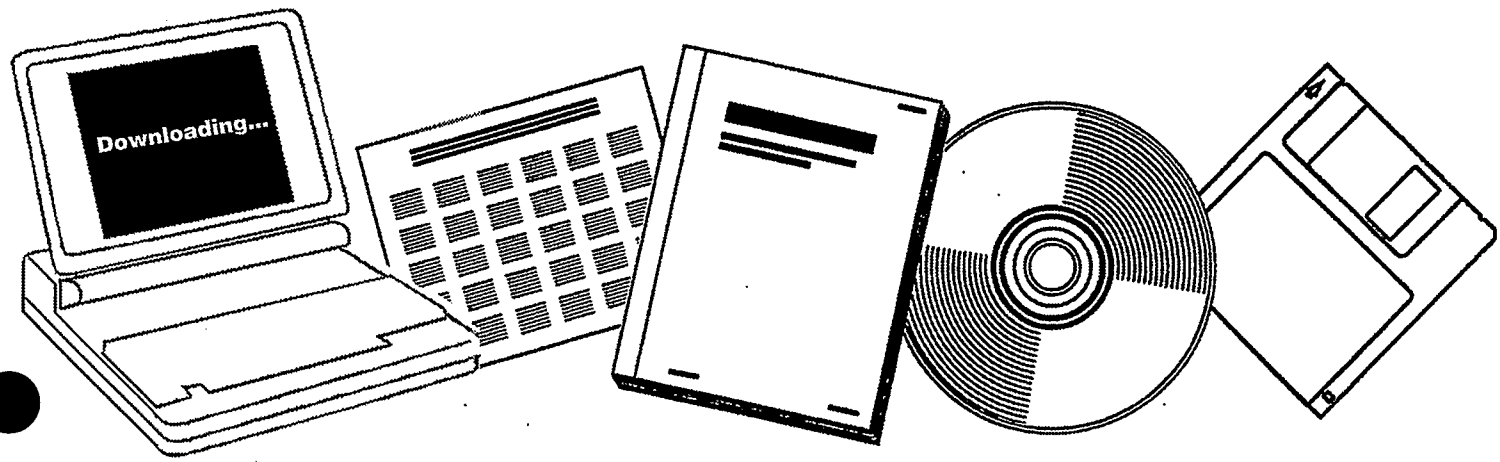
LIQUID HYDROCARBON FUELS FROM SYNGAS. TENTH QUARTERLY REPORT, JUNE-AUGUST 1983

UNION CARBIDE CORP., TARRYTOWN, NY.
TARRYTOWN TECHNICAL CENTER

1983



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DOE/PC/40077--T5

TECHNICAL PROGRESS REPORT
DE-AC22-81PC40077

DOE/PC/40077--T5

DE84 015942

Tenth Quarterly Report
June - August 1983

LIQUID HYDROCARBON FUELS FROM SYNGAS

DISCLAIMER

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

MASTER

Contents

Appendixes

I. CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals ("Molecular Sieves") in combination with transition metals.

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. Only minimal work, if any, is contemplated in the future.

B. Task 2

Twelve catalyst test runs were made from May through July. Ten of these runs used catalysts that contained cobalt as the metal component, while the remaining two runs used catalysts that contained iron as the metal component. Five of the ten cobalt catalyst test runs were made with the catalysts containing one of two different shape selective components (UCC-101 and UCC-108) at two different metal component:shape selective component ratios (1:1 and 3:14). The remaining five cobalt catalyst test runs were made with the catalysts containing different additives incorporated into the cobalt. The two iron test catalysts used potassium and rhodium as additives and UCC-108 as their shape selective components.

The five cobalt catalyst test runs using UCC-101 and UCC-108 at the two different levels showed these catalysts performed best at the 3:14 metal component:shape selective component (MC:SSC) ratio. This ratio, unlike the 1:1 MC:SSC ratio used in the past for iron catalysts, makes available more molecular sieve to

handle the larger quantity of the more paraffinic intermediate produced by the more active, but less concentrated cobalt component.

While this 3:14 MC:SSC ratio worked well with both UCC-101 and UCC-108, the UCC-108 containing catalyst produced a more olefinic, less waxy, and lower pour point product than did the UCC-101 containing product.

The five cobalt catalyst test runs using catalysts with different additives showed that these additives had pronounced effects on the catalysts' activity, selectivity, and stability. The most outstanding effect was realized with the additive used in the Run 9 catalyst. This additive greatly improved the stability of the catalyst. While having the same initial activity of an additive-free catalyst, its deactivation rate was only one fourth of that of the additive-free catalyst. Furthermore, this additive improved the quality of the hydrocarbon product, which had a high, stable yield of olefins, and, unlike the product of any other cobalt/UCC-101 catalyst, was free of suspended wax. This lack of suspended wax resulted in jet fuel and diesel oil fractions that had substantially lower pour points than did the fractions produced from an additive-free catalyst.

The two iron/UCC-108 catalyst test runs gave disappointing results. The catalyst promoted with rhodium had poor activity and selectivity. The catalyst promoted with potassium had an activity that while high initially, deactivated rapidly. By the time sufficient product had been collected to measure the RON,

the catalyst was producing a product that was far less isomerized than its initially produced product, and that had a RON of only 57.6.

C. Task 3

Studies at the University of California at Berkeley, under the direction of Professor G. A. Somorjai, have concentrated on clean and sulfided molybdenum surfaces, as well as the effect of potassium and oxygen promoters on rhenium and iron surfaces. The molybdenum catalyst produced a high turnover of ethylene, giving a yield of ethylene that was three times that of ethane. The addition of potassium to either rhenium or iron shifted the product distribution down to higher molecular weight products. Conversely, the addition of oxygen to either rhenium or iron shifted the product distribution towards methane. Furthermore, the oxygen also appears to decrease the deactivation rate, apparently because of a decreased build-up of graphitic type carbon.

V. CHANGES

There were no contract changes during the tenth quarter.

VI. FUTURE WORK

Efforts during the next quarter will be directed at a continued examation 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 twelve tests conducted from May through July 1983 are detailed in this Quarterly Report. Ten of the tested catalysts have metal components containing cobalt. The other two have iron metal components.

The tests can be divided into three categories. In runs 1-5 appropriate ratios of MC to SSC are established for cobalt containing catalysts for both UCC-101 and UCC-108 as the SSC's. In runs 6-10, additives to the cobalt metal components are tested to see if they can improve the product quality and stability of the catalysts. The results of the two iron catalysts are reported in runs 11 and 12.

The data is presented in the same format as was used in the previous Quarterly Reports.

The catalysts are generally formulated in the same manner. The catalysts used in all the tests except number 10 were prepared as a physical mixture of the MC and SSC. Of those physical mixtures, all but the one used in run number 11 were formed as SiO_2-bonded extrudates. The catalyst used in run number 11 was pressed into tablets with no binder. The catalyst used in run number 10 had the MC pore-filled into a preformed 20 percent Al_2O_3 bonded UCC-101 extrudate.

II. RUN 1 (10225-06) with Catalyst 1 (Co/Th on UCC-101)

This catalyst, intended for use in establishing a base line for determining the most productive ratio of cobalt to Molecular Sieve, is to be compared with Catalyst 2, which follows (Run 10112-14). The metal component was prepared by precipitating cobalt oxide with sodium carbonate from an aqueous solution of cobalt nitrate, washing and drying the cobalt oxide, and impregnating it with thorium nitrate solution to give two weight percent thorium on the catalyst. The metal component and the Molecular Sieve (UCC-101) were then physically mixed in a 1:1 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 42:42:15.

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 two samples are plotted in Figs. 5-6. Carbon number product distributions are plotted in Figs. 7-13. Chromatograms from simulated distillations are reproduced in Figs. 14-20. Detailed material balances appear in Tables 1-3.

Conversion of both hydrogen and carbon monoxide was almost complete at both 280C and 250C; at this level of metal component,

the space velocity should have been higher. The water gas shift activity was good, with 70 percent of oxygen rejected as carbon dioxide at 250C and 80 percent at 280C. Usage of the 1:1 H_2:CO syngas was excellent, with ~0.95 moles of H_2 converted per mole of CO converted. Deactivation was hard to detect with such high conversion; even if present, it may have been masked because not all the active sites may have been used.

Methane production at 280C was extremely high, 60 percent, and down to ~40 percent, still unacceptably high, at 250C. Production of C_2-C_4 (ordinarily low with cobalt catalysts) was high at both temperatures. There was a little condensed liquid at 250C, and almost none at 280C. Total C_5^+ at 280C was minimal (~10 percent), and only up to 40 percent at 250C. As would be expected with so light a distribution, there were no heavies. The pentane was poorly isomerized, and the C_4's deficient in desirable olefins. When a gasoline fraction was distilled, the FIA showed it was 85 percent saturated. In agreement with the pentane findings, chromatograms of the simulated distillations show that the liquid was poorly isomerized. Although the Schulz-Flory plots for 280C are highly non-linear, the quantities of heavier hydrocarbons were negligibly small and hence relatively inaccurate. At 250C, with a heavier and more accurate distribution, the plots are fairly straight.

The combination of high productivity and poor selectivity suggests that the metal component may be too active, while the poor isomerization suggests that the Molecular Sieve may have

been overwhelmed. This undesirable effect can obviously be remedied by increasing the ratio of Molecular Sieve to metal component, thus raising the ratio of space velocity to metal component and lowering the ratio of space velocity to Molecular Sieve.

Fig. 1

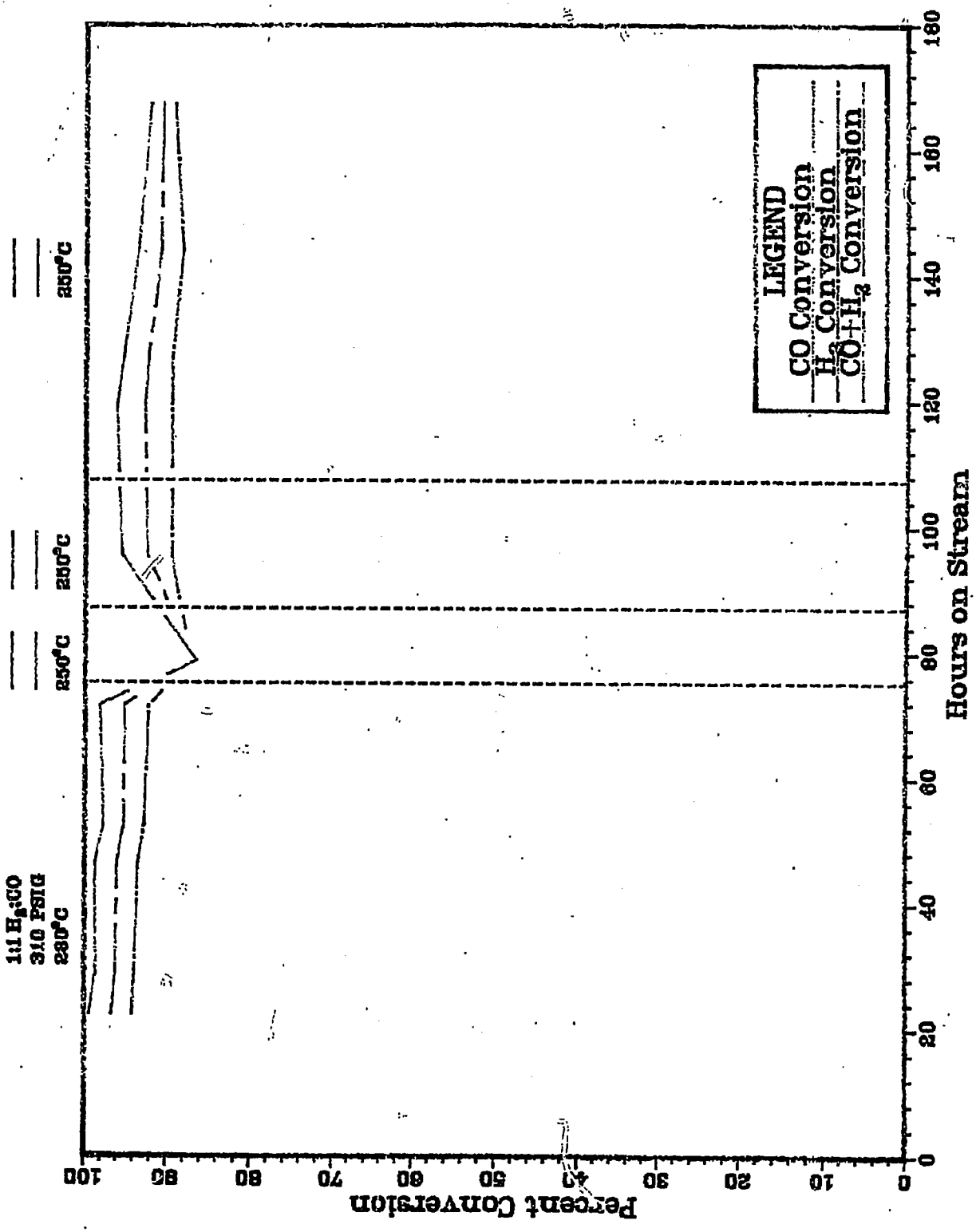

RUN 10225-06
1:1 H2:CO
310 PSIG
230°C
250°C
250°C
250°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 2

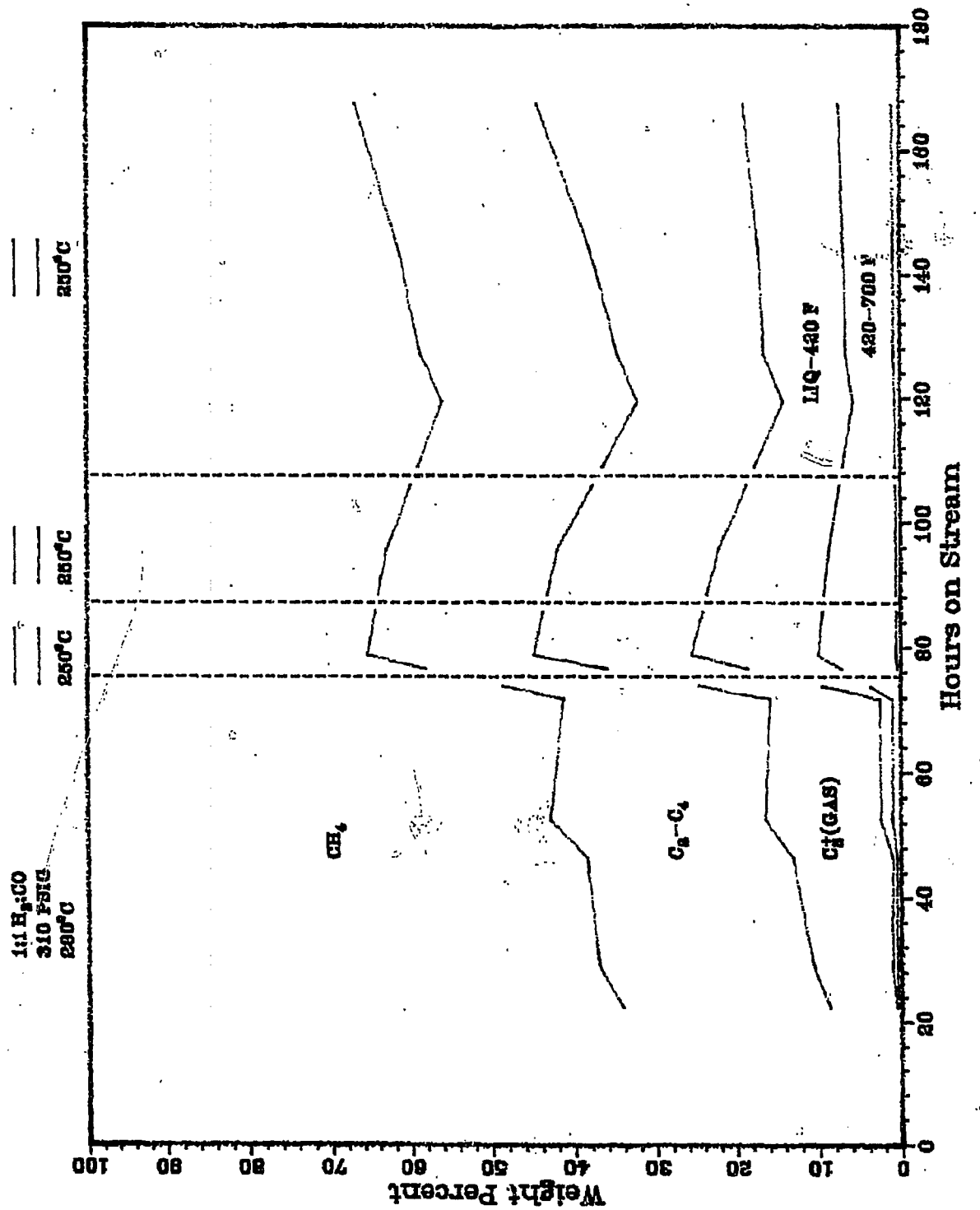

RUN 10225-06
1:1 H2:CO
310 PSIG
230°C
250°C
250°C
250°C
CH4
C2-C4
C5+(GAS)
LIQ-430 F
430-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 3

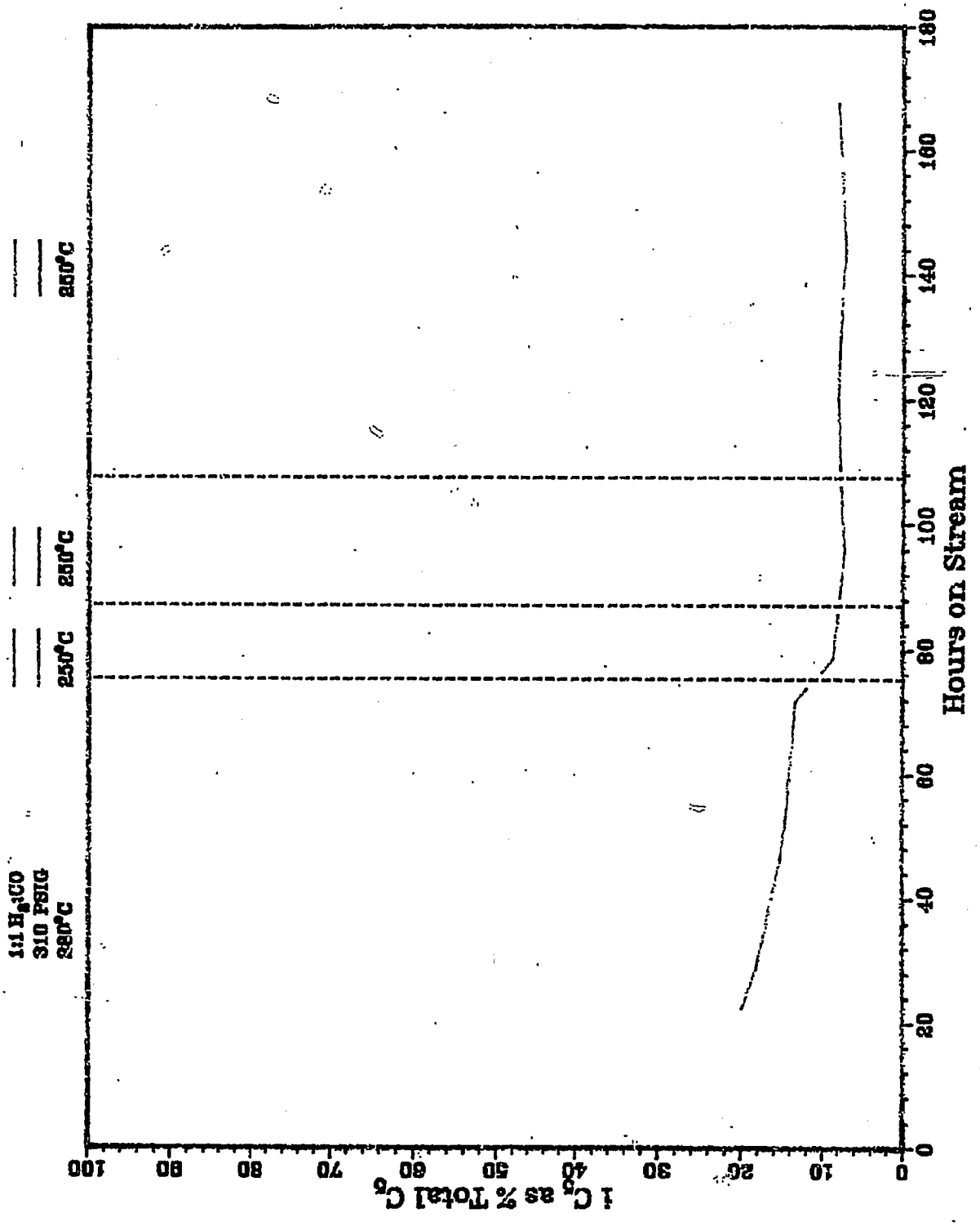

RUN 10225-06
1:1 H2:CO
310 PSIG
280°C
250°C
250°C
250°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 4

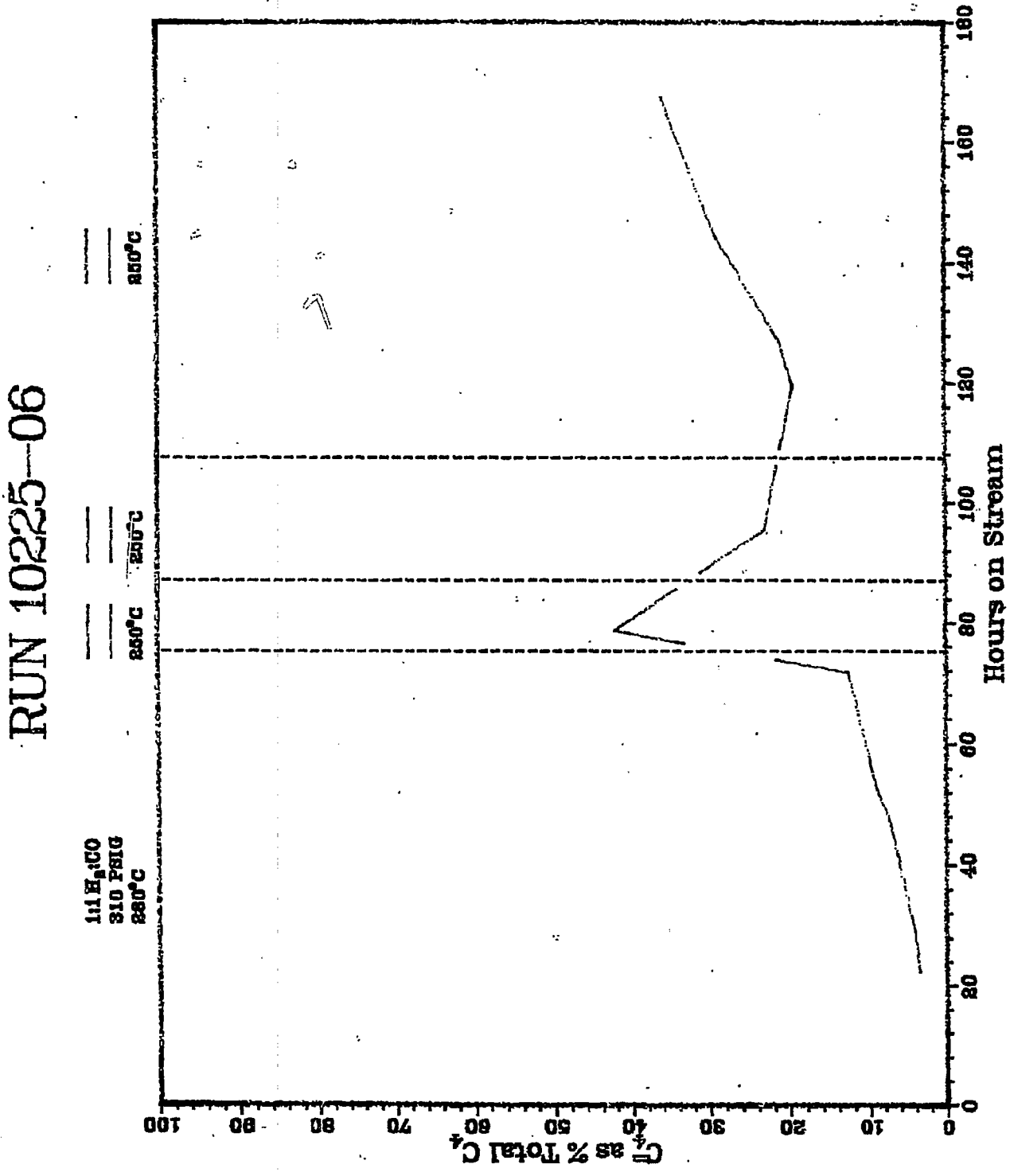

RUN 10225-06
1:1 H_2:CO
310 PSIG
280°C
250°C
250°C
250°C
$C_4^=$ as % Total C_4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 5

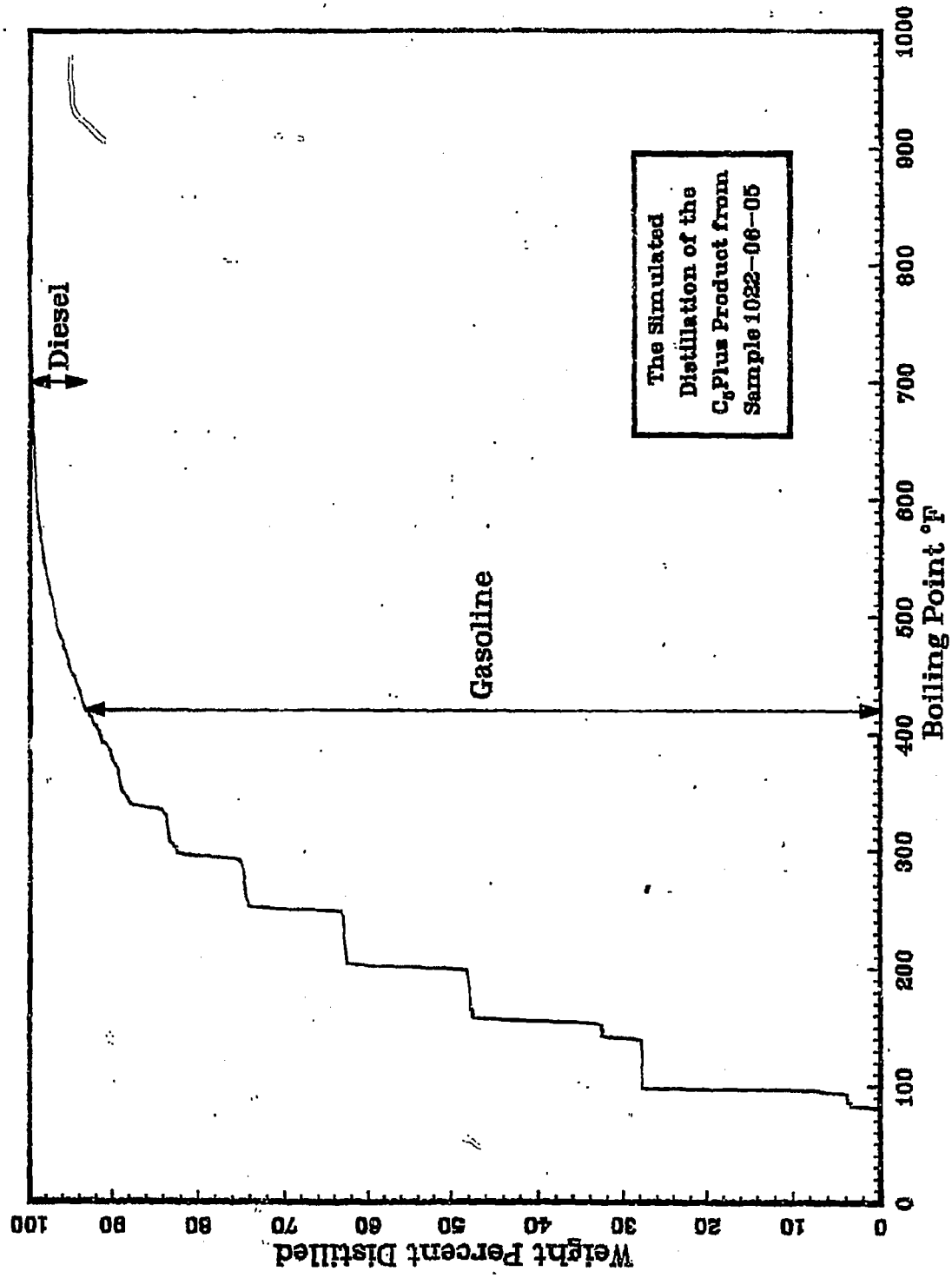

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
The Simulated Distillation of the C5 Plus Product from Sample 1022-06-05

Fig. 6

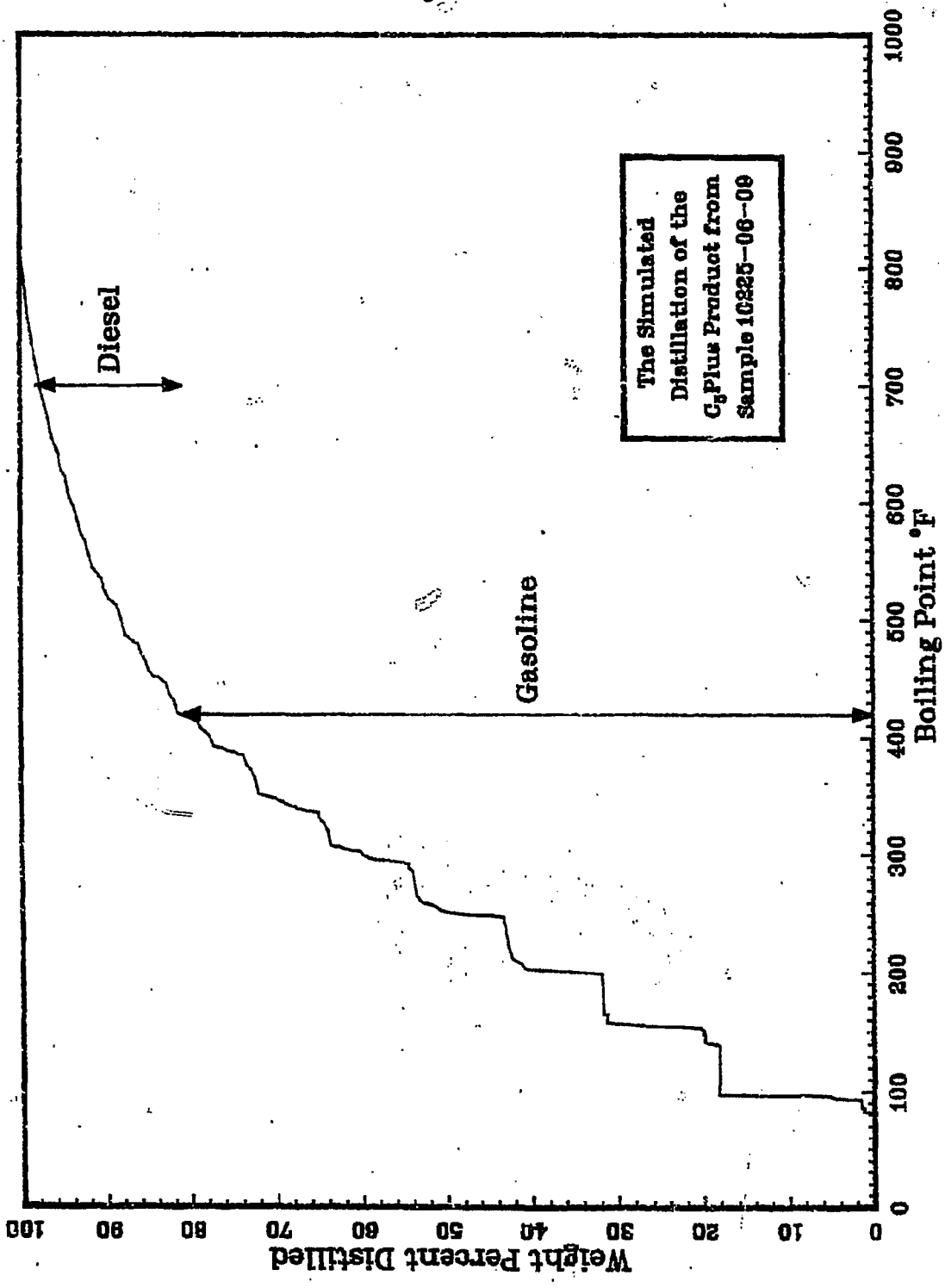
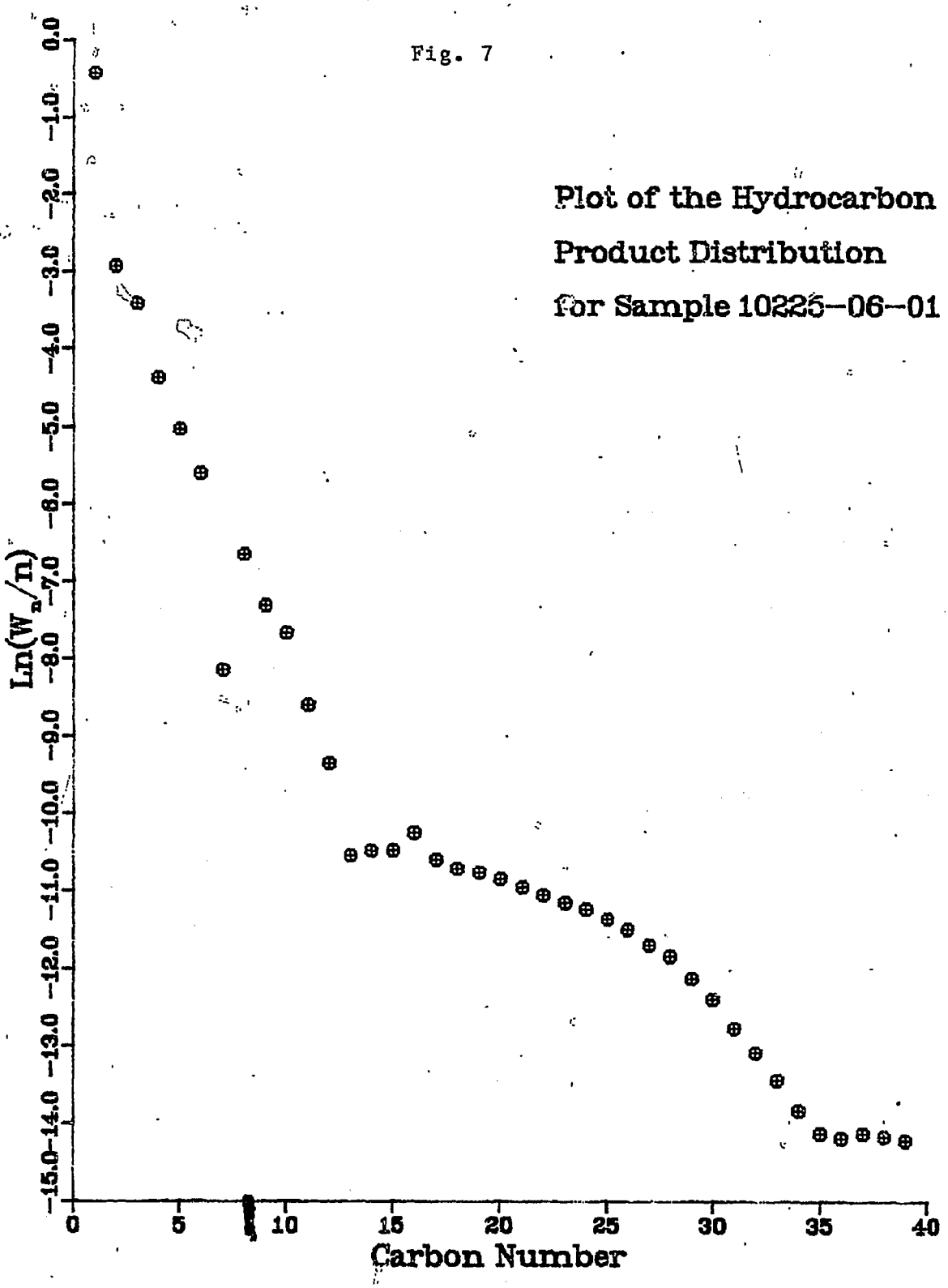

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10325-06-09

Fig. 7



Plot of the Hydrocarbon Product Distribution for Sample 10225--06--01

Fig. 8

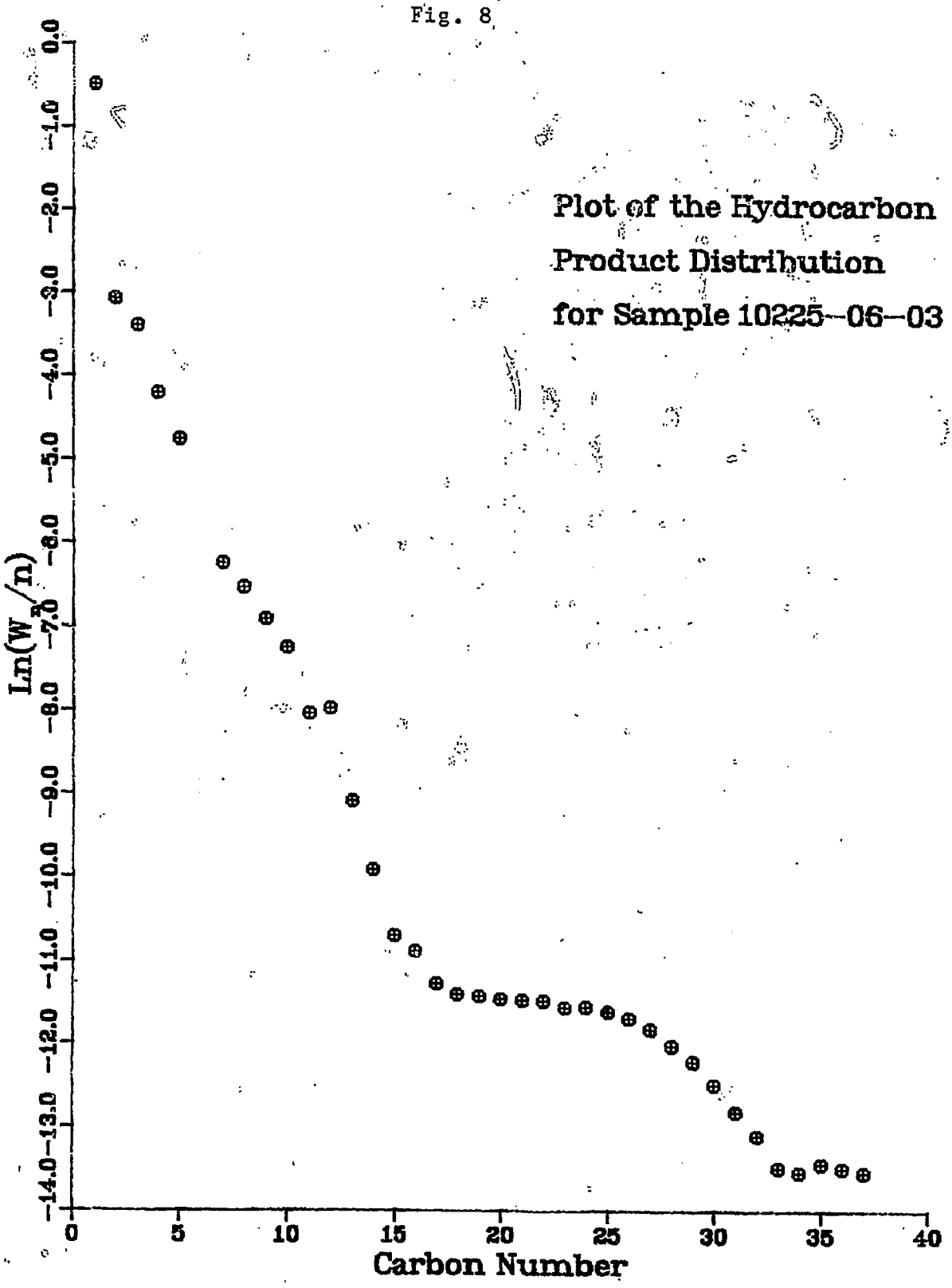
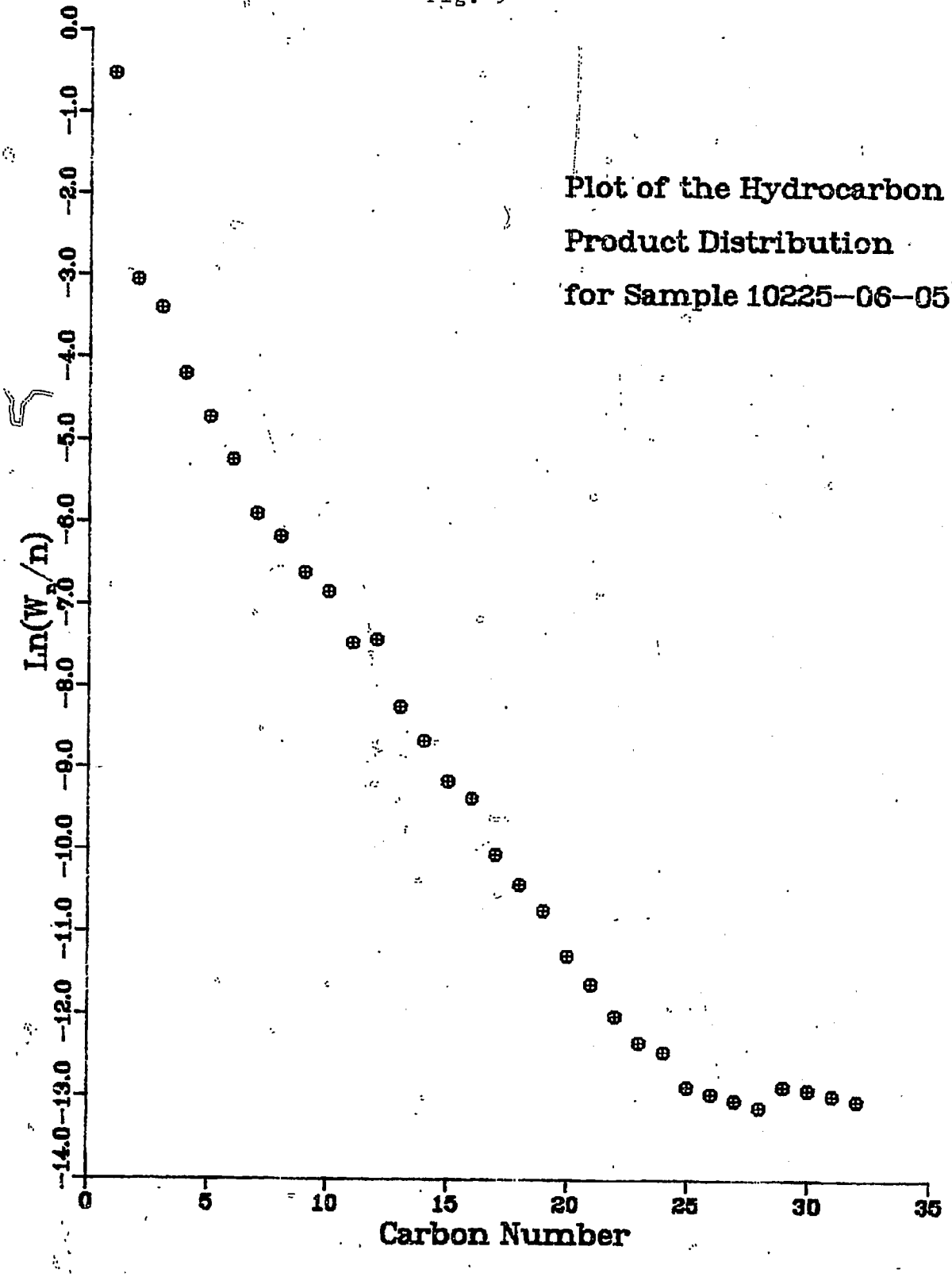

Plot of the Hydrocarbon
Product Distribution
for Sample 10225--06--03
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
-14.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 9



Plot of the Hydrocarbon Product Distribution for Sample 10225-06-05

Fig. 10

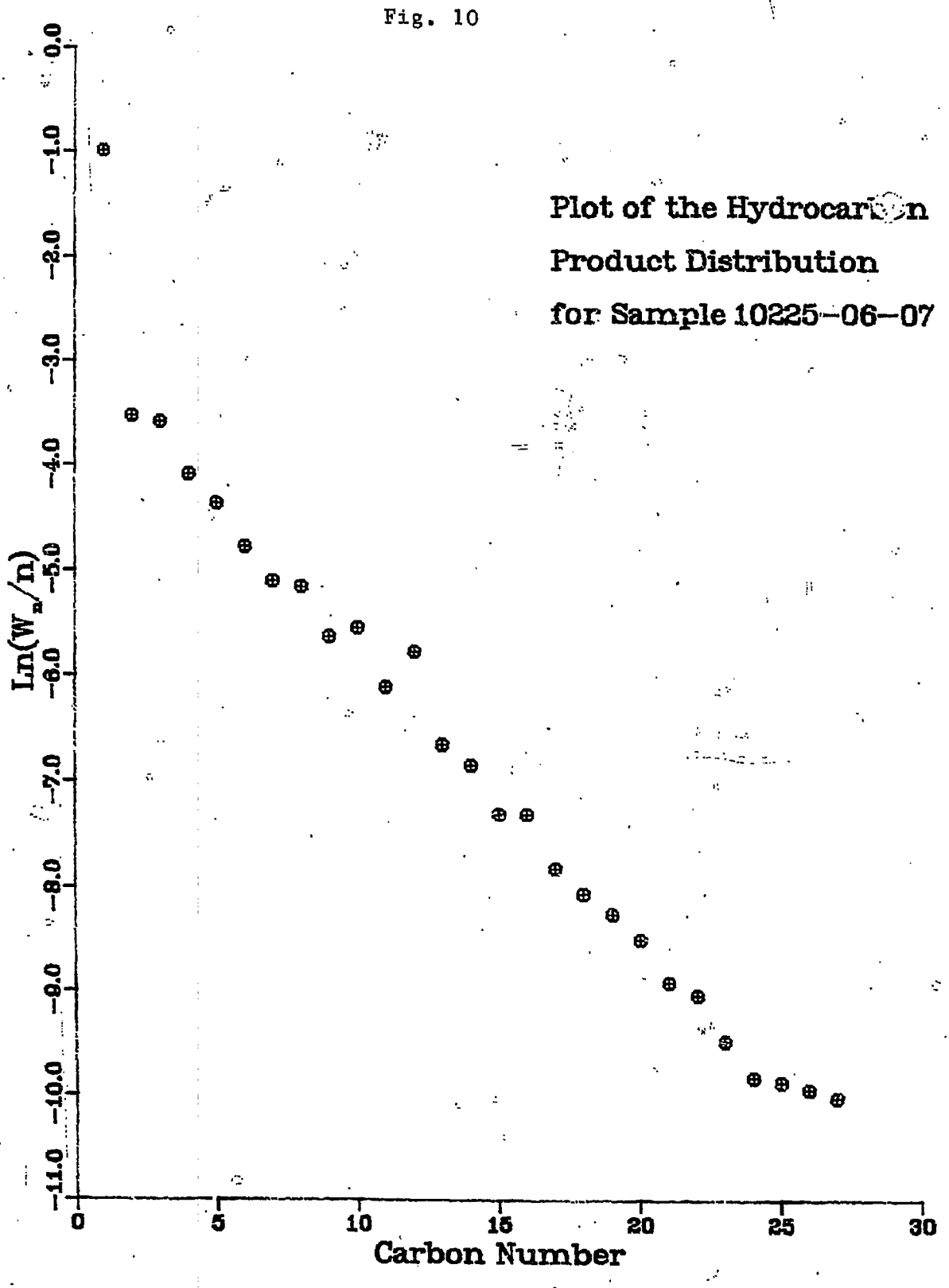

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-06-07
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 11

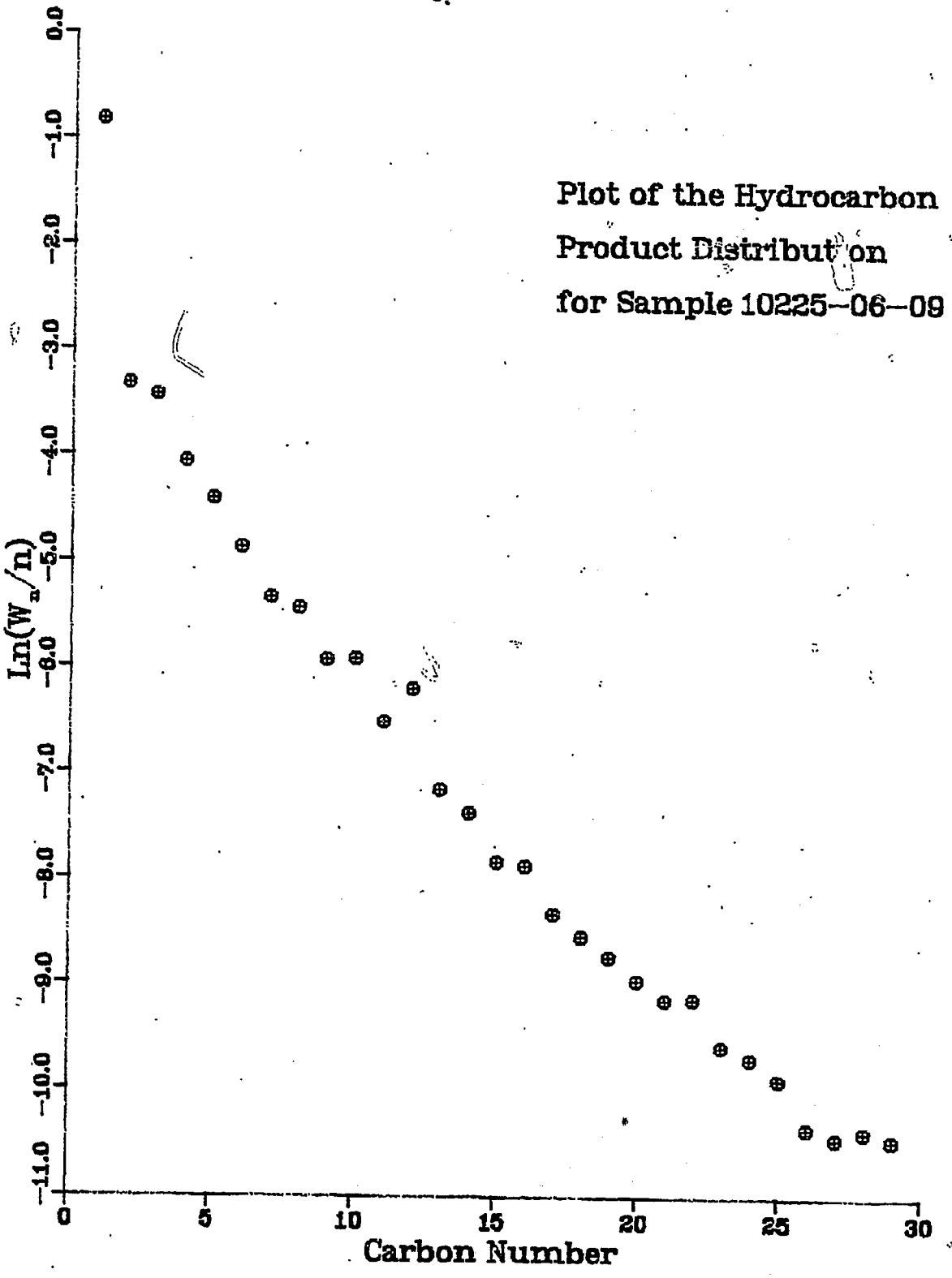

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-06-09
Ln(W_x/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 12

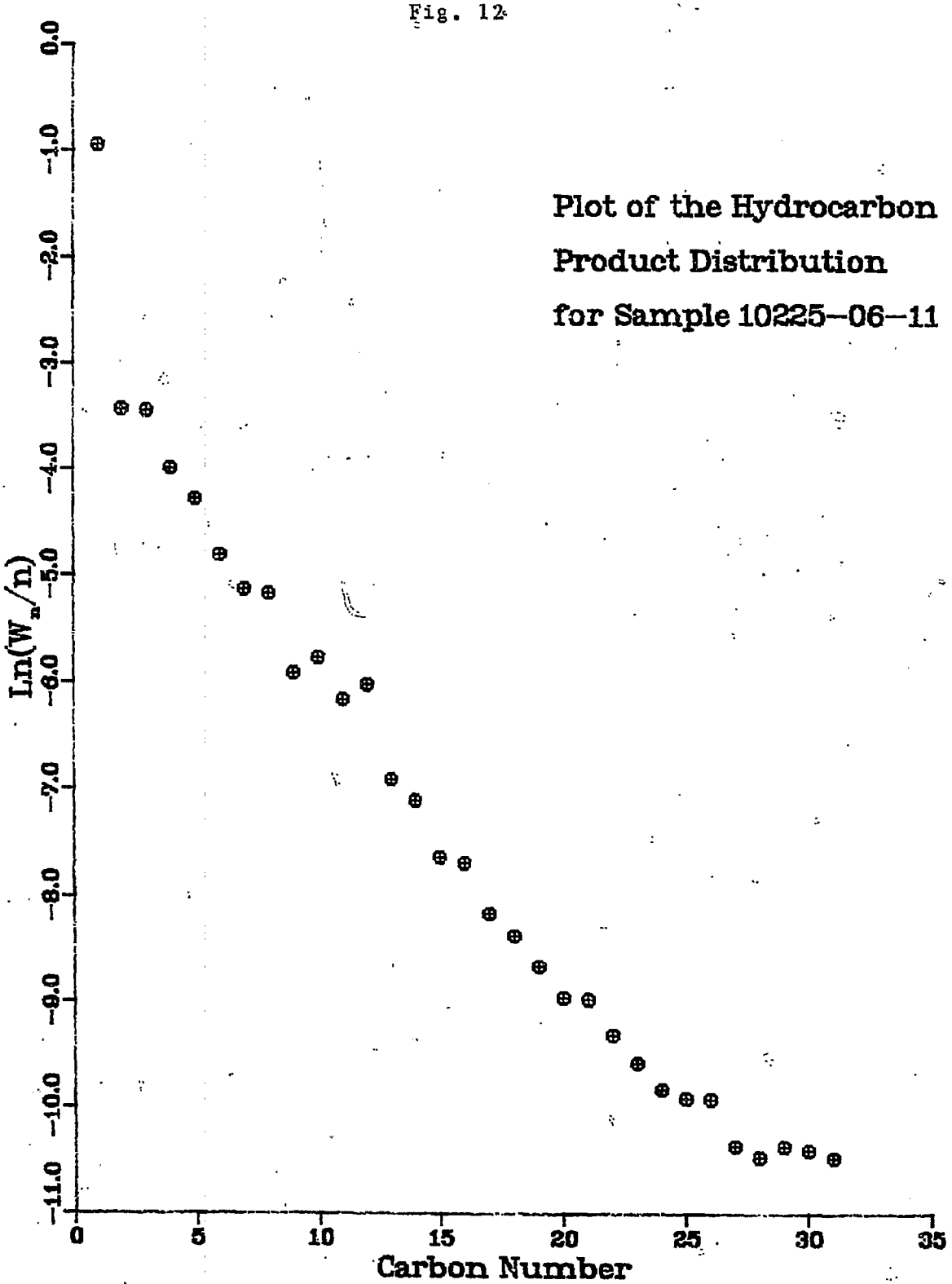
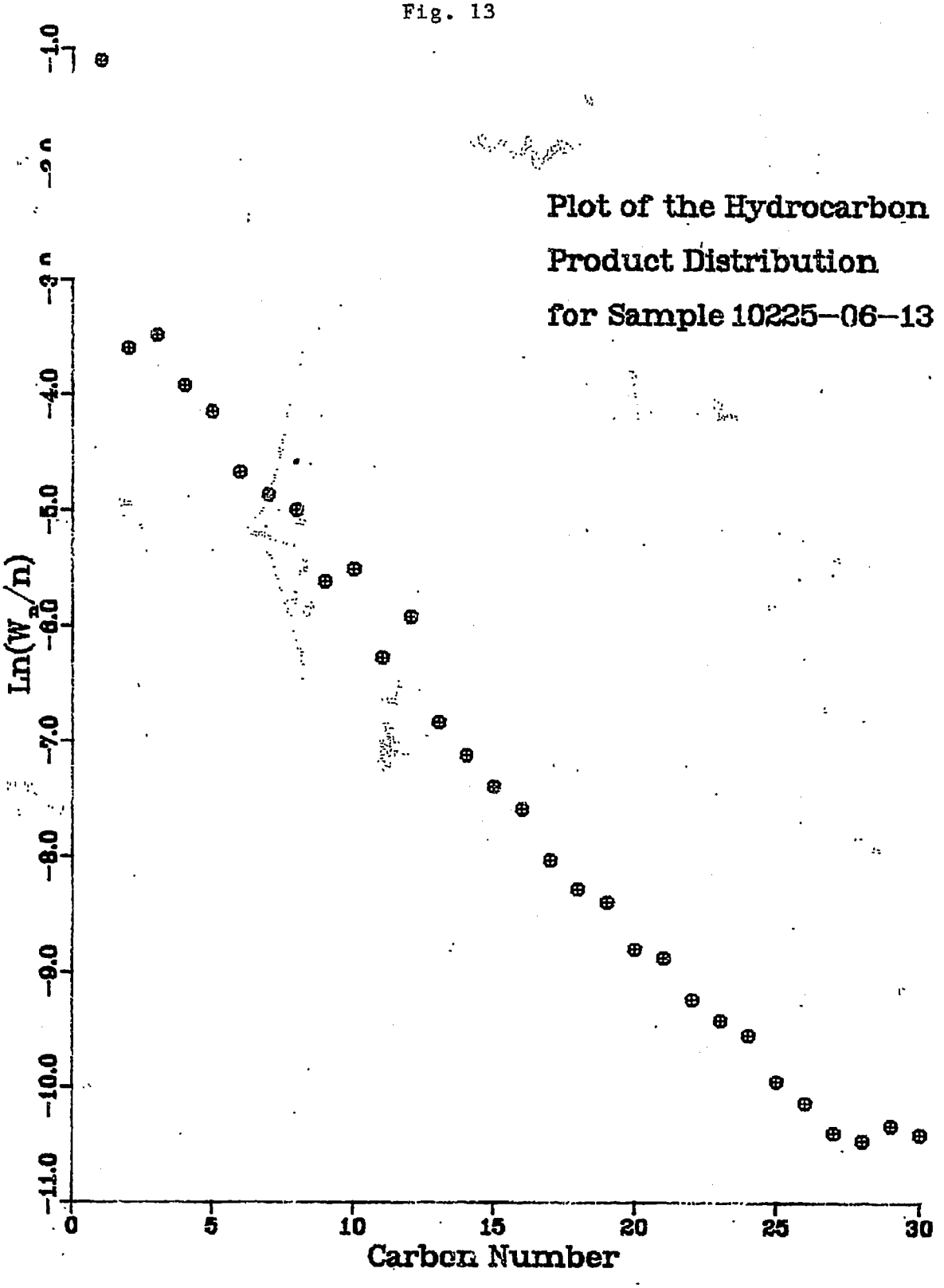

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-06-11
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 13


Plot of the Hydrocarbon
Product Distribution
for Sample 10225-06-13
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
0
5
10
15
20
25
30
Carbon Number

Fig. 14

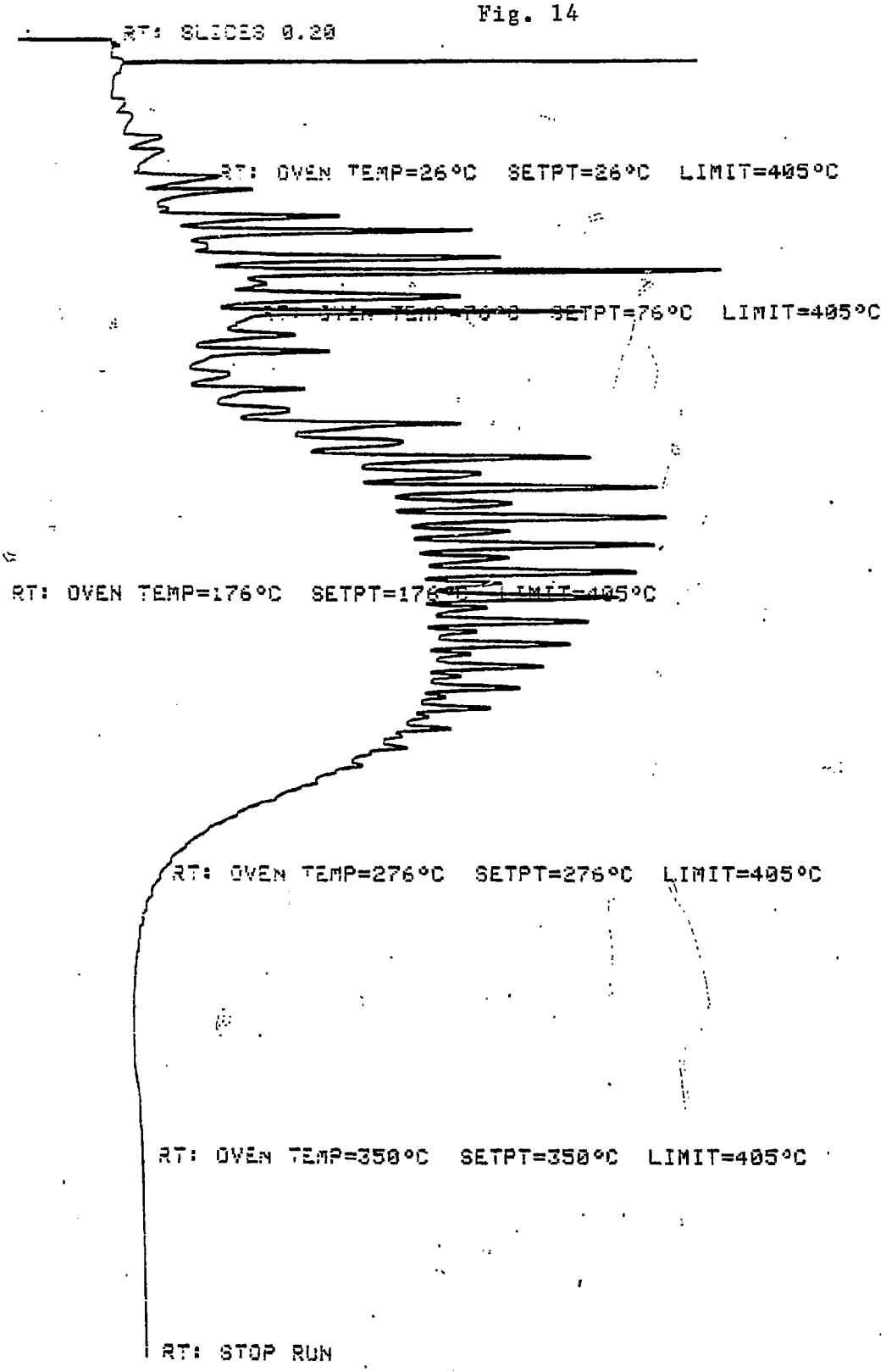
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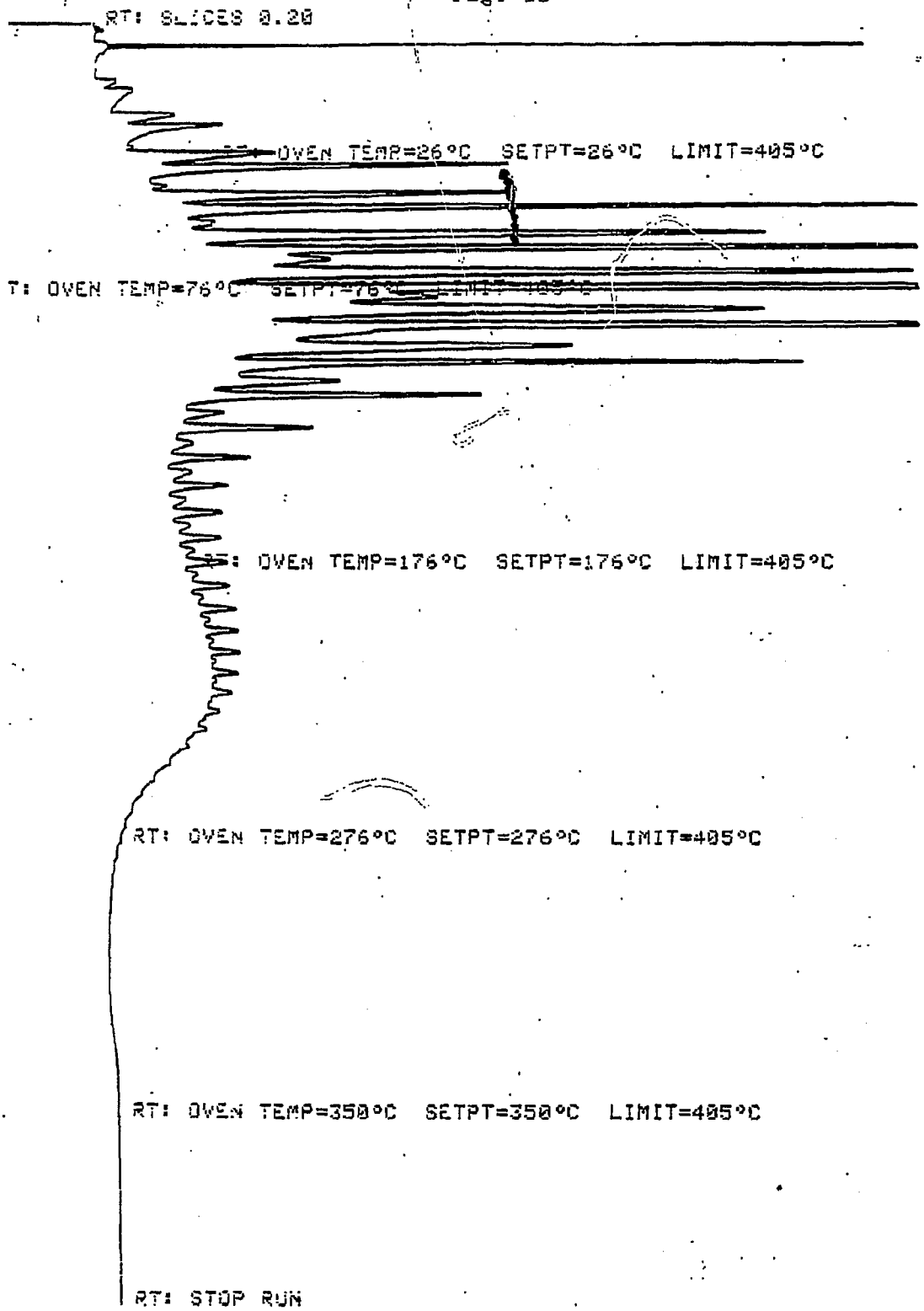
Fig. 15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: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
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RT: STOP RUN
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Fig. 16

