LIQUID HYDROCARBON FUELS FROM SYNGAS. ELEVENTH QUARTERLY REPORT, SEPTEMBER-NOVEMBER 1983

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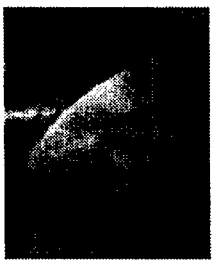

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TECHNICAL PROGRESS REPORT
DE-AC22-81PC40077

Eleventh Quarterly Report
September - November 1983

LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Contents

Appendixes

II. SCHEDULE

The contract work was planned for the 36-month period beginning March 6, 1981.

Work on the program is divided into four tasks.

Task 1, essentially completed, was the conversion of low molecular weight liquids, such as methanol and propylene, to gasoline and diesel fuel, with catalysts consisting of only a Molecular-Sieve component, commonly designated as the shape-selective component (SSC).

Task 2 is the conversion of syngas (carbon monoxide and hydrogen) to gasoline and diesel fuel, using catalysts consisting of both an SSC and a transition-metal component (MC).

Task 3 is a study of the surface effects and reaction intermediates present on various catalysts during the hydrogenation of carbon monoxide. This task is conducted under a subcontract with the University of California at Berkeley, and is directed by Dr. Gabor A. Somorjai.

Task 4 comprises the management and technical reports for the contract.

III. ORGANIZATION

Synthesizing "Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysis conducted by the Molecular Sieve Department, Catalysts and Process Systems Division, Union Carbide Corporation.

The work is performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown NY 10591.

Principal investigator is Dr. Jule A. Rabo.

Program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

Task 1 has been essentially completed. There should be no future Task 1 work.

B. Task 2

Twelve catalyst test runs were made from August through October. Eleven of these runs (Runs 1 through 11) used nine catalysts that contained cobalt or cobalt/thorium as the metal component, while the remaining run (Run 12) used a catalyst that contained iron as the metal component.

Run 1 compared the efficacy of a Co/Th + UCC-101 catalyst at 280C with that of the same catalyst previously run at 270C (Run 3, Tenth Quarterly Report). Runs 2 through 5 examined the performance of catalysts containing the additives X_5, X_6, and X_7 incorporated into their Co or Co/Th metal components and having UCC-101 as their shape selective components. Run 6 compared the performance of a Co/Th/X_4 + UCC-108 catalyst with that of the previously tested Co/Th/X_4 + UCC-101 catalyst (Run 9, Tenth Quarterly Report). Runs 7 and 8 compared the effectiveness of 1/8-inch and 1/16-inch extrudates of Co/Th + UCC-108 (a modification of UCC-101). Run 9 examined the efficacy of ion-exchanged zinc

as a coke inhibitor on the shape selective component of a Co/Th + Zn/UCC-107 catalyst. Runs 10 and 11 examined the performance of a Co/Th + α-Al_2O_3 reference catalyst at different temperatures. Finally, Run 12 examined the effectiveness of a Fe/Rh + UCC-108 catalyst.

Unusually promising results were obtained in Run 4 with the Co/Th/X_6 + UCC-101 catalyst. The small amount of X_6 significantly reduced the yield of methane, increased the yield of olefins, and enhanced the catalyst's stability to a degree not previously observed.

This same type of stability was also found in Runs 7 and 8 with the Co/Th + UCC-103 catalyst. Its unusual stability in both syngas conversion and product distribution is believed to be caused by the mixing of the metal and shape selective components in a manner that gave a more intimate contact between these components than that obtained in the past from the usual mixing method.

The other runs were less successful. Run 6 showed that while the Co/Th/X_4 + UCC-108 had a higher production of olefins than that of last quarter's Co/Th/X_4 + UCC-101 catalyst, it had a poorer C_5^+ yield and poorer stability than that product. Run 9 showed that the exchanged zinc in the Co/Th + Zn/UCC-107 catalyst was not successful in stopping the coking of the UCC-107. Finally, Runs 2, 5 and 12 showed that neither the cobalt catalysts containing the X_5 or X_7 additives, nor the Fe/Rh + UCC-108 catalyst, performed satisfactorily.

C. Task 3

Studies at the University of California at Berkeley, under the direction of Professor G. A. Somorjai, have concentrated this quarter on the catalytic hydrogenation of CO on molybdenum, rhenium and iron surfaces.

Reaction rates, activation energies, and product selectivities were found to be the same for both Mo(100) single crystals and for the closely packed (110) face of bcc crystals. Adding potassium was found to have a promotion effect, with the ethene production nearly tripling from a ~0.1 monolayer of potassium.

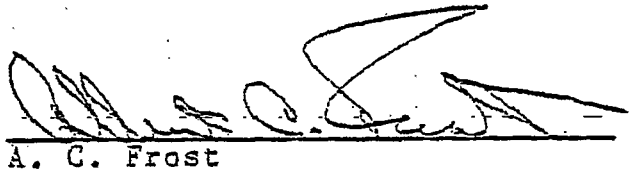
Large differences in the activation energies between Re and Re+Na and between Fe and FeO_x implied that oxygen and sodium changed the rate-determining step of the methanation reaction.

V. CHANGES

There were no contract changes during the Eleventh Quarter.

VI. FUTURE WORK

Efforts during the next quarter will be directed at a continued examination of cobalt catalysts with additional additives.



A. C. Frost
Program Manager

APPENDIXES

Appendix A. CATALYST TESTING

By P. K. Coughlin, C. L. Yang, G. N. Long and L. F. Elek

Contents

I. Introduction

The results of 12 runs conducted from August through October 1983 are detailed in this report. All but one of the runs (Run 12) used catalysts having metal components containing cobalt. The catalyst used in Run 12 had an iron-rhodium metal component. A run with this catalyst under different process conditions was reported last quarter.

Like Run 12, many of the runs reported this quarter flow from previous results. The catalyst in Run 1 is similar to catalysts reported last quarter but tested under different conditions. Runs 2 to 6 are a continuation of the series of runs begun last quarter to investigate the effects of different additives. Three of the additives are new, but one, X_4, was tested again. In the last quarter. X_4 was found to be a useful additive for catalysts containing UCC-101. This quarter X_4 was used in combination with UCC-108. Runs 7 and 8 test an alternative method of combining the cobalt metal component and the Molecular Sieve shape selective component.

A catalyst containing UCC-107 was reported in the Ninth Quarterly Report. Unfortunately the acid activity of the UCC-107 deactivated rapidly. This quarter another catalyst containing UCC-107, ion exchanged with zinc to inhibit coke formation, was tested in Run 9.

The reference catalyst containing α-Al_2O_3 in place of a Molecular Sieve shape selective component is analogous to a similar reference catalyst prepared for comparing the iron catalysts and reported in the Second Annual Report.

II. RUN 1 (10225-14) with Catalyst 1 (Co/Th + UCC-101)

This catalyst, the same as the one in the Tenth Quarter Run 10112-15, is being tested in this run at 280C for comparison with the previous results at 270C. The metal component was prepared by precipitating cobalt oxide with sodium carbonate from an aqueous solution of cobalt nitrate. After washing and drying, the cobalt oxide was impregnated with thorium nitrate solution to give 15 weight percent thorium on the catalyst. The metal component and the Molecular Sieve (UCC-101) were then physically mixed in a 3:14 weight ratio, bonded with 15 weight percent silica, formed as 1/8" extrudates, and calcined in air at 250C before loading into the reactor. The resulting mixture consisted of cobalt/thorium:UCC-101:silica in a weight ratio of 15:70:15.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 1-4. Simulated distillations of the C_5^+ product for three samples are plotted in Figs. 5-7. Carbon number product distributions are plotted in Figs. 8-16. Chromatograms from simulated distillations are reproduced in Figs. 17-25. Detailed material balances for this run appear in Tables 1-3.

This is a highly active catalyst, with good maintenance of H_2 conversion, although with some initial deactivation of CO conversion. Based on the data for the entire run length, the deactiva-

tion rate of this catalyst, tested at 280C, was one half that of the catalyst used in Run 10112-15, tested at 270C. The initial water gas shift activity was good, with two-thirds of the oxygen rejected as CO_2. Usage of the 1:1 H_2:CO syngas, at about 1, was highly efficient. The water gas shift activity deteriorated quickly at first, after which the conversion stabilized. At 100 hours on stream only 28 percent of the oxygen was rejected as CO_2. The H_2:CO usage ratio increased initially due to the loss of water gas shift activity, and later due to the production of more hydrogen-rich hydrocarbons.

The selectivity to liquid hydrocarbons, initially very poor, quickly improved and stabilized, and throughout the stable stage was comparable to the final product distribution of Run 10112-15. Methane production, a very high 32 percent in the initial sample, dropped quickly to 21 percent, then rose gradually to 24 and 27 percent at 150 and 200 hours on stream respectively. At 270C, in Run 10112-15, methane production was 15 percent initially, and 23 and 24 percent at 150 and 190 hours. The C_2-C_4 selectivity, about 14 percent, was almost the same as at 270C. The yield of total motor fuels was 60-55 percent, of which about two-thirds was gasoline, again similar to the yield at 270C. The yield of heavies was low, about 4 percent. In general, the selectivity of this catalyst is almost the same at 280C as at 270C except for the somewhat higher methane production at 280C.

Isomerization of the pentane was fairly high for a cobalt catalyst, with a relatively constant isopentane fraction of about

30 percent; in the earlier run at 270C the isopentane fraction of the pentane was almost 40 percent initially and about 20 percent at the end of the run. The chromatograms from the simulated distillations of the liquid product show that the liquid was also isomerized.

The initial Schulz-Flory plots show an excess of methane and a carbon number cut-off; plots of later samples also show the excess of methane but no carbon number cut-off. The initial non-linearity of the S-F plots does not seem to be due to wax build-up in the reactor.

At 280C this catalyst produced results essentially similar to those at 270C (Tenth Quarter Run 10112-15).

Fig. 2

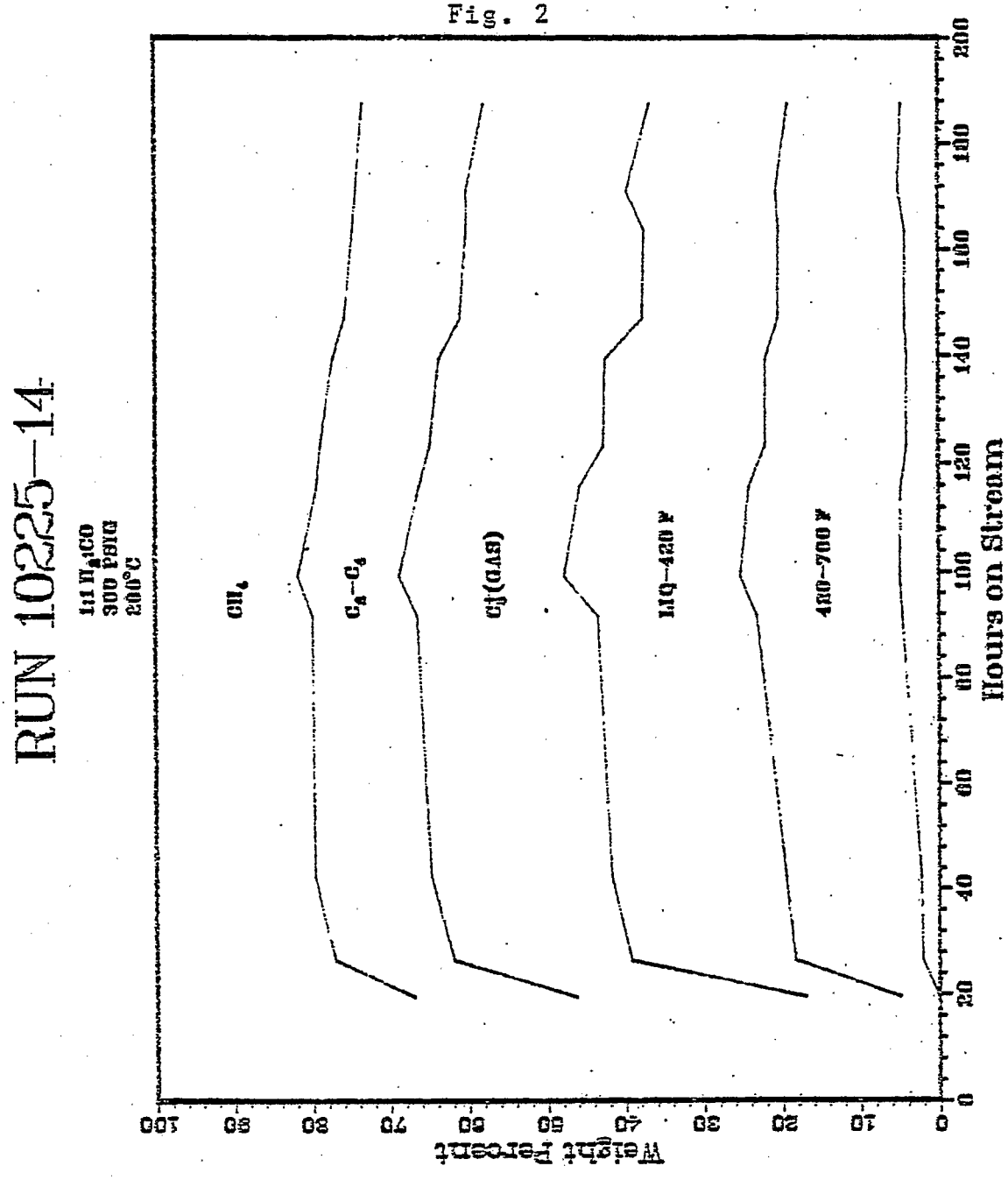

RUN 10225-14
1:1 H2:CO
300 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 3

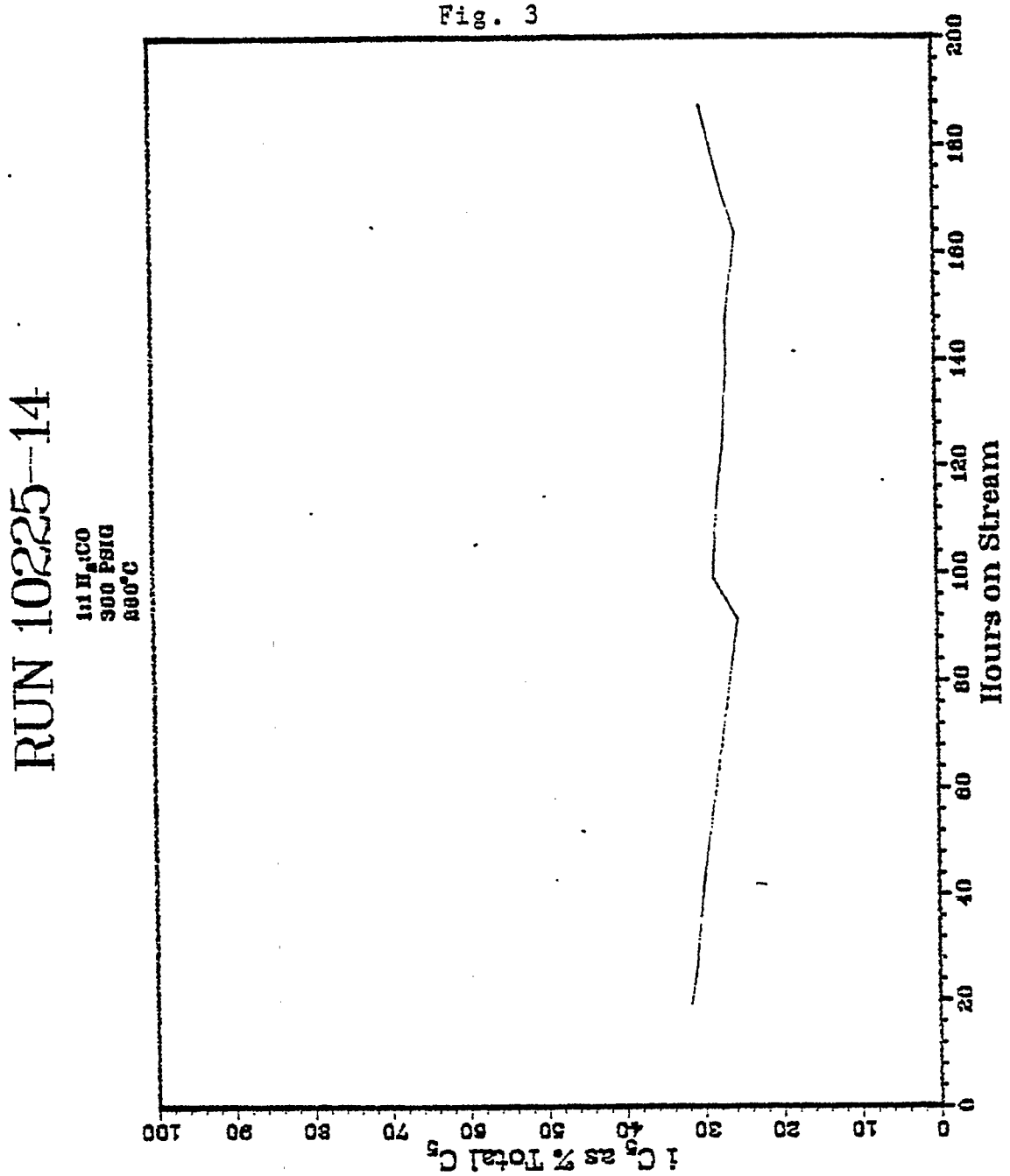

RUN 10225--14
1:1 H2:CO
300 PSIG
280°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 4

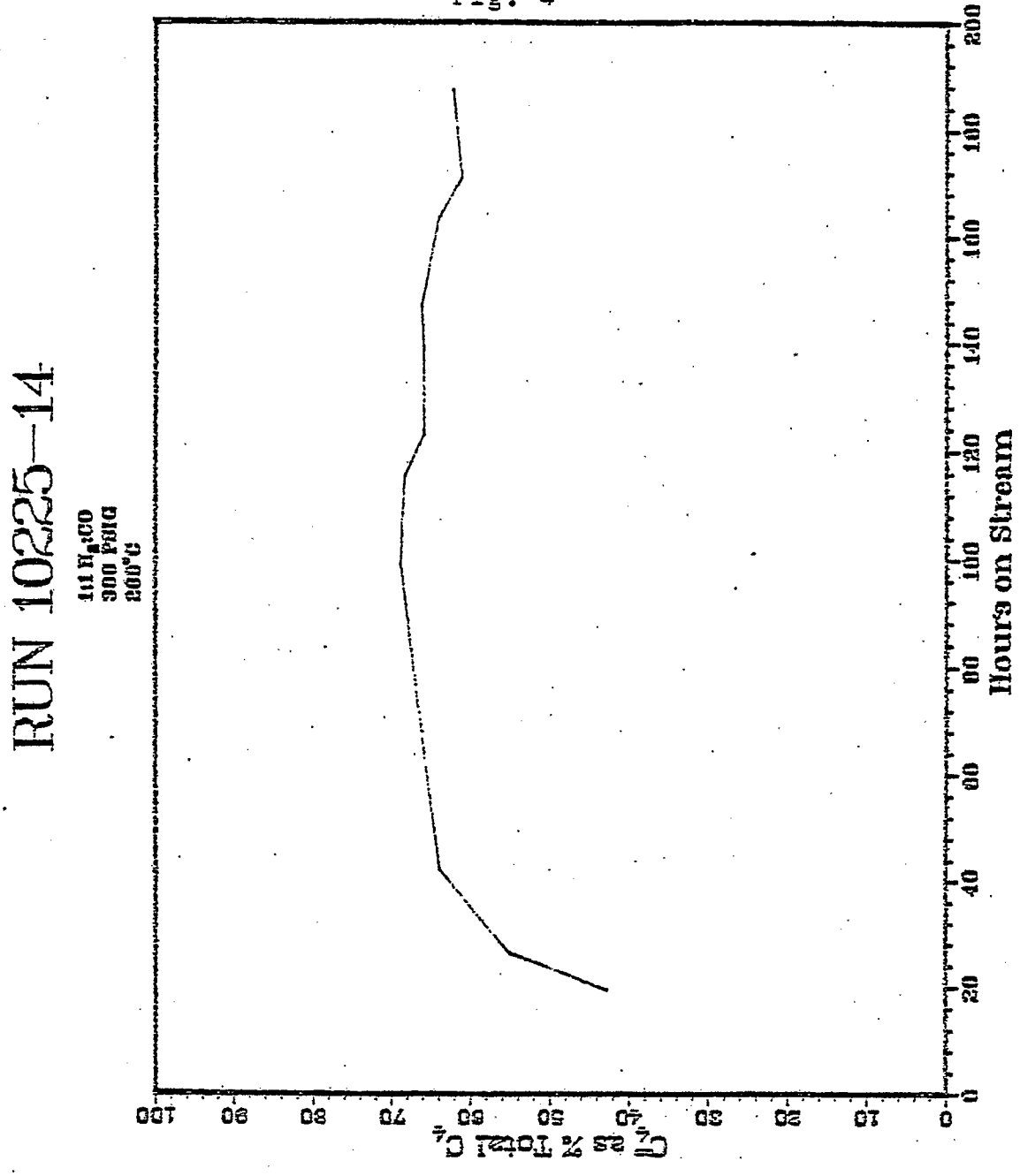

RUN 10225-14
411 H2:CO
300 PSIG
260°C
C4 as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
10
30
50
70
90

Fig. 5

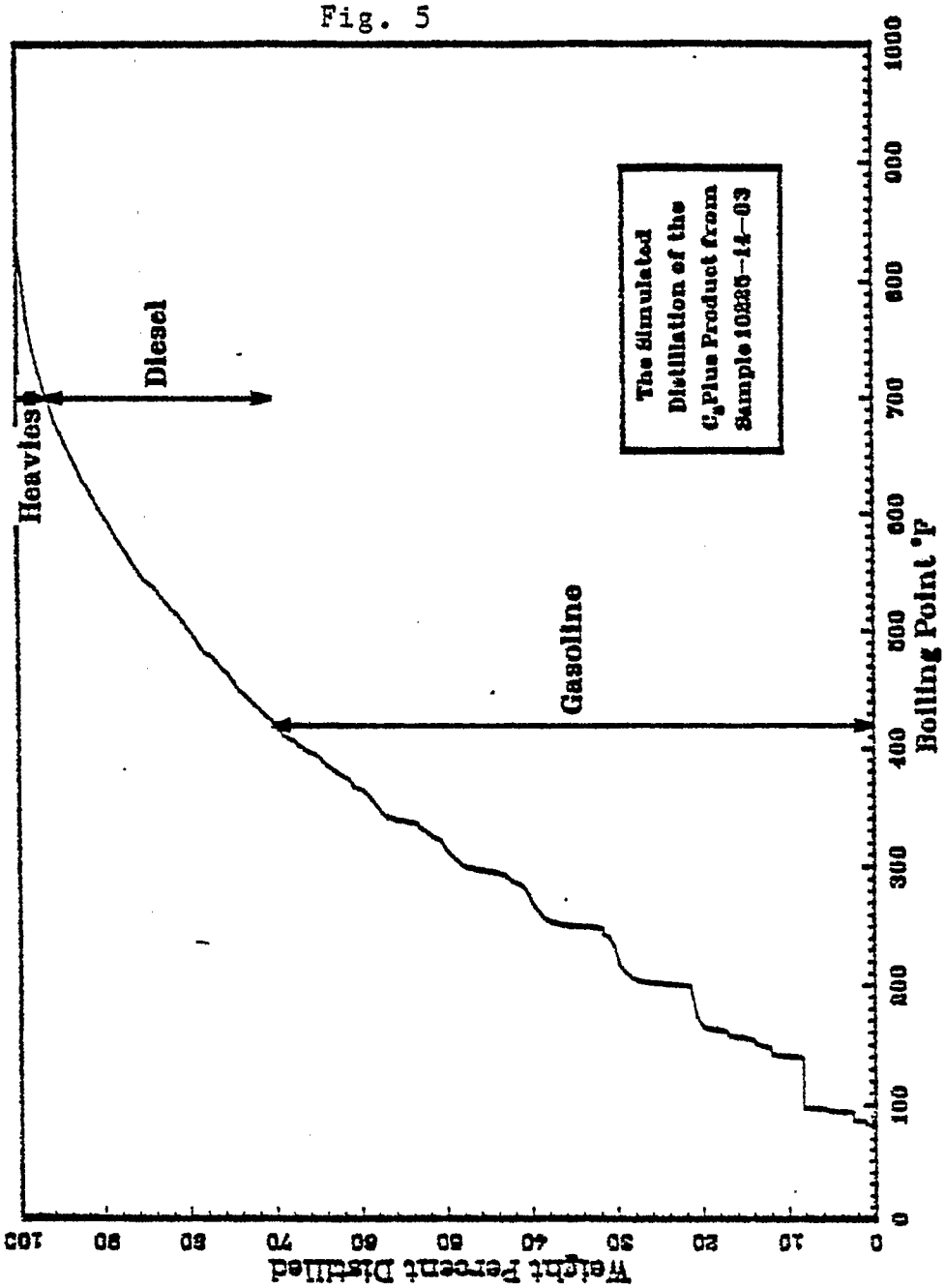

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heaviest
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10225-14-03

Fig. 6

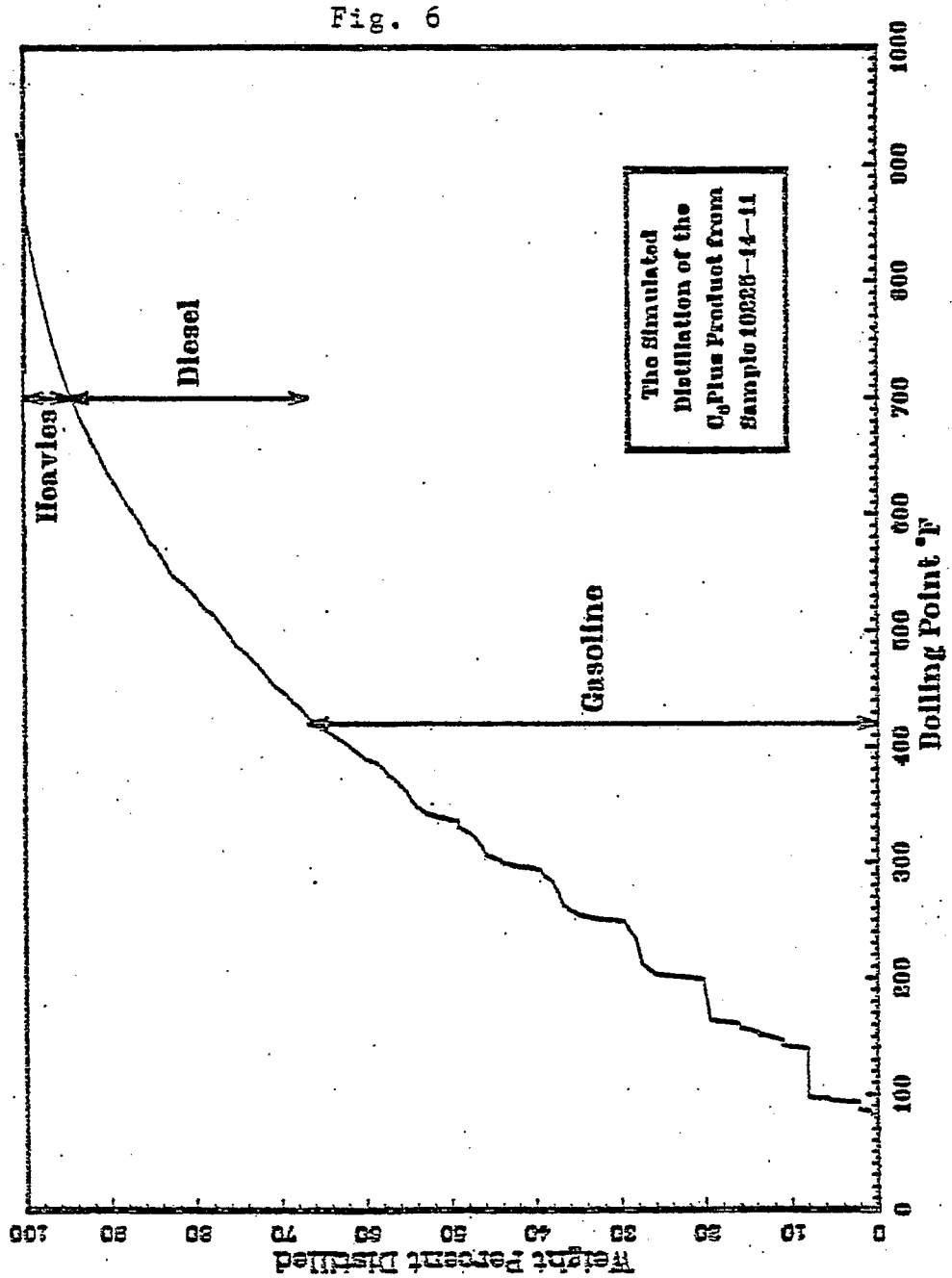

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C6Plus Product from Sample 10226-14-11

Fig. 7

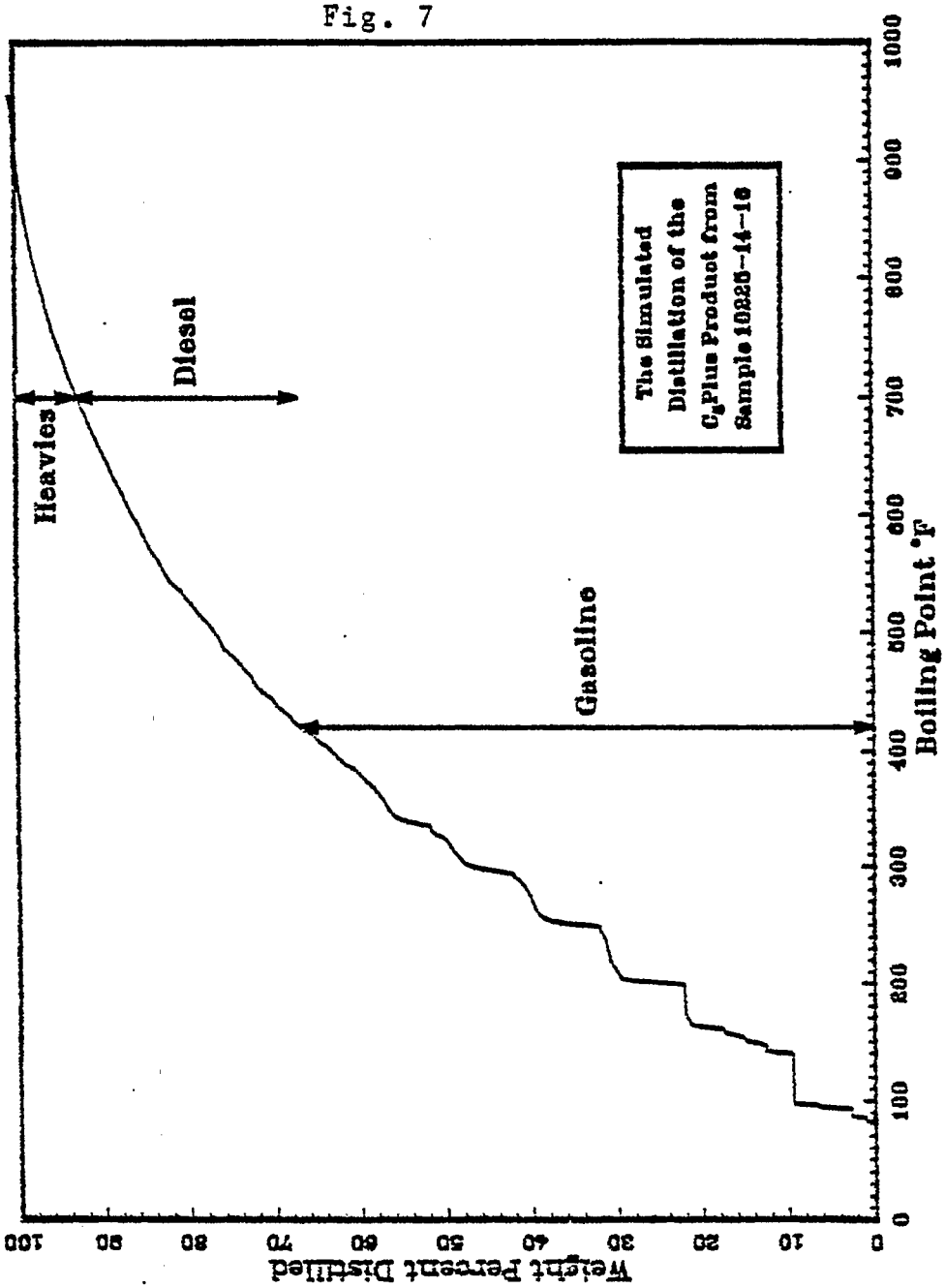
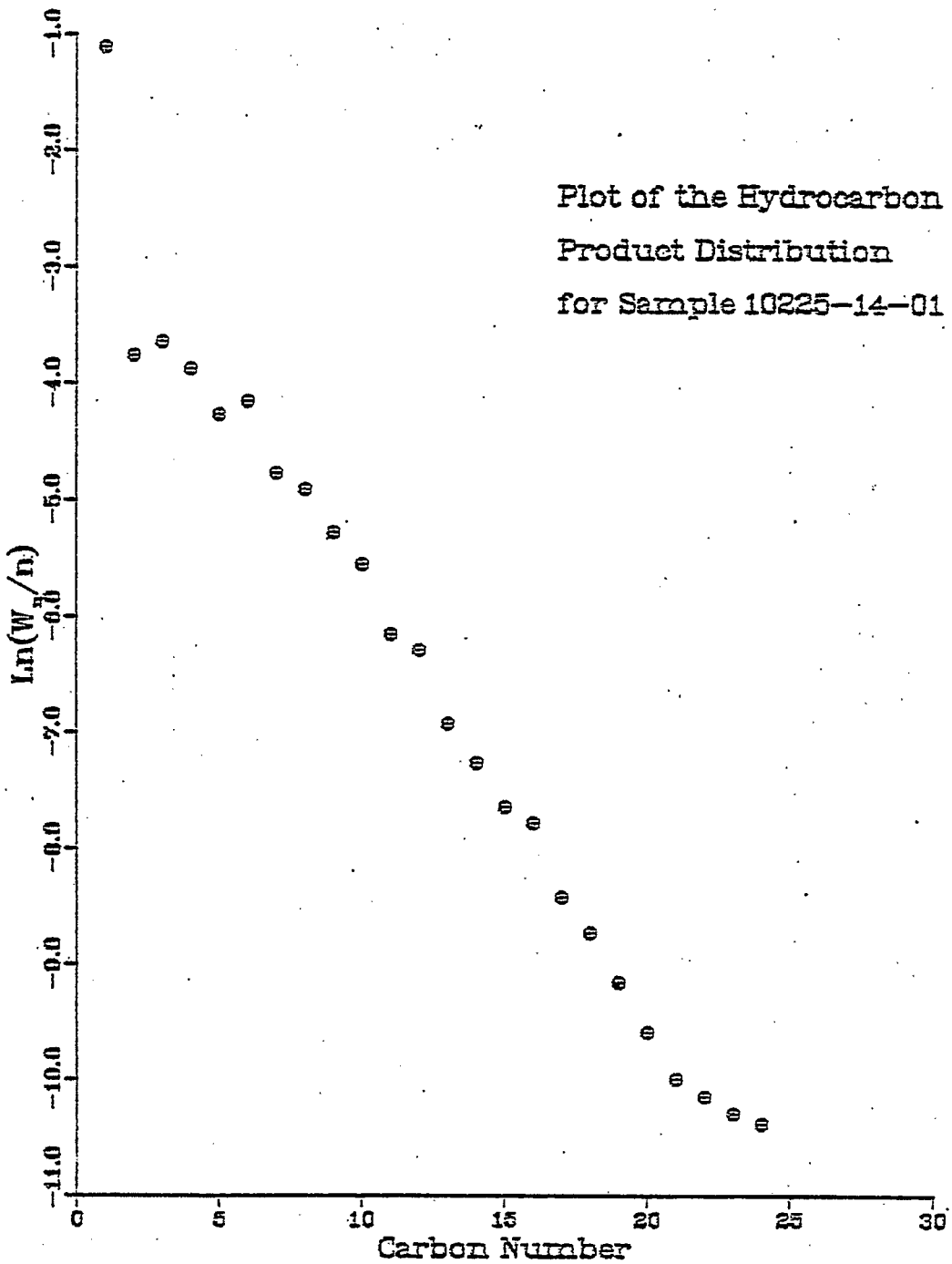

Heavies
Diesel
Gasoline
The Simulated Distillation of the C4 Plus Product from Sample 10225-14-16
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. 8


Plot of the Hydrocarbon
Product Distribution
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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
Carbon Number

Fig. 9

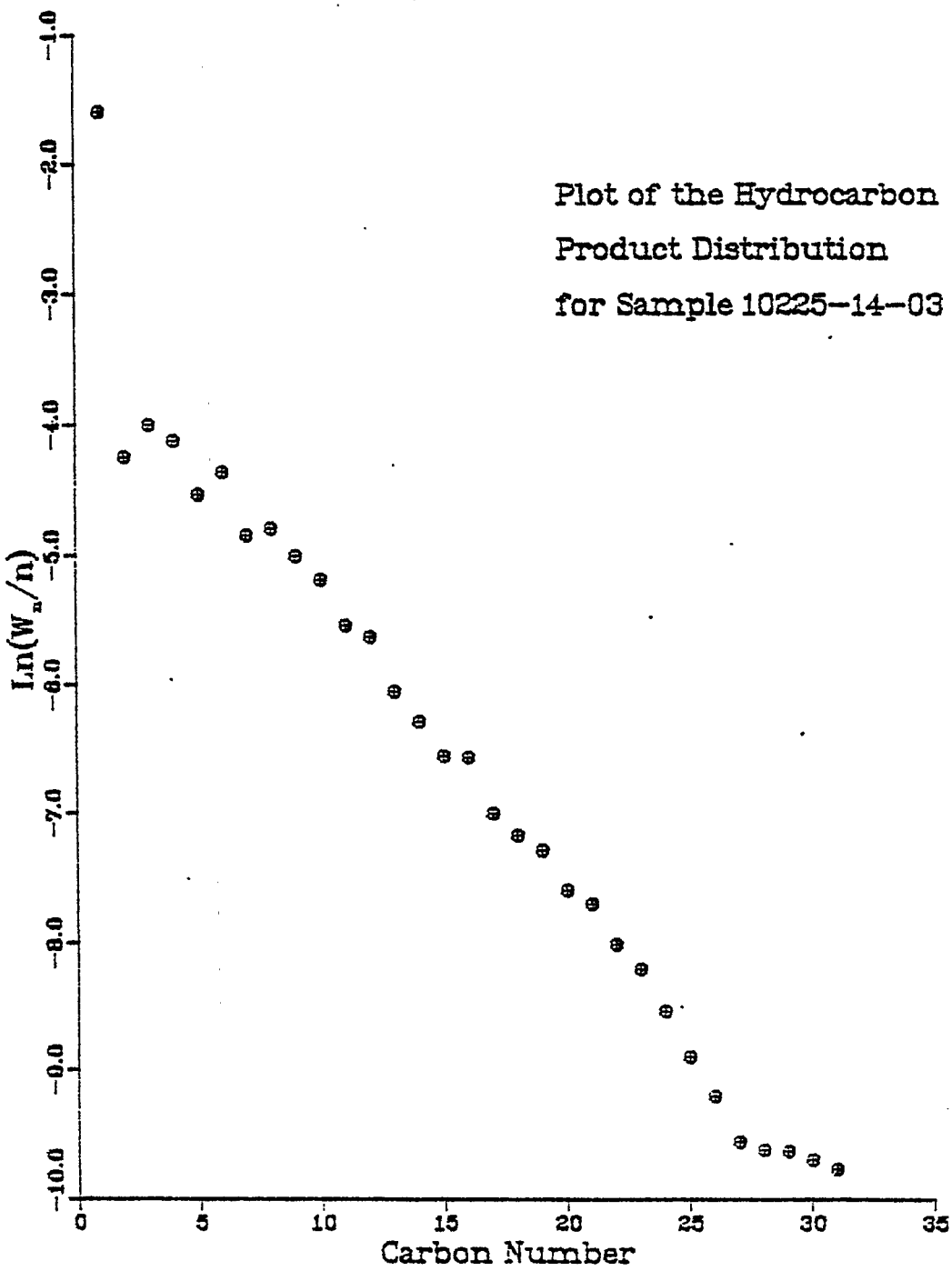
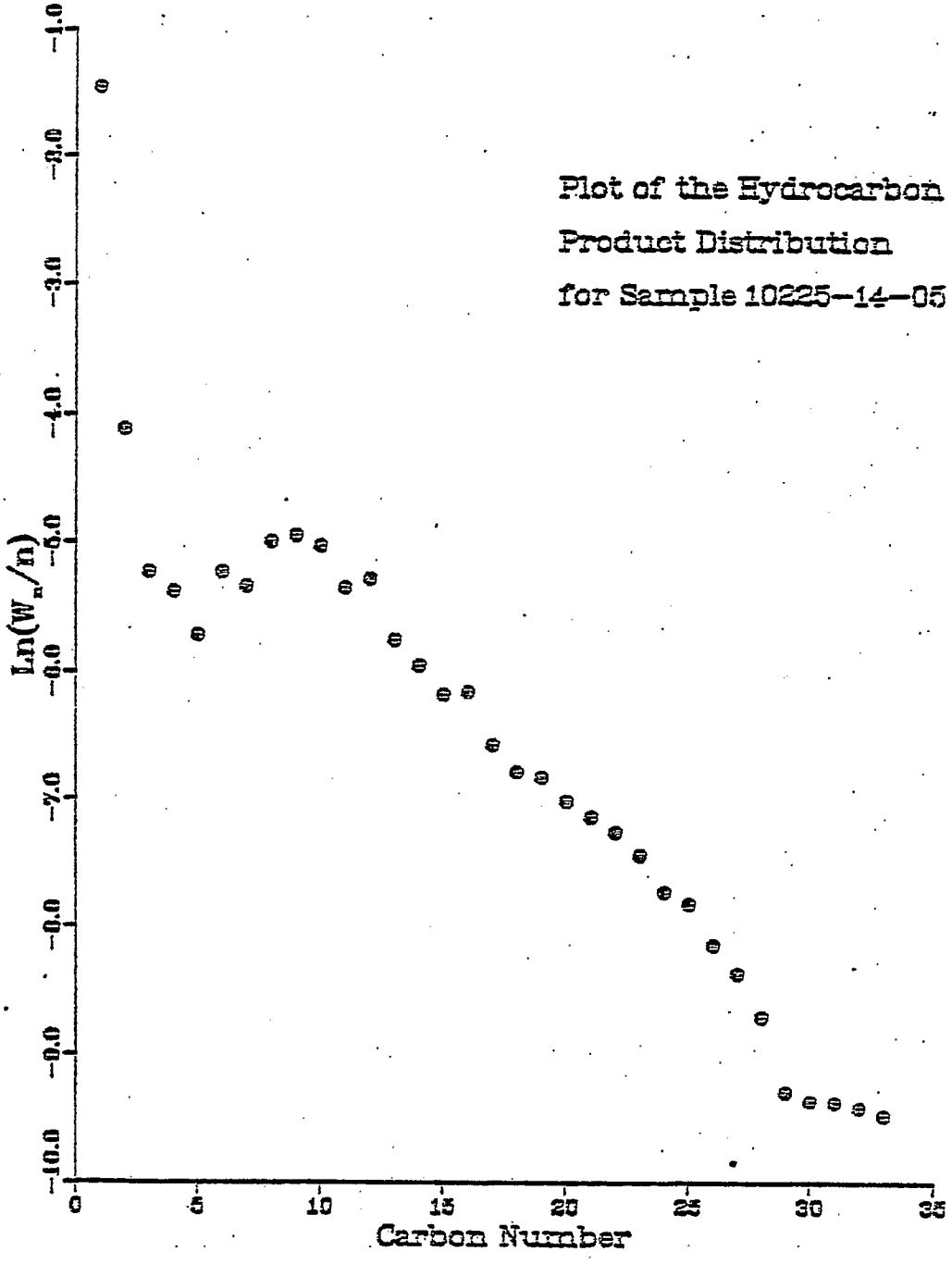

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 10


Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-05
Ln(W_n/n)
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-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. 11

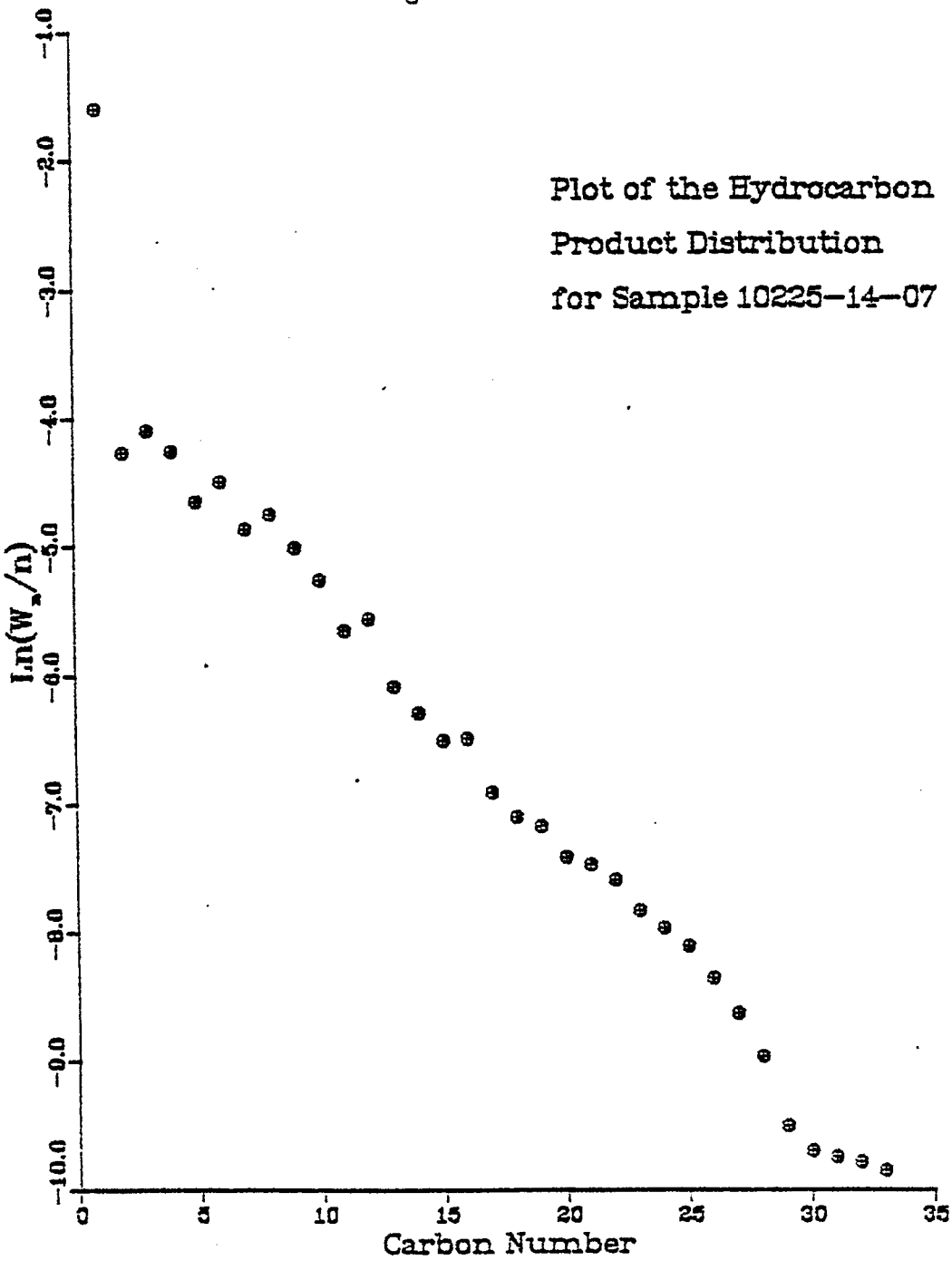
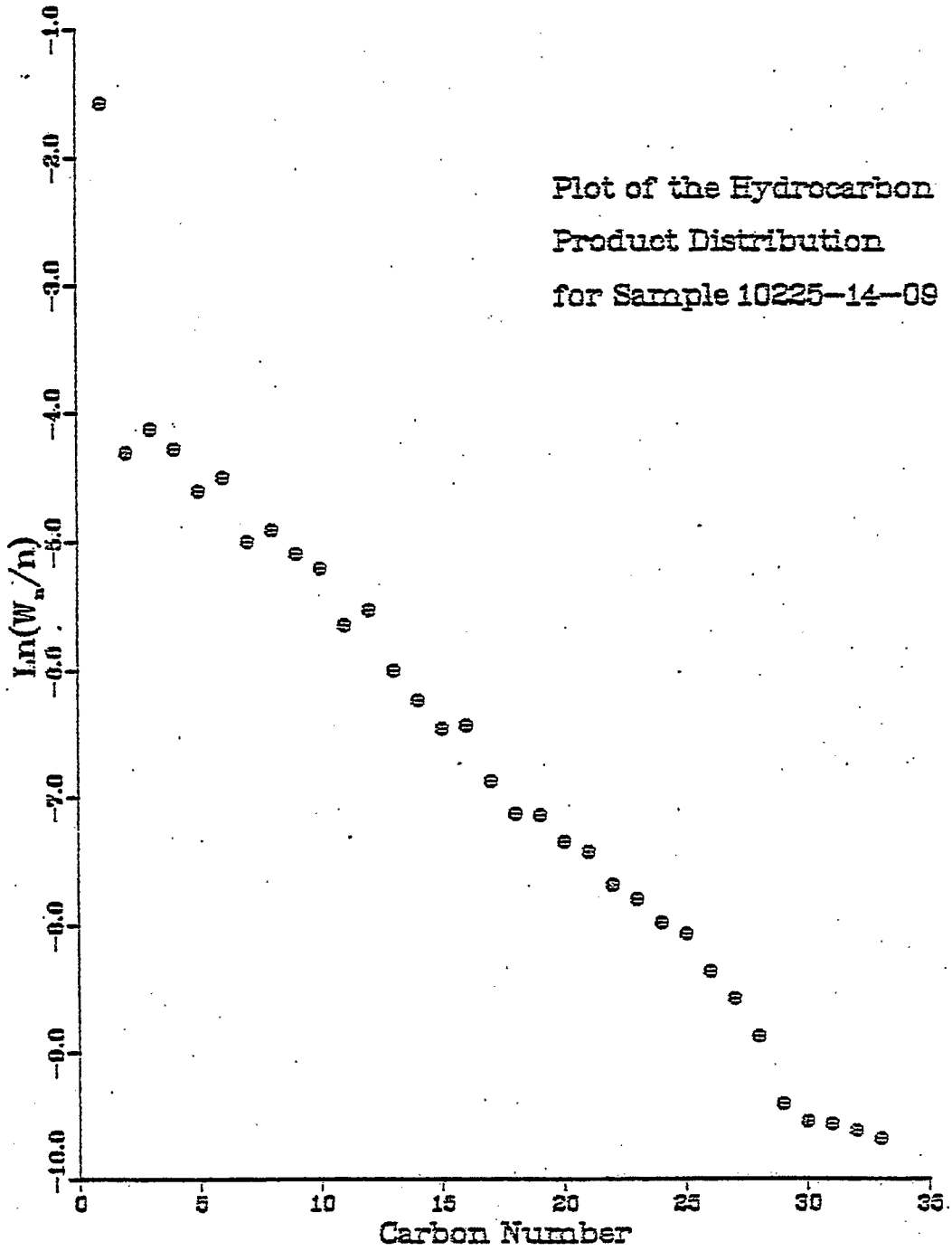

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-07
ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 12


Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-09
ln(W_n/n)
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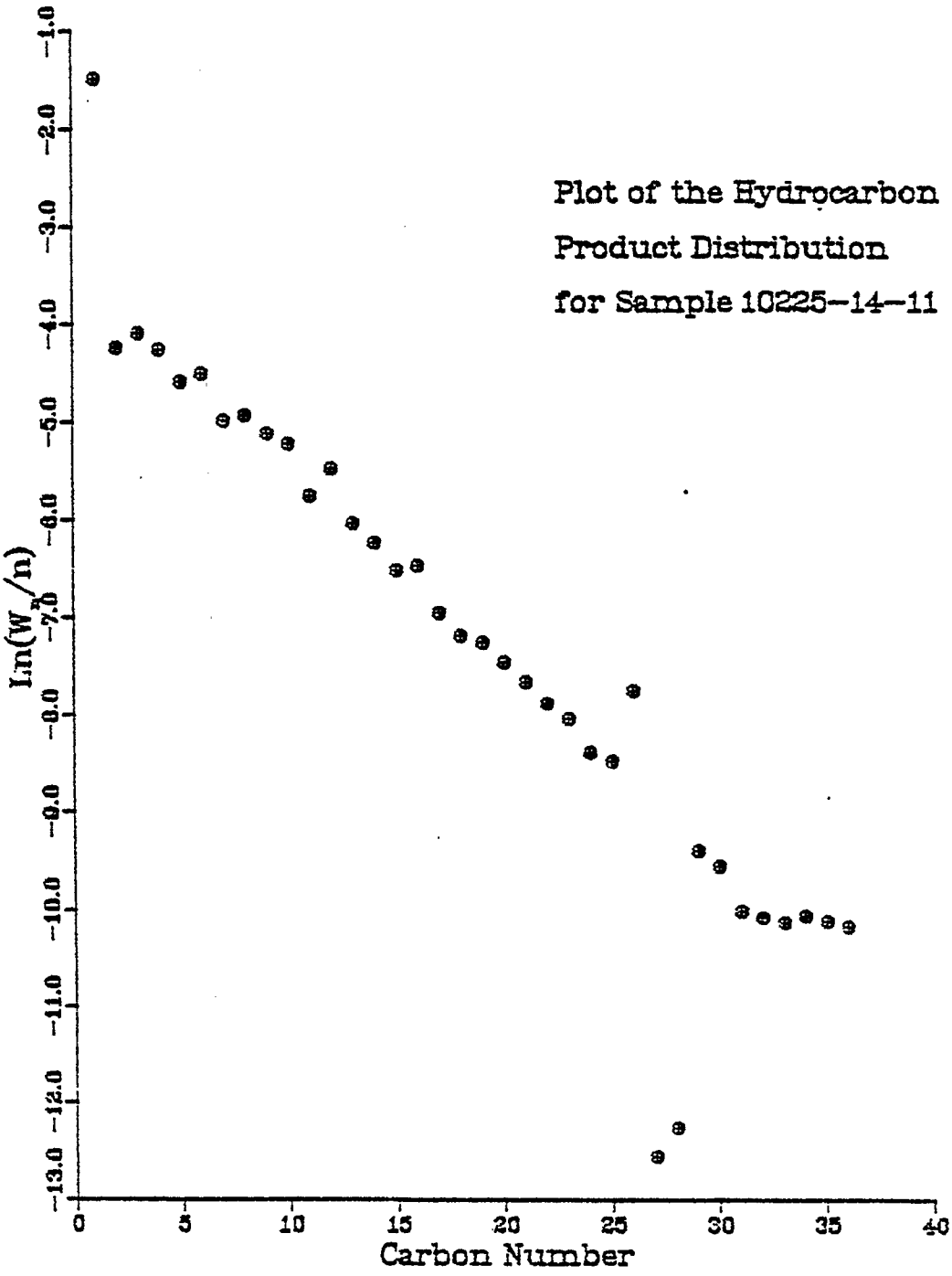
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 13


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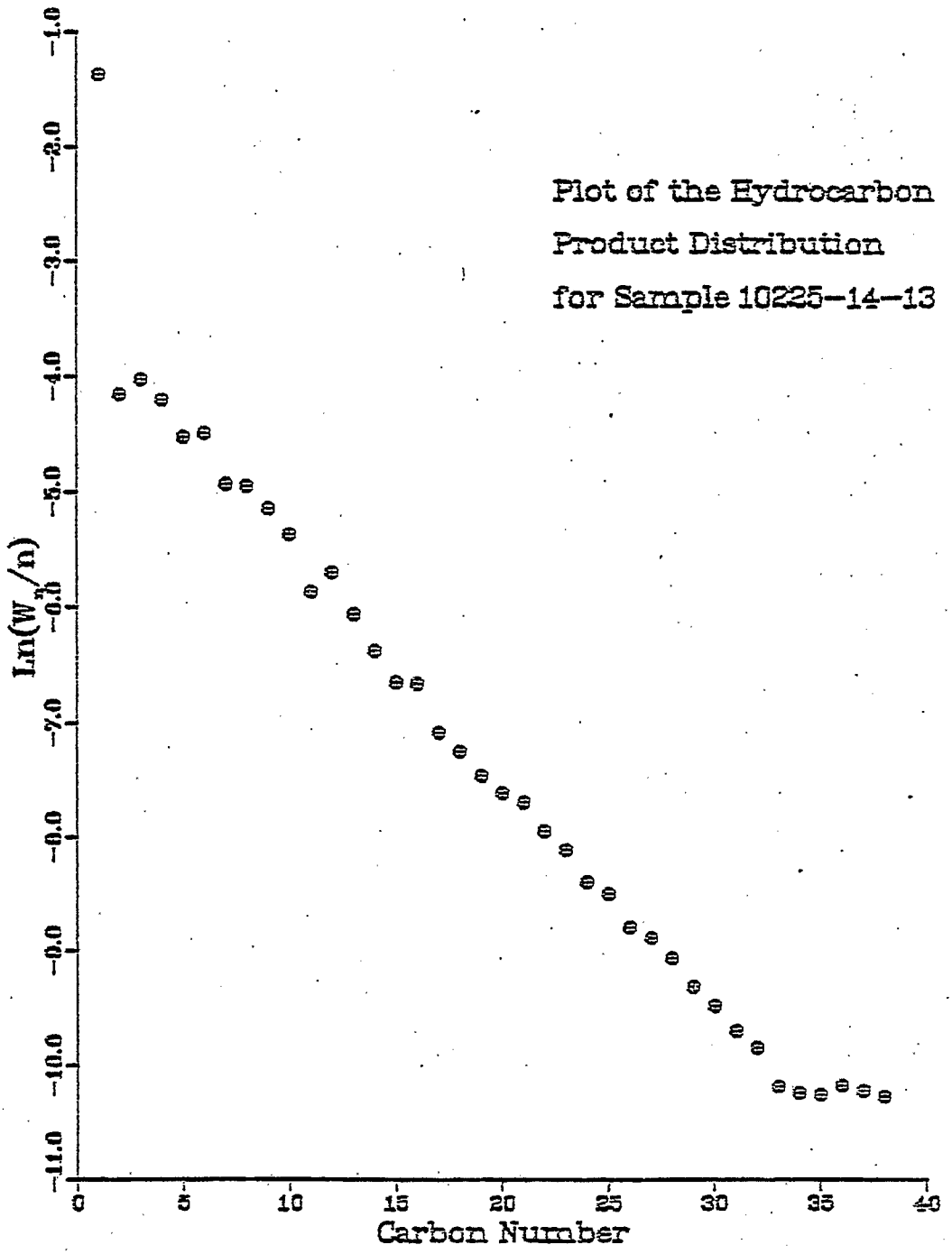
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 14


Plot of the Hydrocarbon
Product Distribution
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Ln(W_n/n)
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-4.0
-5.0
-6.0
-7.0
-8.0
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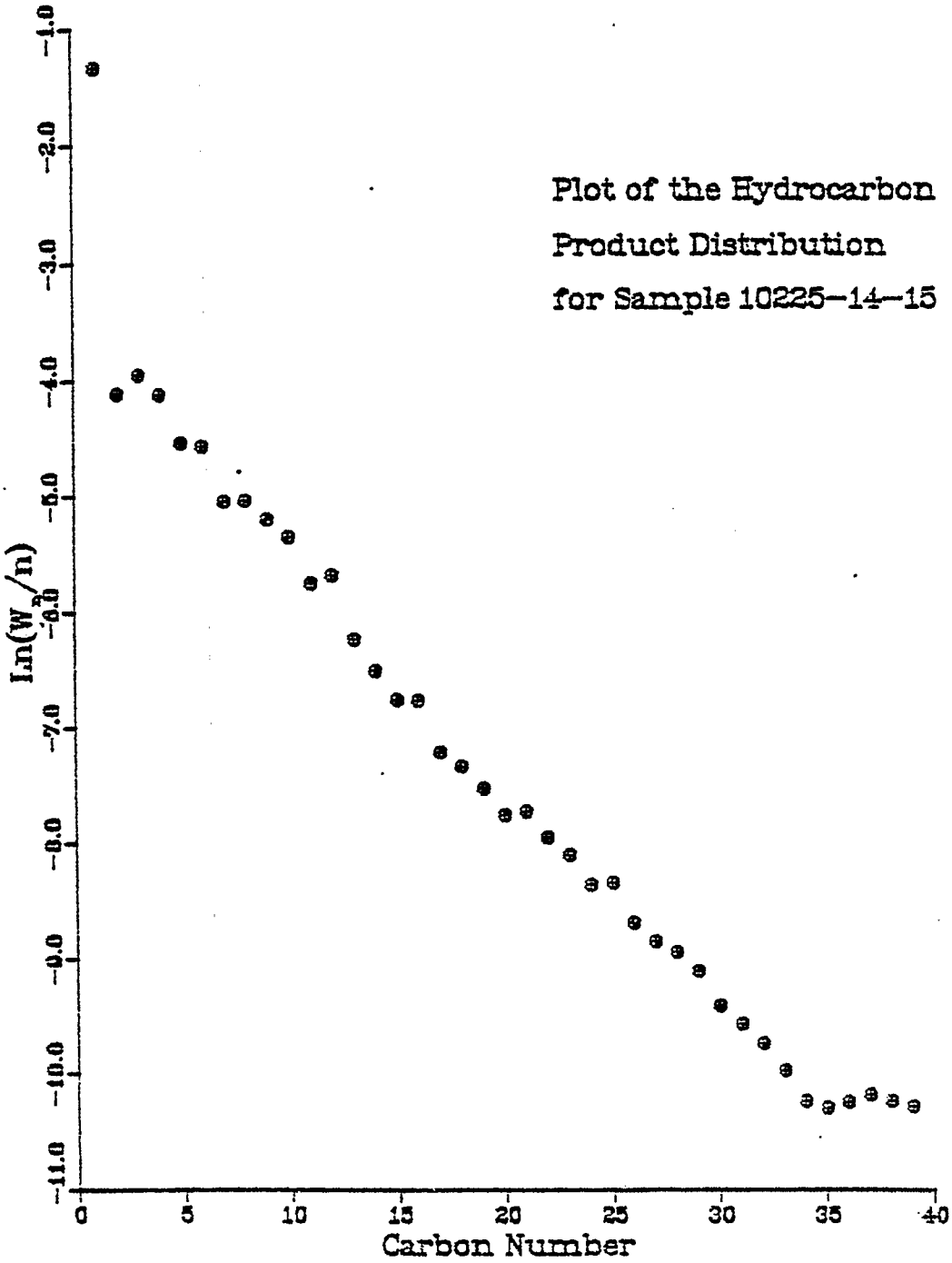
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 15


Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-15
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-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
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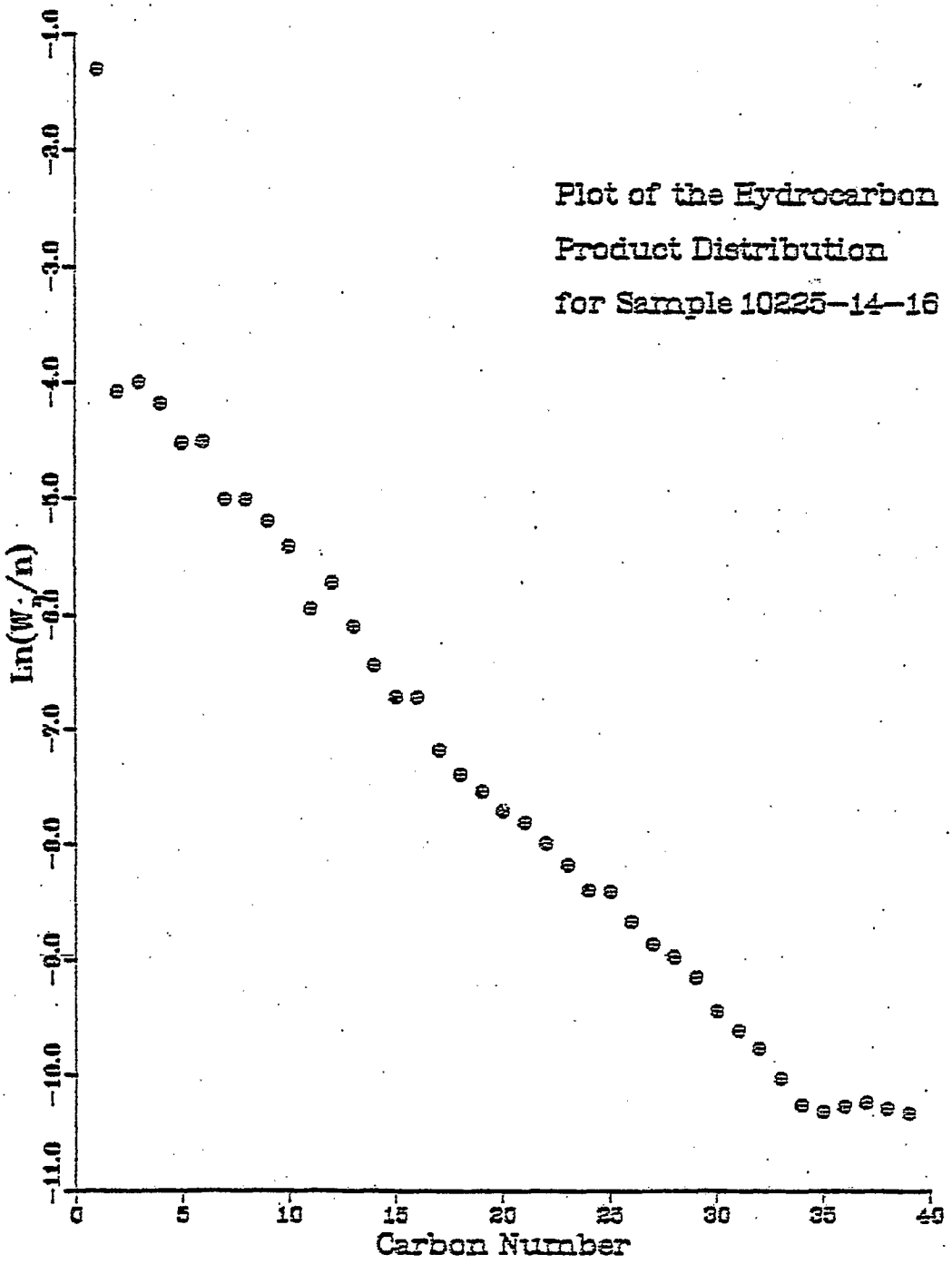
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 16


