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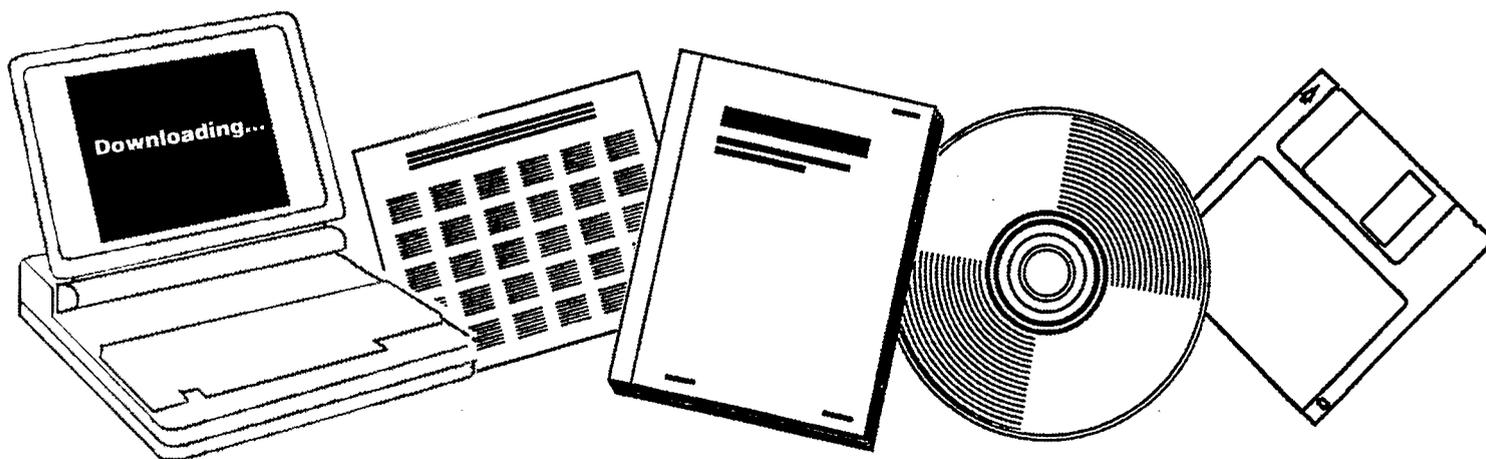
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**EXXON CATALYTIC COAL GASIFICATION PROCESS
DEVELOPMENT PROGRAM. QUARTERLY TECHNICAL
PROGRESS REPORT, JANUARY-MARCH 1980**

**EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX**

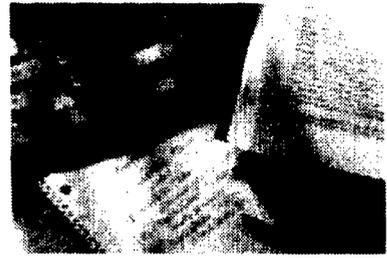
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EXXON CATALYTIC COAL GASIFICATION PROCESS
DEVELOPMENT PROGRAM

Quarterly Technical Progress Report
for January - March, 1980

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Submitted June, 1980

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

ABSTRACT

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

This report covers the activities for the Exxon Catalytic Coal Gasification Development Program during the period January - March, 1980. This work is being performed by the Exxon Research and Engineering Company (ER&E) and is supported by the United States Department of Energy under Contract No. ET-78-C-01-2777 and by the Gas Research Institute.

The highlights of this report are summarized below:

• Bench Scale Research and Development

Bench tests of flocculant treated $\text{Ca}(\text{OH})_2$ digested chars were completed. Tests showed that the flocculant remains effective for multiple cycles of filtration and reslurrying.

An experimental program was initiated to quantify the amounts of various potassium species present in catalyst recovery operations. The preliminary results from analysis of both water washed and digested solutions of old FBG and fresh PDU chars indicate that catalytically inactive sulfur species are not present in fresh PDU char. Inactive species are formed by exposure to air.

• Process Development Unit Operations

Operation of the PDU was directed to study of the causes of chunk formation in the gasifier and the interaction of the severity of feed coal oxidation, the gasifier pressure, and the char particle size distribution on the fluid bed density. By increasing the gas flow through the coal feed line and ensuring that the initial bed height is above the feed line, chunk formation has been essentially eliminated. Bed density can be improved by either

lowering reactor pressure or by mild oxidation of the feed coal followed by a heat soak. Two vessels are being added to the PDU which will allow for fluid bed pretreatment of the coal in a continuous fashion.

The initial train of the catalyst recovery unit was operated in a water wash mode. The slurry transfer line from the PDU char slurry pot, the filter, and the filtrate evaporator/concentrator were operated. Construction is continuing on the process instrumentation and on the second train of the catalyst recovery unit.

- Advanced Study of the Exxon Catalytic Coal Gasification Process

Work was aimed at further defining the effect of temperature, gas composition, gas flow rate, and pressure on the gasification rate. With pure steam feed to the reactor, the apparent activation energy is about 31 kcal/g mole; however, with a feed mixture of H₂ and H₂O in equimolar amounts, the apparent activation energy is increased to about 46 kcal/mole. The gasification rate was found to be rather insensitive to pressure changes but highly sensitive to the ratio of H₂O to H₂ in the feed gas.

Bench scale tests have verified that devolatilization pressure is the most important variable affecting char agglomeration. Initial results indicate that a mild oxidation at 350°F followed by a heat treatment will improve agglomeration properties.

- Engineering Research and Development

Work continued on the catalyst recovery screening studies to evaluate the economic impacts of alternative processing approaches and solid-liquid separation techniques. Five cases are underway. Preliminary economics show that Case 2, Water Wash with Filters has a significant advantage over Case 1, Lime Digestion with Filters because of greater difficulty in filtering lime-digested solids. Economics will be developed shortly for Case 3, Water Wash with Gravity Settlers. Process bases are being set for two new studies: Case 4, Water Wash with Hydroclones and Case 5, Water Wash with Centrifuges.

Inquiries have been made to several European manufacturers as part of a study to determine the types and performance of coal crushing equipment appropriate for commercial CCG plants.

Based on material and energy balance studies, the preferred process basis for the supplemental steam reformer study has been determined to be a coil outlet temperature of 1500°F for the preheat furnace and 1400°F for the steam reformer, a steam/carbon ratio in the steam reformer of 5/1, and SNG for the plant fuel.

An early laboratory guidance study was conducted to estimate the potential effects of oxygen consumption in coal pretreatment on the CCG system material and energy balance. Pretreatment via air oxidation is one approach under investigation for increasing gasifier fluid bed density.

The results indicate that "mild" pretreatment, with 2-4 wt % O₂ consumption (on dry coal), is a potentially low cost method of increasing density. However, "severe" pretreatment, with greater than 10 wt % O₂ consumption, results in a significant loss in SNG product yield per ton of coal and is not likely to be economically attractive.

An early laboratory guidance study has been completed to estimate the effect of reduced gasifier pressure on the CCG process. Based on material and energy balances, it appears that reducing gasifier pressure from 500 psia to 300 psia is potentially a low cost method of increasing gasifier fluid bed density. However, gasifier operation at 100 psia is not likely to be economically attractive.

Material and energy balances have been developed to help select gasifier conditions for both the PDU process variable studies and more detailed engineering screening studies on gasifier process conditions. The effects of catalyst loading, gasifier temperature, gasifier feed steam rate, carbon conversion, and gasifier pressure were investigated.

Activities continued in the engineering technology programs:

- The materials evaluation program using corrosion racks and probes in the PDU is proceeding as planned. In addition, analyses were conducted of two equipment components which failed in PDU service.
- Wilco Research Company has completed seven of the twelve runs planned under their subcontract to measure vapor-liquid equilibria in sour water/catalyst systems.
- The available data bases for boiling points, enthalpies, and densities of aqueous potassium hydroxide and potassium carbonate solutions were analyzed. A literature search was begun on the properties of aqueous potassium sulfide and potassium bisulfide.
- A series of filtration and cake washing experiments was completed using water-washed char in the laboratory batch unit with a new 120 ml test cell. Initial evaluation of the results indicated that use of 25 ppm of flocculant doubled the filtration rate and that in-situ washing of the filter cake was effective in recovering potassium.
- A detailed plan was prepared for characterizing waste waters, spent solids, and solids slurries produced in the PDU. These data will provide the basis for quantitative estimates of the treatment needs and environmental impact of liquid and solid wastes from the commercial CCG process.
- Gas sampling and analysis plans for the PDU were reviewed from the perspective of estimating potential atmospheric emissions. PDU data will be used to assess the air quality impact of a commercial CCG plant and identify control alternatives for potential problem emissions.

- Work continued on the gasifier module in the dynamic simulation of the CCG reactor system. The portion of the gasifier module which integrates to define the product gas stream has been completed.
- A catalytic gasifier solids balance model, which assumes there are two solid species, is being developed.

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LABORATORY PROCESS RESEARCH AND DEVELOPMENT

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

1.1 Flocculant Pretreatment of Catalyst Recovery Slurry

Bench scale experiments were continued on lime digested slurries to determine the effect of flocculant dosage and integrity of flocculated particles in a multi-stage filtration operation.

The digested slurries were prepared in a bench scale digester by mixing 1 part (by weight) of FBG fines, 2.5 parts of FBG char, 1.7 parts of lime and 28 parts of 2.8 wt % KOH solution. The slurries were then heated to 300°F, while stirring, for 1-1/2 hours and allowed to cool to room temperature. The slurries contained 11.3 wt % solids, 3.4 wt % KOH (pH=13.7) and 20 wt % particles less than 10 microns. Figure 1.1-1 gives the particle size distribution of a typical slurry sample. The samples were heated to 200°F while stirring. A measured amount of flocculant D-25A was added. Table 1.1-1 gives relative filtration and settling rates of the slurries at various flocculant dosages.

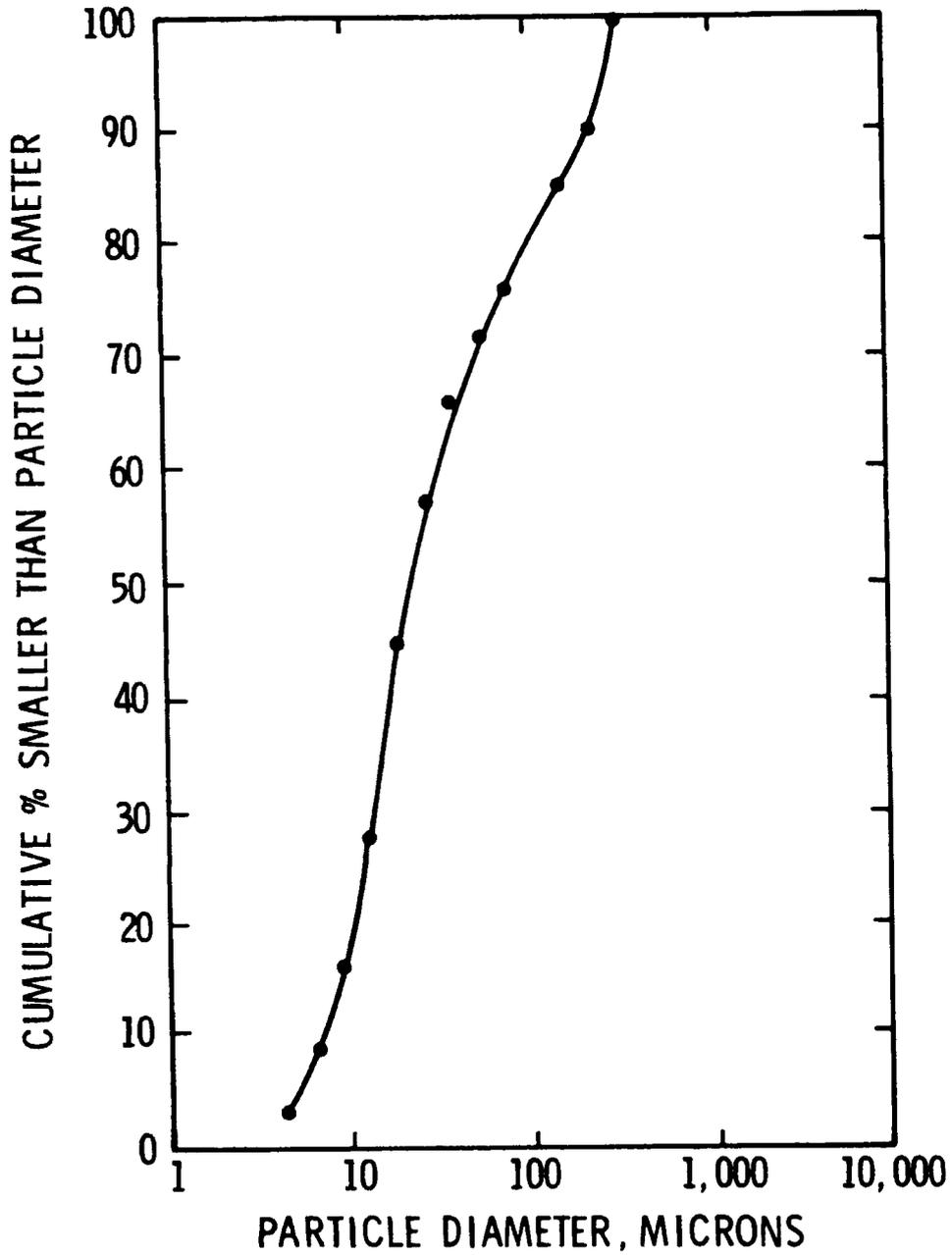
Table 1.1-1

Determination of Optimum Flocculant Dosage
for Lime Digested Slurries

<u>Flocculant</u>	<u>Dosage</u> <u>ppm</u>	<u>Relative</u> <u>Filtration</u> <u>Rate,</u> <u>% of Base</u>	<u>Relative</u> <u>Settling</u> <u>Rate,</u> <u>% of Base</u>	<u>Slurry Solid</u> <u>Content</u> <u>wt %</u>
None	0	Base	Base	12.2
D-25A	25	170	150	12.8
D-25A	50	260	165	11.6
D-25A	75	240	170	12.0

The data show that the effect of dosage saturates at about 50 ppm for digested char samples. Therefore, 50 ppm of flocculant D-25A was used for the tests of flocculated particle integrity. Filtration rate measurements were taken. After the first measurement was made, the filter cake was reslurried, stirred and reheated to 200°F for 30 minutes. The filtration rate was again

FIGURE 1.1-1
PARTICLE SIZE DISTRIBUTION OF
LIME DIGESTED SLURRY



measured. The procedures were repeated for six cycles for both blank and flocculated slurry cases. The D-25A flocculant was added into the slurry before the initial cycle. No flocculant was added on subsequent cycles.

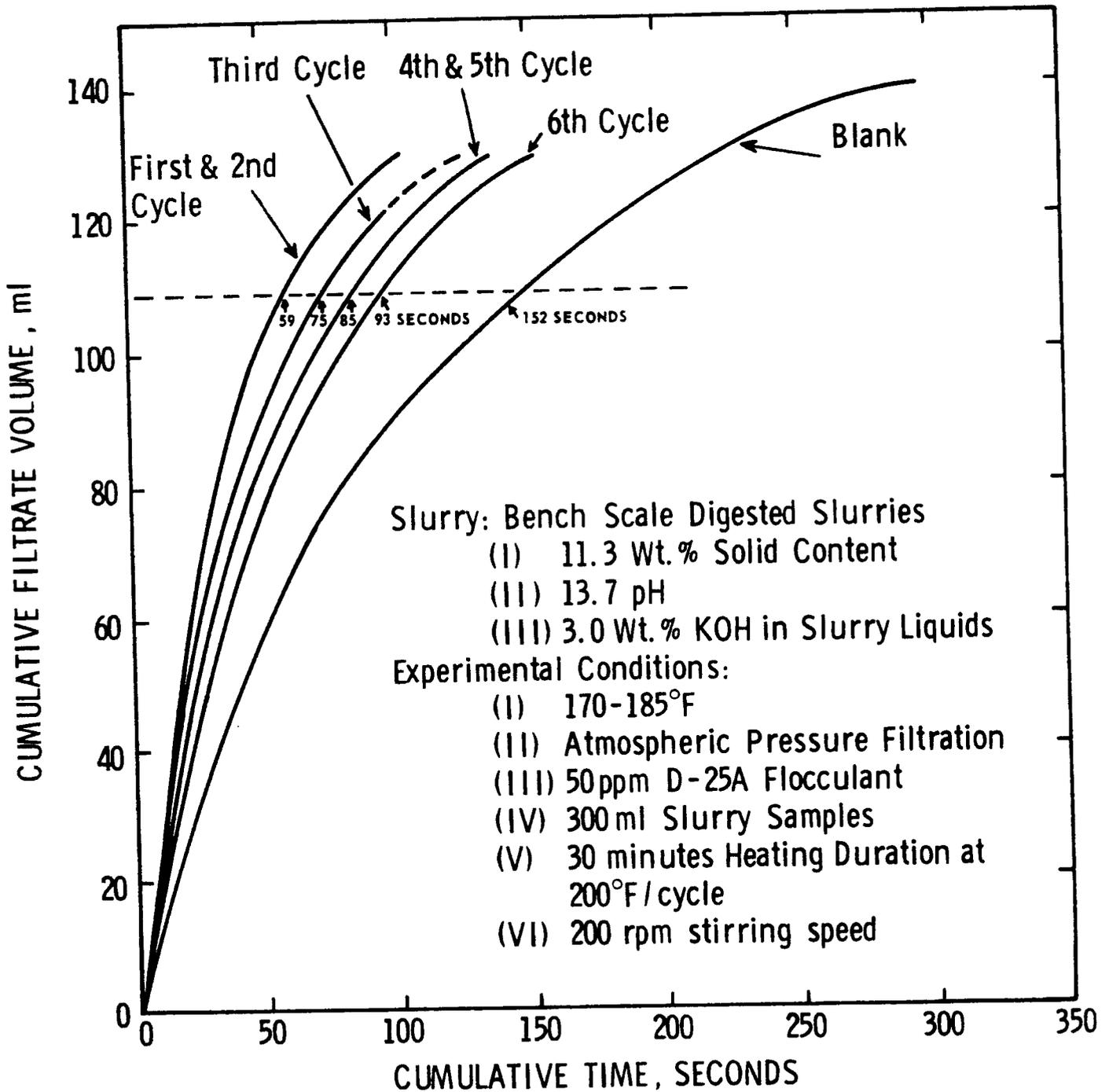
Figure 1.1-2 shows experimental results of gravity filtration. Data for the various cycles of the blank runs form a single curve. The data for 50 ppm D-25A pretreatment runs can be grouped into four curves; namely, one for the first and second cycles, another for the third cycle, a third for the fourth and fifth cycles and a fourth for the sixth cycle. Filtration time required to collect 110 ml of filtrate (which is about 80% of the total cumulative filtrate that can be collected from the 300 ml slurry samples) for the four grouped curves and blank runs are 59, 75, 85, 93 and 152 seconds, respectively. The data show that the flocculant pretreatment will improve filtration rate for multiple reslurry cycles, although the effect diminishes with each cycle.

This work concludes the experimental program of flocculant pretreatment of catalyst recovery slurries. Experiments may be resumed in the future on fresh PDU char to verify the experimental results obtained from FBG char.

The principal results for water washed slurries were reported in the October - December, 1979 Quarterly Report along with initial screening results for digested slurries. The principal results of flocculant pretreatment on the lime digested slurries are summarized below:

- The solid particles of the digested slurries carry a positive surface charge.
- Anionic flocculants are the best type of flocculants for the lime-digested catalyst recovery slurries. The D-25A, T-352A and R-10A samples appeared to be the best flocculants among those that have been tested.
- The recommended dosage of the D-25A flocculant is about 50 ppm.
- Filtration and settling rates were increased by a factor of 2.6 and 1.7 of the base case (blank run), respectively, when the digested slurries were pretreated with 50 ppm of the D-25A flocculant.
- The extent of potential improvement in either filtration or settling rate with the flocculant pretreatment was less for the lime digested slurries than that for the water washed ones tested previously (July - September, 1979 Quarterly Report), namely 2.6 versus 4.7 in filtration rate and 1.7 versus 4.5 in settling rate.
- The flocculant D-25A remains effective for multiple cycles in a filtration operation. Therefore, it should not be necessary to add flocculant into every stage in a multi-stage filtration unit.

FIGURE 1.1-2
INTEGRITY OF LIME DIGESTED SLURRY FLOCCULES



1.2 Catalyst (potassium) Forms in Catalyst Recovery Solution

An experimental program was initiated in January with the objective of determining the forms of catalyst on the char produced in the PDU. Potassium forms washed off char into solution are needed to determine both the energy balance and the chemistry of the gasification process. Different potassium forms have different heats of formation which will affect the overall gasification energy requirements. Furthermore, some of the potassium forms, such as K_2SO_4 and $K_2O \cdot nSiO_2$, are not catalytically active. These inactive forms will affect the catalyst makeup requirement.

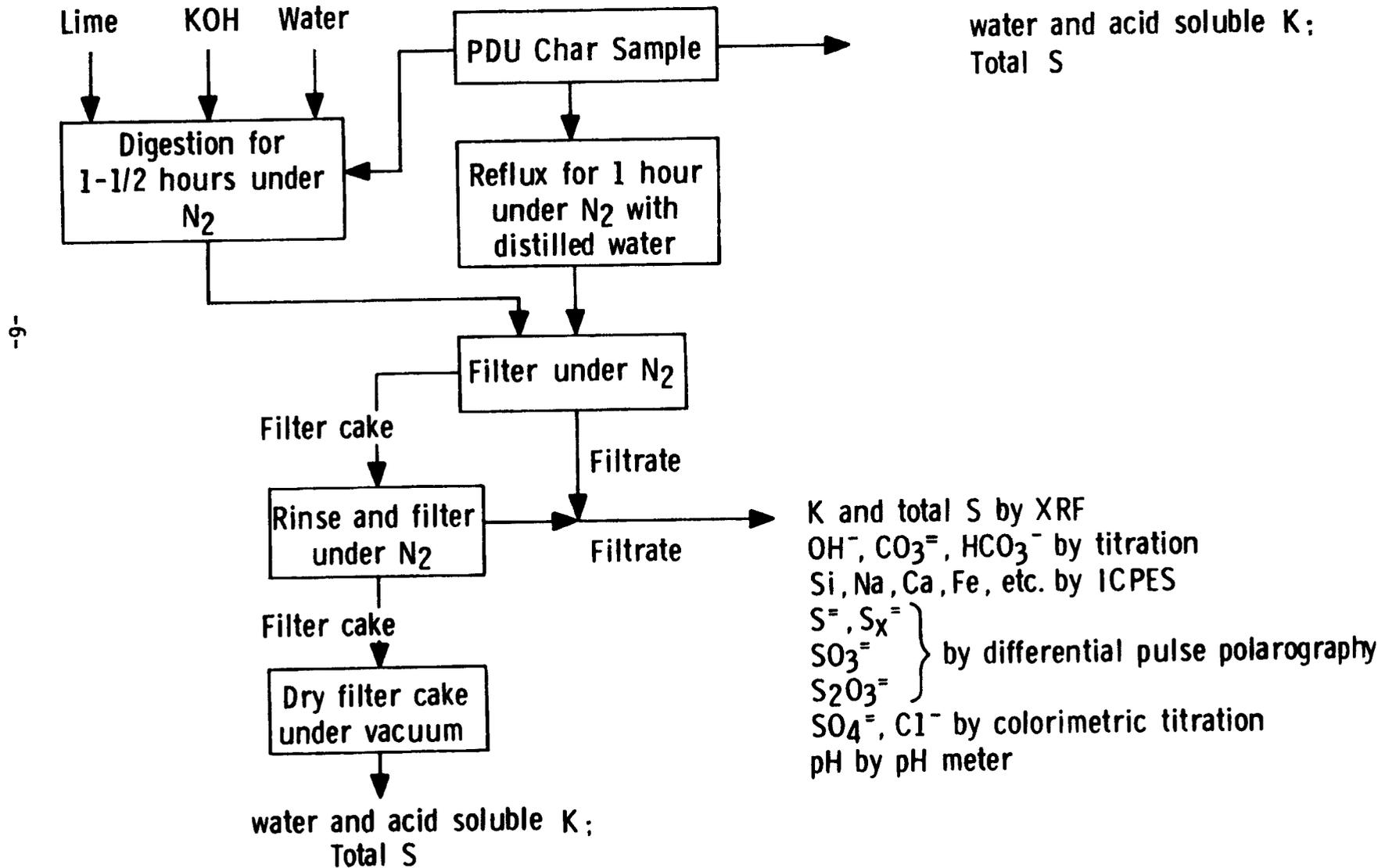
A bench scale reflux apparatus has been designed and placed in a N_2 glove box for water washing tests. An existing bench scale digester was recommissioned for lime digestion runs. Sampling bombs for obtaining inerted PDU char directly from the gasifier were designed and fabricated.