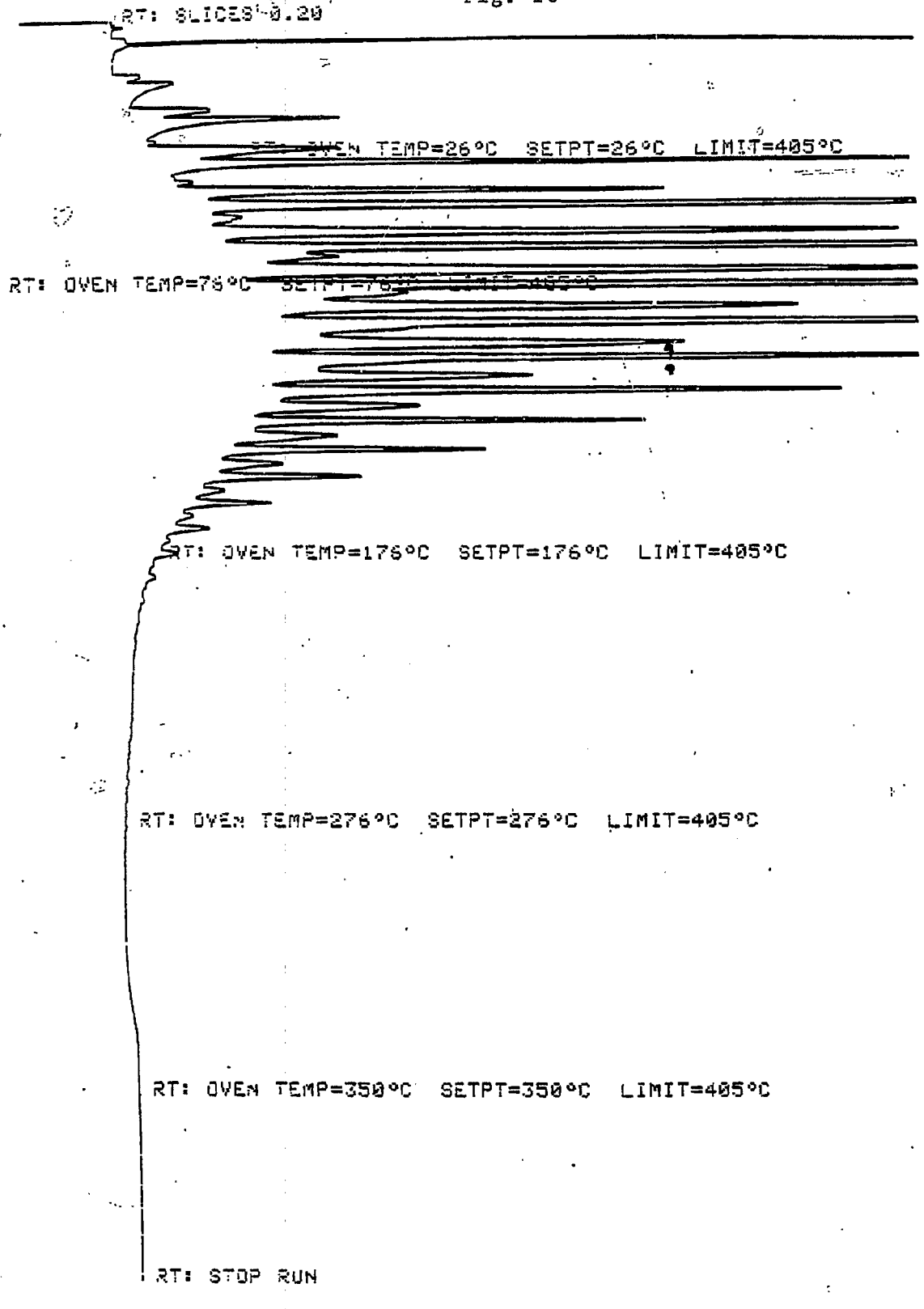
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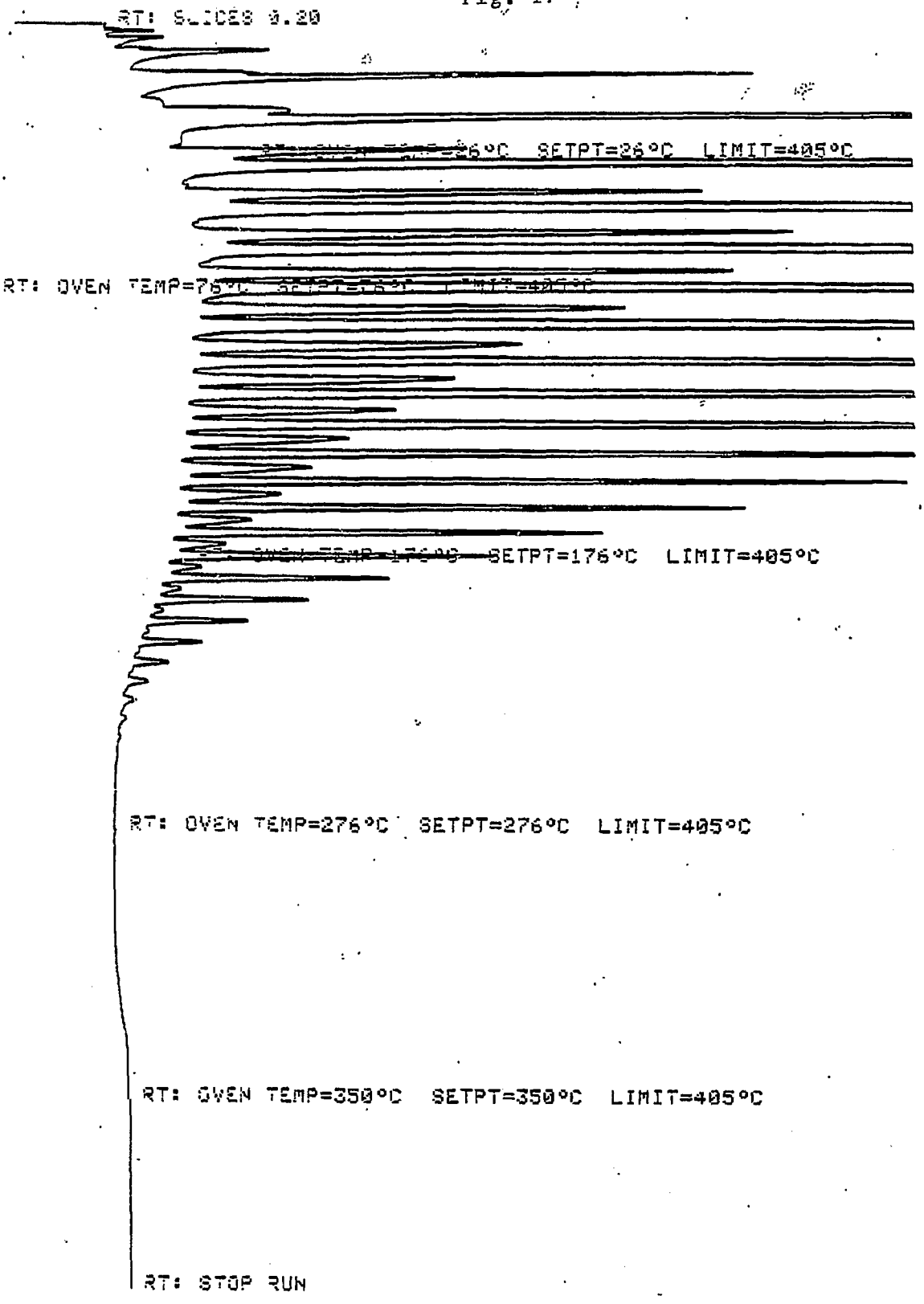
Fig. 17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RT: STOP RUN
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Fig. 18

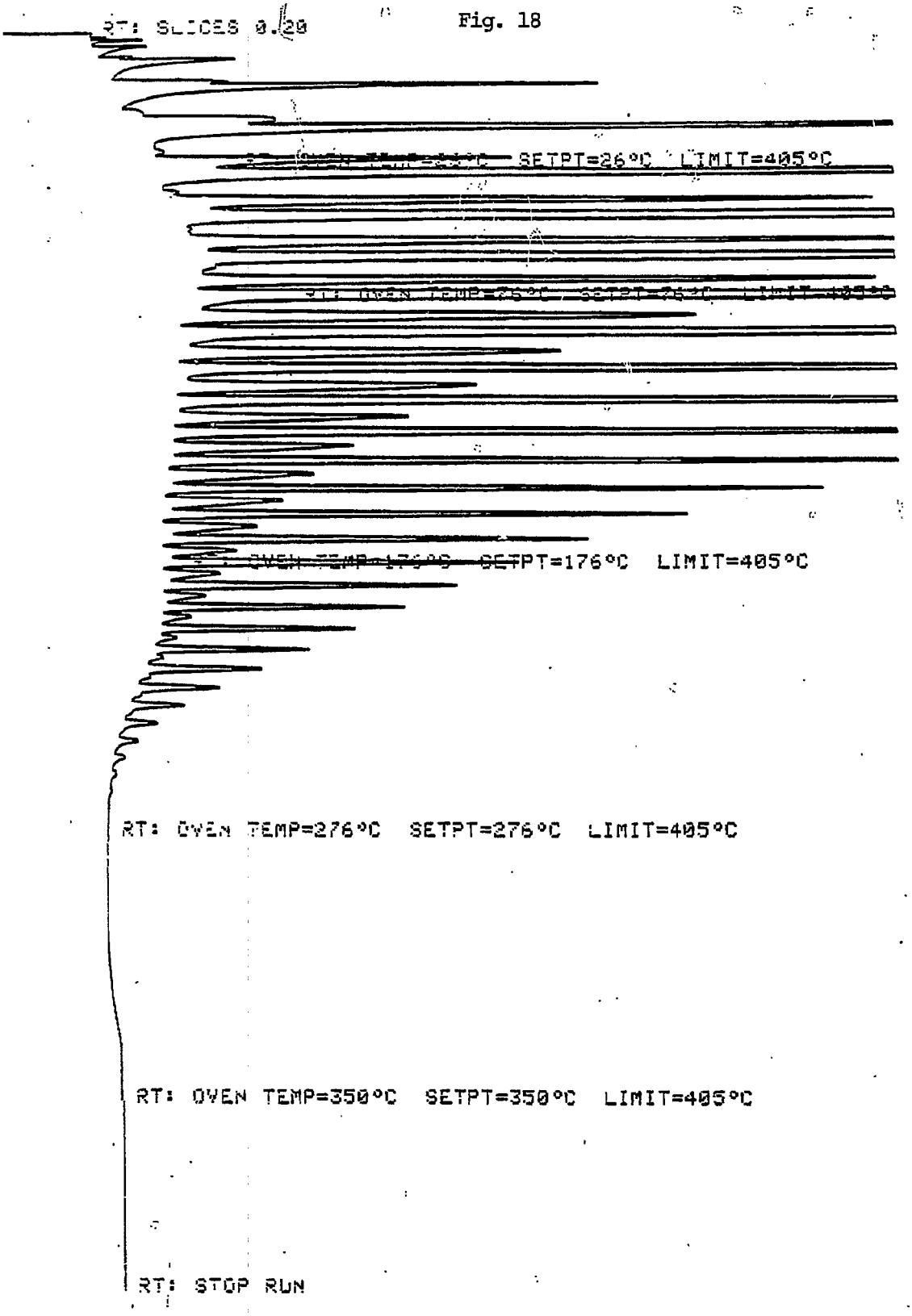
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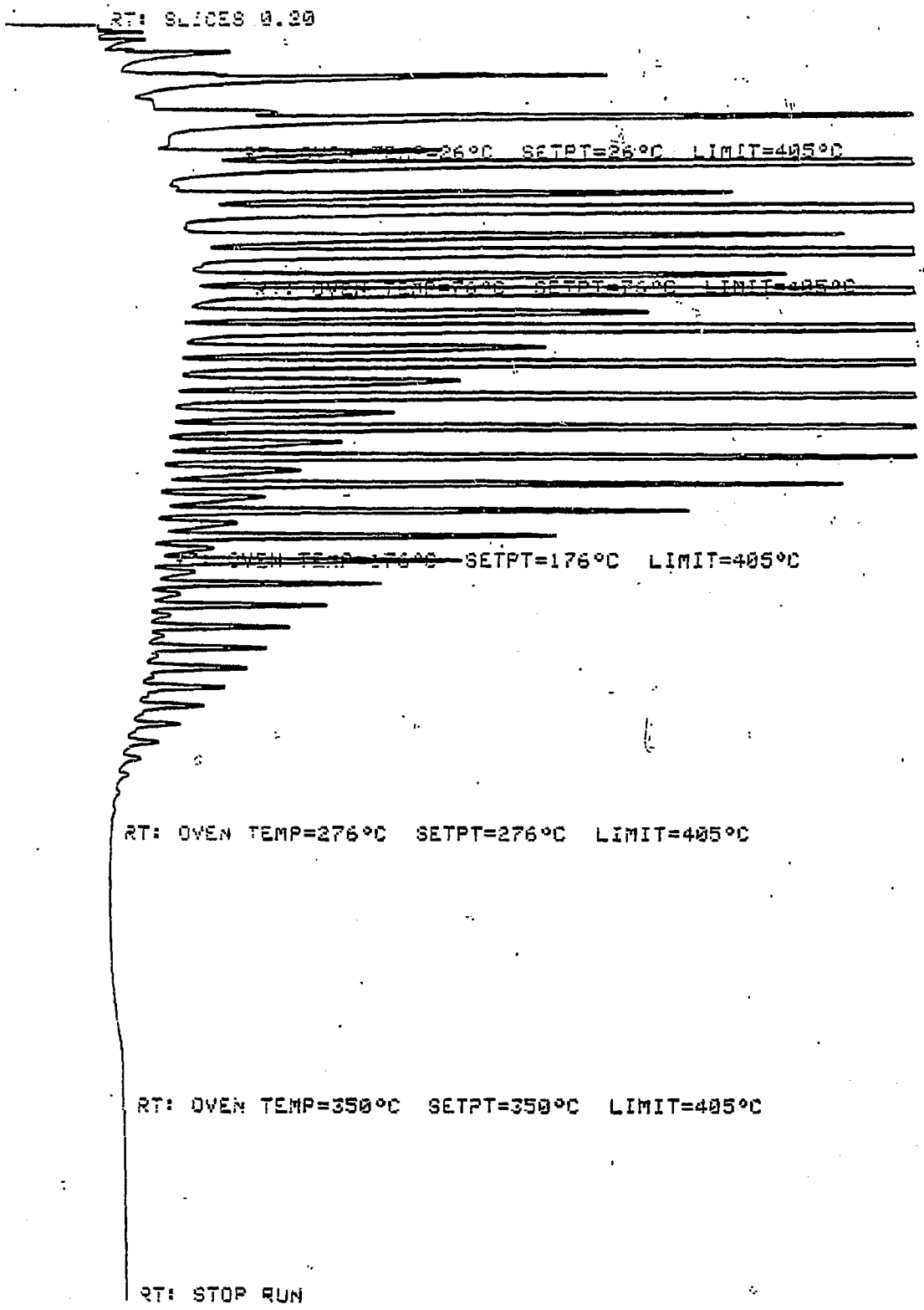
Fig. 19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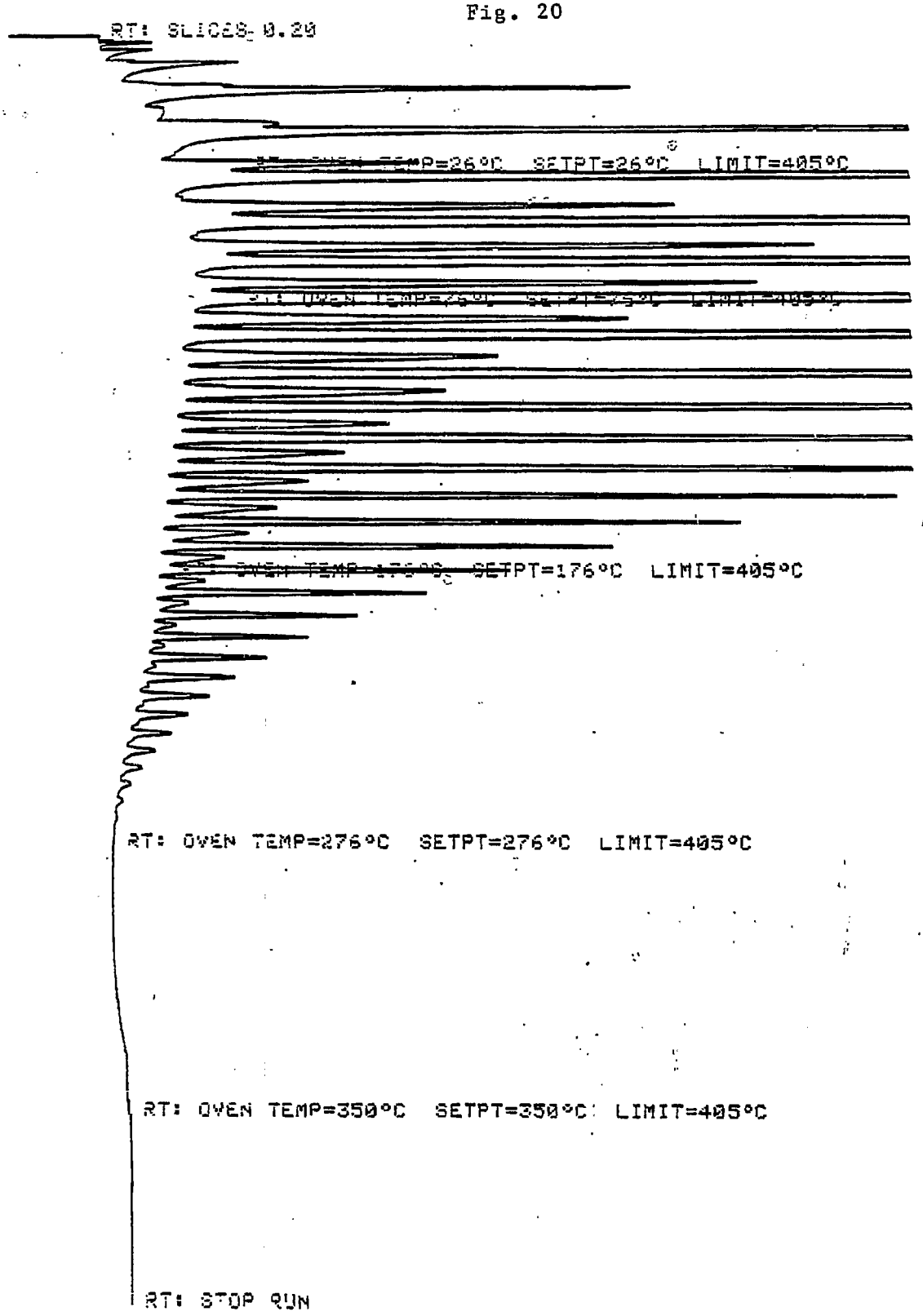
SAMPLE:10225-6-11L

Fig. 20



SAMPLE:10225-6-13L

TABLE 1 RESULT OF SYNGAS OPERATION

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CATALYST CO/TH +UCC-101 #10252-30C 80 CC 35.8GM (34.6 AFTER RUN -1. G)
FEED H2:CO:ARGON OF 50:50:0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-06-01	225-06-02	225-06-03	225-06-04	225-06-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.5	29.0	46.5	52.5	71.7
PRESSURE,PSIG	302	310	308	309	309
TEMP. C	279	278	278	278	278
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.50	6.50	24.00	6.00	25.17
EFFLNT GAS LITER	236.90	68.30	250.70	62.30	261.25
GM AQUEOUS LAYER	11.57	3.98	14.70	4.34	18.20
GM OIL	0.58	0.27	1.00	0.55	2.30
MATERIAL BALANCE					
GM ATOM CARBON %	91.76	92.56	92.75	93.27	91.84
GM ATOM HYDROGEN %	97.25	97.50	100.17	97.93	97.43
GM ATOM OXYGEN %	94.37	96.12	93.00	96.66	96.07
RATIO CHX/(H2O+CO2)	0.9484	0.9312	0.9950	0.9351	0.9186
RATIO X IN CHX	3.5000	3.4477	3.4075	3.3230	3.3443
USAGE H2/CO PRODT	0.9889	0.9837	1.0210	0.9782	0.9731
RATIO CO2/(H2O+CO2)	0.8529	0.8345	0.8297	0.8125	0.8122
K SHIFT IN EFFLNT	59.88	22.53	25.62	14.23	19.03
CONVERSION					
ON CO %	99.39	98.54	98.64	97.66	98.09
ON H2 %	94.06	93.82	93.38	92.68	92.09
ON CO+H2 %	96.65	96.12	95.91	95.11	95.00
PRDT SELECTIVITY,WT %					
CH4	65.76	62.89	61.54	57.05	58.74
C2 HC'S	10.66	10.43	9.31	9.46	9.41
C3H8	9.70	10.34	9.80	10.22	9.51
C3H6=	0.10	0.12	0.24	0.34	0.49
C4H10	4.90	5.37	5.57	5.90	5.24
C4H8=	0.17	0.22	0.41	0.57	0.74
C5H12	3.12	3.63	3.99	4.38	3.89
C5H10=	0.12	0.15	0.31	0.41	0.51
C6H14	2.18	2.56	3.22	3.57	3.11
C6H12= & CYCLO'S	0.04	0.03	0.09	0.25	0.03
C7+ IN GAS	2.53	3.12	4.42	5.38	5.80
LIQ HC'S	0.70	1.13	1.10	2.47	2.52
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	91.30	89.38	86.87	83.55	84.13
C5 -420 F	8.12	10.06	12.59	15.39	14.79
420-700 F	0.36	0.37	0.36	1.02	1.04
700-END PT	0.22	0.19	0.18	0.04	0.04
C5+-END PT	8.70	10.62	13.13	16.45	15.87
ISO/NORMAL MOLE RATIO					
C4	0.1162	0.1055	0.0870	0.0821	0.0781
C5	0.2498	0.2226	0.1812	0.1713	0.1551
C6	0.5407	0.4891	0.3869	0.3609	0.3245
C4=	0.4140	0.3806	0.2160	0.1620	0.1320
PARAFFIN/OLEFIN RATIO					
C3	93.2300	82.2922	38.8404	28.3561	18.6704
C4	27.1787	23.1114	12.9851	10.0334	6.8197
C5	24.4467	24.2034	12.3818	10.4409	7.4000
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	-	SL CLDY	-	SL CLDY
DENSITY					0.759
N, REFRACTIVE INDEX					1.4271
SIMULT'D DISTILATN					
10 WT % @ DEG F	352		300		288
16	403		330		307
50	617		418		407
84	770		706		523
90	804		764		563
RANGE(16-84 %)	367		376		216
WT % @ 420 F	17.70	51.00	51.00	57.00	57.00
WT % @ 700 F	69.00	83.45	83.45	98.35	98.35

TABLE 2 RESULT OF SYNGAS OPERATION

RUN NO. 10225-06
CATALYST CO/TH +UCC-101 #10252-30C 80 CC 35.8GM (34.6 AFTER RUN -1. G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-06-06	225-06-07	225-06-09	225-06-10	225-06-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	78.75	95.5	119.5	127.0	144.0
PRESSURE,PSIG	302	306	306	309	302
TEMP. C	255	247	252	253	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.08	23.83	24.00	7.50	24.50
EFFLNT GAS LITER	64.10	217.25	239.10	73.70	240.60
GM AQUEOUS LAYER	9.52	32.03	24.80	8.72	28.48
GM OIL	5.59	18.81	12.52	4.63	15.12
MATERIAL BALANCE					
GM ATOM CARBON %	86.74	90.47	93.75	94.28	93.87
GM ATOM HYDROGEN %	86.40	96.01	98.70	100.29	97.26
GM ATOM OXYGEN %	93.88	96.44	97.81	97.73	98.32
RATIO CHX/(H2O+CO2)	0.8554	0.8903	0.9243	0.9360	0.9166
RATIO X IN CHX	2.7849	2.8615	3.0276	2.9721	2.9062
USAGE H2/CO PRODT	0.9586	0.9616	0.9586	0.9794	0.9531
RATIO CO2/(H2O+CO2)	0.6646	0.6958	0.7540	0.7289	0.7263
K SHIFT IN EFFLNT	1.87	5.56	8.59	6.40	5.00
CONVERSION					
ON CO %	86.43	95.37	96.02	95.26	93.50
ON H2 %	87.14	89.41	89.40	89.40	88.19
ON CO+H2 %	86.78	92.30	92.63	92.24	90.80
PRDT SELECTIVITY,WT %					
CH4	34.63	37.10	44.18	41.46	38.70
C2 HC'S	5.71	5.84	7.18	6.89	6.46
C3H8	5.98	7.54	8.96	9.11	8.46
C3H6=	2.13	0.76	0.68	0.68	1.09
C4H10	3.92	5.20	5.58	5.74	5.30
C4H8=	2.77	1.51	1.30	1.49	2.08
C5H12	3.89	5.03	4.90	5.04	5.01
C5H10=	2.46	1.35	1.14	1.25	1.90
C6H14	3.61	4.64	4.36	4.26	4.57
C6H12= & CYCLO'S	0.28	0.11	0.07	0.06	0.12
C7+ IN GAS	9.07	8.77	7.50	7.52	9.25
LIQ HC'S	25.56	22.15	14.15	16.50	17.08
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	55.13	57.95	67.88	65.37	62.08
C5 -420 F	34.90	33.41	26.46	28.03	31.09
420-700 F	9.34	8.09	4.97	5.78	5.99
700-END PT	0.63	0.55	0.68	0.82	0.85
C5+-END PT	44.87	42.05	32.12	34.63	37.92
ISO/NORMAL MOLE RATIO					
C4	0.0508	0.0386	0.0450	0.0454	0.0392
C5	0.0943	0.0785	0.0886	0.0859	0.0771
C6	0.1645	0.1501	0.1677	0.1619	0.1434
C4=	0.0000	0.1627	0.1848	0.1757	0.1290
PARAFFIN/OLEFIN RATIO					
C3	2.6850	9.4355	12.5361	12.7247	7.4043
C4	1.3677	3.3335	4.1454	3.7318	2.4668
C5	1.5388	3.6270	4.1883	3.9134	2.5644
LIQ HC COLLECTION					
PHYS. APPEARANCE	-	CLR OIL	CLR OIL	-	CLR OIL
DENSITY		0.737	0.742		0.741
N, REFRACTIVE INDEX		1.4161	1.45171		1.4169
SIMULT'D DISTILAIN					
10 WT % @ DEG F		249	254		253
16		261	266		263
50		390	391		393
84		542	567		553
90		596	628		622
RANGE(16-84 %)		281	301		290
WT % @ 420 F	61.00	61.00	60.00	60.00	60.00
WT % @ 700 F	97.52	97.52	95.16	95.04	95.04

TABLE 3 RESULT OF SYNGAS OPERATION

RUN NO. 10225-06
CATALYST CO/TH +UCC-101 #10252-30C 80 CC 35.8GM (34.6 AFTER RUN -1. G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-06-13
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	167.5
PRESSURE,PSIG	310
TEMP. C	251
FEED CC/MIN	400
HOURS FEEDING	23.50
EFFLNT GAS LITER	225.80
GM AQUEOUS LAYER	29.82
GM OIL	16.95
MATERIAL BALANCE	
GM ATOM CARBON %	97.17
GM ATOM HYDROGEN %	99.19
GM ATOM OXYGEN %	98.02
RATIO CHX/(H2O+CO2)	0.9840
RATIO X IN CHX	2.7846
USAGE H2/CO PRODT	0.9845
RATIO CO2/(H2O+CO2)	0.7021
K SHIFT IN EFFLNT	3.26
CONVERSION	
ON CO %	91.96
ON H2 %	89.12
ON CO+H2 %	90.53
PRDT SELECTIVITY,WT %	
CH4	33.13
C2 HC'S	5.46
C3H8	7.87
C3H6=	1.35
C4H10	5.12
C4H8=	2.78
C5H12	5.40
C5H10=	2.46
C6H14	5.15
C6H12= & CYCLO'S	0.27
C7+ IN GAS	12.11
LIQ HC'S	18.90
TOTAL	100.00

SUB-GROUPING	
C1 -C4	55.71
C5 -420 F	36.92
420-700 F	6.49
700-END PT	0.88
C5+-END PT	44.29
ISO/NORMAL MOLE RATIO	
C4	0.0360
C5	0.0868
C6	0.1362
C4=	0.0881
PARAFFIN/OLEFIN RATIO	
C3	5.5557
C4	1.7745
C5	2.1349
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLR OIL
DENSITY	0.744
N, REFRACTIVE INDEX	1.4171
SIMULT'D DISTILATN	
10 WT % @ DEG F	253
16	262
50	390
84	557
90	622
RANGE(16-84 %)	295
WT % @ 420 F	61.00
WT % @ 700 F	95.33

III. RUN 2 (10112-14) With Catalyst 2 (Co/Th on UCC-101)

Like Catalyst 1, with which it is to be compared, this catalyst is to be used in establishing the most favorable ratio of metal component to Molecular Sieve in cobalt catalysts. It was prepared in the same way as Catalyst 1 except that the metal component contained 17 weight percent ThO_2 and the weight ratio of Molecular Sieve to metal component was 14:3, with 15 weight percent SiO_2 binder.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 21-24. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 25-26. Carbon number product distributions are plotted in Figs. 27-33. Chromatograms from simulated distillations are reproduced in Figs. 34-40. Detailed material balances appear in Tables 4-6.

As expected with its lower concentration of metal component, this catalyst was much less active (~45 percent conversion) at 250C than Catalyst 1; there was an initial deactivation, followed by a steady conversion. At 270C the conversion was substantially higher than at 250C, but still not as good as with Catalyst 1. Because the water gas shift activity was poor, the conversion of H_2 was higher than that of CO; 85 percent of the oxygen was rejected as H_2O at 250C, and 75 percent at 270C--an inefficient use

of 1:1 syngas. Due to the high conversion of hydrogen and the CSTR behavior of the Berty reactor, the effective exposure of this catalyst to the H_2:CO syngas was in a ratio of only 0.4:1.

The selectivity at 250C was variable, at 270C fairly stable. Methane production was 17-18 percent, a high yield but common with cobalt catalysts. The C_2-C_4 fraction was low. The C_5^+ product was fairly high: 42 percent of the total product was gasoline, 20 percent diesel oil, and 7.5 percent heavies. The total motor fuel yield, however, was lower than the Schulz-Flory limit. The C_4 fraction was more olefinic than that of Catalyst 1; measurements varied, but without discernible trends. Isomerization of the pentane, while approximately twice that of Catalyst 1, was still low. Pentane production, in moles per hour, was about half that of Catalyst 1, so that absolute isomerization was the same with both. The Schulz-Flory plots are linear except for the excess methane and some error in the C_6-C_7 measurements, and there is no indication of a carbon number cut-off. The condensed liquid contains wax, even though only 16 percent of it boiled above the diesel range. The chromatograms of the simulated distillations show mostly straight chain hydrocarbons; isomerization of the pentanes was substantially higher than with Catalyst 1, but total isomerization was only a little higher.

The ratio of metal component to Molecular Sieve in this catalyst is much lower than that in Catalyst 1, and the Molecular Sieve is not being overwhelmed. Methane production is still excessive, and a higher degree of isomerization would be desirable.

To test the possibility that in the initial part of the run at 250C the catalyst may have lost some of its isomerizing ability, which it could not thereafter recover, it may be useful to run it first at 270C to see if the isomerization improves.

Fig. 21

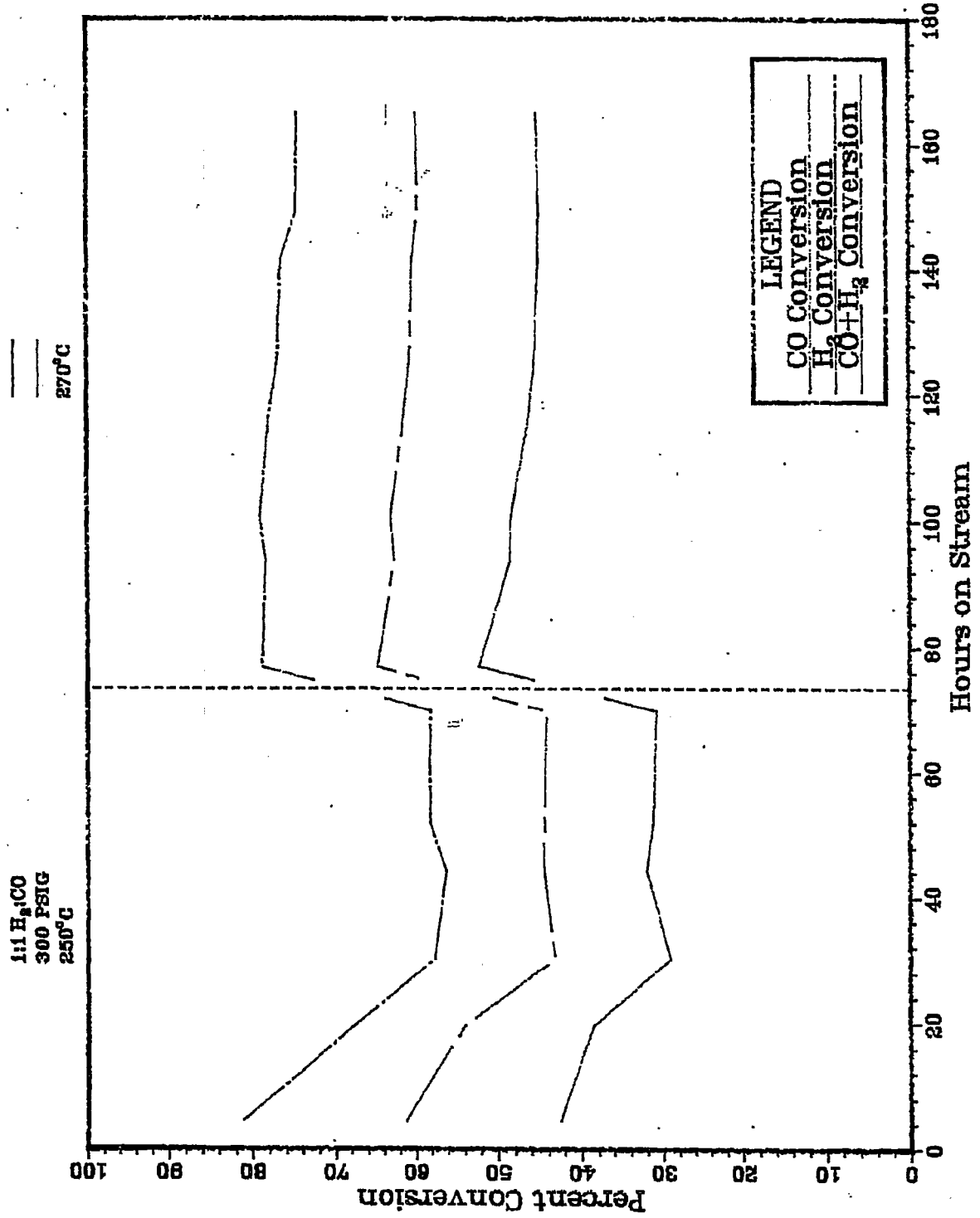
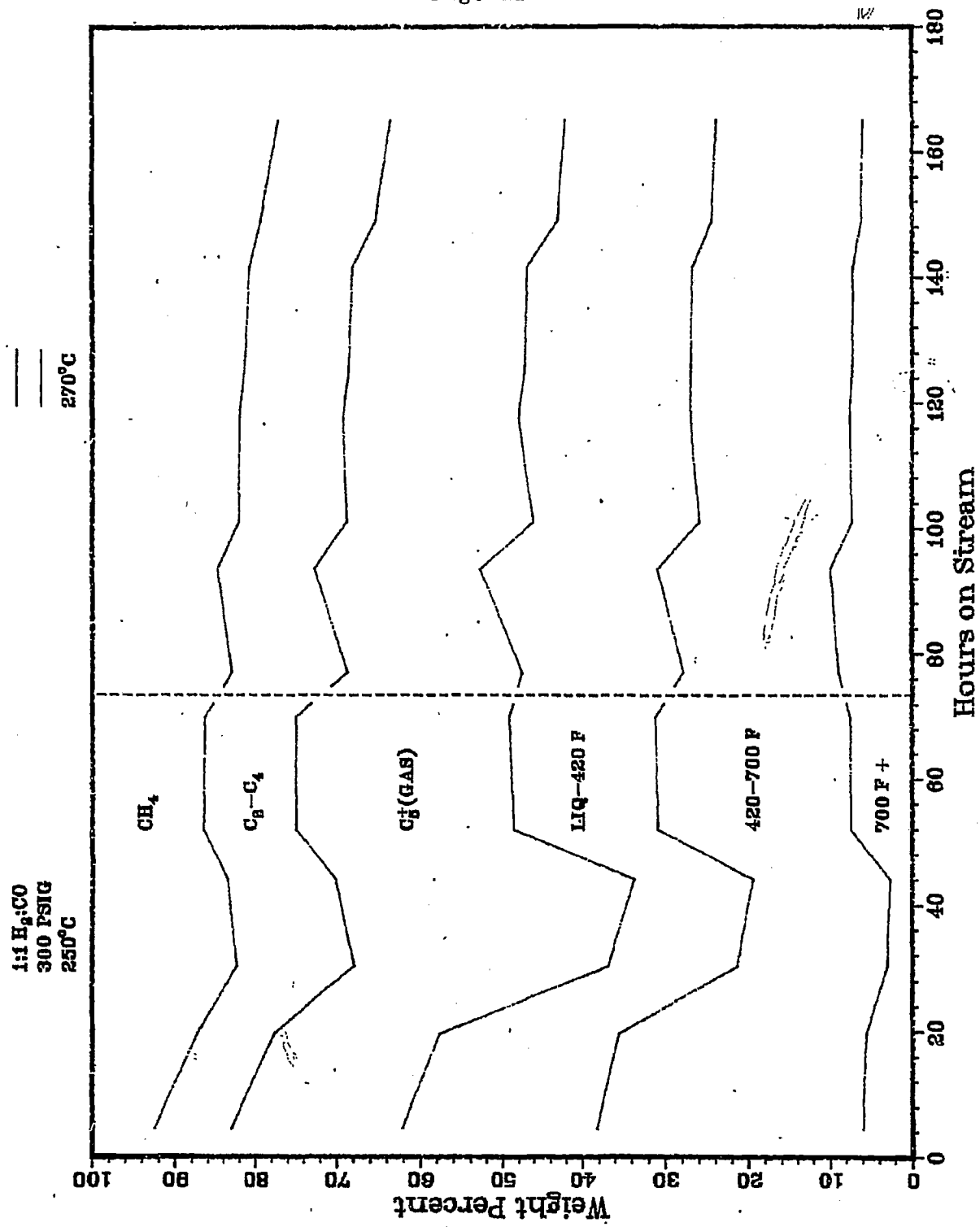

RUN 10112-14
1:1 H_2:CO
300 PSIG
250°C
270°C
LEGEND
CO Conversion
H_2 Conversion
$CO+H_2$ Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 22


RUN 10112-14
1:1 H2:CO
300 PSIG
250°C
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

RUN 10112–14

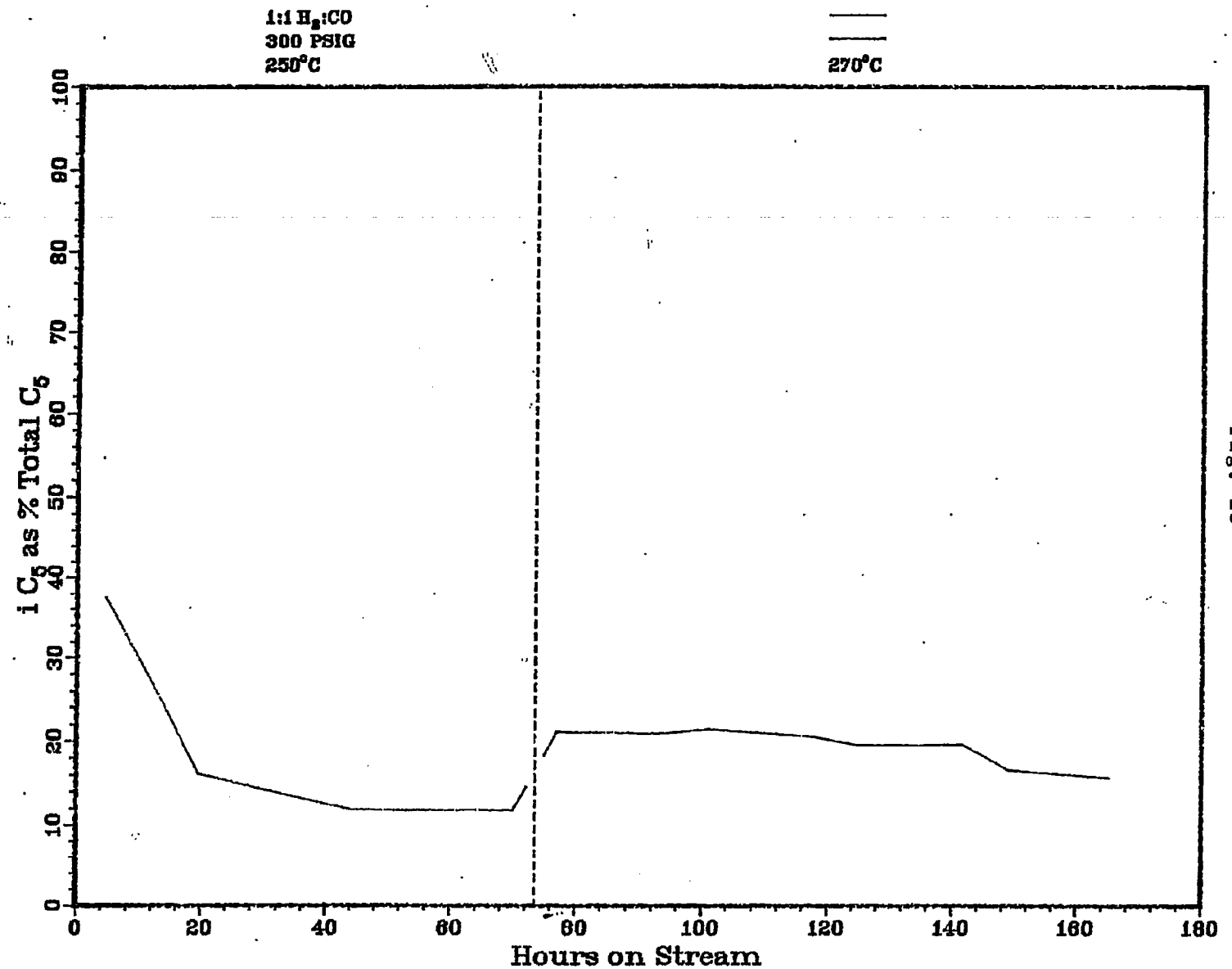


Fig. 23

Fig. 24

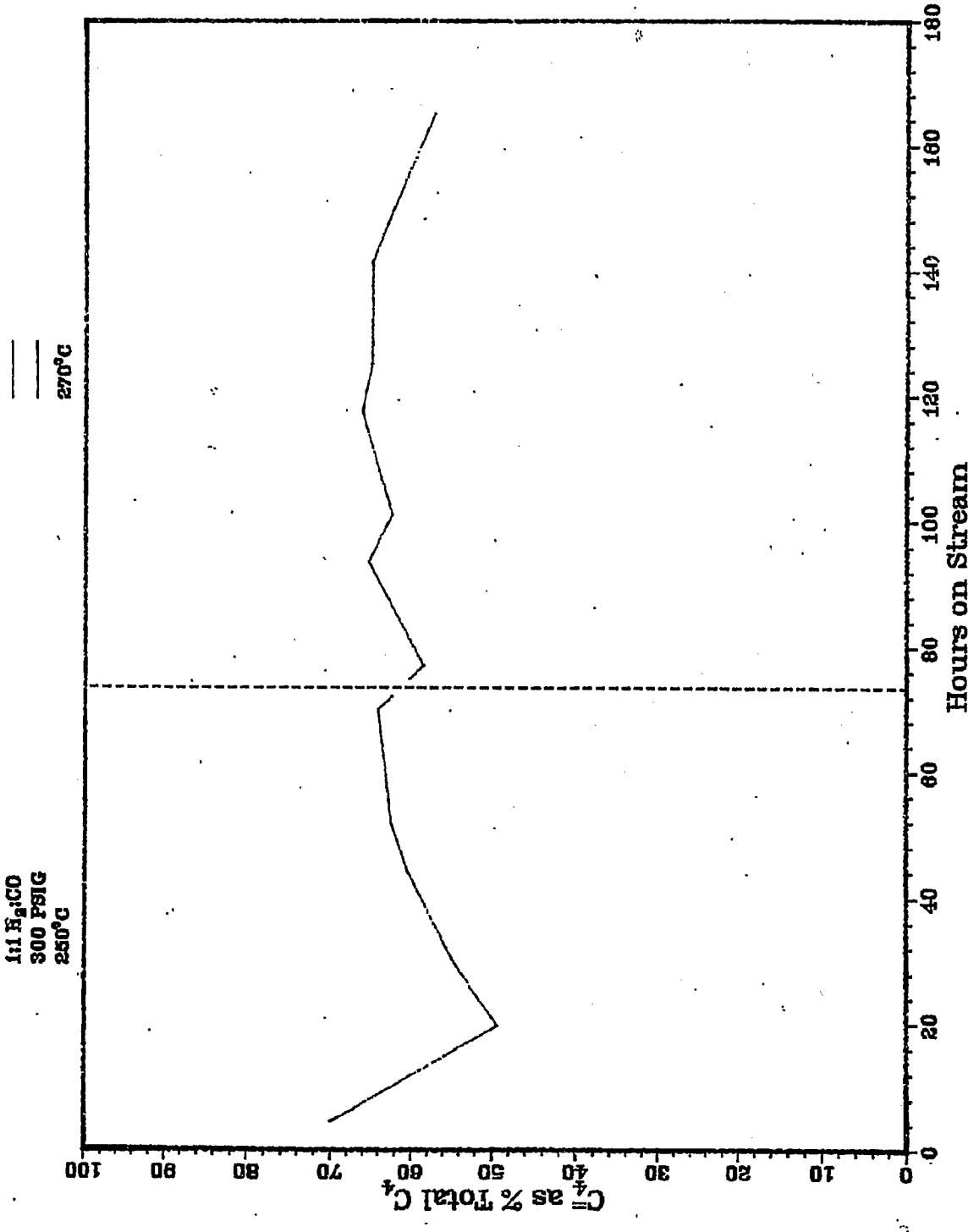

RUN 10112-14
1:1 H2:CO
300 PSIG
250°C
270°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. 25

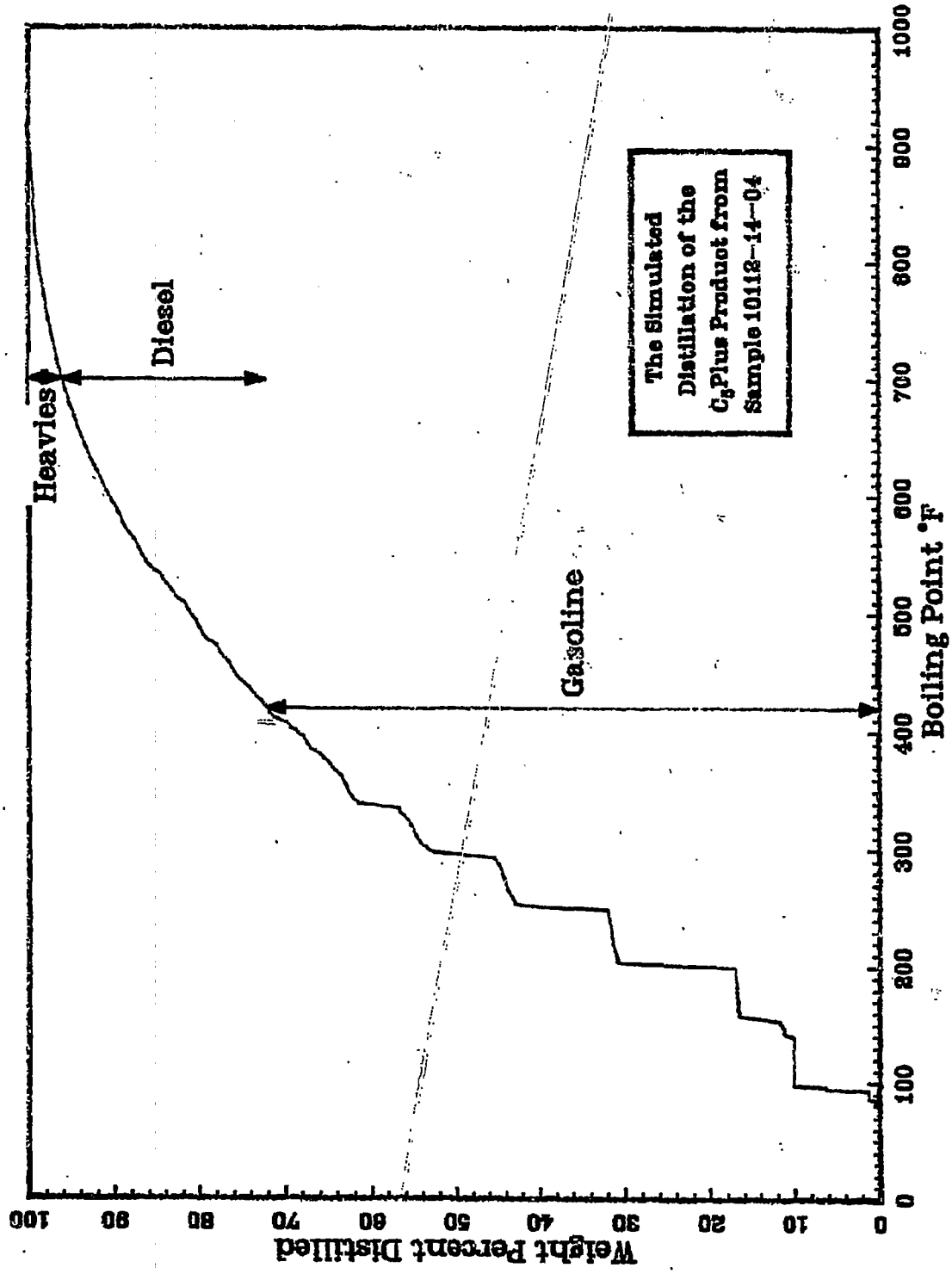

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10112-14-04

Fig. 26

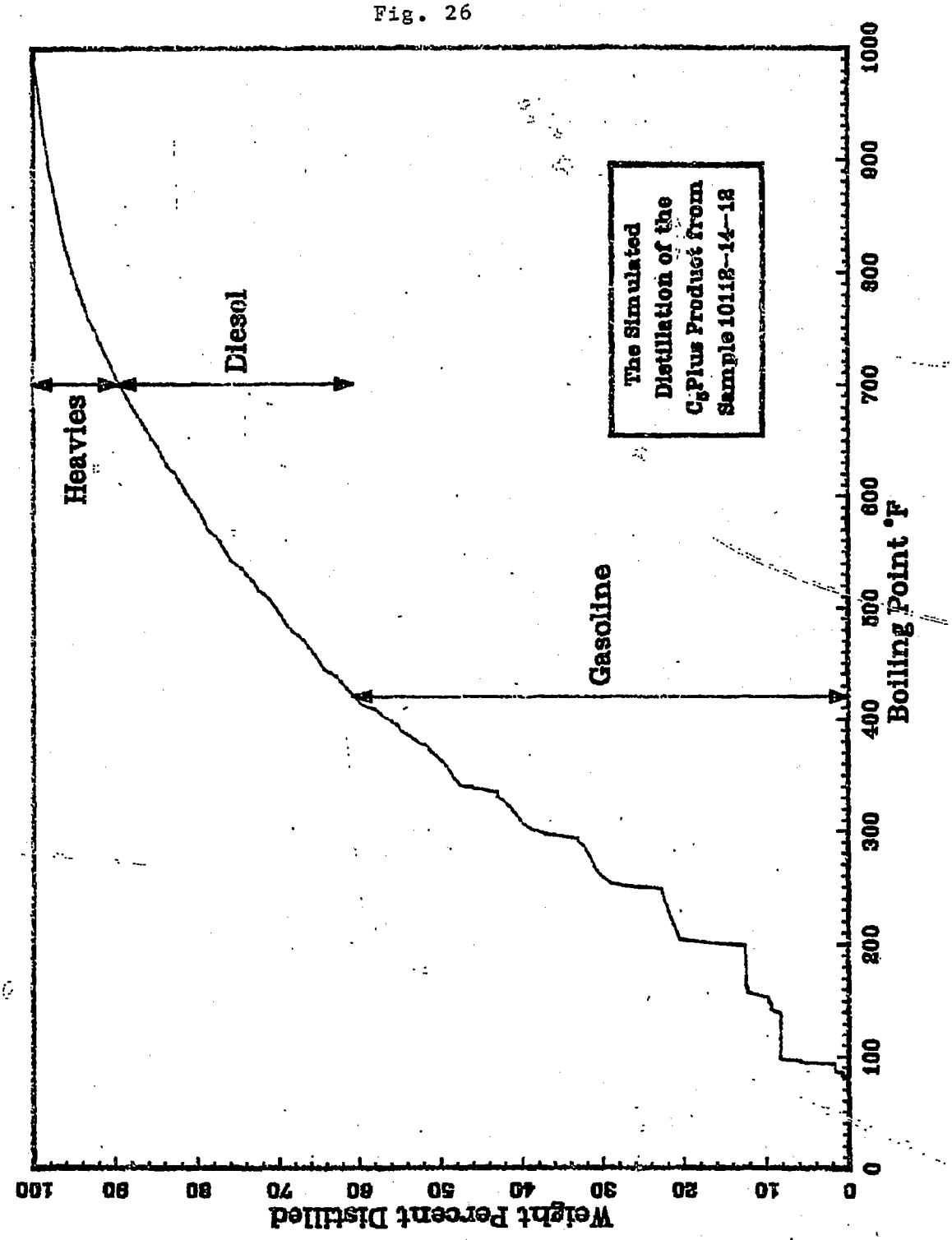

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10118-14-1B

Fig. 27

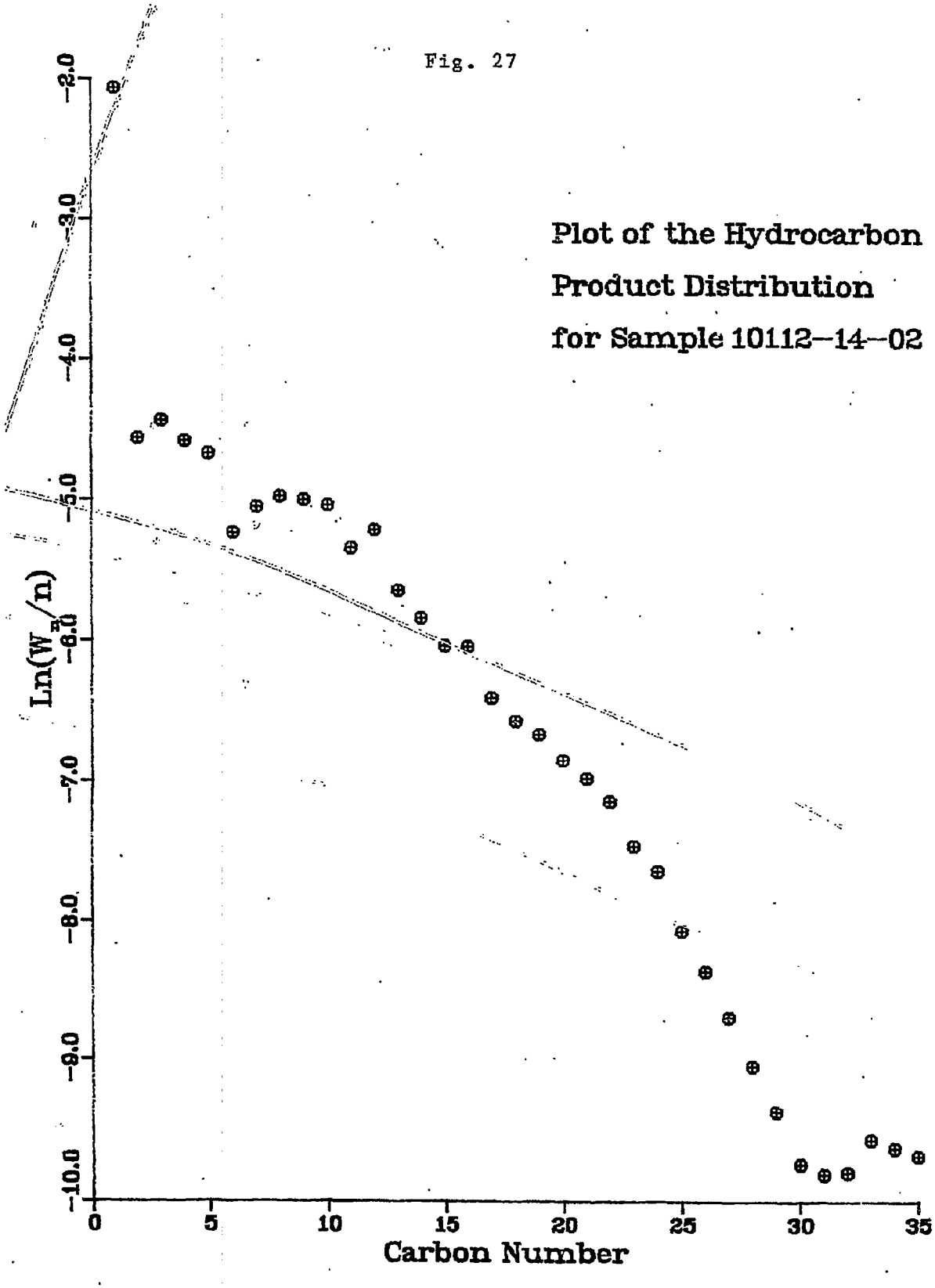
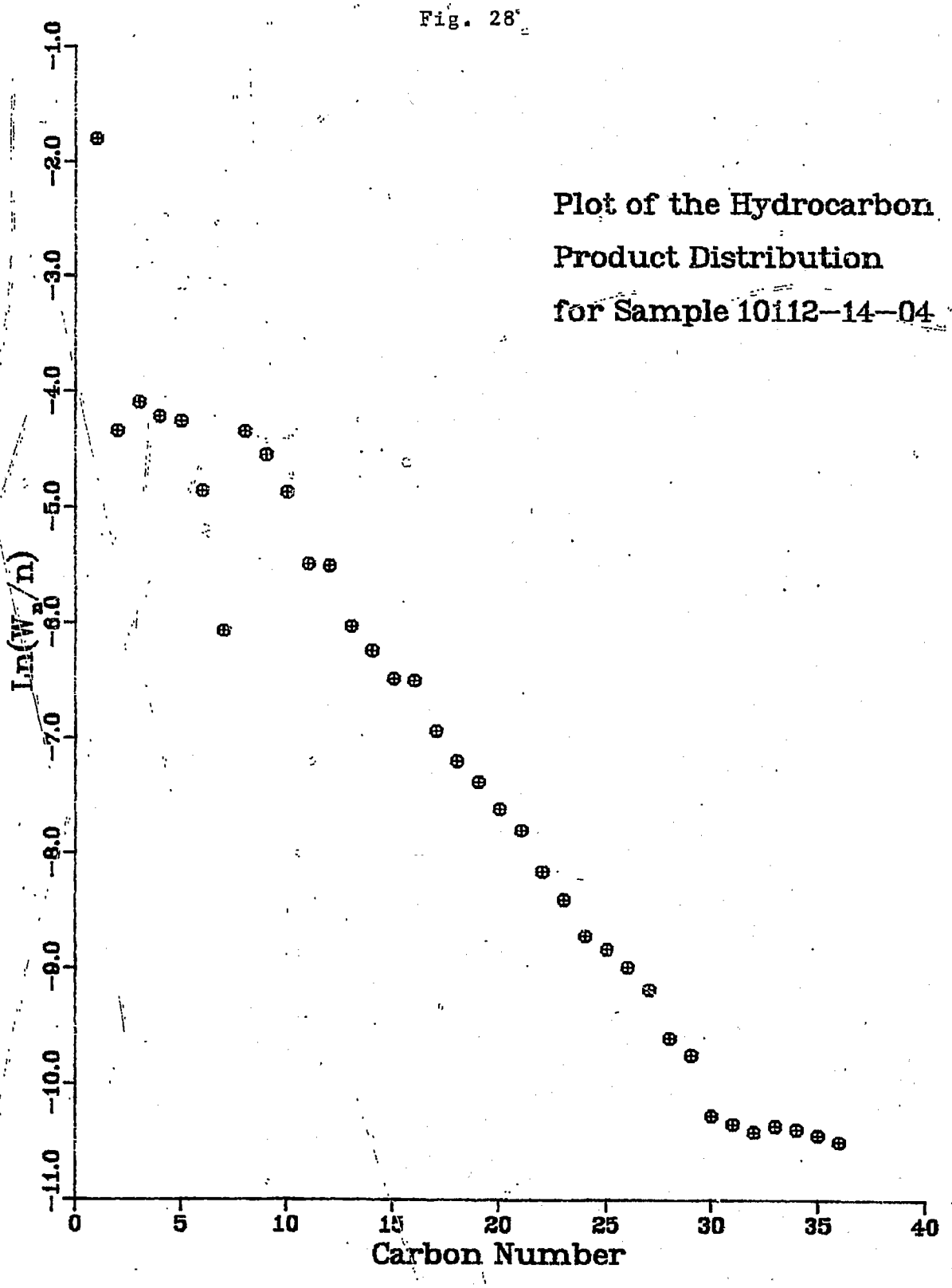

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--14--02
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 28



