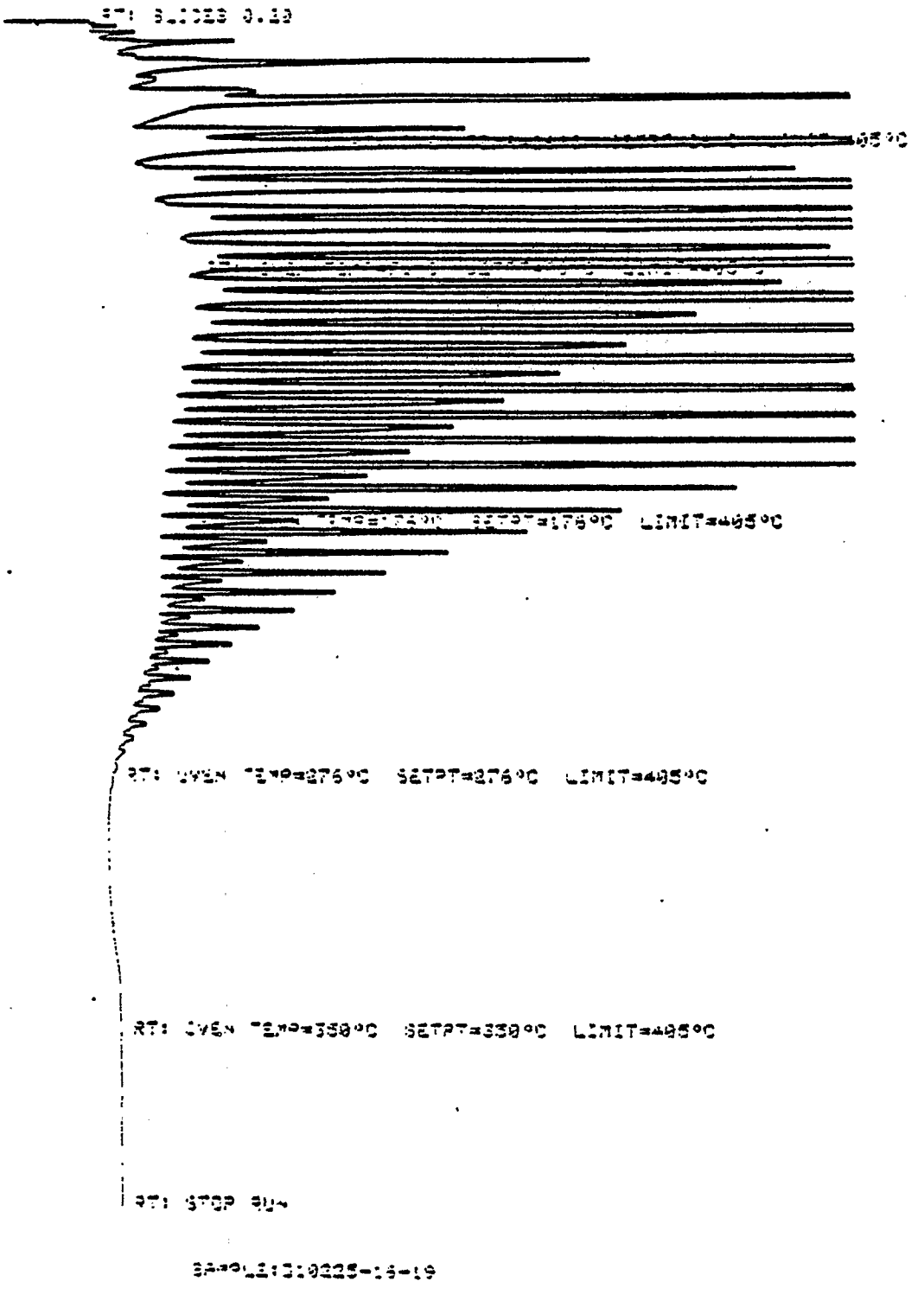
Fig. 125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RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

TABLE 13 RESULT OF SYNGAS OPERATION

RUN NO. 10225-16
CATALYST CO/TH÷UCC-103 11684-12C 80CC 37.9G (37.8 AFTER RUN -.1 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-16-01	225-16-02	225-16-03	225-16-04	225-16-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.5	27.0	43.0	51.0	67.5
PRESSURE,PSIG	295	292	296	295	291
TEMP. C	272	272	272	272	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.50	7.50	23.50	8.00	24.50
EFFLNT GAS LITER	170.65	61.90	197.60	68.25	210.90
GM AQUEOUS LAYER	48.67	18.58	58.21	21.05	64.46
GM OIL	26.00	10.24	32.09	10.70	32.76
MATERIAL BALANCE					
GM ATOM CARBON %	93.54	89.04	89.44	89.51	89.57
GM ATOM HYDROGEN %	98.20	94.85	95.19	96.02	97.06
GM ATOM OXYGEN %	96.79	91.01	90.25	91.90	91.26
RATIO CHX/(H2O+CO2)	0.9342	0.9578	0.9820	0.9478	0.9627
RATIO X IN CHX	2.5007	2.4683	2.4750	2.4583	2.4720
USAGE H2/CO PRODT	1.2848	1.3391	1.3878	1.4202	1.4456
RATIO CO2/(H2O+CO2)	0.4051	0.3725	0.3517	0.3231	0.3153
K SHIFT IN EFFLNT	0.27	0.24	0.21	0.18	0.18
CONVERSION					
ON CO %	70.87	69.40	67.12	64.87	64.48
ON H2 %	88.85	88.63	88.11	87.64	87.28
ON CO+H2 %	80.08	79.32	77.94	76.65	76.33
PRDT SELECTIVITY,WT %					
CH4	20.71	19.59	20.03	19.26	19.89
C2 HC'S	3.61	3.36	3.42	3.34	3.34
C3H8	4.77	4.19	4.06	3.91	4.00
C3H6=	1.63	1.54	1.49	1.58	1.53
C4H10	4.00	3.62	3.53	3.53	3.54
C4H8=	1.23	2.59	2.59	2.66	2.63
C5H12	4.75	4.33	4.26	4.22	4.30
C5H10=	1.95	1.84	1.82	1.88	1.88
C6H14	5.92	5.39	5.26	5.32	5.36
C6H12= & CYCLO'S	1.55	1.45	1.50	1.51	1.59
C7+ IN GAS	9.70	9.25	8.92	9.61	9.00
LIQ HC'S	40.19	42.86	43.13	43.17	42.92
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	35.95	34.88	35.12	34.29	34.94
C5 -420 F	47.75	45.76	45.40	46.14	45.60
420-700 F	15.22	17.30	17.41	17.16	17.07
700-END PT	1.08	2.06	2.07	2.40	2.39
C5+-END PT	64.05	65.12	64.88	65.71	65.06
ISO/NORMAL MOLE RATIO					
C4	0.0244	0.0236	0.0242	0.0246	0.0238
C5	0.1079	0.1050	0.1078	0.1022	0.1078
C6	0.3000	0.2989	0.3064	0.3002	0.3087
C4=	0.5027	0.1711	0.1739	0.1675	0.1729
PARAFFIN/OLEFIN RATIO					
C3	2.7932	2.6012	2.5963	2.3579	2.4957
C4	3.1539	1.3454	1.3154	1.2785	1.3012
C5	2.3633	2.2937	2.2711	2.1800	2.2281
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7776		0.8044		0.8047
RATIO CH4/(1-A)**2	4.1874		5.2355		5.2161
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.748		0.750		0.751
N, REFRACTIVE INDEX	1.4176		1.4200		1.4198
SIMULT'D DISTILATN					
10 WT % @ DEG F	255		258		258
16	263		288		290
50	391		410		410
84	544		586		590
90	599		642		647
RANGE(16-84 %)	281		298		300
WT % @ 420 F	59.44	54.83	54.83	54.67	54.67
WT % @ 700 F	97.32	95.20	95.20	94.43	94.43

TABLE 14 RESULT OF SYNGAS OPERATION

RUN NO. 10225-16
CATALYST CO/TH+UCC-103 11684-12C 80CC 37.9G (37.8 AFTER RUN -.1 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-16-06	225-16-07	225-16-09	225-16-11	225-16-12
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	74.0	91.5	116.3	139.5	144.8
PRESSURE,PSIG	298	298	302	299	298
TEMP. C	272	272	272	272	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.50	24.00	24.75	23.25	5.25
EFFLNT GAS LITER	57.15	210.80	241.24	228.23	48.65
GM AQUEOUS LAYER	17.49	64.59	67.53	64.00	14.54
GM OIL	8.63	31.88	31.83	25.61	6.54
MATERIAL BALANCE					
GM ATOM CARBON %	90.73	91.68	97.03	94.14	92.13
GM ATOM HYDROGEN %	97.63	99.14	101.91	99.21	98.14
GM ATOM OXYGEN %	92.88	91.90	98.79	98.08	94.87
RATIO CHX/(H2O+CO2)	0.9525	0.9951	0.9619	0.9129	0.9383
RATIO X IN CHX	2.4665	2.4599	2.5047	2.5215	2.4844
USAGE H2/CO PRODT	1.4618	1.4893	1.4819	1.5121	1.5368
RATIO CO2/(H2O+CO2)	0.3037	0.2966	0.3025	0.2805	0.2666
K SHIFT IN EFFLNT	0.16	0.16	0.16	0.14	0.13
CONVERSION					
ON CO %	62.91	63.38	60.19	57.26	58.13
ON H2 %	87.08	87.46	86.21	85.15	86.00
ON CO+H2 %	75.44	75.89	73.52	71.57	72.51
PROT SELECTIVITY,WT %					
CH4	19.64	19.43	21.42	22.06	20.57
C2 HC'S	3.31	3.28	3.61	3.79	3.44
C3H8	3.94	3.85	4.35	4.42	4.16
C3H6=	1.62	4.59	1.68	1.80	1.72
C4H10	3.53	3.41	3.81	4.00	3.69
C4H8=	2.70	2.54	2.67	2.93	2.71
C5H12	4.34	4.21	3.98	4.25	3.88
C5H10=	1.97	1.81	1.79	2.12	1.80
C6H14	5.31	5.17	5.10	5.36	5.00
C6H12= & CYCLO'S	1.55	1.49	1.02	1.52	1.02
C7+ IN GAS	9.20	8.75	10.25	10.55	10.32
LIQ HC'S	42.87	41.47	40.33	37.18	41.69
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.75	37.10	37.53	39.01	36.29
C5 -420 F	45.40	43.71	43.80	43.64	44.41
420-700 F	16.90	16.34	15.81	14.24	16.25
700-END PT	2.95	2.85	2.86	3.11	3.05
C5+-END PT	65.25	62.90	62.47	60.99	63.71
ISO/NORMAL MOLE RATIO					
C4	0.0227	0.0252	0.0000	0.0225	0.0000
C5	0.1017	0.1052	0.0982	0.0967	0.0928
C6	0.2973	0.2938	0.3312	0.3091	0.3180
C4=	0.1696	0.1751	0.1796	0.1756	0.1749
PARAFFIN/OLEFIN RATIO					
C3	2.3185	0.8011	2.4755	2.3372	2.3095
C4	1.2618	1.2935	1.3759	1.3183	1.3165
C5	2.1409	2.2600	2.1594	1.9477	2.0919
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8075	0.8098	0.8111	
RATIO CH4/(1-A)**2		5.2449	5.9207	6.1820	
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLR OIL	CLR OIL	CLR OIL	
DENSITY		0.748	0.750	0.753	
N, REFRACTIVE INDEX		1.4201	1.4206	1.4208	
SIMULT'D DISTILATN					
10 WT % @ DEG F		258	257	258	
16		290	291	293	
50		411	411	411	
84		601	601	619	
90		662	665	678	
RANGE(16-84 %)		311	310	326	
WT % @ 420 F	53.71	53.71	53.71	53.33	53.71
WT % @ 700 F	93.12	93.12	92.92	91.64	92.69

TABLE 15 RESULT OF SYNGAS OPERATION

RUN NO. 10225-16
CATALYST CO/TH+UCC-103 11684-12C 80CC 37.9GM(37.8 AFTER RUN -.1 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-16-13	225-16-14	225-16-15	225-16-16	225-16-17
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	163.5	171.0	187.5	195.0	211.5
PRESSURE,PSIG	296	294	302	302	292
TEMP. C	272	272	272	272	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	7.50	24.00	7.50	24.00
EFFLNT GAS LITER	235.88	68.85	218.65	66.10	217.70
GM AQUEOUS LAYER	66.49	20.80	66.55	20.96	67.09
GM OIL	29.91	9.64	30.84	9.25	29.59
MATERIAL BALANCE					
GM ATOM CARBON %	96.36	91.34	91.69	88.62	89.89
GM ATOM HYDROGEN %	102.31	98.64	99.21	96.76	98.39
GM ATOM OXYGEN %	97.25	92.84	92.58	90.75	92.04
RATIO CHX/(H2O+CO2)	0.9800	0.9654	0.9796	0.9508	0.9506
RATIO X IN CHX	2.4867	2.4649	2.4686	2.4574	2.4778
USAGE H2/CO PRODT	1.5507	1.5724	1.5728	1.5821	1.5800
RATIO CO2/(H2O+CO2)	0.2679	0.2506	0.2536	0.2421	0.2468
K SHIFT IN EFFLNT	0.14	0.12	0.12	0.12	0.12
CONVERSION					
ON CO %	57.84	57.96	58.76	58.27	58.11
ON H2 %	85.15	85.59	86.12	86.18	85.62
ON CO+H2 %	71.91	72.30	72.98	72.83	72.49
PROT SELECTIVITY,WT %					
CH4	20.50	19.71	19.63	19.23	20.14
C2 HC'S	3.46	3.33	3.31	3.29	3.45
C3H8	4.20	3.96	4.23	4.01	4.06
C3H6=	1.75	1.67	1.97	1.89	1.62
C4H10	3.85	3.61	4.03	3.55	3.64
C4H8=	2.78	2.65	2.93	2.75	2.65
C5H12	4.20	3.89	3.93	4.13	4.26
C5H10=	1.94	1.85	1.30	2.08	1.94
C6H14	5.28	5.08	5.17	5.06	5.18
C6H12= & CYCLO'S	1.50	1.43	1.41	1.40	1.48
C7+ IN GAS	10.81	10.09	10.15	10.74	10.07
LIQ HC'S	39.72	42.73	41.93	41.87	41.50
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	36.54	34.94	36.10	34.72	35.57
C5 -420 F	45.07	45.41	44.61	45.88	45.20
420-700 F	15.48	16.59	16.28	16.37	16.23
700-END PT	2.90	3.06	3.01	3.03	3.00
C5+-END PT	63.46	65.06	63.90	65.28	64.43
ISO/NORMAL MOLE RATIO					
C4	0.0221	0.0229	0.0405	0.0237	0.0228
C5	0.0910	0.0944	0.1072	0.1087	0.1040
C6	0.2997	0.3047	0.3103	0.3114	0.3004
C4=	0.1752	0.1746	0.1839	0.1728	0.1788
PARAFFIN/OLEFIN RATIO					
C3	2.2890	2.2633	2.0418	2.0265	2.3881
C4	1.3376	1.3131	1.3266	1.2478	1.3287
C5	2.1021	2.0435	2.9388	1.9315	2.1333
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8088		0.8101		0.8092
RATIO CH4/(1-A)**2	5.6061		5.4462		5.5349
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.752		0.751		0.752
N, REFRACTIVE INDEX	1.4200		1.4201		1.4205
SIMULT'D DISTILATN					
10 WT % @ DEG F	258		258		258
16	293		293		296
50	411		410		411
84	603		599		599
90	667		664		665
RANGE(16-84 %)	310		306		303
WT % @ 420 F	53.71	54.00	54.00	53.67	53.67
WT % @ 700 F	92.69	92.83	92.83	92.77	92.77

TABLE 16 RESULT OF SYNGAS OPERATION

RUN NO. 10225-16
CATALYST CO/TH÷UCC-103 11684-12C 80CC 37.9GM(37.8 AFTER RUN -.1 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-16-18	225-16-19
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	219.0	235.5
PRESSURE,PSIG	299	297
TEMP. C	272	272
FEED CC/MIN	400	400
HOURS FEEDING	7.50	24.00
EFFLNT GAS LITER	70.45	223.60
GM AQUEOUS LAYER	20.83	66.64
GM OIL	8.43	26.97
MATERIAL BALANCE		
GM ATOM CARBON %	91.03	90.45
GM ATOM HYDROGEN %	97.96	98.18
GM ATOM OXYGEN %	93.71	93.08
RATIO CHX/(H2O+CO2)	0.9381	0.9395
RATIO X IN CHX	2.4921	2.5037
USAGE H2/CO PRODT	1.5844	1.5859
RATIO CO2/(H2O+CO2)	0.2452	0.2468
K SHIFT IN EFFLNT	0.12	0.12
CONVERSION		
ON CO %	56.32	56.92
ON H2 %	85.08	85.28
ON CO+H2 %	71.22	71.68
PRDT SELECTIVITY,WT %		
CH4	20.69	21.15
C2 HC'S	3.49	3.73
C3H8	4.26	4.45
C3H6=	1.83	1.92
C4H10	3.78	3.86
C4H8=	2.83	2.73
C5H12	4.49	4.41
C5H10=	1.94	2.14
C6H14	5.38	5.37
C6H12= & CYCLO'S	1.50	1.49
C7+ IN GAS	11.25	10.35
LIQ HC'S	38.56	38.40
TOTAL	100.00	100.00

SUB-GROUPING		
C1 -C4	36.89	37.84
C5 -420 F	45.43	44.55
420-700 F	14.93	14.87
700-END PT	2.76	2.75
C5+-END PT	63.11	62.16
ISO/NORMAL MOLE RATIO		
C4	0.0230	0.0260
C5	0.1015	0.1063
C6	0.2981	0.3122
C4=	0.1737	0.1787
PARAFFIN/OLEFIN RATIO		
C3	2.2184	2.2126
C4	1.2883	1.3656
C5	2.2446	2.0009
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))		0.8052
RATIO CH4/(1-A)**2		5.5730
LIQ HC COLLECTION		
PHYS. APPEARANCE		CLR OIL
DENSITY		0.752
N, REFRACTIVE INDEX		1.4204
SIMULT'D DISTILATN		
10 WT % @ DEG F		258
16		296
50		410
84		598
90		663
RANGE(16-84 %)		302
WT % @ 420 F	54.14	54.14
WT % @ 700 F	92.85	92.85

IX. Run 8 (10225-17) with Catalyst 8 (Co/Th + UCC-103)

This catalyst is the same as Catalyst 7 except that it was formed into 1/16-inch, instead of 1/8-inch, extrudates to investigate possible mass transfer problems.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 126-129. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 130-131. Carbon number product distributions are plotted in Figs. 132-136. Chromatograms from simulated distillations are reproduced in Figs. 137-141. Detailed material balances appear in Tables 17-18.

The initial activity of this catalyst was extremely high, with about 90 percent conversion of the $CO+H_2$ syngas. The water gas shift activity was also very high initially, with 63 percent of the oxygen rejected as CO_2. The initial usage of the 1:1 H_2:CO feed was ideal at a ratio of 1.0:1. The conversion fell off rapidly, however, to stabilize at about 73 percent, nearly all the loss due to deactivation of the CO conversion while the H_2 conversion was remaining relatively stable. The water gas shift activity dropped sharply, to less than 20 percent of the oxygen rejected as CO_2 (lower than that for Catalyst 7). The usage ratio rose to 1.7:1--higher than that for Catalyst 7, but not as high as the loss of water gas shift activity would indi-

cate, since the hydrocarbon products were growing steadily less hydrogen-rich with time. Despite its high initial activity, therefore, the net overall activity of this catalyst was little different from that of Catalyst 7. The greatest difference between the two was in their water gas shift activities.

The selectivity was poor at the start of the run, yielding a product predominant in lights: 35 percent methane, high in C_2-C_4, and only about 40 percent total motor fuels, most of which was gasoline. It improved rapidly, however, so that by about 60 hours on stream methane production had dropped to the more nearly normal level of 20 percent, and C_2-C_4 production to the usual low level for a cobalt catalyst. Production of motor fuels, meanwhile, rose to 63 percent--almost the same as that of Catalyst 7 and much higher than that of the reference catalyst (Tenth Quarter Run 10112-15). Isomerization of the pentanes, initially slight, fell off even further to the same low level as with Catalyst 7. Olefinic content of the C_4, initially low, stabilized at a level above that of Catalyst 7 but below the level of most cobalt catalysts. The liquid product was poorly isomerized, and does not show a carbon number cut-off.

The final activity of this catalyst is similar to that of Catalyst 7, the principal difference being its much higher initial activity. If there is a diffusion restriction due to the larger extrudate of Catalyst 7, it lowers the initial activity but improves the stability.

Fig. 126

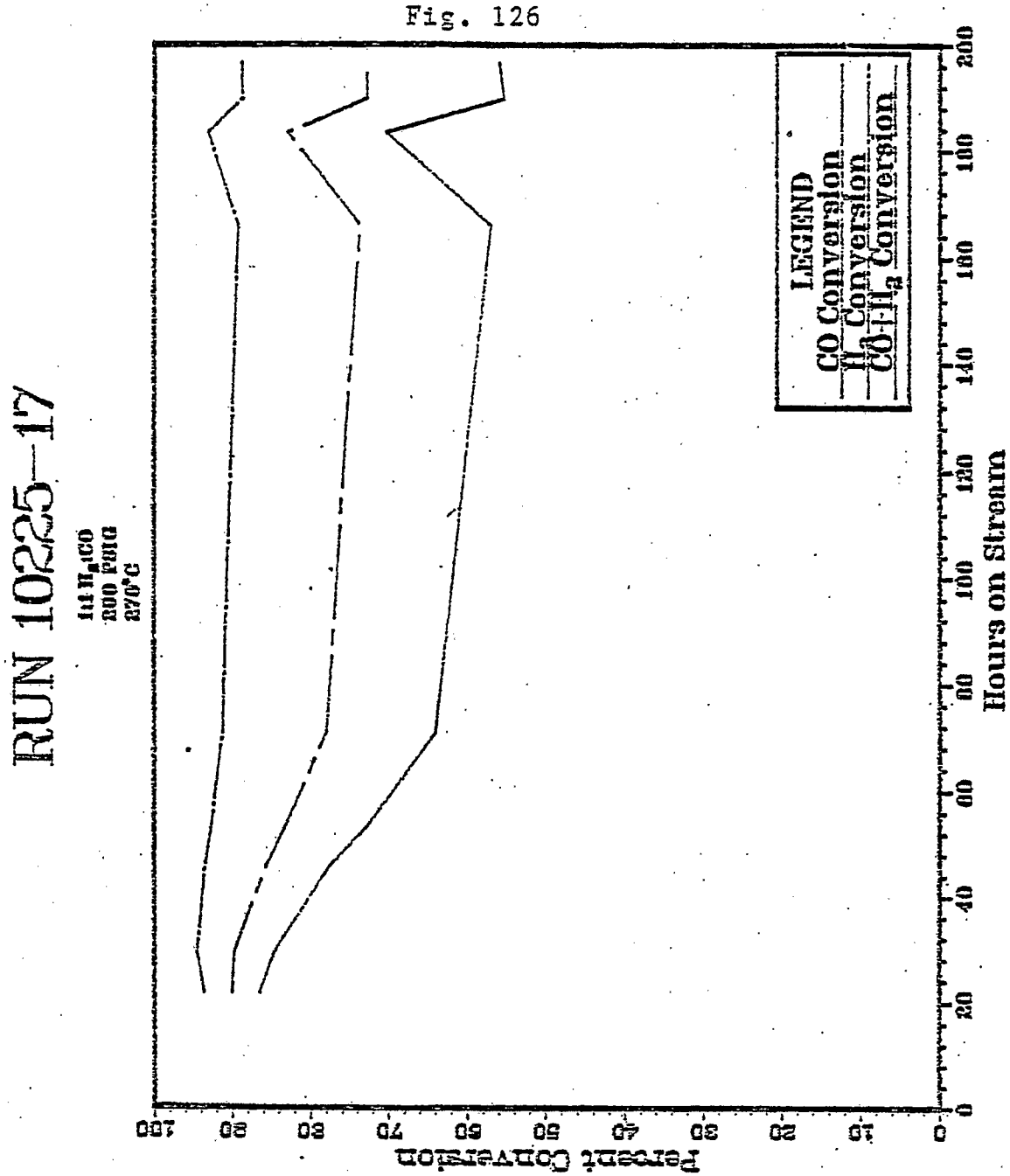
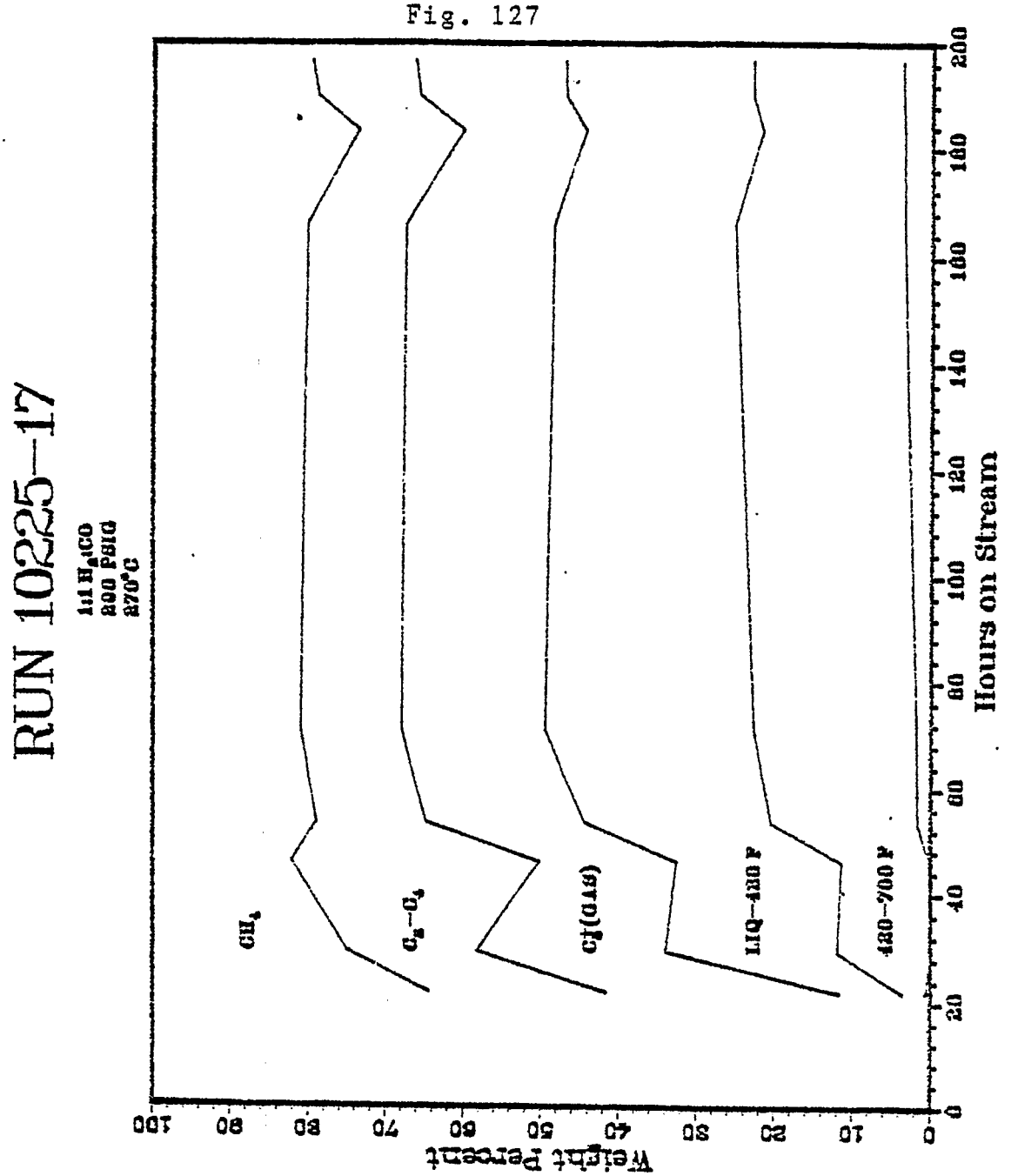

RUN 10225-17
1:1 H_2:CO
200 Psig
270°C
LEGEND
CO Conversion
H_2 Conversion
CO+H_2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 127


RUN 10225-17
1:1 H2:CO
200 Psig
270°C
CH4
C2-C4
C5(GAS)
LIQ-430 F
430-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

RUN 10225-17

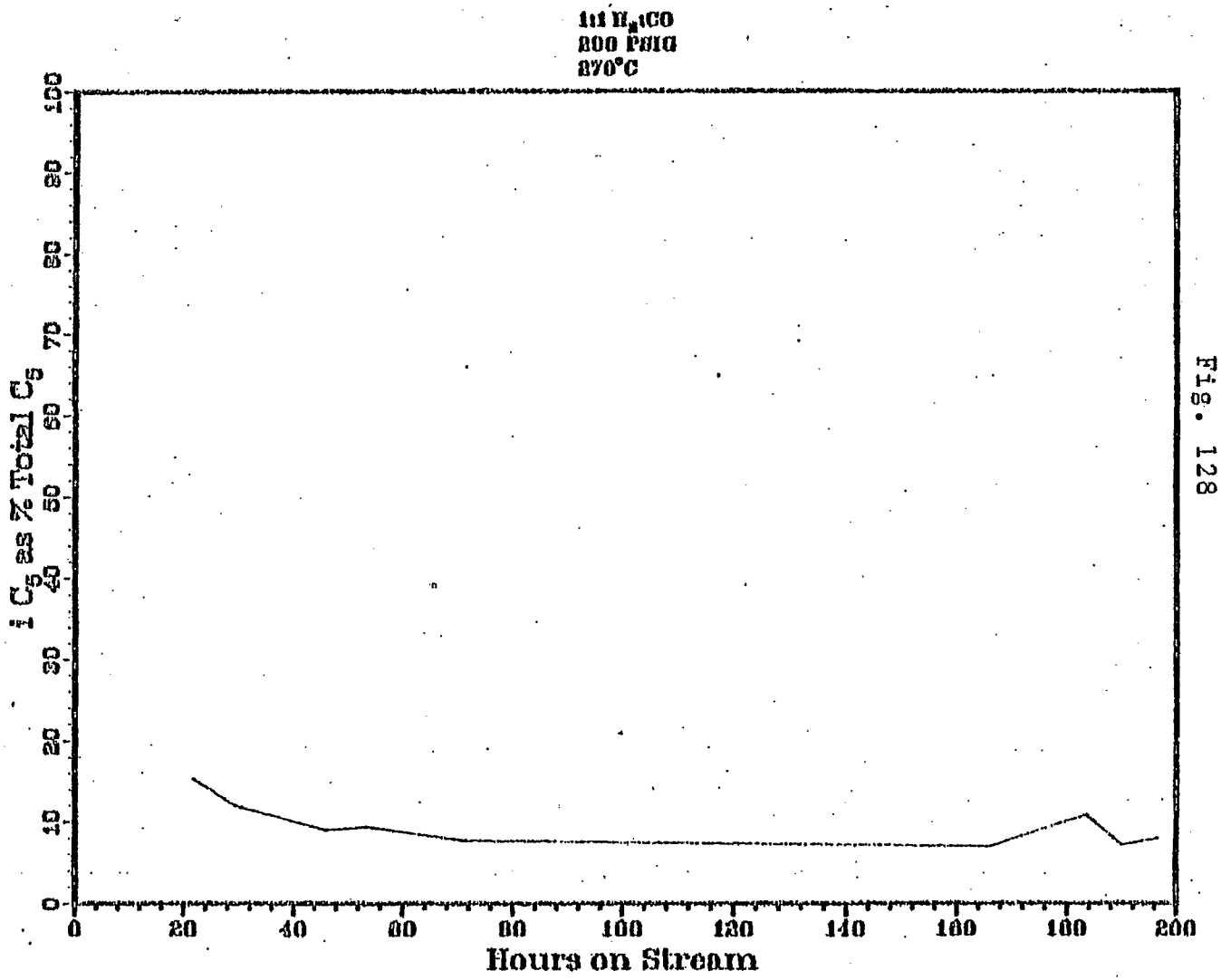


Fig. 128

Fig. 129

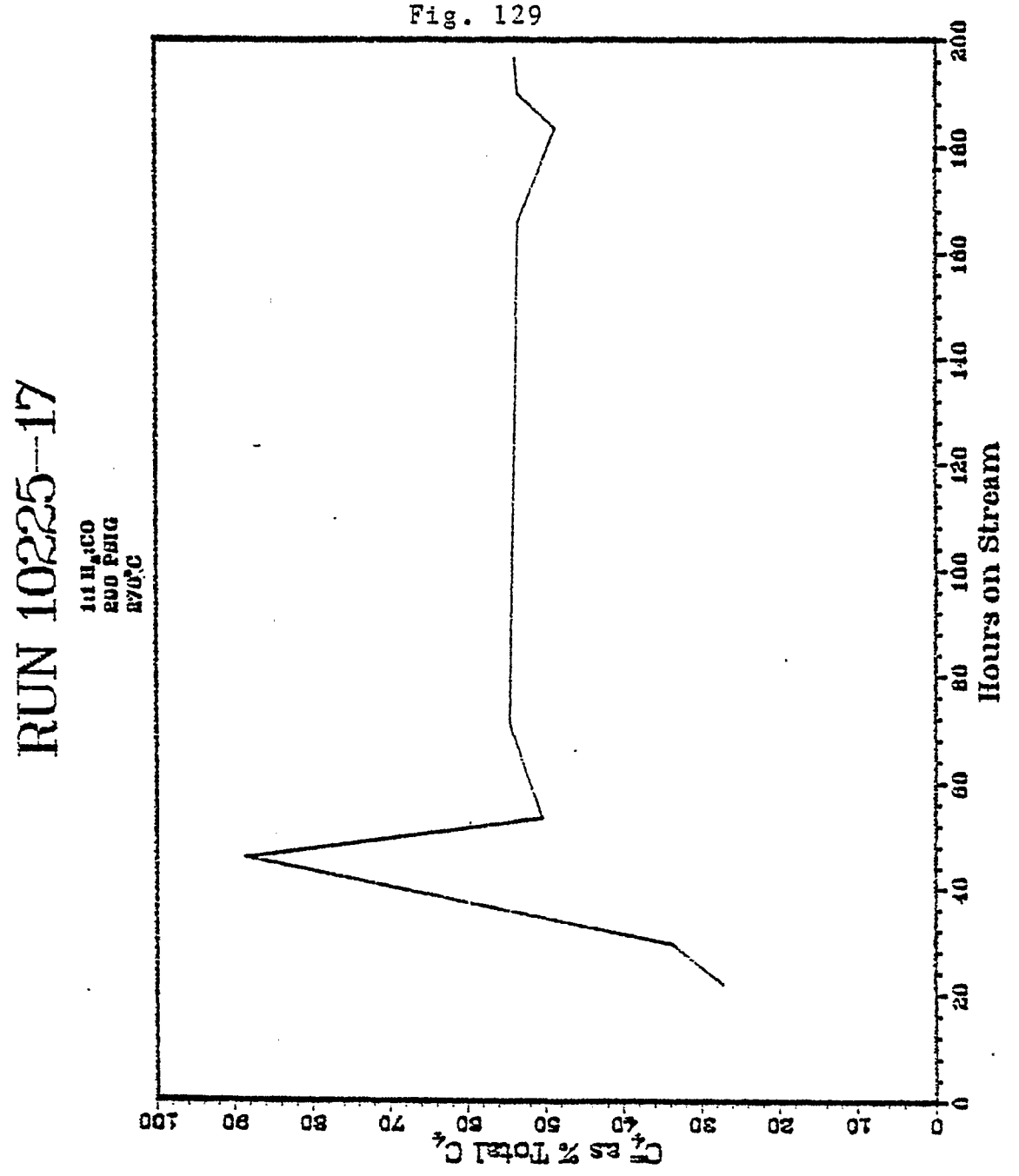

RUN 10225--17
1:1 H2:CO
200 PSIG
270°C
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
140
160
180
200

Fig. 130

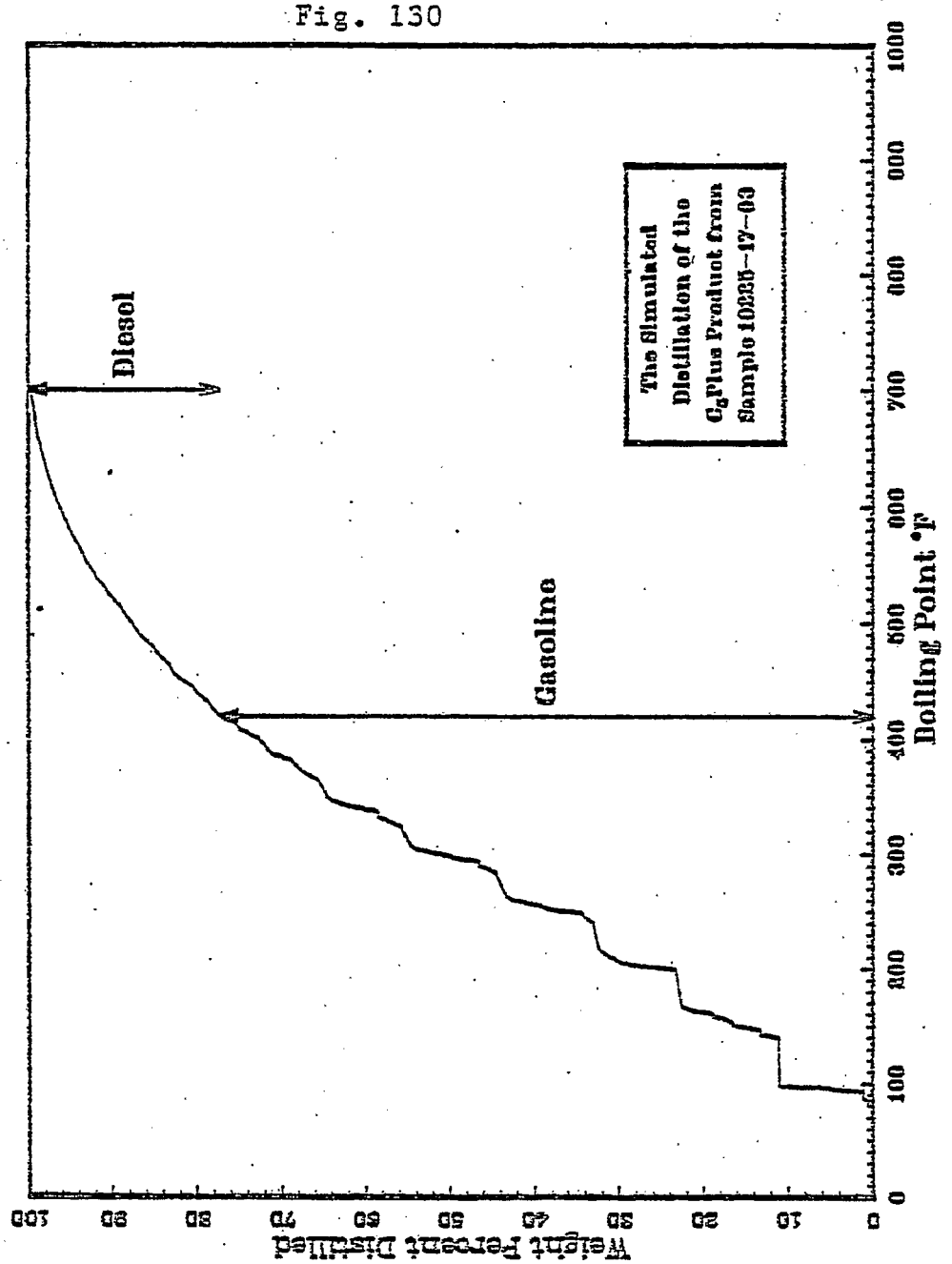

The Simulated Distillation of the C6 Plus Product from Sample 102285-17-03
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 131

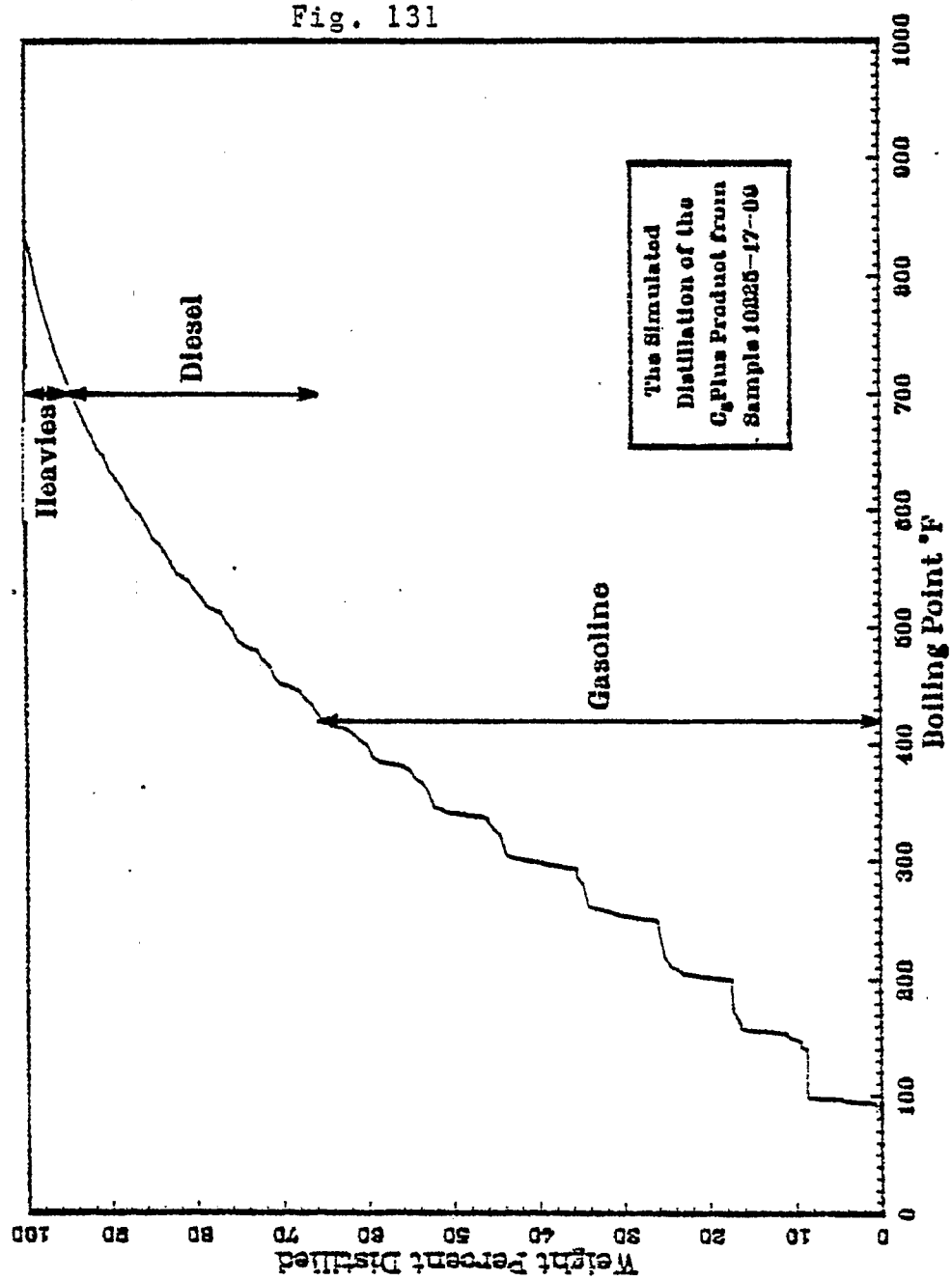
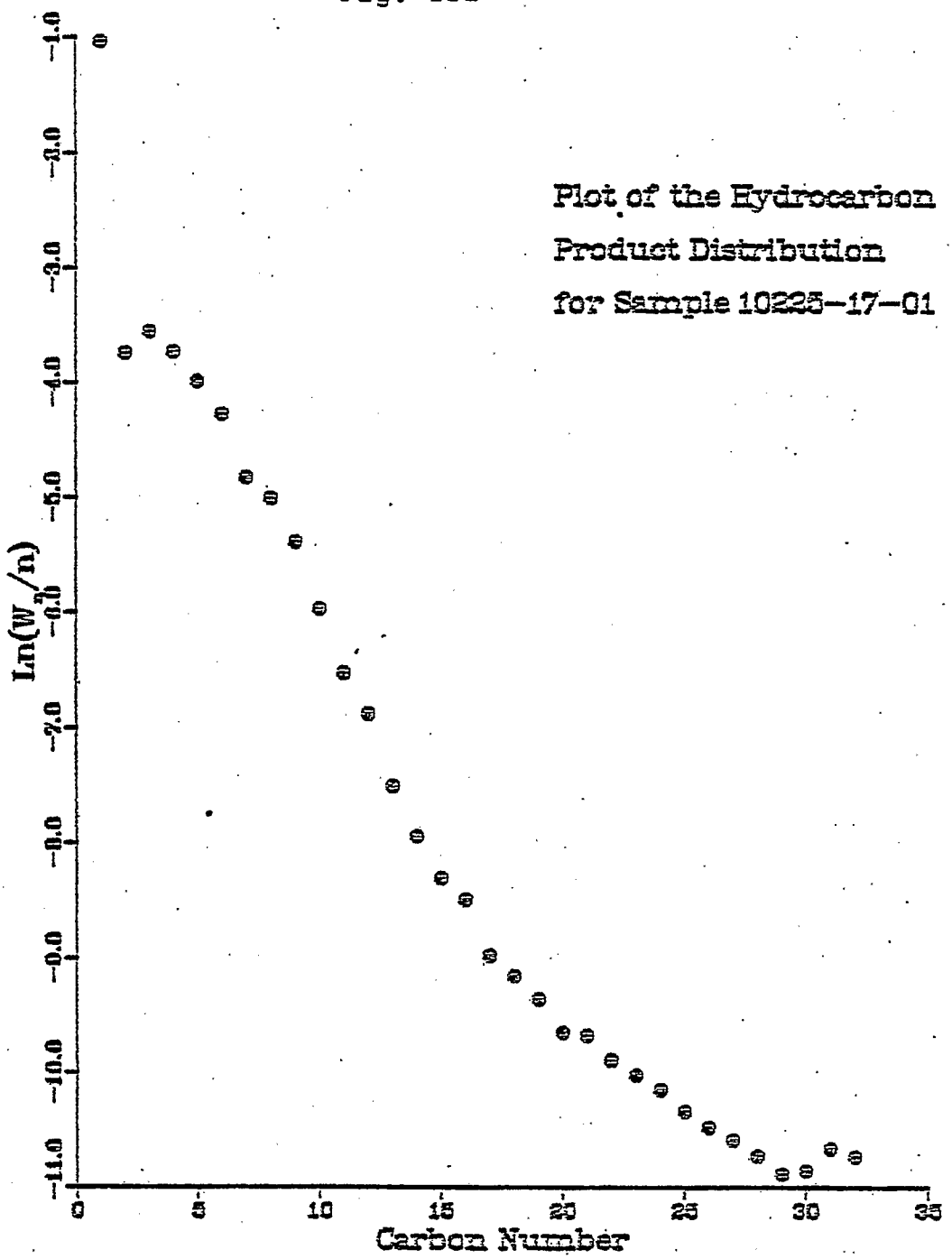

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10225-17-09
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 132



Plot of the Hydrocarbon Product Distribution for Sample 10225-17-01

Fig. 133

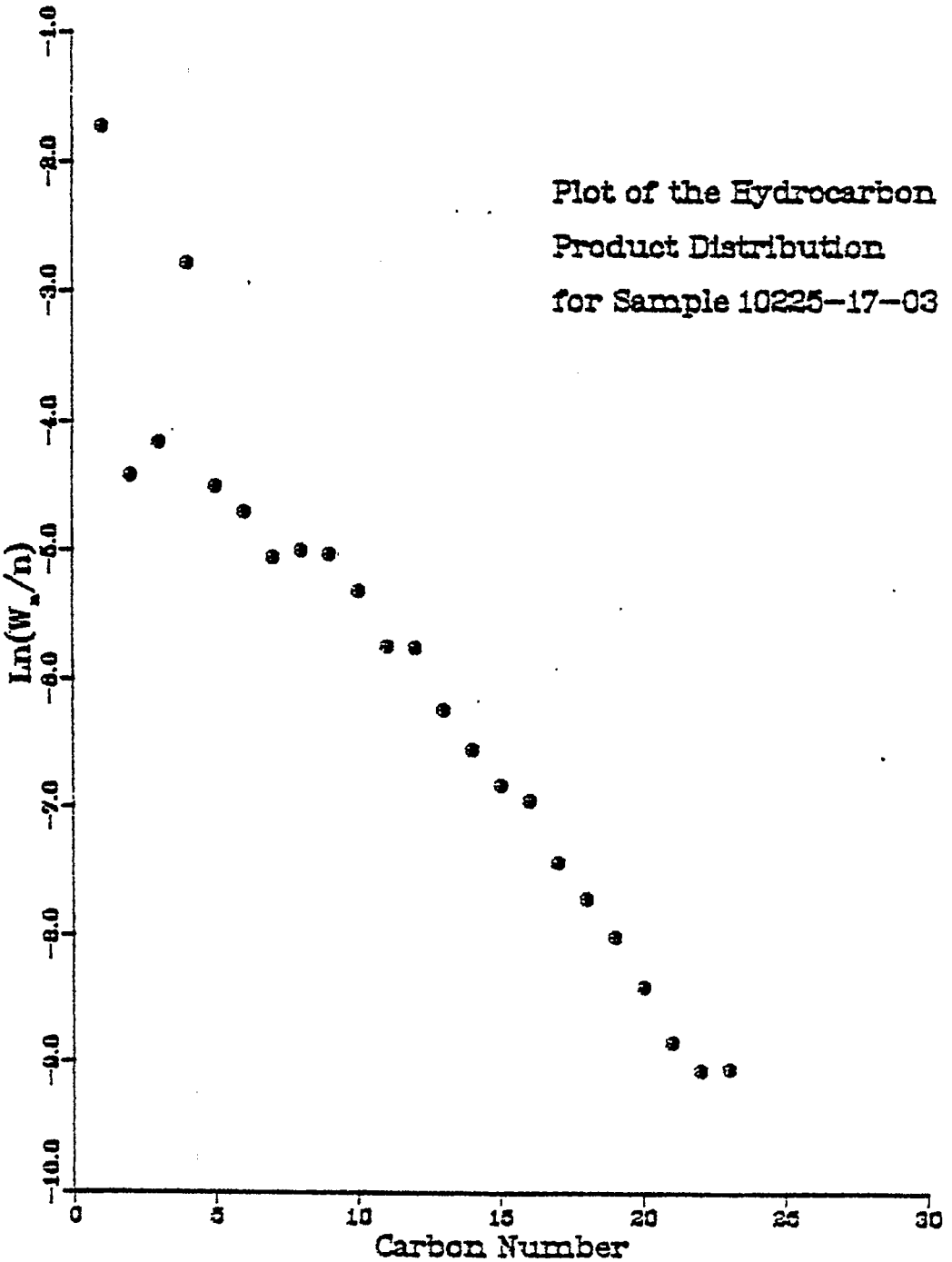

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-17-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 134

