Fig. 121

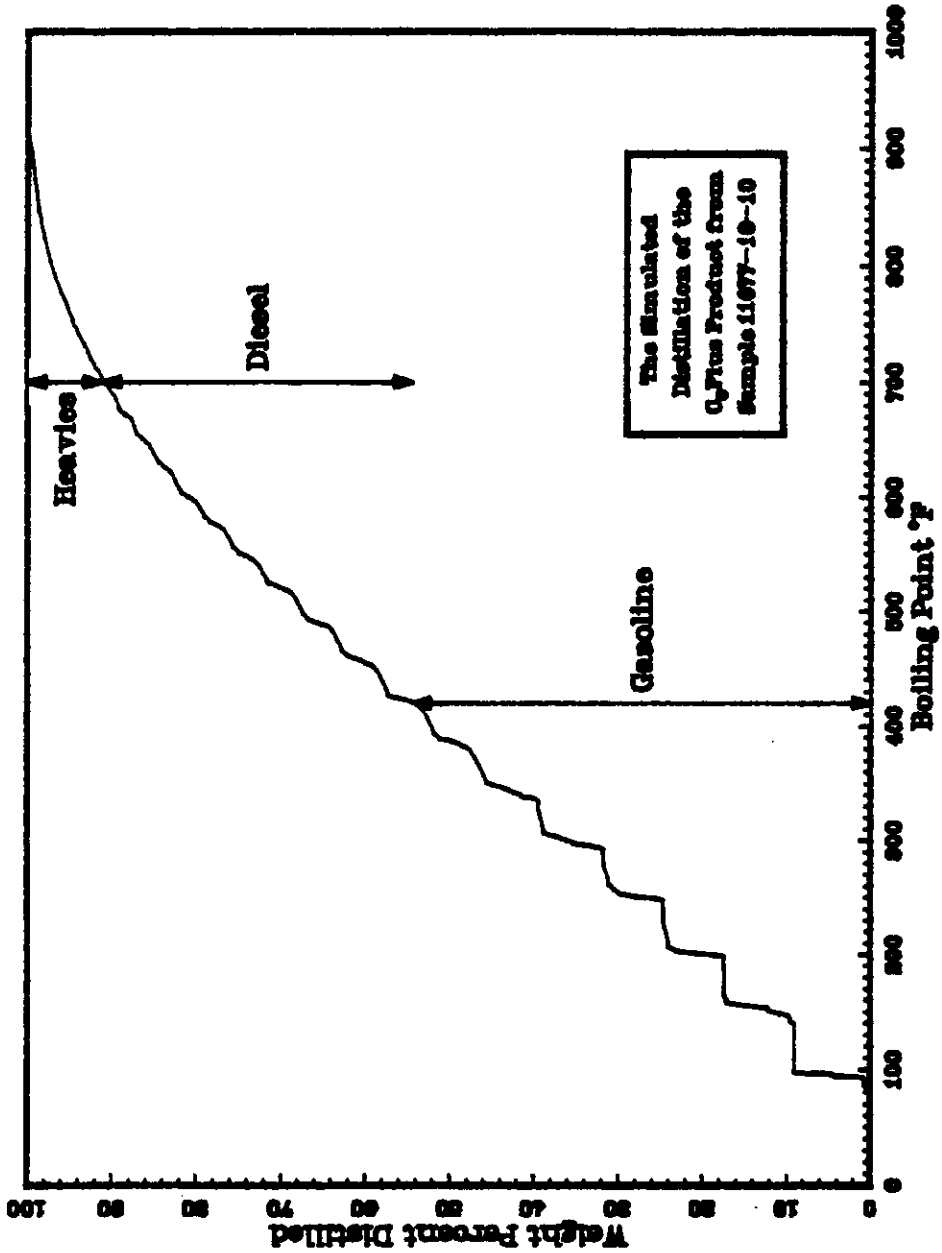

Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F

Fig. 122

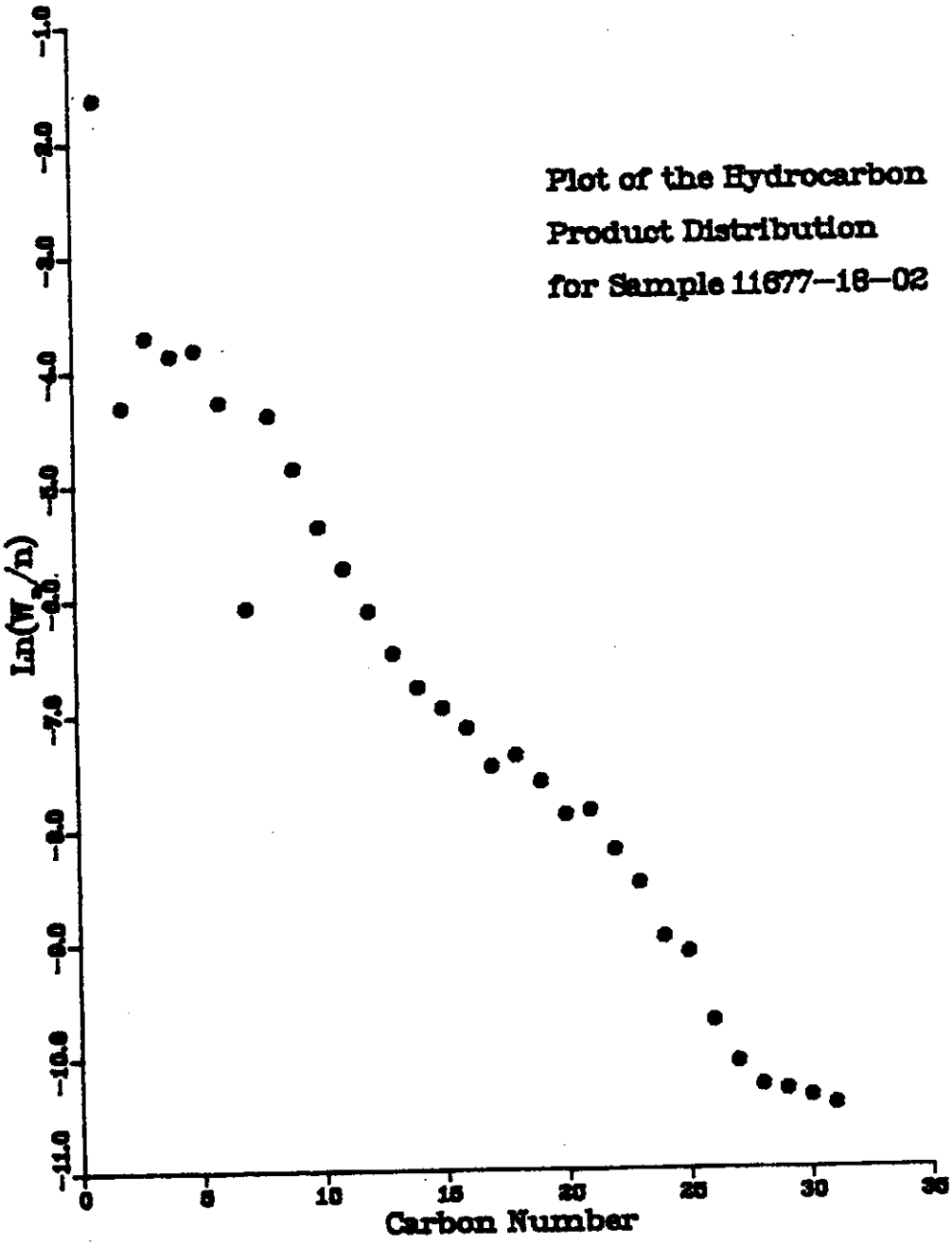

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-18-02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 123

