Table 29

## RESULT OF SYNGAS OPERATION

RUN NO. 11723-13
CATALYST CoTh+U103+U101+CuZn/MS-A 250 CC 111.GM (Cat#11684-99C +17 G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

| RUN & SAMPLE NO. | 11723-13-21 |
|---|---|
| FEED H2:CO:AR | 66:33: 0 |
| HRS ON STREAM | 259.0 |
| PRESSURE,PSIG | 295 |
| TEMP. C | 254 |
| FEED CC/MIN | 945 |
| HOURS FEEDING | 24.00 |
| EFFLNT GAS LITER | 654.40 |
| GM AQUEOUS LAYER | 172.85 |
| GM OIL | 46.47 |
| MATERIAL BALANCE | |
| GM ATOM CARBON % | 91.93 |
| GM ATOM HYDROGEN % | 98.89 |
| GM ATOM OXYGEN % | 99.74 |
| RATIO CHX/(H2O+CO2) | 0.8591 |
| RATIO X IN CHX | 2.5828 |
| USAGE H2/CO PRODT | 2.3676 |
| FEED H2/CO FRM EFFLNT | 2.1537 |
| RESIDUAL H2/CO RATIO | 1.9110 |
| RATIO CO2/(H2O+CO2) | 0.0224 |
| K SHIFT IN EFFLNT | 0.0438 |
| SPECIFIC ACTIVITY SA | 0.3910 |
| CONVERSION | |
| ON CO % | 53.16 |
| ON H2 % | 58.44 |
| ON CO+H2 % | 56.77 |
| PRDT SELECTIVITY,WT % | |
| CH4 | 23.53 |
| C2 HC'S | 2.41 |
| C3H8 | 4.60 |
| C3H6= | 1.26 |
| C4H10 | 4.35 |
| C4H8= | 2.17 |
| C5H12 | 4.60 |
| C5H10= | 2.32 |
| C6H14 | 4.77 |
| C6H12= & CYCLO'S | 1.50 |
| C7+ IN GAS | 12.68 |
| LIQ HC'S | 35.80 |
| TOTAL | 100.00 |

Table 29 (continued)

| | |
|---|---|
| SUB-GROUPING | |
| C1 -C4 | 38.32 |
| C5 -420 F | 42.52 |
| 420-700 F | 16.10 |
| 700-END PT | 3.05 |
| C5+-END PT | 61.68 |
| ISO/NORMAL MOLE RATIO | |
| C4 | 0.0216 |
| C5 | 0.0278 |
| C6 | 0.0497 |
| C4= | 0.0974 |
| PARAFFIN/OLEFIN RATIO | |
| C3 | 3.4733 |
| C4 | 1.9343 |
| C5 | 1.9269 |
| SCHULZ-FLORY DISTRBTN | |
| ALPHA (EXP(SLOPE)) | 0.8041 |
| RATIO CH4/(1-A)**2 | 6.1319 |
| LIQ HC COLLECTION | |
| PHYS. APPEARANCE | CLDY/SLD |
| DENSITY | 0.7460 |
| N, REFRACTIVE INDEX | 1.4214 |
| SIMULT'D DISTILATN | |
| 10 WT % @ DEG F | 262 |
| 16 | 304 |
| 50 | 426 |
| 84 | 624 |
| 90 | 685 |
| RANGE(16-84 %) | 320 |
| WT % @ 420 F | 46.50 |
| WT % @ 700 F | 91.47 |
| | 46.50 |
| | 91.47 |

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## XIII. Run 12 (11677-19) with Catalyst 12 (Co/Th/UCC-103+UCC-101+Cu/Zn/A)

This catalyst is the same as Catalyst 9 except that the zinc was ion-exchanged into the A zeolite before the copper was loaded.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the $C_4$'s are plotted against time on stream in Figs. 166-169. Simulated distillations of the $C_5^+$ product are plotted in Figs. 170-171. Carbon number product distributions are plotted in Figs. 172-174. Chromatograms from simulated distillations are reproduced in Figs. 175-177. Detailed material balances appear in Table 30.

The Fischer-Tropsch component in this catalyst, when it was tested without a water gas shift component as Catalyst 3 of the Third Annual Report, was above average in conversion and selectivity. When combined with the water gas shift component in this run, however, both components were almost totally inactive.

Fig. 166

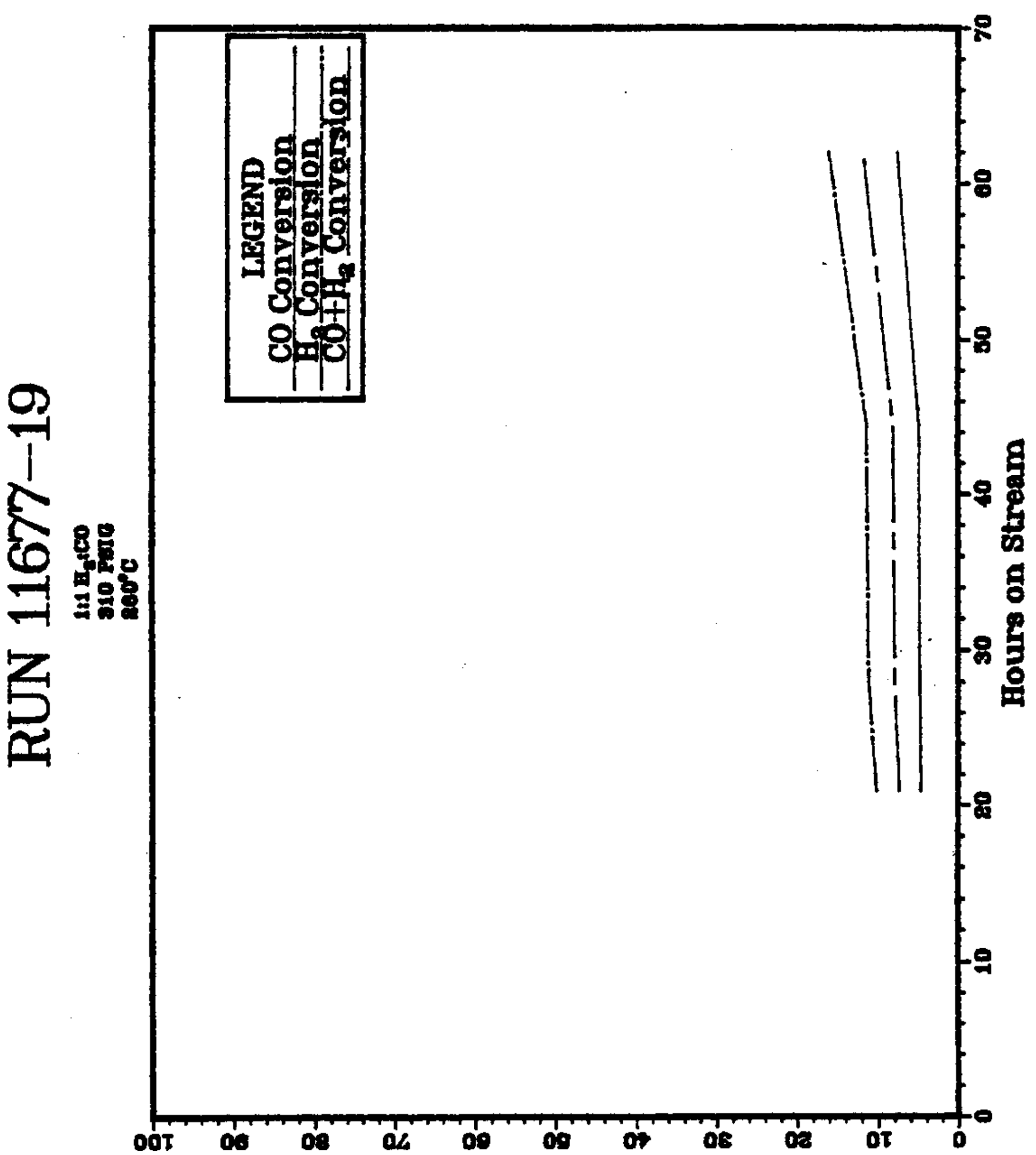

RUN 11677–19
1:1 H2:CO
310 PSIG
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100

