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UPGRADING OF COAL LIQUIDS

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Progress Report
For November, 1977

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TABLE OF CONTENTS

ABSTRACT

Series flow second-stage hydrocracking of high nitrogen H-Coal liquid to gasoline has been completed. Complete conversion to gasoline was attained at moderate process conditions.

Because of the presence of significant amounts of heptane insolubles, the raw EDS process gas oil was not suitable as hydrocracker charge stock. Hydrotreating converted these insolubles completely to distillate and lowered the nitrogen content well below the level required for a second-stage hydrocracking feedstock.

Hydrotreating process variable studies on raw EDS liquid product have been started. The first series of experiments was conducted at 250 psig above base pressure, 25°C above base temperature, and three space velocities.

The preparative H-Coal gas oil hydrotreating run for preparing a FCC feedstock with 11% hydrogen was completed. Another preparative run, aimed at preparing a 13% hydrogen feedstock, is now near completion.

Task 1

Work Accomplished

Series flow second-stage hydrocracking of high nitrogen H-Coal liquid to gasoline was carried out in Plant 536 (Run 678). The feedstock is a blend of first-stage hydrocrackates from Plant 638H, Run 9B (reported in FE-2556-06). Table 1 gives the inspections of this feedstock.

In the series flow system, the first reactor was loaded with a UOP-DCB catalyst, and the second reactor was loaded with a UOP-HCA catalyst

(See Table 13, FE-2566-07). The fractionator was operated at maximum gasoline yield mode with 375°F$^+$ fractionator bottoms recycled back to the first reactor. Hydrocracking was conducted at 500 psig below base pressure, base fresh feed (FF) space velocity, and 1.18 x base combined feed ratio (CFR). The first reactor was operated at a constant temperature of 14°C below base temperature. Temperature was varied in the second reactor to a level where there was no net make of 375°F$^+$ bottoms. Startup temperature was 65°C below base temperature (Figure 1). The temperature was then increased stepwise until the conversion to 375°F$^-$ distillate reached 100%. This level of conversion was attained at 1°C above base temperature (Figure 1). The run was on stream for 545 hours. Analyses of the products are in progress.

The hydrotreated H-Coal gas oils from Plant 859 (reported in FE-2566-08) were blended. Analysis showed a hydrogen content of 10.89 wt-%. Initial plan was to use this five gallons of liquid in a hydrocracking run to explore the feasibility of hydrocracking hydrotreated gas oil to gasoline. However, in view of this low hydrogen content (only 0.20% higher than the first-stage hydrocrackate 3531-5) it was decided not to carry out the exploratory hydrocracking run.

The Exxon Donor Solvent (EDS) process gas oil as received contained heptane insolubles ranging from 6.51 to 8.61 wt-% (Table 2). To be a suitable hydrocarbon feed these insolubles contents must normally be kept below 0.1%

In order to conserve the limited supply of charge stock, a short exploratory run was carried out in Plant 505 (Run 860) with a black oil hydrotreating catalyst to determine if the heptane insoluble content could be reduced to an acceptable level by hydrotreating instead of by flash distillation. Within

the range of conditions studied, all heptane insolubles were converted to distillate. The hydrotreatment also substantially lowered the nitrogen content. Results are summarized in Table 3. At near base pressure, base space velocity, and 10°C above base temperature, initial nitrogen conversion was essentially 100%. After 84 hours on stream (Period 5) conversion lined out at about 99.9%. The nitrogen content dropped from 4580 ppm to a level well below that required for a second-stage hydrocracking charge stock. The system appeared to be somewhat unstable when the pressure was lowered to 750 psig below base pressure.

Based on results obtained from these exploratory studies, a program for hydrotreating studies on EDS process gas oil has been scheduled for Plant 505. The primary objective of these studies is to investigate the effects of process variables, and to arrive at optimum conditions for preparing suitable feedstocks for subsequent hydrocracking. Studies are to be made at two pressures, three space velocities, and three temperatures.