Plot of the Hydrocarbon Product Distribution for Sample 10112-14-04

Fig. 29

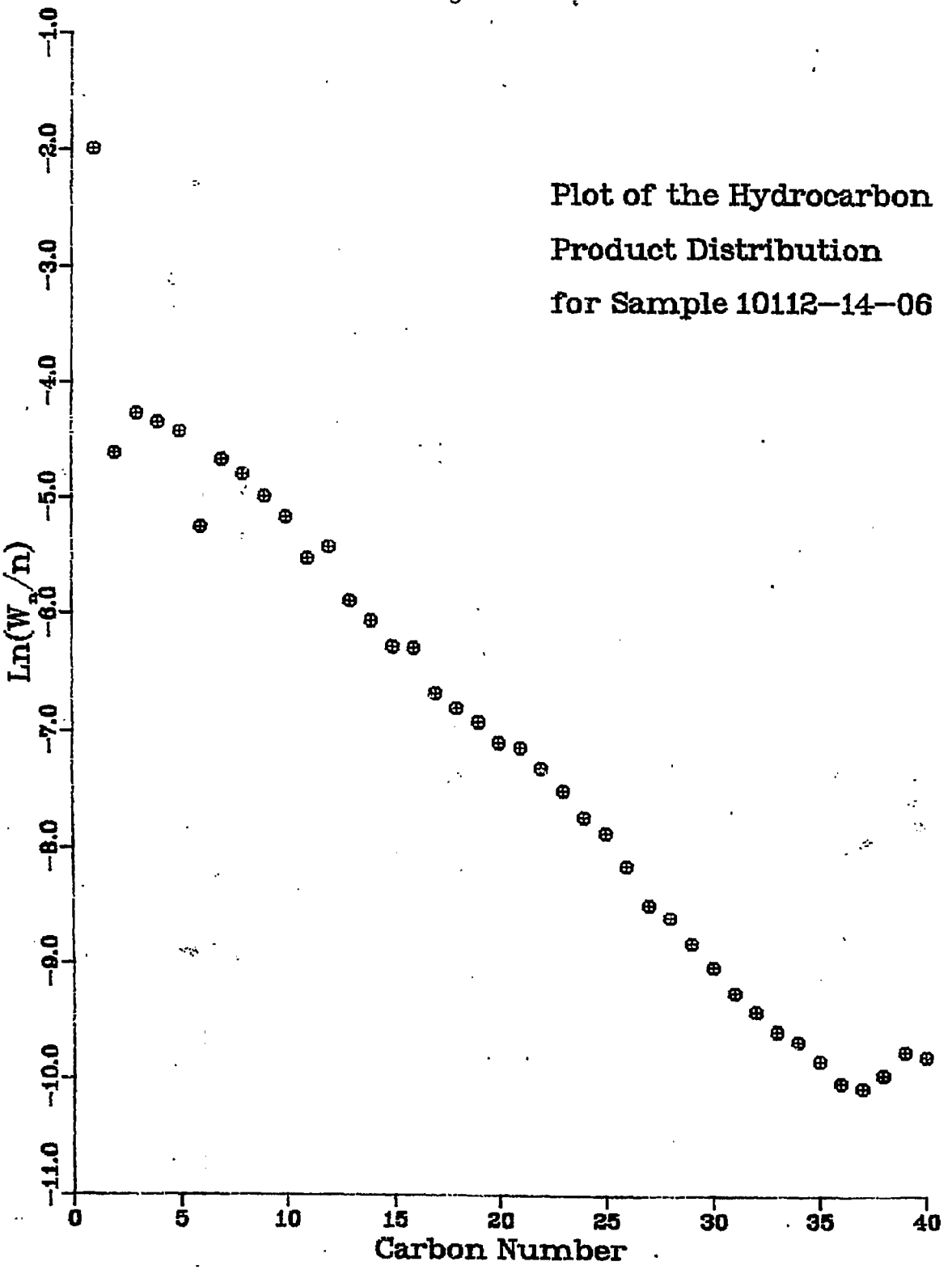

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–14–06
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 30

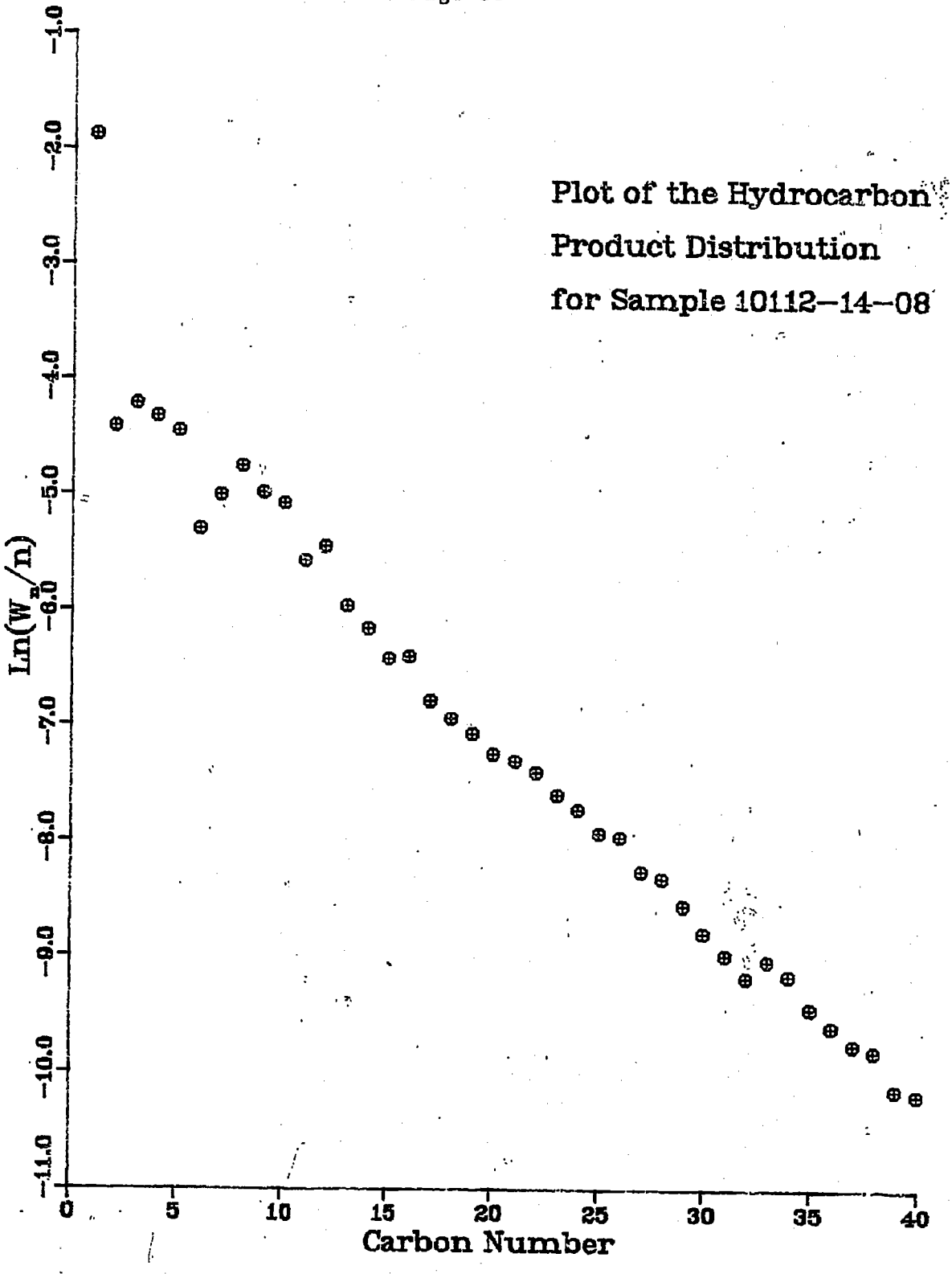

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-14-08
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 31

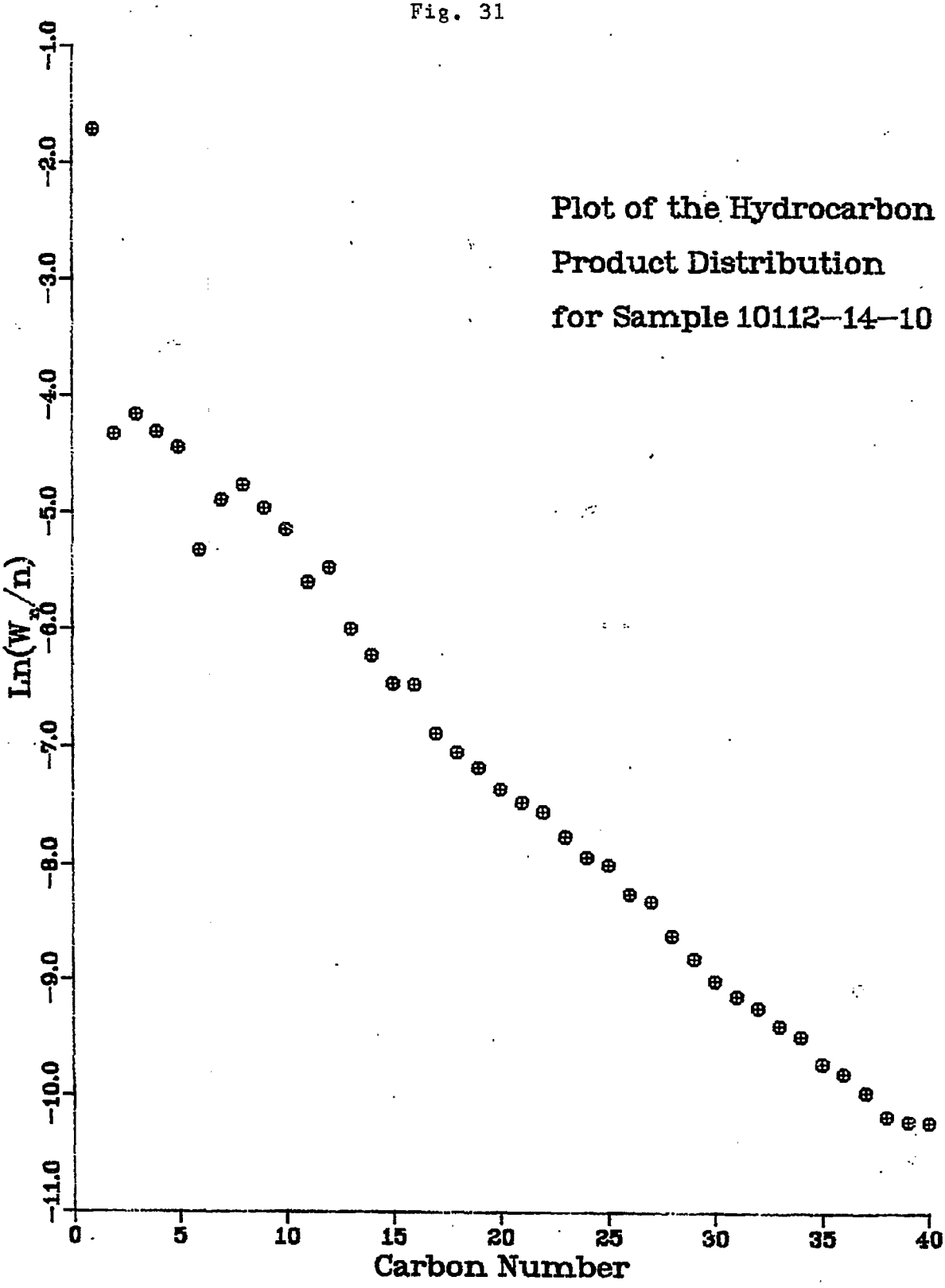

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-14-10
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 32

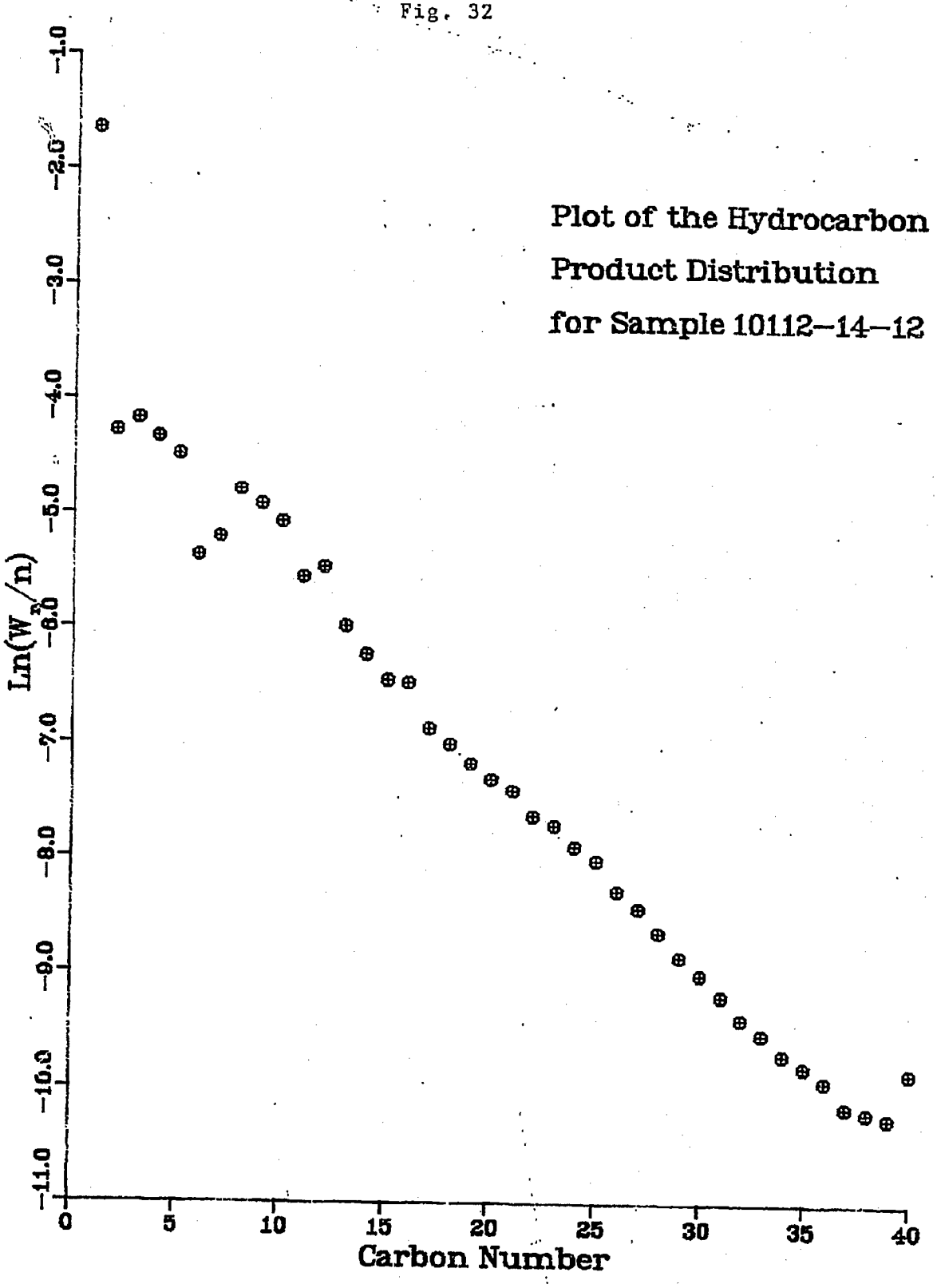

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-14-12
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 33

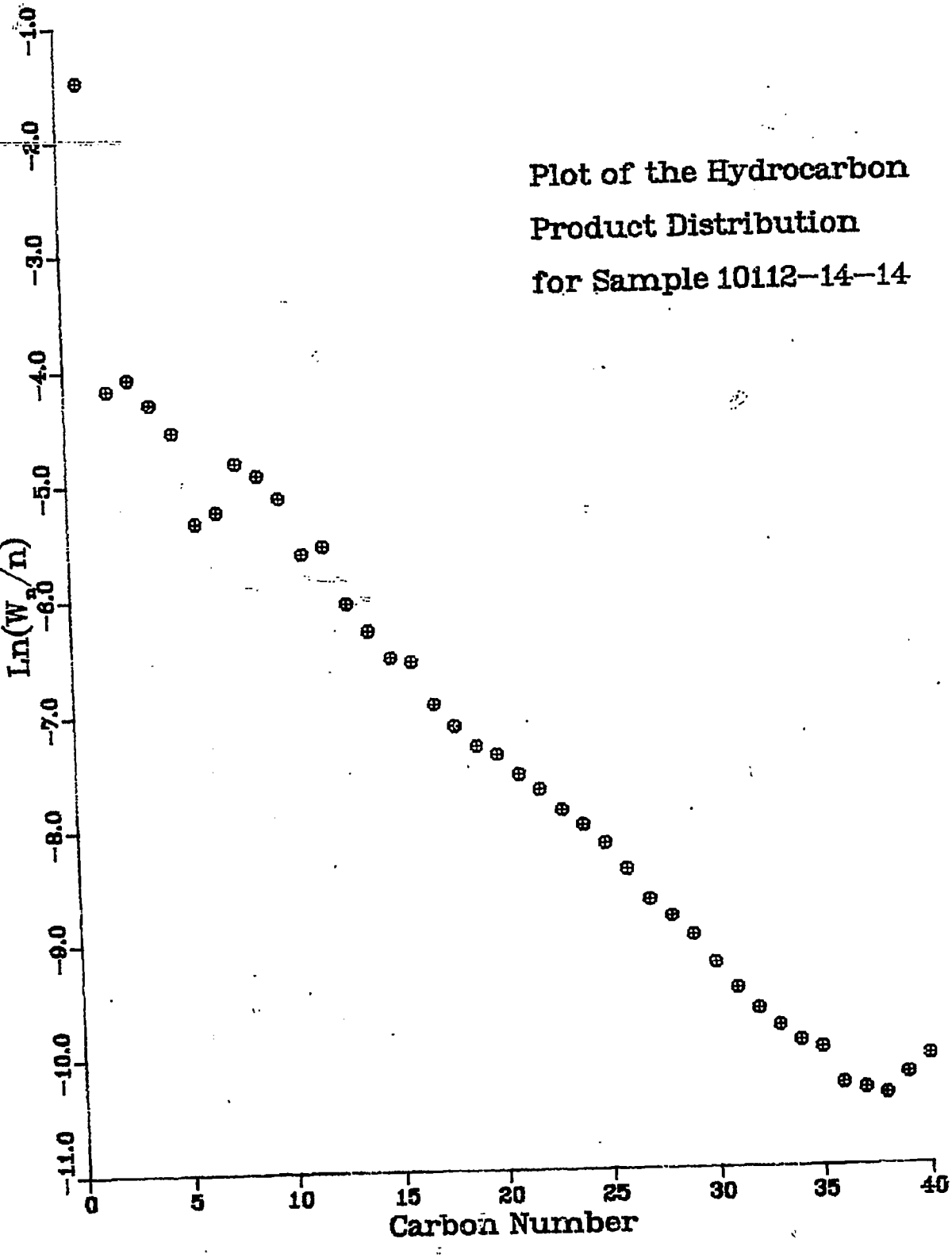
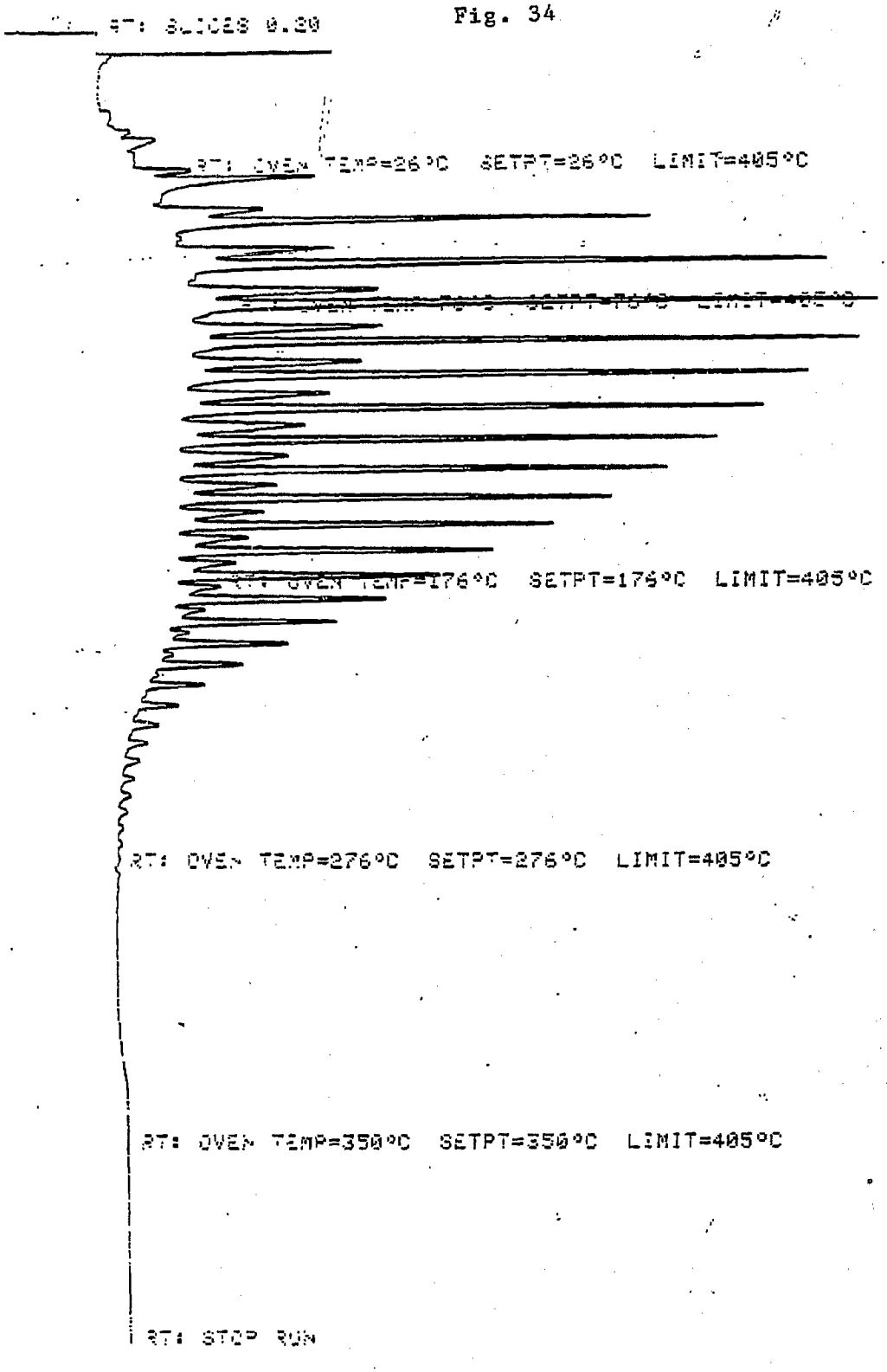
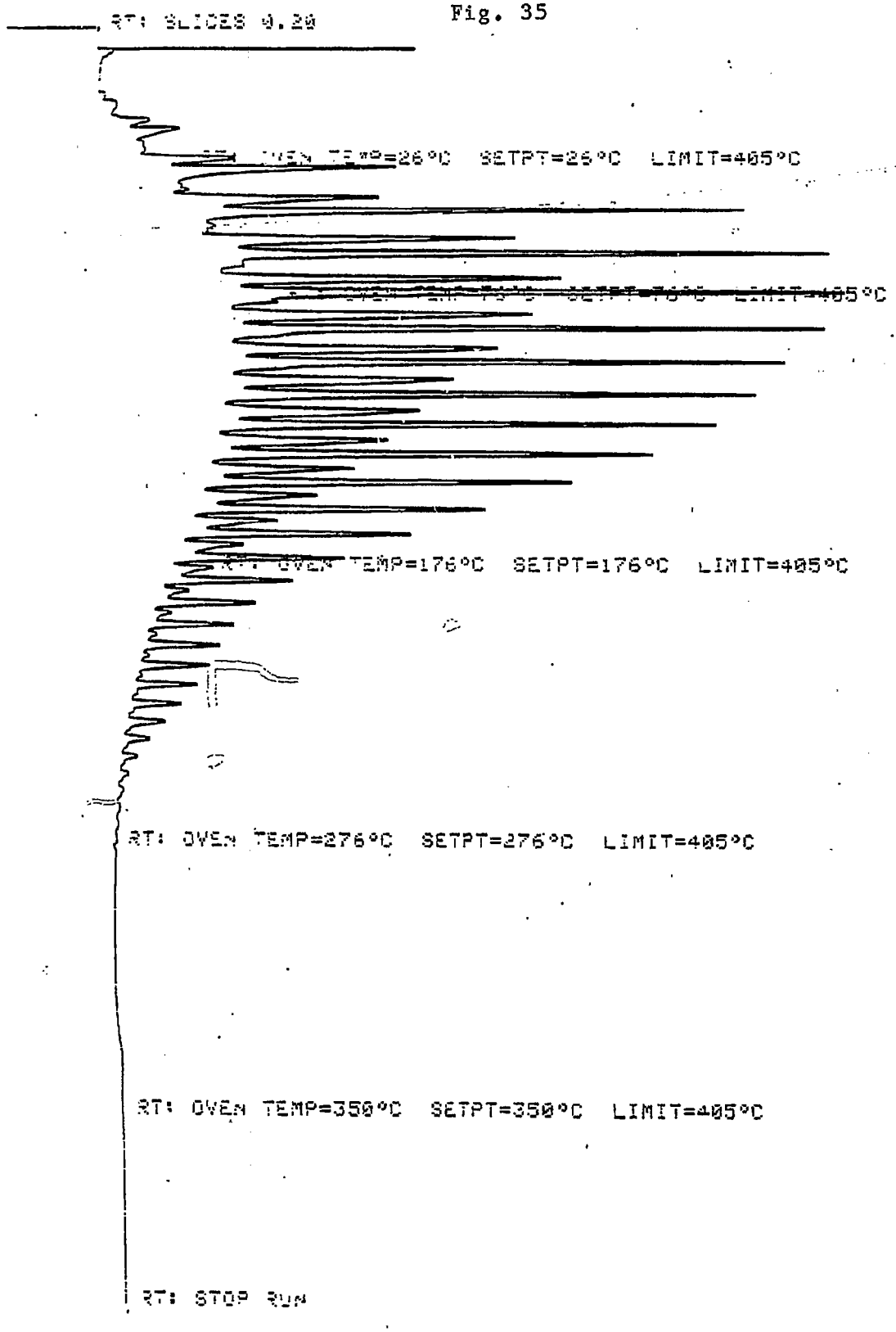

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-14-14
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 34



SAMPLE:10112-14-2L

Fig. 35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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:10112-14-4L

Fig. 36

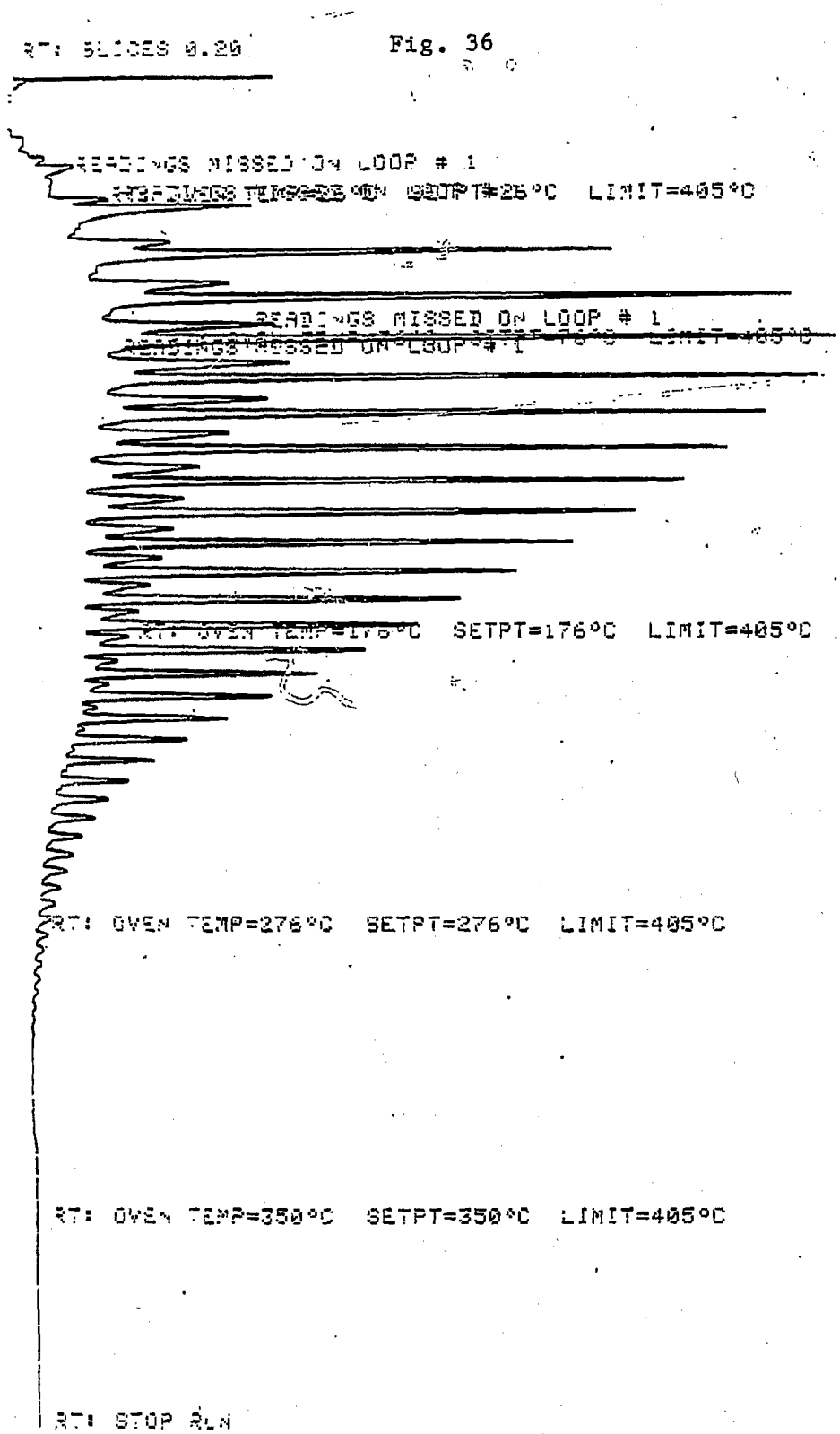

RT: SLICES 0.20
READINGS MISSED ON LOOP # 1
READINGS MISSED ON LOOP # 1
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-14-6L

Fig. 37

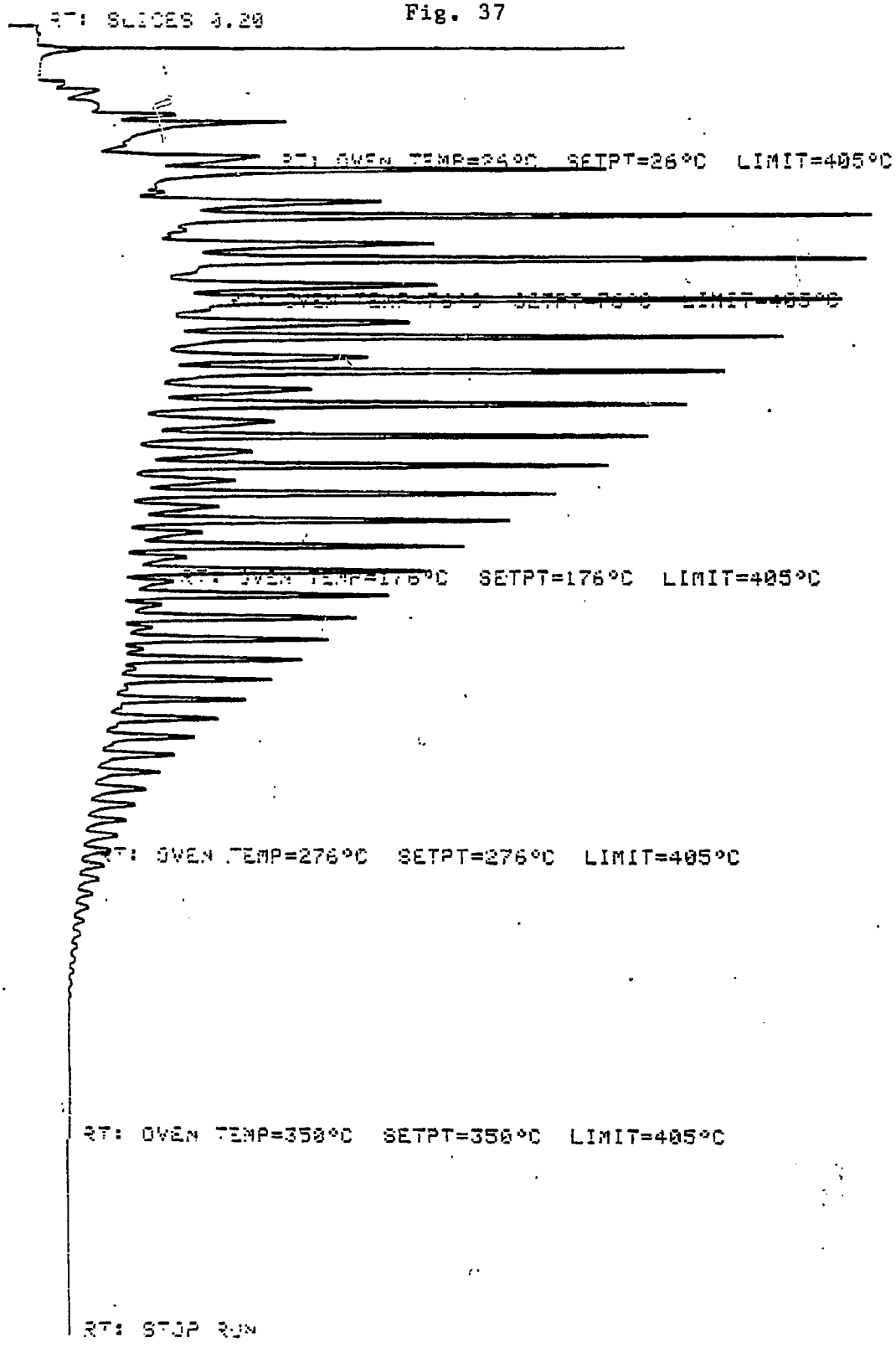
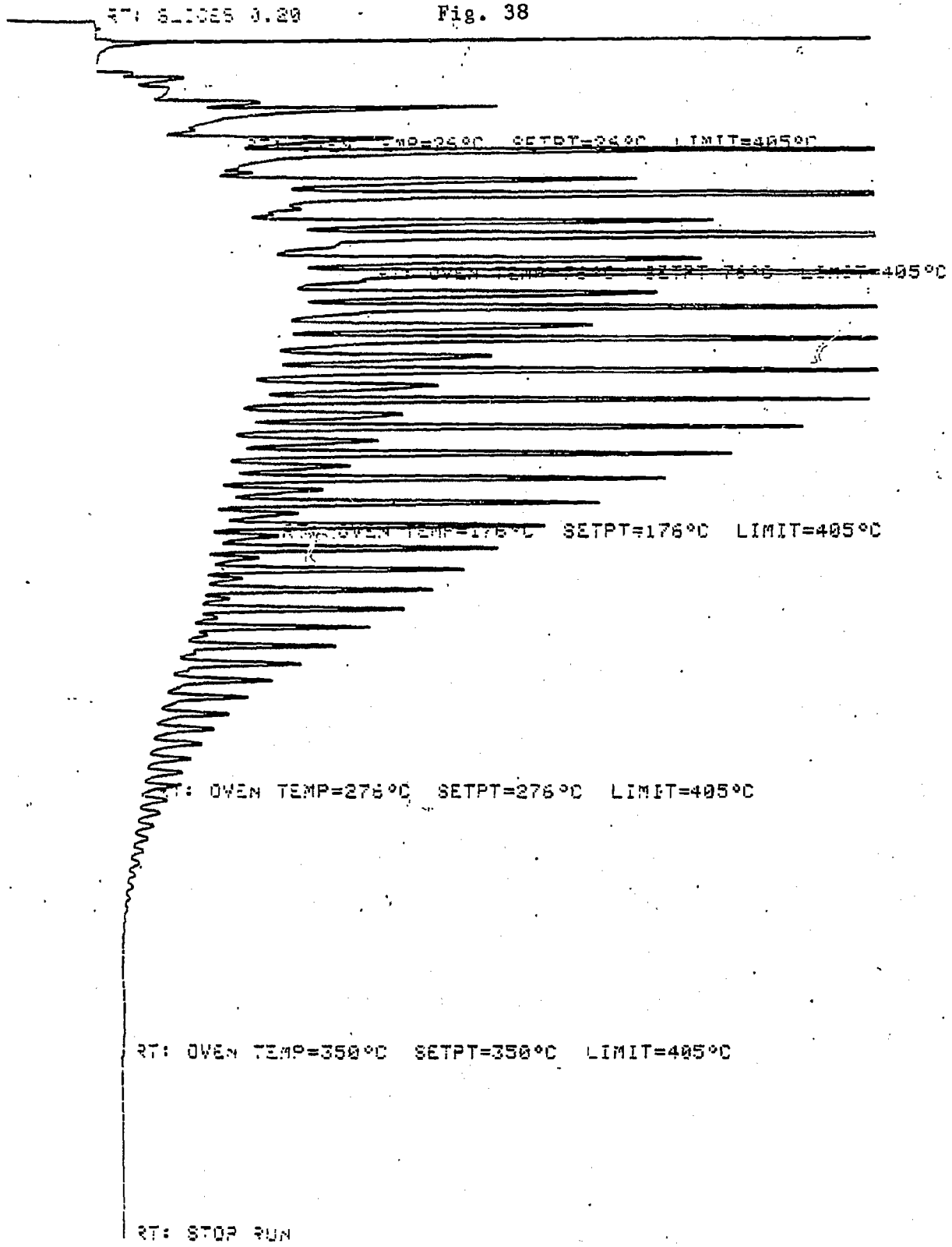
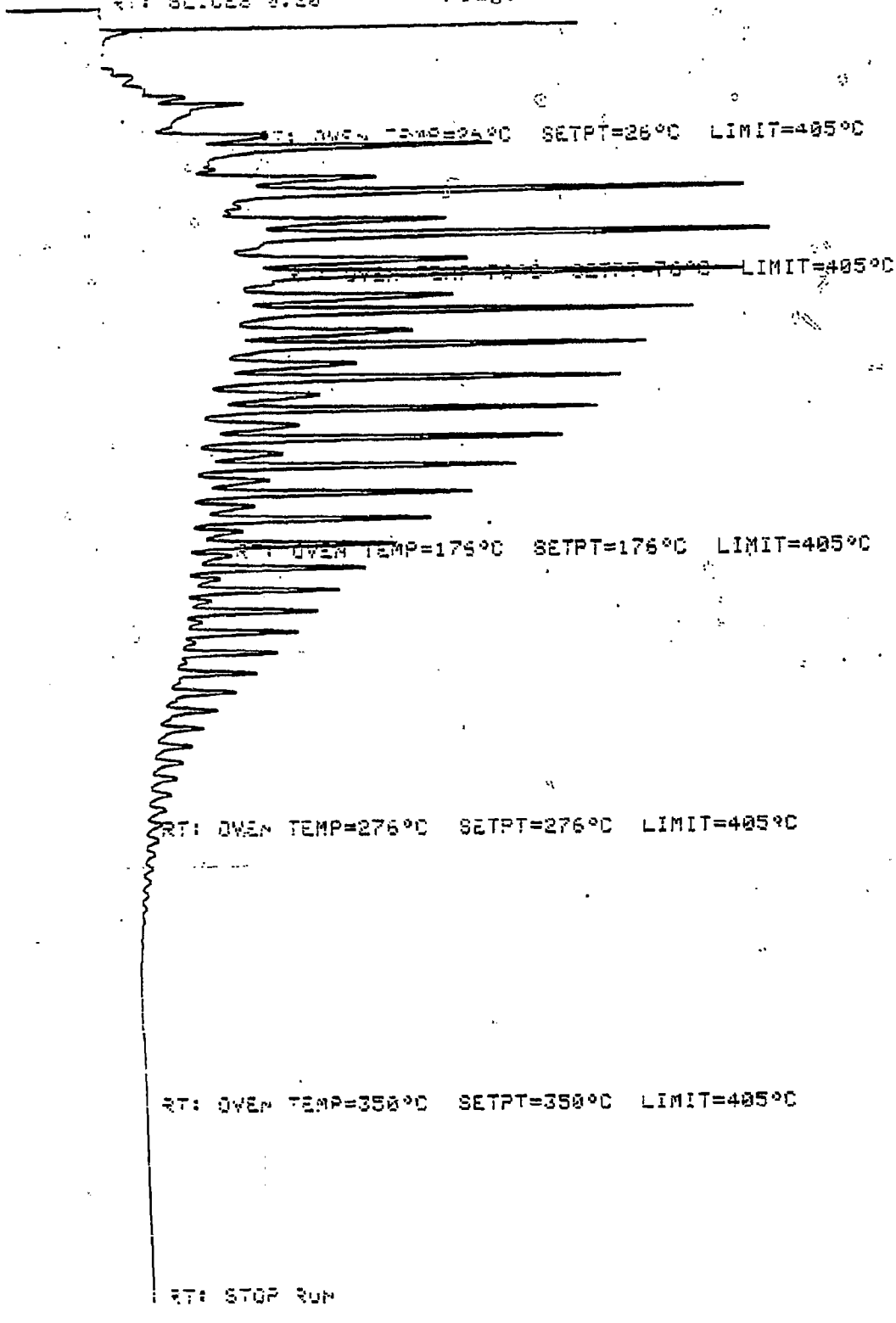

RT: SLICES 4.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-14-SL

Fig. 38

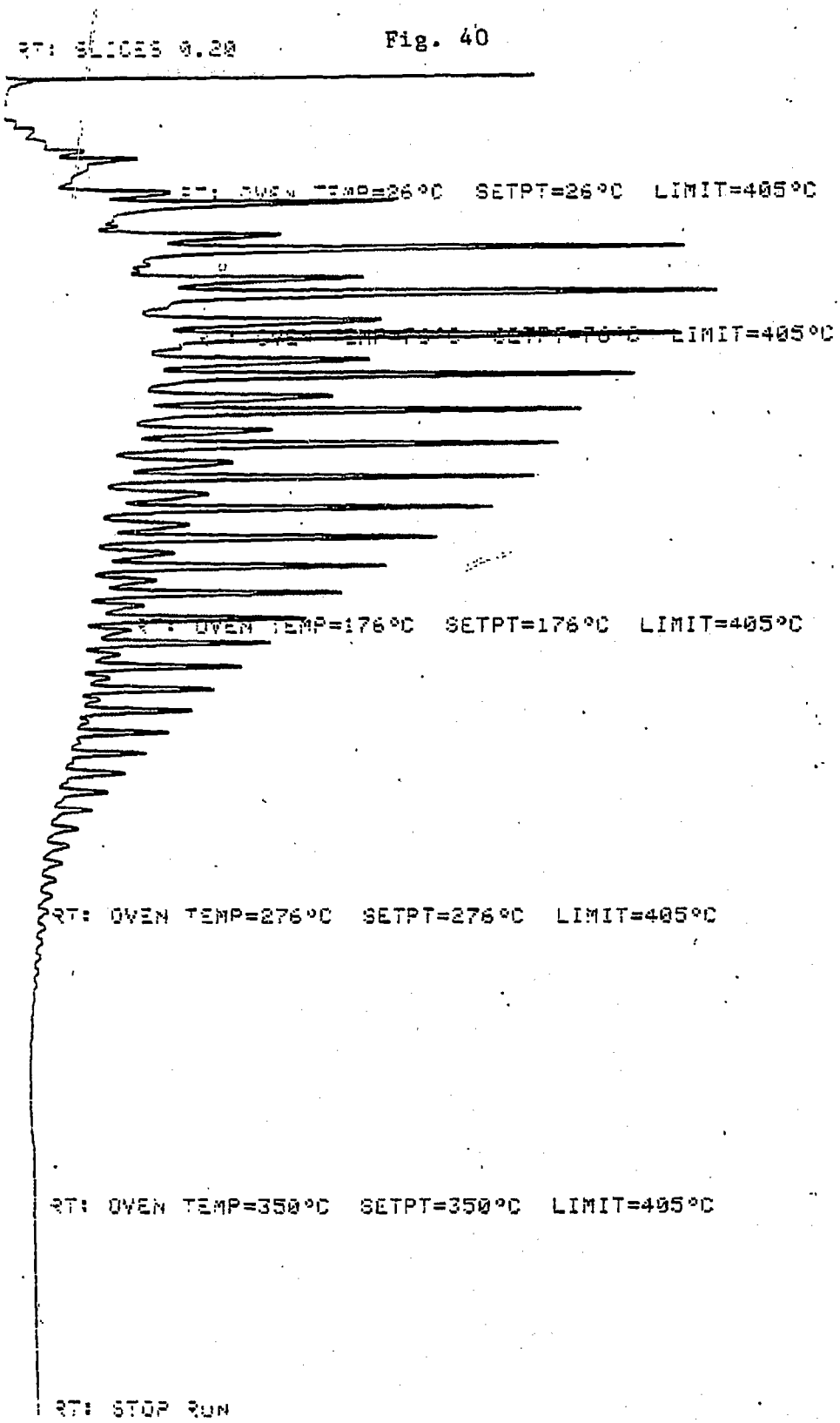

RT: SLIDES 0.20
SETPT=260°C LIMIT=405°C
405°C
SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-14-10L

. Fig. 39



SAMPLE:10112-14-12L

Fig. 40



SAMPLE:10112-14-14L

TABLE 4 RESULT OF SYNGAS OPERATION

RUN NO. 10112-14
CATALYST CO/TH +UCC-101 #10252-42C 80 CC 30.0GM (43.7 AFTER RUN +14 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-14-01	112-14-02	112-14-03	112-14-04	112-14-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	4.5	19.75	30.25	44.13	52.0
PRESSURE,PSIG	294	295	295	297	296
TEMP. C	252	251	251	251	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	4.50	19.75	10.50	24.38	7.87
EFFLNT GAS LITER	36.80	214.30	148.65	346.65	112.95
GM AQUEOUS LAYER	11.39	49.99	22.26	51.70	15.89
GM OIL	4.94	21.67	6.03	14.00	7.10
MATERIAL BALANCE					
GM ATOM CARBON %	75.17	81.30	92.97	90.33	98.18
GM ATOM HYDROGEN %	70.54	90.23	90.97	97.13	94.92
GM ATOM OXYGEN %	86.48	89.02	102.40	97.44	101.39
RATIO CHX/(H2O+CO2)	0.6903	0.7770	0.6983	0.7711	0.8907
RATIO X IN CHX	2.1798	2.2921	2.4108	2.3778	2.3074
USAGE H2/CO PRODT	1.5204	1.7321	1.6498	1.6823	1.7132
RATIO CO2/(H2O+CO2)	0.1854	0.1286	0.1663	0.1592	0.1504
K SHIFT IN EFFLNT	0.07	0.09	0.12	0.13	0.10
CONVERSION					
ON CO %	42.54	38.57	29.09	31.95	31.18
ON H2 %	81.12	67.61	57.61	56.14	58.15
ON CO+H2 %	61.22	53.85	43.20	44.48	44.44
PRDT SELECTIVITY,WT %					
CH4	7.51	12.66	17.69	16.46	13.46
C2 HC'S	1.53	2.07	2.96	2.58	2.09
C3H8	1.39	2.45	3.44	3.01	2.52
C3H6=	2.06	1.08	1.90	1.95	1.73
C4H10	1.40	2.11	2.79	2.37	2.00
C4H8=	3.14	1.98	3.28	3.49	3.23
C5H12	2.02	2.56	3.40	3.02	2.49
C5H10=	3.31	2.10	3.70	4.04	3.58
C6H14	2.79	3.04	4.08	4.27	3.11
C6H12= & CYCLO'S	0.17	0.14	0.26	0.38	0.27
C7+ IN GAS	12.59	12.15	19.63	24.70	16.84
LIQ HC'S	62.07	57.67	36.87	33.74	48.68
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	17.04	22.34	32.07	29.85	25.03
C5 -420 F	44.75	42.15	46.47	50.51	44.02
420-700 F	32.21	29.93	18.47	16.90	23.43
700-END PT	6.00	5.58	2.99	2.73	7.51
C5+-END PT	82.96	77.66	67.93	70.15	74.97
ISO/NORMAL MOLE RATIO					
C4	0.3564	0.1006	0.0912	0.0827	0.0778
C5	0.5998	0.1927	0.1662	0.1352	0.1346
C6	0.8712	0.3216	0.2781	0.2349	0.2299
C4=	0.2793	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.6429	2.1752	1.7240	1.4733	1.3893
C4	0.4293	1.0280	0.8204	0.6559	0.5990
C5	0.5931	1.1808	0.8940	0.7279	0.6761
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL WAX		OIL WAX	
DENSITY		0.775		0.768	
N, REFRACTIVE INDEX		1.4304		1.4302	
SIMULT'D DISTILAIN					
10 WT % @ DEG F		305		300	
16		338		329	
50		475		453	
84		654		626	
90		697		677	
RANGE(16-84 %)		316		297	
WT % @ 420 F	38.43	38.43	41.80	41.80	36.43
WT % @ 700 F	90.33	90.33	91.90	91.90	84.57

TABLE 5 RESULT OF SYNGAS OPERATION

RUN NO. 10112-14
CATALYST CO/TH +UCC-101 #10252-42C 80 CC 30.0GM (43.7 AFTER RUN +14 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-14-06	112-14-07	112-14-08	112-14-09	112-14-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	70.0	77.0	93.5	101.0	117.5
PRESSURE,PSIG	296	295	296	296	296
TEMP. C	251	270	270	271	271
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	25.87	7.00	23.50	7.50	24.00
EFFLNT GAS LITER	371.00	89.60	275.00	84.45	273.05
GM AQUEOUS LAYER	52.25	16.34	54.84	17.95	57.44
GM OIL	23.35	10.93	36.70	9.40	30.07
MATERIAL BALANCE					
GM ATOM CARBON %	97.81	116.99	106.94	100.62	99.61
GM ATOM HYDROGEN %	94.58	105.70	98.04	94.17	93.25
GM ATOM OXYGEN %	101.08	114.17	103.53	101.76	101.03
RATIO CHX/(H2O+CO2)	0.8880	1.0651	1.0891	0.9709	0.9626
RATIO X IN CHX	2.3071	2.3904	2.3383	2.3972	2.3926
USAGE H2/CO PRODT	1.7295	1.3981	1.5330	1.5123	1.5571
RATIO CO2/(H2O+CO2)	0.1435	0.3459	0.2653	0.2681	0.2439
K SHIFT IN EFFLNT	0.10	0.21	0.14	0.14	0.12
CONVERSION					
ON CO %	30.76	52.11	48.42	48.26	45.98
ON H2 %	58.00	78.77	78.29	78.90	77.66
ON CO+H2 %	44.15	64.76	62.71	63.07	61.30
PRDT SELECTIVITY,WT %					
CH4	13.64	16.98	15.24	17.94	18.02
C2 HC'S	1.98	2.82	2.41	2.67	2.65
C3H8	2.40	3.28	2.43	2.90	2.56
C3H6=	1.77	1.98	1.97	2.04	2.12
C4H10	1.89	2.60	1.86	2.15	1.85
C4H8=	3.26	3.54	3.38	3.46	3.51
C5H12	2.37	3.08	2.29	2.47	2.18
C5H10=	3.56	3.52	3.49	3.68	3.74
C6H14	2.86	3.49	2.59	2.72	2.54
C6H12= & CYCLO'S	0.27	0.33	0.38	0.35	0.37
C7+ IN GAS	16.75	10.74	11.11	13.42	12.31
LIQ HC'S	49.24	47.65	52.87	46.22	48.14
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	24.95	31.20	27.28	31.16	30.71
C5 -420 F	43.75	40.83	41.68	42.81	42.17
420-700 F	23.70	18.96	21.04	18.67	19.45
700-END PT	7.60	9.02	10.00	7.36	7.67
C5+-END PT	75.05	68.80	72.72	68.84	69.29
ISO/NORMAL MOLE RATIO					
C4	0.0748	0.1460	0.1390	0.1373	0.1306
C5	0.1345	0.2683	0.2660	0.2734	0.2600
C6	0.2178	0.4573	0.4199	0.4338	0.4018
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.2954	1.5787	1.1782	1.3606	1.1559
C4	0.5598	0.7085	0.5299	0.5988	0.5089
C5	0.6468	0.8481	0.6379	0.6521	0.5676
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX		GR OIL WAX		GR OIL WAX
DENSITY	0.784		0.775		0.768
N, REFRACTIVE INDEX	1.4316		1.4305		1.4305
SIMULT'D DISTILATN					
10 WT % @ DEG F	306		274		271
16	339		305		302
50	485		473		452
84	696		731		699
90	751		801		769
RANGE(16-84 %)	357		426		397
WT % @ 420 F	36.43	41.29	41.29	43.67	43.67
WT % @ 700 F	84.57	81.08	81.08	84.07	84.07

TABLE 6 RESULT OF SYNGAS OPERATION

RUN NO. 10112-14
CATALYST CO/TH +UCC-101 #10252-42C 80 CC 30.0GM (43.7 AFTER RUN +14 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-14-11	112-14-12	112-14-13	112-14-14
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	125.0	141.5	149.0	165.0
PRESSURE,PSIG	296	294	299	296
TEMP. C	271	271	271	272
FEED CC/MIN	400	400	400	400
HOURS FEEDING	7.50	24.00	7.50	23.50
EFFLNT GAS LITER	86.55	281.75	90.25	288.05
GM AQUEOUS LAYER	17.88	57.23	17.87	55.98
GM OIL	9.18	29.37	8.26	25.89
MATERIAL BALANCE				
GM ATOM CARBON %	99.40	100.34	99.21	100.05
GM ATOM HYDROGEN %	94.22	95.47	97.15	99.62
GM ATOM OXYGEN %	100.61	100.94	101.10	101.35
RATIO CHX/(H2O+CO2)	0.9678	0.9838	0.9497	0.9654
RATIO X IN CHX	2.4052	2.4168	2.4488	2.4924
USAGE H2/CO PRODT	1.5793	1.6063	1.5918	1.6128
RATIO CO2/(H2O+CO2)	0.2365	0.2285	0.2358	0.2366
K SHIFT IN EFFLNT	0.13	0.12	0.14	0.14
CONVERSION				
ON CO %	45.43	44.89	44.86	45.20
ON H2 %	76.70	76.29	74.47	74.26
ON CO+H2 %	60.64	60.20	59.51	59.70
PRDT SELECTIVITY,WT %				
CH4	18.59	19.26	20.68	22.78
C2 HC'S	2.74	2.77	2.85	3.10
C3H8	2.64	2.63	3.02	3.18
C3H6=	2.03	1.97	2.26	1.93
C4H10	1.91	1.89	2.23	2.37
C4H8=	3.43	3.37	3.59	3.06
C5H12	2.29	2.16	2.19	2.25
C5H10=	3.64	3.49	3.51	3.05
C6H14	2.46	2.46	2.56	2.56
C6H12= & CYCLO'S	0.38	0.35	0.34	0.34
C7+ IN GAS	12.56	12.72	13.56	13.08
LIQ HC'S	47.31	46.93	43.21	42.30
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	31.36	31.90	34.62	36.42
C5 -420 F	41.52	41.20	40.75	39.47
420-700 F	19.76	19.60	18.38	18.00
700-END PT	7.36	7.30	6.24	6.11
C5+-END PT	68.64	68.10	65.38	63.58
ISO/NORMAL MOLE RATIO				
C4	0.1238	0.1202	0.1215	0.1093
C5	0.2438	0.2455	0.2001	0.1865
C6	0.3807	0.3656	0.3749	0.3614
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	1.2403	1.2703	1.2767	1.5720
C4	0.5383	0.5403	0.5978	0.7467
C5	0.6117	0.6009	0.6053	0.7187
LIQ HC COLLECTION				
PHYS. APPEARANCE		GR OIL WAX		GR OIL WAX
DENSITY		0.773		0.767
N, REFRACTIVE INDEX		1.4319		1.4310
SIMULT'D DISTILATN				
10 WT % @ DEG F		287		288
16		310		311
50		458		454
84		696		686
90		758		748
RANGE(16-84 %)		386		375
WT % @ 420 F	42.67	42.67	43.00	43.00
WT % @ 700 F	84.44	84.44	85.55	85.55

IV. RUN 3 (10112-15) With Catalyst 3 (Co/Th on UCC-101)

This is a second preparation of Catalyst 2, identical in formulation and composition, to be run only at 270C as a test of any possible effect of temperature on degree of isomerization.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C4's are plotted against time on stream in Figs. 41-44. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 45-46. Carbon number product distributions are plotted in Figs. 47-51. Chromatograms from simulated distillations are reproduced in Figs. 52-56. Detailed material balances appear in Tables 7-8.

There was an initial loss of activity to ~55 percent CO and H_2 conversion, slightly below the level of Catalyst 2. Water gas shift activity was low; initially ~37 percent of the oxygen was rejected as CO_2, dropping to 20 percent by the end of the run. Due to the high conversion of hydrogen, the effective exposure of the catalyst to the H_2:CO syngas was in a ratio of only 0.5:1.

The product selectivity was essentially the same as in the previous run, evidently having been unaffected by the difference in temperature. Based on total hours on stream, as distinct from hours at 270C, the selectivity was poorer. At 120 hours on stream the methane production was slightly higher at ~20 percent. Wax production was a little lower. There was no essential dif-

ference in production of gasoline and diesel fuel, in percent olefins of C_4, or in pentane isomerization. Total motor fuels were again below the Schulz-Flory limit. The S-F plots show excessive methane, as well as an apparent carbon number cut-off above the diesel range. The condensed liquid was waxy, even though only ~11 percent of it boiled above the diesel range. The chromatograms of the simulated distillations can be almost exactly superimposed on those of the previous run. There was little isomerization of the liquid hydrocarbons.

Distillation and subsequent analysis of the liquid hydrocarbons showed that the olefin content of the gasoline fraction was 36 percent, and that of the jet fuel fraction was 32 percent (three times higher than with Catalyst 1, and similar to the previous run). The lower percentage of metal component equates to shorter metal component contact time, curtailing the formation of secondary products. The higher olefins, and possibly the slight isomerization, both contribute to the very low pour point of ØF for the jet fuel fraction, in contrast to the pour point of 65F for the jet fraction from an iron catalyst without Molecular Sieve, and the diesel fraction's pour point of 50F.

Results were similar to those of the previous run. The initial testing at 250C evidently had little effect on the results at 270C.

