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RUN 252 WITH ILLINOIS NO. 6 COAL

Technical Progress Report

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Work Performed Under Contract No. AC22-82PC50041

For
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Catalytic, Inc.
Wilsonville, Alabama

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ADVANCED COAL LIQUEFACTION
RESEARCH AND DEVELOPMENT FACILITY

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Wilsonville, Alabama

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Run 252 with Illinois No. 6 Coal

Published: May 1990

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Birmingham, Alabama 35202
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PREFACE

Operations at the Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama, are funded by the U. S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI). Southern Company Services, Inc. (SCS) manages the Wilsonville program on behalf of DOE and EPRI. Catalytic, Inc. operates the facility under a subcontract with SCS.

The Wilsonville R & D Facility combines three process units: a thermal liquefaction unit (TLU), a Critical Solvent Deashing (CSD) unit, and a catalytic hydrogenation (HTR) unit. The TLU was designed by Catalytic, Inc., using technology initially developed in Germany and later refined by the Pittsburg and Midway Coal Mining Co. Until November 1985, with the inception of close-coupled operations, this unit was used for coal dissolution. Currently the TLU is used for coal preparation, gas scrubbing and recompression and solvent distillation. The CSD unit was designed and developed by the Kerr-McGee Corporation. The HTR unit uses H-Oil® technology, developed by Hydrocarbon Research, Inc. (HRI), and was constructed by Catalytic, Inc. The HTR unit has been modified by Catalytic, Inc. to allow close-coupled operations. The modification primarily consisted of adding a new reactor in close proximity to the existing HTR reactor. These close-coupled reactors can be used for both thermal-catalytic and catalytic-catalytic modes of operation. The two reactors are commonly referred to the 1st and 2nd stage reactors. The combined three-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 1st and 2nd stages may be independently varied, allowing for improvement in product slate flexibility as compared with single-stage liquefaction. Accordingly, a heavy fuel oil with low sulfur may be produced, or alternatively, emphasis may be placed on maximum production of low nitrogen distillate products with efficient hydrogen utilization.

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ABSTRACT

This reports presents the operating results for Run 252 at the Advanced Coal Liquefaction R & D Facility in Wilsonville, Alabama. This run operated in the Close-Coupled Integrated Two-Stage Liquefaction mode (CC-ITSL) using Illinois No. 6 bituminous coal. The primary run objective was demonstration of unit and system operability in the CC-ITSL mode with catalytic-catalytic reactors and with ash recycle.

Run 252 began on 26 November 1986 and continued through 3 February 1987. During this period 214.4 MF tons of Illinois No. 6 coal were fed in 1250 hours of operation.

1. INTRODUCTION

Run 252 was in the CC-ITSL mode. Prior runs in the CC-ITSL mode included Run 250 (Ref. 1) and Run 251 (Ref. 2).

In the CC-ITSL mode the product from the first stage reactor is sent to the second stage reactor without prior fractionation or deashing. Interstage cooling and gas separation are possible. The 2nd stage bottoms product is sent to the CSD unit, and the deashed resid is recycled to the slurry mix tanks along with 2nd stage distillate solvent. A block flow diagram of CC-ITSL is shown in Figure 1.

A brief summary of recent and future Two-Stage Liquefaction (TSL) runs at Wilsonville is given below:

Run	Coal	Mode	Comments
242	Illinois	ITSL	SCT(1)
243	Illinois	ITSL	
244	Illinois	ITSL	
245	Illinois	ITSL	Continuous HTR catalyst addition/withdrawal
246	Wyoming	DITSL(2)/ITSL	FeS catalyst in TLU(3)
247	Illinois	RITSL	TLU dissolver tracer study
248	Illinois	DITSL(2)/ITSL	LCT(4)
249	Wyoming	RITSL	Forced Back-mixed Dissolver
250	Illinois	CC-ITSL	Thermal-Catalytic
251	Ill/Wyo.	CC-ITSL	Catalytic-Catalytic and Thermal-Catalytic
252	Illinois	CC-ITSL	Catalytic-Catalytic
Future:			
253	Illinois	CC-ITSL	Catalytic-Catalytic

(1) SCT denotes Short Contact Time Liquefaction. No dissolver was used.

(2) DITSL is Double Integrated Two-Stage Liquefaction.

(3) Iron oxide and dimethyl disulfide added, which formed FeS catalyst in TLU.

(4) LCT denotes Low Contact Time Liquefaction. A 5.2" ID dissolver was used.

(5) In Runs 242-250 the first stage is a thermal liquefaction stage and the second stage hydrotreater is a catalytic stage.

Figure 2 shows, in block diagram form, all of the operating modes tested at Wilsonville prior to the CC-ITSL mode. Flow diagrams of each of the operating units are presented in Figures 3, 4, 5 and 6.

Objectives

The objectives of Run 252 were:

1) To determine the viability of catalyst cascading from the second stage to the first stage reactor. With catalyst cascading, fresh catalyst is added to the second stage reactor and the catalyst withdrawn from the second stage is added to the first stage. The viability of catalyst cascading can be determined by determining the catalyst deactivation curve of the first stage catalyst which was initially aged in the second stage in prior runs.

2) To evaluate the utilization of pulverized aged catalyst as a coal slurry additive.

3) To determine the effects on first stage and TSL system performance with fresh catalyst addition as makeup to the first stage reactor.

4) To evaluate unit and TSL performance with Amocat 1C 1/16" catalyst, along with unit and TSL yield structures in the ash recycle mode of operation.

5) To evaluate the impact on TSL and second stage catalyst performance of the close-coupled operation without the interstage vapor separation.

Objective (3) was studied only briefly (31 January - 3 February) as Run 252 was ended when the first stage ebullating pump suddenly stopped running due to overheating and could not be restarted. Without the flow from the ebullating pump a plug quickly formed in the reactor. Objectives 2 and 5 were not achieved but included for Run 253.

A summary of base operating conditions for the 1st and 2nd stages during Run 252 is shown below:

Run no.	252A-C1
Start date	26 Nov 86
End date	3 Feb 87
Coal type	Ill. 6
Mine	Burning Star
Interstage separator	Yes
• 1st stage	
Coal feed rate, lb/hr MF	300/350/385
Slurry conc., wt % MF	33
Resid in process solvent, wt %	38
CI in process solvent, wt %	12
Feed gas flow, scfh	5000
Gas purity, mol % H_2	85
R1235 H_2 partial pressure, psi	2500
R1235 target temperature, °F	810
Catalyst type (a)	Amocat 1C
Catalyst charge, lbs	340
• 2nd stage	
Total gas flow, scfh	7000
Feed gas purity, mol % H_2	94
R1236 H_2 partial pressure, psi	2600
R1236 target temperature, °F	680/750
Catalyst type (a)	Amocat 1C
Catalyst charge, lbs	340

(a) The mixed Amocat 1C (a blend of 37.5 wt % from Run 251-I, 37.5 wt % from Run 250 and 25 wt % fresh sulfided) with an age of 1500 lb(resid + CI)/lb cat (915 lb MF coal/lb cat) was charged in the 1st stage and a fresh sulfided Amocat 1C was charged in the 2nd stage. This catalyst age corresponds to a replacement rate of 2 lb catalyst/ton MF coal. The addition of a fresh sulfided catalyst in the 1st stage reactor at 2 lb cat/ton MF coal started on 31 January.

In order to evaluate the catalyst deactivation trend with a mixed catalyst, Amocat 1A batch deactivation data obtained in Run 251-I were used for an example calculation. Catalyst age studied was 1500 to 3000 lb (resid+CI)/lb catalyst. The activity calculated for the mixed catalyst showed a similar deactivation trend to that for the batch catalyst, only improving the resid + UC conversion by 1 to 2 wt % feed. This improvement of the mixed catalyst over the batch catalyst may influence the mixed catalyst activity experimentally measured in Run 252 with Amocat 1C, although the effect is considered to be relatively small.

2. CONCLUSIONS AND RECOMMENDATIONS

2.1 Conclusion - Observation

- Process performance in the CC-ITSL catalytic/catalytic mode using Amocat 1C bimodal catalyst in each stage was similar to process performance using the Amocat 1A/1C combination.

- The long term physical integrity of the bimodal catalyst in the ebullated bed reactors needs to be further evaluated; the catalyst recovery was only 63% in the first stage reactor.

- Under batch catalyst aging, the concentration of preasphaltenes in the CSD feed stream gradually increased thus the DAS was gradually strengthened to both reduce energy rejection to the ash concentrate and improve resid recovery.

- Although the plant operation did not completely simulate catalyst cascading in Run 252, the first stage batch deactivation curve with the mixed catalyst showed similar catalyst activity and deactivation coefficient values to those batch aging data without having the mixed catalyst (Run 251-I). The catalyst age range studied was 1500 to 2600 lb resid+CI/lb catalyst. In addition, the second stage catalyst activity and deactivation coefficient values are very similar for both runs with Amocat 1C catalyst (Figures 17, 18, 19 and 20). Note that Amocat 1A catalyst was used in the first stage for Run 251-I.

- The above catalyst activity data with the mixed catalyst in the first stage show that the cascading catalyst activity from the second stage to the first stage is significant in the high-low configuration. The first stage cascaded catalyst has a much higher activity than the second stage catalyst and similar to that with Amocat 1A in Run 251-I.

2.2 Recommendations

- Test actual catalyst cascading when an addition/withdrawal system is available on both reactors.

3. OPERATING DATA AND PROCESS PERFORMANCE

Run 252 began on 26 November with Illinois No. 6 bituminous coal in the CC-ITSL mode of operation. Mixed Amocat 1C (37.5 wt % from Run 251-I, 37.5 wt % from Run 250 and 25 wt % fresh sulfided) with an age of 1500 lb(resid + CI)/lb cat was charged in the first stage and fresh sulfided Amocat 1C catalyst was charged in the second stage. The amount of each catalyst was 340 lbs. The ash recycle was continued during Run 252 by using the CSD unit to purge the ash from the system and to remove distillate solvent and resid for blending in the recycle process solvent. The recycled atmospheric bottoms contained the ash and unconverted coal (UC) that were not purged. R1235 reactor was used as the 1st stage and R1236 reactor was used as the 2nd stage.

During Run 252, the Close-Coupled Reactor (CCR) unit operated 1,250 hours out of a total of 1,628 hours, for an on-stream factor of 76.8%.

3.1 TSL System Stability

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

- Mass balance closure errors for TSL, CCR (1st & 2nd), and CSD must be less than 10 wt % MAF coal.
- The sum of the absolute values of inventory changes (including drum-outs) must be less than 15 wt % MAF coal, based on the following locations:
  - (a) Between the 2nd stage and CSD unit
  - (b) Between the CSD unit and 1st stage
  - (c) Between the 2nd and 1st stages

Twenty-one stable days were selected during Run 252. Elementally balanced yields were calculated on these stable days for each unit and the TSL system. Yields on days with similar operating conditions were then averaged. For final characteristic yields for each set of operating conditions, 17 of the 21 stable days were selected. The operating conditions and the corresponding days are shown below. A description of the elemental balancing procedure and a more detailed description of selection criteria are given in Section 8, Material Balance Methodology.

Run 252 Operating Periods

Operating Period	Description	Number of Selected Days	Element Balance Days (1986-87)
252A	Transitional Coal feed rate = 300 MF lb/hr 1st stage catalyst = Amocat 1C temp. = 810°F WHSV = 2.8 hr^{-1} 2nd stage catalyst = Amocat 1C temp. = 680°F WHSV = 2.7 hr^{-1} CSD DAS = 4100 Recycle process solvent (wt %) Solvent = 50, resid = 38 UC = 4, ash = 8	2	Dec 16, 17
252B	Coal feed rate = 350 MF lb/hr 2nd stage temp. = 750°F	4	Dec 24, 25, 29, 30
252B1	New coal pile (see page 14)	4	Jan 4, 5, 7, 8
252C	Transitional Coal feed rate = 385 MF lb/hr	2	Jan 20, 21
252C1	New coal pile (see page 14)	5	Jan 26, 27, 28, 29, 30

Period 252B1 was selected for product quality testing. Samples of products from selected days were blended, fractionated and analyzed by boiling point range. Results from product quality testing are presented in Section 4, Distillate Product Quality and Unit Solvents.

3.2 1st Stage

Run 252 started in the catalytic-catalytic mode of operation. Mixed Amocat 1C catalyst was used in the 1st stage reactor.

Catalyst preconditioning, a "soft start" of the R1235 reactor catalyst, was completed during 24-26 November.

Plant start-up conditions in the 1st stage were:

(1) Average reaction temperature of 810°F.

(2) Inlet hydrogen partial pressure of 2,500 psia.

(3) Feed gas hydrogen purity of 85 mol % at a rate of 5,000 scfh.

(4) Coal feed rate of 300 MF lb/hr.

Process adjustments made in the 1st stage during Run 252 were:

(1) The coal feed rate was increased from 300 to 350 MF lb/hr on 21 December to evaluate TSL process performance at a higher coal feed rate.

(2) The coal feed rate was further increased from 350 to 385 MF lb/hr on 17 January to continue the evaluation.

Plant operations were smooth except for outages to repair the 1st stage ebullating pump on two occasions (29 November - 10 December and 18-20 December), and to clear the 2nd stage ebullating pump of catalyst carryover (22-24 January). Run 252 ended on 3 February because of a 1st stage reactor plug formed during an ebullating pump shutdown.

The first several coal batches were mixed with process solvent produced from Runs 250 and 251-I (bituminous coal runs). The recycle process solvent consisted of 50 wt % solvent, 38 wt % resid, 4 wt % UC and 8 wt % ash for the entire period of Run 252.

Solvent quality (by equilibrium test) of the recycle process solvent (V131B) for 252A, 252B, 252B1, and 251-IE was similar, 84-87%, as shown below:

Run	251-IE	252A	252B	252B1
Catalyst type				
1st stage	Amocat 1A	Amocat 1C	Amocat 1C	Amocat 1C
2nd stage	Amocat 1C	Amocat 1C	Amocat 1C	Amocat 1C
Reaction temp., °F				
1st stage	808	811	810	810
2nd stage	758	679	751	750
Catalyst age, lb (res+CI)/lb cat				
1st stage	2159-2245	1841-1884	2117-2416	2662-2867
2nd stage	2313-2374	290-319	487-708	893-1043
Catalyst age, lb MF coal/lb cat				
1st stage	1254-1298	1090-1112	1232-1386	15113-1619
2nd stage	1519-1560	190-210	320-465	587-685
Coal feed rate, MF lb/hr	301	300	353	347
Resid content in V131B, wt %	40	38	38	38
Hydrogen content, wt %				
V131B (as-is)	7.74	8.47	8.25	8.15
Resid	7.08	7.64	7.99	7.87
Distillate	9.93	10.34	10.11	10.20
Solvent quality, % (a)	84	84	87	85

(a) Tests were done with CI-free samples.

In periods 252B and 252B1 at younger catalyst ages in the 2nd stage compared to Run 251-IE (600-1000 vs 2350), hydrogen contents of recycle process solvent and resid and distillate portions of recycle process solvent were significantly higher by 0.4-0.5, 0.8-0.9 and 0.2-0.3 wt %, respectively. The 2nd stage catalyst age appears to mainly affect the hydrogen content. Solvent quality slightly increased from 84 to 85-87%.

Figure 7 shows hydrogen contents of resid and distillate of recycle process solvent and of 1st stage reaction products (2nd stage feed) for Run 252. Detailed discussion on solvent quality related to hydrogen transfer is reported in Section 3.5 Overall TSL Yields - Correlations of TSL Hydrogenation.

The total exotherm between the inlet and the outlet of the R1235 reactor was very high during Run 252, due to high catalytic hydrogenation reactions by Amocat 1C in the 1st stage. The temperature gradient between the bottom (10% volume location) and the outlet (100% volume location) was also high as similarly observed in Run 251. Figures 8 and 9 show the relative (actual x factor) preheater outlet temperature, total exotherm and reactor temperature gradient trends. The actual exotherm and gradient are proprietary.

Catalyst Activity Trends in Resid + UC Conversion

Daily resid + UC conversion data for selected days during Run 252 are summarized below. These data were obtained from Phase 2 results.

Date, 1986-87	1st stage temp., °F	Catalyst age lb coal/lb cat	Catalyst age lb(res+CI)/lb cat	WHSV hr^{-1}	WHSV lb coal/hr-ft^3	Resid+UC conv., wt %	Rate Constant K, hr^{-1}
12/12	812	1018.5	1672	2.76	37.78	37.9	1.648
12/15	810	1081.9	1799	2.75	37.16	36.3	1.567
12/16	811	1103.1	1841	2.75	37.03	36.8	1.601
12/17	811	1124.3	1884	2.75	37.16	36.5	1.577
12/23	811	1215.1	2067	3.23	44.07	30.1	1.394
12/24	809	1239.8	2117	3.18	43.21	30.2	1.376
12/25	809	1264.7	2167	3.20	43.58	30.9	1.430
12/29	810	1362.6	2365	3.15	43.46	38.8	1.275
12/30	811	1387.8	2416	3.18	44.07	31.4	1.454
1/1	810	1437.3	2515	3.17	42.84	28.4	1.256
1/4	810	1310.4	2677	3.14	42.72	30.6	1.382
1/5	810	1536.5	2730	3.10	42.59	29.6	1.306
1/7	810	1603.2	2834	3.20	42.84	28.9	1.286
1/8	812	1627.8	2884	3.21	43.09	30.6	1.412
1/20	811	1885.3	3337	3.45	46.30	26.3	1.229
1/21	811	1912.0	3391	3.48	46.67	25.3	1.181
1/26	811	1991.6	3554	3.50	46.54	26.2	1.239
1/27	811	2018.3	3609	3.47	46.91	27.6	1.320
1/28	810	2045.3	3664	3.49	47.28	26.6	1.264
1/29	811	2072.8	3720	3.48	48.15	27.3	1.307
1/30	811	2099.2	3775	3.48	46.17	25.5	1.188
2/1	811	1972.2	3678	3.51	46.67	25.0	1.170
2/2	810	1891.8	3533	3.50	46.91	25.9	1.221

The catalyst deactivation coefficient (α) was calculated for two different groups as shown below and plotted in Figure 17. In Group I (Run 252A), the catalyst is at younger ages and exhibit high activity and high deactivation rate. This may be due to a portion of the catalyst charge being fresh. Also, in period 252A, the second stage temperature was very low (679°F), and as a result, the second stage activity was low which may affect the apparent first stage activity.

Group I (Catalyst age: 1600-2000 lb (resid+CI)/lb cat)

$$\ln K = \ln A - (E/R)(1/T) - \alpha t$$
$$\alpha = 0.00031 \pm 0.00013$$
$$\ln A - (E/R)(1/T) = 1.03$$
$$r^2 = 0.74$$

Group II (Catalyst age: 2000-3800 lb (resid+CI)/lb cat)

$$\alpha = 0.000077 \pm 0.000019$$
$$\ln A - (E/R)(1/T) = 0.49$$
$$r^2 = 0.50$$

The gradual decrease and the low value of the catalyst deactivation coefficient in the range 2000-3800 lb (resid+CI)/lb cat catalyst age indicates a significant catalyst residual activity.

Catalyst activity in resid + UC conversion and heteroatom removal are discussed in detail in the Overall TSL section and compared with those for Run 251-I with Amocat 1A charged in the 1st stage.

1st Stage Yields

1st stage yields for operating periods 252A to C1 are summarized on the following pages. The 1st stage yields are averages of elementally balanced yields from the days listed in Section 3.1 in the table of Run 252 operating periods. A trend plot of 1st stage C_4+ distillate yields is given in Figure 10. Average operating and performance data are given in Tables 3 and 4. 1st stage yields before elemental balancing are presented in Table 5.

1st Stage Yields
(Phase 3 Data)

Operating Period	252A	252B
Dates, 1986	12/16-12/17	12/24-12/30
Days selected	12/16,12/17	12/24,12/25 12/29,12/30
Coal feed rate, MF lb/hr	300	353
Coal space velocity, MF lb/hr/cu ft cat	37.0	43.6
Coal conc. in slurry, wt % MF	33	33
Process solvent, wt %		
Resid, wt % (a)	38(43)	38(43)
CI, wt %	12	12
Hydrogen, wt %	8.47	8.25
H/C atomic ratio	1.22	1.20
1st stage		
Reaction temp., °F (average)	811	810
Inlet H_2 part. press., psia	2560	2520
Space velocity, lb feed/hr/lb cat	2.76	3.18
Catalyst type	Amocat 1C	Amocat 1C
Catalyst age, lb(res+CI)/lb cat	1841-1884	2117-2416
lb MF coal/lb cat	1103-1124	1240-1388
2nd stage		
Reaction temp., °F (average)	679	751
Inlet H_2 part. press., psia	2660	2580
Space velocity, lb feed/hr/lb cat	2.69	3.05
Catalyst type	Amocat 1C	Amocat 1C
Catalyst age, lb(res+CI)/lb cat	290-319	487-708
lb MF coal/lb cat	192-213	327-476
Hydrogen consumption, wt % MAF	4.7±0.0	3.9±0.3
Coal conversion, wt % MAF (b)	91.8±0.1	91.2±0.8
Yield, wt % MAF coal		
Water	9.1±0.0	8.4±0.7
H_2S, CO, CO_2, NH_3	4.0±0.1	2.9±0.4
C_1-C_3 gas	5.0±0.0	4.1±0.2
C_4+ distillate	59.5±0.6	46.8±1.4
C_4+ naphtha	13.2±0.3	10.2±0.7
Middle distillate	7.2±0.0	5.7±0.3
Distillate solvent	39.1±0.3	30.9±1.4
Resid	19.0±0.8	33.0±0.5
UC	8.2±0.1	8.8±0.8
Selectivity of C_1-C_3 gas to C_4+ distillate yield (X100)	8	9
Resid + UC conversion, wt % feed (c)	37.1±0.0(72.8±0.7)	29.9±0.7(58.3±1.4)

(a) Data in parentheses on CI-free basis.
(b) Cresol solubles.
(c) MAF coal as 100 wt % UC. Data in parentheses are based on wt % MAF coal.

1st Stage Yields
(Phase 3 Data)

Operating Period	252B1(d)	252C	252C1(d)
Dates, 1987	1/4-1/8	1/20-1/21	1/26-1/30
Days selected	1/4,1/5 1/7,1/8	1/20,1/21	1/26,1/27,1/28 1/29,1/30
Coal feed rate, MF lb/hr	347	377	381
Coal space velocity, MF lb/hr/cu ft cat	42.8	46.5	47.0
Coal conc. in slurry, wt % MF	33	33	33
Process solvent, wt %			
Resid, wt % (a)	38(44)	38(43)	39(45)
CI, wt %	12	12	12
Hydrogen, wt %	8.15	8.02	7.93
H/C atomic ratio	1.19	1.17	1.15
1st stage			
Reaction temp., °F (average)	810	811	811
Inlet H_2 part. press., psia	2500	2440	2580
Space velocity, lb feed/hr/lb cat	3.15	3.46	3.49
Catalyst type	Amocat 1C	Amocat 1C	Amocat 1C
Catalyst age, lb(res+CI)/lb cat	2662-2867	3337-3391	3554-3775
lb MF coal/lb cat	1510-1628	1885-1912	1992-2099
2nd stage			
Reaction temp., °F (average)	750	749	750
Inlet H_2 part. press., psia	2580	2580	2600
Space velocity, lb feed/hr/lb cat	3.03	3.32	3.26
Catalyst type	Amocat 1C	Amocat 1C	Amocat 1C
Catalyst age, lb(res+CI)/lb cat	893-1043	1471-1515	1662-1792
lb MF coal/lb cat	598-697	972-999	1066-1175
Hydrogen consumption, wt % MAF	3.8±0.2	3.2±0.3	3.4±0.2
Coal conversion, wt % MAF (b)	91.5±0.9	89.0±0.5	93.2±0.6
Yield, wt % MAF coal			
Water	6.8±1.2	6.3±0.1	7.3±0.6
H_2S, CO, CO_2, NH_3	3.7±0.2	2.8±0.1	3.0±0.2
C_1-C_3 gas	3.7±0.0	3.3±0.1	3.0±0.2
C_4+ distillate	48.9±2.5	42.2±0.4	44.6±1.4
C_4+ naphtha	9.1±1.0	7.3±0.7	8.2±0.8
Middle distillate	5.2±0.5	5.3±0.2	5.1±1.0
Distillate solvent	34.7±2.4	29.6±0.6	31.3±1.5
Resid	32.2±1.3	37.7±1.3	38.6±1.2
UC	8.5±0.9	11.0±0.5	6.8±0.6
Selectivity of C_1-C_3 gas to C_4+ distillate yield (X100)	8	8	7
Resid + UC conversion wt % feed (c)	29.9±1.0(59.4±1.9)	25.9±0.5(51.3±0.8)	27.2±0.8(54.6±1.5)

(a) Data in parentheses on CI-free basis.
(b) Cresol solubles.
(c) MAF coal as 100 wt % UC. Data in parentheses are based on wt % MAF coal.
(d) Process performance improved without any process variable changes.

The 1st stage elemental balance errors for each operating period are shown below. These errors are calculated from measured stream analyses and flow rates for all feed and product streams. The interstage slurry flow rate was obtained by difference since it could not be accurately measured. Thus, there is zero overall mass closure in the 1st stage for Run 252.

Operating Period	1st Stage Elemental Balance Error, Wt % MAF Coal					
	C	H	N	S	O	Ash
252A	2.5	-0.9	0.6	0.2	-2.3	-0.1
252B	1.0	-0.1	0.7	0.5	-2.0	-0.1
252B1	0.0	0.2	0.6	0.0	-0.4	-0.3
252C	-0.7	-0.5	0.7	1.9	-1.5	0.1
252C1	0.9	-0.4	0.1	0.1	-0.5	-0.3

Yields calculated from measured stream analyses and flow rates are given in Table 5.

Analysis of 1st Stage Performance

C_4+ distillate yield responses for TSL, 1st and 2nd stages due to process variable changes are plotted in Figure 10. Three different coal piles were processed during Run 252 and process performance improved without any process variable changes on 4 and 26 January. Some data suggests that coal piles 1 and 2 may have been partially oxidized. However, there was an addition of Run 251 catalyst to the first stage on January 7 that might affect the catalyst activity (see Section 6.1). At the start of Run 252, 50 tons of coal that had been on the ground for 6 months, contained 0.46 wt % sulfate sulfur and the microautoclave (long) test gave 66-73% coal conversions (low). New coal was ordered. The new pile (Pile 1) was sampled (11/11/86) and contained 0.19 wt % sulfate sulfur which is marginal, however, when the totebin composite samples were analyzed later (Table 1, p. 62), the sulfate sulfur was 0.34 wt %. The second pile, received about 12/4/86, showed 0.14 wt % sulfate sulfur from the pile and 0.26 wt % sulfate sulfur when tested from the totebins on 1/9-14/87. Pile 3 received about 12/29/86 and used after 1/26/87 showed low sulfate sulfur of 0.086 from the totebins. Microautoclave (long test) results on the pile samples showed Pile 1 was of lower reactivity, however, Piles 2 and 3 were good. The respective autoclave results for Piles 1, 2 and 3 were 79.8, 85.0, 82% coal conversion. The microautoclave reactivity tests are done with a 25 wt % tetralin in 1-methylnaphthalene mixture at the conditions stated on page 58.

Good TSL system process performance responses were observed during Run 252 in the catalytic-catalytic mode of operation. The 1st stage process performance and responses were the main contributions to the TSL system performance and responses except for the response due to process variable changes from 252A to 252B. This was due to a high catalyst activity of Amocat 1C in the 1st stage reactor.

Because of relatively significant catalyst deactivation of Amocat 1C in the 1st stage, the averaged Phase 3 yields previously presented in this section cannot be used for calculation of process responses without considering catalyst ages. Estimated trend lines from experimental data are drawn in Figure 10 in order to see instant or zero-time process responses due to process variable changes. Comparisons for TSL, 1st and 2nd stages are summarized and discussed in the Section 3.5, Overall TSL Yields.

The table below for periods 252A, 252B, 252B1 and 252C shows the effects of 1st stage reaction residence time on 1st stage C_4+ distillate yields. The 1st stage reaction temperature was 810°F and the 2nd stage reaction temperature was 680°F for 252A and 750°F for the other periods.

Period	252A	252B	252B1	252C
Coal feed rate, MF lb/hr	300	353	347	377
Space velocity, hr^{-1}	2.76	3.18	3.15	3.46
$\frac{1}{\text{Space velocity}}$, hr	0.362	0.314	0.317	0.289
(Δ, % increase)		(-13)		(-9)
Catalyst age, lb(res+CI)/lb cat				
1st stage (average)	1863	2267	2765	3364
(Δ)		(+404)		(+599)
Catalyst age, lb MF coal/lb cat				
1st stage (average)	1101	1309	1566	1874
(Δ)		(+208)		(+308)
1st stage C_4+ dist. yield change, wt % MAF coal				
(Δ) zero-time		(-9)		(-3)
(Δ) avg. Phase 3		(-13)		(-7)

The table shows that the zero-time 1st stage C_4+ distillate decreased by 3-9 wt % MAF coal, as the 1st stage reaction residence time decreased by 9-13%. Larger responses in averaged Phase 3 data were observed due to different catalyst ages, that is, 7-13 wt % MAF coal decreases.

For periods 252B1 and 252C1 (Figure 10) the zero-time 1st stage C_4+ distillate increased by 4-7 wt % MAF coal without any process variable changes. These process performance improvements were possibly due to the three different coal piles processed.

Run 252 Comparison with Run 251

Period 252B (CC-ITSL, catalytic-catalytic mode of operation with Amocat 1C in both stages) is compared with 251-IE (CC-ITSL, catalytic-catalytic mode of operation with Amocat 1A 1st stage catalyst and Amocat 1C 2nd stage catalyst) as follows. First stage catalyst ages for the runs were similar (2100-2400 lb resid+CI/lb cat)(1224-1378 lb MF coal/lb cat). Period 252B had a higher coal feed rate (350 vs 300 MF lb/hr), a slightly lower 2nd stage reaction temperature (751 vs 758°F) and a lower 2nd stage catalyst age (500-700 vs 2300-2400 lb resid + CI/lb cat) (329-430 vs 1511-1577 lb MF coal/lb cat). Period 252B showed lower 1st stage process performance with lower C_4+ distillate by 10 wt % MAF coal, higher resid by 7 wt % MAF coal, lower hydrogen consumption by 0.6 wt % MAF coal, lower coal conversion by 2 wt % MAF coal and lower resid + UC conversion by 4 wt % feed (by 9 wt % MAF coal). The 1st stage catalyst activity was similar for both runs as shown in Figures 17 and 19. A detailed comparison is shown in the following table:

Operating Period	251-IE	252B
Dates, 1986	6/3-6/5	12/24-12/30
Operation mode		
1st stage	Catalytic	Catalytic
2nd stage	Catalytic	Catalytic
Catalyst type		
1st stage	Amocat 1A	Amocat 1C
2nd stage	Amocat 1C	Amocat 1C
Reaction temperature, °F		
1st stage	808	810
2nd stage	758	751
Inlet H_2 part. press., psia		
1st stage	2470	2520
2nd stage	2470	2580
Coal space velocity (1st/2nd stage) MF lb/hr/cu ft cat	36.3/37.2	43.6
Space velocity, lb feed/hr/lb cat		
1st stage	2.67	3.18
2nd stage	2.28	3.05
Catalyst age, lb(res+CI)/lb cat		
1st stage	2159-2245	2117-2416
2nd stage	2313-2374	487-708
Catalyst age, lb MF coal/lb cat		
1st stage	1077-1119	1240-1388
2nd stage	1483-1525	327-476
Coal feed rate, MF lb/hr	301	353
Hydrogen consumption , wt % MAF coal	4.5±0.3	3.9±0.3
Coal conversion, wt % MAF coal (a)	92.9±0.7	91.2±0.8
Yields, wt % MAF coal		
Water	5.9±0.1	8.4±0.7
H_2S, CO, CO_2, NH_3	3.5±0.2	2.9±0.4
C_1-C_3 gas	4.7±0.1	4.1±0.2
C_4+ distillate	57.2±0.3	46.8±1.4
C_4+ naphtha	12.1±0.9	10.2±0.7
Middle distillate	6.4±1.0	5.7±0.3
Distillate solvent	38.7±0.5	30.9±1.4
Resid	26.1±0.7	33.0±0.5
UC	7.1±0.7	8.8±0.8
Selectivity of C_1-C_3 gas to C_4+ distillate yield (X100)	8	9
Resid + UC conversion wt % feed (b)	33.8±0.2(66.8±0.1)	29.9±0.7(58.3±1.4)

(a) Cresol solubles.
(b) MAF coal as 100 wt % UC. Data in parentheses are based on wt % MAF coal.

