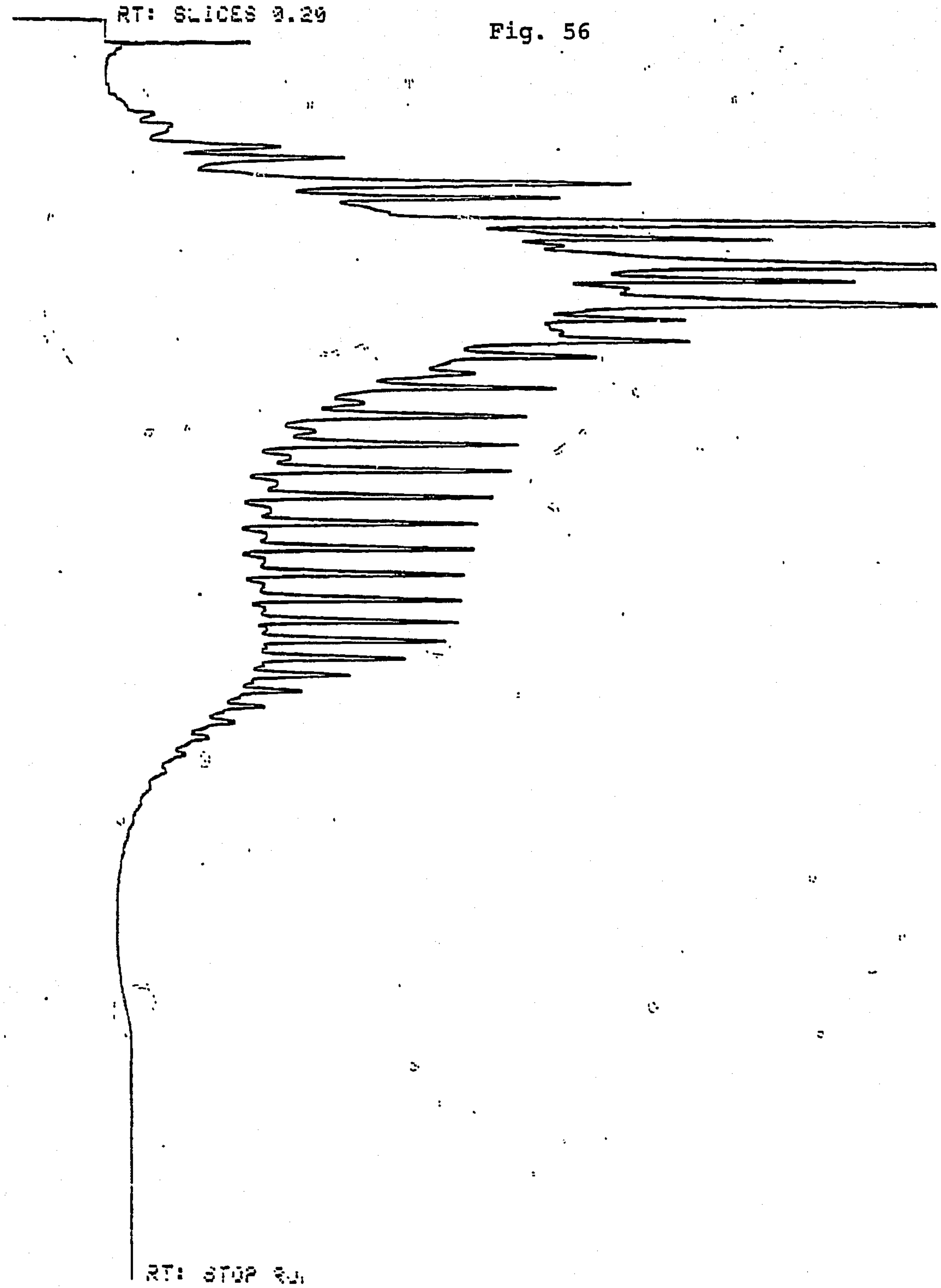
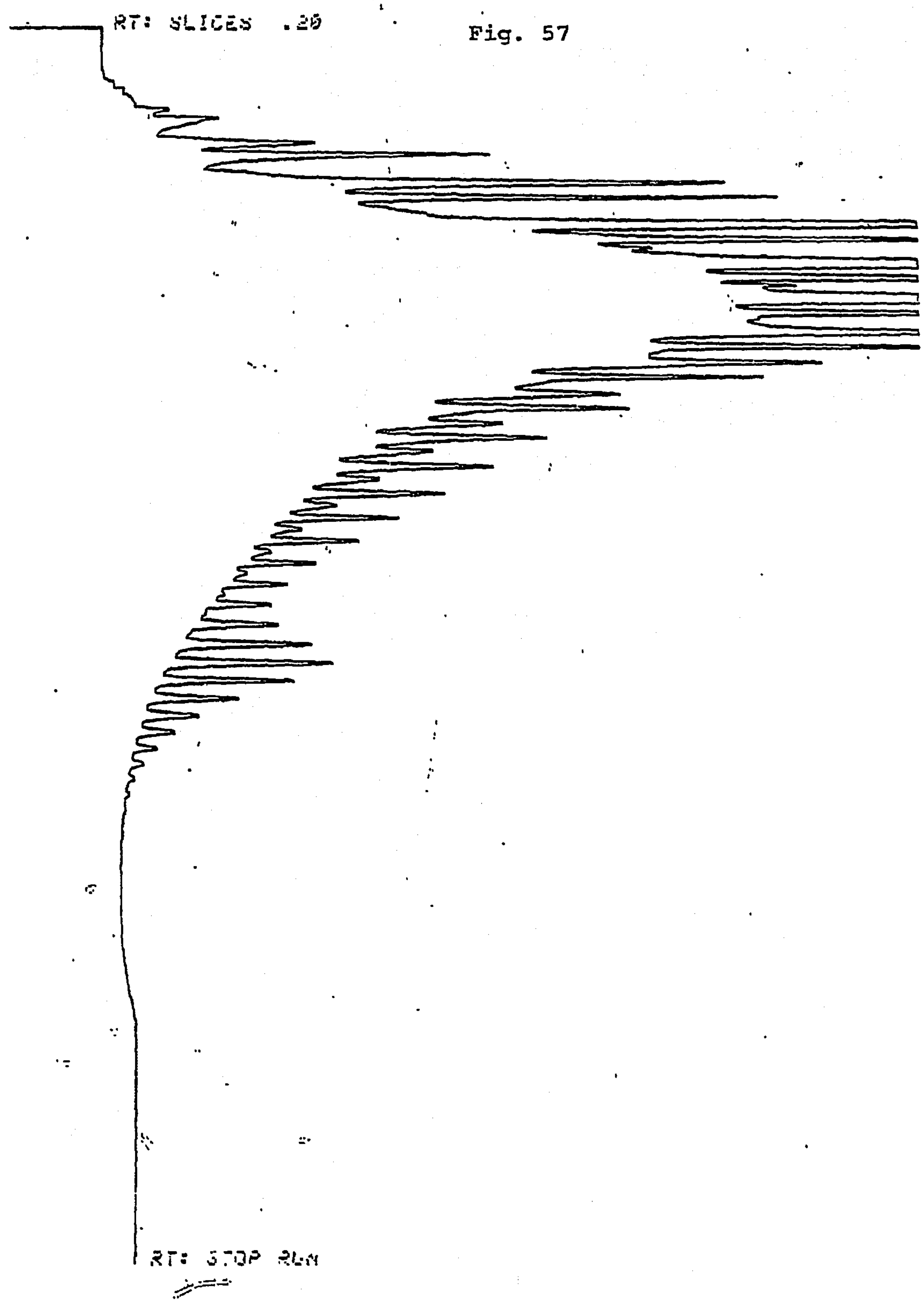
Fig. 56