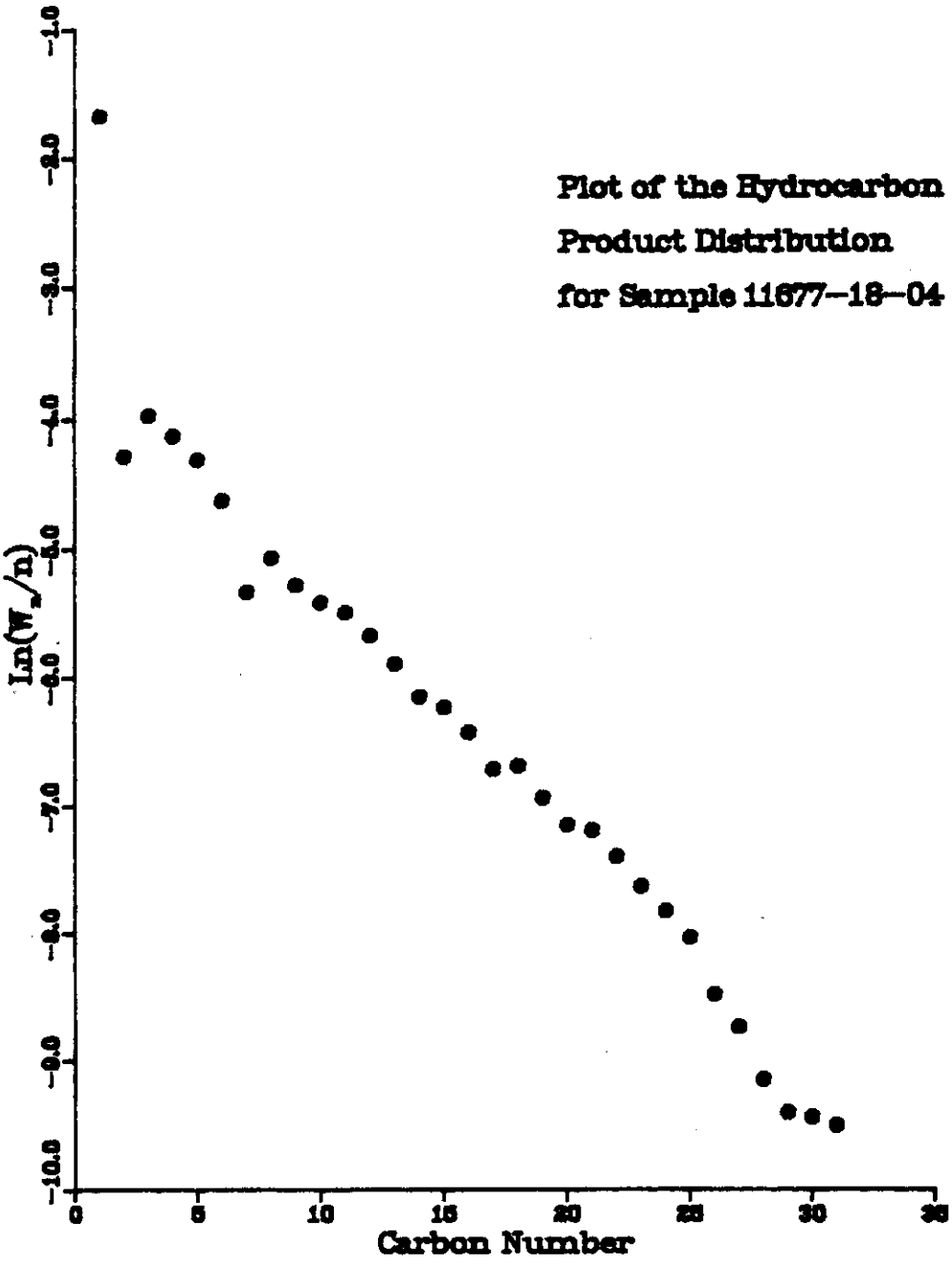

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-18-04
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 124

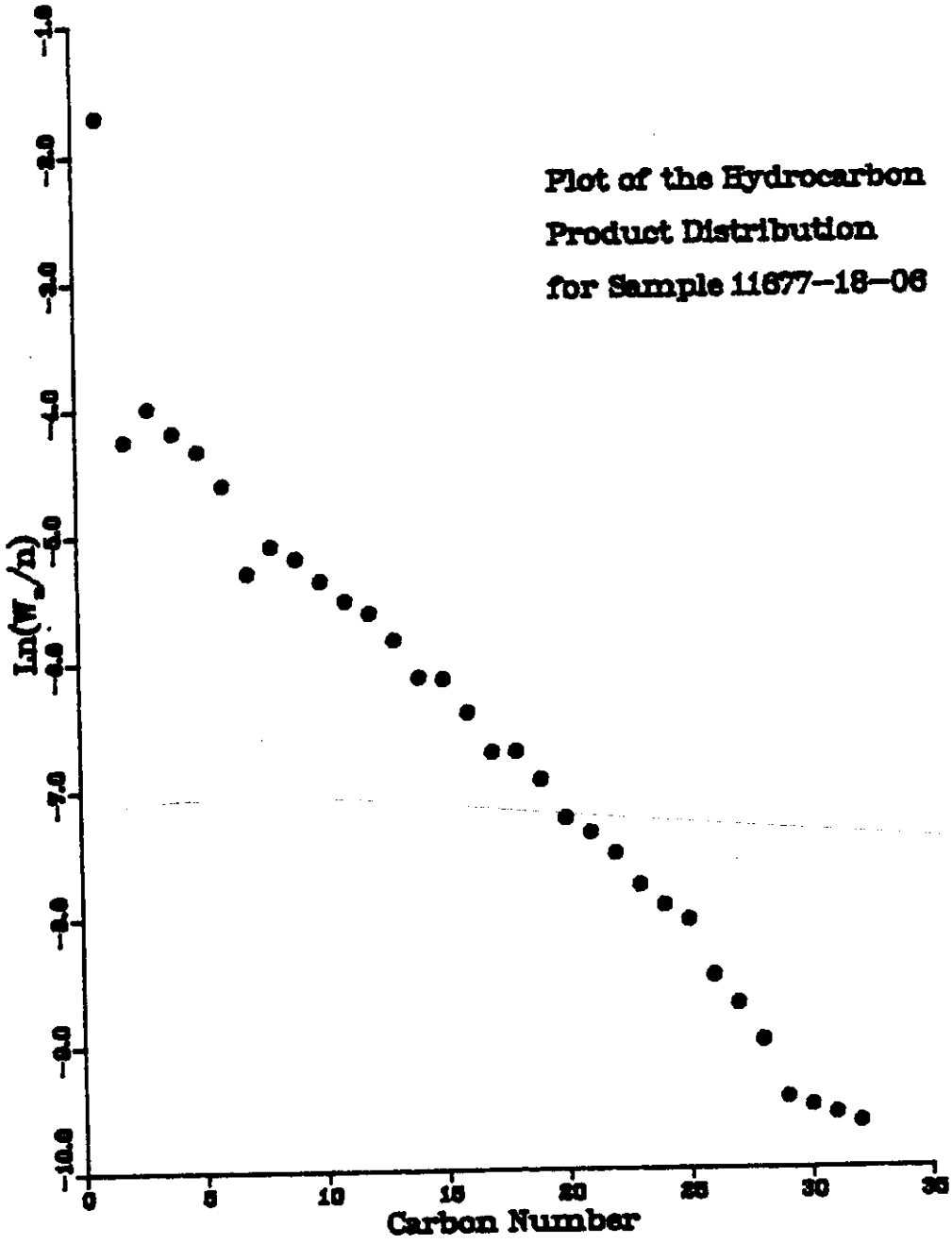

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-18-06
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 125

