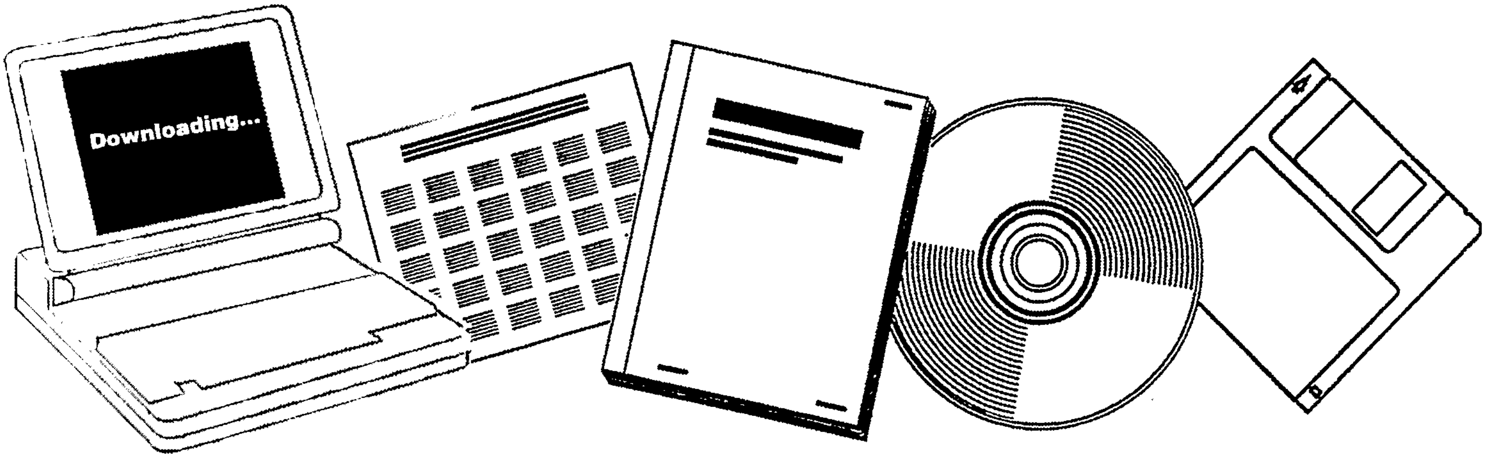
EXXON CATALYTIC COAL-GASIFICATION PROCESS DEVELOPMENT PROGRAM. QUARTERLY TECHNICAL PROGRESS REPORT, JULY-SEPTEMBER 1979

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

DEC 1979



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EXXON CATALYTIC COAL-GASIFICATION PROCESS DEVELOPMENT PROGRAM

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
July - September, 1979

C. A. Euker,Jr. - Program Manager

EXXON RESEARCH AND ENGINEERING COMPANY
Baytown, Texas 77520

December, 1979

MASTER

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

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Quarterly Technical Progress Report
for July-September, 1979

C. A. Euker, Jr. - Program Manager

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ABSTRACT

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

The highlights of this report are summarized below:

- Bench Scale Research and Development

Catalyst recovery studies indicate that $Ca(OH)_2$ digestion in dilute KOH (0.1 M) solutions may be as effective as in concentrated solutions (1.0 M).

The lack of adequate mixing of char, lime, and process solution prior to digestion was found to increase the amount of inactive potassium silicates in the recovered catalyst solution. This result may be due to agglomeration of lime prior to digestion, preventing the full utilization of the calcium in the lime for the digestion reaction.

Experiments have shown that soluble potassium can be extracted from flocculant treated chars. Furthermore, flocculant pretreatment was found to increase sedimentation and filtration rates by a factor of 2 to 5 depending on process conditions of temperature, pH, and weight percent solids in the slurry. A combination of a cationic and an anionic flocculant gave even better filtration and sedimentation rates and liquid clarity than the use of either one of them alone.

The recycle gas furnace bench reactor continued to be troubled with some deposition of carbon in the heated zone during operation. Neither SO_2 pretreatment of the reactor internals nor use of a quartz sleeve were effective in completely eliminating the carbon deposits.

- Process Development Unit Operations

Guidelines and recommendations for the safe operation of the PDU gasifier were formulated and carried out. The gasification section of the PDU was operated at 500 psia and 1200°F using nitrogen and steam as the fluidizing gases for short periods of up to 14 hours while the feed and withdrawal systems were debugged. Afterwards, a sustained operation of 165 hours at conditions of 1200-1250°F and 500 psia was completed. Feed rates were 150 lbs/hour steam, 3500 SCFH total nitrogen, and 90 lbs/hour catalyzed Illinois coal. Material balances were in the 95-98% range.

In the present turnaround, mechanical and operational changes are being made to enable operation with a CO/H_2 mixture instead of nitrogen as fluidizing gas in order to simulate gas recycle to a commercial gasifier.

The foundation and structural drawings were completed for the PDU catalyst recovery system, and work began on the foundation. Preliminary experiments are being made using rental filters to gain experience in filter operation.

- Advanced Study of the Exxon Catalytic Coal Gasification Process

Modifications were made to the feed system of the mini-fluid bed unit. Good reproducibility of gasification rate data has resulted from these modificatons. Initial results indicate that gasification rate increases with increasing potassium-to-carbon ratio even beyond the region where this effect was previously believed to saturate.

Study of the devolatilization process has shown that oxidation level of catalyzed coal accounts for variations in the density of gasifier chars. Catalyst form and coal soak time have been shown not to be significant factors in char density.

The equilibrium concentration of potassium ion remaining on char in catalyst recovery solutions was found to be independent of pH below about pH 11.5 and to increase with higher pH.

- Engineering Research and Development

The Integral Steam Reformer Study was completed and showed a gas cost savings of about 3% compared to the CCG Study Design. Most of the cost savings for this study result from designing for higher steam conversion than the Study Design. This is possible because of the greater flexibility provided by the use of steam reforming for heat input. Carbon laydown was identified as a potential problem for this system and will be addressed in future lab and engineering studies.

A study to optimize the Methane Recovery Section of the CCG process has been initiated. Work in this area will be based on a system proposed by Air Products and Chemicals, Inc. under contract to DOE. This system includes a low pressure stripping tower and autorefrigeration.

Work continued on catalyst recovery system screening studies to evaluate the economic impacts of alternative processing approaches and solid-liquid separation techniques. A material and energy balance has been completed for a first case combining calcium hydroxide digestion with countercurrent water washing using filters. Process bases are being established for two cases which use water washing without digestion, employing filters or gravity settlers for the solid-liquid separations.

An early guidance study to evaluate the cost of additives which may be used to improve filtration performance has been completed. Use of a filter aid as a body feed appears prohibitively expensive, but use as a precoat may be acceptable. Flocculating chemicals offer the most promise as an economical approach to increasing filtration rates.

Ten manufacturers of coal crushing equipment have been contacted as part of a study to determine the types and performance of coal crushing equipment appropriate for commercial CCG plants.

Work is continuing on the development of a material and energy balance model for the CCG gasifier system. The gasifier solids balance model block is now essentially complete. A block to incorporate the gasifier kinetics/contacting model is being programmed.

Activities continued in the engineering technology programs:

- The first set of materials corrosion racks has been installed in the PDU and a second set has been fabricated.

- A subcontract was executed by ER&E and Wilco Research Company covering measurement of vapor-liquid equilibria in sour water/catalyst systems at Wilco.

- Methods were identified for predicting the temperature and composition dependence of viscosity for aqueous solutions of potassium hydroxide and potassium carbonate. A literature search to find enthalpy data for such solutions is continuing.

- A laboratory batch filter was used to collect additional data on filtration rates for digested char samples. Some tests showed commercially acceptable rates, especially when a flocculant was added. However, no definitive conclusions could be drawn at this time because of the variability between different char samples.

- Analytical results were obtained on the leachate from char samples as part of the continuing environmental control programs.

- A proprietary dynamic solids balance computer model is being adapted for use in the CCG process. After validation using data from the PDU, the model will be used to predict equilibrium particle size distributions and gasifier solids balances.

- A program has been initiated to study the dynamic response, stability and control requirements for the CCG reactor and associated recycle gas system.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

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

1.1 Catalyst Recovery Studies

Digestion

The effect of slurry liquid pH on potassium recovery from Illinois No. 6 char was further studied during this quarter. A potassium recovery of 89% was obtained at digestion conditions of one hour, 300°F, 60 RPM agitator speed, Ca/K=0.7, using a 0.1M KOH process liquid with a pH of 12.9. Earlier results at similar conditions using a 1.0M KOH solution (pH ≈ 14.0) showed potassium recoveries of 91 and 92%. Thus, the preliminary indication is that a slurry liquid pH of between 13 and 14 has a minimal effect on potassium recovery from Illinois No. 6 char under these digestion conditions. However, the method used for preparing the char-lime slurry for digestion was found to affect both the overall catalyst recovery and the catalyst forms present after digestion.

A digestion run was made at 300°F, one hour residence time, Ca/K=0.7, with mild agitation, and with 0.1M KOH process solution. The feed to the digestor was prepared by mixing char and lime separately with digestion process liquid, then mixing them together. Of the initial potassium on the char, 93% was solubilized. Further, concentrations of carbonate and silicon in digested liquid were low, 400 and 23 ppm respectively. Two additional runs were made at the same conditions on char and lime which were mixed together, then slurried. Potassium recovery was decreased to 89% and 85% for these runs. Carbonate concentration increased to 2900 and 1500 ppm while silicon concentration increased to 812 ppm and 680 ppm for these digestion runs.

Large white particles were observed in the solids produced from the latter set of digestion runs. This may indicate that lime agglomerated prior to digestion. Consequently, full utilization of the calcium in the lime was not attained, and significant silicon remained in the digestion liquid. Therefore, these results show that predigestion mixing of char, lime and process solution affects digestion.

An attempt was made to digest char which had been water washed to remove 75% of the potassium. This char contained no water soluble potassium. Further, since carbonate concentration on the char was lower, it was hoped that less lime would be needed for digestion since less calcite would be produced. The potassium lean char was digested at 300°F for one hour and Ca/K=1.56 with mild agitation. Of the remaining potassium, 31% was recovered. This corresponds to an overall potassium recovery of 83%.

Potassium Forms from Char

Previous bench scale char washing studies (May, 1979 Monthly Report) showed considerable amounts of potassium in solution in the form of $K_2S_2O_3$ and K_2SO_4. Since these potassium compounds may be formed by exposure of the char to air, a large nitrogen blanketed box was constructed to house char samples to minimize air exposure. In addition, FBG Illinois No. 6 char having less air exposure than that used in previous bench scale studies will be tested for catalyst forms. Both of these changes should reduce the concentrations of sulfate and thiosulfate forms of sulfur in solution. Fresh PDU char will be tested as soon as it is available to determine catalyst forms on fresh char where air exposure has been minimized.

Leaching

Four char leaching runs were made to determine the effect flocculants have on solids entrainment during leaching. Figure 1.1-1 shows the results of two runs at 5 wt.% K^+ in liquid. Flocculant D-25A was used at a dosage of 50 ppm for one run; no flocculant was used in the other run. Char with the same particle size distribution was used in both runs. The flocculant greatly reduces the solids entrained at all liquid superficial velocities.

Similar runs were made at 10 wt.% K^+ in liquid. Figure 1.1-2 shows similar improvement in solids entrainment because of flocculant in the slurry liquid, but greater quantities of char are entrained at these conditions.

Potassium recovery in all four of these runs was approximately 70-75%. This represents essentially all of the water soluble potassium on the char. These results indicate that leaching will extract water soluble potassium from char treated with flocculants.

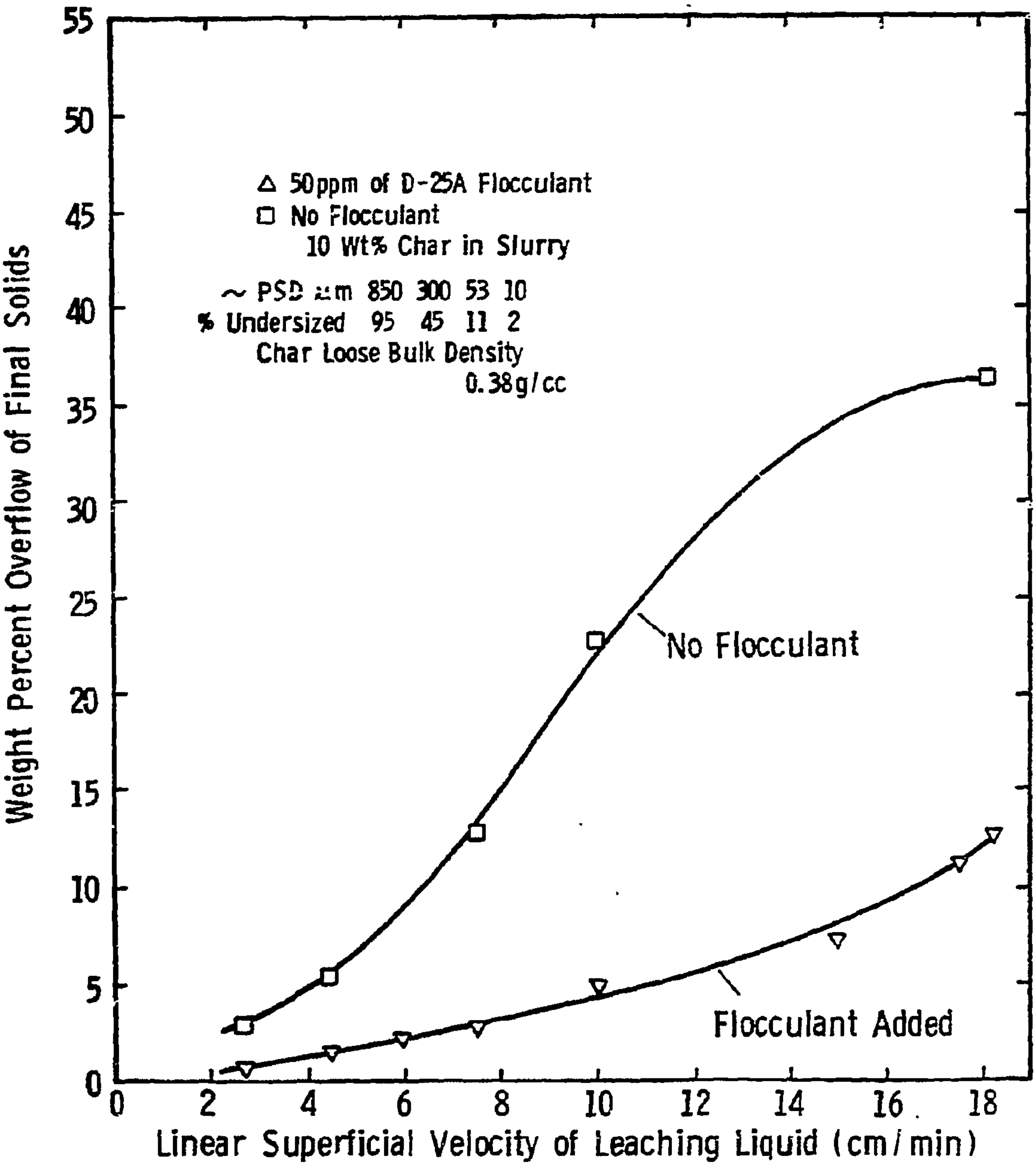
1.2 Flocculant Pretreatment of Catalyst Recovery Slurry

Bench scale tests were initiated in July to study the potential benefits of flocculant pretreatment of the water washed char-catalyst slurry for solid-liquid separation at PDU conditions. PDU water washed char-catalyst slurries were simulated by mixing two parts (by weight) of FBG char and one part of FBG fines with eight parts of water. The mixture was stirred and heated to 200°F for one hour and allowed to cool to room temperature before a measured amount of flocculant was added. Table 1.2-1 gives a typical analysis of the slurry. The solid content of the slurry samples varied from 6.0 to 8.0 wt.%.

Screening tests were carried out at room temperature with three types of flocculant samples (anionic, non-ionic and cationic). Table 1.2-2 gives a list of the flocculants tested. Table 1.2-3 shows the results of the screening tests. D-25A flocculant appeared to be the best among the flocculants that have been tested. Filtration and sedimentation rates were increased by a factor of about 2 and 4, respectively, above the base values when 50 ppm of D-25A flocculant was used. A combination of D-25A and R-7C flocculants gave

FIGURE 1.1-1

CHAR LEACHING 5% K+ IN SLURRY LIQUID



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even better filtration and sedimentation rates and better clarity of the supernatant liquid than the use of either one of them alone. For example, a combination of 25 ppm of D-25A and 12 ppm of R-7C resulted in an increase in filtration rate by about a factor of 3.8 and an increase in sedimentation rate by about a factor of 5, compared to the base values.

In order to examine temperature and pH effects on stability and performance of the flocculant, the slurries were heated up to 200°F. This is the temperature expected to be run in PDU solid-liquid separation operations. Various amounts of potassium hydroxide were used in order to give potassium concentrations of 2, 4, 6, 10, and 16, wt.% in the slurry.

Experimental results indicate that D-25A flocculant is stable and works even at severe conditions; namely, 200°F, 16 wt.% K^+ ($pH=14^+$) and 9 wt.% solid loading. Table 1.2-4 gives the results of temperature and pH effects on flocculant performance in the water washed slurry. Runs 1 and 3 show that the heating process itself increased both sedimentation and filtration rates by about a factor of 5 and 2.5, respectively, compared to the base values (run 1). This is because of the decrease in density and viscosity of the slurry at high temperature. For example, the density and viscosity of a 5 wt.% KOH solution decreases from 1.01 gram/cc and 1.1 cp at 80°F to 0.97 gram/cc and 0.35 cp at 200°F. Although the supernatant liquid from these experiments remained a cloudy, clarity of the supernatant liquid was improved by the flocculant treatment.

Figure 1.2-1 and 1.2-2 clearly illustrate that flocculant pretreatment of the slurries improved both filtration and sedimentation. These figures show that filtration and sedimentation rates decrease as potassium concentration in the slurries isncreases because slurry density and viscosity increases. Nevertheless, flocculant pretreatment improves both filtration and sedimentation rates even at potassium concentration as high as 16 wt.%. The extent of improvement in filtration and sedimentation rates is, however, somewhat less for high potassium concentration cases than for lower ones. For example, as shown in Table 1.2-4, with an addition of 25 ppm of D-25A flocculant to a 2 wt.% K^+ slurry at 200°F, run 4 shows the sedimentation rate to be increased by about a factor of 4.5 compared to the base value (run 3). However, run 12 shows a doubling of the sedimentation rate compared to run 11 for a 16 wt.% K^+ slurry. Filtration rate for these same slurry runs increased by a factor of 4.7 times the base value for 2 wt.% K^+ slurry and a factor of 3 times the base value for 16 wt.% K^+ slurry.

Future work will address the integrity of flocs of the water washed slurry as well as the effect of flocculant pretreatment on $Ca(OH)_2$ digested char-catalyst slurries.