Plot of the Hydrocarbon
Product Distribution
for Sample 10225-14-16
ln(Wn/n)
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-3.0
-5.0
-7.0
-9.0
-11.0
0
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20
25
30
35
40
Carbon Number

Fig. 17

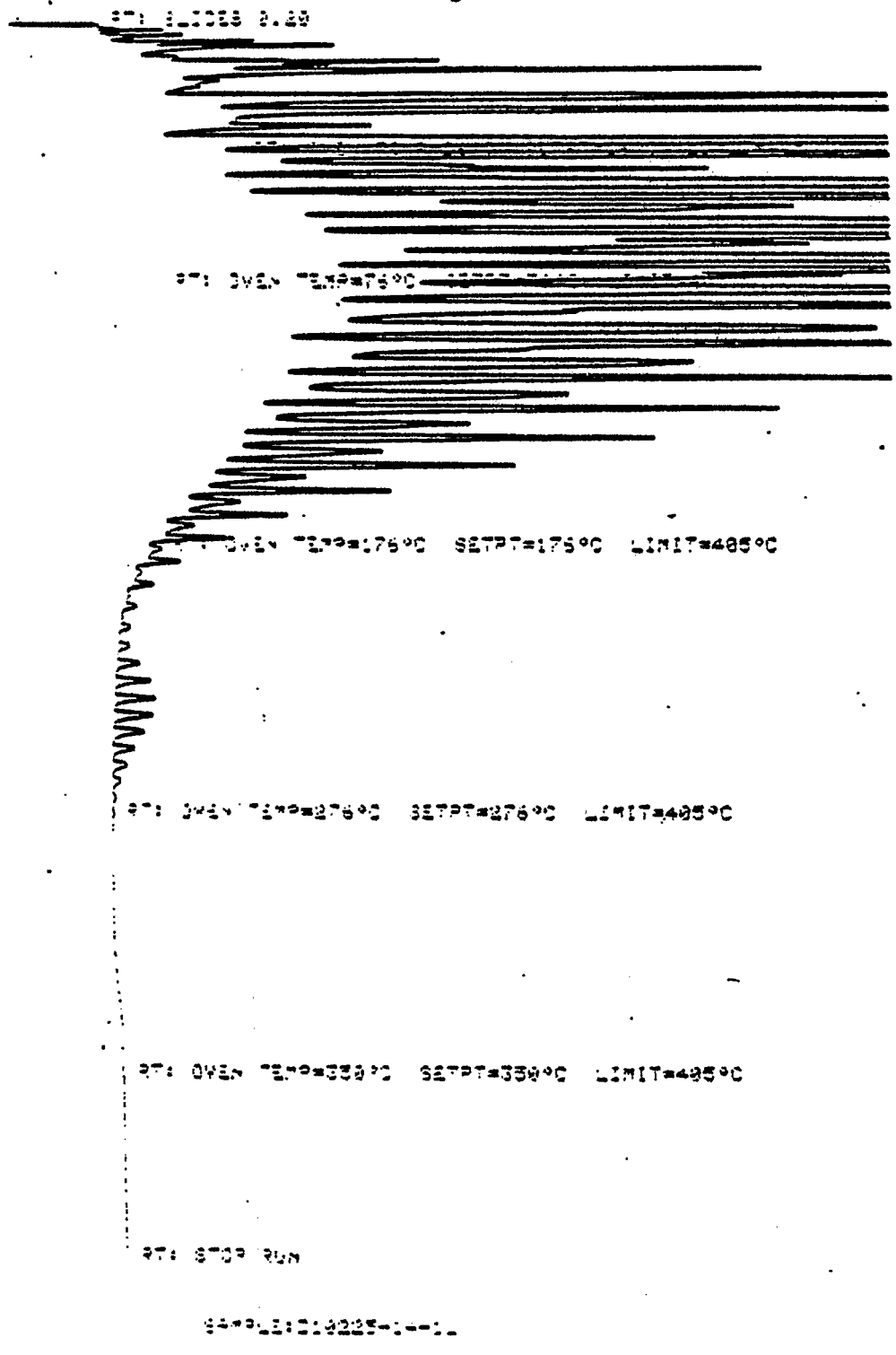

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Fig. 18

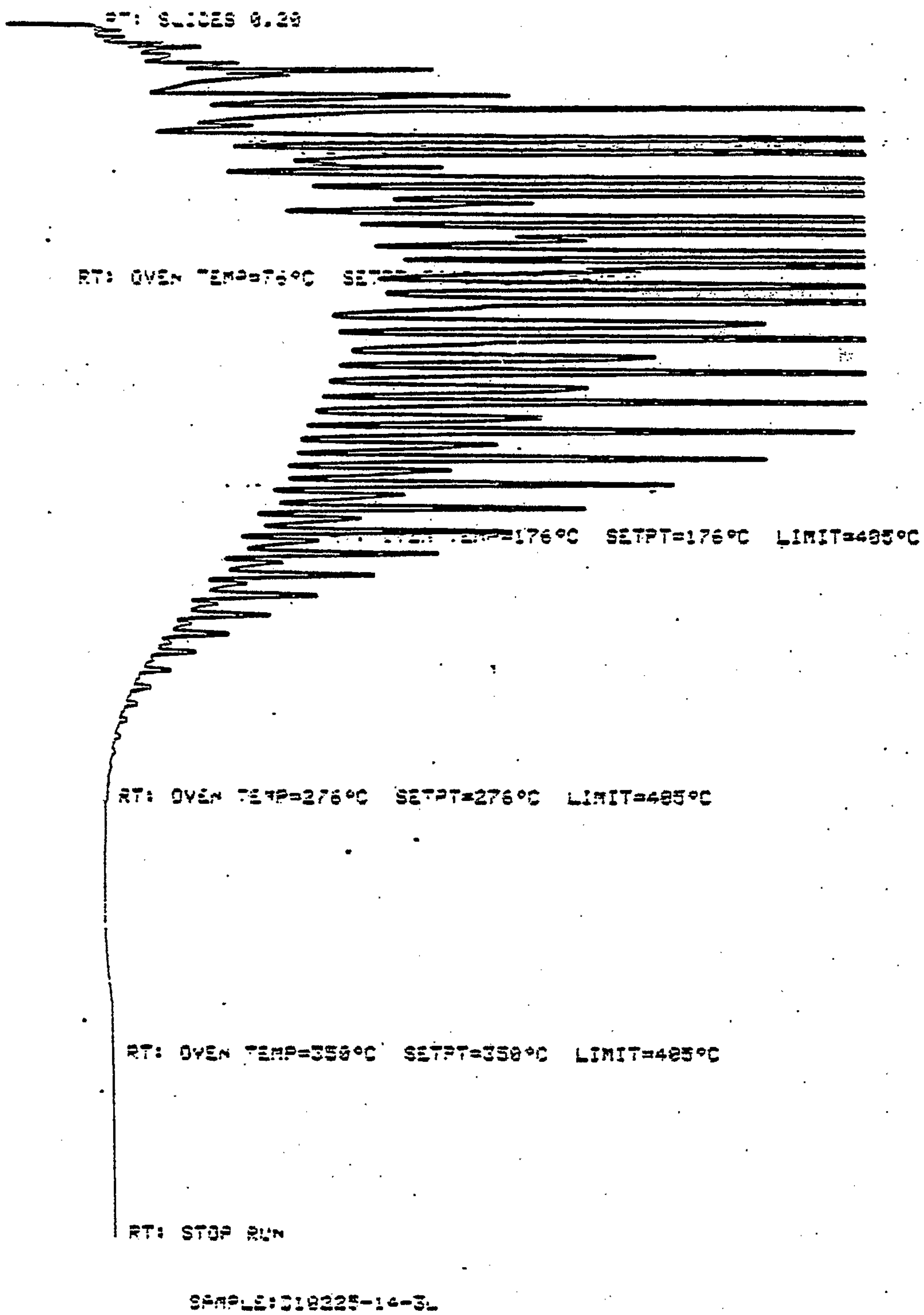
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Fig. 19

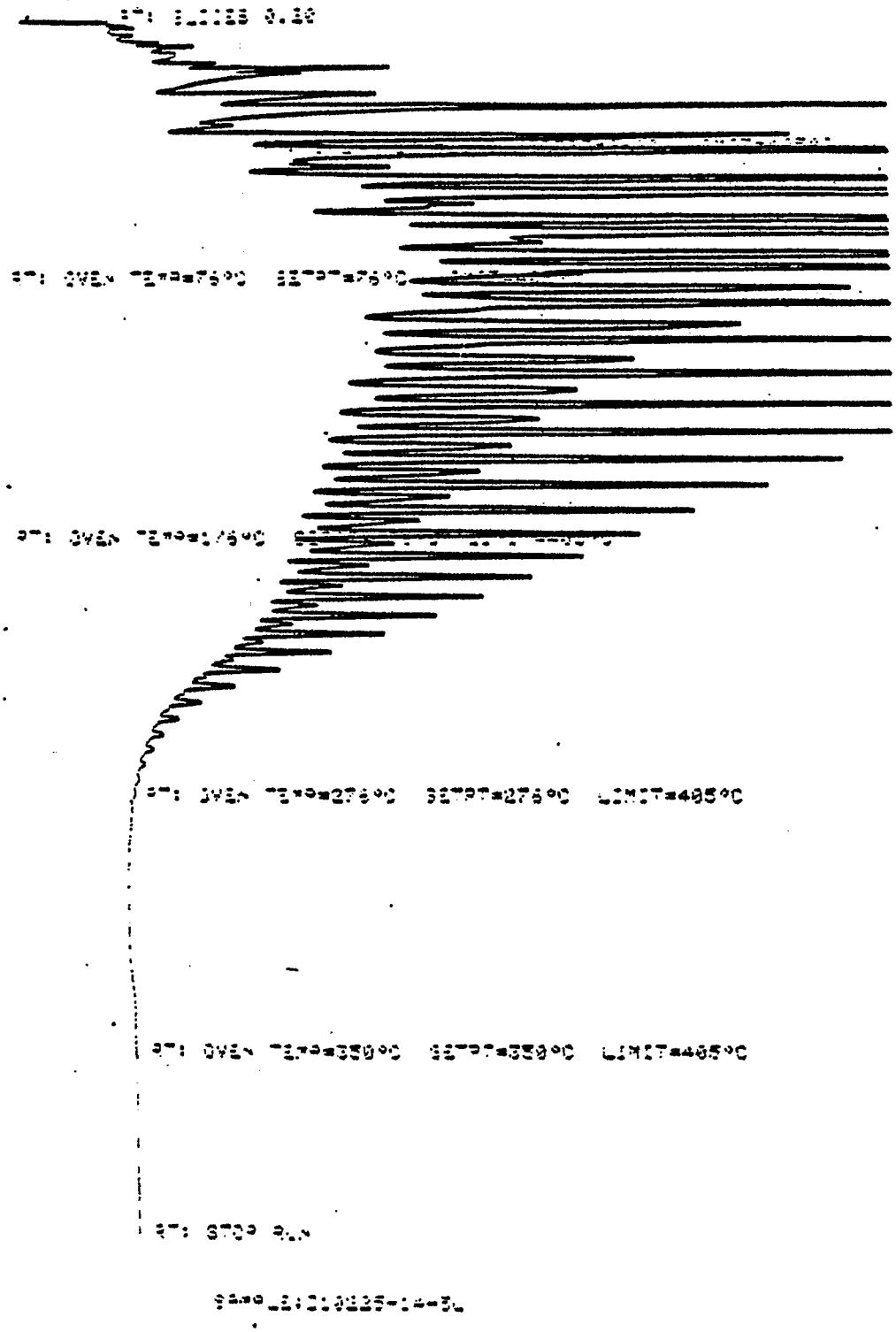
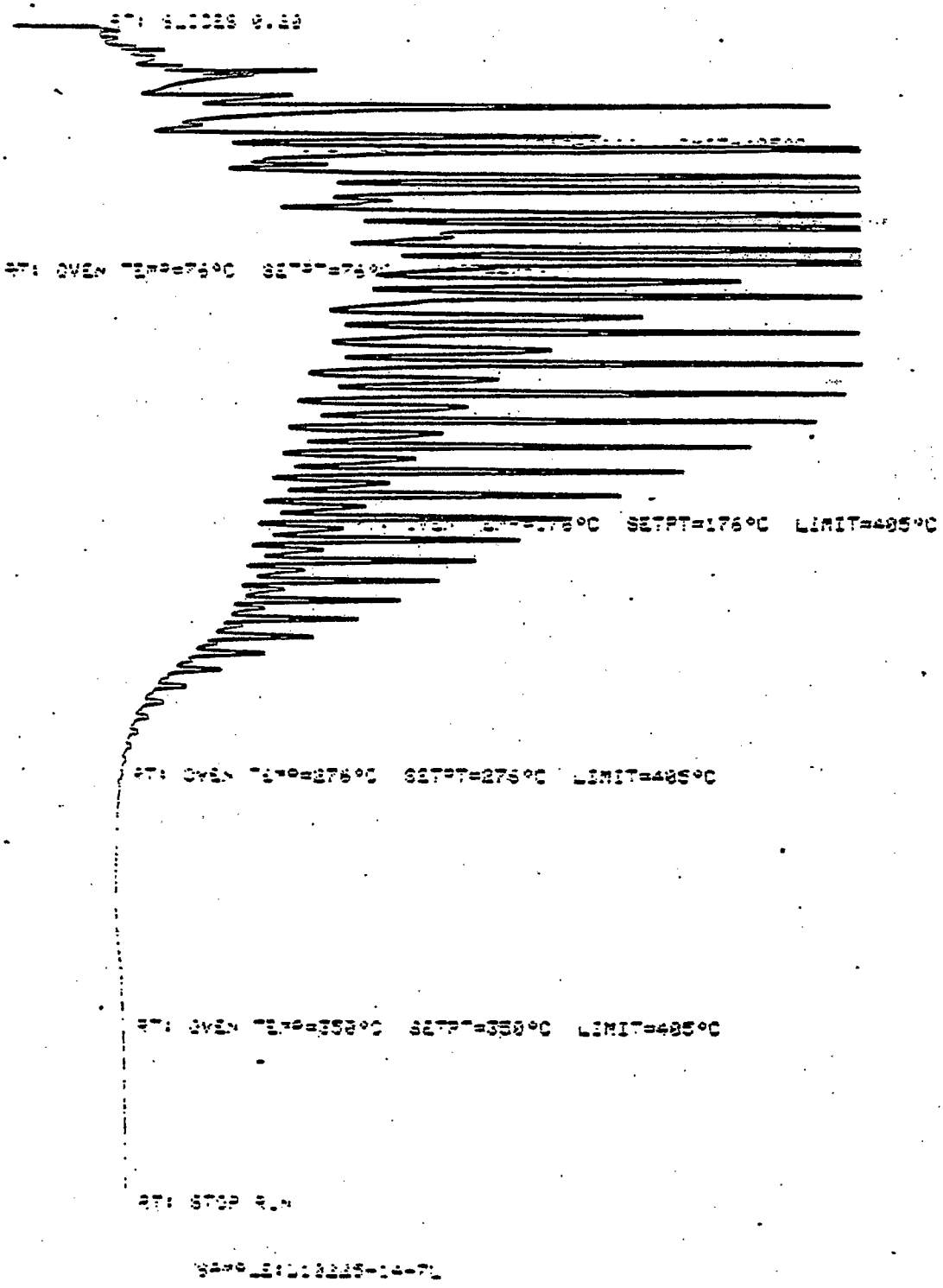


Fig. 20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PT: STOP RUN

Fig. 21

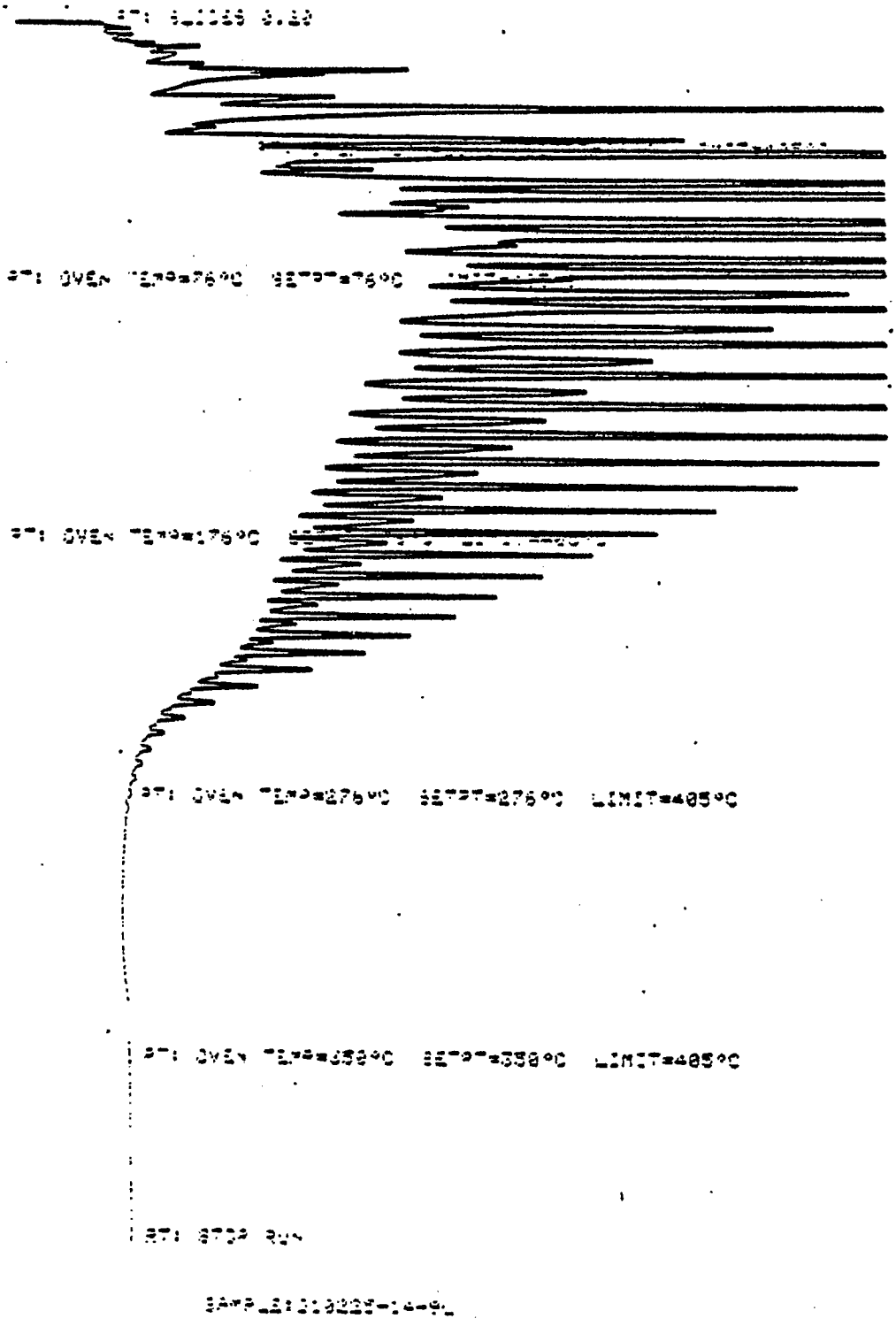

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Fig. 22 -

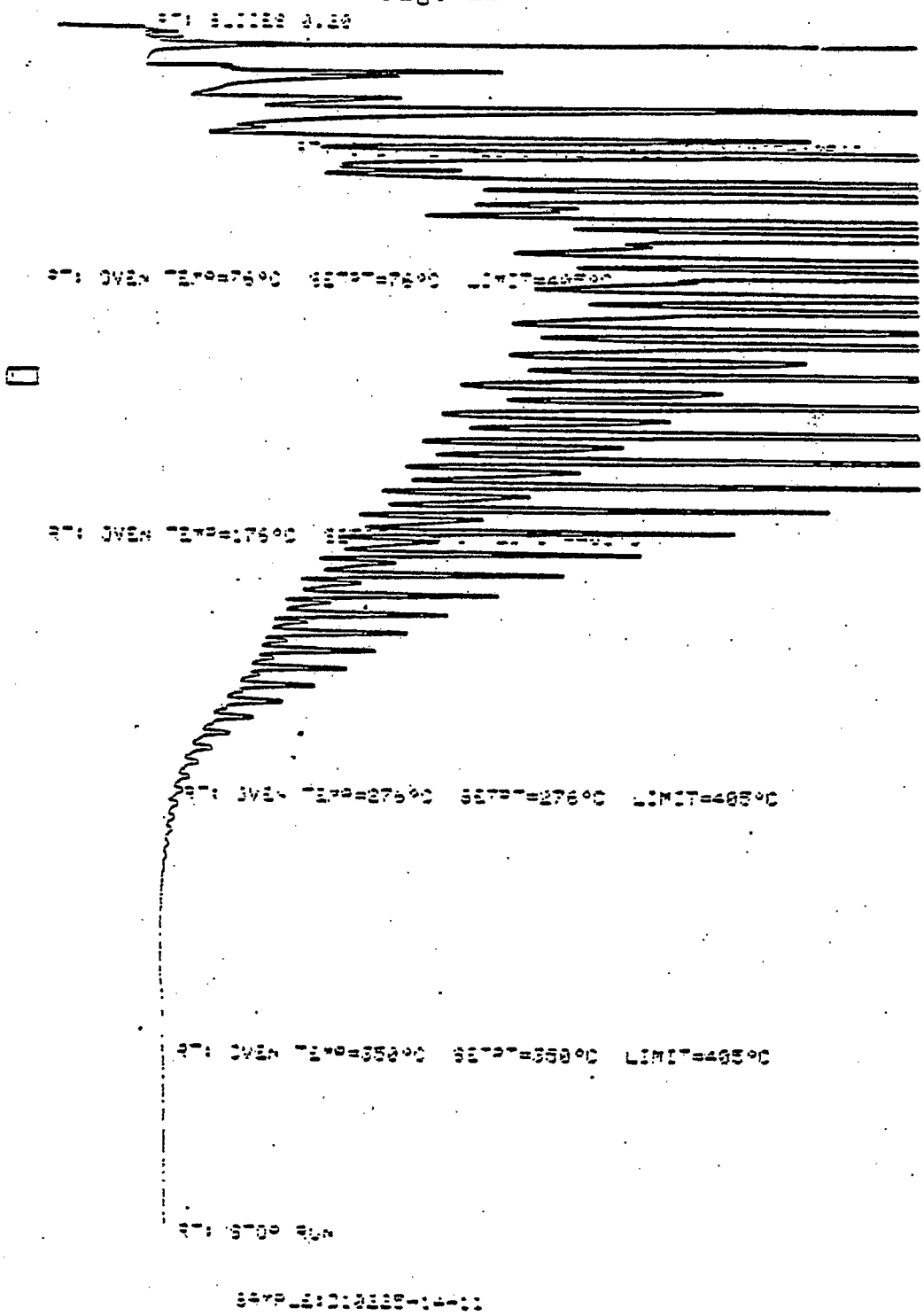
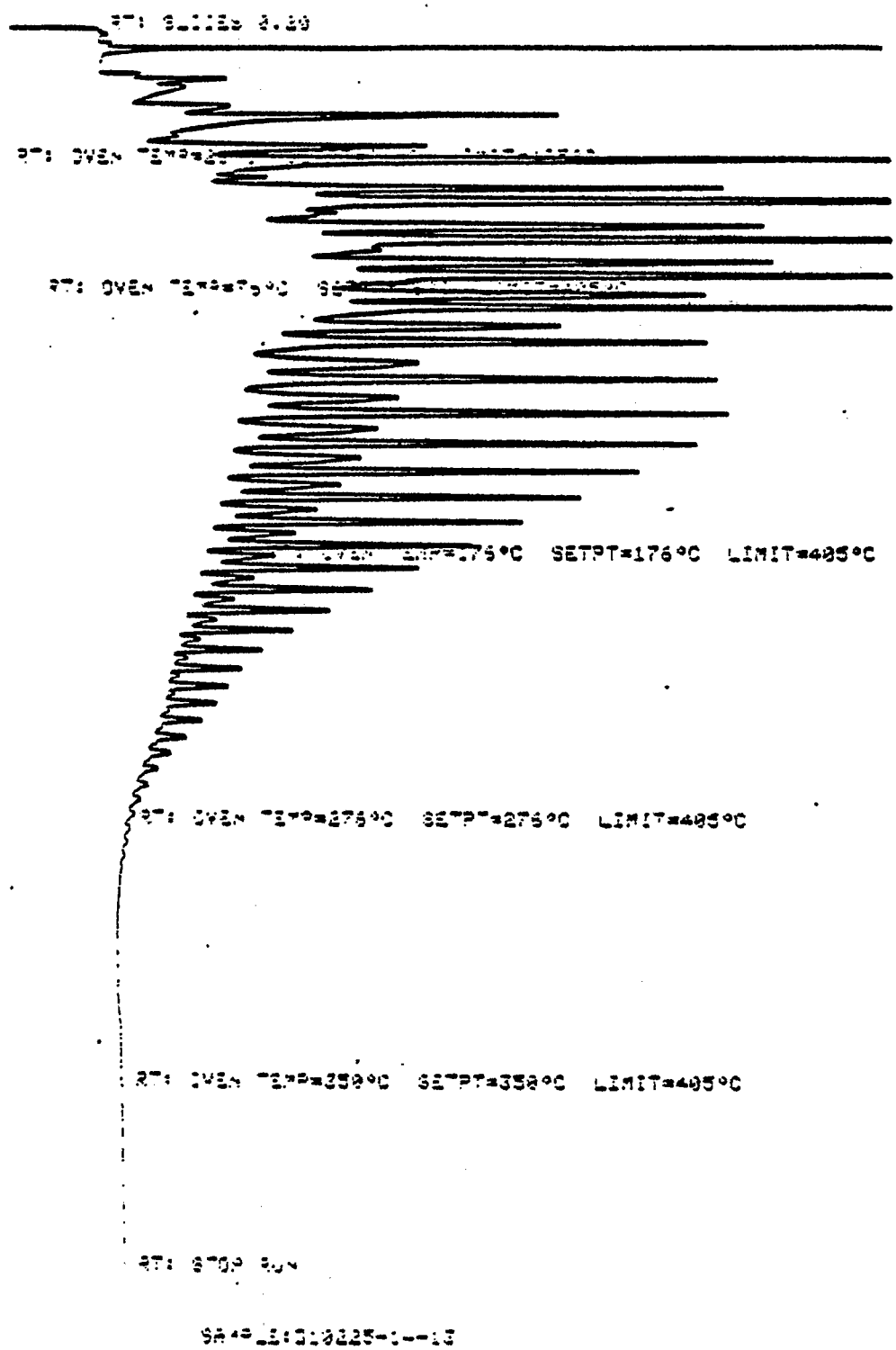


Fig. 23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RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 24

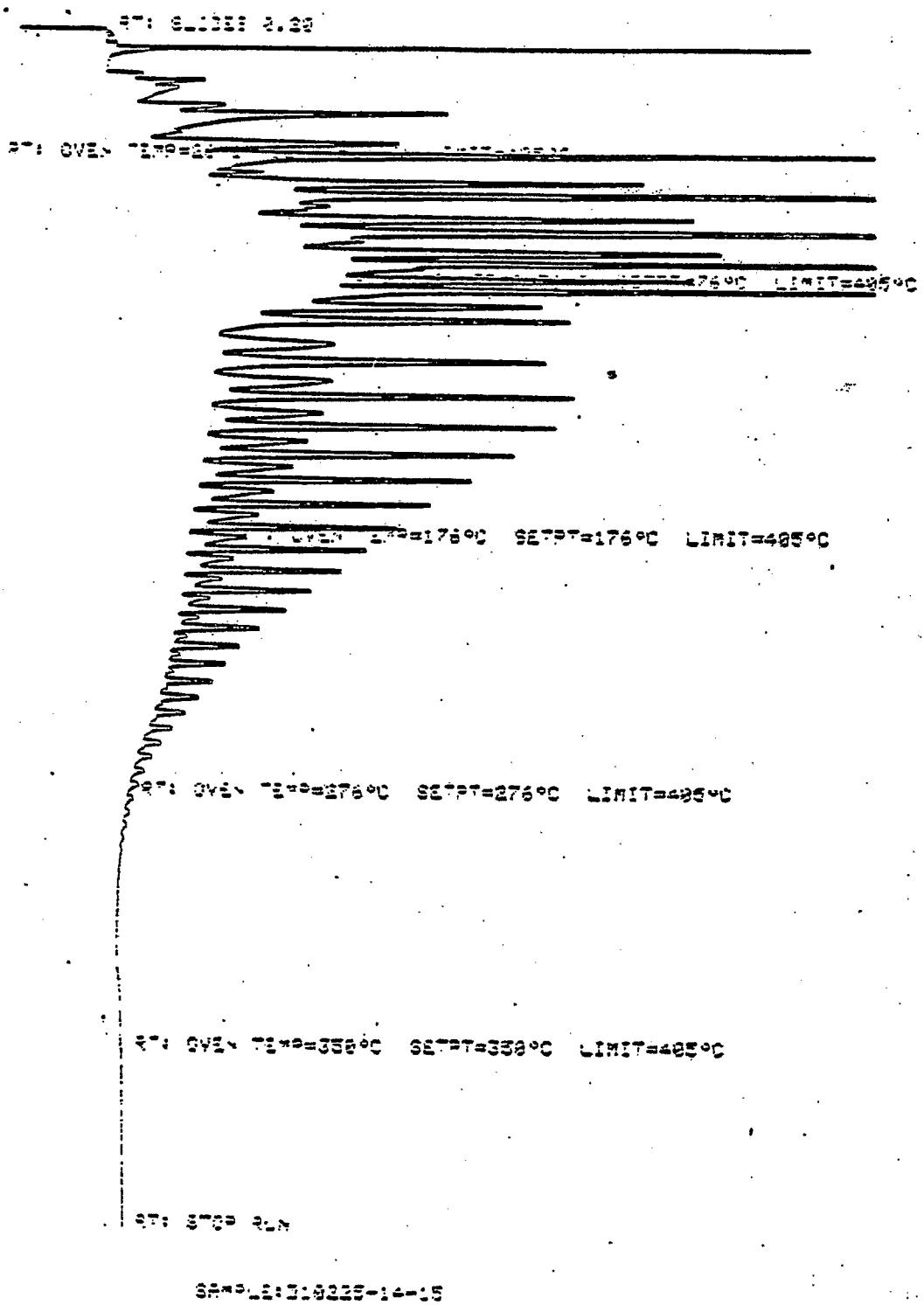

PT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
PT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 25

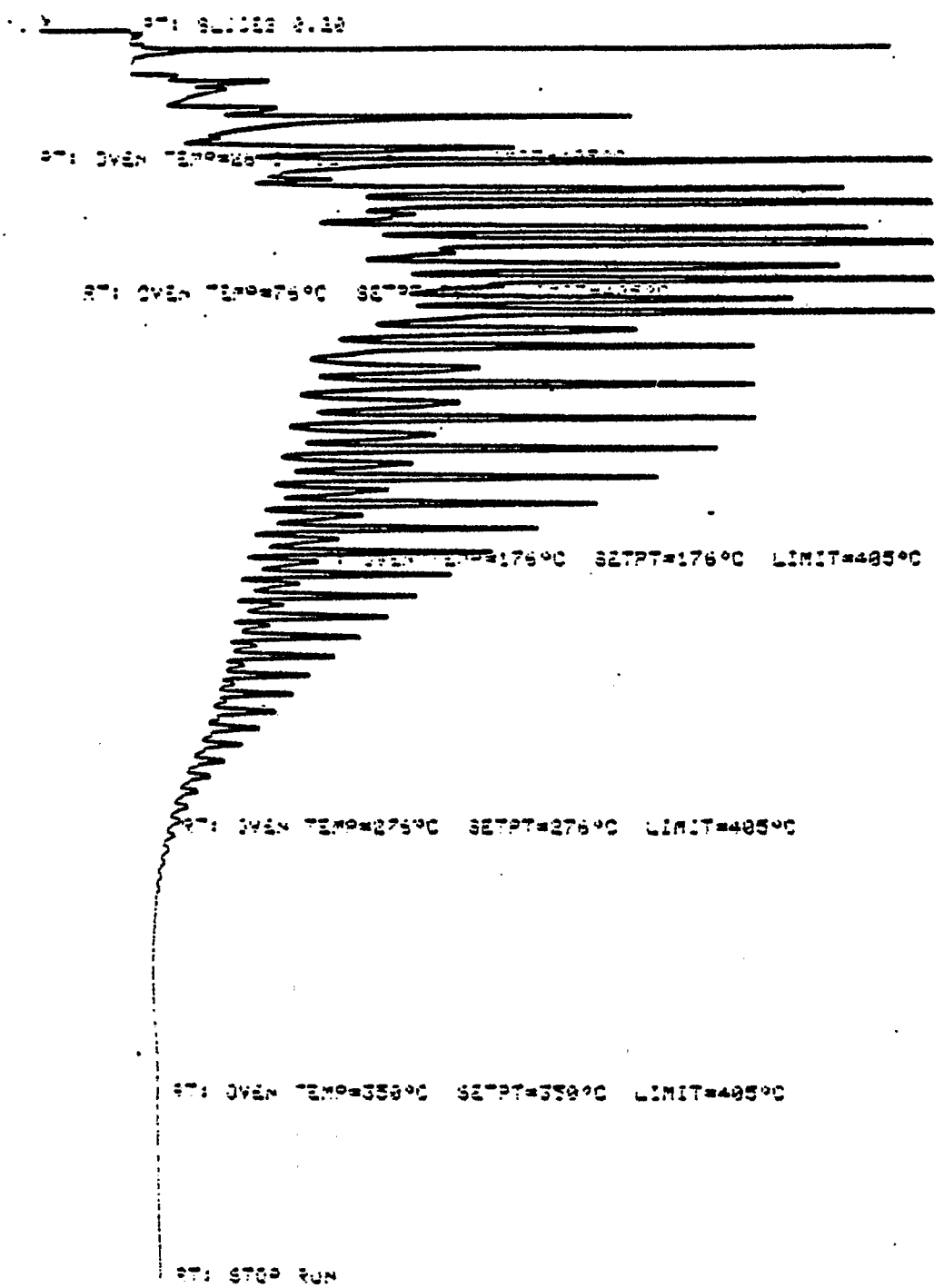

ST: SLIDE 0.10
ST: OVEN TEMP=175°C SETPT=176°C LIMIT=405°C
ST: OVEN TEMP=275°C SETPT=276°C LIMIT=405°C
ST: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
ST: STOP RUN
SAMPLE:810225-14-16

TABLE 1 RESULT OF SYNGAS OPERATION

RUN NO. 10225-14
CATALYST CO/TH +UCC-101 #11684-01C 80 CC 35.1GM (44.8 AFTER RUN +9.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-14-01	225-14-02	225-14-03	225-14-07	
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	
HRS ON STREAM	19.5	26.5	42.3	91.5	
PRESSURE,PSIG	303	306	300	301	
TEMP. C	276	277	277	277	
FEED CC/MIN	400	400	400	400	
HOURS FEEDING	19.50	7.00	25.75	23.17	
EFFLNT GAS LITER	176.00	54.30	205.74	209.87	
GM AQUEOUS LAYER	26.38	14.93	54.91	66.63	
GM OIL	11.03	9.60	35.10	34.15	
MATERIAL BALANCE					
GM ATOM CARBON %	91.43	90.07	89.79	98.30	
GM ATOM HYDROGEN %	86.92	93.51	89.56	101.89	
GM ATOM OXYGEN %	97.10	93.32	89.58	100.48	
RATIO CHX/(H2O+CO2)	0.8882	0.9372	1.0047	0.9562	
RATIO X IN CHX	2.7600	2.5108	2.4484	2.4311	
USAGE H2/CO PRODT	0.9612	1.1211	1.2345	1.4189	
RATIO CO2/(H2O+CO2)	0.6722	0.5142	0.4442	0.3202	
K SHIFT IN EFFLNT	1.35	0.52	0.28	0.14	
CONVERSION					
ON CO %	86.63	83.59	73.26	64.49	
ON H2 %	90.72	92.22	90.53	89.80	
ON CO+H2 %	88.62	87.98	81.89	77.37	
PRDT SELECTIVITY,WT %					
CH4	32.97	22.84	20.40	20.10	
C2 HC'S	4.64	3.21	2.86	2.80	
C3H8	5.81	3.65	2.84	2.45	
C3H6=	2.00	2.01	2.67	2.56	
C4H10	4.80	2.89	2.39	1.84	
C4H8=	3.45	3.43	4.09	3.83	
C5H12	4.74	2.86	2.36	1.75	
C5H10=	2.24	2.45	2.99	3.00	
C6H14	7.06	4.78	4.05	3.22	
C6H12= & CYCLO'S	2.06	2.50	3.16	3.22	
C7+ IN GAS	13.05	10.09	10.41	11.77	
LIQ HC'S	17.18	39.29	41.80	43.46	
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	53.66	38.04	35.24	33.58
C5 -420 F	41.38	43.67	45.29	43.30
420-700 F	4.84	16.12	17.15	18.47
700-END PT	0.11	2.18	2.32	4.65
C5+-END PT	46.34	61.96	64.76	66.42
ISO/NORMAL MOLE RATIO				
C4	0.1957	0.2143	0.2366	0.1861
C5	0.4634	0.4481	0.4272	0.3385
C6	1.2554	1.4251	1.5003	1.4117
C4=	0.0473	0.0574	0.0754	0.0800
PARAFFIN/OLEFIN RATIO				
C3	2.7703	1.7275	1.0160	0.9129
C4	1.3399	0.8129	0.5647	0.4645
C5	2.0536	1.1333	0.7679	0.5654
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.7089		0.8031	0.8217
RATIO CH4/(1-A)**2	3.8904		5.2619	6.3175
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLR OIL		CLR OIL	GRN OIL
DENSITY	0.742		0.755	0.752
N, REFRACTIVE INDEX	1.4192		1.4264	1.4306
SIMULT'D DISTILATN				
10 WT % @ DEG F	237		251	258
16	255		283	296
50	358		407	437
84	486		598	654
90	530		650	707
RANGE(16-84 %)	231		315	358
WT % @ 420 F	71.16	53.43	53.43	46.80
WT % @ 700 F	99.35	94.46	94.46	89.30

TABLE 2 RESULT OF SYNGAS OPERATION

RUN NO. 10225-14
CATALYST CO/TH +UCC-101 #11684-01C 80 CC 35.1GM (44.8 AFTER RUN +9.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-14-08	225-14-09	225-14-10	225-14-11	225-14-12
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	99.0	115.5	123.0	139.5	147.0
PRESSURE,PSIG	300	305	300	305	305
TEMP. C	277	277	277	276	277
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.50	24.00	7.50	24.00	7.50
EFFLNT GAS LITER	55.30	203.92	66.40	223.00	73.60
GM AQUEOUS LAYER	21.68	69.40	21.32	68.24	19.94
GM OIL	11.23	35.92	10.30	32.88	8.85
MATERIAL BALANCE					
GM ATOM CARBON %	84.43	92.45	93.60	94.50	95.61
GM ATOM HYDROGEN %	95.25	100.07	99.77	102.69	100.78
GM ATOM OXYGEN %	86.57	94.27	95.23	96.01	96.54
RATIO CHX/(H2O+CO2)	0.9536	0.9616	0.9651	0.9676	0.9791
RATIO X IN CHX	2.3944	2.4434	2.4544	2.4876	2.5202
USAGE H2/CO PRODT	1.5010	1.4865	1.4982	1.5189	1.5122
RATIO CO2/(H2O+CO2)	0.2701	0.2883	0.2851	0.2815	0.2935
K SHIFT IN EFFLNT	0.12	0.13	0.13	0.14	0.15
CONVERSION					
ON CO %	66.84	64.30	62.33	61.51	59.24
ON H2 %	90.61	89.66	88.82	87.10	85.68
ON CO+H2 %	79.44	77.48	76.00	74.84	72.81
PRDT SELECTIVITY,WT %					
CH4	18.26	20.74	21.19	22.83	24.26
C2 HC'S	2.43	2.70	2.76	2.90	3.03
C3H8	2.39	2.39	2.46	2.69	2.92
C3H6=	2.51	2.45	2.64	2.31	2.56
C4H10	1.78	1.79	2.14	1.97	2.15
C4H8=	3.83	3.75	4.01	3.69	4.10
C5H12	1.99	1.96	2.01	2.08	2.39
C5H10=	3.08	3.06	3.18	3.02	3.19
C6H14	3.24	3.16	3.30	3.33	3.54
C6H12= & CYCLO'S	3.28	3.18	3.54	3.14	3.40
C7+ IN GAS	9.40	9.01	10.14	9.60	10.78
LIQ HC'S	47.80	45.79	42.64	42.44	37.69
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	31.21	33.83	35.20	36.39	39.02
C5 -420 F	43.54	41.98	42.70	41.61	40.53
420-700 F	20.26	19.40	18.07	17.99	16.19
700-END PT	5.00	4.78	4.03	4.01	4.26
C5+-END PT	68.79	66.17	64.80	63.61	60.98
ISO/NORMAL MOLE RATIO					
C4	0.1871	0.1741	0.3917	0.1603	0.1553
C5	0.3964	0.3845	0.3715	0.3603	0.3613
C6	1.3984	1.3888	1.3469	1.2751	1.1888
C4=	0.0809	0.0796	0.0800	0.0823	0.0828
PARAFFIN/OLEFIN RATIO					
C3	0.9104	0.9324	0.8911	1.1106	1.0886
C4	0.4495	0.4612	0.5160	0.5137	0.5078
C5	0.6270	0.6232	0.6147	0.6704	0.7307
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8263		0.8185	
RATIO CH4/(1-A)**2		6.8748		6.9278	
LIQ HC COLLECTION					
PHYS. APPEARANCE		GRN OIL		OIL & SLD	
DENSITY		0.764		0.763	
N, REFRACTIVE INDEX		1.4303		1.4300	
SIMULT'D DISTILATN					
10 WT % @ DEG F		257		259	
16		295		296	
50		434		431	
84		650		633	
90		704		694	
RANGE(16-84 %)		355		337	
WT % @ 420 F	47.17	47.17	48.17	48.17	45.75
WT % @ 700 F	89.55	89.55	90.55	90.55	88.70

TABLE 3 RESULT OF SYNGAS OPERATION

RUN NO. 10225-14
CATALYST CO/TH +UCC-101 #11684-01C 80 CC 35.1GM (44.8 AFTER RUN +9.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-14-13	225-14-14	225-14-15	225-14-16
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	163.5	171.0	187.5	194.0
PRESSURE,PSIG	301	306	304	304
TEMP. C	277	280	280	280
FEED CC/MIN	400	400	400	400
HOURS FEEDING	24.00	7.50	24.00	6.50
EFFLNT GAS LITER	244.40	60.90	215.20	66.10
GM AQUEOUS LAYER	63.82	18.85	60.33	17.32
GM OIL	28.32	8.57	27.44	7.97
MATERIAL BALANCE				
GM ATOM CARBON %	97.04	81.84	89.61	100.92
GM ATOM HYDROGEN %	103.01	92.21	97.40	105.81
GM ATOM OXYGEN %	97.48	83.43	89.21	99.56
RATIO CHX/(H2O+CO2)	0.9901	0.9619	1.0093	1.0295
RATIO X IN CHX	2.5431	2.5522	2.5689	2.5783
USAGE H2/CO PRODT	1.5359	1.5246	1.5194	1.5178
RATIO CO2/(H2O+CO2)	0.2881	0.2899	0.3056	0.3126
K SHIFT IN EFFLNT	0.16	0.16	0.16	0.15
CONVERSION				
ON CO %	58.30	63.63	62.71	61.07
ON H2 %	84.67	87.41	87.36	87.43
ON CO+H2 %	71.88	76.23	75.55	74.56
PRDT SELECTIVITY,WT %				
CH4	25.40	25.83	26.59	27.20
C2 HC'S	3.13	3.20	3.28	3.37
C3H8	3.01	3.09	3.18	3.00
C3H6=	2.35	2.08	2.60	2.48
C4H10	2.19	2.26	2.52	2.16
C4H8=	3.78	3.45	4.01	3.93
C5H12	2.33	2.33	2.31	2.28
C5H10=	3.08	2.79	3.07	3.17
C6H14	3.44	3.32	3.16	3.30
C6H12= & CYCLO'S	3.24	2.94	3.12	3.31
C7+ IN GAS	10.64	9.04	9.40	9.85
LIQ HC'S	37.42	39.66	36.76	35.95
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	39.86	39.92	42.17	42.14
C5 -420 F	39.85	39.46	38.71	39.17
420-700 F	16.07	15.57	14.43	14.11
700-END PT	4.23	5.06	4.69	4.58
C5+-END PT	60.14	60.08	57.83	57.86
ISO/NORMAL MOLE RATIO				
C4	0.1475	0.1611	0.2061	0.1632
C5	0.3370	0.3683	0.4226	0.3770
C6	1.1078	1.1292	1.2849	1.2988
C4=	0.0827	0.0904	0.0983	0.0893
PARAFFIN/OLEFIN RATIO				
C3	1.2238	1.4170	1.1689	1.1552
C4	0.5590	0.6334	0.6052	0.5310
C5	0.7351	0.8144	0.7309	0.6987
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.8255		0.8306	0.8296
RATIO CH4/(1-A)**2	8.3441		9.2621	9.3647
LIQ HC COLLECTION				
PHYS. APPEARANCE	OIL SLD		OIL SLD	OIL SLD
DENSITY	0.765		0.764	0.767
N, REFRACTIVE INDEX	1.4310		1.4305	1.4315
SIMULT'D DISTILATN				
10 WT % @ DEG F	263		263	264
16	299		299	299
50	438		427	437
84	653		668	665
90	715		733	732
RANGE(16-84 %)	354		369	366
WT % @ 420 F	45.75	48.00	48.00	48.00
WT % @ 700 F	88.70	87.25	87.25	87.25

III. RUN 2 (10225-12) with Catalyst 2 (Co/X_5 + UCC-101)

This test continues a series, begun in the Tenth Quarter, in which the metal component (MC) is treated with an additive (the exact nature of which is not, in general, being discussed). It was prepared in the same way as Catalyst 1 except that the cobalt was impregnated, not with thorium, but with the additive X_5 to give 4 weight percent X_5 on the catalyst.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 26-29. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 30-31. Carbon number product distributions are plotted in Figs. 32-35. Chromatograms from simulated distillations are reproduced in Figs. 36-39. Detailed material balances appear in Tables 4-5.

The conversion of syngas, although steady, was low, and there was little water gas shift activity, only 7 percent of the oxygen having been rejected as CO_2. The selectivity also was steady but poor, with a high production not only of methane (about 25 percent) but, uncharacteristically for a cobalt catalyst, of C_2-C_4 as well. The total yield of motor fuels was correspondingly poor, with less than 55 percent as C_5^+ and 2.5 percent as heavies. Isomerization of the pentane was about the same as in last quarter's Run 10112-15, which was lower than with Catalyst 1.

The C_4's are about one-half olefins, lower than with most catalysts reported thus far. The Schulz-Flory plots show the high methane and suggest a possible carbon number cut-off, while the chromatograms from the simulated distillations reflect the poor isomerization of the pentane.

Although the activity of this catalyst was fairly steady during the short run of less than 100 hours on stream, its level of activity was low and its selectivity no better than average. The additive tested is evidently of little or no value.

RUN 10225-12

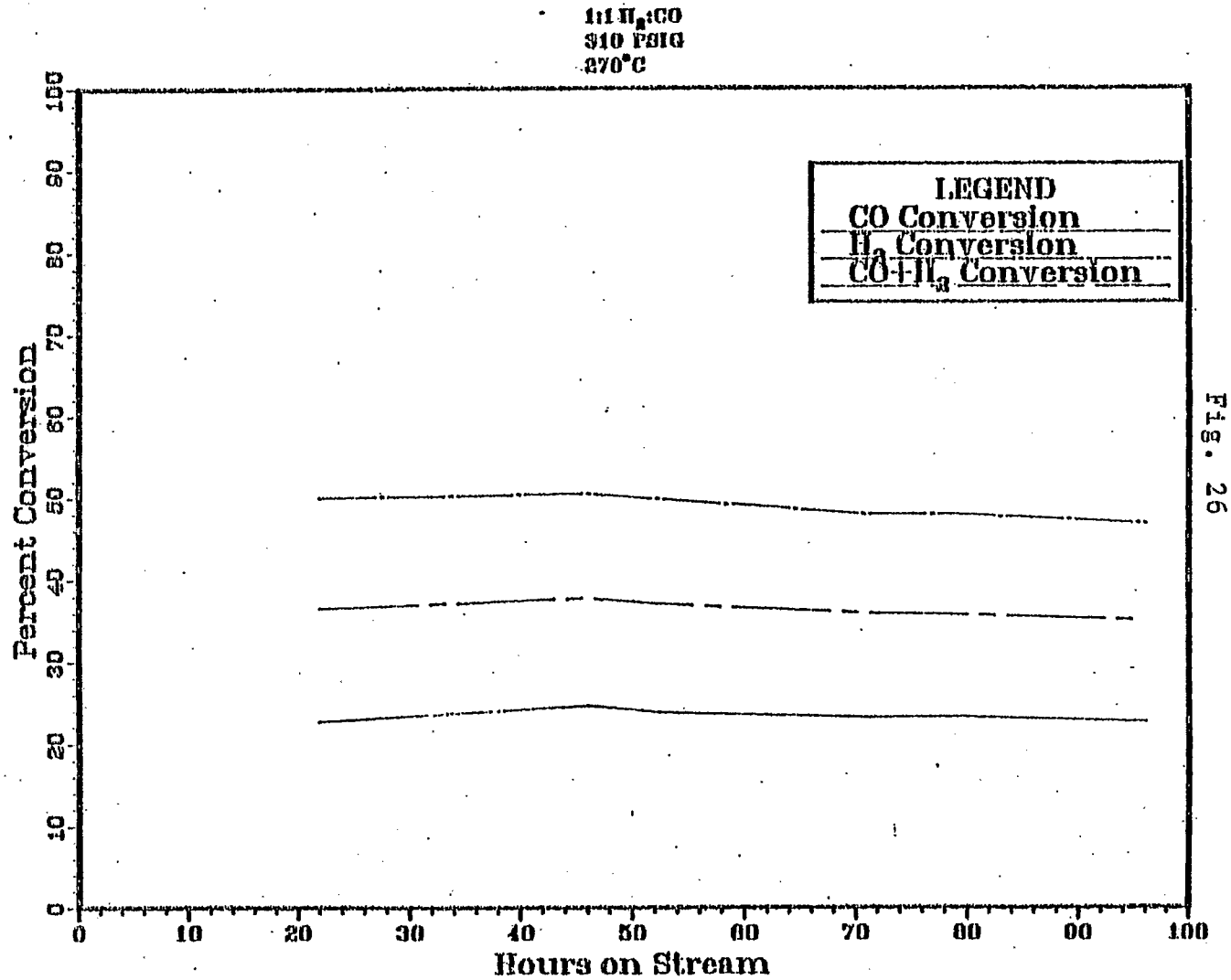
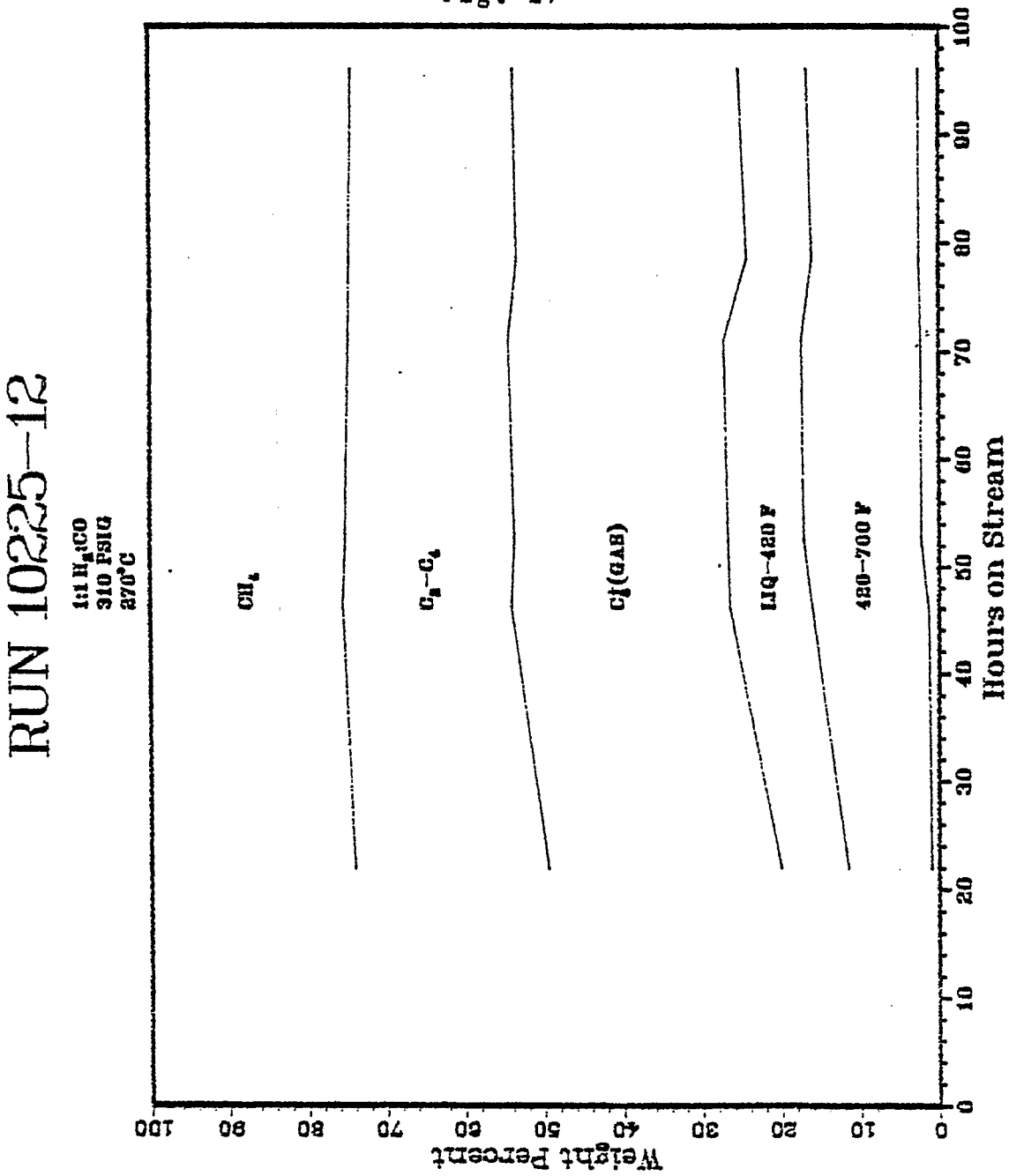


Fig. 26

Fig. 27


RUN 10225-12
1:1 H2:CO
310 PSIG
270°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

RUN 10225–12

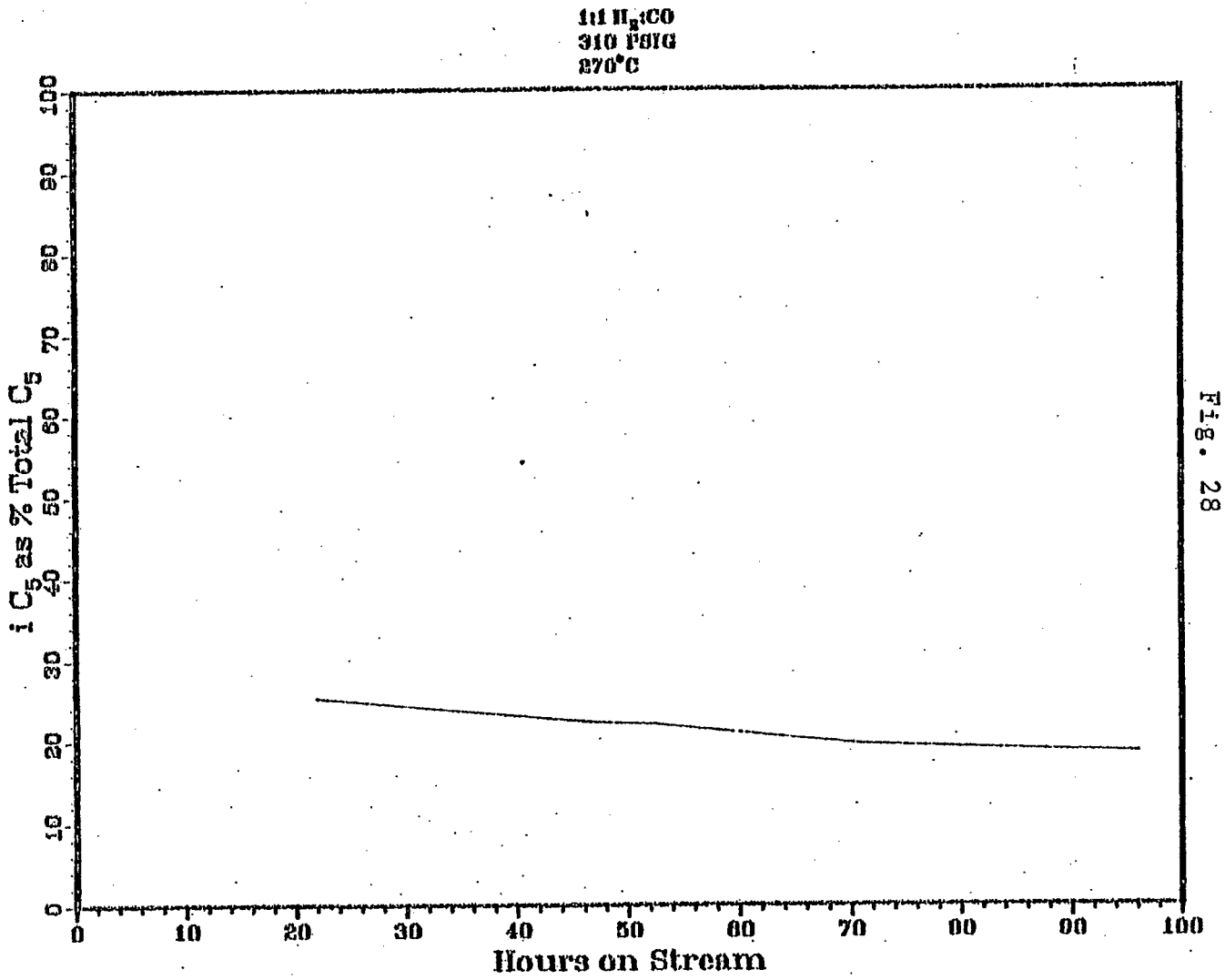


Fig. 28

RUN 10225--12

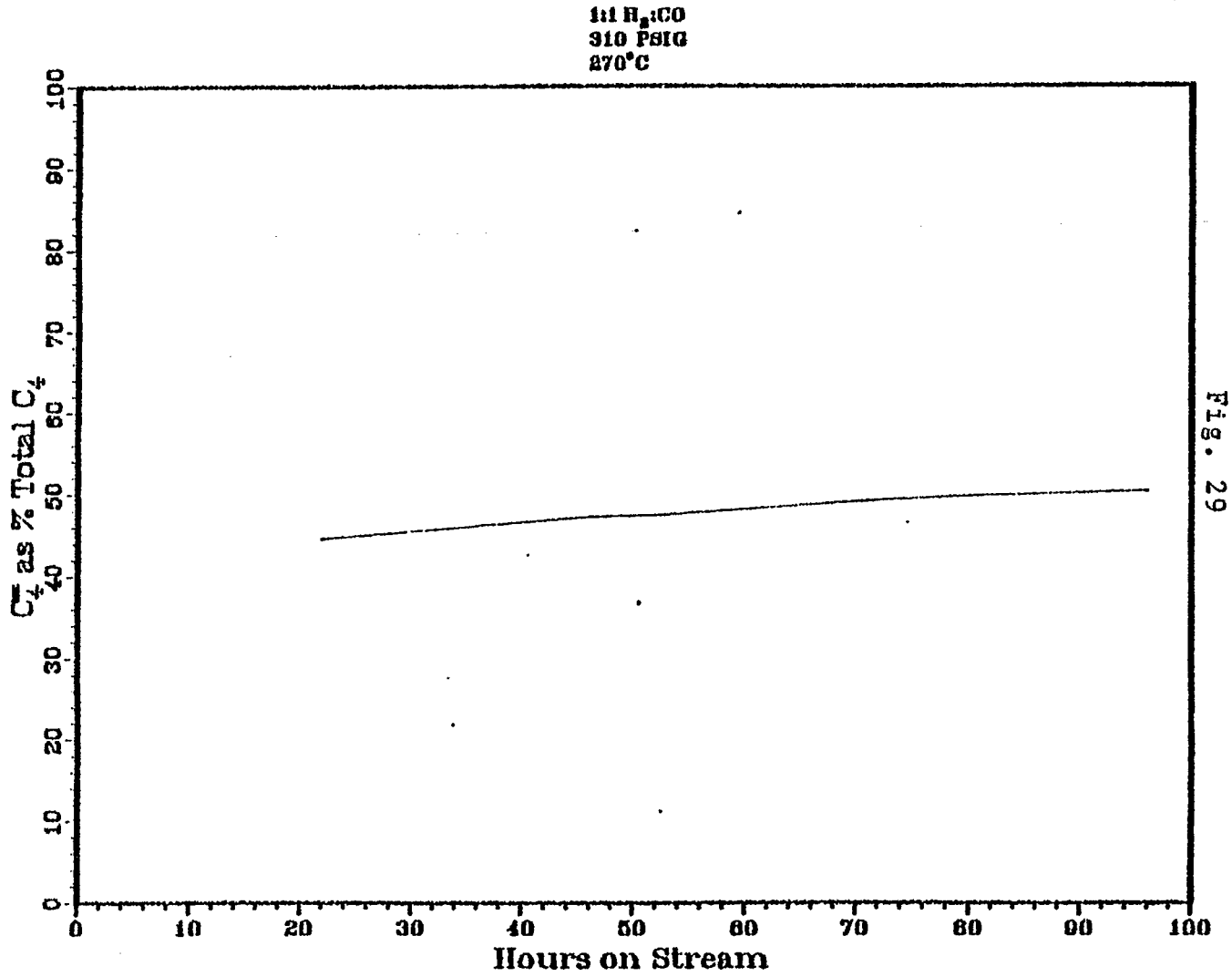


Fig. 29

Fig. 30

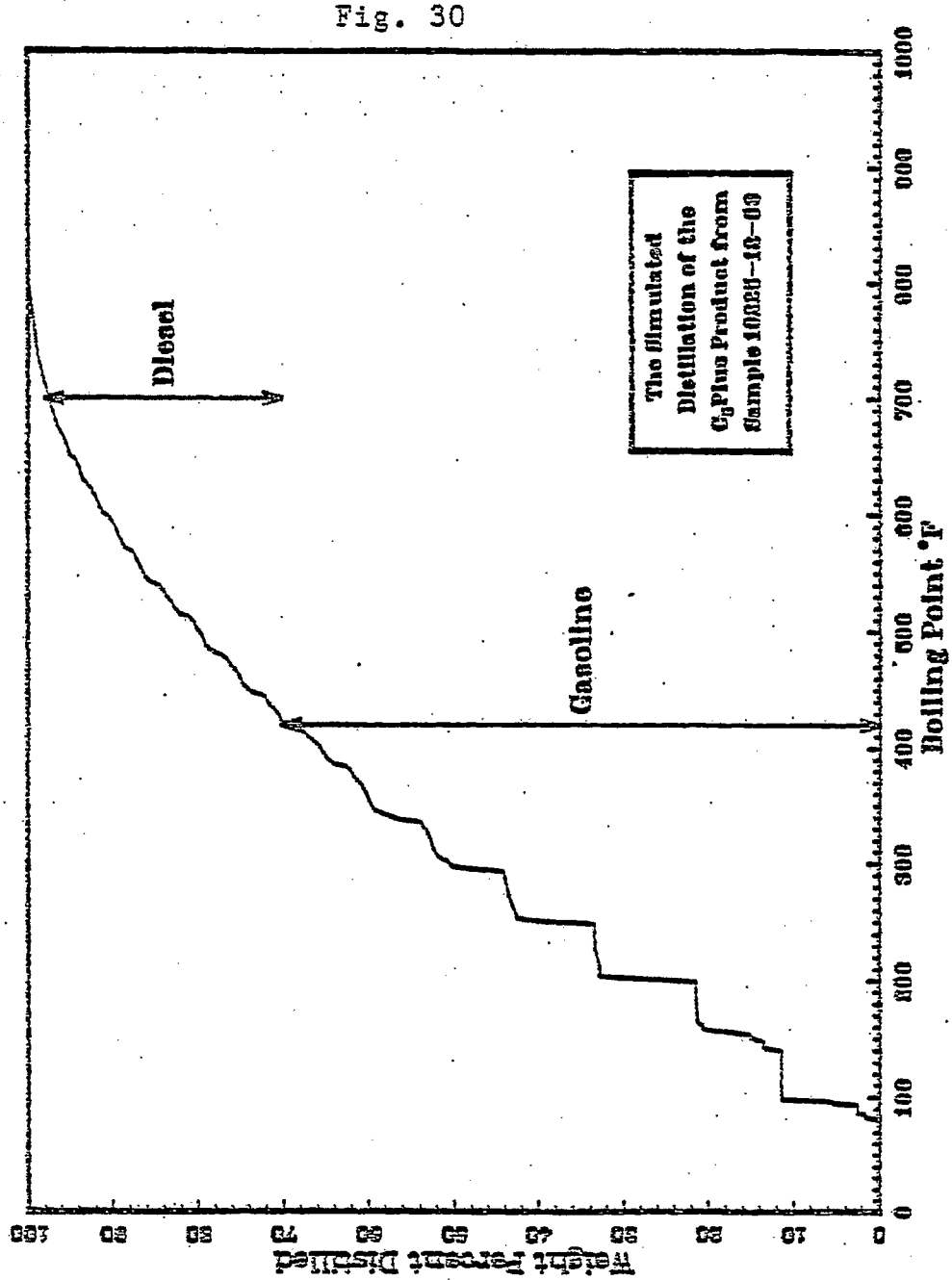

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Diesel
Gasoline
The Simulated Distillation of the C9 Plus Product from Sample 10525-18-09