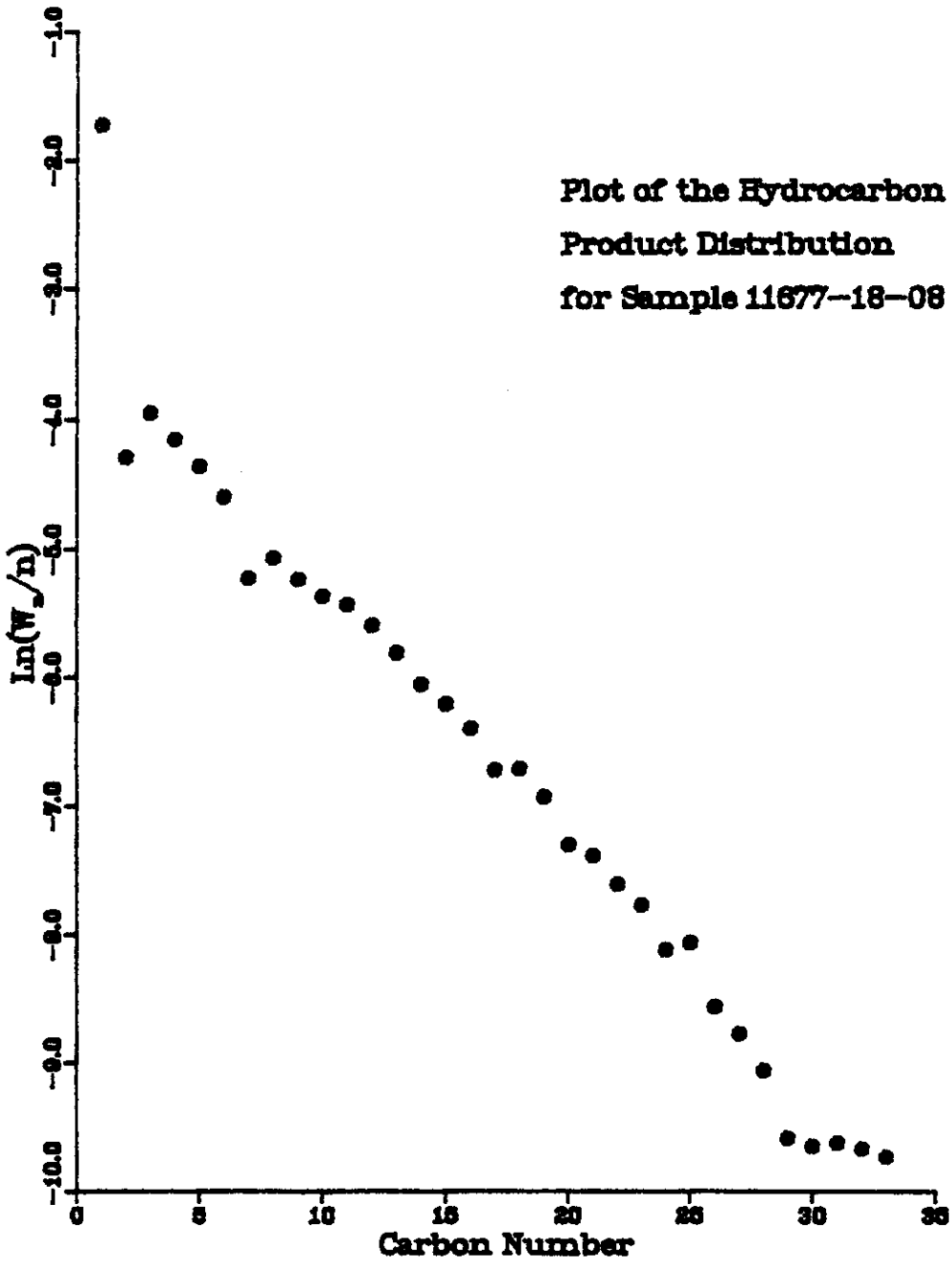

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-18-08
ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 126

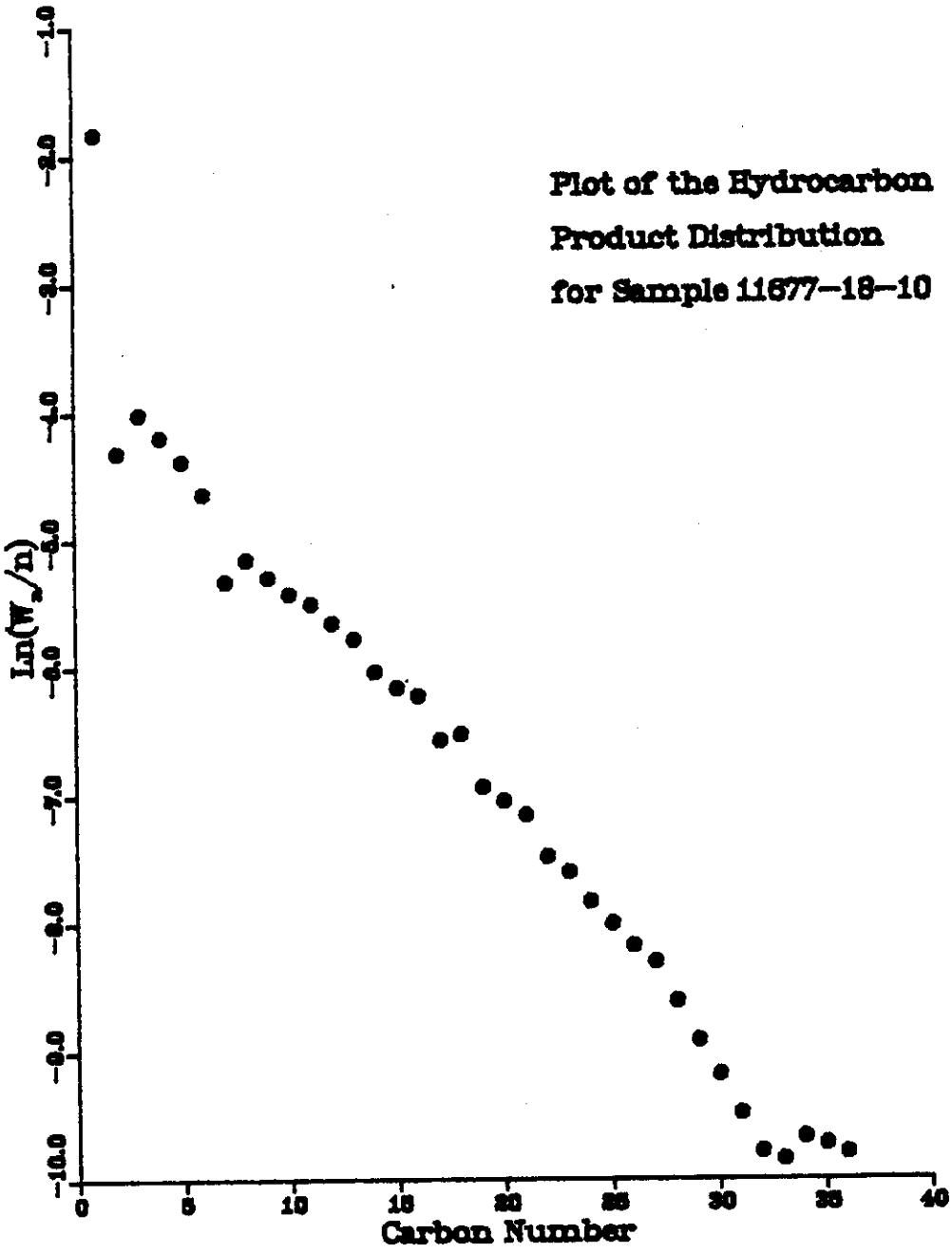

Plot of the Hydrocarbon
Product Distribution
for Sample 11677-18-10
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 127