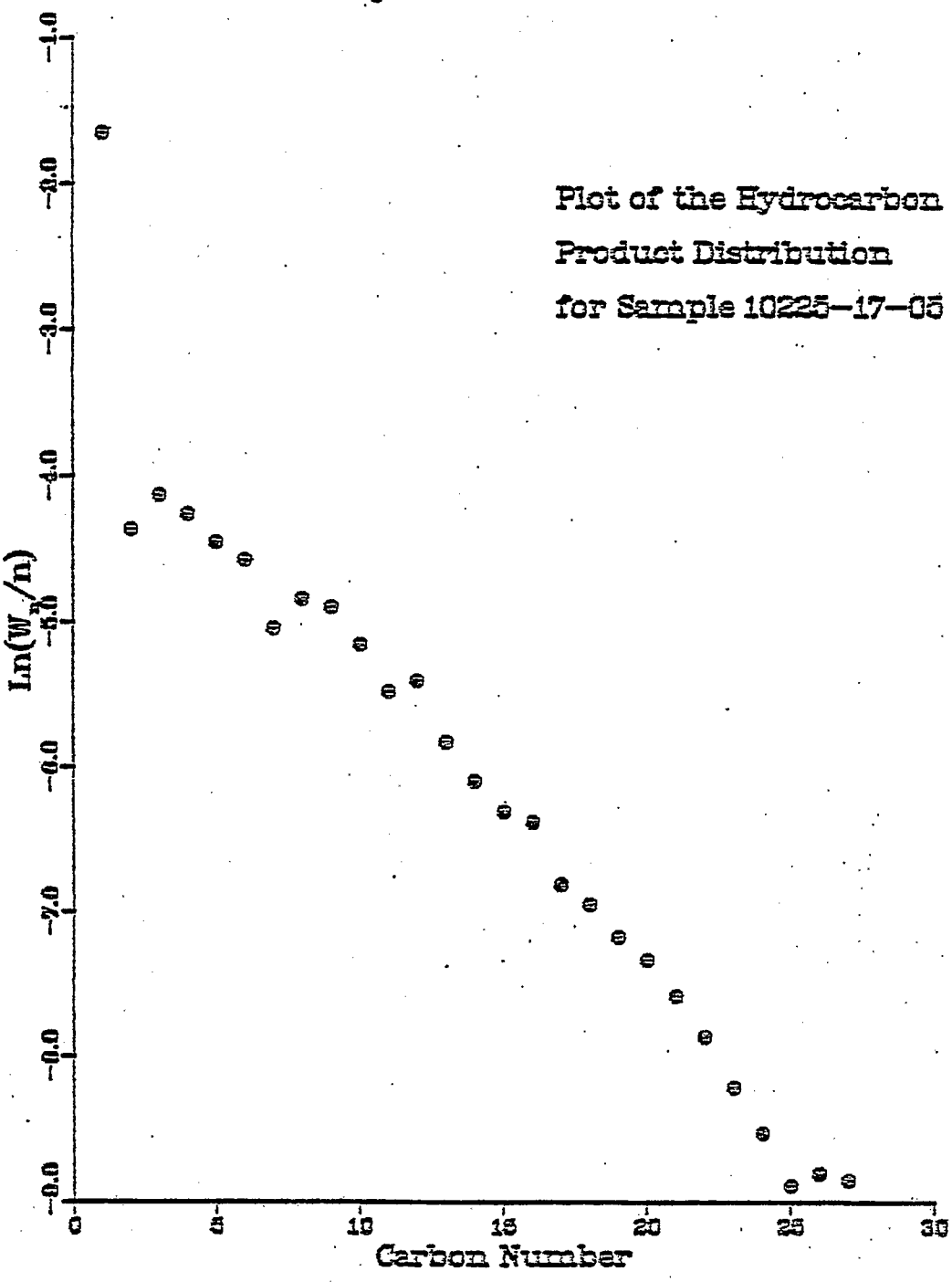

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-17-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. 135

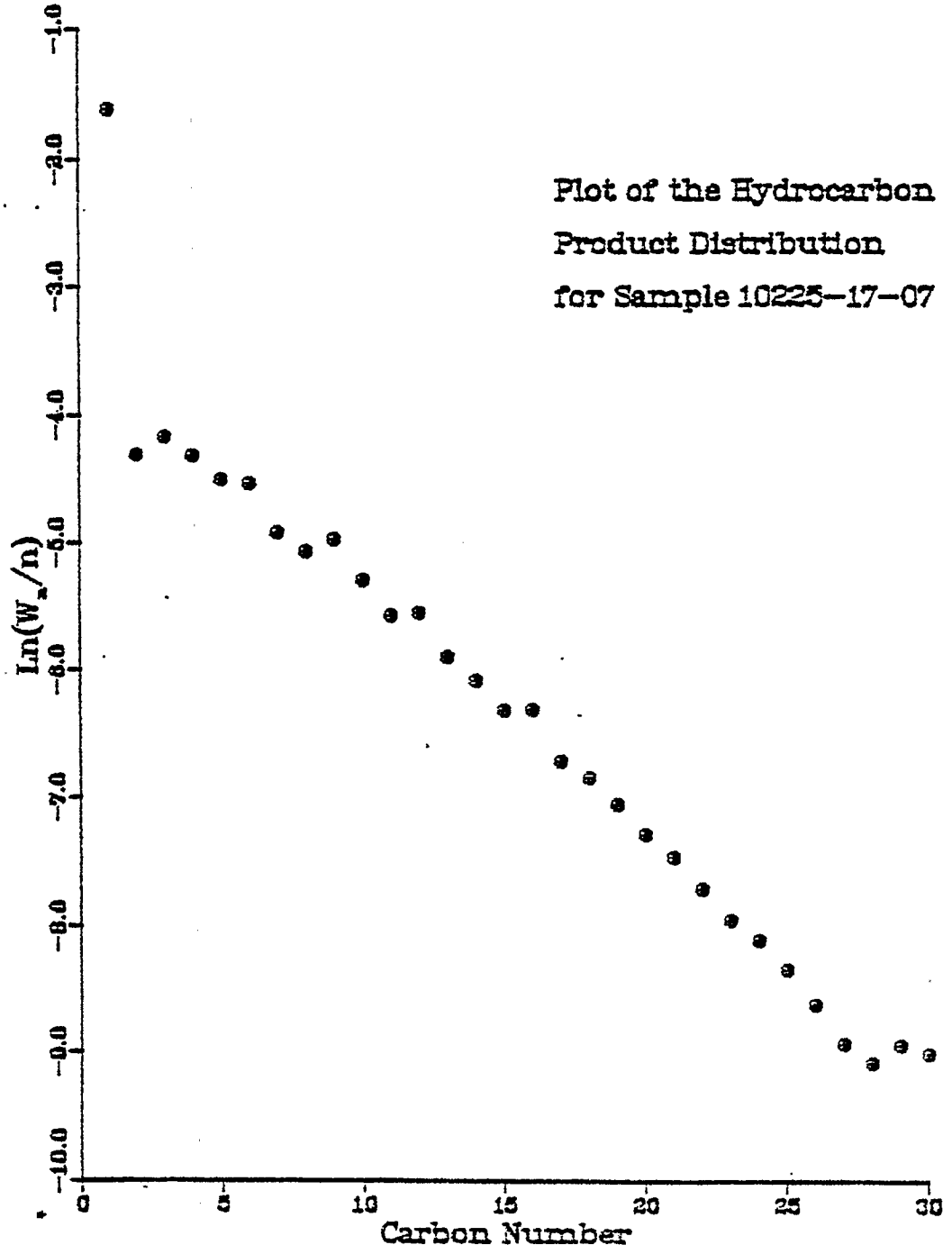

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-17-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 136

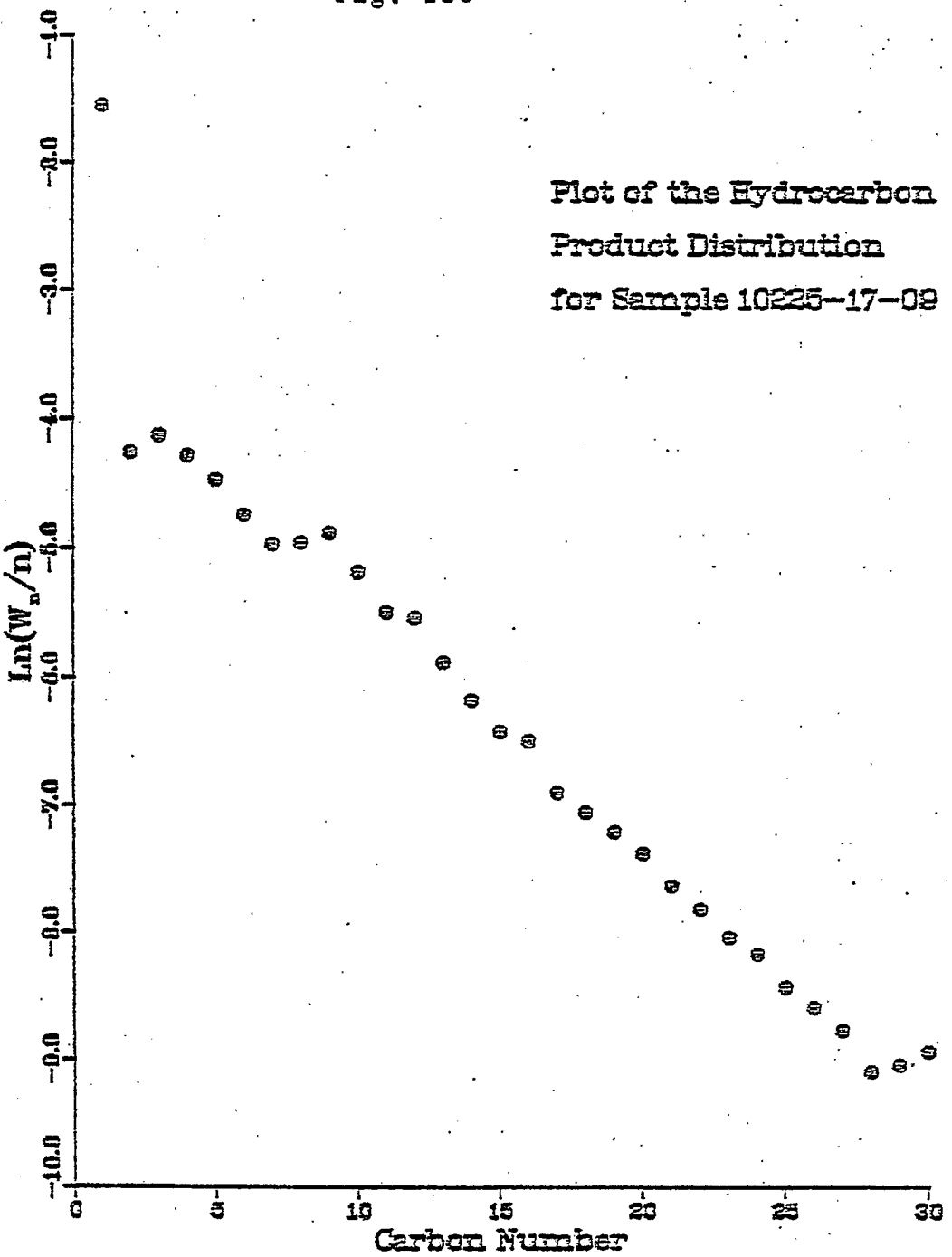

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-17-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 137

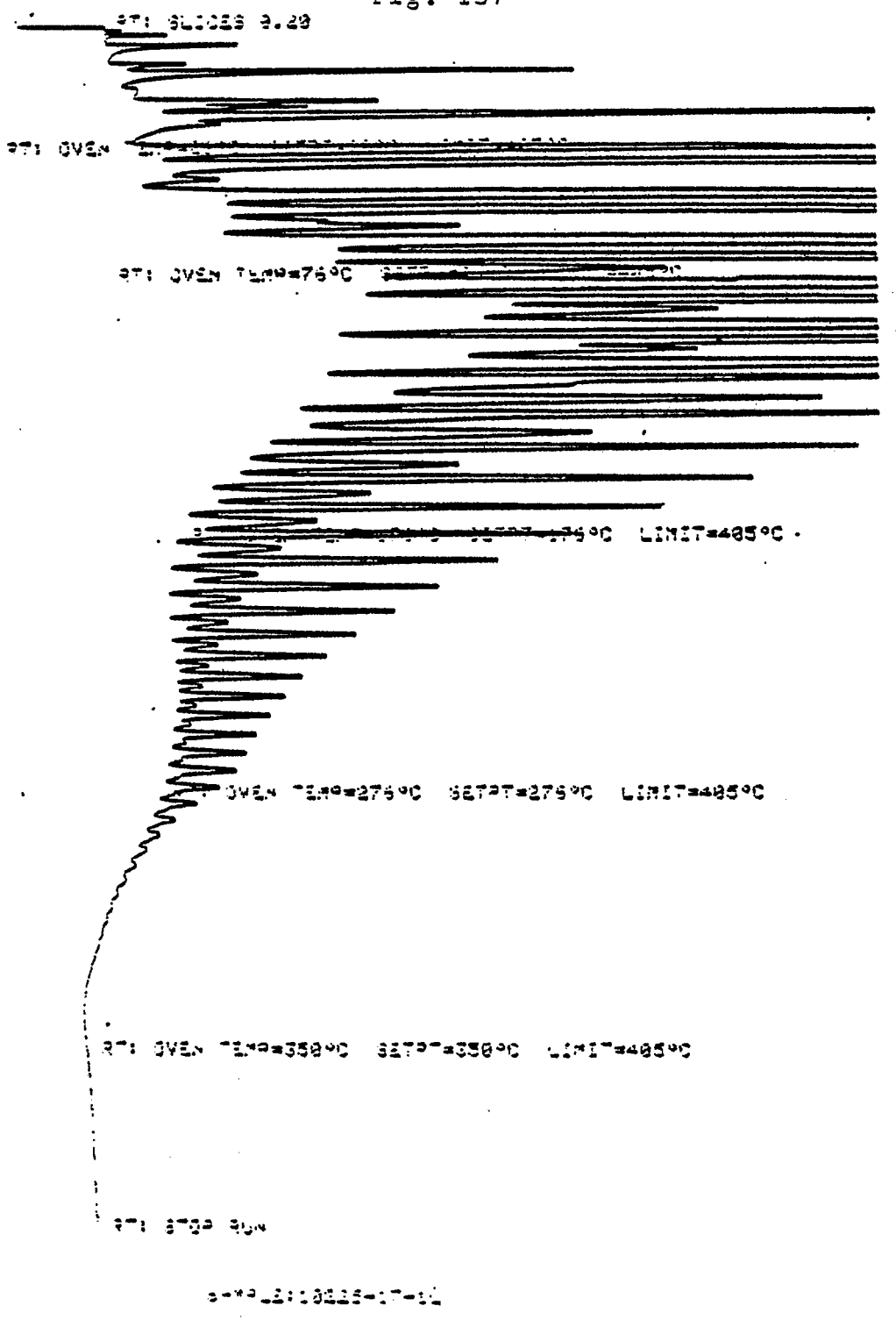

OVEN TEMP=76°C
LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 138

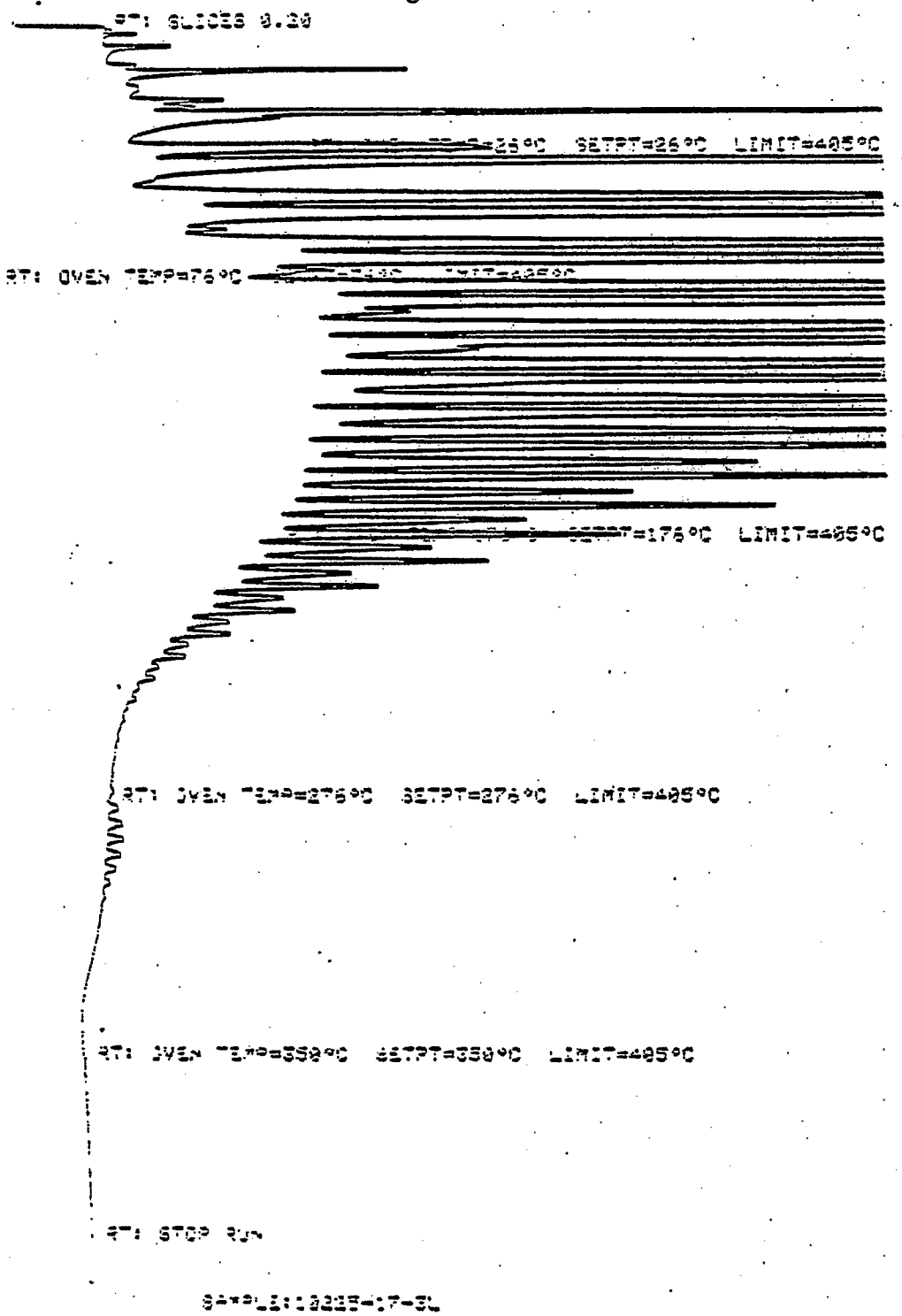

RT: SLIDES 0.20
SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C
SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 139

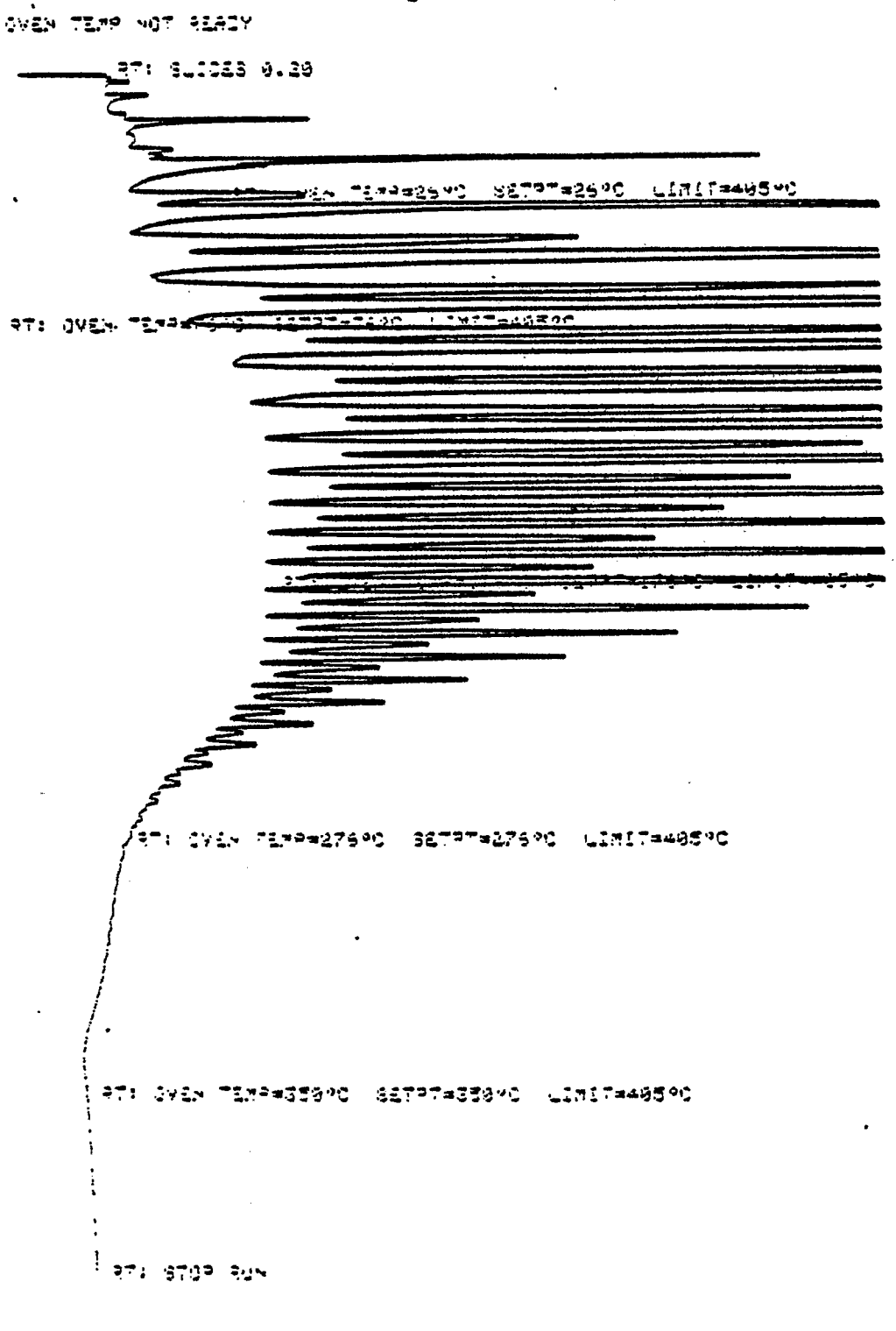

OVEN TEMP NOT READY
ST: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
ST: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
ST: STOP RUN

Fig. 140

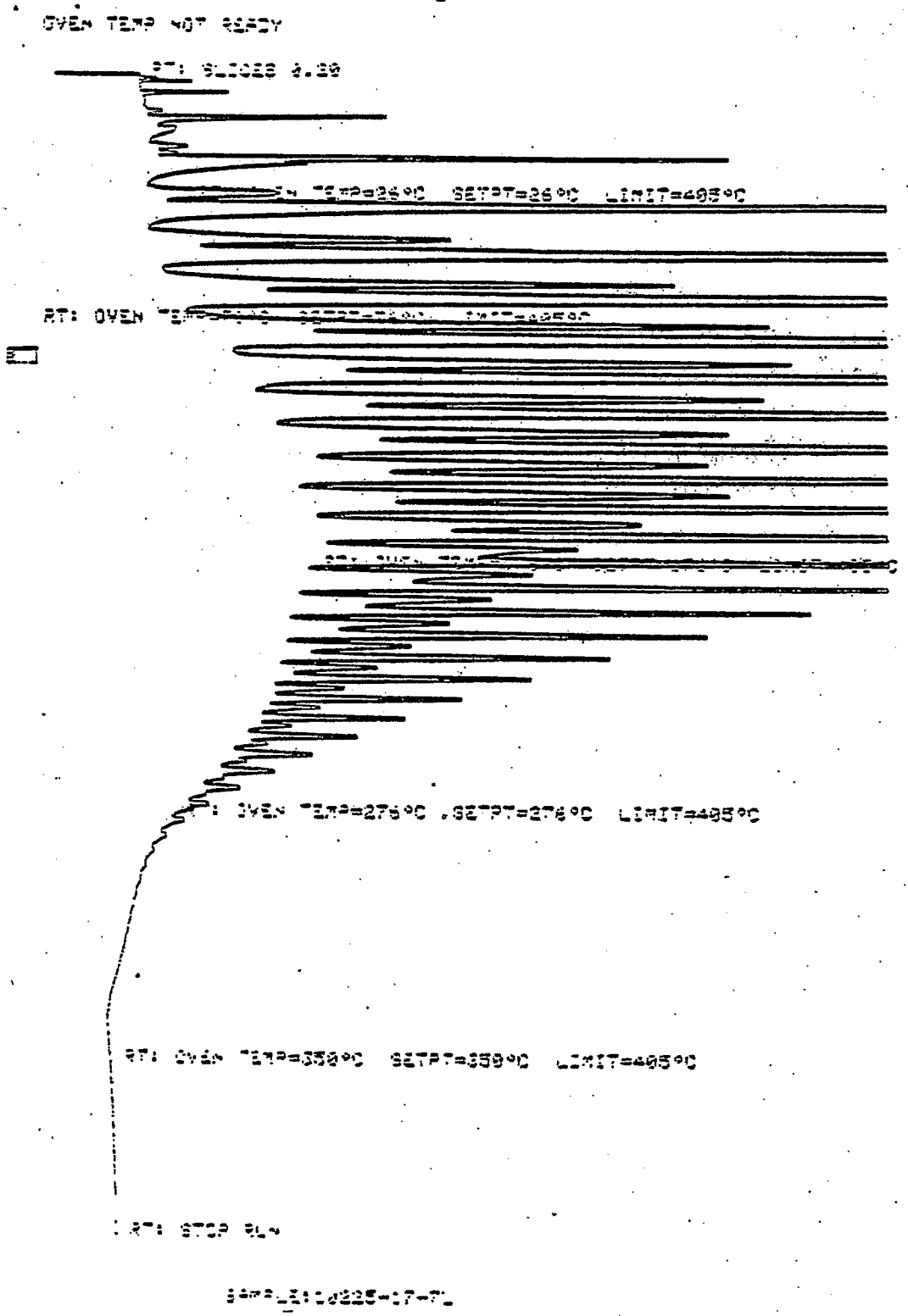

OVEN TEMP NOT READY
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 141

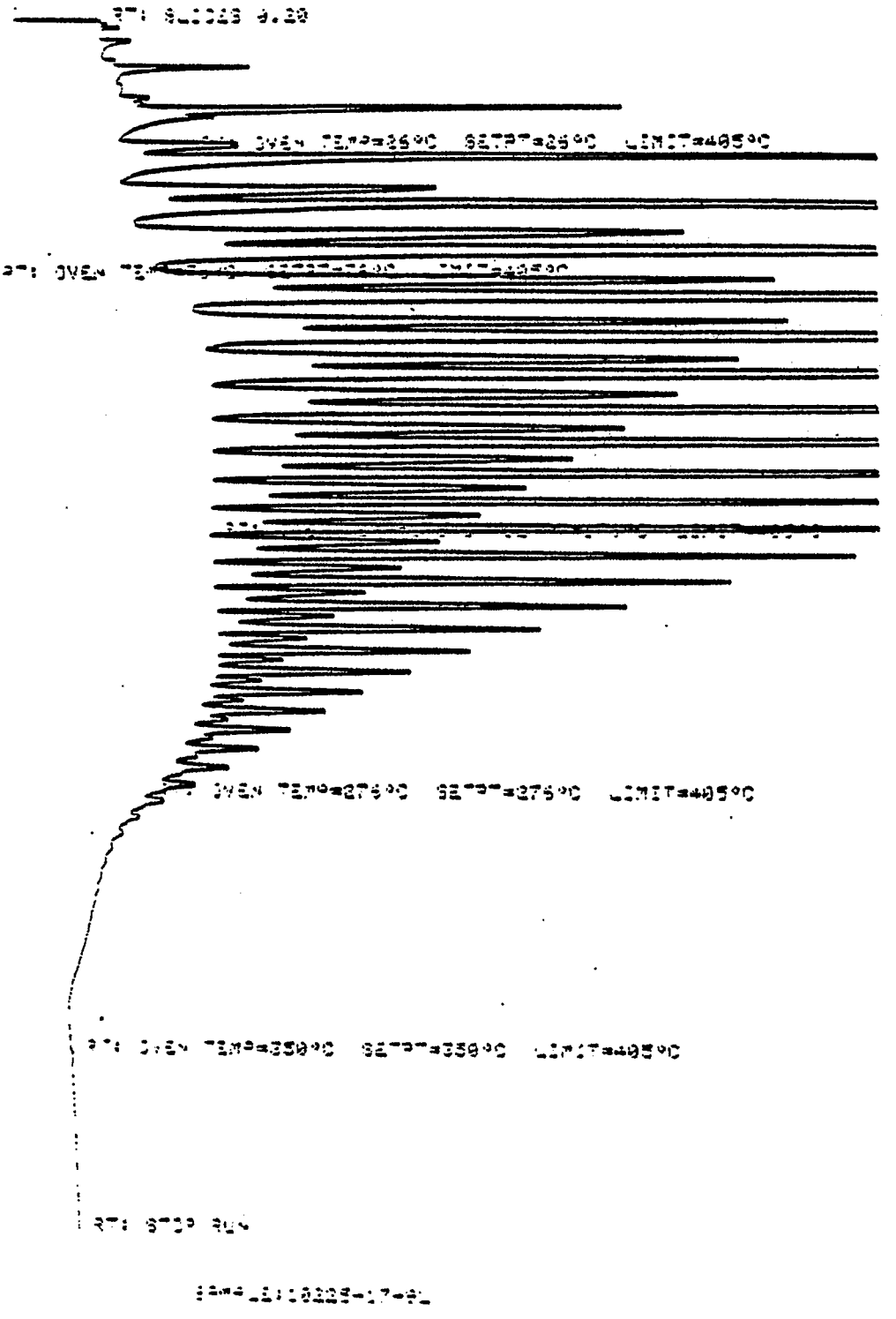


TABLE 17 RESULT OF SYNGAS OPERATION

RUN NO. 10225-17
CATALYST CO/TH+UCC-103 11684-21C 80 CC 37.9G(43.5 AFTER RUN +5.6 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	10225-17-01	225-17-02	225-17-03	225-17-04	225-17-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.0	29.5	46.0	53.5	71.0
PRESSURE,PSIG	294	295	297	295	290
TEMP. C	273	273	273	273	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.00	7.50	24.00	7.50	25.00
EFFLNT GAS LITER	195.25	60.80	193.85	60.95	202.75
GM AQUEOUS LAYER	33.93	17.60	56.32	21.62	72.08
GM OIL	9.00	10.09	32.29	11.95	39.84
MATERIAL BALANCE					
GM ATOM CARBON %	91.80	97.45	92.37	95.12	91.56
GM ATOM HYDROGEN %	91.62	104.79	95.04	103.21	97.09
GM ATOM OXYGEN %	95.82	97.19	92.96	97.80	93.40
RATIO CHX/(H2O+CO2)	0.9214	1.0046	0.9878	0.9492	0.9609
RATIO X IN CHX	2.8450	2.5829	2.5178	2.4734	2.4242
USAGE H2/CO PRODT	1.0525	1.2011	1.2746	1.3560	1.4869
RATIO CO2/(H2O+CO2)	0.6331	0.4968	0.4294	0.3618	0.2842
K SHIFT IN EFFLNT	0.82	0.38	0.23	0.17	0.10
CONVERSION					
ON CO %	86.51	84.70	74.37	72.76	64.02
ON H2 %	93.54	94.47	92.52	92.69	91.18
ON CO+H2 %	90.02	89.76	83.58	83.13	78.00
PRDT SELECTIVITY,WT %					
CH4	35.50	24.94	22.67	21.07	19.10
C2 HC'S	4.73	3.46	3.03	2.75	2.53
C3H8	7.40	4.95	3.93	3.43	2.85
C3H6=	1.12	1.24	1.95	1.85	1.96
C4H10	7.00	4.84	3.72	3.05	2.62
C4H8=	2.52	2.39	3.06	2.99	3.01
C5H12	6.95	5.04	4.08	3.37	2.83
C5H10=	1.88	1.78	2.29	2.26	2.39
C6H14	7.35	5.58	4.86	4.29	3.78
C6H12= & CYCLO'S	1.28	1.44	1.98	2.21	2.42
C7+ IN GAS	12.46	10.58	9.31	8.33	7.15
LIQ HC'S	11.83	33.76	39.11	44.40	49.36
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	58.26	41.81	38.36	35.15	32.08
C5 -420 F	38.21	46.37	47.95	44.49	45.28
420-700 F	2.86	11.64	13.49	18.70	20.79
700-END PT	0.67	0.18	0.20	1.66	1.85
C5+-END PT	41.74	58.19	61.64	64.85	67.92
ISO/NORMAL MOLE RATIO					
C4	0.0431	0.0354	0.0216	0.0228	0.0214
C5	0.1793	0.1351	0.0974	0.1030	0.0824
C6	0.7161	0.5967	0.5283	0.5675	0.5063
C4=	0.2742	0.2011	0.1305	0.1211	0.0993
PARAFFIN/OLEFIN RATIO					
C3	6.3197	3.8122	1.9274	1.7713	1.3829
C4	2.6805	1.9604	1.1707	0.9851	0.8378
C5	3.5960	2.7512	1.7337	1.4517	1.1534
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7610		0.7763		0.8148
RATIO CH4/(1-A)**2	6.2150		4.5305		5.5702
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.742		0.743		0.752
N, REFRACTIVE INDEX	1.4175		1.4206		1.4218
SIMULT'D DISTILATN					
10 WT % @ DEG F	214		240		255
16	251		258		282
50	346		373		412
84	523		519		584
90	607		560		631
RANGE(16-84 %)	272		261		302
WT % @ 420 F	70.16	65.00	65.00	54.13	54.13
WT % @ 700 F	94.33	99.48	99.48	96.25	96.25

TABLE 18 RESULT OF SYNGAS OPERATION

RUN NO. 10225-17
CATALYST CO/TH+UCC-103 11684-21C 80 CC 37.9G(43.5 AFTER RUN +5.6 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	10225-17-07	225-17-08	225-17-09	225-17-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	166.0	173.5	190.0	196.5
PRESSURE,PSIG	294	293	296	296
TEMP. C	272	278	272	272
FEED CC/MIN	400	400	400	400
HOURS FEEDING	95.00	7.50	24.00	6.50
EFFLNT GAS LITER	830.05	52.20	206.20	59.89
GM AQUEOUS LAYER	291.57	23.09	73.90	19.95
GM OIL	145.26	10.31	32.98	9.94
MATERIAL BALANCE				
GM ATOM CARBON %	93.30	79.31	89.28	97.02
GM ATOM HYDROGEN %	100.79	97.89	98.03	103.56
GM ATOM OXYGEN %	93.84	84.89	92.12	96.08
RATIO CHX/(H2O+CO2)	0.9879	0.8852	0.9358	1.0211
RATIO X IN CHX	2.4395	2.5714	2.4615	2.4527
USAGE H2/CO PRODT	1.6809	1.5521	1.7016	1.7075
RATIO CO2/(H2O+CO2)	0.1993	0.2645	0.1868	0.1945
K SHIFT IN EFFLNT	0.07	0.11	0.06	0.07
CONVERSION				
ON CO %	57.03	70.39	55.63	55.94
ON H2 %	89.18	92.94	88.68	88.71
ON CO+H2 %	73.73	82.85	72.92	72.86
PRDT SELECTIVITY,WT %				
CH4	19.88	26.33	20.91	20.40
C2 HC'S	2.69	3.24	2.78	2.64
C3H8	2.74	3.51	2.84	2.88
C3H6=	1.91	1.44	1.93	2.04
C4H10	2.53	2.80	2.61	2.71
C4H8=	2.79	2.55	2.86	3.04
C5H12	2.78	2.68	2.87	3.35
C5H10=	2.16	1.90	2.21	2.36
C6H14	4.02	3.57	4.17	3.90
C6H12= & CYCLO'S	2.40	1.89	2.14	2.18
C7+ IN GAS	7.77	5.75	8.27	7.60
LIQ HC'S	48.33	44.33	46.38	46.90
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	32.54	39.89	33.95	33.70
C5 -420 F	42.20	38.49	43.43	43.42
420-700 F	21.77	18.17	19.01	19.23
700-END PT	3.48	3.45	3.61	3.65
C5+-END PT	67.46	60.11	66.05	66.30
ISO/NORMAL MOLE RATIO				
C4	0.0194	0.0276	0.0195	0.0186
C5	0.0744	0.1209	0.0757	0.0858
C6	0.4259	0.5170	0.3683	0.4171
C4=	0.1003	0.1543	0.1012	0.0971
PARAFFIN/OLEFIN RATIO				
C3	1.3651	2.3234	1.4057	1.3471
C4	0.8752	1.0566	0.8806	0.8601
C5	1.2509	1.3753	1.2644	1.3790
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.8268		0.8241	
RATIO CH4/(1-A)**2	6.6305		6.7617	
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLDY WH		CLDY WH	
DENSITY	0.756		0.756	
N, REFRACTIVE INDEX	1.4242		1.4240	
SIMULT'D DISTILATN				
10 WT % @ DEG F	257		257	
16	296		294	
50	436		416	
84	622		619	
90	671		674	
RANGE(16-84 %)	326		325	
WT % @ 420 F	47.75	51.22	51.22	51.22
WT % @ 700 F	92.80	92.21	92.21	92.21

X. Run 9 (10225-15) with Catalyst 9 (Co/Th + Zn/UCC-107)

When UCC-107 was used in a Fischer-Tropsch catalyst in Run 10112-11, reported in the Ninth Quarter, it seemed to deactivate rapidly, presumably due to coking. Ion exchanged zinc has been shown to protect Molecular Sieves in hydrocracking catalysts from deactivation, and the purpose of this run was to test its efficacy with UCC-107. UCC-107 was ion exchanged to about 45 percent of its ion exchange capacity with zinc to constitute the shape selective component. The catalyst was then prepared by the same procedure as was used for Catalyst 1, with Zn/UCC-107 in place of UCC-101.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 142-145. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 146-147. Carbon number product distributions are plotted in Figs. 148-153. Chromatograms from simulated distillations are reproduced in Figs. 154-159. Detailed material balances appear in Tables 19-20.

The initial conversion of the $CO+H_2$ syngas was 74 percent, nearly as high as the 76 percent initial conversion of the reference catalyst (Tenth Quarter Run 10112-15). But this catalyst was much more stable than the reference; after 115 hours on stream its conversion was still 73 percent as against 58 percent

for the reference catalyst. At 280C the conversion was 82 percent. The water gas shift activity was a little better than normal, with 24 percent of oxygen rejected as CO_2. At 280C, however, the water gas shift activity had risen to 40 percent oxygen rejected as CO_2, so that despite the production of lighter, more hydrogen-rich hydrocarbons, the H_2:CO usage ratio fell off.

The selectivity at 270C was very steady. The methane yield remained just under 20 percent, compared with 24 percent for the reference catalyst. The yield of C_2-C_4 was 15 percent, normal for a cobalt catalyst. Total motor fuels held constant at 61-63 percent, with a 2:1 ratio of gasoline to diesel oil. The yield of heavies remained at 4-5 percent. All products were much more paraffinic than those of the reference catalyst. The olefin content of the C_4, initially 40 percent, increased during the run to more than 55 percent. The same pattern held true for the C_3 and C_5 hydrocarbons. Even more extreme was the drop in isomerization of the pentane, from an initial isopentane content of almost 70 percent to less than 20 percent just before the temperature was raised. Chromatograms from the simulated distillations show the same high initial isomerization and the same rapid decrease with time. The Schulz-Flory plots show the excess methane, and what may be a carbon number cut-off above C_{25}.

The metal component of this catalyst is both active and stable. But the Molecular Sieve seems to deactivate as rapidly with the zinc as without it. The zinc appears to act as a hydrogenation catalyst, and to deactivate as the Molecular Sieve cokes up.

Fig. 142

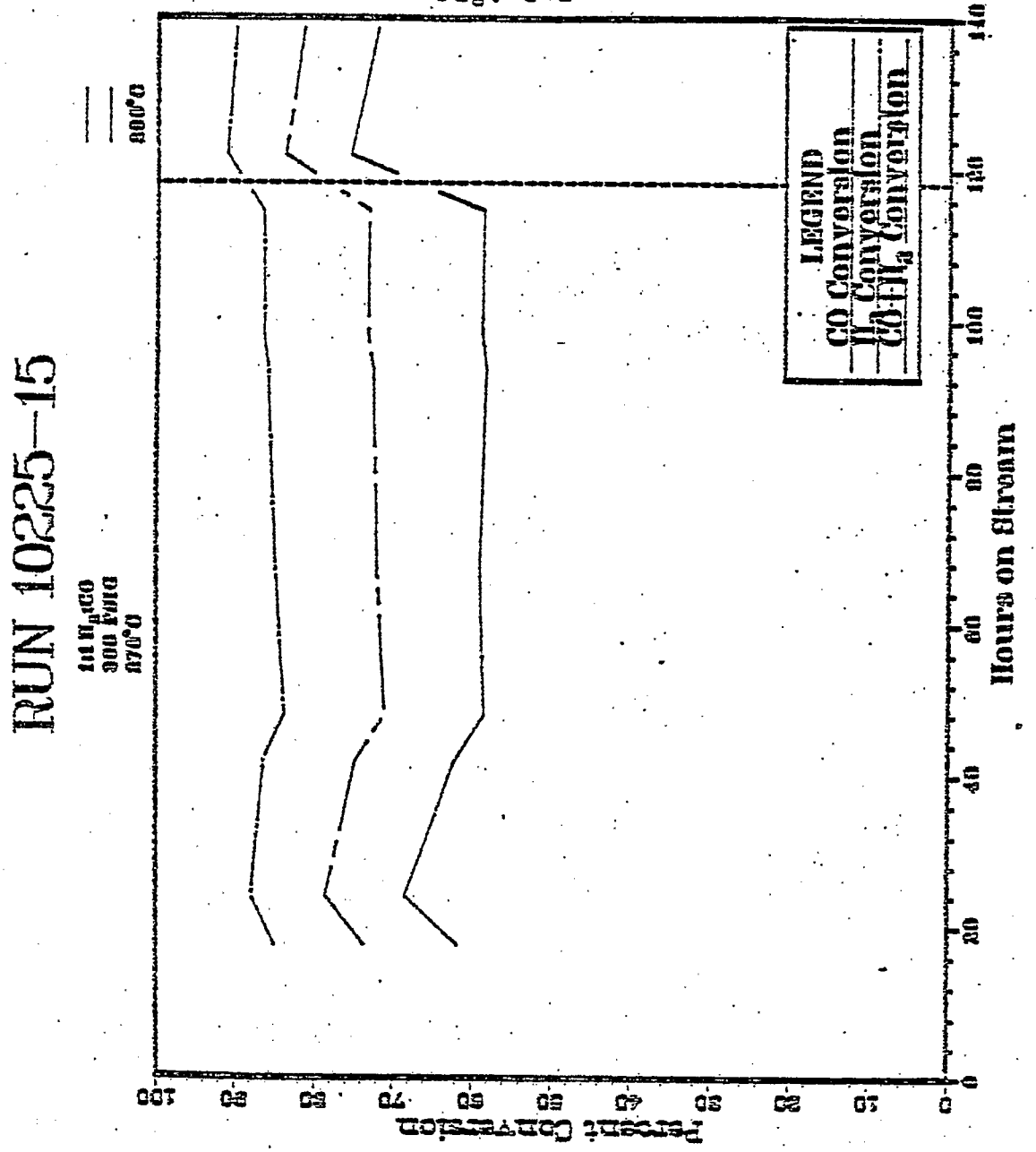
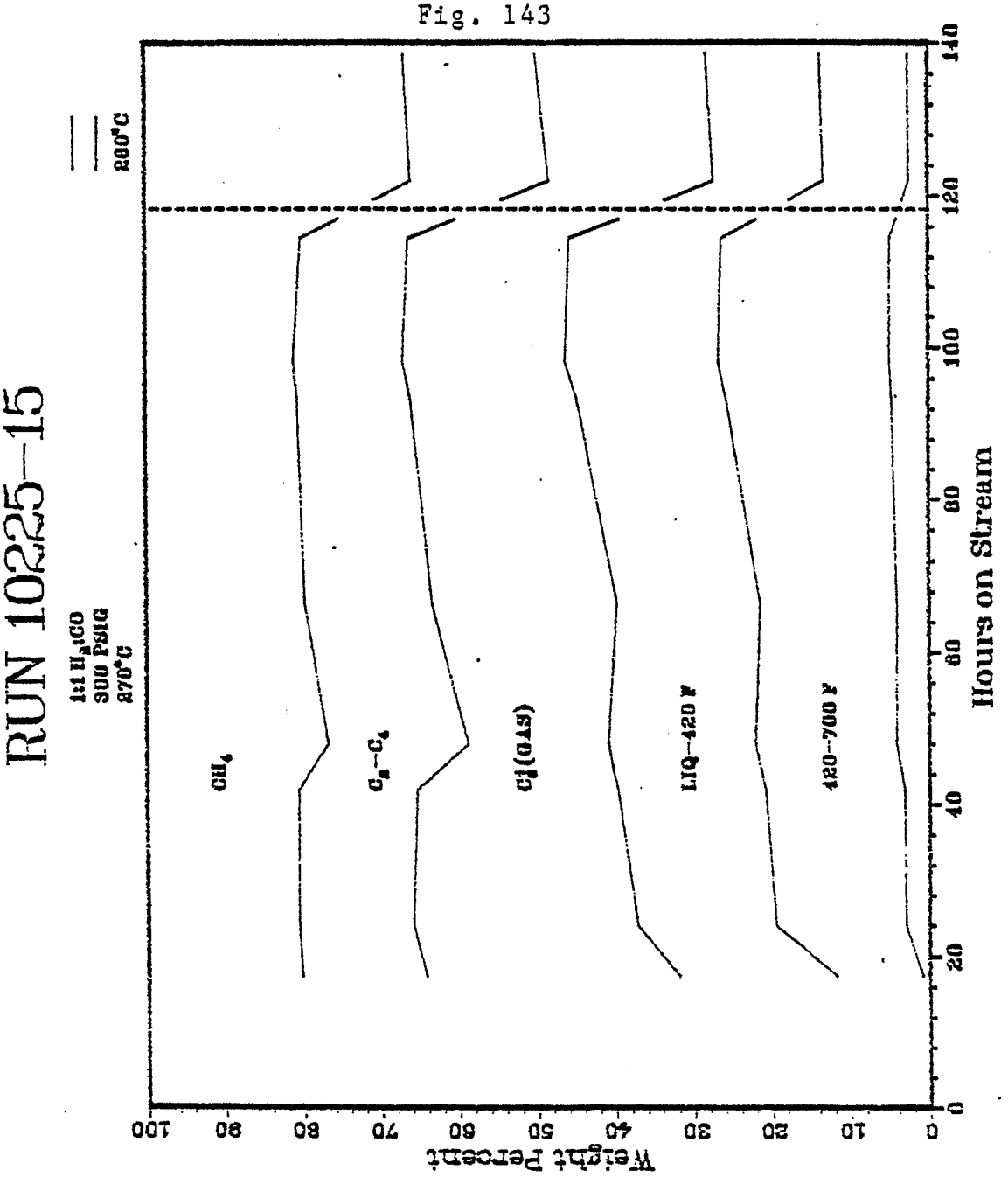

RUN 10225-15
LEGEND
CO Conversion
H_2 Conversion
Hours on Stream
Percent Conversion

Fig. 143


RUN 10225-15
1:1 H2:CO
300 PSIG
270°C
280°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
120
140