3.3 2nd Stage

The second stage catalyst was 340 lbs of Amocat 1C. Catalyst samples were not obtained from R1236 during the run because the reactor does not have a catalyst addition/withdrawal system. See Section 6 for details of catalyst pretreatments and for the end of the run catalyst analysis.

From the startup of Run 252 to 18 December the coal feed rate was 300 MF lb/hr and the second stage temperature was 680°F. On 21 December, the coal feed rate was increased to 350 MF lb/hr and the second stage temperature was increased to 750°F. The coal feed rate was increased to 385 MF lb/hr on 17 January 1987.

The feed to the second stage consisted of the interstage separator bottoms and the T104 bottoms. T104 is used to fractionate the overhead stream of the interstage separator.

The flashed distillates from the second stage were fractionated using T105 and T102. Only distillates from T102 bottoms were returned to the process solvent. Until 13 January 1987, T102 bottoms distillate was also returned to the first stage as withdrawal tube flush; after this time the T104 bottoms was used as withdrawal tube flush.

Process adjustments made in support of second stage unit operations and upset conditions are summarized below:

	Process Adjustments/ Upset Conditions	Rationale/ Explanation
•	Dilute coal feed at 06:30 on 26 November.	"Soft start".
•	33% coal feed at 19:00 on 26 November.	
•	On solvent circulation at 01:35 on 29 November.	P1222 failure.
•	Restarted coal feed on 10 December at 13:35.	
•	Started operating T102 on 11 December.	
•	Started first stage solvent injection on 13 December at 02:25.	
•	On solvent at 17:00 on 18 December.	To change P1222.

On coal feed at 00:01 on 21 December. Coal feed = 350 MF lb/hr R1236 temp. = 750°F	
V1082 was down for several hours 2-3 January 1987. Two batches of process solvent were mixed with excess V1067 material.	Dowtherm system problems and FV6945 failure.
V1082 was down 11 January.	Due to CSD outage.
Unit on solvent at 12:00 on 12 January.	Due to CSD outage.
Unit on coal feed at 11:00 on 13 January.	
The coal feed rate was increased from 350 to 385 MF lb/hr at 18:15 on 17 January.	To stop negative resid yield.
Had power failures on 22 January 1987. P1236 would not restart after switching to emergency power at 07:30. On solvent at 08:50.	Off feed to clear catalyst from P1236.
On coal feed at 10:15 on 24 January.	
V1082 out of service from 04:30 to 08:30 on 28 January.	P1042 problems.
The level control valve for the interstage separator plugged at 10:15 on 28 January. Out of service until 13:05.	
Adjusted the solvent injection rate to R1236.	The solvent injection rate did not equal the T104 bottoms rate.
P1222 shutdown and could not be restarted at 01:50 on 3 February 1987. A plug formed in R1235.	End of Run 252.

Discussion of 2nd Stage Performance

For period 252A, the coal feed rate was 300 MF lb/hr and the 2nd stage temperature was 680°F. The hydrogen contents of the interstage separator resid and the V131B resid were 6.9 and 7.6 wt %, respectively. The V131B distillate contained 10.4 wt % hydrogen. The resid + UC conversion was very low (7.0 wt %).

For periods 252B and 252B1, the coal feed rate was 350 MF lb/hr and the 2nd stage temperature was 750°F. The hydrogen contents of the interstage separator resid and the V131B resid were 7.1 and 8.0 wt %, respectively. The V131B distillate averaged 10.15 wt % hydrogen. The resid + UC conversion averaged 18.0 wt % of solvent and ash free feed.

For periods 252C and 252C1, the coal feed rate was 385 MF lb/hr and the 2nd stage temperature was 750°F. The hydrogen contents of the interstage separator resid and the V131B resid were 6.7 and 7.5 wt %, respectively. The V131B distillate contained 10.0 wt % hydrogen. The resid + UC conversion averaged 16.1 wt % of solvent and ash free feed.

The wt % hydrogen in the process solvent distillate was fairly constant due to fractionation of the product and the subsequent recycle of only the heavy fraction. The wt % hydrogen in the process solvent resid dropped from 8 to 7.5 wt % when the coal feed rate was increased from 350 to 385 MF lb/hr. Also, the wt % hydrogen in the interstage resid decreased slightly when the coal feed rate was increased from 350 to 385 MF lb/hr.

When the coal feed rate was increased from 350 to 385 MF lb/hr, the second stage WHSV increased from 3 to 3.3 hr^{-1} and was accompanied by a decrease in resid + UC conversion of 1.8 wt % of solvent and ash free feed. The catalyst age was about 500 lb resid + CI/lb catalyst (329 lb MF coal lb cat) higher in 252C than in 252B1.

The second stage arrhenius constant for Run 252 was 0.81 compared to 0.96 in Run 250FGH. Run 250FGH operated in the thermal/catalytic mode with ash recycle. The second stage arrhenius constant in Run 251-IAF (catalytic-catalytic) was similar to the constant from Run 252. Operation with catalyst in the first stage reactor reduces second stage reactivity.

2nd Stage Performance Summary for Run 252

Operating Period	252A	252B	252B1	252C	252C1
Operating conditions					
R1235 avg. temp., °F	811	810	810	811	811
R1236 avg. temp., °F	679	751	750	749	750
Interstage Separator					
Bottoms, wt % solvent	48.95	45.18	44.53	44.15	43.44
R1236 WHSV, lb feed/hr/lb cat.	2.69	3.05	3.03	3.32	3.26
lb MF coal/lb cat	37.00	43.60	42.80	46.50	47.00
Atmospheric flashed bottoms, wt % solvent	51.5	48.9	47.1	45.9	44.0
Performance Data					
Resid + UC conversion wt % solvent & ash-free feed	7.0	18.2	17.7	15.9	16.2
H_2 consumption, wt % MAF	2.02	3.00	3.26	3.14	2.74
Process solvent (distillate) wt % hydrogen	10.4	10.1	10.2	10.0	10.0
Process solvent (resid-CI) wt % hydrogen	7.6	8.0	7.9	7.4	7.5
Catalyst age lb(resid+UC+ash)/lb cat	304	598	968	1493	1707
lb MF coal/lb cat	203	401	648	986	1120
Elementally balanced yields wt % solvent & ash-free feed					
H_2	-1.63	-2.20	-2.34	-2.14	-1.87
CO, CO_2	0.00	0.01	0.00	0.00	0.00
H_2O	1.11	1.71	2.03	2.04	1.62
NH_3	0.41	0.67	0.63	0.60	0.69
H_2S	0.30	0.41	0.40	0.73	0.68
C_1-C_3	1.85	1.96	2.00	2.15	1.59
C_4+ distillate	5.02	15.67	14.98	12.51	13.44
C_4-C_6	0.56	0.43	0.44	0.41	0.39
Naphtha	3.04	5.08	5.58	5.80	5.03
Middle distillate	0.79	1.58	1.88	1.93	1.59
Distillate solvent	0.63	8.57	7.07	4.37	6.43
UC	11.79	11.86	11.37	10.95	11.40
Resid	81.17	69.92	70.94	73.16	72.45

3.4. CSD Unit

The primary objectives of CSD unit operations during Run 252 were as follows:

1) To establish and maintain efficient first stage deashing to produce a low ash containing full range resid to blend with recycle solvent for coal slurrying.

2) To produce an optimum resid recovery with energy rejection <25 % of the feed coal heating value in the ash concentrate.

3) To evaluate CSD operations in the catalytic/catalytic, CC-ITSL mode of operation with Amocat 1C during batch aging and also during catalyst addition/withdrawal operations.

DAS type and first stage operating conditions were adjusted to produce efficient CSD operations. The CSD feed solvency index, resid recovery, energy rejection, and resid content of the ash concentrate were monitored on a frequent basis as performance indicators.

DAS type 4100 was used from the start of Run 252 until 5 Jan. Before then, the CSD feed characteristics (solubility in the DAS, solvent content, and preasphaltene content) did not allow the CSD operations to be optimized. First and second stage operating conditions were changed to prevent ash carryover and optimize resid recovery. Between 5 and 10 Jan, the DAS was gradually strengthened from 4100 to 2304. During this time, the energy rejection did not change but the resid recovery improved from 74.0 to 78.9%. Between 14 and 18 Jan, a gradual weakening of the DAS from type 2304 to 2204 was required to maintain acceptable deashing performance. After 19 Jan, the feed solvency index was in a range to increase the strength of the DAS. Thus, the DAS was gradually strengthened from 2304 to 2504. As expected, the strongest DAS had the best performance parameters: 82.0% resid recovery and 16.7% energy rejection on 2 Feb.

Batch catalyst aging effect on the CSD was predicted accurately. As the catalyst aged, the concentration of preasphaltenes in the CSD feed stream gradually increased and the feed solvency index decreased. This response is most clearly shown before the DAS was changed.

Catalyst addition/withdrawal began on 31 Jan. Since the run ended on 3 Feb an evaluation of CSD operations was inappropriate. A summary of CSD unit yields is given in the following table:

CSD Unit Yield Structure

Operating Period Date, (1986-87) DAS Type	252A 16,17 Dec 4100	252B 24-25,29-30 Dec 4100	252B1 4-5,7-8 Jan 4100/2204/2254	252C 20-21 Jan 2354/2404	252C1 26-30 Jan 2404/2504
Input, wt % CSD feed					
Distillate solvent	7.6	6.5	5.1	5.6	3.3
Resid	62.2	61.9	63.1	65.1	67.3
UC	10.1	10.7	10.4	10.4	10.4
Ash	20.1	20.9	21.4	18.9	19.0
Yield, wt % CSD feed					
Ash concentrate	47.8	48.4	49.1	45.0	45.3
Distillate solvent	0.9	1.0	0.9	0.2	0.4
Resid	15.5	14.8	15.5	13.5	11.6
UC	10.5	11.4	11.0	11.6	13.9
Ash	20.9	21.2	21.7	19.7	19.4
CSD resid	52.2	51.6	50.9	55.0	54.7
Distillate solvent	3.5	6.2	4.3	6.9	4.1
Resid	48.3	45.3	46.5	48.0	50.6
Ash	0.4	0.1	0.1	0.1	0.0
Resid recovery, wt % cresol solubles	76.9	76.2	75.6	80.3	78.7
Energy rejection, % of coal heating value	20.0	19.9	19.6	18.3	19.0
Organic rejection, % of adjusted ash concentrate (2nd Phase Balance Data)	18.5	17.7	17.3	17.8	17.8

Summary of DAS Changes

The DAS type was changed throughout Run 252 to minimize the energy rejection to the ash concentrate. The DAS type is chosen to allow acceptable first stage deashing while minimizing the energy rejection. A summary of DAS changes for Run 252 is shown below:

Date	DAS Type
28 Nov 86	4100
6 Jan 87	2154
7 Jan	2204
8-9 Jan	2254
10 Jan	2304
14 Jan	2254
17 Jan	2204
19 Jan	2304
20 Jan	2354
21 Jan	2404
30 Jan	2504

Observations

During this period of Run 252, the CSD feed solvency index ranged from 0.68 to 0.84 and the preasphaltene content of the CSD feed ranged from 0.0 to 11.5 wt % on a TI-CI basis. The feed had an average ash content of 20.1 wt %, an average UC content of 10.2 wt %. The ash concentrate consistency varied from gummy, grainy, chunky to powdery. The toluene soluble content of the ash concentrate ranged from 37.5 wt % in December to 11.2 wt % near the end of the run.

3.5 Overall TSL Yields

Averaged, elementally balanced TSL yields and contributions from each unit are summarized on the following pages for operating periods 252A to 252C1. The TSL yield contributions are also shown schematically in Material Balance Flow Diagrams (Figures 11 to 15).

Overall TSL Yields
(Phase 3 Data)

Operating Period	252A	252B
Date, 1986	12/16-12/17	12/24-12/30
Days selected	12/16, 12/17	12/24, 12/25 12/29, 12/30
Coal feed rate, MF lb/hr	300	353
Coal space velocity, MF coal/hr/cu ft cat	37.0	43.6
Coal conc. in slurry, wt % MF	33	33
Process solvent, wt %		
Resid (a)	38(43)	38(43)
CI	12	12
1st stage		
Reaction temp., °F (average)	811	810
Inlet H_2 part. press., psia	2560	2520
Space velocity, lb feed/hr/lb cat	2.76	3.18
Catalyst type	Amocat 1C	Amocat 1C
Catalyst age, lb(resid+CI)/lb cat	1841-1884	2117-2416
lb MF coal/lb cat	1103-1124	1240-1388
2nd stage		
Reaction temp., °F (average)	679	751
Inlet H_2 part. press., psia	2660	2580
Space velocity, lb feed/hr/lb cat	2.69	3.05
Catalyst type	Amocat 1C	Amocat 1C
Catalyst age, lb(resis+CI)/lb cat	290-319	487-708
lb MF coal/lb cat	192-213	327-476
CSD		
DAS type	4100	4100
H_2 consumption, wt % MAF	6.8±0.2	6.9±0.3
Energy rejection, %	20.1±0.2	19.9±1.4
Yield, wt % MAF coal		
Water	10.5±0.1	10.7±0.3
H_2S, CO, CO_2, NH_3	4.8±0.1	4.4±0.2
C_1-C_3 gas	7.3±0.4	6.7±0.3
C_4+ distillate	62.9±1.3	68.0±0.9
C_4+ naphtha	17.6±0.2	17.8±1.0
Middle distillate	8.2±0.5	7.9±0.1
Distillate solvent	37.0±2.1	42.4±1.8
Resid (b)	2.7±1.3	-0.8±0.7
Ash concentrate	18.7±0.1	17.9±1.5
H_2 efficiency		
lb C_4+ dist/lb H_2 cons	9.3±0.0	9.9±0.3
C_1-C_3 selectivity (X100)		
to C_4+ distillate	12.0±1.0	10.0±0.0
Coal conversion, wt % MAF (c)		
1st stage	91.8±0.1	91.2±0.8
1st and 2nd stages	92.9±0.3	92.9±0.4
Two stage	92.4±0.1	92.3±0.7
Resid + UC conversion, wt % feed (d)		
1st stage (e)	37.1±0.0(72.8±0.7)	29.9±0.7(58.3±1.4)
2nd stage	7.0±0.5(9.1±0.3)	18.2±1.8(25.1±3.1)

(a) Data in parentheses on CI-free basis.
(b) Includes TSL system UC accumulation.
(c) Cresol solubles.
(d) Data in parentheses are based on MAF coal.
(e) MAF coal as 100 wt % UC.

Overall TSL Yields
(Phase 3 Data)

Operating Period	252B1(f)	252C	252C1(f)
Date, 1987	1/4-1/8	1/20-1/21	1/26-1/30
Days selected	1/4,1/5 1/7,1/8	1/20,/21	1/26,1/27,1/28 1/29,1/30
Coal feed rate, MF lb/hr	347	377	381
Coal space velocity, MF lb/hr/cu ft cat	42.8	46.5	47.0
Coal conc. in slurry, wt % MF	33	33	33
Process solvent, wt %			
Resid (a)	38(44)	38(43)	39(45)
CI	12	12	12
1st stage			
Reaction temp., °F (average)	810	811	811
Inlet H_2 part. press., psia	2500	2440	2580
Space velocity, lb feed/hr/lb cat	3.15	3.46	3.49
Catalyst type	Amocat 1C	Amocat 1C	Amocat 1C
Catalyst age, lb(resid+CI)/lb cat	2662-2867	3337-3391	3554-3775
lb MF coal/lb cat	1510-1628	1885-1912	1992-2099
2nd stage			
Reacton temp., °F (average)	750	749	750
Inlet H_2 part. press., psia	2580	2580	2600
Space velocity, lb feed/hr/lb cat	3.03	3.32	3.26
Catalyst type	Amocat 1C	Amocat 1C	Amocat 1C
Catalyst age, lb(resid+CI)/lb cat	893-1043	1471-1515	1662-1792
lb MF coal/lb cat	598-697	972-999	1066-1175
CSD			
DAS type	4100-2204	2354	2404-2504
H_2 consumption, wt % MAF	7.1±0.1	6.3±0.1	6.1±0.3
Energy rejection, %	19.6±0.3	18.3±1.4	19.0±1.0
Yield, wt % MAF coal			
Water	9.6±0.8	9.3±0.9	9.7±0.4
H_2S, CO, CO_2, NH_3	5.1±0.1	4.7±0.1	5.1±0.2
C_1-C_3 gas	6.5±0.2	6.4±0.3	5.3±0.3
C_4+ distillate	69.4±2.0	61.7±0.3	64.9±1.7
C_4+ naphtha	17.5±0.9	16.5±0.8	16.2±0.6
Middle distillate	7.8±0.5	8.1±0.5	7.5±0.6
Distillate solvent	44.1±2.3	37.1±0.9	41.3±1.9
Resid (b)	-1.0±1.7	6.1±0.7	3.3±2.2
Ash concentrate	17.4±0.5	18.0±1.8	17.9±1.1
H_2 efficiency			
lb C_4+ dist/lb H_2 cons	9.9±0.3	9.8±0.1	10.6±0.3
C_1-C_3 selectivity (X100)			
to C_4+ distillate	9.0±0.0	11.0±1.0	8.0±1.0
Coal conversion, wt % MAF (c)			
1st stage	91.5±0.9	89.0±0.5	93.2±0.6
1st and 2nd stages	93.4±0.2	92.7±0.5	93.2±0.6
Two stage	93.0±0.3	91.7±0.1	92.2±0.8
Resid + UC conversion, wt % feed (d)			
1st stage (e)	29.9±1.0(59.4±1.9)	25.9±0.5(51.3±0.8)	27.2±0.8(54.6±1.5)
2nd stage	17.7±0.9(24.4±0.9)	15.9±0.7(24.2±0.6)	16.2±1.4(23.4±1.4)

(a) Data in parentheses on CI-free basis.
(b) Includes TSL system UC accumulation.
(c) Cresol solubles.
(d) Data in parentheses are based on MAF coal.
(e) MAF coal as 100 wt % UC.
(f) TSL process performance improved without any process variable changes.

	Product Withdrawal Point (a)				
	252A	252B	252B1	252C	252C1
TSL Yield, wt % MAF					
H_2	-6.75	-6.89	-7.05	-6.30	-6.13
CO, CO_2	0.31	0.28	.27	0.51	0.46
H_2O	10.49	10.70	9.64	9.28	9.68
NH_3	1.46	1.55	1.62	1.40	1.53
H_2S	3.06	2.57	3.22	2.82	3.06
C_1-C_3	7.25	6.73	6.52	6.42	5.28
C_4+ distillate	62.81	67.97	69.38	61.65	64.93
C_4-C_6	3.07	2.21	3.27	1.94	1.69
IBP-350	14.53	15.55	15.22	14.52	14.46
350-450	8.19	7.85	7.80	8.11	7.46
450-EP	37.02	42.35	44.10	37.08	41.31
Resid	2.26	-1.09	-1.21	6.14	3.56
Int. Accum. - UC	0.47	0.27	0.24	0.13	-0.23
Ash Conc. (ash-free)	18.65	17.92	17.38	17.97	17.85
1st Stage Contribution, wt % MAF					
H_2	-4.73	-3.89	-3.79	-3.15	-3.39
CO, CO_2	0.31	0.26	0.27	0.51	0.46
H_2O	9.11	8.36	6.81	6.28	7.32
NH_3	0.96	0.63	0.75	0.51	0.52
H_2S	2.69	2.01	2.66	1.75	2.06
C_1-C_3	4.97	4.05	3.73	3.25	2.96
C_4+ distillate	5.59	12.07	12.63	7.69	15.03
C_4-C_6	2.38	1.63	1.65	1.33	1.12
IBP-350	8.23	7.15	6.89	5.55	6.34
350-450	3.81	3.15	3.33	2.92	2.51
450-EP	-8.83	0.13	0.76	-2.11	5.05
2nd Stage Contribution, wt % MAF					
H_2	-2.02	-3.00	-3.26	-3.14	-2.74
CO, CO_2	0.00	0.01	0.00	0.00	0.00
H_2O	1.38	2.34	2.83	3.00	2.36
NH_3	0.50	0.92	0.87	0.88	1.01
H_2S	0.37	0.56	0.56	1.08	1.00
C_1-C_3	2.28	2.68	2.79	3.17	2.32
C_4+ distillate	57.31	56.28	56.95	53.19	49.48
C_4-C_6	0.69	0.59	0.62	0.61	0.57
IBP-350	6.31	8.40	8.33	8.98	8.12
350-450	4.37	4.70	4.47	5.18	4.95
450-EP	45.94	42.60	43.53	38.41	35.84
Int. Accum. - Resid	3.41	1.68	1.52	0.86	-1.51
Int. Accum. - UC	0.47	0.27	0.24	0.13	-0.23
CSD Contribution, wt % MAF					
450-EP	-0.09	-0.38	-0.20	0.78	0.42
Resid	-1.14	-2.77	-2.74	5.28	5.06
Ash Conc. (ash-free)	18.65	17.92	17.38	17.97	17.85

(a) Unit contributions denote where products were withdrawn from the TSL system.

Discussion of TSL Performance

Process conditions were varied during Run 252 to improve TSL process performance. Major process adjustments are summarized below:

(1) 2nd stage reaction temperature: 680-750°F

(2) 1st stage space velocity (WHSV): 2.8-3.5 hr^{-1}

(3) 2nd stage space velocity (WHSV): 2.7-3.3 hr^{-1}
37-47 MF lb/hr/cu ft cat

(4) CSD DAS type: 4100, 2204-2504

(5) Catalyst aging during the run:
1st stage Amocat 1A, 1500-3533 lb (res+CI)/lb cat
964-1892 lb MF coal/lb cat
2nd stage Amocat 1C, 0-1921 lb (res+CI)/lb cat
35-1255 lb MF coal/lb cat

TSL process performance data varied significantly due to these process variable changes as shown below:

	Range for 252A to 252C1
H_2 efficiency, lb C_4+ dist/lb H_2 cons	9.3-10.6
C_1-C_3 selectivity (X100) to C_4+ dist	8-12
Energy rejection, %	18-20
Coal conversion, wt % MAF coal	93
TSL yield, wt % MAF coal	
H_2 consumption	6.1-7.1
C_1-C_3	5-7
C_4+ distillate	62-69
Resid (a)	-1-+6
Ash concentrate (ash-free)	17-19

(a) Includes TSL system UC accumulation.

As discussed in Section 3.2 1st Stage - Analysis of 1st Stage Performance, good TSL system process performance responses were observed during Run 252 in the catalytic-catalytic mode of operation. Figure 10 shows C_4+ distillate yield responses for TSL, 1st and 2nd stages due to process variable changes. The 1st stage process performance and responses were main contributions to the TSL system performance and responses except for the response due to process variable changes from 252A to 252B. This was due to a high catalyst activity of Amocat 1C in the 1st stage reactor.

Instant or zero-time process responses due to process variable changes were estimated by extrapolation of trend lines from experimental data (Figure 10) with consideration of catalyst ages. This is summarized below:

Period	252A		252B		252B1(b)		252C		252C1(b)
Temp., °F									
1st stage	811		810		810		811		811
2nd stage	679		751		750		749		750
Coal feed rate									
MF lb/hr	300		353		347		377		381
C_4+ dist. yield wt % MAF coal									
TSL		+11		+9		-2		+6	
1st stage		-9		+7		-3		+4	
2nd stage		+20		+2		+1		+2	
Yield distribution wt %									
1st stage	95		69		71		68		69
2nd stage	5		31		29		32		31

(a) These yield responses cannot be seen by comparing average Phase 3 yields for each period because of rapid catalyst deactivation trends. Estimated trend lines are drawn by evaluation of catalyst activity trends in both reactors, which will be discussed later in the catalyst activity section.

(b) Process performance was improved for unknown reasons. Several catalyst adjustments were made in January (see Section 6.1). Three different coal piles were processed during Run 252:

Pile #1 for 12-30 December
Pile #2 for 31 December - 19 January
Pile #3 for 20 January - 3 February

Comparisons of periods 252A, 252B, 252B1 and 252C were discussed in the section 3.2 1st Stage - Analysis of 1st Stage Performance, to evaluate the effect of the 1st stage reaction residence time on the 1st stage C_4+ distillate yield. The effect on the TSL C_4+ distillate yield response is different from the 1st stage response for 252A and 252B, because the 2nd stage reaction temperature was increased by 72°F at the same time.

The effect of the 2nd stage reaction temperature increase by 72°F on the TSL C_4+ distillate yield are summarized below:

Period	252A		252B
Temp., °F			
2nd stage	679		751
(Δ)		(+72)	
Catalyst age lb(res+CI)/lb cat			
2nd stage (average)	305		598
(Δ)		(+293)	
Catalyst age lb MF coal/lb cat			
2nd stage (average)	200		393
(Δ)		(+193)	
C_4+ dist. yield change wt % MAF coal			
2nd stage			
(Δ) zero-time		(+20)	
(Δ) avg. Phase 3		(+18)	
TSL			
(Δ) zero-time		(+11)	
(Δ) avg. Phase 3		(+5)	

The zero-time TSL C_4+ distillate yield was increased by 11 wt % MAF coal due to the zero-time 1st stage decrease by 9 wt % and the 2nd stage increase by 20 wt %. A different response in Phase 3 data was observed because of different catalyst ages in both 1st and 2nd stages, that is, 5 wt % MAF coal increase.

For 252B1 and 252C the effect on the TSL C_4+ distillate yield response due to the 1st stage reaction residence time change is similar to the 1st stage response because there was no significant response observed in the 2nd stage.

Periods 252B1 and 252C1 show the zero-time TSL C_4+ distillate increases by 6-9 wt % MAF coal for unknown reasons. No process variables were changed during these periods however different coal piles were processed and several catalyst adjustments were made (see Section 6.1). The 1st stage response (4-7 wt % MAF coal) was the main contribution to the TSL response. The 2nd stage response was relatively small, 2 wt % MAF coal.

TSL Comparisons - Run 252 and 251

TSL process performance is compared for CC-ITSL, catalytic-catalytic mode Run 252 and 251-I. Period 252B with Amocat 1C in both stages, and period 251-IE with Amocat 1A 1st stage catalyst and Amocat 1C 2nd stage catalyst were selected for comparison because of similar 1st stage catalyst ages (2100-2400 lb resid + CI/lb cat) (1380-1577 lb MF coal/lb cat). Several process operating conditions were different for these runs such as (1) higher coal feed rate for 252B,

(2) slightly lower 2nd stage reaction temperature for 252B, and (3) lower 2nd stage catalyst age for 252B. A comparison of the 1st and 2nd stage rate constant for the two periods indicates that the difference in 2nd stage catalyst age was the primary reason for differences in yields.

- Run 252B with Amocat 1C in the 1st stage reactor at younger catalyst ages in the 2nd stage reactor achieved an "all-distillate" yield slate while operating with a coal feed rate 17% higher, compared to Run 251-IE.
- The C_4+ distillate yield was similar, 68-70 wt % MAF coal. Run 252B had lower C_4+ naphtha by 2 wt % MAF coal.
- Run 252B showed higher organic rejection by 3 wt % MAF coal compared to Run 251-IE, probably due to highly soluble CSD feed produced during Run 252B. The organic rejection did not improve throughout the run.
- Run 252B showed lower 1st stage resid + UC conversion by 4 wt % of feed (9 wt % MAF coal), but higher 2nd stage resid + UC conversion by 4 wt % of feed (6 wt % MAF coal).

A detailed performance comparison is given below:

Operating Period Dates, 1986	251-IE 6/3-6/5	252B 12/24-12/30
Operating mode		
1st stage	Catalytic	Catalytic
2nd stage	Catalytic	Catalytic
Catalyst type		
1st stage	Amocat 1A	Amocat 1C
2nd stage	Amocat 1C	Amocat 1C
Reaction temperature, °F		
1st stage	808	810
2nd stage	758	751
Inlet H_2 part. press., psia		
1st stage	2470	2520
2nd stage	2470	2580
Coal space velocity (1st/2nd stage), MF lb/hr/cu ft cat	36.3/37.2	43.6
Space velocity, lb feed/hr/lb cat		
1st stage	2.67	3.18
2nd stage	2.28	3.05
Catalyst age, lb(resid+CI)/lb cat		
1st stage	2159-2245	2117-2416
2nd stage	2313-2374	487-708
Catalyst age lb MF coal/lb cat		
1st stage	1077-1119	1240-1388
2nd stage	1483-1525	327-476
Catalyst age, lb MF coal/lb cat		
1st stage	1254-1278	1232-1386
2nd stage	1520-1560	320-465
Coal feed rate, MF lb/hr	301	353
H_2 consumption, wt % MAF coal	6.8±0.0	6.9±0.3
Energy rejection, %	16.5±0.2 (DAS 2504)	19.9±1.4 (DAS 4100)
Yield, wt % MAF coal		
Water	10.3±0.1	10.7±0.3
H_2S, CO, CO_2, NH_3	4.6±0.1	4.4±0.2
C_1-C_3 gas	7.4±0.0	6.7±0.3
C_4+ distillate	70.2±0.6	68.0±0.9
C_4+ naphtha	19.6±0.9	17.8±1.0
Middle distillate	7.9±0.7	7.9±0.1
Distillate solvent	42.8±0.4	42.4±1.8
Resid (a)	-0.7±0.7	-0.8±0.7
Ash concentrate	15.1±0.3	17.9±1.5
H_2 efficiency		
lb C_4+ dist/lb H_2 cons.	10.3±0.1	9.9±0.3
C_1-C_3 selectivity (X100)		
to C_4+ distillate	11.0±1.0	10.0±0.0
Coal conversion, wt % MAF (b)		
1st stage	92.9±0.7	91.2±0.8
1st and 2nd stages	93.8±0.5	92.9±0.4
Two stage	92.9±0.5	92.3±0.7
Resid + UC conversion, wt % feed (c)		
1st stage (d)	33.8±0.2(66.8±0.1)	29.9±0.7(58.3±1.4)
2nd stage	14.6±0.7(19.0±1.1)	18.2±1.8(25.1±3.1)

(a) Includes TSL system UC accumulation.
(b) Cresol solubles.
(c) Data in parentheses are based on wt % MAF coal.
(d) MAF coal as 100 wt % UC.

