2. Process Development Unit Operations
(Reporting Category C02)

2.1 PDU Operations

Operation of the Process Development Unit (PDU) for Catalytic Coal Gasification began in July, 1979. After a period of equipment and systems shakedown, the PDU operated successfully, investigating a number of different operating conditions before completing a run to demonstrate operability of the catalytic gasifier at the end of the contract period. Several months were taken at the beginning of operations to debug and line out the equipment. For the remainder of the first year of operations, several process problems were solved. The major problems were: plugging in the coal feedlines, occasional formation of agglomerates in the gasifier, and production of char with an unexpectedly low fluid bed density. Once these problems were addressed, the PDU program investigated a range of operating conditions for the Catalytic Coal Gasification process. This program was culminated by a demonstration run of the gasifier section of the PDU. The demonstration run was successful in providing data for the next stage of development. This report includes a brief description of the PDU and is followed by a detailed summary of the operations of the PDU for this contract.

Description of the PDU

The PDU is a fully integrated pilot unit including: continuous coal feeding, char withdrawal, product gas cleanup, cryogenic fractionation of methane, synthesis gas recycle and catalyst recovery and recycle. The unit was sized for a nominal coal feed rate of 1.0 ton-per-day. The base case temperature and pressure were designed to be 1275°F and 500 psig, respectively. A simplified flow diagram of the PDU is shown in Figure 2.1-1. The unit can be separated into three sections to describe it in more detail. The three sections - gasification, gas separation, and catalyst recovery - are discussed below.

Gasification Section

Fresh coal which has been dried, washed, and screened to 16 x 100 mesh size is transported under nitrogen to a storage hopper. A rotary vane feeder on the bottom of the hopper meters coal to a ribbon mixer in which catalyst solution is added to the coal. The catalyzed coal is then dried in a series of steam heated screw conveyor dryers. The dry coal is transported to a surge bin for storage before feeding to the gasifier.

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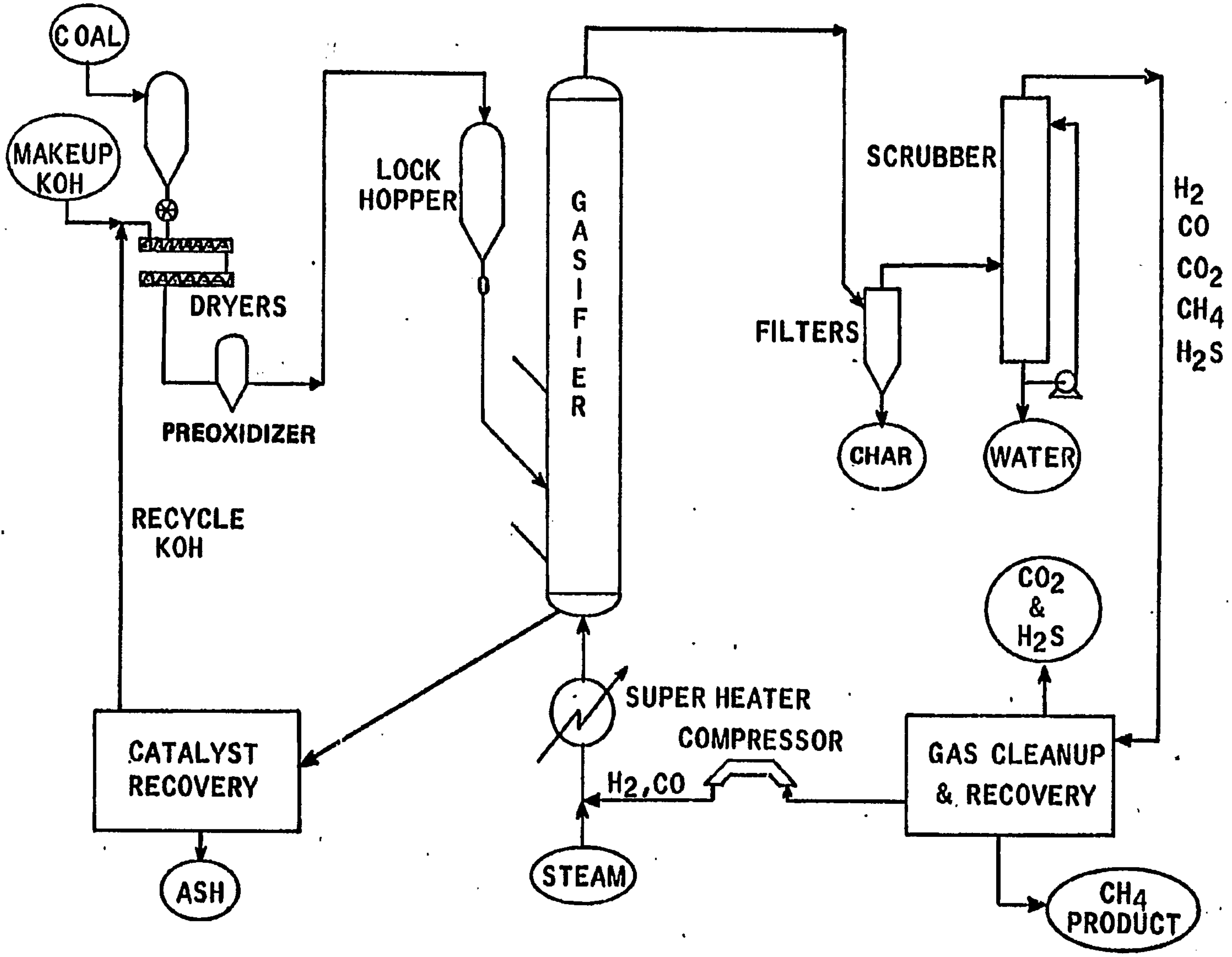
FIGURE 2.1-1

PDU FLOW DIAGRAM



The reactor coal feed system consists of two parallel pressurized lock hoppers holding about one ton of catalyzed coal each, with a small lockpot under each hopper. One hopper is feeding while the other is being depressured, filled from the surge bin and repressured for use when the on-line hopper is emptied. The lockpot feeder cycles approximately 25 times per hour to feed 100 lb/hour to the gasifier. The lockpot drops the coal into a vertical two-inch line, reducing to a 3/4-inch line from which the coal is blown into the side of the gasifier by driver gas at a 45° downward angle. The feed coal can be injected 5 feet, 25 feet, or 45 feet from the bottom of the gasifier.

The gasification reactor itself is a vertical vessel, with flange closures on each end, 83 feet high with approximately 10 inch i.d. and 13 inch o.d. It is heated electrically by radiant ceramic heaters arranged into 16 separate control sections. It is constructed of HK-40, a cast stainless steel alloy similar in composition to 310 stainless steel.

Steam and synthesis gas are injected into the bottom center of the reactor. Steam is generated at 600 psig in an electrically heated vaporizer, then mixed with the synthesis gas and passed through a superheater. The superheater is an electrically heated, fluidized sandbath which heats the gases to 1200°F. A small amount of H_2S is added to the synthesis gas before preheating to prevent carbon deposition on hot metal surfaces.

Synthesis gas is recycled gas from the cryogenic fractionator. Trailer supplies of H_2 and CO are also available for makeup gas and start-up purposes. Two recycle gas compressors are used to raise the synthesis gas supply to 600 psig.

Product gas leaving the top of the gasifier passes through filters to remove the entrained char. It then passes through a scrubber to condense the unreacted steam which is removed as water and weighed.

Gas Separation Section

The product gas then enters the gas cleanup section to remove CO_2, H_2S, and small amounts of ammonia and water. Monoethanolamine (MEA) is used to absorb the acid gases in a packed tower at 250 psi and ambient temperature. The MEA is regenerated in another packed tower where it is heated and depressurized to atmospheric pressure. The regenerated MEA is then returned to the absorber to form a closed loop. After the MEA tower, the gas passes through a molecular sieve absorber and an activated carbon absorber for removal of final trace impurities before entering the cryogenic system.

The cryogenic fractionator system operates at 250 psig and approximately -250°F, using liquid N_2 as the coolant. Extensive feed-effluent heat exchange is used to reduce the amount of liquid N_2 required. All of the low temperature equipment is inside an insulated, evacuated containment vessel to minimize heat transfer from the atmosphere. Methane is removed as a bottom product from the fractionator and CO and H_2 are the overhead product. The CO and H_2 are sent to the compressors for recycle to the gasifier.

Catalyst Recovery Section

Char is removed from the bottom of the gasifier through two parallel char withdrawal lines. The lines contain two valves which are cycled in a lockpot manner to lock out a volume of char approximately three feet long in a three-inch diameter pipe. The char drops into a slurry pot on each line which contains water to quench the hot char. An agitator mixes the char into the water and the char is then drawn off as a slurry. The pots operate at 500 psi to minimize the pressure drop and wear on the ball valves which would result from the hot abrasive char.

The char slurry is sent to the catalyst recovery system before the char is finally dumped. The slurry is washed with water and filtered in two countercurrent stages to recover the potassium. The rich solution is concentrated by evaporation to approximately 20% potassium salts and then recycled to the catalyst addition section where it is applied to fresh coal entering the gasifier. Further details of the catalyst recovery operation are contained in the next section of this report.

Initial Gasifier Operation

Operations of the gasification section of the PDU were begun the first of July 1979. During these operations, the gasifier temperature ranged from 1200-1250°F and the pressure was 500 psia. The feed was Illinois No. 6 coal catalyzed with 12 to 12.5 wt % KOH and fed at a rate of 40 to 80 lbs per hour. The fluidizing gas was nitrogen, introduced at a rate of 1500 to 3000 SCFH, (nitrogen was used in place of synthesis gas (H_2 + CO) in the interest of maximizing the operating safety during the start-up of new equipment and the operator training period). Steam was injected at a rate of 150 to 170 lbs hour. The preheaters and superheater were used to raise the nitrogen and steam injection temperatures to 1200°F.

All of the pieces of equipment in the gasification section were operated. Most of the equipment operated well after making the usual adjustments required of new equipment. The catalyst addition equipment, automatic coal feed system, steam generation equipment, entrained char removal system, and the product gas water scrubber system all worked well. The first operational problems encountered on the PDU were associated with the coal feed injection lines.

Feed Line Plugging

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

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

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

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

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

Feed Line Modifications

Several modifications were made to the feed line to help delay devolatilization until the coal is inside the char bed. As shown in Figure 2.1-2, a thermal sleeve was added to the feed line on the last two feet before injection. The sleeve helps to shield the coal from the hot char temperatures until it reaches the actual tip of the injection point. Cooling gas is blown into the tip of the annulus between the feed line and its thermal sleeve. This gas is routed so that it does not enter the process. The cut off angle of the tip of the feed line was also changed so that the coal may enter the fluidized bed horizontally rather than at a 45° downward angle. In addition, the temperature along the length of the entire feed line was reduced from 400-500°F to 250-350°F. The injection gas rate in the feed line was also increased to speed the flow of solids through the heated zones.

These changes produced a dramatic improvement in feed line operation. Five sustained periods of feeding were accomplished (2-14 hours), in which coal feed was stopped voluntarily in each case to perform other maintenance or modifications to the unit. As further work was directed toward optimizing the operating conditions of the gasifier, longer and longer sustained runs were made.

First Sustained PDU Operation

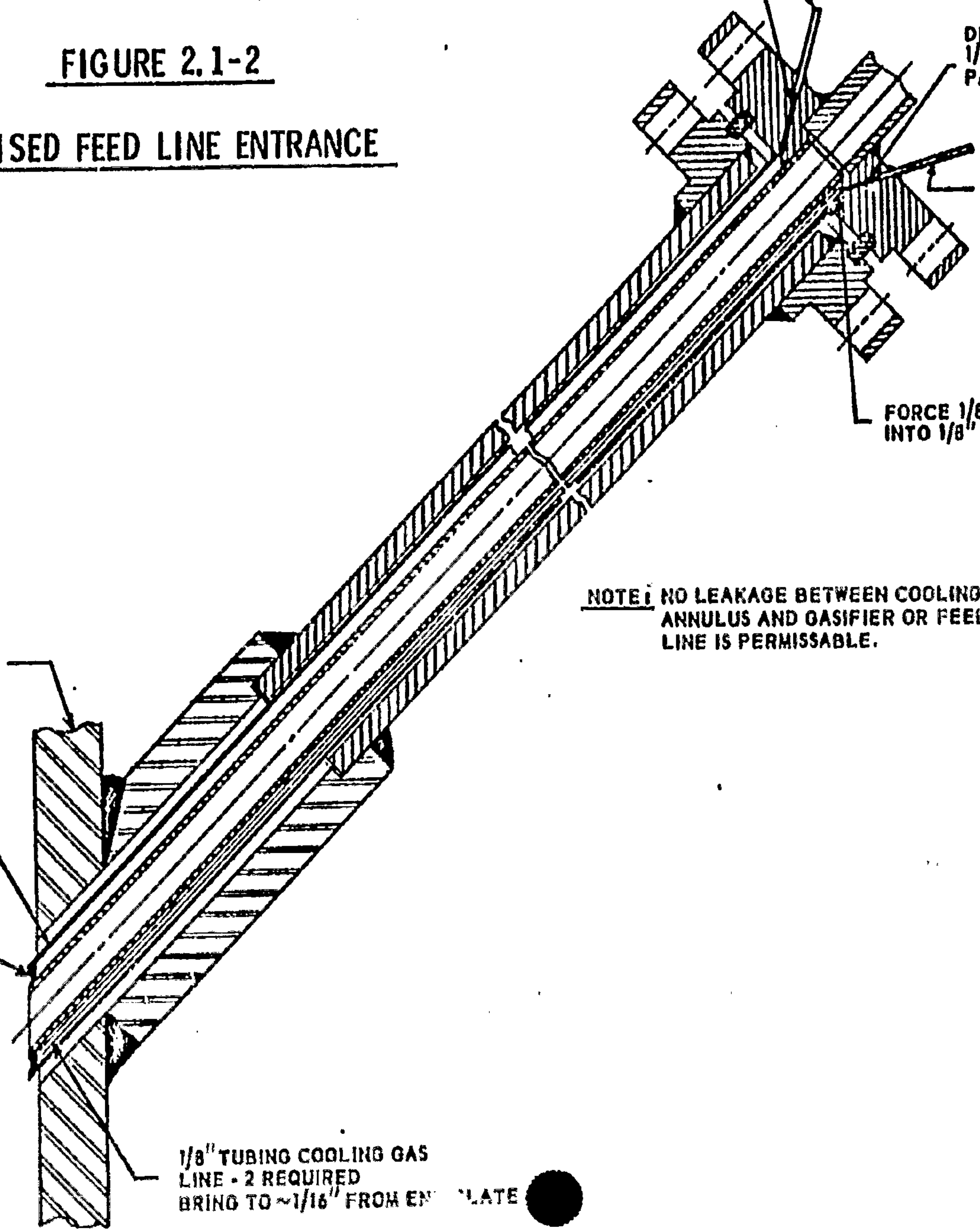
The highlight of August 1979 was a sustained operation of the gasification section for 165 hours. Only a minor interruption of feeding for less than three hours occurred. Otherwise the operation was very smooth and well-controlled. The run was terminated by the loss of a liquid N_2 pump used to supply feed nitrogen to the gasifier.

