Fig. 30

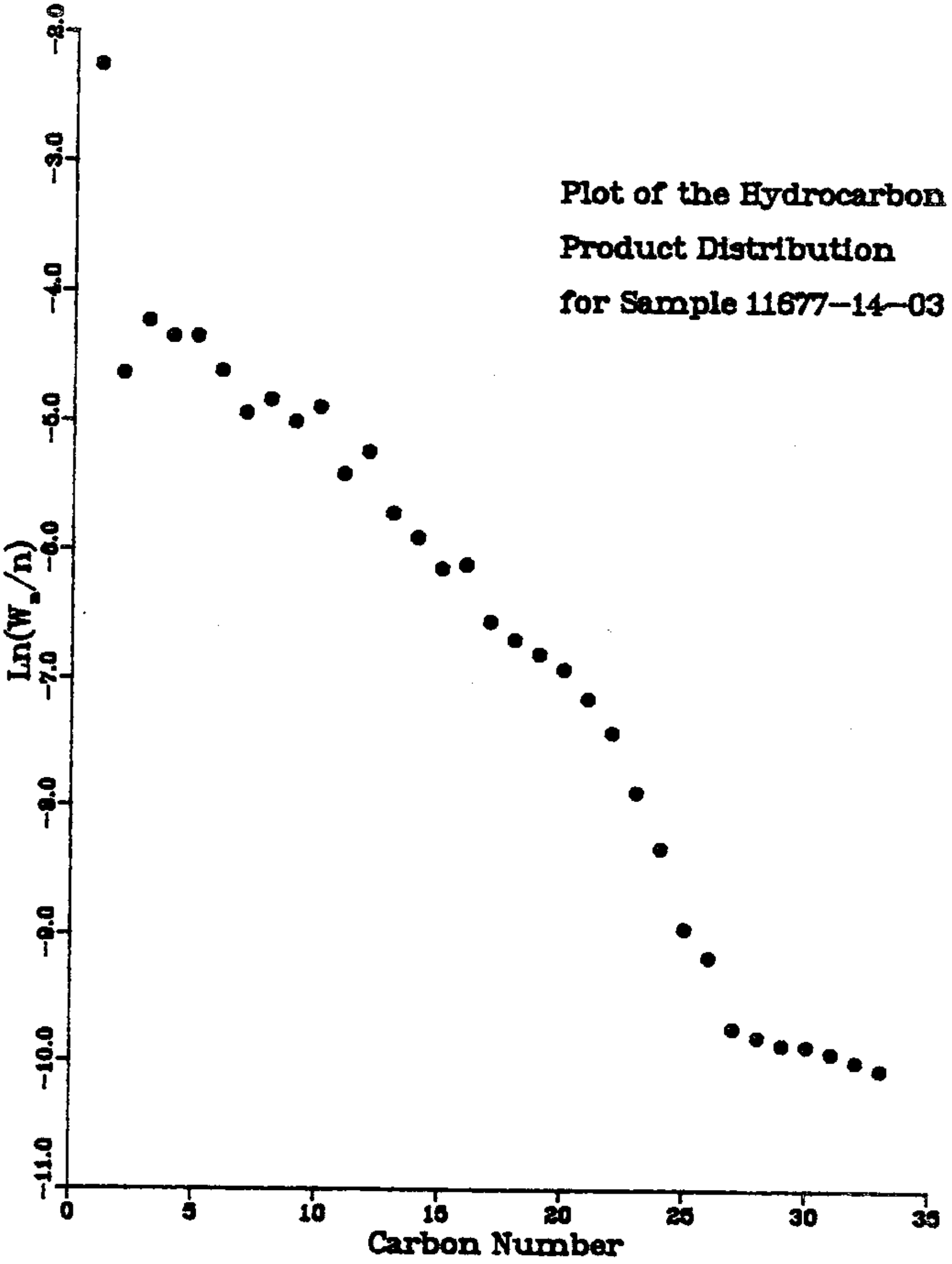
Plot of the Hydrocarbon
Product Distribution
for Sample 11677-14-03
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 31

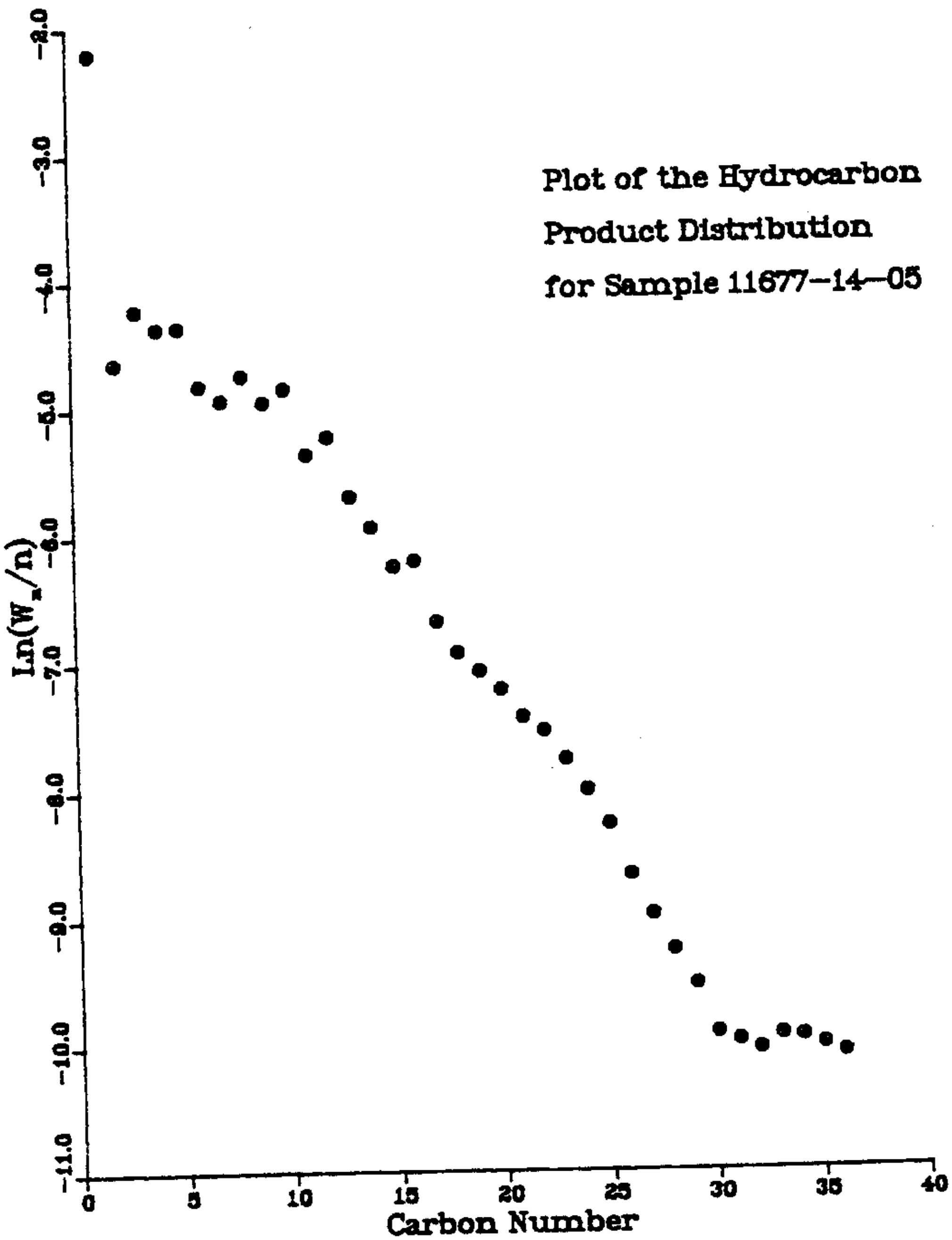
Plot of the Hydrocarbon
Product Distribution
for Sample 11677-14-05
Ln(W$_x$/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 32