Figure 1.2-1 shows an analysis scheme for identifying potassium forms in the catalyst recovery solution. The scheme consists of two different routes, one for water washing, the other for lime digestion. For water washing tests, the solution was prepared by mixing 1 part (by weight) of char with 10 parts of extra purified distilled water inside the N_2 glove box to eliminate air exposure. The slurry was refluxed in the reflux apparatus for 60 minutes inside the N_2 box and then filtered. For lime digestion runs, the solution was prepared by mixing 1 part (by weight) of char, 0.5 part of lime and 5 parts of 0.51 wt % KOH solution. The slurry was digested for 1-1/2 hours at 325°F under N_2 atmosphere in the bench scale digester. Four trial water washing runs were carried out on PDU and FBG char; three for PDU char and one for FBG char. Two trial lime digestion tests were carried out on PDU char.

Table 1.2-1 shows preliminary results of the distribution of sulfur species in the water washed catalyst recovery solution of PDU and FBG char. The PDU char samples used were exposed to air for short periods, while the FBG char was exposed to air for almost two years. A significant portion of the sulfur species exists as sulfide and polysulfide in the fresh filtrate of PDU char. After two days of air exposure, the sulfide and polysulfide were completely oxidized and converted to sulfite, thiosulfate and sulfate. In the meantime, color of the fresh filtrate changed from dark green to colorless after air exposure. The FBG char solution contains no sulfide or polysulfide and is colorless. The dark green color of the fresh PDU solution may be due to a combined color effect of the polysulfide and potassium iron sulfide ($KFeS_2$) ions.

FIGURE 1.2-1

ANALYSIS SCHEME FOR CATALYST FORMS OF PDU CHAR



-9-

Table 1.2-1

DISTRIBUTION OF SULFUR SPECIES IN WATER WASHED
CATALYST RECOVERY SOLUTION OF PDU AND FBG CHAR

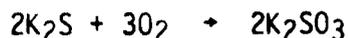
(Mole % of sulfur in given species)

	<u>PDU Char 10/18/79 Fresh Filtrate</u>	<u>PDU Char 10/18/79 Filtrate After 2-day Air Exposure</u>	<u>PDU Char 1/3/80 Filtrate</u>	<u>FBG Char 1978 Filtrate</u>
S ⁼	50.60	0.00	32.90	0.20
S _x ⁼	3.00	0.00	1.40	0.00
SO ₃ ⁼	1.90	16.80	0.00	0.10
S ₂ O ₃ ⁼	21.40	56.90	47.40	43.50
SO ₄ ⁼	<u>23.00</u>	<u>26.30</u>	<u>18.30</u>	<u>56.20</u>
Total	100.00	100.00	100.00	100.00
Color of Product Solution	Dark Green	Colorless	Light Green & Pale Yellowish	Colorless
pH of Product Solution, Measured	12.1	12.1	12.1	10.2
pH, Calculated from OH ⁻ Concentration	13.1	13.1	13.1	12.4
Si, ppm	861	861	948	164

There are many chemical reactions involved in oxidizing aqueous sulfur anions. A species with a lower oxidation state can be converted to the higher oxidation state species by oxidation. For example, the first step in oxidizing a solution of sulfide (K_2S) may be the following reaction:



Thiosulfate and polysulfide are formed from the sulfide. The following reaction will also occur simultaneously but is thought to be somewhat slower:



Once formed, sulfite may then back-react with some of the polysulfide to produce thiosulfate:



Note that some sulfide is regenerated. This is simply a release of the sulfide from the polysulfide. There is no oxidation or reduction involved. The above chemical reactions gravitate toward thiosulfate. Thus, thiosulfate is a prominent species of the sulfur forms in the oxidized char solution or in the solution prepared from the oxidized char.

Table 1.2-2 gives preliminary results of catalyst forms and sulfur species distribution in the lime digested solution of a PDU char. Hydroxide is a prominent species in the solution and there is no carbonate or bicarbonate being detected analytically. Only a very small amount of silicon compounds exist in the digested solution; namely 3 to 4 ppm. It is believed that any carbonate ions or silicon compounds are precipitated by lime under digestion conditions.

Sulfide is a predominant component among the sulfur species. Thiosulfate is a second large sulfur species in the digested solution. This indicates that the PDU char sample has been partially exposed to air. The pH of the product solution calculated from analytic hydroxide concentration agrees reasonably with that measured by a pH meter.

Table 1.2-2

CATALYST FORMS AND DISTRIBUTION OF SULFUR SPECIES IN LIME DIGESTED
CATALYST RECOVERY SOLUTION OF PDU CHAR SAMPLE (JAN. 3, 1980)

I. Catalyst Forms

		<u>First Run</u>	<u>Second Run</u>
CO ₃ ⁼	Mole %	0.00	0.00
HCO ₃ ⁼		0.00	0.00
S ⁼		9.49	11.63
S _x ⁼		0.08	0.06
SO ₃ ⁼		0.11	0.10
S ₂ O ₃ ⁼		2.86	2.77
SO ₄ ⁼		1.26	0.85
SiO ₃ ⁼		0.02	0.02
OH ⁼		<u>86.18</u>	<u>84.57</u>
Total		100.00	100.00

II. Distribution of Sulfur Forms (Mole % of sulfur in given species)

S ⁼	68.80	75.50
S _x ⁼	0.60	0.40
SO ₃ ⁼	0.80	0.60
S ₂ O ₃ ⁼	20.70	18.00
SO ₄ ⁼	<u>9.10</u>	<u>5.50</u>
Total	100.00	100.00
Color of Product Solution	Colorless	Colorless
pH of Product Solution, Measured	13.3	13.6
pH, Calculated from OH ⁼ Concentration	13.7	13.6
Si, ppm	4.0	2.8

2. Process Development Unit Operations (Reporting Category CO2)

2.1 PDU Operations

Controlling Chunk Formation

In late December a run was made to test the possible effects that the gasifier startup procedure has on chunk formation in the unit. The reactor was heated to 1300°F and pressured to 500 psia with nitrogen. Petroleum coke was loaded into the gasifier to a level above the coal feed point (25 feet). Synthesis gas (CO and H₂) and steam were then added to fluidize the bed. Coal was fed, bringing the bed up to about 35 feet; then char withdrawal was started to maintain bed height. Operation was smooth. There were occasional feedline plugs, and occasional withdrawal problems as well. The unit was voluntarily brought down after 60 hours for scheduled computer maintenance.

This opportunity was taken to empty the bed and inspect the walls for deposits. Care was taken to maintain a fluid bed while cooling down the reactor. A soft bridge was found within five feet of the bottom of the reactor. This deposit accounted for the occasional problems with char withdrawal. The bed above the bridge contained agglomerates that were soft, plastic, low-conversion material. These agglomerates were possibly formed at the feedline.

The unit was brought back up on petroleum coke. Gas flow through the feed line was increased from 7 ft/sec to 14 ft/sec. The number of feed line plugs reduced appreciably. The run continued for eleven days with extended periods of smooth operation interrupted occasionally by difficulties in char removal because of small chunks. This long run demonstrates that the formation of agglomerates in the gasifier can be eliminated as an operational problem by maintaining the fluid bed above the coal feed point and by keeping the feed line gas velocity above 14 ft/sec.

Redesign of Fines Filters

The run was terminated when the fines filters failed which caused the product gas scrubber to become restricted with fines which in turn caused the scrubber to overheat. Increasing the gas flow to the feedlines not only increased the overall quantity of product gas to the filters, but also increased the amount of fines carryover. Fines accumulated in the filter shell and bridged around the elements. The regeneration backflush was not adequate to dislodge these packed solids. Large pressure differentials across the elements caused them to bend and even to tear near the header. The 12 filter elements (per filter) were replaced with 6 elements, spaced further apart to

prevent bridging. Mechanical supports were added to hold the elements perpendicular to the head. Vibrators were also added to help knock down the fines during regeneration, and plans were made to increase the backflush velocity.

PDU operations in February focused on the study of gasifier bed properties, integration of the gas clean-up loop, and startup of the catalyst recycle loop. Since the PDU gasifier operability has been demonstrated by previous runs, operation of the gasifier concentrated on variables that affect the gasifier fluid bed density. In addition, progress has been made toward smoothing out the integrated operations of the gas clean-up loop. Startup and initial shake-down of the catalyst recycle loop was also underway in March.

Variables Affecting Gasifier Bed Density

In operations to date, the PDU fluidized bed density has been somewhat lower than originally expected. The PDU density has been 6-10 lbs/ft³ compared to the FBG predevelopment runs which were 11-20 lbs/ft³. In runs on the FBG earlier in this contract, the fluidized bed density was about 6-8 lbs/ft³. The degree of oxidation of the coal was believed to be the major reason for the difference in char density observed during development contract runs on the FBG and those under the predevelopment program. By exposing the feed coal to air, the density in the FBG was increased to 10-12 lbs/ft³.

A program has been initiated to study variables which effect the PDU fluidized bed char density. The variables being considered include coal/catalyst oxidation, gasifier pressure, superficial gas velocity, catalyst impregnation technique and low temperature heat soak treatments.

During the month of February, several runs were made to begin studying the effects of the different variables on the PDU fluidized bed char density. Five gasification runs were made. These runs are highlighted in Table 2.1-1.

For the five gasification runs, three different batches of oxidized coal were prepared and run at three different pressures. The first run was made with PDU catalyzed coal which had been mildly oxidized in a fluidized bed at 300°F for 30 hours. This first run was made at 500 psi pressure. Operation of the gasifier was very smooth, but the fluidized bed density was 5-6 lbs/ft³.

The second run was made using the same mildly oxidized coal as the first run, but the gasifier pressure was 250 psi. Unit operability was again good, but the fluidized char density was low, 8 lbs/ft³. The fines content of the char bed was much lower than that of earlier PDU operations. The weight percent of particles less than 200 mesh for this second run was 12-16% as opposed to 35-60% for PDU runs in December and January.

Table 2.1-1

SUMMARY OF PDU RUNS IN FEBRUARY

<u>Run Number</u>	<u>Pressure Psig</u>	<u>Air Pretreatment</u>	<u>Fluid Bed Density (lbs/ft³)</u>
1	500	Mild	5-6
2	250	Mild	8
3	250	Severe	8-11
4	100	Mild	10-13
5	100	Minimal	12-15

The third run was started by introducing a more severely oxidized batch of coal at the end of the second run. The coal for the third run was oxidized in a fluidized bed at 400°F for 45 hours. The pressure was held at 250 psi pressure. As the more severely oxidized coal replaced the existing bed, the fluidized bed density went up to 8-11 lbs/ft³. The fines content of the bed dropped to 10-13%.

For the fourth run, the pressure was reduced to 100 psi pressure, and the batch of mildly oxidized coal was reintroduced. Once the unit lined out, the fluidized bed char density was up to 10-13 lbs/ft³. The amount of fines retained in the bed was very low, 4-9 wt % less than 200 mesh particle size.

The unit was held at 100 psi pressure, and a batch of minimally oxidized coal was introduced to the PDU for the fifth run. This coal had been impregnated with catalyst and exposed to air for two hours while drying. The fluidized bed density went up to 12-15 lbs/ft³, and the fines (-200 mesh) content of the bed was up slightly to between 5 and 15 wt %.

Three gasifier runs on six more batches of coal were made to test the effects of pretreatment on gasifier bed density. The first run was on coal oxidized at 350°F for 28 hours, then heat soaked at 250°F for 34 hours. The pressure for this run was 250 psi. The bed density lined out at 14 lbs/ft³ and the fines content of the bed was between 17 and 24%. This run demonstrated that a good bed density is attainable when the coal is pretreated with a mild oxidation step followed by a low temperature heat soak when the gasifier is operated at 250 psi.

The next batch of coal was used to test mild oxidation combined with heat treating at a gasifier pressure of 500 psi. Coal oxidized at 285°F for 26 hours and then heat soaked at 270°F for 45 hours showed an average bed density of 7 lbs/ft³ at 500 psi. The fines content built up rapidly and went as high as 58%. This high level of fines is believed to be partly responsible for the low bed density.

Constant total feed gas rate to the gasifier results in very different superficial gas velocities through the gasifier as the pressure varies from run to run. Five hundred (500) psi operation has half the superficial gas velocity of 250 psi operation when the total gas fed to the gasifier is held constant. This difference in superficial gas velocity may be responsible for the fines buildup in the gasifier, which occurs especially at 500 psi operation. Thus, it was decided that further 500 psi operation would run with the same superficial gas velocity as the 250 psi operation, since the fines content of the bed was low at 250 psi, giving a good bed density.

The third batch of coal received a very mild oxidation treat, and was run at 250 psi. This batch of coal was oxidized at 220°F for seven hours, followed by an average heat soak, 230°F for 24 hours. This coal resulted in a poor bed density at 250 psi. The average bed density was 8 lbs/ft³. The fines content of the bed ranged between 17 and 25%. The unit was brought down when the process coil in the steam superheater ruptured.

At this point, it was desired to determine if a coal pretreatment of oxidation combined with a heat soak would give bed densities above 15 lbs/ft³ at 500 psi. The next three batches were all run at 500 psi with slightly more severe oxidation treats than used formerly.

The first batch was oxidized at 425°F for 66 hours, then heat soaked at 200°F for 12 hours. The next batch was oxidized at 405°F for 12 hours and heat soaked at 200°F for 28 hours. The third batch was oxidized at 400°F for 14 hours and heat soaked at 280°F for 7 hours. All three batches gave a bed density of 10 lbs/ft³.

The fines content of the bed at 500 psi did not go down for these three batches of coal, even though the superficial gas velocity was doubled. The fines content ranged from 36 to 48% of the run.

At this time, it has been shown that pretreating the gasifier feed coal through a mild oxidation, plus a low temperature, heat soak can improve the density of the gasifier fluid bed. It has been shown that this pretreatment can produce a gasifier feed which shows a density of 12-15 lbs/ft³ at 250 psi.

Two vessels are being added to the PDU which will allow for fluid bed pretreatment of the coal in a continuous fashion. The first vessel will serve as an oxidizer, and the second vessel will be for the heat soak. Installation and initial operation of these vessels is expected to be complete in early April.

Operation of Gas Clean-up and Separation Section

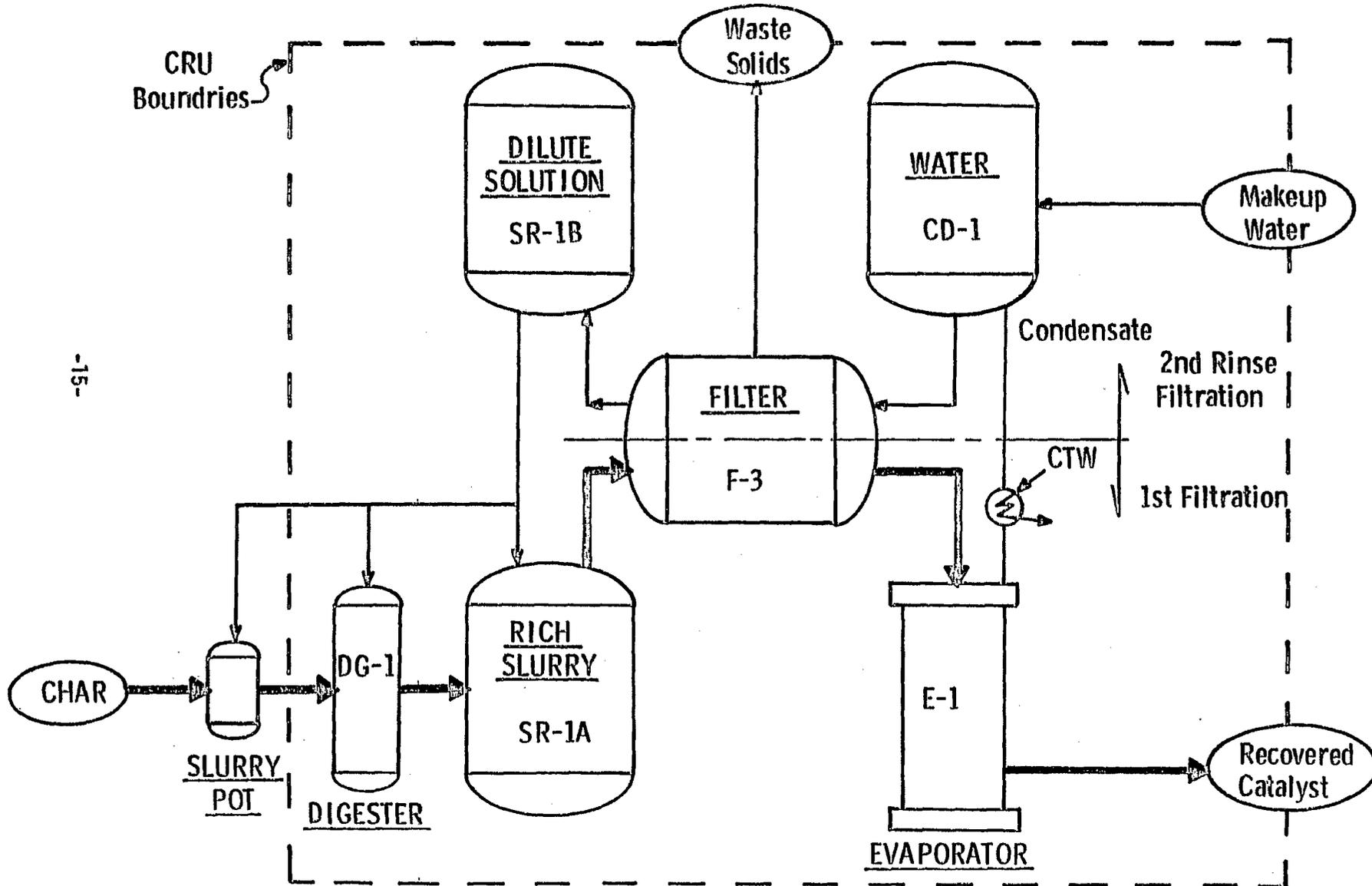
Integrated operations of the gas clean-up and recycle loop began at the end of January. The MEA, molecular sieve, and cryogenic distillation systems were started up and shutdown several times during this quarter. By the end of February, CO₂ concentrations off the MEA system were lowered to 0.5-1.0%. The remaining CO₂ was completely removed by the molecular sieves. A product gas was taken from the cryogenic distillation column which, on nitrogen-free basis, contained 94% methane. The PDU was run in the recycle mode for approximately 200 hours during this quarter. Familiarizing the operators with the equipment, debugging, and optimization of the equipment is continuing.

2.2 PDU Catalyst Recovery Unit Construction and Initial Operations

Process

Initially, the PDU Catalyst Recovery Unit (CRU) will be run as a two-stage water wash process. In this mode no effort is made to enhance catalyst recovery by Ca(OH)₂ digestion to solubilize potassium forms chemically tied up with clays in the coal ash. Typically for Illinois coal, 70% of the initial catalyst loading is recoverable via water wash alone. Figure 2.2-1 is a schematic of the water wash process. Char from the PDU gasifier is slurried in the slurry pots with dilute catalyst solution from a prior catalyst recovery cycle. The

FIGURE 2.2-1
CRU PROCESS SCHEMATIC
TWO STAGE WATER WASH CATALYST RECOVERY



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slurry is then pressured into the digester, which in this mode acts only as a receiving vessel. The digester has the capacity to receive char slurry for approximately eight hours which constitutes a catalyst recovery cycle time. The slurry from the digester is then transferred to the rich slurry surge tank and further diluted with the remainder of the dilute solution before filtering. The filtrate from the first-stage filtration is then collected in the evaporator and concentrated to a 15 wt % K^+ solution before being recycled to the catalyst addition unit of the PDU. The second-stage rinse is accomplished by adding water to the filter and sparging with nitrogen to disperse the cake for better contact. The filtrate is then recycled to the pump section until the solids are recaked on the filter element. The volume of dilute solution remaining in the filter vessel will then be retained in a surge tank for the next catalyst recovery cycle.

Figure 2.2-2 shows the relation between soluble catalyst recovery and second-stage rinse water. Catalyst is lost by being retained in the filter cake. The amount of wash water will dilute the solution in the cake and increase recovery. In the operation of the CRU we can expect 98% soluble catalyst recovery. Also shown in Figure 2.2-2 is the soluble catalyst recovery versus slurring water for a single-stage catalyst recovery process without the second rinse. In this mode, water is added to the slurry pots instead of dilute catalyst solution. The maximum catalyst recovery obtainable for this mode using the CRU is 90% of the water soluble catalyst.

Construction Status

At the beginning of January all general construction work on the catalyst recovery unit was directed towards completing one train of water wash. Completion of construction was given priorities in the order of the process sequence. Figure 2.2-3 shows a complete CRU schematic including the process links between equipment. The shaded region in Figure 2.2-3 denotes the equipment necessary to join a single train of water wash catalyst recovery as described in the previous section. Figure 2.2-4 shows the progress of construction during this quarter. Second train construction of the spare equipment began in early February. The spare process surge tanks were completed in this month and work on the additional digesters and evaporators was initiated.

Construction was interrupted temporarily during February to modify the existing sparge system in the filter for improved operation. In March, the second train evaporator and digesters were completed. Also, insulation of all the process vessels was finished. Construction next month will continue in an effort to complete installation of the lime and precoat slurry tanks necessary for the digestion mode of catalyst recovery. The second train filter will be the last piece of equipment assembled. Also, next month, an emphasis will be placed on instrument hook-up to aid in material balancing the unit and process piping insulation for 200°F operation.

FIGURE 2.2-2

CATALYST RECOVERY UNIT PROCESS

CATALYST RECOVERY VS. PROCESS WATER

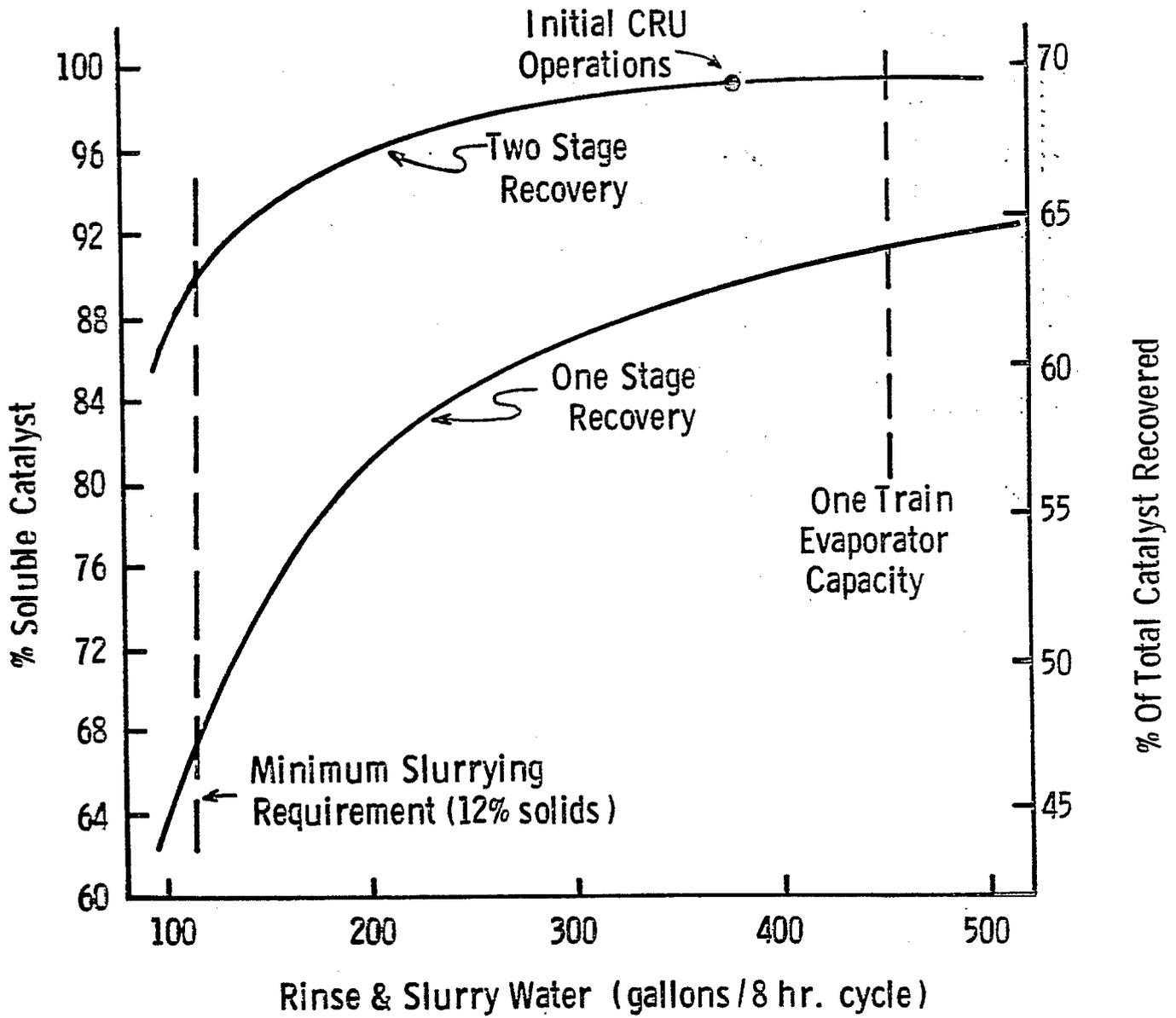
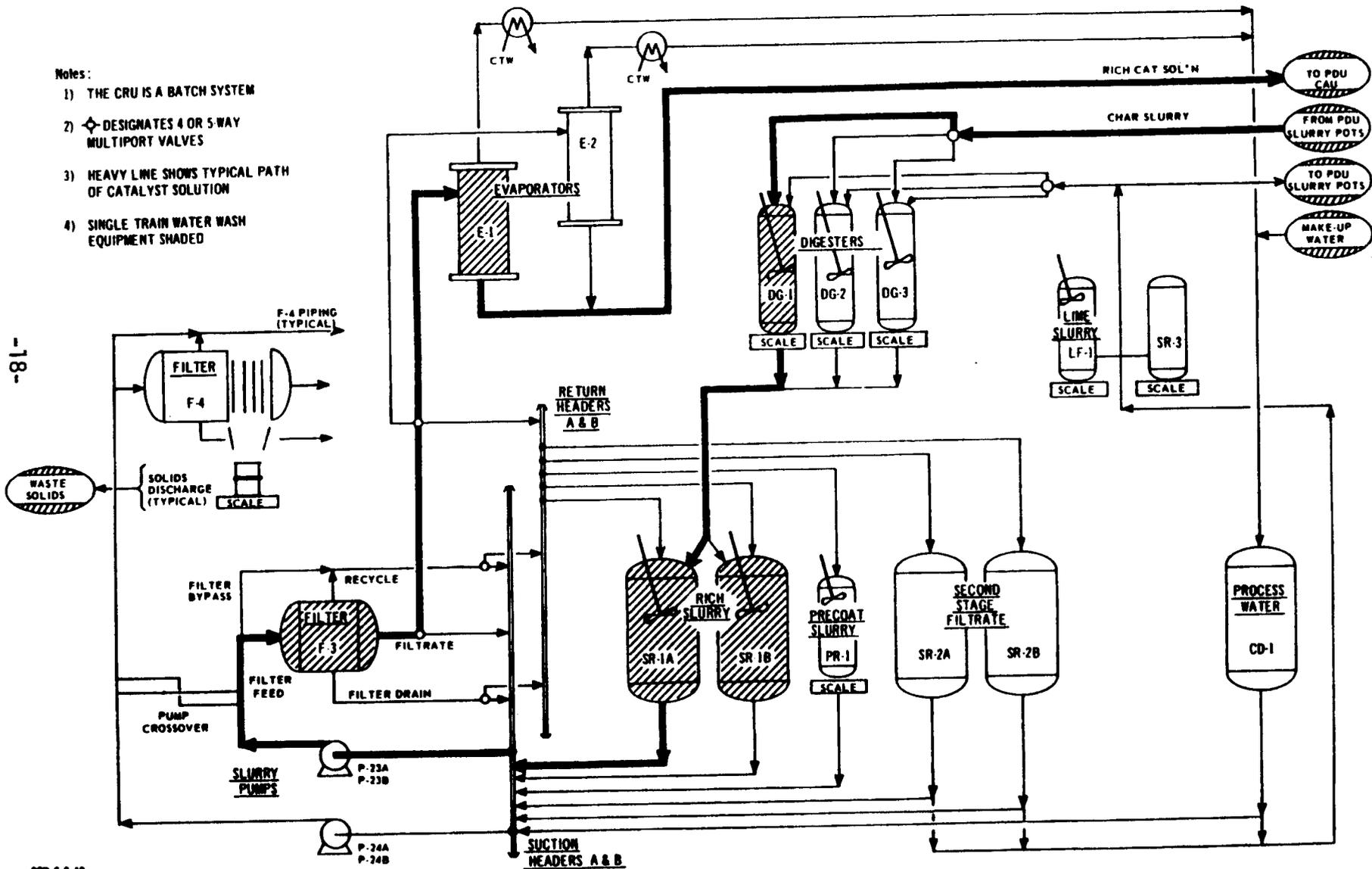