1.3 Recycle Gas Furnace Studies

Work during this quarter was directed at minimizing the lay down of carbon in the internals of the reactor in order to clearly distinguish the effects of incremental amounts of wire mesh on CO_2 production. Two techniques were tried:

Table 1.2-3

Flocculant Screening for Water Wash Slurry

Flocculant and Dosage	Filtration Rate, ml/min.	Relative Filtration Rate, % of Base	Sedimentation Rate, mm/min.	Relative Sedimentation Rate, % of Base	Note
Single Flocculants					
Blank 0 ppm	32	100	4	100	Supernatant liquid remained cloudy after 30 min., solid-liquid interface was not clear.
R-7C 50 ppm	56	180	9	230	Liquid is clear, few particles suspended in liquid though.
R-10A 50 ppm	44	140	5	130	Supernatant liquid remained black and cloudy; solid particles suspended.
A-585C 50 ppm	50	160	3	80	
A-1839A 50 ppm	53	170	5	130	Liquid was milky and cloudy; particles suspended.
A-1906N 50 ppm	51	160	3	80	
T-362C 50 ppm	54	170	3	80	
D-43C 50 ppm	39	120	7	180	
D-25A 50 ppm	68	210	16	400	Both sedimentation and filtration rates were improved substantially. Liquid remained black and cloudy.
Multiple Flocculants					
D-25A 45 ppm and D-43C 5 ppm	62	190	28	700	
D-25A 45 ppm and R-7C 5 ppm	88	280	37	930	Clear supernatant liquid.
D-25A 25 ppm and R-7C 6 ppm	111	350	17	430	Clear supernatant liquid.
D-25A 25 ppm and R-7C 12 ppm	122	380	20	500	Clear supernatant liquid.

FIGURE 1.2-1

FLOCCULANTS IMPROVE FILTRATION RATE

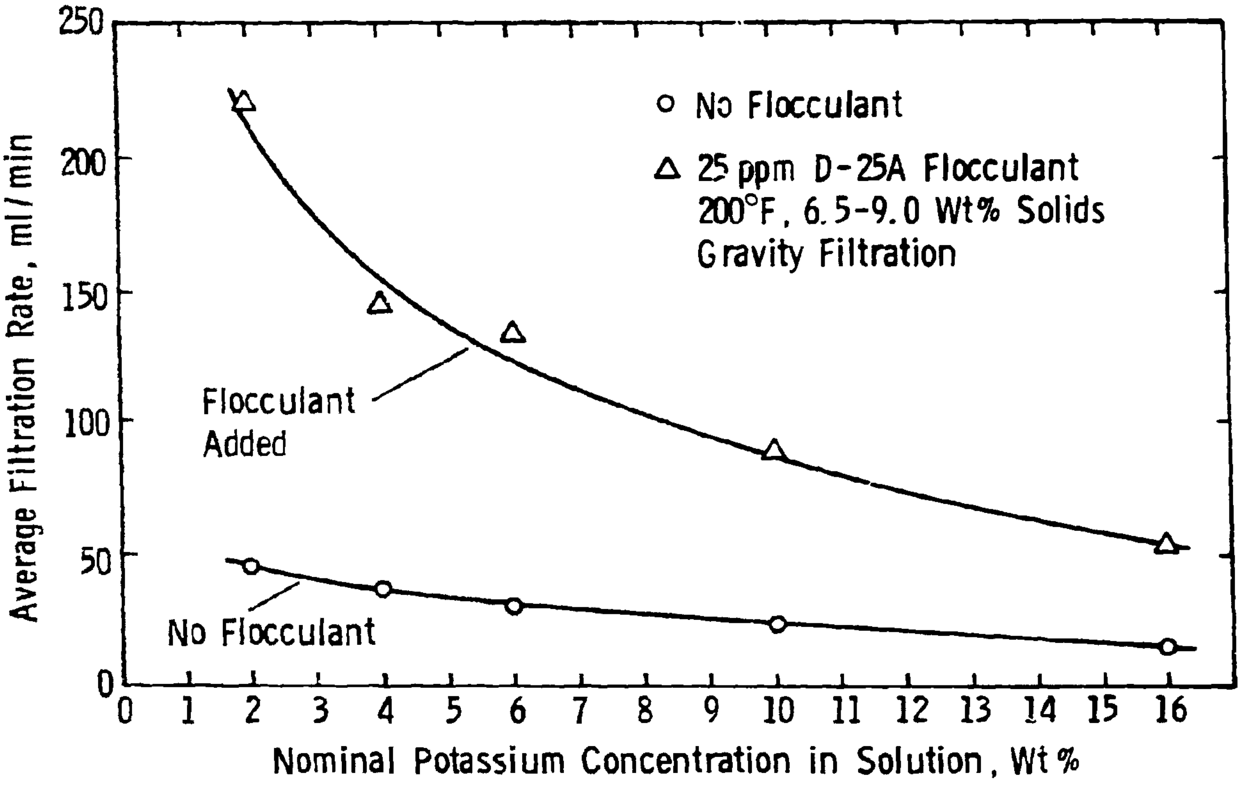


Table 1.2-4

Temperature and pH Effects on Flocculant Performance in Undigested Catalyst Slurries

Run No.	Flocculant Dosage, ppm	Temperature °F	Solution Concentration wt.% K+	Solids Slurry wt.%	pH	Average Filtration Rate, ml/MIN.	Relative Filtration Rate	Average Sedimentation mm/MIN.	Relative Sedimentation Rate
1	0.0	80.	2	6.77	10.2	17.2	0.4 x Base	4.5	0.2 X Base
2	25.0	80.	2	7.47	10.2	67.2	1.4 X Base	22.5	0.8 X Base
3	0.0	200	2	6.77	10.2	46.7	1.0 X Base	30.0	1.0 X Base
4	25.0	200	2	7.47	10.2	221	4.7 X Base	135.0	4.5 X Base
5	0.0	200	4	6.63	12.8	37.2	0.8 X Base	20.0	0.7 X Base
6	25.0	200	4	7.31	12.8	147	3.2 X Base	77.1	2.6 X Base
7	0.0	200	6	6.83	13.5	31.1	0.7 X Base	16.4	0.6 X Base
8	25.0	200	6	7.83	13.5	135	2.9 X Base	60.0	2.0 X Base
9	0.0	200	10	8.28	14.4	23.3	0.5 X Base	15.8	0.5 X Base
10	25.0	200	10	8.91	14.4	91.3	2.0 X Base	28.4	1.0 X Base
11	0.0	200	16	8.48	14.6	17.6	0.4 X Base	14.2	0.5 X Base
12	25.0	200	16	8.92	14.6	53.5	1.2 X Base	28.4	1.0 X Base

Note:

1. Flocculant is D-25A (anionic type)
2. Gravity filtration only
3. Stirring speed 180 rpm
4. Heating duration at 200°F is 5 minutes after flocculant addition.
5. Initial slurry sample is 300 ml.

Table 1.2-1

Analysis of Water Washed Slurry

K^+ in liquid, wt.%	1.78
Solid content, wt.%	6.50
pH of the liquid	10.0

Particle size distribution:

Size, Micron	Wt.% Undersize
300	100.0
212	94.9
150	89.4
106	79.6
75	68.9
53	58.4
38	46.7
27	38.2
19	29.2
13	21.4
9.4	15.5
6.6	9.4
4.7	4.6

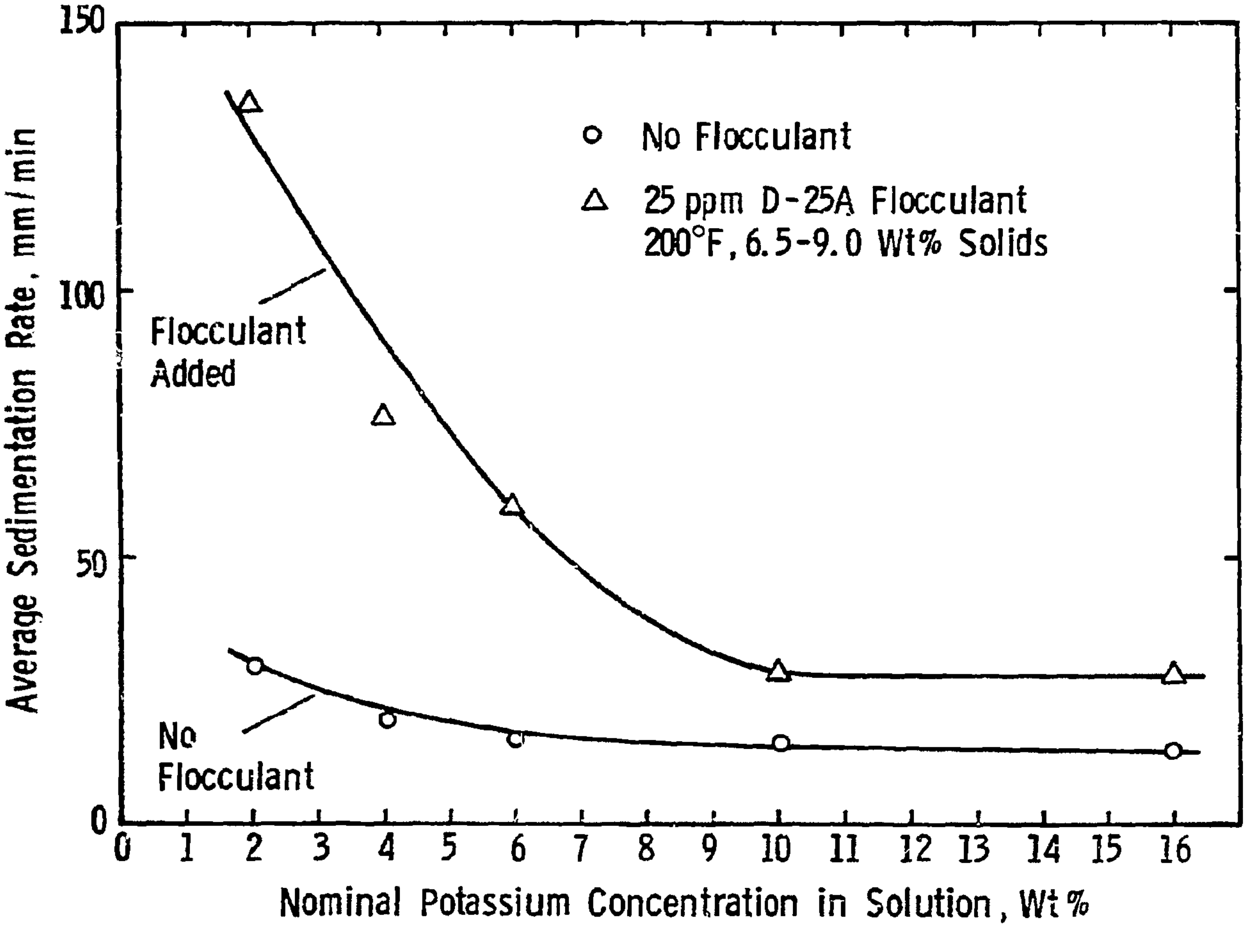
Table 1.2-2

Flocculants Tested

Flocculant	Type
A-585C	Cationic
A-1839A	Anionic
A-1906N	Nonionic
T-362C	Cationic
T-365A	Anionic
D-43C	Cationic
D-25A	Anionic
H-1129A	Anionic
H-1141A	Anionic
H-1142A	Anionic
R-3C	Cationic
R-7C	Cationic
R-10A	Anionic

FIGURE 1.2-2

FLOCCULANTS IMPROVE SEDIMENTATION RATE



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- SO_2 pretreatment of the reactor
- Use of quartz tubing as a masking device to prevent the gas from contacting thermocouple and product gas line surfaces.

Table 1.3-1 presents the CO_2 concentration in the product gas when SO_2 pretreatment of the reactor internals was carried out prior to operation, while Table 1.3-2 presents the CO_2 concentration when both SO_2 pretreatment and quartz tubing were used. It is estimated that the quartz tubing masked approximately 80% of the internal metal area from the gas.

Table 1.3-1

Product Gas Compositions
SO_2 Pretreatment

Reaction Zone Temperature, °F	CO_2 Composition of Product Gas, mole %	Equilibrium CO_2 Concentration, mole %
1110	0.1	5.4
1226	0.2	5.2
1315	0.4	5.0
1431	0.7	4.5
1524	1.2	4.3
1556	1.5	4.3

Table 1.3-2

Product Gas Compositions
SO_2 Pretreatment/Quartz Tubing

Reaction Zone Temperature, °F	CO_2 Composition of Product Gas, mole %	Equilibrium CO_2 Concentration, mole %
1166	0.1	5.3
1423	0.5	4.5
1617	2.0	4.2

These data indicate that the quartz tubing had very little effect on CO_2 formation. Carbon specks appeared in the product line condenser during both of these runs as well.

Future work will use sulfur injection in the feed in order to determine what level of sulfur addition is required to prevent carbon laydown. The possible catalytic effect of the mullite internals of the reactor toward carbon laydown will also be examined.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

2. Process Development Unit Operations (Reporting Category C02)

2.1 PDU Startup and Initial Operations

The gasification section of the PDU was started up the first of July. Gasifier temperature ranged from 1200-1250°F and the pressure was 500 psia. The feed was Illinois No. 6 coal catalyzed with 12 to 15 wt.% KOH, fed at a rate of 40 to 80 lbs per hour. The fluidizing gas was nitrogen at a rate of 1500 to 3000 SCFH. Nitrogen was used in place of synthesis gas (H_2 + CO) in the interest of maximizing the operating safety during the startup of new equipment and the operator familiarization and training period. Steam was generated at 600 psi and injected at a rate of 150 to 170 lbs per hour. The preheaters and superheater were used to raise the nitrogen and steam injection temperatures to 1200°F.

All of the coal feed and solids handling equipment were operated, including the raw coal transporter, the catalyst addition pumps and weighing equipment, the rotary coal feeder and ribbon mixer, the series of four screw conveyor dryers, the catalyzed coal transporter, the automatic lockhopper fill system, and the pressurized lock pots and automatic feed system. All of this equipment operated well, after the usual debugging required of new equipment, with the exception of the actual feed injection lines to the gasifier. By the end of the month the problems associated with the feed injection lines had also been solved.

Other equipment operated included all of the steam generation equipment, consisting of the water storage and weighing scales, pumps, steam condensation equipment for off-line steam startup, and the steam generator itself with its associated level, pressure control, and alarm systems. The automatic fines removal filter systems and scrubber were also operated, as well as the sour water weighing system and stripper.

Initially both feed lines plugged after one to two hours. In each case the line could be cleared by pushing gas into it, but it would soon plug again. The unit was shut down and the feed lines examined. It was found that a specially machined swage fitting designed to smooth the flow of solids through the part of a ball valve had been misaligned during assembly so that it restricted the solids flow. It was also found in bench scale devolatilization tests that the catalyst loading on the coal was low and the coal had a tendency to swell and become sticky. This load of coal was dumped and a new batch prepared. A richer catalyst solution was next used, 45% KOH instead of 30% previously used, and a longer wet soak time was employed by turning off the steam heat on the first of four screw conveyer dryers.

Modifications were made in the catalyst addition system to provide smoother coal feeding to the ribbon mixer. It was discovered that the bags in the dust collector above the raw coal hopper (LH-3) had charred and pieces of the bags were hanging up in the feeder. This caused erratic coal feeding to the ribbon mixer so that the catalyst loading on the coal varied. The bags had been charred by blowing down the feed line plugs into the dust collector. The blowdown line was subsequently rerouted to a new cyclone to prevent recurrence of this problem.

Feed line plugs continued to occur in the upper part of the line after the newly catalyzed coal was prepared. One entire feed line plugged badly and required replacement. The catalyst solution concentration was then reduced to 20% because of the possibility that the 45% solution was extracting humic acids from the coal and causing surface stickiness on the coal particles.

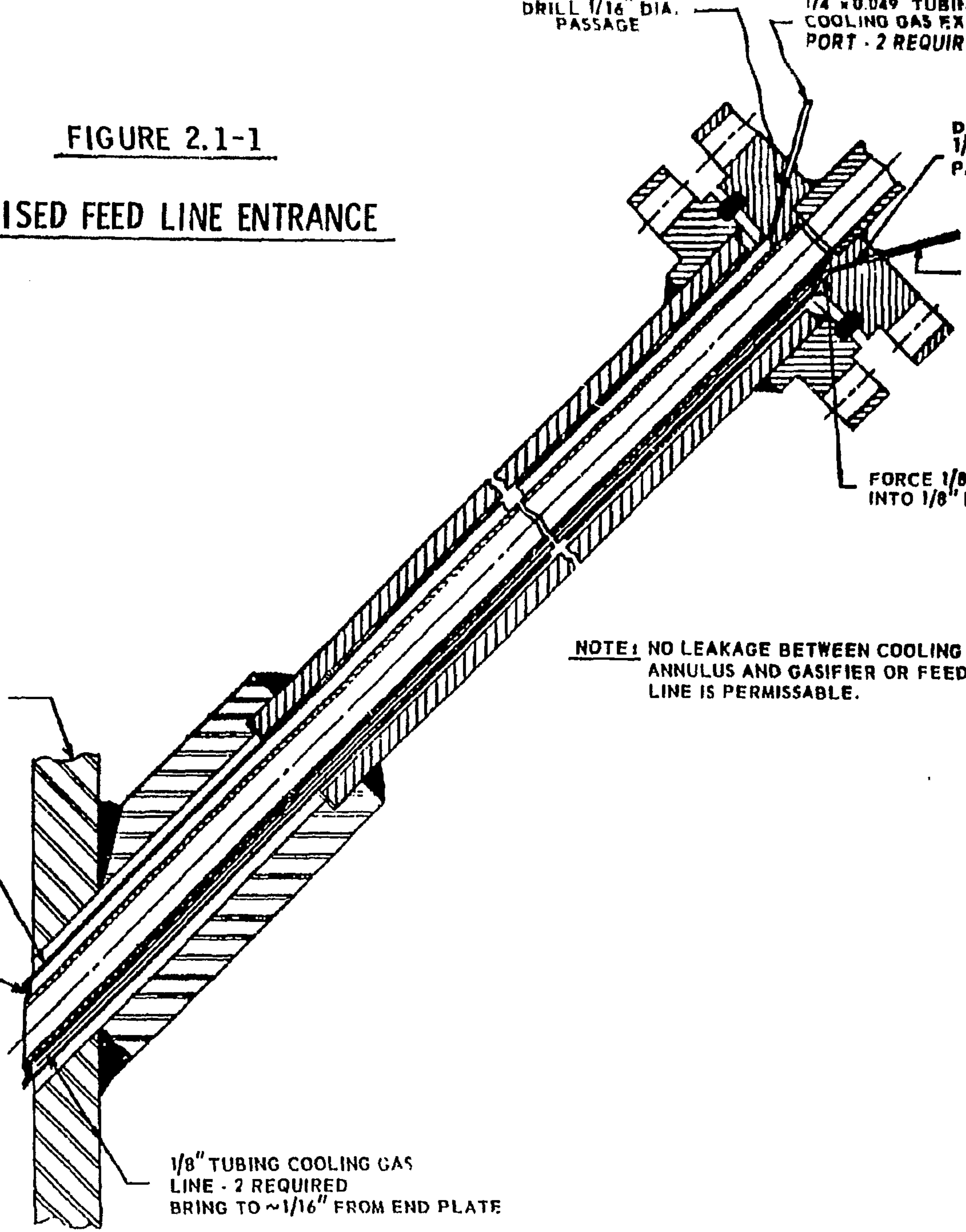
The reduction in catalyst concentration helped the operability of the upper part of the feed line, which is a 20 foot vertical two-inch pipe under full reactor pressure. The coal drops through this pipe and is simultaneously blown downward by gas during coal injection. The feed line makes a 45° turn into 3/4" tubing for injection into the side of the reactor at a 45° downward angle. Driver gas is injected at the 45° transition block. As the plugging problems in the upper, vertical section of the line were eliminated, they next appeared in the injection tip, the hottest part of the 45° section of the feed line.