RUN 10225–15

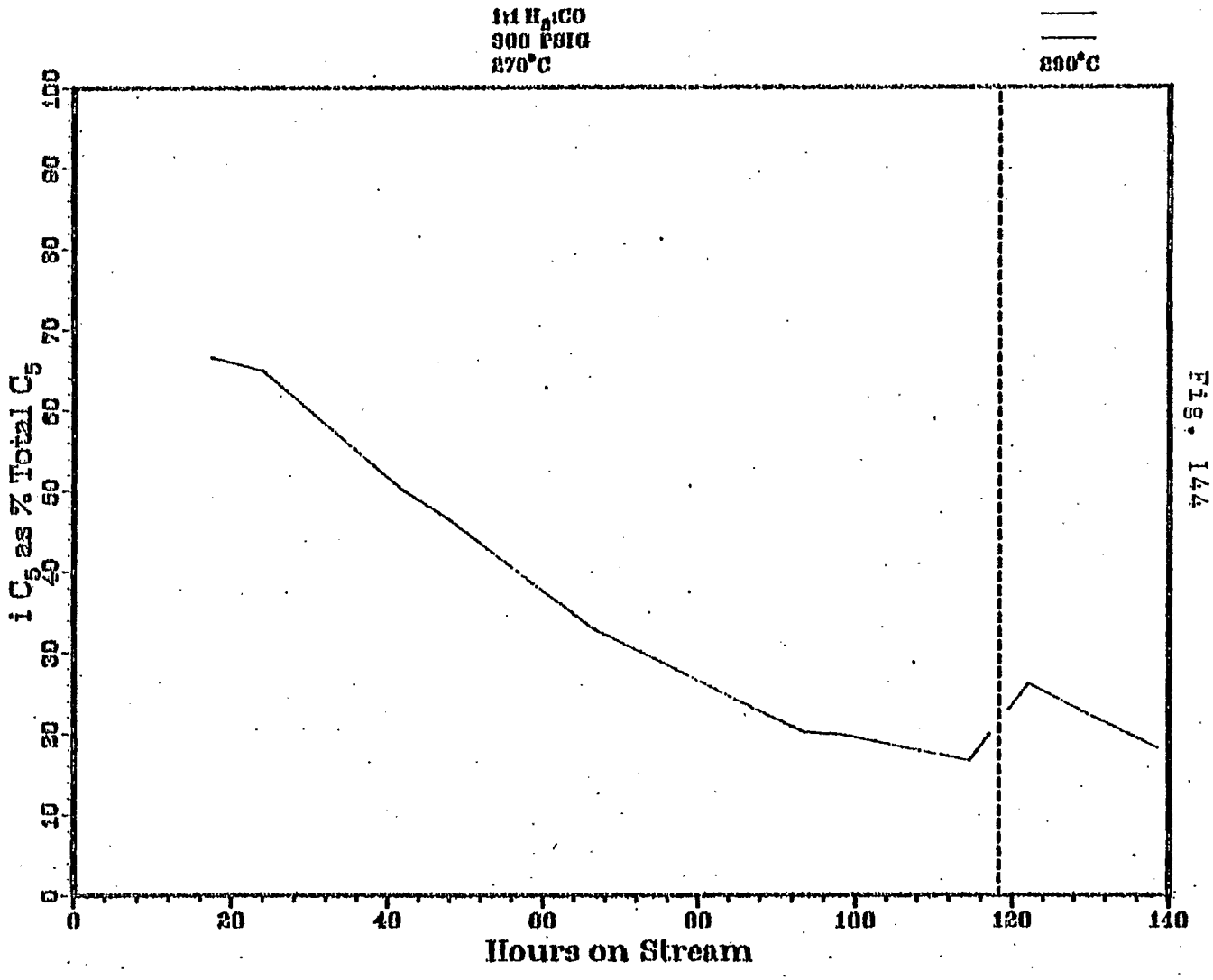


Fig. 144

RUN 10225–15

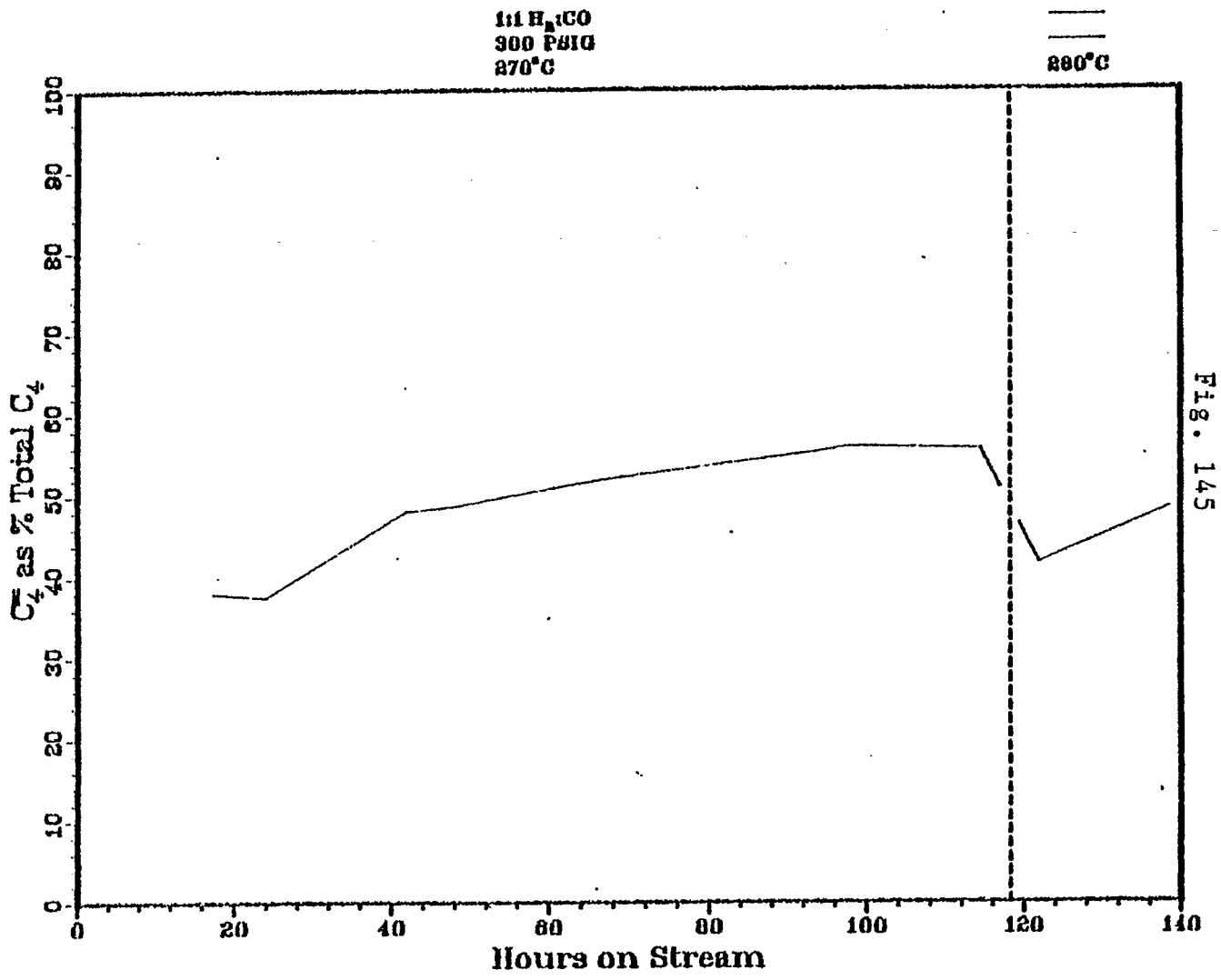


Fig. 145

Fig. 146

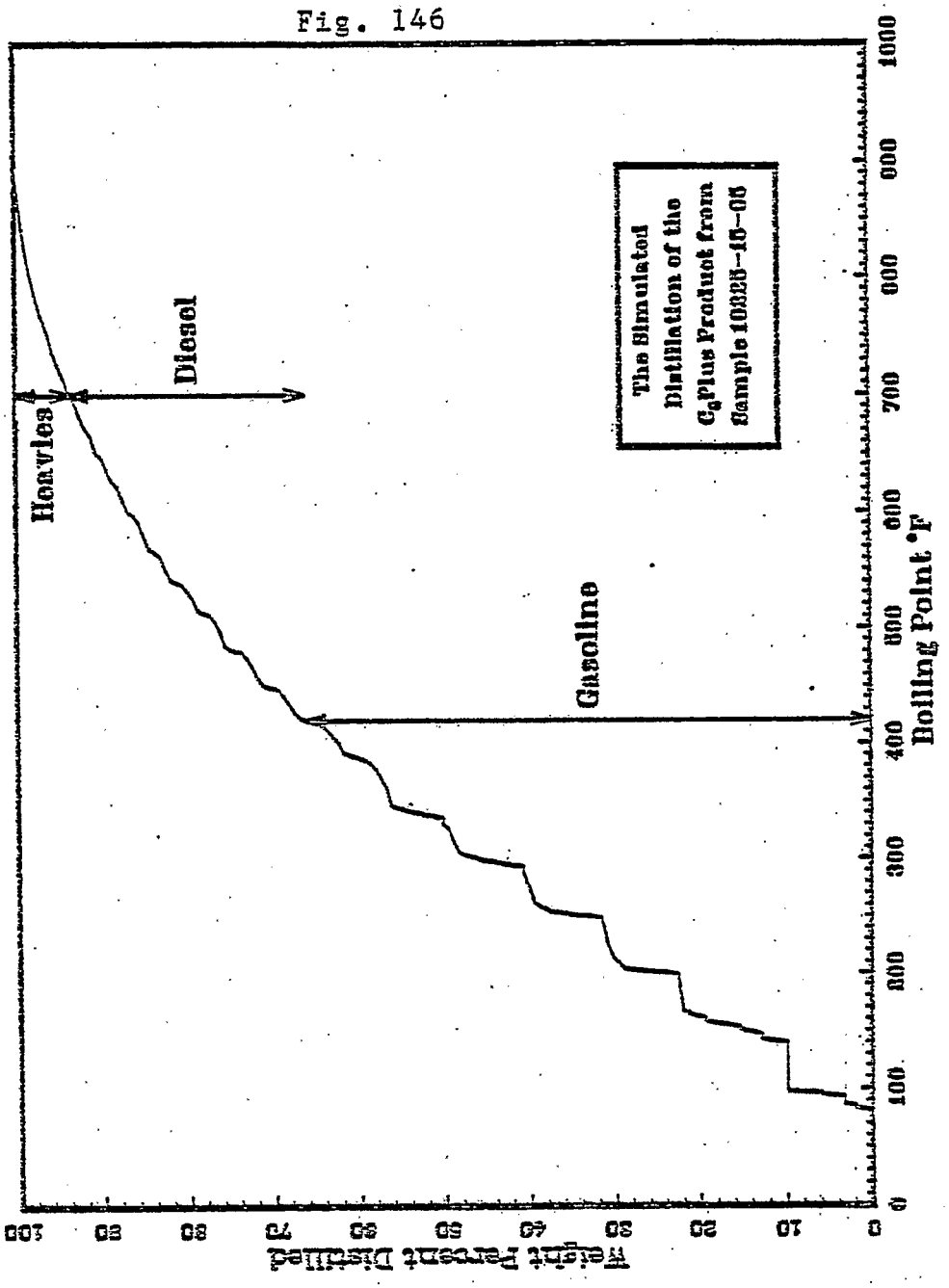

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 10326-16-05

Fig. 147

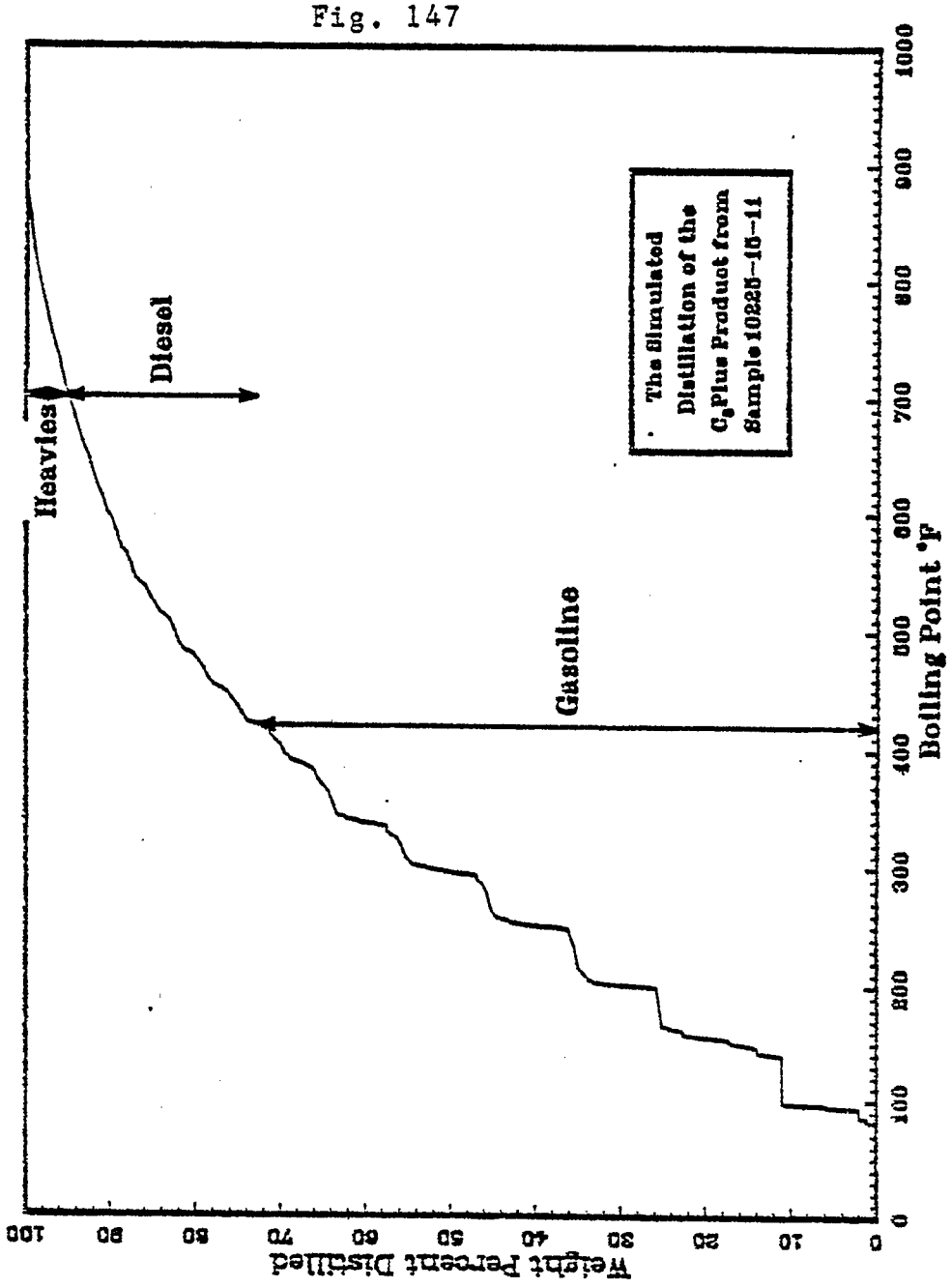

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10225-16-11
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. 148

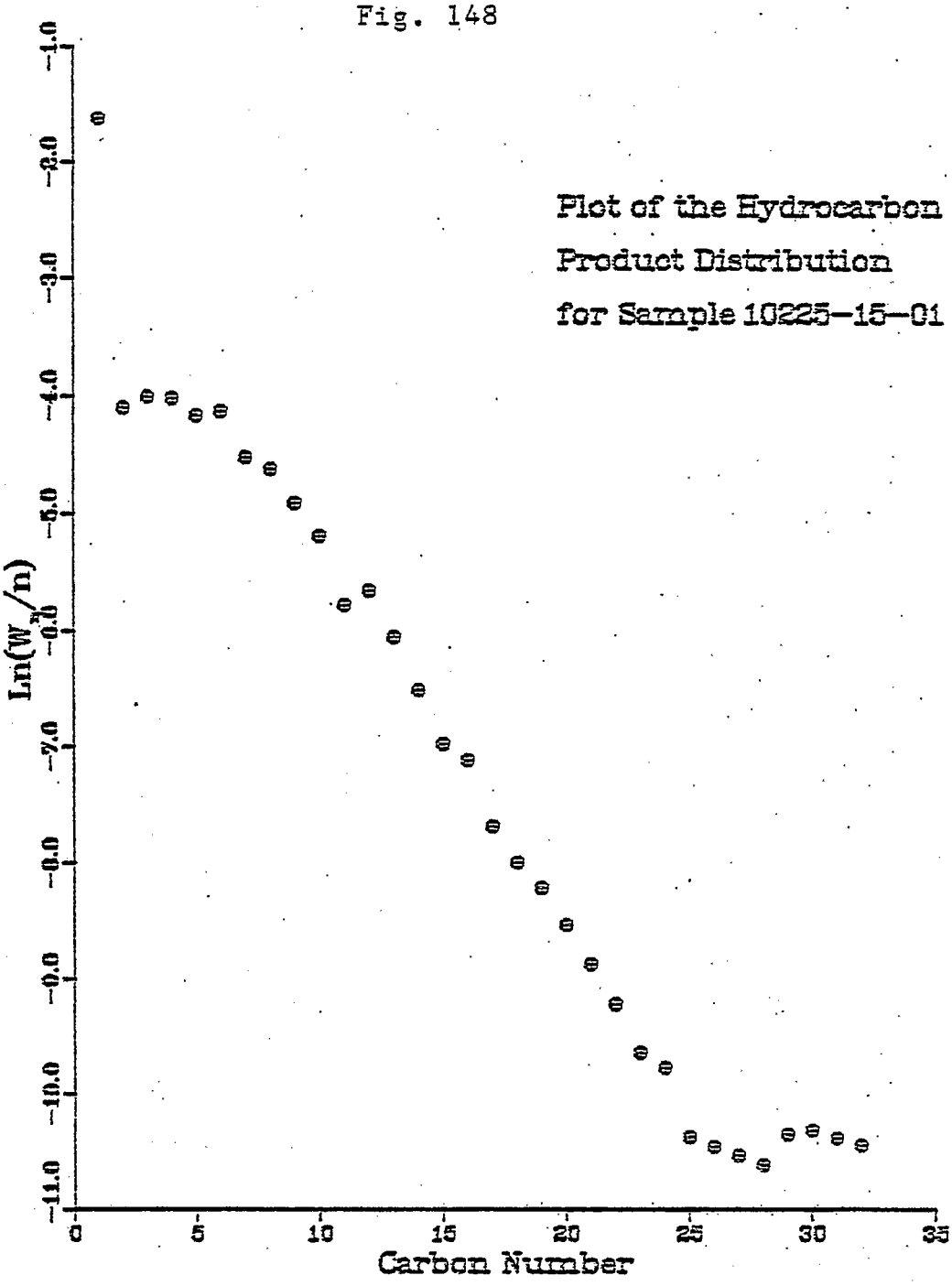

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 149

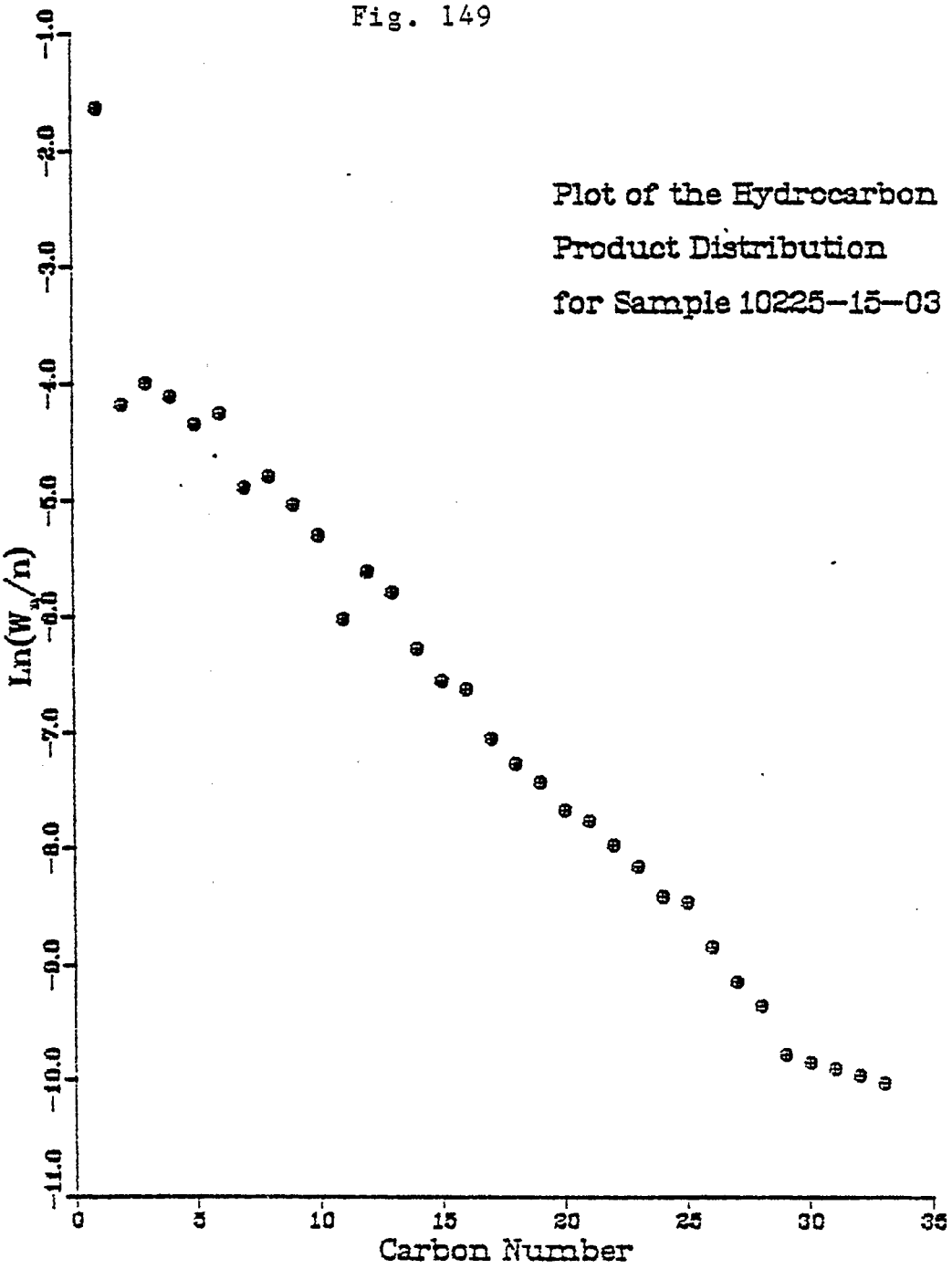

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 150

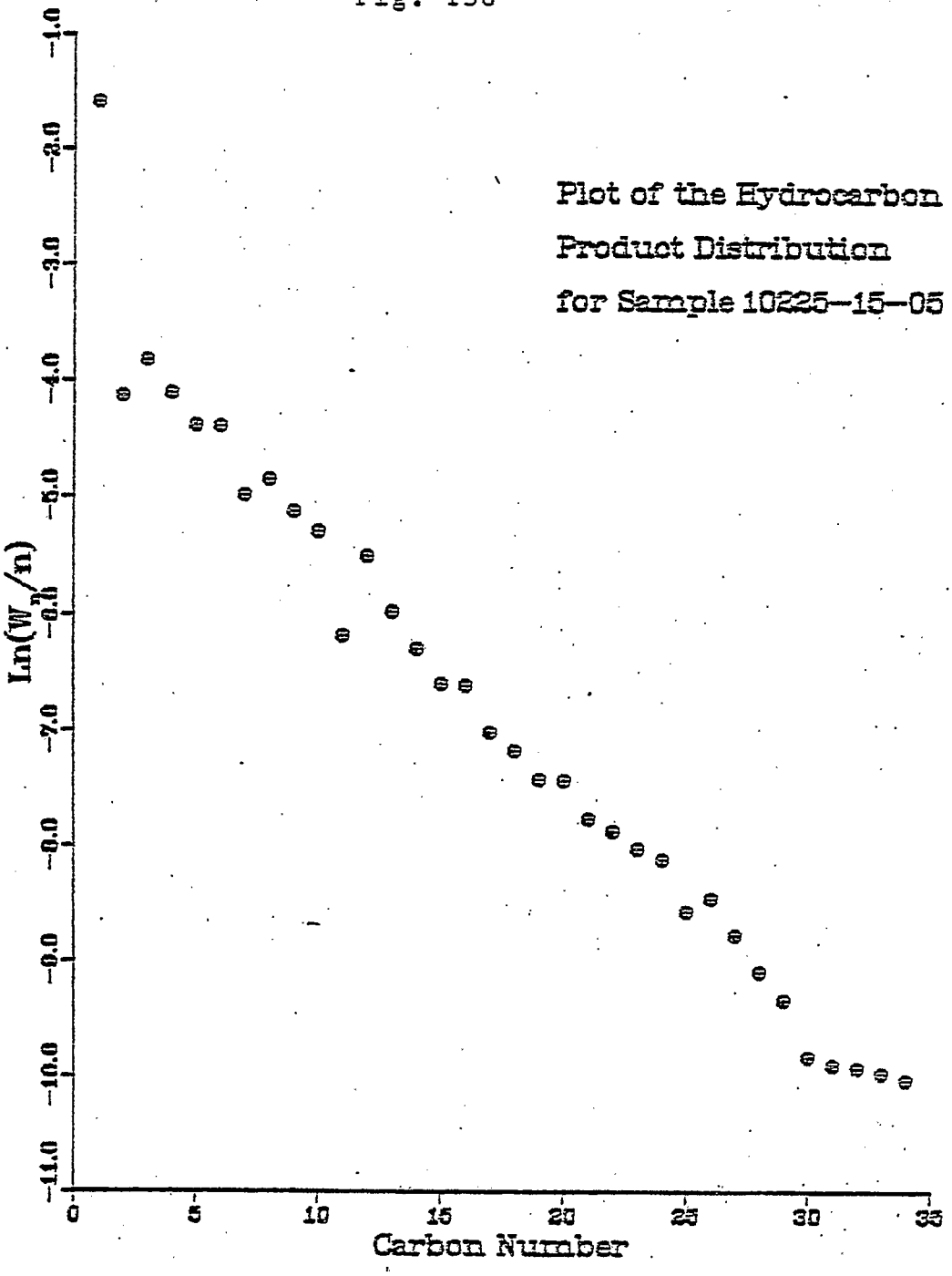

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-05
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 151

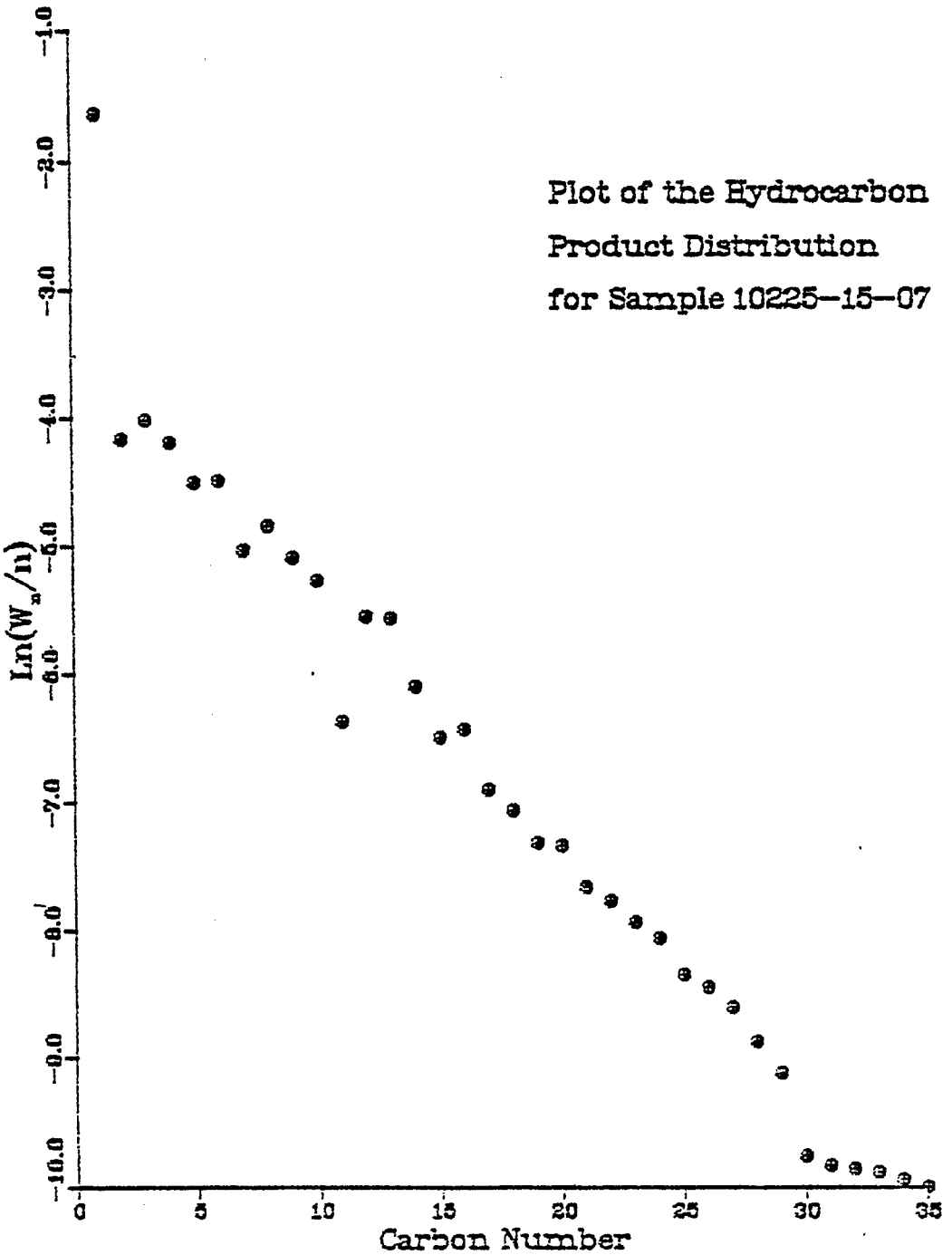

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 152

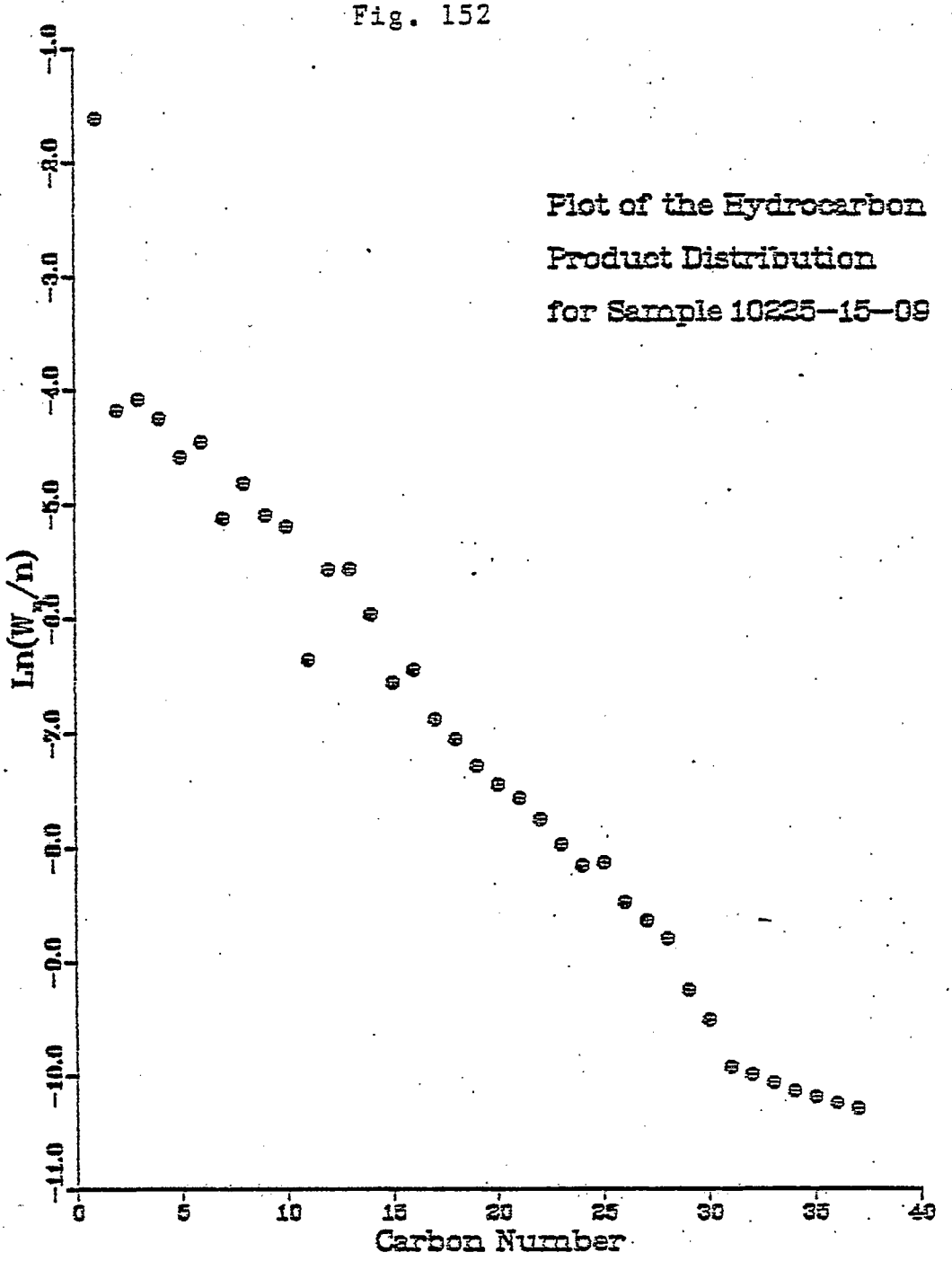

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-09
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 153

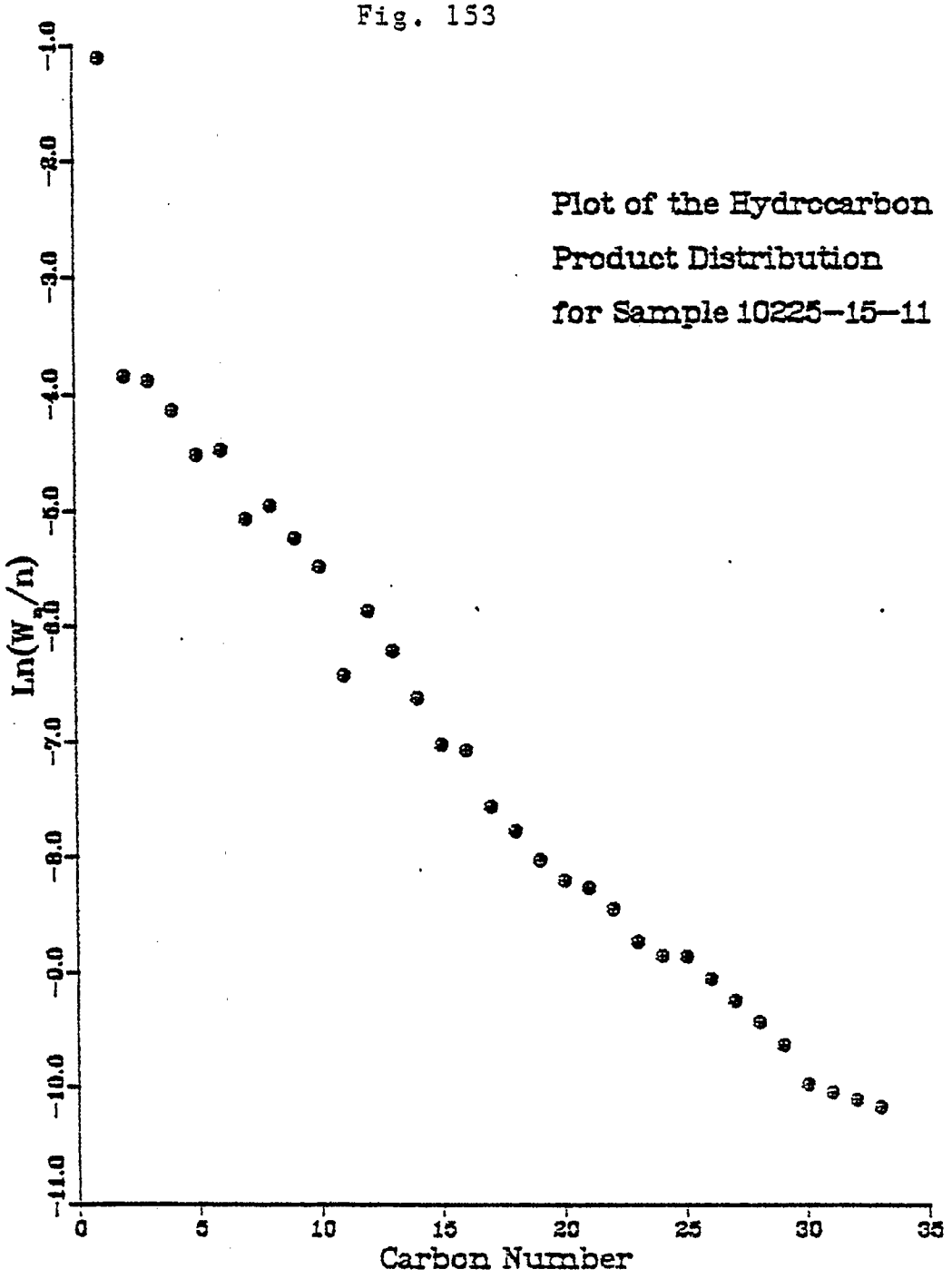

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-15-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 154 -

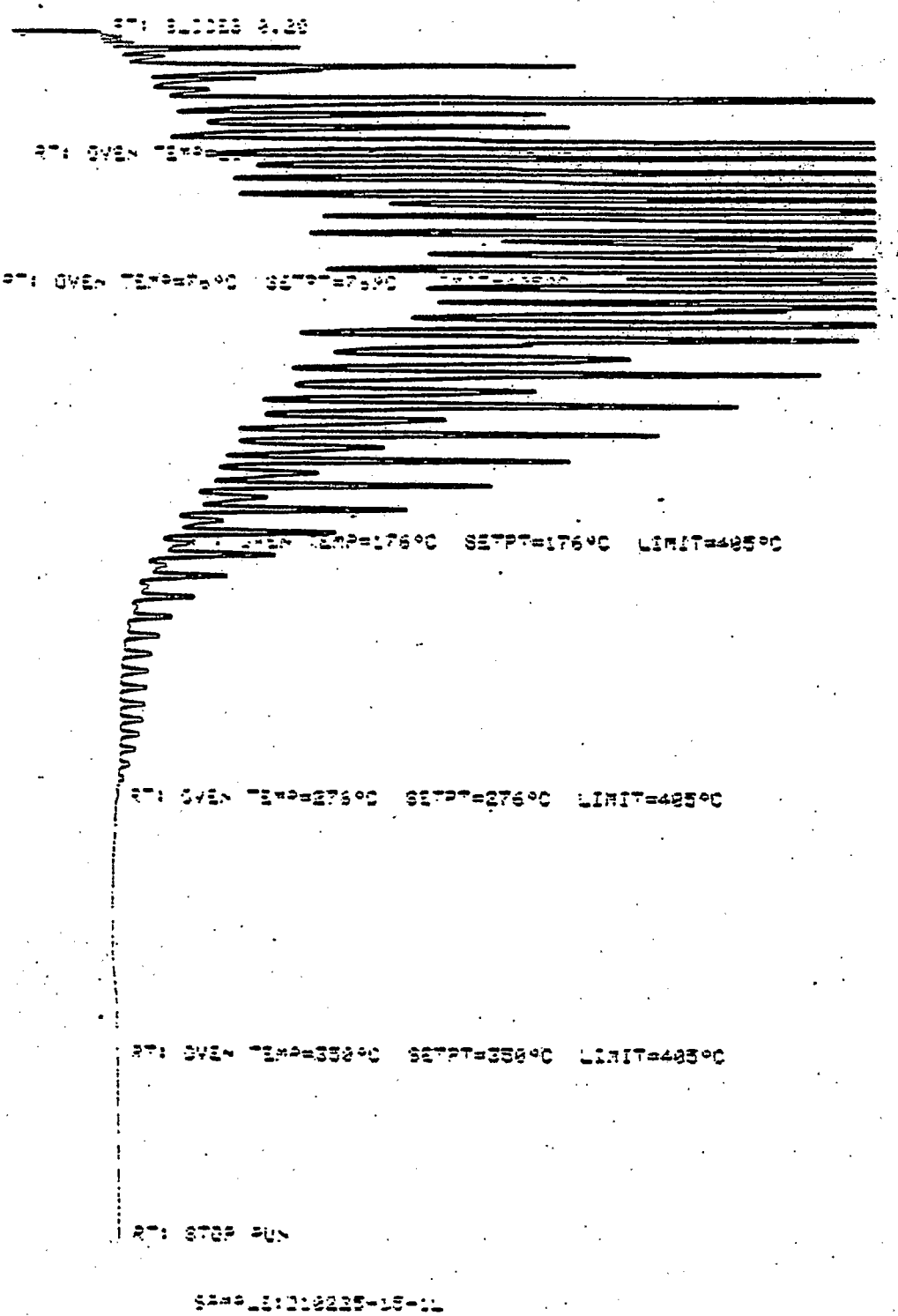

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=485°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=485°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=485°C
RT: STOP RUN

Fig. 155

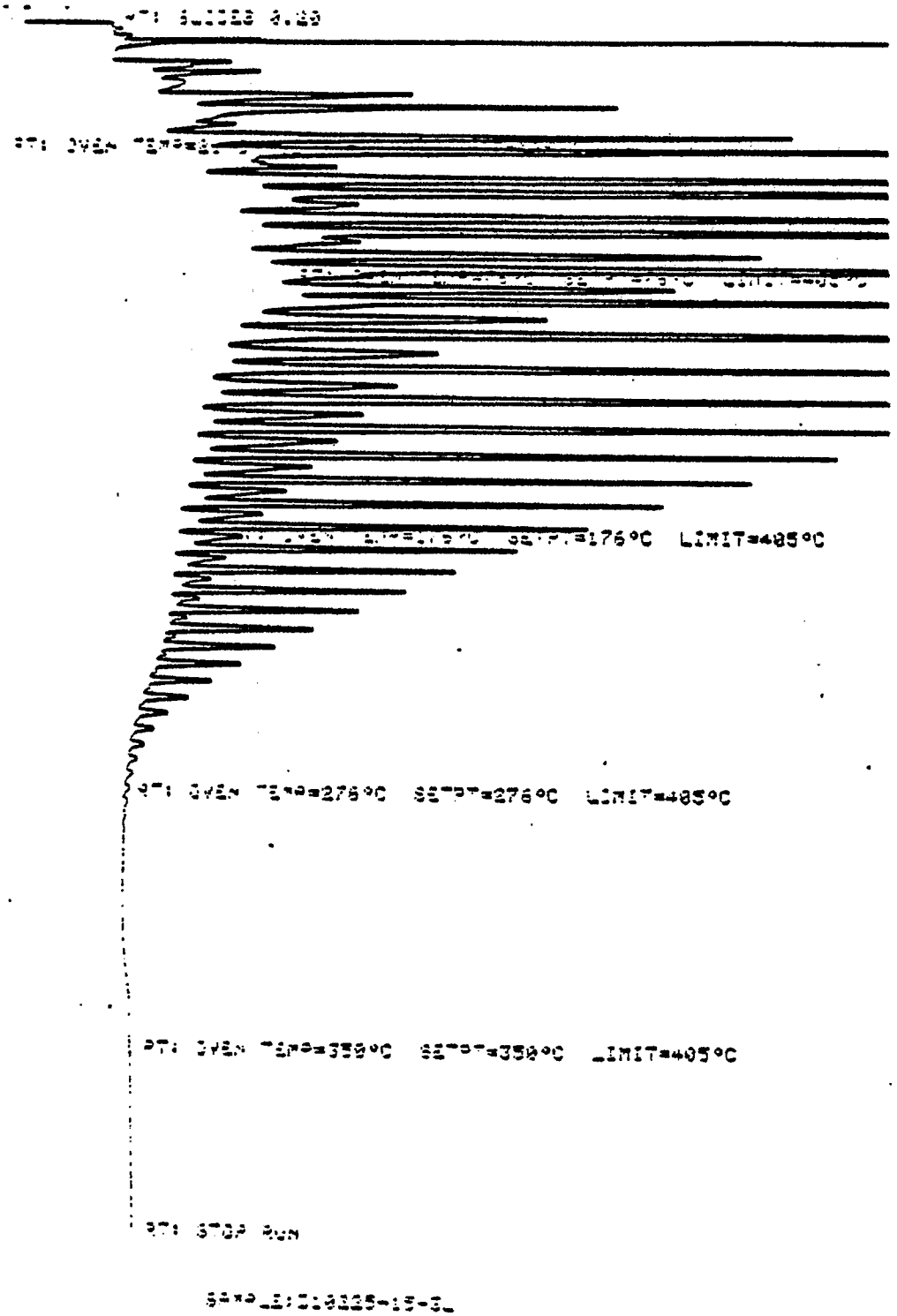

PT: OVEN TEMP=176°C SETPT=176°C LIMIT=485°C
PT: OVEN TEMP=276°C SETPT=276°C LIMIT=485°C
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
PT: STOP RUN

Fig. 156

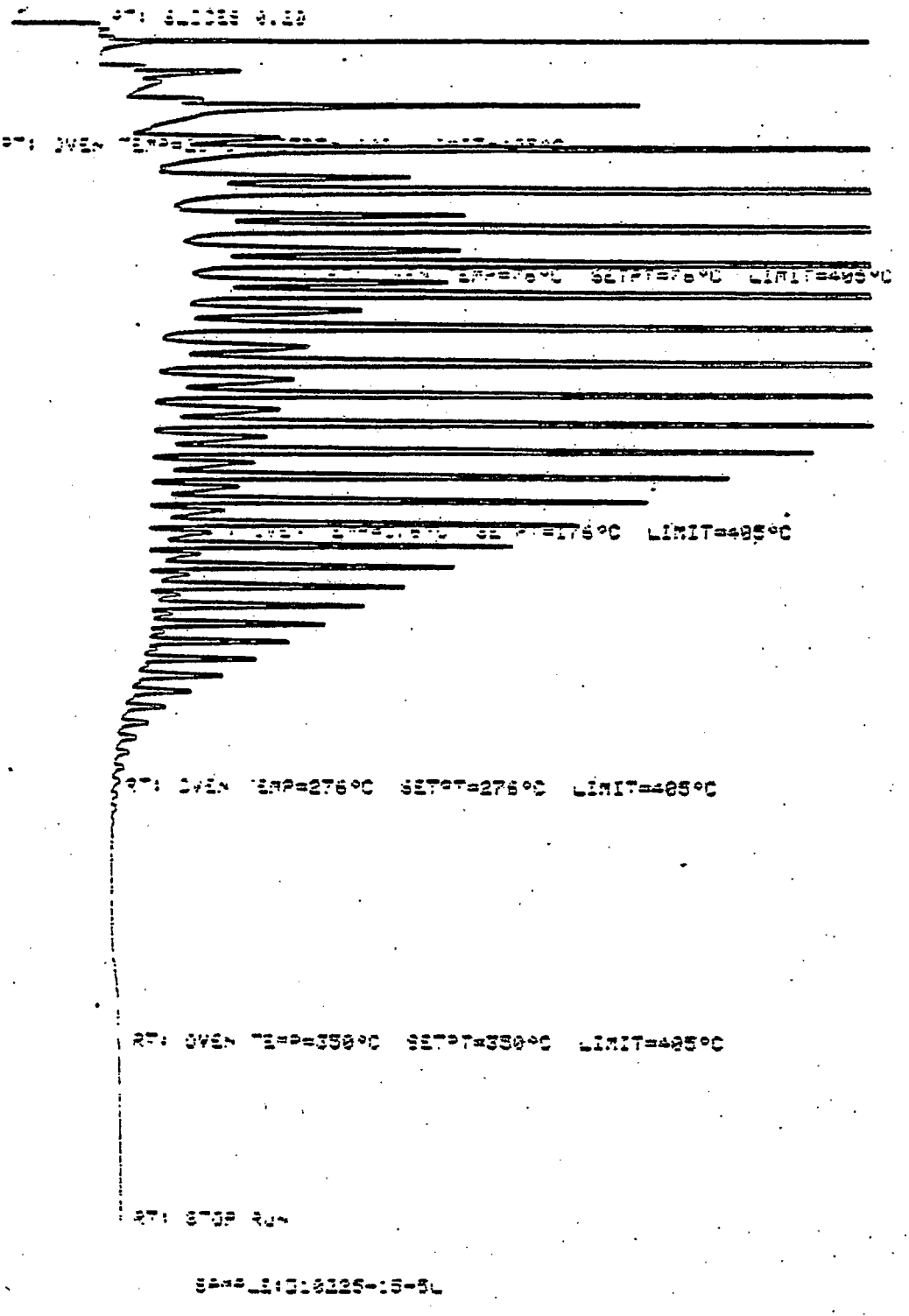

SET=275°C LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 157

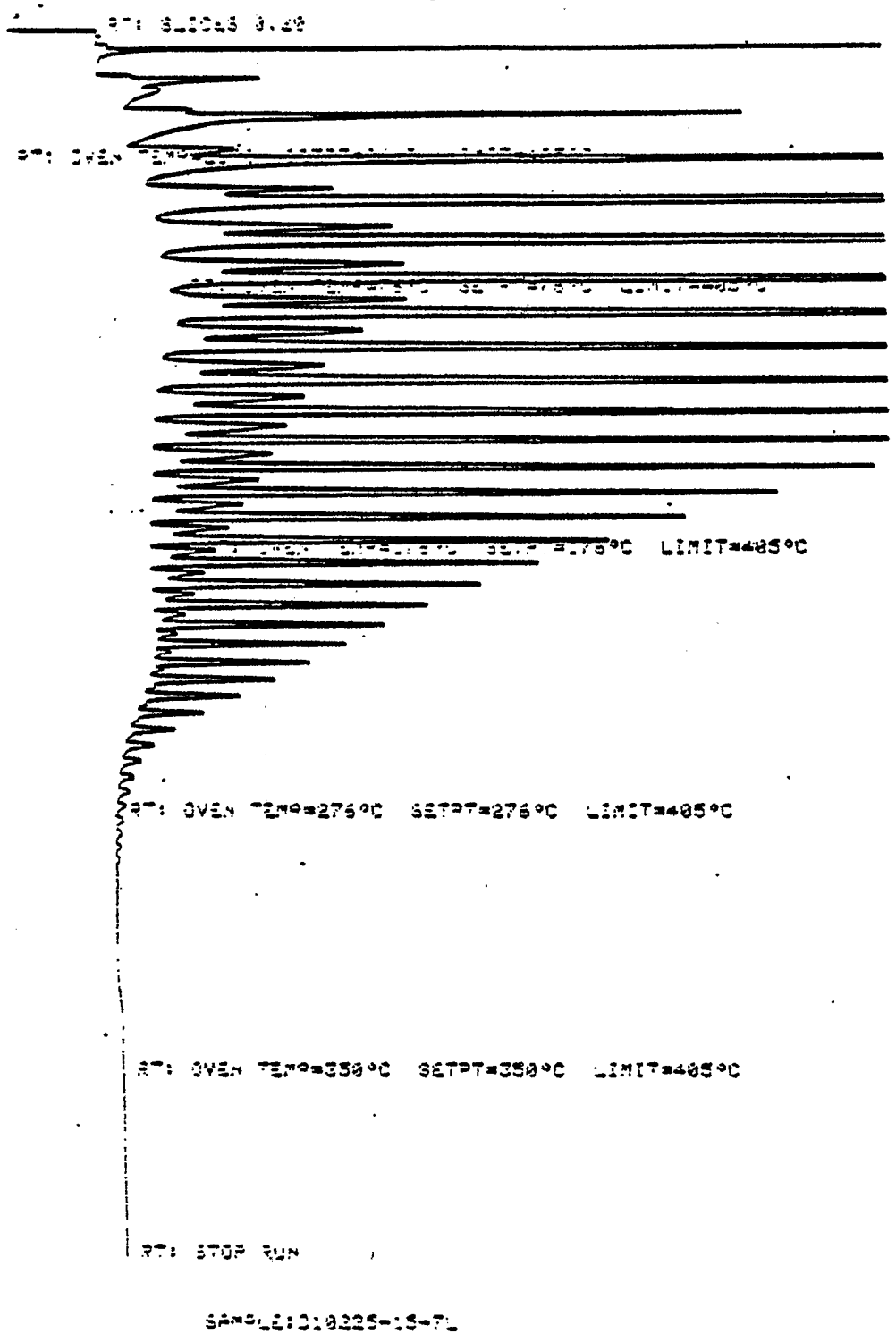

RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 158

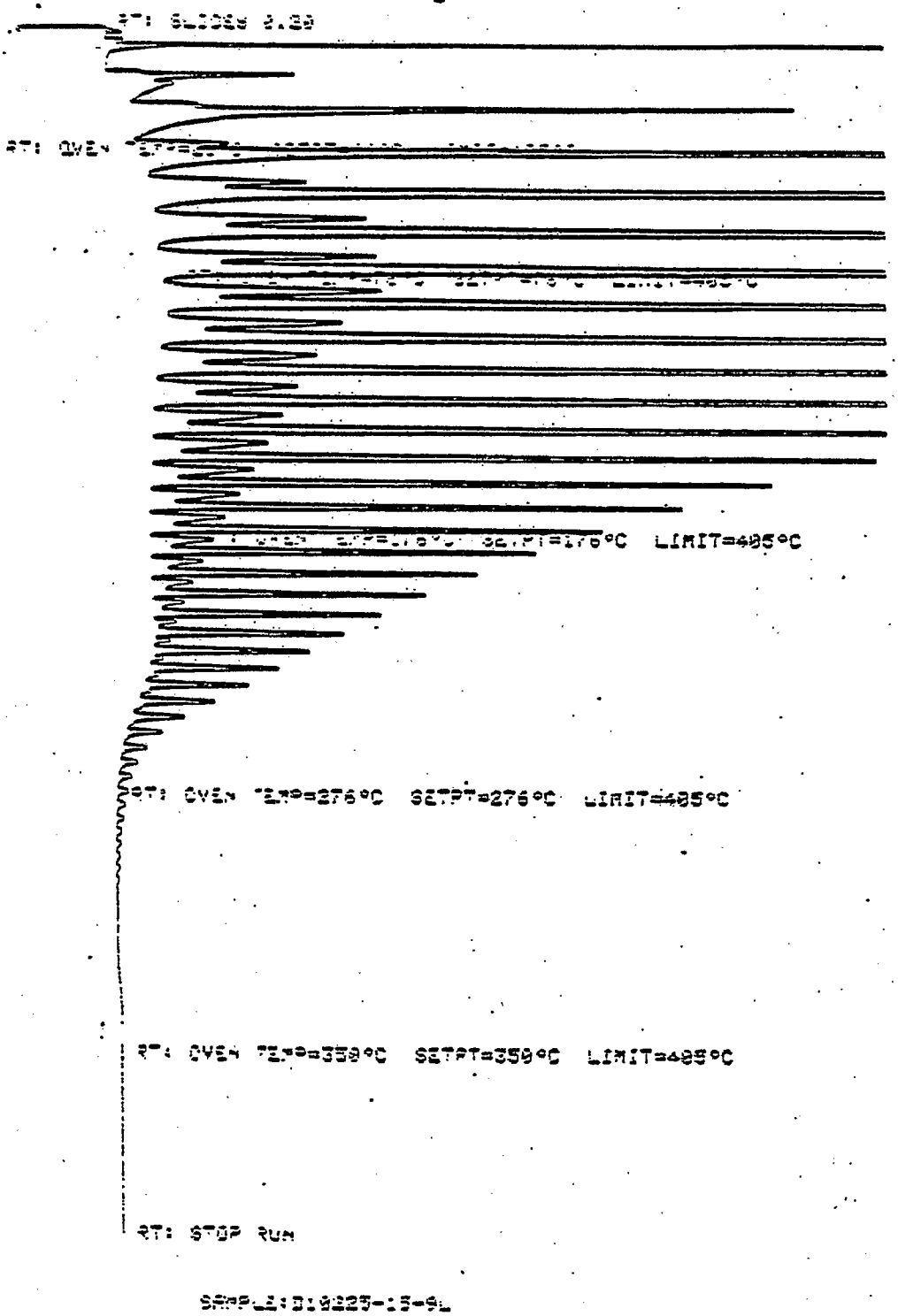

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=485°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=485°C
RT: OVEN TEMP=359°C SETPT=359°C LIMIT=485°C
RT: STOP RUN