During the run the unit was operating at conditions of 1225°F and 500 psia, with feed rates of 150 lb/hr steam, 3500 SCFH total nitrogen, 2200 SCFH fluidization N_2, and 90 lb/hr catalyzed Illinois coal. Catalyst loading was 15% KOH on coal. Superficial gas velocity at the bottom of the reactor was 0.25 to 0.3 ft/sec. Carbon conversions were in the 80-90% range and steam conversion of approximately 50% was achieved. Material balances were in the 95-98% range. Some of the automatic data acquisition systems, such as the process gas chromatograph (GC) analyzer, were still being brought on-line and were not operating at the time of the run.

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

FIGURE 2.1-2

REVISED FEED LINE ENTRANCE



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

As the problems with the coal feed system were being solved, improvements were also being made in the char withdrawal system. The char was initially withdrawn as dry solids in a manual operation. Construction and programming of equipment later allowed for a continuous automatic withdrawal of the char as a water slurry.

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

Work continued on the gas cleanup and recovery section. The MEA system start-up progressed as unit operator time was available. Construction was completed on the molecular sieve system in August and start-up was initiated when the programming was completed and checked out on the programmable controller. The cryogenic fractionator construction proceeded on schedule. As the equipment in this section became operable, it was tested by operation on gasifier product gas on a once-through basis.

Before the sustained operation in August, the 2-1/2 inch diameter carbon steel studs in the top and bottom flanges were replaced by B8M stainless steel studs and retorqued on 4400 ft-lb. It had been found during the July 1979 operations that the flanges had to operate hot enough that the carbon steel studs crept and the flanges leaked. During that downtime, filter elements in both the entrained char removal filters were replaced; leaks were repaired in the steam generator drum and sight glasses; the slow depressure valves were repaired; and entrained char was washed out of the scrubber, sour water accumulator drums, and sour water stripper.

First Major Turnaround

After the sustained operations of August 1979, the first major turnaround of the gasification section was begun. This extended through the month of September. The goals of the turnaround included completing work in four major areas: (1) mechanical repair, maintenance, and testing; (2) process improvements; (3) installation of hydrogen/carbon monoxide supply system; and (4) miscellaneous data, instrumentation, and control systems.

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

Several process vessels downstream of the product gas filter had to be cleaned because of the accumulation of fine char. These included the scrubber, which condenses unreacted steam from the product gas, and sour water accumulators, which hold the condensate for weighing before discharge. Both filter elements were replaced while a longer term solution to the problem was being actively pursued.

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

Process lines supplying gas necessary to feed coal were replaced with lines of larger diameter so the required flow at the desired pressure could be maintained at all times. Also, several three-way valves were installed so that gas flow could be conveniently switched from nitrogen to synthesis gas. This allowed critical systems such as coal feed gas supply and pressure taps to remain on nitrogen when syn gas was first introduced to the gasifier. This proved to be advantageous from an operations standpoint.

Other improvements included (1) a direct reference system for pressure taps, eliminating the offset caused by a regulator in the old system; (2) a back pressure reference system for the steam generator which operates independent of the gasifier; (3) the use of house nitrogen (160 psi) for critical air actuated valves rather than instrument air (55 psi); and (4) the installation of a backup programmable logic controller to ensure maximum reliability of automatic valve cycling.

During the turnaround period, the hydrogen/carbon monoxide (syn gas) supply system was completed. All lines from the gas cylinder trailers to the unit and all manifold lines, valves and instruments were thoroughly leak tested to ensure safe operation with these flammable gases. As a precaution, the body purges on the char withdrawal valves were pressured with nitrogen slightly above unit pressure to assure no flammable gas leaks through these valve stem packings. Finally, the carbon monoxide detectors were calibrated and the process analyzer was brought on stream to ensure safe operation of the unit.

The next period of PDU operations consisted of flow tests, fluidization tests, and the introduction of hydrogen and carbon monoxide (syn gas) as the feed to the gasifier. The turnaround of the unit for syn gas start-up was completed in the first part of October 1979. This was followed by a series of flow and fluidization tests aimed at increasing the precision of measurement of several process variables. Near the end of the month, the unit was started up and ran for seven days with steam and syn gas as feed to the bottom of the reactor.

Flow Tests

After the turnaround, operations of the PDU began with several flow tests. These tests were conducted in an effort to increase the accuracy of the information used in the PDU material balance program. Several of the studies dealt with pressure drop measurements across the fluidized bed and the sensitivity of the new instrumentation used. Pressure taps are purged with gas that flows into the reactor to keep solids from plugging the line to the transmitter. It was found that pressure readings were sensitive to the gas purge rates. An increase in the superficial velocity of the purge gas caused a decrease in the pressure reading. By maintaining all pressure tap purge rates equal and constant, the problem has been eliminated.

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

Synthesis Gas Introduced to Gasifier

Leak testing of the PDU with syn gas was delayed for several days by failures of the programmable controller and the C-2 compressor. Once the problem with the programmable controller was found, several days were spent reworking and replacing all of the system input/output housings. Shortly thereafter, a connecting rod in the C-2 compressor came loose. Compressor C-1 was also inspected and found to be heavily worn. The compressors were rebuilt after consulting with the factory representative. Three possible causes of the compressor failure were discussed: poor quality control in the construction of the compressor; a hydraulic relief valve that was set at too high pressure; and the use of non-recommended oil in the compressor.

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

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

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

A new type of stainless steel filter element was installed in October 1979 to remove char carried over in the product gas stream. The previous system used a glass weave construction that would tear when subjected to high pressure drops resulting in contamination and plugging of the water scrubber. The new filter element consisted of 316 stainless steel wires drawn in a random matrix, compressed and sintered. This provided a rugged medium which could be cleaned by backflushing. The new filter element was found to be a definite improvement, but the new system started leaking solids into the scrubber after several weeks of operation. It was found that the unsupported filters fail when subjected to large pressure drops during unit upsets.

First Syn Gas Runs

In November 1979 operations continued with four sustained runs of the gasifier section using syn gas (75% H_2 and 25% CO) in the bottom of the gasifier. The service factor of the gasifier for the entire month increased to 30%. During the runs, the unit was operating at conditions of 1250-1300°F and 500 psia with feed rates of 100 lbs/hr steam, 2500-3500 SCFH syn gas and 40 to 100 lbs/hr coal. The catalyst loading was 12.5 wt.% KOH on coal. Superficial velocity at the bottom of the reactor was 0.2 to 0.25 ft/sec.

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

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

Further Agglomerate Formations

The unsteady coal feed rate was due to occasional feed line plugs and slow char withdrawal operation. Pressure tap readings showed the presence of small bridges at or above the feed point on a few occasions. The bridges were probably formed when the coal was fed above the bed in the reactor. The char withdrawal legs were plugged by chunks a few times. There were two types of chunks--a porous, shiny type with high carbon content (62%) and harder chunks with low carbon (3%) and high ash (88%) contents. The chunks with high carbon content were thought to be caused by collapsed bridges. Those with high ash content probably resulted from stagnant zones at the gasifier bottom. In the latter part of November 1979 the bed level was always kept above the feed point and bed slumping was avoided. This helped reduce the formation of chunks.

In December 1979, after a short turnaround where the char withdrawal valves were repacked, another six-day gasification run was made. During start-up a gas leak was discovered coming from the middle char withdrawal valve going to char slurry pot D-6. The packing material used on these valves was an asbestos weave impregnated with graphite. In service, this packing was found to harden causing the valve stem to stick and to promote leaks. Consultation with the valve manufacturer revealed that this leakage is a common problem. Packing on all char withdrawal valves was changed to an all graphite compressed ribbon on the four inner packing rings and an all graphite weave packing on the ends. The new packing has given excellent service with no leakage and has not required replacement to date.

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

Gasification Chemistry

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

Table 2.1-1

GASIFICATION CHEMISTRY APPROACHES STUDY DESIGN

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

Deposits End December 1979 Run

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

Controlling Chunk Formation

Late in December 1979 a run was made to test the possible effects that the gasifier start-up procedure had 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 H_2) 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 feed line plugs, and occasional withdrawal problems as well. The unit was voluntarily brought down after 60 hours for scheduled computer maintenance.

The computer maintenance provided an opportunity 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. This deposit accounted for the occasional problems with char withdrawal. The bed above the bridge contained agglomerates that were soft, plastic, low-conversion material. It was determined that these agglomerates were most likely being formed at the feed line.

The unit was brought back up in January 1980 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 due to small chunks. This long run demonstrated that the operational problem of agglomerates formation in the gasifier could be minimized by maintaining the fluid bed above the coal feed point and by keeping the feed line gas velocity above 14 ft/sec.

Redesign of Entrained Char Filters

The run was terminated when the entrained char filters failed and caused the product gas scrubber to become restricted with solids and overheat. Increasing the gas flow to the feed lines not only increased the overall quanity of product gas to the filters, but also increased the amount of char entrainment. Solids 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 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.

Variables Affecting Gasifier Bed Density

In operations up through February 1980, the PDU fluidized bed density had been somewhat lower than originally expected. The PDU density was 6-10 lbs/ft^3 compared to the FBG predevelopment runs which had bed densities in the range of 11-20 lbs/ft^3. In runs on the FBG earlier in this contract, the fluidized bed density was about 6-8 lbs/ft^3. 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 during drying, the density in the FBG was increased to 10-12 lbs/ft^3.

Starting in February 1980, a program was initiated to study variables which affect the PDU fluidized bed char density. The variables considered included coal/catalyst oxidation, gasifier pressure, superficial gas velocity, catalyst impregnation technique and low temperature heat soak treatments.

February 1980 Operations

During the next several months, a number of runs were made to begin studying the effects of the different variables on the PDU fluidized bed char density. Five gasification runs made in February are highlighted in Table 2.1-2.

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/ft^3.

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/ft^3. 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 2.1-2

SUMMARY OF PDU RUNS IN FEBRUARY 1980

Run Number	Pressure Psig	Air Pretreatment	Fluid Bed Density (lbs/ft^3)
1	500	300°F, 30 hr.	5-6
2	250	300°F, 30 hr.	8
3	250	400°F, 45 hr.	8-11
4	100	300°F, 30 hr.	10-13
5	100	300°F, 2 hr.	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. As the more severely oxidized coal replaced the existing bed, the fluidized bed density went up to 8-11 lbs/ft^3. The fines content of the bed dropped to 10-13%.

For the fourth run, the pressure was reduced to 100 psi, and the batch of mildly oxidized coal was reintroduced. Once the unit lined out, the fluidized bed char density had risen to 10-13 lbs/ft^3. 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/ft^3, and the fines (-200 mesh) content of the bed was up slightly to between 5 and 15 wt %.

March 1980 Operations

During March 1980 six more gasifier runs on different batches of treated coal were made to test the effects of pretreatment on gasifier bed density. These runs are summarized in Table 2.1-3. The first run was conducted on coal

Table 2.1-3

SUMMARY OF PDU RUNS IN MARCH 1980

Run Number	Pressure psi	Air Pretreatment Time (hrs)	Air Pretreatment Temp (°F)	Heat Soak Time (hrs)	Heat Soak Temp (°F)	Fluid Bed Density (lbs/ft^3)
1	250	28	350	34	250	14
2	500	26	285	45	270	7
3	250	7	220	24	230	8
4	500	66	425	12	200	10
5	500	12	405	28	200	10
6	500	14	400	7	280	10

oxidized 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/ft^3 and the fines content of the bed was between 17 and 24%. This run demonstrated that a good bed density could be attained when the coal was pretreated with a mild oxidation step followed by a low temperature heat soak at a gasifier pressure of 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/ft^3 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 operations had half the superficial gas velocity of 250 psi operations when the total gas fed to the gasifier was held constant. This difference in superficial gas velocity may be responsible for the fines buildup which occurred in the gasifier, especially at 500 psi operation.

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 a heat soak at 230°F for 24 hours. This coal resulted in a poor bed density at 250 psi. The average bed density was 8 lbs/ft^3. 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.

The next three runs were made to determine if feed coal oxidation combined with a heat soak would give bed densities above 15 lbs/ft^3 at 500 psi. Batch number four 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 final batch of March 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/ft^3. 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.

The February and March 1980 runs demonstrated that pretreating the gasifier feed coal through a mild oxidation, plus a low temperature heat soak, could improve the density of the gasifier fluid bed. This type of pretreatment produced a gasifier feed which shows a density of 12-15 lbs/ft^3 at 250 psi.

Initial Operation of Gas Cleanup and Separation Section

Initial integrated operations of the gas cleanup and recycle loop began at the end of January 1980. The MEA, molecular sieve, and cryogenic distillation were started up and shut down several times during the first quarter of 1980. By the end of February 1980, CO_2 concentrations off the MEA system were lowered to 0.5-1.0%. The remaining CO_2 was completely removed by the molecular sieves. A product gas was taken from the cryogenic distillation column which, on a nitrogen-free basis, contained 94% methane. The PDU was operated in the recycle mode for approximately 200 hours during the quarter.

Installation of Continuous Pretreatment

Due to the success of the oxidation and heat soaking steps, two vessels were added to the PDU to allow for continuous pretreatment of the coal. These vessels were fabricated and installed in the PDU during a ten-day major turnaround at the beginning of April 1980. The two fluid bed pretreatment vessels have capacities of 1100 pounds each. They can be fluidized with hot air and nitrogen and are traced with 600 psi steam to maintain a temperature up to 450°F.

During the next three months, three sustained runs were made on the PDU to study some of the CCG process variables. The first run period lasted for 195 hours with the first pretreat vessel serving as an oxidizer and the second as a heat soaker. The temperatures of the oxidizer and heat soaker were set at 330°F; however, operations were erratic. The oxygen content in the oxidizer feed gas was between 5 and 10%. The gasifier was at 340 psia and 1230°F. The nominal coal and steam rates were 65 and 110 lbs/hr, respectively. The gas superficial velocity in the gasifier from bottom to top ranged between 0.4 to 0.7 ft/sec for the entire period. The fluid bed density was only about 7-8 lbs/ft^3. The entrained char rate was 11 lbs/hr, about the same as previous operations, but the entrained char contained 35% larger-than-80 mesh particles. This was due to the higher superficial velocity at the top of the gasifier. The operations were stopped due to a planned shutdown of the site utilities.