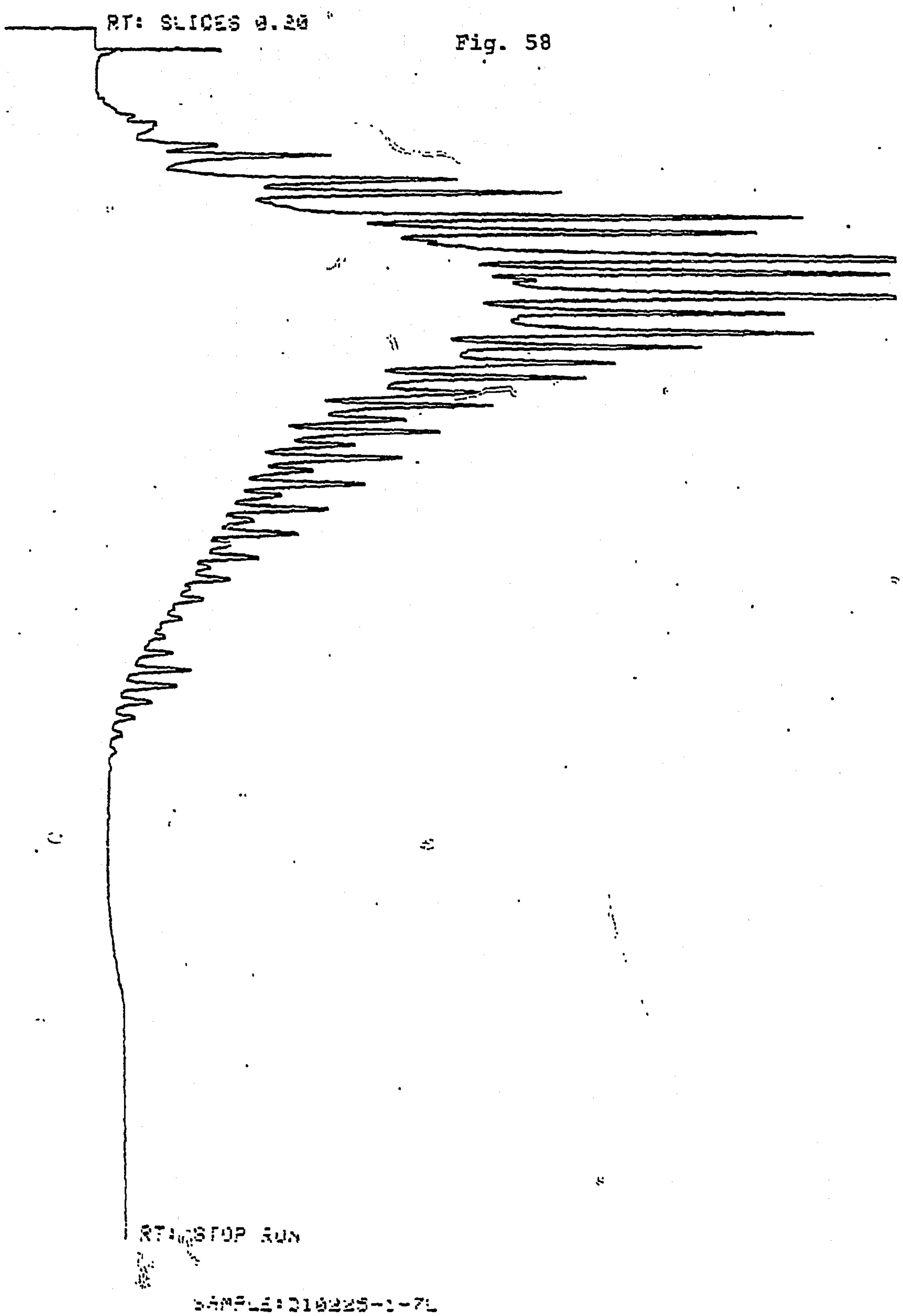
SAMPLE:010225-1-3L

Fig. 57



SAMPLE:01:225-1-5L

Fig. 58



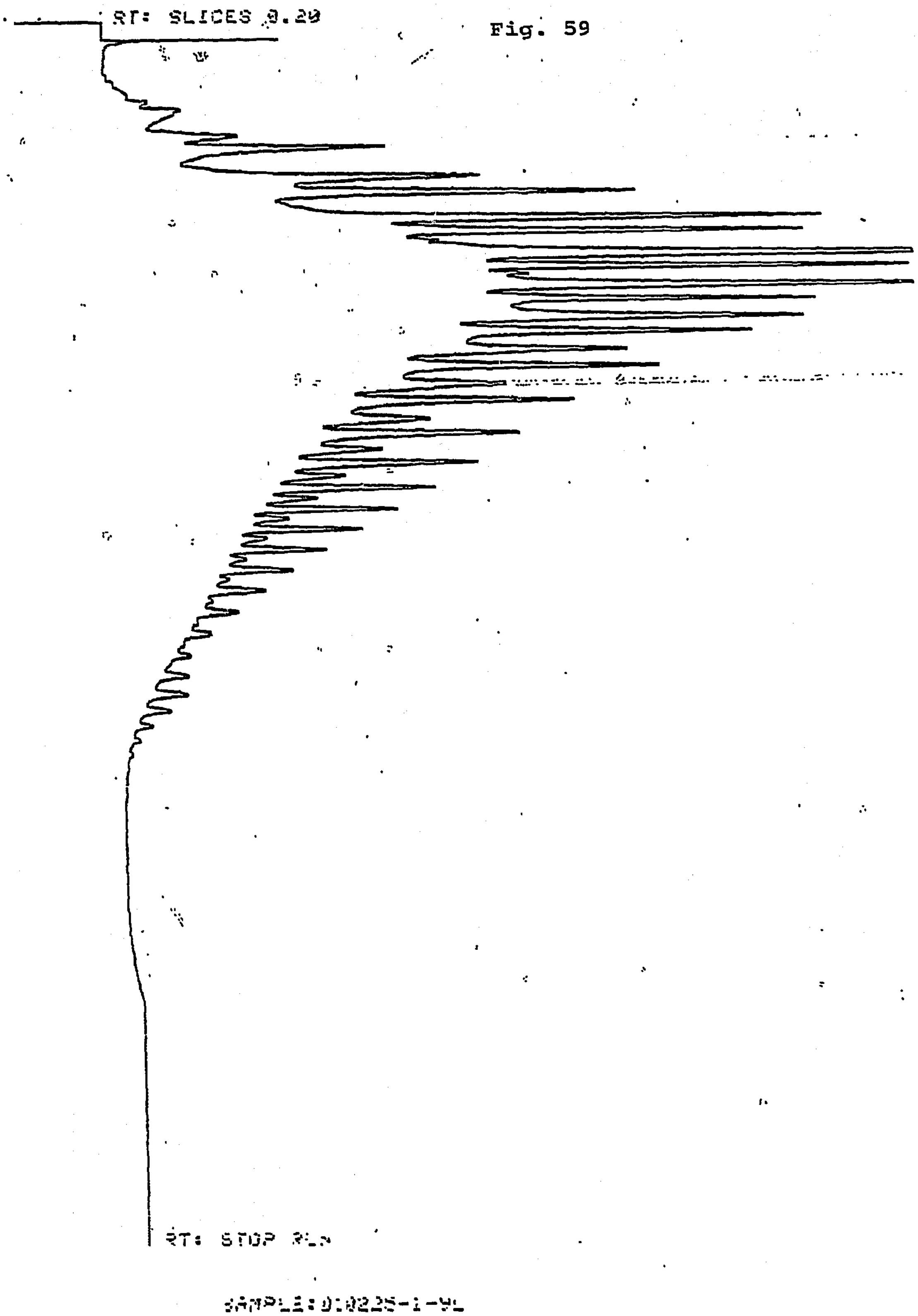


Fig. 59

Fig. 60.

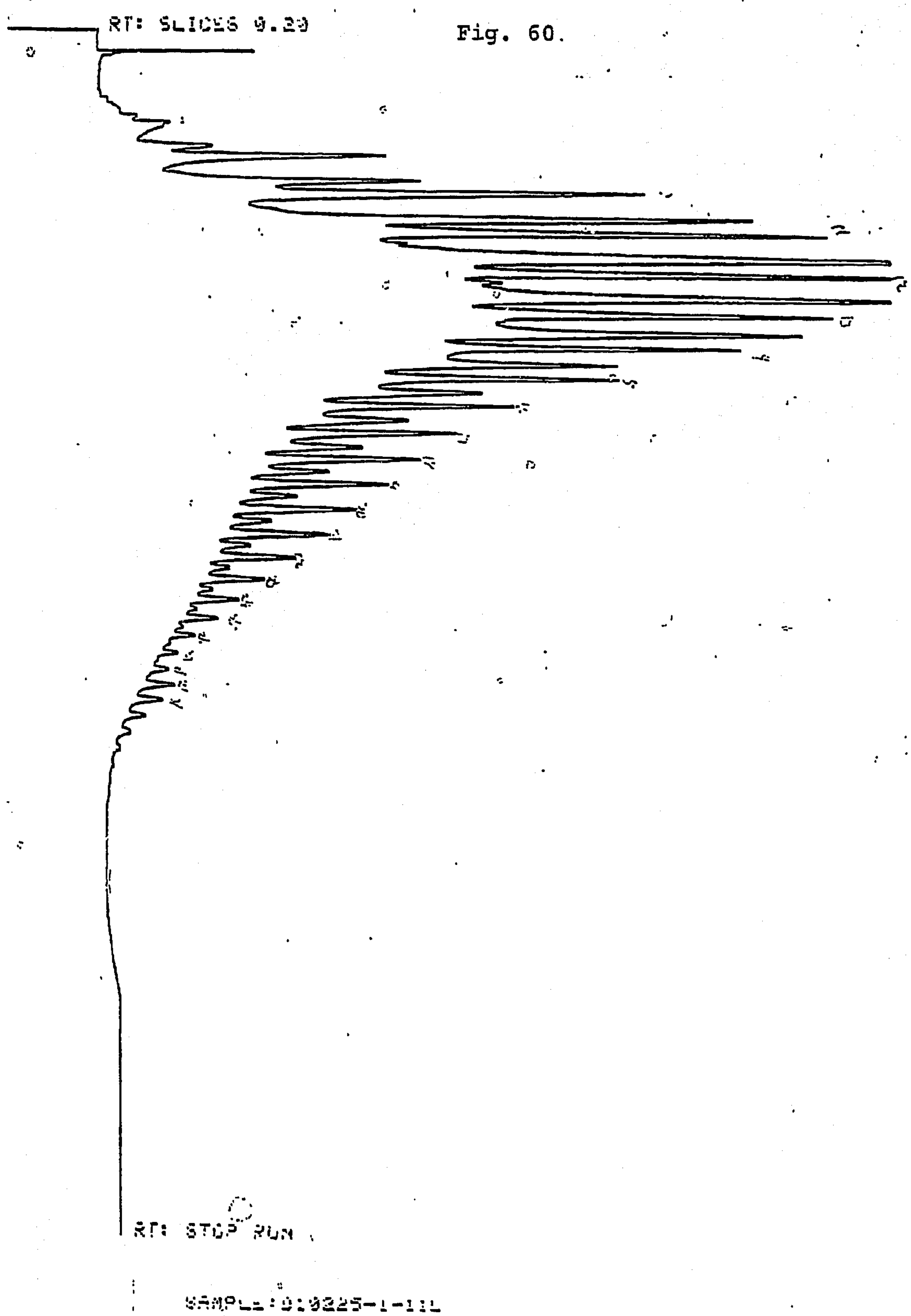
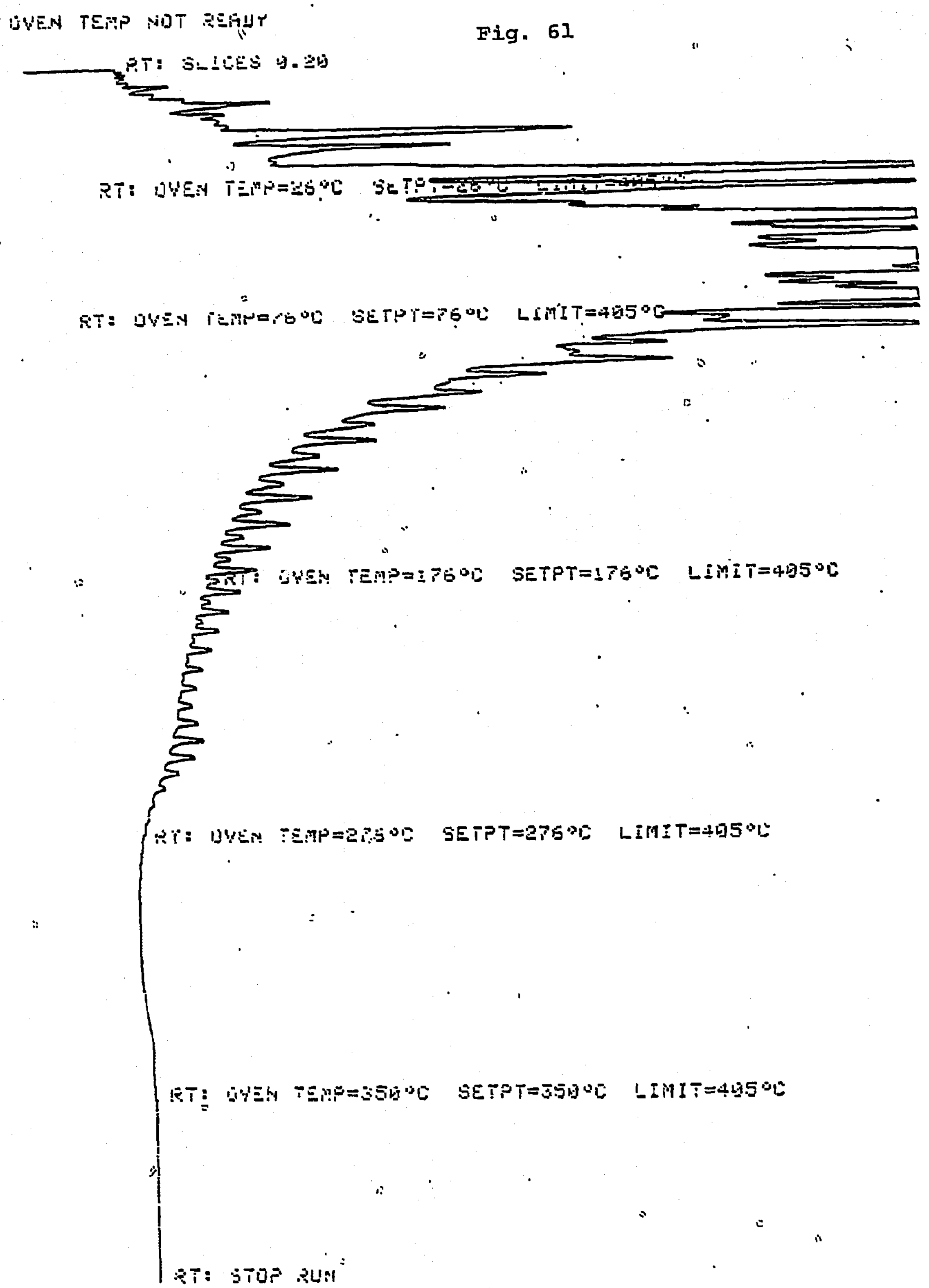


