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ADVANCED COAL LIQUEFACTION
RESEARCH AND DEVELOPMENT FACILITY

Wilsonville, Alabama

TECHNICAL PROGRESS REPORT

Run 262 with Black Thunder Subbituminous Coal

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PREFACE

Operation of the Advanced Coal Liquefaction R & D Facility at the Clean Coal Research Center in Wilsonville, Alabama, is funded by the U. S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), and Amoco Corporation. Southern Company Services, Inc. (SCS) manages the Wilsonville program on behalf of DOE, EPRI and Amoco.

The Wilsonville R & D Facility combines two process units: a Close-Coupled Reactors (CCR) unit and a Residuum Oil Supercritical Extraction - Solids Rejection (ROSE-SR^{SM}) unit. The CCR unit uses H-Oil® technology, developed by Hydrocarbon Research, Inc. (HRI) and was constructed and modified by Catalytic, Inc. to allow close-coupled operation. The modification primarily consisted of adding a second reactor in close proximity to a pre-existing reactor. These close-coupled reactors can be used for various modes of operation --- thermal/catalytic, catalytic/catalytic and catalytic/thermal. The ROSE-SR^{SM} unit uses a proprietary solid-liquid separation process developed by the Kerr-McGee Corporation. The process separates ash and unconverted coal (UC) from resid as a heavy fluid phase, termed bottoms product, using a deashing solvent near its critical point. The combined two-unit system is generally known as a Two-Stage Liquefaction (TSL) process.

The TSL process is an advanced coal liquefaction concept, where the severities in the first and second stage can be independently varied, allowing for improvement in product slate flexibility. During Run 262, the main emphasis was to evaluate the performance of the TSL system using a dispersed molybdenum catalyst with and without the supported Criterion 324 1/16" catalyst in the second stage.

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ABSTRACT

This report presents the results of Run 262 performed at the Advanced Coal Liquefaction R & D Facility in Wilsonville, Alabama. The run started on July 10, 1991 and continued until September 30, 1991, operating in the Close-Coupled Integrated Two-Stage Liquefaction mode processing Black Thunder Mine subbituminous coal (Wyodak-Anderson seam from Wyoming Powder River Basin). A dispersed molybdenum catalyst was evaluated for its performance. The effect of the dispersed catalyst on eliminating solids buildup was also evaluated. Half volume reactors were used with supported Criterion 324 1/16" catalyst in the second stage at a catalyst replacement rate of 3 lb/ton of MF coal. The hybrid dispersed plus supported catalyst system was tested for the effect of space velocity, second stage temperature, and molybdenum concentration. The supported catalyst was removed from the second stage for one test period to see the performance of slurry reactors. Iron oxide was used as slurry catalyst at a rate of 2 wt % MF coal throughout the run (dimethyl disulfide (DMDS) was used as the sulfiding agent).

The close-coupled reactor unit was on-stream for 1271.2 hours for an on-stream factor of 89.8% and the ROSE-SR^{SM} unit was on-feed for 1101.6 hours for an on-stream factor of 90.3% for the entire run.

1. INTRODUCTION

The Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) mode was used in Run 262 in the thermal/catalytic, high/low temperature mode of operation. Prior runs in the CC-ITSL configuration include Runs 250-261 (Ref. 1-12).

In the CC-ITSL mode, the product from the first stage reactor was sent directly to the second stage reactor, without depressurizing or deashing. A high pressure gas-liquid flash separator was used between the two stages to remove the recycle and vent gases, water, and light hydrocarbons that were produced in the first stage. The remainder of the first stage product was sent to the second stage.

The effluent from the second stage was separated using three flashes: a high pressure flash, an atmospheric flash, and a vacuum flash. A portion of the bottoms of the vacuum flash, which contains resid, unconverted coal, and ash, was recycled to provide the CI content in the process solvent. The remaining portion of the bottoms from the vacuum flash were fed to the Residuum Oil Supercritical Extraction-Solids Rejection (ROSE-SR^{SM}) unit. The solids-free resid recovered in the ROSE-SR^{SM} unit was recycled with second stage distillate (heavy gas oil) and the vacuum flashed bottoms for coal slurry preparation. A simplified flow diagram of the CC-ITSL process is shown in Figure 1.

Dispersed molybdenum catalyst was introduced into the CC-ITSL system in concentrations ranging from 1000 to 100 ppm. The second stage contained Criterion 324 1/16" supported catalyst for all tests except the last period. In the last test period, the supported catalyst was removed from the second stage to evaluate the performance of slurry reactors. On the last day of the run, the reactor temperatures and coal feed rate were varied to find the flexibility of the slurry reactor system for the next run.

The new resid circulation system was used in the beginning of the run. In this system, coal was slurried with a mixture of heavy gas oil and deashed resid. The vacuum flash underflow stream containing the solids were injected directly into the preheater/reactor feed line. The resid circulation system was discontinued for the remainder of the run since the solids recycle pumps had frequent problems in handling the process stream.

In the following, a brief summary of Integrated Two-Stage Liquefaction (ITSL) runs conducted at Wilsonville is given:

Table A. Summary of Runs Since 242

Run	Coal	Configuration	Comments/Process Mode
242	Illinois No. 6	ITSL(1)	SCT(2)
243	Illinois No. 6	ITSL	
244	Illinois No. 6	ITSL	
245	Illinois No. 6	ITSL	On-line cat. replacement in second stage
246	Wyoming	DITSL/ITSL	Iron oxide addition in first stage(3)
247	Illinois No. 6	RITSL(4)	First stage dissolver tracer study
248	Illinois No. 6	DITSL/ITSL	Low Contact Time liquefaction(5)
249	Wyoming	RITSL(4)	Forced back-mixed dissolver
250	Illinois No. 6	CC-ITSL	Thermal/Catalytic
251	Ill./Wyo.	CC-ITSL	Thermal/Catalytic and Catalytic/Catalytic(6)
252	Illinois No. 6	CC-ITSL	Catalytic/Catalytic
253	Illinois No. 6	CC-ITSL	Catalytic/Catalytic
254	Ohio No. 6	CC-ITSL	Catalytic/Catalytic
255	Texas Lignite	CC-ITSL	Thermal/Catalytic and Catalytic/Catalytic
256	Ohio No. 6	CC-ITSL	Catalytic/Catalytic(7)
257	Illinois No. 6	CC-ITSL	Catalytic/Catalytic(8)
258	Bl. Thunder/Sp. Creek	CC-ITSL	Thermal/Catalytic(9,10)
259	Pittsburgh No. 8	CC-ITSL	Catalytic/Catalytic
260	Black Thunder	CC-ITSL	Thermal/Catalytic and Catalytic/Thermal(11)
261	Illinois No. 6	CC-ITSL	Catalytic/Catalytic(12)
262	Black Thunder	CC-ITSL	Thermal/Catalytic(10,13)

(1) In Runs 242-250, the first stage was a thermal liquefaction stage and the second stage was a catalytic stage.

(2) SCT denotes Short Contact Time liquefaction. A dissolver was not used.

(3) Iron oxide and dimethyl disulfide (to form sulfided iron catalyst in first stage) are usually added in low rank coal runs

(4) RITSL was a precursor to CC-ITSL. RITSL differs from CC-ITSL in that the reactor interstage stream is cooled and depressured.

(5) A 5.2" ID dissolver was used.

(6) Catalytic/catalytic mode denotes that a supported catalyst was present in both reactors.

(7) On-line catalyst replacement capability added to second reactor.

(8) Also tested half-volume reactors and low/high temperature severity operation.

(9) Spring Creek/Black Thunder Mine coals from Powder River Basin.

(10) Half-volume reactors were used throughout the run.

(11) Full-volume thermal stage and three-quarters-volume catalytic stage.

(12) EXP-AO-60 and Criterion catalysts used.

(13) Used dispersed molybdenum and supported Criterion catalysts.

Figure 2 shows, in a block diagram form, all of the operating modes tested at Wilsonville since Run 242. Figures 3, 4, and 5 are flow diagrams of the coal slurry preparation system, ebullated bed reactor, and the ROSE-SR^{SM} unit, respectively. The resid circulation system used in period 262A and 262B is described in Section 3. The nomenclature and definitions are given in Appendix A.

Objectives

The primary objectives of Run 262 were:

- To evaluate the performance of a dispersed molybdenum catalyst processing a low-rank coal, and
- To investigate and reduce/eliminate solids buildup processing a low rank coal.

During Run 262, the following modifications and tests were done to attain the objectives set forth.

- Modified the catalyst withdrawal tube flush system in both the reactors for use with a hot, heavier V1074 flush solvent.
- Installed a new injection system to feed the Molyvan L slurry catalyst.
- Start up the plant for process equilibration with Black Thunder mine coal.
- Evaluate the performance of the Molyvan L slurry catalyst at 1000 ppm molybdenum addition rate, operating with a Criterion 324 catalyst replacement rate of 3 lb/ton MF coal in the second stage and at 825°F first stage and 760°F second stage reaction temperatures and 250 MF lb/hr coal feed rate.
- Evaluate the performance of the Molyvan L slurry catalyst at a 500 ppm molybdenum addition rate.
- Switch to the batch slurry blend system using V131B, V101A and V101B tanks due to problems with the resid circulation system.
- Determine the effects of the increase in the second stage reaction temperature to 790°F and the increase in coal feed rate to 300 MF lb/hr on process performance.
- Evaluate the performance of the Molyvan L slurry catalyst at a 200 ppm molybdenum addition rate.
- Evaluate the performance of Molyvan L slurry catalyst at a

100 ppm molybdenum addition rate.

- Determine the effect of a dispersed catalyst system by removing the Criterion 324 catalyst from the second stage.
- Conduct a short test to observe the process responses at 810°F first stage and 825°F second stage reaction temperatures and 300 MF lb/hr coal feed rate.

The evaluation of a dispersed molybdenum catalyst in the CC-ITSL system was designed in a step-by-step manner. Since Runs 258 and 260 were performed in thermal/catalytic mode with Criterion (Shell) 324 supported catalyst in the second stage, the first tests were to add the dispersed molybdenum catalyst to the familiar system for comparison and to maintain smooth operation and system stability as in previous runs. Near the end of the run, the supported catalyst was withdrawn from the second stage to obtain data with dispersed iron and molybdenum catalysts alone. This was done in order to observe the operational stability in preparation for Run 263 where slurry reactors using only dispersed molybdenum and iron catalysts will be tested by varying the molybdenum concentration, second stage temperature, and coal space rate with an optional test of using another molybdenum precursor.

The second objective of the run was to reduce/eliminate the solid deposits experienced while liquefying low-rank coal. The dispersed molybdenum may give acceptable conversions at moderate reaction temperatures and reduce the coking reactions that are likely to cause solids to deposit in the transfer lines.

2. CONCLUSIONS AND RECOMMENDATIONS

2.1 Conclusions

The conclusions for Run 262 are:

- The "all-distillate" product slate was achieved with resid extinction in periods A, B, C, D and E. The TSL excess resid yield was -0.5 to 3 wt % MAF coal with 16-20 wt % organic rejection.
- Periods 262C and D had high C_4+ distillate yields (61 wt % MAF coal) with 17-20 wt % organic rejection. The highest C4+ distillate yield obtained in Run 262 was 65 wt % MAF coal, achieved in period C1 (Table D), with -4 wt % resid yield and 17 wt % organic rejection. Resid content in the process solvent was high (39.1 wt %) during this period.
- The addition of Molyvan L as a dispersed molybdenum slurry catalyst seemed to improve resid and coal conversions allowing lower temperature and higher space velocity operation. The use of even a low 100 ppm molybdenum concentration gave good performance in period E with resid extinction at the highest space velocity ever used at the Wilsonville pilot plant (91.5C lb MF coal/hr/cuft-reactor in first stage (C: a constant) or 110 lb MF coal/hr/cuft-catalyst in second stage).
- No solid deposits were found in the transfer lines or the second stage. A small amount of deposit was found in the interstage separator and the first stage. The reduction of deposits in the system was not necessarily due to the molybdenum or the process configuration alone. The system was not run at high temperatures which readily form deposits.
- Criterion 324 catalyst in the second stage significantly improved resid conversion generating more process exothermic heat, and as a result, allowing lower temperature operation of the interstage heater without exceeding the second stage reaction temperature.
- Operational difficulties were experienced with the new resid circulation system due to high variation in flow rate. The new resid circulation system did not improve resid conversion reactivity compared to the batch slurry blend system which had longer residence time for the resid in the process.

Major Observations in Run 262 were:

- Reducing the molybdenum concentration from 1000 to 500 ppm seemed to reduce the resid conversion and the coal conversion, although the 500 ppm moly test was operated at a higher resid recycle.

- Dispersed molybdenum appears to increase coal conversion. Compared to Run 258 at similar coal feed rates, higher coal conversions were obtained in Run 262 due to dispersed molybdenum, despite lower thermal reactor temperature.

- Persistent problems were experienced with the pumps handling the vacuum flash bottoms containing resid and about 35-40 wt % CI. The flowrate of the new pumps injecting the recycle CI's (P1091) exhibited swings of as much as 150 lbs/hr during a typical day. This in effect caused swings throughout the system and resulted in inconsistent samples and analytical data during period 262A.

- The interstage stream had about 7.2 wt % hydrogen during the part of the run with molybdenum catalyst concentration of 500 ppm. In comparison, periods 260A-C had only about 6.1 - 6.5 wt % hydrogen in the interstage stream. Both iron and molybdenum slurry catalysts were used in Run 262, but in Run 260 only iron slurry catalyst was used.

- The carbon on the second stage Criterion catalyst (at 790°F second stage reactor temperature) was around 8.5-9.0 wt %. In comparison, carbon on the Shell (same as Criterion) catalyst during periods 260A-C was in the range 11 to 15 wt % (790°F second stage reactor temperature).

- The ROSE-SR^{SM} resid recovery was low and the organic rejection was high for Run 262. When comparing Run 262A-D to periods 258H and 260C, ash content in the bottoms product averaged 34.0 vs. 46.2 wt % and resid recovery averaged 65.9 vs. 82.2%. This is probably due to the higher coal conversions observed in 258H and 260C.

- ROSE-SR^{SM} unit feed properties for Run 262 were found to have differences from feeds in Run 260 with the same coal. They had higher viscosities and also contained more hydrogen and oxygen compared to a feed product from period 260C. These differences may be a factor why lab analysts in this run are having difficulty filtering the insoluble matter from ROSE-SR^{SM} feed solubility tests.

- The GC cut point of the distillate product (T102 overheads) from GC simulated distillation and by the equal weight percent overlap method did not vary much during the run (783 - 793°F, with an overlap of 6-11 wt %). The laboratory workup for the distillate product quality using the ASTM D1160 method gave end points between 723-775°F except for period 262A. These end points are for the combined distillate product (T105 and T102 column overheads) for each period. As in previous runs, the GC simulated cut points are 10-40°F higher than those estimated by the D1160 method.

- Varying the molybdenum concentration from 100 to 1000 ppm seemed not to affect resid conversion, but increasing the molybdenum concentration improved coal conversion.

- The second stage catalyst activity (in terms of calculated rate constant) declined at 810°F, even with catalyst replacement at 3 lb/ton MF coal, indicating more rapid deactivation compared to operation at 790°F.

- Apparent activation energy determined for the second stage catalytic conversion was high, 89,000-94,000 Btu/lb-mole, indicating that the Molyvan L addition was more effective at higher temperature operation for resid+UC conversion.

- Catalytic resid+UC conversion with Criterion 324 catalyst seemed more than three times greater than thermal conversion. This was observed in operation with 100-200 ppm molybdenum concentration.

- A good linear correlation was observed between organic rejection and coal conversion, processing low-rank coals and lignite.

- Distillate properties were generally the same throughout this run. Molyvan L concentrations seemed to have little effect on product properties within the range studied.

- Hydrogen content in the distillate product averaged 11.32 wt %. Nitrogen content in the distillate product averaged 5,303 ppm and increased as the boiling point of the fractions increased.

- The distillate product properties were similar to those in Run 260D period except for slightly higher nitrogen.

- At a high space velocity of 110 lb coal/hr/ft^3 catalyst, the distillate yield and coal conversion were 57.2 and 91.6 wt % MAF coal, respectively (262E).

- When the supported catalyst was taken out in period 262F, the distillate yield was only 47.5 wt %.

- The solvent quality decreased in 262F once the Criterion 324 catalyst was taken out of the second stage from about 80 to 74%.

- At the end of the run, no solids were found in the transfer lines or in the second stage. A significantly lower amount of solid deposits were found in the interstage separator and in the first stage. The solid deposition in this run was of a semi-solid type with much lower ash content (21-32 wt %) compared to the solids in Run 258 and Run 260 with higher ash contents (56-67 wt %) and of a dry, hard type.

- After September 19, the V1258 and V1250 overheads contained a waxy material which were paraffinic in nature. The paraffins appeared when the weather became cooler and shortly after increasing the coal feed rate to 350 lb MF coal/hr. There does not seem to be any correlation with taking the Criterion catalyst out of the second stage reactor and the appearance of the paraffins.

2.2 Recommendations

- Continue testing with the new dispersed molybdenum catalyst, Molyvan L, in the absence of a supported catalyst and to increase the distillate production at resid recycle levels higher than 40 wt % in the process solvent.
- Test at first/second stage reaction temperatures higher than 825/810°F to increase the distillate production.
- Test at molybdenum concentrations lower than 200 ppm MF coal to improve the process economics by reducing the slurry catalyst cost.
- Determine the effects of solids recycle levels and iron-oxide (+DMDS) slurry catalyst concentrations on process performance in the presence of Molyvan L slurry catalyst.
- Test with Texas lignite in the slurry catalyst system to evaluate distillate production, yield and selectivity at coal conversion higher than 90 wt % MAF coal.
- Test the low/high thermal severity configuration in the catalytic/catalytic mode to improve the thermal efficiency, catalyst utilization, distillate selectivity, and hydrogen efficiency.
- Evaluate the performance of EXP-AO-60 bimodal catalyst in processing subbituminous coals and lignite.
- Molybdenum precursors other than Molyvan L should be tested such as Molyvan 822 for higher levels of hydrogenation.
- Evaluate process economics with variations of catalyst type such as the hybrid, supported plus dispersed catalyst system, slurry reactors, and supported catalyst only.
- Dispersed molybdenum catalyst allows higher throughput, however, the nitrogen content is much higher in the distillate product. Thus, there is a need to investigate and add a packed bed reactor to improve the product quality.
- Test SO_2 pretreated subbituminous coal to evaluate the elimination/reduction of solid deposits during liquefaction by removing calcium so as not to form calcium carbonate.

3. OPERATING DATA AND PROCESS PERFORMANCE

The main objective of this run is to test a dispersed molybdenum catalyst to study its effects on solids buildup and yield performance. Molyvan L, which is an organic liquid additive containing molybdenum, sulfur, and phosphorous, was used as a precursor to obtain dispersed molybdenum catalyst in situ. These tests were made in thermal/catalytic, high/low mode with Criterion 324 catalyst in the second stage. The effects of various parameters such as dispersed molybdenum concentration, second stage temperature, and space velocity were studied. At the end of the run, most of the Criterion 324 catalyst was taken out of the second stage reactor and a datapoint was obtained.

3.1 TSL System Stability

TSL system stability is judged by evaluating the material balance closure errors, plant operation stability, and plant performance stability. Criteria for selection of stable days include:

- Mass balance closure errors for CCR unit (first and second stages), and ROSE-SR^{SM} unit must be less than 10 wt % MAF coal.

- The sum of absolute values of inventory changes including drumouts, must be less than 15 wt % MAF coal for the following locations.

    a) Between the second stage and ROSE-SR^{SM} unit,
    b) Between the ROSE-SR^{SM} unit and the first stage.

A description of the elemental balancing procedure and a more detailed description of the selection criteria are given in Appendix B (Material Balance Methodology).

Run 262 was started on July 10 and was interrupted on July 11 with a hole in the V1067 to V1082 line. Coal feed resumed on July 11. There were multiple problems during July 11-22 (period 262A). The centrifugal pumps on V1082 bottoms were changed out many times due to seal or seal oil system failures. Also, the circulation rate was not high enough. The P1091 pumps on the CI recycle from V1082 would not pump or leaked at the head. Also, the ROSE-SR^{SM} unit would not deash. Due to continued ash carryover, the ROSE-SR^{SM} unit plugged on July 22. While the ROSE-SR^{SM} unit was being cleaned out, several mechanical problems were found that would explain the poor performance during the July 11-22 period. The gate from a gate valve had come loose and was restricting the V1082 bottoms circulation. Also several holes were found in the V1082 overheads condenser -- the source of poor vacuum and high solvent content in the ROSE-SR^{SM} feed.

Coal feed resumed on August 6. The ROSE-SR^{SM} unit started deashing. On August 10, the recycle gas compressor packing began to leak excessively and the overhead condenser on T102 failed. The condenser had only been in service for 20 months. The tubes at the inlet looked like metal had been removed on the side facing the vapor. One of the tubes was cracked.

The run resumed on August 12 without T102. The V1082 vacuum flashed overheads was used for blending with the coal until August 15 when the T102 overhead condenser was repaired.

Another problem was that the P1091 resid+CI injection pumps on the V1082 bottoms recycle continued to pump slower until the recycle line plugged on August 16. Since the resid and CI inventory was low, it took about three days to go back to target recipe using the V1082 recycle via V131B, the process solvent tank. Periods 262C1, C2, D, E and F did not have resid and CI recycle via the resid injection system.

During the latter part of August, the valve on the interstage separator failed to control the level and at times allowed gas to flow through to the second stage. On inspection, the valve trim was worn. Normally the valve can be repaired while running. However, the bypass line was plugged. There were indications of solids in the separator both by high density/level reading on the separator and by the low mid temperature reading on the separator for August 26-27. The coal feed was stopped on August 29 to repair the separator level valve.

After the feed rate was increased to 350 lb/hr, presence of wax was more apparent; in periods 262E and 262F, the separator overheads would not flow through the water/oil separator or through the lines to T105. Also, the flashed overheads from the second stage high pressure letdown valve were waxy and would not flow. During the outage, these sections of the plant will be steam traced although they have never needed tracing in the past.

On September 24, period 262F, the V1079 calibration tank was bypassed which caused material balance problems. The discharge valve would not open completely.

DIFFICULTY OR CHANGE	**CONSEQUENCE**
Molyvan L + DMDS addition tank and pumps installed.	New for Run 262.
V1074 to both withdrawal tube flushes completed.	New for Run 262.
On coal feed, July 10.	

Hole in V1067 to V1082 line.	Off coal feed, July 11.
On coal feed, July 11.	
Multiple problems July 12-22.	
Pumps on V1082 would not circulate.	
Pumps on CI recycle would leak at packing or not pump.	
ROSE-SR^{SM} unit would not deash.	
Pumps on coal slurry would not pump at 48.5% coal.	Changed to 45% coal, July 19.
Line to ROSE-SR^{SM} second stage plugged, July 22.	Off coal feed.
Condenser on V1082 was leaking. Holes in several tubes, July 22.	Probable cause of ROSE-SR^{SM} unit not deashing.
Gate valve had come off of V1082 recirculation valve.	Probable cause of V1082 recirculation problem.
On coal feed, August 6.	
Moly addition reduced to 500 ppm, August 7.	
Large leak at packing on recycle gas compressor.	Off coal feed, August 10.
During outage leak developed in T102 overhead condenser, August 10.	Some water carried to reactors. T102 shutdown.
On coal feed, August 12, with T102 bypassed.	
CI/resid pumps leaking with diminished output, August 6-15.	
Condenser replaced on T102, August 15.	T102 back in service.
Resid+CI/resid pumps not functioning. Line or check valves plugged, August 16.	Direct pumping of resid+CI discontinued. Using V131B for blending process solvent.
Increased coal feed rate to 300 lb MF /hr, August 16.	

Low recycle ash due to transition from resid injection to V131B blend. Also DMDS rate not increased with coal feed.	Low coal conversion for August 16-18.
DMDS and Molyvan L addition rate increased to 500 ppm, August 19.	
Increased second stage temperature to 790°F, August 19.	
Level control valve on V1258 is not controlling the flow. Gas blowing through to second stage. V1258 density/level gauge showing high level, August 22.	Upset condition.
Bypass on V1258 level valve is plugged, August 23.	Can not repair V1258 level valve.
Mid temperature of V1258 showed low, August 26-27.	Usual indication of solids in separator.
Four power failures, August 27.	Upset conditions.
To 200 ppm Mo, August 28.	
V1258 level very difficult to control, August 29.	Off coal feed.
V1258 had a large clump in bottom of the vessel. Trim on V1258 valve was worn.	
Viscosity in V101A and B became high. Tanks were diluted with T102 OH distillate, September 3.	
On coal feed, September 6.	
P1222 ebullating pump on R1235 not pumping, September 7.	Blew suction to drum to get flow.
V1258 level valve plugged, September 9.	Loss of flow, upset.
To 100 ppm Mo, R1236 to 810°F and coal feed rate set to 350 lb/hr, September 13.	
Target process solvent composition set at 42% resid, 38% distillate,	

September 16.	
V1258 OH and V1250 OH are waxy, September 19.	Pipes are plugging. Will have to be steam traced.
To 300 ppm Mo for 1/2 day, then to 200 ppm Mo and most of the catalyst removed, September 23.	
Valve on V1079 calibration tank not functioning, September 24.	Flow rate to be estimated.
Lost circulation on V101B, September 28.	Short feed outage. Low temperatures in reactors.
First stage to 810°F and second stage to 825°F. Lowered feed rate to 300 lb MF/hr at 1130 for 5 1/2 hours.	
End of run, October 1.	

In Figure 7, the forced ash balance coal conversion is shown for Run 262. The coal slurry viscosity is shown in Figure 8. From July 10 to August 17, the coal slurry contained 40-48 wt % coal in V1074 solvent plus deashed resid. After August 17, the viscosity of the whole slurry, with 30 wt % coal, is shown. The slurry viscosity is not a good indicator of whether the high coal concentration slurries would pump or not. When the coal concentration was changed from 45 wt % coal to 48.5 wt % coal during July 17-19, the slurry viscosity did not change, however, the centrifugal pumps would not move the coal slurry resulting in plugged suction lines. The maximum coal concentration that was functional was 45 wt % coal.

Historically, the inventory of process solvent has been high (22-35 hours for one turnover) at the pilot plant due to the nature of batch processing of coal plus process solvent slurries. Ideally, continuous coal addition would significantly reduce process solvent inventory, however, due to cost, the resid injection system was proposed to reduce the inventory of resid plus CI but would increase the inventory of distillate.

The normal method of preparing process solvent is to add resid from the ROSE-SR^{SM} unit, CI containing heavy resid from V1082 (vacuum bottoms) and heavy distillate from T102 bottoms (V1074) to V131B to make the process solvent recipe which is usually 12% CI, 50% resid, and 38% distillate for bituminous coals or 20% CI, 30-40% resid and 50-40% distillate for subbituminous coals. Coal is then added to the process solvent to make a 30-33 wt % slurry. For the resid injection system operation, the coal is added to the heavy distillate (V1074) alone or as a mixture of V1074 plus ROSE-SR^{SM} deashed resid to make a slurry of less than 48 wt % coal. The CI containing resid (V1082) is then pumped into the same feed line that the coal slurry is pumped into (see Figure 6). Also, the ROSE-SR^{SM} resid can be pumped into the same feed line. The equipment installed consisted of measuring tanks for the ROSE-SR^{SM} unit deashed resid (V1090) and for the V1082 vacuum bottoms (V1091). Two high pressure pumps (P1090A/B pump and spare) were used to pump the ROSE-SR^{SM} resid and two high pressure pumps (P1091A/B pump and spare) were used to pump the V1082 vacuum bottoms.

3.2 Feed Coal

Black Thunder subbituminous coal from the Thunder Basin Coal Company in Wright, Wyoming, served as the feed coal for Run 262. This Powder River Basin Coal was last used in Run 260. Typical analysis of the feedstock are summarized in Table 1. The elemental data remained about the same throughout Run 262. Black Thunder coal is low in sulfur compared to bituminous coal and it is almost devoid of pyritic sulfur commonly found in bituminous coals. Pyritic sulfur is a natural catalyst and aids in coal conversion in the liquefaction process. Hence for Run 262, the pyritic sulfur had to be generated by the addition of iron oxide and dimethyl disulfide (DMDS).

The Black Thunder coal contains about twice the oxygen content of bituminous coals. The oxygen is distributed into various functional groups, with each having its own particular influence on process performance. Much of the oxygen will combine with hydrogen to make water. Carbonyl oxygens can easily combine with the high calcium and magnesium content to form scale deposits in lines and vessels.

Black Thunder coal for Run 262 contained about 22 wt % moisture. This water is driven off in the slurry drying system before the coal ever reaches the first reactor. The drying takes time and is a limiting step in achieving high coal feed rates with subbituminous coals. Typically, slurry batches consist of two parts recycle solvent (V131B) and one part moisture free coal. However in Run 262, a resid injection system was used which changed the usual sequence of steps for coal slurry preparation. Slurry preparation is discussed in the following section.

3.2.1 Slurry Preparation

For periods 262A and 262B, the resid circulation system was in operation. A description of the new system is given in Section 3.1 TSL System Stability. Since a sample of the complete process solvent is not available with this system, analysis of the recycle process solvent is available only for periods 262C-F in Table 2.

After August 16, the batch coal slurry preparation began using V131B, V101A, and V101B tanks. With this system, the process solvent used for coal slurry blend was a mixture of V1074 heavy gas oil (T102 vacuum column bottoms), full range ROSE-SR^{SM} resid, and the V1082 vacuum flashed bottoms.

Targeted conditions for the recycle process solvent were 40 wt % resid, 20 wt % CI, and 40 wt % distillate. From period 262C onwards, the resid concentration in the process solvent was floated. The resid made in the system was recycled back to the process.

3.3 Close-Coupled Reactor (CCR) Unit

The close-coupled reactor (CCR) unit had the following objectives for Run 262:

1) Evaluate the performance of the CCR unit using a dispersed molybdenum catalyst.

2) Eliminate solid deposition in the process when processing a low rank coal.

3) Evaluate process performance with the resid injection system in service.

4) Evaluate process performance using dispersed molybdenum catalyst, with and without the supported Criterion 324 1/16" catalyst in the second stage.

5) Test the slurry reactors in low/high temperature mode and lower coal feed rate to find the range of operability for the next run.

Feed slurry composition, coal feed rate, dispersed molybdenum catalyst concentration, and reactor temperature were changed to maintain smooth operation and obtain performance data for the molybdenum catalyst. Coal conversion, hydrogen consumption, and resid and distillate yields were monitored daily as performance indicators. Catalyst samples were routinely analyzed to evaluate the catalyst for activity and integrity.

3.3.1 Unit Operations

Before the unit was put on coal feed for Run 262, a simple reactor heat loss test was performed. The unit was on solvent recycle during the tests and the ebullating pump was on for half of the tests. The results of the heat loss test are presented in Section 7.1 Reactor Heat Loss Test.

During the shutdown, a system was implemented to inject a hot, heavier boiling material as the withdrawal tube flush. The V1074 material (bottoms of the vacuum distillation column) was used as the flush in Run 262. The flush was heated by a dowtherm jacket before entering the withdrawal tube.

Also implemented before the run was a system to inject a mixture of Molyvan L and DMDS (dimethyl disulfide) into the feed line before the preheater (B1200). Drums of these two materials are pumped into a vessel. The mixture from the vessel is pumped to the feed line.

The CCR unit went on coal feed on July 10. However on July 11, a hole in the line between V1067, the atmospheric flash, and V1082, the vacuum flash, caused the unit to go off feed for the day. The first full operating day, therefore, was July 12. The target conditions for the start of Run 262 are shown below:

<u>Coal</u>	
Type	Black Thunder Sub.
Feed rate	250 lb/hr
Conc. in Slurry	30 wt %
<u>Process Solvent</u>	
Resid	40 wt %
CI	20 wt %
<u>First Stage</u>	
Temperature	825 °F
Dispersed Moly Cat Conc.	1000 ppm moly
Fe_2O_3 Conc.	2 wt %
Reactor Volume	Half
<u>Second Stage</u>	
Temperature	760 °F
Catalyst Type	Criterion 324
Catalyst Charge	170 lbs
Cat. Replacement Rate	3 lb cat/ton coal
Reactor Volume	Half

The process changes from the initial test period are listed below.

August 7	Moly conc. decreased from 1000 to 500 ppm.
August 13	T102 taken out of service.
August 15	T102 in service.
August 16	Resid injection system out of service. Coal feed increased from 250 to 300 lb MF/hr.

August 19	Second stage temp. increased from 760 to 790°F. Moly conc. set at 500 ppm.

The resid injection system was in service at this time. Since the best conditions to operate this system is at 45 wt % coal concentration in the slurry mix tank (before injecting the solids recycle stream), the coal concentration in the total slurry was lower than the target of 30 wt %. To try to get closer to the target, the coal concentration was increased to 46-48 wt % in the coal slurry tank between July 17 and 19. However, due to circulation pump problems and longer coal addition time, the coal concentration was set at 45 wt % on July 19th.

Criterion 324 1/16" unimodal, supported catalyst was charged to the second stage reactor (R1236) from Run 260. This catalyst was already at an age equivalent to 3 lb catalyst/ton coal from operation in Run 260. At the beginning of the run, 145 lbs of catalyst was charged to R1236. On July 14, the charge was increased to the target of 170 lbs.

During July 12 through July 21, there were many operational problems. From July 12-15, the vent system on the coal slurry tank was not pulling a good vacuum causing longer coal addition times. A new fan was installed and modified to eliminate the problem.

Throughout July 12-21, the vacuum flash (V1082) circulation pumps would not pump without frequent flushing. This caused the temperature in the vacuum flash to be lower sending more solvent to the ROSE-SR^{SM} unit. The flush material was V178 material or T102 product.

The ROSE-SR^{SM} unit could not deash the resid during this time. The strength of the deashing solvent became the weakest available to Wilsonville. This may be due to high solvent in the feed to the ROSE-SR^{SM} or characteristics of the feed caused by the dispersed molybdenum catalyst. See Section 3.4 for more details on the ROSE-SR^{SM} unit operation.

Starting July 20, the solids recycle injection pumps would not pump consistently at the rate required for 20 wt % CI concentration. The solids concentration for these positive displacement pumps was too high. The solids recycle rate swung quite a bit until August 16 when the resid injection was discontinued. A problem resulting from the recycle rate swings was swings in the system causing the samples and the analytical data to be inconsistent. Figure 9 shows the solids recycle injection rate for August 6 to August 15.

On July 22, the plant went off coal feed due to excessive plugging of the ROSE-SR^{SM} unit. Just before going off coal feed, a leak in the vacuum flash system was found. The overhead condenser (E1012) of the vacuum flash had tubes leaking. The ROSE-SR^{SM} second stage and exchanger were hydroblasted and the E1012 was repaired before the plant was put on coal feed on August 6.

On August 7, the molybdenum concentration (in the form of Molyvan L) was decreased from 1000 to 500 ppm. Decreasing the concentration of dispersed molybdenum catalyst gives a more realistic and economic amount of catalyst in the process.

The plant went off coal feed on August 10 to repack the gas recycle compressor (C1206). Upon going on solvent recycle, the T102 column lost vacuum. When the system was checked over, water was found in T102 and the overhead product vessel (V138). The cooling water on the T102 overhead partial condenser (E113) was leaking into T102.

On August 12, the plant was on coal feed without the T102 column in service. The atmospheric distillation column bottoms was sent to V178, the T102 product vessel. Vacuum flash overheads (V1072) was sent to the T102 bottoms vessel (V1074) for use as recycle. On August 15, the distillation system was set up with T102 in service.

The solids recycle injection pumps would not operate and a plug formed in the line from the pumps to the feed line on August 16. Therefore, the solids recycle was added to the solvent mix tank (V131B). The resid injection was discontinued on August 16. Also on August 16, the coal feed rate was increased from 250 to 300 lb MF coal/hr. The Molyvan L concentration was not increased until August 19 to give 500 ppm molybdenum at a 300 lb/hr coal feed rate. The second stage temperature was also increased on August 19 from 760 to 790°F. From August 16 to 19, the resid in the process solvent was lower than the targeted 40 wt % until the resid inventory could be increased.

From August 23 to 28, there were several indications of solids buildup in the interstage separator (V1258). On August 23, the bypass around the V1258 level control valve was found to be plugged. This bypass was possibly plugged from the beginning of the run. The level control valve was not controlling and leaking through causing swings in the system. This level control valve normally can be repaired on line, however, with the bypass plugged, repair of the valve was not possible. Since the valve was leaking through, the pressure drop between the reactors was lowered so that the valve would hold. Also during this time, the nuclear density/level indicator steadily increased indicating solids were depositing on the vessel walls. On August 26 to 28, the mid temperature indicator in V1258 was low meaning that solids were depositing on the thermocouple.

On August 29, the plant was taken off coal feed to inspect the lines and vessels for deposits, take samples, clean V1258 and the ROSE-SR^{SM} unit of solids. The places where flanges were broken to inspect the lines were located at the outlet of R1235, from R1235 to V1258, at the inlet of V1258, at the outlet of V1258, and from V1258 to the high pressure sampler. The V1258 was opened up and inspected. The lines between the first stage and the interstage separator and between the interstage separator and the high pressure sampler were found clean. About 12 lbs of semi-solids, a much lower amount compared to previous runs, was found in V1258.

When the plant was put on coal feed on September 6, the conditions were the following:

Coal	
Type	Black Thunder Sub.
Feed rate	300 lb/hr
Conc. in Slurry	30 wt %
Process Solvent	
Resid	40 wt %
CI	20 wt %
First Stage	
Temperature	825 °F
Dispersed Moly Conc.	500 ppm
Fe_2O_3 Conc.	2 wt %
Reactor Volume	Half
Second Stage	
Temperature	790 °F
Catalyst Type	Criterion 324 1/16"
Catalyst Charge	170 lbs
Cat. Replacement Rate	3 lb cat/ton coal
Reactor Volume	Half

The process changes from these test conditions are listed below.

Aug 28	Moly conc. decreased from 500 to 200 ppm.
Sep 13	Second stage temp. increased from 790 to 810°F. Coal feed increased from 300 to 350 lb/hr. Moly conc. decreased from 200 to 100 ppm.
Sep 23	Criterion 324 catalyst withdrawn from R1236. Moly conc. increased from 100 to 200 ppm.
Sep 30	First stage temp. decreased from 825 to 810°F. Second stage temp. increased from 810 to 825°F. Coal feed decreased from 350 to 300 lb/hr.

On September 6, the plant was put on coal feed and the molybdenum concentration was set at 200 ppm. Based on cost, a molybdenum concentration of 200 ppm is equivalent to catalyst replacement at a rate of 3 lb catalyst/ton coal. For process economics, the molybdenum concentration should be less than 200 ppm. In the next test, the molybdenum concentration was lowered to 100 ppm.

The interstage preheater (B1201) outlet temperature was low enough that the second stage temperature could be increased. Since there was no positive resid make, the feed rate also had to be raised so that enough resid would be available with operations at the higher second stage temperature. On September 13, the molybdenum concentration was decreased from 200 to 100 ppm, the second stage temperature was increased from 790 to 810°F, and the coal feed rate was increased from 300 to 350 lb/hr.

The process solvent was targeted for 42 wt % resid, 38 wt % solvent, and 20 wt % CI on September 16. Consistently, the actual amount of resid in the process solvent is sampled to be about 2 wt % lower than the target.

In order to see the contribution the dispersed moly catalyst has on the system when using a hybrid supported and dispersed catalyst system, the catalyst bed was withdrawn from R1236 on September 23. The molybdenum concentration was also increased from 100 to 200 ppm on September 23. When testing the slurry reactors, the second stage bed exotherm decreased to near 1 or 2°F, and there was a rapid buildup of resid at a high coal feed rate of 350 lb/hr.

A waxy gel started to be noticed by operations in the interstage separator overheads (V164) and the atmospheric flash overheads (V1250) after September 19. See Section 7.2 for a discussion on the wax observations. Towards the end of the run, the line from V105 (V1258 overheads) to V164 to V160 would plug with this waxy material and have to be cleared. Also, V1251 (atmospheric flash overheads separation vessel) had level control problems due to the gel from September 25 to 29.

On September 24, the V1079 dump pot was not working properly, and so it was bypassed. This necessitated that the V1079 flow rate be estimated by a material balance around V1082 vacuum flash vessel.

For the next run, the flexibility of the process using only dispersed molybdenum catalyst needed to be tested. On the last day of the run (September 30), low/high temperature mode was tested to see if the process would be able to run. The temperature was changed to 810/825°F in the first and second stages, respectively. Then, several hours later, the coal feed rate was reduced from 350 to 300 lb/hr to see if the temperatures could be maintained.

With the temperatures in low/high mode, it resulted in a 5°F increase in the interstage heater outlet temperature. After the coal feed was decreased, the conversion increased, however, the amount of material converted decreased so that the exotherm went down. When the coal feed was 300 lb/hr, the interstage heater outlet temperature increased by 10°F. Operable conditions were obtained with the lower feed rate.

In Run 260 with the reactors in low/high temperature mode, the target second stage temperature of 825°F could not be achieved. In attempt to increase the second stage temperature, the coal feed was increased but the highest reactor temperature attained was 804°F. Using slurry reactors, low/high temperature mode seems achievable from the brief test at the end of Run 262.

When the reactors were opened at the end of the run, the Criterion 324 catalyst recovery was assessed for R1236. The recovery was low at 76.2%. The probable cause for the low recovery was crushing of the catalyst by the impingement of the feed flow on the top face of the plenum chamber since the top surface of the plenum chamber had eroded grooves on it. Corrective action was taken after the run ended to minimize erosion.

3.3.2 Solids Buildup

The deposits from Run 258 during Black Thunder coal operation were analyzed by Pennsylvania State University and were found to be largely caused by mesophase-derived semicoke.(13) Therefore, Run 260 was operated in the catalytic/thermal mode with the intent of running at a low first stage temperature and a high second stage temperature to prevent coke formation along with retrogressive reactions.

The deposits formed during the catalytic/thermal operation of Run 260 (sample numbers 16411 and 16403) were also analyzed by Pennsylvania State University.(14) These samples were from the second stage thermal reactor. In their report, the minerals found by X-ray diffraction for both samples were similar. Calcite, halite, and pyrrhotite were the more predominant minerals along with spinel and quartz. The presence of halite was not expected because Black Thunder Mine coal typically does not contain chlorine. A recent analysis may explain the presence of chlorine in the solid deposit samples. Chlorine was found to be present at 2.02% in the iron oxide (purchased from Kerr-McGee Chemical Company, Mobile, Alabama) that was used as a slurry catalyst with DMDS as the sulfiding agent in Run 262. The same brand iron oxide was used in Run 260. A new brand of iron oxide (purchased from Bailey Engineers, Fairfield, Alabama) will be used in Run 263 that contains only 0.28% chlorine.

Optical microscopy analysis showed that the reactor bottoms sample was composed of calcium carbonate spheres, pyrrhotite aggregates with carbonate rims and coal-derived minerals cemented together with a thin layer of process-derived mesophase. The reactor wall scale was composed mainly of calcium carbonate cement. The deposits were mainly formed by the deposition or formation and accretion of calcium carbonate with the other process and coal derived inerts. These results suggest that the process conditions of catalytic/thermal mode to prevent coking may have been effective. However, the larger problem of process-derived calcium carbonate formation has not and may not be eliminated by changes in process conditions. This problem may have to be addressed by the removal of organically bound calcium ions before liquefaction.

In Run 262, the solid deposition problem associated with low rank coal was addressed by the use of a dispersed molybdenum catalyst to reduce the retrogressive coking reactions. The dispersed catalyst seemed to eliminate the deposits in the lines in between the reactors. However, the interstage separator had some deposition. The deposits in V1258 were semi-solid with a solid block floating in the bottom. This type of deposit (semi-solid) differs from the deposit seen in Runs 258 and 260. The transfer line deposit in Run 260 and the interstage separator deposit in Run 258 were very dense solids.

To detect the appearance and growth of any deposition, the pressure drop between the reactors and between the first stage and the interstage separator, the gas flow rate from the overheads of the interstage separator, and the interstage separator temperatures were monitored.

There was no increase in pressure drop between the reactors or between the first stage and the interstage separator like what was seen in Run 260. This gave evidence that the lines between the first and second stages were clean and free of deposits throughout the run. See Figure 10 for the pressure drops in Runs 262 and 260. The pressure drop between the reactors was purposefully decreased gradually (operation days (OD) 27-32) to prevent leaking through the level control valve of the interstage separator. The valve trim was eroded and the bypass around the valve was plugged, therefore, the valve could not be repaired.

The V164 rate or the interstage separator gas overheads rate, did not decrease gradually indicating there was adequate gas-liquid separation space and no great amount of solid deposits. The rate ranged 55 to 65 lb/hr. In Run 260 the rate decreased from 50 to 14 lb/hr. Figure 11 shows the V164 rate for both Runs 262 and Run 260.

Figure 12 shows the interstage separator temperatures of the bottoms, the overheads, and the downstream points. On OD=30, the temperature of the process stream in the interstage separator dropped dramatically. This was due to solids depositing on the thermowell.

From August 23 to 28, there were several indications of solids buildup in the interstage separator (V1258). During this time, the nuclear density/level indicator steadily increased which signified there were growing deposits in the interstage separator (starting on the day the coal feed rate was increased to 300 lb/hr). On August 26 to 28, the mid-temperature indicator in V1258 was low meaning that solids were depositing on the thermowell. On August 29, the plant was taken off coal feed for an orderly shutdown to inspect lines and vessels for deposition.

After we shut down, a number of flanges were unbolted to check for deposits in various lines. The location of the flanges were 1) at the 50% outlet of R1235, 2) between the first stage and the interstage separator, 3) the inlet to the interstage separator, 4) the bottom flange of V1258, and 5) between V1258 and the high pressure sampler. The top head of V1258 was removed and the vessel was inspected and cleaned.

No deposits were found in the lines before or after V1258. Semi-solids in the bottom of the interstage separator 18 to 22 inches in height were discovered. Also, in the bottom of the separator there was a big chunk of solid, hard material. The semi-solid material and the solid chunk weighed about 12 lbs. The amount of deposit is much less compared to previous runs. In the top of V1258, there was a small amount of wall scale.

V1258 solid samples from the August 29th shutdown are shown in Table 3 along with deposit samples from Runs 258 and 260. The solid chunks had higher UC (unconverted coal, UC = CI -Ash; CI is cresol insolubles) than the semi-solids type deposits (66.9 vs. 38.2 wt %). Compared to Runs 260 and 258, the ash content of the V1258 solids in Run 262 was much lower than the ash content of the deposits in Runs 260 and 258 (21-32 wt % vs. 56-67 wt %). The semi-solid metal analysis in the bottom of V1258 in Run 262 compares closely with the metal analysis of the Black Thunder coal ash. Also, the analysis of the chunk in the bottom of V1258 and the Run 258 solids found in V1258 are comparable. In this run, the solids had more calcium and less aluminum and sodium than the solids in Runs 258 and 260.

At the conclusion of Run 262, both reactors, the line from the high pressure sampler to the second stage, and the interstage separator were inspected. Neither the transfer lines nor the second stage showed any appreciable deposits upon inspection. This was expected since the pressure drop between the reactors or between the first stage and V1258 did not increase during the run.

The interstage separator had a thin deposit in the upper section on the walls. Semi-solids were found in the bottom of the separator. There was also a hard solid chunk in the bottom of the vessel measuring about 12 inches in height. The total amount of solids taken out of the interstage separator including the chunk weighed approximately 17 lbs. The nuclear density/level indicator did not show any appreciable indication of solids buildup prior to shutdown.

When the first stage reactor was inspected, there was a buildup in the bottom of the reactor. A solid deposit of 6 to 8 inches thick was found 10 to 12 inches above the top section of the bottom head. The remainder of the solids was scale around the plenum chamber that seemed to be deposited in layers (a normal occurrence due to dead space in the reactor). The total amount of solids removed from the first stage weighed 37 lbs. The solids found in the first stage reactor accumulated over the entire run since the first stage reactor was not opened and inspected during the August 29th shutdown. Upon inspection, no deposit was observed in the second stage reactor.

Figure 13 indicates locations where deposits were observed upon inspection at the end of the run. Samples 1, 2 and 3, indicated in the figure, refer to the first stage reactor solids, the V1258 chunk and the V1258 semi-solids in the bottom of the separator, respectively. Samples of the deposits were taken and the ash and CI results are shown in Table 4. The first stage deposits have much more ash than the solids in the interstage separator. The chunk in the interstage separator contained a large amount of cresol insolubles with not much ash.

Comparing these results with what is usually found when operating in thermal/catalytic mode, this run with dispersed moly catalyst is a great improvement in significantly reducing the solid deposition.

3.3.3 Process Performance

For Run 262, the CCR unit on stream efficiency was 89.8% with 1271.2 hours on stream. The resid and coal conversion, hydrogen consumption, and distillate and resid yields were monitored daily as process performance indicators. Phase 2 TSL yields are summarized in Table 5 for each period of the run. In Table 5 and Table C, the internal accumulation of UC and ash in the recycle loop, "Int. Accum. (Res. Free)", was calculated for each period and is included in the table to evaluate the TSL system performance stability. This value is affected by the imbalances of yield components (UC, ash, etc.) caused by experimental errors. In previous reports, this term was reported as part of resid yield. A detailed discussion of process performance and unit conversions is given in Section 4.0.

The first stage resid + UC conversion remained fairly constant throughout the run even when the molybdenum concentration was decreased from 1000 to 500 ppm (OD=13). See Figure 14. When the second stage temperature was increased from 760 to 790°F (OD=23), the second stage conversion increased and the first stage conversion decreased slightly. During this time the first and second stage conversions were nearly the same at around 21 wt %. The overall resid + UC conversion did not change when the molybdenum concentration was changed from 500 to 200 ppm (OD=33), however, the second stage conversion decreased slightly. The second stage resid + UC conversion did decrease significantly once the supported catalyst was removed from the second stage (17 to 10 wt %).

The ebullation rates are plotted in Figure 15 (the ordinate is not labelled in the figure since ebullation rates are proprietary). The ebullation rate in the thermal first stage was constant throughout the run. The second stage ebullation rate was as low as we could operate during the 1000 ppm molybdenum test. Lower resid + UC conversion in the first stage caused the second stage ebullation rate to gradually decrease with the higher feed rate of 300 lb/hr in spite of the higher second stage temperature of 790°F (OD=23-33). With the increase in the second stage temperature to 810°F (OD=39), the ebullation rate increased.

As seen in Figure 16, the temperature rise across the first stage reactor (□ symbol data, called as total exotherm) decreased slightly when the molybdenum concentration was lowered to 500 ppm in period B and increased when the resid injection was discontinued in period C. When the second stage had higher resid + UC conversion at 790°F (periods C and D), the total exotherm (x symbol data) increased greatly in the second stage. The in-bed temperature rise in the second stage (◊ symbol data) remained fairly constant throughout the run, as illustrated in the figure and also shown in Table 6. When the coal feed rate was increased to 350 lb/hr (OD=39) in period E, the first stage bed exotherm (△) increased by about 4°F (Table 6). Without supported catalyst in the second stage reactor in period F, the bed exotherm (◊ symbol data) decreased greatly from 9.5 to 2.6°F.

3.4 Residuum Oil Supercritical Extraction - Solids Rejection (ROSE-SR^{SM}) Unit

The objectives of Run 262 for the Residuum Oil Supercritical Extraction - Solids Rejection (ROSE-SR^{SM}) unit were to

- Evaluate unit performance while using Criterion 324 catalyst in the second stage reactor and Molyvan L as a dispersed catalyst for Black Thunder coal.

- Recover full range resid used in coal slurry preparation while achieving acceptable deashing.

- Obtain optimum resid recovery with minimum energy rejected into the solid bottoms product.

3.4.1 Unit Operation and Process Performance

The temperature and pressure of the separating vessels and the strength of the deashing solvent were varied to prevent letdown header pluggage and to improve process performance and operability. Aside from problems due to expected, routine maintenance problems and due to the introduction of resid from the previous run for the start-up of Run 262, several additional problems developed. The vacuum flash overhead condenser (E-1012) leaked causing inconsistent flow to the ROSE-SR^{SM} unit plus higher than normal solvent in the feed (7.4 wt % average for July 17-21). As shown in Figure 17, preasphaltenes in the ROSE-SR^{SM} feed were low for this initial startup period with dispersed catalyst (ranging 1-6 wt %), which could be due to high solvent in the feed (Table 8). The use of Molyvan L as a dispersed catalyst has an unknown effect on the operation of the ROSE-SR^{SM} unit. A combination of these factors caused the unit to carry-over ash for 10 days which resulted in plugging of the first stage condenser and the lines between the first and second stages.

After the initial plugging problems subsided, operations in the ROSE-SR^{SM} unit were consistent for the remainder of the run. However, as shown in Tables 7 and 8 and Figures 18 and 19, the ash content in the bottoms product and the resid recovery were low for Run 262 compared to previous subbituminous runs. Several attempts were made to improve the unit performance, but improving ash content in the bottoms product and resid recovery resulted in ash carry-over in each case.

One contributing factor to the low resid recovery was the low preasphaltenes in the feed; in Run 262A-D, the preasphaltenes were in the range of 1-9 wt % (4.6 wt % average). Also the use of Molyvan L as a dispersed catalyst may have contributed to the poor performance of the ROSE-SR^{SM} unit. This issue will be investigated further during Run 263.

3.5 Distillation System

The objectives of the V1082/T105/T102 distillation system for Run 262 were:

- To remove low boiling point products in T105 from the interstage separator overheads and from the liquids flashed overhead after the second stage reactor.

- To split in T102, the T105 bottoms and heavy vacuum flashed overheads from V1082 into a product stream and a recycle distillate that is in balance with the recycle distillate needs for blending with the coal.

Run 262 was the fourth consecutive run to use the T102 vacuum column for adjusting the entire split between recycled distillates and product distillates. Another variation for this run is that the V1074 (T102 column bottoms) was used for withdrawal tube flush (about 60 lbs/hr) to both reactors. Essentially all of the cut points (obtained from GC simulated distillation and by equal weight percent overlap method) were above 783°F (Table 9, Figure 20) similar to previous runs. Two periods were below 783°F. In period 262A, there were several operational problems including a hole in the V1082 vacuum overhead condenser possibly causing a loss of solvent and hence a lower cut point. Period 262C1 occurred shortly after a change over from the resid injection method (August 16-19) to resid/CI recycle in V131B which involves a substantial change in solvent inventory. The overlap for the test periods ranged from 6 to 13 wt % (Figure 21).

The lightest distillate (V161 in Figure 22) was primarily the overheads from the second stage. The T105 overheads had a boiling point below 550°F. Except for the start up period, about 45-53% of the overheads boiled below 350°F. For most of the run, the T102 overheads (V182, Figure 23) had little material boiling above 850°F by GC simulated distillation. The recycle distillate (V1074, Figure 24) was very heavy with 70-80 wt % boiling above 850°F except in period 262A. It is interesting to note that for period 262A with a 700°F cut point there was about 15% of a 650-750°F cut present which thereby reintroduces low boiling liquids into the recycle stream.

4. OVERALL TWO-STAGE LIQUEFACTION YIELDS

The overall TSL yields are the result of averaged elemental balances around the unit. The analytical data used for these balances are presented in Tables 10 to 12. The operating conditions, averaged elementally balanced overall yields and unit contributions are summarized in Tables B, C and D for all representative periods. Internal accumulation of UC in the recycle loop, "Int. Acc. UC", was calculated for each period and is included in Tables C and D to evaluate the TSL system performance stability. This value is affected by the imbalances of yield components (UC, ash, etc.) caused by experimental errors. The yield contributions are also shown schematically in material balance flow diagrams (Figures 25 to 30).

4.1 TSL Performance

The primary purpose of the run was to determine the merits of using a dispersed molybdenum catalyst on process performance and solids buildup. Molyvan L, which is an organic liquid containing molybdenum, sulfur, and phosphorous, was used as a precursor to give dispersed molybdenum. The molybdenum and sulfur contents in Molyvan L are about 8.1-8.5 wt % and 12.3 wt %, respectively. In this run, the effects of molybdenum concentration, second stage temperature, and space velocity were studied in high/low, thermal/catalytic mode with Criterion 324 catalyst in the second stage. A catalyst replacement rate of 3 lb/ton was used in the second stage. Iron-oxide along with a sulfiding agent was used to increase coal conversion. Half-volume reactors were used with an interstage separator. Seven material balance periods were obtained and each of these periods is discussed below.

In period 262A, the reactor temperatures were 826/760°F at a coal feed rate of 242 lb/hr. The dispersed molybdenum concentration was about 1000 ppm on a MF coal basis. The resid and CI concentrations in process solvent were 32.1 and 19.3 wt %, respectively. The ash-free bottoms product was 16.4 wt %. The heteroatom and C_1-C_3 gas yields were low.

In period 262B, the molybdenum concentration was lowered from 1000 to 500 ppm MF coal. Due to improved resid inventory, resid concentration in the process solvent could be increased to 37.7 wt % (target was 40 wt %). Although the molybdenum concentration was lowered to 500 ppm, 58 wt % distillate was obtained due to higher resid concentration.

After completing period 262B, the second stage temperature was increased from 760 to 790°F; simultaneously, the coal feed rate was increased from 250 to 300 lb/hr. The dispersed molybdenum concentration was maintained at 500 ppm MF coal. In this period, 262C, the C_4+ distillate yield, resid yield and the TSL coal conversion were 60.7, 1.5, and 92.0 wt % MAF coal, respectively.

The distillate yield was slightly higher than that in period 262B despite an increase in the coal feed rate. This may be due to higher conversions at the higher second stage temperature. The C1-C3 gas yield slightly increased because of the higher temperature. However, under these conditions, there was a distinct variation in resid concentration in the process solvent, which could have affected the distillate yield. This variation in resid in the process solvent could have resulted due to changeover from the resid circulation system to batch preparation of the process solvent. Thus, Phase 3 yields were also obtained for two short periods, 262C1 and 262C2, to facilitate data analysis (Table D). In period 262C1, the C_4+ distillate yield and TSL coal conversion were 64.7 and 91.7 wt % MAF coal, respectively, at a resid concentration of 39.1 wt % in the process solvent. In period 262C2, the C_4+ distillate yield and TSL coal conversion were 56.7 and 92.2 wt % MAF coal, respectively, at a resid concentration of 35.8 wt % in the process solvent.

In period 262D, the dispersed molybdenum concentration was lowered from 500 to 200 ppm. The C_4+ distillate yield and TSL coal conversion were 60.8 and 90.1 wt % MAF coal, respectively. Within the variation of experimental data, the distillate appears to be comparable to that in period 262C2, despite lower molybdenum concentration in 262D. However, TSL coal conversion appears to have decreased from 92 to 90 wt % in 262D.

In period 262E, the coal feed rate was increased from 300 to 350 lb/hr, the second stage temperature was increased from 790 to 810°F, and the molybdenum concentration was decreased from 200 to 100 ppm MF coal. Under these conditions, the C_4+ distillate yield and TSL coal conversion were 57.2 and 91.6 wt % MAF coal, respectively.

After completing period 262E, most of the Criterion 324 catalyst was withdrawn from the second stage while on-stream. Simultaneously, the dispersed molybdenum concentration was increased from 100 to 200 ppm and period 262F was obtained. This period is termed unstable because one of the major streams (feed to vacuum flash unit, V1079) could not be measured due to dump pot malfunction. The vacuum flash overhead stream (V1072) was also estimated. There was a significant reduction in the C_4+ distillate yield, i.e., it decreased from 57.2 wt % in 262E to 47.5 wt % in 262F. The resid yield was about 11 wt % in 262F. The resid + UC conversion in the second stage decreased significantly due to removal of the Criterion 324 catalyst.

In general, in Run 262, the C_1-C_3 gas make was low due to lower thermal first stage temperatures, i.e., C_1-C_3 was in the range of 5-6 wt % MAF coal. However, at high coal space velocities, the coal conversion decreased thereby increasing the organics in the ash-free bottoms product.

Table B. Summary of Operating Conditions

Operating Period	262A(transitional)	262B	262C
Date, 1991	July 17-20	Aug 8,9,14,15	Aug 22-25
Operation Days	6-9	14,15,18,19	26,29
Coal			
Feed rate, MF lb/hr	242.0	247.7	298.6
Ash, wt % MF	6.4	6.3	6.5
Conc. in slurry, wt % MF	29.6	29.7	29.7
Process solvent, wt %			
Resid	32.1	37.7	37.5
CI	19.3	18.7	18.9
First Stage			
Reactor temp.,°F	826	825	825
Inlet H_2 part. press., psia	2740±12	2708±30	2719±48
Total gas flow, scfh	5096	4814	4447
Recycle gas, scfh	1024	920	555
Space velocity, lb MF coal/hr/cu.ft. reactor	63.9C	65.4C	78.8C
Iron Oxide, wt % MF coal	2	2	2
Moly Conc., ppm MF coal	1000	500	500
Second Stage			
Reactor temp.,°F	760	761	790
Inlet H_2 part. press., psia	2505±8	2500±5	2556±9
Total gas flow, scfh	4570	4755	5127
Recycle gas, scfh	3310	3367	2875
Space velocity,			
lb feed/hr-lb cat	4.7	4.8	5.8
lb MF coal/hr-ft^3 cat	76.9	78.7	94.8
Catalyst type	Criterion 324	Criterion 324	Criterion 324
Cat. age, lb(R+CI)/lb cat	1545±37	1424±60	1343±47
lb MF coal/lb cat	706±17	692±22	688±24
Catalyst replacement rate, lb cat/ton MF coal	3	3	3
ROSE-SR^{SM} Unit			
DAS type	2114	2164	2249

Table B. Summary of Operating Conditions (Cont...)

Operating Period	262D	262E	262F(Unstable)
Date, 1991	Sep 8-12	Sep 18-22	Sep 24,26,27,29
Operation Days	34-38	44-48	50,52,53,55
Coal			
Feed rate, MF lb/hr	299.7	346.2	342.8
Ash, wt % MF	6.4	6.3	6.5
Conc. in slurry, wt % MF	29.7	29.8	30.0
Process solvent, wt %			
Resid	36.2	38.3	41.3
CI	19.6	20.0	20.1
First Stage			
Reactor temp., °F	825	824	824
Inlet H_2 part. press., psia	2795±26	2840±25	2862±15
Total gas flow, scfh	4461	4900	4967
Recycle gas, scfh	187	672	784
Space velocity, lb MF coal/hr/cu.ft. reactor	79.2C	91.5C	90.6C
Iron Oxide, wt % MF coal	2	2	2
Moly Conc., ppm MF coal	200	100	200
Second Stage			
Reactor temp., °F	790	810	809
Inlet H_2 part. press., psia	2530±9	2541±23	2530±24
Total gas flow, scfh	5125	5057	5165
Recycle gas, scfh	3054	2160	2663
Space velocity,			
lb feed/hr-lb cat	5.8	6.6	-
lb MF coal/hr-ft^3 cat	95.2	110.0	-
Catalyst type	Criterion 324	Criterion 324	-
Cat. age, lb(R+CI)/lb cat	1404±49	1315±51	-
lb MF coal/lb cat	727±25	674±26	-
Catalyst replacement rate, lb cat/ton MF coal	3	3	-
ROSE-SR^{SM} Unit			
DAS type	2234	2294	2404

Table C. Overall TSL Yields with Black Thunder Mine Coal

Operating Period Date, 1991 Operation Days	262A(transitional) July 17-20 6-9	262B Aug 8,9,14,15 14,15,18,19	262C Aug 22-25 26-29
Yield, wt % MAF coal			
H_2	-4.4±0.2	-5.4±0.1	-5.6±0.2
Water	16.1±0.6	15.4±0.5	14.2±1.2
H_2S	0.5±0.1	0.1±0.3	0.4±0.3
CO, CO_2	5.0±0.7	7.3±0.2	6.8±0.2
NH_3	0.7±0.0	0.8±0.0	0.8±0.0
C_1-C_3 gas	4.9±0.3	5.2±0.3	5.8±0.1
C_4+ distillate	57.7±2.3	58.0±2.1	60.7±4.9
C_4-C_6	1.3±0.1	2.5±0.2	2.7±0.1
IBP-350°F	14.8±2.7	9.9±1.4	13.0±2.2
350-450°F	8.2±1.1	7.2±1.2	8.1±0.6
450°F-EP	34.4±3.0	38.4±3.4	36.9±5.9
Resid	2.3±3.0	-0.1±2.3	1.5±5.2
Int. Acc. UC	0.7±0.6	1.7±0.9	-0.5±0.8
Bottoms Product (ash-free)	16.4±1.8	17.0±0.7	15.9±1.4
H_2 Efficiency, (%)	13.0±0.6	10.8±0.4	10.9±0.7
C_1-C_3 Selectivity, (%)	8.5±0.6	9.0±0.3	9.7±0.7
Coal Conv., wt % MAF			
First stage	89.9±2.6	87.0±2.1	89.3±2.0
Second stage	93.0±1.1	92.2±0.5	92.8±0.4
Overall TSL	92.8±1.3	91.1±0.9	92.0±0.4
Resid+UC Conv., wt % feed			
First stage	29.7±1.5	28.9±0.9	22.4±2.5
Second stage	11.8±2.0	11.8±1.9	19.7±2.1
Resid+UC Conv., wt % MAF coal			
First stage	61.9±1.5	62.8±1.3	49.6±6.4
Second stage	18.7±1.6	18.7±2.6	33.4±3.9
Overall	80.6±2.6	81.4±2.0	83.0±4.8

Table C. Overall TSL Yields with Black Thunder Mine Coal (Cont...)

Operating Period	262D	262E	262F(Unstable)
Date, 1991	Sep 8-12	Sep 18-22	Sep 24,26,27,29
Operation Days	34-38	44-48	50,52,53,55
<u>Yield, wt % MAF coal</u>			
H_2	-5.5±0.2	-5.5±0.4	-4.2±0.3
Water	13.9±1.1	15.5±0.7	13.1±0.6
H_2S	0.5±0.1	0.5±0.1	0.4±0.1
CO, CO_2	5.5±0.3	6.3±0.4	6.9±0.6
NH_3	0.7±0.0	0.6±0.1	0.3±0.0
C_1-C_3 gas	5.3±0.3	6.0±0.4	5.5±0.3
C_4+ distillate	60.8±3.2	57.2±1.8	47.5±0.5
C_4-C_6	2.1±0.1	2.3±0.3	2.2±0.2
IBP-350°F	10.8±2.7	13.1±3.5	9.0±0.9
350-450°F	7.7±0.9	8.6±1.3	8.9±0.9
450°F-EP	40.1±6.2	33.2±3.2	27.4±1.1
Resid	-0.3±3.1	-0.4±2.5	11.0±2.0
Int. Acc. UC	0.6±0.6	-0.1±1.1	0.4±1.2
Bottoms Product (ash-free)	19.0±0.8	19.8±1.3	19.1±2.6
<u>H_2 Efficiency, (%)</u>	11.1±0.5	10.4±0.6	11.3±1.0
<u>C_1-C_3 Selectivity, (%)</u>	8.8±0.8	10.5±0.6	11.6±0.7
<u>Coal Conv., wt % MAF</u>			
First stage	89.1±2.6	86.7±2.5	86.3±3.0
Second stage	91.9±0.5	92.3±0.8	92.3±0.3
Overall TSL	90.1±0.5	91.6±0.8	91.3±0.9
<u>Resid+UC Conv., wt % feed</u>			
First stage	24.7±1.3	21.4±1.6	22.9±2.7
Second stage	16.5±2.0	18.8±1.1	9.8±4.8
<u>Resid+UC Conv., wt % MAF coal</u>			
First stage	53.5±2.0	47.5±4.3	51.7±7.8
Second stage	27.3±2.9	33.1±2.8	17.8±8.1
Overall	80.8±2.9	80.6±1.7	69.5±1.2

Table D. Overall TSL Yields of 262C1 and 262C2 with Black Thunder Mine Coal

Operating Period	262C1*	262C2*
Date, 1991	Aug 22-23	Aug 24-25
Operation Days	26-27	28-29
<u>Process solvent, wt %</u>		
Resid	39.1	35.8
CI	18.6	19.2
<u>Yield, wt % MAF coal</u>		
H_2	-5.8±0.2	-5.4±0.1
Water	14.1±1.7	14.2±1.1
H_2S	0.6±0.0	0.2±0.3
CO, CO_2	6.8±0.2	6.7±0.0
NH_3	0.8±0.0	0.7±0.1
C_1-C_3 gas	5.9±0.1	5.8±0.2
C_4+ distillate	64.7±2.5	56.7±1.3
C_4-C_6	2.8±0.0	2.7±1.3
IBP-350°F	13.0±3.5	13.0±1.3
350-450°F	8.3±0.8	7.8±0.3
450°F-EP	40.6±6.9	33.2±0.4
Resid	-3.0±0.6	6.0±0.8
Int. Acc. UC	-1.1±0.5	0.1±0.7
Bottoms Product (ash-free)	16.9±1.3	15.0±0.3
<u>H_2 Efficiency, (%)</u>	11.3±0.8	10.5±0.3
<u>C_1-C_3 Selectivity, (%)</u>	9.1±0.5	10.2±0.1
<u>Coal Conv., wt % MAF</u>		
First stage	90.6±1.4	88.0±1.8
Second stage	92.9±0.4	92.7±0.4
Overall TSL	91.7±0.5	92.2±0.3
<u>Resid+UC Conv., wt % feed</u>		
First stage	23.8±1.5	20.9±2.8
Second stage	19.7±1.5	19.6±3.3
<u>Resid+UC Conv., wt % MAF coal</u>		
First stage	53.8±4.1	45.4±5.9
Second stage	33.4±2.9	33.5±6.1
Overall	87.1±1.2	78.9±0.2

* Period 262C is subdivided into periods 262C1 and 262C2 to reduce scatter in yields, especially on resid yield. The main difference between periods 262C1 and C2 is the resid content in process solvent (39.1 wt % in 262C1 vs. 35.8 wt % in 262C2). Other process conditions are the same as those listed for period 262C in Table B.

4.2 Process Solvent Quality and Hydrogenation

The process solvent quality is given in the following table (Table E) for Run 262. Solvent quality data for the beginning of the run was not available since there was no whole solvent sample of what was fed to the reactor unit when the solids recycle stream was directly injected into the line feeding the reactor. The process solvent quality remained around 80% during the run except for period 262F. After the supported catalyst was removed from the second stage in 262F, the process solvent quality decreased greatly to 73.7%. Period 262C2 had the highest quality (83.4%) of the run.

Table E
Process Solvent Quality

Date	Period	Total Process Solvent Quality, %
Aug 21	C1	78.7
Aug 27	C2	83.4
Sep 11	D	79.4
Sep 15	E	80.4
Sep 23		82.4
Sep 29	F	73.7

The hydrogen content in the total stream of the process solvent and the interstage stream is shown in Figure 31. On operation day (OD) 21, the injection of the solids recycle stream was discontinued. After this time, the interstage stream hydrogen decreased from 7.4 wt % to 7.1 wt %. Once the supported catalyst was removed from the second stage (OD=49), the hydrogen in both streams decreased only slightly. The total process solvent hydrogen decreased from 7.1 to 6.9 wt %. The decrease in the total interstage stream hydrogen was from 6.8 to 6.7 wt %. The slight decrease in hydrogen was probably due to the molybdenum not coming to an equilibrium concentration in the recycle stream.

The interstage hydrogen in Runs 260A-C and Run 262 is compared in Figure 32. The hydrogen content of the interstage stream was higher at 7.1 to 7.3 wt % in Run 262 compared to 6.1 to 6.5 wt % in Run 260A-C. The presence of higher hydrogen in the process stream may slow down the deposits of solids since there will be less of a chance of forming coke.

The hydrogen content in the resid and distillate portions of the interstage stream is shown in Figure 33. The distillate hydrogen averaged around 10 wt % and the resid hydrogen averaged 7.1 wt % until the molybdenum concentration was lowered to 100 ppm (OD=39). During 100 ppm molybdenum operation and with slurry reactors, the hydrogen content decreased slightly in both the distillate and resid portions but more so in the resid.

Comparing to Run 260 in the thermal/catalytic mode, the resid hydrogen in Run 260 was lower than in Run 262. In Run 260A-C, the resid hydrogen was 6.1 to 6.5 wt % and distillate hydrogen was 9 to 9.3 wt %. The resid hydrogen in this run was comparable to having catalyst in the first stage in the catalytic/thermal mode of Run 260.

Resid and distillate hydrogen content of the recycle stream is shown in Figure 34. In the recycle stream, the distillate hydrogen decreased slightly more than the resid hydrogen with the lower molybdenum concentrations.

The resid hydrogen content in both the process solvent and the interstage stream are compared in Figure 35. With 100 ppm molybdenum concentration (262E) and at higher coal feed rate (350 lb/hr), the interstage resid hydrogen dropped from 7 to 6.5 wt %. The increase in the second stage reaction temperature to 810°F and the increase in space velocity may have affected the hydrogen content much more than due to any change in molybdenum concentration.

5. CATALYST

Criterion 324 1/16" unimodal, supported catalyst from the first stage at the end of Run 260, which was aged at 790°F reaction temperature, was charged to the second stage reactor (R1236). This catalyst was already at an age equivalent to 3 lb catalyst/ton MF coal from operation in Run 260. The initial catalyst ages were 628 lb MF coal/lb catalyst and 1470 lb resid + CI/lb catalyst. No presulfiding of fresh catalyst was necessary since there was enough in inventory from previous runs (Runs 260 and 261). Table 13 compares the properties of Criterion 324 catalyst with other catalysts that were tested before at Wilsonville.

At the beginning of the run, 145 lbs of catalyst was charged to R1236. On July 14, the charge was increased to the target of 170 lbs. Catalyst replacement continued every other day until September 23 to keep the catalyst at an age equivalent to 3 lb catalyst/lb MF coal. On August 29 (OD=32) before going off feed to clean out V1258 of solids, catalyst was withdrawn from R1236 without the appropriate addition of fresh catalyst. When the plant was put on coal feed on September 6, the addition of fresh catalyst was performed to complete the catalyst replacement procedure.

In order to see the contribution the dispersed molybdenum catalyst has on the system when using a hybrid supported and dispersed catalyst system, the supported catalyst bed was withdrawn from R1236 on September 23 (OD=49). The amount of catalyst that was removed from the reactor was 108 lbs dry catalyst. The remainder of the catalyst charge was assumed to be left in the reactor (approximately 60 lbs dry catalyst) and the catalyst ages were calculated from this catalyst loading. At the end of the run, it was found that the actual amount left in the reactor was 29 lbs dry catalyst.

The second stage catalyst ages are shown in Figure 36. Since the Criterion (Shell) 324 catalyst was taken from the end of Run 260, the resid + CI age decreased until it reached an equilibrium age. After taking the catalyst out of the second stage, the catalyst ages were calculated assuming a catalyst charge of 60 lbs dry catalyst.