RUN 10112–15

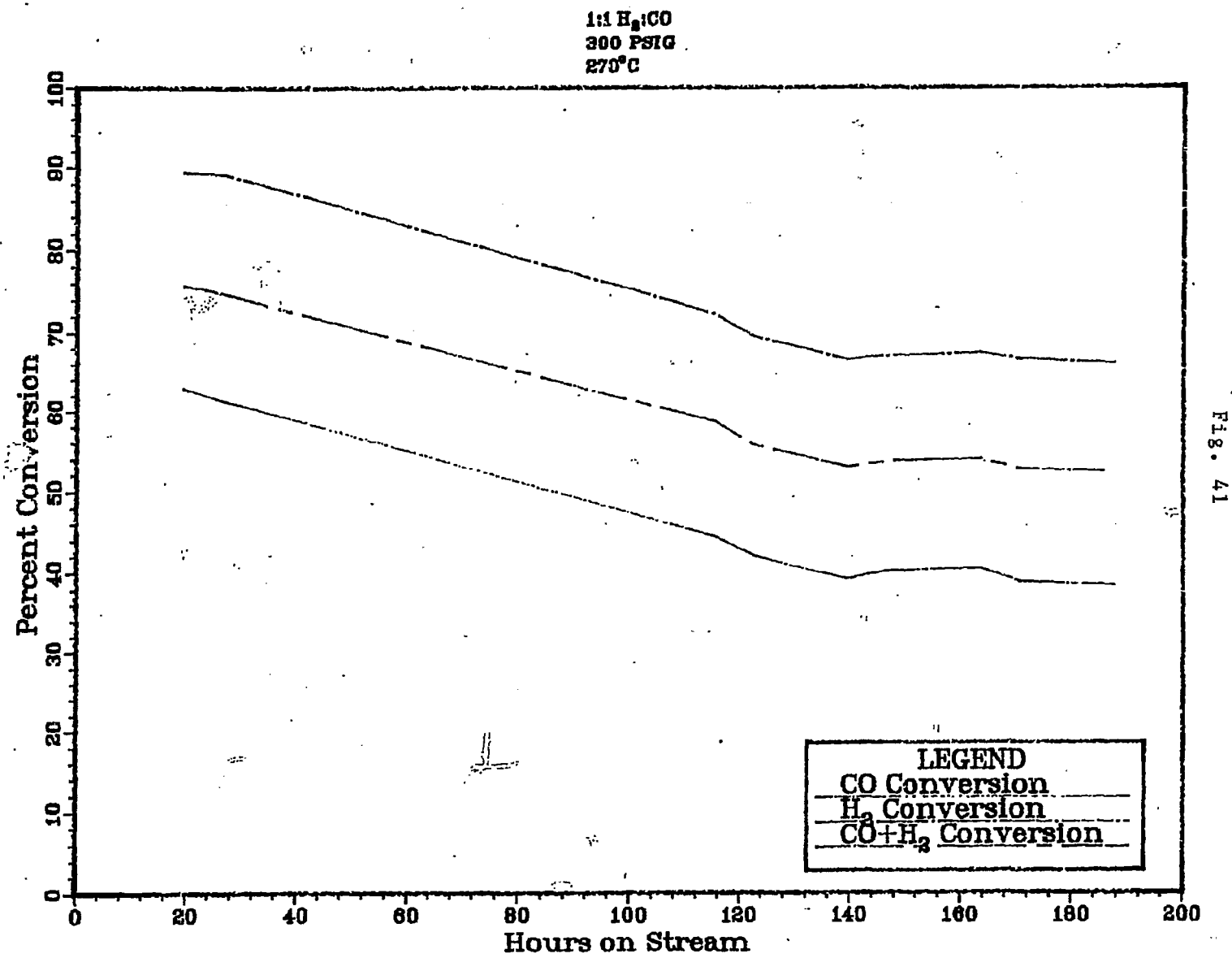


Fig. 41

Fig. 42

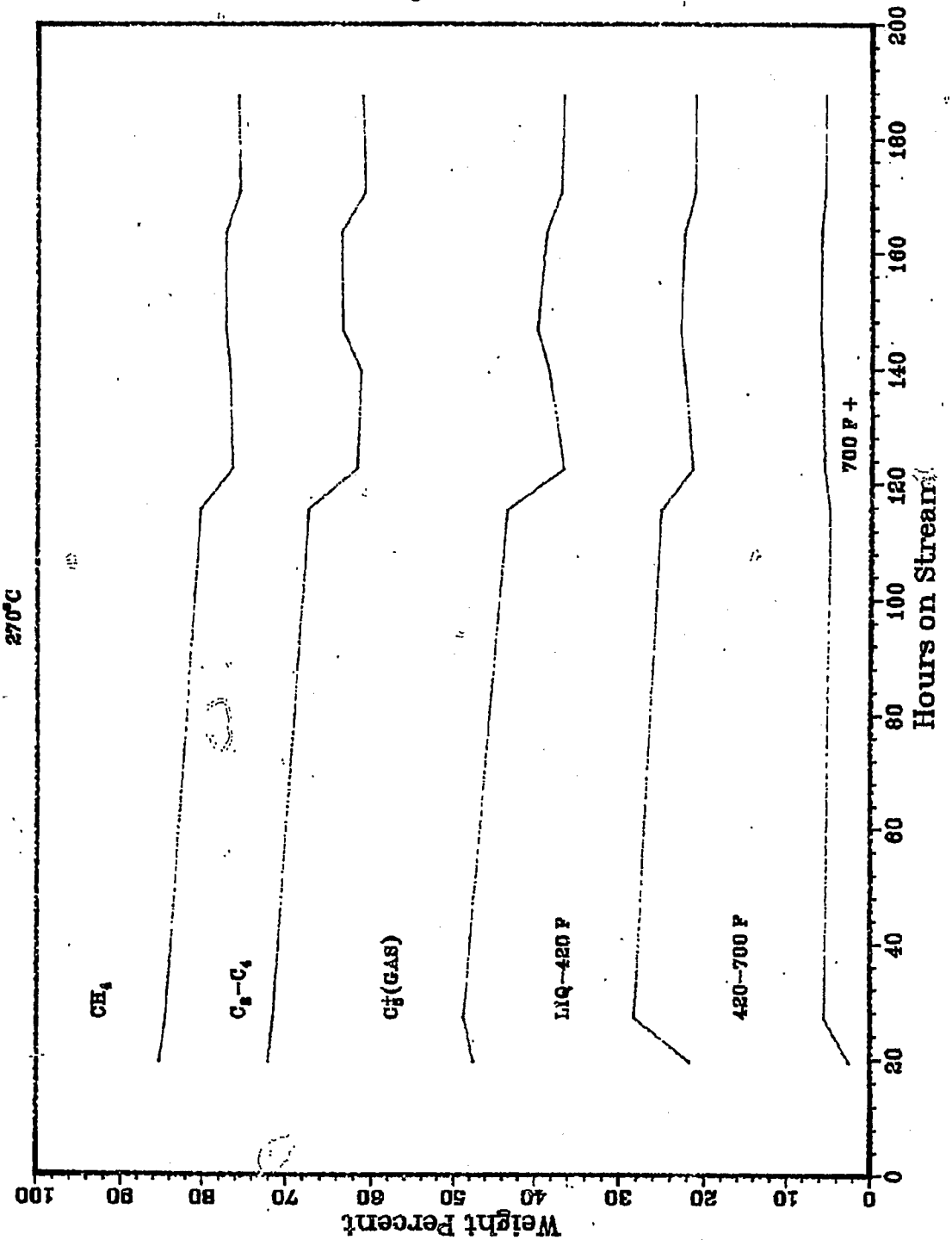

RUN 10112-15
1:1 H2:CO
300 PSIG
270°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 43

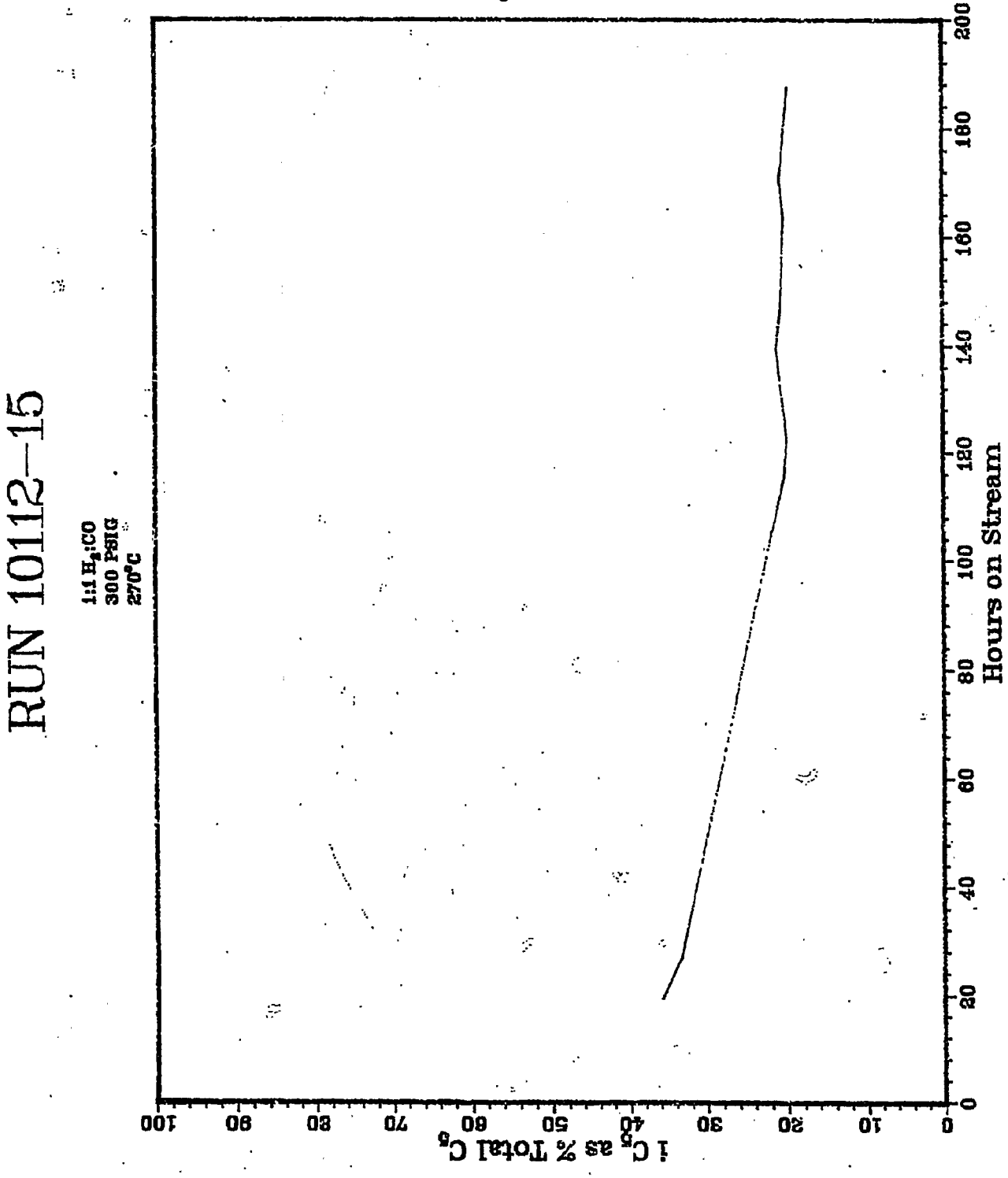

RUN 10112-15
1:1 H2:CO
300 PSIG
270°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 44

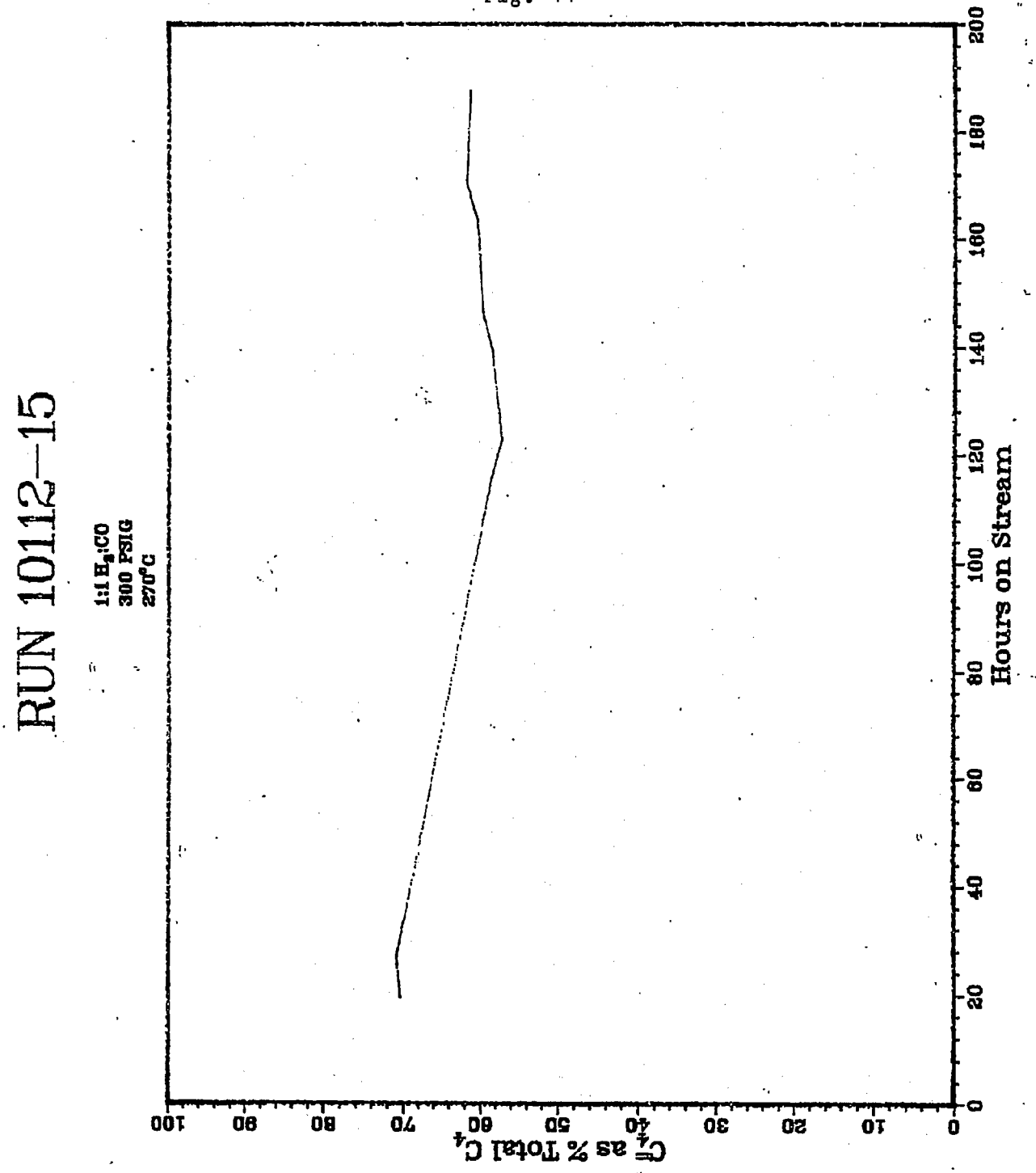

RUN 10112-15
1:1 H2:CO
300 PSIG
270°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 45

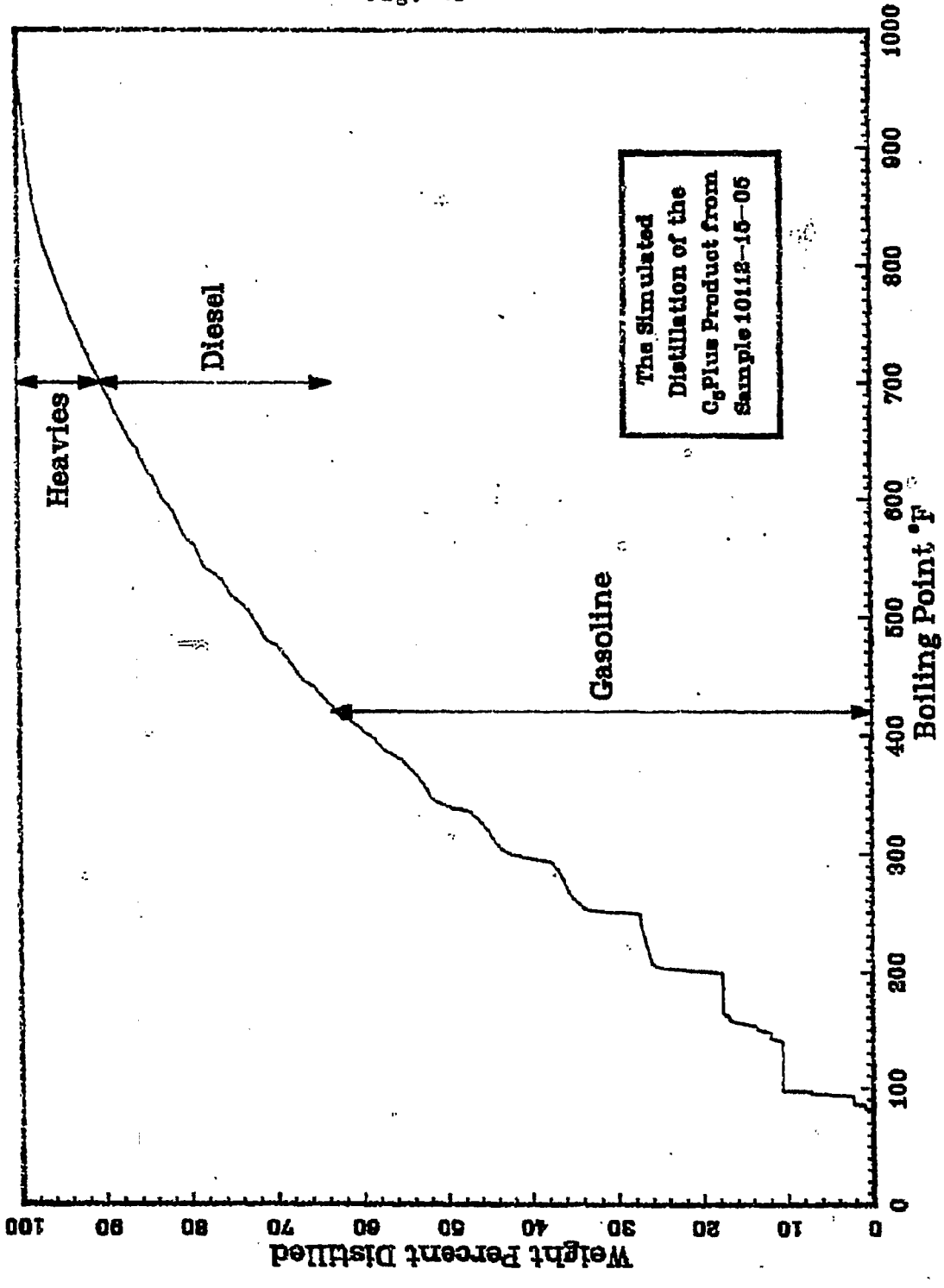

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point, °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C6Plus Product from Sample 10113-15-06

Fig. 46

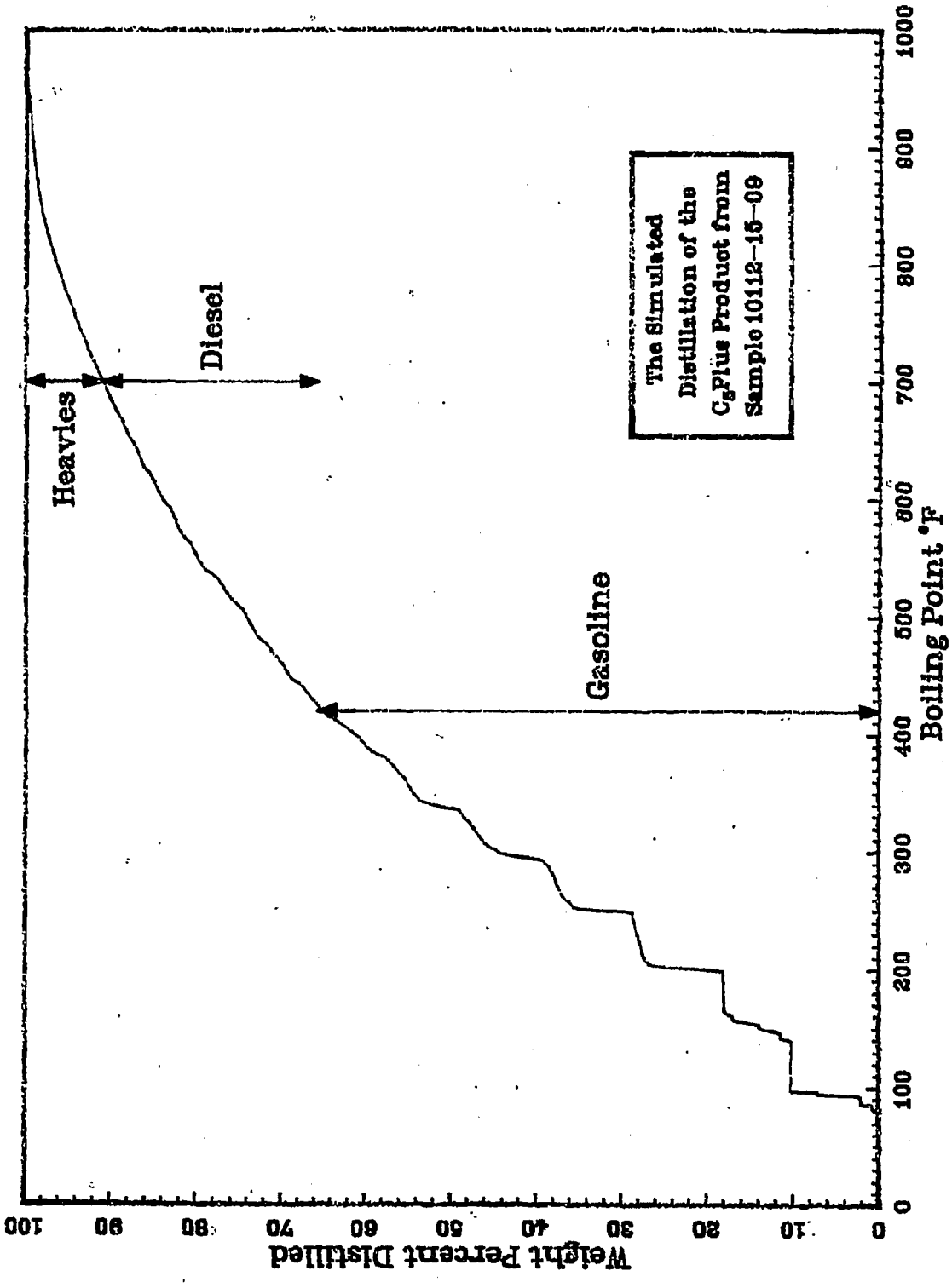

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5Plus Product from Sample 10112-15-09

Fig. 47

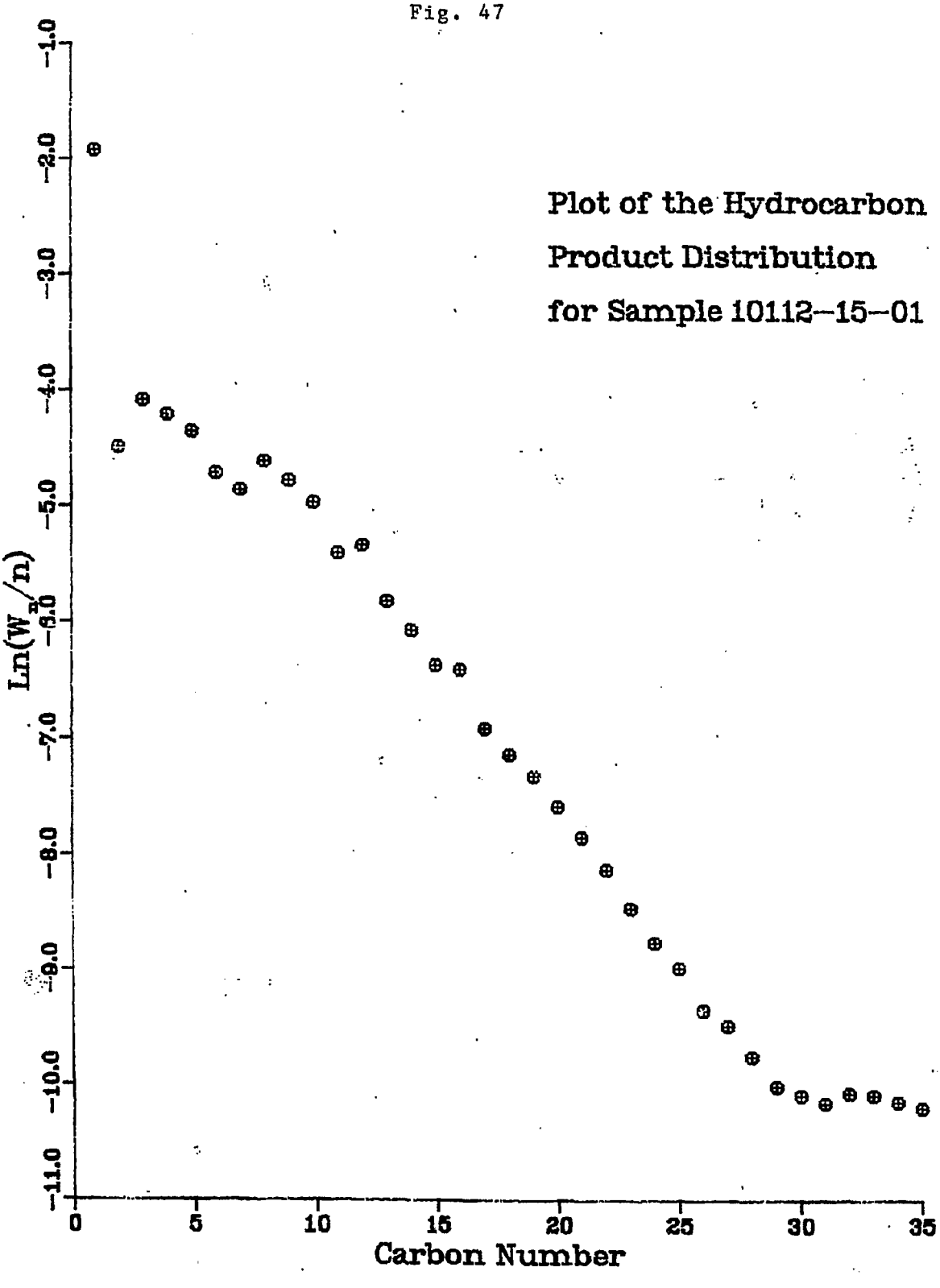
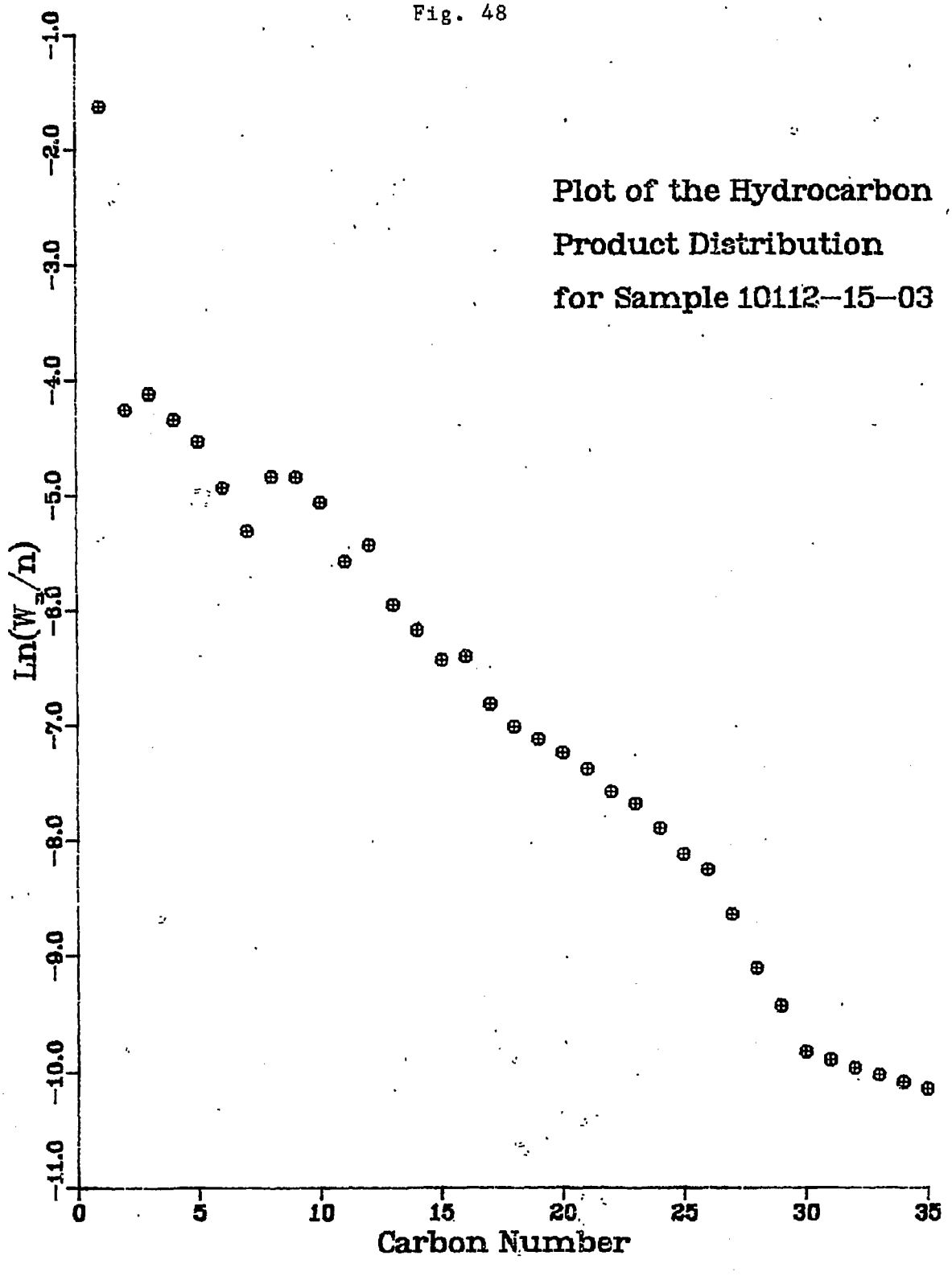

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–15–01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 48



Plot of the Hydrocarbon Product Distribution for Sample 10112–15–03

Fig. 49

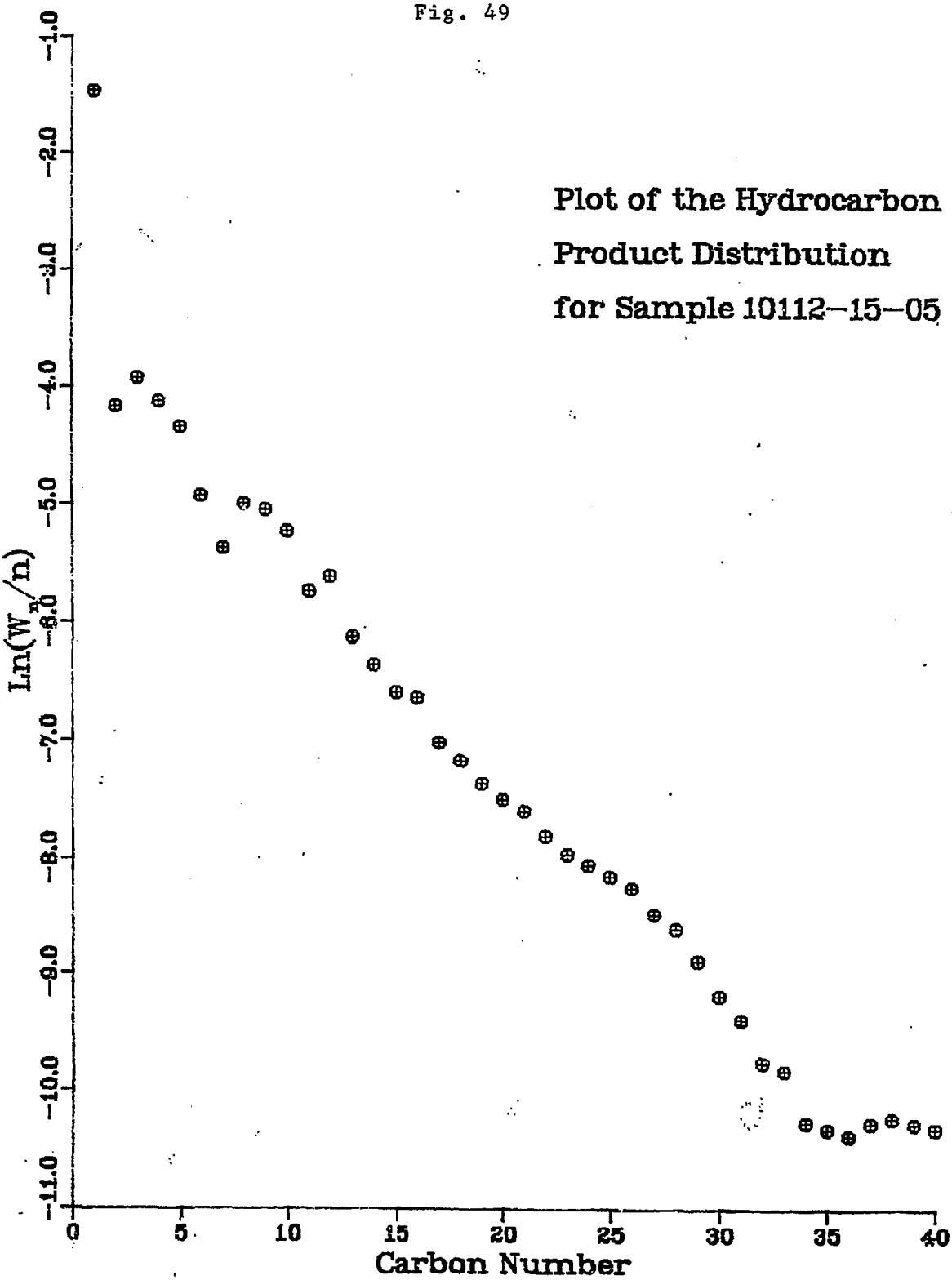

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-15-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 50

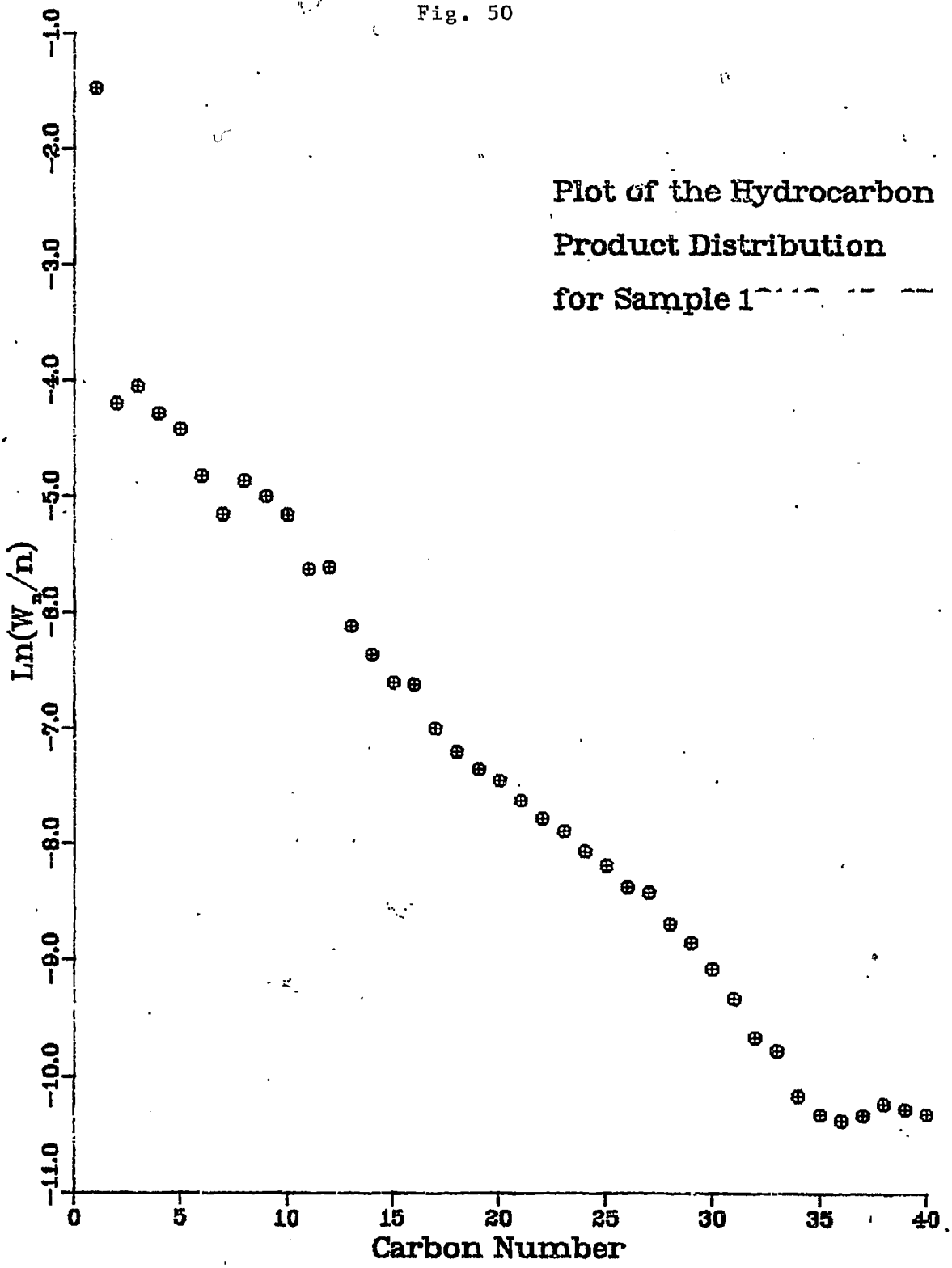
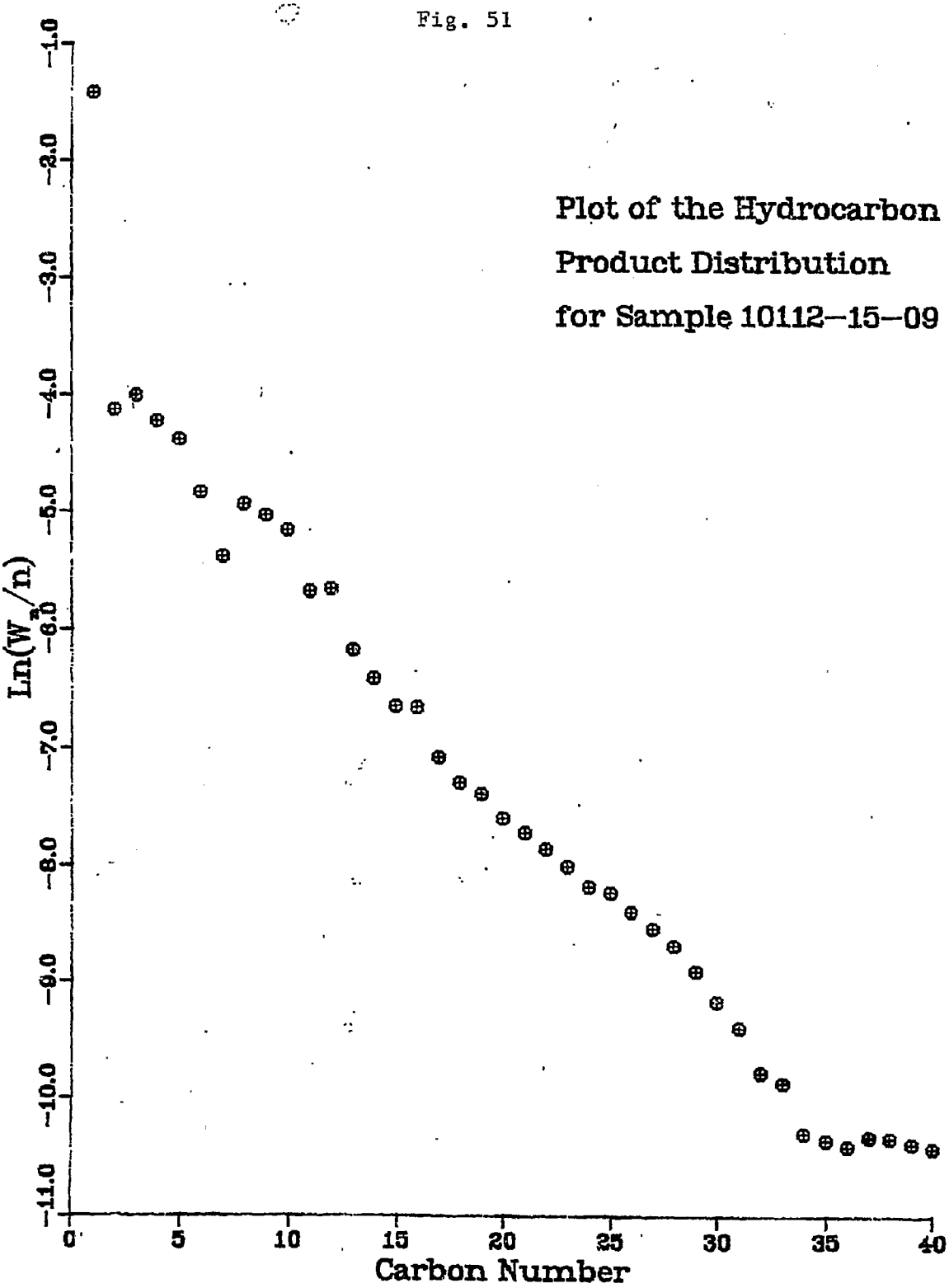

Plot of the Hydrocarbon
Product Distribution
for Sample 1
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 51



Plot of the Hydrocarbon Product Distribution for Sample 10112–15–09

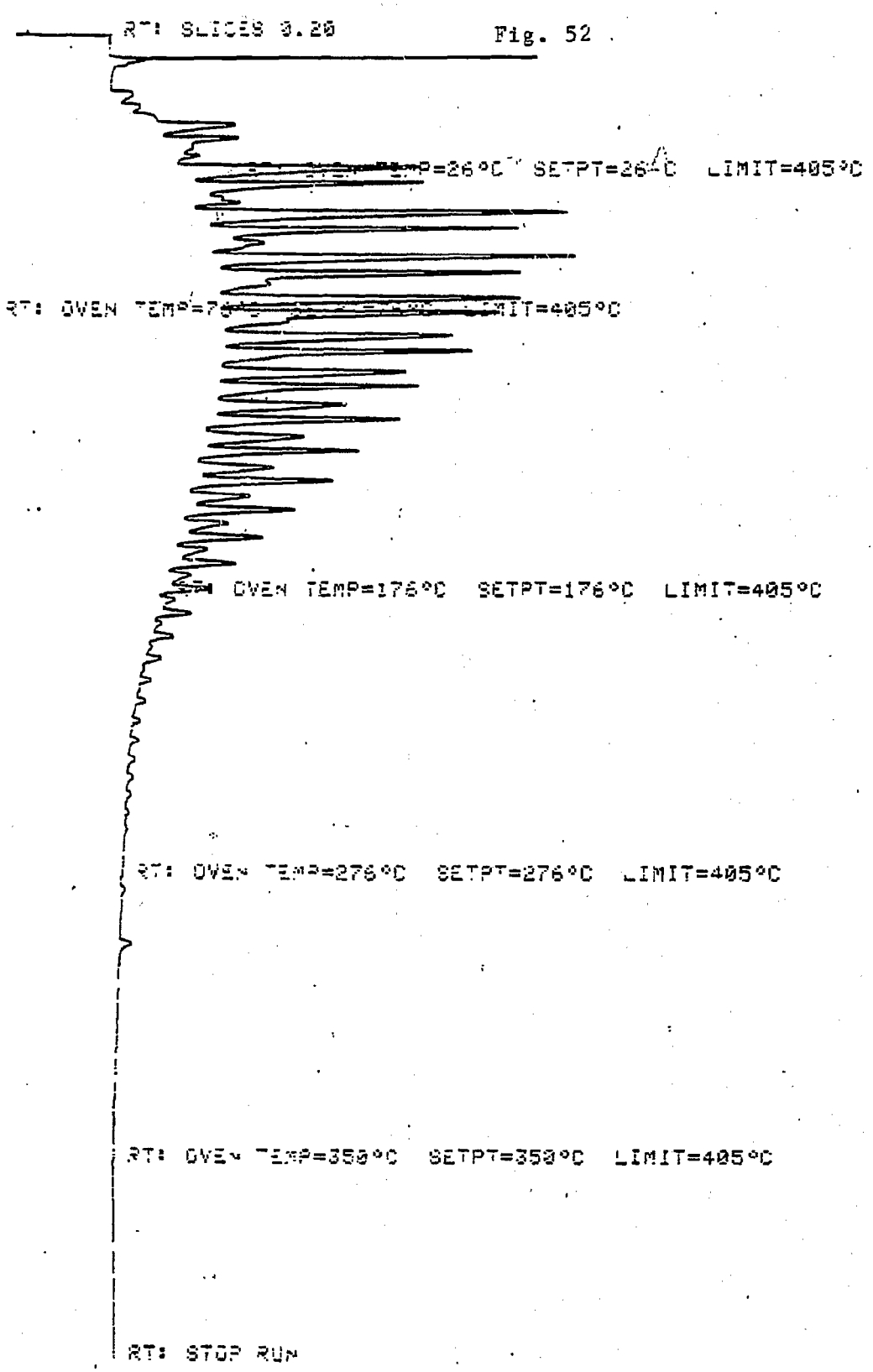
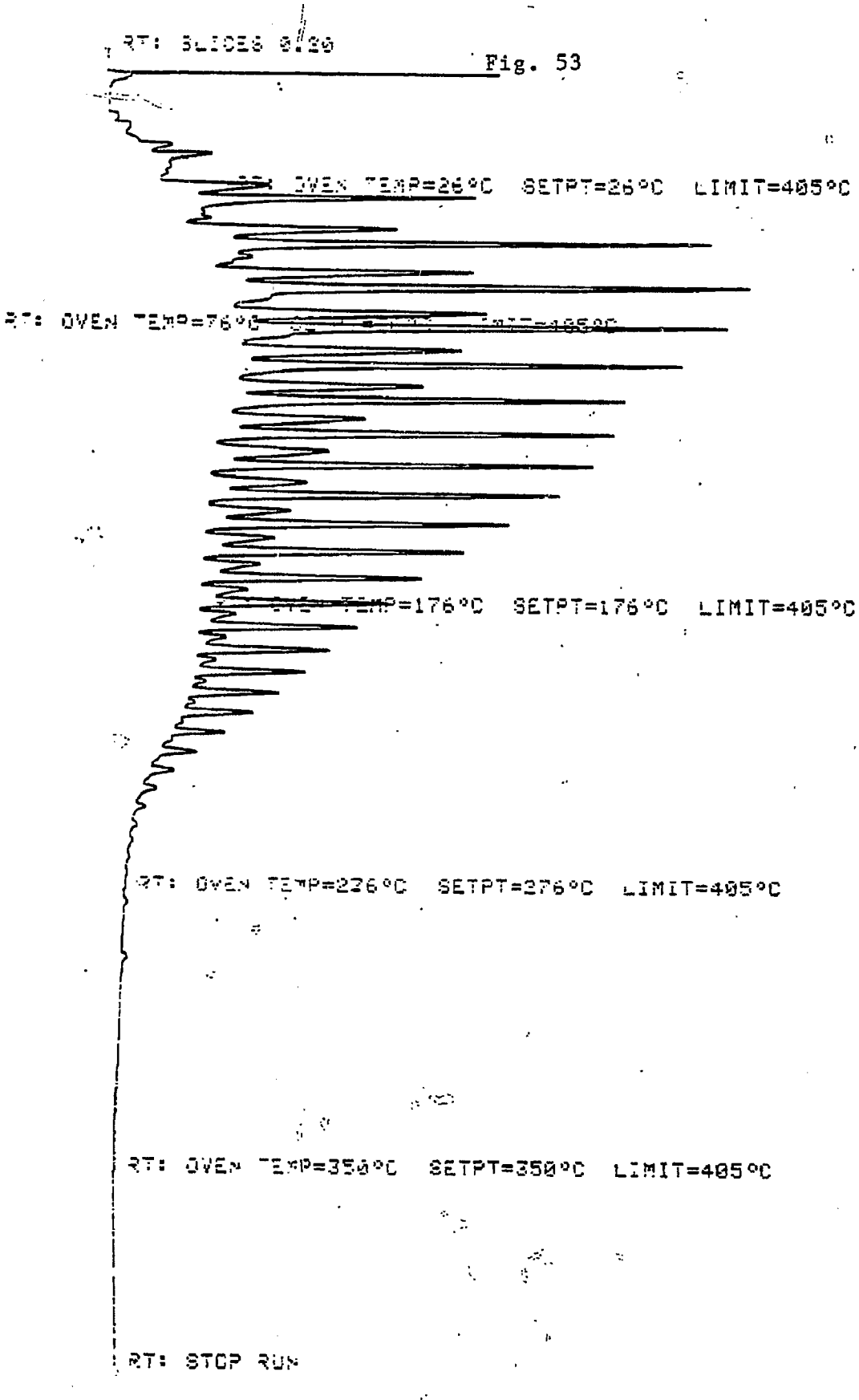

RT: SLICES 0.20
OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D:0:12-15-1L

Fig. 52

Fig. 53


RT: SLICES 0:30
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=226°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:010112-15-3L

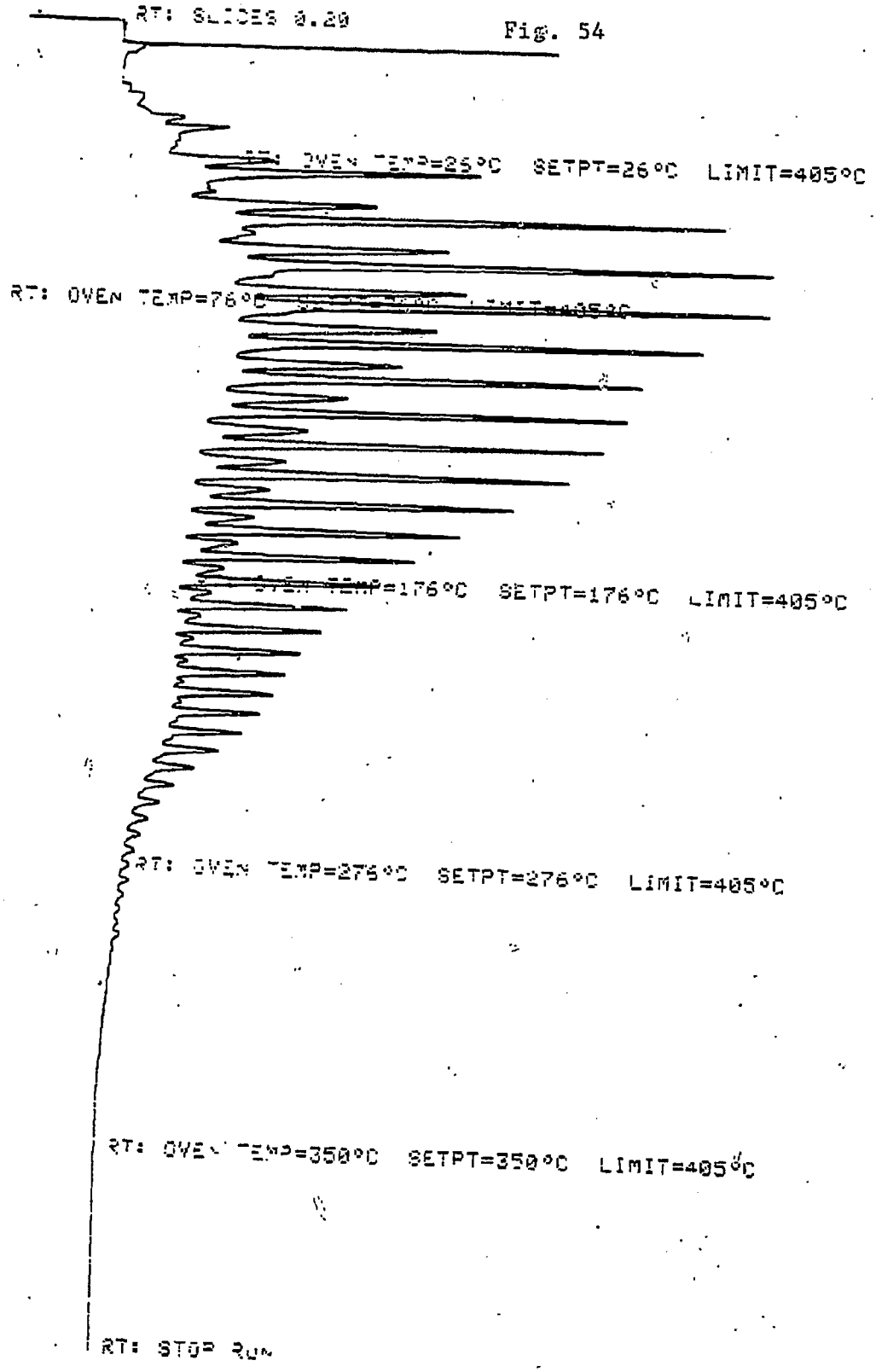
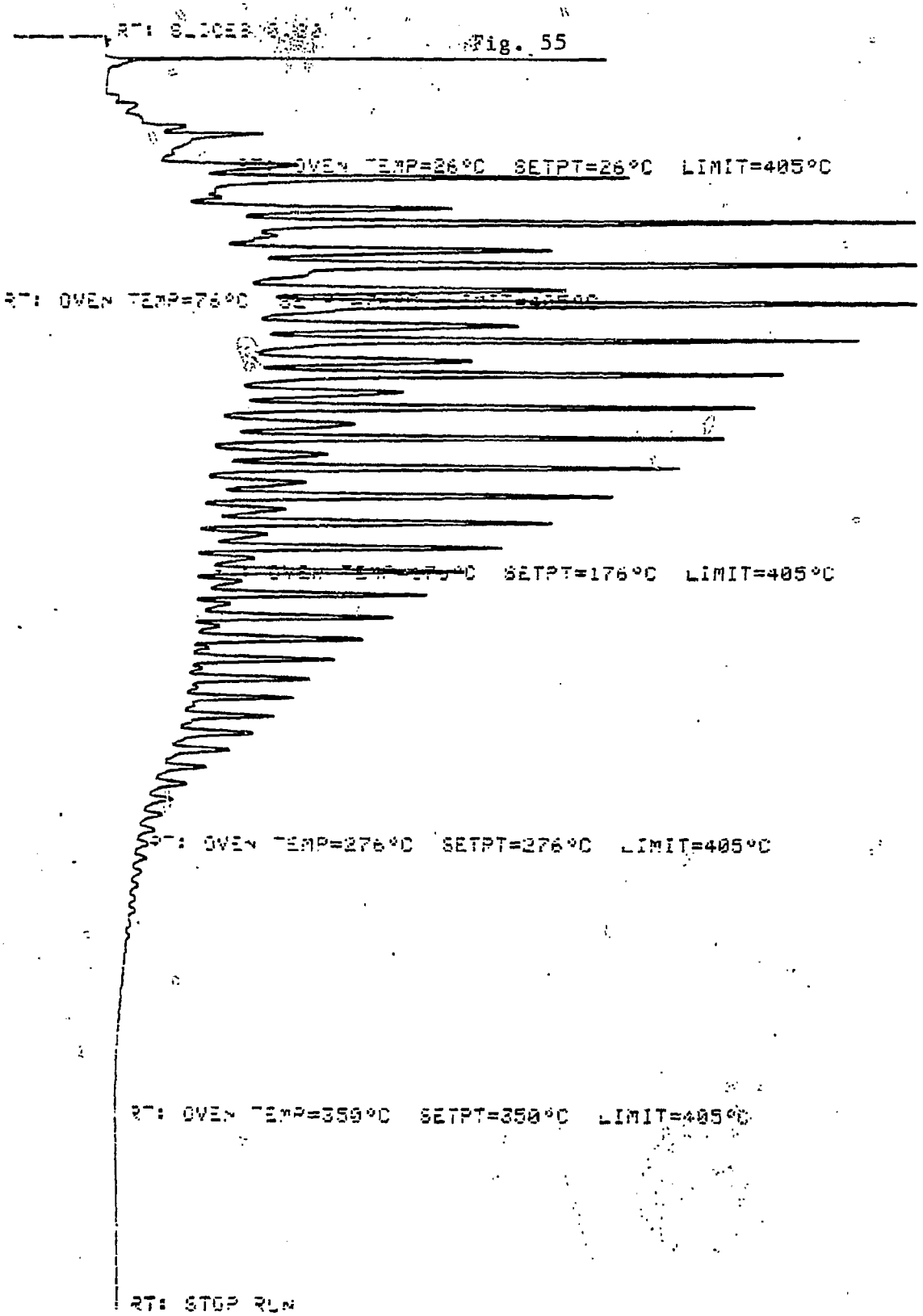

RT: SLICES 0.20
RT: OVEN TEMP=25°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D10113-15-SL

Fig. 54

Fig. 55


RT: SLICE
OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°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: D10112-15-7L

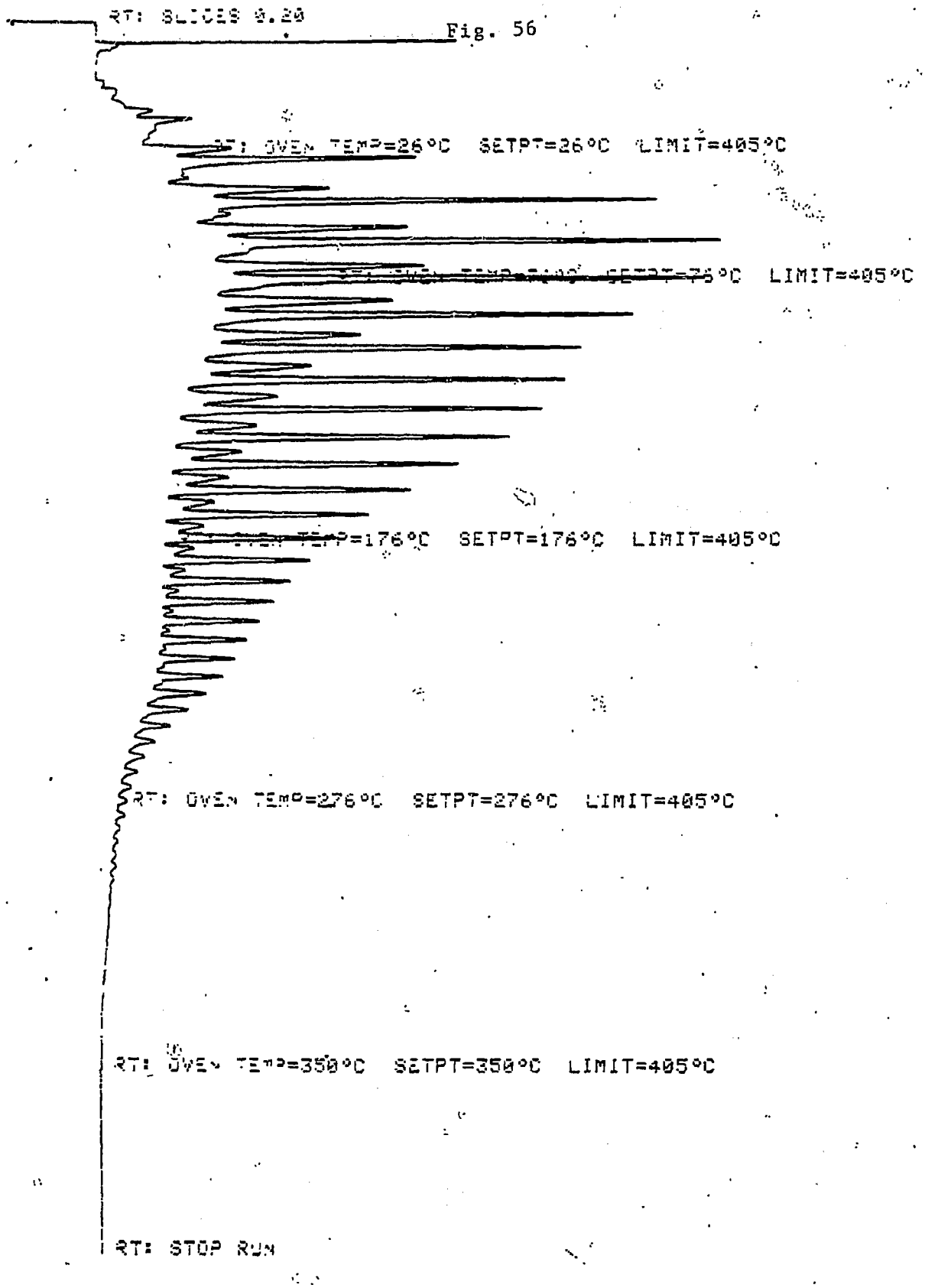

RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D10112-15-9L

Fig. 56

TABLE 7 RESULT OF SYNGAS OPERATION

RUN NO. 10112-15
CATALYST CO/TH +UCC-101,#10252-46C 80 CC 37.2GM (52.1 AFTER RUN +15 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-15-01	112-15-02	112-15-03	112-15-04	112-15-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.5	27.0	115.5	122.5	139.5
PRESSURE,PSIG	302	299	303	302	302
TEMP. C	272	271	269	269	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.50	7.50	88.50	7.00	24.00
EFFLNT GAS LITER	156.55	61.50	1049.40	91.50	324.55
GM AQUEOUS LAYER	47.27	18.12	208.20	14.74	50.54
GM OIL	24.32	9.60	96.37	6.24	21.39
MATERIAL BALANCE					
GM ATOM CARBON %	85.88	86.83	95.01	99.73	99.31
GM ATOM HYDROGEN %	79.97	80.49	98.12	98.28	99.38
GM ATOM OXYGEN %	94.42	94.44	95.50	99.88	99.73
RATIO CHX/(H2O+CO2)	0.8123	0.8293	0.9862	0.9955	0.9870
RATIO X IN CHX	2.3242	2.3375	2.4283	2.5101	2.5037
USAGE H2/CO PRODT	1.2272	1.2590	1.6739	1.6228	1.6902
RATIO CO2/(H2O+CO2)	0.3735	0.3620	0.2001	0.2403	0.2068
K SHIFT IN EFFLNT	0.16	0.15	0.13	0.17	0.14
CONVERSION					
ON CO %	62.86	61.20	44.21	41.99	39.12
ON H2 %	89.40	89.06	72.07	69.26	66.43
ON CO+H2 %	75.66	74.61	58.36	55.53	52.78
PRDT SELECTIVITY,WT %					
CH4	14.67	15.46	19.66	23.52	23.12
C2 HC'S	2.23	2.29	2.82	3.07	3.09
C3H8	2.12	2.11	2.90	3.27	3.29
C3H6=	2.93	2.82	1.96	2.23	2.63
C4H10	1.80	1.74	2.18	2.64	2.72
C4H8=	4.14	4.08	3.00	3.44	3.73
C5H12	2.18	2.06	2.27	2.72	2.71
C5H10=	4.24	4.17	3.09	3.62	3.78
C6H14	2.98	2.63	2.55	2.88	2.80
C6H12= & CYCLO'S	2.37	2.30	1.77	2.02	1.56
C7+ IN GAS	12.74	11.58	14.13	13.78	11.90
LIQ HC'S	47.58	48.77	43.68	36.81	38.66
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	27.90	28.49	32.52	38.17	38.59
C5 -420 F	50.41	43.30	42.22	40.22	38.71
420-700 F	19.19	22.72	20.35	15.94	16.74
700-END PT	2.51	5.49	4.91	5.67	5.95
C5+-END PT	72.10	71.51	67.48	61.83	61.41
ISO/NORMAL MOLE RATIO					
C4	0.2857	0.2632	0.1226	0.1367	0.1778
C5	0.5572	0.4990	0.2546	0.2493	0.2698
C6	0.9660	0.8647	0.4117	0.4098	0.4181
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.6912	0.7154	1.4156	1.3971	1.1943
C4	0.4206	0.4117	0.7010	0.7401	0.7044
C5	0.5004	0.4803	0.7141	0.7302	0.6954
LIQ HC COLLECTION					
PHYS. APPEARANCE	GR YL OIL		GR OIL WAX		GR YL OIL
DENSITY	0.741		0.765		0.769
N, REFRACTIVE INDEX	1.4266		1.4309		1.4310
SIMULT'D DISTILATN					
10 WT % @ DEG F	257		292		292
16	286		318		320
50	406		457		465
84	578		662		694
90	635		712		755
RANGE(16-84 %)	292		344		374
WT % @ 420 F	54.40	42.16	42.16	41.29	41.29
WT % @ 700 F	94.72	88.75	88.75	84.60	84.60

TABLE 8 RESULT OF SYNGAS OPERATION

RUN NO. 10112-15
CATALYST CO/TH +UCC-101,#10252-46C 80 CC 37.2GM (52.1 AFTER RUN +15 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-15-06	112-15-07	112-15-08	112-15-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	146.5	163.5	170.5	187.5
PRESSURE,PSIG	302	300	302	301
TEMP. C	269	270	269	269
FEED CC/MIN	400	400	400	400
HOURS FEEDING	7.00	24.00	7.00	24.00
EFFLNT GAS LITER	94.55	326.45	94.30	328.00
GM AQUEOUS LAYER	14.55	49.89	14.55	49.89
GM OIL	6.71	23.01	5.88	20.15
MATERIAL BALANCE				
GM ATOM CARBON %	100.50	101.89	98.59	99.45
GM ATOM HYDROGEN %	100.39	101.30	97.96	99.16
GM ATOM OXYGEN %	99.42	100.08	99.44	99.78
RATIO CHX/(H2O+CO2)	1.0334	1.0559	0.9737	0.9896
RATIO X IN CHX	2.4875	2.4874	2.5214	2.5200
USAGE H2/CO PRODT	1.6872	1.6911	1.6860	1.7093
RATIO CO2/(H2O+CO2)	0.2121	0.2136	0.2099	0.2017
K SHIFT IN EFFLNT	0.15	0.15	0.14	0.14
CONVERSION				
ON CO %	40.12	40.43	38.74	38.31
ON H2 %	66.85	67.26	66.47	65.97
ON CO+H2 %	53.48	53.81	52.56	52.12
PRDT SELECTIVITY,WT %				
CH4	22.57	22.63	24.24	24.15
C2 HC'S	2.95	2.99	3.23	3.23
C3H8	3.05	2.98	3.15	3.14
C3H6=	2.16	2.22	2.34	2.34
C4H10	2.33	2.22	2.37	2.32
C4H8=	3.37	3.29	3.72	3.56
C5H12	2.42	2.38	2.41	2.43
C5H10=	3.29	3.60	3.68	3.84
C6H14	2.81	2.72	2.69	2.72
C6H12= & CYCLO'S	2.02	2.06	2.09	2.07
C7+ IN GAS	13.06	13.88	12.88	13.28
LIQ HC'S	39.97	39.03	37.20	36.92
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	36.43	36.33	39.05	38.74
C5 -420 F	40.39	41.04	39.43	39.90
420-700 F	17.06	16.65	15.90	15.78
700-END PT	6.13	5.98	5.62	5.58
C5+-END PT	63.57	63.67	60.95	61.26
ISO/NORMAL MOLE RATIO				
C4	0.1292	0.1370	0.1316	0.1327
C5	0.2615	0.2540	0.2620	0.2473
C6	0.4047	0.4006	0.3968	0.3892
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	1.3523	1.2831	1.2830	1.2776
C4	0.6684	0.6503	0.6155	0.6289
C5	0.7168	0.6438	0.6376	0.6146
LIQ HC COLLECTION				
PHYS. APPEARANCE		CLDY GR		CLDY GR
DENSITY		0.747		0.769
N, REFRACTIVE INDEX		1.4316		1.4319
SIMULT'D DISTILATN				
10 WT % @ DEG F		291		293
16		318		320
50		462		460
84		694		692
90		755		754
RANGE(16-84 %)		376		372
WT % @ 420 F	42.00	42.00	42.14	42.14
WT % @ 700 F	84.67	84.67	84.89	84.89

V. RUN 4 (10112-13) with Catalyst 4 (Co/Th on UCC-108)

This is another base line catalyst for use in determining the most productive ratio of metal component to Molecular Sieve. Except for the substitution of UCC-108 for UCC-101, it is identical in preparation and composition to Catalyst 1.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 57-60. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 61-62. Carbon number product distributions are plotted in Figs. 63-68. Chromatograms from simulated distillations are reproduced in Figs. 69-74. Detailed material balances appear in Tables 9-11.

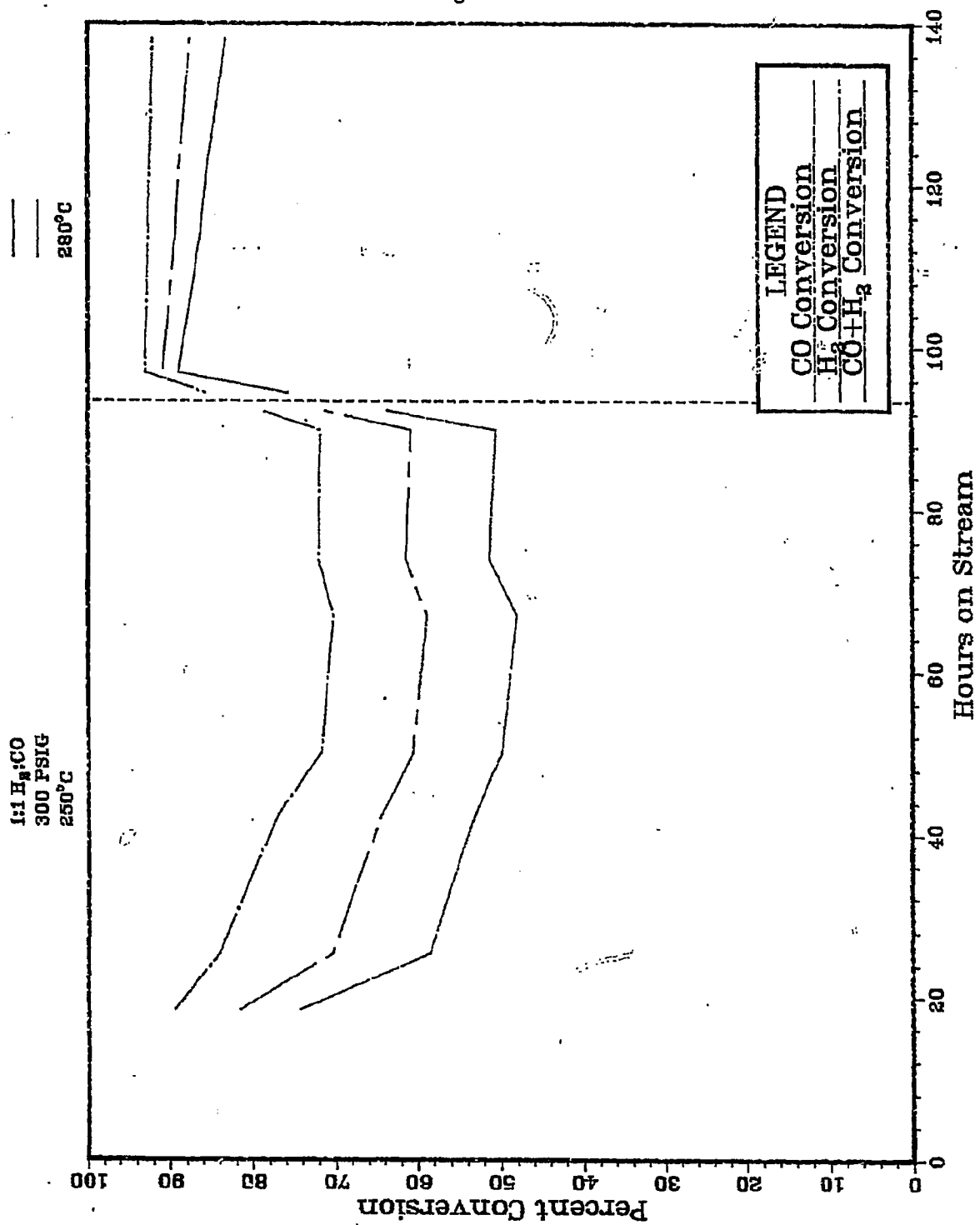
At 250C the conversion of this catalyst was 60 percent, much lower than the 90 percent plus of Catalyst 1. The difference at 280C was smaller: 88 percent for this catalyst, 95 percent for Catalyst 1. The lower activity is hard to explain in a physically mixed catalyst, since the Molecular Sieve should not be mixed intimately enough with the metal component to affect its activity. The water gas shift activity was lower than for Catalyst 1. At 250C the percent of oxygen rejected as CO_2 was initially 50 percent, then fell off to 35 percent; at 280C it was 75 percent.

The general selectivity at 280C was similar to that of Catalyst 1 at 250C, with similar conversion. Methane and C_5^+ pro-

duction were each ~40 percent, with low wax yield. At 250C, however, the selectivity was substantially better: methane production was ~15 percent, C_5^+ was more than 70 percent, and the combined total of gasoline plus diesel oil was ~60 percent. At first the gasoline plus diesel oil was 74 percent of the total product, beyond the Schulz-Flory limit, but this was a false measurement caused by wax build-up in the reactor; note the increase of heavies with hours on stream, and the low material balance until Sample 4 because this product was not coming out of the reactor. The percent olefins in the C_4 fraction varied widely, with no apparent relationship to time or temperature. Isomerization of the pentane was even lower than with Catalyst 1; characterization of the liquid indicates that it was highly saturated straight chain hydrocarbons, much like that of Catalyst 1. The initial Schulz-Flory plots show what appears to be a carbon number cut-off, again a false measurement caused by wax build-up in the reactor; by Sample 5 the distribution is linear except for the excess methane. The last two samples seem to show excess heavies--yet another false measurement, due this time to the built-up wax leaving the reactor at high temperature.