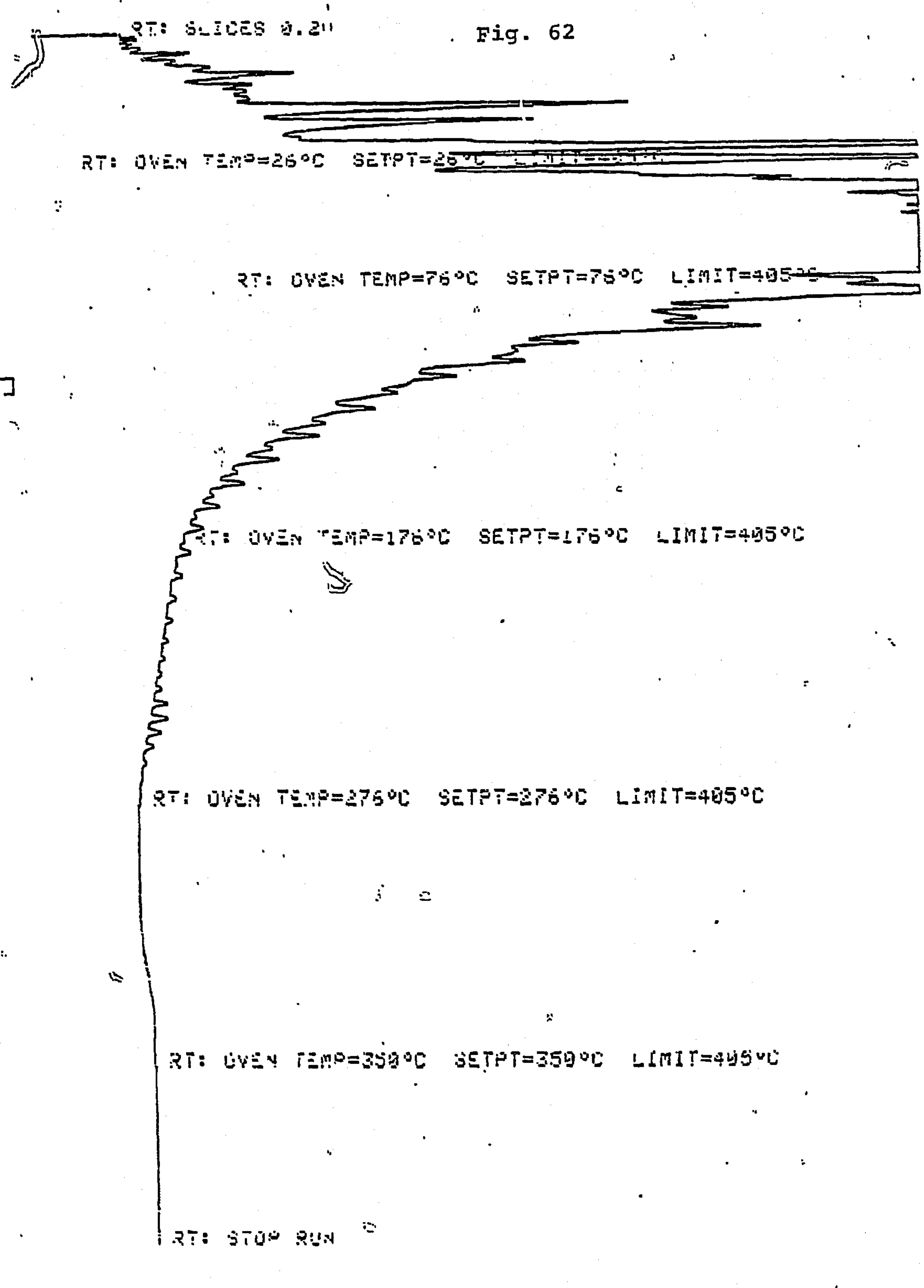
Fig. 61



SAMPLE:D10225-1-13L

152

Fig. 62



SAMPLE:210225-1-15L

TABLE 3A RESULT OF SYNGAS OPERATION

RUN NO. 10225-01
CATALYST FE,K ON LZ-105-6 #10042-88 80 CC 51.6GM (53.3 AFTER RUN+1.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-01-01	225-01-02	225-01-03	225-01-04	225-01-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	2.22	4.67	22.0	26.75	45.00
PRESSURE,PSIG	305	299	295	302	296
TEMP. C	255	250	250	250	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	2.22	4.67	22.00	4.75	23.00
EFFLNT GAS LITER	33.63	79.70	393.36	83.21	408.50
GM AQUEOUS LAYER	2.04	4.29	20.20	4.96	24.02
GM OIL	0.23	0.48	2.27	0.45	2.18
MATERIAL BALANCE					
GM ATOM CARBON %	74.23	84.74	96.70	94.93	94.27
GM ATOM HYDROGEN %	85.83	95.59	102.69	102.27	105.63
GM ATOM OXYGEN %	85.01	92.17	99.49	98.86	97.64
RATIO CHX/(H2O+CO2)	0.5308	0.6634	0.8860	0.8446	0.8663
RATIO X IN CHX	2.7190	2.5827	2.4431	2.4295	2.4211
USAGE H2/CO PRODT	1.0529	1.1654	1.1535	1.1868	1.2007
RATIO CO2/(H2O+CO2)	0.4460	0.4098	0.4618	0.4259	0.4218
K SHIFT IN EFFLNT	0.88	0.72	0.85	0.73	0.76
CONVERSION					
ON CO %	30.24	27.96	34.06	33.83	34.39
ON H2 %	34.15	33.41	38.56	39.55	38.76
ON CO+H2 %	32.33	30.85	36.38	36.80	36.70
PRDT SELECTIVITY,WT %					
CH4	26.81	21.94	15.43	14.94	14.61
C2 HC'S	9.92	9.54	12.54	12.08	11.76
C3H8	5.16	4.58	5.64	5.53	5.62
C3H6=	0.84	1.91	10.02	10.05	10.39
C4H10	8.65	5.87	3.18	3.10	3.02
C4H8=	2.66	4.66	9.48	9.51	9.75
C5H12	9.01	6.05	2.75	2.68	2.68
C5H10=	1.12	2.53	8.11	8.32	8.45
C6H14	9.25	8.08	2.10	2.18	2.10
C6H12= & CYCLO'S	1.21	3.50	4.02	4.35	4.64
C7+ IN GAS	13.75	21.60	20.09	21.05	20.89
LIQ HC'S	11.66	9.73	6.67	6.21	6.09

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	54.00	48.50	56.28	55.20	55.15
C5 -420 F	39.94	46.35	40.17	41.76	41.83
420-700 F	5.01	3.60	2.50	2.61	2.59
700-END PT	1.05	1.56	1.05	0.44	0.42
C5+-END PT	46.00	51.50	43.72	44.80	44.85
ISO/NORMAL MOLE RATIO					
C4	0.9600	0.5344	0.1308	0.1178	0.1071
C5	1.5358	0.8921	0.3681	0.3289	0.3188
C6	3.2255	3.3413	0.6199	0.5776	0.5096
C4=	1.4588	0.6103	0.0949	0.0926	0.0915
PARAFFIN/OLEFIN RATIO					
C3	5.8483	2.2896	0.5370	0.5253	0.5166
C4	3.1399	1.2156	0.3233	0.3144	0.2991
C5	7.8268	2.3220	0.3297	0.3134	0.3085
LIQ HC COLLECTION					
PHYS. APPEARANCE			YLW OIL		YLW OIL
DENSITY	-	-	0.797	-	0.786
N, REFRACTIVE INDEX	-	-	1.4469	-	1.4386
SIMULT'D DISTILATN					
10 WT % @ DEG F			313		310
16			332		331
50			433		419
84			698		590
90			753		656
RANGE(16-84 %)			366		259
WT % @ 420 F			46.66		50.50
WT % @ 700 F			84.20		93.06

TABLE 3B RESULT OF SYNGAS OPERATION

RUN NO. 10225-01
CATALYST FE,K ON LZ-105-6 #10042-88 80 CC 51.6GM (53.3 AFTER RUN+1.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-01-06	225-01-07	225-01-08	225-01-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	50.25	69.25	77.00	93.58
PRESSURE,PSIG	294	296	303	295
TEMP. C	250	250	250	250
FEED CC/MIN	400	400	400	400
HOURS FEEDING	5.25	24.25	7.75	24.33
EFFLNT GAS LITER	91.67	432.19	138.94	435.62
GM AQUEOUS LAYER	5.60	25.87	8.69	27.27
GM OIL	0.50	2.30	0.74	2.31
MATERIAL BALANCE				
GM ATOM CARBON %	93.82	96.70	98.74	97.89
GM ATOM HYDROGEN %	101.19	101.91	104.37	103.87
GM ATOM OXYGEN %	98.12	100.70	102.01	101.39
RATIO CHX/(H2O+CO2)	0.8254	0.8378	0.8724	0.8610
RATIO X IN CHX	2.4266	2.3850	2.3889	2.4012
USAGE H2/CO PRODT	1.2201	1.2135	1.2352	1.2502
RATIO CO2/(H2O+CO2)	0.3999	0.3994	0.3962	0.3868
K SHIFT IN EFFLNT	0.65	0.63	0.62	0.59
CONVERSION				
ON CO %	32.12	31.56	32.86	32.08
ON H2 %	38.92	38.72	40.33	39.91
ON CO+H2 %	35.65	35.23	36.70	36.11
PRDT SELECTIVITY,WT %				
CH4	14.80	12.67	13.36	13.84
C2 HC'S	11.78	11.62	11.02	11.00
C3H8	5.69	5.70	5.31	5.48
C3H6=	10.68	10.80	11.06	11.57
C4H10	3.05	3.01	3.06	3.07
C4H8=	9.76	9.68	9.94	10.31
C5H12	2.66	2.67	2.64	2.66
C5H10=	8.91	8.94	8.48	8.23
C6H14	2.16	2.12	1.80	2.02
C6H12= & CYCLO'S	4.93	5.04	4.94	4.97
C7+ IN GAS	19.00	21.30	22.37	20.70
LIQ HC'S	6.57	6.45	6.01	6.15

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	55.77	53.49	53.76	55.27
C5 -420 F	40.88	43.20	43.06	41.45
420-700 F	2.96	2.94	2.76	2.85
700-END PT	0.39	0.37	0.42	0.43
C5+-END PT	44.23	46.51	46.24	44.73
ISO/NORMAL MOLE RATIO				
C4	0.1081	0.1131	0.1027	0.1014
C5	0.2919	0.2826	0.2844	0.2670
C6	0.4774	0.4185	0.5196	0.4314
C4=	0.0890	0.0882	0.0894	0.0875
PARAFFIN/OLEFIN RATIO				
C3	0.5087	0.5035	0.4584	0.4520
C4	0.3020	0.3003	0.2972	0.2875
C5	0.2901	0.2899	0.3028	0.3134
LIQ HC COLLECTION				
PHYS. APPEARANCE		CLR OIL		CLR OIL
DENSITY		0.776		0.775
N, REFRACTIVE INDEX		1.4366	-	1.4366
SIMULT'D DISTILATN				
10 WT % @ DEG F		314		311
16		334		333
50		424		429
84		592		610
90		649		666
RANGE(16-84 %)		258		277
WT % @ 420 F		48.66		46.66
WT % @ 700 F		94.19		93.07

TABLE 3C RESULT OF SYNGAS OPERATION

RUN NO. 10225-01
CATALYST FE,K ON LZ-105-6 #10042-88 80 CC 51.6GM (53.3 AFTER RUN+1.7G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-01-11	225-01-13	225-01-14	225-01-15
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	118.67	143.0	148.5	167.0
PRESSURE,PSIG	296	301	301	293
TEMP. C	250	275	281	281
FEED CC/MIN	400	400	400	400
HOURS FEEDING	25.08	24.33	5.50	24.00
EFFLNT GAS LITER	455.08	362.03	76.27	330.80
GM AQUEOUS LAYER	27.68	18.28	3.60	15.71
GM OIL	2.49	8.49	2.61	11.40
MATERIAL BALANCE				
GM ATOM CARBON %	99.44	107.67	102.51	102.03
GM ATOM HYDROGEN %	104.75	113.57	107.50	106.34
GM ATOM OXYGEN %	102.47	109.61	101.65	102.49
RATIO CHX/(H2O+CO2)	0.8787	0.9598	1.0194	0.9898
RATIO X IN CHX	2.3940	2.5916	2.5636	2.5846
USAGE H2/CO PRODT	1.2500	0.8356	0.8476	0.8351
RATIO CO2/(H2O+CO2)	0.3901	0.7763	0.7852	0.7892
K SHIFT IN EFFLNT	0.60	6.21	6.55	6.77
CONVERSION				
ON CO %	31.97	77.84	78.31	78.93
ON H2 %	39.74	62.38	62.95	63.42
ON CO+H2 %	35.95	69.90	70.45	71.01
PRDT SELECTIVITY,WT %				
CH4	13.62	20.87	19.92	20.80
C2 HC'S	10.79	12.31	11.75	12.30
C3H8	5.34	5.50	5.25	5.55
C3H6=	11.30	1.93	1.84	1.95
C4H10	3.11	5.37	5.13	5.00
C4H8=	10.41	4.46	4.25	4.32
C5H12	2.69	5.29	5.05	4.64
C5H10=	8.98	5.59	5.34	4.37
C6H14	2.09	3.79	3.62	3.53
C6H12= & CYCLO'S	5.35	3.14	3.00	3.11
C7+ IN GAS	20.00	21.30	20.32	19.74
LIQ HC'S	6.33	10.43	14.52	14.69