The plug material had the appearance of partially devolatilized coal, which had not been observed before in either atmospheric pressure or 100 psi devolatilization of catalyzed coal. A number of laboratory experiments were run which indicated that high pressure devolatilization causes the particles to go through a sticky stage. This is theorized to be caused by liquids being retained inside or on the particle surface at high pressure. These liquids would vaporize away from the surface at low pressure. The best solutions for feed line plugging appeared to be lower temperatures or shorter residence times at elevated temperatures in the feed line. In this way the coal particles could be injected into the 1300°F char bed where devolatilization and coking of the liquids would be very rapid, and the feed coal particles would be quickly diluted by char. This should minimize the effects of any liquid evolution from the particles.

Several modifications were made to the feed line to help produce devolatilization inside the char bed. As shown in Figure 2.1-1, a thermal sleeve was added to the feed line on the last two feet before injection. This is to shield the coal from the hot char temperatures until it reaches the actual tip of the injection point. Cooling gas is blown into the tip of the annulus between the feed line and its thermal sleeve. This gas is routed so that it does not enter the process. The cut off angle of the tip of the feed line was also changed so that the coal may enter the fluidized bed horizontally rather than at a 45° downward angle. In addition, the temperature along the length of the entire feed line was reduced from 400-500°F to 250-350°F. The injection gas rate in the feed line was also increased to speed the flow of solids through the heated zones.

FIGURE 2.1-1

REVISED FEED LINE ENTRANCE



NOTE: NO LEAKAGE BETWEEN COOLING ANNULUS AND GASIFIER OR FEED LINE IS PERMISSABLE.

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These changes produced a dramatic improvement in feed line operation. The plugging ceased and feeding at will became routine. Five sustained periods of feeding were accomplished:

Date	Time of Feeding (hours)
7/25	14
7/25	2.5
7/27	5
7/29	2
7/31	5

Feed was stopped voluntarily in each case to perform other maintenance or modifications to the unit. Further work is being directed toward optimizing the operating conditions of the feed line.

Work was also emphasized in the char withdrawal area. During July, the char was being withdrawn as dry solids in manual operations. Construction and programming of equipment was completed in order to permit continuous automatic withdrawal of the char as a water slurry.

The highlight of August operations was a sustained operation of the gasification section for 165 hours. Only a minor interruption of feeding for less than three hours occurred. Otherwise the operation was very smooth and well-controlled. The run was terminated by the loss of a liquid N_2 pump used to supply feed nitrogen to the gasifier.

During the run the unit was operating at conditions of 1200-1250°F, and 500 psia, with feed rates of 150 lb/hr steam, 3500 SCFH total nitrogen, 2200 SCFH fluidization N_2, and 90 lb/hr catalyzed Illinois coal. Catalyst loading was 15 to 18% KOH on coal. Superficial gas velocity at the bottom of the reactor was 0.25 to 0.3 ft/sec. Carbon conversions up to the 80-90% range and steam conversion of approximately 50% were achieved. Material balances were in the 95-98% range. These results are very preliminary since they are based on spot samples. Some of the automatic data acquisition systems, such as the process GC analyzer, are still being brought on-line and were not operating at the time of the run.

The sustained operation of nearly one week demonstrated gasifier operability over extended periods. The feeding problems encountered in July initial operations appeared to be solved by the modification made at that time. Coal feeding was very smooth and virtually trouble-free. The long continuous run provided an opportunity to test and develop operating procedures for the char removal system.

The water slurry pots for char removal were activated for the first time in a wet operation. After initial periods of slow char removal caused by char chunks plugging the lines, the operation became smooth and routine. It is believed the chunks were formed during the periods of erratic coal feeding and were no longer formed after the feeding problems were solved. They had accumulated in the reactor and were gradually removed with the char. In the last several days of operation, no chunks were seen in the char slurry. However, after the run was terminated, approximately three gallons of chunks were removed from the bottom of the reactor. These were probably slowing down the removal of char even during the smooth operations by interfering with the flow into the char withdrawal legs. Only about one-half the expected char withdrawal rate was achieved by the char removal lock valve system.

Before bringing the unit up in August, the 2-1/2-inch diameter carbon steel studs in the top and bottom flanges were replaced by B8M stainless steel studs and retorqued to 4400 ft/lb. It had been found during the July operations that the flanges had to operate hot enough that the carbon steel studs crept and the flanges leaked. During that downtime, filter elements in both the char fines removal filters were replaced; leaks were repaired in the steam generator steam drum and sight glasses; the slow depressure valves were repaired; and fines were worked out of the scrubber, sour water accumulator drums, and sour water stripper.

Work continued on the gas cleanup and recovery section. The MEA system startup was continued as unit operator time was available. Construction was completed on the molecular sieve system and startup will be initiated as soon as the programming can be completed and checked out on the programmable controller. The cryogenic fractionator construction is proceeding on schedule. As this equipment becomes operable, it will be tested by operation on gasifier product gas on a once-through basis.

After the sustained operations of August, the gasification section began its first major turnaround. This extended through the month of September. The goals of the turnaround included completing work in four major areas: (1) mechanical repair, maintenance, and testing; (2) process improvements; (3) installation of hydrogen/carbon monoxide supply system; and (4) miscellaneous data, instrumentation, and control systems.

Mechanical work included rebuilding the valves associated with the coal feeding system. The slow and fast depressure valves were reworked and the packing was replaced on some of the char withdrawal valves.

Several process vessels downstream of the product gas fines removal filter had to be cleaned because of the accumulation of fine material. These included the scrubber which condenses unreacted steam from the product gas and sour water accumulators which hold the condensate for weighing before discharge. Both filter elements were replaced; however, a longer term solution to the problem is being actively pursued and progress will be discussed in future reports.

Several materials testing coupons were located at strategic points in process vessels. The locations, types of coupons, and the testing program are described in the July, 1978 - June, 1979 Annual Report.

During the turnaround, char was removed from the gasification vessel. It was found that some solid material in the form of chunks or deposits had accumulated in the reactor. These were flushed out with water derived from steam condensate and a visual inspection was made to ensure a clean gasifier. In subsequent operations, care will be taken to maintain the bed of char in a fluidized state at all times and never to let it slump completely at reactor temperature. The gasifier will be cooled to at least 750°F if it is necessary to cut off all flows. Also, efforts will be made to maintain the bed level above the feed point so that fresh coal fed will not impinge directly on the vessel wall. After the visual inspection, the unit was thoroughly pressure tested.

Several process modifications were indicated during August operations and these were instituted during the turnaround period. Process lines supplying gas necessary to feed coal were replaced with ones of larger diameter so the required flow at the desired pressure could be maintained at all times. Also several three-way valves were installed so that gas flow could be conveniently switched from nitrogen to synthesis gas. This allows critical systems such as coal feed gas supply and pressure taps to remain on nitrogen while syn gas is first introduced to the gasifier. This is advantageous from an operations standpoint.

Other improvements include: (1) direct reference system for pressure taps eliminating offset caused by regulator in old system; (2) back pressure reference system for steam generator independent of gasifier; and (3) use of house nitrogen (160 psi) for critical air actuated valves rather than instrument air (55 psi).

During the turnaround period the hydrogen/carbon monoxide supply system was completed. The next operational phase of the gasification program calls for the inclusion of these gases along with steam and the exclusion of nitrogen. All lines from the gas cylinder trailers to the unit and all manifold lines, valves, and instruments have been thoroughly leak tested to ensure safe operation when these flammable gases are brought to the unit. Also, as a precaution, the body purges on the char withdraw valves will be pressured with nitrogen slightly above unit pressure assuring no flammable gas leakage through valve stem packing. Additionally the syn gas supply system requires a 50 ppm bleed of hydrogen sulfide to suppress carbon formation and hence plugging in the preheater and superheater.

Finally the carbon monoxide detectors were calibrated and the process analyzer brought on stream to ensure safe operations and enable nearly continuous analysis of all gas streams. Also a backup programmable logic controller was installed to ensure maximum reliability of automatic valve cycling without which the unit cannot operate in a continuous manner.

2.2 PDU Catalyst Recovery System

Design and Construction

During this quarter, work began on the detailed flow diagrams for the catalyst recovery system outlined in the June, 1978 - July, 1979 Annual Report. The flow diagram for the digester system and an initial pass of the flow diagram for the filter system were completed. In addition, all major pieces of equipment, including the digesters, surge tanks, filters, and evaporators were designed. The digesters, designed to hold 450 gallons of slurry at 500 psig and 450°F, were ordered with delivery expected in November. The surge tanks, designed to hold 1500 gallons of slurry at 20 psig and 200°F, were ordered with delivery also expected in November. The evaporators, designed to evaporate 4,900 pounds of 1 wt.% K^+ solution down to 20 wt.% K^+ will be built by Exxon as the material arrives. As mentioned in the May, 1979 report, the filters were ordered in May. Conversations with the manufacturers indicate delivery will not be until late November instead of the middle of October as originally planned.

Foundation and structural drawings for the catalyst recovery unit were completed during this quarter. The foundation was poured and completed. Bids for fabrication and erection of the structure indicates that outside contractors could not provide an erected structure in the time frame desired. Consequently it was decided that Exxon would erect the structure. Steel was ordered and construction is scheduled to commence next month.

Filtering Procedure Being Developed

Experiments have been initiated to establish the operating procedure for the filter system of the PDU catalyst recovery unit. Rented filters, identical to those on order for the Catalyst Recovery Unit (CRU) will serve as training for the operators in addition to developing techniques for filtering the PDU char slurry.

A thin, even layer of precoat was applied to the filter surface by filtering a 0.1-0.3 wt % cellulose fiber precoat slurry. Recycling 30% of the slurry from the top of the filter created an upward movement of slurry across the cake which was necessary for adequate solids dispersion. The residual liquid in the filter body was removed without upsetting the precoat layer by pressurizing the vessel with nitrogen and blowing the solution out as filtrate.

In future filter experiments, both digested and undigested char from the PDU will be used. Filtration and slurry handling procedures will be developed at ambient and elevated temperatures. Also, the effectiveness of a second char rinse step in one filter will be examined to determine whether the filters can be operated in parallel or whether they must be operated in series. The results of these tests will serve as the basis for developing detailed CRU operating procedures.

3. Data Acquisition and Correlations
(Reporting Category C03)

3.1 Process Modeling

The objectives of modeling the fluid bed gasifier are two-fold: to better characterize the reactor behavior and therefore provide a better basis for correlating the data; and to provide a method for extending the data base beyond the experimental range. The model will therefore serve both as a learning tool and a predictive tool for design purposes.

A fluid bed gasifier model was developed during the predevelopment contract E(49-18)-2369. The current modeling effort is geared toward validating the existing model against data from FBG runs as well as data that will be generated by the PDU and other laboratory scale units. It is our goal to improve upon the existing model so as to reflect all observed kinetic data and to eliminate, as much as possible, uncertainties associated with using the model for process definition of commercial catalytic gasifiers.

Two aspects of the FBG data were analyzed during this quarter:

- How well does the existing fluid bed reactor model predict the overall carbon conversion observed in FBG runs.
- To what extent were the FBG gasification rates influenced by the interphase mass transfer between the bubble and the particulate phases (i.e., how serious was gas bypassing in the FBG runs).

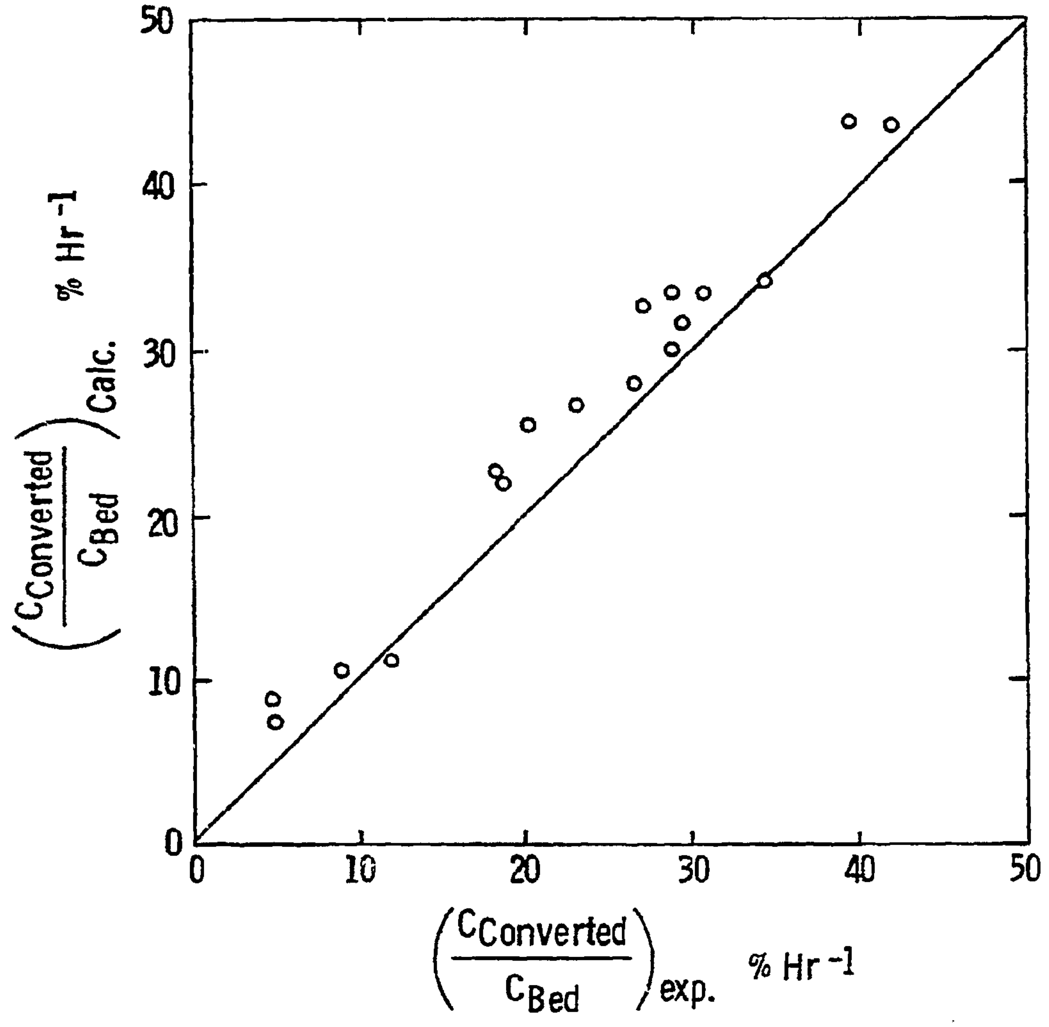
On the basis of overall carbon conversion, the existing model agrees well with the FBG data (Figure 3.1-1). However, a number of assumptions in the model still need careful reevaluation. Chief among these are the questions of maximum bubble size, the effect of high K/C ratio upon gasification rate, devolatilization yield and the gasification and methanation kinetics. These uncertainties will be examined more closely in future studies.

Interphase mass transfer between bubbles and the particulate phase is an important consideration in all fluid bed reactor modeling. Two factors are important in determining the interphase mass transfer: the rate of mass transfer per unit time and surface area (i.e. mass transfer coefficient), and the residence time of the bubbles in the bed. These factors in turn are dependent upon the physical characteristics of the bed (i.e. bed height, gas flow rate, reactor configuration, gas and particle properties).

While there are several empirical or semi-empirical correlations in the literature, none is universally accepted or "proven" to be true in a general sense. Though the variability among the correlations is large, the following relationship is agreed upon by many researchers in this field:

FIGURE 3.1-1

COMPARISON OF MODEL WITH FBG DATA: TOTAL CARBON CONVERSION RATE



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$$X \propto \frac{L_{mf}}{D_B^n} \qquad (3.1\text{-}1)$$

where X = number of times the bubble volume is exchanged with the particulate phase
L_{mf} = bed height at minimum fluidization
D_B = bubble diameter
n = exponent of D_b, generally lies between 1.0 and 2.0

The significance of X can best be seen in the following example. Suppose a bubble containing tracer gas is injected into a large fluidized bed maintained at minimum fluidization with zero tracer concentration. The concentration of the tracer gas in the bubble upon exiting the bed is given by:

$$\frac{C}{C_o} = e^{-X} \qquad (3.1\text{-}2)$$

where C = tracer concentration in the bubble exiting the bed
C_o = Initial tracer concentration in the bubble

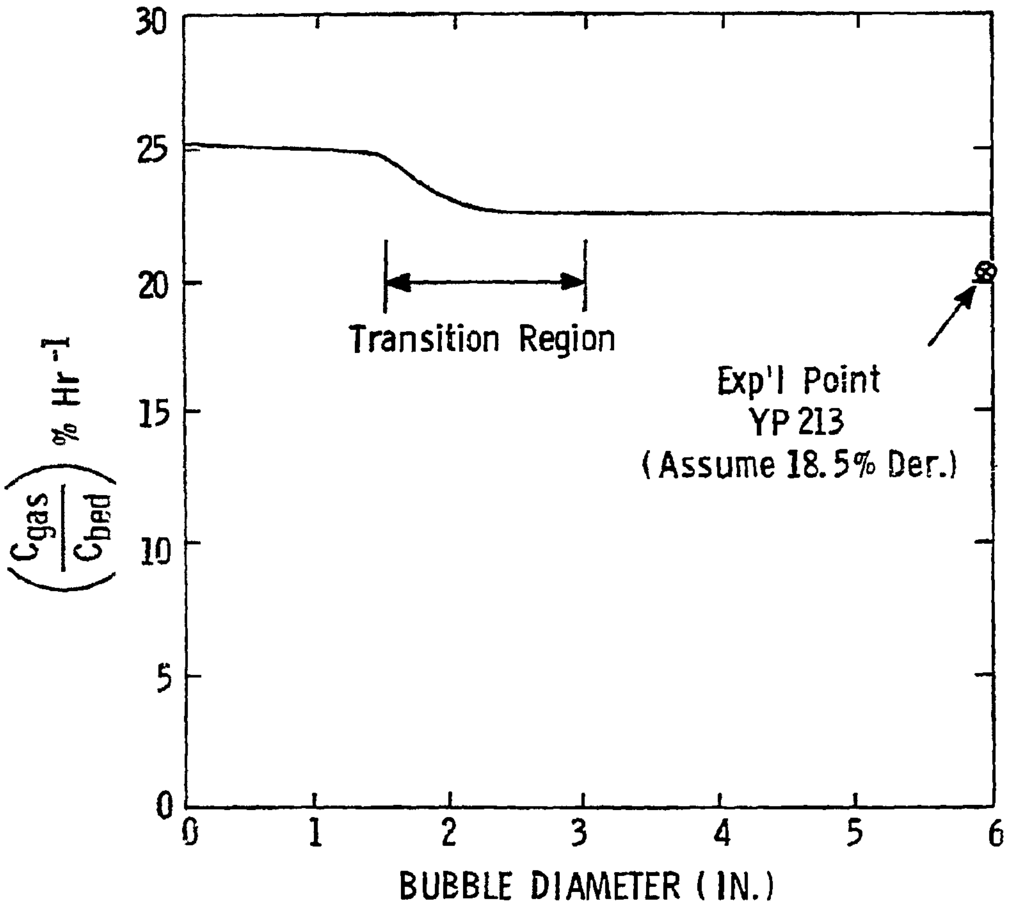
From equation (3.1-2), it can be calculated that the tracer concentration in the bubble is reduced to less than 1% of its initial value after five complete interchanges with the surroundings (i.e. $x = 5$). Consequently, further increasing from five to ten will improve the overall interphase mass transfer little.

Based on the above understanding and using a conservative estimate of bubble mass transfer (i.e. Kunii and Levenspiel's bubble-cloud-emulsion model) and Hormond and Davidson's mass transfer model for slugs, it was concluded that gasification rates for the FBG runs are not significantly constrained by interphase mass transfer. Figure 3.1-2 shows a typical case in the example of yield period 213. By assuming the bubble diameter is within the range of 1/4" to 6", the gasification rate is altered by only 10%. The gasification rates of the FBG runs are relatively insensitive to bubble size variations because the beds are relatively tall (minimum fluidization bed height ranges from 16 to 32 feet) and the reactor diameter limits bubble size to 6 inches. Consequently, the bubbles have sufficient time to interchange with the surroundings before exiting the bed.