Throughout the run, a dispersed molybdenum catalyst was used in the form of Molyvan L. A description of Molyvan L is given in Section 5.1.4, Dispersed Molybdenum Catalyst. Also, iron oxide slurry catalyst was added to the system at 2 wt % MF using dimethyl disulfide (DMDS) as the sulfiding agent through the entire run.

5.1 Analytical Results and Recovery

Analytical results of each catalyst sample include an elemental analysis, a screen analysis, an ash evaluation, and a naphthalene activity test. The carbon content was evaluated to determine any buildup that would inhibit catalyst activity. The naphthalene activity test determines the hydrogen consumption during the hydrogenation of a fixed volume of catalyst in a laboratory microautoclave reactor, measured in units of millimoles of hydrogen consumed per 100 g of liquid sample. Naphthalene is the model compound used to measure relative catalyst activity in a laboratory microautoclave reactor and is independent of pilot plant reactor or TSL system performance.

When the reactors were opened at the end of the run, the Criterion 324 catalyst recovery was assessed for R1236. By adding the Criterion 324 catalyst withdrawn on September 23 (108 lbs minus 15.4 wt % non supported catalytic fines = 92.2 lbs), what was left in the reactor at the end of the run (28.6 lbs), and the catalyst left in the addition pot due to leaking addition valves (8.7 lbs), the total recovery was 76.2%. The probable cause for this low recovery was crushing of the catalyst by the impingement of the feed flow on the top face of the plenum chamber since the top surface of the plenum chamber had eroded grooves on it. Corrective action was taken after the run ended to minimize erosion.

5.1.1 Catalyst Size and Recovery

In previous runs at Wilsonville with Criterion 324 1/16" catalyst, no problems were observed with breakage or fracturing of the catalyst during the run. During Run 262, no signs of breakage or fracturing occurred during the run, however, the end-of-run sample screen analysis showed 81.5% +14 mesh size. Other end-of-run Criterion 324 catalyst samples have not had as much breakage. For example, the Shell 324 (same as Criterion) catalyst end-of-run sample from Run 260 withdrawn from the first stage had a 91.9% +14 mesh screen analysis. For Run 258, the second stage end-of-run sample contained 86.7% +14 mesh with Shell 324 catalyst.

The screen analysis of the end-of-run sample showed that 15.4 wt % of the catalyst charge consisted of non-supported catalytic fines (mainly agglommerated iron compounds). The end-of-run screen analysis in Table 14 was prorated by excluding the fines.

5.1.2 Catalyst Elemental Analysis and Naphthalene Activity

Figure 37 gives the carbon and the sulfur on the THF extracted catalyst. The carbon on the Criterion catalyst decreased during the 1000 ppm moly concentration period due to the catalyst replacement program. Carbon on the catalyst decreased after the coal feed rate was increased to 300 lb/hr due to the catalyst not reaching an equilibrium carbon amount. After the second stage temperature was increased to 790°F (OD=23), the carbon on the catalyst gradually increased from 8 to 9.4 wt %. Once the temperature was again increased to 810°F (OD=39), the carbon on the catalyst started to increase from 9.5 to 10.7 wt %. With lower molybdenum concentrations of 200 and 100 ppm, the sulfur on the catalyst decreased gradually from 7 to 6.5 wt %.

Figure 38 shows both the hydrogen and nitrogen on the THF extracted catalyst. The hydrogen on the Criterion catalyst decreased from 0.8 to 0.7 wt % when the molybdenum concentration was decreased from 1000 to 500 ppm (OD=13). The hydrogen on the catalyst increased slightly from 0.7 to 0.8 wt % with 100 ppm moly concentration, 350 lb/hr coal feed rate, and 810°F second stage temperature. The nitrogen concentration was constant at 0.18 wt % throughout the run.

Figure 39 gives the carbon to hydrogen atomic ratio for the THF extracted Criterion catalyst. The carbon to hydrogen atomic ratio of the Criterion catalyst decreased from 1.15 to 1 when the moly concentration was decreased from 1000 to 500 ppm. Usually, the carbon to hydrogen ratio is 1.1 to 1.2 and in this run it is 1.0, therefore, it seems that the molybdenum catalyst has an effect on this ratio. With lower moly concentrations of 200 and 100 ppm, the carbon to hydrogen ratio increased to the normal range of 1.1 to 1.2.

The naphthalene activity of the Criterion catalyst declined rapidly during the 1000 ppm moly period (Figure 40). Once the coal feed rate was increased to 300 lb/hr (OD=39), the naphthalene activity increased from 20 to 30. The naphthalene activity of the catalyst stayed within the range of 30 to 40 for the last part of the run.

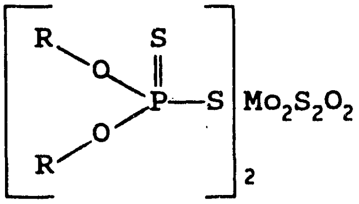
Table 15 gives the metal analysis of the withdrawn catalyst samples from the entire run. Within some variation, there was no apparent nickel loss and no gradual buildup of metal oxides throughout the run.

5.1.3 Comparison of Catalyst Analysis to Previous Runs

When comparing Run 260A-C and 262 (both operated in the thermal/catalytic mode), the carbon on the Criterion catalyst was higher in Run 260 than in Run 262 (Figure 41). When comparing both runs at a 790°F second stage temperature (Run 262 : OD=23-39; Run 260 OD=0-52), the carbon was 11 to 15 wt % in Run 260A-C and 9 wt % in Run 262.

5.1.4 Dispersed Molybdenum Catalyst

To disperse molybdenum into the process stream before entering the TSL system, Molyvan L, sold as a friction reducer and antiwear agent, was injected before the B1200 preheater along with DMDS. Molyvan L is a stable organic liquid additive containing molybdenum, sulfur, and phosphorous. It is manufactured by R.T. Vanderbilt Company, Inc., Norwalk, Connecticut. Molyvan L contains 8.1% molybdenum, 6.4% phosphorous, and 12.3% sulfur. It is soluble in petroleum oils and greases and aliphatic and aromatic solvents. At room temperature, Molyvan L is in a liquid state with a flash point of 330°F. The structure of Molyvan L is a sulfurized oxymolybdenum organophosphorodithioate shown below:



R is an alkyl group

In order to monitor the molybdenum content in the recycle ash, mineral analysis was performed on the vacuum bottoms ash (V1082) for selected days in different periods. The results are given in Table F. A sample calculation involving feed-coal ash content, iron oxide and molybdenum input indicated that at 1000 ppm molybdenum feed (on MF coal basis), the wt % of molybdenum in the ash under equilibrated conditions could be about 1.6 wt %. The recycle molybdenum concentration is expected to decrease in proportion to decreasing molybdenum concentration in the feed, if the process stream compositions are equilibrated.

In period 262A, the molybdenum wt % in the ash was about 1.6 wt % indicating that the moly in the recycle has reached a steady value. In periods 262B and 262C2 at 500 ppm molybdenum levels, the wt % in the ash was 0.9 and 0.8, respectively. The molybdenum wt % in 262B is slightly higher than the expected equilibrated value (0.8). In period 262D, at 200 ppm molybdenum level, the molybdenum wt % in ash was 0.5, which is higher than the expected value of about 0.3 wt %. In 262E period, at 100 ppm level, the wt % molybdenum in ash was about 0.2 wt %, which is somewhat closer to the expected value of about 0.17 wt %.

It appears that molybdenum in the recycle ash had reached a reasonable level in periods 262A, 262C2 and 262E. In general, it appears that it may take up to about a week to reach the expected wt % in the recycle ash after a change in molybdenum concentration in the feed.

Table F
Molybdenum Analysis in Recycle Ash in Different Periods

Period	Date	Mo_2O_5 Wt % in Recycle Ash
262A	07/17/91	1.6
262B	08/14/91	0.9
262C2	08/25/91	0.8
262D	09/11/91	0.5
262E	09/20/91	0.2

5.2 Run 262 Catalyst Activity and Thermal Conversion Analysis

Criterion (Shell) 324 1/16" catalyst activity in the second stage and thermal conversion in the first stage were evaluated and analyzed for Black Thunder coal, based on Phase 2 and 3 resid + UC conversion trend data. The first stage thermal conversion, the second stage catalytic conversion, and the overall two-stage conversion for both first and second stage conversions were compared for TSL performance evaluation. The new resid injection system was used until August 16 (OD=20) when the injection pump discharge line was plugged. After August 16 the slurry blend system used V131B pasting solvent tank, V101A slurry blend tank and V101B slurry feed tank. The interstage separator was used in this run, and the hot, heavier V1074 (heavy vacuum gas oil from T102 Vacuum Column bottoms) was used for the withdrawal tube flush in both reactors.

Run 262 in the thermal/catalytic mode of operation began on July 10 with half-volume reactors in both stages and continued for the entire run (July 12 - September 29, 1-55 operation days (OD)). Initial targeted conditions were: 250 MF lb/hr coal feed rate, 40 wt % resid and 20 wt % CI in the recycle process solvent, 825°F first stage and 760°F second stage reaction temperatures, 2 wt % MF iron-oxide and DMDS addition and 1000 ppm moly with Molyvan L (a dispersed molybdenum catalyst) as the precursor addition. The start-up process solvent was derived from the previous run (Run 261) processing Illinois No. 6 Burning Star Mine bituminous coal. Criterion 324 catalyst charge in the second stage was 170 lbs (aged in Run 260). Catalyst replacement started on July 15 (OD=4) in the second stage at 3 lb/ton MF coal.

There were operational difficulties with the ROSE-SR^{SM} deashing unit during the start-up period July 12-21 (OD=1-10). The ROSE-SR^{SM} unit did not perform proper deashing, experiencing serious ash carryover and, as a result, plugged on July 22. Initial start-up performance data (Phase 2 data, July 17-21) showed 92-95 wt % coal conversion, 0-12 wt % excess resid and 13-19 wt % organic rejection. Difficulties were experienced in calculating performance data, due to high variation in the flow rate from the new resid injection system and the V1082 Vacuum Flash Vessel bottoms recirculation pump requiring frequent solvent flushing through the pump. The material balance closure error was high in the range of 8-28 wt % MAF coal. Coal concentration in the feed slurry to the reactor was 27-30 wt %; recycle resid and CI were 29-34 wt % (below the target 40 wt %) and 17-21 wt % in the recycle process solvent.

There is normally several days of minor ash carryover when starting up the ROSE-SR^{SM} unit due to the initial adjustment of operating conditions for optimum resid recovery. For the start-up of Run 262, several additional problems developed. The vacuum flash overhead condenser (E1012) leaked causing inconsistent flow to the ROSE-SR^{SM} unit plus higher than normal solvent content in the feed (7.4 wt %). Preasphaltenes in the ROSE-SR^{SM} feed were low, 1-5 wt % (3.7 wt % average) for July 17-21 indicating more soluble material was produced in the prior reaction stages than usual. The use of Molyvan L as a dispersed molybdenum catalyst has an unknown effect on the operation of the ROSE-SR^{SM} unit. A combination of these factors caused serious ash carryover for 10 days, which resulted in plugging of the first stage condenser and the lines between the first and second stages in the ROSE-SR^{SM} unit.

The plugging problems in the ROSE-SR^{SM} unit at the start of Run 262 could have been related to feed property characteristics. Observations and analytical test results indicated the feed material was different from the feed material in Run 260C when the same coal was in use. The insoluble residues from routine solubility tests were very difficult to filter at the start of Run 262. Run 262 feed had more oxygen and a higher viscosity compared to the 260C feed. The preasphaltenes content was lower, 1-5 wt %, compared to 10-15 wt % for the 260C feed.

On August 6, after inspection of the ROSE-SR^{SM} unit and equipment repairs, the plant operation resumed at a reduced Molyvan L slurry catalyst addition rate (500 ppm). During August 13-16 (OD=17-20) with the T102 vacuum column bypassed due to a leak that developed in the overhead condenser (E113), V1072 vacuum flash overhead solvent was used for recycle and hot solvent withdrawal tube flush in both reactors. Coal feed rate was increased to 300 MF lb/hr on August 16 (OD=20) to increase the resid inventory. The recycle resid concentration was low, 35-40 wt % in the recycle process solvent. The new resid injection system was plugged on August 16. The old slurry blend system was reestablished using the V131B pasting solvent tank, V101A slurry blend tank and V101B slurry feed tank for the continuous plant operation. On August 19, the second stage reaction temperature was increased to 790°F to improve the process performance.

During the period after August 19, reaction temperatures studied were 825°F in the first stage and 790-810°F in the second stage. Coal feed rates were 300-350 MF lb/hr, and targeted recycle resid and CI concentrations in the recycle process solvent were 40 and 20 wt %, respectively. The resid concentration varied from 35-43 wt %. Molyvan L addition rate was at 100, 200, and 500 ppm molybdenum. Iron-oxide addition was maintained at 2 wt % MF coal and DMDS was used as a sulfiding agent. The plant was shutdown on August 29 (OD=33) to inspect the V1258 interstage separator and operation resumed on September 6 after completion of inspection and equipment repairs. Minor solids buildup occurred in the separator, but not in the transfer lines. On September 23 (OD=49), Criterion catalyst in the second stage was withdrawn to determine the effect of a supported catalyst on performance and evaluate the performance of Molyvan L slurry catalyst in the absence of Criterion catalyst. The addition rate of the Molyvan L slurry catalyst was increased from 100 to 200 ppm. Total reactor exotherm in the second stage decreased significantly indicating that Criterion 324 catalyst improved hydrogenation and hydrocracking. The outlet temperature of the B1201 interstage heater had to be increased close to the maximum allowable temperature in order to maintain the targeted second stage reaction temperature of 810°F. On September 30 (OD=56), before the completion of the run, a test of about 8 hours duration was performed to evaluate the process responses at 810°F first stage and 825°F second stage reaction temperatures and 300 MF lb/hr coal feed rate.

Results are illustrated in Figures 42 to 49. Cracking activity (resid conversion) is not the only function of the catalyst. Hydrogenation activity of the catalyst was not considered in these catalyst activity analyses. Trend data for the catalyst hydrogenation were discussed based on hydrogen contents of recycle resid and distillate in Section 4.2, Process Solvent Quality and Hydrogenation.

5.2.1 Overall Two-Stage Conversion Activity

Overall two-stage conversion activities were calculated for periods 262A-F, and are illustrated in Figures 42 and 43. TSL resid yields are listed below for these periods along with Phase 3 data. Two different common organic rejection (COR) values were selected for trend analysis. Standard deviation of the resid yield was 0.2-3.7 wt % MAF coal for periods 262B-E and was high, 5-6 wt %, with Phase 2 data for periods 262A (transitional) and 262F (unstable).

Period		Resid with COR = 20/15 wt % wt % MAF coal	
		Phase 2	Phase 3
262A	(transitional)		
	(COR=15)	6.9 ± 4.9	4.4 ± 2.6
	(COR=20)	1.9 ± 4.9	-0.6 ± 2.6
262B	(COR=15)	7.1 ± 2.7	3.6 ± 2.0
	(COR=20)	2.1 ± 2.7	-1.4 ± 2.0
262C	(COR=15)	-2.6 ± 3.1	-3.1 ± 4.8
	(COR=20)	2.4 ± 3.1	2.0 ± 4.8
262C1	(COR=15)	0.2 ± 0.4	-2.2 ± 1.1
	(COR=20)	-4.8 ± 0.4	-7.2 ± 1.1
262C2	(COR=15)	4.6 ± 3.0	6.1 ± 0.2
	(COR=20)	-0.4 ± 3.0	1.1 ± 0.2
262D	(COR=15)	7.1 ± 2.2	4.2 ± 2.9
	(COR=20)	2.1 ± 2.2	-0.8 ± 2.9
262E	(COR=15)	7.9 ± 3.7	4.4 ± 1.7
	(COR=20)	2.9 ± 3.7	-0.6 ± 1.7
262F	(unstable)		
	(COR=15)	18.5 ± 6.0	15.4 ± 1.2
	(COR=20)	13.5 ± 6.0	10.4 ± 1.2

Key process variable changes are summarized below.

Period	Process condition
262A (transitional)	startup w/ bituminous resid; thermal/catalytic mode; new resid injection system in operation; hot V1074, heavier solvent for withdrawal tube flush in reactors; catalyst replacement = 3 lb/ton MF; Molyvan L addition = 1000 ppm Molybdenum (1.3 wt % MF); Fe_2O_3 (+ DMDS) addition = 2 wt % MF; $T_{1st}/_{2nd}$ = 825/760°F, 250 lb MF coal/hr; coal concentration in slurry to reactor = 29.6 (29.2-30.0) wt %; process solvent composition (wt %) resid = 32.1 (29.1-33.7) CI = 19.4 (16.9-21.0).
262B	Molyvan L addition = 500 ppm molybdenum; coal concentration in slurry to reactor = 29.9 (28.6-30.9) wt %; process solvent composition (wt %) resid = 37.2 (35.6-40.4) CI = 18.6 (18.2-19.1).
262C1	old slurry blend using V131B, V101A/B;

	T_{2nd} = 790°F, 300 lb MF coal/hr; resid = 39.0 wt % in process solvent.
262C2	resid = 35.8 wt % in process solvent.
262D	Molyvan L addition = 200 ppm molybdenum; resid = 36.1 wt % in process solvent.
262E	Molyvan L addition = 100 ppm molybdenum; T_{2nd} = 810°F, 350 lb MF coal/hr; resid = 38.3 wt % in process solvent.
262F (unstable)	2nd stage Criterion catalyst withdrawn; Molyvan L addition = 200 ppm molybdenum; resid = 41.3 wt % in process solvent.

Resid + UC conversion data for these periods are listed below. Standard deviation of the overall two-stage conversion was 0.2-3.7 wt % MAF coal for periods 262B-E and was high, 5-6 wt %, with Phase 2 data for periods 262A (transitional) and 262F (unstable). Standard deviation of each stage conversion was higher, 2-7 wt % for periods 262B-E, than that of the overall conversion.

		Resid + UC conversion wt % MAF coal	
Period		Phase 2	Phase 3
262A	1st stage	57.4 ± 2.8	61.9 ± 1.5
	2nd stage	20.7 ± 2.6	18.5 ± 1.9
	Overall	78.1 ± 4.9	80.3 ± 2.8
262B	1st stage	60.5 ± 3.4	62.8 ± 1.3
	2nd stage	17.4 ± 5.3	18.7 ± 2.6
	Overall	77.9 ± 2.7	81.4 ± 2.0
262C	1st stage	47.1 ± 4.2	49.6 ± 6.4
	2nd stage	35.5 ± 2.7	33.4 ± 3.9
	Overall	82.7 ± 3.1	83.1 ± 4.8
262C1	1st stage	48.3 ± 1.8	53.8 ± 4.2
	2nd stage	36.6 ± 2.2	33.4 ± 2.9
	Overall	84.9 ± 0.4	87.2 ± 1.2
262C2	1st stage	45.9 ± 6.6	45.4 ± 5.9
	2nd stage	34.5 ± 3.5	33.5 ± 6.1
	Overall	80.5 ± 3.0	79.0 ± 0.2
262D	1st stage	53.3 ± 3.4	53.5 ± 2.0
	2nd stage	24.6 ± 2.4	27.3 ± 2.9
	Overall	78.0 ± 2.2	80.8 ± 2.9
262E	1st stage	46.0 ± 4.8	47.5 ± 4.3
	2nd stage	31.2 ± 5.5	33.1 ± 2.8
	Overall	77.1 ± 3.7	80.6 ± 1.7
262F	1st stage	50.5 ± 4.1	51.7 ± 7.8
	2nd stage	16.0 ± 6.4	17.9 ± 8.1
	Overall	66.5 ± 6.0	69.5 ± 1.2

The "all-distillate" product slate was achieved with resid extinction in periods 262A, B, C1, D and E. The TSL excess resid yield was -4 to 3 wt % MAF coal with 16-20 wt % organic rejection. Periods 262C2 and F did not achieve the "all-distillate" product slate. The reasons these periods did not achieve the "all distillate" product slate was probably due to fluctuation in the process solvent composition used for the slurry blend in period 262C2 and due to the absence of Criterion catalyst in the second stage in period F. Period 262A was transitional for the following reasons: (1) the lower recycle resid concentration (32 wt %), (2) the ash carryover in the ROSE-SR^{SM} unit, and (3) the unexpectedly low hydrogen consumption. Period F was unstable with high variation in the TSL excess resid yield (±6 to 8 wt %).

In periods 262A and B, the new resid injection system and the addition of Molyvan L as a dispersed molybdenum slurry catalyst seemed to improve the resid conversion in both thermal and catalytic stages allowing lower temperature operation. They also seemed to improve the coal conversion. Reducing the molybdenum concentration from 1000 to 500 ppm seemed to lower the coal conversion, although the 500 ppm molybdenum test was operated at a higher resid recycle. The molybdenum concentration and solids recycle significantly increased the thermal stage exotherm indicating improved hydrogenation and hydrocracking reactions, while decreasing the catalytic second stage exotherm.

In period 262C, the increase of the second stage reaction temperature to 790°F significantly increased the resid conversion in the second stage. Operating without using the new resid injection system, allowed a higher coal space velocity (300 MF lb/hr coal feed rate) while achieving the "all-distillate" product slate. Resid reactivity did not deteriorate when the old slurry blend system was used with longer residence time for the resid in the process.

From September 13 (OD=39) to September 22 (OD=48) during which time 262E period data was collected, performance trend data in each stage showed high variation having transitional responses (Figures 42 and 43). Three process variable changes (Molyvan L addition, coal feed and second stage reaction temperature) at the same time were the probable cause for the high performance variation. The resid + UC conversion in the second stage declined by about 20 wt % MAF coal, while in the first stage it increased by about 15 wt %. The decrease in overall conversion appeared to be 5 wt %. The Criterion catalyst in the second stage appeared to deactivate more rapidly at 810°F, even with 3 lb/ton MF coal catalyst replacement.

In period 262F, without the presence of Criterion catalyst in the second stage, the overall resid + UC conversion decreased by about 10-11 wt % MAF coal, although operated at a higher addition rate of Molyvan L catalyst (200 ppm moly), compared to 262E. The resid + UC conversion decrease was primarily in the second stage due to the absence of Criterion catalyst. However, coal conversion improved by 1-2 wt % (Phase 2 data), apparently due to the increase of the Molyvan L addition and/or the increased residence time in the second stage without the presence of Criterion catalyst. In contrast, Phase 3 data showed similar coal conversion for both periods 262E and F.

Trend analyses are summarized in Tables 16 to 18. Resid + UC conversion, TSL excess resid yield, coal conversion and organic rejection data are compared.

5.2.2 First Stage Thermal Conversion Activity

Thermal resid + UC conversion activities were calculated, assuming that the resid + UC conversion reaction follows first-order kinetics for a continuous stirred tank reactor. The conversion rate constant (K) is expressed in terms of two experimentally determined quantities: feed weight-hourly space velocity (SV) and resid + UC conversion (ϵ).

$$K/C = (SV/C)\ \epsilon/(1-\epsilon),$$

where C: constant equating thermal reaction volume to catalytic reaction volume.

The dependence of the conversion rate constant on temperature (T) is described by the Arrhenius equation.

$$K/C = (A/C)\ e^{-E/RT},$$

where K: rate constant, [hr^{-1}]
SV: feed space velocity, [lb feed/hr/cu ft-reactor]
ϵ: resid + UC conversion, [wt % feed]
A: frequency factor
E: apparent activation energy, [Btu/lb-mole]
R: ideal gas constant, [Btu/lb-mole-°R]
T: temperature, [°R]

The linear regression analysis equation becomes:

$$\ln(K/C) = \ln(A/C) - E/R(1/T)$$

Thermal conversion activities in the first stage were analyzed based on Phase 2 resid + UC conversion data. Results are illustrated in Figures 50 to 52.

The average ln K/C values for periods 262A-F were calculated and are listed below. Reactor volume was used in calculation of the conversion rate constant (K).

Period	Average ln K/C (1/hr) Phase 2	Phase 3
262A	4.48 ± 0.08	4.57 ± 0.05
262B	4.49 ± 0.05	4.55 ± 0.04
262C	4.34 ± 0.11	4.38 ± 0.14
262C1	4.37 ± 0.06	4.46 ± 0.06
262C2	4.32 ± 0.17	4.30 ± 0.17
262D	4.52 ± 0.09	4.52 ± 0.07
262E	4.42 ± 0.12	4.46 ± 0.09
262F	4.49 ± 0.10	4.54 ± 0.15

In Figure 51, the effect of Molyvan L addition rate on thermal conversion seems not significant when data for all periods were included in the linear regression analysis. However, as shown in Figure 52, periods 262C1-F using the old slurry blend system indicate that there is an optimum point at about 250 ppm molybdenum for the conversion. A second order curve fit was used for the trend analysis of periods 262C1-F data. The linear regression results were:

(For periods 262A-F)
$Y = 4.45 - 0.00002X, \ r^2 = 0.01$

(For periods 262C1-F using the old slurry blend)
$Y = 4.27 + 0.00189X - (3.46E-06)X^2, \ r^2 = 0.94$

Comparing 262B and C1C2 periods at the same Molyvan L addition rate of 500 ppm molybdenum in Figure 52, there appears to be an advantage of the new resid injection system as opposed to the old slurry blend system in having higher thermal conversion. However, several different operating variables (coal feed, second stage reaction temperature, etc.) might have affected the performance for these periods. Trend analyses are summarized in Table 19.

Figure 53 (Arrhenius plot) compares the first stage thermal conversion for runs processing Black Thunder coal with Criterion (Shell) 324 catalyst (Runs 258A-J, 260BC and 262AB). The calculated rate constant value (ln K/C) was plotted with respect to inverse temperature (1/T). Run 262AB with resid injection and Molyvan L addition showed much higher conversion than other runs (258A-J and 260BC). These runs operated in the thermal/catalytic mode with a half-volume reactor for Runs 258 and 262 and a full-volume reactor for Run 260 in the thermal first stage. Run 260BC operated without interstage separation.

5.2.3 Second Stage Catalyst Activity

Criterion (Shell) 324 1/16" catalyst activities at both batch and steady-state operation with catalyst replacement in the second stage were analyzed based on Phase 2 resid + UC conversion data. Results are illustrated in Figures 50 and 54.

Catalyst activities were calculated assuming that the resid + UC conversion reaction follows first-order kinetics for a continuous stirred tank reactor. The conversion rate constant (K) is expressed in terms of two experimentally determined quantities: feed weight-hourly space velocity (WHSV) and resid + UC conversion (ϵ).

$$K = WHSV\ \epsilon/(1-\epsilon)$$

The dependence of the conversion rate constant on temperature (T) is described by the Arrhenius equation and the decline of the rate constant due to deactivation with catalyst age (t) is described by a deactivation model.

$$K = A\ e^{-E/RT}\ e^{-\alpha t}$$

In this equation, A is the frequency factor, E is the apparent activation energy, and α is the deactivation coefficient. The equilibrium catalyst activity (K_{eq}) with catalyst replacement is projected by using the residence time distribution function, RTD(t).

$$K_{eq} = \int_0^\infty RTD(t)\ K(t)\ dt$$

The linear regression analysis equation for the conversion rate constant (K) becomes:

$$\ln K = \ln A - E/R\ (1/T) - \alpha t$$

K: second stage resid + UC conversion activity
A: frequency factor
E: apparent activation energy, Btu/lb-mole
R: ideal gas constant, Btu/lb-mole °R
T: reaction temperature, °R
α: deactivation coefficient, [1/t]
t: second stage catalyst age

The average ln K values for periods 262A-F were calculated and are listed below. Catalyst volume was used in calculation of the conversion rate constant (K).

	Average ln K (1/hr)	
Period	Phase 2	Phase 3
262A	3.77 ± 0.21	3.59 ± 0.17
262B	3.63 ± 0.28	3.61 ± 0.16
262C	4.48 ± 0.07	4.40 ± 0.14
262C1	4.52 ± 0.04	4.41 ± 0.11
262C2	4.44 ± 0.08	4.40 ± 0.21
262D	4.11 ± 0.04	4.18 ± 0.15
262E	4.41 ± 0.14	4.49 ± 0.07
262F[a]	4.66 ± 0.46	4.65 ± 0.63

[a] Primarily thermal reactor with a small amount of catalyst which could not be withdrawn on September 23. The catalyst left in the reactor was estimated to be 60 lbs which was used for rate calculations.

Temperature dependency on the second stage catalytic conversion for periods 262B-C2, DE, and A-E are shown in Figure 54 using the Arrhenius plot. Days selected for MB periods and transitional data on September 14-17 for the initial response at 810°F were used for calculation. Apparent activation energy was determined by the linear regression analysis technique. Results are:

(For periods 262B and C2 at 760-790°F w/ 500 ppm moly)
$\ln K = 42.1 - 47000\ (1/T),\ r^2 = 0.82$

(For periods 262D and E at 790-810°F w/ 100-200 ppm moly)
$\ln K = 28.6 - 30500\ (1/T),\ r^2 = 0.56$

(w/ initial response on September 14-17 and period 262D)
$\ln K = 39.6 - 44300\ (1/T),\ r^2 = 0.90$

(For periods 262A-E at 760-810°F w/ 100-1000 ppm moly)
$\ln K = 26.2 - 27500\ (1/T),\ r^2 = 0.73$

Apparent activation energy for periods 262B and C1C2 was very high, 94000 Btu/lb-mole, indicating that the Molyvan L addition is more effective at higher temperature operation for resid + UC conversion. For period 262D and the initial response at 810°F on September 14-17, apparent activation energy was also high, 88600 Btu/lb-mole; however, as shown in Figure 50, because of the rapid decline of the second stage conversion activity, the activation energy became less, 61000 Btu/lb-mole. Including all data generated for periods 262A-F, the activation energy was 55000 Btu/lb-mole. These energy values might have been affected by different operation variables (coal feed, reaction temperature, Molyvan L addition, etc.). All these values are much higher than those observed in previous runs with low-rank coals (30000-40000 Btu/lb-mole) in the absence of the Molyvan L addition. A likely problem with the analysis of catalyst activation energy and a better explanation of the high calculated values is the use of a catalyst that had not reached steady-state activity at the given operational temperatures. The spent catalyst employed had been aged at a higher temperature (790°F in Runs 260 and 258), exhibiting high carbon laydown suggestive of prior deactivation. A catalyst aged only at 760°F, for instance, would have a lower carbon content, and as a result would exhibit a higher rate constant at that temperature. A subsequent increase in temperature would then result in a smaller rate improvement, thus generating a lower calculated activation energy, or vice versa. It seems that the old way of slurry blending in periods 262C-E did not deteriorate the resid reactivity with longer residence time of the resid in the process.

The average K value significantly increased by 127% in periods 262C1C2 due to an increase in reaction temperature from 760 to 790°F compared to period 262B; the average K value initially increased by 89% in period 262E due to an increase in temperature to 810°F (based on the initial response during September 14-17) and later the increase became 37% due to a gradual decline in conversion activity (Figure 50), compared to period 262D. These K value increases might have been affected by different operation variables (coal feed, Molyvan L addition, etc.).

The high average K value in period 262F was due to the artifact in calculation using the low catalyst charge (60 lbs) left behind after the catalyst withdrawal on September 23 (Figure 55). The second reactor became a mixed one with both thermal and catalytic reactions. The catalytic reactor volume was approximately 1.11 ft^3 of slump catalyst (about 35% of the slump catalyst volume with 170 lbs charge before withdrawal). If the reactor is assumed to be 100% thermal, then the average K/C value for the thermal reaction is low and estimated to be 33.4 hr^{-1} (Figure 56). The majority of this low value stems from the catalytic conversion by the catalyst left. The estimate of catalytic conversion for 60 lbs catalyst charge is 7.1 wt % feed resid + UC by using the second stage rate constant value (83 hr^{-1}) for 262E. The observed conversion in 262F was 9.5 wt % (Table 20). The thermal contribution appears to be very small. After the completion of the run, the reactor was opened and the amount of catalyst found was approximately 30 lbs, half of the estimated 60 lbs. Based on this lower catalyst charge left in the second reactor, the thermal contribution in conversion becomes more important. The resid + UC conversion is estimated to be 3.7 wt % for catalytic reaction with 17.5% reactor volume. Then, the thermal conversion becomes higher (5.8 wt %) with 82.5% reactor volume. It seems that the catalytic conversion is 3 times higher than the thermal conversion. In this comparison, the volume ratio of catalytic to thermal reaction and the additional effect of the Molyvan L addition were not considered in analysis. Trend analyses are summarized in Table 20.

Figure 57 compares the second stage catalytic conversion for runs processing Black Thunder coal with Criterion (Shell) 324 catalyst (Runs 258H-M, 260BC and 262AB). The calculated rate constant value (ln K) was plotted with respect to second stage catalyst age. Run 262AB at 760°F with resid injection and Molyvan L addition showed higher conversion than Run 258KL at 760°F and Run 260BC at 790°F. Runs 262 and 258 operated in the thermal/catalytic mode with a half-volume reactor in the catalytic second stage. Run 260 operated with a 3/4-volume reactor in the second stage without interstage separation. Periods 262C-E, operated at 790°F without resid injection and with Molyvan L addition, showed much higher rate constant values ($\ln K = 4.2\text{-}4.5\ hr^{-1}$, as discussed before and compared in the Arrhenius plot, Figure 54) than those for Runs 260BC ($3.1\text{-}3.3\ hr^{-1}$) and 258M ($3.8\ hr^{-1}$) at the same 790°F reaction temperature and 3 lb/ton MF coal catalyst replacement rate.

5.3 Catalyst Requirement Comparisons

Phase 3 overall resid + UC conversion data for periods 262A-F, Runs 258H-M and 260A-F with Black Thunder coal and Criterion (Shell) 324 catalyst are plotted in Figures 58 and 59. Figure 59 is plotted with respect to coal space rate using CCR reactor volume, whereas, in Figure 58, it is plotted with respect to coal space velocity using catalyst volume.

Coal space velocity was selected as the x-coordinate variable to evaluate process responses in resid + UC conversion and catalyst requirement. To better evaluate the catalyst requirement and coal throughput for Run 262 with Criterion (Shell) 324 1/16" catalyst (unimodal), coal feed rates were projected for resid extinction by using process performance responses estimated by assuming CSTR first-order kinetics as shown in Figures 60-71 based on catalyst or reactor volume. Catalyst replacement rates for steady-state operation were calculated for comparison with actual replacement rates used at the plant. Results are listed in Tables 21 and 22.

Periods 262A-E with Molyvan L addition (and with the new resid injection system in periods 262A and B) showed a similar or higher resid + UC conversion than Run 260A-F (Figures 58 and 59). Run 262 operated at higher coal space velocities and Run 260 operated without interstage separation. Several operating conditions were different for these two runs such as reaction temperature, catalytic stage reactor volume, reactor severity sequence, etc.

Periods 262C-E with Molyvan L addition showed a similar or slightly higher conversion than that for Run 258J-M (Figures 58 and 59). Run 262 operated at lower first stage reaction temperature and similar coal space velocities (93-110 lb MF coal/hr/ft^3-catalyst per stage). Both runs operated with half-volume reactors in the thermal/catalytic mode with interstage separation. Catalyst replacement was 3 lb/ton MF coal for Run 262 and 0-3 lb/ton for 258J-M. Periods 262A and B with the new resid injection system and Molyvan L addition at a similar coal space velocity (77-79 lb MF coal/hr/ft^3-catalyst per stage) had a slightly higher conversion than Run 258HI. Run 258HI operated at higher reaction temperatures and with a lower catalyst replacement rate (1.5 vs 3 lb/ton MF coal).

Figure 72 compares coal conversion for Black Thunder coal runs with Criterion catalyst (Runs 258, 260 and 262). Reactor and catalyst volumes for these runs are summarized below.

Run No.	262,258	260
reactor volume	half/half[b]	full/tqs[a]
reactor volume ratio	0.47	1.00/0.71[a]
catalyst volume		
(slump) ft^3	- /3.1[b]	-/5.6[a]
(ratio)	- /0.38[b]	- /0.68[a]

[a] A three-quarters-volume reactor in the catalytic stage.
[b] A half-volume reactor in the catalytic second stage.

Periods 262C-E with Molyvan L addition showed a similar or slightly higher coal conversion than that for Run 258J-M (Figure 72). Run 262 operated at lower first stage reaction temperature and similar coal space velocities (93-110 lb MF coal/hr/ft^3-catalyst per stage). Both runs operated with half-volume reactors in the thermal/catalytic mode with interstage separation. Catalyst replacement was 3 lb/ton MF coal for Run 262 and 0-3 lb/ton for 258J-M. Periods 262A and B with the new resid injection system and Molyvan L addition at a similar coal space velocity (77-79 lb MF coal/hr/ft^3-catalyst per stage) had a slightly lower coal conversion than Run 258HI. Run 258HI operated at higher reaction temperatures and with a lower catalyst replacement rate (1.5 vs 3 lb/ton MF coal). Molyvan L addition seemed to improve coal conversion, allowing operation at a lower reaction temperature.

Figure 73 illustrates a flat response with respect to coal space velocity in Run 262A-F, probably due to other process variable changes made at the same time (Molyvan L addition, second stage reaction temperature, etc.).

The effects of Molyvan L addition on resid + UC conversion and coal conversion are shown in Figures 74 and 75, respectively. The variation of molybdenum concentration in the range of 100-1000 ppm in the slurry did not significantly affect resid + UC conversion in both thermal first stage and overall two-stage. There seems to be an optimum concentration at about 250 ppm molybdenum in the thermal first stage for periods 262C1-E (Figure

74). The increase in molybdenum concentration improved coal conversion in both thermal first stage and thermal/catalytic close-coupled reactors (CCR) as shown in Figure 75. Other operating variables could have affected resid + UC and coal conversions (coal space rate, second stage reaction temperature, recycle resid level, etc.).

A good correlation between recycle resid concentration and resid + UC conversion in Figure 76 was not observed because of other operating variables affecting the performance (coal space rate, second stage reaction temperature, Molyvan L addition, etc.).

A thermal reaction severity factor (TRSF) is defined as a function of system pressure (P), coal space velocity above 700°F (SV) and average reaction temperature (T), as shown below, in order to evaluate process responses in coal and resid + UC conversions.

$$\begin{aligned} TRSF &= f(P, SV, T) \\ &= a(P^b)(1/SV)\exp(c/T) \end{aligned}$$

where P: system pressure [psia]
SV: coal space vel. [MF lb/hr/ft^3-reaction volume]
T: volumetric average reaction temperature [°R]
a,b,c: constants

Run 262 coal conversion data are compared in Figure 77 with the second-order correlation developed for Run 260A-F. This comparison suggests that Molyvan L addition in Run 262 improved coal conversion by approximately 3-5 wt % MAF coal in both thermal first stage and thermal/catalytic first and second stage.

Run 262 resid + UC conversion data are compared in Figure 78 with correlations (power function, $Y = \alpha X^{\beta}$) developed for Runs 260 and 258. This comparison suggests that Molyvan L addition improved resid + UC conversion by approximately 0-10 wt % MAF coal in the thermal first stage and 5-10 wt % in overall two-stage except for period 262F with a small amount of catalyst left in the second stage.

A good linear correlation between organic rejection and coal conversion is shown in Figure 79. Data generated for low-rank coals and lignite runs (251-II, 251-III, 255, 258, 260 and 262) are used for the linear regression calculation. Results are:

$$Y = 179.0 - 1.76X, \quad r^2 = 0.92$$

where Y: organic rejection [wt % MAF coal]
X: coal conversion [wt % MAF coal]
r^2: determination coefficient

No apparent effect in the correlation was found by the addition of Molyvan L in the slurry in Run 262A-F.

5.4 Thermal History in TSL Process System

Thermal histories during July 17 - August 21 in Run 262 are illustrated in Figures 80 and 81. The thermal first stage exotherm decreased by 25-30% during August 6-15 at a lower Molyvan L addition rate of 500 ppm molybdenum indicating that the molybdenum concentration significantly affects the exothermic reactions such as hydrogenation and hydrocracking. When the solids were low in the recycle stream on August 16, the exotherm further declined by 25% indicating that the solids recycle significantly affects the exothermic reactions. Coal conversion decreased to about 85 wt % MAF coal with solids recycle. However, this conversion decline might be partly affected by the lower resid recycle during August 16-17 (10-20 wt % in the pasting solvent with 43-46 wt % coal concentration as shown in Figures 48 and 49). As the solids recycle gradually increased to the target 20 wt % in the process solvent during August 17-21 by using the old slurry blend system (V131B, V101A and V101B tanks), the first stage exotherm continuously increased back to the high value observed at a higher Molyvan addition rate of 1000 ppm molybdenum during July 18-21, although the addition rate was kept at 500 ppm. The coal conversion improved to about 92 wt % MAF coal.

The catalytic second stage exotherm continuously increased as opposed to the decline in the thermal first stage as shown in Figure 81. The increase of the second stage reaction temperature to 790°F on August 19 increased the second stage exotherm by 55% indicating more hydrogenation and hydrocracking reactions in the second stage.

Figure 81 includes a trend plot of B1201 interstage heater outlet temperature. The interstage heater outlet temperature was similar or lower than the second stage reaction temperature after August 12. This was due to the increased exotherm in the second reactor. The hot, heavier V1074 (or V1072) solvent flushing system used for the catalyst withdrawal tube flush in both reactors might be partly contributing in lowering the B1201 outlet temperature.

Figures 82 to 85 show trends in system pressure, differential pressure, gas flow, and ebullation and backmixing pump flows for this period. Black Thunder subbituminous coal was processed during this portion of Run 262 (August 21 - September 29, 25-55 operation days (OD)). The slurry blend system used V131B pasting solvent tank, V101A slurry blend tank and V101B slurry feed tank. The interstage separator was used, and the hot, heavier V1074 was used for the catalyst withdrawal tube flush in both reactors during this period.

Thermal histories during September 11-30 in Run 262 are illustrated in Figures 86 and 87. The thermal first stage and catalytic second stage exotherms increased by 15% and 35%, respectively, when coal feed rate was increased from 300 to 350 MF lb/hr, second stage reaction temperature was increased from 790 to 810°F, and Molyvan L addition rate was decreased from 200 to 100 ppm molybdenum on September 13. When the Criterion 324 catalyst was withdrawn from the second stage and the Molyvan L addition was increased to 200 ppm molybdenum on September 23, the thermal first stage exotherm increased by 10% indicating that partial compensation occurring in one stage for a loss in the other stage; however, the second stage exotherm significantly declined by more than 100%, primarily due to the absence of Criterion catalyst. Criterion catalyst significantly affected the exothermic reactions by improving hydrogenation and hydrocracking. The outlet temperature of the B1201 interstage heater had to be increased close to the maximum operable temperature in order to maintain the targeted second stage reaction temperature of 810°F. On September 30, before completion of the run, a short test of about 8 hrs duration was conducted to evaluate the process responses at 810/825°F reaction temperatures and 300 MF lb/hr coal feed rate. The first stage exotherm decreased by 10-15%, primarily due to the lower reaction temperature and coal feed rate; the second stage exotherm increased from a negative to a positive value, primarily due to the increased second stage reaction temperature. Figures 88 to 91 show trends in system pressure, differential pressure, gas flow, and ebullation and backmixing pump flows for the period September 11-30, 1991.

Thermal histories during periods 262E and F are illustrated in Figures 92 and 93 by using temperature profiles and approximate relative residence times through the TSL process system. Run 262 was operated with half-volume reactors and an interstage separator. Process times for slurry blend and feed tanks, and process solvent storage tank were significantly reduced for illustration.

Key Equipment	Location Number	Description
V101A	6-10	slurry blend tank
V101B	10-14	slurry feed tank
B1200	16-18	preheater
R1235	19-29	1st stage reactor
V1258	31	interstage separator
B1201	33-35	interstage heater
R1236	37-47	2nd stage reactor
V1247	49	high press separator
V1069	51	atm. flash vessel
V1082	53	vac. flash vessel
V131B	55-59	process sol. storage

6. DISTILLATE PRODUCT QUALITY AND UNIT SOLVENTS

6.1 Product Quality

This section summarizes the distillate product properties obtained from liquefying Black Thunder Coal. Similar product evaluations were performed in Runs 258 and 260 when the same coal was used as feedstock. Run 262 does have some process differences to the previous runs although Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) was common in all three runs. One difference in Run 262 was the use of Molyvan L as a dispersed disposable slurry catalyst. This was a first time use at Wilsonville. The other difference was the use of the T-102 vacuum bottoms (V-1074) as the withdrawal tube flush, an internal stream, as opposed to the T-102 vacuum column middle oil (V-182) as the flush. Catalyst activity can have a direct effect on product quality properties while the withdrawal tube flush can effect the product properties indirectly by compositional (blending) changes.

6.1.1 Methodology and Product Preparation

Tests indicative of product quality were performed on oils from six material balance periods. The tests included hydrogen, carbon, nitrogen, and sulfur. All were performed by combustion methods. Oxygen content was determined by difference. Simulated distillation was also a test performed. It was done by gas chromatography and the information was used to estimate the percentage of various boiling range fractions. Specific gravities were determined by pycnometer and the end points were obtained by distilling a sample by the ASTM D1160 procedure. Then, approximately 600 grams was distilled using an Oldershaw Column to give typical petroleum boiling cuts of Naphtha, Middle Distillate, and Vacuum Gas Oil. This gave the actual percentages of each cut in the total product and the yield of each fraction was sufficient enough to allow for their characterization.

The total product oil was prepared from process product streams, in proportion to their respective flow rates. In every case, the oils were prepared from a combination of distillation column overhead streams. Figure 94 is a partial schematic of the CC-ITSL process showing the distillation columns and product collection vessels. The atmospheric column overhead material collects in vessel V-161 and usually constitutes 40 wt % of the oil product. It has naphtha-like properties and boils from 75 to 500°F. The sample is generally low in nitrogen and sulfur and it contains about 12.0 wt % hydrogen. Vacuum column overhead, V-182 oil, is the major source of the other oil component and accounts for about 60 wt % of the product. It boils from 400 to 800°F and contains about 10.5 wt % hydrogen. The amount of each stream used in preparing the respective blends is summarized in Table

23. Since the use of the T-102 Vacuum Column Bottoms (V-1074) as withdrawal tube flush, the percentage of the V-182 Oil in the total product has risen by about 5.0 wt %.

6.1.2 Product Quality Data and Results

Total Oil

Table 24 summarizes the properties of the total oil product obtained from liquefying Black Thunder coal. Overall, the properties measured were influenced very little by changes in process conditions. There was a slight decrease in hydrogen, from 11.2 wt % to 10.96 wt %, when the Molyvan L concentration in the coal slurry was reduced from 1000 ppm down to 500 ppm. This transition took place in going from 262A to 262B. However, the hydrogen increased back to 11.45 wt % in 262C when only the second stage temperature was increased from 760 to 790°F. The Molyvan L concentration remained at 500 ppm. Low hydrogen in the 262B oil could be attributed to product composition as the oil from this period contained the least amount, 27.1 wt % of atmospheric overhead material (V-161). The overhead stream contributes a significant portion of hydrogen to the total oil product.

Period 262C was divided into two parts because of resid concentration differences in the recycle stream. The difference was about 3.0 wt % and it had no effect on product quality. The Molyvan L concentration remained at 500 ppm. In period 262D, the Molyvan L concentration was lowered from 500 ppm in 262C to 200 ppm. Since this was the only change in these respective periods, 262C2 and 262D affords the best comparison for the effects of Molyvan L on product quality properties. Basically, there is no difference in the product oil properties between the two periods. There is a slight elevation in end point with the lower Molyvan L concentration of 200 ppm in 262D. This was also observed in periods 262A and 262B when the Molyvan L concentration was lowered from 1000 ppm in 262A down to 500 ppm in 262B. The 262D and 262E oil properties were about the same with the latter product resulting from a temperature change and also a Molyvan L concentration change from 200 ppm to 100 ppm.

Hence, for all periods, hydrogen averaged 11.32 wt %, nitrogen 5,303 ppm, sulfur 0.035 wt % and oxygen, by difference, 1.84 wt %. No outstanding trends are evident except for a slight increase in nitrogen as the run progressed. End points averaged 748°F as measured by D-1160 distillation and excluding the 262A end point of 646°F. The reason for the lower end point in 262A was found in the V-182 oil composition. The simulated distillation data in Table 25 shows that the oil is much lighter in the early stages of the run which include the 262A period and the use of 1000 ppm Molyvan L. However, the oil became considerably heavier in August when data were collected for the

262B period.

Table 24 shows characteristics of the product oil from the 260D period. The properties of the 262 oils are similar except for slightly higher nitrogen.

Naphtha (IBP-350°F)

Table 26 summarizes the properties of the Black Thunder naphtha. They all have similar hydrogen contents which average 13.47 wt %. Oxygen is the highest heteroatom followed by nitrogen and then sulfur. Nitrogen averaged 1,633 ppm, sulfur 0.07 wt %, and oxygen by difference was 2.21 wt %. This cut showed an increasing heteroatom content as the run progressed. Run 262 naphtha was slightly poorer in quality compared to the 260D naphtha. This is based on the Run 262 naphtha having lower hydrogen content and slightly higher heteroatoms. Naphtha comprised about 14.0 wt % of the total oil.

Middle Distillate (350-450°F)

This boiling range distillate comprised 12.0 wt % of the total oil product. Its hydrogen content averaged 11.56 wt % and was basically unchanged for all periods. Oxygen was the highest heteroatom and averaged 3.09 wt %. Nitrogen was the next highest heteroatom and averaged 2,882 ppm. Nitrogen remained about the same for all periods except for 262E when it decreased almost half compared to the other periods. Sulfur averaged 0.04 wt % and showed no trend. Table 27 summarizes the middle distillate properties along with those from period 260D. The 260D middle distillate is slightly better in terms of hydrogen and heteroatom comparisons.

Middle Distillate (450-650°F)

The middle distillate properties are summarized in Table 28. The properties of this cut remained steady throughout the run except for a slight increase in nitrogen beginning about the middle of the run. Oxygen was again the highest heteroatom averaging 1.66 wt % followed by nitrogen at 6,191 ppm, and then sulfur at 0.03 wt %. Unlike the Run 262 naphtha and lower middle distillate cuts, the middle distillate properties compared similarly to the same cut from Run 260D. This fraction accounts for a major part of the total oil product and, therefore, is a contributing factor in why the overall oil properties are about the same throughout Run 262.

Vacuum Gas Oil (650°F+)

The gas oil fraction was a significant component of the total oil product and averaged 34.1 wt % except for 262A when it was only 6.8 wt %. The vacuum gas oil fractions had a narrow boiling range starting around 650°F and ending at approximately 748°F. Their properties are similar throughout the run and no trends are evident. The gas oil was high in nitrogen compared to the other fractions. For some periods, nitrogen was higher than oxygen but, overall oxygen was greater than nitrogen and averaged 0.91 wt % while nitrogen was 6,500 ppm. Sulfur was typically 0.02 wt % and hydrogen averaged 10.41 wt %. Neither showed much change for the respective periods. The gas oil characteristics are about the same as those for the 260D gas oil except for slightly higher nitrogen in the 262D fractions. The gas oil properties for the 262A-F and 260D cuts are summarized in Table 29.

6.1.3 Summary

The following is a summary of observations concerning the Run 262 product oils.

- Their properties were generally the same throughout the run.
- Within concentration ranges studied, Molyvan L seemed to have little effect on product properties.
- Product end points (by ASTM D1160 method) were 723-775°F except for the 262A period.
- Oxygen was the highest heteroatom in the distillates followed by nitrogen and then sulfur.
- Hydrogen content averaged 11.32 wt %.
- Nitrogen content averaged 5,303 ppm and increased as the boiling point of the fractions increased.
- The product properties were similar to those in period 260D except for slightly higher nitrogen.

6.2 Unit Solvents

6.2.1 CCR Unit Recycle Solvent

The recycle solvent was made up of ROSE-SR^{SM} deashed resid, vacuum flash bottoms (V1082) providing the solids recycle material, and vacuum distillation column bottoms (V1074). During 262A and 262B, the resid circulation system was in service. A description of the system is described in Section 3.1 TSL Stability. With the resid circulation system in service, the targeted coal concentration of 30 wt % could not be achieved. An attempt was made to increase the coal concentration to the target between July 17 and 19, however, the target could not be reached. After discontinuing the use of the resid circulation system, the coal concentration was maintained at 30 wt % throughout the run.

The targeted recycle solvent composition for the entire run was 40 wt % resid, 20 wt % CI, and 20 wt % distillate. Throughout the run, the resid concentration floated so that whatever resid made in the TSL system was fed back to the coal slurry preparation site. However, in all periods except for 262E and F (with 350 lb/hr coal feed rate), there was no positive resid make and no extra resid was available to recycle back.

The withdrawal tube flush for both reactors was vacuum distillation column bottoms material (V1074) for Run 262. The flush was heated by dowtherm jackets before entering the reactors. This is the first run in which V1074 material was used as flush solvent.

6.2.2 ROSE Unit Deashing Solvent

The ROSE-SR^{SM} unit uses a proprietary deashing solvent to process material containing ash. These deashing solvents are designated by numerical designations in order to prevent their disclosure. The deashing solvent was strengthened whenever necessary to optimize resid recovery while minimizing energy rejection to the ROSE-SR^{SM} bottoms product and maintaining efficient, stable deashing in the first stage.

7. Special Topics

7.1 Reactor Heat Loss Tests

Heat loss tests were conducted for both R1235 and R1236 on July 6 and 7, 1991 prior to the start up of Run 262. Conditions for the test were set as follows:

R1235	half reactor.
R1236	half reactor.
Feed rate	1000 lb/hr.
Gas recycle rate	5500 scfh.
Inlet temperatures on both reactors	about 700°F.

No DMDS addition to either reactor.
No withdrawal tube flush addition to either reactor.
No heat media on R1236 skin.
Heat media on both preheater to reactor lines.

The inlet temperatures were held steady for about ten hours until temperatures were stable (see Figures 95 and 96). The first test was performed without the ebullating pumps on to determine the amount of heat loss along the reactor. The second test was performed with the ebullation pumps on to determine the amount of heat loss due to ebullating pump operation. Temperatures and flow rates were averaged during the last hour of each test to determine the heat loss (see Figure 97). Overall heat loss from the preheater through the reactors with the ebullating pumps on was 49,000 and 57,000 Btu/hr for R1235 and R1236 respectively. The heat loss for R1236 is higher primarily because this reactor has a horizontal ebullating pump and the lines are much longer. The reactor heat losses are essentially the same for both reactors.

Heat Loss	R1235 Btu/hr	R1236 Btu/hr
Preheater outlet to reactor inlet	21,000	20,000
Reactor inlet to within reactor, includes bottom head	10,000	13,000
Within reactor	9,000	9,000
Due to ebullating pump	9,000	16,000

7.2 Evidence of Paraffins in Process Streams

The presence of paraffins in subbituminous coal distillates is not surprising since aliphatic groups have been postulated as bridges between aromatic clusters in this rank of coal. Toward the end of Run 262, the first stage distillate (V164) and second stage distillate (V1078) began to gel at room temperature.

Operators experienced transfer problems in lines that carried these distillates, especially on cool nights. It was speculated that the grainy-like material was paraffinic in nature. An investigation revealed information that was consistent with higher molecular weight paraffins whose carbon chains began around C16 and went as high as C32.

The grainy texture of distillate samples began to appear in early September close to the conclusion of Run 262. Warming the samples would cause the material to disappear resulting in a homogeneous liquid. We found that the substance could be precipitated by adding a portion of the sample to cold acetone. Suction filtration then yielded a white product having a melting point of about 100°F.

Elemental analysis of the solid revealed that it contained 85.3 wt % carbon and 14.2 wt % hydrogen. These values are consistent with the paraffinic formulation of C_nH_{2n+2}. The solid was then chromatographed and its spectrum is shown in Figures 98 and 99. The peak at 1690 seconds has the same retention time as the C_{20} paraffin eiocosane. The peaks are evenly spaced and the one at 2380 seconds corresponded to the C_{28} paraffin octacosane. Figure 98 is the G.C. spectrum of the total sample V164. Evenly spaced paraffin responses are clearly evident throughout the whole spectrum. However, paraffins are more prevalent toward the heavy end and boil primarily above 650°F. Similar experiments with the vacuum column bottoms (V1074) confirmed that the paraffins concentrate in this stream. However, the data indicate that no trends are evident in this stream throughout the run.

It was suspected that the reason the paraffins became noticeable was that supported catalyst was removed from the second stage reactor in late September toward the conclusion of the run. To confirm this suspicion, the waxes in first and second stage distillate products were precipitated by adding equal sample weights to cold acetone. The product was then suction filtered, air dried, and weighed.

Table G shows the relative percentage of paraffins present for each material balance period. There is not a lot of difference in the paraffinic nature of the respective products. The percentage of paraffins begins to show an increase for period 262E for both reactor products. The increase is not consistent with removal of supported catalyst as it was still present in period 262E.

Table G

Wax in Run 262 Oils

Period	V164 wt %	V1078 wt %	V1074 wt%
262A	3.0	2.3	7.5
262B	4.3	2.2	14.3
262C	7.3	3.4	23.5
262D	5.2	4.9	27.7
262E	8.0	8.7	16.0
262F	8.5	8.7	12.4

Procedure: Add 25.0 g of oil into about 200 ml of cold acetone. Store contents in freezer for about 3 hours. Filter precipitate.

7.3 Filtering Problems During Sample Analysis

Laboratory analysts experienced difficulties in filtering the insoluble matter from ROSE feed solubility tests in Run 262. The usual five minute filtration step in the solubility tests was easily extended to thirty minutes to one hour using typically a 10 gram sample weight for extraction. This problem may have been experienced some in Run 260, when the feed was derived from the same coal, but analysts do not recall the problem lasting as long as it has for the current run. An investigation of the feed materials from the respective runs indicated some noticeable differences in their physical and chemical properties.

These properties are summarized in the table below (Table H) and they show, for example, that viscosity is different. The Run 262 feed samples were found to have a much higher viscosity when measured on the Brookfield viscometer at 500°F at a shear of 8.5 1/sec. There was an increasing viscosity trend noted for Run 262. It first started in the 700 to 900 centipoise range for period 262A and then increased to the 1100 to 1500 centipoise range for period 262B.

We measured the viscosity in a feed sample for period 260C and found it to have a lower value at 266 centipoise. Another difference that was found was in hydrogen and oxygen values with the Run 262 feeds having higher values. Hydrogen content from whole sample feeds for this current run are ranging from 5.5 to 6.0 wt % while for the 260C feed product the typical hydrogen was 4.5 wt %. A sample of the feed was extracted to remove all solids and analyzed again for elements. Oxygen, by difference, in the current feed resid was around 8.5 wt % but found to be only 2.1 wt % in the 260C feed resid. Whole sample elementals allowed the same conclusions for oxygen content even though the values were much different from resid oxygens.

Preasphaltenes in whole sample feeds have been relatively low to only moderate for Run 262 ROSE feeds. They started out very low and reached the 1 to 5 wt % range for 262A and then showed a modest increase to the 5 to 9 wt % range for 262B. The preasphaltenes were higher in period 260C feed sample and ranged from 9 to 14 wt %. Hence, there is not a clear cut relationship between feed viscosity and preasphaltenes. The actual cresol insoluble matter removed from the filtration step was also investigated and found to have differences in elemental properties. One conclusion is that the current feed insolubles is more organic in nature as it contains more carbon and hydrogen compared to Run 260. Carbon was found to be 42.7 wt %, hydrogen 2.7 wt %, and nitrogen 0.60 wt % from a Run 262 cresol insoluble product. A similar type sample was isolated from a Run 260C feed sample. In it carbon was 29.4 wt %, hydrogen 0.60 wt %, and nitrogen 0.30 wt %.

These test results only help to illustrate that apparent differences do exist between ROSE unit feed properties between Run 260 and Run 262 despite both feeds being derived from the same coal. We have never encountered filtering problems with this magnitude in previous runs with subbituminous coals.

Table H

ROSE-SR^{SM} Feed Characteristics for Runs 260C, 262A, and 262B from Black Thunder Coal

	260C			262A			262B		
Test	Feed	Resid (wt %)	CI	Feed	Resid (wt %)	CI	Feed	Resid (wt %)	CI
CI	35.6	-	-	35.3	-	-	38.6	-	-
Ash	23.3	-	-	20.1	-	-	19.7	-	-
Solvent	3.6	-	-	5.5	-	-	2.8	-	-
Carbon	71.8	90.3	29.4	70.6	83.6	42.7	72.0	-	41.9
Hydrogen	4.8	6.2	1.6	5.7	6.8	2.7	5.7	-	2.6
Nitrogen	1.0	1.3	0.3	0.9	1.1	0.6	0.9	-	0.6
Sulfur	2.2	0.1	-	2.2	-	-	2.2	-	-
Oxyg.(diff)	-3.1	2.1	-	0.5	8.5	-	-0.5	-	-
Pasp	9-14	-	-	1-5	-	-	5-9	-	-
Viscosity, cp	266	-	-	700-900	-	-	1100-1500	-	-

CI - cresol insoluble
pasp - preasphaltenes
viscosity - in centipoise measured at 500°F and shear 8.5 1/sec

8. REFERENCES

1. Catalytic, Inc., Technical Progress Report, "Run 250 with Illinois No. 6 Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. 50041-81, November 1987.

2. Catalytic, Inc., Technical Progress Report, "Run 251 with Illinois No. 6 and Wyodak Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-88, April 1988.

3. Catalytic, Inc., Technical Progress Report, "Run 252 with Illinois No. 6 Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-98, May 1990.

4. Catalytic, Inc., Technical Progress Report, "Run 253 with Illinois No. 6 Coal", DOE Contract No. DE-AC22-82PC500-41, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-99, February 1991.

5. Catalyst, Inc., Technical Progress Report,"Run 254 with Ohio No. 6 Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-111, February 1990.

6. Catalytic, Inc., Technical Progress Report, "Run 255 with Martin Lake Texas Lignite Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-113, May 1991.

7. Southern Electric International, Inc., Technical Progress Report, "Run 256 with Ohio No. 6 Coal", DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-114, May 1991.

8. Southern Electric International, Inc., Technical Progress Report, "Run 257 with Illinois No. 6 Coal", DOE Contract No. De-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document NO. DOE/PC/50041-121, March 1991.

9. Southern Electric International, Inc., Technical Progress Report, "Run 258 with Subbituminous Coal", DOE Contract No. DE-AC-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-130, May 1991.

10. Southern Electric International, Inc., Technical Progress Report, "Run 259 with Pittsburgh No. 8 (Ireland Mine) Coal", DOE Contract No. DE-AC-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/50041-14, May 1991.

11. Southern Electric International, Inc., Technical Progress Report, "Run 260 with Black Thunder Mine Subbituminous Coal from Powder River Basin", DOE Contract No. DE-AC-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/90033-16, January, 1992.

12. Southern Electric International, Inc., Technical Progress Report, "Run 261 with Black Thunder Mine Subbituminous Coal from Powder River Basin", DOE Contract No. DE-AC-90PC90033, EPRI Contract No. RP1234-1-2, Document No. DOE/PC/90033-21, Sepetmber, 1992.

13. Davis, A. Schobert, H.H., Mitchell, G.D. and Artok, L., (1990). "Catalyst Dispersion and Activity Under Conditions of Temperature-Staged Liquefaction", DOE Technical Progress Report for the Period April-June, 1990, No. DOE-PC-89877-3.

14. Davis, A. Schobert, H.H., Mitchell, G.D. and Artok, L., (1991). "Catalyst Dispersion and Activity under Conditions of Temperature-Staged Liquefaction", DOE Technical Progress Report for the Period April-June, 1991, No. DOE-PC-89877-7.

APPENDIX A

Nomenclature and Definitions

All-distillate: For experimental data, the resid yield is in the range of ±5 wt % MAF coal. Projected values are based on a zero resid yield.

Ash: Non-organic material obtained by muffle furnace burning at 800°C for 4 hours (adapted ASTM D-482).

Asphaltenes: A toluene-soluble and pentane-insoluble material which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.

B102: T102 Vacuum Column Reboiler

B1200: First stage reactor preheater

B1201: Interstage heater

CC-ITSL: Close-Coupled Integrated Two-Stage Liquefaction

CCR: Close-Coupled Reactor Unit

CI: Material which is insoluble in hot cresol. This material is composed of both ash and unconverted coal.

COR: Common Organic Rejection

DAS (Deashing Solvent): Deashing solvent in the ROSE-SR^{SM} unit. A solvent used to extract the resid from the feed to the ROSE-SR^{SM} unit.

Distillate solvent: A coal-derived distillate fraction which boils between 450°F and 600°F at 0.1 mm Hg in a laboratory batch distillation apparatus.

DITSL: Double Integrated Two-Stage Liquefaction

Dowtherm: Heat transfer fluid used in the process. Dowtherm is a trademark of the Dow Chemical Company.

DMDS: Dimethyl disulfide

Energy rejection: The heating value lost to the bottoms product as a percent of the feed coal heating value.

Feed Solvency Index: Laboratory analysis for fraction of ROSE-SR^{SM} feed soluble in actual deashing solvent compared to its solubility in a solvent standard.

HTR: Hydrotreater. Catalytic hydrogenation reactor unit.

Appendix A (continued)

IBP: Initial Boiling Point

ITSL: Integrated Two-Stage Liquefaction

K111: Vacuum System Precondenser. The vessel used as the middle distillate product condenser in T102 Vacuum Column.

LTR: Light Thermal Resid

MAF coal: Moisture- and Ash-Free coal

MB period: Material Balance period

MF coal: Moisture-Free coal

Middle distillate: A coal-derived distillate fraction which boils between 350 and 450°F at 760 mm Hg (GC and ASTM D-86).

Naphtha: A coal-derived distillate fraction which boils less than 350°F at 760 mm Hg (GC and ASTM D-86).

Naphthalene Activity: Catalyst activity test: Millimoles of hydrogen consumed per 100 g of 10% naphthalene solution.

OD: Operation Days

Oils: A pentane-soluble material which is non-distillable at 600 and 0.1 mm Hg in the laboratory.

Preasphaltenes: A cresol-soluble and toluene-insoluble material which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.

Process solvent: The material mixed with coal in slurry preparation which is normally a blend of distillate solvent, resid and CI in specified concentrations.

P171: Pump used to transfer T102 overhead material to product storage. Also designates a sample point.

P1222 & P1236: Ebullation pumps on R1235 and R1236, respectively.

P1090: Pump used in the resid circulation system to inject deashed resid from the ROSE-SR^{SM} unit into the CCR unit feed line.

P1091: Pump used in the resid circulation system to inject the solids recycle stream (V1082 bottoms material) into the CCR unit feed line.

R1235 OTL: Interstage sample.

Appendix A (continued)

Resid: A cresol-soluble material which is non-distillable at 600°F and 0.1 mm Hg in the laboratory. Normally refers to deashed resid from the ROSE-SR^{SM} unit.

Resid + UC conversion: The fraction of the feed resid and UC that is converted to material that is distillable at 600°F and 0.1 mm Hg.

$$\text{Percent Conversion} = \frac{\text{Resid+UC in} - \text{Resid+UC out}}{\text{Resid+UC in}} \times 100$$

Resid recovery: The percent of ROSE-SR^{SM} feed resid that is recovered in the deashed resid and not lost to bottoms product.

RITSL: Reconfigured Integrated Two-Stage Liquefaction

ROSE-SR^{SM}: Residuum Oil Supercritical Extraction-Solids Rejection Unit. The unit used to remove ash and unconverted coal from the process.

Bottoms Product: A product of the Kerr McGee ROSE-SR^{SM} unit first stage separator that is rich in cresol insolubles (ash and UC) with lesser amounts of resid and solvent (previously known as ash concentrate).

Solvent (SOLV): A coal-derived distillate fraction which boils above 450°F and is distillable at 600°F at 0.1 mm Hg in a laboratory batch distillation apparatus.

TLU: Thermal Liquefaction Unit. Reactor operating in thermal mode.

TR: Thermal Resid

T102: Vacuum Distillation Column

T105: Atmospheric Distillation Column

Unconverted Coal (UC): Ash free organic material that is insoluble in hot cresol.

V101A: Coal Slurry Blend Tank. The vessel in which coal is added to process solvent to form a coal slurry for feed to the reactors.

V101B: Coal Slurry Feed Tank

V131B: Process Solvent Blend Tank. The vessel used to blend material from V1067 (or V1082) and V1074 with deashed resid from the ROSE-SR^{SM} unit to make process solvent for recycle to the coal slurry blend section of the plant.

Appendix A (continued)

V138: T102 Tray 3 Pot. The vessel used as the collection drum for the T102 Vacuum Column Tray 3 product draw.

V161: T105 Distillate Overhead Tank. The vessel used to collect T105 overhead material for transfer to product storage.

V182: Oil/Water Separator. This vessel is used to remove water from the middle distillate product stream from the T102 Vacuum Column.

V1067: Bottoms Product Hold Tank. The vessel used to collect bottoms material from the atmospheric flash vessel.

V1072: Vacuum Overhead Drum. The vessel used to collect overhead material from the vacuum flash drum.

V1074: Distillate Bottoms Tank. The vessel used as a surge drum for the T102 Column bottoms material used in the recycle solvent.

V1078: Atmospheric Overhead Pot. The vessel used to measure overhead material from the atmospheric flash vessel.

V1079: Bottoms Measuring Pot. The vessel which measures the amount of material transferred from the atmospheric flash vessel to the V1067 Bottoms Product Hold Tank.

V1080: Sour Water Measuring Pot. The vessel ultimately used to measure the amount of water removed from the second stage reactor effluent via a series of flash drums and separators.

V1082: Vacuum Flash Vessel

V1090: Calibration dump pot vessel used to collect and measure the flow rate of the deashed resid from the ROSE-SR^{SM} unit used in the resid circulation system.

V1091: Calibration dump pot vessel used to collect V1082 bottoms material (solids recycle stream) and to measure the flow rate when the resid circulation system is in service.

V1247: The vessel used to separate the liquid and gas fractions of the second stage reactor effluent.

V1258B: Interstage Separator. The vessel used to separate the liquid and gas fractions of the first stage reactor effluent.

WHSV: Weight Hourly Space Velocity, lb/hr feed per lb catalyst. Space velocity with catalyst volume units are lb MF coal/hr-ft^3 settled catalyst.

APPENDIX B

MATERIAL BALANCE METHODOLOGY

B.1 Elemental Balancing of Yields

The total mass and elemental balances around each process unit are determined from the measured stream flow rates and laboratory analyses for the following elements in each stream.

- Carbon
- Hydrogen
- Nitrogen
- Sulfur
- Oxygen
- Ash

Elemental analyses (C, H, N, S, O) are not adjusted. Weighing factors, based on assumed flow rate errors for each stream and relative stream flow rate sizes, are applied to the process flow rates. The method minimizes the required adjustments to a stream flow rate to close the mass and elemental balance for each unit.

Since the streams are composed primarily of hydrogen and carbon, the balance is first developed based on these elements. Next, sulfur, nitrogen, an oxygen are balanced along with carbon and hydrogen, primarily by adjusting hydrogen sulfide, ammonia, and water rates. Ash is balanced by adjusting the ash analysis of output streams to equal the ash that entered with the coal. For ash recycle operations, the vacuum bottoms (V1082) rate to the ROSE-SR^{SM} unit is adjusted based on both coal ash and vacuum bottoms ash to ensure that all of the coal ash was purged in the ash concentrate (steady-state assumption). The adjusted stream flow rates between units are then corrected for inventory changes to achieve steady-state flow rate.

The CCR unit balance is developed with the above procedure. Since the ROSE-SR^{SM} has fewer streams than components, the measured stream flow rates and elemental analyses are used to calculate elemental errors. The errors are used as the basis for adjusting the compositions of the streams to close the balance.

The overall two-stage (TSL) yields are calculated by combining the balances of the CCR and the ROSE-SR^{SM} units.

B.2 Material Balance Methodology

Material balance data are routinely available for plant monitoring. In calculating the final yields, there are two intermediate stages of data. The "as-is" material balance data (Phase 2) uses measured flow rates in calculating yields.

Included with Phase 2 data are the mass balance closure errors. These data for Run 261 can be found in Table 5. When elemental analyses are complete on all input and output streams for a given day, elementally balanced yields (Phase 3) are calculated for that day. Phase 3 elementally balanced yield data are averaged for each set of stable operating conditions to obtain the final yield used throughout this report (Phase 4).

An evaluation of the material balance methodology was conducted to assess the usefulness of the different phases of material balance reports for plant monitoring, daily decision making, and technical accuracy of yields. Quantitative guidelines were desired to screen the data as it continued through the data phase system from Phase 2 to Phase 3 to Phase 4. For the evaluation, a statistical approach was used to assess the variance of the material balance data before and after elemental balancing.

In general, it was found that the Phase 2 and Phase 3 yields were in good agreement. Thus, the Phase 2 yields are considered to be adequate for plant monitoring and daily decision making. As an exception to this rule, only Phase 3 data is used to monitor plant performance with regard to production of C_4+ distillate. Daily comparison of Phase 2 and Phase 3 data proved to be useful in locating and correcting sources of balance errors.

For final yield characterization (Phase 4), Phase 3 yields are averaged for stable operating periods. These are the yields that have been used throughout this report.

B.3 Material Balance Data Selection Criteria

Statistical analysis was used to develop selection criteria for deciding which days to include in Phase 3 and Phase 4 data.

Phase 2-3 Selection Criteria are related to flow closure error, inventory changes, and plant stability. A total of ±10 wt % MAF flow closure error and ±15 wt % MAF inventory changes are allowed. Both are obtained by summing the contributions from individual units. In addition, days may be eliminated due to plant upsets or step changes in operating conditions.

Phase 3-4 Selection Criteria are related to elemental balance closure errors. Elemental closure error should be within the 95% confidence intervals for each individual unit and overall TSL system. Yields on days highlighted by excessive elemental closure errors are then compared with yields from the other elemental balance days in the Phase 4 period. If important yields on these days are outside an 80% confidence interval, the days are eliminated from the Phase 4 yields. The averages and standard deviations of the Phase 3-4 Selection Criteria are reported in Table 30 for each representative operating period (Phase 4 Period).

In addition to the selection criteria, changes in Phase 2 or Phase 3 yields from one day to the next are used to assess TSL stability. Material balance data have defined quantitative guidelines, that indicate system stability, as the data flow through the data phase system from Phase 2 to Phase 3 to Phase 4.

APPENDIX C

Microautoclave Activity Test Descriptions

C.1 Solvent Quality

Solvent quality is determined in the Wilsonville laboratory as follows:

Standard coal (Indiana V) and solvent are charged to a 30 cc microautoclave reactor to which a mixing ball is added. The slurry is mixed and heated to a specific temperature (±5°F) within a three minute period and is maintained for a specific period of time. The microautoclave is quenched in water and the reaction products are washed and extracted with tetrahydrofuran (THF).

The ratio of the amount of reacted coal to the original sample weight is expressed as percentage conversion which is referred to as "solvent quality".