Like Catalyst 1, this catalyst contains too high a proportion of metal component to Molecular Sieve. The ratio should be adjusted.

Fig. 57


RUN 10112-13
1:1 H_2:CO
300 PSIG
250°C
280°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

RUN 10112–13

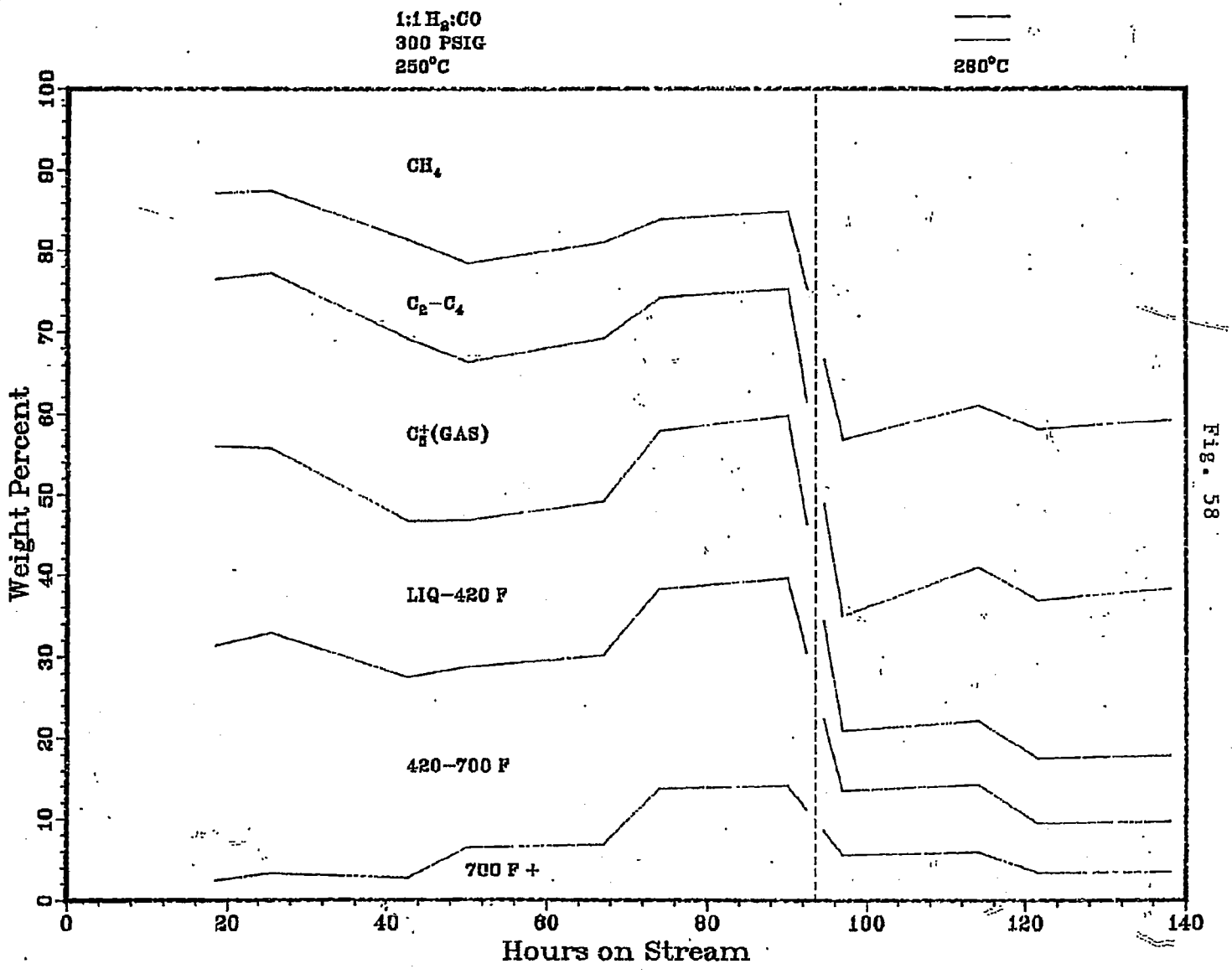
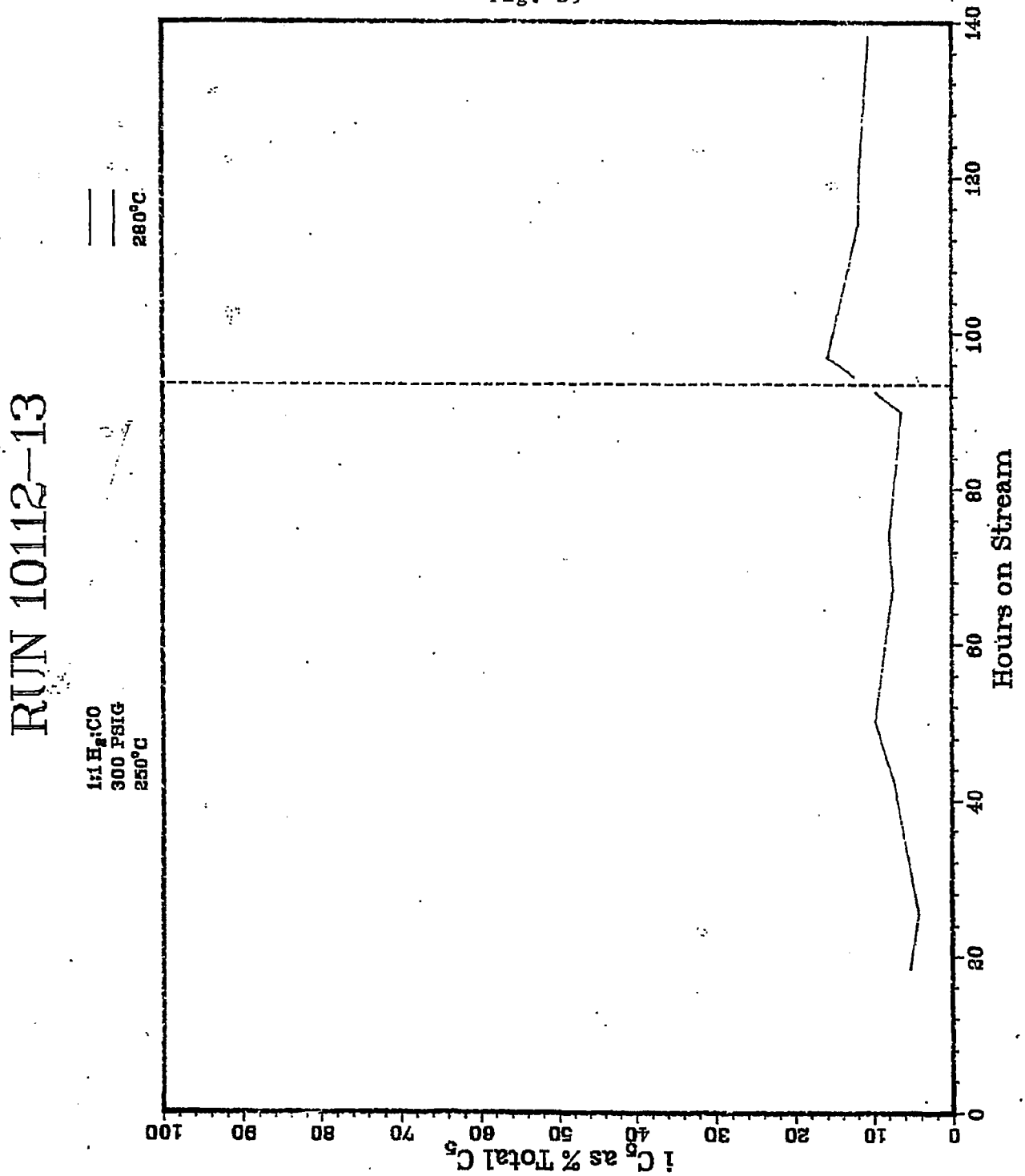


Fig. 58

Fig. 59


RUN 10112-13
1:1 H2:CO
300 PSIG
250°C
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

RUN 10112–13

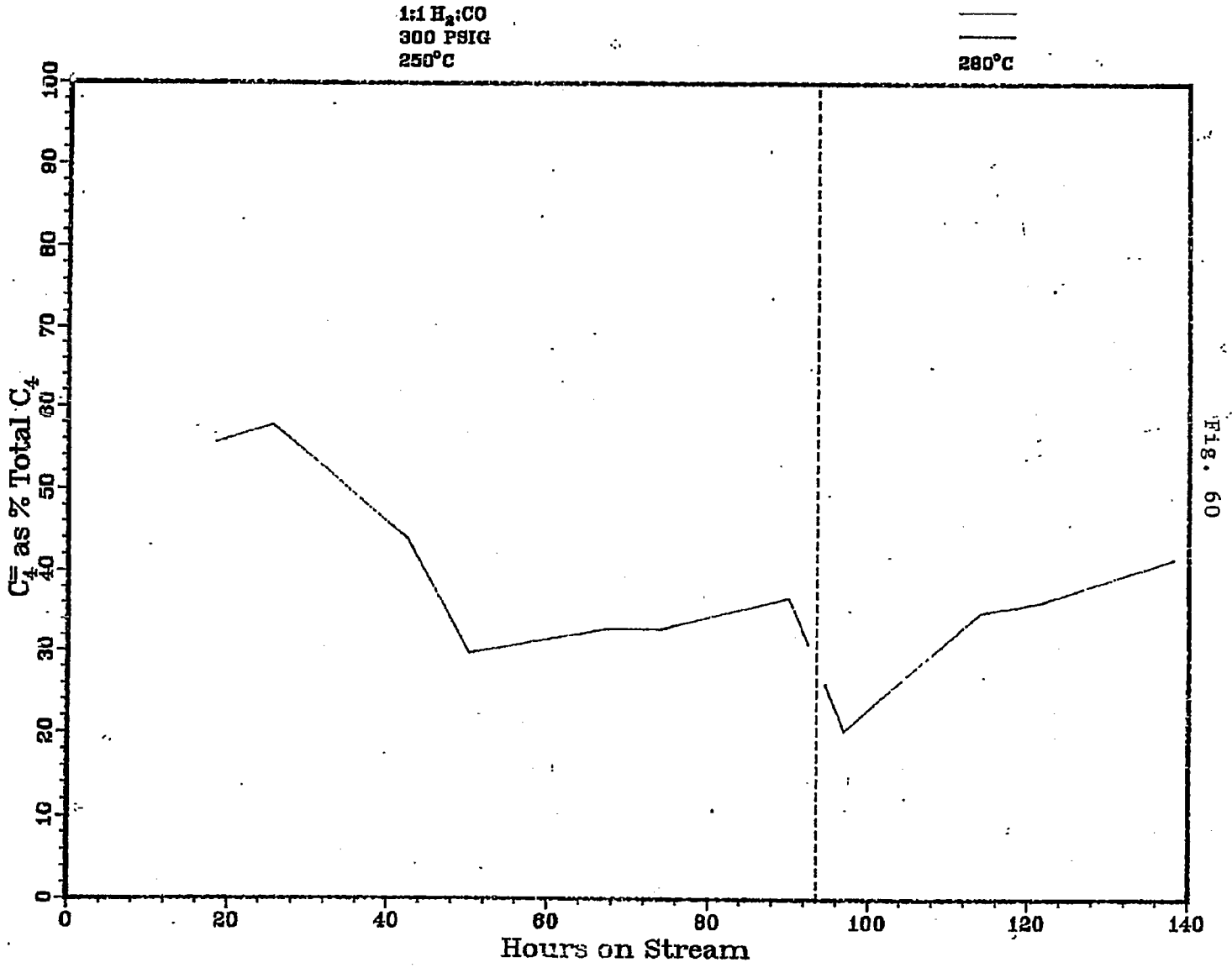


Fig. 60

Fig. 61

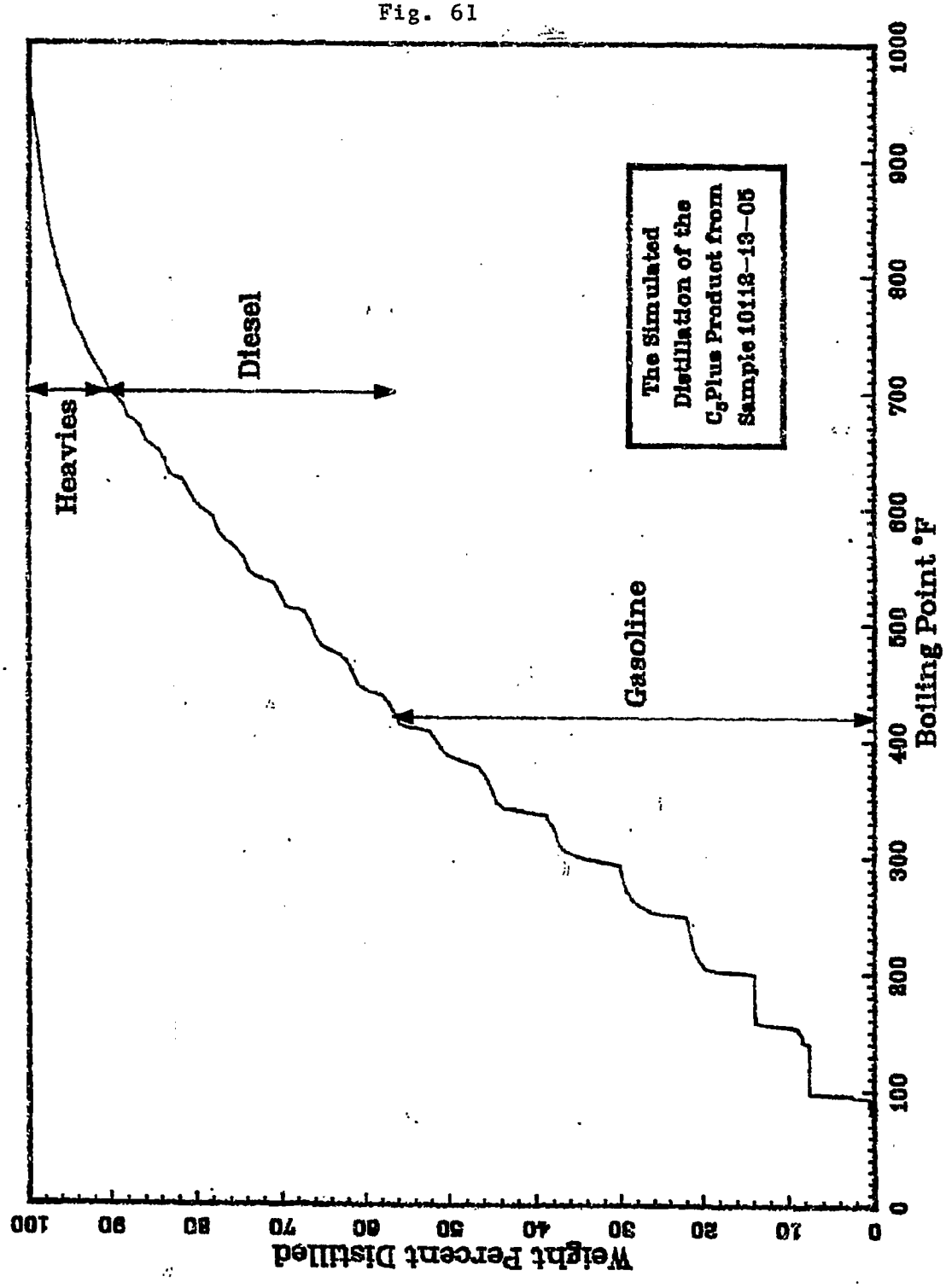

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 10113-13-05

Fig. 62

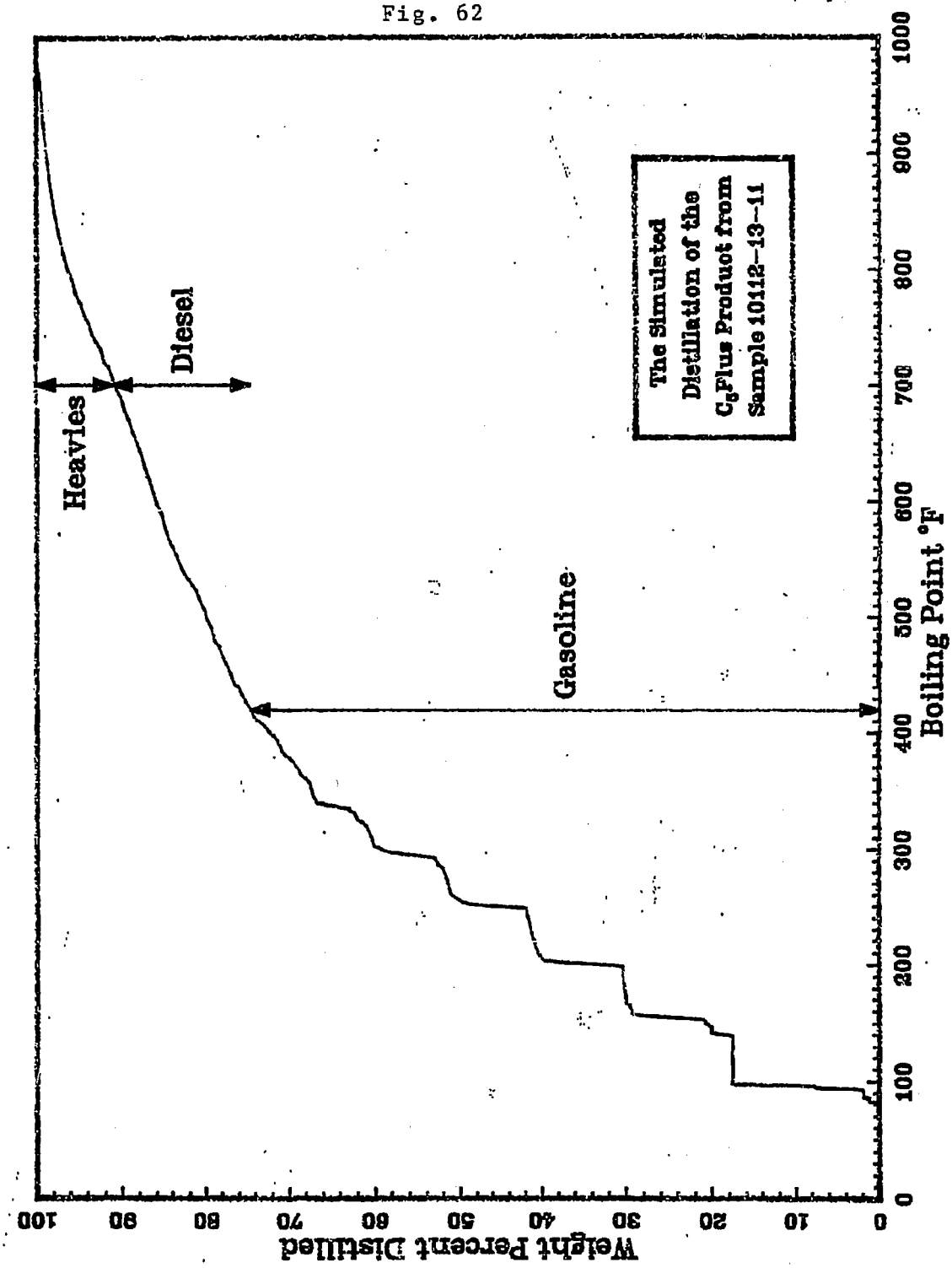

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5Plus Produot from Sample 10112-13-11

Fig. 63

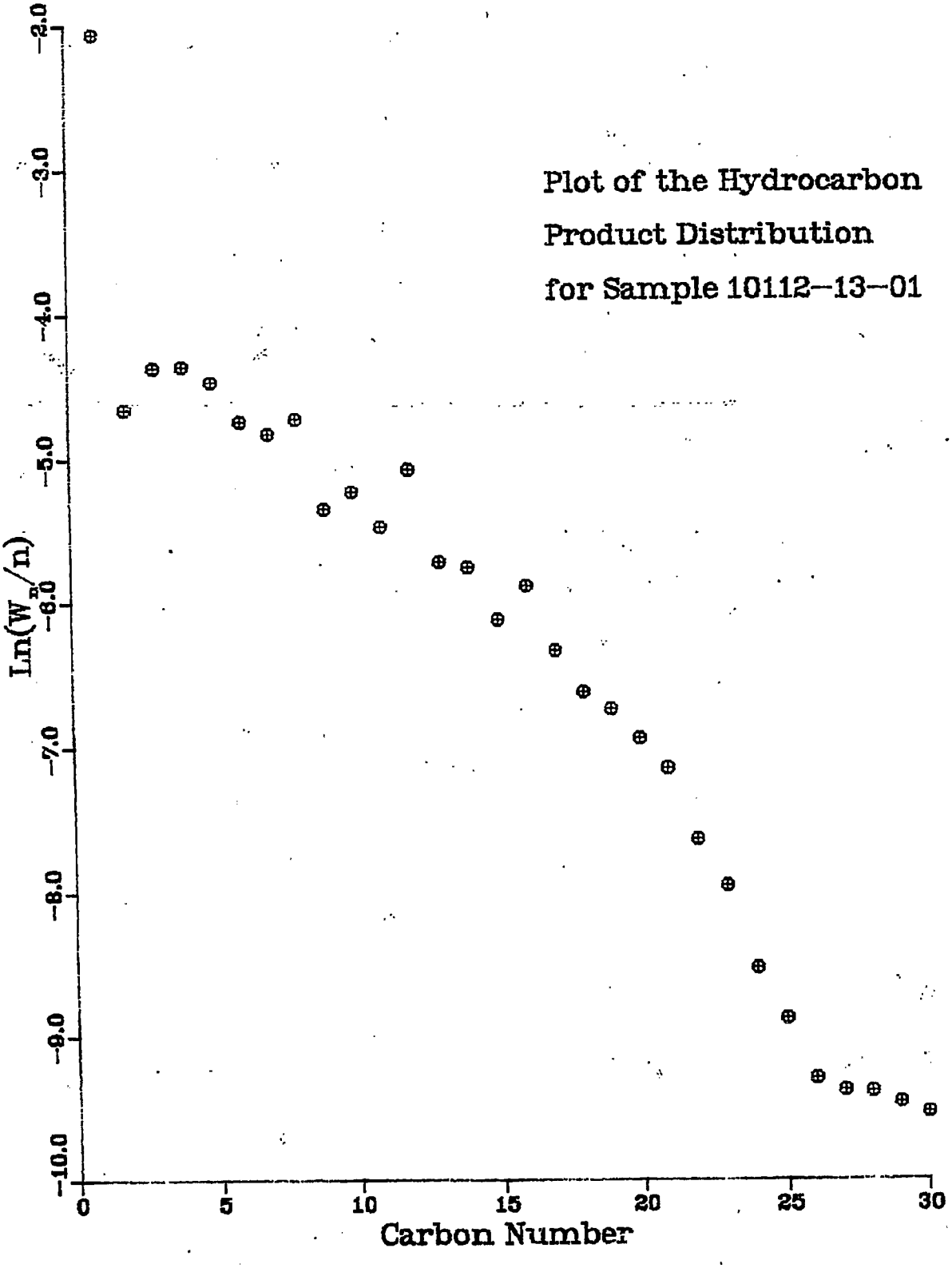

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--13--01
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 64

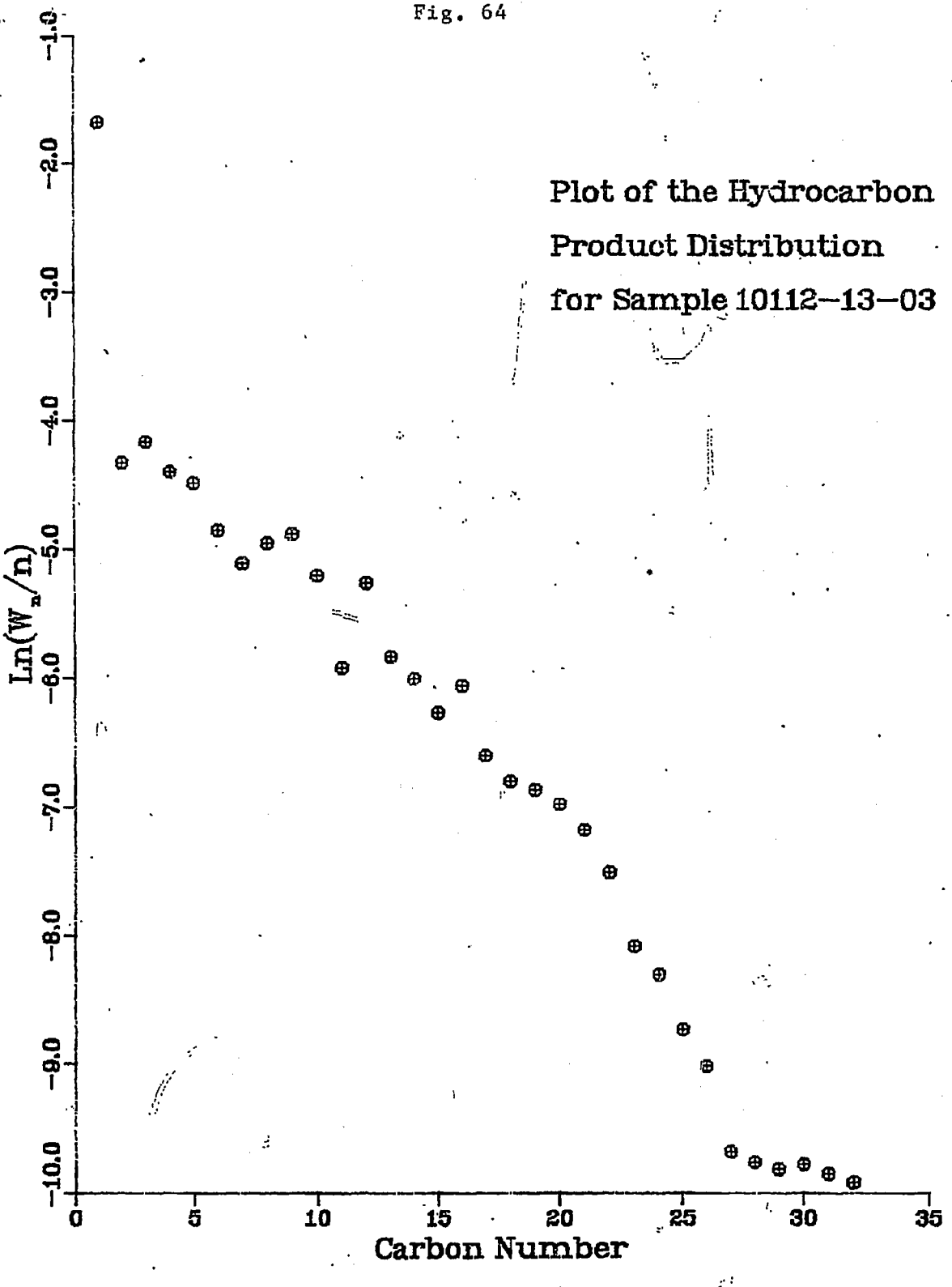

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-13-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 65

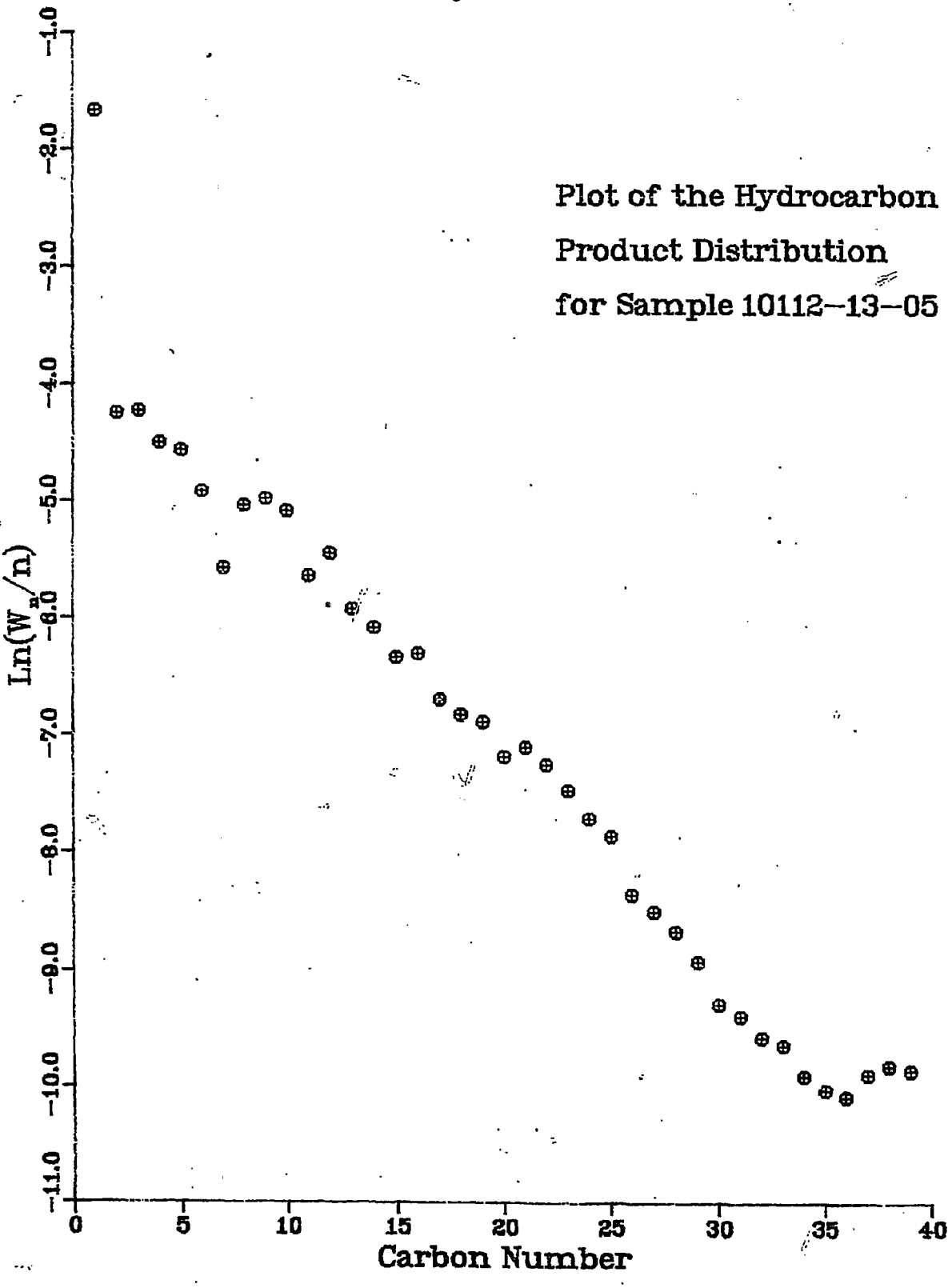

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--13--05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 66

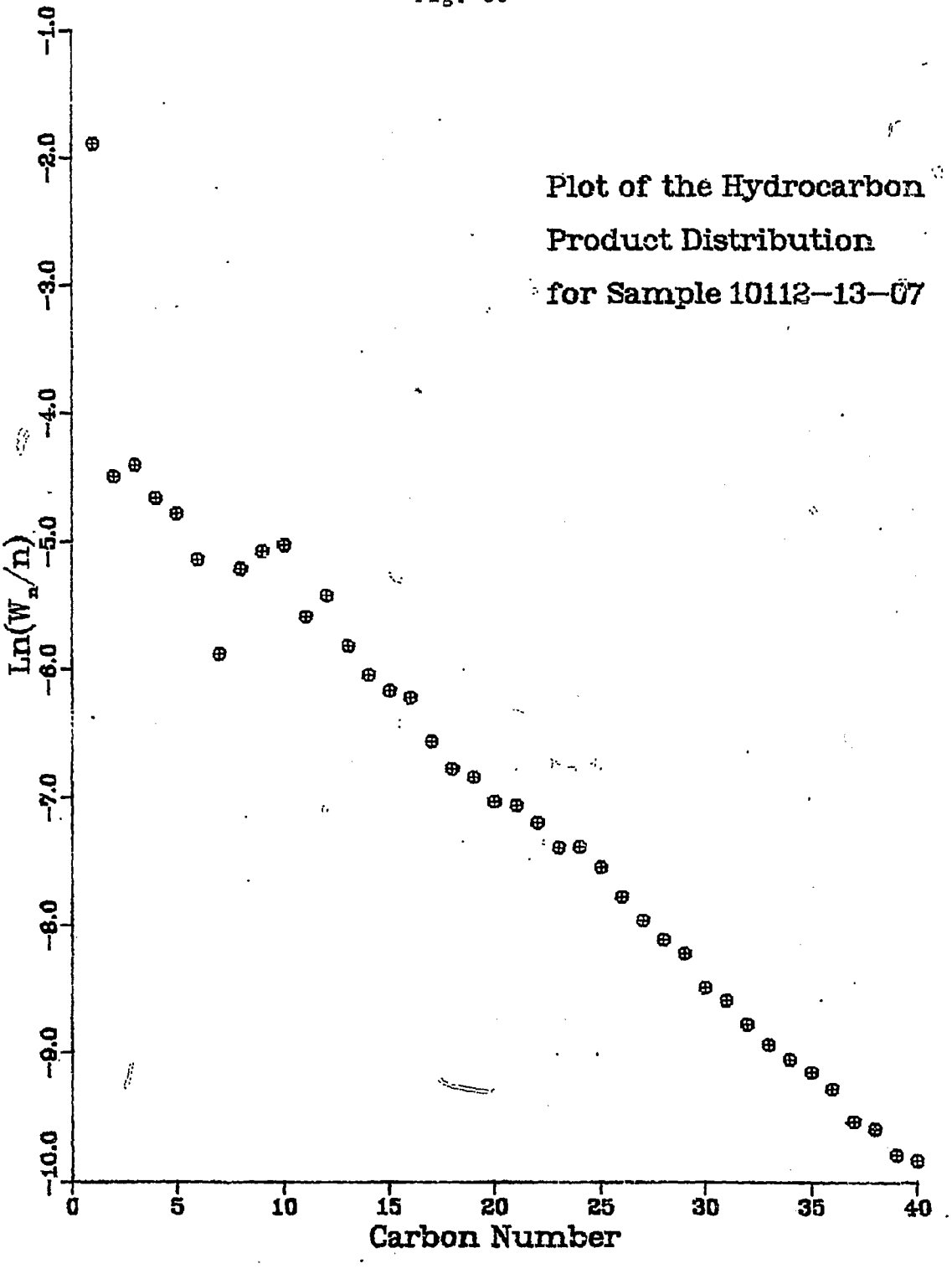

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-13-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 67

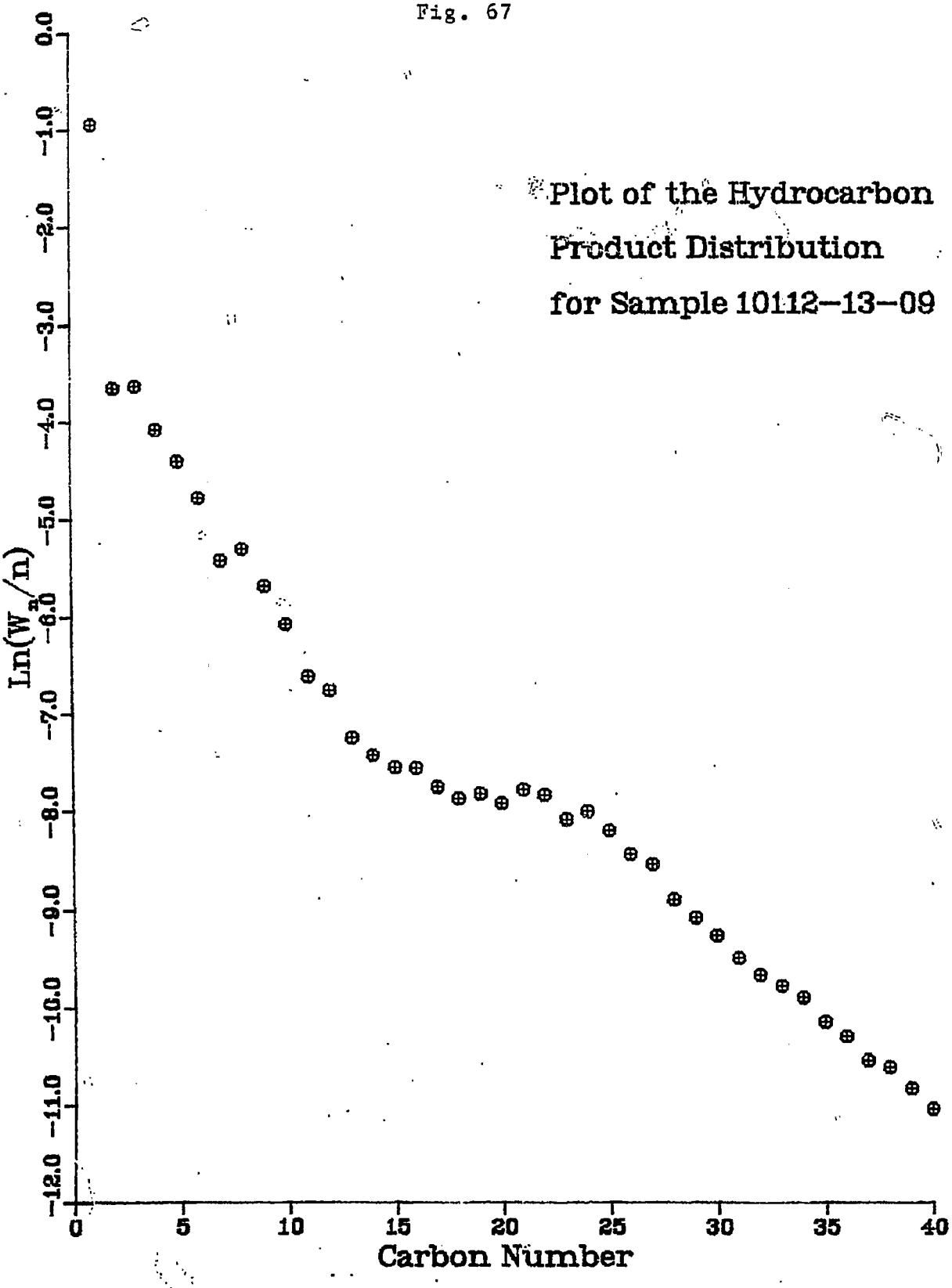

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-13-09
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 68

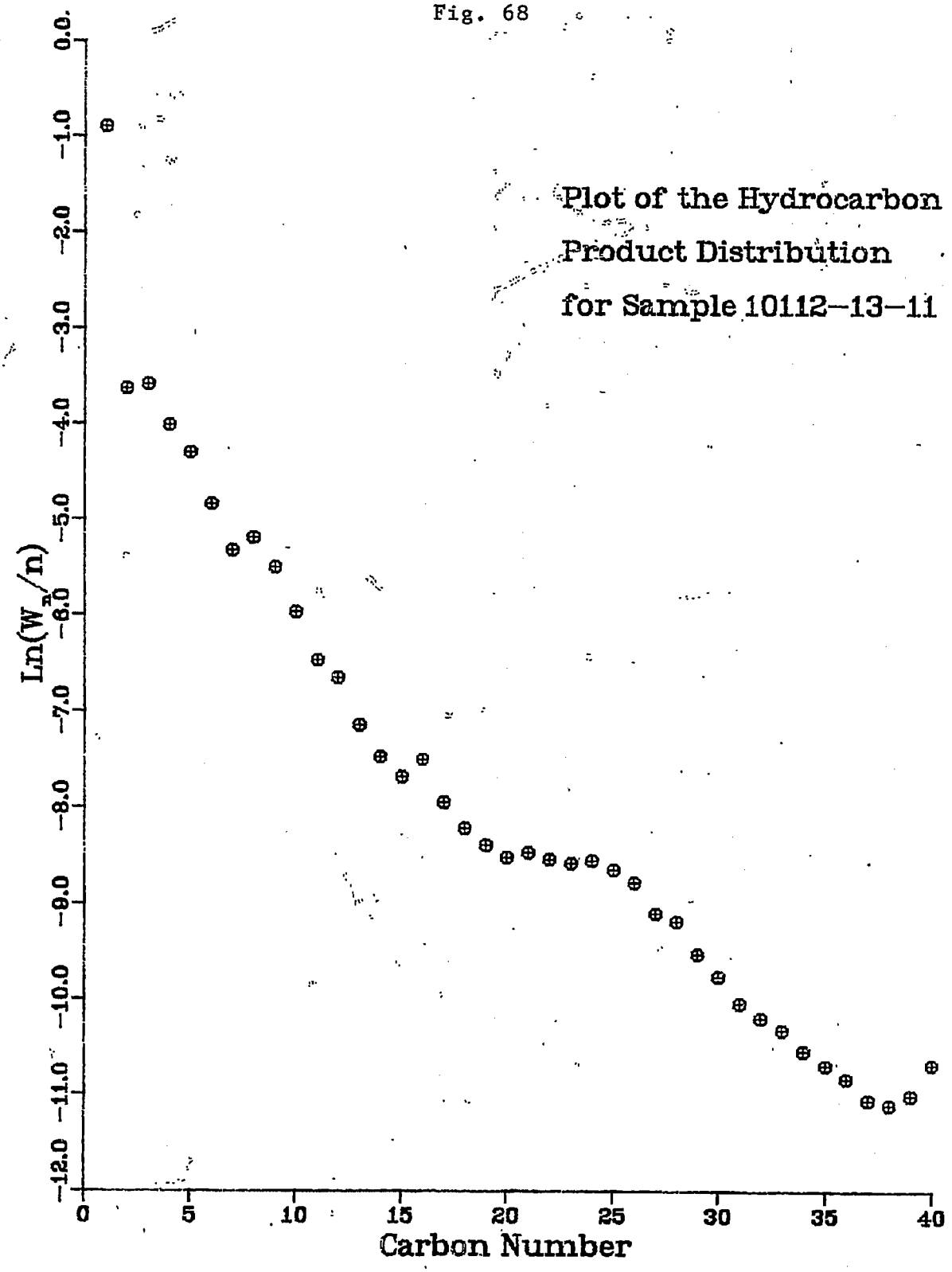

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-13-11
Ln(W_n/n)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 69

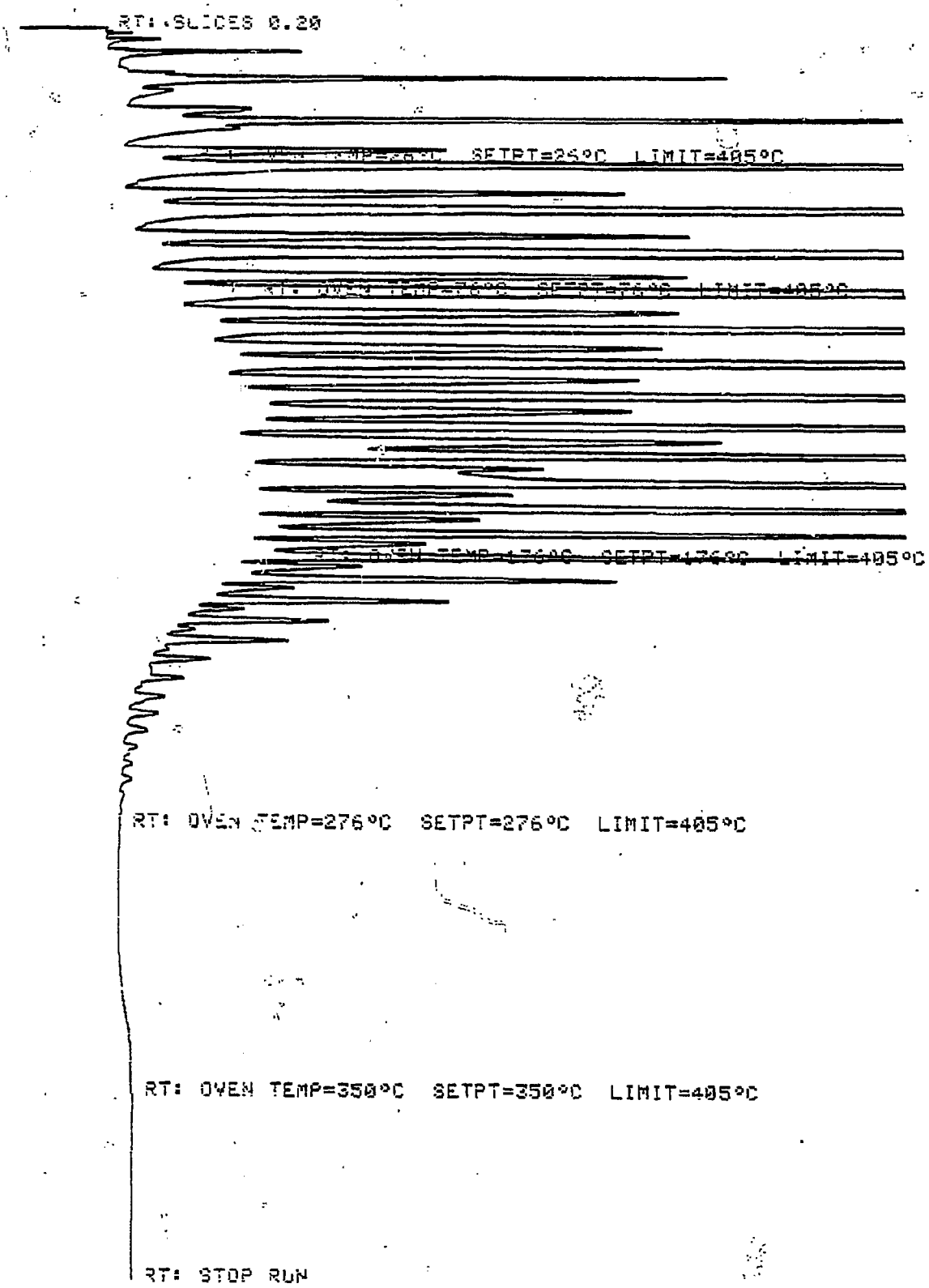
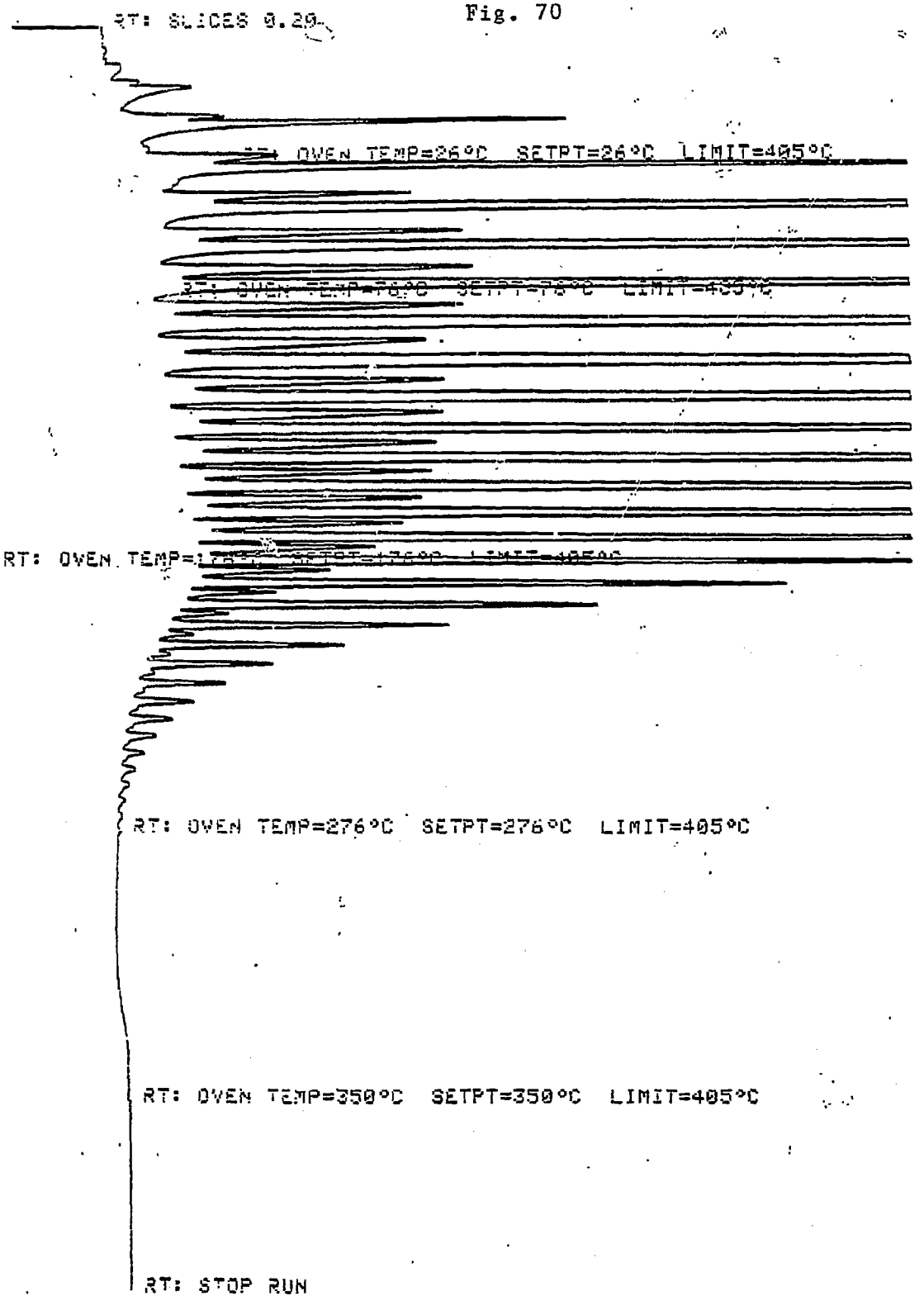

OVEN TEMP NOT READY?
RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-13-1L

Fig. 70



SAMPLE:10112-13-3L

Fig. 71

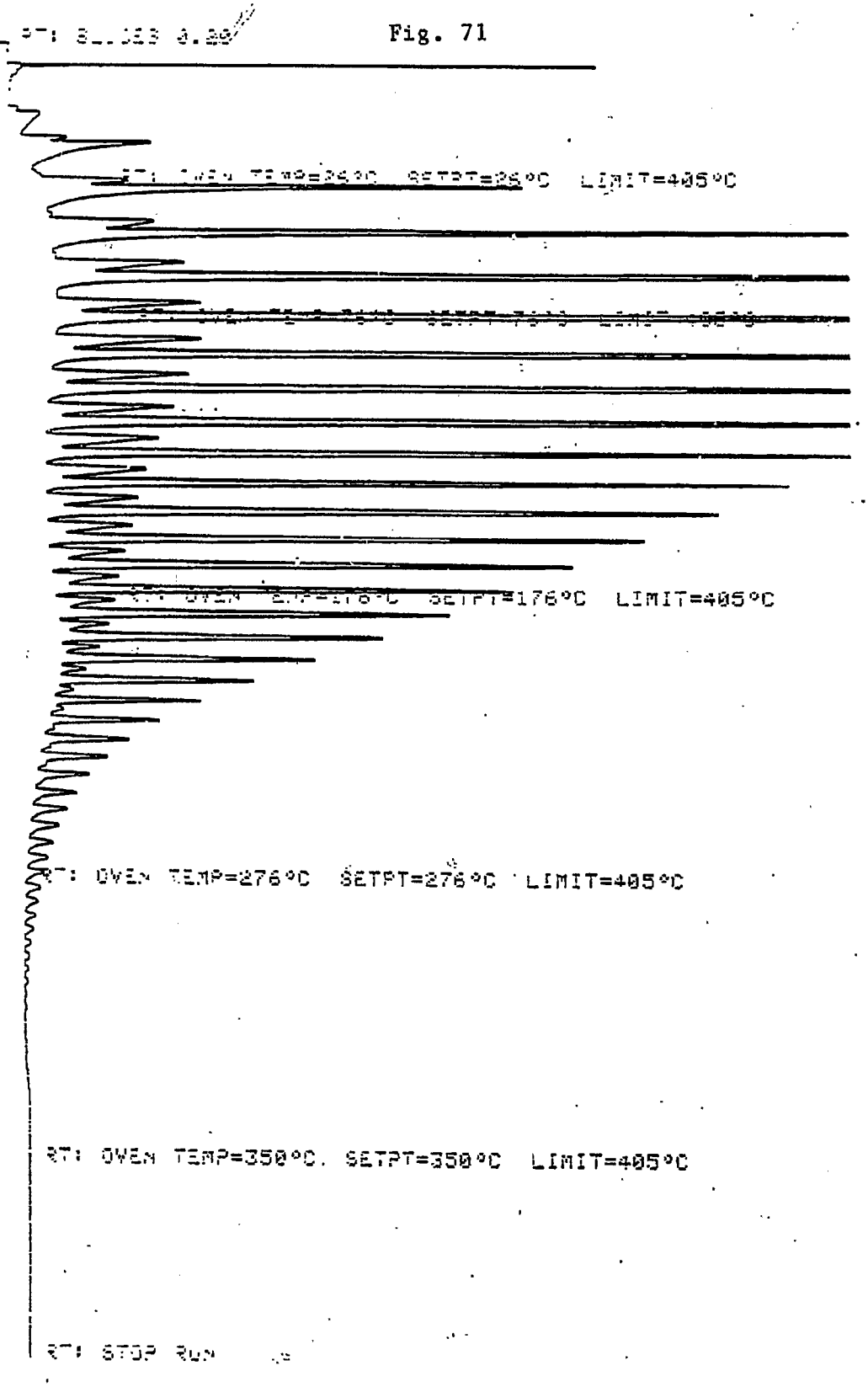
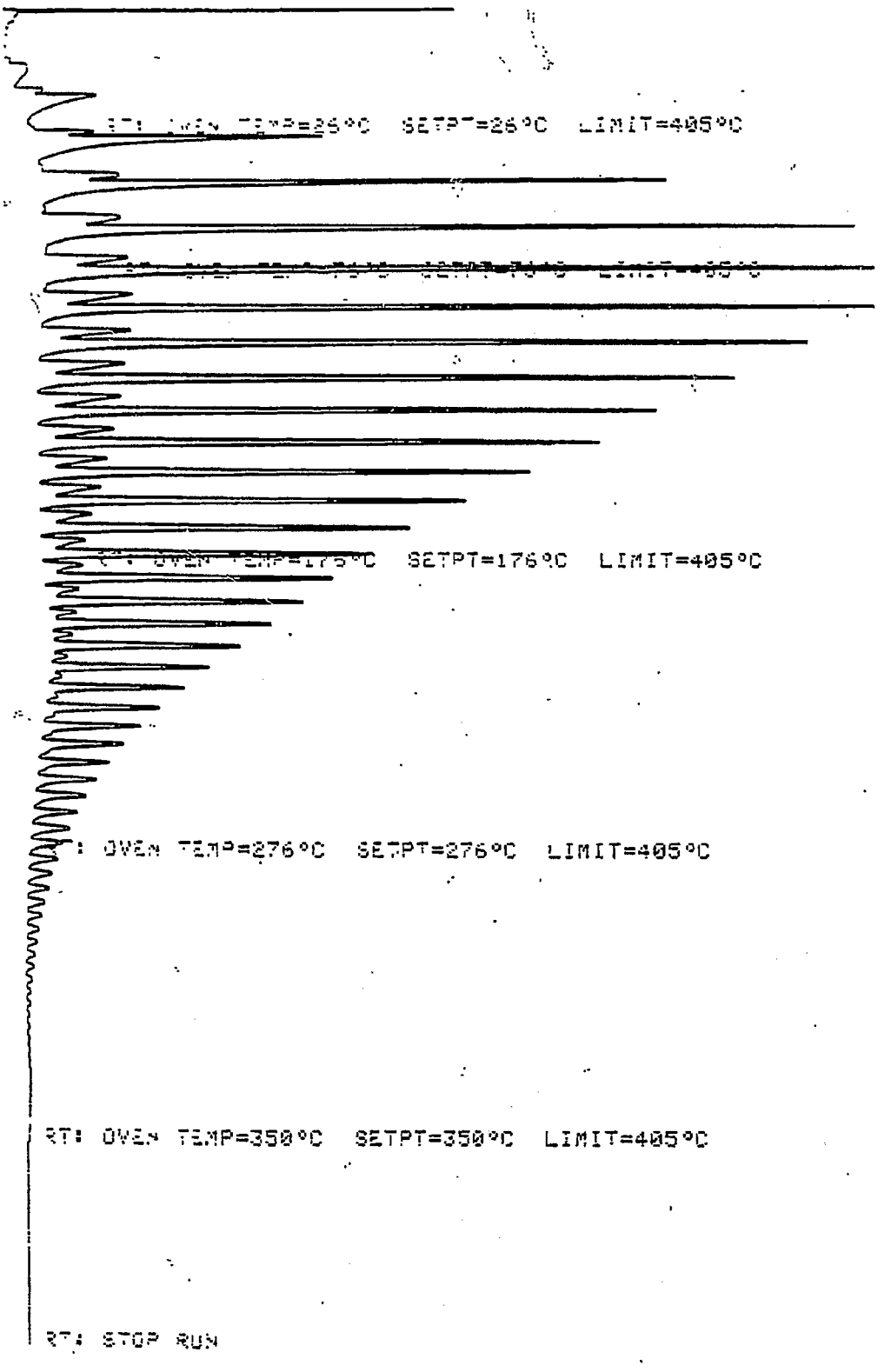

RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C. SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-13-SL

Fig. 72



SAMPLE:10112-13-7L

OVEN TEMP NOT READY

Fig. 73

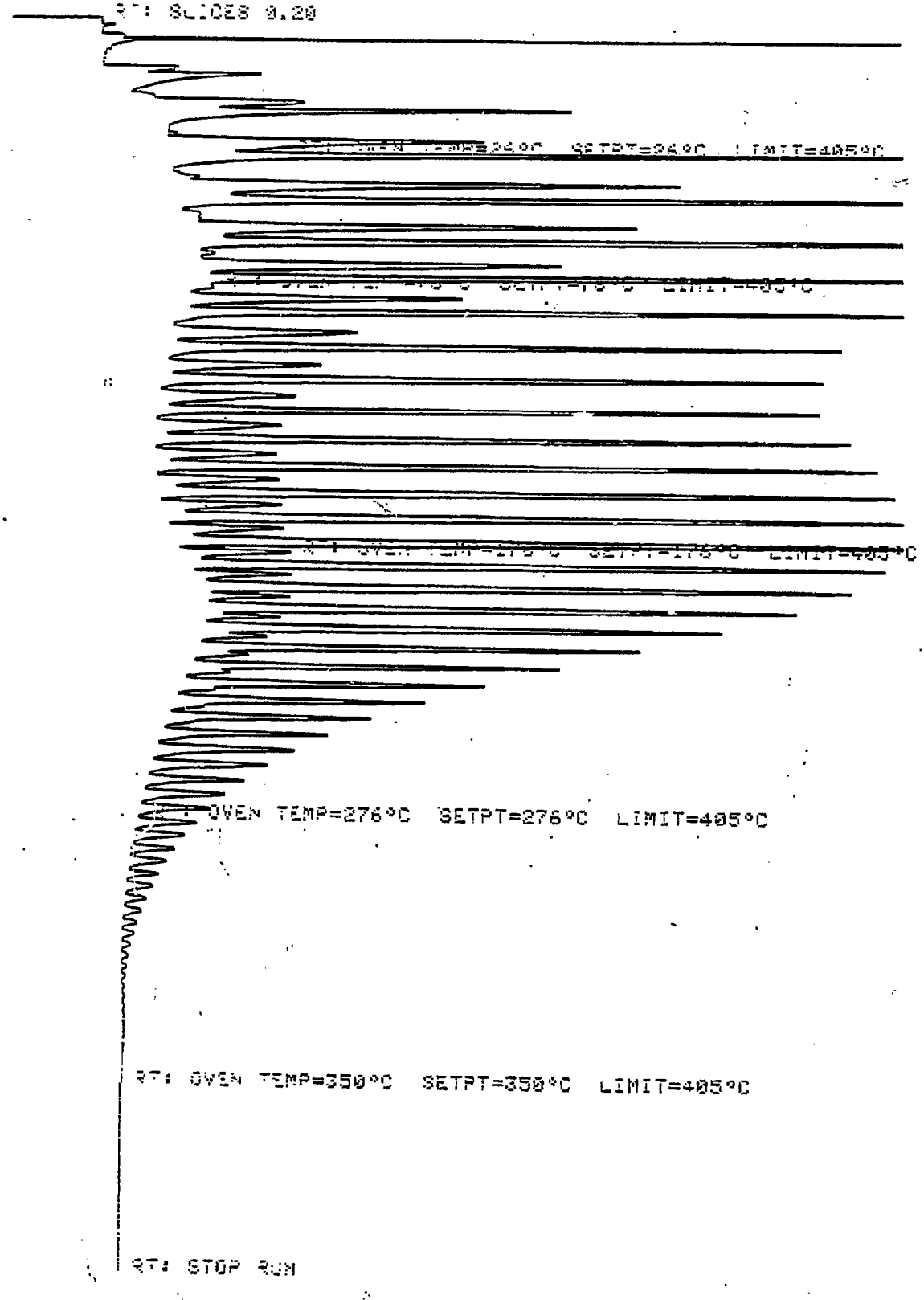


Fig. 74

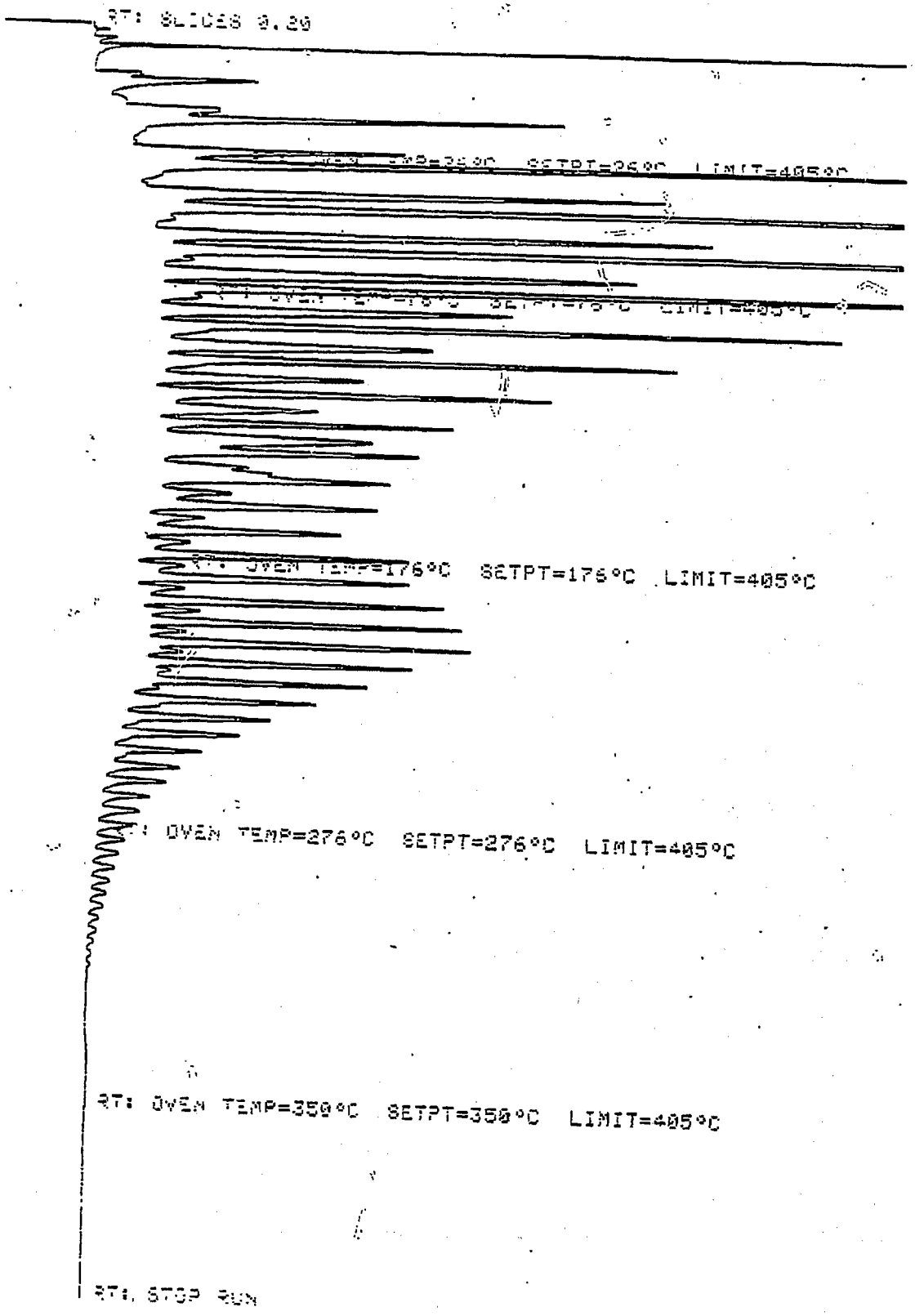

OVEN TEMP NOT READY
RT: SLIDES 0.20
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10112-13-11L