Fig. 167

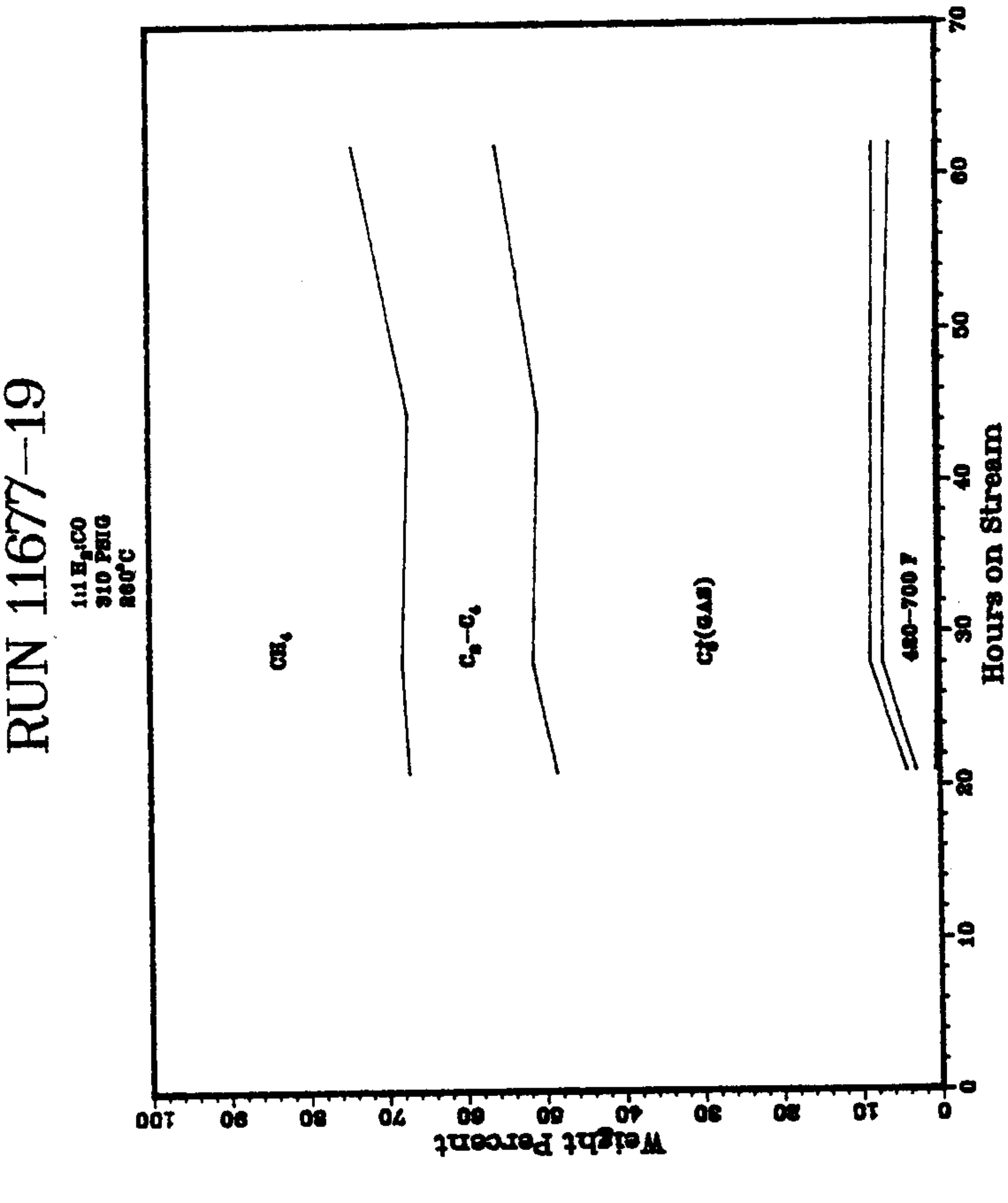
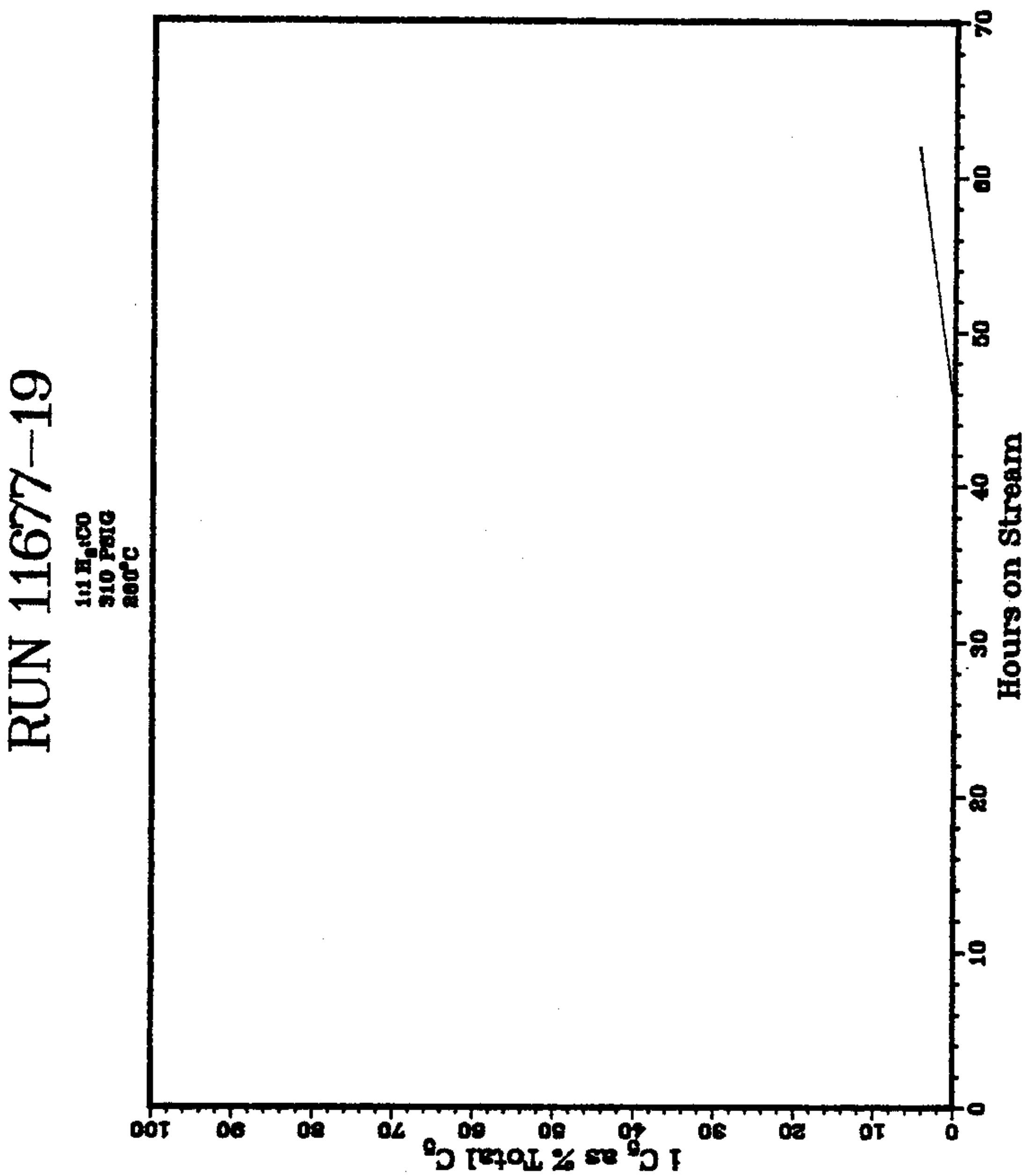