Fig. 159

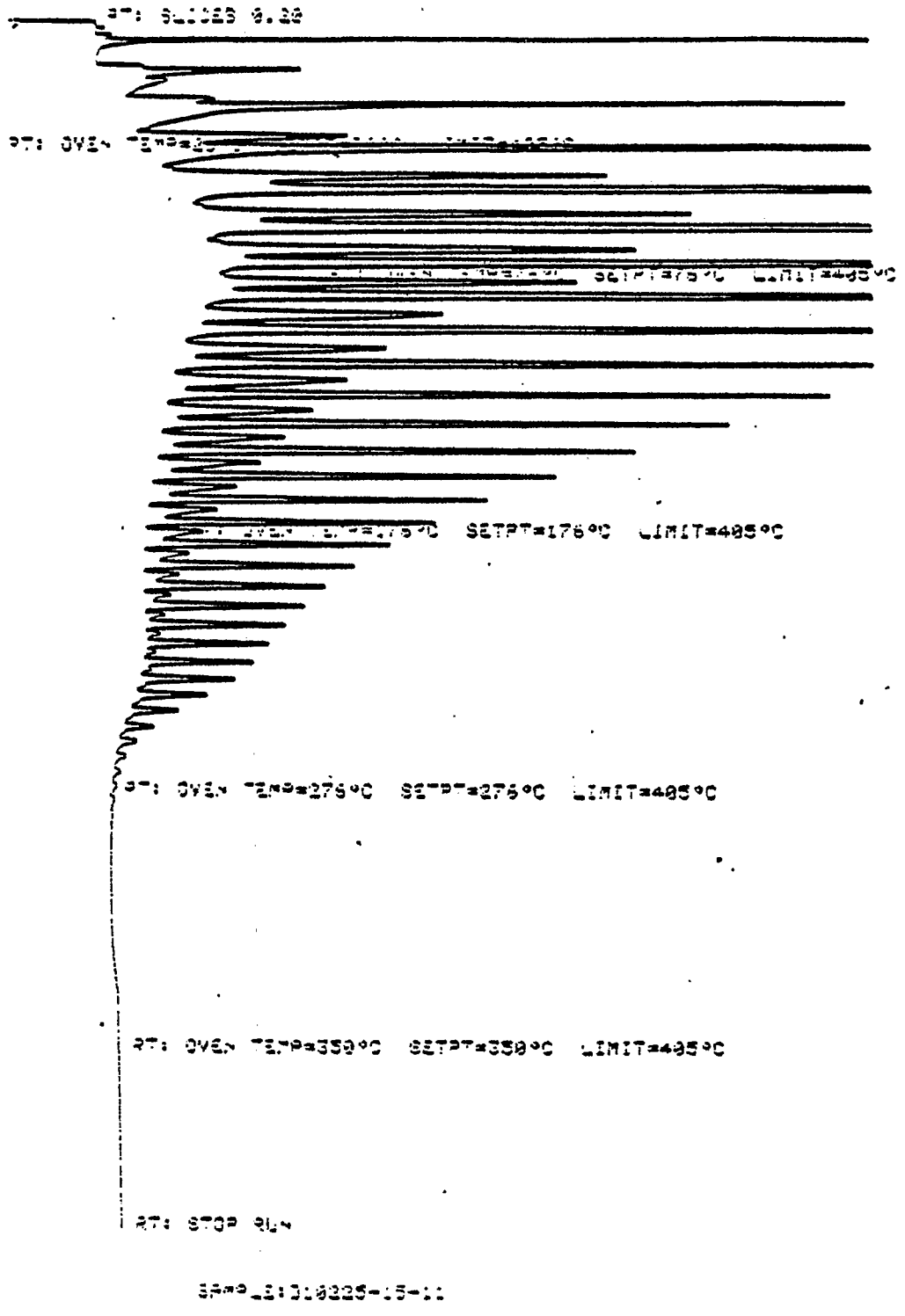

RT: SLIDES 0.00
RT: OVEN TEMP=
SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=175°C SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:010325-15-11

TABLE 19 RESULT OF SYNGAS OPERATION

RUN NO. 10225-15
CATALYST CO/TH+ZN-UCC-107 11684-06C 80CC 33.1GM (38.7 AFTER RUN +5.6G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-15-01	225-15-02	225-15-03	225-15-04	225-15-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	17.5	24.0	42.0	48.0	66.5
PRESSURE,PSIG	297	303	301	296	293
TEMP. C	268	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.50	6.50	24.50	6.00	24.50
EFFLNT GAS LITER	156.45	58.60	226.95	66.45	249.65
GM AQUEOUS LAYER	44.14	18.38	69.28	15.04	61.41
GM OIL	15.11	8.07	30.41	7.78	31.78
MATERIAL BALANCE					
GM ATOM CARBON %	86.20	94.75	93.62	104.31	100.49
GM ATOM HYDROGEN %	90.32	103.44	100.65	102.77	101.65
GM ATOM OXYGEN %	93.73	99.49	97.59	106.91	98.37
RATIO CHX/(H2O+CO2)	0.8337	0.9078	0.9167	0.9444	1.0488
RATIO X IN CHX	2.4875	2.4692	2.4542	2.5417	2.4738
USAGE H2/CO PRODT	1.3444	1.3508	1.4450	1.3814	1.4795
RATIO CO2/(H2O+CO2)	0.3431	0.3540	0.3027	0.3599	0.3152
K SHIFT IN EFFLNT	0.22	0.23	0.17	0.22	0.17
CONVERSION					
ON CO %	61.87	68.47	62.12	58.48	59.05
ON H2 %	84.99	87.82	86.34	83.73	84.83
ON CO+H2 %	73.70	78.57	74.67	71.01	72.01
PROT SELECTIVITY,WT %					
CH4	19.75	19.42	19.54	23.33	20.38
C2 HC'S	3.31	3.04	3.06	3.59	3.19
C3H8	3.71	3.62	3.63	4.32	4.50
C3H6=	1.74	1.51	1.89	2.29	2.05
C4H10	4.52	4.12	3.47	4.07	3.22
C4H8=	2.68	2.40	3.10	3.73	3.35
C5H12	6.38	5.58	4.42	4.99	3.63
C5H10=	1.40	1.30	2.05	2.63	2.56
C6H14	8.02	6.68	4.02	4.21	4.39
C6H12= & CYCLO'S	1.14	2.56	4.12	5.35	2.92
C7+ IN GAS	15.46	12.63	11.01	0.67	10.11
LIQ HC'S	31.88	37.14	39.69	40.82	39.69
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	35.71	34.10	34.69	41.32	36.69
C5 -420 F	52.50	46.40	44.48	36.63	41.88
420-700 F	10.91	16.53	17.66	17.91	17.42
700-END PT	0.88	2.97	3.18	4.13	4.02
C5+-END PT	64.29	65.90	65.31	58.68	63.31
ISO/NORMAL MOLE RATIO					
C4	0.6628	0.5819	0.3199	0.2921	0.1982
C5	1.9847	1.8495	1.0041	0.8634	0.4903
C6	3.4970	3.5003	3.5018	3.4986	0.7671
C4=	0.0364	0.0404	0.0430	0.0409	0.0456
PARAFFIN/OLEFIN RATIO					
C3	2.0390	2.2785	1.8314	1.7974	2.0979
C4	1.6297	1.6580	1.0778	1.0536	0.9257
C5	4.4156	4.1678	2.1012	1.8471	1.3755
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7657		0.8082		0.8162
RATIO CH4/(1-A)**2	3.5971		5.3113		6.0333
LIQ HC COLLECTION					
PHYS. APPEARANCE	GRN OIL		OIL SLD		OIL SLD
DENSITY	0.752		0.757		0.755
N, REFRACTIVE INDEX	1.4217		1.4266		1.4255
SIMULT'D DISTILATN					
10 WT % @ DEG F	241		255		258
16	261		289		299
50	378		424		440
84	517		622		647
90	566		677		701
RANGE(16-84 %)	256		333		348
WT % @ 420 F	63.00	47.50	47.50	46.00	46.00
WT % @ 700 F	97.23	92.00	92.00	89.88	89.88

TABLE 20 RESULT OF SYNGAS OPERATION

RUN NO. 10225-15
CATALYST CO/TH+ZN-UCC-107 11684-06C 80CC 33.1GM (38.7 AFTER RUN +5.6G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-15-07	225-15-08	225-15-09	225-15-10	225-15-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	93.5	98.0	114.5	122.0	138.5
PRESSURE,PSIG	301	303	297	300	303
TEMP. C	270	270	270	281	281
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	27.00	4.50	21.00	7.50	24.00
EFFLNT GAS LITER	241.80	40.50	192.00	55.05	178.40
GM AQUEOUS LAYER	73.52	13.21	61.64	14.72	47.09
GM OIL	36.19	6.42	29.96	5.81	18.59
MATERIAL BALANCE					
GM ATOM CARBON %	90.26	91.88	93.09	75.11	74.76
GM ATOM HYDROGEN %	96.90	100.74	101.74	84.38	83.09
GM ATOM OXYGEN %	91.03	93.78	94.51	77.23	76.41
RATIO CHX/(H2O+CO2)	0.9819	0.9579	0.9686	0.9483	0.9581
RATIO X IN CHX	2.4402	2.4297	2.4463	2.7570	2.7272
USAGE H2/CO PRODT	1.5699	1.5824	1.5922	1.3301	1.3644
RATIO CO2/(H2O+CO2)	0.2499	0.2380	0.2382	0.4341	0.4105
K SHIFT IN EFFLNT	0.12	0.11	0.11	0.31	0.28
CONVERSION					
ON CO %	58.27	58.80	58.62	75.53	72.16
ON H2 %	85.84	86.35	86.51	91.09	89.94
ON CO+H2 %	72.55	73.21	73.18	83.76	81.52
PROT SELECTIVITY,WT %					
CH4	19.43	19.05	19.98	34.15	33.25
C2 HC'S	3.10	2.95	3.06	4.55	4.29
C3H8	3.42	3.26	3.19	5.05	4.51
C3H6=	2.00	1.91	1.87	1.41	1.65
C4H10	2.75	2.62	2.57	3.95	3.35
C4H8=	3.29	3.22	3.12	2.74	3.04
C5H12	2.96	2.72	2.60	3.54	3.06
C5H10=	2.54	2.47	2.47	2.18	2.41
C6H14	3.85	3.84	3.76	4.26	4.14
C6H12= & CYCLO'S	2.89	2.88	2.86	2.37	2.65
C7+ IN GAS	9.01	8.92	8.95	8.56	9.49
LIQ HC'S	44.74	46.17	45.57	27.25	28.14
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.00	33.01	33.79	51.84	50.10
C5 -420 F	40.28	40.37	39.93	34.94	36.25
420-700 F	21.12	21.70	21.42	10.82	11.17
700-END PT	4.61	4.93	4.86	2.40	2.48
C5+-END PT	66.00	66.99	66.21	48.16	49.90
ISO/NORMAL MOLE RATIO					
C4	0.1419	0.1384	0.1167	0.1809	0.1318
C5	0.2523	0.2492	0.2004	0.3551	0.2237
C6	0.5644	0.5399	0.5140	0.6128	0.5722
C4=	0.0532	0.0557	0.0586	0.0987	0.0898
PARAFFIN/OLEFIN RATIO					
C3	1.6323	1.6305	1.6224	3.4280	2.6006
C4	0.8057	0.7859	0.7946	1.3928	1.0638
C5	1.1326	1.0732	1.0222	1.5812	1.2344
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8231		0.8242		0.8049
RATIO CH4/(1-A)**2	6.2097		6.4619		8.7388
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL SLD		OIL SLD		OIL SLD
DENSITY	0.754		0.754		0.753
N, REFRACTIVE INDEX	1.4250		1.4250		1.4229
SIMULT'D DISTILATN					
10 WT % @ DEG F	258		257		256
16	300		300		290
50	448		448		416
84	648		648		614
90	703		710		685
RANGE(16-84 %)	348		348		324
WT % @ 420 F	42.50	42.33	42.33	51.50	51.50
WT % @ 700 F	89.70	89.33	89.33	91.19	91.19

XI. Run 10 (11723-01) with Catalyst 10 (Co/Th + α-Al_2O_3)

This is a reference catalyst, the same as Catalyst 1 except that the Molecular Sieve was replaced with inactive α-Al_2O_3 polishing powder with a 1-micron particle size. The test is very short, but the same catalyst is tested again in Run 11.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 160-163. A simulated distillation of one C_5^+ product is plotted in Fig. 164. Carbon number product distributions are plotted in Figs. 165-166. Chromatograms from the simulated distillations of two samples are reproduced in Figs. 167-168. Detailed material balances appear in Table 21.

Conversion of the H_2+CO syngas was extremely high at 270C. The water gas shift activity was excellent, with 80 percent of the oxygen rejected as CO_2. Usage of the 1:1 H_2:CO syngas was less than 1.0:1 even though the product was exceptionally hydrogen rich (3.2 hydrogens per carbon vs. the usual 2.3 to 2.4).

The selectivity, however, was very poor, yielding a product made up of 50 percent methane, 23 percent C_2-C_4, 23 percent gasoline, 2 percent diesel oil, and 0.2 percent heavies.

Evidently this catalyst is a strong methanator. Why the Co/Th metal component acted so differently in this run than it has done in other contexts is hard to explain.

Fig. 160

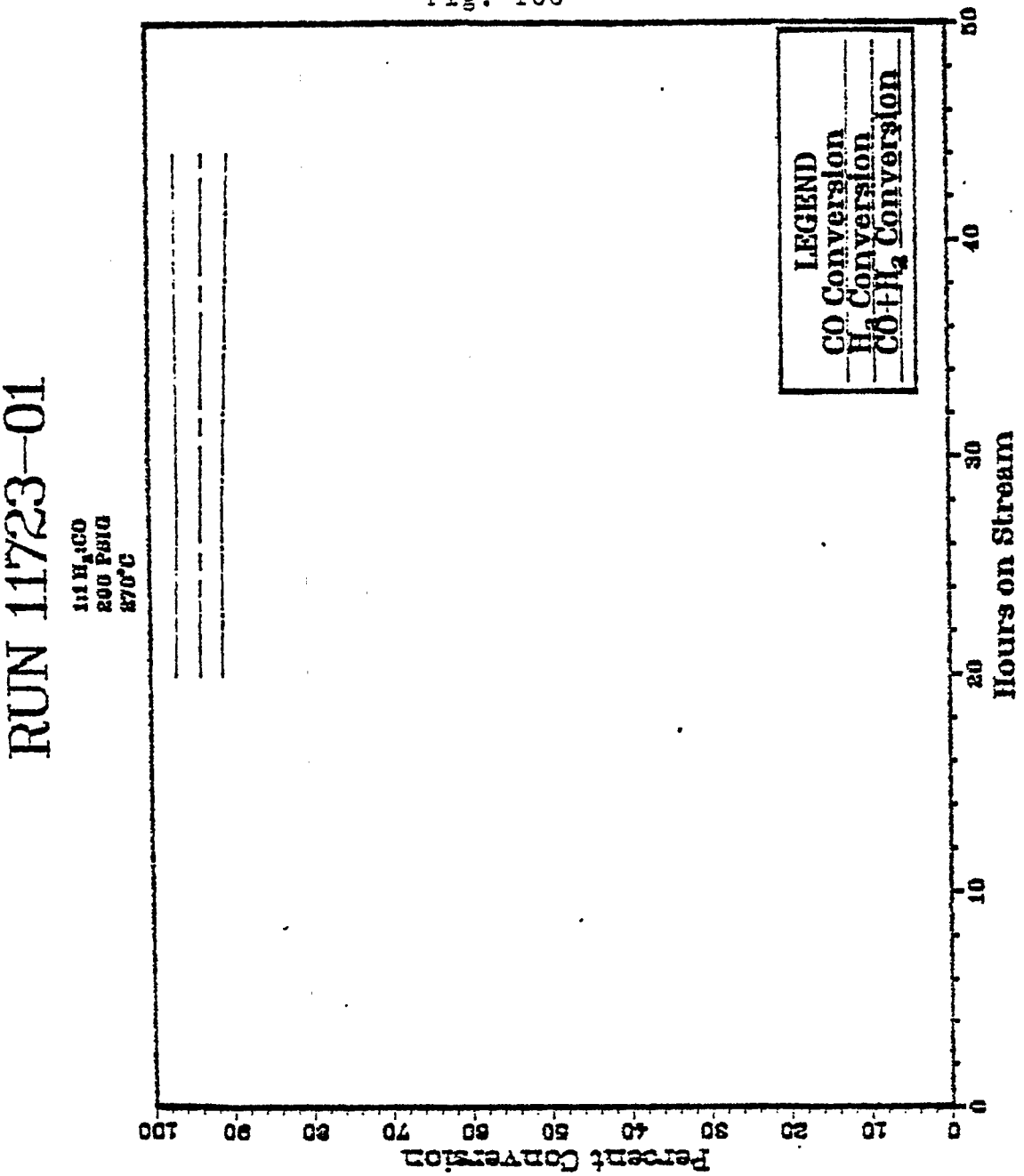
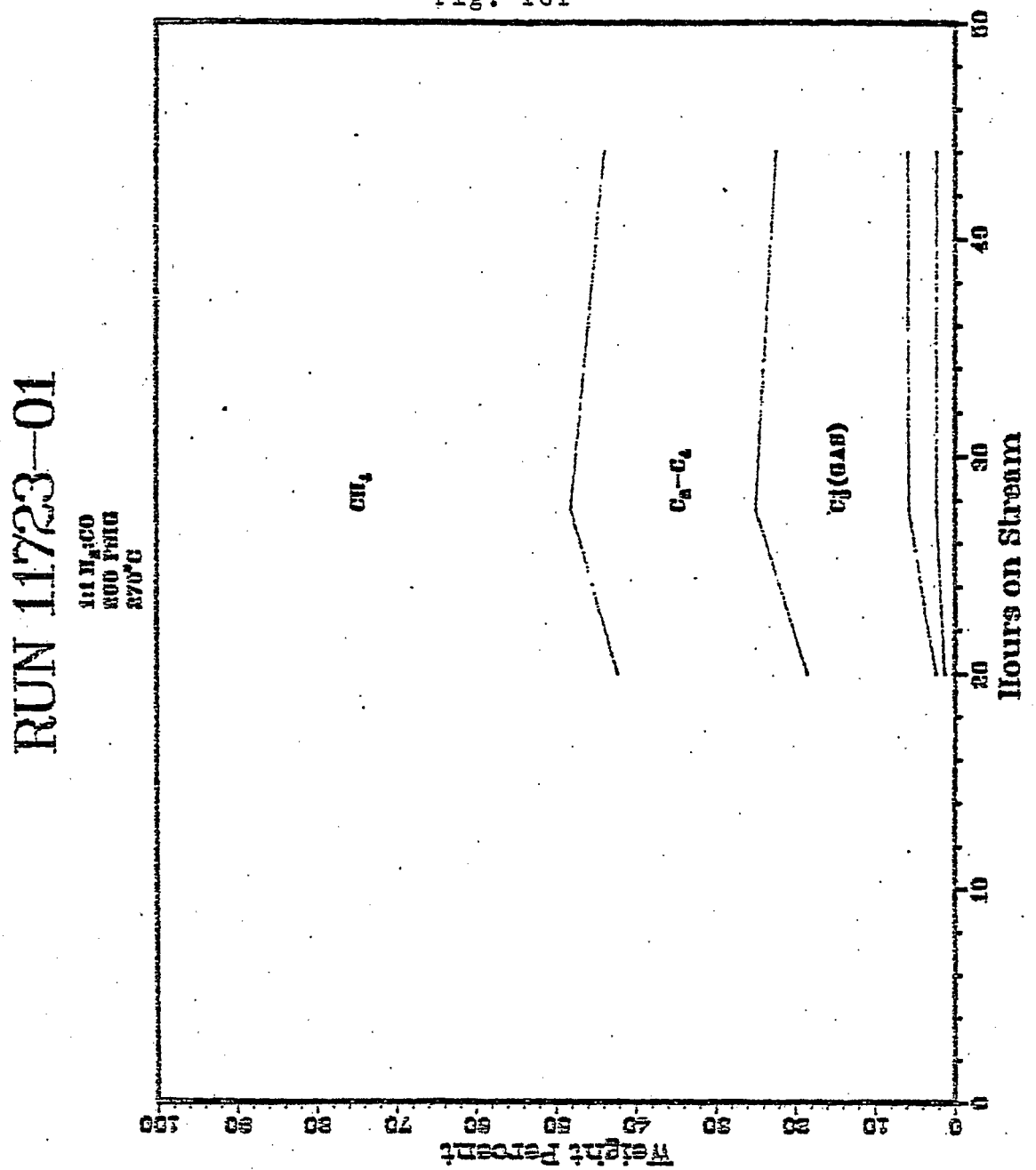

RUN 11723-01
1:1 H2:CO
200 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 161


RUN 11723-01
111 H2:CO
8000 VHSV
270°C
CH4
C2-C4
C5(GAS)
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

RUN 11723-01

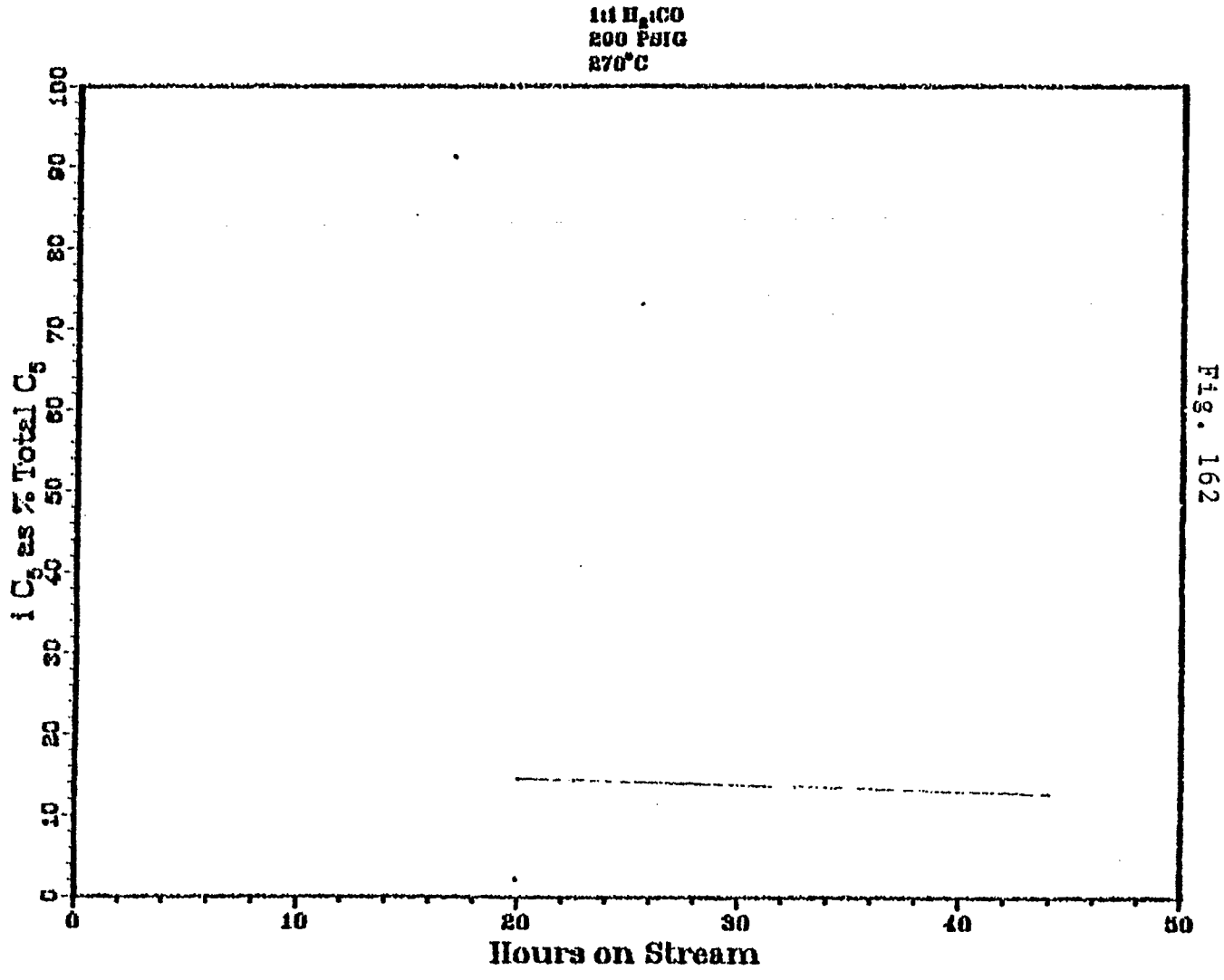


Fig. 162

RUN 11723--01

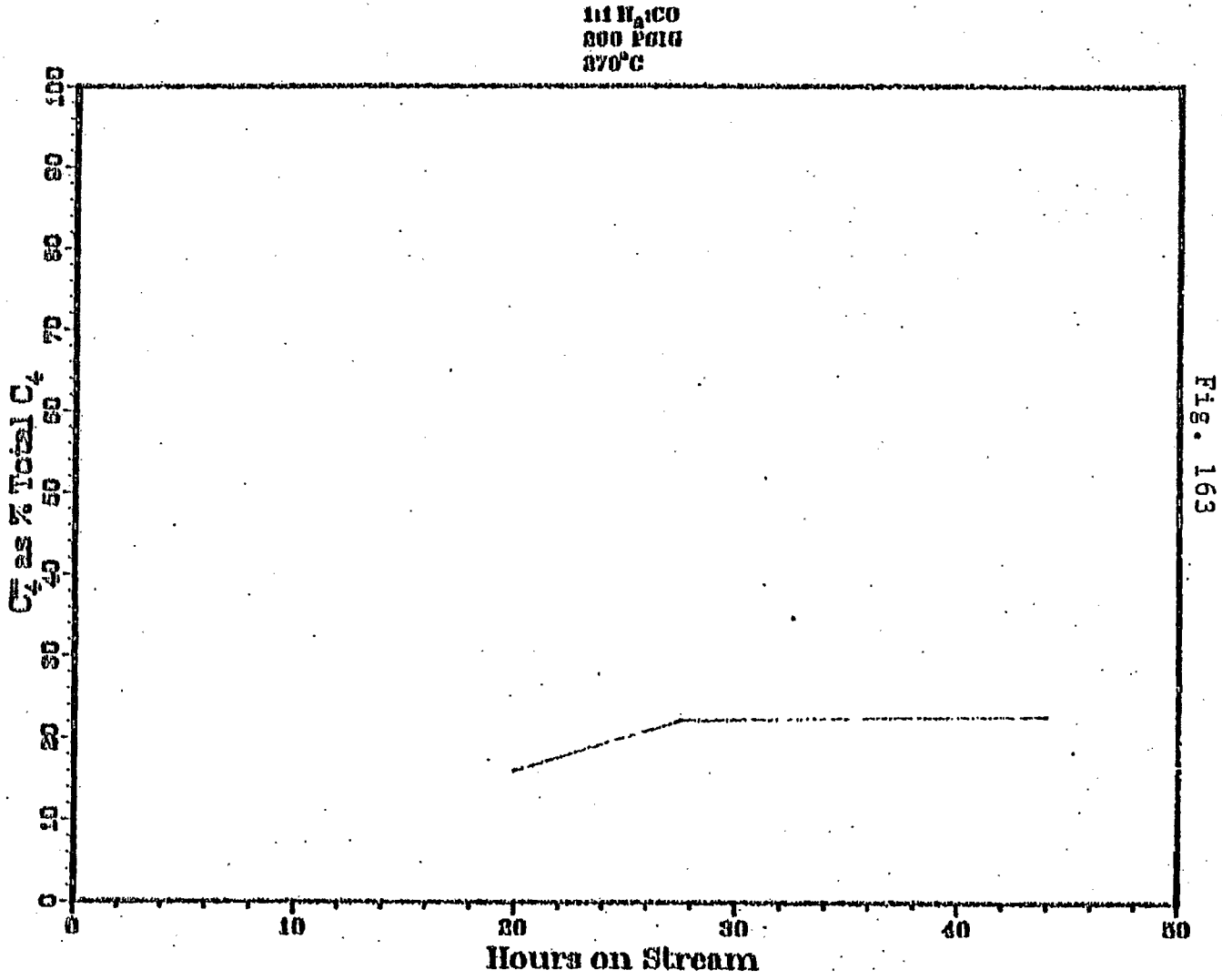


Fig. 163

Fig. 164

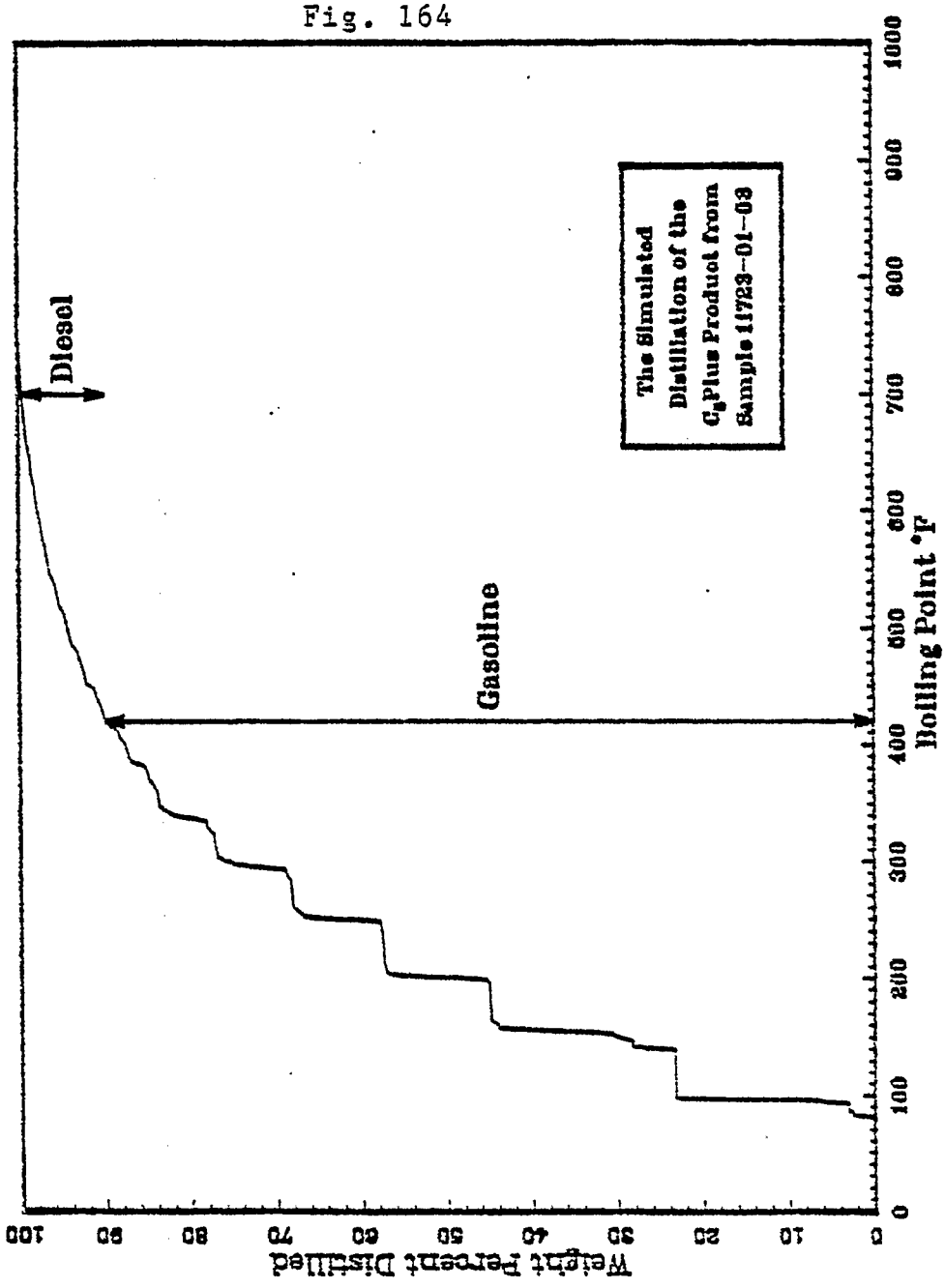

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11723-01-03
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. 165

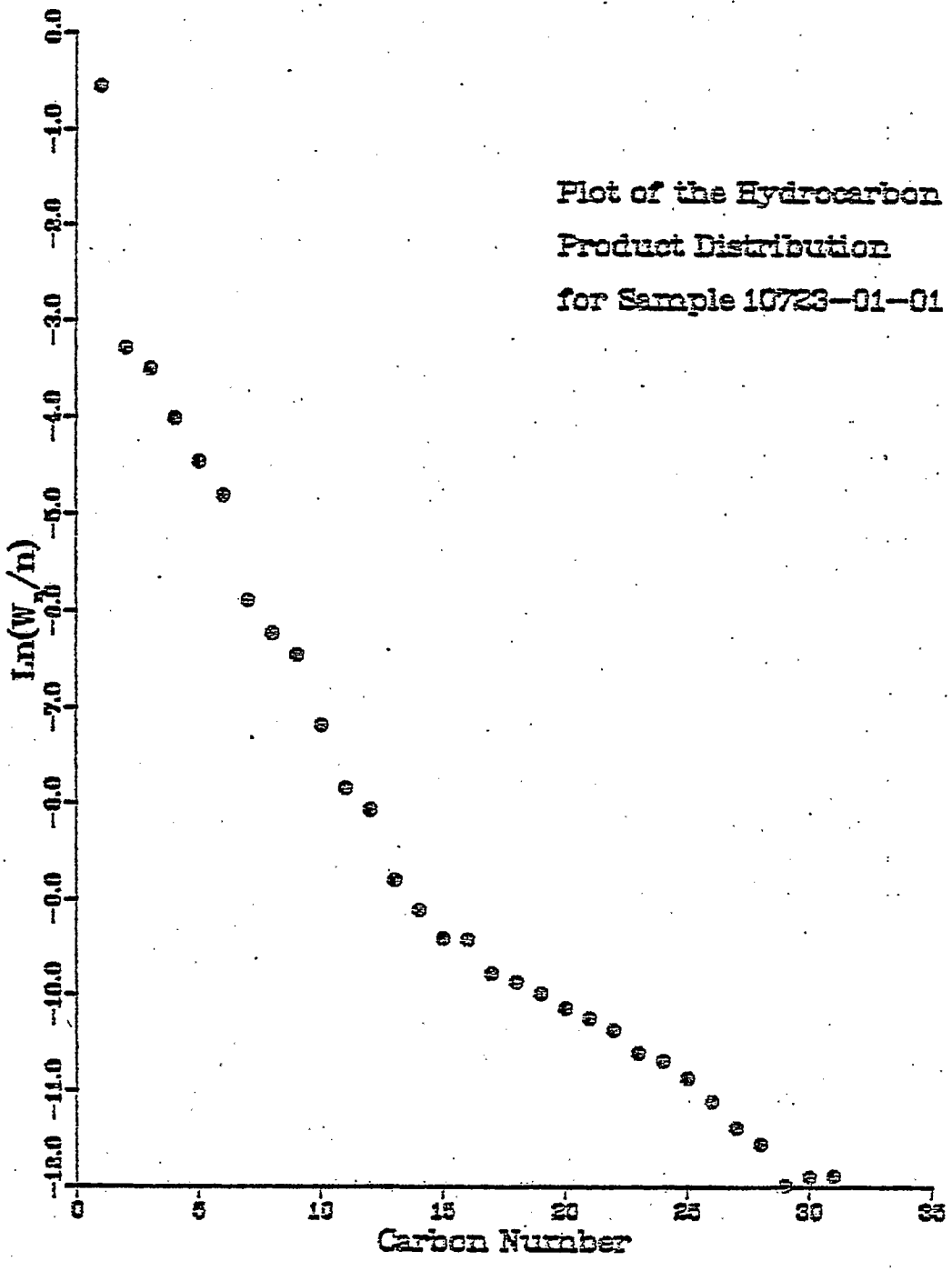

Plot of the Hydrocarbon
Product Distribution
for Sample 10723-01-01
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 166

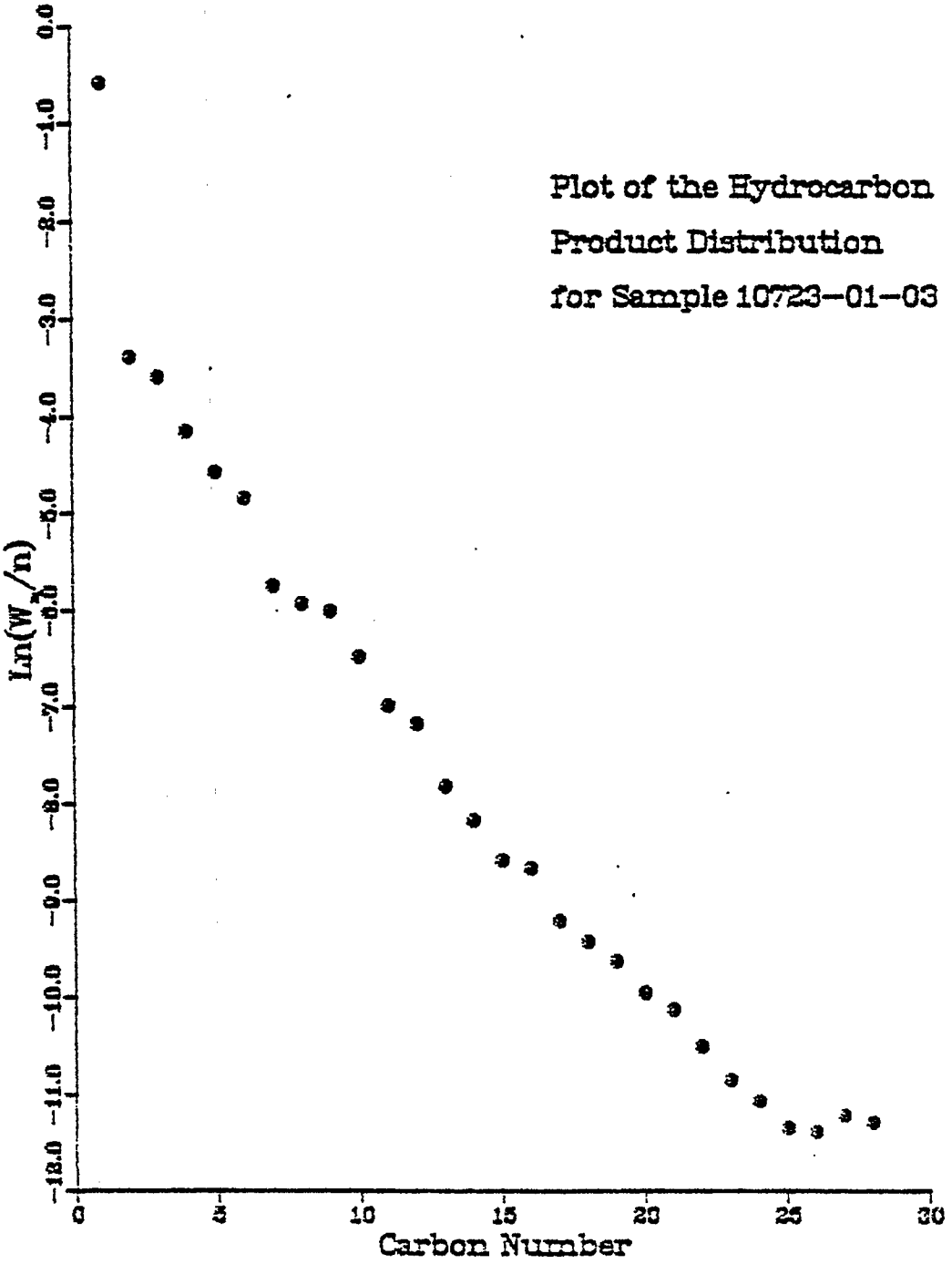

Plot of the Hydrocarbon
Product Distribution
for Sample 10723-01-03
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
Carbon Number

Fig. 167

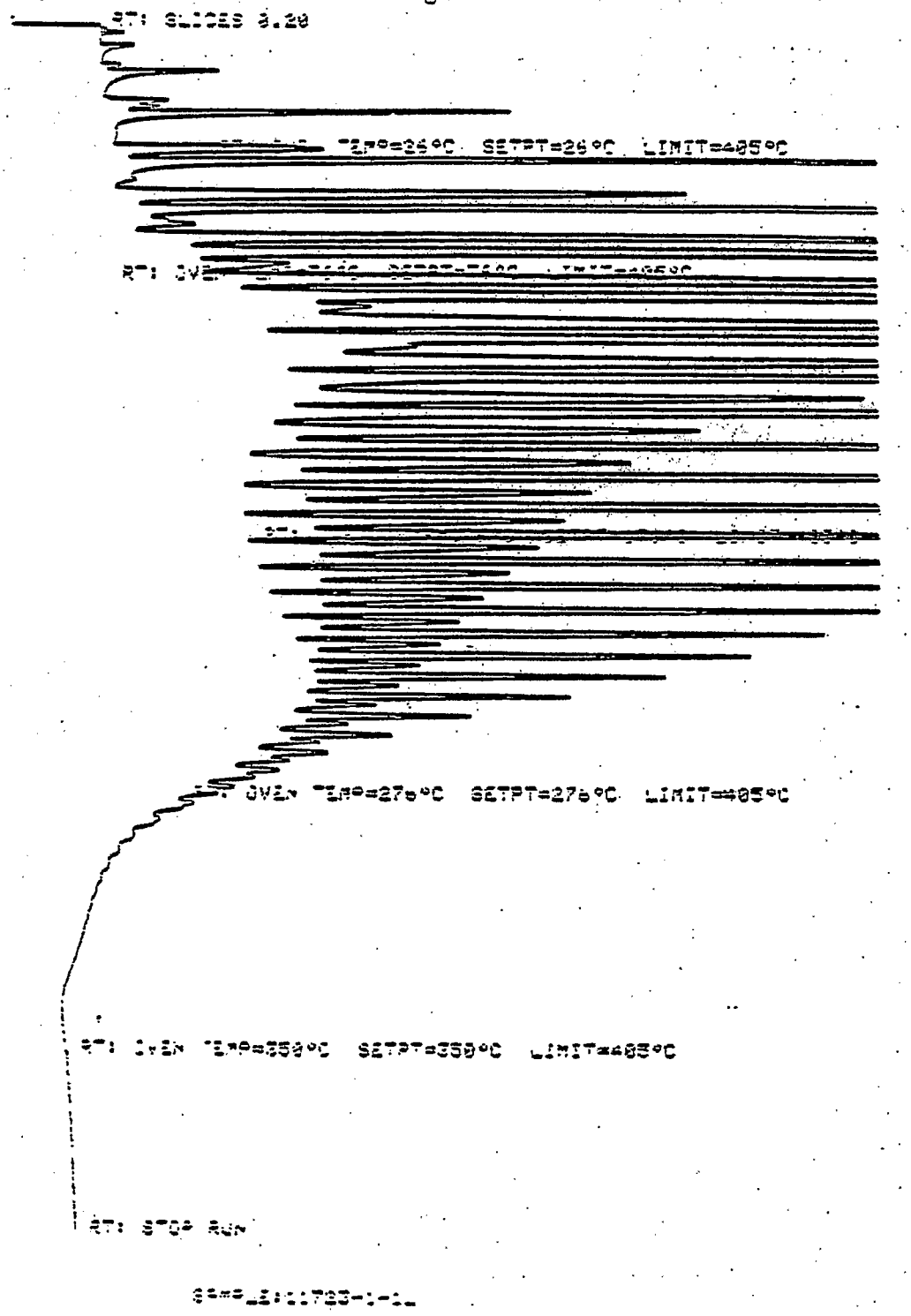

RT: SLICES 0.20
SETPT=26°C LIMIT=405°C
SETPT=275°C LIMIT=405°C
SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 168

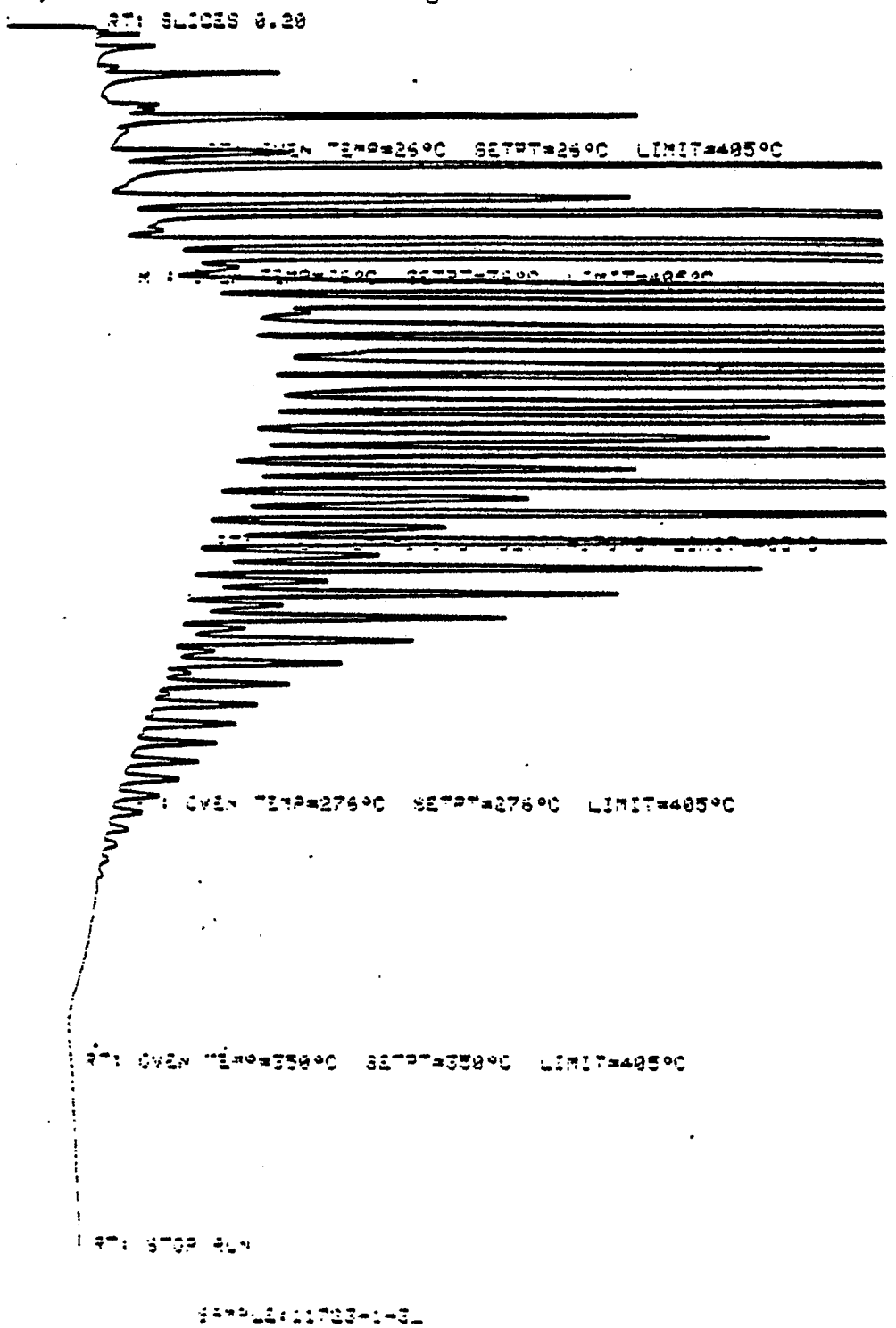

RT: SLICES 0.20
OVEN TEMP=25°C SETPT=25°C LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

TABLE 21 RESULT OF SYNGAS OPERATION

RUN NO. 11723-01
CATALYST CO/TH +AL2O3 #11684-28C 80 CC 48.9GM (47.1 AFTER RUN -1.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11723-01-01	723-01-02	723-01-03
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	20.0	27.5	44.0
PRESSURE,PSIG	290	293	288
TEMP. C	273	273	274
FEED CC/MIN	400	400	400
HOURS FEEDING	20.00	7.50	24.00
EFFLNT GAS LITER	207.45	77.10	249.15
GM AQUEOUS LAYER	13.13	6.03	19.31
GM OIL	1.79	1.62	5.20
MATERIAL BALANCE			
GM ATOM CARBON %	91.41	94.08	91.70
GM ATOM HYDROGEN %	95.78	100.12	100.11
GM ATOM OXYGEN %	94.41	94.54	93.47
RATIO CHX/(H2O+CO2)	0.9402	0.9910	0.9650
RATIO X IN CHX	3.3087	3.1801	3.2510
USAGE H2/CO PRODT	0.9692	0.9997	1.0052
RATIO CO2/(H2O+CO2)	0.8203	0.7904	0.7884
K SHIFT IN EFFLNT	13.07	10.28	12.15
CONVERSION			
ON CO %	96.69	96.40	96.59
ON H2 %	90.95	90.78	89.83
ON CO+H2 %	93.75	93.50	93.06
PROT SELECTIVITY,WT %			
CH4	57.72	51.93	56.12
C2 HC'S	7.45	6.72	6.79
C3H8	8.53	8.32	7.66
C3H6=	0.50	0.70	0.66
C4H10	6.10	5.78	4.95
C4H8=	1.13	1.60	1.41
C5H12	4.97	5.21	4.38
C5H10=	0.81	0.90	0.84
C6H14	4.40	4.88	4.07
C6H12= & CYCLO'S	0.49	0.70	0.64
C7+ IN GAS	5.41	7.52	6.59
LIQ HC'S	2.50	5.72	5.89
TOTAL	100.00	100.00	100.00

SUB-GROUPING			
C1 -C4	81.42	75.06	77.59
C5 -420 F	17.21	22.67	20.07
420-700 F	1.07	2.09	2.15
700-END PT	0.29	0.18	0.18
C5+-END PT	18.58	24.94	22.41
ISO/NORMAL MOLE RATIO			
C4	0.0729	0.0587	0.0497
C5	0.1703	0.1627	0.1457
C6	0.3786	0.3895	0.3540
C4=	0.3368	0.2819	0.2595
PARAFFIN/OLEFIN RATIO			
C3	16.2488	11.2902	11.0043
C4	5.2347	3.4888	3.3974
C5	5.9476	5.6225	5.0774
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))	0.7447		0.7221
RATIO CH4/(1-A)**2	8.8530		7.2650
LIQ HC COLLECTION			
PHYS. APPEARANCE	CLR OIL		CLR OIL
DENSITY	0.763		0.749
N, REFRACTIVE INDEX	1.4268		1.4202
SIMULT'D DISTILATN			
10 WT % @ DEG F	286		259
16	303		299
50	448		389
84	668		543
90	716		598
RANGE(16-84 %)	365		244
WT % @ 420 F	45.40	60.33	60.33
WT % @ 700 F	88.30	96.87	96.87

XII. Run 11 (11677-07) with Catalyst 11 (Co/Th + α-Al_2O_3)

This catalyst, the same as Catalyst 10, was rerun to obtain reference data for a catalyst without a Molecular Sieve.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 169-172. Simulated distillations of the C_5^+ product are plotted in Figs. 173-178. Carbon number product distributions are plotted in Figs. 179-188. Chromatograms from simulated distillations are reproduced in Figs. 189-198. Detailed material balances appear in Tables 22-25.