The second run started after all utilities were again available, and it lasted for 160 hours. Since the oxidation and heat treatment at 330°F did not improve the bed density, the oxidizer and soaker temperatures were raised to 520°F. On a few occasions, the temperatures in the oxidizer went as high as 650°F. The higher temperature oxidation did not improve the fluid bed density. Again the operation of the pretreaters was erratic. At the latter part of the run, the unit pressure was dropped from 340 to 250 psia to study the pressure effect. A surge of bed density started just after the lowering of the pressure. The density went up to 9.5 lbs/ft^3 for a few hours then it leveled off at 8 lbs/ft^3 after 24 hours.

It seemed that the steady state oxidization at temperatures between 300°F to 600°F did not produce high density char in the fluid bed. The bed density was lower than those produced by batch coal treatments in previous months. However, the gasifier operations were very smooth, and no chunks were formed in the unit. The coal feed and char withdrawal were very steady. The coal feedline gas velocity was reduced to 14 ft/sec at the tip (i.e., 6 ft/sec just below the feed hopper).

During these two runs the operation of the MEA system was improved by optimizing the temperature of the regeneration tower. The temperature was raised to 240°F to aid the release of CO_2 and H_2S from the MEA. Prior to this time, the temperature was 212°F, which allowed some CO_2 to remain in the MEA. This inhibited the absorption of CO_2 on the next pass through the absorber, and the MEA absorber off-gas at times contained up to 0.5% CO_2. When the regenerator temperature was raised to 240°F, the CO_2 and H_2S contents of the MEA off-gas dropped to less than 0.1%.

The molecular sieve absorbers functioned satisfactorily once the MEA system was lined out. Prior to that, the molecular sieves were overloaded with CO_2, which allowed CO_2 break through in the molecular sieve off-gas.

The cryogenic fractionator operation was hampered by a malfunctioning valve in the liquid nitrogen condenser. It had experienced excessive wear due to very rapid on-off action. A time delay was installed in the level control system to prevent the chattering and wear. During subsequent operations of the cryogenic fractionator, a frozen plug formed in the outlet of the methane product line. The temperature of the cryogenic system was raised to melt the plug. The plug material, most likely ice, probably entered the system during the unsteady operating period of the MEA system.

Longest Sustained Run

During April 1980, the PDU began a continuous run period of 33 days. During this run, the decision was made to remove the -16/+30 mesh size fraction from the feed due to the observed swelling tendency of these larger particles.

During this long continuous run, the operation of the oxidizer vessels for preparing coal was changed from a continuous to a cyclic mode. The two vessels ran on a staggered four-hour cycle during which one was allowed to heat up by means of external steam coils and air mixed with fluidizing nitrogen while the other was allowed to cool by cutting off the steam and air. After four hours, the operation was reversed so that air was flowing to one vessel at all times. Temperatures cycled between 125 and 300°F in the first oxidizer and between 175 and 400°F in the second oxidizer. The first oxidizer ran cooler because of the added heat load required to dry the freshly catalyzed coal that entered it.

This cyclic mode of coal pretreatment resulted in the highest fluid bed density attained to date in the PDU. The bed density lined out at about 18 lbs/ft^3 with a solids entrainment of 6-10 lbs/hr. The weight percent of char particles in the gasifier less than 200 mesh was between 10 and 15%.

Gasifier pressure was maintained at 265 psi. On two occasions, however, the pressure was increased to 300 psi and the char density decreased slowly to about 13 lbs/ft^3 but only after showing a transient spike of high density.

Progress was made toward attaining PDU target design conditions. Material balances were in the 95-100% range. From the beginning of May 1980, carbon conversions of 85-90% were achieved with steam conversions of 30-40%. The gasifier operated at 1290°F with feed rates of 55-60 lbs/hr catalyzed coal, 115 lbs/hr steam and 3500 SCFH syn gas. Methane content of the dry product gas was 18%. The nitrogen in the product gas was reduced to only 5% by using syn gas in the coal feed line on a regular basis rather than nitrogen and also by turning off the nitrogen purges on the bodies of the char withdrawal valves.

Progress was also made in fully integrating the operation of the catalyst recovery and gas recycle sections of the PDU. In early May, recovered catalyst started providing about 25% of the total potassium requirement. This catalyst was obtained by a once-through water washing of withdrawn char.

Work continued to bring the gas recycle system into full operation. This work was being completed in stages as individual systems were checked out and brought on line. The operation of the MEA column and molecular sieve adsorbers was optimized. They ran successfully during May, removing carbon dioxide and hydrogen sulfide from the gasifier product gas.

Starting in the second week of May 1980, the longest continuous period of gas recycle was begun. It lasted for 12 days and was terminated only because of the voluntary shutdown of the entire unit for turnaround. During this period, 60% of the clean product gas was recycled back to the gasifier. Full recycle was not employed because the gas still contained methane. It was discovered that the fractionator's reboiler could not attain a low enough temperature without the inclusion of a valve to restrict the amount of warm feed gas going through the reboiler. The feed gas provided the heating duty to the reboiler.

Operations at 265 psia After the Long Run

The unit was brought down for a turnaround after the long run and then operations continued at 265 psia to demonstrate a high fluid bed density. During the 265 psia operations, a high bed density run was accomplished, syngas feed to the reactor was reduced, and the freeze-out problem in the cryogenic tower was solved.

Changes were made in the treatment of feed coal to improve char density.

Gas fluidization velocity in the oxidizers was increased in order to improve the agitation in these vessels. Agglomerated deposits found in the oxidizers indicated a lack of agitation in these vessels. In addition, it was desired to run the oxidizers at the higher flow conditions used in bench scale testing. The higher flow necessitated installation of a second air compressor so that the oxygen level would still be about 6% by volume.

Treatment time was reduced by more than half by flowing only nitrogen to the first vessel. Treatment time in the second vessel was about 11 hours. Oxidizer operations were at constant conditions during start-up to test the effects of oxygen concentration and treatment temperature. External steam coils provided the vessel with any supplemental heat required. During normal operation, high nitrogen flow rate and heat losses were sufficient to maintain constant temperature. If this cooling was not sufficient, the air was turned off momentarily to reduce the heat generated.

Due to higher flows in the oxidizers, a problem was encountered in operation of the dust collector. It was designed to retain small particles elutriated from the oxidizer vessel and to clean the gas stream vented to the atmosphere. Because of the greater solids loading and larger volume of hot gases, dust collector bags began to fail frequently. This problem was solved during downtime by rerouting effluent gases through a supplemental dust collector located on top of the coal lock hopper. This arrangement gave the hot gases time to cool and the elutriated particles somewhere to collect.

PDU coal oxidizer operations continued using one 11 hour residence time vessel. During the first two weeks of operation after the downtime, the oxidizer temperature control range was narrowed. The char bed density was 8-10 lbs/ft^3 for this period. Once close temperature control of 180-200°C was maintained in the oxidizer, the reactor fluid bed char density increased to 18-20 lbs/ft^3. This represented a substantial step in the operation of the oxidizer.

Gasifier operations were aimed at bringing the unit into syngas balance. The make-up hydrogen to carbon monoxide ratio was changed from 3:1 to 8.5:1.5, and the overall syngas feed rate was reduced. Syngas feed was reduced incrementally in both the reactor bottom and the coal feed line. While the syngas feed was eliminated from the bottom and significantly reduced in the feed line, syngas balance was not achieved using this reactor coal feed configuration.

The recurrent freeze-out problems in the cryogenic tower were also solved during this period. Several gases were identified as potential causes of the freeze-out: CH_4, CO_2, H_2O, and C_2H_6. All of the clean-up and recovery section equipment was analyzed to determine the gas causing the problems.

Gases were systematically eliminated to discover the cause of the freeze-outs. The cryogenic tower's coldest operating temperature was -165°C. Due to their low freezing points (-183°C and -172°C) methane and ethane were ruled out as causes. Nitrogen was saturated with water and passed through the system for eight days without freezing up in the tower. When no water was detected breaking through the molecular sieve columns, liquid water freeze-out was eliminated as a potential cause.

This left CO_2 as the cause of the freeze-outs. While testing the molecular sieves, CO_2 breakthrough was noted after just a few hours of operation, which suggested that the columns were not regenerating properly. Further investigations confirmed this hypothesis. The regeneration gas line entering each column had filled with molecular sieve pellets, restricting the flow of gas to the columns.

Gas distributors were designed and installed in the columns to keep the problem from re-occuring. When the columns were put back together, the gas clean-up and recovery section was put back on line with the gasifier. The system ran smoothly for 31 hours before the PDU was shut down to prepare for the expected landfall of Hurricane Allen.

Early in September 1980 a rupture occurred in a product gas line connected to the cryogenic distillation column. This rupture required breaking into the cryogenic containment vessel resulting in a major turnaround.

Besides repairing the ruptured line, breaking into the containment vessel allowed for other changes which were needed. Methane product lines were rerouted and bad level detectors were replaced. Three of five sonic level detectors had failed due to thermal cycling. These were replaced.

Turnaround

While the PDU was down, several items were repaired or replaced. The product gas filters, gasifier heaters, steam generators and steam/syngas superheater were inspected and repaired.

Neither of the product gas filters were leaking solids; however, inspection of the filters showed several damanged elements in one filter and a failed vibrator on the others. Both of these items were replaced and the filters reinstalled. Several of the gasifier radiant heater sections had failed in the last several months of operation. The elements were replaced and conditioned during the turnaround.

All of the heater elements in the steam generator were also replaced. A number of the elements had failed during the last run and an inspection of the elements showed a substantial quantity of mineral deposits built up on the elements. A regular schedule for blowing down the contents of the steam generator was instituted to prevent a reoccurrence.

The coil in the steam/syngas superheater was inspected as part of the continuing plan to monitor any metal dusting occurring in the superheater tubing. The coil was hydrostatically tested, and failed at 5000 psi; the tubing had thinned in several places.

Return to 500 psia Operations

After successfully demonstrating a high fluid bed density at 265 psia, PDU operations returned to 500 psia during September 1980. These operations first concentrated on moving the gasifier more toward syngas balance. Cracks were discovered and repaired in the bottom flange area during these operations. Then a number of variables was studied before trying to identify target conditions for the process demonstration run. After these target conditions were identified, 23-day run was made to demonstrate the process and provide data for a design basis leading to further scale-up of the process. These events are described in more detail below.

Improving Syngas Balance

Due to the greater methane make at 500 psia, the syngas rates in the coal feedlines had to be lowered to maintain syngas balance. These lower rates resulted in velocities too low to feed coal. In order to increase the feedline injection velocity, the 3/4-inch feed nozzles were replaced with 1/2-inch nozzles. This modification allowed a velocity of 14-20 feet/second to be maintained while feeding coal with a minimal amount of syngas usage. However, initial attempts of feeding with the smaller nozzles were unsuccessful. The feedlines were removed and the reactor was inspected. A large (approximately five feet long) chunk was found to be blocking the feed inlets to the gasifier. It appeared as though the chunk had been building during the previous unsuccessful feed attempts. The mass was rodded out and the feedlines were moved to the 25 foot level in case some of the chunk remained. At the 25 foot level, coal feeding was successful through the 1/2-inch feedlines. The gasifier ran smoothly near syngas balance for 6 days before developing problems in the product gas filters.

Excessive amounts of char began to show up in the scrubber water. In addition, the inlet and outlet filter block valves were leaking through to the extent that the filters could not be depressured sufficiently for blow down. Thus, in the middle of October, the unit was shut down to replace the filter elements, replace and rebuild the filter block valves, and replace selected piping to improve corrosion resistance.

Both F-1 and F-2 filter element headers were removed for inspection. All twelve filter elements on F-1 header were replaced since several were torn. In addition, a new vibrator was installed with new tubing for the vibrator inlet and outlet. Only the vibrator on F-2 and its associated inlet and outlet tubing were replaced since the filter elements on the F-2 header were all in good shape.

The four best filter block valves were rebuilt and four new valves were installed in place of the original block valves. The new valves were installed in the upstream position of F-1 and F-2 inlet and outlet lines. The new valves were expected to seal better and for a longer period of time because the new valves contained metal seats while the original valves had a carbon-graphite seat.

In order to decrease the possibility of corrosion problems, the carbon steel piping on the filter inlets, outlets, and around the block valves was replaced with alloy 800H pipe. Approximately five feet of the product gas line immediately upstream of the filters was also replaced with alloy 800H pipe. Finally, all of the stainless steel tubing around the filter-scrubber bypass valves was replaced with alloy C-276 tubing. The tubing was socket welded to an alloy 625 coupling which was welded to the new alloy 800H pipe in the product gas line. This eliminated all stainless steel tubing and fittings in the bypass line until well past the bypass valves.

The unit was reassembled and leak testing was begun. While pressure testing with nitrogen, a large crack was discovered in the D-6 char withdrawal nozzle about two inches below the gasifier bottom flange. The crack extended almost 180° around the 316SS nozzle. A dye penetrant test on the D-7 char withdrawal nozzle indicated the presence of a crack in a similar location. Cracks were indicated in two nozzles and it was thought to be extremely likely that the remaining three nozzles of the blind flange would also have cracks. Therefore, the turnaround was extended into a major one, allowing inspection of the entire gasifier.

Extent of Damage

With the gasifier bottom blind flange removed, the surfaces in contact with the process were found to be extensively cracked. A widespread granular crack pattern on the bore was clearly visible to the naked eye.

A dye penetrant test showed the cracks propagating around the edge onto the face of the flange. The cracks extended about fourteen inches up into the reactor and disappeared approximately four inches below the flange-reactor weld. The cracks were parallel, vertical, and of a non-branching nature.

The blind flange was also cracked extensively. Once more, the granular cracking patterns were found to be extensive in both the socket welded portion of the nozzle and the base 316SS metal of the blind flange. The cracks continued on the bore of the withdrawal hole all the way through the blind flange. The cracks were also present in the D-7 withdrawal hole and pulser hole, and the thermocouple hole, but not as extensively as in the D-7 opening. No cracks were indicated in the steam/syngas nozzle.

The char withdrawal legs appeared, at first, to be in good shape. However, subsequent examination showed that the alloy 800H pipe in the withdrawal legs did have some cracking, although far less than the 316SS of the nozzles. The 316SS char withdrawal valves were discovered to be cracked along the bore and the body of the valve. The alloy 625 hubs showed no signs of cracking either visually or by a dye penetrant test. Table 2.1-4 summarizes the location and type of material where cracks were found.