RUN 11677–19
1:1 H2:CO
310 PSIG
260°C
CH4
C2–C4
480–700 F
Hours on Stream
Weight Percent
0
10
20
30
40
50
60
70
80
90
100

Fig. 168



RUN 11677—19
1:1 $H_2$:CO
310 PSIG
i $C_5$ as % Total $C_5$
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50
60
70

Fig. 169

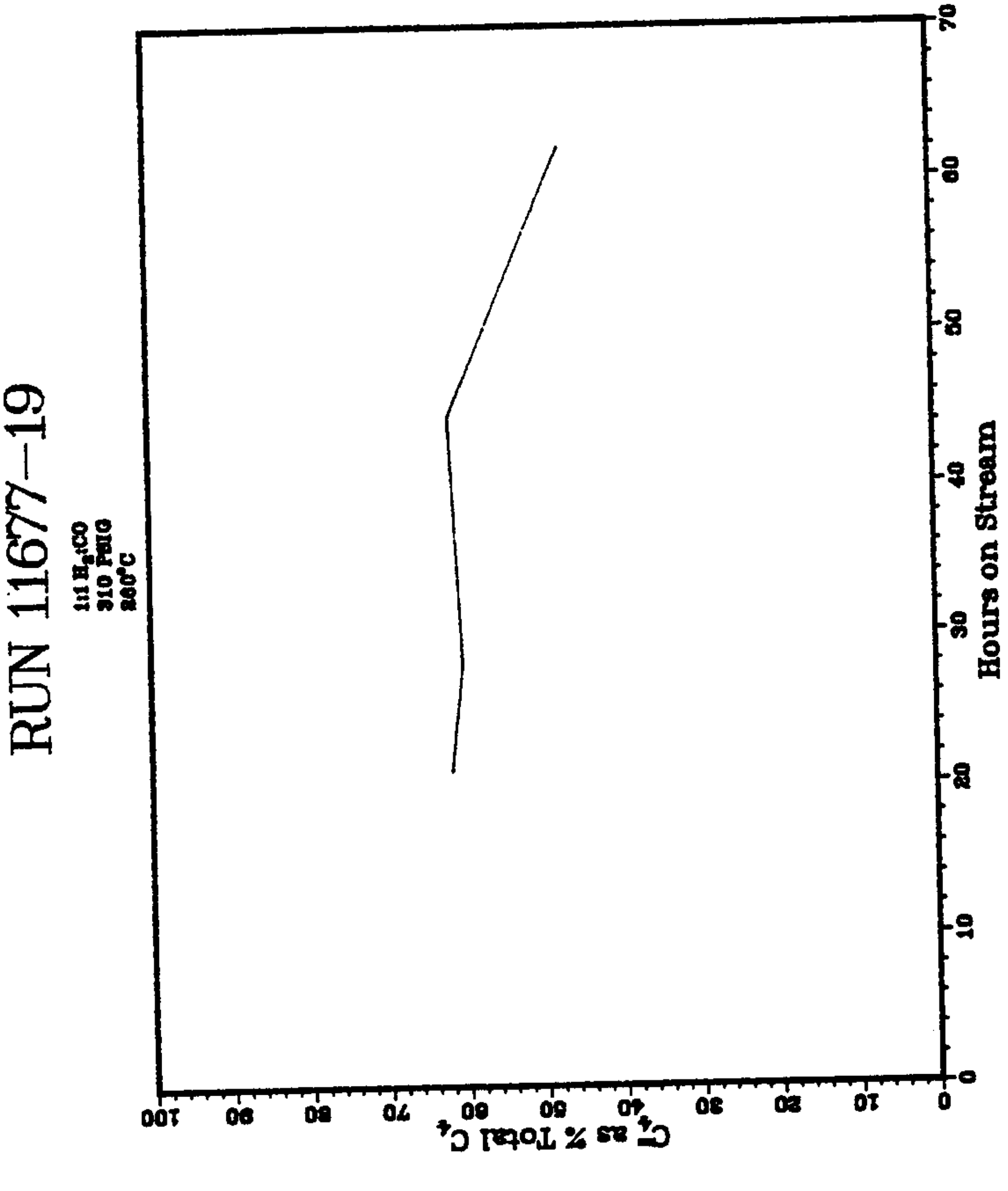
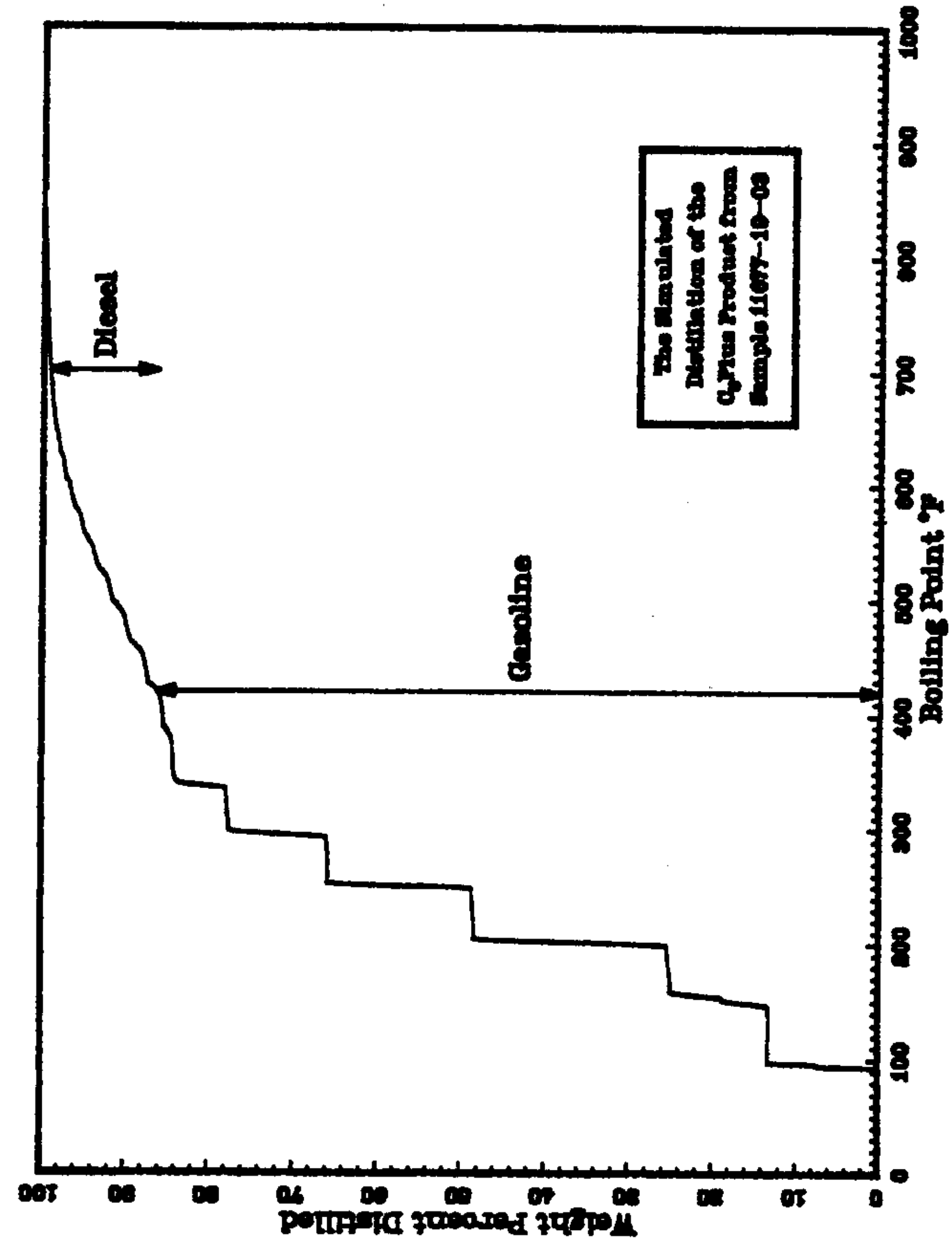