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	54.56	50.46	48.15	49.92
C5 -420 F	42.06	46.57	48.44	46.63
420-700 F	2.88	2.45	3.09	3.12
700-END PT	0.50	0.52	0.32	0.33
C5+-END PT	45.44	49.54	51.85	50.08
ISO/NORMAL MOLE RATIO				
C4	0.1007	0.5772	0.5772	0.5078
C5	0.2633	1.4480	1.4480	1.4092
C6	0.3681	2.5070	2.5070	2.3917
C4=	0.0876	0.6057	0.6057	0.5715
PARAFFIN/OLEFIN RATIO				
C3	0.4508	2.7201	2.7201	2.7231
C4	0.2889	1.1638	1.1638	1.1174
C5	0.2911	0.9192	0.9192	1.0326
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLDY OIL	LT YL OIL		LT YL OIL
DENSITY	0.761	0.778		0.781
N, REFRACTIVE INDEX	1.4360	1.4394		1.4393
SIMULT'D DISTILATN				
10 WT % @ DEG F	313	251		249
16	335	278		276
50	429	361		352
84	619	507		459
90	676	588		513
RANGE(16-84 %)	284	229		183
WT % @ 420 F	46.66	71.50		76.50
WT % @ 700 F	92.07	95.03		97.75

V. RUN 10225-4, Fe/K on UCC-104

This catalyst was prepared by the same procedure used for the previous one (10225-1), except that UCC-104 was used instead of LZ-105-6. It was formed into tablets without a binder.

A similar catalyst using UCC-108 (an optimized, more active version of UCC-104) was previously found to be almost completely inactive for syngas conversion. The Molecular Sieve components of many catalysts have been deactivated by the metal ions. Not since the shake-down runs a year ago, however, has a metal component been so poisoned as to lose almost all activity. To determine whether this is a general phenomenon or merely some problem with a particular batch, this catalyst was prepared. That the phenomenon is in fact a general one for this method of metal loading is indicated in Fig. 63. Product selectivity is given in Fig. 64, and detailed material balances in Table 4.

A physical mixture of promoted iron and UCC-104 is an excellent F-T catalyst with good selectivity for high-octane gasoline. When the iron is precipitated onto the UCC-104 by this method, however, the catalyst is inactive.

Fig. 63

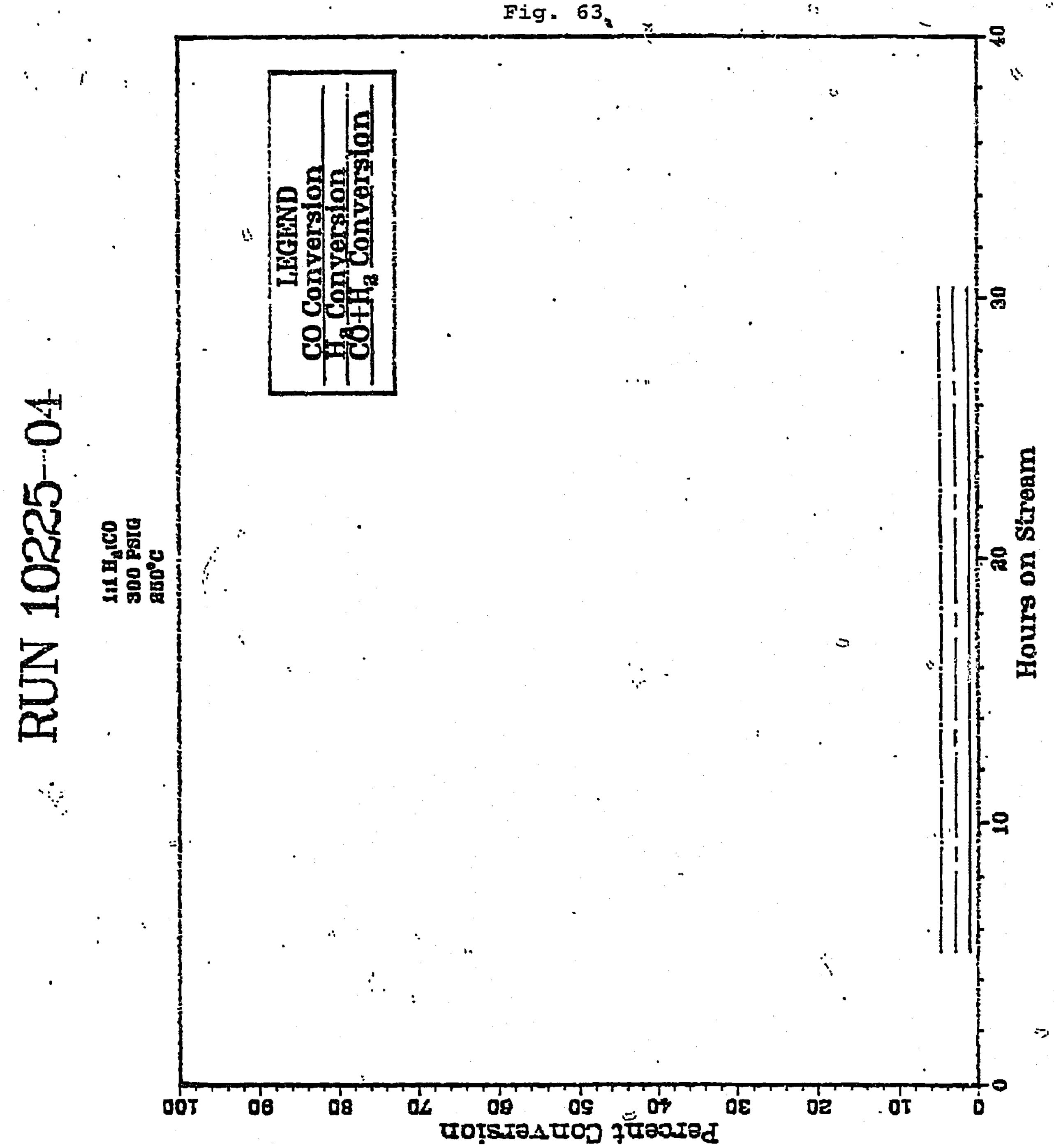
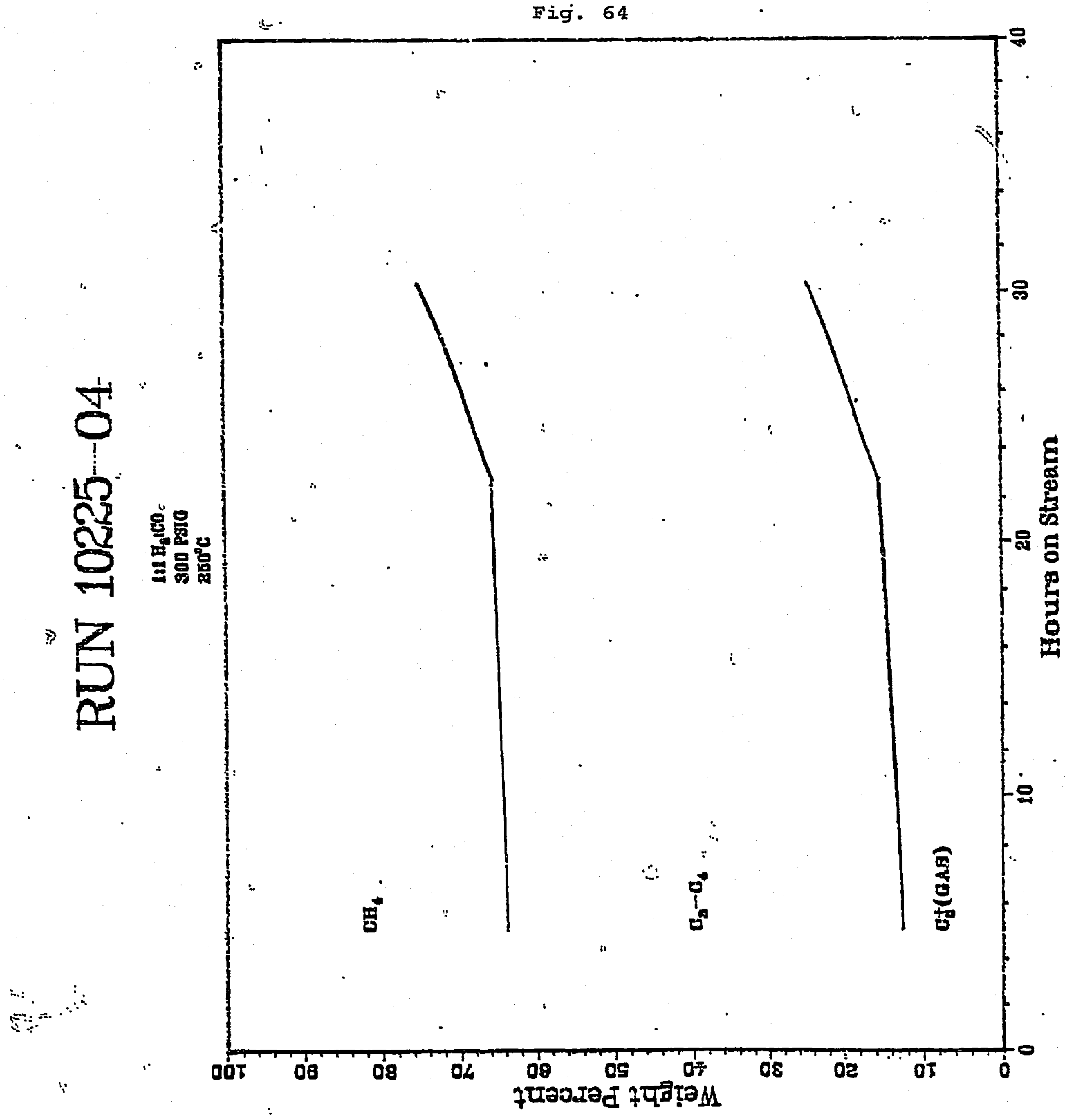

RUN 10225-04
1:1 H2:CO
300 PSIG
250°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100

Fig. 64



RUN 10225-04
1:1 H2:CO
300 PSIG
250°C
CH4
C2-C4
C5+(GAS)
Hours on Stream
0
10
20
30
40
Weight Percent
0
10
20
30
40
50
60
70
80
90
100