Run 252 TSL Hydrogenation of Process Solvent

Figures 7 and 16 are plots of catalyst hydrogenation and process solvent hydrogen donor activity properties including hydrogen content of recycle and product resid and distillate, 1st and 2nd stage reactor exotherm, and 1st and 2nd stage hydrogen consumption. Hydrogen transfer, hydrogen consumption and exotherm data are shown below in comparison to data from Run 251-IC and 251-IE. Hydrogen transfer data for the 1st stage were approximated by the hydrogen content differences of resid and distillate portions of recycle process solvent (V131B) and 2nd stage feed which relatively indicate net dehydrogenation of recycle process solvent. This net dehydrogenation is considered to be a result of the combination of thermal dehydrogenation (hydrogen transfer from recycle process solvent to coal) and catalytic rehydrogenation with gaseous hydrogen.

Run	251-IC	251-IE	252A	252B	252B1	252C	252C1
Operation mode							
1st stage	← Catalytic →						
2nd stage	← Catalytic →						
Catalyst type							
1st stage	← Amocat 1A →		← Amocat 1C →				
2nd stage	← Amocat 1C →		← Amocat 1C →				
Reaction temp., °F							
1st stage	806	808	811	810	810	811	811
2nd stage	759	758	679	751	750	749	750
Catalyst age, lb(resid+CI)/lb cat							
1st stage	1181-1722	2159-2245	1841-1884	2117-2416	2662-2867	3337-3391	3554-3775
2nd stage	1570-1992	2313-2374	290-319	487-708	893-1043	1471-1515	1662-1792
Coal feed rate, MF lb/hr	482	301	300	353	347	377	381
Hydrogen transfer wt % hydrogen (V131B-R1235)							
Resid	0.6	0.2	0.6	0.8	0.8	0.7	0.4
Distillate	0.5	0.3	0.5	0.5	0.5	0.3	0.2
Total	1.1	0.5	1.1	1.3	1.3	1.0	0.6
H_2 consumption wt % MAF coal							
TSL	6.0	6.8	6.8	6.9	7.1	6.3	6.1
1st stage	3.3	4.5	4.7	3.9	3.8	3.2	3.4
2nd stage	2.7	2.3	2.1	3.0	3.3	3.1	2.7
Exotherm, °F(a)							
1st stage	0.97	0.96	1.0	0.77	0.72	0.62	0.67
2nd stage	3.43	2.48	1.0	3.39	3.30	3.74	3.52

(a) Exotherm is relative to 252A.

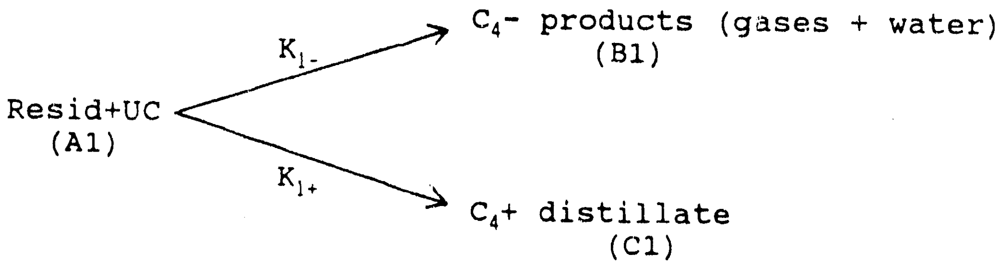
Periods 252B, B1 and C compared to 251-IE at younger 2nd stage catalyst ages (600-1500 vs 2350 lb (res + CI)/lb cat) (394-986 vs 1544 lb MF coal/lb cat) and at a higher coal feed rate (350 vs 300 MF lb/hr) had higher hydrogen transfer values (1.0-1.34 vs 0.5). This is probably due to higher hydrogen contents of recycle process solvent (8.01-8.25 vs 7.74 wt %), which appear to reduce catalytic rehydrogenation in the 1st stage. Less hydrogen consumption and less total exotherm in the 1st stage confirmed lower catalytic rehydrogenation in the 1st stage, while more hydrogen consumption and more total exotherm in the 2nd stage confirmed higher catalytic hydrogenation in the 2nd stage.

In period 252C1 at high 1st stage catalyst ages (3500-3800 lb (res+CI)/lb cat) (1944-2099 lb MF coal/lb cat) the hydrogen transfer value declined to 0.6, indicating a decline of recycle process solvent quality. During this period process solvent quality was 81-82% as compared to the early periods of 84-87%. Further studies are necessary to investigate the effect of this decline of hydrogen transfer at high catalyst ages on TSL process performance.

Parity Plots and Steady-State Catalyst Requirement Calculations

Parity plots and catalyst addition/withdrawal requirements are calculated using a first order kinetics model for the following conversions:

First stage conversion:



$$-r_{A1} = K_1 C_{A1} = (K_{1+} + k_{1-}) C_{A1} = r_{B1} + r_{C1}$$
$$r_{B1} = k_{1-} C_{A1}$$
$$r_{C1} = K_{1+} C_{A1}$$

In these equations, K_1 is the first stage resid + UC conversion rate constant and K_{1+} and K_{1-} are the first stage rate constants for the production of C_4+ distillate and C_4- products (gases + H_2O) respectively. The various rate constants can be calculated as follows:

$$K_1 = WHSV_1 \frac{\epsilon_1}{(1-\epsilon_1)}$$

$$K_{1+} = f_1 K_1$$

$$K_{1+} = f_1 WHSV_1 \frac{Y_{C1}'}{(f_1 C_1 - Y_{C1}')}$$

$$K_{1-} = (1-f_1) K_1$$

where Y_{C1}' is the distillate yield (wt % MAF coal/100), f_1 is the fraction of C_4+ distillate produced per pound of resid + UC converted (experimental value of f_1 ranges from 0.515 to 0.719), and C_1 is a unit conversion factor of resid + UC conversion from wt % feed to wt % MAF coal (1.948-2.001). For first stage, correlation of experimental data yields (Run 252B-C1, Figure 17).

$$\ln K_1 = 0.49 - 0.000077t$$

A similar reaction scheme can be formulated for the second stage + ROSE-SR^{SM} unit conversion of resid + UC. The reactions and equations for the second stage are similar to those obtained for the first stage (substitute subscript 1 by 2 in the above equations). The constants f_2 and C_2 are in the range 1.041-1.523 and 1.366-1.472 respectively and the correlation of experimental data for the second stage yields (Figure 18).

$$\ln K_2 = -0.21 - 0.00005t$$

The overall two-stage C_4+ distillate yield can be expressed as a sum of each stage yield:

$$Y_C' = Y_{C1}' + Y_{C2}'$$

$$= \frac{f_1\ C_1\ K_{1+}}{(f_1\ \mathrm{WHSV}_1 + K_{1+})} + \frac{f_2\ C_2\ K_{2+}}{(f_2\ \mathrm{WHSV}_2 + K_{2+})}$$

Using the rate constant equations obtained by correlating the experimental data, the distillate yield is calculated and compared with experimental yield in the following table. A parity plot involving the distillate yields is given in Figure 21.

The table also compares experimental coal feed rates with those predicted using the rate constant equations. For a run period, the feed rate is predicted for the given experimental distillate yield. The feed rate can be calculated using the above equations and the experimental value for the ratio of $\mathrm{WHSV}_2/\mathrm{WHSV}_1$. A parity plot involving coal feed rates is given in Figure 21. For comparison, values obtained from Run 251-I are also plotted in Figure 21.

The comparisons in the table and the parity plots give an indication of how well the experimental rate constant data are correlated using the first order kinetics. Because of large scatter in data, the errors obtained in correlating rate constants may not be sufficient to judge the accuracy of the correlation. Alternatively, the parity plots in Figure 21 and the errors in distillate yield and coal feed rates reported in the table, suggest that the rate constant correlations are fairly accurate. Thus, the first order kinetics model is sufficiently accurate in the range of experimental data.

The coal feed rates projected to achieve resid extinction with a common organic rejection of 15 wt % MAF coal are given in the next table along with mean catalyst ages. The projected coal feed rates for the given achievable distillate yields are then calculated as described above. The catalyst addition/withdrawal rates necessary to maintain catalyst ages at a steady-state at the projected coal feed rates are also given in the table. For example, for period 252C, the addition/withdrawal rates necessary to maintain catalyst ages at 1899 and 986 lb MF coal/lb catalyst in the first and second stages are 1.03 and 1.94 lb catalyst/ton MF coal, respectively. With these addition/withdrawal rates and a coal feed rate of 317 lb MF/hr, the distillate yield will be 69 wt % MAF coal with an organic rejection of 15 wt % MAF coal and resid extinction. It is important to note that the addition/withdrawal rates calculated are only valid for the experimental run conditions of catalyst age distribution, catalyst activity, and the deactivation rate.

Catalyst ages can be maintained with the addition/withdrawal rates calculated above, but the catalyst activity is continuously changing since the age distribution changes with every addition/withdrawal. For design calculations as well as for comparison between various runs, it is useful to calculate addition/withdrawal rates necessary to maintain an equilibrium activity level. Such calculations take into account an equilibrium catalyst age distribution and activity levels and deactivation rates over a broad range of catalyst ages. If the experimental data is available over a wide range of catalyst ages, then addition/withdrawal rates based on equilibrium activity levels is more accurate and useful in design calculations.

Experimental and Model Predicted Coal Feed Rate and Distillate Yield Comparisons

					Model Predicted		Experimental		C_4+ dist. yield wt % MAF coal			Coal feed MF lb/hr		
Run	Stage	Temp. (°F)	Rate constant (K), hr^{-1} lnK = (lnA-E/RT)-αt	Catalyst age (t) lb res+CI/lb cat	Rate constant (K), 1/hr	Conversion wt % feed	Rate constant (K) 1/hr	Conversion wt % feed	Model (a)	Expt.	Error % (c)	Model (b)	Expt.	Error % (c)
252B	1st	810	0.49-0.00008t	2266	1.362	30	1.356	29.9	72.8	68.0	6.6	385	353	8.4
	2nd	751	-0.21-0.00005t	598	0.787	20.5	0.679	18.2						
252B1	1st	810	0.49-0.00008t	2764	1.309	29.4	1.344	29.9	74.6	69.4	7.0	381	347	8.9
	2nd	750	-0.21-0.00005t	968	0.772	20.3	0.652	17.7						
252C	1st	811	0.49-0.00008t	3364	1.247	26.5	1.209	25.9	65.6	61.7	5.9	415	377	9.2
	2nd	749	-0.21-0.00005t	1493	0.752	18.5	0.628	15.9						
252C1	1st	811	0.49-0.00008t	3664	1.218	25.9	1.304	27.2	65.6	64.9	1.1	394	381	3.2
	2nd	750	-0.21-0.00005t	1707	0.744	18.6	0.630	16.2						
251-IB	1st	792	23.3-28200/T-0.00034t	949	1.574	27.4	1.546	27.0	61.4	61.0	0.7	476	472	0.6
	2nd	760	17.2-21300/T-0.00005t	1394	0.720	15.9	0.733	16.1						
251-IC	1st	806	23.3-28200/T-0.00034t	1532	1.592	27.4	1.654	28.2	60.8	60.6	0.3	484	482	0.4
	2nd	759	17.2-21300/T-0.00005t	1845	0.730	16.2	0.662	14.9						
251-ID	1st	807	23.3-28200/T-0.00034t	1922	1.476	30.4	1.401	29.3	68.0	62.3	8.4	434	385	11.3
	2nd	759	17.2-21300/T-0.00005t	2143	0.684	18.6	0.528	15.0						
251-IE	1st	808	23.3-28200/T-0.00034t	2202	1.366	33.8	1.363	33.8	78.7	70.2	10.8	346	301	13.0
	2nd	758	17.2-21300/T-0.00005t	2344	0.667	22.6	0.390	14.6						

(a) C_4+ distillate yield predicted for the experimental coal feed rate.
(b) Coal feed rate predicted for the experimental C_4+ distillate yield.
(c) % error = (1 - experimental/predicted) x 100.

Projection of Coal Feed Rate for Resid Extinction, and Calculation of Steady State Catalyst Addition

Run	Stage	Temp. (°F)	Coal feed lb MF/hr	Yield (wt % MAF coal)			Achievable C_4+ dist. yield (a) (wt % MAF coal)	Projected coal feed rate (MF lb/hr)	Catalyst age (lb MF coal) / lb cat	Calculated steady-state catalyst A/W (lb/ton MF)	
				C_4+ dist.	Organic rejection	Resid				-	Total
252B	1st	810	353	68	18	-1	70	339	1314	1.47	5.93
	2nd	751							401	4.46	
252B1	1st	810	347	69	17	-1	70	346	1569	1.24	4.11
	2nd	750							648	2.87	
252C	1st	811	377	62	18	6	69	323	1899	1.03	2.97
	2nd	749							986	1.94	
252C1	1st	811	381	65	18	3	70	344	2045	0.96	2.67
	2nd	750							1120	1.71	
251-IB	1st	792	472	61	20	5	65	425	474	3.73	5.87
	2nd	760							876	2.14	
251-IC	1st	806	482	61	18	6	68	405	763	2.43	4.08
	2nd	759							1168	1.65	
251-ID	1st	807	385	62	17	7	69	335	958	1.98	3.39
	2nd	759							1364	1.41	
251-IE	1st	808	301	70	15	-1	69	310	1098	1.76	3.06
	2nd	758							1504	1.30	

(a) Assuming 20 wt % MAF for operation at 790°F and 15 wt % MAF at 810°F as achievable organic rejection.

TSL Catalyst Selectivity in TSL Hydrogenation and Heteroatom Removal (Run 251-I vs 252) (Amocat 1A vs Amocat 1C) 1st Stage

Catalyst selectivities in TSL hydrogenation and heteroatom removal versus TSL hydrogen consumption, (which is an indication of TSL process severity) are compared in Figures 22-27 for Runs 251-I and 252.

Several process operating conditions for the runs were different, as shown below:

Run	251-I	252
Catalyst type		
1st stage	Amocat 1A	Amocat 1C
2nd stage	Amocat 1C	Amocat 1C
Catalyst age lb(res+CI)/lb cat		
1st stage	0-2800	1500-3800(high)
2nd stage	0-2800	0-2000(low)
Catalyst age lb MF coal/lb cat		
1st stage	0-1584	
2nd stage	0-1840	
Coal feed rate, MF lb/hr	300-480	300-335
Reaction temp., °F		
1st stage	775-825	810
2nd stage	760-775	690-750
T105-T102 Col. operation	No	Yes

Major observations in catalyst selectivities at the above process operating conditions are:

- Run 252 with highly aged Amocat 1C in the 1st stage showed a slightly higher selectivity for the potential liquid yield (C_4+ resid) production by 1-2 wt % MAF coal, compared to Run 251-I with less aged Amocat 1A in the 1st stage.

- There appears to be a breakeven point for hydrogen efficiency and product quality. TSL hydrogen consumption for the breakeven is approximately 6.5 wt % MAF coal. Run 252 with highly aged Amocat 1C in the 1st stage showed a slightly lower hydrogen efficiency in the high severity process conditions with hydrogen consumption above 7 wt % MAF coal. The opposite is true in the low severity process conditions with hydrogen consumption below 6 wt % MAF coal.

- Run 252 with highly aged Amocat 1C in the 1st stage showed less C_1-C_3 gas make in the high severity process conditions. This indicates that hydrogen was more efficiently used in the C_4+ distillate make.

- Run 252 had higher nitrogen removal and lower oxygen removal activity than 251-I. Sulfur removal activity was similar for both runs.

  Overall heteroatom (N, S, O) removal was similar for both runs, or slightly better in Run 251-I.

- Run 252 showed an indication of a catalytic water-gas shift reaction processing Illinois No. 6 bituminous coal (see page 103):

$$CO_2 + H_2 \underset{\text{Catalyst}}{\rightleftarrows} H_2O + CO$$

- From results of linear regression slope analyses in relation to the contributions of TSL hydrogen consumption in products as listed below, Run 252 showed a higher hydrogen consumption contribution in H_2O make, lower in C_1-C_3 gas and NH_3 make and similar in C_4+ distillate and H_2S make, compared to Run 251-I.

Run	Product	Linear regression slope (Product/H_2 Cons)	H_2 required theoretically (% MAF coal)	Contribution (%)
251-I	C_1-C_3	2.77	0.16	16
	H_2O	0(a)	0	0
	C_4+ dist	11.0	0.8(b)	80
	H_2S	0(a)	0	0
	NH_3	0.20	0.04	4
			=1.00	=100
252	C_1-C_3	1.33	0.08	8
	H_2O	0.93	0.1	10
	C_4+ dist	4.89(c)	0.82(b)	82
	H_2S	0(a)	0	0
	NH_3	0(a)	0	0
			=1.00	=100

(a) The slope in the linear regression analysis is assumed to be zero because of a poor correlation ($r^2 < 0.4$).

(b) By difference.

(c) Questionable data because process performance was improved without any process variable changes during Run 252.

TSL Catalyst Characterization (Amocat 1C Cascading)

For Run 252 with Amocat 1C catalyst cascading, elemental and mineral analysis data of fresh and aged 1st and 2nd stage Amocat 1C catalysts are summarized in the Section 6.0 - Catalyst. Several catalyst physical and chemical properties such as coke and carbon deposits, atomic ratios of H/C and S/Mo are plotted in Figures 28 and 29 in addition to naphthalene activity of aged catalyst. Coke is defined as (100% - % catalyst) in the THF-extracted aged catalyst, where % catalyst is defined as (% ash + % sulfur).

Major observations in characterization of the mixed catalyst used for the cascading experiment (a batch deactivation test with the catalyst aged in the 2nd stage) during Run 252 were:

- 2nd stage catalyst had lower carbon deposits by 5-10 wt % of catalyst than 1st stage catalyst.
- 2nd stage catalyst showed a higher H/C atomic ratio by 0.5 than 1st stage catalyst.
- 2nd stage catalyst showed a lower S/Mo atomic ratio by 0.3 than 1st stage catalyst probably due to no DMDS addition in the 2nd stage during this run.

  Note that 1st stage catalyst collected after the reactor plug on 3 February showed a lower S/Mo atomic ratio by 0.2-0.4 compared to those collected in the normal operation.
- 2nd stage catalyst showed higher naphthalene activity by 40-50 (m gr-mole of H_2 consumed) than 1st stage catalyst.
- A good linear correlation was observed between naphthalene activity (Y) of aged catalyst and carbon deposits (X) on catalyst.

  $Y = 198.38 - 8.35\ X$
  r (correlation coefficient) = 0.972

  A similar trend was observed with Shell 324 processing Wyodak coal during Run 251-III (Ref. 2).

  $Y = 225.04 - 11.66\ X$
  r (correlation coefficient) = 0.921

  Run 252 Amocat 1C catalyst showed a slower decline of the naphthalene activity as the carbon deposits on the catalyst increased and a higher activity at the same catalyst age than Run 251-III Shell 324. A similar result was also observed as the catalyst age increased. This indicates that Run 252 Amocat 1C catalyst processing Illinois No. 6 coal has a lower deactivation rate and higher catalyst activity in hydrogenation than Run 251-III Shell 324 catalyst processing Wyodak coal.

  In addition, Run 252 Amocat 1C catalyst showed lower carbon deposits on the catalyst and a higher atomic ratio of hydrogen to carbon at the same catalyst age.

In comparison with Run 251-I (Amocat 1A catalyst in the 1st stage processing Illinois No. 6 coal), Run 252 (Amocat 1C catalyst in the 1st stage) showed similar trends in the carbon deposits on catalyst and atomic ratio of hydrogen to carbon, as the catalyst age increases. These results may be affected because of two different extraction solvents used for catalyst preparation before analyses (toluene for Run 251-I and THF for Run 252). Run 252 Amocat 1C showed higher naphthalene activity than Run 251-I Amocat 1A, indicating that Amocat 1C has higher catalyst activity in hydrogenation.

Both Run 251-I and 252 used Amocat 1C in the 2nd stage. Characterization results of the 2nd stage Amocat 1C catalyst are compared below:

Run	251-I	252
Catalyst age (end-of-run) lb res+CI/lb cat	2783	1921
Catalyst age (end-of-run) lb MF coal/lb cat	1958	1262
Carbon deposits wt % of catalyst	13.5	8.4-10.9
H/C atomic ratio	1.04	1.12-1.32
S/Mo atomic ratio	1.96	1.82
Naphthalene activity m gr-mole of H_2 consumed	72	95-114

(Note) Extraction solvents used in preparation of catalyst samples for analyses were toluene for Run 251-I and THF for Run 252.

Run 252 2nd stage Amocat 1C catalyst at a lower catalyst age (1921 vs 2783) at the end of the run showed lower carbon deposits, a higher H/C atomic ratio and higher naphthalene activity indicating higher catalyst activity in hydrogenation, compared to that for Run 251-I at a higher catalyst age at the end of the run.

4. DISTILLATE PRODUCT QUALITY AND UNIT SOLVENTS

The primary products in Run 252 were distillates produced in the 1st and 2nd stages. These distillates were analyzed by gas chromatography to determine boiling range fractions and by an elemental analyzer to determine elemental composition such as carbon, hydrogen, nitrogen, sulfur and oxygen by difference. The GC boiling range fractions are defined as: naphtha (IBP-350°F), middle distillate (350-450°F), and distillate solvent (450°F-EP).

The 1st stage produces three distillate products: T104 Solvent Recovery Column overhead, T104 bottoms, and V182 Slurry Drying System overhead. The T104 overhead is predominantly IBP-450°F naphtha, T104 bottoms is 450-850°F, and V182 solvent is a wide-boiling range stream.

The 2nd stage produces four distillate products: T105 atmospheric column overhead (V161), T102 vacuum column overhead (P171), T102 vacuum column tray 3 distillate (V138) and V1074 solvent. The T105 overhead product is mainly a mixed naphtha product. The T102 overhead consists mainly of water in small quantity. The tray 3 distillate consists mainly of a mix of 850°F minus products. The V1074 solvent is a 650°F-EP product from T102 vacuum column bottom, which is a major component of the process solvent used to slurry the feed coal.

In Run 252 CC-ITSL operations with the distillation system in operation, the distillate products were:

Wt % of Total Distillate Products	Product Streams
12 - 17	T104 Overhead
-2 - 10	T104 Bottoms
15	T105 Overhead
0.01	T102 Overhead
56	T102 Tray #3
10	T102 Bottoms (V1074)
3	V1072

4.1 Distillate Product Quality

The distillate products from the TSL process were characterized in two ways:

(1) Each distillate product stream analyzed individually.

(2) Blend of distillate products prepared, fractionated and analyzed by boiling point range.

Typical stream analyses are shown below for operating period 252-B1.

Stream	H/C Atomic Ratio	Elemental Composition, wt % C	H	N	S	O(diff)
T104 Overhead	-	84.7	14.2	0.10	0.07	0.9
T104 Bottoms	-	88.3	11.1	0.29	0.04	0.3
T105 Overhead	1.88	84.3	13.3	0.23	0.01	2.2
T102 Overhead	-		(all H_2O)			
T102 Tray #3	1.52	88.5	11.3	0.20	0.01	0.0
T102 Bottoms (V1074)	1.34	89.4	10.1	0.32	0.01	0.2
V1072	1.39	89.3	10.4	0.27	0.01	0.07

There were five (5) operating periods in Run 252: A, B, B1, C, and C1. Operating period 252B1 was selected as the representative period for product quality evaluation. In 252-B1, the recycle distillate was fractionated in a vacuum column to reduce the light ends in the recycle solvent.

Analyses of Product Blends

Blends of products were prepared for period 252-B1 in proportion to their elementally balanced production rates. These blends were fractionated into four boiling point cuts, and then each cut and the blend were analyzed separately by GC simulated distillation.

For period 252-B1 the blend was:

T104 Overhead	15.8 wt %
T104 Bottoms	0.9 wt %
T105 Overhead	14.6 wt %
T102 Tray #3	55.9 wt %
T102 Bottoms (V1074)	9.6 wt %
V1072 Solvent	3.2 wt %
Total Blend	100.0 wt %

The analyses of the 252-B1 blend and individual fractions are given below:

Product Quality Data
Period 252-B1

Fraction	IBP-350°F	350-450°F	450-650°F	650°F-EP	Calc Blend (c)	Actual Blend (b)
Wt % of blend(a)	20.90	12.50	38.40	28.20	100.00	100.00
GC dist., wt %						
IBP-350°F	91.51	2.06	0.00	0.00	19.38	22.06
350-450°F	8.49	78.96	0.00	0.00	11.64	14.60
450-550°F	0.00	18.98	29.12	0.00	13.55	14.17
550-650°F	0.00	0.00	40.68	0.00	15.62	18.78
650-850°F	0.00	0.00	30.20	78.87	33.84	29.25
850°F-EP	0.00	0.00	0.00	21.13	5.96	1.15
EP, °F (d)	359.60	484.90	721.90	1000.40(d)		872.30(d)
Specific Gravity	0.803	0.872	0.932	1.002	0.912	0.913
Elem. Comp., wt %						
Carbon	85.53	87.16	87.85	89.30	87.69	87.80
Hydrogen	14.22	12.28	11.60	10.38	11.89	11.77
Nitrogen (e)	0.02	0.08	0.09	0.17	0.10	0.10
Sulfur	0.05	0.03	0.01	0.01	0.02	0.02
Oxygen-by diff.	0.18	0.45	0.45	0.14	0.31	0.31
H/C atomic ratio	1.98	1.68	1.57	1.39	1.62	1.60

TSL products 252-B1 were blended according to Elementally Balanced product rates for (4) days: 04 January 87, 05 January 87, 07 January 87, 08 January 87

(a) Obtained from lab Oldershaw Fractionation.
(b) Obtained from GC b.p. simulation distillation on blend sample.
(c) Calculated from data generated from GC b.p. simulated distillation on individual fraction.
(d) EP = Simulated E.P. is defined as the final b.p. at which a cumulative area count equal to 99.5% of the total area under the chromatogram is obtained. This routine results in a different end boiling point for the 650-EP and the total blend. For this particular case only 0.5 wt % of the total blend boils between 872 and 1000°F.
(e) Nitrogen by Kjeldahl.

A comparison of the two distillate product blends from periods 251-IE, and 252-B1 is shown below:

Product Quality Data
Comparison of Blends

Period	252B1	251-IE
1st stage temp., °F	810	808
2nd stage temp., °F	750	758
Coal, MF lb/hr	347	300
1st stage WHSV, 1/hr	3.2	2.7
2nd stage WHSV, 1/hr	3.0	2.3
GC dist., wt %		
IBP-350°F	22.06	25.97
350-450°F	14.60	11.65
450-650°F	32.95	32.26
650°F-EP	30.40	30.13
EP, °F	872	875
Specific gravity	0.913	0.900
Elem. comp., wt %		
Carbon	87.80	87.18
Hydrogen	11.77	11.62
Nitrogen (1)	0.10	0.16
Sulfur	0.02	0.03
Oxygen-by diff.	0.31	1.01
H/C atomic ratio	1.60	1.59
Blend composition, wt %		
T104 overhead	15.76	17.81
T104 bottoms	0.92	22.89
V1078 distillate	-	51.64
V1072 solvent	3.24	7.66
T105 overhead	14.50	-
T102 tray 3	55.89	-
V1074 (T102 bottom)	9.63	-

(1) Nitrogen by Kjeldahl.

When comparing blend product quality for these periods, the following observations are made:

Although small improvements were noticed with fractionation in Run 252, there were no major differences between Run 251-IE (no fractionation) and Run 252-B1 (with fractionation). This results indicates that on the whole there was no major shift in the distribution of the distillation cuts by a simple recycling a heavier distillation cut.

However, should distillation system be operated in conjunction with the changing in the reaction conditions, it is anticipated that a shift in the distribution of the distillation cuts would occur.

To simulate the non-distillation mode, a fictious sub period was created within the 252-Bl period in which it is assumed that the distillation system is not in operation and the final products are V1078 and V1072 instead of final products of T102 Tray 3, T105 overhead and T102 bottoms when the distillation system is operating.

A comparison of the results with and without fractionation shows small improvements in product quality with fractionation. The gas oil was 30% of the blend with fractionation versus 35% without fractionation. The product end-point was reduced from 910°F without fractionation to 870°F with fractionation. Also, the API gravity of the gas fraction was higher with fractionation.

A comparison of the properties of the distillate products for Runs 251-IE, 252 Bl with and without distillation is given below:

Properties of Distillate Products

Distillation Cut	Wt % of crude	Elemental (wt %) C	H	N(1)	S	O(diff)	°API
CC-ITSL (Run 251-IE (no fractionation, 70% distillate)							
Naphtha (IBP-350°F)	26.0	85.90	13.98	0.03	0.05	0.04	50.85
Distillate (350-650°F)	43.9	87.77	11.81	0.13	0.02	0.27	24.17
Gas oil (650°F+)	30.1	89.64	10.04	0.21	0.03	0.08	9.44
CC-ITSL (Run 252-B1) (with fractionation, 69% distillate)							
Naphtha (IBP-350°F)	32.1	85.53	14.22	0.02	0.05	0.18	44.71
Distillate (350-650°F)	47.6	87.68	11.77	0.09	0.01	0.45	22.81
Gas oil (650°F+)	30.4	89.30	10.38	0.17	0.01	0.14	9.72
CC-ITSL (Run 252-B1) (without fractionation, 69% distillate)							
Naphtha (IBP-350°F)	24.1	85.10	14.26	0.02	0.03	0.59	45.80
Distillate (350-650°F)	40.6	86.97	11.68	0.09	0.00	1.26	18.20
Gas Oil (650°F+)	35.3	89.45	10.26	0.27	0.00	0.02	2.90

(1) Nitrogen by Kjeldahl.

4.2 Unit Solvents

4.2.1 1st Stage

Run 252 was made with bituminous coal in the ash recycle mode of operation. The T105/T102 distillation system was in operation. This system processed the second stage distillates to remove the distillates lighter than 450°F and then separate under a vacuum the distillates boiling less than approximately 650°-850°F. The heavy bottoms from the T105/T102 system (V1074), the atmospheric flashed bottoms (V1067) and the CSD resid were blended to make the process solvent. For Run 252 the process solvent nominally contained 12% CI and 40 wt % resid. Until 14 January, the V1074 material was also used to help keep the catalyst withdrawal tube clear. After 14 January, lighter process solvent (V178) was used.

The elemental analysis of the V1067 material and the CSD resid are given in Tables 8 and 12. The elemental composition of the process solvent components are given in Table 10.

4.2.2 2nd Stage

The feed to the 2nd stage reactor was the bottoms of the interstage separator plus excess T104 bottoms. Compositions of the second stage feed are given in Tables 9. The feed contained from 44-45 wt % distillate, 39-41 wt % resid, and 15.2-16.5 wt % CI in periods 252B thru C1. In period 252A the solvent was about 5% higher and the resid was about 5% lower.