The first series of experiments was carried out at 250 psig above base pressure, about 25°C above base temperature, and three space velocities. Data are summarized in Table 4. At 2 x base space velocity, nitrogen conversion lined out at about 99.5% after 52 hours on stream. At the lowest space velocity (Period 11-13), nitrogen conversion was practically complete. Near the end of this series of studies catalyst activity check tests were made at conditions similar to the initial conditions (Periods 2-7). A comparison of data from Periods 14-15 with those of Periods 2-7 shows that no significant deactivation occurred. The run is now continuing at lower temperatures.

Figure 2 is a semi-logarithmic plot of percentage residual nitrogen versus reciprocal reduced space velocity. Data from the following periods were used in

this figure: Periods 4-10 and 14-16.

Task 1

Work Forecast

Hydrotreating process variable studies on EDS process gas oil will continue into December. These studies should be completed by the middle of January, 1978.

All hydrocracking runs on H-Coal gas oil have been completed (see Figure 3). Preparation of the interim report will be under way when all required analyses of hydrocracked products have been completed.

Task 2

Work Accomplished

A preparative, H-Coal gas oil hydrotreating run (Plant 601, Run 760) was completed. Object was to process twelve gallons of gas oil and obtain a feedstock containing 10-11% hydrogen for FCC studies. Inspections of the charge stock are given in Table 5. A log of the hydrotreating operation is given in Table 6. The hydrotreated products were blended. Analysis shows this FCC feedstock to have a hydrogen content of 10.68%.

The second preparative hydrotreating run (Plant 638H, Run 17) on H-Coal gas oil has been started to prepare another FCC feedstock with 12-13% hydrogen. Data obtained to date are summarized in Table 7.

Task 2

Work Forecast

The second preparative H-Coal gas oil hydrotreating run will be completed in the first week of December.

Task 3

Status

All Platforming(R) runs on H-Coal process naphthas have been completed (Figure 3). All required mass spectroscopy analyses of the hydrocracked naphthas before and after Platforming(R) should be completed in the beginning of December. Preparation of the interim report will start thereafter.

Table 1

Inspections of First-Stage H-Coal Hydrocrackate 3531-14

Sample No.	3531-14
°API @ 60°F	15.0
Sp. Gr. @ 50°F	0.9659
Distillation, ASTM D-1160	
IBP, °F	377
5%	463
10%	484
20%	502
30%	519
40%	540
50%	560
60%	580
70%	607
80%	641
90%	685
95%	729
EP	790
% Over	99.0
% Bottoms	1.0
Hydrogen, Wt-%	10.49
Carbon, Wt-%	89.43
Sulfur, Wt-ppm	7.6
Nitrogen, Wt-ppm	619
Oxygen, Wt-ppm	1413
FIA, Vol-%	
A	81.5
P&N	18.5

Table 2

Inspections of Raw EDS Liquid Product

Drum No.	1	3	2
UOP Sample No.	3531-20	3531-21	3531-22
°API @ 60°F	7.9	8.0	8.0
SP. Gr. @ 60°F	1.0151	1.0143	1.0143
Distillation, ASTM D-1160			
IBP, °F	404	400	406
5%	422	426	423
10%	434	438	435
20%	458	457	458
30%	490	485	488
40%	535	520	526
50%	582	565	572
60%	642	623	632
70%	745	726	735
80%	845	830	840
90%	950	931	949
% Over	90.0	90.0	90.0
% Bottoms	10.0	10.0	10.0
Heptane Insolubles, Wt-%	6.54	8.61	8.11
882°F- Liquid			
Vol-%			86.7
Heptane Insolubles, Wt-%			1.75
Benzene Insolubles, Wt-%			0.01