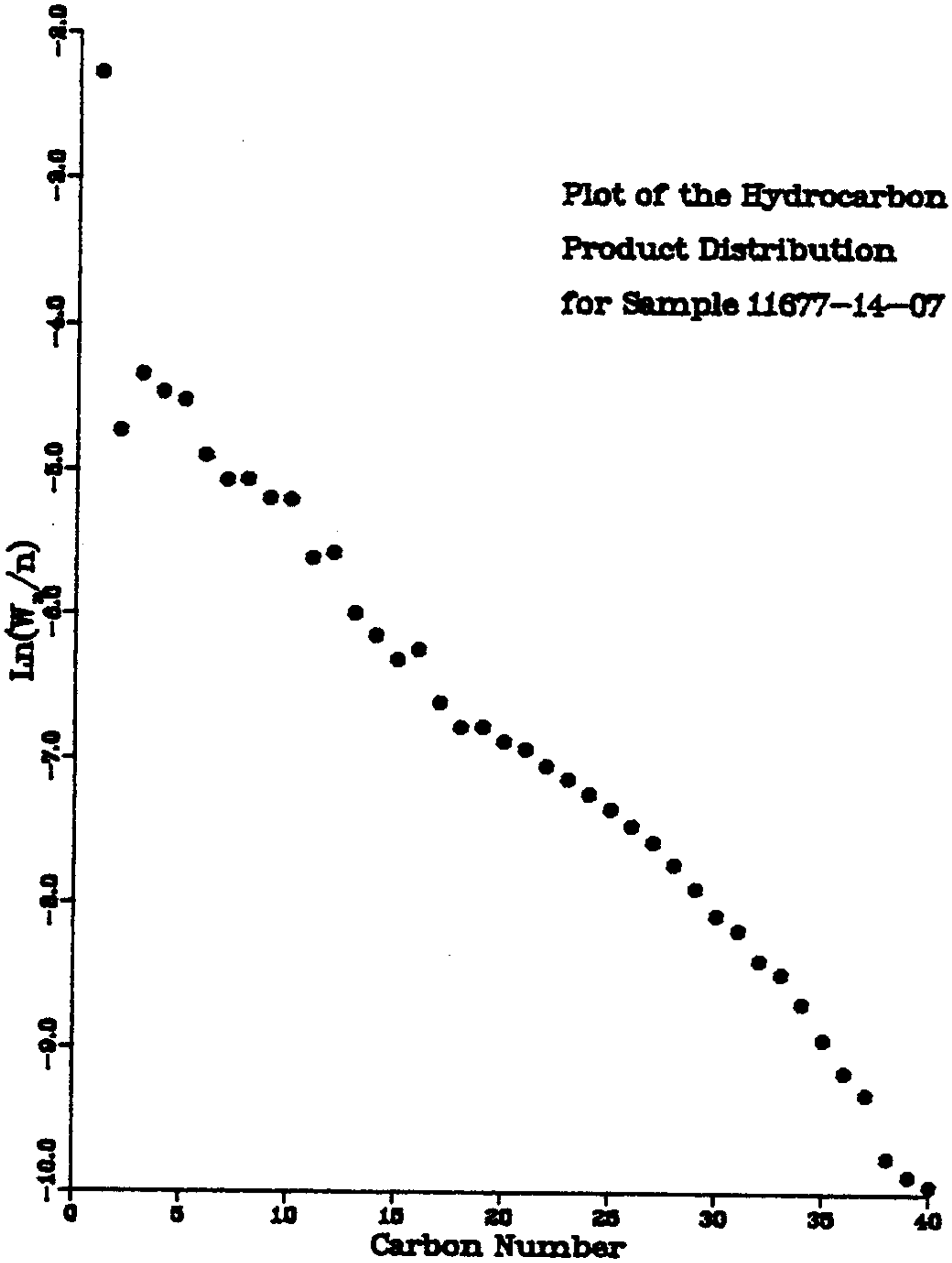
Plot of the Hydrocarbon
Product Distribution
for Sample 11677-14-07
Ln(W$_n$/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Table 5

## RESULT OF SYNGAS OPERATION

RUN NO. 11677-14
CATALYST HiCoThU103+U101 11684-70C 66 CC 26.5GM (31.8 AFTER RUN +5.3G)
FEED H2:CO:ARGON OF 50:50:0 @ 330 CC/MN OR 300 GHSV

| RUN & SAMPLE NO. | 11677-14-01 | 677-14-02 | 677-14-03 | 677-14-04 | 677-14-05 |
|---|---|---|---|---|---|
| FEED H2:CO:AR | 50:50: 0 | 50:50: 0 | 50:50: 0 | 50:50: 0 | 50:50: 0 |
| HRS ON STREAM | 19.5 | 26.0 | 44.0 | 49.5 | 68.5 |
| PRESSURE,PSIG | 299 | 303 | 299 | 304 | 303 |
| TEMP. C | 260 | 259 | 259 | 260 | 259 |
| FEED CC/MIN | 330 | 330 | 330 | 330 | 330 |
| HOURS FEEDING | 19.50 | 6.50 | 24.50 | 5.50 | 24.50 |
| EFFLNT GAS LITER | 122.45 | 45.70 | 179.75 | 42.50 | 194.60 |
| GM AQUEOUS LAYER | 51.39 | 17.09 | 64.41 | 14.00 | 62.37 |
| GM OIL | 19.28 | 6.92 | 26.08 | 5.53 | 24.62 |
| MATERIAL BALANCE | | | | | |
| GM ATOM CARBON % | 77.17 | 84.75 | 86.85 | 89.06 | 86.99 |
| GM ATOM HYDROGEN % | 81.45 | 86.43 | 88.97 | 89.16 | 91.52 |
| GM ATOM OXYGEN % | 88.64 | 93.70 | 94.49 | 96.01 | 94.50 |
| RATIO CHX/(H2O+CO2) | 0.7232 | 0.7843 | 0.8136 | 0.8270 | 0.8108 |
| RATIO X IN CHX | 2.2904 | 2.2963 | 2.3091 | 2.3259 | 2.3237 |
| USAGE H2/CO PRODT | 2.0825 | 2.0243 | 2.0421 | 2.0109 | 2.0648 |
| FEED H2/CO FRM EFFLNT | 1.0555 | 1.0198 | 1.0244 | 1.0012 | 1.0520 |
| RESIDUAL H2/CO RATIO | 0.2335 | 0.2486 | 0.2663 | 0.2773 | 0.3491 |
| RATIO CO2/(H2O+CO2) | 0.1045 | 0.1034 | 0.0913 | 0.0992 | 0.0874 |
| K SHIFT IN EFFLNT | 0.0273 | 0.0287 | 0.0268 | 0.0305 | 0.0334 |
| SPECIFIC ACTIVITY SA | 6.8252 | 6.1339 | 5.6323 | 4.7041 | 3.4957 |
| CONVERSION | | | | | |
| ON CO % | 44.45 | 43.43 | 42.69 | 41.76 | 40.97 |
| ON H2 % | 87.71 | 86.21 | 85.10 | 83.87 | 80.41 |
| ON CO+H2 % | 66.66 | 65.03 | 64.15 | 62.83 | 61.19 |
| PRDT SELECTIVITY,WT % | | | | | |
| CH4 | 9.56 | 9.77 | 10.44 | 11.36 | 11.07 |
| C2 HC'S | 1.67 | 1.82 | 1.95 | 2.00 | 1.93 |
| C3H8 | 2.07 | 2.18 | 2.30 | 2.46 | 2.53 |
| C3H6= | 2.14 | 2.01 | 2.06 | 2.10 | 1.87 |
| C4H10 | 1.67 | 1.71 | 1.79 | 1.96 | 1.97 |
| C4H8= | 3.41 | 3.44 | 3.36 | 3.58 | 3.14 |
| C5H12 | 1.98 | 2.11 | 2.11 | 2.28 | 2.32 |
| C5H10= | 4.38 | 4.25 | 4.35 | 4.41 | 4.10 |
| C6H14 | 2.27 | 2.21 | 2.33 | 2.36 | 2.51 |
| C6H12= & CYCLO'S | 3.76 | 3.66 | 3.59 | 3.73 | 2.34 |
| C7+ IN GAS | 10.54 | 10.76 | 11.05 | 11.93 | 12.79 |
| LIQ HC'S | 56.55 | 56.09 | 54.67 | 51.83 | 53.42 |
| TOTAL | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Table 5 (continued)