Interstage Separator Bottoms

	252A	252B	252B1	252C	252C1
Resid	35.5	38.7	39.1	39.8	41.4
CI	15.5	16.2	16.4	16.1	15.2

4.2.3 CSD Unit

The CSD unit uses proprietary deashing solvents to process ash containing feed. These deashing solvents are identified by numerical designations for reporting purposes. The deashing solvent type was strengthened when possible to optimize resid recovery and energy rejection to the ash concentrate yet maintain efficient, stable first stage deashing. During Run 252 the CSD unit operated in Mode II of the DAS Recycle System. A summary of DAS losses, their distribution, and DAS type employed during the run follows:

DAS Losses

Operating	Total DAS loss		Loss to Products			
period	Lb/hr	Wt % feed	Lb/hr	Wt % feed	Wt % total loss	DAS type
252A	5.2	4.8	0.8	0.8	15.5	4100
252B	8.7	7.8	0.6	0.5	8.1	4100
252B1	10.7	10.3	1.0	1.0	11.6	4100/2204/2254
252C	8.2	5.7	1.6	1.1	19.4	2354/2404
252C1	8.5	7.0	1.2	1.0	16.9	2404/2504

Efforts were not dedicated to reducing DAS losses.

5. FEED COAL

In Run 252, pulverized coal was ground to 95% less than 200 mesh, mixed with process solvent in a 1 to 2 ratio in V101A Slurry Blend Tank (Figure 4) and fed to the 1st stage. The process solvent used for slurry preparation was V1074 distillate solvent, resid from the CSD second stage, and V1067 atmospheric bottoms.

Elemental analyses of Illinois 6 feed coal (Burning Star Mine) are presented in Tables 1 and 6. Detailed analyses such as minerals, sulfur forms, proximate, and ultimate analyses of selected tote bin coal composite samples are presented in Table 1. Averaged data for Run 252 are presented below:

Run	252A-C1
Period, 1986-87	26 Nov-3 Feb
<u>Coal analysis, wt % MF</u>	
Carbon	70.10±0.48
Hydrogen	4.82±0.12
Nitrogen	1.40±0.06
Sulfur	3.40±0.24
Oxygen (by difference)	8.60±0.51
Ash	11.69±0.31
Water as-is wt %	3.03-3.42
<u>Sulfur forms, wt % MF</u>	
Pyritic	1.36
Sulfate	0.26-0.34
Sulfide	<0.01
Organic	1.70-2.05
Chlorine wt % MF	0.11-0.12
Volatile matter as-is wt %	35.02-35.21
Ferric oxide in ash, %	16.69-17.35
H/C atomic ratio	0.83

The standard deviations of coal analyses show that coal physical and chemical properties did not vary significantly in Run 252. The ash content of feed coal was 11.4 to 12.0 wt %, the pyritic sulfur content was 1.4 wt %, and the total sulfur content was 3.2 to 3.6 wt %.

6.0 CATALYST

6.1 Analytical Results and Recovery

First Stage Catalyst

The first stage catalyst charge was 340 lb of a 1500 average age blend consisting of the following:

25% sulfided Amocat 1C
37.5% 1200 age (lb resid+CI/lb cat) Amocat 1C from Run 250
37.5% 2800 age (lb resid+CI/lb cat) Amocat 1C from Run 251-I

The catalyst from Run 250 was aged in the second stage reactor with the reactor temperature between 700 and 750°F. The catalyst from Run 251-I was initially aged during Run 250 in the second stage reactor with the reactor temperature between 740 and 760°F; the catalyst was further aged in the second stage during Run 251-I. During 251-I, the second stage temperature ranged from 760 to 775°F. During Run 250 and 251-I, Illinois No. 6 coal was used.

Since 25% of the catalyst was not aged, it was preconditioned prior to high temperature operation using the following sequence:

16 hours of operation at 700°F using a heavy solvent
16 hours of operation at 750°F using process solvent
16 hours of operation at 775°F using a 20% coal slurry

After the P1222 failure on 29 November, the R1235 catalyst charge consisted of 120 lb of the 1500 (915 lb MF coal/lb cat) age blend and 220 lb of catalyst removed from R1235 after shutdown on 29 November. The average catalyst age at the end of the run was 3533 (1961 lb MF coal/lb cat); however, the age of some portions of the blend was as high as 5400 (2923 lb MF coal/lb cat).

Naphthalene activity tests were not regularly performed. Since the laboratory activity tests utilize a very small amount of catalyst and the catalyst charge was a blend, it was believed that representative samples could not be obtained. Catalyst samples were withdrawn from R1235 approximately once per week. Regular catalyst additions/withdrawals, at a rate of 2 lb catalyst per ton of MF coal, were planned, but only two additions/withdrawals were made before the run ended.

Catalyst fines were observed in some withdrawals. The catalyst that contained fines was not added back to the reactor; the broken catalyst was replaced. On 5 January 1987, due to plugging of the catalyst withdrawal tube, 23.2 lbs (dry weight) of catalyst was removed from R1235. Since this catalyst had some crushed catalyst and tar in it, it was not returned to the reactor but was replaced with Run 251-I catalyst (age = 1841 lb MF coal/lb catalyst) on 7 January. More withdrawal tube plugging on 9 January and 11 January resulted in a loss of another 42 lbs (dry weight) catalyst which was partially replaced on 15 January with 22 lbs of Run 251-I catalyst. On 19 January 36.9 lbs more catalyst was returned. On 20 January, 10.4 lbs of Run 250 catalyst (age = 727 lb MF/lb catalyst) was added to bring the sum of additions and withdrawals to an inventory of 340 lbs in the reactor. During this period it was observed that the T102 bottoms distillate, used as withdrawal tube flush, contributed to the plugging problems. On 13 January withdrawal tube flush was changed to a lighter solvent from V178. The samples seemed to contain fines when actions were taken to clear plugs in the withdrawal system; however, the catalyst recovery at the end of the run was only 63%. The high loss of catalyst from the reactor could be the result of high attrition of the high age catalyst, since the catalyst is not normally aged as high as 5000 lb resid + CI/lb catalyst (2717 lb MF coal/lb cat). At the end of the run, 22% of the catalyst in the reactor had an age higher than 5000 lb resid + CI/lb catalyst (2717 lb MF coal/lb cat).

Four nickel balances during the last month of Run 252 indicate that the catalyst was gradually lost from R1235. The nickel balances indicate a loss of 2.6 pounds per day and the actual loss averaged 2.4 pounds per day. A gradual loss mechanism for the catalyst is also supported by the catalyst samples, that were taken from the reactor after shutdown; samples from the upper portion of the reactor contained more fines. Also, nuclear scans of the reactor before the end of Run 252 indicated reduced densities in the upper portion of the bed.

Four molybdenum balances during the last month of the run gave inconsistent results. Catalyst losses calculated from molybdenum balances ranged from 2.2 to 17.5 pounds per day.

Table 17 shows the analyses of various withdrawn catalyst samples.

Second Stage Catalyst

The second stage catalyst charge was 340 lb of fresh sulfided Amocat 1C. The end of run catalyst age was 1921 (lb resid + CI/lb cat or 1255 lb MF coal/lb cat). The catalyst recovery from R1236 was 99%. Catalyst samples from R1236 are available only for the end of the run, since R1236 has no catalyst withdrawal system.

During the "soft start", effluent from the first stage was fed through the second stage via the normal flow path. The second stage temperature was between 600 and 650°F during this conditioning step.

Table 18 shows the analyses of various catalyst samples.

6.2 Catalyst Sulfiding Procedure

The fresh catalyst was sulfided with dimethyl disulfide (DMDS) at a 1.5 wt % initial concentration in recirculating No. 2 diesel (fuel) oil. The feed gas rate was maintained at 3,000 scfh, and catalyst bed ebullation began when the reactor temperature reached 250°F. The reactor was heated from 250 to 400°F at a rate of 50°F/hr and held at that temperature until hydrogen sulfide "breakthrough" occurred, indicating the end point of the sulfiding procedure. During the sulfiding the hydrogen-rich vent gas was recycled and DMDS was added (6 lbs/hr) to the diesel oil. The reactor temperature was then increased by 50°F/hr to 500°F, 600°F and 700°F and held at each level until breakthrough occurred. The temperature was held at 700°F until analyses of catalyst samples indicated a sulfur content (wt % S = "as is" wt % S/wt % ash x 100) of at least 7.5 wt % for Amocat 1C. The reactor was then cooled at a maximum rate of 100°F/hr to <250°F. The catalyst was withdrawn and stored in drums at ambient conditions.

7.0 ENVIRONMENTAL PROTECTION

7.1 Regulatory Compliance

The purpose of the wastewater treatment facilities is to maintain compliance with permit limitations established by the Alabama Department of Environmental Management (ADEM). Both the sanitary and process wastewater treatment facilities are operated under a National Pollutant Discharge Elimination System (NPDES) permit. This permit was issued by ADEM, which was authorized by the Environmental Protection Agency (EPA) to administer the NPDES program in Alabama. This permit was effective on 1 July 1983 and expires on 30 June 1988. The permit established average and maximum limits for specific parameters. The performances of the treatment facilities and the applicable permit limitations, are shown on the following tables:

Process Wastewater Treatment Facility (Outfall 001)

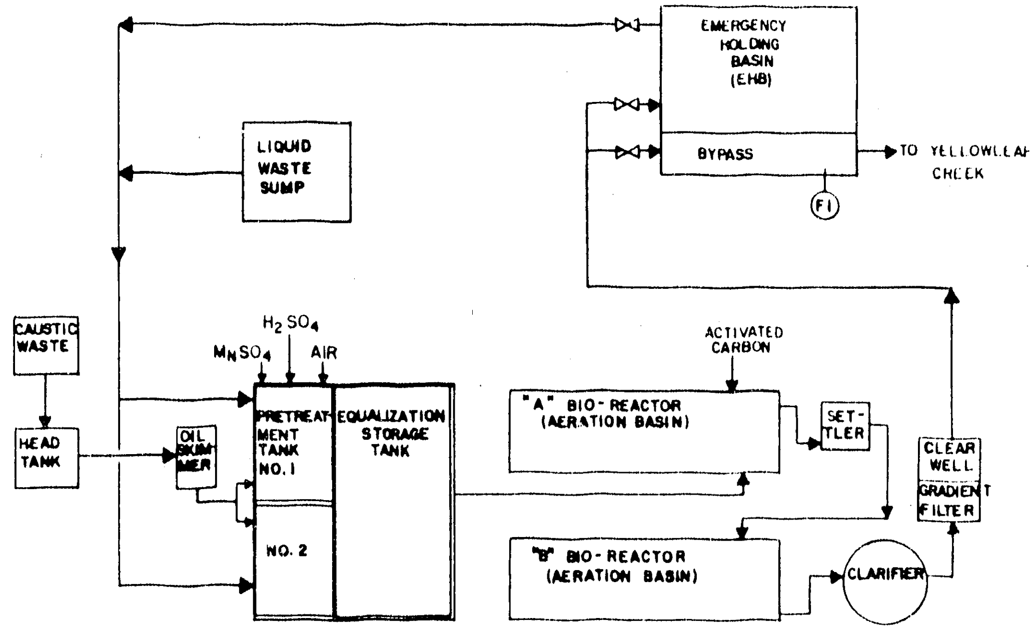
	Allowable Daily Average	Actual Daily Average 26 Nov 86 to 3 Feb 87	Allowable Daily Average	Actual Daily Maximum 26 Nov 86 to 3 Feb 87
Flow, gpd	-	26,303	-	36,130
BOD_5, mg/l	30	<1.4	45	4.8
Suspended solids, mg/l	30	4.2	45	14.0
Phenolics, mg/l	0.25	<0.063	0.50	0.15
Sulfides, mg/l	0.10	<0.056	0.20	0.13
pH (range)	N/A	N/A	6-9	7.0-7.9

Sanitary Wastewater Treatment Facility (Outfall 002)

	Allowable Daily Average and Maximum	Actual Daily Average 26 Nov 86 to 3 Feb 87	Actual Daily Maximum 26 Nov 86 to 3 Feb 87
Flow, gpd	-	644	1800
BOD_5, mg/l	30	2.1	2.1
Suspended Solids, mg/l	30	13.9	17.5
Fecal Coliforms, N/100 ml	200	4.1	32
Chlorine, mg/l	0.2	<0.1	<0.1
pH (range)	6-9	N/A	7.0-8.0

The above results are based on weekly (or monthly) samples collected by the plant operators and analyzed by an outside laboratory. As the tables show, all results were in compliance with the limitations.

The treatment facilities consist of oil removal, chemical oxidation for removal of sulfide, two-stage activated sludge (with optional addition of powdered activation carbon), and sand filtration. A schematic flow diagram is shown below:



WASTEWATER TREATMENT SYSTEM

8.0 MATERIAL BALANCE (MB) METHODOLOGY

8.1 Elemental Balancing of Yields (Ref. 3)

The mass and elemental balance 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. Weighting 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 in order to close the mass and elemental balances 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, and oxygen are balanced along with carbon and hydrogen, primarily by adjusting hydrogen sulfide, ammonia, and water rates. Finally ash is balanced by adjusting the ash analysis of output streams to equal the ash that entered with the coal[1]. The adjusted stream flow rates between units are then corrected for inventory changes to achieve steady-state flow rates.

The 1st and 2nd stage balances are developed with the above procedure. Since the CSD unit 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.

Two-stage yields are developed by combining the balances of the three process units.

8.2 MB Methodology

Beginning in Run 247, elementally balanced yields were calculated for several days each week and were reported within 2 to 5 days. Elementally balanced yields were calculated for 21 days during Run 252.

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[1] During the ash recycle operations the HTR vacuum bottoms rate to the CSD unit is prorated based on coal ash and HTR vacuum bottoms ash so that all of the coal ash will be purged in the ash concentrate (steady-state assumption).

In prior runs, elementally balanced yields were calculated only for 8 to 10 selected days each run. These calculations were done after run completion.

With the advent of the routine element balances in Run 247, better material balance data is 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 closure errors. When elemental analyses are completed on all input and output streams for a given day, elementally balanced yields are calculated for that day (Phase 3). Phase 3 elementally balanced yield data is averaged for each set of stable operating conditions to obtain the final yield used throughout this report (Phase 4).

An evaluation of the MB methodology was conducted to assess the usefulness of the different phases of MB reports for plant monitoring, daily decision making, and technical accuracy of yields. Quantitative guidelines were desired to screen the data as it flowed 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 Run 247 MB 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, Phase 3 are 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 MB errors.

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

8.3 MB 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. The averages and standard deviations of the Phase 2-3 Selection Criteria are reported in Table 14 for each Operating Period (Phase 4 Period).

Phase 3-4 Selection criteria are related to element balance closure errors. 95% confidence intervals are calculated for element closures for each individual unit and the TSL system. Yields on days highlighted by excessive element closure errors are then compared with yields from the other element balance days in the Phase 4 periods. 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 15 for each 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. The most sensitive indicators of TSL stability are the 1st and 2nd stage contributions to the TSL distillate solvent yield. Slow trends in solvent composition in process inventory can lead to relatively large swings in unit contributions from day to day. Standard deviations of the distillate solvent unit contributions from the 1st and 2nd stages would thus be much larger than the standard deviation of the TSL yield of distillate solvent. This indicates that the TSL system is not truly at equilibrium, although TSL yields are relatively constant.

To summarize the MB methodology, significant improvements were implemented in Run 247. The improvements center on routine elemental balancing of yield data and quantitative guidelines for screening the material balance data as it flows through the data phase system from Phase 2 to Phase 3 to Phase 4.

9. REFERENCES

1. Catalytic, Inc., Technical Progress Report, "Run 250 with Illinois No. 6 Coal," DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP 1234-1-2, Document No. DOE/PC-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-, report not yet published.

3. Catalytic, Inc., Topical Report No. 11, "The Wilsonville ACL R&D Facility Material Balance Procedure," DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE/PC-50041-41, September 1984.

APPENDIX A

Microautoclave Activity Test Descriptions

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 unit to which a mixing ball is added. The slurry is mixed and heated to a specific temperature (±5°F) within a two 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 a percentage conversion which is referred to as "solvent quality".

Two tests are done. They are the kinetic and equilibrium tests. The conditions used for both tests are listed below:

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

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.

Catalyst Activity

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 test determines hydrogen consumption during the hydrogenation of a model compound, naphthalene, in the presence of the catalyst. This gives an indication of relative catalyst activity, independent of reactor and/or TSL system performance. The activity is based on a fixed volume of catalyst.

The test also may be used for measuring the completeness of catalyst presulfiding.

APPENDIX B

Nomenclature and Definitions

Ash	Non-organic material obtained by muffle furnace burning at 800°C for 4 hours (adapted ASTM D-482).
Ash concentrate	A product of the Kerr-McGee CSD unit first stage separator that is rich in cresol insolubles (ash and UC) with lesser amounts of residue and solvent.
Asphaltenes	A benzene-soluble and pentane-insoluble product of the coal liquefaction process which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.
CC-ITSL	Close Coupled Integrated Two-Stage Liquefaction.
CSD feed solvency index	Laboratory analysis for fraction of CSD feed soluble in actual deashing solvent compared to solubility in a solvent standard.
Deashing solvent (DAS)	A solvent used to deash the feed to the CSD unit.
Distillate solvent	A coal-derived distillate fraction boiling above 450°F that is distillable at 600°F at 0.1 mm Hg in a laboratory batch distillation apparatus.
DITSL	Double Integrated Two-Stage Liquefaction
DMDS	Dimethyl disulfide
Energy rejection	The heating value lost to the ash concentrate as a fraction of the feed coal heating value.

APPENDIX B (continued)

Nomenclature and Definitions

ITSL	Integrated Two-Stage Liquefaction
LCT	Low Contact Time
LTR	Light Thermal Resid
MAF	Moisture and Ash Free
MB Period	Material Balance Period
MF	Moisture Free
Middle distillate	A coal derived distillate fraction with a boiling range between 350 and 450°F at 760 mm Hg (GC and ASTM D-86).
Naphtha	A coal derived distillate fraction with an IBP-350°F boiling range at 760 mm Hg (GC and ASTM D-86).
Oils	A pentane-soluble product of the coal liquefaction process which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.
Preasphaltenes	A cresol-soluble and benzene-insoluble product of the coal liquefaction process which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.
Process solvent	Feed solvent to the TL unit which is normally a blend of distillate solvent and resid in variable concentrations.
Resid	A cresol-soluble product of the coal liquefaction process which is non-distillable at 600°F and 0.1 mm Hg in the laboratory.

Nomenclature and Definitions

Resid conversion	The fraction of the resid feed to the HTR unit that is converted to gases and liquids. $$\text{Percent conversion} = \frac{\text{Resid in} - \text{resid out}}{\text{resid in}} \times 100$$
Resid recovery	The percent of CSD feed resid that is recovered in the deashed resid and is not lost to the ash concentrate.
RITSL	Reconfigured Integrated Two-Stage Liquefaction
TR	Thermal Resid
T102 Vacuum Column bottoms	A nonvolatile mixture of resid, distillate solvent, ash, and UC.
Unconverted Coal (UC)	Organic material that is insoluble in hot cresol.
WHSV	Weight Hourly Space Velocity, lb/hr feed per lb catalyst.

Table 1

FEED COAL ANALYSES

Coal	Illinois 6	
Mine	Burning Star	
Run	252	252
Date	22-27 Dec 1986	9-14 Jan 1987
<u>Proximate analysis, wt %</u>		
Volatile matter	35.21	35.02
Fixed carbon	49.94	50.12
Ash	11.43	11.83
Moisture	3.42	3.03
<u>Ultimate analysis, wt %</u>		
Carbon	69.62	69.25
Hydrogen	5.00	4.96
Nitrogen	1.35	1.25
Sulfur	3.40	3.67
Chlorine	0.11	0.12
Ash	11.83	12.20
Oxygen (by difference)	8.69	8.55
H/C atomic ratio	0.87	0.86
Dry heating value, Btu/lb	12,411	12,425
<u>Sulfur forms, wt %</u>		
Pyrite	1.36	1.36
Sulfate	0.34	0.26
Sulfide	<0.01	<0.01
Organic	1.70	2.05
<u>Mineral analysis, wt % (ignited basis)</u>		
Phos. pentoxide, P_2O_5	0.08	0.06
Silica, SiO_2	46.64	46.65
Ferric oxide, Fe_2O_3	16.69	17.35
Alumina, Al_2O_3	16.94	17.23
Titania, TiO_3	0.69	0.72
Lime, CaO	6.59	5.41
Magnesia, MgO	0.92	0.87
Sulfur trioxide, SO_3	6.92	6.52
Potassium oxide, K_2O	1.75	1.97
Sodium oxide Na_2O	1.13	0.92
Undetermined	1.65	2.30

Table 2

COAL CONVERSION (FORCED ASH BALANCE BASIS)

	Coal conversion, wt % MAF coal	
MB Period	Via Interstage sample	Via CSD feed
252A	93.3	93.2
252B	92.7	93.1
252B1	93.0	93.4
252C	91.3	92.5
252C1	93.1	93.0

Table 3

CCR UNIT OPERATING DATA

Operating period	R1235 Reactor Temp. Volume average	R1235 Reactor Temp. Variation(a)	Catalyst age(b/c)	Coal conversion wt %(d)	WHSV(e)	R1236 Reactor Temp. Volume average	R1236 Reactor Temp. Variation(a)	Catalyst age(b/c)	Coal conversion wt %(d)	WHSV(e)	K Value(f)
252A	811	4	1863/1114	92.5	2.75	679	9	304/203	93.8	2.69	0.27
252B	810	6	2266/1314	91.6	3.18	751	8	598/401	93.0	3.05	0.69
252B1	810	10	2764/1569	91.3	3.16	750	9	968/648	93.1	3.03	0.66
252C	811	6	3364/1849	89.9	3.47	749	8	1493/986	93.0	3.32	0.65
252C1	811	7	3664/2045	93.2	3.48	750	11	1707/1120	93.5	3.26	0.63

(a) Variation is defined as the maximum average reactor temperature during the day, minus the minimum average reactor temperature; used as a stability guide.

(b/c) Catalyst age units are (lb resid + CI/lb catalyst)/(lb MF coal/lb catalyst).

(d) Conversion is resid + UC conversion, based on elemental balance.

(e) WHSV units are lb feed/hr/lb catalyst.

(f) K Value = WHSV $\frac{\varepsilon}{1-\varepsilon}$, where WHSV is the weight hourly space velocity and ε is resid + UC converison.

Table 4

CCR UNIT OPERATING DATA

	T104 Atmospheric Column		
Operating Period	Overhead rate, lb/hr	Bottoms rate, lb/hr	Inventory change, lb/hr
252A	38.8	54.5	-4.5
252B	33.0	49.4	0.6
252B1	30.9	48.1	2.4
252C	29.0	46.9	-2.2
252C1	24.6	56.3	6.5

Table 5

FIRST STAGE YIELDS BEFORE ELEMENTAL BALANCING
(WT % MAF COAL)

Operating Period	H_2	H_2O NH_3	H_2S CO_x	C_1-C_3	C_4-C_6	Naphtha	Mid Distillate	Distillate Solvent	C_4+ Distillate	Resid	Unconverted Coal
252A	-5.65	10.94	0.87	4.89	2.33	11.02	7.31	40.59	61.24	20.60	7.54
252B	-4.02	10.00	0.82	3.99	1.59	8.42	5.72	32.59	48.32	32.64	8.36
252B1	-3.73	10.27	0.97	4.35	1.77	7.52	5.27	33.02	47.58	32.16	8.75
252C	-3.68	8.13	2.51	3.17	1.30	5.85	5.12	29.02	41.31	38.64	10.17
252C1	-3.86	8.57	1.77	2.91	1.11	7.25	4.78	31.11	44.24	39.85	6.76

Table 6

ANALYTICAL DATA OF STREAMS USED IN ELEMENTAL BALANCE

Operating Period	Coal, wt % MF							T102 Btms, V1074 wt %					CSD Resid, wt %				
	C	H	N	S	O(a)	Ash	H_2O(b)	C	H	N	S	O(a)	C	H	N	S	O(a)
252A	69.52	4.80	1.32	3.26	9.21	11.90	0.25	89.28	10.27	0.32	0.01	0.12	90.65	7.67	0.91	0.72	0.00
252B	70.13	4.75	1.39	3.10	6.71	11.92	0.27	89.52	10.08	0.37	0.01	0.03	90.64	8.26	0.75	0.05	0.14
252B1	70.18	4.77	1.43	3.66	8.18	11.81	0.31	89.41	10.14	0.32	0.01	0.12	90.56	7.92	0.81	0.12	0.36
252C	70.53	4.83	1.41	3.42	8.35	11.48	0.25	89.17	9.71	0.46	0.04	0.62	90.24	7.76	0.90	0.20	0.87
252C1	70.07	4.89	1.42	3.52	8.74	11.36	0.30	89.32	10.13	0.40	0.02	0.13	90.06	7.69	0.91	0.22	1.12

(a) Determined by difference.
(b) From as-is coal analysis.

Table 7

ANALYTICAL DATA OF STREAMS USED IN ELEMENTAL BALANCE

Operating	T104 Overhead, wt %					T104 Bottoms, wt %					2nd Stage Feed, wt %						CSD Feed, wt %					
Period	C	H	S	N	O(a)	C	H	N	S	O(a)	C	H	N	S	O(a)	Ash	C	H	N	S	O(a)	Ash
252A	85.02	13.62	0.12	0.04	1.21	88.27	11.44	0.24	0.01	0.05	79.67	7.65	0.66	0.93	0.66	10.45	71.04	5.70	0.71	1.47	0.39	20.20
252B	85.05	13.52	0.16	0.06	1.22	88.62	10.96	0.30	0.02	0.11	79.61	7.56	0.73	0.99	0.75	10.38	70.78	5.92	0.69	1.62	0.04	20.95
252B1	84.74	14.18	0.07	0.10	0.92	88.31	11.11	0.29	0.04	0.26	79.12	7.45	0.71	1.03	0.99	10.70	69.87	5.67	0.76	1.76	0.50	21.45
252C	84.62	13.64	0.28	0.20	1.27	87.24	10.98	0.40	0.10	1.28	79.68	7.27	0.81	1.22	1.19	9.85	71.45	5.58	0.88	1.75	1.40	18.95
252C1	85.52	14.22	0.15	0.14	0.28	87.28	10.93	0.36	0.09	1.34	79.63	7.40	0.86	1.16	1.10	9.84	71.51	5.51	0.90	1.70	1.39	18.98

Table 8

ANALYTICAL DATA OF STREAMS USED IN ELEMENTAL BALANCE

Operating	V1078, wt %					V1067 Recycle, wt %						V1072, wt %				
Period	C	H	N	S	O	C	H	N	S	O	Ash	C	H	N	S	O
252A	87.21	12.56	0.15	0.02	0.08	79.33	8.05	0.55	0.83	0.00	11.25	89.03	10.38	0.31	0.01	0.28
252B	87.32	12.07	0.17	0.01	0.20	78.96	7.91	0.52	0.87	0.07	11.68	89.42	10.27	0.29	0.01	0.01
252B1	86.97	12.30	0.10	0.01	0.62	78.47	7.81	0.53	0.93	0.01	12.25	89.25	10.41	0.27	0.01	0.07
252C	86.87	12.17	0.21	0.02	0.73	79.73	7.53	0.61	0.98	0.01	11.15	89.44	10.19	0.35	0.02	0.00
252C1	87.26	12.19	0.21	0.02	0.32	79.15	7.54	0.70	0.95	0.17	11.48	89.34	10.18	0.17	0.01	0.30

Table 9

CCR UNIT ANALYTICAL DATA

	Interstage Sample wt %									
					CI Free Residue			Distillate		
Operating Period	Solv %	Resid %	UC %	Ash %	C %	H %	N %	C %	H %	N %
252A	48.9	35.6	5.1	10.4	89.26	6.92	0.96	88.90	9.82	0.34
252B	45.5	38.5	5.6	10.6	89.18	7.06	1.14	88.45	9.72	0.37
252B1	44.7	39.0	5.6	10.8	89.71	7.06	0.99	89.37	9.75	0.43
252C	44.2	40.0	6.2	9.8	88.60	6.67	1.27	89.81	9.70	0.49
252C1	43.4	41.5	5.3	9.7	89.22	6.94	1.11	89.24	9.86	0.37

Table 10

PROCESS SOLVENT ANALYTICAL DATA

Operating Period	V131B					
	Residue, wt %			Distillate, wt %		
	C	H	N	C	H	N
252A	90.35	7.64	0.93	89.41	10.34	0.45
252B	90.22	7.99	0.85	89.33	10.11	0.33
252B1	89.91	7.87	0.84	89.28	10.19	0.31
252C	89.69	7.40	1.03	89.65	9.97	0.39
252C1	89.72	7.35	0.95	89.37	10.03	0.36

Table 11

2ND STAGE YIELDS BEFORE ELEMENTAL BALANCING

Operating Period	Wt % Ash & Solv. Free Feed														Conversion % Resid + UC
	H_2	CO, CO_2	Sour Water	H_2S	C_1–C_3	C_4+ dist.	C_4–C_6	Naphtha	Mid. Dist.	Dist. Solv.	Resid	UC	Ash	Closure Error	
252A	-1.16	0.00	3.04	0.03	1.90	3.31	0.58	2.79	0.61	0.36	79.26	11.41	0.98	1.26	9.35
252B	-1.89	0.01	2.65	0.04	2.01	15.08	0.44	5.09	1.63	7.92	69.55	11.73	0.14	0.50	18.72
252B1	-1.91	0.00	2.60	0.06	2.08	16.95	0.46	5.62	1.90	8.97	70.17	11.44	0.53	1.93	18.38
252C	-1.78	0.00	2.65	0.09	2.22	12.84	0.43	5.83	1.98	4.61	71.97	11.32	0.05	0.62	16.71
252C1	-1.72	0.00	2.62	0.04	1.60	13.08	0.39	5.03	1.69	5.96	72.21	11.20	-0.0	1.01	16.58

Table 12

CSD UNIT ANALYTICAL DATA
RUN 252

Operating Period	252A	252B	252B1	252C	252C1
CSD feed composition					
Wt % Ash	20.1	20.9	21.4	18.9	19.0
Wt % UC	10.1	10.7	10.4	10.4	10.4
Wt % Solv	7.6	6.5	5.1	5.6	3.3
Wt % Preasphaltenes					
(BI-CI)	0.2	-	3.0	-	6.2
(TI-CI)	0.6	1.5	4.9	7.6	9.6
% Carbon	71.03	71.63	70.02	71.45	71.57
% Hydrogen	5.70	5.90	5.72	5.58	5.51
% Nitrogen	0.71	0.69	0.76	0.88	0.90
% Sulfur	1.50	1.60	1.80	1.75	1.70
% Oxygen (a)	0.96	0.00	0.30	1.44	1.32
Soft. Pt. (°F)	153.0	134.3	154.0	160.5	156.4
Fusion Pt. (°F)	165.5	144.3	181.7	174.5	172.4
Ash Concentrate Composition					
Wt % Ash (b)	43.7	43.8	44.2	43.8	42.8
Wt % UC (b)	22.0	23.5	22.4	25.9	25.7
Wt % Resid (b)	32.5	30.6	31.6	29.9	30.6
Wt % Solv (b)	1.9	2.1	1.9	0.4	0.9
Wt % DAS	0.4	0.3	0.4	1.2	1.2
% Carbon	48.90	48.57	48.48	48.09	49.43
% Hydrogen	3.18	3.17	3.19	2.95	2.99
% Nitrogen	0.68	0.64	0.75	0.86	0.91
% Sulfur	3.10	3.21	3.40	3.30	3.42
% Oxygen (a)	0.44	0.61	0.00	1.00	0.45
Deashed Resid Composition					
Wt % Ash (b)	0.70	0.17	0.10	0.11	0.01
Wt % Solvent (b)	6.75	11.93	8.50	12.50	7.46
Wt % DAS	0.75	0.53	0.98	1.10	1.00
% Sulfur	0.88	0.71	0.11	0.20	0.23
Soft. Pt. (°F)	128.5	106.0	113.3	103.0	119.8
Fusion Pt. (°F)	147.5	117.5	150.7	115.0	135.4
% Carbon	90.58	90.97	90.31	90.24	90.07
% Hydrogen	7.70	8.25	8.06	7.76	7.64
% Nitrogen	0.71	0.05	0.78	0.90	0.92

(a) Results calculated by difference.