TABLE 4 RESULT OF SYNGAS OPERATION

RUN NO. 10225-04
CATALYST FE,K-PPT ON UCC-104 #10252-9 80 CC 29.8GM(29.0 AFTER RUN-.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-04-01	225-04-02	225-04-03
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	5.08	22.75	30.42
PRESSURE,PSIG	298	298	306
TEMP. C	249	249	249
FEED CC/MIN	400	400	400
HOURS FEEDING	5.08	17.67	7.67
EFFLNT GAS LITER	115.56	408.22	179.67
GM AQUEOUS LAYER	0.00	0.00	0.00
GM OIL	0.00	0.00	0.00
MATERIAL BALANCE			
GM ATOM CARBON %	93.62	94.97	95.74
GM ATOM HYDROGEN %	96.81	98.54	100.91
GM ATOM OXYGEN %	96.62	98.04	98.62
RATIO CHX/(H2O+CO2)	0.2024	0.1945	0.2530
RATIO X IN CHX	2.7739	2.7413	2.6064
USAGE H2/CO PRODT	1.9242	1.9214	1.9473
RATIO CO2/(H2O+CO2)	0.0424	0.0407	0.0372
K SHIFT IN EFFLNT	0.04	0.04	0.04
CONVERSION			
ON CO %	0.98	0.94	1.17
ON H2 %	4.81	4.74	4.94
ON CO+H2 %	2.93	2.88	3.10
PRDT SELECTIVITY,WT %			
CH4	36.19	34.67	25.13
C2 HC'S	14.99	14.45	16.48
C3H8	5.58	4.59	4.54
C3H6=	18.46	16.64	16.34
C4H10	3.04	3.08	2.63
C4H8=	9.09	11.19	10.39
C5H12	0.00	0.00	2.18
C5H10=	3.43	4.83	8.08
C6H14	0.00	0.00	1.18
C6H12= & CYCLO'S	0.00	0.00	0.00
C7+ IN GAS	9.23	10.55	13.05
LIQ HC'S	0.00	0.00	0.00

TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	87.34	84.62	75.51
C5 -420 F	12.66	15.38	24.49
420-700 F	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00
C5+-END PT	12.66	15.38	24.49
ISO/NORMAL MOLE RATIO			
C4	0.0000	0.0000	0.0000
C5	0.0000	0.0000	0.0000
C6	0.0000	0.0000	0.0000
C4=	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO			
C3	0.2885	0.2634	0.2650
C4	0.3229	0.2655	0.2444
C5	0.0000	0.0000	0.2619
LIQ HC COLLECTION			
PHYS. APPEARANCE			
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F			
16			
50			
84			
90			
RANGE(16-84 %)			
WT % @ 420 F			
WT % @ 700 F			

VI. RUN 10112-11, Fe/K on UCC-107

This precipitation catalyst was prepared like the two previous ones, except with UCC-107 as the Molecular Sieve component. It was tested for one day, found to be inactive, and shut down. The material balance for the single sample is shown in Table 5. The cause of the inactivity is unknown.

TABLE 5 RESULT OF SYNGAS OPERATION

RUN NO. 10112-11
CATALYST FE,K-PPT-UCC-107 #10252-13C 80 CC 34.7GM(34.9 AFTER RUN +.2G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-11-01
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	23.75
PRESSURE,PSIG	308
TEMP. C	251
FEED CC/MIN	400
HOURS FEEDING	23.75
EFFLNT GAS LITER	569.55
GM AQUEOUS LAYER	0.00
GM OIL	0.00
MATERIAL BALANCE	
GM ATOM CARBON %	99.16
GM ATOM HYDROGEN %	104.88
GM ATOM OXYGEN %	101.30
RATIO CHX/(H2O+CO2)	0.5379
RATIO X IN CHX	2.5705
USAGE H2/CO PRODT	1.5953
RATIO CO2/(H2O+CO2)	0.1790
K SHIFT IN EFFLNT	0.22
CONVERSION	
ON CO %	3.34
ON H2 %	6.67
ON CO+H2 %	5.05
PRDT SELECTIVITY,WT %	
CH4	19.07
C2 HC'S	15.23
C3H8	7.58
C3H6=	12.13
C4H10	4.84
C4H8=	9.58
C5H12	4.25
C5H10=	5.76
C6H14	4.04
C6H12= & CYCLO'S	1.30
C7+ IN GAS	16.23
LIQ HC'S	0.00

TOTAL	100.00
SUB-GROUPING	
C1 -C4	68.42
C5 -420 F	31.58
420-700 F	0.00
700-END PT	0.00
C5+-END PT	31.58
ISO/NORMAL MOLE RATIO	
C4	0.1705
C5	0.4079
C6	0.6038
C4=	0.0839
PARAFFIN/OLEFIN RATIO	
C3	0.5966
C4	0.4871
C5	0.7181
LIQ HC COLLECTION	
PHYS. APPEARANCE	
DENSITY	
N, REFRACTIVE INDEX	
SIMULT'D DISTILATN	
10 WT % @ DEG F	
16	
50	
84	
90	
RANGE(16-84 %)	
WT % @ 420 F	
WT % @ 700 F	

VII. RUN 10112-6, Co on LZ-105-6

This catalyst was prepared by precipitating $CoO \cdot XH_2O$ with sodium carbonate from a slurry of cobalt nitrate and LZ-105-6. The cobalt-loaded Molecular-Sieve powder was pressed into pellets and calcined at 250C. Cobalt loading level was 20 percent.

Conversion, product selectivity, isomerization of the pentanes, and percent olefins of the C_4's are plotted against time on stream in Figs. 65-68. Simulated distillations of the pentane$^+$ products from two representative samples are shown in Figs. 69-70. Carbon number product distributions are shown in Figs. 71-76. Chromatograms of simulated distillations of the condensed products are reproduced in Figs. 77-82. Detailed material balances are given in Tables 6A and 6B.

At the initial reaction temperature of 220C, conversion of the syngas is only 20-25 percent (Fig. 65), which is similar to the conversion with a corresponding iron-on-LZ-105 catalyst at 250C. Gram for gram of metal, cobalt catalysts seem much more active than iron. At 250C the conversion increases significantly, but so also does the rate of deactivation. At this higher temperature the carbon monoxide and hydrogen conversion levels are almost equal, leading to a hydrogen:carbon monoxide usage ratio close to the 1:1 hydrogen:carbon monoxide feed ratio, indicating that this catalyst has enough WGS to use the hydrogen-lean syngas efficiently. Few cobalt-containing catalysts have significant WGS activity, nor is the Molecular Sieve known to have it.

Product selectivity is shown in Fig. 66. Selectivity to methane is quite high even at the lower temperature, where it averaged more than 15 percent. At 250C, more than 30 percent of the hydrocarbon product was methane, fairly typical for cobalt F-T catalysts. The extent to which the methane yield differs from that of other hydrocarbons is best illustrated by the carbon-number product distributions, plotted in Figs. 71-76. The data points for methane are unrelated to the line connecting the data points for the other hydrocarbons. The same phenomenon was observed for all the cobalt catalysts reported last quarter as well as this quarter.

The yield of the C_2-C_4 hydrocarbons is low. For the samples taken at 250C, this fraction is lower than predicted from extrapolation of the C_5^+ product distribution, since it has a flatter carbon number distribution in the C_2-C_4 region. This behavior is not unusual for cobalt catalysts at most conditions. At this lower temperature the total motor fuels yield, C_5 - 700F, averaged a respectable 68 percent. Cobalt pore-filled on UCC-101 (Second Annual Report, Run 10011-14) produced a similar yield of motor fuels at reaction temperatures of both 220 and 250C. This catalyst, however, performed poorly at 250C, producing less than half its hydrocarbons in the motor fuels range, a yield more typical of an iron rather than a cobalt catalyst. With its poor motor fuel yield and high methane yield, this catalyst is inferior to most iron catalysts.

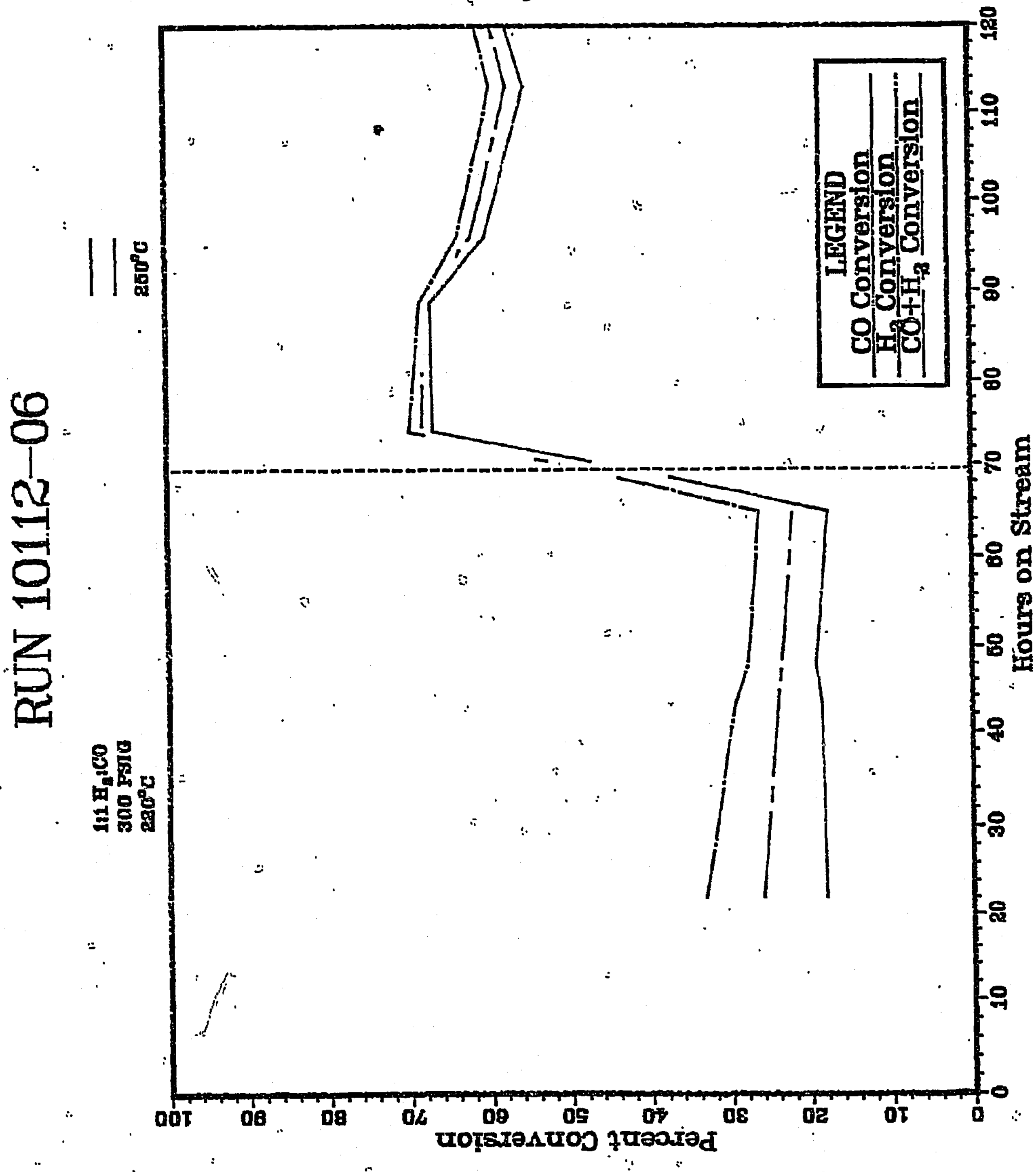
Heavies produced by this catalyst were only about 5 percent, except only Sample 5 with 20 percent. This anomaly was caused by a heavies build-up in the reactor during the first 65 hours at 220C. When the reactor temperature was raised to 250C the heavies moved more quickly out of the reactor, giving Sample 5 an apparently high selectivity for heavies. This explanation is corroborated by the high material balance for Sample 5, compared to that of all the other samples. Enough heavies were leaving the reactor after 48 hours on stream to convert the condensed product of this catalyst into a solid wax. This was probably the first sample in which the effluent products reflected the true steady-state products at those reactor conditions.

Diesel oil produced from this catalyst, unlike that from similar iron catalysts, can be expected to have a high pour point. The C_4's are less olefinic than the 70 percent olefins in iron-catalyst C_4's (Fig. 68). The pentane is barely isomerized at all (Fig. 67). Chromatograms of the simulated distillations show the condensed product to be primarily straight-chain paraffins (Figs. 77-82). Straight-chain material packs well in the solid state, leading to very high pour points for diesel range products. The low reaction temperature and partial ion exchange of the cobalt contributed to the low isomerization of the product. Conversely, the partially ion-exchanged Fe/K-on-LZ-105 catalyst isomerized the liquid very efficiently (Run 10225-1), which it was able to do because of the higher reaction temperature.