At 270C, as in the previous run, the conversion was extremely high (93 percent), and deactivated only slightly; the water gas shift activity was very high, with more than 80 percent of the oxygen rejected as CO_2; and the H_2:CO usage ratio was less than 1:1. When the temperature was lowered to 250C the conversion dropped to about 65 percent. The water gas shift activity also dropped, to 68 percent of oxygen rejected as CO_2, still much higher than the initial values of other catalysts at higher temperatures. But at 250C, even though the water gas shift activity was lower than at 270C, the hydrocarbon products were poorer in hydrogen, so that the H_2:CO usage ratio was lower as well--0.83:1, down from 0.90:1 at 270C. At 260C the conversion rose again, to 85 percent; the water gas shift activity rose to the

same level as at 270C; and the usage ratio was between the 250C and 270C levels.

At 270C the selectivity of this catalyst was poor, as it was in the previous run. The product was extremely hydrogen-rich: predominantly lights (more than 45 percent methane, 20 percent C_2-C_4, less than 30 percent gasoline, 4 percent diesel oil, and 0.5 percent heavies), all of which were almost completely saturated.

When the temperature was lowered to 250C, the methane production dropped to less than 15 percent. C_2-C_4 production dropped to 15 percent. The lights were more olefinic. The selectivity to gasoline and diesel oil improved. The liquid product was distinctly waxy, which was to be expected since the α-Al_2O_3 has no acid activity. The yield of total motor fuels was between 68 and 71 percent, near the 72 percent maximum for a Schulz-Flory distribution.

At 260C the methane production was again rather high at 32 percent, C_2-C_4 production was up to about 21 percent, the lights were highly paraffinic, and the production of total motor fuels was low. The Schulz-Flory plots, as expected, show a straight line distribution except for the excess methane. The chromatograms from the simulated distillations show that the liquid product, like the pentane, was mostly n-paraffins.

The most significant finding of this test is the differential sensitivity of the catalyst to temperature. Since its selectivity varies much more widely with temperature than its conversion,

lowering the temperature substantially improves the yield of useful products. The yield of C_2^+ hydrocarbons was 2.1 gm per hour at 250C, 2.37 gm per hour at 260C, and 1.99 gm per hour at 270C. At 270C, although the conversion was highest, the yield of C_2^+ was lowest. This same behavior was also observed for the C_5^+ product, which was produced at 1.18 gm per hour at 270C, 1.60 gm per hour at 260C, and 1.73 gm per hour at 250C.

At 250C, therefore, as compared with 260C and 270C, the yield from this catalyst was both highest in desirable fractions and lowest in undesirable by-products. These findings point up the value of an active catalyst whose selectivity can be improved by controlling the temperature.

Fig. 169

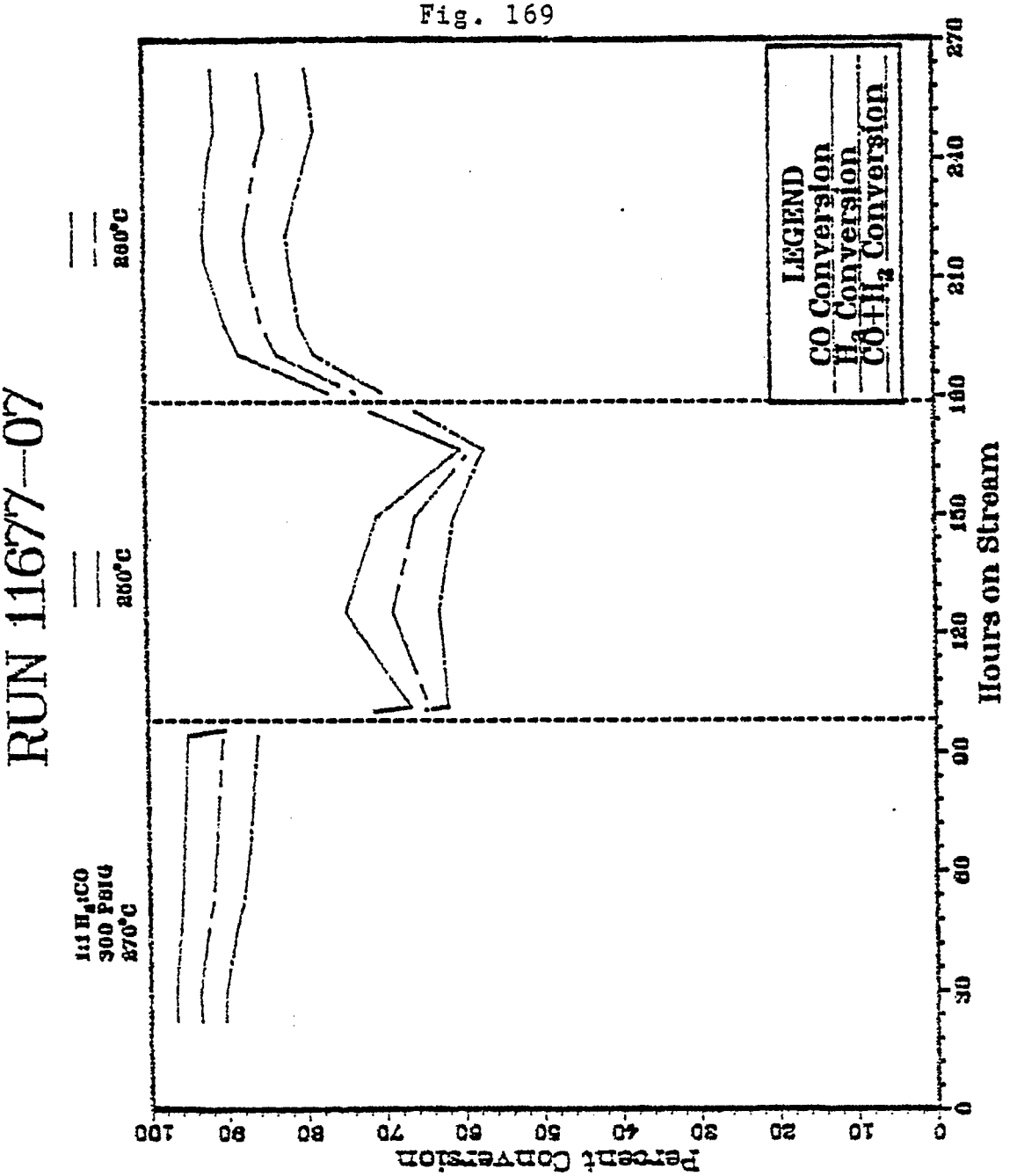

RUN 11677-07
1:1 H2:CO
300 PSIG
270°C
260°C
280°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270

Fig. 170

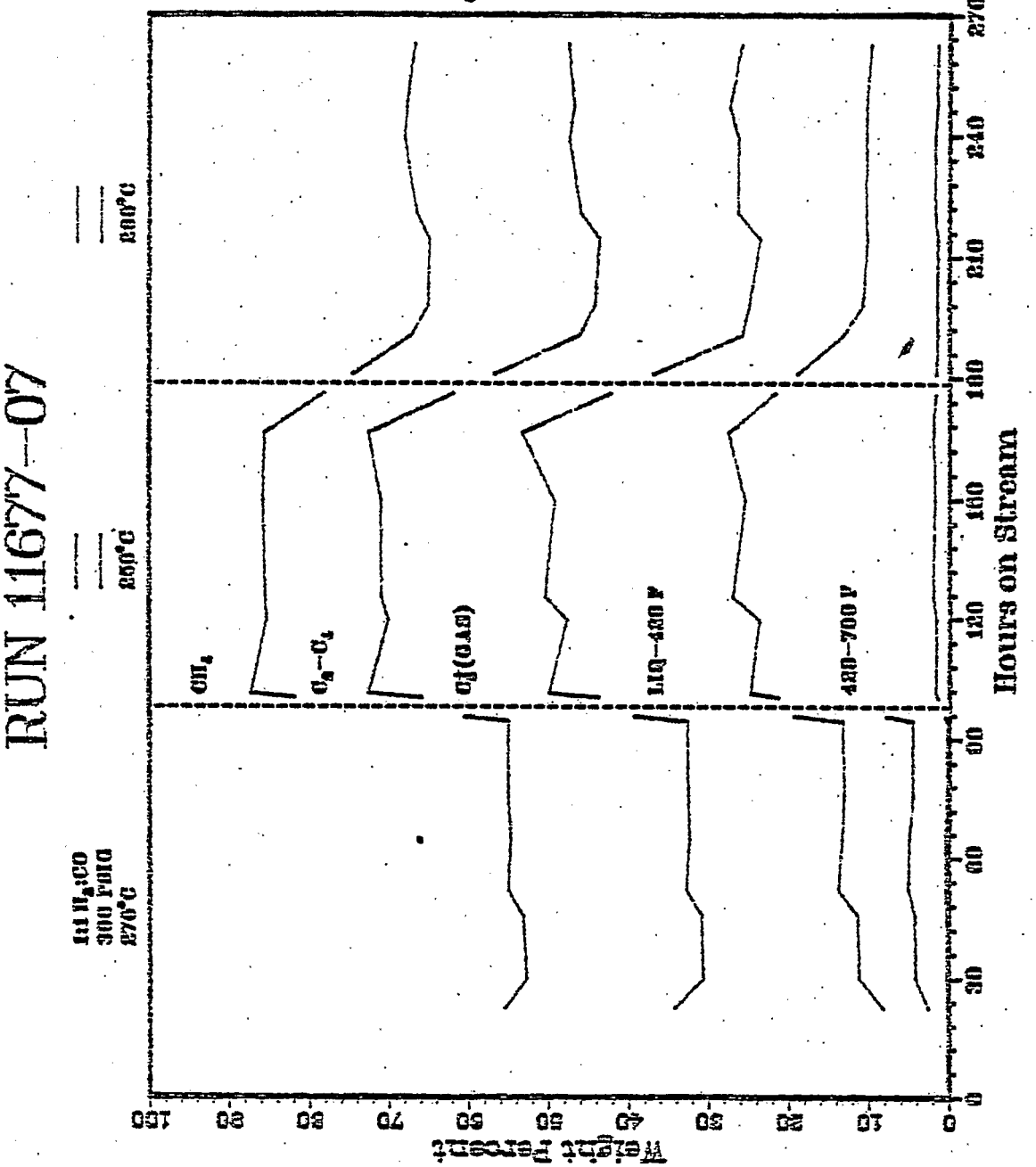

RUN 11677-07
Weight Percent
Hours on Stream
CH_4
C_2-C_4
C_5(GAS)
LIQ-430 F
430-700 F
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280

Fig. 171

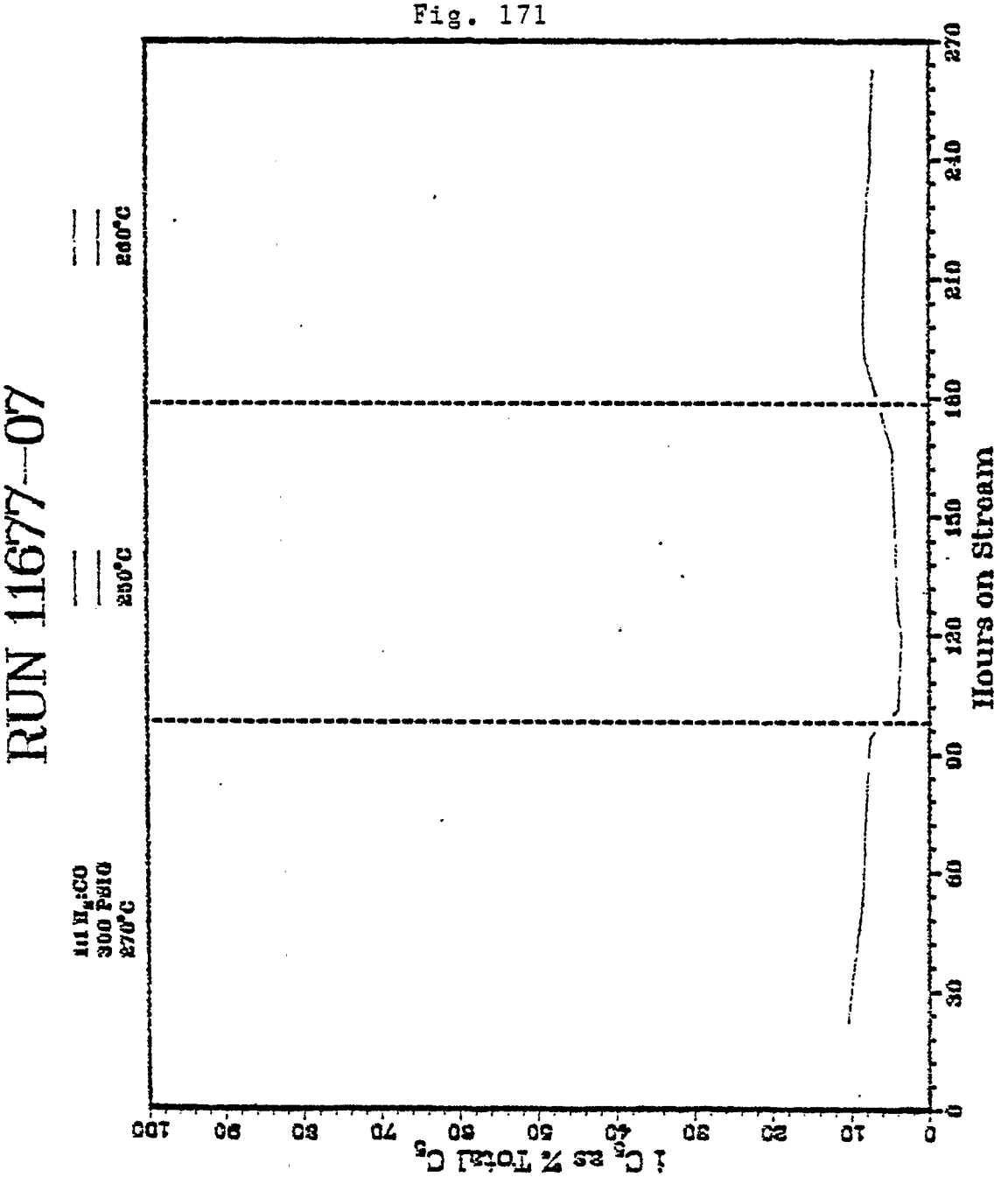

RUN 11677-07
1:1 H2:CO
300 PSIG
270°C
250°C
260°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270

Fig. 172

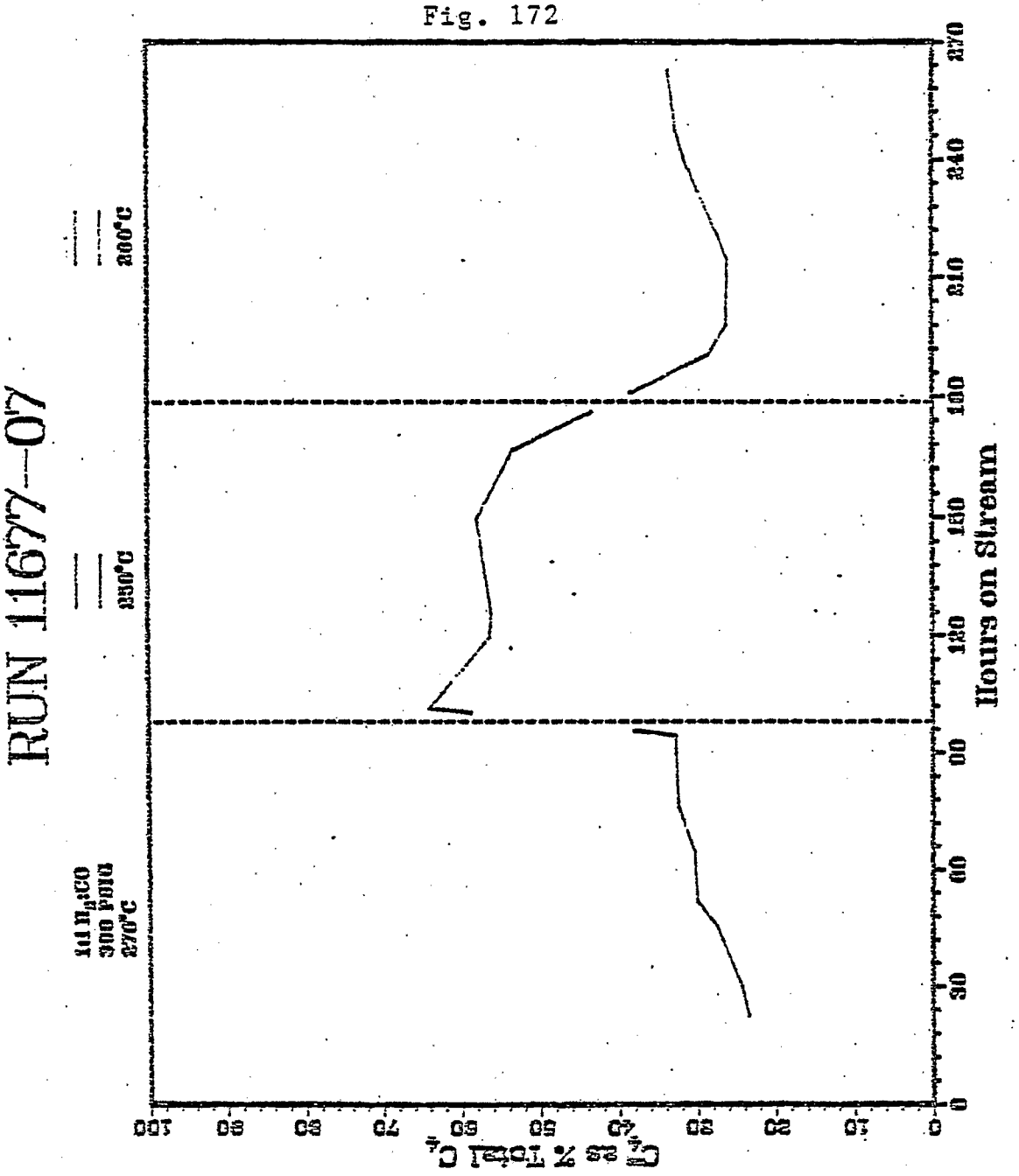

RUN 11677-07
111 lb/hr CO
300 PSIA
270°C
350°C
300°C
C_4 as % Total C_4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
130
140
150
160
180
210
240
270

Fig. 173

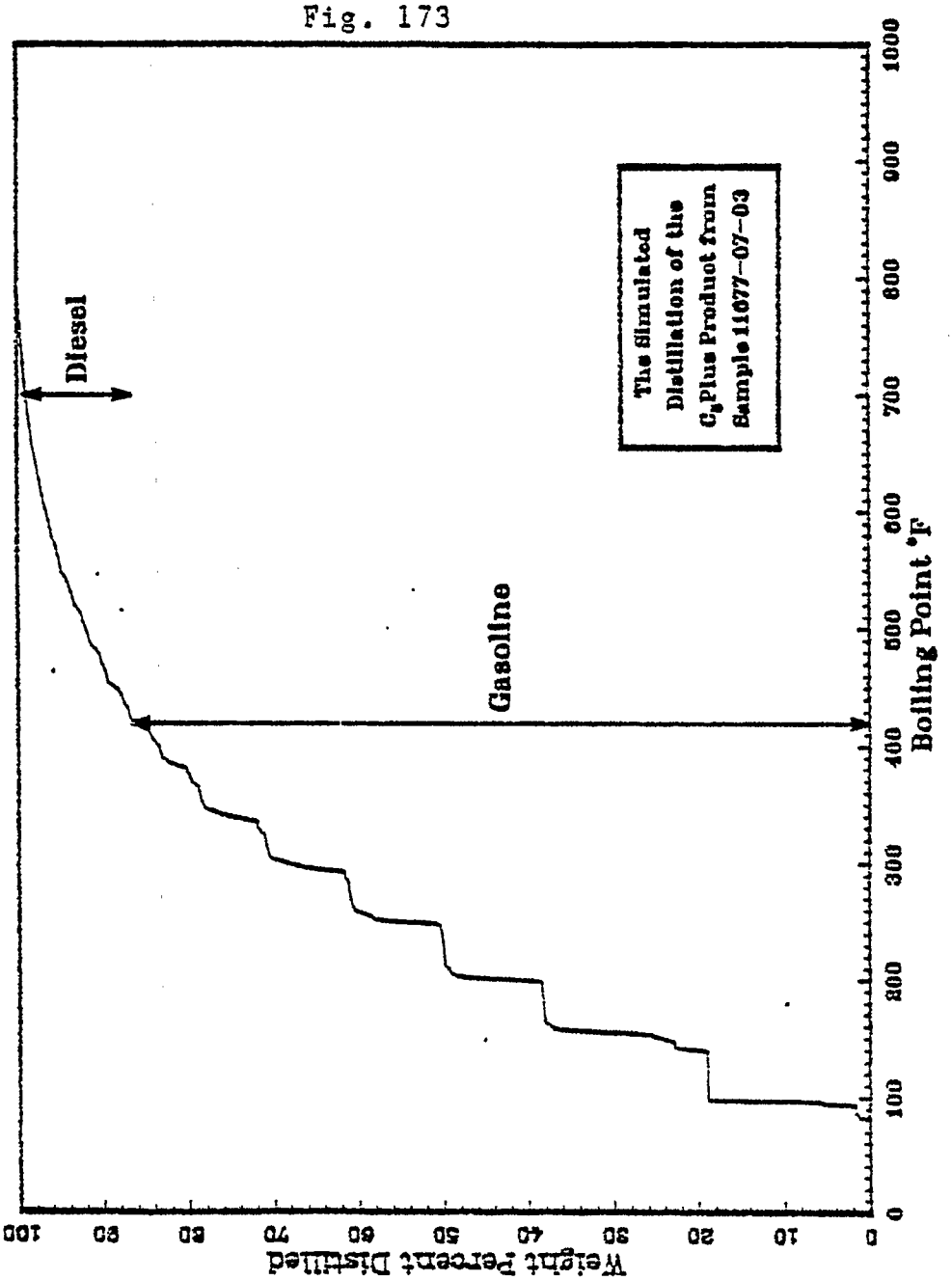

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-07-03
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. 174

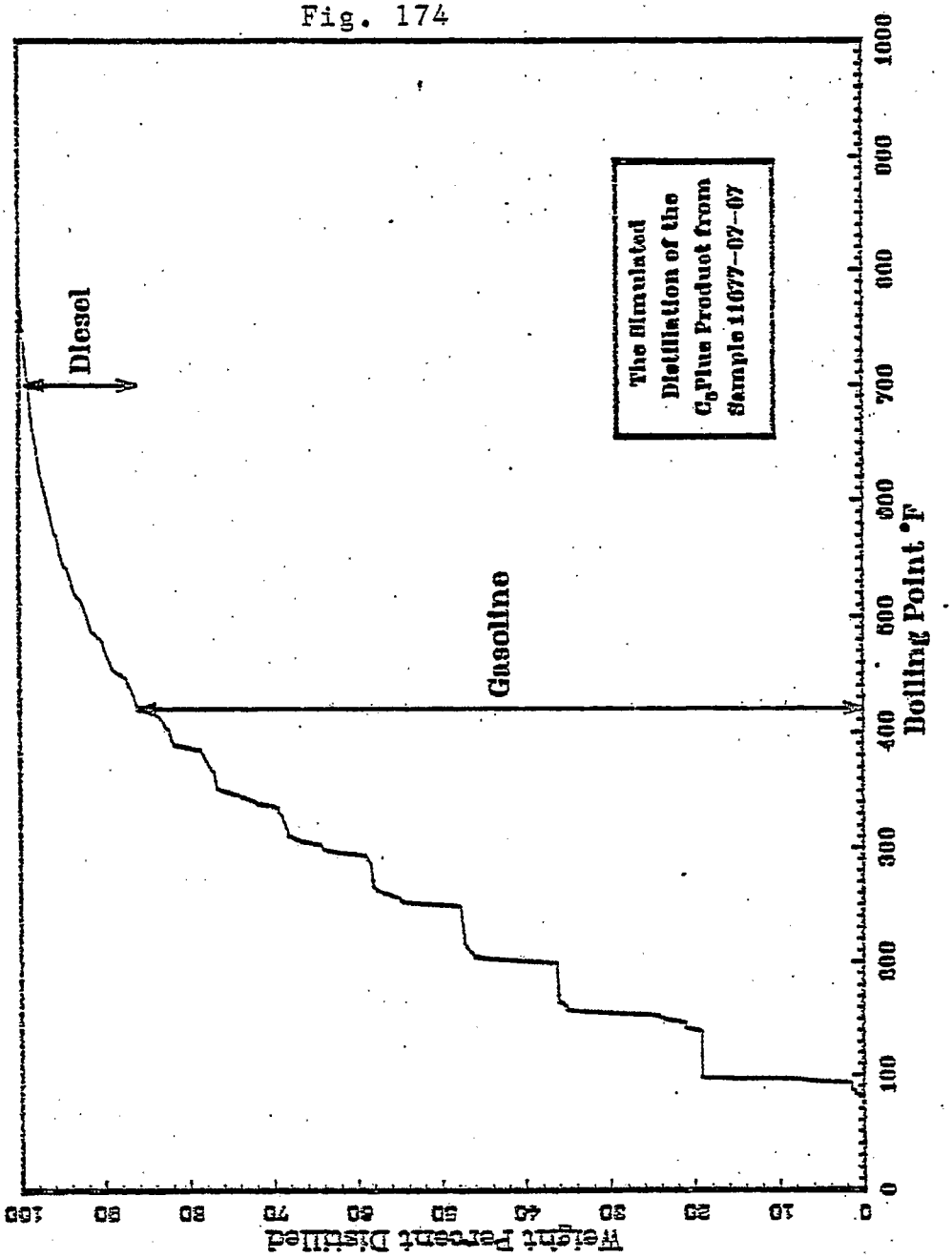

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-07-07
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 175

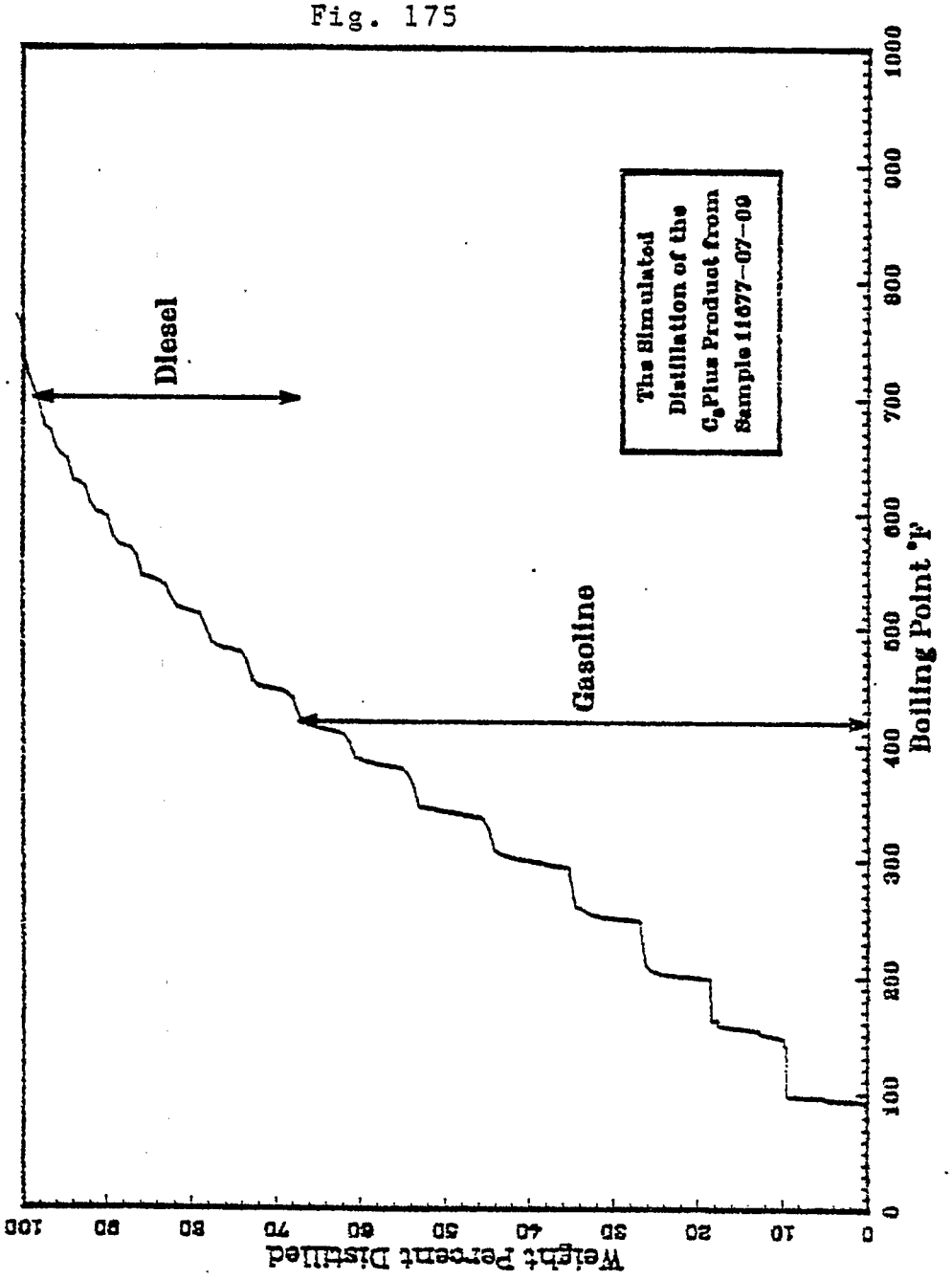

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-07-09

Fig. 176

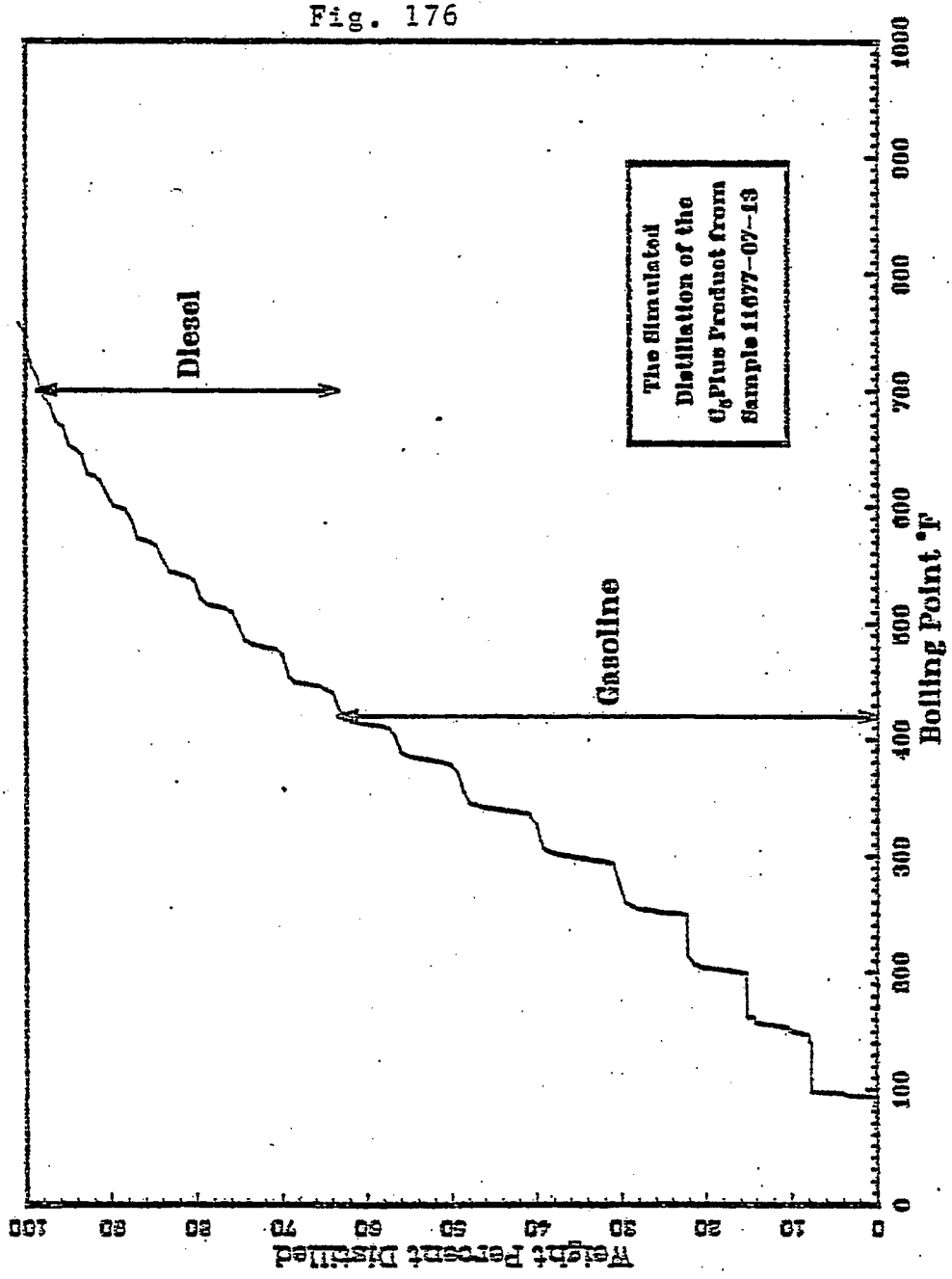

Diesel
Gasoline
The Simulated Distillation of the C_5 Plus Product from Sample 11677-07-13
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 177

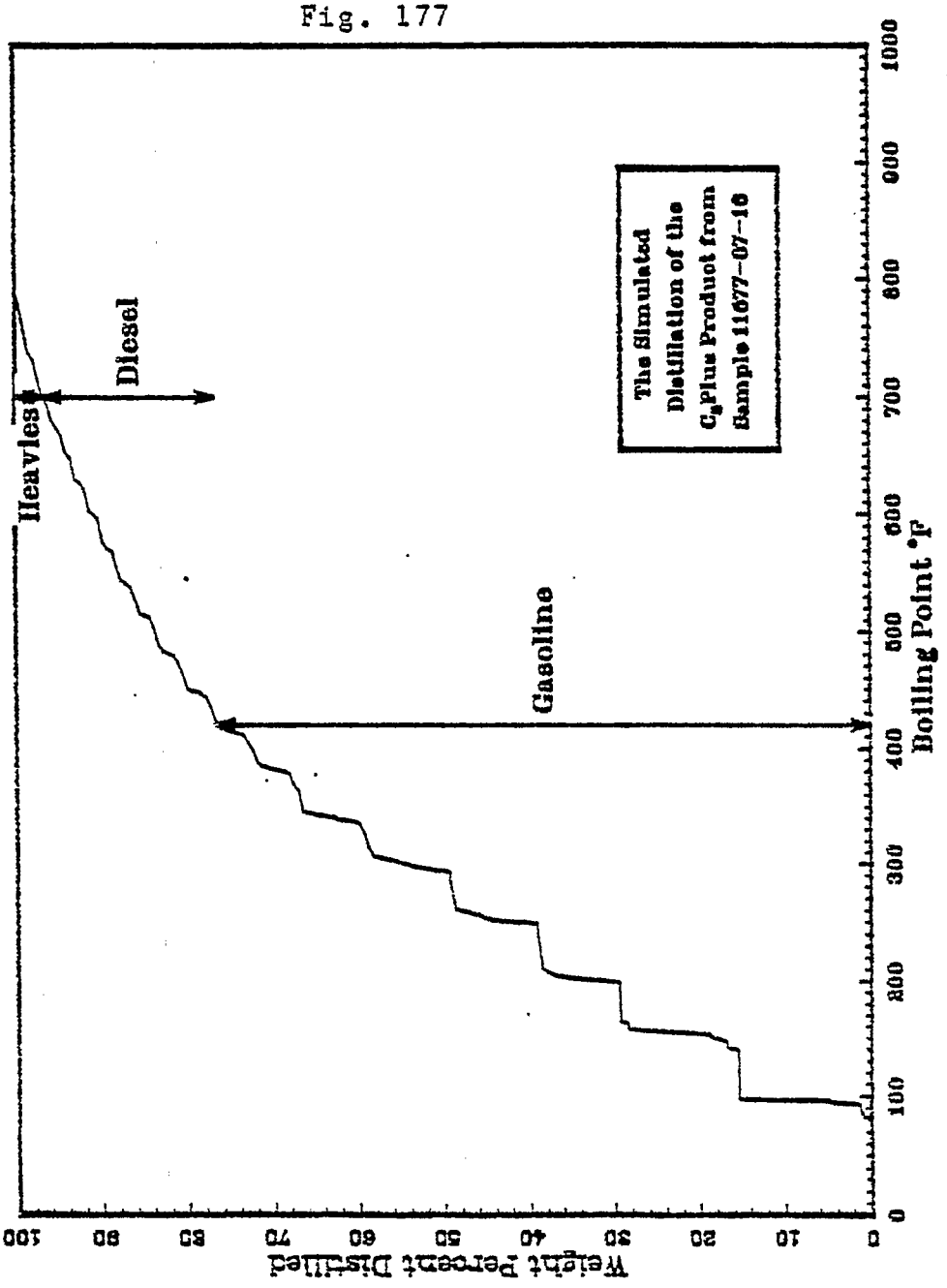

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11677-07-16

Fig. 178

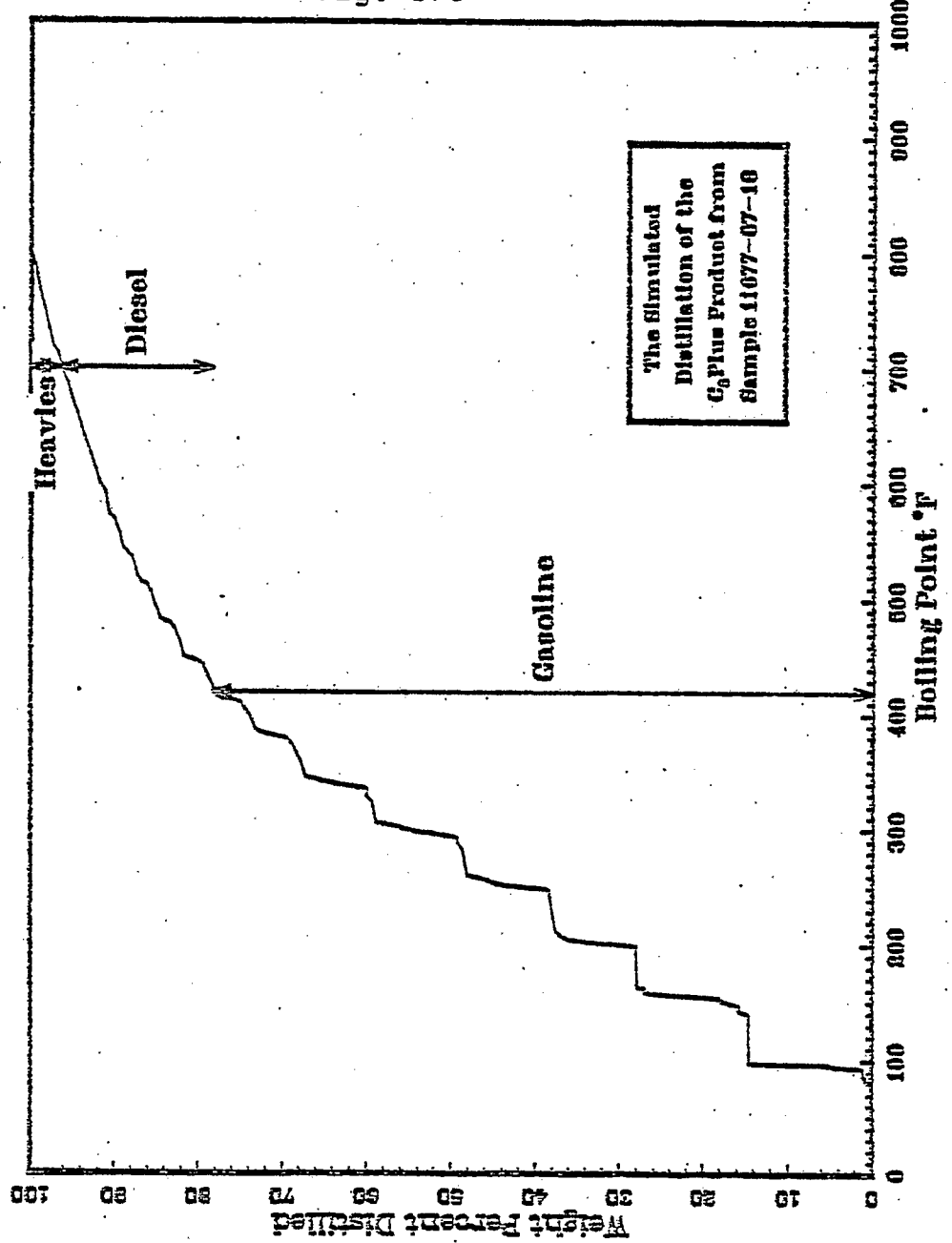

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11077-07-10
Weight Percent Distilled
Boiling Point °F
0
20
40
60
80
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 179

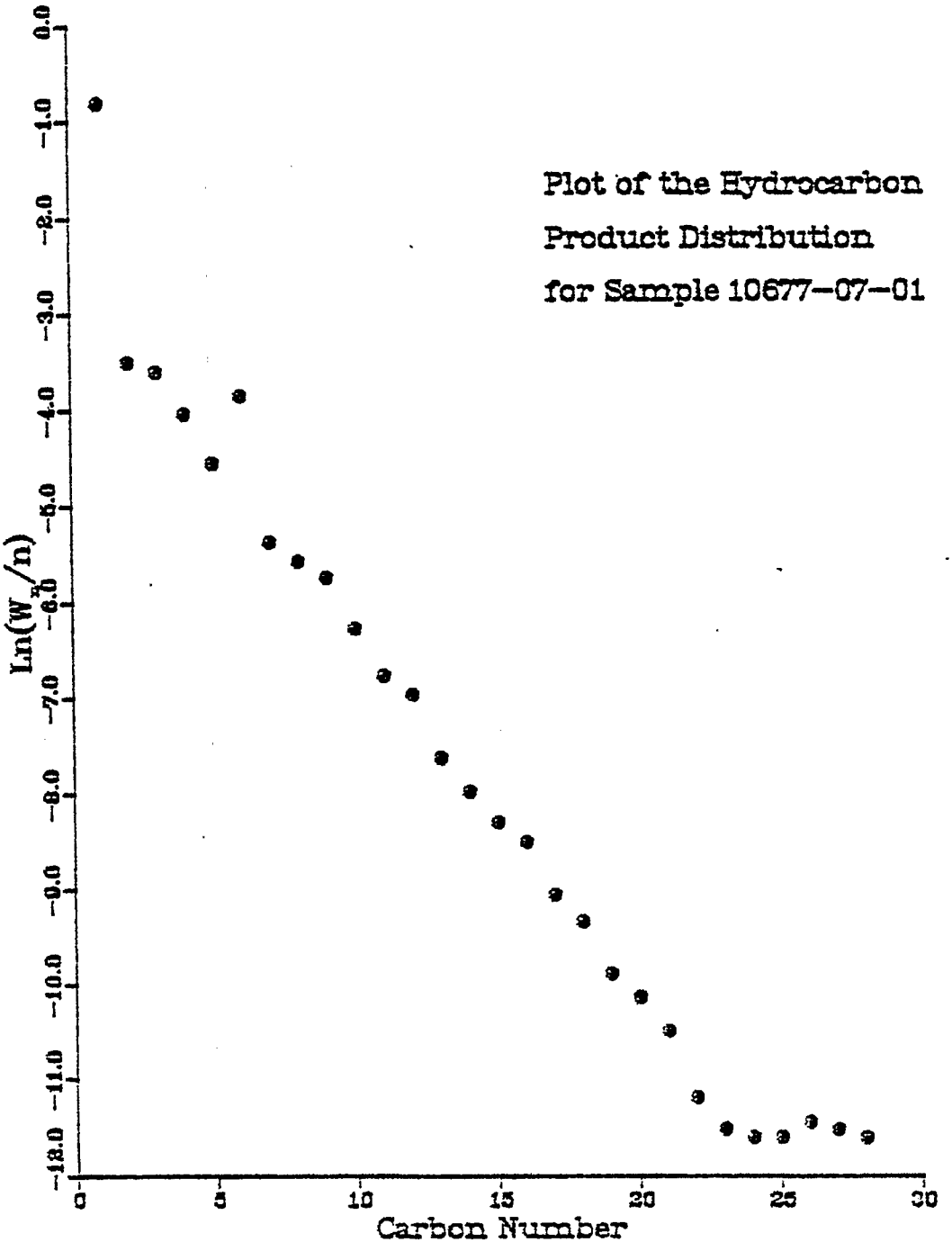

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-01
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
Carbon Number

Fig. 180

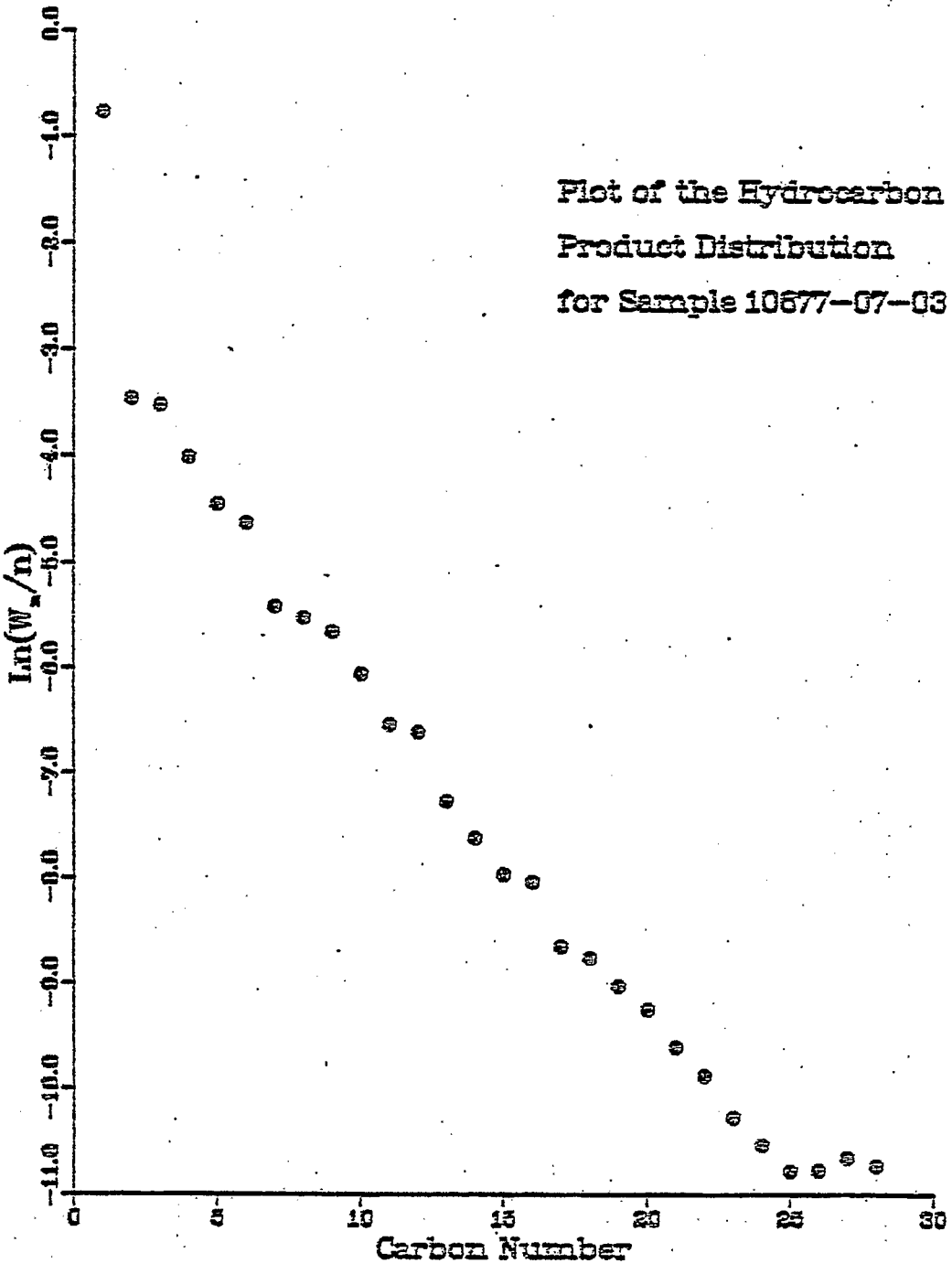

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-03
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 181

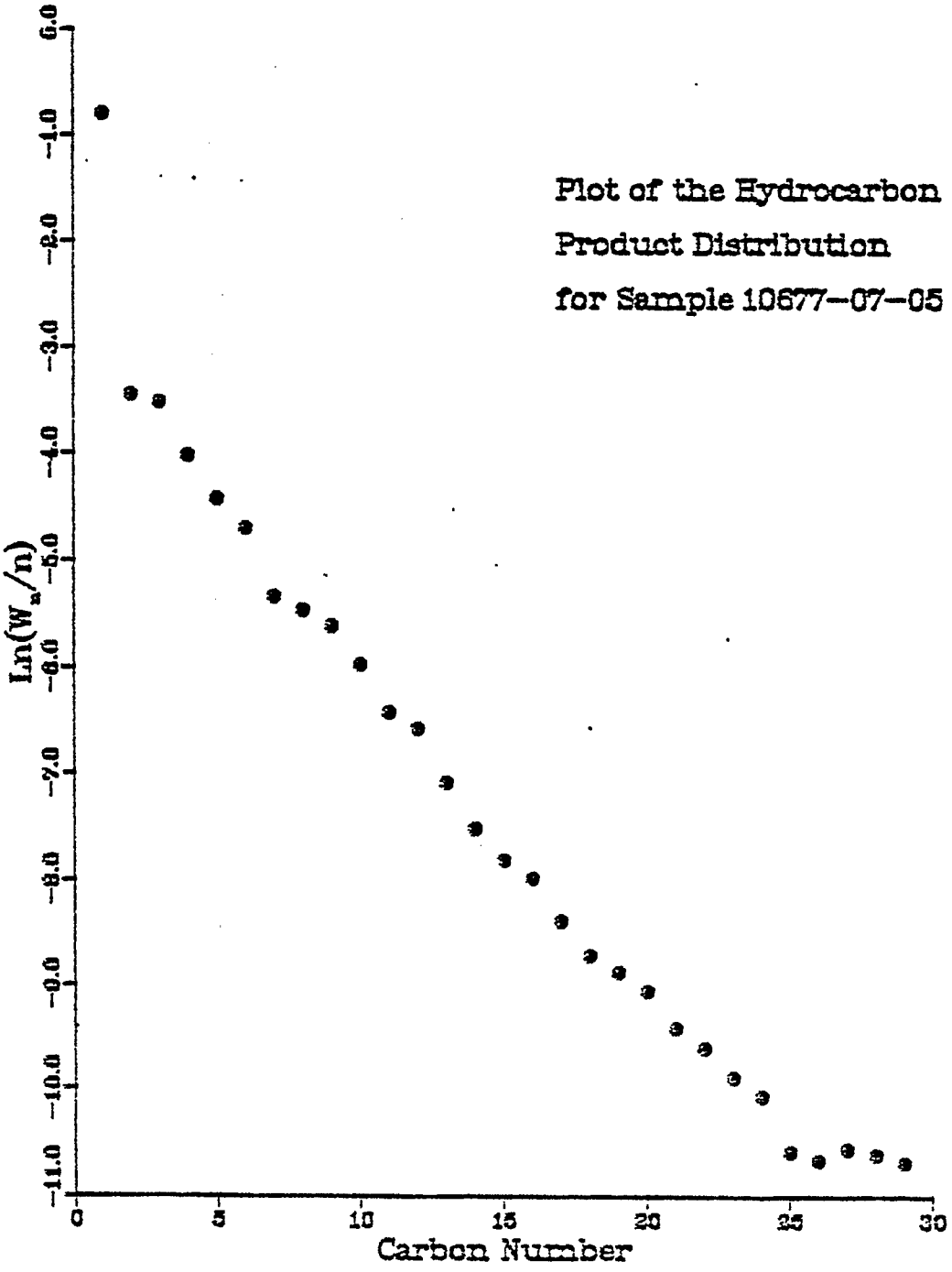

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-05
Ln(W_n/n)
6.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 182