TABLE 9 RESULT OF SYNGAS OPERATION

RUN NO. 10112-13
CATALYST CO/TH +UCC-108 #10252-28C 80 CC 31.8GM (33.6 AFTER RUN +1.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-13-01	112-13-02	112-13-03	112-13-04	112-13-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.5	25.5	42.67	50.17	67.08
PRESSURE,PSIG	307	302	299	301	299
TEMP. C	252	251	250	251	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	18.50	7.00	24.17	7.50	24.42
EFFLNT GAS LITER	142.05	53.65	246.95	94.13	305.56
GM AQUEOUS LAYER	40.78	14.82	51.18	14.59	47.49
GM OIL	28.73	6.60	22.79	9.38	30.53
MATERIAL BALANCE					
GM ATOM CARBON %	86.09	71.97	86.56	101.73	100.19
GM ATOM HYDROGEN %	79.40	62.28	77.56	97.85	95.63
GM ATOM OXYGEN %	97.75	91.36	101.42	101.93	101.12
RATIO CHX/(H2O+CO2)	0.7705	0.5520	0.6552	0.9945	0.9744
RATIO X IN CHX	2.3015	2.2841	2.4213	2.4880	2.4363
USAGE H2/CO PRODT	1.0183	1.0088	1.1175	1.3802	1.3824
RATIO CO2/(H2O+CO2)	0.4881	0.4219	0.4101	0.3616	0.3451
K SHIFT IN EFFLNT	0.36	0.24	0.31	0.31	0.29
CONVERSION					
ON CO %	74.24	58.55	53.03	49.82	47.96
ON H2 %	89.45	83.96	76.85	71.62	70.13
ON CO+H2 %	81.54	70.33	64.29	60.51	58.79
PRDT SELECTIVITY,WT %					
CH4	12.75	12.53	18.58	21.53	18.98
C2 HC'S	1.88	1.84	2.64	2.99	2.86
C3H8	2.37	1.83	2.99	3.66	3.39
C3H6=	1.41	2.19	1.67	0.83	1.00
C4H10	2.30	1.88	2.80	3.25	3.02
C4H8=	2.79	2.49	2.11	1.34	1.43
C5H12	3.59	2.73	3.55	3.76	3.70
C5H10=	2.10	2.52	2.06	1.21	1.53
C6H14	4.24	3.15	3.91	4.00	4.01
C6H12= & CYCLO'S	0.45	1.08	0.76	0.28	0.40
C7+ IN GAS	10.03	11.89	12.14	10.21	10.34
LIQ HC'S	56.08	55.86	46.80	46.94	49.33
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	23.51	22.76	30.78	33.60	30.69
C5 -420 F	45.08	44.32	41.64	37.58	39.02
420-700 F	28.98	29.67	24.86	22.29	23.42
700-END PT	2.43	3.25	2.72	6.53	6.87
C5+-END PT	76.49	77.24	69.22	66.40	69.31
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0110	0.0264	0.0355	0.0294
C5	0.0557	0.0443	0.0797	0.1081	0.0807
C6	0.1192	0.0611	0.1271	0.1871	0.1532
C4=	0.4558	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.6088	0.8006	1.7139	4.2227	3.2498
C4	0.7953	0.7305	1.2823	2.3508	2.0377
C5	1.6586	1.0545	1.6753	3.0211	2.3520
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		OIL WAX
DENSITY	.745 .747		.755 .759		.743 .757
N, REFRACTIVE INDEX	1.4195 1.4208		1.424 1.4245		1.4260
SIMULT'D DISTILATN					
10 WT % @ DEG F	258		298		299
16	304		328		333
50	451		466		478
84	605		628		688
90	649		664		737
RANGE(16-84 %)	301		300		355
WT % @ 420 F	44.00	41.07	41.07	38.60	38.60
WT % @ 700 F	95.67	94.19	94.19	86.08	86.08

TABLE 10 RESULT OF SYNGAS OPERATION

RUN NO. 10112-13
CATALYST CO/TH +UCC-108 #10252-28C 80 CC 31.8GM (33.6 AFTER RUN +1.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-13-06	112-13-07	112-13-08	112-13-09	112-13-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	74.0	90.0	97.0	114.0	121.5
PRESSURE,PSIG	295	297	298	296	297
TEMP. C	251	251	280	280	281
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.92	22.92	7.00	24.00	7.50
EFFLNT GAS LITER	85.54	281.89	78.90	258.05	78.35
GM AQUEOUS LAYER	12.93	42.84	7.01	24.02	9.42
GM OIL	11.94	39.57	6.69	22.92	5.20
MATERIAL BALANCE					
GM ATOM CARBON %	105.81	105.09	113.80	110.73	103.74
GM ATOM HYDROGEN %	100.67	98.48	111.90	104.37	101.38
GM ATOM OXYGEN %	99.34	99.67	105.99	102.79	102.16
RATIO CHX/(H2O+CO2)	1.1833	1.1539	1.1470	1.1583	1.0308
RATIO X IN CHX	2.3658	2.3448	2.9797	2.8745	2.9399
USAGE H2/CO PRODT	1.4217	1.4074	1.0689	1.0559	1.0667
RATIO CO2/(H2O+CO2)	0.3500	0.3477	0.7547	0.7419	0.6929
K SHIFT IN EFFLNT	0.29	0.28	1.94	1.47	1.15
CONVERSION					
ON CO %	51.22	50.30	88.83	86.12	85.35
ON H2 %	71.96	71.68	92.84	92.46	92.33
ON CO+H2 %	61.33	60.64	90.82	89.19	88.80
PRDT SELECTIVITY,WT %					
CH4	16.06	15.09	43.08	38.91	41.86
C2 HC'S	2.34	2.22	6.44	5.21	5.49
C3H8	2.87	2.72	7.83	6.57	6.84
C3H6=	0.82	0.91	0.76	1.39	1.60
C4H10	2.48	2.41	5.38	4.49	4.62
C4H8=	1.17	1.36	1.34	2.33	2.55
C5H12	3.05	2.99	4.51	4.32	4.51
C5H10=	1.18	1.17	1.14	1.88	2.09
C6H14	3.29	3.18	3.75	4.23	4.32
C6H12= & CYCLO'S	0.27	0.34	0.16	0.70	0.31
C7+ IN GAS	8.38	7.73	4.46	7.64	8.08
LIQ HC'S	58.06	59.88	21.14	22.32	17.71
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	25.75	24.71	64.83	58.90	62.96
C5 -420 F	35.74	35.57	21.58	26.75	27.45
420-700 F	24.77	25.55	7.91	8.35	6.12
700-END PT	13.74	14.17	5.68	5.99	3.46
C5+-END PT	74.25	75.29	35.17	41.10	37.04
ISO/NORMAL MOLE RATIO					
C4	0.0243	0.0220	0.0720	0.0426	0.0454
C5	0.0853	0.0670	0.1879	0.1340	0.1319
C6	0.1487	0.1334	0.4844	0.3372	0.3339
C4=	0.0000	0.0000	0.5016	0.2165	0.2085
PARAFFIN/OLEFIN RATIO					
C3	3.3276	2.8423	9.7854	4.5185	4.0772
C4	2.0379	1.7126	3.8795	1.8571	1.7493
C5	2.5135	2.4745	3.8362	2.2380	2.0936
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL WAX		OIL WAX	
DENSITY		.765 .759		0.798	
N, REFRACTIVE INDEX		1.4274		1.4304	
SIMULT'D DISTILATN					
10 WT % @ DEG F		303		262	
16		339		302	
50		514		540	
84		770		773	
90		845		827	
RANGE(16-84 %)		431		471	
WT % @ 420 F	33.67	33.67	35.73	35.73	45.86
WT % @ 700 F	76.33	76.33	73.14	73.14	80.44

TABLE 11 RESULT OF SYNGAS OPERATION

RUN NO. 10112-13
CATALYST CO/TH +UCC-108 #10252-28C 80 CC 31.8GM (33.6 AFTER RUN +1.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-13-11
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	138.0
PRESSURE,PSIG	296
TEMP. C	281
FEED CC/MIN	400
HOURS FEEDING	24.00
EFFLNT GAS LITER	251.05
GM AQUEOUS LAYER	30.15
GM OIL	16.65
MATERIAL BALANCE	
GM ATOM CARBON %	103.74
GM ATOM HYDROGEN %	99.53
GM ATOM OXYGEN %	101.54
RATIO CHX/(H2O+CO2)	1.0440
RATIO X IN CHX	2.9077
USAGE H2/CO PRODT	1.0753
RATIO CO2/(H2O+CO2)	0.6837
K SHIFT IN EFFLNT	0.99
CONVERSION	
ON CO %	83.07
ON H2 %	91.93
ON CO+H2 %	87.41
PRDT SELECTIVITY,WT %	
CH4	40.68
C2 HC'S	5.31
C3H8	6.37
C3H6=	1.94
C4H10	4.26
C4H8=	2.94
C5H12	4.33
C5H10=	2.43
C6H14	4.21
C6H12= & CYCLO'S	0.38
C7+ IN GAS	9.10
LIQ HC'S	18.05
TOTAL	100.00

SUB-GROUPING	
C1 -C4	61.50
C5 -420 F	28.73
420-700 F	6.24
700-END PT	3.53
C5+-END PT	38.50
ISO/NORMAL MOLE RATIO	
C4	0.0343
C5	0.1176
C6	0.2927
C4=	0.1585
PARAFFIN/OLEFIN RATIO	
C3	3.1353
C4	1.3990
C5	1.7334
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL WAX
DENSITY	0.751
N, REFRACTIVE INDEX	1.4255
SIMULT'D DISTILATN	
10 WT % @ DEG F	258
16	298
50	443
84	731
90	778
RANGE(16-84 %)	433
WT % @ 420 F	45.86
WT % @ 700 F	80.44

VI. RUN 5 (110225-07) with Catalyst 5 (Co/Th + UCC-108)

Like Catalysts 2 and 3, this catalyst was intended for use in determining a favorable metal loading ratio of cobalt metal component to Molecular Sieve, in this case UCC-108. Preparation and composition were identical to those of Catalyst 2 except the substitution of UCC-108 for 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. 75-78. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 79-80. Carbon number product distributions are plotted in Figs. 81-88. Chromatograms from simulated distillations are reproduced in Figs. 89-96. Detailed material balances appear in Tables 12-14.

At 270C this catalyst was more active than Catalyst 4 at 250C, but less active than Catalyst 4 at 280C. The initial conversion was similar to that of Catalyst 3, the two runs having been the same except for the different Molecular Sieves. Deactivation was much lower than with Catalyst 3, resulting in ~25 percent higher syngas conversion at the end of the run. The water gas shift activity was low, with ~20 percent of the oxygen rejected as CO_2, the rest as H_2O. Thus the catalyst was effectively exposed to the H_2:CO syngas in a ratio of only 0.25:1. Even in such a hydrogen-poor environment, however, the catalyst was unu-

sually stable.

There was some deactivation, the product becoming lighter with time and the proportion of methane higher. The product distribution was similar to that of Catalyst 3, the principal difference being in the 700+ fraction, of which this catalyst produced only 2.5 percent and Catalyst 3 produced 6 percent.

The distribution was much better than that of Catalyst 4 at 280C, and generally better than that of Catalyst 4 at 250C. The initial selectivity to total motor fuels was fairly good at ~69 percent. This time, however, the fall-off was due not to wax build-up in the reactor, since the wax did not increase and the initial material balance was good, but to a true shift in selectivity as with Catalyst 3.

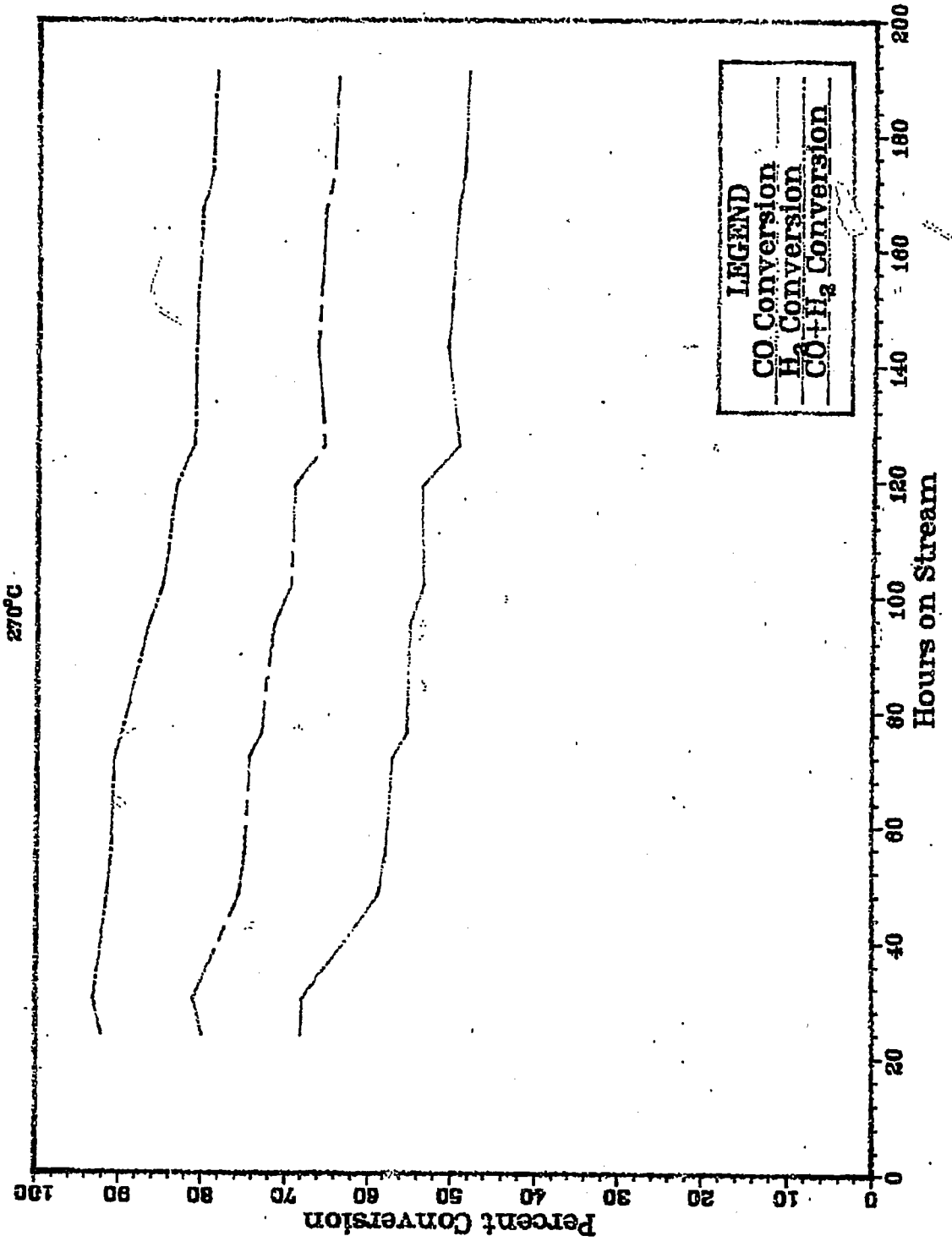
The C_4's were only slightly more olefinic than with Catalyst 3, but much more so than with Catalyst 4. The pentane was less isomerized than with Catalyst 3--a result contrary to that with iron catalysts, in which isomerization is higher with UCC-108 than with UCC-101. Consistent with this result, chromatograms of the simulated distillations show that the liquid was poorly isomerized.

Both the gasoline and jet fuel fractions were substantially more olefinic than with Catalyst 3--respectively ~63 vs. 36 percent, and ~52 vs. 32 percent--even though the C_4's were equally olefinic for both. The fall-off of percent olefins with increasing carbon number, common with F-T catalysts, was more gradual with this catalyst than with Catalyst 3. The olefins also affect

the pour points of the jet and diesel fuels; compared with Catalyst 3 the jet fuel pour point is -15F vs. ØF, and the diesel fuel pour point 10F vs. 50F, both being signs of improved product. The Schulz-Flory plots, aside from the usual excess of methane, are fairly straight, with a possible slight decrease in above the diesel range.

This formulation is far superior to Catalyst 4, in which the Molecular Sieve was overwhelmed by the metal component. From comparison of this catalyst with Catalyst 3, however, it is still not clear whether UCC-101 or UCC-108 is more effective in combination with cobalt.

Fig. 75


RUN 10225-07
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

RUN 10225-07

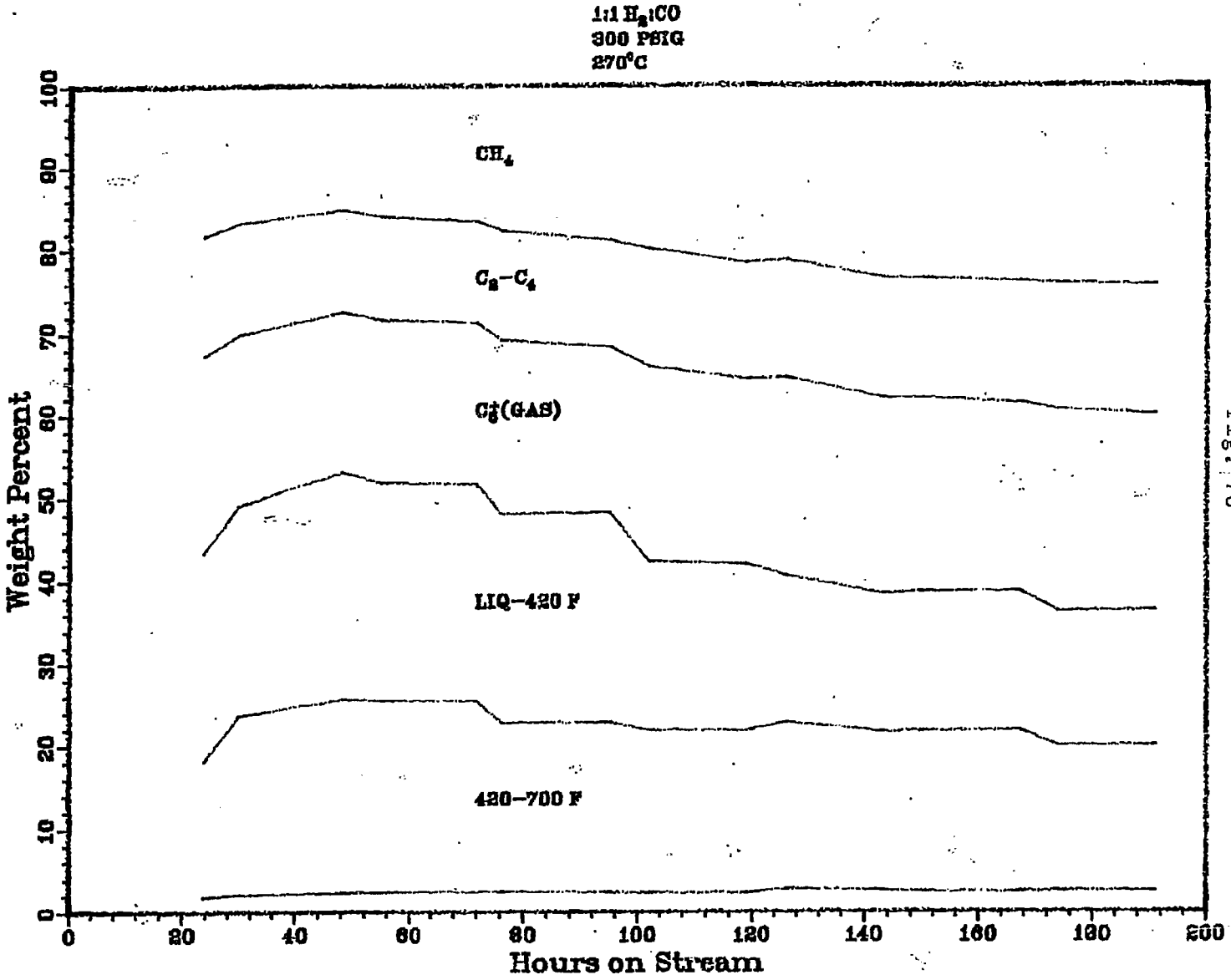


Fig. 76

RUN 10225--07

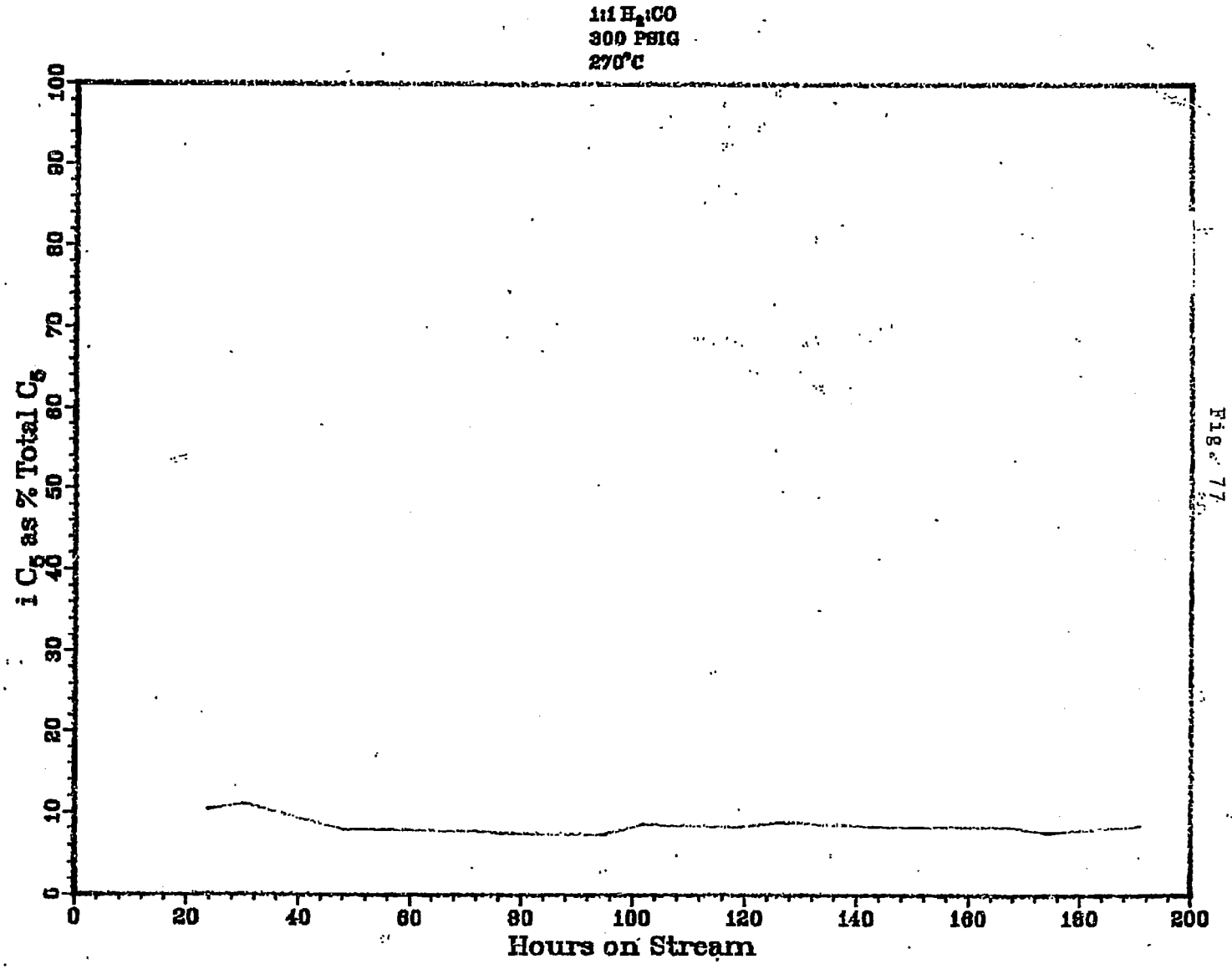


Fig. 77

RUN 10225-07

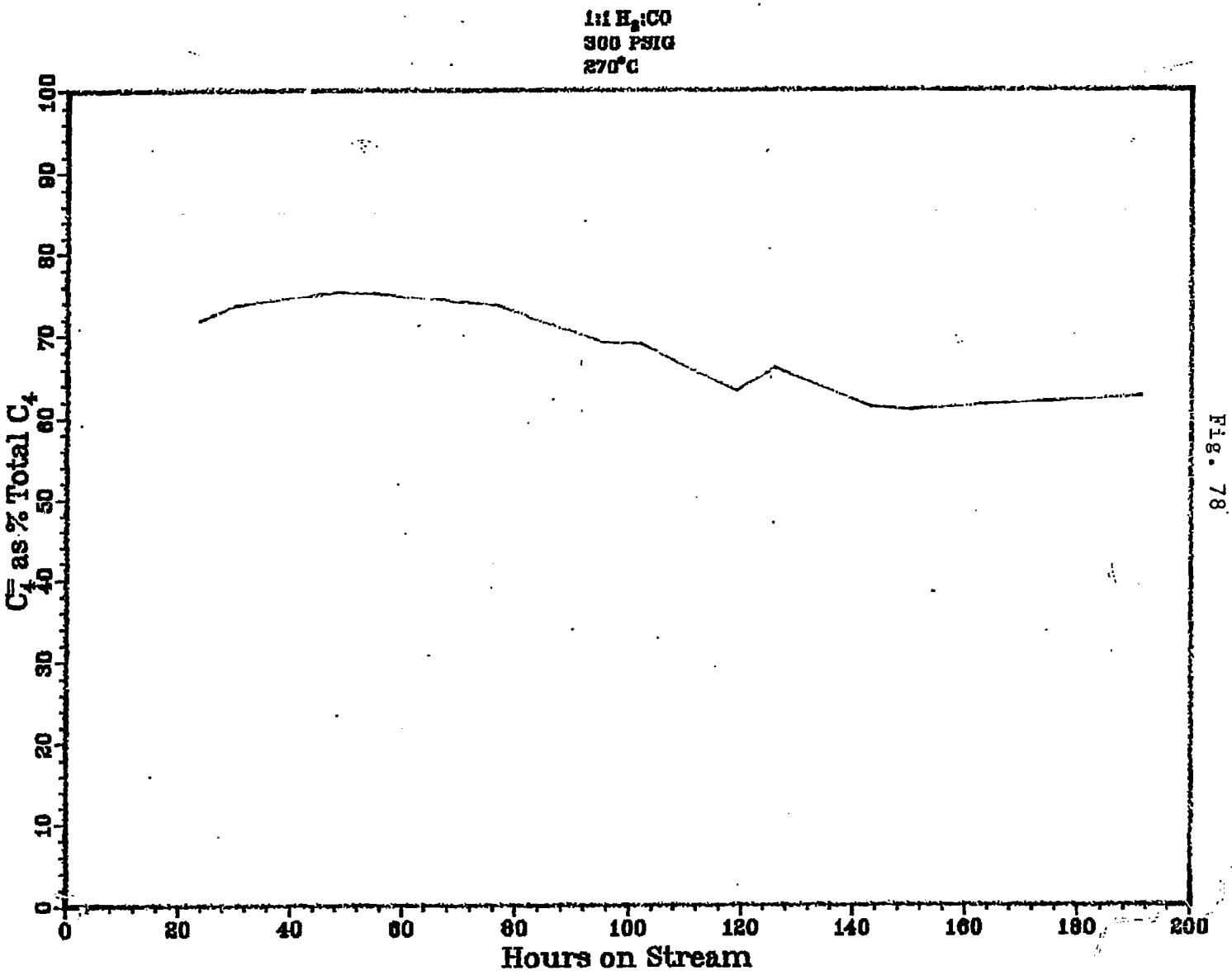


Fig. 78

Fig. 79

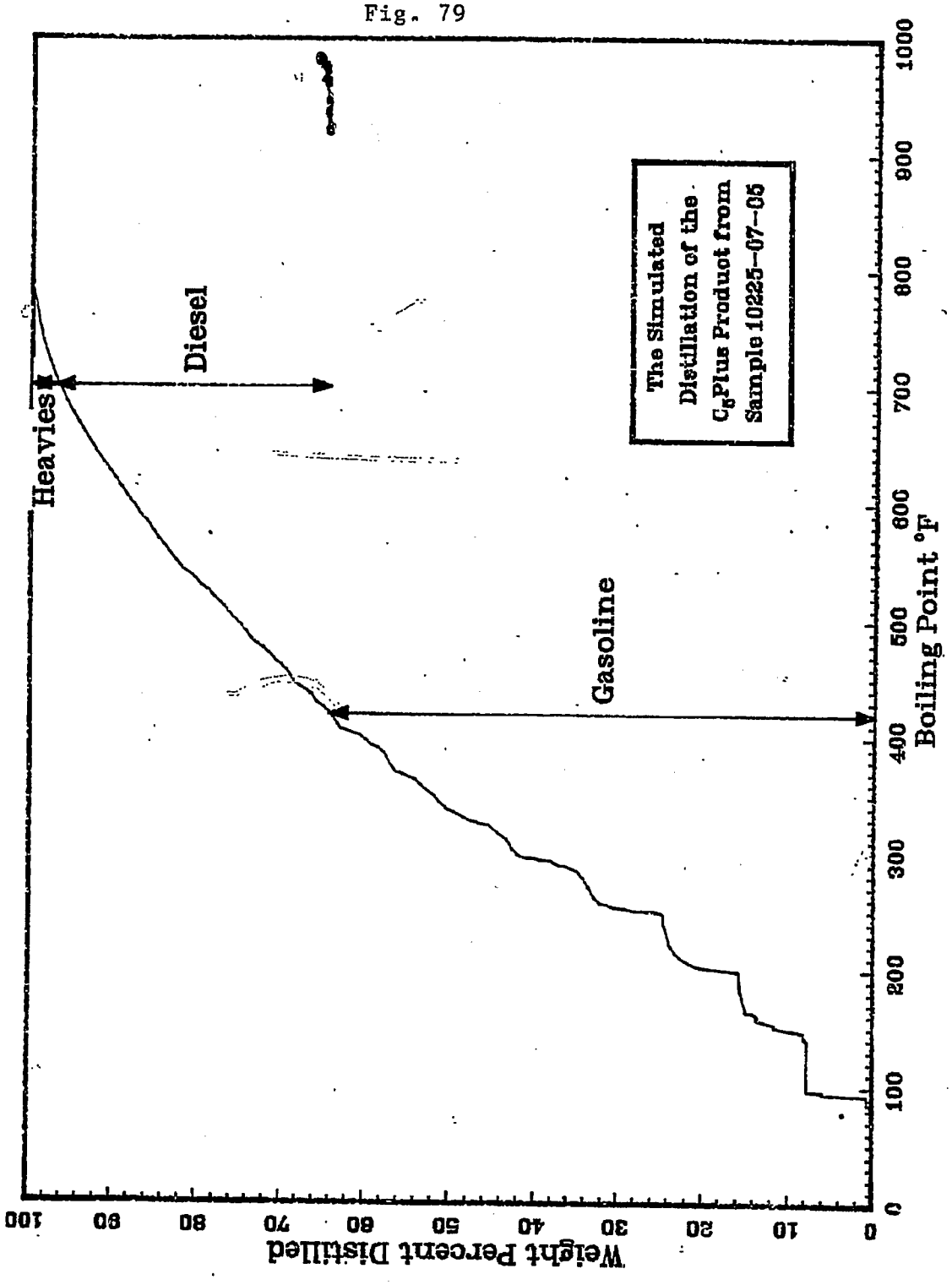

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C_5Plus Product from Sample 10225-07-05

Fig. 80

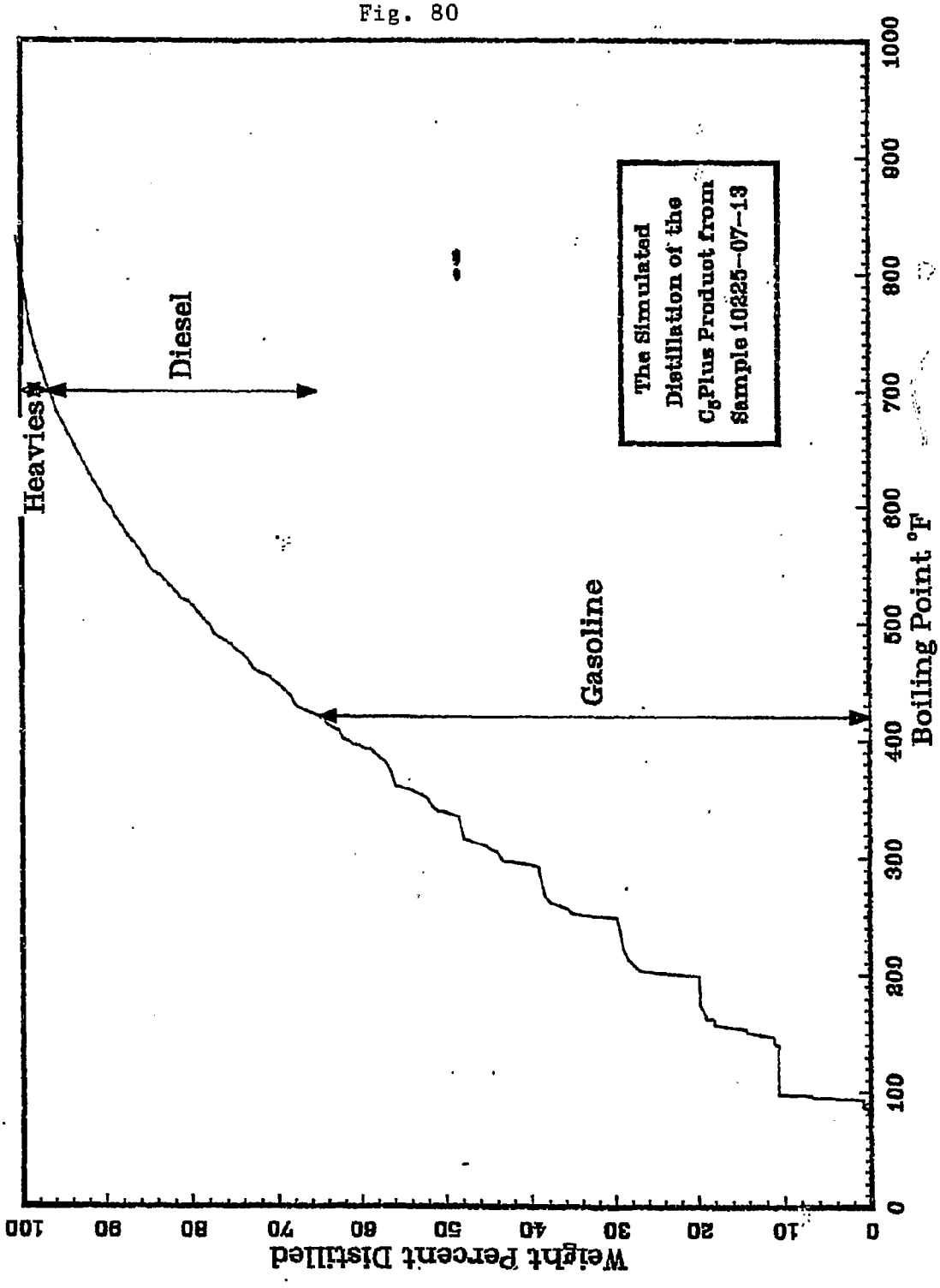

The Simulated Distillation of the C_5 Plus Product from Sample 10225-07-13
Heavies
Diesel
Gasoline
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000

Fig. 81

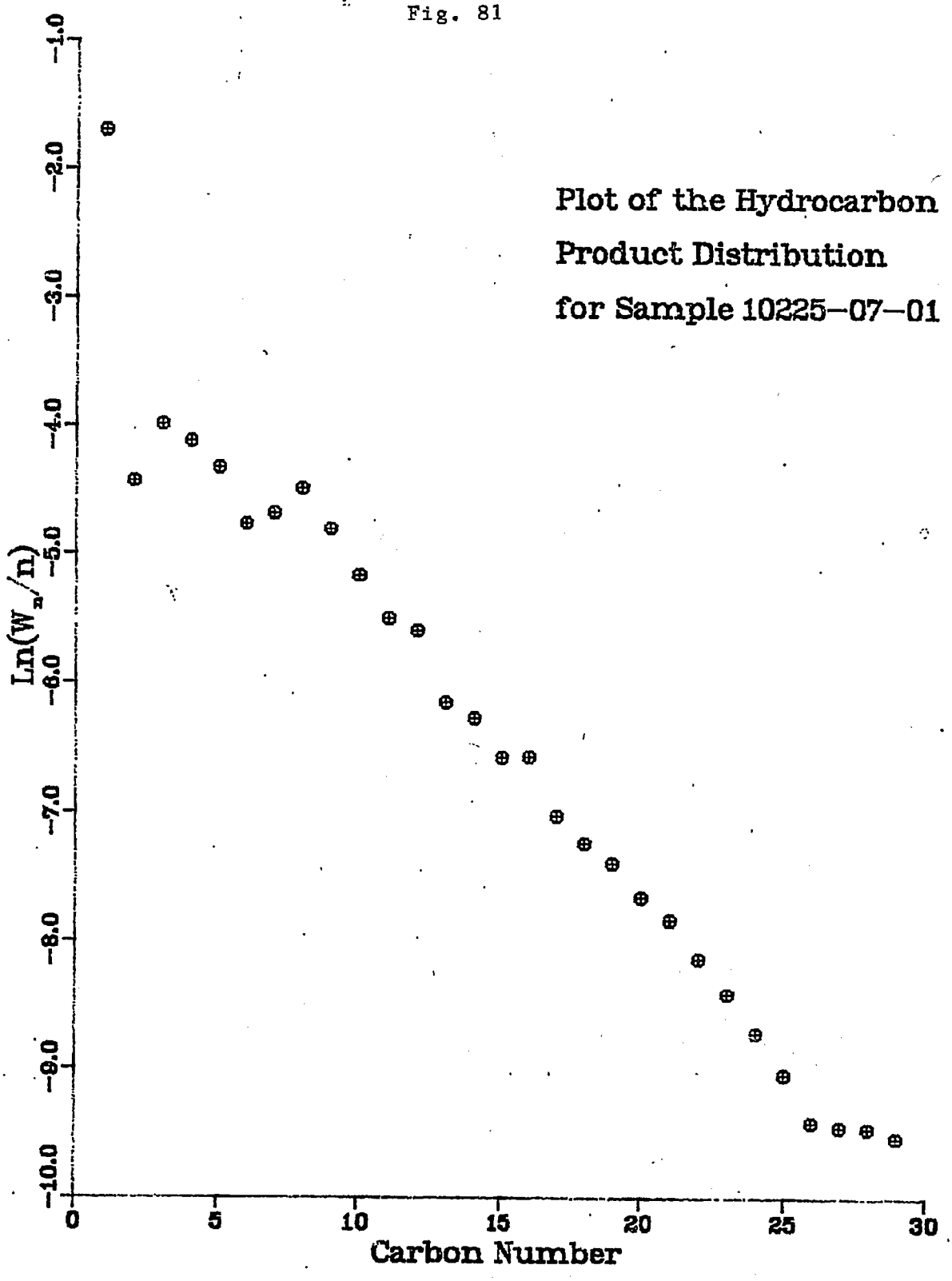

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-07-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 82

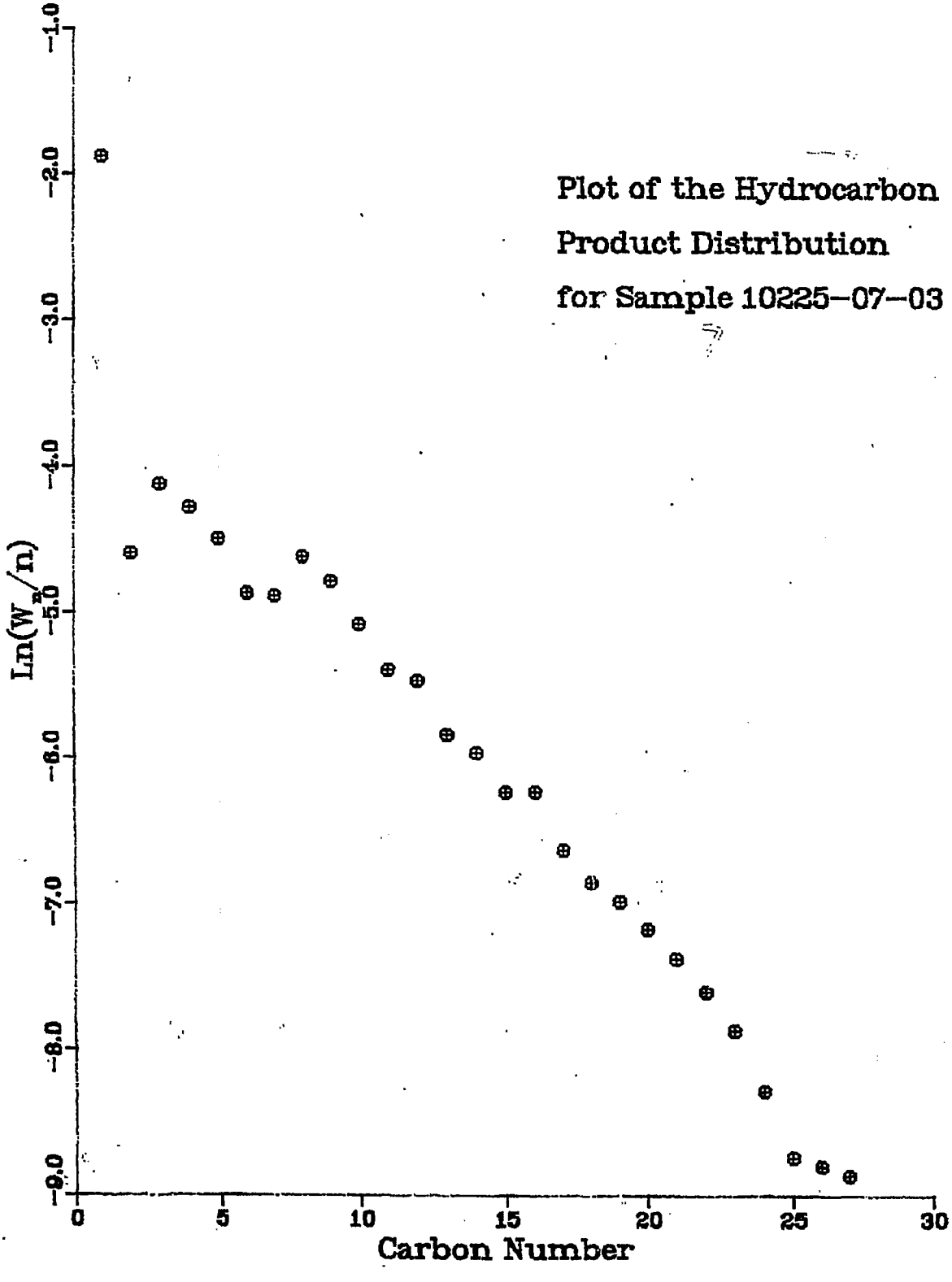

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-07-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. 83

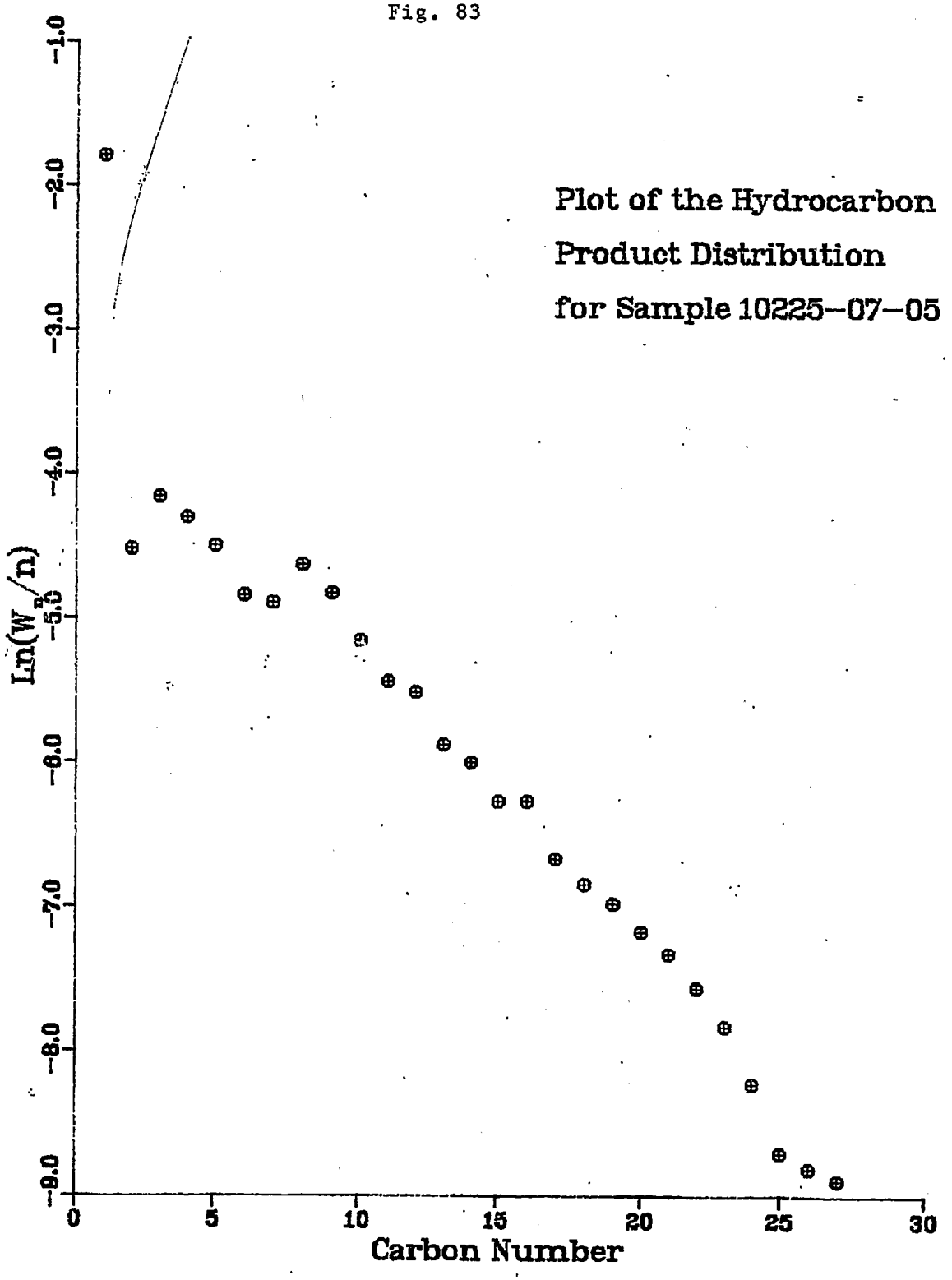

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-07-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. 84

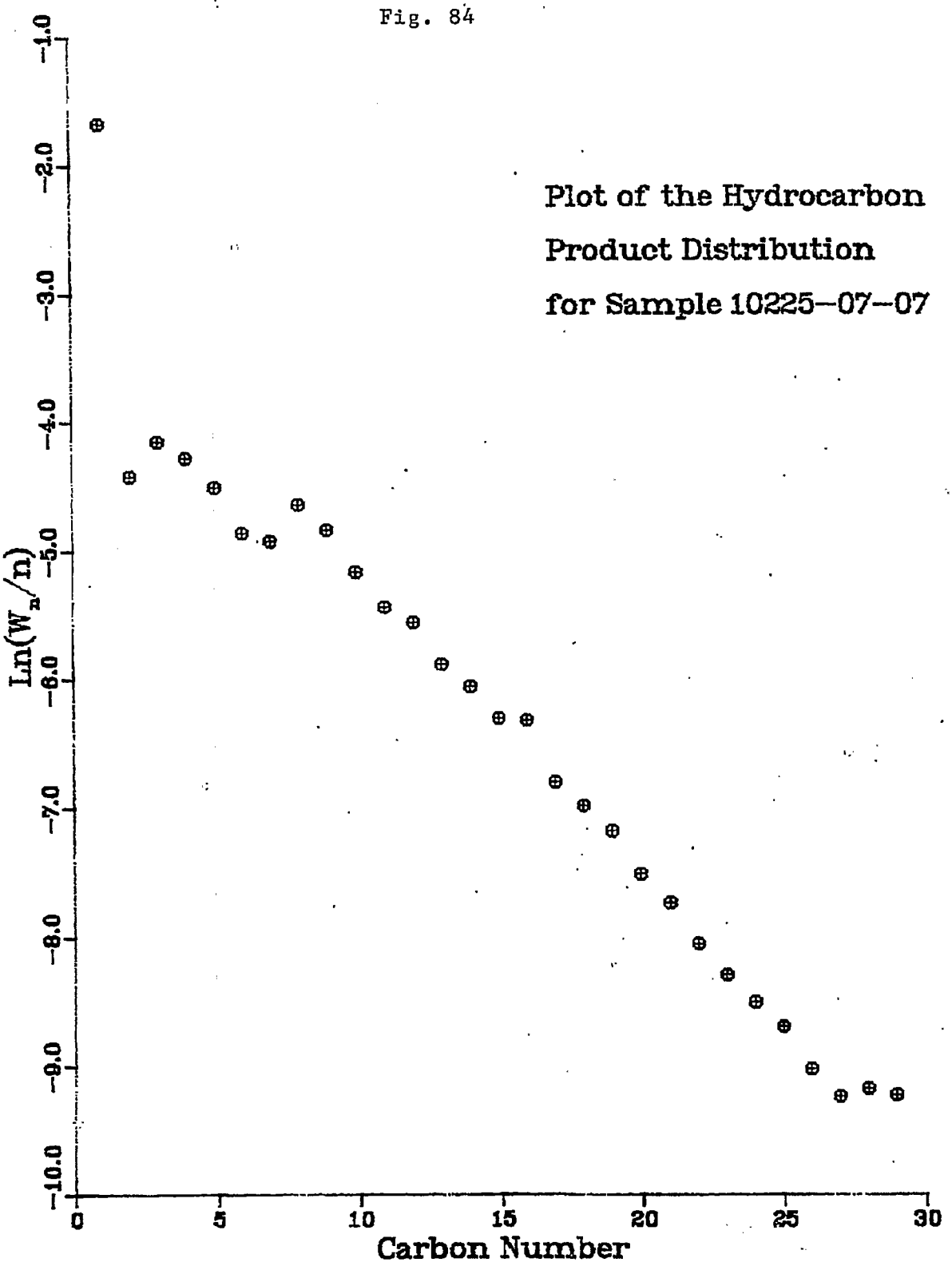

Plot of the Hydrocarbon
Product Distribution
for Sample 10225--07--07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 85

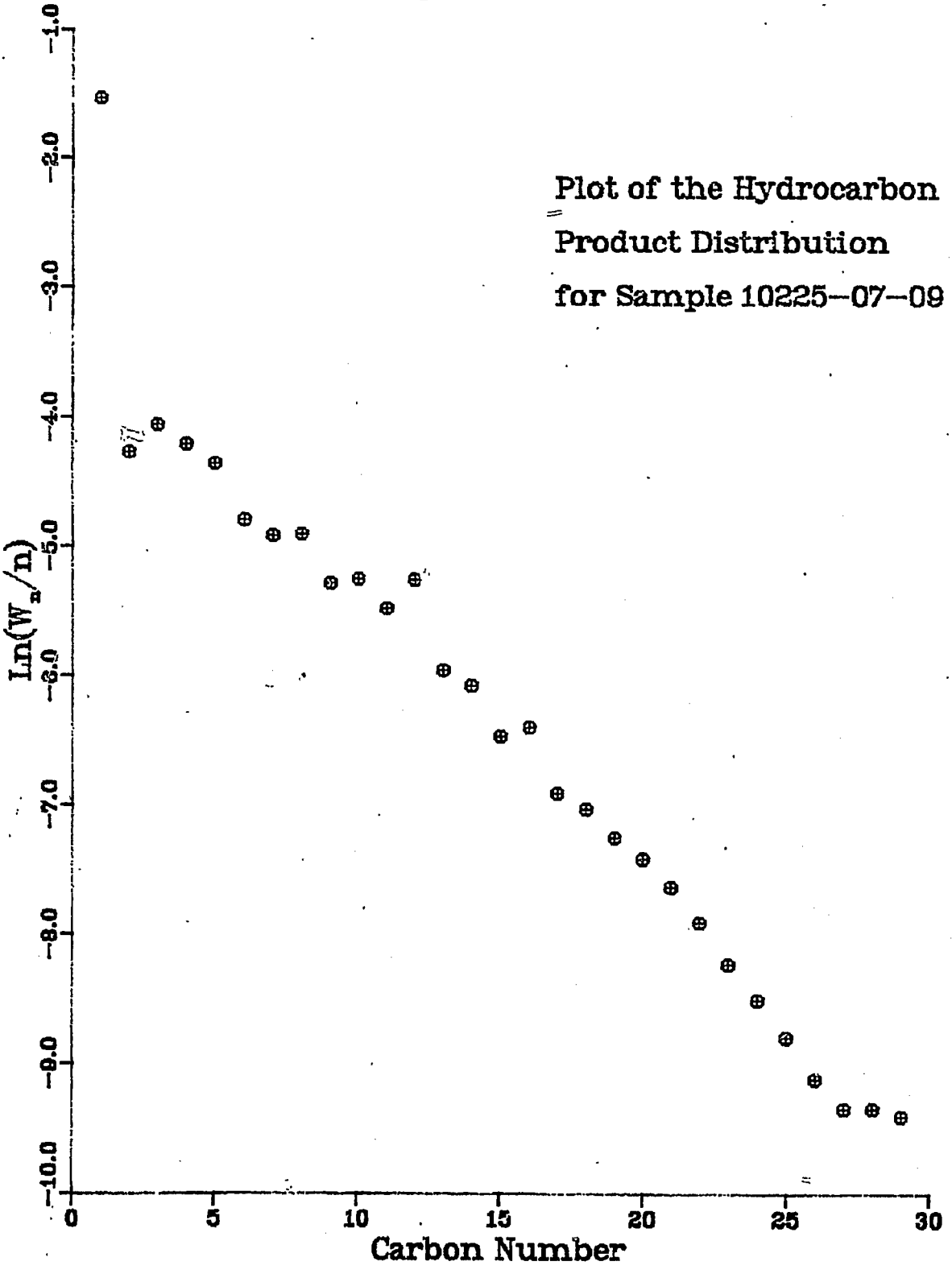

Plot of the Hydrocarbon
Product Distribution
for Sample 10225--07--09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 86

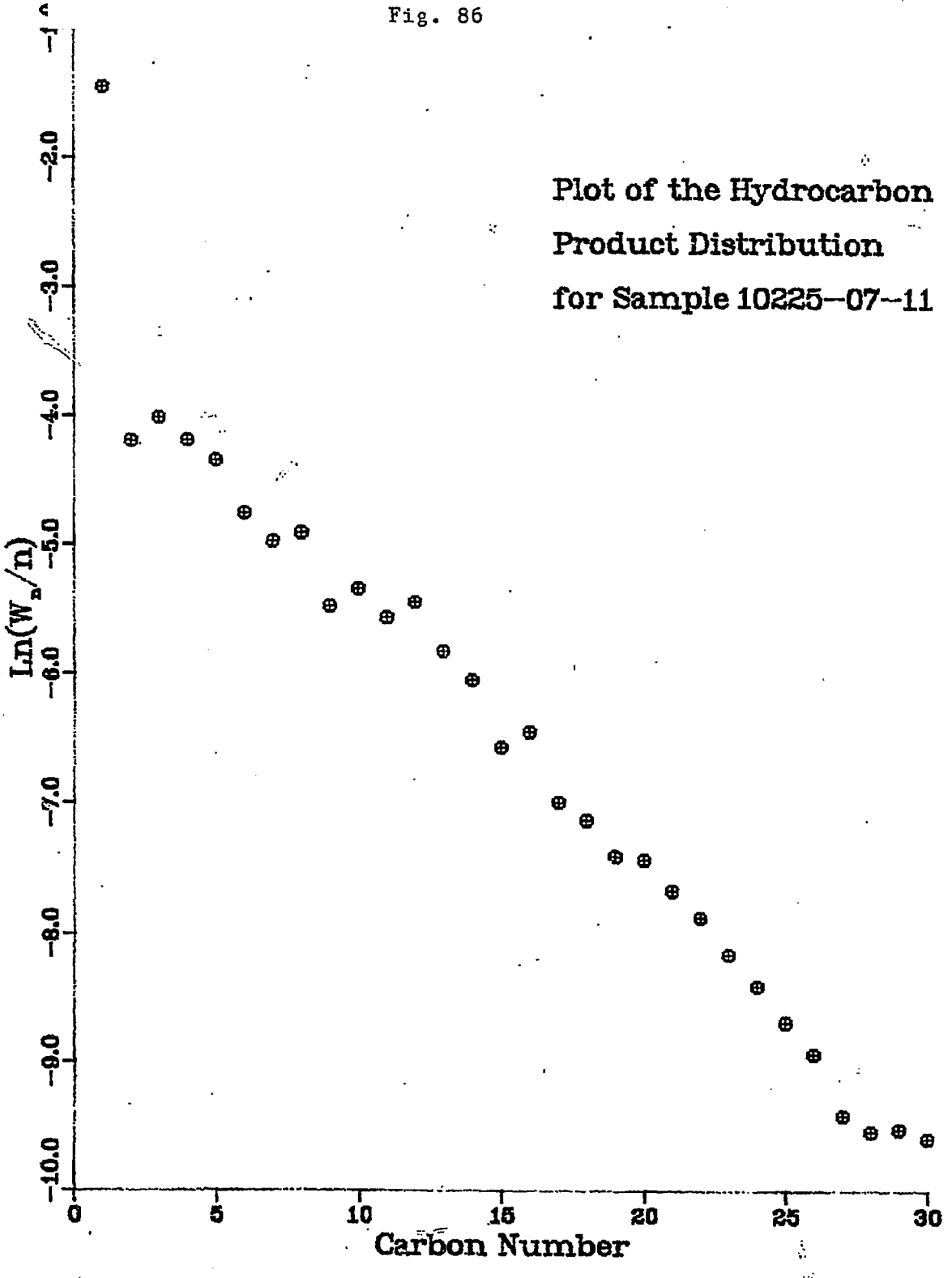

Plot of the Hydrocarbon
Product Distribution
for Sample 10225--07--11
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 87

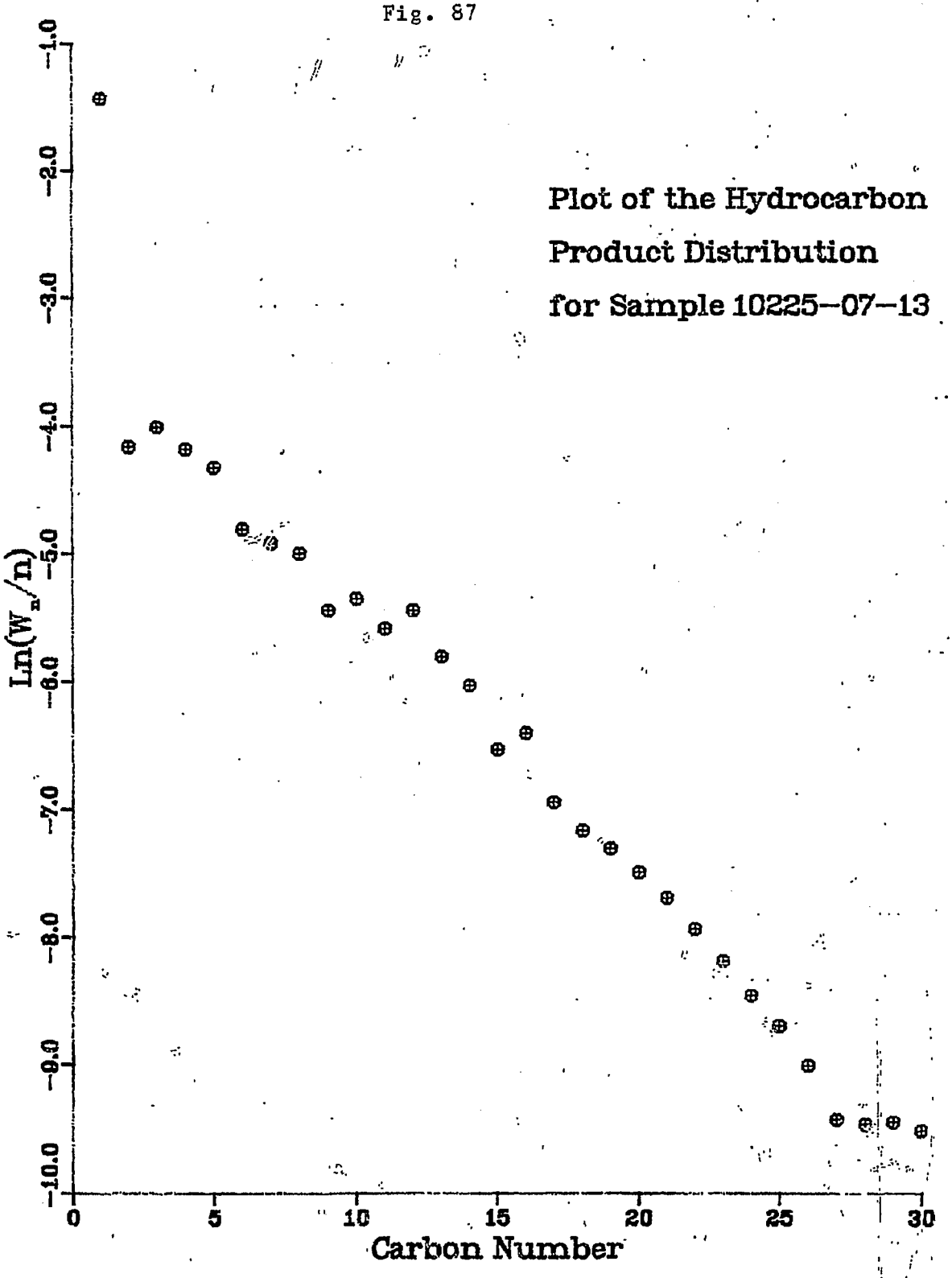

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-07-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 88