Fig. 31

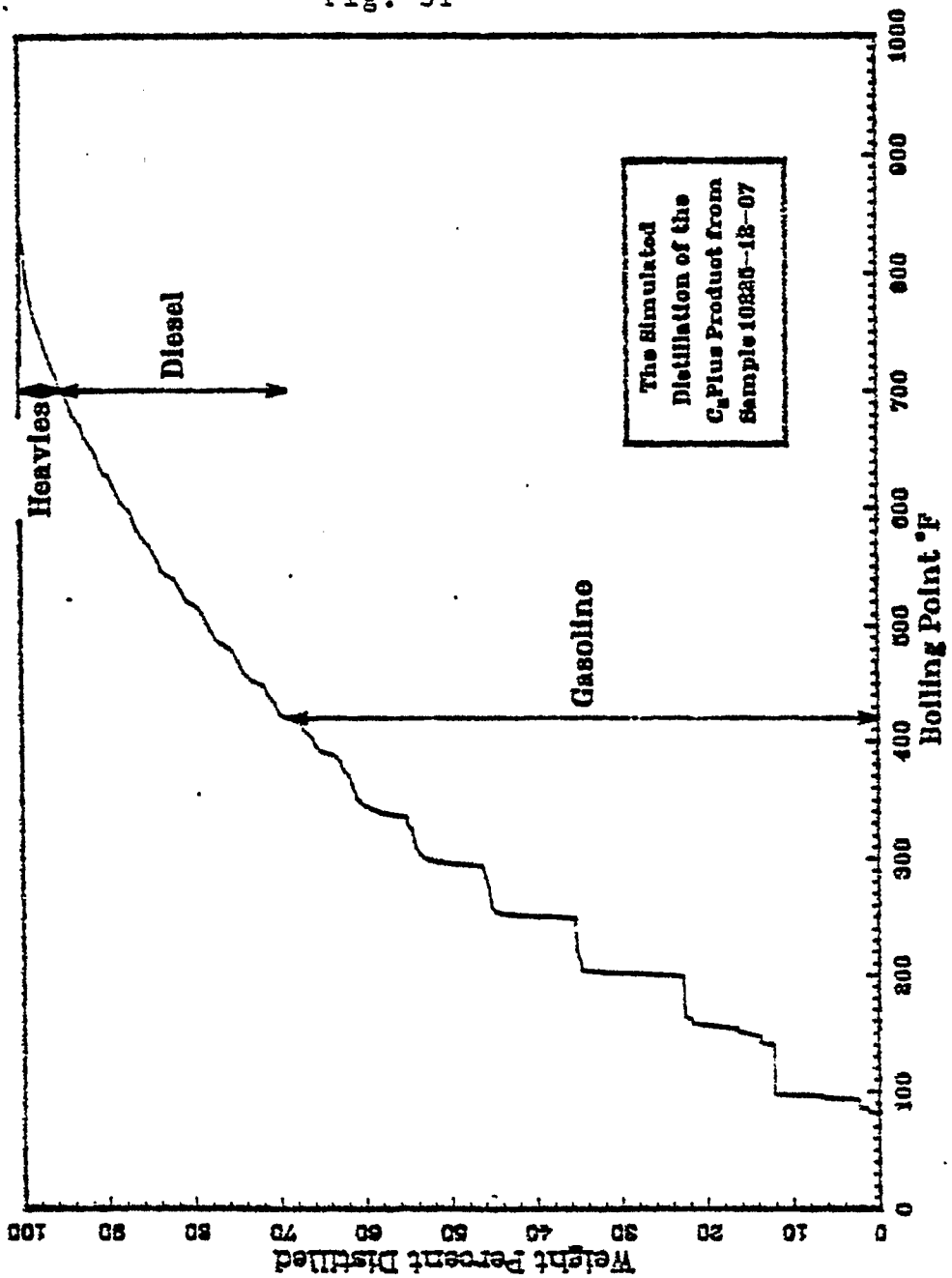

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 103285-13-07
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 32

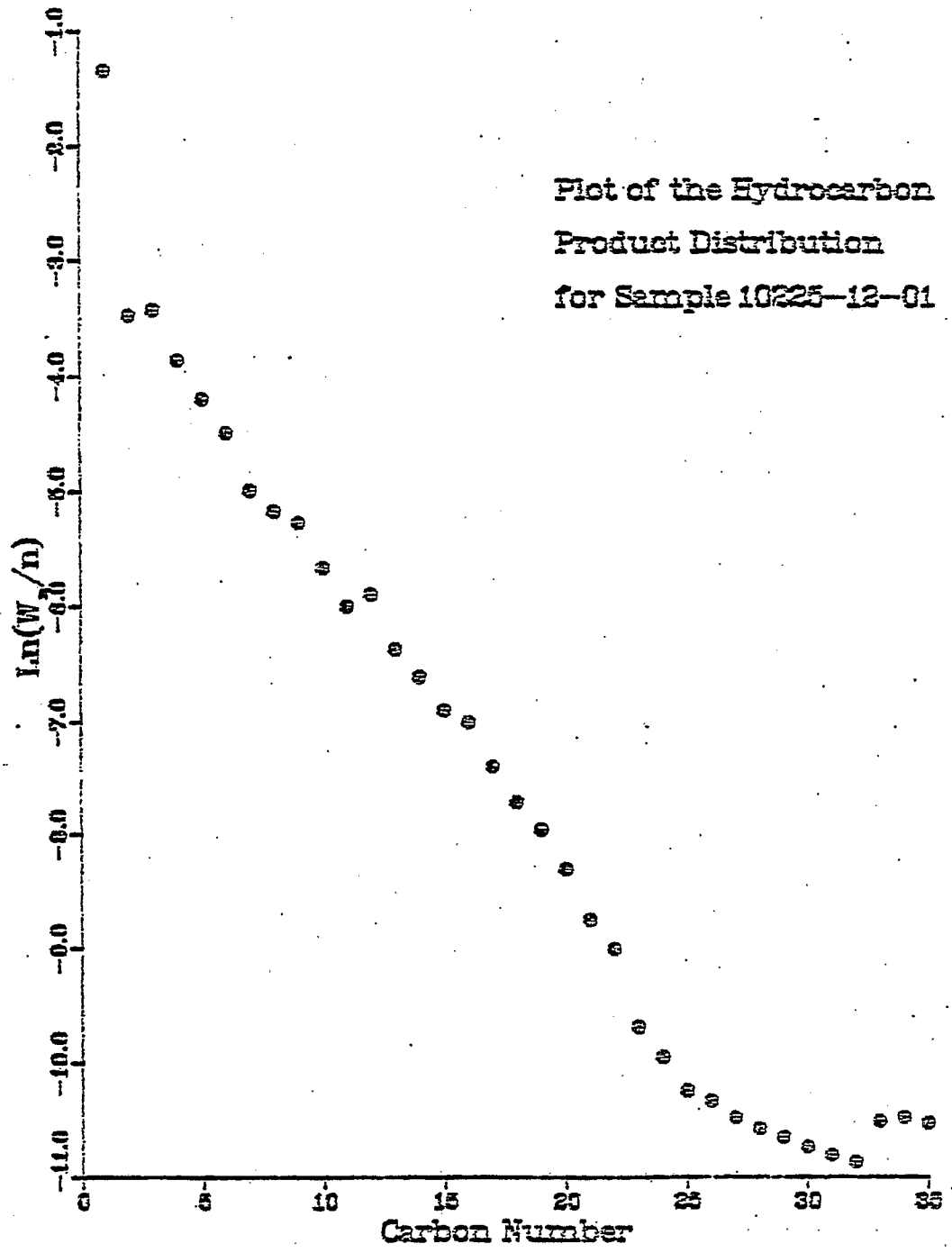

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-12-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 33

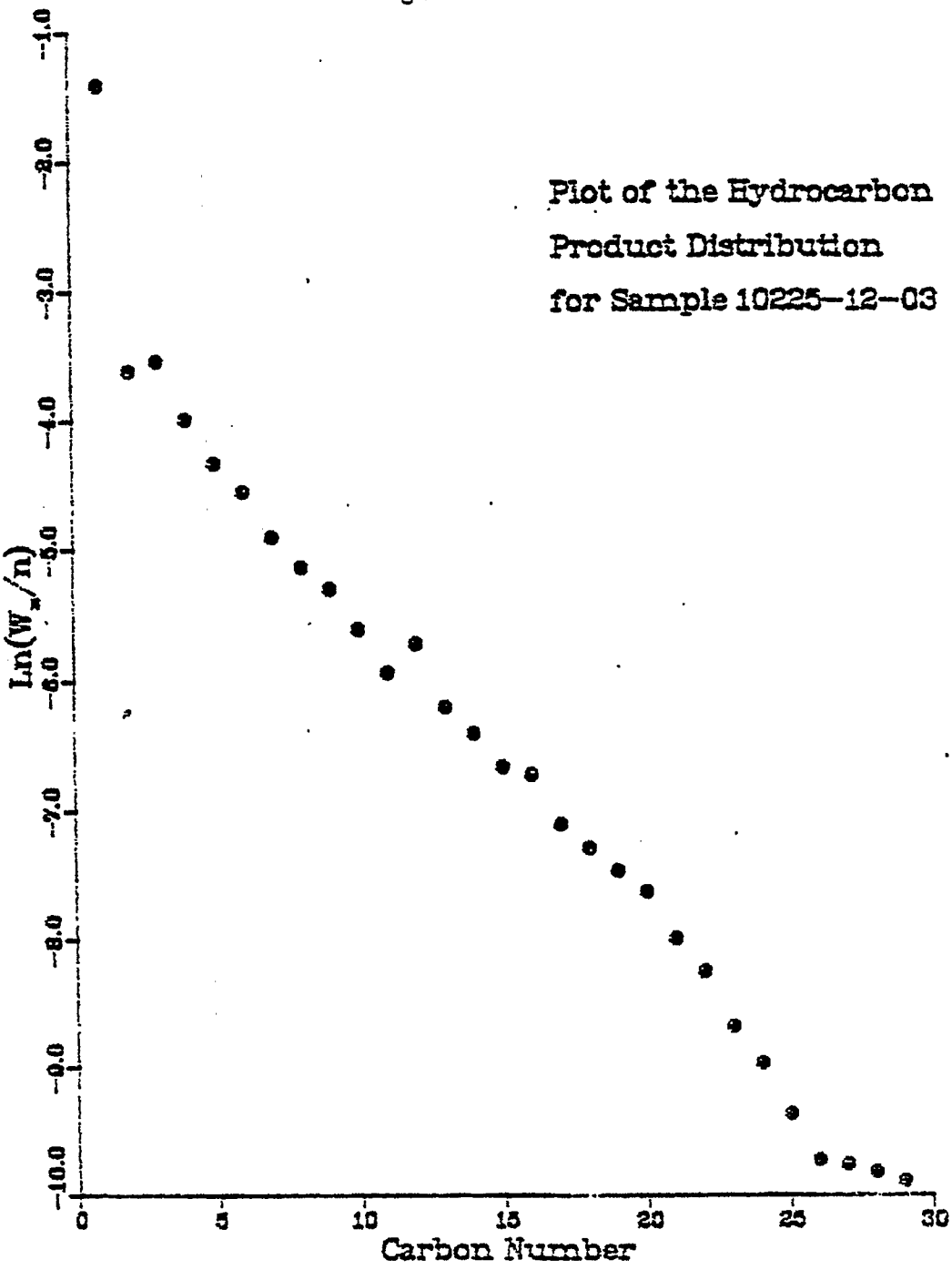

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-12-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 34

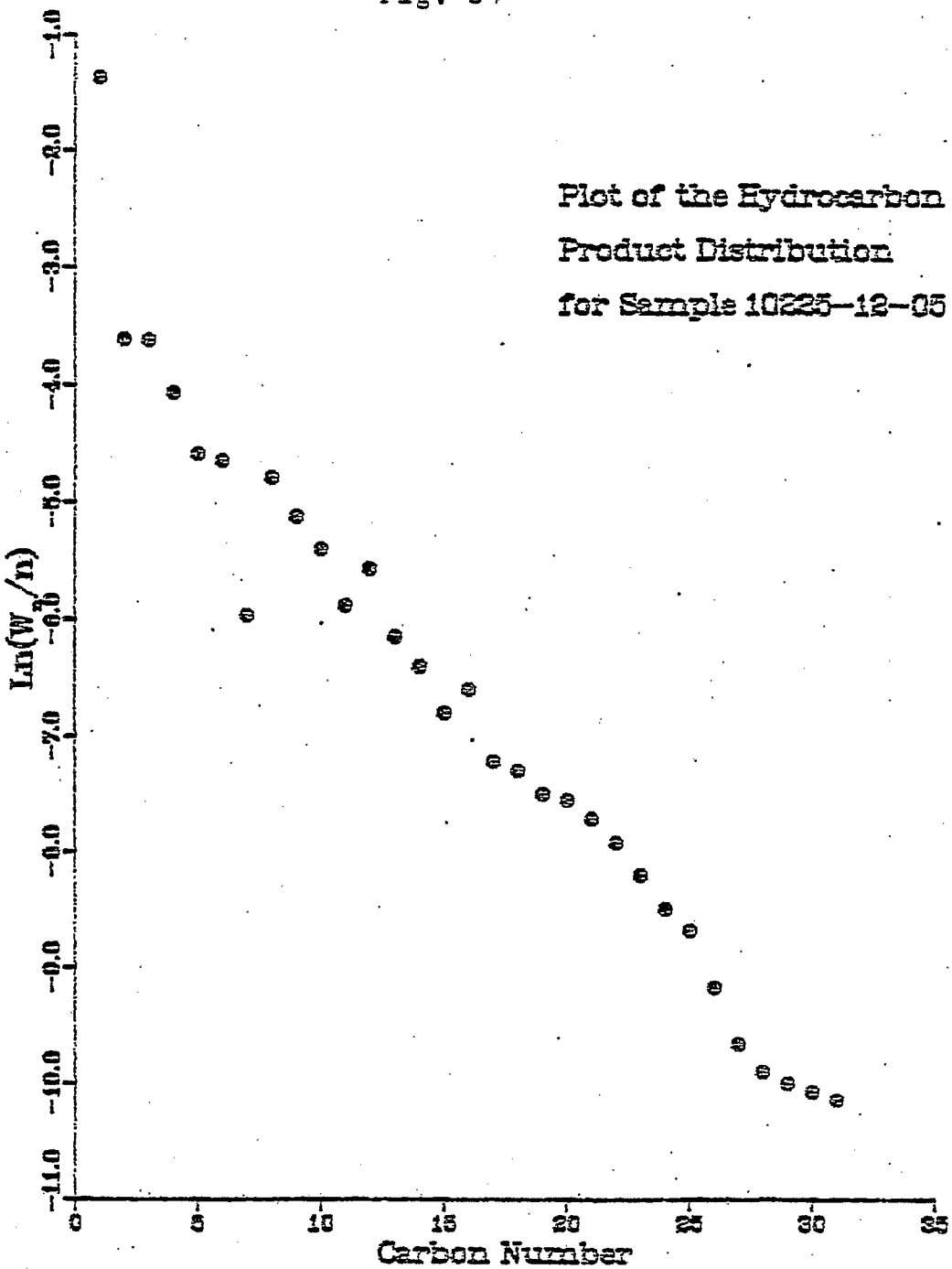

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-12-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 35

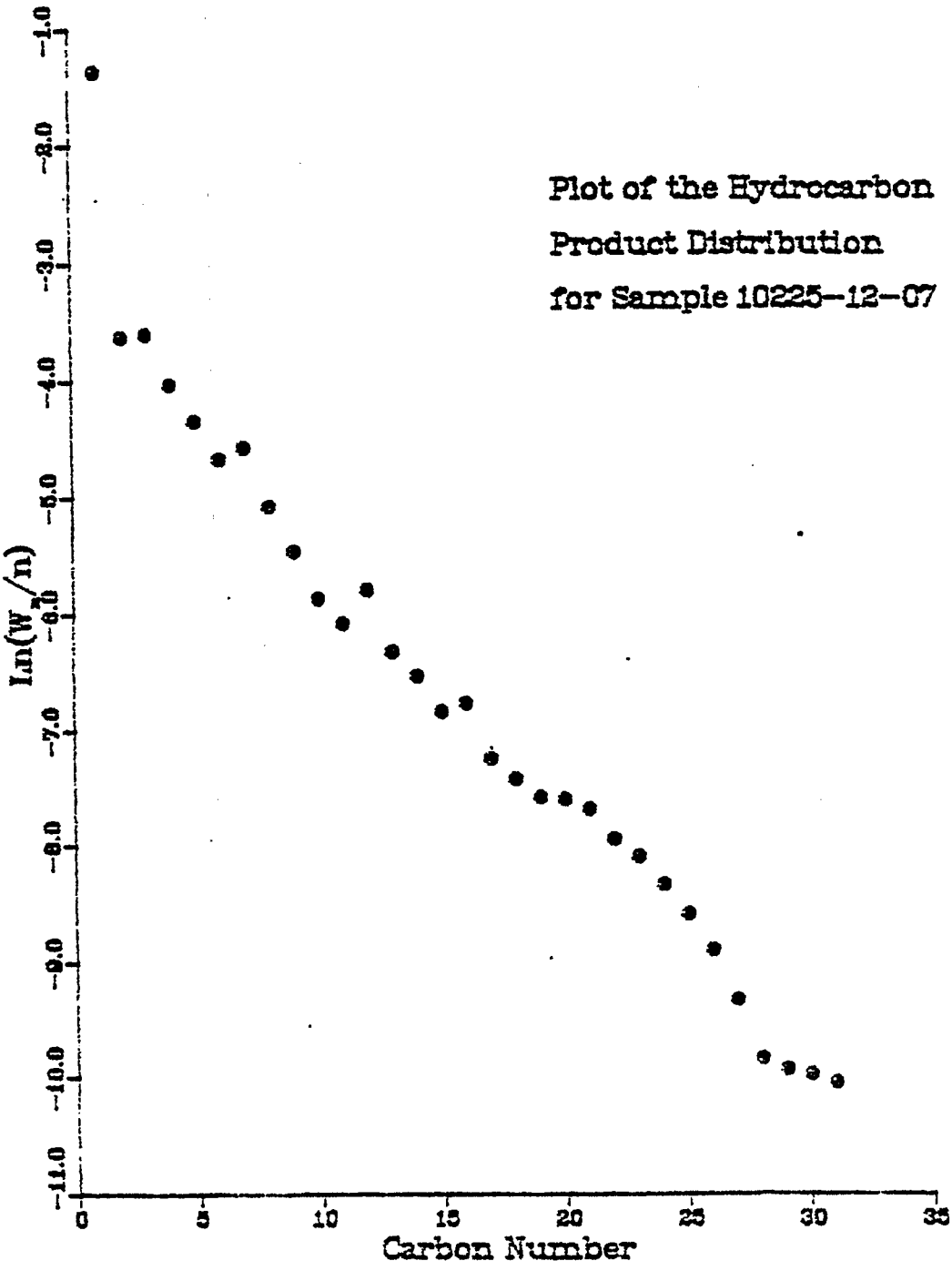

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-12-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 36

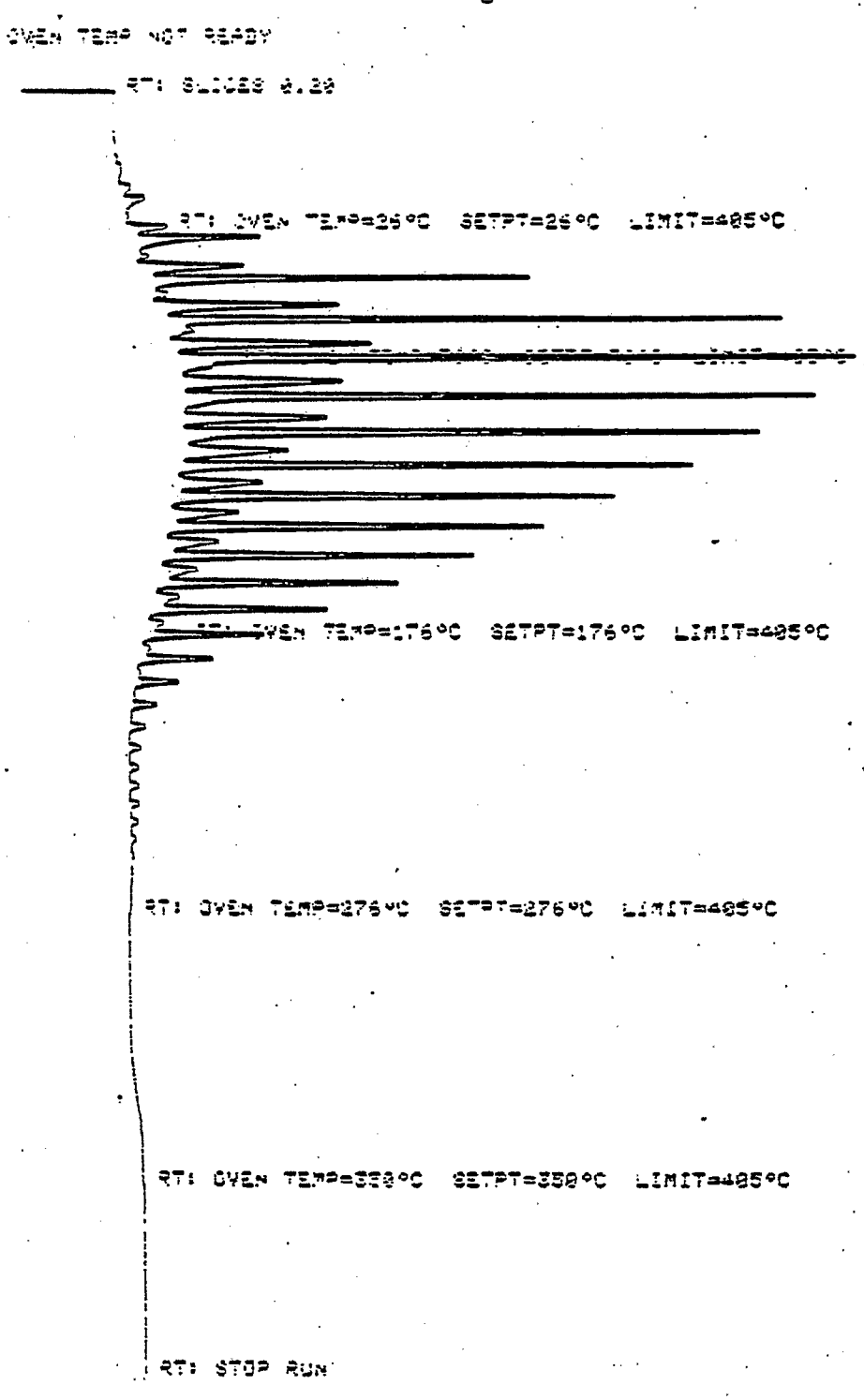

OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D:0225-13-1L

Fig. 37

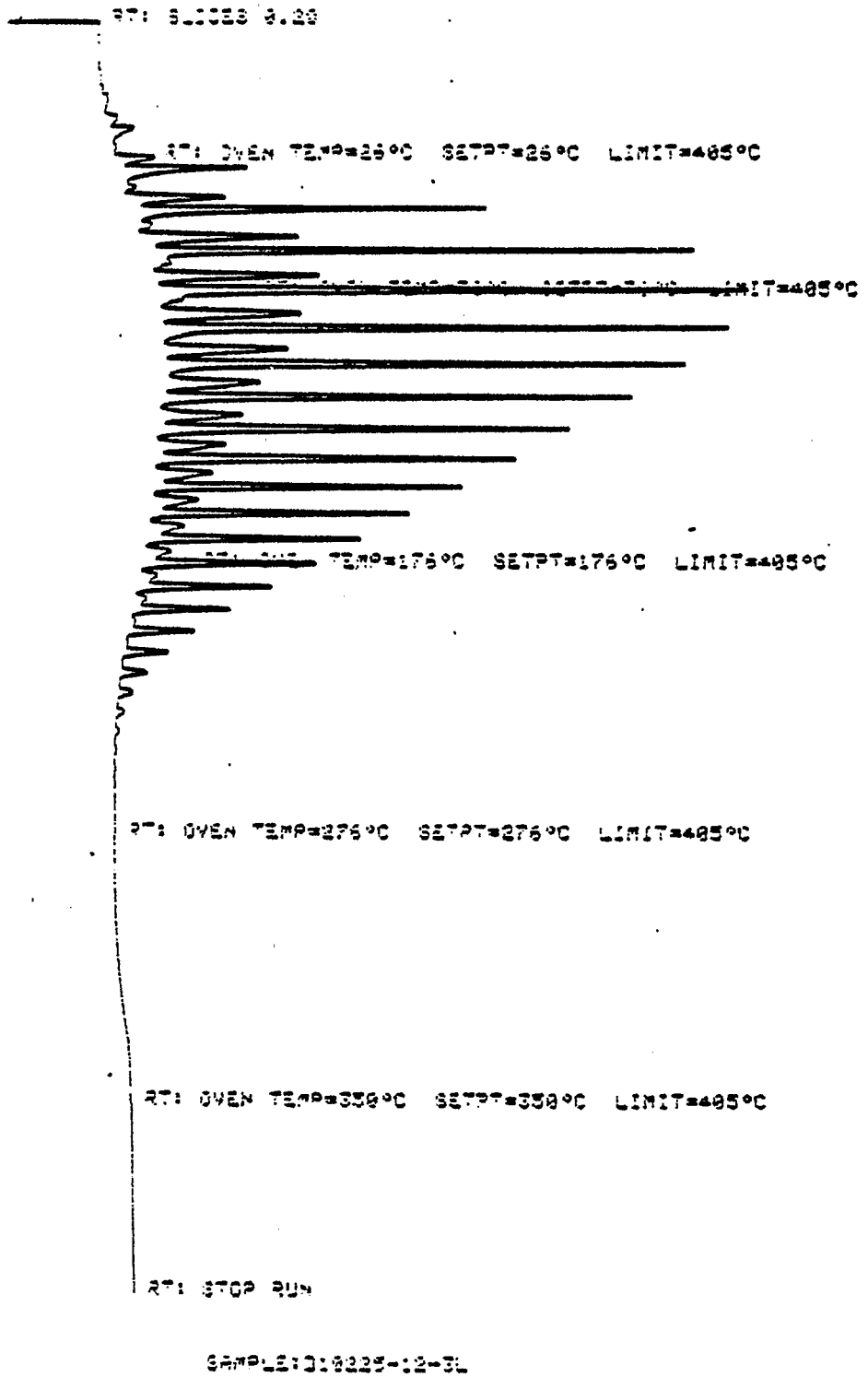

RT: SLICED 0.20
RT: OVEN TEMP=25°C SETPT=25°C LIMIT=405°C
LIMIT=405°C
TEMP=175°C SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:010225-12-3L

Fig. 38

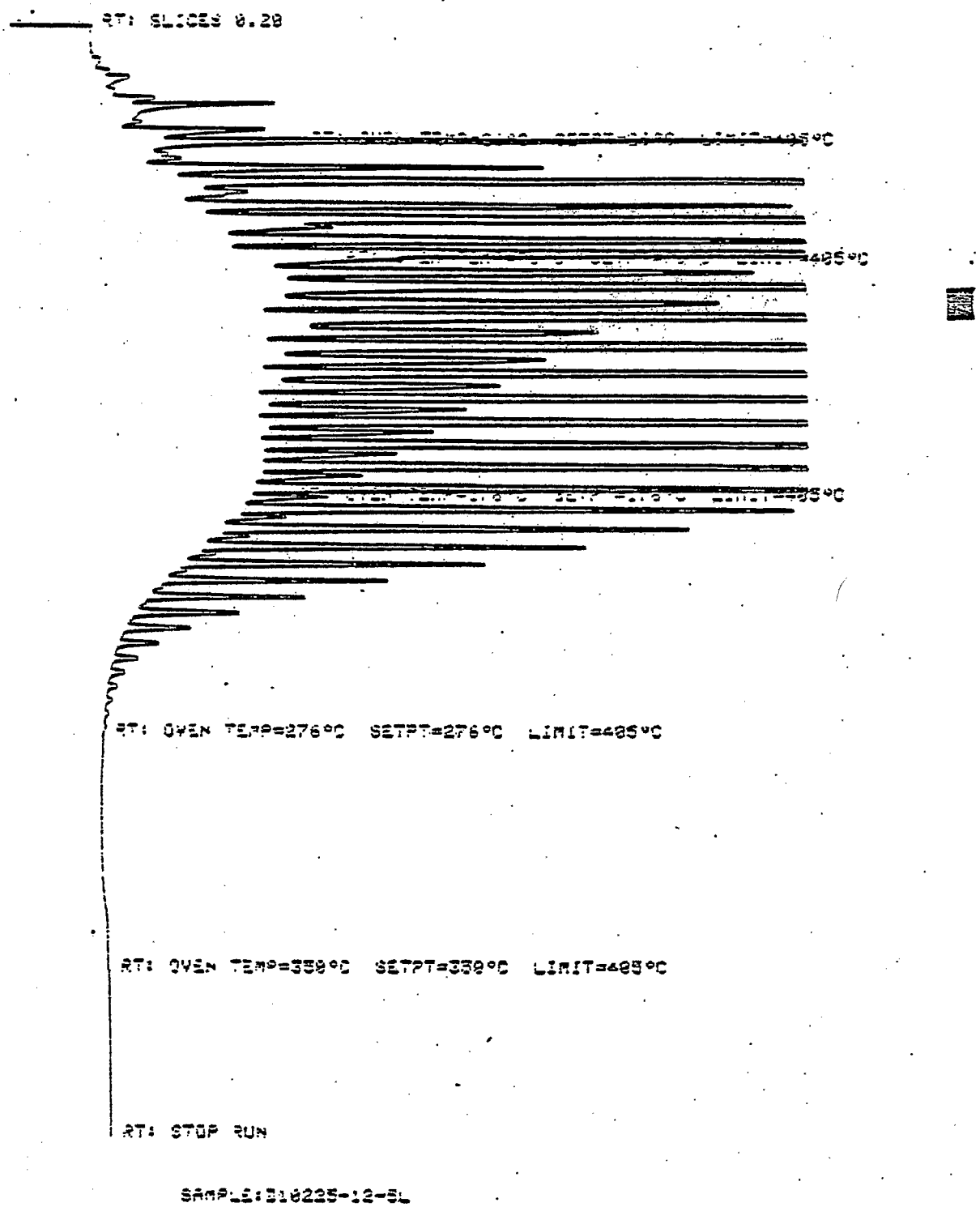

RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=330°C SETPT=330°C LIMIT=405°C
RT: STOP RUN
SAMPLE:B10225-12-SL

Fig. 39

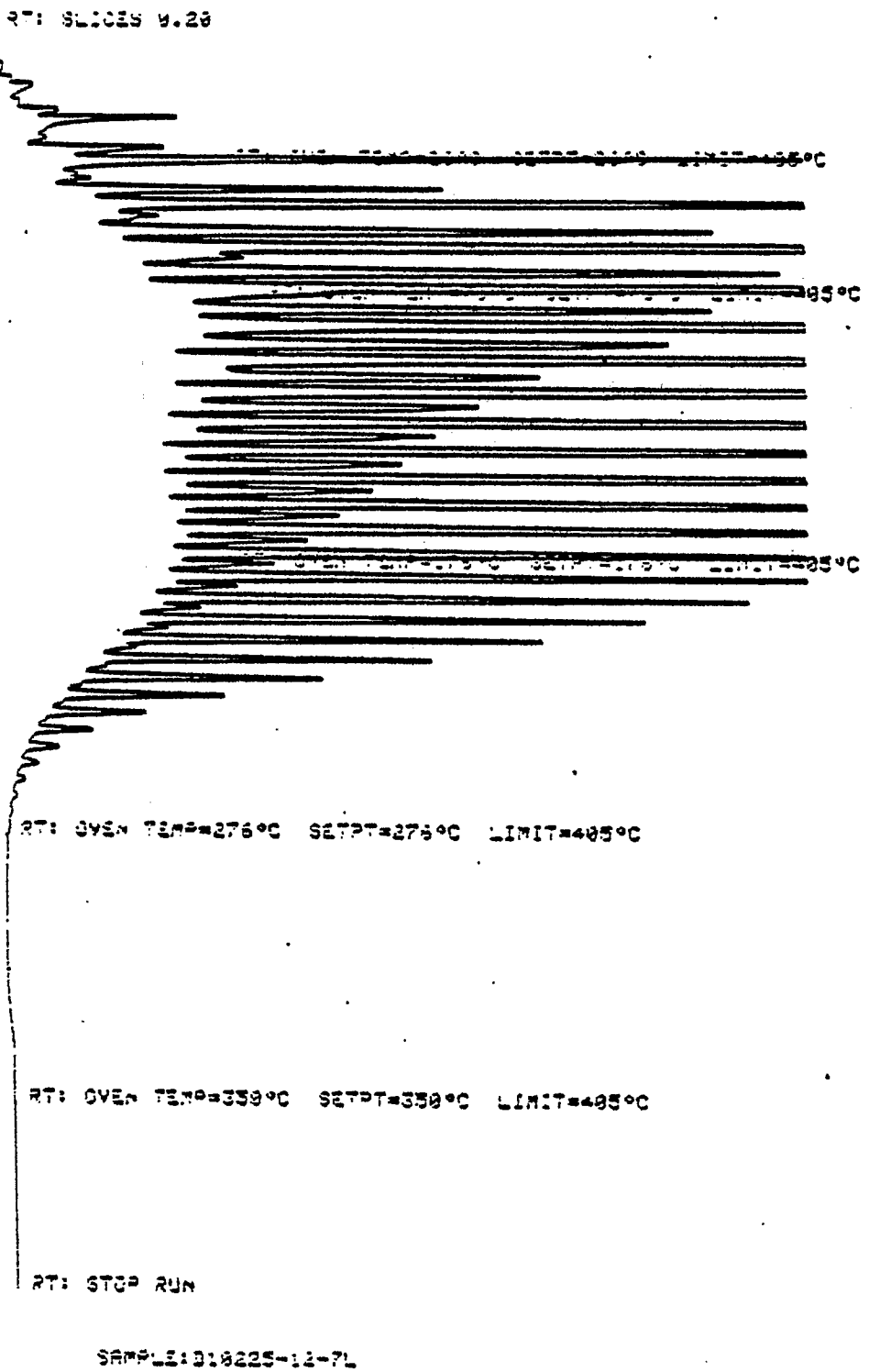

RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

TABLE 4 RESULT OF SYNGAS OPERATION

RUN NO. 10225-12
CATALYST CO/X5 +UCC-101 #10252-80C 80 CC 35.7GM (36.7 AFTER RUN +1. G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-12-01	225-12-03	225-12-04	225-12-05	225-12-06
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.0	46.0	52.5	71.0	78.5
PRESSURE,PSIG	315	319	316	313	310
TEMP. C	266	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.00	24.00	6.50	25.00	7.50
EFFLNT GAS LITER	370.65	383.95	104.75	417.00	127.85
GM AQUEOUS LAYER	40.70	41.67	11.36	43.68	12.53
GM OIL	6.69	9.95	2.63	10.12	2.80
MATERIAL BALANCE					
GM ATOM CARBON %	99.41	95.34	95.33	96.24	99.27
GM ATOM HYDROGEN %	102.12	99.35	99.07	102.14	102.43
GM ATOM OXYGEN %	103.68	97.53	98.36	99.67	101.33
RATIO CHX/(H2O+CO2)	0.8305	0.9084	0.8735	0.8570	0.9113
RATIO X IN CHX	2.6415	2.5863	2.5932	2.5936	2.6008
USAGE H2/CO PRODT	2.0625	2.0373	2.0353	2.0381	2.0388
RATIO CO2/(H2O+CO2)	0.0683	0.0760	0.0744	0.0721	0.0779
K SHIFT IN EFFLNT	0.05	0.06	0.06	0.06	0.06
CONVERSION					
ON CO %	22.77	24.64	23.84	23.18	23.22
ON H2 %	50.03	50.41	49.81	47.94	47.93
ON CO+H2 %	36.58	37.79	37.07	35.93	35.77
PRDT SELECTIVITY,WT %					
CH4	26.06	24.52	24.84	25.29	25.38
C2 HC'S	6.26	5.37	5.48	5.41	5.63
C3H8	6.81	5.61	5.78	5.32	5.50
C3H6=	3.01	3.09	2.82	2.72	2.89
C4H10	4.75	3.98	3.95	3.54	3.71
C4H8=	3.69	3.43	3.44	3.31	3.54
C5H12	4.77	3.90	3.96	3.65	3.74
C5H10=	2.75	2.73	2.12	1.40	2.81
C6H14	4.87	4.39	4.10	3.83	4.23
C6H12= & CYCLO'S	1.87	1.95	1.24	1.89	2.04
C7+ IN GAS	15.10	14.52	15.51	16.40	16.22
LIQ HC'S	20.07	26.50	26.76	27.24	24.30
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	50.57	46.01	46.31	45.59	46.65
C5 -420 F	37.82	37.94	36.56	36.97	37.31
420-700 F	10.60	14.73	14.94	15.21	13.55
700-END PT	1.00	1.32	2.19	2.23	2.49
C5+-END PT	49.43	53.99	53.69	54.41	53.35
ISO/NORMAL MOLE RATIO					
C4	0.1952	0.1891	0.1571	0.1380	0.1394
C5	0.3389	0.2885	0.2837	0.2439	0.2381
C6	0.4520	0.4057	0.3742	0.3525	0.3465
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	2.1606	1.7331	1.9574	1.8654	1.8164
C4	1.2432	1.1206	1.1081	1.0328	1.0129
C5	1.6821	1.3902	1.8178	2.5385	1.2954
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7799	0.7846		0.7986	
RATIO CH4/(1-A)**2	5.3776	5.2849		6.2326	
LIQ HC COLLECTION					
PHYS. APPEARANCE	YL OIL	YL OIL		YL OIL	
DENSITY	0.759	0.762		0.766	
N, REFRACTIVE INDEX	1.4288	1.4290		1.4306	
SIMULT'D DISTILATN					
10 WT % @ DEG F	315	312		316	
16	341	343		346	
50	448	461		478	
84	594	616		648	
90	632	651		686	
RANGE(16-84 %)	253	273		302	
WT % @ 420 F	42.17	39.40	36.00	36.00	34.00
WT % @ 700 F	95.00	95.00	91.83	91.83	89.75

TABLE 5 RESULT OF SYNGAS OPERATION

RUN NO. 10225-12
CATALYST CO/X5 +UCC-101 #10252-80C 80 CC 35.7GM (36.7 AFTER RUN +1.0G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-12-07
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	96.0
PRESSURE,PSIG	311
TEMP. C	270
FEED CC/MIN	400
HOURS FEEDING	25.00
EFFLNT GAS LITER	426.20
GM AQUEOUS LAYER	41.78
GM OIL	9.32
MATERIAL BALANCE	
GM ATOM CARBON %	97.61
GM ATOM HYDROGEN %	102.42
GM ATOM OXYGEN %	100.53
RATIO CHX/(H2O+CO2)	0.8747
RATIO X IN CHX	2.6005
USAGE H2/CO PRODT	2.0348
RATIO CO2/(H2O+CO2)	0.0758
K SHIFT IN EFFLNT	0.06
CONVERSION	
ON CO %	22.64
ON H2 %	46.79
ON CO+H2 %	35.00
PROT SELECTIVITY,WT %	
CH4	25.67
C2 HC'S	5.32
C3H8	5.36
C3H6=	2.78
C4H10	3.59
C4H8=	3.52
C5H12	3.69
C5H10=	2.82
C6H14	3.79
C6H12= & CYCLO'S	1.84
C7+ IN GAS	16.26
LIQ HC'S	25.37
TOTAL	100.00

SUB-GROUPING	
C1 -C4	46.23
C5 -420 F	37.02
420-700 F	14.15
700-END PT	2.60
C5+-END PT	53.77
ISO/NORMAL MOLE RATIO	
C4	0.1239
C5	0.2280
C6	0.3036
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	1.8400
C4	0.9858
C5	1.2710
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8008
RATIO CH4/(1-A)**2	6.4698
LIQ HC COLLECTION	
PHYS. APPEARANCE	YL OIL
DENSITY	0.766
N, REFRACTIVE INDEX	1.4311
SIMULT'D DISTILATN	
10 WT % @ DEG F	325
16	348
50	484
84	660
90	701
RANGE(16-84 %)	312
WT % @ 420 F	34.00
WT % @ 700 F	89.75

IV. RUN 3 (11677-01) with Catalyst 3 ($Co/Th/X_6$ + UCC-101)

This catalyst continues the series of tests of metal component additives. It was prepared in the same way as Catalyst 1 except that the thorium-promoted cobalt was impregnated with the additive X_6 to give 2 weight percent X_6 on the catalyst.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 40-43. A simulated distillation of the C_5^+ product is plotted in Fig. 44. Carbon number product distributions are plotted in Figs. 45-46. The chromatograms from the simulated distillations are reproduced in Figs. 47-48. Detailed material balances appear in Table 6.

Due to a number of mechanical failures this test had to be aborted after only 41 hours on stream. During the run the catalyst's activity was only fair; the water gas shift activity was very low, with less than 10 percent of the oxygen rejected as CO_2; and the usage of the H_2:CO syngas was in a ratio of about 2:1. The selectivity was about average for a cobalt catalyst: methane production was high; production of C_5-700F was about 60 percent, with a 3:1 ratio of gasoline to diesel fuel; and both the pentane and the liquids were somewhat isomerized.

The C_4's, however, were highly olefinic, more typical of an iron than a cobalt catalyst. For this reason, and to investigate

the possibility of lowering the methane production, the test was re-run and is reported next.

Fig. 40

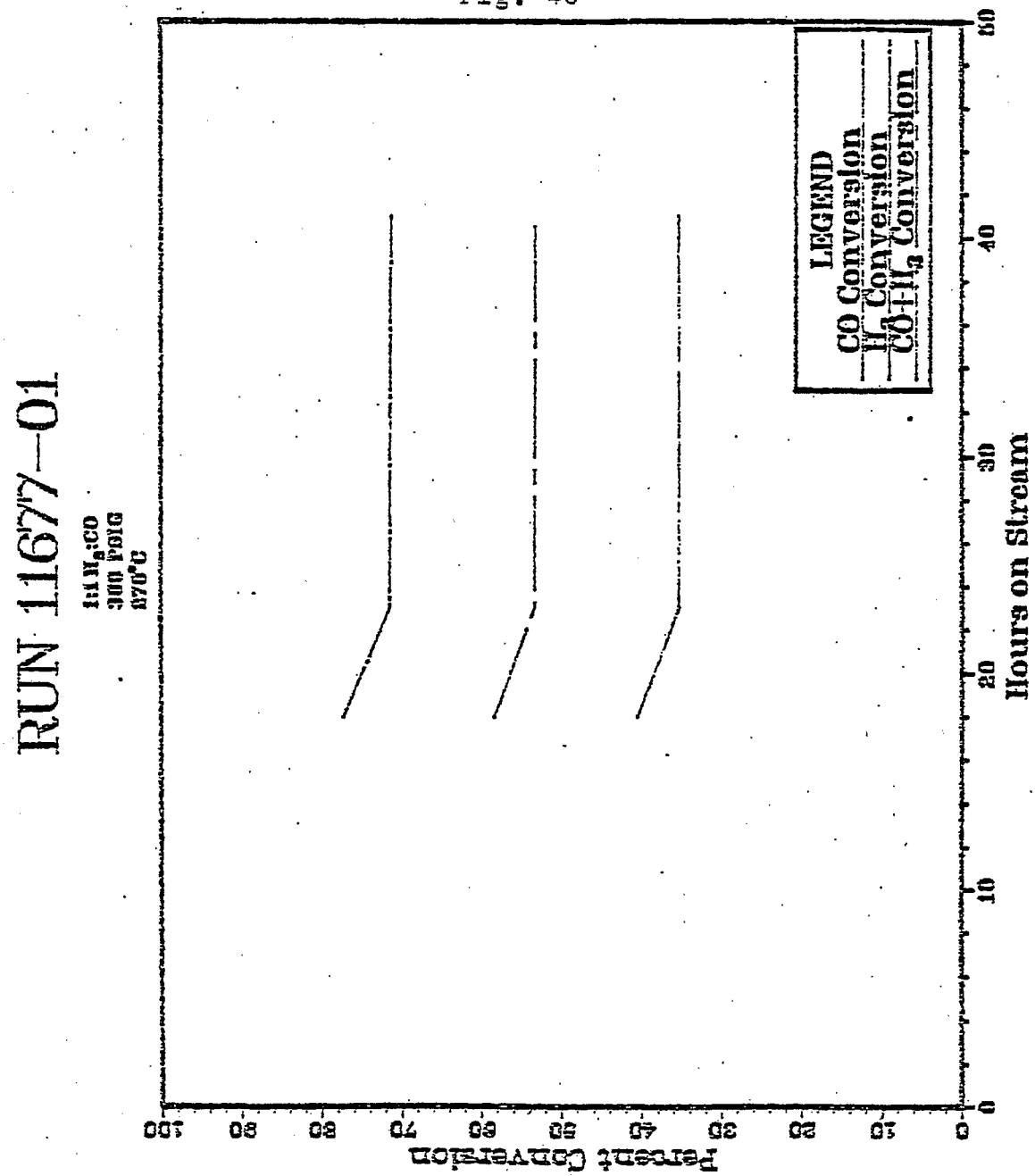

RUN 11677-01
1:1 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 41

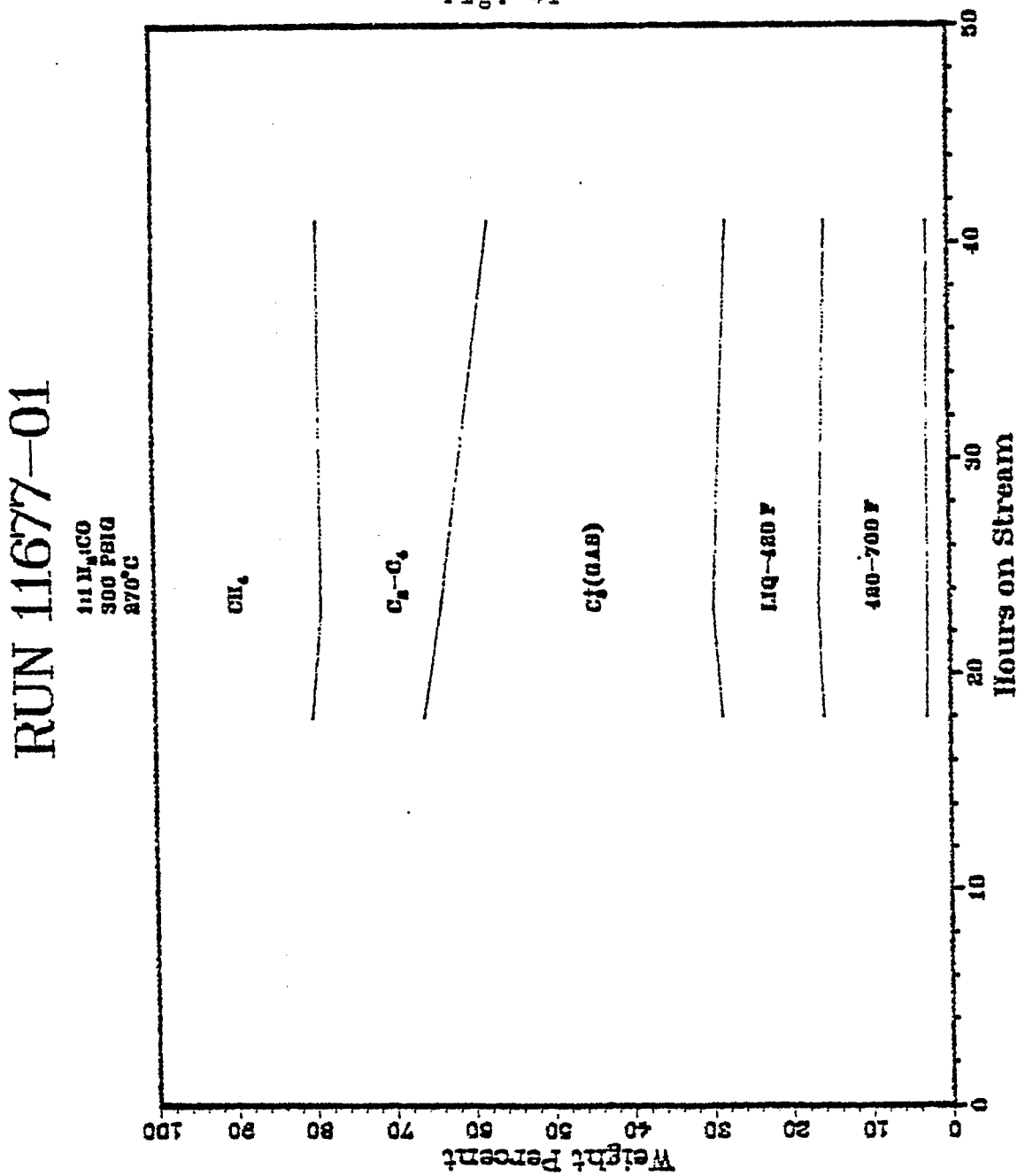
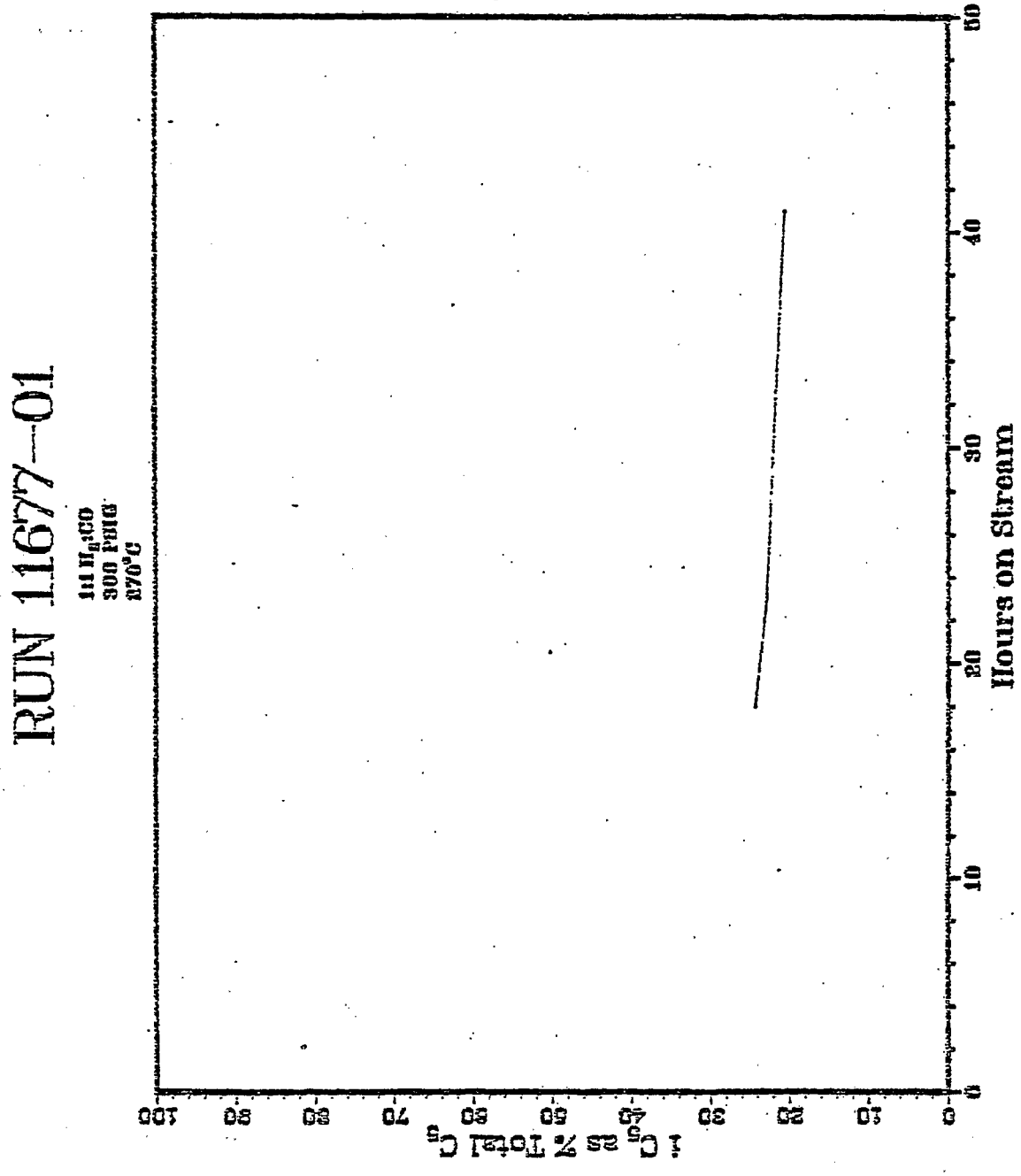

RUN 11677-01
1:1 H2:CO
300 PSIG
270°C
CH4
C2-C4
C5+(BTU)
110-400 F
400-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 42


RUN 11677-01
1:1 H_2:CO
300 Psig
270°C
i C_5 as % Total C_5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

RUN 11677--01

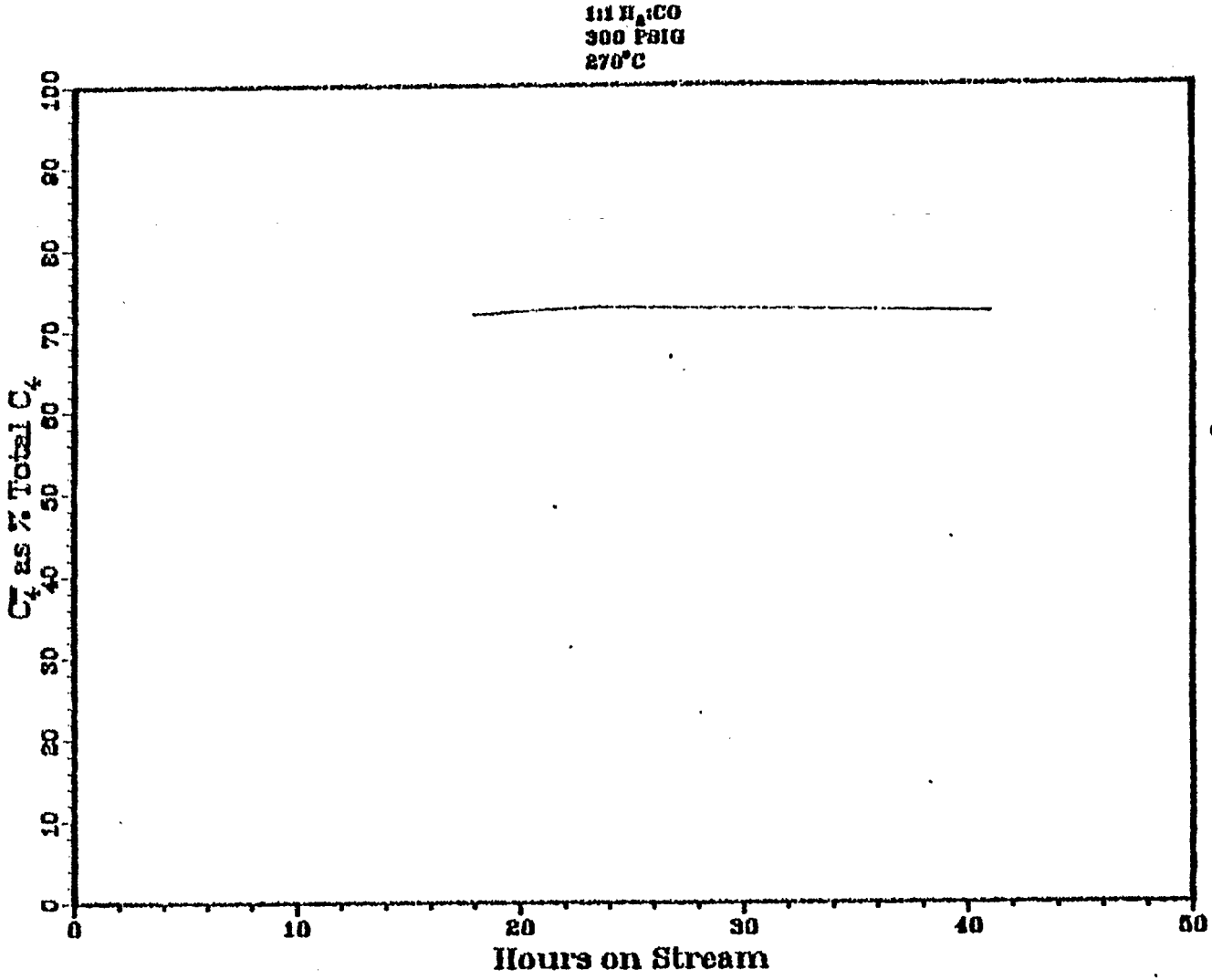


Fig. 43

Fig. 44

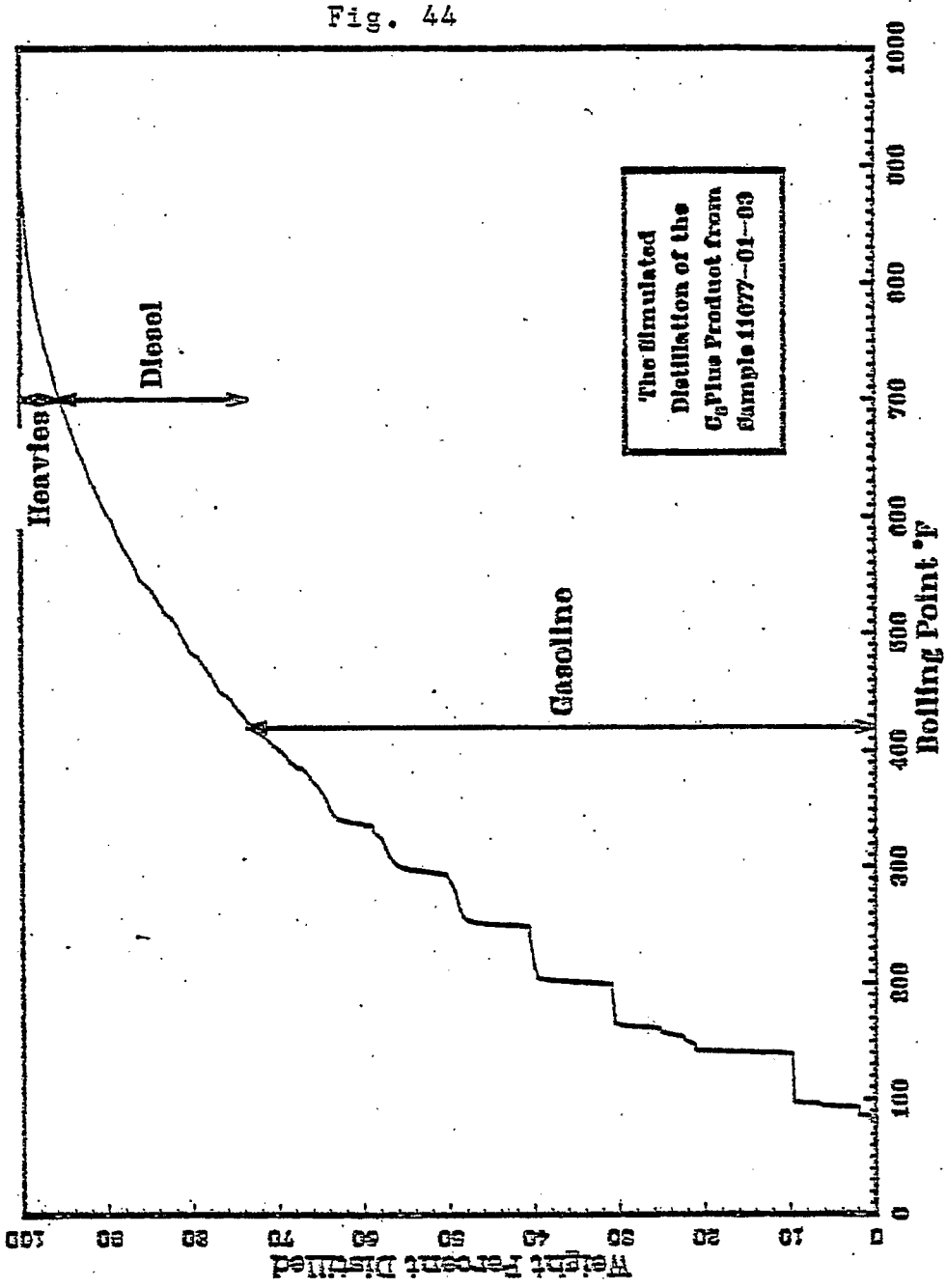

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-01-03
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 45

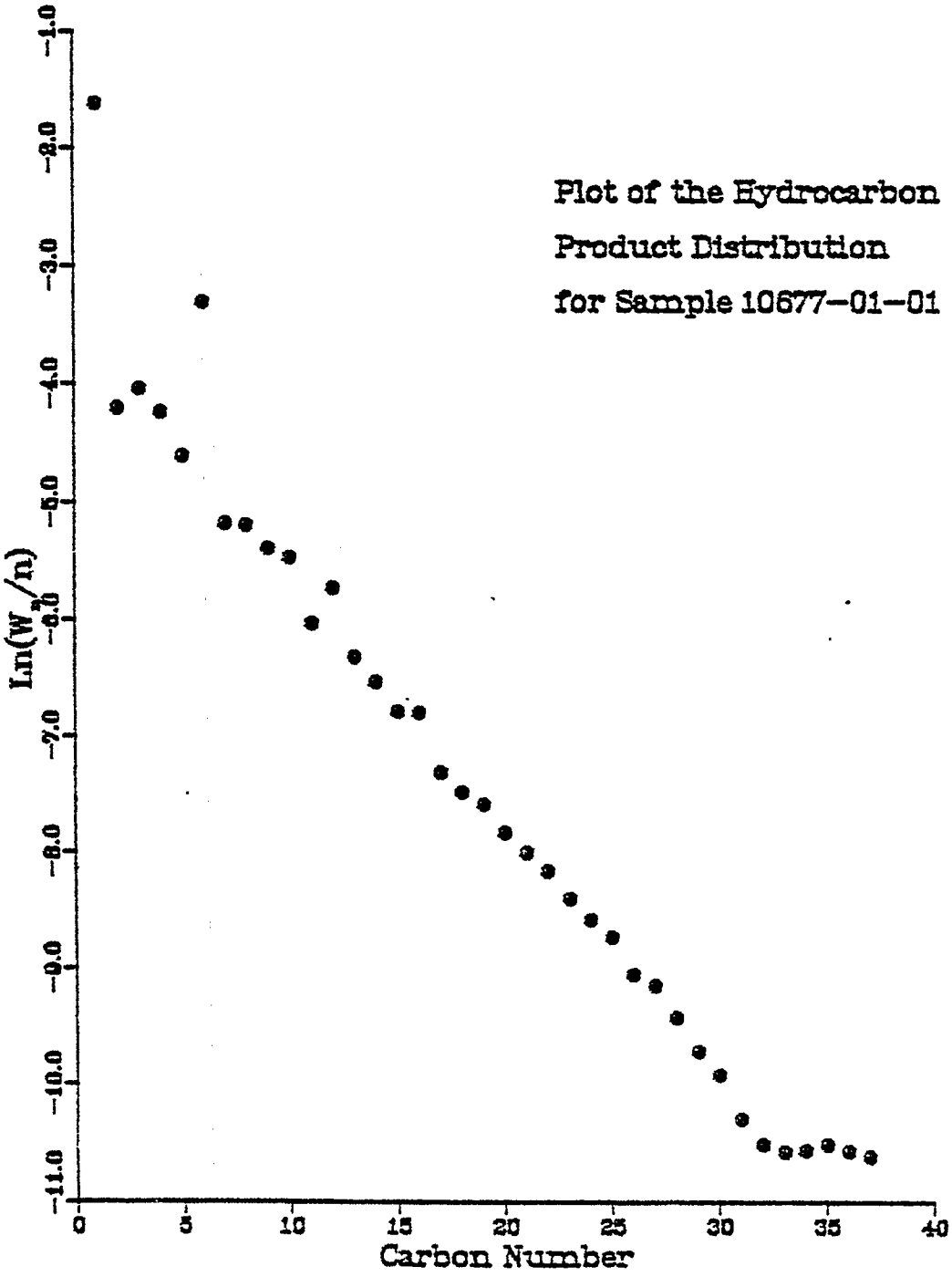

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-01-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 46