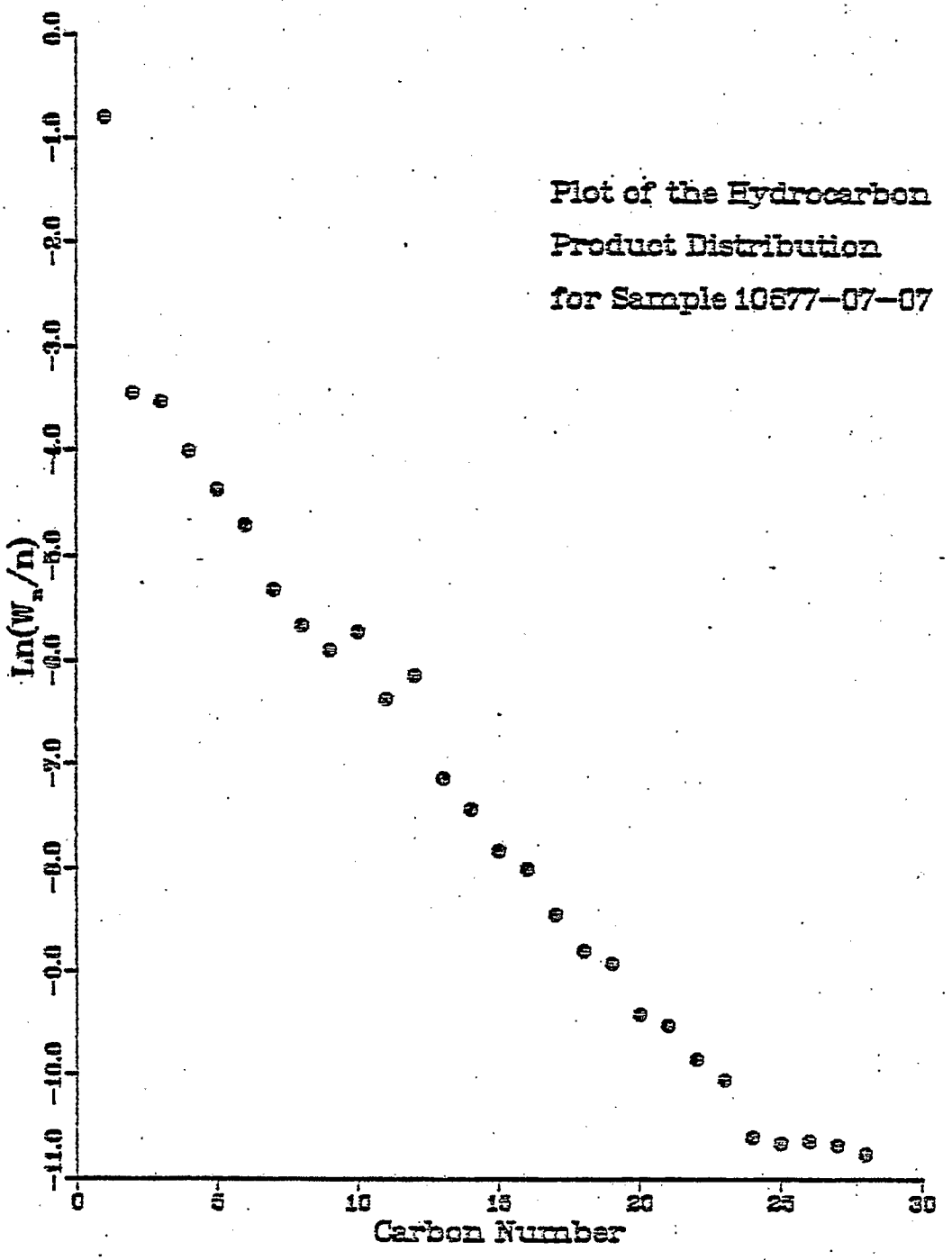

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-07
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 183

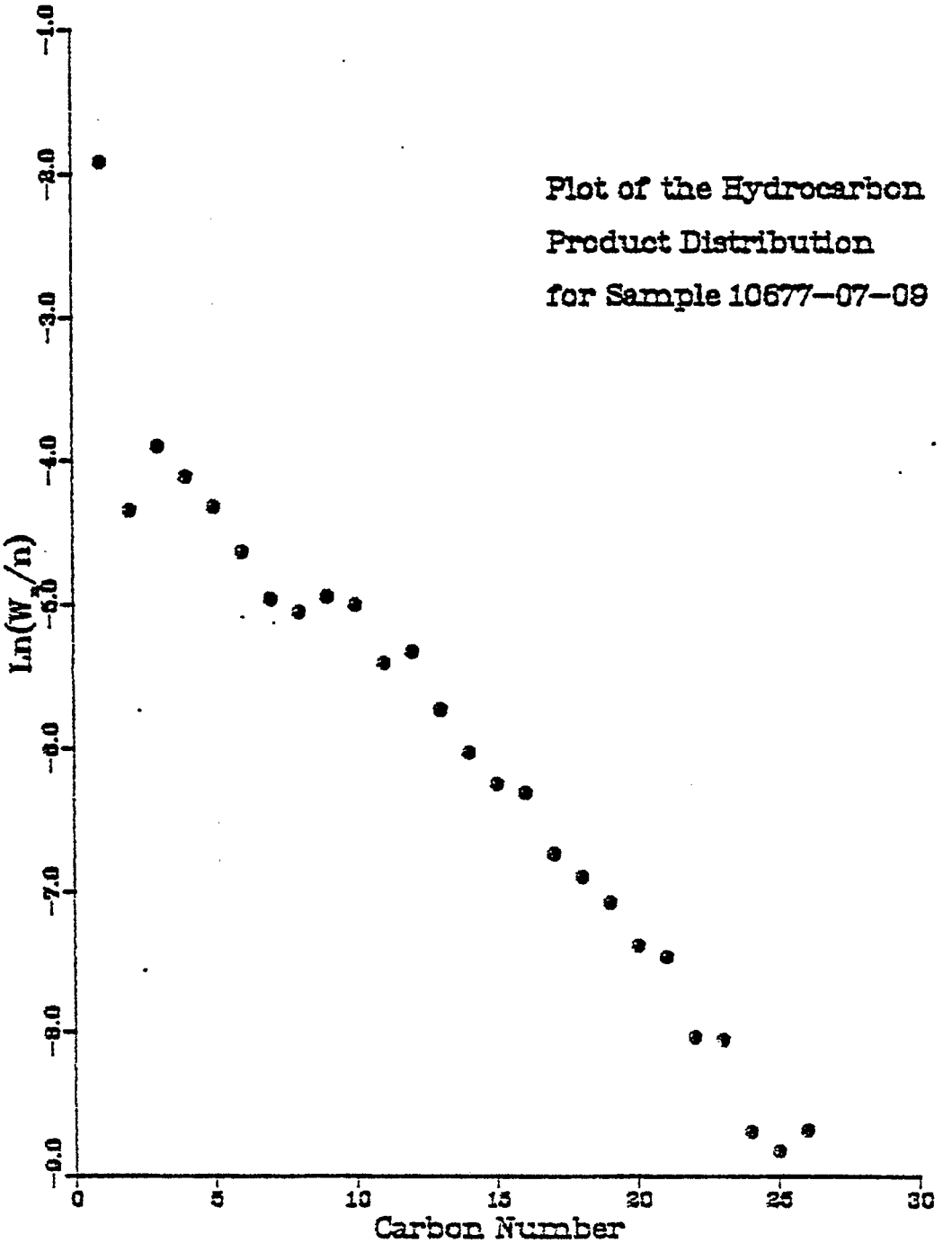

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-09
Ln(W_x/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. 184

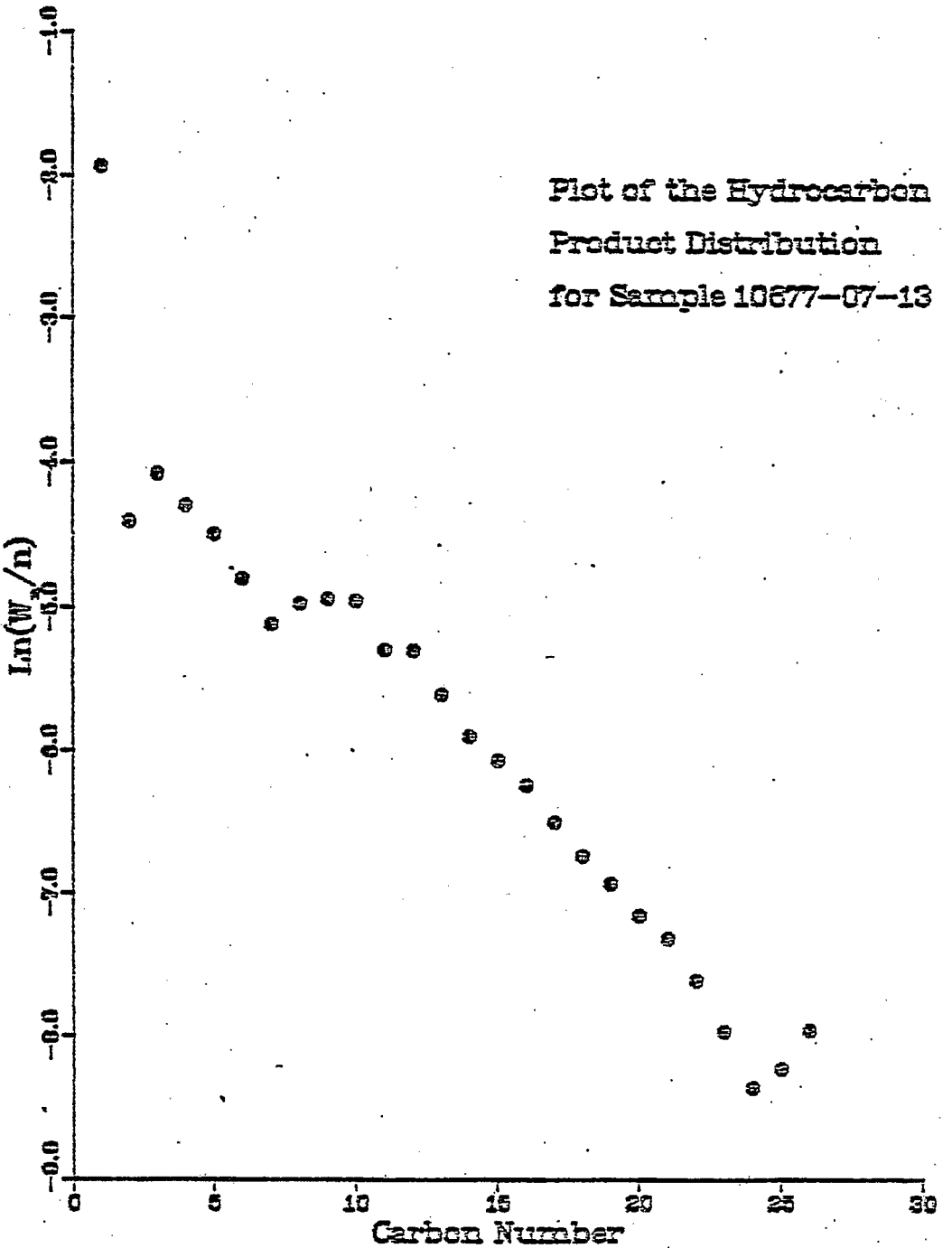

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. 185

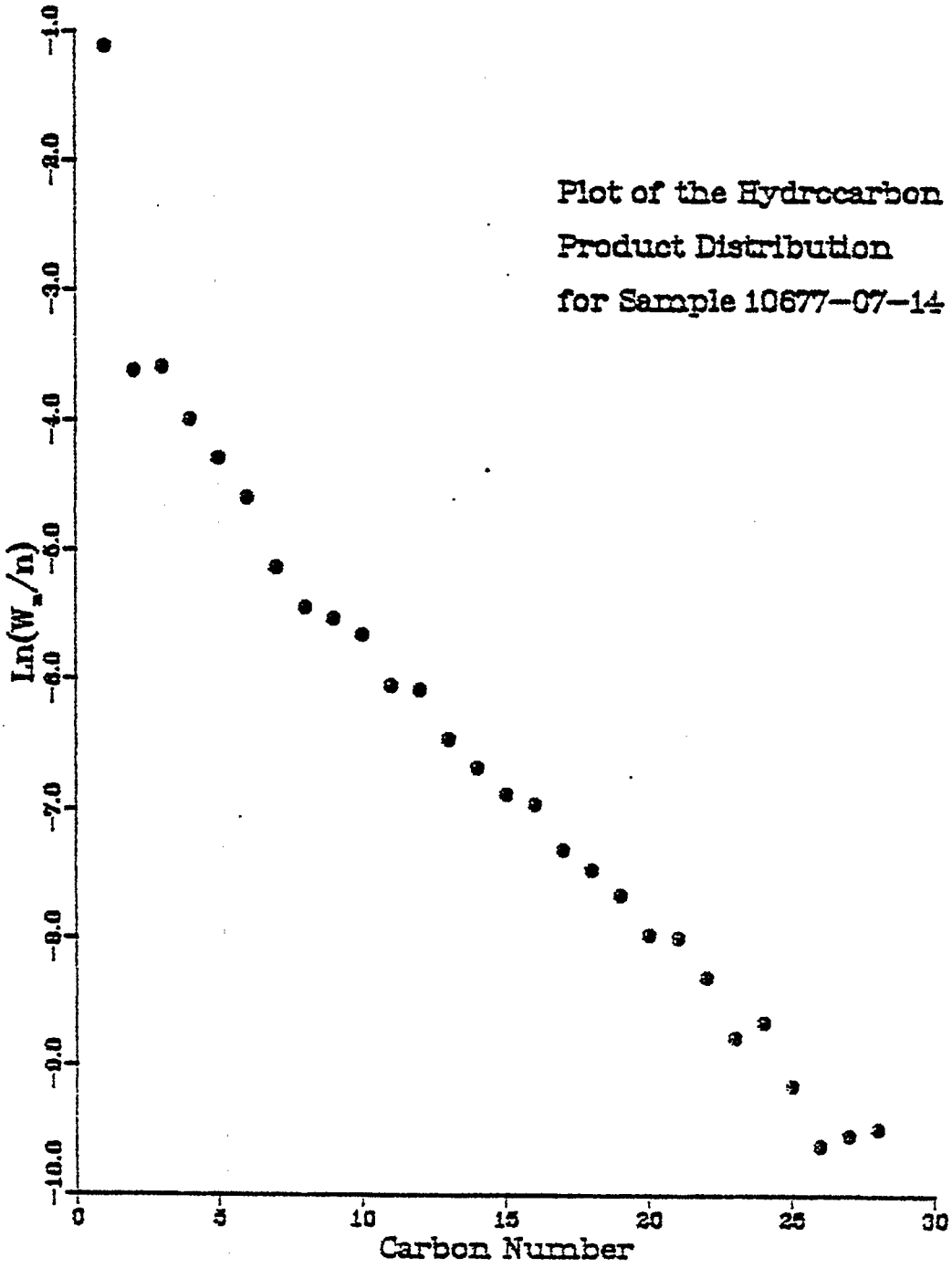

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-14
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 186

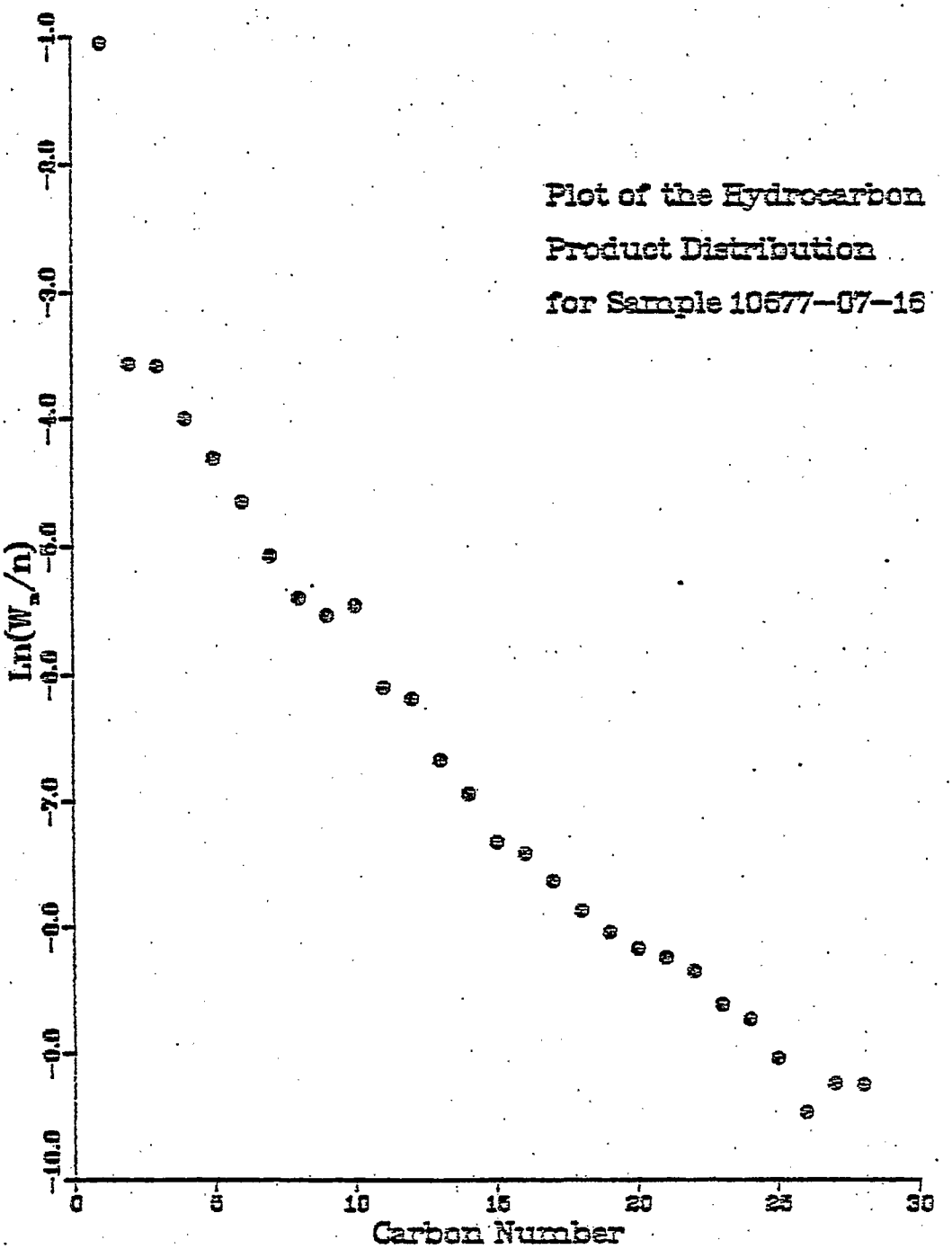

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-16
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 187

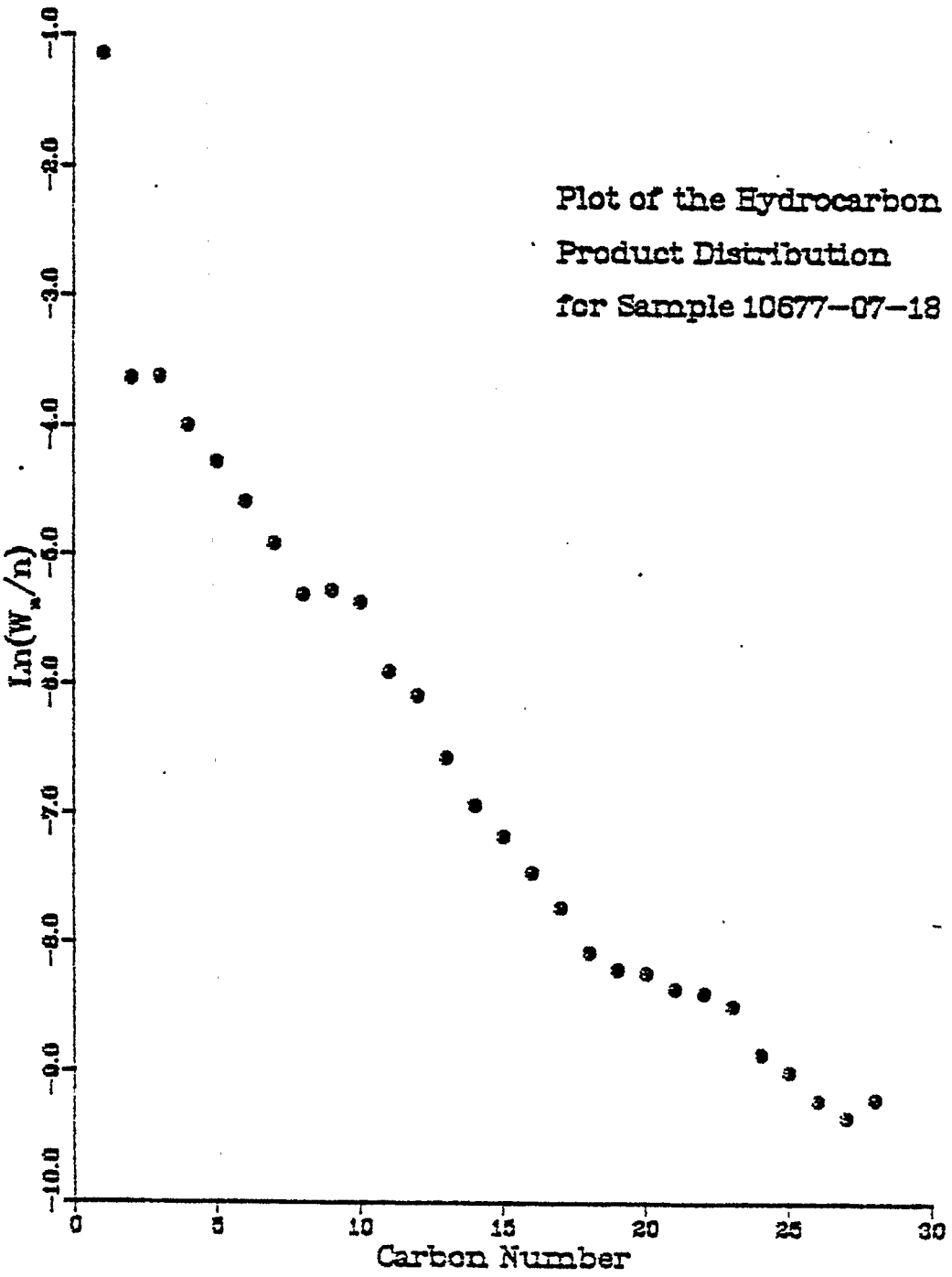

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-18
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 188

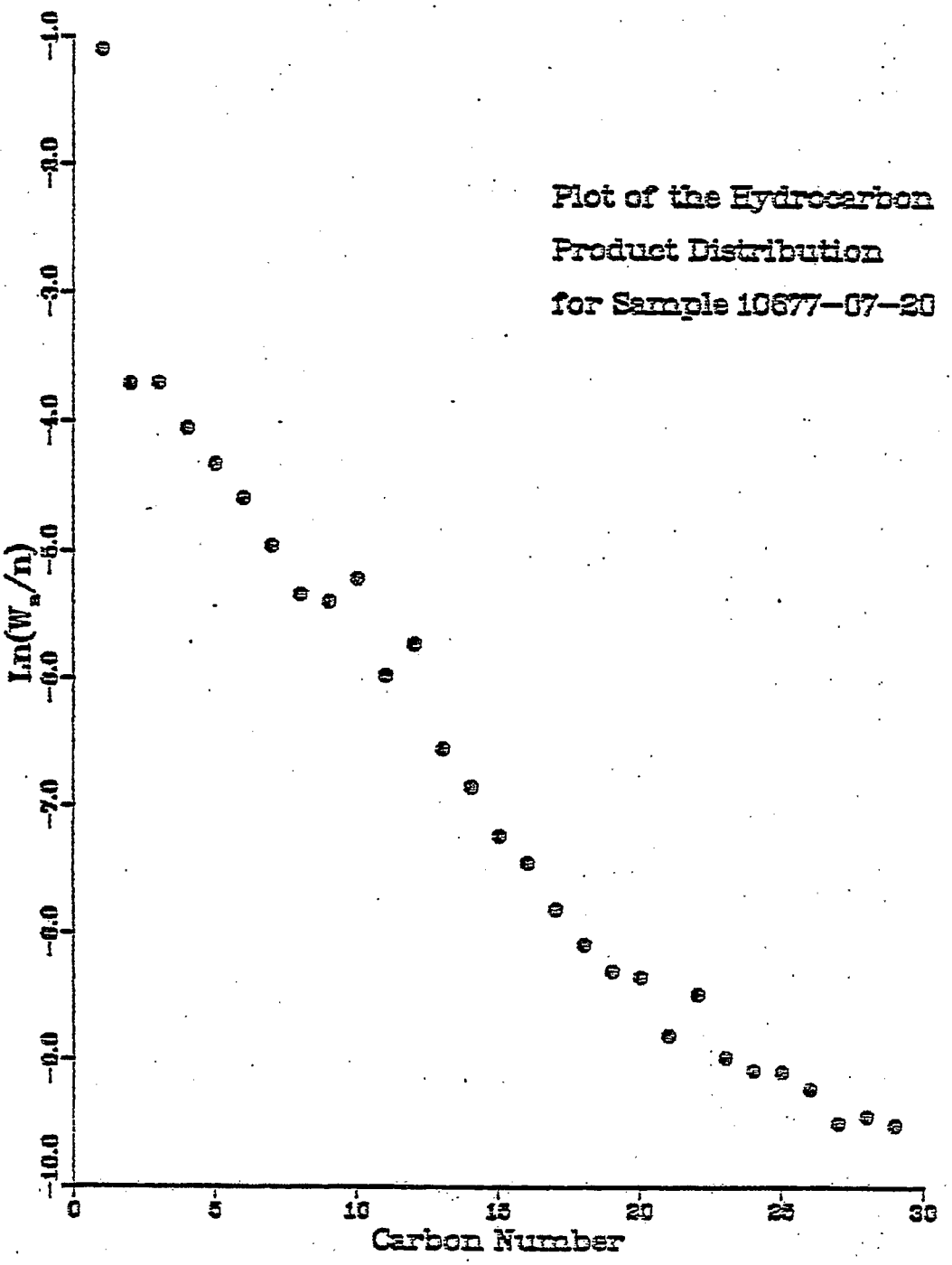

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-07-20
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 189

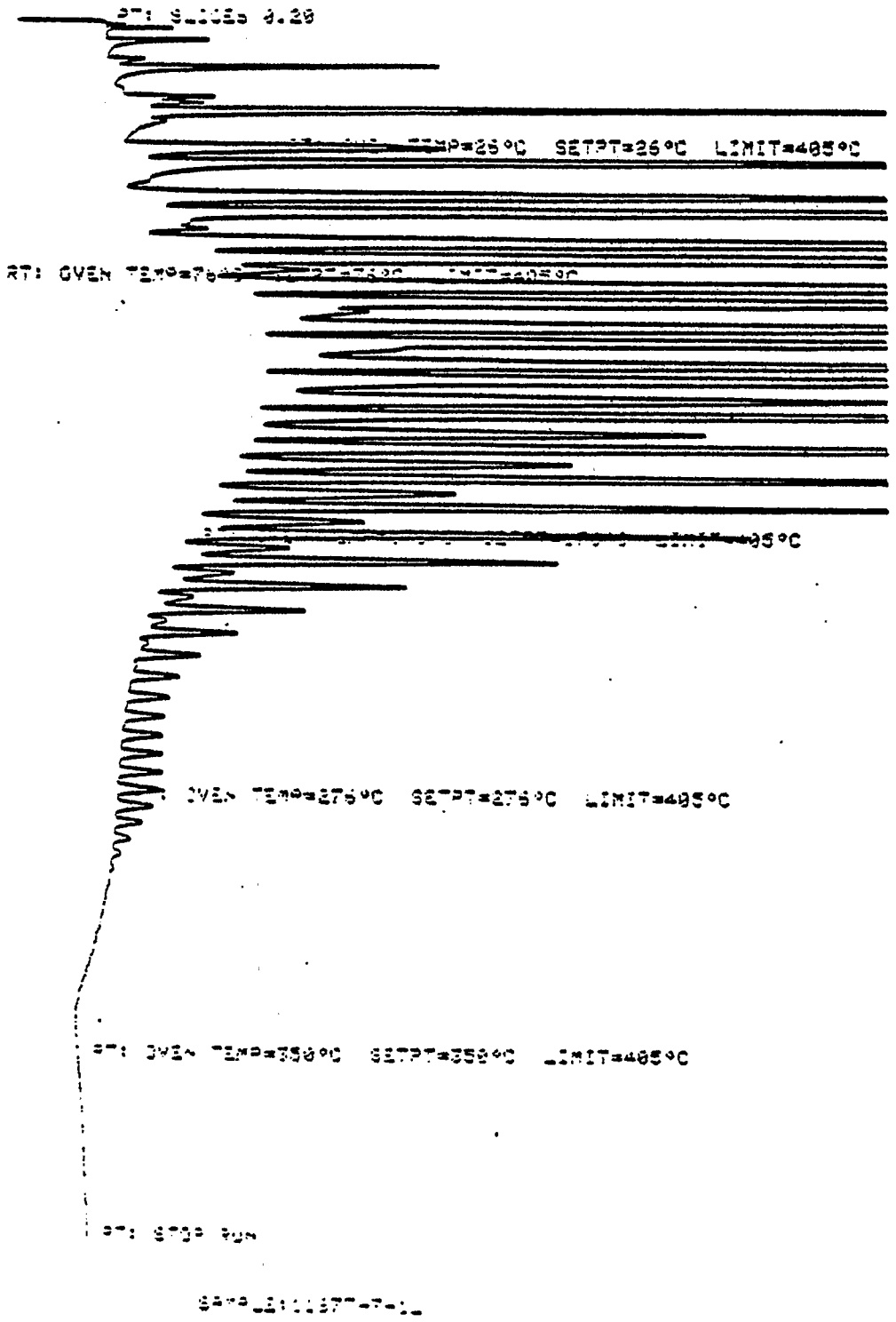

SETPT=25°C LIMIT=405°C
SETPT=275°C LIMIT=405°C
SETPT=350°C LIMIT=405°C

Fig. 190

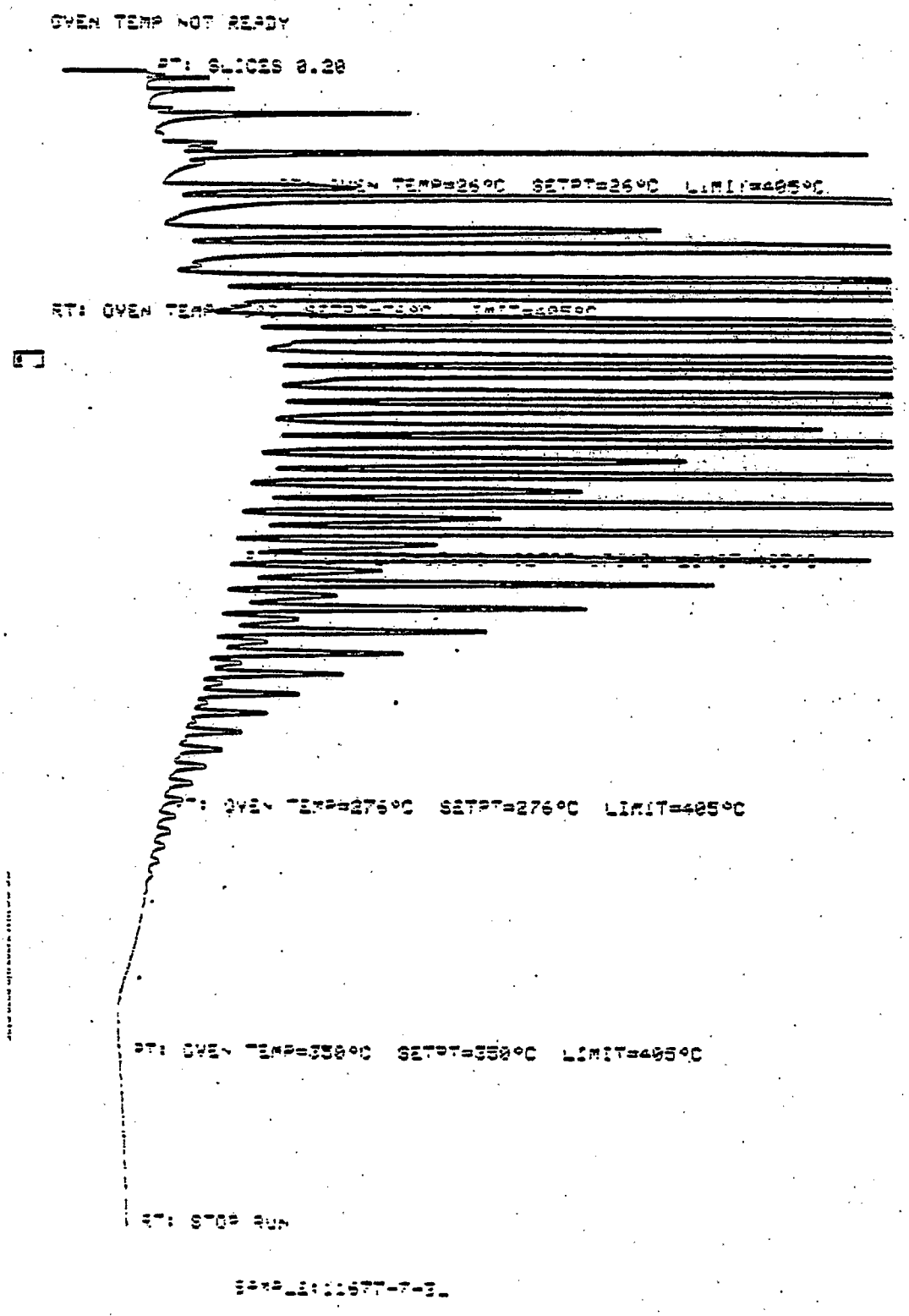

OVEN TEMP NOT READY
RT: SLICES 0.28
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 191

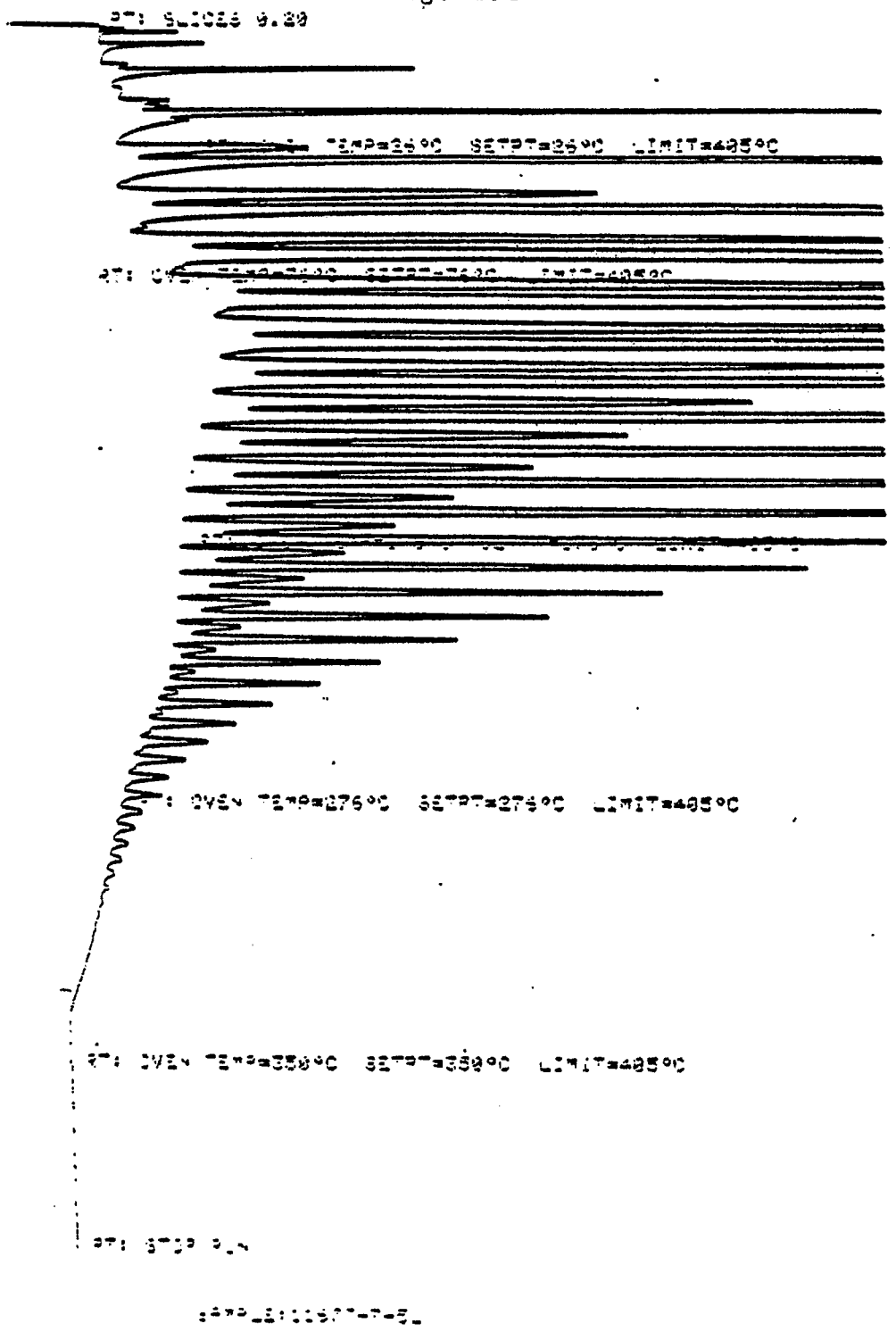


Fig. 192

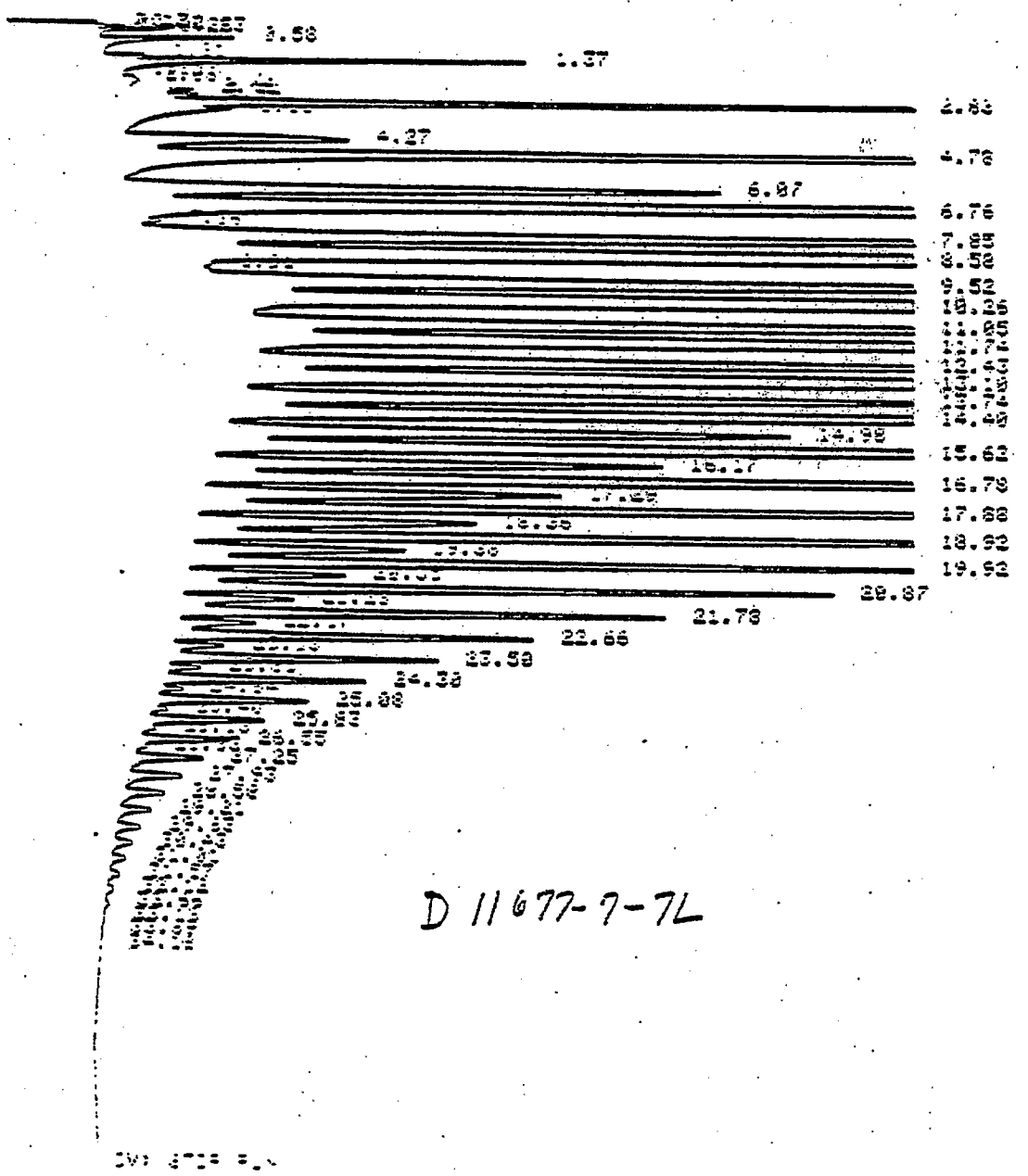

1.37
4.27
6.87
15.62
16.78
17.88
19.92
21.78
22.66
23.58
24.38
D 11677-7-7L

Fig. 193

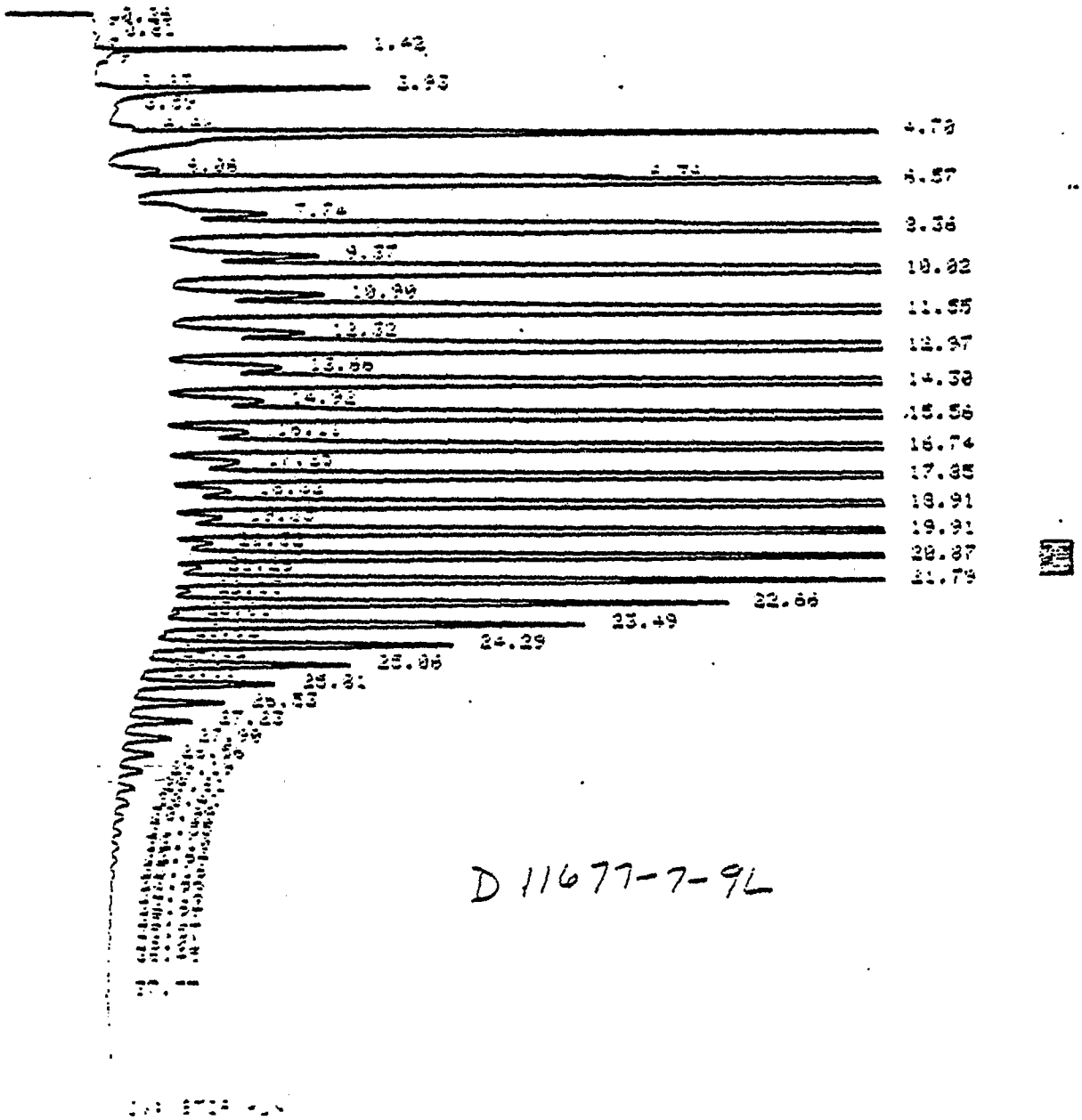
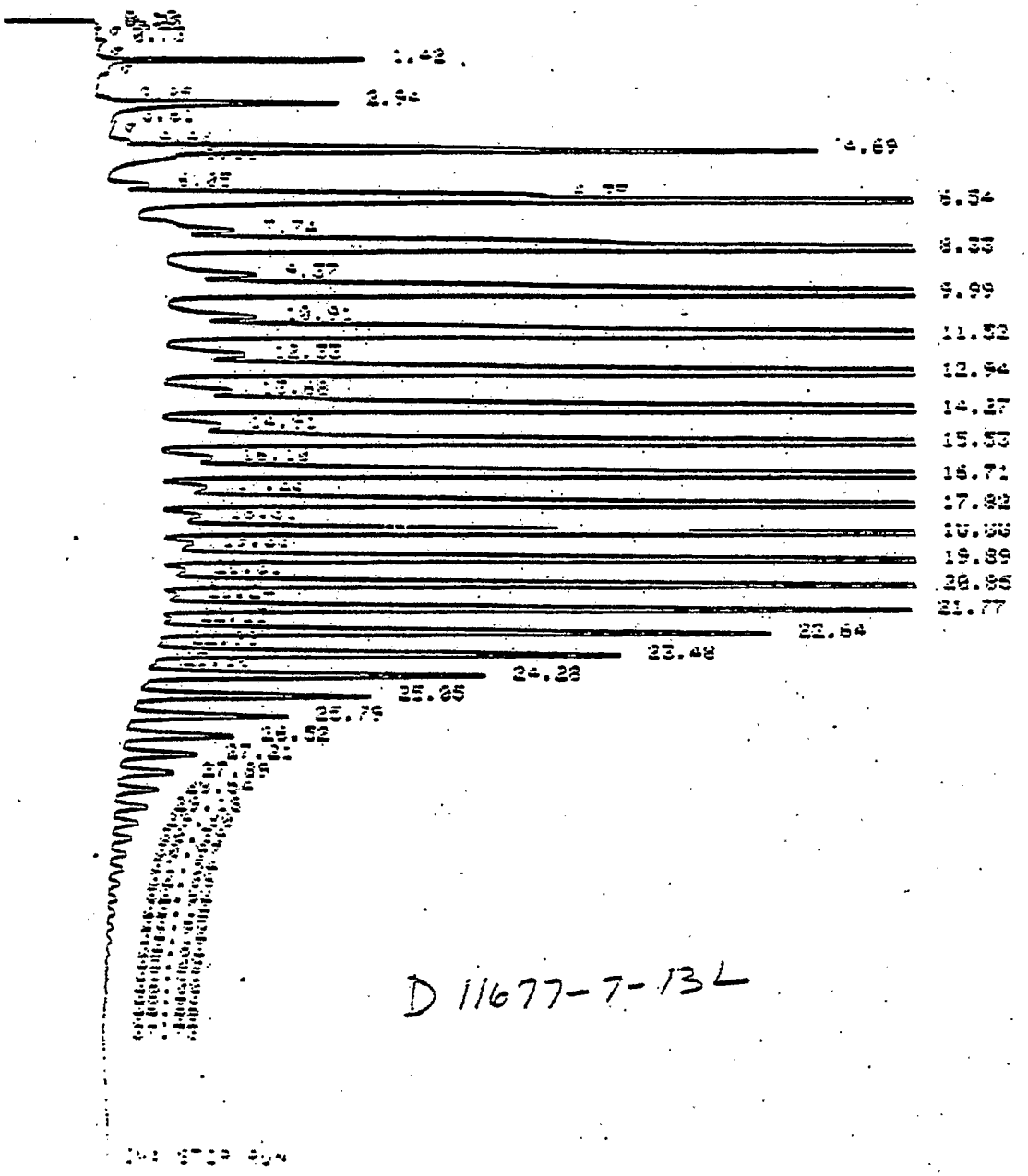
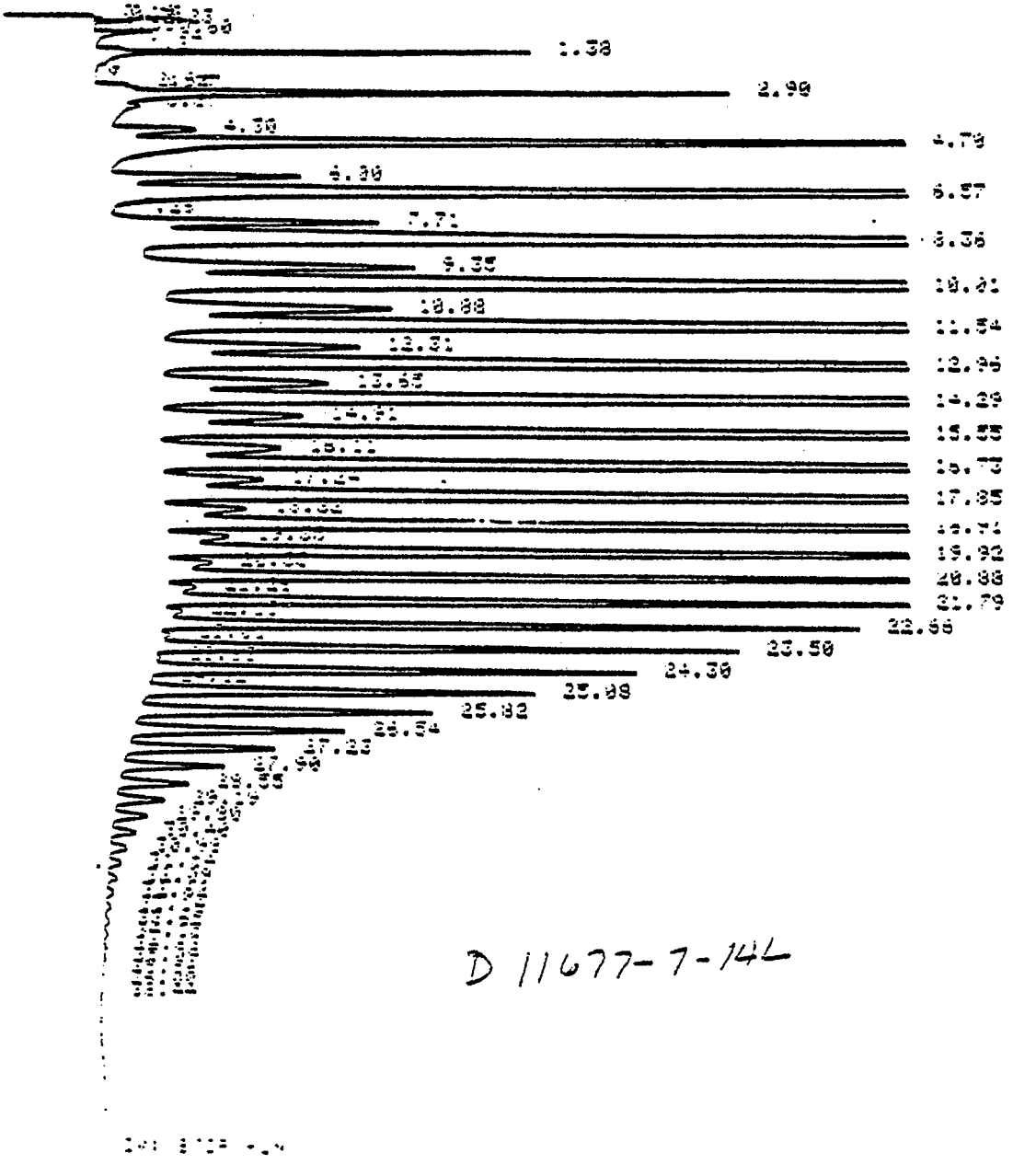