Table 2.1-4

SUMMARY OF CRACKING OF THE PDU BOTTOM FLANGE AREA

Location	Material	Cracks
Reactor Weld Neck Flange	Cast 316SS with 1/8" 310SS Weld Overlay on Bore	Extensive Cracking on Bore and Flange Face
Reactor Blind Flange	Forged 316SS	Extensive Cracking on the Bore of the Holes
Reactor Blind Flange Nozzles	Forged 316SS	Extensive Cracking on the Bore of the Nozzles with Large Crack Completely through the Wall of D-6 Nozzle
Char Withdrawal Pipe	800H	Slight Cracking on D-6 Side with no Visual Effect on D-7
Char Withdrawal Grayloc Hubs	625	No Visual or Dye Penetrant Indications of Cracks
Char Withdrawal Valves	Cast 316SS & Forged 316SS Co/Cr/W Alloy	Both Cast & Forged 316SS had Cracks - The Co/Cr/W Alloy Ball Showed no Cracks

Metallurical examination of the cracked area of the D-6 char withdrawal leg showed that the cracks were definitely transgranular and generally propagated in a straight path without branches. EDAX analysis showed extreme amounts of potassium in the crack with only slight amounts of chlorine present. Based on these results, it was concluded that the cracking problem was the result of caustic stress corrosion cracking.

Repair of the Unit

Since the weld neck flange was physically part of the reactor, it became immediately evident that any repair plan hinged on whether or not the weld neck flange would still be useable. Extensive ultrasonic testing by company and outside experts along with x-ray inspection proved that the basic flange was sound and that the cracks were only surface cracks. Thus, by machining off part of the wall of the flange, the cracks would be removed leaving sound metal. Approximately 9/16-inch of metal was removed from the weld neck flange wall. This allowed at least 1/16-inch of sound metal to be removed past the last crack. The cracks were also machined off the face of the flange. Once the machining was complete, the bore was smoothed and honed in preparation for testing. No cracks were evident and ultransonic testing confirmed that all the cracks had been removed. In order to afford more protection to the 316SS of the bore and to replace at least some of the metal, a weld overlay of alloy 625 was added.

Once it became apparent that the weld neck flange could be reused, repair efforts were also begun on the blind flange. All nozzles were cut off and examined for cracks. Both char withdrawal nozzles were extensively cracked, the D-6 nozzle was much worse than D-7. The steam/syngas inlet nozzle showed no visual cracks while the pulser inlet and thermocouple nozzle both had small visual cracks. The blind flange had extensive cracks on the bore of the char withdrawal holes and cracks were also present at the face of the flange on the corner where the holes started.

To machine these cracks out in a manner similar to what was done on the reactor would have required removal of an excessive amount of metal. Therefore, the blind flange was reworked completely. The first step consisted of removing the bad metal on the outside of the flange. This was done by machining the knob on the bottom completely off. The second step consisted of removing the bad metal on the face of the flange. This was done by machining out a plug of bad metal about 14 inches in diameter and about 2 inches deep. A new plug of 316SS was then welded in place. The third step was to remove the bad metal on the bore of the five holes. This was done by machining the bore until all of the cracks were gone, and lining these holes with new nozzles made of 625. The final step consisted of a weld overlay of 625 on the flange face.

Preventing a Reoccurrence

Stress corrosion cracking of austenitic stainless steels is a fairly common occurrence. Low flange operating temperatures were undoubtedly a factor in allowing the cracking to occur. To eliminate this factor, additional heaters and thermocouples were installed in order to effectively monitor and control temperatures at the bottom part of the gasifier and avoid potential condensation.

The fact that no cracks were found at other locations besides the gasifier bottom flange area was attributed to the high temperatures maintained in these areas. Higher operating temperatures coupled with alloy 625 material should prevent a reoccurrence of caustic cracking in the gasifier bottom flange area in the future.

Several other items were worked on during the turnaround. These included:

- Installation of the char withdrawal legs with block valves.
- Installation of a thermocouple network with heating tapes on the top flange and lines to prevent cooling to the point where caustic condenses.

- Installation of the new six hour residence time oxidizer.

Other items of lesser importance to actual operation were also repaired or installed. These items include:

- Replacement of the fast depressure line due to caustic cracks forming in the dead-space beyond the block valve.
- Installation of a water knock-out drum just prior to the product gas dry test meters to trap all condensate prior to these meters.

While the reworking of the bottom flange was being completed, additional cracks were discovered in the flange groove and char withdrawal valves.

Upon welding the new plug into the face of the blind flange, cracks appeared around the face and in the seal ring groove. These cracks were removed by machining off about 1/8" from the flange face and groove ring. Dye penetrant tests after installing the weld overlay gave no indication of cracks anywhere on the flange. With this rework of the flange, alloy 625 would be the only metal in contact with the process on the weld neck flange bore and face, the blind flange face, and the nozzles of the blind flange.

Cracks in the char withdrawal valves and lines were also repaired. Three of the valves were cut out of the char withdrawal legs and sent back to the manufacturer to be rebuilt. After disassembly, it became evident that the valve body and other parts of the valve were cracked. Due to the extensive nature of the cracking and the inaccessible locations, it was decided that the valves were not readily repairable. Therefore, the decision was made to replace the valves with new valves. While three spare valves were available at Exxon, none were available from any manufacturer in a reasonable time. Fortunately, one of the valves on the D-7 withdrawal leg showed only small amounts of cracking on the bore. This valve was repairable by machining out the bad metal and rebuilding the bore with an alloy 625 weld overlay. This left four valves available for the char withdrawal system instead of six as in the original layout. Although the first valve in each leg was originally designed as a backup shut-off valve, these valves have not proven to be necessary in practice, thus, they were eliminated. Then the three spare valves were installed in conjunction with the rebuilt valve. Finally, the alloy 800H pipe of the char withdrawal legs was replaced with new alloy 800H. Replacement with alloy 625 was preferred but the material was unavailable in pipe form.

Other parts of the gasifier were inspected for signs of cracks. The feed point nozzles were visually and ultrasonically inspected but no cracks were indicated. The inside of the gasifier top flange was inspected with a flexible optical fiberscope and, once more, no cracks were found. Suspect pieces of 316SS piping, however, were replaced with new 316SS piping and additional heaters and thermocouples were installed. Finally, the dipleg on the gasifier was a highly suspect location for cracking due to low temperatures and stagnant conditions. Since fines carryovers had not been excessive, the dipleg was separated just below the cyclone and just before the reactor and plugs were welded at each location.

Modification of Gasifier Top Flange Heaters and Thermocouples

During the repair of the cracks at the bottom flanges of the gasifier, additional cracks were found at the fast depressure line just above the gasifier top flange. These cracks were also caused by a potassium-related caustic stress corrosion. It is necessary to maintain the gasifier top flange area hot to avoid steam condensation and to avoid a reoccurrence of the cracks. The status of existing heaters and thermocouples were reviewed to effectively monitor and control temperatures at the top flange area. Several findings resulted:

- No heaters had been installed around the fast depressure line. The line had been heated by raw product gas and thus the dead space area (most of the 2" pipe section of the fast depressure line) was cold even with the gasifier running.
- Some thermocouple positions were not consistent with those shown in the flow diagram.
- Pressure tap PT-1, which was shown as being tapped to the fast depressure line, was actually tapped to the slow depressure line.

Several modifications of heaters and thermocouples were made as a result of these findings.

After the cracks had been repaired, PDU operations were focused on studying the effects of several variables before preparations were begun for the process demonstration run in February, 1981. These variables included: oxidizer residence time, oxidizer oxygen concentration, coal feed top size, gasifier fluid bed density and carbon conversion.

New Six-Hour Oxidizer Installed

A new shorter residence time oxidizer was installed during this turnaround. This oxidizer was installed to allow for the testing of pretreatment times of six hours and less. Experiments were begun at the end of October 1980 to determine the effects on oxygen pickup, hydrogen loss and carbon loss of shorter residence times.

The PDU was brought up on November 18, 1980 after all repairs and changes had been made. The only real difficulty encountered in operating the PDU was the slow rate at which the bed height increased.

The unit was idled after one week's operation due to a lack of coal. The coal preparation unit (CPU) had been shut down because of a breakdown in the coal grinding equipment. Upon completion of the CPU repairs, more coal was received at the PDU and after catalyst impregnation, the unit was readied to continue the run. As the unit was being brought back on line, fines began appearing in the gas scrubber indicating a filter failure. The unit was brought down and repaired. The filter repair consisted of replacing the metal cloth filter elements and steam cleaning the gas scrubber.

While the filter repair was underway and the unit was being readied for start-up, a problem arose in withdrawing char. Upon investigation, it became evident that char was plugging the withdrawal legs and reactor bottom. After several unsuccessful attempts to remove this plug, the reactor was cooled to near ambient conditions and the plug was washed out using steam condensate.

The six hour oxidizer ran successfully. The oxidizer was originally designed for a coal residence time of six hours with a coal feed rate of 35 kg/hr. Upon start-up, the coal feed rate had to be decreased to a low of 18 kg/hr. This low feed rate was unable to keep up with the PDU's feed rate of 40 kg/hr. To raise the feed rate, the percent oxygen in the oxidizing gas was raised from 6% to 10%. This increased oxygen percentage allowed the coal feed rate to be raised to 40 kg/hr.

Operation of Gas Clean-Up and Cryogenic Section

The first run of the gas clean-up and recovery section indicated a problem in the recycle gas stream of the cryogenic distillation tower. The methane content of the recycle gas could only be reduced to the desired 10% level at very low product gas rates. This observation led to the hypothesis that a methane reflux from the cryogenic tower condenser was not being maintained at high gas rates. At low gas rates the gas velocity through the condenser was low enough to allow the methane to trickle down to the column packing area, while at high gas rates, the liquid methane was being blown overhead. Two solutions to this problem were identified, (1) redesign the condenser to reduce gas velocities, and (2) design a precooling heat exchanger cooled by liquid nitrogen to liquefy the methane in the feed to the distillation column. The precooler system would operate in a manner such that the recycle gas stream would be of the proper purity at the distillation column feed point. The precooler fix was chosen since it could be built quickly and mounted easily. The precooler would be mounted externally to the cryogenic tower in contrast to the condenser which would require breaking into the cryogenic containment vessel where it would be mounted. The precooler was installed during the major turnaround and tested during the second run of this reporting period.

The PDU ran long enough at the end of December 1980 to test out the gas separations system, including the cryogenic distillation tower precooler. During this run the cryogenic tower was on line for seven days without developing a freeze-out plug, and a liquid methane level was maintained in the cryogenic tower reboiler. The precooler to the cryogenic tower had been installed and was operating, however, it did not significantly reduce the methane level in the recycle gas. As a result of this test, the condenser in the cryogenic distillation column was rebuilt in order to stop the entrainment of methane in the recycle gas at high product gas feed rates.

No major operational difficulties occurred on the PDU in January 1981; however, numerous minor problems in critical areas kept the unit down for most of the month. These problems occurred in three areas: bottom flange problems, fines filter problems, and problems caused by the sudden depressurization of the nitrogen ground pack.

Leaks in the Bottom Flange Area

The unit was operating smoothly in early January when a small leak was detected in the bottom flange area. The unit was immediately switched from syngas to N_2 and the coal feed was stopped. The whole area was leak-tested and some leaks were found in the vicinity of one of the char withdrawal block valves. These leaks were repaired and a nitrogen purge line was added. This purge line was to provide a diluent gas to the area preventing the concentration of flammable gases.

After this repair was completed, the unit was reheated and syngas introduced. Unfortunately, another leak in the bottom flange area forced the unit down again. The decision was made to remove all insulation from the bottom flange area and tighten the bolts to 93.1 MPa.

While the bolts were being tightened, cracks were discovered in the purge nozzles on the D-6 char withdrawal leg block valve. The withdrawal leg was removed and the nozzle to the gasifier was blinded-off. The bottom flange area was then reinsulated and brought back up to operating temperature.

Fines Filter Area

Bakersfield coke was being added to the unit, in preparation for start-up, when problems with the filters began. As the Bakersfield coke was being loaded, BV-59, a ball valve leading to the first filter, developed a leak around its flange. This leak required the unit to be depressured and the valve removed for repair. The valve was repaired and the unit was put into operation.

After three days of operation, char was discovered in the scrubber, indicating the fines filters had failed. The unit was brought down again and the filters were repaired using all new elements in the first filter. The best of the remaining elements were installed in the second filter.

This work was almost complete when it was noticed that a filter inlet valve (BV-59) was not operating properly. After removal of the valve, the shaft was found to be twisted nearly 90° off the actuator. In consulting the manufacturer about the twisting, it was decided that there was too much packing between the valve body and the ball. The packing thickness was reduced by 5 thousandths of an inch and the problem was apparently corrected.

The unit was readied for start-up of coal feed when a large amount of fines were again found in the scrubber water. This discovery necessitated removal of the filters for another repair. During this downtime, all valves surrounding the filters were reworked and the filters were rebuilt so that more rugged filter elements could be installed. The scrubber was cleaned of all fines during this period as well.

Depressurization of Nitrogen Storage

The unit was then brought up smoothly and another problem arose. The rupture disk on the liquid nitrogen ground pack blew, venting all nitrogen. The gasifier bed was maintained by using plant nitrogen. Full operations were not possible because of the low pressure of this gas. The rupture disk was replaced, and the cause for the rupture repaired. During this period, the pulser line plugged due to low N_2 pressure.

In late January 1981, operations of the PDU were begun to prepare the unit for a process demonstration run of the gasification section. Three runs were made prior to the demonstration run. The first run lasted nine days and entered into a new operating regime for the CCG process. The second run lasted six days and was characterized by rough operations. The third run took place after a long turnaround and operations were much smoother. During this third run, demonstration run target conditions were identified. Finally, in late March 1981, a 23-day demonstration run was made of the PDU gasifier section.

High Carbon Conversion Operating Regime

Several material balance periods were obtained in the nine-day run of January 1981, and a new operating regime was discovered. Material Balance periods 45 through 48 were very informative for the following reasons:

- The top size of the feed coal was switched from 30 mesh to 16 mesh with no change in unit operability.
- The solids entrainment rate was higher than previously experienced, while the char withdrawal rate was slower than usual.
- The carbon conversion of the bottom char climbed to 97 percent.
- The bed density climbed to approximately 32 lb/ft^3.

Material Balance period 49 was different from the previous four in that the bed density was around 32 lb/ft^3, while the swelling index of the feed coal varied widely. The new operating regime had the high bulk density of 51 lb/ft^3 and bed carbon conversions in excess of 95%.

The PDU gas separations system was successfully operated during the nine-day run. The focus of these operations was to establish the operability of the new methane condenser which had been installed in the cryogenic distillation tower. Previously, the methane content of the recycle gas was greater than 10 percent. With the new condenser, recycle gas methane contents as low as 6 percent were attained. The system gave no sign of freeze-out plugging during these runs.