RUN 11677—19
1:1 H2:CO
310 PSIG
260°C
Hours on Stream
C4= as % Total C4
0
10
20
30
40
50
60
70
80
90
100

Fig. 170



Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. 171

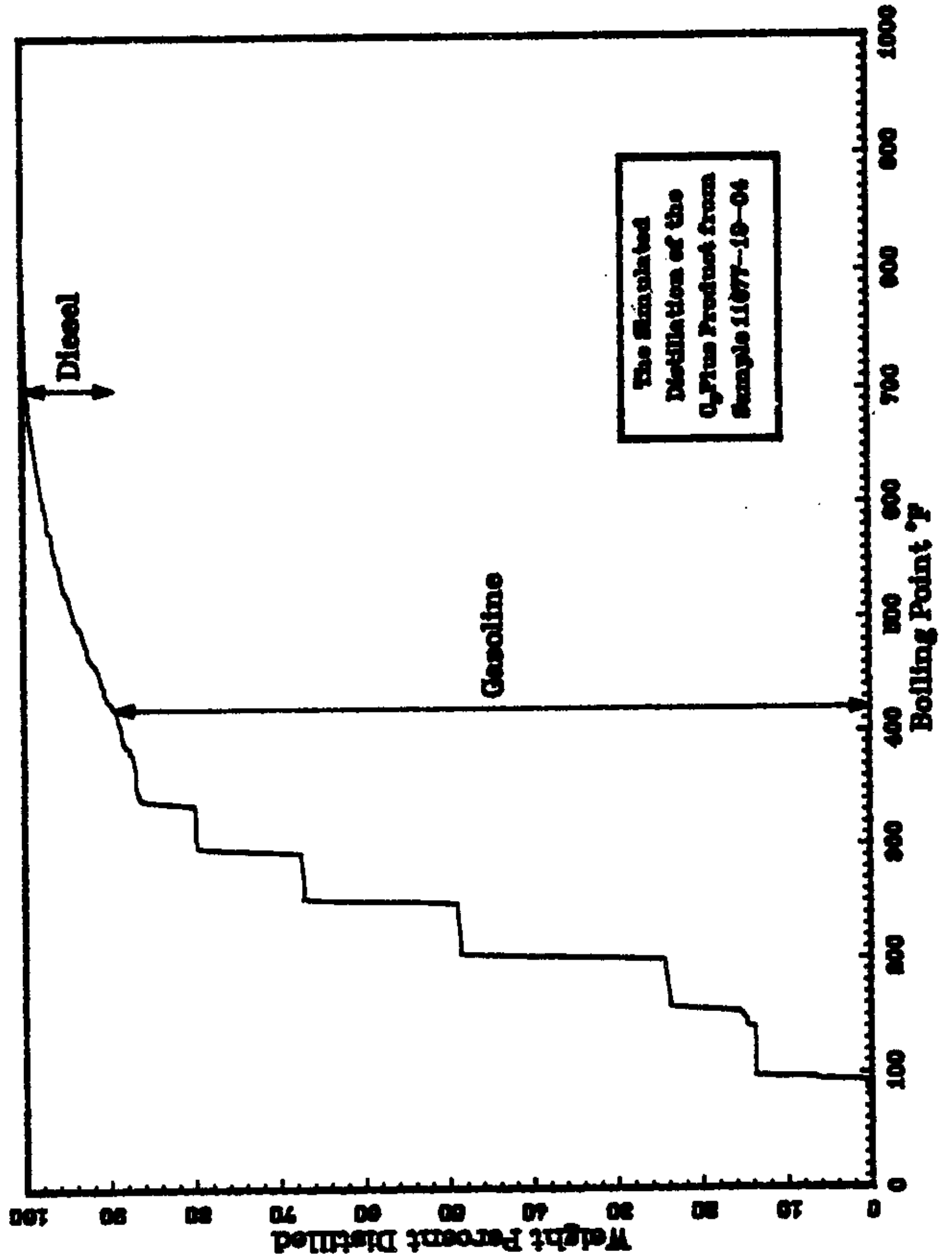

Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. 172

