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ZINC HALIDE HYDROCRACKING PROCESS FOR DISTILLATE FUELS FROM COAL

Annual Technical Progress Report for 1975, Including the Quarter Ending January 31, 1976

MASTER

CONOCO COAL DEVELOPMENT COMPANY
Research Division
Library, Pennsylvania 15129

Date Published: February 15, 1976

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ABSTRACT

The objective of this contract is the further development of the zinc halide process to produce clean gaseous and liquid fuels from coal, with emphasis on the production of high-octane gasoline. The major effort in this first year has been reconstruction of continuous, bench-scale, zinc chloride hydrocracking and catalyst regeneration units. These units were revised to handle coal feed and spent melt from direct coal hydrocracking as well as coal extract. Operation was demonstrated with both subbituminous coal and a coal extract derived therefrom by continuous hydroextraction at 825°F and 1750 psig pressure. The bench-scale regeneration unit has investigated the effect of cyclone temperature and ash content of the feed on the amount of zinc recovered in the ash solids.

Supporting laboratory work has defined the hydrocracking rate for subbituminous coal in the temperature range 725 to 775°F at 3000 psig of hydrogen pressure. Similar runs at 2000 psig of hydrogen are underway.

Material and energy balances, process flow diagrams and instrumentation drawings for a 100 lb/hr Process Development Unit have been prepared. Mechanical design for the high-pressure vessels has been completed and long-lead-time items ordered.

An economic evaluation was completed comparing the costs of producing gasoline from coal extract via (1) zinc chloride processing versus (2) ebullated-bed hydrocracking plus desulfurization, distillate hydrocracking and reforming to make the same product. The study shows that zinc chloride processing could save from 7.4 to 15.7% for a refinery whose chief product is 45,000 BPD of gasoline.

The bench-scale units will continue the program to define catalyst losses using coal feed and to explore ways of minimizing such losses. It is anticipated that construction of the PDU can begin in late summer and be completed by the summer of 1977.

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I. Objective and Statement of Work

A. Objective

1. The objective of this contract is the production of clean liquid and gaseous fuels of which approximately 50 percent will be distillate, equivalent to four barrels per ton of coal on a moisture, ash-free (MAF) basis.

2. The work to be performed under this contract will be directed toward conducting a systematic experimental study, entailing both continuous bench-scale and process development unit work on the above process, involving investigation of zinc halide as a Lewis acid "catalyst" for the hydrogenation and hydrocracking of coal extract and of subbituminous coals and development of an economical regeneration process for the efficient recovery of zinc halide from the spent melt.

B. Statement of Work (Abbreviated)

The following experimental work will be performed to demonstrate the viability and economic potential of the zinc halide hydrocracking process for production of distillate fuels from coal with economic regeneration and recycle of the zinc halide.

Task 1 Refurbish Existing Continuous Unit

The existing continuous bench-scale zinc halide hydrocracking unit (2 lb/hr capacity) and the continuous fluidized-bed combustion unit for regeneration of spent zinc halide melt (5 lb/hr capacity) will be refurbished. This will include modification of the hydrocracking feed system to permit feeding of coals.

Task 2 Continuous Bench-Scale Hydrocracking

An experimental program will be conducted to demonstrate the utility of the continuous bench-scale hydrocracking unit for direct hydrogenation and hydrocracking of subbituminous coal using zinc halide as the catalyst or regenerable intermediate. This will be divided into the following activities:

a. Prepare Feedstocks for the Continuous Hydrocracker

This includes drying and grinding a subbituminous coal, followed by hydroextraction of some of same to prepare coal extract for start-up operations of the continuous unit.

b. Break-in Operation of Continuous Bench-Scale Hydrocracker

Initial break-in operations will be done with coal extract to facilitate shake-down of equipment and provide comparison with previous work.

c. Hydrocracking of Coal and Preparation of Spent Melt for Regeneration Tests

The first operating period for the hydrocracker will confirm operability with coal, focusing on relatively severe conditions to produce a low-carbon spent melt. A batch of 300 pounds of spent melt will be produced for the first series of regeneration runs. This study will be limited in scope to permit early operation of the regeneration unit and expedite a decision to proceed with construction of the PDU.

d. Evaluation of the Low-Conversion Hydrocracking

After the first series of regeneration runs, hydrocracking variables will again be explored, focusing on milder conditions to produce a spent melt suitable for production of fuel gas.

e. Evaluate Another Coal

If time permits, one additional coal may be evaluated following the second series of regeneration tests.

Task 3 Continuous Bench-Scale Regeneration

a. Regeneration of "Low-Carbon" Spent Melt

The bench-scale, fluidized-bed combustor will be operated on low-carbon spent melt, emphasizing confirmation of previous work with synthetic spent melts and recovery of zinc halide. Successful completion of Task 3a will be one milestone pertinent to construction of the PDU.

b. Regeneration of "High-Carbon" Spent Melt

The second series of tests will operate on high-carbon melt to seek conditions for effective melt regeneration simultaneously with production of a low-Btu fuel gas or synthesis gas.

Task 4 Design of a Process Development Unit (PDU)

PDUs for zinc halide hydrocracking and regeneration will be designed based on feeding 100 lb/hr of coal or extract. This unit is to provide information on the commercial potential for the process, effect of equipment size on reaction rate, performance of mechanical components, suitability of materials of construction, and overall reliability.

Task 5 Construction of PDU

After ERDA's authorization to proceed, construction is to be undertaken by the contractor and is expected to require about 15 months.

Task 6 Operation of PDU

A program for testing in the PDUs will be prepared to emphasize:

a. Hydrocracking to produce light distillates from both coal and coal extract as feedstocks.

b. Integrated operation of hydrocracking and regeneration following initial separate operation.

c. Operation under 3 different modes:

   (1) High severity hydrocracking to maximize light distillates.

   (2) Low pressure hydrocracking with a high-temperature final stage to increase the gas/distillate ratio.

   (3) Mild hydrocracking conditions, producing a high-carbon spent melt which in regeneration will produce a synthesis gas useful for hydrogen production.

Task 7 Supporting Laboratory Studies

Laboratory studies will be carried out simultaneously with operation of the continuous bench-scale units and PDUs. The objectives will be to:

a. Provide a more fundamental understanding of the basic physical parameters and mechanism of the zinc halide hydrocracking process as an aid to process improvements and scaleup.

b. Provide supporting tests for operation of the continuous units.

Task 8 Process and Economic Studies

Process and economic studies of commercial plant scale will be conducted in two periods:

a. Near the beginning of the contract it is desirable to define the incentive for development. This will be done first by comparing the cost of gasoline made by alternate routes of zinc halide hydrocracking and ebullated-bed hydrocracking using a coal extract derived via hydroextraction of subbituminous coal. A second study will compare direct hydrocracking of subbituminous coal with hydroextraction plus extract hydrocracking, both with molten zinc chloride catalyst.

b. After operation of the PDUs economic studies will be made to evaluate the commercial potential of the process.

Task 9 Preparation of a Final Report

The final report will summarize all the work done with appropriate data, calculations and conclusions. An economic appraisal will be part of this report.

II. SUMMARY

Bench-Scale Work

The major effort in the first year has been reconstruction of continuous, bench-scale, zinc halide hydrocracker and regenerator units used previously in the OCR work of 1963-1968.(1,2) Major revisions were made in both units to permit continuous operations with direct hydrocracking of coal and regeneration of the spent melts derived therefrom. Prior work in the 1963-1968 period in continuous units was confined to the use of coal extract as the feed. Break-in operations were completed in October for the hydrocracker and in November for the regenerator using coal extract as the feed. Subbituminous coal from the Rosebud Seam in Montana was dried and ground to -100 mesh for use in the program. A portion of this coal was hydroextracted continuously at 825°F and 1750 psig pressure at a space rate of 24 lb MF coal/hr-ft^3. The product was filtered to provide a low-ash coal extract for the first hydrocracking run.

A successful hydrocracking run with extract was made at 775°F and 3500 psig using a zinc chloride-to-extract weight ratio of 1.0. This work uncovered a frothing problem associated with batch-type depressuring of spent catalyst. This problem has been resolved by a revised method for depressuring the melt.

The bench-scale hydrocracker was then converted to feed a slurry of coal in distillate oil. The first successful run feeding coal was completed in December.

The bench-scale regenerator has shown that spent melts with relatively high ash levels are operable. A study of zinc recovery as affected by cyclone temperature and ash content of feed is underway with a synthesized spent melt. Preliminary results indicate decreased zinc loss with the cyclone underflow solids at a reduced cyclone temperature of 1350°F. The zinc loss also does not appear to increase with increased ash content of the feed.

Supporting Batch Work

The kinetics of zinc chloride hydrocracking of subbituminous coal have been explored in batch supporting work at 725, 750, 775°F and 3000 psig of hydrogen pressure. Although this work is incomplete, it is clear that most of the conversion occurs within the first 15 minutes, even at 725°F.

Process Development Unit

Process design for a 100 lb/hr Process Development Unit (PDU) to feed either coal or coal extract is about 90 percent complete. Mechanical design for high-pressure vessels has been completed and the long-lead-time items have been ordered for delivery in the fall of 1976. Piping and instrumentation drawings have been completed for the hydrocracking section, and are 80 percent complete for the regeneration section. Engineering of the fractionation section is 50 percent complete.

Economic Studies

An economic evaluation has been completed comparing the costs of producing gasoline from coal extract via zinc chloride processing with that via more conventional ebullated-bed hydrocracking plus reforming. The results show that zinc chloride processing could save from 7.4 to 15.7% for a refinery whose chief product is 45,000 BPD of gasoline. This provides further incentive to develop the zinc chloride process based on either coal or coal extract.

Program Schedule

The bench-scale hydrocracker will be operated with coal feed to determine the minimum zinc chloride-to-coal weight ratio which can be fed and to define conditions required to produce a 300-pound batch of spent catalyst having < 7% carbon content. The 300 pounds of spent catalyst will be used in regeneration studies. Prior to the availability of this natural spent melt, a synthesized melt will be used to study the efficiency of zinc recovery as affected by cyclone temperature, ash level in the feed, and HCl content of the fluidizing air. After demonstrating good recovery of zinc from regeneration of natural spent melt, the bench-scale units will be used to demonstrate the other operational mode with subbituminous coal: hydrocracking at high throughput, yielding a high-carbon spent catalyst, followed by regeneration with substoichiometric oxygen or air to yield a synthesis and/or fuel gas. If time permits, one or more other coals will be tested.

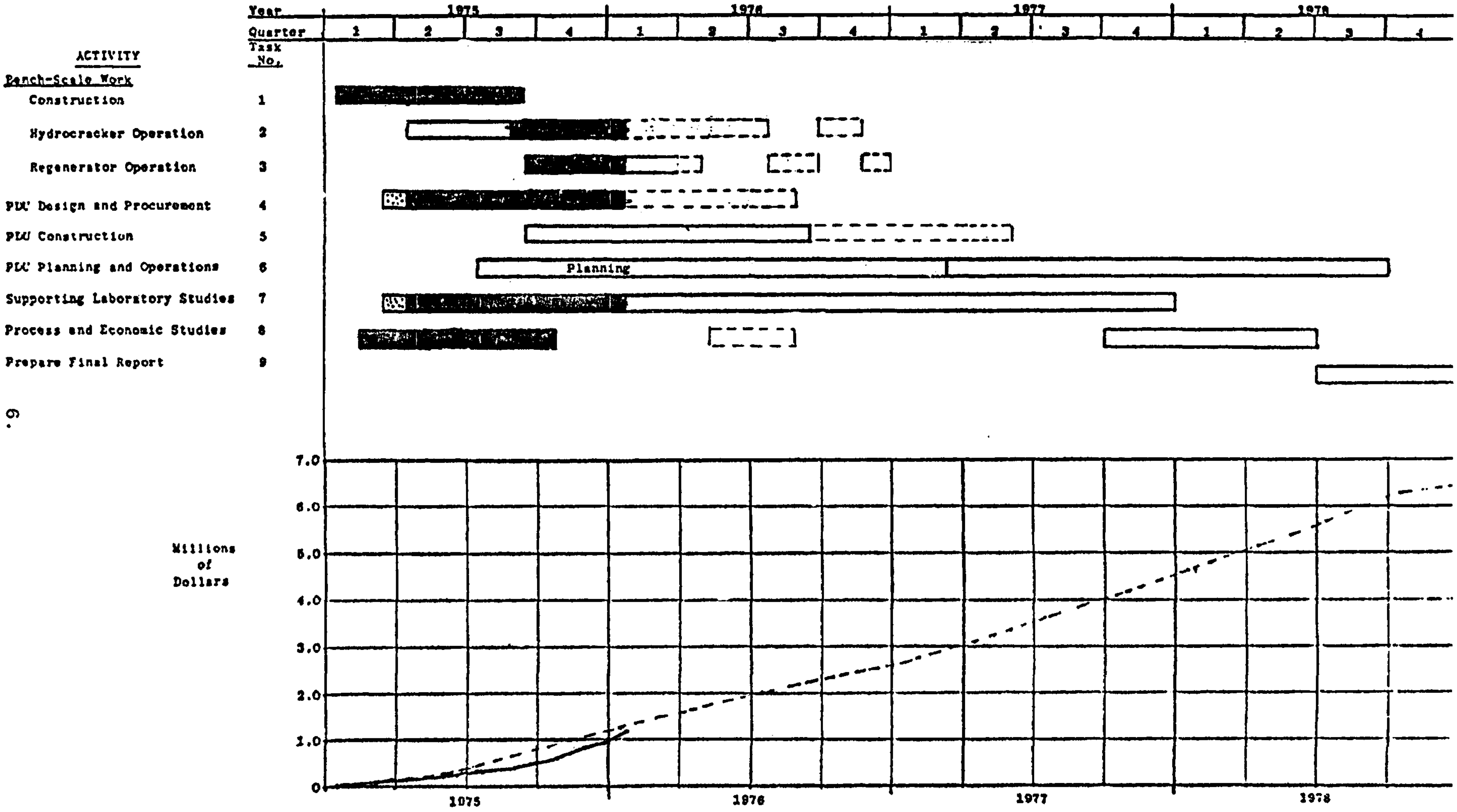
Supporting laboratory work will expand the matrix of variables in defining the kinetics of coal conversion with zinc chloride. A major effort will involve study of chemical equilibria and interactions existing between zinc chloride ash components, and to elucidate means for secondary recovery of zinc trapped in such ash.

Design of the PDU will be completed, procurement provided, and construction begun by the summer of 1976. Program planning will proceed concurrently with construction, which is currently estimated to be completed by the summer of 1977.

After bench-scale results are complete, an economic study will be initiated to compare the costs for zinc chloride hydrocracking of coal with that for hydroextraction of coal followed by zinc chloride hydrocracking of the low-ash extract.

PROJECT PLAN AND PROGRESS REPORT

Under ERDA Contract No. E(49-18)-1743



III. DESCRIPTION OF TECHNICAL PROGRESS BY TASKS

Task 1a Reactivation of the Bench-Scale Hydrocracker

The bench-scale continuous zinc chloride ($ZnCl_2$) hydrocracker used in the previous $ZnCl_2$ work under OCR Contract No. 14-01-0001-310(1) was rebuilt and modified to accommodate the use of coal feed as well as coal extract feed. The previous unit could be used with coal extract but not with coal feed.

A simplified flow diagram of the modified unit is shown in Figure 1. The unit has a nominal capacity of two pounds of coal per hour. It is rated at 5000 psig at 850°F design pressure (4250 operating pressure). Most of the vessels for the modified unit were used in the previous unit.

The feed coal, ground to -100 mesh is mixed with oil and fed as a slurry, along with $ZnCl_2$ catalyst and hydrogen, to the first of two tandem reactors. The reactors are stirred autoclaves. The liquid level in each reactor is controlled by a weir through which all gaseous and liquid products exit. Only a single reactor may be used or both reactors may be used simultaneously. The products pass from the reactor(s) to the melt-vapor separator. This is an empty vessel held at the same temperature as the reactor. The spent melt flows by gravity from the separator to the dead-ended spent melt collection system. The gases and vapors pass to the distillate collection system where the condensable products are collected. The fixed gases are then let down through a back pressure control valve and the gases are sampled and metered.

A satisfactory cold pressure test of the bench-scale continuous hydrocracker was obtained on May 12. By June 12, all heaters, thermocouples and insulation were installed and calibrations of instruments and pumps completed. However, it was impossible to achieve a satisfactory hot pressure test at 3500 to 4500 psig despite continuing efforts toward this end during the next seven weeks. Unexpected difficulties were encountered with 9/16" x 5/16" Inconel tubing connected to type 316 ss fittings and with valves leaking through seats and through packed stems.