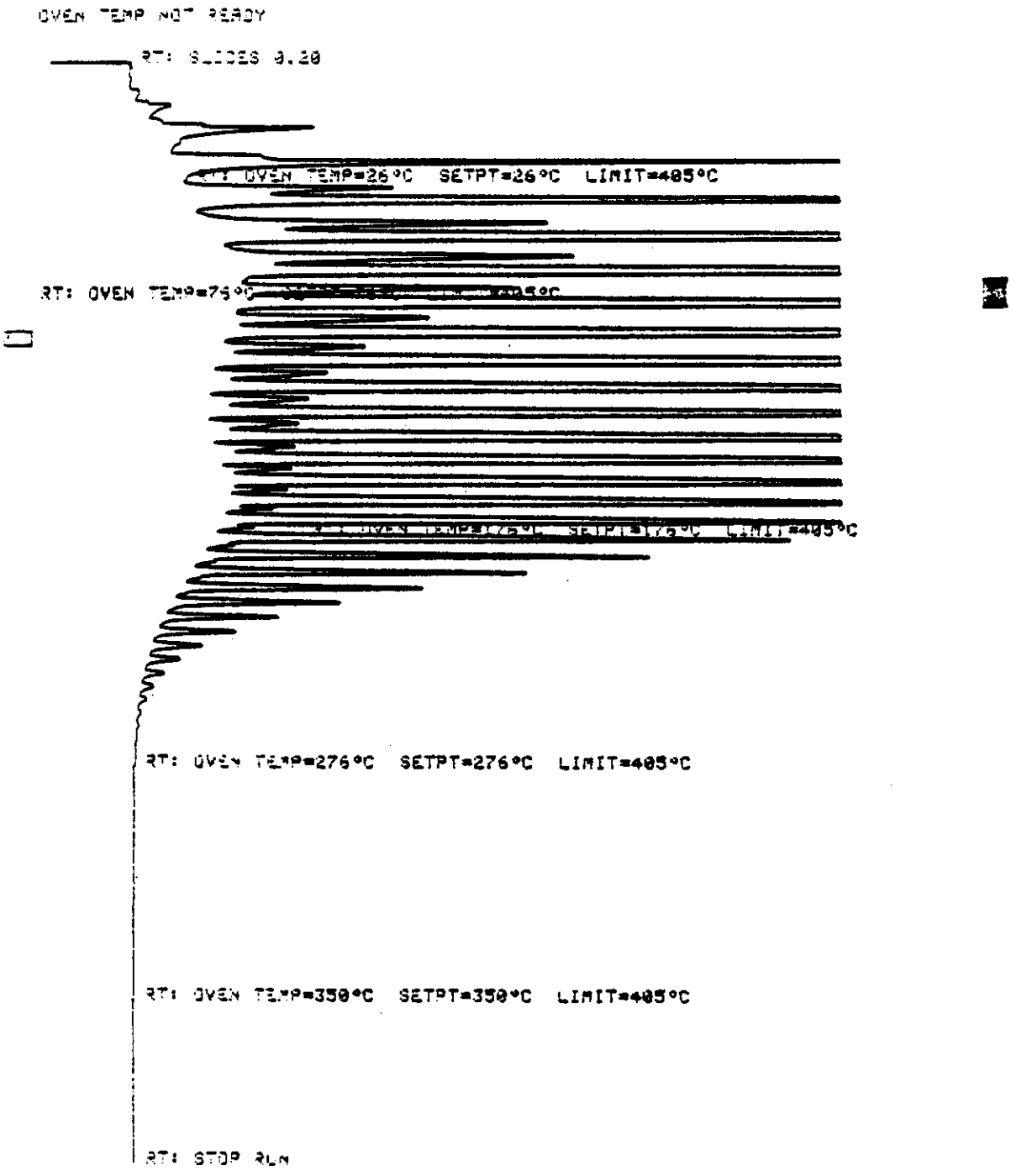
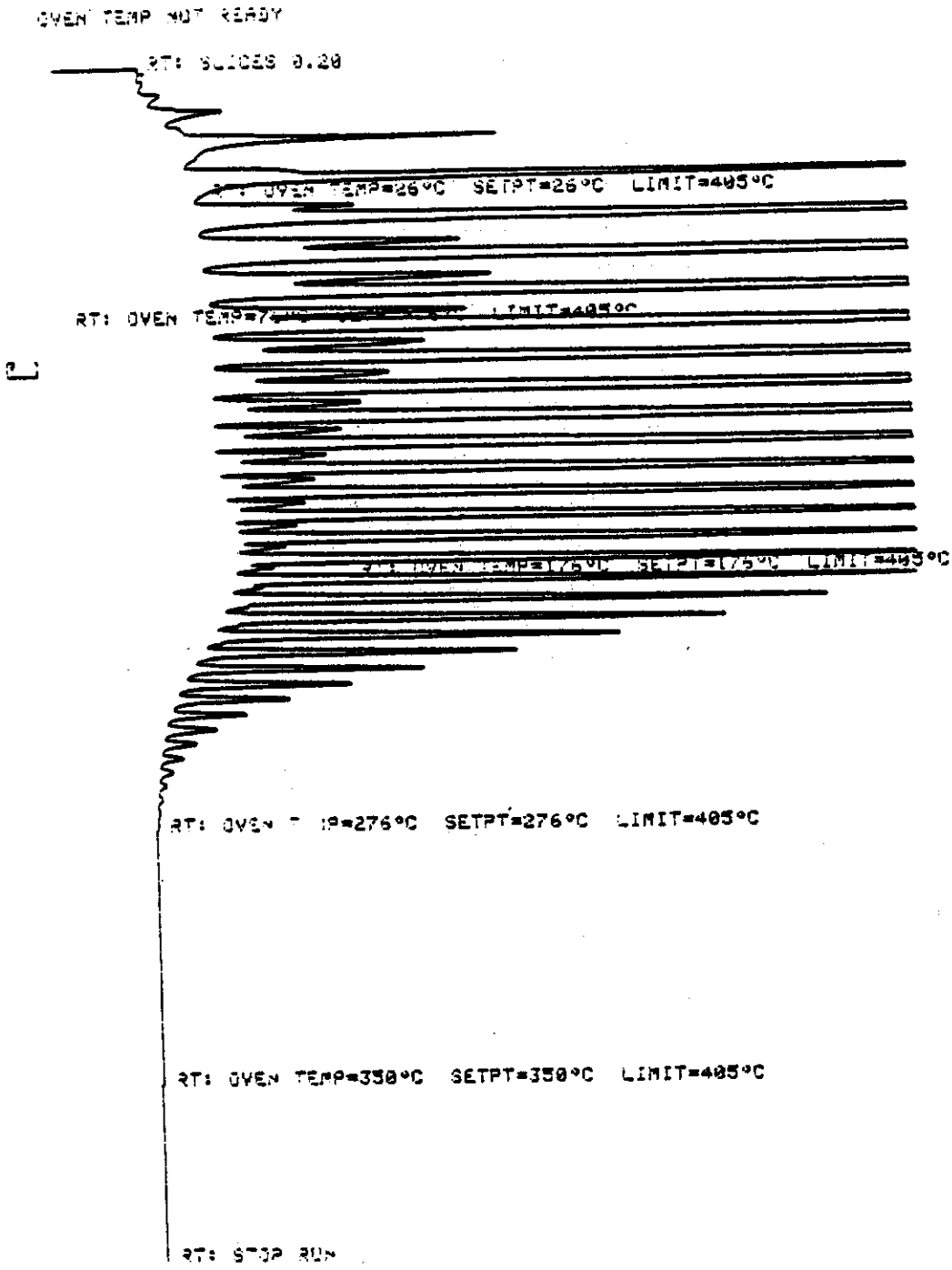

OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE: 11677-18-2L

Fig. 128



SAMPLE: 11677-18-4L

Fig. 129

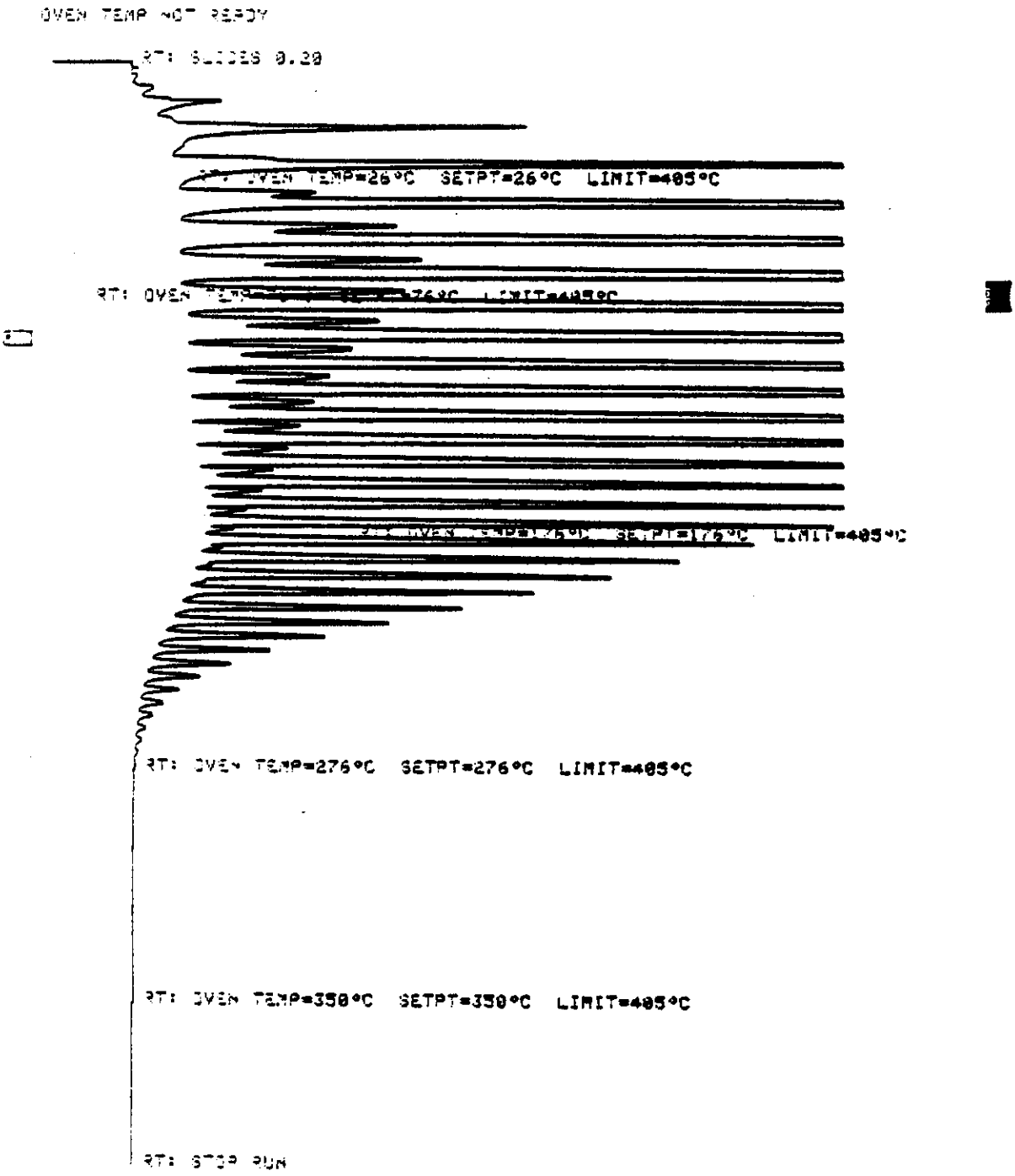
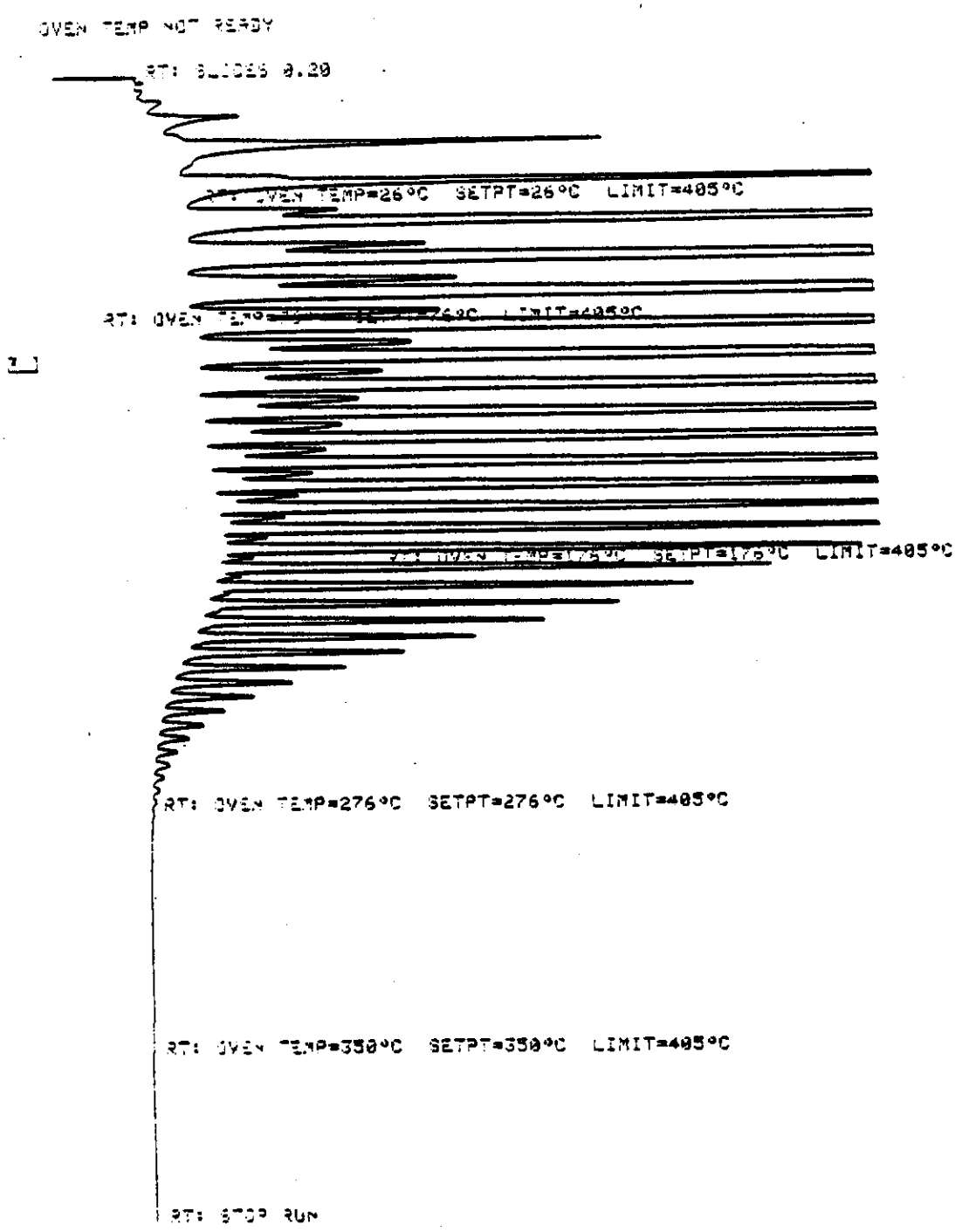

OVEN TEMP NOT READY
RT: SLIDES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE: 11677-18-6L