| | | | | | |
|---|---|---|---|---|---|
| SUB-GROUPING | | | | | |
| C1 -C4 | 20.52 | 20.92 | 21.90 | 23.46 | 22.52 |
| C5 -420 F | 50.72 | 48.65 | 48.45 | 49.23 | 49.30 |
| 420-700 F | 25.55 | 27.56 | 26.86 | 23.06 | 23.79 |
| 700-END PT | 3.21 | 2.87 | 2.79 | 4.26 | 4.39 |
| C5+-END PT | 79.48 | 79.08 | 78.10 | 76.54 | 77.48 |
| ISO/NORMAL MOLE RATIO | | | | | |
| C4 | 0.1119 | 0.0882 | 0.0694 | 0.0694 | 0.0622 |
| C5 | 0.1666 | 0.1532 | 0.1204 | 0.1217 | 0.1114 |
| C6 | 0.3604 | 0.2526 | 0.2427 | 0.2059 | 0.2087 |
| C4= | 0.0569 | 0.0573 | 0.0572 | 0.0601 | 0.0601 |
| PARAFFIN/OLEFIN RATIO | | | | | |
| C3 | 0.9246 | 1.0350 | 1.0649 | 1.1178 | 1.2895 |
| C4 | 0.4727 | 0.4785 | 0.5158 | 0.5271 | 0.6057 |
| C5 | 0.4399 | 0.4828 | 0.4713 | 0.5025 | 0.5513 |
| SCHULZ-FLORY DISTRBTN | | | | | |
| ALPHA (EXP(SLOPE)) | 0.8090 | | 0.8115 | | 0.8246 |
| RATIO CH4/(1-A)**2 | 2.6217 | | 2.9395 | | 3.5975 |
| LIQ HC COLLECTION | | | | | |
| PHYS. APPEARANCE | CLDY | | CLR OIL | | OIL/SLD |
| DENSITY | 0.7562 | | 0.7553 | | 0.7621 |
| N, REFRACTIVE INDEX | 1.4276 | | 1.4276 | | 1.4276 |
| SIMULT'D DISTILATN | | | | | |
| 10 WT % @ DEG F | 263 | | 278 | | 281 |
| 16 | 302 | | 304 | | 304 |
| 50 | 426 | | 444 | | 437 |
| 84 | 599 | | 618 | | 627 |
| 90 | 648 | | 657 | | 681 |
| RANGE(16-84 %) | 297 | | 314 | | 323 |
| WT % @ 420 F | 49.14 | 45.75 | 45.75 | 47.25 | 47.25 |
| WT % @ 700 F | 94.33 | 94.89 | 94.89 | 91.78 | 91.78 |

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Table 6

## RESULT OF SYNGAS OPERATION

RUN NO. 11677-14
CATALYST HiCoThU103+U101 11684-70C 66 CC 26.5GM (31.8 AFTER RUN +5.3G)
FEED H2:CO:ARGON OF 50:50:0 @ 330 CC/MN OR 300 GHSV

| RUN & SAMPLE NO. | 11677-14-06 | 677-14-07 |
|---|---|---|
| FEED H2:CO:AR | 50:50: 0 | 50:50: 0 |
| HRS ON STREAM | 73.0 | 91.5 |
| PRESSURE,PSIG | 305 | 301 |
| TEMP. C | 260 | 260 |
| FEED CC/MIN | 330 | 330 |
| HOURS FEEDING | 4.50 | 23.00 |
| EFFLNT GAS LITER | 38.15 | 202.70 |
| GM AQUEOUS LAYER | 10.70 | 54.73 |
| GM OIL | 6.75 | 34.48 |
| MATERIAL BALANCE | | |
| GM ATOM CARBON % | 98.65 | 104.67 |
| GM ATOM HYDROGEN % | 101.82 | 101.181 |
| GM ATOM OXYGEN % | 95.05 | 99.83 |
| RATIO CHX/(H2O+CO2) | 1.0951 | 1.1289 |
| RATIO X IN CHX | 2.2866 | 2.3089 |
| USAGE H2/CO PRODT | 1.8025 | 1.8115 |
| FEED H2/CO FRM EFFLNT | 1.0322 | 0.9666 |
| RESIDUAL H2/CO RATIO | 0.3830 | 0.3078 |
| RATIO CO2/(H2O+CO2) | 0.0992 | 0.0918 |
| K SHIFT IN EFFLNT | 0.0422 | 0.0311 |
| SPECIFIC ACTIVITY SA | 3.3850 | 4.4495 |
| CONVERSION | | |
| ON CO % | 45.73 | 43.81 |
| ON H2 % | 79.87 | 82.11 |
| ON CO+H2 % | 63.07 | 62.64 |
| PRDT SELECTIVITY,WT % | | |
| CH4 | 9.10 | 10.29 |
| C2 HC'S | 1.50 | 1.77 |
| C3H8 | 2.10 | 2.16 |
| C3H6= | 1.44 | 1.76 |
| C4H10 | 1.62 | 1.68 |
| C4H8= | 2.51 | 2.95 |
| C5H12 | 1.97 | 1.97 |
| C5H10= | 3.10 | 3.49 |
| C6H14 | 1.97 | 1.96 |
| C6H12= & CYCLO'S | 2.42 | 2.52 |
| C7+ IN GAS | 10.10 | 8.93 |
| LIQ HC'S | 62.17 | 60.52 |
| TOTAL | 100.00 | 100.00 |

Table 6 (continued)

| | | |
|---|---|---|
| SUB-GROUPING | | |
| C1 -C4 | 18.27 | 20.60 |
| C5 -420 F | 39.62 | 38.41 |
| 420-700 F | 25.51 | 24.83 |
| 700-END PT | 16.60 | 16.16 |
| C5+-END PT | 81.73 | 79.40 |
| ISO/NORMAL MOLE RATIO | | |
| C4 | 0.0634 | 0.0579 |
| C5 | 0.1097 | 0.1005 |
| C6 | 0.1877 | 0.1685 |
| C4= | 0.0624 | 0.0613 |
| PARAFFIN/OLEFIN RATIO | | |
| C3 | 1.3889 | 1.1740 |
| C4 | 0.6221 | 0.5505 |
| C5 | 0.6175 | 0.5496 |
| SCHULZ-FLORY DISTRBTN | | |
| ALPHA (EXP(SLOPE)) | 0.8646 | 0.8748 |
| RATIO CH4/(1-A)**2 | 4.9661 | 6.5581 |
| LIQ HC COLLECTION | | |
| PHYS. APPEARANCE | | OIL/SLD |
| DENSITY | | 0.7649 |
| N, REFRACTIVE INDEX | | SOLIDIF'D |
| SIMULT'D DISTILATN | | |
| 10 WT % @ DEG F | | 300 |
| 16 | | 337 |
| 50 | | 540 |
| 84 | | 776 |
| 90 | | 828 |
| RANGE(16-84 %) | | 439 |
| WT % @ 420 F | 32.27 | 32.27 |
| WT % @ 700 F | 73.30 | 73.30 |

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IV. <u>Run 3 (11723-14) with Catalyst 3 (Co/Th/UCC-101+UCC-101)</u>

This catalyst is similar to Catalyst 1, except that UCC-101 is used in place of the intimately mixed UCC-103, resulting in a formulation that has UCC-101 present as both intimately and physically mixed components. It is similar also to Catalyst 1 of the Third Annual Report, except with a larger proportion of UCC-101. The final cobalt content was approximately 8.3 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the $C_4$'s are plotted against time on stream in Figs. 33-36. Simulated distillations of the $C_5^+$ product are plotted in Figs. 37-42. Carbon number product distributions are plotted in Figs. 43-54. Chromatograms from simulated distillations are reproduced in Figs. 55-65. Detailed material balances appear in Tables 7-10.

Throughout the 260 hour run the conversion of syngas fell off slowly and steadily. The rate of deactivation, one percent every 36 hours, was two-thirds that of Catalyst 1 in this Report and almost exactly the same as that of Catalyst 1 in the Third Annual Report, but higher than that of the $X_4$-containing Catalyst 6 of the Third Annaual Report. The usage ratio was high, more than 2:1, showing very little water gas shift activity. In this catalyst the cobalt was not used as effectively as in Catalyst 1; the level of cobalt loading was the same in both catalysts but the specific activity of this catalyst was lower.