At the end of July it was decided that further efforts to get the existing 316 ss - Inconel slimline 9/16" x 5/16" tubing system leak tight were futile. Therefore, the following major changes were made to eliminate the Inconel 316 ss joint problem and to alleviate the valve leak problem:

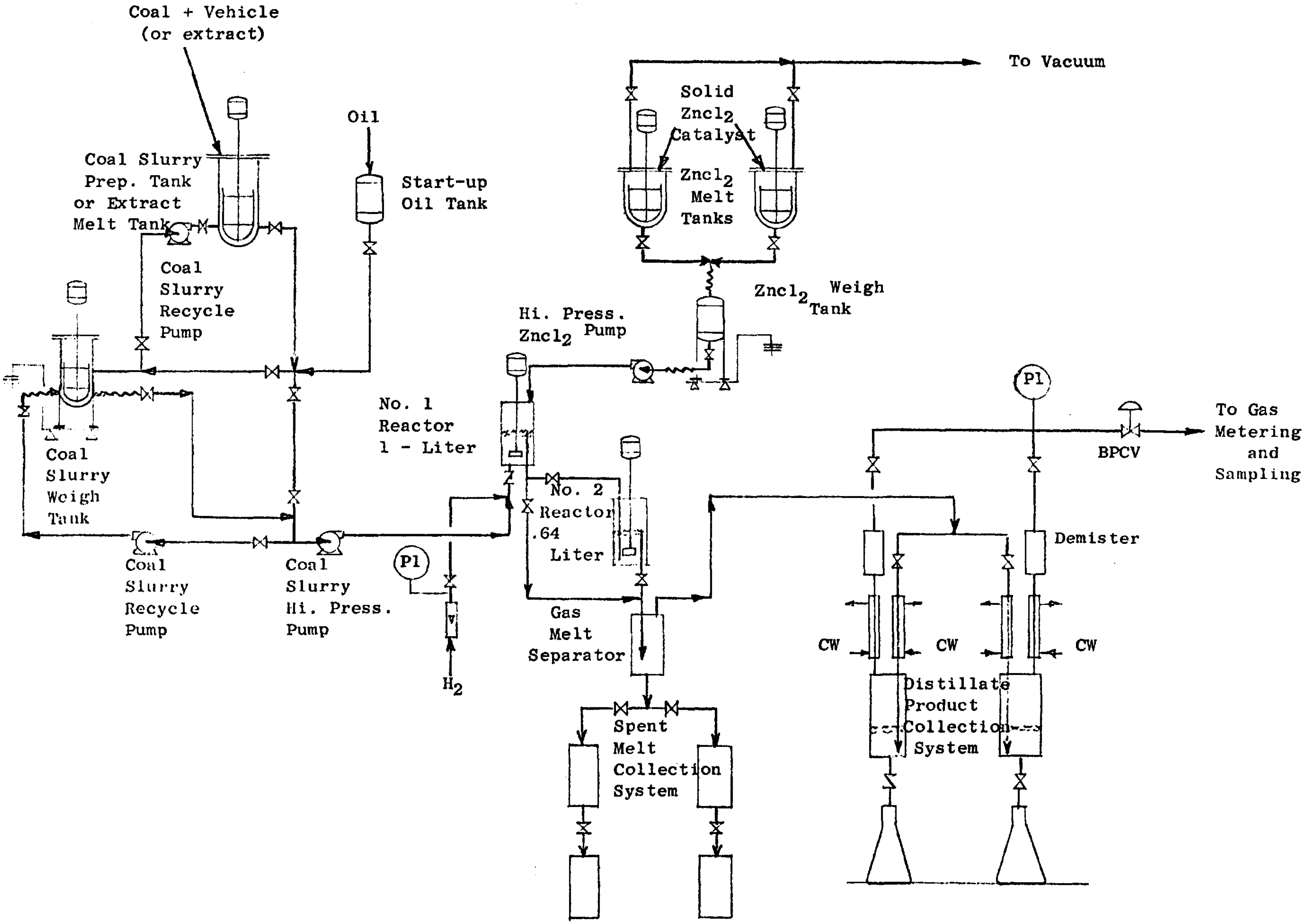
1. All 9/16" Inconel tubing was replaced by type 316 ss tubing. Although this metal is subject to chloride stress corrosion cracking in wet environments, past experience suggested that it would serve adequately for an experimental unit if kept above the dew point. In the situation that existed where Inconel fittings were unavailable this "calculated risk" was taken to eliminate one possible source of leaks.

2. Key vessels were spring mounted, to eliminate sources of stress when short lines between them are heated.

3. All lines which have sufficient pressure to maintain flow with smaller bore (1/8"), were changed from 9/16" x 5/16" to 3/8" x 1/8" size. This increased flexibility and reduced stresses on heating or when changing valves, etc.

Figure 1

Simplified Flow Diagram of Bench-Scale (2 lb/hr) Hydrocracker



4. Valve packing was replaced with more-flexible "Graphoil" precision rings to eliminate leaks through the packing.

5. Valve seats were lapped in to reduce leaking through the seats.

The rather extensive changes were made and a satisfactory hot pressure test was achieved by August 22.

The rapid achievement of a pressure tight unit after the revisions were made indicated that the revisions were effective in overcoming the previous leak problems.

By the end of August, it was considered that Task 1a had been completed.

Task 1b <u>Reactivation of the Continuous Bench-Scale Regenerator</u>

The existing bench-scale, continuous, fluidized-combustion-type regeneration unit was refurbished for carrying out regeneration studies of spent melt produced from processing of coal in the bench-scale hydrocracker.

A simplified flow diagram of the unit is shown in Figure 2. The flow of the unit is fairly obvious from Figure 2. The melt is fed into the air-fluidized bed (silica sand) via a remote drip tip. The impurities are burned out of the melt in the fluidized bed and the $ZnCl_2$ is vaporized. The $ZnCl_2$ vapor leaves the reactor along with the combustion gases and the entrained coal ash. The coal ash is removed from this gas stream via a cyclone. The "ash-free" regenerated $ZnCl_2$ melt is then condensed. The combustion gases then pass through the caustic scrubber where the $ZnCl_2$ fog, water, and HCl are removed from the gas stream. The gases finally pass through a drying tower and they are then let down to atmospheric pressure after which they are metered and sampled.

The fluidized combustor for burning the impurities out of the melt, the cyclone for separating coal ash from the $ZnCl_2$ vapor and combustion gases stream, and the cooler for condensing the regenerated $ZnCl_2$ on the existing unit were not changed. These pieces of equipment were used satisfactorily during the previous campaign on regeneration of simulated spent melt from direct hydrocracking of coal. The primary changes made in the refurbishment were modifications of the spent melt feed and the gas cleanup system just downstream from the regenerated melt receivers.

The reactivation of the regenerator was completed by October 7.

Task 2a <u>Preparation of Feedstocks for the Continuous Hydrocracker</u>

<u>Coal</u>

A five-ton batch of nominally -100 mesh Colstrip coal, a subbituminous coal originating from the Rosebud Seam in Montana, was dried and ground to nominally -100 Tyler mesh for use as a feedstock in the bench-scale hydrocracker, and for use as a feedstock for preparing Colstrip coal extract. A typical analysis of this coal is given in Table I.

Figure 2

Simplified Flow Diagram of Bench-Scale (4 lb/hr) Regenerator

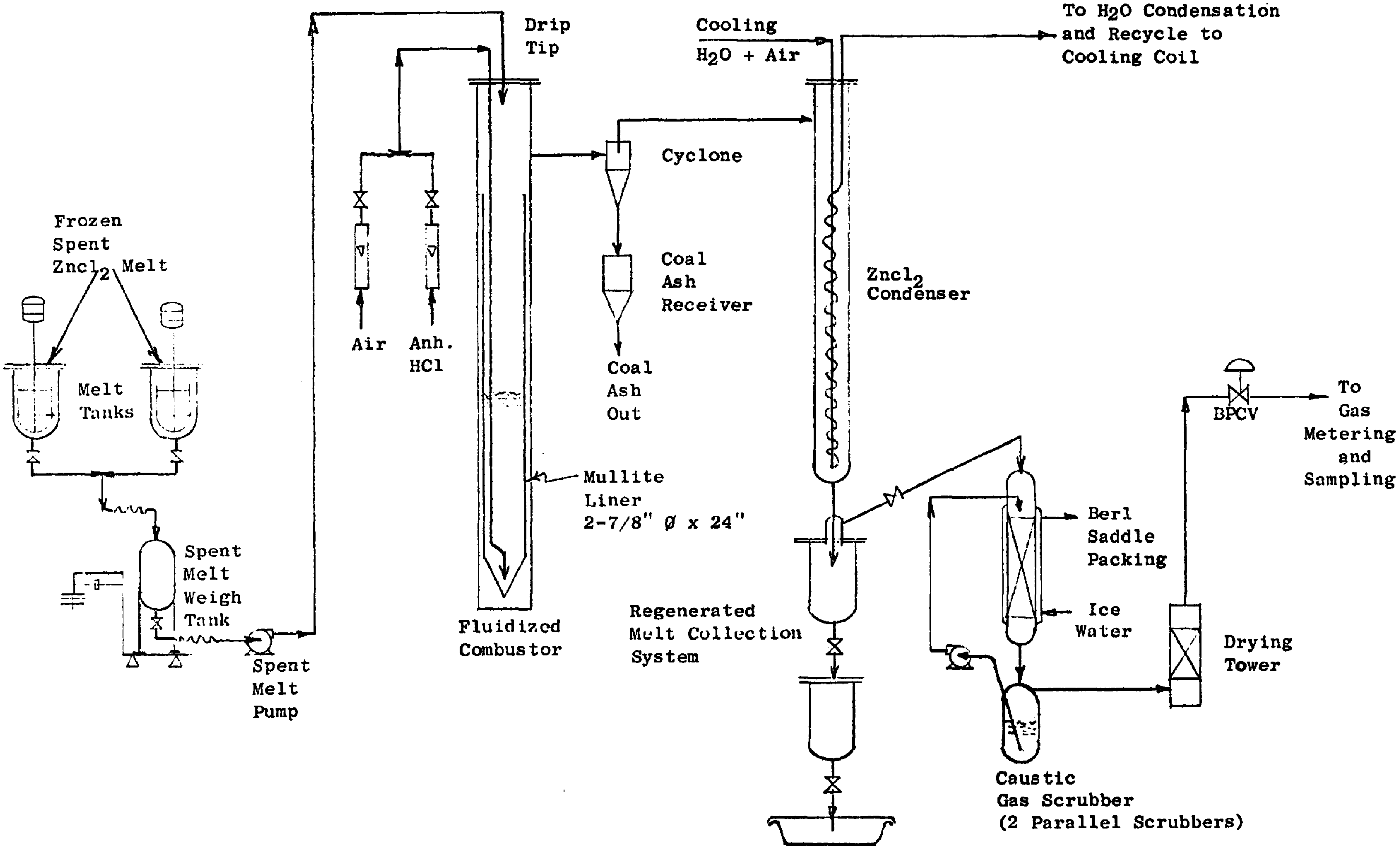


TABLE I

Colstrip Feed Coal Analysis
(Kiln Dried)

Moisture, wt %	3.59
Proximate Analysis, MF wt %	
Volatile Matter	41.73
Fixed Carbon	47.58
Ash Oxidized (SO_3 Free Basis)	10.69
Ultimate Analysis, MF wt %	
Hydrogen	4.39
Carbon	66.93
Nitrogen	1.01
Oxygen (By Diff.)	16.10
Sulfur Total	0.88
Sulfide Sulfur	0.00
Pyritic Sulfur	0.31
Sulfate Sulfur	0.01
Organic Sulfur	0.56
BTU/lb, MF Basis	11570
Ash, Elemental	
Na_2O	0.27
K_2O	0.26
CaO	10.50
MgO	4.38
Fe_2O_3	5.97
TiO_2	0.83
P_2O_5	0.06
SiO_2	46.28
Al_2O_3	18.64
So_3	9.83
Other	2.98
Screen Size, Tyler Mesh, wt %	
on 8	0.0
14	0.0
28	0.3
48	0.3
100	2.7
200	21.6
325	28.8
-325	46.3

Colstrip Coal Extract

About 65 pounds of "ash-free" Colstrip coal extract was produced in the CCDC bench-scale, continuous hydroextraction unit. This material was made for use as a startup and shakedown feedstock in the reactivated bench-scale hydrocracker. Conveniently also this work provided needed hydroextraction and solids separation data for comparative economic studies to be made in the future of direct hydrocracking of coal with zinc chloride versus extraction plus extract hydrocracking.

The hydroextraction program was carried out with -100 mesh Colstrip coal fed as a slurry in natural hydroextraction solvent generated from Illinois No. 6 coal in previous work. The work was conducted at a single set of conditions: 825°F extraction temperature, 1750 psig extraction pressure (about 1400 psia hydrogen partial pressure), 23-25 lb MF coal/hr-ft^3 space rate, 35-38 SCF hydrogen/lb of MAF coal, and a solvent-to-coal weight ratio of 2. A coal conversion of 68% of the MAF coal was obtained with a total hydrogen consumption by both the coal and solvent of 2.5 wt % of the MAF coal. The product distribution was as follows:

	Wt. % of MAF Coal
MAF Residue	32.0
+535°C Extract	39.1
Water	12.6
Gases	14.6
-206°C Distillate	+7.8
206 x 535°C Distillate	-3.6
Total	102.5

An analysis of the extract feedstock produced is given in Table II.

The conclusions from the feedstock preparation are:

1. Hydroextraction of Colstrip coal at the conditions studied is an operable process.
2. It is likely that a higher hydrogen pressure would be required to produce enough solvent to keep in solvent balance. A deficit of +3.6 wt % of the MAF coal of solvent boiling in the extraction solvent range was experienced in the above operation.
3. Successful continuous separation of solids via settling of the unconverted coal and ash from extract and solvent is achieved by the addition of a precipitating solvent, n-decane, at a weight ratio of 0.77 n-decane to extraction solvent. A solvent-free extract having 0.38 wt % ash was obtained in this manner.

Natural Spent Melt from Hydrocracking Operations

One of the objectives of zinc chloride hydrocracking operations in the bench-scale unit is to produce large amounts of both low-carbon (7 wt % or less) and high-carbon (about 15 wt %) spent melts for testing in the bench-scale regenerator. Sufficient amounts of these feedstocks are not available for regeneration studies at this writing. Preparation of the large batch of low-carbon spent melt will be undertaken in March, 1976.

TABLE II

Deashed Colstrip Extract Analysis
(Feedstock for $ZnCl_2$ Hydrocracker)

Proximate Analysis, MF Wt %	
Volatile Matter	62.72
Fixed Carbon	36.73
Ash Oxidized	0.55
Ultimate Analysis, MF Wt %	
Hydrogen	5.48
Carbon	87.04
Nitrogen	1.37
Oxygen (by difference)	5.36
Sulfur Total	0.20
Btu/lb, MF Basis	15,935
Ring and Ball Softening Point, °C	153
Solvent Fractionation	
Benzene Insolubles	21.3
Asphaltenes	41.8
Oils	36.9
Wt % Solvent (-290°C at 1 torr)	6.1

Task 2b Operation of the Bench-Scale Hydrocracker on Coal Extract

The initial operation of the hydrocracker was begun in September using coal extract as the organic feedstock and molten pure $ZnCl_2$ as the catalyst. The main objectives of this work were to:

1. Shake down the unit to determine if it would operate satisfactorily and simultaneously train the operating personnel.
2. Make one or more runs at relatively severe conditions of temperature and pressure to get data with Colstrip coal extract as the feed for comparison with later runs feeding coal directly and with runs in the previous unit that fed extract derived from bituminous coal.

Extract was used as the feedstock in the initial operations instead of coal for comparison with previous continuous hydrocracking with extract feed, to provide comparative data for subsequent runs with coal, and to break-in the new unit.

The work was terminated at the end of October after the main objectives had been achieved and the supply of Colstrip coal extract had been exhausted.

The main difficulties encountered during the shakedown period in September were:

1. Difficulties in pumping extract.
2. Difficulties in pumping zinc chloride.
3. Frothing of spent melt into lines when a receiver was depressured.

The pumping difficulties were overcome by the end of September, but the frothing difficulty gave trouble more or less during the entire operating campaign using extract as the feedstock. The problem was alleviated but not totally solved by operating the residue receivers at 575°F instead of 700°F, and operating the receivers on a shorter cycle to decrease the amount of material present during depressuring.

During October, the second objective was accomplished in that a successful run feeding coal extract was made (Run 1E). Four startups with premature shutdowns were required before the successful fifth attempt. The four starts were terminated because of a variety of difficulties that included leaks, frothing of residue, stirrer problems and cold spots. After the successful run, work was directed toward making a similar run at a lower throughput rate. Three attempts were made before the supply of extract was exhausted at the end of October. The runs were prematurely shut down because of residue frothing and reactor stirrer problems. The first attempt (Run 2A) was the most successful. An attempt will be made to get an estimate of conversion in Run 2A even though a balance was not made.

The conditions and results of Run 1E and the conditions of Run 2A are given in Table III. There are no directly comparable runs to Run 1E from the previous extract campaign, but it appears that the results with the Colstrip coal extract are fairly similar to what would be expected at similar conditions using Ireland Mine coal extract which is a Pittsburgh Seam bituminous coal extract.

No further work with extract is contemplated at this time.

The reactor inventories or bed densities in the runs with extract were much lower than would be expected on the basis of previous work. The previous campaign with extract indicated that the stirred pool density would be about 1.5 or 1.6 gm/cc at 775°F with a stirring speed of 1100 rpm instead of the actual values obtained of between 0.68 and 1.03. To clarify the situation, a series of three tests were in which the density of a stirred inventory of pure $ZnCl_2$ in the reactor was determined as a function of the stirring speed. Pure $ZnCl_2$ was used to preclude frothing that might come from organic vapors if organic feed was also used. The conditions of the tests were:

$ZnCl_2$ Feed Rate	1.0 lb/hr
H_2 Feed Rate	30 SCF/lb $ZnCl_2$
Reactor Temperature	775°F
Total Pressure	3500 psig
Feed Time	3 hours or more

Figure 3 shows the reactor bed density as a function of stirrer speed. This is a corrected plot from that given in the quarterly report, and allows an accurate estimation of the stirrer speed required for a desired residence time.

