

**ZINC HALIDE HYDROCRACKING PROCESS
FOR DISTILLATE FUELS FROM COAL**
**Quarterly Technical Progress Report
for the Period:
February 1 to April 30, 1976**

-NOTICE-

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ABSTRACT

Continuous hydrocracking of subbituminous coal with zinc chloride was demonstrated at zinc chloride-to-coal ratios of 2.0, 1.5 and 1.0. This bench-scale unit is now engaged in producing 300 pounds of spent catalyst for regeneration studies; 197 pounds are in hand at the end of April.

The continuous bench-scale regenerator made eight runs with synthesized melt and three runs with natural spent catalyst melt. The natural melt was found to have a somewhat lower sintering temperature than the synthesized one, but a successful regeneration of natural melt was demonstrated at 1700°F with good carbon removal.

Reliability of the bench-scale units is much improved over earlier experience, the only significant failure being in the low-pressure system when zinc chloride vapor is condensed.

Significant progress was made in assuring high recovery of zinc in the regeneration process. The coal ash, which is recovered via a cyclone from the regenerator offgases contains between 0.5 and 1.5% of the zinc fed. Batch tests have shown that up to 99% of this zinc can be stripped out as zinc chloride by treatment of this coal ash with 10% HCl in nitrogen at cyclone temperature. Since this is the only major place for zinc loss, the potential recovery of zinc can be up to 99.98% of that fed to regeneration.

Results of the batch kinetics study on zinc chloride hydrocracking of subbituminous coal are reported for 2000 and 3000 psig at temperatures of 725, 750 and 775°F.

Process design of a 100 lb/hr Process Development Unit has been completed and engineering design is underway.

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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 18 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

Successful operation of the continuous bench-scale hydrocracker was demonstrated using zinc chloride-to-coal ratios of 2.0, 1.5 and 1.0. The Colstrip coal was fed in 240 x 395°C aromatic solvent using a 1.5 ratio of solvent-to-coal. The emphasis was then shifted to preparation of 300 pounds of spent catalyst from coal hydrocracking with zinc chloride - to be used for regeneration studies. In order to also produce distillates representative of that from coal only, the vehicle for coal feeding was changed to benzene containing 8% polystyrene. This vehicle produces light, identifiable products in hydrocracking, and was successful as a vehicle when the coal concentration was lowered to 25 to 30%. One hundred and ninety seven pounds of spent melt have been produced. Some pumping failures caused interruptions largely due to more rapid wear on the check valve seats with the benzene vehicle. Runs up to 32 hours in length were obtained, limited by pumping problems or eventual plugging of coal vent lines from low-pressure melt receivers. The only failures due to stress corrosion occurring in the high-pressure sections since converting the distillate lines to Inconel 600 have been a 316 ss stirrer shaft and a 316 ss overflow tube in the reactor.

The continuous bench-scale regenerator explored a number of operating variables as they affect zinc and chlorine recovery. The eight additional runs this quarter with a synthesized spent melt produced the following conclusions:

1. Cyclone temperature between 1350 and 1650°F had no effect on zinc recovery.
2. A small gas flow out the bottom of the cyclone helped maintain cyclone operation.
3. The cyclone operated successfully without frequent hammering, but efficiency of solids collection decreased somewhat.
4. Increasing the mol percent HCl in the feed air to the regenerator decreased the zinc retained in the cyclone solids.
5. Increased amounts of ash in the melt fed resulted in only a slight increase in zinc retained in recovered ash. From 0.56 to 1.34% of feed zinc was collected with the cyclone solids, and only 0.03 to 0.11% was collected by the bed solids. The fraction of chlorine retained by solids was even less.
6. Adding ferrous chloride (4% of the feed melt) had no effect on operability. Over half of the iron was retained by solids, indicating an equilibrium situation where FeCl_2 would not be expected to build up in the recycled catalyst.

Run conditions and details of the product properties and distributions of zinc and chlorine are given.

Three regeneration runs (two in May) have been made with natural spent melt produced by zinc chloride hydrocracking of subbituminous coal at 775°F and 3500 psig. The first two runs showed sintering of the coal ash in the 1800°F bed. The 1700°F run was normal in all respects and showed good carbon burnout. The lower sintering temperature with the natural melt versus

the synthesized melt (which used oxidized ash from the same coal) is believed to be due to formation of chlorides of alkali or alkaline earths in the hydrocracker. This may reverse in the regenerator if sufficient fine silica and alumina from the coal is present. Further runs will be made to define the operating limits and demonstrate high recovery of zinc and chlorine.

The regeneration equipment held up well except for two points:

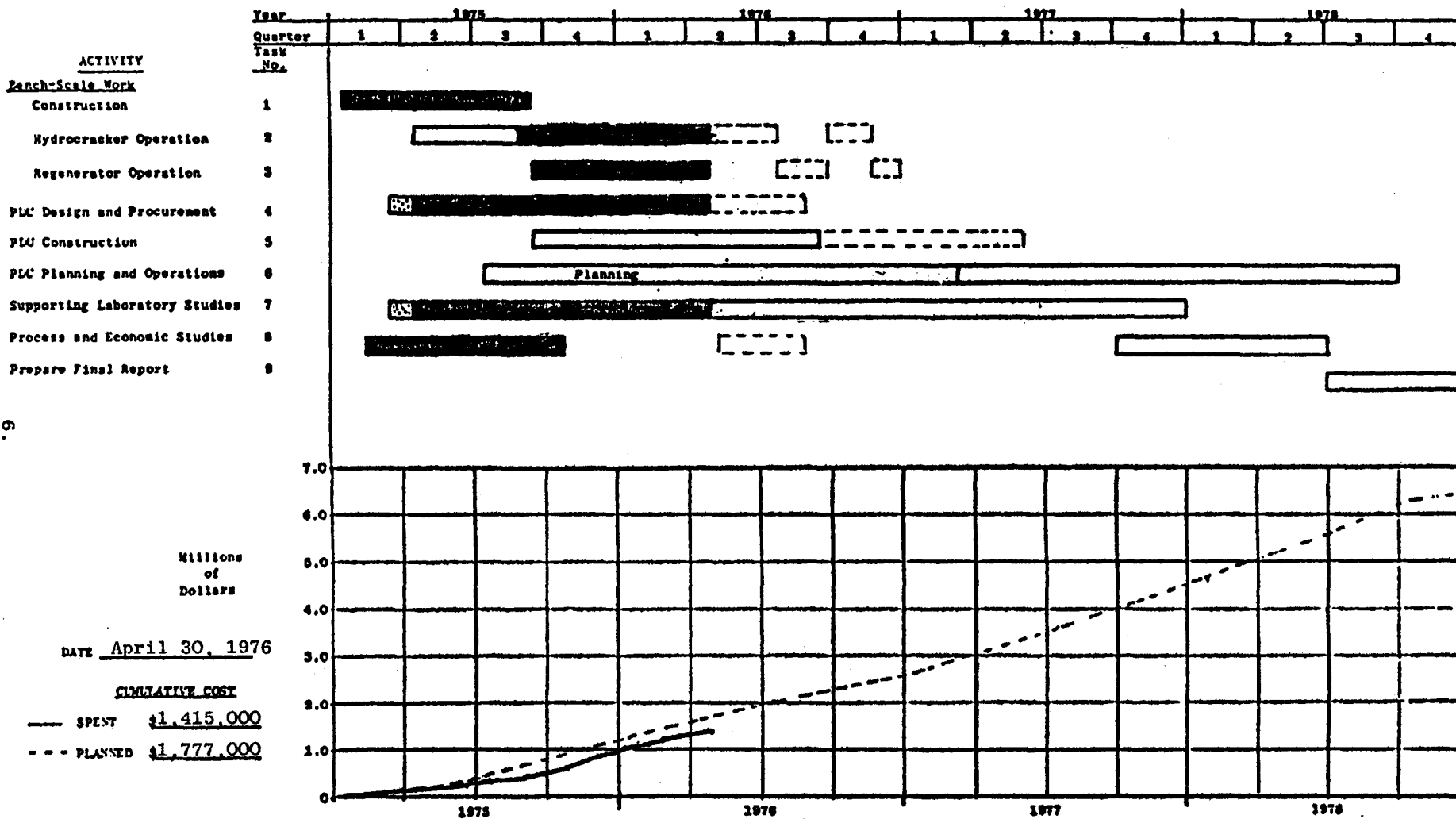
1. The Inconel 600 tube which conducts entering air and HCl to the bottom of the fluidized bed reactor gradually corrodes away at its lower extremity where oxygen concentration is high. This design will not be used on larger scale units.
2. The Inconel 600 condenser tube and adjacent thermowell corroded through after 30 hours at the level where zinc chloride starts to condense. Corrosion coupons of other materials have been placed in this location and in the regenerator proper. The PDU design of this cooler has been revised to flood the critical area with recycled zinc chloride.

A few more batch kinetics runs hydrocracking subbituminous coal were completed at 2000 psig of hydrogen. Results are reported in the tables and figures. The supporting laboratory effort was then diverted to a study of secondary zinc recovery from coal ash recovered by cyclone from the regenerator offgas stream. The major potential loss of zinc in the process is in coal ash collected by cyclone following the regenerator (0.5 to 1.5% of total zinc circulated). It was shown that batch treatment of this ash with 10% HCl in N₂ at 1400-1700°F (i.e., cyclone temperature) removed 90 to 99% of the zinc present, presumably as ZnCl₂. Thus, a secondary treatment of this type could result in overall zinc recoveries up to 99.98%, well above that needed for economic reasons. Further work is needed to get rate data for design of a continuous stage.

Process design of the Process Development Unit (PDU) is substantially complete and a design package has been forwarded to ERDA. Engineering design, piping and instrumentation specifications and layouts are underway. The building to house the unit is essentially complete.

The status of the work by Tasks is shown on the Plan of Progress on the next page.

PROJECT PLAN AND PROGRESS REPORT
Under ERDA Contract No. E(49-18)-1743



III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

- Task 1 Reactivation of the Continuous Bench-Scale Hydrocracker and Regenerator - Complete
- Task 2a Preparation of Feedstocks - Complete
- Task 2b Bench-Scale Hydrocracking of Coal Extract - Complete
- Task 2c Bench-Scale Hydrocracking of Coal

The work was continued with direct hydrocracking of Colstrip coal using $ZnCl_2$ catalyst at relatively severe conditions of temperature and pressure designed to produce a low-carbon spent melt, i.e., 7 wt % carbon or less. All of the work was done using a single reaction stage. The work was done in three areas:

1. Completion of the study of the effect of $ZnCl_2/MF$ coal ratio on unit operability and coal conversion that was in progress at the close of the last quarter.
2. Investigation of unit operability and coal conversion using polystyrene-thickened benzene as the vehicle for the feed coal slurry instead of the high-boiling complex Neville solvent that had been used in the previous studies with coal. It is desired to use the simple low-boiling vehicle so that the yields from coal can be defined and collected for use in subsequent reactivity studies. This could not be done using the high-boiling complex aromatic Neville solvent. This is possible with the polystyrene-thickened benzene because the benzene in the vehicle is essentially inert to $ZnCl_2$ hydrocracking, and the polystyrene goes largely to known low-boiling products as shown by a batch autoclave run (see Task 7 below).
3. Operate to produce 300 pounds of low-carbon melt for use in regeneration studies.

Effect of Zinc Chloride-to-Coal Ratio

In the last quarter, successful, high, coal-conversion operation was demonstrated in material balance runs employing $ZnCl_2/MF$, solvent-free coal ratios of 2.0 and 1.5. The -100 mesh Colstrip coal was fed to the unit in a slurry consisting of 40 wt % coal-60 wt % Neville solvent.

This study was completed this month when it was demonstrated in 26 hours of operation (comprised of three periods) that the unit can be operated successfully at a $ZnCl_2/MF$, solvent-free coal feed ratio of 1.0. The work further demonstrated that a low-carbon spent melt (less than 7 wt % C) can be produced in a single-stage at a $ZnCl_2$ /coal ratio as low as 1.0. One of the operating periods was over 12 hours duration consisting of a 6 hour lineout and a 6 hour material balance; another startup was 7.9 hours duration with a 4.9 hour lineout and a 3.0 hour balance.

The concern that this low a ratio possibly would not be operable stemmed from the fact that a relatively high solids content (coal ash plus unconverted carbon) accumulates in the melt. The fact that a $ZnCl_2$ /coal ratio of 1.0 (or perhaps even lower) can be conducted successfully is favorable for the economics of the direct coal hydrocracking process vis-a-vis hydrocracking coal extract, since in the latter case a $ZnCl_2$ /extract ratio of about 1.0 probably would be used for best results.

The conditions of the runs in this study are given in Table I along with the carbon content of the spent $ZnCl_2$ residue. At all three ratios, a low-carbon "spent" $ZnCl_2$ residue was obtained. It should be noted that the runs were conducted using a constant coal feed rate per unit volume of reactor so that the melt residence time increased from a low of 77 minutes to a high of 130 minutes as the $ZnCl_2$ /coal ratio was decreased from 2 to 1.