FIGURE 2.2-3 CATALYST RECOVERY UNIT EQUIPMENT SCHEMATIC

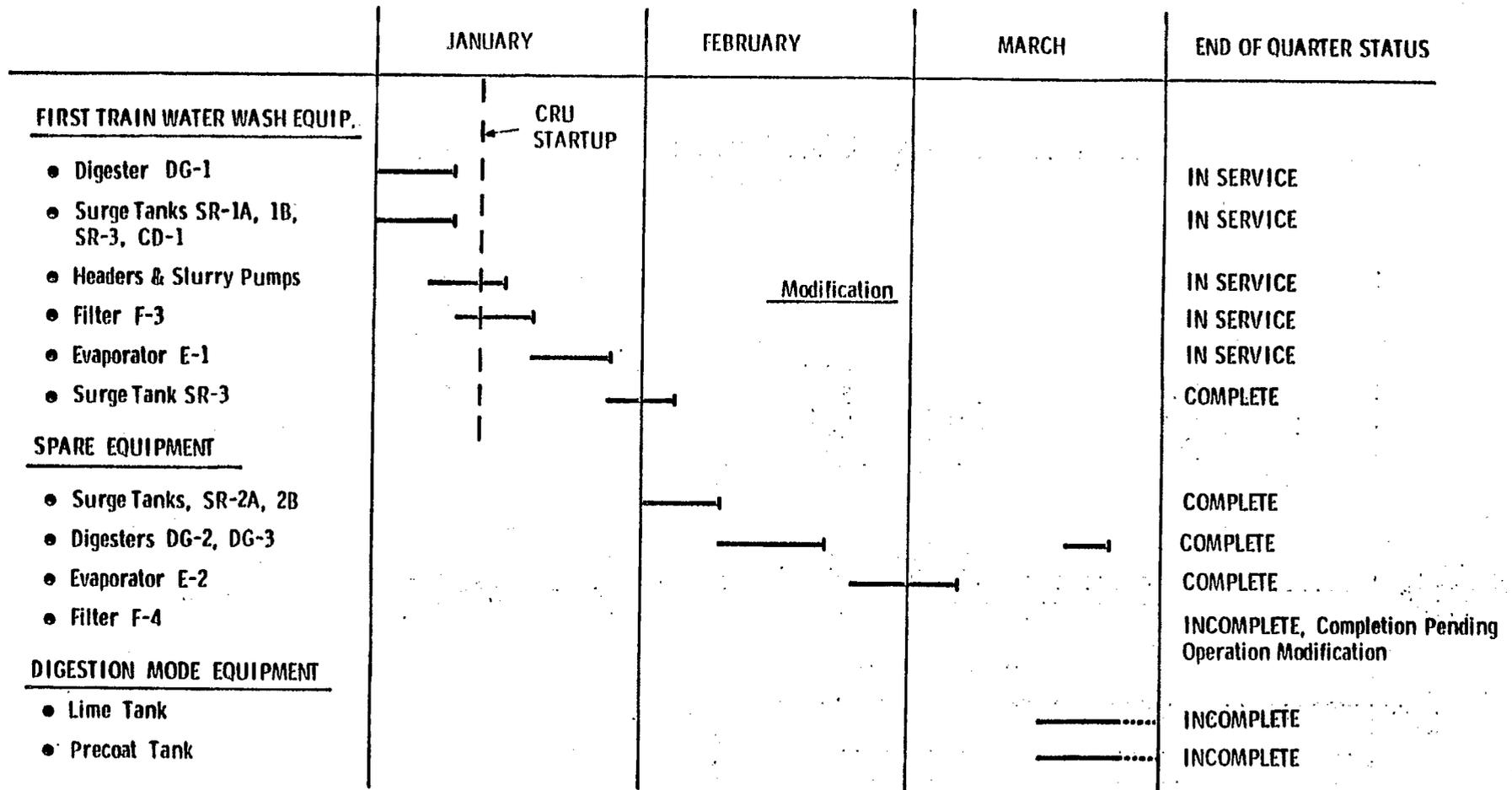


- Notes:
- 1) THE CRU IS A BATCH SYSTEM
 - 2) \diamond DESIGNATES 4 OR 5-WAY MULTI-PORT VALVES
 - 3) HEAVY LINE SHOWS TYPICAL PATH OF CATALYST SOLUTION
 - 4) SINGLE TRAIN WATER WASH EQUIPMENT SHADED

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FIGURE 2.2-4

CRU CONSTRUCTION COMPLETION SCHEDULE



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Operations

The catalyst recovery unit was started up this quarter in a one-stage water wash mode. As reported in the October - December, 1979 Quarterly Report, this operation scheme requires a minimum of process vessels and equipment. In addition, this mode of operation allows us to gain experience in operating the unit before construction is complete, allowing operations to impact on final construction. Operations in the one-stage water wash mode have proceeded smoothly with only minor problems.

Char slurry was initially transferred into the unit from barrels. Chunks of char plugged the suction side of the transfer pump and had to be removed before the bulk of the char slurry could be pumped into the digester. The transfer proceeded smoothly as long as no chunks were in the barrels. In the later part of the quarter, a slurry transfer line between the PDU slurry pots and the catalyst recovery unit was started up. Transferring operations have been very smooth with the line plugging only once. The plug was cleared quickly by using the high pressure nitrogen flush connection. Inspection of the char from the plug showed that it was dry char instead of a slurry. Consequently, steps were taken to insure that the char is completely wetted before transfer. Also, to avoid plugging the transfer line with chunks, strainers were installed at the point the slurry transfer line exits the slurry pots.

Next, the char slurry was transferred from the digester to a surge tank using pressurizing gas. No problems were encountered during the transfer, so it is possible to transfer slurry from one tank to another within the catalyst recovery unit as planned.

Considerable experience has been gained in filtering the char slurry during this quarter. To filter, slurry is pumped out of the surge tank and into the filter until it is full. Once the filter is full, part of the slurry is recycled back to the surge tank while the clear filtrate is sent to the evaporator. When the filtration operation is complete, the remaining slurry in the filter is pressurized back into the surge tank. The filter cake, in general, is uniformly deposited on the filter leaves and approximately one quarter of an inch thick. However, a large quantity of solids are left on the bottom of the filters. These deposits cause concern that the solids are not being suspended well enough within the filter body.

A nitrogen sparge system was originally installed in the filter to help disperse the solids during the preliminary steps of the second wash. It was hoped that the sparge system would prevent the solids from settling but not force the cake off the filter leaves. Experiments during this quarter proved that the cake would stay on the leaves with the sparge system in operation; however, this sparge system was unable to suspend the solids in the slurry during the second wash. Therefore, the sparge system was improved to allow a more thorough sparging of the filter vessel. With the incorporation of

additional sparging during the filtering step, a uniform cake has been consistently formed on the leaves with negligible solids settling in the filter vessel. Finally, two-wash runs have been made, however, further two-wash runs are being temporarily postponed to allow effort to be concentrated on material balance operations.

Once a clean filtrate is produced from the filter, it must be concentrated in an evaporator before being applied to the PDU feed coal. The filtrate in current once-washed operations has a concentration of about 0.3 wt % K^+ . This is below the value planned for integrated operation because large amounts of water are temporarily being used to slurry the char in the PDU char slurry pots. The evaporation step seems to work smoothly but at a significantly lower throughput than designed. At the design condensate rate of 4.0 GPM, an excessive amount of K^+ is present in the condensate. The carryover disappears only when the rate of condensate production is lowered to 2.3 GPM. This carryover of K^+ in the condensate is due to poor disengaging of the steam generated and entrained liquid. Therefore, a demister will be installed to condense entrained liquid from the gas and thus allow the design evaporation rate to be achieved.

During the later part of this quarter, attempts were made to calculate an approximate material balance in the once-washed operation mode. The data is approximate since only some of the instruments necessary for an accurate balance are currently installed. Samples of slurry were analyzed to get the information normally obtained directly from the instruments. For the one run for which data are available, a 73% balance of potassium was achieved while recovery was 33% of all the potassium present. In comparison, about 70% of the potassium could be recovered in a water washed mode. Thus, almost 50% of the water soluble potassium has been recovered in one wash.

Next month's work will focus on integrating the catalyst recovery unit operations with the rest of the PDU. Also, further work will be done to improve the evaporator throughput as well as to improve material balances.

3. Data Acquisition and Correlations (Reporting Category C03)

3.1 Correlation and Modeling

There are two principal parts in the modeling of a fluidized bed reactor such as the CCG gasifier; the hydrodynamics of the gas-solid suspension, and the intrinsic kinetics of the chemical reactions. The performance of the reactor is determined by the combined effects of these two factors. During this quarter, efforts were concentrated in trying to understand the hydrodynamics of the system. This is important from the viewpoint of understanding gas-solid contacting.

It is well known that a fluidized bed consists of two distinct phases: the dense phase or the emulsion phase and the lean phase or the bubble phase. The two-phase theory of fluidization stipulates that all excess gas beyond that required for minimum fluidization goes through the bed in the form of bubbles. The emulsion phase of the bed, therefore, always remains at minimum fluidization voidage with the interstitial flow equal to the minimum fluidization velocity. The operating experience of the PDU, however, indicates that the ideal two-phase theory is probably not applicable when the char particles are extremely fine and light, especially when operating under 500 psi pressure.

In recent PDU operations at about 500 psi, the gasifier mid char contained as much as 50 wt % less than 200 mesh particles. At the same time, the bed density was about one third of the initial loose bulk density. One possible explanation for the low bed density is that the emulsion phase has expanded considerably beyond the minimum fluidization voidage assumed in the two-phase theory. Consequently, the interstitial flow could be significantly greater than the minimum fluidization velocity and the bubble flow appreciably less than that predicted by the two-phase theory.

Figure 3.1-1 shows all of the PDU bed density measurements up to mid-March, 1980. A clearer trend can be detected by making the variables dimensionless (normalized against bulk density and U_{mf} , respectively) as shown in Figure 3.1-2. Figure 3.1-3 shows that the measured PDU bed densities cannot be reasonably explained by assuming a bubbling or slugging bed under the ideal two-phase theory. The measured bed densities, in fact, are better estimated by the Richardson - Zaki correlation developed for the particulate fluidized beds (i.e., bubble-free expansion).

Figure 3.1-4 shows the comparison between the measured bed densities with those calculated from the Richardson - Zaki correlation. The Richardson - Zaki correlation is seen to provide an estimate of the bed density within about 25% of the measured densities. The approximate agreement between the measured bed densities and those calculated by the Richardson - Zaki correlation does not mean that there are no bubbles in the bed. Many different combinations of bubble size/emulsion phase voidage can be postulated to

FIGURE 3.1-1
PDU BED DENSITY MEASUREMENTS

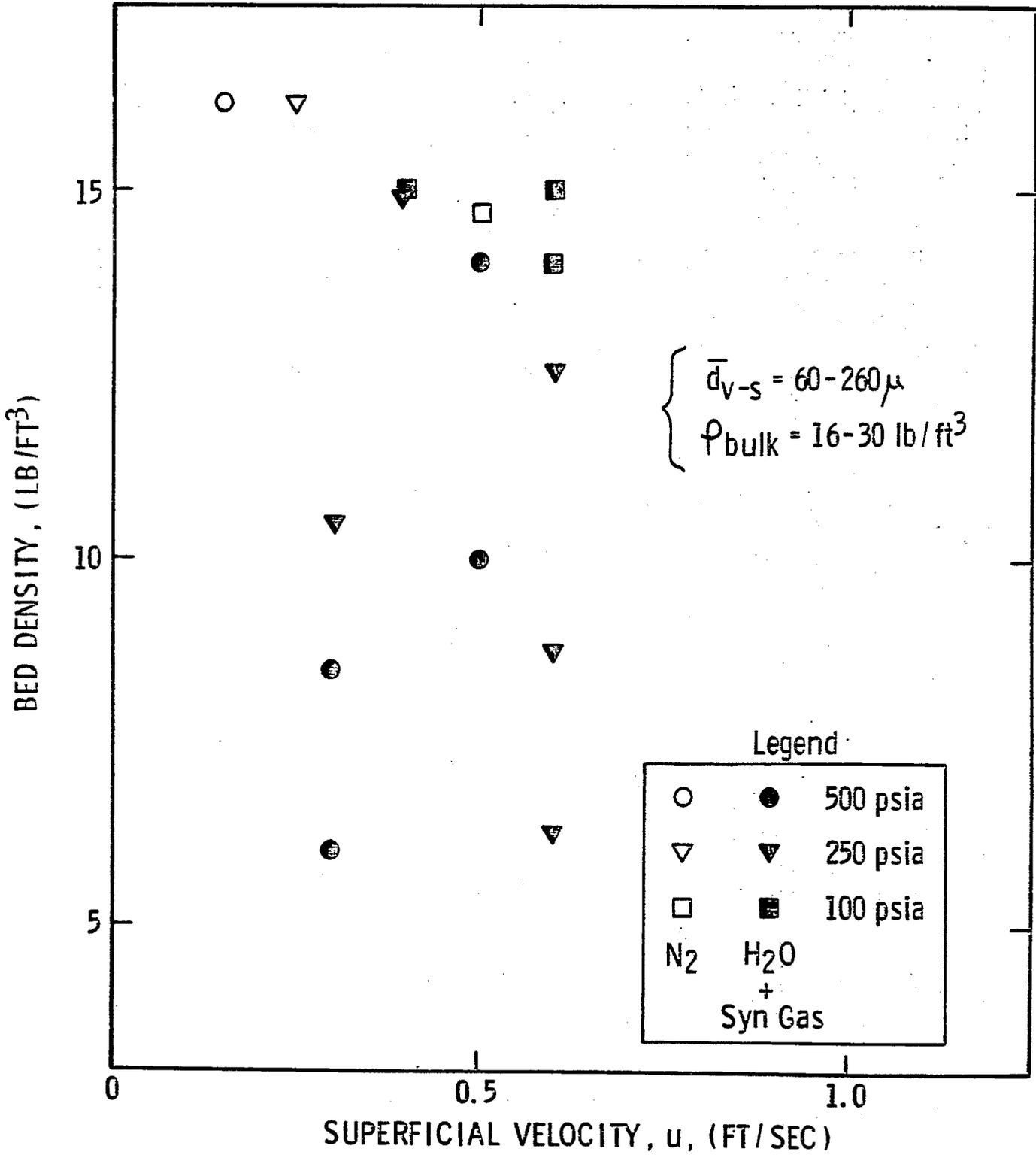
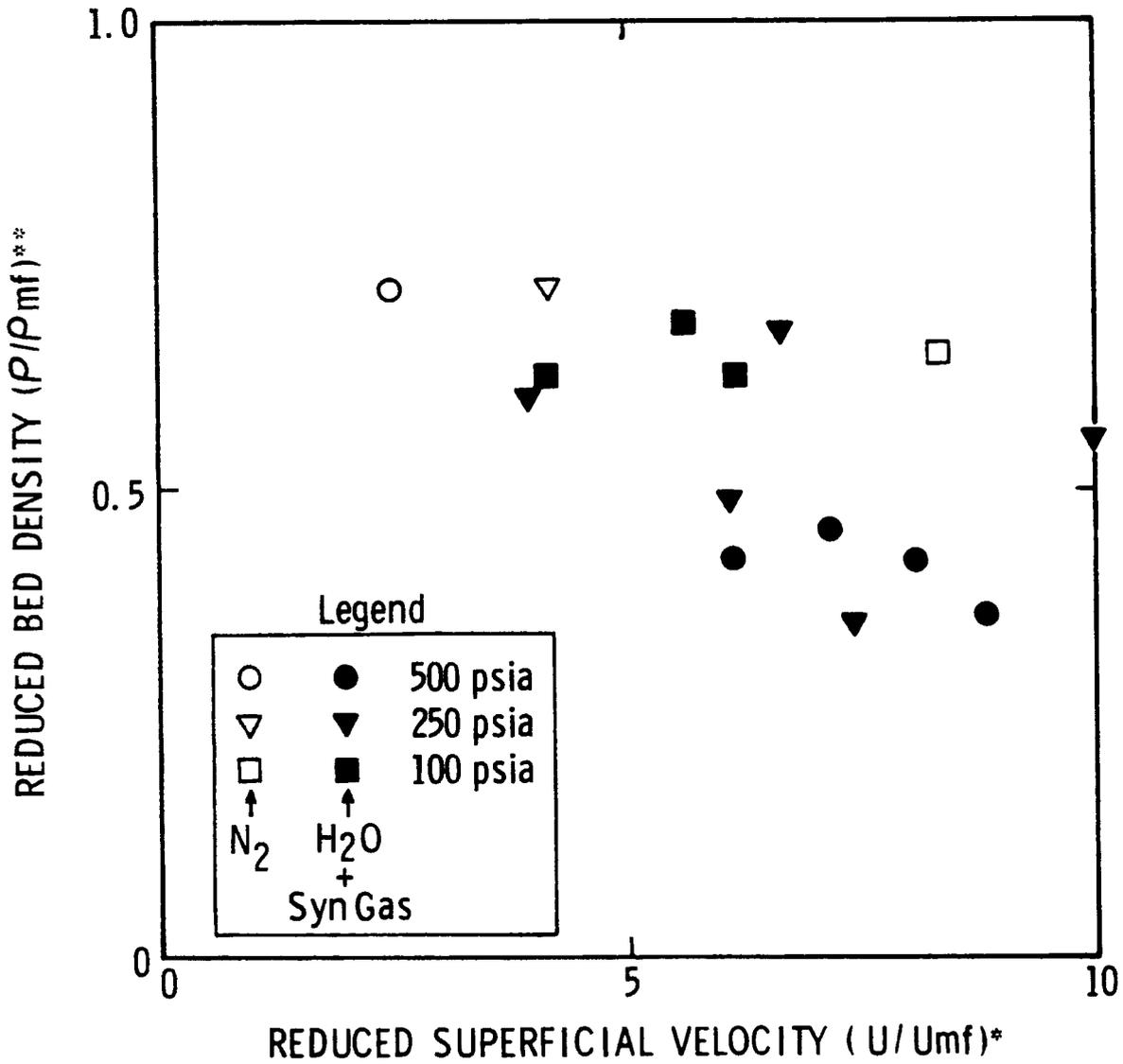