Task 2c Operation of the Bench-Scale Hydrocracker on Coal

Operation of the hydrocracker in which Colstrip coal is hydrocracked directly using molten $ZnCl_2$ catalyst was started early in November. In this work the coal was fed to the hydrocracker as a slurry consisting of 40 wt % -100 mesh Colstrip coal and 60 wt % Neville solvent (248-396°C petroleum-derived aromatic solvent). The work was focused on the use of the more severe conditions of temperature and pressure (775°F, 3500 psig total pressure) designed to produce a "low-carbon" melt containing less than 7% carbon.

The objectives of the work were to:

1. Establish and demonstrate the operability of the unit with coal feed.
2. Establish conditions at which a low-carbon melt can be produced so that conditions are defined for producing at the earliest feasible time, a large amount (ca 300 lb) of low-carbon spent melt for use in regeneration studies.
3. Explore the effect of $ZnCl_2$/coal ratio to establish the minimum ratio that can be used when feeding coal since the lowest ratio compatible with achieving operability and high conversion is economically desirable.

TABLE III

Bench-Scale Hydrocracker Runs

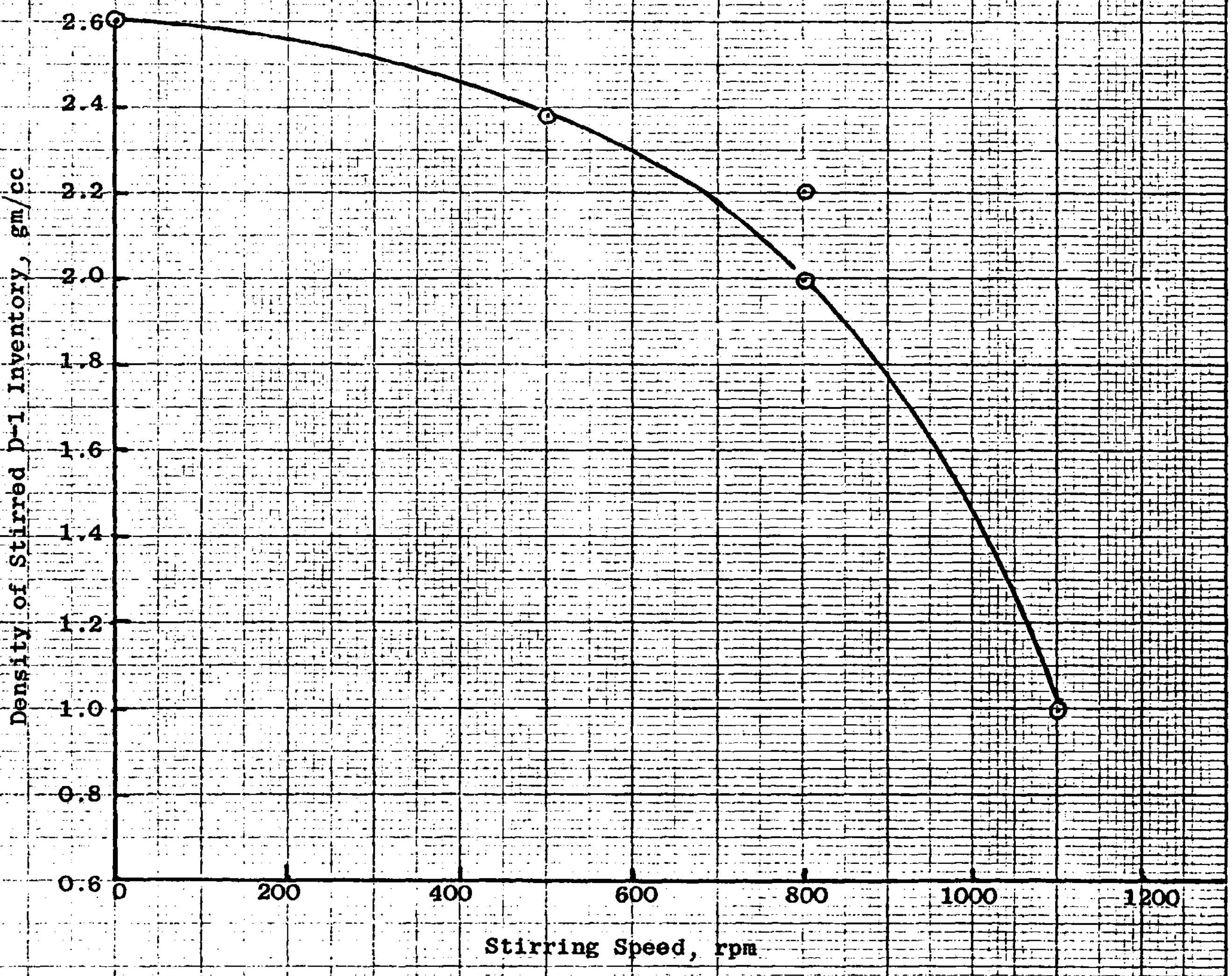
Run No. 518.02-	1-E	2-A	3-O	3-J
Temperature, °F	← 775 →			
Total Pressure, psig	← 3500 →			
Organic Feed Composition, Wt %				
Colstrip Coal Extract	99.4	85	--	--
Minus 100 Mesh Colstrip Coal	--	--	40	40
248 x 396°C Neville Solvent	0.6	15	60	60
Catalyst	← "Pure" $ZnCl_2$ →			
$ZnCl_2$/Solvent-Free Extract or Solvent-Free Coal	1.0	1.0	2.0	1.5
Organic Feed Rate, lb/hr	1.27	0.87	~ 1.34	2.0
$ZnCl_2$ Feed Rate, lb/hr	1.17	~ 0.80	~ 1.07	~ 1.2
H_2 Feed Rate, SCF/lb org. feed	← 30 →			
Stirring Speed, rpm	1100	1100	800	800
Pool Depth, cm	19.5	19.5	19.5	29.2
WHSV*	1.2	0.8	~ 0.37	~ 0.37
Lineout Running Time, hours	3.0	5.9	4.0	4.4
Balance Running Time, hours	3.0	--	6.0	3.8
Conversion to -475°C Product, wt % MAF feed extract or coal	69.0		90	
Melt Residue Carbon Content, wt %	17.1		3.7	
Yields, Wt % MAF Solvent-Free Feed				
CH_4	0.9			
C_2H_6	0.9			
C_3H_8	2.5			
iC_4H_{10}	3.5			
nC_4H_{10}	0.9			
CO	0.0			
CO_2	0.3			
H_2O	--			
C_5 x 200°C Distillate	31.5			
200 x 230°C Distillate	6.9			
230 x 325°C Distillate	8.2			
325 x 475°C Distillate	5.7			
+475°C MEK Soluble Product	24.1			
+475°C MEK Insoluble Product	6.8			
Σ	92.2			
H_2 Consumed, wt % MAF	4.3			

* Grams of solvent-free extract or solvent-free MF coal fed/hr-gm bed.

FIGURE 3

Measured Density of Stirred Inventory of Pure $ZnCl_2$ in the D-1 Reactor

$ZnCl_2$ Feed Rate	1.0 lb/hr
H_2 Feed Rate	30 SCF/lb $ZnCl_2$
Pool Depth	3.6 inches
Temperature	775°F



Two successful runs were made: one run using a $ZnCl_2$/solvent-free MF coal weight ratio of 2 (Run 3-O) and a similar run at a ratio of 1.5 (Run 4-J). These runs achieved objectives 1 and 2 and, while they have not established the minimum possible ratio of $ZnCl_2$/coal as per objective 3, they have shown that the hydrocracker is operable at a ratio at least as low as 1.5.

The conditions of Runs 3-O and 4-J are given in Table III under Task 2b. A couple of results of Run 3-O are also shown in this table. Run 3-O showed a coal conversion of about 90%, which will be reduced somewhat when results on the +475°C material carried overhead are available. The spent melt contained 3.7 wt % carbon which is well below the concentration of about 6-7 percent that is required for adiabatic regeneration of the melt via combustion of the carbon with excess air.

A large number of starts with premature shutdowns were required before Run 3-O and 4-J, respectively, were successfully made.

The main reasons for premature shutdown of hydrocracking runs were: (1) frothing of spent melt into lines when a receiver was depressured, and (2) cracking of type 316 ss lines in the distillate system. The first of these was corrected by depressuring to 800 psig through a heated line and the low-pressure receiver, and by taking the final melt depressuring via throttling of the melt. The second problem is being overcome by replacing the 316 ss fittings and tubing with Inconel 600 which is not subject to stress corrosion cracking.

Work planned for the next quarter includes:

1. Complete the study to establish the minimum $ZnCl_2$/coal ratio that can be used when feeding coal to the hydrocracker.
2. Make a run at one of the conditions already tested, but with use of a slurry consisting of Colstrip coal in benzene thickened with polystyrene. (The benzene must be thickened to give it sufficient viscosity to make a pumpable slurry.) This vehicle should give known products so that the product yields from the coal can be defined and collected. This cannot be done using the complex Neville solvent as a vehicle in the slurry.
3. Produce 300 pounds of low-carbon spent melt, for use in regeneration studies, at one of the conditions defined by the foregoing work. Thickened benzene will be used as the vehicle if possible to allow collection of relatively large amounts of the natural middle and heavy oils produced from the coal for later studies on its reactivity upon recycle as a vehicle for the feed coal.

Task 3 Operation of the Continuous Bench-Scale Regenerator

The unit was essentially completed at the end of September but initial operations were not started until the middle of October. The unit has been operated up to this writing with synthetic spent melt since natural spent melt from the bench-scale hydrocracker has not been available in large enough quantities.

The spent melt feedstocks for all of the operations thus far have been synthetic spent melts that simulate low-carbon spent melt (6 wt % C + organic H) from direct hydrocracking of Colstrip coal at $ZnCl_2$/solvent-free MF coal ratios of 2.0 and 1.0.

The runs conducted so far have had the following objectives:

1. Determination of the preferred cyclone temperature, and the preferred rate of gas underflow through the cyclone as judged by cyclone operability and the efficiency of $ZnCl_2$ recovery and ash recovery.

2. Determination of the effect of ash content of the spent melt feedstock on $ZnCl_2$ recovery. This work will indicate whether zinc losses to the ash are caused by interaction of ZnO with the ash components or by simple kinetic or equilibrium limitations regarding the reverse hydrolysis reaction:

   $$ZnO + 2\ HCl = ZnCl_2 + H_2O.$$

   If the former is true the Zn content of the cyclone underflow will be approximately directly proportional to the underflow ash weight, whereas, if the latter is true the zinc content will be lower in the case of the feed with the higher ash content. The chemical form of the zinc in the ash is of interest regarding the recovery of residual zinc from the cyclone underflow solids in a second stage.

All of the runs were made using 115% of stoichiometric air except for one run in which 153% of stoichiometric air was used when the melt feed rate was inadvertently low. Cyclone temperatures of 1350, 1500 and 1650 were studied at otherwise constant conditions. Also, the effect of ash content of the spent melt feedstock was studied, i.e., it was varied from 4.3 and 7.9 wt % of the feedstock corresponding to spent melt from hydrocracking at $ZnCl_2$/MF coal ratios of 2 and 1, respectively. The conditions of the runs and some preliminary results are given in Table IV.

Based on the zinc content of the cyclone underflow solids (ash) and the rate of zinc collection in the cyclone underflow solids as shown in Table I, the following preliminary conclusions can be made:

1. The zinc losses to the cyclone solids increase substantially as the cyclone temperature is increased above 1350°F, although no large difference is noted between 1500 and 1650°F.

2. The zinc content of the underflow cyclone solids decreases when the ash collection at the cyclone increases because of increased ash content of the feed. However, the rate of zinc collection is nearly constant. These results imply that the zinc "losses" in the cyclone solids are not due to chemical interaction of the zinc with ash constituents such as silica and alumina, but due to simple ZnO formation by hydrolysis of $ZnCl_2$. A further implication is that the 5.5 mol % HCl in the feed gas is too low to completely prevent formation of ZnO by hydrolysis of $ZnCl_2$.

TABLE IV

Regenerator Runs With Synthetic Spent Melt

Common Conditions

Temperature, °F	1800
Pressure, psig	3
Inlet Gas Comp., mol %	94.5 Air-5.5 HCl
Superficial Fluid. Vel, fps	1
Bed Depth, inches	12
Bed Solids	28-48 M Silica Sand

Other Conditions

Run No. 518.05-	1-C	2	2-B	3-B	4	5
Amount of Air, % stoich.	115	153	← 115 →			
Cyclone Temp., °F	1350	1500	1500	1650	1500	1500
Cyclone Gas Underflow Rate, SCFM	*	*	*	*	~ .0006	~ .0017
Ash Content of Feedstock, wt %	← 4.3 →				7.9	7.9
C + Organic H Content of Feedstock, wt %	← 6.0 →					

* Control of the gas underflow rate was not achieved.

Preliminary Results

	1-C	2	2-B	3-B	4	5
Solids Collected at Cyclone, wt % feedstock	74	66	73	67	75	80
Rate of Solids Collected at Cyclone, gm/min	0.73	0.52	0.75	0.65	1.24	1.53
Wt Ash Fed/min	0.98	0.79	1.03	0.98	1.82	1.90
Zinc Content of Cyclone Solids, wt %	3.35	4.97	9.50	7.74	5.30	
Rate of Zinc Collected at Cyclone, gm/min	0.024	0.026	0.071	0.050	0.066	
CO content of the Acid-Gas-Free Effluent Gas, mol %		0.11	0.78			

3. It appears that the higher cyclone gas underflow in Run 5 as compared with Run 4 resulted in greater efficiency of solids collection at the cyclone.

An increase in the amount of stoichiometric air from 115 to 153% of stoichiometric reduced the CO content of the gas very substantially, i.e., from 0.78 to 0.11 mol %. This, of course, is desirable from the environmental aspect; however, the capacity of the unit decreases with increasing excess air.

Work planned for the next quarter includes:

1. Using synthetic spent melts as feedstocks, complete the experimental study on the effects of cyclone temperature and ash content of the feedstock on cyclone operability, ash collection efficiency and zinc loss. This will involve one or two more runs.
2. Investigate the effect of increased HCl content of the feed gas on zinc recovery using synthetic spent melt feedstocks.
3. Investigate regeneration of low-carbon natural spent melt (7% C or less) from direct hydrocracking of Colstrip coal. This campaign will be started as soon as spent melt is available from the bench-scale hydrocracker. The main objectives are:
    a. To establish operability using excess air and to define, in a run of prolonged duration the efficiency of zinc and chlorine recovery.
    b. To determine the conditions and method of operation to improve or optimize zinc and chlorine recovery.
4. If there are delays in obtaining the natural spent melt, further work will be done with synthetic spent melt regarding the collection efficiency of iron in a high-iron content spent melt. Some work may also be done using a high-carbon spent melt with a deficiency of air to further define operability limits regarding sintering of the ash in the fluidized bed.

Task 4 Design of the Process Development Unit

A. Introduction

The purpose of the Process Development Unit (PDU) is to demonstrate hydrocracking with and regeneration of zinc halide on a large enough scale to obtain a meaningful analysis of the commercial potential of the overall process. Items to be demonstrated include:

1. Performance of mechanical components.
2. Suitability of materials of construction.
3. Operability and reliability of the system.
4. Effect of equipment size on reaction rate.
5. Yields from coal and extract feed.
6. Catalyst losses.
7. Effect of process variables.
8. Relative attractiveness of competing process options.

A PDU has been designed to process 100 lb/hr of coal or extract feed. The design includes hydrocracking, regeneration, pressure letdown and fractionation sections. A prime consideration in the design has been inclusion of sufficient flexibility to evaluate competing process options and to evaluate individual items of equipment.

B. Summary of Work Accomplished

1. Material and energy balances were made for four anticipated modes of operation of the hydrocracking, letdown and fractionation sections and for operation of the regeneration section with 115% of stoichiometric air at the minimum and maximum anticipated carbon feed rates to the unit.

2. Long-lead-time items (8 vessels, 2 compressors and Hastelloy B tubing) for the hydrocracking section were identified and designed. Bids were obtained and orders placed to purchase these items. Design of the long-lead-time hydrocracking reactors (a 7.25" ID stirred reactor and a 5" ID sparged reactor) included analysis of mass transfer and axial mixing characteristics of the reactor.

3. Process flow diagrams and process and instrumentation (P&I) drawings for sections 100 and 200 (hydrocracking), section 300 (regeneration) and section 400 (letdown) were prepared and issued.

4. Tentative process flow diagrams and P&I drawings for section 500 (fractionation) were prepared and issued. These documents will become final when the design has been checked against output from Conoco's computer simulation model.

5. Mechanical design of the regenerator reactor began.

C. Material and Energy Balances - Hydrocracking

Material and energy balances were prepared for four different cases of operation of the hydrocracking, letdown and fractionation sections. The purpose of these balances was to provide input for the process flow diagrams and P&I drawings. More specifically, these balances were used for equipment sizing, selection of materials of construction, selection of instrumentation and layout of equipment. As mentioned earlier, flexibility is a prime consideration in design of the PDU. Accordingly, no single, "typical" material and energy balance would properly characterize the system. Rather, the four balances were made to check extreme conditions and inclusion of foreseeable steps in the alternate processing schemes.