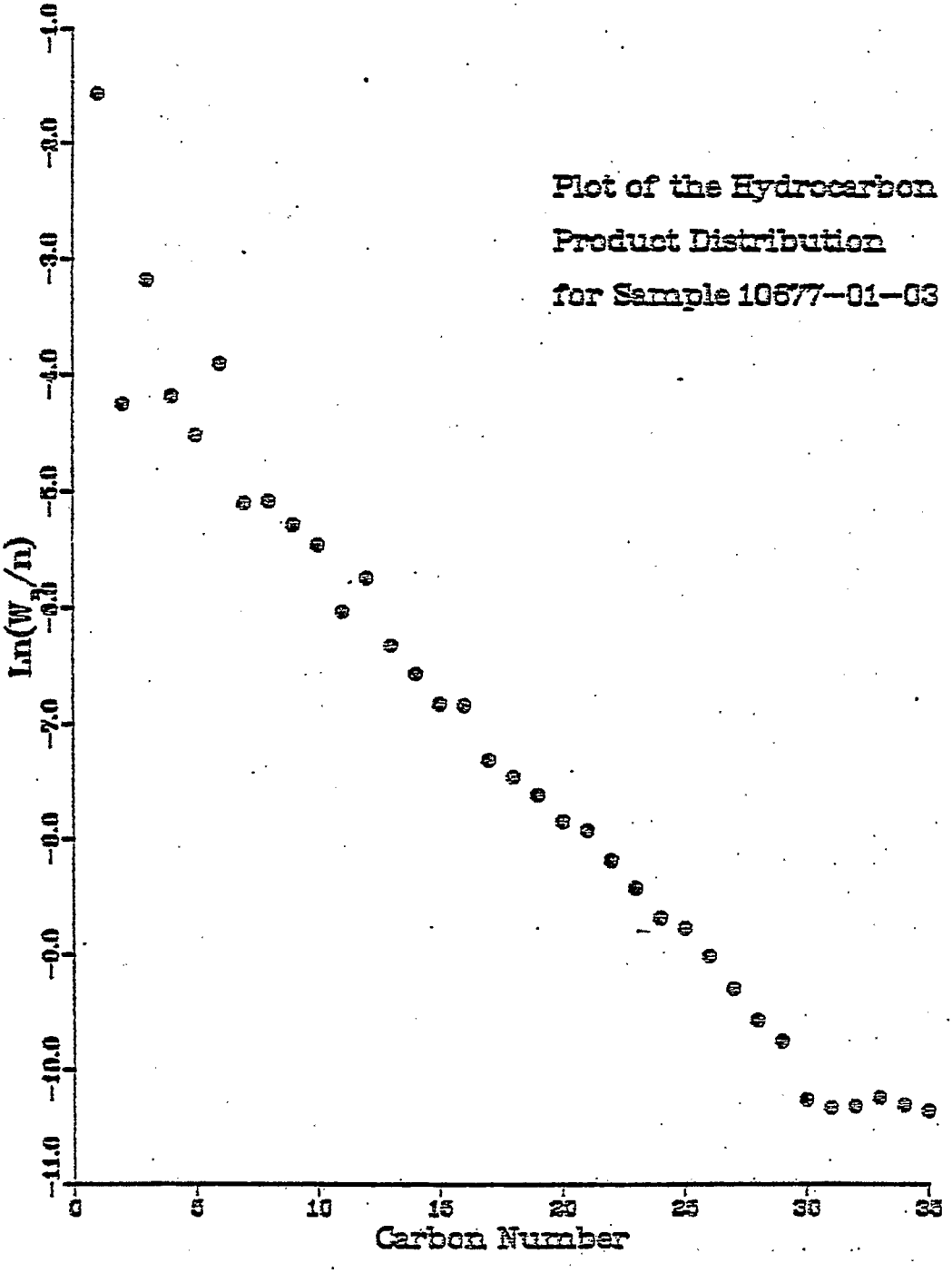
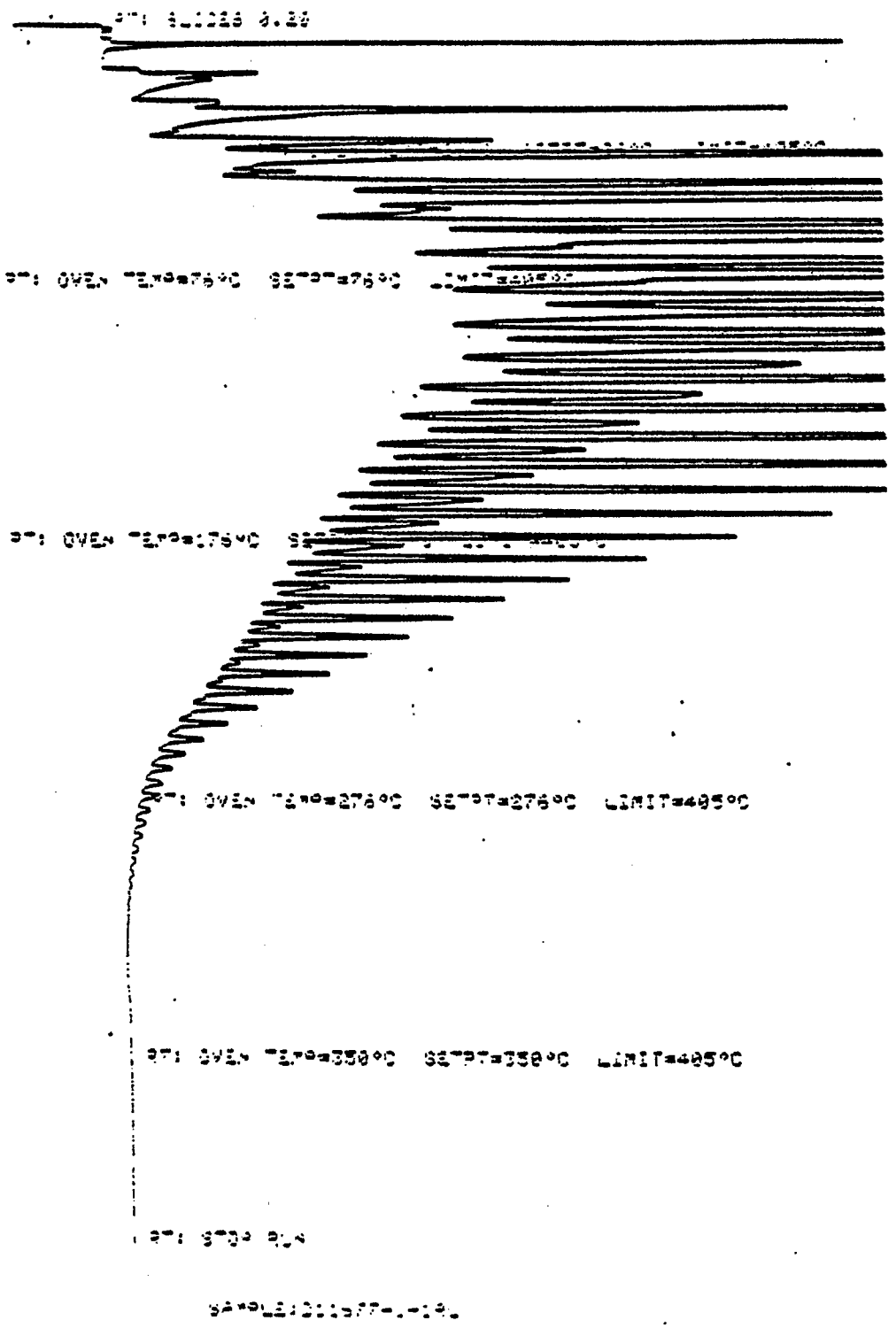
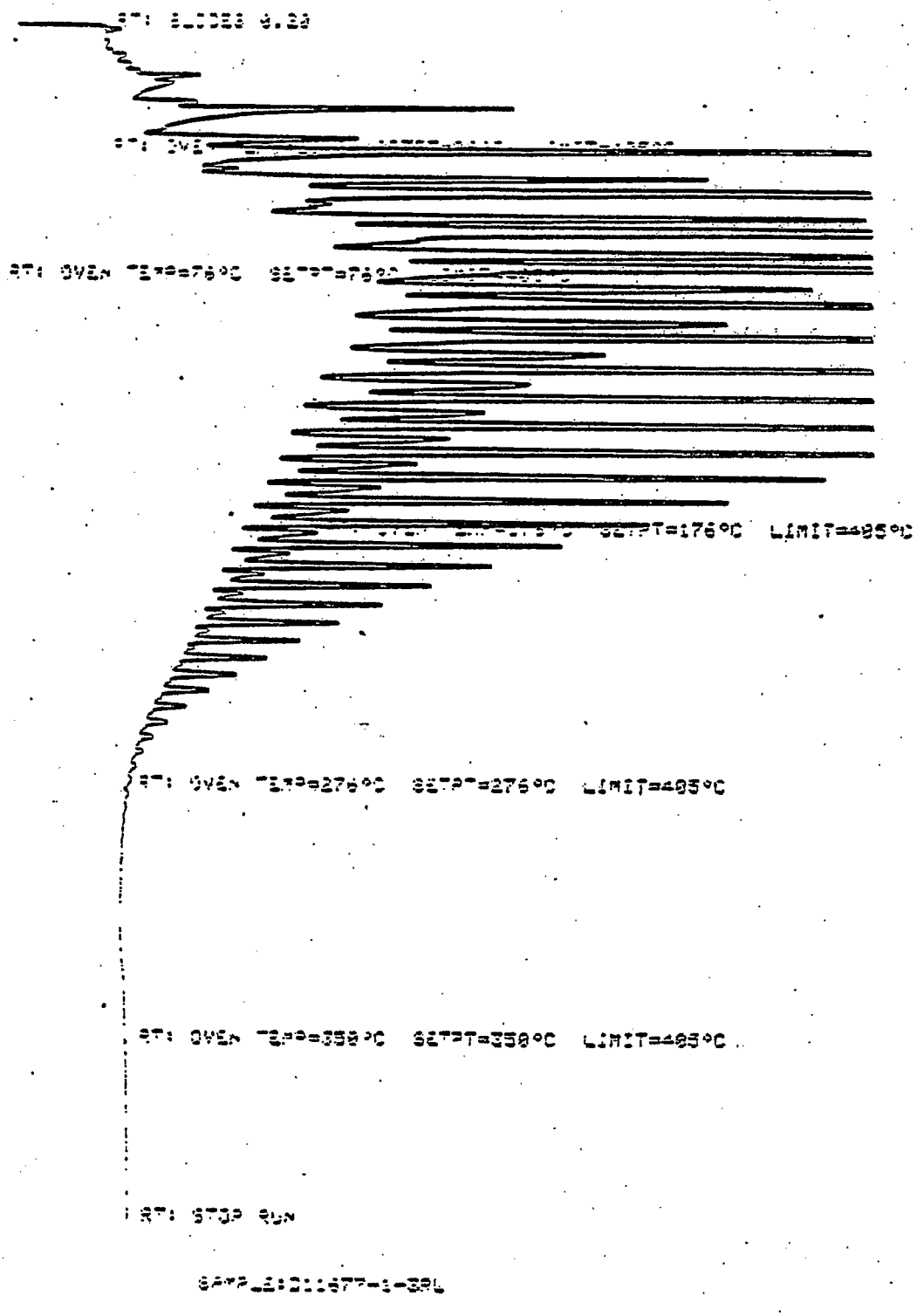

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-01-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 47



- 76 -

Fig. 48


RT: SETPT=176°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

RUN 11677-03

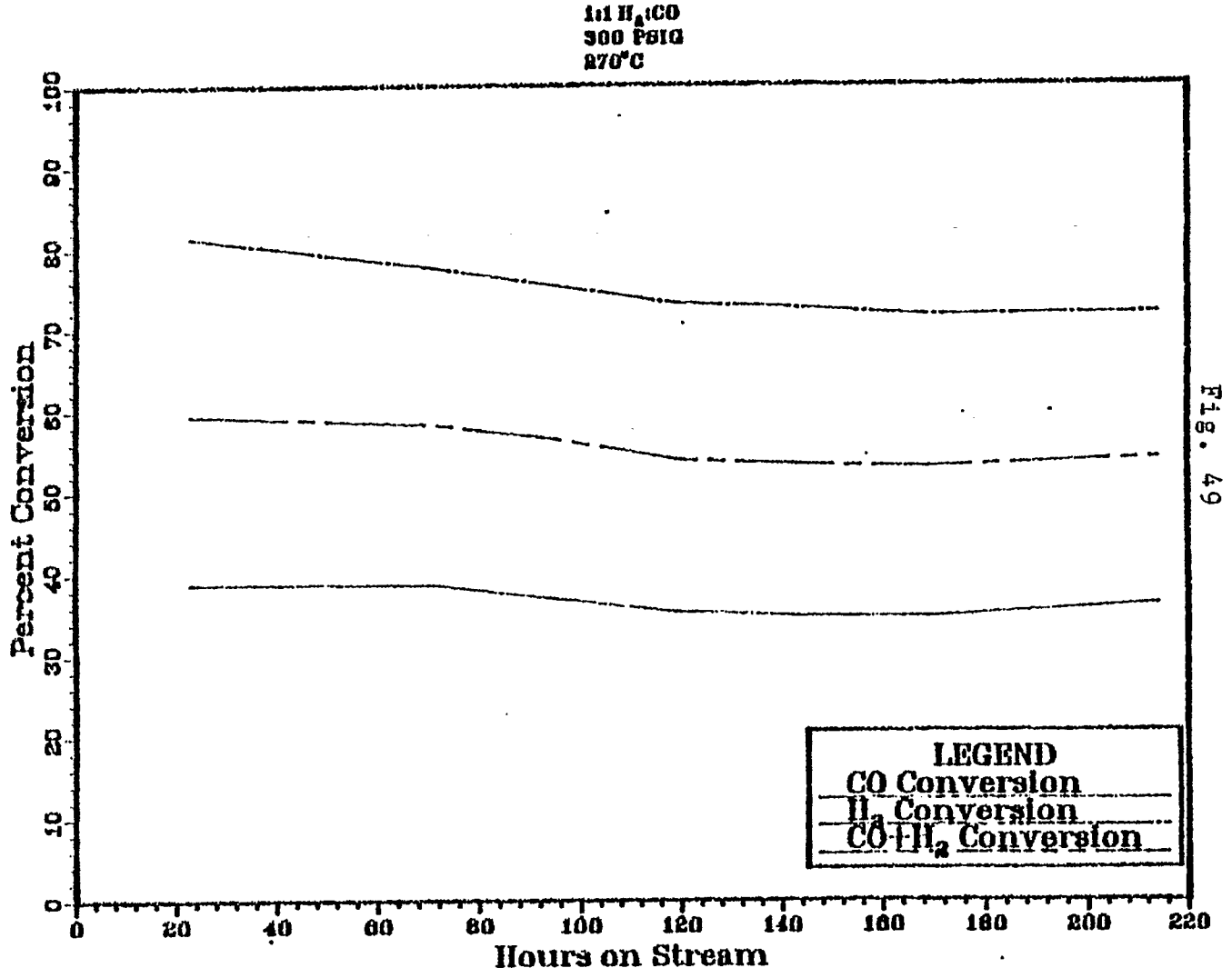


Fig. 49

TABLE 6 RESULT OF SYNGAS OPERATION

RUN NO. 11677-01
CATALYST CO/TH/X6÷UCC-101 11684-3C 80 CC 35.7GM (39.1 AFTER RUN ÷3.4G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	11677-01-01	677-01-02	677-01-03
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.0	23.0	41.0
PRESSURE,PSIG	298	300	306
TEMP. C	275	270	270
FEED CC/MIN	400	400	400
HOURS FEEDING	18.00	6.00	24.00
EFFLNT GAS LITER	239.40	74.60	315.80
GM AQUEOUS LAYER	45.47	14.65	58.60
GM OIL	15.81	4.02	16.10
MATERIAL BALANCE			
GM ATOM CARBON %	108.37	94.22	98.31
GM ATOM HYDROGEN %	100.88	93.58	96.12
GM ATOM OXYGEN %	106.16	96.43	100.31
RATIO CHX/(H2O÷CO2)	1.0648	0.9303	0.9570
RATIO X IN CHX	2.5115	2.4867	2.5081
USAGE H2/CO PRODT	1.9662	2.0095	2.0238
RATIO CO2/(H2O÷CO2)	0.1036	0.0722	0.0711
K SHIFT IN EFFLNT	0.04	0.03	0.03
CONVERSION			
ON CO %	36.69	33.73	32.60
ON H2 %	75.34	70.62	69.59
ON CO÷H2 %	55.32	52.12	50.89
PRDT SELECTIVITY,WT %			
CH4	23.69	22.68	23.75
C2 HC'S	3.55	3.27	3.24
C3H8	2.49	2.33	2.49
C3H6=	3.76	3.64	3.77
C4H10	1.97	1.89	1.99
C4H8=	4.87	4.86	4.97
C5H12	2.20	2.24	2.32
C5H10=	3.69	3.80	3.88
C6H14	3.51	4.15	3.99
C6H12= & CYCLO'S	3.90	4.19	4.30
C7+ IN GAS	12.59	15.22	13.95
LIQ HC'S	33.76	31.73	31.37
TOTAL	100.00	100.00	100.00

SUB-GROUPING			
C1 -C4	40.35	38.67	40.21
C5 -420 F	40.82	43.66	42.33
420-700 F	15.33	14.63	14.47
700-END PT	3.51	3.03	3.00
C5+-END PT	59.65	61.33	59.79
ISO/NORMAL MOLE RATIO			
C4	0.1606	0.1419	0.1313
C5	0.3216	0.2955	0.2585
C6	1.2222	1.2475	1.1515
C4=	0.0667	0.0627	0.0653
PARAFFIN/OLEFIN RATIO			
C3	0.6314	0.6114	0.6288
C4	0.3913	0.3760	0.3865
C5	0.5799	0.5725	0.5808
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))	0.8084		0.8039
RATIO CH4/(1-A)**2	6.4546		6.1745
LIQ HC COLLECTION			
PHYS. APPEARANCE	GRN OIL		GRN OIL
DENSITY	0.767		0.764
N, REFRACTIVE INDEX	1.4312		1.4306
SIMULT'D DISTILATN			
10 WT % @ DEG F	289		291
16	313		317
50	448		447
84	647		641
90	704		695
RANGE(16-84 %)	334		324
WT % @ 420 F	44.20	44.33	44.33
WT % @ 700 F	89.60	90.45	90.45

V. RUN 4 (11677-03) with Catalyst 4 ($Co/Th/X_6$ + UCC-101)

This catalyst, the same as in Run 3 (11677-01), was retested due to mechanical failures in the first trial.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 49-52. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 53-54. Carbon number product distributions are plotted in Figs. 55-60. Chromatograms from simulated distillations are reproduced in Figs. 61-66. Detailed material balances appear in Tables 7-8.

The initial syngas activity was 59 percent, as against 76 percent with the reference catalyst (Run 10112-15). Most of the difference was due to lower CO conversion, resulting in turn from low water gas shift activity, with only about 6 percent of the oxygen having been rejected as CO_2 in contrast to 37-20% for the reference catalyst. Usage of the 1:1 H_2:CO syngas was in a ratio of about 2:1. Because of the back-mixed nature of the Berty reactor, the effective exposure of the catalyst to the syngas was in a ratio of only 0.4:1. Ordinarily, in such a CO-rich environment the catalyst should deactivate quickly, but this catalyst proved remarkably stable, much more so than the reference catalyst (10112-15). From the initial level of 59 percent and after more than 200 hours on stream, its conversion had dropped to only

54 percent; conversion of the reference catalyst, by contrast, in a little less time on stream dropped from 76 to 52 percent. After only 40 hours on stream this catalyst was more active than the reference catalyst.

The selectivity was generally rather good; more significantly, it was relatively very stable throughout the run. Methane production, initially 14 percent, rose after nearly 200 hours on stream to less than 18 percent; with the reference catalyst, in contrast, the corresponding values were 15 and 24 percent. In about the same time on stream, therefore, this catalyst's rate of methane production rose less than half as rapidly as that of the reference catalyst, and its total production of methane was some 26 percent lower.

Production of C_2-C_4 was also initially lower than with the reference catalyst, and remained lower throughout the run; thus the yield of C_5^+ was substantially higher. Since the wax yield was only 5 to 6 percent, the selectivity for total motor fuels is exceptionally good--69 percent initially, the same as with the reference catalyst, but falling only to 62 percent by the end of the run as against 55 percent with the reference catalyst. What sets this catalyst apart, in short, is not merely its better-than-average selectivity, but its stability over time. If run at a slightly lower temperature, both its selectivity and stability may possibly be still further improved.

The total motor fuel fraction consists, by calculation with a 420F gasoline cut point, of approximately two parts gasoline to

one part diesel fuel. If the cut between gasoline and diesel fuel is made at 300F (a reasonable starting point for diesel fuel), then this catalyst produces more diesel fuel than gasoline. The yield of heavies is low, as it was for the reference catalyst; the liquid product of this catalyst, however, is all liquid, while that of the reference contained solid hydrocarbons. The difference is quantified in the pour points of the heavier fractions. The jet fuel from this catalyst has a pour point of -5F, as against ØF for the reference catalyst; the pour points of the diesel fractions from both catalysts are the same at about 50F. These values suggest that the heavies from this catalyst may be less waxy than those from the reference. Isomerization of the hydrocarbons does not seem to be the cause; both this catalyst and the reference have similar isopentane yields, and the chromatograms from the simulated distillations show that the liquid product is not highly isomerized. All major fractions of the product from this catalyst are more olefinic than those from the reference catalyst: the C_4 being slightly more olefinic; the gasoline fraction having 46 percent olefins as against 36 percent; and the jet fuel fraction containing 45 percent olefins as against 32 percent. Up to about Sample 11 the Schulz-Flory plots show a possible carbon number cut-off, but since it does not appear thereafter it may or not be real.

This catalyst is especially promising by reason of its relatively low yield of methane, its high yield of olefins, and its exceptional stability.

Fig. 50

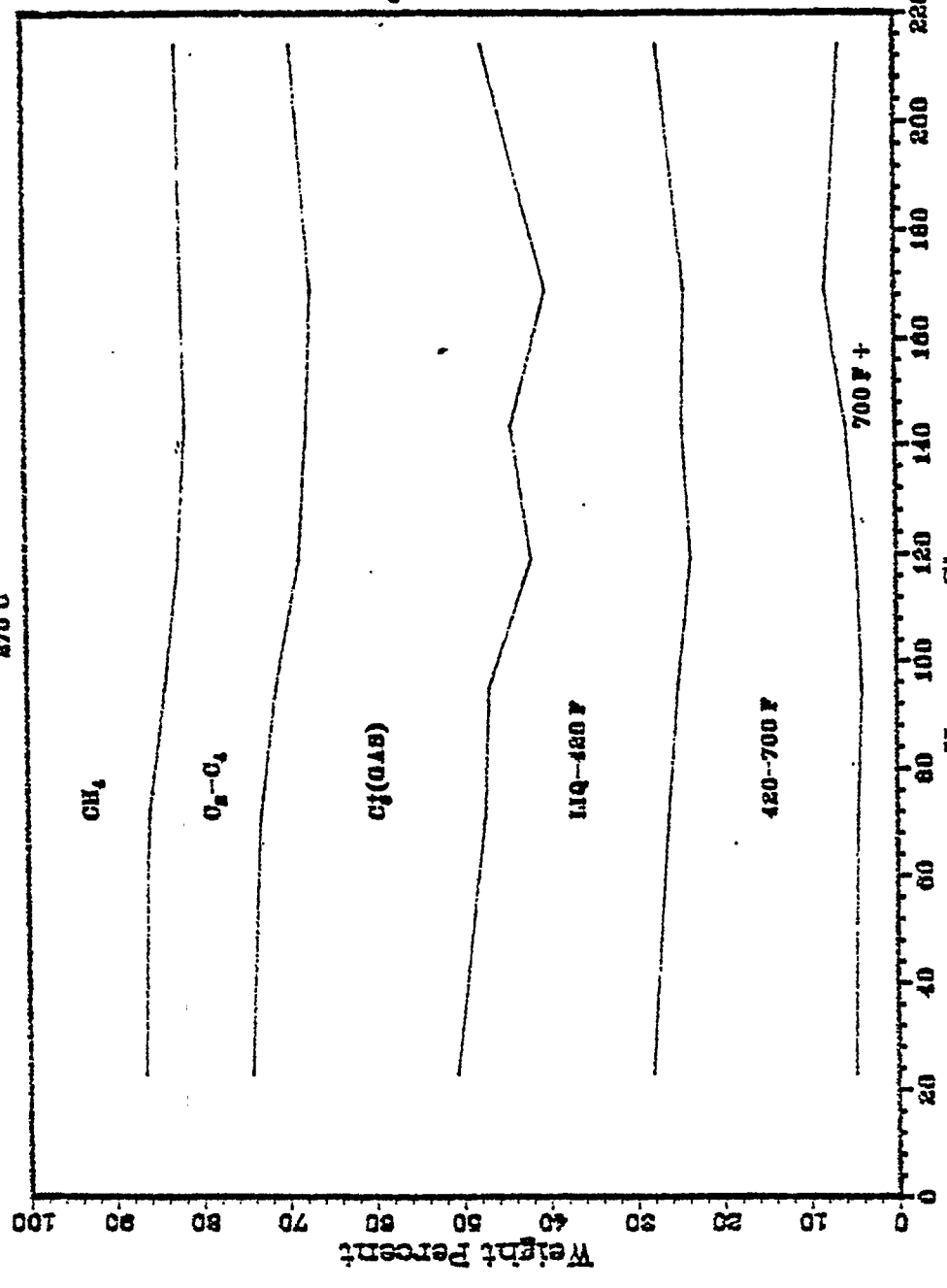

RUN 11677-03
1:1 H2:CO
300 PSIG
270°C
CH4
C2-C4
C5(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220

Fig. 51

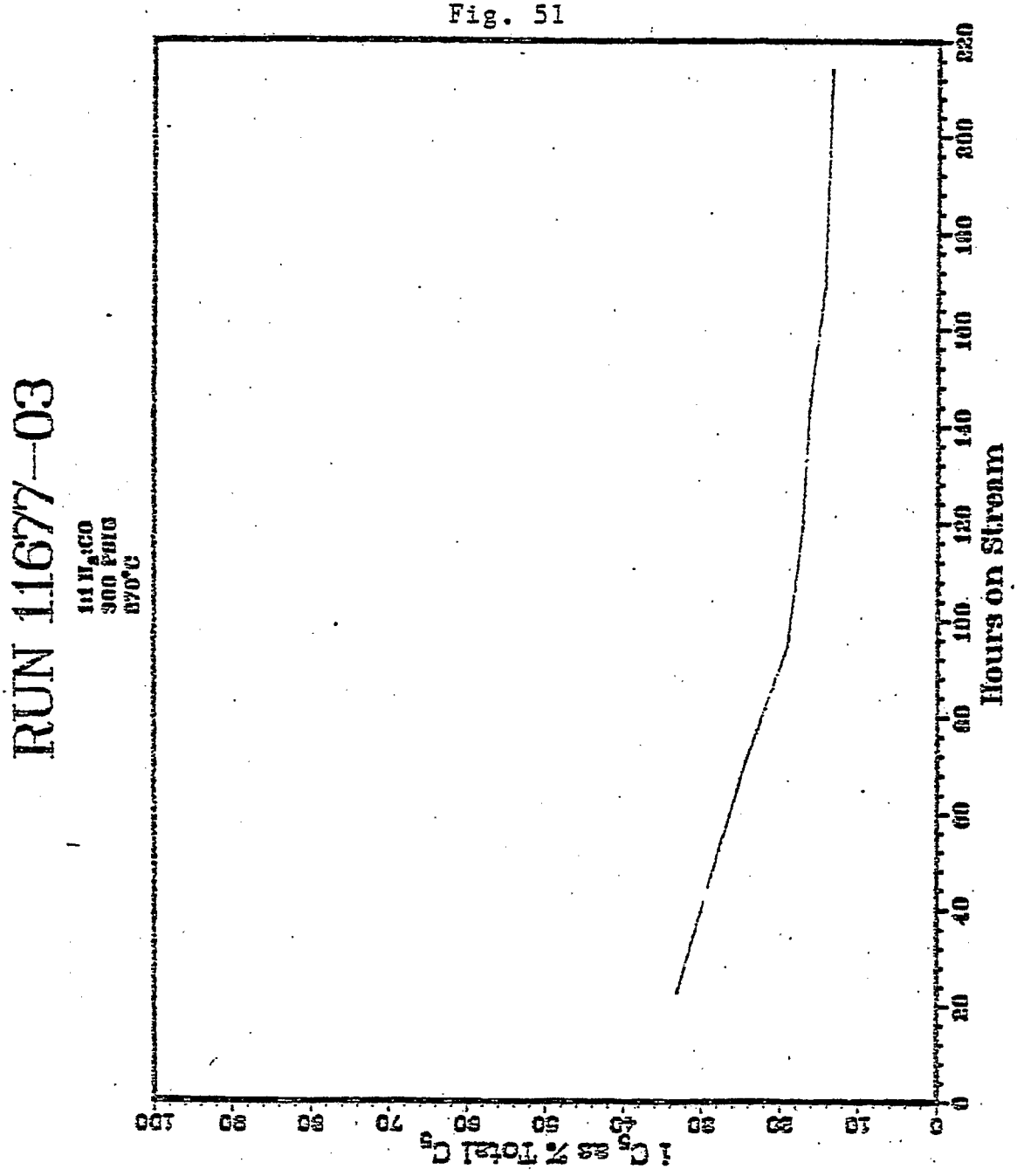

RUN 11677-03
111 Hg:CO
900 PSIG
870°C
i C5 as % Total C5
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220

Fig. 52

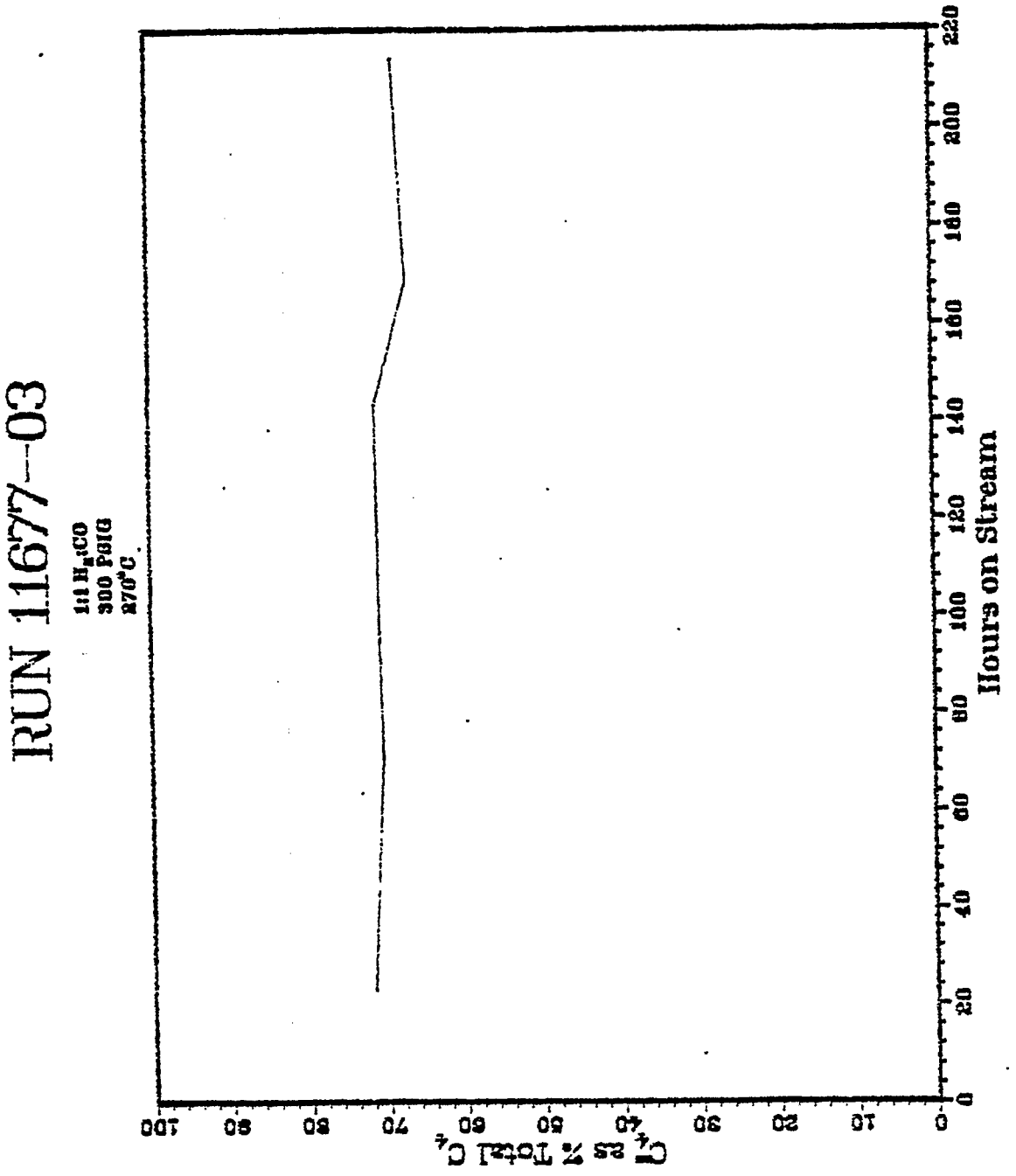

RUN 11677--03
1:1 H2:CO
300 PSIG
270°C
C4 as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
10
20
30
40
50
60
70
80
90
100

Fig. 53

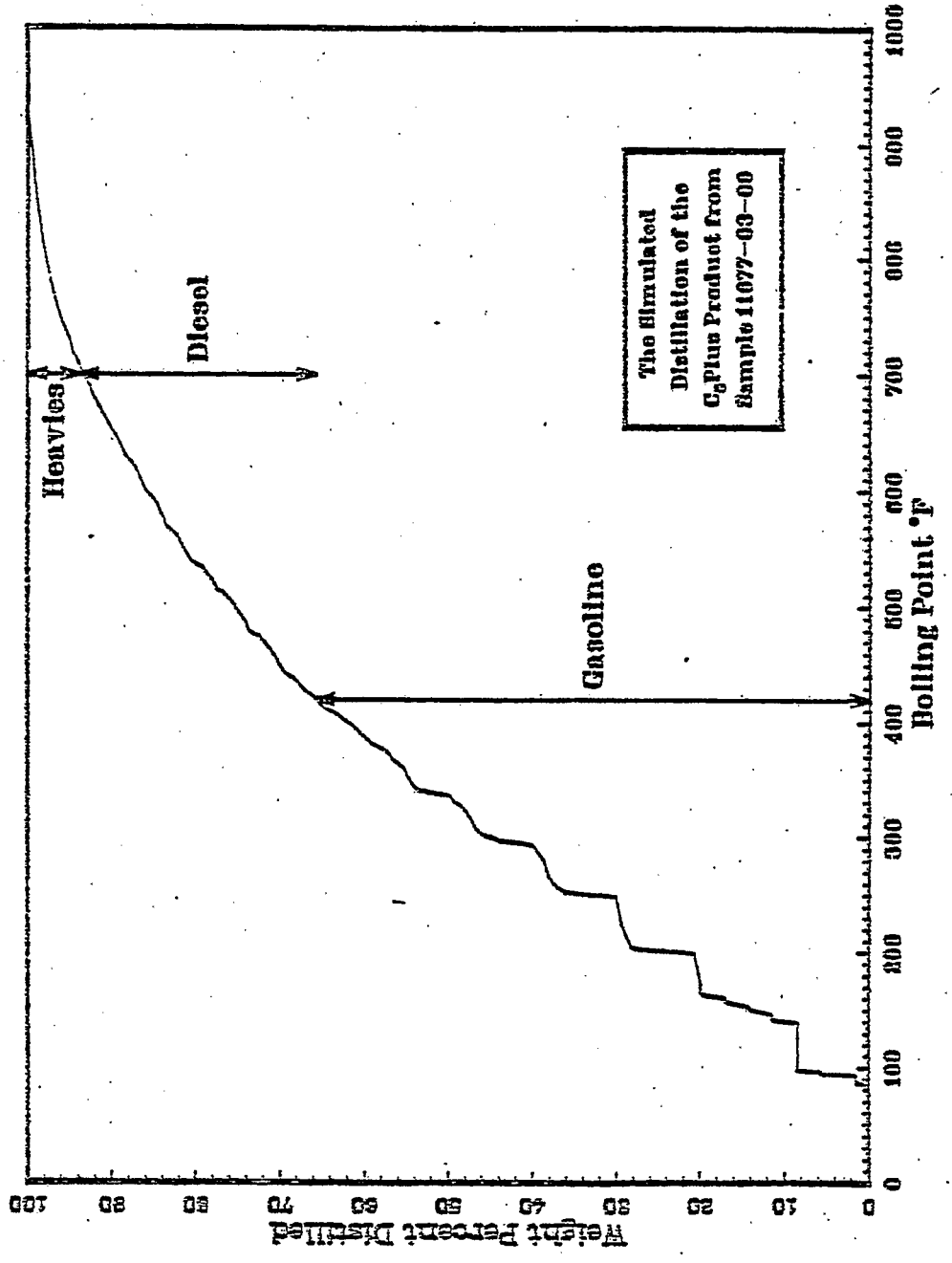

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11077-03-00

Fig. 54

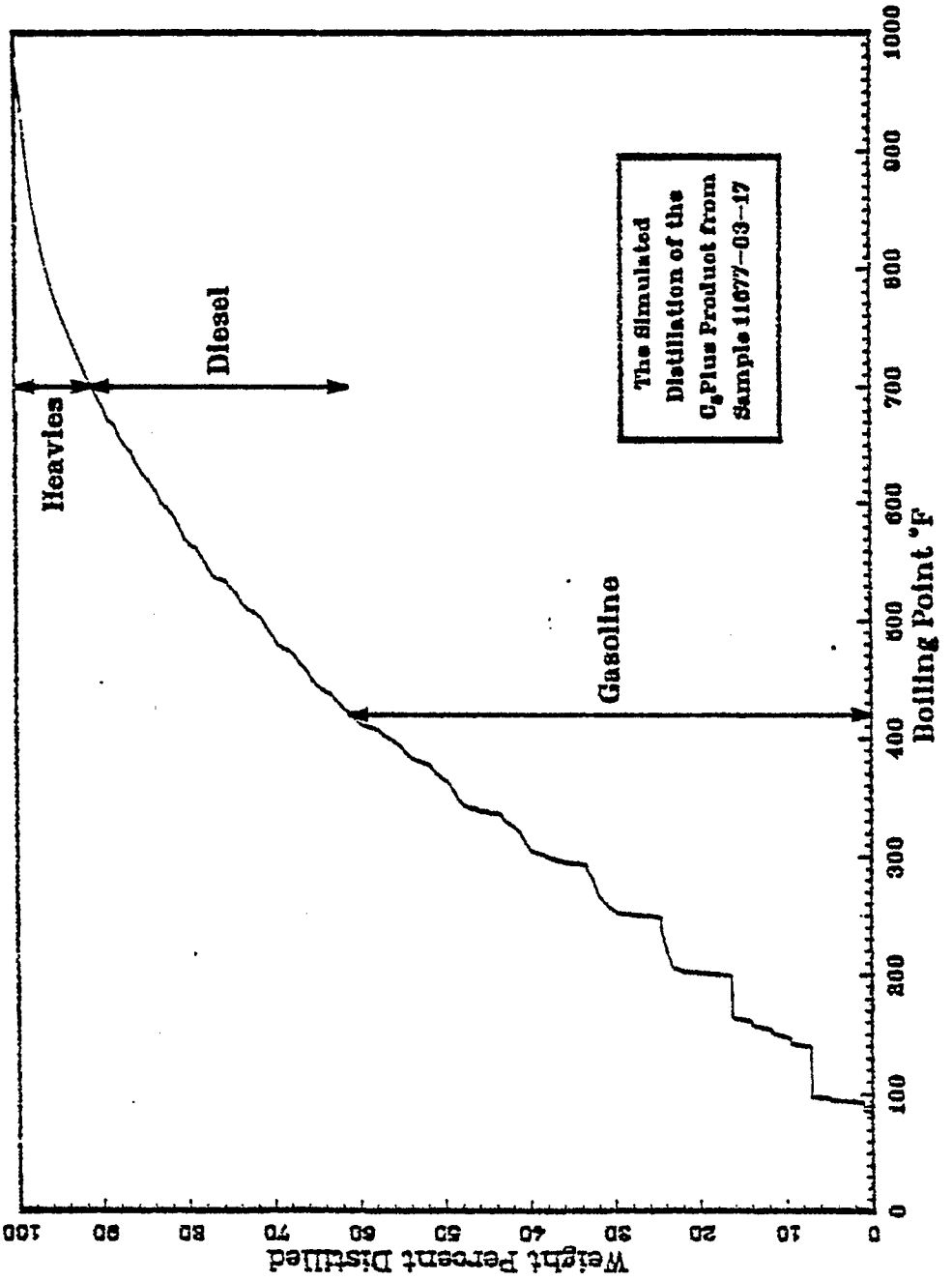

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-03-17
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 55

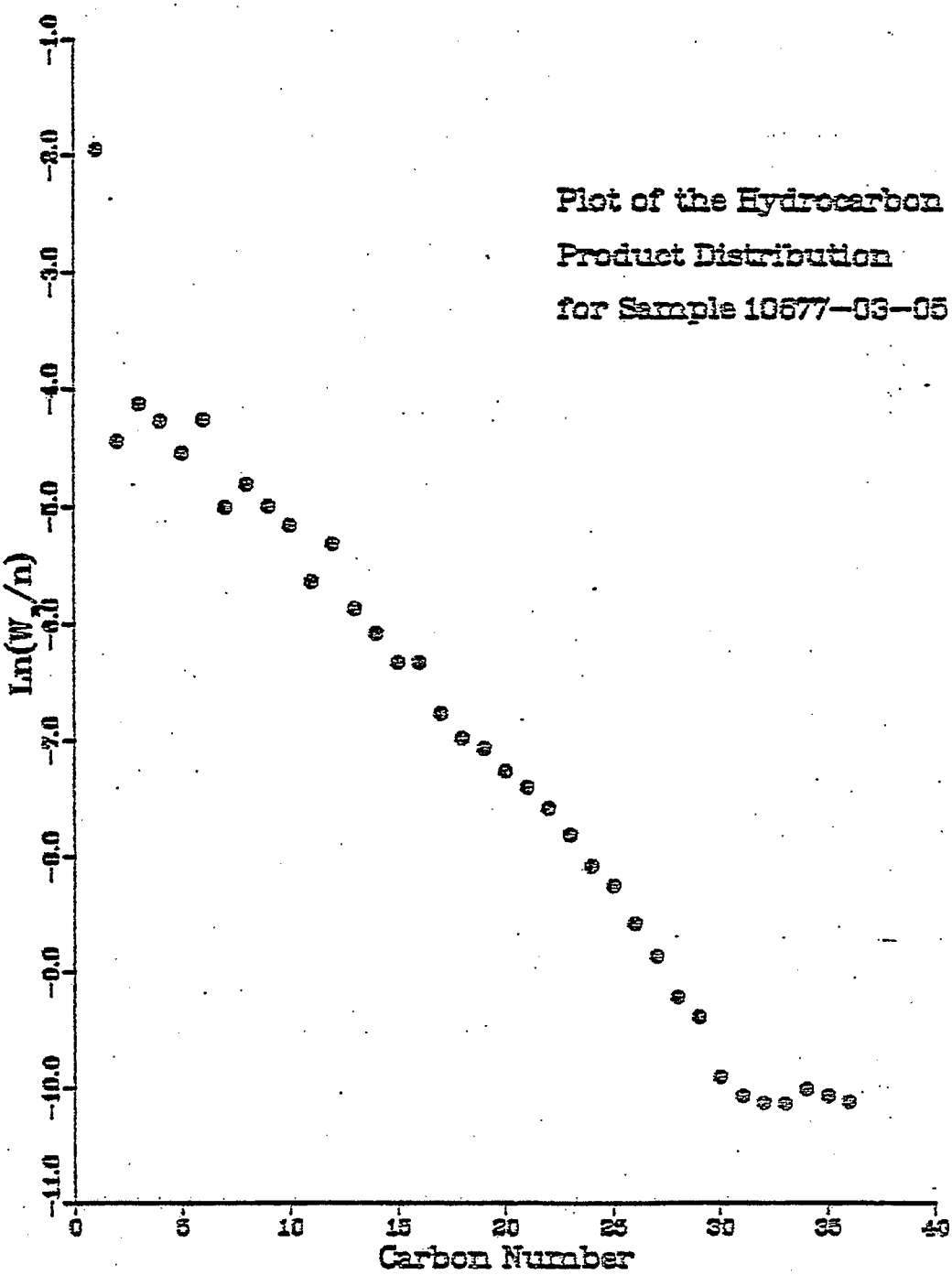

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 56

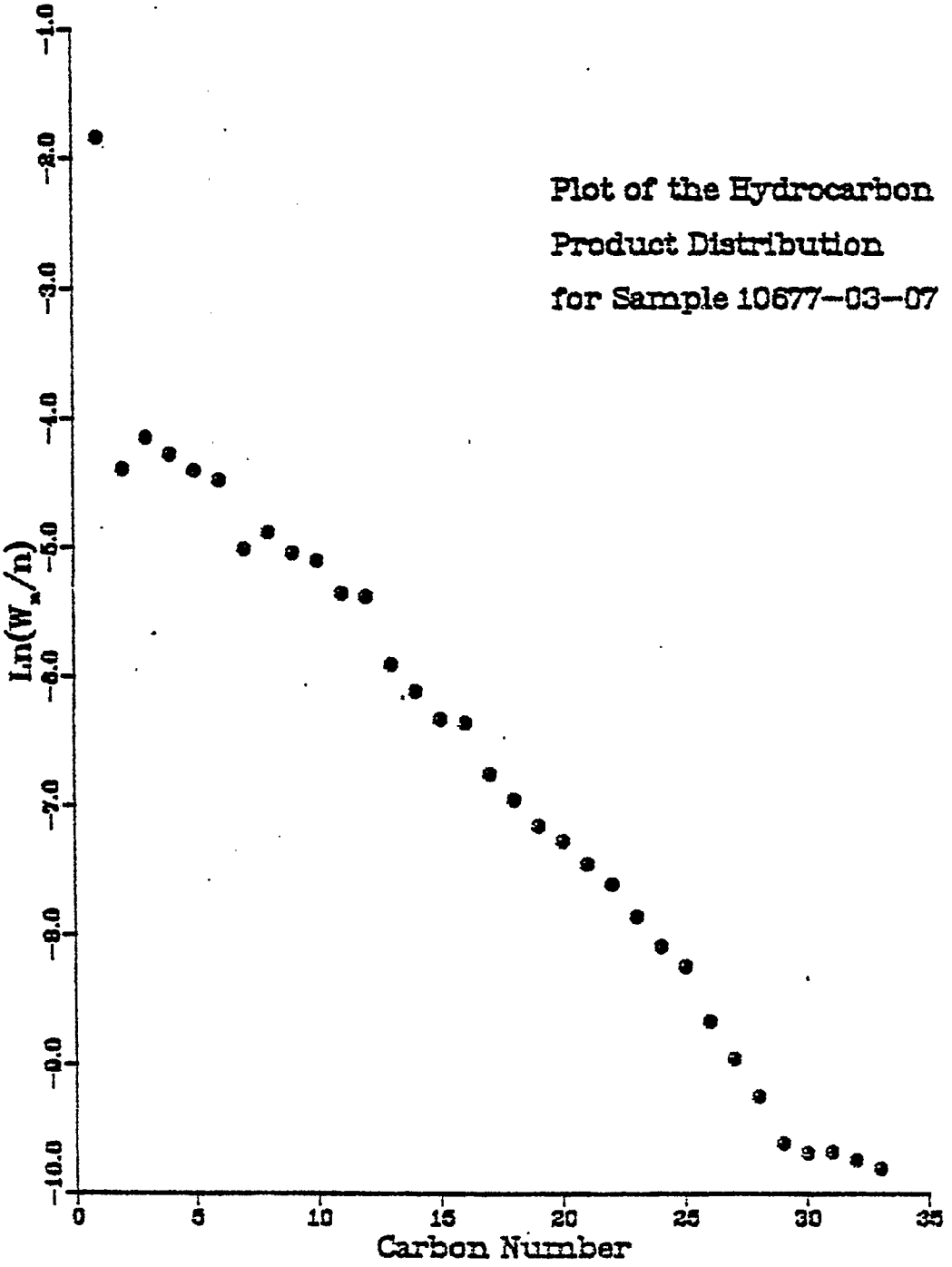

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 57

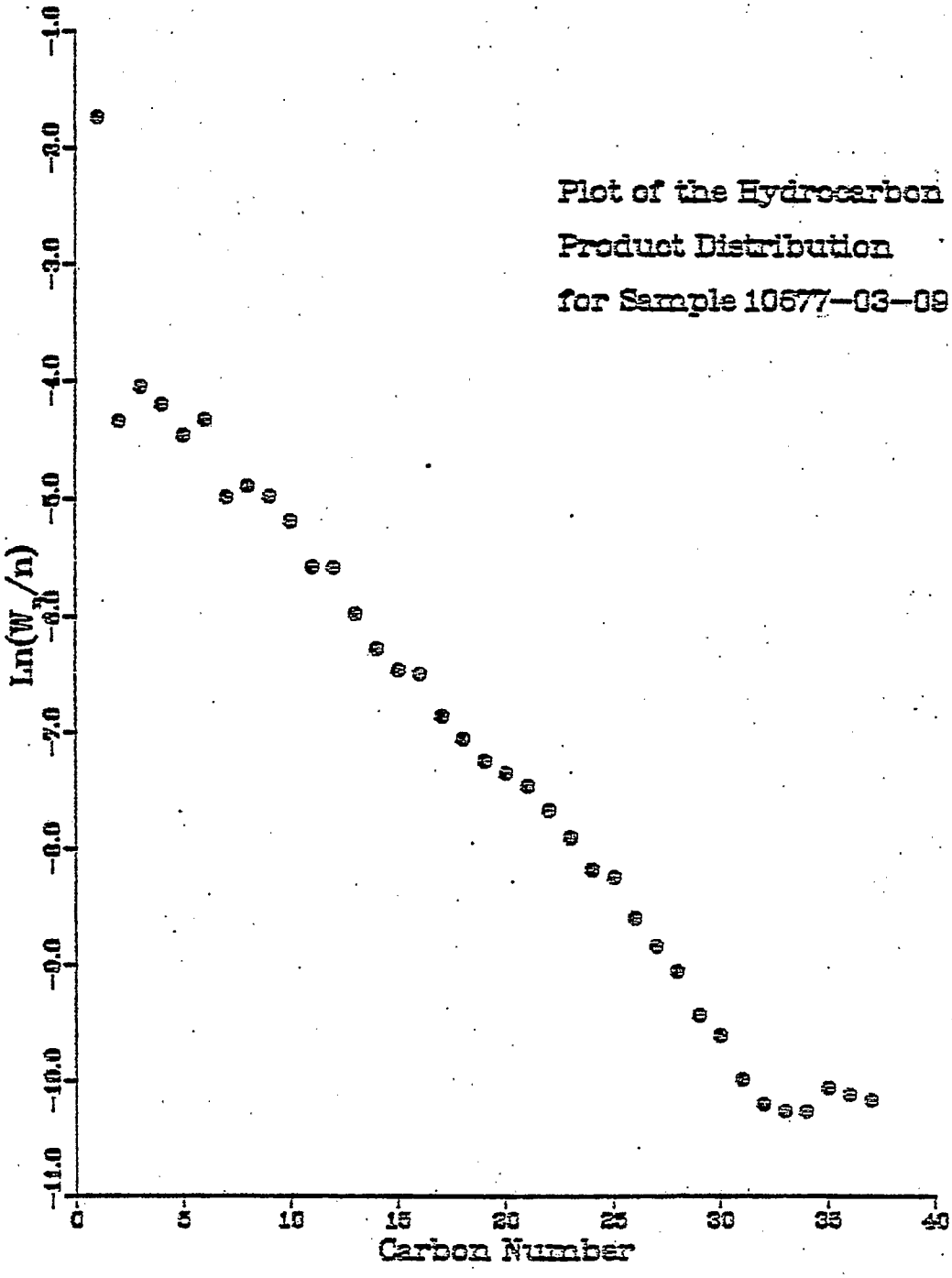

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 58

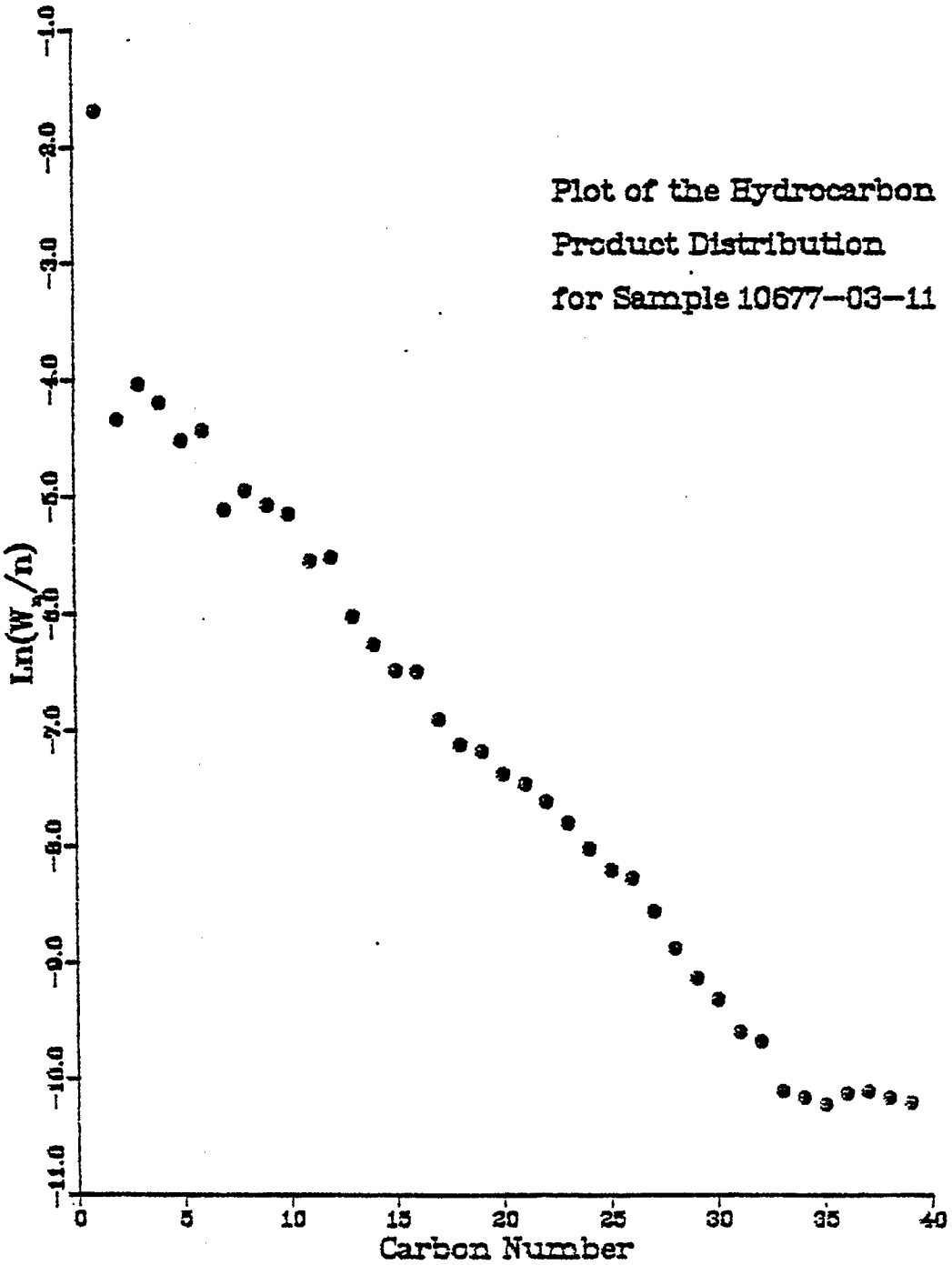

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 59

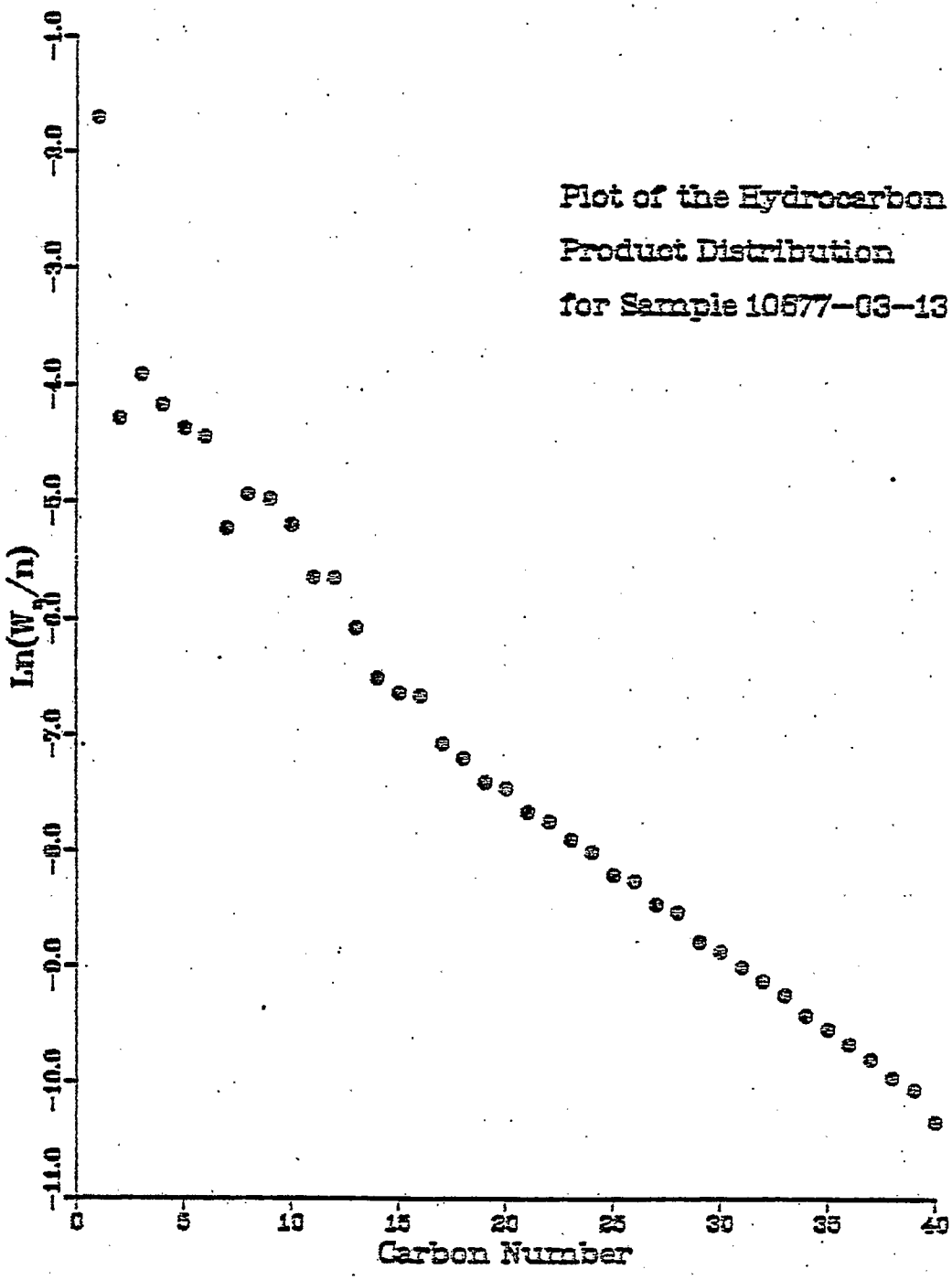

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 60

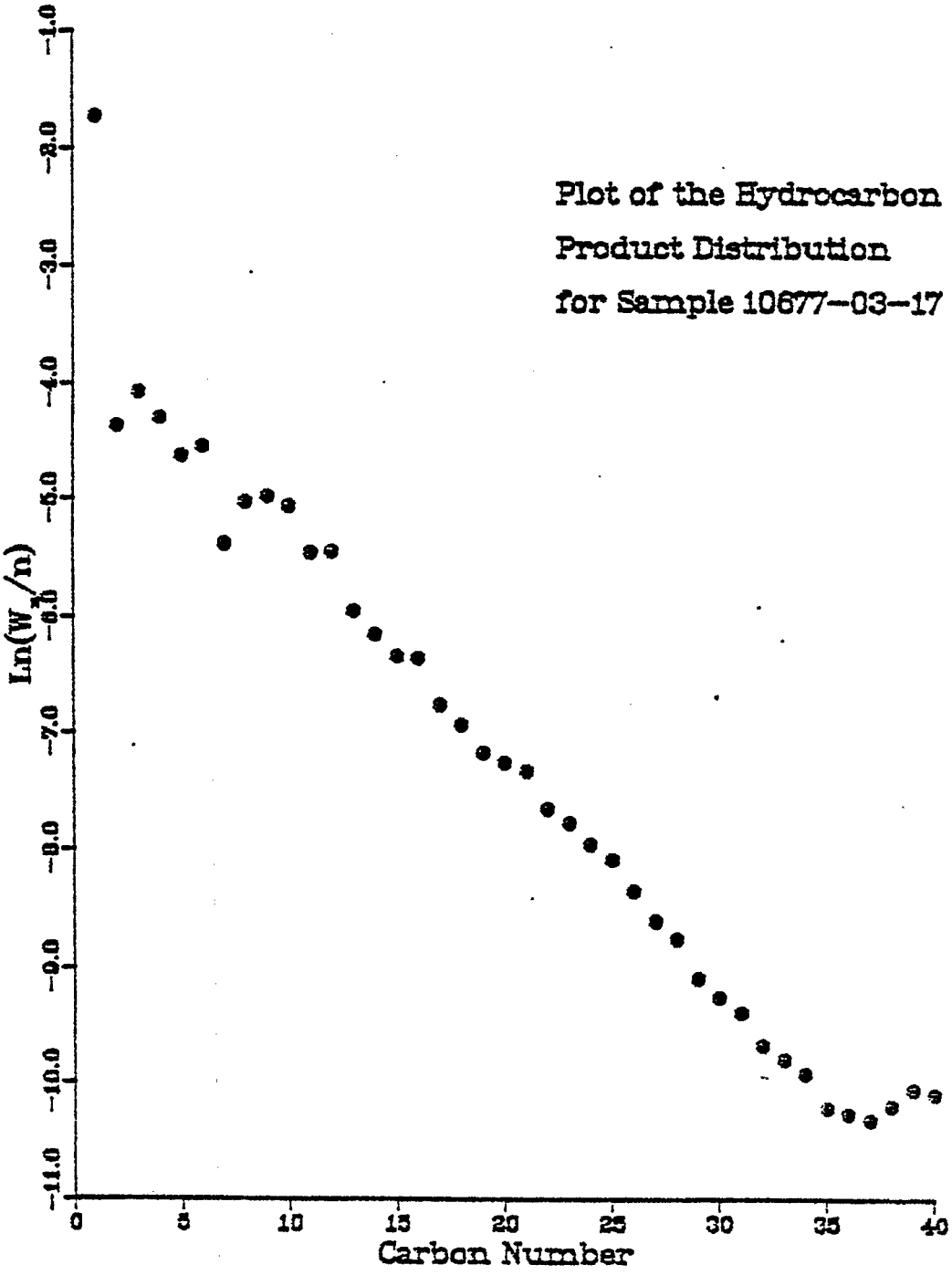

Plot of the Hydrocarbon
Product Distribution
for Sample 10677-03-17
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 61

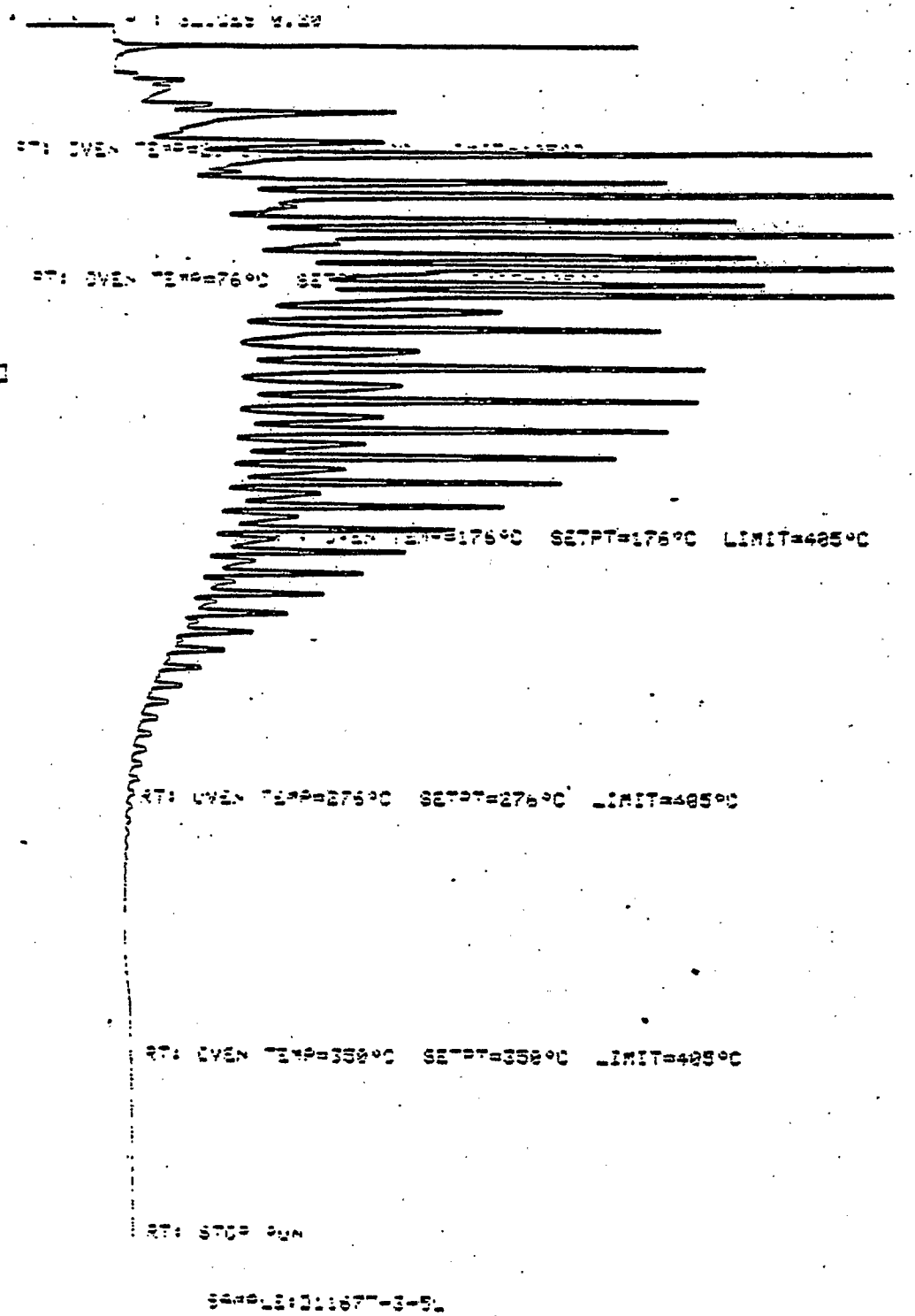

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=352°C SETPT=352°C LIMIT=405°C
RT: STOP RUN