(b) Results are adjusted to a 'DAS Free' basis.

Table 13

SUMMARY OF CSD PARAMETERS

Operating period	DAS type	Resid recovery, wt %	Energy rejection, %	Ash concentrate toluene solubles, wt %	Feed solv. index	Ash consistency
252A	4100	76.95	20.0	28.35	0.74	Gummy
252B	4100	76.18	19.9	26.65	0.82	Gummy/Powder/Grainy
252B1	4100/2204/2404	75.55	19.6	21.97	0.74	Gummy/Grainy/Powder
252C	2354/2404	80.30	18.3	13.17	0.73	Chunky/Grainy/Powder
252C1	2404/2504	78.74	19.0	14.04	0.71	Chunky/Extruded/Powder

Table 14

PHASE 2-3 CRITERIA
MASS BALANCE CLOSURES & INVENTORY CHANGES (a)(b)
STATISTICAL SUMMARY
(WT % MAF)

Operating Period	252A	252B	252B1	252C	252C1
CCR closure	1.56±0.14	0.67±0.95	-2.68±0.85	0.92±1.98	1.50±1.59
CSD closure	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Total closure	1.56±0.14	0.67±0.95	-2.68±0.85	0.92±1.98	1.50±1.59
Abs. tot. clo.	1.56±0.14	0.80±0.80	2.68±0.85	1.40±1.30	1.77±1.20
CCR2-CSD inv. (c)	11.08±13.61	-0.89±2.74	1.65±0.87	-1.95±3.01	1.15±3.92
CSD-CCR1 inv. (c)	-11.11±5.02	-1.02±4.03	-1.17±2.05	3.62±1.49	4.12±5.33
CCR2-CCR1 inv. (c)	10.55±5.20	-2.33±7.27	-3.37±6.23	4.02±7.31	-1.03±6.90
Abs. tot. inv. (d)	32.74±13.43	11.42±6.06	8.55±4.23	10.92±6.95	13.58±6.23

(a) Inv. changes include resid, UC and ash comp. only. Increases are positive.

(b) Mass Balance closure sign convention is that losses are negative.

(c) The CCR2-CSD, CSD-CCR1 and CCR2-CCR1 inventory changes include any net resid, UC or ash make or depletion.

(d) Absolute total is the absolute total of the inventory changes between all three process units which gives a measure of overall plant and process stability.

Table 15

PHASE 3-4 CRITERIA
STATISTICAL SUMMARY
UNIT AND TSL ELEMENTAL CLOSURE ERRORS (a)
(WT % MAF)

Operating Period	252A	252B	252B1	252C	252C1
CCR1 Unit Data					
Carbon	2.51±0.23	1.01±1.21	-0.03±0.64	-0.68±0.69	0.92±1.32
Hydrogen	-0.87±0.03	-0.12±0.29	0.16±0.16	-0.54±0.26	-0.42±0.23
Nitrogen	0.61±0.01	0.68±0.11	0.60±0.10	0.65±0.01	0.14±0.42
Sulfur	0.18±0.07	0.50±0.45	0.01±0.34	1.88±0.10	0.13±0.47
Oxygen	-2.30±0.48	-1.95±1.05	-0.41±1.16	-1.45±0.26	-0.45±0.48
Ash	-0.14±0.26	-0.10±1.40	-0.32±0.20	0.13±0.28	-0.31±0.70
CCR2 Unit Data					
Carbon	-4.24±0.69	-1.56±1.74	0.97±1.12	-0.52±0.71	-0.94±2.50
Hydrogen	0.29±0.02	0.24±0.19	0.62±0.21	0.38±0.26	0.08±0.36
Nitrogen	0.12±0.10	-0.27±0.08	-0.20±0.09	-0.27±0.10	-0.36±0.17
Sulfur	0.54±0.07	0.30±0.16	0.36±0.32	-0.18±0.08	-0.37±0.21
Oxygen	0.59±0.13	-0.04±0.81	-0.71±1.30	-0.49±0.91	0.30±0.93
Ash	1.13±1.04	0.57±0.98	0.86±0.46	0.03±0.02	-0.15±0.33
CSD Unit Data					
Carbon	-0.28±0.20	-0.38±0.25	-0.08±0.31	-0.27±0.22	0.02±0.55
Hydrogen	-0.19±0.06	-0.13±0.10	-0.10±0.08	-0.07±0.01	-0.01±0.04
Nitrogen	0.07±0.04	0.00±0.02	0.02±0.01	0.01±0.01	0.01±0.03
Sulfur	0.30±0.01	-0.02±0.12	-0.01±0.03	-0.11±0.05	-0.02±0.07
Oxygen	-0.52±0.18	-0.31±0.43	-0.07±0.17	-0.14±0.42	-0.21±0.64
Ash	0.63±0.27	0.24±0.27	0.24±0.31	0.60±0.15	0.22±0.23
Totaled Data(b)					
Carbon	-2.01±0.71	-0.93±0.71	0.85±0.85	-1.47±1.62	0.00±1.15
Hydrogen	-0.76±0.10	-0.01±0.28	0.69±0.13	-0.24±0.01	-0.35±0.38
Nitrogen	0.80±0.05	0.41±0.04	0.41±0.03	0.39±0.08	-0.21±0.34
Sulfur	1.02±0.00	0.78±0.36	0.37±0.25	1.59±0.08	-0.26±0.45
Oxygen	-2.24±0.54	-1.68±0.52	-1.19±1.49	-2.08±0.23	-0.36±0.45
Ash	1.63±0.50	0.71±0.84	0.78±0.52	0.75±0.10	-0.24±0.81
Absolute Sum Data					
Carbon	7.03±0.25	3.40±2.45	1.66±1.44	1.47±1.62	4.02±1.44
Hydrogen	1.35±0.06	0.61±0.22	0.90±0.11	0.99±0.51	0.71±0.30
Nitrogen	0.80±0.05	0.96±0.18	0.82±0.19	0.93±0.12	0.66±0.42
Sulfur	1.02±0.00	0.90±0.28	0.67±0.26	2.18±0.13	0.75±0.31
Oxygen	3.42±0.79	2.85±1.63	2.38±0.66	2.38±0.23	1.66±1.12
Ash	1.95±0.96	2.16±1.36	1.44±0.82	0.82±0.00	1.01±0.32

(a) Closure Error sign convention is that losses are negative.
(b) Total is the arithmetic sum of the individual unit errors.
(c) Absolute Total is the sum of the absolute values of the individual unit errors.

Table 16

RUN 252 SOUR WATER ANALYSES (a)

Operating Period	252A	252B	252B1	252C
V105 From First Stage				
Total Organic Carbon	5,306	4,586	17,567	34,140
Kjeldahl Nitrogen	16,630	13,711	22,294	16,020
Sulfide Sulfur	18,160	19,720	12,120	404
Chloride	<1	<1	-	-
Phenols	785	1,167	2,837	1,891
Inorganic Carbon	904	958	3,380	3,250
V180 From Second Stage				
Total Organic Carbon	6,568	466	3,816	769
Kjeldahl Nitrogen	6,772	13,048	12,768	9,408
Sulfide Sulfur	8,080	13,760	9,400	8,280
Phenols	220	213	844	883
Inorganic Carbon	56	88	145	158

Table 17

RUN 252
AMOCAT 1C 1/16" FIRST STAGE CATALYST

Date, 1986-87	Average Catalyst Age	Description of Sample	As-is S	wt % Ash	Analysis of THF-Extracted Catalyst, wt % Oil	C	H	N	S	Ash	Naphthalene Activity
11/13	-	Composite of Sulfided Batch 1	4.25	60.9	34.2	1.69	0.62	0.18	6.49	92.7	181
11/15	-	Composite of Sulfided Batch 2	4.84	60.9	34.1	1.34	0.62	0.08	6.75	93.1	198
11/18	-	Composite of Sulfided Batch 3	4.24	60.7	33.9	2.65	0.76	0.12	6.31	89.8	186
11/26	1500	1st WD	4.1	59.5	31.7	9.30	0.86	0.24	6.14	81.9	105(104)
12/01	1628	Removed after shutdown	3.75	57.8	28.8	14.10	1.05	0.30	5.64	78.4	65
12/05	1600	Composite used to restart run	4.0	57.5	-	13.72	0.96	0.26	5.53	79.4	63(54)
12/10	1600	WD for Lab Sample	4.3	58.7	-	18.75	1.69	0.28	5.31	79.6	-
12/12	1672	WD for Lab Sample	4.0	57.3	-	18.31	1.41	0.31	5.51	78.3	-
12/27	2266	WD for Lab Sample	5.5	54.5	-	13.71	0.80	0.23	5.66	79.2	51
01/06	2784	WD for Lab Sample	5.9	62.4	-	15.01	0.82	0.21	5.65	77.0	69
01/10	2992	WD for Lab Sample	5.1	59.1	-	14.30	1.88	0.21	5.70	78.3	-
01/30	3775	WD for Lab Sample	4.1	58.1	-	15.63	0.83	0.24	5.17	77.2	-
01/31	3615	1st WD for A/W	4.3	57.4	-	-	-	-	-	-	-
02/02	3533	2nd WD for A/W	4.9	-	-	15.24	0.83	0.36	6.40	79.3	-

Table 18

RUN 252
AMOCAT 1C 1/16" SECOND STAGE CATALYST

Date, 1986-87	Catalyst Age	Description of Sample	As-is S	wt % Ash	Analysis of THF-Extracted Catalyst, wt %						Naphthalene Activity
					Oil	C	H	N	S	Ash	
11/12	-	Composite of Sulfided Batch 1	4.25	60.9	34.2	1.69	0.62	0.18	6.49	92.7	181
11/15	-	Composite of Sulfided Batch 2	4.84	60.9	34.1	1.34	0.62	0.08	6.75	93.1	198
11/18	-	Composite of Sulfided Batch 3	4.24	60.7	33.9	2.65	0.76	0.12	6.31	89.8	186
02/13	1921	End of Run 4' to 9' Level	3.83	58.8	33.5	7.66	0.84	0.21	5.42	85.6	114
02/13	1921	End of Run Above 9' Level	4.02	59.8	32.0	9.71	0.90	0.23	5.31	84.1	95

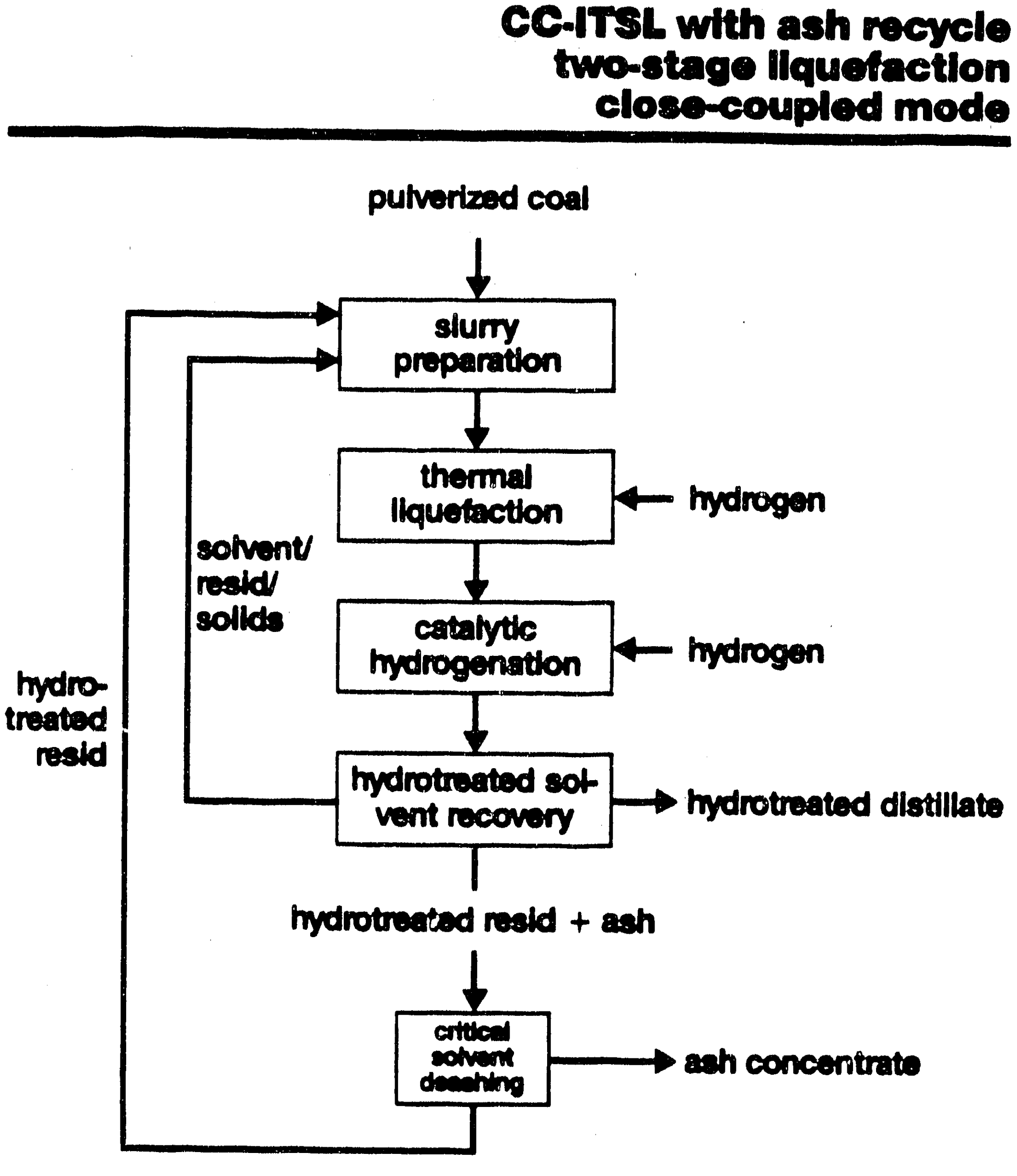
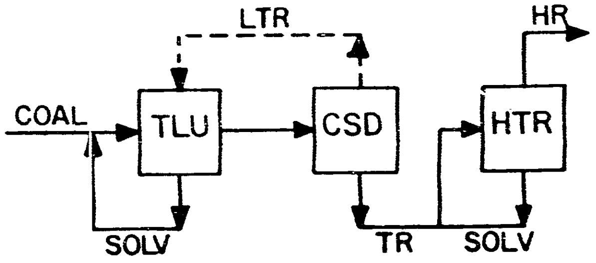


FIGURE 1. BLOCK FLOW DIAGRAM OF CC-ITSL OPERATION WITH SOLIDS RECYCLE

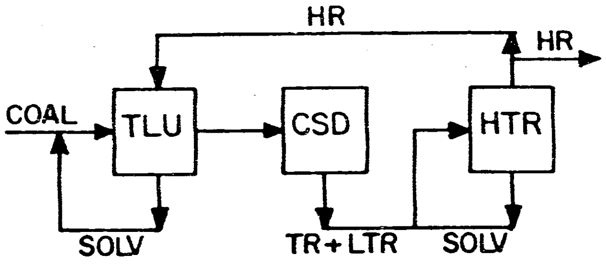
FIGURE 2

TWO STAGE LIQUEFACTION MODES TESTED

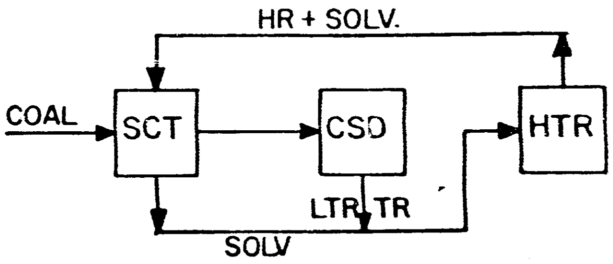
PRIOR TO CC-ITSL MODE



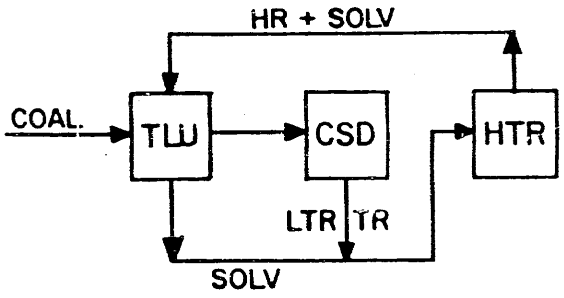
NTSL (W/WO LTR)
(RUNS: 228-236, 240-241)



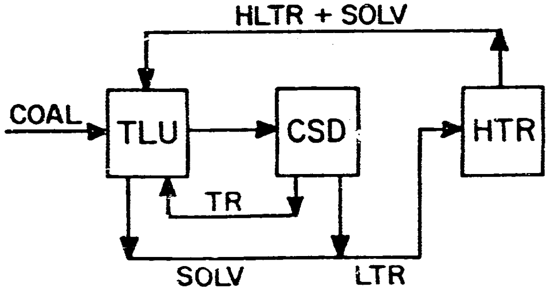
PITSL
(RUNS: 238-239)



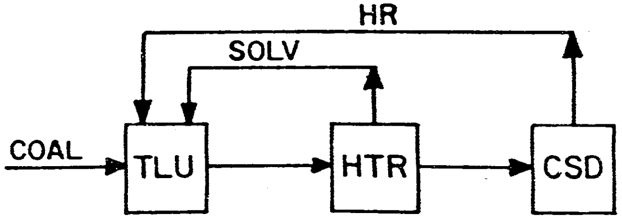
SCT - ITSL
(RUN: 242)



ITSL
(RUNS: 243-1,2, 244, 245, 246)



DITSL
(RUNS: 246, 248)



RITSL
(RUNS: 247, 249)

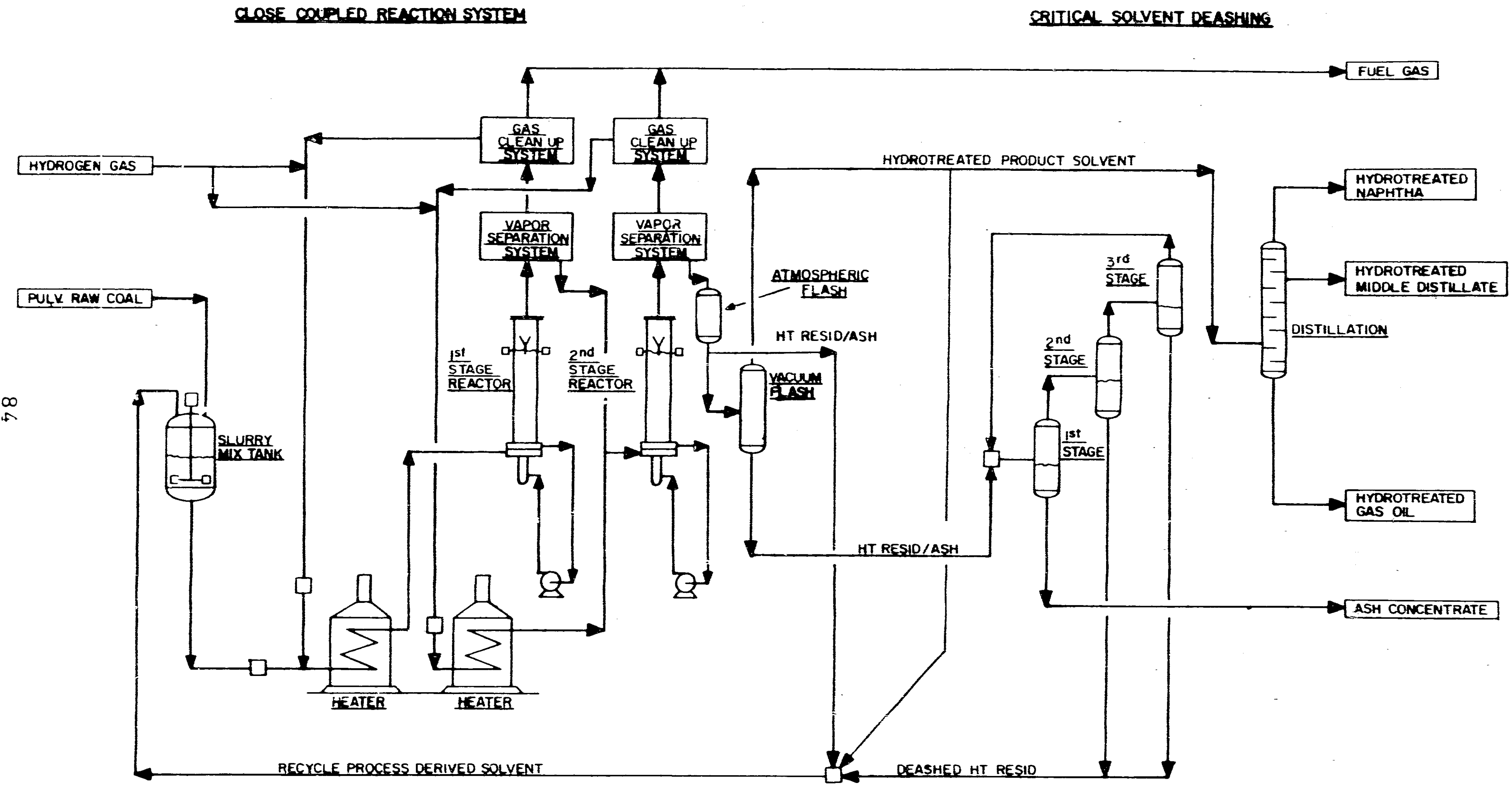
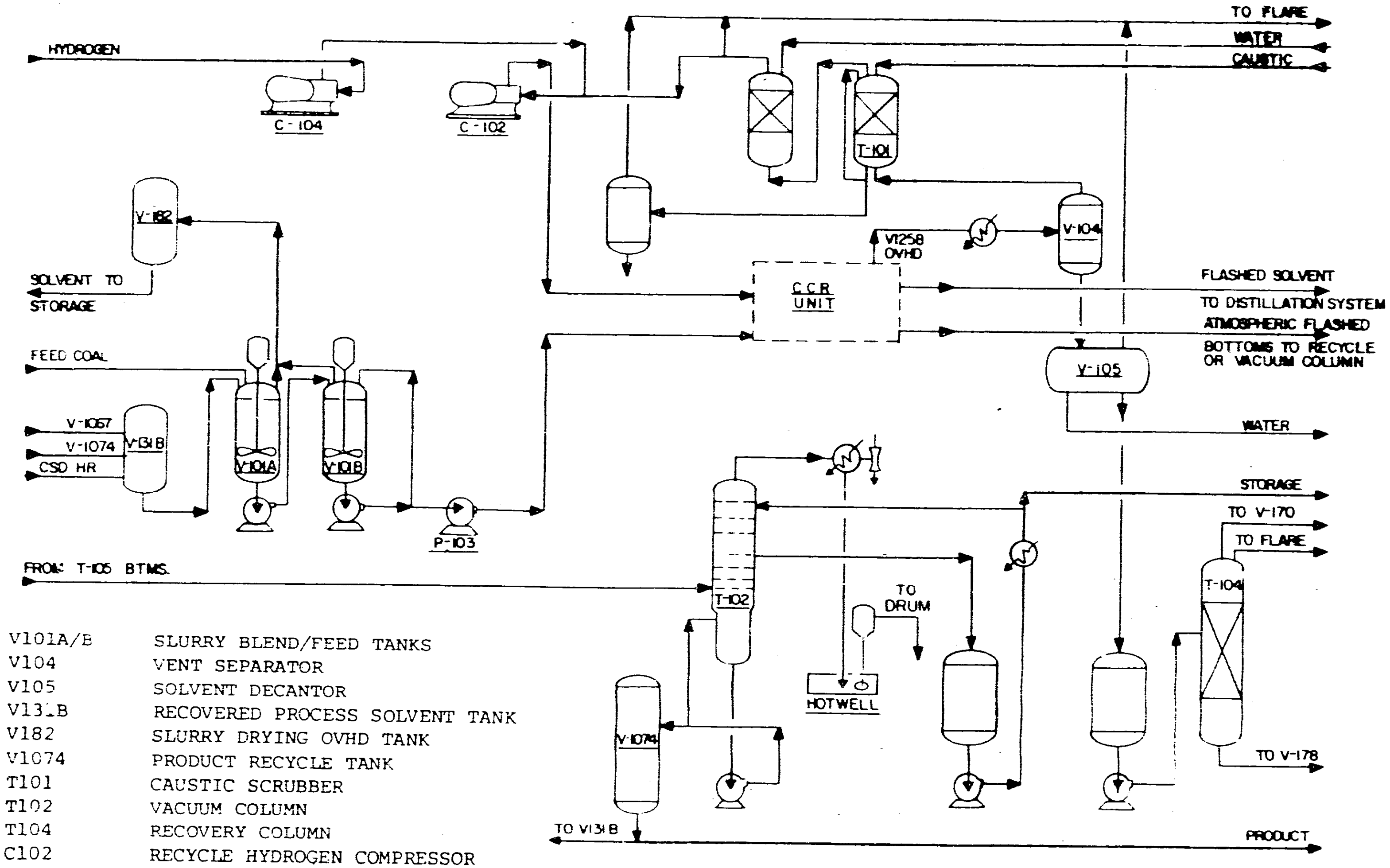
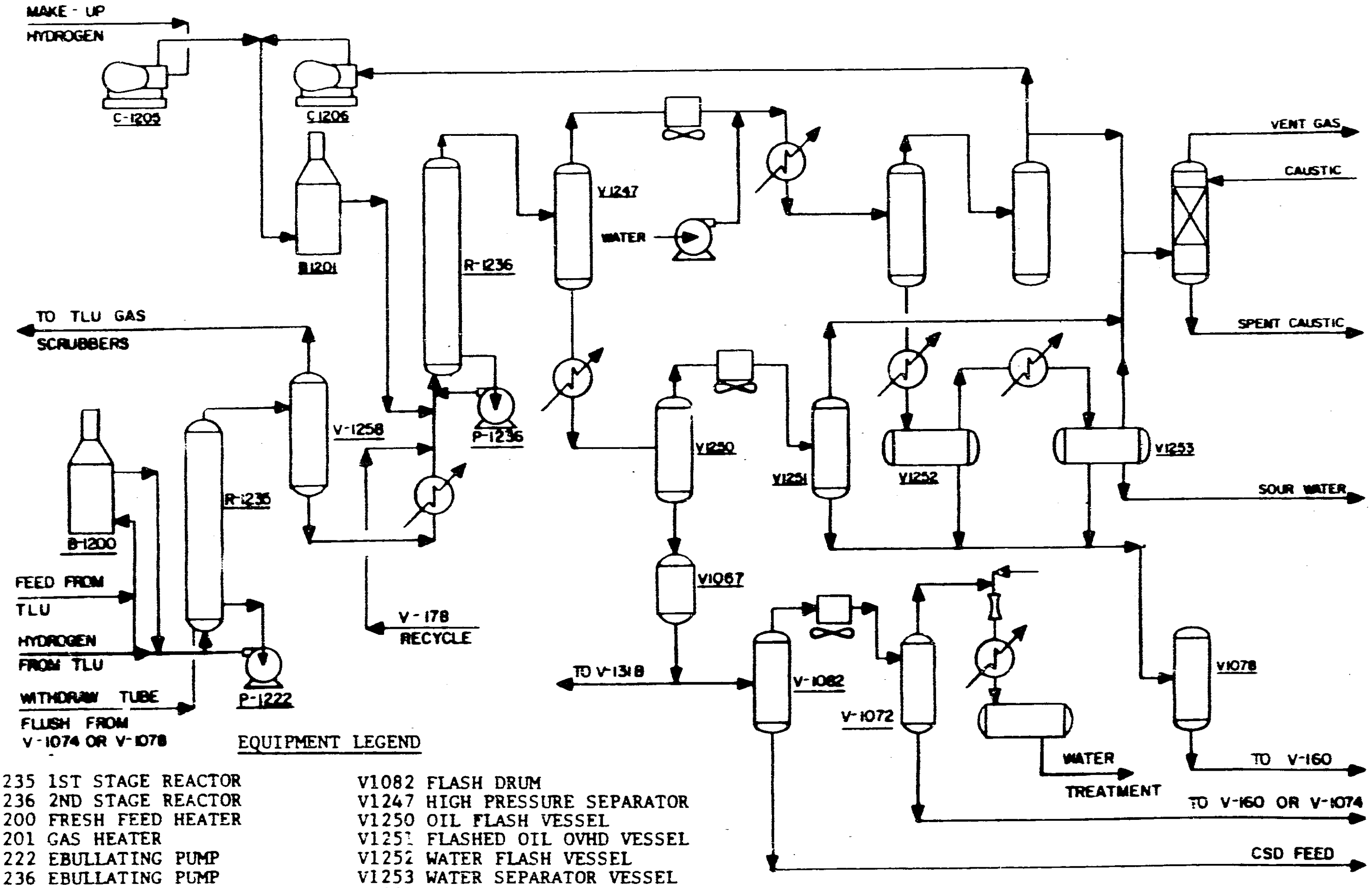


FIGURE 3. SCHEMATIC FLOW DIAGRAM OF CCR UNIT WITH ASH RECYCLE



V101A/B	SLURRY BLEND/FEED TANKS
V104	VENT SEPARATOR
V105	SOLVENT DECANTOR
V131B	RECOVERED PROCESS SOLVENT TANK
V182	SLURRY DRYING OVHD TANK
V1074	PRODUCT RECYCLE TANK
T101	CAUSTIC SCRUBBER
T102	VACUUM COLUMN
T104	RECOVERY COLUMN
C102	RECYCLE HYDROGEN COMPRESSOR
C104	FRESH HYDROGEN COMPRESSOR
P103	HIGH PRESSURE FEED PUMP