Both kinetic and equilibrium tests can be performed. The equilibrium test is used to monitor solvent quality and is more commonly used. The kinetic test gives a relative indication of the hydrogen transfer rate and hydrogen shuttling ability of the solvent. The equilibrium test gives a relative indication of the concentration of donatable hydrogen in the solvent. The conditions used for these tests are listed below:

Test type	Temp., °F	Reaction Solvent-to-coal ratio	Time min.
Kinetic	750	8:1	10
Equilibrium	750	2:1	30

C.2 Catalyst Activity

Supported catalyst activity is determined in the Wilsonville laboratory as follows:

Two grams of 10% naphthalene in hexadecane is catalytically hydrogenated in a microautoclave reactor at the following conditions:

Temperature, °F	720
Hydrogen pressure, psig	1,000 (cold)
Agitation, strokes/min	800 (no ball or rod added)
Reaction time, min.	15

The reactor is quenched with cold water and the contents are filtered. The concentrations of tetralin and decalin, which are the products of naphthalene hydrogenation, and naphthalene are determined by gas chromatography. The hydrogen consumption is then determined by stoichiometric calculations. The catalyst activity or naphthalene activity is the millimoles of hydrogen consumed per 100 g of 10% naphthalene solution.

Table 1

BLACK THUNDER MINE FEED COAL ANALYSIS FOR RUN 262

Period	262A	262B	262C1	262C2	262D	262E	262F
Proximate (MF) %							
Volatile matter	49.6	49.9	49.7	49.5	49.4	49.9	49.2
Fixed carbon	44.1	44.0	43.9	44.3	44.3	44.1	44.5
Ash	6.2	6.1	6.4	6.1	6.3	6.0	6.3
Moisture	20.8	20.4	20.8	20.9	22.9	22.2	22.2
Ultimate (MF) %							
Carbon	69.6	69.3	68.7	69.7	69.5	68.4	68.8
Hydrogen	5.3	5.2	4.7	4.7	5.0	4.8	5.1
Nitrogen	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	0.6	0.4	0.5	0.5	0.5	0.5	0.5
Ash	6.4	6.3	6.5	6.5	6.4	6.3	6.5
Oxygen (diff.)	17.1	17.8	18.5	18.5	17.6	18.8	18.0
Chlorine (ppm)	49	..	..	75	..	..	<10
Pyritic Sulfur	0.046	..	..	0.055	..	..	0.04
H/C atomic ratio	0.91	0.89	0.81	0.81	0.86	0.84	0.88
Dry heating value (Btu/lb)	11,794	11,855	..	..	..	..	..
Mineral analysis, (wt % of ash)							
Silica, SiO_2	28.8	32.1	..	..	30.7	..	30.9
Ferric oxide, Fe_2O_3	5.3	5.0	..	..	5.8	..	5.4
Alumina, Al_2O_3	18.1	17.9	..	..	15.6	..	16.2
Lime, CaO	26.2	25.1	..	..	22.4	..	23.2
Magnesia, MgO	4.5	4.5	..	..	4.3	..	4.5
Potassium oxide, K_2O	1.1	1.4	..	..	1.2	..	1.9
Sodium oxide, Na_2O	0.7	0.7	..	..	0.7	..	0.7

Table 2

RECYCLE PROCESS SOLVENT ANALYTICAL DATA

Operating Period	V131B					
	CI-Free Resid, wt %			Distillate, wt %		
	C	H	N	C	H	N
262A	-	-	-	-	-	-
262B	-	-	-	-	-	-
262C1	88.57	7.31	1.14	89.50	10.02	0.45
262C2	-	-	-	-	-	-
262D	88.86	7.45	1.07	87.96	10.26	0.43
262E	88.50	6.99	1.17	88.94	9.53	0.49
262F	88.63	6.53	1.32	89.52	9.46	0.60

Table 3

Metal Analysis of Solid Deposits - August 29 Shutdown Samples

Run	262	262	262	260	260	258	262A
Sample No.	23527	23528	23532	16403	16411	1477	
Description	Top Wall Scale in V1258	Semi-Solids in V1258	Bot.Solid Chunk in V1258	Second Stg Settl Solids	Second Stg Deposits	Solids in V1258	BT Coal Ash
Ash, wt%	26.5	32.0	21.6	62.1	67.3	56.3	6.2
CI, wt%	30.5	38.2	66.9	72.3	76.7		
Metal Oxides, wt%							
Aluminum	12.3	10.9	11.6	14.3	24.1	14.4	16.6
Calcium	18.0	19.6	14.9	12.0	14.6	12.8	24.2
Iron	23.9	22.7	24.7	31.5	14.5	21.8	6.0
Magnesium	3.6	3.2	3.3	4.9	9.7	3.8	4.6
Manganese	0.7	0.6	0.7	..	..	0.7	0.1
Molybdenum	0.8	0.6	0.7	..	..	..	0.1
Potassium	0.2	0.1	0.4	0.3	0.2	0.3	1.0
Silicon	17.3	21.1	26.9	11.5	5.8	27.6	32.4
Sodium	0.4	0.4	0.5	2.7	5.1	1.5	0.7
Sulfur Trioxide	14.3	17.0	14.6	19.6	15.6	15.1	11.2
Titanium	2.8	1.9	1.0	1.4	5.4	1.4	1.4
Iron-free Basis							
Aluminum	16.2	14.1	15.4	20.9	28.2	18.4	17.6
Calcium	23.6	25.4	19.8	17.5	17.1	16.4	25.7
Iron	0.0	0.0	0.0	0.0	0.0	0.0	6.4
Magnesium	4.7	4.1	4.4	7.2	11.4	4.9	4.9
Manganese	0.9	0.8	0.9	..	..	0.9	0.1
Molybdenum	1.1	0.8	0.9	..	..	..	0.1
Potassium	0.3	0.1	0.5	0.4	0.2	0.4	1.1
Silicon	22.7	27.3	35.7	16.8	6.8	35.3	34.5
Sodium	0.5	0.5	0.7	3.9	6.0	1.9	0.7
Sulfur Trioxide	18.8	22.0	19.4	28.6	18.2	19.3	11.9
Titanium	3.7	2.5	1.3	2.0	6.3	1.8	1.5

Table 4

Solid Deposits from End of Run 262

Sample No.	24807	24804	24852	
Description	R1235 Btm Wall	R1235 Btm Solids	V1258 Semi-Solids	V1258 Chunks
Ash, wt %	55.7	53.4	21.2	10.5
CI, wt %	90.6	73.4	49.6	80.7
Total Wt, lbs	37.2		17.0	

Table 5

TSL Yields Before Elemental Balancing
(Phase 2 Data)

	Operating Period					
Yield, wt % MAF	262A	262B	262C	262D	262E	261F
H_2 consumed	-6.9	-6.3	-6.1	-6.7	-5.4	-4.4
CO, CO_2	4.8	6.9	6.5	5.5	6.3	7.1
Sour Water	12.5	12.9	14.5	15.9	16.2	15.0
H_2S	-0.2	0.2	0.2	0.03	0.1	0.1
C_1-C_3 gases	4.2	4.7	5.5	4.9	5.8	5.3
C_4+ distillate	59.4	57.5	65.6	61.5	57.2	46.4
C_4-C_6	1.3	2.4	2.8	2.2	2.4	2.3
IBP-350°F	14.7	10.3	13.3	10.9	13.0	9.1
350-450°F	8.9	7.3	8.7	8.1	8.5	8.8
450-750°F	37.9	31.2	30.1	32.5	28.0	22.3
750-850°F	4.6	14.0	12.3	5.8	13.6	22.3
850°F-EP	-7.9	-7.6	-1.6	2.0	-8.4	-6.4
Int. Accum.(Res. Free)	0.9	3.9	1.5	1.3	0.8	0.6
Resid	5.2	1.5	-0.2	1.2	2.7	11.9
Bottoms Product(Ash-free)	15.8	16.7	16.1	18.6	19.3	18.7
Closure	4.3	2.0	-3.5	-2.1	-2.9	0.2
Resid+UC conv. wt % feed						
1st stage	28.0	28.0	21.7	24.4	20.7	22.5
2nd stage	13.8	11.8	20.9	16.0	17.7	10.2
Coal Conversions % MAF						
1st stage	88.8	88.4	85.6	88.5	85.2	86.7
TSL	92.5	89.9	90.4	90.2	92.0	92.8

Table 6

Close-Coupled Reactors Operating Data

Operating period	Coal feed rate MF lb/hr	First Stage Avg temp.,(°F)	First Stage Bed exotherm (°F)	Second Stage Avg temp.,(°F)	Second Stage Bed exotherm (°F)
262A	242	826	12.5	760	5.3
262B	248	825	12.2	761	7.8
262C1	301	825	14.5	790	8.5
262C2	296	825	14.0	790	6.9
262D	300	825	12.5	790	8.5
262E	346	824	17.7	810	9.5
262F	343	824	18.6	809	2.6

Table 7
Summary of ROSE-SR Performance Parameters

Operating Period	DAS Type	Resid Recov (wt %)	Energy Rej (%)	Organic Rej (wt %)	Tol Solubles (wt %)	FSI (a)	Ash Consistency
262A	2114	63.7	18.2	15.8	25.9	0.66	Powder
262B	2164	68.7	17.0	16.7	20.5	0.67	Powder
262C	2254	67.4	17.1	16.1	17.5	0.68	Powder
262D	2224	63.6	18.7	18.6	20.1	0.68	Powder
262E	2284	56.1	20.3	19.4	23.7	0.60	Extruded
262F	2404	69.2	18.7	18.7	18.3	0.67	Powder

(a) Feed solvency index: Ratio of feed soluble in deashing solvent to feed soluble in cresol.

Table 8

ROSE Unit Analytical Data - Run 262

Operating Period	262A	262B	262C	262D	262E	262F
Day						
Date						
Feed Comp (Wt%)						
Ash	18.2	19.7	20.9	20.0	19.5	17.7
UC	18.3	18.9	19.1	20.4	17.2	15.9
Resid (a)	56.3	59.3	57.8	57.6	61.4	63.1
Solvent	7.3	2.2	2.2	2.1	2.4	3.3
Carbon	70.6	71.6	70.6	71.9	71.9	73.5
Hydrogen	5.7	5.7	5.5	5.6	5.3	5.4
Nitrogen	0.9	0.9	0.9	1.0	1.0	1.1
Sulfur	2.2	2.2	2.2	2.1	2.1	1.9
Oxygen	2.5	-0.1	-0.1	-0.6	0.2	0.4
Preasphaltenes	5.5	5.3	4.0	3.4	10.3	10.4
Soft Point (deg F)	131	179	180	170	161	200
Fusion Pt (deg F)	149	207	205	195	193	247
Bottoms Prod Comp (Wt%)						
Ash (b)	34.1	34.0	35.6	32.4	30.4	32.7
UC (b)	29.0	32.4	32.7	35.4	30.2	31.2
Resid (a) (b)	35.7	29.3	27.9	31.2	38.3	35.0
Solvent (b)	2.0	1.9	3.6	1.0	1.1	1.0
DAS	0.7	1.3	0.9	1.0	1.2	0.9
Carbon	58.6	58.7	58.6	60.1	62.0	60.2
Hydrogen	3.9	3.9	3.8	3.9	4.0	3.8
Nitrogen	0.9	0.9	0.9	1.0	1.0	1.0
Sulfur	3.5	3.4	3.5	3.3	3.2	3.3
Oxygen (a)	-0.9	-0.9	-2.4	-0.7	-0.6	-1.1
Recycle Resid Comp (Wt%)						
Ash (b)	1.9	0.2	0.4	0.9	0.1	0.7
UC (b)	1.7	0.2	0.2	0.6	0.0	1.1
Resid (a) (b)	74.2	94.2	94.0	90.4	93.8	87.7
Solvent (b)	22.7	5.5	5.5	8.0	6.1	10.0
DAS	0.1	1.7	1.6	1.3	1.1	0.6
Carbon	87.0	89.4	88.7	89.7	89.4	88.4
Hydrogen	7.9	7.9	7.5	7.8	7.3	7.1
Nitrogen	0.9	1.0	1.0	1.0	1.1	1.3
Sulfur	0.5	0.0	0.1	0.1	0.1	0.2
Oxygen	1.8	1.5	2.4	0.5	2.1	2.4
Soft Point (deg F)	68	154	153	123	137	136
Fusion Pt (deg F)	82	182	177	140	171	170

(a) Calculated by difference
(b) "DAS-free" basis

Table 9

T102 Operating Conditions Summary

	262A	262B(a)	262C1	262C2	262D	262E	262F
T102 Tray 2 temp, °F	483	470	449	458	463	457	452
T102 Tray 3 temp, °F	489	492	464	479	494	483	478
T102 Top pack temp, °F	532	533	519	539	562	552	549
T102 Tray 8 temp, °F	570	589	571	578	604	580	579
T102 Bottom temp, °F	623	623	623	622	622	623	623
T102 TR3 reflux temp, °F	254	253	230	234	240	238	237
T102 Top pres, psia	2.9	1.6	2.0	1.7	1.5	1.6	1.9
T102 Reflux flow, lb/hr	639	637	532	625	634	634	635
B102 Inlet temp, °F	610	610	612	612	611	612	610
B102 Outlet temp, °F	664	672	664	666	664	667	665
B102 Process flow, GPM	24	21	24	25	25	24	24
GC Cut Point, °F	706±22	783±2	765±2	790	792±2	793±4	783±13
GC Equal wt % Overlap	7	11	6	11	13	9	7

(a) Aug 8-9 only.

Table 10

ANALYTICAL DATA FOR THE INTERSTAGE STREAM

Operating Period	Interstage Sample, wt %									
					CI-Free Residue			Distillate		
	Solv	Resid	UC	Ash	C	H	N	C	H	N
262A	45.8	33.5	10.2	10.6	88.61	7.39	1.15	88.35	9.84	0.57
262B	42.1	36.7	10.6	10.7	83.34	8.15	0.89	87.75	10.01	0.60
262C1	38.2	39.8	10.7	11.3	88.00	6.98	1.13	87.39	9.80	0.58
262C2	39.2	38.5	10.7	11.7	..	..	..	..	..	..
262D	40.6	37.8	10.6	11.0	88.42	7.29	1.11	88.09	9.85	0.52
262E	37.3	40.1	11.8	10.8	86.80	6.48	1.22	88.73	9.55	0.59
262F	36.8	41.2	11.3	10.7	88.30	6.76	1.23	87.55	9.28	0.64

Table 11

ANALYTICAL DATA OF STREAMS USED IN THE ELEMENTAL MATERIAL BALANCES

Operating Period	Coal, wt % MF					
	C	H	N	S	O(a)	Ash
262A	69.6	5.3	1.1	0.6	17.1	6.4
262B	69.3	5.2	1.0	0.4	17.8	6.3
262C1	68.8	4.8	1.0	0.5	18.5	6.5
262C2	68.8	4.8	1.0	0.5	18.5	6.5
262D	69.5	5.0	1.0	0.5	17.6	6.4
262E	68.5	4.9	1.0	0.5	18.8	6.3
262F	68.8	5.1	1.1	0.5	18.0	6.5

Operating Period	Recycle Material (V1082), wt %					
	C	H	N	S	O(a)	Ash
262A	70.0	5.6	0.9	2.4	0.6	20.5
262B	71.4	5.7	0.9	2.2	0.1	19.8
262C1	70.1	5.4	0.9	2.2	1.1	20.4
262C2	70.0	5.5	0.9	2.3	1.3	20.0
262D	71.4	5.6	1.0	2.1	0.1	19.9
262E	71.8	5.3	1.1	2.1	0.7	19.2
262F	73.1	5.3	1.2	2.0	0.5	18.0

Operating Period	Flashed Distillate (V1078), wt %				
	C	H	N	S	O(a)
262A	86.3	11.6	0.0	0.01	1.6
262B	86.2	11.7	0.4	0.01	1.7
262C1	85.8	11.5	0.3	0.01	2.4
262C2	86.4	11.7	0.4	0.01	1.5
262D	86.4	11.7	0.4	0.02	1.4
262E	86.1	11.5	0.4	0.04	1.9
262F	85.5	10.8	0.7	0.12	2.9

Operating Period	T102 Bottoms (V1074) + Withdrawal Tube Flush, wt %				
	C	H	N	S	O(a)
262A	87.1	9.8	0.5	0.04	2.6
262B	87.6	10.0	0.5	0.09	1.8
262C1	89.0	10.2	0.5	0.01	0.4
262C2	88.7	10.2	0.5	0.01	0.7
262D	89.0	10.2	0.5	0.02	0.3
262E	89.1	9.9	0.5	0.11	0.5
262F	89.1	9.5	0.6	0.02	0.8

Table 11 (continued)

ANALYTICAL DATA OF STREAMS USED IN THE ELEMENTAL MATERIAL BALANCES

Operating	Vaccum Flash Overhead (V1072), wt %				
Period	C	H	N	S	O(a)
262A	88.6	9.5	0.5	0.04	1.4
262B	88.6	10.3	0.5	0.05	0.6
262C1	88.5	10.1	0.4	0.01	1.0
262C2	88.3	10.0	0.5	0.01	1.3
262D	88.4	10.1	0.4	0.00	1.0
262E	89.0	9.8	0.5	0.02	0.7
262F	88.7	9.4	0.7	0.02	1.2

Operating	ROSE-SR^{SM} Resid, wt %					
Period	C	H	N	S	O(a)	Ash
262A	87.1	7.9	0.9	0.50	1.8	1.8
262B	89.4	8.0	1.0	0.04	1.5	0.2
262C1	88.7	7.5	1.0	0.06	2.4	0.4
262C2	89.4	7.6	1.1	0.05	1.5	0.4
262D	89.7	7.8	1.0	0.06	0.5	0.9
262E	89.3	7.3	1.1	0.06	2.1	0.1
262F	88.4	7.1	1.2	0.20	2.1	1.1

(a) Oxygen by difference.

Table 12

Run 262 Sour Water Analysis

	1st Stage	2nd Stage
Period	V105 Water (mg/liter)	V1080 water (mg/liter)
Kjeldahl nitrogen	7,280	7,966
Total organic carbon	19,791	4,320
Inorganic carbon	2,004	925
Phenols	8,750	2,750
Sulfide sulfur	985	11,375
Chloride	67.9	197.0

Table 13

COMPARISON OF CATALYST PROPERTIES

	Criterion 324 (Shell 324)	Shell 317	Amocat 1C	Amocat 1C	EXP-AO-60
Run	256,259,261,262	253,254,256	257,259	251,252	261
Support	Unimodal	Bimodal	Bimodal	Bimodal	Bimodal
Size, inches	1/16	1/20	1/12	1/16	1/16
Shape	Cylindrical	Trilobe	Cylindrical	Cylindrical	Cylindrical
Bulk density, lb/ft^3	54	37	35	42	33
Surface area (Sqm/g)	165	235	185	190	241
Metals, wt %					
Ni	2.70	2.65	2.35	2.33	2.5
Mo	13.20	11.58	10.60	10.42	10.7
Pore volume, cc/g	0.48	0.75	0.86	0.85	0.78
Catalyst charge, lb					
Full-volume	440	300	290	340	270
Half-volume	170	..	110	..	..

Table 14

R1236 Catalyst Age and Analytical Data

Date	Operating Day	Description	Catalyst Age R+CI	Catalyst Age MF Coal	<-------As is-------> S	Ash (wt %)	Oil	<----THF Extracted C	H	N (wt %)	S	Ash	Naph	14.0	18.0 Screen Size	25.0	-25.0 ---->
11-NOV-90		Run 260 Aged Cat	1470	628	6.0	66.9	18.4	11.8	0.9	0.2	7.1	76.2	59	91.9	6.7	1.5	0.0
14-JUL-91	3		1707	745	5.9	70.7	19.0	9.8	0.9	0.2	7.3	84.5	53	91.6	4.7	1.1	2.6
15-JUL	4	1st A/W	1588	701	5.8	75.4	15.9	12.4	0.9	0.2	7.0	84.8	44	95.5	2.7	0.9	0.9
17-JUL	7	2nd A/W	1541	693	5.8	73.2	18.5	11.0	0.8	0.2	7.0	85.5	33	97.2	1.9	0.3	0.6
19-JUL	9	3rd A/W	1494	685	5.8	73.1	17.8	11.0	0.8	0.2	7.1	89.0	20	95.3	3.8	0.5	0.4
21-JUL	11	4th A/W	1442	674	5.7	70.9	17.7	9.7	0.8	0.2	7.3	86.5	12	97.0	2.4	0.4	0.3
07-AUG	13	5th A/W	1448	688	5.7	71.7	18.7	9.7	0.6	0.2	7.2	84.2	22	98.5	1.2	0.1	0.2
09-AUG	15	6th A/W	1417	680	5.8	71.8	18.1	9.8	0.7	0.2	7.1	84.3	22	97.4	2.2	0.2	0.2
13-AUG	17	7th A/W	1369	667	5.9	71.0	19.2	9.4	0.7	0.2	6.8	82.7	9	98.9	0.6	0.2	0.3
15-AUG	19	8th A/W	1341	664	5.9	69.3	17.4	9.7	0.8	0.2	7.1	84.5	41	99.1	0.6	0.1	0.2
17-AUG	21	9th A/W	1333	671	5.7	69.3	18.0	9.2	0.8	0.2	7.1	86.4	28	98.7	0.9	0.3	0.2
19-AUG	23	10th A/W	1329	681	5.6	70.7	16.4	8.3	0.7	0.2	6.5	82.0	32	99.4	0.4	0.2	0.0
21-AUG	25	11th A/W	1314	674	5.9	72.5	17.2	8.1	0.7	0.2	7.2	83.4	27	99.3	0.4	0.1	0.2
23-AUG	27	12th A/W	1303	668	6.0	71.9	16.9	8.4	0.7	0.2	7.3	84.7	28	98.7	0.4	0.4	0.5
25-AUG	29	13th A/W	1289	661	6.0	71.7	16.9	8.5	0.7	0.2	7.3	84.8	45	99.7	0.1	0.2	0.1
27-AUG	31	14th A/W	1279	656	5.9	72.5	15.5	8.0	0.8	0.1	6.2	87.2	25	99.1	0.4	0.2	0.3
29-AUG	33	15th A/W	1387	713	5.7	66.7	21.5	8.9	0.7	0.2	7.0	85.7	35	97.9	0.5	0.5	1.1
09-SEP	35	16th A/W	1473	762	5.9	73.5	16.9	8.9	0.7	0.2	7.0	85.2	37	99.5	0.5	0.0	0.1
10-SEP	36	17th A/W	1366	708	5.7	71.7	16.3	8.9	0.7	0.2	6.5	82.2	34	99.2	0.7	0.0	0.1
12-SEP	38	18th A/W	1343	697	5.6	72.2	16.2	9.1	0.7	0.2	6.8	83.5	49	99.3	0.4	0.2	0.1
14-SEP	40	19th A/W	1316	682	5.4	71.8	15.7	9.2	0.7	0.2	6.7	83.0	39	99.6	0.4	0.0	0.1
16-SEP	42	20th A/W	1303	670	5.7	71.5	17.2	9.4	0.8	0.2	6.7	84.3	39	99.5	0.4	0.1	0.0
18-SEP	44	21st A/W	1285	661	6.2	71.2	16.8	9.3	0.8	0.2	6.5	84.7	20	98.0	1.0	0.4	0.6
20-SEP	46	22nd A/W	1275	654	6.2	72.0	15.5	9.4	0.7	0.2	6.5	86.1	27	99.7	0.2	0.0	0.2
22-SEP	48	23rd A/W	1527	787	5.8	73.0	16.2	10.1	0.8	0.2	6.6	82.4	26	98.4	0.9	0.3	0.4
23-SEP	49	End of Run Comp	1527	787	5.7	72.9	20.3	10.7	0.7	0.2	6.1	86.4	37	81.5	12.7	5.8	0.0
03-OCT	55	Btm Head	3472	1755										89.0	5.0	0.7	5.3

Table 15

Metal Analysis of Second Stage (R1236) Criterion 324 Catalyst (Wt % Metal Oxides)

Sample No.	22115	22307	22806	23211	23525	24129	24392
Date, 1991	7/15	7/19	8/15	8/23	8/29	9/18	9/22
Period	____	262A	262B	262C	____	262E	262E
Metal Oxides (Original Analysis)							
Aluminum	63.5	59.5	62.6	58.6	58.8	68.3	62.5
Calcium	0.2	0.3	0.2	0.2	0.3	0.3	1.5
Iron	0.5	0.4	0.3	0.3	1.4	0.2	1.6
Magnesium	0.2	0.2	0.2	0.2	0.1	0.2	0.5
Molybdenum	18.0	17.9	18.1	18.3	18.6	18.2	15.8
Nickel	3.5	2.9	3.4	3.8	3.1	3.6	3.1
Titanium	0.1	0.1	0.1	0.1	0.3	0.1	0.3
Silicon	0.3	0.3	0.4	0.4	0.4	0.2	0.4
Metal Oxides (Base: 100% Molybdenum Oxide)							
Aluminum	352.8	332.4	345.8	320.2	316.1	375.3	395.6
Calcium	1.1	1.7	1.1	1.1	1.6	1.6	9.5
Iron	2.8	2.2	1.6	1.6	7.5	1.1	10.1
Magnesium	1.1	1.1	1.1	1.1	0.5	1.1	3.2
Molybdenum	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Nickel	19.4	16.2	18.8	20.8	16.7	19.8	19.6
Titanium	0.6	0.6	0.6	0.5	1.6	0.5	1.9
Silicon	1.7	1.7	2.2	2.2	2.2	1.1	2.5

Table 16

TSL SYSTEM RESPONSES IN RESID + UC CONVERSION, EXCESS RESID, AND COAL CONVERSION
Run 262 with Black Thunder Coal, Jul. 12 - Sep. 30, 1991
Phase 2 data

unit: wt % MAF coal

		resid+UC conversion					Resid	Resid	coal conversion	
Date	Days	First	Second	Overall	TSL resid	Org.Rej.	w/ OR=15%	w/ OR=20%	First	Second
12-Jul-91	1	43.9	23.5	67.4	1.5	31.1	17.6	12.6	84.8	88.9
13-Jul-90	2	65.0	30.0	95.0	-8.4	13.4	-10.0	-15.0	88.5	94.9
14-Jul-91	3	66.7	20.4	87.1	-3.0	15.9	-2.1	-7.1	93.8	93.8
15-Jul-91	4	56.5	18.2	74.7	11.1	14.2	10.3	5.3	88.3	92.1
16-Jul-91	5	64.8	1.6	66.4	14.6	19.0	18.6	13.6	93.2	88.7
17-Jul-91	6	60.4	22.7	83.1	-2.0	18.9	1.9	-3.1	92.6	92.9
18-Jul-91	7	55.3	22.0	77.3	8.2	14.5	7.7	2.7	86.9	91.4
19-Jul-91	8	54.7	17.0	71.7	14.0	14.3	13.3	8.3	89.5	93.7
20-Jul-91	9	59.1	21.1	80.2	4.3	15.5	4.8	-0.2	86.1	91.9
21-Jul-91	10	56.5	21.2	77.7	4.5	17.8	7.3	2.3	87.8	91.8
06-Aug-91	12	44.6	52.8	97.4	-13.8	16.4	-12.4	-17.4	92.6	94.9
07-Aug-91	13	58.6	26.4	85.0	-1.8	16.8	-0.0	-5.0	89.0	92.7
08-Aug-91	14	63.4	12.7	76.1	7.6	16.3	8.9	3.9	89.3	89.0
09-Aug-91	15	63.9	10.7	74.6	9.7	15.7	10.4	5.4	88.6	89.6
13-Aug-91	17	57.1	20.6	77.7	5.1	17.2	7.3	2.3	88.9	89.5
14-Aug-91	18	56.9	22.8	79.7	2.7	17.6	5.3	0.3	87.4	90.4
15-Aug-91	19	61.3	20.0	81.3	1.7	17.0	3.7	-1.3	88.4	90.4
18-Aug-91	22	48.4	14.5	62.9	19.2	17.9	22.1	17.1	82.3	93.5
19-Aug-91	23	52.2	22.3	74.5	6.0	19.5	10.5	5.5	91.8	89.6
20-Aug-91	24	43.8	31.4	75.2	5.0	19.8	9.8	4.8	87.5	91.9
21-Aug-91	25	47.2	35.1	82.3	-2.3	20.0	2.7	-2.3	88.7	93.1
22-Aug-91	26	49.6	35.0	84.6	-2.2	17.6	0.4	-4.6	87.9	89.9
23-Aug-91	27	47.0	38.1	85.1	-0.7	15.6	-0.1	-5.1	82.4	90.5
24-Aug-91	28	41.3	37.0	78.3	6.3	15.4	6.7	1.7	86.4	90.0
25-Aug-91	29	50.6	32.0	82.6	1.6	15.8	2.4	-2.6	85.8	91.4
26-Aug-91	30	47.7	29.2	76.9	7.2	15.9	8.1	3.1	88.3	90.6
27-Aug-91	31	59.8	20.2	80.0	3.9	16.1	5.0	0.0	89.7	92.4
28-Aug-91	32	53.3	32.0	85.3	2.1	12.6	-0.3	-5.3	86.2	93.4
08-Sep-91	34	54.9	22.2	77.1	4.1	18.8	7.9	2.9	85.0	89.9
09-Sep-91	35	57.3	23.8	81.1	0.1	18.8	3.9	-1.1	89.4	91.2
10-Sep-91	36	49.7	27.8	77.5	4.5	18.0	7.5	2.5	89.3	88.7
11-Sep-91	37	51.3	24.8	76.1	4.2	19.7	8.9	3.9	89.3	90.8
12-Sep-91	38	50.3	32.6	82.9	-0.8	17.9	2.1	-2.9	89.4	90.5
13-Sep-91	39	47.8	29.8	77.6	4.1	18.3	7.4	2.4	84.8	91.0
14-Sep-91	40	41.1	39.6	80.7	1.2	18.1	4.3	-0.7	88.1	96.5
15-Sep-91	41	34.6	44.1	78.7	3.5	17.8	6.3	1.3	80.7	91.5
16-Sep-91	42	35.7	41.5	77.2	4.3	18.5	7.8	2.8	82.4	95.0
17-Sep-91	43	42.7	35.5	78.2	1.2	20.6	6.8	1.8	81.2	94.4
18-Sep-91	44	44.0	38.5	82.5	-2.6	20.1	2.5	-2.5	84.2	95.4
19-Sep-91	45	38.9	34.9	73.8	8.4	17.8	11.2	6.2	84.4	90.3
20-Sep-91	46	49.6	29.7	79.3	0.6	20.1	5.7	0.7	85.8	93.2
21-Sep-91	47	51.1	25.0	76.1	4.4	19.5	8.9	3.9	87.4	92.9
22-Sep-91	48	46.2	27.7	73.9	6.9	19.2	11.1	6.1	84.3	88.4

Table 16 (continued)

23-Sep-91	49	56.4	17.5	73.9	7.4	18.7	11.1	6.1	85.8	92.9
24-Sep-91	50	50.7	12.9	63.6	17.5	18.9	21.4	16.4	88.1	93.5
25-Sep-91	51	43.9	19.5	63.4	17.8	18.8	21.6	16.6	86.7	96.0
26-Sep-91	52	54.3	16.3	70.6	9.8	19.6	14.4	9.4	87.4	92.6
27-Sep-91	53	53.9	19.9	73.8	10.4	15.8	11.2	6.2	86.6	93.1
28-Sep-91	54	52.7	4.9	57.6	22.8	19.6	27.4	22.4	86.6	92.0
29-Sep-91	55	47.2	22.7	69.9	9.5	20.6	15.1	10.1	84.8	91.8
PERIOD 262A : July 17-20										
Average		57.4	20.7	78.1	6.1	15.8	6.9	1.9	88.8	92.5
Stan. Dev. (σn)		2.4	2.2	4.2	5.8	1.8	4.2	4.2	2.5	0.9
Stan. Dev. (σn-1)		2.8	2.6	4.9	6.7	2.1	4.9	4.9	2.9	1.0
PERIOD 262B : August 8,9,14,15 including 13										
Average		60.5	17.4	77.9	5.4	16.8	7.1	2.1	88.5	89.8
Stan. Dev. (σn)		3.0	4.8	2.4	3.0	0.7	2.4	2.4	0.6	0.5
Stan. Dev. (σn-1)		3.4	5.3	2.7	3.3	0.8	2.7	2.7	0.7	0.6
PERIOD 262C : August 22-25										
Average		47.1	35.5	82.7	1.3	16.1	2.4	-2.6	85.6	90.5
Stan. Dev. (σn)		3.6	2.3	2.7	3.2	0.9	2.7	2.7	2.0	0.6
Stan. Dev. (σn-1)		4.2	2.7	3.1	3.7	1.0	3.1	3.1	2.3	0.7
PERIOD 262C1 : August 22-23										
Average		48.3	36.6	84.9	-1.5	16.6	0.2	-4.8	85.2	90.2
Stan. Dev. (σn)		1.3	1.5	0.3	0.8	1.0	0.3	0.3	2.8	0.3
Stan. Dev. (σn-1)		1.8	2.2	0.4	1.1	1.4	0.4	0.4	3.9	0.4
PERIOD 262C2 : August 24-25										
Average		45.9	34.5	80.5	4.0	15.6	4.6	-0.4	86.1	90.7
Stan. Dev. (σn)		4.6	2.5	2.1	2.4	0.2	2.2	2.2	0.3	0.7
Stan. Dev. (σn-1)		6.6	3.5	3.0	3.3	0.3	3.0	3.0	0.4	1.0
PERIOD 262D : September 8-12										
Average		53.3	24.6	78.0	3.2	18.8	7.1	2.1	88.3	90.1
Stan. Dev. (σn)		3.0	2.0	1.9	1.8	0.6	1.9	1.9	1.9	1.0
Stan. Dev. (σn-1)		3.4	2.4	2.2	2.1	0.7	2.2	2.2	2.2	1.1
PERIOD 262E : September 18-22										
Average		46.0	31.2	77.1	3.5	19.3	7.9	2.9	85.2	92.0
Stan. Dev. (σn)		4.3	4.9	3.4	4.0	0.8	3.4	3.4	1.2	2.4
Stan. Dev. (σn-1)		4.8	5.5	3.7	4.5	0.9	3.7	3.7	1.4	2.7
PERIOD 262F : September 24-29										
Average		50.5	16.0	66.5	14.6	18.9	18.5	13.5	86.7	93.2
Stan. Dev. (σn)		3.8	5.8	5.5	5.0	1.5	5.5	5.5	1.0	1.4
Stan. Dev. (σn-1)		4.1	6.4	6.0	5.5	1.6	6.0	6.0	1.1	1.5

wt % MAF coal

Table 17

TSL SYSTEM RESPONSES IN RESID+UC CONVERSION AND EXCESS RESID
Run 262 with Black Thunder Coal, Jul. 17 - Sep. 30, 1991
Phase 3 Data

unit: wt % MAF coal

Date	Days	resid+UC conversion First	Second	Overall	TSL resid	Org.Rej.	Resid w/OR=15%	w/OR=20%
17-Jul-91	6	63.0	17.5	80.5	0.5	19.0	4.5	-0.5
18-Jul-91	7	61.3	16.9	78.2	5.3	15.3	5.6	0.6
19-Jul-91	8	60.0	18.3	78.3	6.6	15.1	6.7	1.7
20-Jul-91	9	63.1	21.1	84.2	-0.5	16.3	0.8	-4.2
08-Aug-91	14	64.0	19.3	83.3	-0.2	16.9	1.7	-3.3
09-Aug-91	15	62.8	18.3	81.1	2.7	16.3	4.0	-1.0
14-Aug-91	18	61.0	21.6	82.6	-0.5	17.9	2.4	-2.6
15-Aug-91	19	63.3	15.4	78.7	4.2	17.0	6.2	1.2
22-Aug-91	26	50.8	35.4	86.3	-4.2	17.8	-1.4	-6.4
23-Aug-91	27	56.7	31.3	88.0	-3.9	16.0	-2.9	-7.9
24-Aug-91	28	41.2	37.8	79.1	6.1	14.8	5.9	0.9
25-Aug-91	29	49.6	29.2	78.8	6.0	15.2	6.2	1.2
08-Sep-91	34	56.3	27.1	83.4	-2.5	19.1	1.6	-3.4
09-Sep-91	35	54.2	28.6	82.8	-1.8	18.9	2.1	-2.9
10-Sep-91	36	53.8	22.3	76.1	5.7	18.1	8.8	3.8
11-Sep-91	37	52.3	29.2	81.5	-1.7	20.2	3.5	-1.5
12-Sep-91	38	51.0	29.2	80.1	1.3	18.6	4.9	-0.1
18-Sep-91	44	46.0	34.5	80.5	0.4	19.1	4.5	-0.5
19-Sep-91	45	42.4	35.5	77.9	4.2	17.9	7.1	2.1
20-Sep-91	46	54.0	28.7	82.7	-4.0	21.3	2.3	-2.7
21-Sep-91	47	49.2	32.0	81.2	-1.6	20.4	3.8	-1.2
22-Sep-91	48	46.0	34.8	80.8	-1.1	20.3	4.2	-0.8
24-Sep-91	50	48.9	19.5	68.4	13.0	18.6	16.6	11.6
26-Sep-91	52	61.1	7.7	68.7	11.7	19.5	16.2	11.2
27-Sep-91	53	54.1	16.8	70.8	13.2	16.0	14.2	9.2
29-Sep-91	55	42.8	27.4	70.2	7.5	22.2	14.7	9.7

Table 17 (continued)

PERIOD 262A : July 17-20							
Average	61.9	18.5	80.3	3.0	16.4	4.4	-0.6
Stan. Dev. (σ_n)	1.3	1.6	2.4	3.0	1.6	2.2	2.2
Stan. Dev. (σ_{n-1})	1.5	1.9	2.8	3.5	1.8	2.6	2.6
PERIOD 262B : August 8,9,14,15							
Average	62.8	18.7	81.4	1.6	17.0	3.6	-1.4
Stan. Dev. (σ_n)	1.1	2.2	1.8	2.0	0.6	1.7	1.7
Stan. Dev. (σ_{n-1})	1.3	2.6	2.0	2.3	0.7	2.0	2.0
PERIOD 262C : August 22-25							
Average	49.6	33.4	83.1	1.0	16.0	2.0	-3.1
Stan. Dev. (σ_n)	5.5	3.4	4.1	5.1	1.2	4.1	4.1
Stan. Dev. (σ_{n-1})	6.4	3.9	4.8	5.8	1.3	4.8	4.8
PERIOD 262C1 : August 22-23							
Average	53.8	33.4	87.2	-4.1	16.9	-2.2	-7.2
Stan. Dev. (σ_n)	3.0	2.1	0.8	0.1	0.9	0.7	0.7
Stan. Dev. (σ_{n-1})	4.2	2.9	1.2	0.2	1.3	1.1	1.1
PERIOD 262C2 : August 24-25							
Average	45.4	33.5	79.0	6.1	15.0	6.1	1.1
Stan. Dev. (σ_n)	4.2	4.3	0.1	0.0	0.2	0.2	0.2
Stan. Dev. (σ_{n-1})	5.9	6.1	0.2	0.1	0.3	0.2	0.2
PERIOD 262D : September 8-12							
Average	53.5	27.3	80.8	0.2	19.0	4.2	-0.8
Stan. Dev. (σ_n)	1.8	2.6	2.6	3.0	0.7	2.6	2.6
Stan. Dev. (σ_{n-1})	2.0	2.9	2.9	3.4	0.8	2.9	2.9
PERIOD 262E : September 18-22							
Average	47.5	33.1	80.6	-0.4	19.8	4.4	-0.6
Stan. Dev. (σ_n)	3.9	2.5	1.6	2.7	1.2	1.6	1.6
Stan. Dev. (σ_{n-1})	4.3	2.8	1.7	3.0	1.3	1.7	1.7
PERIOD 262F : September 24-29							
Average	51.7	17.9	69.5	11.4	19.1	15.4	10.4
Stan. Dev. (σ_n)	6.7	7.0	1.0	2.3	2.2	1.0	1.0
Stan. Dev. (σ_{n-1})	7.8	8.1	1.2	2.7	2.6	1.2	1.2

Table 18

TSL SYSTEM RESPONSES IN COAL CONVERSION AND RESID + UC CONVERSION
Run 262 with Black Thunder Coal, Jul. 17 - Aug. 15, 1991
Phase 3 Data

		unit :	wt % MAF coal		wt% feed	hr^{-1}	hr^{-1}	wt% feed	hr^{-1}	hr^{-1}
		coal conversion			1st stage rate constant			2nd stage rate constant		
Date	Days	First	Second	TSL	Conv.	K_Vol	LN K_Vol	Conv.	K_Vol	LN K_Vol
17-Jul-91	6	93.0	91.4	91.1	29.2	96.3	4.57	9.9	30.9	3.43
18-Jul-91	7	88.5	93.0	92.7	29.4	94.2	4.55	11.9	36.7	3.60
19-Jul-91	8	90.8	94.1	93.9	28.5	91.3	4.51	10.7	33.0	3.50
20-Jul-91	9	87.1	93.3	93.5	31.8	103.7	4.64	14.5	45.3	3.81
08-Aug-91	14	88.4	92.3	91.4	29.7	96.9	4.57	12.1	37.9	3.64
09-Aug-91	15	88.9	92.7	92.2	27.6	90.6	4.51	10.8	34.6	3.54
14-Aug-91	18	84.2	91.9	90.3	28.9	92.7	4.53	14.3	45.7	3.82
15-Aug-91	19	86.6	91.7	90.4	29.5	97.6	4.58	10.0	31.1	3.44
22-Aug-91	26	89.6	92.6	91.4	22.7	82.8	4.42	20.8	89.1	4.49
23-Aug-91	27	91.6	93.2	92.1	24.8	90.7	4.51	18.7	76.1	4.33
24-Aug-91	28	89.2	92.4	92.4	19.0	65.0	4.17	22.0	94.1	4.54
25-Aug-91	29	86.7	93.0	92.1	22.9	82.8	4.42	17.3	70.1	4.25
08-Sep-91	34	85.8	92.1	89.6	26.4	100.8	4.61	16.8	68.2	4.22
09-Sep-91	35	88.1	92.6	90.6	25.3	94.1	4.54	17.3	69.8	4.25
10-Sep-91	36	92.8	91.9	90.3	24.9	92.8	4.53	13.0	50.3	3.92
11-Sep-91	37	88.5	91.6	89.7	23.6	86.6	4.46	16.9	68.5	4.23
12-Sep-91	38	90.1	91.5	90.4	23.4	84.9	4.44	18.2	74.4	4.31
18-Sep-91	44	85.5	93.3	91.6	20.7	82.8	4.42	18.9	88.9	4.49
19-Sep-91	45	85.0	92.5	92.8	19.5	78.0	4.36	20.0	96.7	4.57
20-Sep-91	46	91.1	92.3	90.5	23.6	99.4	4.60	17.1	79.9	4.38
21-Sep-91	47	85.2	92.2	91.3	22.3	91.4	4.52	18.6	87.5	4.47
22-Sep-91	48	86.5	91.0	91.8	20.9	84.3	4.43	19.6	93.5	4.54
24-Sep-91	50	86.0	92.1	92.1	21.9	88.7	4.49	11.5	139.9	4.94
26-Sep-91	52	90.6	92.1	90.1	26.4	114.0	4.74	4.0	45.1	3.81
27-Sep-91	53	84.7	92.7	92.1	23.6	95.7	4.56	8.3	95.5	4.56
29-Sep-91	55	83.7	92.2	91.1	19.9	79.4	4.38	15.4	198.3	5.29

Table 18 (continued)

PERIOD 262A : July 17-20									
Average	89.9	93.0	92.8	29.7	96.4	4.57	11.8	36.5	3.59
Stan. Dev. (σn)	2.2	1.0	1.1	1.2	4.6	0.05	1.7	5.5	0.15
Stan. Dev. (σn-1)	2.6	1.1	1.2	1.4	5.3	0.05	2.0	6.4	0.17
PERIOD 262B : August 8,9,14,15									
Average	87.0	92.1	91.1	28.9	94.4	4.55	11.8	37.4	3.61
Stan. Dev. (σn)	1.8	0.4	0.8	0.8	2.9	0.03	1.6	5.4	0.14
Stan. Dev. (σn-1)	2.1	0.4	0.9	0.9	3.3	0.04	1.9	6.2	0.16
PERIOD 262C : August 22-25									
Average	89.3	92.8	92.0	22.4	80.4	4.38	19.7	82.4	4.40
Stan. Dev. (σn)	1.7	0.3	0.4	2.1	9.4	0.12	1.8	9.6	0.12
Stan. Dev. (σn-1)	2.0	0.4	0.4	2.4	10.9	0.14	2.1	11.1	0.14
PERIOD 262C1 : August 22-23									
Average	90.6	92.9	91.8	23.8	86.8	4.46	19.8	82.6	4.41
Stan. Dev. (σn)	1.0	0.3	0.3	1.0	3.9	0.05	1.0	6.5	0.08
Stan. Dev. (σn-1)	1.4	0.4	0.5	1.5	5.6	0.06	1.5	9.2	0.11
PERIOD 262C2 : August 24-25									
Average	88.0	92.7	92.3	21.0	73.9	4.30	19.7	82.1	4.40
Stan. Dev. (σn)	1.3	0.3	0.2	1.9	8.9	0.12	2.4	12.0	0.15
Stan. Dev. (σn-1)	1.8	0.4	0.2	2.8	12.6	0.17	3.3	16.9	0.21
PERIOD 262D : September 8-12									
Average	89.1	91.9	90.1	24.7	91.8	4.52	16.4	66.2	4.18
Stan. Dev. (σn)	2.3	0.4	0.4	1.1	5.7	0.06	1.8	8.3	0.14
Stan. Dev. (σn-1)	2.6	0.4	0.4	1.2	6.3	0.07	2.0	9.3	0.15
PERIOD 262E : September 18-22									
Average	86.7	92.3	91.6	21.4	87.2	4.46	18.8	89.3	4.49
Stan. Dev. (σn)	2.3	0.7	0.7	1.4	7.5	0.08	1.0	5.7	0.07
Stan. Dev. (σn-1)	2.5	0.8	0.8	1.6	8.4	0.09	1.1	6.4	0.07
PERIOD 262F : September 24-29									
Average	86.3	92.3	91.4	23.0	94.5	4.54	9.8	119.7	4.65
Stan. Dev. (σn)	2.6	0.2	0.8	2.4	12.7	0.13	4.2	56.4	0.55
Stan. Dev. (σn-1)	3.0	0.3	1.0	2.8	14.6	0.15	4.8	65.2	0.63

Table 19

RUN 262 FIRST STAGE THERMAL ACTIVITY IN RESID + UC CONVERSION
Black Thunder Coal, Jul. 12 - Sep. 30, 1991
Half-Volume Reactor
Phase 2 Data

Date	Days	Temp.	SV/C_Vol	Factor	Resid + UC Conv.	K/C	LN K/C	T_Inv.
12-Jul-91	1	825	64.8	3.81	19.9	61.3	4.12	0.000778
13-Jul-90	2	823	63.8	3.97	26.1	89.4	4.49	0.000779
14-Jul-91	3	826	66.9	3.91	27.6	99.7	4.60	0.000778
15-Jul-91	4	824	65.7	3.62	27.0	87.9	4.48	0.000779
16-Jul-91	5	824	65.6	3.79	28.6	99.5	4.60	0.000779
17-Jul-91	6	825	65.1	3.59	28.5	93.1	4.53	0.000778
18-Jul-91	7	825	64.2	3.52	27.0	83.7	4.43	0.000778
19-Jul-91	8	826	64.9	3.53	26.4	82.1	4.41	0.000778
20-Jul-91	9	829	61.5	3.62	30.2	96.2	4.57	0.000776
21-Jul-91	10	826	60.4	3.89	26.1	83.0	4.42	0.000778
06-Aug-91	12	813	65.6	3.65	22.1	67.9	4.22	0.000786
07-Aug-91	13	824	63.8	3.79	26.3	86.2	4.46	0.000779
08-Aug-91	14	825	64.0	3.58	29.1	94.1	4.54	0.000778
09-Aug-91	15	825	64.7	3.67	27.5	90.2	4.50	0.000778
13-Aug-91	17	825	65.9	3.38	27.4	84.1	4.43	0.000778
14-Aug-91	18	825	66.7	3.42	27.0	84.3	4.43	0.000778
15-Aug-91	19	825	66.4	3.51	28.4	92.5	4.53	0.000778
18-Aug-91	22	826	80.8	3.47	24.4	90.4	4.50	0.000778
19-Aug-91	23	826	79.4	3.49	24.7	91.0	4.51	0.000778
20-Aug-91	24	826	79.2	3.51	19.8	68.7	4.23	0.000778
21-Aug-91	25	825	79.8	3.50	21.9	78.3	4.36	0.000778
22-Aug-91	26	826	80.8	3.49	22.6	82.4	4.41	0.000778
23-Aug-91	27	825	78.4	3.51	21.5	75.3	4.32	0.000778
24-Aug-91	28	825	78.2	3.55	19.4	66.7	4.20	0.000778
25-Aug-91	29	825	78.1	3.57	23.4	85.2	4.44	0.000778
26-Aug-91	30	825	79.6	3.52	22.4	80.8	4.39	0.000778
27-Aug-91	31	826	78.7	3.50	27.4	103.8	4.64	0.000778
28-Aug-91	32	825	78.0	3.50	24.4	88.2	4.48	0.000778
08-Sep-91	34	825	79.3	3.54	25.8	97.7	4.58	0.000778
09-Sep-91	35	824	79.5	3.50	26.4	99.7	4.60	0.000779
10-Sep-91	36	825	79.5	3.52	23.2	84.5	4.44	0.000778
11-Sep-91	37	824	79.3	3.53	23.4	85.6	4.45	0.000779
12-Sep-91	38	825	78.3	3.55	23.0	83.1	4.42	0.000778
13-Sep-91	39	825	87.0	3.51	21.9	85.7	4.45	0.000778
14-Sep-91	40	825	92.1	3.43	19.1	74.5	4.31	0.000778
15-Sep-91	41	825	88.8	3.58	15.8	59.7	4.09	0.000778
16-Sep-91	42	825	92.0	3.48	16.8	64.6	4.17	0.000778
17-Sep-91	43	825	91.5	3.48	20.1	80.2	4.38	0.000778
18-Sep-91	44	824	91.0	3.49	19.9	78.8	4.37	0.000779
19-Sep-91	45	824	92.0	3.50	17.7	69.2	4.24	0.000779
20-Sep-91	46	825	92.1	3.50	22.3	92.4	4.53	0.000778
21-Sep-91	47	824	90.8	3.51	22.7	93.5	4.54	0.000779
22-Sep-91	48	824	91.4	3.49	20.8	83.8	4.43	0.000779

Table 19 (continued)

23-Sep-91	49	824	[illegible].7	3.48	25.2	108.8	4.69	0.000779
24-Sep-91	50	824	90.6	3.49	22.1	89.7	4.50	0.000779
25-Sep-91	51	824	90.9	3.49	19.3	76.0	4.33	0.000779
26-Sep-91	52	824	91.5	3.47	24.0	100.4	4.61	0.000779
27-Sep-91	53	824	88.2	3.51	23.0	92.5	4.53	0.000779
28-Sep-91	54	824	90.3	3.48	23.2	95.0	4.55	0.000779
29-Sep-91	55	823	92.0	3.48	20.9	84.5	4.44	0.000779
PERIOD 262A : July 17-20								
Average		826	63.9	3.56	28.0	88.8	4.48	0.000777
Stan. Dev. ($\sqrt{n}$)		2	1.4	0.04	1.5	6.0	0.07	0.000001
Stan. Dev. ($\sqrt{n-1}$)		2	1.7	0.04	1.7	6.9	0.08	0.000001
PERIOD 262B : August 8,9,14,15 including 13								
Average		825	65.5	3.51	27.9	89.0	4.49	0.000778
Stan. Dev. ($\sqrt{n}$)		0	1.0	0.11	0.8	4.1	0.05	0.000000
Stan. Dev. ($\sqrt{n-1}$)		0	1.2	0.12	0.9	4.6	0.05	0.000000
PERIOD 262C : August 22-25								
Average		825	78.9	3.53	21.7	77.4	4.34	0.000778
Stan. Dev. ($\sqrt{n}$)		0	1.1	0.03	1.5	7.1	0.09	0.000000
Stan. Dev. ($\sqrt{n-1}$)		1	1.3	0.04	1.7	8.2	0.11	0.000000
PERIOD 262C1 : August 22-23								
Average		826	79.6	3.50	22.1	73.9	4.37	0.000778
Stan. Dev. ($\sqrt{n}$)		1	1.2	0.01	0.6	3.5	0.04	0.000000
Stan. Dev. ($\sqrt{n-1}$)		1	1.7	0.01	0.8	5.0	0.06	0.000000
PERIOD 262C2 : August 24-25								
Average		825	78.1	3.56	21.4	75.9	4.32	0.000778
Stan. Dev. ($\sqrt{n}$)		0	0.0	0.01	2.0	9.2	0.12	0.000000
Stan. Dev. ($\sqrt{n-1}$)		0	0.1	0.02	2.8	13.0	0.17	0.000000
PERIOD 262D : September 8-12								
Average		825	79.4	3.52	24.7	91.9	4.52	0.000779
Stan. Dev. ($\sqrt{n}$)		1	0.1	0.02	1.4	6.8	0.07	0.000000
Stan. Dev. ($\sqrt{n-1}$)		1	0.1	0.02	1.6	7.9	0.09	0.000000
PERIOD 262E : September 18-22								
Average		824	91.5	3.50	20.7	83.5	4.42	0.000779
Stan. Dev. ($\sqrt{n}$)		0	0.5	0.01	1.8	9.0	0.11	0.000000
Stan. Dev. ($\sqrt{n-1}$)		0	0.6	0.01	2.0	10.1	0.12	0.000000
PERIOD 262F : September 24-29								
Average		824	90.6	3.49	22.1	89.7	4.49	0.000779
Stan. Dev. ($\sqrt{n}$)		0	1.2	0.01	1.6	7.8	0.09	0.000000
Stan. Dev. ($\sqrt{n-1}$)		0	1.3	0.01	1.7	8.5	0.10	0.000000
		deg F	$\frac{\text{lb MF coal/hr}}{\text{cuft-reactor}}$		wt % of feed r+UC	hr^{-1}	hr^{-1}	deg R^{-1}

Table 20

RUN 262 SECOND STAGE CATALYST ACTIVITY IN RESID + UC CONVERSION
Criterion 324 1/16", Black Thunder Coal, Molyvan L and Fe203 Addition
Resid Injection: Jul. 12-Aug. 15, Old Slurry Blend: Aug. 17 - Sep. 30
Catalyst Replacement At 3 lb/ton MF Coal : Jul. 15 - Sep. 22
Half-Volume Reactor, 170 lbs Charge, 110 lbs Removed on Sep. 23, 60 lbs Left
Phase 2 Data

Date	Days	Temp.	MF_Age	SV_Cat_Vol	Resid + UC Conv.	Age_Vol	K_Vol	LN K_Vol	T_Inv.
12-Jul-91	1	760	684	91.3	12.7	3.69	50.6	3.92	0.000820
13-Jul-90	2	759	724	89.9	11.0	3.91	44.1	3.79	0.000820
14-Jul-91	3	761	745	80.4	6.4	4.02	21.5	3.07	0.000819
15-Jul-91	4	760	701	79.0	11.8	3.79	38.2	3.64	0.000820
16-Jul-91	5	760	736	78.8	0.8	3.97	2.4	0.88	0.000820
17-Jul-91	6	760	693	78.3	13.7	3.74	44.6	3.80	0.000820
18-Jul-91	7	760	728	77.1	15.8	3.93	51.0	3.93	0.000820
19-Jul-91	8	760	685	78.0	10.4	3.70	31.9	3.46	0.000820
20-Jul-91	9	760	718	73.9	15.4	3.88	48.6	3.88	0.000820
21-Jul-91	10	759	674	72.6	13.2	3.64	42.9	3.76	0.000820
06-Aug-91	12	755	731	78.9	31.7	3.95	133.6	4.89	0.000823
07-Aug-91	13	758	688	76.7	15.7	3.72	54.1	3.99	0.000821
08-Aug-91	14	762	722	76.9	10.0	3.90	30.6	3.42	0.000818
09-Aug-91	15	761	680	77.8	8.3	3.67	25.9	3.25	0.000819
13-Aug-91	17	759	667	79.2	14.5	3.60	45.4	3.82	0.000820
14-Aug-91	18	761	703	80.2	15.4	3.80	49.9	3.91	0.000819
15-Aug-91	19	760	664	79.8	13.4	3.59	43.4	3.77	0.000820
18-Aug-91	22	759	714	97.1	13.4	3.86	52.1	3.95	0.000820
19-Aug-91	23	776	681	95.5	13.4	3.68	51.6	3.94	0.000809
20-Aug-91	24	790	723	95.3	18.6	3.90	76.5	4.34	0.000800
21-Aug-91	25	789	674	96.0	19.8	3.64	82.9	4.42	0.000801
22-Aug-91	26	790	717	97.2	20.9	3.87	89.7	4.50	0.000800
23-Aug-91	27	789	668	94.3	22.3	3.61	95.0	4.55	0.000801
24-Aug-91	28	790	710	94.1	21.2	3.83	89.7	4.50	0.000800
25-Aug-91	29	790	661	93.9	19.3	3.57	80.2	4.38	0.000800
26-Aug-91	30	790	704	95.7	19.0	3.80	78.9	4.37	0.000800
27-Aug-91	31	789	656	94.7	14.0	3.54	53.9	3.99	0.000801
28-Aug-91	32	790	698	93.7	19.5	3.77	79.5	4.38	0.000800
08-Sep-91	34	790	720	95.4	14.8	3.89	58.7	4.07	0.000800
09-Sep-91	35	789	762	95.5	15.2	4.11	59.8	4.09	0.000801
10-Sep-91	36	790	708	95.6	16.1	3.82	64.6	4.17	0.000800
11-Sep-91	37	790	750	95.3	15.1	4.05	59.9	4.09	0.000800
12-Sep-91	38	790	697	94.2	19.0	3.76	78.5	4.36	0.000800
13-Sep-91	39	803	743	104.6	17.9	4.01	80.1	4.38	0.000792
14-Sep-91	40	810	682	110.8	23.6	3.68	117.3	4.76	0.000787
15-Sep-91	41	810	729	106.8	24.7	3.94	125.5	4.83	0.000787
16-Sep-91	42	811	670	110.6	23.6	3.62	118.8	4.78	0.000787
17-Sep-91	43	811	719	110.0	20.4	3.88	98.2	4.59	0.000787
18-Sep-91	44	811	661	109.4	21.4	3.57	103.9	4.64	0.000787
19-Sep-91	45	810	710	110.6	17.5	3.83	82.1	4.41	0.000787
20-Sep-91	46	810	654	110.8	17.5	3.53	82.1	4.41	0.000787
21-Sep-91	47	810	703	109.2	16.1	3.80	73.5	4.30	0.000787
22-Sep-91	48	808	647	109.9	16.1	3.49	73.6	4.30	0.000789

Table 20 (continued)

23-Sep-91	49	809	787	315.6	10.8	4.25	133.1	4.89	0.000788
24-Sep-91	50	807	924	308.5	8.5	4.99	100.0	4.61	0.000789
25-Sep-91	51	809	1062	309.5	11.9	5.73	146.1	4.98	0.000788
26-Sep-91	52	810	1201	311.8	8.6	6.49	101.9	4.62	0.000787
27-Sep-91	53	809	1334	300.3	10.8	7.20	127.7	4.85	0.000788
28-Sep-91	54	803	1471	307.8	4.0	7.94	44.6	3.80	0.000792
29-Sep-91	55	809	1610	313.4	12.9	8.69	161.3	5.08	0.000788
PERIOD 262A : July 17-20									
Average		760	706	76.8	13.8	3.81	44.0	3.77	0.000820
Stan. Dev. (σn)		0	18	1.7	2.1	0.10	7.3	0.18	0.000000
Stan. Dev. (σn-1)		0	20	2.0	2.5	0.11	8.5	0.21	0.000000
PERIOD 262B : August 8,9,14,15 including 13									
Average		761	687	78.8	12.3	3.71	39.0	3.63	0.000819
Stan. Dev. (σn)		1	22	1.2	2.7	0.12	9.2	0.25	0.000001
Stan. Dev. (σn-1)		1	25	1.4	3.0	0.13	10.3	0.28	0.000001
PERIOD 262C : August 22-25									
Average		790	689	94.9	20.9	3.72	88.6	4.48	0.000800
Stan. Dev. (σn)		0	25	1.3	1.1	0.13	5.3	0.06	0.000000
Stan. Dev. (σn-1)		1	29	1.6	1.2	0.15	6.2	0.07	0.000000
PERIOD 262C1 : August 22-23									
Average		790	693	95.8	21.6	3.74	92.3	4.52	0.000800
Stan. Dev. (σn)		1	25	1.4	0.7	0.13	2.7	0.03	0.000000
Stan. Dev. (σn-1)		1	35	2.1	1.0	0.19	3.8	0.04	0.000000
PERIOD 262C2 : August 24-25									
Average		790	686	94.0	20.3	3.70	85.0	4.44	0.000800
Stan. Dev. (σn)		0	25	0.1	1.0	0.13	4.8	0.06	0.000000
Stan. Dev. (σn-1)		0	35	0.1	1.3	0.19	6.8	0.08	0.000000
PERIOD 262D : September 8-12									
Average		790	735	95.5	15.3	3.97	60.7	4.11	0.000800
Stan. Dev. (σn)		0	22	0.1	0.5	0.12	2.3	0.04	0.000000
Stan. Dev. (σn-1)		1	25	0.1	0.6	0.14	2.6	0.04	0.000000
PERIOD 262E : September 18-22									
Average		810	675	110.0	17.7	3.64	83.0	4.41	0.000788
Stan. Dev. (σn)		1	26	0.6	1.9	0.14	11.1	0.13	0.000001
Stan. Dev. (σn-1)		1	29	0.7	2.2	0.16	12.4	0.14	0.000001
PERIOD 262F : September 24-29									
Average		808	1267	308.6	9.5	6.84	113.6	4.66	0.000789
Stan. Dev. (σn)		2	234	4.2	2.9	1.26	37.9	0.42	0.000001
Stan. Dev. (σn-1)		3	256	4.6	3.2	1.38	41.5	0.46	0.000002
NOTE:									
unit		deg F	$\frac{\text{lb MF coal}}{\text{lb cat}}$	$\frac{\text{lb ccal/hr}}{\text{cuft-cat}}$	wt % of feed resid+UC	$\frac{\text{lb MF coal}}{\text{cuft-cat}}$	hr^{-1}	hr^{-1}	deg R^{-1}

Table 21

TSL Process Performance Summary

Period	Reactor volume %	Recycle Resid (wt %)	Reaction temp.(F) 1st	Reaction temp.(F) 2nd	Coal feed (MF lb/hr)	Yield (wt % MAF coal) C4+ dist	Yield (wt % MAF coal) Organic rejection	Yield (wt % MAF coal) Resid	Catalyst replacement (lb/ton MF)	Catalyst age (lb MF coal/ lb cat)	Coal space velocity (lb MF coal/ hr/cuft cat)	Interstage separator	Inlet H2 pp (psia) 1st	Inlet H2 pp (psia) 2nd
262A(a)	50/50(c)	32	826	760	242	58	16	3	3	706	76.9	Yes	2740	2510
262B	50/50	38	825	761	248	58	17	2	3	692	78.7	Yes	2710	2500
262C1	50/50	39	825	790	301	65	17	-4	3	692	95.7	Yes	2720	2550
262C2	50/50	36	825	790	296	57	15	6	3	685	94.0	Yes	2720	2560
262D	50/50	36	825	790	300	61	19	0	3	727	95.2	Yes	2800	2530
262E	50/50	38	824	810	346	57	20	-1	3	674	110.0	Yes	2840	2540
262F(b)	50/50	41	824	809	343	48	19	11	-	-	(90.6)(d)	Yes	2860	2530

Note: (a) Transitional.
(b) Unstable. Primarily thermal reactor with a small amount of catalyst left in the second stage reactor (about 30-60 lbs).
(c) Half-volume in both thermal first and catalytic second stages.
(d) Unit = lb MF coal/hr/cuft reactor (1st stage).

Table 22

Projection of Coal Feed Rate for Resid Extinction and
Calculation of Steady-State Catalyst Replacement

Period	Projected (a) coal feed rate (MF lb/hr)	Projected (a) space velocity (MF lb/hr/cuft-cat)	Adjusted yield (wt % MAF coal) C4+ dist	Adjusted yield (wt % MAF coal) Common(b) organic rej.	Calculated steady-state catalyst replacement (lb/ton MF)
262A(c)	-	-	60.4	16	2.7
262B	220.5	70.0	60.6	16	2.7
262C1	311.0	99.0	62.5	16	2.7
262C2	266.1	84.5	59.6	16	2.7
262D	281.3	89.6	61.0	19	2.6
262E	339.1	107.8	57.0	19	2.7
262F(d)	265.0	(70.0)(e)	55.4	19	-

Note: (a) Projected by using CSTR 1st order kinetics.
(b) Estimated.
(c) Transitional.
(d) Unstable. Primarily thermal reactor with a small amount of catalyst left in the second stage reactor (about 30-60 lbs).
(e) Unit = lb MF coal/hr/cuft reactor (1st stage).

Table 23

Blending Proportions of Atmospheric Overhead (V161) and Vacuum Tower Overhead (V182) Used To Prepare Product Quality Blends

Period	Atm. Overhead (V161) wt %	Vac. Overhead (V182) wt %
262A	30.4	69.6
262B	27.1	72.9
262C1	38.5	61.5
262C2	33.6	66.4
262D	34.3	65.7
262E	40.4	59.6

Table 24

PROPERTIES OF TOTAL OIL PRODUCTS

PERIOD	262A	262B	262C1	262C2	262D	262E	260D
Elemental wt %							
C	86.43	86.88	85.30	86.15	86.74	86.30	87.09
H	11.28	10.96	11.45	11.46	11.42	11.37	11.13
N(ppm)	5100	4754	5282	5581	5373	5728	4500
S	0.05	0.01	0.02	0.03	0.03	0.05	0.04
O(dif)	1.73	1.36	2.68	2.31	1.27	1.71	1.29
Gravity (°API)	21.4	18.1	23.1	21.6	19.6	23.5	22.1
G.C. Sim. Dist., °F							
IBP	97	176	97	134	156	97	97
10%	307	424	265	268	358	265	250
20%	399	492	360	364	466	360	350
30%	475	539	435	460	516	436	450
40%	511	586	496	515	568	496	502
50%	549	638	563	568	629	563	561
60%	586	671	617	629	672	626	611
70%	631	707	659	664	722	670	652
80%	648	740	694	706	762	722	652
90%	676	756	750	749	799	760	722
95%	709	793	763	773	810	783	751
EP	746	838	815	821	868	838	813
Distribution, Wt.%[a]							
IBP-350°F	13.4	5.6	18.5	16.4	10.4	19.9	15.2
350-450°F	13.0	9.7	14.6	13.3	11.4	10.0	8.2
450-650°F	66.8	51.0	37.3	33.1	38.5	43.9	44.0
650-EP °F	6.8	33.7	33.8	37.2	39.7	26.2	32.5
EP°F(D1160)	646 675[b]	775	710	735	771	748	723

a) performed by laboratory distillation
b) rerun

Table 25

SIMULATED DISTILLATION FOR V182 OIL

DATE	PERIOD	IBP 350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	850°F+
7/16	262A	0.0	1.7	18.7	42.4	35.6	1.6	0.0
7/17	262A	0.0	1.9	23.9	49.2	24.4	0.6	0.0
7/18	262A	0.0	2.1	22.8	39.9	34.3	0.7	0.0
8/08	262B	0.0	0.8	9.9	24.7	38.1	24.9	1.6
8/09	262B	0.0	1.1	11.2	25.8	37.1	24.4	0.4

All analyses are wt %.

Table 26

PROPERTIES OF NAPHTHA (IBP-350°F)

PERIOD	262A	262B	262C1	262C2	262D	262E	260D
Elemental wt %							
C	84.24	85.26	84.33	83.27	83.78	83.66	85.14
H	13.56	13.28	13.52	13.58	13.49	13.38	14.34
N(ppm)	1654	1137	1556	1558	1981	1909	1200
S	0.08	0.06	0.07	0.05	0.05	0.10	0.06
O(dif)	1.95	1.29	1.92	2.94	2.48	2.67	0.34
Gravity (°API)	49.5	47.0	49.1	47.1	47.5	47.5	53.5
G.C. Sim. Dist., (°F)							
IBP	70	88	88	88	91	69	69
10%	156	176	161	161	164	156	156
20%	176	231	176	176	176	176	176
30%	231	241	231	227	237	237	231
40%	241	249	241	241	241	241	241
50%	249	272	250	250	253	252	248
60%	269	301	270	270	281	281	270
70%	291	316	291	291	306	306	281
80%	308	339	327	327	320	324	291
90%	357	360	350	350	343	342	309
95%	360	360	358	360	357	350	335
EP	360	367	360	360	366	362	360

Table 27

PROPERTIES OF MIDDLE DISTILLATE (350-450°F)

PERIOD	262A	262B	262C1	262C2	262D	262E	260D
Elemental wt %							
C	84.79	85.12	84.53	84.99	85.51	85.26	86.25
H	11.45	11.47	11.60	11.49	11.74	11.60	12.03
N(ppm)	3400	3318	2732	2831	3055	1598	1600
S	0.06	0.03	0.03	0.03	0.04	0.07	0.08
O(dif)	3.38	3.05	3.57	3.21	2.40	2.91	1.48
Gravity (°API)	25.4	25.7	26.9	26.5	26.2	27.9	28.6
G.C. Sim. Dist., (°F)							
IBP	323	323	325	334	334	330	306
10%	360	364	360	360	363	360	350
20%	366	376	364	365	363	366	361
30%	389	395	381	381	394	366	369
40%	405	405	393	397	405	383	383
50%	416	424	405	405	424	389	405
60%	434	437	424	436	436	399	405
70%	443	444	435	450	448	424	436
80%	466	466	458	460	460	435	451
90%	476	476	460	466	466	435	460
95%	485	476	466	466	492	449	460
EP	492	492	492	492	492	460	483

Table 28

PROPERTIES OF MIDDLE DISTILLATE (450-650°F)

PERIOD	262A	262B	262C1	262C2	262D	262E	260D
Elemental wt %							
C	87.26	87.34	86.51	86.85	86.80	86.36	87.15
H	10.82	11.05	10.90	10.98	10.62	10.70	10.94
N(ppm)	5732	5146	6765	5889	6758	6850	5000
S	0.04	0.01	0.02	0.02	0.02	0.04	0.03
O(dif)	1.31	1.09	1.89	1.56	1.88	2.21	1.38
Gravity (°API)	17.3	17.5	17.0	16.9	18.5	17.7	18.4
G.C. Sim. Dist., (°F)							
IBP	441	445	405	449	449	377	415
10%	492	492	487	492	492	460	475
20%	516	531	516	516	510	483	501
30%	549	563	539	549	549	496	538
40%	568	580	572	580	568	531	560
50%	591	614	591	614	593	568	575
60%	618	638	616	636	620	598	600
70%	643	652	648	652	643	619	625
80%	661	668	664	668	661	643	651
90%	676	676	676	676	676	668	672
95%	676	676	685	685	685	668	676
EP	685	685	685	722	685	722	705

Table 29

PROPERTIES OF VACUUM GAS OIL (650°F+)

PERIOD	262A	262B	262C1	262C2	262D	262E	260D
Elemental wt %							
C	87.53	88.41	87.64	87.52	88.54	88.56	88.30
H	10.41	10.58	10.49	10.29	10.50	10.17	10.27
N(ppm)	7641	4439	6982	6497	5899	7539	5800
S	0.05	0.01	0.02	0.02	0.01	0.02	0.03
O(dif)	1.25	0.56	1.15	1.52	0.46	0.50	0.82
Gravity (°API)	11.9	12.8	11.9	11.9	13.6	12.3	10.6
G.C. Sim. Dist., (°F)							
IBP	722	740	740	686	722	685	685
10%	722	740	740	686	722	694	685
20%	722	740	740	686	740	722	722
30%	722	751	751	696	753	740	722
40%	740	769	764	707	772	757	722
50%	740	769	770	713	789	767	722
60%	754	782	770	723	789	779	740
70%	754	801	781	736	813	779	754
80%	754	817	796	748	838	798	763
90%	775	838	796	760	852	817	787
95%	794	854	816	760	852	838	812
EP	898	937	877	833	910	878	905

Table 30

PHASE 3-4 CRITERIA
UNIT AND ELEMENTAL CLOSURE ERRORS
WT% MAF COAL

PERIODS ->	262A	262B	262C1	262C2	262D	262E	262F
CCR1 UNIT DATA							
CARBON	4.46±1.65	1.66±0.49	0.87±0.38	-0.86±0.29	0.30±1.36	0.24± 1.08	2.25± 2.59
HYDROGEN	-2.25±0.53	-1.53±0.18	-1.44±0.64	-1.36±0.08	-1.58±0.63	-1.15± 0.37	-0.74± 0.38
NITROGEN	0.04±0.09	-0.06±0.12	0.04±0.09	0.08±0.08	-0.11±0.13	-0.01± 0.04	-0.14± 0.10
SULFUR	0.06±0.41	0.36±0.28	0.28±0.01	0.79±0.07	0.38±0.12	0.28± 0.15	-0.28± 0.71
OXYGEN	-2.28±2.88	-2.90±1.74	-1.36±0.48	-2.51±0.53	-0.72±1.74	-1.38± 1.68	-0.46± 3.25
ASH	0.94±3.59	2.73±2.22	2.45±0.62	4.75±0.19	2.61±0.55	2.14± 1.27	0.18± 2.26
CCR2 UNIT DATA							
CARBON	-2.78±6.20	-7.71±6.16	9.57±5.17	10.02±1.10	-2.71±4.32	-2.16±10.88	-2.00±10.37
HYDROGEN	-0.59±0.47	-0.19±0.70	1.80±0.64	1.76±0.42	0.39±0.62	1.08± 0.81	0.67± 0.85
NITROGEN	-0.31±0.13	-0.36±0.13	-0.30±0.01	-0.21±0.09	-0.19±0.13	-0.21± 0.15	0.17± 0.21
SULFUR	-0.73±0.62	-0.83±0.13	-0.23±0.03	-0.21±0.71	-0.53±0.25	-0.24± 0.13	0.45± 0.64
OXYGEN	-1.39±3.63	0.00±1.92	1.60±2.54	1.48±1.43	1.54±2.11	0.99± 1.81	1.26± 3.63
ASH	-1.42±5.18	-3.00±2.09	-3.27±0.51	-4.09±0.71	-3.58±1.32	-2.91± 0.84	0.15± 3.63
ROSE-SR UNIT DATA							
CARBON	-0.15±0.51	0.04±0.09	-0.53±0.18	-0.10±0.94	-0.48±0.23	-0.36± 0.51	-0.32± 0.64
HYDROGEN	-0.08±0.09	-0.14±0.07	-0.13±0.08	-0.07±0.08	-0.16±0.04	-0.11± 0.05	-0.05± 0.04
NITROGEN	0.01±0.01	0.02±0.01	0.01±0.00	0.02±0.02	0.03±0.05	0.02± 0.01	-0.01± 0.02
SULFUR	-0.09±0.09	-0.19±0.11	-0.09±0.03	-0.33±0.35	-0.01±0.05	-0.03± 0.02	-0.02± 0.03
OXYGEN	0.53±0.19	0.31±0.04	-0.17±0.57	0.25±0.06	0.13±0.18	0.40± 0.14	0.37± 0.20
ASH	-0.46±0.86	-0.04±0.13	0.20±0.22	0.01±0.38	0.23±0.41	-0.27± 0.24	0.42± 0.27
TOTALED DATA							
CARBON	1.53±5.62	-6.00±6.45	9.91±5.72	9.06±2.33	-2.89±4.32	-2.28±10.97	-0.07±12.45
HYDROGEN	-2.93±0.57	-1.86±0.58	0.24±0.08	0.33±0.26	-1.35±0.43	-0.19± 0.57	-0.11± 1.06
NITROGEN	-0.27±0.07	-0.40±0.06	-0.25±0.08	-0.11±0.03	-0.27±0.08	-0.20± 0.13	0.03± 0.16
SULFUR	-0.77±0.29	-0.66±0.18	-0.03±0.01	0.25±0.28	-0.16±0.26	0.02± 0.09	0.15± 0.54
OXYGEN	-3.13±0.60	-2.59±0.56	0.07±1.49	-0.78±0.96	0.95±0.84	0.01± 0.27	1.17± 0.64
ASH	-0.94±2.00	-0.31±0.37	-0.62±0.33	0.67±0.52	-0.74±1.05	-1.04± 1.82	0.75± 2.28
ABSOLUTE SUM DATA							
CARBON	10.24±3.96	9.43±5.91	10.97±5.36	11.55±0.67	5.77±1.74	11.03± 1.73	9.56± 6.31
HYDROGEN	2.94±0.57	2.24±0.40	3.36±1.19	3.19±0.58	2.24±1.03	2.35± 1.11	1.75± 0.32
NITROGEN	0.40±0.17	0.47±0.11	0.38±0.07	0.31±0.15	0.37±0.05	0.26± 0.17	0.36± 0.24
SULFUR	1.12±0.83	1.39±0.45	0.60±0.02	1.62±0.01	0.95±0.26	0.55± 0.25	1.25± 0.52
OXYGEN	6.08±2.71	4.59±1.43	3.56±2.98	4.23±2.01	3.43±2.53	3.36± 2.93	6.03± 2.92
ASH	8.26±3.38	5.84±4.32	5.92±1.35	9.10±0.53	6.58±1.85	5.33± 1.47	5.07± 1.29

NOTES: (a) Closure error sign convention is that losses are negative. (b) Total is the arithmetic sum of the individual unit errors.