FIGURE 3.1-2

DIMENSIONLESS BED DENSITY-VELOCITY
PLOT FROM PDU DATA



* $U_{mf} = \sum_i X_i U_{mf,i}$; X_i = Wt. Fraction of size i

** Assume $\rho_{mf} \approx \rho_{bulk}$

FIGURE 3.1-3

PDU BED EXPANSION SIGNIFICANTLY GREATER THAN PREDICTED BY THE IDEAL TWO-PHASE THEORY

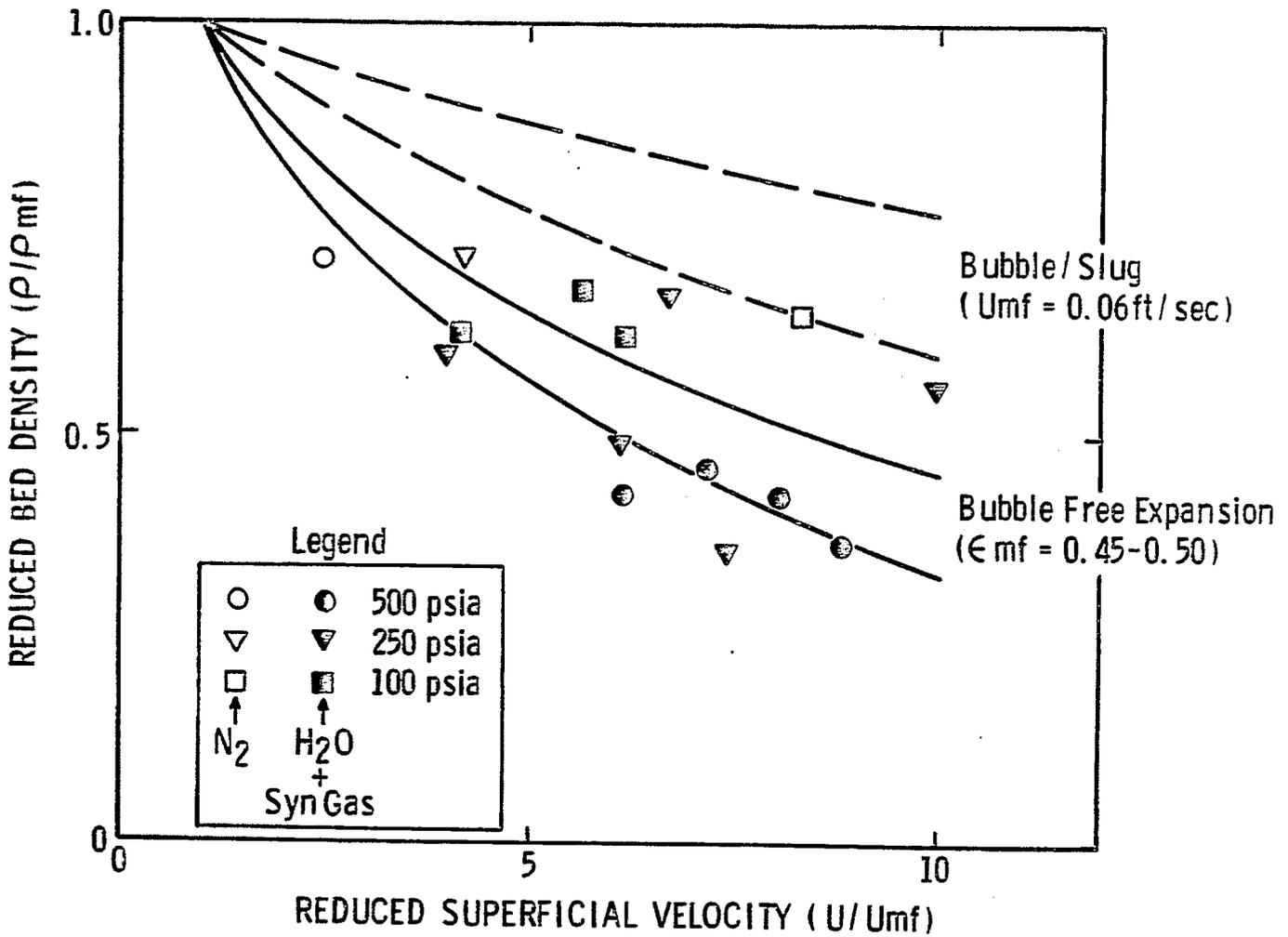
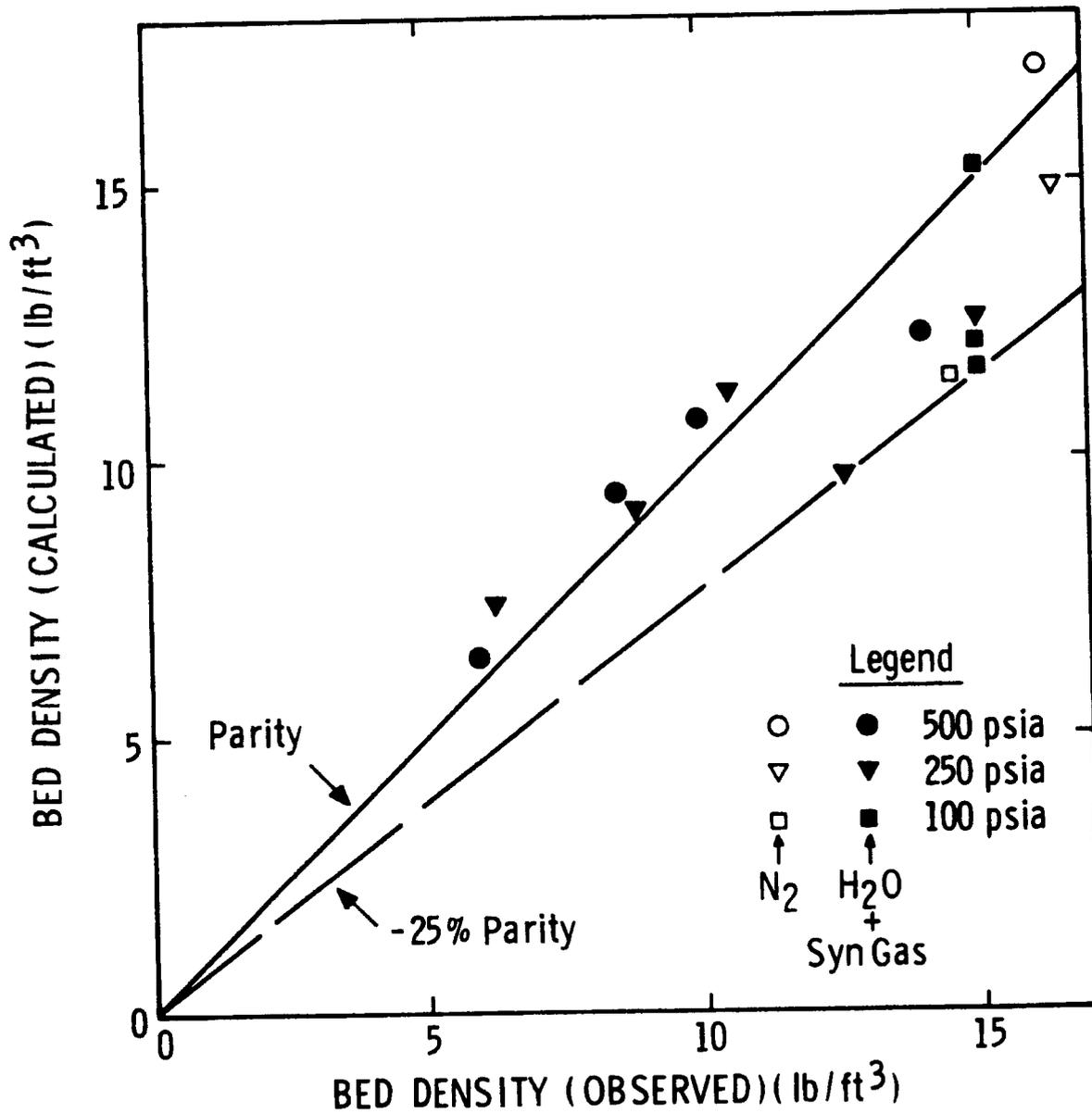


FIGURE 3.1-4

RICHARDSON-ZAKI CORRELATION
PREDICTS THE OBSERVED BED DENSITIES



80B-6-4-30

account for the overall bed expansion. The agreement does indicate, however, that bubble size cannot be deduced from bed expansion measurements alone.

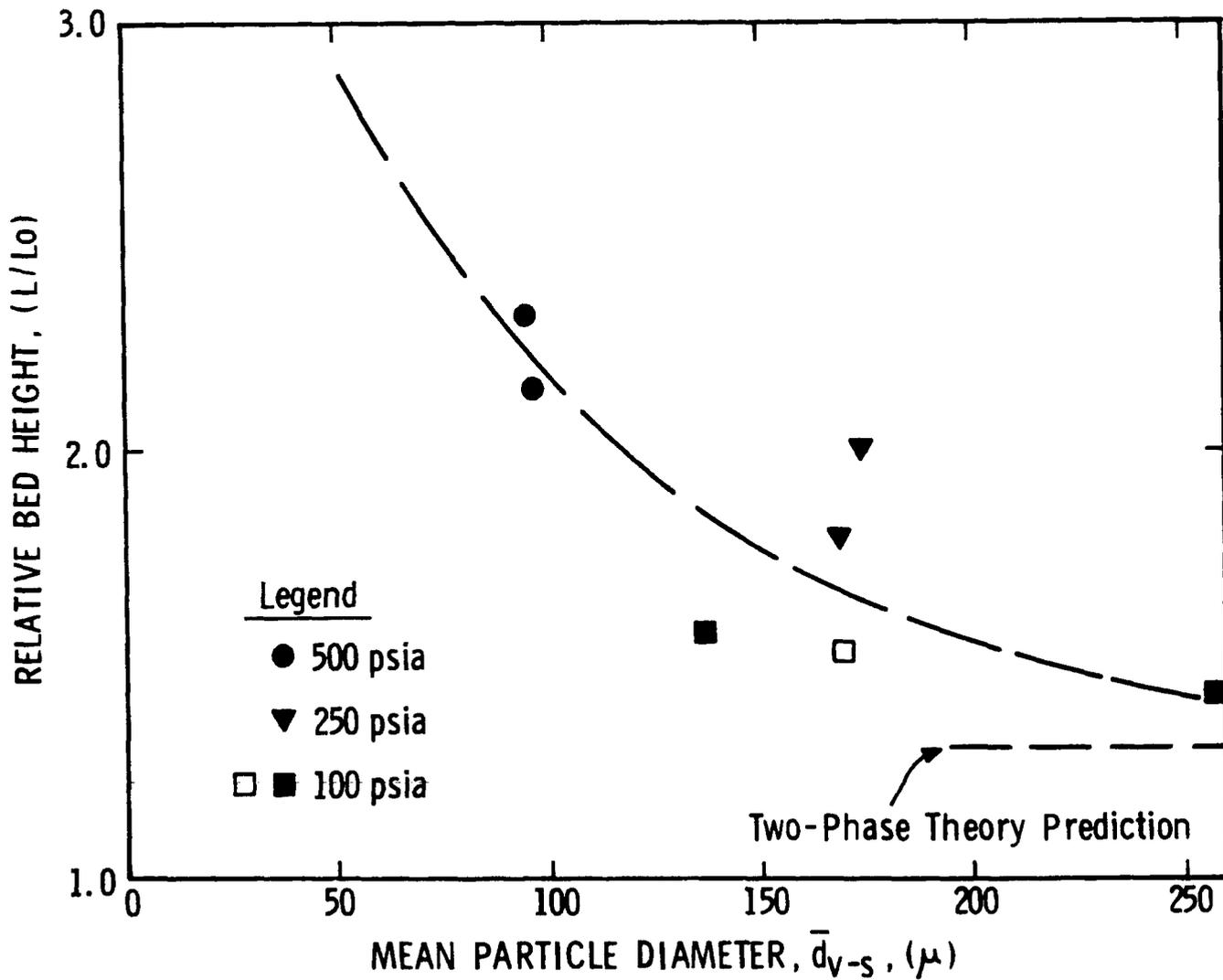
Figure 3.1-5 shows that in addition to the pressure effect, particle size plays an important role in determining bed expansion. As the volume-surface mean particle size increases to 250, it is seen that bed expansion asymptotically approaches the level predicted by the ideal two-phase theory. On the other hand, the deviation from the two-phase theory increases sharply with decreasing particle size.

In summary, the PDU bed density studies lead to two conclusions:

1. The ideal two-phase theory is in error when applied to the PDU system with fine particles and operating under high pressures. The emulsion phase could, in fact, be expanded appreciably beyond the minimum fluidization voidage.
2. Particle size, in addition to pressure, exerts a large influence on the degree of bed expansion and deviation from the ideal two-phase theory.

Both conclusions are supported by recent literature data.

FIGURE 3.1-5
BED EXPANSION DEPENDENT ON PARTICLE SIZE



$u = 0.55 \text{ ft/sec}$

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

4.1 Kinetics of Gasification

Effect of Temperature

The dependence of gasification rate on temperature was studied in the 1/4-inch diameter mini-gasifier, both with and without H₂ in the feed gas. The experimental conditions and the observed reaction rates for this series of experiments are summarized in Table 4.1-1.

Figure 4.1-1 shows the measured reaction rates as a function of reciprocal temperature for experiments both with and without H₂ in the reactor. The apparent activation energy changes as the composition of the gas fed to the reactor changes. When only steam is fed to the reactor, the apparent activation energy is about 31 kcal/mole. When a mixture of H₂O + H₂ is fed to the reactor, the apparent activation energy increases to about 46 kcal/mole. From Figure 4.1-1 it is seen that for H₂O + H₂ in the feed gas, gasification rate is very sensitive to temperature changes. Gasification rate approximately halves for each 50°F drop in reactor temperature below 1300°F.

There is an interaction between feed gas composition and apparent activation energy because the mini-reactor is an integral reactor. For example, when pure steam is introduced at the bottom of the bed of char, a mixture of H₂O + H₂ issues from the top of the bed. As the rate of reaction changes, the gas composition at various locations in the reactor changes even though the feed gas remains the same. Therefore, as temperature changes, some of the change in rate is due to activation energy, but some of the change is due to gas composition. The apparent activation energy is based on an overall rate measurement; therefore, the apparent activation energy ignores the interaction between temperature and gas composition. The reactor model performs the integration required to account for both effects. Future modeling work will distinguish the true activation energy.

Effect of H₂ in the Feed Gas

A series of five experiments were run in the one atmosphere mini-reactor to study the effect of H₂ concentration in the feed gas on gasification rates. Increasing the H₂ to H₂O molar ratio in the feed gas from 0.0 to 0.93 lowers the gasification rate to approximately half its initial value. Further increasing the H₂/H₂O ratio in feed gas to 2.3 only marginally lowers the gasification rate. The experimentally measured gasification rates at various levels of H₂ in the feed gas are presented in Table 4.1-2. Gasification rate increases approximately linearly with the mole fraction of H₂O in the total molar flow of H₂O and H₂ in the feed gas as shown in Figure 4.1-2. Additional experiments are planned at other H₂O mole fractions.

Table 4.1-1
GASIFICATION RATE MEASUREMENTS

<u>Reactor Temperature (°F)</u>	<u>(H₂O/C) (mole/mole) hr⁻¹</u>	<u>(H₂/H₂O) (mole/mole)</u>	<u>Observed Reaction Rate (mole/hr-mole)</u>
1000	10	0	0.132
1094	10	0	0.564
1190	10	0	2.04
1286	10	0	4.74
1373	10	0	9.30
1100	10	0.93	0.084
1194	10	0.93	0.492
1290	10	0.93	2.22
1386	10	0.93	4.80

Steady State FBG Char (Dated 2/3/79) Containing Approximately 30% Carbon and K/C = 0.233

Sample Size = 0.5 grams of char

FIGURE 4.1-1

APPARENT ACTIVATION ENERGY DEPENDS ON
FEED GAS COMPOSITION

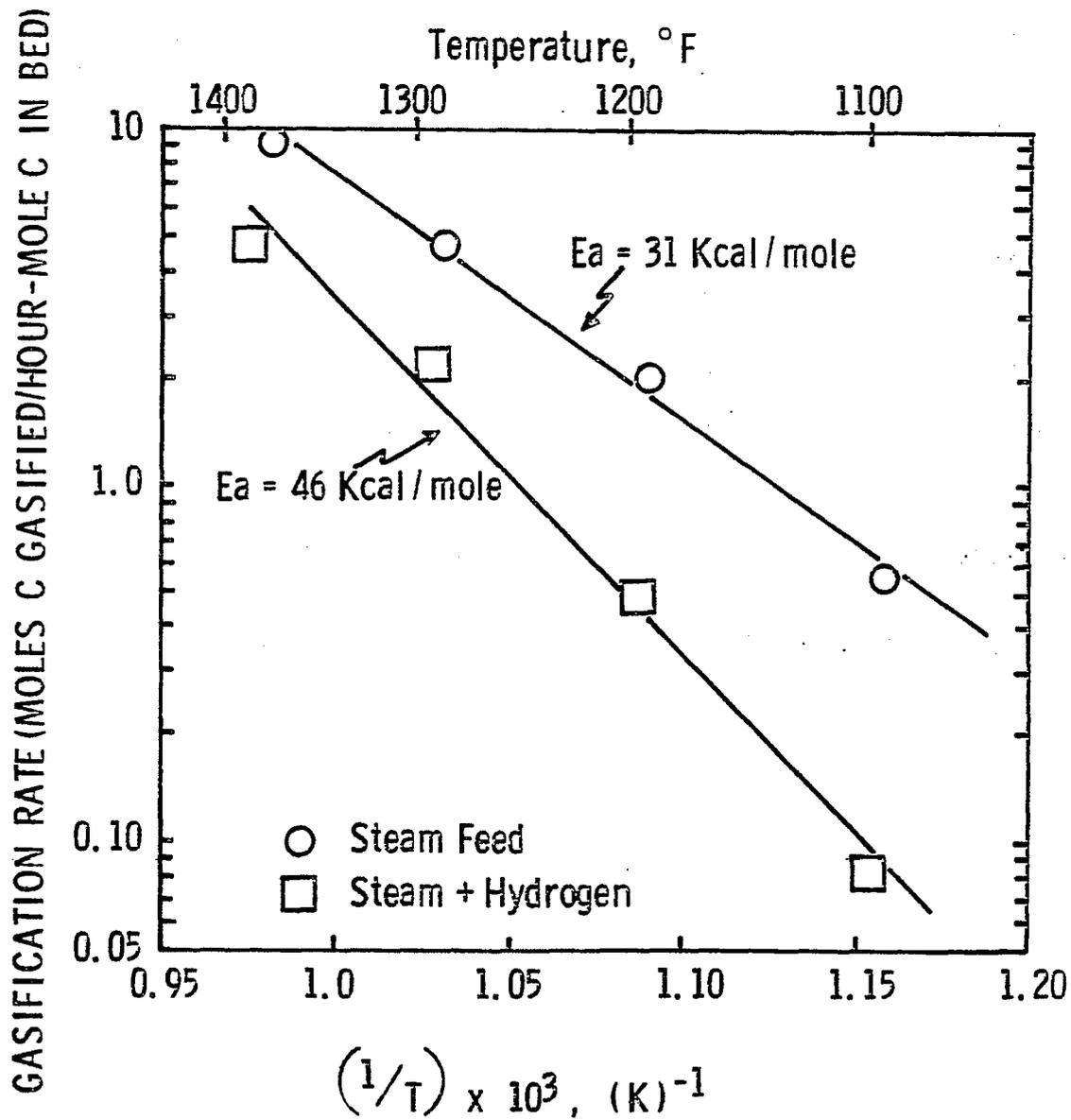


Table 4.1-2

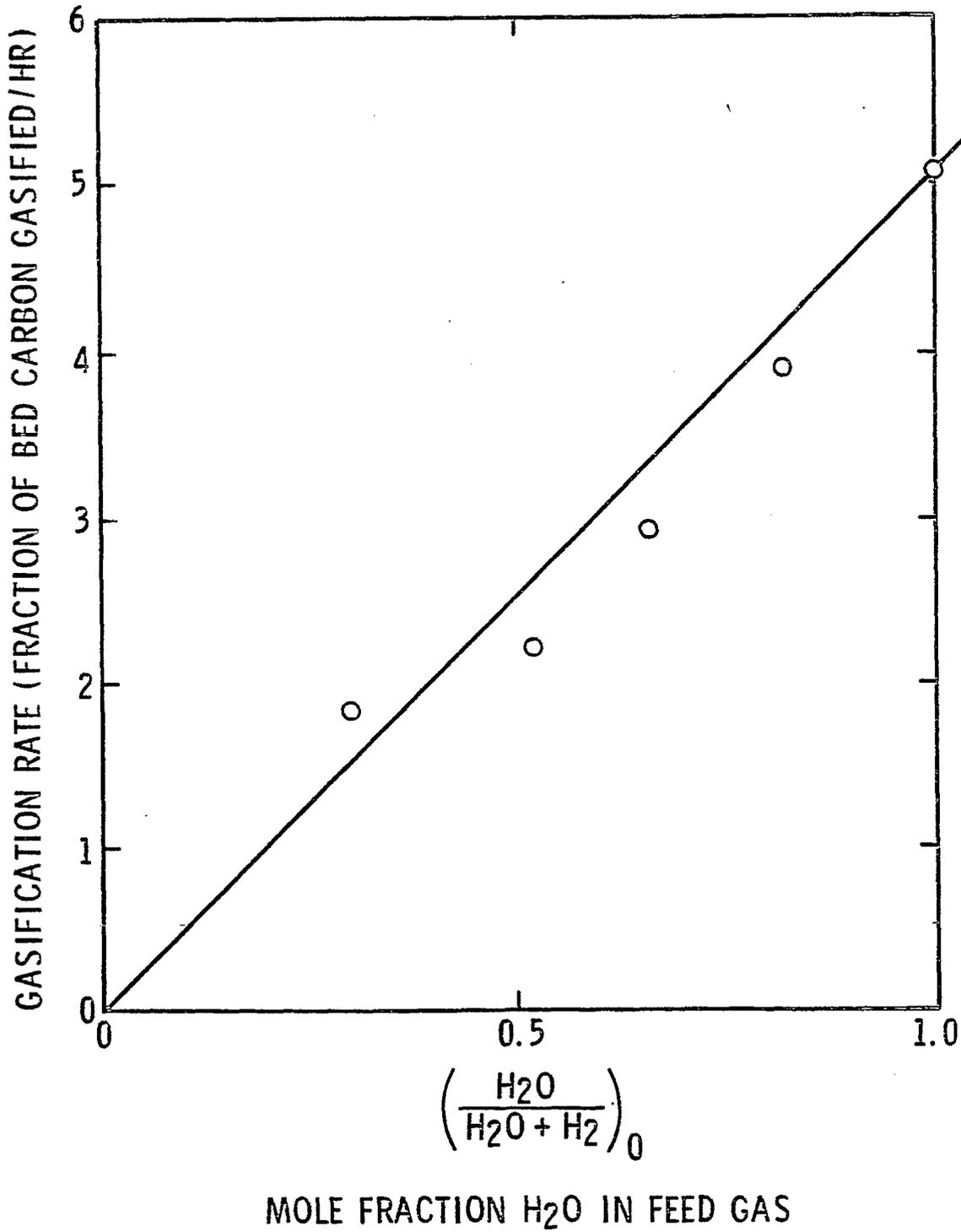
DEPENDENCE OF GASIFICATION RATE ON H₂ IN FEED GAS

(Reactor Temp.: 1300°F; char: 0.5 g FBG char dated 2/3/79)

<u>H₂/H₂O</u> <u>Mole Ratio</u>	$\left(\frac{\text{H}_2\text{O}}{\text{H}_2\text{O}+\text{H}_2}\right)$ <u>Mole Ratio</u>	<u>Reaction Rate</u> <u>(mole/hr-mole)</u>
0.0	1.0	5.10
0.22	0.82	3.90
0.50	0.66	2.94
0.93	0.52	2.22
2.30	0.30	1.86

FIGURE 4.1-2

EFFECT OF H₂ IN FEED GAS ON GASIFICATION RATES



Effects of H₂O Feed Rate

A series of experiments over a four-fold change in reactor sample size (0.25 g to 1.0 g) and three-fold change in H₂O feed rate (0.72 to 2.25 ml per hour) were conducted. The measured reaction rates in moles carbon gasified per hour per mole of carbon in the bed are shown in Table 4.1-3. Gasification rates were found to increase linearly with the square root of the steam rate/carbon in bed ratio as shown in Figure 4.1-3.

Table 4.1-3

Dependence of Gasification Rate on H₂O Rate and Reactor Charge

(Reactor Temp.: 1300°F; char: FBG char dated 2/3/79)

<u>Charge (g)</u>	<u>H₂O Rate (ml/hr)</u>	<u>(H₂O/C) hr⁻¹</u>	<u>Reaction Rates mole/hr-mole</u>
1.0	2.25	5.0	3.06
1.0	1.40	3.1	2.57
1.0	0.72	1.6	1.62
0.5	2.25	10.0	4.62
0.5	1.40	6.2	3.60
0.25	2.25	20.0	6.72

Comparison with Model Predictions

The measured effects of H₂O/C and H₂/H₂O ratios on the gasification rates are in agreement with the interim reactor model. Figure 4.1-4 shows the good agreement between model calculations and the measured gasification rates. In using the interim model kinetic expressions, (October - December, 1979 Quarterly Report) the f_G term must be fixed equal to 1.0 in order to obtain the good agreement shown. According to the interim model, f_G should decrease with increasing potassium-to-carbon mole ratio. For the mini-bed runs, the initial f_G is calculated to be 0.72, and f_G should continue to decrease in the course of the gasification run. However, this is not observed. The good agreement between model calculations (with $f_G = 1.0$) and the measured gasification rates is one indication that the f_G term in the interim model may be in error. Another indication was found in previous mini-fluid bed work (October - December, 1979 Quarterly Report) dealing with the effects of potassium-to-carbon ratio on gasification rate. The f_G factor will be investigated more fully in future work.