1.42
3.93
4.79
6.57
8.36
10.02
11.55
12.97
14.38
15.56
16.74
17.85
18.91
19.91
20.87
21.79
22.66
23.49
24.29
25.06
25.81
D 11677-7-9L

Fig. 194



D 11677-7-13L

Fig. 195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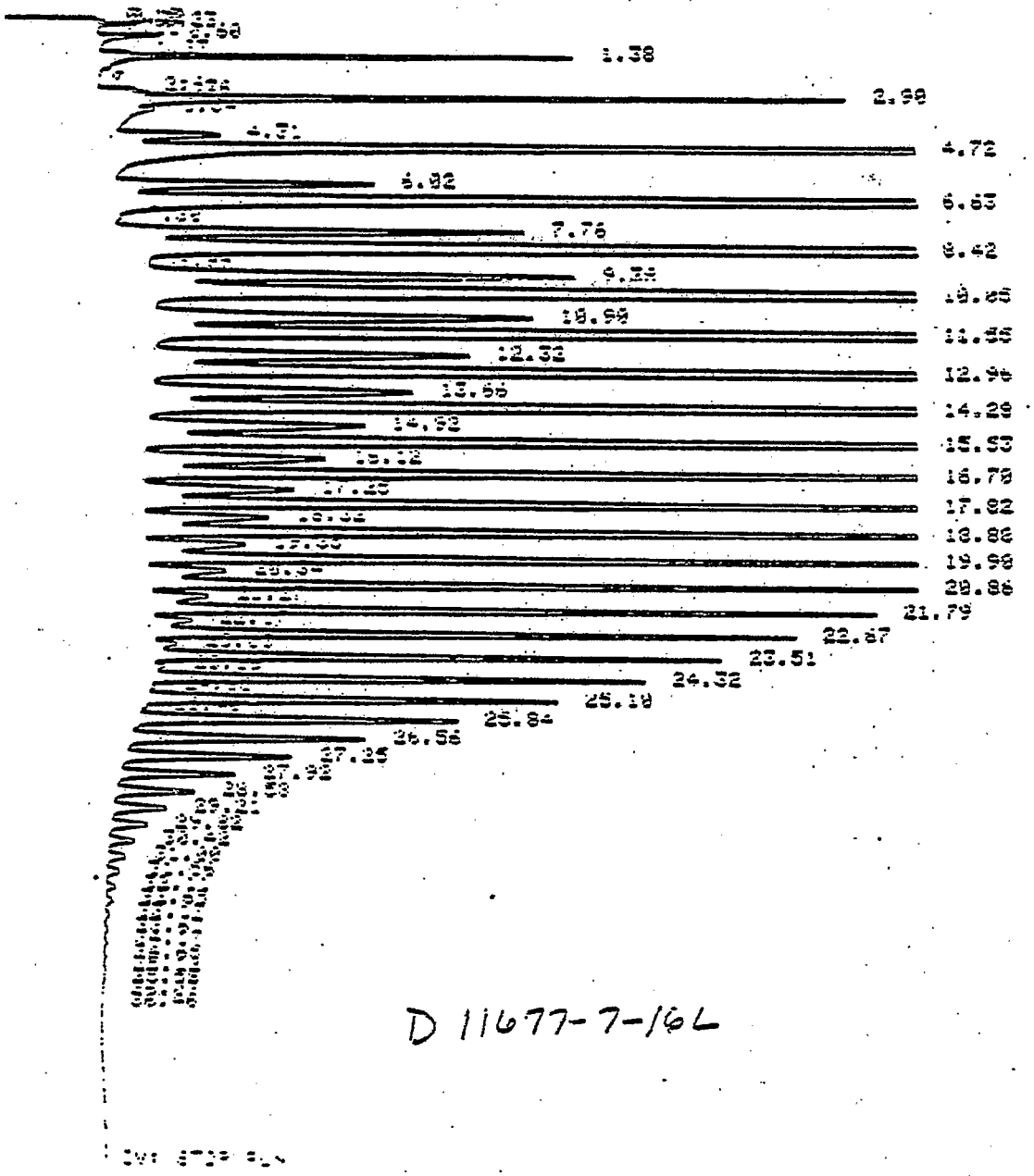
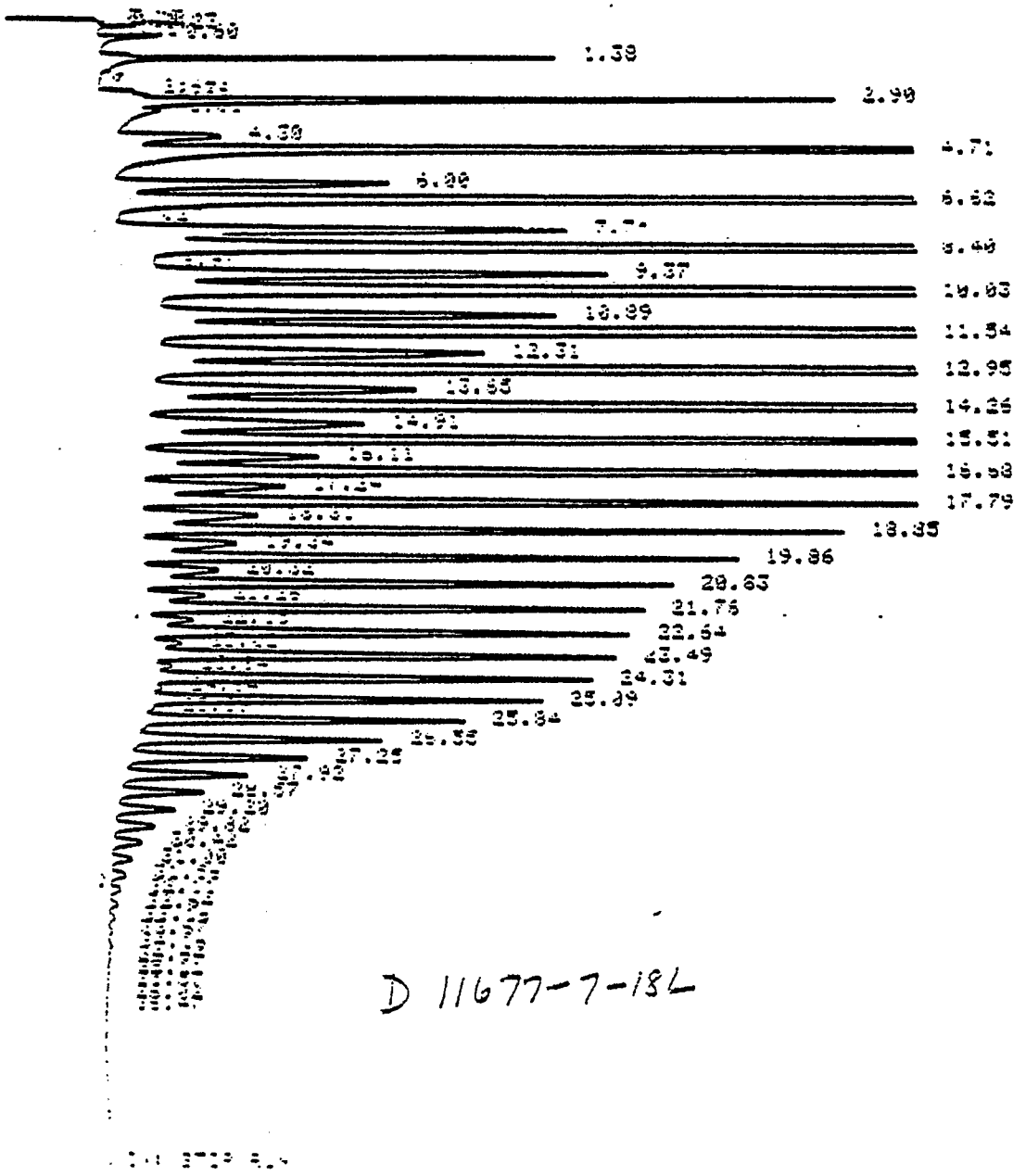
2.99
4.79
6.57
8.36
10.01
11.54
12.96
14.29
15.55
16.73
17.85
19.92
20.88
21.79
22.66
23.50
24.30
25.08
25.82
26.54
27.23
27.90
D 11677-7-14L

Fig. 196



D 11677-7-16L

Fig. 197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4.71
6.62
8.40
9.37
10.83
11.84
12.95
14.26
15.51
16.58
17.79
18.85
19.86
20.63
21.76
22.64
23.49
24.31
25.09
25.84
26.58
27.25
D 11677-7-18L

Fig. 198

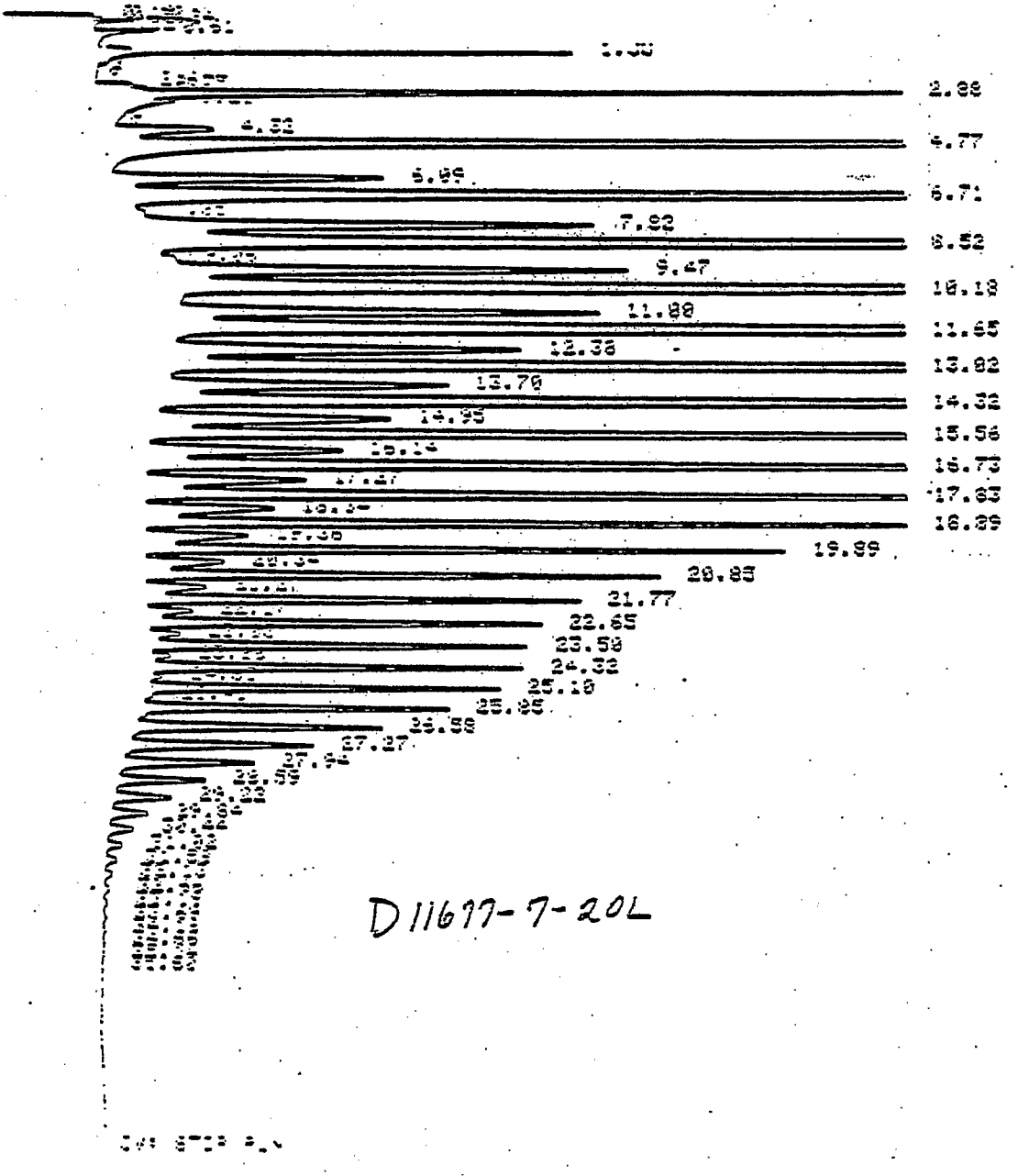

2.88
4.77
6.71
8.52
10.18
11.65
13.02
14.32
15.56
16.73
17.83
18.89
19.89
20.83
21.77
22.65
23.58
24.32
25.10
27.27
D11617-7-20L

TABLE 22 . RESULT OF SYNGAS OPERATION

RUN NO. 11677-07
CATALYST CO/TH + AL2O3 #11684-31C 80 CC 46.3GM (51.8 AFTER RUN +5.5G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-07-01	677-07-02	677-07-03	677-07-04	677-07-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.5	30.0	45.5	52.0	64.5
PRESSURE,PSIG	307	303	301	298	305
TEMP. C	272	272	272	271	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.50	7.50	23.00	6.50	24.00
EFFLNT GAS LITER	218.55	74.45	231.00	63.90	248.05
GM AQUEOUS LAYER	15.50	4.61	14.14	4.04	14.90
GM OIL	6.81	3.08	9.44	3.17	11.72
MATERIAL BALANCE					
GM ATOM CARBON %	89.91	93.41	92.83	91.16	94.52
GM ATOM HYDROGEN %	90.00	92.85	92.50	91.08	94.81
GM ATOM OXYGEN %	93.23	94.07	94.17	92.07	95.48
RATIO CHX/(H2O+CO2)	0.9332	0.9869	0.9729	0.9812	0.9807
RATIO X IN CHX	3.0902	3.0714	3.0595	3.0161	3.0217
USAGE H2/CO PRODT	0.9152	0.9251	0.9148	0.9130	0.9101
RATIO CO2/(H2O+CO2)	0.8131	0.8293	0.8282	0.8235	0.8274
K SHIFT IN EFFLNT	12.40	13.93	13.47	13.17	13.75
CONVERSION					
ON CO %	96.44	96.62	96.01	95.73	95.49
ON H2 %	89.86	90.25	88.80	87.93	87.09
ON CO+H2 %	93.15	93.45	92.41	91.83	91.28
PRDT SELECTIVITY,WT %					
CH4	47.80	47.22	46.80	44.86	45.19
C2 HC'S	6.47	6.27	6.29	6.14	6.35
C3H8	8.01	7.73	7.60	7.47	7.60
C3H6=	0.81	0.88	1.25	1.33	1.28
C4H10	5.87	5.53	5.31	5.25	5.03
C4H8=	1.74	1.71	1.94	2.17	2.11
C5H12	4.69	4.71	4.56	4.33	4.27
C5H10=	1.10	1.08	1.28	1.26	1.73
C6H14	5.30	4.97	4.80	4.69	4.16
C6H12= & CYCLO'S	0.87	0.75	0.87	0.97	1.09
C7+ IN GAS	8.59	7.93	7.87	7.69	7.79
LIQ HC'S	8.75	11.22	11.44	13.85	13.42
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	70.70	69.35	69.18	67.21	67.54
C5 -420 F	26.59	26.53	26.62	27.68	27.51
420-700 F	2.56	3.80	3.88	4.63	4.49
700-END PT	0.15	0.32	0.33	0.47	0.46
C5+-END PT	29.30	30.65	30.82	32.79	32.46
ISO/NORMAL MOLE RATIO					
C4	0.0448	0.0429	0.0397	0.0353	0.0325
C5	0.1165	0.1109	0.0984	0.0932	0.0897
C6	0.3557	0.3469	0.3360	0.3198	0.1938
C4=	0.2572	0.2451	0.1950	0.1842	0.1640
PARAFFIN/OLEFIN RATIO					
C3	9.3905	8.3751	5.8129	5.3685	5.6770
C4	3.2518	3.1172	2.6384	2.3375	2.2988
C5	4.1429	4.2493	3.4526	3.3340	2.4060
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7038		0.7373		0.7499
RATIO CH4/(1-A)**2	5.4470		6.6735		7.2231
LIQ HC COLLECTION					
PHYS. APPEARANCE	YL GN OIL		YL GR OIL		YL GN OIL
DENSITY	0.737		0.742		0.744
N, REFRACTIVE INDEX	1.4180		1.4181		1.4184
SIMULT'D DISTILATN					
10 WT % @ DEG F	248		256		256
16	260		285		282
50	368		384		383
84	503		539		542
90	544		592		599
RANGE(16-84 %)	243		254		260
WT % @ 420 F	69.00	63.25	63.25	63.13	63.13
WT % @ 700 F	98.30	97.13	97.13	96.57	96.57

TABLE 23 RESULT OF SYNGAS OPERATION

RUN NO. 11677-07
CATALYST CO/TH + AL2O3 #11684-31C 80 CC 46.3GM (51.8 AFTER RUN +5.5G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-07-06	677-07-07	677-07-08	677-07-09	677-07-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	76.0	94.5	101.5	119.5	125.5
PRESSURE,PSIG	302	304	300	305	302
TEMP. C	271	271	249	249	249
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.50	25.00	7.00	25.00	6.50
EFFLNT GAS LITER	64.95	250.85	76.80	277.00	66.60
GM AQUEOUS LAYER	3.67	14.11	7.03	25.10	5.61
GM OIL	2.99	11.49	8.23	29.39	7.90
MATERIAL BALANCE					
GM ATOM CARBON %	90.98	90.41	84.39	85.16	80.15
GM ATOM HYDROGEN %	90.78	89.95	82.89	85.97	81.17
GM ATOM OXYGEN %	91.75	92.02	86.93	90.71	83.36
RATIO CHX/(H2O+CO2)	0.9840	0.9663	0.9291	0.8624	0.9137
RATIO X IN CHX	3.0151.	3.0124	-2.2941	2.3434	2.3391
USAGE H2/CO PRODT	0.9037	0.8928	0.8924	0.8300	0.8313
RATIO CO2/(H2O+CO2)	0.8337	0.8335	0.6368	0.6763	0.6952
K SHIFT IN EFFLNT	14.01	13.59	1.96	2.90	3.38
CONVERSION					
ON CO %	95.23	94.84	66.52	72.78	74.63
ON H2 %	86.62	85.91	61.81	62.52	62.90
ON CO+H2 %	90.93	90.39	64.19	67.62	68.73
PRDT SELECTIVITY,WT %					
CH4	44.89	44.86	12.76	14.72	14.55
C2 HC'S	6.18	6.36	2.41	2.59	2.52
C3H8	7.66	7.39	1.91	2.51	2.53
C3H6=	1.29	1.40	3.83	3.57	3.15
C4H10	5.03	4.91	2.37	2.91	2.79
C4H8=	2.33	2.31	4.07	3.63	3.45
C5H12	4.33	4.30	2.46	3.24	3.06
C5H10=	1.83	1.98	3.47	3.39	2.62
C6H14	4.15	4.08	3.42	3.67	3.86
C6H12= & CYCLO'S	1.11	1.18	2.49	2.17	2.01
C7+ IN GAS	8.02	7.78	10.93	9.93	9.05
LIQ HC'S	13.18	13.44	49.90	47.68	50.42
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	67.38	67.25	27.35	29.92	28.99
C5 -420 F	28.05	28.10	47.83	46.36	43.91
420-700 F	4.23	4.31	23.08	22.05	25.02
700-END PT	0.34	0.35	1.75	1.67	2.08
C5+-END PT	32.62	32.75	72.65	70.08	71.01
ISO/NORMAL MOLE RATIO					
C4	0.0322	0.0304	0.0214	0.0177	0.0177
C5	0.0873	0.0815	0.0418	0.0370	0.0418
C6	0.1870	0.1787	0.2373	0.0563	0.1799
C4=	0.1606	0.1495	0.0708	0.0743	0.0722
PARAFFIN/OLEFIN RATIO					
C3	5.6508	5.0237	0.4752	0.6702	0.7640
C4	2.0848	2.0510	0.5622	0.7742	0.7822
C5	2.2947	2.1151	0.6889	0.9274	1.1370
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.7375		0.8132	
RATIO CH4/(1-A)**2		6.5111		4.2177	
LIQ HC COLLECTION					
PHYS. APPEARANCE		YL OIL		OIL SLD	
DENSITY		0.742		0.769	
N, REFRACTIVE INDEX		1.4180		1.4228	
SIMULT'D DISTILATN					
10 WT % @ DEG F		258		286	
16		287		302	
50		386		418	
84		521		596	
90		573		628	
RANGE(16-84 %)		234		294	
WT % @ 420 F	65.33	65.33	50.25	50.25	46.25
WT % @ 700 F	97.43	97.43	96.50	96.50	95.88

TABLE 24 RESULT OF SYNGAS OPERATION

RUN NO. 11677-07
CATALYST CO/TH + AL2O3 #11684-31C 80 CC 46.3GM (51.8 AFTER RUN +5.5G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-07-12	677-07-13	677-07-14	677-07-15	677-07-16
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	149.5	166.5	190.5	198.0	214.4
PRESSURE,PSIG	299	298	295	297	302
TEMP. C	249	249	260	260	261
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.00	24.00	24.00	7.50	23.92
EFFLNT GAS LITER	79.20	282.90	274.45	79.15	257.50
GM AQUEOUS LAYER	6.65	22.81	17.83	4.70	15.00
GM OIL	8.37	28.70	22.46	6.49	20.68
MATERIAL BALANCE					
GM ATOM CARBON %	85.52	84.19	100.52	94.37	97.97
GM ATOM HYDROGEN %	86.01	86.39	100.29	93.44	96.83
GM ATOM OXYGEN %	90.01	84.19	100.25	93.45	97.39
RATIO CHX/(H2O+CO2)	0.8839	1.0001	1.0054	1.0200	1.0118
RATIO X IN CHX	2.3331	2.3312	2.7711	2.8132	2.8202
USAGE H2/CO PRODT	0.8358	0.9752	0.8908	0.8914	0.8778
RATIO CO2/(H2O+CO2)	0.6776	0.6027	0.7932	0.8112	0.8221
K SHIFT IN EFFLNT	2.82	1.67	6.85	8.11	10.69
CONVERSION					
ON CO %	70.65	60.14	87.92	89.65	92.12
ON H2 %	60.90	57.15	78.38	80.28	81.55
ON CO+H2 %	65.76	58.63	83.16	84.99	86.87
PRDT SELECTIVITY,WT %					
CH4	14.29	14.41	32.81	34.91	35.09
C2 HC'S	2.27	2.44	5.36	5.73	5.60
C3H8	2.49	2.56	7.18	7.04	7.39
C3H6=	3.40	2.50	1.08	0.95	0.90
C4H10	2.79	2.58	5.32	5.31	5.46
C4H8=	3.72	2.85	2.04	1.82	1.85
C5H12	3.29	2.92	5.13	5.04	5.13
C5H10=	3.26	2.67	1.72	1.52	1.65
C6H14	3.50	3.10	4.79	4.48	4.58
C6H12= & CYCLO'S	2.13	1.83	1.07	0.79	0.95
C7+ IN GAS	9.56	8.75	7.60	7.38	7.72
LIQ HC'S	49.30	53.37	25.91	25.03	23.68
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	28.96	27.35	53.79	55.75	56.30
C5 -420 F	45.54	45.04	32.87	33.34	33.38
420-700 F	23.70	25.66	11.86	9.37	8.87
700-END PT	1.80	1.95	1.48	1.53	1.45
C5+-END PT	71.04	72.65	46.21	44.25	43.70
ISO/NORMAL MOLE RATIO					
C4	0.0171	0.0179	0.0313	0.0341	0.0313
C5	0.0461	0.0491	0.0886	0.0913	0.0894
C6	0.0577	0.0712	0.1402	0.1580	0.1449
C4=	0.0904	0.0789	0.1623	0.1828	0.1797
PARAFFIN/OLEFIN RATIO					
C3	0.6977	0.9770	6.3485	7.1032	7.8246
C4	0.7256	0.8734	2.5228	2.8218	2.8429
C5	0.9785	1.0635	2.8933	3.2227	3.0299
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8351	0.7915		0.7932
RATIO CH4/(1-A)**2		5.2950	7.5498		8.2032
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL SLD	OIL SLD		OIL SLD
DENSITY		0.769	0.757		0.748
N, REFRACTIVE INDEX		1.4241	1.4226		1.4196
SIMULT'D DISTILATN					
10 WT % @ DEG F		293	259		256
16		302	300		285
50		441	439		405
84		599	610		603
90		645	654		666
RANGE(16-84 %)		297	310		318
WT % @ 420 F	48.27	48.27	48.50	56.43	56.43
WT % @ 700 F	96.35	96.35	94.28	93.88	93.88

TABLE 25 RESULT OF SYNGAS OPERATION

RUN NO. 11677-07
CATALYST CO/TH + AL203 #11684-31C 80 CC 46.3GM (51.8 AFTER RUN +5.5G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-07-17	677-07-18	677-07-19	677-07-20
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	220.7	239.1	247.1	262.5
PRESSURE,PSIG	300	298	299	303
TEMP. C	262	262	261	261
FEED CC/MIN	400	400	400	400
HOURS FEEDING	6.25	24.67	8.00	23.42
EFFLNT GAS LITER	61.00	254.60	85.00	250.70
GM AQUEOUS LAYER	3.65	14.42	5.04	14.76
GM OIL	5.68	22.40	7.47	21.87
MATERIAL BALANCE				
GM ATOM CARBON %	90.68	93.41	94.90	96.16
GM ATOM HYDROGEN %	89.73	92.08	94.03	96.93
GM ATOM OXYGEN %	88.65	92.63	94.96	94.04
RATIO CHX/(H2O+CO2)	1.0451	1.0168	0.9988	1.0450
RATIO X IN CHX	2.7816	2.7489	2.7384	2.7612
USAGE H2/CO PRODT	0.8872	0.8592	0.8550	0.8869
RATIO CO2/(H2O+CO2)	0.8194	0.8236	0.8157	0.8140
K SHIFT IN EFFLNT	10.75	11.27	10.40	10.42
CONVERSION				
ON CO %	92.42	91.63	90.94	91.25
ON H2 %	81.86	79.50	78.50	79.31
ON CO+H2 %	87.17	85.61	84.75	85.26
PRDT SELECTIVITY,WT %				
CH4	33.44	31.96	31.53	33.23
C2 HC'S	5.43	5.27	5.21	4.93
C3H8	7.12	6.85	6.68	6.20
C3H6=	0.89	1.14	1.26	1.20
C4H10	5.22	5.10	5.04	4.67
C4H8=	1.89	2.25	2.35	2.28
C5H12	4.94	5.00	4.91	4.67
C5H10=	1.61	1.91	1.98	1.94
C6H14	4.44	4.61	4.57	4.52
C6H12= & CYCLO'S	1.02	1.18	1.23	1.29
C7+ IN GAS	7.58	8.44	8.28	9.17
LIQ HC'S	26.43	26.31	26.95	25.92
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	53.99	52.56	52.07	52.50
C5 -420 F	35.56	37.03	37.71	37.67
420-700 F	8.68	8.64	8.66	8.33
700-END PT	1.77	1.77	1.56	1.50
C5+-END PT	46.01	47.44	47.93	47.50
ISO/NORMAL MOLE RATIO				
C4	0.0327	0.0271	0.0265	0.0261
C5	0.0896	0.0810	0.0812	0.0772
C6	0.1490	0.1315	0.1330	0.1214
C4=	0.1768	0.1503	0.1418	0.1374
PARAFFIN/OLEFIN RATIO				
C3	7.6372	5.7423	5.0468	4.9284
C4	2.6676	2.1945	2.0721	1.9832
C5	2.9857	2.5446	2.4131	2.3407
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))		0.7907		0.7884
RATIO CH4/(1-A)**2		7.2961		7.4187
LIQ HC COLLECTION				
PHYS. APPEARANCE		OIL SLD		OIL SLD
DENSITY		0.738		0.744
N, REFRACTIVE INDEX		1.4187		1.4176
SIMULT'D DISTILATN				
10 WT % @ DEG F		254		257
16		261		265
50		384		386
84		593		569
90		660		638
RANGE(16-84 %)		332		304
WT % @ 420 F	60.44	60.44	62.09	62.09
WT % @ 700 F	93.29	93.29	94.21	94.21

XIII. Run 12 (10225-11) with Catalyst 12 (Fe/Rh + UCC-108)

According to UK Patent Application GB2099716A, a catalyst with Fe/Rh and ZSM-5 has very high selectivity for gasoline; the purpose of this catalyst was to test the properties of the same metal component in combination with UCC-108. A precipitate of $Fe_2O_3 \cdot XH_2O$ was prepared in the same way as for the Tenth Quarter Catalyst 11, and impregnated with a solution of $RhCl_3$ to give 2 percent rhodium on the catalyst. This metal component was then physically mixed with an equal quantity of UCC-108, bonded with 15 percent SiO_2, and formed as extrudates.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 199-202. Simulated distillations of the C_5^+ product are plotted in Figs. 203-204. Carbon number product distributions are plotted in Figs. 205-207. Chromatograms from simulated distillations are reproduced in Figs. 208-210. Detailed material balances appear in Tables 26-27.

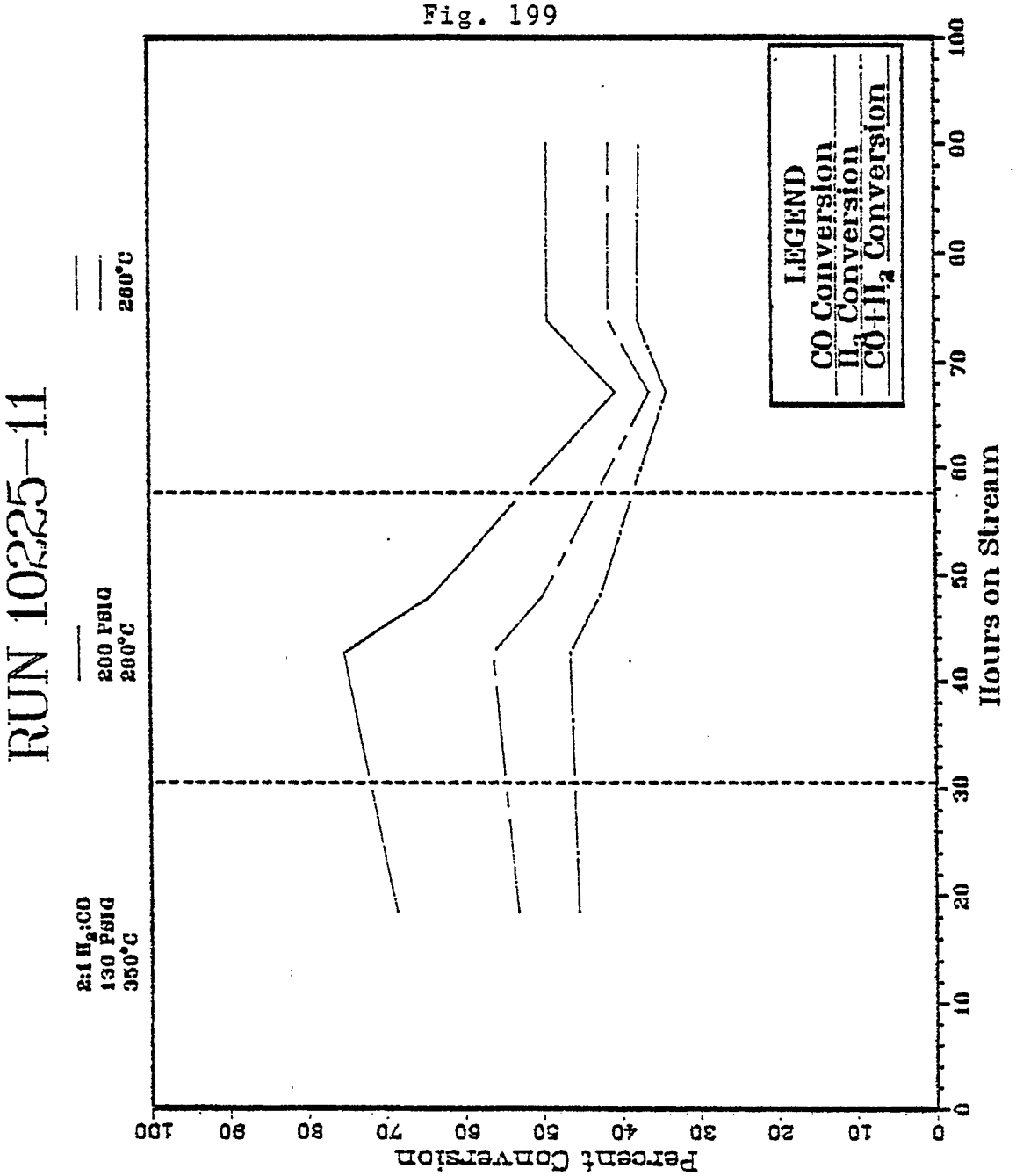
The activity was low at 260C and improved very little at higher temperatures. The water gas shift activity was no better than average.

The selectivity was very poor, with high methane, very high C_2-C_4, and very little C_5^+. Isomerization of the pentane decreased with time on stream. The C_4 was highly olefinic, as

usual with an iron catalyst, and the olefin content varied inversely with the temperature. The chromatograms from the simulated distillations show loss of isomerization with time.

This does not appear to be a useful catalyst.

Fig. 199


RUN 10225-11
2:1 H2:CO
130 PSIG
350°C
200 PSIG
200°C
200°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

RUN 10225–11

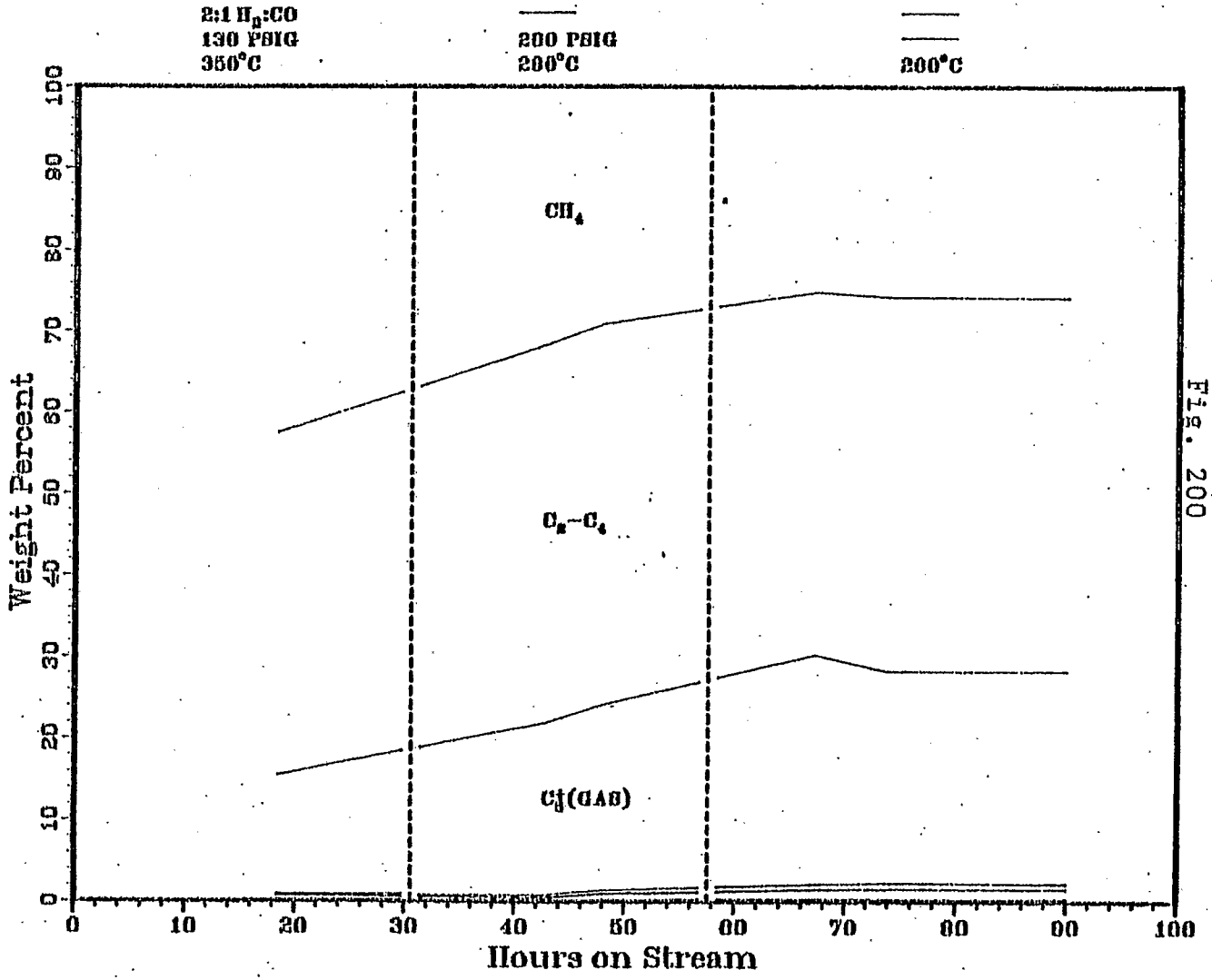


Fig. 200

Fig. 201

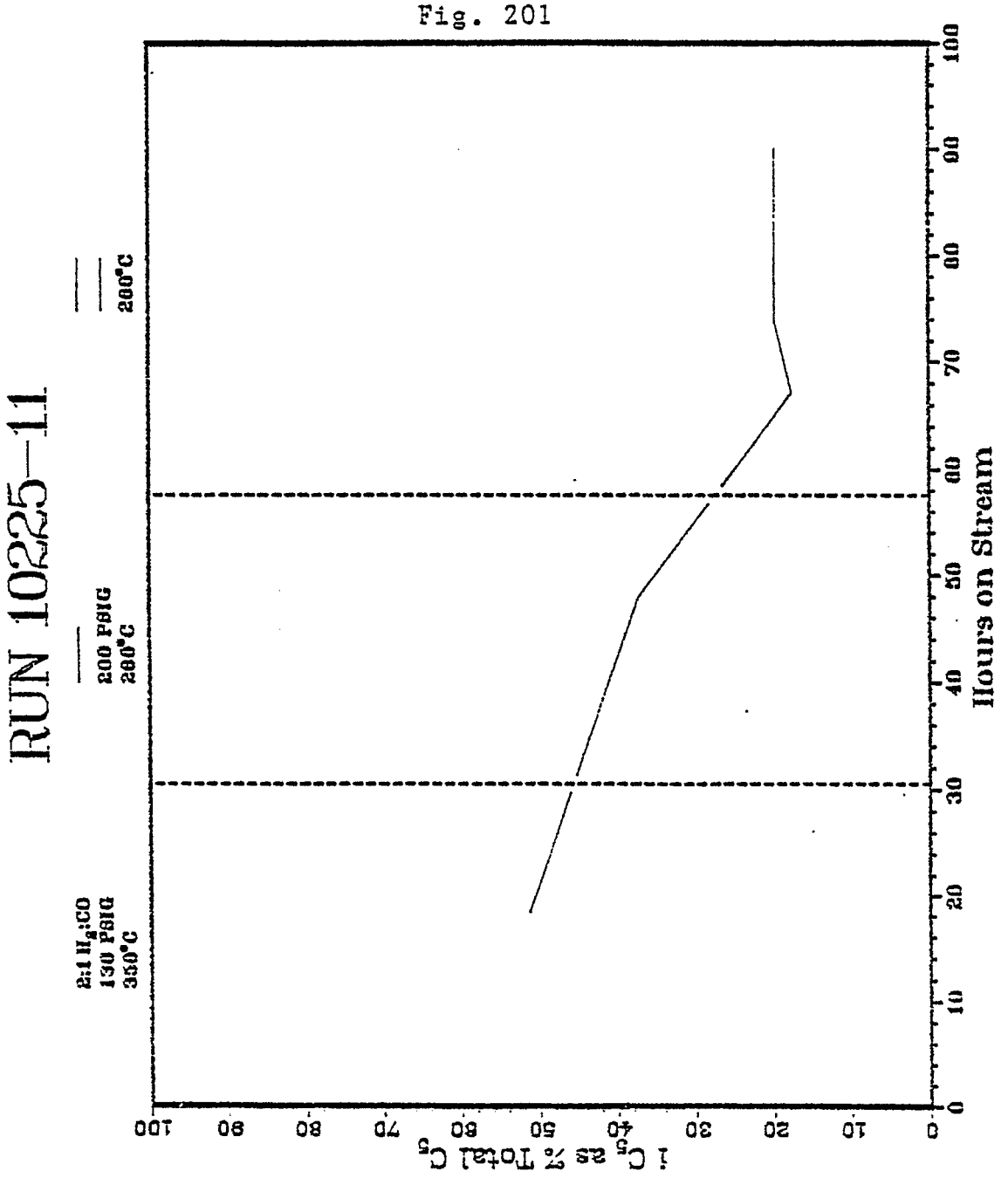

RUN 10225–11
2:1 H2:CO
130 PSIG
350°C
200 PSIG
280°C
280°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 202

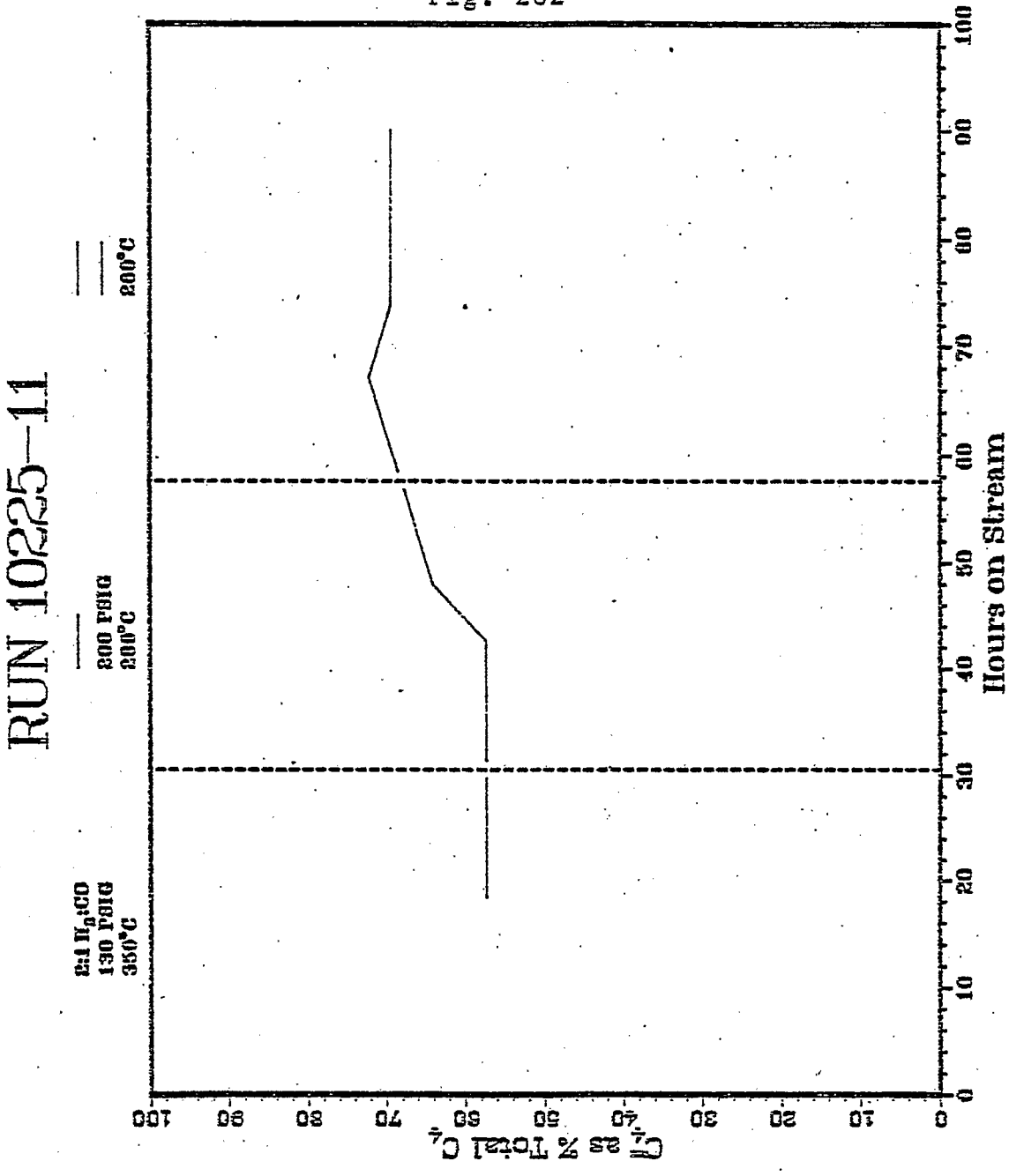

RUN 10225-11
2:1 H2:CO
130 PSIG
350°C
300 PSIG
200°C
200°C
C2= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 203

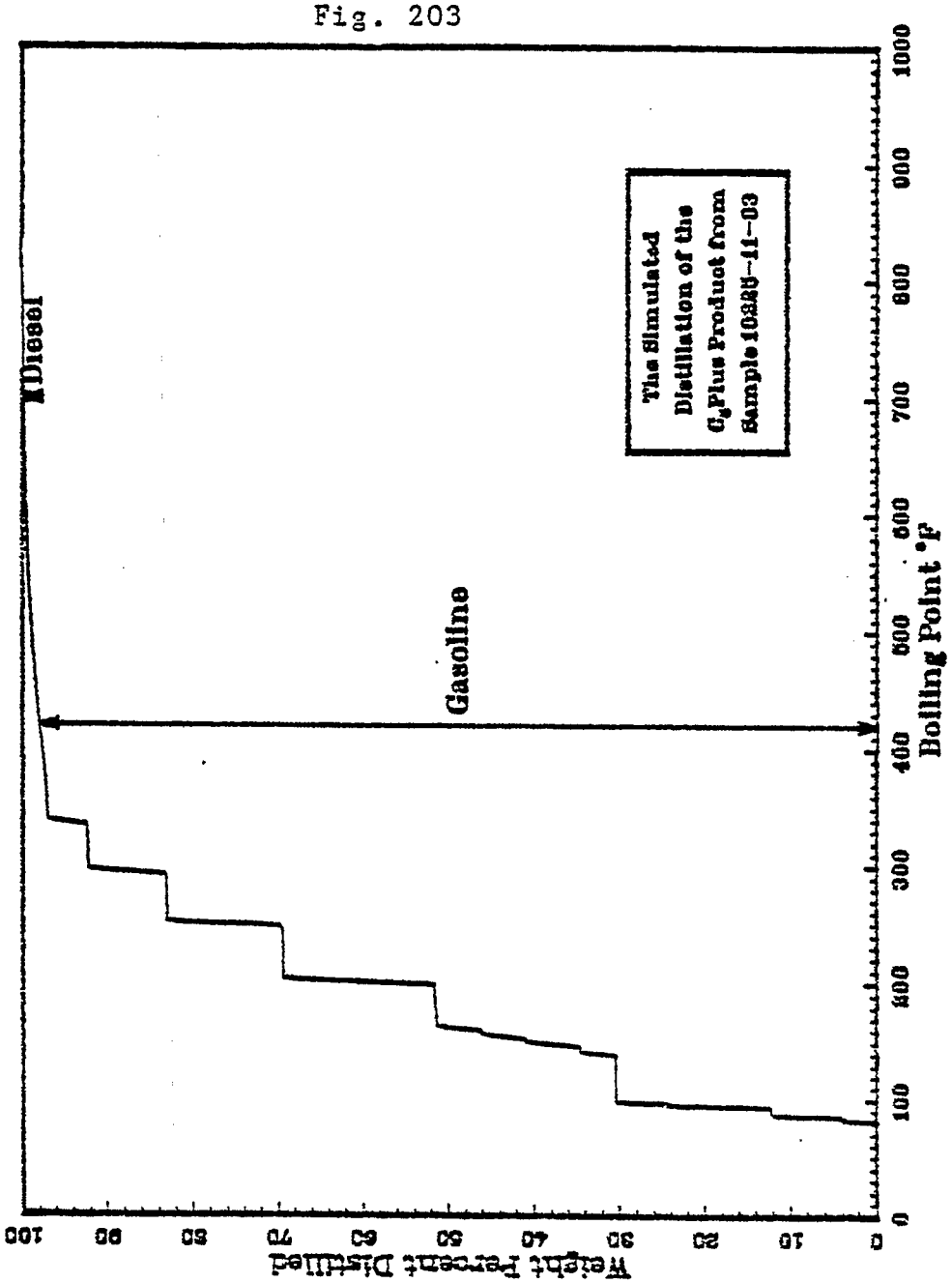

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10825-11-03
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. 204