Fig. 62

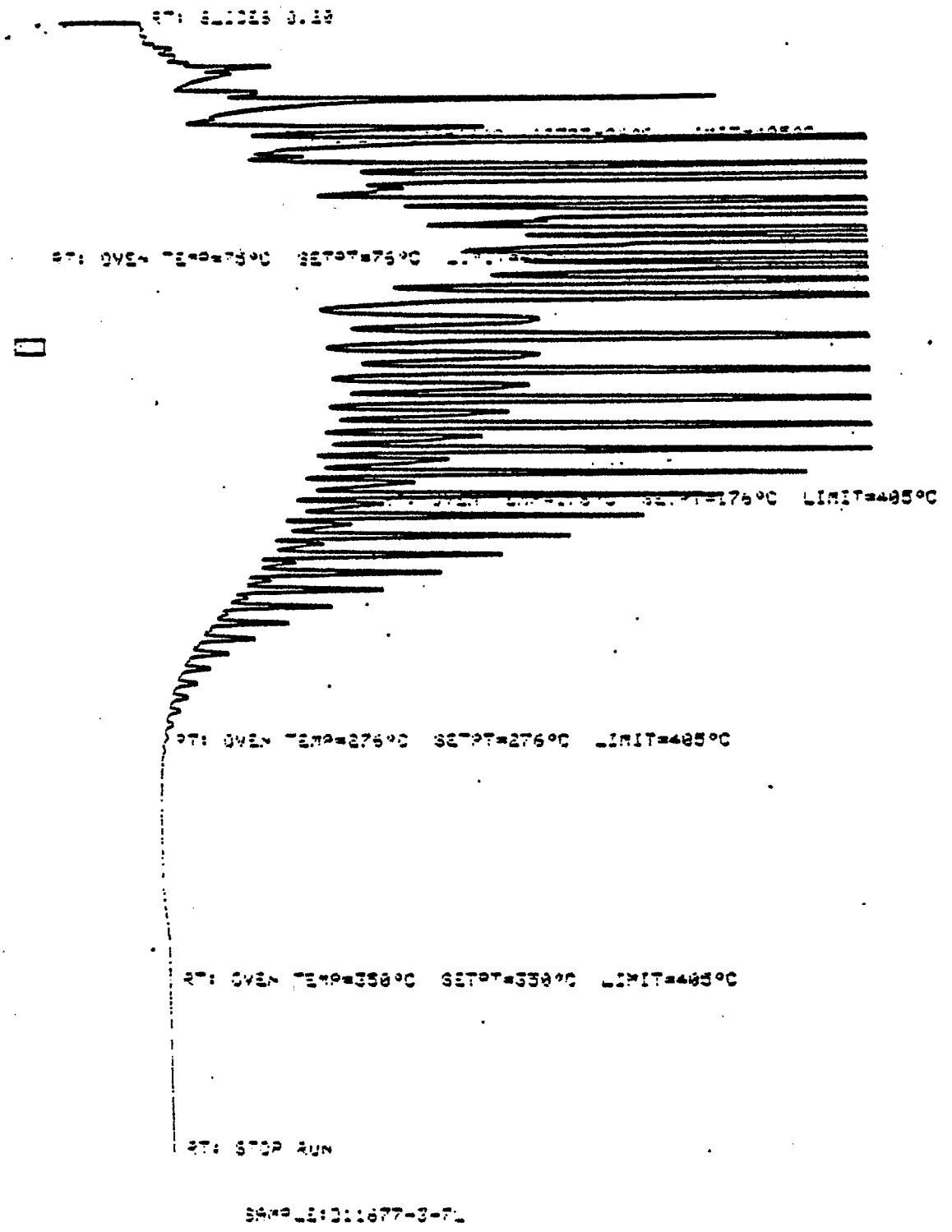


Fig. 63

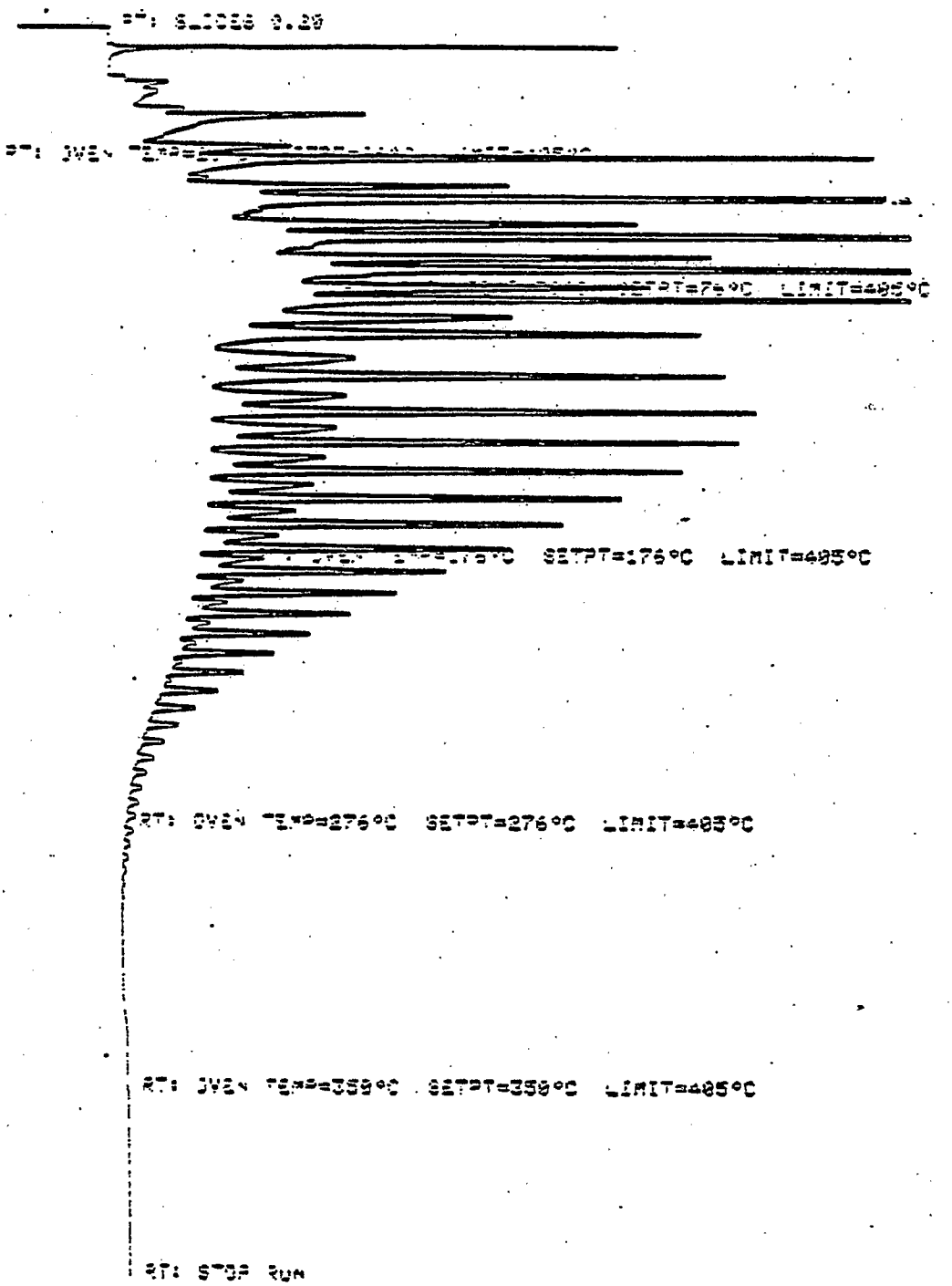

SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=359°C SETPT=359°C LIMIT=405°C
RT: STOP RUN

Fig. 64

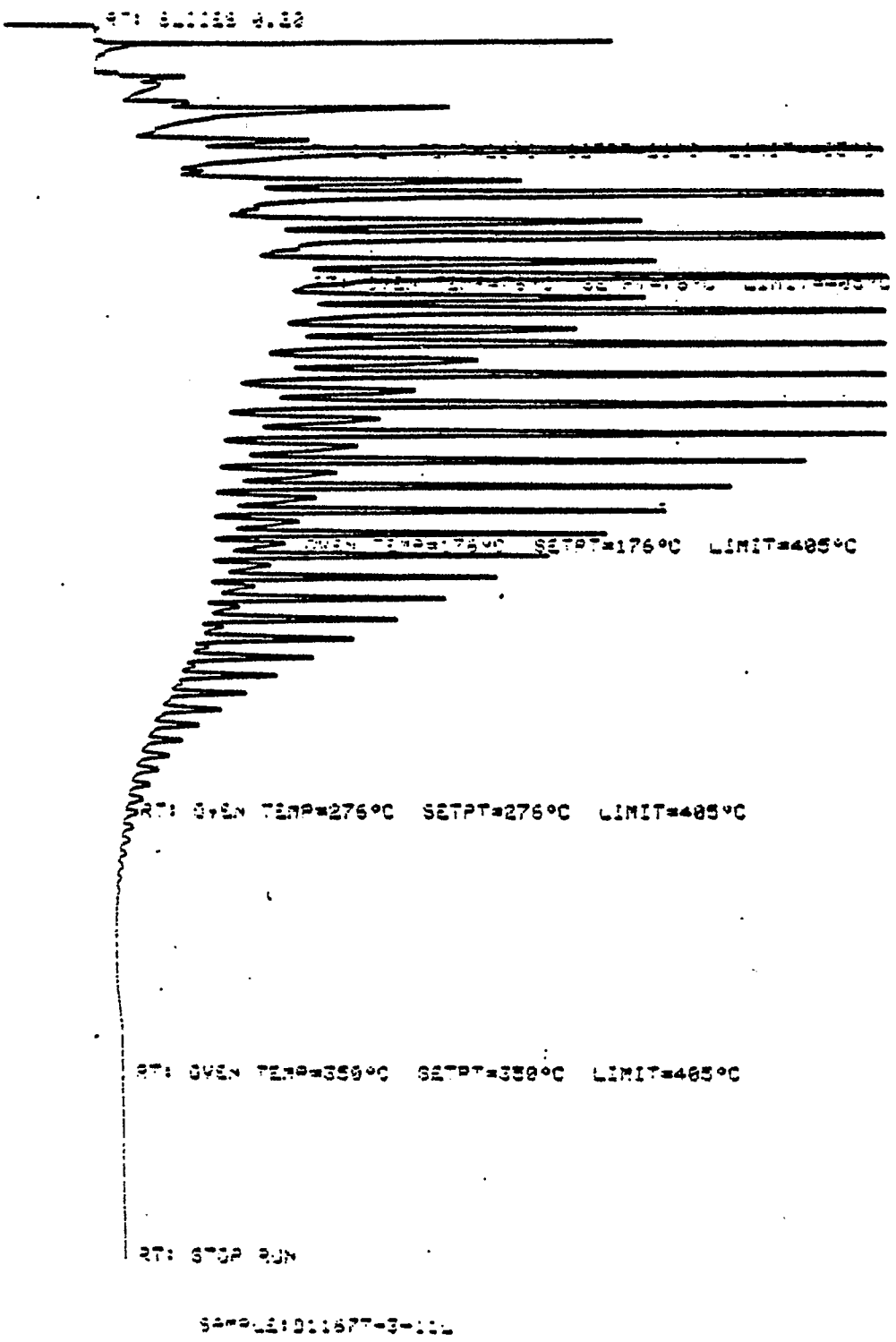

SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: STOP RUN

Fig. 65

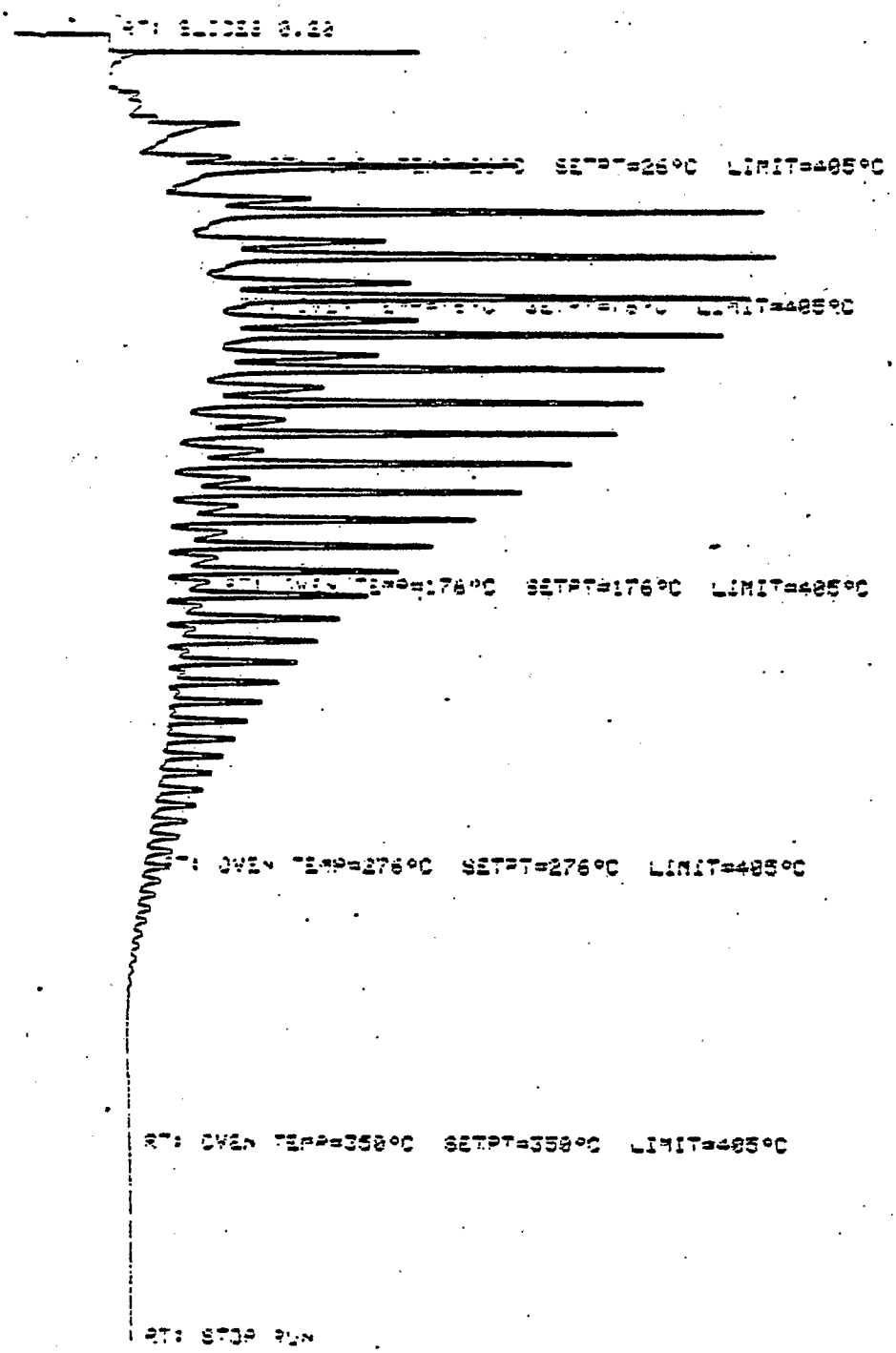

SETPT=26°C LIMIT=405°C
SETPT=176°C LIMIT=405°C
SETPT=276°C LIMIT=405°C
SETPT=350°C LIMIT=405°C

Fig. 6.6

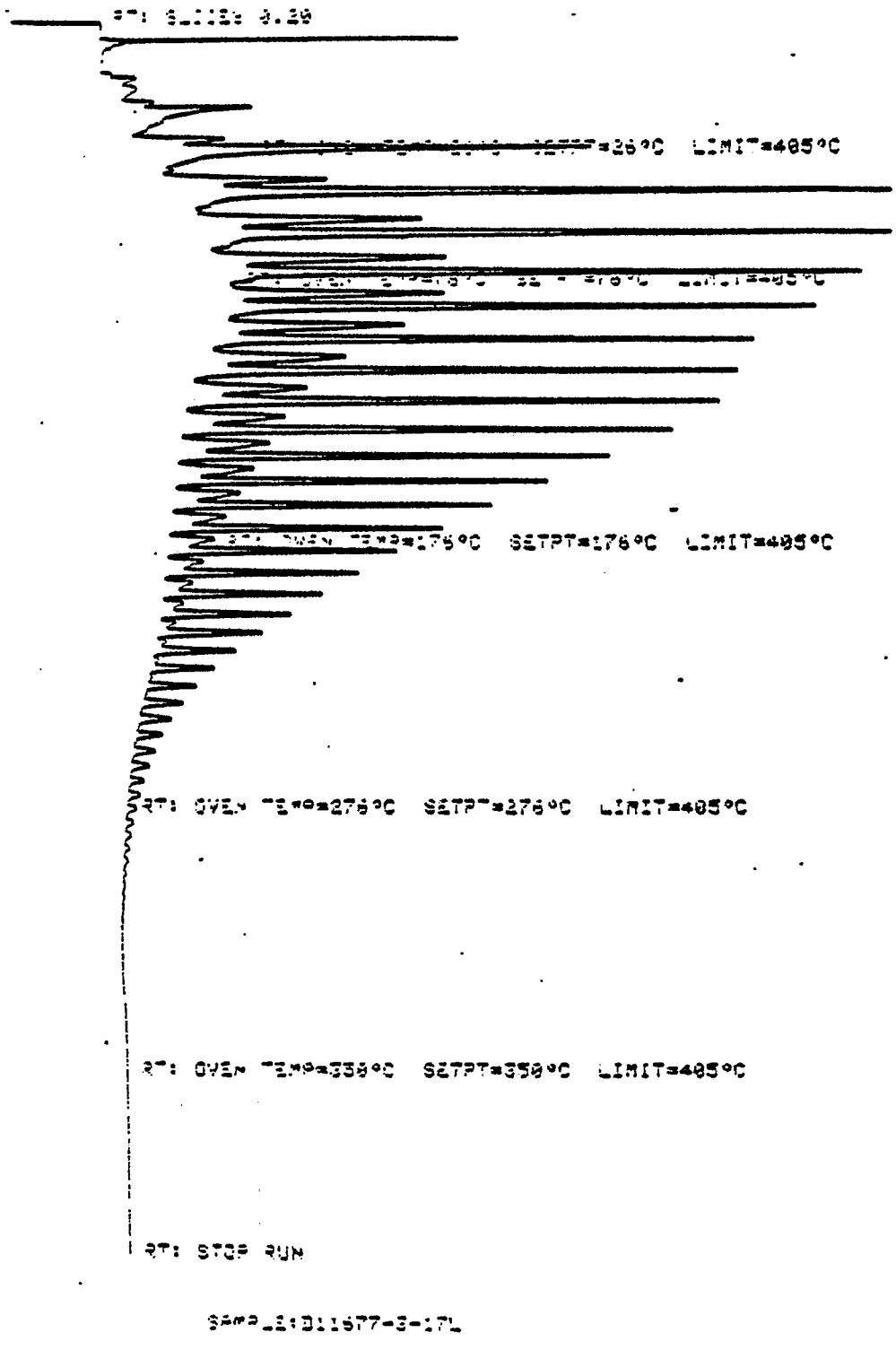

RT: SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

TABLE 7 RESULT OF SYNGAS OPERATION

RUN NO. 11677-03
CATALYST CO/TH/X6 +UCC-101 11684-3C 80CC 35.8GM (38.6 AFTER RUN +2.6G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-03-01	677-03-05	677-03-07	677-03-09	677-03-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	23.0	70.9	94.9	118.9	143.4
PRESSURE,PSIG	295	297	297	293	301
TEMP. C	272	271	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	23.00	23.00	24.00	24.00	24.50
EFFLNT GAS LITER	209.30	249.70	275.00	284.95	296.20
GM AQUEOUS LAYER	59.13	65.52	69.17	58.07	59.23
GM OIL	23.83	26.40	26.50	22.83	24.36
MATERIAL BALANCE					
GM ATOM CARBON %	82.63	94.04	94.89	95.73	96.51
GM ATOM HYDROGEN %	78.23	95.23	97.80	92.48	93.04
GM ATOM OXYGEN %	87.17	95.79	97.92	94.93	96.12
RATIO CHX/(H2O+CO2)	0.8643	0.9514	0.9165	1.0259	1.0123
RATIO X IN CHX	2.3018	2.3503	2.3853	2.4191	2.4342
USAGE H2/CO PRODT	1.8562	1.9844	2.0136	2.0225	2.0185
RATIO CO2/(H2O+CO2)	0.0926	0.0609	0.0543	0.0636	0.0667
K SHIFT IN EFFLNT	0.03	0.02	0.02	0.03	0.03
CONVERSION					
ON CO %	38.72	38.68	37.01	35.34	34.85
ON H2 %	81.30	77.62	75.41	73.11	72.54
ON CO+H2 %	59.43	58.27	56.50	53.90	53.35
PROT SELECTIVITY,WT %					
CH4	13.56	14.14	16.03	17.70	18.58
C2 HC'S	2.12	2.35	2.49	2.62	2.62
C3H8	1.85	1.99	1.99	2.20	2.20
C3H6=	2.74	2.87	2.76	3.03	3.11
C4H10	1.59	1.70	1.66	1.79	1.78
C4H8=	3.94	3.90	3.88	4.21	4.24
C5H12	2.07	2.05	2.02	2.20	2.06
C5H10=	3.22	3.28	4.10	3.56	3.38
C6H14	3.69	3.63	3.36	3.99	3.50
C6H12= & CYCLO'S	3.34	4.85	3.46	3.92	3.65
C7+ IN GAS	11.23	11.97	11.46	12.93	10.76
LIQ HC'S	50.65	47.29	46.79	41.85	44.12
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	25.80	26.94	28.81	31.55	32.53
C5 -420 F	46.14	46.86	46.07	44.95	43.03
420-700 F	23.25	21.70	21.13	19.01	18.82
700-END PT	4.81	4.49	3.98	4.50	5.63
C5+-END PT	74.20	73.06	71.19	68.45	67.47
ISO/NORMAL MOLE RATIO					
C4	0.2716	0.1913	0.1453	0.1272	0.1092
C5	0.4937	0.3226	0.2364	0.2085	0.1966
C6	1.7074	1.2078	1.0986	1.0447	0.9495
C4=	0.0533	0.0631	0.0634	0.0625	0.0616
PARAFFIN/OLEFIN RATIO					
C3	0.6435	0.6638	0.6895	0.6912	0.6770
C4	0.3908	0.4198	0.4125	0.4097	0.4061
C5	0.6249	0.6082	0.4788	0.6016	0.5933
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8188	0.8180	0.8208	0.8314
RATIO CH4/(1-A)**2		4.3060	4.8372	5.5158	6.5387
LIQ HC COLLECTION					
PHYS. APPEARANCE	GRN OIL	CLDY OIL	GRN OIL	CLDY OIL	CLDY OIL
DENSITY		0.765	0.765	0.765	0.768
N, REFRACTIVE INDEX		1.4300	1.4294	1.4306	1.4311
SIMULT'D DISTILATN					
10 WT % @ DEG F		282	285	287	285
16		304	306	308	305
50		444	434	444	443
84		645	633	654	671
90		695	685	709	730
RANGE(16-84 %)		341	327	346	366
WT % @ 420 F	44.60	44.60	46.33	43.83	44.60
WT % @ 700 F	90.50	90.50	91.50	89.25	87.25

TABLE 8 RESULT OF SYNGAS OPERATION

RUN NO. 11677-03
CATALYST CO/TH/X6 +UCC-101 11684-3C 80CC 35.8GM (38.6 AFTER RUN +2.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11677-03-13	677-03-17
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	168.8	214.1
PRESSURE,PSIG	304	303
TEMP. C	270	270
FEED CC/MIN	400	400
HOURS FEEDING	25.42	22.25
EFFLNT GAS LITER	295.41	269.76
GM AQUEOUS LAYER	58.80	53.55
GM OIL	21.81	25.07
MATERIAL BALANCE		
GM ATOM CARBON %	91.57	97.09
GM ATOM HYDROGEN %	89.64	96.58
GM ATOM OXYGEN %	91.15	94.29
RATIO CHX/(H2O+CO2)	1.0142	1.0914
RATIO X IN CHX	2.4274	2.4189
USAGE H2/CO PRODT	2.0369	2.0560
RATIO CO2/(H2O+CO2)	0.0592	0.0556
K SHIFT IN EFFLNT	0.03	0.03
CONVERSION		
ON CO %	34.69	36.25
ON H2 %	71.71	71.93
ON CO+H2 %	53.00	54.04
PRDT SELECTIVITY,WT %		
CH4	18.17	17.78
C2 HC'S	2.75	2.54
C3H8	2.51	2.20
C3H6=	3.51	2.91
C4H10	2.10	1.75
C4H8=	4.10	3.69
C5H12	1.93	1.78
C5H10=	4.38	3.09
C6H14	3.61	3.24
C6H12= & CYCLO'S	3.46	3.13
C7+ IN GAS	13.43	10.74
LIQ HC'S	40.04	47.16
TOTAL	100.00	100.00

SUB-GROUPING		
C1 -C4	33.14	30.86
C5 -420 F	42.76	42.07
420-700 F	16.18	20.85
700-END PT	7.92	6.23
C5+-END PT	66.86	69.14
ISO/NORMAL MOLE RATIO		
C4	0.1471	0.1122
C5	0.1678	0.1561
C6	1.0217	1.0011
C4=	0.0687	0.0706
PARAFFIN/OLEFIN RATIO		
C3	0.6824	0.7207
C4	0.4937	0.4593
C5	0.4282	0.5622
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8457	0.8361
RATIO CH4/(1-A)**2	7.6346	6.6188
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL SLD	OIL SLD
DENSITY	0.761	0.763
N, REFRACTIVE INDEX	1.4338	1.4311
SIMULT'D DISTILATN		
10 WT % @ DEG F	296	295
16	326	321
50	474	457
84	737	672
90	809	734
RANGE(16-84 %)	411	351
WT % @ 420 F	39.83	42.60
WT % @ 700 F	80.23	86.80

VI. RUN 5 (10112-21) with Catalyst 5 (Co/X_7 + UCC-101)

This catalyst continues the series of metal additive tests. The metal component (MC) was prepared by precipitating a 1:1 weight solution of cobalt and additive X_7, physically mixing the MC with Molecular Sieve (UCC-101) in a 3:14 weight ratio, bonding with 15 weight percent silica, forming as 1/8" extrudates, and calcining in air at 250C. The resulting mixture consisted of cobalt/X_7:UCC-101:silica in a weight ratio of 15:70:15.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 67-70. A simulated distillation of the C_5^+ product is plotted in Fig. 71. A carbon number product distribution is plotted in Fig. 72, and the chromatogram from a simulated distillation is reproduced in Fig. 73. Detailed material balances appear in Table 9.

The activity of this catalyst was very low, almost nil. Its water gas shift activity was sufficient to match the low Fischer-Tropsch activity. Selectivity was poor as well, with only about 30 percent of the product as C_5^+.

This is an ineffective catalyst, with no apparent advantages over the reference catalyst.

Fig. 67

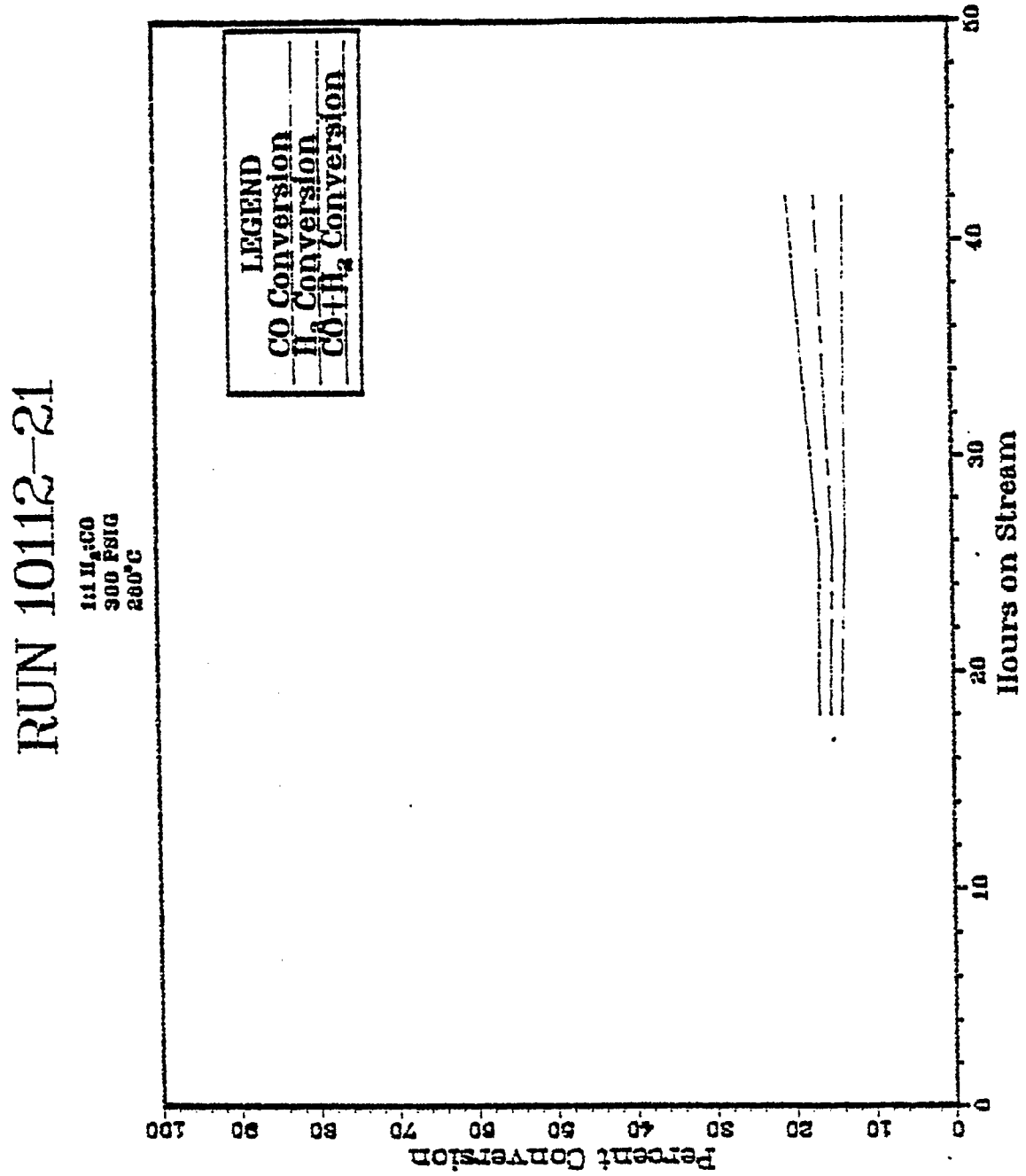

RUN 10112-21
1:1 H2:CO
300 PSIG
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 68

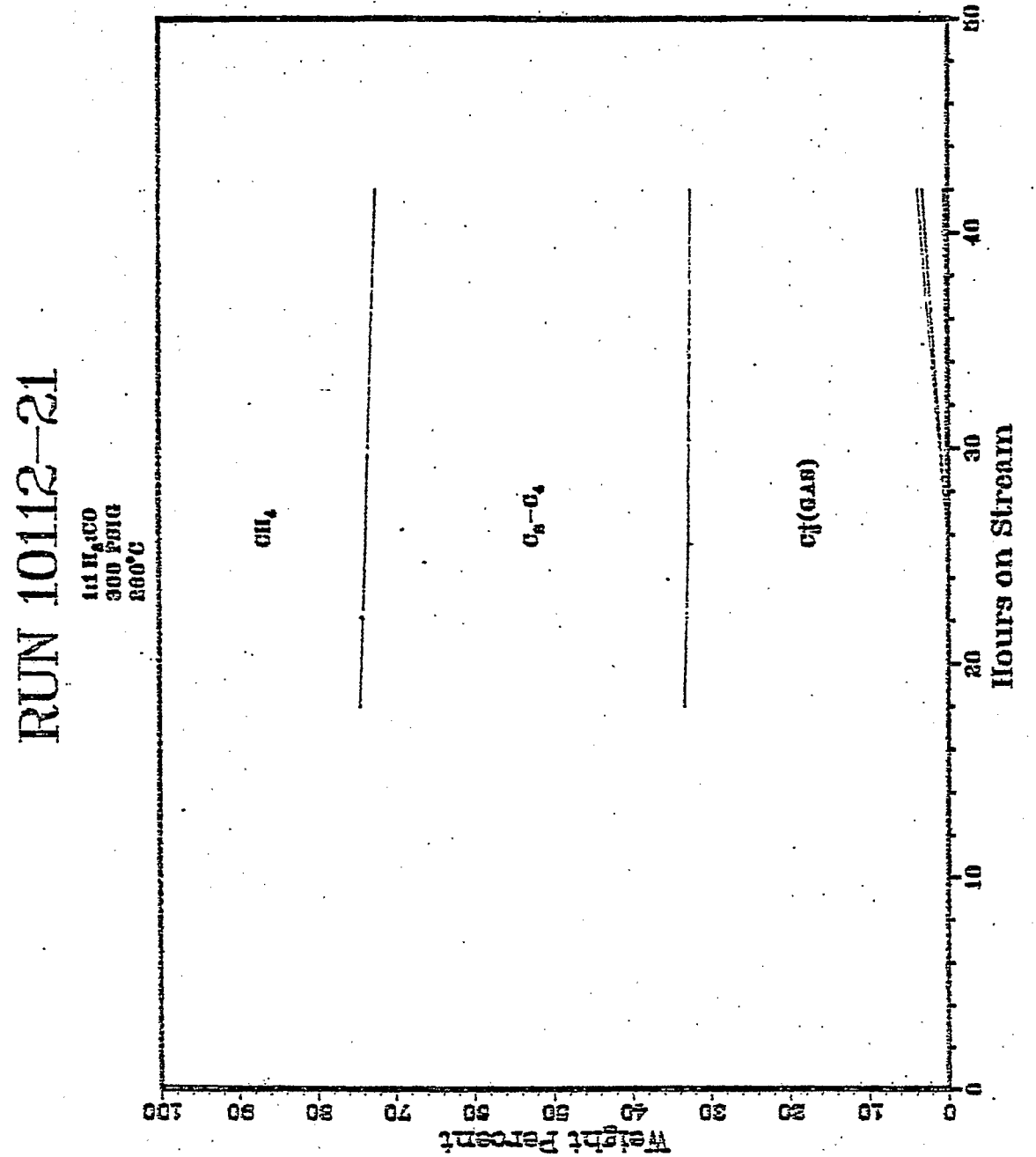
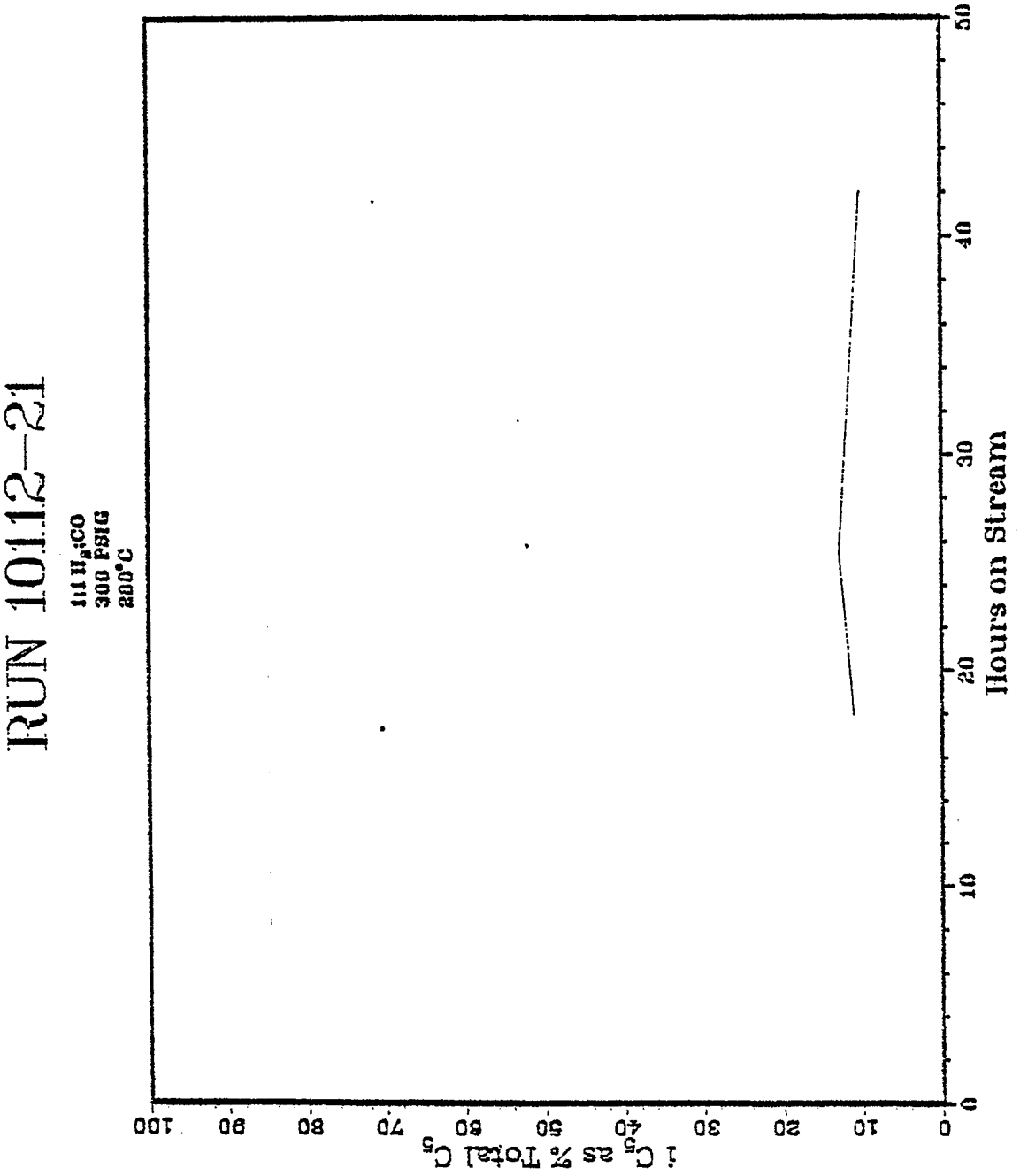

RUN 10112–21
1:1 H_2:CO
300 psig
280°C
CH_4
C_2–C_4
C_5^+(GAS)
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. 69


RUN 10112-21
1:1 H2:CO
300 PSIG
280°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

RUN 10112–21

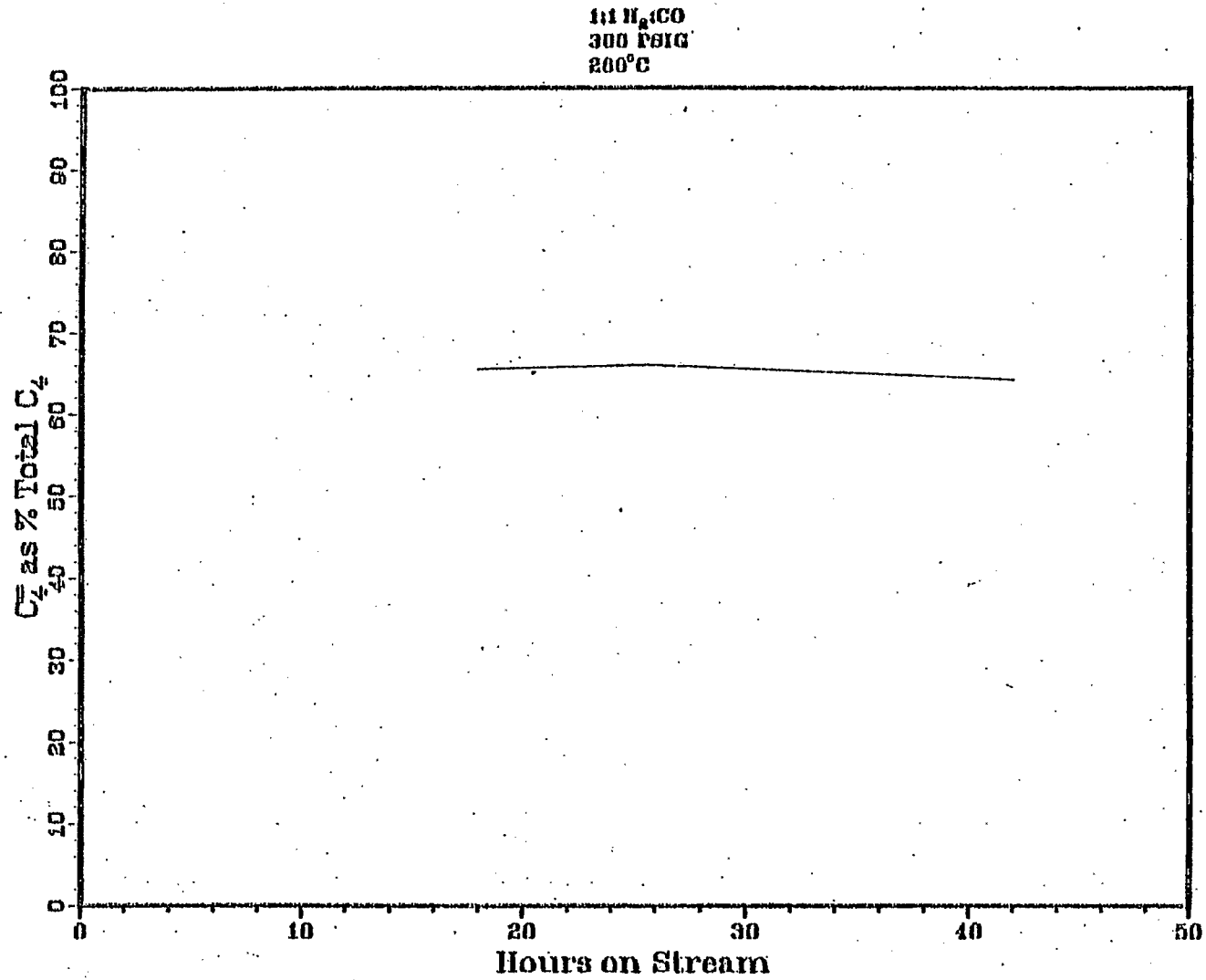


FIG. 70

Fig. 71

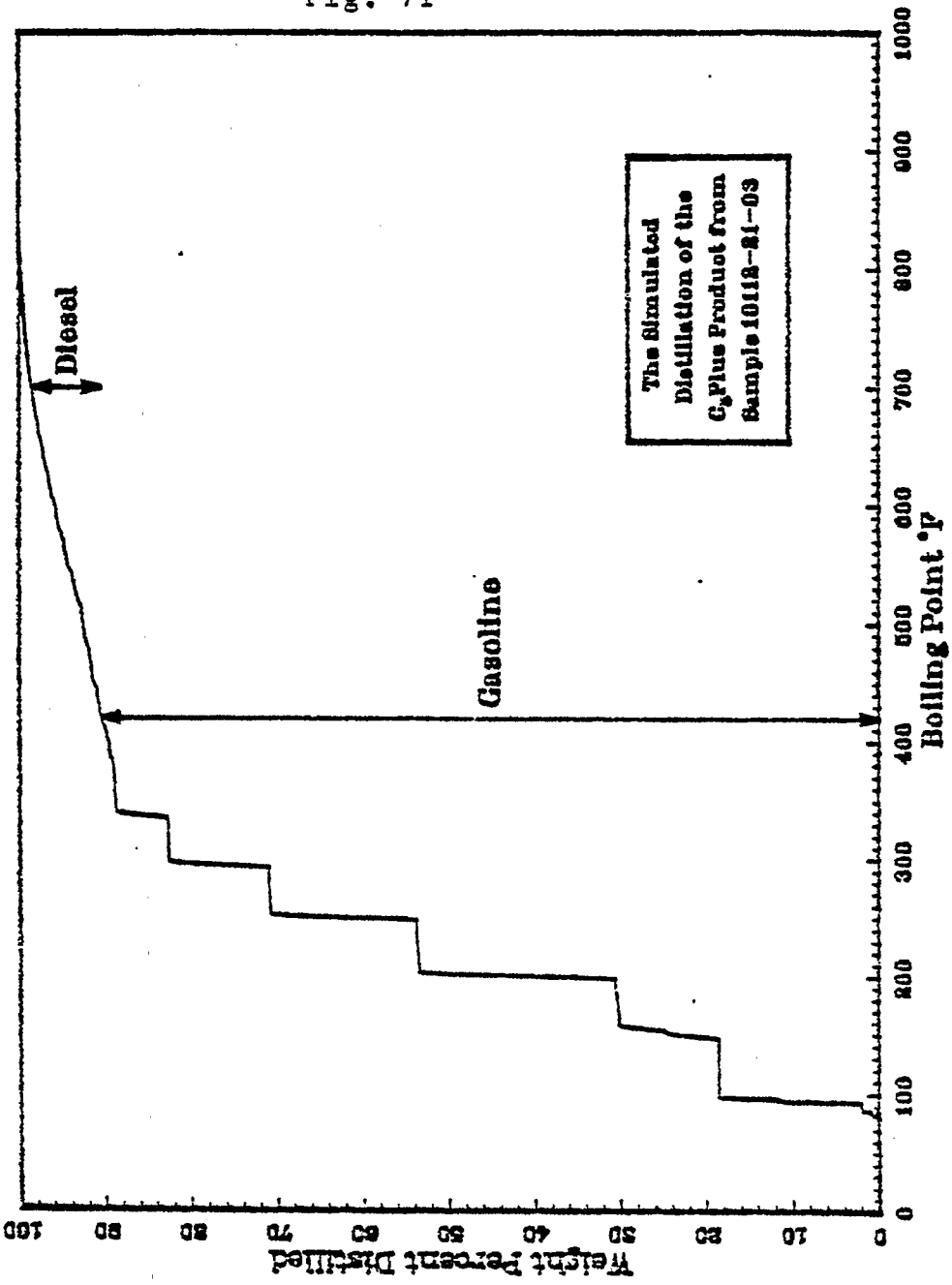

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10118-81-03
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 72

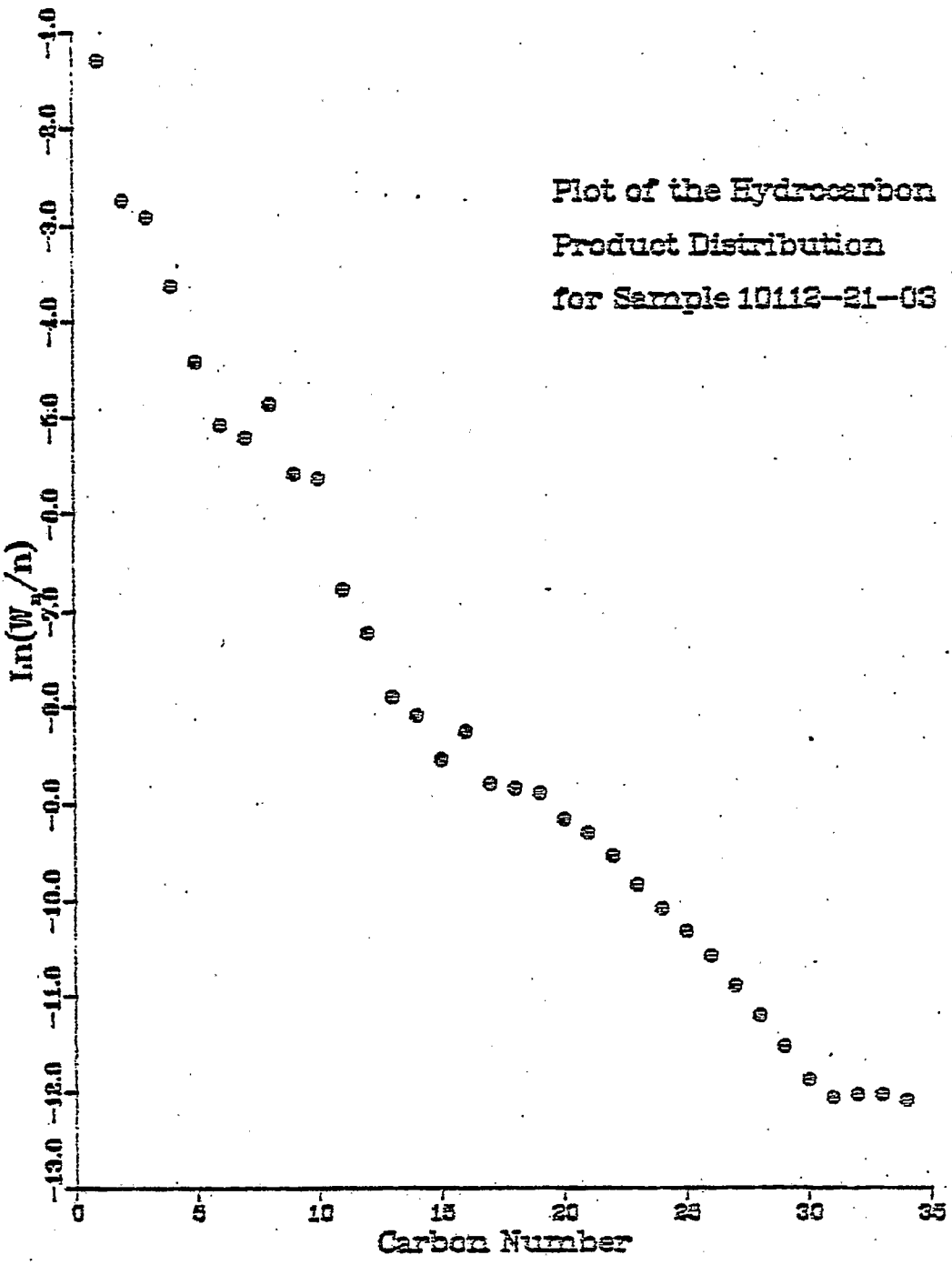

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-21-03
ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 73

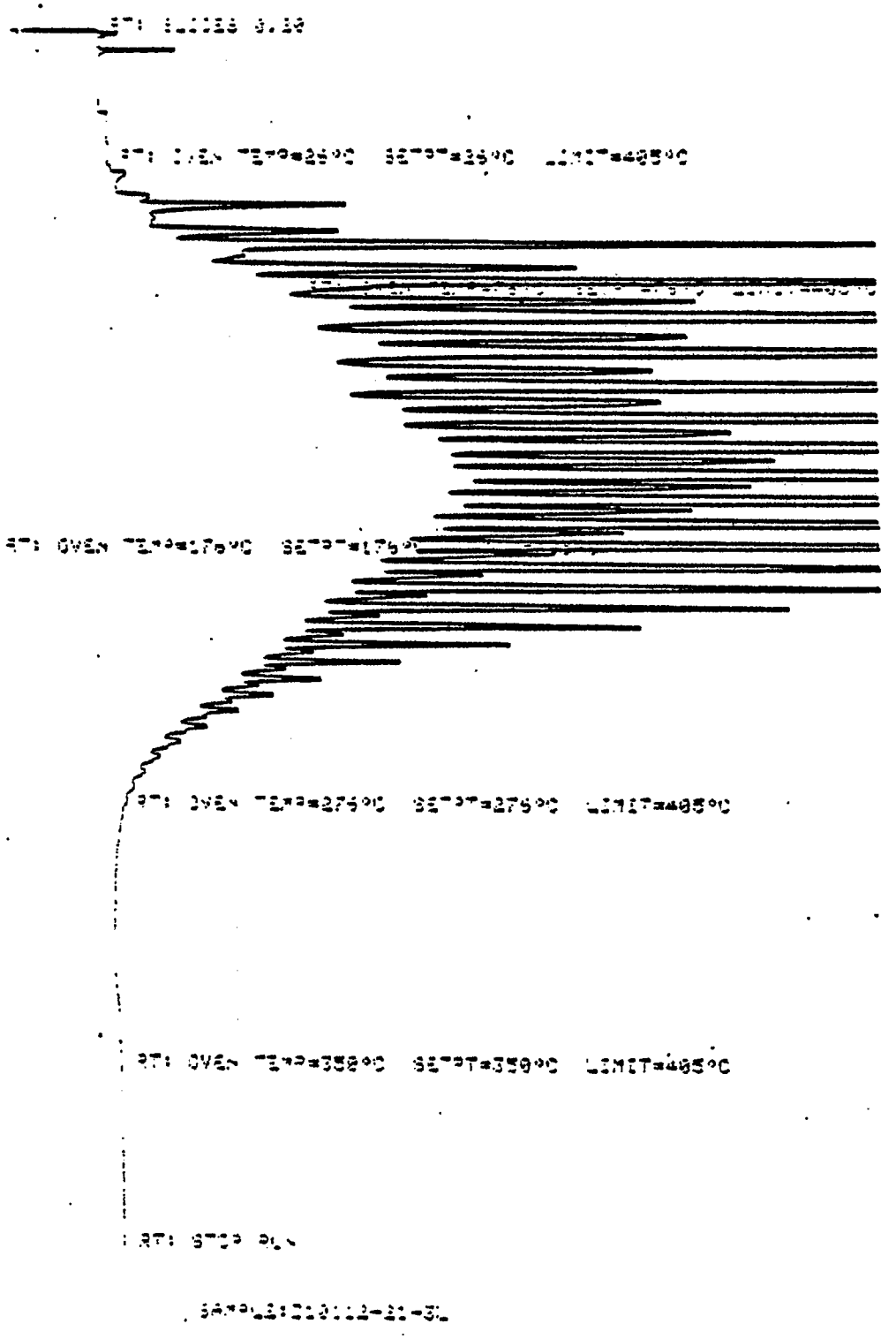


TABLE 9 RESULT OF SYNGAS OPERATION

RUN NO. 10112-21
CATALYST CO/X7 + UCC-101 10252-71C 80 CC 33.9GM (34.1 AFTER RUN +0.2G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-21-01	112-21-02	112-21-03
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.0	25.5	42.0
PRESSURE,PSIG	295	297	302
TEMP. C	250	250	250
FEED CC/MIN	400	400	400
HOURS FEEDING	18.00	7.50	16.50
EFFLNT GAS LITER	383.55	162.60	356.85
GM AQUEOUS LAYER	0.00	0.00	6.40
GM OIL	0.00	0.00	0.45
MATERIAL BALANCE			
GM ATOM CARBON %	99.30	100.82	100.54
GM ATOM HYDROGEN %	96.16	97.59	102.03
GM ATOM OXYGEN %	97.04	98.37	102.28
RATIO CHX/(H2O+CO2)	1.3009	1.3380	0.8490
RATIO X IN CHX	2.6276	2.6466	2.6739
USAGE H2/CO PRODT	1.2683	1.3245	1.4528
RATIO CO2/(H2O+CO2)	0.5510	0.5258	0.3229
K SHIFT IN EFFLNT	1.15	1.03	0.44
CONVERSION			
ON CO %	14.02	13.38	13.40
ON H2 %	16.86	16.65	20.42
ON CO+H2 %	15.42	14.99	16.94
PROT SELECTIVITY,WT %			
CH4	25.54	26.33	27.65
C2 HC'S	12.58	12.30	12.96
C3H8	5.38	5.42	5.40
C3H6=	11.76	11.71	10.94
C4H10	4.03	4.00	3.89
C4H8=	7.40	7.49	6.74
C5H12	2.85	2.93	2.50
C5H10=	4.02	4.30	3.52
C6H14	1.94	2.16	1.77
C6H12= & CYCLO'S	2.36	2.71	1.99
C7+ IN GAS	22.14	20.67	18.80
LIQ HC'S	0.00	0.00	3.85
TOTAL	100.00	100.00	100.00

SUB-GROUPING			
C1 -C4	66.69	67.24	67.58
C5 -420 F	33.31	32.76	29.28
420-700 F	0.00	0.00	2.61
700-END PT	0.00	0.00	0.54
C5+-END PT	33.31	32.76	32.42
ISO/NORMAL MOLE RATIO			
C4	0.0549	0.0650	0.0619
C5	0.1241	0.1475	0.1129
C6	0.0000	0.0944	0.0000
C4=	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO			
C3	0.4365	0.4420	0.4708
C4	0.5260	0.5152	0.5571
C5	0.6891	0.6618	0.6917
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))			0.7485
RATIO CH4/(1-A)**2			4.3715
LIQ HC COLLECTION			
PHYS. APPEARANCE			LT YW OIL
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F			391
16			414
50			546
84			688
90			727
RANGE(16-84 %)			274
WT % @ 420 F	18.29	18.29	18.29
WT % @ 700 F	86.00	86.00	86.00

VII. RUN 6 (10112-22) with Catalyst 6 (Co/Th/X_4 + UCC-108)

This catalyst was run as a further test of X_4, the additive used in the exceptionally productive Catalyst 9 (Run 10225-8) reported in the Tenth Quarterly Report. The metal component was prepared by impregnating cobalt with 15 weight percent thorium, and impregnating the mixture with 13 weight percent X_4. This was physically mixed with Molecular Sieve UCC-108 in a Co/Th/X_4:UCC-108 weight ratio of 3:14, bonded with 15 weight percent silica, and formed as extrudates. The final product was identical to the Tenth Quarter Catalyst 9, except that UCC-108 was used 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. 74-77. Simulated distillations of the C_5^+ product for three samples are plotted in Figs. 78-80. Carbon number product distributions are plotted in Figs. 81-89. Chromatograms from simulated distillations are reproduced in Figs. 90-98. Detailed material balances appear in Tables 10-12.

Conversion of the syngas was 73 percent initially, as against 76 percent with the non-X_4 containing reference catalyst (Catalyst 3 in the Tenth Quarter Run 10112-15), and 53 percent at the end of the run. Maintenance of activity was slightly better than with the reference catalyst, but not as good as with this quar-

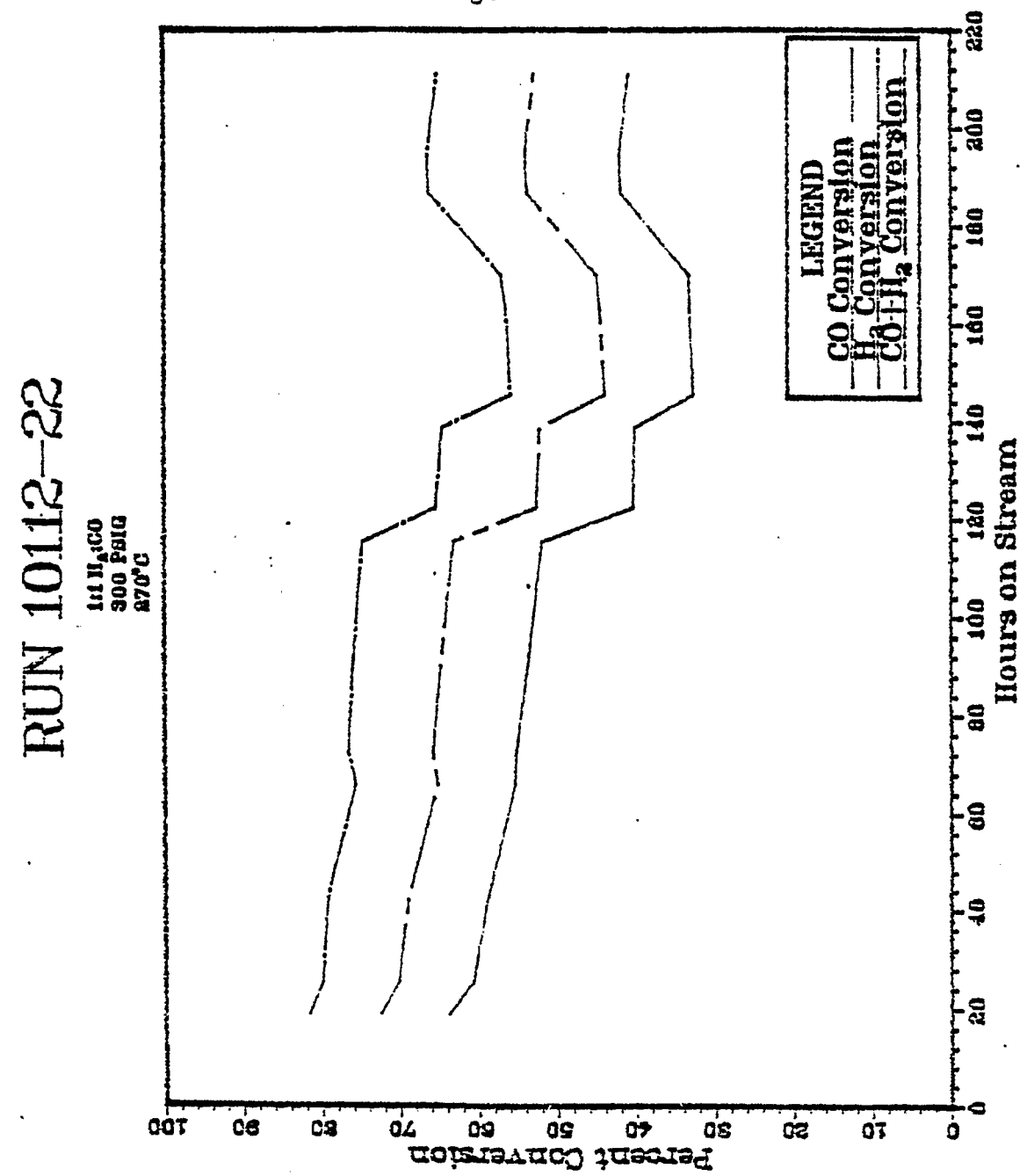
ter's X_6-containing Catalyst 4, and far below that of the Tenth Quarter's X_4-containing Catalyst 9. The conversion minimum at 160 hours on stream is probably due to a problem which was corrected during the run; the resulting deactivation appears to have been overcome by the catalyst, so that the final conversion was at a level which might have been predicted from the initial slow deactivation before the sudden drop in conversion between 140 and 180 hours on stream. The water gas shift activity was superior: initially more than 40 percent of the oxygen was rejected as CO_2, and by the end of the run it had dropped to only about 30 percent, as against 20 percent for the non-X_4 containing reference catalyst (Catalyst 3 in the Tenth Quarter Run 10112-15).

The selectivity is rather good, and similar to that of the reference catalyst. Methane production was 16 percent initially, and rose to about 25 percent by the end of the run; corresponding values for the reference catalyst were 15 and 24 percent. High production of C_2-C_4, as with Tenth Quarter Catalyst 9, led to relatively low production of motor fuels, only 64-51 percent, some 5 percent lower than with the reference catalyst. The yield of heavies was also lower than with the reference catalyst. The proportion of gasoline to diesel oil was about 3:1. Isomerization of the pentane was very low, only about 10 percent--something of an anomaly since UCC-108 ordinarily produces a more highly isomerized product than does UCC-101. Olefinic content of the C_4 hydrocarbons was high, and increased with time on stream, apparently a characteristic property of additive X_4. The liquid

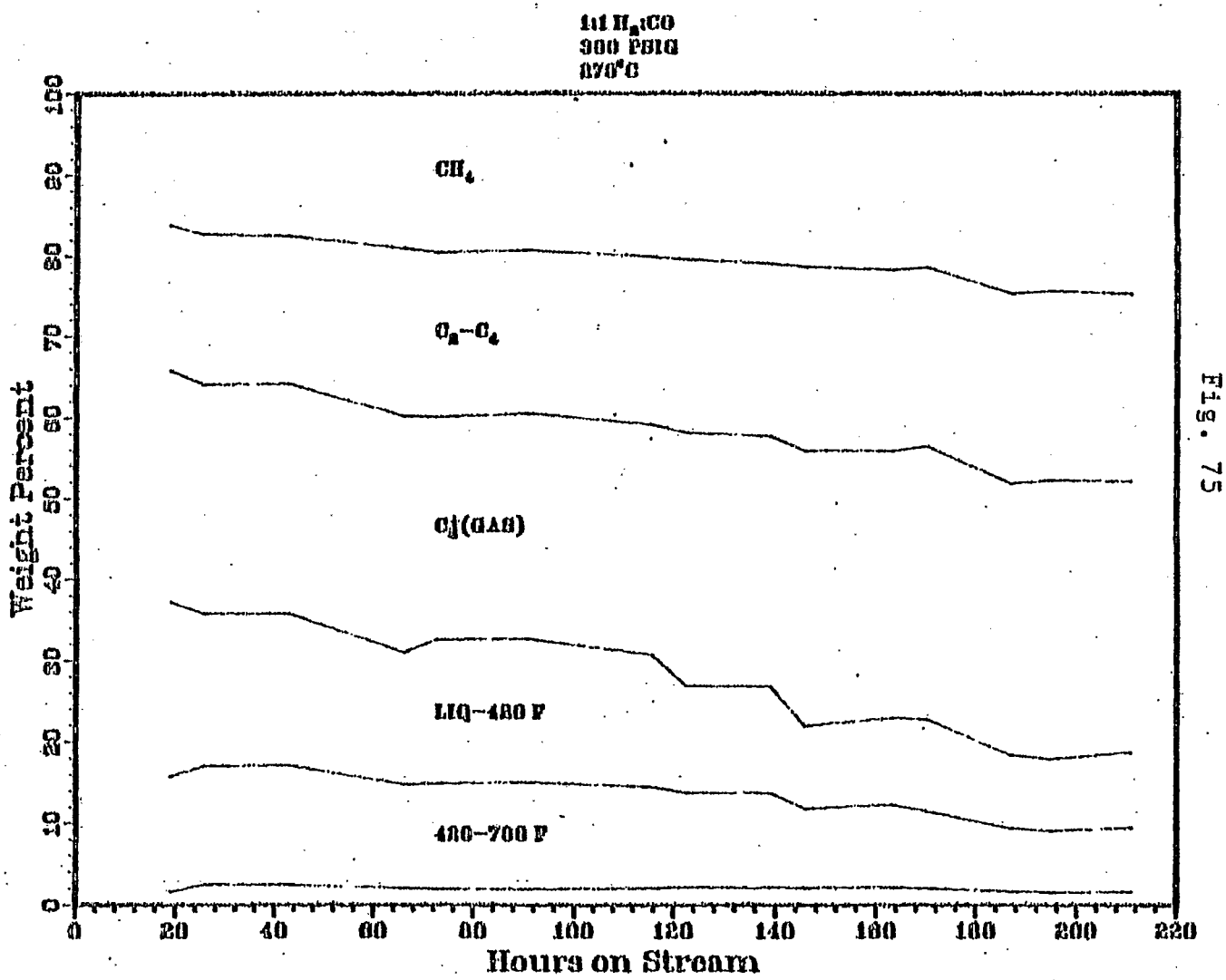
product was high in olefins as well: 65 percent in the gasoline and 45 percent in the jet fuel, as against 36 and 32 percent for the reference catalyst. The pour point of the jet fuel was -10F and that of the diesel oil 10F, as against ØF and 50F for the reference catalyst. Since the Schulz-Flory plots show no carbon number cut-off, the improved pour points may be attributed to the high olefin content.

This is a useful and important catalyst, but it still falls short of Tenth Quarter's X_4-containing Catalyst 9. While the substitution of UCC-108 for UCC-101 did improve the production of olefins (the lighter fractions of which could be oligomerized to improve the yield of total motor fuels), it lowered the catalyst's stability and somewhat impaired its product distribution.