The selectivity, although not as good initially as that of Catalyst 1, deactivated more slowly; by about 150 hours on stream the two patterns were essentially the same. From an initial level of 13.1 percent, the production of methane increased at the rate of one percent every 72 hours to 16.7 percent at 260 hours on stream. This was accompanied by the customary decrease in production of $C_5^+$ but at a lower rate than usual, resulting in a declining output of $C_2$-$C_4$ over time. The yield of motor fuels, about 69 percent initially, fell off at the rate of one percent every 70 hours. Gasoline production, which fell at one percent every 39 hours, was partially offset by an increase in the yield of diesel fuel at one percent every 87 hours, resulting in an increasing ratio of diesel to gasoline with time on stream.

The products were considerably olefinic, with about 70 percent of the $C_4$'s in the form of butenes, and more highly isomerized than with most catalysts which contain UCC-103. Catalyst 1 of the Third Annual Report, which also contained UCC-101 in place of UCC-103, likewise yielded more highly isomerized pentanes than did the UCC-103 catalysts. Isomerization of the pentane is confirmed both in the liquid product and in the chromatograms from the simulated distillations; with time on stream, however, it decreased ultimately to its usual low level. Except for the excess of methane, plots of the carbon number product distributions follow the typical Schulz-Flory pattern.

While this is by no means the most stable catalyst yet tested, its slow, steady deactivation rate is nevertheless remarkable for the low ratios of hydrogen to carbon monoxide in the syngas to which it was exposed. It was active initially in a syngas with $H_2$:CO ratio of only 0.28:1, and although the ratio increased steadily, by the end of the run it still did not exceed 0.4:1. These are very low-hydrogen environments for the maintenance of catalytic activity; usually in such an environment a Fischer-Tropsch catalyst will rapidly coke and deactivate.

Fig. 33

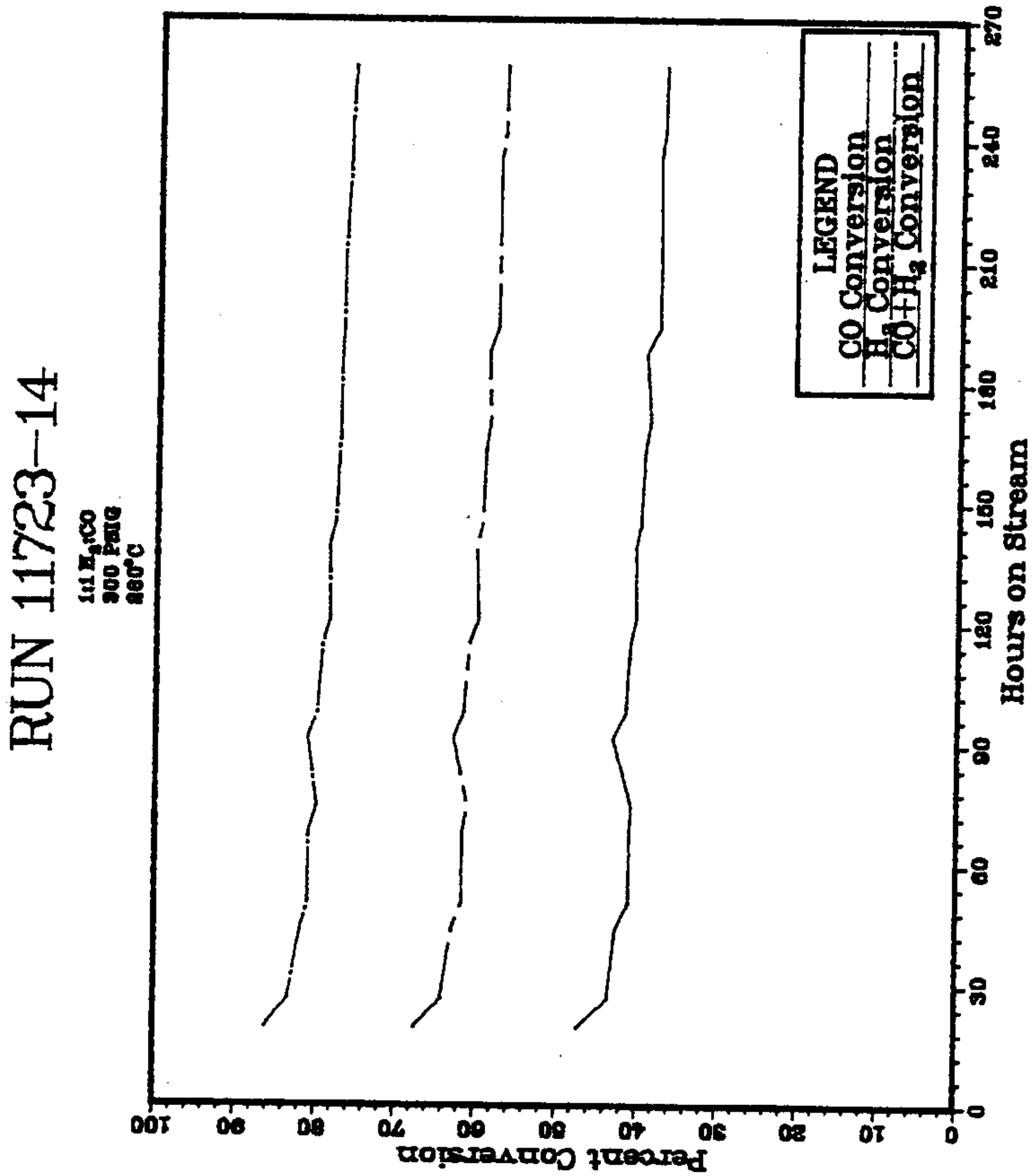

RUN 11723–14
LEGEND
CO Conversion
$H_2$ Conversion
$CO+H_2$ Conversion
Hours on Stream
Percent Conversion
0 30 60 90 120 150 180 210 240 270
0 10 20 30 40 50 60 70 80 90 100