Table II presents preliminary balance results from 518.02-3-O and 518-4-J which are the runs at $ZnCl_2$ /coal ratios of 2.0 and 1.0, respectively. The yields of the various products generated from the feed coal cannot be defined because large amounts of light distillates and hydrocarbon gases, which are indistinguishable from those made from the coal, are made from the Neville solvent used as a vehicle to feed the coal. Only roughly 26-27% of the products listed in Table II derive from the feed coal. Thus, the yields have been presented in Table II on two bases: weight % of the total organic MAF feed (MAF coal plus Neville solvent) and yield in grams per 100 grams of MAF feed coal. It is apparent from the results that the Neville solvent underwent extensive hydrocracking. A blank run using Neville solvent without coal would be required to resolve the product yields from coal. It is unlikely, however, that this would be very satisfactory because the amount of the total liquid derived from coal is relatively small.

Nomenclature Change

In the last report and in this report what formerly had been termed 400°C regarding distillate cuts of hydrocracking products or extract has been changed to 475°C. This is deemed a more accurate translation of the distillation conditions (240°C, 1 torr on the distillation pot) used in obtaining this cut to a normal boiling point. Pot conditions are used because there is insufficient boil up to get an equilibrium boiling point. It is stressed that this change in nomenclature does not affect the yields.

Production of 300 Pounds of Low-Carbon Spent Melt Using Polystyrene-Thickened Benzene as the Coal Slurry Vehicle

The work of areas 2 and 3 outlined above fall in this category. First, an exploratory run established that -100 mesh Colstrip coal could be successfully fed to the unit and hydrocracked when the vehicle in the coal feed slurry was polystyrene-thickened benzene. Furthermore, this run showed that the spent melt produced contained only 3.95% C, i.e., less than 7 wt % carbon, which is suitable for use as a feedstock for adiabatic regeneration studies of natural low-carbon spent melt.

The thrust of the work has since been directed to producing 300 pounds of spent melt using polystyrene-thickened benzene as the coal slurry vehicle at the following nominal conditions:

Temperature, °F	775
Total Pressure, psig	3500
ZnCl ₂ /Vehicle-free Coal, Wt Ratio	1.5
<u>Coal Slurry Composition, Wt %</u>	
-100 Mesh Colstrip Coal, MF	25-30
Vehicle (7-8 wt % polystyrene in benzene)	75-70
Melt Residence Time in Reactor, minutes	~ 95-100
H ₂ Rate, SCF/lb of coal feed slurry	30

It was necessary to reduce the coal concentration in the slurry to 25-30 wt %, as opposed to 40 wt % using Neville solvent as the vehicle, to get a pumpable slurry with the lighter vehicle. The polystyrene is necessary to give the benzene sufficient viscosity to make the slurry pumpable on this scale. In one run toluene was substituted for benzene with the hope that this would give an improved slurry regarding pumpability; however, no improvement was observed and the use of toluene was abandoned.

By the end of the quarter, 197 pounds of spent melt that meets the desired low-carbon specifications had been produced. This weight represents about 151 hours of running time since the production rate of spent melt was about 1.3 pounds per hour. The longest continuous running time in the production campaign thus far has been 32 hours. Running times of 10.8, 7.3, 9.7, 8, 11.7, 12, 14, 17.5, 8.2 and 26 hours were also achieved. Three 6 hour material balances and one 4-3/4 hour material balance were included in the production work. Calculations for these material balances are not yet complete.

The chief reasons for the shutdowns during the production work were slurry pumping difficulties and plugging of the vent lines out of the low-pressure spent melt receivers after "long" term operation. Other reasons were: a failed ZnCl₂ transfer line heater, valves associated with the high-pressure melt receivers becoming inoperative and plugging of the inlet feed line in the slurry feed line where the hydrogen tees into it and in the dip tube where the slurry and hydrogen feeds are discharged at the bottom of the reactor pool.

The equipment has held up well regarding stress corrosion cracking problems in the high-pressure section of the unit. Essentially no problems have been encountered in this regard since January 20. The metallurgy in the hot high-pressure active sections of the unit now consists of essentially all 316 ss except for the Inconel 600 transfer lines, valves and fittings that carry distillate from the melt-vapor separator to the distillate receivers. It is believed that Inconel was required here because of exposure to stress cracking by caustic from the distillate receivers instead of HCl, since the 316 ss upstream from this region has generally held up well. However, the reactor stirrer shaft and a newly-installed reactor weir, both of 316 ss, broke, presumably due to stress corrosion.

A new higher capacity slurry pump (Bran and Lubbe) was tested, but it was not used because it did not pump as well as the existing Hills-McCanna pump. Different style checks will be tested in the B&L pump.

The Esterline-Angus PD2064 Programmable Data Logger was put into operation. This instrument automatically records the temperature at 124 thermocouple locations on the unit every thirty minutes.

Work planned for the next quarter includes:

1. Complete the production of 300 pounds of low-carbon spent melt; 103 pounds are still required which represents about 79 hours operating time.
2. Distill all distillate from the production campaign and save all of the +150°C materials for future tests of these materials for reactivity on recycle and for using as coal slurring materials in future pumping tests.
3. Calculate the results of all of the material balance runs made in the hydrocracker since the start of operations.

Task 3 Operation of the Continuous Bench-Scale Regenerator

Investigation of the effects of the variables on regeneration of low-carbon spent melt (less than 7% C) from direct hydrocracking of Colstrip coal using excess air (115% of stoichiometric) was continued this quarter.

Eight runs were made using synthetic spent melt feedstocks that simulate spent melt from direct hydrocracking of Colstrip coal at a $ZnCl_2/MF$ feed coal ratio of 1.5. In the previous quarter runs were made with synthetic feedstocks that simulate spent melts produced in a hydrocracker at $ZnCl_2/MF$ feed coal ratios of 1.0 and 2.0. The synthetic spent melt was used because natural spent melt had not been produced in sufficient quantity for use in this work.

In addition, three runs were made with natural spent melt feedstock. The natural spent melt used as a feedstock was produced in the continuous bench-scale hydrocracker at a $ZnCl_2/MF$, solvent-free Colstrip coal feed ratio of 1.5 at 3500 psig total pressure and a temperature of 775°F. One hundred fifty-six pounds of this material were blended in a molten state to give a uniform feedstock for regeneration studies. The feedstock contains about 6.9 wt % carbon and about 6.0 wt % ash.

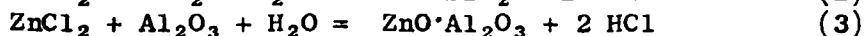
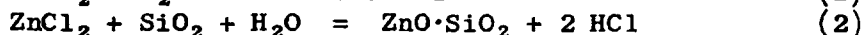
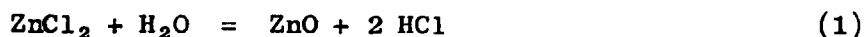
The general objectives of the work with natural spent melt feedstock are to demonstrate operability of the unit at conditions based on the variable study with synthetic melts and define in longer runs the losses of zinc and chlorine during regeneration.

Runs with Synthetic Spent Melt Feedstock

General

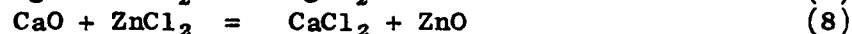
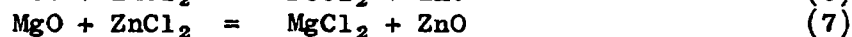
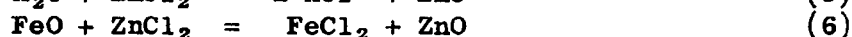
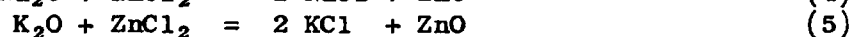
The conditions of the runs and the results of the runs made during the quarter are given in Table IV. The conditions of the runs and results of runs made during the last quarter are given in Table III. The latter are given because data are somewhat more complete than presented previously. The results include the amount of cycle underflow solids expressed as weight percent of the feed ash which is a measure of the efficiency of ash removal in the regeneration process. In addition, the zinc and chlorine contents of the cyclone ash are given. Finally, the zinc and chlorine distribution in the products are given. The distributions of these materials in the bed solids and cyclone underflow solids are a measure of the "loss" of zinc and chlorine. Any zinc not retained in these products is conserved in the process cycle in the melt and any chlorine

not retained in these products is conserved in the process cycle in the melt or in the gas. Zinc may be lost to the bed solids or cyclone solids as zinc oxide, zinc silicate or zinc aluminate as a result of interaction with the ash components or bed solids by reactions of the type:



Hydrogen chloride gas is fed to the regenerator along with air to minimize the extent of these reactions. In addition to these compounds, some ZnCl_2 is retained in the cyclone underflow solids as a result of absorption and diffusion.

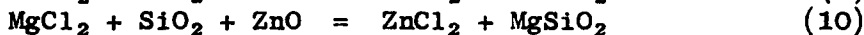
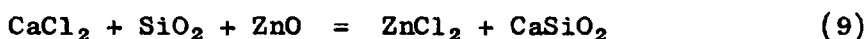
Possible reactions that could result in retention of chlorine in the bed or cyclone solids are:



or similar reactions where ZnCl_2 is replaced by HCl . Of course, chlorine can also be retained in the cyclone solids as ZnCl_2 . The amount of water-soluble zinc retained in the cyclone solids is a measure of the zinc chloride equivalent retained in the cyclone solids. As Table III shows, the water-soluble zinc varies from about 21 to 50% of the zinc retained in the cyclone solids.

The zinc losses to the cyclone solids expressed as percent of the feed zinc varied among the runs from a low of 0.56% to a high of 1.36%. In general, zinc losses to the bed solids were very small, from 0.03 to 0.11% of the feed zinc.

The chlorine losses to the cyclone solids varied from 0.19 to 0.62% of the chlorine in the feed melt whereas the losses to the bed solids were in general zero. The latter fact indicates that, in general, reactions such as:



take place to purge chlorine from the bed. If this were not so, it would be expected that considerable CaCl_2 , which is essentially nonvolatile at regeneration temperatures would be retained in the bed.

Zinc losses are more critical economically than chlorine losses since zinc is about 7 times as expensive as chlorine: 36-37¢/lb vs 5.5¢/lb.

Discussion of Specific Runs

Runs 1 through 5 were discussed in the last quarterly report, and they will not be discussed here again. Detailed conditions and material balances for these runs are given in Table V. These data are given to show the general reliability of the data and how well the conditions can be controlled. The higher HCl "out" versus "in" is largely due to HCl released from NH_4Cl in the feed melt. This will be made clear when elemental balances are presented.

Runs 6 through 13A represent the runs with synthetic melt made in this quarter. The purposes of the runs and the conclusions are given in the following paragraphs.

Run 9 was made to check whether a 1350°F cyclone temperature is indeed preferred over 1500 or 1650°F, regarding zinc losses, as indicated in previous work. The results of Run 9 versus Run 6 indicate that 1350°F gives no improvement over 1500°F. Cyclone and reactor operability were equally good in both cases.

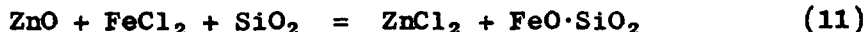
Runs 6, 7B and 8 were an investigation of the effect of HCl concentration in the feed air. Increasing the HCl concentration in the feed air from 5.5 to 11.5 mol % resulted in lower zinc in both the bed and the cyclone solids. Operability was good in all three runs.

Run 10 was made at the same conditions as Run 7B except that the cyclone was not hammered as it was in all the other runs. This is of interest regarding the PDU and commercial operation since hammering becomes impractical in larger scale operation, especially if the cyclone is fabricated from ceramics. Run 10 showed that the cyclone was operable without hammering, but ash recovery efficiency was moderately lower.

Run 11 was similar to Run 7B except that 4.0 wt % of FeCl₂ was added to the melt feed. This amounts to 0.67 mols of FeCl₂ per mol of SiO₂ in the feedstock ash. The purpose of the run was to determine the distribution of iron in the products. The iron, expressed as weight percent of iron in the feed was distributed as follows:

In bed solids	24.3%
In cyclone solids	32.1%
Presumably in the product ZnCl ₂	43.6%

It is therefore concluded that some reaction such as,



occurs to some extent and an equilibrium situation should prevail that would limit the buildup of FeCl₂ in the recycled melt. Operability in this run was very good; the FeCl₂ had no adverse effect.

Run 12 investigated regeneration at 1700°F at conditions similar to Run 7B at 1800°F. The run gave good operability and good carbon burnout. Analyses are required to determine whether a lower nitrogen removal was obtained than at 1800°F.

Run 13A investigated regeneration at 1900°F at conditions similar to Run 7B at 1800°F. Shutdown was forced after 3.5 hours because the reactor outlet plugged with ash. Incipient sintering of the coal ash apparently occurs at 1900°F. No extraordinary size growth of the bed solids or ash in the bed solids was noted, however.