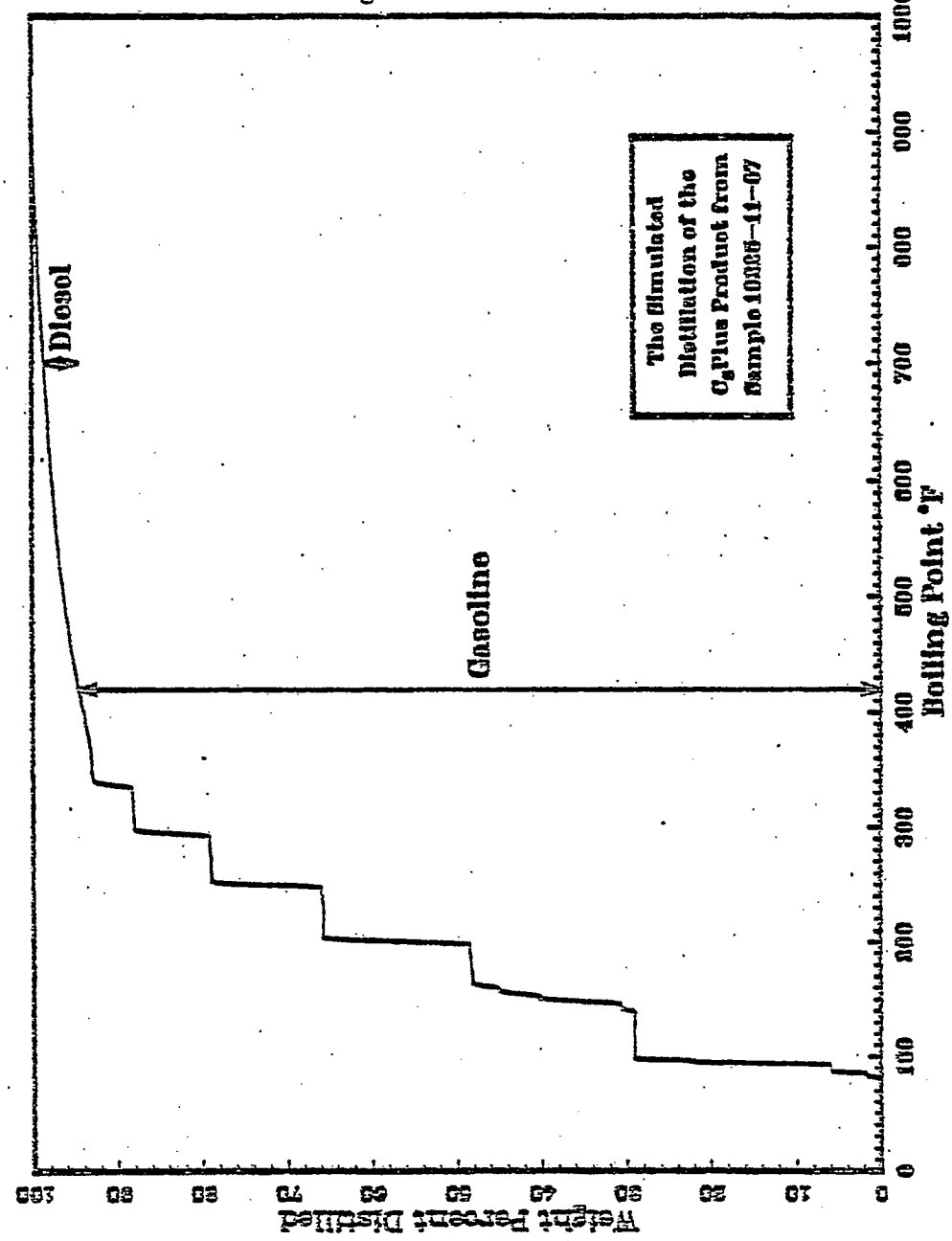
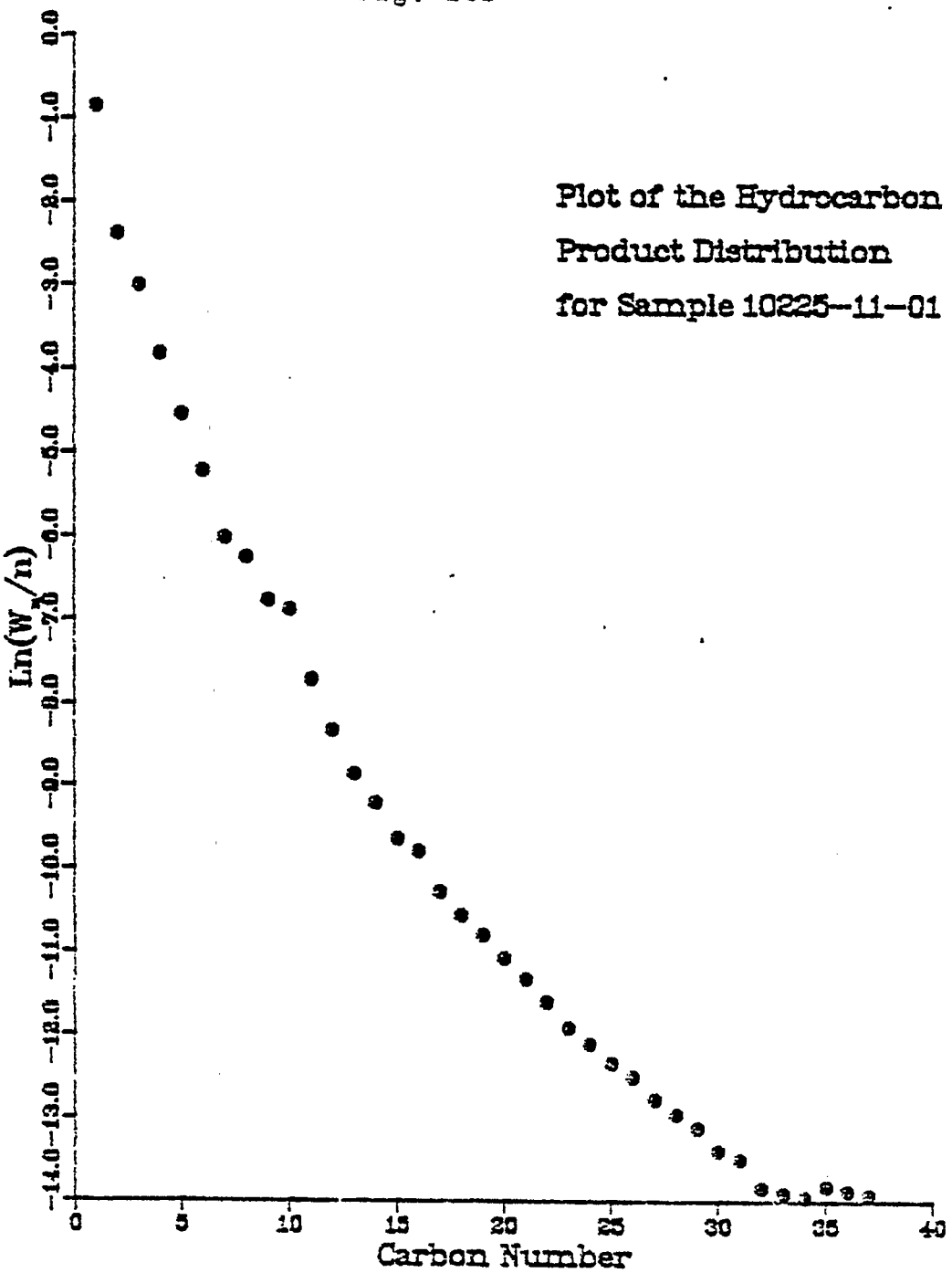

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10336-11-07
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 205



Plot of the Hydrocarbon Product Distribution for Sample 10225-11-01

Fig. 206

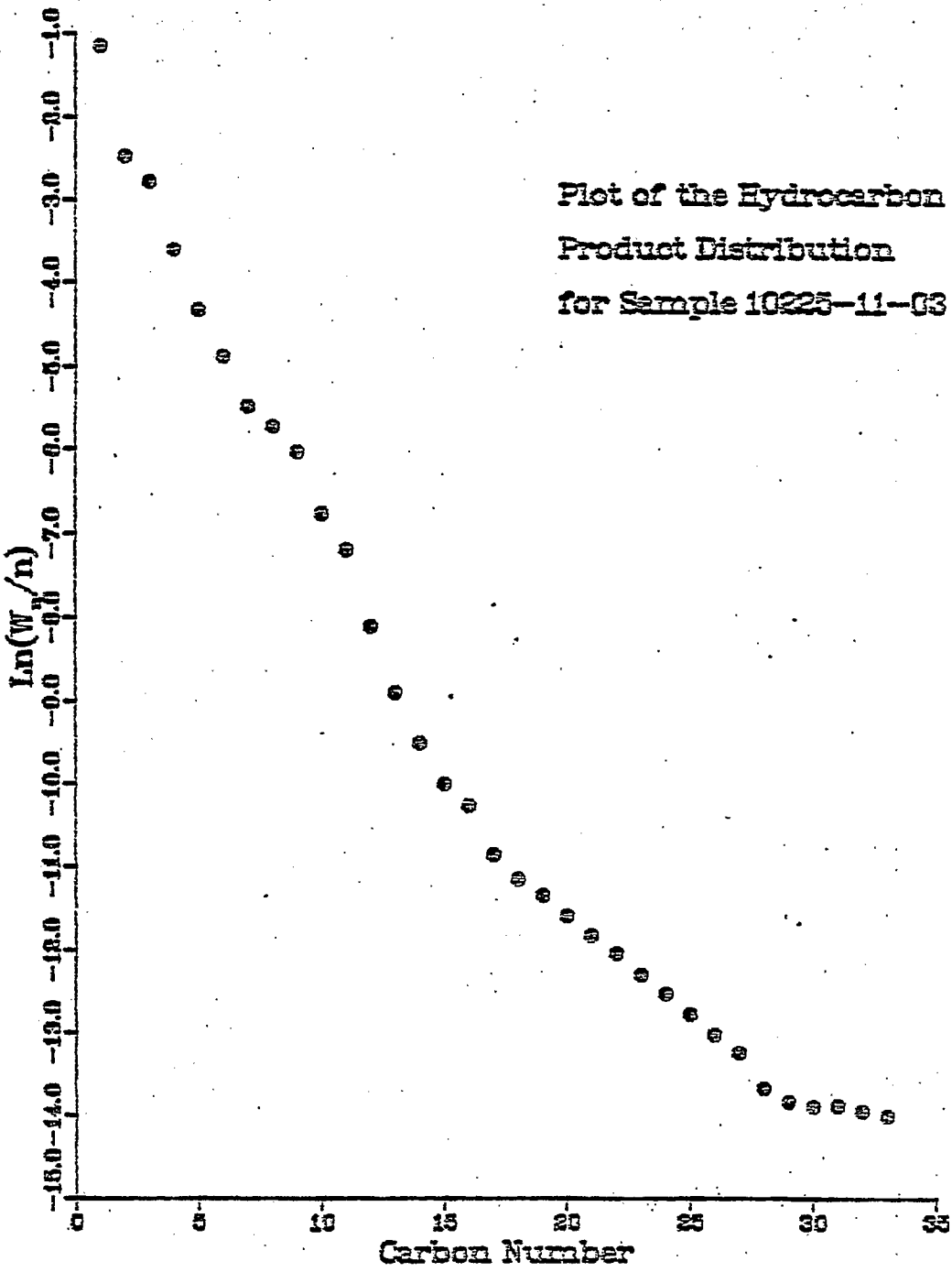
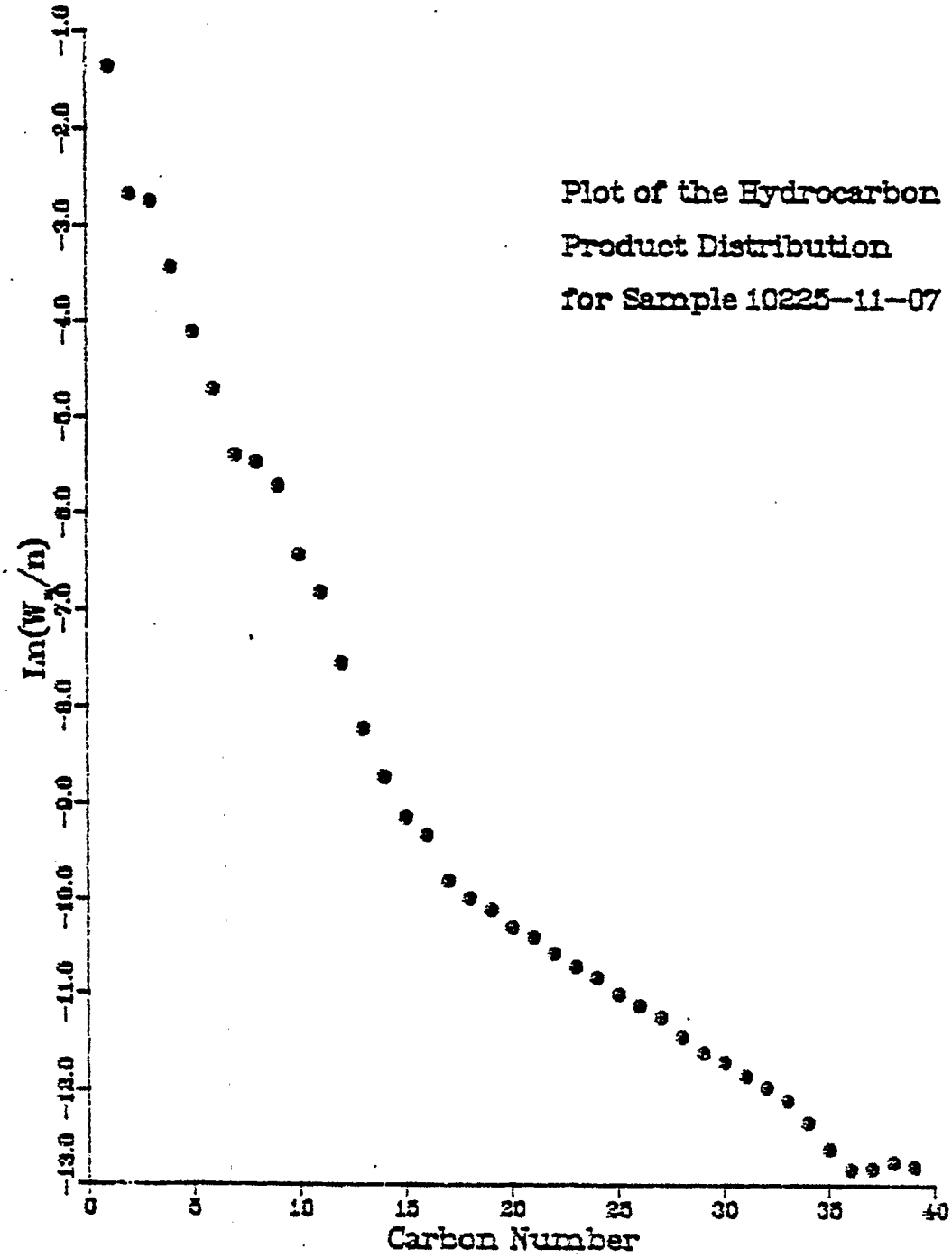

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-11-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
-14.0
-15.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 207



Plot of the Hydrocarbon Product Distribution for Sample 10225-11-07

Fig. 208

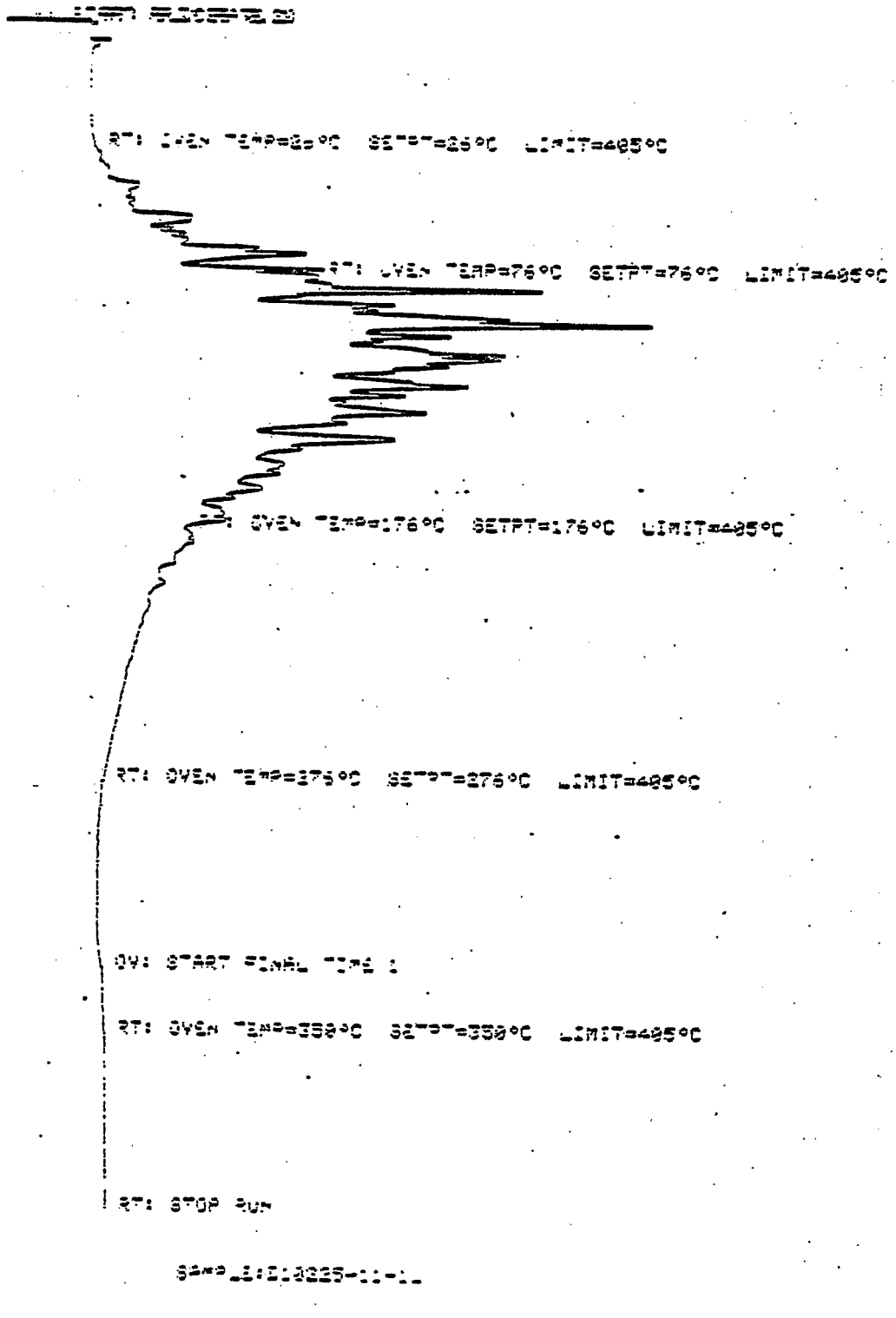

RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
OV: START FINAL TIME 1
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 209

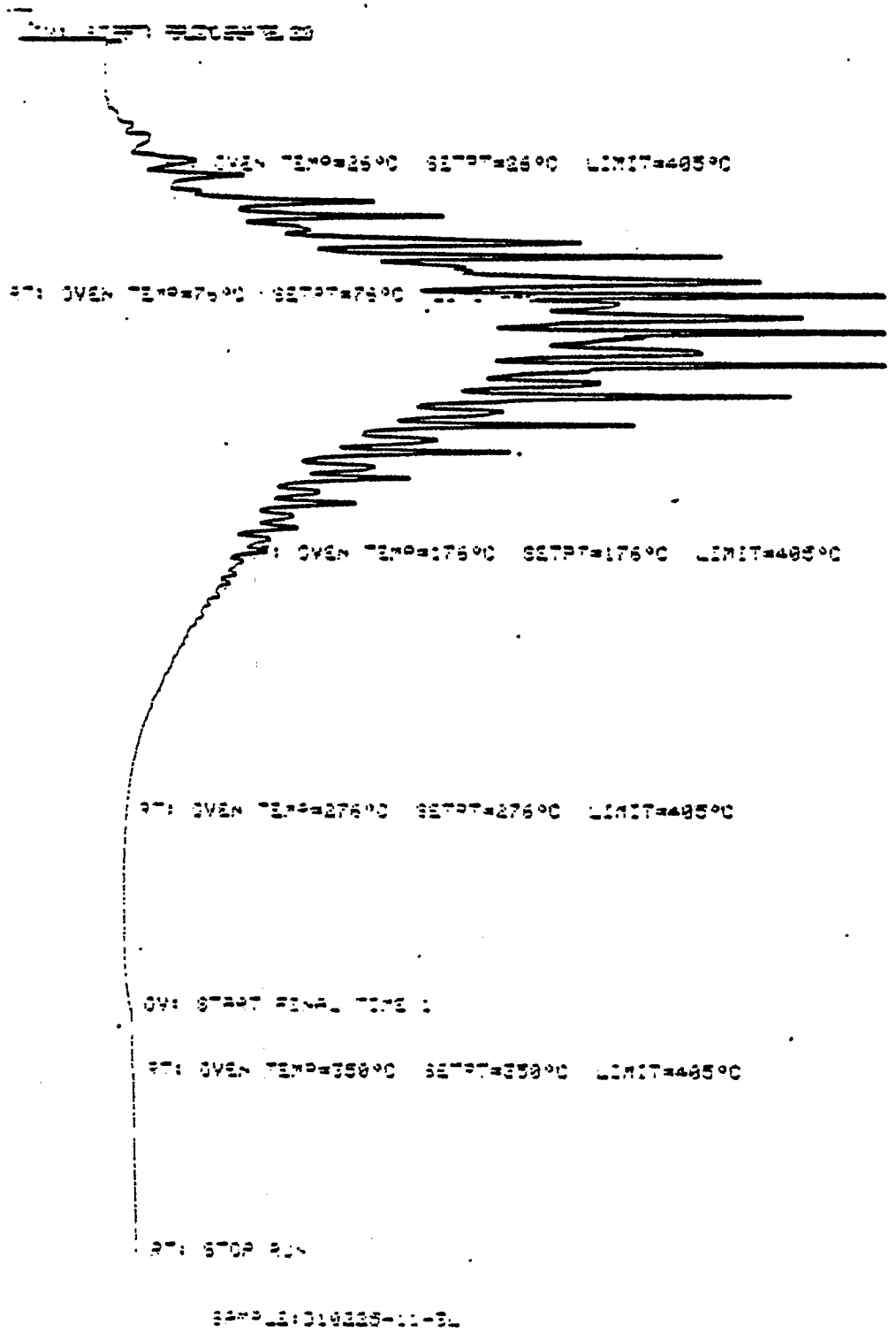

OVEN TEMP=25°C SETPT=25°C LIMIT=485°C
PT: OVEN TEMP=75°C SETPT=75°C
PT: OVEN TEMP=175°C SETPT=175°C LIMIT=485°C
PT: OVEN TEMP=275°C SETPT=275°C LIMIT=485°C
OV: START FINAL TIME :
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=485°C
PT: STOP RUN

Fig. 210

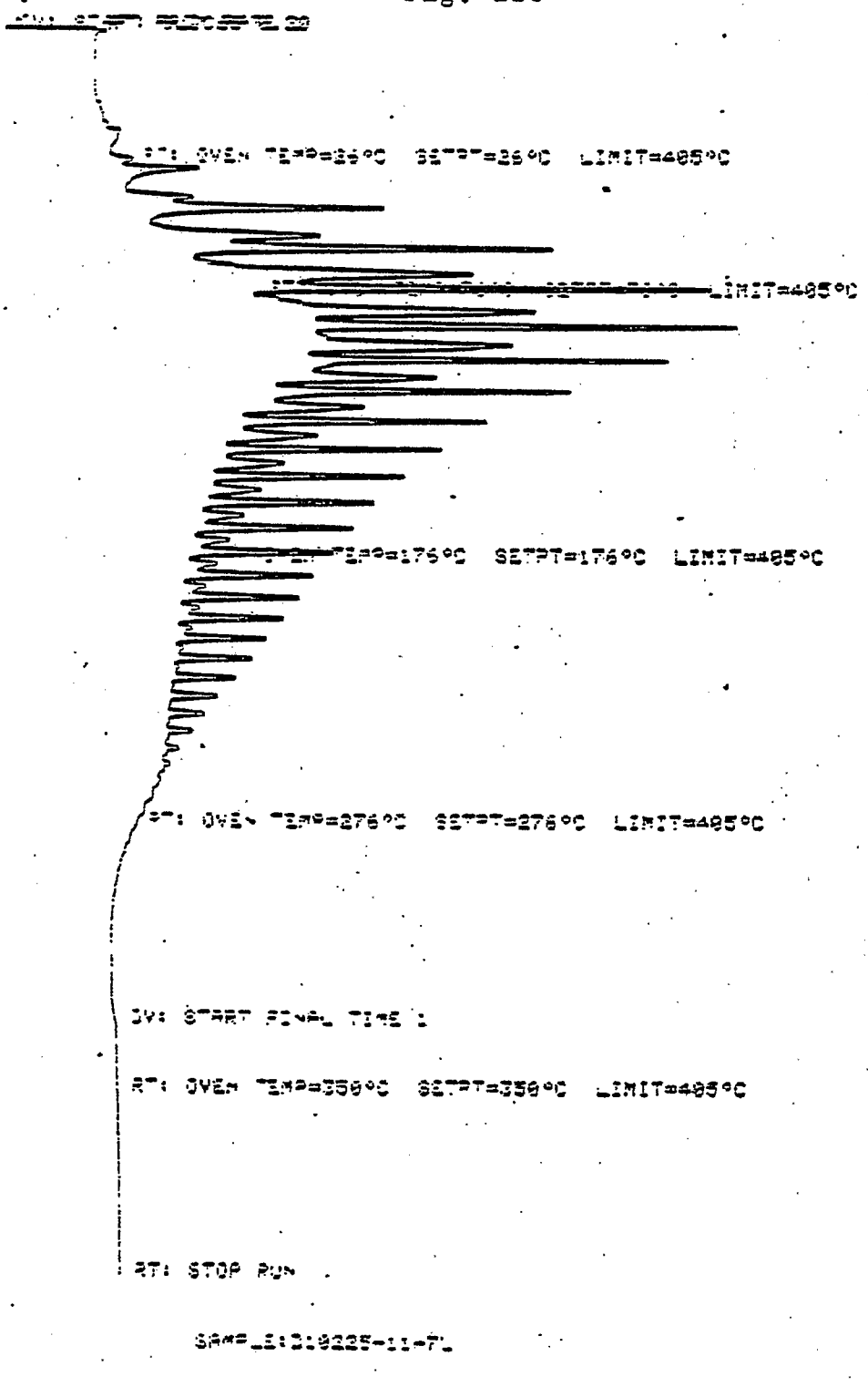

RT: OVEN TEMP=25°C SETPT=25°C LIMIT=485°C
LIMIT=485°C
TEMP=175°C SETPT=175°C LIMIT=485°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=485°C
OV: START FINAL TIME :
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=485°C
RT: STOP RUN
SAMP_I:3:0225-11-7L

TABLE 26 RESULT OF SYNGAS OPERATION

RUN NO. 10225-11
CATALYST FE/RH +UCC-108 #10252-88C 80 CC 39.3GM (40.1 AFTER RUN +.8 G)
FEED H2:CO:ARGON OF 66:33: 0 @1350 CC/MN OR 1013GHSV

RUN & SAMPLE NO.	10225-11-01	225-11-03	225-11-04	225-11-05	225-11-06
FEED H2:CO:AR	66:33: 0	66:33: 0	66:33: 0	66:33: 0	66:33: 0
HRS ON STREAM	18.5	42.6	48.0	67.2	73.8
PRESSURE,PSIG	133	212	198	211	201
TEMP. C	350	282	275	258	265
FEED CC/MIN	1350	1350	1350	1350	1350
HOURS FEEDING	18.50	24.08	6.42	24.58	6.58
EFFLNT GAS LITER	981.90	1294.54	349.11	1337.40	348.97
GM AQUEOUS LAYER	68.63	81.14	25.18	96.48	27.33
GM OIL	1.29	1.65	0.65	2.50	0.86
MATERIAL BALANCE					
GM ATOM CARBON %	100.83	108.49	103.62	92.11	93.82
GM ATOM HYDROGEN %	100.74	105.03	102.08	92.12	94.09
GM ATOM OXYGEN %	101.96	103.89	102.45	94.10	95.62
RATIO CHX/(H2O+CO2)	0.9756	1.0943	1:0264	0.9367	0.9502
RATIO X IN CHX	3.0725	2.8794	2.7987	2.6692	2.7025
USAGE H2/CO PRODT	1.3141	1.2291	1.3232	1.6315	1.5081
RATIO CO2/(H2O+CO2)	0.5188	0.5780	0.4716	0.2547	0.3243
K SHIFT IN EFFLNT	3.74	5.75	2.81	0.76	1.18
CONVERSION					
ON CO %	68.60	75.31	64.12	40.68	49.20
ON H2 %	45.48	46.45	42.68	34.06	37.71
ON CO+H2 %	53.19	56.28	49.90	36.26	41.53
PRDT SELECTIVITY,WT %					
CH4	42.47	31.84	29.12	25.23	25.81
C2 HC'S	18.37	16.83	15.64	13.10	13.84
C3H8	9.61	12.94	11.29	8.47	10.01
C3H6=	5.29	5.66	7.39	10.03	9.19
C4H10	3.81	4.73	4.55	3.69	4.03
C4H8=	4.94	6.14	7.84	9.21	8.82
C5H12	1.77	2.19	2.29	2.34	2.36
C5H10=	3.57	4.45	5.41	5.98	5.82
C6H14	1.50	2.02	1.97	1.90	1.80
C6H12= & CYCLO'S	1.76	2.57	2.29	3.82	3.58
C7+ IN GAS	5.99	9.86	10.85	14.11	12.41
LIQ HC'S	0.92	0.77	1.36	2.11	2.32
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	84.50	78.14	75.83	69.74	71.71
C5 -420 F	14.78	21.40	23.24	28.81	26.69
420-700 F	0.63	0.41	0.69	1.07	1.18
700-END PT	0.09	0.05	0.25	0.38	0.42
C5+-END PT	15.50	21.86	24.17	30.26	28.29
ISO/NORMAL MOLE RATIO					
C4	0.4979	0.1526	0.1654	0.0960	0.1045
C5	1.0571	0.6629	0.5932	0.2133	0.2459
C6	1.2784	0.8025	0.7116	0.2602	0.3067
C4=	1.1536	0.5399	0.2076	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.7336	2.1819	1.4568	0.8054	1.0387
C4	0.7436	0.7439	0.5601	0.3871	0.4414
C5	0.4815	0.4783	0.4121	0.3802	0.3947
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7263	0.6805			
RATIO CH4/(1-A)**2	5.6699	3.1181			
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR LT GR	CLR LT GR			
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	388	329			
16	404	354			
50	498	447			
84	646	600			
90	700	656			
RANGE(16-84 %)	242	246			
WT % @ 420 F	21.67	41.00	31.33	31.33	31.33
WT % @ 700 F	90.00	93.47	81.88	81.88	81.88

TABLE 27 RESULT OF SYNGAS OPERATION

RUN NO. 10225-11
CATALYST FE/RH +UCC-108 #10252-88C 80 CC 39.3GM (40.1 AFTER RUN +.8 G)
FEED H2:CO:ARGON OF 66:33: 0 @1350 CC/MN OR 1013GHSV

RUN & SAMPLE NO.	10225-11-07
FEED H2:CO:AR	66:33: 0
HRS ON STREAM	90.0
PRESSURE,PSIG	205
TEMP. C	261
FEED CC/MIN	1350
HOURS FEEDING	22.83
EFFLNT GAS LITER	1257.03
GM AQUEOUS LAYER	94.78
GM OIL	2.99
MATERIAL BALANCE	
GM ATOM CARBON %	97.40
GM ATOM HYDROGEN %	97.30
GM ATOM OXYGEN %	98.51
RATIO CHX/(H2O+CO2)	0.9699
RATIO X IN CHX	2.7031
USAGE H2/CO PRODT	1.5039
RATIO CO2/(H2O+CO2)	0.3314
K SHIFT IN EFFLNT	1.22
CONVERSION	
ON CO %	49.18
CN H2 %	37.45
CN CO+H2 %	41.36
PROT SELECTIVITY,WT %	
CH4	25.84
C2 HC'S	13.86
C3H8	10.01
C3H6=	9.20
C4H10	4.04
C4H8=	8.83
C5H12	2.37
C5H10=	5.83
C6H14	1.80
C6H12= & CYCLO'S	3.58
C7+ IN GAS	12.42
LIQ HC'S	2.24
TOTAL	100.00

SUB-GROUPING	
C1 -C4	71.77
C5 -420 F	26.69
420-700 F	1.13
700-END PT	0.41
C5+-END PT	28.23
ISO/NORMAL MOLE RATIO	
C4	0.1045
C5	0.2459
C6	0.3067
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	1.0387
C4	0.4414
C5	0.3947
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.7658
RATIO CH4/(1-A)**2	4.7111
LIQ HC COLLECTION	
PHYS. APPEARANCE	YL-GN OIL
DENSITY	0.783
N, REFRACTIVE INDEX	1.4405
SIMULT'D DISTILATN	
10 WT % @ DEG F	343
16	376
50	489
84	720
90	783
RANGE(16-84 %)	344
WT % @ 420 F	31.33
WT % @ 700 F	81.88

XIV. Summary

The results from the tests reported this quarter are again very informative. The series of additives for cobalt catalysts has yielded another important modifier of cobalt activity. The chemistry of a previously identified additive was further explored in combination with a different shape selective component. The alternate means of combining the metal component and the shape selective component had dramatic effects on the stability and product distribution of the catalyst. Runs with the reference catalyst containing α-Al_2O_3 pointed out the great changes in selectivity possible with slight temperature changes. Even the poor catalysts have contributed to the understanding of cobalt Fischer-Tropsch catalysts.

The low percentage of additive X_6 used in Catalyst 4 had a large effect on the catalyst's stability and final product distribution. The major disadvantage of most cobalt Fischer-Tropsch catalysts is the excessive methane production. This additive reduced the methane yield significantly, especially later in the run. Furthermore, this additive also increased the yield of olefins significantly.

Last quarter, the additive, X_4, was shown to have effects similar to X_6 in a catalyst containing UCC-101. This quarter it was shown to again increase the selectivity for olefins, this

time in a catalyst containing UCC-108. However, in this formulation, X_4 did not impart the previously observed great stability to the catalyst. The X_4 catalyst again produced a higher than usual C_2-C_4 yield, which this time led to a slightly inferior product distribution.

A catalyst with enhanced properties was produced when the metal component and the shape selective component were put in more intimate contact as is shown in the results from Runs 7 and 8. The catalyst had extraordinary stability in both syngas conversion and the product distribution. There was a slight deactivation during the first 140 hours on stream, but it was rock steady thereafter. Formation of the catalyst as 1/16-inch extrudates increased the catalyst's initial activity, especially the water gas shift activity. However, there was a greater initial deactivation followed by a slight deactivation to an activity similar to that of the 1/8-inch extrudate. This method of formulation appears to be an outstanding way to combine a cobalt metal component and a shape selective component.

The catalyst which combined thorium-promoted cobalt with α-Al_2O_3 had the largest temperature dependence of the product selectivity observed for any Fischer-Tropsch catalyst in this program. The change of 20C in the reactor temperature had little effect on the conversion but drastically affected the selectivity. The highest yield of liquids (C_5^+), in grams per hour, was obtained at the lowest temperature, 250C, which also had the lowest total conversion. This just demonstrates the need for an

active catalyst which can be run at a lower temperature to improve selectivity.

The zinc ion exchanged into UCC-107 to hydrogenate coke precursors seemed to be better at hydrogenating the desired Fischer-Tropsch products than it was at stopping deactivation of the UCC-107.

The results this quarter were very encouraging. Hopefully many of these results can be combined into one catalyst exhibiting great stability and improved product quality.

Appendix B. Surface Studies

By M. Logan, B. Naasz, and G. A. Somorjai

The study of the catalytic hydrogenation of carbon monoxide has continued this quarter with our work on molybdenum and rhenium surfaces.

Molybdenum

Rates and activation energies for the hydrogenation of CO were determined (see Figs. B-1 and B-2) on Mo(100) single crystals and Mo foils, composed mainly of the closest packed (110) face of bcc crystals. The reaction is structure insensitive on these surfaces, the rates and product distributions being nearly identical. The molybdenum work was extended by adsorbing submonolayer quantities of potassium on the surface as a promoter. Adding potassium is found to have a promotion effect (see Figure B-3) for up to ~0.2 monolayers (AES peak ratio $K_{252}/Mo_{221} = 0.4$). The rate of ethene production nearly tripled from the potassium-free surface to a potassium coverage of ~0.1 monolayers. The selectivity of the reaction remains constant for the conditions of our experiments. The effect of adding more than 0.2 monolayers of potassium seems to be one of site blocking.

Iron and Rhenium

Work on the Fe and Re systems continued this quarter with

major emphasis placed on their oxides. Activation energies for methanation on Re, Re+Na, Fe and FeO_x are shown in Figs. B-4 and B-5. The large changes in activation energy, E_a, with the addition of oxygen or sodium imply that the rate-determining step is changed. We have also confirmed that the product distributions are altered as the surface is changed from clean to oxide and alkali promoted metal surfaces. Again, with the oxide, less change in product distribution is seen, but the catalyst surface stays active for a much longer period of time. With alkali promoters the product distribution is shifted to hydrocarbons with a higher molecular weight.

Fig. B-1

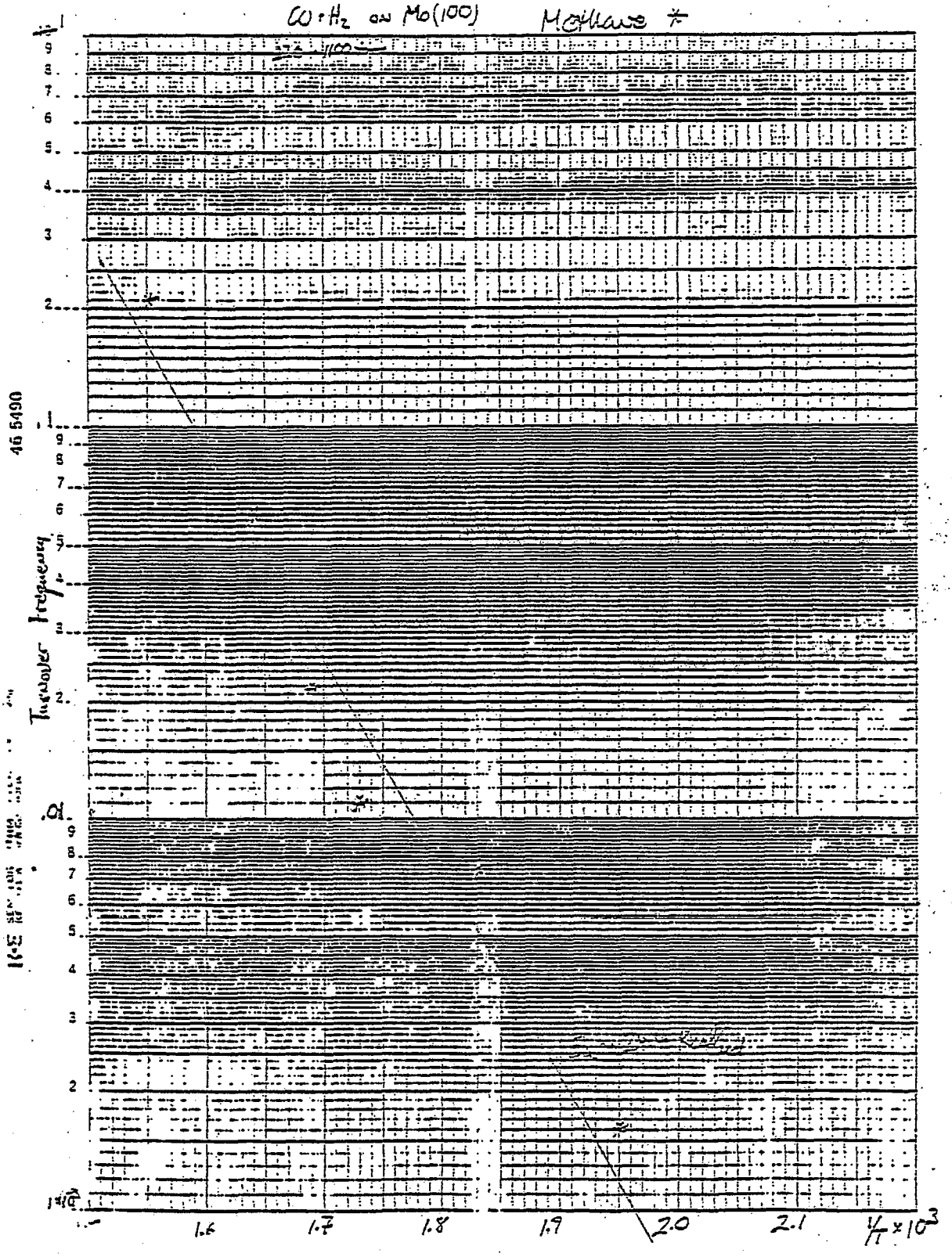

CO + H2 on Mo(100)
Methane *
Temperature Programmed Reaction Spectroscopy
46 5490
Temperature Frequency
1.6
1.7
1.8
1.9
2.0
2.1
1/T x 10^3

Fig. B-2

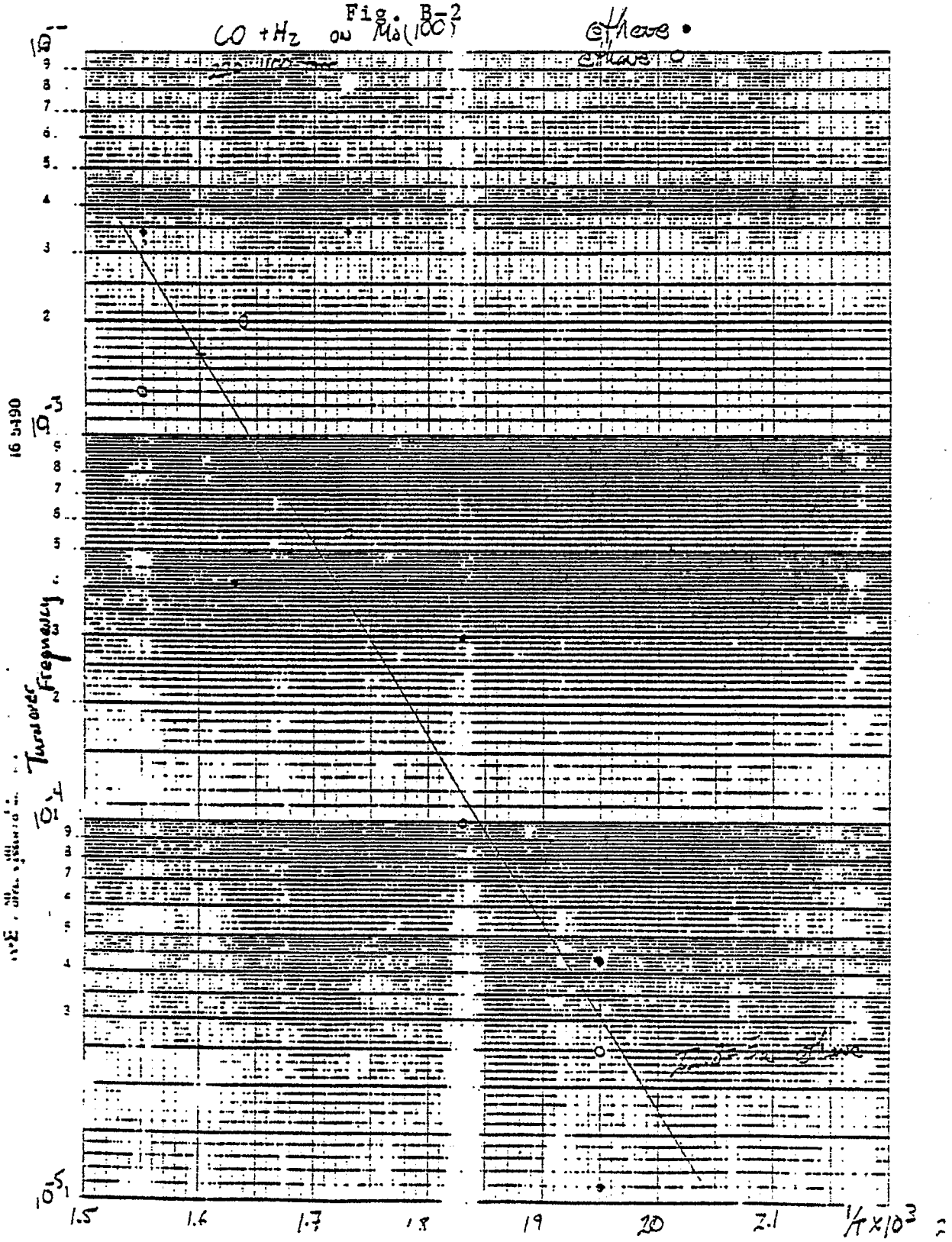

CO + H2 on Mo(100)
Ethene •
Ethane ○
Turnover Frequency
1.5
1.6
1.7
1.8
1.9
2.0
2.1
1/T x 10^3

Fig. B-3

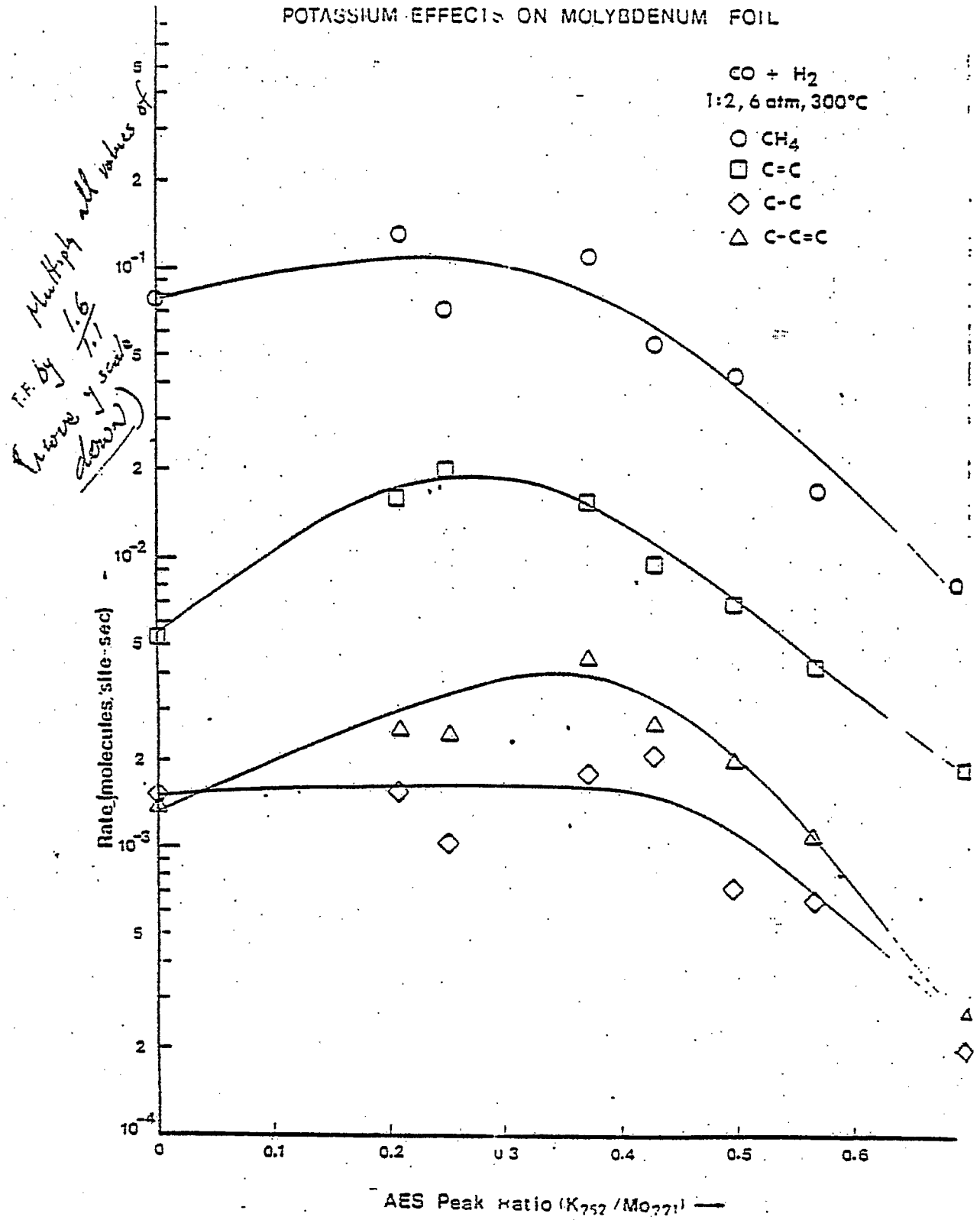
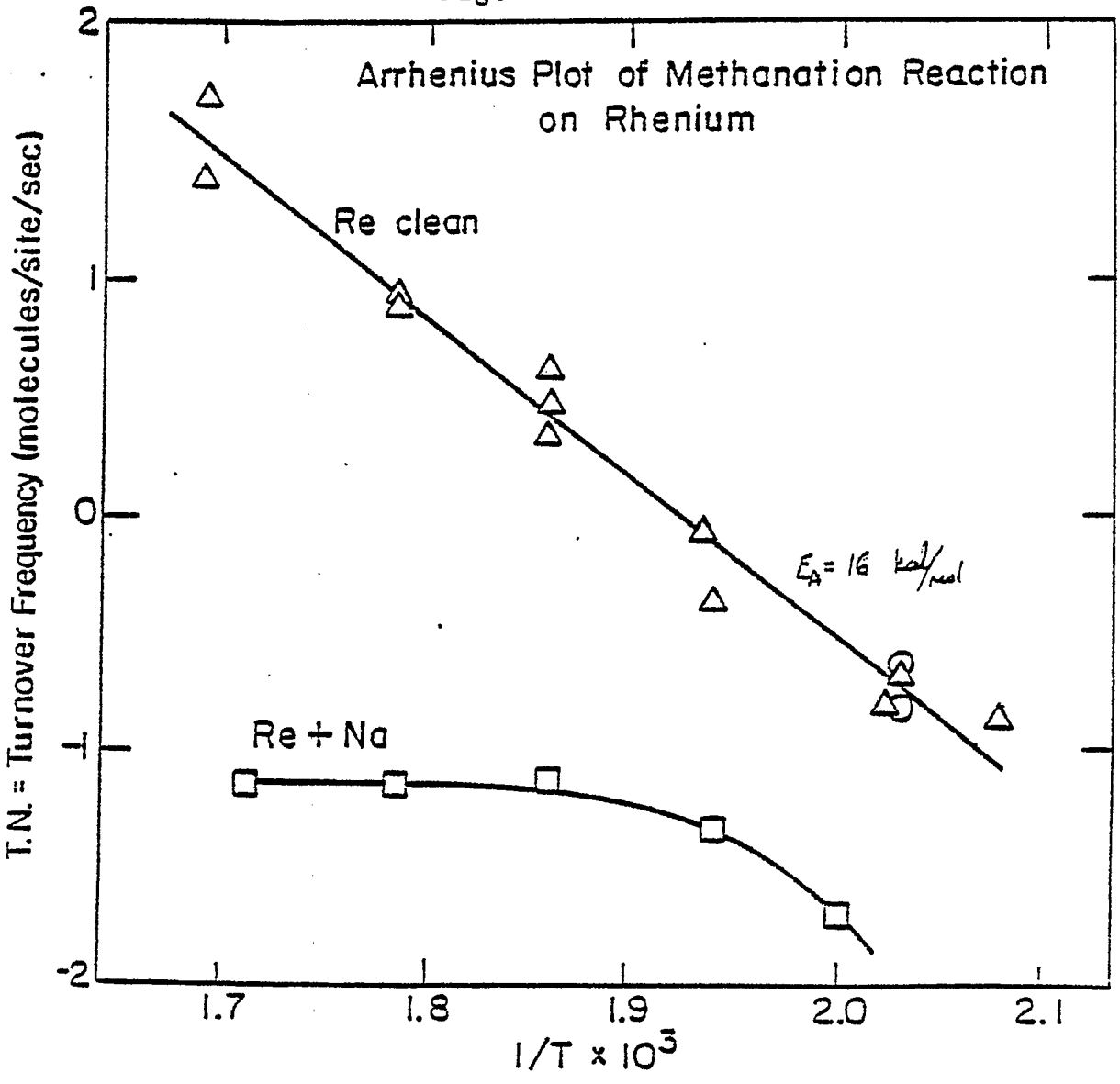

POTASSIUM EFFECTS ON MOLYBDENUM FOIL
CO + H2
1:2, 6 atm, 300°C
CH4
C=C
C-C
C-C=C
Rate (molecules/site·sec)
AES Peak Ratio (K252 /Mo221)
0
0.1
0.2
0.3
0.4
0.5
0.6

Fig. B-4



XBL 837-6025

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