Table 3

Hydrotreating Raw EDS Process Liquid Product(3531-22)
Plant 505, Run 860

Period No.	Hours on Stream	P-P(base), psig	LHSV / LHSV(base)	T-T(base), °C	Prod. N Content,ppm	N Conv., Wt-%
Feed					4580	
1	24-36	20	1.08	10	0.2	99.99
2	36-48	20	1.10	11	1.2	99.97
3	48-60	20	1.14	10	2.7	99.94
4	60-72	20	1.02	11	5.1	99.89
5	72.84	20	1.00	11	4.2	99.91
6	84.96	20	1.06	11	4.7	99.90
7	96-104	20	1.06	11	7.1	99.85
8	116-128	-750	1.00	12	13.5	99.71
9	128-140	-750	1.06	11	16.5	99.64
10	140-152	-750	1.00	11	17.7	99.61
11	152-164	-760	1.00	11	25.6	99.44
12	164-176	-750	1.14	11	32.0	99.30
13	176-188	-770	1.04	11	43.1	99.06
14	188-200	-770	1.12	11	-	-
15	212-244	-770	2.20	28	211.9	95.37
16	224-236	-760	2.00	30	-	-
17	236-248	-750	2.00	30	-	-
18	248-260	-750	2.00	29	393.8	91.40

Table 4

Hydrotreating Raw EDS Process Liquid Product (3531-22)
Plant 505, Run 861

Period No.	Hours on Stream	P-P(base), psig	LHSV / LHSV(base)	T-T(base), °C	Prod. N Content, ppm	N Conv., Wt-%
Feed					4580	
1	20-28	250	2.00	30	6.7	99.85
2	28-36	250	2.20	25	15.4	99.66
3	36-44	250	2.20	26	17.3	99.62
4	44-52	250	2.20	24	23.0	99.50
5	52-60	250	2.20	26	26.5	99.42
6	60-68	250	2.00	25	25.7	99.44
7	68-76	250	2.20	25	17.2	99.62
8	84-90	250	3.20	26	66.7	98.54
9	90-96	250	3.20	25	93.4	97.96
10	96-102	250	3.20	26	95.1	97.92
11	117-127	250	0.80	26	1.1	99.98
12	127-137	250	0.80	26	0.7	99.99
13	137-147	250	0.80	26	1.1	99.98
14	157-167	250	2.00	25	17.8	99.61
15	167-177	250	2.00	26	22.4	99.51
16	177-187	250	2.00	26	16.1	99.65

Table 5

Inspections of H-Coal Atmospheric Still Bottoms

	As Received		After Flash Distillation
HRI Sample No.	LO-585	LO-586	
UOP Sample No.	37-1118	37-1117	3531-11
°API @ 60°F	7.4	12.1	8.9
Sp. Gr @ 60°F	1.0187	0.9854	1.0078
Distillation, ASTM D-1160			
IBP, °F	412	410	415
5%	463	467	462
10%	485	474	490
20%	509	495	518
30%	530	519	538
40%	558	545	553
50%	580	566	571
60%	603	591	590
70%	631	621	615
80%	661	666	645
90%	715	710	689
95%	768	772	715
EP	857	855	769
% Over	99.0	99.0	99.0
% Bottoms	1.0	1.0	1.0
Hydrogen, Wt-%			9.14
Carbon, Wt-%			88.98
Sulfur, Wt-ppm	951	690	600
Nitrogen, Wt-ppm	3534	2066	4100
Oxygen, Wt-ppm	5006	5480	
Con. Carbon, Wt-%	0.41	0.49	<0.01
Heptane Insolubles, Wt-%	0.37	0.53	0.05
FIA, Vol-%			
A	90.9	83.7	90.2
O	0	0	-
P&N	9.1	16.3	9.8
Stm.Jet Gum, mg/100 ml	620	933	37

Table 6

Hydrotreating Rerun H-Coal Atmospheric Still Bottoms (3531-11)

Plant 601, Run 760

(Preparative Run)