Fig. 34

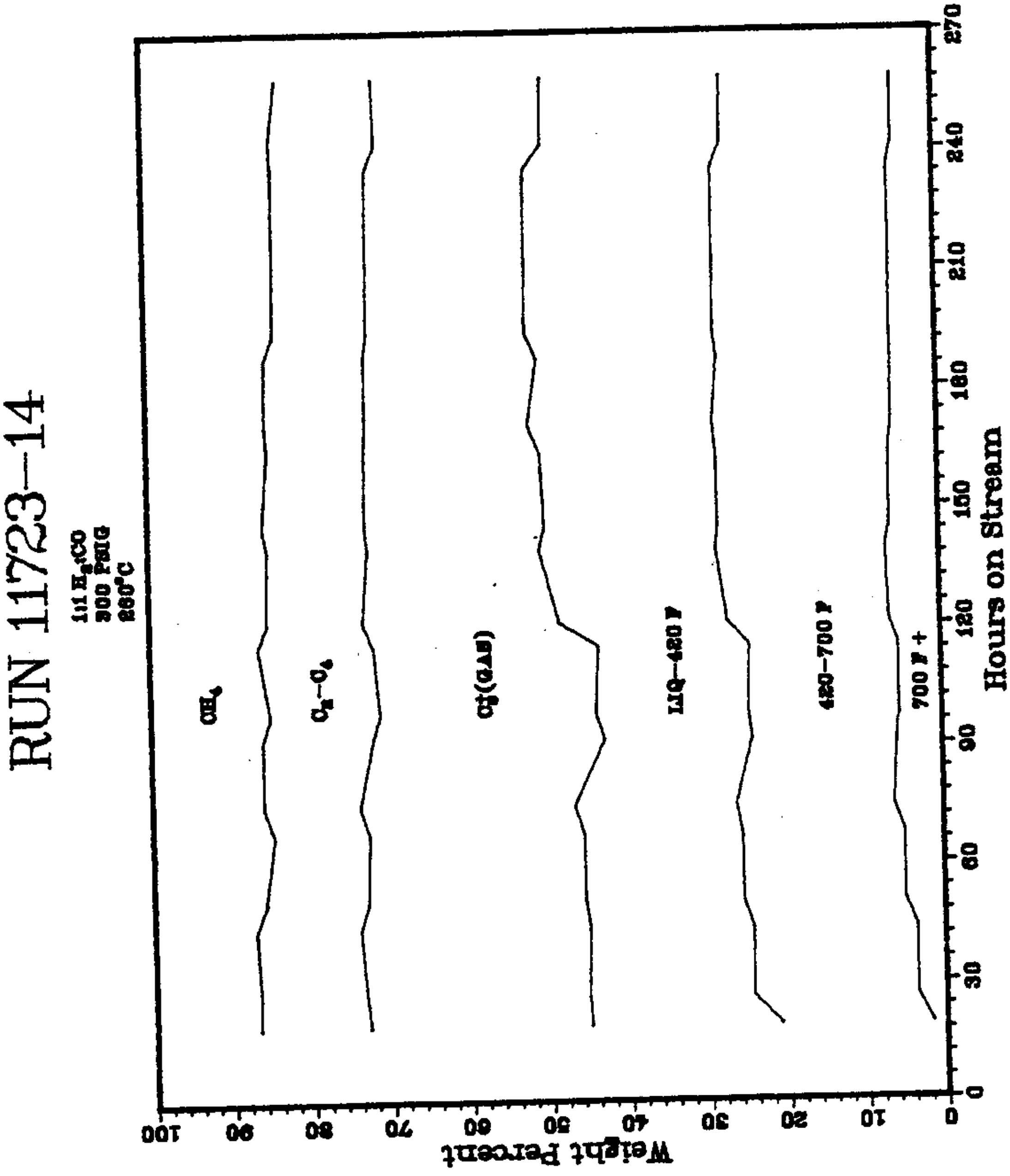

RUN 11723—14
1:1 H2:CO
300 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
Weight Percent
0
30
60
90
120
150
180
210
240
270
0
10
20
30
40
50
60
70
80
90
100

Fig. 35

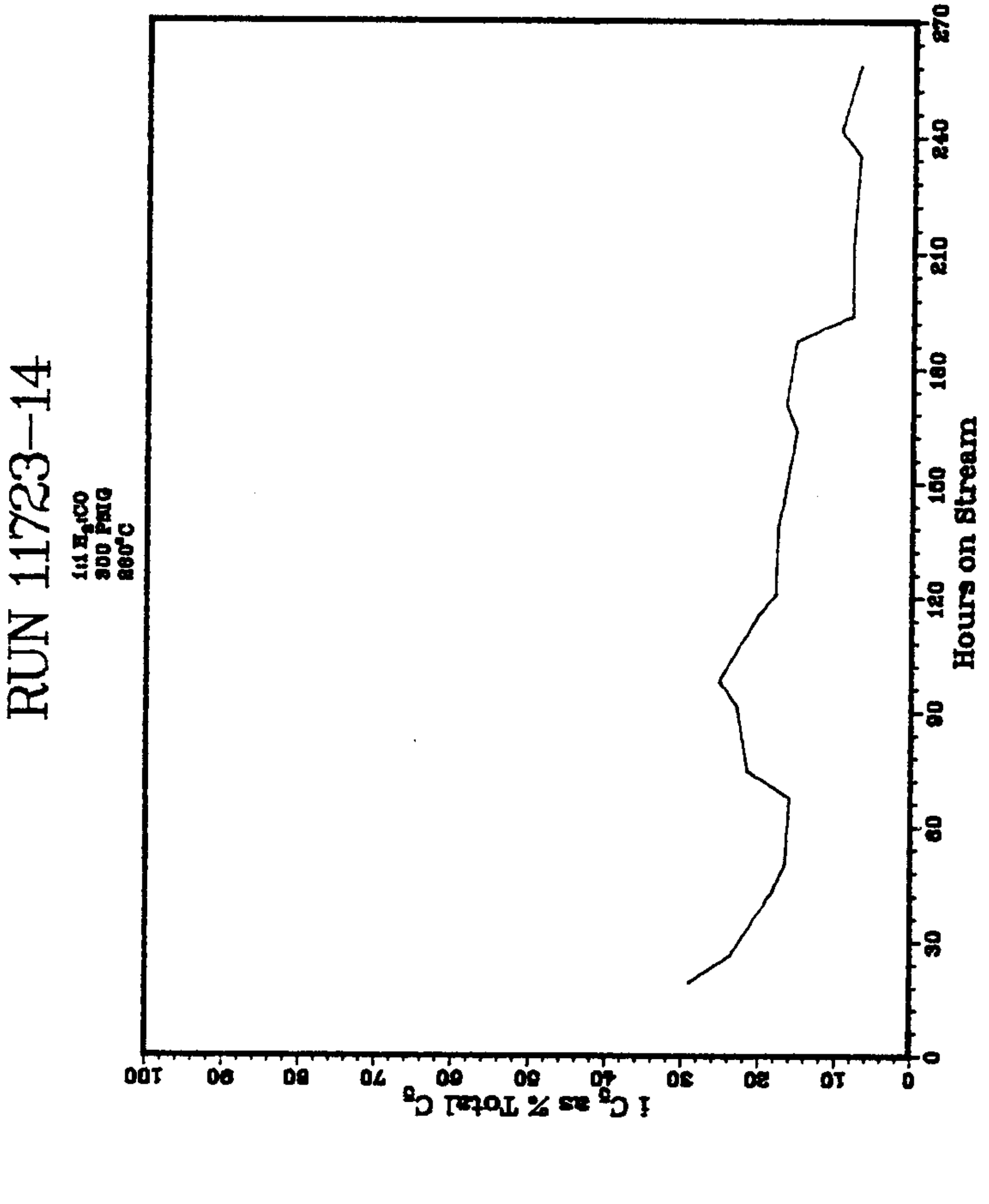
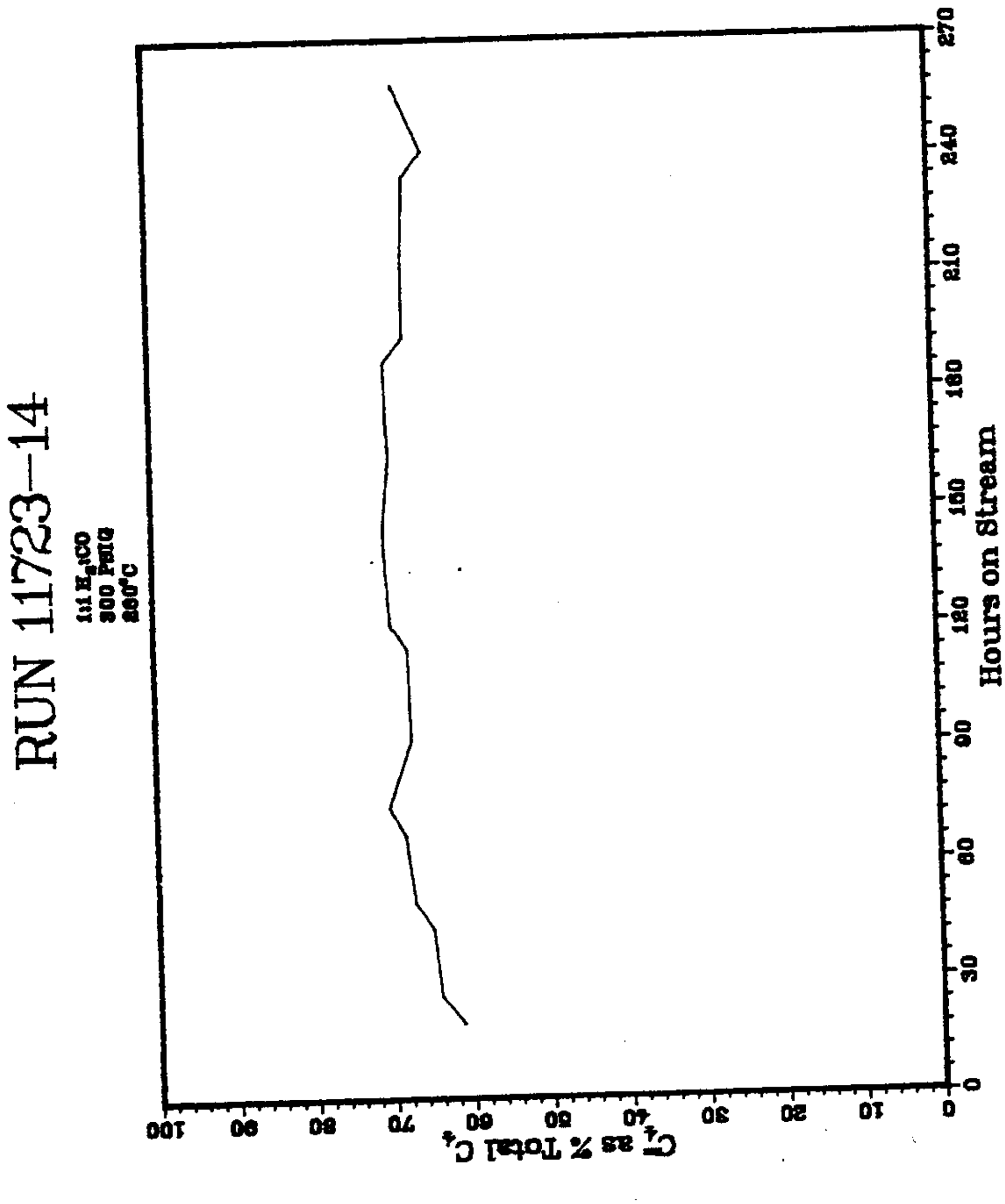
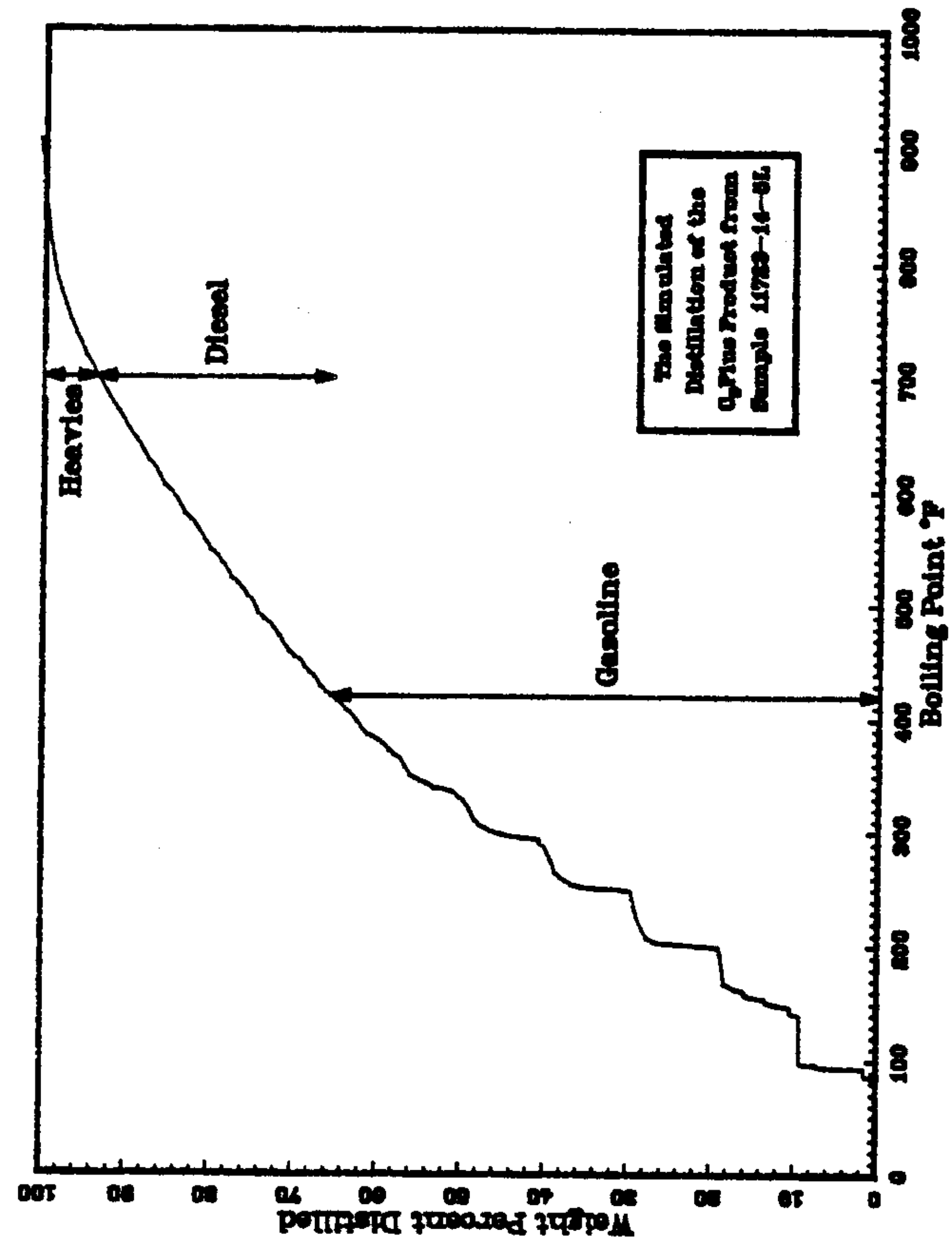