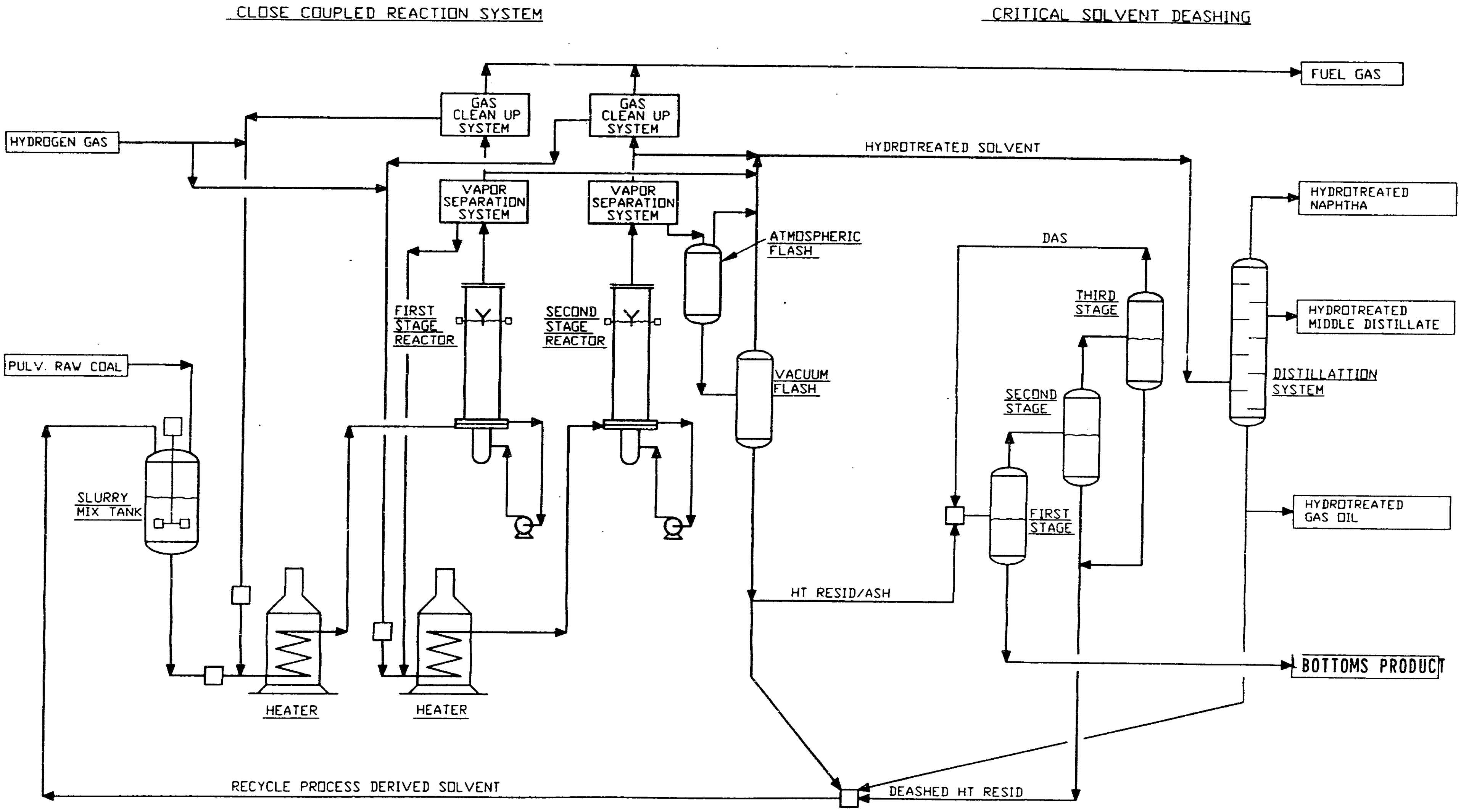
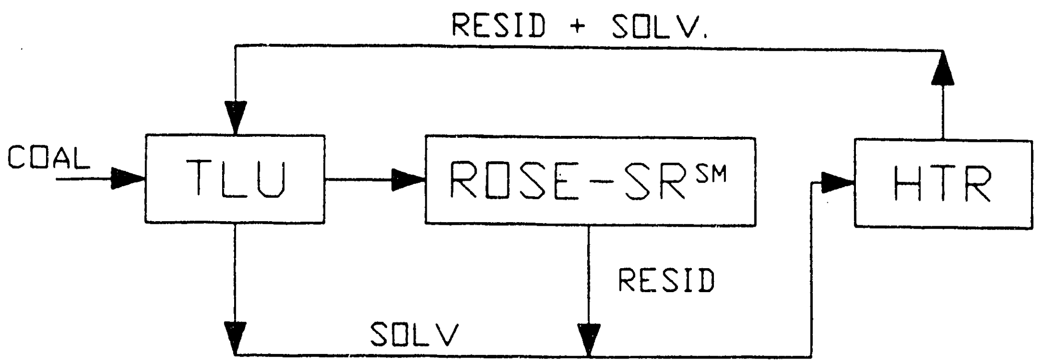
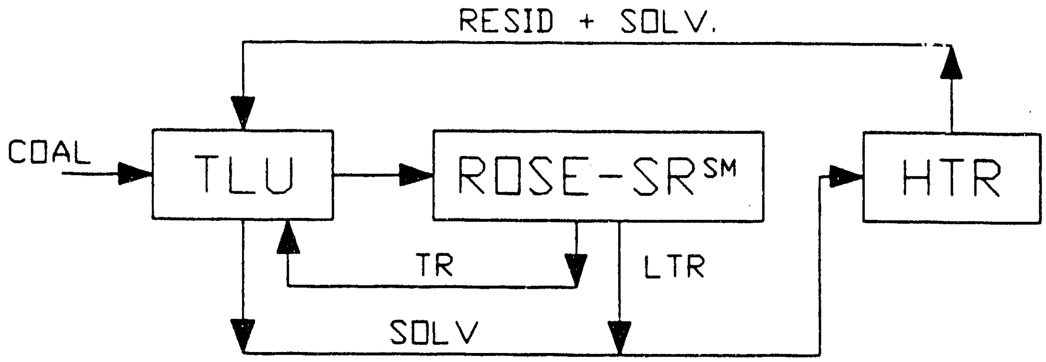


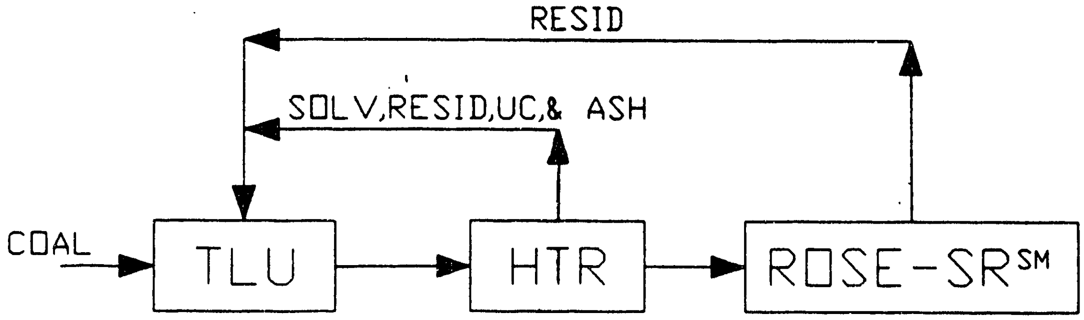
FIGURE 1. SIMPLIFIED FLOW DIAGRAM OF THE CLOSE-COUPLED ITSL COAL LIQUEFACTION SYSTEM WITH INTERSTAGE SEPARATION



INTEGRATED TWO-STAGE LIQUEFACTION

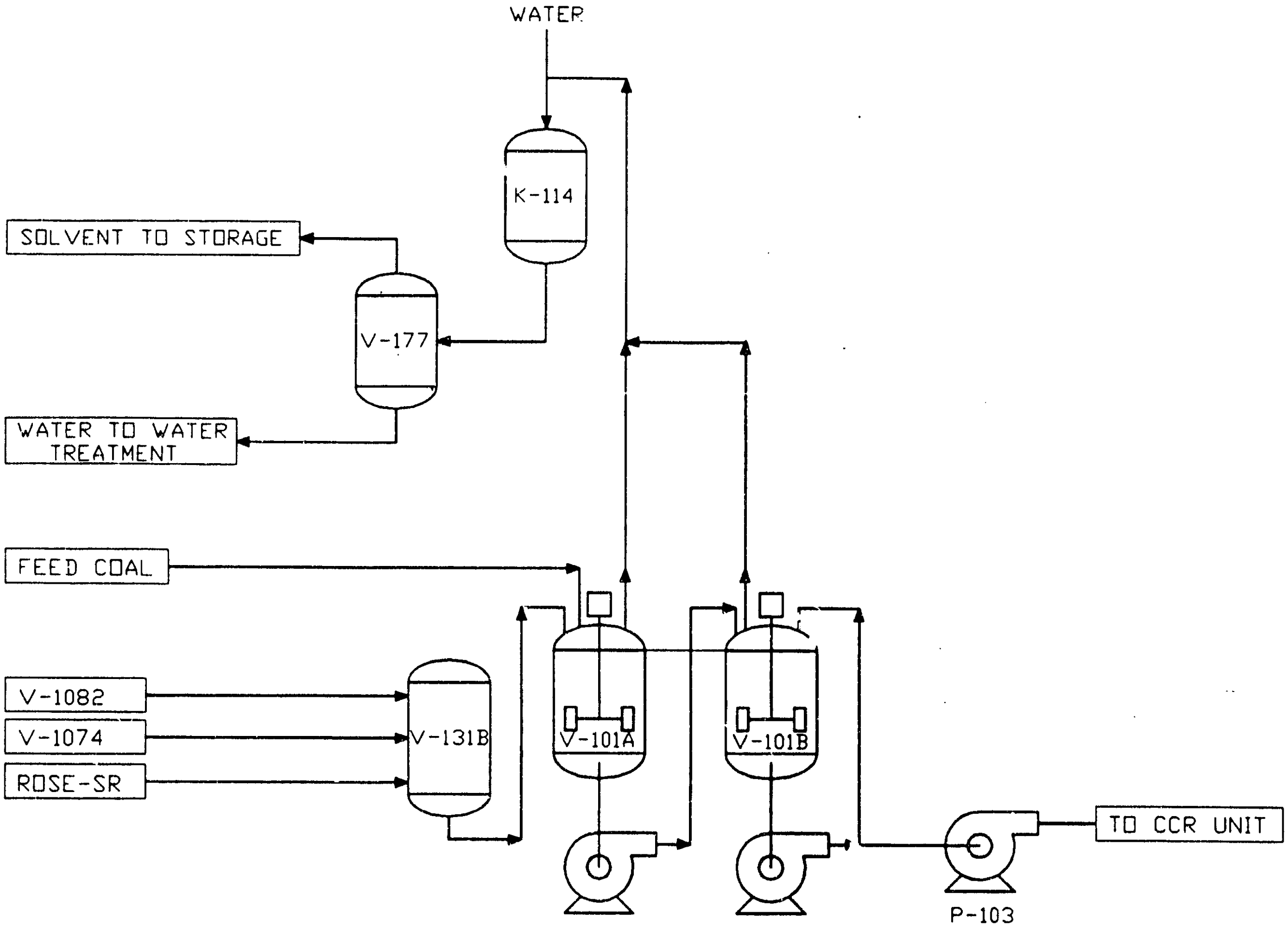


DOUBLE INTEGRATED TWO-STAGE LIQUEFACTION



CLOSE-COUPLED INTEGRATED TWO-STAGE LIQUEFACTION

FIGURE 2. LIQUEFACTION MODES TESTED SINCE RUN 242



V101A	SLURRY BLEND TANK
V101B	FEED TANK
V131B	RECYCLE PROCESS SOLVENT TANK
P103	HIGH PRESSURE FEED PUMP
K-114	WATER CONTACT SCRUBBER
V-177	SETTLING TANK

FIGURE 3. FLOW DIAGRAM OF COAL SLURRY PREPARATION SYSTEM

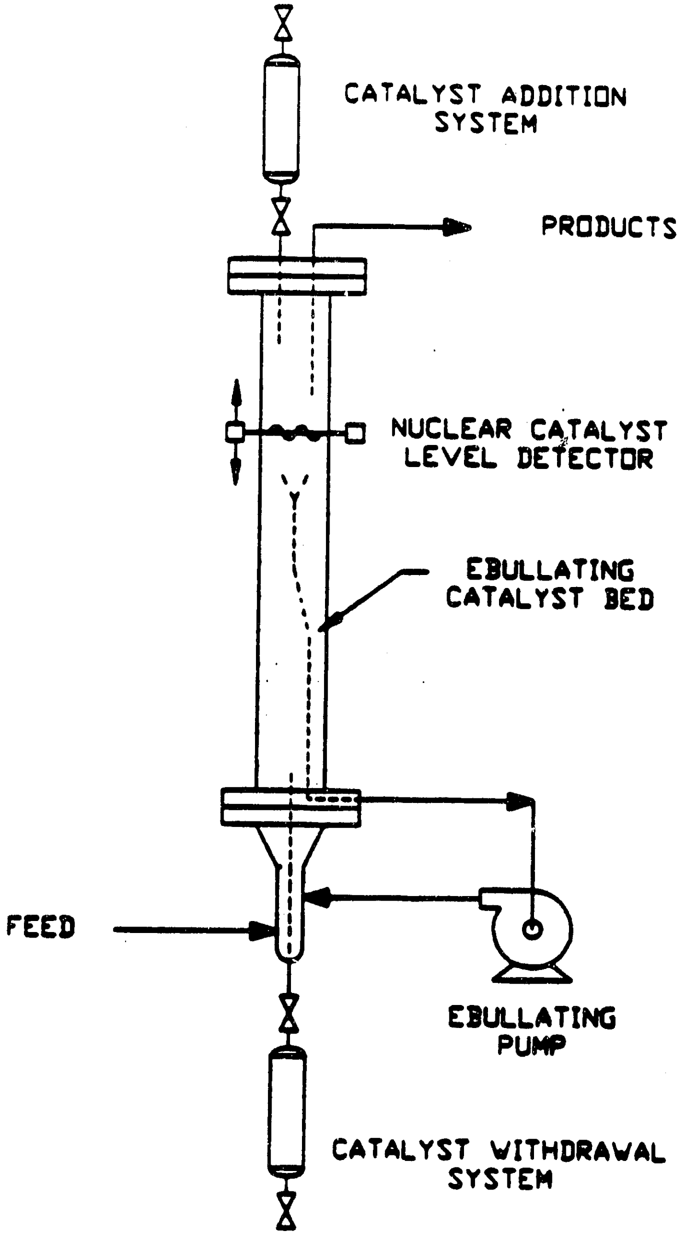


FIGURE 4. H-OIL® EBULLATED BED REACTOR

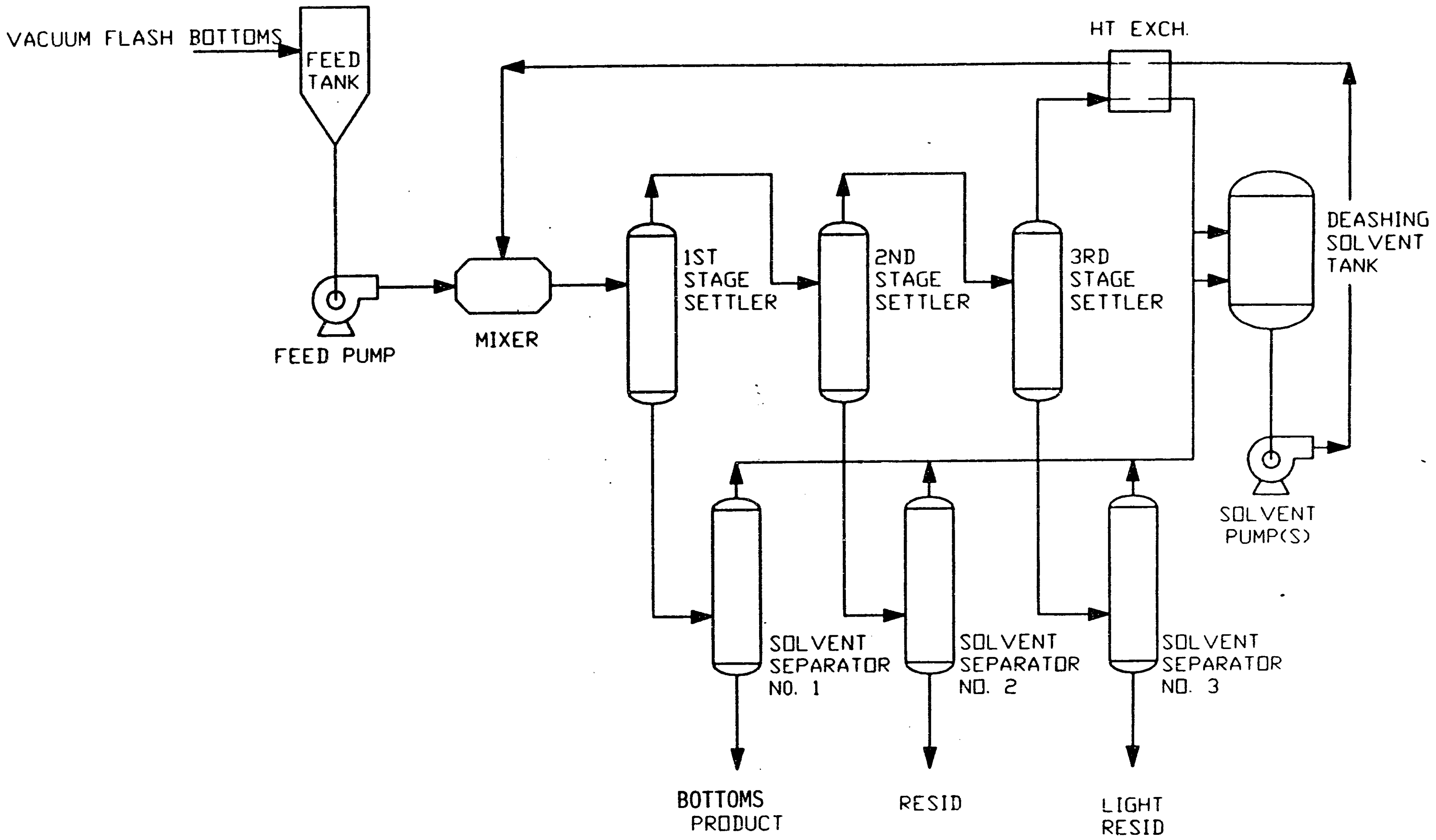


FIGURE 5. FLOW DIAGRAM OF THE RESIDUUM OIL SUPERCRITICAL EXTRACTION - SOLIDS REJECTION UNIT

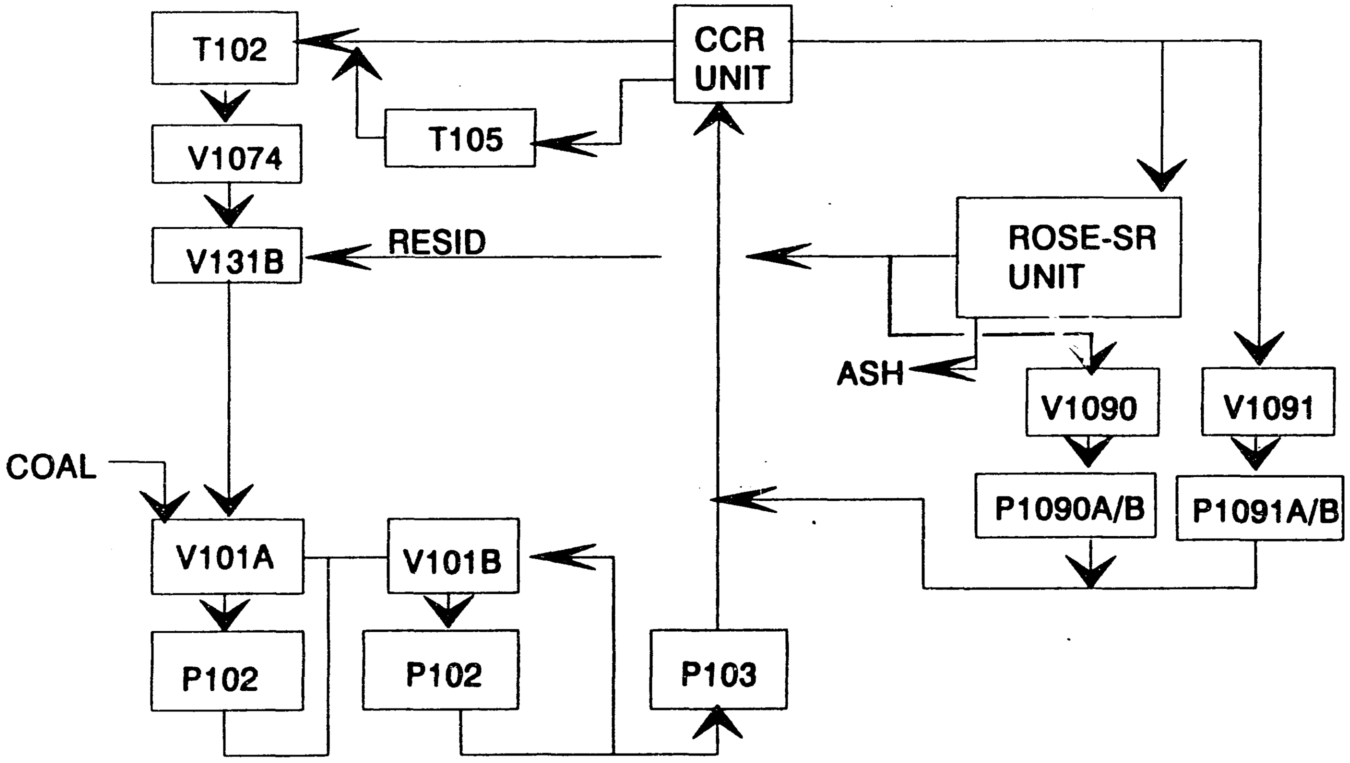


FIGURE 6. SIMPLIFIED FLOW CHART OF STREAMS DURING RESID INJECTION

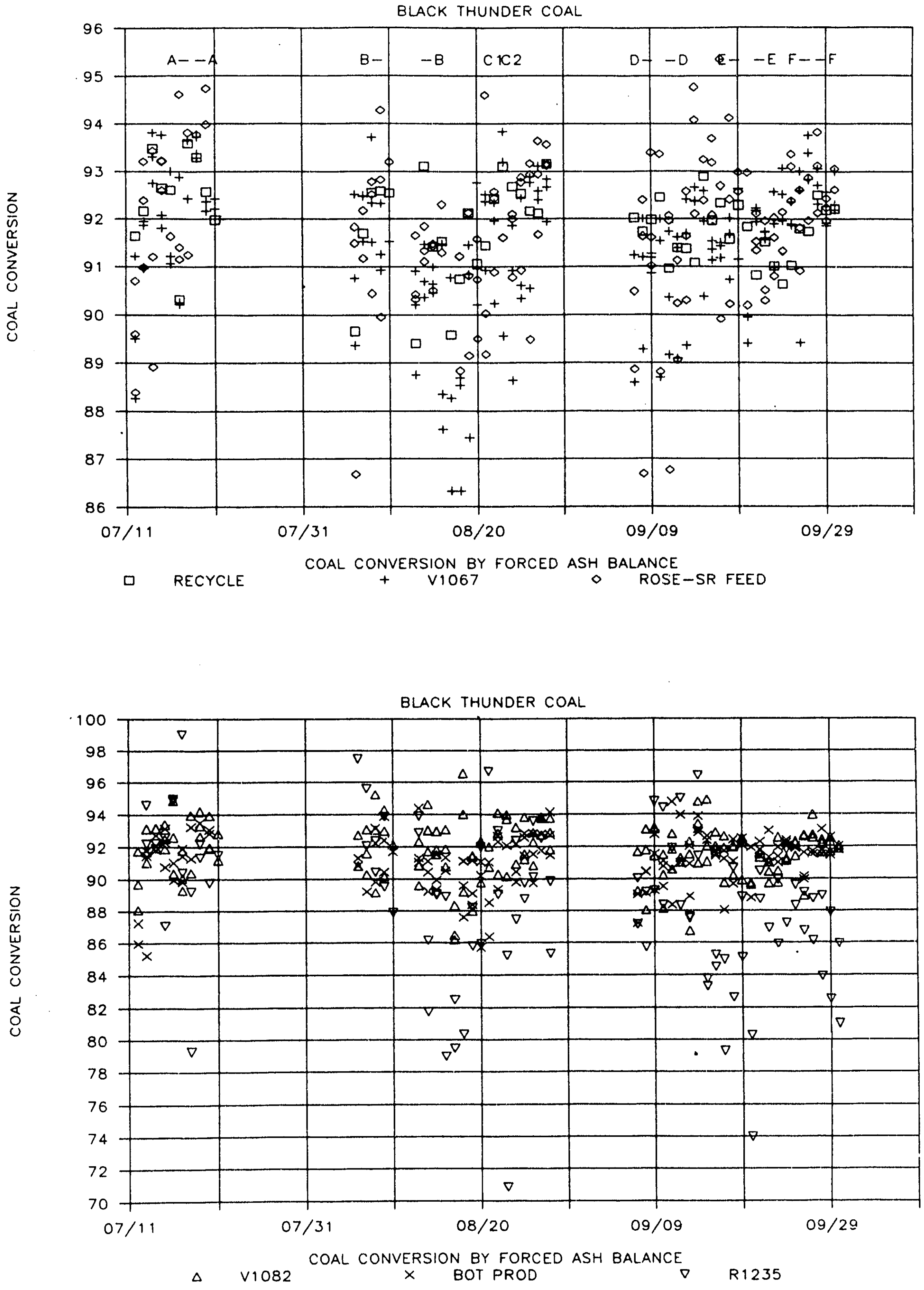


FIGURE 7. COAL CONVERSION BY FORCED ASH BALANCE

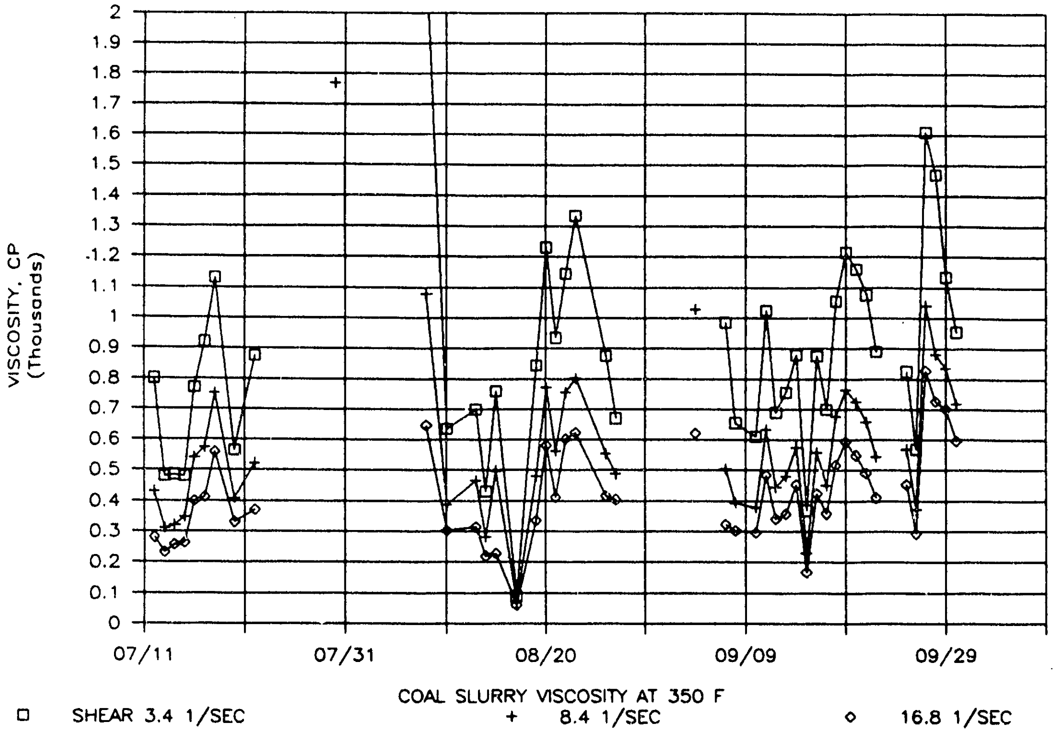


FIGURE 8. COAL SLURRY VISCOSITY

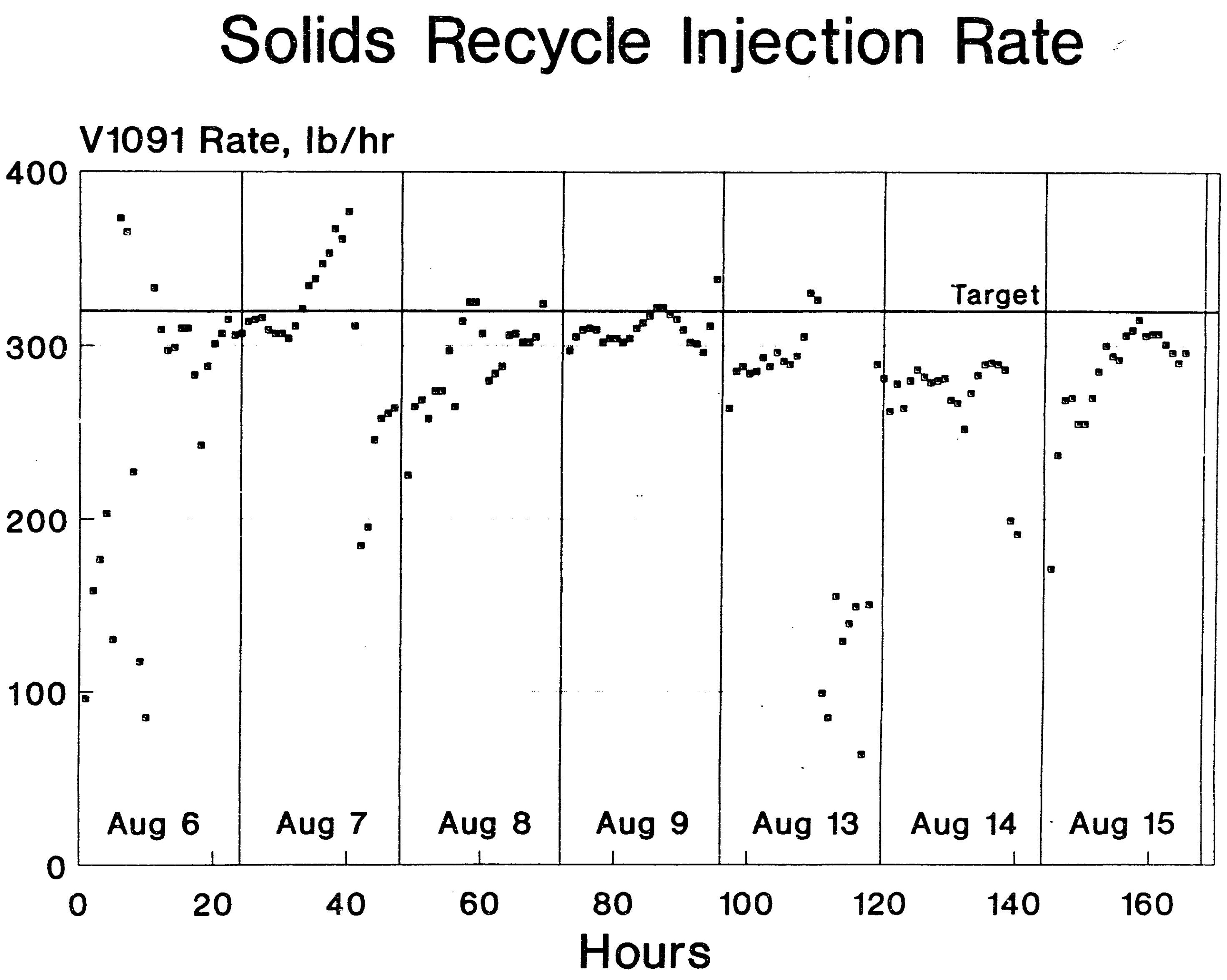


FIGURE 9. SOLIDS RECYCLE INJECTION RATE USING THE RESID CIRCULATION SYSTEM FOR AUGUST 6-15, 1991

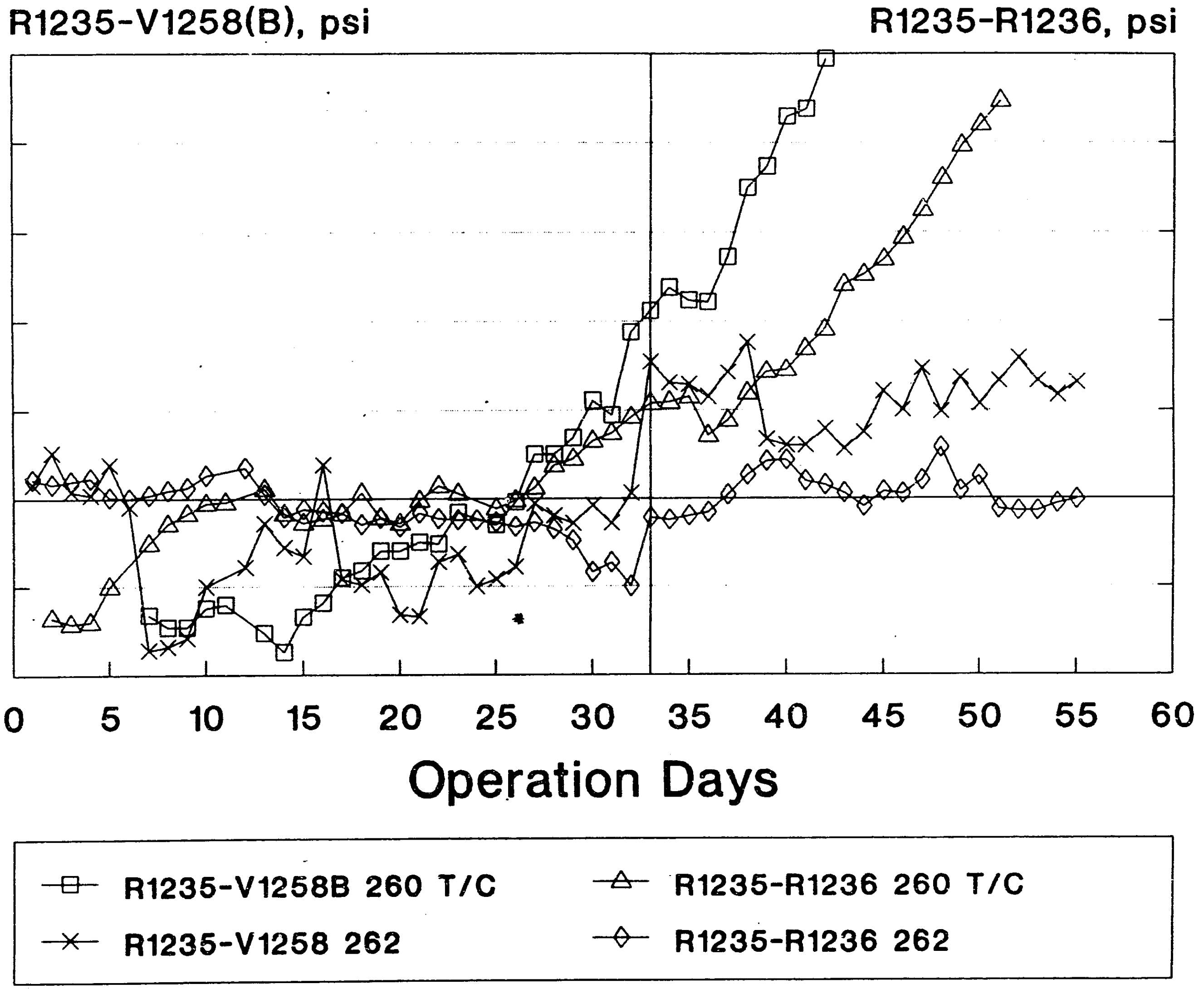


FIGURE 10. PRESSURE DROP BETWEEN FIRST REACTOR AND INTERSTAGE SEPARATOR AND BETWEEN THE REACTORS FOR RUNS 260 AND 262.
RUN 262 CONTINUED AFTER A SHUTDOWN FOLLOWING OPERATING DAY 32.

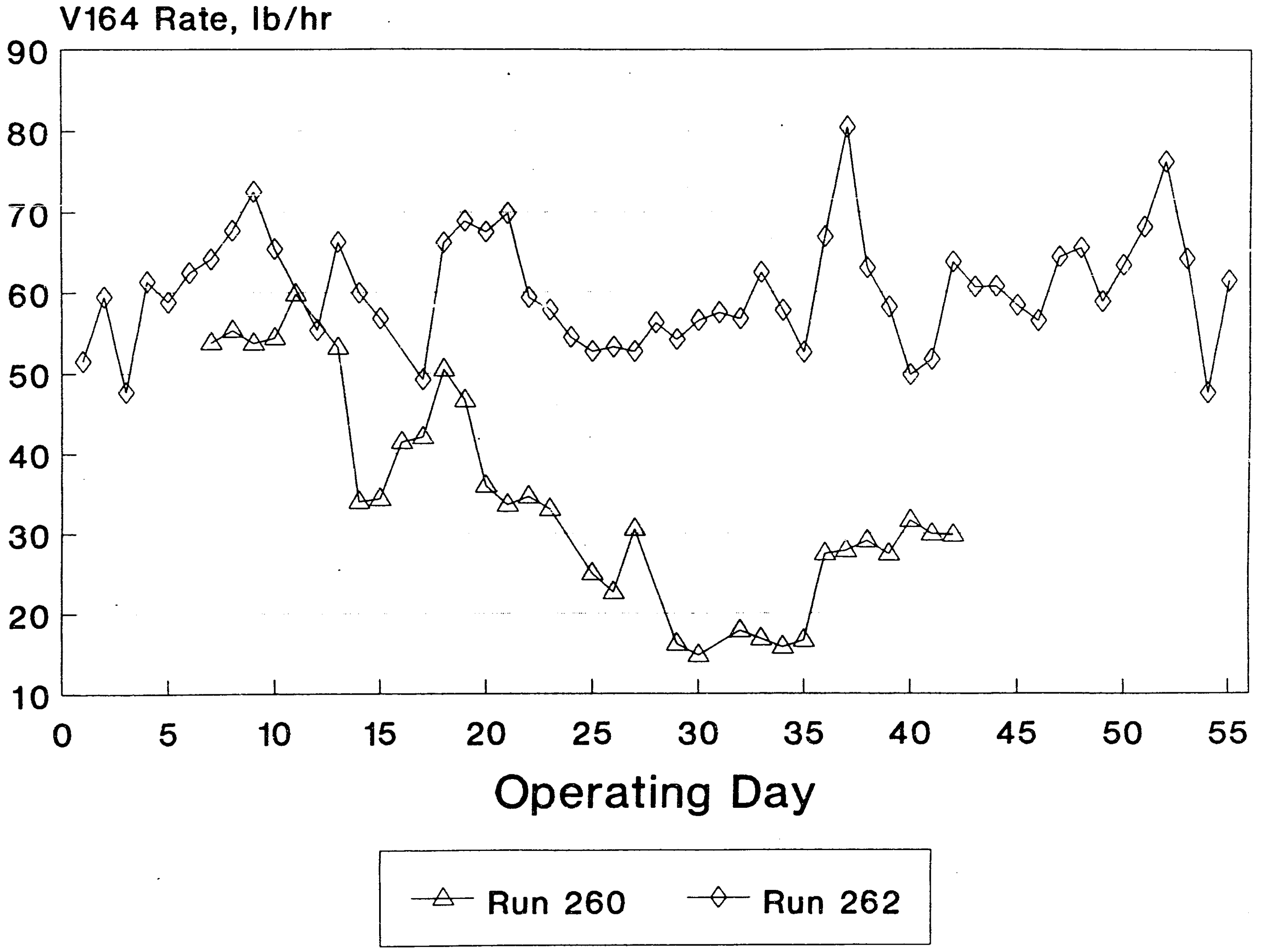


FIGURE 11. COMPARISON OF V164 FLOW RATE (V1258 OVERHEADS) FOR RUN 260AB AND RUN 262

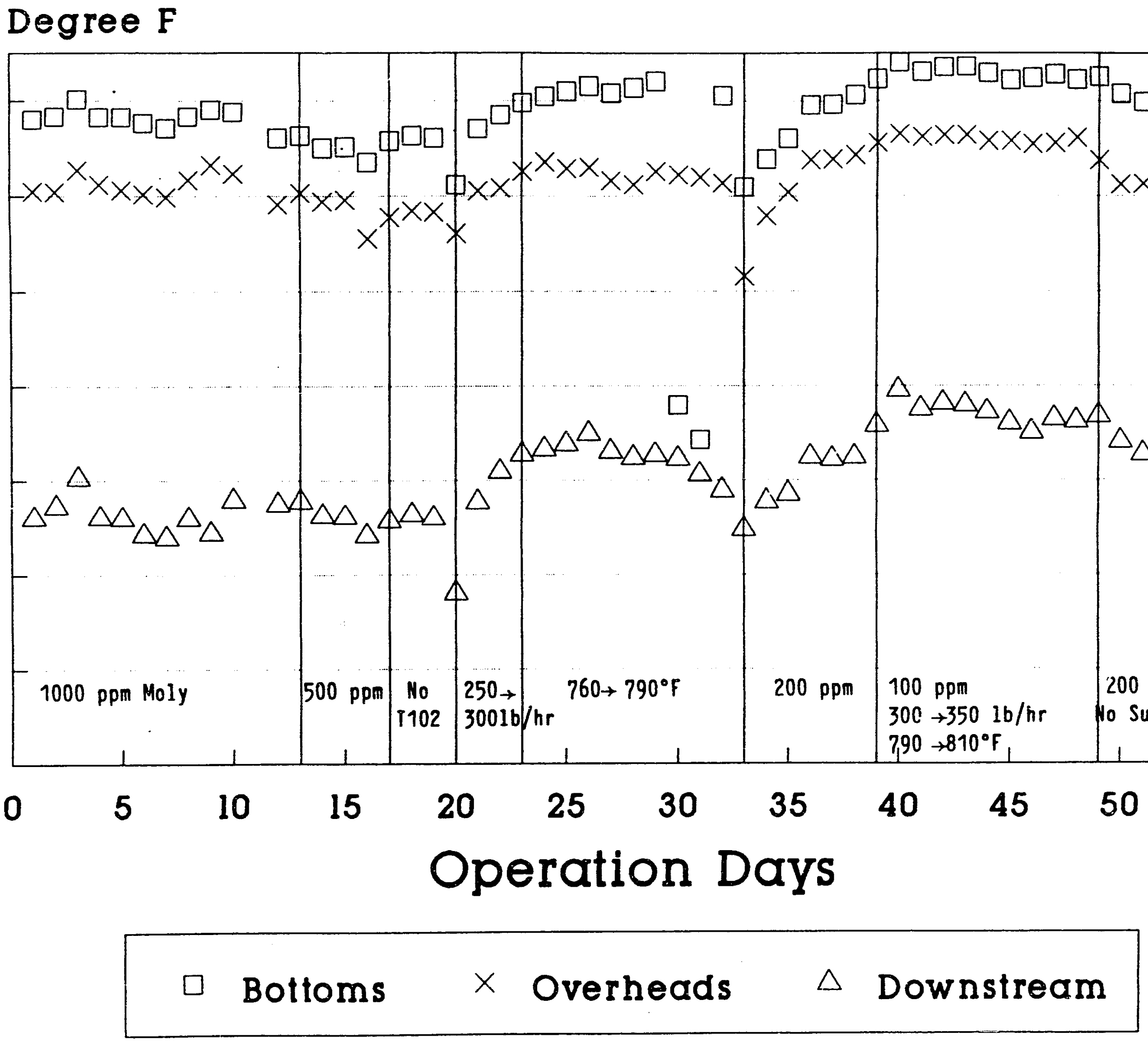


FIGURE 12. V1258 TEMPERATURES

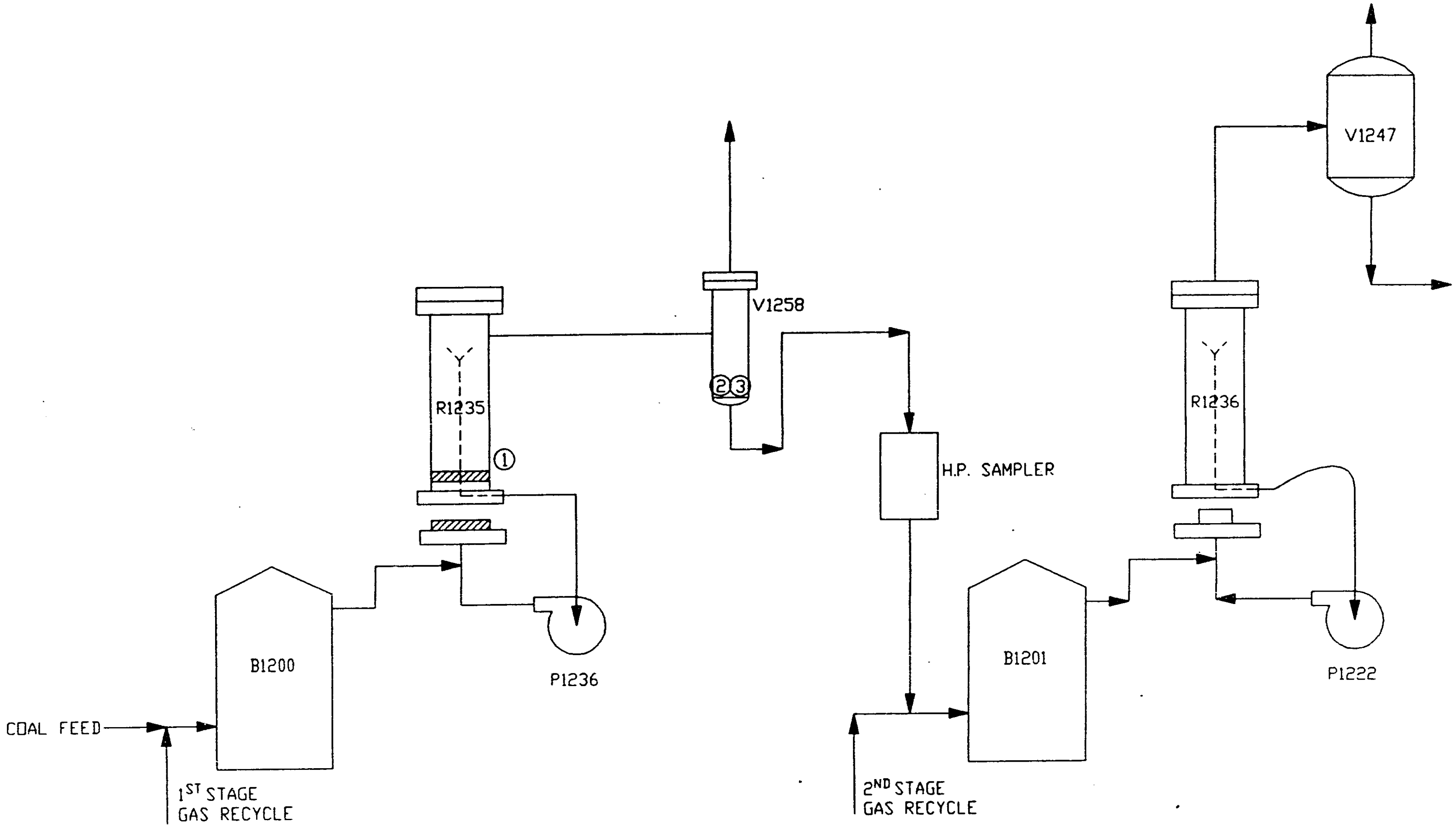


FIGURE 13. LOCATION OF SOLID DEPOSIT SAMPLES FROM END OF RUN 262
ANALYSES IS GIVEN IN TABLE 4

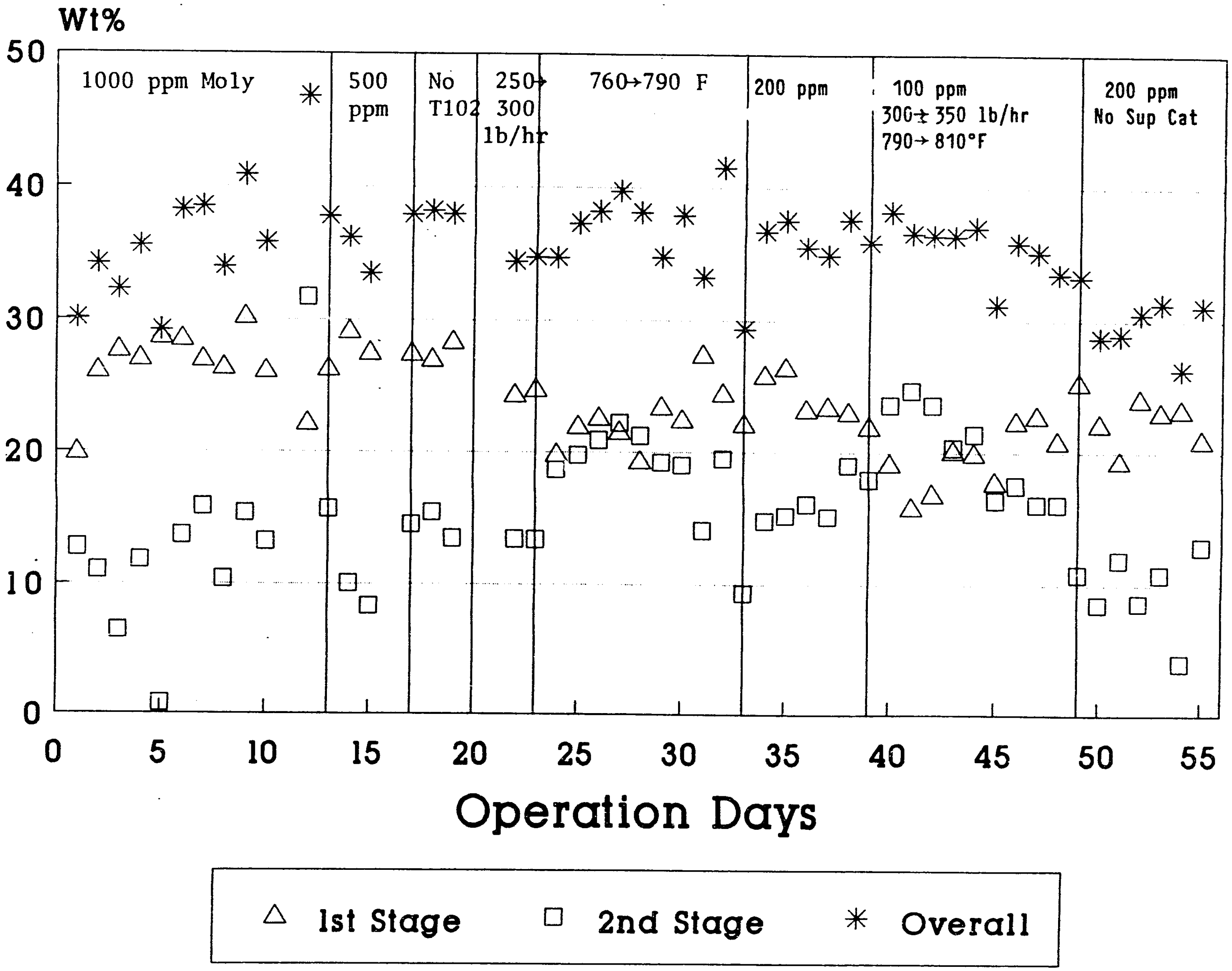


FIGURE 14. RESID + UC CONVERSION

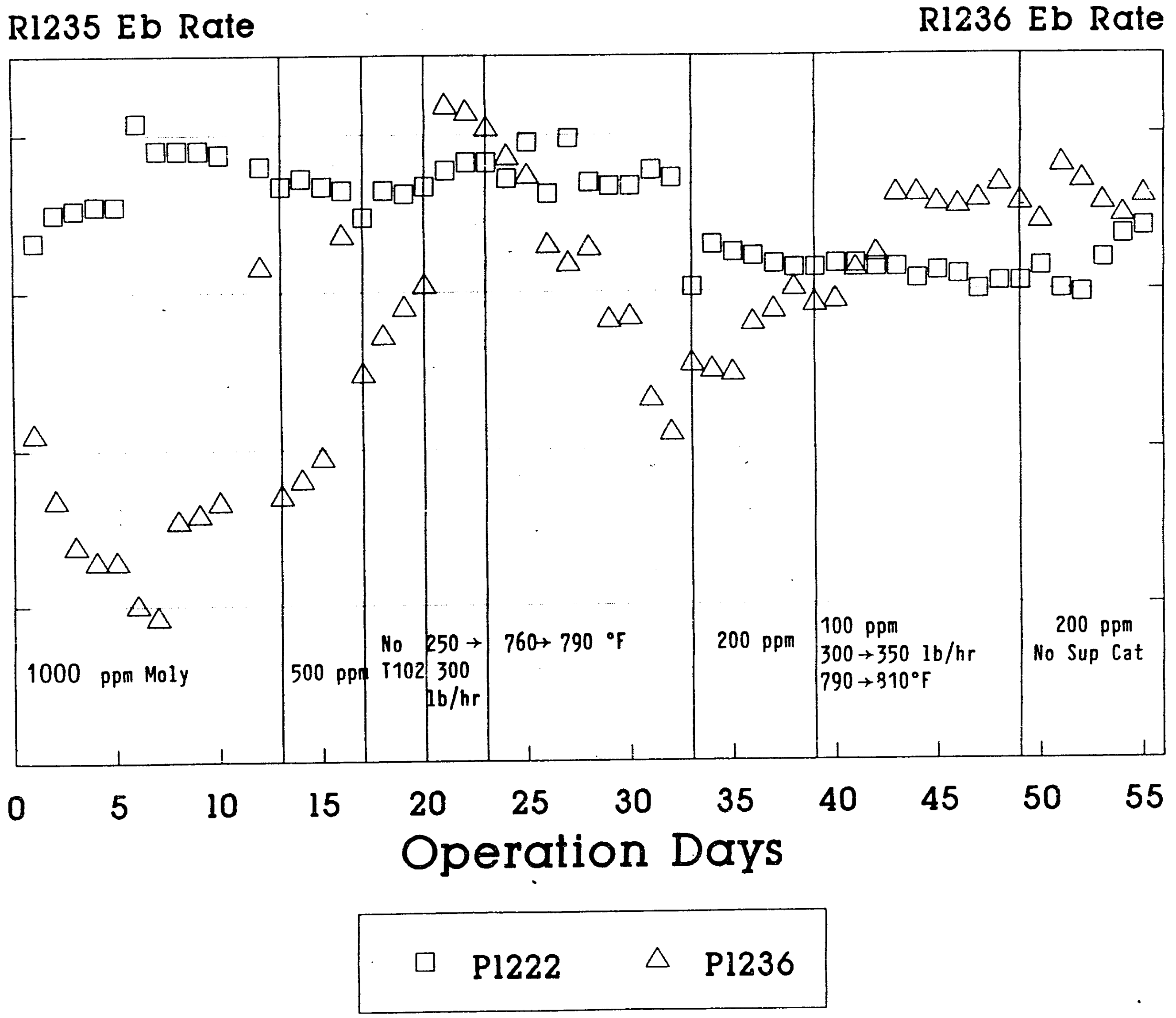


FIGURE 15. FIRST (P1222) AND SECOND STAGE (P1236) EBULLATION RATE

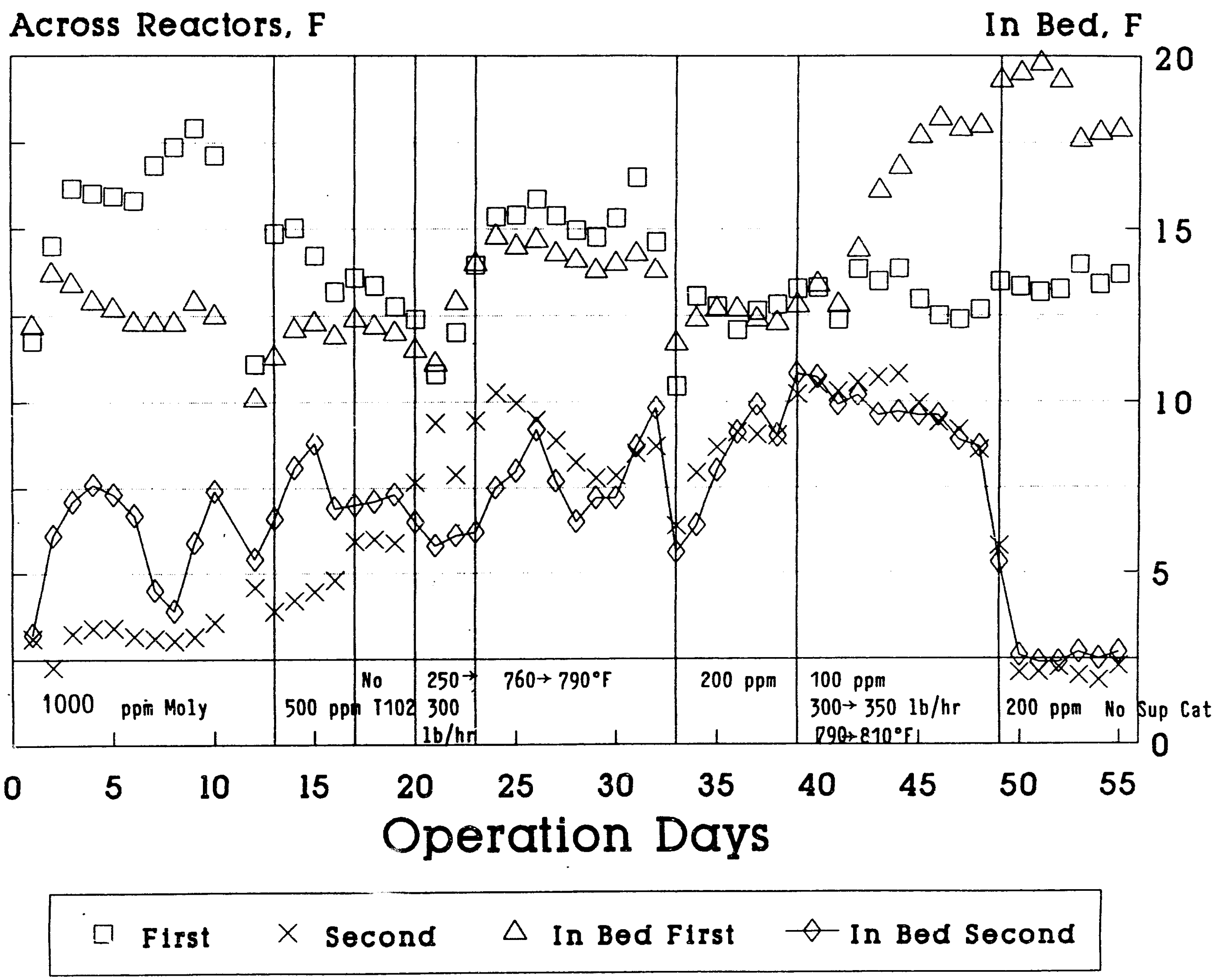
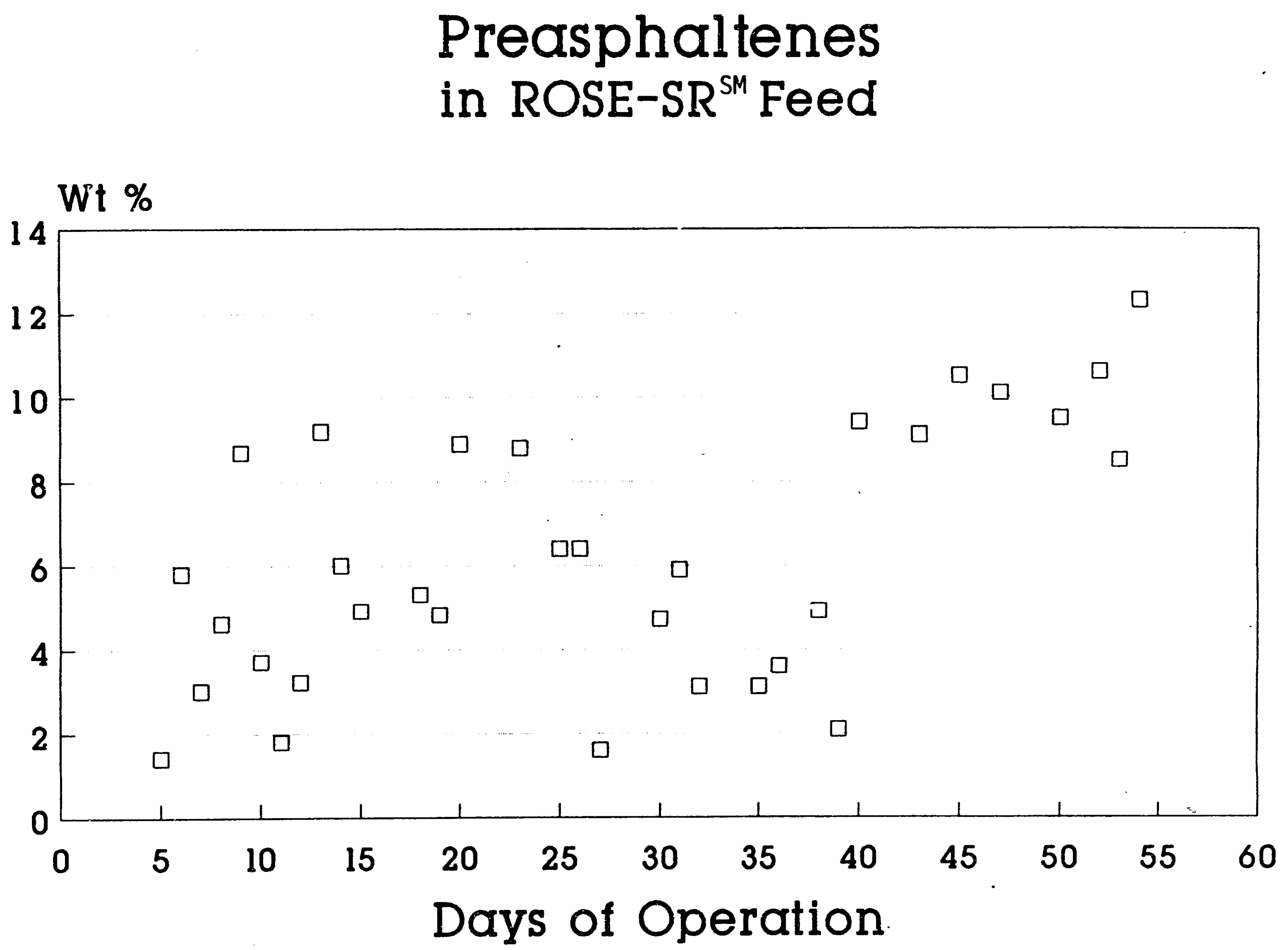
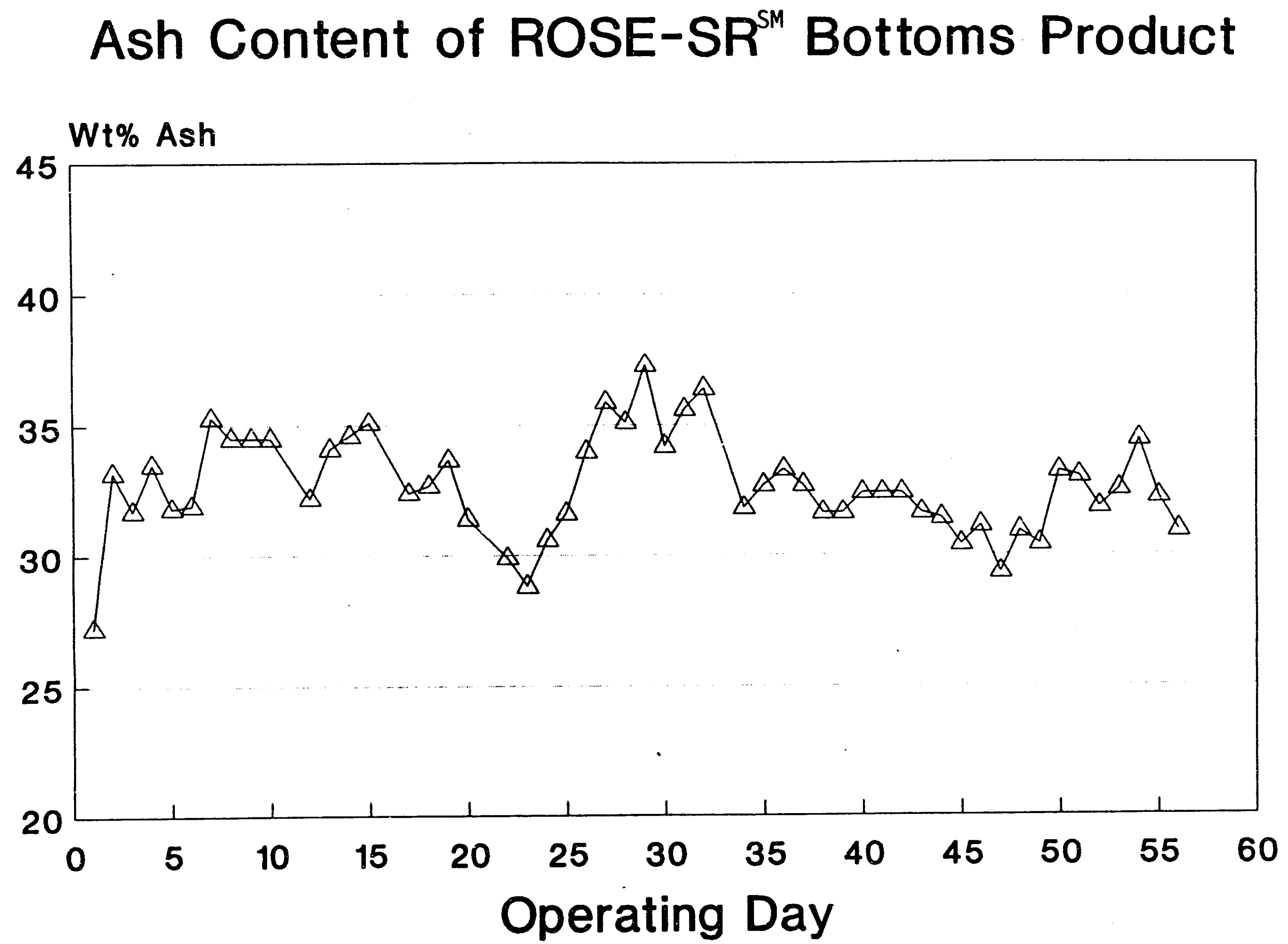


FIGURE 16. FIRST AND SECOND STAGE TEMPERATURE RISES ACROSS THE REACTOR AND IN THE BED



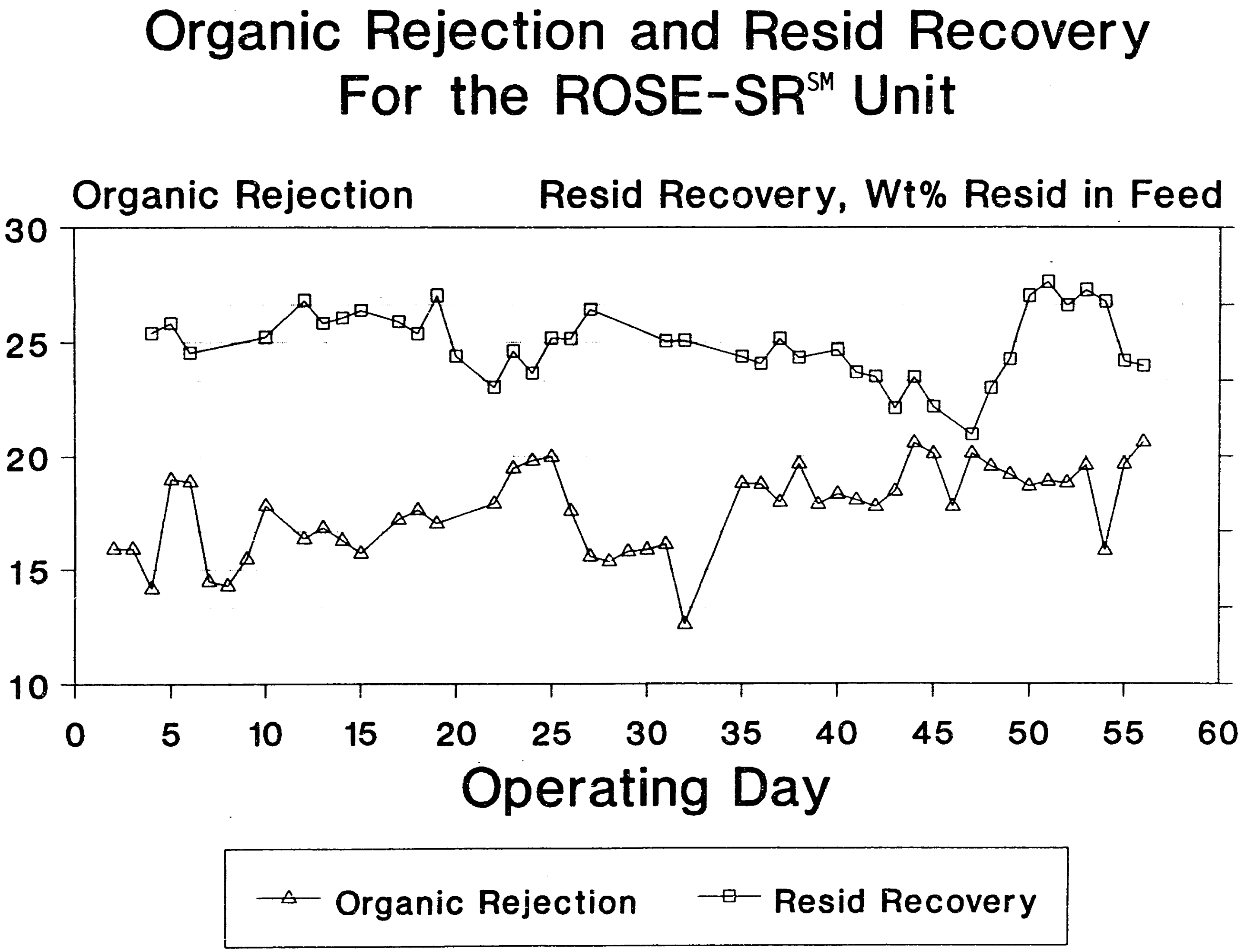
Day 1 = 7/12/91; Day 30 = 8/26/91
Day 10 = 7/22/91; Day 40 = 9/13/91
Day 20 = 8/16/91; Day 50 = 9/26/91

FIGURE 17. PREASPHALTENE CONTENT IN THE ROSE-SR^{SM} FEED



Day 1 ▪ 7/12/91; Day 30 ▪ 8/26/91
Day 10 ▪ 7/22/91; Day 40 ▪ 9/13/91
Day 20 ▪ 8/16/91; Day 50 ▪ 9/23/91

FIGURE 18. ASH CONTENT IN THE ROSE-SR^{SM} BOTTOMS SOLID PRODUCT



Day 1 = 7/12/91; Day 30 = 8/26/91
Day 10 = 7/22/91; Day 40 = 9/13/91
Day 20 = 8/16/91; Day 50 = 9/23/91