The simulated distillation of Sample 9 (Fig. 70) is unlike those of the other samples, which resemble Fig. 69. The unusual distillation leads to an unusual carbon number distribution (Fig. 76). Some of the C_{10}-C_{15} material could have been dimerized into the C_{20}-C_{30} range, a distribution which has been seen with other acidic catalysts, but more likely the aberration is an error in the simulated distillation. This catalyst does not yield a very olefinic product and shows low acid activity, both of which would be needed to oligomerize the C_{10}-C_{15} products.

The product distribution of this catalyst at 250C, where its conversion activity was significant, is just too light to make it an important Task 2 catalyst.

Fig. 65



RUN 10112-06
1:1 H_2:CO
300 PSIG
230°C
250°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
110
120

Fig. 66

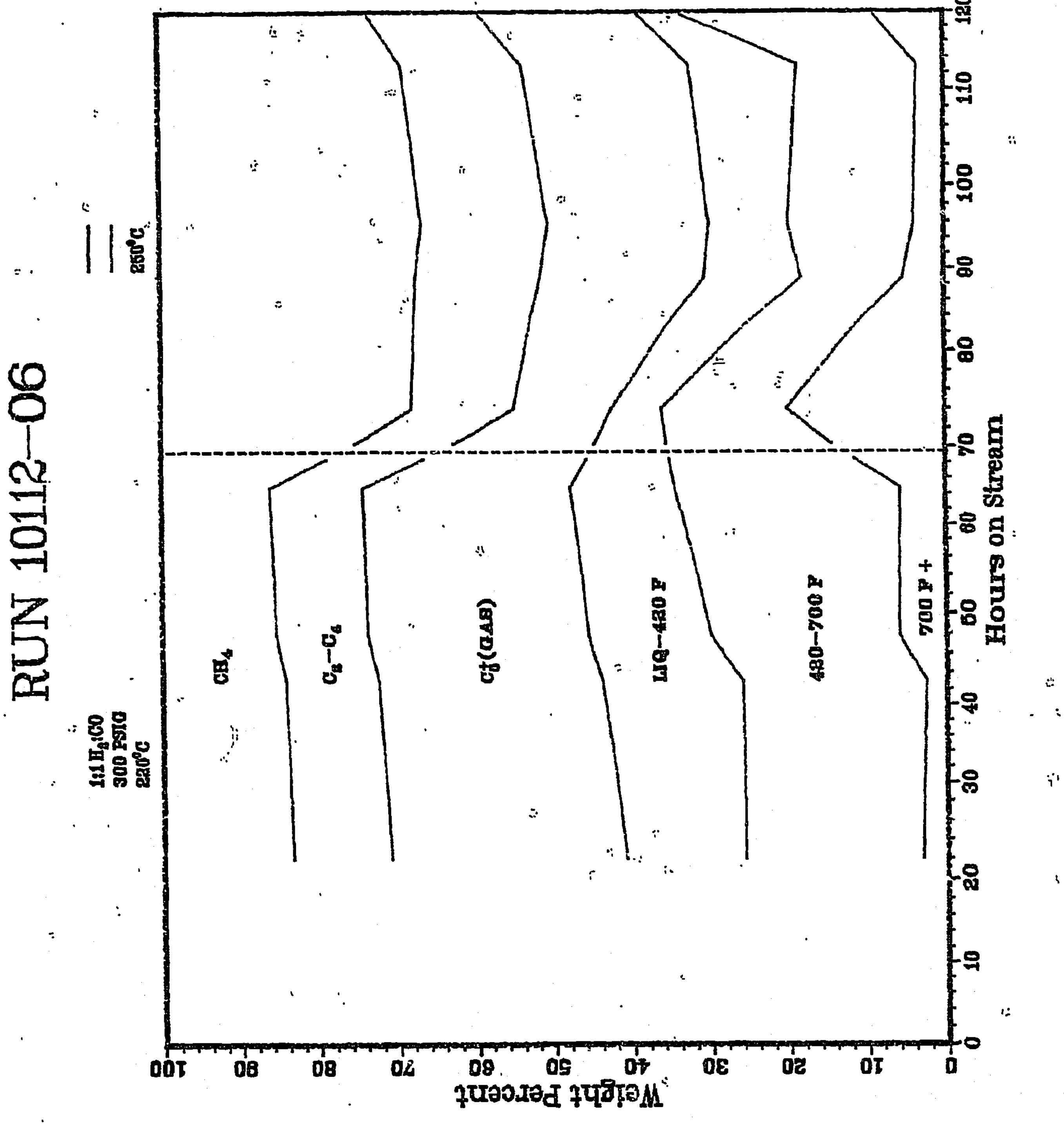

RUN 10112-06
1:1 H2:CO
300 PSIG
220°C
250°C
CH4
LIQ-430 F
430-700 F
700 F +
Hours on Stream
Weight Percent

Fig. 67

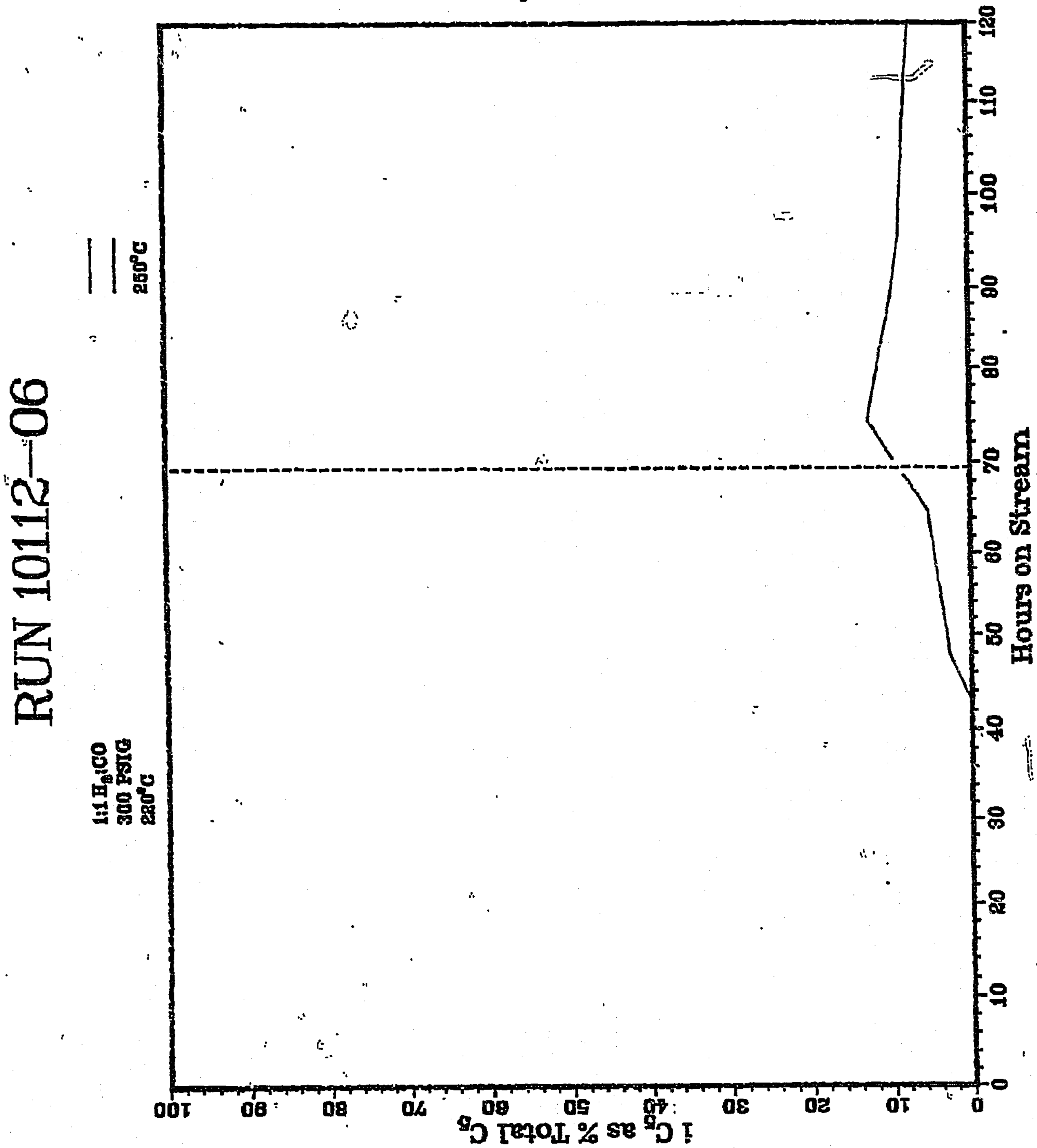
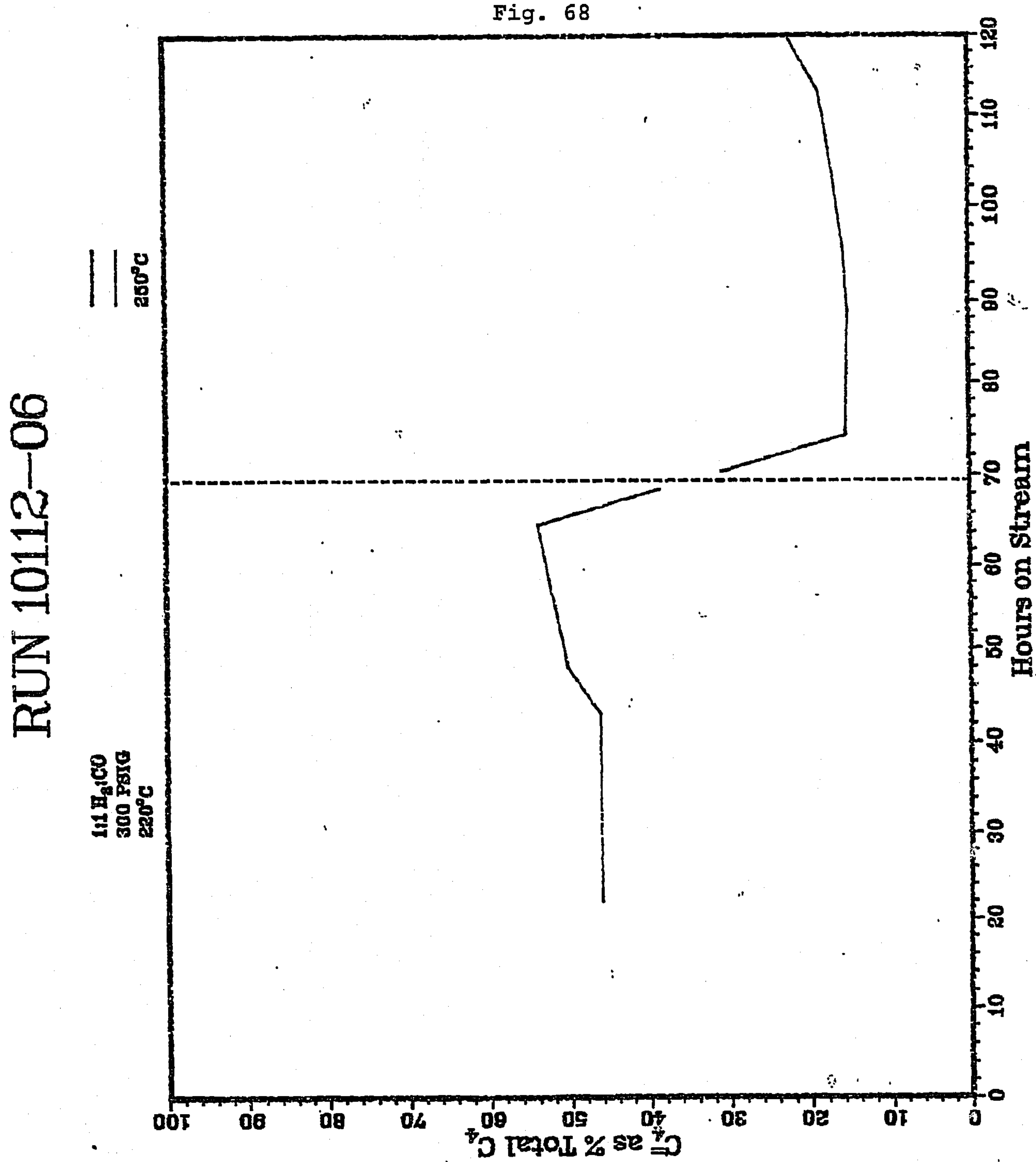