Fig. 130



SAMPLE: 11677-18-8L

Fig. 131

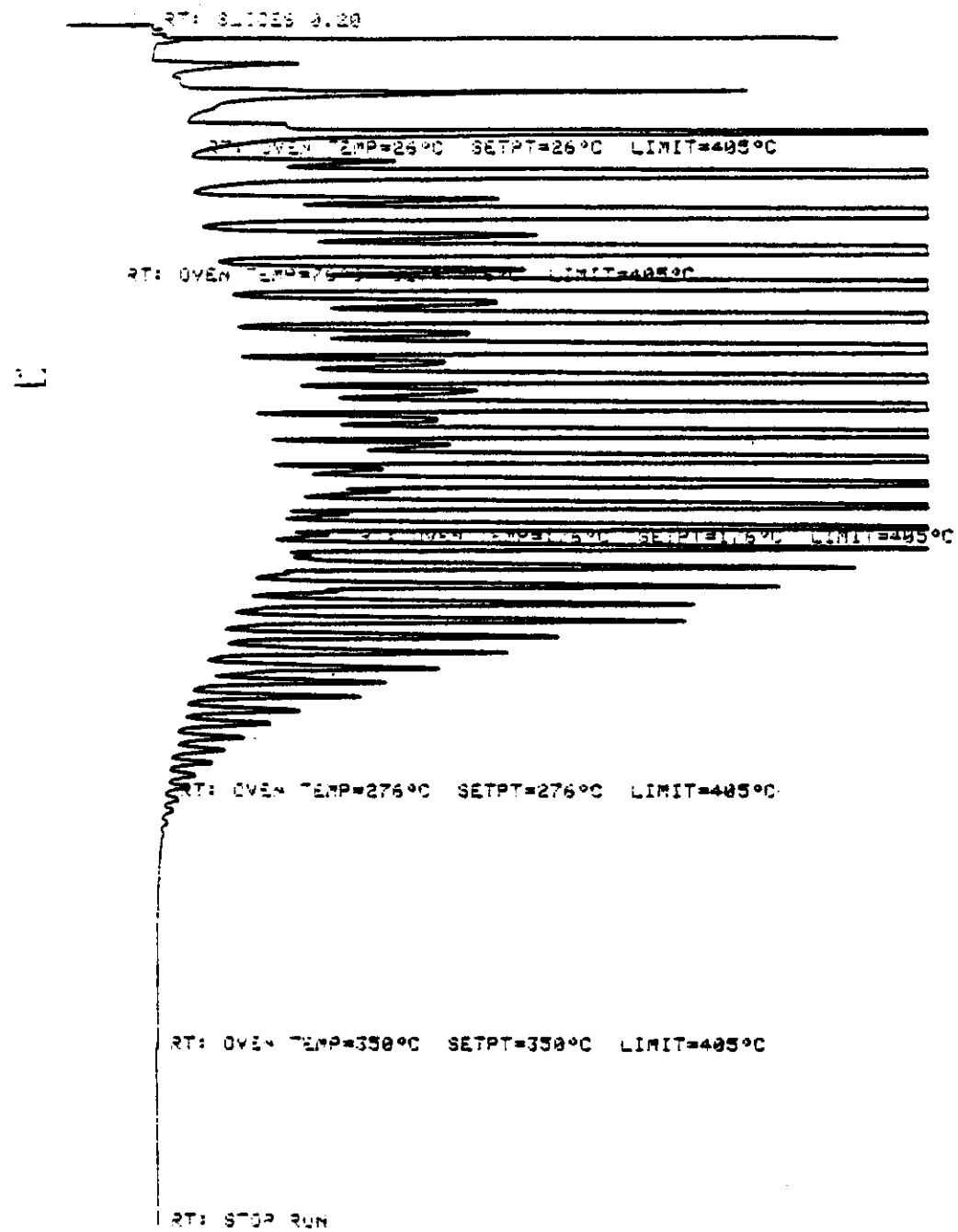

RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Table 23

RESULT OF SYNGAS OPERATION

RUN NO. 11677-18
CATALYST CoThU103+CuZnLZ105-6 250 CC 128.GM (146.3AFTER RUN+18.7G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11677-18-01	677-18-02	677-18-03	677-18-04	677-18-05
FEED H2:CO:AR	49:50: 0	49:50: 0	49:50: 0	49:50: 0	49:50: 0
HRS ON STREAM	2.0	19.0	26.5	43.0	50.5
PRESSURE,PSIG	301	301	300	297	301
TEMP. C	263	262	262	262	261
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	2.00	19.00	7.50	24.00	7.50
EFFLNT GAS LITER	119.60	1002.10	358.20	1124.05	343.75
GM AQUEOUS LAYER	10.01	95.10	49.90	159.69	53.92
GM OIL	1.77	16.85	16.97	54.30	18.46
MATERIAL BALANCE					
GM ATOM CARBON %	103.01	99.14	94.96	95.82	94.30
GM ATOM HYDROGEN %	107.56	97.80	98.93	98.23	100.12
GM ATOM OXYGEN %	107.07	101.17	101.11	100.92	100.55
RATIO CHX/(H2O+CO2)	0.8137	0.9092	0.7803	0.8196	0.7911
RATIO X IN CHX	2.4136	2.4929	2.4720	2.4880	2.4669
USAGE H2/CO PRODT	2.2062	2.0211	2.1871	2.1148	2.1782
FEED H2/CO FRM EFFLNT	1.0113	0.9554	1.0094	0.9929	1.0283
RESIDUAL H2/CO RATIO	0.7408	0.6418	0.6085	0.5798	0.5899
RATIO CO2/(H2O+CO2)	0.0582	0.0979	0.0809	0.0919	0.0795
K SHIFT IN EFFLNT	0.0458	0.0696	0.0536	0.0587	0.0509
SPECIFIC ACTIVITY SA	0.2939	0.4843	0.5868	0.6790	0.7059
CONVERSION					
ON CO %	18.46	22.73	25.40	26.91	27.60
ON H2 %	40.27	48.10	55.03	57.32	58.46
ON CO+H2 %	29.43	35.13	40.28	42.06	43.25
PRDT SELECTIVITY,WT %					
CH4	15.23	19.75	18.14	18.83	17.63
C2 HC'S	1.67	2.69	2.64	2.77	2.71
C3H8	5.11	4.69	3.56	3.77	3.54
C3H6=	2.53	2.72	1.90	1.91	1.83
C4H10	4.93	4.01	3.16	3.45	3.36
C4H8=	5.83	4.39	2.94	3.03	2.83
C5H12	5.09	4.66	3.40	3.63	3.48
C5H10=	7.23	6.34	2.82	3.08	2.81
C6H14	5.63	5.11	3.57	3.71	3.97
C6H12= & CYCLO'S	3.15	3.22	1.93	2.19	1.92
C7+ IN GAS	21.76	23.43	10.76	11.10	10.49
LIQ HC'S	21.85	18.99	45.19	42.53	45.42
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 23 (continued)

SUB-GROUPING					
C1 -C4	35.29	38.25	32.32	33.76	31.90
C5 -420 F	50.18	49.12	38.31	38.60	39.25
420-700 F	12.80	11.13	24.51	23.07	24.05
700-END PT	1.73	1.50	4.86	4.57	4.79
C5+-END PT	64.71	61.75	67.68	66.24	68.10
ISO/NORMAL MOLE RATIO					
C4	0.1548	0.0492	0.0417	0.0449	0.0321
C5	0.3659	0.1133	0.1065	0.0931	0.0897
C6	0.6918	0.1457	0.1350	0.1025	0.1022
C4=	0.4074	0.1060	0.0967	0.0997	0.0958
PARAFFIN/OLEFIN RATIO					
C3	1.9243	1.6480	1.7916	1.8822	1.8462
C4	0.8158	0.8829	1.0371	1.1012	1.1459
C5	0.6841	0.7143	1.1749	1.1460	1.2022
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.7816		0.8326	
RATIO CH4/(1-A)**2		4.1428		6.7228	
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLDY/SLD		CLDY/SLD	
DENSITY		0.7600		0.7604	
N, REFRACTIVE INDEX		1.4266		1.4265	
SIMULT'D DISTILATN					
10 WT % @ DEG F		306		303	
16		346		342	
50		488		487	
84		651		669	
90		688		709	
RANGE(16-84 %)		305		327	
WT % @ 420 F	33.50	33.50	35.00	35.00	36.50
WT % @ 700 F	92.09	92.09	89.25	89.25	89.45