Runs with Natural Spent Melt Feedstock

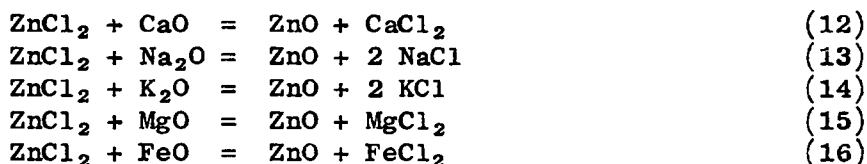
Runs 14, 15 and 16 were made with natural spent melt from zinc chloride hydrocracking of Colstrip coal. Sintering of the coal ash occurred in Run 14 at 1800°F with 8.5 mol % HCl in the feed gas. The run was forcibly shut down

after 1.4 hours because the outlet port of the reactor plugged with ash fines. There was no extraordinary size growth of the bed solids, however. Microscopic examination of the cyclone solids indicated incipient sintering.

Run 15 was similar to Run 14 except that the HCl feed content was lowered to 5.5 mol % of the inlet air. This run was shut down after 3.0 hours because the feed ash remained in the bed as indicated by the pressure drop across the bed and the fact that essentially no ash was collected at the cyclone. The ash had formed clinkers in the bed as large as 2.5 inches indicating that the ash was molten. The feed bed solids did not enter into the clinker formation - only the ash.

Run 16 was similar to Run 15 except that the regeneration temperature was 1700°F instead of 1800°F. This was a satisfactory operable run in all respects. Initially there appeared to be a tendency for plugging at the reactor outlet but as the run proceeded this tendency disappeared.

It is apparent from this work that the natural melt tends to form sticky bed materials at lower temperatures than the synthetic. This may be due to the presence of chlorides in the natural melt resulting from chlorine exchange between ZnCl₂ and the "metallic" ash metals in the hydrocracker by reactions such as:



These metal chlorides are molten and of low volatility and can act as ash fluxes in the regenerator. Operability depends on these chlorides being scavenged by reactions such as 9, 10 and 11 above. If this is so, it may be that once adequate fine silica and alumina from coal ash is built up in the bed, fluxes such as CaCl₂ would react and a higher temperature could be tolerated.

Equipment

The equipment held up well except that the cooling coil in the zinc chloride condenser failed due to corroding through of 1/4" OD x .035" wall Inconel 600 tubing after about 33 hours operation in one instance and 30 hours in another. The 3/8" OD x .035" wall Inconel thermowell also failed after 33 hours operation. The failure occurred in the region where the coil has a temperature of about 1100°F, i.e., in the region where ZnCl₂ first starts to condense. The Inconel tubing air inlet tube and thermowell in the reactor also corrode at their lower ends where the atmosphere is rich in oxygen.

Stressed coupons of Incoloy, Inconels and Hastelloys have been located within the regenerator and in the ZnCl₂ condenser to help select metallurgy for the PDU.

The caustic scrubbers just downstream of the condenser were replaced after Run 5 with electrostatic precipitation to knock down ZnCl₂ fog and condensers to remove make water from the gas stream. This change was made in the interest of getting better material balances.

Planned Activities for the Next Quarter

Work will be continued using the natural melt feedstock with the following objectives:

1. Define experimentally the operating limits for regeneration of natural spent melt.
2. Make long runs to define operability and zinc and chlorine losses at a preferred condition defined under 1 above.

Task 4 Design of the Process Development Unit

A. General Task Work and Scheduling

A design package was prepared and forwarded to ERDA.

A cost estimate and work schedule for the PDU was prepared and presented to ERDA. We were requested to prepare an alternate extended schedule which would permit a longer operating period for the PDU. This was done and the proposed extension of the project to restore the original operating period is under review by ERDA.

B. Regenerator Design

The regenerator design was completed and a preliminary drawing issued. Only review by Harbison-Walker and in-house refractory experts remains to be carried out prior to finalizing the design.

The vessel has hemispherical heads to allow good refractory retention. The grid plate, the liner for the gas inlet and the liner for the bottom of the bed are to be Inconel. The bed itself is 9" ID.

The refractory consists of 3-1/2" of Varnon BF hardface backed by 14" of lightweight insulating castable. The inner surface of the metal shell is to be painted with an impermeable acid-resistant coating. A pressurized steam jacket surrounds the vessel as extra protection against hot spots.

C. Flow Sheet and P&I Reviews

The flow sheets and P&I sheets were given an intensive review which resulted in a number of minor changes.

It was decided to limit tests of absorber operation to the case in which both reactors in series are operated. In that instance, the reactor overhead is cooled, condensate is removed, and the gas is reheated before entering the absorber. In the single reactor mode with extraction, the overhead gas is cooled slightly and any condensed hydrocarbons would be recombined with the melt in the absorption step. It is felt that the dual reactor mode would be more operable and meaningful than to put the hydrocarbons back into the melt. In addition, this case would utilize, as the absorber, vessel D-205, which is somewhat larger than vessel E-201, and therefore is expected to more readily effect good gas-liquid separation at the top of the vessel.

In the same vein, P&I drawing No. AF-3662 will be broken up into two separate drawings in order to more easily understand and carry out the piping design for the two modes of operation which drawing AF-3662 contains.

Originally, overhead condensed product from the $ZnCl_2$ melt still was pumped from vacuum to full system pressure. This necessitated an expensive pump and raised some questions about the ease of maintaining the condensate neutralized if the receivers were operated on a batch letdown mode with its attendant surges of acid condensate. The high-pressure pump was replaced with a lower duty model, and the condensate is instead sent to a low-pressure separator. The hydrocarbon phase is overflowed to the large F-406 separator where it joins the main stream of hydro product.

Some problems were encountered in the $ZnCl_2$ condenser of the bench-scale regenerator with respect to accumulation of ash fines and corrosion of the thermowell. To forestall any problems of this nature from occurring in the PDU, a $ZnCl_2$ recycle pump was added to the C-302 melt condenser. The washing action of the relatively cool liquid melt will carry away settled ash fines and also help to keep the tube walls from becoming too hot.

Provision was made for pumping spent melt directly to F-301 for weighing. This permits elimination of the large weigh scale under the hold tank, makes the product rate more accurate, and reduces the lag time which would otherwise have been associated with integrated operations.

Finally, sample connections and flow measuring instruments were added as needed to fully define the conditions and results of the plant operations.

P&I drawings for the utilities sections were made up and issued.

The equipment list was revised consistent with the P&I changes, and utility and offsite items were added.

The system was reviewed with respect to changes which might be required for startup, shutdown and safety. This work is still in progress and has not been translated into flow sheet changes.

D. Layouts and Mechanical Design

Layouts and mechanical designs are ongoing activities which will take some time to complete.

Vessels and pumps for Section 100, Coal and Catalyst Feeds, have been located along with piping layout. Section 200 Hydrocracking equipment in the barricade has been placed. Work has started on Section 200 equipment outside the barricade. Work on laying out Section 300 Regeneration equipment is well underway.

The conventional cyclone design was received from Shell. It will be constructed of Inconel 600 and surrounded by an insulating castable refractory and a metal outer shell.

Work continues on review of design for Inconel 600 high-pressure valves for this plant. Inquiry has been made of possible vendors as to cost and delivery of these special material items.

Computer calculations showed that the main fractionator will have to be 9" in diameter rather than 8". Due to limited availability of materials, the unit will be designed for 10". Minor changes in the unit accessories were also indicated. The secondary fractionation column is unchanged.

There should be no difficulty in obtaining GC equipment for on-line analysis of product streams. Detailed specification of the equipment will be carried out later in the program.

E. Metallurgy

A review meeting on metallurgy resulted in the conclusion that the vent line from the $ZnCl_2$ feed tank could be 316 ss. However, the Section 100 vent line will be separate from the Section 200 reactor vent system.

Instrumentation such as pressure indicators and differential pressure cells which can be protected by inert purges will be of lower metallurgy than the process vessels. The specification break will be at the last valve in the purge line to the vessel.

Corrosion coupons for testing in the batch regenerator and the regenerator condenser were obtained and will be installed soon. Earlier, a set of tungsten carbide ball checks in the $ZnCl_2$ feed pump had corroded. Wear resistant materials will be needed for the melt letdown valves and for the stirrer bearings in the hydro reactor. Both of the above services require resistance to ash suspended in molten $ZnCl_2$. A corrosion program to test various metal carbides and stellite for use in the process will be setup.

To reduce the potential damage from corrosive carryover from the F-207 High-Pressure Separator, the line from F-207 to knockout pot F213 was specified as Inconel and F-213 itself was enlarged to permit installation of a demister pad.

F. Work Forecast for Next Quarter

1. Finalize the regenerator design.
2. Evaluate corrosion data so that firm specification of the regenerator condenser tubes, now Inconel 600, can be made. Based on corrosion data, specify bearing and letdown valve materials for the process.
3. Review, revise and issue P&I's to take into account safety, startup and shutdown considerations.
4. Continue mechanical design and layout of the plant.

Task 5 Procurement and Construction of the PDU

A requisition for high-pressure Hastelloy tubing for condensers was placed with the Cabot Corporation. This is a long-lead item.

Quotations for the electric control panel have been obtained. A purchase order for these items will be issued as soon as approval is received from ERDA.

Preliminary inquiry for high-pressure Hastelloy pumps has been made. These items appear to require long delivery so that orders for them must be placed as rapidly as possible.

The building to house the PDU has been completed except for heating and ventilating ducts.

During the next quarter, equipment specifications will be drawn up to permit purchasing across the board to begin as soon as ERDA approval is received.

Task 6 PDU Program Planning and Operation

No activity scheduled until construction begins.

Task 7 Supporting Laboratory Work

A. Batch Autoclave Work

1. Kinetics Studies

The batch autoclave operations were curtailed during the quarter because emphasis of the work was shifted to secondary recovery of zinc from regenerator cyclone underflow solids. Three runs were made in the kinetics study of direct hydrocracking of Colstrip coal with $ZnCl_2$ catalyst. These runs are part of a series comprising a study of residence time at 725 and 750°F while holding the hydrogen partial pressure constant at 2000 psig.

This work from its inception comprises 19 runs including Run 1A with extract feed and Run 14 with a feed consisting of reconstituted Colstrip coal, i.e., the solvent-free product from hydroextraction of coal at 825°F and 1750 psig. Complete data for these runs with the exception of the last two runs (19 and 20) are given in Tables VI through X. These data include:

Table VI	-	Feed Materials Analyses
VII	-	Run Conditions and Yields
VIII	-	Organic Products Analyses
IX	-	Effluent Catalyst Analyses
X	-	Effluent Ash Analyses

Figures 1, 2 and 3 are graphical presentations of the newer data at 2000 psig as a function of time and temperature (725 and 750°F). Also shown on these same figures are previously obtained data at 3000 psig at 725°F to show the effect of pressure. Only data at 60 minutes at 750°F and 2000 psig are shown; data at 15 minutes (Run 19 on the tables) are omitted because the data are probably in error, as shown by a poor material balance. The data of these figures show the following:

Effect of Time

(1) At both 2000 and 3000 psig hydrogen pressure the reaction rate is very rapid during the initial 15 minutes after which it decreases. This is shown by both the conversion and hydrogen consumption. Both of these parameters continued to increase, albeit at a decreasing rate, up to 120 minutes residence time.

(2) The yields of $C_4 \times 200^\circ C$ distillate and C_1 to C_3 gases increase with residence time whereas the heavier products decrease.

Effect of Temperature (725°F vs 750°F) at 60 min Residence Time and 2000 psig of H_2

Increasing the temperature at 2000 psig from 725°F to 750°F at 60 minutes residence time tends to be detrimental since the gas yield and +475°C MEK-insoluble residue increase substantially even though hydrogen consumption, conversion and the yield of $C_4 \times 200^\circ C$ distillate remain essentially constant.

Effect of Pressure

Increasing the hydrogen pressure from 2000 to 3000 psig at 725°F is favorable as might be expected in that it results in higher conversion, higher $C_4 \times 200^\circ C$ distillate yield, lower gas yield and lower +475°C MEK-insolubles.

Product Properties

Noteworthy with respect to product properties is that the $-250^\circ C$ distillate (Table VIII) has low nitrogen and sulfur contents. Furthermore, this material generally contains roughly 25 to 30% of aromatics, the remainder being saturates. In a few runs there is an indication in the tables of a small amount of olefins, but it is believed that this reflects analytical error.