RUN 10112–06
1:1 H_2:CO
300 PSIG
230°C
250°C
Hours on Stream
i C_5 as % Total C_5

Fig. 68



RUN 10112—06
1:1 H_2:CO
300 PSIG
220°C
260°C
Hours on Stream
0 10 20 30 40 50 60 70 80 90 100 110 120
$C_4^=$ as % Total C_4
0 10 20 30 40 50 60 70 80 90 100

Fig. 69

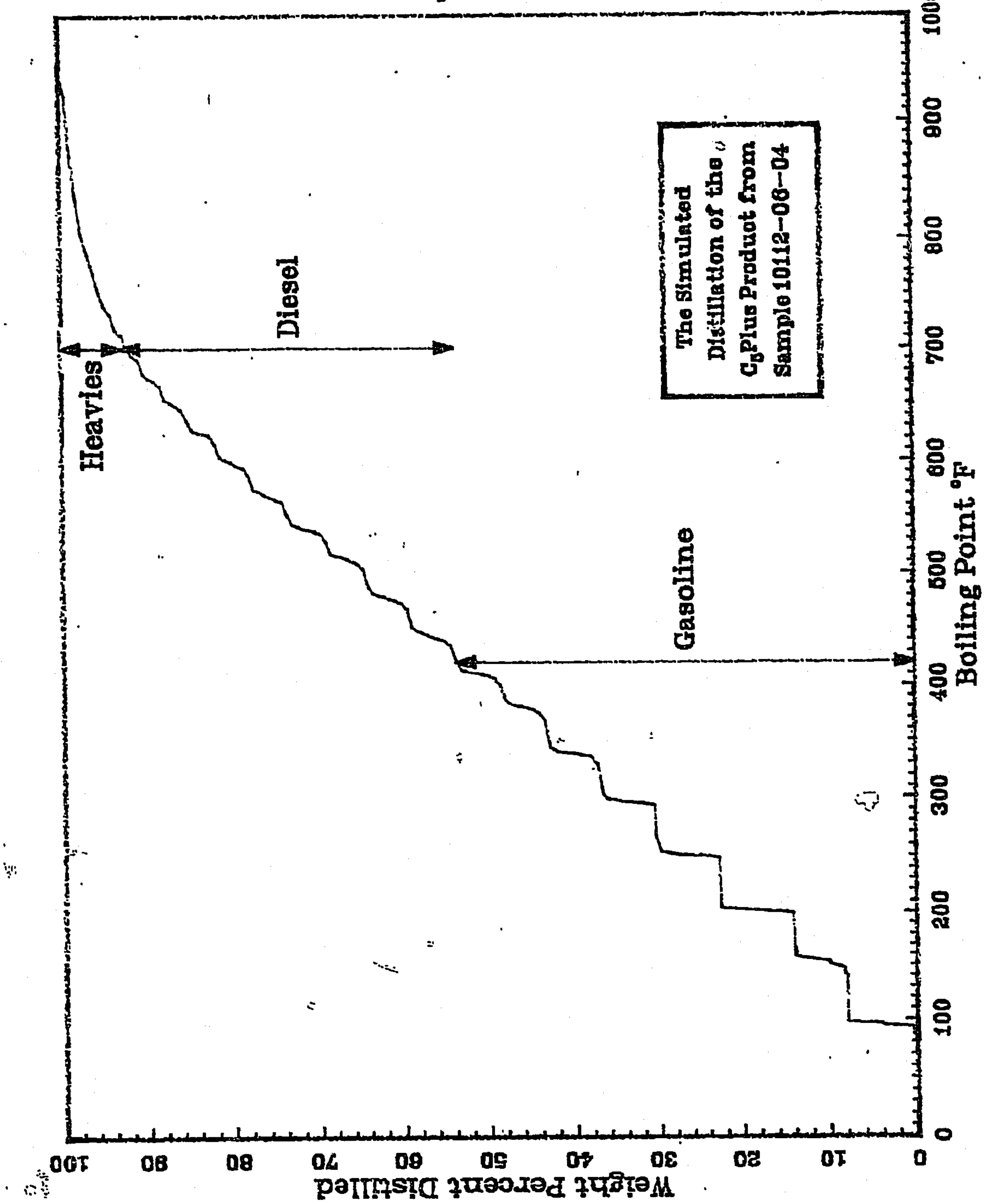

The Simulated
Distillation of the
C5Plus Product from
Sample 10112-06-04
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 70

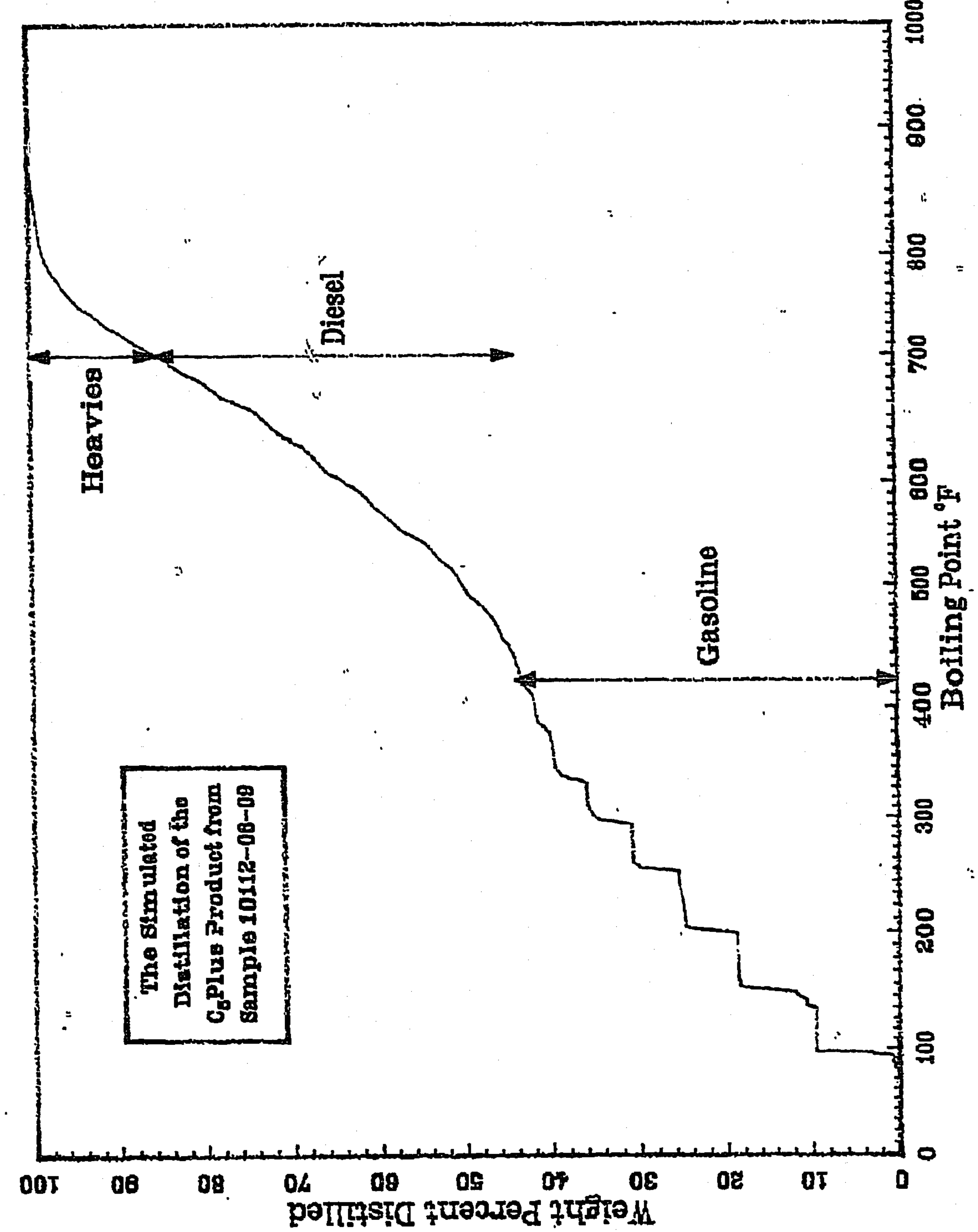

The Simulated Distillation of the C5Plus Product from Sample 10112-06-09
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 71

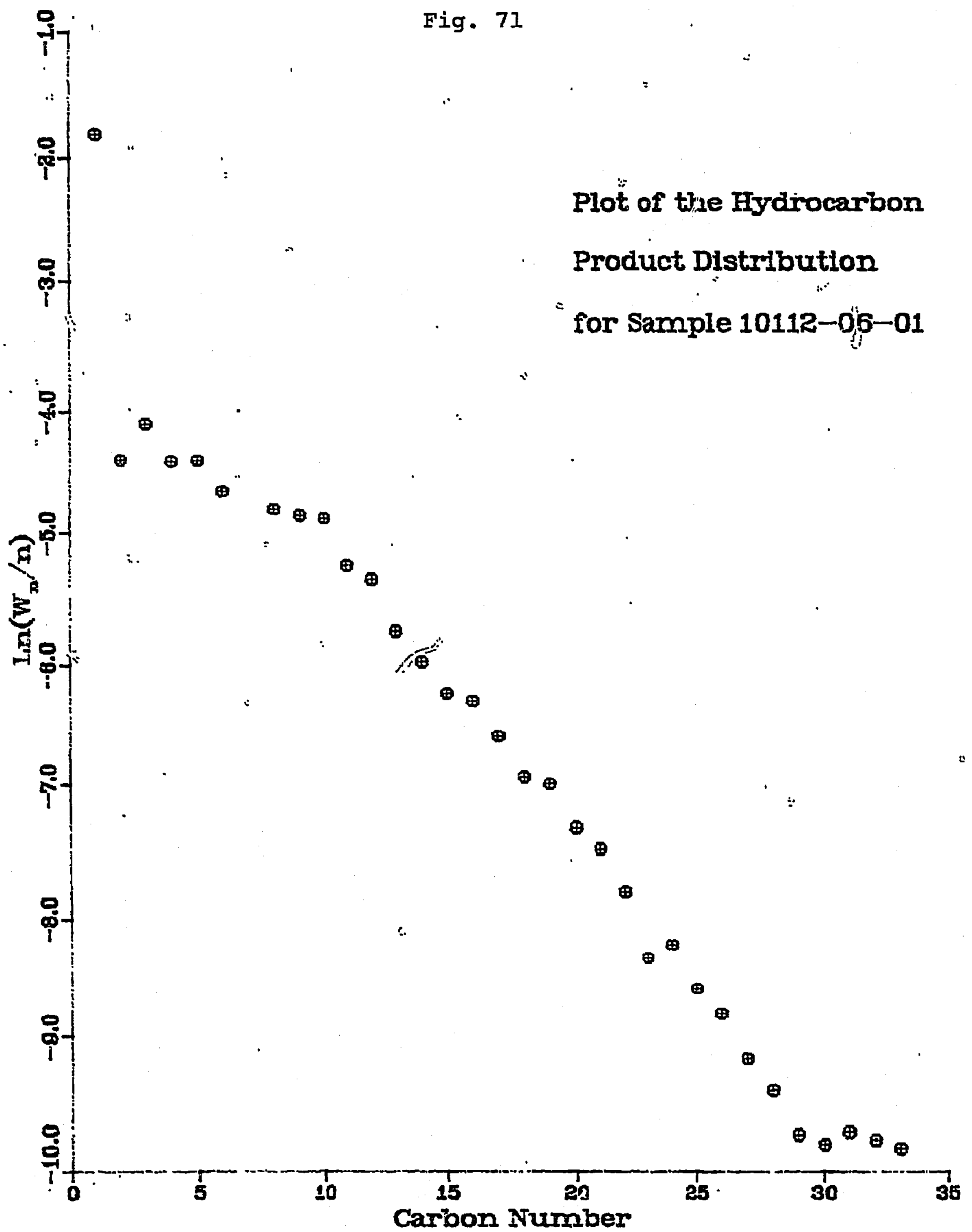

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-06-01
ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 72