NEW FORMAT AUG 29,84

Table 24

RESULT OF SYNGAS OPERATION

RUN NO. 11677-18
CATALYST CoThU103+CuZnLZ105-6 250 CC 128.GM (146.3AFTER RUN+18.7G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11677-18-06	677-18-07	677-18-08	677-18-09	677-18-10
FEED H2:CO:AR	49:50: 0	49:50: 0	49:50: 0	49:50: 0	49:50: 0
HRS ON STREAM	70.08	74.08	93.5	98.5	115.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	261	261	261	261	261
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	27.00	4.00	23.42	5.00	21.50
EFFLNT GAS LITER	1223.06	176.02	1027.37	217.71	937.92
GM AQUEOUS LAYER	194.12	29.98	175.55	37.45	161.02
GM OIL	66.47	10.18	59.59	14.41	61.98
MATERIAL BALANCE					
GM ATOM CARBON %	95.72	93.94	94.80	95.41	96.45
GM ATOM HYDROGEN %	99.22	98.60	98.81	99.80	99.21
GM ATOM OXYGEN %	101.15	100.44	100.59	100.01	100.94
RATIO CHX/(H2O+CO2)	0.8198	0.7909	0.8141	0.8521	0.8558
RATIO X IN CHX	2.4784	2.4729	2.4707	2.4540	2.4387
USAGE H2/CO PRODT	2.1294	2.1663	2.1388	2.0940	2.0795
FEED H2/CO FRM EFFLNT	1.0039	1.0166	1.0094	1.0130	0.9962
RESIDUAL H2/CO RATIO	0.5555	0.5481	0.5370	0.5383	0.5233
RATIO CO2/(H2O+CO2)	0.0864	0.0835	0.0843	0.0844	0.0857
K SHIFT IN EFFLNT	0.0525	0.0500	0.0494	0.0496	0.0491
SPECIFIC ACTIVITY SA	0.8033	0.8353	0.8783	0.9153	0.9478
CONVERSION					
ON CO %	28.49	28.95	29.49	30.52	30.39
ON H2 %	60.43	61.69	62.49	63.08	63.43
ON CO+H2 %	44.49	45.46	46.07	46.90	46.88
PRDT SELECTIVITY,WT %					
CH4	18.31	17.96	17.84	17.04	16.15
C2 HC'S	2.87	2.75	2.75	2.66	2.70
C3H8	3.68	3.64	3.67	3.36	3.40
C3H6=	1.90	1.90	2.12	1.90	2.03
C4H10	3.22	3.21	3.37	3.13	3.15
C4H8=	2.88	2.92	2.92	2.84	2.94
C5H12	3.64	3.55	3.60	3.51	3.54
C5H10=	2.94	2.79	2.80	2.76	2.74
C6H14	3.90	3.82	3.99	3.72	3.90
C6H12= & CYCLO'S	2.11	1.97	2.09	1.92	1.93
C7+ IN GAS	11.02	10.34	11.03	9.64	10.20
LIQ HC'S	43.52	45.14	43.82	47.53	47.32
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 24 (continued)

SUB-GROUPING					
C1 -C4	32.87	32.39	32.66	30.92	30.36
C5 -420 F	39.49	39.40	39.95	37.08	37.78
420-700 F	23.04	23.74	23.05	25.58	25.47
700-END PT	4.59	4.47	4.34	6.42	6.39
C5+-END PT	67.13	67.61	67.34	69.08	69.64
ISO/NORMAL MOLE RATIO					
C4	0.0315	0.0266	0.0318	0.0315	0.0320
C5	0.0920	0.0920	0.0977	0.0890	0.0900
C6	0.0892	0.0997	0.0912	0.0949	0.1021
C4=	0.0956	0.0950	0.0999	0.0995	0.1064
PARAFFIN/OLEFIN RATIO					
C3	1.8453	1.8256	1.6536	1.6877	1.5968
C4	1.0804	1.0616	1.1153	1.0626	1.0337
C5	1.2035	1.2375	1.2498	1.2348	1.2563
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8310		0.8278		0.8426
RATIO CH4/(1-A)**2	6.4085		6.0185		6.5165
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY/SLD		CLDY/SLD		CLDY/SLD
DENSITY	0.7590		0.744		0.7465
N, REFRACTIVE INDEX	1.4255		1.4254		1.4271
SIMULT'D DISTILATN					
10 WT % @ DEG F	302		302		304
16	338		334		344
50	478		464		491
84	655		650		676
90	706		699		732
RANGE(16-84 %)	317		316		332
WT % @ 420 F	36.50	37.50	37.50	32.67	32.67
WT % @ 700 F	89.45	90.09	90.09	86.50	86.50

NEW FORMAT AUG 29,84

XII. Run 11 (11723-13) with Catalyst 11 (Co/Th/UCC-103+UCC-101+Cu/Zn/A)

In this catalyst, as in Catalyst 10, the Fischer-Tropsch and water gas shift components were made up in separate particles. The Fischer-Tropsch component was a typical Co/Th/UCC-103+UCC-101 catalyst. The water gas shift component consisted of a 5A zeolite loaded with a 2:1 mixture of zinc and copper, bonded with SiO_2, and formed as an extrudate. The pores of this zeolite are small enough so that the zinc and copper should be isolated from some of the Fischer-Tropsch products, while still being able to react with carbon monoxide and water. The ratio of Fischer-Tropsch to water gas shift components was 4:1, and the final catalyst contained 3.5 percent cobalt.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 132-135. Simulated distillations of the C_5^+ product are plotted in Figs. 136-143. Carbon number product distributions are plotted in Figs. 144-154. Chromatograms from simulated distillations are reproduced in Figs. 155-165. Detailed material balances appear in Tables 25-29.

As usual with cobalt catalysts containing water gas shift components, there was no water gas shift activity. The conversion activity was low, both absolutely and per gram cobalt.

These tests, in which this catalyst has been subjected to a variety of conditions, have yielded valuable information on how the specific activity term compensates for different ratios of hydrogen to carbon monoxide, and different reactor temperatures, to which the catalyst is exposed, as well as on its intrinsic activity. With a feed of 1:1 syngas (0.66:1 H_2:CO in the reactor), and at a reactor temperature of 263C, the catalyst converted 39 percent of the feed and had a specific activity of 0.54. When the feed ratio was changed to 2:1, and the ratio in the reactor nearly tripled to more than 1.8:1, the conversion increased to 70 percent. The specific activity term reacted to this drastic change in conditions by dropping only slightly to 0.43 (it should be independent of reaction conditions, and decrease only when the catalyst deactivates). When the reaction temperature was lowered 10C, the conversion dropped from 69 to 54 percent, and the specific activity again reacted by dropping only from 0.40 to 0.36. These findings highlight the value of the specific activity term, allowing comparison of catalysts exposed to different reaction temperatures and to different ratios of water to carbon monoxide.

The selectivity was not especially good. At 263C, with a 1:1 feed, the product was more than 17 percent methane; this rose to 30 percent when the feed was changed to 2:1. The C_5^+ was as high as 70 percent with the 1:1 feed, but fell to 52 percent when the feed was changed to 2:1. With about 5 percent of the product as heavies, the selectivity for motor fuel was as high as 66 percent, and the gasoline fraction was considerably larger than that

of diesel fuel.

The olefin content of the product varied strongly with the H_2:CO ratio in the reactor. At a 1:1 ratio, more than 60 percent of the C_4's were butenes; at the 2:1 ratio, this was cut in half. Lowering the reactor temperature resulted in a small increase in olefin content. There was a possible carbon number cut-off with the 1:1 feed, but not with the feed of 2:1.

This is not a promising catalyst. It has been useful, however, in bringing out the value of the specific activity in comparing catalysts with different usage ratios or tested under different conditions.