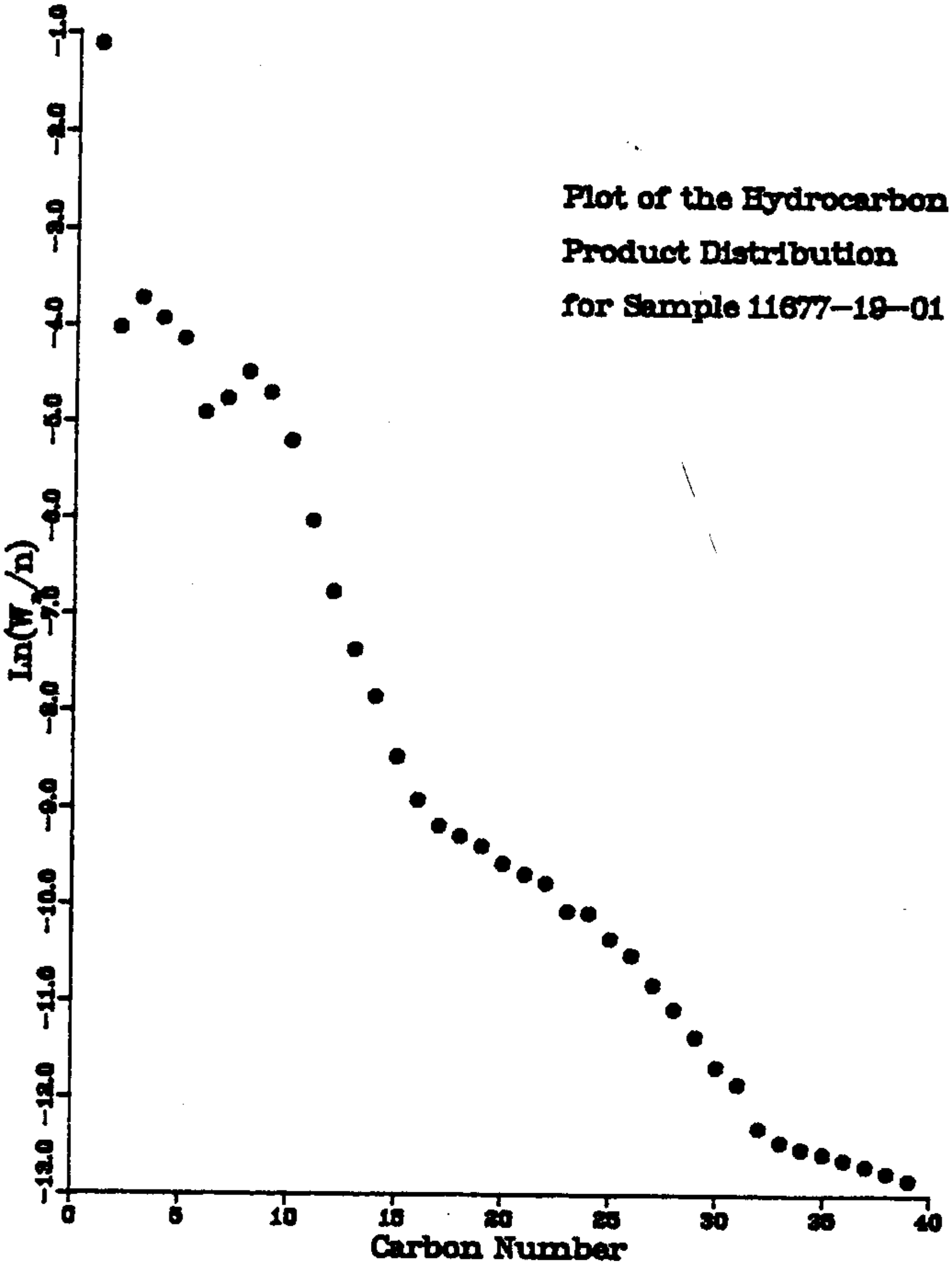

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-19-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 173

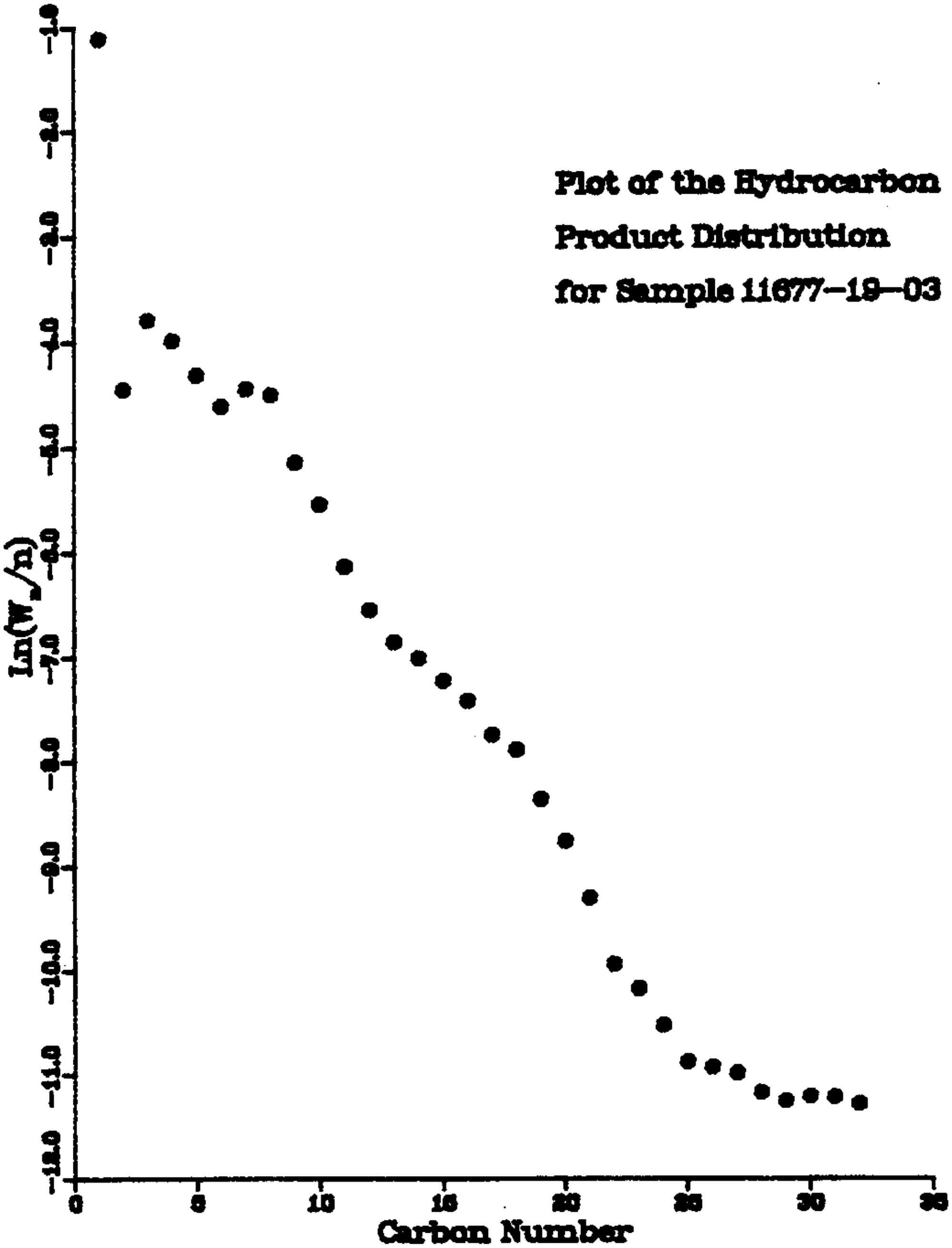
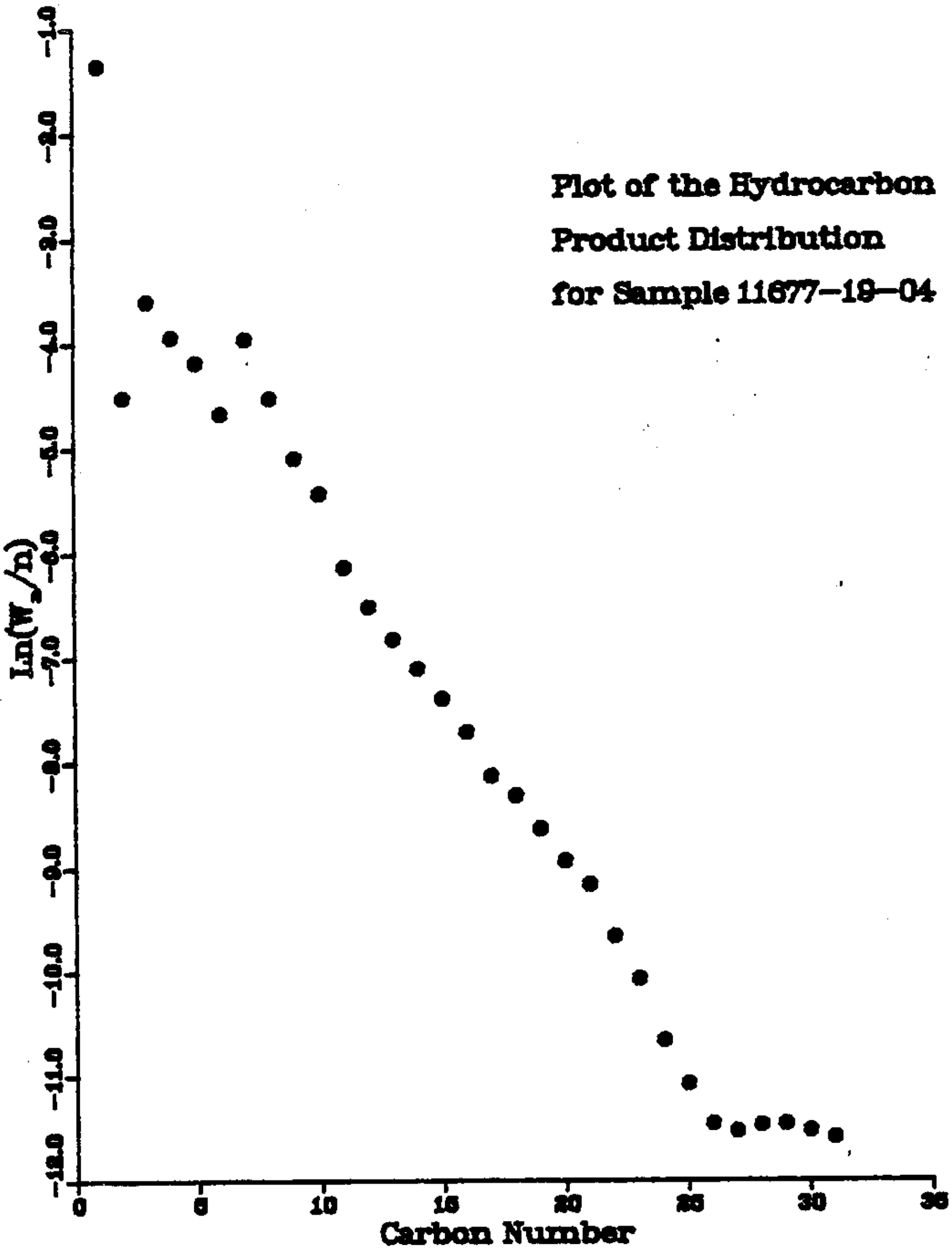