Other Operations Prior to Demonstration Run

When the unit was brought down after the nine-day run, several items were scheduled for replacement or repair prior to the process demonstration run. These scheduled items included:

- Replacing the product gas filter elements with a new design to reduce the number of elements needed.
- Rebuilding the filter valves.
- Replacing the heating elements in the steam generator.
- Rerouting the boiler feed water supply to bypass an unnecessary, failed heat exchanger.
- Bypassing the 12-hour oxidizer.
- Replacing the shaft bearings on the screw dryers.
- Reinstallation of D-6 withdrawal leg.
- Modification of the product gas-metering system to achieve a higher degree of accuracy.

The unit start-up after this short turnaround was very difficult due to numerous problems. These problems were, in order of occurrence:

- Leaks on char withdrawal valves caused by packing failure.
- Leak in a feed line resulting from a bad gasket.
- Leak on a char withdrawal valve caused by a "C" ring failure.
- Leakage through product gas filter valves due to actuator twisting valve stems.
- Plugging in both feed lines caused by insufficient gas velocity in feed lines forming chunks in feed lines.
- Plugging in withdrawal lines caused by the chunks which made it through the feed lines.

The second run was plagued with operating difficulties. The major problems encountered were:

- Numerous plugs in the feed and char withdrawal lines.
- Coal swelling indices from the preoxidizer were marginally acceptable, typically being above 1.10.

- Fluctuation of the bed density over a wide range of values indicating steady state had not been achieved.

Although operations were more difficult than in the past, four material balance periods were declared. Data from these material balances should serve to broaden the current data base of the CCG process. This run was terminated by the nearly simultaneous plugging of both char withdrawal legs.

Long Turnaround to Prepare for Demonstration Run

After the unit was shut down, a turnaround was conducted to correct several items which had contributed to the operating difficulties of the second run. The items repaired and/or replaced during the turnaround include:

- Removal of chunks from the bottom of the reactor (caused by the feedline plugging).
- Installation of smaller feed lockpots to provide more continuous feeding (to alleviate slugs of feed coal which may in turn form chunks).
- Replacement of the coal pre-oxidizer with one of larger capacity. (The smaller pre-oxidizer was found to have a defective baffle, which explained the poor coal swelling indices.)
- Replacing the electric heating coils in the steam super-heater and make-up gas heater.
- Rebuilding of the catalyst additions pump in the catalyst addition unit (CAU).
- Rebuilding the coal star feeder in the CAU.

After the turnaround, the unit was brought back up for a third run which lasted five days. During the third run, the operating difficulties which characterized the second run were not experienced. The turnaround items had been successful in smoothing out problems. The unit operating variables were adjusted to approach the targets identified for the demonstration run. There have been three material balance times, all of which have had in excess of 95% closure over their 24 hour duration. These balances provided additional input into the final target conditions for the demonstration run.

Demonstration Run

The highlight of the development program was a successful Demonstration Run of the PDU. During the 23 days of continuous operation, the PDU verified the viability of the CCG gasification system and generated a volume of data at target conditions. This data (discussed further in Section 3.2) was used to confirm the predictive capability of the CCG kinetic model (discussed in Section 3.1).

The objective of this run was to demonstrate gasifier operability by operating in a controlled, stable mode with a bed density greater than 10 pounds per cubic foot and a carbon conversion greater than 85%. The catalyst loading was 12% KOH on Illinois coal and the target run length was two to three weeks. The demonstration was conducted at the end of March/early April of 1981 and a successful 23 day run was achieved. Table 2.1-5 shows the conditions achieved vs. the targets that we set prior to the run. During the run the gasifier operated at slightly less than the target temperature. The pressure was held constant at 500 PSI and the coal feed rate was close to target. The steam to coal ratio was somewhat higher than target at 1.9. The bed density was stable at 15 lbs per cubic foot. The steam conversion was 35% and the carbon conversion was on target at 85 to 90%. The methane in the product gas was the main target that was not achieved. It was only 21% vs. a target of greater than 25%. However, the methane level achieved was consistent with the high steam to coal ratio that was used. The run length achieved was 23 days and exceeded the target. The run ended because of mechanical problems with char withdrawal valves. This run demonstrated the operability of the gasifier and provided a data base to confirm the predictive ability of the CCG Kinetic Model.

TABLE 2.1-5

SUMMARY OF DEMONSTRATION RUN MATERIAL BALANCES

MATERIAL BALANCE NO.	CRITERION	TARGET	AVERAGE	54	65	56	57	58	59	60	61	62	63	64	65	66	67
FEED RATES, LBS/HR																	
COAL + CATALYST	WITHIN 10% OF DAILY AVE.	132	119	114	122	120	130	130	132	121	120	123	114	127	115	81	122
STEAM	WITHIN 10% OF DAILY AVE.	198	197	201	210	199	192	193	190	199	194	195	198	207	196	193	194
SYN GAS	WITHIN 10% OF DAILY AVE.	---	73	63	54	53	77	87	87	82	76	80	77	76	72	78	70
PROCESS CONDITIONS																	
AVG. GASIFIER TEMP., °F.	NONE	1300	1278	1274	1281	1272	1285	1283	1281	1283	1279	1285	1283	1276	1271	1269	1267
STEAM/RAW COAL RATIO	NONE	1.7	1.9	2.0	2.0	1.9	1.7	1.7	1.6	1.9	1.8	1.8	2.0	1.9	2.0	2.7	1.8
SYN GAS BALANCE, %	----	≥80	84	82	88	91	77	71	77	79	65	83	66	90	92	88	86
PERFORMANCE PARAMETERS																	
RAW MAT. BAL. CLOSURE	WITHIN 95-105%	100	94	94	95	103	102	96	93	100	94	91	93	91	85	87	90
CARBON CONVERSION, %	---	≥85	84	82	85	86	85	90	83	86	83	85	85	84	80	81	82
STEAM CONVERSION, %	WITHIN 3% OF DAILY AVE.	≥30	35	29	33	34	36	36	37	35	38	38	36	39	38	30	38
METHANE IN PROD. GAS, %	WITHIN 3% OF DAILY AVE.	≥25	20	20	20	18	23	25	22	21	21	20	19	19	18	15	21
AVE. BED DENSITY, LBS/FT^3	WITHIN 20% OF DAILY AVE.	≥10	15	16	19	21	17	18	16	16	13	13	12	13	10	9	12

2.2 PDU Catalyst Recovery Unit

After the coal has been reacted in the gasifier, the char consisting of unreacted carbon, mineral matter, and catalyst is removed from the gasifier and processed in the catalyst recovery section. Bench scale experiments during the predevelopment program (Contract No. E[49-18]-2369) demonstrated that part of the catalyst could be recovered from the char by leaching with water. Catalyst recoveries of approximately 70% of the total potassium present were obtained. The remaining 30% of the catalyst was present in a water insoluble complex of potassium with mineral matter that could not be recovered by water washing alone. Hydrothermal digestion of the char with lime can recover most of the water-insoluble potassium (see Section 1.1).

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

During the construction of the CRU, however, preliminary results of engineering studies (see section 5.1) became available which indicated that digestion was not competitive with water wash alone. Thus, the capability to do digestion was built into the CRU, but this equipment was never used for that purpose.

PDU Catalyst Recovery Unit Design Considerations.

There are two overall requirements for the PDU Catalyst Recovery Unit (CRU). The first is that the system recycle 90% of the soluble catalyst fed to the CRU. The second requirement is that the recycled catalyst solution be 10-20% (wt.) K^+, which is the concentration needed in the catalyst addition unit. Any lower concentration would result in excessive drying requirements in the downstream coal feed dryers. However, this concentration need not be reached in the countercurrent water wash since the number of stages required would not be practical or convenient in a plant of this size. Instead the recovered catalyst solution is concentrated to the 10-20% (wt.) K^+ level in an evaporation step prior to recycle to the CAU.

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

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

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

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

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

The leaching tank system was the preferred PDU catalyst recovery system at the beginning of the development contract. To examine the operablity of this concept, a full PDU scale leaching tank was constructed and operated in conjuction with the prototype digester. This prototype equipment yielded important material balance and particle size distribution information as well as providing the necessary performance data to design a leaching tank system. It was found that the leaching tanks worked well on particles that were larger

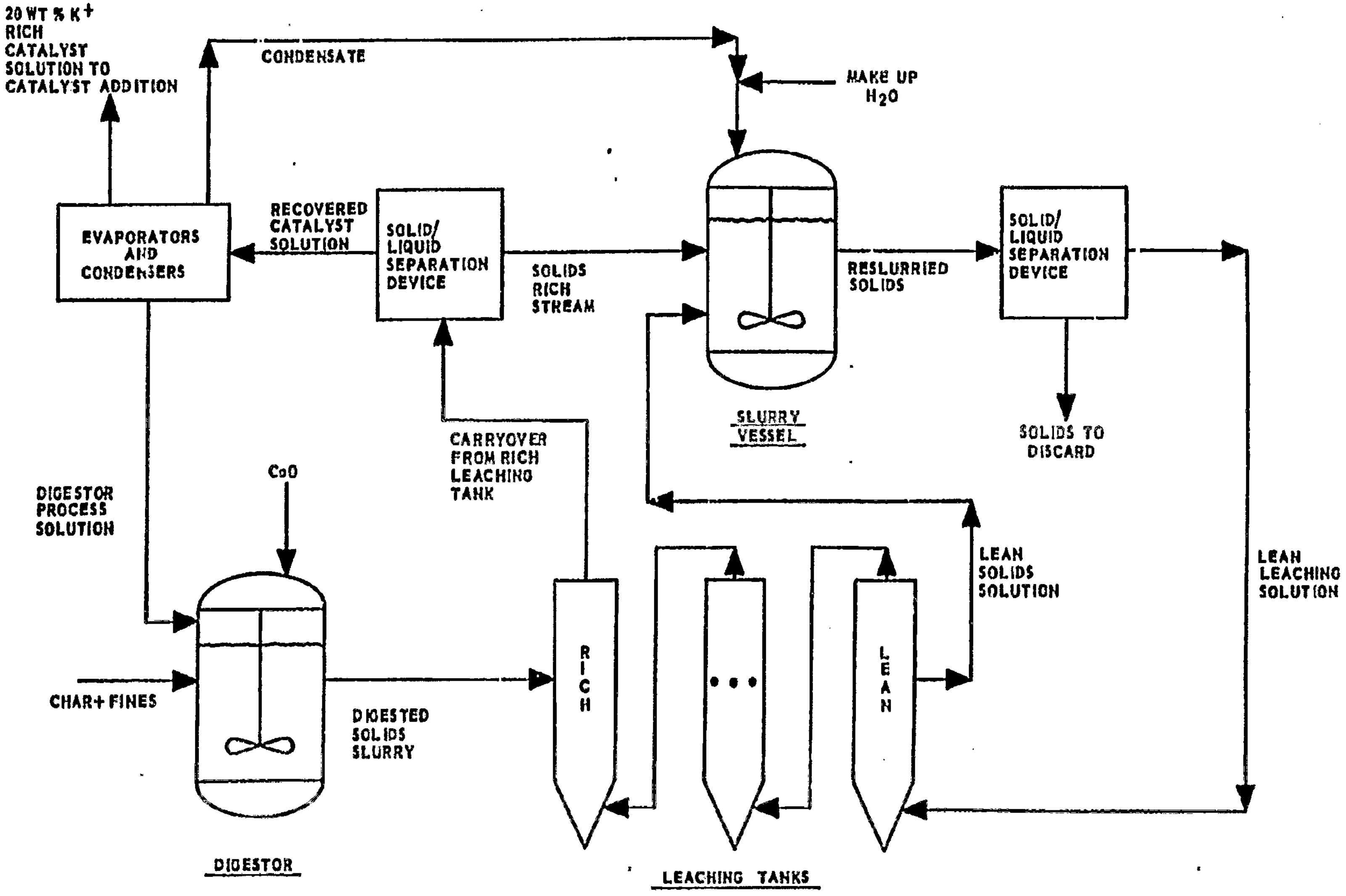
Table 2.2-1

CATALYST RECOVERY CONCEPTUAL MATERIAL BALANCE BASIS

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

FIGURE 2.2-1

LEACHING TANKS IN SERIES



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than 75µm in diameter. Particles smaller than 75µm, however, were likely to be carried out of the leaching vessel in the overflow solution. Unfortunately, 15% of the PDU bottoms char and all of the cyclone fines are expected to be digester should be present as a fine precipitate. The result is that approximately 50% of the solids fed to the leaching tanks would be carried out the top of the first stage. Half of the solids in the system will see only one stage of water wash. Therefore, potassium recoveries of 90% are possible only at extremely dilute recovered catalyst solution concentrations. In addition, any further particle degradation in the digester or char slurry valves would make this problem even worse. Because of these problems with fines, it was decided not to use leaching tanks as the catalyst recovery system for the PDU.

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

This system is probably the simplest that could be devised. Only one solid-liquid separation is required. However, recovered catalyst solution concentrations are of necessity very low To achieve 90% recovery of the soluble potassium, the concentration would have to be approximately 0.5% (wt) K^+. This results in an excessive evaporation duty in order to achieve the 10-20% (wt.) K^+ solution needed in catalyst addition.

Figure 2.2-3 gives the flow plan for a countercurrent water wash using mixing tanks and separators. This is the system that was used to recover catalyst in the PDU. Each stage of the countercurrent wash consists of a mixing tank followed by a solid-liquid separation device. Thus the digester serves as the mixing tank for the first stage. The solids slurry leaving the digester is fed to a solid-liquid separation device. The solution from this device is the recovered catalyst solution which is sent to an evaporation step to be concentrated to a 10-20% (wt.) K^+ solution. The solids from the separator are sent to the second mixing tank where it is slurried with the catalyst solution from the separator associated with stage 3. This countercurrent processing continues until the final stage where the water condensed in the evaporator is added to the nth mixing tank along with any makeup water required.