2. Run Feeding 10 Wt % Polystyrene in Benzene

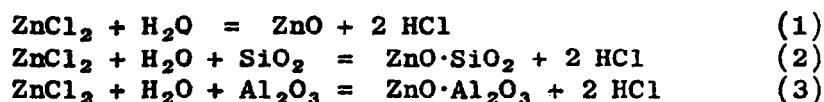
One additional run was made during the quarter involving a feed consisting of 90 wt % benzene and 10 wt % polystyrene. The run was made at 775°F, with a hydrogen partial pressure of 3000 psig, a residence time of 60 minutes, and a $ZnCl_2$ /feed weight ratio of 1.0. The purpose of this run was to determine the breakdown of products obtained from this type of feed in anticipation of the use of polystyrene-thickened benzene in the continuous bench-scale hydrocracker as a vehicle in the coal slurry feed to replace the complex aromatic 248 x 396°C Neville solvent that had been used as a vehicle previously. It was shown in the past that benzene is essentially inert to $ZnCl_2$ cracking, and it was believed that the polystyrene would crack to a few relatively simple low-boiling compounds that could be easily identified. Such a vehicle would allow the products from hydrocracking coal to be defined and collected, which cannot be done when the complex Neville solvent is used as the vehicle as was brought out in a previous section. The purpose of the batch autoclave run was to determine if the benzene-polystyrene system would respond to exposure to $ZnCl_2$ catalyst as anticipated.

The conditions and results of the runs are given in Table XI. It is apparent from these results that the system behaved largely as anticipated. The main products in the effluent are light and largely identifiable. Thus,

products from this vehicle can be largely distinguished from those produced from coal in continuous hydrocracker operation. Furthermore, since the products are largely low-boiling, the heavier products from coal can be collected for further study regarding reactivity with only minor dilution.

**B. Investigation of Secondary Recovery of Zinc
From Regenerator Cyclone Underflow Solids**

It was shown under the results of Task 3 that from 0.56 to as high as 1.36% of the feed zinc to regeneration was retained in the cyclone underflow solids. Since a 1% zinc loss is equivalent to about 1.5¢/gallon of gasoline, when coal is hydrocracked using a ZnCl₂/MF coal ratio of 1.0, it is apparent that from the economic aspect, and as from the ecological aspect, secondary recovery is of importance. The subject study is aimed toward converting any zinc in the cyclone solids, not already in the form of ZnCl₂ but in the form of zinc oxide, zinc aluminate, zinc silicate, or other zinc compounds, to volatile zinc chloride which would be evaporated from the ash and recovered as zinc chloride. The latter three compounds would be found in the cyclone ash as a result of the following types of equilibria:



The amounts of ZnO, ZnO·SiO₂ or ZnO·Al₂O₃ that form in the regenerator and are retained in the cyclone solids thus depends on the ratio

$$\frac{(P_{\text{HCl}})^2}{(P_{\text{ZnCl}_2})(P_{\text{H}_2\text{O}})}$$

In the regenerator this ratio in the gases leaving the reactor is of the order of 0.33 to 1.45 depending on the feed HCl concentration. In secondary treatment this ratio can be made very large by treating the cyclone solids in a second stage with fresh gas containing HCl but no ZnCl₂ or H₂O. Since in the secondary treatment the steam and ZnCl₂ partial pressures are extremely low, whereas the HCl pressure is relatively high, the driving force for converting the zinc compounds in the ash to ZnCl₂ is much higher than in the primary recovery step in the regenerator. Thus, reactions 1, 2 and 3 would be driven from right to left to form ZnCl₂ which would be evaporated from the cyclone solids at the elevated temperature of the secondary recovery.

The apparatus for the secondary recovery work is shown in Figure 4.

The work consisted of passing a continuous stream of gas over a sample of ash contained in a porcelain boat in a mullite tube at elevated temperatures. Runs were made at temperatures of 1400, 1500, 1600 and 1700°F using feed gases consisting of 10 mol % HCl-90 mol % N₂, pure N₂ and 10 mol % HCl-90 mol % air for a total of 12 runs. The residence time was 2.25 hours. The offgases were scrubbed to remove volatile chlorides from the gas stream. Both the effluent cyclone solids and the scrubber liquid were analyzed for zinc and iron as well as other ash metals. Any salts that condensed at the cool outlet of the combustion tube were washed out with water and these washings were combined with the scrubber liquid before analysis.

The conditions of the runs and the results available at the end of the quarter are given in Table XII. The data show:

1. From 91% at 1400°F to 99% at 1700°F of the 8.76% of the zinc was removed from the feed cyclone solids by treatment with 10 mol % HCl-90 mol % N₂ for two hours. The zinc in the feed solids represents 1.36 wt % of the feed zinc to the regeneration process. Thus, after the secondary treatment, the overall zinc loss was reduced to only 0.12 wt % at 1400°F and less than 0.02 wt % at 1700°F.
2. The 10 mol % HCl treatment also volatilized and removed a substantial amount of the iron from the feed ash but considerably less as a percent of the feed than in the case of zinc. It is desirable that the amount of iron volatilization be minimized.
3. About 35% of the zinc in the feed melt was removed by pure nitrogen, an inert gas. This removal undoubtedly represents the zinc that exists in the feed cyclone solids as ZnCl₂.

This work shows the maximum removal and recovery of ZnCl₂ that can be achieved by a second stage of treatment of the cyclone solids with HCl. The work shows that, in principle, zinc lost to the cyclone underflow ash could be reduced to a value as low as 0.02% of the zinc fed to regeneration. The work, however, gives no indication of the rate. Further work must be done to determine the rate of secondary zinc removal with HCl. The rate will determine the method that would be used feasibly in commercial practice for secondary zinc recovery.

C. Work Planned for the Next Quarter

An investigation of the kinetics of removal and recovery of zinc from regenerator cyclone underflow solids will be initiated after an apparatus for this purpose is designed and built.

As time permits the batch autoclave data on the kinetics of zinc chloride hydrocracking of Colstrip coal will be continued by making runs to round out the existing matrix of data.

Task 8 Process and Economic Studies

One study completed; no activity scheduled.

TABLE I

Conditions

ZnCl₂ Continuous Hydrocracker Runs
ZnCl₂/Coal Study

Run Number 518.02-	<u>3-O</u>	<u>4-J</u>	<u>5-B</u>	<u>5-D</u>
Reactor Temperature, °F	775	—————→		
Reactor Pressure, psig	3500	—————→		
Coal Feed Rate, lb/hr	0.53	0.80	—————→	
ZnCl ₂ /Coal Feed Ratio	2.0	1.5	1.0	1.0
Reactor Inventory, grams	669	966	905	--
Reactor Volume, cc	400	600	—————→	
Estimated Melt Residence Time, min	77	95	130	130
Coal Concentration in Neville Solvent, wt %	40	—————→		
Coal Conversion to -400° C Product, wt %	79.0	75.3		
Carbon in Residue, wt %	3.7	6.4	5.9	6.8

TABLE II

Product YieldsZnCl₂ Continuous Hydrocracker Runs
ZnCl₂/Coal Study

Components	518.02-3-0		518.02-4J	
	<u>Percent of Organic MAF Feed</u>	<u>Grams per 100 gm of MAF Coal Feed</u>	<u>Percent of Organic MAF Feed</u>	<u>Grams per 100 gm of MAF Coal Feed</u>
<u>Feed</u>				
MAF Coal	36.10	100.00	36.10	100.00
<u>Neville Solvent</u>				
230 x 325°C Cut	38.61	106.95	38.61	106.95
325 x 475°C	18.02	49.92	18.02	49.92
+475°C	7.27	20.13	7.27	20.13
	<u>100.00</u>	<u>277.00</u>	<u>100.00</u>	<u>277.00</u>
<u>Organic Products*</u>				
CO	0.31	0.87	0.44	1.22
CO ₂	1.00	2.78	0.71	1.96
CH ₄	0.53	1.49	0.57	1.57
C ₂ H ₆	1.09	3.03	1.29	3.56
C ₃ H ₈	9.74	26.98	6.00	16.62
i-C ₄ H ₁₀	12.29	34.04	5.45	15.09
n-C ₄ H ₁₀	1.26	3.49	0.60	1.65
C ₅ x 200°C	41.78	115.73	39.29	108.84
200 x 230°C	9.42	26.10	11.92	33.01
230 x 325°C	11.41	31.60	12.12	33.56
325 x 475°C	18.90	52.36	10.49	29.06
+475°C	5.60	15.50	5.94	16.46
MEK Insolubles	1.98	5.49	2.95	8.18
	<u>115.31</u>	<u>319.46</u>	<u>102.78</u>	<u>270.78</u>

* Excluding H₂O.

TABLE III

Regenerator Runs with Synthetic Spent Melt

Common Conditions

Temperature, °F	1800
Pressure, psig	3
Superficial Fluid. Vel., fps	1
Bed Depth, inches	12
Bed Solids	28-48 M Silica Sand

Other Conditions

Run No. 518.05	<u>1-C</u>	<u>2</u>	<u>2-B</u>	<u>3-B</u>	<u>4</u>	<u>5</u>	<u>6</u>
Amount of Air, % Stoich.	115	153	115	1650	1500	~ .0017	~ .0017
Cyclone Temperature, °F	1350	1500	1500	1650	1500	~ .0017	~ .0017
Cyclone Gas Underflow Rate, SCFM	(1)	(1)	(1)	(1)	~ .0006	~ .0017	~ .0017
Ash Content of Feedstock, Wt %	4.3(2)	4.3(2)	4.3(2)	4.3(2)	7.9(3)	7.9(3)	6.1
C + Organic H Content of Feedstock, Wt %	6.0	6.0	6.0	6.0	6.0	6.0	6.0
<u>Inlet Gas Composition, Mol %</u>							
Air	94.5	94.5	94.5	94.5	94.5	94.5	94.5
Anh. HCl	5.5	5.5	5.5	5.5	5.5	5.5	5.5

Results

Cyclone Solids, Wt % Feed Ash	71.6	65.5	73.8	74.5	77.9	81.3	78.4
<u>Zinc in Cyclone Solids, Wt %</u>							
Water Soluble	2.4	2.0	5.7	6.8	3.7	2.8	4.3
Water Insoluble	8.6	6.2	7.9	7.0	5.1	5.4	5.2
Total	11.0	8.2	13.6	13.8	8.8	8.2	9.5
Chlorine in Cyclone Solids, Wt %	3.6	3.5	6.8	8.2	3.5	4.2	4.9
Zinc Distribution, % of Zinc in Feed Melt							
Cyclone Solids	0.83	0.56	1.06	1.09	1.36	1.34	1.12
Bed Solids	0.03	0.09	0.06	0.07	0.09	0.11	0.11
Effluent Melt (by diff.)	99.14	99.35	98.88	98.84	98.55	98.55	98.77
Chlorine Distribution, % of Chlorine in Feed Melt							
Cyclone Solids	0.25	0.22	0.48	0.58	0.49	0.62	0.52
Bed Solids	0.00	0.00	0.00	0.00	0.00	0.00	0.00

- (1) Control of gas underflow was poor; rate was probably about .0017 SCFM.
 (2) Simulates melt produced in a hydrocracker at a ZnCl₂/MF coal wt ratio of 2.0.
 (3) Simulates melt produced in a hydrocracker at a ZnCl₂/coal wt ratio of 1.0.

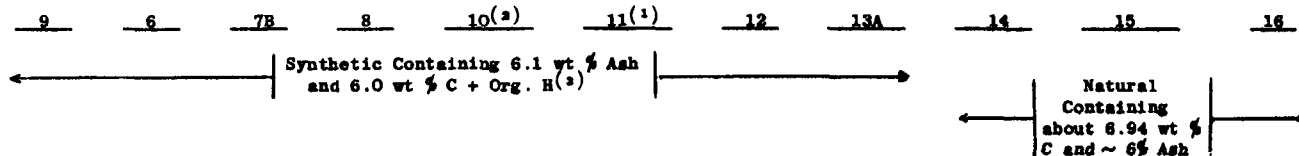
TABLE IV
Continuous Bench-Scale Regeneration

Common Conditions

Pressure, psig 3
 Superficial Fluid Velocity, ft/sec 1
 Bed Depth, inches 12
 Bed Solids 28 x 48 M silica sand
 Amount of Air, % of Stoichiometric 115

Run Number 518.05

Feedstock



Reactor Temperature, °F

Cyclone Temperature, °F

Feed Gas Composition, mol %

air
 anhydrous HCl

Run Time, hr

Melt Feed Rate, lb/hr

Run	9	6	7B	8	10(a)	11 ⁽¹⁾	12	13A	14	15	16	
Reactor Temperature, °F	1800					1700		1800	1800	1800	1700	
Cyclone Temperature, °F	1350						1500					
Feed Gas Composition, mol %												
air	94.5	94.5	91.5	88.5	91.5		91.5		94.5	94.5	94.5	
anhydrous HCl	5.5	5.5	8.5	11.5	8.5		8.5		5.5	5.5	5.5	
Run Time, hr	4.0			6.0			4.0	3.5	1.4	3.0	4.0	
Melt Feed Rate, lb/hr	3.20	3.10	3.25	3.39	3.20	3.27	3.41	3.08	2.64	2.74	2.82	

Results

Cyclone Solids, wt % of Feed Ash

Zinc in Cyclone Solids, wt %

Chlorine in Cyclone Solids, wt %

Zn Dist., % of Zn in Feed Melt

Cyclone Solids

Bed Solids

Effluent Melt (by diff.)