Fig. 74


RUN 10112-22
1:1 H_2:CO
300 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
220

RUN 10112–22



E18 • 75

RUN 10112–22

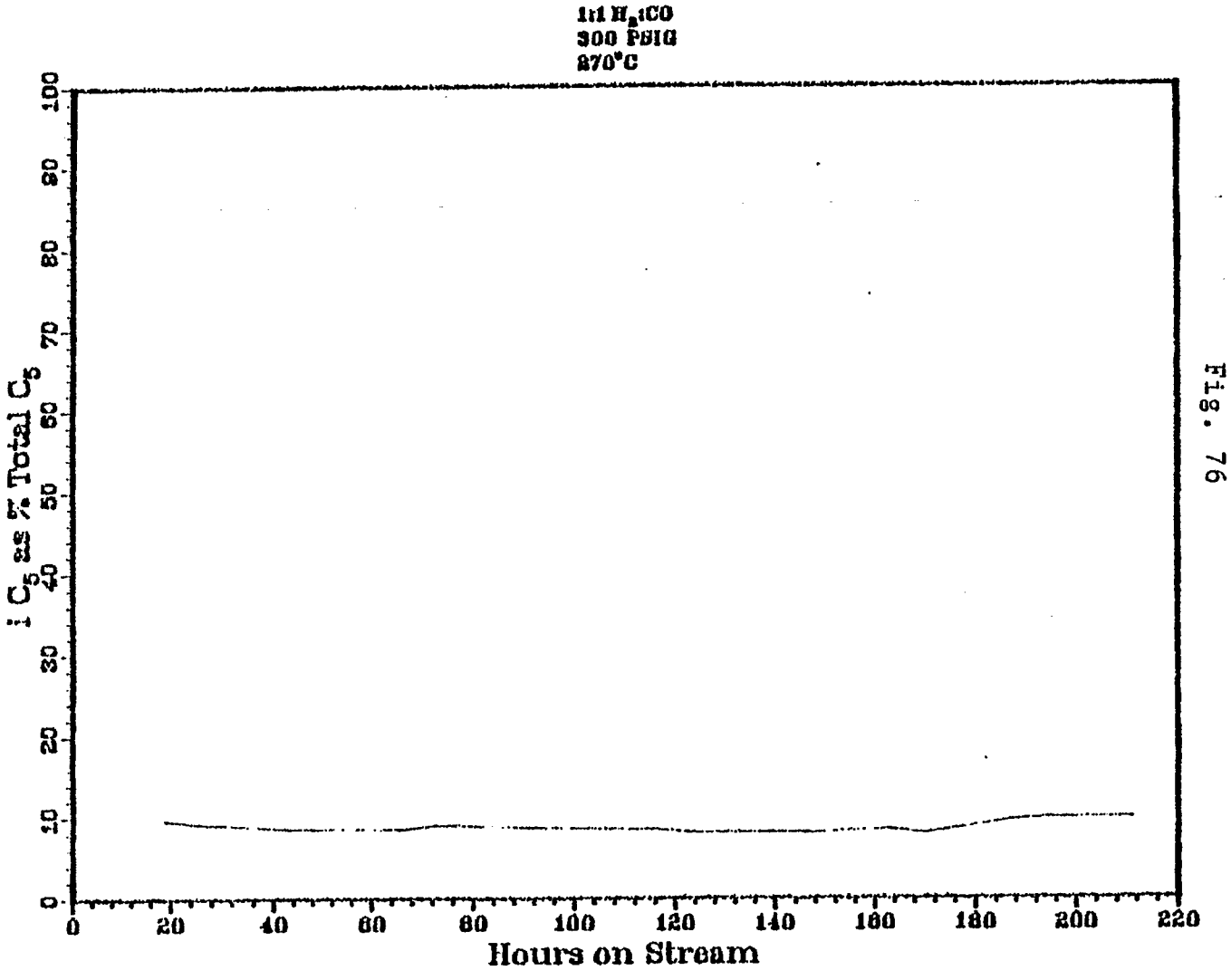


Fig. 76

Fig. 77

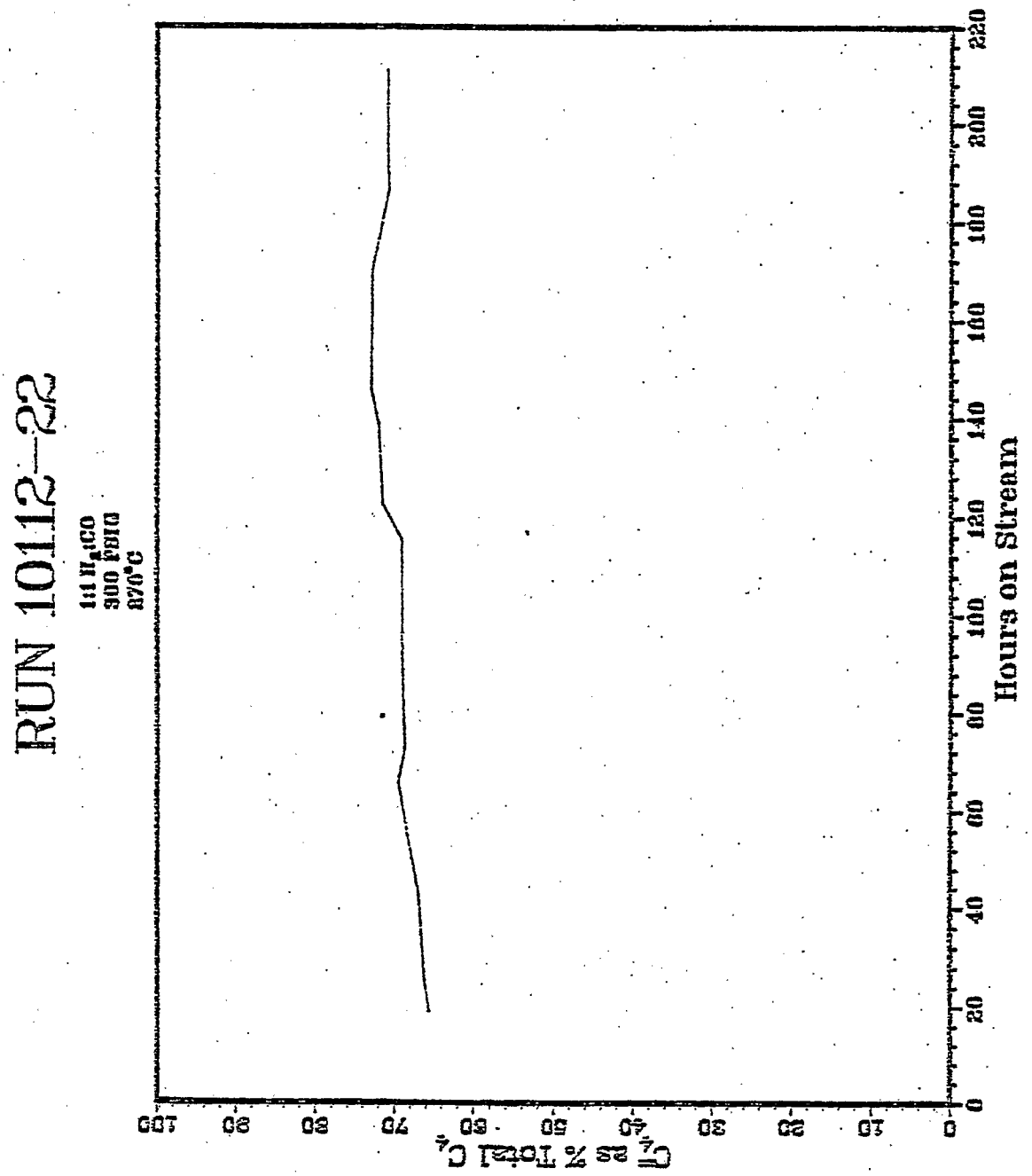

RUN 10112-22
1:1 H2:CO
300 PSIG
270°C
C2= as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
10
30
50
70
90

Fig. 78

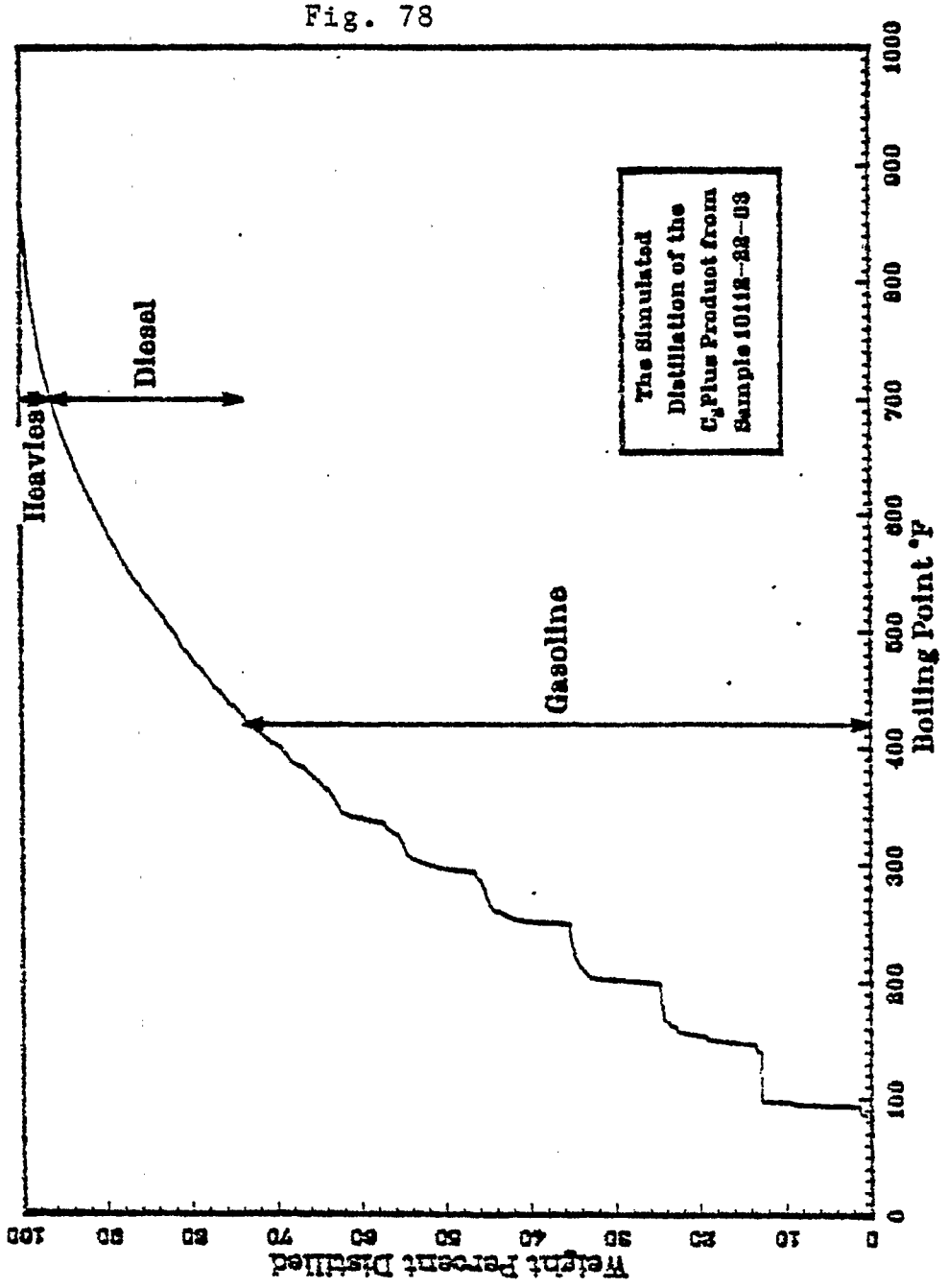

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 10118-22-03

Fig. 79

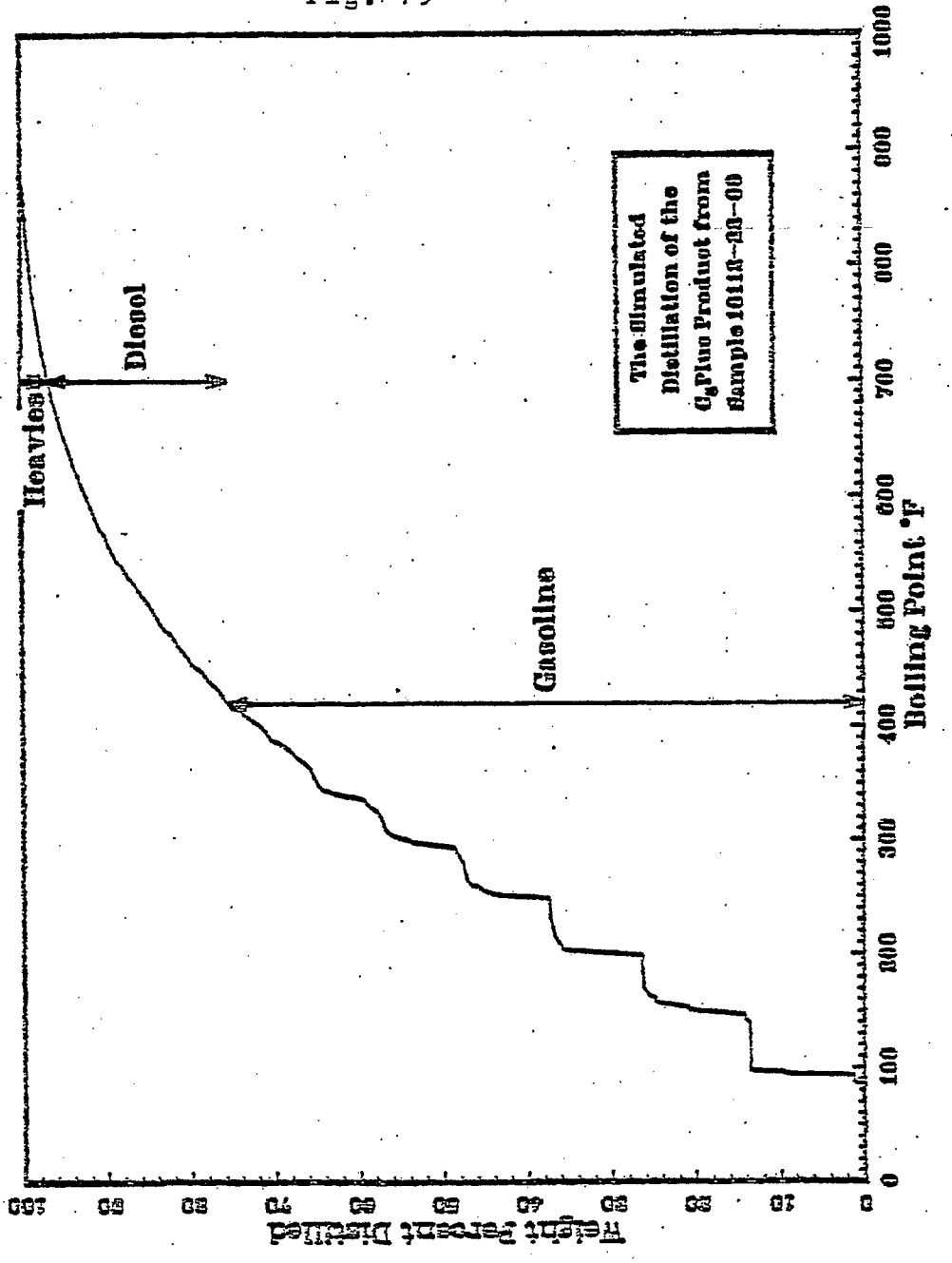

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000
Boiling Point °F
Gasoline
Diesel
Heavies
The Simulated Distillation of the C9 Plus Product from Sample 10113-23-09

Fig. 80

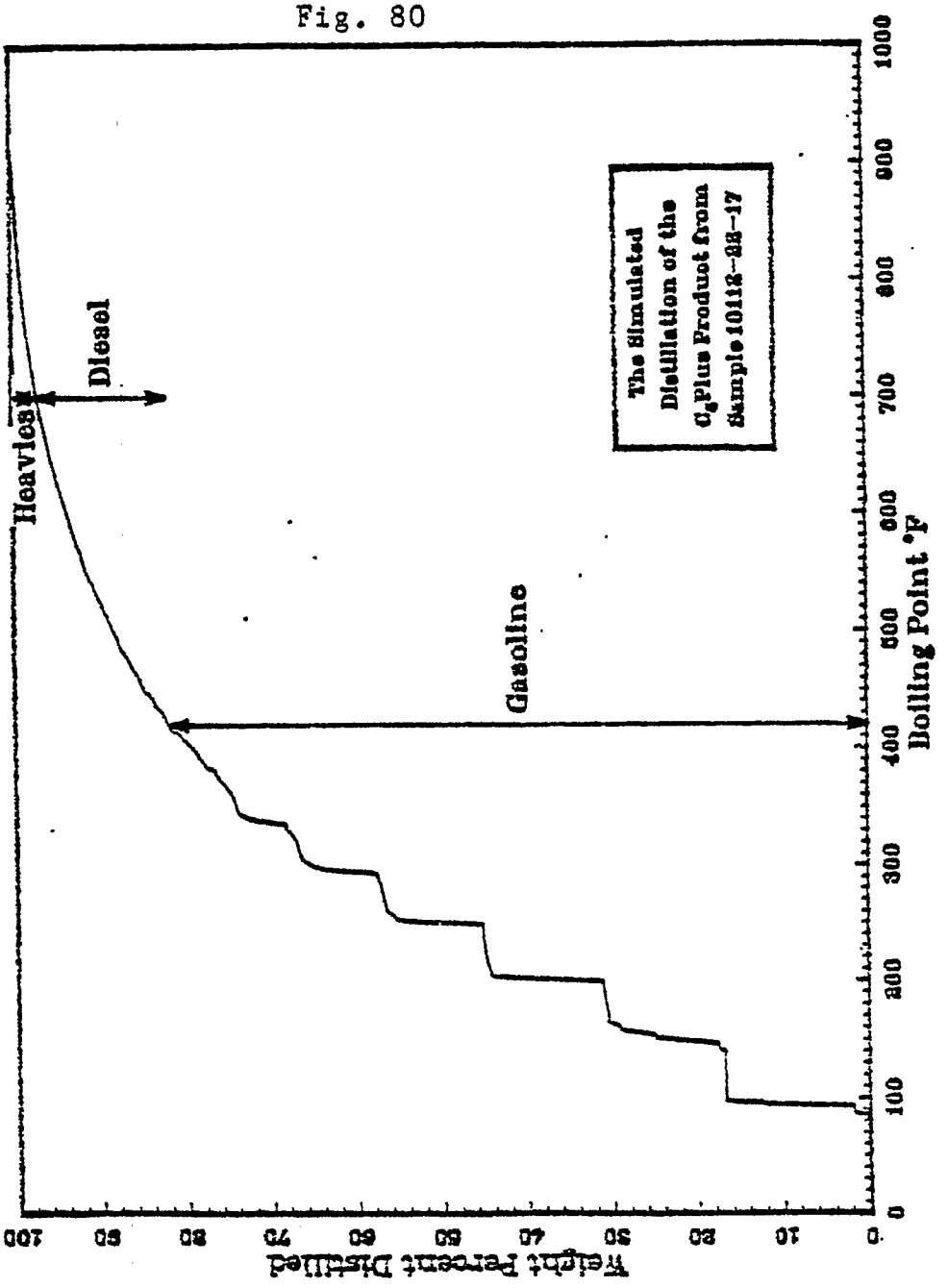

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10112-23-17
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 81

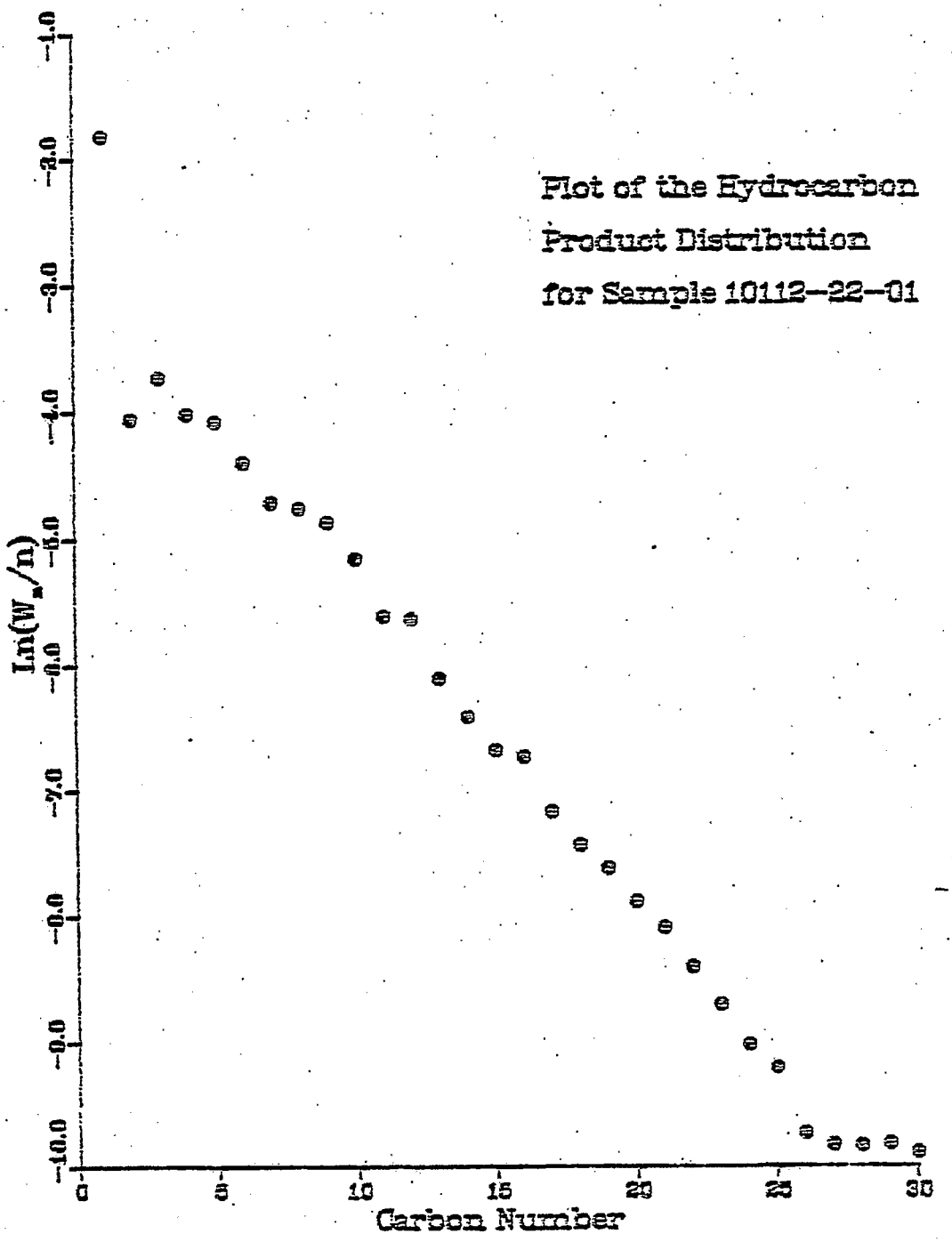

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 82

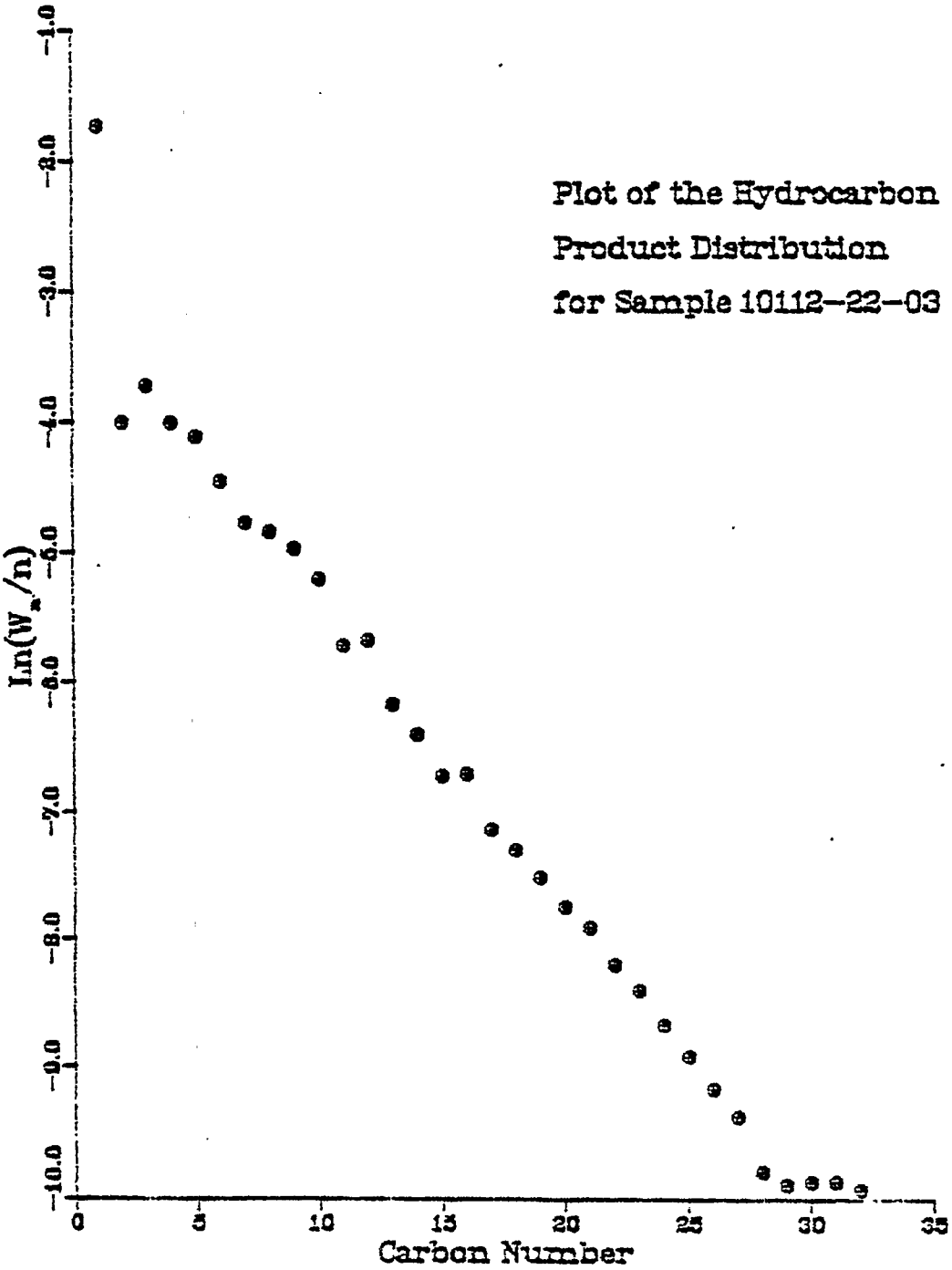

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 83

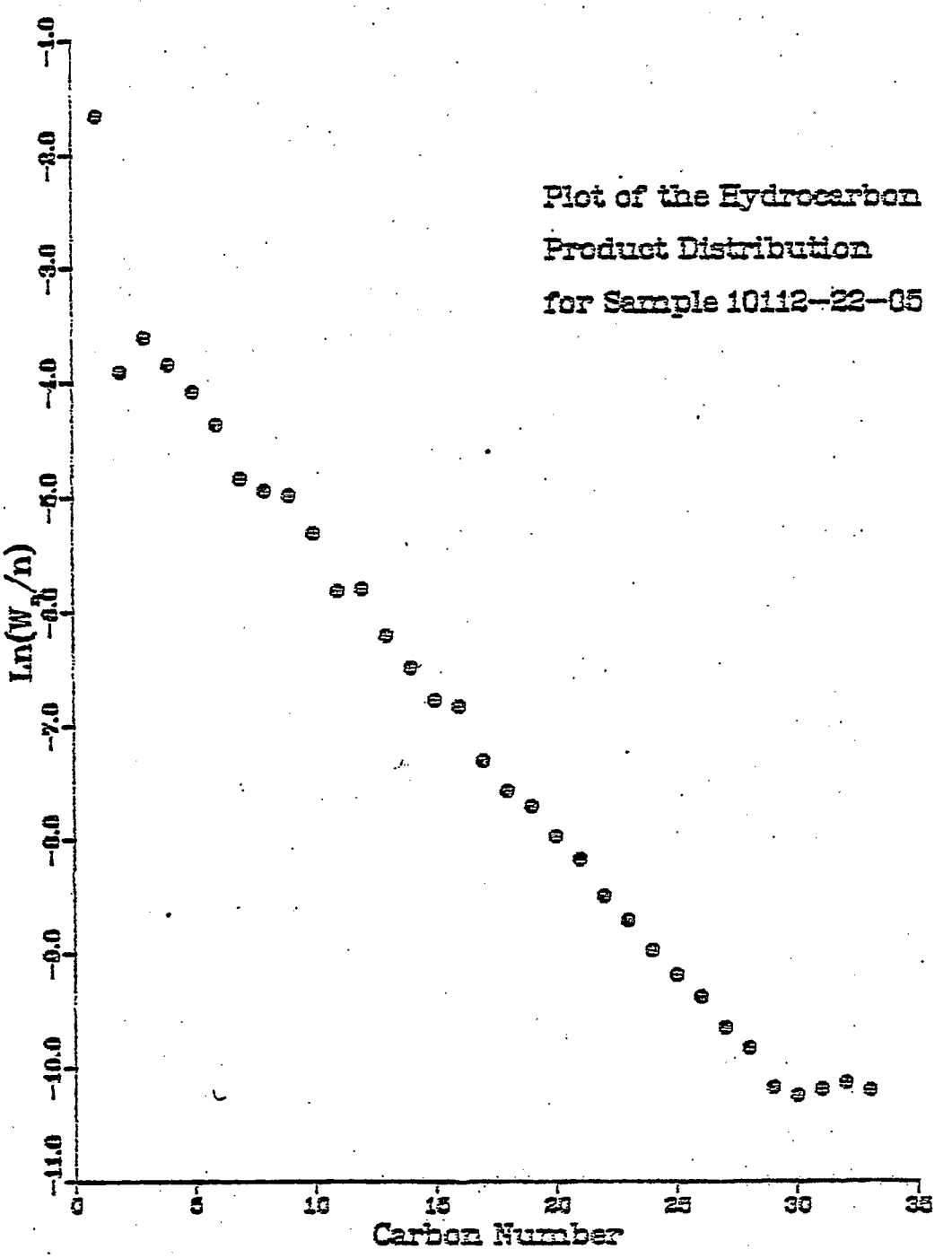

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-05
Ln(W_n/n)
-1.0
-3.0
-5.0
-7.0
-9.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 84

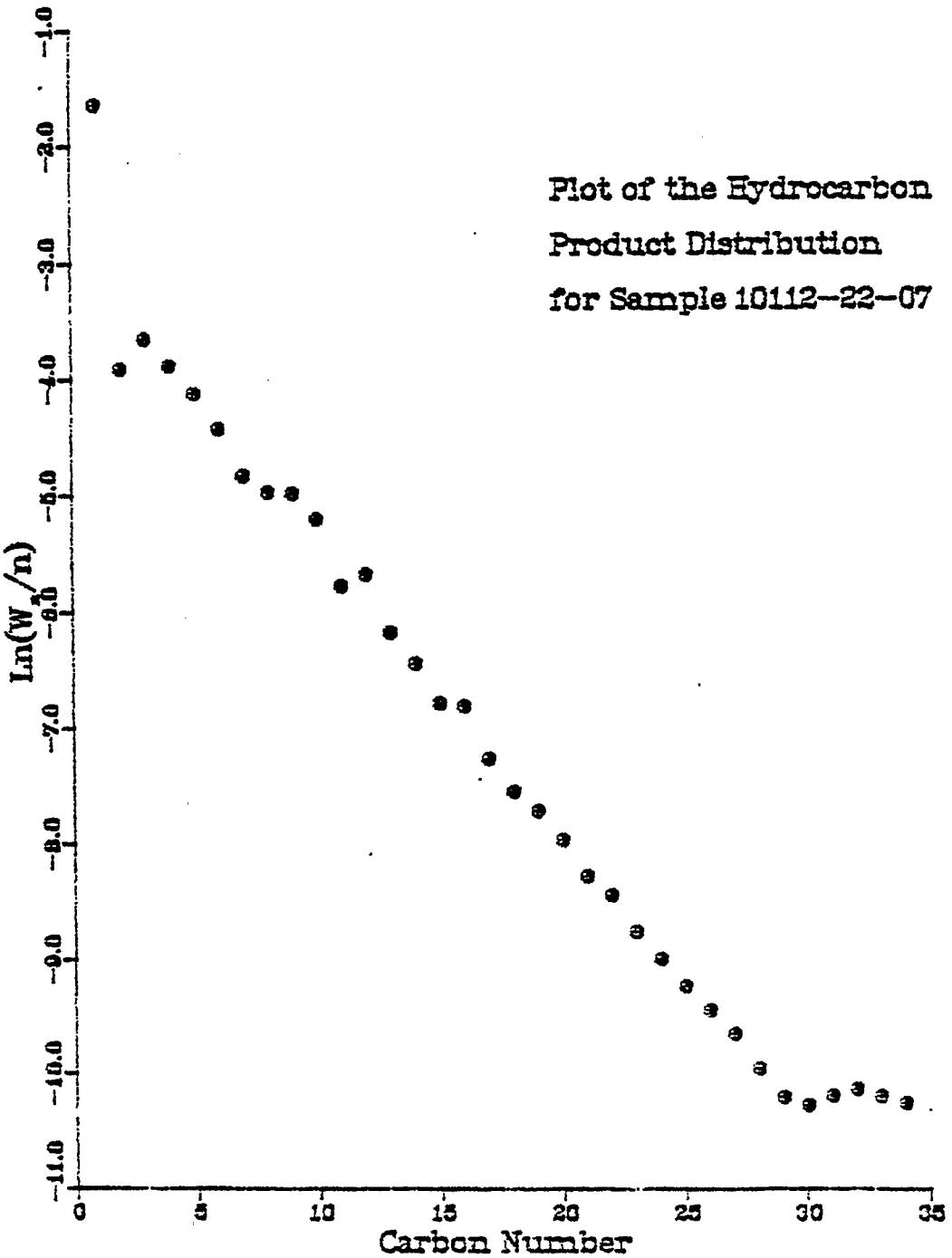

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 85

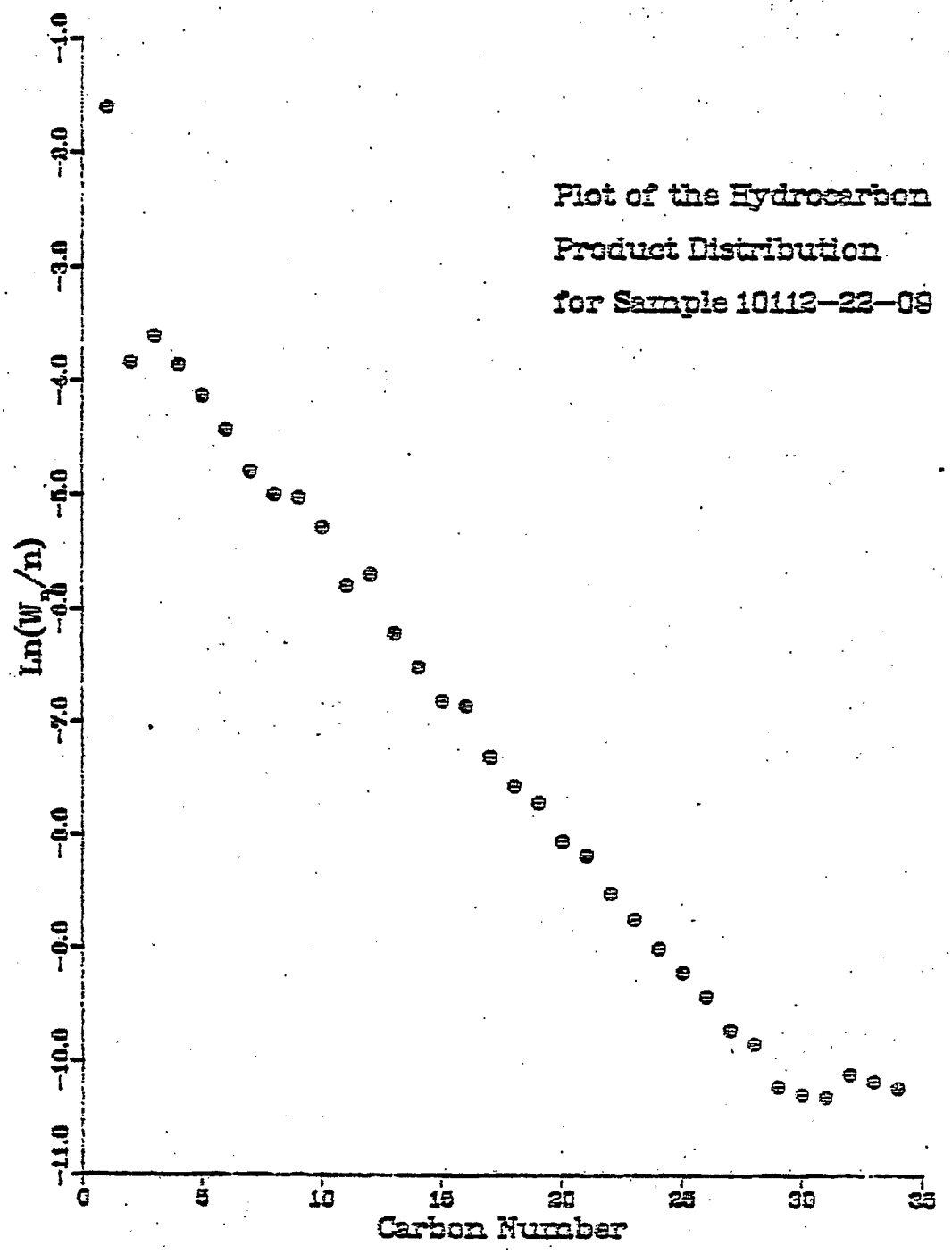

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 86

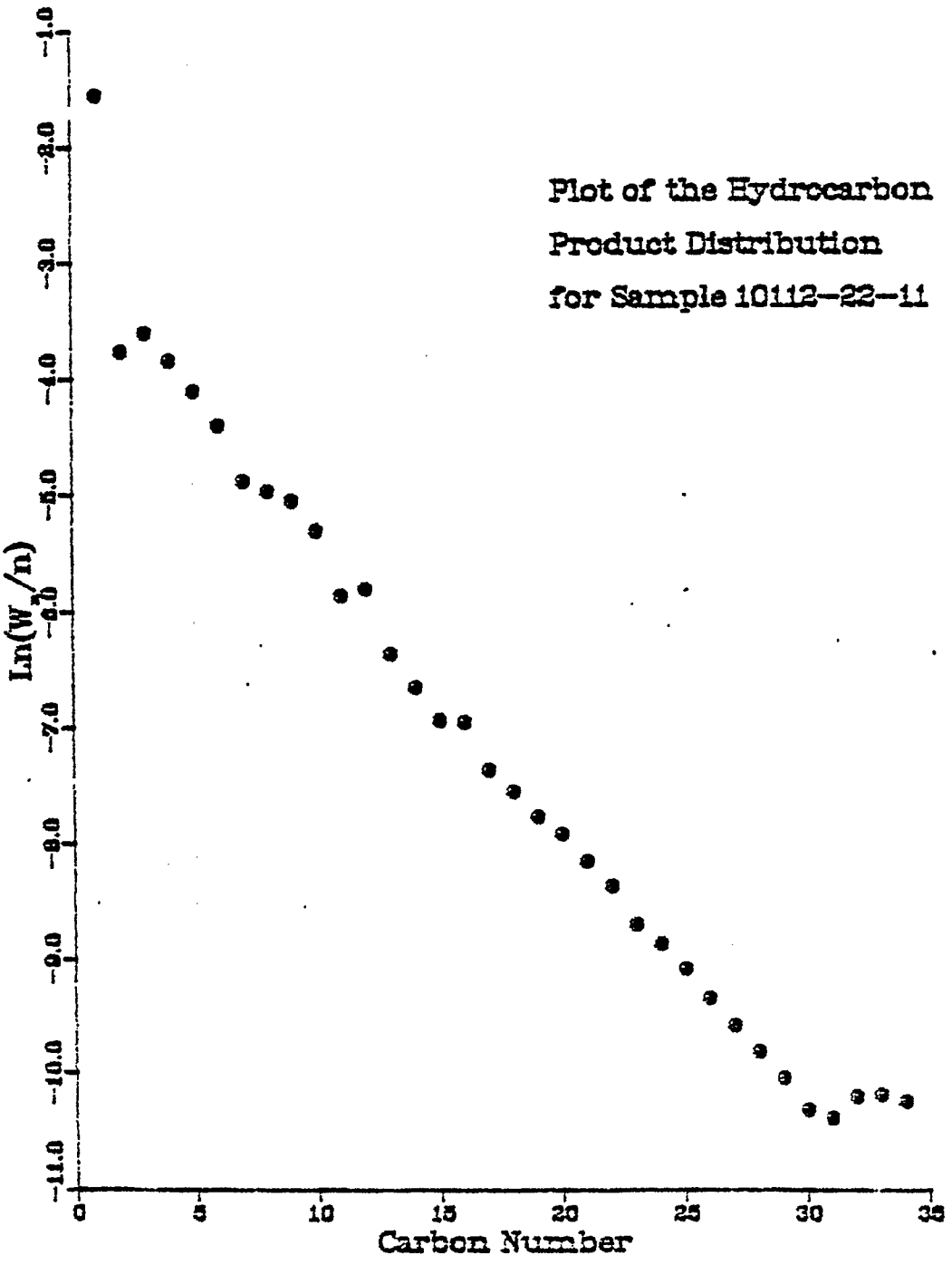

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 87

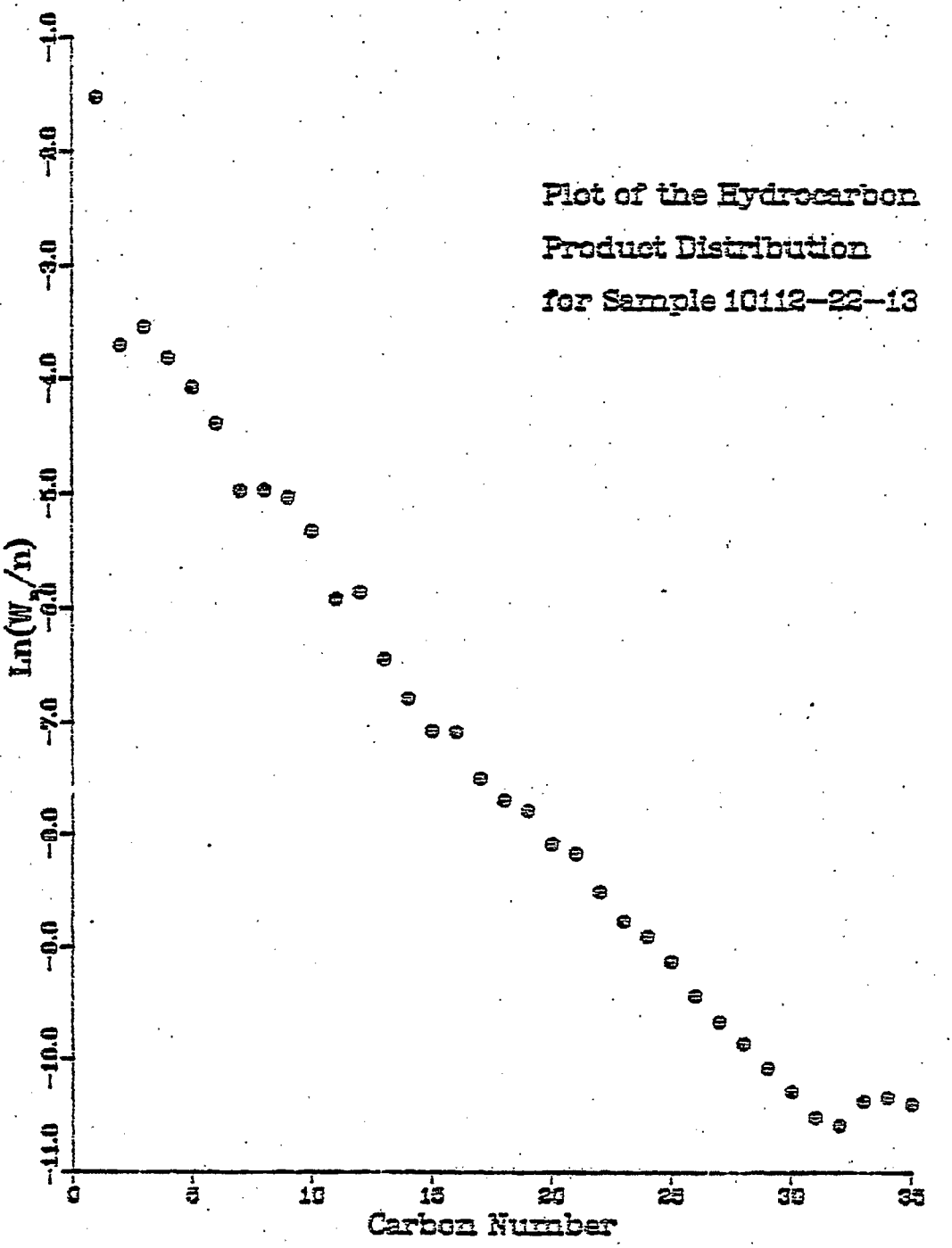

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 88

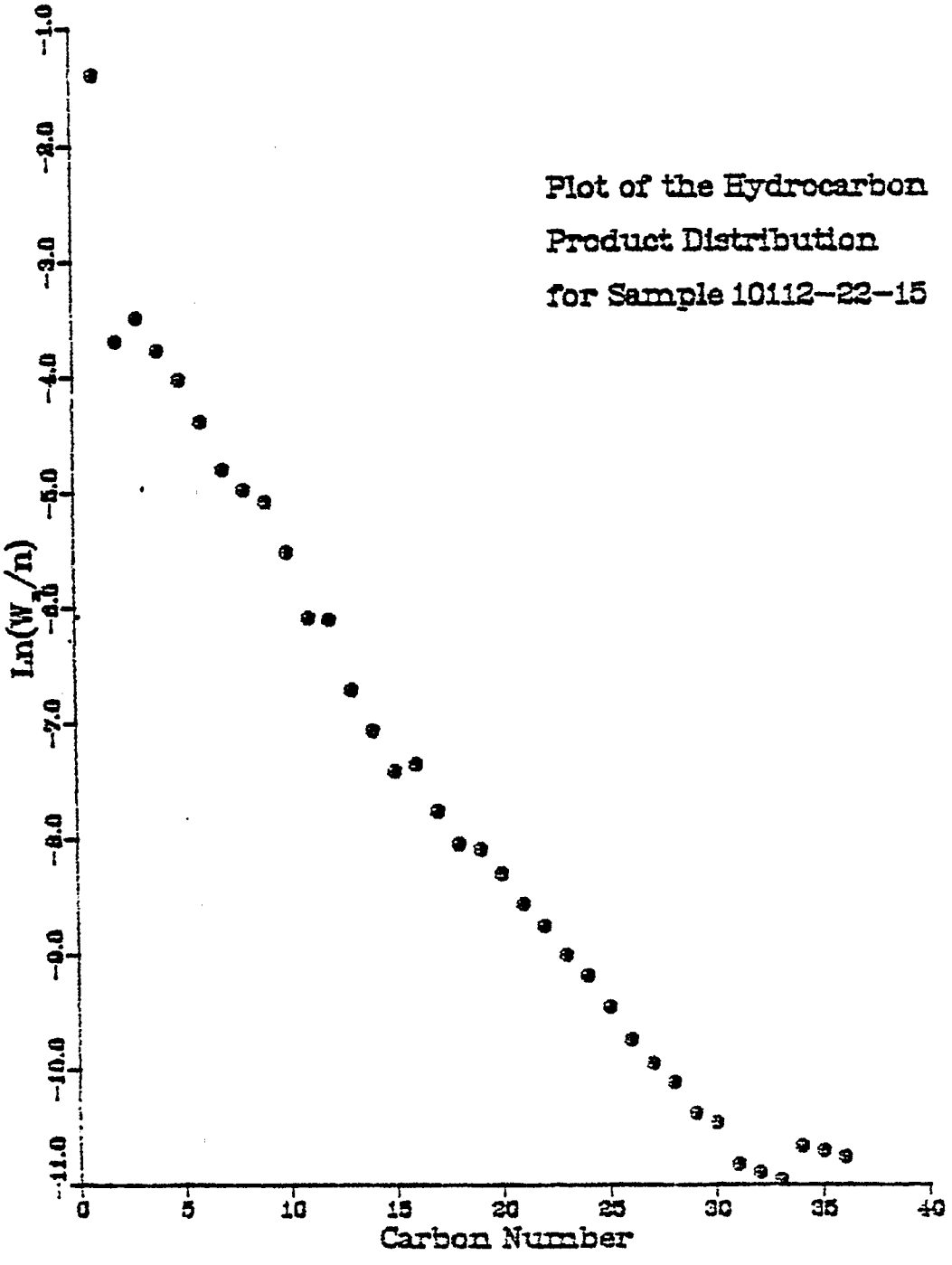

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-15
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 89

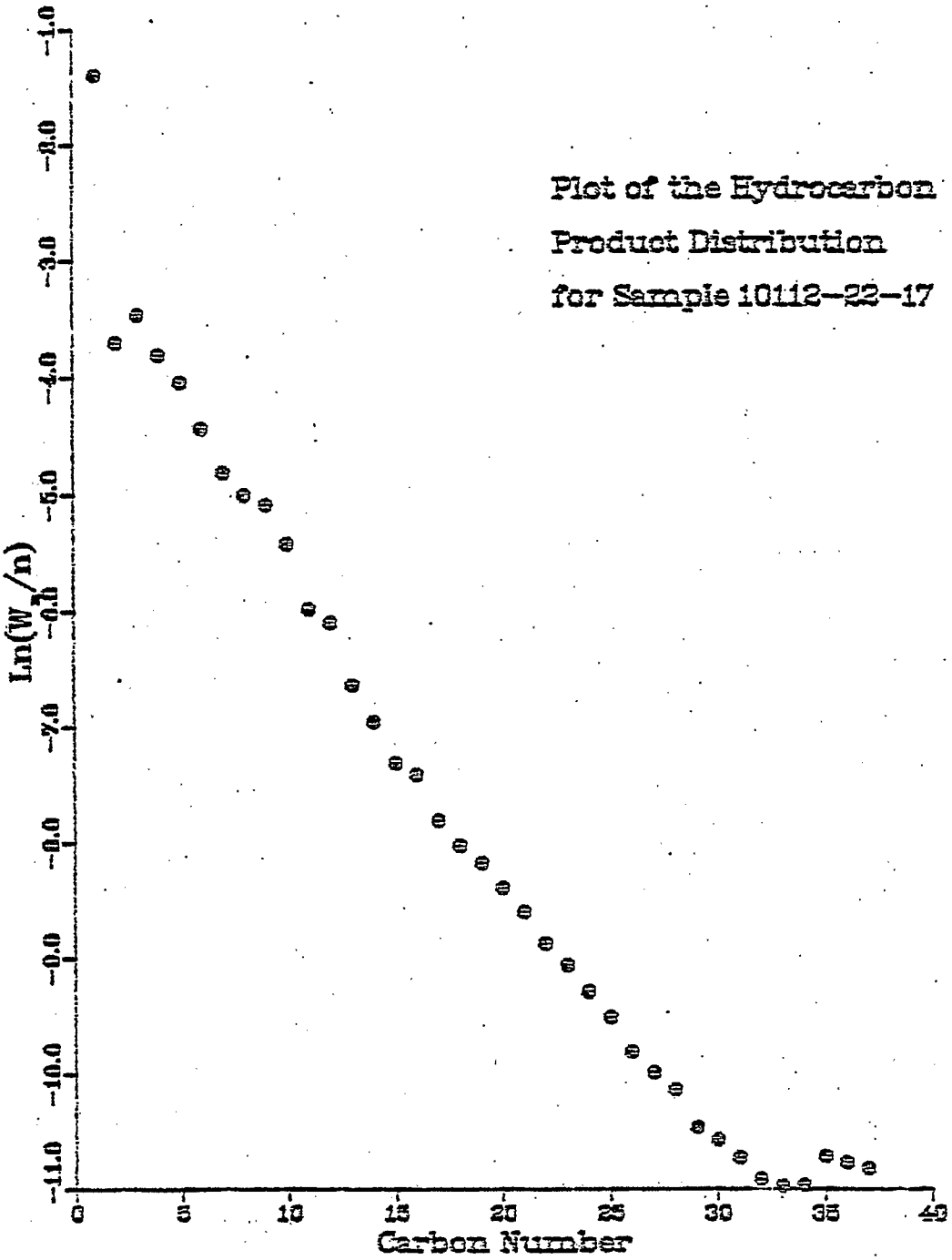

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-22-17
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 90

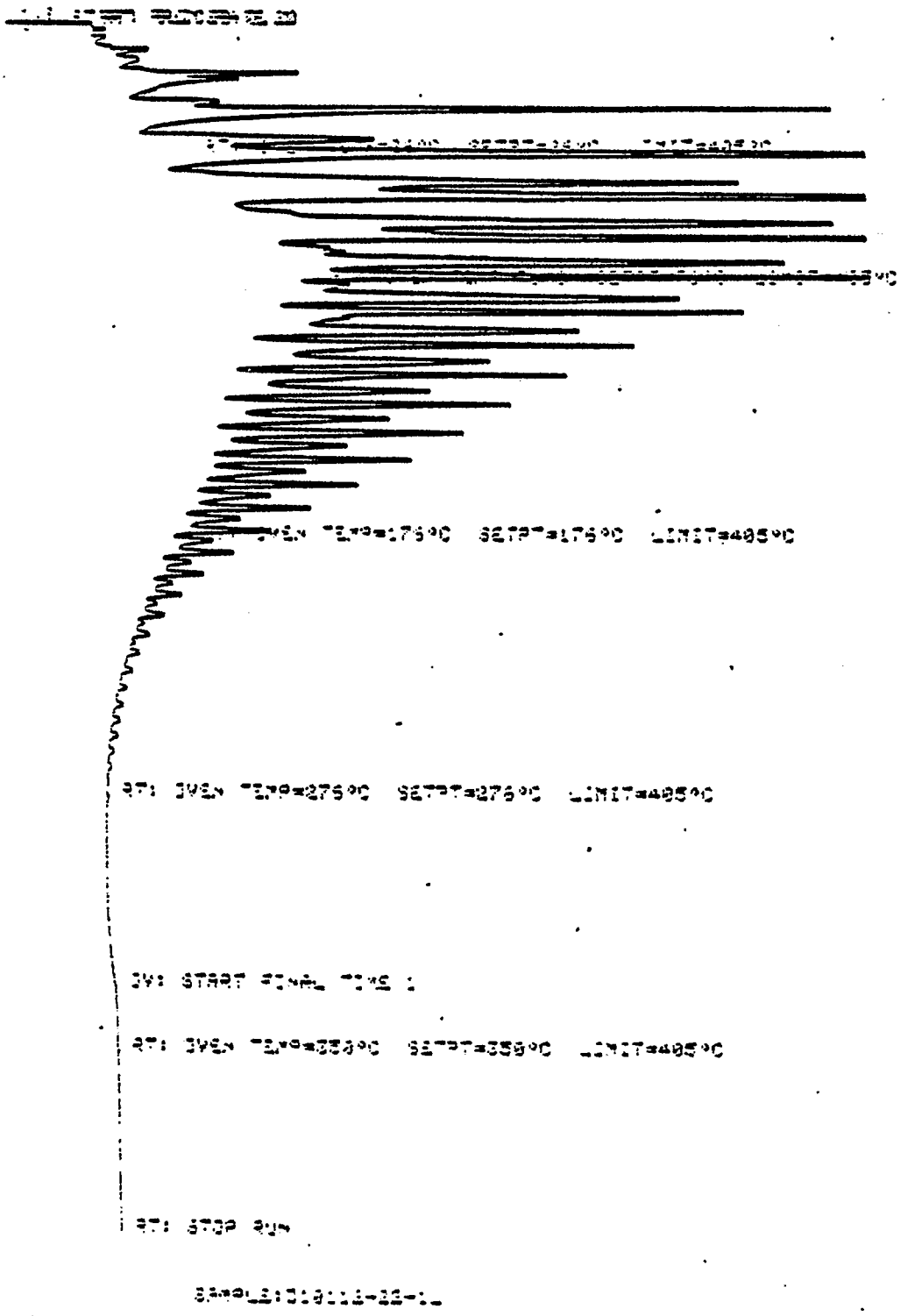

ST: START TEMPERATURE
ST: SOAK TEMP=175°C SETPT=175°C LIMIT=405°C
ST: SOAK TEMP=275°C SETPT=275°C LIMIT=405°C
RT: START FINAL TIME
ST: SOAK TEMP=350°C SETPT=350°C LIMIT=405°C
ST: STOP RUN

Fig. 91

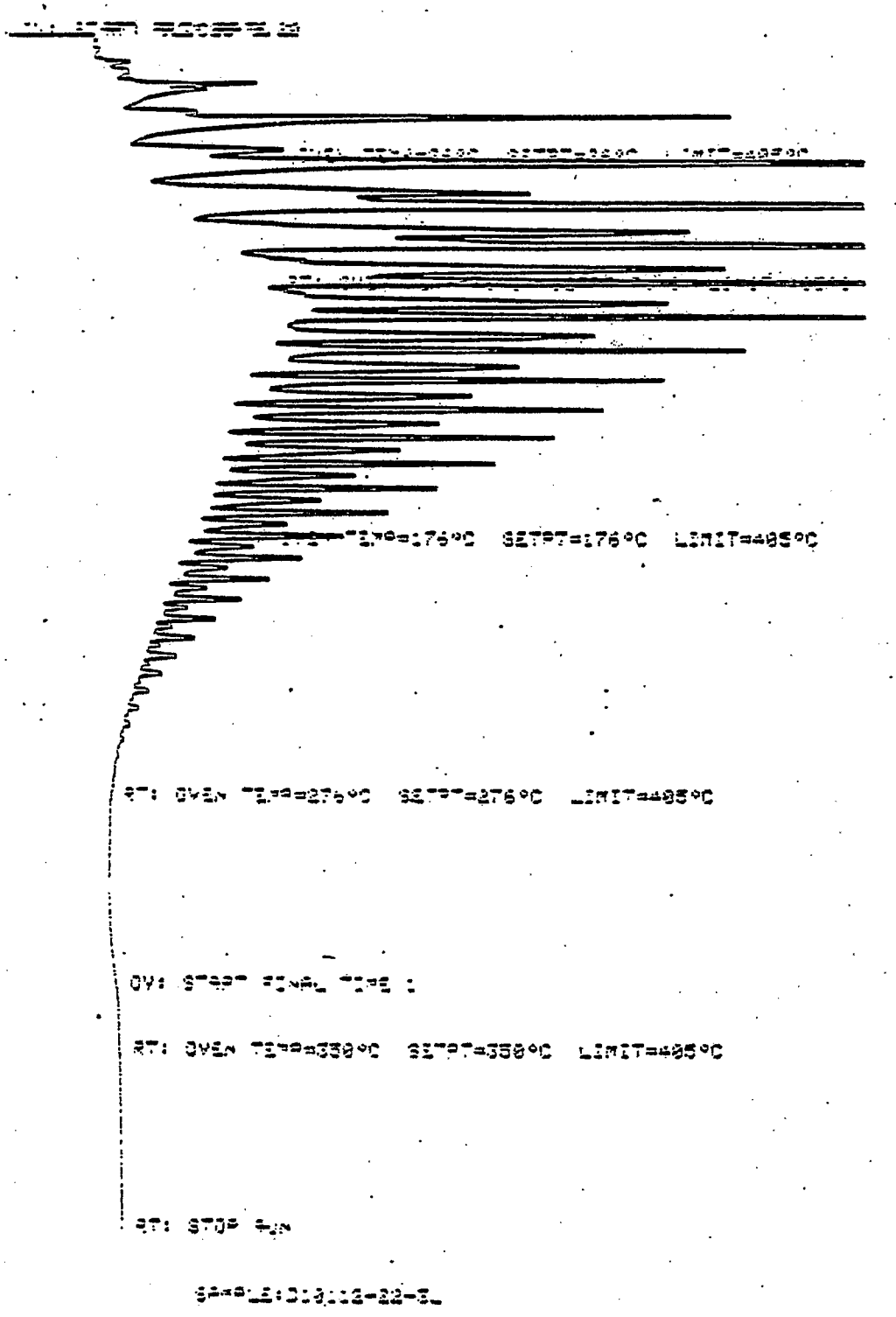
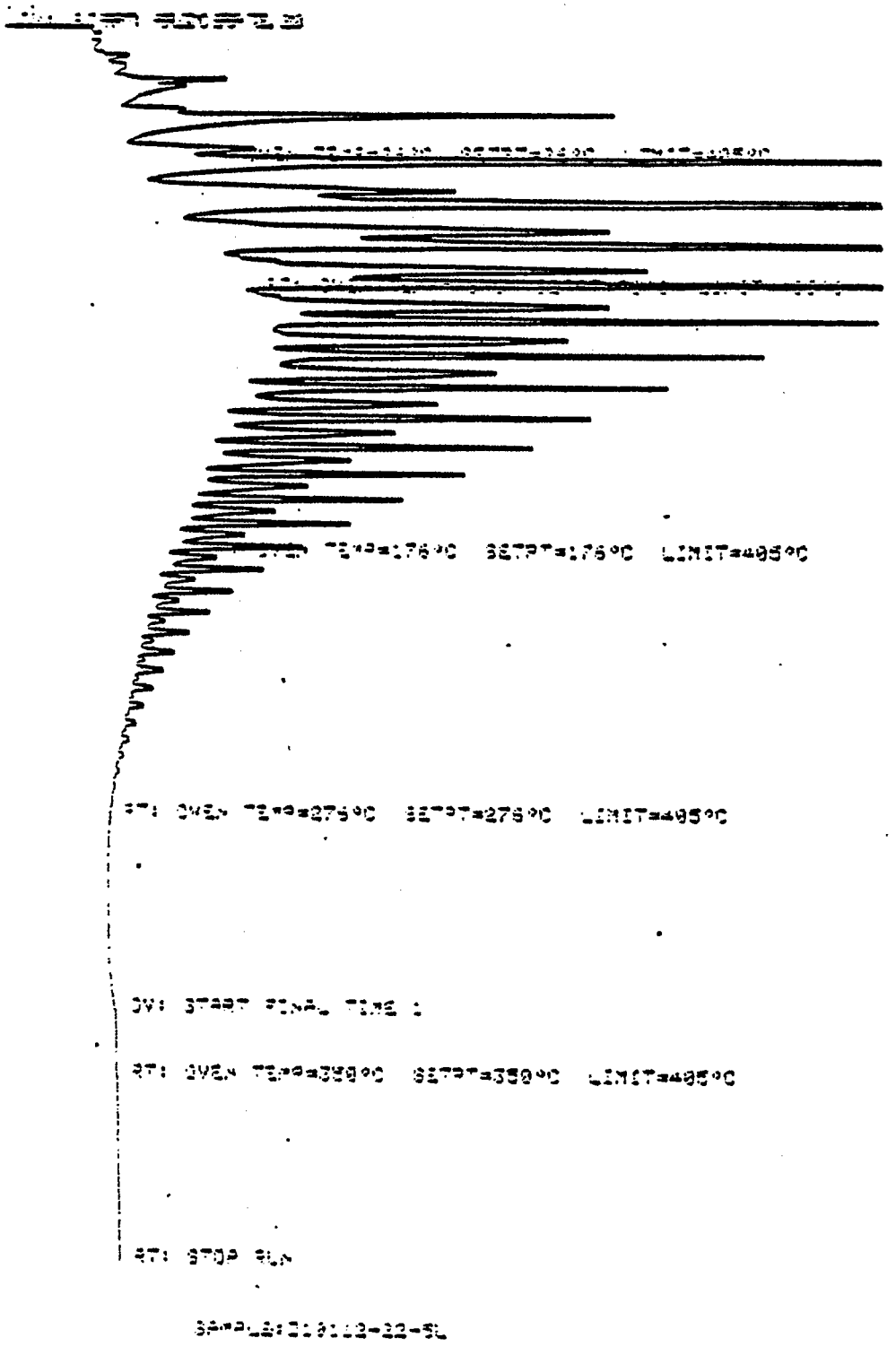

SET=176°C LIMIT=405°C
RT: OVEN SET=275°C LIMIT=405°C
RT: OVEN SET=350°C LIMIT=405°C
RT: STOP RUN

Fig. 92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T=275°C SETPT=275°C LIMIT=405°C
T=350°C SETPT=350°C LIMIT=405°C