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

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

FIGURE 2.2-2

ONE STAGE RECOVERY

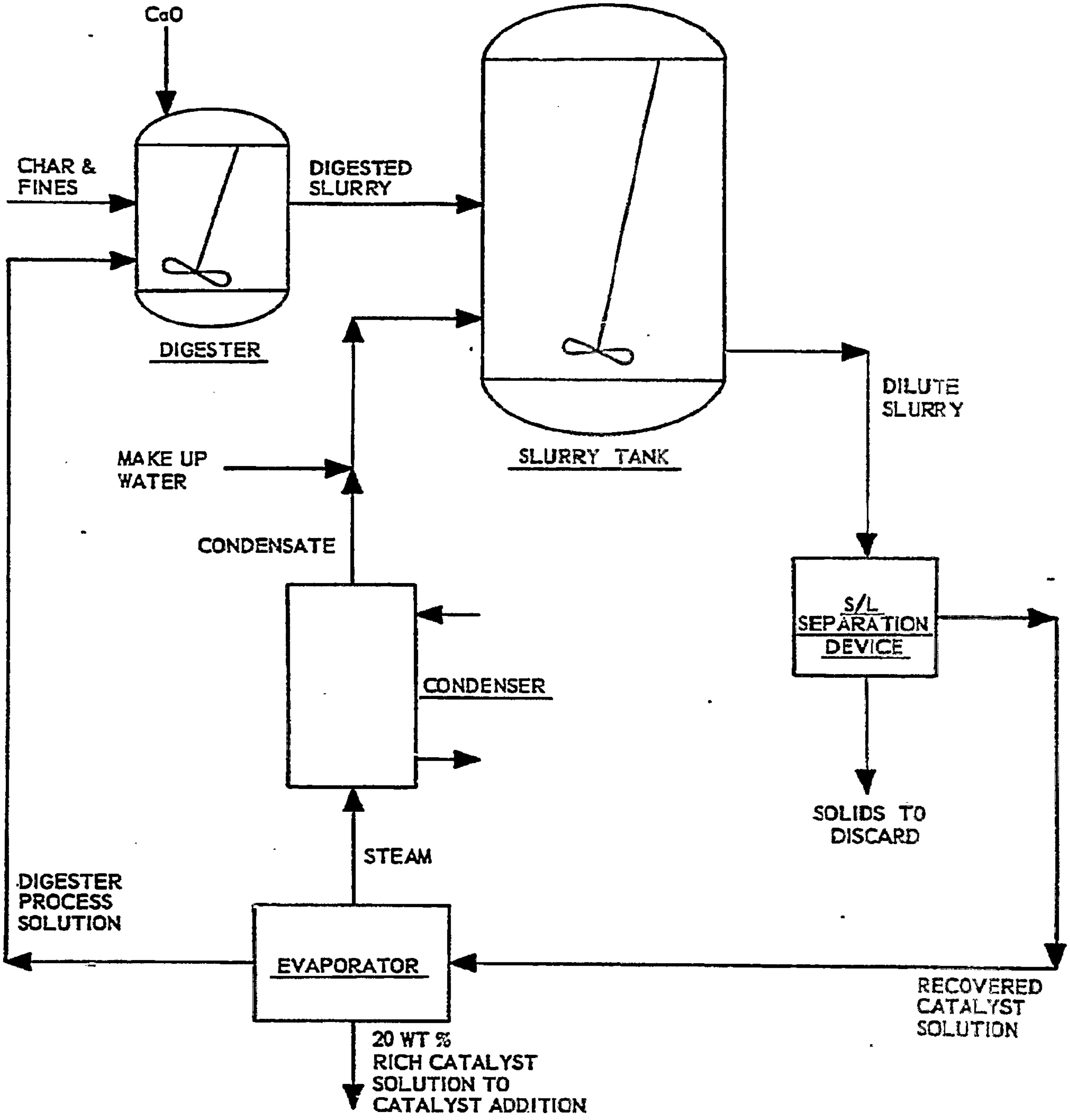

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FIGURE 2.2-3

SEPARATORS AND MIXING TANKS IN SERIES

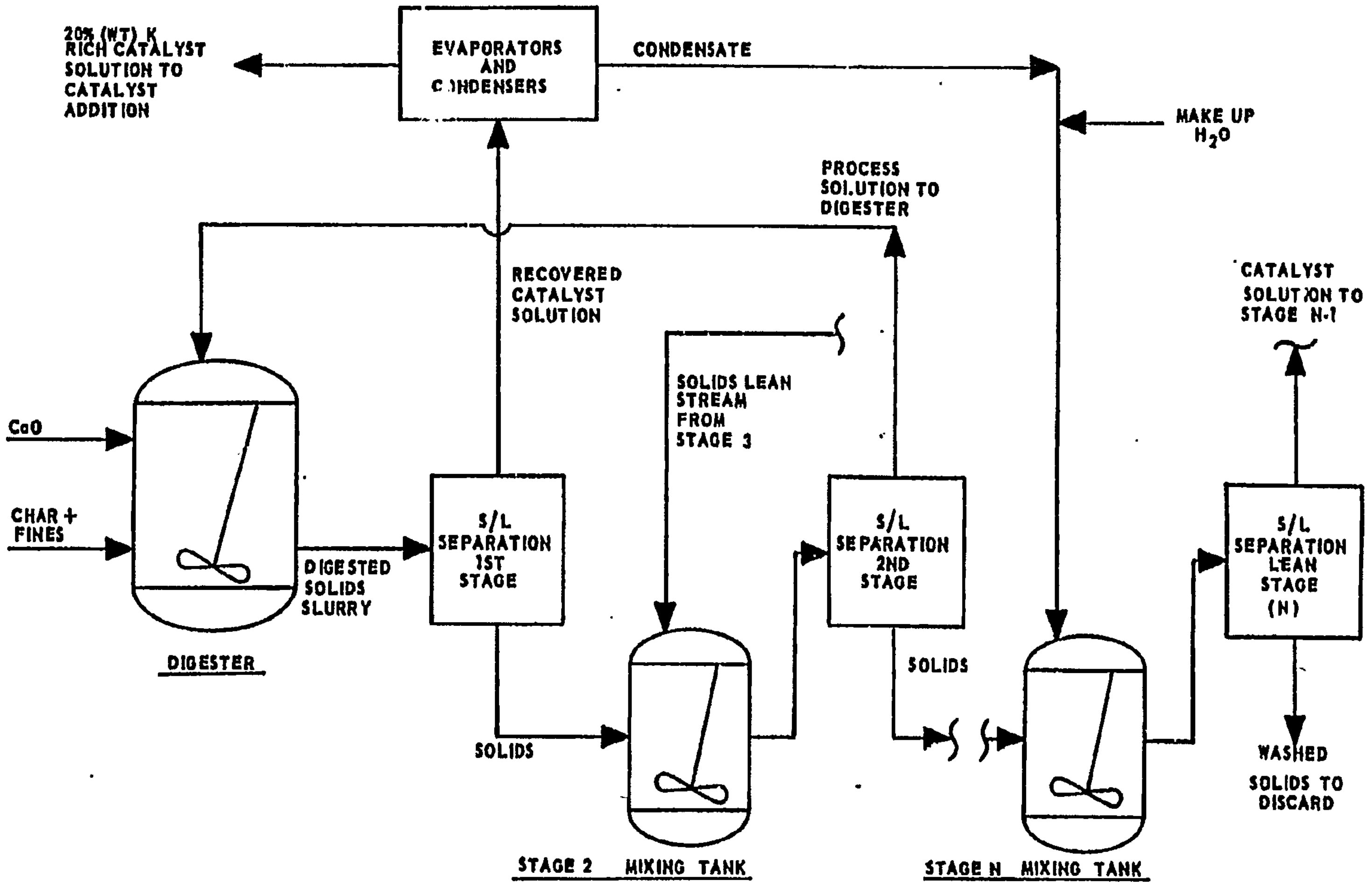

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Table 2.2-2

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

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

---

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

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

This goal was achieved by recovering dilute solutions. The PDU catalyst recovery system consisted of two stages recovering 90% of the soluble catalyst in a 1% (wt.) K^+ solution. Additional data on the impact of higher concentrations of K^+ on the performance of the solid-liquid separation device was obtained off-line.

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

Vendor Filter Tests

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

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

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

Table 2.2-3

SUMMARY OF BATCH FILTRATION TESTS ON CCG CHAR SLURRIES

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

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

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

Selection of CRU Filters

The next step in the design was to choose the actual filter equipment for the CRU. Several types of filtration equipment were examined to determine which would best fulfill the CRU requirements. The types of filters evaluated included rotary vacuum filters, horizontal belt filters, filter presses, and several types of pressure filters. After obtaining and evaluating information concerning the operation of each of these filtration devices, it was decided that two horizontal tank vertical leaf pressure filters would best meet the requirements of the PDU catalyst recovery system. Orders were placed for these filters in May 1979.

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

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

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

Design and Construction of CRU

In the third quarter of 1979, work began on detailed flow plans, process equipment design, and equipment procurement with the exception of the vertical-leaf pressure filters which had already been ordered.

The flow diagram for the digester system and an initial pass of the flow diagram for the filter system were completed. In addition, all major pieces of equipment, including the digesters, surge tanks, filters, and evaporators were designed. The digesters, designed to hold 450 gallons of slurry at 500 psig and 450°F, were ordered. The surge tanks, designed to hold 1500 gallons of slurry at 20 psig and 200°F, were also ordered. The evaporators, designed to evaporate 4,900 pounds of 1 wt % K^+ solution down to 20 wt % K^+ were built by Exxon. Foundation and structural drawings for the CRU were completed.

The foundation was poured and completed. Bids for fabrication and erection of the structure indicated that outside contractors could not provide an erected structure in the time frame desired. Consequently it was decided that Exxon would erect the structure.

During the fourth quarter of 1979, the structure and platform were erected. This platform is twelve feet high and supports the filter and evaporators. Supporting the filters above ground level allows the filter cake to fall into drums on the ground level where it can be easily weighed. In addition, the platform allows easy access for service and repair of the agitators on the surge tanks.

Next the vessel weigh platforms were installed and the surge tanks were placed in the structure on the weigh platforms as they were received. A char slurry transfer line was installed between the PDU char withdrawal system and the digesters. Utilities such as industrial water, plant air, and plant nitrogen were installed in the unit. At the end of the quarter, all major equipment items were in place and process piping was nearing completion for the digester.

During the first quarter of 1980, most of the process construction was completed. Figure 2.2-4 is a simple schematic of the CRU. In order to begin start-up of the unit as soon as possible, it was decided to concentrate upon building the main train of the system for use in the water wash mode. This train consists of one digester, two surge tanks, one filter, one slurry pump, and one evaporator.

This equipment is shaded in Figure 2.2-5 which is a complete schematic of the CRU and includes the piping between equipment. With completion of this single train, catalyst recovery operations without lime digestion were possible while construction of the spare train proceeded. As another step to further facilitate unit start-up, process piping for the major equipment items of the single train was completed sequentially. This meant that all the necessary piping for the digester was completed first followed by that for surge tank 1A, then the filter, and so on until the entire train was completed. This allowed test operation with the major equipment items to discover and correct problems before the train as a whole was ready for operations.

Construction on all of the second train equipment with the exception of the filter, lime tank, and filter precoat tank was completed. Also, insulation of all the process vessels was finished.

During the second quarter of 1980, very little construction was done. Work on the spare filter, the lime slurry tank, and the precoat slurry tank was delayed since these pieces of equipment were not required at that time. Process piping was insulated and work was started on instrument hook-up.

FIGURE 2.2-4
PDU CATALYST RECOVERY FLOW PLAN

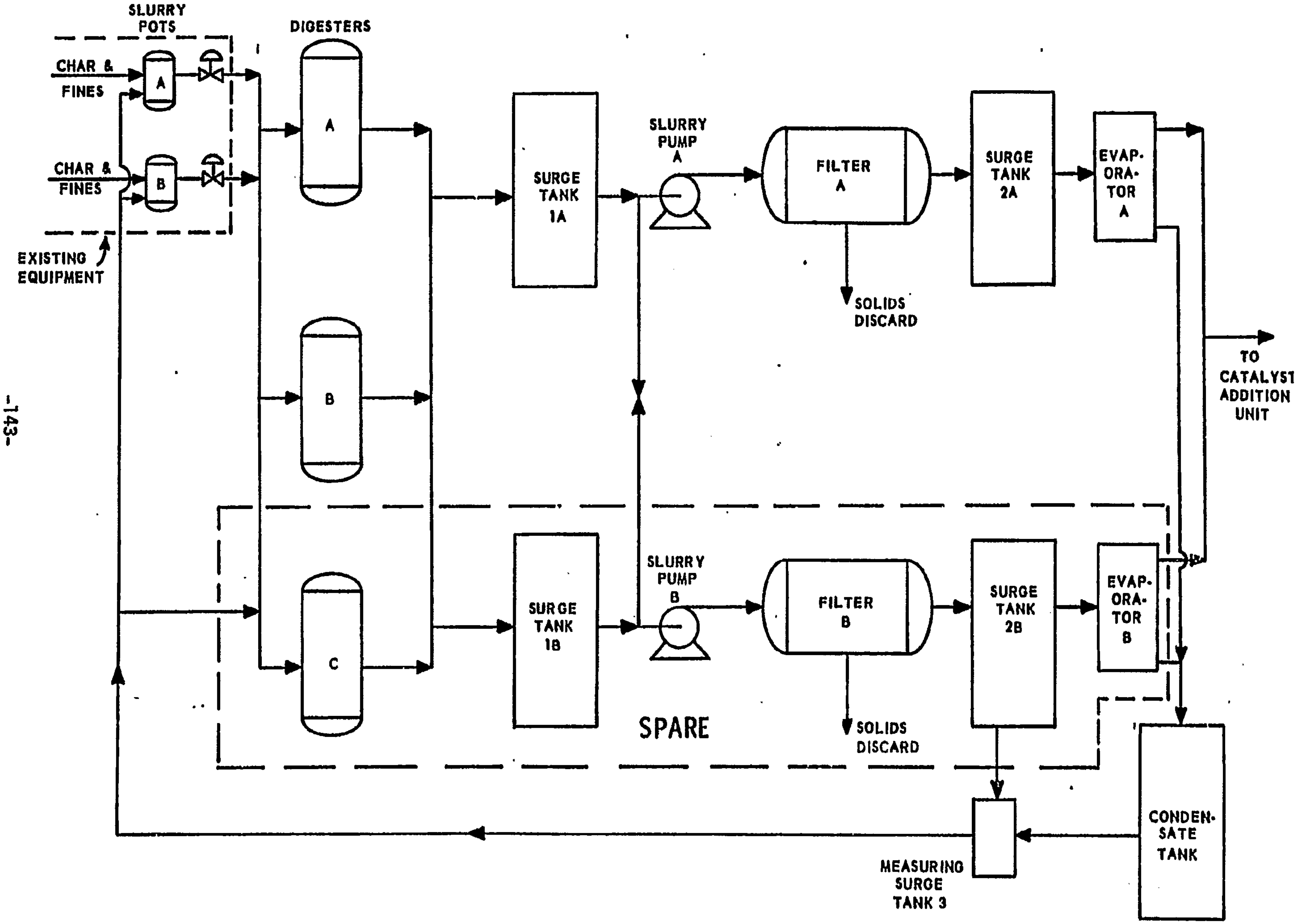
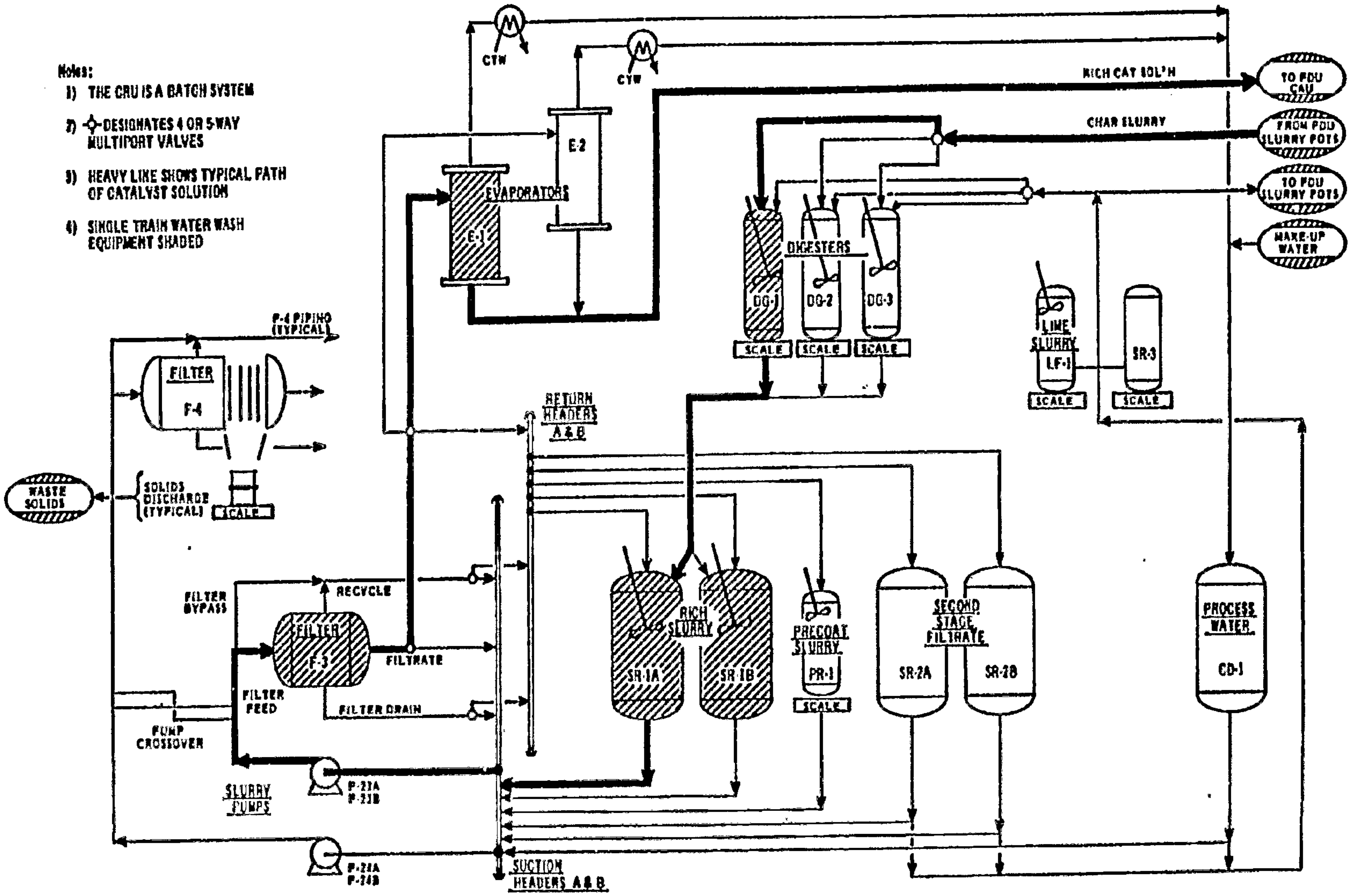