FIGURE 19. ORGANIC REJECTION AND RESID RECOVERY FOR THE ROSE-SR^{SM} UNIT

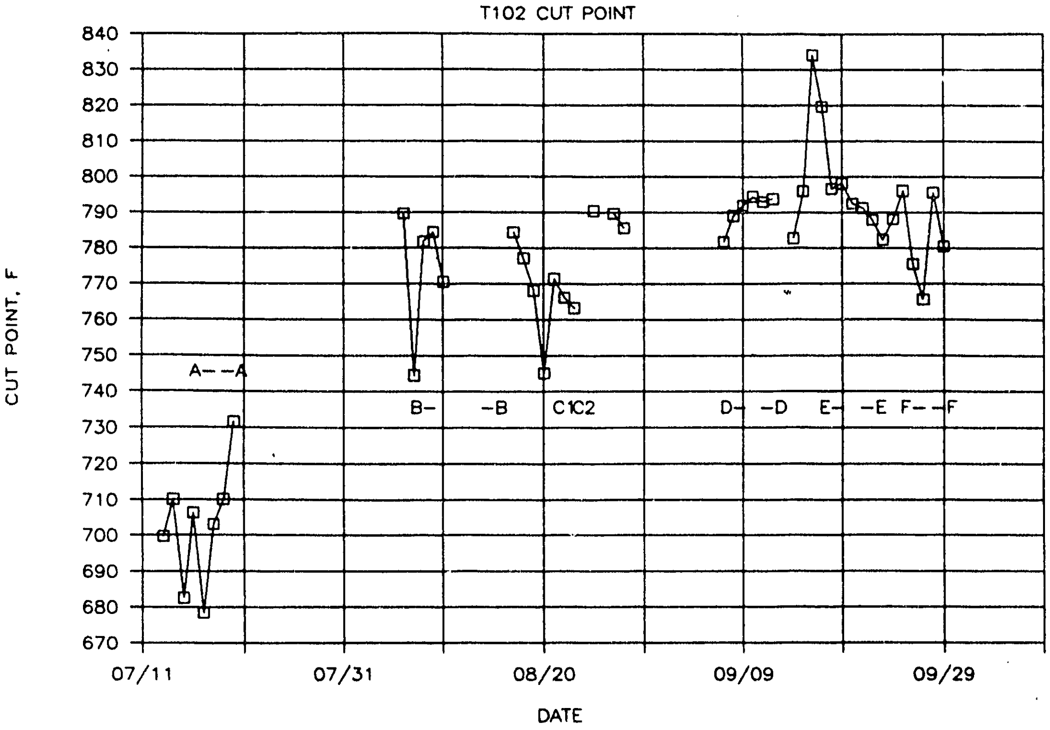


FIGURE 20. T102 VACUUM COLUMN CUT POINT BY GC

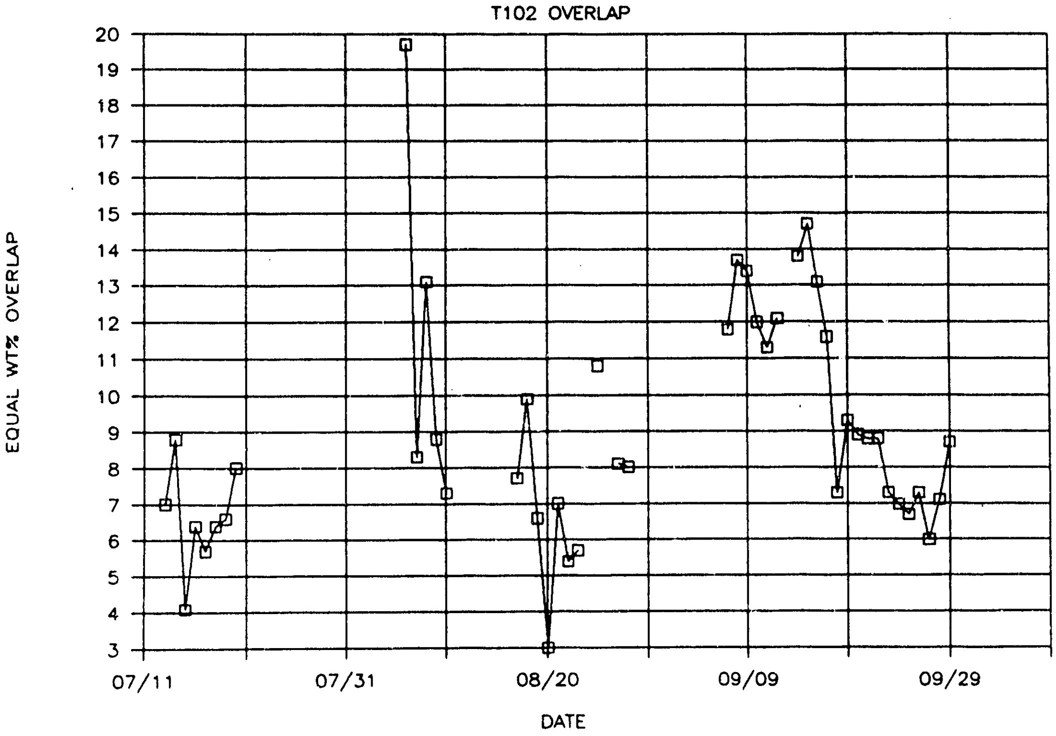


FIGURE 21. T102 VACUUM COLUMN OVERLAP BETWEEN OVERHEADS AND BOTTOMS

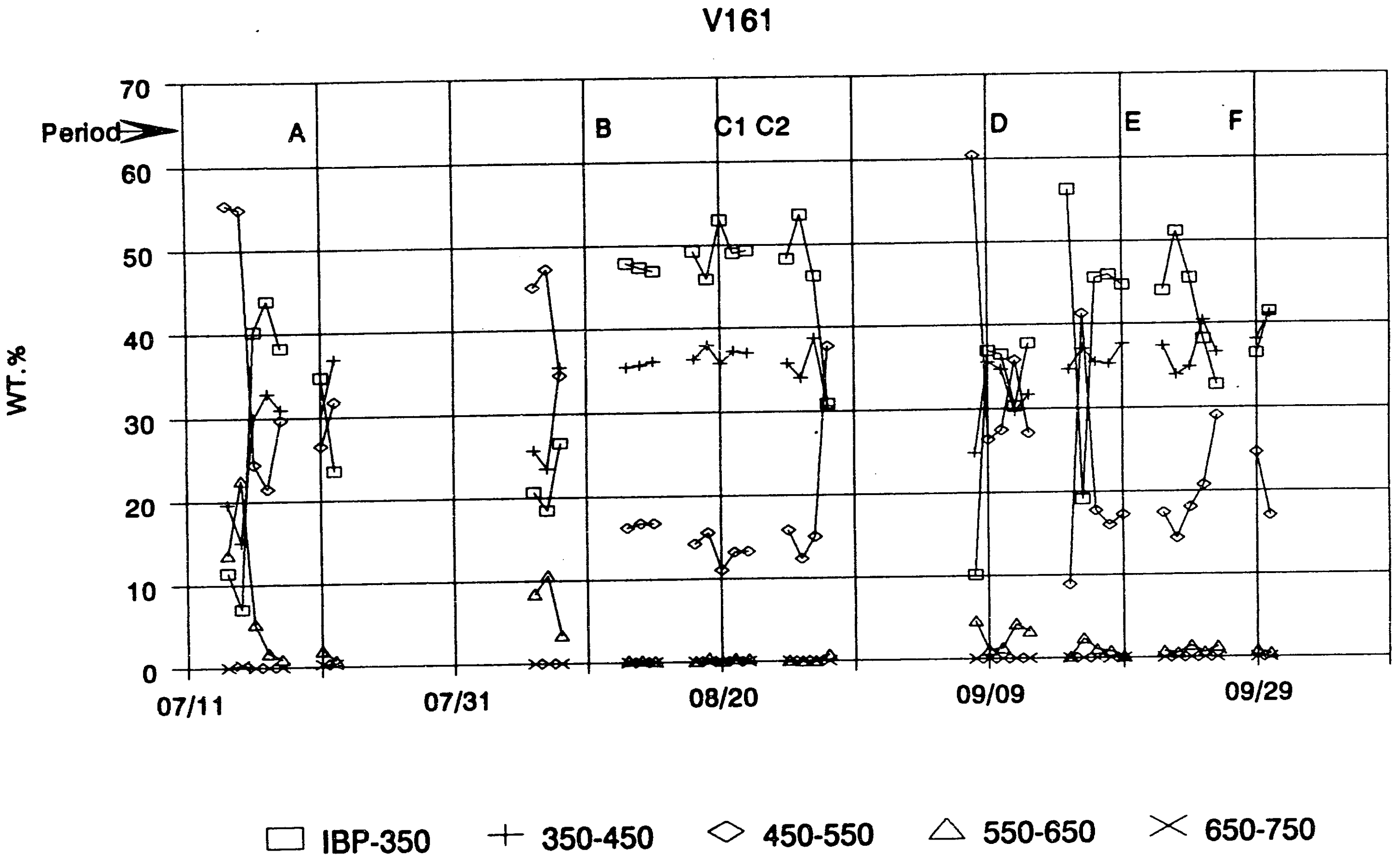


FIGURE 22. T105 OVERHEADS DISTRIBUTION

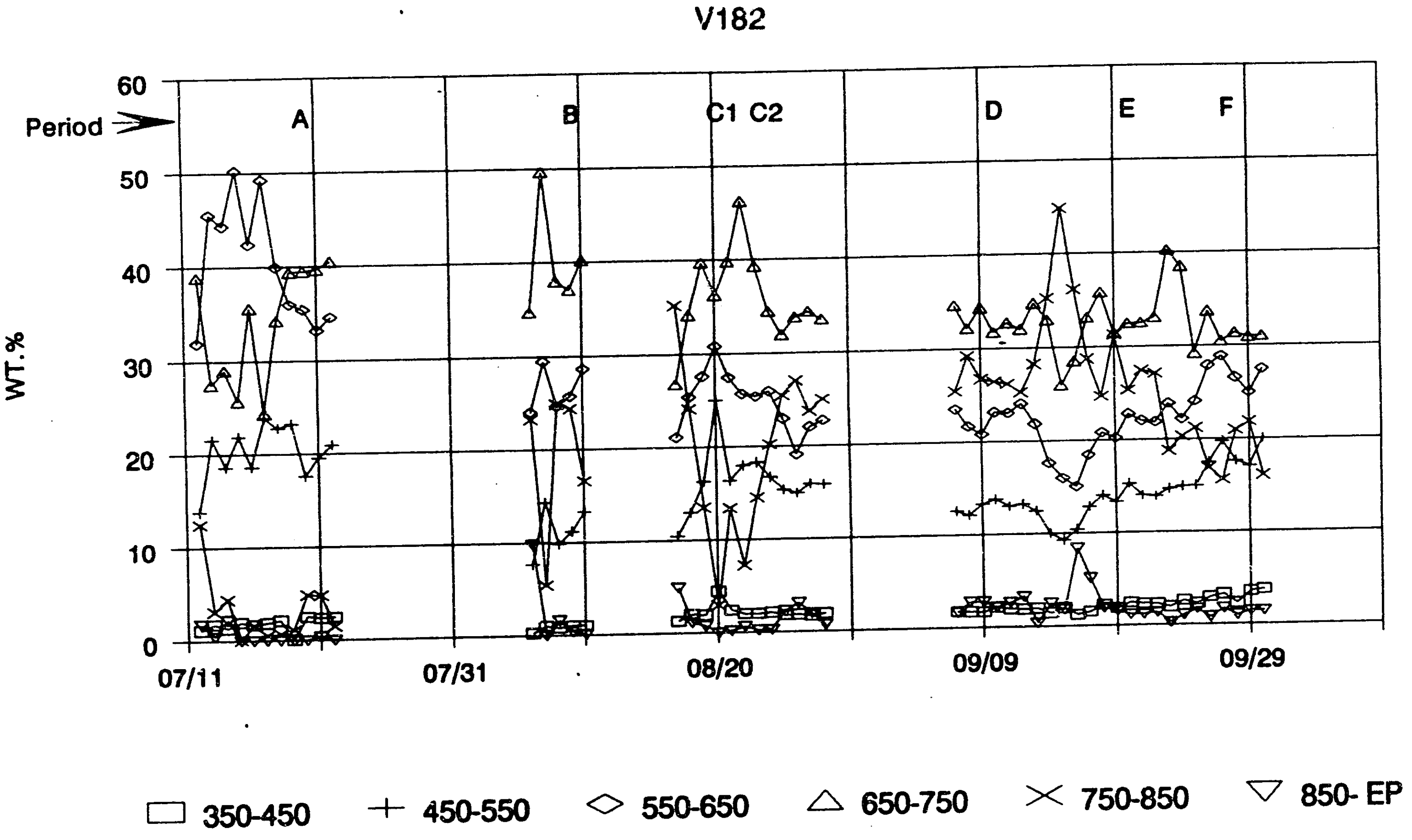


FIGURE 23. T102 OVERHEADS DISTRIBUTION

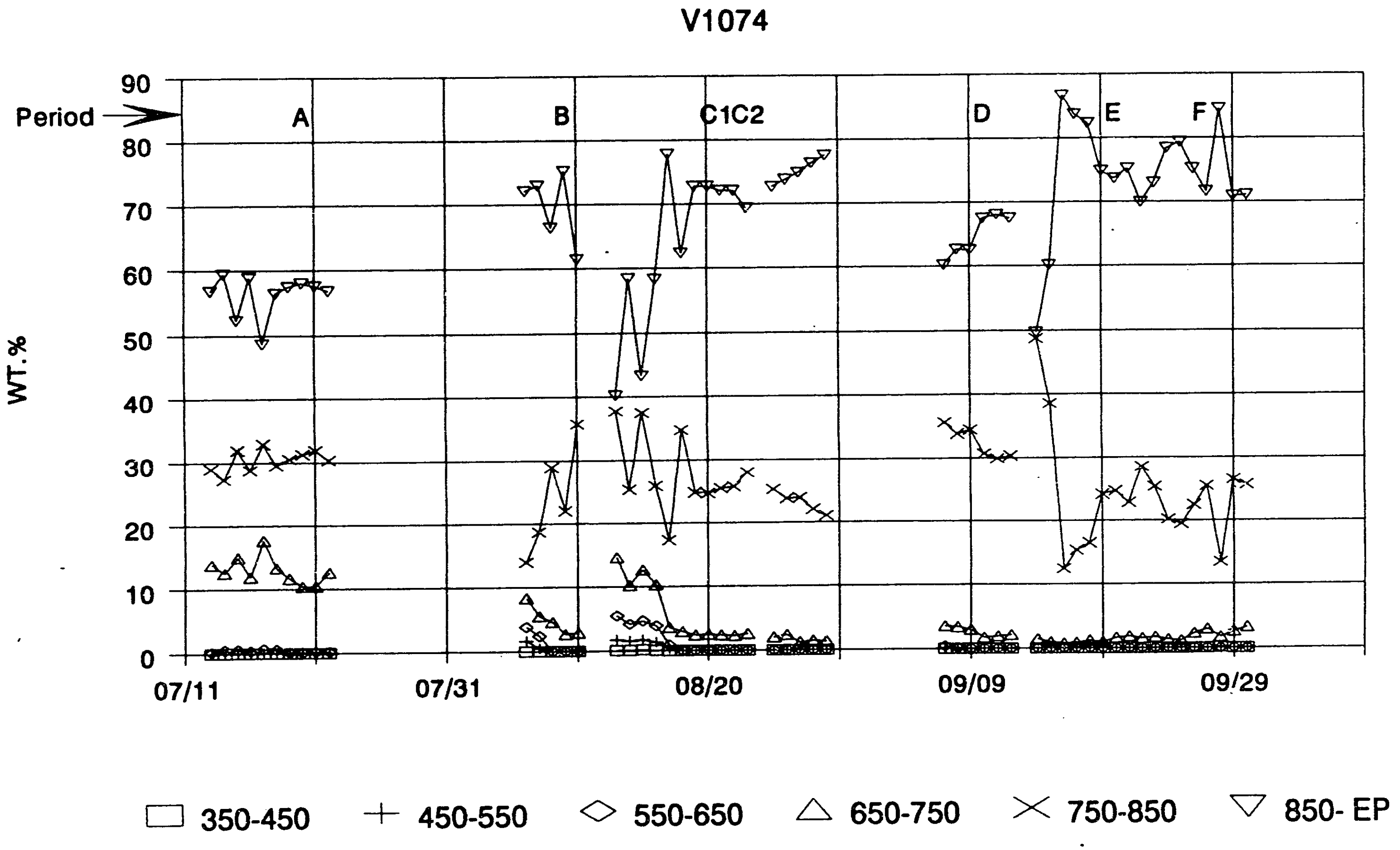


FIGURE 24. T012 BOTTOMS DISTRIBUTION

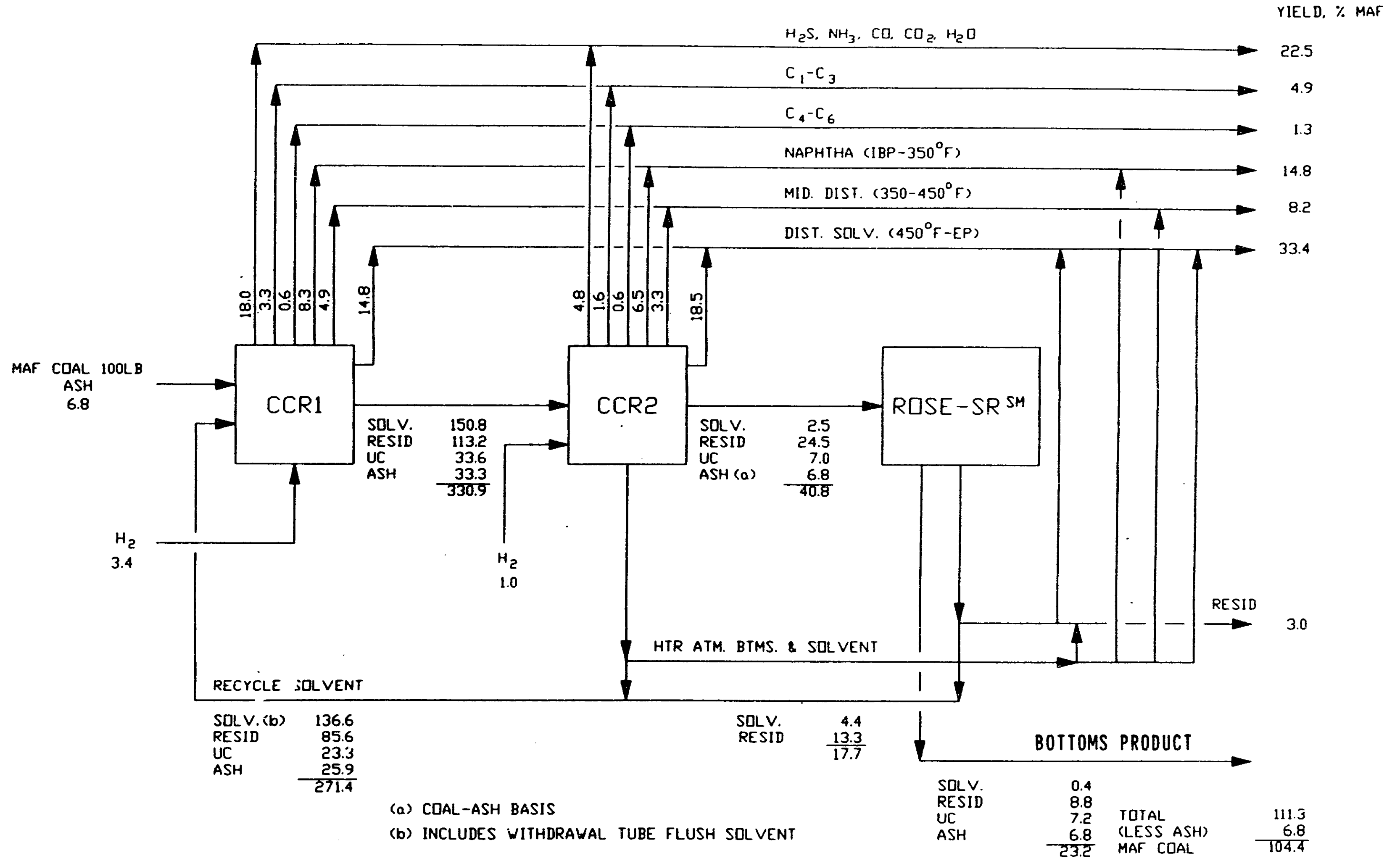


FIGURE 25. MATERIAL BALANCE FLOW DIAGRAM FOR PERIOD 262A

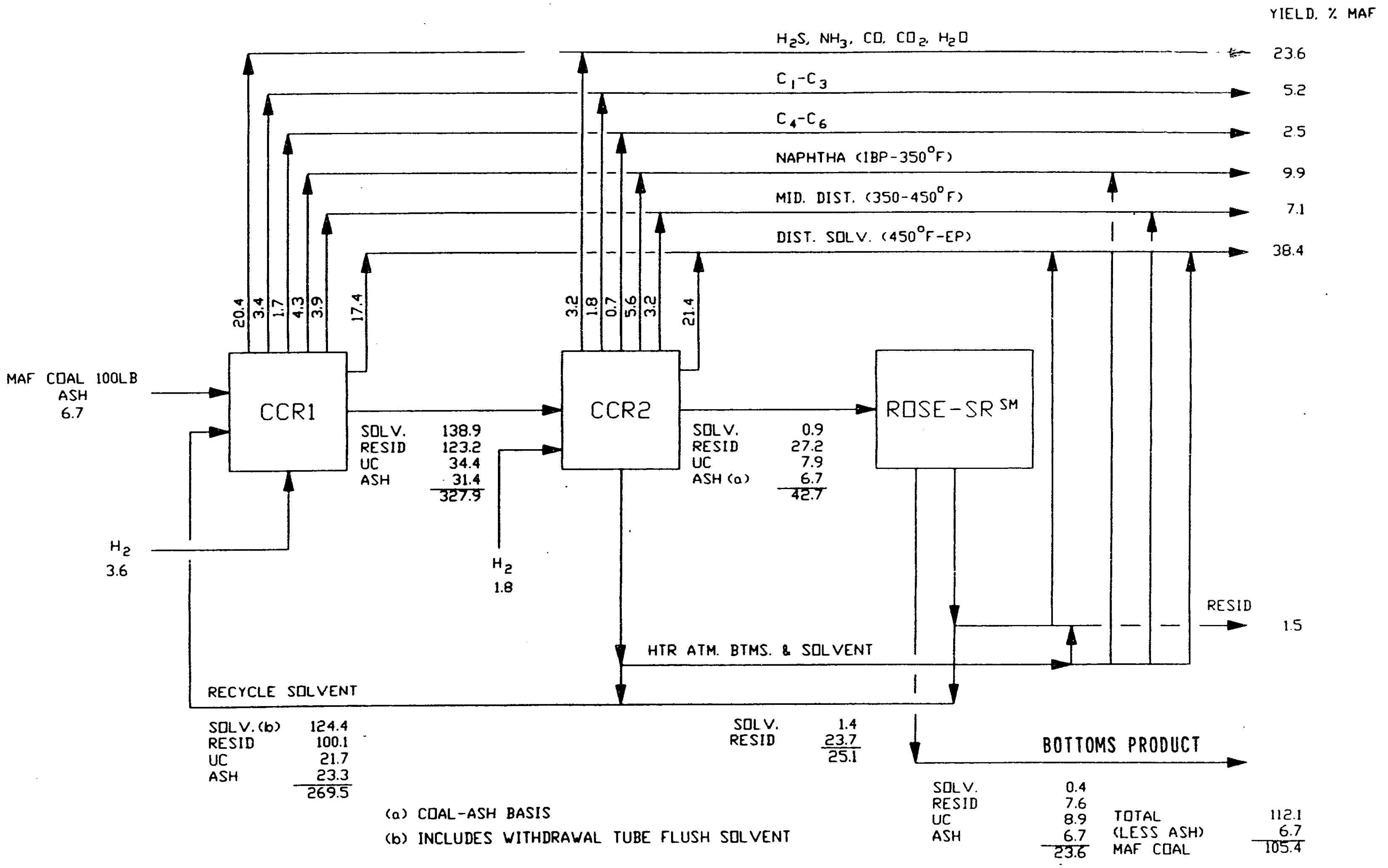


FIGURE 26. MATERIAL BALANCE FLOW DIAGRAM FOR PERIOD 262B

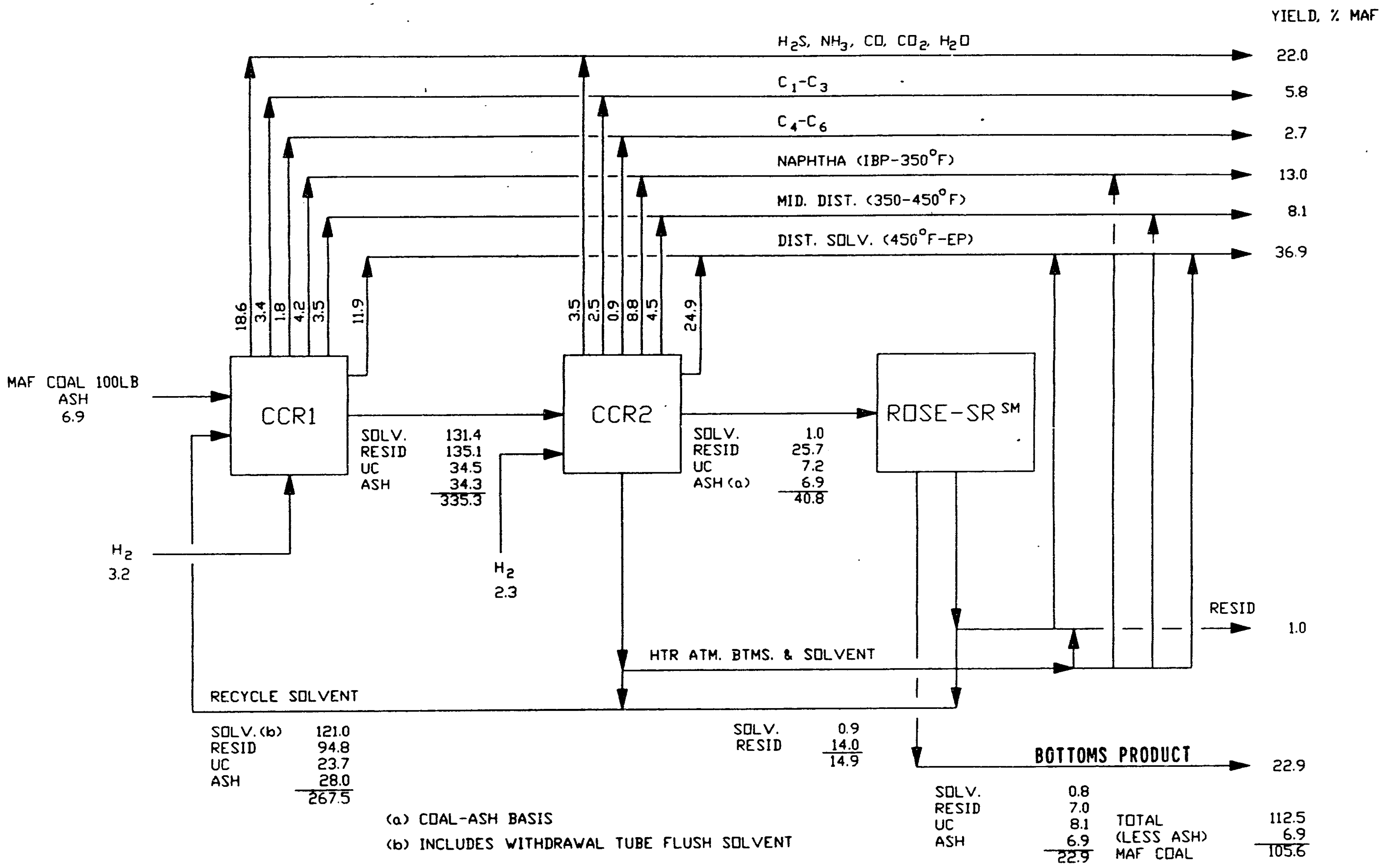


FIGURE 27. MATERIAL BALANCE FLOW DIAGRAM FOR PERIOD 262C

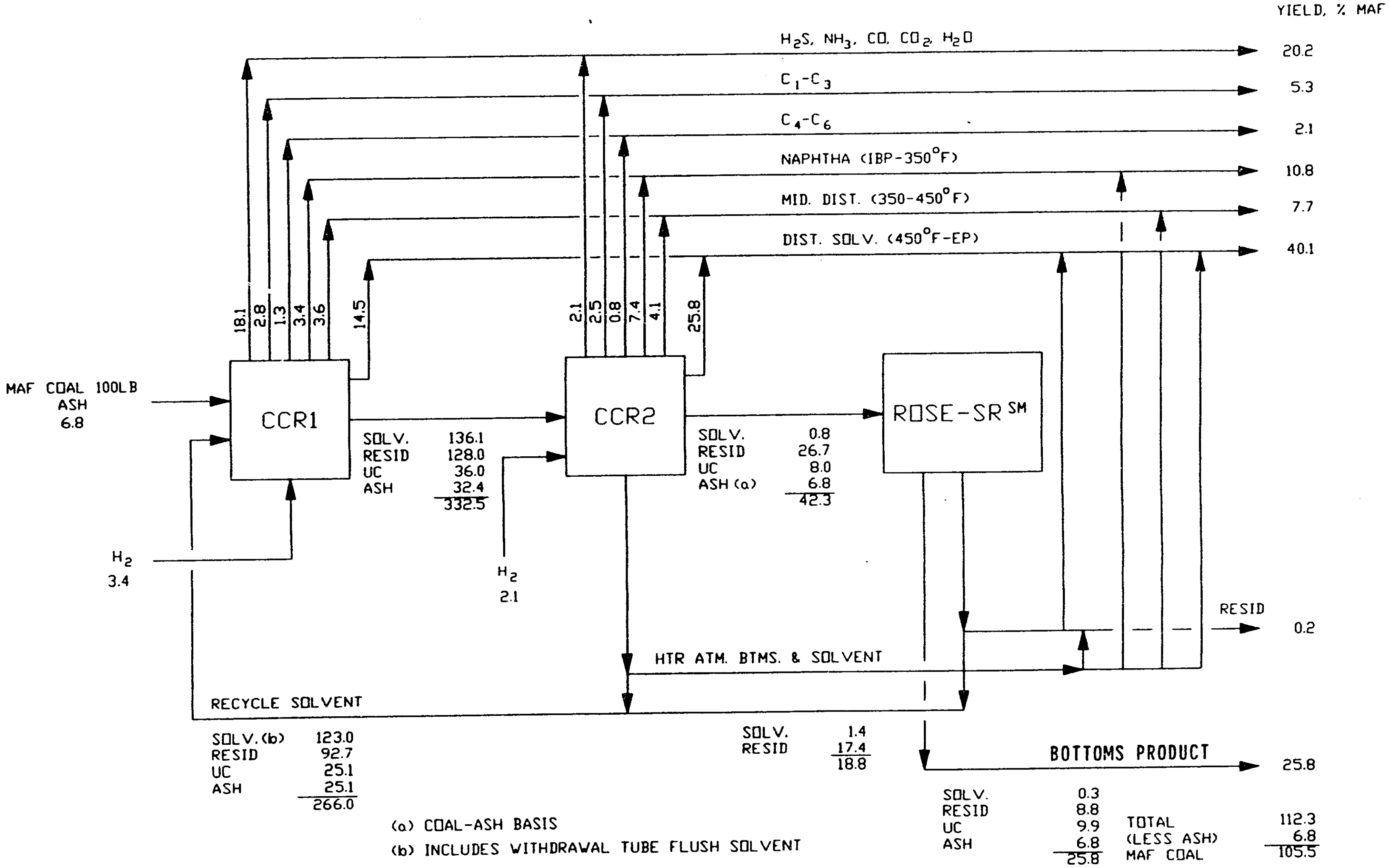
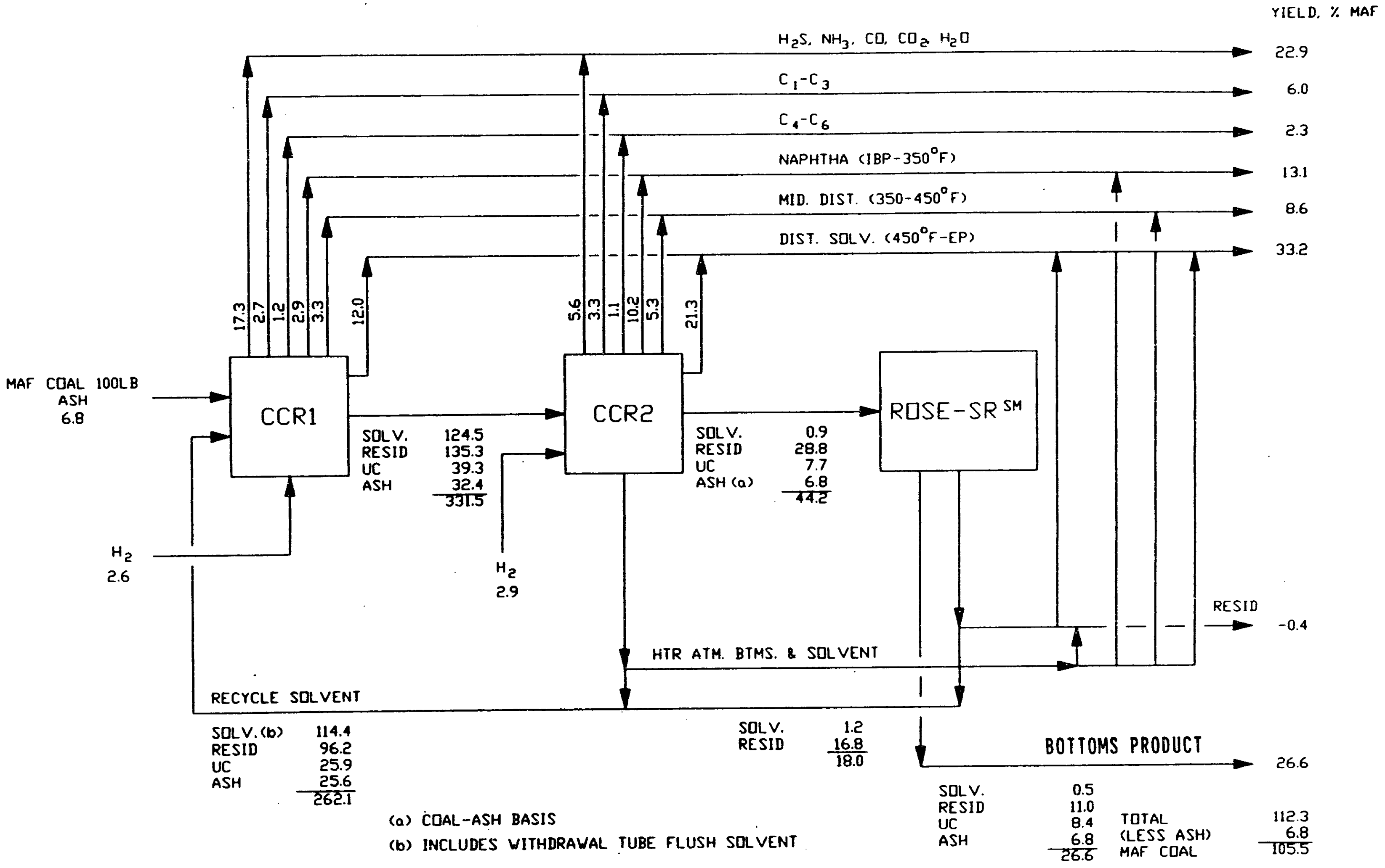


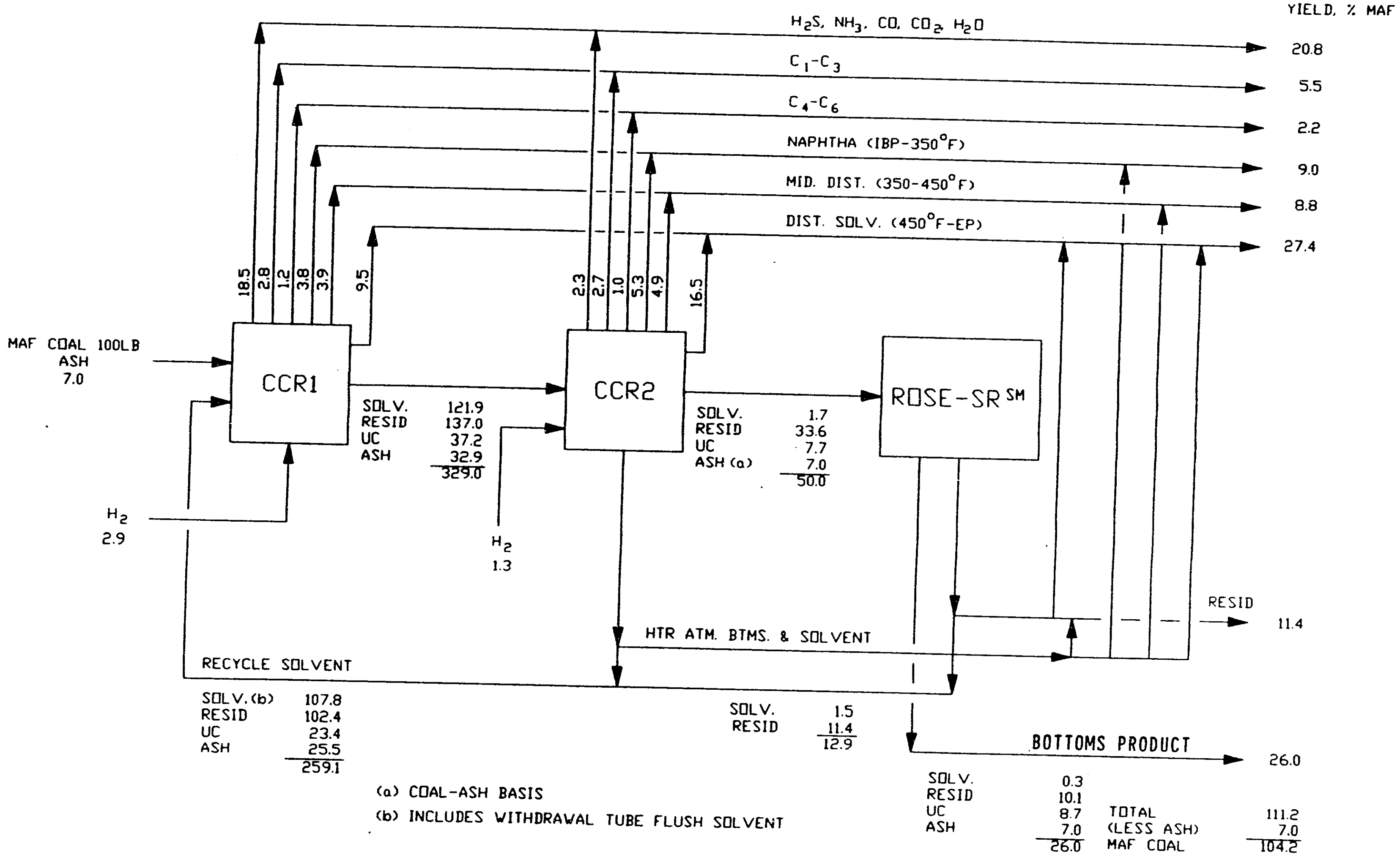
FIGURE 28. MATERIAL BALANCE FLOW DIAGRAM FOR PERIOD 262D



(a) COAL-ASH BASIS

(b) INCLUDES WITHDRAWAL TUBE FLUSH SOLVENT

FIGURE 29. MATERIAL BALANCE FLOW DIAGRAM FOR PERIOD 262E



(a) COAL-ASH BASIS

(b) INCLUDES WITHDRAWAL TUBE FLUSH SOLVENT

FIGURE 30. MATERIAL BALANCE DIAGRAM FOR PERIOD 262F

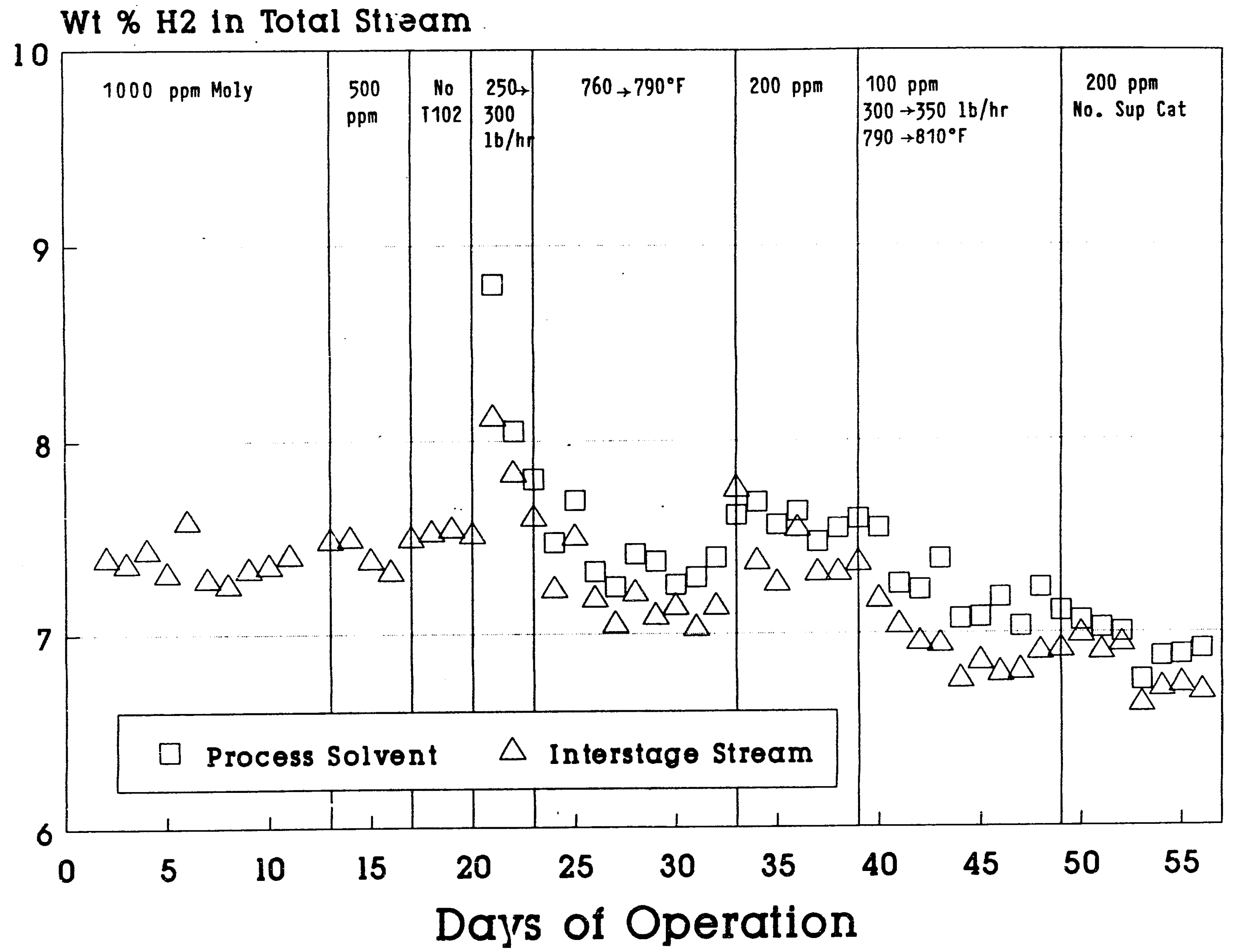


FIGURE 31. HYDROGEN CONTENT IN THE PROCESS SOLVENT AND INTERSTAGE STREAM

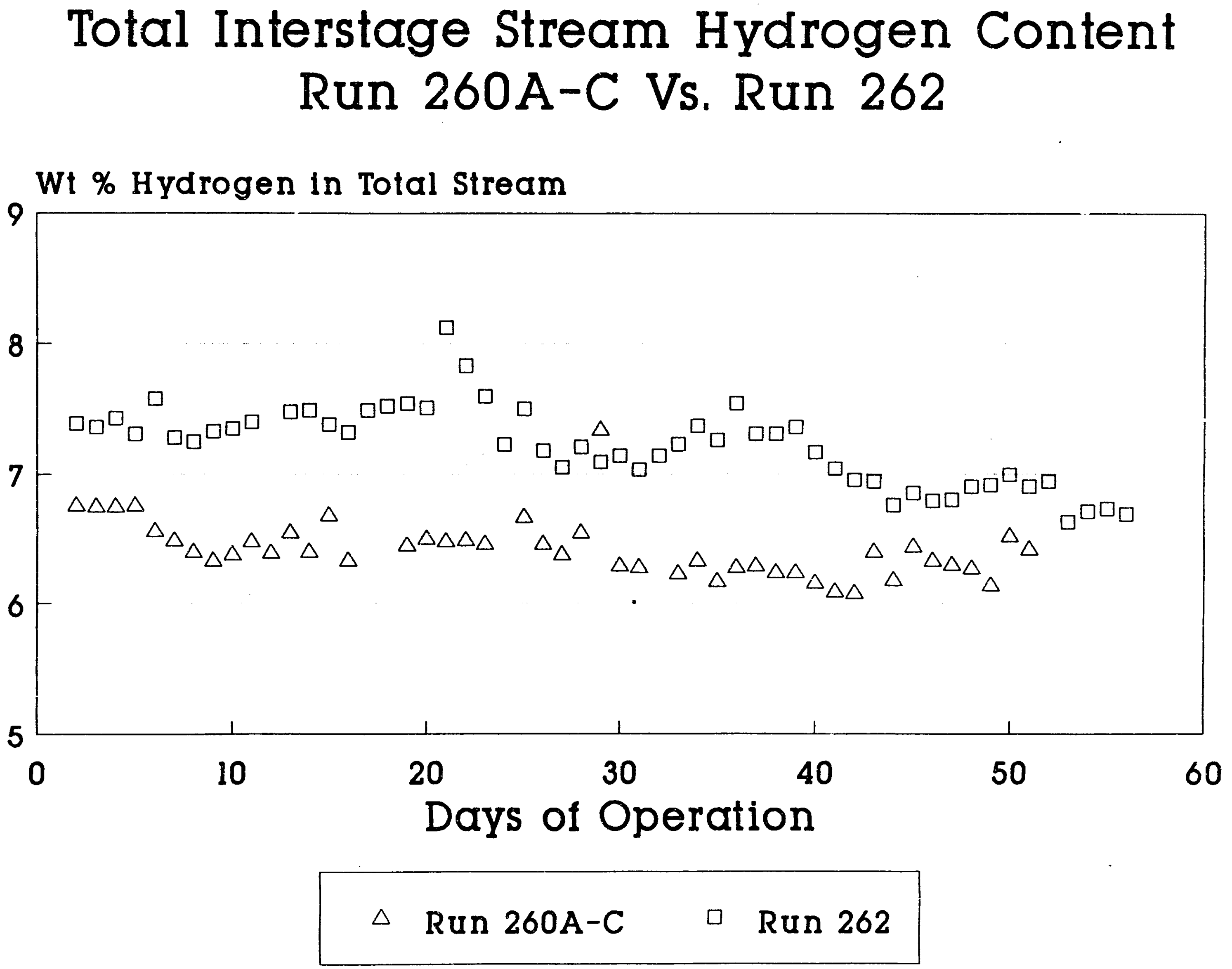

Total Interstage Stream Hydrogen Content
Run 260A-C Vs. Run 262

FIGURE 32. COMPARISON OF HYDROGEN CONTENT IN THE INTERSTAGE STREAM FOR RUN 260A-C and Run 262

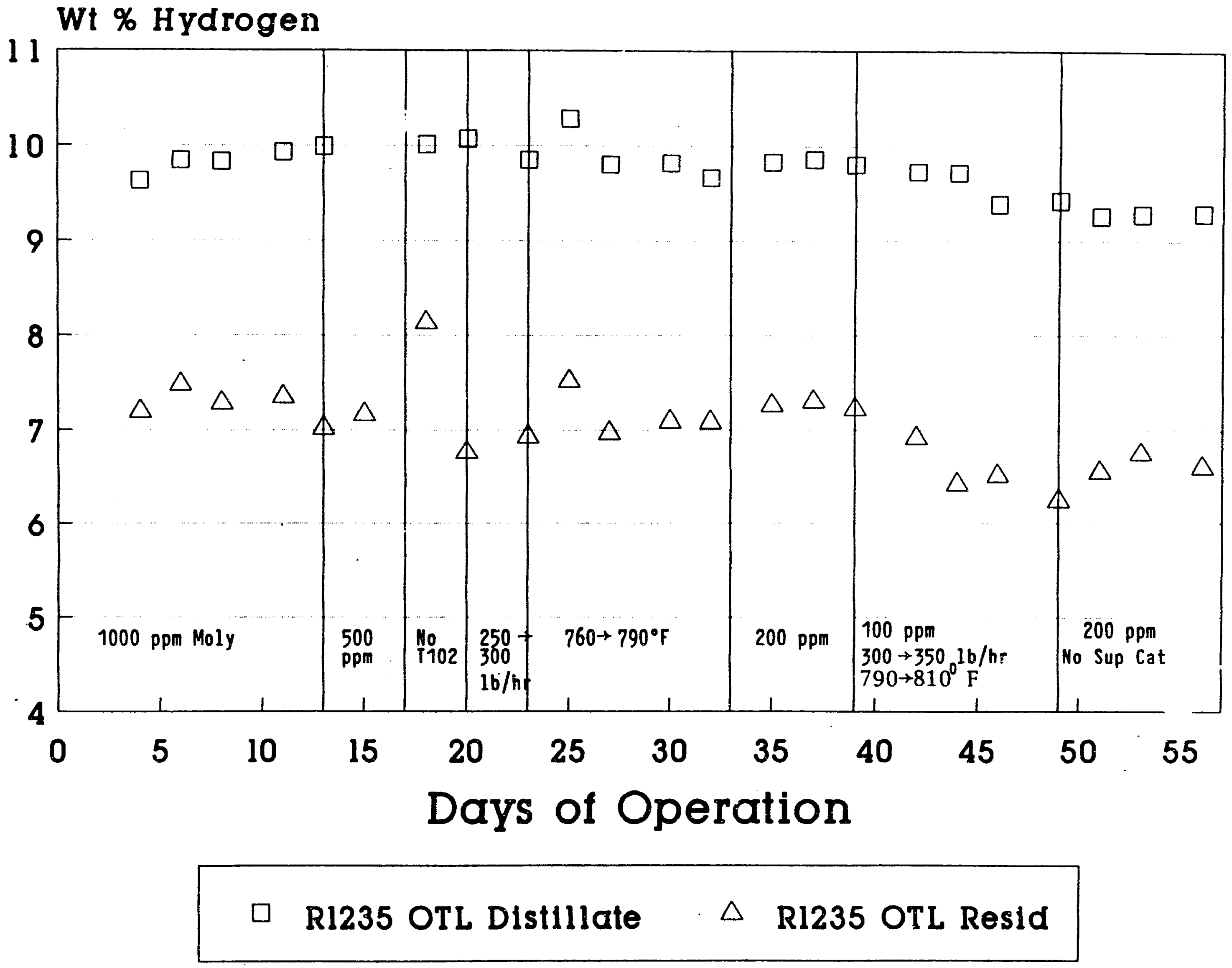


FIGURE 33. HYDROGEN CONTENT IN THE DISTILLATE AND RESID PORTIONS OF THE INTERSTAGE STREAM

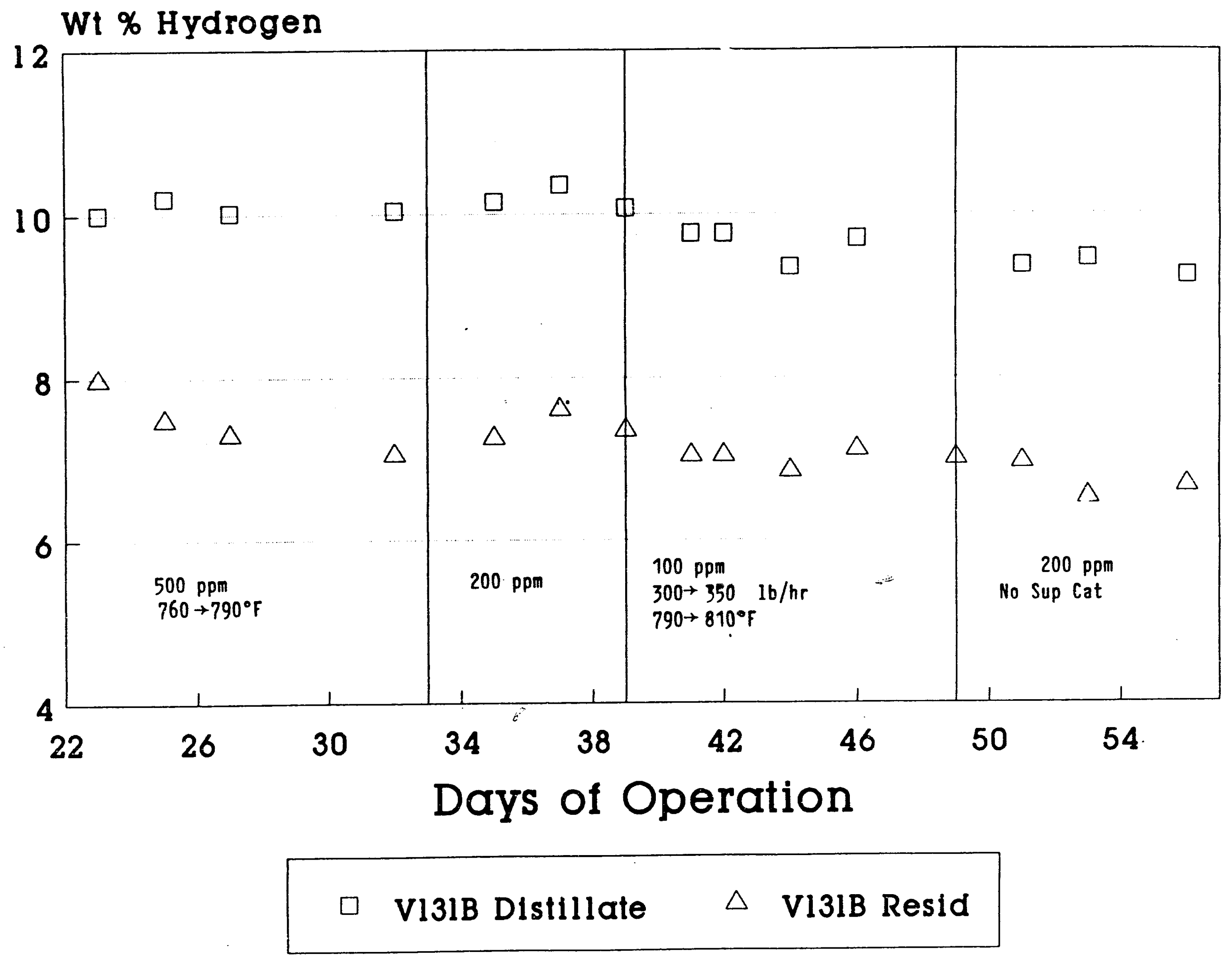


FIGURE 34. HYDROGEN CONTENT IN THE DISTILLATE AND RESID PORTIONS OF THE PROCESS SOLVENT

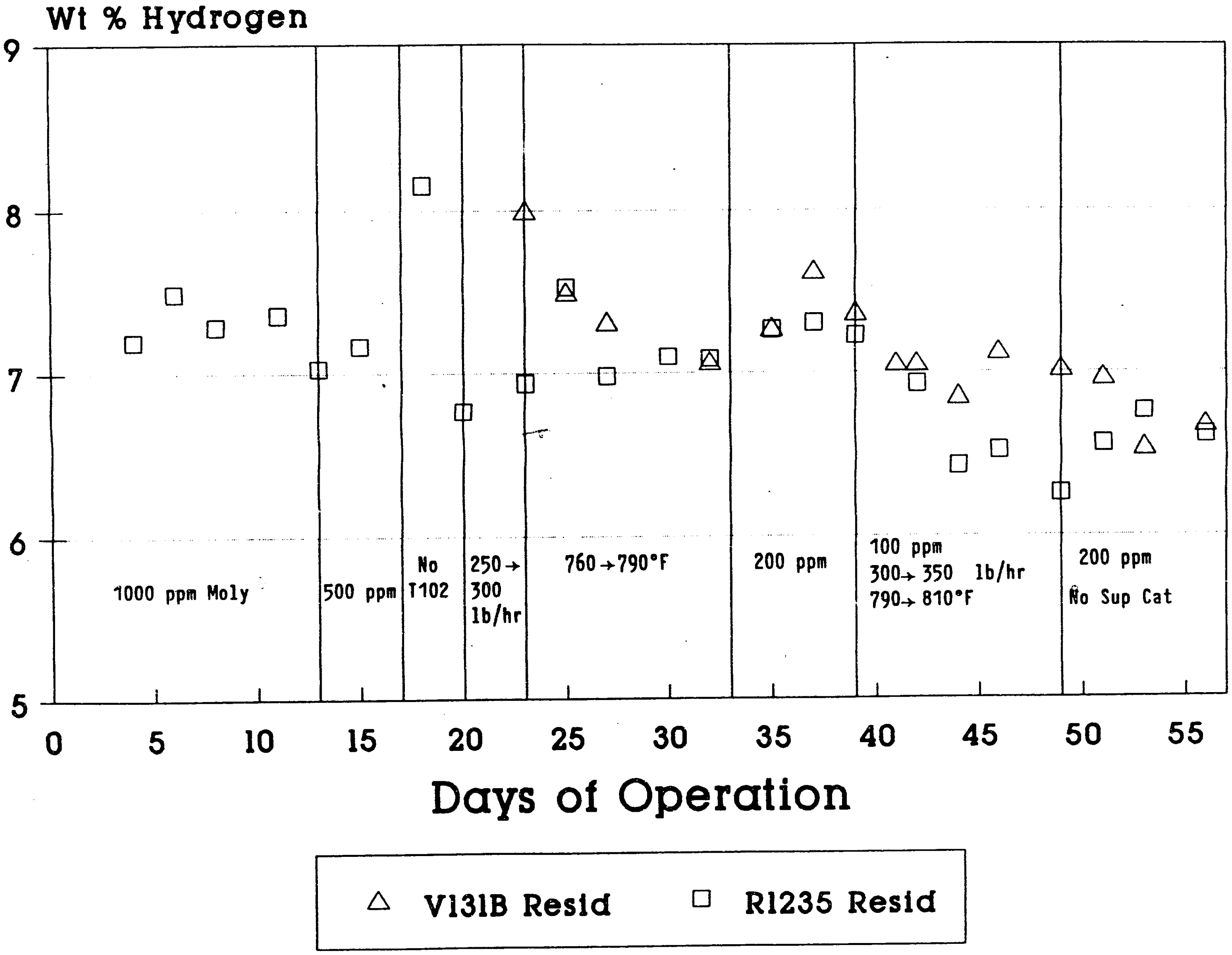


FIGURE 35. COMPARISON OF RESID HYDROGEN IN THE PROCESS SOLVENT AND INTERSTAGE STREAM

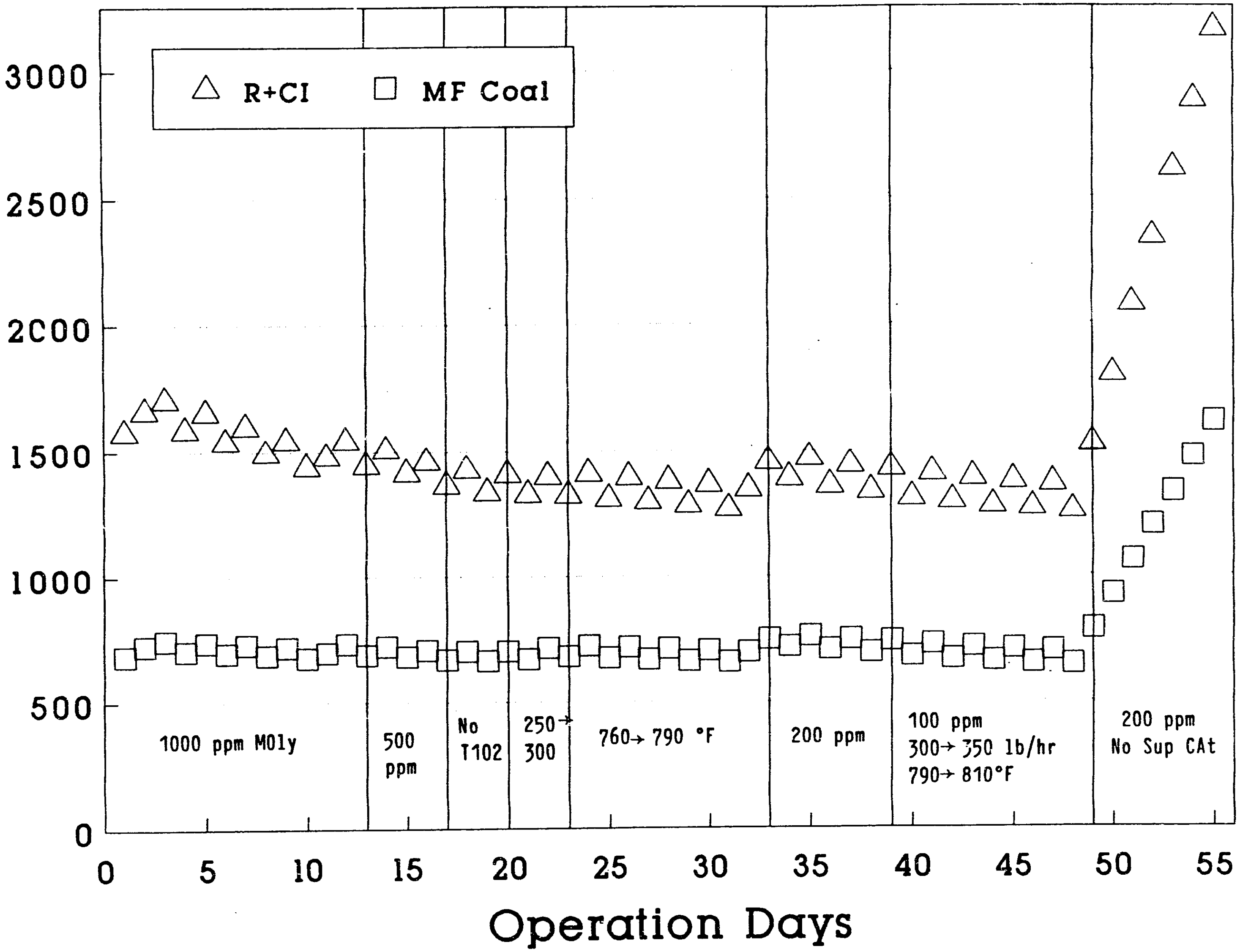


FIGURE 36. SECOND STAGE SUPPORTED CATALYST AGE

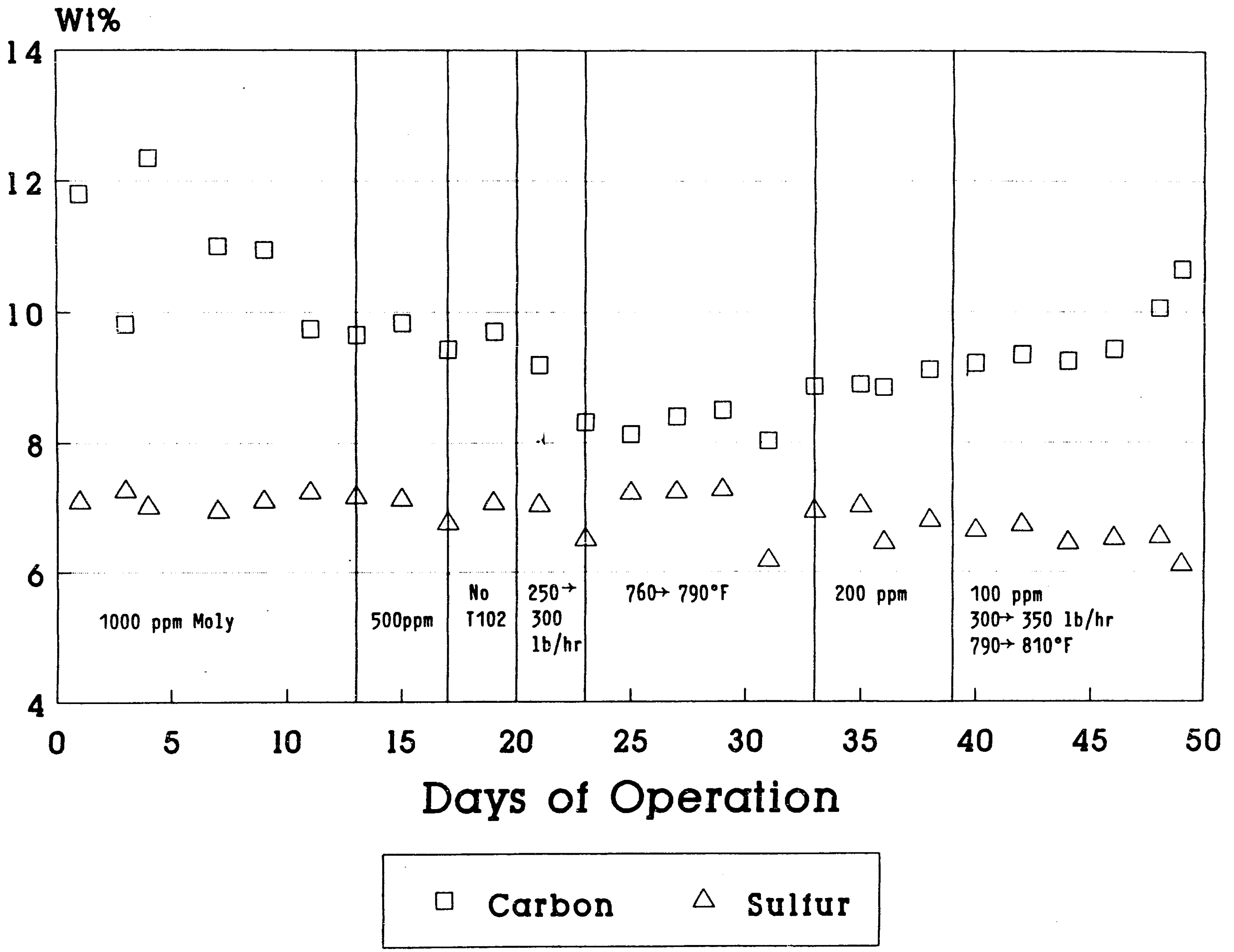


FIGURE 37. THF EXTRACTED CARBON AND SULFUR DEPOSITS ON THE SECOND STAGE SUPPORTED CATALYST

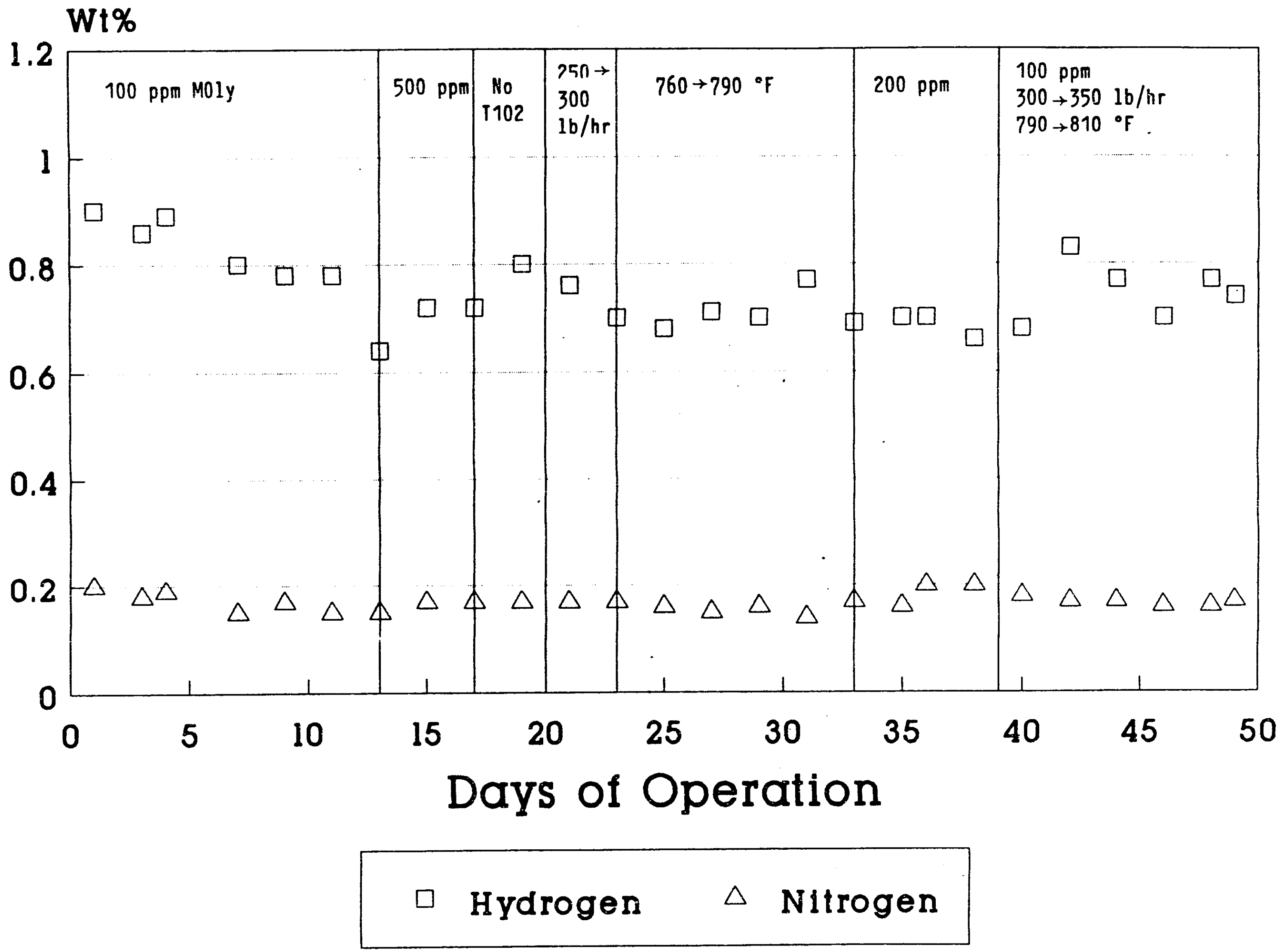


FIGURE 38. THF EXTRACTED HYDROGEN AND NITROGEN DEPOSITS ON THE SECOND STAGE SUPPORTED CATALYST

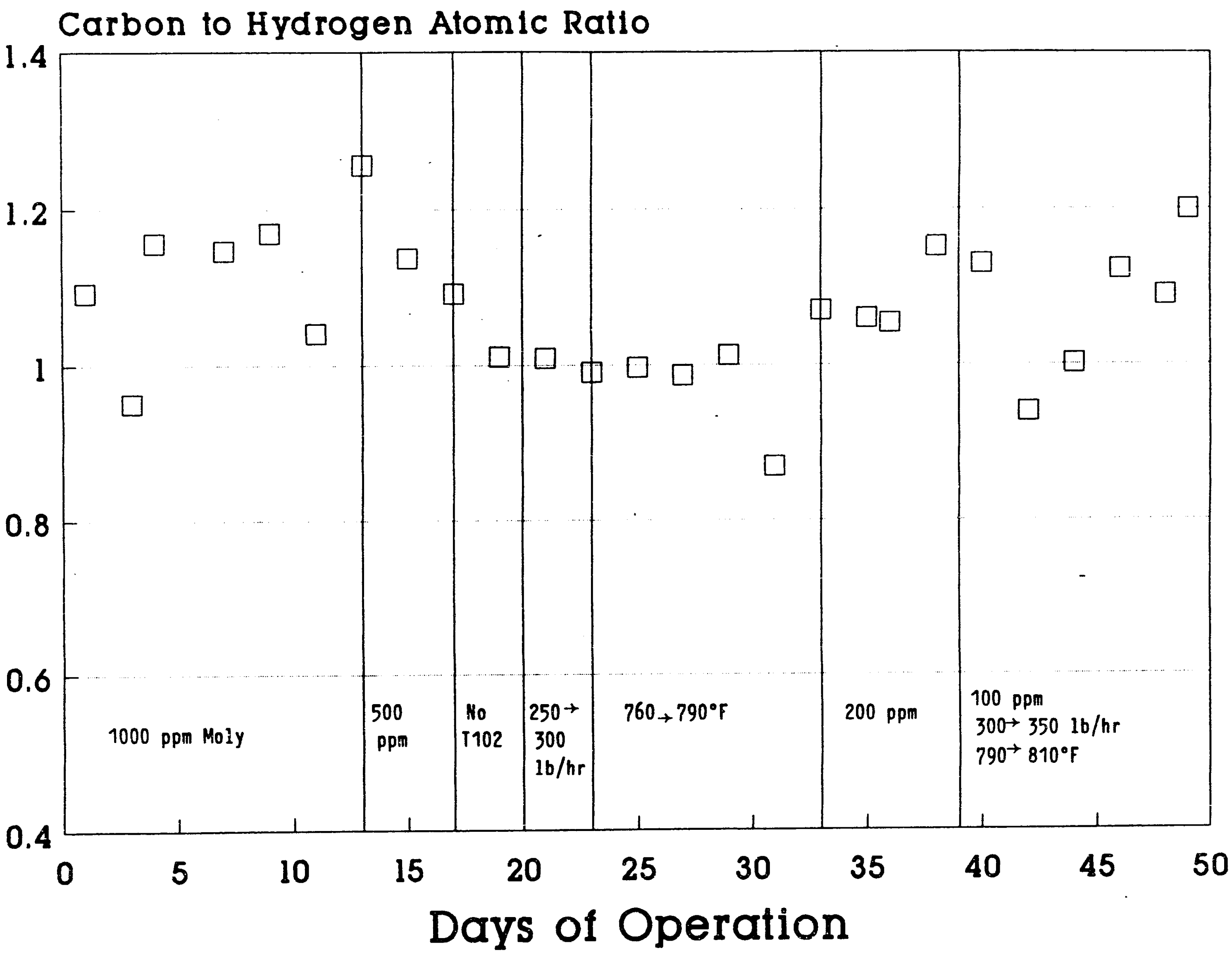


FIGURE 39. CARBON TO HYDROGEN ATOMIC RATIO ON THE SECOND STAGE SUPPORTED CATALYST

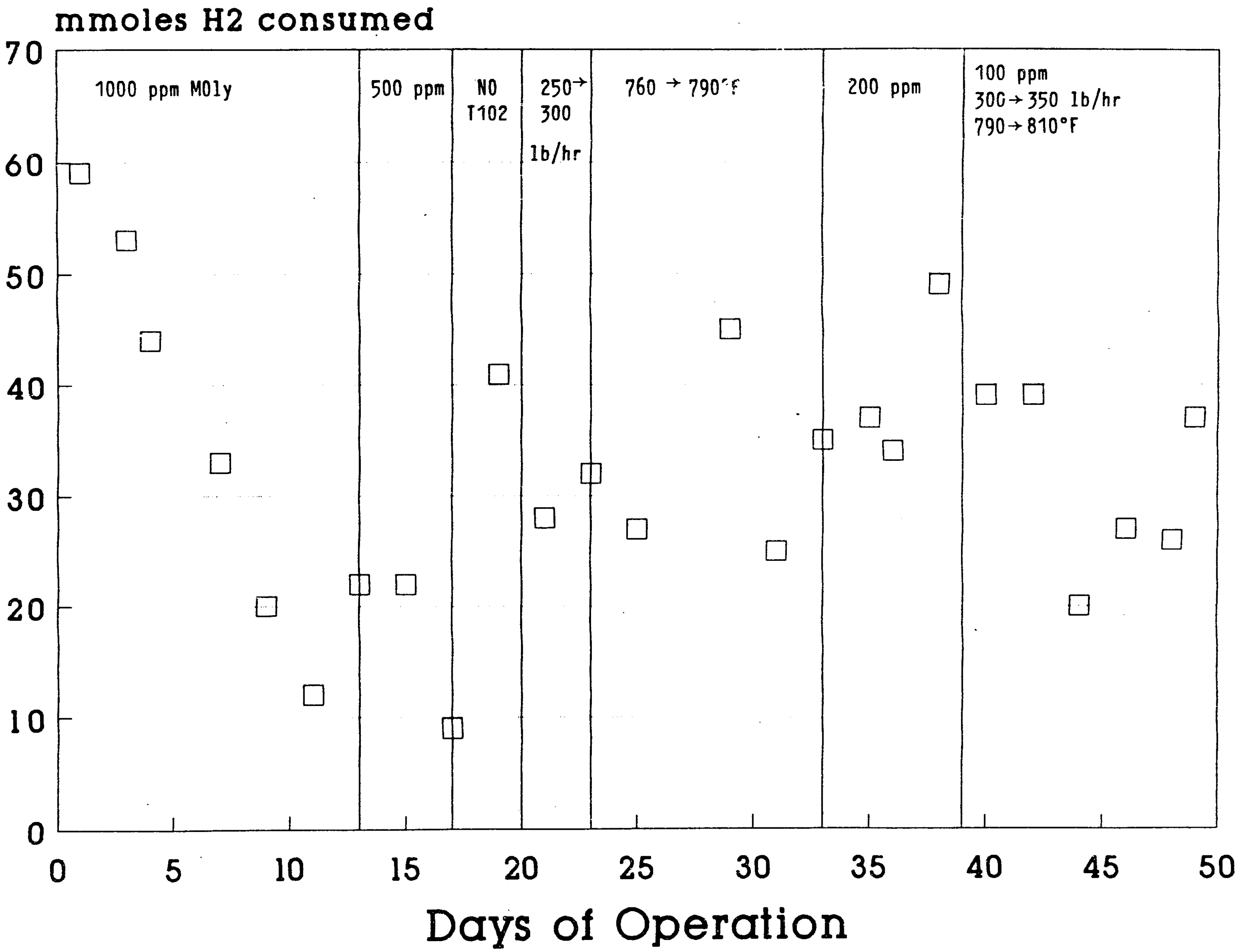


FIGURE 40. NAPHTHALENE ACTIVITY OF SECOND STAGE SUPPORTED CATALYST

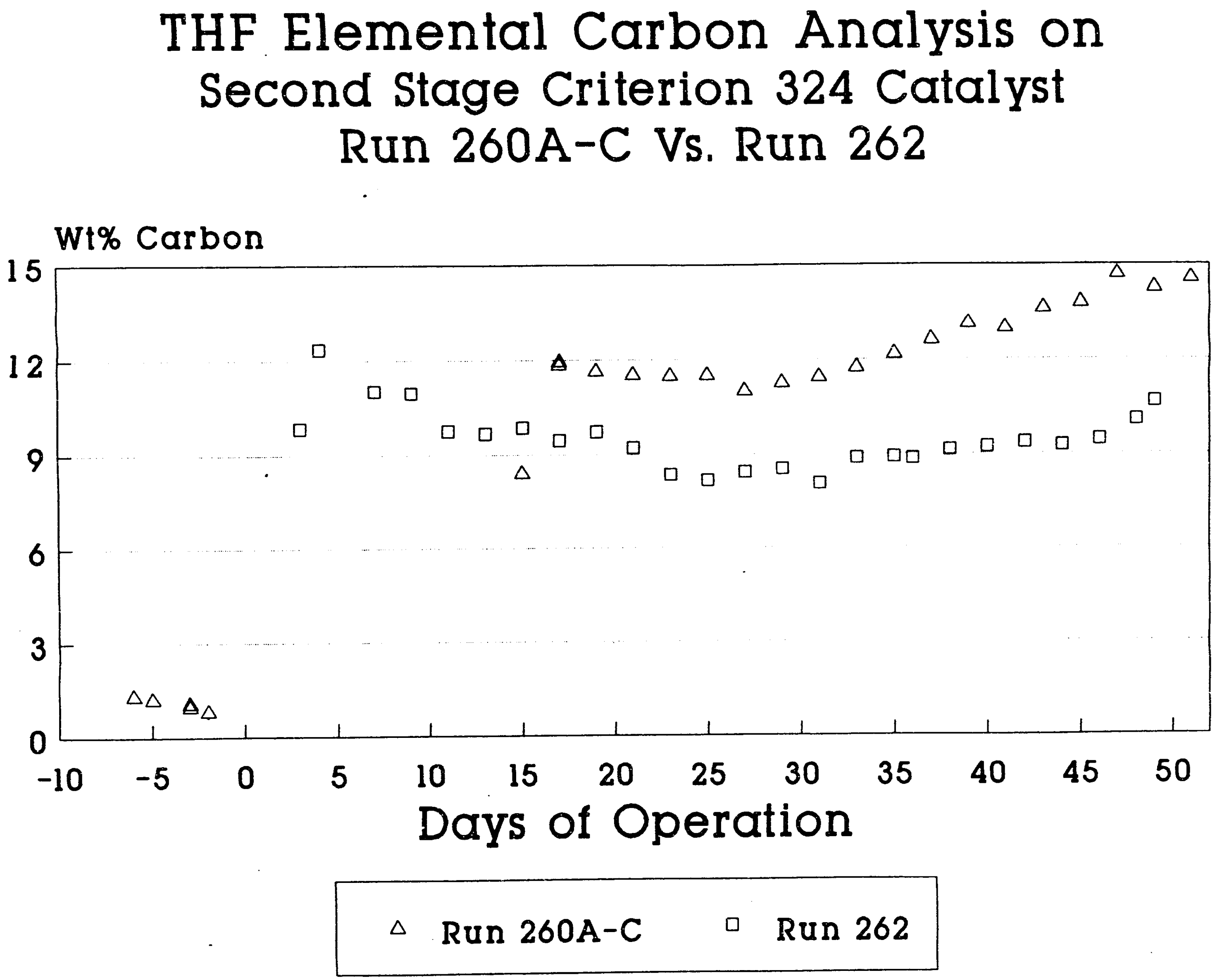
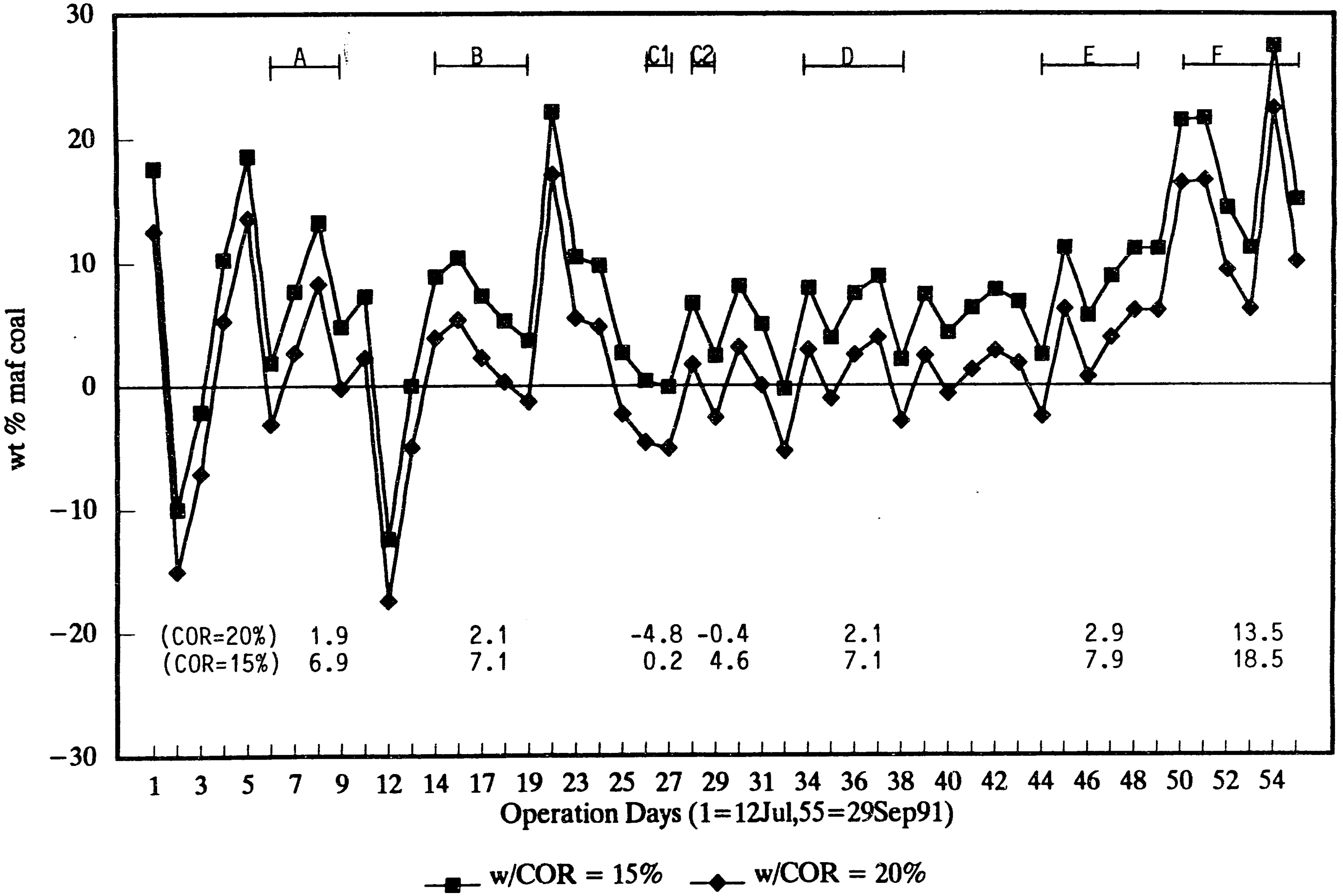