Fig. 93

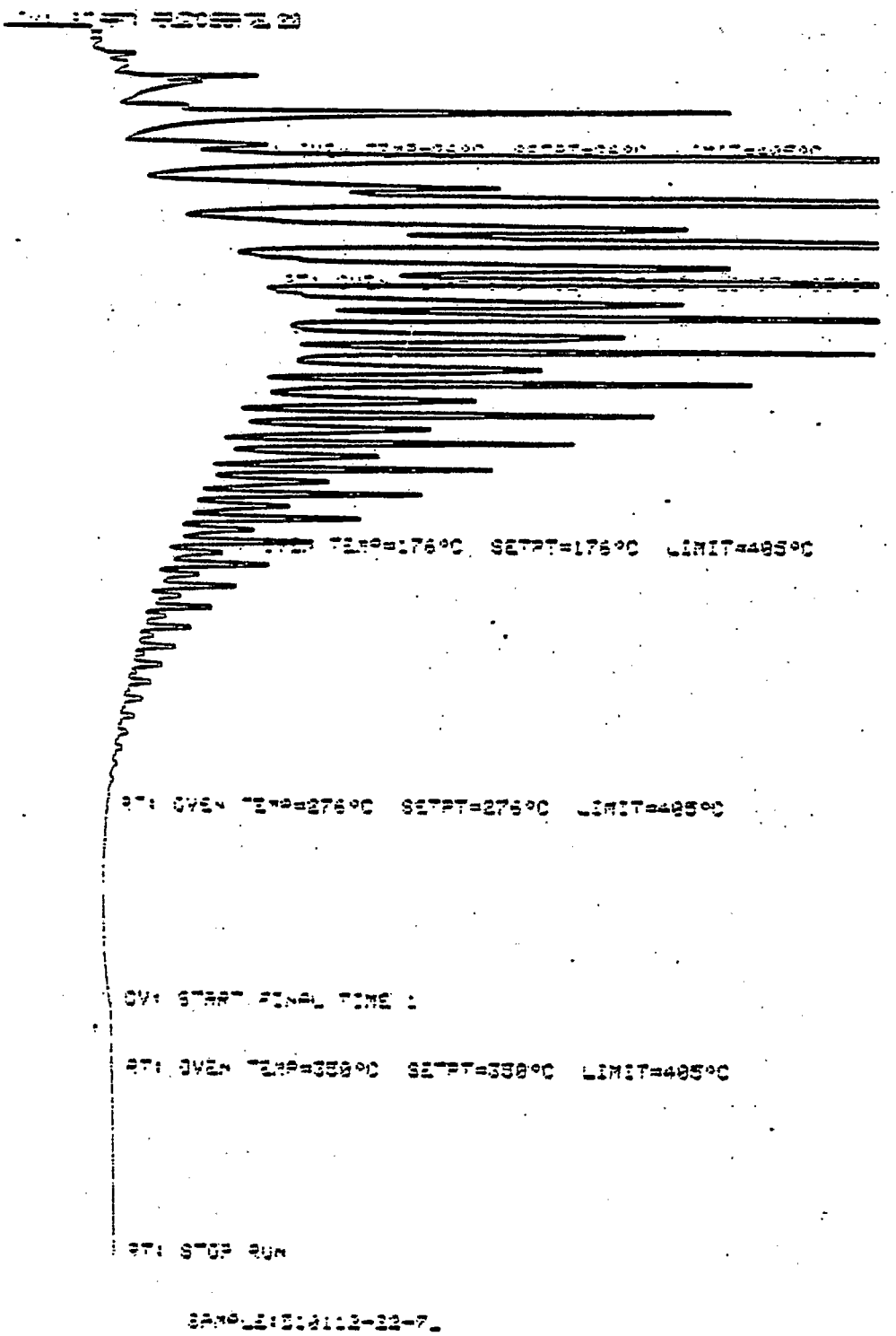
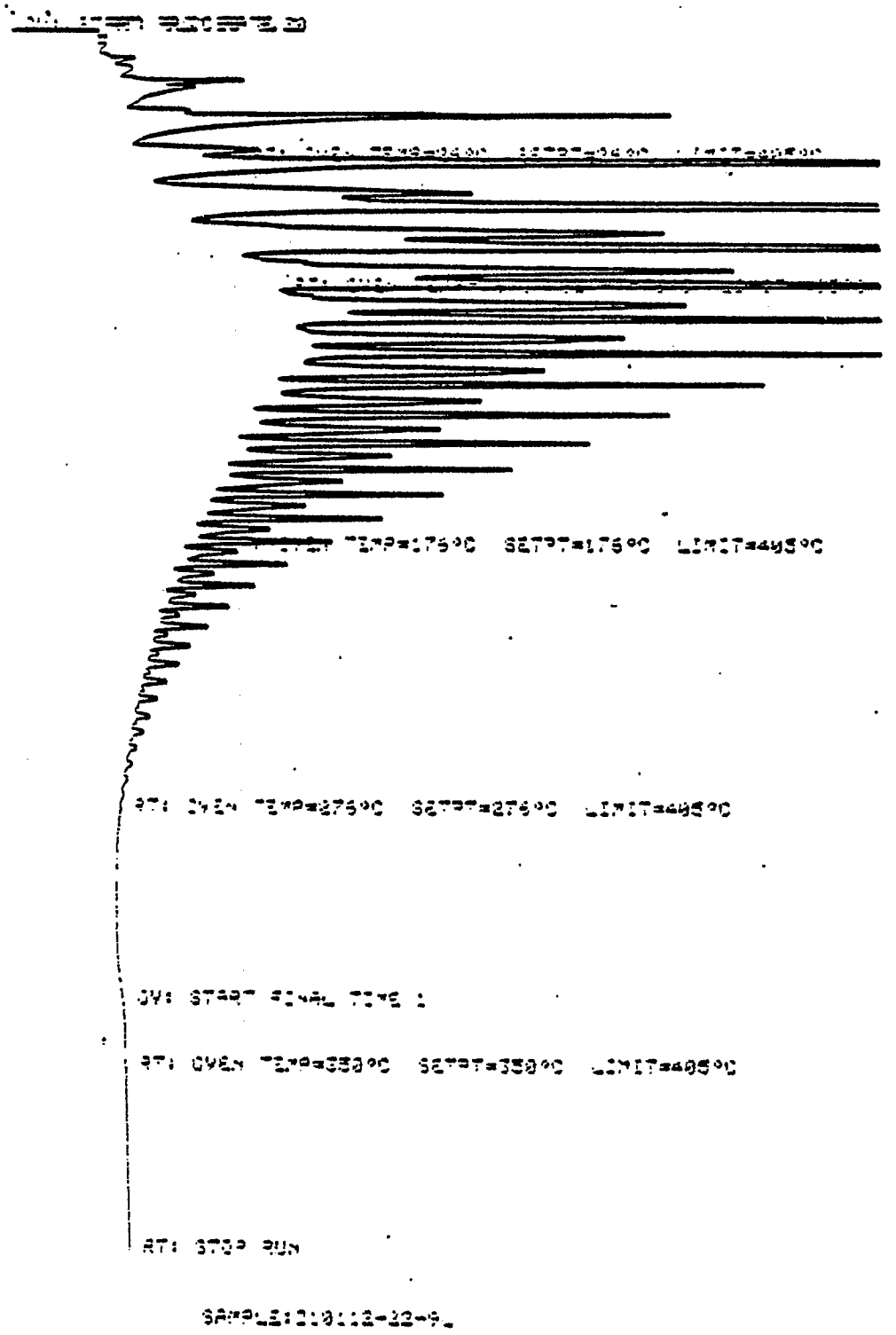

OVEN TEMP=176°C SETPT=175°C LIMIT=405°C
PT: OVEN TEMP=276°C SETPT=275°C LIMIT=405°C
OV: START FINAL TIME :
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
PT: STOP RUN

Fig. 94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AT: OVEN TEMP=275°C SETPT=275°C LIMIT=445°C
OV: START FINAL TIME :
AT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
AT: STOP RUN

Fig. 95

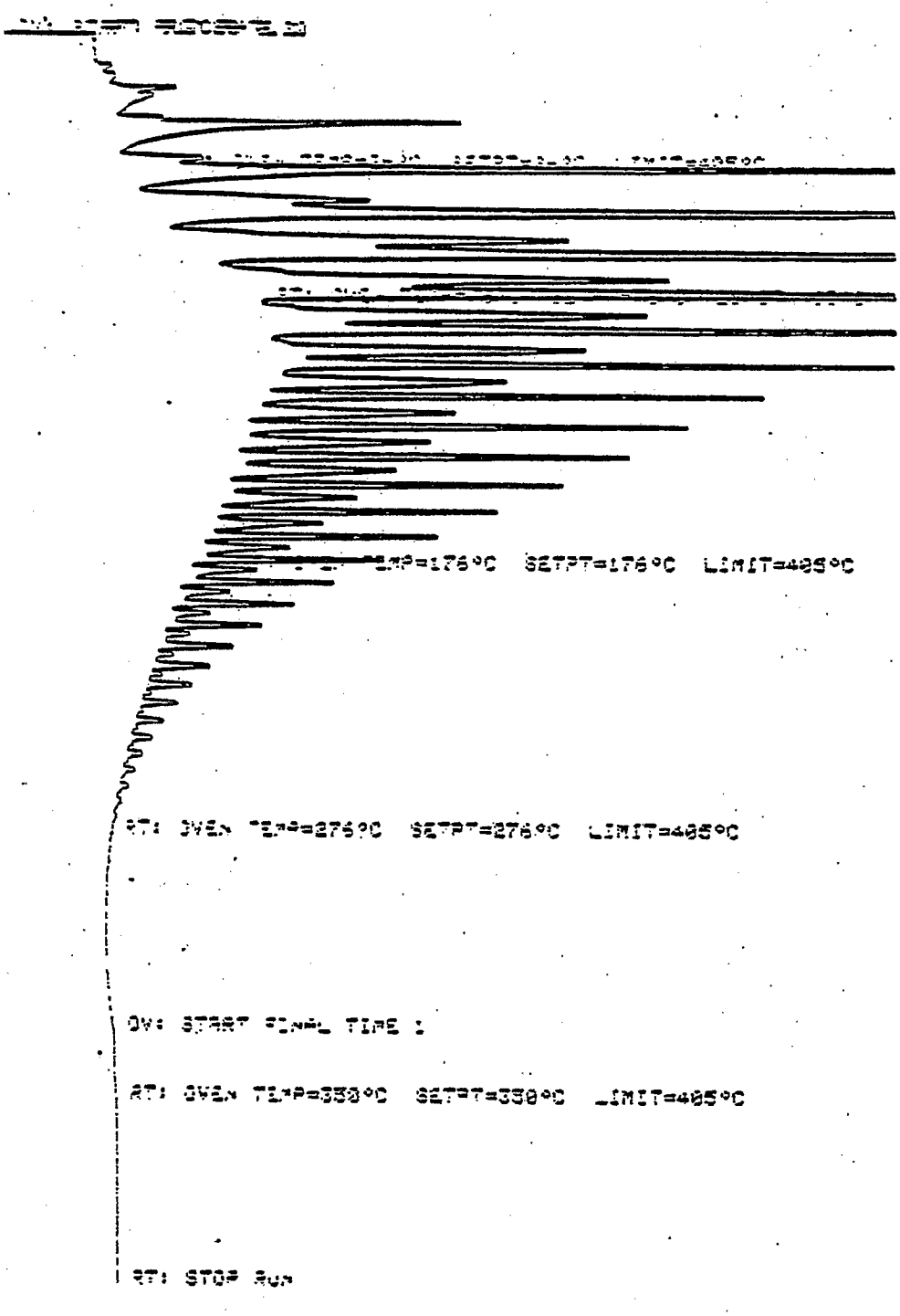

SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
OV: START FINAL TIME :
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP Run

Fig. 96

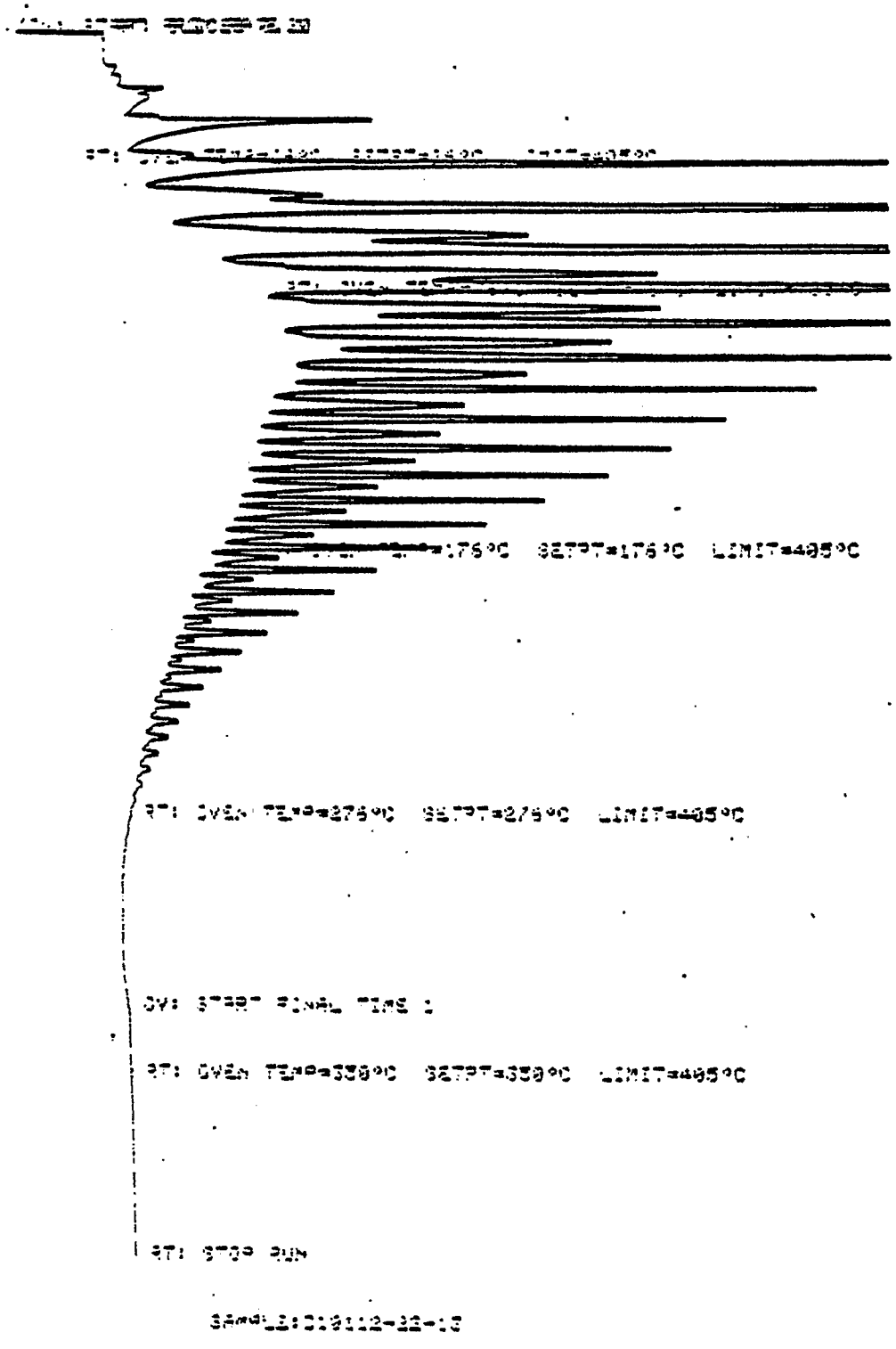

ST: SET=175°C LIMIT=405°C
ST: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
OV: START FINAL TIME :
ST: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
ST: STOP RUN

Fig. 97

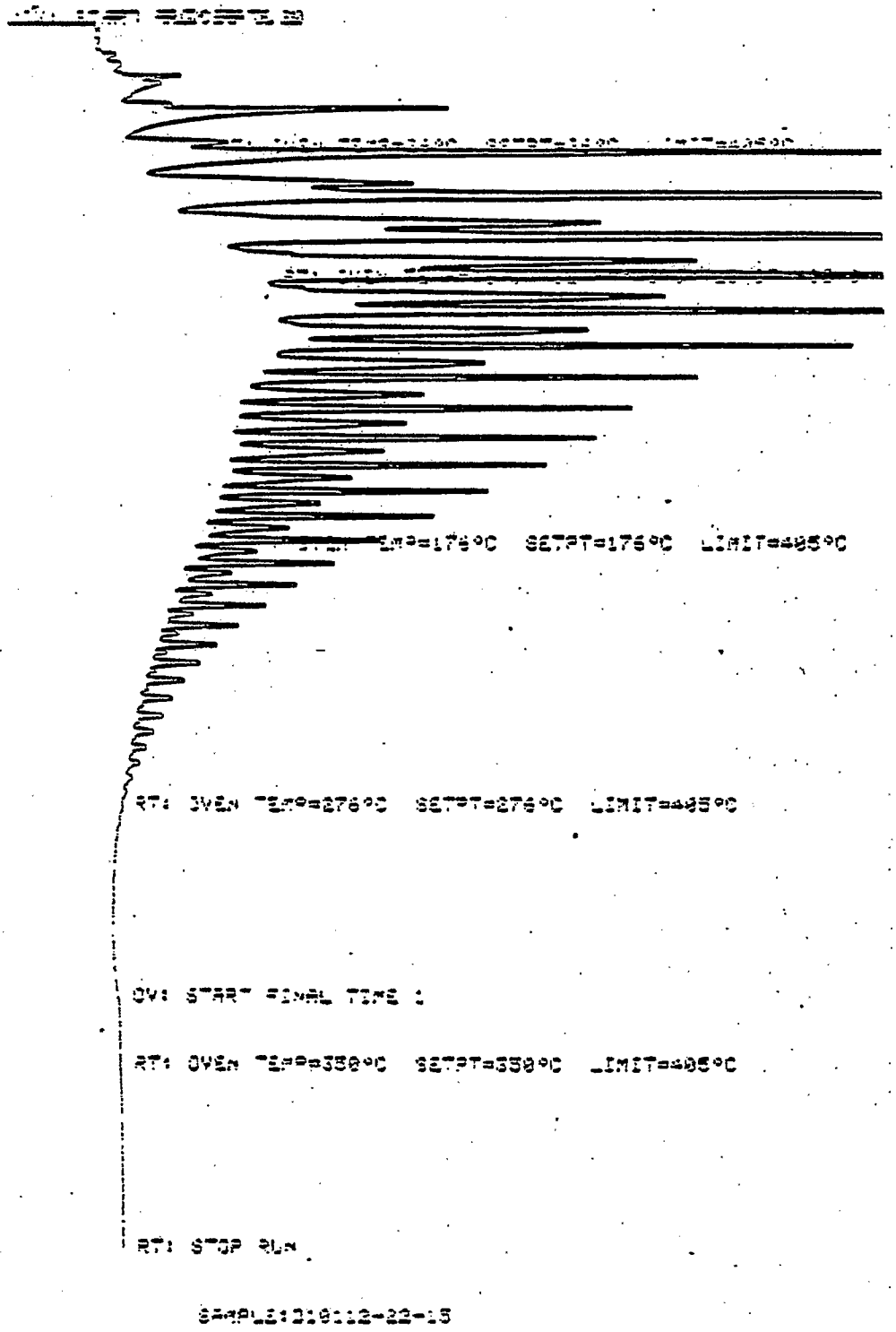

SET PT=175°C LIMIT=405°C
RT: OVEN TEMP=275°C SET PT=275°C LIMIT=405°C
OV: START FINAL TIME :
RT: OVEN TEMP=350°C SET PT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 98

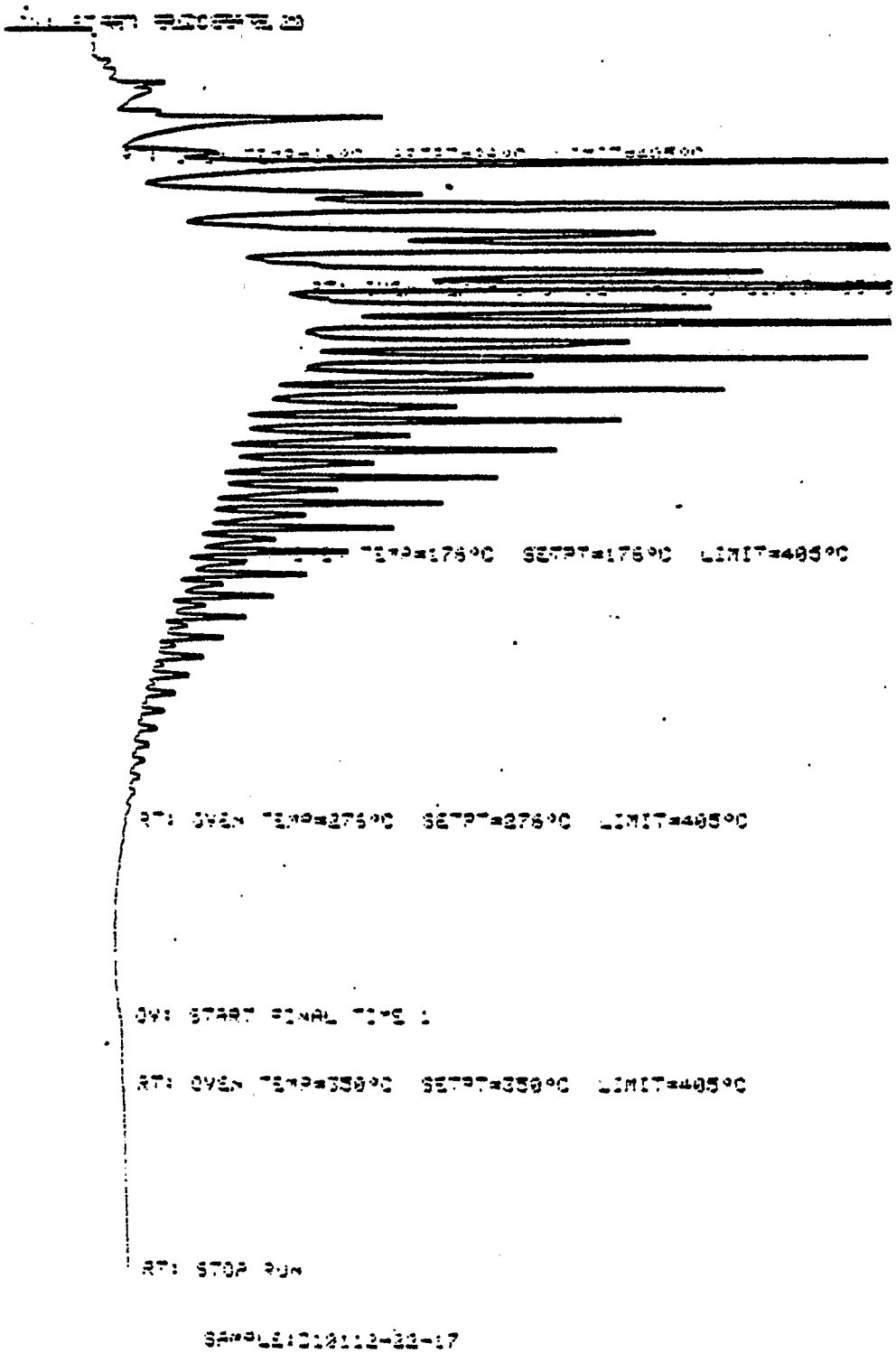

RT: OVEN TEMP=175°C SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=375°C SETPT=375°C LIMIT=405°C
OV: START SIGNAL TYPE 1
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:010112-32-17

TABLE 10 RESULT OF SYNGAS OPERATION

RUN NO. 10112-22
CATALYST CO/TH/X4+UCC-108 10252-90C 80CC 39.9GM (42.6 AFTER RUN +2.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-22-01	112-22-02	112-22-03	112-22-05	112-22-06
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.0	25.5	43.0	66.0	72.5
PRESSURE,PSIG	299	298	297	313	309
TEMP. C	272	272	272	271	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.00	6.50	24.00	23.00	6.50
EFFLNT GAS LITER	177.05	69.55	260.60	305.70	75.10
GM AQUEOUS LAYER	38.25	14.50	53.54	48.59	14.32
GM OIL	19.82	6.87	25.36	23.05	5.93
MATERIAL BALANCE					
GM ATOM CARBON %	89.19	98.32	98.56	114.22	98.93
GM ATOM HYDROGEN %	87.22	95.89	96.87	107.25	97.50
GM ATOM OXYGEN %	91.30	101.95	100.48	112.68	101.78
RATIO CHX/(H2O+CO2)	0.9493	0.9194	0.9556	1.0350	0.9320
RATIO X IN CHX	2.3829	2.4054	2.4092	2.4420	2.4534
USAGE H2/CO PRODT	1.2270	1.2441	1.3018	1.3008	1.3333
RATIO CO2/(H2O+CO2)	0.4199	0.4063	0.3815	0.4087	0.3666
K SHIFT IN EFFLNT	0.36	0.34	0.31	0.35	0.30
CONVERSION					
ON CO %	63.79	60.80	58.78	55.26	55.11
ON H2 %	81.53	79.92	79.15	75.62	76.51
ON CO+H2 %	72.56	70.24	68.88	65.12	65.73
PROT SELECTIVITY,WT %					
CH4	16.26	17.33	17.66	19.08	19.62
C2 HC'S	3.46	3.67	3.64	4.01	4.05
C3H8	4.03	4.12	4.02	4.27	4.33
C3H6=	3.21	3.28	3.24	3.87	3.54
C4H10	2.55	2.60	2.46	2.67	2.69
C4H8=	4.69	4.90	4.81	5.89	5.70
C5H12	2.57	2.59	2.51	2.59	2.60
C5H10=	5.88	5.86	5.70	5.85	5.62
C6H14	2.74	2.71	2.66	2.65	2.63
C6H12= & CYCLO'S	4.36	4.38	4.32	4.88	4.29
C7+ IN GAS	13.10	12.81	13.19	13.25	12.33
LIQ HC'S	37.15	35.75	35.79	30.99	32.60
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.18	35.90	35.83	39.79	39.93
C5 -420 F	49.99	46.99	47.04	45.38	45.08
420-700 F	14.25	14.74	14.75	12.85	13.09
700-END PT	1.58	2.37	2.38	1.98	1.90
C5+-END PT	65.82	64.10	64.17	60.21	60.07
ISO/NORMAL MOLE RATIO					
C4	0.0377	0.0338	0.0033	0.0342	0.0350
C5	0.1054	0.1004	0.0940	0.0931	0.0985
C6	0.1812	0.1670	0.1532	0.1413	0.1459
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1993	1.2000	1.1831	1.0531	1.1679
C4	0.5240	0.5110	0.4943	0.4380	0.4557
C5	0.4254	0.4299	0.4276	0.4304	0.4501
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7829		0.7973	0.7902	
RATIO CH4/(1-A)**2	3.4491		4.2995	4.3371	
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL	CLR OIL	
DENSITY	0.750		0.753	0.754	
N, REFRACTIVE INDEX	1.4241		1.4261	1.4256	
SIMULT'D DISTILATN					
10 WT % @ DEG F	253		259	259	
16	280		295	297	
50	398		414	414	
84	569		603	594	
90	623		659	651	
RANGE(16-84 %)	289		308	297	
WT % @ 420 F	57.40	52.14	52.14	52.17	54.00
WT % @ 700 F	95.76	93.36	93.36	93.62	94.16

TABLE 11 RESULT OF SYNGAS OPERATION

RUN NO. 10112-22
CATALYST CO/TH/X4+UCC-108 10252-90C 80CC 39.9GM (42.6 AFTER RUN +2.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-22-07	112-22-09	112-22-10	112-22-11	112-22-12
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	90.5	115.5	122.5	139.0	145.8
PRESSURE,PSIG	302	298	305	306	306
TEMP. C	271	271	272	271	272
FEED CC/MIN	400	400	543	600	651
HOURS FEEDING	24.50	25.00	7.00	23.50	6.75
EFFLNT GAS LITER	286.05	298.95	128.00	470.95	180.50
GM AQUEOUS LAYER	53.98	53.30	17.85	64.33	18.85
GM OIL	22.36	20.73	5.65	20.37	4.89
MATERIAL BALANCE					
GM ATOM CARBON %	99.33	99.22	98.38	96.43	107.53
GM ATOM HYDROGEN %	97.99	97.01	94.19	93.03	102.16
GM ATOM OXYGEN %	101.05	100.90	99.37	97.51	107.97
RATIO CHX/(H2O+CO2)	0.9580	0.9574	0.9691	0.9653	0.9846
RATIO X IN CHX	2.4463	2.4660	2.4677	2.4788	2.4857
USAGE H2/CO PRODT	1.3748	1.3879	1.5298	1.5285	1.6130
RATIO CO2/(H2O+CO2)	0.3478	0.3443	0.2726	0.2746	0.2384
K SHIFT IN EFFLNT	0.27	0.27	0.21	0.22	0.20
CONVERSION					
ON CO %	53.64	51.74	40.33	40.12	32.65
ON H2 %	75.96	74.64	65.25	64.45	55.78
ON CO+H2 %	64.72	63.06	52.52	52.07	43.92
PRDT SELECTIVITY,WT %					
CH4	19.34	20.21	20.58	21.05	21.49
C2 HC'S	4.01	4.27	4.23	4.62	4.51
C3H8	4.27	4.35	4.00	3.88	3.96
C3H6=	3.57	3.68	4.33	4.23	5.11
C4H10	2.62	2.65	2.55	2.45	2.52
C4H8=	5.65	5.72	6.19	6.09	6.58
C5H12	2.53	2.53	2.39	2.38	2.46
C5H10=	5.56	5.49	5.79	5.84	6.21
C6H14	2.55	2.59	2.45	2.50	2.46
C6H12= & CYCLO'S	4.57	4.57	4.81	4.85	4.79
C7+ IN GAS	12.69	13.26	15.85	15.33	17.95
LIQ HC'S	32.66	30.68	26.82	26.78	21.93
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	39.45	40.88	41.89	42.32	44.18
C5 -420 F	45.53	44.64	44.38	43.97	44.01
420-700 F	13.12	12.54	11.64	11.62	9.86
700-END PT	1.91	1.94	2.09	2.09	1.94
C5+-END PT	60.55	59.12	58.11	57.68	55.82
ISO/NORMAL MOLE RATIO					
C4	0.0347	0.0322	0.0402	0.0327	0.0400
C5	0.0950	0.0919	0.0876	0.0879	0.0870
C6	0.1305	0.1329	0.1099	0.1235	0.1130
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1407	1.1274	0.8818	0.8767	0.7393
C4	0.4483	0.4462	0.3980	0.3875	0.3701
C5	0.4422	0.4473	0.4013	0.3954	0.3858
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7931	0.7931		0.7946	
RATIO CH4/(1-A)**2	4.5178	4.7214		4.9892	
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL		CLR OIL	
DENSITY	0.753	0.753		0.758	
N, REFRACTIVE INDEX	1.4256	1.4259		1.4280	
SIMULT'D DISTILATN					
10 WT % @ DEG F	259	260		287	
16	296	300		304	
50	410	413		428	
84	583	591		619	
90	642	650		674	
RANGE(16-84 %)	287	291		315	
WT % @ 420 F	54.00	52.80	48.80	48.80	46.17
WT % @ 700 F	94.16	93.69	92.20	92.20	91.14

TABLE 12 RESULT OF SYNGAS OPERATION

RUN NO. 10112-22
CATALYST CO/TH/X4+UCC-108 10252-90C 80CC 39.9GM (42.6 AFTER RUN +2.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 800 CC/MN OR 600 GHSV

RUN & SAMPLE NO.	10112-22-13	112-22-14	112-22-15	112-22-16	112-22-17
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	163.0	170.0	187.0	194.5	211.0
PRESSURE,PSIG	304	304	305	297	302
TEMP. C	272	272	281	281	281
FEED CC/MIN	800	800	800	800	800
HOURS FEEDING	24.00	7.00	24.00	7.50	24.00
EFFLNT GAS LITER	707.05	213.00	678.25	210.75	673.70
GM AQUEOUS LAYER	77.96	25.29	86.72	27.26	87.22
GM OIL	20.22	6.09	20.89	6.46	20.67
MATERIAL BALANCE					
GM ATOM CARBON %	96.53	99.70	102.92	102.66	100.76
GM ATOM HYDROGEN %	93.32	98.14	97.70	98.32	97.28
GM ATOM OXYGEN %	97.73	102.08	102.87	101.80	100.90
RATIO.CHX/(H2O+CO2)	0.9553	0.9183	1.0014	1.0265	0.9955
RATIO X IN CHX	2.4931	2.4840	2.5606	2.5526	2.5580
USAGE H2/CO PRODT	1.6155	1.6323	1.5010	1.5263	1.5371
RATIO CO2/(H2O+CO2)	0.2338	0.2184	0.3119	0.3023	0.2915
K SHIFT IN EFFLNT	0.19	0.18	0.25	0.24	0.23
CONVERSION					
ON CO %	33.10	33.13	41.81	42.02	40.83
ON H2 %	56.35	56.92	66.08	66.29	65.12
ON CO+H2 %	44.53	44.93	53.63	53.89	52.76
PRDT SELECTIVITY,WT %					
CH4	21.76	21.43	24.75	24.37	24.77
C2 HC'S	4.90	4.56	5.02	4.90	4.93
C3H8	3.84	3.83	4.62	4.67	4.54
C3H6=	4.82	4.88	4.58	4.66	4.83
C4H10	2.45	2.46	2.76	2.75	2.64
C4H8=	6.34	6.39	6.47	6.50	6.23
C5H12	2.43	2.38	2.62	2.57	2.49
C5H10=	6.07	6.20	6.30	6.24	6.28
C6H14	2.57	2.54	2.68	2.63	2.60
C6H12= & CYCLO'S	4.88	4.81	4.80	5.03	4.54
C7+ IN GAS	17.07	17.77	17.00	17.73	17.37
LIQ HC'S	22.88	22.75	18.41	17.94	18.78
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	44.11	43.56	48.20	47.85	47.94
C5 -420 F	43.57	44.95	42.51	43.14	42.63
420-700 F	10.29	9.52	7.71	7.52	7.87
700-END PT	2.03	1.97	1.59	1.49	1.56
C5+-END PT	55.89	56.44	51.80	52.15	52.06
ISO/NORMAL MOLE RATIO					
C4	0.0355	0.0377	0.0417	0.0407	0.0416
C5	0.0915	0.0853	0.1047	0.1090	0.1092
C6	0.1058	0.1154	0.1563	0.1729	0.1749
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.7619	0.7492	0.9621	0.9560	0.8987
C4	0.3725	0.3724	0.4119	0.4088	0.4090
C5	0.3889	0.3731	0.4038	0.4013	0.3861
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7948		0.7894		0.7919
RATIO CH4/(1-A)**2	5.1693		5.5804		5.7171
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.761		0.758		0.758
N, REFRACTIVE INDEX	1.4289		1.4281		1.4282
SIMULT'D DISTILATN					
10 WT % @ DEG F	299		285		290
16	324		303		306
50	437		423		421
84	630		625		616
90	687		683		677
RANGE(16-84 %)	306		322		310
WT % @ 420 F	46.17	49.50	49.50	49.80	49.80
WT % @ 700 F	91.14	91.36	91.36	91.69	91.69

VIII. RUN 7 (10225-16) with Catalyst 7 (Co/Th + UCC-103)

This catalyst was prepared by promoting cobalt oxide with thorium while in contact with UCC-103 powder (a modification of UCC-101). The mixture was bonded with 20 percent silica, and formed as 1/8-inch extrudates. The final product contained 10 weight 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. 99-102. Simulated distillations of the C_5^+ product for three samples are plotted in Figs. 103-105. Carbon number product distributions are plotted in Figs. 106-115. Chromatograms from simulated distillations are reproduced in Figs. 116-125. Detailed material balances appear in Tables 13-16.

Compared with the reference catalyst (Tenth Quarter Run 10112-15), this catalyst is both more active and more stable. At the end of the run (235 hours on stream) the conversion of $CO+H_2$, initially about 80 percent, had dropped only to 72 percent; corresponding values for the reference catalyst were 76 percent initially and 52 percent after 188 hours on stream. The water gas shift activity was higher, although only slightly, with 40 percent of the oxygen rejected as CO_2 initially and 25 percent at the end of the run, as against 37 and 20 percent for the reference catalyst. Usage of the 1:1 H_2:CO syngas was less than 1.3:1

initially and remained below 1.6:1, as against 1.23:1 and 1.71:1 for the reference catalyst. The higher initial ratio is due in part to the fact that this catalyst produced a hydrogen-rich product with a constant 2.5 hydrogens per carbon, whereas the reference catalyst produced 2.3 carbons per hydrogen initially and 2.5 at the end of the run.

The selectivity also was unusually stable. While the initial methane production was rather high at 20 percent, by the end of the run it had risen only to 21 percent; corresponding values for the reference catalyst were 15 and 24 percent. Furthermore, since production of C_2-C_4 rose only from 15 to 17 percent (reference values 13 and 15 percent), the yield of C_5^+ was above average. Production of total motor fuels, although somewhat lower initially than for the reference catalyst (63 vs. 69 percent), was again more stable; at 188 hours on stream (the term of the reference run), this catalyst was producing 61 percent total motor fuels as against 55 percent for the reference catalyst, and after 235 hours it was still producing nearly 60 percent. Olefinic content of the C_4's was not very high, with only 40 percent as butenes--the most paraffinic product yet produced. The same was true for the gasoline and jet fuel fractions, in which the olefins were 15 and 12 percent respectively, as against 36 and 32 percent for the reference catalyst.

While no carbon number cut-off is evident from the Schulz-Flory plots, a possible cut-off may be inferred from the physical properties of the liquid product. The pour point of the jet fuel

was 5F (vs. ØF for the reference), which is consistent with its low degree of isomerization and unsaturation. However, the pour point of the diesel oil was 35F, well above the 20F value of Catalyst 6, which was much higher in olefins, but substantially below the reference value of 50F. In addition, although the liquid product was poorly isomerized and highly saturated, it nevertheless contained no solids. The lack of very heavy hydrocarbons is consistent with the lower pour point of the diesel oil.

This is another entry in our growing catalog of promising catalysts. Its product distribution and stability are both excellent, and its heavier products, despite their high paraffin content, still have good flow properties. The catalyst demonstrates the potential benefits of intimate contact of the metal component and the shape selctive component, effectuated by its method of preparation.

Fig. 99

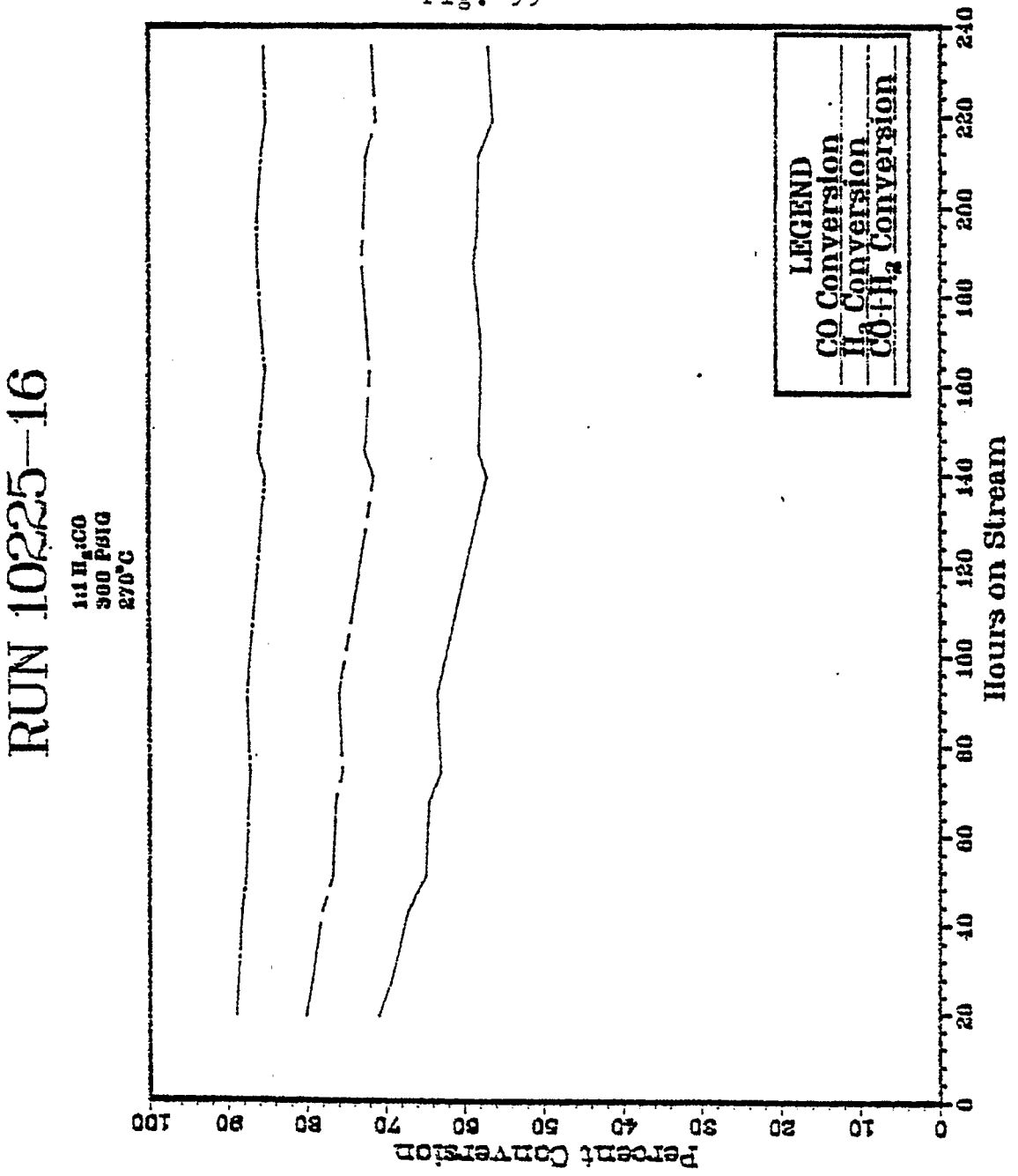
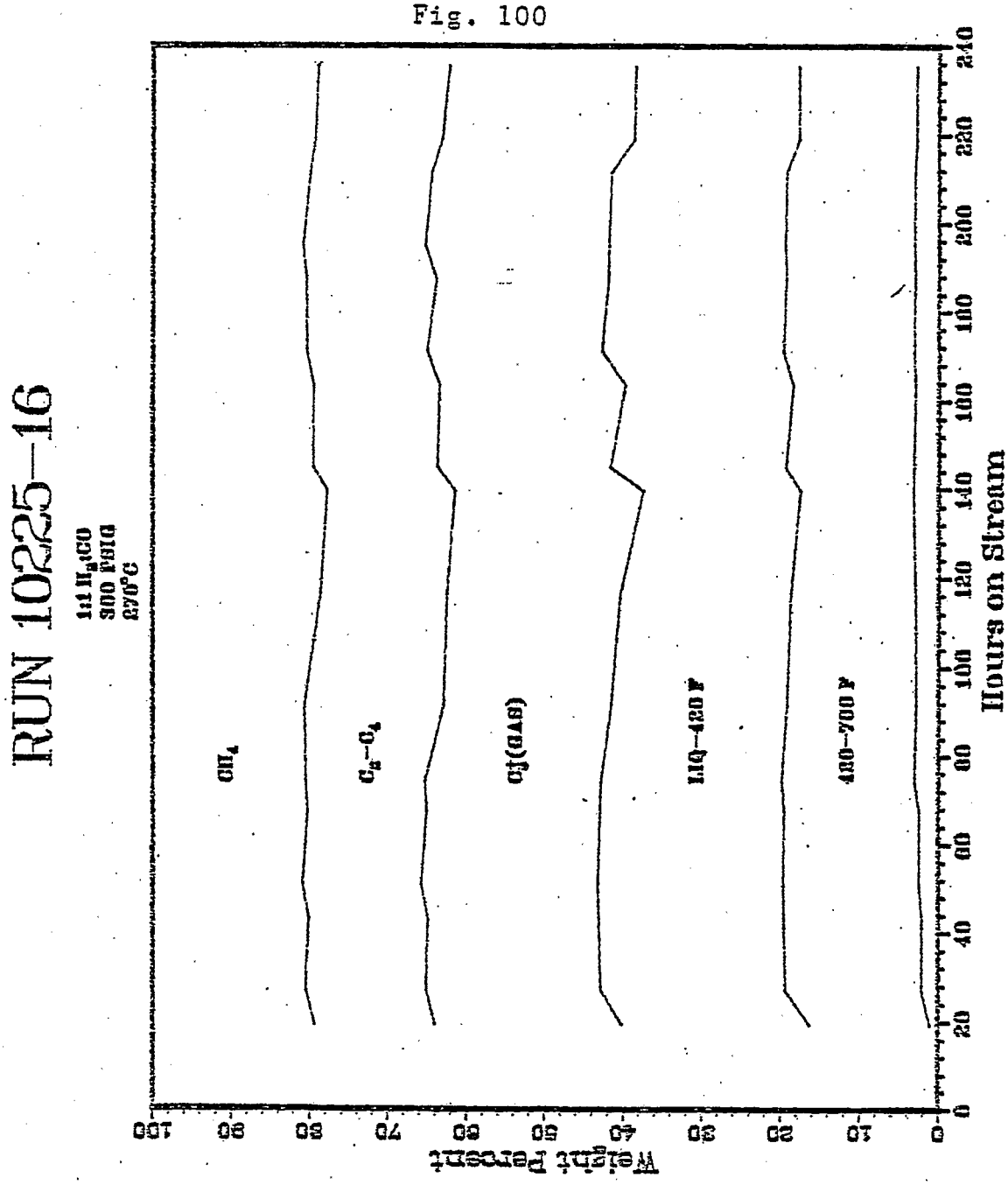

RUN 10225-16
1:1 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 100


RUN 10225-16
1:1 H2:CO
300 PSIG
270°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
20
40
60
80
100
120
140
160
180
200
220
240

RUN 10225–16

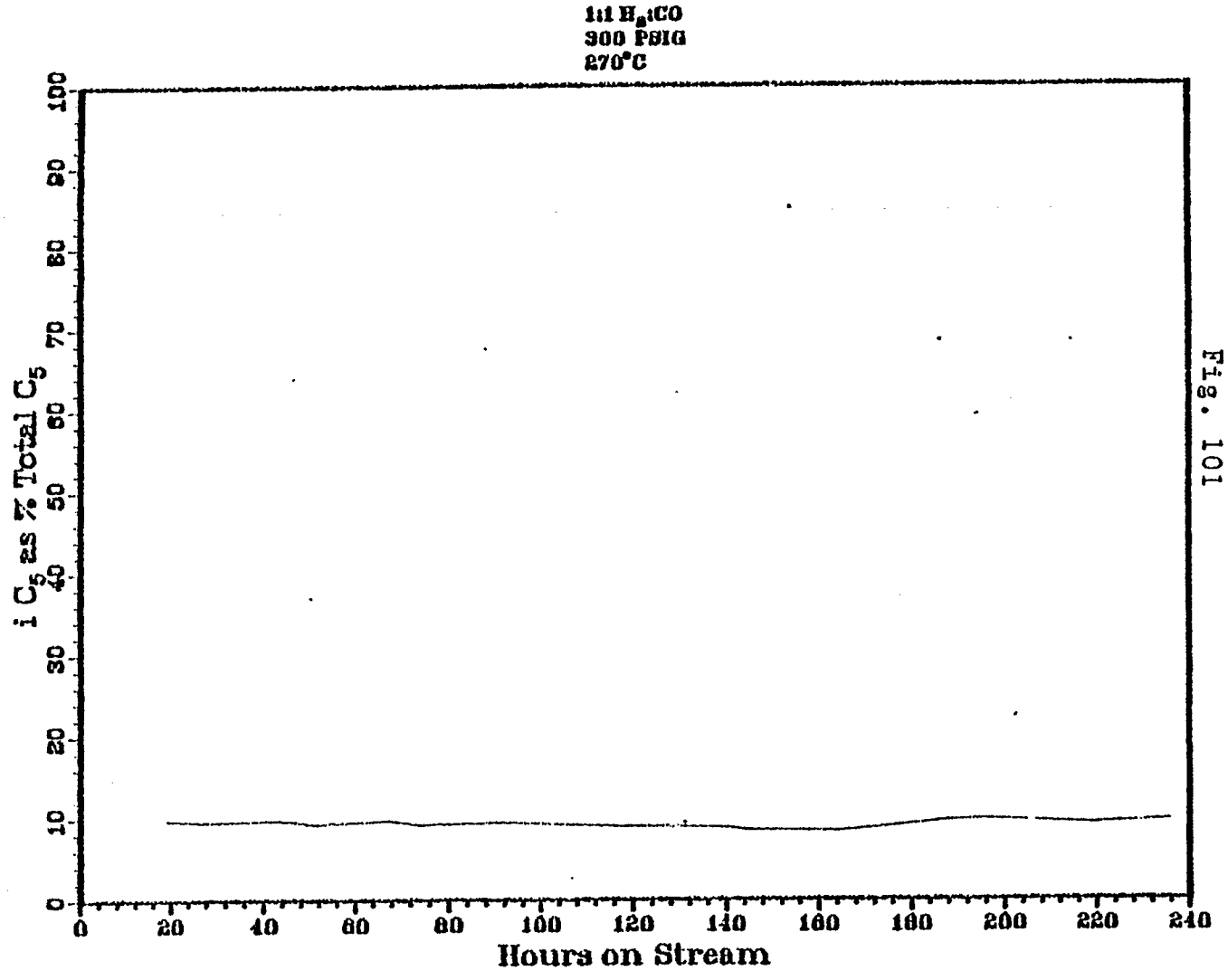


Fig. 101

Fig. 102

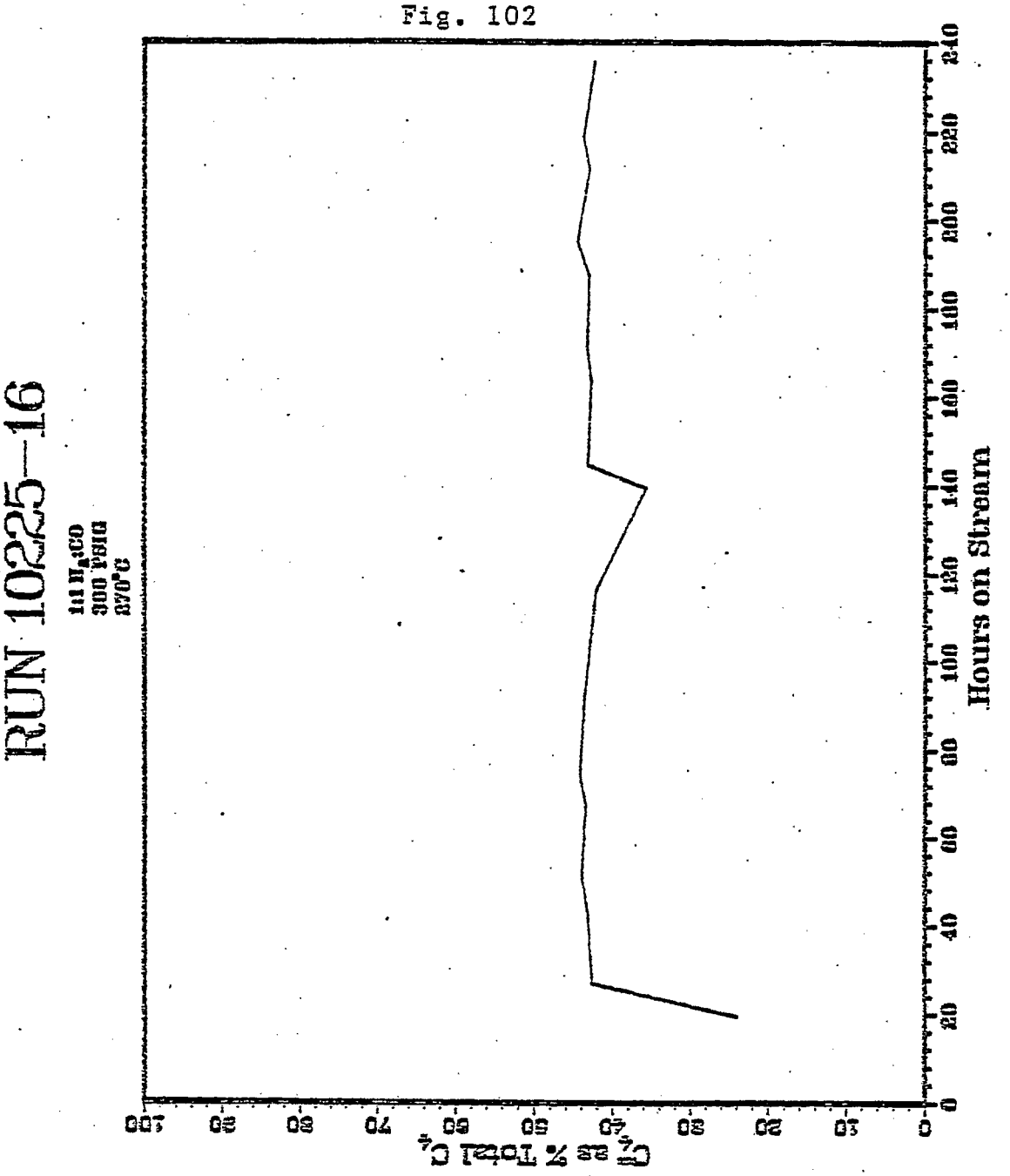

RUN 10225-16
111 H2:CO
300 PSIG
270°C
C4 as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 103

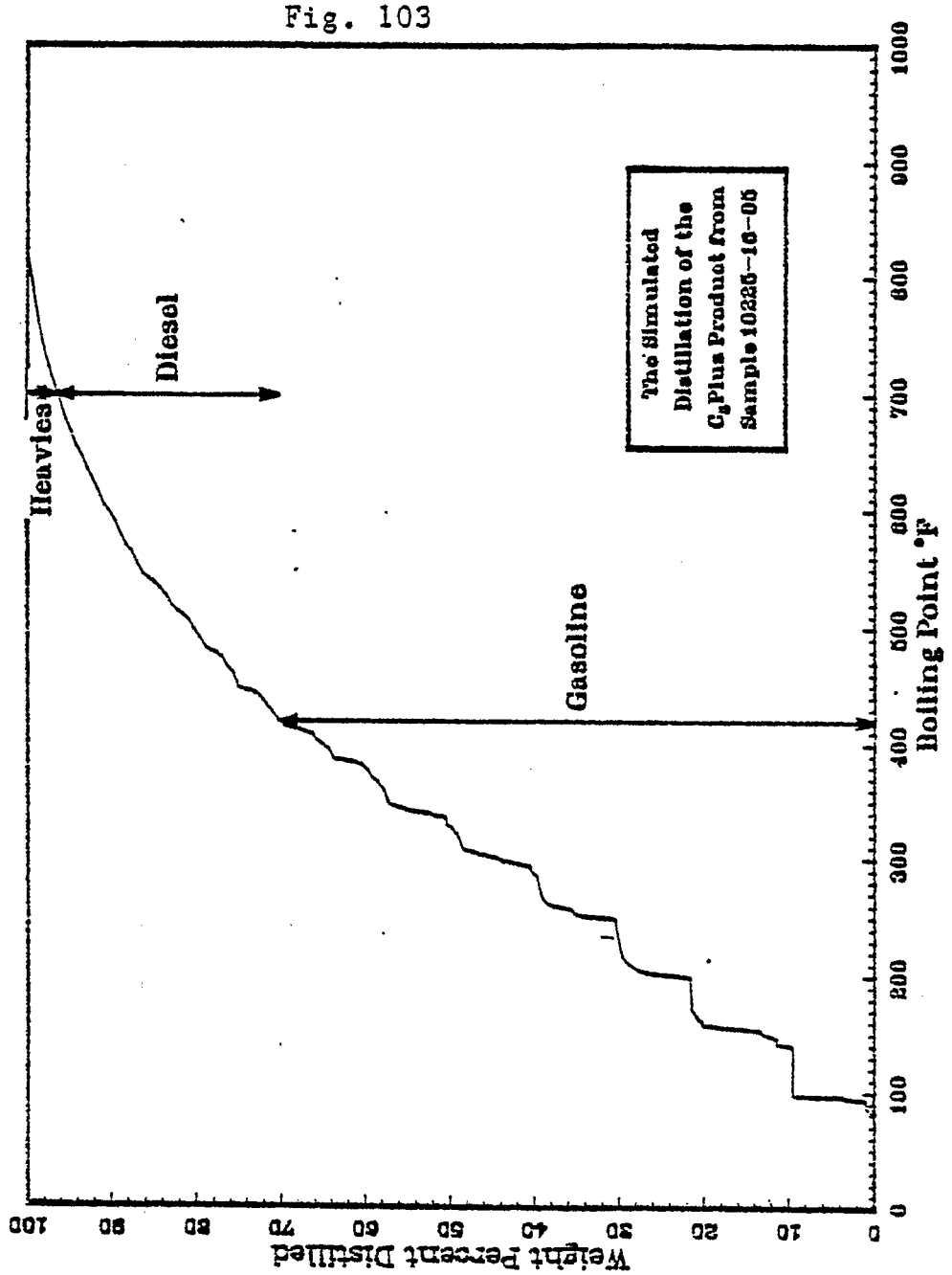

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 10225-16-05

Fig. 104

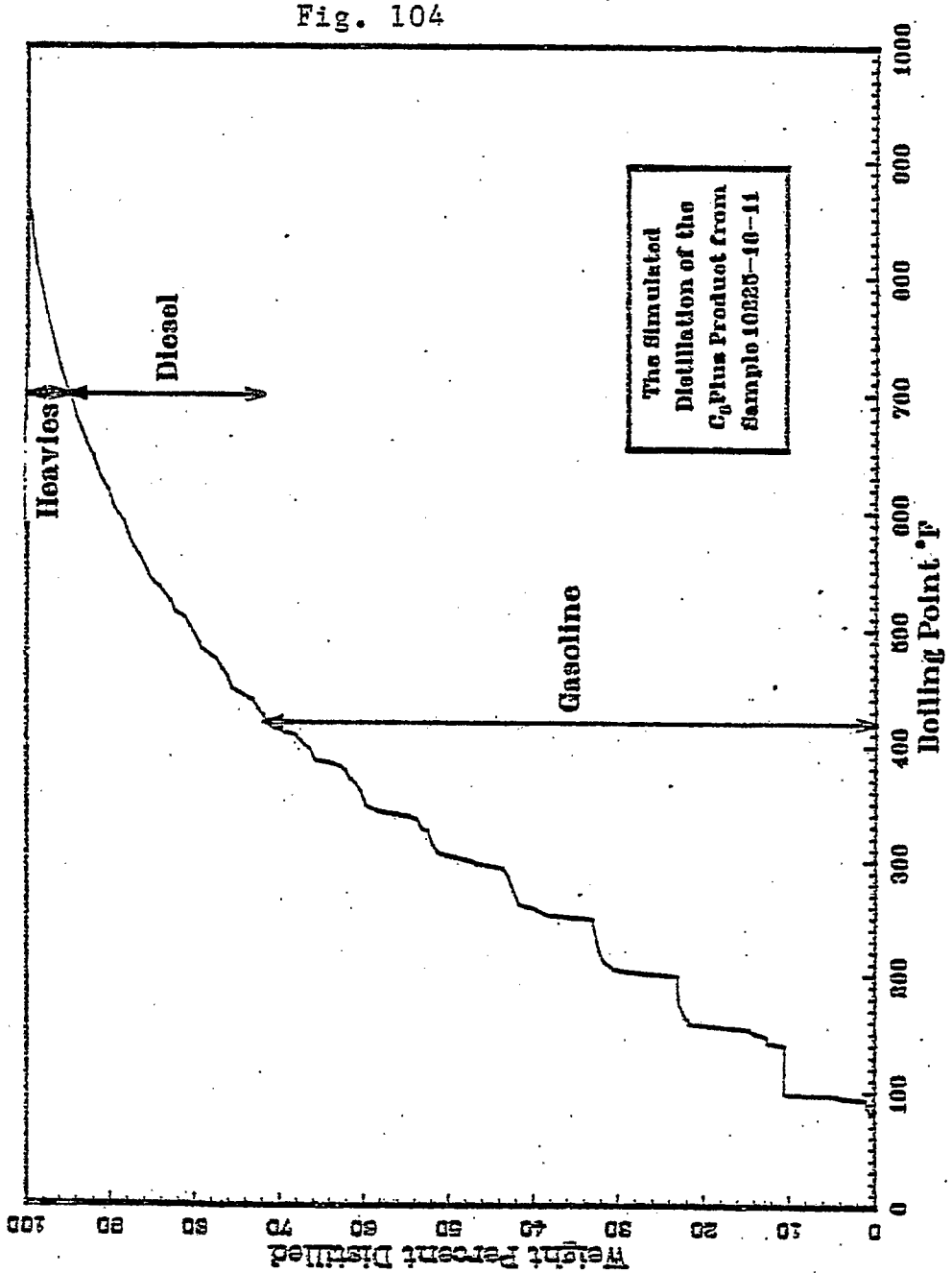

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 10325-10-11

Fig. 105

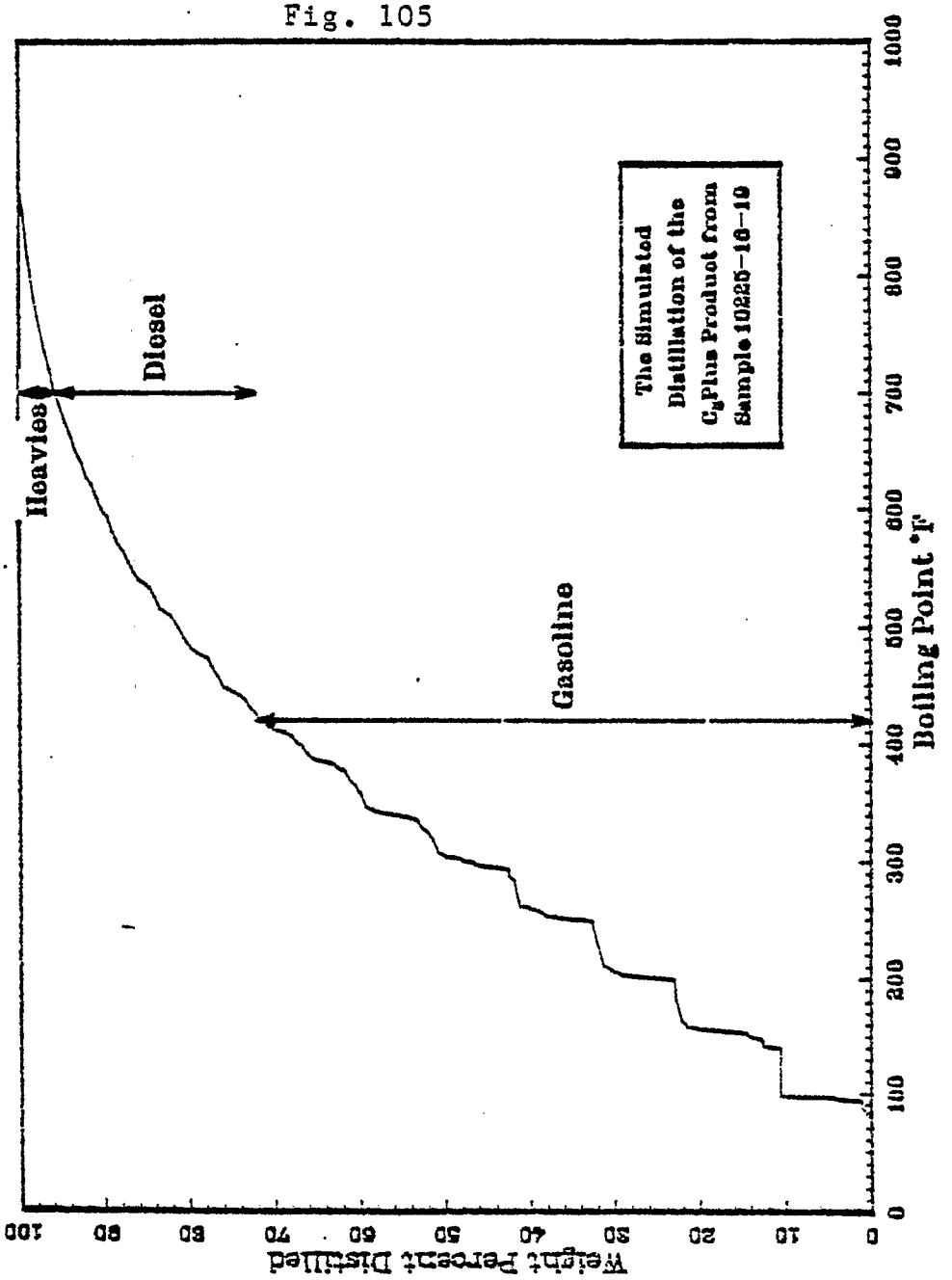

The Simulated Distillation of the C9Plus Product from Sample 10225-16-10
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 106