FIGURE 3.1-2

FBG CONVERSION NOT SENSITIVE TO ASSUMED BUBBLE SIZE (MODEL PREDICTION)

BASIS: FBG YP 213



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

4.1 Kinetics of Gasification and Devolatilization

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

The kinetics of char gasification have previously been investigated during the predevelopment phase of catalytic gasification research (Contract No. E(49-18)-2369). The majority of the kinetic data was obtained using a fixed bed reactor at 1300°F and catalyst loadings of 10 and 20 wt.% potassium carbonate on dry Illinois coal. The coal was devolatilized under an inert atmosphere before loading in the fixed bed reactor. Some data was also obtained at 1200°F.

On the basis of these data, engineering studies have established 15 wt.% potassium carbonate equivalent as the preferred catalyst loading and 1275°F as the study design temperature. Engineering sensitivity studies using the limited temperature data have indicated an economic incentive for lowering the gasifier temperature below 1275°F. Additional kinetic data at various temperatures on steady state char is necessary before a confident optimization of the gasifier conditions can be made.

In view of these needs, a laboratory program is in progress to expand the kinetic data base for gasification of Illinois char. The chars used for this study were produced earlier this year by the Fluid Bed Gasifier (FBG) under steady state conditions. 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.

The reactant gas feed to the mini-fluid bed unit consists of steam and hydrogen. Hydrogen is used to simulate the presence of syn gas (75% hydrogen) in the feed to a commercial gasifier. The hydrogen and steam feed rates used in the current study are chosen to match either (a) the conditions under which the FBG was operated during the predevelopment phase of catalytic gasificatio research (Contract No. E(49-18)-2369), or (b) the conditions specified in the predevelopment commercial study design. These two sets of conditions are different because the FBG reactor was limited to 100 psig operations whereas the commercial reactor is designed for 500 psia.

Several modifications were made to the mini-fluid bed gasifier during this quarter to improve unit operability and data reproducibility. Argon gas is now added to the feed stream to ensure good fluidization of the char sample and to eliminate gas channeling in the bed. In addition, the feed system has been modified to allow the gas and water streams to enter the reactor separately, rather than allowing the two streams to mix upstream of the reactor. This modification produced a more uniform water feed rate to the reactor, and resulted in good reproducibility in the gasification rate data.

Gasification rate data has been obtained in the mini-fluid bed gasifier for two steady state Illinois chars. Figure 4.1-1 shows the rates obtained in the atmospheric mini-fluid bed reactor and those obtained in the 100 psig FBG at similar flow conditions. The solid line representing FBG data is a correlation of rate data from 17 yield periods obtained during the predevelopment phase of gasification research. The mini-fluid bed data were determined at approximately the 10% carbon conversion level of each reactor charge. Each point shown in the figure is an average value calculated from two or more runs. These results indicate that carbon gasification rates measured in the mini-fluid bed reactor are higher than those measured in the FBG. This is probably due to the lower pressure in the mini-fluid bed reactor which favors the carbon gasification thermodynamics. In both the FBG and the mini-fluid bed, the gasification rate increases with potassium-to-carbon molar ratio (K/C).

The reactant flow conditions used in the FBG operations were different from those selected for the commercial study design (SD) because of the pressure difference between the two units. Figure 4.1-2 shows gasification rates obtained in the mini-fluid bed reactor at FBG and SD conditions. The higher gasification rates obtained under SD conditions are a result of the greater steam flow rate and lesser syn gas flow rate to the reactor under SD conditions (see Figure 4.1-2 for actual values).

The effect of hydrogen inhibition on the carbon gasification rate of steady state char was also investigated. For this study, a high steam flow rate to the reactor (5.0 moles steam/ hr per mole carbon initially in the reactor) was used to ensure that the reaction was not equilibrium limited. Gasification rate data was obtained both with and without hydrogen feed to the unit. When hydrogen was used, its flow rate was chosen to match the SD hydrogen/steam feed ratio. The results of this study are shown in Figure 4.1-3. The data indicate that the addition of hydrogen to the gasification reactor reduces the carbon gasification rate by approximately 20-35%.

In order to evaluate the effect of high catalyst loadings on the gasification behavior of these steady-state chars, additional potassium hydroxide catalyst was added to the FBG char whose K/C ratio was 0.12. Two char samples were prepared in this fashion. The K/C values for these chars were approximately

FIGURE 4.1-1

MINI-FLUID BED GASIFIER GIVES HIGHER GASIFICATION RATES THAN FBG

OPERATING CONDITIONS

1300°F

$$0.53 \ \frac{\text{Mole } H_2O/\text{Hr}}{\text{Mole Carbon in Reactor}}$$

$$1.54 \ \frac{\text{Moles Syn Gas/Hr}}{\text{Mole } H_2O/\text{Hr}}$$

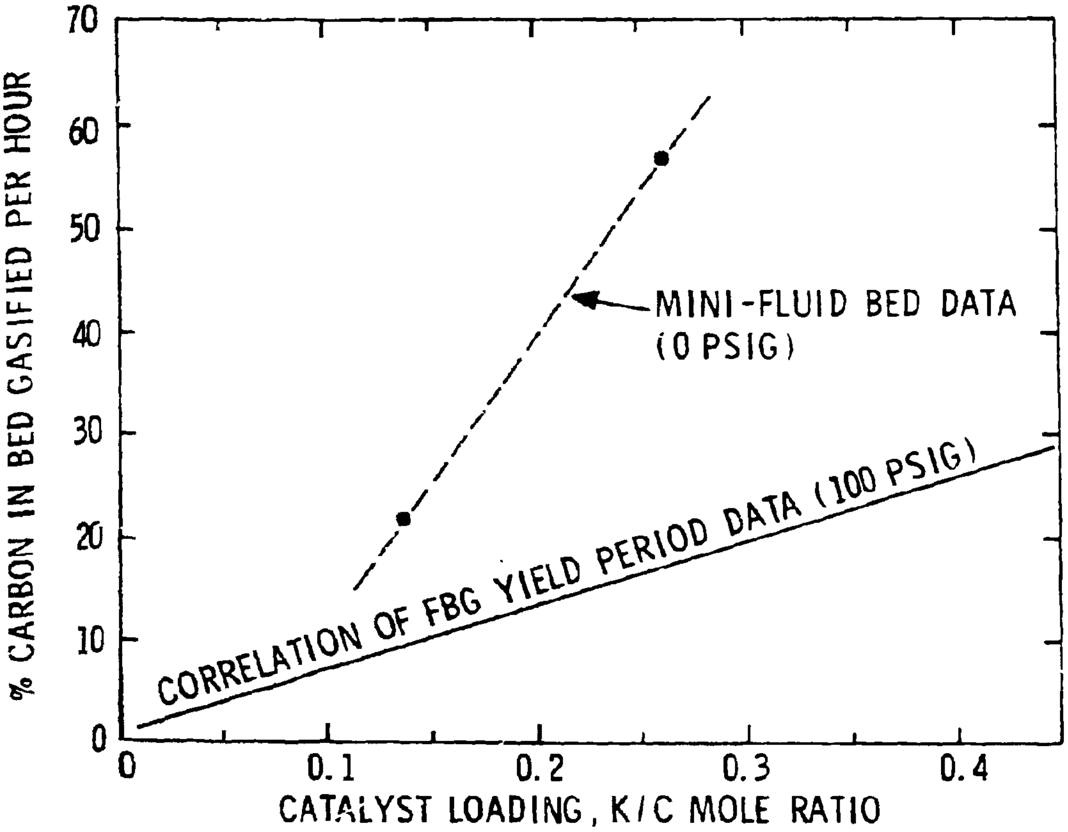

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FIGURE 4.1-2

HIGHER GASIFICATION RATES MEASURED UNDER SD CONDITIONS THAN UNDER FBG CONDITIONS

1300°F; 0 PSIG

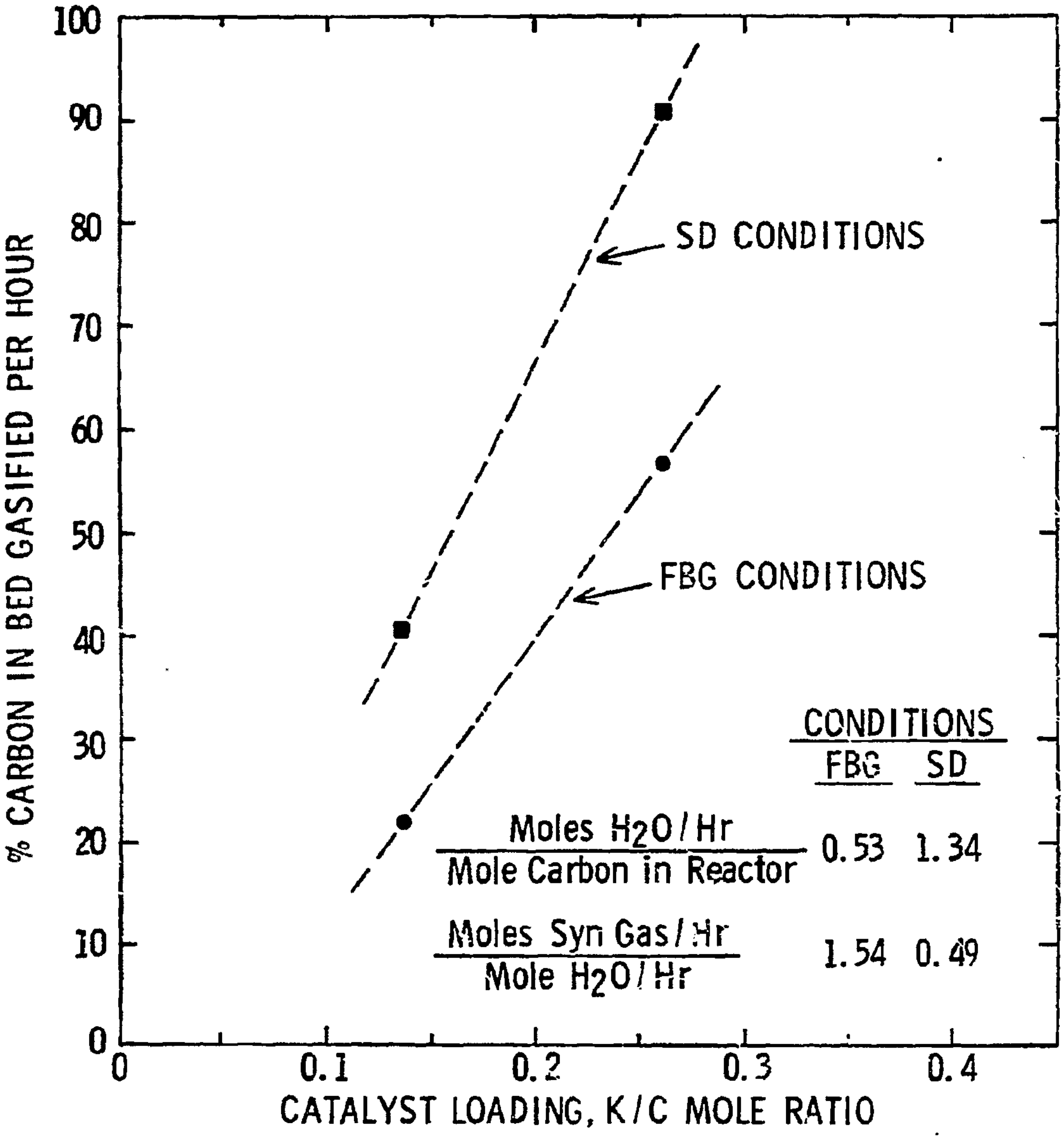
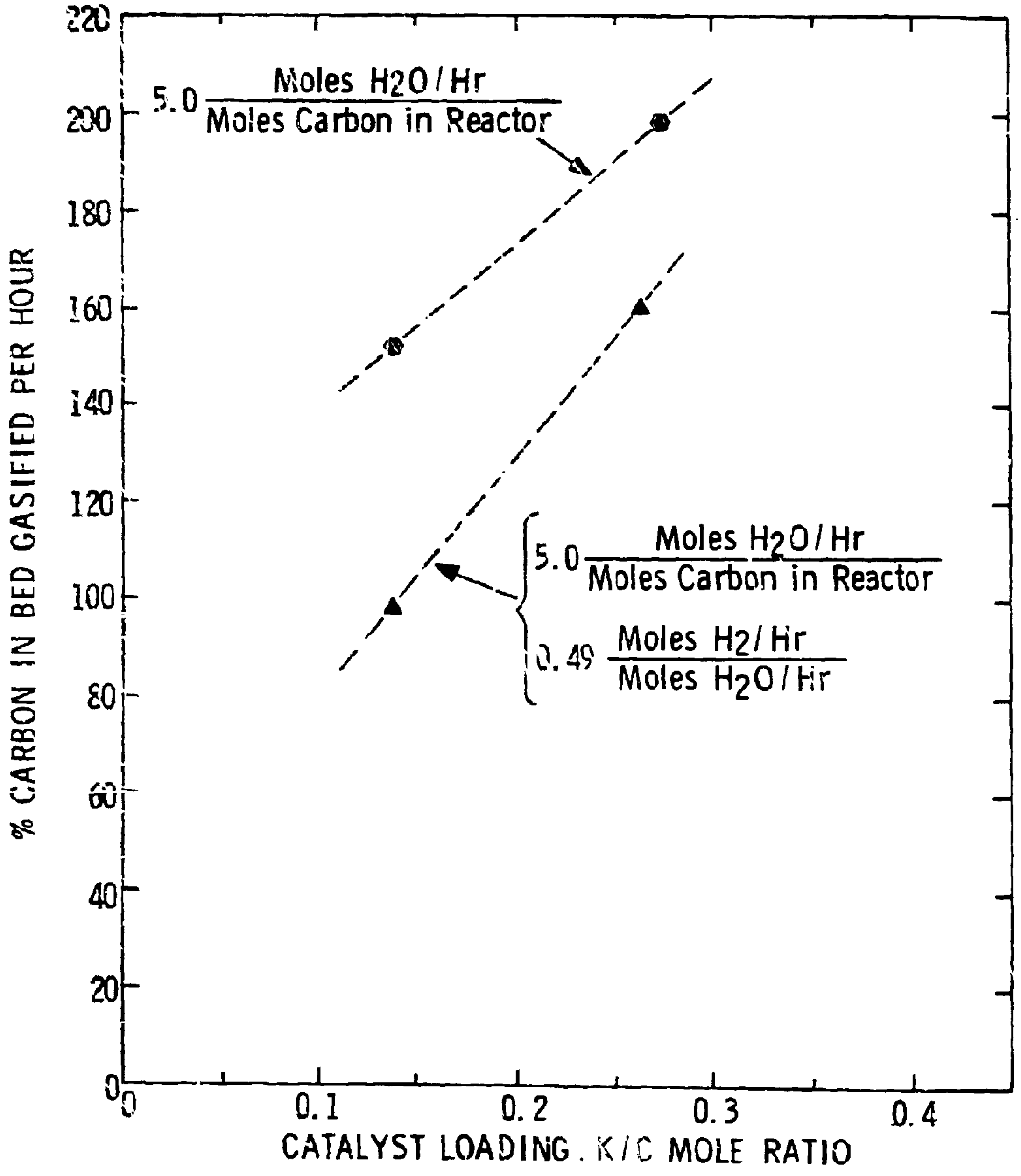


FIGURE 4.1-3

ADDITION OF HYDROGEN REDUCES GASIFICATION RATE BY 20-35%

1300°F; 0 PSIG



0.4 and 0.6. Unfortunately, these chars could not be fluidized at reaction conditions even at high argon flow rates. The char particles agglomerated in the reactor and gas channelling was observed. This agglomeration is believed to be due to the presence of molten potassium hydroxide at the reaction temperature of 1300°F.

To circumvent this problem, potassium carbonate was used to impregnate the same original FBG char to a K/C loading of 0.4. At 1300°F, potassium carbonate is still in the solid phase and, thus, agglomeration should not occur. Initial tests indicate that good fluidization can be obtained, but only with an argon flow rate approximately three times that required to fluidize the original FBG char. Apparently, the K_2CO_3 impregnated char particles are more dense than the original char particles. Mini-fluid bed runs with the K_2CO_3 impregnated char are planned to assess the kinetic effect of the additional catalyst.

4.2 Catalyst Reactions with Coal and Ash

As reported in the October-December, 1978 Quarterly Report the Fluid Bed Gasifier (FBG) had been operated successfully during the predevelopment contract (1977) on a feedstock of potassium carbonate (K_2CO_3) catalyzed Illinois No. 6 coal. During the last quarter of 1978, operation with a new carload of Illinois No. 6 coal and with potassium hydroxide (KOH) as the catalyst was accompanied by some initial operability problems as well as a lower fluidized bed density than was experienced in the predevelopment work. Operations were improved by removing the large (+16 mesh) particles from the feed coal and fluidized bed density was increased by exposing the catalyzed coal to air prior to loading in the FBG. As a result of this experience, bench scale studies were initiated to address questions involving the effect of variables in catalyst impregnation on both agglomeration and the bulk density of the devolatilized coal.

Effect of Soak Time on Catalyst Distribution

Previously reported analytical data (October-December, 1978 Quarterly Report) shows that the large (+20 mesh) particles in the 1978 FBG feed coal had a lower catalyst loading than the remainder of the feed. Laboratory chars prepared from these particles showed a high degree of agglomeration. However, agglomeration was no longer observed when the large (+20 mesh) particles were impregnated separately to ensure proper catalyst loading (July, 1978 - June, 1979 Annual Report). Since it is desirable to use larger size particles in a commercial gasifier feed than the -16 + 100 mesh range that is currently used in the PDU, a study was designed to test the effect of increasing the length of time the catalyst solution is in contact with the coal before drying on the uniformity of catalyst distribution.

Table 4.2-1

Effect of Increased Contact Time on KOH Impregnation of Coal

Contact Time (hr)	-100 Mesh	-60+100 Mesh	-20+60 Mesh	-8+20 Mesh
1	12.72	14.66	15.50	12.12
8	14.20	15.32	15.27	10.97
16	13.64	13.40	14.50	13.70
24	14.19	14.31	14.80	13.53

The data in Table 4.2-1 were obtained using dried Illinois No. 6 coal and a 33% KOH solution. Samples of coal were treated with catalyst solution, allowed to stand under nitrogen for the specified contact time, and then dried in a vacuum oven at 100°C.

The data indicate that for a laboratory prepared sample, increasing the contact time to 16 hours causes some improvement in uniformity of catalyst distribution on particles of all sizes. However, all of the laboratory samples have a more uniform catalyst loading than the samples prepared by the FBG Catalyst Addition Unit. This suggests that adjusting the contact time would be of little benefit for catalyst impregnation of Illinois coal and effective mixing in the catalyst addition unit should be more important. Therefore, no further work is planned in the area of contact time and catalyst impregnation in the bench scale program.

Char Density

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. A small fluidized bed reactor is being used for this study (April, 1979 Monthly Report). The unit simulates coal addition to a hot, fluidized bed gasifier in all respects except pressure conditions.