FIGURE 41. COMPARISON OF CARBON DEPOSITS ON THE SECOND STAGE SUPPORTED CATALYST FOR RUN 260A-C and Run 262

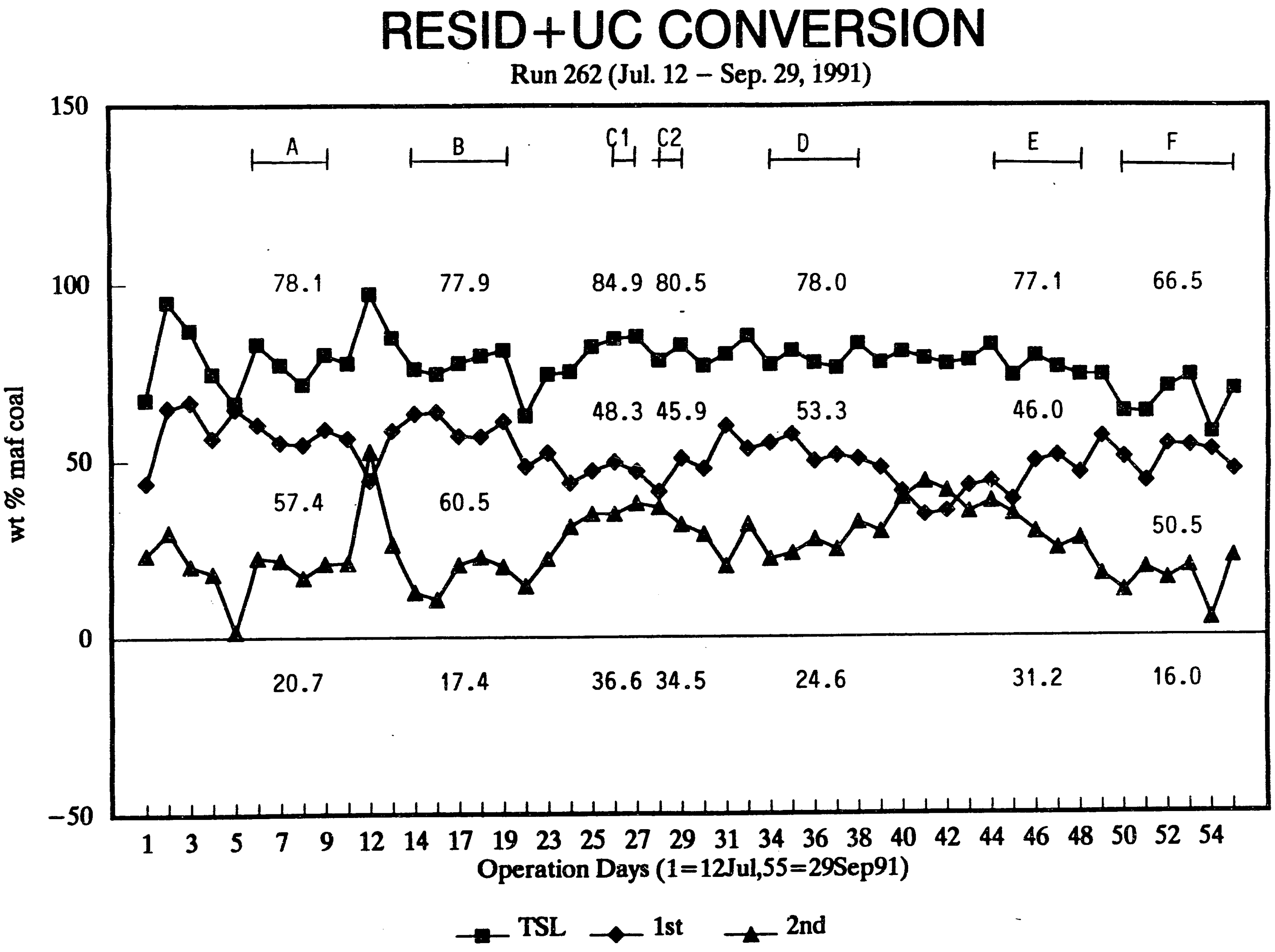
TSL RESID WITH COMMON ORGANIC REJECTION

Run 262 (Jul. 12 – Sep. 29, 1991)



* Black Thunder coal in thermal/catalytic mode

FIGURE 42. TREND DATA OF OVERALL TWO-STAGE EXCESS RESID YIELD WITH COMMON ORGANIC REJECTION (262A-F)



* Phase 2 data measured

FIGURE 43. TREND DATA OF OVERALL TWO-STAGE RESID + UC CONVERSION(262A-F)

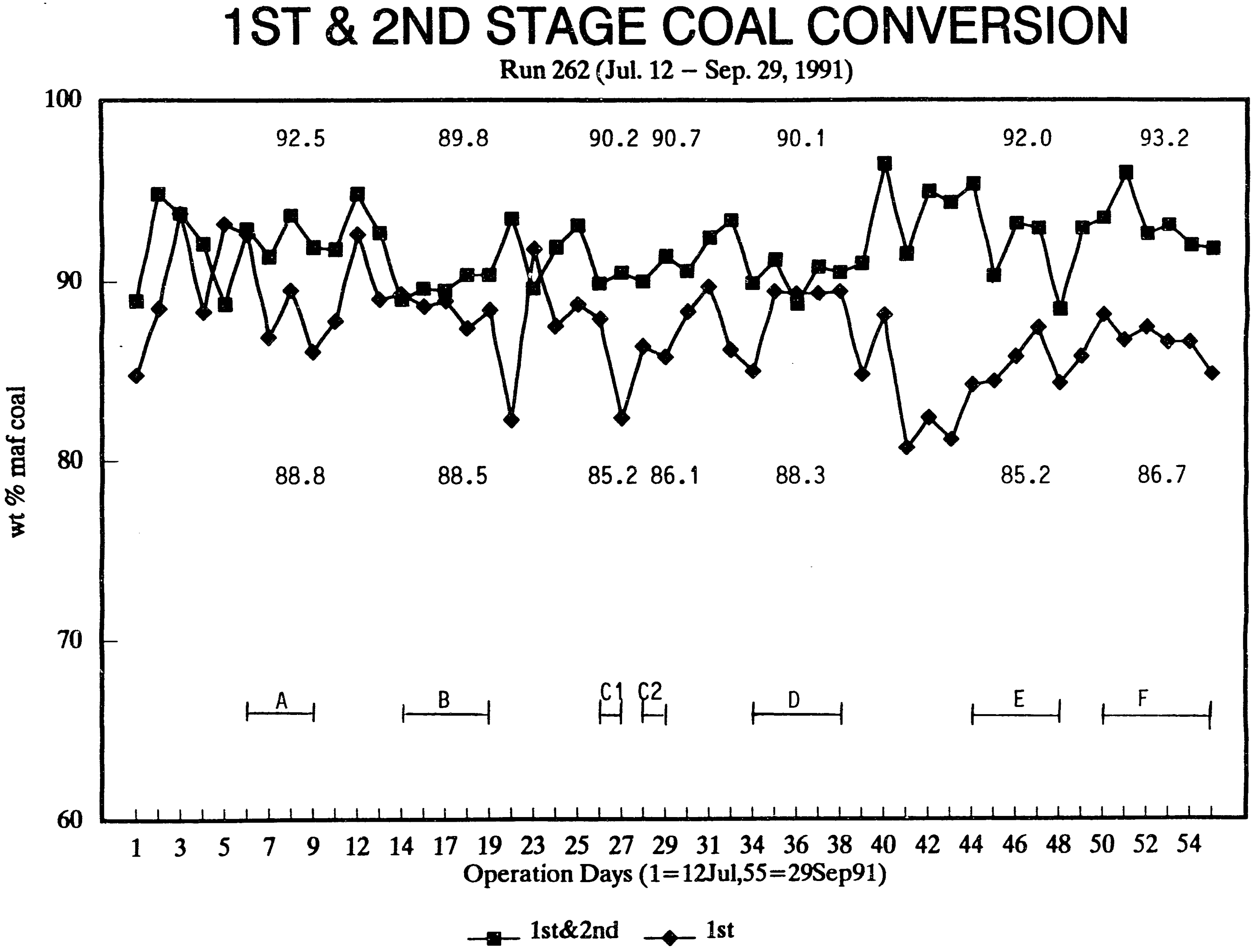


FIGURE 44. TREND DATA OF COAL CONVERSION (262A-F)

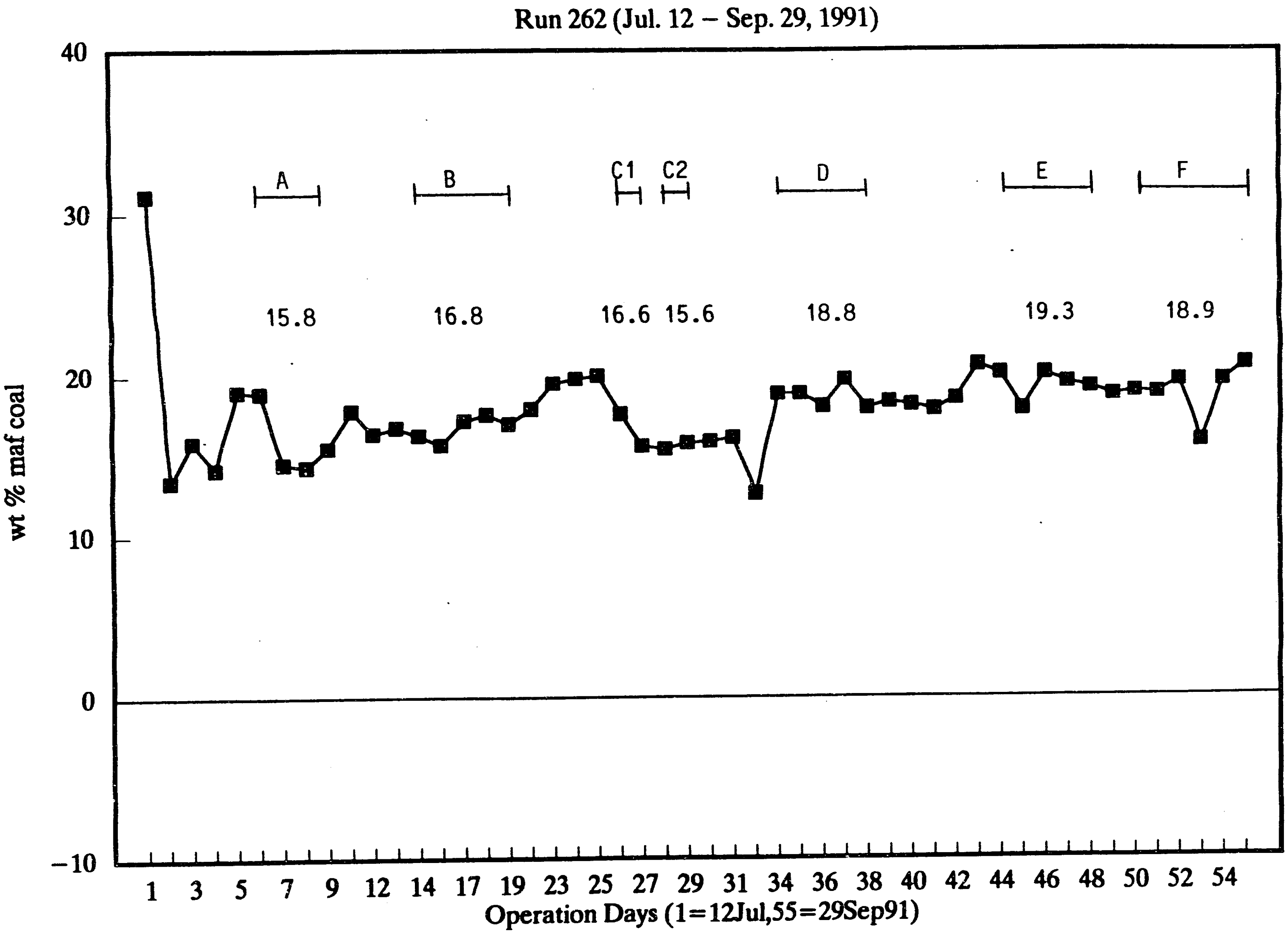


FIGURE 45. TREND DATA OF ORGANICS IN BOTTOMS PRODUCT(262A-F)

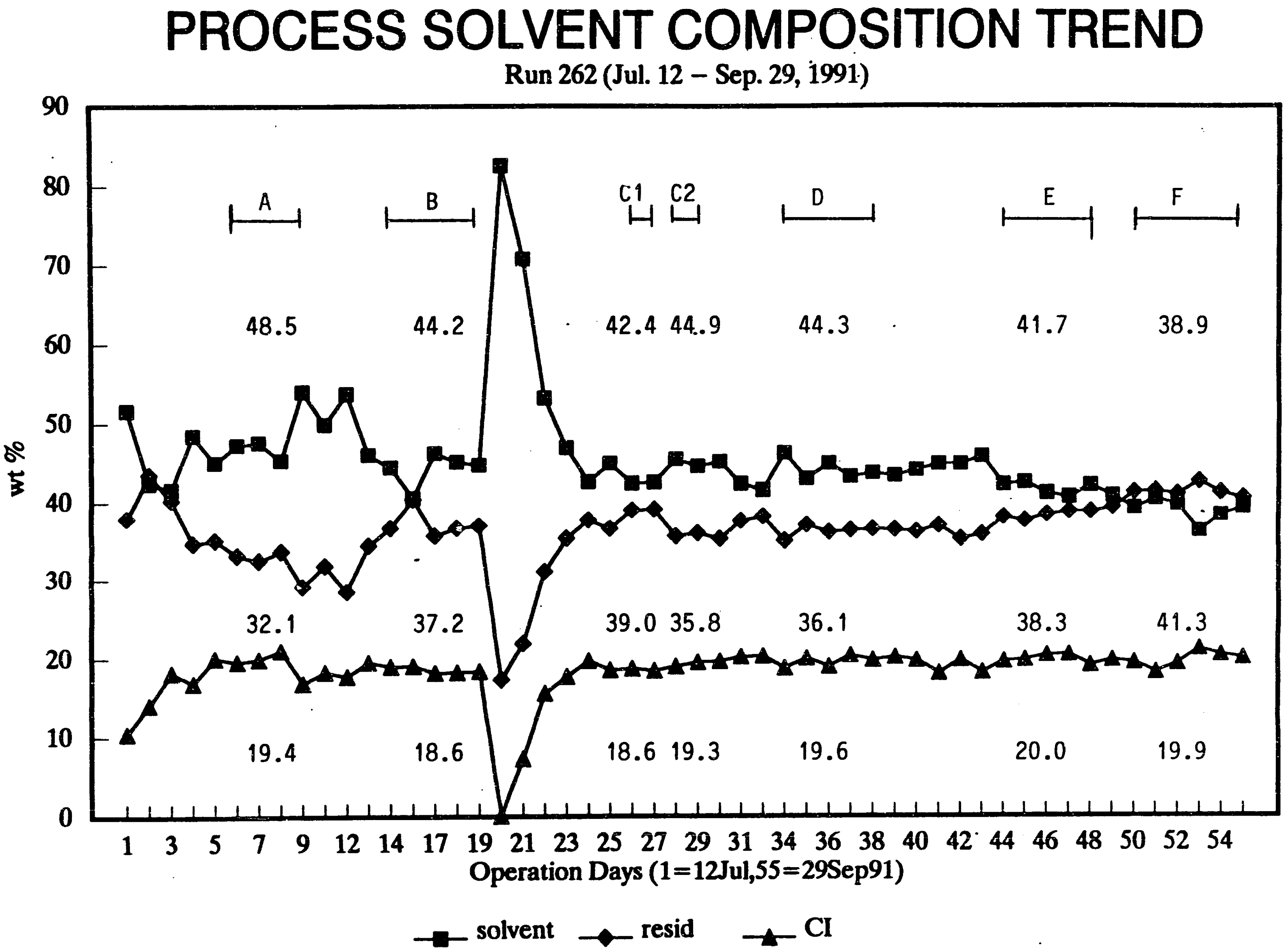


FIGURE 46. TREND DATA OF PROCESS SOLVENT COMPOSITION (262A-F)

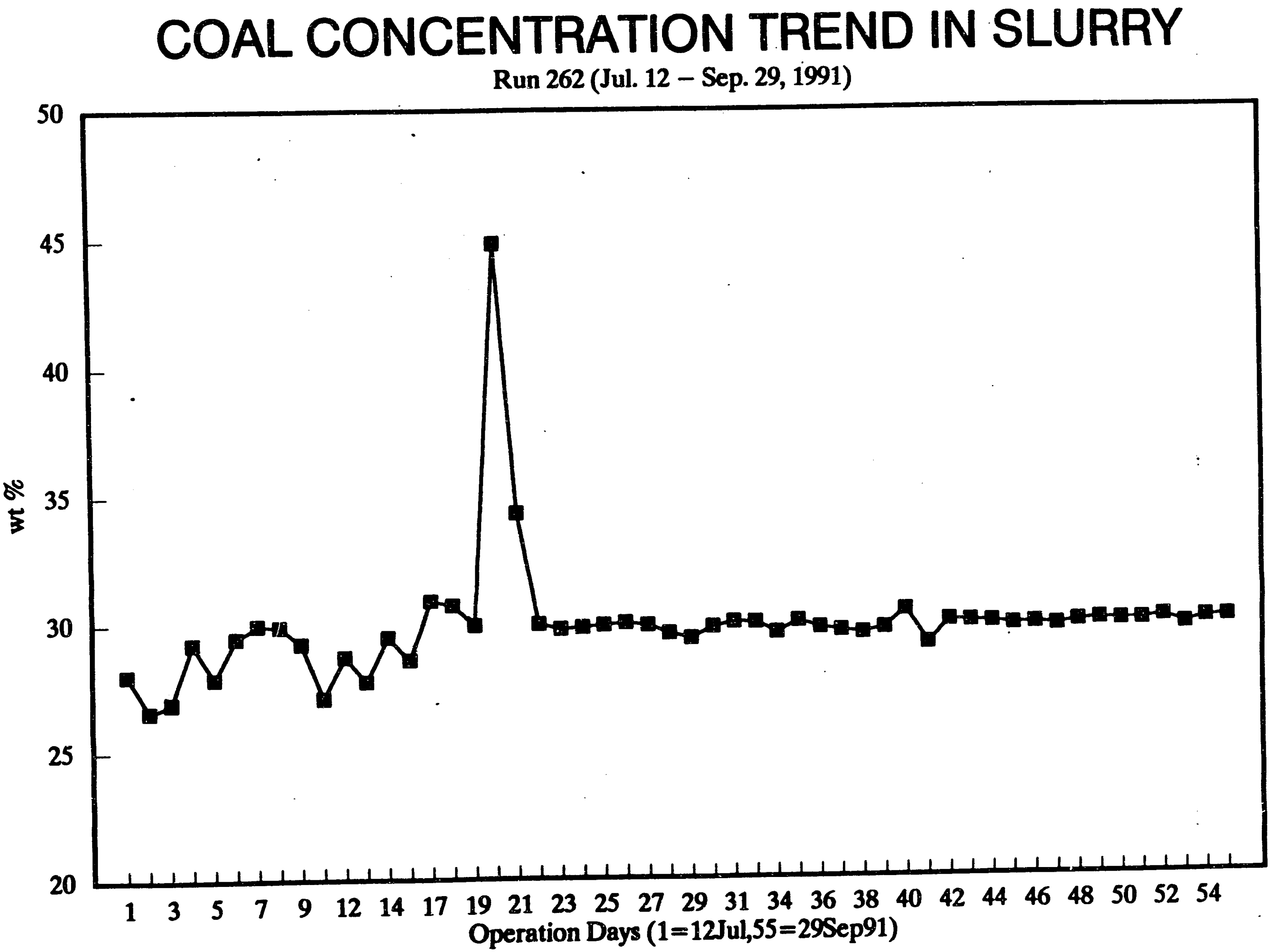


FIGURE 47. TREND DATA OF COAL CONCENTRATION IN SLURRY

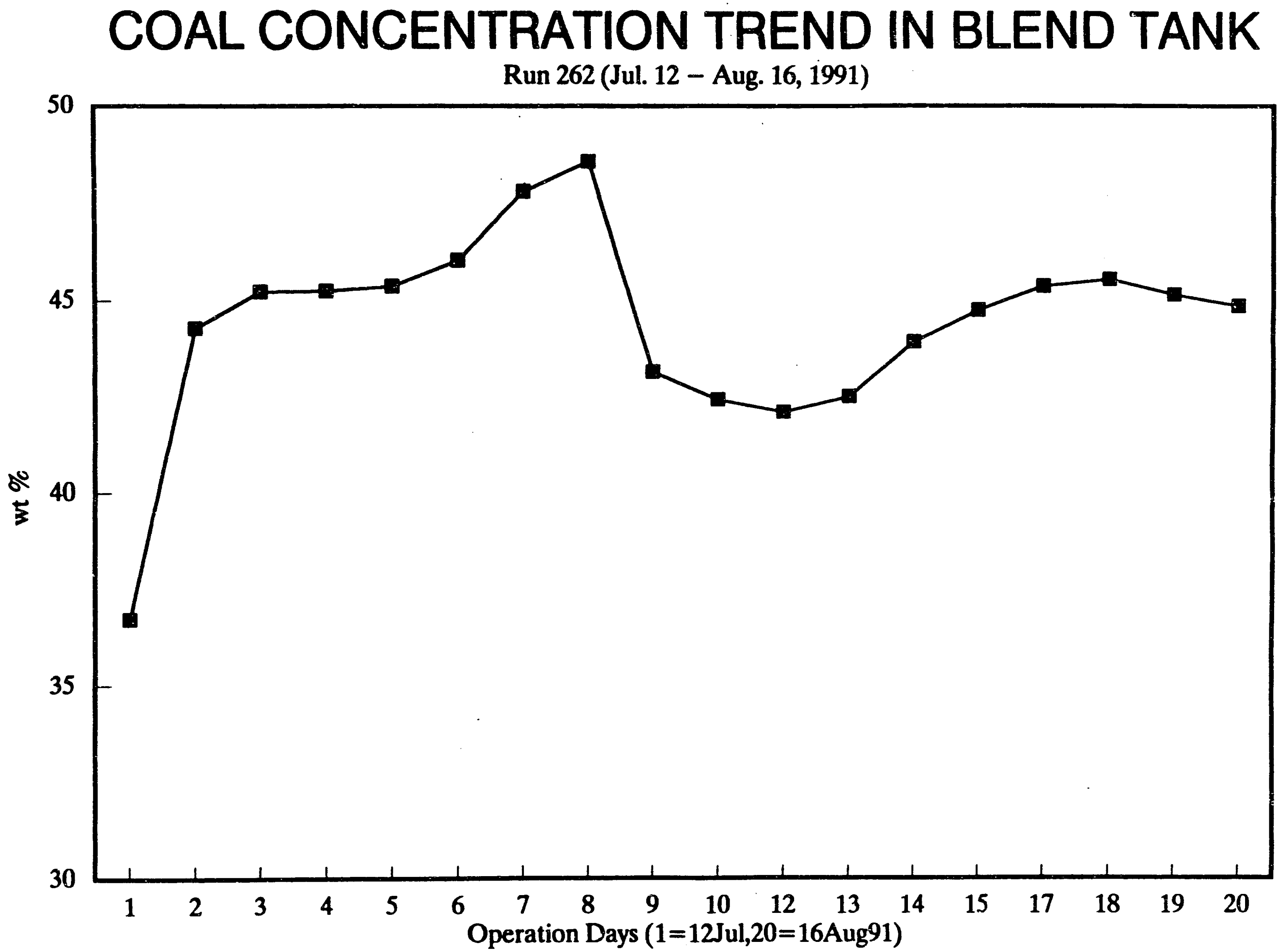


FIGURE 48. TREND DATA OF COAL CONCENTRATION IN BLEND TANK WITH NEW RESID CIRCULATION SYSTEM (262AB)

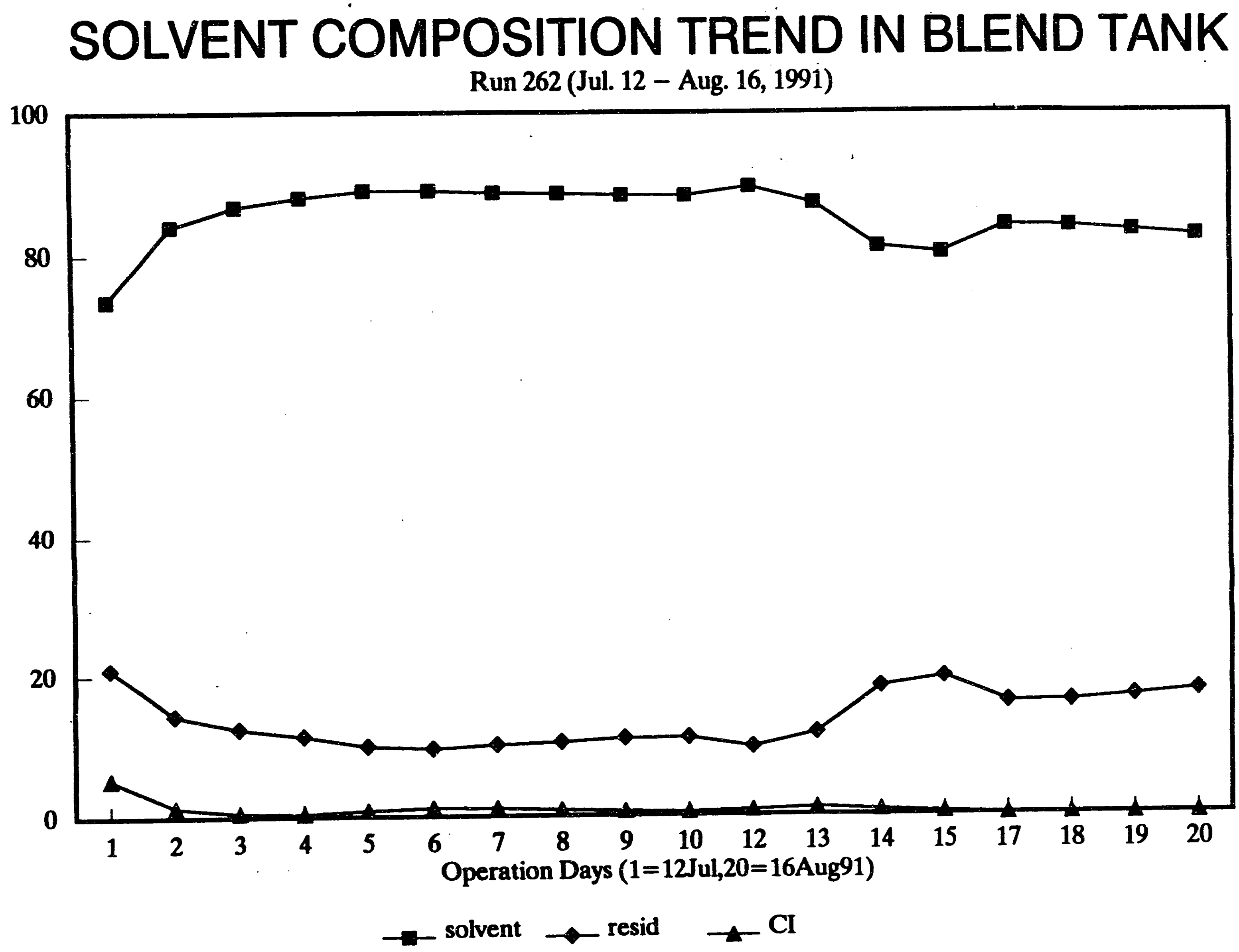


FIGURE 49. TREND DATA OF SOLVENT COMPOSITION IN BLEND TANK WITH NEW RESID CIRCULATION SYSTEM (262A-B)

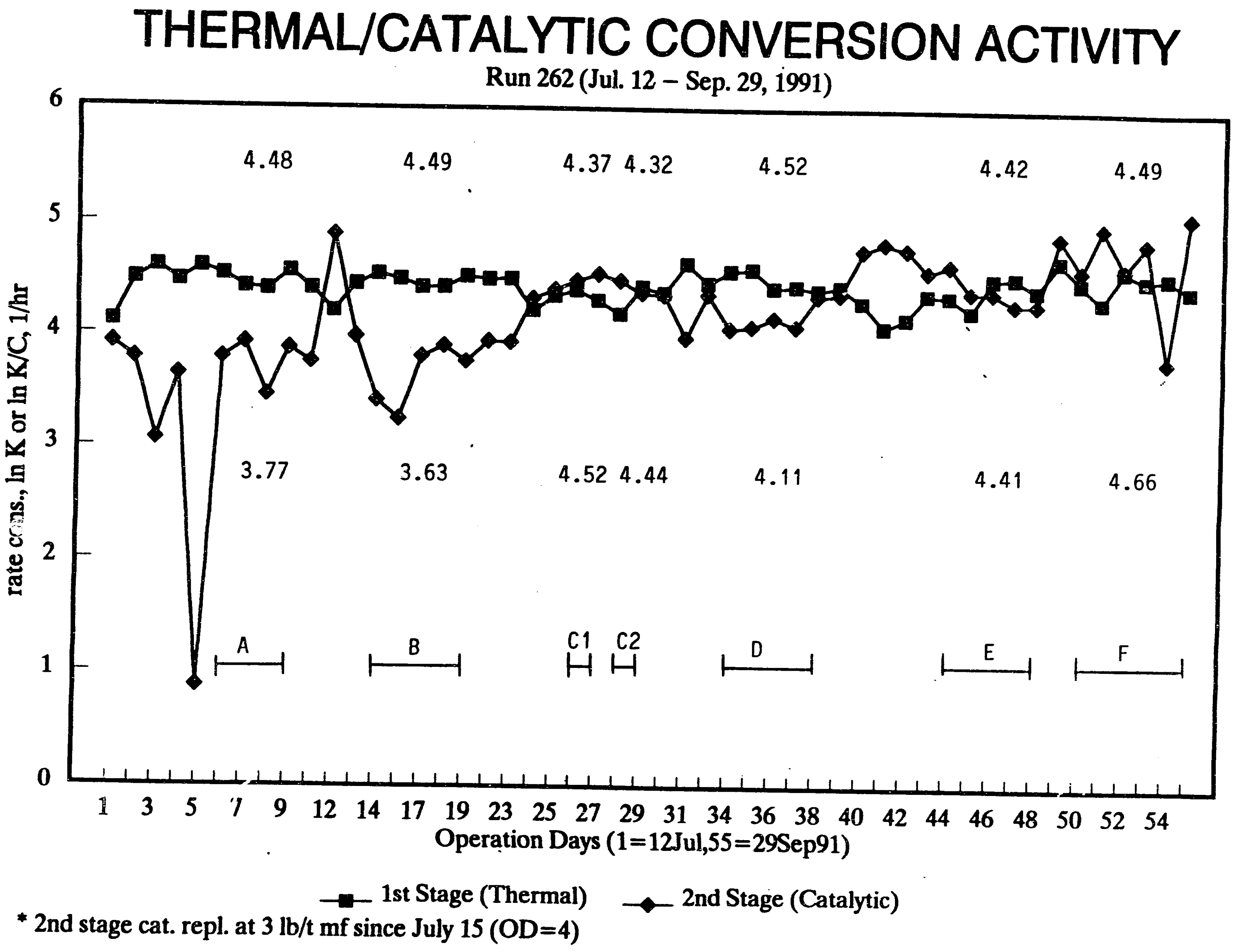


FIGURE 50. FIRST STAGE THERMAL AND SECOND STAGE CATALYTIC CONVERSION ACTIVITY TRENDS (262A-F)

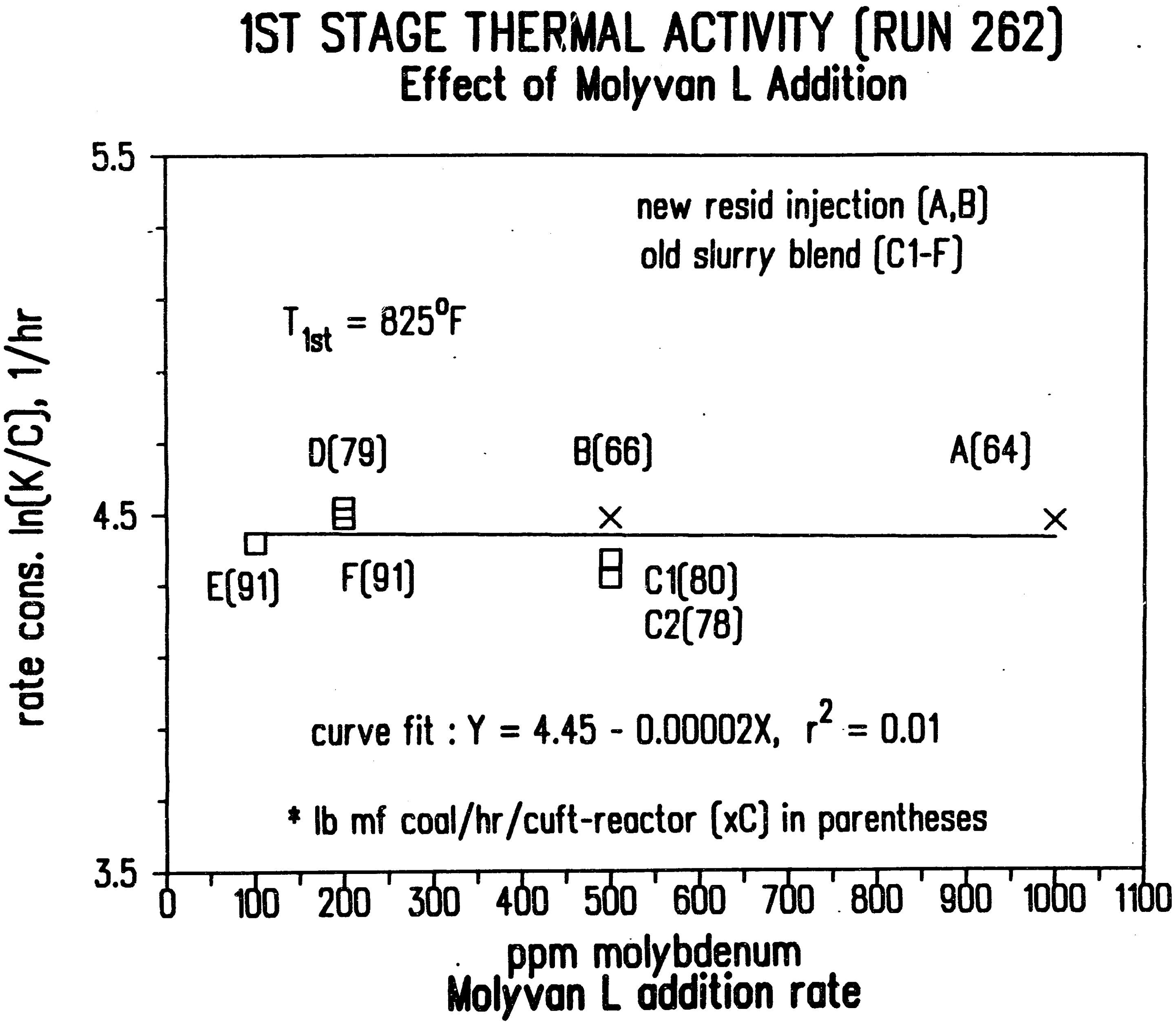


FIGURE 51. EFFECT OF MOLYBDENUM CONCENTRATION ON FIRST STAGE TERMAL CONVERSION ACTIVITY (262A-F)

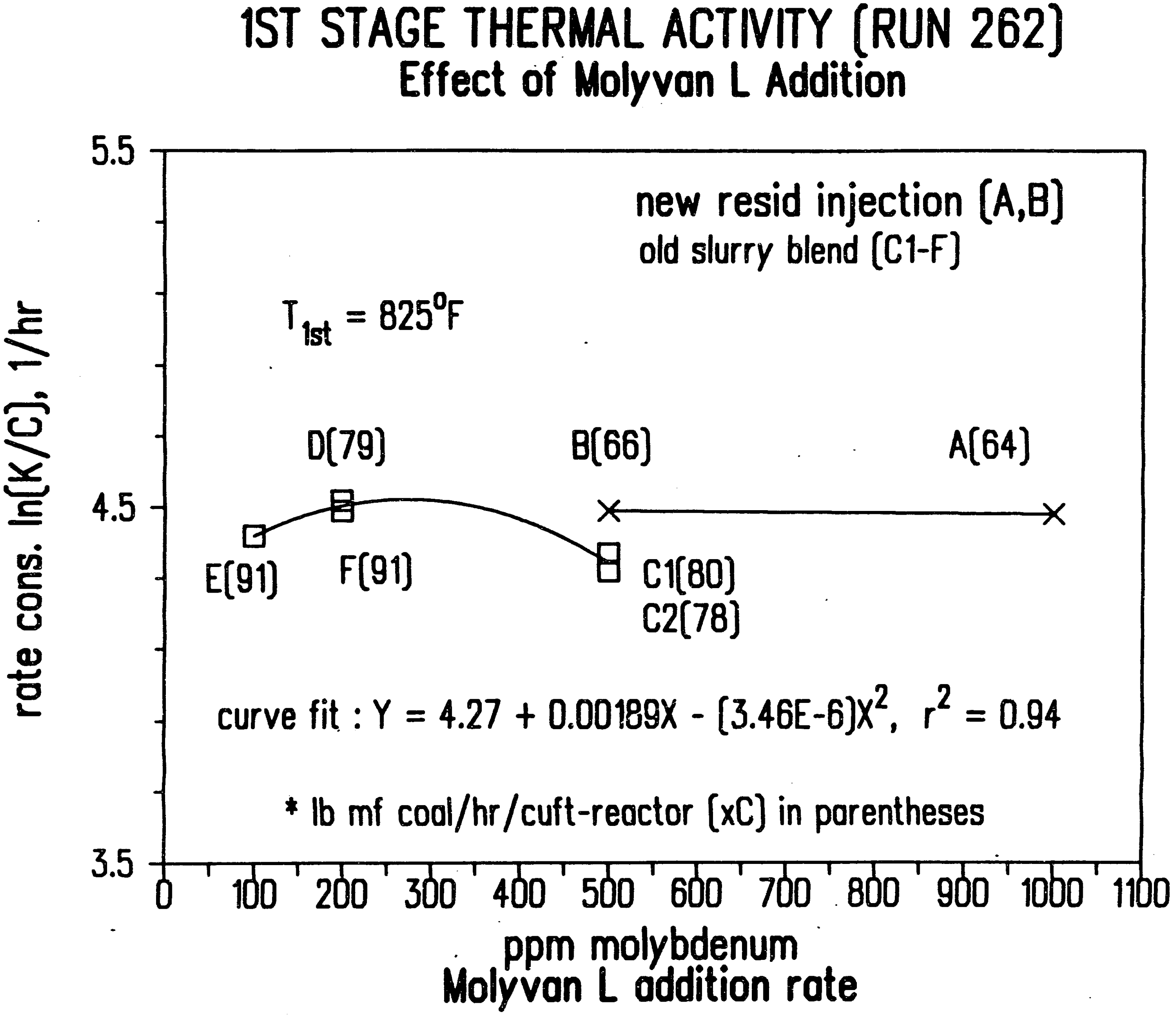


FIGURE 52. EFFECT OF MOLYBDENUM CONCENTRATION OF FIRST STAGE THERMAL CONVERSION ACTIVITY (262AB/262C-F)

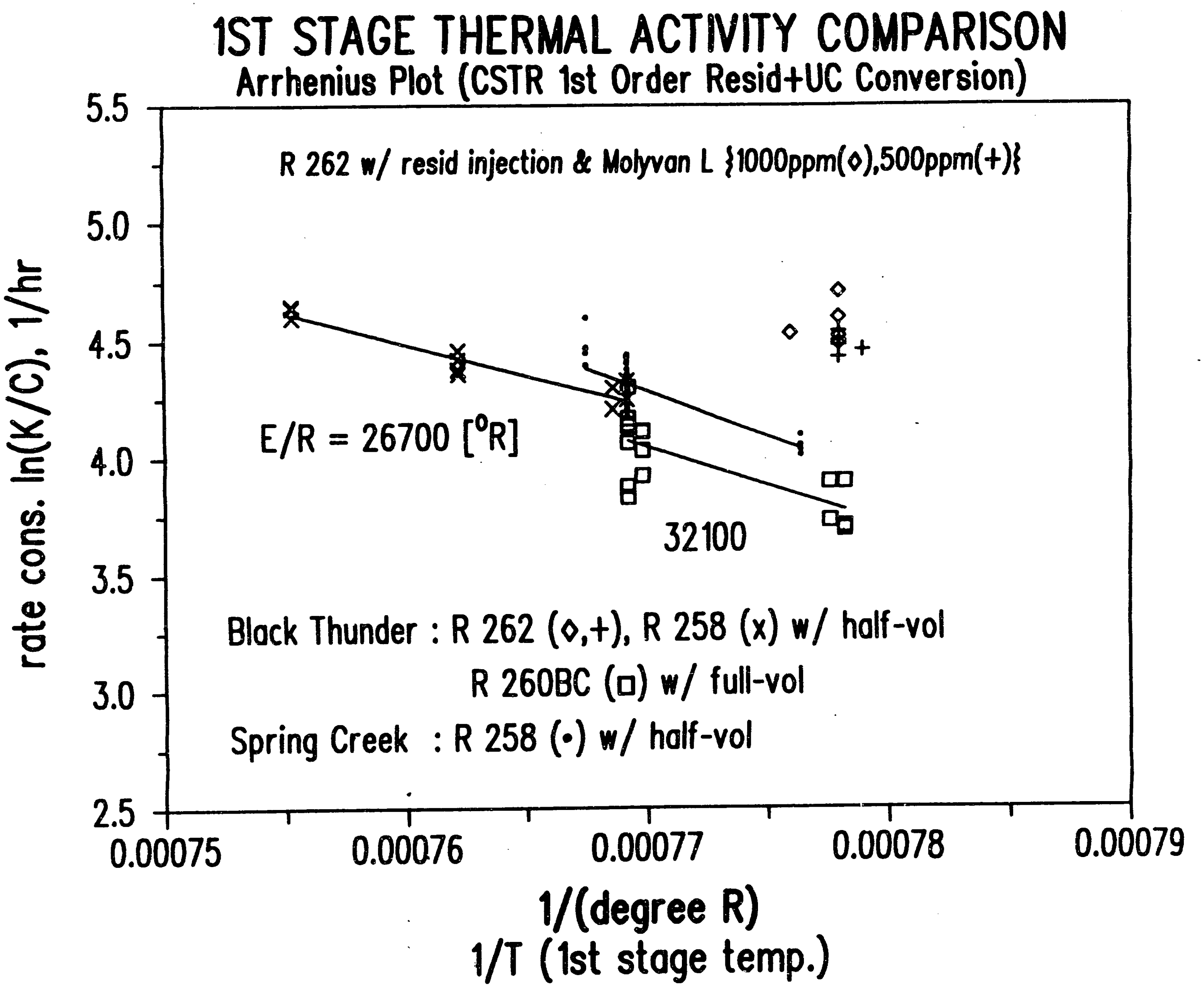


FIGURE 53. FIRST STAGE THERMAL ACTIVITY COMPARISON AND ARRHENIUS PLOT FOR THERMAL ACTIVATION ENERGY (Runs 262AB, 260, 258)

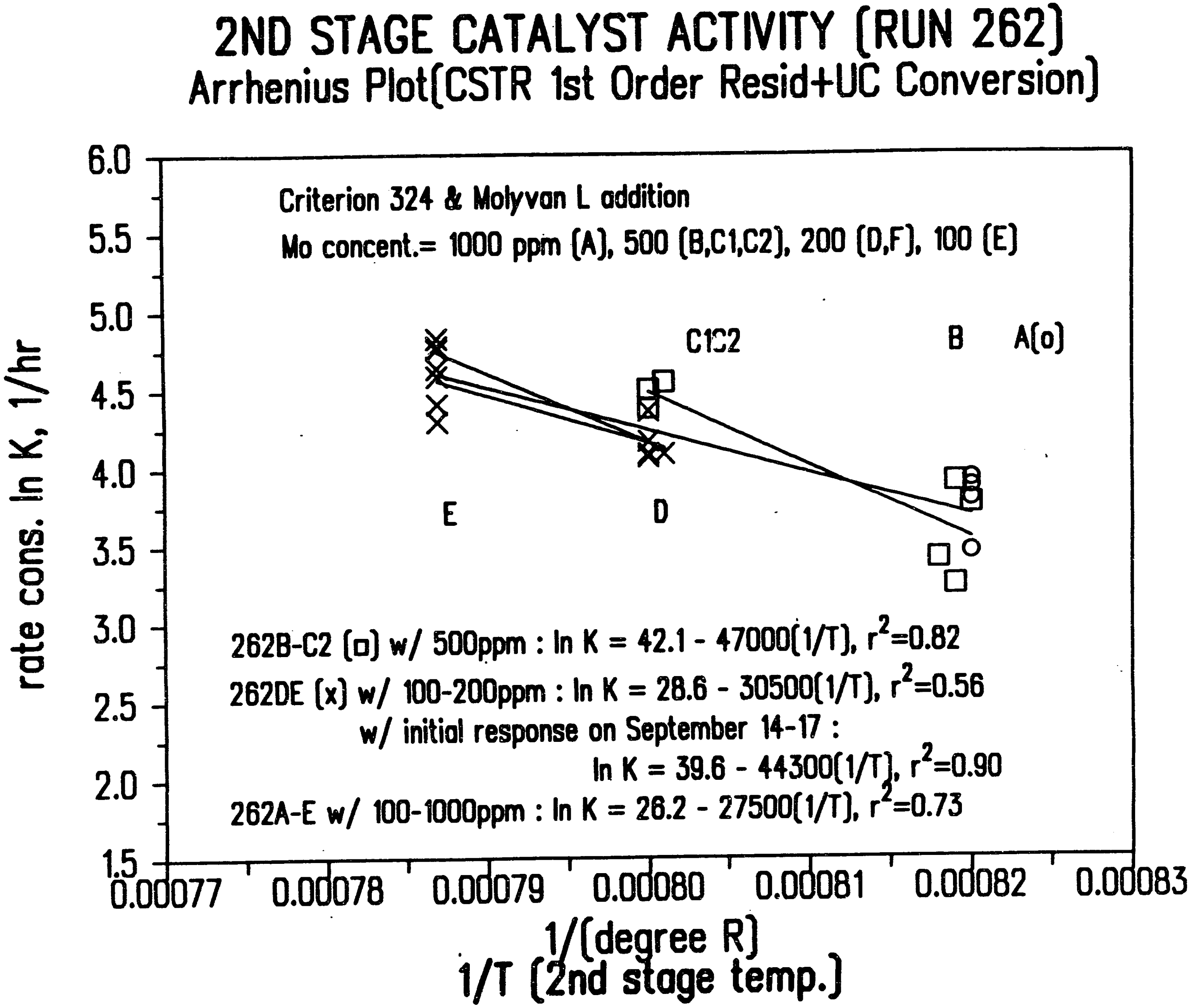


FIGURE 54. SECOND STAGE ARRHENIUS PLOT FOR CATALYTIC ACTIVATION ENERGY (262A-E)

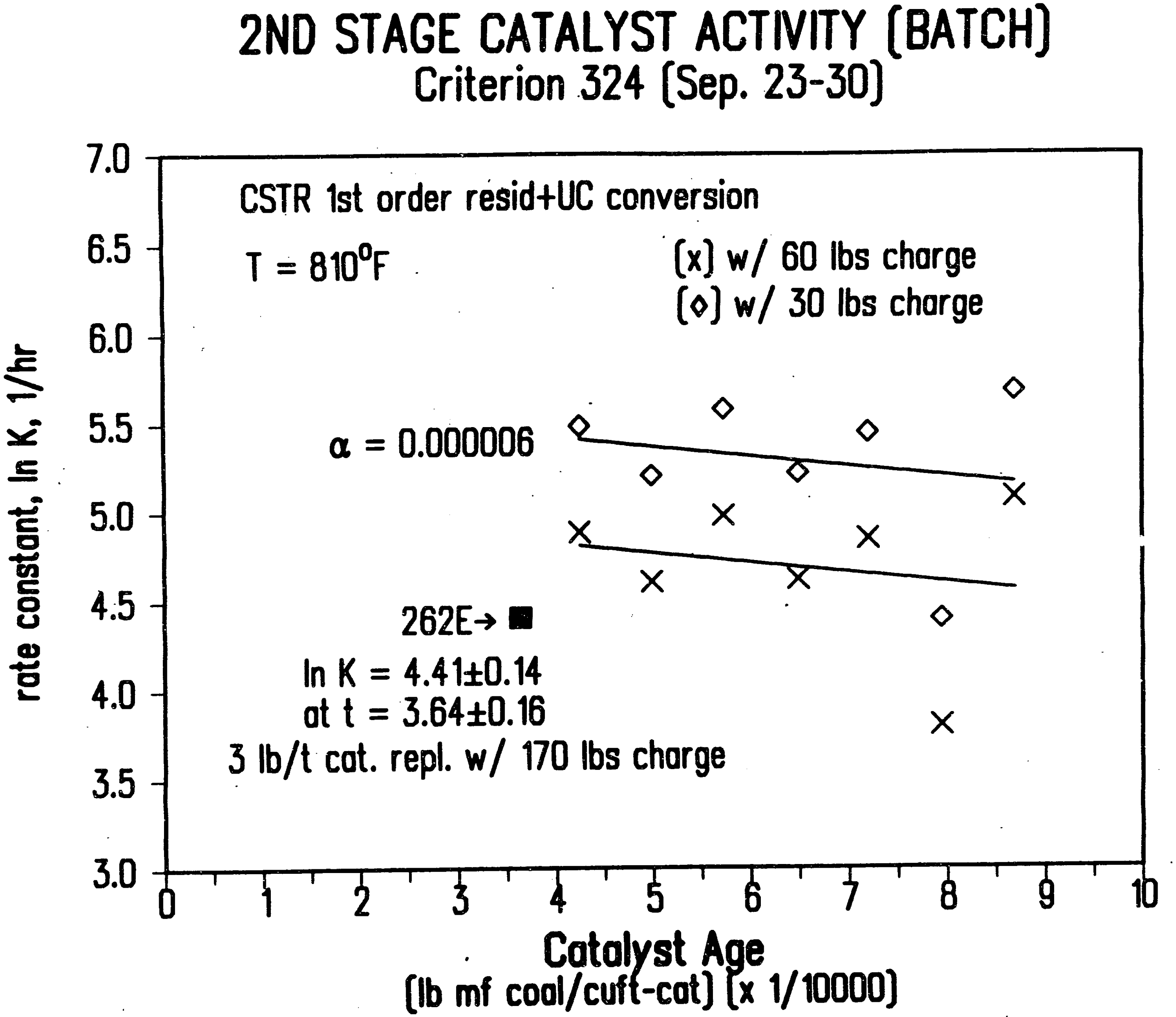


FIGURE 55. LINEAR REGRESSION ANALYSIS OF SECOND STAGE CONVERSION ACTIVITY WITH 30 OR 60 LBS CATALYST CHARGE (262F) (CRITERION 324 CATALYST; BATCH DEACTIVATION)

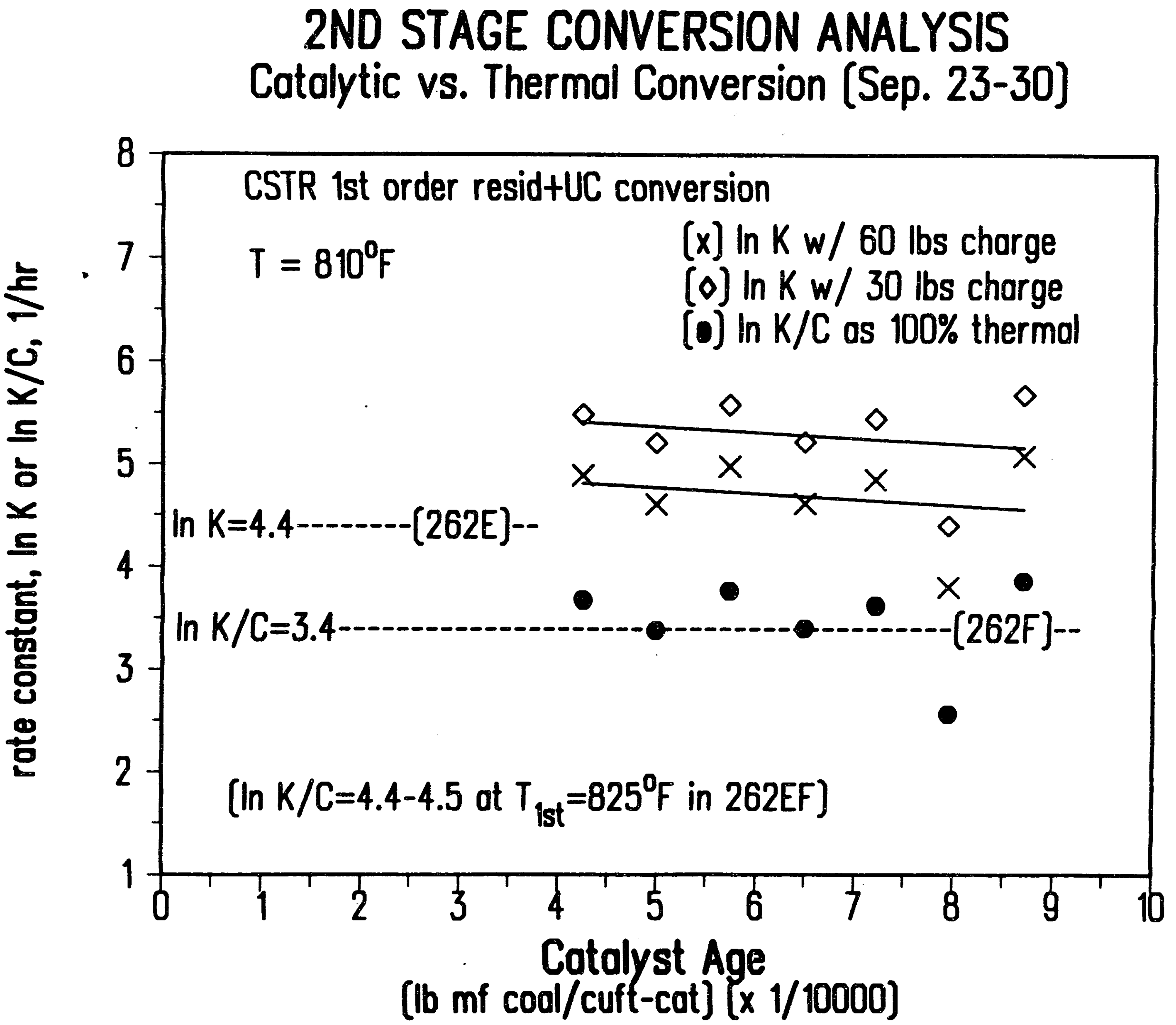


FIGURE 56. SECOND STAGE CONVERSION ANALYSIS - CATALYTIC VS. THERMAL CONVERSION (262F)

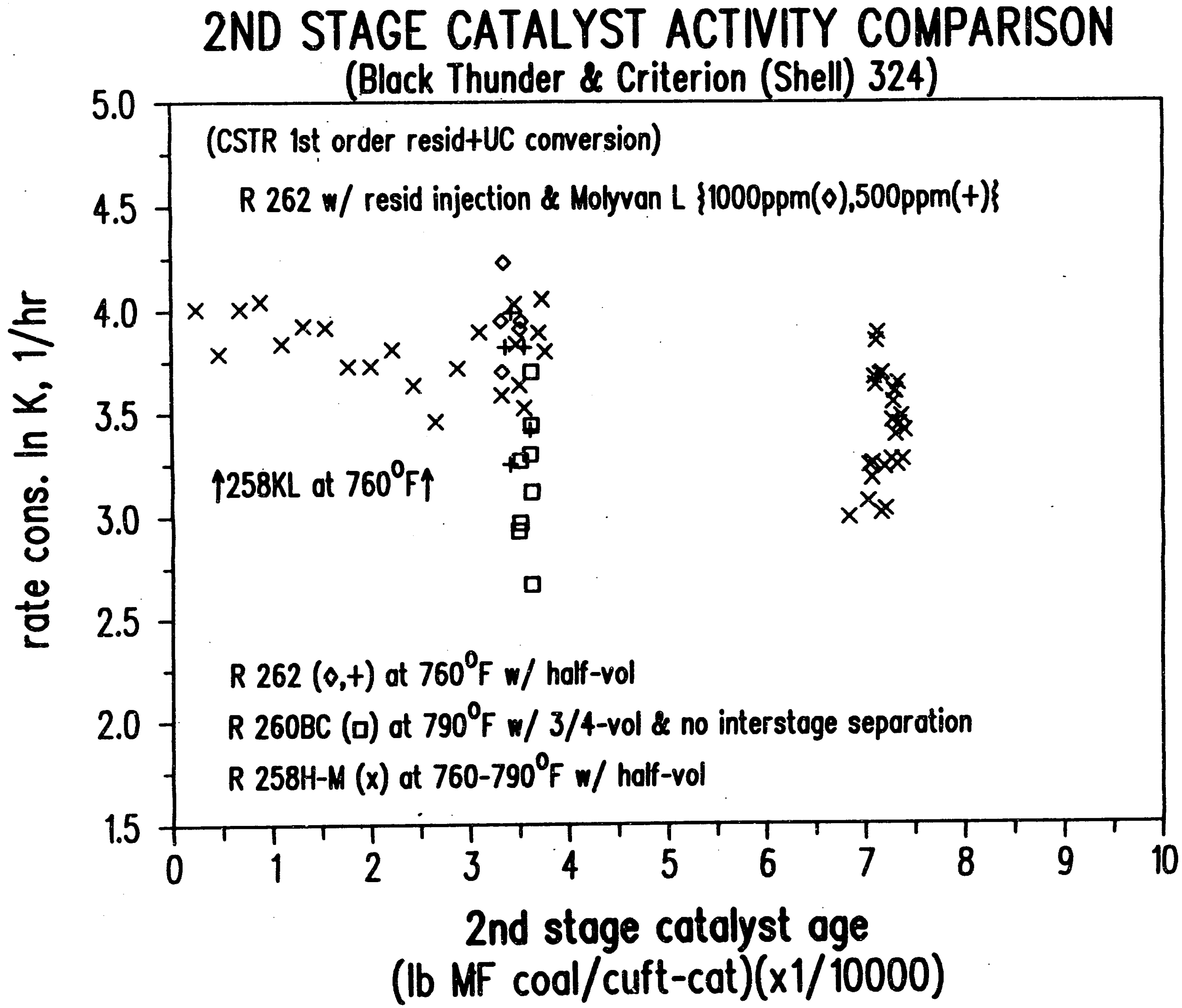


FIGURE 57. SECOND STAGE CATALYST ACTIVITY COMPARISON
(RUNS 262AB, 260BC, 258H-M)

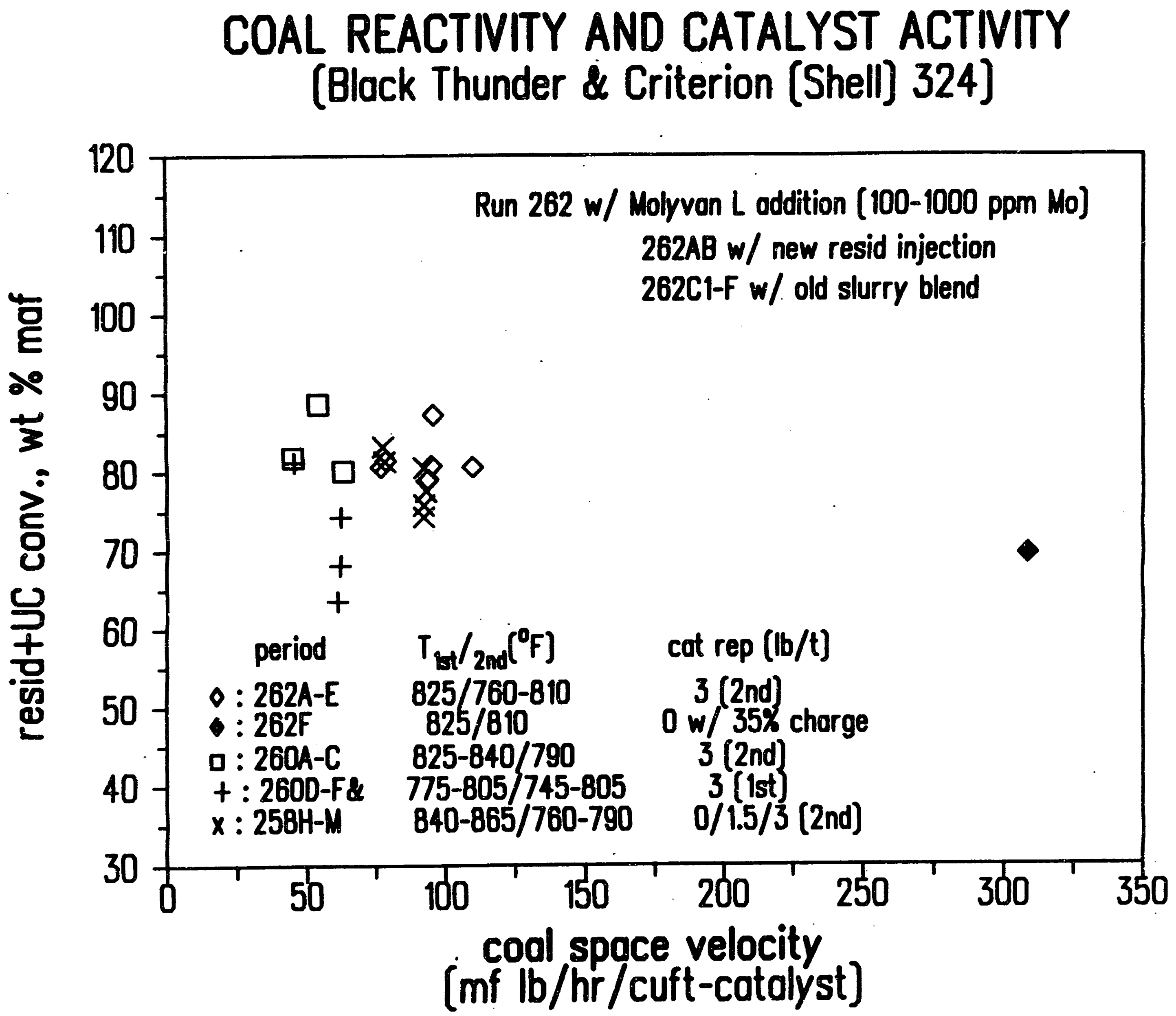


FIGURE 58. OVERALL TWO-STAGE RESID + UC CONVERSION COMPARISON (RUNS 262A-F, 260A-F, 258H-M) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT-CATALYST (2ND)