The four design cases were:

		Conversion to -475°C Material			
Feed	Reactors	Basis Fresh Feed	Overall	Extractor	+475°C Recycle
Extract	1 stirred	80.0%	84.1%	Yes	Yes
Coal	1 sparged	78.6%	85.9%	Yes	Yes
Extract	2 in series	87.6%	87.6%	No	No
Coal	2 in series	87.6%	87.6%	No	No

In the two cases involving use of an extractor and recycle of +475°C material, the process lineup was as follows:

1. Fresh H_2, recycle H_2, recycle hydrocarbons, feed and catalyst are fed to a single reactor.

2. Reactor offgases are cooled to 100°F. Recycle H_2 is recovered by phase separation. After removal of water, the condensate is fractionated to produce products and hydrocarbons for recycle.

3. Spent catalyst from the reactor is extracted with 200-475°C boiling range solvent to recover +475°C material. The extract (solvent and +475°C material) is vacuum flashed to recover recycle solvent. The raffinate (catalyst + residual solvent) is also vacuum flashed to provide a solvent-free spent catalyst for regeneration.

In the two cases not involving use of an extractor or recycle of +475°C material, the process lineup was as follows:

1. Fresh H_2, recycle H_2, recycle -475°C hydrocarbons, feed and catalyst are fed to the stirred reactor. Total product from the first reactor plus additional H_2 are fed to the sparged reactor.

2. Offgas from the sparged reactor is cooled to 450°F, condensing high-boiling hydrocarbons. The high-boiling hydrocarbons are sent to fractionation.

3. Offgas from the partial condensation is reheated and contacted with spent melt from the sparged reactor. HCl is removed from the gases by the reaction,

$$ZnCl_2 \cdot NH_3 + HCl \rightleftarrows ZnCl_2 \cdot NH_4Cl$$

4. Offgases from the HCl scrubber are cooled to 100°F. Recycle H_2 is recovered by phase separation. After removal of water, the condensed liquids are routed to fractionation along with the products from partial condensation. The bottoms from fractionation are flashed to reject +475°C material and then recycled to the reactor.

5. Spent melt is vacuum flashed for cleanup and sent to regeneration.

The details of and assumptions inherent in the hydrocracking material balances have been fully documented in previous quarterly technical progress reports.(4,5) In examining the individual balances, one should carefully note the assumptions used in each case. To insure that all reasonable possibilities were considered, assumptions on the reactivity of recycle material and on product distributions from coal were altered from case to case.

The primary function of the material and energy balances was to provide a basis for selection and sizing of equipment. Thus, the balances are the source of many of the details presented elsewhere on process flow diagrams. Salient points uncovered by the balances include:

1. The critical case from the standpoint of heat removal is extract feed to a single stirred reactor. Allowing for reasonable wall losses, the necessary heat removal can be accomplished at hydrogen flows only slightly higher than those used in previous bench-scale work.

2. The limiting case from the standpoint of heat addition is coal feed to a single sparged reactor. With the sparged reactor, very high hydrogen flow is required. The hydrogen must be preheated to near reactor temperature.

3. When two reactors are operated in series, the type of feed (coal versus extract) has a strong influence on the heat balances. Accordingly, independent control of hydrogen inlet temperature for the two reactors is required.

4. When coal feed is used, recycle of unreactive 150-200°C material will be necessary to provide adequate slurry oil to act as carrier for the coal. Two fractionation columns are required to make the necessary heart cut.

5. When the solvent extractor is used, "low-carbon" spent melt can be produced even with recycle of unconverted +475°C material. However, when solvent extraction is not practiced, recycle of unconverted +475°C material may be inconsistent with production of "low-carbon" spent melt at catalyst/feed ratios of 1/1.

6. When the extractor is used, experiments on removal of HCl from offgases by absorption with spent melt will be difficult. However, when the extractor is not used, absorption experiments should be straightforward.

D. Material and Energy Balances - Regeneration

Regeneration of spent melt involves vaporization of $ZnCl_2$ using heat generated by combustion of carbon in a fluidized bed. Two modes of operation are possible. One may operate with stoichiometric (or excess) air in which case CO_2 is the primary product of combustion. Alternatively, one may operate with substoichiometric air (or O_2) in which case a low-Btu (or synthesis gas) product gas is made. To date, only the stoichiometric air option has been used in making material balances and in design of the regeneration section. The substoichiometric option will be included at a later date.

The regenerator heat balance dominates the regeneration section. Bench-scale results indicate use of 1800-1900°F regenerator temperature. The primary heat source is combustion of carbon and the primary heat sink is vaporization of $ZnCl_2$. For adiabatic operation, one cannot independently specify temperature, oxygen supply and concentration of carbon in the $ZnCl_2$. Thus, if temperature must be 1800-1900°F and stoichiometric air is used, carbon concentration in the feed $ZnCl_2$ is not a free variable. The concept of operation of the regenerator is that carbon concentration in the feed to the regenerator will be controlled. If the carbon content of spent melt from the hydrocracking section is too high, regenerated $ZnCl_2$ will be added to the regenerator feed. If the carbon content of spent melt is too low, hydrocracking conditions will be changed to bring the regenerator into heat balance. With this concept of operation, the carbon feed rate becomes a free variable. Material balances for the regenerator consisted of a "low-carbon" case which represented the maximum overall conversion expected in the hydrocracking section and a "high-carbon" case representing low hydrocracking conversion.

The primary difference between spent melts produced by coal versus extract feed to hydrocracking is the high-ash content when coal is used. Accordingly, if ash is included in the regenerator feed, there is no necessity for different balances for the two types of feed.

The flows in the regenerator section are as follows:

1. Spent melt is combined with recycle regenerated $ZnCl_2$ to provide about 6.3% carbon in the total melt feed to the regenerator.

2. Air in an amount equal to 115% of that required to convert carbon to CO_2, hydrogen to H_2O and sulfur to SO_2, is introduced into the bottom of the regenerator. The inlet gas also contains 5.5 mol % HCl which inhibits hydrolysis of $ZnCl_2$.

3. Ash, combustion products, nitrogen and vaporized $ZnCl_2$ leave the regenerator through a cyclone which collects ash particles larger than about 5 microns in diameter.

4. The cyclone overflow is cooled to about 650°F, condensing $ZnCl_2$. Uncondensed gases are neutralized with caustic, cooled and vented.

5. Molten $ZnCl_2$ is collected and recycled to the regenerator or routed to the hydrocracking section as regenerated catalyst.

In addition to providing input for equipment selection and sizing, the material and energy balances uncovered the following items:

1. Preheating of the input air to the regenerator will be necessary. Wall losses from the regenerator reactor will be about 20,000 Btu/hr. Preheating the air compensates for wall losses. Temperature control on the inlet air will also be used to control short term regenerator reactor temperature variation.

2. Performance of the fluidized bed and gas residence time is controlled by volumetric gas flow. Since carbon feed rate and hence mass flow of air will vary, reactor pressure must be adjusted to insure constant volumetric gas flows.

3. Ash particles too small to be collected by the cyclone will be recycled to the hydrocracker with regenerated $ZnCl_2$. Since spent melt from the hydrocracker returns to the regenerator, there could be a buildup of small ash particles in the system. The particles may agglomerate. If not, some sort of purge will be necessary.

E. Hydrocracker Reactor Design Considerations

Two types of reactors will be used for the PDU. Reactor D-201 will be a stirred vessel while D-202 will be a sparged reactor. The stirred vessel is analogous to the type of reactor used in the bench-scale program. It can be operated with H_2/feed ratios near those expected commercially. However, large commercial stirred reactors are difficult to build and maintain. Accordingly, a sparged reactor (the more likely commercial design) is also provided. The sparged reactor has the inherent problem that H_2/feed ratios must be much higher on the PDU scale than on the commercial scale. In essence, the stirred reactor is provided to obtain yield data for scaleup and the sparged reactor is provided to obtain rate data for scaleup. The two types of reactors can be operated in series to obtain high conversion provided the stirred reactor is first.

To design the stirred reactor, a power input per volume analogous to that obtained in the bench-scale unit at 1020 rpm was used. This requires 688 rpm and 4.8" diameter turbines for the 7.25" ID PDU reactor.

To design the sparged reactor, some estimate of the effect of reactor superficial velocity on mass transfer of hydrogen to the reactants was necessary. Two models were developed. Model 1 assumed physically separate but emulsified melt and reactant phases. Model 2 assumed a homogeneous mixture. Hydrogen solubility was taken from available data. Diffusivities and mass transfer coefficients were estimated. Gas holdup and interfacial areas were then estimated as a function of reactor superficial velocity. Using the two models, saturation ratios (ratio of concentration of hydrogen in bulk reactor liquid to equilibrium concentration) were then calculated and compared with saturation ratios estimated for the bench-scale reactor at 1020 rpm. At 1.0 ft/sec superficial velocity and 60 minutes hold time, the sparged reactor provides saturation ratios which, while not as high as the bench-scale reactor at 1020 rpm, are comfortably above those for the bench-scale reactor at 340 rpm (a known unsuitable condition). Thus, it is deemed likely that a sparged reactor at 1.0 ft/sec superficial velocity will not suffer from hydrogen starvation with the attendant coking.

Increasing superficial velocity above 1.0 ft/sec would not be expected to provide any advantage and, if model 1 applies, a superficial velocity of 0.5 ft/sec would be adequate from the standpoint of hydrogen starvation.

Axial mixing in the sparged reactor was then estimated using liquid axial Peclet Numbers - dimensionless groups for comparing degree of deviation from perfect mixing. The expected axial mixing at 1.0 ft/sec superficial velocity in the PDU reactor is not as good as one would expect in a commercial unit but should be adequate.

The considerations listed above led to specification of a 5" ID for the sparged reactor. Further, the hydrogen system was sized to provide a 1.0 ft/sec superficial velocity. It is anticipated that the 5" ID reactor will be completely adequate. However, in the course of reactor design it became apparent that the 7.25" ID shell provided for the stirred reactor could be designed to allow operation as a sparged reactor with superficial velocities up to 0.5 ft/sec. With such a modification, the PDU would have the capability of testing effect of reactor superficial velocity at constant gas/liquid ratios. Also, the axial mixing in a 7.25" ID, 0.5 ft/sec superficial velocity would be equivalent to that in a commercial reactor.

To summarize, the PDU will have two reactors. There will be a 5" ID by 25' long reactor designed to operate as a sparged reactor with superficial velocities up to 1.0 ft/sec. There will also be a 7.25" ID by 12' reactor designed to operate either as a stirred reactor with H_2/feed ratios near those expected commercially or as a sparged reactor operated at superficial velocities up to 0.5 ft/sec.

Complete details of the reactor design calculations are given in a previous quarterly technical progress report.(4)

F. Process Flow Diagrams and P&I Drawings

The normal design procedure at CCDC is to prepare flow diagrams showing equipment sizes, ratings, materials of construction and orientation along with design flows for line sizing. The process flow diagrams are used to prepare more detailed P&I drawings which show instrumentation, piping layout and size, valving details and insulation. These two types of drawings are used as the basis for mechanical design of equipment items, plant layout, detailed piping drawings, ordering of valves, pumps, instruments, etc., and all other factors which go into actual construction of the PDU.

Process flow and P&I drawings have been transmitted to ERDA for review. Essentially, the drawings constitute specification of the PDU. It is anticipated that a separate design report will be issued for the "as built" plant. To provide a reasonably detailed overview of the PDU, the following process flow diagrams are included as Appendix A;

Drawing No.	Description
AF-3658	Hydrocracking Section - Case I
AF-3682	Hydro Letdown Section - Case I
AF-3659	Hydrocracking Section - Case II
AF-3683	Hydro Letdown Section - Case II
AF-3684	Fractionation Section - Both Cases
AF-3676	Regeneration Section - Both Cases

Case I provides for operation with solvent extraction to recover +400°C material from spent melt. Both reactors are shown on the drawing. However, Case I will involve operation with a single reactor at about 80% conversion of fresh feed and with recycle of unconverted +200°C material (plus some 150-200°C gasoline as slurry oil when coal is fed).

Case II provides for operation without solvent extraction but with scrubbing of HCl from the reactor offgas. In Case II, both reactors, operating in series, will be used. Anticipated conversion (fresh feed basis) is about 87% and recycle of +475°C material will not be practiced.

The two cases use the same equipment. However, drawings designed to include both cases would be too complex for reasonably easy understanding. Accordingly, separate flow drawings were used.

The drawings presented here and the associated P&I diagrams are in "final" form, and will be used for the detail work necessary to construct the PDU. There will be inevitably minor changes and corrections which become obvious as the work progresses. However, the only factors which might lead to substantive changes are:

1. If the physical properties of the extract feed preclude use of bin storage and a screw feeder, or if drying of the extract is required, additional facilities must be provided.

2. The fractionation section was designed using "short cut" techniques. The design is being checked using rigorous tray-to-tray calculations. The more rigorous design might necessitate minor changes.

3. As results from bench-scale work become available, they will be examined for impact on PDU design. As an example, problems with spent melt pressure letdown on the bench-scale unit have already led to modification of the PDU design.

4. The substoichiometric air case (regeneration section) has not been designed. Preliminary consideration of substoichiometric air operation indicates that the only modifications required will be a change in regenerator dimensions and a provision for CO_2 feed to the regenerator reactor. However, other modifications may be dictated by detailed consideration of the substoichiometric air case.

G. Mechanical Design of the Regenerator Reactor

As outlined in the material balance section, the regenerator must be designed to operate over a range of conditions. Specifically, 180 to 325 lb/hr of 94.5% air-5.5% HCl gas will be used to combust 7.3-14.7 lb/hr of carbon, releasing sufficient heat to vaporize 104-212 lb/hr of $ZnCl_2$. From bench-scale work, gas residence times of 1-2 seconds are required. Further, the regenerator must be designed to provide adequate fluidization of the bed without significant loss of bed solids by elutriation. Anticipated operating temperature is 1800-1900°F.

With the above requirements as input, the regenerator reactor bed size was selected. The bed will be 9" in diameter with the option of operating at a depth of either 2 or 4 feet. The depth is to be controlled by overflow weirs. Bed solids will be 28 x 48 mesh sand. Freeboard above the bed will be 4' to 6' depending on bed height. Plans are to increase regenerator ID to 12" above the bed to provide extra insurance against elutriation. Gases entering the bottom of the bed will pass through a distributor designed for 0.5-1.0 psi pressure drop and jet velocities on the order of 150 ft/sec.

The basic control for operation of the bed described above over a wide range of inputs is variation of unit pressure. As the required gas mass rate increases, unit pressure will be raised to provide essentially constant volumetric gas flows. Specifically, at 180 lb/hr of gas feed, regenerator pressure will be 40 psia, and at 325 lb/hr of gas feed, regenerator pressure will be 70 psia. These pressure-flow rate adjustments both provide a superficial velocity of 2.4 ft/sec in a 9" ID bed. This gives about 0.8 sec residence time with the 2' high bed and 1.6 sec residence time with the 4' high bed.

Since the regenerator must operate at 1800-1900°F, very good insulation is required to control wall losses. A conflicting requirement is that the bed be contained in a high density refractory which has good resistance to gas diffusion and abrasion by solids, but poor insulating properties. As a result, the regenerator will be built as follows: The bed will be contained in an inner core of high density refractory. The inner core will be surrounded by approximately 12" of insulating refractory. The insulating refractory is contained by a steel shell. Finally, a water jacket will be provided around the shell. The water jacket, operated at unit pressure, serves two purposes. First, it controls wall temperature above the dew point of water. Second, it provides a safety factor in the event of hot spots on the metal wall. A refractory supplier is currently reviewing refractory requirements. The mechanical design problems are also being reviewed by the in-house experts.

H. Work Forecast for February-April Quarter

The goals for the next quarter are:

1. Conduct safety, startup and shutdown reviews of the PDU.
2. Review PDU design for additional long-lead-time items.
3. Review PDU design to insure that the necessary data and samples can be obtained from the unit.
4. Complete mechanical design of the regenerator.
5. Begin mechanical design of such items as the regenerator cyclones, HCl feed system, solids feed system to the regenerator, etc.
6. Prepare and issue an instrument list for the PDU.
7. Prepare an up-to-date cost estimate for construction of the PDU.

Task 5 Procurement and Construction of the PDU

Eight high-pressure Inconel vessels (D-201, D-202, D-205, D-206, E-201, F-204, F-205 and F-207, Dwg. AF-3658) and two compressors (JC-201, JC-202) were identified as long-lead-time items. These items were designed in sufficient detail to obtain bids from potential suppliers. These items were ordered in January, 1976. Delivery time for the Inconel vessels is 42-45 weeks. Delivery time for the compressors is 36 weeks.

A contract to construct the building to house the PDU has been signed and construction has begun.

Task 6 PDU Program Planning and Operation

No activity scheduled until construction begins.

Task 7 Supporting Laboratory Work

A. Batch Autoclave Work

The batch autoclave operations were largely confined to a kinetics study of direct hydrocracking of Colstrip coal with zinc chloride catalyst. The purpose of the work is to get data for development of a kinetics model. This model will be useful for interpreting the performance of direct coal hydrocracking in continuous units as a function of the operating temperature, the number of stages, and the hydrogen partial pressure.

Twelve runs were made that comprise a study of residence time at temperature levels of 725, 750 and 775°F while holding the hydrogen partial pressure constant at 3000 psig. A single run with extract feed was also made. The conditions and results of these runs are given in Table V and Figures 4, 5 and 6. Some highlights of the results are:

1. The results show that Colstrip coal is a good feedstock for direct hydrocracking by $ZnCl_2$ catalyst. It's reactivity is quite similar to that of Pittsburgh Seam bituminous coal.

2. The Colstrip coal extract that was used was a somewhat less reactive feedstock than Colstrip coal. However, this may be caused by overheating of this extract in its preparation. Further work with other extracts would be required for an unequivocal conclusion.