FIGURE 4. SCHEMATIC FLOW DIAGRAM OF TLU



EQUIPMENT LEGEND

R1235	1ST STAGE REACTOR	V1082	FLASH DRUM
R1236	2ND STAGE REACTOR	V1247	HIGH PRESSURE SEPARATOR
B1200	FRESH FEED HEATER	V1250	OIL FLASH VESSEL
B1201	GAS HEATER	V1251	FLASHED OIL OVHD VESSEL
P1222	EBULLATING PUMP	V1252	WATER FLASH VESSEL
P1236	EBULLATING PUMP	V1253	WATER SEPARATOR VESSEL
V1072	LIGHT OIL OVHD DRUM	V1258	INTERSTAGE SEPARATOR
V1078	DISTILLATE MEASURING POT	C1205	FRESH HYDROGEN COMPRESSOR
V1067	BOTTOMS PRODUCT TANK	C1206	RECYCLE HYDROGEN COMPRESSOR

FIGURE 5. SCHEMATIC FLOW DIAGRAM OF HTR UNIT AND 1ST STAGE REACTOR

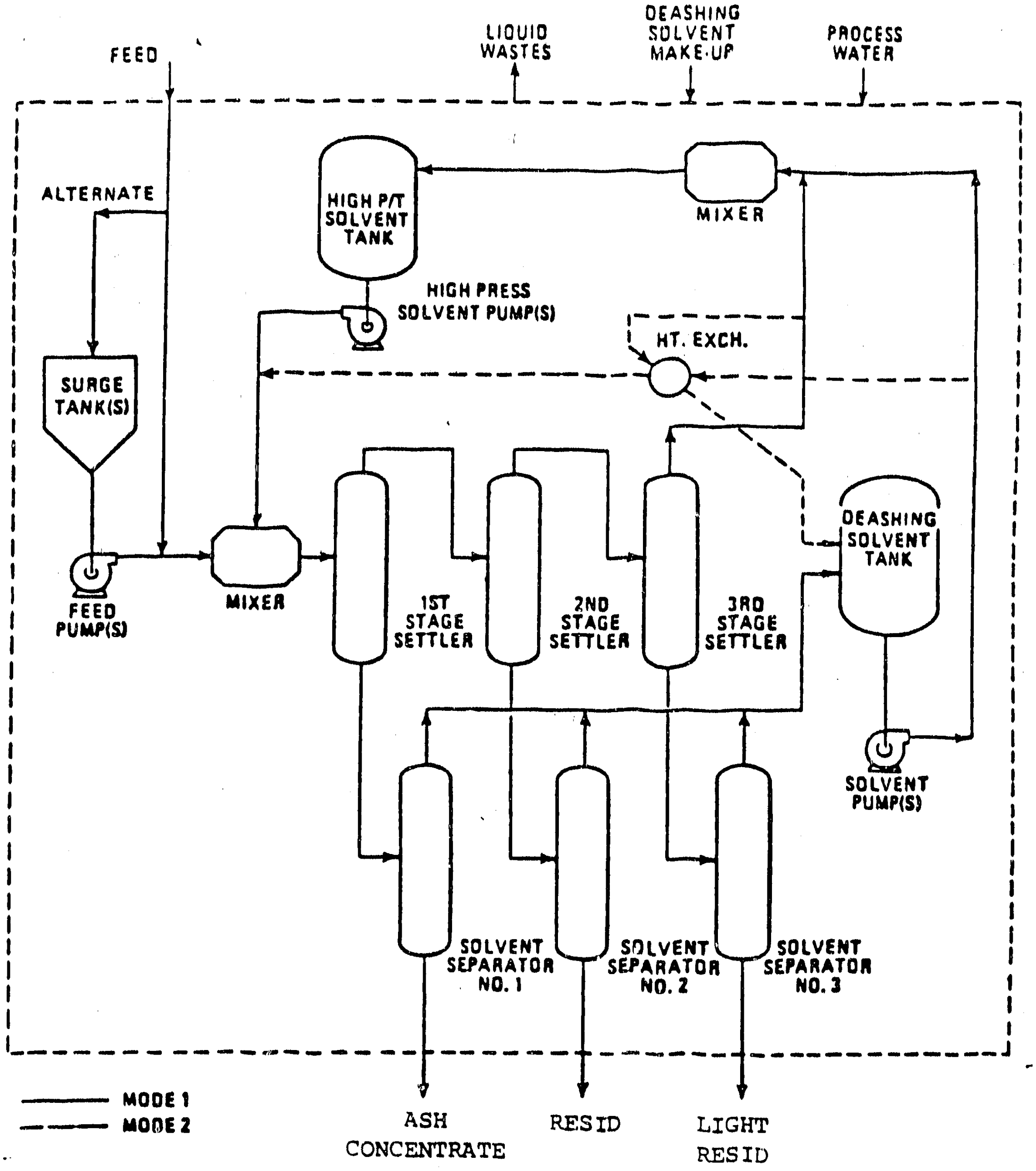


FIGURE 6 . SCHEMATIC FLOW DIAGRAM OF CSD UNIT

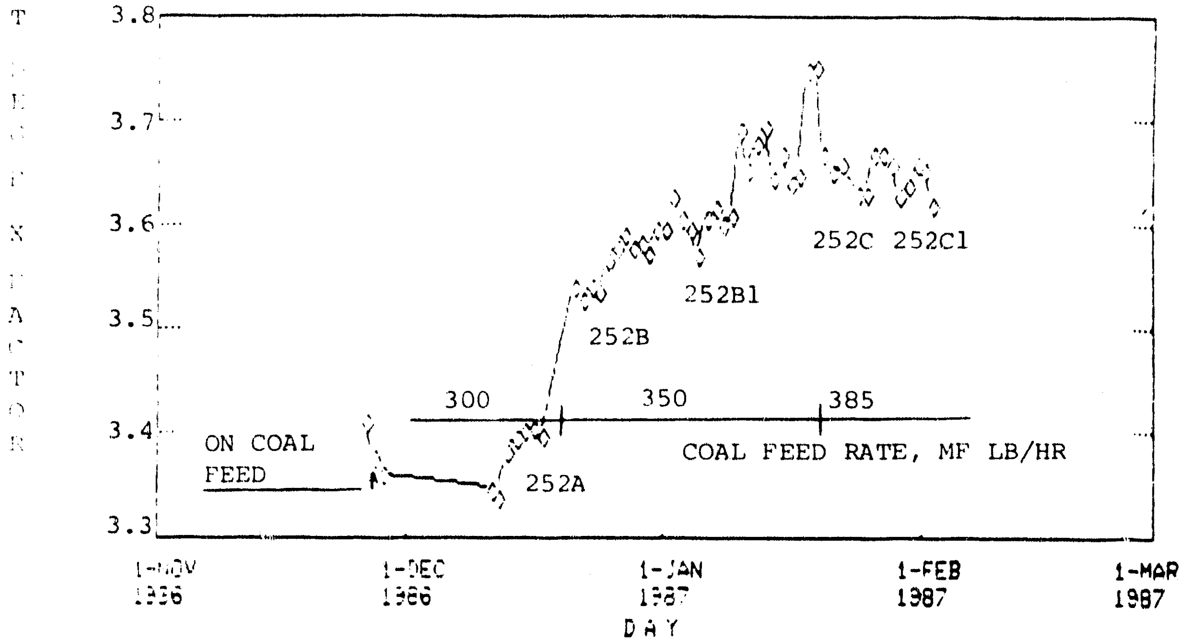


FIGURE 8
PREHEATER OUTLET TEMPERATURE

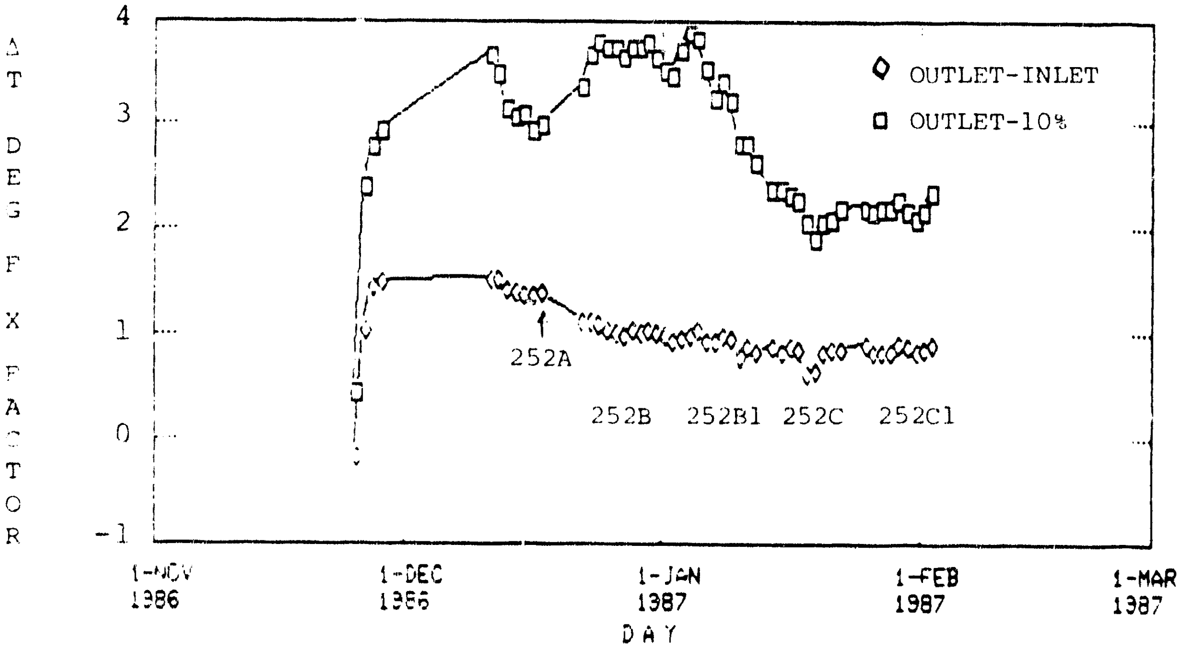


FIGURE 9
R1235 REACTOR EXOTHERM

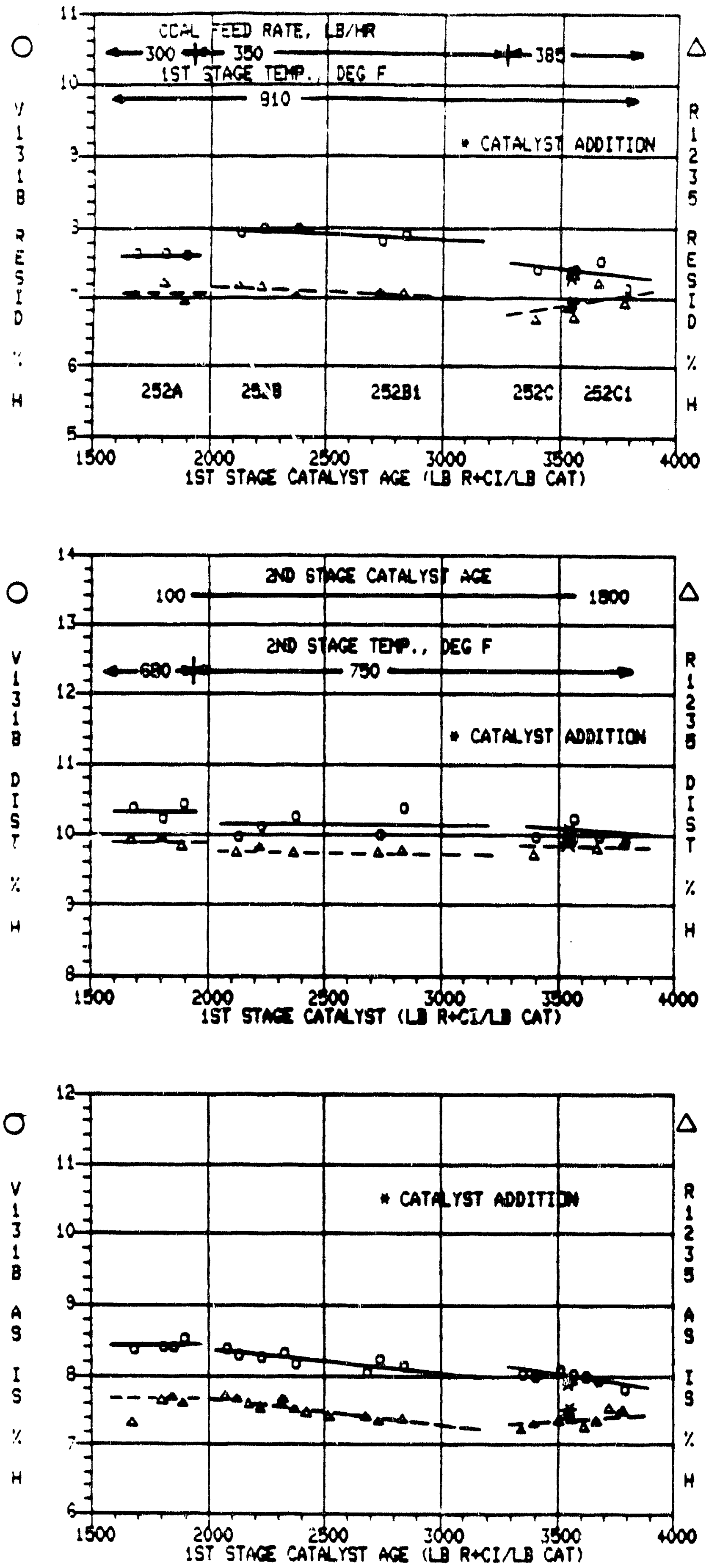


FIGURE 7. HYDROGEN CONTENTS OF RECYCLE AND PRODUCT RESID AND DISTILLATE, AND OF RECYCLE PROCESS SOLVENT (252A-C1)

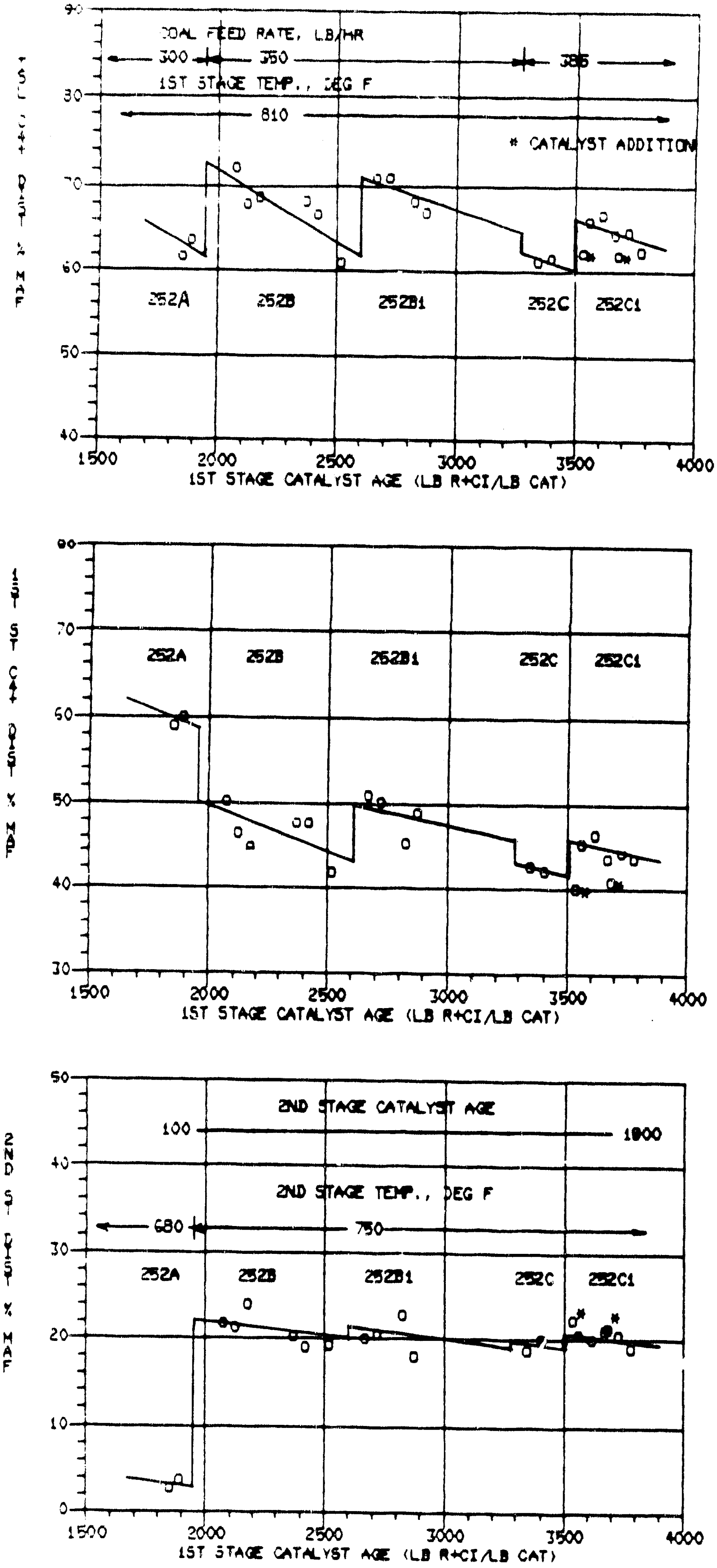


FIGURE 10. C4+ DISTILLATE YIELD RESPONSES (TSL, 1ST AND 2ND)