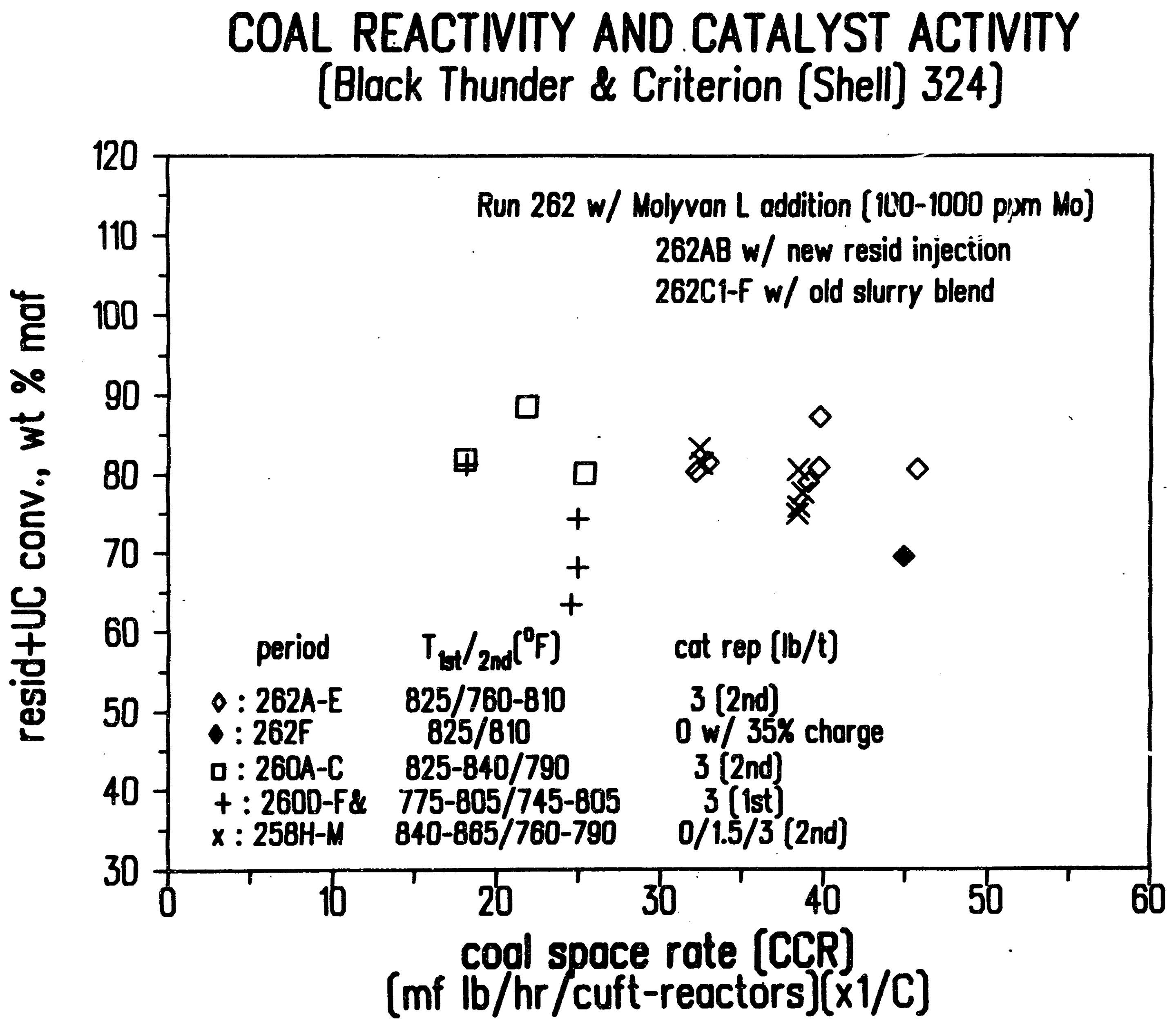


FIGURE 59. OVERALL TWO-STAGE RESID + UC CONVERSION COMPARISON (RUNS 262A-F, 260A-F, 258H-M) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT-REACTORS (CCR)

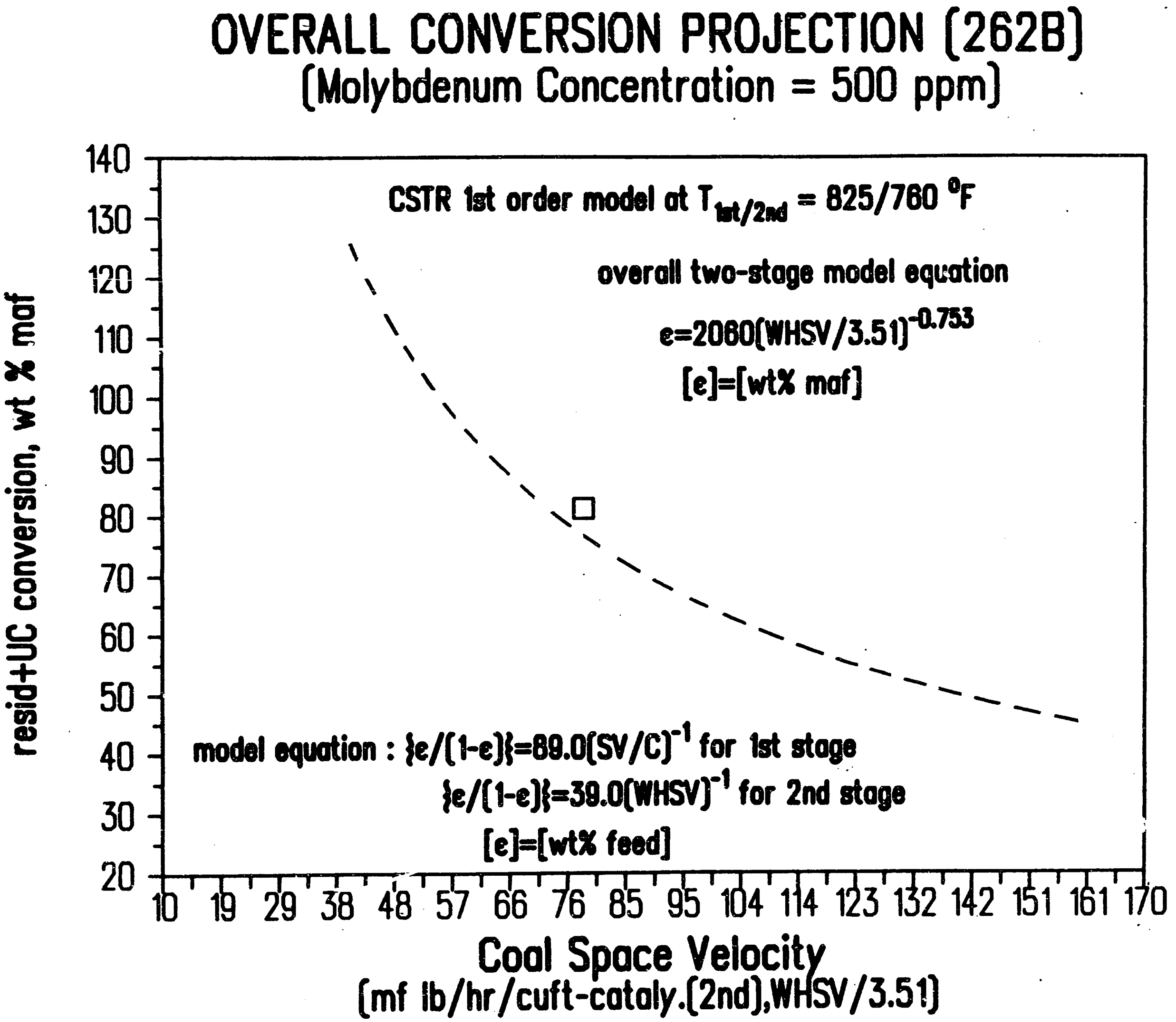


FIGURE 60. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262B) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT CATALYST (2ND)

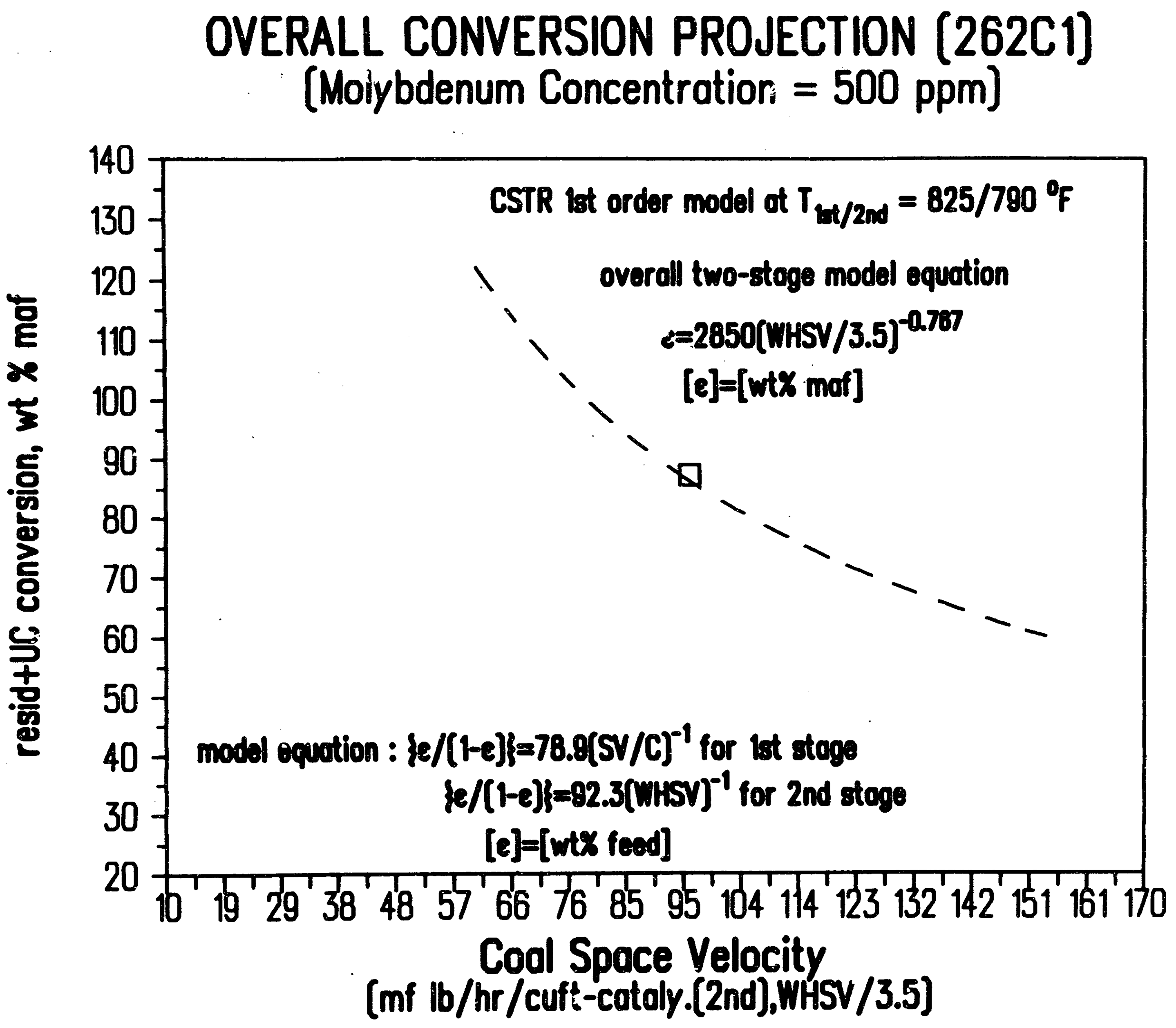
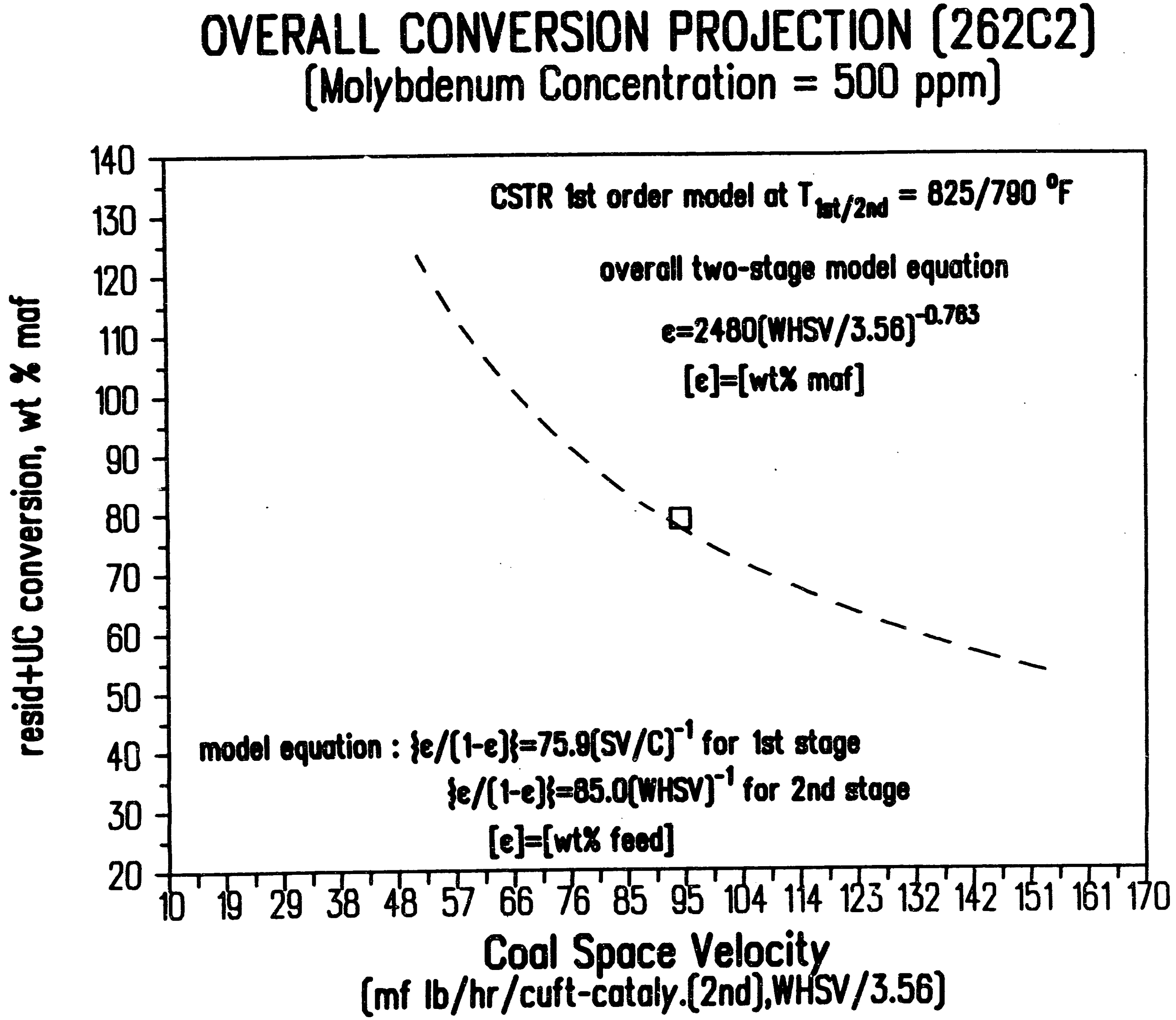


FIGURE 61. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262C1) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT CATALYST (2ND)


OVERALL CONVERSION PROJECTION (262C2)

(Molybdenum Concentration = 500 ppm)

FIGURE 62. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262C2) - SPACE VELOCITY: LB MF COAL/HR/CU FT CATALYST (2ND)

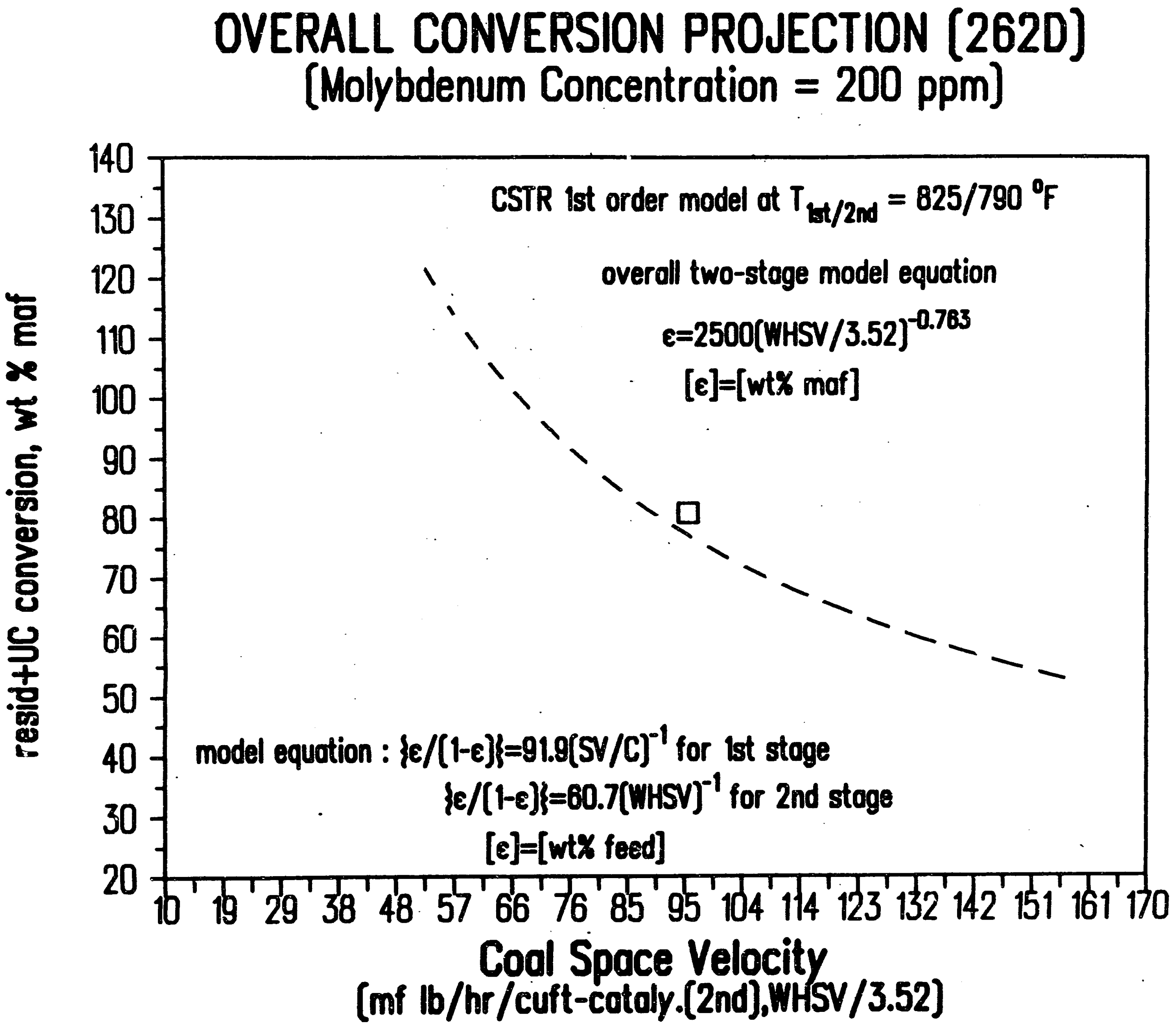


FIGURE 63. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262D) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT CATALYST (2ND)

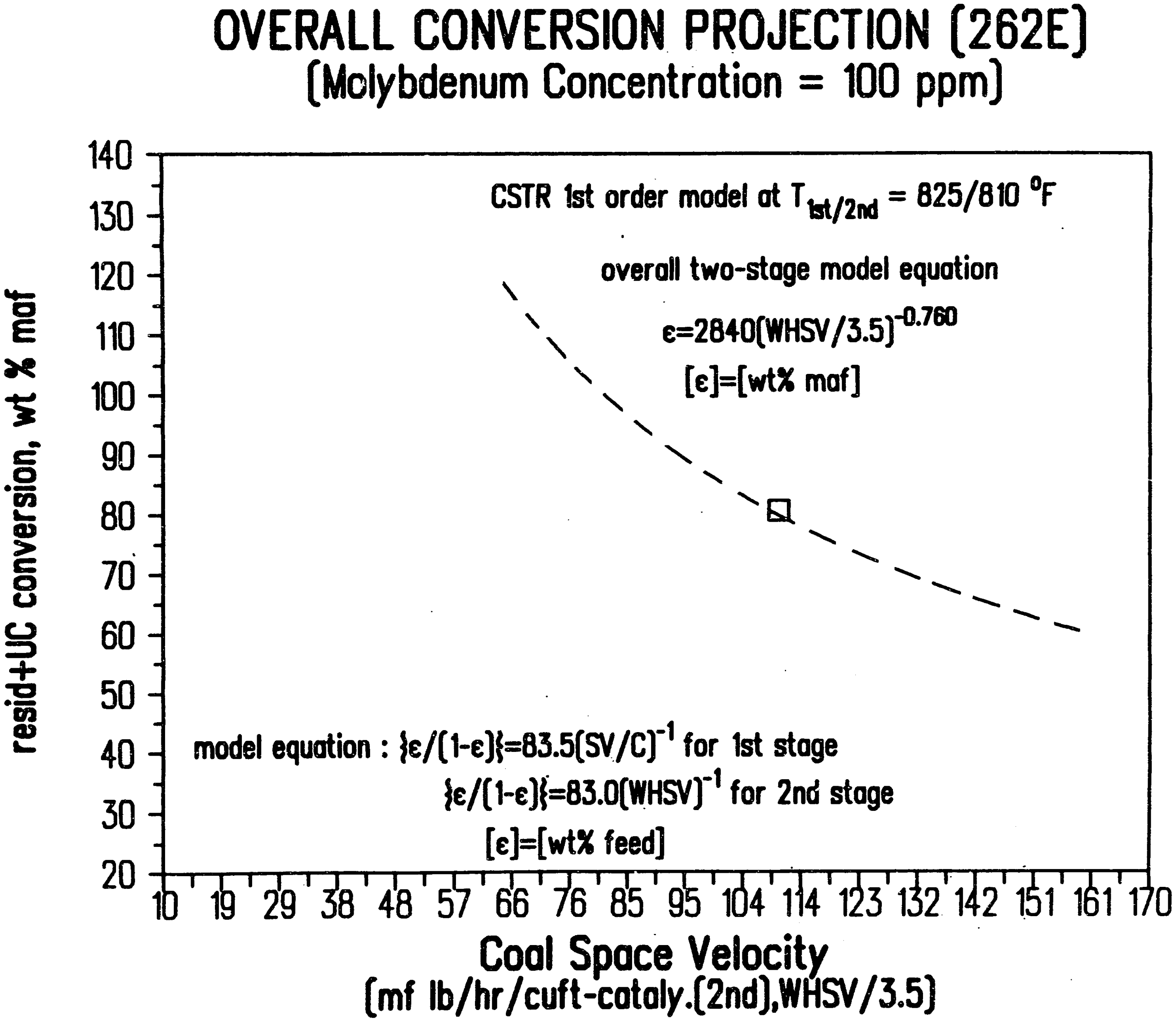


FIGURE 64. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262E) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT CATALYST (2ND)

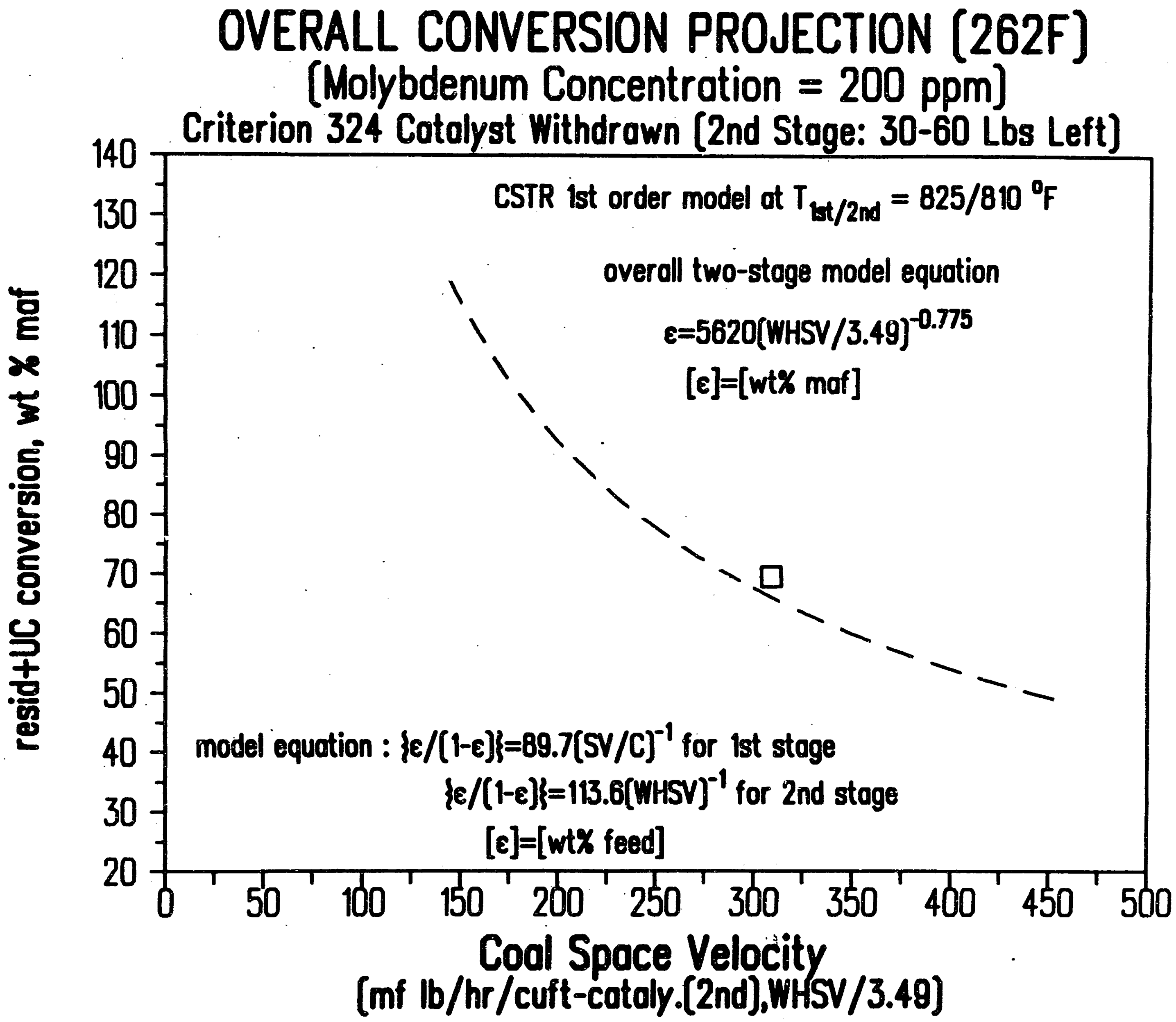


FIGURE 65. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262B) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT CATALYST (2ND)

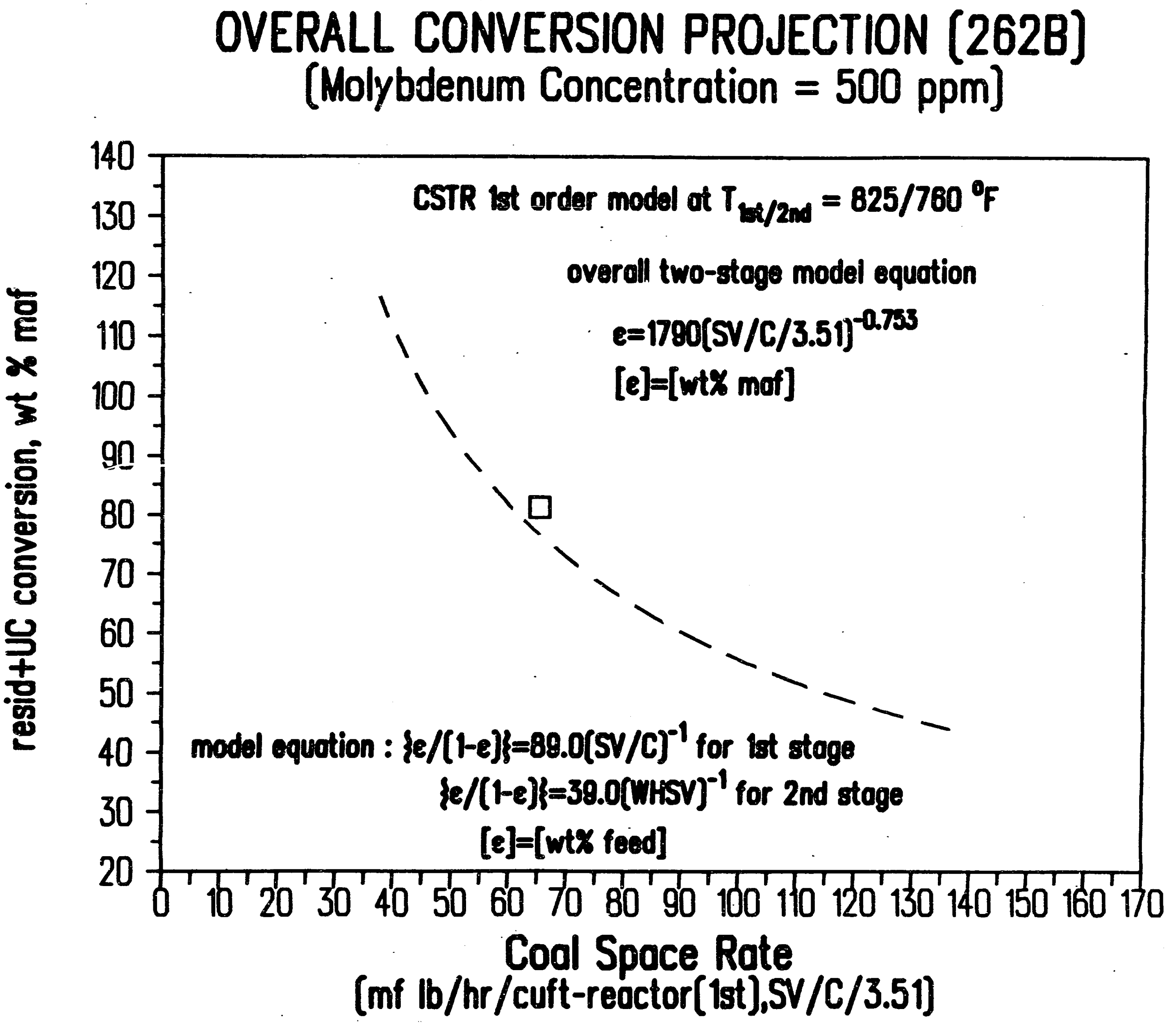


FIGURE 66. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262B) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)

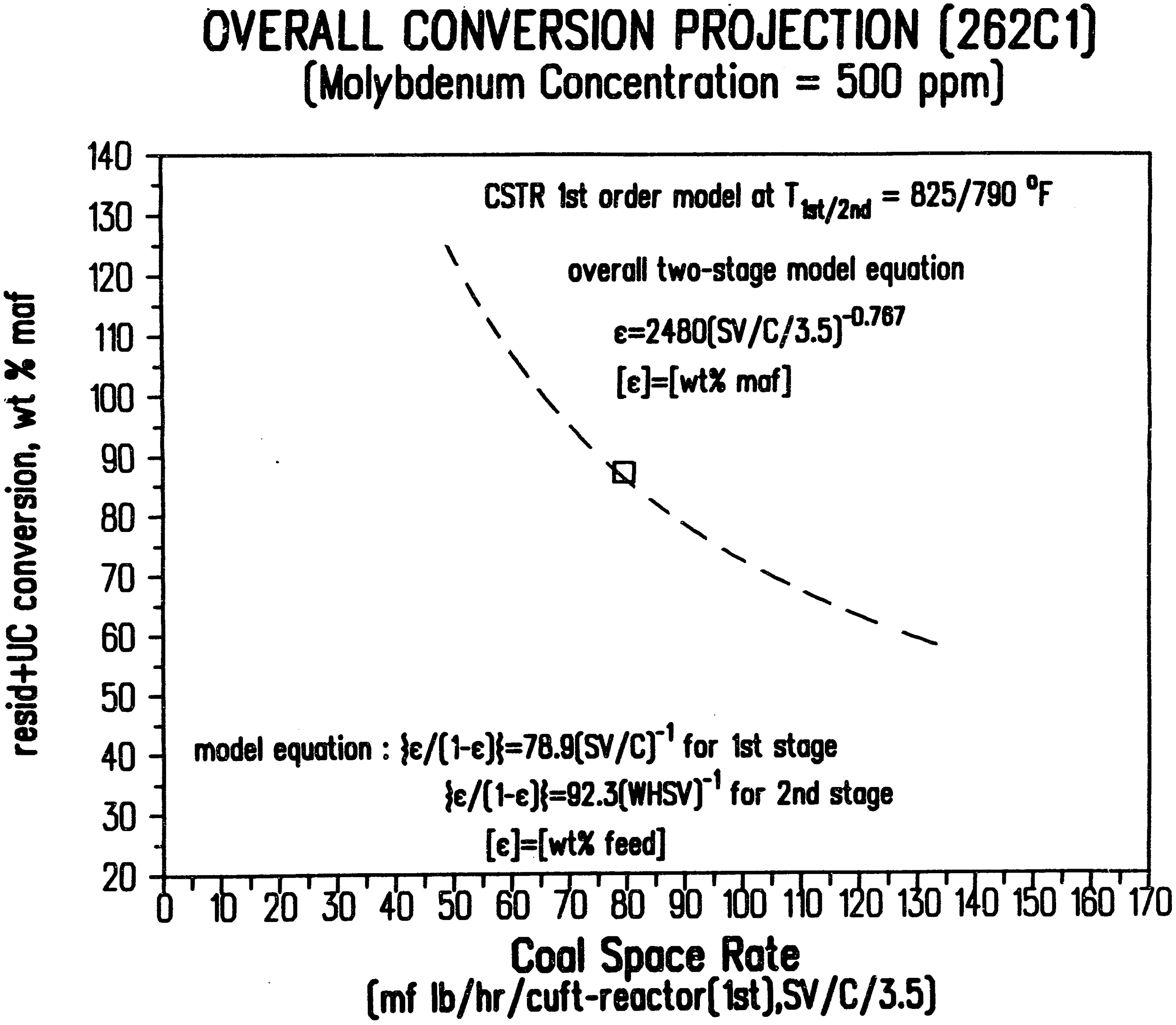
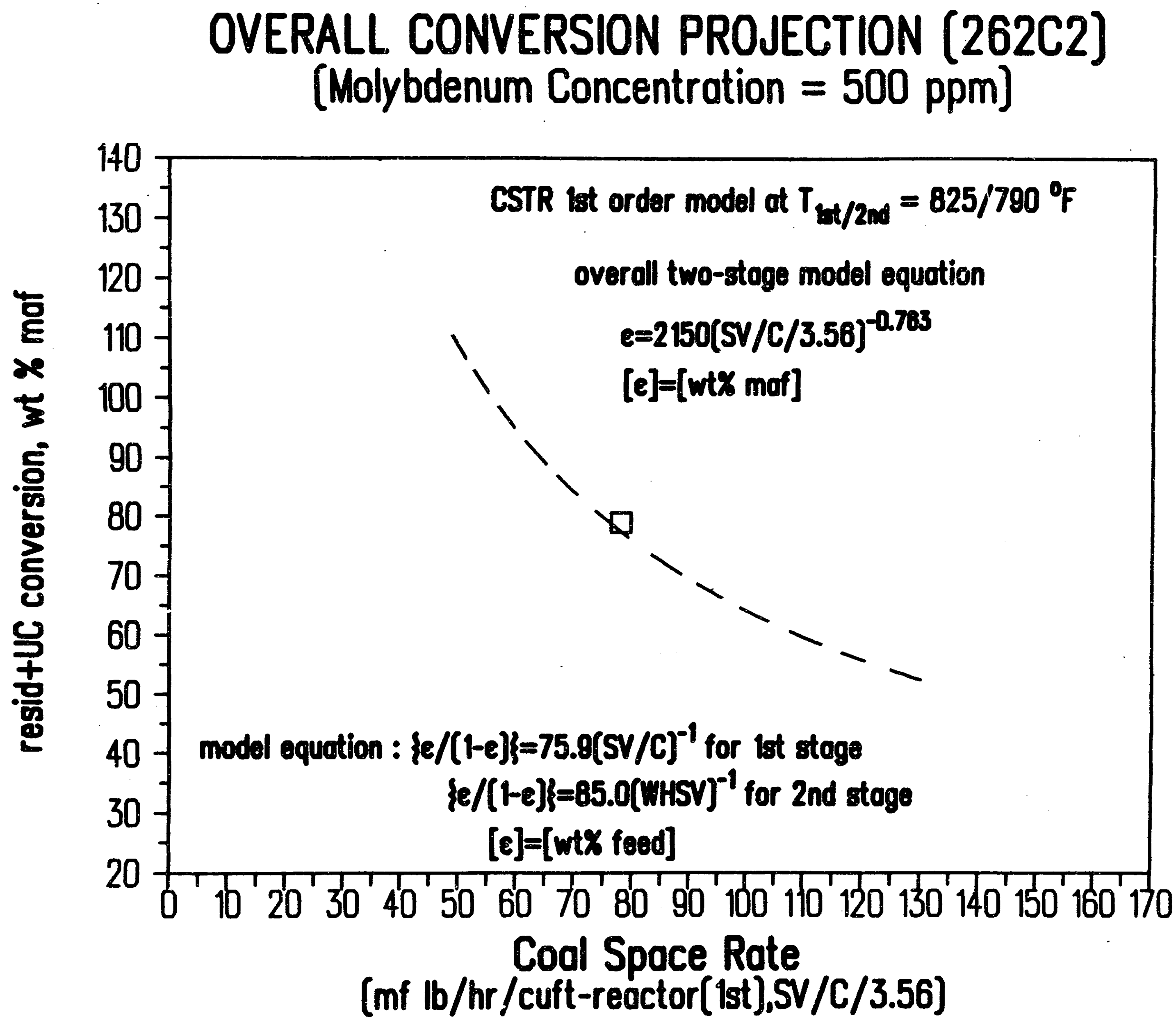


FIGURE 67. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262C1) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)



OVERALL CONVERSION PROJECTION (262C2)
(Molybdenum Concentration = 500 ppm)

FIGURE 68. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262C2) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)

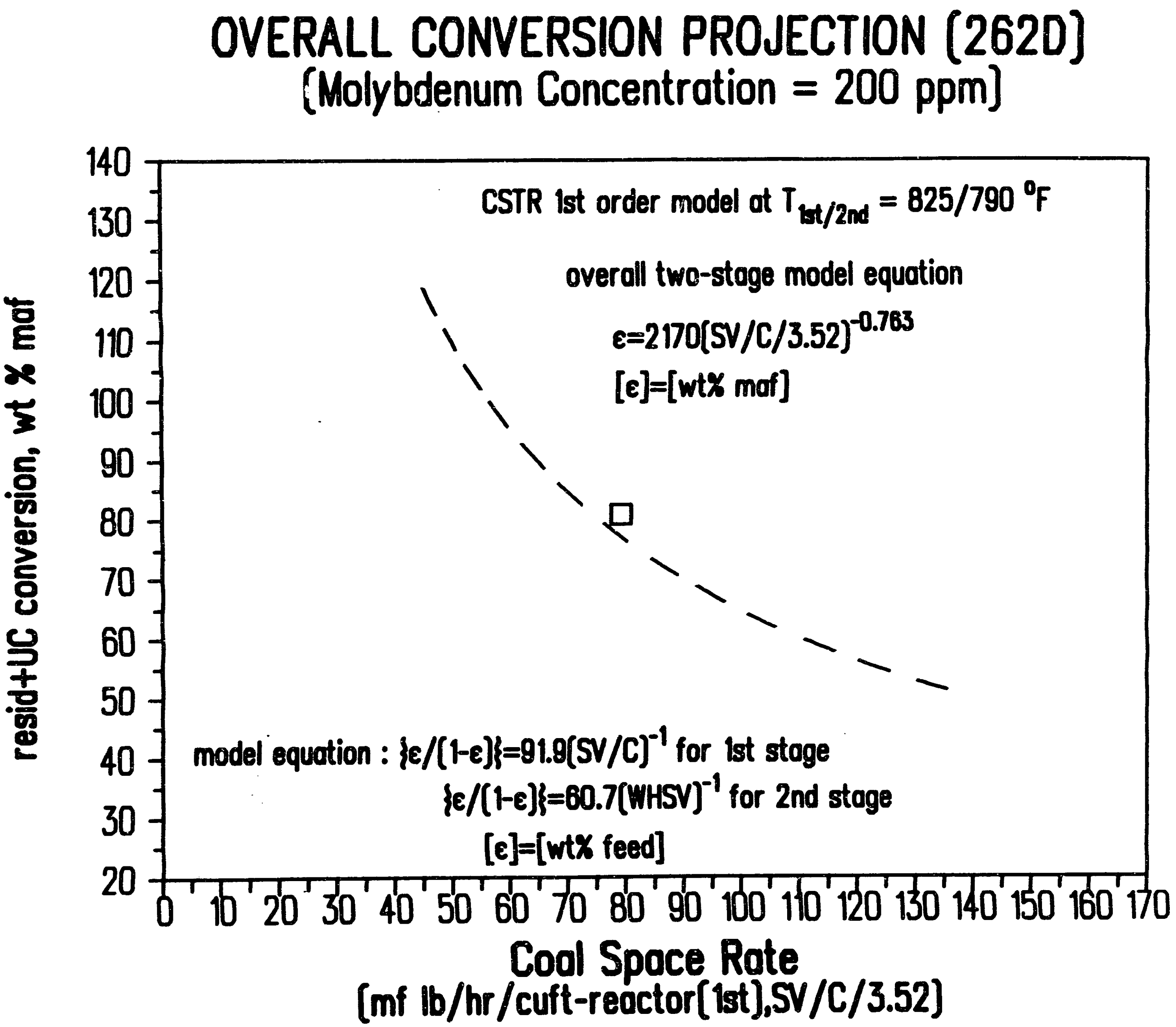


FIGURE 69. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262D) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)

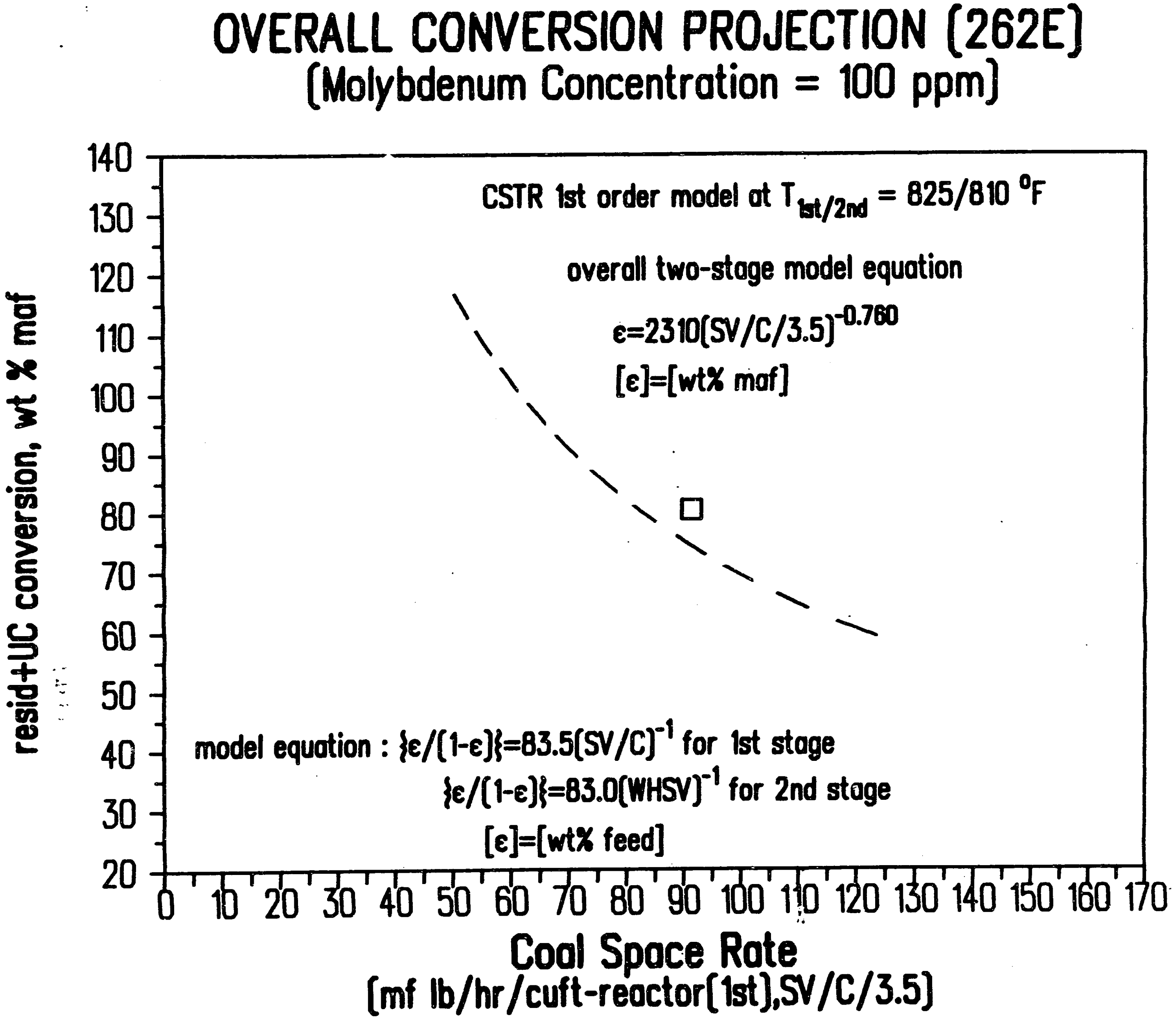


FIGURE 70. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262E) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)

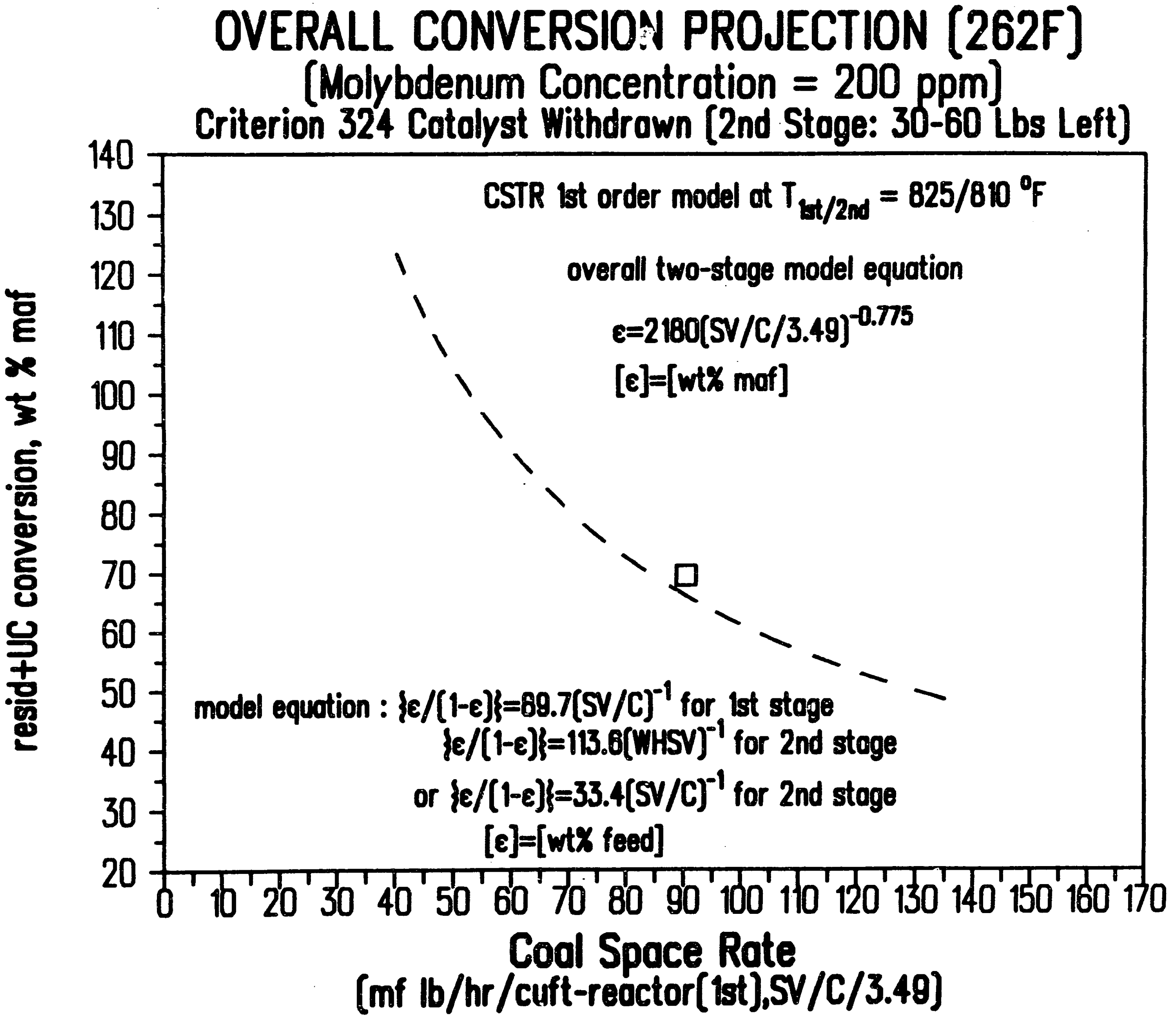


FIGURE 71. PROJECTION USING CSTR FIRST ORDER RESID + UC CONVERSION MODEL (262F) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT REACTOR (1ST)

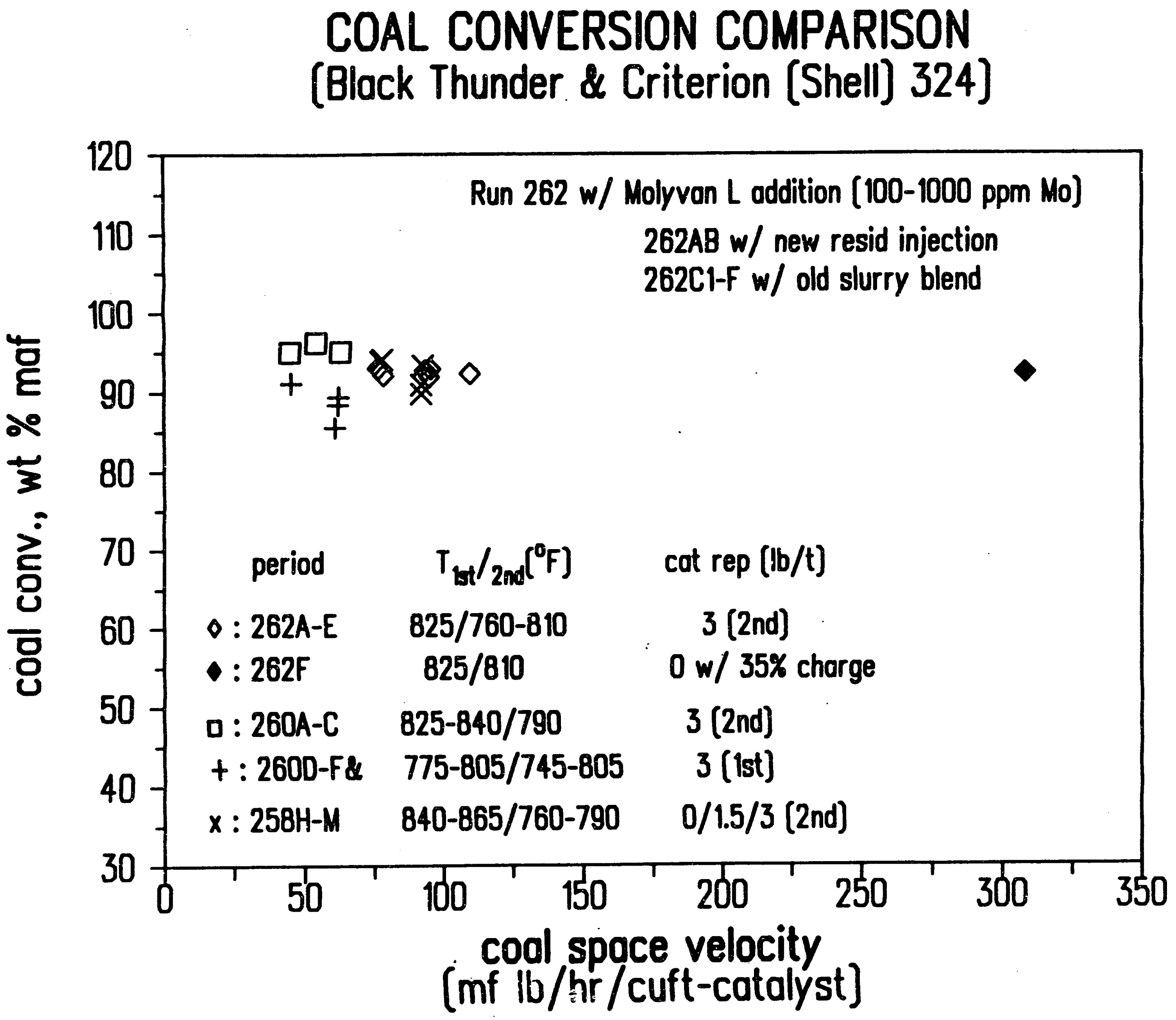


FIGURE 72. COAL CONVERSION COMPARISON (RUNS 262A-F, 260A-F, 258H-M) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT-CATALYST (2ND)

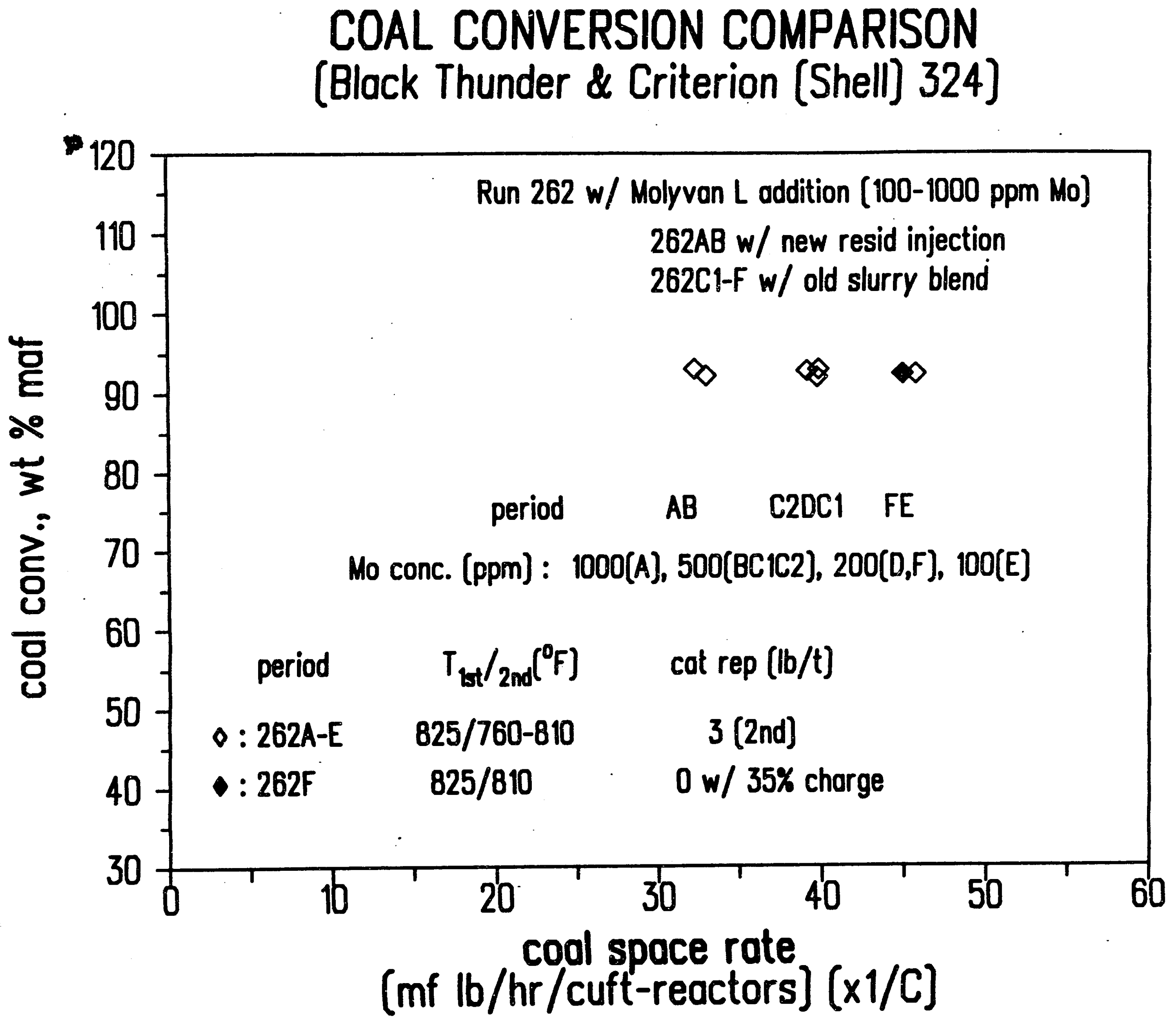


FIGURE 73. COAL CONVERSION COMPARISON (262A-F) - SPACE VELOCITY UNIT: LB MF COAL/HR/CU FT - REACTOR (CCR)

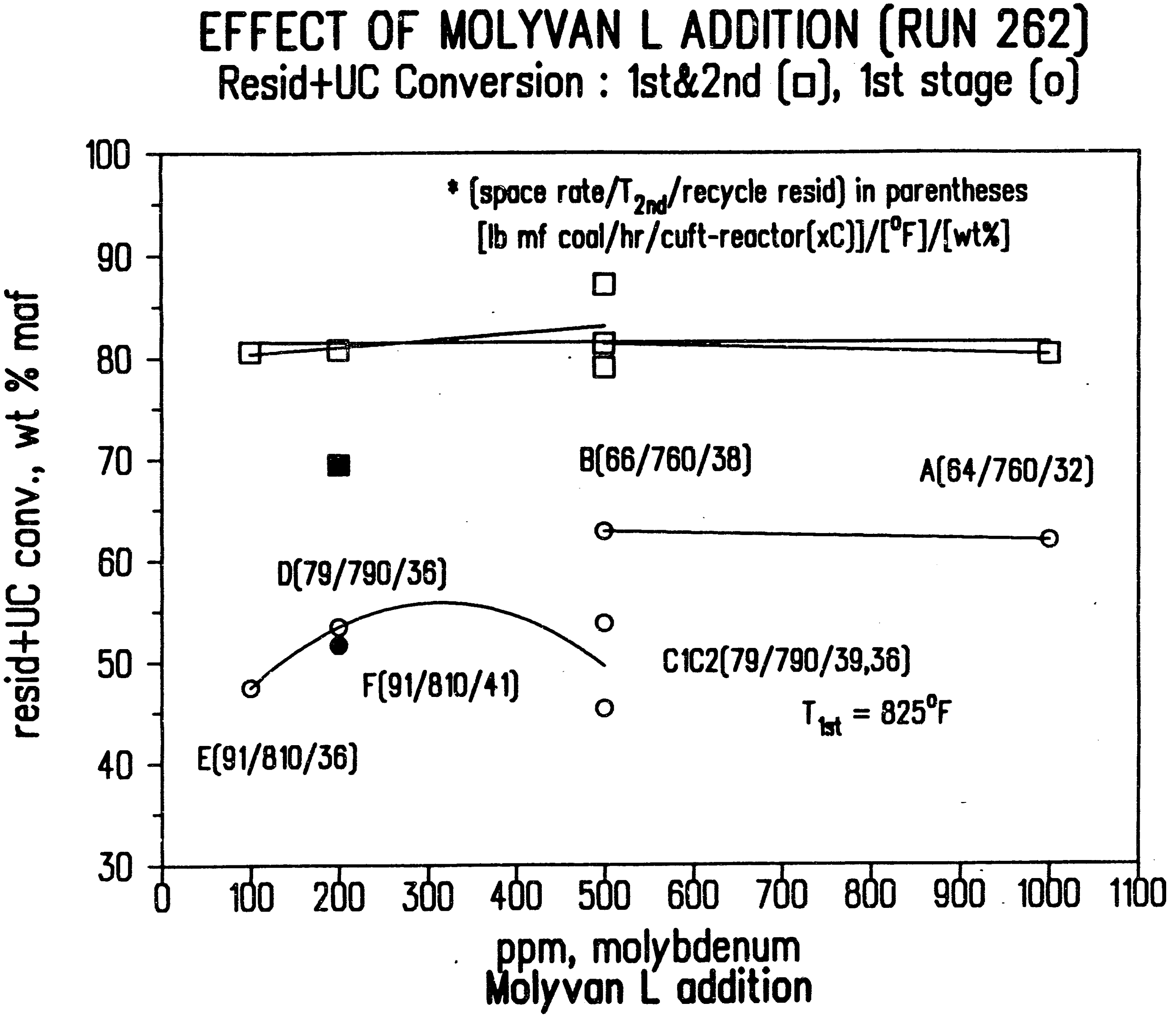


FIGURE 74. EFFECT OF MOLYBDENUM CONCENTRATION ON RESID + UC CONVERSION (262A-F)

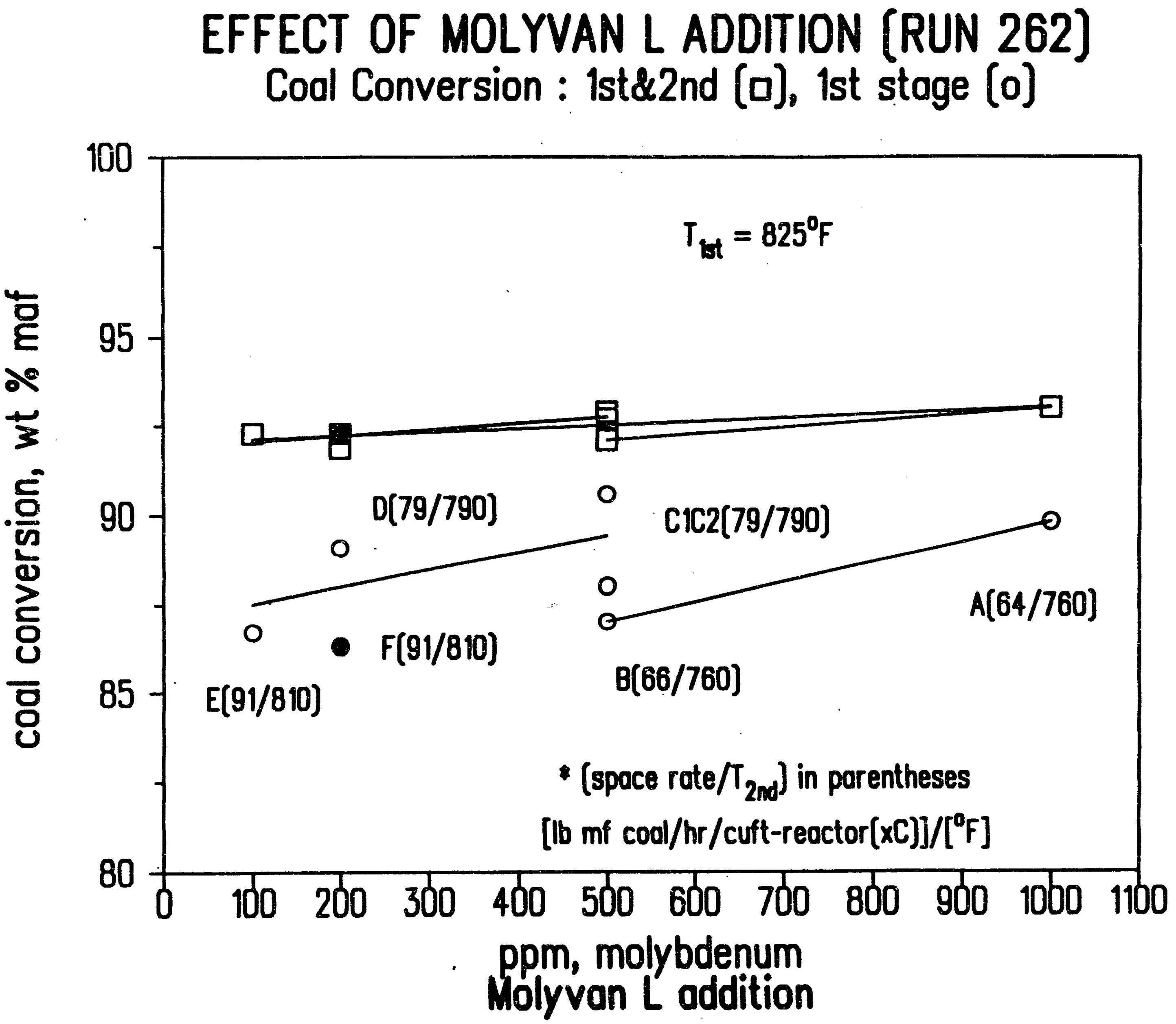


FIGURE 75. EFFECT OF MOLYBDENUM CONCENTRATION ON COAL CONVERSION (262A-F)

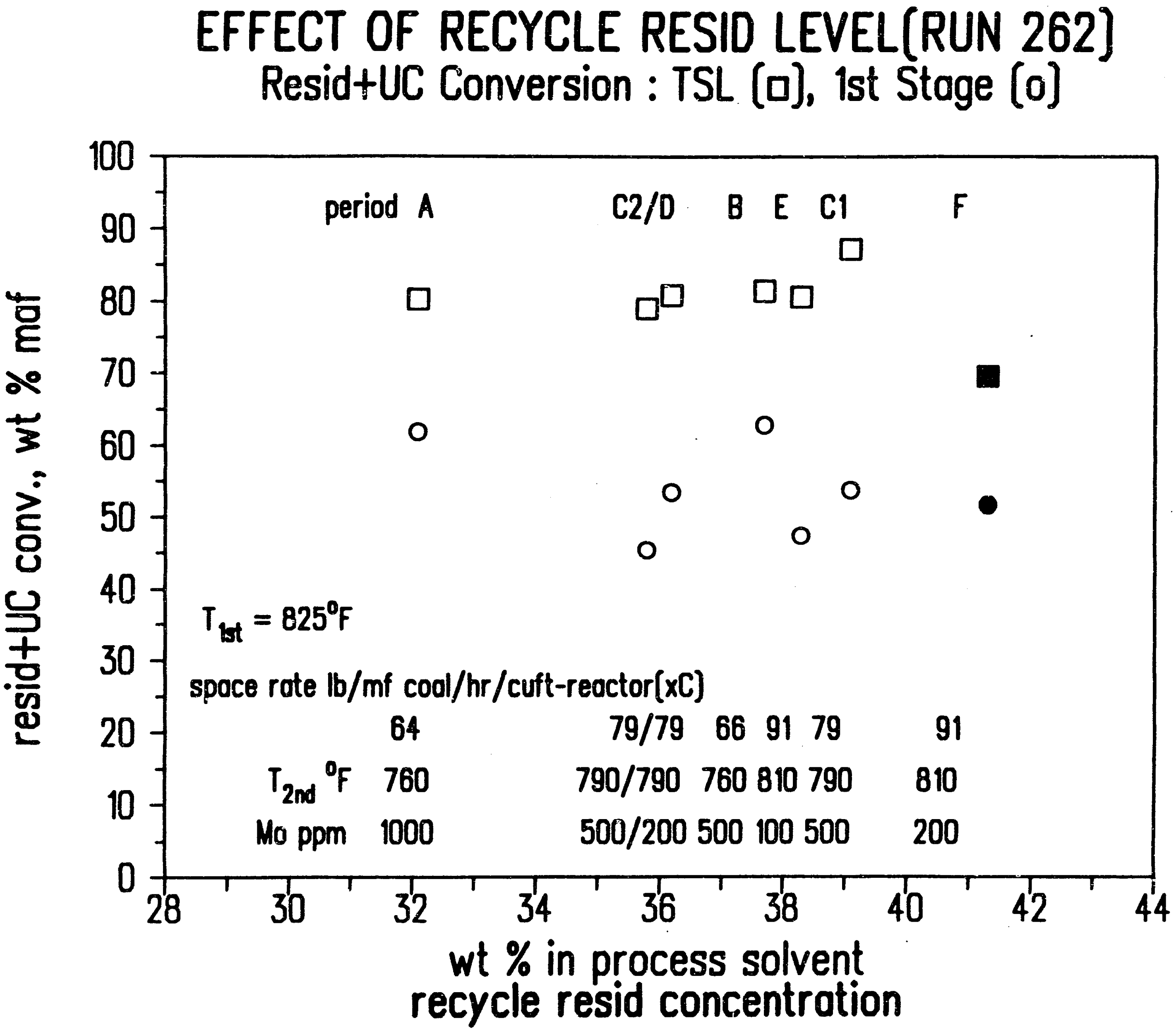


FIGURE 76. EFFECT OF RECYCLE RESID CONCENTRATION ON RESID + UC CONVERSION (262A-F)

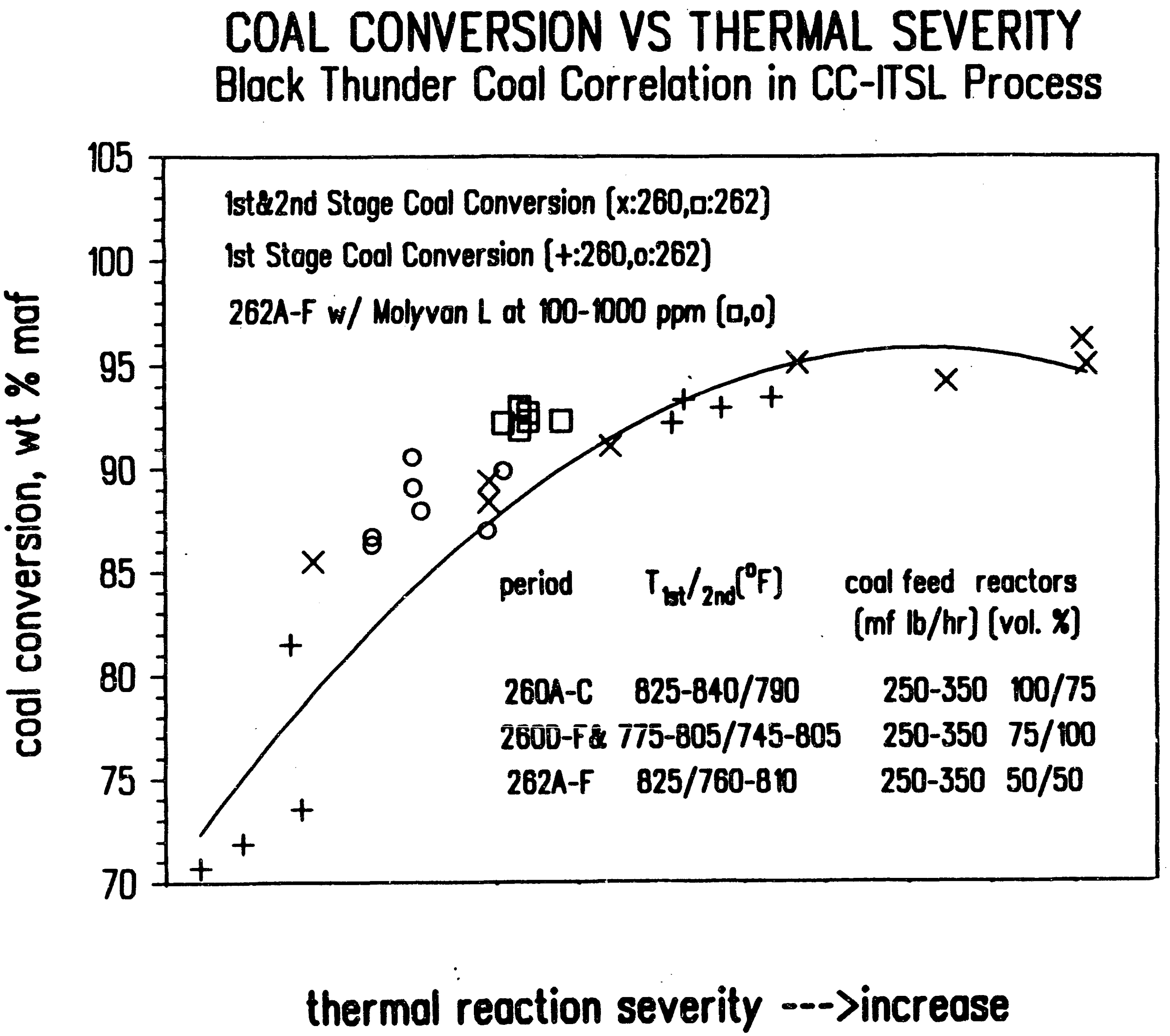


FIGURE 77. EFFECT OF THERMAL REACTION SEVERITY ON COAL CONVERSION (RUNS 262A-F, 260A-F)

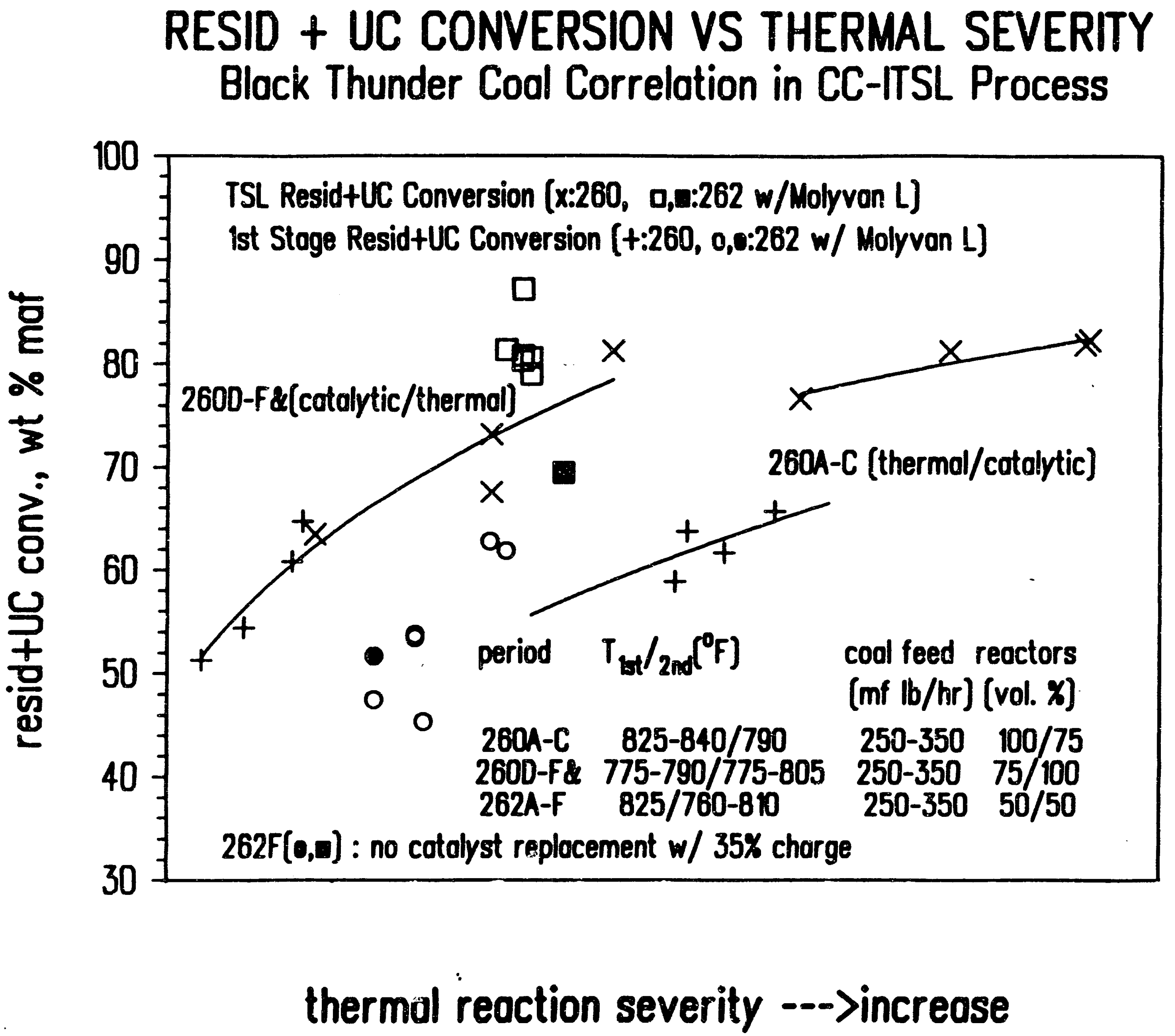


FIGURE 78. EFFECT OF THERMAL REACTION SEVERITY ON RESID + UC CONVERSION (RUNS 262A-F, 260A-F)