Cl Dist., % of Cl in Feed Melt

Cyclone Solids

Bed Solids

Run	9	6	7B	8	10(a)	11 ⁽¹⁾	12	13A	14	15	16
Cyclone Solids, wt % of Feed Ash	79.7	78.4	74.2	67.0	61.9	82.8	70.3	60.5			
Zinc in Cyclone Solids, wt %	11.79	9.46	8.34	6.67	6.74	9.36	8.04				
Chlorine in Cyclone Solids, wt %	4.75	4.28	4.60	6.01	2.29	4.72	3.99	6.67			
<u>Zn Dist., % of Zn in Feed Melt</u>											
Cyclone Solids	1.42	1.16	0.94	0.68	0.63	1.17	0.86				
Bed Solids	0.08	0.11	0.05	0.02	0.03	0.09					
Effluent Melt (by diff.)	98.50	98.73	99.01	99.30	99.34	98.74					
<u>Cl Dist., % of Cl in Feed Melt</u>											
Cyclone Solids	0.40	0.47	0.47	0.55	0.19	0.53	0.38	0.55			
Bed Solids	0.00	0.00	0.00	0.00	0.07	0.00	0.18	0.00			

Comments:

Plug at Reactor Outlet Plug at Reactor Outlet Clinker Formation in Bed

- (1) Feedstock was spiked with 4.0 wt % of FeCl₃.
- (2) Cyclone was not hammered during this run.
- (3) Simulates melt produced in a hydrocracker at a ZnCl₂/MF coal wt ratio of 1.5.

TABLE V

Detailed Conditions and Material Balances

For all runs: Pressure = 30 psig
 Superficial Linear Velocity = 1.0 fps
 Fluidized Bed Depth = 12"
 Superficial Residence Time in the Fluidized Bed = 1.0 sec
 Bed Solids = 12-48 mesh silica sand
 Feedstock = synthetic spent melt

Other Conditions

Run No. 518.05-	1C	2	2B	3B	4	5
Reactor Temperature, °F	1800					
<u>% of Stoichiometric Air</u>						
Nominal	115					
Actual	123	154 ⁽²⁾	118	125	120	116
<u>Inlet Gas Composition, Mol %</u>						
Air	94.5					
Anhydrous HCl	5.5					
<u>Melt Feed Properties</u>						
Wt % C + Organic H	6.0					
Wt % Ash	4.3				7.9	7.9
Cyclone Temperature, °F	1350	1500	1500	1650	1500	
Cyclone Gas Underflow Rate, SCFM	(1)	(1)	(1)	(1)	~ .0006	~ .0017
Average Melt Feed Rate, gm/min	22.95	18.24	23.89	22.49	23.08	23.76
Running Time, min	240	240	241	215	240	207
<u>Inlet Gas Rates, SCFM</u>						
Air	.712					
Anhydrous HCl	.041					
Argon Purges	.048					
Bed Solid Charge, grams	1362	1362	1364	1362	1363	1362

Material Balances

<u>In, gm/100 gm Feed Melt</u>						
Feed Melt	100.00	100.00	100.00	100.00	100.00	100.00
Air (ex Argon)	113.59	141.13	107.71	114.41	111.50	108.33
Anhydrous HCl	8.23	10.36	7.91	8.40	8.19	7.95
Bed Solids	24.73	31.12	23.73	28.17	24.64	27.69
Total	246.55	282.61	239.35	250.98	244.33	243.97
<u>Out, gm/100 gm Feed Melt</u>						
Product Melt	80.66	81.27	80.39	81.38	79.42	78.09
Cyclone Solids	3.12	2.87	3.25	3.31	6.27	6.52
Bed Solids	25.61	31.37	24.80	29.04	25.53	28.75
HCl	11.06	13.74	12.63	9.31	9.33	9.13
H ₂ O	7.24	6.97	6.88	6.97	6.70	7.06
CO ₂	20.79	19.92	22.77	19.20	21.75	21.72
CO	0.69	0.14	1.08	1.03	0.51	0.59
SO ₂	1.64	1.73	1.39	1.06	1.92	1.86
N ₂	83.80	103.24	79.86	83.20	81.34	78.99
O ₂	4.85	13.04	3.63	6.59	6.58	5.34
Total	239.46	274.29	236.67	240.91	239.33	238.05
(Out/In)(100)	97.13	97.06	98.88	95.99	97.95	97.57

(1) Control of gas underflow was poor; rate probably was between .0006 and .0017 SCFM.

(2) High stoichiometric air was deliberately investigated when the melt feed rate was found to be low.

TABLE VI

Rocking Autoclave Data
Feed Materials Analyses

Feed	Colstrip Coal Extract	Reconstituted Colstrip Coal	-100 Mesh Colstrip Coal
<u>Wt %, MF Basis</u>			
Volatile Matter	62.9	46.54	36.45
Non-oxidized Ash ⁽¹⁾		12.19	11.25
Oxidized Ash ⁽²⁾	.68	11.79	11.01
Hydrogen	5.44	4.61	4.54
Carbon	86.76	80.21	66.20
Nitrogen	1.31	1.14	1.17
Oxygen (By Difference)	3.59	1.63	16.35
Total Sulfur	.22	.50	.88
Organic Sulfur ⁽³⁾	.22	.19	.45
Pyritic Sulfur	0	.12	.39
Sulfate Sulfur	0	.03	.04
Sulfide Sulfur		.16	.00
<u>Oxidized Ash Analyses</u>			
SO ₃	11.15	7.78	12.52
Na ₂ O	1.43	.27	.28
K ₂ O	.40	.37	.22
CaO	10.09	11.72	10.77
MgO	5.45	4.27	4.52
Fe ₂ O ₃	3.30	6.69	4.23
TiO ₂	1.50	1.07	.59
SiO ₂	46.95	44.38	42.73
Al ₂ O ₃	15.59	19.12	19.56
Σ	95.86	95.67	95.42

- (1) Calculated from the oxidized ash value, assuming that FeS₂ was converted to Fe₂O₃ during the ashing.
- (2) The Fe₂O₃ has not been corrected back to FeS₂.
- (3) Total sulfur minus inorganic sulfur.

TABLE VII

Rocking Autoclave - Run Conditions and Yields

Run Number 518.03-
Feed

	1A	14	5	4	6	7	8	3	9	10
Colstrip Coal	Colstrip Coal	Colstrip Reconst. Coal	← -100 Mesh Colstrip Coal →							
Extract	50.0		← 45.0 →							
Moisture Content of Feed (Wt %)	0.0	4.7	1.7	1.2	2.0	1.8	1.4	1.0	1.8	1.0
ZnCl ₂ /MF Feed Wt Ratio	1.0					2.5				
Temperature, °F	← 775 →		← 725 →			← 3000 →		← 750 →		
H ₂ Partial Pressure, psig	← 3000 →									
Final Total Pressure, psig	4000	4100	3850	4100	4300	4300	4100	4250	4550	4600
Residence Time, minutes	60	60	15	60	120	180	15	60	120	180
<u>Time-Temperature History, Minutes</u>										
Ambient to 600°F	46	49	42	41	44	36	35	44	41	43
600°F to Maximum Temperature	17	18	10	8	10	16	16	11	16	8
Maximum Temperature to 600°F	8	12	7	8	8	5	7	8	7	6
<u>Yields, Wt % MAF Feed</u>										
CH ₄	0.9	3.3	0.3	0.4	0.8	0.7	0.4	0.9	0.8	1.4
C ₂ H ₆	0.9	3.0	0.3	0.6	1.0	1.1	0.7	1.0	1.3	1.8
C ₃ H ₈	1.5	8.0	1.8	2.2	4.6	5.7	3.8	2.9	8.8	10.3
iC ₄ H ₁₀	2.8	7.6	4.1	8.6	7.7	10.1	6.8	7.0	12.5	16.6
nC ₄ H ₁₀		1.7			0.9	1.0	0.8	4.7	1.4	1.9
CO	.02	0.03	1.2	0.8	1.2	0.7	1.2	0.9	0.7	0.5
CO ₂	.04	0.10	2.9	1.2	2.4	1.5	2.5	1.6	1.3	1.2
H ₂ O	2.7	0.4	14.9	15.3	14.8	15.9	16.3	13.4	17.5	16.9
C ₅ x 150°C Distillate	44.8	25.4	27.3	41.0	42.7	39.1	29.0	46.3	44.0	42.3
150 x 200°C Distillate	5.9	2.3	3.7	3.7	5.8	4.9	4.8	3.4	3.5	2.1
200 x 475°C Distillate	15.5	1.6	7.8	6.2	3.2	2.5	5.5	3.3	1.6	0.7
+475°C MEK Soluble Residue	25.4	9.2	34.8	22.7	17.8	20.3	28.3	17.0	11.1	9.5
+475°C MEK Insoluble Residue	4.6	42.2	5.7	4.0	3.5	3.4	5.3	4.4	3.5	2.8
Nitrogen to Catalyst	1.1	1.0	0.9	1.1	1.2	1.2	1.0	1.1	1.2	1.2
Oxygen to Catalyst	0.6	0.7	0.7	0.8	0.8	0.9	0.8	1.2	0.9	0.6
Sulfur to Catalyst	0.1	0.3	0.5	0.5	0.5	0.5	0.5	0.2	0.5	0.5
Hydrogen to Catalyst	0.3	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.4
Σ Including H ₂ Consumed	107.1	107.0	107.1	109.3	109.2	109.8	108.0	109.6	110.9	110.7
H ₂ Consumed, Wt % MAF Feed	7.1	7.0	7.0	9.3	9.2	9.8	8.1	9.6	10.9	10.7
Conversion, Wt % MAF Feed	70.0	48.7	59.5	73.4	78.7	76.4	66.4	78.6	85.4	87.7
(C ₁ -C ₃) x 100/Conversion	4.7	29.5	3.9	4.3	8.2	9.8	7.4	6.0	12.8	15.4
% H ₂ Consumed as C ₁ -C ₃ Gas	9.6	41.5	6.4	6.4	13.6	14.8	11.7	10.0	19.0	24.2
Conversion to MEK-Soluble Products, Wt % MAF Feed	95.4	57.8	94.3	96.0	96.5	96.6	94.7	95.6	96.5	97.2
Carbon Content of Spent Melt (MEK Insol. + H ₂ O Sol.) Wt %	4.7	10.9	1.8	2.1	2.0	3.4	2.5	2.0	1.6	1.8

TABLE VII (Cont'd.)

Rocking Autoclave - Run Conditions and Yields

Run Number 518.03-	11	12	2	13	16	15B	17	19	20
Feed	← -100 Mesh Colstrip Coal →								
Feed Wt (Grams)	← 45.0 →								
Moisture Content of Feed (Wt %)	1.6	2.0	3.3	4.7	1.2	2.0	3.1	1.4	1.3
ZnCl ₂ /MF Feed Wt Ratio	← 2.5 →								
Temperature, °F	← 775 →				← 725 →			← 750 →	
H ₂ Partial Pressure, psig	← 3000 →				← 2000 →			← 2000 →	
Final Total Pressure, psig	4350	4400	4500	4800	2500	3100	2900	2900	3100
Residence Time, minutes	15	30	60	120	15	60	120	15	60
<u>Time-Temperature History, Minutes</u>									
Ambient to 600°F	41	41	44	44	43	32	45	32	43
600°F to Maximum Temperature	15	15	15	13	8	6	7	15	10
Maximum Temperature to 600°F	9	10	10	6	7	5	6	7	6
<u>Yields, Wt % MAF Feed</u>									
CH ₄	0.7	0.9	1.3	1.5	0.2	0.6	0.8	0.6	0.9
C ₂ H ₆	1.1	1.4	1.5	2.1	0.5	1.0	1.5	1.0	1.5
C ₃ H ₈	6.0	7.8	3.4	12.2	2.1	2.3	6.5	7.6	6.6
iC ₄ H ₁₀	9.5	12.0	13.0	16.2	2.6	1.3	8.0	11.9	6.9
nC ₄ H ₁₀	1.1	2.0		2.0	0.3	.1	0.8	1.1	0.8
CO	1.4	1.3	0.7	0.7	0.9	1.4	1.2	1.5	1.5
CO ₂	2.4	2.5	1.4	1.1	4.0	4.0	3.7	4.4	3.7
H ₂ O	16.3	14.8	15.5	16.4	14.3	14.2	13.9	13.8	14.5
C ₅ x 150°C Distillate	34.1	41.1	46.9	39.1	18.6	39.2	35.1	20.5	28.1
150 x 200°C Distillate	4.7	4.0	4.1	2.6	4.2	4.4	3.7	3.4	6.8
200 x 475°C Distillate	3.3	2.7	2.4	0.8	6.7	5.4	3.0	4.4	2.4
+475°C MEK Soluble Residue	19.6	12.7	12.9	10.0	30.1	23.3	19.1	22.5	15.8
+475°C MEK Insoluble Residue	5.3	3.7	4.3	3.6	18.6	8.0	9.1	11.4	15.6
Nitrogen to Catalyst	1.1	1.2	1.2	1.0	0.8	1.0	0.9	.8	0.9
Oxygen to Catalyst	1.0	0.8	0.9	0.8	0.8	1.0	1.0	.9	1.2
Sulfur to Catalyst	0.5	0.5	0.5	0.5	0.5	0.3	0.3	.4	0.4
Hydrogen to Catalyst	0.2	0.3	0.3	0.5	0.2	0.2	0.2	.2	0.2
Σ Including H ₂ Consumed	108.3	109.7	110.3	111.1	105.4	107.7	108.8	106.4	107.8
H ₂ Consumed, Wt % MAF Feed	8.4	9.7	10.3	11.1	5.4	7.7	8.8	6.4	7.8
Conversion, Wt % MAF Feed	75.1	83.7	82.8	86.4	52.8	68.7	71.8	66.1	68.6
(C ₁ -C ₃) x 100/Conversion	10.5	12.0	7.4	18.3	5.3	5.6	12.3	14.0	13.1
% H ₂ Consumed as C ₁ -C ₃ Gas	17.8	19.9	12.1	27.4	9.9	9.8	19.3	27.4	22.2
Conversion to MEK-Soluble Products, Wt % MAF Feed	94.7	96.3	95.7	96.4	81.4	92.0	90.9	88.6	84.4
Carbon Content of Spent Melt (MEK Insol. + H ₂ O Sol.) Wt %	2.4	1.8	1.9	2.5	6.7	3.3	3.7	5.4	5.4