Shakedown runs have indicated that the original nitrogen entrained feed system is not suitable for feeding raw coal into the hot bed. The feed line becomes sufficiently hot that the coal begins to react and the line plugs. However, feeding coal directly into the top of the reactor appears to simulate pilot unit production of char. Uncatalyzed Illinois coal agglomerated as expected, and coal catalyzed with 15% K_2CO_3 and exposed to air at ambient temperature for 64 hours did not agglomerate. The density of the latter char was 0.38 g/cc. This value is comparable to the high density char produced in the FBG at low carbon conversions during the predevelopment contract.

In order to determine whether air exposure or catalyst form was responsible for the high density char, data was obtained using Illinois No. 6 coal catalyzed with KOH and oxidized to varying degrees. Thus, samples of -20+60 mesh Illinois coal were catalyzed with KOH, dried, and exposed to air by blowing air through a packed bed of coal. Each sample was rehomogenized after air exposure to prevent anomalous results due to sampling errors. A 10g aliquot was then devolatilized in the fluidized bed pyrolyzer. The results, shown in Figure 4.2-1, indicate that exposure to air increases the density of chars produced from KOH catalyzed Illinois coal. This result agrees with pilot unit experience.

Since KOH is known to react with CO_2 to form K_2CO_3 and water, it was not clear from these data alone whether it was O_2 or CO_2 which caused the high density char. Therefore, K_2CO_3 catalyzed coal was studied to learn if CO_2 pretreatment rather than oxidation would be sufficient to produce a high density char from KOH catalyzed coal. It is desirable to avoid oxidation if possible since oxidation may adversely affect the sulfur forms present in recycled catalyst. The results of this study are shown in Figure 4.2-2.

The data indicate that oxidation is required to produce a high density char from K_2CO_3 catalyzed coal. This also demonstrates that oxidation of KOH catalyzed coal, not reaction of KOH with CO_2 to form K_2CO_3, is responsible for the increase in densities shown in Figure 4.2-1.

Further studies will quantify the extent of oxidation required under conditions simulating those used in the catalyst addition unit of the PDU. Modification of catalyst addition procedures will also be studied.

4.3 Catalyst/Char Equilibrium Studies

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

Bench scale studies are in progress to determine the effects of variable pH and potassium ion concentration on the amount of catalyst remaining on the char. The equilibrium concentration of potassium on digested char, undigested char, and fines will be determined as a function of potassium concentration in solutions of constant pH and as a function of the pH of solutions of constant potassium concentration. Data have been obtained at room temperature for all three types of solids over a potassium concentration range of 0.4-15 wt.% aqueous K^+. In these experiments, the pH was varied by changing the relative amounts of KOH and KCl in solution for a fixed concentration of total K^+.

The data for 0.4 wt.% K^+ solutions are presented in Figure 4.3-1. The results indicate that at the upper end of the pH range studied, K^+ absorption is dependent on pH. For all three types of solids, the K^+ absorbed

FIGURE 4.2-1

CHAR DENSITY INCREASES WITH AIR EXPOSURE FOR KOH CATALYZED COAL

- ILLINOIS #6 COAL
- 12% KOH CATALYZED
- -20 + 60 MESH
- AIR EXPOSED AT AMBIENT TEMPERATURE

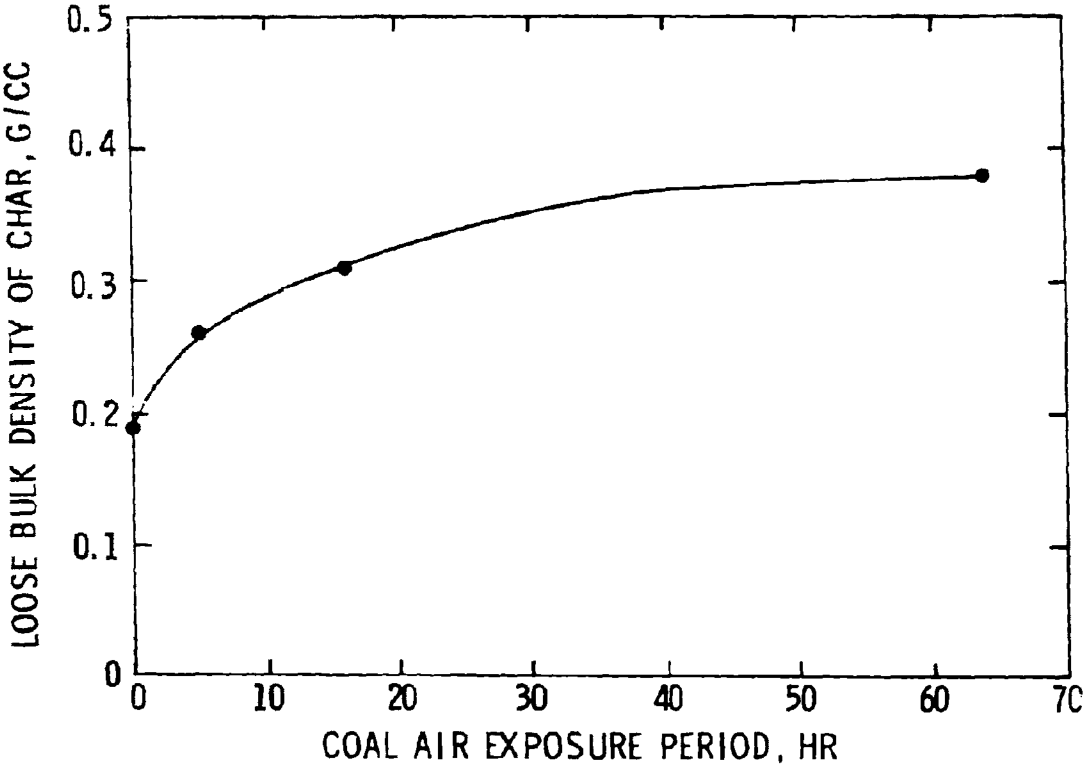


FIGURE 4.2-2

CHAR DENSITY INCREASES WITH AIR EXPOSURE FOR K_2CO_3 CATALYZED COAL

- ILLINOIS #6 COAL
- 15% K_2CO_3 CATALYZED
- -20 + 60 MESH

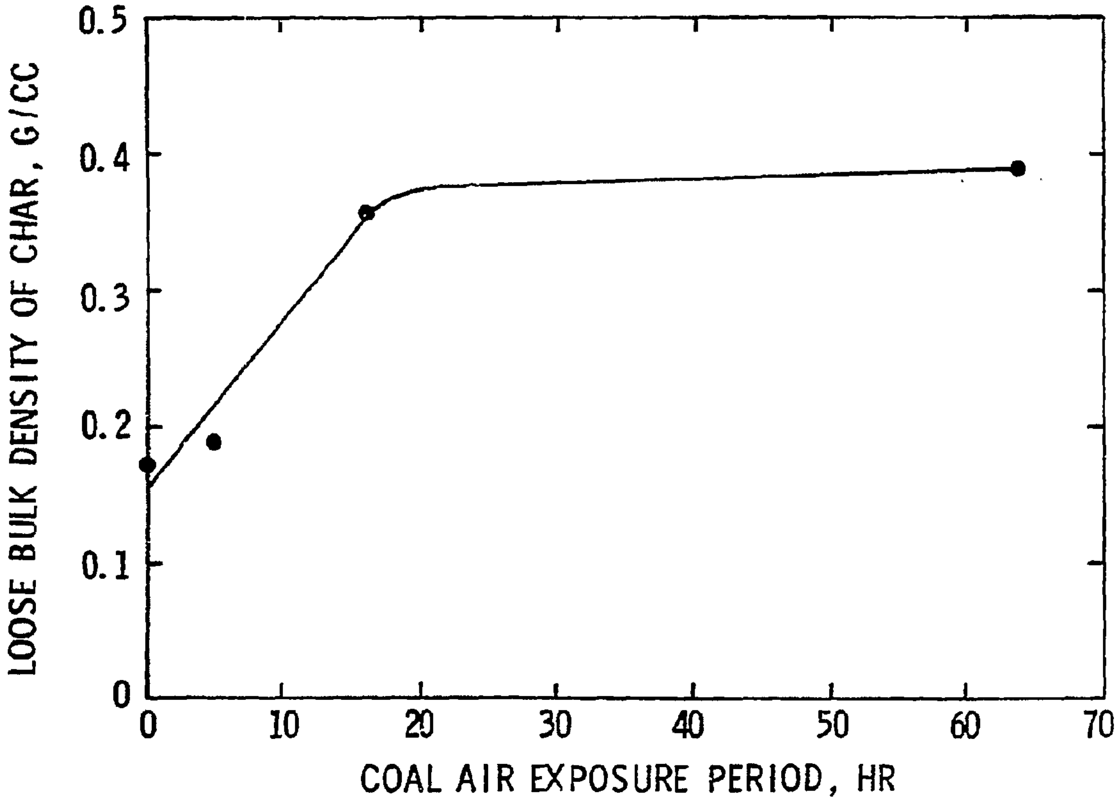


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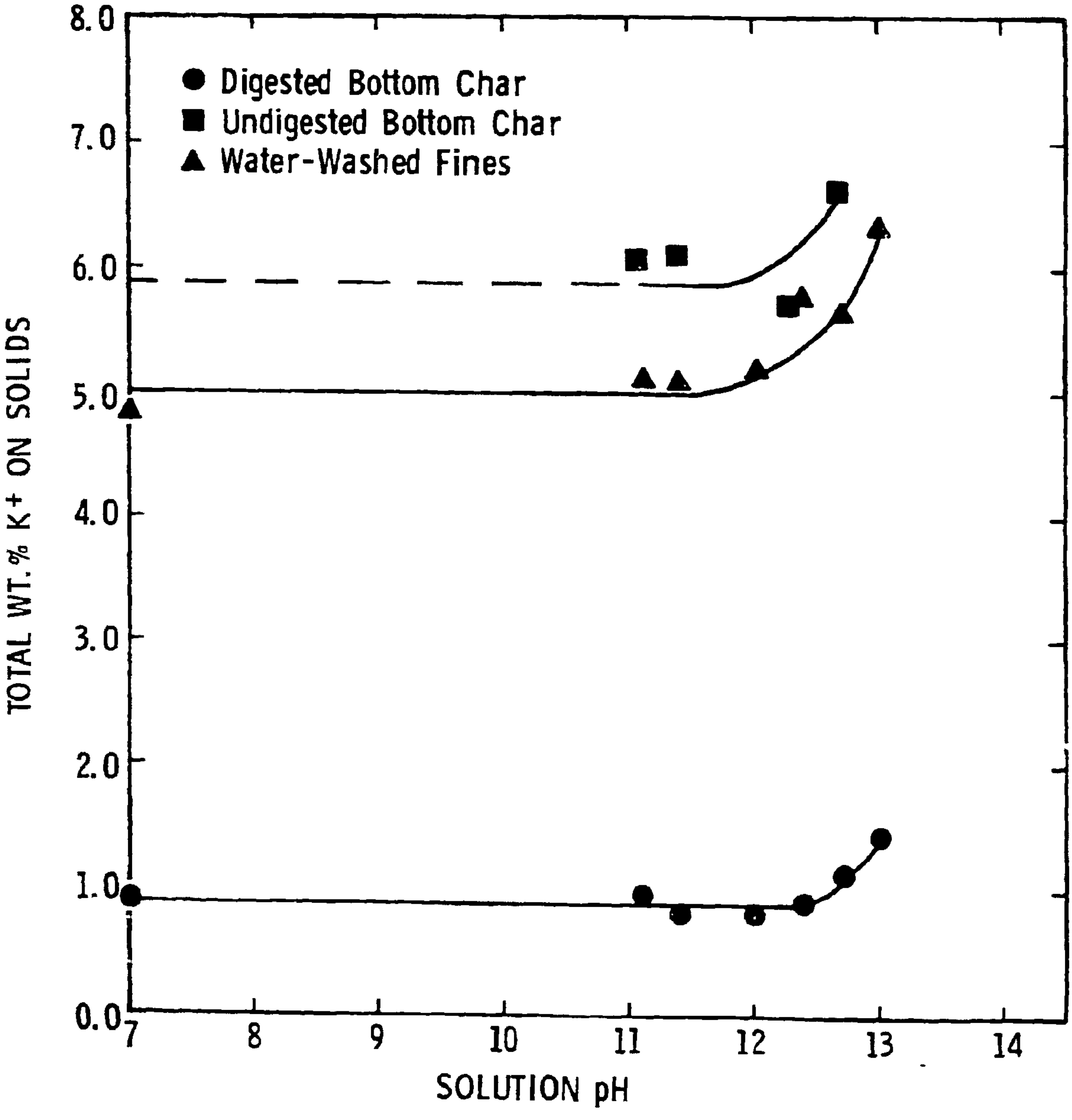
FIGURE 4.3-1

EQUILIBRIUM K^+ ABSORBED ON SOLIDS INCREASES AT HIGH pH

- 24°C
- 0.1 M K^+ (0.4 WT.%)
- KOH + KCl
- FBG Chars



increases with increasing pH from about a pH of 11.5. The total K^+ concentration is lowest for the digested solids due to the absence of K^+ tied up with mineral matter in the char. The small difference between the fines and the undigested char is due to a difference in carbon conversion. The fines have a lower carbon conversion than the bottom char; therefore, the same quantity of K^+ tied up with the mineral matter will appear as a lower weight percentage.

Since less K^+ is absorbed by the char at pH values below 11.5, leaching or other water wash operations may be performed more efficiently in solutions whose pH has been lowered. This might be accomplished by contacting the solutions with the acid gas mixture separated from the gasification product gas.

Figure 4.3-2 contains data obtained under the same conditions for two different K^+ concentrations. The data indicate that for digested solids, an increase in potassium concentration in solution from 0.1M to 1.0M (0.4 wt.%K to 4.0 wt.% K^+) causes no increases in K^+ absorption on the solids. This would mean that a leaching system does not need to operate at very low concentrations on the lean end in order to maximize K^+ recovery.

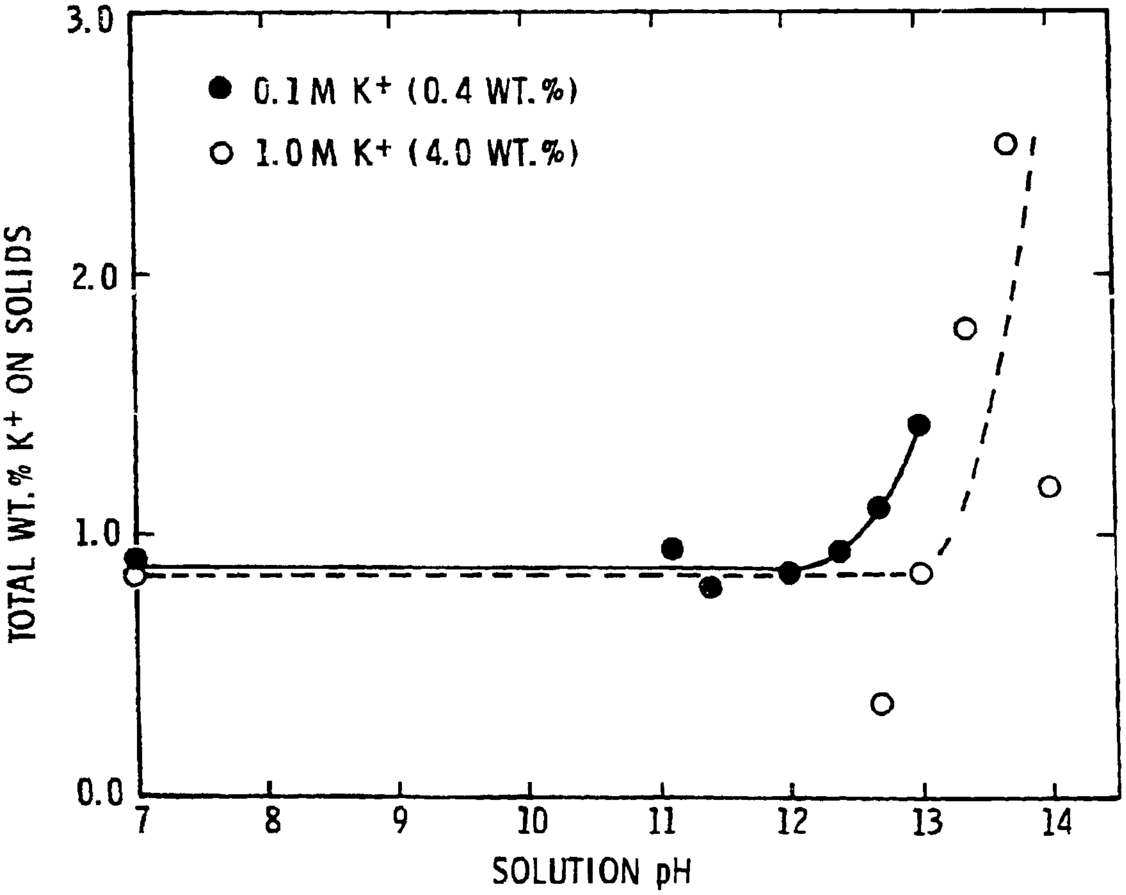
However, the scatter in the 1.0M data and problems observed in obtaining reproducible analytical results at still higher concentrations of K^+ cause the above conclusions to be tentative. Further analyses are in progress.

As mentioned above, all of the results shown were obtained by changing the relative amounts of potassium chloride and potassium hydroxide in solution as a method of pH variation. Since chloride ion will not be a major component of a recovered catalyst solution, further studies are in progress using potassium carbonate-potassium hydroxide mixtures to vary the pH. Elevated temperature studies are also planned.

FIGURE 4.3-2

EQUILIBRIUM K^+ ABSORBED ON DIGESTED SOLIDS SHOWS NO CONCENTRATION DEPENDENCE

- 24°C
- Digested FBG Char
- KOH + KCl



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 July, 1980.