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-19-03
Ln(Wn/n)
Carbon Number
0
5
10
15
20
25
30
35

Fig. 174



Plot of the Hydrocarbon
Product Distribution
for Sample 11677-19-04
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 175

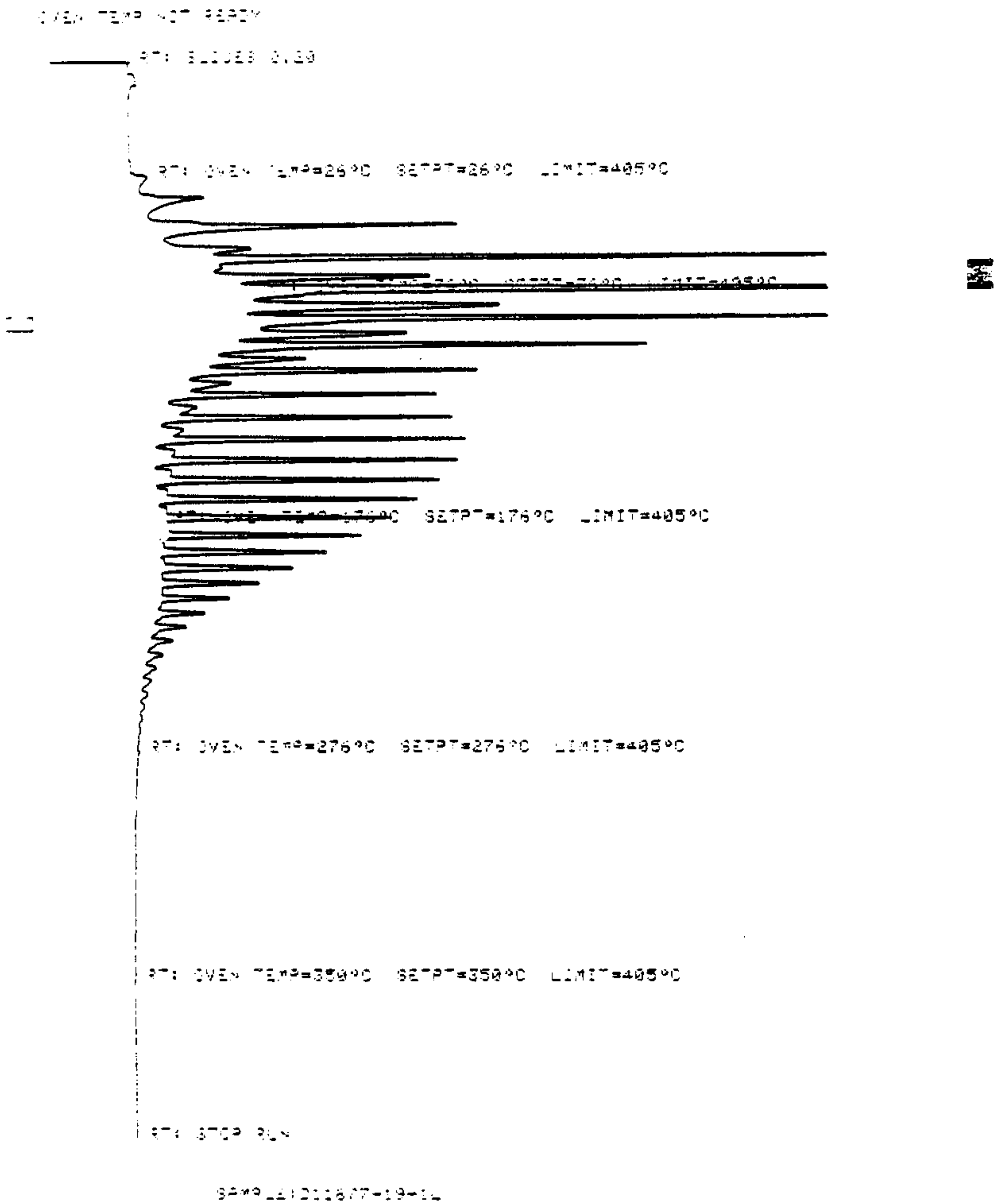