3. Conversions to -475°C products as high as 88 wt % of the MAF feed coal are obtained.

4. C_5-200°C distillate yields as high as 52 wt % of the MAF feed coal are obtained.

5. There is an optimum time for the maximum yield of C_5-200°C distillate.

6. The maximum yield of C_5-200°C distillate occurs at increasingly shorter times and tends to increase slightly as the temperature is increased from 725 to 775°F.

Two runs have been made in a series comprising a study of residence times at various temperature levels while holding the hydrogen partial pressure constant at 2000 psig but results are not available.

In addition to the above runs, Run 14 was made with reconstituted Colstrip coal, i.e., the solvent-free product from hydroextraction of coal at 825°F and 1750 psig. It was hoped that this product would permit use of a lower ratio of zinc chloride than with raw coal because of the liquids produced in hydroextraction. Unfortunately, this particular sample of reconstituted coal, at least, was considerably less reactive to zinc chloride hydrocracking than raw coal itself. This could, however, be due to overheating in the solvent recovery step.

TABLE V

Batch Kinetics
Study of Hydrocracking -100 Mesh Colstrip Coal

For all Runs: Constant H_2 Partial Pressure = 3000 Psig

Run Number 518.03-	1A	5	4	6	7	8	3	9	10	11	12	2	13	14
Feed	Colstrip Coal Extract	-100 Mesh Colstrip Coal												Reconstituted Colstrip Coal
Feed Wt, grams	50.0	45.0												
$ZnCl_2$/MF Feed Wt Ratio	1.0	2.5												
Moisture Content of Feed, wt %	0.0	1.7	1.2	2.0	1.8	1.4	1.0	1.8	1.0	1.6	2.0	3.3	1.3	4.7
Temperature, °F	775	725				750				775				
Residence Time, minutes	60	15	60	120	180	15	60	120	180	15	30	60	120	60
Final Total Pressure, psig	4000	3850	4100	4300	4300	4100	4250	4550	4600	4350	4400	4500	4800	4100
Time-Temperature History, Minutes														
Ambient to 600°F	46	42	41	44	36	35	44	41	43	41	41	44	44	49
600°F to Maximum Temperature	17	10	8	10	16	16	11	16	8	15	15	15	13	18
Maximum Temperature to 600°F	8	7	8	8	5	7	8	7	6	9	10	10	6	12
Yields, Wt % MAF Feed														
CH_4	0.9	0.2	0.4	0.8	0.7	0.4	0.9	0.8	1.4	0.7	0.9	1.3	1.5	3.4
C_2H_6	0.9	0.3	0.6	1.0	1.1	0.7	1.0	1.3	1.8	1.1	1.4	1.5	2.1	3.1
C_3H_8	1.5	1.6	2.2	4.6	5.7	3.8	3.9	8.8	10.3	6.0	7.8	3.4	12.2	8.2
iC_4H_{10}	2.8	3.9	8.6	7.7	10.1	6.8	11.8	12.5	16.6	9.6	12.0	7.2	16.2	7.6
nC_4H_{10}				0.9	1.0	0.8		1.4	1.9	1.2	2.0	5.8	2.1	1.7
CO	0.02	1.1	0.8	1.2	0.7	1.2	0.9	0.7	0.5	1.3	1.4	0.7	0.7	0.04
CO_2	0.04	2.6	1.2	2.4	1.6	2.6	1.0	1.3	1.2	2.4	2.5	1.3	1.1	0.1
H_2O	2.7	14.6	15.3	14.8	15.0	10.3	13.4	17.6	10.9	16.3	15.0	15.5	16.4	
C_5 x 150°C Distillate	44.8	29.3	41.0	42.7	39.1	20.0	46.3	44.0	42.3	34.1	41.8	46.9	39.0	
150 x 200°C Distillate	5.9	3.9	3.7	5.8	4.9	4.8	3.4	3.5	2.1	4.7	4.2	4.1	2.6	
200 x 475°C Distillate	15.6	7.9	6.2	3.2	2.5	5.5	3.3	1.6	0.7	3.3	2.8	2.4	0.8	
+475°C MEK Soluble Residue	25.4	33.6	22.7	17.8	20.3	28.4	17.0	11.1	9.6	10.6	11.8	12.9	10.0	
+475°C MEK-Insoluble Residue	4.6	5.4	4.0	3.5	3.4	6.3	4.4	3.5	2.8	6.3	3.5	4.3	3.6	
N to Catalyst	1.1	0.9	1.1	1.2	1.2	1.0	1.1	1.2	1.2	1.1	1.2	1.2	1.0	
O to Catalyst	0.6	0.9	0.8	0.8	0.9	0.8	1.2	0.9	0.6	1.0	0.7	0.9	0.8	
S to Catalyst	0.1	0.5	0.5	0.5	0.5	0.5	0.2	0.5	0.5	0.5	0.5	0.5	0.5	
H to Catalyst	0.3	0.2	0.2	0.3	0.3	0.2	0.2	0.3	0.4	0.2	0.3	0.3	0.5	
Σ, Including H_2 Consumed	107.1	106.9	109.3	109.4	109.8	108.1	109.6	110.9	110.7	108.4	109.7	110.3	111.1	
H_2 Consumed, wt % MAF Feed	7.1	6.9	9.3	9.4	9.8	8.1	9.6	10.9	10.7	8.4	9.7	10.3	11.1	7.2
Conversion, wt % MAF Feed	70.0	61.0	73.4	78.7	76.4	66.3	78.6	85.4	87.7	75.1	84.7	82.8	86.4	
(C_1-C_4) x 100/Conversion	4.7	3.4	4.4	8.2	9.8	7.4	6.0	12.8	15.4	10.5	11.9	7.4	18.3	
% H_2 Consumed as C_1-C_4 Gas	9.6	5.7	6.4	13.6	14.6	11.7	10.0	20.0	24.2	27.8	16.6	12.1	27.4	

FIGURE 4

BATCH KINETICS STUDY OF HYDROCRACKING -100 MESH COLSTRIP COAL WITH $ZnCl_2$

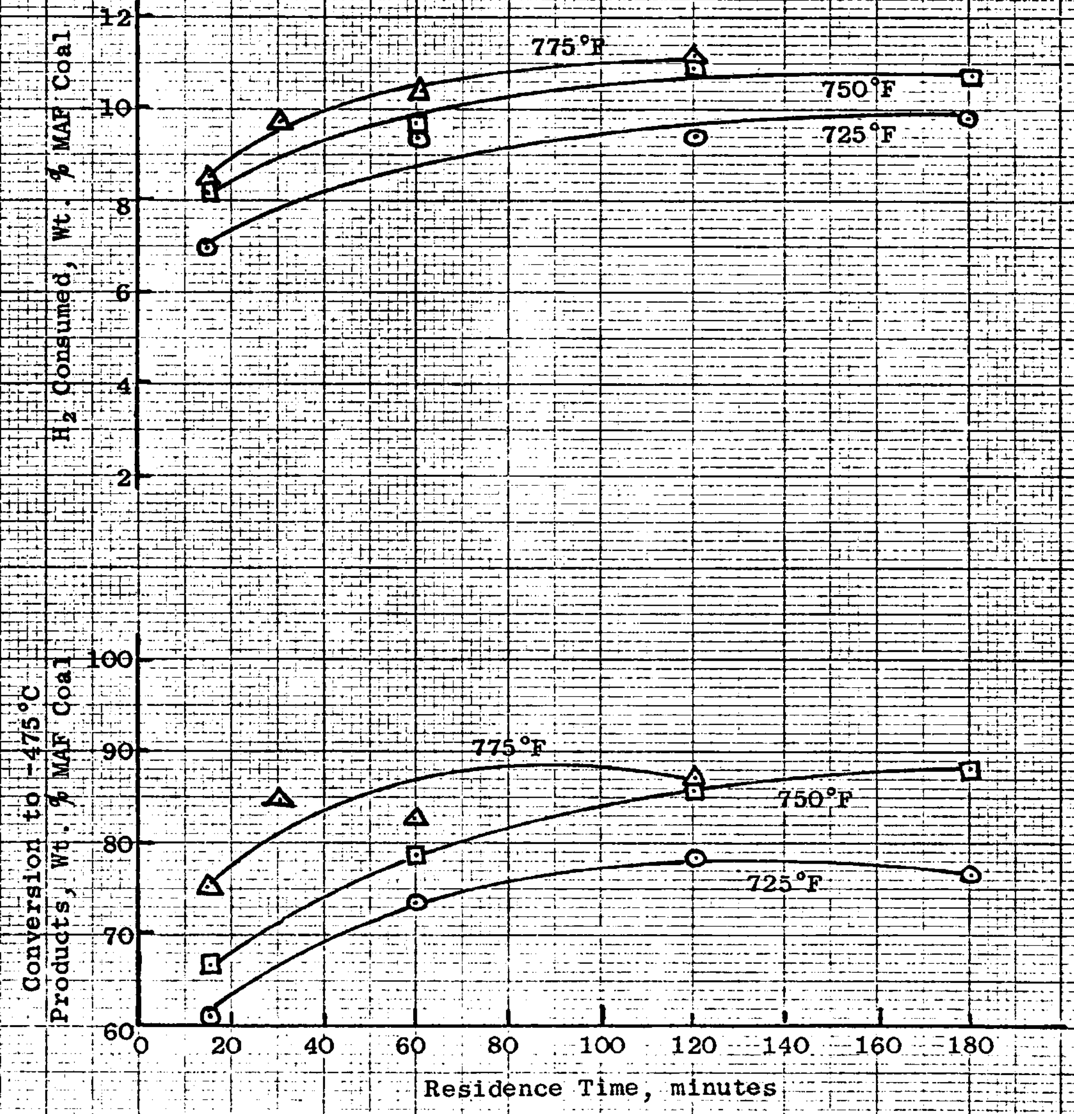


FIGURE 5

BATCH KINETICS STUDY OF HYDROCRACKING -100 MESH COLSTRIP COAL WITH $ZnCl_2$

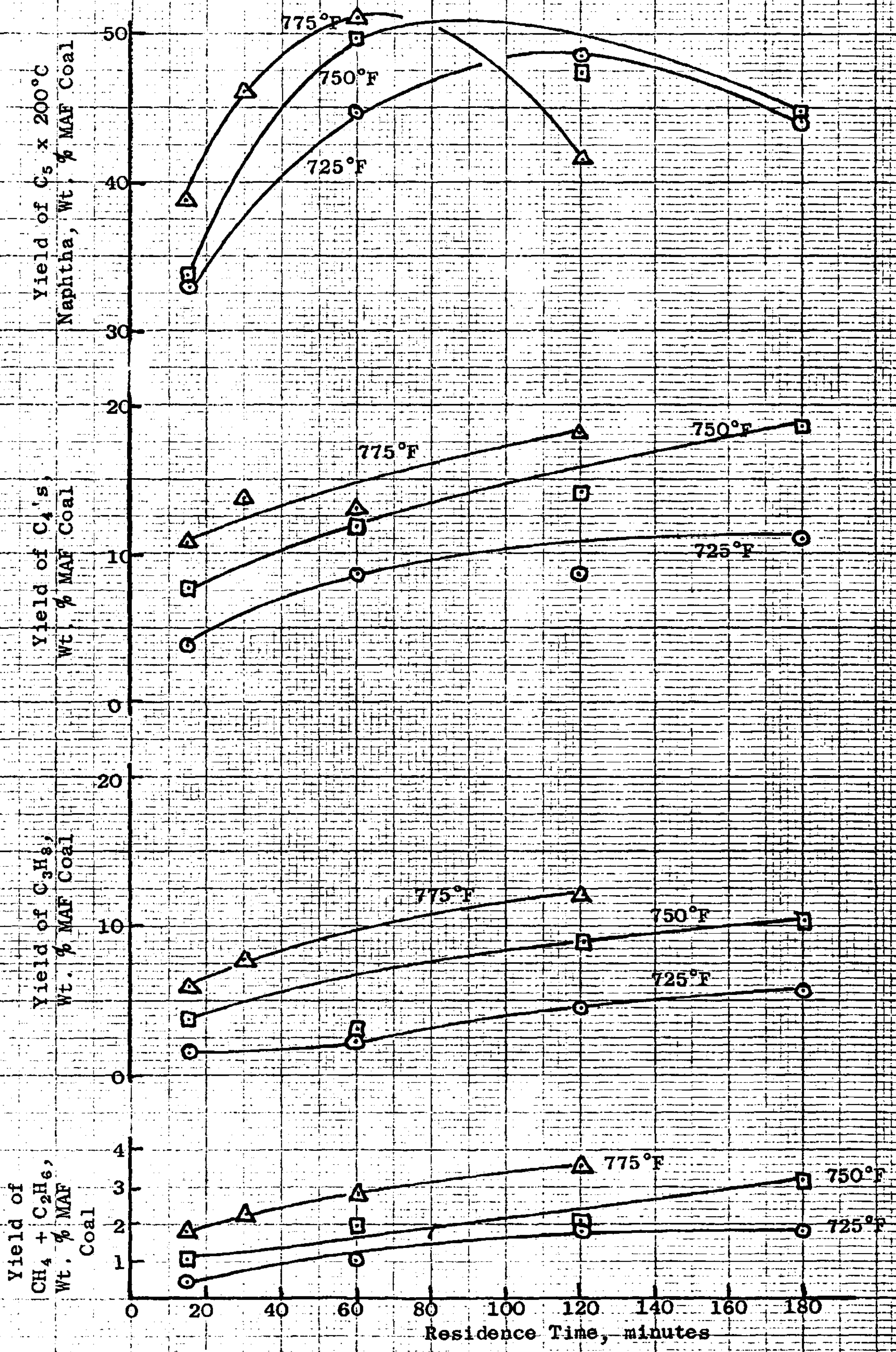
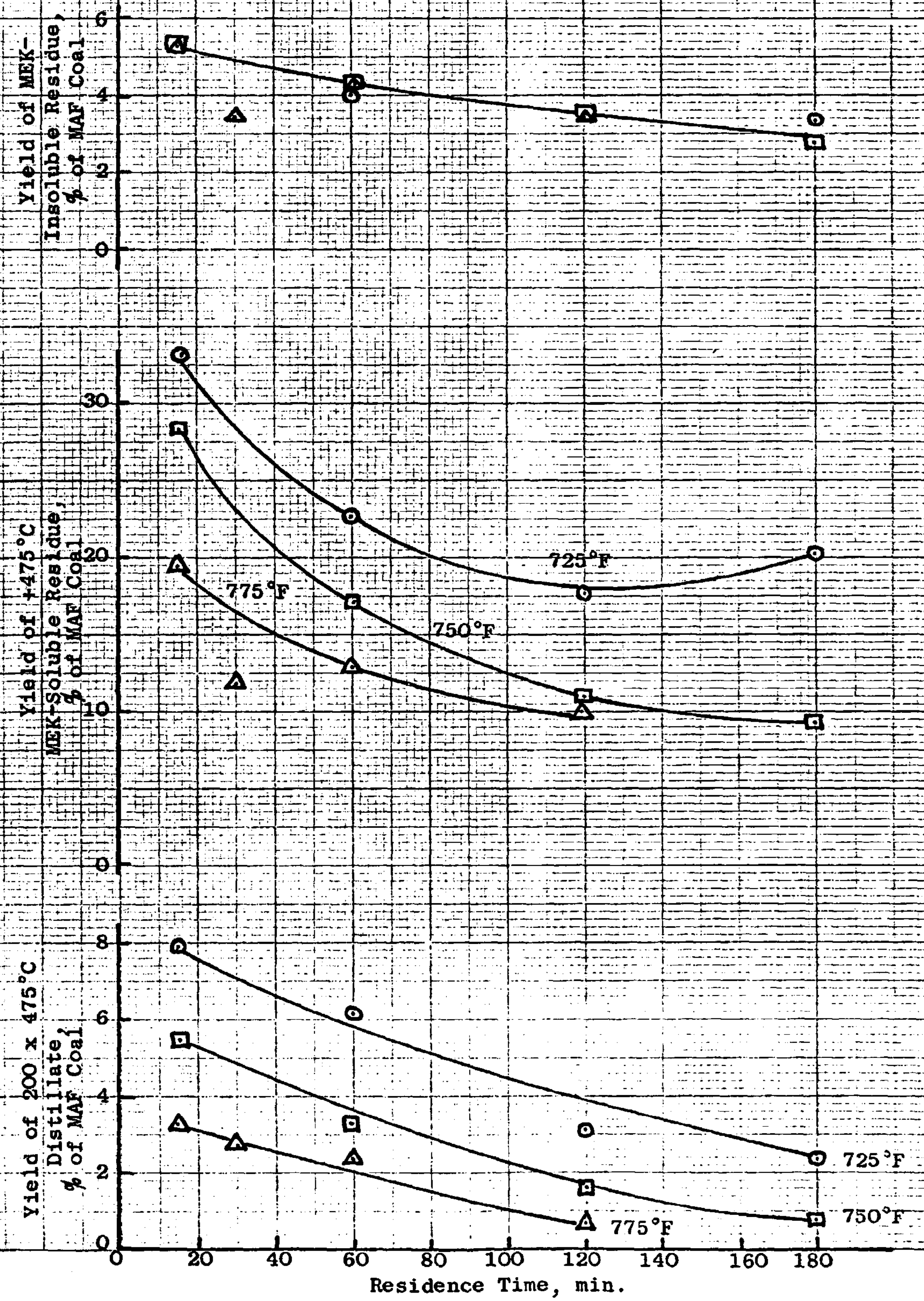


FIGURE 6

Batch Kinetics Study of Hydrocracking -100 Mesh Colstrip Coal with $ZnCl_2$



B. Supporting Work for PDU Design

1. Distillate - Caustic Phase Separation

A short study was made for scrubber design information. Its purpose was to determine whether the overhead distillate, produced during coal or extract hydrocracking, forms stubborn emulsions with caustic solutions when the immiscible phases are subjected to high shear forces such as when the mix is throttled to lower pressure through a valve, or whether reasonably rapid phase separation is obtained. The assessment was made by observing the rate of separation of caustic and overhead distillate oil phases that were mixed in a Waring Blendor. The method and results are given in Table VI. The conclusion is that separation of the two phases may reasonably be expected in two and one-half minutes time or less.