TABLE VIII

Rocking Autoclave - Organic Product Analyses

Run Number 518.03-

	<u>1A</u>	<u>14</u>	<u>5</u>	<u>4</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>3</u>	<u>9</u>	
Feed	Colstrip Coal Extract	Reconst. Colstrip Coal	← -100 Mesh Colstrip Coal →							
Feed Wt (Grams)	50.0		← 45.0 →							
H ₂ Partial Pressure, psig			← 3000 →							
Final Total Pressure, psig	4000	4100	3850	4100	4300	4300	4100	4250	4550	
Temperature, °F	← 775 →		← 725 →			← 750 →				
Residence Time, minutes	← 60 →		15	60	120	180	15	60	120	
<u>+250°C Oil, Wt %</u>										
Hydrogen	13.21	11.76	12.59	12.84	12.70	12.62	12.48	12.78	12.69	
Carbon	86.27	87.73	86.71	85.25	84.84	85.61	86.79	82.24	85.77	
Nitrogen	0.04	0.03	0.17	0.02	0.02	0.02	0.00	0.02	0.02	
Oxygen (Direct)	0.42	0.43	0.51	1.86	2.35	1.70	.69	4.96	1.54	
Sulfur	0.06	0.05	0.02	0.02	0.09	0.05	0.04	0.00	0.00	
<u>FIA Analysis, Volume %</u>										
Aromatics	23.0	42.0	27.9	22.3	29.9	24.0	34.3	22.6	28.3	
Saturates	77.0	58.0	72.1	77.7	69.6	75.4	65.2	77.4	71.0	
Olefins	0	0	0	0	0.5	0.6	0.5	0	0.7	
<u>200 x 400°C Distillate, Wt %</u>										
Hydrogen	9.70	--	9.89	10.06	10.38	10.35	9.80	--	--	
Carbon	89.30	--	87.02	83.57	85.25	85.32	85.25	--	--	
Nitrogen	0.25	--	.65	--	.97	--	.89	--	--	
Oxygen (Direct)	0.72	--	2.36	--	--	--	3.96	--	--	
Sulfur	0.03	--	.08	--	--	--	.10	--	--	
<u>+475°C MEK-Soluble Residue, Wt %</u>										
Hydrogen	7.44	7.92	8.33	8.97	8.80	9.20	8.09	9.06	9.20	
Carbon	90.53	84.95	86.51	83.38	86.26	83.70	87.64	83.77	85.62	
Nitrogen	0.45	0.63	.47	.59	.44	.37	.66	.47	.60	
Oxygen (Direct)	1.19	5.76	4.06	6.61	3.48	6.17	2.95	6.32	3.34	
Sulfur	0.08	0.14	.10	.12	.20	.18	.13	.03	.11	
Ash ⁽¹⁾	0.31	.60	.53	.33	.82	.38	.53	.35	1.13	
C ₁ -C ₃ , Wt % MAF Feed	3.3	14.4	2.3	3.2	6.4	7.5	4.9	4.7	10.9	
<u>C₄ x 200°C Distillate, Wt %</u>										
MAF Feed	53.6	37.0	35.1	53.3	57.1	55.2	41.4	61.5	61.3	
<u>C₄ x 475°C Distillate, Wt %</u>										
MAF Feed	69.1	38.6	42.9	59.5	60.2	57.7	46.9	64.8	62.9	
<u>C₄ x MEK-Soluble Material,</u>										
Wt % MAF Feed	94.5	47.7	77.8	82.2	78.0	78.0	75.2	81.8	73.9	
iC ₄ /nC ₄	--	4.6	--	--	8.9	9.7	8.1	--	8.9	

(1) This ash is essentially ZnCl₂.

TABLE VIII (Cont'd.)

Rocking Autoclave - Organic Product Analyses

Run Number 518.03-

	<u>10</u>	<u>11</u>	<u>12</u>	<u>2</u>	<u>13</u>	<u>16</u>	<u>15B</u>	<u>17</u>	<u>19</u>	<u>20</u>	
Feed	←----- -100 Mesh Colstrip Coal -----→										
Feed Wt (Grams)	←----- 45.0 -----→										
H ₂ Partial Pressure, psig	←----- 3000 -----→					←----- 2000 -----→					
Final Total Pressure, psig	4600	4350	4400	4500	4800	2500	3100	2900	2900	3100	
Temperature, °F	750	←----- 775 -----→				←----- 725 -----→			←----- 750 -----→		
Residence Time, minutes	180	15	30	60	120	15	60	120	15	60	
<u>+250° C Oil, Wt %</u>											
Hydrogen	12.94	12.95	12.70	12.91	12.55	12.43	12.90	13.07	12.75	12.16	
Carbon	84.99	85.53	85.29	84.03	84.14	86.39	86.30	83.72	85.97	87.69	
Nitrogen	0.01	0.04	0.00	0.06	0.05	0.00	0.00	0.00	0.00	0.15	
Oxygen (Direct)	1.99	1.38	2.00	2.99	3.23	1.18	.79	3.20	1.26	0	
Sulfur	0.07	0.10	0.01	0.01	0.02	0.00	0.01	0.01	0.02	0.00	
<u>FIA Analysis, Volume %</u>											
Aromatics	26.0	27.7	31.9	26.4	23.1	29.6	23.8	21.6	33.8	26.8	
Saturates	73.2	72.3	68.1	73.6	76.9	70.4	75.5	78.4	66.2	72.8	
Olefins	0.8	0	0	0	0	0	0.7	0	0	0.4	
<u>200 x 400° C Distillate, Wt %</u>											
Hydrogen	--	9.91	10.10	10.12	--	9.54	9.79	9.97	9.55	--	
Carbon	--	87.12	83.51	78.52	--	86.84	86.58	85.40	87.86	--	
Nitrogen	--	--	--	--	--	.56	.77	--	0.50	--	
Oxygen (Direct)	--	--	--	--	--	3.01	2.74	--	--	--	
Sulfur	--	--	--	--	--	.05	.12	--	--	--	
<u>+475° C MEK-Soluble Residue, Wt %</u>											
Hydrogen	8.65	7.63	8.54	9.48	9.77	7.63	7.90	7.89	7.55	8.12	
Carbon	82.17	86.05	84.02	82.86	84.71	88.92	88.51	87.95	87.63	85.19	
Nitrogen	.35	.50	.46	.29	.29	.72	.44	.73	.52	.59	
Oxygen (Direct)	8.42	2.33	5.74	6.89	4.41	2.08	2.57	2.25	3.30		
Sulfur	.29	.11	.09	.07	.18	.12	.11	.13	.07		
Ash ⁽¹⁾	.12	3.38	1.15	.41	.64	.53	.47	1.05	.93	.63	
C ₁ -C ₃ , Wt % MAF Feed	13.5	7.8	10.1	6.2	15.8	2.8	3.8	8.9	9.3	9.0	
C ₄ x 200° C Distillate, Wt %											
MAF Feed	63.0	49.5	59.1	64.0	59.9	25.8	44.95	47.6	36.9	42.6	
C ₄ x 475° C Distillate, Wt %											
MAF Feed	63.6	52.8	61.8	66.4	60.7	32.4	50.3	50.60	41.3	45.0	
C ₄ x MEK- Soluble Material,											
MAF Feed	73.2	72.4	74.4	79.4	70.7	62.5	73.7	69.7	63.8	60.8	
iC ₄ /nC ₄	8.5	8.3	6.1	--	7.9	8.0	16.3	9.9	10.4	8.5	

(1) This ash is essentially ZnCl₂.

TABLE IX

Rocking Autoclave Effluent Catalyst Analyses

Run No. 518.03-	1A	14	5	4	6	7	8	3	9	10
Feed	Colstrip Coal Extract	Recon. Colstrip Coal	-100 Mesh Colstrip Coal							
Feed, Wt grams	50.0		45.0							
H ₂ Partial Pressure, psig	3000									
Final Total Pressure, psig	4000	4100	3850	4100	4300	4300	4100	4250	4550	4600
Temperature, °F	775		725				750			
Residence Time, Minutes	60	60	15	60	120	180	15	60	120	180
ZnCl ₂ /M ² Feed Wt Ratio	1.0	2.5								
<u>Water-Soluble Material</u>										
Weight Recovered, grams	47.89	103.55	111.01	109.40	109.14	110.48	108.85	108.40	110.73	106.84
<u>Elemental Analysis</u>										
Hydrogen	0.35	0.19	.38	.37	.35	.44	.43	.43	.31	.39
Carbon	1.00	0.31	.94	.90	.83	2.34	1.03	.84	.72	.70
Inorganic Nitrogen	1.20	0.41	.28	.38	.38	.33	.17	.36	.34	.30
Organic Nitrogen	0	.02	.03	.01	.01	.13	.13	0	0	.01
Total Sulfur	0	0	.01	.01	0	.02	.02	.11	.03	.01
Zinc	45.07	46.85	46.21	46.37	45.77	46.07	46.15	46.22	45.80	45.94
Chlorine	60.83	51.23	48.23	46.25	47.62	50.91	50.78	47.16	50.87	51.15
Ash	--									
Oxygen (by diff.)	2.30									
<u>Water and MEK-Insoluble Material</u>										
Weight Recovered, grams	5.84	22.41	10.83	9.82	9.64	9.89	9.94	10.21	9.58	9.17
<u>Elemental Analysis, Wt %</u>										
Hydrogen	3.23	2.74	2.03	1.65	1.89	1.47	1.81	1.69	1.14	.45
Carbon	36.53	60.10	20.36	18.46	13.74	13.40	18.57	14.63	12.13	12.90
Nitrogen	.68	.39	.30	.22	.19	.16	0.28	.27	.21	.15
Inorganic Sulfur	-	.89	.52	2.77	{ 3.61	{ 3.80	2.39	2.95	{ 3.98	3.64
Organic Sulfur	.29	.38	3.02	.36			.29	.29		.37
Zinc	35.07	10.56	24.94	27.94	28.61	29.92	27.21	29.44	31.09	25.80
Chlorine	5.33	1.42	4.20	2.65	4.02	4.06	4.18	2.18	3.07	4.49
Ash	-	14.34		36.83	26.37	33.27	32.58	35.37	24.21	25.11
Oxygen (by diff.)	-	7.40		11.12	11.87	14.82	13.71	13.17	10.17	17.09
<u>Calculated Organic Analyses, Wt %⁽¹⁾</u>										
Hydrogen	7.93	4.31	1.80	9.33	-	-	8.64	10.01	-	3.24
Carbon	29.69	94.51	79.19	27.39	-	-	28.84	26.67	-	63.01
Nitrogen	1.67	.61	1.17	1.24	-	-	1.34	1.60	-	1.08
Sulfur	.72	.87	11.74	2.04	-	-	1.28	1.72	-	2.67
<u>Overall Zinc and Chlorine Balances⁽²⁾</u>										
Zn in - Zn Out, Moles	.008	.051	.004	.013	.023	.008	.022	.017	.009	.043
Cl in - Cl Out, Moles	.080	.131	.112	.304	.161	.039	.069	.188	.041	.085
Moles of Cl Lost in Excess of That as ZnCl ₂	.014	.029	.109	.178	.115	.027	.023	.154	.023	-.001
<u>Catalyst Composition, Mol %</u>										
ZnCl ₂	85.3	92.8	92.8	81.0	91.0	91.3	92.1	90.2	91.2	91.1
ZnCl ₂ ·5H ₂ O	0	1.8	3.2	4.1	4.3	0.4	0.8	4.8	.3	0
ZnCl ₂ ·2NH ₄ Cl	7.8	1.8	0	0	0	3.8	2.7	0	3.8	3.1
ZnS	.5	.4	0.7	0.8	0.7	0.7	0.7	.4	.7	.7
ZnO	5.7	3.8	3.6	4.1	4.0	4.1	3.7	5.2	4.0	3.1

(1) This is the normalized analysis of the organic portion of the water- and MEK-insoluble material.