Fig. 176

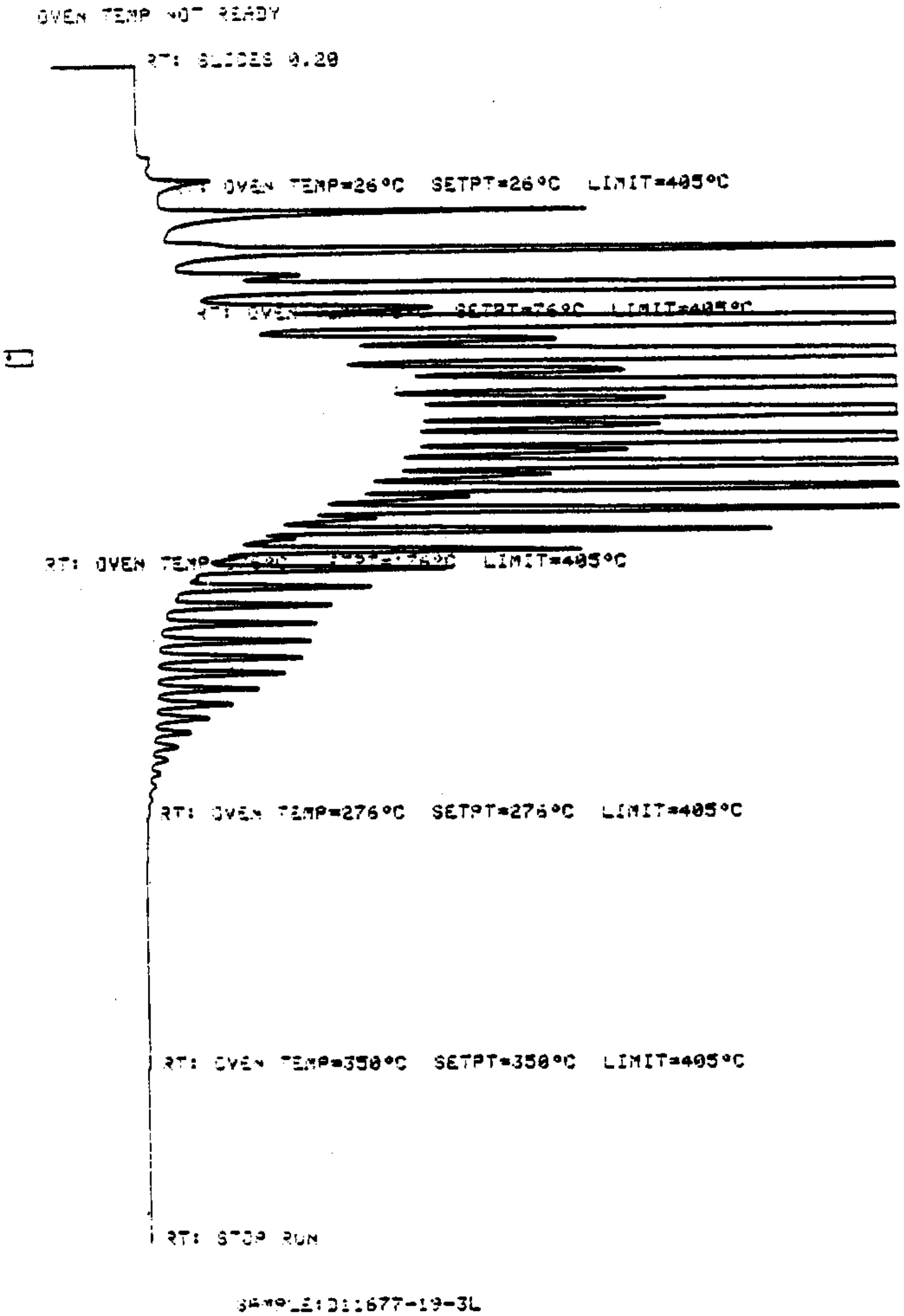
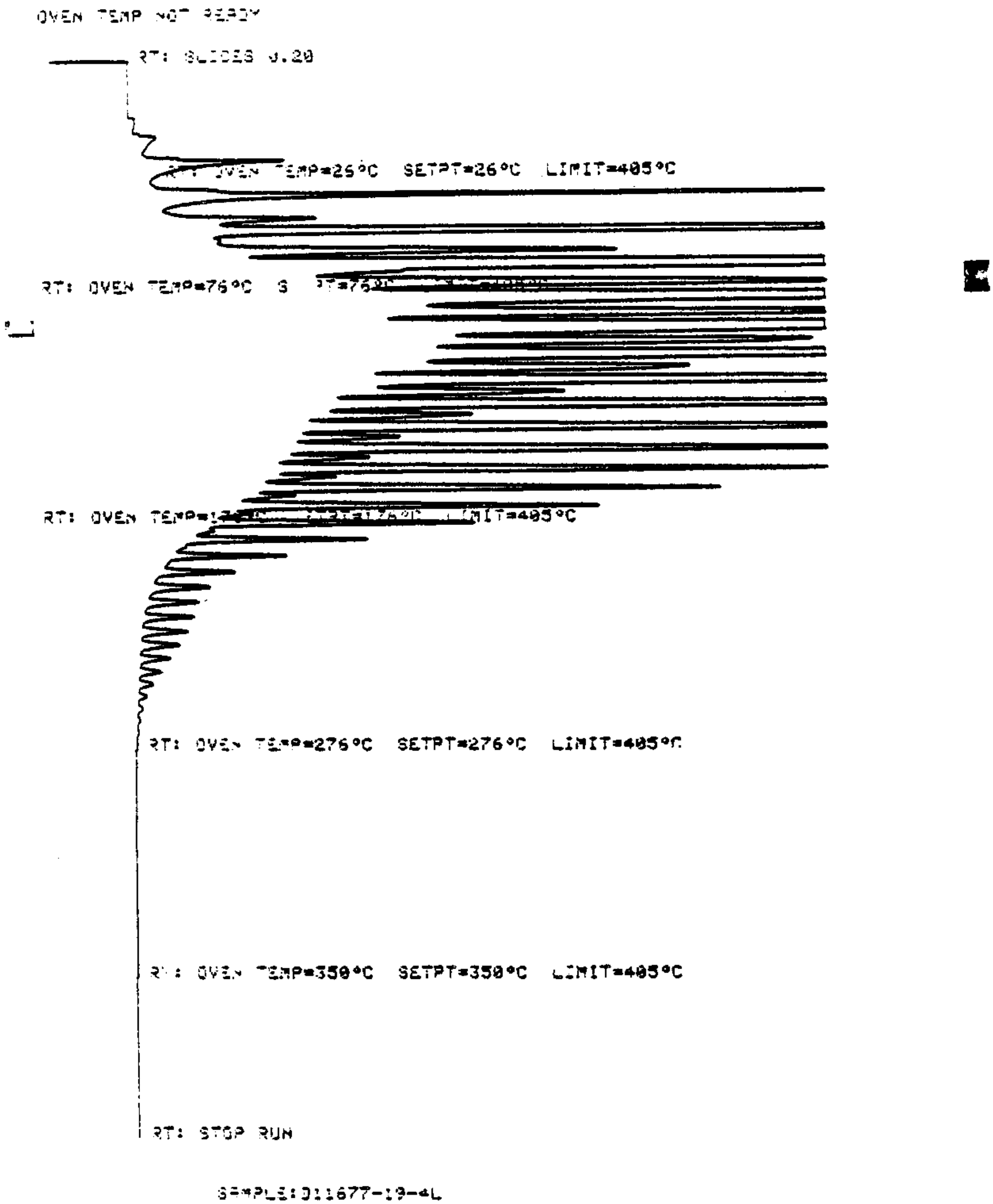

OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D11677-19-3L

Fig. 177



OVEN TEMP NOT READY
RT: SLIDES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Table 30