2. Spent-Melt Viscosity Properties

A study of how the spent melt from direct coal hydrocracking behaves with respect to storage stability regarding viscosity and frothing has been initiated.

C. Program for the Next Quarter

The work planned for the next quarter includes:

1. Continuation of the batch autoclave coal hydrocracking kinetics study at 2000 psig hydrogen partial pressure. The existing 3000 psig work may also be expanded to a study at a temperature of 800°F.

2. Another area of work that will be initiated is a batch-type investigation of secondary recovery of zinc and chlorine from the ash obtained in the cyclone underflow of the continuous regenerator. This will consist of experiments in which a batch of ash is treated at 1400-1900°F with a flow of air only or air together with anhydrous HCl to recover zinc contained in the ash as $ZnCl_2$ or other forms.

Task 8a Economic Study of Extract Hydrocracking: Zinc Chloride versus Ebullated Bed

An economic study leading to comparative costs of gasoline produced by alternate routes of zinc chloride ($ZnCl_2$) hydrocracking and ebullated-bed hydrocracking of coal extract was completed.

The process design for the $ZnCl_2$ case was developed from laboratory data on Ireland Mine extract hydrocracking and on laboratory regeneration studies with natural and synthetic spent melts. The process design for the ebullated-bed case was an update of a previous Consolidation Coal Company study. The quality of the data used in developing each case was roughly equivalent. Both designs used the same amount and composition of extract feed - specifically 9080 TPD including 8300 TPD of +475°C extract, 400 TPD of LTC pitch, 300 TPD of extract residue and 80 TPD of LTC char. Make-up hydrogen was assumed to be available. The projected yields of 90 research octane, 10 RVP gasoline were 48,305 BPD from the $ZnCl_2$ process and 45,820 BPD from the ebullated-bed process. Each process produced minor amounts of byproducts.

TABLE VI

Phase Separation Studies of Hydrocracker Overhead Distillate from Caustic Solution After Undergoing High Shear Forces

Apparatus: Waring Blender ~ 25,000 RPM

Feed Materials

1) Whole overhead distillate from bench-scale hydrocracker Run 3B (density of .902 gm/ml at 23°C)
2) 0.1 N NaOH solution
3) 1.0 N NaOH solution

Procedure

1. Stir prescribed amount of distillate and caustic for 1 minute at 25,000 RPM.
2. Turn off stirrer.
3. Determine interface level as a function of time.

Charge to Runs

<table>
<tr><th>Run Number</th><th>1</th><th>2</th><th>3</th><th>4</th></tr>
<tr><td>Dist. Unstirred Charge Depth, inches</td><td colspan="4">← 2.00 →</td></tr>
<tr><td>0.1 N NaOH Unstirred Charge Depth, inches</td><td>.25</td><td>.50</td><td>--</td><td>--</td></tr>
<tr><td>1.0 N NaOH Unstirred Charge Depth, inches</td><td>--</td><td>--</td><td>.25</td><td>.50</td></tr>
</table>

Data

	Interface Level, Inches			
Run Number	1	2	3	4
Before Stirring	.25	.50	.25	.50
Time After Stirring Was Stopped				
0 sec	0	0	0	0
30	.10	.30	.15	.40
60	.20	.35	.20	.45
120	.25	.45	.25	.50
150		.50		

From the process designs, bare equipment costs were estimated. Installation factors or multipliers were then used to convert equipment costs to total installed costs of plants based on the two processes. This portion of the estimate was done by Shell Oil's Cost Estimation Department for both processes. The estimates are internally consistent and are suitable for comparative costs.

The capital estimates were based on a Gulf Coast location with costs adjusted to January 1, 1975. There was no inflation allowance. Construction in the period 1975-1978 was assumed and startup was projected in late 1978. The Gulf Coast basis was selected because equipment costs and installation factors for the Gulf Coast were more readily available to the estimators. The January 1, 1975 base date was selected so that the results would reflect current dollars more closely.

The costs of extract and hydrogen are important factors in estimation of operating costs. Extract was valued at $45/ton and hydrogen at 85¢/MSCF. The value of extract was estimated by CCDC, based on a proprietary, in-house study of coal extraction. The hydrogen cost was based on information submitted by various companies to the FPC for Lurgi coal gasification plants.

Comparative gasoline costs were prepared for two cases. In the SMR (Steam-Methane Reformer) cases, offgas (H_2-C_4H_{10}) was used internally as fuel and the excess was fed to steam-methane reformers to generate hydrogen for the hydrocracking sections of the plants. In both cases additional hydrogen makeup was still required. The SMR cases are convenient for comparison because an assumed fuel value for the hydrocarbon offgases is not required and, by minimizing make-up hydrogen requirements, the comparison is made less sensitive to hydrogen cost.

The second comparison was made on the basis that process offgases are fed to a cryogenic unit which recovers hydrogen for recycle and produces hydrocarbon gas for internal use and for sale at $2.30/MM Btu. The cryogenic cases show a lower cent/gal gasoline cost but are more sensitive to hydrogen and fuel costs.

Percent discounted cash flow was a parameter in the estimates. Gasoline costs were estimated using 10, 13 and 16% DCF for each option and each process. Cash flows over the 20-year process life were discounted to January 1, 1975. Summarized results were as follows:

	$ZnCl_2$	Ebullated-Bed
Feed		
Colstrip Coal Extract, TPSD	9080	9080
Purchase H_2, MM SCFD	170	200
Products		
Gasoline, BPSD	48,300	45,800
Fuel Oil, TPSD	430	1,685
Ammonia, TPSD	--	140
Sulfur, TPSD	--	30
Investment, $ MM	570	610
Operating Costs, $ MM/year	235	240

Percent Saving in Gasoline Cost Using Zinc Chloride vs Ebullated-Bed Processing	Base Case	Alternate Case
at 10% DCF	7.4	13.5
at 13% DCF	8.3	13.7
at 16% DCF	8.9	15.7

In all cases, the gasoline cost by $ZnCl_2$ hydrocracking was lower than the cost by ebullated-bed hydrocracking. Using steam reforming, the $ZnCl_2$ advantage was 7.4 to 8.9 percent. For the cryogenic cases, the $ZnCl_2$ advantage was 13.5 to 15.7 percent. Part of the $ZnCl_2$ advantage stems from a more favorable yield of gasoline (5.5% higher on a volumetric basis). Another advantage of the $ZnCl_2$ process is a 40-65 MM$ lower investment cost which translates to a 1-3¢/gal advantage. The lower investment cost for $ZnCl_2$ occurs because the extra equipment required for regeneration of spent catalyst in the $ZnCl_2$ case is less expensive than the conventional hydrocracker, reformer and hydrotreater required in the ebullated-bed case. Also, the reactors are more expensive in the ebullated-bed case. Operating costs for the competing processes differ in detail but are within 2% or 5 $MM/year.

To summarize, cost estimates considered adequate for differential cost comparisons have been made for both $ZnCl_2$ and ebullated-bed hydrocracking of extract. The $ZnCl_2$ process shows a persistent advantage of 7-16% in cost per gallon of gasoline. This result is quite encouraging.

The next step under Task 8a is an economic comparison of direct hydrocracking of subbituminous coal against hydrocracking of extact, both with $ZnCl_2$ catalyst. Data to be generated in other phases of the zinc halide project are a necessary input to the direct hydrocracking estimate. Accordingly, additional work under Task 8a will be deferred pending availability of data. A probable starting date for the next phase of Task 8a is the fourth quarter of 1976.

IV. PUBLICATION DURING THE YEAR

Hydrocracking of Coal by Molten Zinc Chloride Catalysts. by Everett Gorin, Paper presented to the Spring Symposium of the Pittsburgh Catalysis Society, April 1975 (to be published in the Symposium Proceedings).

V. REFERENCES CITED

1. Gorin, Everett, et al., Research on Zinc Chloride Catalyst for Converting Coal to Gasoline, U.S. Dept. of the Interior R&D Report No. 39, Vol III, Book 1, OCR Contract 14-01-0001-310 with Consolidation Coal Company, 1968.

2. Ditto, Vol III, Book 2, Regeneration of Zinc Chloride Catalyst, 1968.

3. Conoco Coal Development Co., Zinc Halide Hydrocracking Process for Distillate Fuels from Coal, ERDA Contract E(49-18)-1743, Quarterly Technical Progress Report for the Period Jan. 7 to April 30, 1975, May 15, 1975.

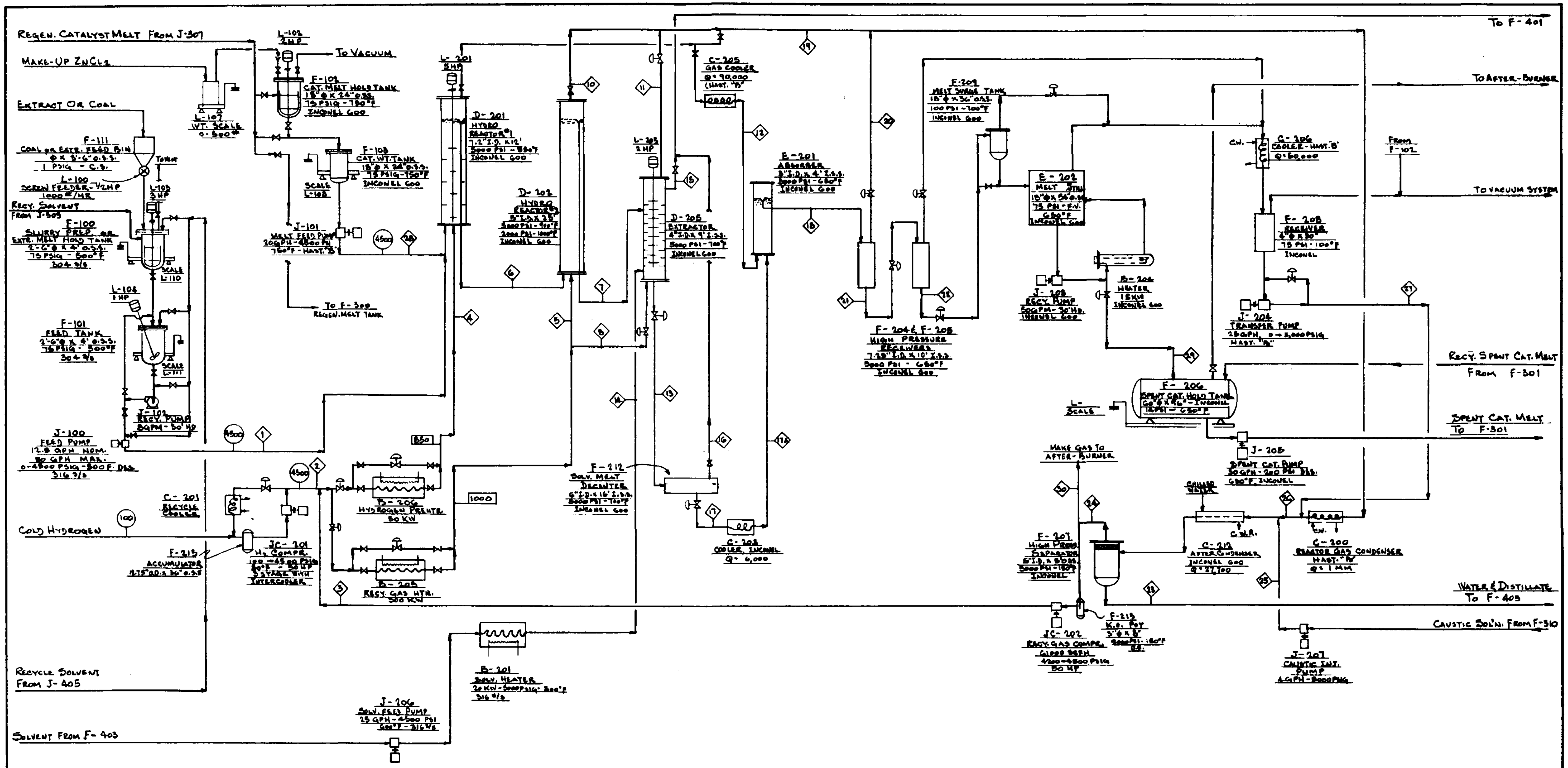
4. Ditto, Quarterly Technical Progress Report for the Period May 1 to July 31, 1975, August 15, 1975.

5. Ditto, Quarterly Technical Progress Report for the Period August 1 to October 31, 1975, November 17, 1975.

APPENDIX

Flow Sheets for PDU

Drawing No.	Description
AF-3658	Hydrocracking Section - Case I
AF-3682	Hydro Letdown Section - Case I
AF-3659	Hydrocracking Section - Case II
AF-3683	Hydro Letdown Section - Case II
AF-3684	Fractionation Section - Both Cases
AF-3676	Regeneration Section - Both Cases



— TABLE OF FLOWS FOR EQUIPMENT SIZING ONLY —

STREAM NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17/17A	18	19	20	21	22	23	24	25	26	27	28	29	30
STREAM DESIGNATION	SLURRY FEED	HYDROGEN FEED	RECYCLE GAS	RX.#1 GAS	RX.#2 GAS	RX.#1 O'FLOW	RX.#2 O'FLOW	EXTR. GAS	RX.#1 O'HEAD	RX.#2 O'HEAD	EXTR. O'HEAD	ABSORB. GAS	EXTR. U'FLOW	SOLV. TO EXTR.	EXTR. O'FLOW	DECANT. O'FLOW	DECANT. U'FLOW	ABSORB. O'FLOW	RX. PROD. GAS	RCY. R. GAS	SPENT MELT L.D	SPENT MELT L.D	COND. U'FLOW	RECYCLE GAS	CAUSTIC NEUT.	COND. PRODUCT	STILL O'HEAD	FEED MELT	SPENT MELT	MAKE GAS
COAL/EXTRACT, #/HR.	100																													
ZnCl2, #/HR.						200	200						100				200	200			200	200						300	200	
RES. ORGANIC/ASH, #/HR.						50	50						50		50	50	20	20			20	20							20	
DISTILLATES, #/HR.	200					250			250	250	50	150	200	200	300	200	50	300	300		75	75	300			300	75			
WATER, #/HR.	5					20			20	20		30						12/20	12/20	12/20	Pr.	Pr.	33.5		13.5	20	20			
HCl, #/HR						1.2			1.2	1.2		1.2						1.2	1.2	1.2	Pr.	Pr.					1.2			
RECYCLE GAS, SCFH			60,000	10,000	50,000	5,000		4,000	6,000	50,000	4,000	6,000						10,000	60,000	10,000				60,000		60,000				5,000
HYDROGEN, SCFH		5,500																												
NaOH, #/HR.																									1.5					
LIQUID/SLURRY, GPM	10-50						20						60																	
TEMPERATURE, °F	200/500	60	60	850	850/1000	850	725	600	850	850	600	500	600	500	850	600	600/500	600	850	500	600	600	100	100	100	100	150	700	600	100
PRESSURE, PSIG	5,000	3,000	5000/3000	5,000	5000/3000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	Atm.	5,000	Atm.	5,000/5,000

LEGEND:
◇ STREAM NUMBER
○ PRESSURE, PSIG
▭ TEMPERATURE, °F

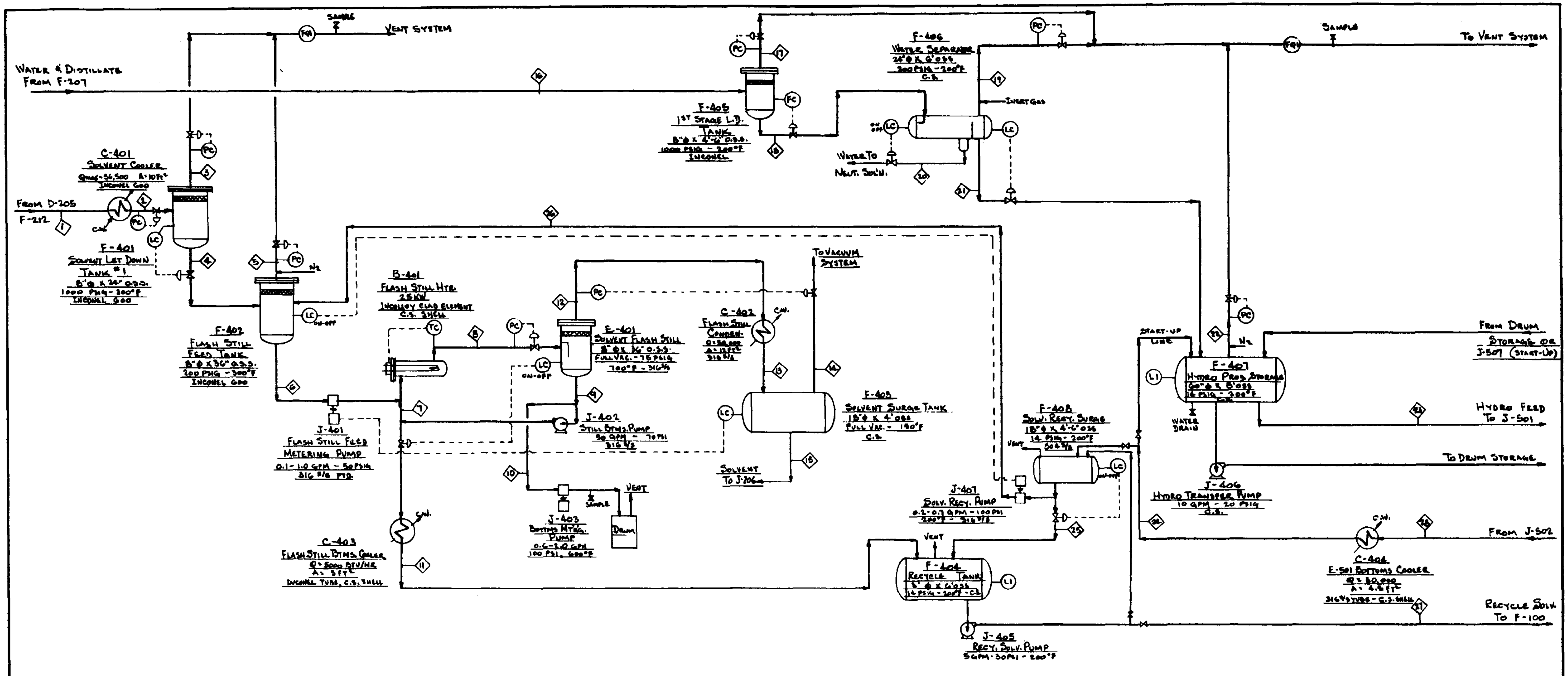
Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date 9-18-75
Drn.
Chk.
App.
Issued For Const.