FIGURE 2.2-5

CATALYST RECOVERY UNIT EQUIPMENT SCHEMATIC



Notes:

1) THE CRU IS A BATCH SYSTEM
2) -◇- DESIGNATES 4 OR 5-WAY MULTIPORT VALVES
3) HEAVY LINE SHOWS TYPICAL PATH OF CATALYST SOLUTION
4) SINGLE TRAIN WATER WASH EQUIPMENT SHADED

Operation of Rented Filter

During the last half of 1979, experiments were conducted to establish the operating procedure for the filter system of the CRU. Operation of rented filters, identical to those on order for the CRU, served as training for the operators in addition to developing techniques for filtering the PDU char slurry.

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

As was expected, it was found that precoat was not necessary for filtration of water washed char. Filtration experiments were carried out using PDU char in the rented filter. The PDU chars used in these tests were obtained from initial gasifier operations.

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

Start-up and Initial Operation of the CRU

The start-up of the CRU was initiated in January 1980. As reported above, it was planned that initial operations would be in the one-stage water wash mode. This operation mode requires a minimum of process vessels and equipment. Operations in the one-stage water wash mode 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 March 1980, a slurry transfer line between the PDU slurry pots and the CRU was started up. Transferring operations were 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 was possible to transfer slurry from one tank to another within the CRU as planned.

Considerable experience has been gained in filtering the char slurry. 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 have proven 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.

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 once-washed operations has a concentration of about 0.3 wt % K^+. This was below the value planned for integrated operation because large amounts of water were temporarily being used to slurry the char in the PDU char slurry pots. The evaporation step worked smoothly but at a significantly lower throughput than designed. At the design condensate rate of 4.0 gpm, an excessive amount of K^+ was present in the condensate. The carryover disappeared only when the rate of condensate production was lowered to 2.5 gpm. Since the carryover of K^+ in the condensate at high flow rates was possibly due to poor disengaging of the steam and entrained liquid, a demister was installed to disengage entrained liquid. The demisters were only partially successful. Since there was enough spare capacity, more work to debottleneck the evaporators was deferred.

For twelve days in May 1980, catalyst solution from the CRU was recycled to the PDU Catalyst Addition Unit at a rate of about 25% of total PDU catalyst needs. The recycled catalyst was rich catalyst solution which had been concentrated by evaporation to 10.4 wt % K^+ (equivalent to about 15 wt % KOH). The percentage of recycle to total catalyst could have been increased by adding PDU entrained char to the CRU feed and by employing a second wash.

Results of Single-Wash Operations

Early attempts were made to calculate an approximate material balance for once-washed operations. Slurry samples were used to calculate the amount of solids fed into the CRU. Unfortunately, representative slurry samples were very difficult to obtain. Typically, the closure on material balances was no better than 70%. Weigh scales for the catalyst recovery unit were installed, checked, zeroed and calibrated. The steam condensate was weighed and used to slurry char in the char slurry pots. The char slurry was weighed when it entered the unit. The difference between these weights should be the amount of char withdrawn from the gasifier. However, the operation of the PDU char slurry pots was not steady enough to allow this technique to be effective.

As shown in Table 2.2-4, total K^+ recovery from one wash was approximately 30%, and filter operations were possible with much higher feed slurry solids concentrations than originally planned. Feed slurry solids concentrations of up to 10 wt % were run with no operational problems. In addition, the filter cakes produced contained much less catalyst solution than anticipated. Cake solids contents of 40-45% were common.

Table 2.2-4

TYPICAL RESULTS FOR ONCE-WASHED FILTER RUN

Run	% Solids of Slurry	% Solids of Cake	% Potassium Recovery
5	3.25	46.4	26.4
10	6.96	43.6	30.1
11	10.18	42.8	37.0
Design	4.3	30.0	93.4

Notes:

1) All potassium referenced to acid soluble potassium.
2) Design numbers are for twice-washed digested char.
3) Average recovery for runs 5, 10, and 11: 30.58%

Table 2.2-5

IONIC FORMS IN FRESH PDU SLURRY

Ion	Composition, Molar %
K^+	99.3
Na^+	0.7
Ca^{++}	0.0
Fe^{++}	0.0
Total Cationic	100.0
Cl^-	3.2
$CO_3^=$	49.7
HCO_3^-	0.4
$S^=$	15.6
HS^-	7.1
$S_x^=$	0.1
$SO_3^=$	0.3
$S_2O_3^=$	0.7
$SO_4^=$	2.9
$HSiO_3^-$	1.8
$SiO_3^=$	3.5
OH^-	14.7
Total Anionic	100.0

The rich catalyst solution from the CRU was analyzed for the various species in solution. The results of these analyses are given in Table 2.2-5. The slurry sample had a minimum of air exposure and was analyzed immediately after the sample was taken. The data show that K^+ is the dominant cation while $CO_3^=$ makes up about half the anions and is over three times more prevalent than OH^-. Thus, almost seven times more K^+ is associated with the $CO_3^=$ ion than with the OH^- ion. In addition, the oxidized sulfur forms are quite low.

In order to investigate the effects of air exposure on the catalyst forms, the fresh slurry was exposed to air for two days and analyzed. Table 2.2-6 presents a summary of sulfur species for the fresh slurry and the air exposed sample. The sulfur forms changed from predominantly $S^=$ and HS^- to catalytically less active $S_2O_3^=$ and $SO_4^=$. Furthermore, total sulfur present in the solution decreased from 26.7 mole % to 8 mole %, probably because of precipitation of elemental sulfur.

Two-Stage Water-Wash Operations

Two-stage water-wash operations of the Catalyst Recovery Unit (CRU) to recover water soluble potassium from PDU spent char were begun in the third quarter of 1980. Previous operations resulted in the recovery of 30% of the total potassium using a one-stage wash. The CRU was designed to recover 90% of the water soluble potassium or approximately 70% of the total potassium. During this period, the two-stage water-wash enabled 70-75% of the total potassium to be recovered.

Batch mixing and filtration are used for the double-wash operations. The steps are summarized below.

(1) Gasifier spent char and water (or lean catalyst solution) are mixed at the PDU and accumulated in an agitated tank (digester) at the CRU. Soluble forms of potassium are extracted into the liquor.

(2) The slurry is transferred to the first-wash mix tank and is then pumped through a drop leaf filter to separate the potassium rich liquor from the solids. This filtrate from the first-wash is sent to an evaporator where it is concentrated to 10.4 wt % potassium for recycle to the PDU. The heel of slurry remaining in the filter body is drained back to the first-wash mix tank. As a result, a cake is left on the filter leaves for the second stage wash.

(3) Water and lean catalyst solution (including a residual lean heel from the previous run) are pumped into the filter for the second-wash. The wet cake and second-wash liquor are mixed by vibrating the leaves to knock off cake while pumping the resulting slurry around through the second-wash mix tank and the filter body.

Table 2.2-6

AIR EXPOSURE OF PDU SLURRY

Ion	Fresh, Molar %	Exposed, Molar %
$S^=$ & HS^-	22.7	0.1
$S_x^=$	0.1	0.0
$SO_3^=$	0.3	1.1
$S_2O_3^=$	0.7	3.3
$SO_4^=$	2.9	3.5
Total S	26.7	8.0

(4) After the streams are well mixed, filtrate (lean catalyst solution) is drawn off and cake is redeposited on the leaves. This lean catalyst solution is concentrated for recycle to the PDU or used to slurry the gasifier spent char. The heel from the second-wash is sent back to the agitated second-wash mix tank (to be slurried with the next run).

(5) To complete the run, the spent cake on the filter leaves is blown with N_2 to reduce the moisture content of the cake to 60-65 wt % moisture. The filter body is then opened and the cake is discharged by vibrating the leaves.

This procedure differed from the original flow scheme because of particle segration in the slurry. Due to the low velocity through the filter body, large particles (>75 um) tended to settle in the bottom of the filter body and thus enriched the heel with solids. These accumulated in the system causing both operation and material balance problems. Operations were improved by adding an agitated vessel for handling the solids enriched heels.

To improve the flow pattern within the filter body, the bottom was swept with sparge nitrogen. This reduced stagnant zones that decrease wash efficiency, and helped reslurry the cake for the second-wash.

Transfer of PDU Entrained Char to CRU

Also in the third quarter of 1980, efforts were made to include the dry entrained char from the PDU as part of the feed to the CRU. These solids were slurried in open drums at the CRU. This resulted in the air exposure of the dry solids and slurry. As seen in the results from earlier operations, the form of recovered catalyst is very sensitive to air exposure. In February and March 1981, a new system was developed which slurried the solids as they were collected. This system proved effective in delivering non-air exposed char to the CRU. Unfortunately, the system was not flexible enough to handle the high gasifier entrainment rate experienced in late March. Therefore, during the gasifier demonstration run the solids were collected dry and were not processed in the CRU.

CO_2 Treatment of CRU Slurries

Bench-scale research has established the need for CO_2 treatment to remove silicates and sulfides from the catalyst loop. For ease of implementation on the CRU it has been decided to strip the char and fines slurries by bubbling CO_2 through the digestors which were being used as holding tanks. Good contacting between the CO_2 and char slurry was identified in the bench-scale program as an important factor in CO_2 treatment. A baffled five-liter agitated vessel was built to test sparger designs. It was found that the agitator dispersed the CO_2 bubbles sufficiently such that the design of the sparger was not critical. Because sparger plugging has been a problem in the CRU filters, spargers were designed with large holes (3/16-inch) and with the capability to be easily flushed out.

In the fourth quarter of 1980, a sparger was installed on one digester to test the design. Because of an extensive turnaround on the PDU, there was no fresh slurry available at the time to test the CO_2 treatment procedure. Washed filter cake, concentrated catalyst solution, and water were mixed, pumped into the digester, and then stripped with CO_2. Since this initial run demonstrated the operability of the system, spargers were installed on the remaining two digester vessels.

Starting in December 1980, char and fines slurries from the PDU were treated with CO_2 as a normal part of the CRU operations. Batches of char and fines slurry (1600-2000 kg) were sparged with 500-700 SCFH of CO_2 until the pH dropped to 8.5 or less. Off gas containing H_2S was flared. After allowing sufficient time for the silica precipitate to form, the slurry was subjected to the standard doublewash.

Initial operations reduced silica concentrations from 40% to 95%. In these initial operations, the removal of sulfur from the slurries was not as good as expected. The slurries contained oxidized solids; therefore, most of the sulfur was present in oxidized forms, which are not affected by CO_2 treatment.

In the first quarter of 1981, all slurries were treated with CO_2 until a pH of 8.5 was reached before filtering in the CRU. The effectiveness of silicon removal in several runs is given in Table 2.2-7. These operations highlighted several operating concerns to which satisfactory solutions were proposed and implemented. Problems encountered were redissolution of silica, incomplete sulfur removal and gel formation in the evaporators.

Potassium silicate and carbon dioxide react to form potassium bicarbonate and an insoluble silica, which can be removed during filtration. This reaction reverses if solution pH is allowed to increase before filtration. To insure stable slurry pH in the CRU, holding tanks were blanketed with CO_2. Precipitation of silica gel onto the char particles is slow relative to gel formation. The solutions needs to be "aged" about one hour after treatment, otherwise the gel would drastically increase filter cake resistance.