FIGURE 4.1-3

EFFECT OF H₂O FEED RATE ON THE GASIFICATION RATE

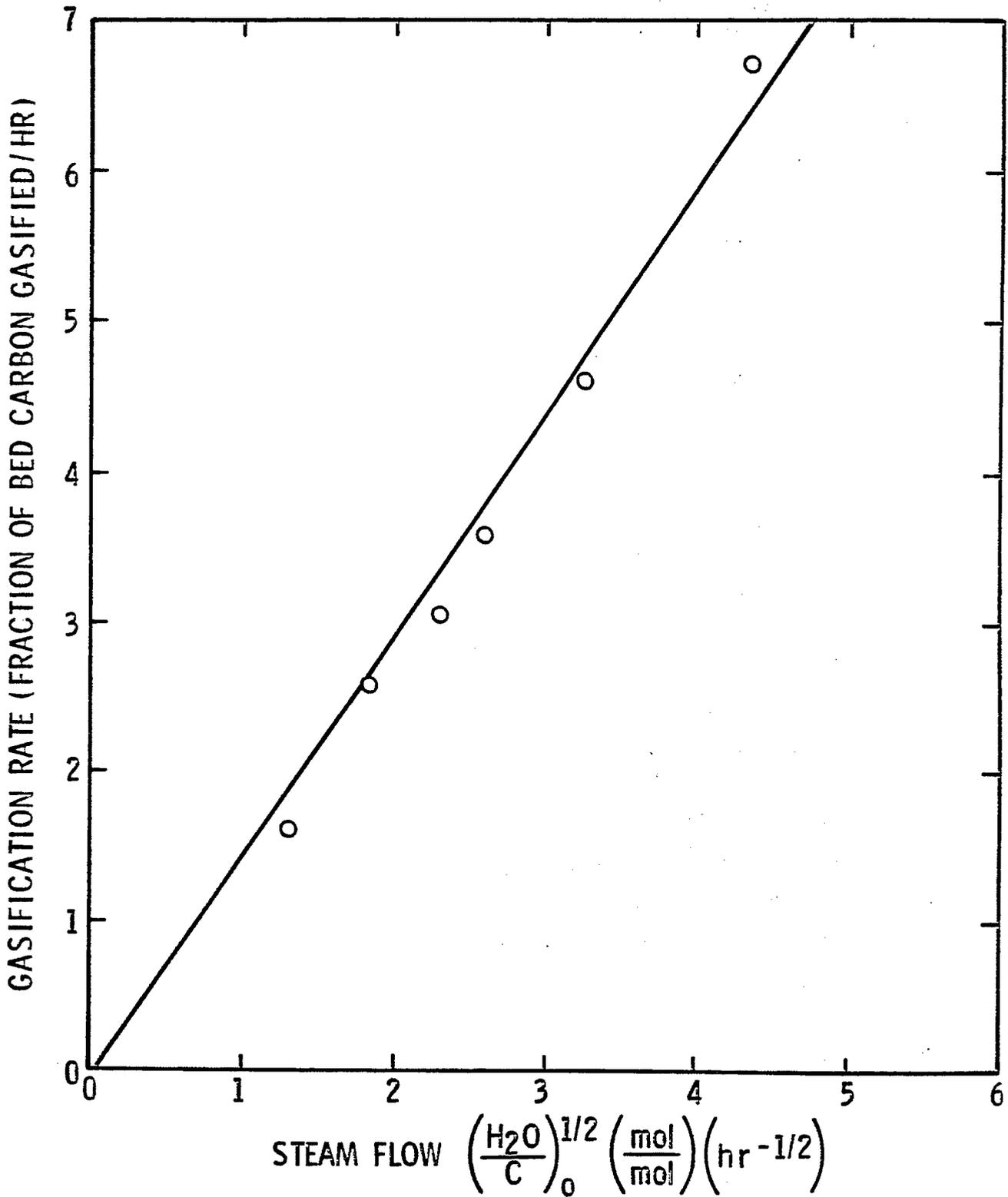
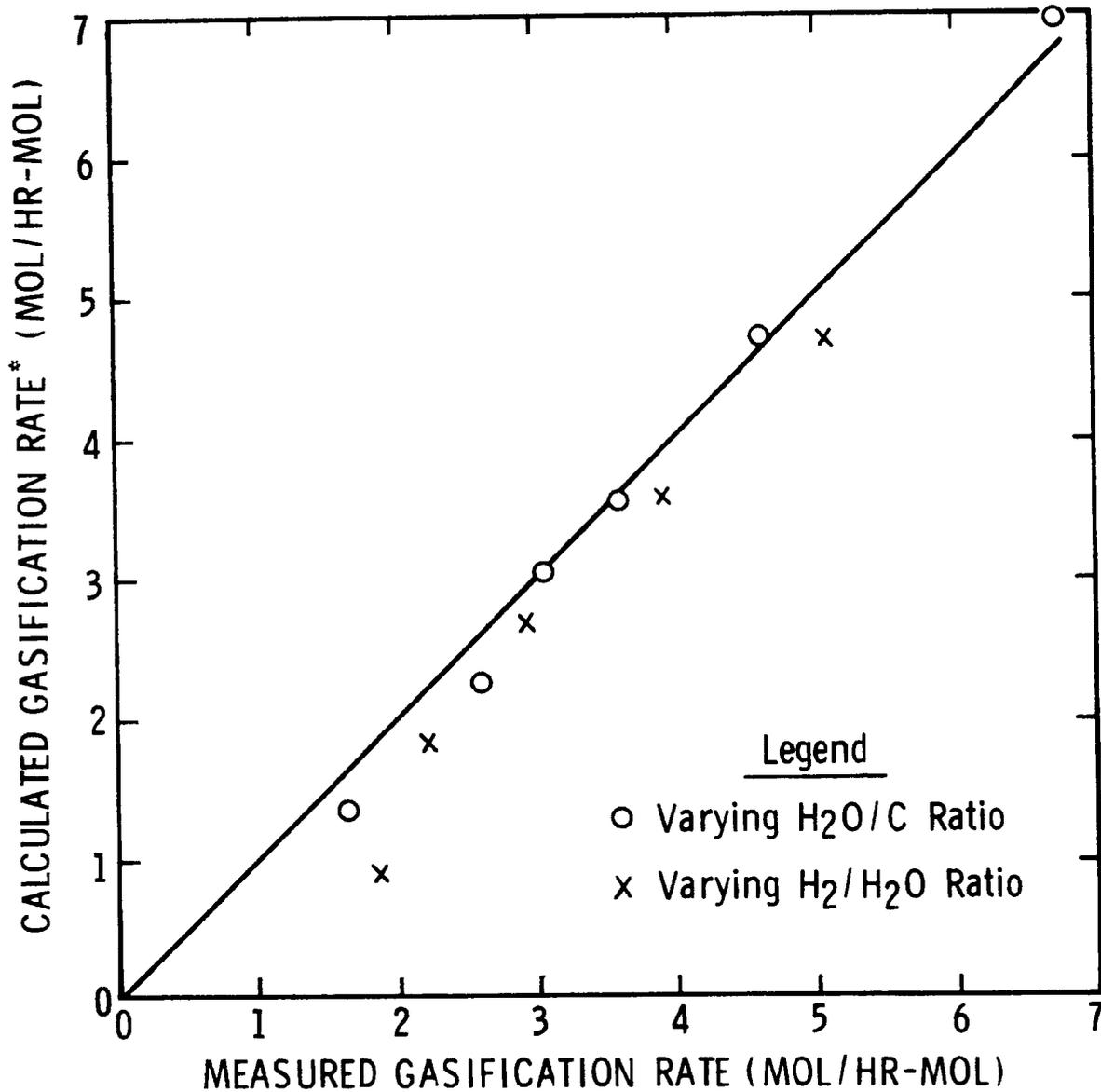


FIGURE 4.1-4

MINI-BED GASIFICATION RATES
CAN BE PREDICTED BY EXISTING MODEL



* Using the Interim model rate expressions with $f_G = 1.0$
(f_G is a function of K/C mole ratio; $f_G = 0.72$ for the
mini-bed runs at the beginning of each run)

High Pressure Reactor Studies

Results obtained in the one atmosphere mini-bed reactor must be verified at commercial reaction conditions. One step in the verification process is a high pressure bench scale test. A high pressure fixed bed reactor has been recommissioned for this purpose. Work this quarter focused on validating the reactor operation against the existing high pressure data base and modifying the unit to allow for a controlled flow of synthesis gas (H₂ and/or CO) into the reactor.

Previous attempts to operate this fixed bed reactor were hindered by analytical problems (July, 1978 - June, 1979 Annual Report). These problems were traced to the gas chromatograph. A different gas chromatograph is now being used, and no analytical problems have been observed.

During the Catalytic Coal Gasification Process predevelopment program (Contract No. E(49-18)-2369), rate studies were conducted using a fixed bed reactor at various pressures and temperatures, but using only pure steam as the feed gas. In order to validate the recommissioned fixed bed for work under this contract, a series of gasification runs was made at pressures ranging from 0 to 500 psig and at steam rates ranging from 0.33 to 1.33 moles per hour. All runs were made at 1300°F using 20 grams of char from Illinois No. 6 coal which had been impregnated with 20 wt % K₂CO₃ and devolatilized in a muffle furnace. These conditions were chosen to match the prior data base.

It was found in the earlier work that gasification rate was not sensitive to pressure but was highly sensitive to steam feed rate. Data from recent runs at both 0 and 500 psig and at both 0.33 and 1.33 moles per hour of steam are shown in Figure 4.1-5. This figure also shows the correlation line from previous runs at these conditions. The agreement between recent data and earlier work validates this reactor.

In order to be able to more closely simulate commercial reaction conditions, the fixed bed unit was modified to allow the introduction of bottled gas into the reactor at a controlled rate. After shakedown of the new feed system, a series of runs was made in the fixed bed reactor at 1300°F and 500 psig with 0.4 moles per hour of H₂ gas fed to the reactor. The steam flow rate varied from 0.33 to 1.33 moles per hour during these runs so that the molar H₂/H₂O ratio ranged from about 0.3 to 1.2.

Data from the one atmosphere mini-bed reactor, shown above, illustrates that the reaction rate is highly sensitive to the ratio of H₂O/H₂ in the reactor. The data at 500 psig confirm this result. Figure 4.1-6 shows data from the two runs where the H₂/H₂O ratio is about 0.3 and 1.2. As shown, the data compare well to the predictions of the simple model shown below.

$$r_G = \frac{0.21 [P_{H_2O} - P_{CO} P_{H_2}/2KG]}{P_{H_2}}$$

FIGURE 4.1-5
RECOMMISSIONED FIXED BED REACTOR
VALIDATED AGAINST PREVIOUS DATA BASE

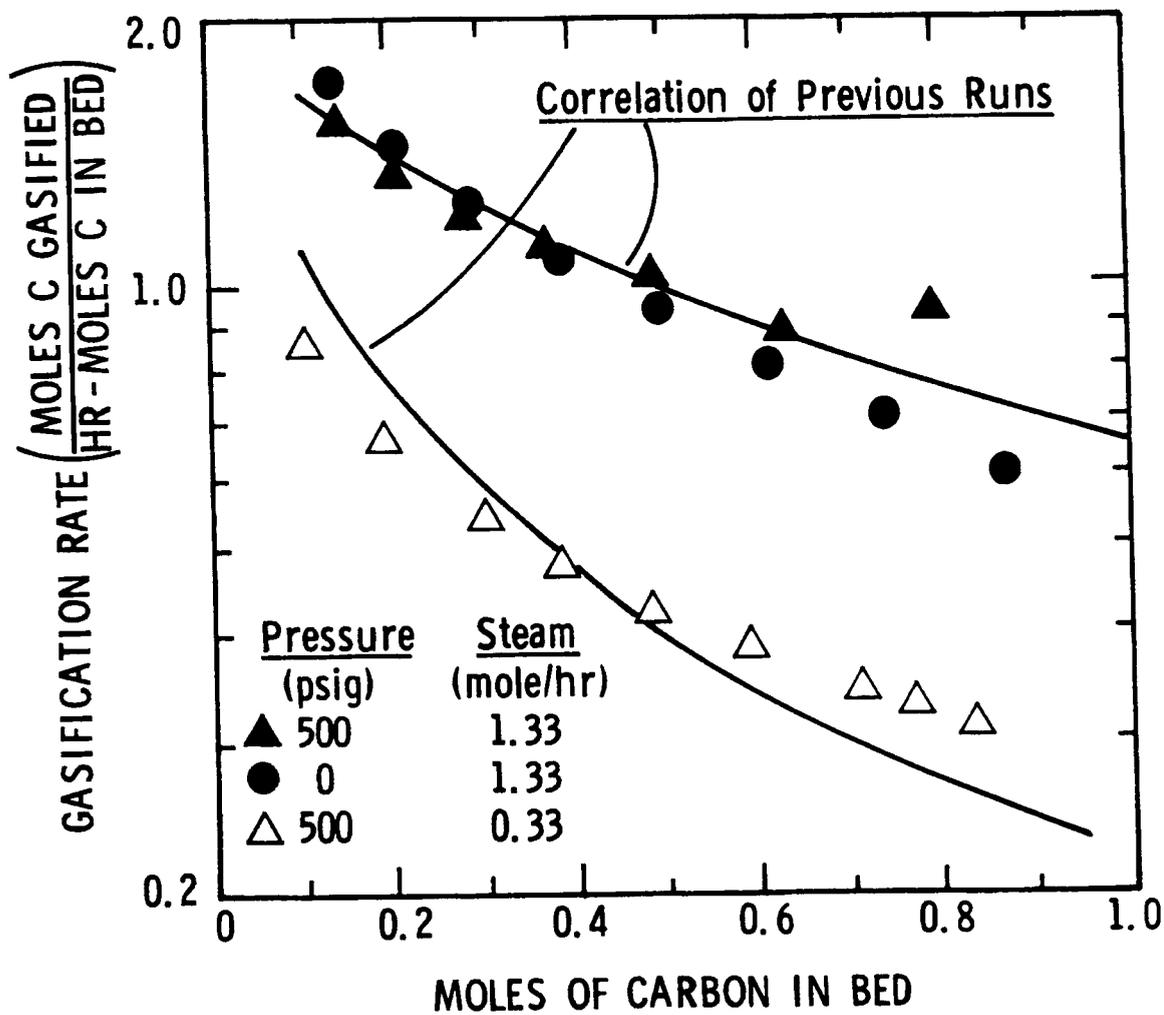
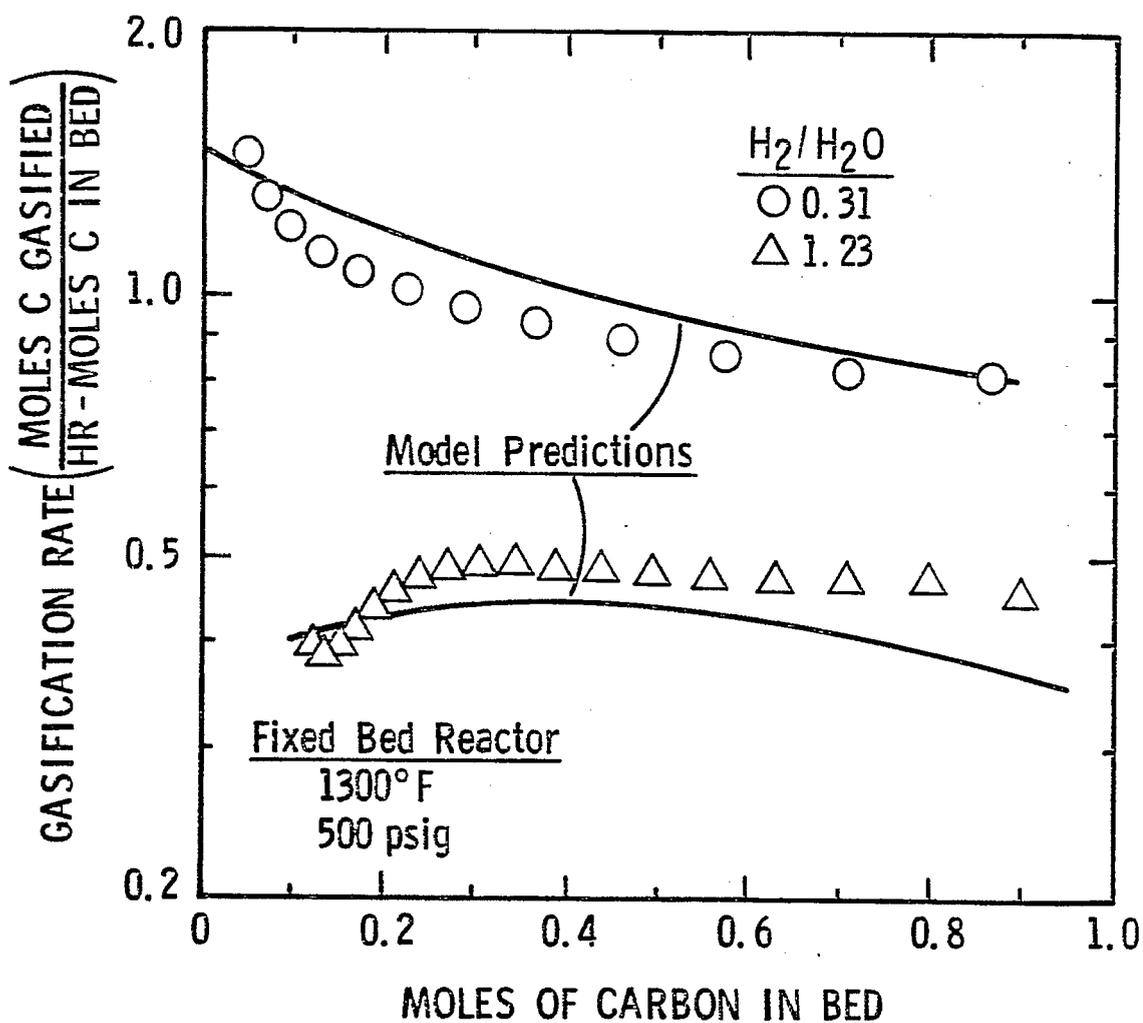


FIGURE 4.1-6

HIGH PRESSURE RUNS WITH HYDROGEN
FIT MODEL DEVELOPED FOR PURE STEAM



$$\text{MODEL: } r_G = 0.21 \frac{(P_{H_2O} - P_{H_2} P_{CO})}{2K_G}$$

P_{H_2}

This model is consistent with data taken for pure steam during the predevelopment program. As shown in the October - December, 1979 Quarterly Report, this simple model can also be used to predict the results from Fluid Bed Gasifier (FBG) operations at 100 psi.

Future work will be aimed at extending the data base to include the effect of various pressures and various combinations of H₂, CO, CO₂, CH₄, and H₂O in the feed gas.

4.2 Catalyst Reactions with Coal and Ash

The goal of recent 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.

Recent bench scale work (October - December, 1979 Quarterly Report) and Process Development Unit (PDU) operations have indicated that pressure is an important variable in coal devolatilization. Therefore, emphasis has shifted from atmospheric pressure studies to pyrolysis at high pressures.

Tubing Bomb Devolatilizations

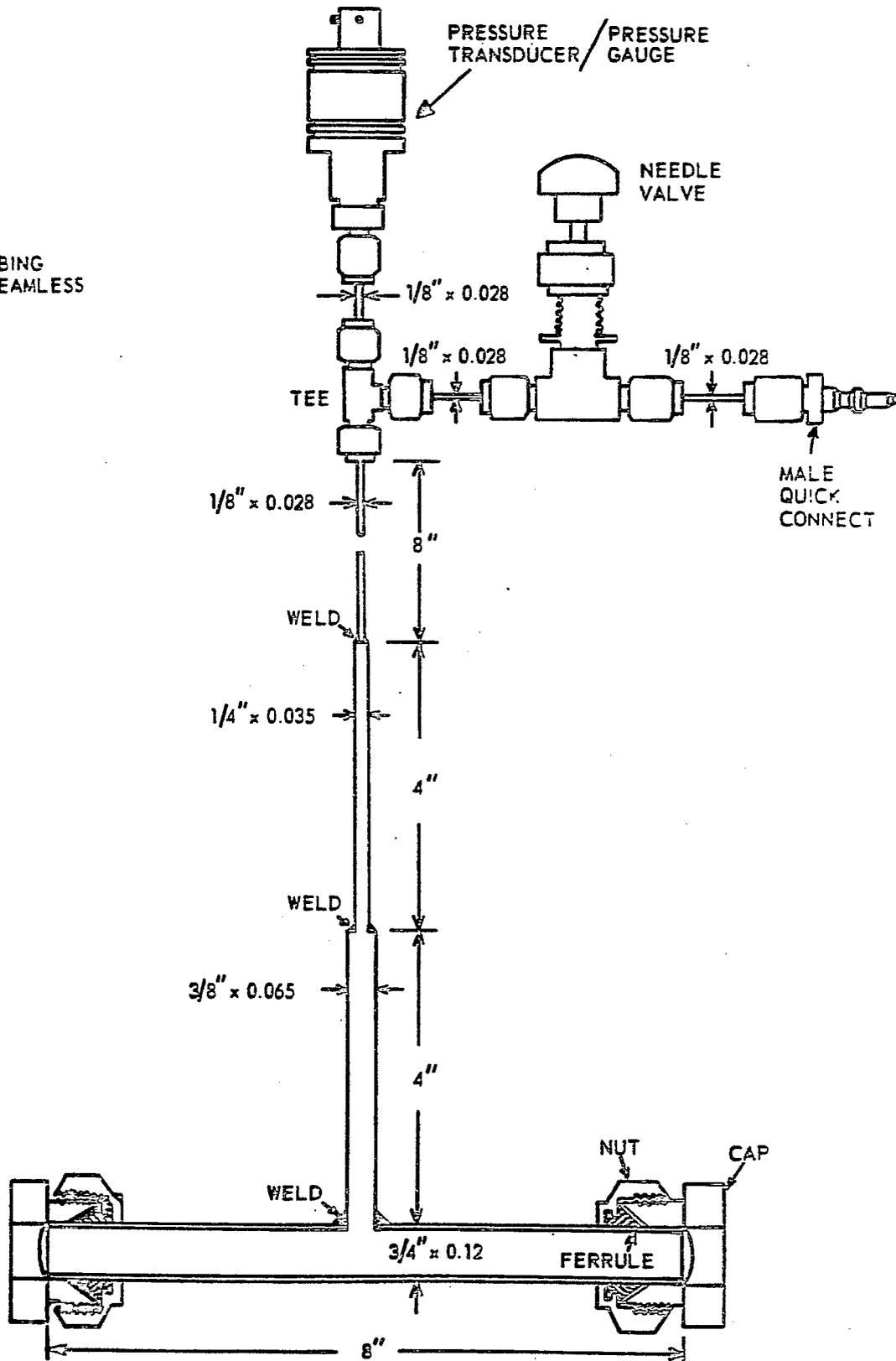
The October - December, 1979 Quarterly Report describes studies conducted using a free fall pyrolysis unit. The service factor for this unit is low because of plugging problems. The most easily operable system for pyrolyzing coal under pressure is a tubing bomb reactor. Figure 4.2-1 illustrates a typical reactor. For these studies, the coal is weighed into ceramic "boats" which are placed in the reactor. The reactor is heated by immersion into a large, fluidized sand bath. The bath temperature used for these studies was 920°F, the maximum allowed on the available equipment. A gauge is used to measure the pressure. A series of screening runs was made in tubing bomb reactors. Table 4.2-1 summarizes the results of these runs.

As found from the earlier Free Fall Unit data and in current PDU operations, pressure was important in determining the extent of agglomeration for the tubing bomb samples. For those samples which did agglomerate, agglomeration increased with increasing pressure. Calcium formate treated samples were highly agglomerated and appeared to have melted in the reactor. Air exposed samples showed less agglomeration than fresh coal. One sample which had been air exposed for six hours at 350°F showed no agglomeration.

Another series of experiments was performed at 1300°F. The tubing bomb was modified so that it could be inserted vertically into a small fluidized sand bath. The results of these tests are shown in Table 4.2-2. The first four samples listed are the same as the correspondingly lettered samples in Table 4.2-1. The results indicate that higher temperature causes somewhat more severe agglomeration.

FIGURE 4.2-1
TUBING BOMB REACTOR

NOTE:
ALL TUBING
SS 316 SEAMLESS



80B-6-3-44

Table 4.2-1

TUBING BOMB DEVOLATILIZATION STUDIES

- 920°F
- Fixed bed
- PDU feed (partially oxidized Illinois #6 with 12% KOH)

Treatment	Result at Final Pressure	
	265 psia	465 psia
A. None (62.1% C, 4.36% H)*	Weakly Agglomerated	Agglomerated
B. 15% Ca(HCO ₂) ₂ added	Agglomerated	Agglomerated
C. Air exposed 41 hr. @ 75°F (61.7% C, 4.32% H)	Very Weakly Agglomerated	Agglomerated
D. Air exposed, 16 hr. @ 200°F (60.4% C, 4.32% H)	Very Weakly Agglomerated	Agglomerated
E. Air exposed, 48 hr. @ 200°F	--	Weakly Agglomerated
F. Air exposed, 24 hr. @ 275°F	--	Weakly Agglomerated
G. Air exposed, 4 hr. @ 350°F	--	Agglomerated
H. Air exposed, 6 hr. @ 350°F (59.4% C, 3.87% H)	No Agglomeration	No Agglomeration
I. Wyodak (56% C, 4.34% H)	No Agglomeration	Very Weakly Agglomerated
J. PDU Fluid Bed Dryer Batch 1	--	Very Weakly Agglomerated

*Analyses on dry coal basis

Table 4.2-2

1300°F TUBING BOMB DEVOLATILIZATIONS

- 1300°F
- Fixed bed
- Illinois #6 coal
- 500 psia final pressure

<u>Sample</u>	<u>Result</u>
A. PDU Feed (CAU)	Agglomerated
D. PDU Feed (CAU), Air Exposed 16 hr @ 200°F	Agglomerated
H. PDU Feed (CAU), Air Exposed 6 hr @ 350°F	Very Weakly Agglomerated
J. Fluid Bed Dryer Batch 1 with Catalyst Redistributed	Agglomerated
K. Fluid Bed Dryer Batch 2	Agglomerated
L. Fluid Bed Dryer Batch 3	Weakly Agglomerated
M. Fluid Bed Dryer Batch 3, N ₂ Exposed 2 hr @ 350°F	Very Weakly Agglomerated

An oxidized coal, the sample labelled Batch 3, showed good agglomeration properties. Allowing this sample to stand for two hours at 350°F in the absence of oxygen further decreased agglomeration. This indicates that the feed coal may be improved by an oxygenless heat treatment after minimal oxidation.

High Pressure Pyrolyzer

It has been shown that pressure is an important variable in determining char density and agglomeration properties. Also, fixed bed reactors do not produce chars with densities comparable to fluid bed reactors. Therefore, a High Pressure Fluidized Bed Pyrolyzer (HPP) has been designed and constructed. A diagram of this unit is shown as Figure 4.2-2. It is similar in operation to the atmospheric pressure fluid bed reactor in that the feed coal is fed into the top of the reactor and falls into a fluidized bed of hot sand. The reactor is continually swept with inert fluidizing gas. The system pressure is maintained by an automated control valve.

The coal feed line is 1/4-inch tubing. Shakedown runs indicated that the coal will agglomerate in the feed line if it extends too far into the reactor. If the feed line does not extend into the reactor at all, some feed coal is carried over into the cold trap. The unit is now operating with a feed line that extends a short distance into the reactor body.