5.1 Cost Reduction and Laboratory Guidance Studies

Integral Steam Reformer Heat Input Study

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

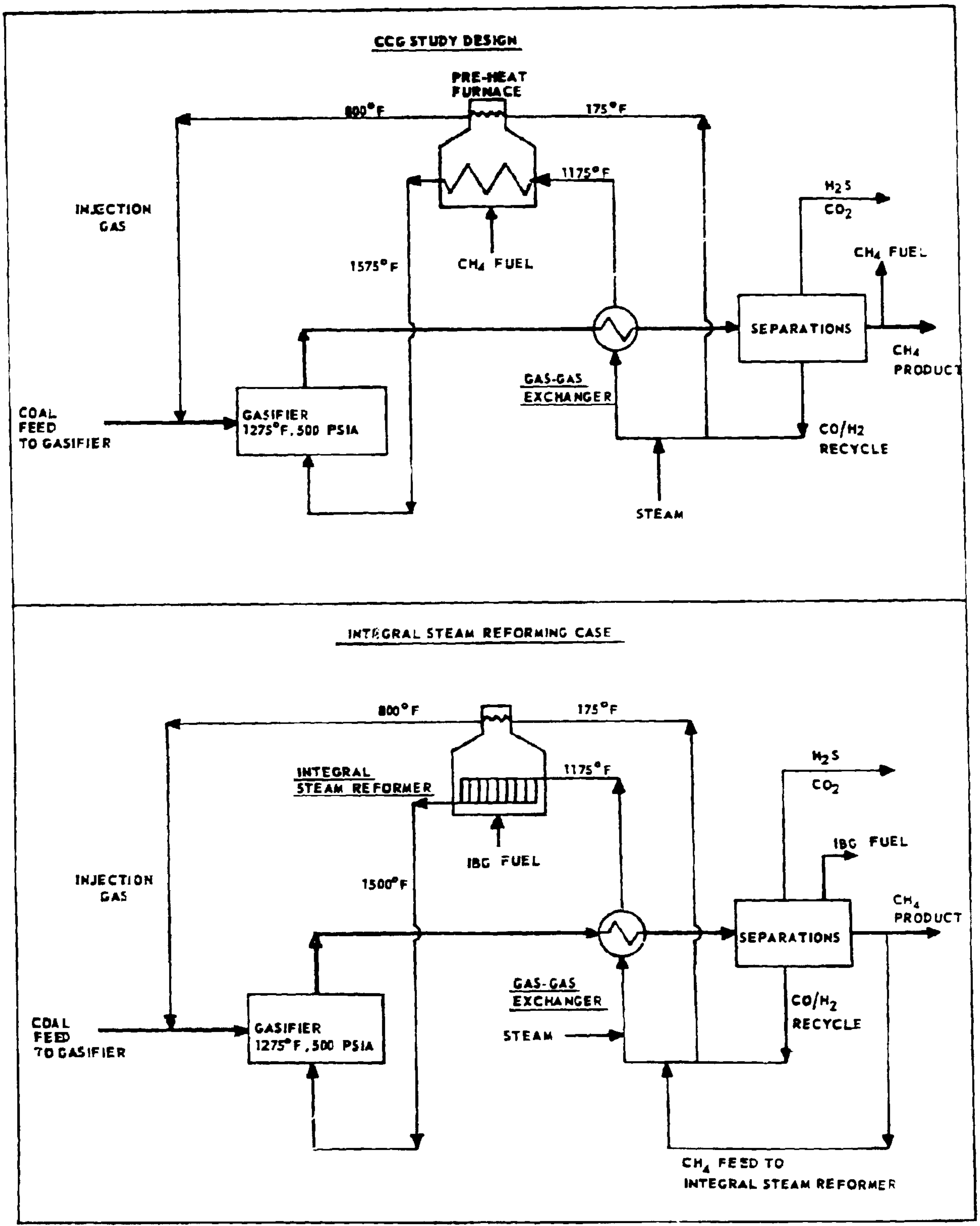
$$\text{Coal} + H_2O \rightarrow CH_4 + CO_2 \qquad \Delta H \simeq 0$$

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

In the 1977 CCG Study Design, this heat input was supplied by heating the steam and recycle gas in a furnace to 1540°F. This preheat is sufficient to provide for the heat input requirements listed above. The preheat furnace design temperature was set at 1575°F to allow for operating flexibility and control. A schematic flow plan for this system is shown in Figure 5.1-1.

FIGURE 5.1-1

INTEGRAL STEAM REFORMING HEAT INPUT STUDIES - SIMPLIFIED SCHEMATIC FLOW PLAN



CCG STUDY DESIGN

INTEGRAL STEAM REFORMING CASE

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

The objective of the current study was to consider the Integral Steam Reformer in greater depth using the CCG Study Design basis. A schematic flow plan for this system is shown in Figure 5.1-1. As discussed in the July, 1978 - June, 1979 Annual Technical Progress Report, several screening studies were carried out to arrive at the final basis which was used for this study. Several alternative processing conditions were evaluated including a range of steam reformer coil outlet temperatures and steam conversions. The important basis items selected as a result of these screening studies are as follows: 1500°F reformer coil outlet temperature, 48% steam conversion, the use of intermediate Btu gas taken from the gasifier product gas stream after sulfur removal as fuel for the reformer, and the use of a small stream of product SNG for process control.

Two final material and energy balances were prepared: a normal balance and a design balance. The bases for the two balances are identical except that, for the design balance, the gasifier heat input requirement is increased by 40 MBtu/hr over calculated requirements to provide an allowance for control of gasifier temperature. This allowance is met by increasing the methane feed and the fuel to the integral reformer in the design case relative to the normal case. These material and energy balances differ from balances developed for the process basis screening studies because the final integral reformer design was used rather than a preliminary design. The design balance was used to develop investments for different sections of the plant by proration from the CCG Commercial Plant Study Design. The normal balance was used to define the plant operating costs. The results of these two balances are summarized below.

	Normal	Design
Coal Feed to Gasifier, ST/SD	14,490	14,490
Gasifier Temperature, °F	1,275	1,275
Raw Gasifier Product Rate, lb-moles/hr	136,600	138,100
Recycle Gas Rate, lb-moles/hr	46,200	46,500
Coil Outlet Temperature, °F	1,500	1,500
Reformer Furnace Duty, MBtu/hr	540	610

As shown above, the inclusion of the gasifier temperature control allowance adds about 1% to the plant gas flow rates and increases the duty of the integral reformer furnace by about 13%. The reformer furnace duty for the design case increases by 70 MBtu/hr compared to the normal case even though the gasifier heat input requirement was increased by only 40 MBtu/hr. In order to increase the radiant duty of the reformer by 40 MBtu/hr, it is necessary to increase the convection section duty by 30 MBtu/hr as well.

A comparison of the Integral Steam Reformer case with the CCG Study Design is shown below:

	Summary of Major Material And Energy Balance Effects	
	CCG Study Design	Integral Steam Reformer Case
Coal Feed to Gasifier, ST/SD	14,490	14,490
Coil Outlet Temperature (COT), °F	1,575	1,500
Normal Furnace Duty, MBtu/hr	485	540
Raw Gasifier Product Rate, lb-moles/hr	159,000	136,600
Recycle Gas, lb-moles/hr	57,500	46,200
Offsite Steam Demand, lb-moles/hr	60,000	46,000
Overall Steam Conversion, %	41	48
Net SNG to Sales, GBtu/SD	256.9	256.2
Relative Gasifier Volume	100	122

The offsite steam requirement is reduced by about 23% for the integral reformer because of the lower steam feed rate to the gasifier for this high steam conversion case. The reduction in recycle rate of 11,300 lb moles/hr is a result of the removal of IBG fuel from the first stage of Acid Gas Removal and higher steam conversion. The gasifier volume increased by 22% as a result of the higher steam conversion.

The investment for all plant facilities excluding the steam reformer was obtained by proration of individual plant sections from the CCG Study Design. The investment for the steam reformer was estimated in detail based on a study design for the furnace. The investment for the Integral Steam Reformer Case and a comparison with the Study Design is presented in Table 5.1-1. The reactor system increased in investment by 12 M$ because of the increased gasifier volume required for higher steam conversion. The steam reformer investment is 14 M$ lower than the Study Design preheat furnace investment because of the lower coil outlet temperature and a revised furnace design for the different service. The reduction in the offsite steam requirement resulted in a 12 M$ reduction in steam generation facilities investment. Overall, the investment for the Integral Steam Reformer case is 4% lower than the CCG Study Design investment.

The gas cost developed for the Integral Steam Reformer case is presented in Table 5.1-2 and is summarized below and compared to the CCG Study Design.

TABLE 5.1-1

INTEGRAL STEAM REFORMER HEAT INPUT STUDY

INVESTMENT FOR PIONEER PLANT

Basis: • January, 1978 Instant Plant
• Eastern Illinois Location

Plant Section	Investment Breakdown - Million $	
	CCG Study Design	Integral Steam Reformer Case
ONSITES		
Coal Drying	27	27
Catalyst Addition	18	18
Preheat Furnace/Steam Reformer	51	37
Reactor System	146	158
Product Gas Cooling and Scrubbing	86	76
Sour Water Stripping and Ammonia Recovery	20	18
Acid Gas Removal and Sulfur Recovery	161	151
Methane Recovery System	44	43
Refrigeration	31	30
Catalyst Recovery	39	39
Common Onsite Facilities	55	55
ONSITES SUBTOTAL	678	652
MATERIALS HANDLING		
Coal Handling Storage	19	19
Coke/Char Handling	5	6
Chemicals Handling and Storage	20	19
By-Products Storage and Shipping	3	3
Waste Solids Handling and Disposal	27	27
MATERIALS HANDLING SUBTOTAL	74	74
UTILITIES		
Raw Water/BFW Treating	29	27
Steam Generation and Distribution	120	108
Cooling Water	9	9
Electric Power Distribution	23	22
Miscellaneous Utilities	5	5
Flue Gas Desulfurization (1)	51	49
UTILITIES SUBTOTAL	237	220
GENERAL OFFSITES		
Wastewater Treating	48	47
Safety and Fire Protection	13	12
Site Preparation	6	6
Miscellaneous Offsites	34	34
GENERAL OFFSITES SUBTOTAL	101	99
TOTAL DIRECT AND INDIRECT COSTS	1,090	1,045
PROCESS DEVELOPMENT ALLOWANCE (25% of Onsites Direct & Indirect Costs)	169	163
PROJECT CONTINGENCY (25% of Total Direct & Indirect Costs)	271	262
TOTAL ERECTED COST	1,530	1,470

Note:

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

TABLE 5.1-2

INTEGRAL STEAM REFORMER
HEAT INPUT STUDY

COST OF SNG FROM PIONEER PLANT WITH 100% EQUITY FINANCING

Basis:
- **January, 1978 Instant Plant, Eastern Illinois Location**
- **256.2 Billion Btu/Stream Day SNG (HHV Basis)**
- **90% Capacity Factor**
- **100% Equity Financing**
- **15% Current Dollar DCF Return**
- **Escalation Rates:**
  - **Operating Costs and By-Product Revenues at 5%/Year**
  - **SNG Revenues at 6%/Year**
- **Total Erected Cost of 1,470 M$**

SNG Cost Components	Requirements (At Full Capacity)	Unit Costs (1978)	SNG Cost Breakdown - $/Million Btu (1978)
• Illinois No. 6 Coal (Cleaned)			
- To Gasifiers	14,490 ST/SD (2)	20 $/ST	1.131
- To Coal Dryer Fuel	710 ST/SD	20 $/ST	0.055
- To Offsite Boiler Fuel	2,620 ST/SD	20 $/ST	0.205
Subtotal	17,820 ST/SD		1.391
• Major Chemicals			
- KOH Solution (30 wt %)	189 ST/SD (Contained)	300 $/ST	0.221
- Lime (90% CaO) to Catalyst Recovery	1,005 ST/SD	39 $/ST	0.153
- Lime (90% CaO) to FGDS	247 ST/SD	39 $/ST	0.038
Subtotal			0.412
• Other Operating Costs			
- Purchased Electric Power	141 MW	2.5 ¢/kWh	0.330
- Raw Water	5,000 gpm	15 ¢/k gal	0.005
- Other Catalysts and Chemicals	Many Items	4.7 M$/yr	0.053
- Wages and Benefits	950 Men	21 k$/man/yr	0.237
- Salaries and Benefits	250 Men	25 k$/man/yr	0.074
- Labor Overheads and Supplies	20% of Wages, Salaries, and Benefits		0.062
- Materials and Overheads	3.3% of Total Erected Cost/Year		0.576
- Ash Disposal	8,300 ST/SD (Wet)	1 $/ST	0.032
Subtotal			1.369
• By-Product Revenues			
- Ammonia (20 wt %)	231 ST/SD (Contained)	160 $/ST	(0.144)
- Sulfur	324 LT/SD (2)	25 $/LT	(0.032)
Subtotal			(0.176)
• Capital Charges	Per Above Basis		2.989
TOTAL SUBSTITUTE NATURAL GAS COST (RISP) (3)			5.985
CALL			5.99

Notes:

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

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

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

	SNG Cost, $/MBtu	
	CCG Study Design	Integral Steam Reformer Case
Illinois No. 6 Coal	1.41	1.39
Major Chemicals	0.41	0.41
Utilities	0.35	0.34
Other Operating Costs	1.08	1.04
By-Product Revenues	(0.18)	(0.18)
Capital Charges (15% DCF)	3.11	2.99
Total SNG Cost (RISP)	6.18	5.99
Savings		3.1%

The economic basis is the same as that for the CCG Study Design. Based on the same coal feed rate to the gasifier, a gas cost of 5.99 $/MBtu was obtained for the Integral Steam Reformer Study. This is a 3% reduction in the gas cost relative to the CCG Study Design. The gas cost reduction is the result of lower plant investment and a slight reduction in coal requirements. The inclusion of a reformer in place of a preheat furnace in the CCG process increases the overall heat input flexibility and thus permits process improvements such as higher steam conversion and the use of IBG for furnace fuel. The gas cost reduction of 3% is mainly a result of these process improvements rather than the integral reformer itself.

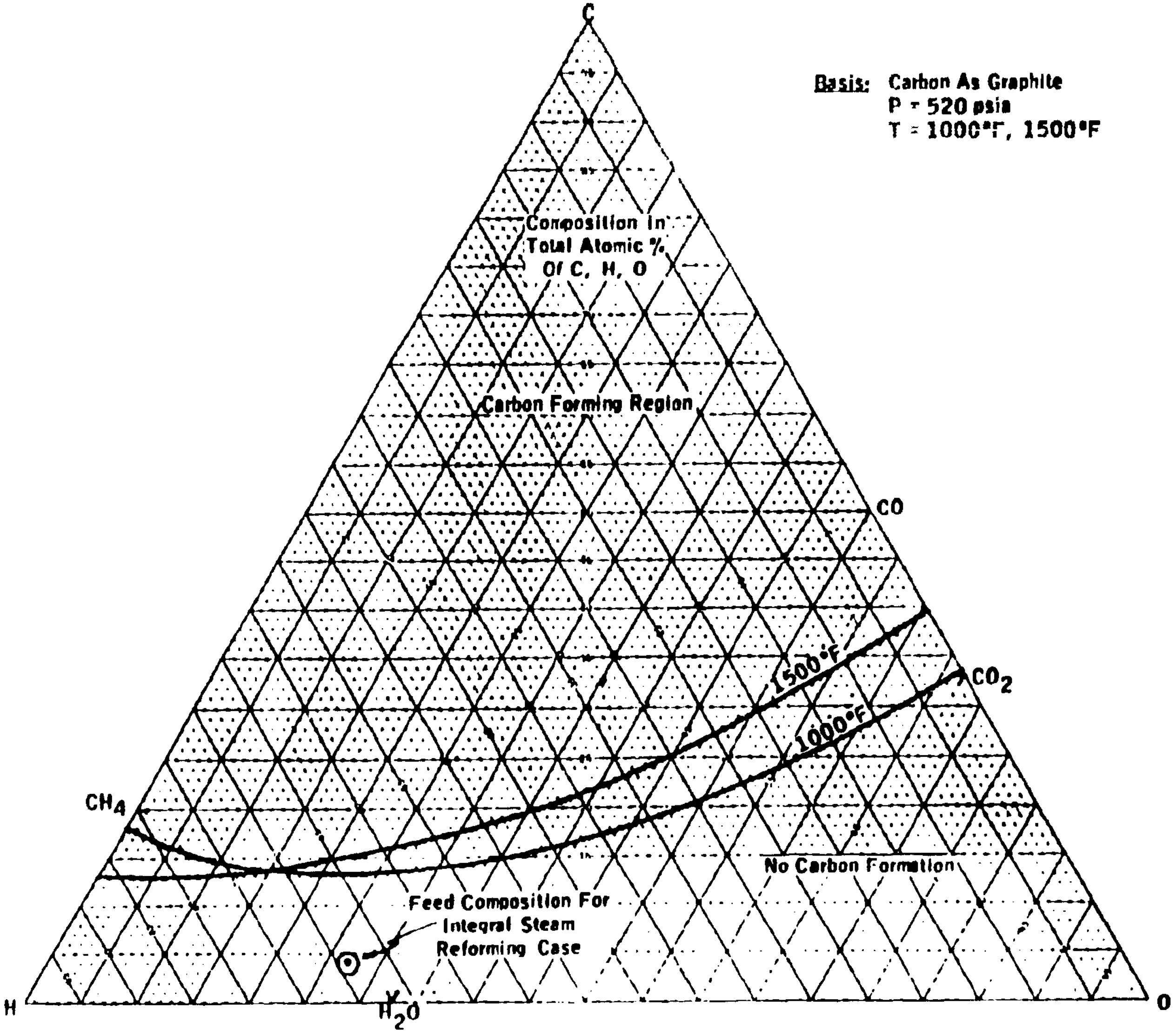
During the process variable studies for the Integral Reformer Study, the potential for carbon formation and laydown on the steam reforming catalyst or upstream equipment was identified as a key data need for the integral steam reformer system. Carbon laydown could result in reformer catalyst deactivation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

$$\begin{aligned} 2CO &\rightarrow CO_2 + C \\ CO + H_2 &\rightarrow H_2O + C \\ CH_4 &\rightarrow 2H_2 + C \end{aligned}$$

Figure 5.1-2 shows the equilibrium curves which define the carbon formation region for C-H-O atomic compositions at 1000°F and 1500°F at 520 psia. The composition of the reformer feed stream on this basis is: 4 mole % carbon, 69 mole % hydrogen, and 27 mole % oxygen. This point is shown on Figure 5.1-2 and is clearly out of the carbon formation region. Thus, with the high steam to carbon ratios for the integral reformer process conditions, equilibrium conditions are not favorable for carbon formation. However, the feed to the integral reformer is <u>not</u> in chemical equilibrium. Thus, it is possible that a non-equilibrium situation may exist in which carbon is laid down (for instance

FIGURE 5.1-2

CARBON FORMATION EQUILIBRIUM ISOTHERMS



Basis: Carbon As Graphite
P = 520 psia
T = 1000°F, 1500°F

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by the reaction $2CO \rightarrow CO_2 + C$) at a rate faster than it can be gasified away by the steam-carbon reaction ($C + H_2O \rightarrow CO + H_2$). Though solid carbon cannot be present at equilibrium, it is possible that it could exist during the time the species are reacting to reach equilibrium. Thus, kinetics of the competing reactions could be important.

Recent data from bench-scale research on Gas Phase Reactions (see Section 1.3 of this report) have shown that carbon laydown can occur in a gas stream with compositions similar to those envisioned commercially for integral reformer feed. However, this research was directed at studies of the shift reaction, and conditions were not commercially representative for carbon laydown in terms of residence times, wall effects, etc. These factors can affect the kinetics of the competing reactions. More representative experiments directed at the issue of carbon laydown are planned as part of the Engineering Technology Studies under the contract. This work will address the issue of carbon formation and, if necessary, explore ways to avoid it.

In the current Integral Reformer Study, it is assumed that carbon laydown does not occur. The observation of carbon laydown in the laboratory was made at the same time that the process basis was set for this study. Approaches for dealing with carbon laydown are being investigated. One potential method for minimizing or eliminating carbon formation upstream of or in the integral steam reformer is to shift a part of or all of the CO to CO_2. For instance, if all the CO were shifted to CO_2, carbon formation via the reaction $2CO \rightarrow CO_2 + C$ would not be possible. A material and energy balance was developed to determine the general impacts of this potential method of avoiding carbon formation. In this case, a shift reactor was added upstream of the integral reformer heat input system. The extent of the shift reaction was set so that 2% of the steam/recycle gas mixture would be CO_2. Directionally, shifting a portion of the gas should reduce the possibility of carbon formation. The basis of 2% CO_2 in the feed to the steam reformer represents a compromise. As more gas is shifted and shift equilibrium is approached, the possibility of carbon formation from CO reversion is reduced. However, increasing the extent of the shift reaction increases the fuel requirement of the integral reformer. Because the shift reaction is exothermic and because the inlet temperature to the integral steam reformer is set at 1175°F by the outlet temperature of the gas-gas exchanger, the chemical heat released in the shift reactor must be made up in the integral steam reformer. This is illustrated in the following table:

	Reformer Without Shift	Reformer With Shift
Heat of Shift Reaction, MBtu/hr	--	-40
Reformer Furnace Duty, MBtu/hr	540	580

Results of the material and energy balance show a 7% increase in the reformer fuel requirement. This translates into a 0.5% reduction in the net SNG product. There were no major changes in gas rates to processing equipment.

It is concluded from this work that altering the composition of the reformer feed gas stream via the shift reaction may be an economical method of preventing carbon formation. The economics of this approach will depend on the extent to which the gas must be shifted.