Residual silica which was not precipitated (40-80 ppm) formed a gel during evaporation and thus caused operating problems in the batch evaporator. Based on bench scale experiments, it was proposed that increasing the pH to 13.5 with KOH before evaporation would prevent the formation of the gel. The amount of KOH needed for this purpose is close to the amount of make-up catalyst required by the process. The CRU was modified to incorporate KOH addition. Subsequent concentrated catalyst solutions were free of gel.

Sulfur removal during CO_2 treatment is the result of the reaction of potassium sulfides with CO_2 to form potassium bicarbonate and hydrogen sulfide. After 3-4 hours of sparging slurries with CO_2, at 20-30 SCF CO_2/ft^3 of slurry, the solution pH dropped to 7-9. However, significant amounts of potassium sulfides were still present. Hydrogen sulfide was found to be present in the offgas for up to an hour after the pH reached this terminal level with continued addition of CO_2. This indicated that pH alone cannot be used as the endpoint for CO_2 treatment as far as sulfur removal is concerned. This effect is shown in Table 2.2-8.

CRU Material Balances

In order to measure potassium recoveries, material balances have been calculated for the CRU. While information is available on streams going out, accumulation and feed slurry streams are not as well defined. Even though slurry into the feed tank is weighed and measured, the char content is uncertain because of unsteady char withdrawal operations. The slurry stream to the filters can change in solids composition because of particle segregation in the tank and in the filter. Therefore, the solids content and density of the slurry can only be roughly estimated. Similar estimations are used to define accumulation around this first stage of filtration. For each individual run these accumulation terms are significant; however, by combining data over several runs, the error in estimating accumulation becomes less significant. Material balances for three such combined operating periods, July 26 through August 8, 1980, August 18 through September 3, 1980, and September 9 through September 16, 1980, are shown in Table 2.2-9.

Table 2.2-7

CO_2 TREATMENT FOR SILICON REMOVAL

Char	Liquid	Final Wt % K	Silicon Content, ppm Before	Silicon Content, ppm After
Fresh Char	Condensate	2.0	534	37
Air Exposed	Condensate	2.3	157	47
Air Exposed	Lean Catalyst Solution	2.3	100	59
Air Exposed	Lean Catalyst Solution	1.5	167	81
Fresh Char	Lean Catalyst Solution	2.0	1150	73
Fresh Char	Condensate	2.0	841	76

Table 2.2-8

CO_2 TREATMENT FOR SULFUR REMOVAL

	Before CO_2 Treatment	After CO_2 Treatment	After Aging Under CO_2
pH	11.0	8.9	8.4
	EQUIVALENT %		
K_2CO_3	76.2	7.4	2.6
$KHCO_3$	6.7	82.5	91.8
KOH	0.3	0.0	0.0
K_2S	5.9	3.9	0.2
KHS	2.9	1.9	0.1
KHS_x, K_2S_x	<.1	<.1	<.1
K_2SO_3	0.1	<.1	<.1
$K_2S_2O_3$	0.6	0.6	1.0
K_2SO_4	0.3	0.2	0.6
K_2SiO_3	0.6	<.1	<.1
$KHSiO_3$	4.1	<.1	<.1
KCl	2.3	3.5	3.7
KBO_2	<.1	<.1	<.1
K_3PO_4	<.1	<.1	<.1

Table 2.2-9

CRU MATERIAL BALANCE SUMMARY

	7/26 - 8/8 (10 Filter Runs)	8/18 - 9/3 (8 Filter Runs)	9/9-9/16 (5 Filter Runs)
	lb		
• **IN**			
Char/Fines Slurry	37700	24100	17400
Water	23300	29400	15700
Total In	61000	53500	33100
• **OUT**			
Cake	7800	4900	3300
Rich Filtrate	31800	22300	14700
Lean Filtrate	26800	27600	16700
Accumulation(1)	-5000	1500	-200
Total Out	61400	56300	34500
Material Balance	99-102%	105-106%	104%

Note: (1) Accumulation is estimated and is only accurate to within 20%.

Potassium recovery was determined based on total potassium out and was defined as potassium recovered in rich and lean filtrate divided by total potassium out. Recovery data is given in Table 2.2-10. Potassium recoveries have varied from 65% to 80%. If unusual operations were discounted then the range of recovery would be 70-75%. The one low recovery in Table 2.2-10 was due to the inclusion of once-washed cake into the feed of that particular period. The two high recovery periods can be characterized as having extremely high wash-to-char ratios (20-30 as opposed to 5-10).

Composition of Recovered Catalyst Solutions

Concentrated catalyst solutions were collected from the CRU in the last half of 1980. During this period the catalyst fed to the gasifier was KOH and there was no CO_2 treatment of slurries in the CRU. The effect of CO_2 treatment on catalyst solution composition is discussed both earlier in this section of the report as well as in Section 1.2. These solutions contained varying amounts of inactive species depending on the feed to the unit. Solution analyses are reported in Table 2.2-11. The sample identification refers to the date on which the liquor was transferred from the CRU evaporators to barrels. The most significant trend to be noted on this table is that samples 6/23/80, 9/8/80, and 10/3/80 all had higher levels of oxidized sulfur forms. In each instance operations at the time led to significant air exposure of the feed to the CRU.

Table 2.2-10

CRU RECOVERY EFFICIENCY

Operation Period	% Recovery
7/26/80-8/8/80	70
8/18/80-9/3/80	75
9/9/80-9/16/80	65
1/13/81-1/30/81	75
2/17/81-2/24/81	71
3/13/81-3/17/81	79
3/27/81-3/31/81	80

Table 2.2-11

COMPOSITION OF CONCENTRATED CATALYST SOLUTIONS

(Equivalent %)

	6/3/80(1)	6/23/80(2)	7/2/80(3)	8/24/80(3)	8/1/80(3)	8/13/80(3)	9/8/80(4)	10/3/80(4)
$CO_3^=$	69.67	60.29	68.83	66.88	68.17	69.08	74.98	76.63
HCO_3^-	0.11	0.04	0.09	0.08	0.11	0.05	0.08	0.18
OH^-	5.57	1.21	1.72	2.16	1.89	1.25	4.27	3.92
$S^=$	1.54	1.80	2.28	2.05	1.87	3.67	0.28	0.09
HS^-	8.23	4.39	9.67	8.70	10.00	7.97	1.08	0.74
HS_X^- & $S_X^=$	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00
$SO_3^=$	0.03	0.06	0.01	0.02	0.02	0.02	0.06	0.07
$S_2O_3^=$	0.99	6.49	1.58	1.97	1.62	1.78	4.82	6.41
$SO_4^=$	0.43	1.56	0.44	0.61	0.43	0.61	1.46	1.24
$SiO_3^=$	9.11	19.74	10.73	12.63	10.87	11.42	8.33	6.92
$HSiO_3^-$	1.17	1.16	1.10	1.29	1.40	0.61	0.76	1.32
Cl^-	1.48	1.92	1.70	1.69	1.76	1.87	2.18	1.79
BO_2^-	1.45	1.94	1.62	1.65	1.62	1.59	1.45	1.45
$PO_4^{=-}$	0.22	0.40	0.24	0.26	0.24	0.27	0.23	0.33
Wt % K^+	11.90	10.80	11.30	11.50	11.20	12.40	11.80	11.90

Notes:

(1)One Wash of PDU char slurry.

(2)Most of the char came from barrels and had been ashed once before (air exposed).

(3)Double Wash of PDU char slurry.

(4)Significant fraction of feed was PDU fines (air exposed).

PDU-CRU Catalyst Loop

During catalyst recycle, various ions may tie up potassium as inactive forms or build-up in the loop to levels that could affect operability. The level of build-up is set by the recycle rate which is in turn a function of recovery efficiency and general operating losses. Points of potential loss around the integrated unit were identified from operating data and are shown in Figure 2.2-6. Hold up around the loop affects the time needed to reach steady state recycle concentrations. Data from operations indicated that the hold up time within the CRU/PDU loop is one to two weeks. At a recycle rate of 70% of the soluble species, which corresponds roughly with recovery of 50% of the total potassium, seven cycles (50-100 days of operation) are needed to reach 90% of the steady state concentration level.

The only attempt to close the catalyst loop during this contract occurred early in 1980 and is documented in this section of the report under "Start-Up and Initial Operations of the CRU". Because of the losses around the loop and the large hold-up in the loop, a steady state integration between the PDU and the CRU was not possible at this time. The loss of catalyst around the loop is documented in more detail below.

Loss of potassium in the PDU-CRU system was identified as the key limitation for how tightly the loop could be closed. During the first quarter of 1981, potassium to the Catalyst Addition Unit (CAU) to the gasifier, to the CRU, and out of the CRU were monitored. The stream data is given in Table 2.2-12. No adjustments were made for accumulation.

Most of the catalyst losses during catalyst addition in January 1981 were due to char entrained from the fluid bed oxidizer. An adjustment to the cyclone reduced this loss later in the period. In March 1981 inadequate pretreatment in the oxidizer produced off spec coal which was dumped. Operation of the CAU was very good from March 23 through April 23, 1981.

Potassium leaves the gasifier either with the entrained char or with the withdrawn char. As discussed earlier, (see "Transfer of PDU entrained char to CRU" of this section of the report) during the 3/23/81 to 4/23/81 period no entrained char, which accounted for 64% of the K^+ leaving the gasifier, were sent to the CRU. In addition char withdrawal problems during the latter part of this period allowed only 27% of the char to be sent to the CRU.

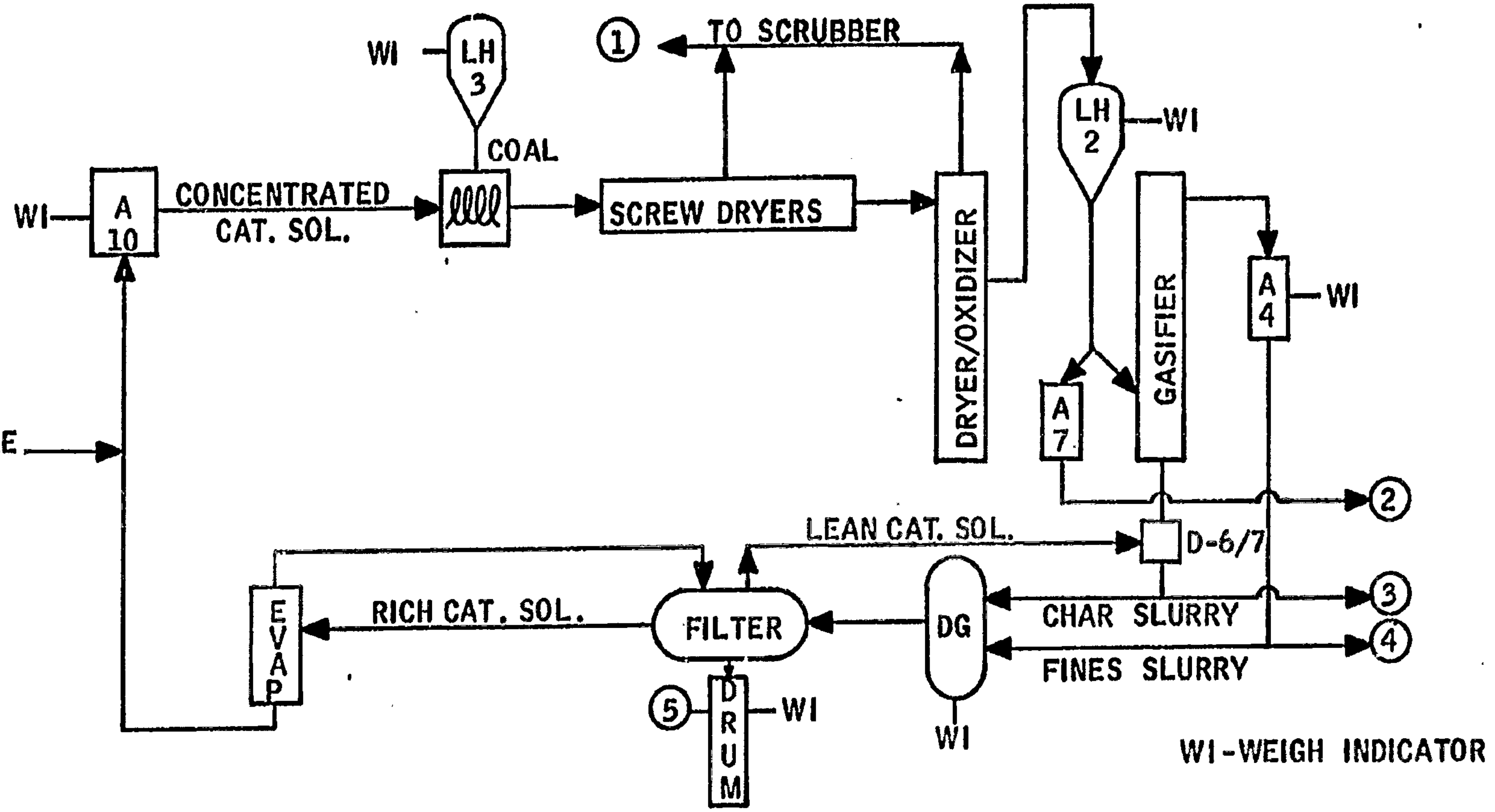
Char losses are closely associated with PDU gasifier operations. Improvements in coal pretreating, bed density control and overall smooth operations are expected to give corresponding improvements in ease of char withdrawal.

Catalyst is lost in the catalyst recovery unit as water insoluble potassium on the filter cake, residual soluble potassium on the cake from high moisture contents, and through losses from the evaporator. Losses in the overhead stream leaving the evaporator have been a continuing problem. Changes in the control strategy for the evaporator have been made to minimize carryover.

81B-3-1

FIGURE 2.2-6

CATALYST RECOVERY LOOP



<u>LOSSES</u>

① ENTRAINED FINES FROM CAU - NOT COLLECTED

② FEEDLINE BLOW DOWN - COLLECTED IN DRUMS

③ SLURRY POT DRAIN - PARTIALLY COLLECTED

④ FINES TRANSFER - NOT COLLECTED

⑤ WASHED CAKE

Table 2.2-12

PDU-CRU CATALYST LOOP - 1981

FLOW OF POTASSIUM	JAN. 11-31	FEB. 1-27	FEB. 28 MAR. 22	MAR. 23 APR. 23
	--------LBS OF POTASSIUM			---------
TO CATALYST ADDITION	2030	1460	3750	4810
TO GASIFIER	1420	1300	1400	4890
IN FILTRATES AND CAKE	1020	540	265	~475
IN FILTRATES	745	380	210	~360
ADDED IN pH CONTROL	0	0	0	710
OUT OF EVAPORATOR	210	0	0	1010