During initial 500 psig operation of the high pressure unit with PDU feed coal, large chunks were formed inside the reactor. These chunks resemble low conversion chunks found in the PDU and described in the October - December, 1979 Quarterly Report. They are much larger than the feed line diameter. Operation with Wyodak coal at high pressure did not form chunks. Chunks were also not formed when a fluidized sand bed pyrolyzer was run at atmospheric pressure. These observations lend support to the theory that the low fluid bed density in the PDU is related to a plastic phase which the feed coal experiences during devolatilization and that high pressure favors the formation of a plastic state. Chunk formation can be avoided by diluting the feed coal with sand of the same size and composition as the sand present in the bed.

Table 4.2-3 contains the densities of chars produced in this manner from a series of PDU feed samples. The pretreatment of these samples and PDU experience with them is summarized in Table 4.2-4.

In all cases, the density is inversely correlated with pressure. The absolute value of the density at the lower pressures is high, relative to the density of the catalyzed coal before devolatilization. This suggests that sand, which has a very high density, is being incorporated into the char. This in turn suggests that at different pressures the char is in a plastic state at different points in the reactor. These conclusions are now being examined.

FIGURE 4.2-2

HIGH PRESSURE FLUIDIZED BED DEVOLATILIZER

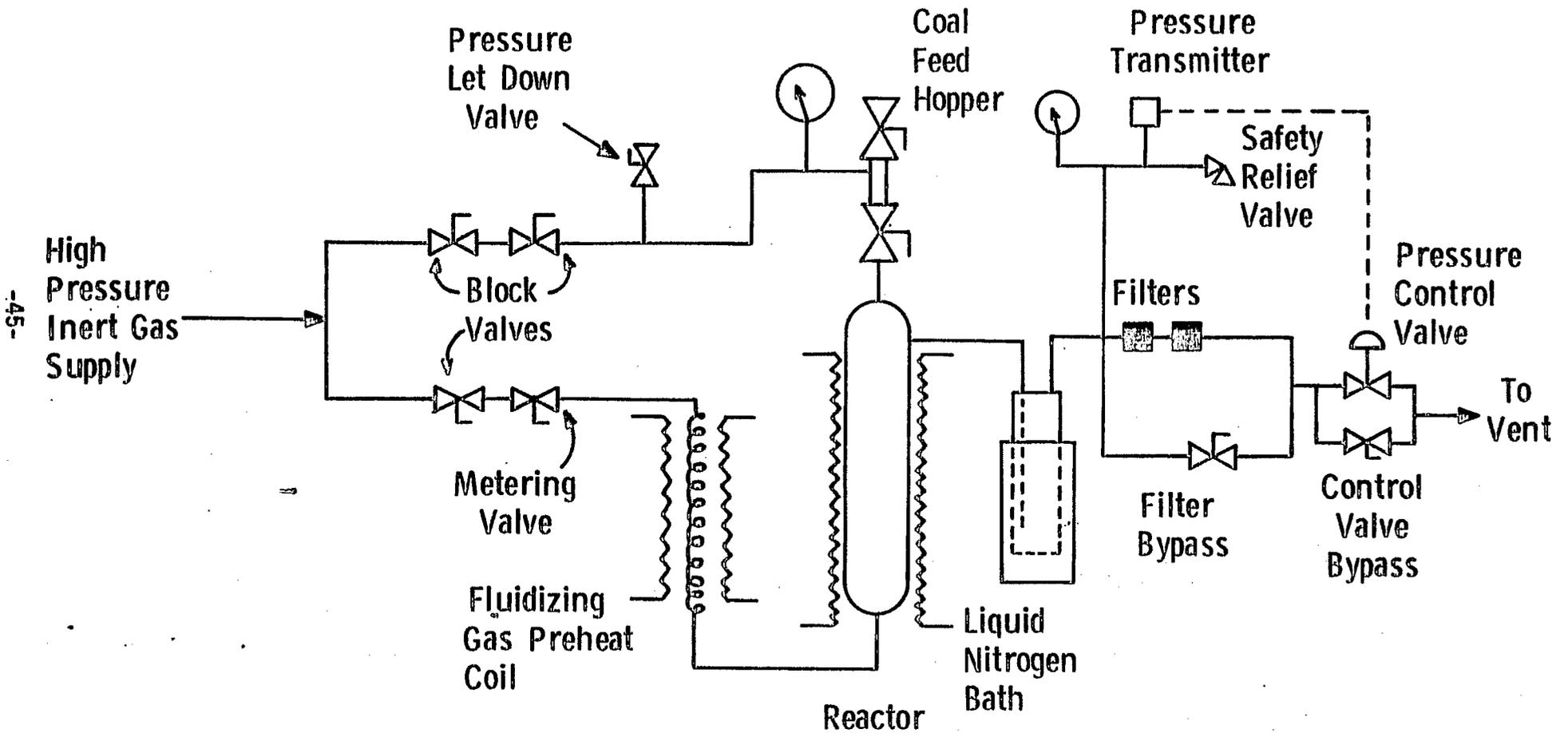


Table 4.2-3

Loose Bulk Densities of Chars
from High Pressure Pyrolyzer

<u>Pressure (psig)</u>	<u>Density (g/ml) Batch Number</u>			
	<u>0</u>	<u>6</u>	<u>7</u>	<u>8</u>
500	0.42	0.44	0.41	-
350	0.51	0.56	-	-
250	0.61	0.60	0.43	0.41
100	0.85	0.73	0.45	0.44
Catalyzed Coal Starting Material	0.74			
Sand	1.56			

Table 4.2-4

PDU Experience with Pretreated Coals

<u>Batch</u>	<u>Pretreatment</u>	<u>PDU Fluid Bed Density</u>
0	None	6-8 lbs/ft ³ @ 500 psig
6	Mild oxidation only	6-8 lbs/ft ³ @ 500 psig
7	Very mild oxidation followed by oxygenless heat treatment	8-9 lbs/ft ³ @ 250 psig
8	Mild oxidation followed by oxygenless heat treatment	8-9 lbs/ft ³ @ 500 psig

Table 4.2-5 contains the densities of these chars relative to the density of the char produced at 100 psig from the same feed coal. These data illustrate that the pretreated coals are less sensitive to pressure variation than the untreated coal. Further, the coals which have received the oxygenless heat treatment show little response to pressure variations regardless of the level of pre-oxidation. This suggests that the oxygenless pretreatment alone may be sufficient. Mass spectrometry data is being gathered to determine the cause of this observed effect.

Table 4.2-5
Pretreated Coals Vary in Extent
of Response to Pressure Change

Relative densities of chars

<u>Pressure</u> <u>(psig)</u>	<u>Batch Number</u>			
	<u>0</u>	<u>6</u>	<u>7</u>	<u>8</u>
500	0.49	0.60	0.91	-
350	0.60	0.77	-	-
250	0.72	0.82	0.96	0.93
100	1.00	1.00	1.00	1.00

4.3 Catalyst/Char Equilibrium Studies

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

Previous work (July - September, 1979 Quarterly Report) looked at solutions of constant potassium concentration but variable pH in order to determine the amount of K^+ which remains on the char. The pH was varied using mixtures of KCl with KOH. Ambient temperature data was presented. Analytical difficulties were encountered, particularly at higher concentrations (4% K^+ in solution and above).

Use of potassium chloride as a neutral salt is not representative of the composition of a recovered catalyst solution. Current data were obtained using mixtures of potassium carbonate and potassium hydroxide to vary the pH. These ions are expected to predominate in recovered catalyst solutions.

Figure 4.3-1 shows that the amount of potassium absorbed on the char is dependent on both the aqueous potassium concentration and the solution pH. As expected, a decrease in the amount of potassium in solution is accompanied by a decrease in the amount of potassium absorbed on the char. There is also a pH dependence, as had been seen earlier. The amount of potassium retained on the char by absorption can be decreased by adjusting the pH to a lower value.

Table 4.3-1 presents data which suggest that the counter ion present does not significantly affect the amount of potassium absorbed, except to the extent that the solution pH is affected.

Further analysis of all data is in progress. The agreement between the complete chloride data set and the carbonate data set will be determined.

Table 4.3-1

Counter Ion Does Not
Affect K⁺ Absorption

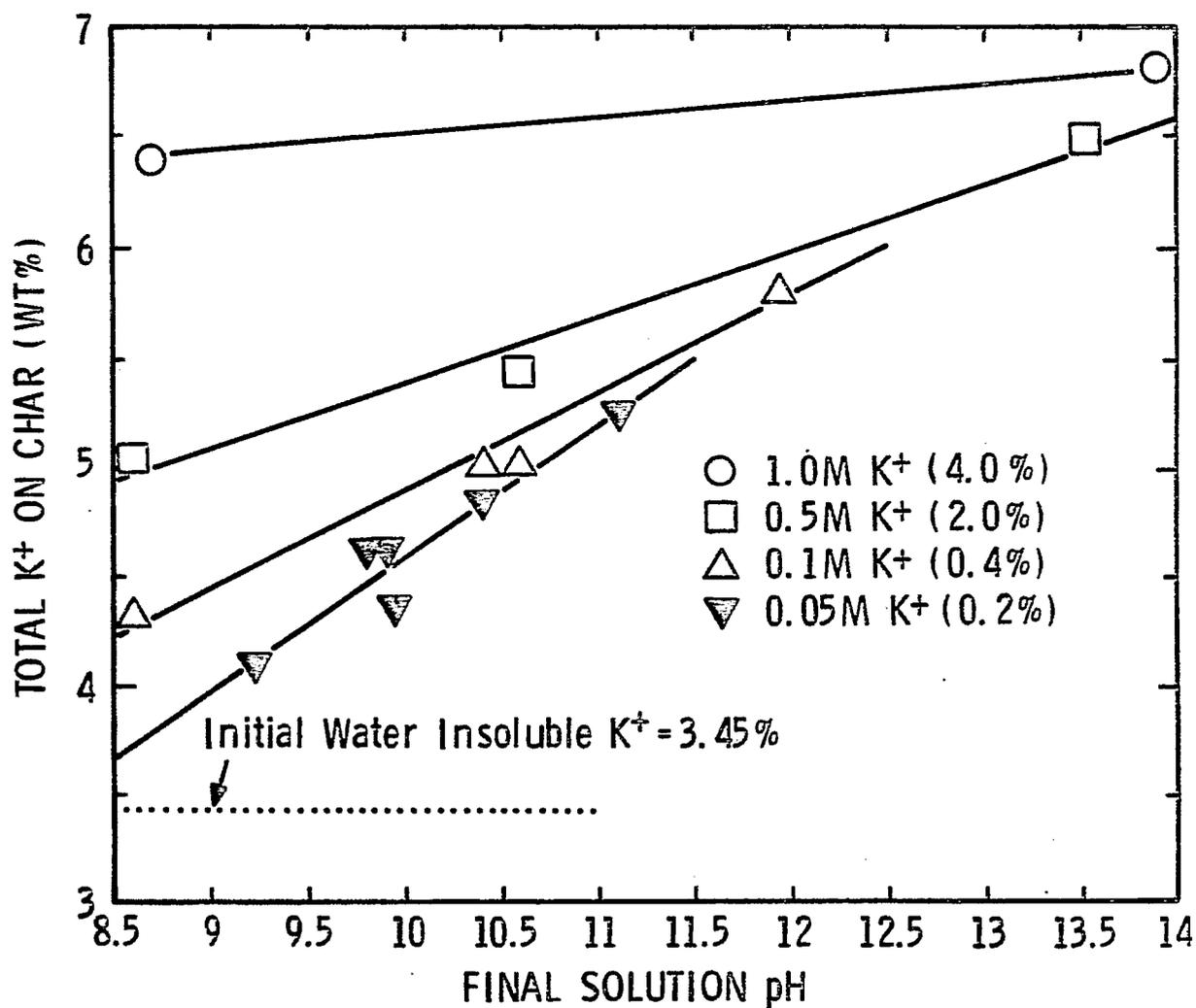
- 1.0 M K⁺ Solutions (4 wt %)
- FBG Char, Water Washed

<u>K⁺ Salt</u>	<u>Total Wt % K⁺ on Char</u>	<u>Original pH</u>
KOH	6.81	14.0
K ₂ CO ₃	6.89	11.2
K ₂ SO ₄	6.49	7.0
KCl	6.35	7.0

FIGURE 4.3-1

POTASSIUM ABSORPTION DECREASES WITH DECREASING pH
AND DECREASING POTASSIUM IN SOLUTION

- FBG CHAR, WATER-WASHED
- $K_2CO_3 + KOH$ SOLUTIONS
- AMBIENT TEMPERATURE ($24^\circ C$)
- 7% SOLIDS CONCENTRATION



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 and fourth sub-tasks. The first and major portion of the Systems Modeling sub-task was completed in December, 1979. Work on the Process Definition is not scheduled until September, 1980.

5.1 Cost Reduction and Laboratory Guidance Studies

Catalyst Recovery Screening Studies

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

Five catalyst recovery screening studies are underway. The cases differ in the type of solid-liquid separation device used in the countercurrent water washing sequence. Only the first case includes lime digestion, which solubilizes 90% of the total potassium in the char and fines. In the remaining cases, which utilize just water wash, only about 70% of the total potassium is soluble. The case numbers, basis, and status of the catalyst recovery screening studies currently in progress are summarized in the following table.

Summary of Catalyst Recovery Screening Studies

Case Number	Basis	Status
1	Lime Digestion with Rotary Drum Filters	Preliminary economics completed
2	Water Wash with Rotary Drum Filters	
3	Water Wash with Gravity Settlers	Cost estimates underway
4	Water Wash with Hydroclones	Process basis development underway
5	Water Wash with Centrifuges	

The work on these cases during the first quarter of 1980 is described below under separate sub-headings.

Cases 1 and 2: Lime Digestion and Water Wash with Rotary Drum Filters

Case 1 is an evaluation of countercurrent water wash combined with lime digestion, using rotary drum filters for the solid-liquid separations. In Case 2, the solid-liquid separations are again carried out using rotary drum filters, but the initial lime digestion step is omitted. The process bases, material and energy balances, and equipment specifications were completed for both of these cases in the previous quarter. During the current quarter, investment and operating cost estimates were prepared for Cases 1 and 2 and preliminary economics were developed. As described in the October - December, 1979 Quarterly Report, the rotary drum filters used in the washing sequence for these two cases were sized based on cake resistances estimated from bench scale filtration tests. As indicated in that report, Case 1 with digested solids requires both more filters and larger average area per filter, when compared to Case 2. However, Case 2 requires more makeup potassium hydroxide. This basic tradeoff is clearly reflected in the preliminary economics for these two cases.

The economics for the catalyst recovery screening cases have been developed on a 1978 dollar basis consistent with the revised CCG Study Design as described in the July, 1978 - June, 1979 Annual Report. However, the investments and operating costs for these screening cases include only the facilities and operating requirements for catalyst recovery, waste solids storage, makeup catalyst, and lime for digestion. Changes in other onsites and offsites sections are incorporated as cost deltas. The cost deltas were calculated using Case 2, Water Wash with Filters, as the "base case". Utilities requirements for the screening cases are reflected by including investments and operating costs which are an allocated share -- based on usage -- of the total CCG Study Design utilities costs.

The investment estimates for catalyst recovery screening Cases 1 and 2 are summarized in Table 5.1-1. The lime digestion step in Case 1 is not expensive in itself; the drums, pumps, and exchangers required for digestion cost only 5 M\$. However, the water wash section is very costly compared to Case 2. The higher investment in Case 1 is due both to the additional lime and lime-derived solids which must be washed, and to the higher filtration cake resistance measured for digested solids in bench-scale tests. These differences are described in detail in the October - December, 1979 Quarterly Report. Lime digestion solubilizes more potassium sulfides than water wash. These sulfides in turn are converted to hydrogen sulfide in the gasifiers. This increases the size of the acid gas removal and sulfur recovery sections in Case 1, but also causes heat effects which reduce preheat furnace investment. Common facilities are larger for Case 1 because of increased process area requirements for catalyst recovery. Additional facilities are needed in Case 1 to handle the lime for digestion and to store the extra waste solids. Utilities consumptions are also larger for Case 1. Case 2 is more costly than Case 1 only in the catalyst receipt and storage area, reflecting the higher potassium hydroxide solution makeup rate (495 ST/SD KOH versus 233 ST/SD KOH in Case 1). Overall, Case 1 requires over three times the investment of Case 2.

The economic comparison between Cases 1 and 2 is presented in Table 5.1-2. Results are shown in terms of 1978 dollars per million Btu's of product SNG (substitute natural gas), based on the CCG Study Design SNG rate of 257 billion Btu/SD. The economic basis is the same used for the CCG Study Design. Based on these initial screening studies, catalyst recovery via lime digestion with rotary drum filters (Case 1) costs a total of 1.75 \$/MBtu, 0.77 \$/MBtu more than water wash with rotary drum filters (Case 2). With water wash, makeup potassium hydroxide costs over 0.30 \$/MBtu more than with lime digestion. However, the cost of the lime for digestion offsets half of this increase. Much larger costs in Case 1 for utilities and other operating requirements, and the capital charges associated with the larger investment discussed above, more than offset the remaining makeup cost delta and add up to an overwhelming deficit for lime digestion. Thus, water wash without lime digestion is likely to have a very significant advantage if rotary drum filters are used for the solid-liquid separations.

The material and energy balances for these screening cases include the estimated impact of adsorption of aqueous potassium ion ($K^+(aq)$) on the char/fines solids. This adsorption effect seems to behave like an equilibrium: the amount of $K^+(aq)$ adsorbed on the solids is apparently a function of the $K^+(aq)$ concentration in the solution. In these initial screening cases, a strong equilibrium potassium adsorption has been assumed based on early, limited experimental results. Inclusion of this equilibrium approximately doubles the solid-liquid separations equipment required to achieve a given potassium recovery, compared to an analogous case with no $K^+(aq)$ adsorption. Recent laboratory studies have indicated that $K^+(aq)$ adsorption may be less strong than assumed in Cases 1 and 2. This would bring down the costs in both cases, but would be unlikely to eliminate the big advantage for Case 2.

Table 5.1-1

CATALYST RECOVERY SCREENING STUDIES
INVESTMENTS FOR ROTARY DRUM FILTER CASES

Basis: ● January, 1978 Instant Pioneer Plant
 ● Eastern Illinois Location

<u>Plant Section</u>	<u>Investment Breakdown, Million \$</u>	
	<u>Case 1</u> <u>Lime Digestion</u> <u>With Filters</u>	<u>Case 2</u> <u>Water Wash</u> <u>With Filters</u>
● Catalyst Recovery		
- Lime Digestion	5	-
- Water Wash	217	62
- Fines Slurry Filtration	3	3
- Rich Solution Evaporation	<u>11</u>	<u>10</u>
Subtotal	236	75
● Changes in Other Onsites		
- Preheat Furnaces	(4)	Base
- Acid Gas Removal and Sulfur Recovery	15	Base
- Common Facilities	4	Base
- Others	<u>0</u>	<u>Base</u>
Subtotal	15	Base
● Catalyst-Related Offsites		
- Catalyst Receipt and Storage	1	3
- Lime Receipt and Storage	10	-
- Onsites Waste Solids Handling	<u>15</u>	<u>12</u>
Subtotal	26	15
● Changes in Other Offsites	4	Base
● Allocated Utilities		
- Raw Water/Cooling Water	4	2
- Steam	15	5
- Electric Power	<u>7</u>	<u>2</u>
Subtotal	<u>26</u>	<u>9</u>
TOTAL DIRECT AND INDIRECT COSTS	307	99
PROCESS DEVELOPMENT ALLOWANCE (25% of Onsites D and I Costs)	63	19
PROJECT CONTINGENCY (25% of Total D and I Costs)	<u>77</u>	<u>25</u>
TOTAL ERECTED COST	447	143

Note:

(1) Excludes lime receipt and storage for flue gas desulfurization.

Table 5.1-2

CATALYST RECOVERY SCREENING STUDIES
ECONOMICS FOR ROTARY DRUM FILTER CASES

- Basis:
- January, 1978 Instant Pioneer Plant, Eastern Illinois Location
 - 257 Billion Btu/Stream Day SNG (HHV Basis)
 - 90% Capacity Factor
 - 100% Equity Financing
 - 15% Current Dollar DCF Return
 - Escalation Rates:
 - Operating Costs and By-Product Revenues at 5%/Year
 - SNG Revenues at 6%/Year

Catalyst Recovery Cost Components	Cost Breakdown, \$/Million Btu SNG	
	Case 1 Lime Digestion With Filters	Case 2 Water Wash With Filters
● Illinois No. 6 Coal @ 20 \$/ST	0.000	Base
● Major Chemicals		
- KOH Solution @ 300 \$/ST KOH	0.272	0.578
- Lime (97% CaO) @ 39 \$/ST	0.153	-
- Flocculant (D-25A) @ 4200 \$/ST	0.042	0.030
Subtotal	<u>0.467</u>	<u>0.608</u>
● Allocated Utilities		
- Raw Water/Cooling Water	0.009	0.005
- Steam	0.017	0.005
- Electric Power	0.050	0.012
Subtotal	<u>0.076</u>	<u>0.022</u>
● Other Operating Costs		
- Wages and Benefits	0.083	0.028
- Salaries and Benefits	0.025	0.009
- Labor Overheads and Supplies	0.022	0.007
- Materials and Overheads	0.162	0.051
- Waste Solids Disposal @ 1 \$/ST	0.014	Base
- Fuel Gas (SNG) @ 6.18 \$/MBtu	(0.008)	Base
- Filter Medium Replacement	0.009	0.001
Subtotal	<u>0.307</u>	<u>0.096</u>
● By-Product Revenues		
- Ammonia @ 160 \$/ST NH ₃	0.000	Base
- Sulfur @ 25 \$/LT	(0.008)	Base
Subtotal	<u>(0.008)</u>	<u>Base</u>
● Capital Charges	<u>0.910</u>	<u>0.256</u>
TOTAL CATALYST-RECOVERY-RELATED COST	1.752	0.982
CALL	1.75	0.98

As indicated previously, these initial catalyst recovery screening studies are intended only to select the more promising process and solid-liquid separation alternatives for further study. There is much uncertainty in the current filtration cake resistance measurements and the resulting filter sizes for digested and water-washed solids, so caution is necessary in trying to draw firm conclusions from the current studies. More bench filtration data are needed, and such data will be obtained when representative char and fines solids are available from the lined-out PDU. In addition, the use of alternative solid-liquid separation devices could narrow or even eliminate the advantage for water wash.

However, these results do support one important recommendation: near-term laboratory and engineering work should emphasize catalyst recovery via water wash. In keeping with this recommendation, the PDU Catalyst Recovery Unit is being operated in the water wash only mode. Similarly, the next three catalyst recovery screening studies in the engineering program, described below, are based on water wash. Some bench laboratory studies on solid-liquid separations with digested solids should continue to be carried out, to provide a firmer data base for a definitive comparison of lime digestion and water wash later in the current program.

The estimated total catalyst-recovery-related costs in Case 2, Water Wash with Filters, are 0.98 \$/MBtu of product SNG. A brief side study was carried out to break out the corresponding cost items from the CCG Study Design. The estimated costs for these same areas in the Study Design are 0.76 \$/MBtu. Thus, catalyst-recovery-related costs for Case 2 are 0.22 \$/MBtu higher than for the Study Design. This increase represents roughly 3-4% of the total Study Design SNG cost of 6.18 \$/MBtu. It is much too early to conclude that overall CCG costs will necessarily increase by this amount. As discussed earlier, costs for these screening studies may be over-estimated because potassium may not adsorb on the solids as strongly as was assumed. Other solid-liquid separation devices such as gravity settlers or hydroclones may be cheaper than the rotary drum filters used in Case 2. Also, no attempt has yet been made to optimize the catalyst recovery processing sequence.

Another key factor is catalyst makeup cost. Studies carried out during the CCG Predevelopment Contract concluded that makeup KOH for commercial CCG plants could cost from 25% to as much as 45% less than the nominal market price, due mainly to lower KOH purity requirements and economies of scale in KOH manufacture (by electrolysis of potassium chloride). The price assumed for KOH in the Study Design economic basis, 300 \$/ST (contained), was only 15% below the then current (1978) market price. If economics for Case 2 were based on KOH at 200 \$/ST, 44% less than the 1978 market price, the increase in catalyst-recovery-related costs would be less than 1% of the Study Design SNG cost.

The initial phase of work on catalyst recovery screening Cases 1 and 2 is now complete. These cases will be compared to other screening cases, including Cases 3, 4 and 5 already in progress (and described below). If rotary drum filters appear promising based on the preliminary economics reported here and on the results of the continuing laboratory programs, Case 2 (and perhaps Case 1) will be updated later this year to permit a more definitive comparison with other leading alternatives.

Case 3: Water Wash with Gravity Settlers

Case 3 is an evaluation of catalyst recovery via water wash using gravity settlers for the solid-liquid separations. Equipment specifications for Case 3 were prepared during the quarter, and the investment cost estimate is nearing completion. Economics for Case 3 will be developed during the next quarter. Laboratory settling tests for gasifier solids at two potassium concentrations were carried out to provide the basis for estimating the size of commercial gravity settlers for this service, as described below. The economic comparison between Case 2 and Case 3 will provide an initial indication as to whether filters or gravity settlers are more attractive for catalyst recovery solid-liquid separations.