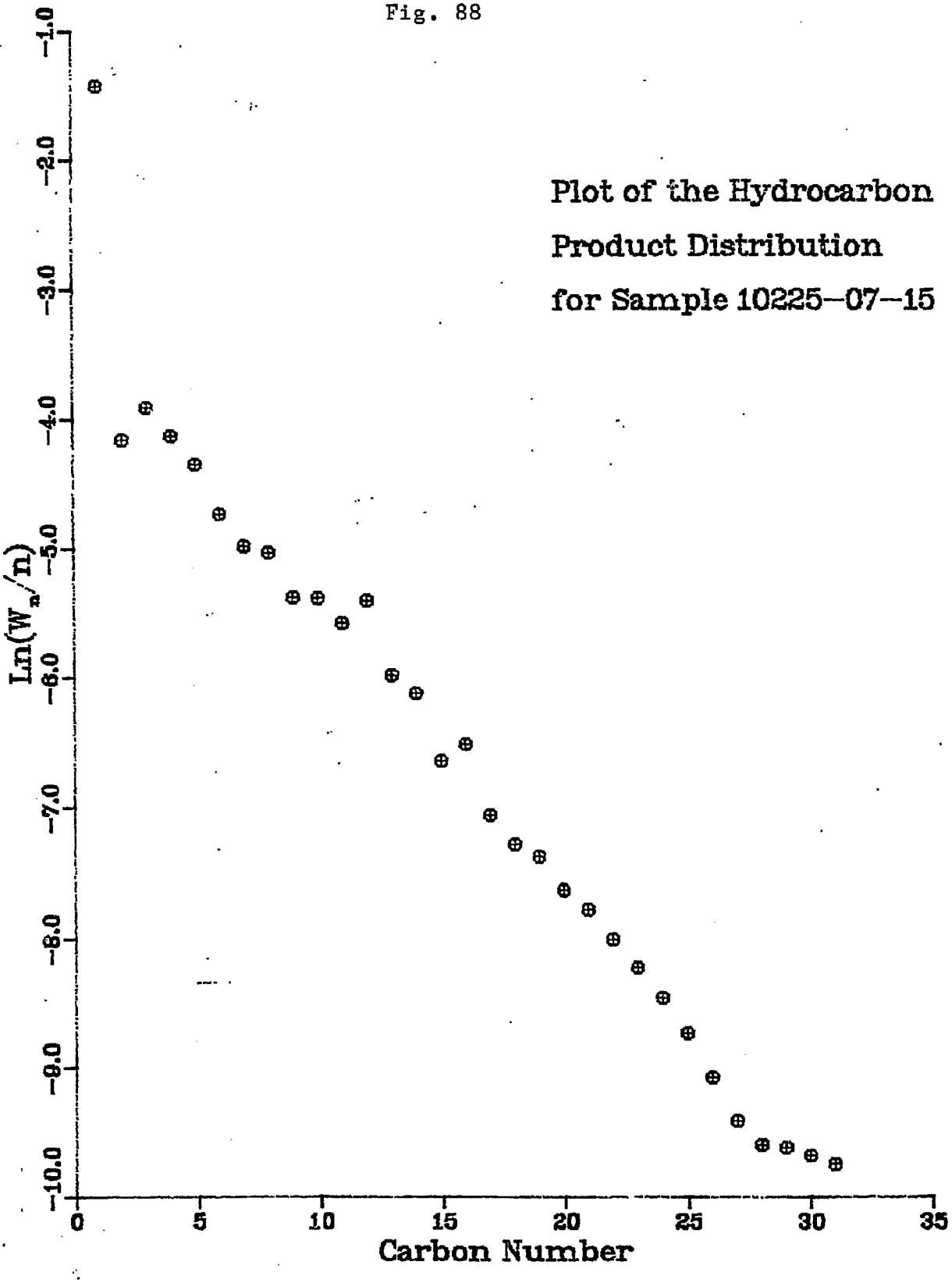
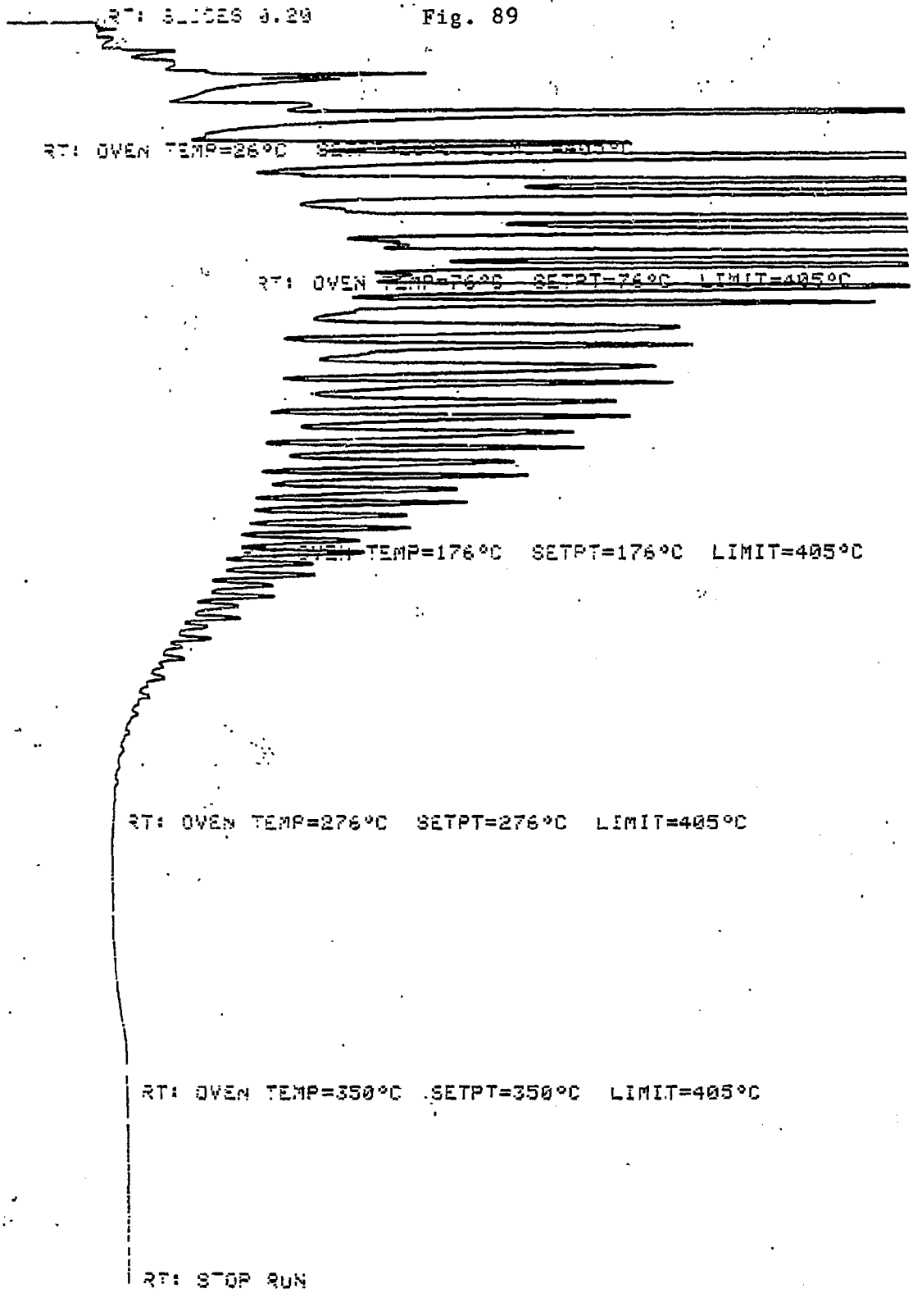

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-07-15
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 89



SAMPLE:10225-7-IL

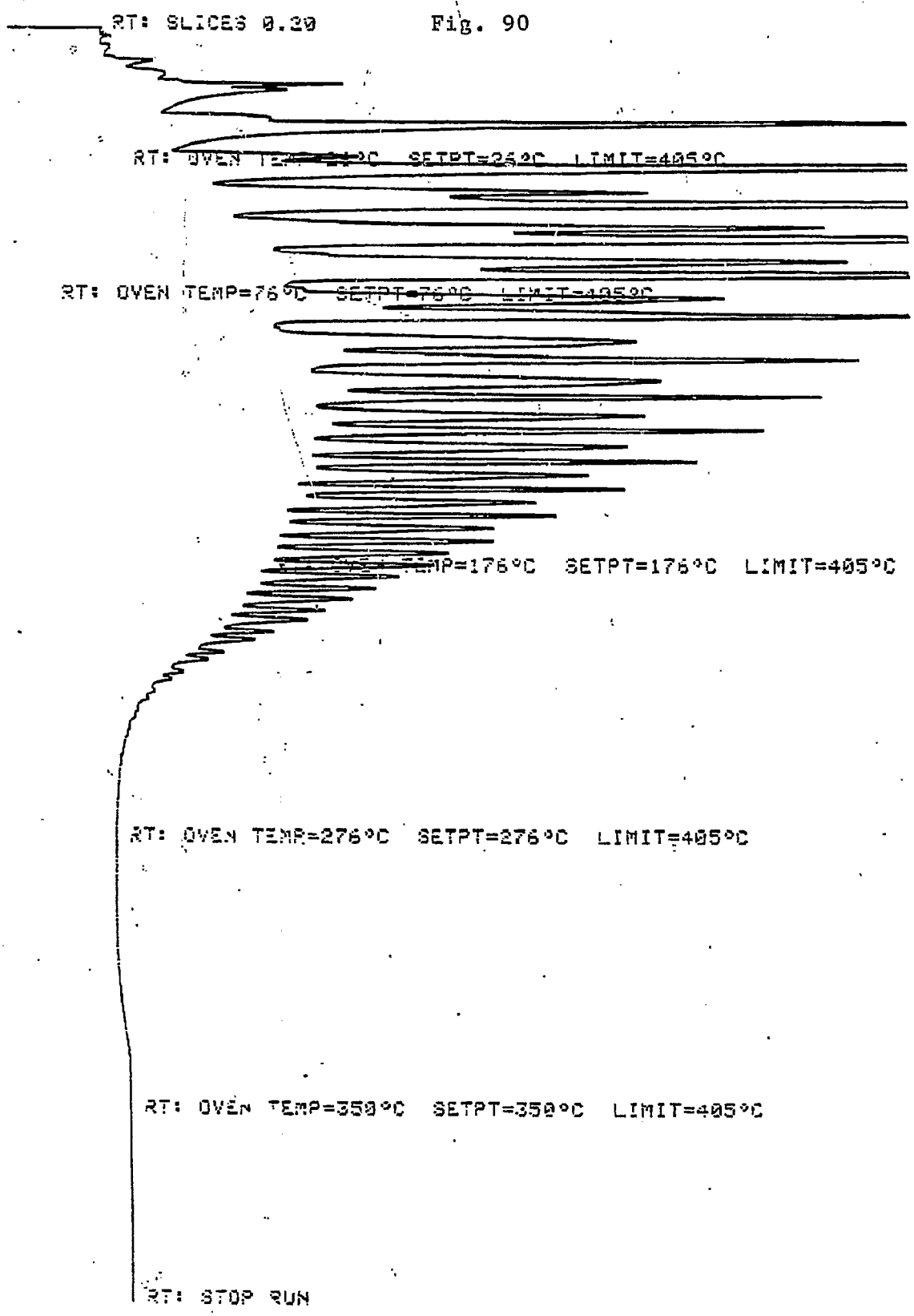
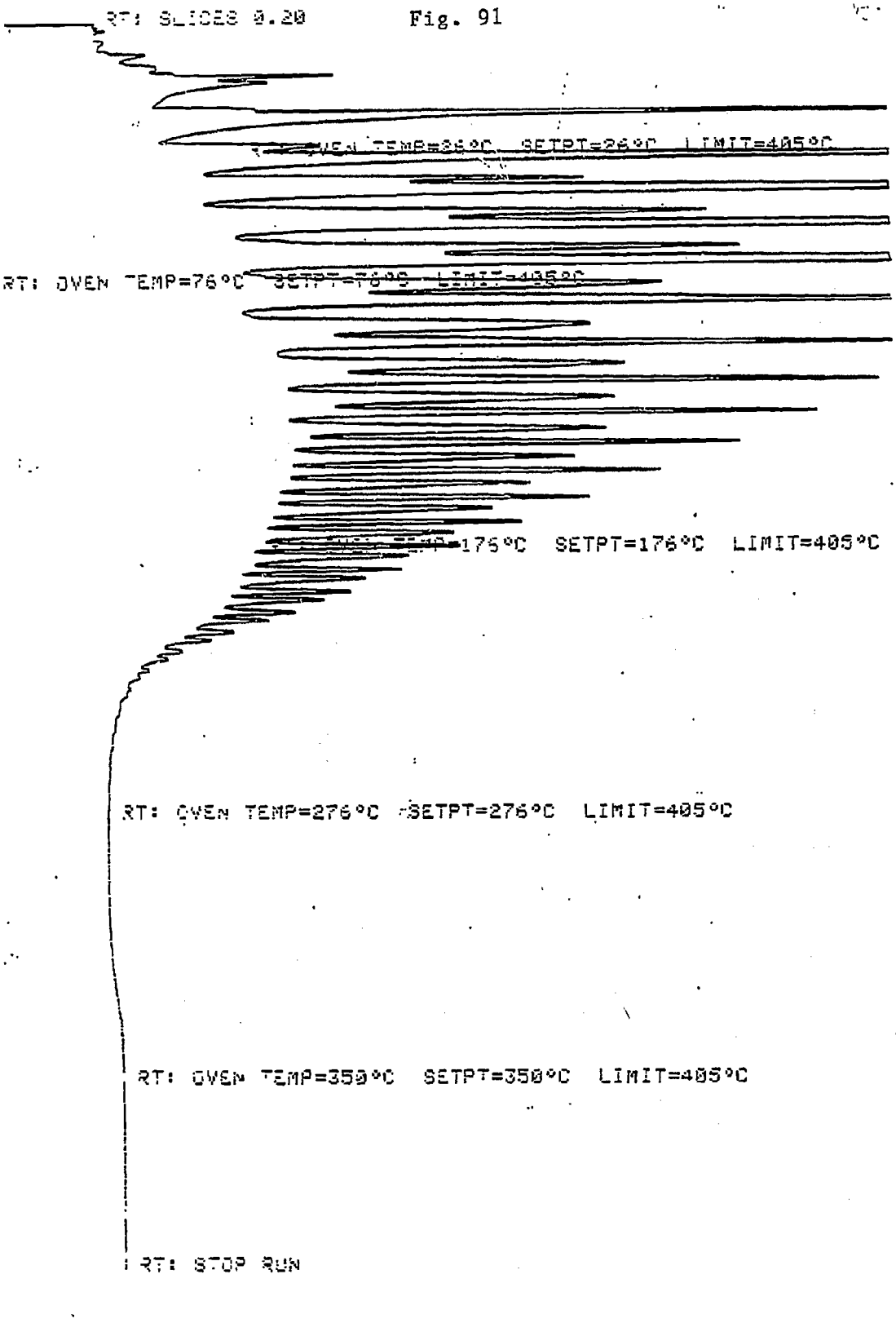

RT: SLICES 0.20
RT: OVEN TEMP=264°C SETPT=264°C LIMIT=405°C
RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:10225-7-3L

Fig. 90

Fig. 91



SAMPLE:10225-7-5L

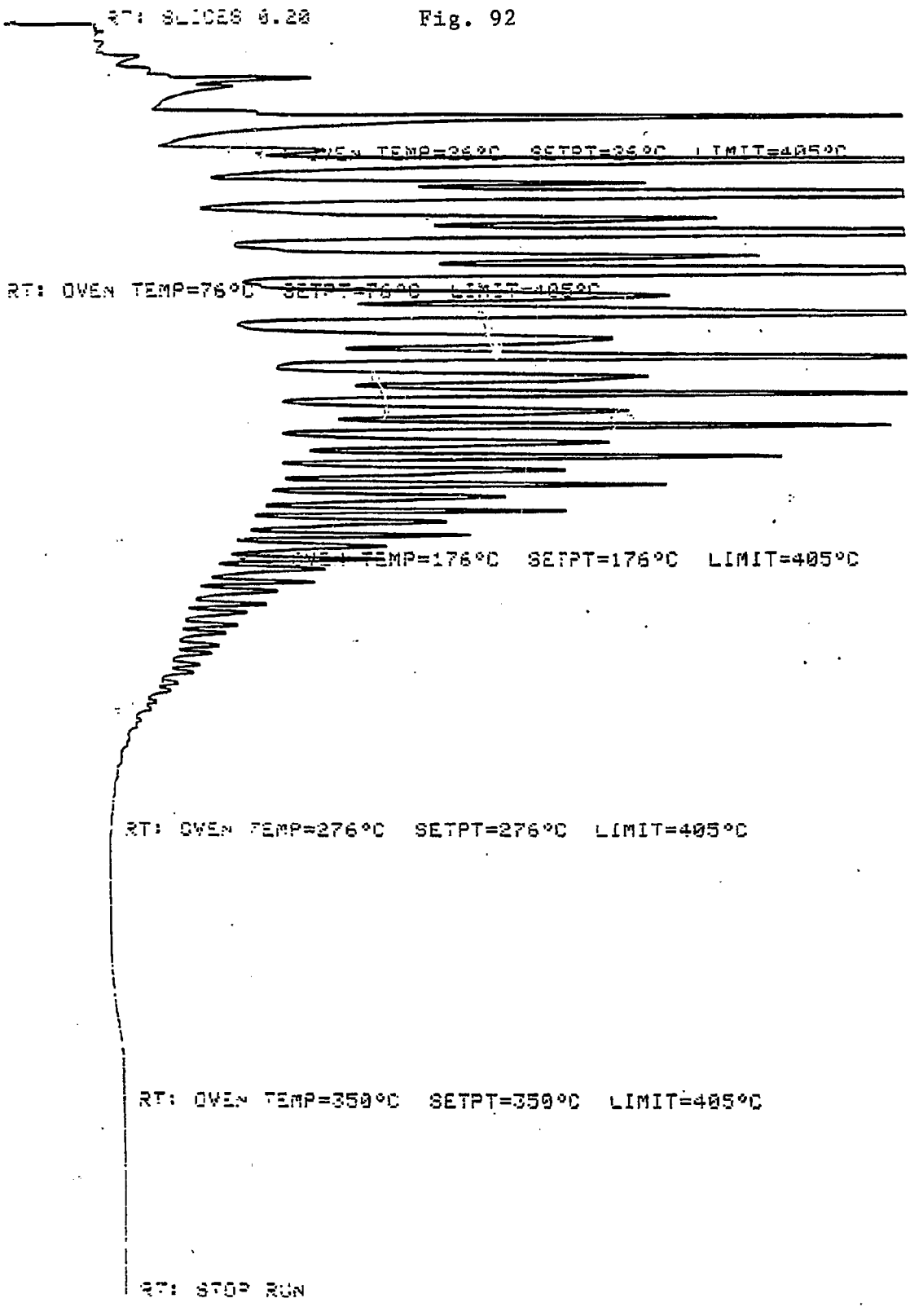
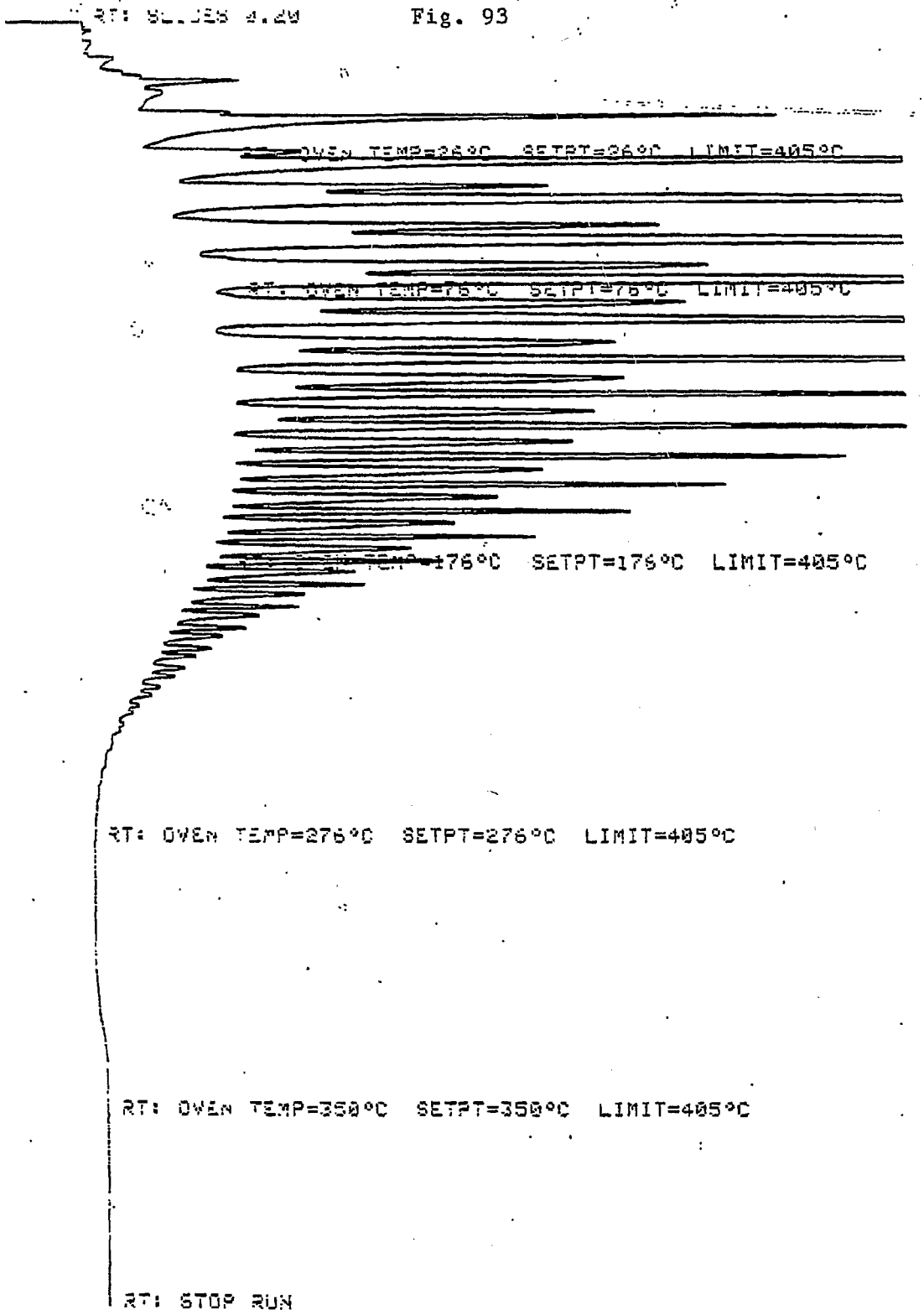


Fig. 92

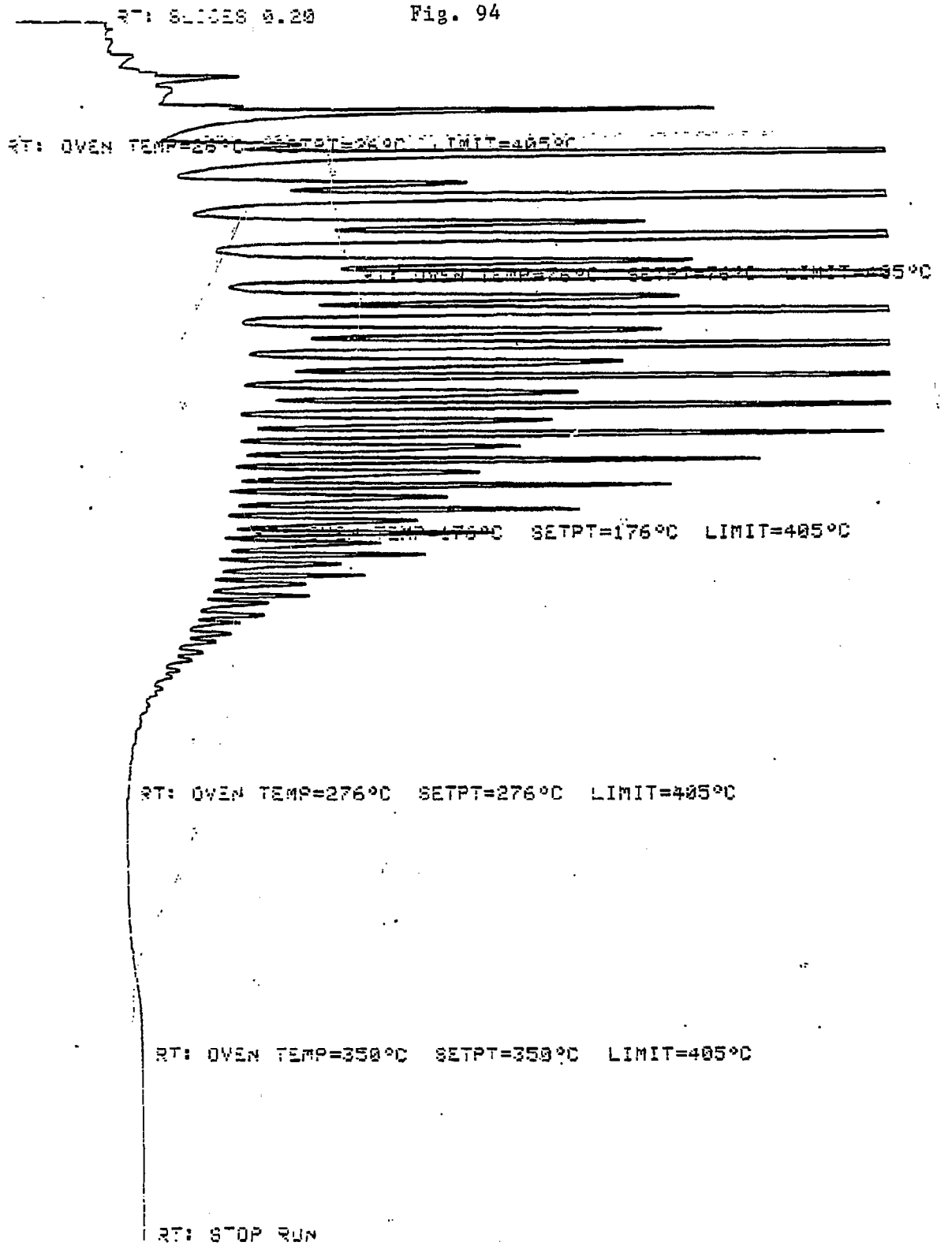
SAMPLE:10225-7-7L

Fig. 93



SAMPLE:10225-7-9L

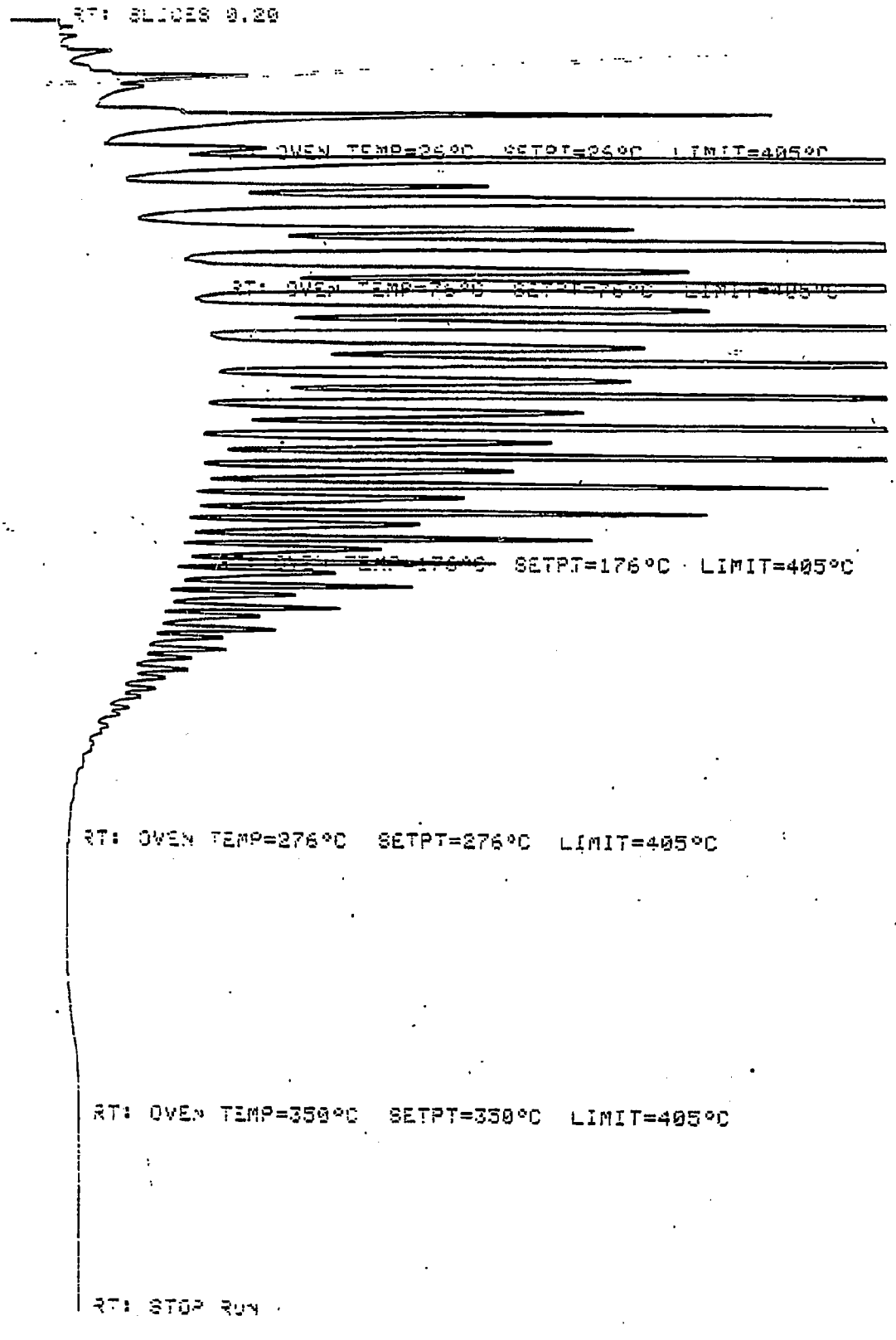
Fig. 94



SAMPLE:10225-7-11L

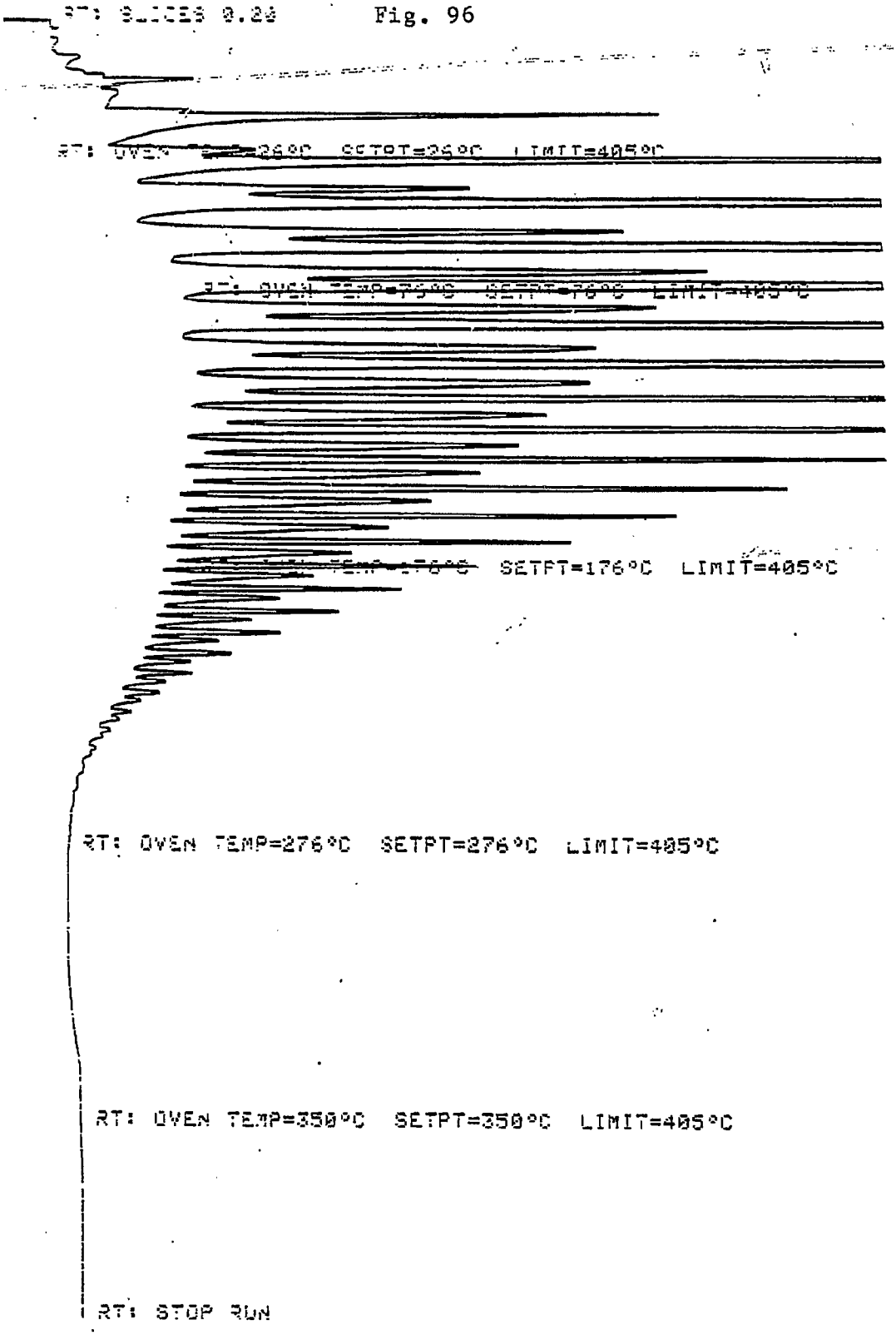
OVEN TEMP NOT READY

Fig, 95



SAMPLE:10225-7-13L

Fig. 96



SAMPLE:10225-7-15L

TABLE 12 RESULT OF SYNGAS OPERATION

RUN NO. 10225-07
CATALYST CO/TH +UCC-108 #10252-44C 80 CC 51.9GM (59.0 AFTER RUN +7. G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-07-01	225-07-02	225-07-03	225-07-04	225-07-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	23.75	30.0	48.08	55.08	72.0
PRESSURE,PSIG	295	299	300	298	300
TEMP. C	273	273	269	269	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	23.75	6.25	24.33	7.00	23.92
EFFLNT GAS LITER	182.05	48.00	193.65	57.70	199.80
GM AQUEOUS LAYER	56.58	20.29	79.01	23.42	80.01
GM OIL	31.51	10.14	39.48	11.05	37.75
MATERIAL BALANCE					
GM ATOM CARBON %	87.71	91.46	90.71	91.90	92.27
GM ATOM HYDROGEN %	86.06	99.43	95.97	97.87	98.68
GM ATOM OXYGEN %	89.64	98.29	95.62	98.18	97.84
RATIO CHX/(H2O+CO2)	0.9568	0.8719	0.8977	0.8725	0.8855
RATIO X IN CHX	2.3926	2.3571	2.3213	2.3367	2.3489
USAGE H2/CO PRODT	1.3068	1.4113	1.5728	1.5808	1.6127
RATIO CO2/(H2O+CO2)	0.3755	0.2931	0.2136	0.2090	0.1989
K SHIFT IN EFFLNT	0.15	0.10	0.06	0.06	0.06
CONVERSION					
ON CO %	68.09	67.95	58.83	57.89	57.10
ON H2 %	92.15	93.05	91.48	91.00	90.65
ON CO+H2 %	80.00	81.03	75.61	74.97	74.44
PRDT SELECTIVITY,WT %					
CH4	18.25	16.73	15.20	15.96	16.56
C2 HC'S	2.39	2.20	2.01	2.07	2.16
C3H8	2.74	2.36	1.97	2.01	2.02
C3H6=	2.81	2.79	2.88	2.76	2.65
C4H10	1.88	1.65	1.39	1.43	1.44
C4H8=	4.63	4.44	4.08	4.17	3.94
C5H12	1.85	1.66	1.39	1.45	1.47
C5H10=	4.77	4.41	4.15	4.26	4.06
C6H14	2.19	1.92	1.63	1.68	1.74
C6H12= & CYCLO'S	2.49	2.57	2.79	2.85	2.85
C7+ IN GAS	12.56	10.17	9.40	9.52	9.44
LIQ HC'S	43.44	49.10	53.12	51.84	51.67
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	32.71	30.17	27.53	28.39	28.77
C5 -420 F	49.05	46.10	46.80	46.06	45.76
420-700 F	16.40	21.59	23.36	23.15	23.07
700-END PT	1.85	2.14	2.32	2.41	2.40
C5+-END PT	67.29	69.83	72.47	71.61	71.23
ISO/NORMAL MOLE RATIO					
C4	0.0458	0.0439	0.0362	0.0400	0.0351
C5	0.1159	0.1243	0.0862	0.0858	0.0838
C6	0.2050	0.2148	0.1454	0.1455	0.1421
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.9307	0.8072	0.6526	0.6964	0.7281
C4	0.3928	0.3584	0.3288	0.3312	0.3526
C5	0.3769	0.3660	0.3268	0.3317	0.3531
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	-	CLR OIL	-	CLR OIL
DENSITY	0.748		0.754		0.753
N, REFRACTIVE INDEX	1.4240		1.4262		1.4266
SIMULT'D DISTILATN					
10 WT % @ DEG F	244		254		254
16	261		283		285
50	391		409		415
84	573		598		604
90	628		645		650
RANGE(16-84 %)	312		315		319
WT % @ 420 F	58.00	51.67	51.67	50.71	50.71
WT % @ 700 F	95.75	95.64	95.64	95.36	95.36

TABLE 13 RESULT OF SYNGAS OPERATION

RUN NO. 10225-07
CATALYST CO/TH +UCC-108 #10252-44C 80 CC 51.9GM (59.0 AFTER RUN +7. G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-07-06	225-07-07	225-07-08	225-07-09	225-07-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	76.33	95.0	102.0	119.0	126.0
PRESSURE,PSIG	303	295	299	303	303
TEMP. C	269	269	269	268	268
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	4.33	23.00	7.00	24.00	7.00
EFFLNT GAS LITER	37.12	207.75	69.45	244.05	73.20
GM AQUEOUS LAYER	14.00	74.33	20.67	70.88	19.35
GM OIL	6.07	32.22	8.80	30.16	7.63
MATERIAL BALANCE					
GM ATOM CARBON %	91.07	90.73	95.90	95.57	93.74
GM ATOM HYDROGEN %	96.09	99.95	100.43	103.41	97.07
GM ATOM OXYGEN %	97.40	97.30	99.00	98.47	97.94
RATIO CHX/(H2O+CO2)	0.8661	0.8607	0.9305	0.9350	0.8992
RATIO X IN CHX	2.3757	2.4002	2.4274	2.4651	2.4559
USAGE H2/CO PRODT	1.6089	1.6224	1.6110	1.6303	1.6253
RATIO CO2/(H2O+CO2)	0.2022	0.1996	0.2200	0.2187	0.2136
K SHIFT IN EFFLNT	0.06	0.08	0.10	0.11	0.11
CONVERSION					
ON CO %	55.40	55.13	53.48	53.78	49.41
ON H2 %	89.77	86.53	84.74	83.31	81.06
ON CO+H2 %	73.05	71.59	69.47	69.13	65.51
PRDT SELECTIVITY,WT %					
CH4	17.79	18.83	19.90	21.56	21.24
C2 HC'S	2.29	2.41	2.62	2.78	2.81
C3H8	2.19	2.44	2.71	2.92	2.80
C3H6=	2.81	2.32	2.57	2.24	2.45
C4H10	1.57	1.75	1.99	2.23	2.07
C4H8=	4.23	3.79	4.24	3.69	3.89
C5H12	1.62	1.78	2.16	2.40	2.20
C5H10=	4.25	3.77	4.50	3.94	4.18
C6H14	1.87	2.04	2.36	2.57	2.45
C6H12= & CYCLO'S	2.97	2.62	2.79	2.36	2.58
C7+ IN GAS	10.26	9.81	11.72	11.15	12.61
LIQ HC'S	48.15	48.42	42.44	42.15	40.72
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	30.88	31.55	34.03	35.42	35.26
C5 -420 F	46.30	45.50	44.04	42.80	41.80
420-700 F	20.39	20.50	19.61	19.48	20.19
700-END PT	2.44	2.45	2.32	2.30	2.75
C5+-END PT	69.12	68.45	65.97	64.58	64.74
ISO/NORMAL MOLE RATIO					
C4	0.0366	0.0301	0.0313	0.0323	0.0316
C5	0.0809	0.0797	0.0941	0.0905	0.0972
C6	0.1406	0.1422	0.1424	0.1497	0.1444
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.7446	1.0041	1.0059	1.2435	1.0886
C4	0.3577	0.4461	0.4516	0.5826	0.5145
C5	0.3697	0.4593	0.4654	0.5939	0.5106
LIQ HC COLLECTION					
PHYS. APPEARANCE	-	CLR OIL	-	CLR OIL	
DENSITY		0.753		0.753	
N, REFRACTIVE INDEX		1.4260		1.4260	
SIMULT'D DISTILATN					
10 WT % @ DEG F		255		262	
16		283		305	
50		407		429	
84		586		603	
90		637		652	
RANGE(16-84 %)		303		298	
WT % @ 420 F	52.60	52.60	48.33	48.33	43.67
WT % @ 700 F	94.94	94.94	94.54	94.54	93.25

TABLE 14 RESULT OF SYNGAS OPERATION

RUN NO. 10225-07
CATALYST CO/TH +UCC-108 #10252-44C 80 CC 51.9GM (59.0 AFTER RUN +7.0G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-07-11	225-07-12	225-07-13	225-07-14	225-07-15
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	143.0	150.0	167.0	174.0	191.0
PRESSURE,PSIG	297	294	301	298	298
TEMP. C	268	269	269	269	269
FEED CC/MIN	400	400	400	414	414
HOURS FEEDING	24.00	7.00	24.00	7.00	24.00
EFFLNT GAS LITER	257.50	75.45	263.60	78.90	272.80
GM AQUEOUS LAYER	66.34	19.34	66.29	19.01	65.19
GM OIL	26.17	7.67	26.31	7.14	24.49
MATERIAL BALANCE					
GM ATOM CARBON %	95.48	95.83	96.51	93.79	93.76
GM ATOM HYDROGEN %	101.51	101.57	102.41	99.51	100.11
GM ATOM OXYGEN %	97.99	98.07	98.65	95.57	95.31
RATIO CHX/(H2O+CO2)	0.9400	0.9462	0.9484	0.9548	0.9603
RATIO X IN CHX	2.5043	2.5050	2.5133	2.5209	2.5243
USAGE H2/CO PRODT	1.6501	1.6632	1.6779	1.6839	1.7031
RATIO CO2/(H2O+CO2)	0.2175	0.2128	0.2081	0.2078	0.2008
K SHIFT IN EFFLNT	0.11	0.11	0.11	0.11	0.11
CONVERSION					
ON CO %	50.77	50.33	49.61	48.86	48.40
ON H2 %	80.84	80.80	80.20	79.05	78.54
ON CO+H2 %	66.27	66.01	65.36	64.40	63.96
PRDT SELECTIVITY,WT %					
CH4	23.32	23.41	23.78	24.04	24.23
C2 HC'S	3.02	3.00	3.10	3.11	3.14
C3H8	3.19	3.15	3.20	3.37	3.33
C3H6=	2.22	2.25	2.25	2.44	2.72
C4H10	2.41	2.39	2.38	2.47	2.48
C4H8=	3.66	3.59	3.68	3.87	3.99
C5H12	2.59	2.54	2.60	2.67	2.65
C5H10=	3.92	3.75	3.95	3.97	3.83
C6H14	2.76	2.72	2.66	2.87	2.88
C6H12= & CYCLO'S	2.40	2.28	2.20	2.43	2.39
C7+ IN GAS	11.92	12.13	11.33	12.31	11.82
LIQ HC'S	38.59	38.79	38.87	36.46	36.54
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	37.81	37.79	38.39	39.30	39.88
C5 -420 F	40.45	40.36	39.71	40.65	40.02
420-700 F	19.13	19.38	19.42	17.56	17.60
700-END PT	2.61	2.47	2.47	2.49	2.50
C5+-END PT	62.19	62.21	61.61	60.70	60.12
ISO/NORMAL MOLE RATIO					
C4	0.0302	0.0347	0.0309	0.0338	0.0311
C5	0.0909	0.0907	0.0908	0.0825	0.0920
C6	0.1420	0.1420	0.1424	0.1385	0.1448
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.3747	1.3364	1.3597	1.3206	1.1650
C4	0.6348	0.6439	0.6248	0.6170	0.5999
C5	0.6423	0.6595	0.6403	0.6535	0.6720
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	-	CLR OIL	-	CLR OIL
DENSITY	0.754		0.752		0.757
N, REFRACTIVE INDEX	1.4255		1.4253		1.4253
SIMULT'D DISTILATN					
10 WT % @ DEG F	268		267		270
16	315		312		312
50	442		442		438
84	618		613		614
90	667		662		666
RANGE(16-84 %)	303		301		302
WT % @ 420 F	43.67	43.67	43.67	45.00	45.00
WT % @ 700 F	93.25	93.64	93.64	93.17	93.17

VII. RUN 6 (10112-16) with Catalyst 6 ($Co/Th/X_1$ + UCC-101)

This catalyst is the first of a series of five in which the thorium-promoted cobalt metal component (MC) is treated with other metals (the exact nature of the metal component will not, in general, be discussed). The metal component was first formed as an equi-molar mixture of cobalt and the additive, then impregnated with thorium to give 15 percent Th. This was physically mixed with UCC-101 in a MC:SSC ratio of 3:14, bonded with 15 percent SiO_2, and formed as an extrudate. Aside from the additive this is much the same as Catalysts 2 and 3, and should be compared to the latter.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 97-100. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 101-102. Carbon number product distributions are plotted in Figs. 103-108. Chromatograms from simulated distillations are reproduced in Figs. 109-114. Detailed material balances appear in Tables 15-17.

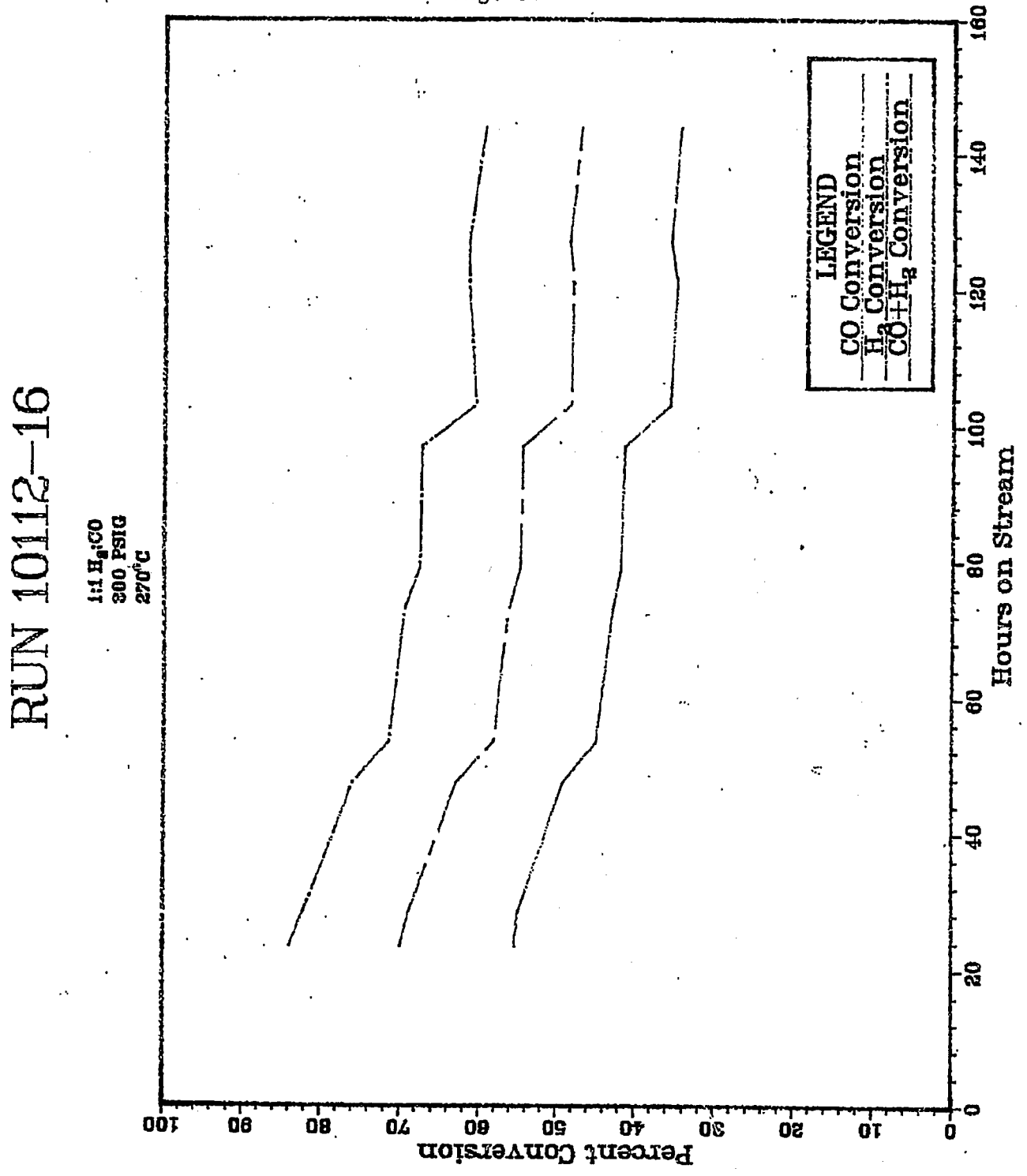
The conversion was 92 percent of that with Catalyst 3, but the cobalt, at only half the level in Catalyst 3, was used much more efficiently. The rate of deactivation was also similar to that of Catalyst 3. The water gas shift activity was low, initially 28 percent and falling to 20 percent of the oxygen reject-

ed as CO_2 (not an efficient use of the 1:1 syngas). Due to the high H_2 conversion the catalyst was effectively exposed to the H_2:CO syngas in a ratio of 0.57:1, without very rapid deactivation.

The initial selectivity was similar to that of Catalyst 3 except that the yield of heavies was lower (less than 2 percent vs. ~6 percent). The total motor fuel yield was ~65 percent, also like that of Catalyst 3 but with more gasoline and less diesel oil. The selectivity is more stable than that of Catalyst 3, the shift toward lighter products with hours on stream having been less pronounced. Percent olefin of the C_4 product was the same as with Catalyst 3, but the pentane was slightly less isomerized. The chromatograms of the simulated distillations appear to show that the liquid was more isomerized than the pentane, but since the liquid contained solid wax this finding may be open to question. The Schulz-Flory plots are typical of cobalt, with no apparent carbon number cut-off.

This catalyst shows little improvement over Catalyst 3. It does, however, use cobalt more efficiently, its selectivity is a little more stable, and its liquid product may be more highly isomerized.

Fig. 97


RUN 10112-16
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

RUN 10112–16

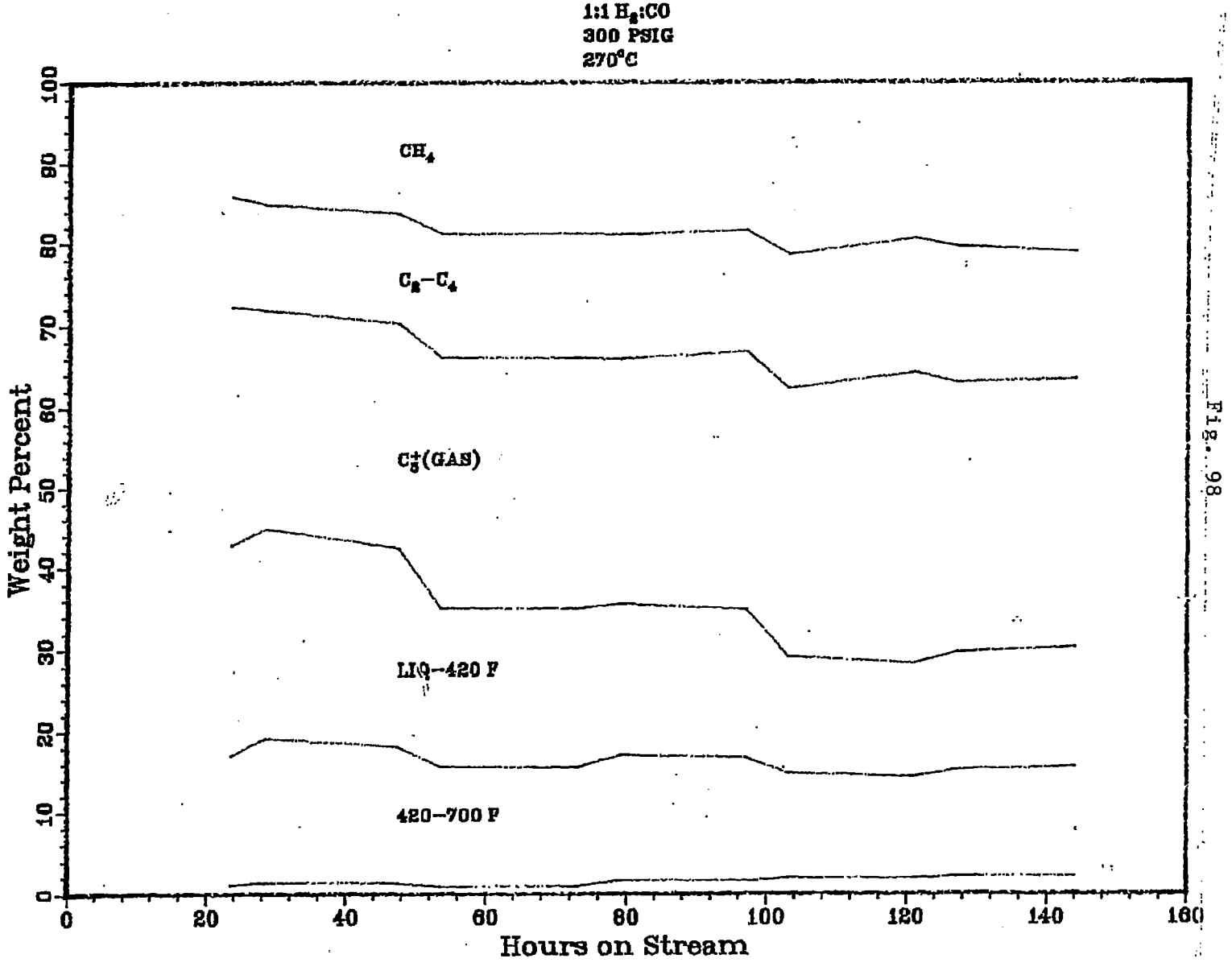


Fig. 98

RUN 10112--16

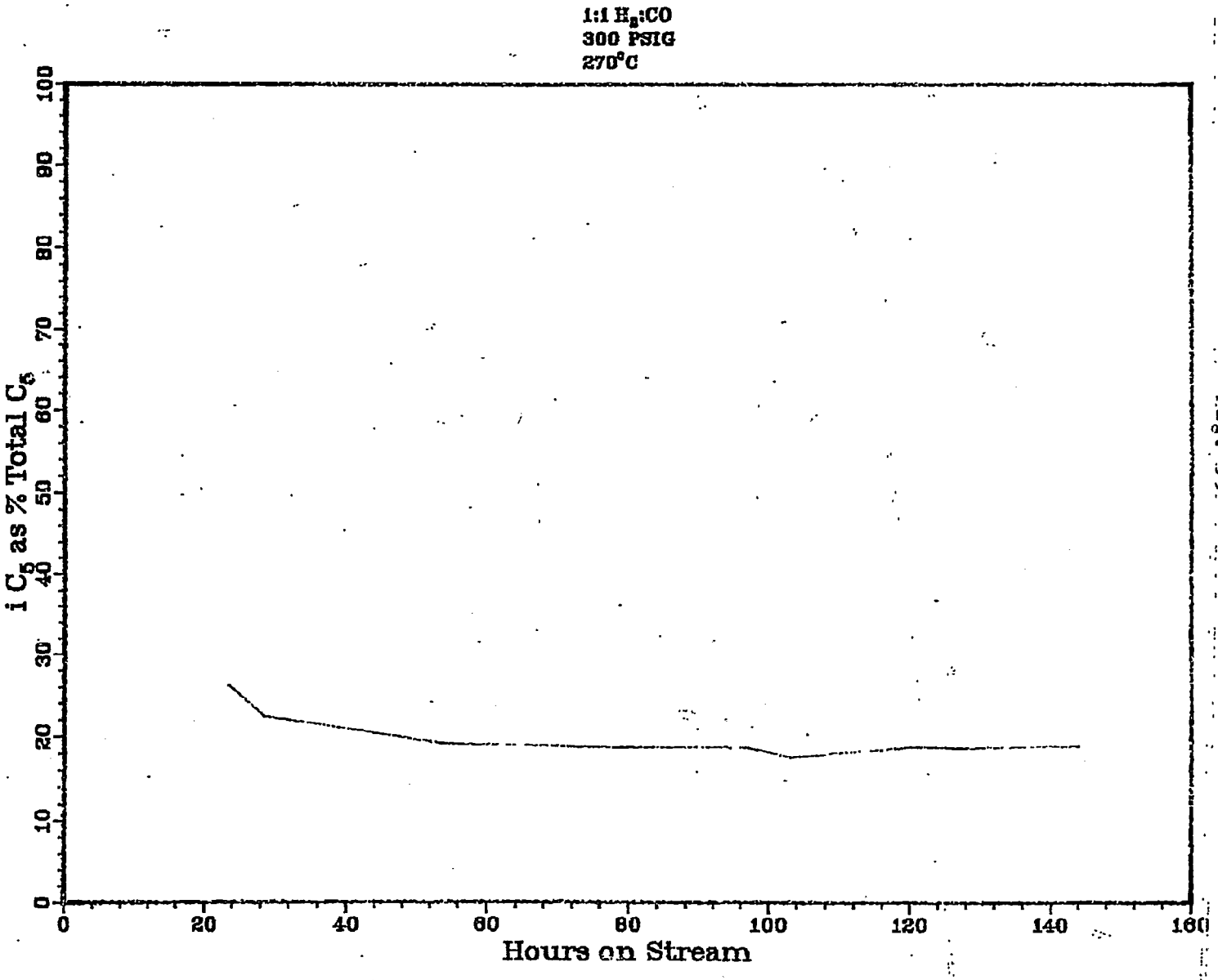


Fig. 99

Fig. 100

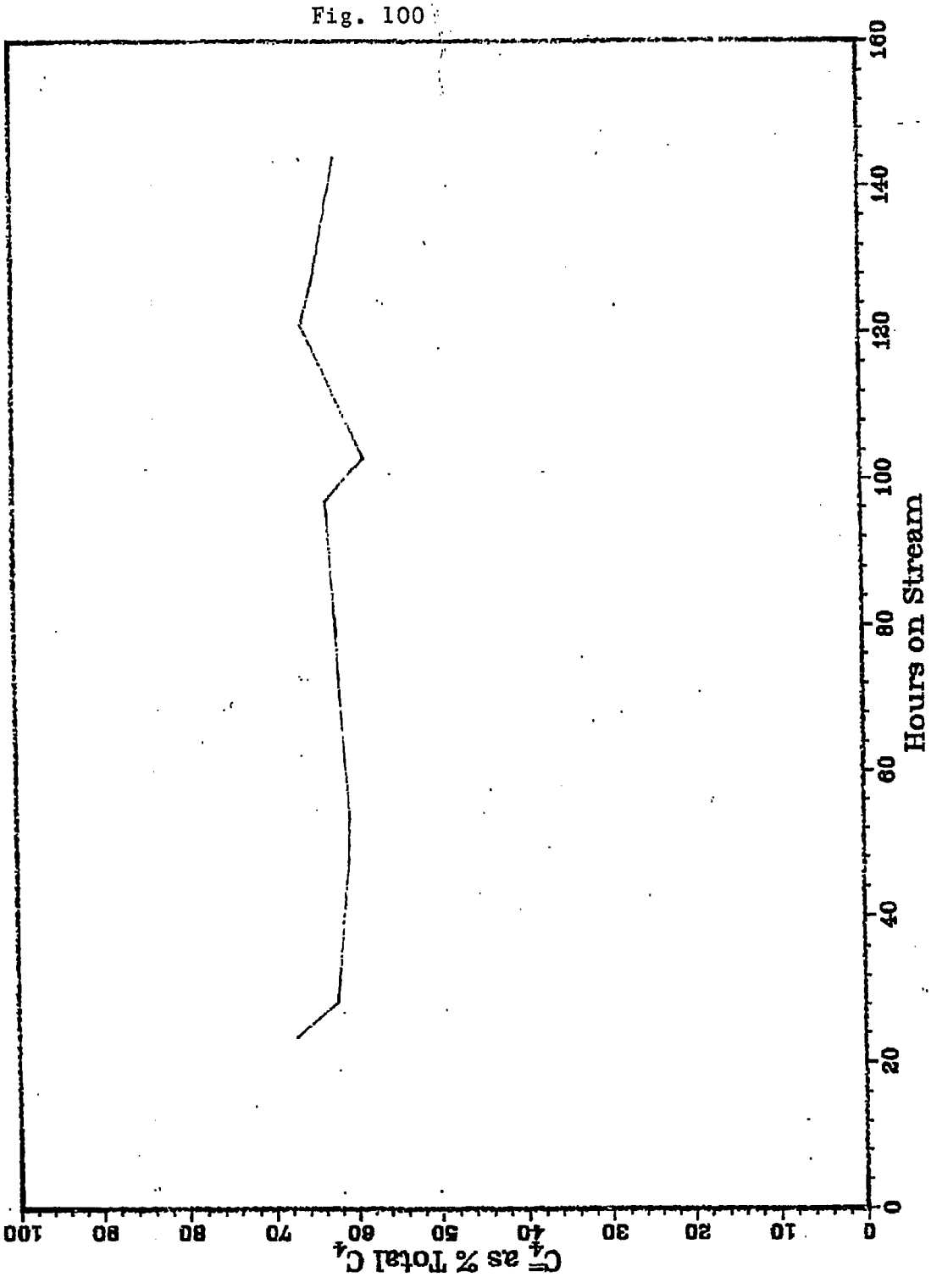

RUN 10112-16
1:1 H2:CO
300 PSIG
270°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160

Fig. 101

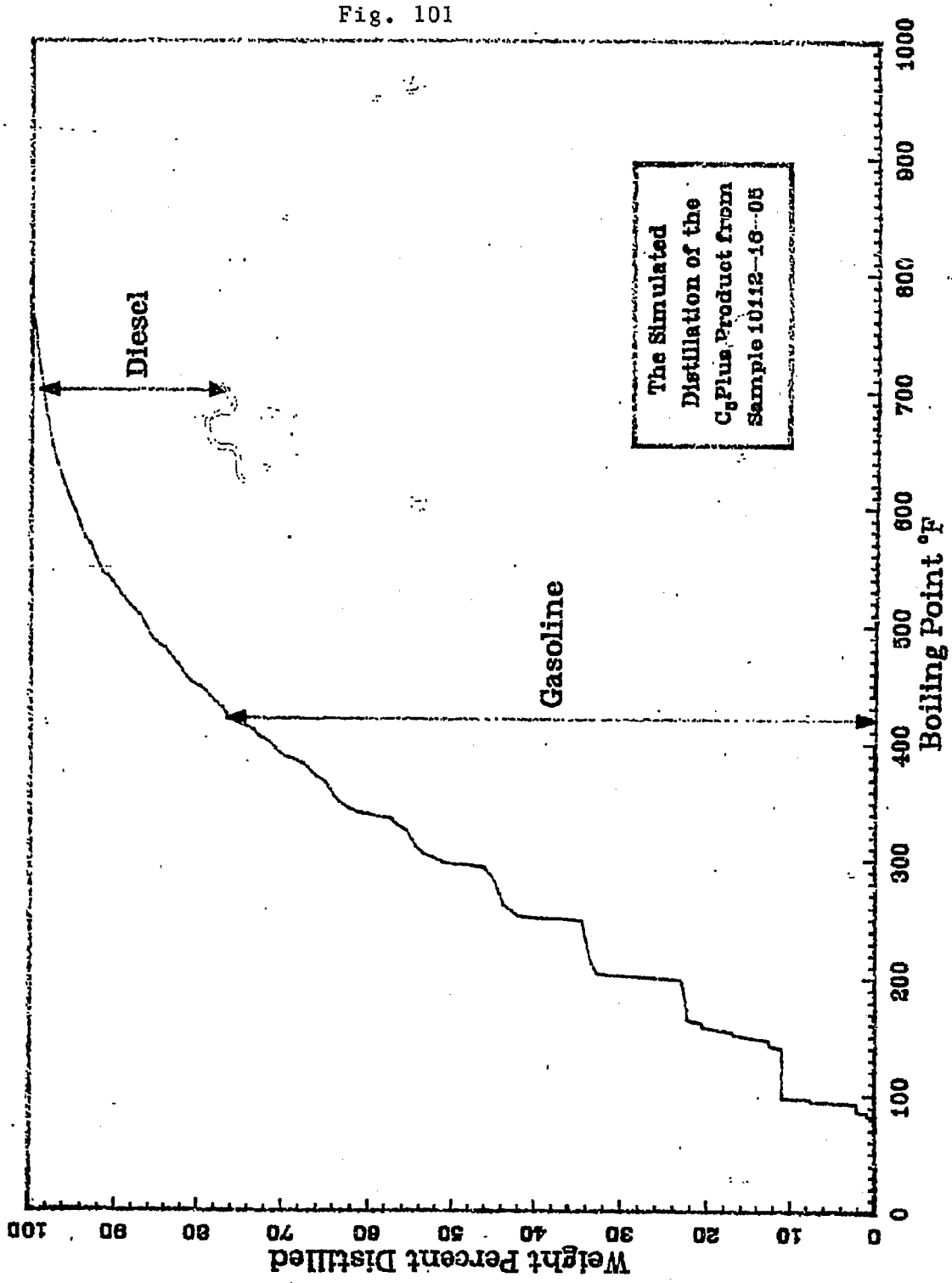

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
The Simulated Distillation of the C5 Plus Product from Sample 10112-16-05

Fig. 102

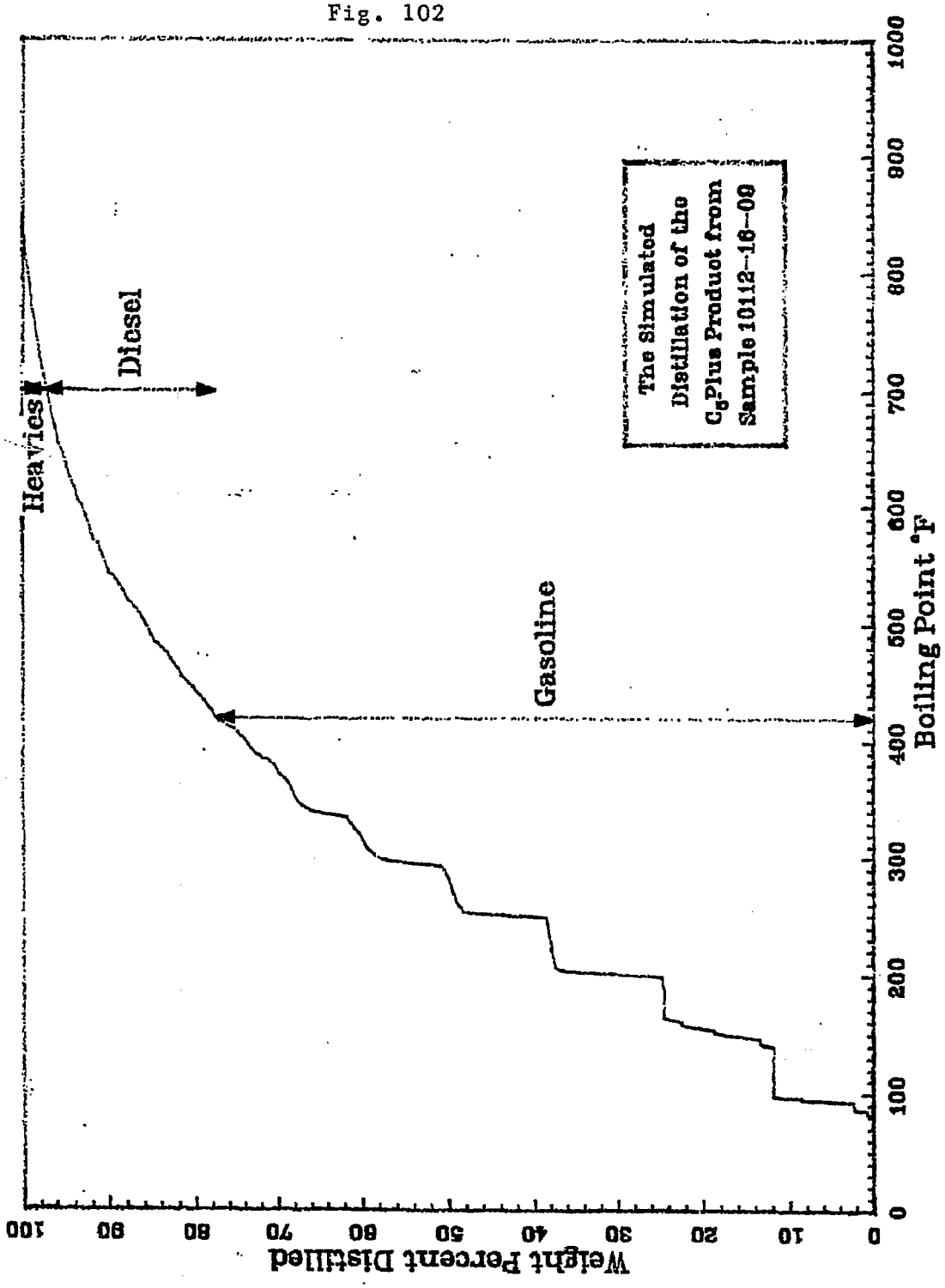

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C6 Plus Product from Sample 10112-16-09