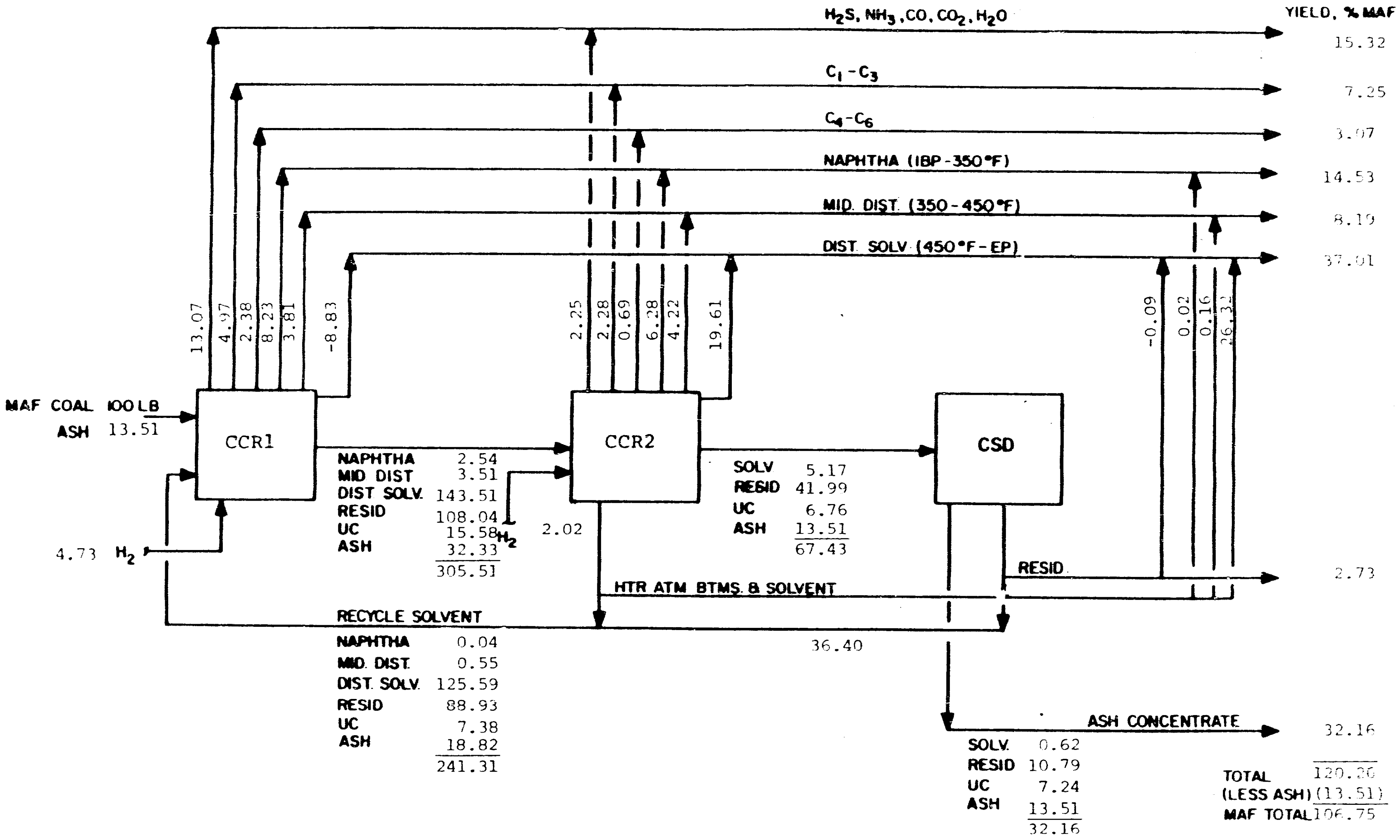


FIGURE 11. MATERIAL BALANCE FLOW DIAGRAM FOR 252A

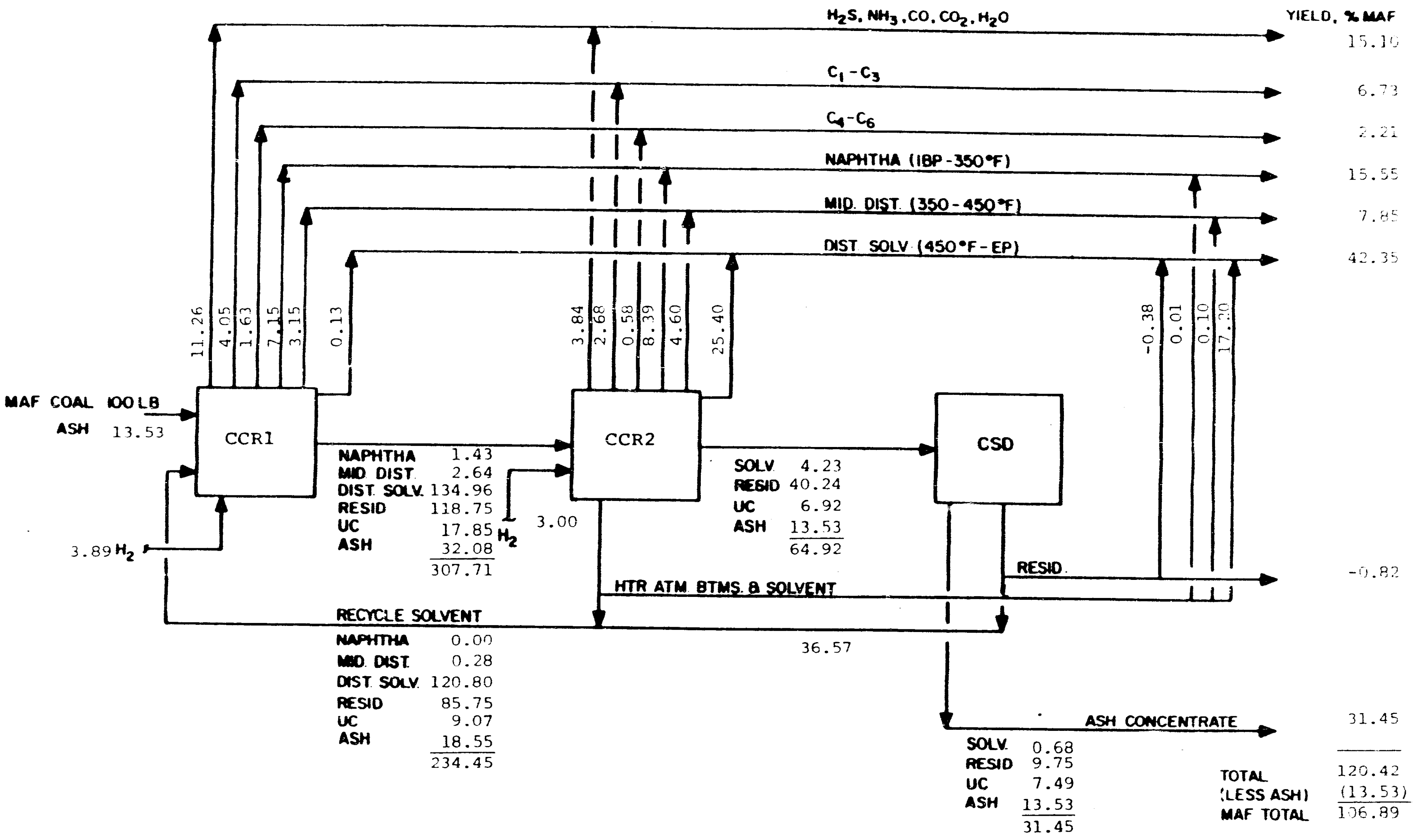


FIGURE 12. MATERIAL BALANCE FLOW DIAGRAM FOR 252B

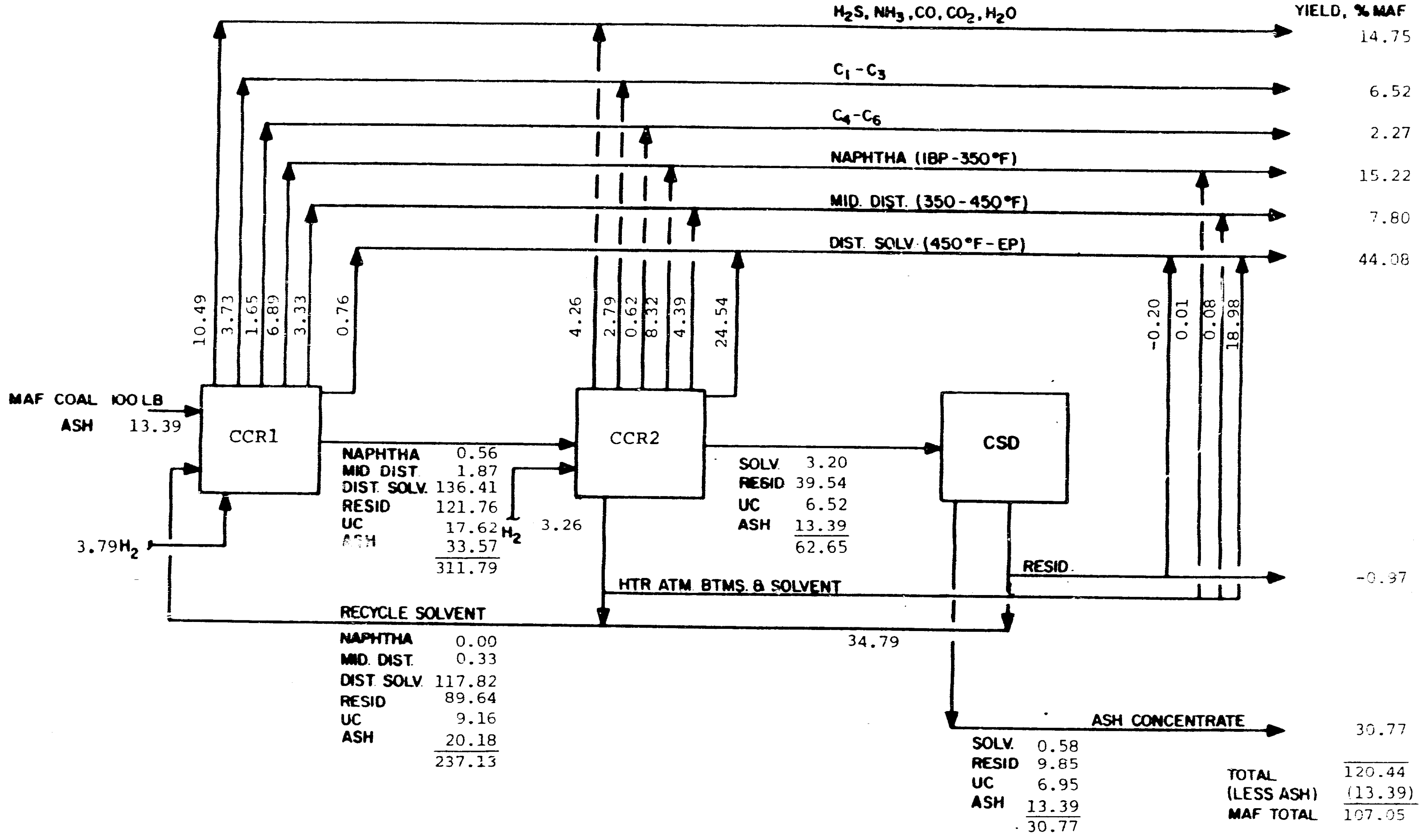


FIGURE 13. MATERIAL BALANCE FLOW DIAGRAM FOR 252B1

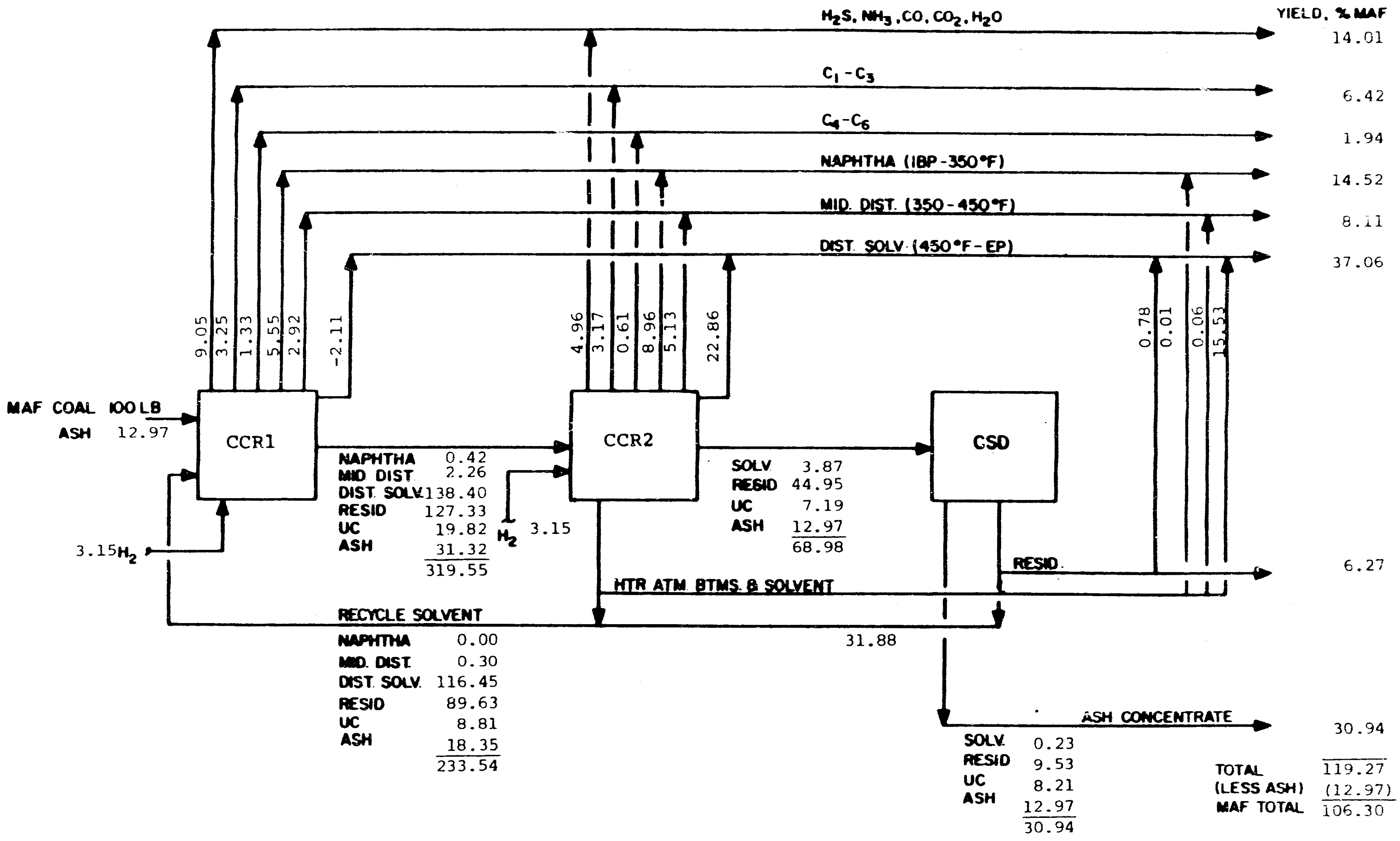


FIGURE 14. MATERIAL BALANCE FLOW DIAGRAM FOR 252C

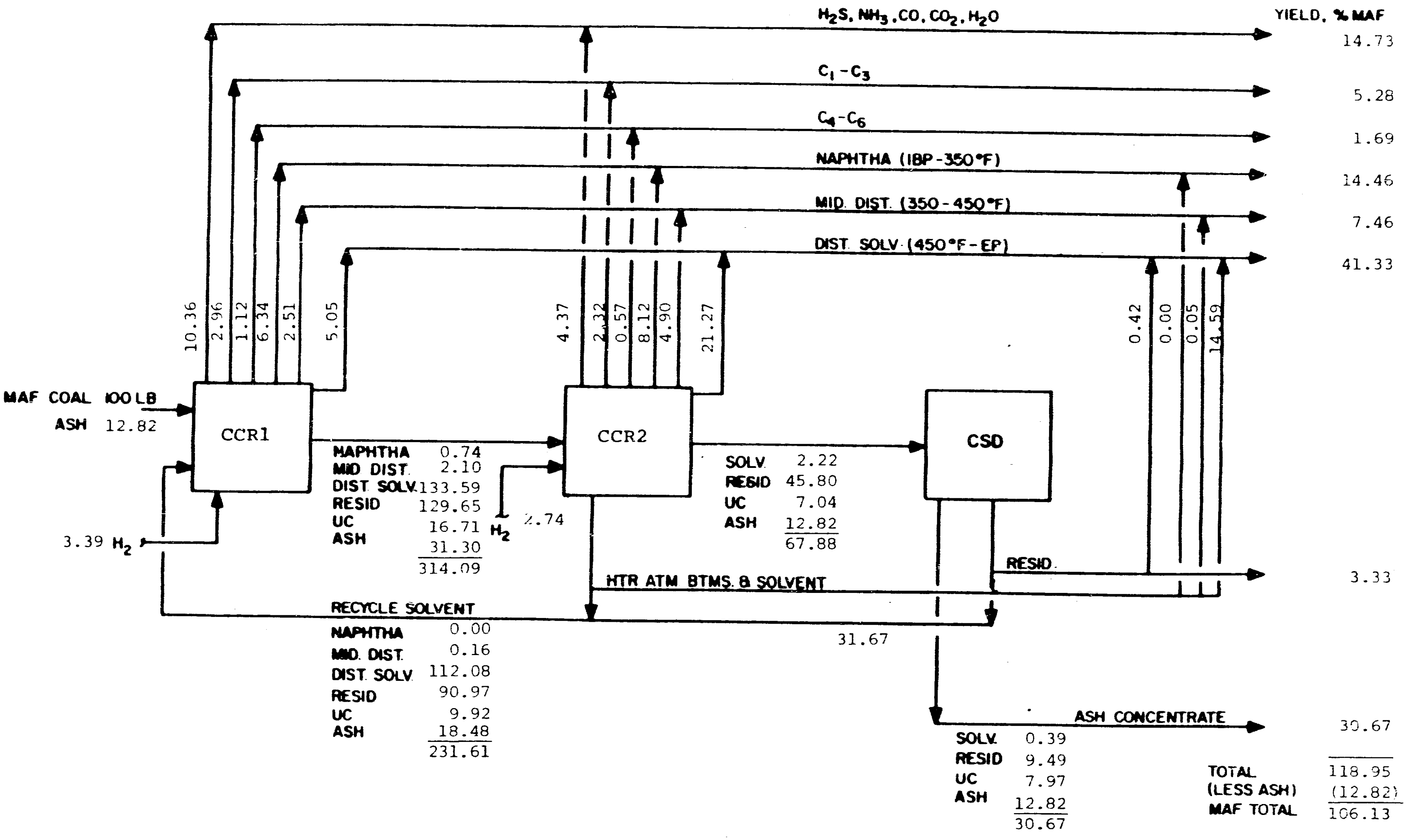
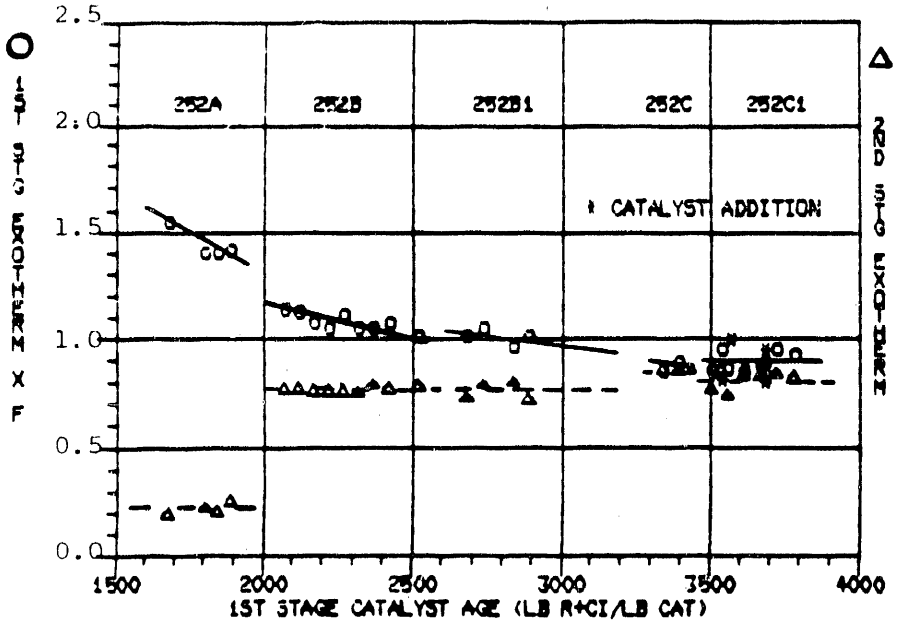


FIGURE 15. MATERIAL BALANCE FLOW DIAGRAM FOR 252C1



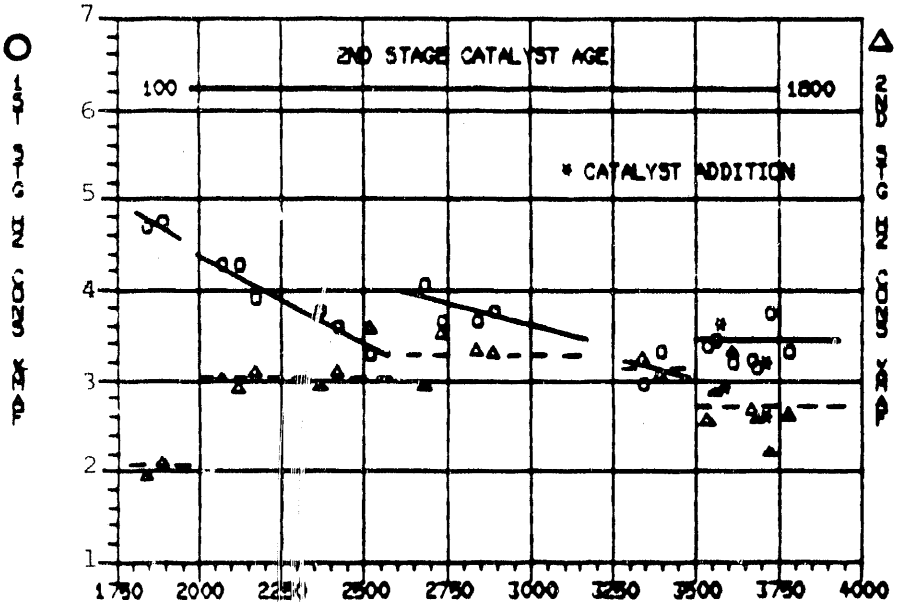


FIGURE 16. REACTOR EXOTHERM AND HYDROGEN CONSUMPTION (1ST AND 2ND STAGES) (252A-C1)

FIGURE 17

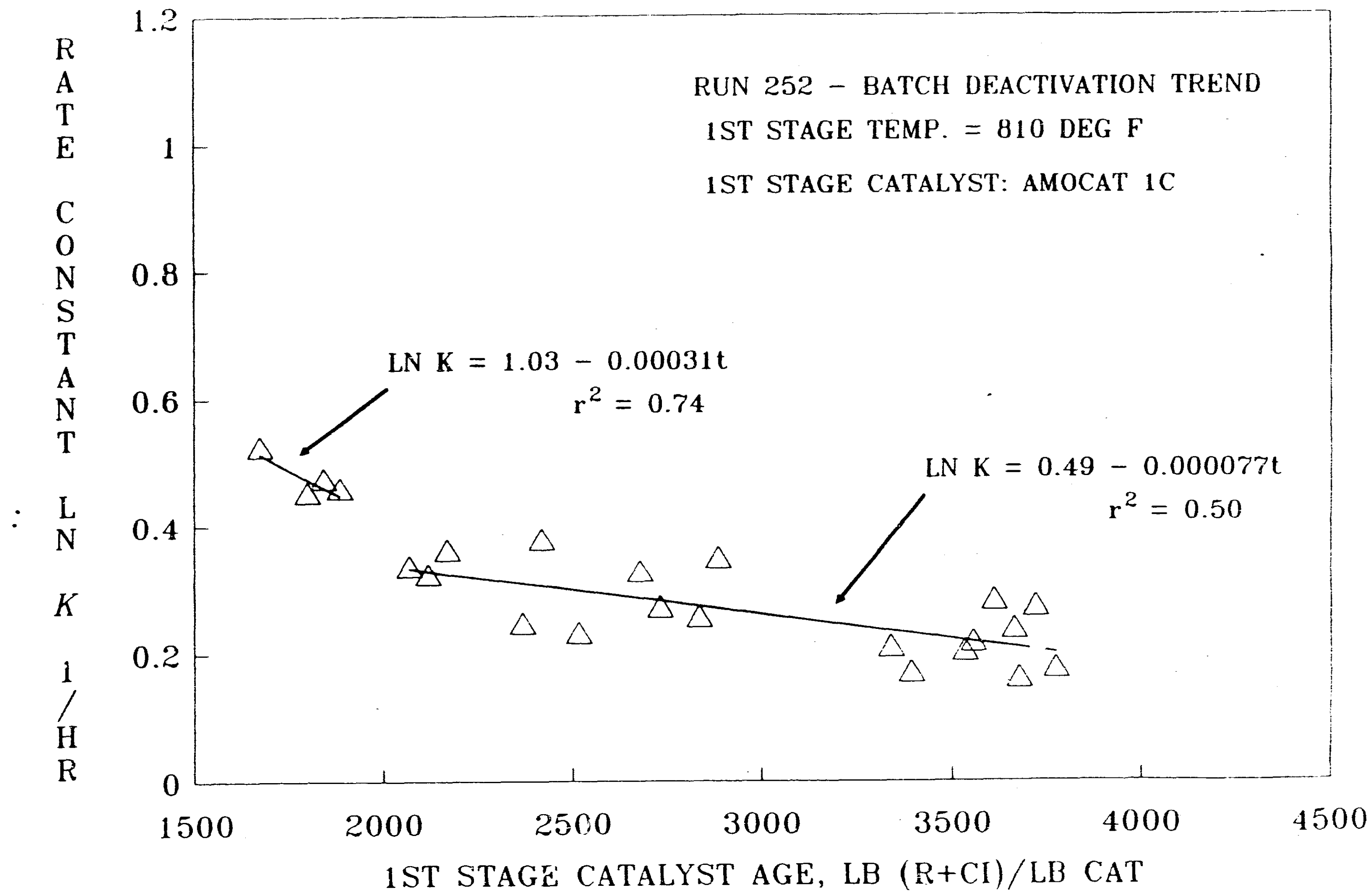

RUN 252 - BATCH DEACTIVATION TREND
1ST STAGE TEMP. = 810 DEG F
1ST STAGE CATALYST: AMOCAT 1C
LN K = 1.03 - 0.00031t
r² = 0.74
LN K = 0.49 - 0.000077t
r² = 0.50
RATE CONSTANT : LN K 1/HR
1.2
1
0.8
0.6
0.4
0.2
0
1500
2000
2500
3000
3500
4000
4500
1ST STAGE CATALYST AGE, LB (R+CI)/LB CAT

FIGURE 18

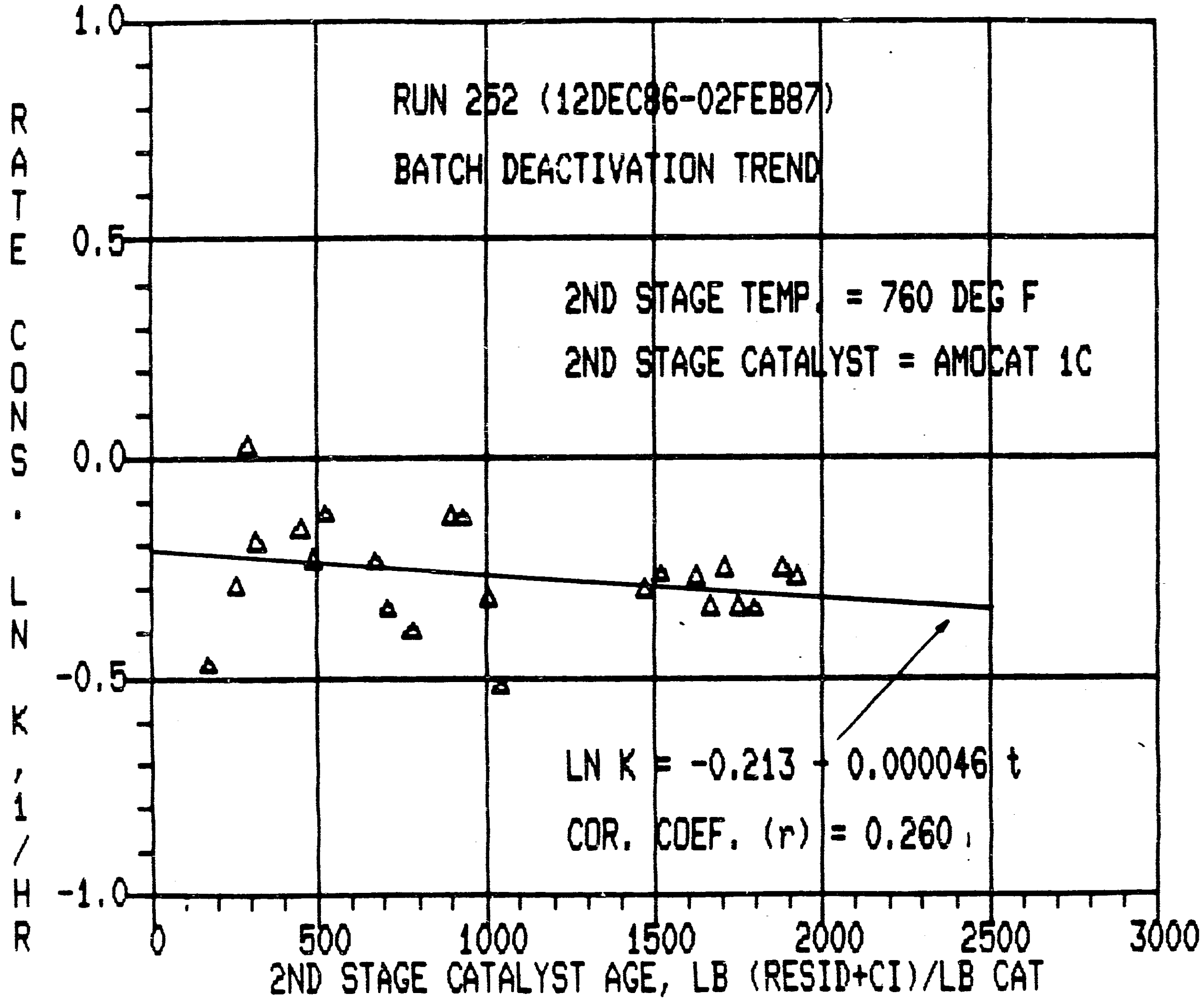

RUN 252 (12DEC86-02FEB87)
BATCH DEACTIVATION TREND
2ND STAGE TEMP. = 760 DEG F
2ND STAGE CATALYST = AMOCAT 1C
LN K = -0.213 - 0.000046 t
COR. COEF. (r) = 0.260
RATE CONS. LN K, 1/HR
1.0
0.5
0.0
-0.5
-1.0
0
500
1000
1500
2000
2500
3000
2ND STAGE CATALYST AGE, LB (RESID+CI)/LB CAT

FIGURE 19

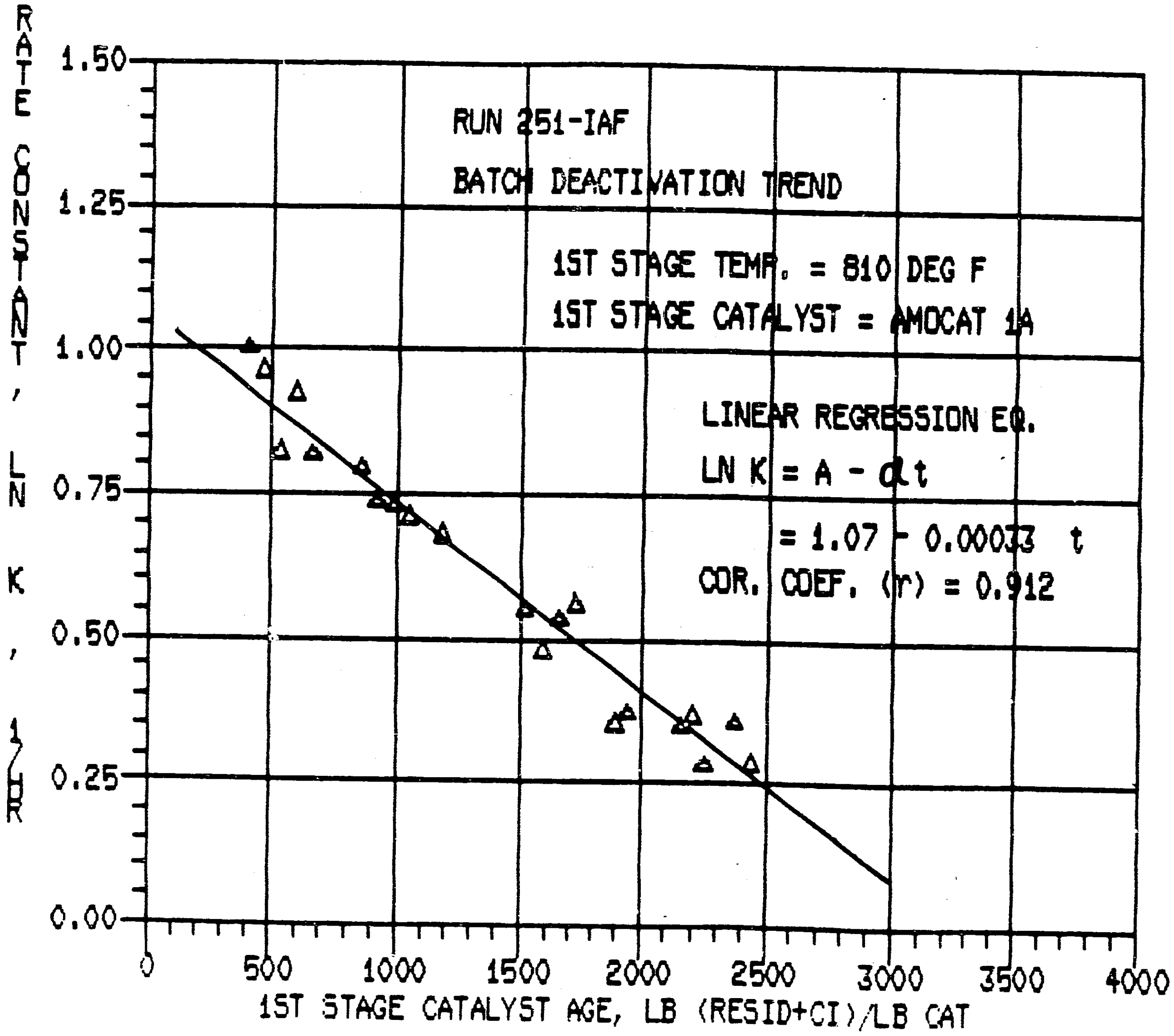

RUN 251-IAF
BATCH DEACTIVATION TREND
1ST STAGE TEMP. = 810 DEG F
1ST STAGE CATALYST = AMOCAT 1A
LINEAR REGRESSION EQ.
LN K = A - αt
= 1.07 - 0.00033 t
COR. COEF. (r) = 0.912
RATE CONSTANT, LN K, 1/HR
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0
500
1000
1500
2000
2500
3000
3500
4000
1ST STAGE CATALYST AGE, LB (RESID+CI)/LB CAT

FIGURE 20

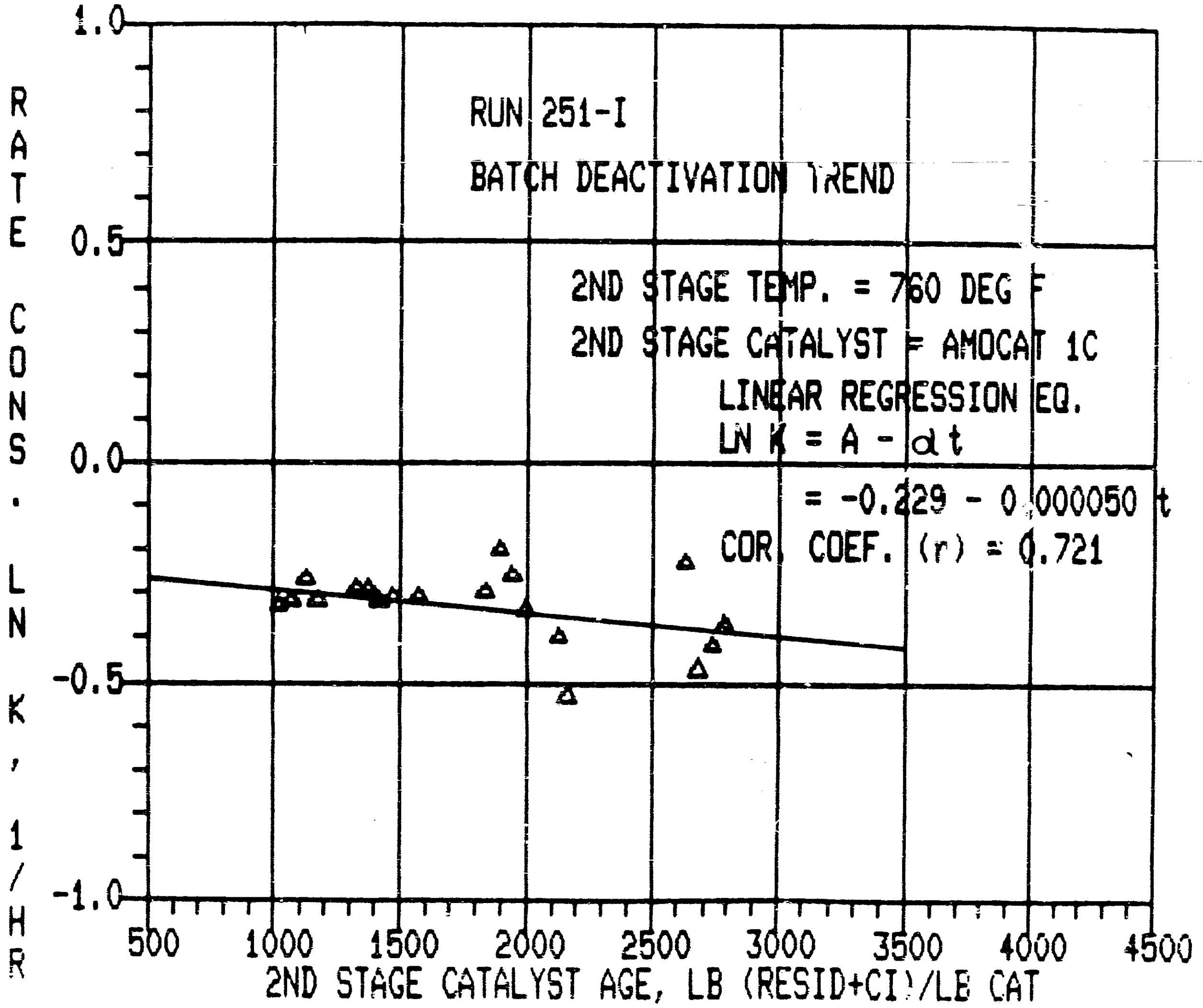
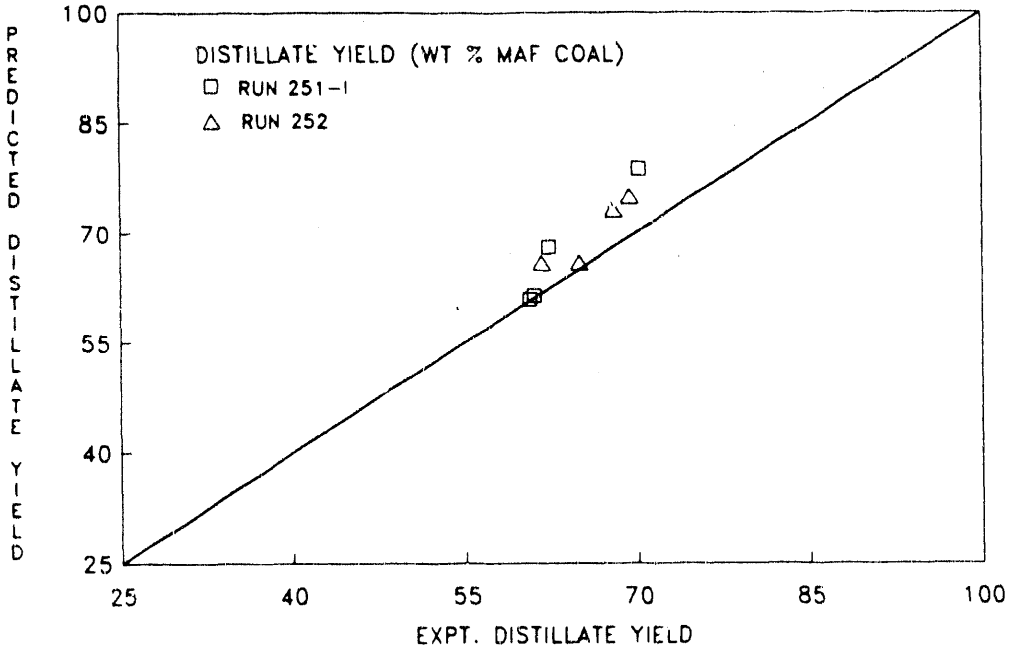
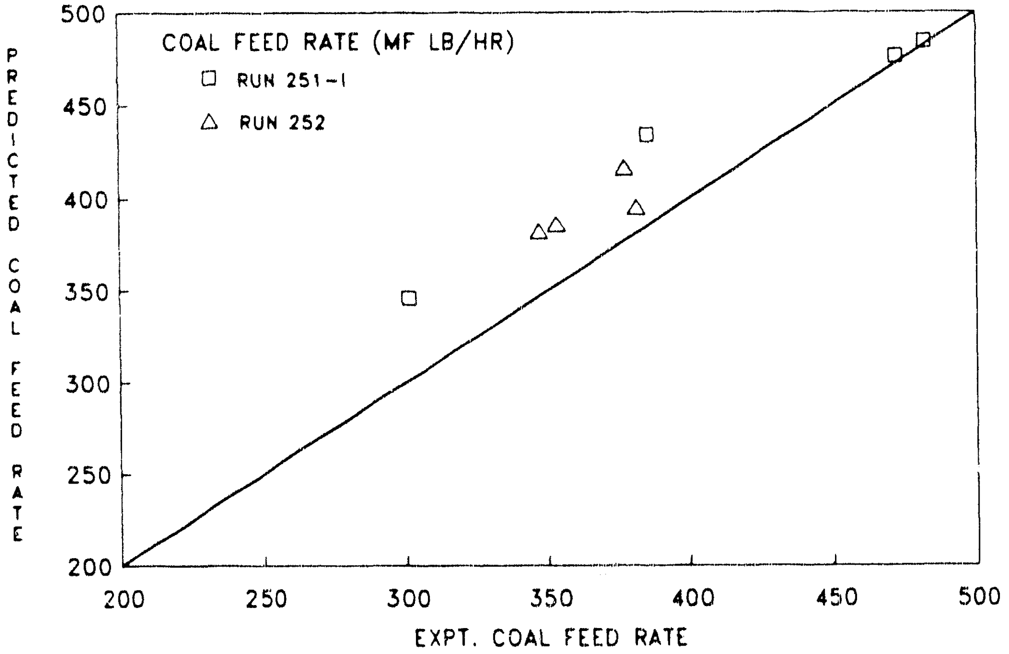
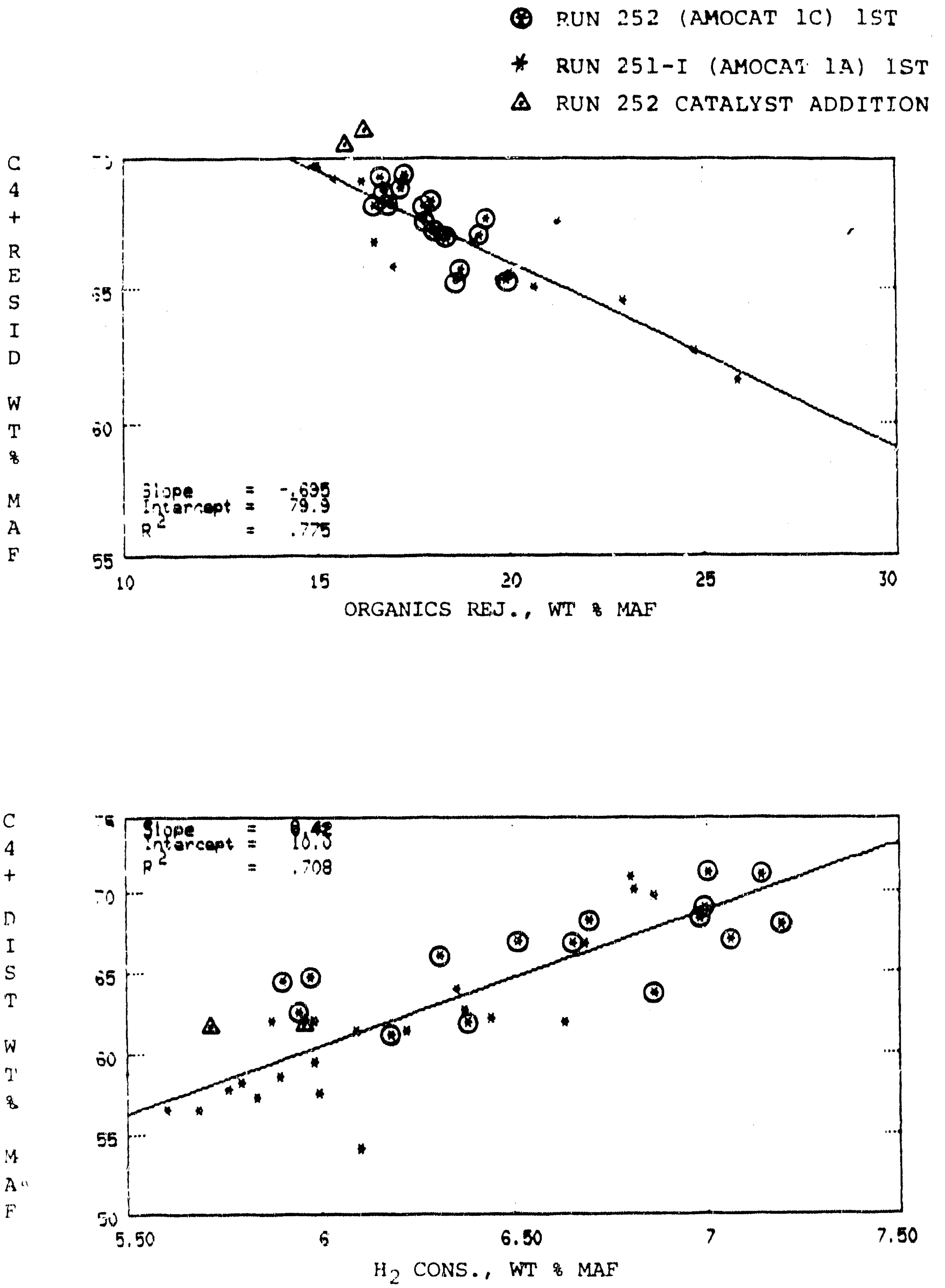