RESULT OF SYNGAS OPERATION

RUN NO. 11677-19
CATALYST CoThU103+U101+CuZnCa(A) 210 CC 96.7GM (93.7 AFTER RUN -3. G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 360 GHSV

| RUN & SAMPLE NO. | 11677-19-01 | 677-19-02 | 677-19-03 | 677-19-04 |
|---|---|---|---|---|
| FEED H2:CO:AR | 49:50: 0 | 49:50: 0 | 50:50: 0 | 49:50: 0 |
| HRS ON STREAM | 21.0 | 28.0 | 44.5 | 62.0 |
| PRESSURE,PSIG | 306 | 306 | 305 | 307 |
| TEMP. C | 260 | 260 | 260 | 260 |
| FEED CC/MIN | 1260 | 1260 | 1260 | 1260 |
| HOURS FEEDING | 21.00 | 7.00 | 23.50 | 17.50 |
| EFFLNT GAS LITER | 1525.35 | 494.95 | 1663.60 | 1205.70 |
| GM AQUEOUS LAYER | 6.09 | 3.71 | 12.47 | 17.53 |
| GM OIL | 0.81 | 0.57 | 1.92 | 2.18 |
| MATERIAL BALANCE | | | | |
| GM ATOM CARBON % | 100.63 | 97.43 | 99.36 | 98.36 |
| GM ATOM HYDROGEN % | 99.60 | 98.79 | 97.45 | 99.98 |
| GM ATOM OXYGEN % | 102.09 | 99.48 | 101.23 | 99.52 |
| RATIO CHX/(H2O+CO2) | 0.7291 | 0.6598 | 0.6932 | 0.8513 |
| RATIO X IN CHX | 2.6976 | 2.6746 | 2.6918 | 2.5916 |
| USAGE H2/CO PRODT | 2.1100 | 2.2885 | 2.2892 | 2.0669 |
| FEED H2/CO FRM EFFLNT | 0.9586 | 0.9821 | 0.9808 | 0.9845 |
| RESIDUAL H2/CO RATIO | 0.9022 | 0.9163 | 0.9134 | 0.8950 |
| RATIO CO2/(H2O+CO2) | 0.1431 | 0.1132 | 0.1052 | 0.1120 |
| K SHIFT IN EFFLNT | 0.1507 | 0.1170 | 0.1074 | 0.1129 |
| SPECIFIC ACTIVITY SA | 0.0822 | 0.0824 | 0.0848 | 0.1366 |
| CONVERSION | | | | |
| ON CO % | 4.66 | 4.80 | 4.90 | 7.64 |
| ON H2 % | 10.27 | 11.18 | 11.43 | 16.04 |
| ON CO+H2 % | 7.41 | 7.96 | 8.13 | 11.81 |
| PRDT SELECTIVITY,WT % | | | | |
| CH4 | 32.81 | 32.00 | 32.87 | 25.93 |
| C2 HC'S | 3.56 | 1.68 | 2.33 | 2.20 |
| C3H8 | 3.11 | 2.89 | 2.64 | 4.72 |
| C3H6= | 4.16 | 4.33 | 4.08 | 3.48 |
| C4H10 | 3.05 | 3.09 | 2.89 | 4.17 |
| C4H8= | 4.77 | 4.54 | 4.52 | 3.61 |
| C5H12 | 3.28 | 3.34 | 2.95 | 4.27 |
| C5H10= | 4.68 | 4.33 | 3.75 | 3.40 |
| C6H14 | 2.86 | 3.57 | 3.19 | 5.31 |
| C6H12= & CYCLO'S | 1.57 | 1.92 | 2.77 | 0.34 |
| C7+ IN GAS | 31.93 | 29.51 | 29.55 | 34.45 |
| LIQ HC'S | 4.22 | 8.79 | 8.45 | 8.12 |
| TOTAL | 100.00 | 100.00 | 100.00 | 100.00 |

Table 30 (continued)

| | | | | |
|---|---|---|---|---|
| SUB-GROUPING | | | | |
| C1 -C4 | 51.47 | 48.53 | 49.34 | 44.11 |
| C5 -420 F | 45.45 | 44.26 | 43.73 | 49.89 |
| 420-700 F | 2.48 | 6.74 | 6.48 | 5.70 |
| 700-END PT | 0.60 | 0.46 | 0.45 | 0.31 |
| C5+-END PT | 48.53 | 51.47 | 50.66 | 55.89 |
| ISO/NORMAL MOLE RATIO | | | | |
| C4 | 0.0000 | 0.0000 | 0.0000 | 0.0746 |
| C5 | 0.0000 | 0.0000 | 0.0000 | 0.0490 |
| C6 | 0.0000 | 0.0000 | 0.0000 | 0.1171 |
| C4= | 0.0732 | 0.0607 | 0.0960 | 0.0576 |
| PARAFFIN/OLEFIN RATIO | | | | |
| C3 | 0.7134 | 0.6366 | 0.6182 | 1.2969 |
| C4 | 0.6174 | 0.6565 | 0.6168 | 1.1146 |
| C5 | 0.6812 | 0.7500 | 0.7637 | 1.2205 |
| SCHULZ-FLORY DISTRBTN | | | | |
| ALPHA (EXP(SLOPE)) | 0.7303 | 0.7323 | 0.7329 | 0.7204 |
| RATIO CH4/(1-A)**2 | 4.5125 | 4.4641 | 4.6086 | 3.3177 |
| LIQ HC COLLECTION | | | | |
| PHYS. APPEARANCE | OIL/SLD | | CLR OIL | CLR OIL |
| DENSITY | | | 0.7681 | 0.7719 |
| N, REFRACTIVE INDEX | | | 1.4328 | 1.4328 |
| SIMULT'D DISTILATN | | | | |
| 10 WT % @ DEG F | 378 | | 385 | 368 |
| 16 | 397 | | 416 | 387 |
| 50 | 481 | | 499 | 477 |
| 84 | 685 | | 609 | 602 |
| 90 | 735 | | 646 | 643 |
| RANGE(16-84 %) | 288 | | 193 | 215 |
| WT % @ 420 F | 27.00 | 18.00 | 18.00 | 26.00 |
| WT % @ 700 F | 85.83 | 94.72 | 94.72 | 96.17 |

NEW FORMAT AUG 29,84

## XIV. Summary

Of the twelve catalysts tested in this quarter, none showed any significant effectiveness. The principal value of the quarter's work has been in whatever guidance may be derived from the negative findings, especially what they may tell us about the design parameters of a good catalyst.

The most effective catalyst developed to date, Catalyst 6 (Run 11677-11) of the Third Annual Report, was composed of Co/Th/$X_4$/UCC-103+UCC-101. This quarter's findings suggest three specifics of that catalyst which should prove useful in shaping further work: First, that the $X_4$ component is probably a key contributor to stability. Second, that the source of the $X_4$ is important; the $X_4$ must be free of known catalyst poisons, or have those poisons completely removed without impairing the cobalt Fischer-Tropsch activity. And third, that extra, physically mixed UCC-101 apparently contributes little if anything to stability.

Eight of the twelve runs were devoted to tests of water gas shift catalysts in different formulations and methods of preparation, and under different operating conditions. Many attempts have been made to develop a copper-zinc water gas shift catalyst which will function effectively in combination with a Fischer-Tropsch catalyst and at the Fischer-Tropsch operating temperatures. The failure of these trials to date suggests that the water gas shift components may be deactivated by intermediates or products of Fischer-Tropsch synthesis. Yet attempts to isolate the water gas shift component from the Fischer-Tropsch products have been equally fruitless.

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