(2) Total moles of ZnCl₂ Fed = 0.819, except for Run 518.03-1A where 0.363 moles were fed.

TABLE IX - Cont'd.

Rocking Autoclave Effluent Catalyst Analyses

Run No. 518-03-

	11	12	2	13	16	15B	17	19	20
Feed	-100 Mesh Colstrip Coal								
Feed, Wt grams	45.0								
H ₂ Partial Pressure, psig	3000				2000				
Final Total Pressure, psig	4350	4400	4500	4800	2500	3100	2900	2900	3100
Temperature, °F	775				725				
Residence Time, minutes	15	30	60	120	15	60	120	15	60
ZnCl ₂ /MF Feed Wt Ratio	2.5								
	<u>Water-Soluble Material</u>								
Weight Recovered, grams	109.95	107.13	107.13	109.95	109.86	108.17	108.38	108.46	109.36
<u>Elemental Analysis</u>									
Hydrogen	.55	.30	.31	.47	.28	.31	.44	.37	.26
Carbon	.78	.82	.72	1.51	.98	1.00	1.01	1.34	.73
Inorganic Nitrogen	.34	.38	.37	.37	.21	.15	.30	.26	.35
Organic Nitrogen	.02	.01	.01	.09	.02	.01	.06	.07	.03
Total Sulfur	0	.01	0	.01	0	.01	0	0	0
Zinc	45.24	47.54	47.34	47.20	46.26	47.08	46.35	46.40	46.17
Chlorine	48.54	51.44	45.03	52.92	50.55	49.32	50.10	49.38	49.56
Ash						1.30	.78	1.13	
Oxygen (by diff.)						.82	.96	1.05	
	<u>Water- and MEK-Insoluble Material</u>								
Weight Recovered, grams	10.30	9.11	9.88	9.58	15.71	11.45	11.89	13.56	15.13
<u>Elemental Analysis, Wt %</u>									
Hydrogen	1.80	1.29	1.50	1.29	2.07	2.00	1.83	2.60	2.37
Carbon	18.00	15.65	14.75	13.35	46.34	24.90	28.04	37.77	39.29
Nitrogen	.19	.13	.09	.12	.44	.17	.16	.27	.22
Inorganic Sulfur	3.42	3.56	3.37	3.38	2.01	2.25	1.98	1.95	1.82
Organic Sulfur	.27	.29	.36	.57	.42	.03	1.16	.57	.65
Zinc	29.24	29.65	28.71	27.87	17.28	24.89	24.09	21.30	23.46
Chlorine	3.63	3.20	3.48	4.25	2.46	2.94	2.77	3.12	3.61
Ash	33.10	38.27	36.06	36.72	18.87	27.02	28.81	21.90	
Oxygen (by diff.)	10.35	7.90	11.68	12.45	9.21	14.00	11.16	10.52	
<u>Calculated Organic Analysis, Wt %⁽¹⁾</u>									
Hydrogen	8.88	7.43	8.98	8.41	5.92	7.14	5.87	6.31	5.43
Carbon	88.84	90.15	88.32	87.09	92.36	88.03	89.90	91.65	89.91
Nitrogen	.94	.75	.54	.78	.88	.61	.51	.66	.50
Sulfur	1.34	1.67	2.16	3.72	.84	3.32	3.72	1.38	4.16
<u>Overall Zinc and Chlorine Balances⁽²⁾</u>									
Zn in - Zn Out, Moles	.022	.009	.011	.000	.011	.008	.032	.015	.003
Cl in - Cl Out, Moles	.120	.074	.268	.000	.060	.123	.125	.111	.091
Moles of Cl Lost in Excess of That as ZnCl ₂	.076	.056	.246	.000	.035	.107	.061	.081	.085
<u>Catalyst Composition, Mol %</u>									
ZnCl ₂	91.1	91.5	90.1	89.8	92.8	91.4	92.4	92.3	91.3
ZnCl ₂ ·NH ₃	3.8	4.0	4.5	0	1.5	3.7	2.1	2.9	3.1
ZnCl ₂ ·NH ₄ Cl	0	0	0	5.8	1.4	0	.8	0	0
ZnS	.8	.8	.9	.8	0.6	0.4	.5	.6	0.6
ZnO	4.3	3.7	4.5	3.6	3.7	4.5	4.4	4.2	5.0

(1) This is the normalized analysis of the organic portion of the water- and MEK-insoluble material.

(2) Total moles of ZnCl₂ Fed = 0.818.

TABLE X

Rocking Autoclave Effluent Ash Analyses

Run No. 518.03

	1A	14	5	4	6	7	8	3	9	10
Feed	Colstrip	Recon.								
	Coal	Coal	← -100 mesh Colstrip Coal →							
Feed Wt, grams	50.0		← 45.0 →							
H ₂ Partial Pressure, psig			← 3000 →							
Final Total Pressure, psig	4000	4100	3850	4100	4300	4300	4100	4250	4550	4600
Temperature, °F		775		725				750		
ZnCl ₂ /MF Feed Wt Ratio	1.0		← 2.5 →							
Residence Time, minutes		60	15	60	120	180	15	60	120	180
<u>Ash In Water-Soluble Material, Wt %</u>										
SO ₃	--	.02	.03	.13	.06	.05	.17	.03	.12	
Na ₂ O	--	.02	.05	.01	.03	.05	.05	.02	.04	
K ₂ O	--	.02	.05	.02	.04	.04	.05	.02	.05	
CaO	--	.56	.54	.49	.50	.47	.40	--	.46	
MgO	--	.11	.20	.24	.19	.22	.21	.21	.22	
Fe ₂ O ₃	--	.00	.00	.46	.03	.14	.30	.37	.10	
TiO ₂	--	.07	.05	.39	.13	.08	.02	.02	.00	
SiO ₂	--	.00	.12	.00	.32	.15	.00	.31	.00	
Al ₂ O ₃	--	--	--	--	--	--	--	--	--	
Total Ash										
<u>Ash In Water and MEK-Insoluble Material, Wt %</u>										
SO ₃	--	.68	.39	.22	.13	.17	.13	.44	.34	
Na ₂ O	--	.03	.03	.04	.11	.05	.03	.02	.10	
K ₂ O	--	.18	.16	.15	.13	.16	.16	.12	.21	
CaO	--	.22	.00	.10	.05	.00	.04	.09	.00	
MgO	--	1.81	.17	.14	.09	.02	.05	.11	.12	
Fe ₂ O ₃	--	1.53	2.81	1.21	1.72	1.03	1.47	1.58	1.39	
TiO ₂	--	.66	.86	.82	1.71	1.83	1.06	1.13	1.39	
SiO ₂	--	34.13	32.31	33.06	31.15	29.14	30.96	30.40	29.57	
Al ₂ O ₃	--	17.57	17.26	16.97	16.57	15.84	16.92	17.10	16.79	
Total Ash		56.81	53.99	52.71	51.69	48.24	50.82	50.99	49.91	
Feed Iron In H ₂ O-Soluble Material (FeCl ₂), %	--	0	0	243	14	75	105	194	54	
Feed Iron In H ₂ O-Insoluble Material (FeS), %	--	28	0	39	51	34	46	54	47	
Total	--	28	0	282	65	109	151	248	101	
Feed Calcium In H ₂ O-Soluble Material (CaCl ₂), %	--	94	110	102	93	99	83		97	
Feed Calcium In H ₂ O-Insoluble Material, %	--	2		1	1	0	1		0	
Total	--	96		103	94	99	84		97	
Feed Magnesium in H ₂ O-Soluble Material (MgCl ₂), %	--	51	97	118	84	110	103	103	111	
Feed Magnesium in H ₂ O-Insoluble Material, %	--	53		4	2	0	1	4	4	
Total	--	104		122	86	110	104	107	115	

TABLE X (continued)

Rocking Autoclave Effluent Ash Analysis

Run No. 518.03

	<u>11</u>	<u>12</u>	<u>2</u>	<u>13</u>	<u>16</u>	<u>15B</u>	<u>17</u>	<u>19</u>	<u>20</u>
Feed	←----- -100 mesh Colstrip Coal -----→								
Feed Wt, grams					←----- 45.0 -----→				
H ₂ Partial Pressure, psig					←----- 2000 -----→				
Final Total Pressure, psig	4350	4400	4500	4800	2500	3100	2900	2900	3100
Temperature, °F	←----- 775 -----→				←----- 725 -----→			←----- 750 -----→	
ZnCl ₂ /MF Feed Wt Ratio					←----- 2.5 -----→				
Residence Time, minutes	15	30	60	120	15	60	120	15	60
<u>Ash In Water-Soluble Material, Wt %</u>									
SO ₃	.05	.03	.07	.02	.28	.03	.01	.00	
Na ₂ O	.30	.02	.02	.02	.00	.00	.01	.01	
K ₂ O	.50	.02	.02	.03	.00	.00	.00	.00	
CaO	.00	.50	.47	.62	.61	.55	.54	.60	
MgO	.21	.10	.24	.23	.22	.23	.00	.23	
Fe ₂ O ₃	.18	.38	.68	.22	.05	.26	.22	.09	
TiO ₂	.05	.00	.09	.02	.00	.00	.00	.00	
SiO ₂	.06	.00	.23	.45	.16	.15	.00	.14	
Al ₂ O ₃						.00	.00	.00	
Total Ash						<u>1.22</u>	<u>.78</u>	<u>1.07</u>	
<u>Ash In Water and MEK-Insoluble Material, Wt %</u>									
SO ₃	.56	1.18	.39	.73	.64	.93	.26	.44	
Na ₂ O	.00	.68	.06	.10	.03	.00	.04	.00	
K ₂ O	.13	.14	.19	.14	.14	.08	.17	.06	
CaO	.04	.07	.03	.08	.00	.00	.00	.00	
MgO	.11	.14	.20	.18	.08	.09	.12	.12	
Fe ₂ O ₃	1.31	1.29	1.07	1.17	2.33	1.61	1.55	1.63	
TiO ₂	.69	.86	1.54	.97	.76	.48	1.16	.44	
SiO ₂	31.15	32.52	30.43	28.49	27.72	30.25	31.61	30.28	
Al ₂ O ₃	<u>17.25</u>	<u>17.46</u>	<u>17.97</u>	<u>18.42</u>	<u>15.66</u>	<u>12.83</u>	<u>14.30</u>	<u>12.87</u>	
Total Ash	51.24	54.34	51.88	50.28	47.36	46.27	49.21	45.84	
Overall Ash Balance, (Out/In) x 100						95	94	88	
Feed Iron In H ₂ O-Soluble Material (FeCl ₂), %	96	199	359	117	27	138	115	48	
Feed Iron In H ₂ O-Insoluble Material (FeS), %	42	40	36	40	71	52	53	51	
Total	138	239	395	157	98	190	168	99	
Feed Calcium In H ₂ O-Soluble Material (CaCl ₂), %	0	102	98	129	127	114	111	124	
Feed Calcium in H ₂ O-Insoluble Material, %	1	1	0	1	0	0	0	0	
Total	1	103	98	130	127	114	111	124	
Feed Magnesium in H ₂ O-Soluble Material (MgCl ₂), %	105	49	118	114	110	114	0	113	
Feed Magnesium in H ₂ O-Insoluble Material, %	3	4	6	6	2	3	37	4	
Total	108	53	124	120	112	117	37	117	

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TABLE XI

Batch Run with 10% Polystyrene-90% Benzene
Run No. 518.03-18

<u>Components</u>	<u>Detailed Yield Breakdown, Wt % MAF Feed</u>		
CO ₂	.18		
CO	.03		
CH ₄	.20		
C ₂ H ₆	.32		
C ₃ H ₈	1.10		
i C ₄ H ₁₀	.61		
n C ₄ H ₁₀	.13		
C ₅ 's	.27		
Pentene	.05		
2-M-1-Butene	.07		
2-M-2-Butene	.08		
Unid.	.002		
Cyclopentane	.02		
2,3-Di-M-Butene	.02		
2-M-Pentane	.07		
3-M-Pentane	.06		
n-Hexane	.02		
Methylcyclopentane	.15		
Benzene	89.17		
Cyclohexane	.04		
Unids. (C.T. oil)	.05		
DMCP's	.04		
Unids. (C.T. oil)	.05		
Toluene	.93		
Unids. (C.T. oil)	.06		
Ethylbenzene	2.34		
150°C Unids	.72		
Isopropylbenzene	.27		
n-propylbenzene	.15		
Unids. (C.T. oil)	.73		
200°C Unids.	.12		
Unids.	2.67		
H ₂ O-Benzene Insol.	<u>.16</u>		
Total Yield, including H ₂ Consumed	100.88		
H ₂ Consumed, Wt % MAF Feed = 0.88			