Two other alternatives for preventing carbon laydown have been identified. The first method is similar to the one described above. It consists of CO_2 injection into the reformer feed to alter the CO_2/CO ratio to prevent carbon laydown by the reaction $2CO \rightarrow CO_2 + C$. The second method consists of replacing the integral reformer with a small conventional steam reformer operated in parallel with a preheat furnace. This small supplemental reformer would feed SNG and steam and thus carbon laydown would not be a problem. The preheat furnace coil outlet temperature could be lowered to reduce its investment and the injection of a small amount of a sulfur compound could be used to prevent carbon laydown as in the study design base case. As stated above, it has been assumed for the current evaluation of the integral reformer that carbon laydown does not occur. Representative experiments directed at the issue of carbon laydown are planned as part of the Engineering Technology Studies under the contract. The economic impact of alternatives to prevent carbon laydown will also be evaluated in future studies.

Gas Separation Screening Studies

A unique part of the Catalytic Coal Gasification process is the methane recovery system where product methane (SNG) is separated from a recycle stream consisting mainly of CO and H_2. Prior to this separation, it is necessary to remove components that could freeze at low temperature. After bulk removal of H_2S and CO_2 in a selective heavy glycol solvent absorption system, trace components are removed by adsorption on activated carbon and molecular sieves. The clean gas is then fed to methane recovery.

In the CCG Study Design, information supplied by a vendor was used for design of the acid gas removal system. The information was of screening quality and was not optimized for the specific application to CCG. The methane recovery separation was made using cryogenic distillation. The system specified in the Study Design was based on work carried out prior to the Predevelopment Contract E(49-18)-2369. In this work, a detailed and optimized study design was developed for one methane recovery process configuration. Time did not permit detailed consideration of other process configurations.

The objective of the current gas separation screening studies is to develop an optimized process basis for these sections of the CCG process. This effort will be based primarily on the work being done by Air Products and Chemicals, Inc. of Allentown, Pennsylvania under DOE contract ET-78-C-01-3044. The objective of that 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 will be devoted to the methane recovery system.

A flow scheme for the Methane Recovery System included in the CCG Study Design is presented in Figure 5.1-3. In this system methane is recovered via cryogenic distillation using external cascade refrigeration cycles. Treated and dried feed gas at approximately 420 psia and 5°F is cooled in the feed/product exchanger before entering the Methane Recovery Tower. In this tower CO and H_2 are separated from CH_4 by cryogenic distillation at about 410 psia. The main condenser duty is supplied by a cascade refrigeration system consisting of propylene, ethylene, and methane refrigeration cycles. The reboiler duty is provided by condensing a portion of compressed methane refrigerant. The tower overhead vapor is warmed in the feed/product exchanger, compressed and sent to the gasifier. The product methane bottoms is flashed to low pressure (88 psia and 70 psia) to supply feed refrigeration and part of the condenser duty. The vaporized bottoms is then compressed to pipeline conditions.

The flow scheme for the alternative Methane Recovery System proposed by Air Products is illustrated in Figure 5.1-4. In this system, methane separation is achieved by autorefrigeration of feed gas followed by stripping of CO and H_2 at low pressure. Treated and dried feed gas at approximately 420 psia and 5°F is cooled and partially condensed in the main exchanger. The cooled vapor portion is rich in CO and H_2 and is withdrawn from the separator drum at 390 psia. The resulting liquid is let down in pressure to 40 psia and fed to the CO stripper to remove dissolved CO and H_2. The stripper overhead vapor and the vapor withdrawn from the separator drum are warmed in the main exchanger, compressed and sent to the gasifier as recycle gas. Evaporation of the stripper bottoms (CH_4) provides the required refrigeration to cool the feed in the main exchanger and reboiler. A portion of the bottoms methane entering the main exchanger is let down to near atmospheric pressure to supply the cold-end duty at the required temperature level. The remaining portion is pumped to about 80 psia so that the vaporization temperature closely matches the feed cooling curve at the warm end. The warmed SNG streams are compressed to product pressure.

Potential advantages for this system relative to the Study Design Methane Recovery System are as follows:

- Separation of CH_4 from CO/H_2 is easier at low pressure due to greater relative volatilities.
- Most of the CO and H_2 are separated from the product methane by simple cooling and a separator drum without having to be fed to the cryogenic low pressure stripper. This permits separation of the remaining CO and H_2 at low pressure while minimizing CO and H_2 recompression costs.
- External refrigeration cycles are eliminated resulting in a simpler process configuration.

Work is currently underway to make a consistent comparison between the two systems. The first step in this work will be to develop material and energy balances for the two systems on a consistent basis.

FIGURE 5.1-3

METHANE RECOVERY VIA CRYOGENIC DISTILLATION

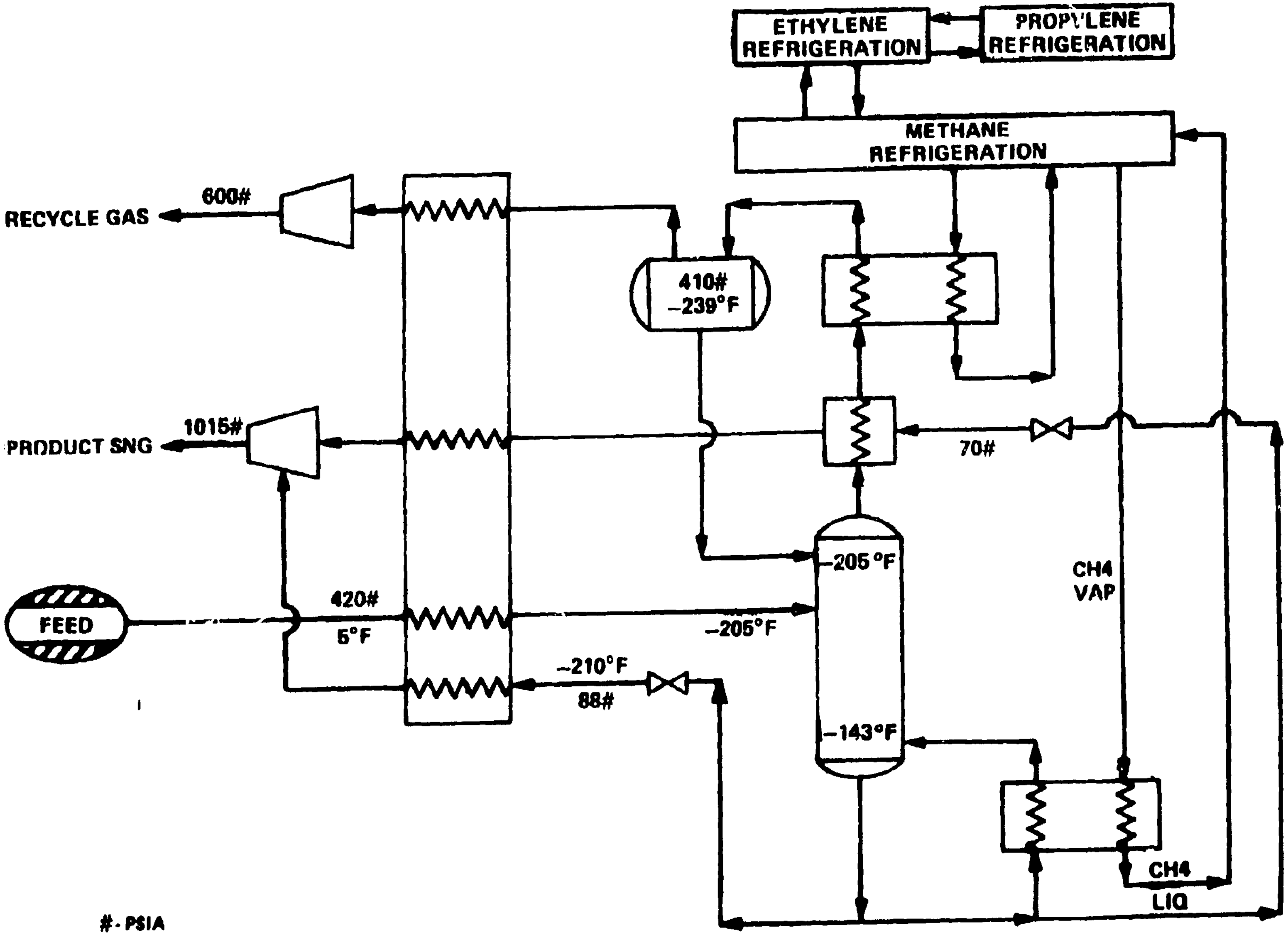

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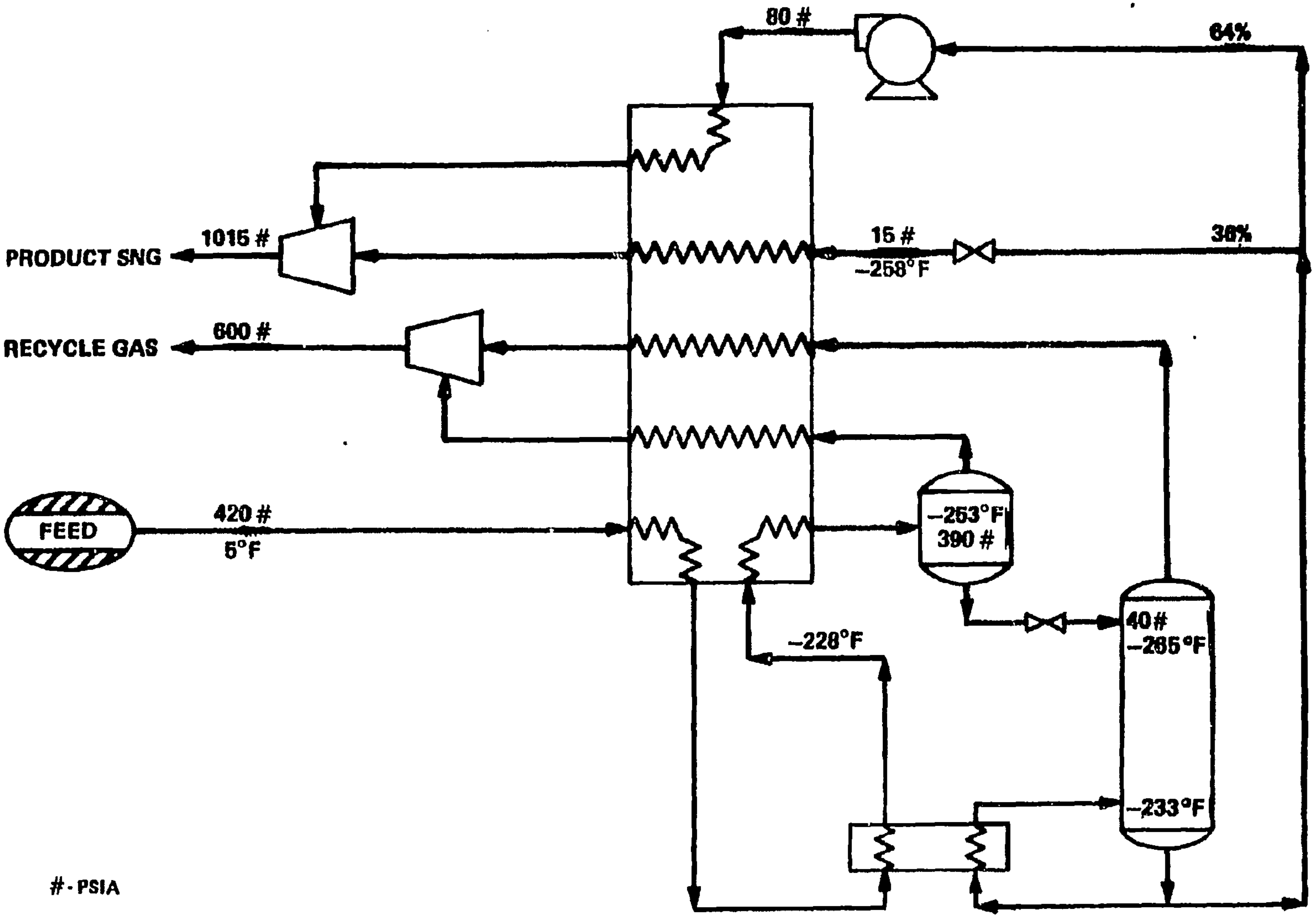
FIGURE 5.1-4

METHANE RECOVERY VIA LOW PRESSURE CO STRIPPING



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Catalyst Recovery System Screening Studies

A series of engineering screening studies are underway 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 calcium hydroxide 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 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.

During the quarter, work continued on the first case (Case 1) which combines countercurrent water-wash with $Ca(OH)_2$ digestion, using filters for the solid-liquid separations. The process basis for this screening study has been finalized, the material and energy balance has been completed, and equipment specifications are being prepared. The basis and flowsheet for this case are discussed in more detail below.

In addition, two more cases have been initiated. Both of these cases will evaluate catalyst recovery using water washing alone, without initial digestion. In Case 2, filters will be used for the solid-liquid separations, and in Case 3, gravity settlers (or "thickeners") will be used. Work has begun on developing the process bases and material and energy balances for these two cases.

The process basis for Case 1 is summarized in Table 5.1-3. A schematic flowsheet is shown in Figure 5.1-5. The rates of spent gasifier solids ("char" and potassium catalyst) fed to catalyst recovery are the same as in the CCG Study Design. The char feed consists of 68% coarse char withdrawn from the bottom of the gasifier and 32% fines collected in external cyclones. The bottoms char and cyclone fines feeds are slurried with "semi-rich" catalyst solution from the second wash stage and are digested at 300°F and 70 psia with a residence time of one hour. Here, lime is added to give a calcium/potassium ratio of 0.7 mole/mole. The lime reacts with insoluble forms of potassium to produce soluble potassium salts. About 90% of the total potassium fed is solubilized during digestion. The slurry from digestion is flashed to 20 psia (lowering the temperature to 230°F) and then filtered in first-stage filters

TABLE 5.1-3

CATALYST RECOVERY SYSTEM SCREENING STUDIES

PROCESS BASIS FOR CASE 1: DIGESTION WITH FILTERS

Principal Material Balance Assumptions

- **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."**
- Concentrations (K^+) of key solutions:

- Rich solution from catalyst recovery	11.8 wt%
- Concentrated solution from evaporators	22.8 wt%
- Makeup catalyst solution	20.9 wt% (30.0 wt% KOH)

Basis for Calcium Hydroxide Digestion

- Digestion conditions:

- Temperature	300°F
- Pressure	70 psia
- Residence Time	1 hour
- Ca/K	0.7 mole/mole

- Resulting K solubilized is 90% of all K in bottoms char and cyclone catch.

Basis for Water Wash/Solid-Liquid Separations

- Water wash conditions:

- Temperature	230°F	Except last stage at 146°F and 15 psia
- Pressure	55 psia	

- Filter performance:
  - Solids content of filter cake is 30 wt%
  - Solids separation efficiency is 99%
- Overall target recovery is 95% of all soluble K fed (including K solubilized in digestion).

Basis for Evaporation

- Double-effect evaporators are provided using 30 psig steam raised in gasifier effluent waste heat boilers.

Basis for Heat Balance

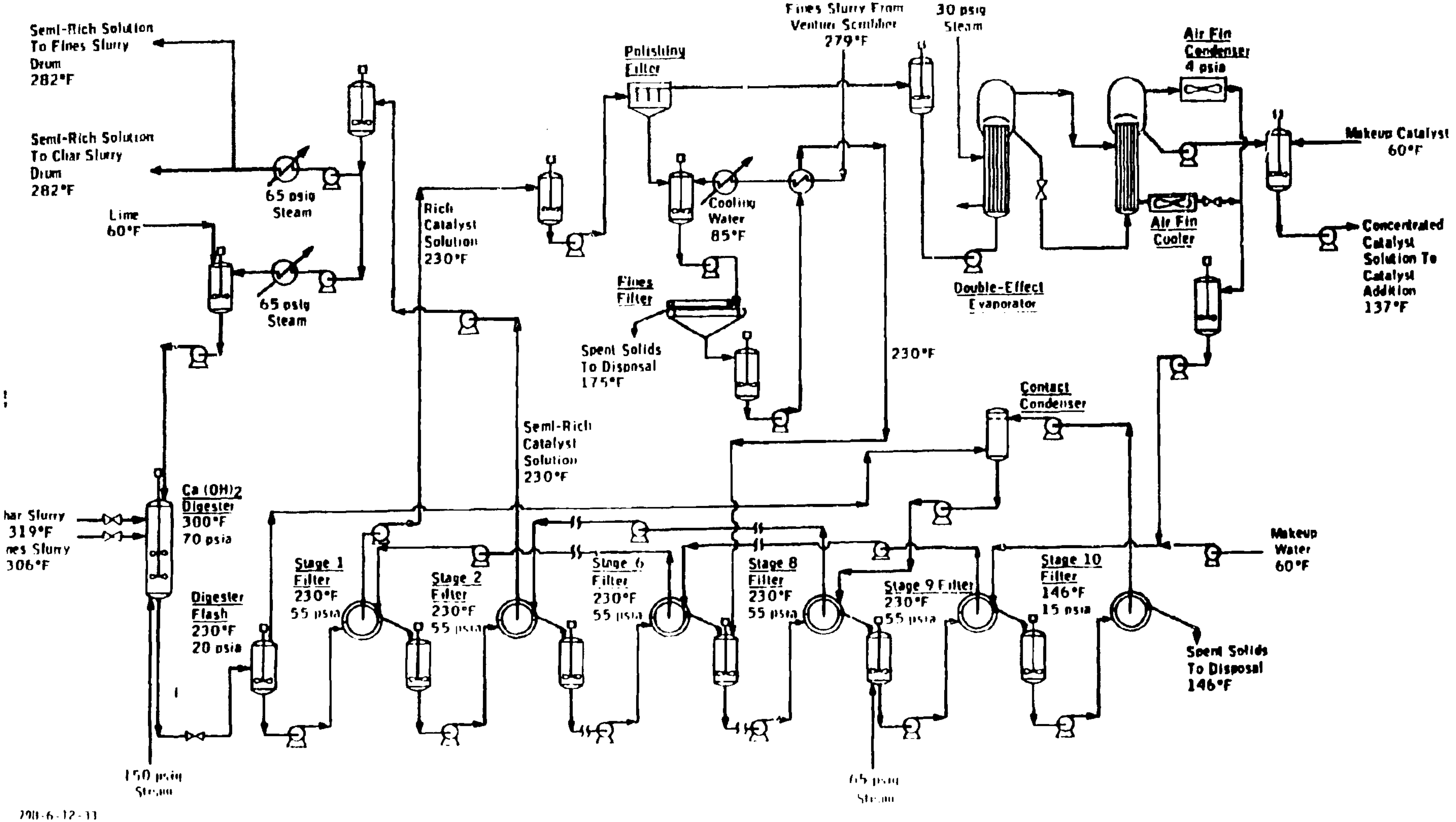
- Temperatures of major feeds:

- Bottoms char	600°F
- Cyclone fines	600°F
- Lime	60°F
- Makeup catalyst solution	60°F
- Makeup wash water	60°F

- Steam supplied at:
  - 150 psig for direct injection to the digesters
  - 65 psig for direct injection to water wash stages and indirect heating of semi-rich catalyst solution
  - 30 psig for evaporators
- The following heat effects are all assumed to be zero:
  - Net heats of mixing
  - Net heats of digestion reactions
  - Heat losses from system

FIGURE 5.1-5

CATALYST RECOVERY: DIGESTION WITH FILTERS



to remove most of the solids. Continuous pressure rotary-drum filters are utilized. The filters operate at an inlet pressure of 55 psia with a 35 psi pressure drop across the cake. The clarified filtrate from this first stage is the "rich" catalyst solution and has a potassium (K^+) concentration of about 12 wt%. This rich solution is filtered a second time in pressure vertical-leaf polishing filters to remove any fines that may have passed through the rotary-drum filters. Following this second filtration, the rich solution is concentrated in double-effect evaporators. The heat to drive the first effect of the evaporators is provided by 30 psig steam generated from onsite waste heat. The concentrated catalyst solution from the evaporators (23 wt% K^+) is combined with makeup KOH solution (21 wt% K^+) and sent to catalyst addition to be applied to the feed coal. The condensate from the evaporators is returned to the last stage of water wash, reducing makeup wash water requirements.