RUN 11723-14
Hours on Stream
0
30
60
90
120
150
180
210
240
270
10
20
30
40
50
60
70
80
90
100

Fig. 36



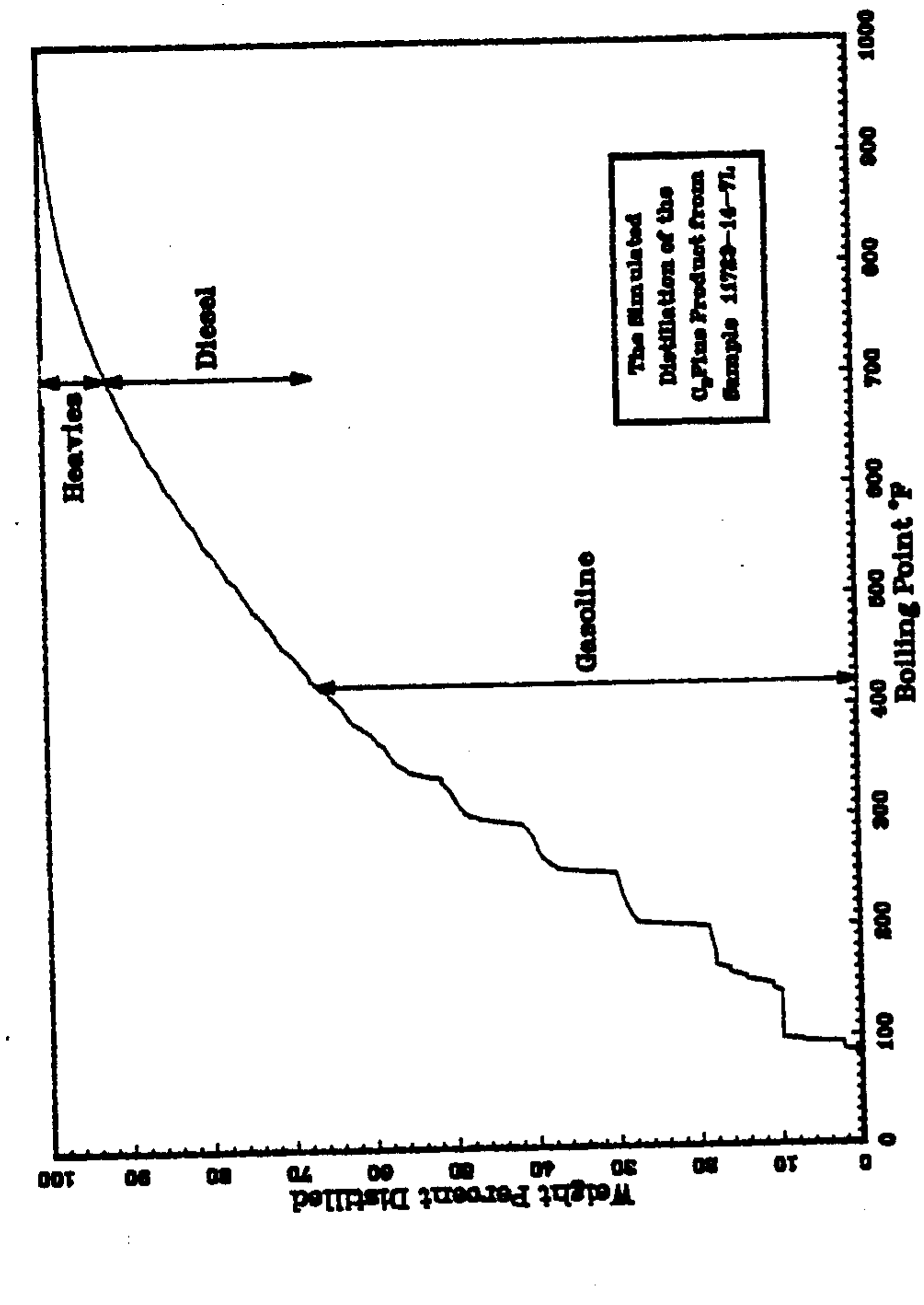
RUN 11723—14
1:1 H2:CO
300 PSIG
260°C
Hours on Stream
C4= as % Total C4
0
30
60
90
120
150
180
210
240
270
0
10
20
30
40
50
60
70
80
90
100