P-P (base), psig: 500

Period No.	Hours on Stream	LHSV / LHSV(base)	T-T (base), °C	Product Analysis, Wt-% H	C
Feed				9.14	88.98
1	30-40	1.20	-39	10.80	88.51
2	40-50	1.20	-39	10.91	89.02
3	50-60	1.20	-39	11.00	89.20
4	60-70	1.20	-39	10.82	88.58
5	70-80	1.20	-39	11.01	88.68
6	80-90	1.21	-38	10.30	88.70
7	90-100	1.21	-39	10.72	89.03
8	100-110	1.20	-39	11.71	88.50
9	110-120	1.20	-39	10.60	89.04
10	120-130	1.18	-39	11.46	88.37
11	130-140	1.22	-39	10.79	88.87
12	140-150	1.24	-39	10.69	89.40
13	150-160	1.21	-40	10.76	89.05
14	160-170	1.18	-38	10.84	89.28
15	170-180	1.18	-41	10.73	88.53
16	180-190	1.21	-38	10.33	89.15
17	190-200	1.22	-38	10.72	88.98
18	200-210	1.24	-40	10.33	88.37
19	210-220	1.20	-39	10.68	89.16
20	220-230	1.20	-40	10.60	89.28
21	230-240	1.18	-39	10.79	89.45
22	240-250	1.19	-39	10.29	89.65
23	250-260	1.19	-41	10.94	88.34
24	260-270	1.19	-41	10.79	89.53
25	270-280	1.23	-40	10.63	89.70
26	280-290	1.19	-38	10.66	89.57
27	290-300	1.21	-38	10.35	89.32

Table 7

Hydrotreating Rerun H-Coal Atmospheric Still Bottoms (3531-11)
Plant 638H, Run 17

(Preparative Run No. 2)

P-P (base), psig: 500

Period No.	Hours on Stream	LHSV / LHSV(base)	T-T(base), °C	Product Analysis, Wt-% H[(a)]	C
Feed				9.14	88.98
1	12-24	0.41	1	12.30	88.21
2	24-36	0.40	1	-	-
3	44-56	0.40	22	11.93	87.20
4	56-68	0.40	21	11.74	87.67
5	68-80	0.39	21	12.08	87.90
6	80-92	0.40	21	12.00	87.72
7	92-104	0.39	22	12.01	87.71
8	104-116	0.39	22	11.89	88.81
9	116-128	0.40	21	11.94	87.56
10	128-135	0.38	22	12.13	87.98
11	147-159	0.30	21		
12	159-171	0.30	23	12.03	87.36
13	171-183	0.30	21	12.33	87.82
14	183-195	0.30	23	12.47	87.11
15	195-207	0.30	23	12.74	87.88
16	207-219	0.30	24	12.82	86.97
17	219-231	0.29	21	12.60	87.78
18	231-243	0.30	23		
19	243-255	0.30	23	12.81	87.56
20	255-267	0.30	23	12.56	87.31
21	267-279	0.29	22	12.71	87.68
22	279-291	0.30	21	12.89	86.40
23	291-303	0.30	22	13.06	86.86
24	303-315	0.30	23	13.36	86.50
25	315-327	0.30	21	13.35	86.37
26	327-339	0.30	21	13.67	86.78

(a) Products which contain less than 12% H are to be reprocessed.

Figure 1

Temperature vs. Time

Series Flow Second-Stage Hydrocracking of H-Coal Gas Oil to Gasoline

Plant 536, Run 678 (Second Reactor)