The solids in the first-stage filter cake continue on through the countercurrent water-wash to recover the remaining soluble catalyst. Each washing stage consists of slurry mixing drums to provide contact between richer solids and leaner solution, and rotary-drum filters for separating the solids. The filters used between each washing stage remove 99% of the solids fed. The filter cake from each stage contains 70% liquid and 30% solids. Ten washing stages are provided to recover 95% of the solubilized catalyst.

In addition to the char and fines, the fines slurry from the product gas venturi scrubbers is also processed in catalyst recovery. This stream is combined with the solids from the rich catalyst solution polishing filters and filtered in atmospheric filter belt presses. The filtrate is added to the seventh stage of the counter-current water wash and the solids are sent to disposal.

Process heat for the 300°F catalyst recovery digesters is provided indirectly with 65 psig steam (by heating the semi-rich catalyst solution prior to slurrying the char, fines, and lime), and directly by injecting live 150 psig steam. Heat to bring the ninth stage up to 230°F is provided by injecting live 65 psig steam and by condensing the steam generated in flashing the digester slurry.

Work on these first three cases will continue through the fourth quarter of 1979. Additional cases to evaluate centrifuges and hydroclones are planned. Economics for the initial three cases are expected to be developed in the first quarter of 1980.

Cost of Additives to Improve Solid-Liquid Separations Performance

An important factor in recovering the CCG catalyst from the spent gasifier solids is the performance of the solid-liquid separation devices used in the countercurrent water wash. Recent laboratory experiments have shown that filter aids (body feeds or precoats) and flocculating chemicals can increase filtration rates for CCG solids. If the filtration rate is increased, the total filter area required for each wash stage can be reduced.

To justify using such an additive, the cost of the additive must be offset by savings in capital charges associated with reduced filter investment. To provide early guidance to the continuing experimental programs, a simple economic evaluation has been made to quantify the potential impact of these additives on the CCG gas cost.

The process and economic bases for calculating the cost impact were taken from the CCG Commercial Plant Study Design. The Study Design gasifier solids production rate was used to determine the total quantity of filter aid and/or flocculating chemical which would be required for a given additive/solids ratio. Typical costs for additives were obtained from manufacturers. The calculated gas cost impacts include only the operating cost of the additive itself. No credit was included for reduced filter area.

The potential gas cost impacts of filter aids and flocculating chemicals are summarized in Table 5.1-4 for a range of typical additive/gasifier solids ratios. These results show that the use of a filter aid (unit cost 100-200 $/ton) as a body feed at high additive/solids ratios would be very costly, perhaps over a dollar per MBtu of SNG. However, if a filter aid is used as a precoat at low additive/solids ratios--e.g., 0.1 pound precoat per pound solids or so--the impact on the gas cost may be acceptable. Flocculating chemicals offer more promise as an economical approach to increasing filtration rates. At typical concentrations (500 wppm on solids), the use of a flocculant would contribute only three cents per MBtu to the SNG cost.

As mentioned above, these gas cost impacts do not include the credit for reduced cost of the solid-liquid separation device. This impact will be investigated and quantified as part of the Catalyst Recovery System Screening Studies which are in progress.

Coal Crushing Machinery for CCG

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

To arrive at appropriate design requirements, the safety requirements in regard to pressure containment in the event of coal dust explosion are being investigated for coal crushing equipment and its associated ductwork, fans, etc. Following the review of National Fire Protection Association (NFPA) standards reported in the July, 1978 - June, 1979 Annual Report, a member of the NFPA Committee on Dust Explosion Hazards was contacted to help determine appropriate design pressure requirements for the coal crusher/dryer system. Per his advice, an interpretation request to the Committee on Dust Explosion Hazards is being prepared requesting their comments as to design pressure requirements for this system.

Also in the past quarter, inquiries were made to ten American manufacturers concerning the type(s) of equipment they manufacture for crushing/drying coal to anticipated commercial CCG requirements. These manufacturers include the makers of rod mills, cage mills, hammer mills, roller mills, and others.

TABLE 5.1-4

GAS COST IMPACT OF ADDITIVES TO IMPROVE SOLID-LIQUID SEPARATIONS

Cost of Filter Aids, $/MBtu SNG

	Requirement (Filter Aid/Solids Ratio) (1)		
Filter Aid Unit Cost	0.1 lb/lb	0.5 lb/lb	1.0 lb/lb
100 $/T	0.13	0.67	1.34
200 $/T	0.27	1.34	2.68

Cost of Flocculants, $/MBtu SNG

	Requirement (Flocculant/Solids Ratio) (1)		
Flocculant Unit Cost	100 wppm	500 wppm	1000 wppm
1000 $/T	<0.01	<0.01	0.01
5000 $/T	<0.01	0.03	0.07

Note:

(1) "Solids" is used here to represent the total dry gasifier solids fed to catalyst recovery, typically including both the coarse char withdrawn from the bottom of the gasifier and the overhead fines recovered in external cyclones. Lime fed for calcium hydroxide digestion is excluded.

They were given the basic crushing/drying requirements and asked to provide information about the type and size mill that they would expect to supply to such a facility in 1985. Manufacturers were also asked to express their views on the system design requirements pertaining to a coal dust explosion, including both the design pressure requirements for the mill itself and the design pressure requirements for the ductwork, fans, cyclones, etc. associated with the mill. The results of these inquiries will be evaluated to determine which proposals merit further investigation.

5.2 Systems Modeling

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

CCG Reactor System Material and Energy Balance Model

The systems modeling effort to develop improved material and energy balance tools for the CCG reactor and recycle gas loop neared completion during the quarter. Work concentrated on the development and validation of the model block to perform the gasifier solids (including catalyst) material and energy balance. The overall modeling approach was described in the July, 1978 - June, 1979 Annual Report. Improved computer tools are being prepared to allow the laboratory guidance and process definition studies planned under the current program to be carried out efficiently and consistently.

The 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 in catalyst fed to gasifier
Hydrogen	K_2CO_3	
Oxygen	K_2S	
Nitrogen	K_2SO_3	
Organic Sulfur	K_2SO_4	
Pyritic Sulfur	$K_2S_2O_3$	
Sulfatic Sulfur	K_2S_2	
Ash*	Inert Forms	
Alumina (Al_2O_3)	K (in K·Char)**	Principal forms in catalyst leaving gasifier, along with K_2CO_3
Silica (SiO_2)	$KFeS_2$	
Coal Moisture (H_2O)	$KAlSiO_4$	
	$K_2O \cdot xSiO_2$	

*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 $K_2CO_3 + 2H\cdot Char \rightarrow 2K\cdot Char + H_2O + CO_2$.

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.

During the third quarter, the gasifier solids balance block was completed except for some final adjustments to the solids enthalpy basis. Subroutines to calculate the catalyst forms out of the gasifier and their enthalpies were programmed and incorporated into the block. The model was then validated with the CCG Commercial Plant Study Design and the catalyst loop balance from the current catalyst recovery system screening studies.

Other work during the quarter included development of input forms to incorporate the current gasifier kinetics/contacting model into its own block. This final block will allow calculation of the gasifier bed size in the same computer run with the material and energy balance. Work in the fourth quarter will include programming and validation of the gasifier model block, finalization of the enthalpy basis for the gasifier solids balance block, and completing the documentation of the overall model.

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 objectives and features of the materials testing/corrosion monitoring program are described in detail in the July, 1978-June, 1979 Annual Report.

The materials evaluation program utilizing corrosion racks and probes is being implemented as planned. Corrosion racks and probes have been installed in the PDU at Test Sites 1-7, described in Table 5.3-1. Test site 8 will be installed during the next quarter. Test sites 9 and 10 will be installed when the catalyst recovery system is completed.

A second set of corrosion racks has been assembled and shipped to the PDU. They are to be installed at the time the first set is removed for evaluation, probably in the first quarter of 1980.

The first 100-hour test run for evaluating materials in simulated CCG environments has been completed at the Bureau of Mines Tuscaloosa Research Center. Exposed test specimens are currently being examined and evaluated.

Vapor-Liquid Equilibria in Sour Water/Catalyst Systems

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

Experimental VLE data on sour water systems are insufficient for developing an accurate model. Therefore, a subcontract was prepared (in the second quarter of this year) for the measurement of VLE data on aqueous mixtures containing ammonia, carbon dioxide, hydrogen sulfide, and potassium hydroxide. This subcontract has been executed by ER&E and Wilco Research Company. Wilco plans to measure these experimental data during the fourth quarter. Future work will include monitoring these experimental measurements.

TABLE 5.3-1

CATALYTIC COAL GASIFICATION PDU CORROSION RACKS AND PROBES

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

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

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

(3) Non-retractable electric resistance probe

Physical and Thermodynamic Properties of Catalyst Recovery Solutions

The objective of this program is to collect the physical and thermodynamic properties needed to design the processing equipment in the catalyst recovery system. This quarter, a brief review was done on viscosity and enthalpy data for aqueous solutions containing KOH and K_2CO_3. Adequate methods were found for predicting the composition dependence of viscosity and for extrapolating experimental viscosity data to higher temperatures. However, the available data base for enthalpy was found to be insufficient. Therefore, a more extensive literature search has been initiated to identify additional sources of enthalpy data.

Three methods of extrapolating viscosity as a function of temperature were tested: (1) $\ln \eta = A_1 + A_2/T$, where η is the viscosity, T is the absolute temperature, and A_1 and A_2 are arbitrary constants; (2) $\ln \eta = A_1 + A_2 \ln T$; and (3) $1/\eta = A_1 (V/A_2 - 1)$ (Hildebrand's fluidity theory), where V is the molar volume (a function of temperature). Results with pure water show that the first equation is the best of the three tested.

For predicting the composition dependence of viscosity at constant temperature, the following equation should be adequate:

$$\eta / \eta_0 = 1 + \Sigma B_i m_i$$

where η is the viscosity of the aqueous solution containing one or more dissolved electrolytes, η_0 the viscosity of pure water at the same temperature, m_i is the molality of electrolyte i, and B_i is a property of each electrolyte i. The B_i's are functions of ionic strength and temperature.

Additional work on viscosity and enthalpy predictions will be deferred until more literature data have been obtained and a better definition is available for the electrolytes present in catalyst recovery solutions. Instead, boiling-point elevation will be studied for aqueous solutions containing potassium compounds.

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. In an initial review of alternative solid-liquid separation devices, filtration was identified as a potentially feasible method for catalyst recovery. Continuous belt filtration combined with in-situ leaching was identified as a promising technique to be further evaluated for this application. Work this quarter focused on measuring filtration rates for digested char slurries and evaluating the use of additives (flocculants) to increase these rates.

A laboratory batch filtration apparatus was used to measure filtration rates, and the effect of additives on filtration rates, for two different samples of digested char designated D39 and D44. A temperature of 190°F and a 5 μ millipore filter were used for all tests. Differential pressure ranged from 30 to 70 psi. Data on initial and final filtration rates along with other experimental results are given in Table 5.3-2. Filtration rates for sample D39 were about five to ten times greater than those for D44, both without and with additives. This variability between samples is probably attributable to variations in particle loading and size distribution, cake properties (porosity, residual moisture and compressibility), and liquid viscosity.

For sample D39, addition of 25 ppm anionic flocculant D-25A was found to increase the initial filtration rate by a factor of 1.7 from 60 gph/ft^2 to 103 gph/ft^2. Cake resistance was lowered from 5.4 x 10^{11} ft/lb to 2.4 x 10^{11} ft/lb. The same addition of D-25A to sample D44 had no effect. Adding A-1906N (a nonionic flocculant) at a concentration of 10 ppm lowered the initial filtration rate of D39 from 60 gph/ft^2 to 48 gph/ft^2. The results of other experiments with flocculants are summarized in the table.

In view of the variability observed, no conclusions can be drawn at this time regarding the potential commercial effectiveness of filtration for catalyst recovery from digested char. For D39 with additives, rates were high enough to approach commercial feasibility -- typical commercial rates are 90 gph/ft^2. For D44 and D26 (reported in the July, 1978 - June, 1979 Annual Report), rates were an order of magnitude lower. Further work to identify the cause(s) of filtration rate variability is planned.

In these filtration rate experiments, a potassium specific ion electrode was used to measure the concentration of K^+ in the filtrate. Measurements were made by analyzing batch samples collected during filtration runs. Liquid viscosity, necessary for cake resistance calculations, was estimated based on the K^+ concentration. Potassium levels for D44 were two to four times greater than for D39.

The batch filter has been modified to include an additional heated liquid reservoir for use in studying cake washing. Cake washing data are needed for design of a continuous belt filter/in-situ leaching system. At the completion of a normal filtration run, liquid from this reservoir will be forced through the filter cake. The concentration of K^+ in the exiting wash liquid will be obtained using the specific ion electrode.

Construction of a laboratory device to study char attritability (discussed in the Annual Report) has been delayed by the unavailability of parts. Such tests are now planned for the first half 1980.

Environmental Control: Water and Solids Effluents

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

TABLE 5.3-2

LABORATORY BATCH FILTER RESULTS (1)

mpl	Differential Pressure (psig)	Filtration Rate Initial (gph/ft^2)	Filtration Rate Final (gph/ft^2)	Cake Resistance (ft/lb x 10^{11})	Residual Cake Moisture (wt%)	Filtrate K+ (wt%)	Feed Solids Concentration (wt%)	Flocculant/ Loading
9	50	60	18	5.4	68	2.24	11.26	--
9	50	103	24	2.4	68	2.33	10.65	D-25A/25 ppm
9	50	69	19	2.2	68	2.57	13.59	D-25A/50 ppm
9	50	48	10	4.1	67	2.31	12.71	A-1906N/10 ppm
	50	50	12	4.8	68	2.28	12.90	A-1906N/5 ppm
	50	68	12	3.1	68	2.32	13.04	D-25A/25 ppm A-1906N/5 ppm
(2	30	12	4	60	64	4.95	7.36	--
(2	40	14	1.2	55	64	5.45	7.36	--
	40	6	0.5	141	54	9.93	19.28	--
(2	70	11	2	57	62	5.83	9.47	D-25A/25 ppm

S:

All tests done at 190°F with 5 μm millipore media.

Water added to dilute the original sample.

During the past quarter, additional analytical results were obtained on the leachate from digested and undigested chars from bench-scale catalyst recovery experiments. Data from analyses for 36 metals showed very low concentrations in both samples--well below ten times the drinking water standards which is one of the criteria listed in the Resource Conservation and Recovery Act (RCRA) for determining hazardous wastes. The metals' levels corresponded closely in both samples with the exception of aluminum and strontium. Al was four times greater in the undigested sample whereas Sr was over two times greater in the digested sample. Other analytical tests determined levels of pollutants most commonly found in gasification wastewaters. The levels reported were quite low and the two samples were almost identical. However, phenol and sulfate concentrations in the two samples were significantly different. The higher phenol concentration in the digested sample contributed to that sample's considerably higher Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD). Further testing is necessary to verify these results and to judge their significance.

Catalytic Gasifier Solids Balance Model

Solids loss rates from the gasifier can have a major impact on vessel design requirements, solids recovery facilities and design bases for the catalyst recovery system. A proprietary solids balance computer model called DYNAMOD, which was developed and validated by Exxon for other fluid-solids processes, can be used to calculate transient and steady-state loss rates and particle size distributions for the gasifier system. The overall objective of this program is to adapt DYNAMOD to model the catalytic gasifier in order to provide a base for more definitive design studies, quantitative predictions of overall losses, improved specifications of fines recovery equipment, and reliable assessments of processing limitations imposed by fines losses.

Work started during this quarter on adapting DYNAMOD for use in the CCG process. Fluidized bed parameters for the gasifier and process characteristics were reviewed to define modifications required for simulating both pilot plant and commercial unit operations. Data from Fluid Bed Gasifier (FBG) operations during the predevelopment research phase are being used to develop a solids attrition model and assess the effects of char/ash density differences on their relative entrainment rates.

Work is continuing on adapting DYNAMOD for use in the CCG process. After the model is developed and validated using data from the PDU, it will be used to evaluate the effects of operating variables, solids properties and reaction parameters on equilibrium particle size distributions and ash/char behavior.

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. A dynamic simulation including a detailed gasifier model and simplified preheat furnace, product gas cooling, acid gas removal and methane recovery tower models will be developed to conduct the study. This simulation will run on a hybrid digital/analog computer which provides interfacing to control instrumentation and significant interactive capabilities.

The dynamic study can be divided into two phases. The first phase involves the development of various process models and the integration of these models with each other and with control instrumentation. The second phase involves the actual dynamic analysis and control system design for the process using the simulation as the principle tool. Planning for each aspect of the project is highlighted below.

The fourth quarter of 1979 will be devoted to the gasifier model. The first quarter of 1980 will be allocated to completing the gasifier model and the product gas cooling and acid gas removal models. The methane recovery section, preheat furnace, and the linking of individual models will be completed during the second quarter. The third quarter will be devoted to dynamic and control system studies.

The dynamic simulation includes several process models, which are outlined below. The reactor model will employ existing kinetic and contacting relationships. The solids will be assumed to be well-mixed and will be characterized by a single mean particle diameter. The gasifier temperature and gasifier bed inventory will be calculated from dynamic material and energy balances. Plug flow of gas in the emulsion and bubble phases will be assumed. A pseudo steady-state assumption will be adopted for the gas phase because of the very low residence time of the gas compared to the solids.

The gas-gas exchangers and waste heat boilers will be simulated using an existing simplified heat exchanger model. The intent will be to calculate the onsite steam generation rate and the temperature of the feed to the preheat furnace. The NH_3 scrubber, the COS converter and acid gas removal will be assumed to function as designed. Dynamic effects in this section of the plant will be estimated.

The methane recovery tower (MRT) will be modeled using an existing pseudo-binary routine to calculate product compositions, flow rates, and the control tray temperature. The MRT feed/product exchanger, condensers, and reboiler will be simulated using the existing heat exchanger routine. The refrigeration section and recycle gas compressor will not be modeled.

The preheat furnace will be simulated using an existing simplified dynamic model involving energy balances for the process gas and flue gas in the radiant and convection sections. The objective will be to calculate the furnace coil outlet temperature, flue gas temperature, and furnace draft.

Once the integration of the various process models is complete, the second phase of the program will begin. The overall process stability at various design parameters will be examined. Dynamic process responses to different input variables will then be determined in an open loop mode. These variables will include:

- Coal feed rate
- Catalyst loading
- Gasifier pressure
- Char withdrawal rate
- Coal properties

- Steam feed rate
- Furnace coil outlet temperatures
- Gas-gas exchanger performance
- Furnace fuel gas composition upsets
- Recycle rate, temperature, and composition changes

From this information, the process stability can be studied and a basic regulatory control scheme established. The process response will be determined for emergencies such as:

- Loss of coal feed
- Loss of offsite steam
- MRT reflux failure
- Recycle gas compressor trip

Alternative control systems will be evaluated and a preferred control strategy identified. The sensitivity of the process to modeling uncertainties will also be examined.

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