Fig. 37



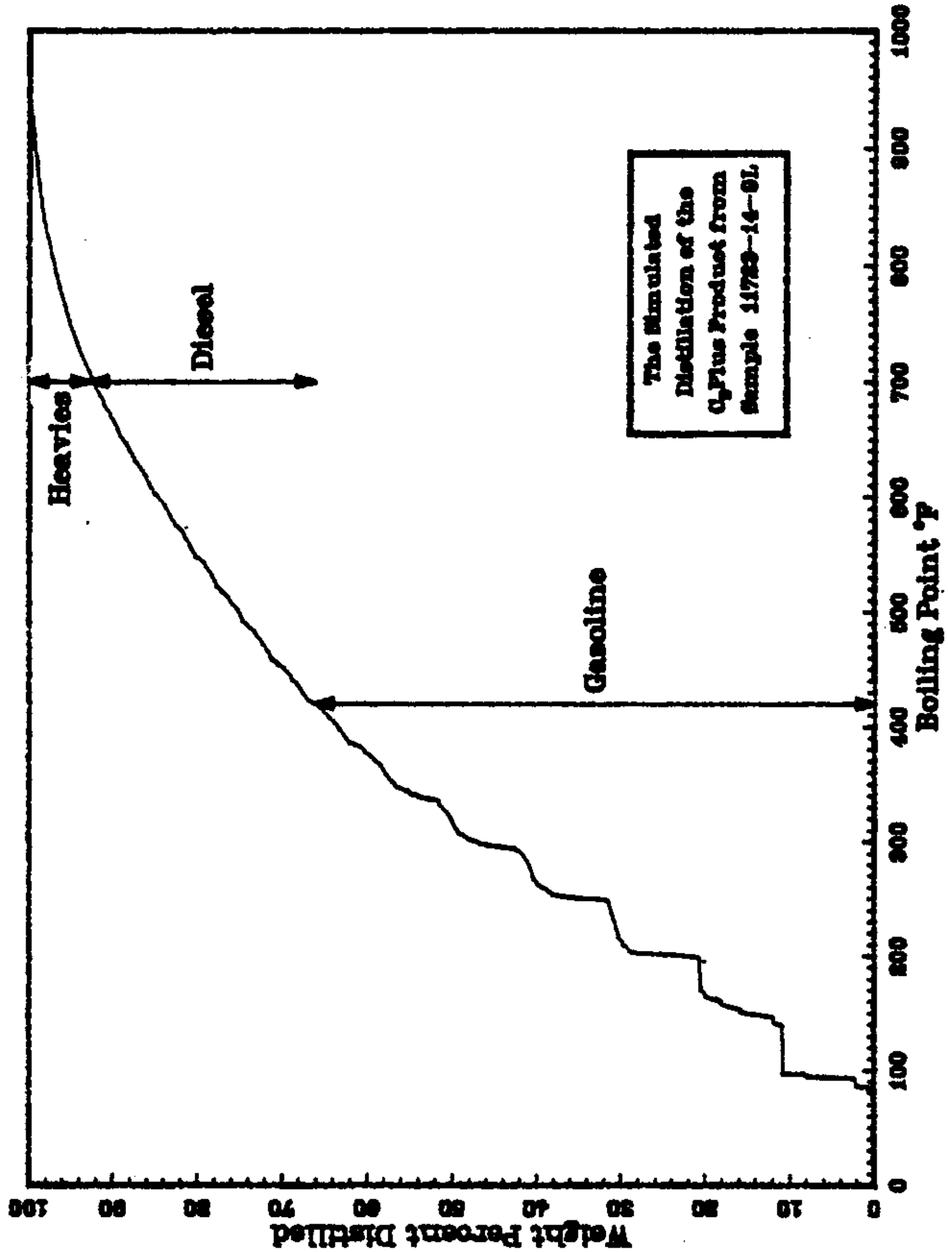
Heavies
Diesel
Gasoline
The Simulated
Distillation of the
Boiling Point °F
Weight Percent Distilled

Fig. 38



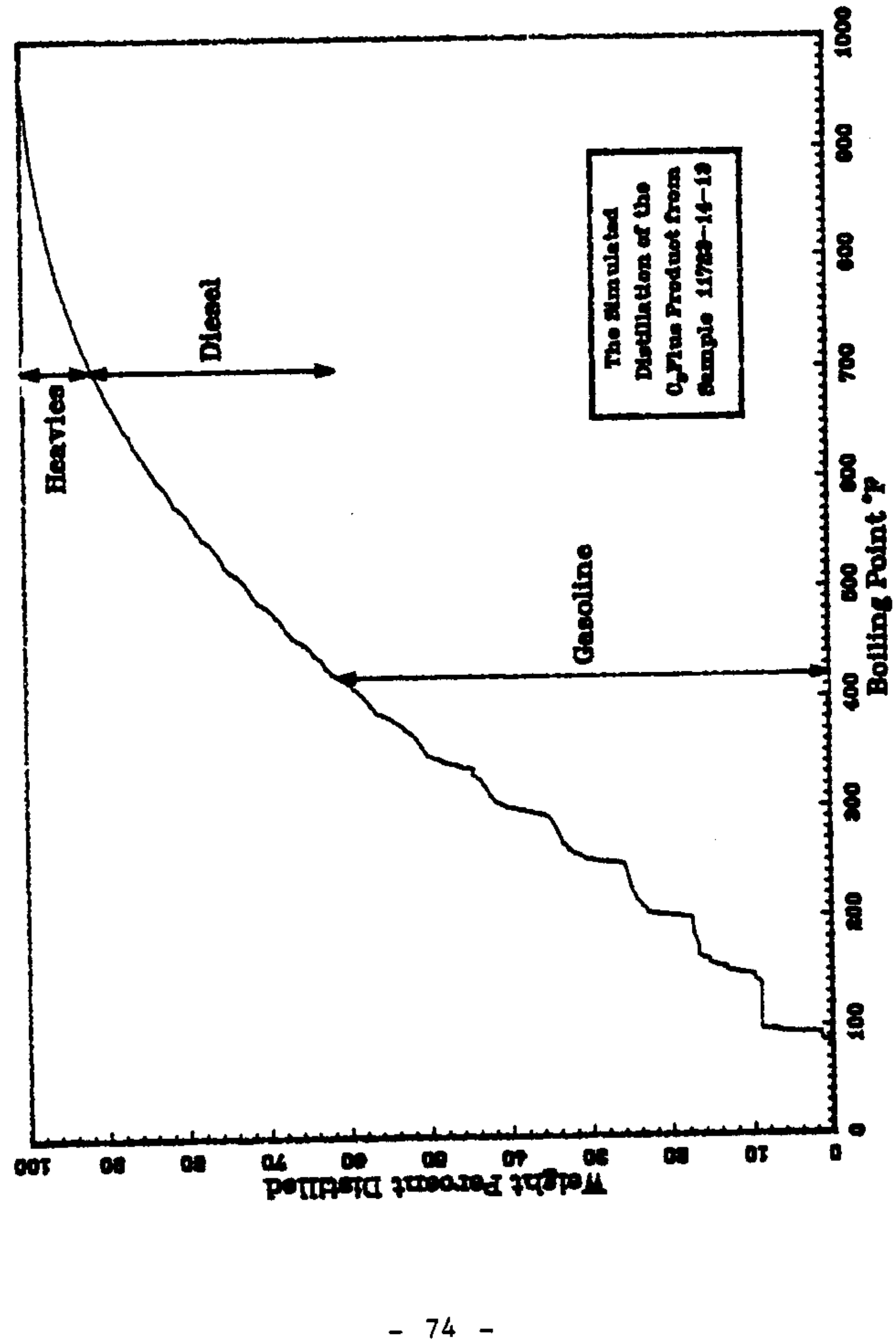
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. 39