RUN 251-I
BATCH DEACTIVATION TREND
2ND STAGE TEMP. = 760 DEG F
2ND STAGE CATALYST = AMOCAT 1C
LINEAR REGRESSION EQ.
LN K = A - αt
= -0.229 - 0.000050 t
COR. COEF. (r) = 0.721
RATE CONS. LN K, 1/HR
1.0
0.5
0.0
-0.5
-1.0
500
1000
1500
2000
2500
3000
3500
4000
4500
2ND STAGE CATALYST AGE, LB (RESID+CI)/LB CAT

FIGURE 21. PARITY PLOTS OF EXPERIMENTAL VS PREDICTED C_4+ DISTILLATE YIELDS AND COAL FEED RATES

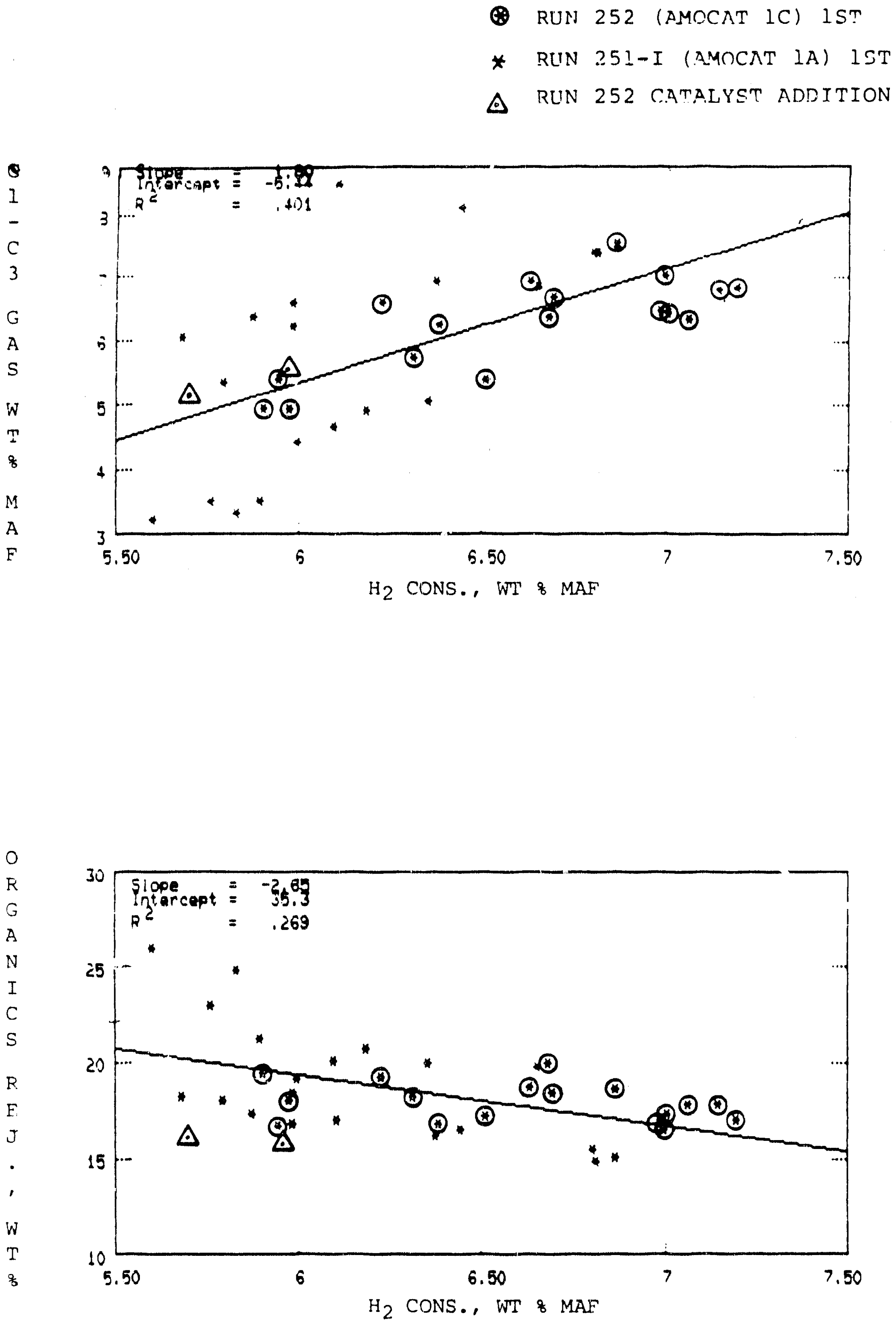






(NOTE) SELECTED DAYS (37)
RUN 252A, B, B1, C, C1 (17)
RUN 251-IA, IB, IC, ID, IE, IF (20)

FIGURE 22. TSL CATALYST SELECTIVITY IN TSL HYDROGENATION (RUNS 251-I and 252) (PART I)



(NOTE) SELECTED DAYS (37)
RUN 252A, B, B1, C, C1 (17)
RUN 251-IA, IB, IC, ID, IE, IF (20)

FIGURE 23. TSL CATALYST SELECTIVITY IN TSL HYDROGENATION (RUNS 251-I AND 252) (PART 2)

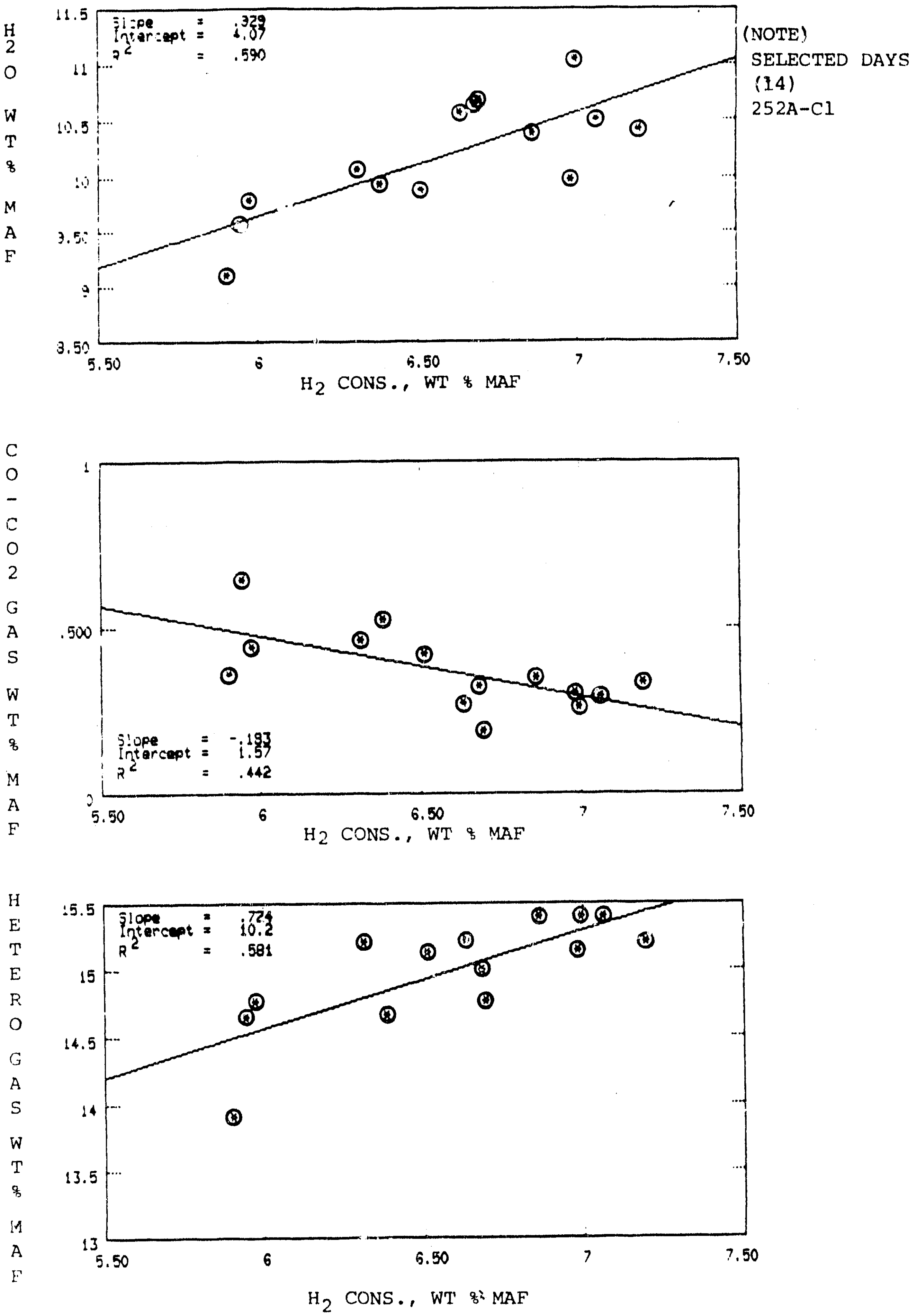
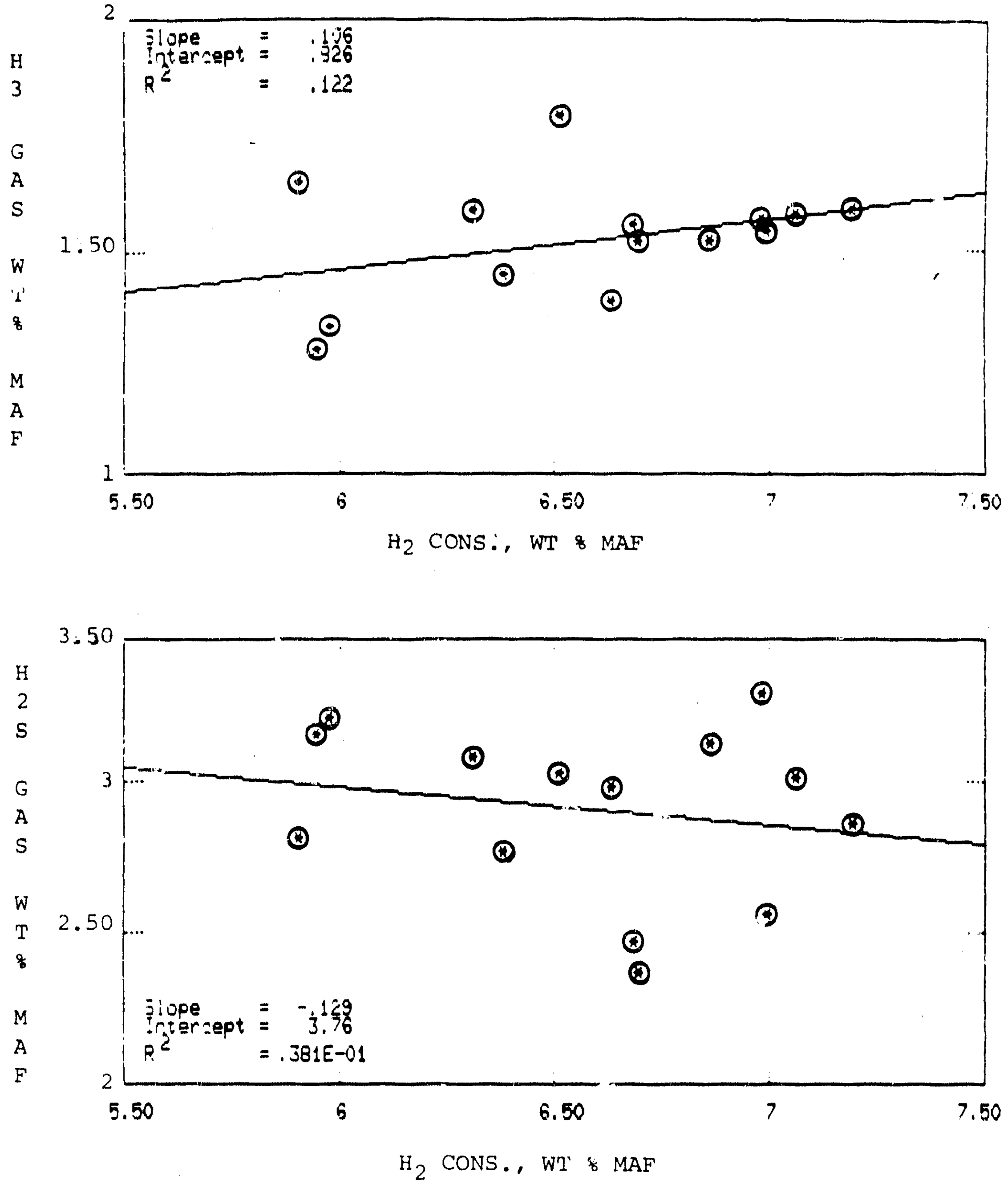

(NOTE)
SELECTED DAYS
(14)
252A-C1

FIGURE 24. TSL CATALYST SELECTIVITY IN TSL HETEROATOM REMOVAL (RUN 252) (PART 1)



(NOTE) SELECTED DAYS (14)

252A : 12/16, 12/17
252B : 12/24, 12/25, 12/29, 12/30
252B1 : 1/7, 1/8
252C : 1/20
252C1 : 1/26, 1/27, 1/28, 1/29, 1/30

DATA FOR 1/4, 1/5 AND 1/20 WERE NOT INCLUDED IN LINEAR REGRESSION ANALYSES.

FIGURE 25. TSL CATALYST SELECTIVITY IN TSL HETEROATOM REMOVAL (RUN 252) (PART 2)

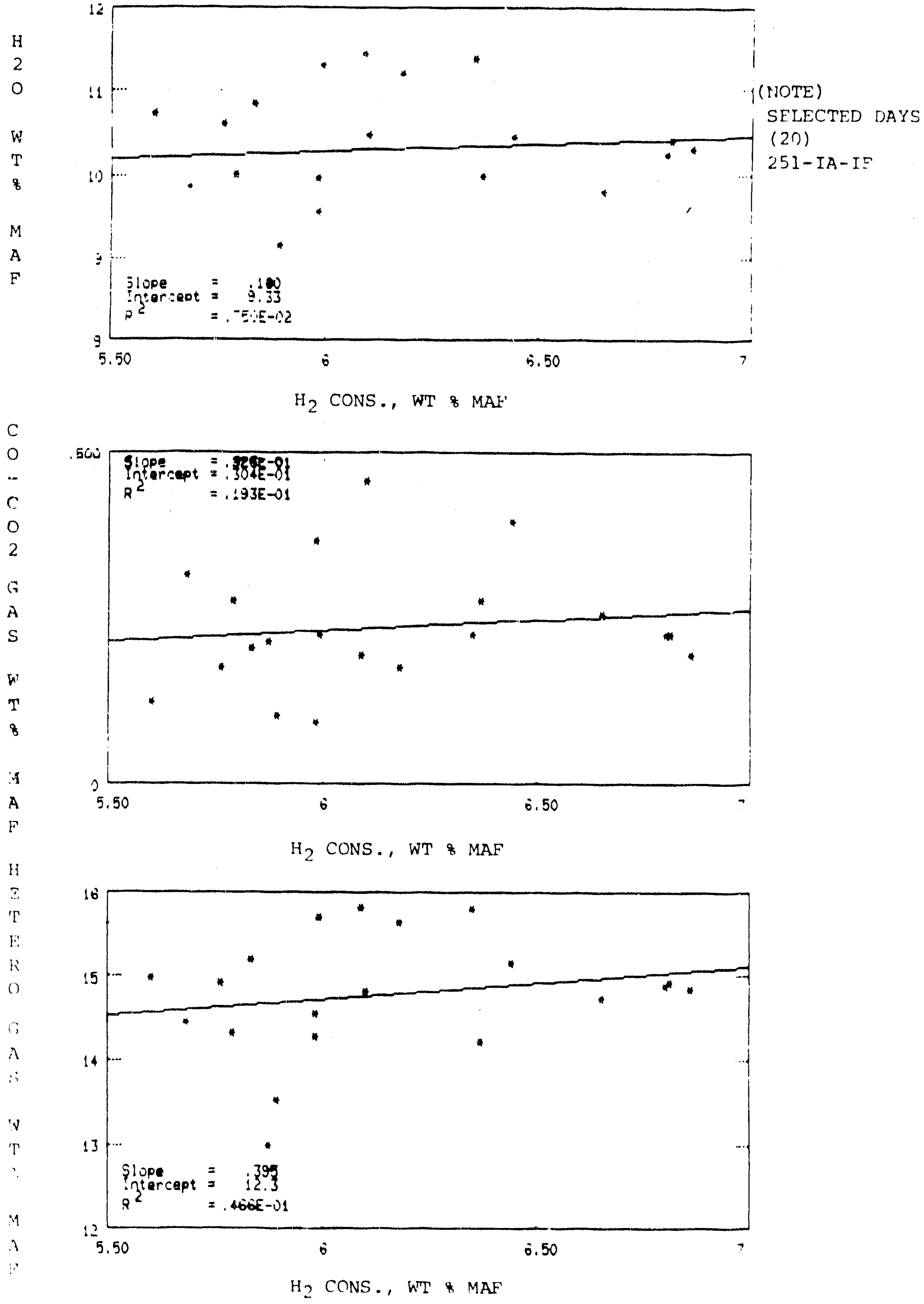
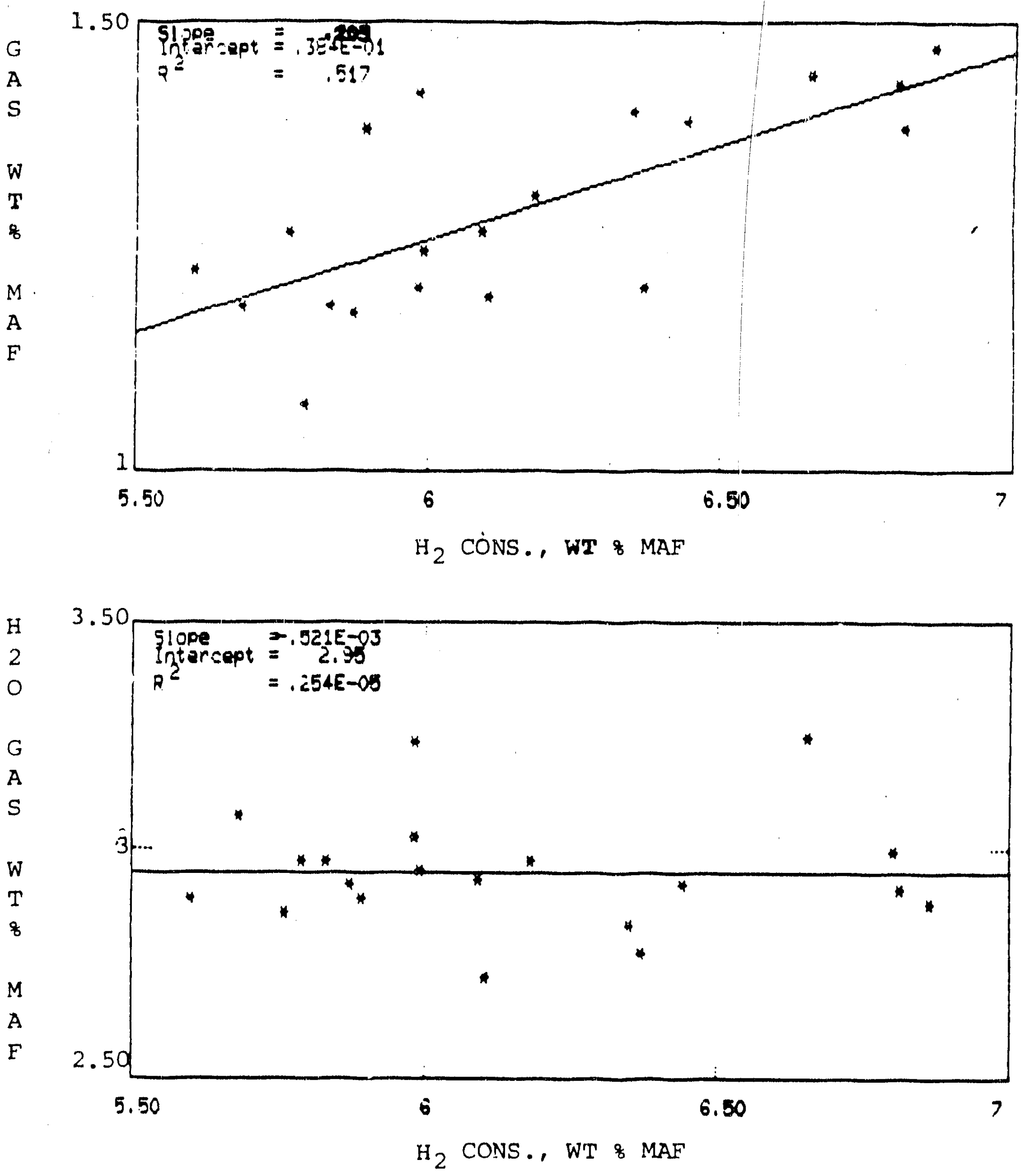


FIGURE 26. TSL CATALYST SELECTIVITY IN TSL HETEROATOM REMOVAL (RUN 251-I) (PART 1)



(NOTE) SELECTED DAYS (20)

251-IA : 5/5, 5/6, 5/7, 5/8
251-IB : 5/11, 5/12, 5/13, 5/14
251-IC : 5/16, 5/22, 5/23, 5/24, 5/25
251-ID : 5/28, 5/29
251-IE : 6/3, 6/4, 6/5
251-IF : 6/7, 6/8

FIGURE 27. TSL CATALYST SELECTIVITY IN TSL HETEROATOM REMOVAL (RUN 251-I) (PART 2)

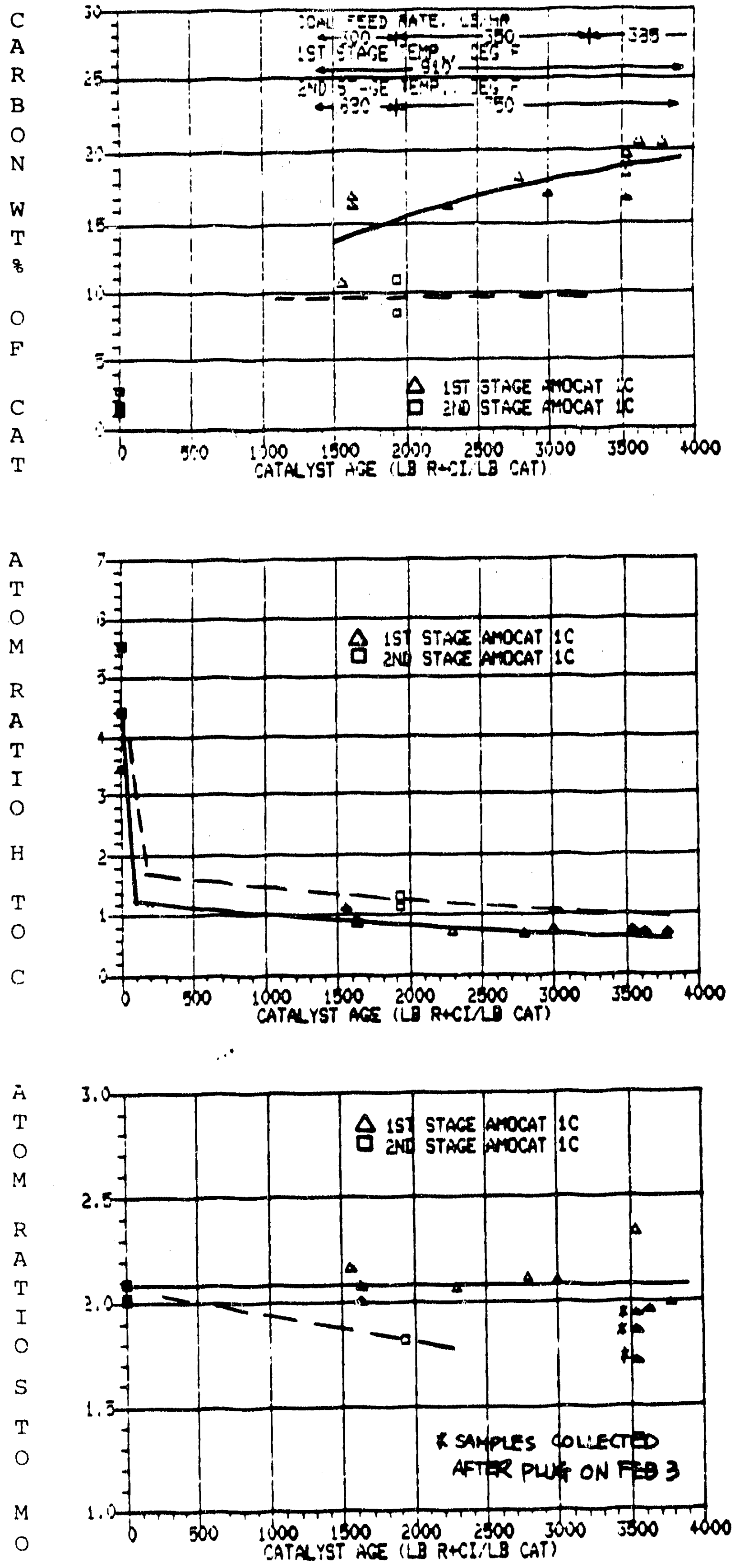
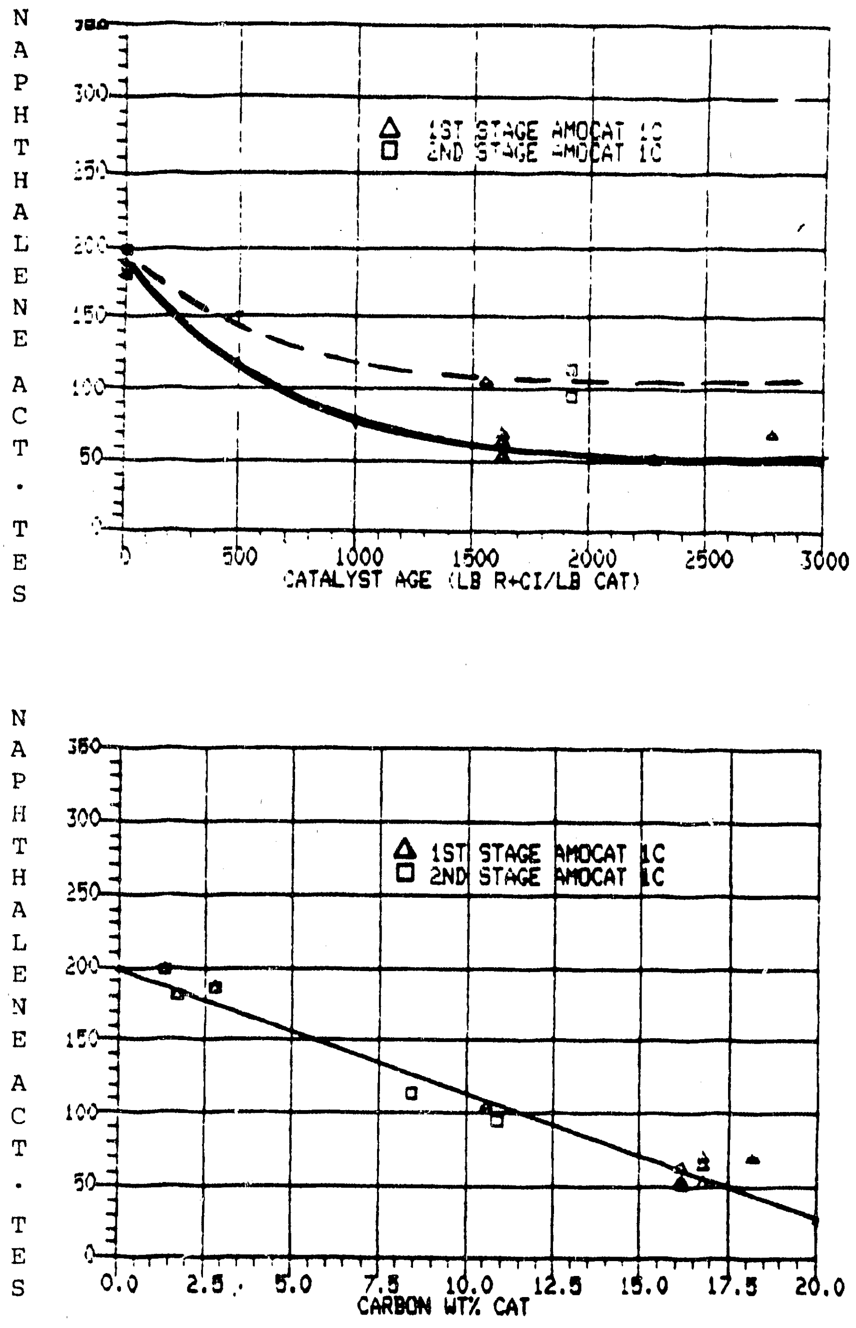


FIGURE 28. CATALYST CHARACTERIZATION DATA (PART I)
(1ST AND 2ND STAGE AMOCAT 1C 1/16") (RUN 252)



LINEAR REGRESSION ANALYSIS

$Y = a + bX$
$a = 198.38$ (intercept)
$b = -8.35$ (slope)
$r = 0.972$ (correlation coefficient)

FIGURE 29. CATALYST CHARACTERIZATION DATA (PART II) (1ST AND 2ND STAGE AMOCAT 1C 1/16") (RUN 252)

END

DATE FILMED

01 / 07 / 91