The gravity settlers (or "thickeners") in Case 3 were designed starting with data from bench-scale batch settling tests conducted in a one-liter graduated cylinder. Results of these tests were reported in the October - December, 1979 Quarterly Report. The graduated cylinder was jacketed with a hot-water bath to maintain the desired temperature. Experiments were conducted by filling the cylinder with solids slurry, and measuring the solids interface height versus time as the solids settled. These data were plotted, and a graphical construction procedure developed by H. H. Oltmann was used to determine the characteristic "critical settling time" (θ_c). (This procedure is described in Fitch, E. B. and Stevenson, D. G., "Solid/Liquid Separation Equipment Scale-Up," ed. Purchas, D. B., Chapter 4, Uplands Press Ltd., Croydon, England 1977.) The experimental θ_c was then translated into a design solids flux rate for commercial-scale gravity settlers using the following equation:

$$G_c = \frac{W}{2 A \theta_c}$$

where, G_c = design solids flux rate, lb/hr-ft²
 W = weight of solids in the batch settling test, lb
 A = cross sectional area in the batch settling test, ft²
 θ_c = critical settling time, hr

The factor of two in the denominator is a typically recommended scale-up allowance or "safety factor."

The bench-scale settling experiments carried out to date have used undigested (water wash only) solids from the Fluidized Bed Gasifier (FBG) unit operating at 100 psig. The design solids flux rates calculated from these test data are shown in the table below.

Design Solids Flux Rates
For Water-Washed FBG Solids

<u>KOH in Liquid</u>	<u>Flocculant</u>	<u>Design Solids Flux</u>
2 wt%	D-25A/25 ppm	52 lb/hr-ft ²
10 wt%	D-25A/50 ppm	33 lb/hr-ft ²

The concentration of KOH in the slurry liquid has a fairly strong influence on the solids settling rate. Settler sizing for Case 3 is based on adding flocculants in the initial dosages shown in the above table. The bench experiments indicated that flocculants increased settling rates substantially.

These design solids fluxes determined from bench data were used to size the gravity settlers in catalyst recovery screening Case 3. The more concentrated solution in the bench experiments, 10 wt% KOH, is equivalent to the catalyst salts concentration in the first or "rich" stage of the Case 3 water wash sequence. Settling rates for leaner stages were based on linear interpolation between the 10 wt% KOH and 2 wt% KOH design solids fluxes. The results of the sizing calculations are summarized below:

Gravity Settler Design Summary for Case 3

<u>Wash Stage</u>	<u>Settler Diameter, ft</u>	<u>Feed Compartment Diameter, ft</u>
1	102	29
2	102	36
3	93	36
4 & 5	90	36
6 & 7 & 8	85	36
9	77	29

A 10-foot deep feed compartment in the center of each settler provides 10 minutes residence time for slurry mixing and solids flocculation. The settlers are all 15 ft deep at the outer wall, and fully enclosed to maintain a temperature near 212°F and to avoid exposure to air. Air exposure must be avoided to prevent oxidation of the KHS and K₂S in solution to K₂SO₄, which has low catalytic activity in gasification. Only eight water-wash stages are required to achieve the design recovery of 93% of the water-soluble potassium. A spare settler is provided in series so that the design recovery can be achieved when any one settler is down for maintenance.

The current data base for sizing gravity settlers for CCG catalyst recovery is very limited. Thus, the settler designs for Case 3 should be regarded only as a first approximation. The initial catalyst recovery screening studies described here are intended only to identify data needs and to select the more promising process and solid-liquid separation alternatives for further study. More bench settling data are needed to provide a firm basis for the design of gravity settlers. Such data will be obtained when representative char and fines solids are available from the lined-out PDU.

Cases 4 and 5: Water Wash with Hydroclones and Centrifuges

Work began in March on process basis setting for two additional catalyst recovery screening studies utilizing water washing only. In the first of these new cases, Case 4, the solid-liquid separations will be carried out using hydroclones (or liquid cyclones). In the second case, Case 5, centrifuges will be used.

For these initial screening studies, estimates of the separations performance of hydroclones and centrifuges will be based primarily on calculations obtained from Exxon-proprietary computer models. Available data on the properties of CCG char and fines are being used to develop a basis for "typical" particle densities and size distributions for input to the computer models. Extensive contacts are planned with equipment vendors and in-house consultants to gather information on equipment types, sizes, performance, and operating limitations for this service.

After the general process basis is set for Cases 4 and 5, material and energy balances will be developed and equipment items will be specified for investment cost estimating. Work on these cases is expected to continue through the second quarter of 1980.

Coal Crushing Machinery for CCG

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

During the quarter, correspondence was completed with the National Fire Protection Association (NFPA) on the subject of crusher/dryer system safety in the event of a coal dust explosion. Their position is that relevant portions of NFPA 85F can be used to provide adequate explosion protection design standards for the system. Thus, the system can either be designed to withstand a 50 psig explosion or inerted or both.

A review of hot-gas-swept mill system designs received from U.S. manufacturers was also completed. Only one design submitted appears to satisfy project requirements. Consequently, several European manufacturers have been contacted and asked to provide information concerning their equipment and systems.

Potential Effects of Coal Pretreatment on the CCG Material and Energy Balance

As described earlier in this report, recent PDU operations have resulted in lower-than-expected densities in the gasifier fluid bed. These low densities appear to be interrelated with swelling of the catalyzed feed coal during devolatilization and the production of added quantities of fines. It is desirable to avoid such conditions in commercial operations for two principal reasons: first, lower bed density will reduce carbon holdup per unit volume and thus lead to larger gasifiers; and second, the added fines make will tend to lower overall carbon conversion and thus reduce the SNG yield per ton of coal fed.

Two main techniques have been identified in the laboratory to increase fluid bed densities and reduce fines production: (1) operating the gasifier at a pressure below the CCG Study Design "base" pressure of 500 psia; and (2) pretreating the coal by exposure to air at relatively mild conditions (1 atm, 300-450°F). Much laboratory work is underway and planned to study various combinations of pressure and pretreatment. This work is directed toward determining the relationships among gasifier pressure, degree of pretreatment, and fluid bed density, and toward defining the preferred conditions for and the material balance impacts of coal pretreatment. To provide guidance to these laboratory studies, a series of gasifier system material and energy balances has been developed to quantify some of the potential effects of reduced pressure and of coal pretreatment on a commercial CCG plant. The impact of coal pretreatment is described immediately below, and the impact of pressure is covered in the next section of this report.

The effects of coal pretreatment via air exposure on the structure and elemental analysis of the coal are not well understood at this time. Early results do indicate that oxygen is consumed in pretreatment and that the amount of oxygen consumption depends on the "severity" (time and temperature) of the air exposure step. Pretreatment at "mild" conditions results in an oxygen consumption of about 2-4 wt% on dry coal, while "severe" pretreatment can result in 10-20 wt% O₂ consumption.

To provide a measure of the effects of pretreatment at different severities, commercial-scale CCG material and energy balances were developed for two assumed levels of oxygen consumption, 2 wt% and 10 wt% on dry coal. The material and energy balance results for these cases are compared to the "base" CCG Study Design in Table 5.1-3. All of the cases shown in the table are based on the same coal feed rate and gasifier conditions as the Study Design. As shown by the first three columns of the table, the most significant impact of coal oxidation on the CCG material balance is that the net SNG product rate decreases relative to the Study Design as the extent of coal oxidation increases. For "mild" pretreatment severity (2 wt% O₂ pickup), the net SNG product dropped to 253.2 GBtu/SD, or 1.4% less than the Study Design. Relatively "severe" pretreatment (10 wt% O₂ pickup) resulted in a product rate of 239.5 GBtu/SD, or 6.8% less than the Study Design. The

Table 5.1-3

**POTENTIAL EFFECTS OF COAL PRETREATMENT
ON THE MATERIAL AND ENERGY BALANCE
FOR A COMMERCIAL CCG PLANT**

- Basis: ● Coal Feed Rate to Pretreatment: 11,980 ST/SD (Dry)
 ● Gasifier Conditions: 500 psia, 1275°F
 ● Carbon Conversion: 90%

	CCG Study Design (Base Case)	Pretreatment Cases			
		O ₂ Combines With Coal(1)	O ₂ Removes H From Coal(2)	O ₂ Removes C From Coal(3)	
Oxygen Consumption in Pretreatment, wt% on Dry Coal	None	2	10	10	10
Temperature of Coal Feed to Gasifer, °F	200	200	200	200	200
Net SNG Product, GBtu/SD	256.9	253.2	239.5	238.7	242.0
Change in Net SNG Product, % of Base	Base	-1.4	-6.8	-7.1	-5.8
Relative Steam-Carbon Equilibrium Constant(4)	1.00 (Base)	1.00	1.00	1.00	1.00
Steam Conversion, % of Steam Fed	41.5	41.0	39.1	43.3	40.9
Steam to Coal Ratio, lb Steam/lb Dry Coal	1.58	1.57	1.53	1.64	1.47
Total Steam Requirement, lb-mole/hr	87,800	87,200	84,900	91,000	81,400
Offsite Steam Requirement, lb-mole/hr	59,200	58,400	55,400	62,900	54,000
Recycle Gas Rate, lb-mole/hr	57,600	57,400	56,800	56,800	54,300
Normal Preheat Furnace Coil Outlet Temp., °F	1541	1555	1597	1595	1554
Preheat Furnace Heat Absorbed, MBtu/hr	480	500	550	580	470

Notes:

- (1) Net SNG reduction results mostly from coal oxygen pickup. Small losses of coal carbon and hydrogen as CO₂ and H₂ are also included.
- (2) Net SNG reduction results mostly from removal of hydrogen as H₂O. Small losses of coal carbon and hydrogen as CO₂ and H₂ are also included.
- (3) Net SNG reduction results mostly from removal of carbon as CO₂. A small loss of coal hydrogen as H₂ is also included.
- (4) Steam-graphite equilibrium equals 1.00.

economic debit associated with a product yield loss of nearly 7% would be quite significant. Additional debits would be incurred for the costs of facilities added to carry out the pretreatment process.

The material and energy balances show that other changes to the gasifier and recycle gas loop would also be required if pretreatment via air oxidation were incorporated into the commercial plant design. In all cases the steam rate to the gasifier was set to maintain the gasifier outlet gas in apparent steam-graphite equilibrium. As the extent of oxidation increases, the total gasification steam requirement decreases, which in turn decreases the steam required from the offsite coal-fired boilers. The recycle gas loop and the associated equipment would be slightly smaller relative to the Study Design. Preheat furnace duty and coil outlet temperature both increase with oxidation extent if it is assumed that the temperature of the gasifier feed coal remains at the Study Design value of 200°F. Heat may be released in pretreatment depending on the severity and the final disposition of the oxygen consumed. This heat may be usable in a way which heats the feed somewhat above 200°F. Increasing the feed coal temperature would lower the preheat furnace duty, coil outlet temperature, and fuel fired, and increase the net SNG product rate enough to offset some of the yield loss due to pretreatment.

The exact manner in which oxygen is consumed in pretreatment is not yet known. The first two pretreatment cases in Table 5.1-3 are based on the assumption that most of the O₂ combines with the solid coal itself, and is thus carried into the gasifier. It is possible that O₂ acts to remove hydrogen or carbon from the coal in pretreatment as H₂O or CO₂. The last two columns of the table show the impacts of these alternative assumptions on the CCG material and energy balance with 10 wt% oxygen consumption in pretreatment. The results still show substantial SNG product yield losses, ranging from 5.8 - 7.1% of the base product rate. Compared to the case in which the O₂ is assumed to combine with the coal, more steam is required if O₂ removes hydrogen from the coal, and the recycle rate is also up. The steam and recycle rates are lower and the SNG yield is higher if the O₂ removes carbon from the coal, but this is judged to be the least likely of the three possible modes of O₂ consumption.

Based on these initial cases, it appears that mild pretreatment of feed coal via air exposure is a potentially low cost method of increasing gasifier fluid bed density. Material balance debits are modest for pretreatment oxygen consumptions in the range of 2-4 wt% on dry coal. Severe pretreatment, with oxygen consumptions above 10 wt%, is not likely to be economically attractive. Extensive laboratory and engineering work is planned to permit more definitive evaluation of the tradeoffs among gasifier pressure, pretreatment level, and bed density. On the engineering side, a first-pass screening study of facilities required for coal pretreatment will begin shortly.

Gasification System Screening Studies

Work has been initiated on engineering screening studies to evaluate the economic impact of alternative gasifier operating conditions. The

results of these studies will be used to provide guidance for PDU gasifier process variable studies and for selection of preferred operating conditions for the PDU demonstration run.

Impact of Reduced Gasifier Operating Pressure on the CCG Material and Energy Balance

As discussed in the preceding article of this report, two main techniques have been identified in the laboratory to increase fluid bed densities and reduce fines production: (1) operating the gasifier at a lower pressure than the CCG Study Design pressure of 500 psia; and (2) pretreating the coal by exposure to air at relatively mild conditions. The purpose of this study was to investigate the impacts of reduced pressure on the CCG system material and energy balance and thus provide guidance to the current laboratory studies.

The major impacts of reduced pressure on CCG process parameters and plant facilities are shown in Table 5.1-4. A series of commercial-scale CCG material and energy balances were prepared to help quantify these impacts. These balances were prepared for gasifier operating pressures of 300 psia and 100 psia and are presented below and compared to operation at the CCG Study Design pressure of 500 psia. These cases are based on the same coal feed rate, solids properties and gasifier operating conditions (except for pressure) as the Study Design.

Impact of Reduced Pressure on CCG Material and Energy Balance

Basis: 14,490 ST/SD Coal Feed Rate to Gasifiers
1275°F Gasifier Temperature

	<u>CCG Study Design</u>	<u>Reduced Pressure Cases</u>	
Gasifier Pressure, psia	500	300	100
Gasifier Effluent, lb-moles/hr	160,000	180,000	270,000
Recycle Gas, lb-moles/hr	60,000	80,000	170,000
CO ₂ Partial Pressure, psia	72	38	8
Relative Fluidized Bed Bubble Size	1.0	1.5	3.6
Relative Gasifier Volume	1.0	1.6	3 - 7
Preheat Furnace COT, °F	1,540	1,500	1,420
Preheat Furnace Duty, MBtu/hr	480	490	560
Net SNG, GBtu/SD	257	256	253

Table 5.1-4

IMPACT OF REDUCED PRESSURE ON CCG PROCESS

Impact on Process Parameters

- Recycle Gas Rate Increases
- Bubble Size in Fluid Bed Gasifier Increases
- CO₂ Partial Pressure Is Lower
- CH₄ Produced in Gasifier Remains Constant
- Preheat Furnace Duty Increases
- Net CH₄ Product Decreases Slightly

Impact on Commercial Plant Facilities

- Lower Cost Mechanical Design
 - Coal Feeding from Lock Hoppers
 - Reduced Wall Thickness for Gasifier, Gas-Gas Exchanger Shell, and Preheat Furnace Tubes
- Increased Gasifier Volume
 - Inhibition Due to Increased Recycle Gas Rate
 - Poorer Mass Transfer
- Small to Moderate Impact on Gas Separations
 - Larger Gas Rates
 - Lower CO₂ Partial Pressure
 - Lower Feed Pressure Increases Energy Requirement for Methane Recovery
- Small Impact on Preheat Furnace
 - Larger Duty
 - Lower Coil Outlet Temperature

As shown in these tables, the most significant impacts of reduced pressure are increased recycle gas rate, increased gasifier volume, and reduced cost for equipment mechanical design. The impact of reduced pressure on other plant sections such as gas separation equipment and the preheat furnace is less significant.

The recycle gas rate is larger at lower pressure because the gasifier effluent is assumed to be in methanation equilibrium and, at lower pressure, this equilibrium results in more moles of CO and H₂ per mole of methane product (which is constant). In addition, the current reactor model indicates that equilibrium may not be as closely approached as pressure is reduced. This impact is not included in this study but will be investigated in future more detailed studies.

The gasifier volume is larger at lower pressure for two main reasons. First, the mass transfer rate between the emulsion and bubble phases in the fluidized bed is lower at reduced pressure because the bubbles are larger. At 500 psia and to a lesser degree at 300 psia, mass transfer is believed to have only a small impact on gasifier volume. However, at 100 psia mass transfer may have a significant impact on gasifier volume; thus, the uncertainties in the bubble size and mass transfer correlations lead to greater uncertainties in the reactor kinetics/contacting model predictions at 100 psia. Secondly, because of the increased recycle of CO and H₂ at lower pressure, the inhibition effect of these components on gasification rate is increased.

However, reducing the gasifier pressure will result in lower cost mechanical designs, directionally offsetting the debits due to increased recycle gas rate and gasifier volume. Design and operation of the lock hoppers, the lock hopper pressurization system, and the preheat furnaces will be simpler at reduced pressure. The preheat furnaces will have both reduced design coil outlet temperatures and reduced design pressure. Based on these initial cases, it appears that reducing the gasifier pressure to 300 psia is potentially a low cost method of increasing gasifier fluid bed densities. The increases in gas flow rates and gasifier volume for a gasifier operating at 300 psia are moderate and will be directionally offset in many sections of the plant by reductions in design pressure. However, because of the excessive increases in gas flow rates and gasifier volume, operating a gasifier at 100 psia is not likely to be economically attractive.

Extensive laboratory and engineering work is planned to permit more definitive evaluation of the tradeoffs among gasifier pressure, pretreatment level, and bed density. An engineering screening study to evaluate gasifier operation at 300 psia will begin shortly.

Impact of Alternative Gasifier Operating Conditions on the CCG Material and Energy Balance

A study of the impact of gasifier operating conditions on the CCG material and energy balance has been completed. The following process

variables were investigated: catalyst loading, gasifier temperature, gasifier feed steam rate, carbon conversion, and gasifier pressure. The study of gasifier pressure is covered in the preceding article.

The operating conditions for the CCG Study Design were used as the base case for this study. These conditions include a gasifier temperature of 1275°F, pressure of 500 psia, catalyst loading of 15 wt% K₂CO₃ equivalent, 90% carbon conversion and a steam rate based on graphite equilibrium at the gasifier effluent. Since the coal char is more active than graphite, setting the feed steam rate in this manner ensures a reasonably consistent gasification driving force in the fluid bed. For the Study Design this resulted in a steam to dry coal weight ratio of 1.58. The present study was also based on the Study Design coal feed rate of 14,490 ST/SD. The impact of changes in operating conditions was investigated by changing one variable at a time while keeping the others constant.

The interim version of the reactor model described in the October - December, 1979 Quarterly Report has been used to predict the gasifier volume for these studies. As indicated in that report, although the interim model is based on the best available data on catalytic coal gasification, considerably more data are required to better define the model. This is particularly true where conditions differ from the data base used to develop the interim model. Since many of the cases in this study explore the impact of process variables where the current data base is limited, the results are preliminary. These cases will be re-examined when the data base and reactor model are updated.

The impacts of changes in gasifier operating conditions on gas flow rates, preheat furnace temperature, and gasifier volume are described below.

The first gasifier process variable investigated was catalyst loading. Since the Study Design was based on a loading of 15 wt% K₂CO₃ equivalent, material and energy balances were developed for loadings of 10 and 20 wt% and are shown below.

Impact of Catalyst Loading

<u>Item</u>	<u>Base Case</u>	<u>Sensitivities</u>	
Catalyst Loading, wt% K ₂ CO ₃	15%	10%	20%
Preheat Furnace Temperature, °F	1540	1500	1580
Gasifier Volume	1.0	1.2	1.0
Catalyst Recycle Rate	1.0	0.7	1.3

With lower catalyst loading of 10 wt%, the preheat temperature is reduced because of the lower sensible heat required to preheat the prepared coal feed to reaction temperature. The gasifier volume increases by 20% but the amount of catalyst which must be recovered and recycled is only 70% of that

in the base case. Opposite effects are observed for the case with higher catalyst loading of 20 wt% except that the gasifier volume is not reduced as would be anticipated. This is due to saturation of the active catalyst sites. However, this phenomenon is not well quantified and is the subject of current laboratory work.

The next gasifier operating variable investigated was operating temperature. Results are shown below.

Impact of Gasifier Temperature

<u>Item</u>	<u>Base Case</u>	<u>Sensitivities</u>			
Gasifier Temperature, °F	1275	1200	1250	1300	1350
Preheat Furnace, Temperature, °F	1540	1410	1500	1570	1620
Gasifier Feed Steam Rate	1.00	1.14	1.05	1.00	0.98
Total Recycle Gas Rate	1.00	0.88	0.96	1.12	1.37
Gasifier Volume	1.0	1.5	1.1	0.9	0.8

With lower gasifier temperature, the preheat furnace temperature drops more than the gasifier temperature because of the lower sensible heat required to preheat the prepared coal feed. The gasifier steam rate is based on apparent steam-graphite equilibrium which requires more steam at lower temperatures. The recycle rate is reduced at lower temperatures because the gasifier effluent is in methanation equilibrium and, at lower temperature, this equilibrium results in less moles of CO and H₂ per mole of methane (which is constant). The reactor model predicts a 50% increase in gasifier volume at 1200°F. However, this is based on preliminary estimates of the gasification reaction activation energy. The temperature dependence of the gasification reaction rate is currently under investigation as part of the laboratory program.

The impacts of changing the gasifier feed steam rate are shown below.

Impact of Gasifier Feed Steam Rate

<u>Item</u>	<u>Base Case</u>	<u>Sensitivities</u>		
Gasifier Feed Steam Rate	1.00	1.40	0.80	0.75
Total Recycle Gas Rate	1.00	1.41	0.82	0.77
Preheat Furnace Temperature, °F	1540	1460	1610	1640
Gasifier Volume	1.0	0.8	1.5	2.0

Near the base case conditions, the change in recycle gas rate is nearly proportional to the change in the gasifier feed steam rate. As both the steam and recycle gas rates increase, there is more gas to carry sensible heat into the gasifiers. The sensible heat in the steam plus recycle gas above the gasifier temperature is used in effect to preheat the feed coal and to make up for heat losses and endothermic reactions between catalyst

and ash. Thus, the preheat furnace temperature is reduced. Gasifier volume increases as steam rate is reduced. The large change in gasifier volume (from 1.5 to 2.0) caused by a change in the feed steam rate from 80% to 75% of the base level shows the impact of approaching the equilibrium steam requirement.

Carbon conversion was the last process variable studied. The results are shown below.

Impact of Carbon Conversion

<u>Item</u>	<u>Base Case</u>	<u>Sensitivities</u>			
Carbon Conversion, %	90%	80%	85%	95%	98%
Gasifier Feed Steam Rate	1.00	0.89	0.94	1.05	1.08
Net SNG	1.00	0.90	0.95	1.05	1.08
Gasifier Volume	1.0	0.8	0.9	1.5	2.9

The change in steam requirement and net SNG product is proportional to the change in carbon conversion. For example, to increase carbon conversion by 5%, the steam requirement must be increased by 5% and the net SNG is thus increased by 5%. The gasifier volume increase is not proportional to carbon conversion since a 5% increase in carbon conversion from 90% to 95% approximately doubles the catalyst to carbon ratio of the char in the gasifier bed and results in a smaller holdup of carbon per unit of volume. This in turn leads to significantly larger gasifier volume requirements. As mentioned in the discussion of the catalyst loading sensitivity cases, the impact of the catalyst to carbon ratio is the subject of current laboratory work.

These studies of the impact of gasifier operating conditions on the CCG material and energy balance will be updated in the future based on laboratory work currently in progress. The results will be used for laboratory guidance in selecting operating conditions for the PDU demonstration run.

Supplemental Steam Reformer Heat Input Study

Work has continued on a study to evaluate supplemental steam reforming as a method of heat input to the catalytic gasifier. With this heat input method, a small steam reformer is operated in parallel with the preheat furnace. A methane/steam mixture is fed to the reformer where CO and H₂ are produced. The CO and H₂ are then fed to the catalytic gasifier where heat is released by forming methane. Recycle CO and H₂ along with the bulk of the gasification steam are fed to the preheat furnace. Because of the extra heat input supplied by the supplemental reformer, the preheat furnace outlet temperature can be reduced, thus significantly reducing its investment. Carbon laydown is avoided with this heat input option because CO is not fed to the reformer and H₂S can be added to the preheat furnace inlet to prevent carbon laydown. The use of steam reforming for heat input increases process flexibility and permits higher steam conversions for the gasifier system.

The process basis described in the July - September, 1979 Quarterly Technical Progress Report for the integral steam reformer study (1500°F coil outlet temperature, gasifier effluent after sulfur removal for fuel, and 48% steam conversion) was used as a starting point for this study. The first alternative investigated was the type of fuel to be used for the preheat and steam reforming furnaces. The options evaluated were gasifier effluent after sulfur removal, which is an intermediate Btu gas (IBG), and product SNG. Material and energy balances were prepared for cases using the different furnace fuels. Results of these material and energy balances are summarized below.

Effect of Fuel Type

<u>Type of Fuel for Furnaces</u>	<u>IBG Fuel</u>	<u>SNG Fuel</u>
Preheat Furnace COT, °F	-----1500-----	-----1500-----
Steam Reformer COT, °F	-----1500-----	-----1500-----
Steam/Carbon Ratio, mole/mole	-----5/1-----	-----5/1-----
Total Recycle Gas, lb-moles/hr	47,300	51,900
Gasifier Effluent, lb-moles/hr	140,400	143,100
Onsite Steam, lb-moles/hr	34,200	31,700
Offsite Steam, lb-moles/hr	42,100	44,400
Preheat Furnace Fuel, MBtu/hr	345	371
Steam Reformer Fuel, MBtu/hr	314	206
Net SNG Product, GBtu/SD	254.4	255.5

Lower gas rates were obtained for the IBG case; however, the total furnace fuel requirement is 14% greater than the SNG case. Based on this material and energy balance study there is no clear advantage for the use of either IBG or SNG for plant fuel. SNG has been chosen as the fuel for the supplemental steam reformer case based on the judgement that the higher product rate for the SNG case may show a small advantage over the lower gas rate for the IBG case.