Fig. 103

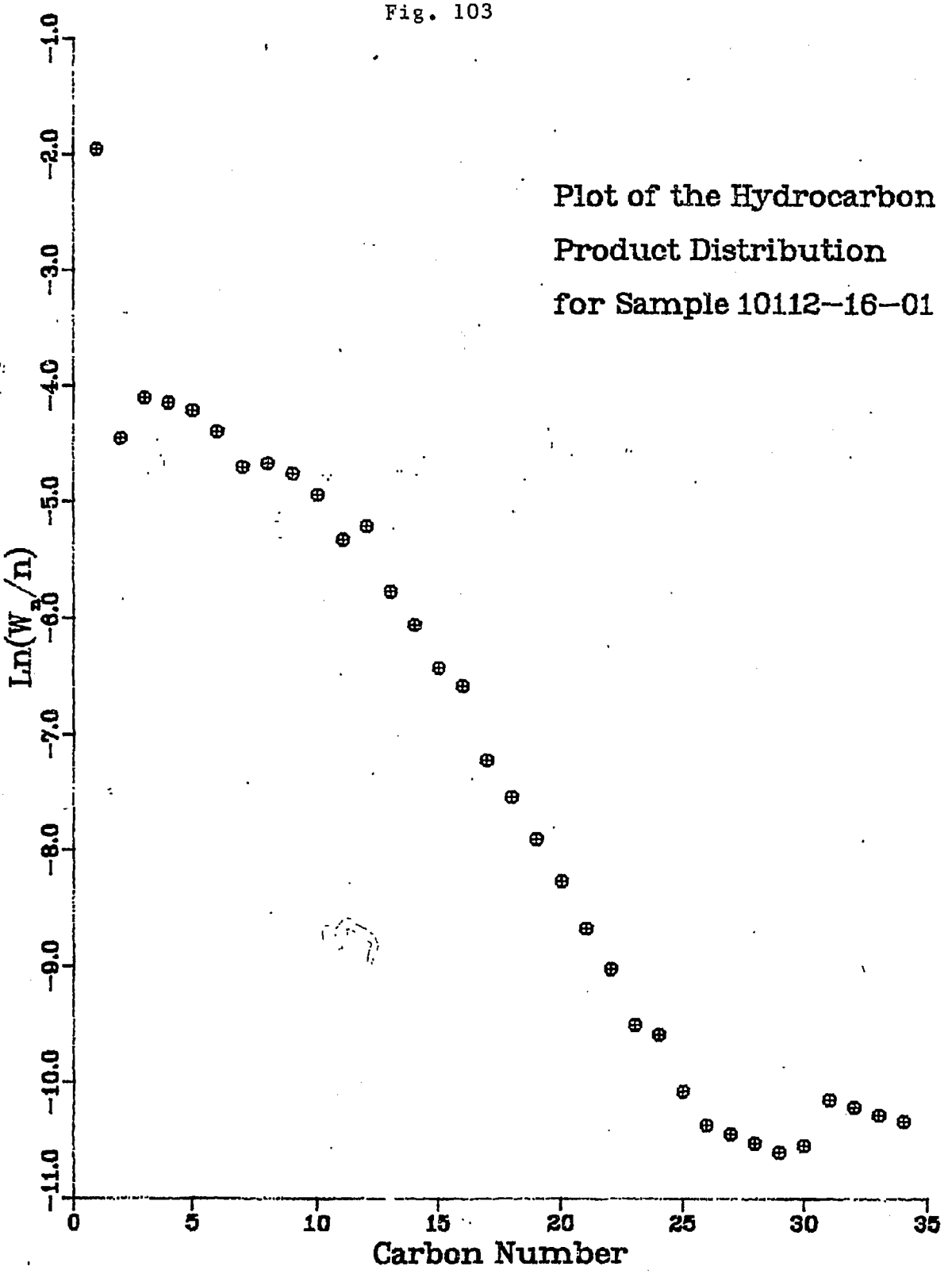

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--16--01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 104

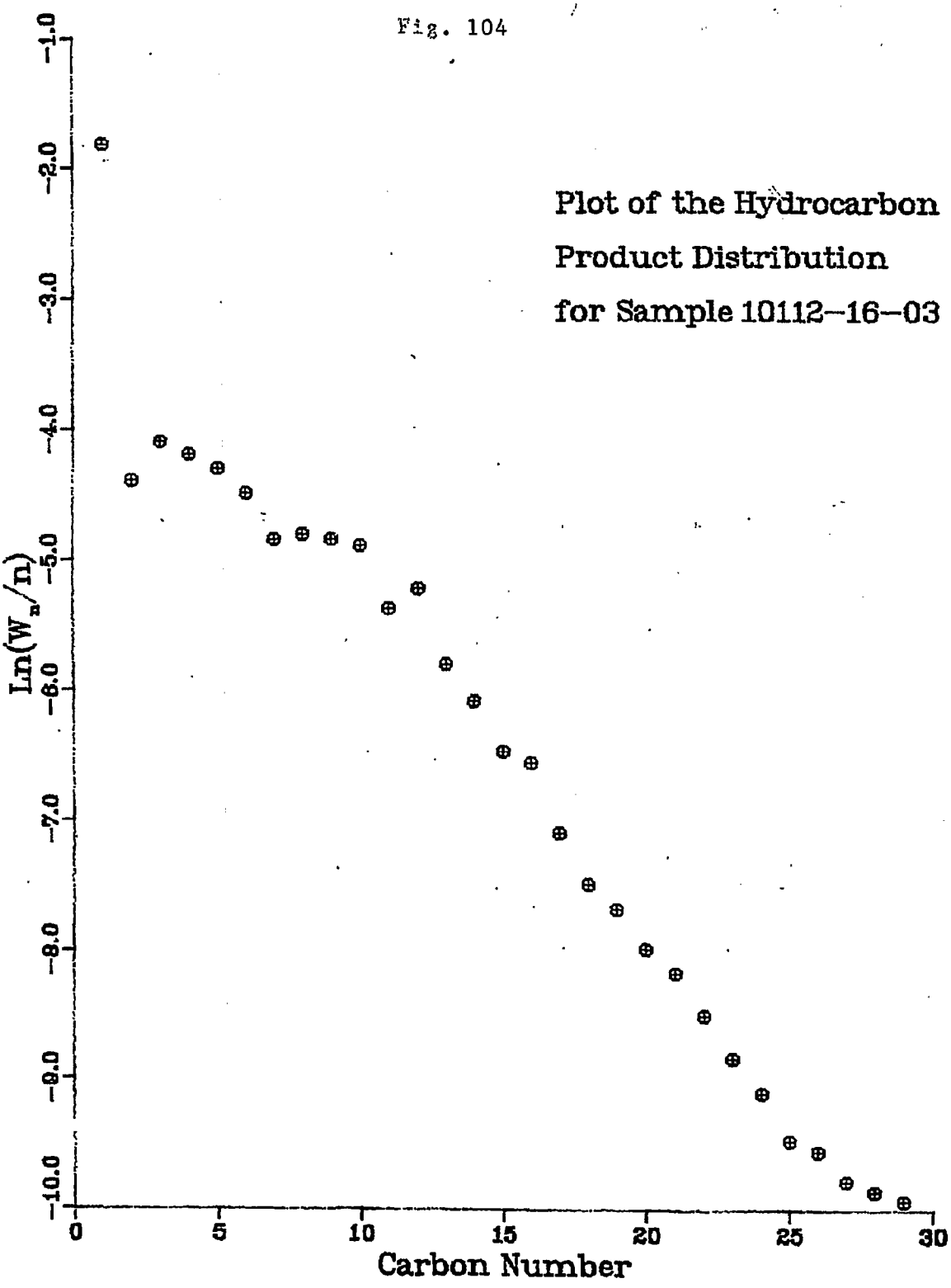
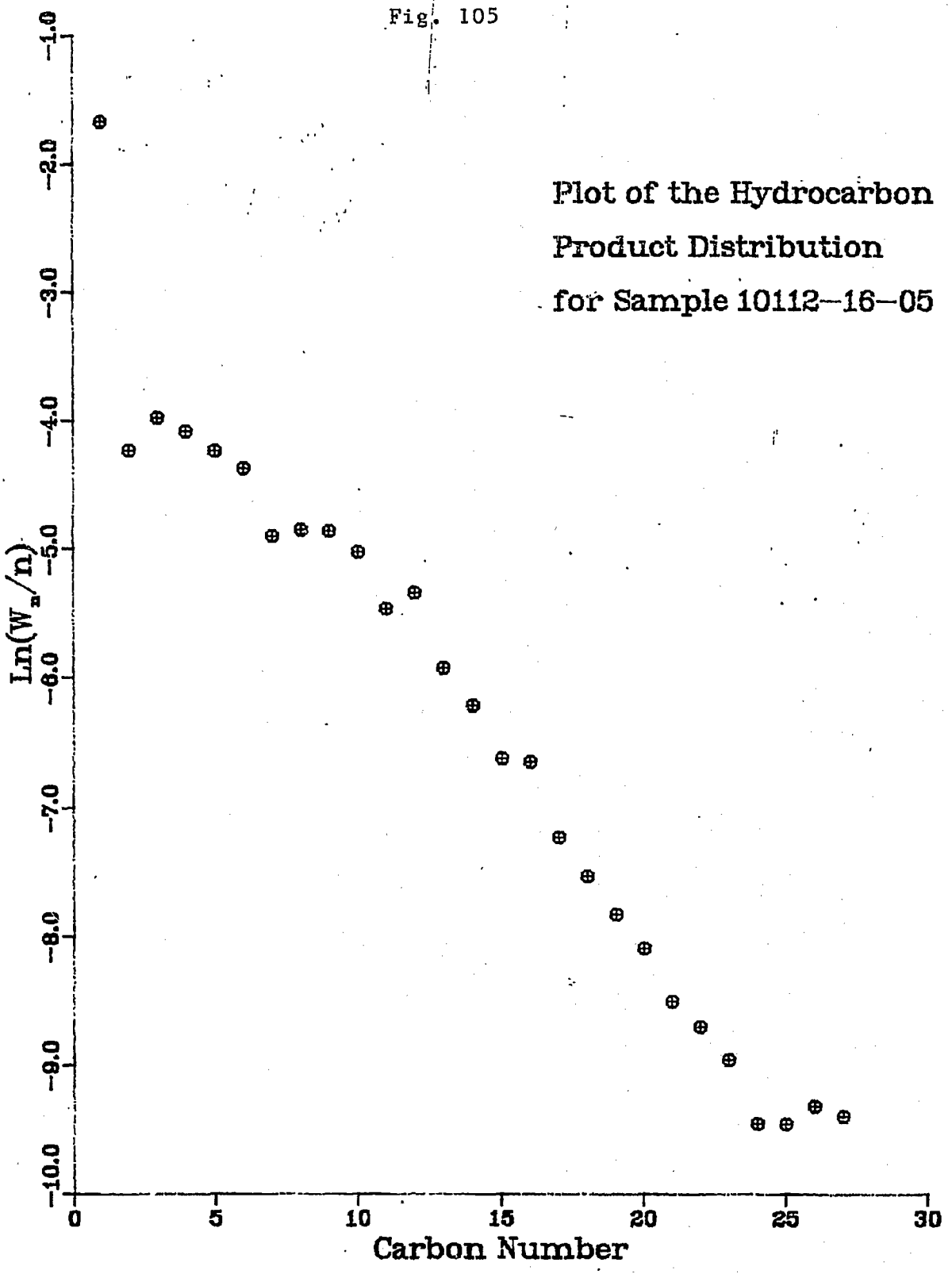

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-16-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 105



Plot of the Hydrocarbon Product Distribution for Sample 10112-16-05

Fig. 106

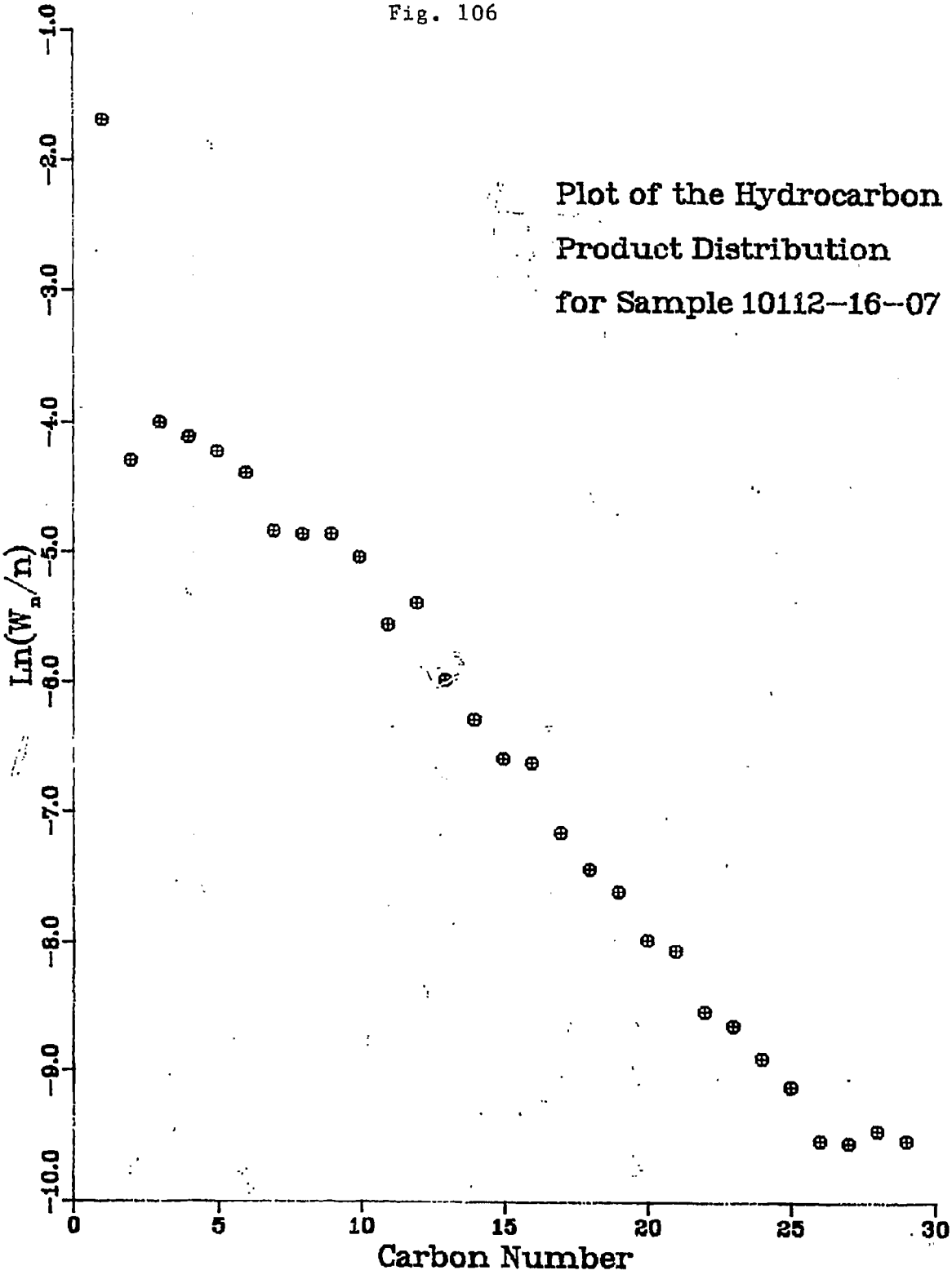

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-16-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 107

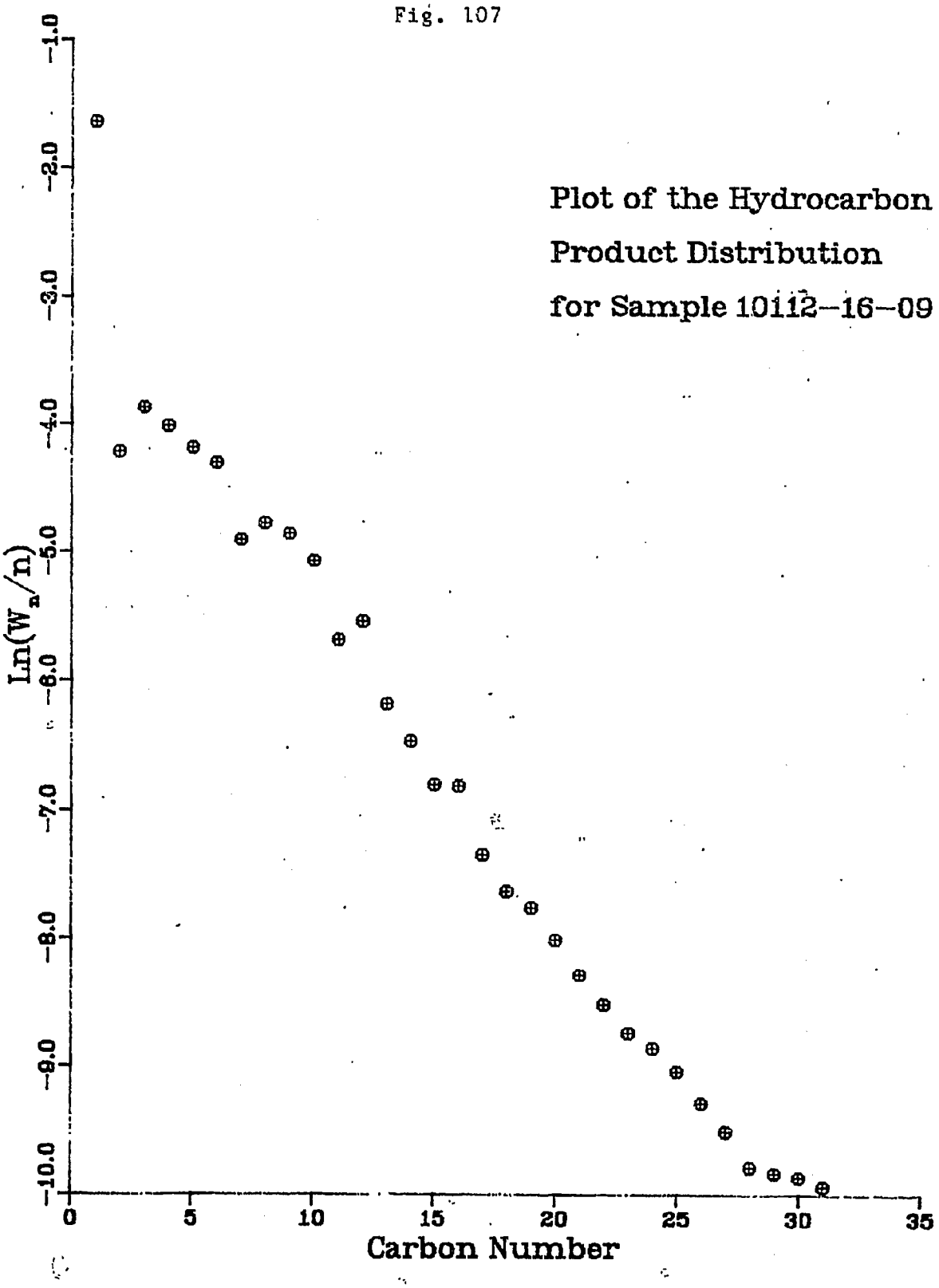
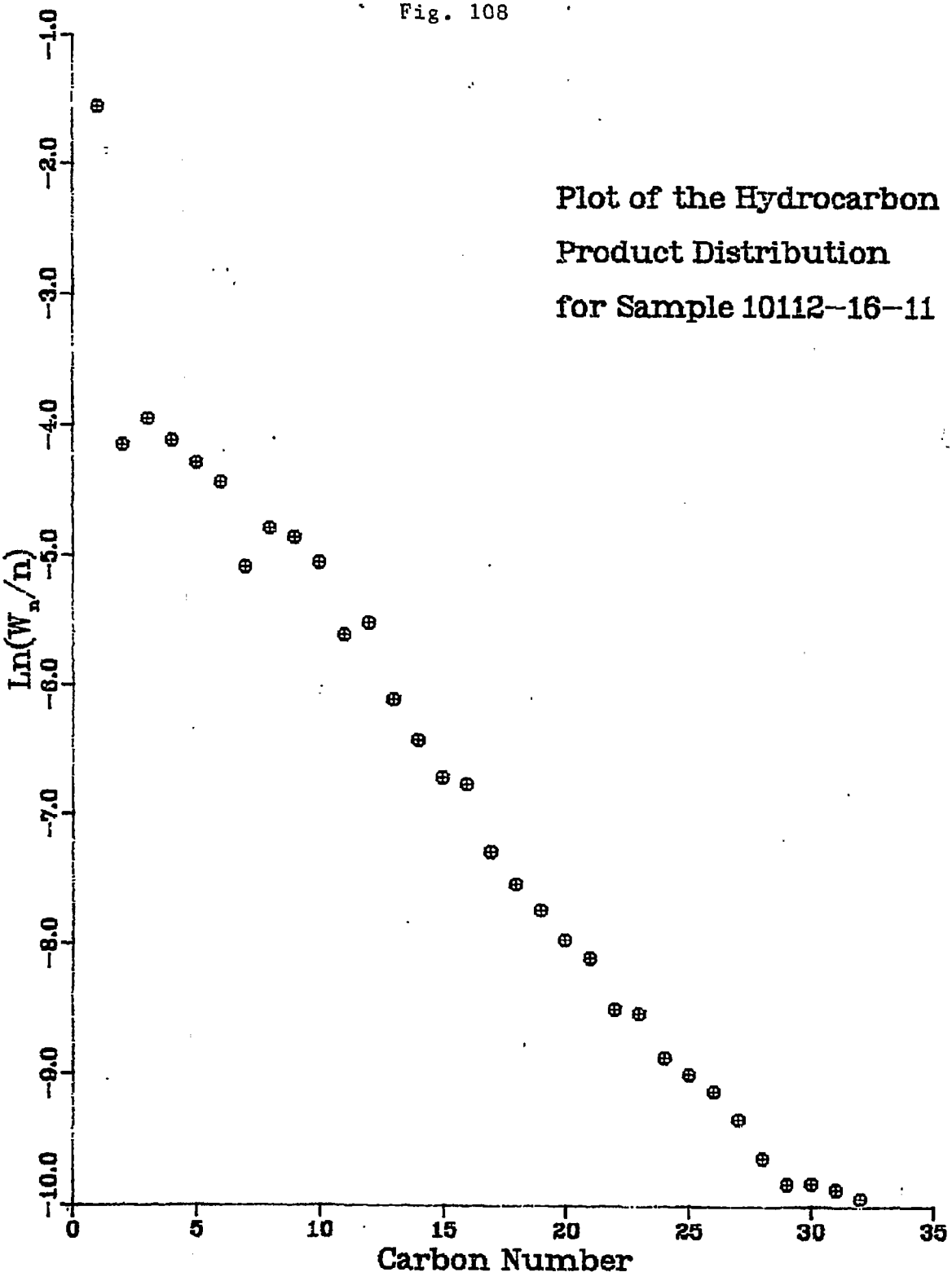
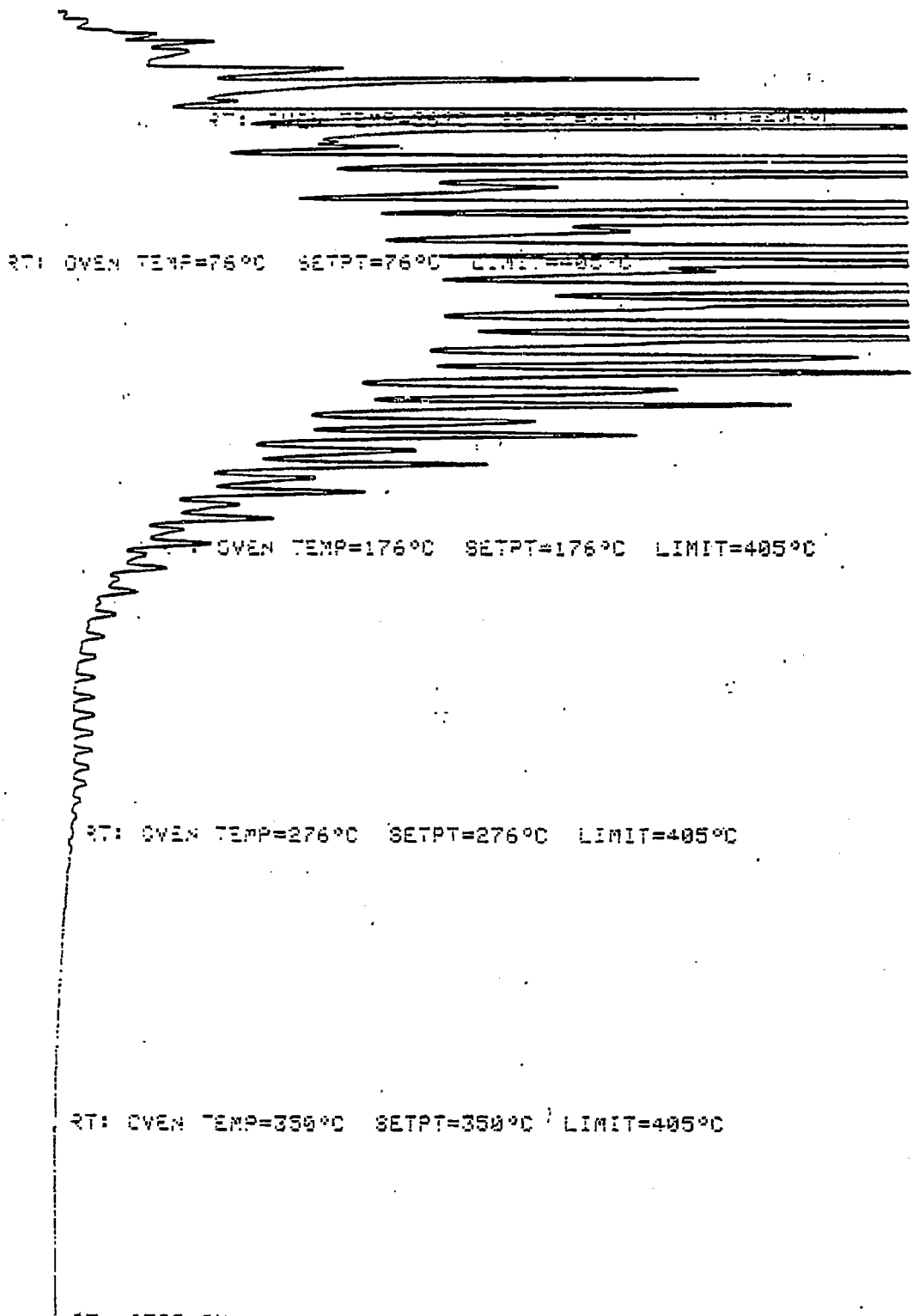

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-16-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 108



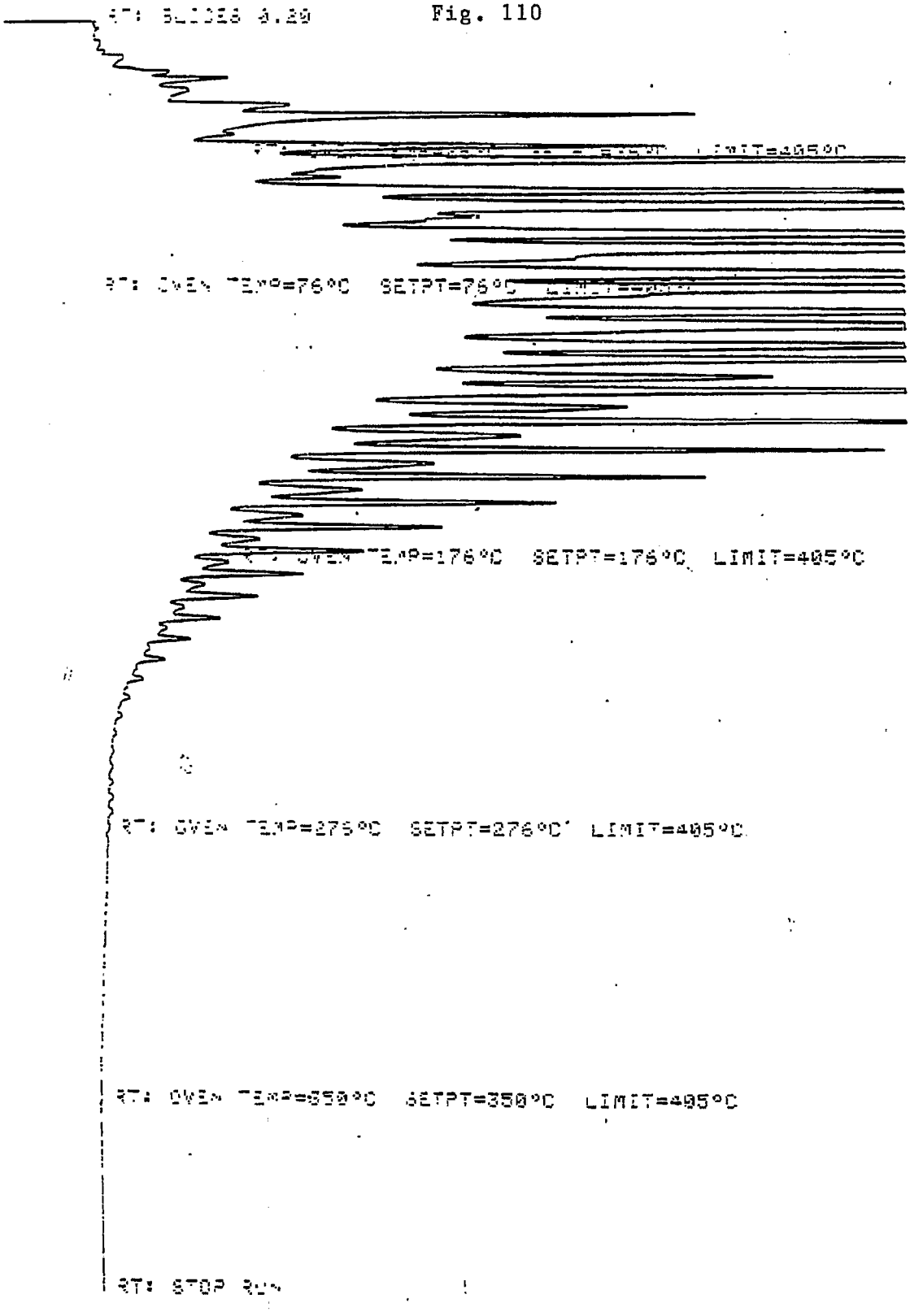
Plot of the Hydrocarbon Product Distribution for Sample 10112--16--11

Fig. 109



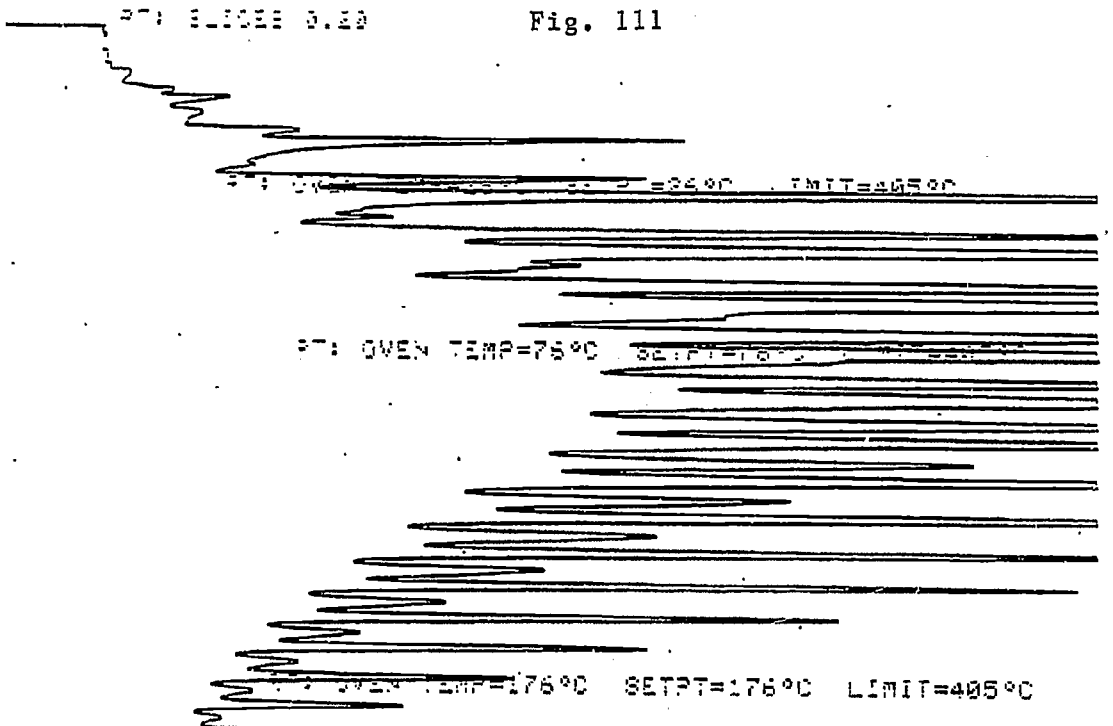
SAMPLE:10112-16-1L

Fig. 110



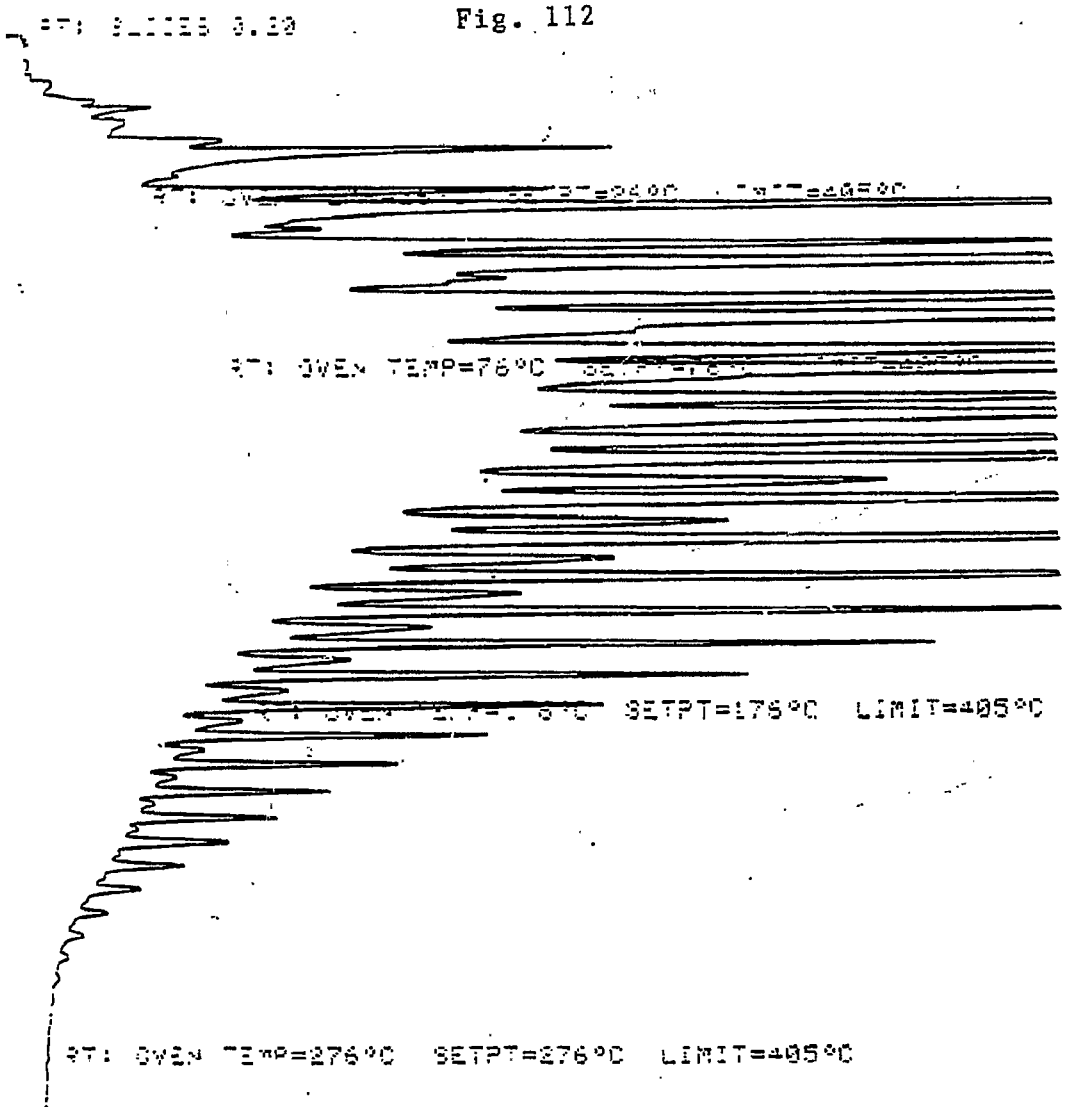
SAMPLE: 10112-16-3L

Fig. 111



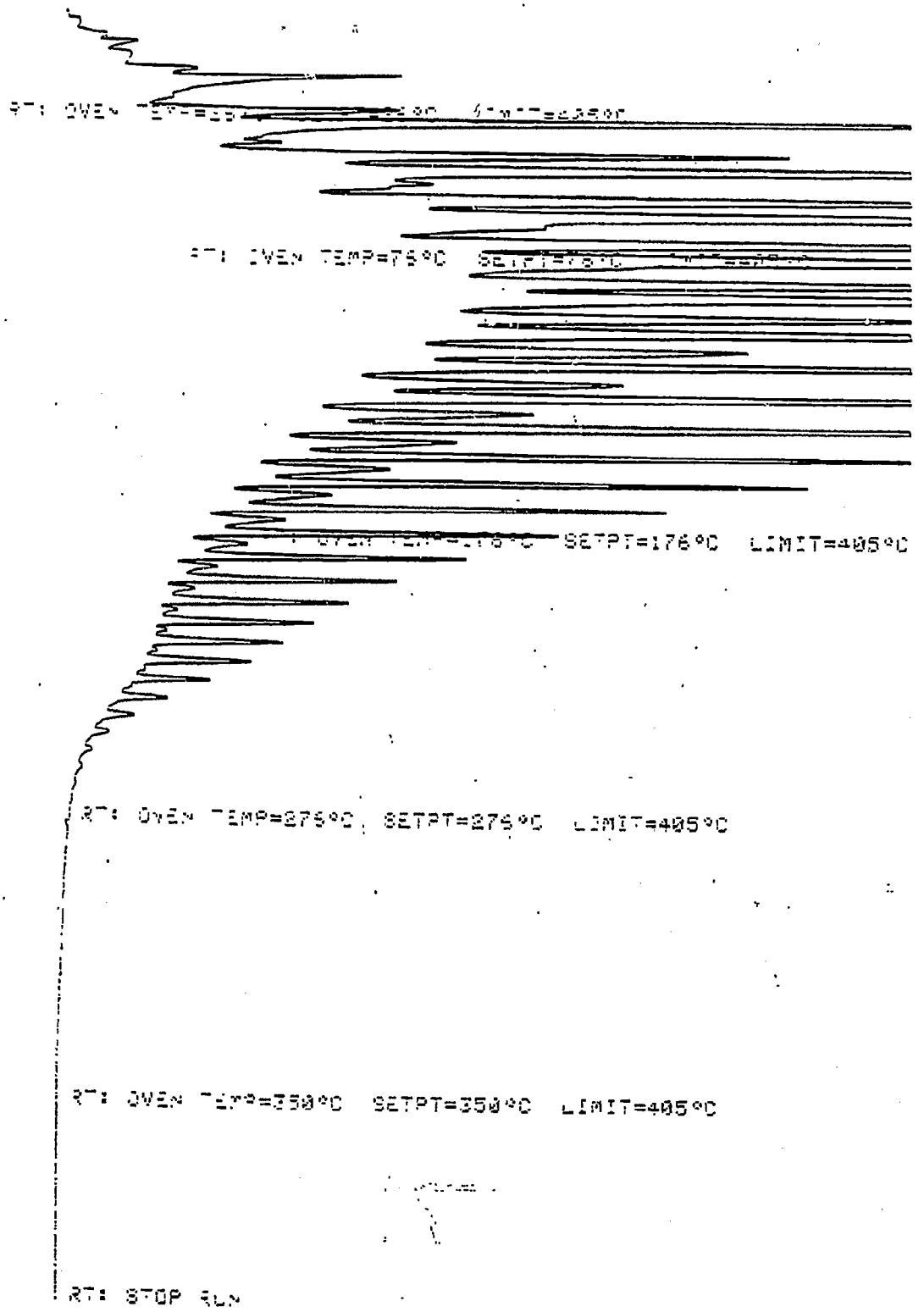
SAMPLE:10112-16-5L

Fig. 112



SAMPLE:10112-16-7L

Fig. 113



SAMPLE: 10112-16-9L

Fig. 114

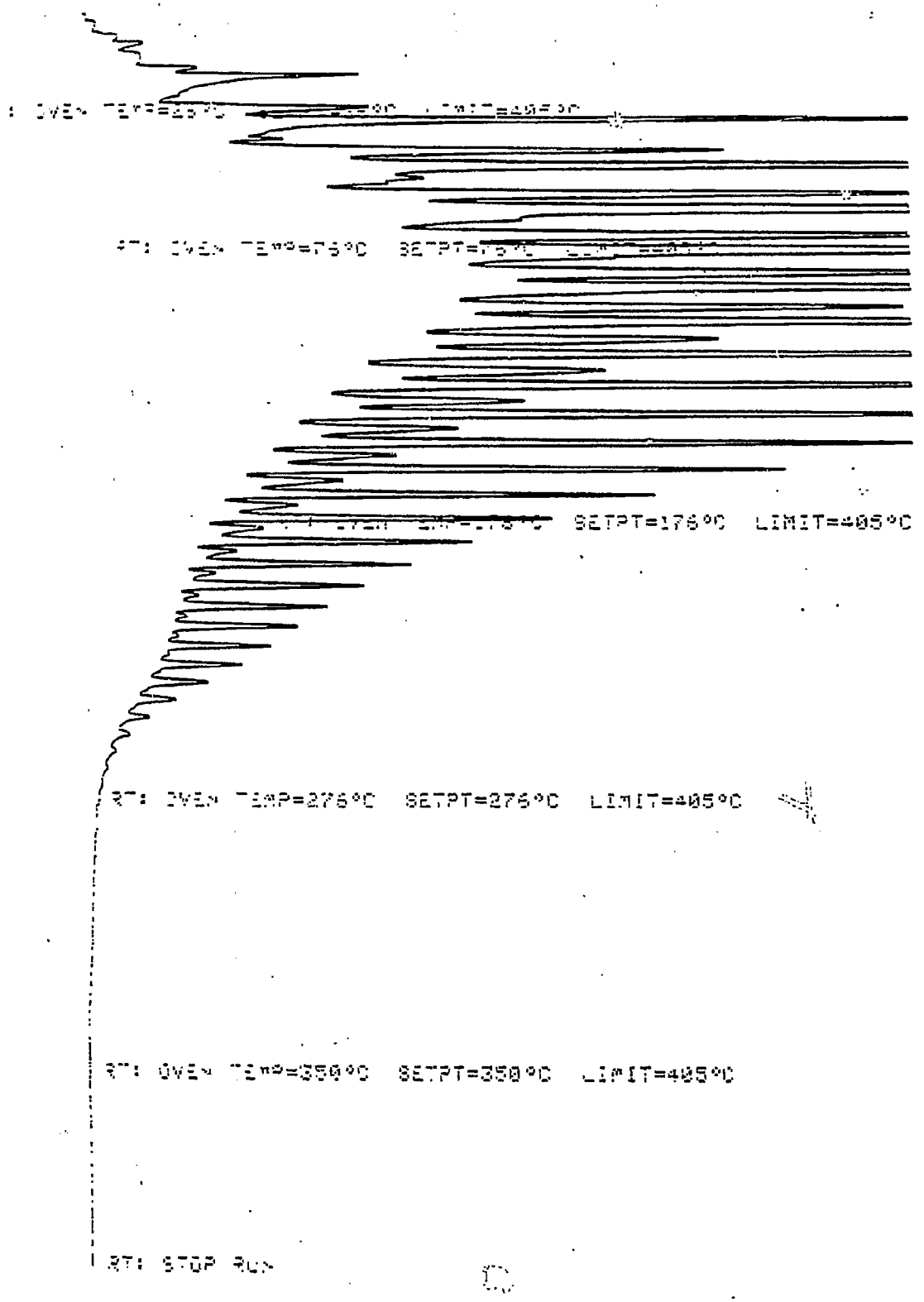

SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

TABLE 15 RESULT OF SYNGAS OPERATION

RUN NO. 10112-16
CATALYST CO/TH/X1+UCC-101 #10252-57C 80 CC 32.0 GM (47.7 AFTER RUN +16G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-16-01	112-16-02	112-16-03	112-16-04	112-16-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	23.5	28.5	47.5	53.5	73.0
PRESSURE,PSIG	300	305	302	301	301
TEMP. C	270	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	23.50	5.00	24.00	6.00	25.50
EFFLNT GAS LITER	195.75	40.70	237.80	70.40	313.00
GM AQUEOUS LAYER	67.31	12.62	60.55	13.76	58.48
GM OIL	21.54	4.75	22.81	4.76	20.22
MATERIAL BALANCE					
GM ATOM CARBON %	78.09	75.28	83.35	92.22	94.05
GM ATOM HYDROGEN %	81.65	78.55	88.43	92.23	95:11
GM ATOM OXYGEN %	94.56	86.79	91.36	98.17	98.66
RATIO CHX/(H2O+CO2)	0.6466	0.7213	0.7972	0.8417	0.8731
RATIO X IN CHX	2.3212	2.3413	2.3668	2.4218	2.4208
USAGE H2/CO PRODT	1.3304	1.3683	1.4922	1.4804	1.5495
RATIO CO2/(H2O+CO2)	0.2811	0.2816	0.2418	0.2645	0.2376
K SHIFT IN EFFLNT	0.15	0.16	0.16	0.19	0.17
CONVERSION					
ON CO %	55.39	55.00	49.20	45.07	42.94
ON H2 %	83.91	82.14	75.95	71.49	69.56
ON CO+H2 %	69.97	68.86	62.97	58.28	56.32
PRDT SELECTIVITY,WT %					
CH4	14.19	15.18	16.28	18.79	18.77
C2 HC'S	2.34	2.36	2.46	2.76	2.91
C3H8	2.39	2.52	2.86	3.23	3.18
C3H6=	2.54	2.25	2.15	2.35	2.44
C4H10	2.12	2.27	2.42	2.74	2.62
C4H8=	4.20	3.62	3.63	4.07	4.11
C5H12	2.46	2.52	2.67	2.91	2.81
C5H10=	4.90	4.16	4.10	4.41	4.42
C6H14	3.05	3.00	3.10	3.42	3.39
C6H12= & CYCLO'S	4.33	3.75	3.64	3.96	4.17
C7+ IN GAS	14.58	13.42	14.22	16.24	16.18
LIQ HC'S	42.90	44.95	42.49	35.14	35.00
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	27.78	28.20	29.79	33.92	34.03
C5 -420 F	55.05	52.56	52.02	50.35	50.31
420-700 F	15.96	17.85	16.87	14.80	14.75
700-END PT	1.20	1.39	1.31	0.92	0.92
C5+-END PT	72.22	71.80	70.21	66.08	65.97
ISO/NORMAL MOLE RATIO					
C4	0.1874	0.1740	0.1345	0.1322	0.1241
C5	0.3554	0.2891	0.2508	0.2388	0.2335
C6	0.6851	0.5262	0.4449	0.4198	0.4129
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.8997	1.0681	1.2690	1.3123	1.2461
C4	0.4873	0.6070	0.6455	0.6501	0.6166
C5	0.4883	0.5889	0.6335	0.6416	0.6185
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR YL OIL		CLDY YG OIL		CLDY BL OIL
DENSITY	0.758		0.797		0.755
N, REFRACTIVE INDEX	1.4246		1.4256		1.4259
SIMULT'D DISTILATN					
10 WT % @ DEG F	258		263		282
16	288		299		303
50	395		403		410
84	527		543		543
90	569		597		594
RANGE(16-84 %)	239		244		240
WT % @ 420 F	60.00	57.20	57.20	55.25	55.25
WT % @ 700 F	97.21	96.91	96.91	97.38	97.38

TABLE 16 RESULT OF SYNGAS OPERATION

RUN NO. 10112-16
CATALYST CO/TH/X1+UCC-101 #10252-57C 80 CC 32.0 GM (47.7 AFTER RUN +16G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-16-06	112-16-07	112-16-08	112-16-09	112-16-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	79.0	97.0	103.0	121.0	127.0
PRESSURE,PSIG	300	301	301	302	299
TEMP. C	270	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.00	24.00	6.00	24.00	6.00
EFFLNT GAS LITER	76.05	308.00	84.05	342.80	84.90
GM AQUEOUS LAYER	13.33	53.31	11.77	47.08	11.65
GM OIL	4.80	19.21	3.50	14.02	3.69
MATERIAL BALANCE					
GM ATOM CARBON %	94.97	96.18	95.22	99.73	98.37
GM ATOM HYDROGEN %	96.18	97.61	97.31	96.46	96.83
GM ATOM OXYGEN %	98.89	98.84	97.70	101.35	99.76
RATIO CHX/(H2O+CO2)	0.8890	0.9236	0.9189	0.9468	0.9544
RATIO X IN CHX	2.4221	2.4111	2.4799	2.4333	2.4550
USAGE H2/CO PROD'T	1.5563	1.5905	1.6635	1.6575	1.6580
RATIO CO2/(H2O+CO2)	0.2374	0.2253	0.2040	0.2026	0.2074
K SHIFT IN EFFLNT	0.18	0.16	0.16	0.15	0.15
CONVERSION					
ON CO %	41.96	41.63	35.96	35.14	35.86
ON H2 %	67.66	67.42	60.64	61.62	61.60
ON COH2 %	54.89	54.62	48.43	48.16	48.63
PROD'T SELECTIVITY,WT %					
CH4	18.89	18.47	21.46	19.46	20.49
C2 HC'S	2.74	2.72	3.10	2.96	3.01
C3H8	3.19	3.01	3.74	3.15	3.33
C3H6-	2.50	2.48	2.51	3.10	3.00
C4H10	2.62	2.47	2.97	2.51	2.63
C4H8-	4.13	4.10	4.05	4.70	4.64
C5H12	2.80	2.63	2.92	2.60	2.74
C5H10-	4.58	4.68	4.36	5.03	4.91
C6H14	3.31	3.22	3.39	3.32	3.24
C6H12- & CYCLO'S	3.96	4.20	4.04	4.78	4.54
C7+ IN GAS	15.65	17.16	18.35	20.05	17.81
LIQ HC'S	35.64	34.87	29.10	28.33	29.66
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.07	33.24	37.84	35.89	37.10
C5 -420 F	48.74	49.93	47.32	49.66	47.47
420-700 F	15.56	15.22	12.89	12.55	13.27
700-END PT	1.64	1.60	1.95	1.90	2.15
C5+-END PT	65.93	66.76	62.16	64.11	62.90
ISO/NORMAL MOLE RATIO					
C4	0.1310	0.1341	0.1242	0.1348	0.1416
C5	0.2330	0.2328	0.2154	0.2346	0.2318
C6	0.4047	0.3940	0.3910	0.3955	0.3843
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.2186	1.1609	1.4204	0.9680	1.0566
C4	0.6108	0.5807	0.7082	0.5148	0.5477
C5	0.5933	0.5469	0.6502	0.5022	0.5417
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLDY BLUE		LT BL OIL	
DENSITY		0.757		0.765	
N, REFRACTIVE INDEX		1.4273		1.4285	
SIMULT'D DISTILATN					
10 WT % @ DEG F		285		293	
16		305		315	
50		416		426	
84		573		600	
90		627		654	
RANGE(16-84 %)		268		285	
WT % @ 420 F	51.75	51.75	49.00	49.00	48.00
WT % @ 700 F	95.41	95.41	93.31	93.31	92.75

TABLE 17 RESULT OF SYNGAS OPERATION

RUN NO. 10112-16
CATALYST CO/TH/X1+UCC-101 #10252-57C 80 CC 32.0 GM (47.7 AFTER RUN +16G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-16-11
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	144.0
PRESSURE,PSIG	300
TEMP. C	271
FEED CC/MIN	400
HOURS FEEDING	23.00
EFFLNT GAS LITER	334.10
GM AQUEOUS LAYER	44.66
GM OIL	14.14
MATERIAL BALANCE	
GM ATOM CARBON %	98.06
GM ATOM HYDROGEN %	99.32
GM ATOM OXYGEN %	99.48
RATIO CHX/(H2O+CO2)	0.9523
RATIO X IN CHX	2.4658
USAGE H2/CO PRODT	1.7017
RATIO CO2/(H2O+CO2)	0.1899
K SHIFT IN EFFLNT	0.15
CONVERSION	
ON CO %	34.69
ON H2 %	59.50
ON CO+H2 %	47.17
PRDT SELECTIVITY,WT %	
CH4	21.14
C2 HC'S	3.15
C3H8	3.24
C3H6=	2.56
C4H10	2.54
C4H8=	3.99
C5H12	2.56
C5H10=	4.29
C6H14	3.05
C6H12= & CYCLO'S	4.07
C7+ IN GAS	19.12
LIQ HC'S	30.28
TOTAL	100.00

SUB-GROUPING	
C1 -C4	36.62
C5 -420 F	47.63
420-700 F	13.55
700-END PT	2.20
C5+-END PT	63.38
ISO/NORMAL MOLE RATIO	
C4	0.1320
C5	0.2367
C6	0.3820
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	1.2084
C4	0.6146
C5	0.5794
LIQ HC COLLECTION	
PHYS. APPEARANCE	LT BL OIL
DENSITY	0.761
N, REFRACTIVE INDEX	1.4291
SIMULT'D DISTILAIN	
10 WT % @ DEG F	297
16	319
50	430
84	604
90	665
RANGE(16-84 %)	285
WT % @ 420 F	48.00
WT % @ 700 F	92.75

VIII. RUN 7 (10112-17) with Catalyst 7 ($Co/Th/X_2$ + UCC-101)

This catalyst, the second of five treated with a metal additive, was formulated in exactly the same way as Catalyst 6 except with a different additive.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 115-118. A simulated distillation of the C_5^+ product for one sample is plotted in Fig. 119. Carbon number product distributions are plotted in Figs. 120-122. Chromatograms from simulated distillations are reproduced in Figs. 123-125. Detailed material balances appear in Table 18.

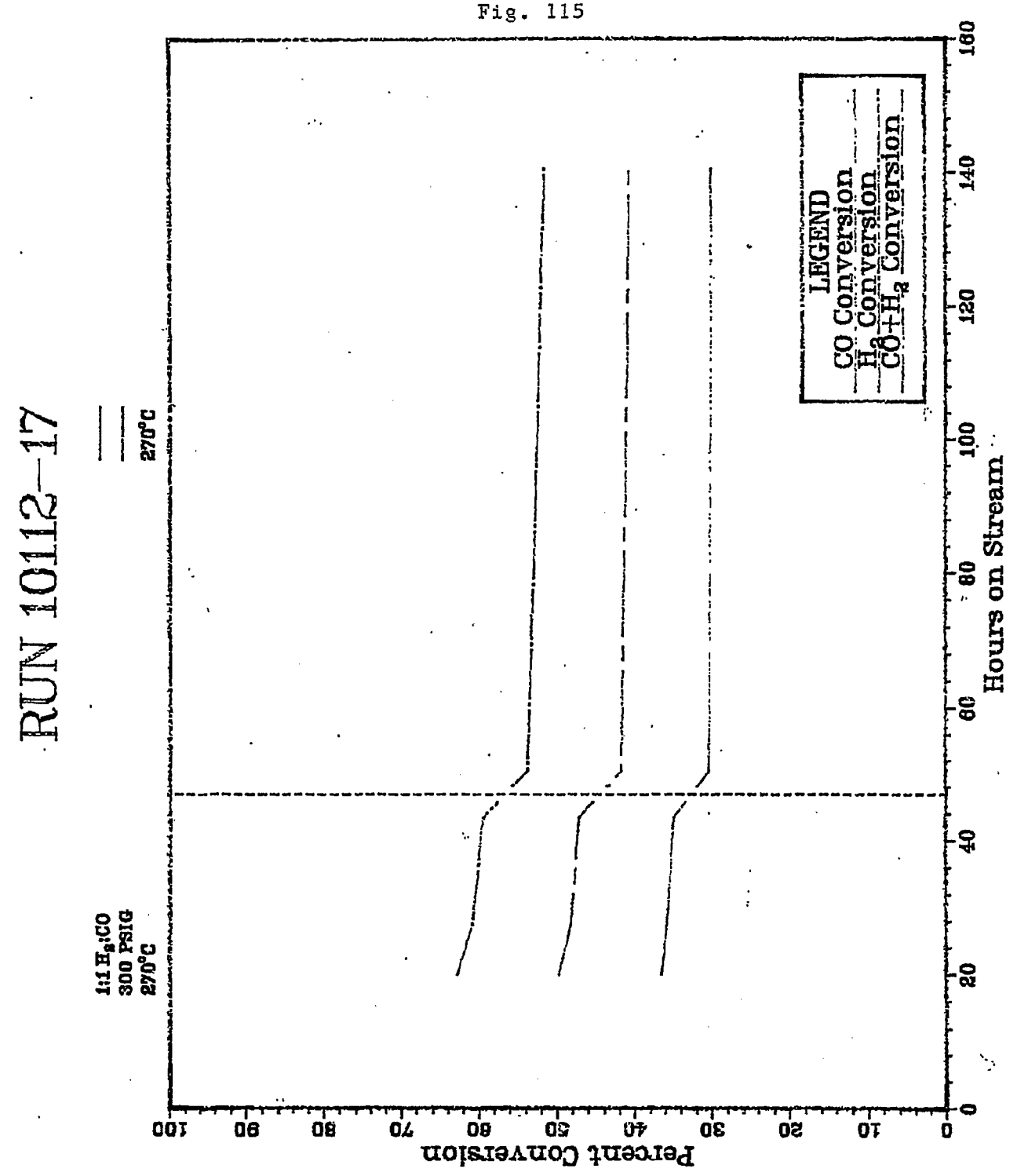
This catalyst performed poorly in comparison with Catalyst 6. The levels of cobalt in both Catalysts 6 and 7 were approximately one half of that of Catalyst 3; but whereas Catalyst 6 was 92 percent as active as Catalyst 3, this catalyst was only 43 percent as active as Catalyst 6 and only 40 percent as active as Catalyst 3. Considering that the additive used may itself have some Fischer-Tropsch activity, this catalyst's use of the cobalt was particularly inefficient. The water gas activity was also low, with 20 percent of the oxygen rejected as CO_2. The H_2:CO usage ratio of 1.65 was an inefficient use of the 1:1 syngas.

Characteristic of cobalt catalysts, the selectivity for methane was high. The C_2-C_4 yield, however, was also high, more like

an iron than a cobalt catalyst. The C_5^+ selectivity was low; very little diesel oil was produced, and practically no heavies. Production of olefins, as measured by the C_4 fraction, was steady, typical of cobalt catalysts. Isomerization of the pentane was similar to that of the Co+UCC-101 catalysts previously tested. Chromatograms of the simulated distillations show that isomerization of the liquids was the same as with Catalyst 6. The Schulz-Flory plots show that the methane production was still excessive, but due to the high production of C_2-C_4, not as high as usual with cobalt catalysts.

The additive used in this catalyst not only fails to enhance the activity of the cobalt, it actually appears to endow cobalt with some of the undesirable properties of iron catalysts which led to abandoning iron in favor of cobalt in the first place.

Fig. 115


RUN 10112-17
1:1 H2:CO
300 PSIG
270°C
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

RUN 10112–17

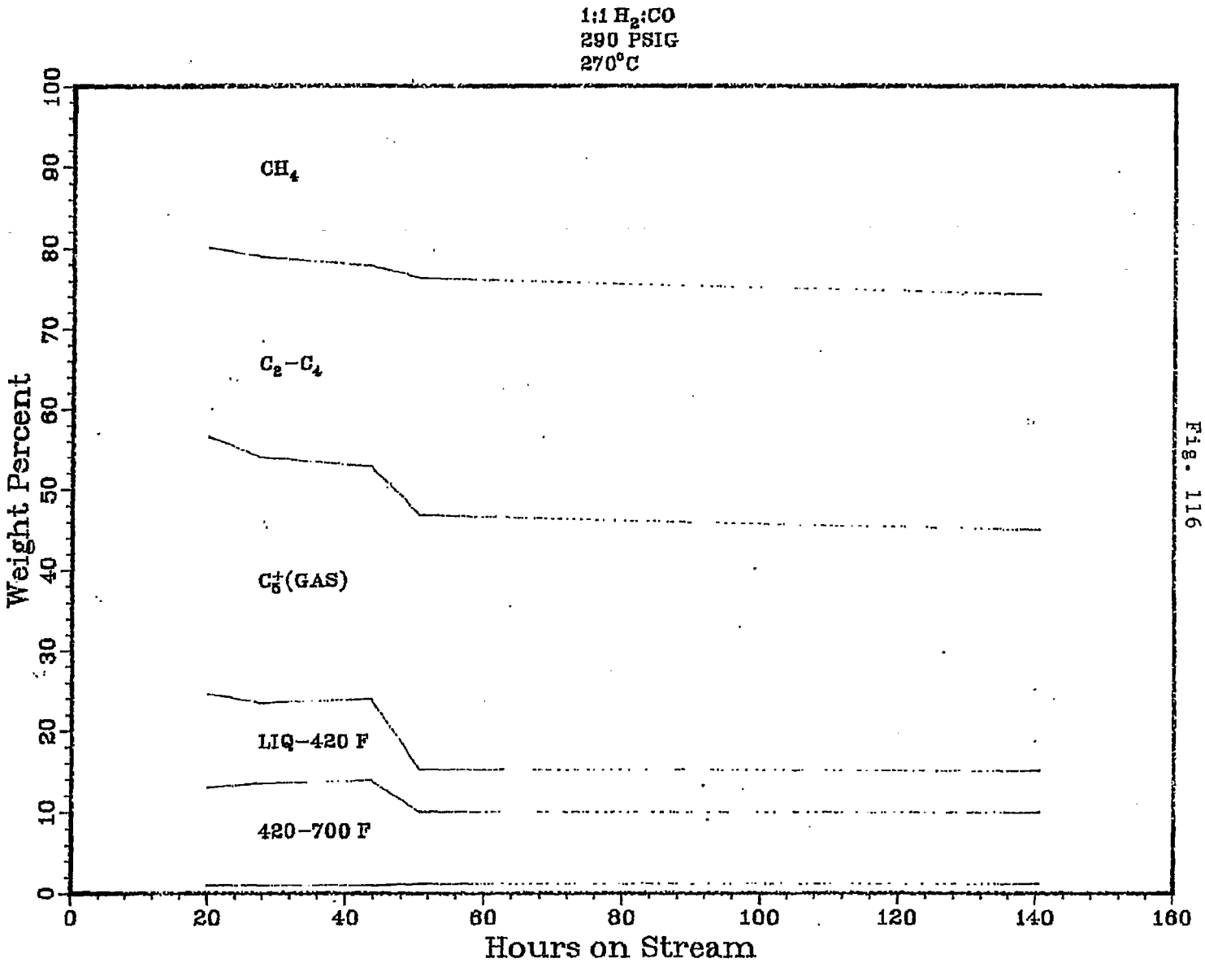


Fig. 116