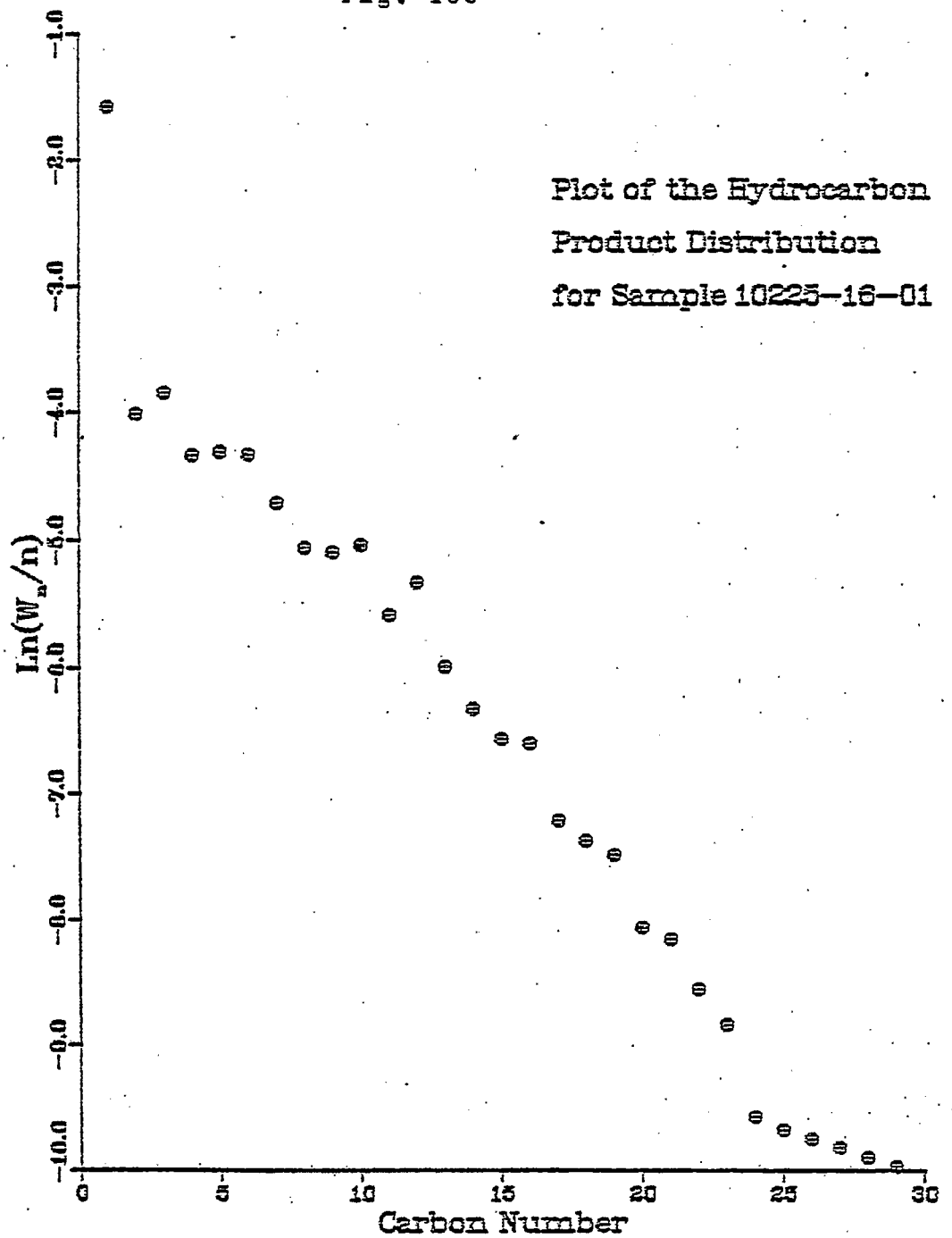

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 107

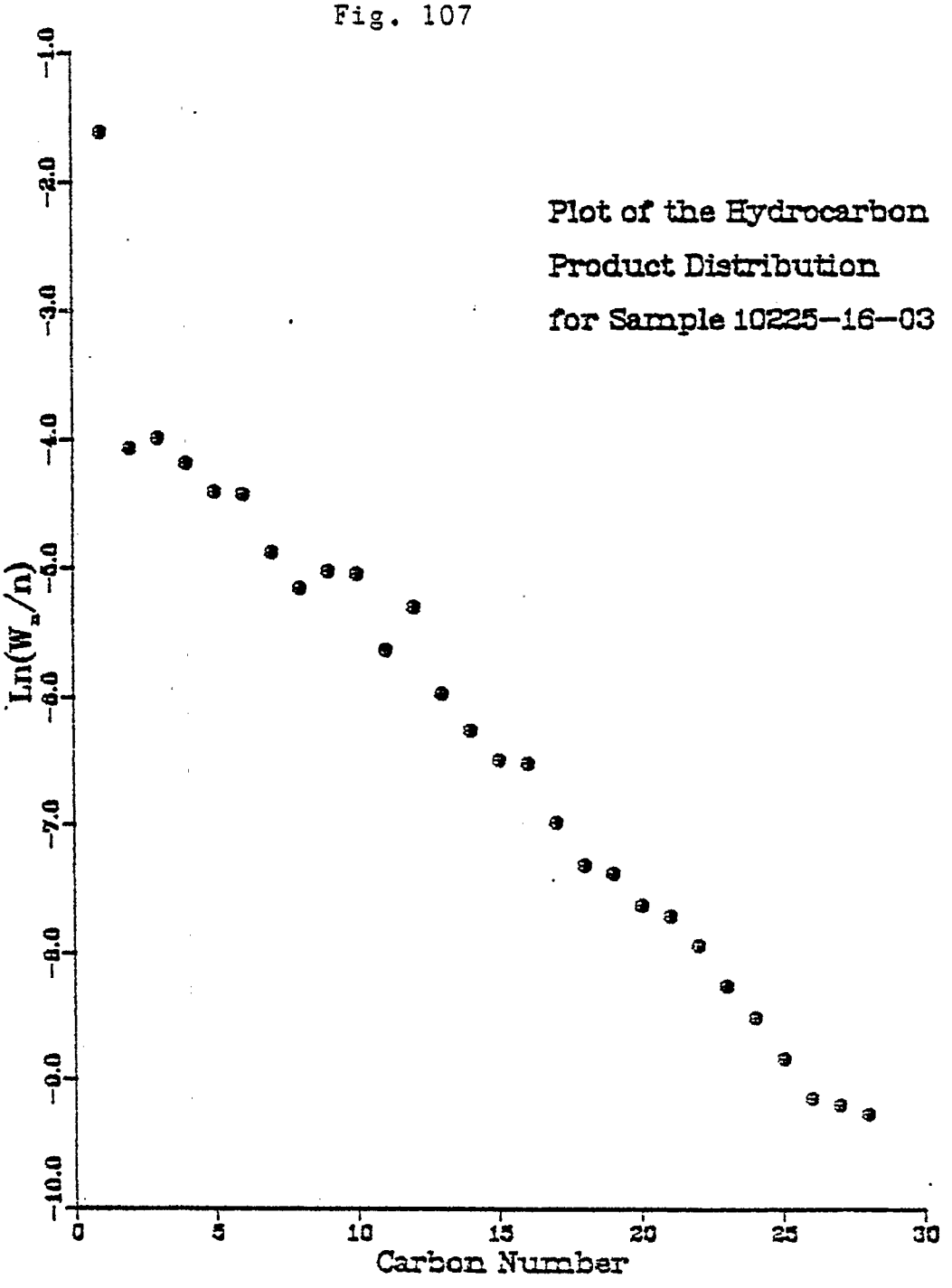

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 108

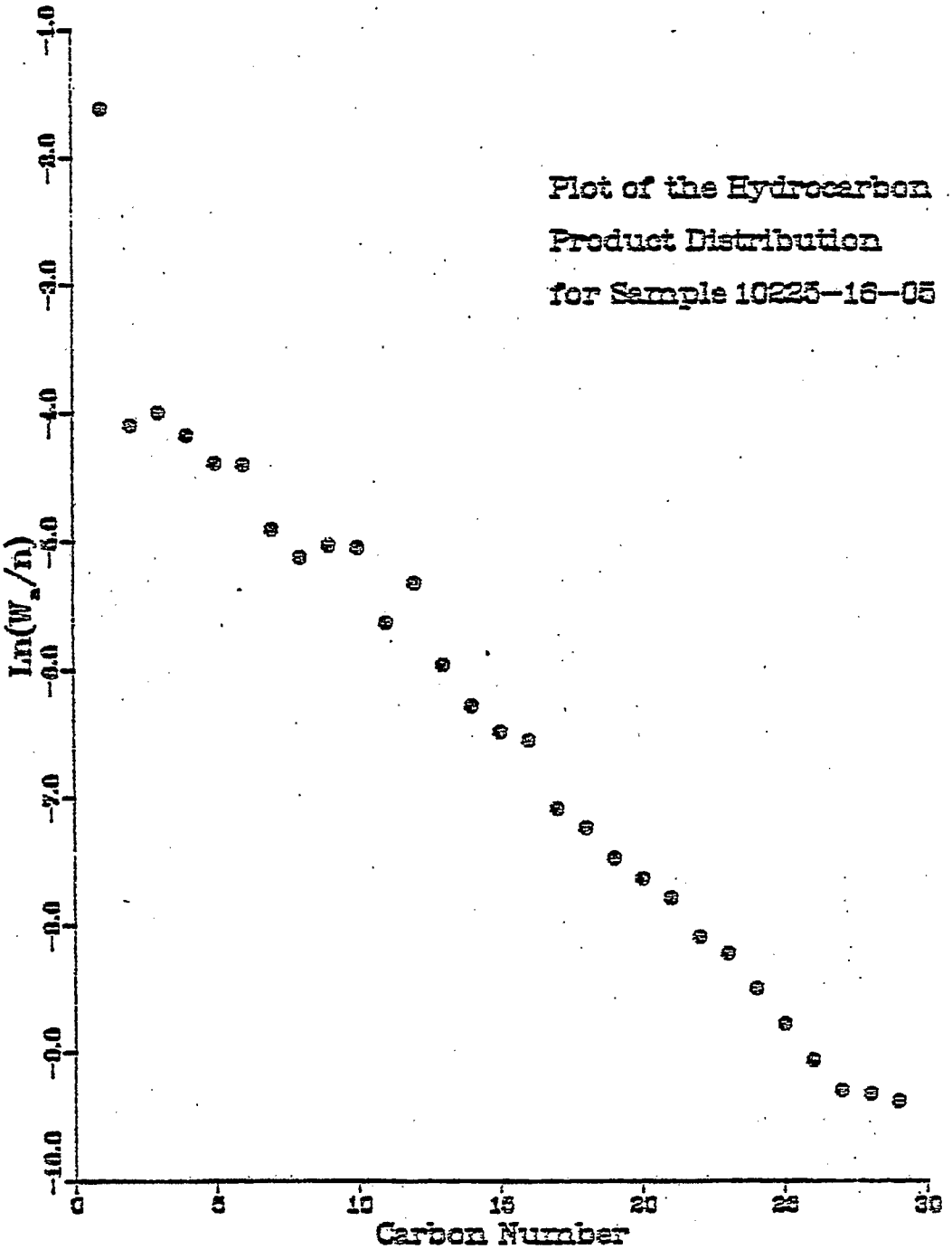

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 109

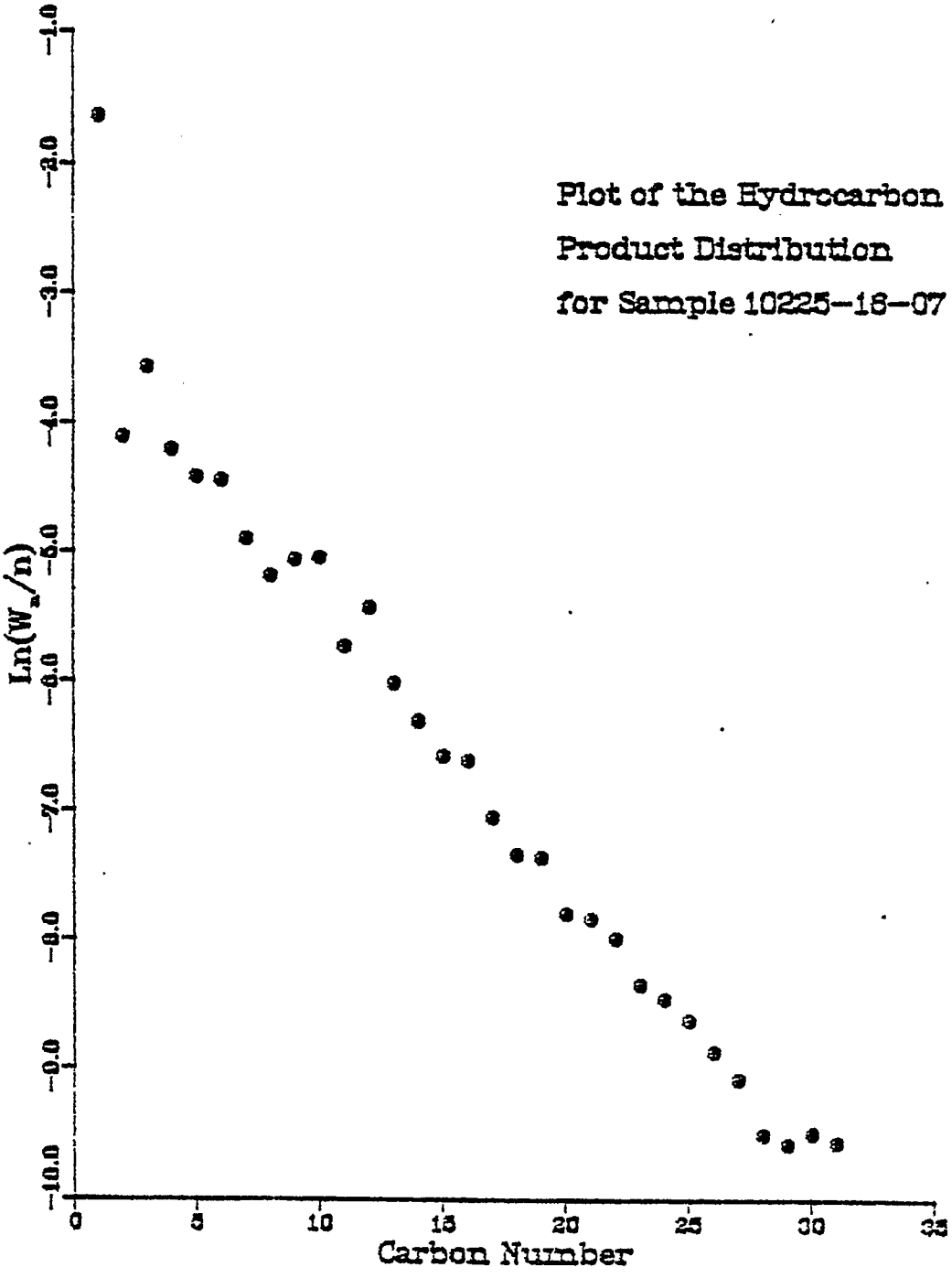

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-18-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 110

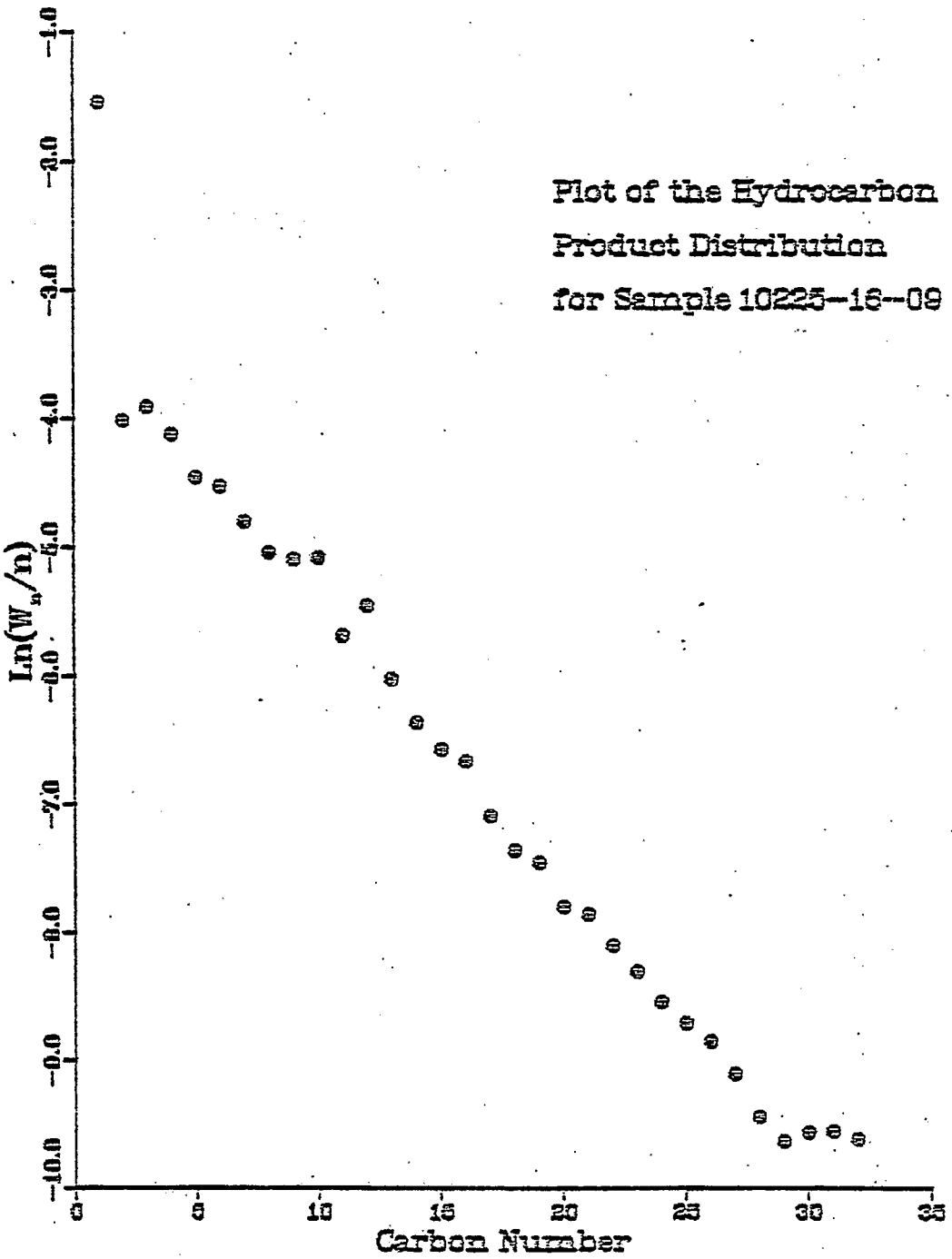

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-09
Ln(W_n/n)
-1.0
-3.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 111

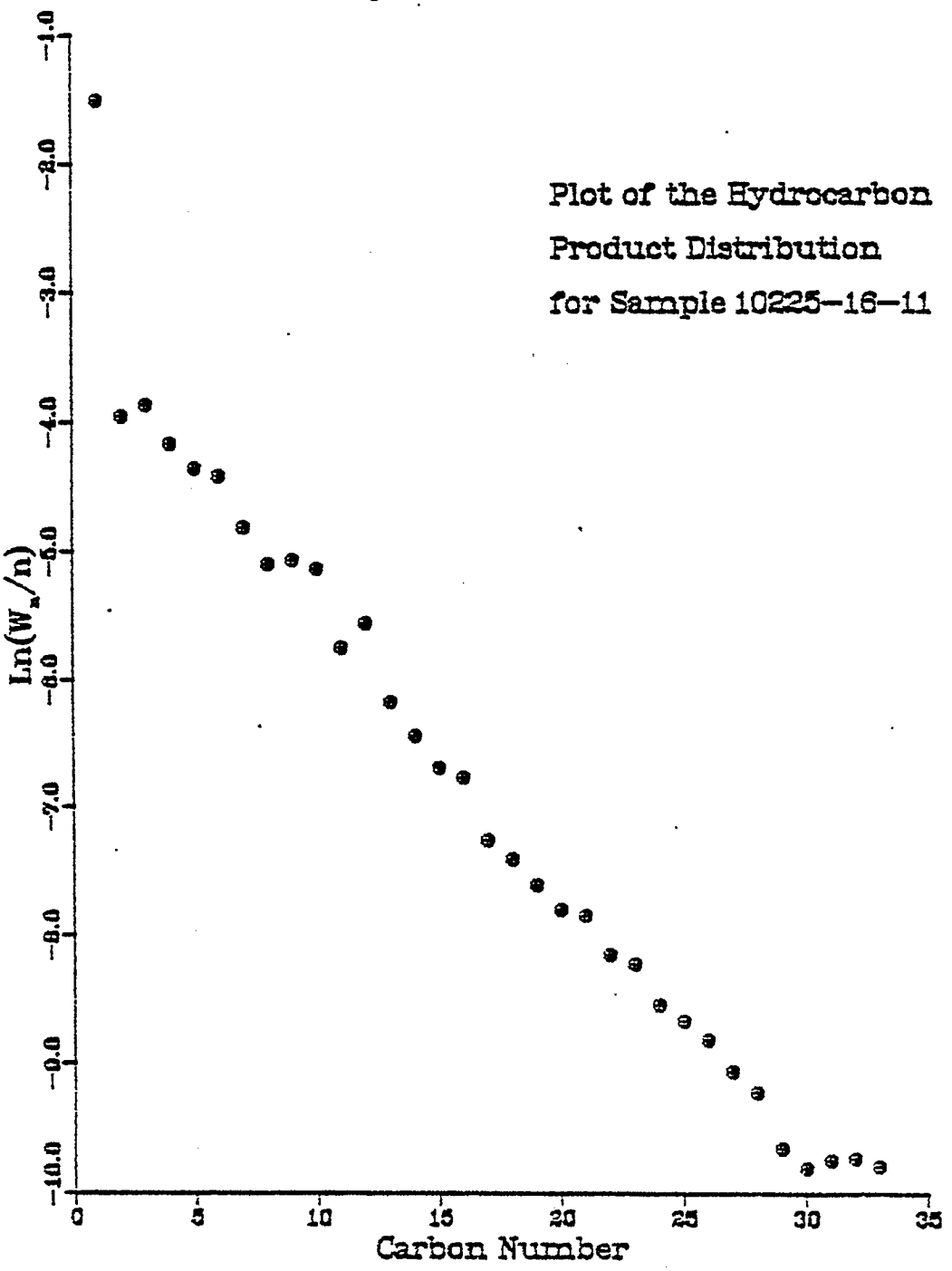

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 112

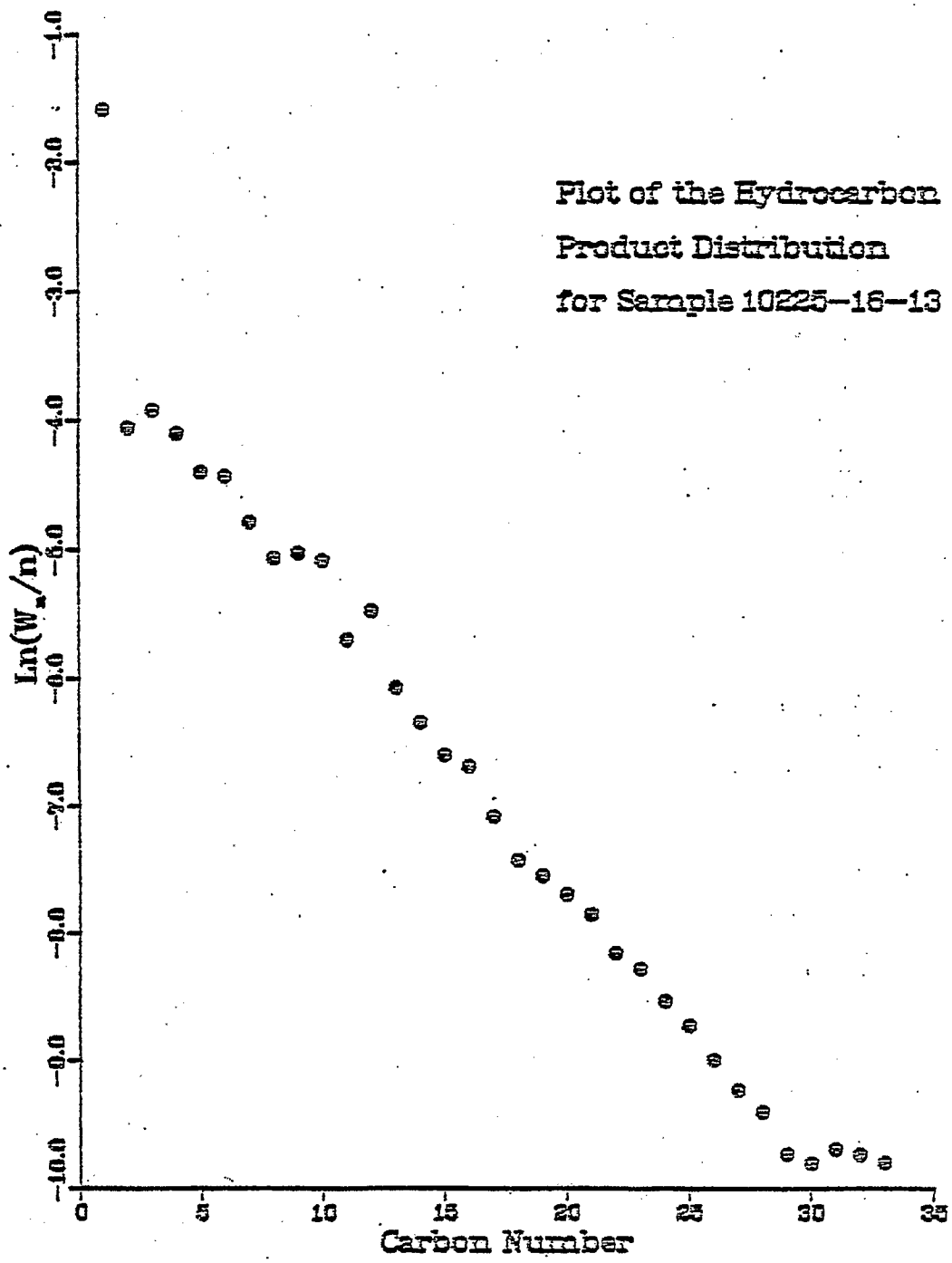

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 113

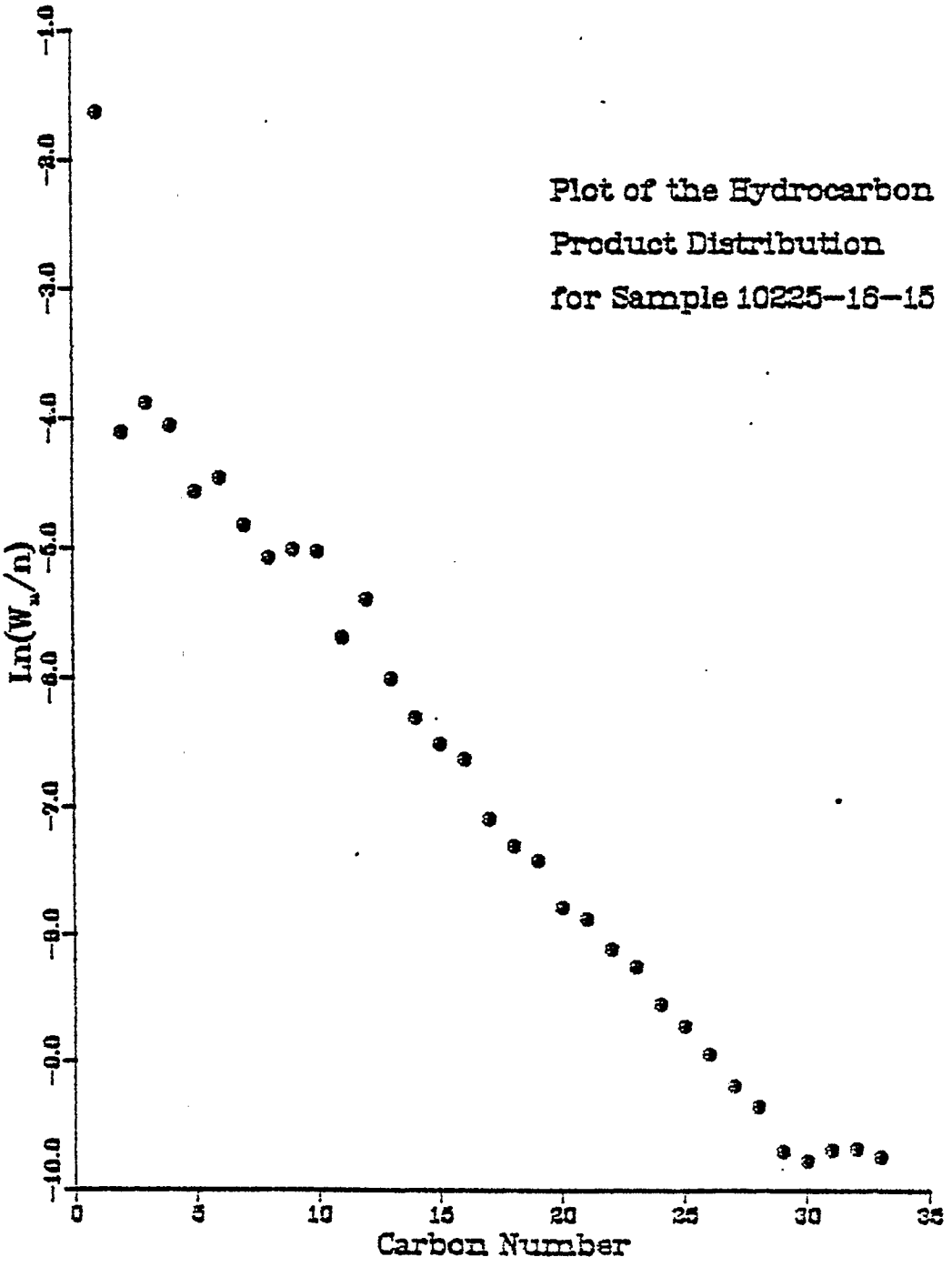

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-15
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 114

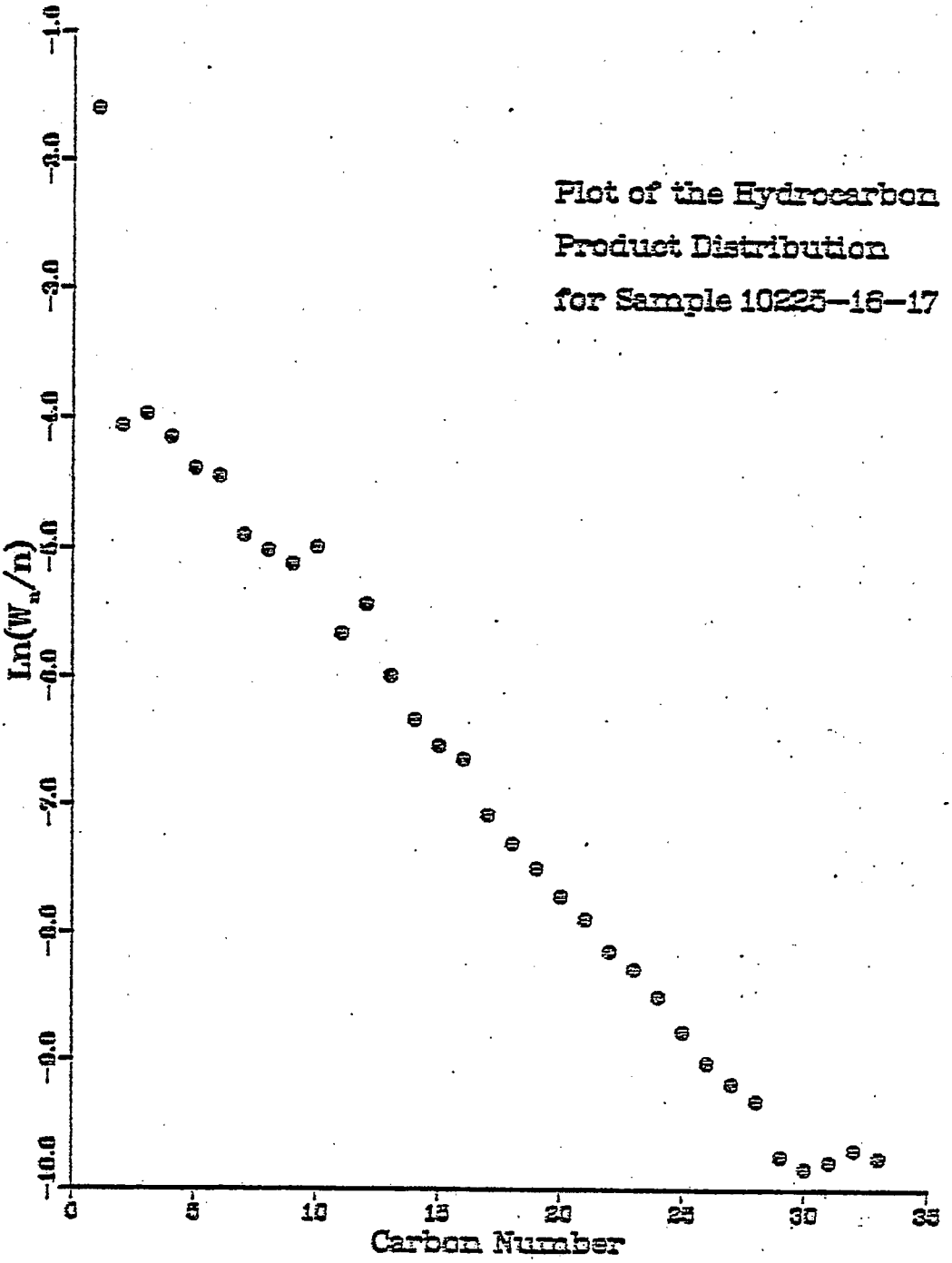

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-17
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 115

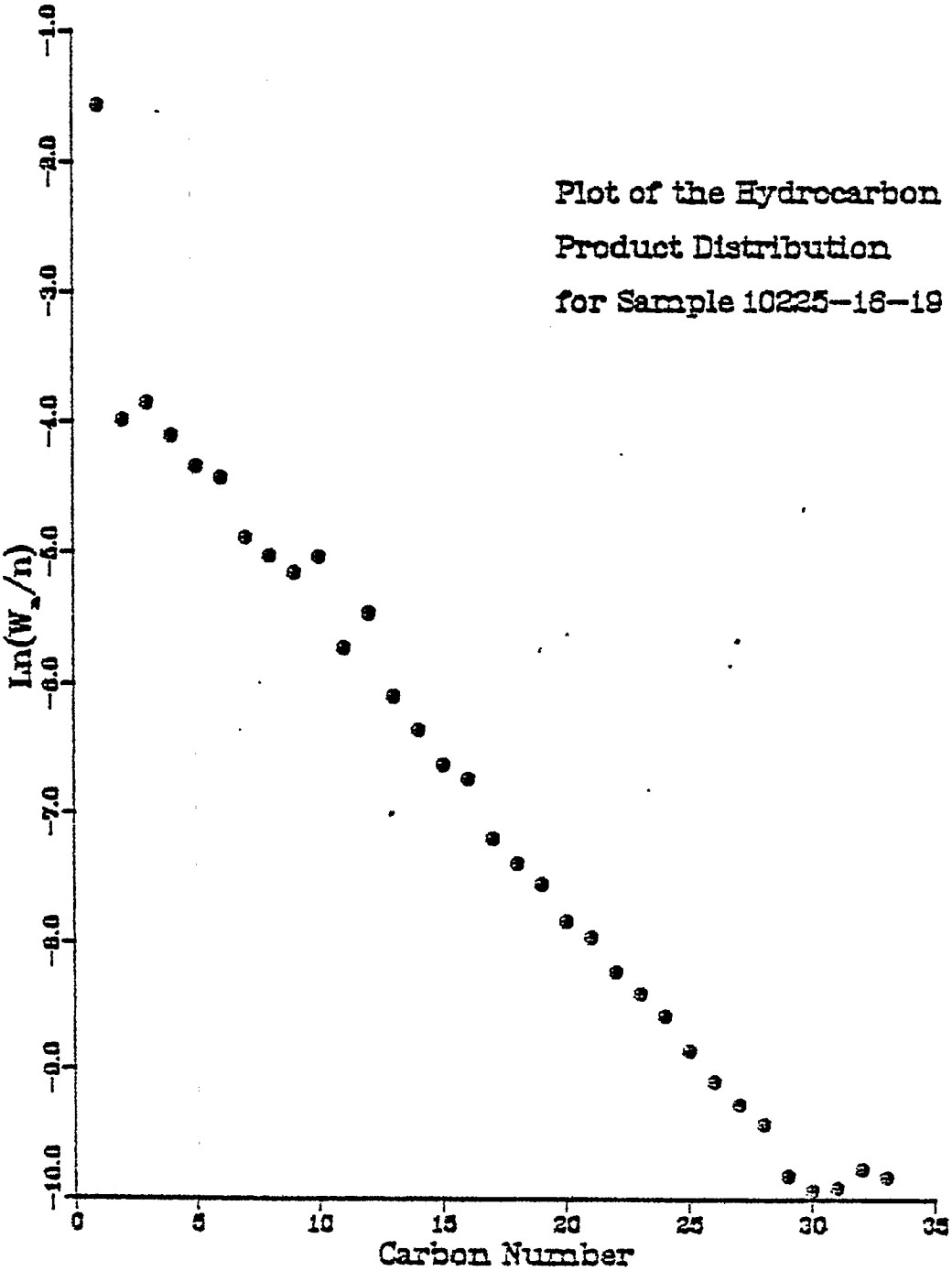

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-16-19
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 116

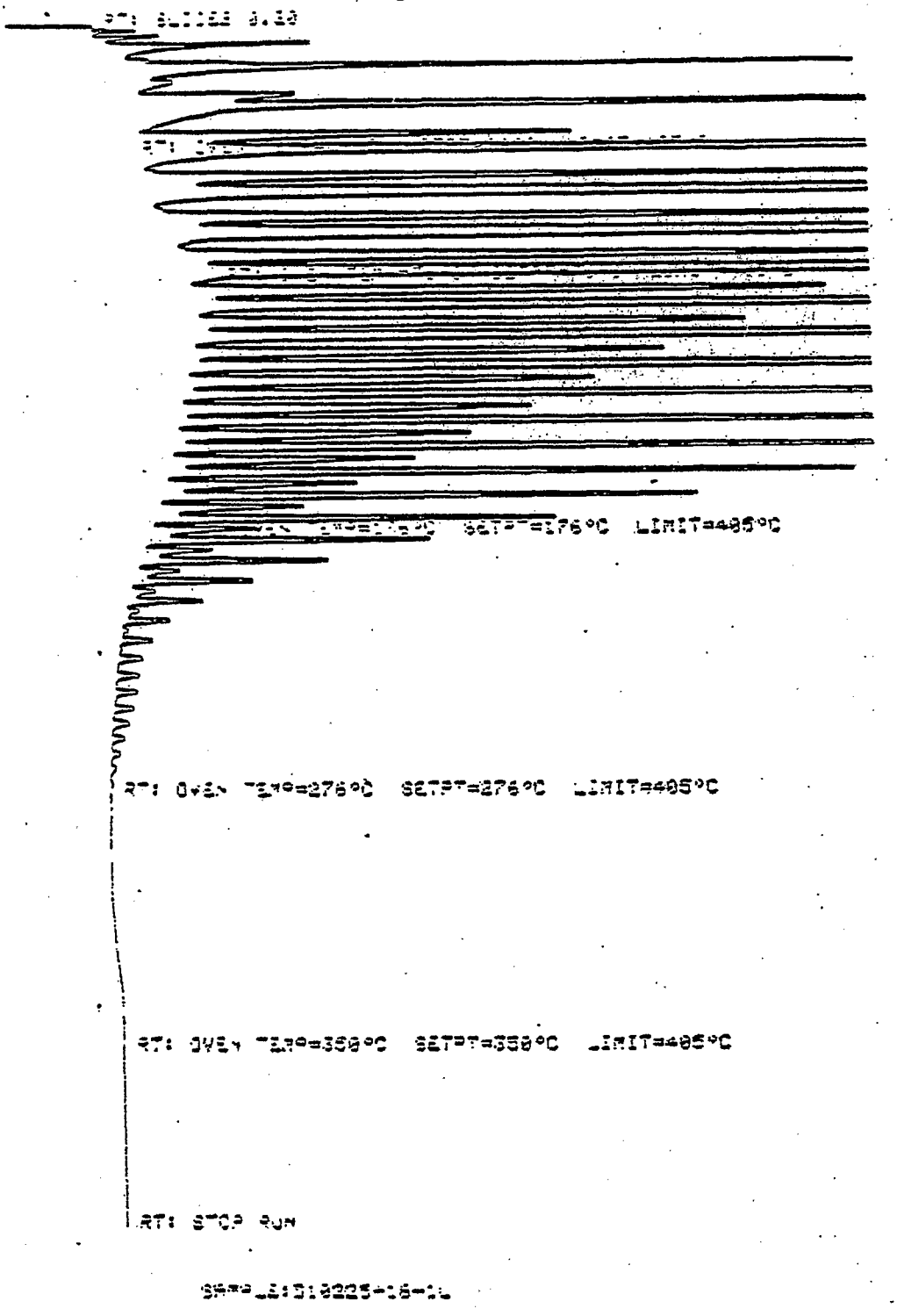

SETPT=175°C LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 117

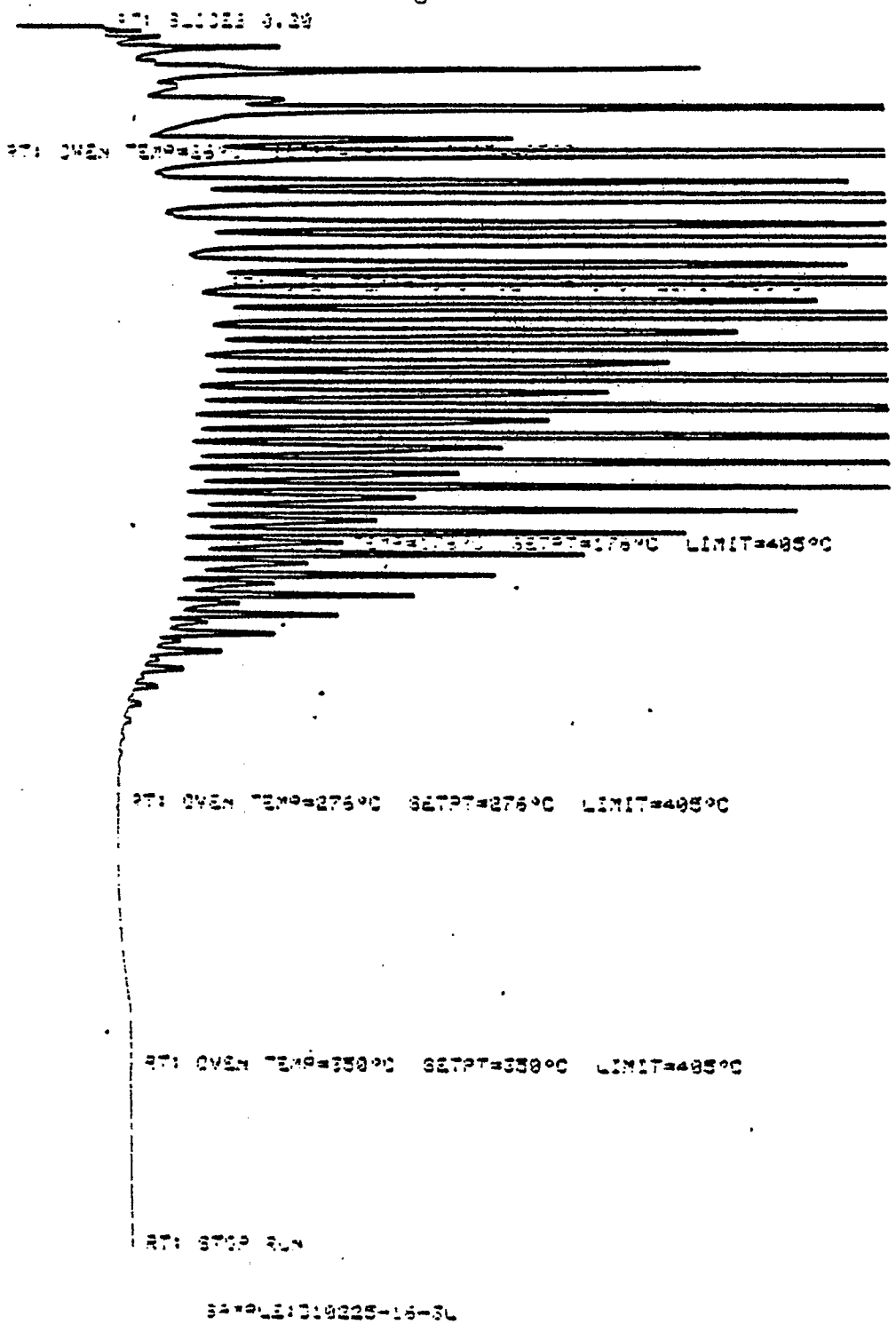

RT: OVEN TEMP=376°C SETPT=376°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 118

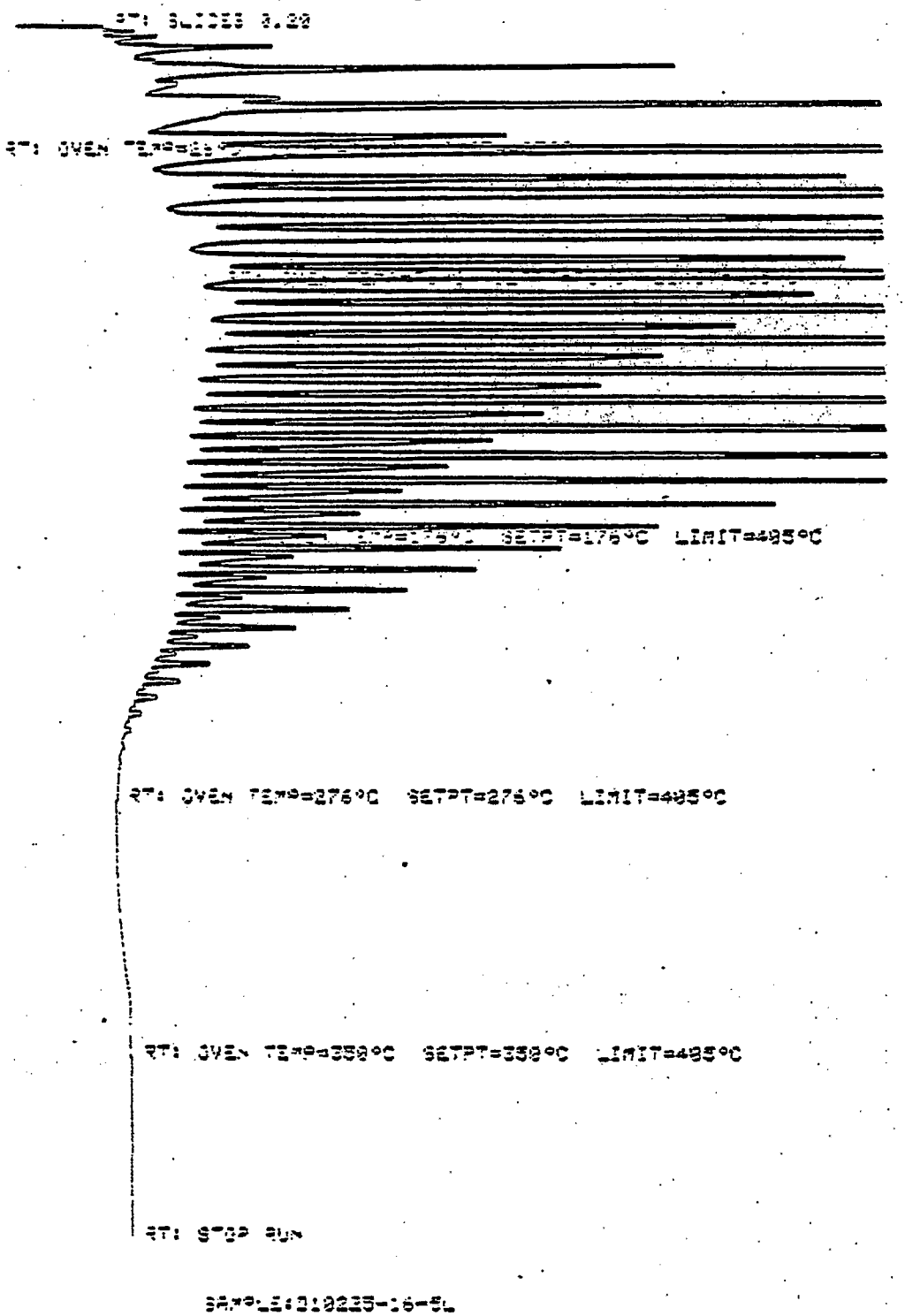

SETPT=175°C LIMIT=495°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=495°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=495°C
RT: STOP RUN

Fig. 119

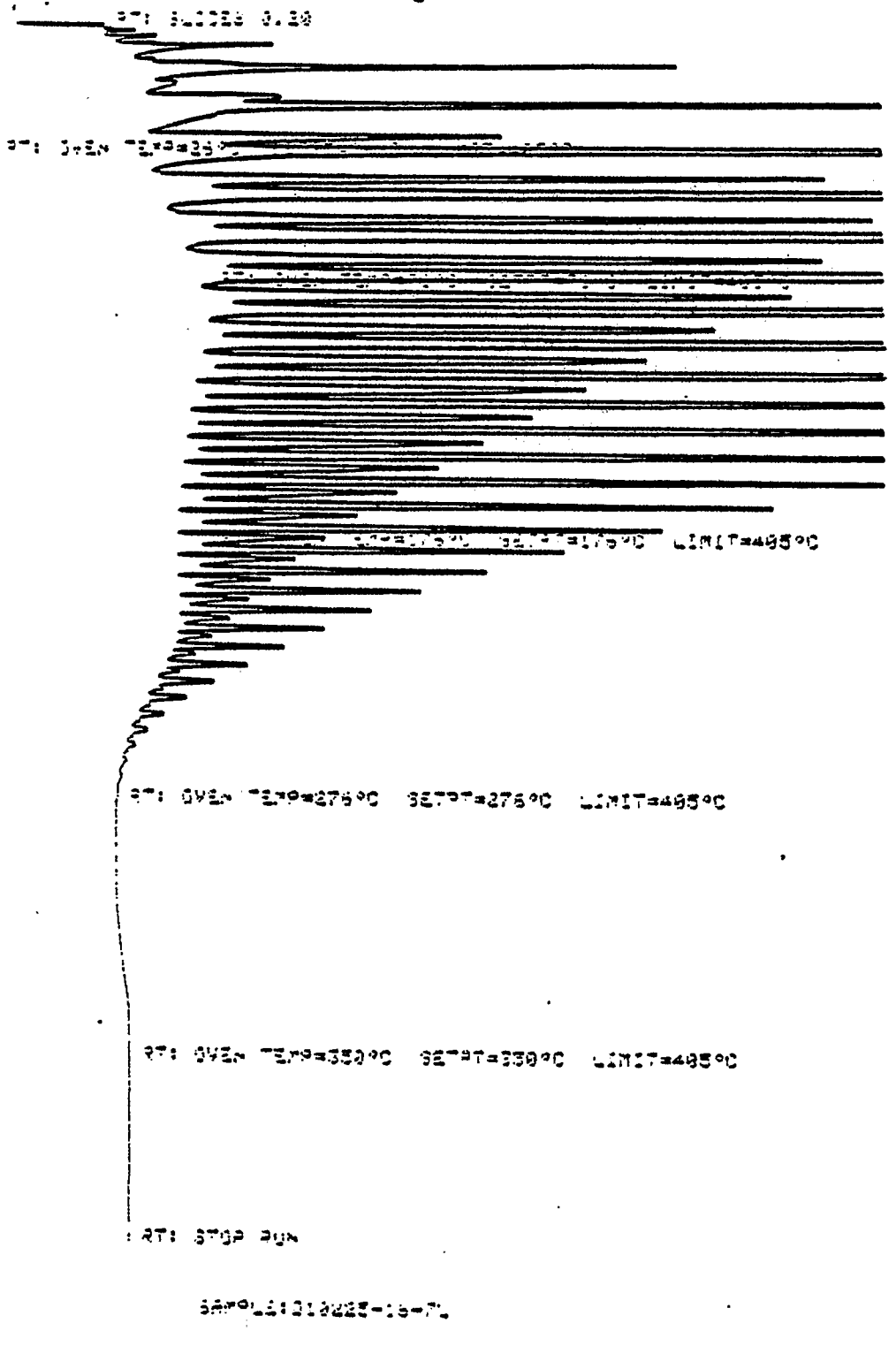

LIMIT=405°C
RT: OVEN TEMP=275°C SET PT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SET PT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 120

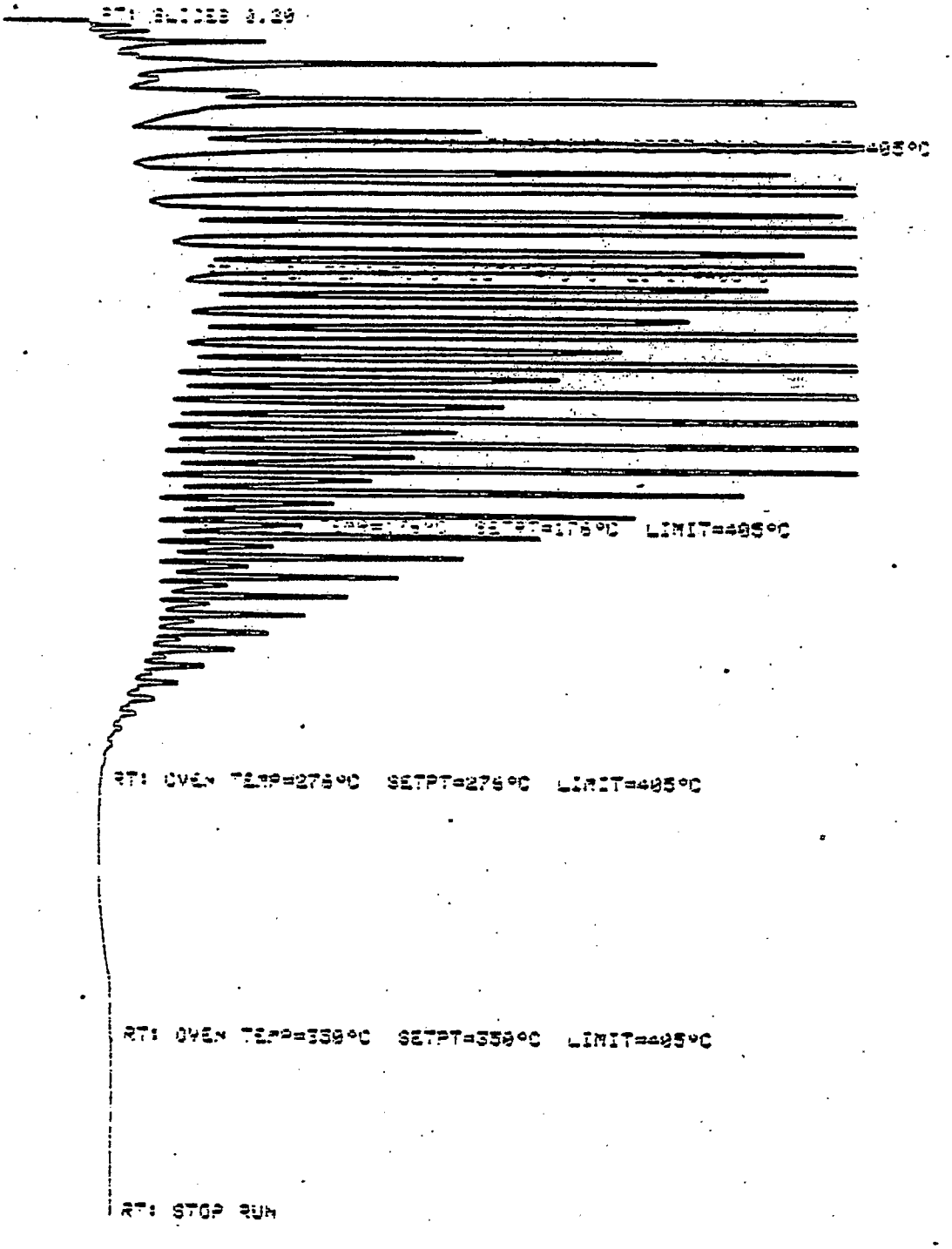

RT: 0.1333 0.39
=405°C
LIMIT=405°C
RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=339°C SETPT=339°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D19225-16-9L

Fig. 121

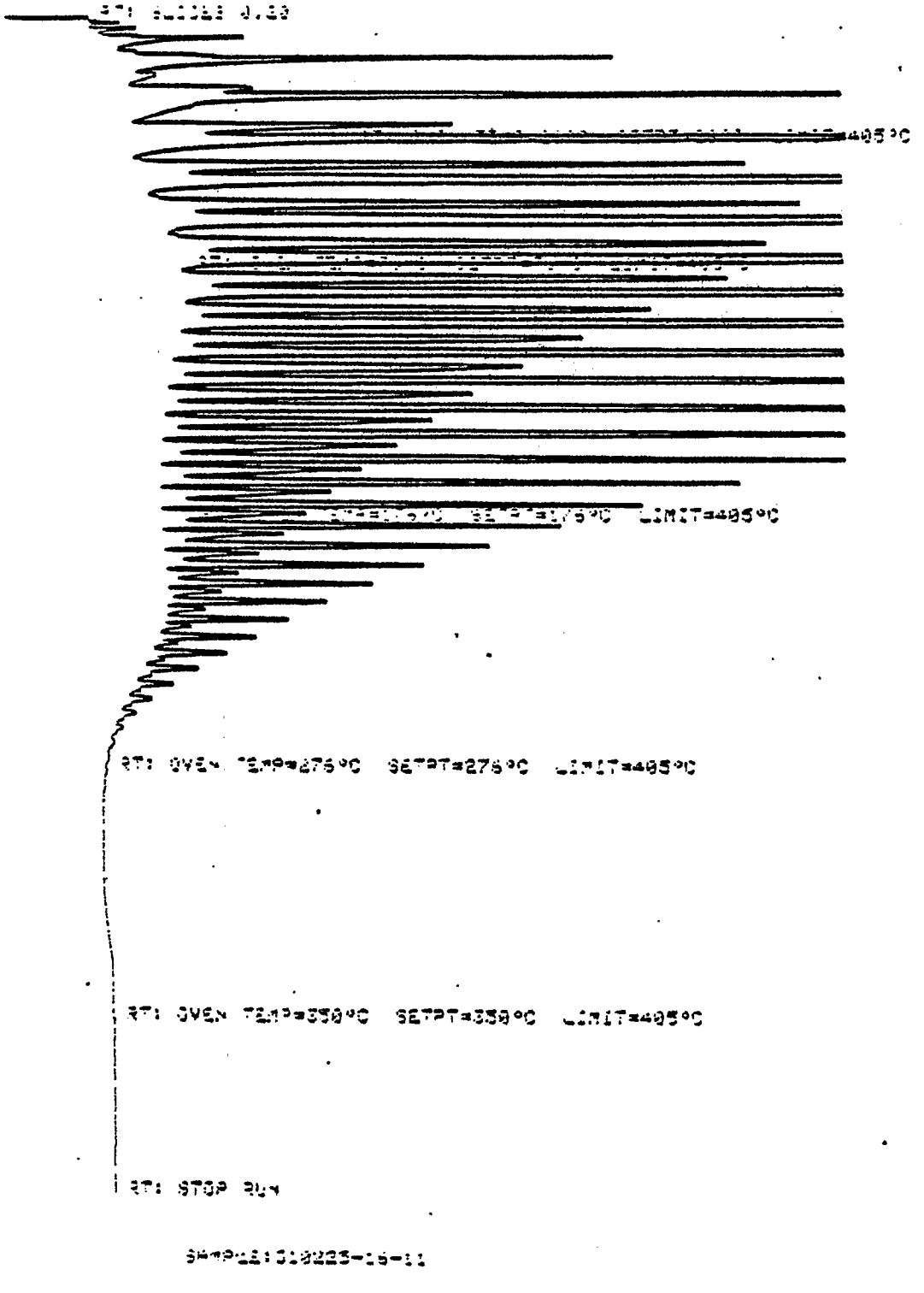

RT: OVEN TEMP=275°C SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 122

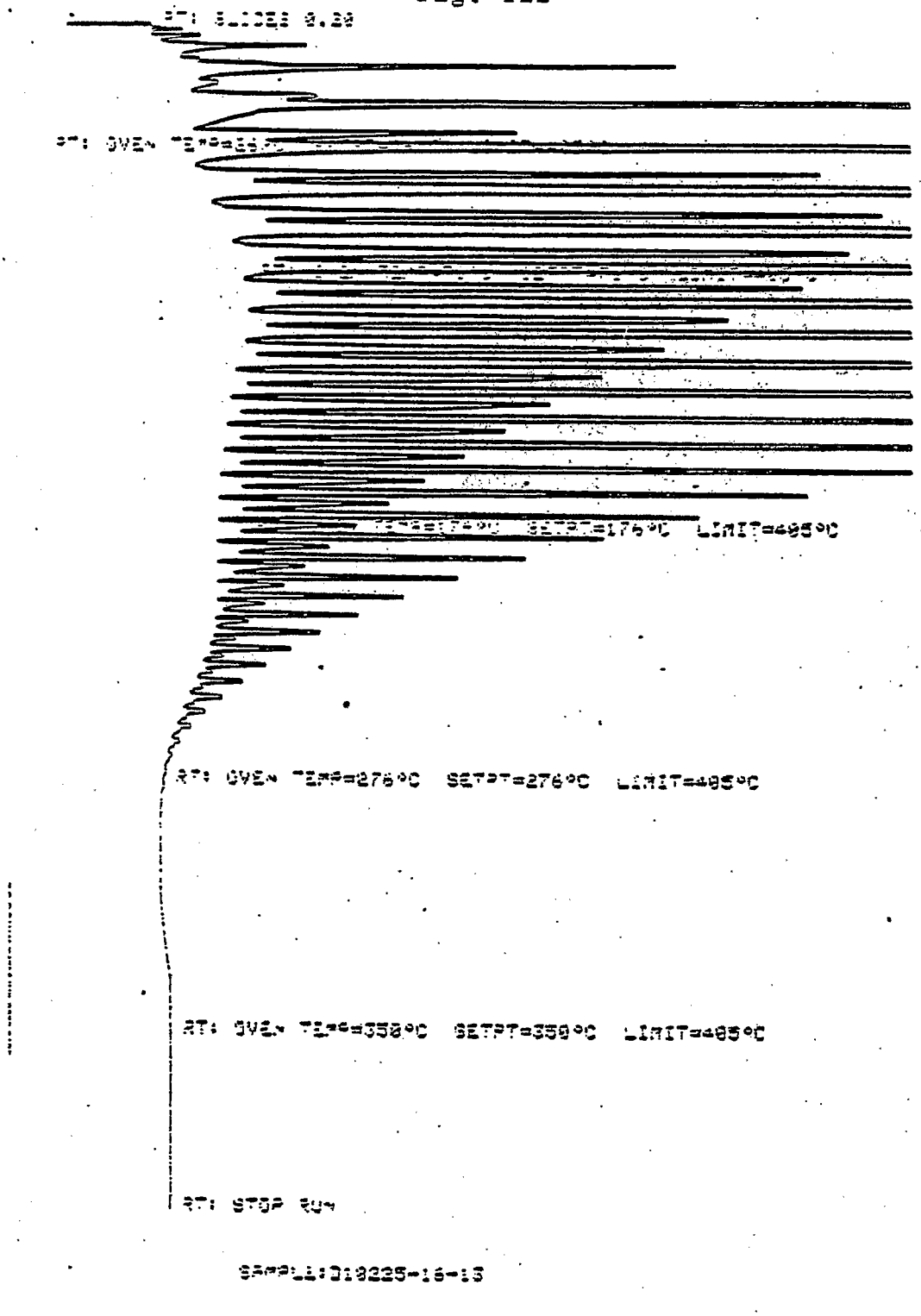

RT: SLICE: 0.00
RT: OVEN TEMP=175°C SETPT=175°C LIMIT=485°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=485°C
RT: OVEN TEMP=359°C SETPT=359°C LIMIT=485°C
RT: STOP RUN
SAMPLE:D19225-16-13

Fig. 123

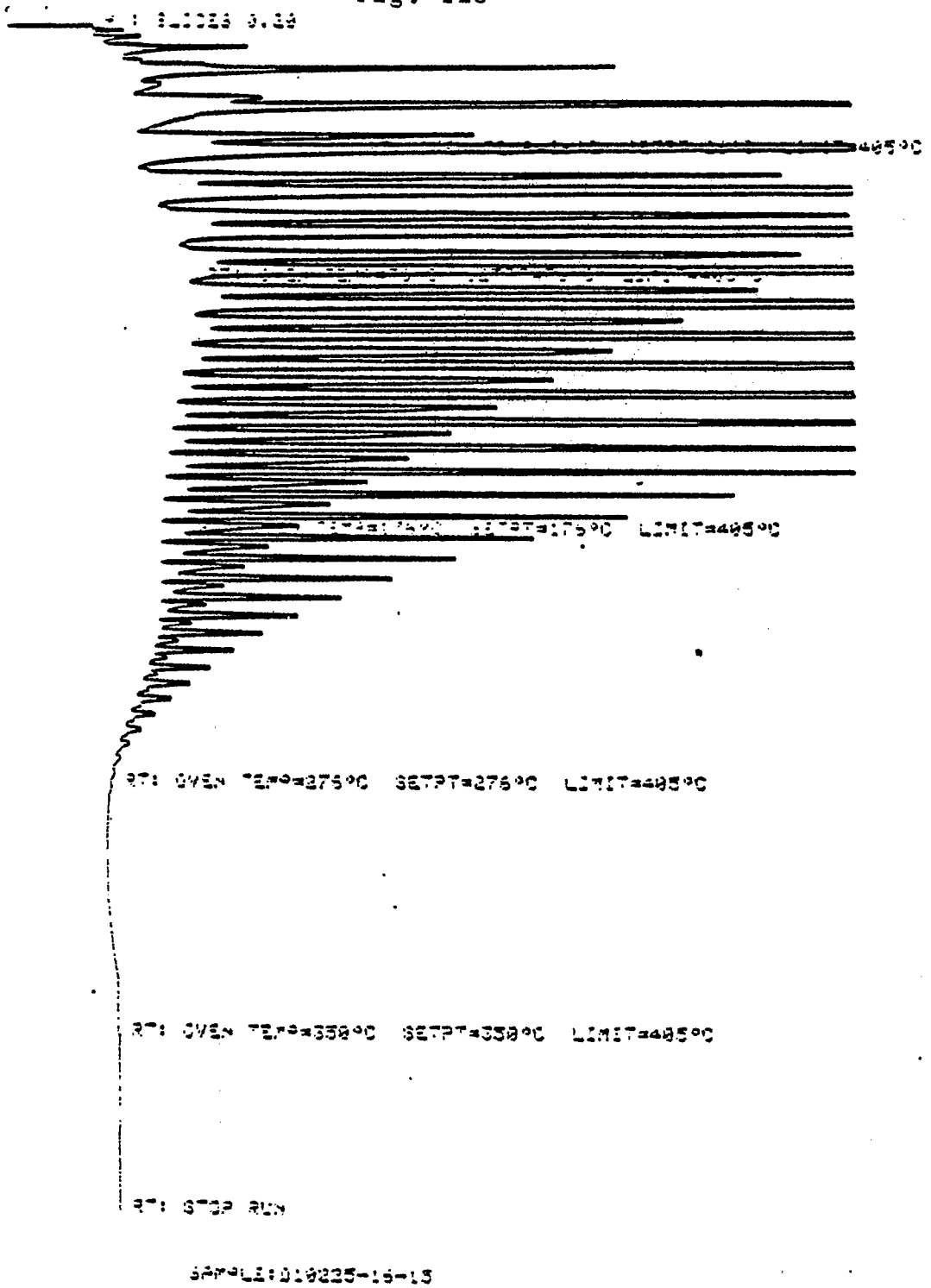
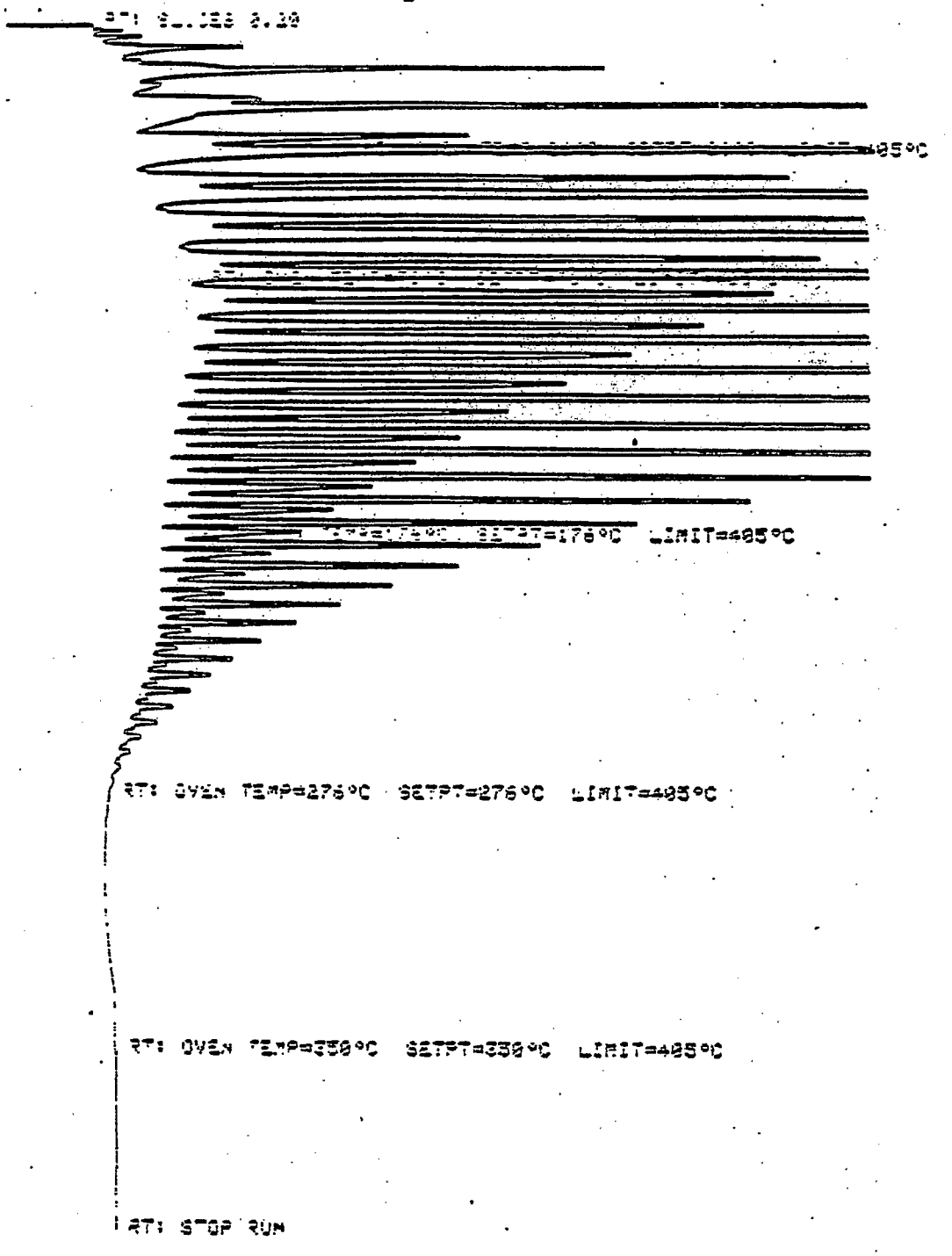

405°C
LIMIT=405°C
RT: OVEN TEMP=375°C SETPT=375°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 124


RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=330°C SETPT=330°C LIMIT=405°C
RT: STOP RUN