Fig. 132

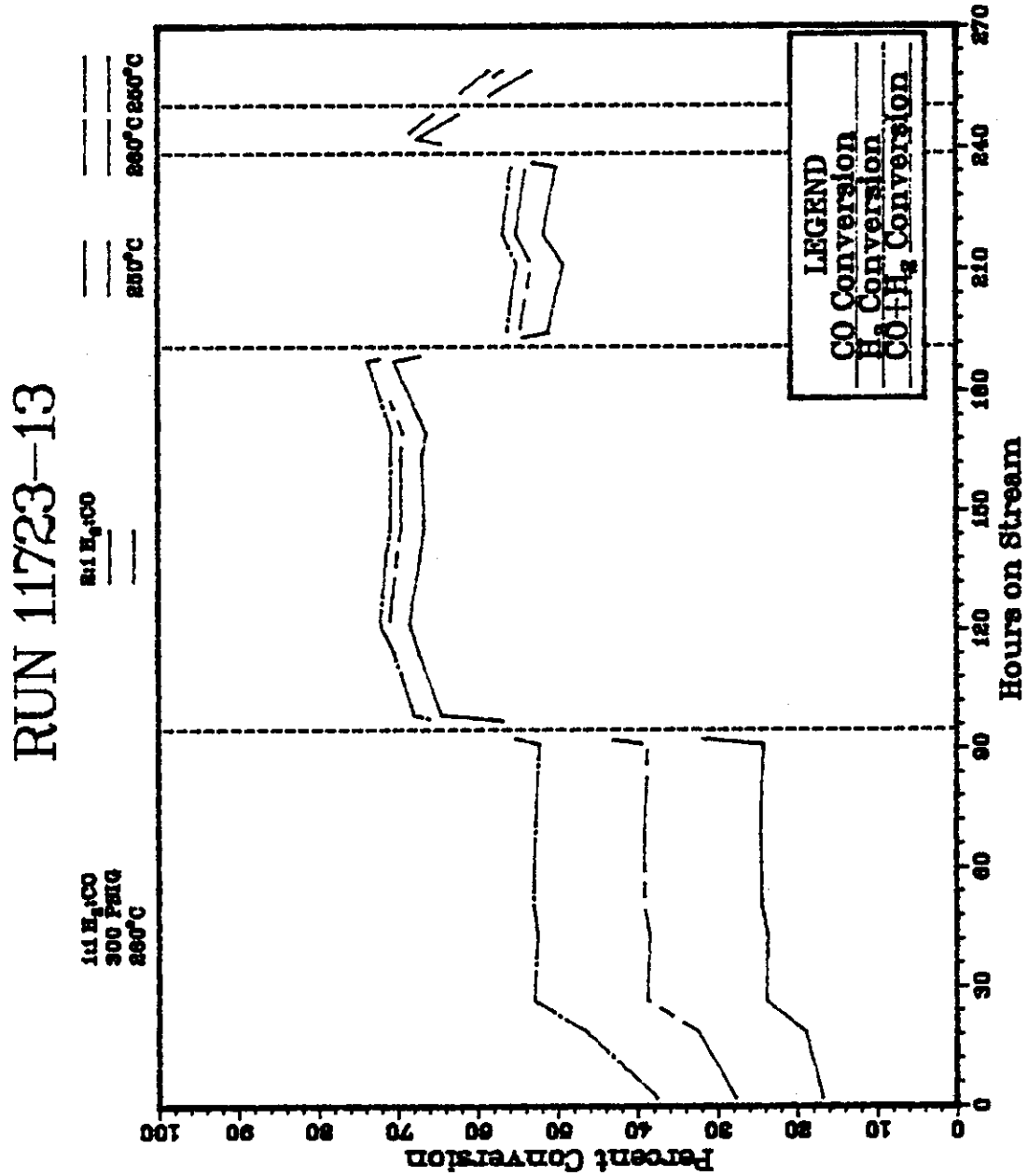
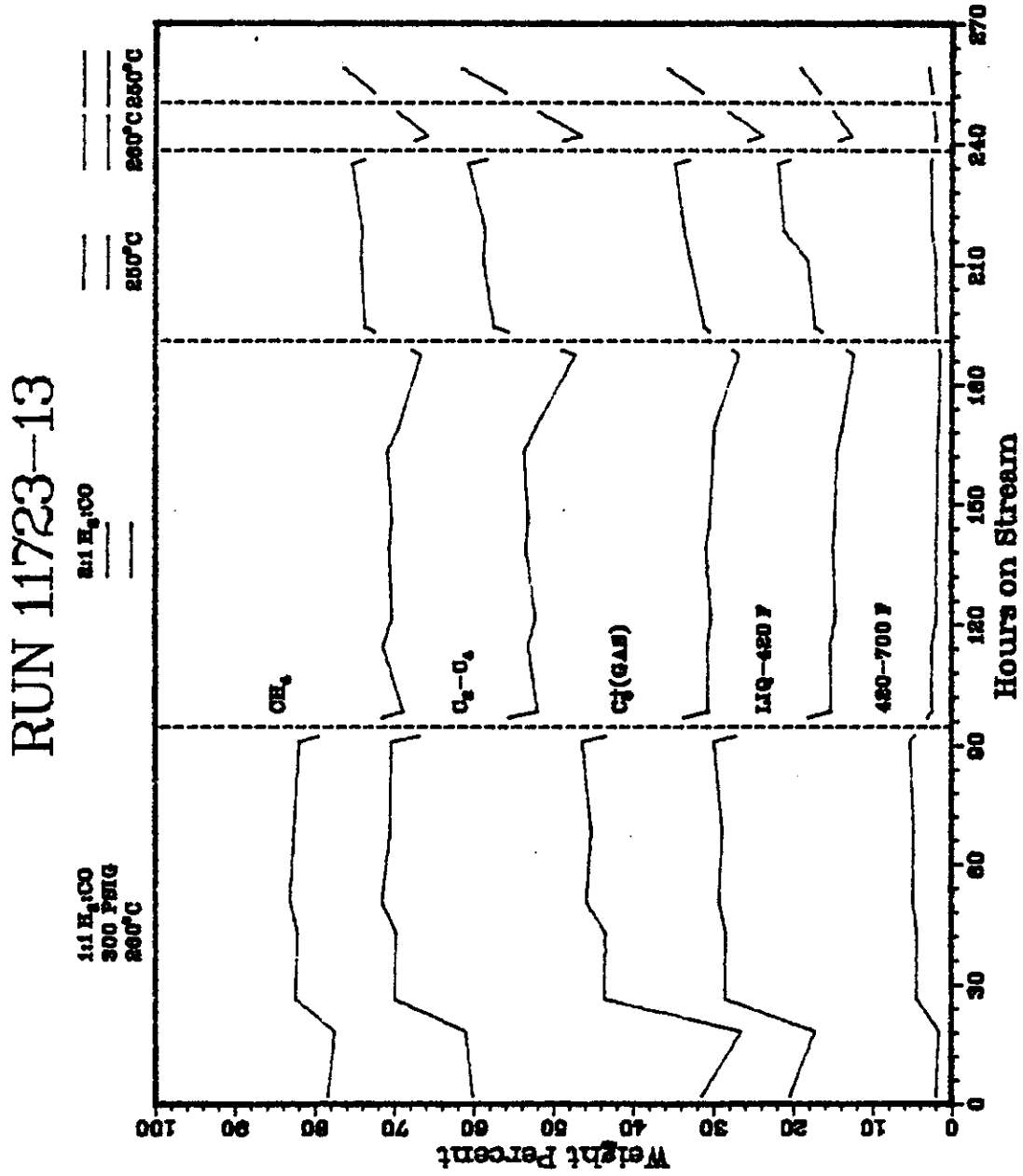

RUN 11723-13
LEGEND
CO Conversion
H_2 Conversion
$CO+H_2$ Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
1:1 H_2:CO
250°C
250°C 250°C
1:1 H_2:CO
300 PSIG
250°C

Fig. 133


RUN 11723-13
1:1 H2:CO
300 PSIG
260°C
2:1 H2:CO
250°C
250°C 250°C
CH4
C2-C4
C5(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270