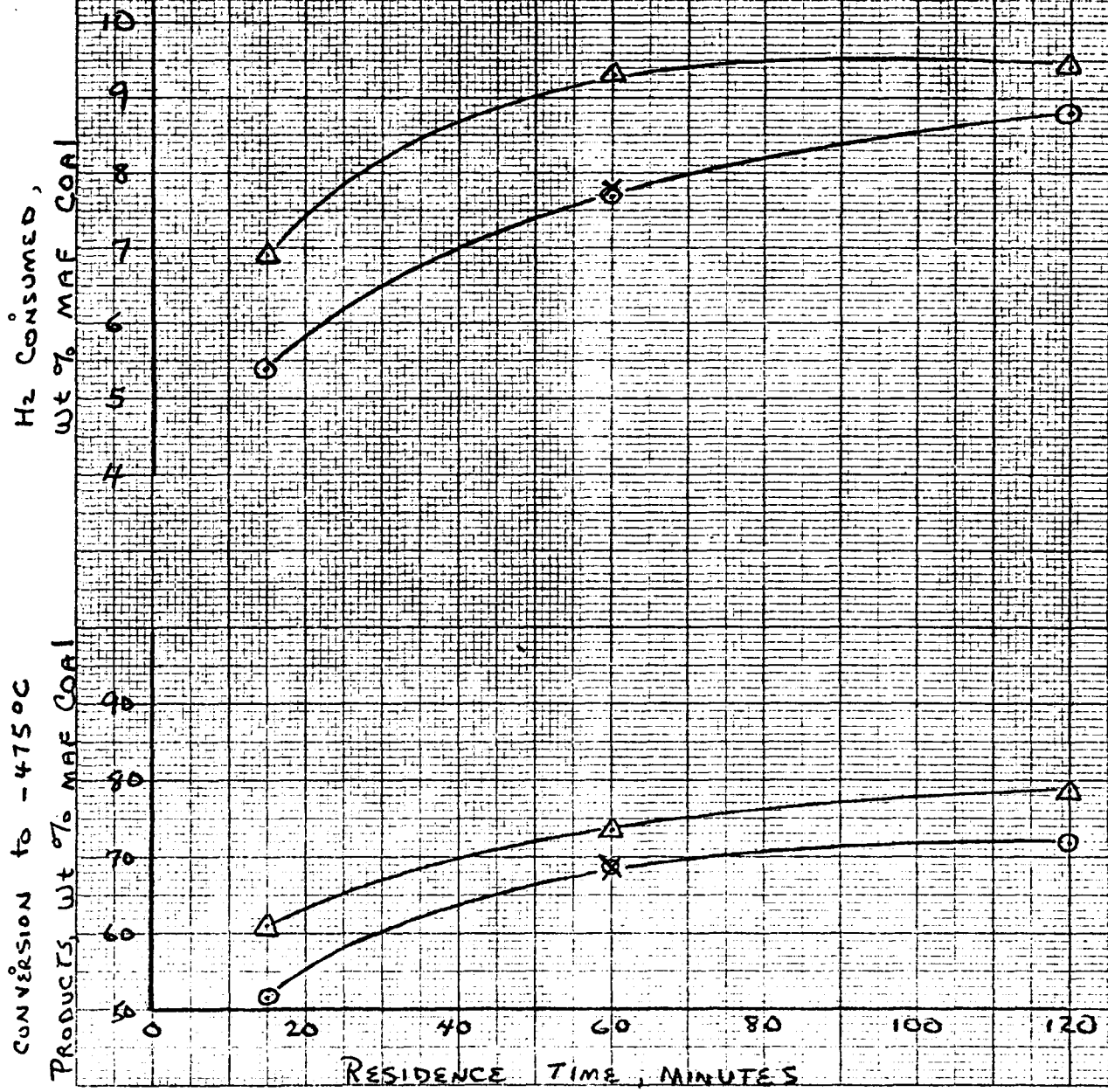
<u>Conditions</u>	
Feed Composition	10% Polystyrene 90% Benzene
Feed Wt, grams	48.90
Wt of ZnCl ₂ , grams	49.99
H ₂ Partial Pressure, psig	3000
Final Total Pressure, psig	4100
Temperature, °F	775
Residence Time, minutes	60

<u>Summary of Yields</u>	
-C ₅	2.57
C ₅ x 150°C Distillates	94.21
150 x 200°C Distillates	1.27
+200 x 475°C Distillates	2.67
+475°C Residue	.00
H ₂ O-Benzene Insolubles	<u>.16</u>
	100.88

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

FIGURE # 1

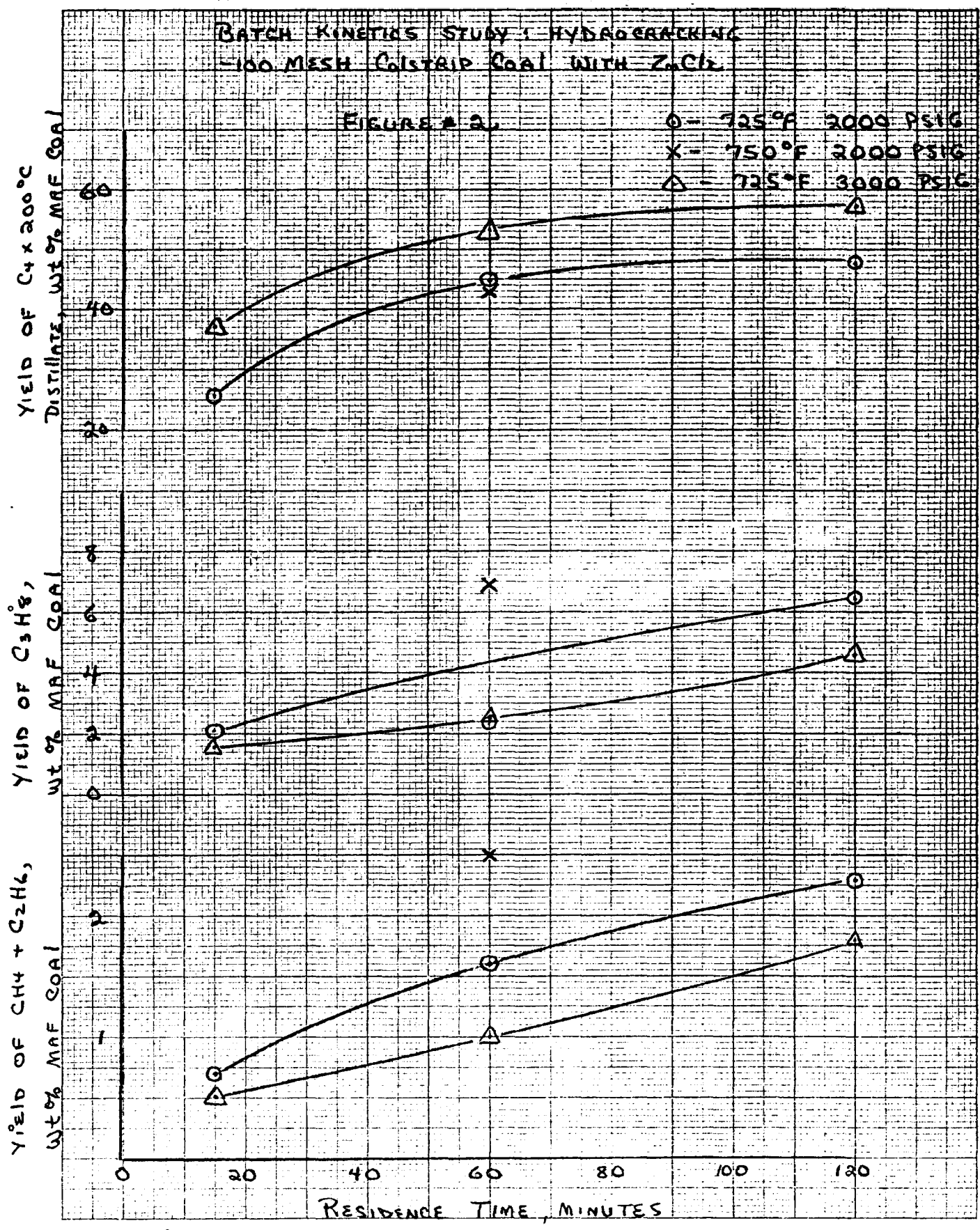
- 725°F 2000 PSIG
- × 750°F 2000 PSIG
- △ 725°F 3000 PSIG



BATCH KINETICS STUDY: HYDROCRACKING
 -100 MESH COALSTRIP COAL WITH $ZnCl_2$

FIGURE # 2.

O - 725°F 2000 PSIG
 X - 750°F 2000 PSIG
 Δ - 725°F 3000 PSIG



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

FIGURE No. 3

○ - 725°F 2000 PSI
 x - 750°F 2000 PSI
 Δ - 725°F 3000 PSI

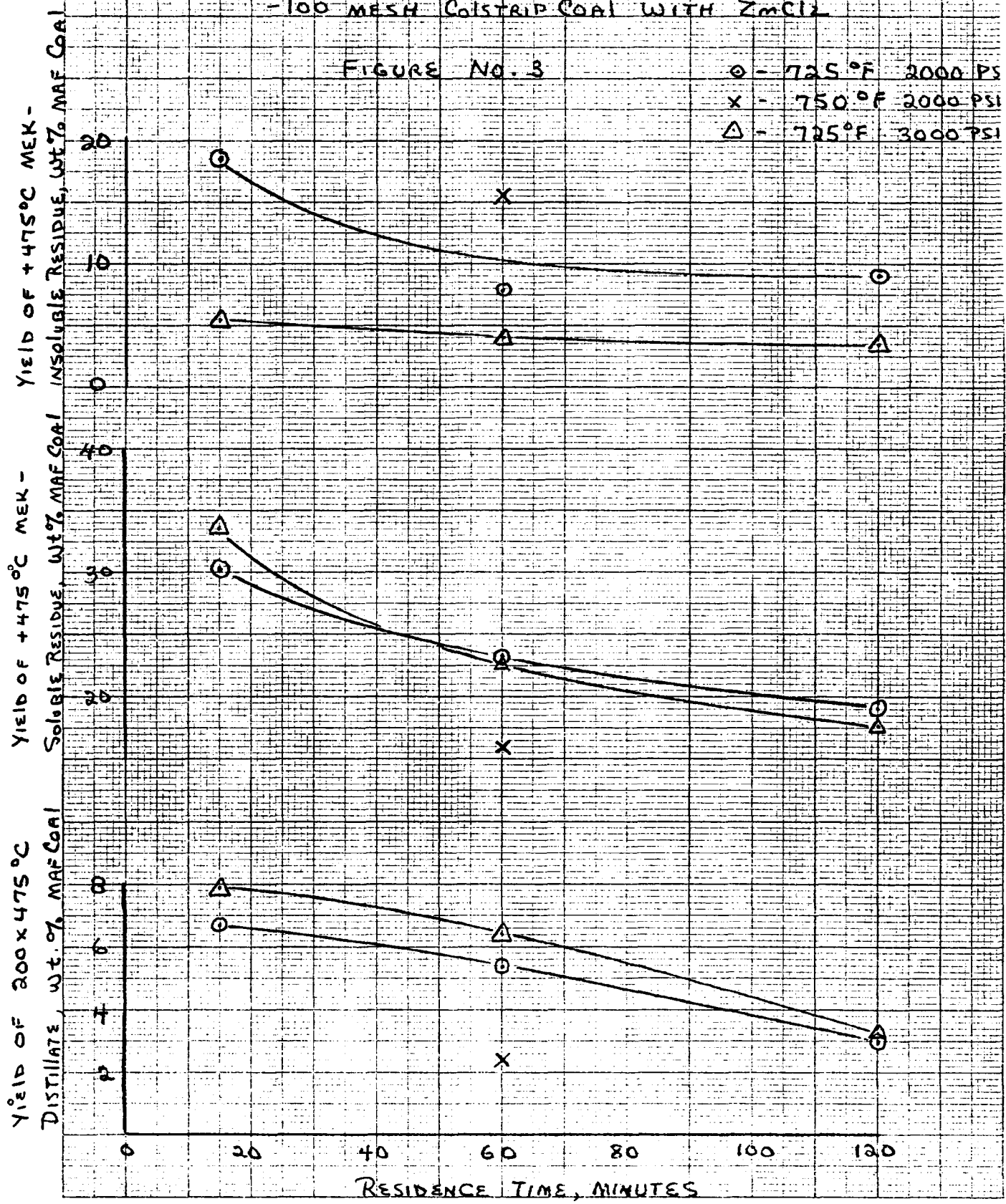


FIGURE 4

**Apparatus for Secondary Zinc
Recovery from Cyclone Solids**