ORGANIC REJECTION VS COAL CONVERSION

Low-Rank Coal Correlation in CC-ITSL Process

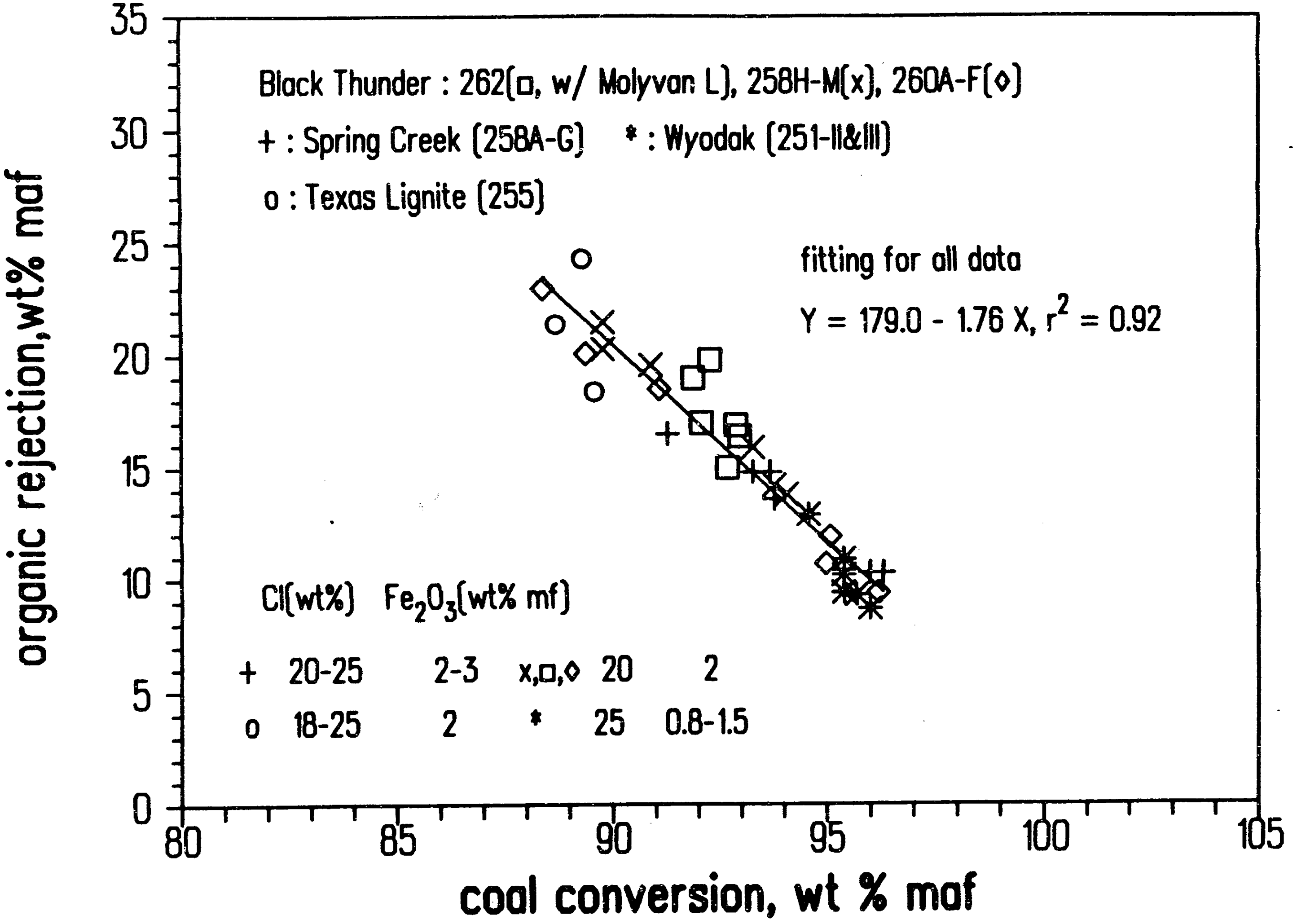


FIGURE 79. LINEAR CORRELATION BETWEEN ORGANIC REJECTION AND COAL CONVERSION IN LOW-RANK COALS (RUNS 262, 260, 258, 255, 251-II, 251-III)

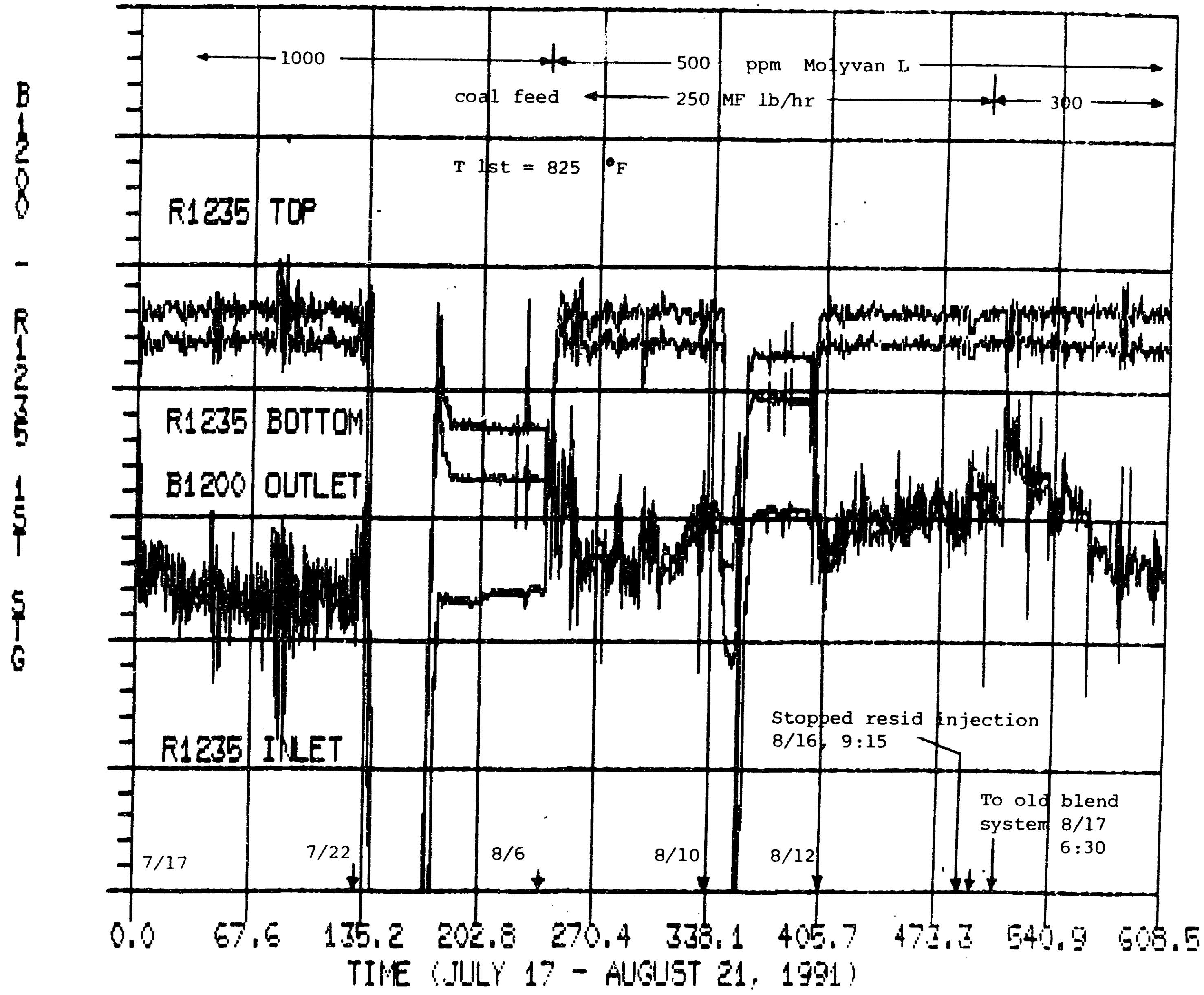


FIGURE 80. PREHEATER OUTLET AND FIRST STAGE REACTOR TEMPERATURE TREND (JULY 17-AUGUST 21, 1991)

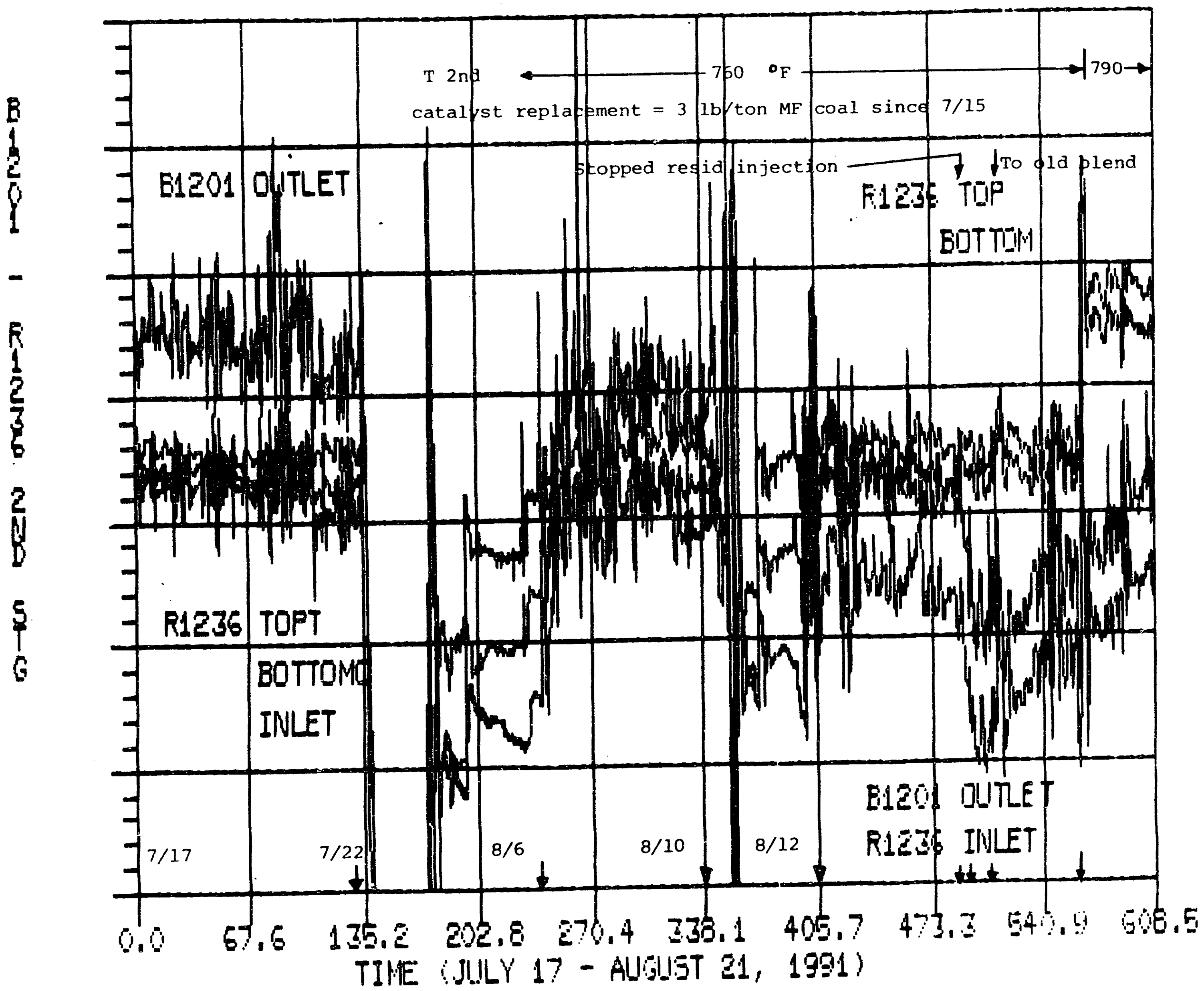


FIGURE 81. INTERSTAGE HEATER OUTLET AND SECOND STAGE REACTOR TEMPERATURE TREND (JULY 17-AUGUST 21, 1991)

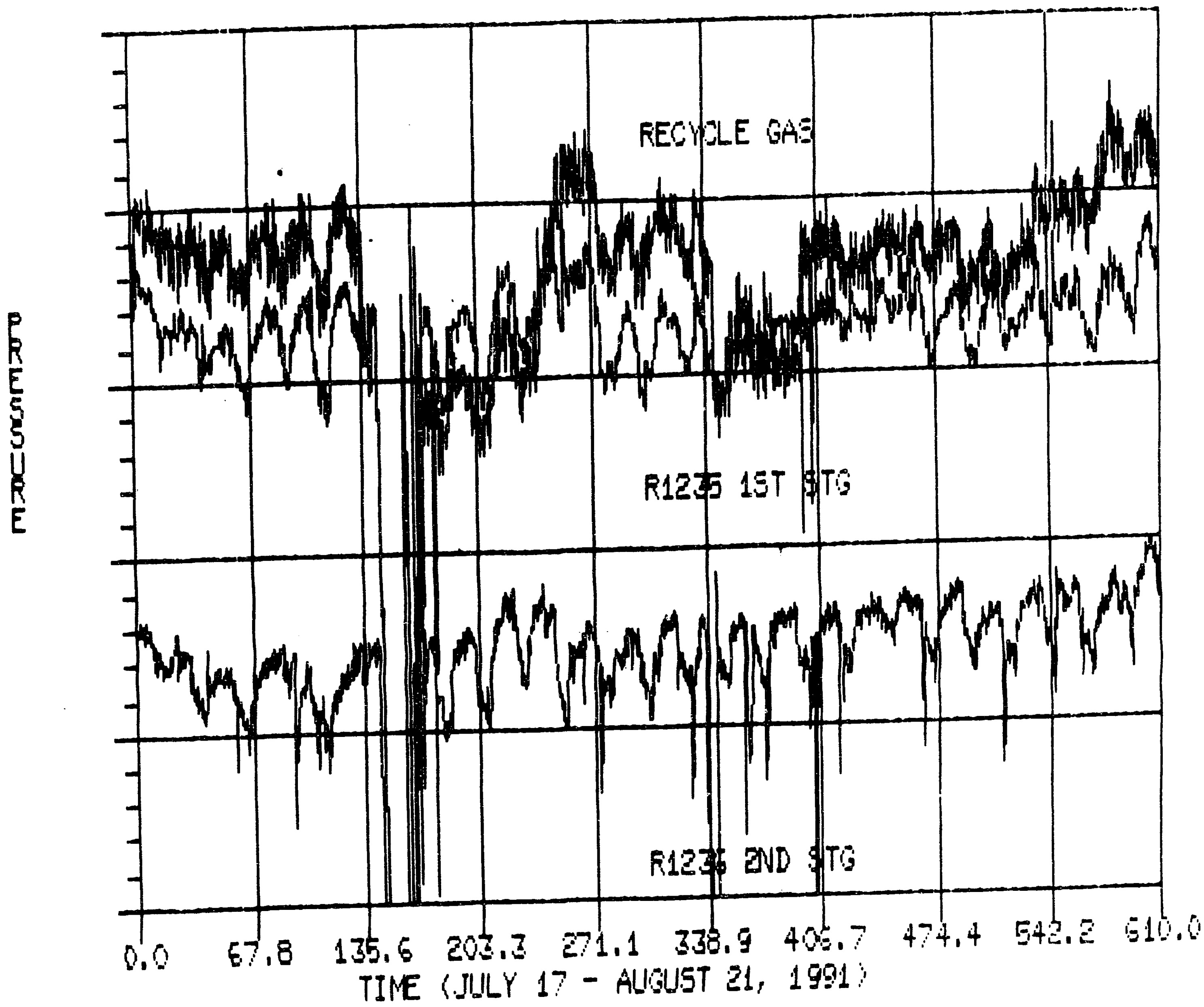


FIGURE 82. SYSTEM PRESSURE TREND (JULY 17-AUGUST 21, 1991)

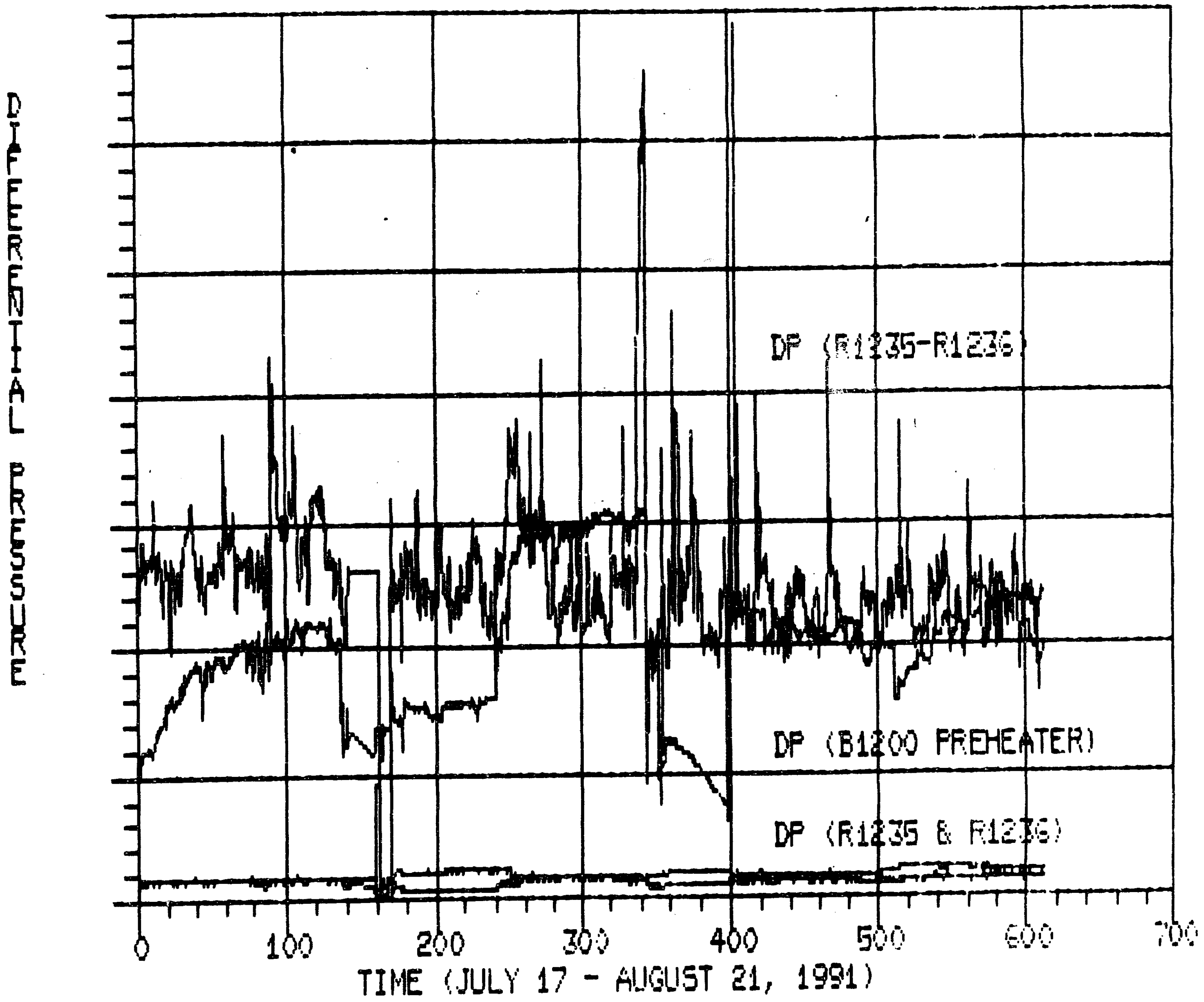


FIGURE 83. DIFFERENTIAL PRESSURE TREND (JULY 17-AUGUST 21, 1991)

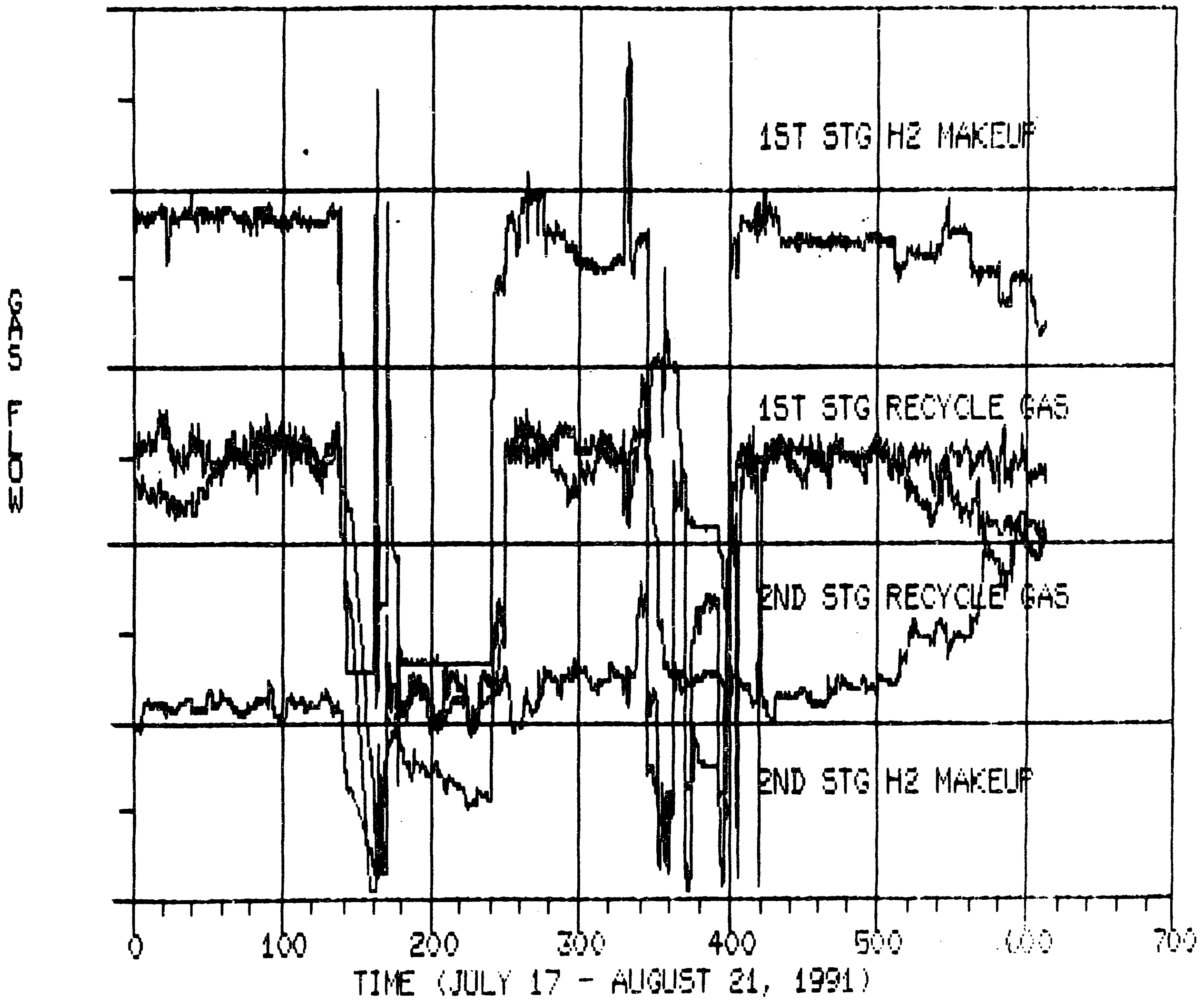


FIGURE 84. GAS FLOW RATE TREND (JULY 17-AUGUST 21, 1991)

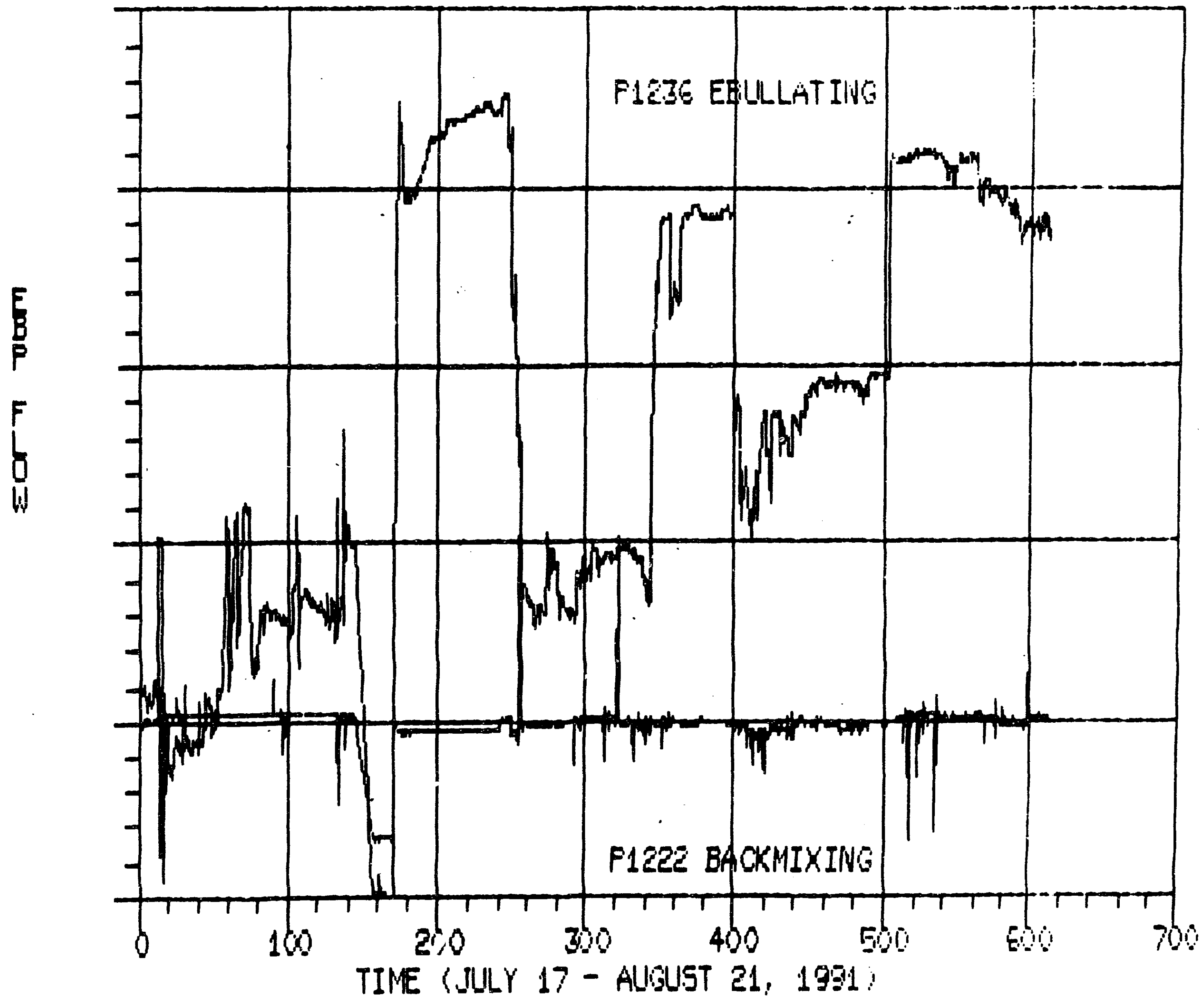


FIGURE 85. EBULLATING AND BACKMIXING PUMP FLOW RATE TREND (JULY 17-AUGUST 21, 1991)

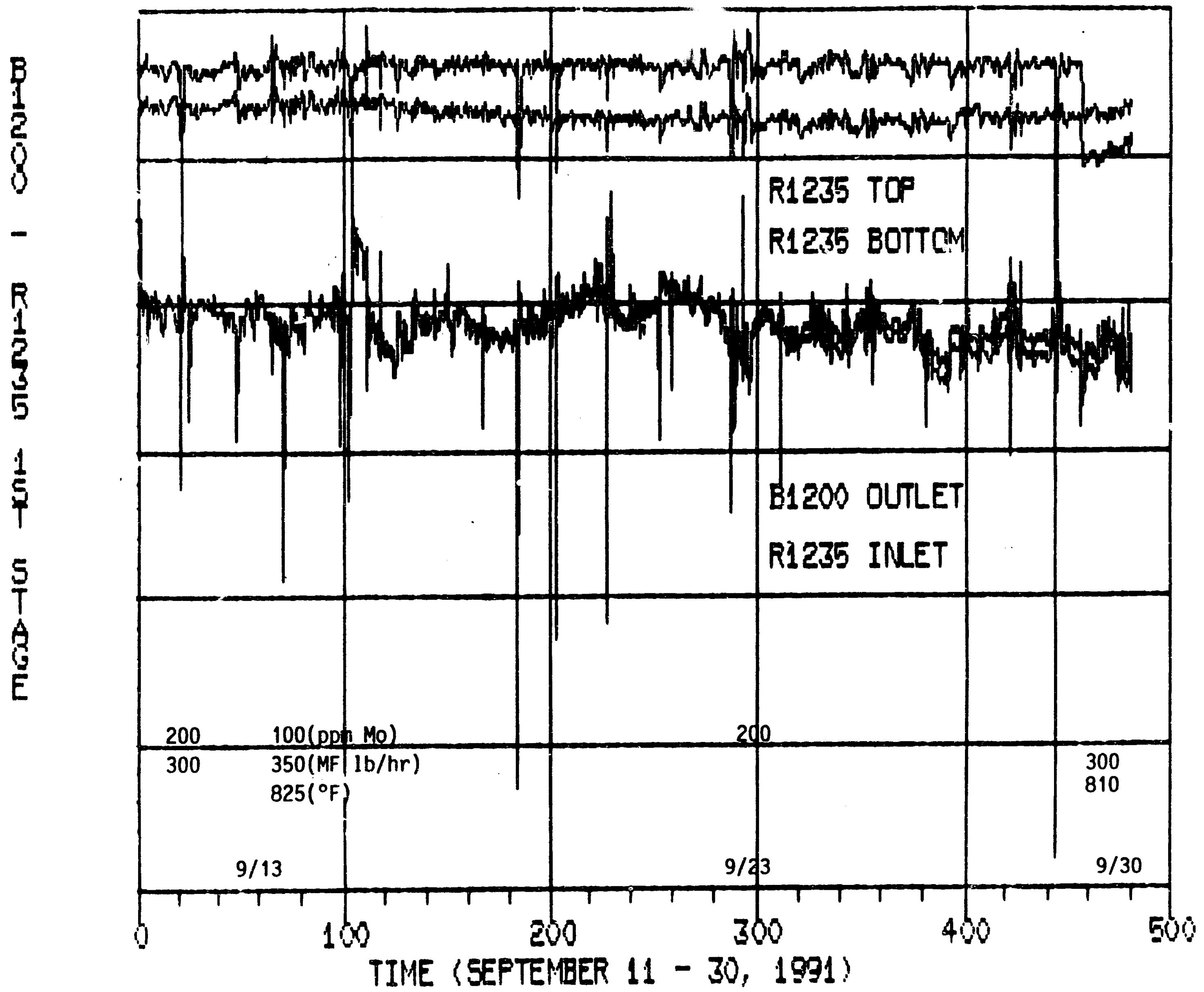


FIGURE 86. PREHEATER OUTLET AND FIRST STAGE REACTOR TEMPERATURE TREND (SEPTEMBER 11-30, 1991)

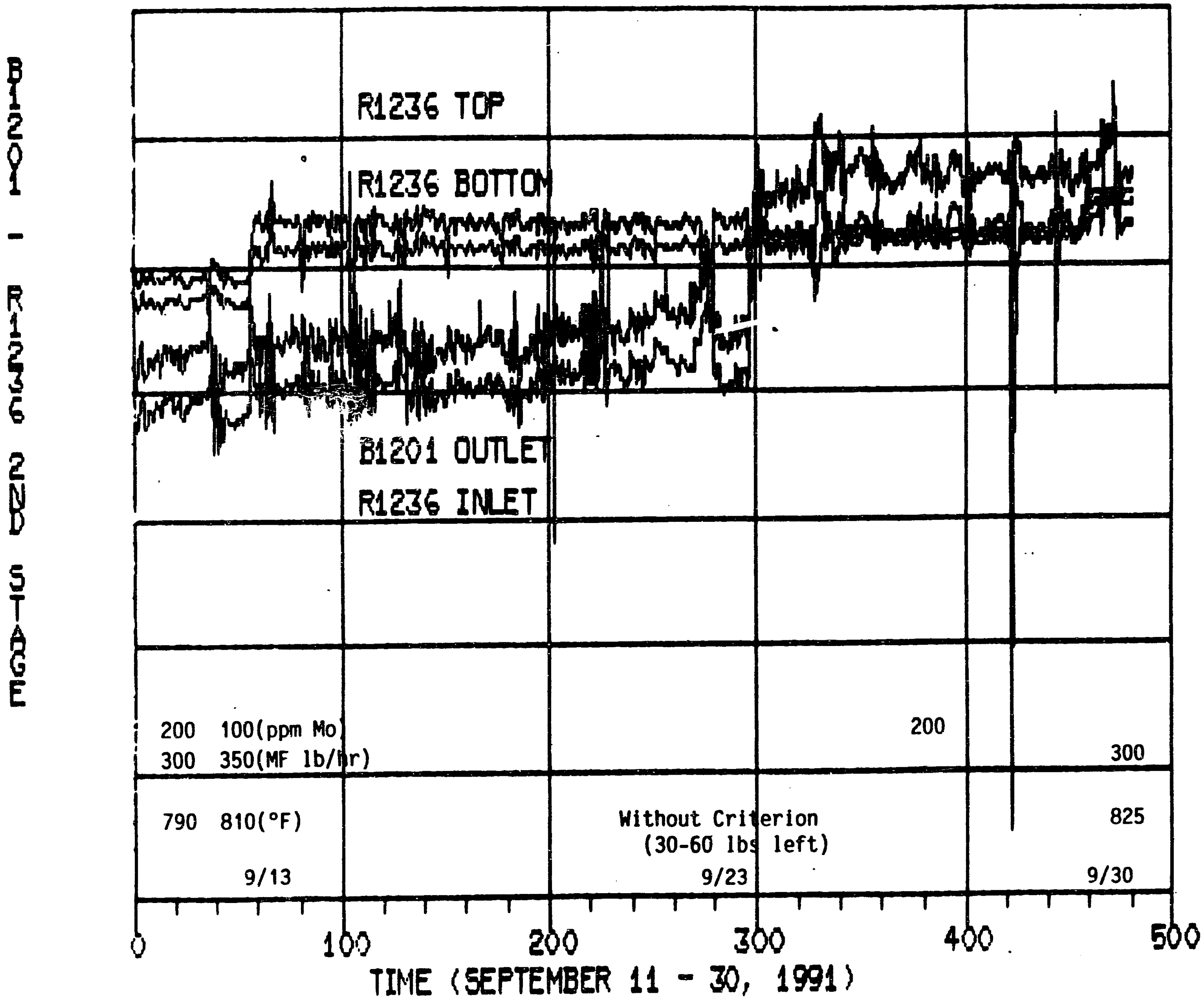


FIGURE 87. INTERSTAGE HEATER OUTLET AND SECOND STAGE REACTOR TEMPERATURE TREND (SEPTEMBER 11-30, 1991)

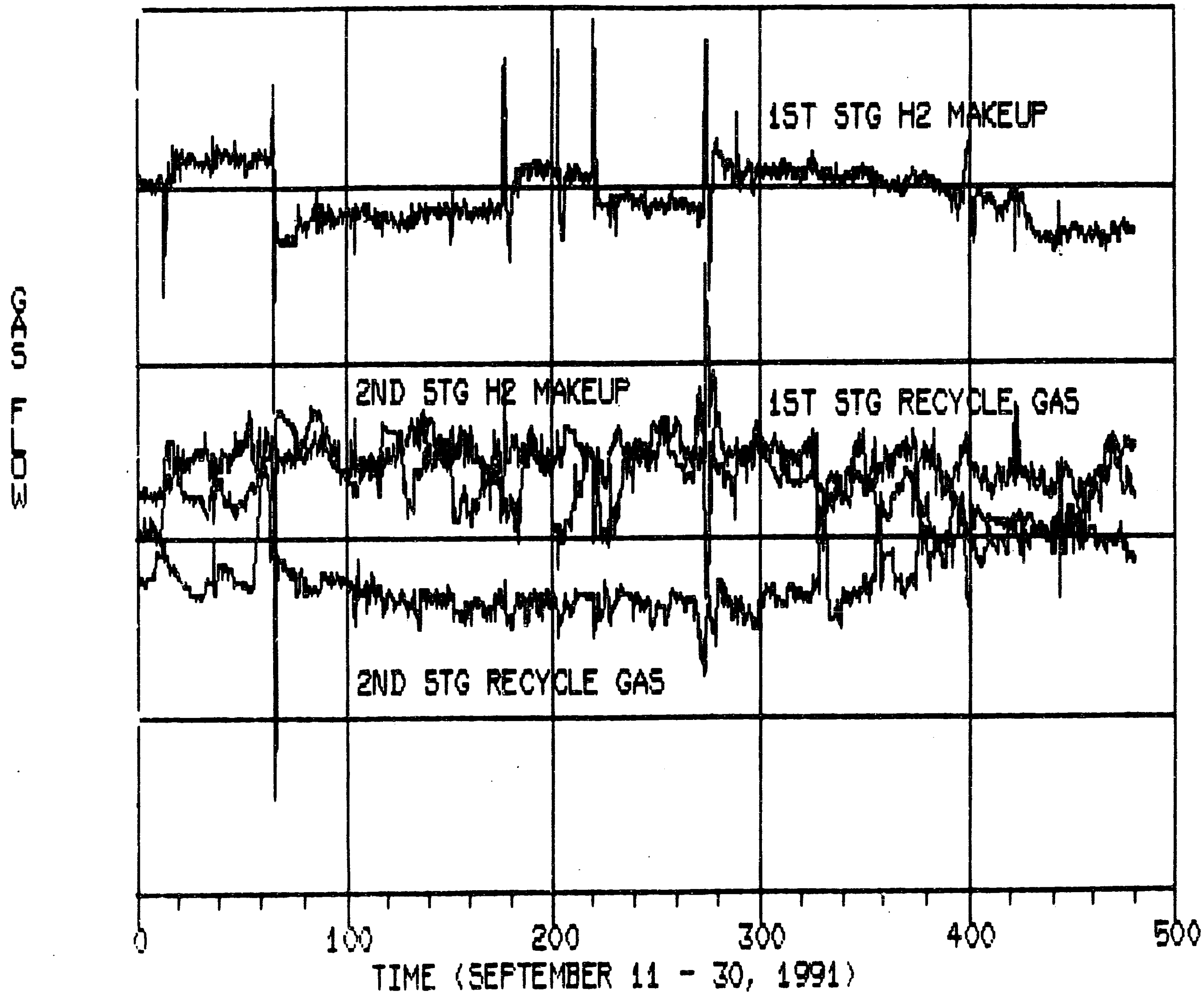


FIGURE 88. GAS FLOW RATE TREND (SEPTEMBER 11-30, 1991)

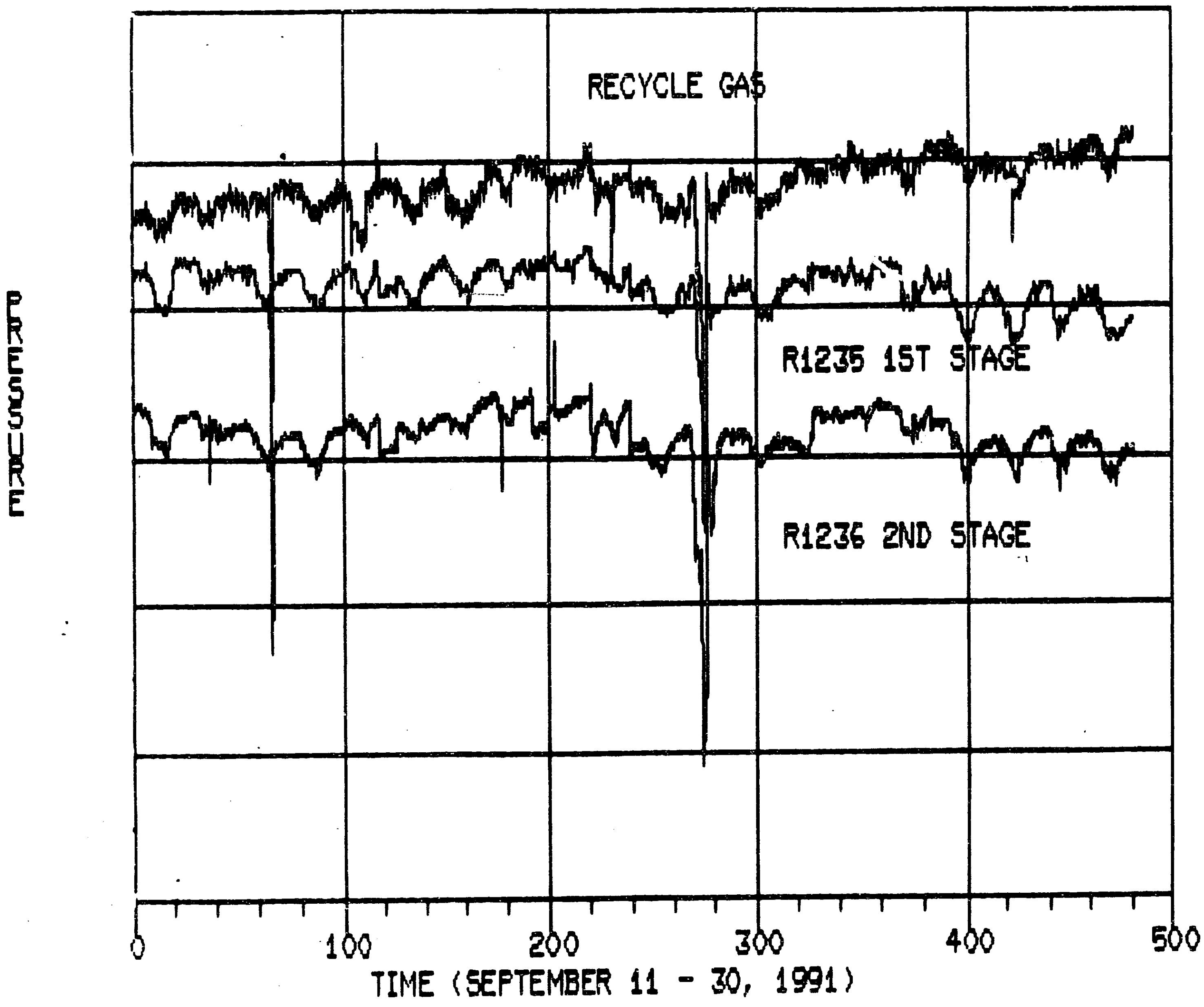


FIGURE 89. SYSTEM PRESSURE TREND (SEPTEMBER 11-30, 1991)

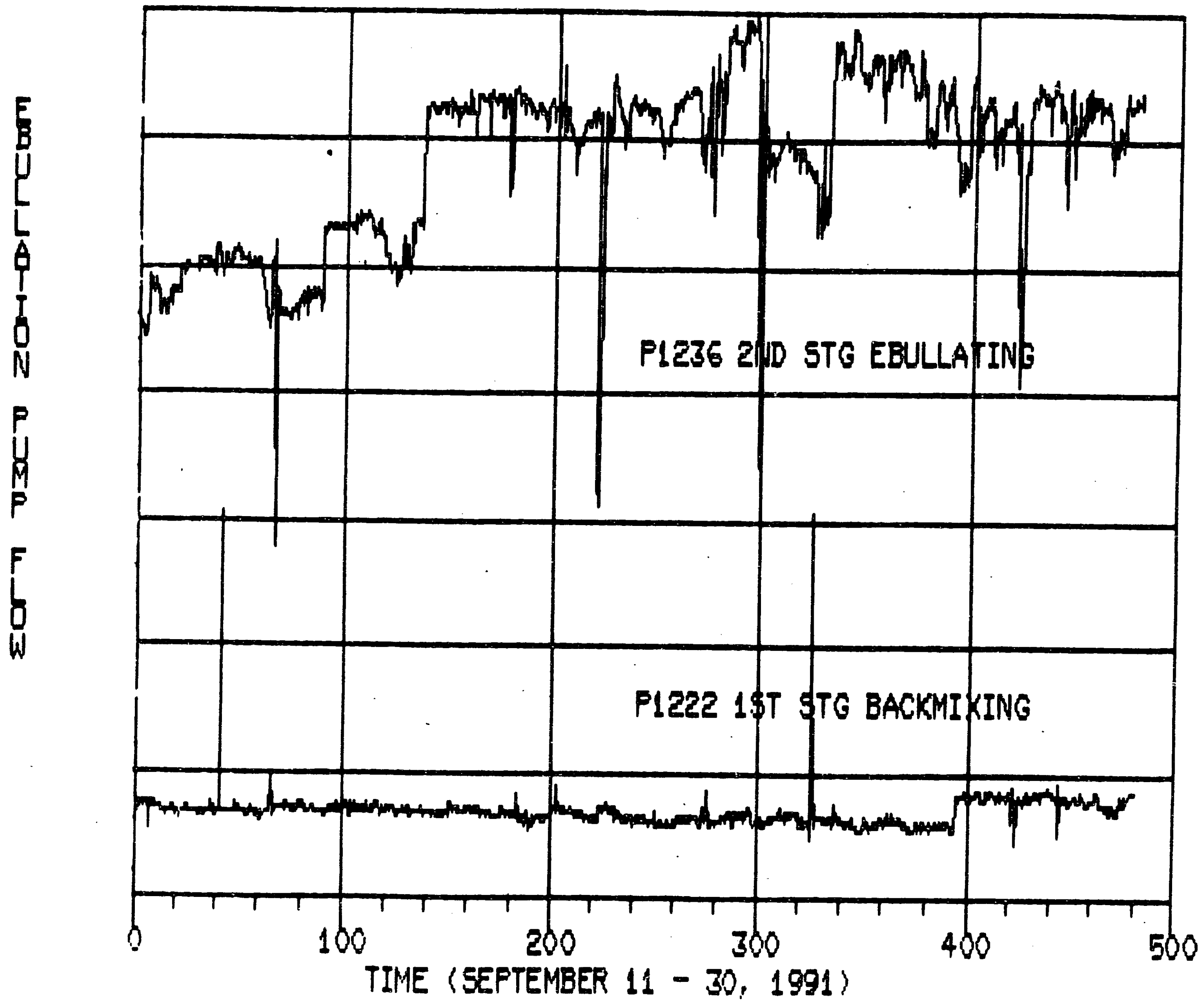


FIGURE 90. EBULLATION AND BACKMIXING PUMP RATE TREND (SEPTEMBER 11-30, 1991)

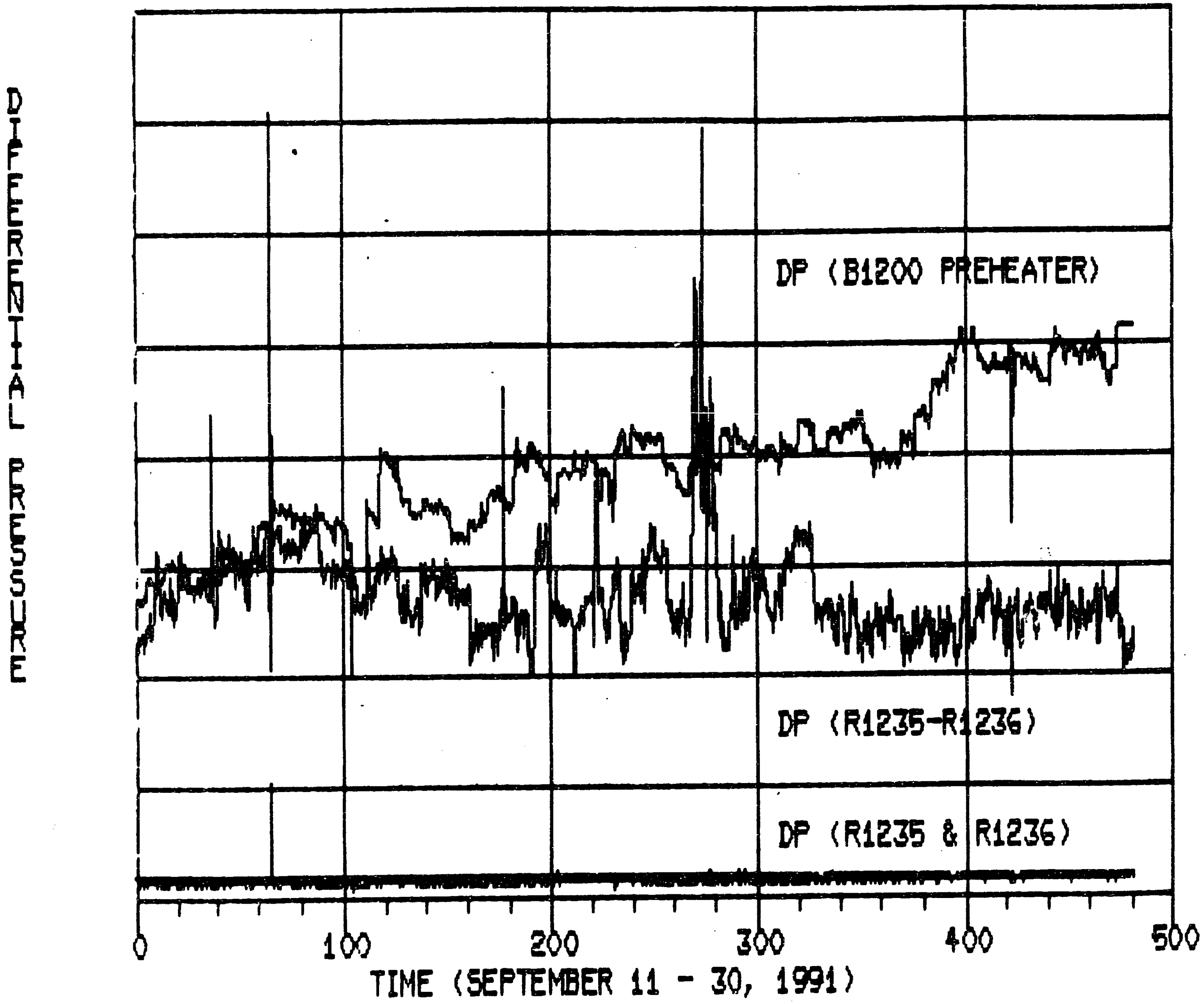


FIGURE 91. DIFFERENTIAL PRESSURE TREND (SEPTEMBER 11-30, 1991)

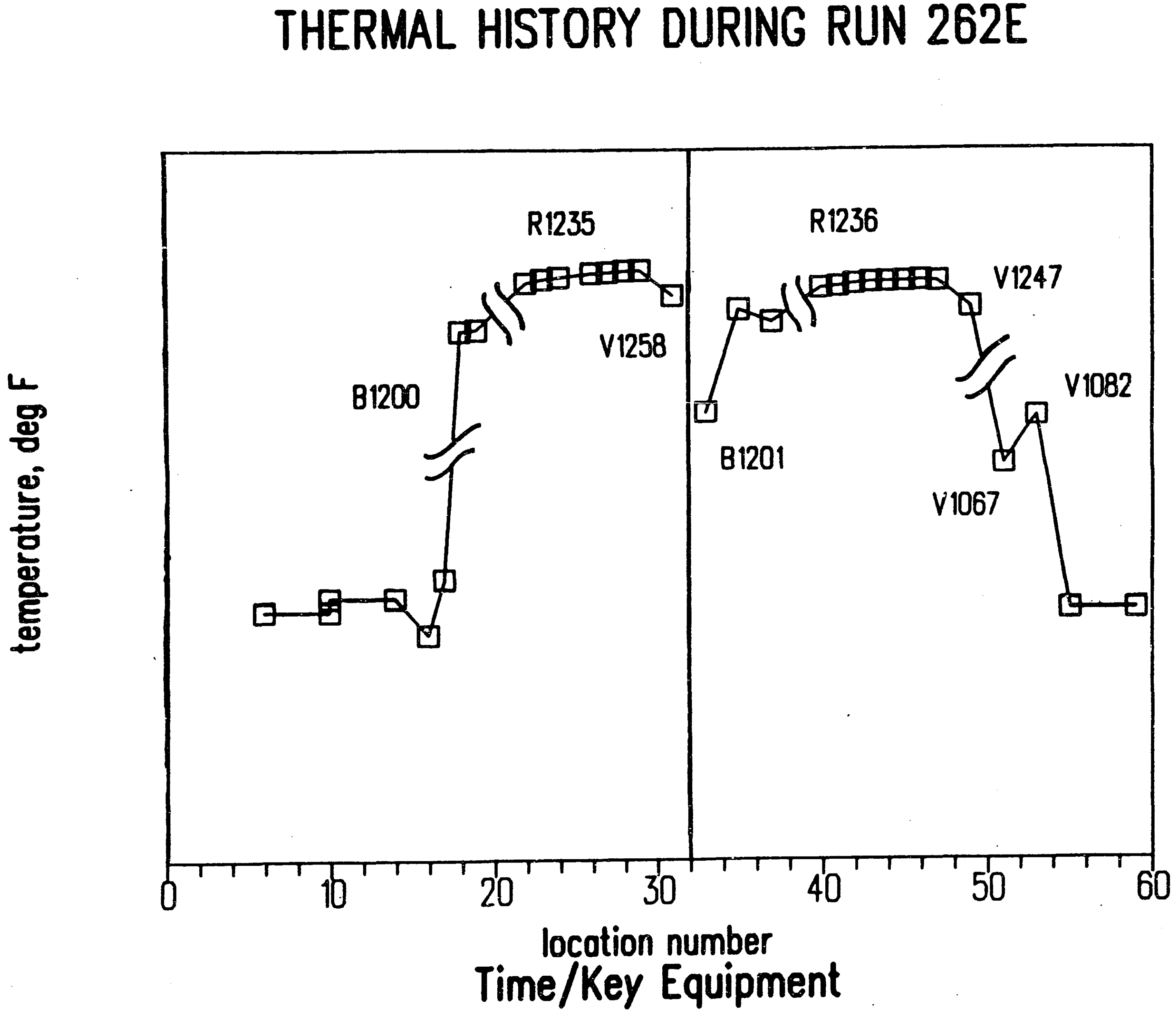


FIGURE 92. TSL THERMAL HISTORY DURING RUN 262E

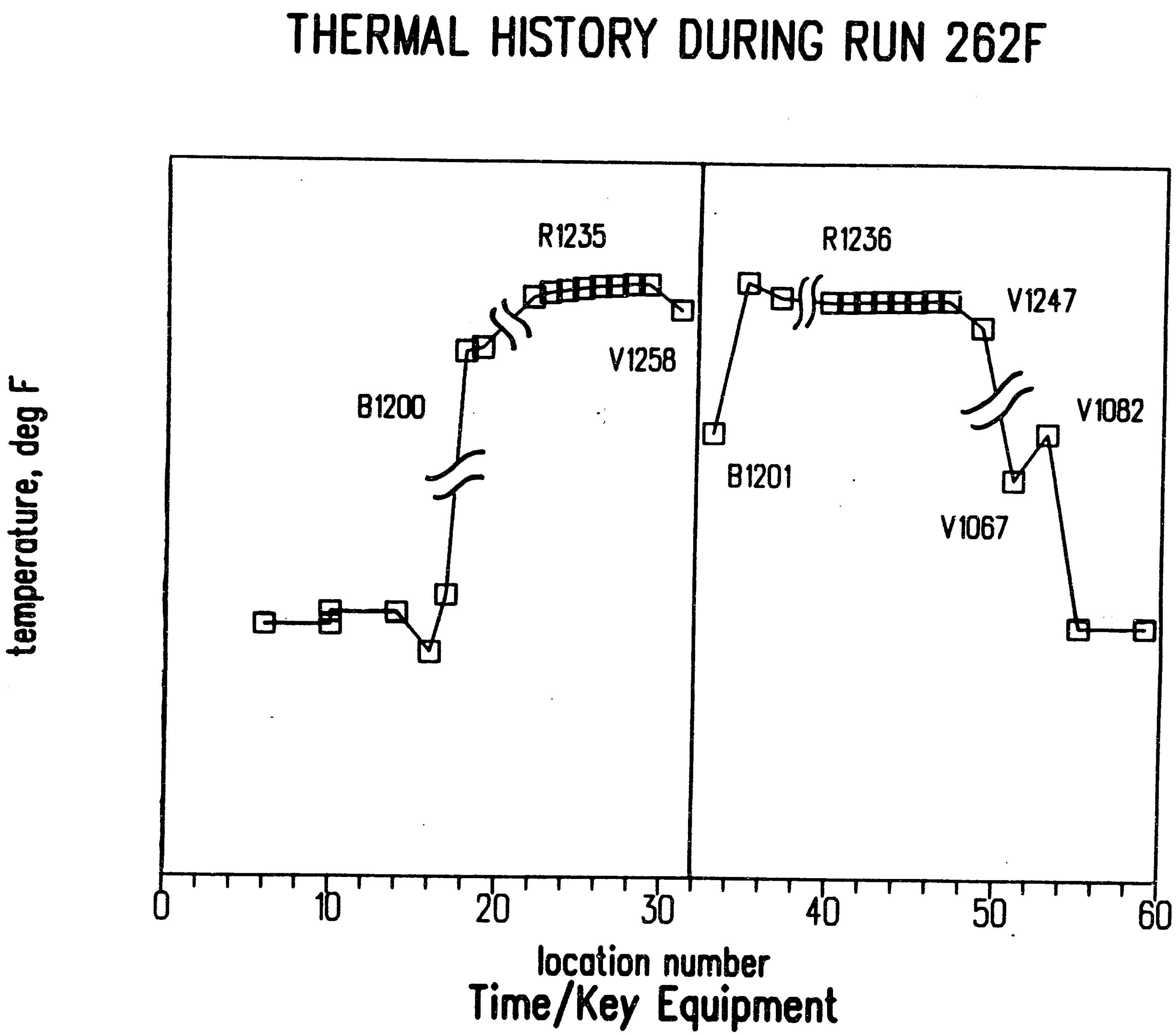


FIGURE 93. TSL THERMAL HISTORY DURING RUN 262F

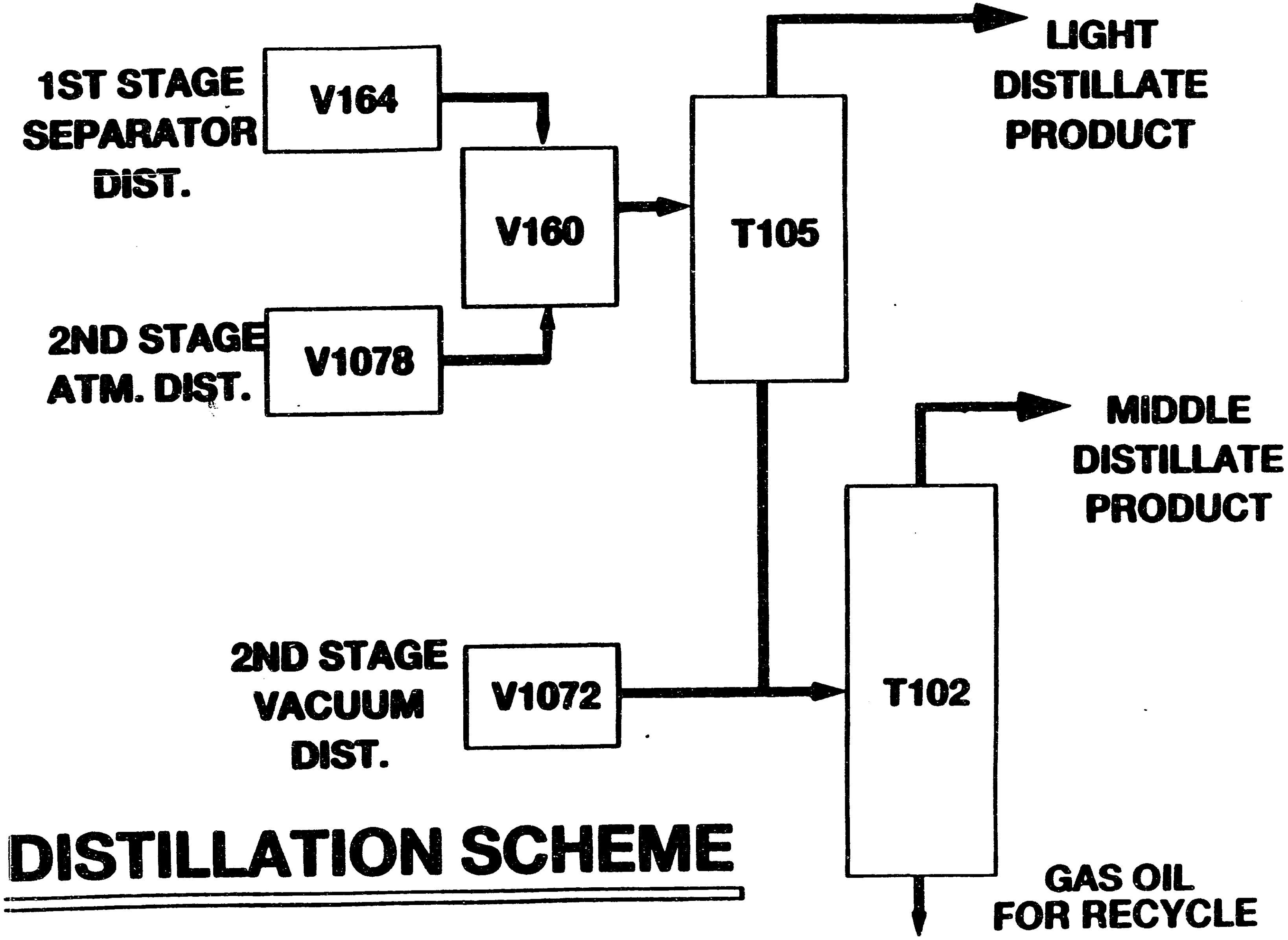


FIGURE 94. SCHEMATIC SHOWING THE FEED AND PRODUCT STREAMS OF THE DISTILLATION COLUMNS

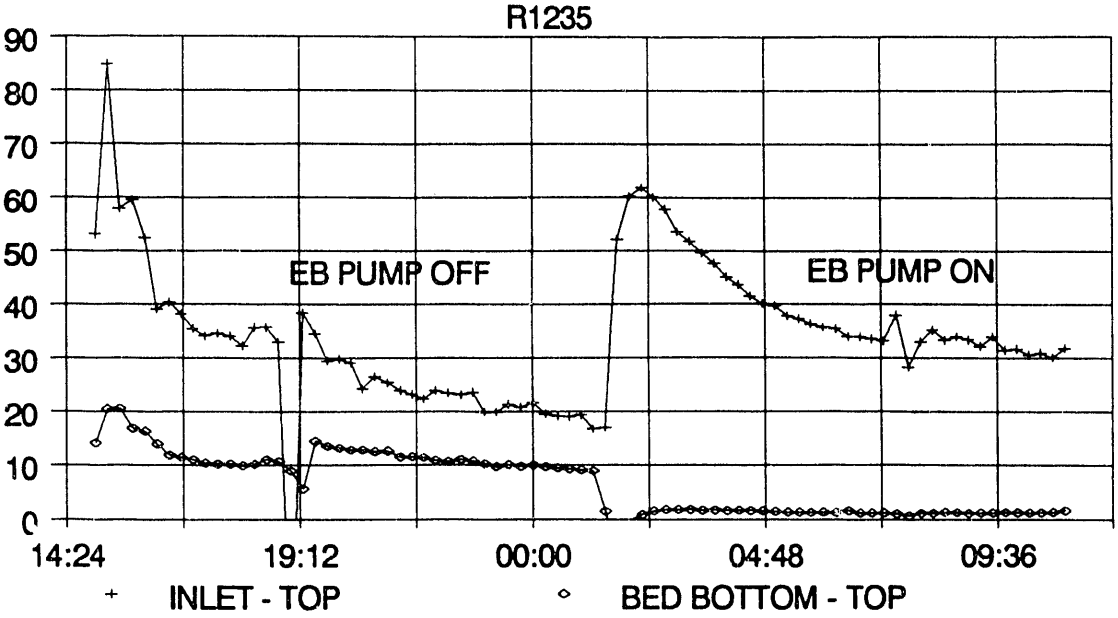


FIGURE 95. R1235 TEMPERATURE DIFFERENCES DURING HEAT LOSS TEST

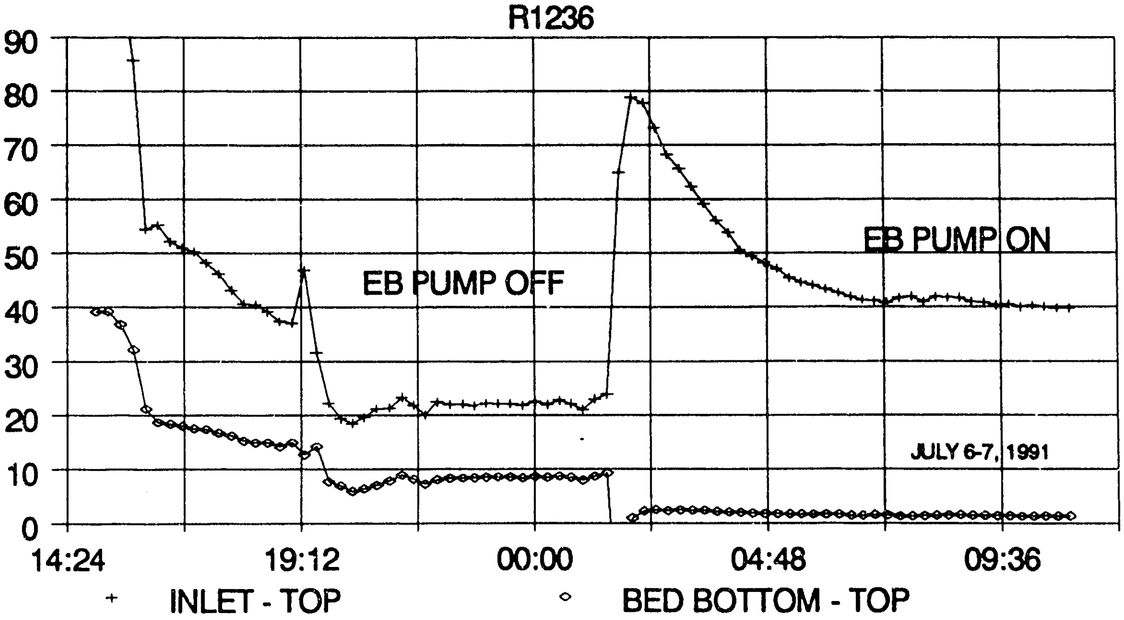


FIGURE 96. R1236 TEMPERATURE DIFFERENCES DURING HEAT LOSS TEST

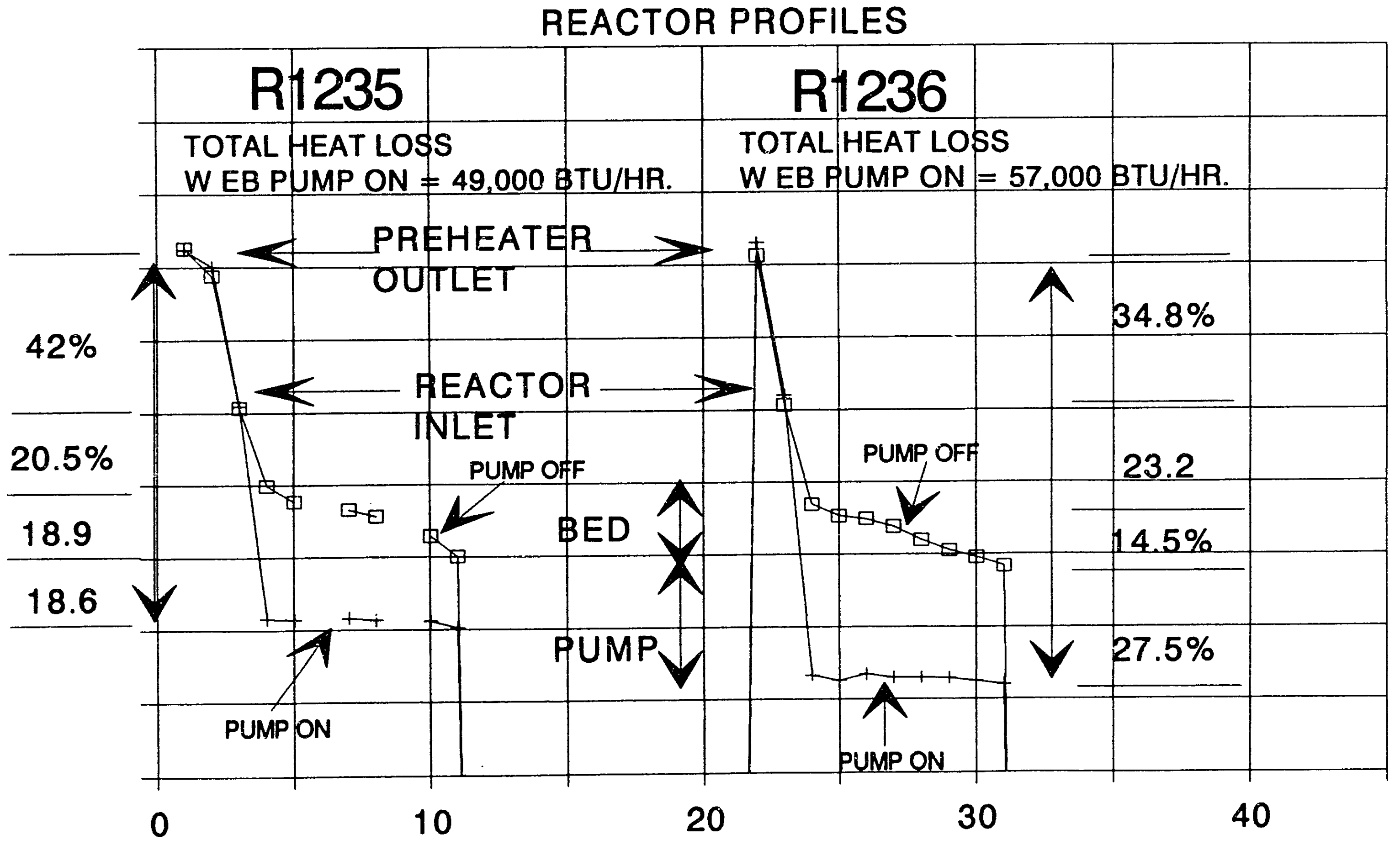
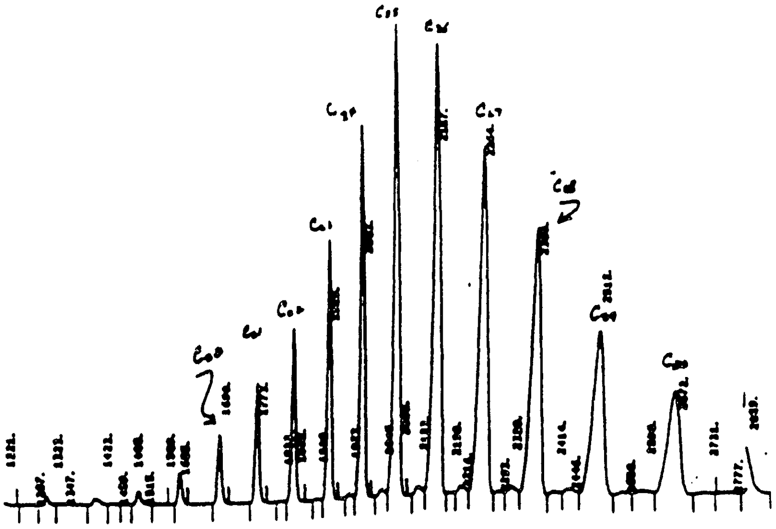


FIGURE 97. REACTOR PROFILES DURING THE HEAT LOSS TESTS

FIGURE 98. GAS CHROMATOGRAPHIC SPECTRUM OF PARAFFINS ISOLATED FROM FIRST STAGE DISTILLATE V164



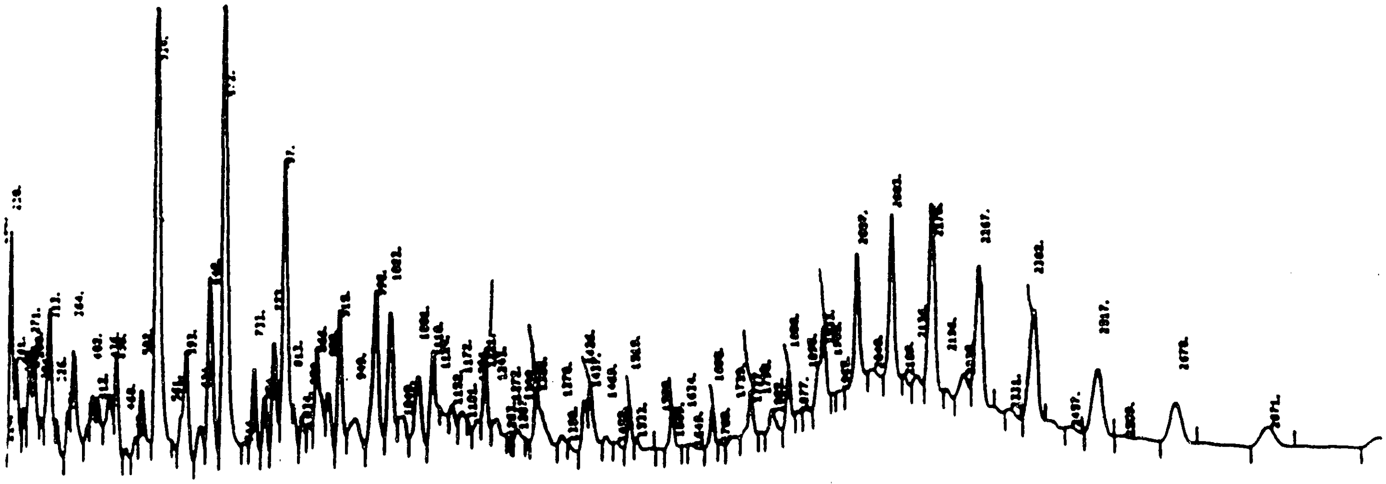


FIGURE 99. GAS CHROMATOGRAPHIC SPECTRUM OF THE TOTAL OIL DISTILLATE

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