Conoco Coal Development Co.
Research Division
Library, Pennsylvania

PROCESS FLOW DIAGRAM — CASE I
PDU SECTION 100 & 200
ZnCl2 HYDROCRACKING

Scale	Project No.	Drawing Number	Rev.
NONE	517.00	AF-3658	



OPERATION WITH SOLVENT EXTRACTION
TABLE OF FLOWS FOR EQUIPMENT SIZING ONLY

STREAM NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
DESCRIPTION	SOLVENT	SOLVENT	VENT GAS	LET DOWN SOLVENT	VENT GAS	SOLVENT FEED TO FLASH	FLASH BOTTOMS RECYCLE	TOTAL FLASHSTILL FEED	TOTAL FLASH BOTTOMS	+400°C PURGE	EXCESS SOLVENT & +400°C	FLASHSTILL VAPOR	CONDENSED VAPOR	VACUUM GAS
°F	550	200	200	200	200	200	300	570-560	500	500	200	500	150	150
PSIA	4000	4000	75	75	50	50	50	50	3.9	75	20	3.9	2.9	2.9
STATE	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Gas	Liquid	Gas
GPM	0.31-0.25	0.27-0.22	-	0.27-0.22	-	0.4-0.3	0.42	0.9-0.73	0.49	0.01-0.03	0.06-0.03	-	0.33-0.28	-
SCFH	-	-	88-70.5	-	20	-	-	-	-	-	-	328-253	-	2
lb/hr TOTAL	*126.5-100.4	126.5-100.4	0.6-0.4	125.9-100.0	1.6	188.6-140.5	200	388.7-340.5	232.7-225.3	5.0-11.5	27.7-14.0‡	156.0-115	156-115	Trace
H_2	0.5-0.4	0.5-0.4	0.5-0.4	Tr-Tr										Trace
CO														
CO_2														
C_1														
C_2														
C_3														
C_4														
C_5-150	3-{2	3-{2		3-{2										
150-200			Tr-Tr			3-2		3-2				3-3	3-2	—
200-400	110-83	110-83	0.1-0.0	109.9-83		163.1-118.9	80-69.4	243.1-188.3	93.1-78.3	2-4	11.1-4.9	150-110	150-110	
+400	13-15	13-15		13-15		22.6-19.6	120-130.6	142.6-150.2	139.6-147.2	3-7.5	16.6-9.1	3-3	3-3	
H_2O														
N_2					1.6									
											‡Average			

STREAM NUMBER	15	16	17	18	19	20	21	22	23	24	25	26	27	28
DESCRIPTION	SOLVENT TO J-206	WATER AND DISTILLATE	VENT GAS	DISTILLATE	VENT GAS	WATER	LET DOWN DISTILLATE	VENT GAS	DIST. FEED TO FRACT.	COOLED +200°C FROM FRACT.	EXCESS +200°C	+200°C FEED TO FLASH SURGE	RECYCLE SOLVENT TO F-110	+200°C FROM FRACT.
°F	150	100	100	100	100	100	100	100	100	200	200	200	200	600
PSIA	40	300	300	300	45	45	45	20	20	30	60	60	60	35
STATE	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Liquid	Gas	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
GPM	0.33-0.28	0.68-0.37	-	0.68-0.37	-	0.04-0.02	0.65-0.35	-	0.64-0.34	0.28-0.13	0.12-0.04	0.13-0.08	0.18-0.07	0.30-0.18
SCFH	-	-	104-85	-	20-20	-	-	20-20	-	-	-	-	-	-
lb/hr TOTAL	156-115	283.6-154.4	1.3-2	282.4-152.4	1.1-1.6	20-10‡	262-141	1.4-2.4	262-136.9	124-61	61.3-21.5‡	62.7-40.6‡	69-34.5‡	124-61‡
H_2		0.6-0.4	0.5-0.4	0.1-Tr	0.1-Tr		Tr-Tr	Tr-Tr	-					
CO		0.2- -	0.1- -	0.1- -	Tr- -		0.1- -	Tr- -	0.1- -					
CO_2		0.3- -	0.1- -	0.2- -	0.1- -		0.1- -	Tr- -	0.1- -					
C_1		- -0.5	- -0.3	- -0.2	- -0.1		- -0.2	- -Tr	- -0.1					
C_2		0.5-1	0.1-0.3	0.4-0.7	0.1-0.3		0.3-0.4	Tr-0.3	0.3-0.1					
C_3		1.5-4.5	0.1-0.5	1.4-4	0.1-0.6		1.3-3.4	Tr-1	1.3-2.4					
C_4		4.5-8	0.2-0.5	4.3-7.5	Tr-0.4		4.3-7.1	Tr-0.9	4.3-6.2					
C_5-150		45}-66	0.1	44.9}66	- -Tr		44.9}66	- -Tr	44.9}66					
150-200	3-2	81	-	81	-		81		81	Tr-Tr	Tr-Tr	Tr-Tr	Tr-Tr	Tr-Tr
200-400	150-110	111-57	-	111-57		-	111-57	-	111-57	105-54	51.9-16.1	53.1-35.5	43-23	105-54
+400	3-3	19-7	-	19-7		-	19-7	-	19-7	19-7	9.4-2.4	9.6-4.6	26-11.5	19-7
H_2O		20-10	-	20-10		20-10		-						
N_2					0.7-0.2			1.4-0.3					‡Avg. Rate	‡Assumed
						*Average					‡Average	‡Average		

*First value-Coal case
Second value-Extract case

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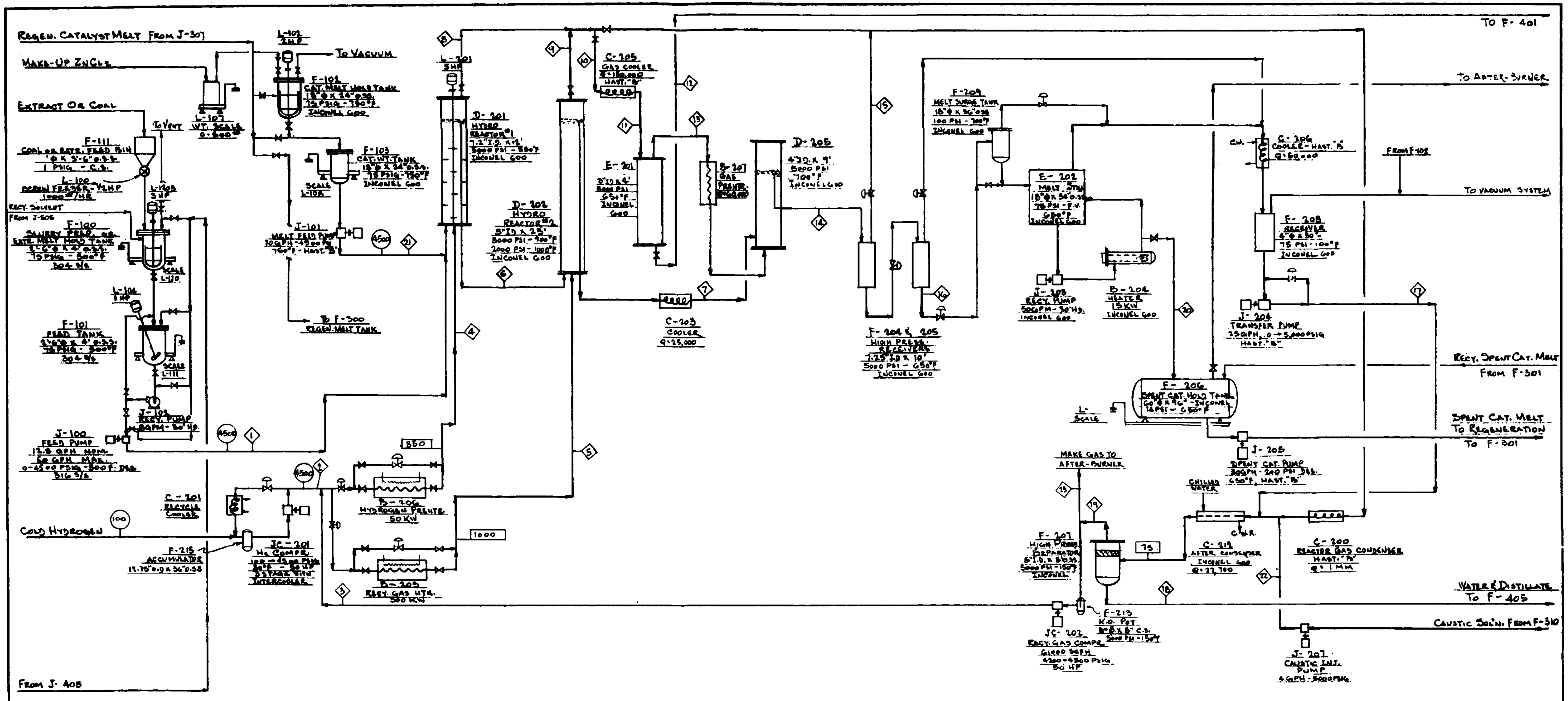
Research Division
Library, Pennsylvania

PROGRESS FLOW DIAGRAM
PDU SECTION 400 HYDRO LET DOWN
CASE I

Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date	1-26-76
Drn.	
Chk.	
App.	
Issued For Const.	

Scale	Project No.	Drawing Number	Rev.
NONE	517.00	AF-3682	



– TABLE OF FLOWS FOR EQUIPMENT SIZING ONLY –

STREAM NO.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
STREAM DESIGNATION		SLURRY FEED	HYDROGEN FEED	RECYCLE GAS	RX.#1 GAS	RX.#2 GAS	RX.#1 O'FLOW	RX.#2 O'FLOW	RX.#1 GAS	RX.#2 GAS	PRODUCT GAS	COOLED GAS	CONDENSATE	STRIPPED GAS	ABS. O'FLOW	MAKE GAS	SPENT MELT L.D.	STILL O'HEAD	COND. U'FLOW	RECYCLE GAS	SPENT MELT	FEED MELT	CAUSTIC NEUT.	MAKE GAS
COAL/EXTRACT,	#/HR.	100																						
$ZnCl_2$,	#/HR.						200	200							200		200				200	200		
RES. ORGANIC/ASH,	#/HR.						50	50							50		50				50			
DISTILLATES,	#/HR.	200					250		250	250	250	250	200	250	100	200	100	100	300	Tr				
WATER,	#/HR.	5					20		12/20	12/20	12/20	12/20		12/20	12/20	12/20	Tr	Tr.	12/20	Tr			13.5	
HCl,	#/HR.						1.2		1.2	1.2	1.2	1.2		1.2	1.2	1.2	1.2	1.2	1.2					
RECYCLE GAS,	SCFH			8,000	5,000	5,000	5,000		5,000	10,000	10,000	10,000		10,000	10,000	10,000				10,000				1,000
HYDROGEN,	SCFH		3,000																					
NaOH,	#/HR.																						1.5	
LIQUID/SLURRY,	GPH	10-50						20																
TEMPERATURE,	°F	200/500	850	850/1000	850	850/1000	850	775	850	850/1000	900	300/500	300	300/500	650	650	650	150	80	80	600	600	100	80
PRESSURE,	Psig	5,000	5,000	5000/2000	5,000	5000/2000	5,000	5,000	5,000	5000/2000	5,000	5,000	5,000.	5,000	5,000	5,000	5,000	Atm.	Atm.	5,000	Atm.	Atm.	5,000	5,000

LEGEND:

◇ STREAM NUMBER

○ PRESSURE, PSIG.

▭ TEMPERATURE, °F

Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date 9-18-75
Drn.
Chk.
App.
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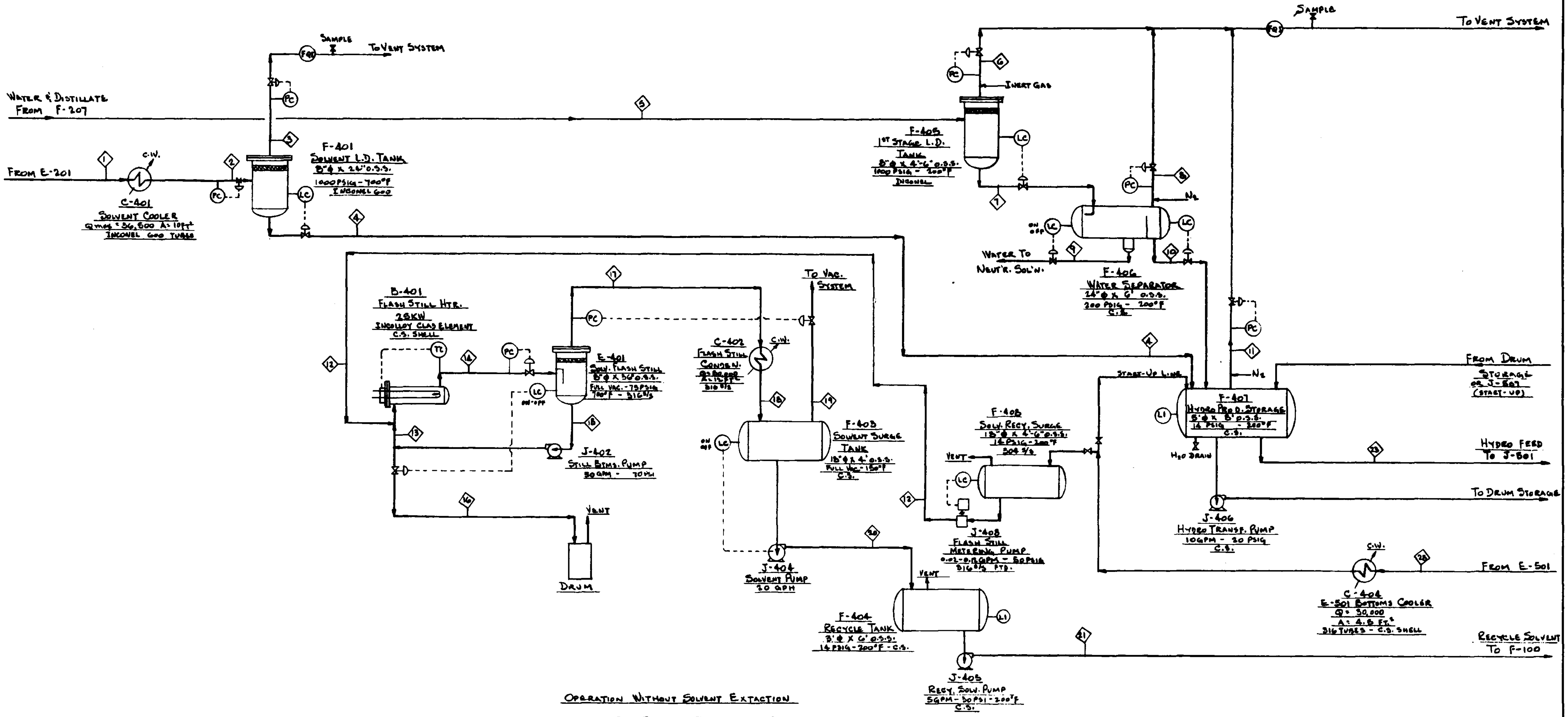
PROCESS FLOW DIAGRAM – CASE II
PDU SECTION 100 & 200
ZnCl2 HYDROCRACKING