Heavies
Diesel
Gasoline
The Simulated
Distillation of the
Boiling Point °F
Weight Percent Distilled

Fig. 40



Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. 41

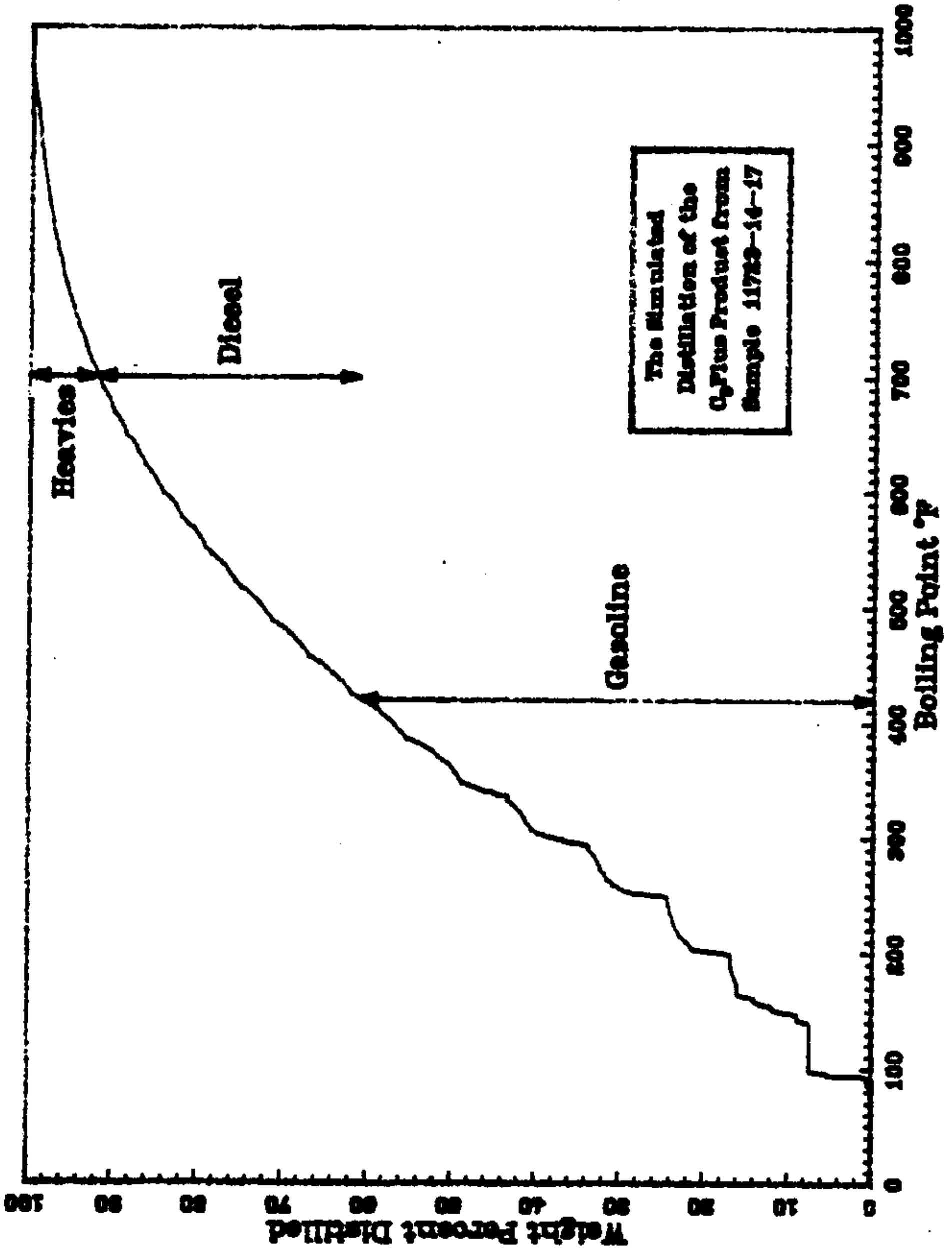
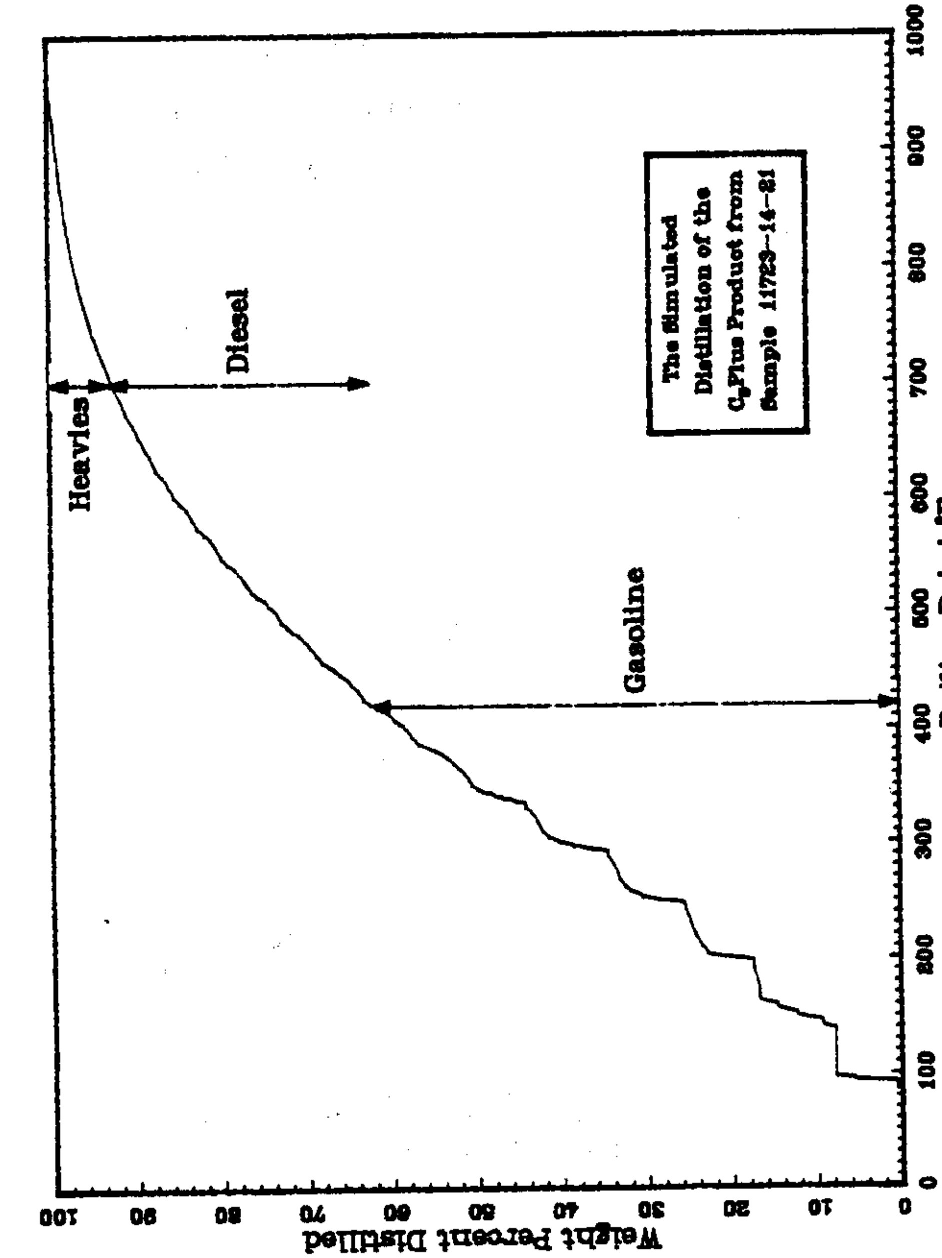

Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
The Simulated
Distillation of the

Fig. 42



The Simulated Distillation of the C5 Plus Product from Sample 11723-14-21
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000