The effects of several process variables on supplemental steam reforming were then examined. Material and energy balances were prepared with SNG as the plant fuel. The process variables examined were preheat furnace coil outlet temperature, steam reformer coil outlet temperature, and steam/carbon ratio in the reformer feed.

Preheat furnace coil outlet temperatures of 1400°F to 1550°F were investigated. For these cases, the supplemental reformer was assumed to operate with a 1500°F coil outlet temperature and a feed steam/carbon ratio of 5/1. A summary of the material and energy balance results is shown below.

Effect of Preheat Furnace Coil Outlet Temperature

Preheat Furnace COT, °F	1400	1450	1500	1550
Steam Reformer COT, °F	-----	1500	-----	-----
Steam/Carbon Ratio, mole/mole	-----	5/1	-----	-----
Total Recycle Gas, lb-moles/hr	53,100	52,500	51,900	51,200
Gasifier Effluent, lb-moles/hr	146,600	144,900	143,100	141,300
Onsite Steam, lb-moles/hr	35,600	33,700	31,700	29,600
Offsite Steam, lb-moles/hr	41,300	42,800	44,400	46,000
Preheat Furnace Fuel, MBtu/hr	231	299	371	446
Steam Reformer Fuel, MBtu/hr	417	315	206	92
Net SNG Product, GBtu/SD	253.4	254.4	255.5	256.6

Credits for higher preheat furnace coil outlet temperatures include lower overall plant fuel requirement, hence higher net product, and lower recycle gas rates. The debits for higher preheat coil outlet temperatures are higher preheat furnace investment and higher offsite steam requirements.

Steam reformer coil outlet temperatures of 1400°F and 1500°F were investigated with the steam/carbon ratio in the feed held constant at 5/1. For these cases, the preheat furnace coil outlet temperature was set at 1500°F. A comparison of the material and energy balances is shown below.

Effect of Steam Reformer Coil Outlet Temperature

Preheat Furnace COT, °F	-----	1500	-----
Steam Reformer COT, °F	1400	-----	1500
Steam/Carbon Ratio, mole/mole	-----	5/1	-----
Total Recycle Gas, lb-moles/hr	52,400	-----	51,900
Gasifier Effluent, lb-moles/hr	144,500	-----	143,100
Onsite Steam, lb-moles/hr	32,100	-----	31,700
Offsite Steam, lb-moles/hr	44,200	-----	44,400
Preheat Furnace Fuel, MBtu/hr	363	-----	371
Steam Reformer Fuel, MBtu/hr	225	-----	206
Net SNG Product, GBtu/SD	255.1	-----	255.5

The credits for higher supplemental reformer coil outlet temperatures include lower recycle gas rates and slightly higher net product. Debits for higher reformer coil outlet temperature are increased investments for the reforming and preheat furnaces which are respectively due to increased process severity and increased duty.

A range of steam/carbon ratios for the feed to the supplemental steam reformer was evaluated with the coil outlet temperature held constant at 1500°F. For these cases, the preheat furnace coil outlet temperature was set at 1500°F. The results of the material and energy balances are shown below.

Effect of Steam/Carbon Ratio in Reformer Feed

Preheat Furnace COT, °F	-----	1500	-----
Steam Reformer COT, °F	-----	1500	-----
Steam/Carbon Ratio, mole/mole		3/1	5/1 7/1
Total Recycle Gas, lb-moles/hr	52,200	51,900	51,700
Gasifier Effluent, lb-moles/hr	143,900	143,100	142,800
Onsite Steam, lb-moles/hr	31,300	31,700	32,000
Offsite Steam, lb-moles/hr	44,900	44,400	44,000
Preheat Furnace Fuel, MBtu/hr	379	371	363
Steam Reformer Fuel, MBtu/hr	195	206	218
Net SNG Product, GBtu/SD	255.5	255.5	255.3

In general, the steam/carbon ratio in the feed to the supplemental steam reformer has small effects on the material and energy balances. For higher steam/carbon ratios the gas rates and the net SNG decrease slightly.

Based on a qualitative analysis of the above material and energy balance cases, the following process basis has been chosen for the supplemental reformer case: a coil outlet temperature of 1500°F for the preheat furnace, a coil outlet temperature of 1400°F for the steam reformer, a steam/carbon ratio in the steam reformer feed of 5/1, and SNG for the plant fuel. The basis for these choices is discussed below (except for the choice of SNG for plant fuel which was discussed previously).

A coil outlet temperature of 1500°F was chosen for the preheat furnace because the furnace investment starts to increase significantly as the coil outlet temperature is increased from 1500 to 1550°F. In addition, in this temperature range, it becomes necessary to use two radiant boxes instead of one in order to reduce the heat flux for the tubes in high temperature service. This reduces tube metal temperatures and permits the use of tube thicknesses within the range of current commercial practice. When it is necessary to use a two-box radiant section design, a step increase in furnace investment occurs. Thus a coil outlet temperature of 1500°F was chosen to avoid the need for two boxes.

An inspection of the material balance cases for steam reformer outlet temperatures of 1400°F and 1500°F shows that gas rates are relatively unaffected by the choice of reformer temperature. Though the product SNG rate is slightly higher at a 1500°F outlet temperature, this benefit is likely outweighed by the increased investment associated with designing the reformer for 1500°F versus 1400°F. This is particularly true since the reformer would be operating with a pressure of over 500 psia. Thus a reformer coil outlet temperature of 1400°F was chosen as the basis for the study.

The material and energy balances for the steam/carbon ratio in the reformer feed cases show little change from one case to another. Since most commercial experience is with steam/carbon ratios of 5/1, this basis was selected for the supplemental reformer study.

The material and energy balance resulting from the final process basis will serve as the design basis for study designs of the preheat furnace and steam reformer. These furnace study designs will be used to develop investment cost estimates for the two furnaces. Work on the economics of supplemental steam reforming will be deferred until those cost estimates are available.

5.2 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 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 using corrosion racks and probes installed in the CCG PDU at Baytown, Texas. Other elements of the ER&E program include stream sampling, analyses of components which fail in PDU service, and nondestructive testing. Work is also underway at the Bureau of Mines Tuscaloosa Research Center (under a separate DOE contract) on materials evaluation in simulated CCG environments.

The corrosion rack exposure program described in the October - December, 1979 Quarterly Report is continuing. Replacement of the first set of racks (Series I) and installation of the second set (Series II) is planned for the next quarter, prior to the start of the PDU process variable studies. It is expected that all ten corrosion racks will be installed during Series II, including movement of Test Site 3 from the dense phase to the dilute phase of the gasifier. Routine stream sampling and analyses will be initiated in the next quarter when process variable studies are begun.

Two failure analyses were conducted this quarter. Metallographic examination of a leaking section of 316SS tubing used to bypass the gasifier overhead filters revealed extensive transgranular cracking, believed to be the result of caustic stress corrosion cracking. This bypass was normally blocked off and was uninsulated, providing an ideal location for formation of aqueous condensate. It is believed that potassium hydroxide or another potassium salt was leached from char particles, resulting in a highly alkaline solution. To avoid this type of failure, replacement with Inconel 600 or 625 was recommended. As an alternative, the piping could be modified so as to eliminate condensate formation by heat tracing and insulating.

Leaking valve stem packing removed from the gasifier char withdrawal valves has been examined and found to have severely hardened in service. This graphite-impregnated asbestos packing (Chesterton 1500) has a maximum recommended use temperature of 1200°F. The manufacturer examined samples of the deteriorated packing and placed the cause of failure on exposure to excessive temperatures, possibly 2000°F. This explanation is implausible because the temperature of the packing is normally maintained at 500-600°F, and probably does not rise appreciably during the brief periods of intermittent char withdrawal. Analytical work is underway to investigate the possibility of chemical reactions between the packing material and the process environment. Grafoil rings are being used for replacement and have performed well to date.

Work is continuing on materials evaluation in simulated CCG environments at the Bureau of Mines Tuscaloosa Research Center. The interim results summarized below are abstracted from the First Progress Report (October, 1979 - February, 1980) under their new contract (DOE/BOM Contract DE-A105-800R20686).

- Determination of Effect of Typical CCG Environments on Candidate Metals and Refractories
 - First 100-hour CCG exposure (730°C, 500 psi):
 - (1) In alkali vapor (estimated 50 ppm KOH)
 - No apparent metal loss, only mild surface reactions
 - (2) In molten KOH/coal mixture
 - 310 SS - Slight pitting
 - 446 SS - Slight pitting
 - Incoloy 800 - Slight pitting
 - 304 SS - Severe attack
 - Aluminized Incoloy 800 - Definite thinning
 - (3) In molten KOH
 - All metals attacked
 - Conclusions:
 - + None of the metals tested have useful resistance under the exposure conditions used.
 - + Aluminizing is not an effective coating.

● Determination of Most Effective Method of Introducing Alkali to the CCG Atmosphere

- In the initial experimental runs, considerable difficulties had been experienced in introducing KOH into the high pressure test chambers. Consequently, several runs were made to study alkali transport and chemical transformation; during these, refractory samples were exposed in the test chamber to determine potassium pickup:

(1) 250-hour run (730°C, 500 psi)

- + Atmosphere was a dynamic steam/argon mixture.
- + 75 g molten KOH in crucible.
- + At end of run, only 22.5 g KOH remained in crucible.
- + Initial condensate from test chamber contained appreciable K_2O but carryover of K_2O decreased rapidly with time.
- + Refractory samples registered up to sixfold increase in K_2O content after exposure.

(2) 50-hour run (730°C, 500 psi)

- + Atmosphere was H_2S -free CCG gas.
- + Molten KOH in crucible.
- + After exposure, most of the alkali remained in the crucible, but was transformed to K_2CO_3 .
- + Refractories did not show any significant K_2O pickup.

(3) 50-hour run (730°C, 500 psi)

- + Atmosphere was CO_2 -free CCG gas.
- + Molten KOH in crucible.
- + After exposure, one third of remaining material in crucible was K_2S .
- + Refractories not yet 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 gasifier effluent gas wet scrubbers and condensate drums and the sour water stripping facilities.

A literature review for data on the volatility of ammonia, carbon dioxide, and hydrogen sulfide in aqueous solutions identified deficiencies in the experimental data base. Therefore, an experimental program to obtain additional VLE data was defined and Wilco Research Company was subcontracted to obtain these data.

Late this quarter, Wilco reported results for seven of the twelve runs planned. Their results are given in Table 5.2-1. Next quarter, these data will be compared with calculations of several models for predicting VLE in sour water systems. These comparisons will help to evaluate the accuracy of the experimental data and the accuracy of the models for predicting VLE at conditions anticipated for the CCG Process.

Physical and Thermodynamic Properties of Catalyst Recovery Solutions

The objective of this program is to collect the physical and thermodynamic properties needed to design the processing equipment in the catalyst recovery system. A review of this system identified the important properties as: viscosity, density, enthalpy, and boiling point for aqueous solutions containing up to about 30 wt% dissolved potassium compounds. Temperatures of interest range from 15°C to 150°C (60°F to 300°F). Potassium hydroxide and potassium carbonate are the potassium compounds of primary interest.

A literature search for properties of aqueous solutions containing potassium hydroxide (KOH) or potassium carbonate (K_2CO_3) was conducted. This quarter, the articles on boiling point, enthalpy, and density were analyzed. For boiling points, accurate data exist for both aqueous KOH and K_2CO_3 . An article by Mashovets et al.⁽⁵⁾ presents accurate data from 25°C to 350°C for solutions containing up to 49 wt% KOH. For aqueous K_2CO_3 , two complementary articles by Puchkov et al.^(6,7) cover the temperature range from 25°C to 300°C for solutions containing up to 51 wt% K_2CO_3 . It is anticipated that all of these boiling point data can be analyzed in terms of the Guggenheim equation for the activity of water as a function of composition⁽³⁾. This equation requires only one empirically-determined parameter for each electrolyte-water binary solution. Preliminary results suggest that this parameter is only a weak function of temperature.

The analysis of enthalpy data identified reliable heat capacity data only for aqueous potassium carbonate⁽²⁾. However, several important literature articles have not been received yet. Further analysis of enthalpy data will be deferred until after these articles become available.

The analysis of density data for aqueous potassium hydroxide and aqueous potassium carbonate is almost complete. Accurate data have been found for each system throughout the temperature and composition ranges of interest. Mashovets et al.⁽⁴⁾ report extensive data for aqueous KOH from 0°C to 400°C for concentrations from 0 to above 50 wt% KOH. These data are supplemented, at the lower temperatures, by the data of Akerlof and Bender⁽¹⁾. For aqueous K_2CO_3 , the data of Puchkov et al.⁽⁷⁾ stretch from 25°C to 300°C for concentrations of up to 50 wt%. Data extending to 0°C have been reported in the International Critical Tables⁽⁸⁾. Next quarter, a method will be chosen for predicting densities in multi-component aqueous solutions.

References: See page 76.

Table 5.2-1

SUMMARY OF MEASURED VAPOR-LIQUID EQUILIBRIUM DATA
ON NH₃-CO₂-H₂S-H₂O-KOH MIXTURES

Run No.	Temp. °C	Pressure psia	Analysis, Mole %								
			NH ₃		CO ₂		H ₂ S		H ₂ O		KOH
			Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.
2	140	85.0	5.52	36.4	0	0	0.617	5.96	93.86	57.5	0
3	50	55.0	3.64	0.052	3.32	71.8	0.454	22.2	92.59	5.97	0
4	130	79.5	2.63	10.73	0.530	28.8	0.436	9.26	96.40	51.2	0
5	130	86.3	6.98	32.6	0.433	8.17	1.64	17.6	90.94	41.6	0
6	170	315	4.59	12.4	0.500	33.3	1.00	19.0	93.90	35.3	0
7	130	65.5	0	0	1.48	27.1	1.52	13.4	94.03	59.5	2.97
8	190	215	0	0	1.50	13.6	1.60	4.12	93.88	82.2	3.00

Previous work has concentrated on aqueous solutions of potassium hydroxide and potassium carbonate. However, other potassium compounds, such as potassium sulfide and potassium bisulfide, may appear in the catalyst recovery streams. Therefore, a literature search was begun on the properties of aqueous potassium sulfide and potassium bisulfide. Few promising data sources have been discovered yet and it is unlikely that extensive data exist for these systems. However, this new literature search will continue next quarter.

References:

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- (6) Puchkov, L. V. and Kurochkina, V. V., "Vapor Pressure of Aqueous Potassium Carbonate Solutions," J. Appl. Chem. USSR, 43(1), 175-177 (1970).
- (7) Puchkov, L. V., Kurochkina, V. V. and Matveeva, R. P., "Density and Saturated Vapor Pressure of Aqueous Solutions of Potassium Carbonate at Temperatures Up to 315°," Zh. Prikl. Khim. (Leningrad), 50(6), 1431 (1977). See Chem. Abstr. 87:58681. Data available through VINITI, No. 3476-76, deposited on September 30, 1976.
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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. During this quarter, the newly modified batch filtration apparatus was used to make a series of runs on water-washed char samples. The purpose of these runs was to obtain data on filtration rate, cake resistance and cake washing for thin cakes (1-2 in.) typical of commercial filtration equipment.

Initial evaluation of the results indicated that the runs had been made quickly enough, as intended, to reduce the tendency for premature cake formation due to settling in the test cell. Use of 25 ppm of D-25A flocculant approximately doubled filtration rate. In-situ leaching of filter cake appears effective for K^+ ion recovery; however, the cake tended to compress during the leaching process, particularly at higher pressure differentials.

Filtration runs were made in the laboratory batch filter apparatus using the new 120 ml test cell and a screen filter medium. The test sample was a slurry containing about 12 wt% CCG gasifier solids in an aqueous solution containing 5 wt% K^+ . After heating the sample in a one-liter supply reservoir to about 190°F, slurry was introduced into the heated test cell using compressed nitrogen. All runs were done in batch mode using only the 120 ml of sample in the test cell. Once the sample was in the cell, the valve at the cell bottom was immediately opened to withdraw the filtrate, and the run was begun. Run lengths with the modified test cell using the screen medium were typically less than one minute compared to over three to six minutes using a 5 μ m millipore filter medium in the old 300 ml cell. Thus, due to the shorter time frame of the experiment, the tendency for premature settling of solids in the filter cell prior to filtration was reduced. Filtrate clarity was achieved with the screen within a few seconds after the start of each run. Filtration rates during tests at equivalent pressure differentials (20.3 psi) for samples with and without 25 ppm D-25A flocculant were about 5 gpm/ft² and 2 to 3 gpm/ft², respectively, for a period in which over 90% of the filtrate volume was collected. This confirmed the improvement achievable by use of such chemical aids.

The possibility of using in-situ leaching to remove potassium from char cakes was evaluated in several runs by washing the wet cakes. Distilled water was introduced into the test cell from an external one-liter heated reservoir using compressed nitrogen at the same pressure as the previous filtration run. Samples of wash liquid were collected in 100 ml increments. The effluent samples were analyzed "off line" using a potassium ion probe. These in-situ leaching test data showed that the potassium level in the wash liquid dropped from 5 wt% in the filtrate to less than 0.2 wt% after only 100 ml of distilled water was passed through the cell. Wash liquid flow rates decreased during the runs due to collapse of the cake. For example, the rate for the second 100 ml flow dropped to 38% of the rate for the

initial 100 ml flow, at a 20 psi pressure differential. The drop off was not as severe at 10 psi. Thus, while the initial wash liquid flow rate was higher at higher pressure differentials, the tendency to compress the cake was also greater.

Complete analysis of the recent filtration data is planned for the next quarter. Based on a detailed evaluation of these data, the need for further experimental work with the modified batch filtration apparatus and on the feasibility of horizontal belt filtration with in-situ washing will be defined.

Construction of the char attrition unit which will be used to evaluate particle size degradation of CCG char during staged slurry processing is nearly complete. Installation of the slurry viscometer, which will be used to evaluate the rheology and pumpability of CCG char slurries, is also underway. Experimental testing with these units will be postponed until representative samples are available from the lined-out PDU.

Environmental Control: Water and Solids Effluents

The overall objective of this program is to generate the data needed for a quantitative assessment of the environmental impact of the commercial CCG process. The main focus of the program is to characterize waste waters, spent solids, and solids slurries produced in the CCG PDU. Specific objectives are to:

- Estimate untreated waste loads from a commercial plant, including the effect of source control.
- Recommend suitable treatment and disposal schemes for solid and liquid wastes.
- Estimate the quantity and quality of any treated wastes discharged.

During the current quarter, a detailed plan was prepared for test programs in this area. An overview of the plans for stream sampling in the PDU is provided in the following paragraphs.

An important consideration in developing a PDU stream sampling plan is that commercial and pilot unit waste streams must correspond as closely as possible, so that pilot unit data can be extrapolated. An efficient way of obtaining the most useful data is to follow a staged sampling and analysis approach. The first stage consists of two parts, of which the first is a preliminary sampling program. This aims at determining absolute rates of pollutants produced per pound of feed, within a factor of three, as outlined in U.S. EPA Industrial Environmental Research Laboratory, "Guide for Level 1 Sampling and Assessment." This is done by extensively analyzing one set of grab samples. The second part of the first stage aims at determining the variability of pollutant production rates. This is done by taking a series of samples over a period of time, and performing only a few analyses.

Following a determination of which streams contain significant levels of pollutants, and which have the least variability, some are selected for a closer examination during the second stage. This is done by taking many samples, and analyzing them exhaustively.

The major commercial plant liquid and solid waste stream and the corresponding PDU streams are summarized in Table 5.2-2. In each case, PDU streams are produced which should provide a reasonable basis for estimating commercial pollutant rates. Judgement will be necessary in interpreting PDU data in some areas, particularly for the product gas cooling and scrubbing streams.

As part of the planning effort, a list has been prepared of the sizes, containers, preservation methods, and analyses for the preliminary samples to be obtained from the PDU. A summary of the frequencies, durations, sizes, containers, and analyses for the time series samples has also been developed. Both preliminary and time series samples are currently scheduled to be taken in the next quarter. Planning will also begin for the more detailed second-stage sampling program.

Environmental Control: Atmospheric Emissions

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

During the quarter, a detailed review was made of the test plans developed by PDU operations personnel. These test plans include provisions for sampling process, product, and waste streams for process and pollutant components. The PDU streams which are expected to be analyzed from the perspective of potential atmospheric emissions are:

- Screw dryer effluent
- Gasifier product gas (at several locations in the gas loop)
- Sour water stripper off-gas
- MEA regenerator off-gas
- Molecular sieve vent gas

Spent water-washed solids from the PDU Catalyst Recovery Unit should also be analyzed with a view toward identifying any toxic organic compounds and toxic metals which may be emitted with fugitive dust particles from the solid waste disposal operations.

Table 5.2-2

MAJOR CCG LIQUID AND SOLID WASTE STREAMS
COMMERCIAL PLANT VS. PDU

<u>Commercial Plant Section and Stream</u>	<u>Closest Corresponding PDU Stream</u>
<u>Coal Drying and Catalyst Addition</u>	
● Entrained Dryer Flue Gas Venturi Scrubber Purge (Slurry)	● Screw Dryer Effluent Gas Scrubber Purge (Slurry)
<u>Product Gas Cooling and Scrubbing</u>	
● Product Gas Venturi Scrubber Purge (Slurry)	● Mixture of: - Product Gas Filter Fines - Product Gas Scrubber Water
● Product Gas Condensates: - Intermediate Separator Sour Water (330°F) - Final Separator Sour Water (120°F)	● Product Gas Scrubber Water (ca. 170°F)
<u>Catalyst Recovery</u>	
● Water-Washed Spent Gasifier Solids (Filter Cake)	● Water-Washed Spent Gasifier Solids (Filter Cake)

In the course of reviewing the gas loop stream sampling needs for trace components (listed in Table 5.1-4 of the October - December, 1979 Quarterly Report), some additional components were identified which are of concern from a hazardous emissions standpoint. These include potentially toxic PHA's (polynuclear aromatics), which are commonly found in coal conversion operations, and trace elements such as mercury, cadmium, vanadium, lead, selenium, and arsenic. The proposed sampling tests for the product gas scrubber effluent should provide this component concentration data. Knowledge of trace component concentrations in the gas loop will help indicate their emissions potential at a commercial facility.

The gas sampling plans developed by PDU operations personnel were sufficient, with one exception, to address the possible atmospheric pollutants of concern. The one exception is the sampling and analysis of the lockhopper depressurization vent emissions. Hydrocarbons, H₂S, and CO may be released during the lockhopper depressurization cycles. A recommendation has been made to sample for these components. Identifying the component pollutants in this vent stream will enable estimates to be developed of potential pollutants expected to be flared to atmosphere from CCG commercial plant lockhopper depressurization.

PDU operations personnel are beginning to develop specifications for the PDU sampling equipment, procedures, and methods, and for the test operating conditions required for an adequate pollutant emissions analysis. These specifications will be reviewed from the atmospheric emissions perspective as they become better defined.

Dynamic Simulation of the CCG Reactor System

The objective of this program is to study the dynamic response, stability, and control requirements for the gasifier reactor and associated recycle gas system. The simulation program is divided into a series of modules. Current work has concentrated on the gasifier module.

The portion of the gasifier module describing the concentration profiles in the emulsion and bubble phases has been completed. This module involves the integration over the reactor length of the steady state material balance equations. Diffusivity, bubble diameter, mass transfer coefficients, and the fraction of gas in the bubble phase are calculated at various points along the reactor length. Existing kinetic relationships are used to calculate reaction rates.

Several integration techniques were investigated for application to the reactor differential material balances. The intent was to find an algorithm which minimized computer time in order to allow a maximum of interaction with the simulation. An Euler technique and a fifth order explicit Runge-Kutta with step size adjustment were successfully applied.

The latter method was more efficient. An implicit technique and a predictor-corrector method were considered but were rejected on the basis of excessive computation.

The remainder of the gasifier module involves dynamic solids and energy balances. Material balances for carbon, ash (including mineral matter and catalyst) and active catalyst have been developed. The catalyst reactions are modeled in a simple way and the material liberated to the gas phase determined. The energy balance is based on correlations for the enthalpy of organic material, ash, moisture, and catalyst. The heat of the catalyst reactions are also included. After coding and testing, the solids and energy balances will be linked to the gas phase equations to form the complete gasifier module.

Catalytic Gasifier Solids Balance Model

The objective of this program is to adapt DYNAMOD, a proprietary solids balance computer model developed and validated for other Exxon fluid-solids processes, to predict the steady-state loss rates and particle size distributions both in the catalytic gasifier and of all streams leaving the vessel. A two species model is being developed that solids balances both char and high conversion "ash" components. Work will continue on programming and validating the two species model after a data base has been established from the PDU. The previously developed single species model will be used initially to evaluate preliminary data and in scaling up PDU results.

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