Scale	Project No.	Drawing Number	Rev.
NONE	517.00	AF-3659	



Operation Without Solvent Extaction

Table Of Flows For Sizing Equipment Only

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	23	28
Description	Solvent	Solvent	Vent Gas	L/D Solvent	Water + Distillate	Vent Gas	L/D Distillate	Vent Gas	Water	L/D Distillate	Vent Gas	+200°C Feed To Flash Still	Flash Bottoms Recycle	Total Flash Feed	Flash Bottoms	+400°C Purge	Flash Still Vapor	Condensed Flash Vapor	Vacuum Gas	Recycle +200°C	Recycle +200°C to F-110	Dist. Feed to Fract'n	+200°C From Fract'n
°F	400	100	100	100	100	100	100	100	100	100	100	200	500	510-535	500	500	500	150	150	150	150	100	600
PSIA	4000	4000	100	100	300	300	300	45	45	45	20	40	40	40	3.9	15.0	3.9	2.9	2.9	20	60	20	25
State	Liquid	Liquid	Gas	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Liquid	Gas	Liquid	Liquid	Liquid	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Liquid	Liquid	Liquid
GPM	0.26-0.10	0.23-0.09		0.23-0.09	0.41-0.21	-	0.40-0.20	-	.06-.01	0.34-0.19	-	0.03-0.10	0.42-0.43	0.45-0.56	0.43-0.45	0.01-0.02	-	0.02-0.06	-	0.02-0.09	0.02-0.09	0.38-0.29	0.04-0.12
SCFH	-	-	.07-53.5	-	-	86-87	-	20-20	-	-	20-20	-	-	-	-	-	22-85	-	2	-	-	-	-
Lbs/Hr																							
Total	*91.6-43.7	91.6-43.7	0.9-0.4	90.7-43.3	162.2-82.9	2.3-2.9	159.9-80	1.5-1.6	♦27.3-6	132.5-73.6	1.6-2.6	13.7-48.4	200	213.7-248.4	204.4-206.9	♦4.4-6.9	9.3-41.5	9.3-41.5	-	♦9.3-41.5	*9.3-41.5	222.5-113.7	13.7-48.4
H_2	0.6-0.3	0.6- .3	0.6-0.3	Tr-Tr	0.4-0.4	0.4-0.4	- -Tr	Tr-Tr		-	Tr-Tr								Tr			- - -	
CO					0.2-	0.1-	0.1-	Tr-		0.1-	Tr-											0.1-	
CO_2					0.3-	0.1-	0.2-	Tr-		0.2-	0.1-											0.1-	
C_1					0.4-0.2	0.2-0.2	0.2-Tr	Tr-Tr		0.2-Tr	0.1-Tr											0.1-Tr	
C_2					0.9-0.9	0.7-0.8	0.2-0.1	Tr-Tr		0.2-0.1	Tr-0.1											0.2-Tr	
C_3					2.8-4.7	0.3-0.8	2.5-3.9	Tr-0.1		2.5-3.8	0.9-1.2											2.3-2.6	
C_4					9.0-8.2	0.5-0.7	8.5-7.5	0.1-0.1		6.4-7.4	0.5-1.1											8.1-6.3	
C_5-150	14-4	14-4	0.3-0.1	13.7-3.9	33.6-36		33.6-35			33.6-35	- -Tr											47.3-38.9	
150-200	69-4.3	69-4.3	Tr-Tr	69-4.3	85.3-11.8		85.3-11.8			85.3-11.8	-	4-0.8	3.2-	7.2-0.8	3.3- -	0.1 -	3.9-0.8	3.9-0.8		3.9-0.8	3.9-0.8	154.3-16.1	4 -0.8
200-400	4-30	4-30	-	4-30	2.0-14.8		2-14.8			3-14.8	-	5.7-42.8	35.8-84	44.5-126.6	39.6-85.9	0.8-2.9	4.9-39.7	4.9-39.7		4.9-39.7	4.9-39.7	8-44.8	5.7-42.6
+400°C	4-4.1	4-4.1	-	4-4.1	-0.9		- -0.9			- -0.9	-	4-5	158-116	162-121	161.5-120	3.5-4.	0.5-1	0.5-1		0.5-1	0.5-1	4-6	4-5
H_2O	-	-			27.3-6		27.3-6		27.3-6		-												
N_2								1.4-1.4			0.9-0.2										*Average		
									♦Average							♦Average				♦Average			

* First Value - Coal Case
Second Value - Extract Case

Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date 1-26-76
Drn.
Chk.
App.
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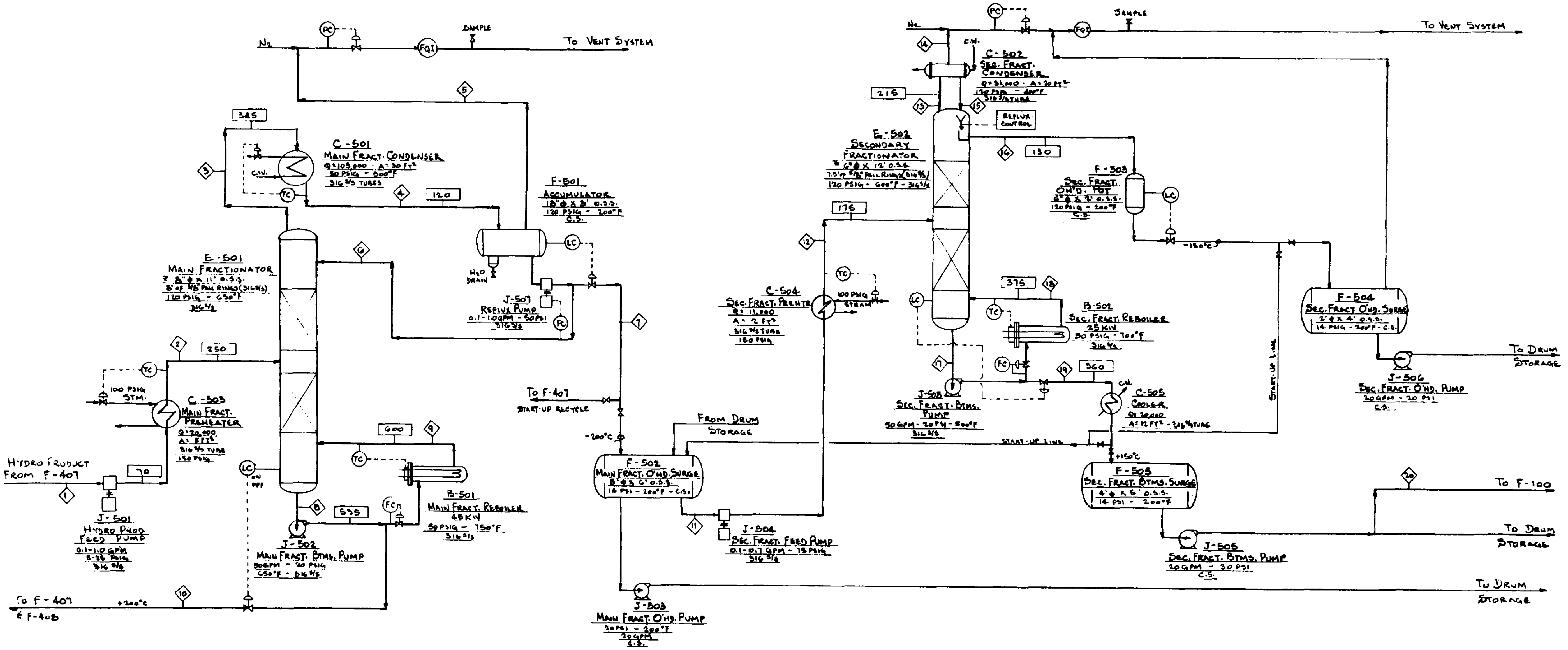
Process Flow Diagram
PDU Section 400 Hydro Let Down
Case II

Scale	Project No.	Drawing Number	Rev.
None	517.00	AF-3683	



Section 500 For Equipment Sizing Only

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Service	Feed to E-501	Heated Feed to E-501	Overhead Vapor to Condenser	Cond. Overhead Vapor	Uncond. Gas to Vent	Reflux	E-501 Overhead Product	E-501 Bottoms Total	Reboiler Liq-Vap to Column E-501	E-501 Bottoms Product	Feed to E-502	Hot Feed to E-502	E-502 Overhead Vapor	Overhead Gas to Vent	Reflux to E-502	E-502 Overhead Product	E-502 Bottoms Total	Reboiler Liq-Vap to Column E-502	E-502 Bottoms Product	150-200°C Material to F-100
°F	70	250	345	120	120	120	120	535	600	510-560	70-120	175	215	110	110	130	360	375	330-360	100°F
PSIA	20	25	24	23	23	24	23	26	26	40	20	24	23	22	23	23	26	26	40	40
State	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Liquid	Liquid	Gas-Liquid (Two Phase)	Liquid	Liquid	Liquid	Gas	Gas	Liquid	Liquid	Liquid	Gas-Liquid (Two Phase)	Liquid	Liquid
GPM	0.24-0.56	0.20-0.61	-	1.06	-	0.57	0.52	2.28		0.02-0.33	0.31-0.51	0.33-0.54	-	-	0.59	0.13-0.15	1.36		0.23-0.43	0.17-0.35
SCFH	-	-	1348	-	4-27	-	-	-		-	-	-	640	4-18	-	-	-		-	-
Lbs/Hr	113-262	113-282	431	431	0.5-3	230	210	843	716	10-130	130-212	130-212	151	0.5-2	151	49-88	480	336	89-154	73-150
Max. or Range of All cases	Range	Range	Max	Max	Range	Max	Max	* Max	* Max	Range	Range	Range	Max	Range	Max	Range	* Max	* Max	Range	Range Avg. Rate

* Does Not Include Liquid Recirculated To Column

Legend

◇ Stream Number

○ Pressure, PSIG

▭ Temperature, °F

Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date 1-26-76
Drn.
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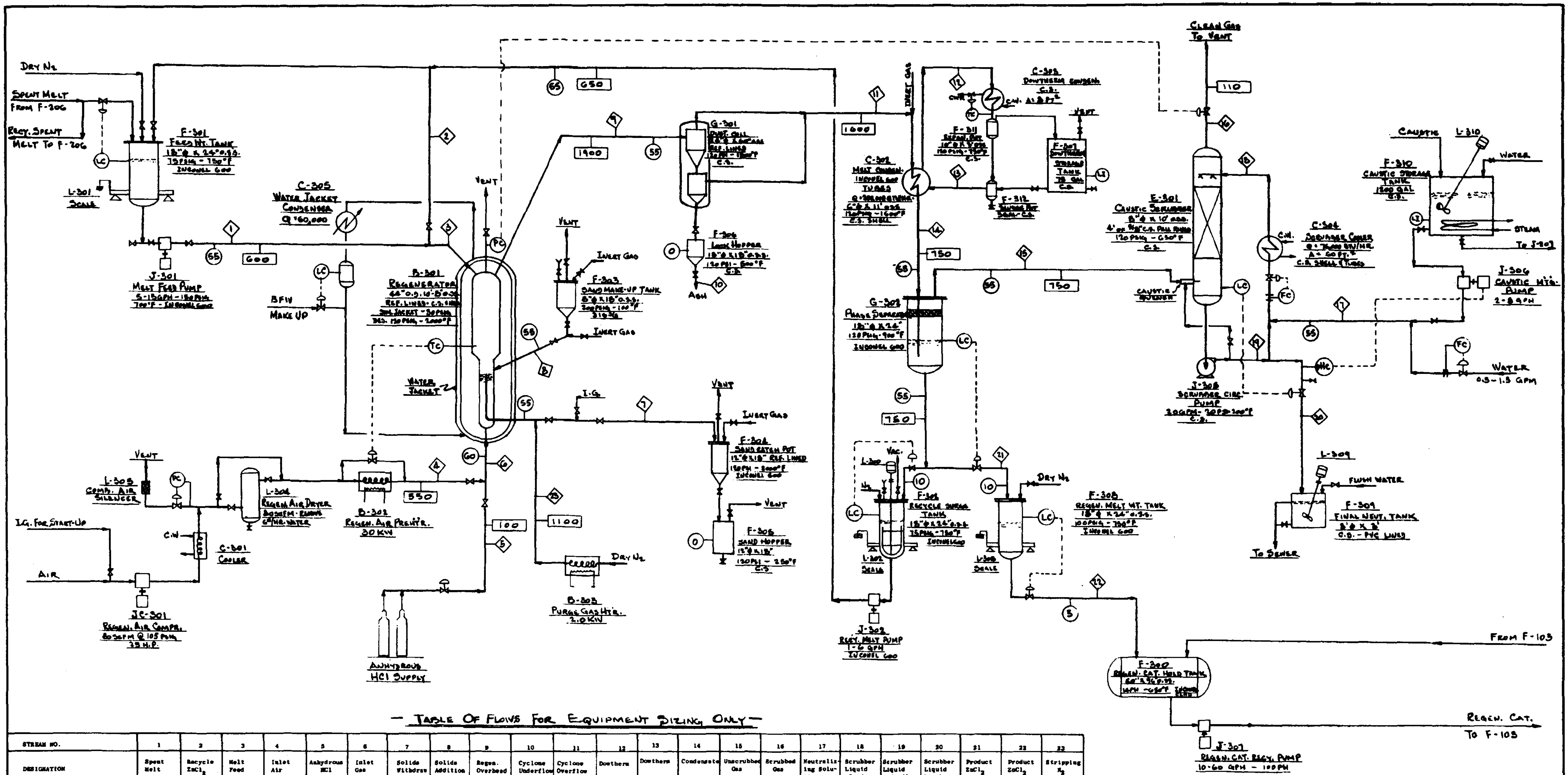
Process Flow Diagram
PDU Section 500 Product Fractionation

Scale	Project No.	Drawing Number	Rev.
None	517.00	AF-3684	



– TABLE OF FLOWS FOR EQUIPMENT SIZING ONLY –

STREAM NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
DESIGNATION	Spent Melt	Recycle $ZnCl_2$	Melt Feed	Inlet Air	Anhydrous HCl	Inlet Gas	Solids Withdraw	Solids Addition	Regen. Overhead	Cyclone Underflow	Cyclone Overflow	Dowtherm	Dowtherm	Condensate	Unscrubbed Gas	Scrubbed Gas	Neutralizing Solution	Scrubber Liquid Feed	Scrubber Liquid Underflow	Scrubber Liquid Discharge	Product $ZnCl_2$	Product $ZnCl_2$	Stripping N_2
STATE	Liquid	Liquid	Liquid	Gas	Gas	Gas	Solid	Solid	Gas	Solids	GAS	Vapor/Liq.	Liquid	Gas/Liquid	Gas	Gas	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Gas
NORMAL OPERATING RANGE																							
GPM	0.13-0.22	0-0.09	0.13-0.24	-	-	-	-	-	-	-	-	-		0.09-0.18	-	-	0.5-1.5	8-12	8-12	0.6-1.6	0.09-0.20	0.09-0.30	-
SCFS	-	-	-	0.6-1.2	0.04-0.06	0.6-1.3	-	-	0.7-1.4	-	0.7-1.4		-	0.6-1.2	0.6-1.2	0.6-1.2	-	-	-	-	-	-	0.005-0.01
ACFS	-	-	-	0.4-0.5	0.02	0.4-0.5	-	-	1.2-1.4	-	1.2-1.4		-	0.5	0.5	0.3	-	-	-	-	-	-	0.008
Temp. °F	600	650	600	350-550	100	350-550	1800-1900	AMB	1800-1900	1400-1800	1400-1800	650	650	750	750	100	AMB	97	110	110	750	650	1100
Pressure PSIG	25-55	25-55	25-55	25-55	25-55	25-55	25-55	25-55	25-55	25-55	25-55	55	36	25-55	25-55	25-55	25-55	25-55	25-55	25-55	0-55	0-30	25-55
lbs/hr																							
Total	114-236	0-104	114-263	155-305	10-25	165-330	16	13	287-600	2-17	288-587	10000-24000	10000-20000	288-587	186-353	168-313	250-750	4000-6000	4000-6000	300-800	100-104	100-345	1-3
$ZnCl_2$	100-200	0-100	100-225	-	-	-	trace	-	100-225	-	100-225	-	-	100-225	trace	-	-	-	-	-	100-200	100-339	-
Ash	1-14	0-2	1-14	-	-	-	3	-	1-14	1-12	1-2	-	-	1-2	trace	-	-	-	-	-	0-2	0-3	-
HCl	trace	trace	trace	-	10-25	10-25	trace	-	10-25	trace	10-25	-	-	10-25	10-25	trace	-	-	-	-	-	-	-
Hydrocarbons (C,H,O,N,S)	13-22	0-2	13-24	-	-	-	trace	-	0-4	0-2	0-4	-	-	0-4	-	-	-	-	-	-	0-2	0-3	-
Solids (SiO_2, ZnO)	-	-	-	-	-	-	13	13	1-4	1-3	1-3	-	-	1-3	-	-	-	-	-	-	-	-	-
Gases (O_2, N_2, CO_2, CO)	-	-	-	155-305	-	155-305	-	-	160-300	-	160-300	-	-	160-300	160-300	160-300	-	-	-	-	-	-	1-3
Water	-	-	-	trace	-	trace	-	-	15-25	trace	15-25	-	-	15-25	15-25	7-10	236-712	3800-5700	3800-5700	280-760	-	-	-
SO_2	-	-	-	-	-	-	-	-	1-3	-	1-3	-	-	1-3	1-3	1-3	-	-	-	-	-	-	-
Chemicals (NaOH, NaCl)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	14-38	100-300	100-300	15-40	-	-	-

LEGEND:
◇ STREAM NUMBER
○ PRESSURE, PSIG
▭ TEMPERATURE, °F

Dwg. No.	Reference Drawings	No.	Date	Revision	By	Chk.	App.

Date 1-13-76
Drn.
Chk.
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PROCESS FLOW DIAGRAM
PDU – SECTION 300 - MELT REGENERATION

Scale	Project No.	Drawing Number	Rev.
NONE	51700	AF-3676	