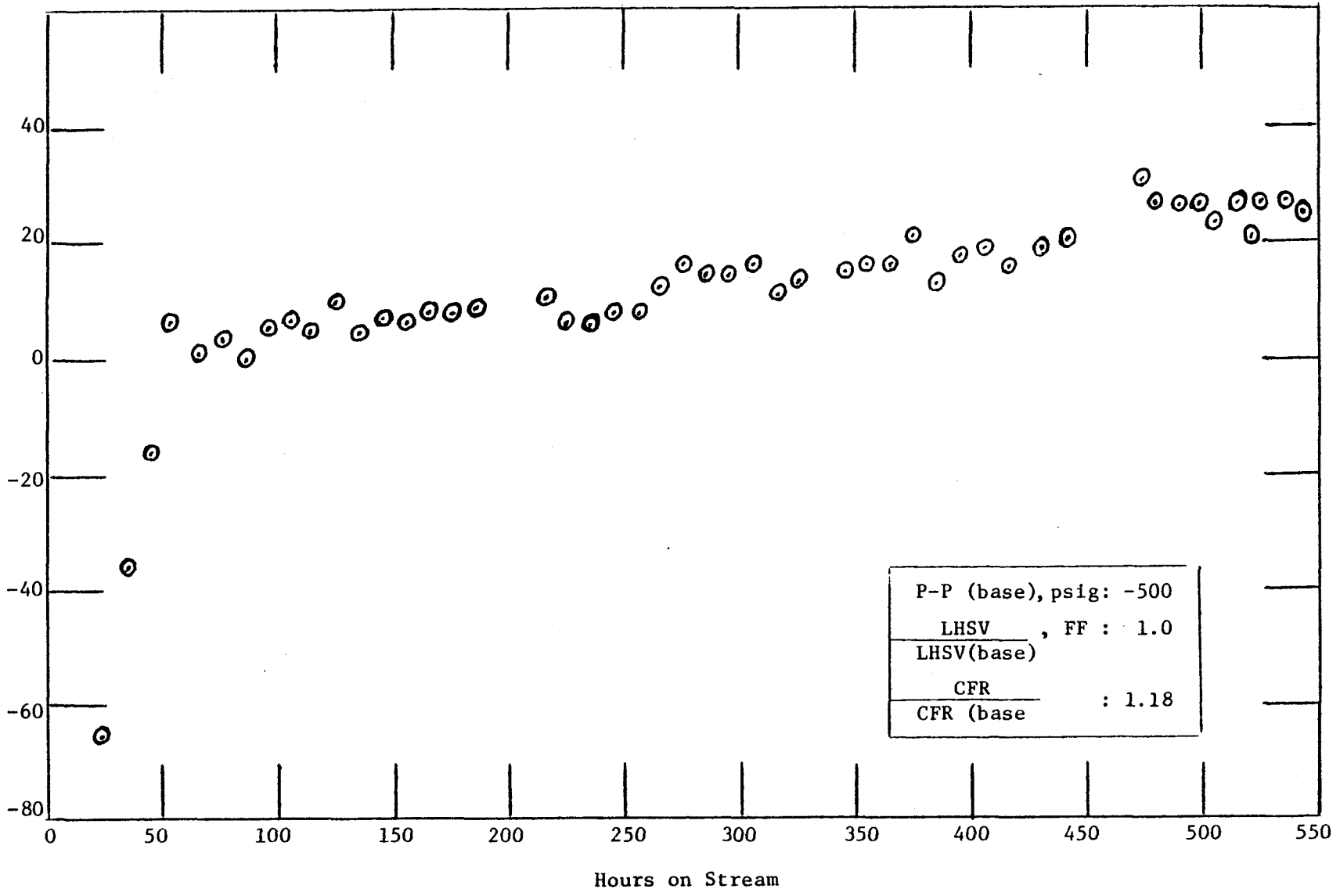


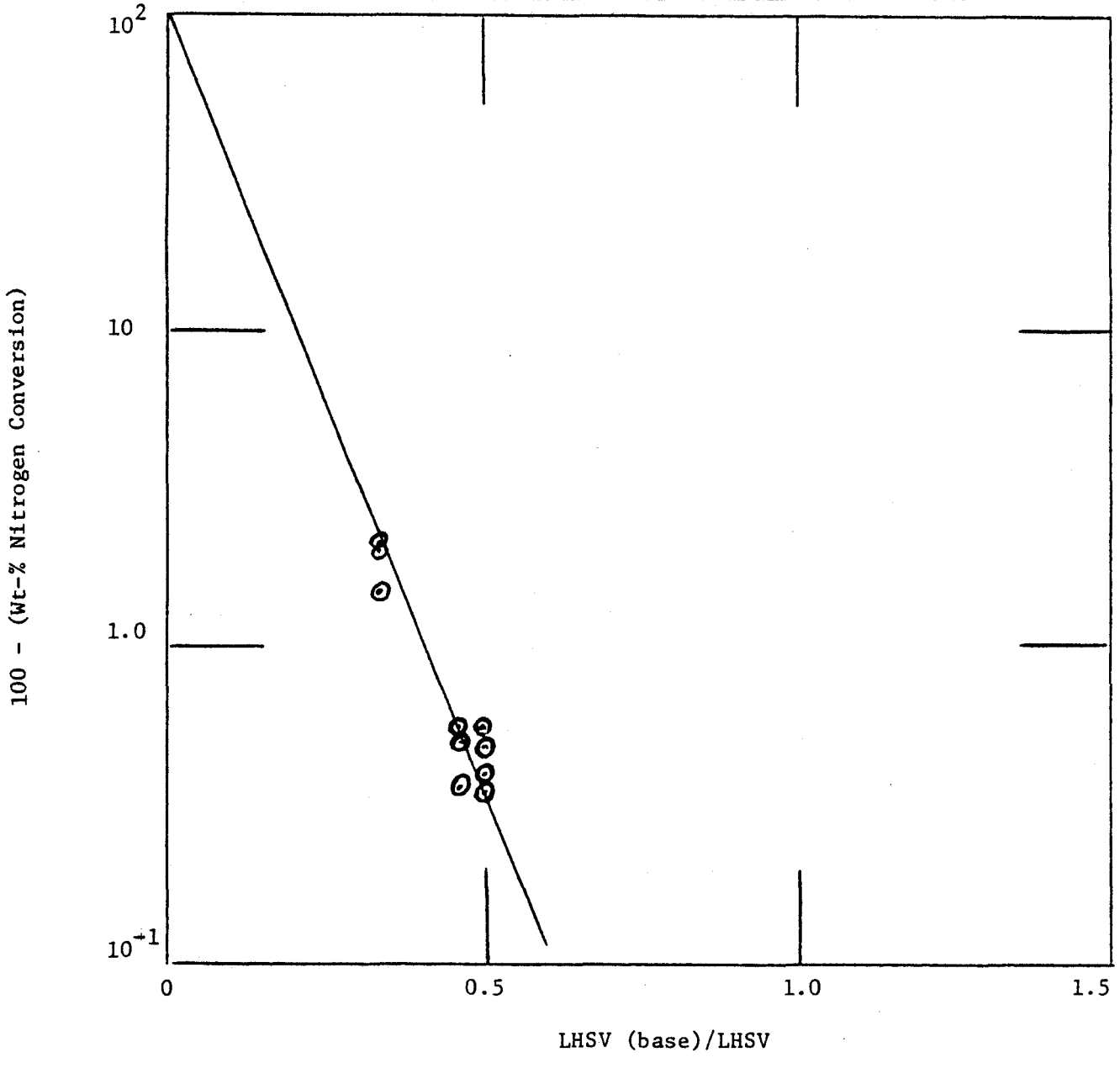
Figure 2

Percentage Residual Nitrogen vs. Reciprocal ReducedSpace Velocity

Hydrotreating Raw EDS Liquid Product (3531-22)

Plant 505, Run 861

P-P (base), psig: 250; T-T (base), °C: 24/26



r. rerunning
p.v. process variable study
prep. preparative run
U Unifining
P Platforming

Figure 3

Work Plan and Progress

Legend

--- H-Coal Liquids
--- EDS Liquids
Scheduled
Completed