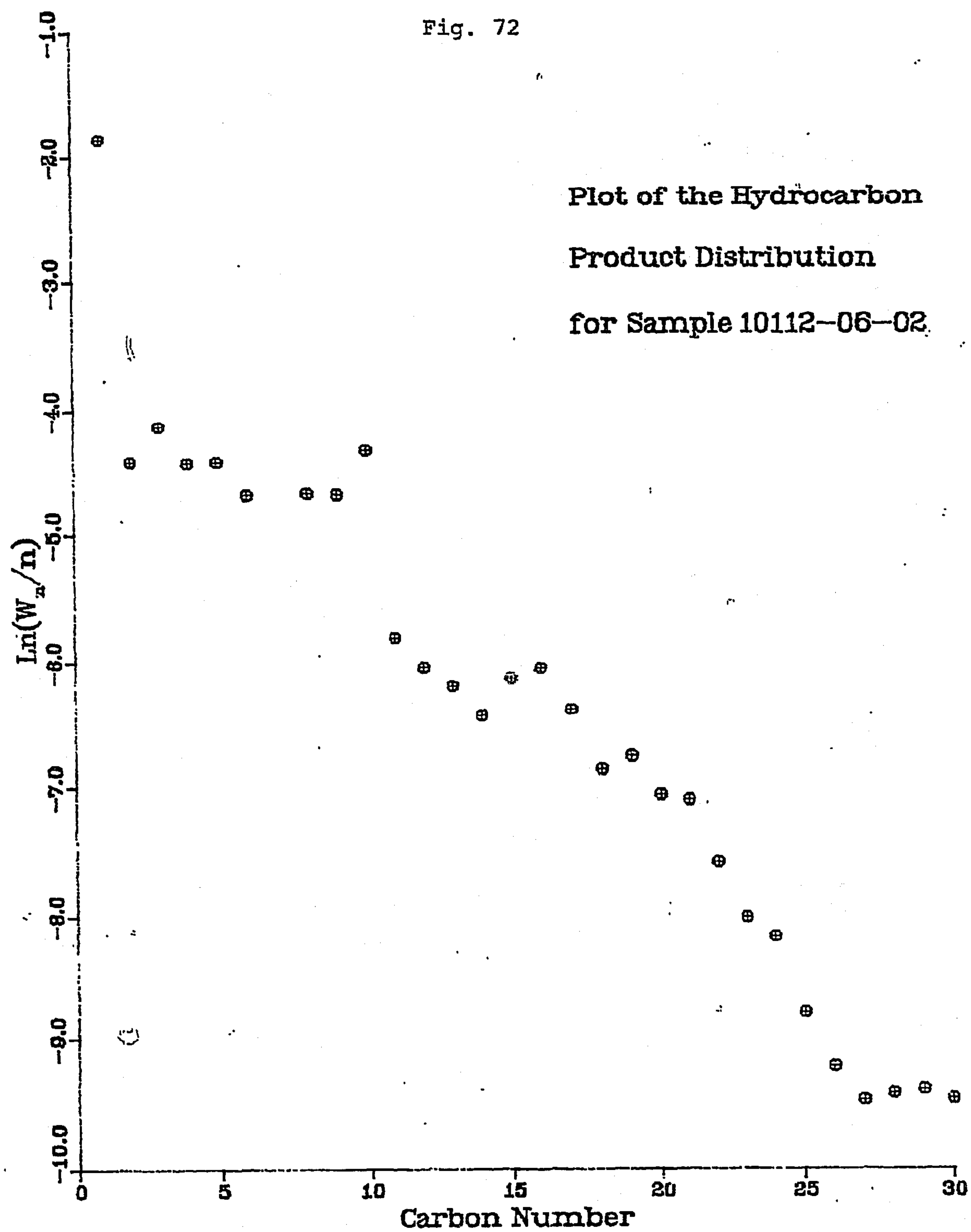

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–06–02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 73

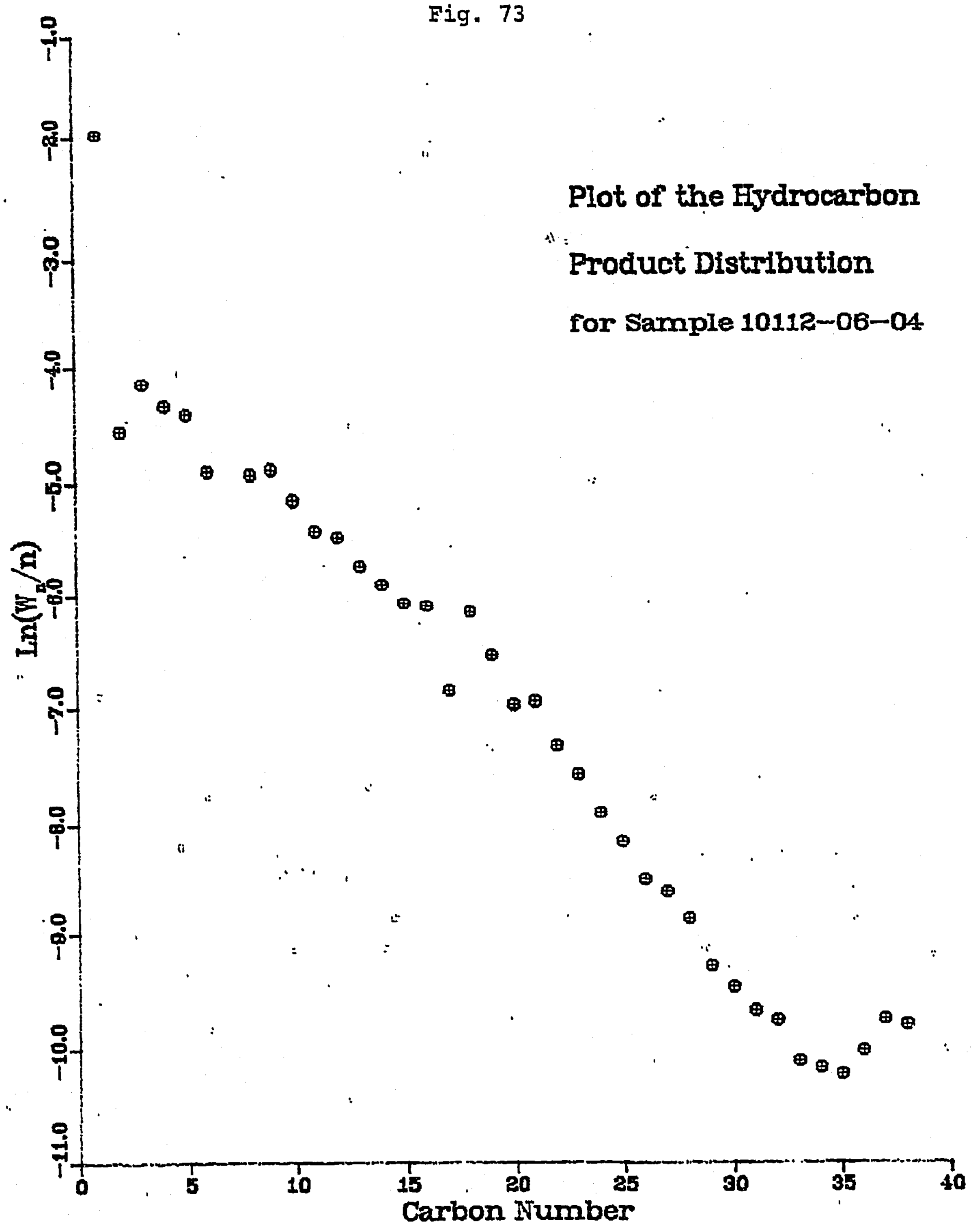

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-06-04
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 74

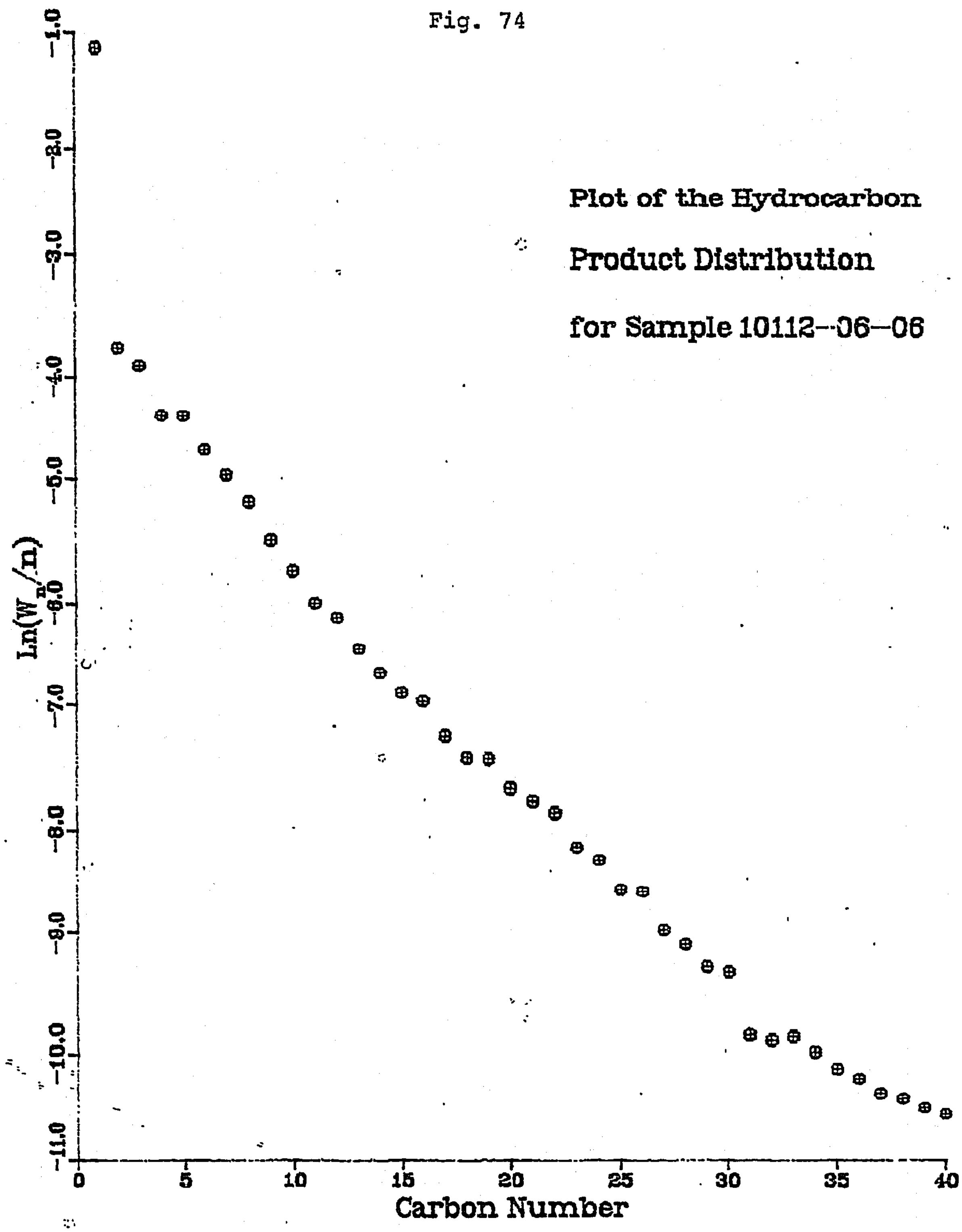

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-06-06
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 75

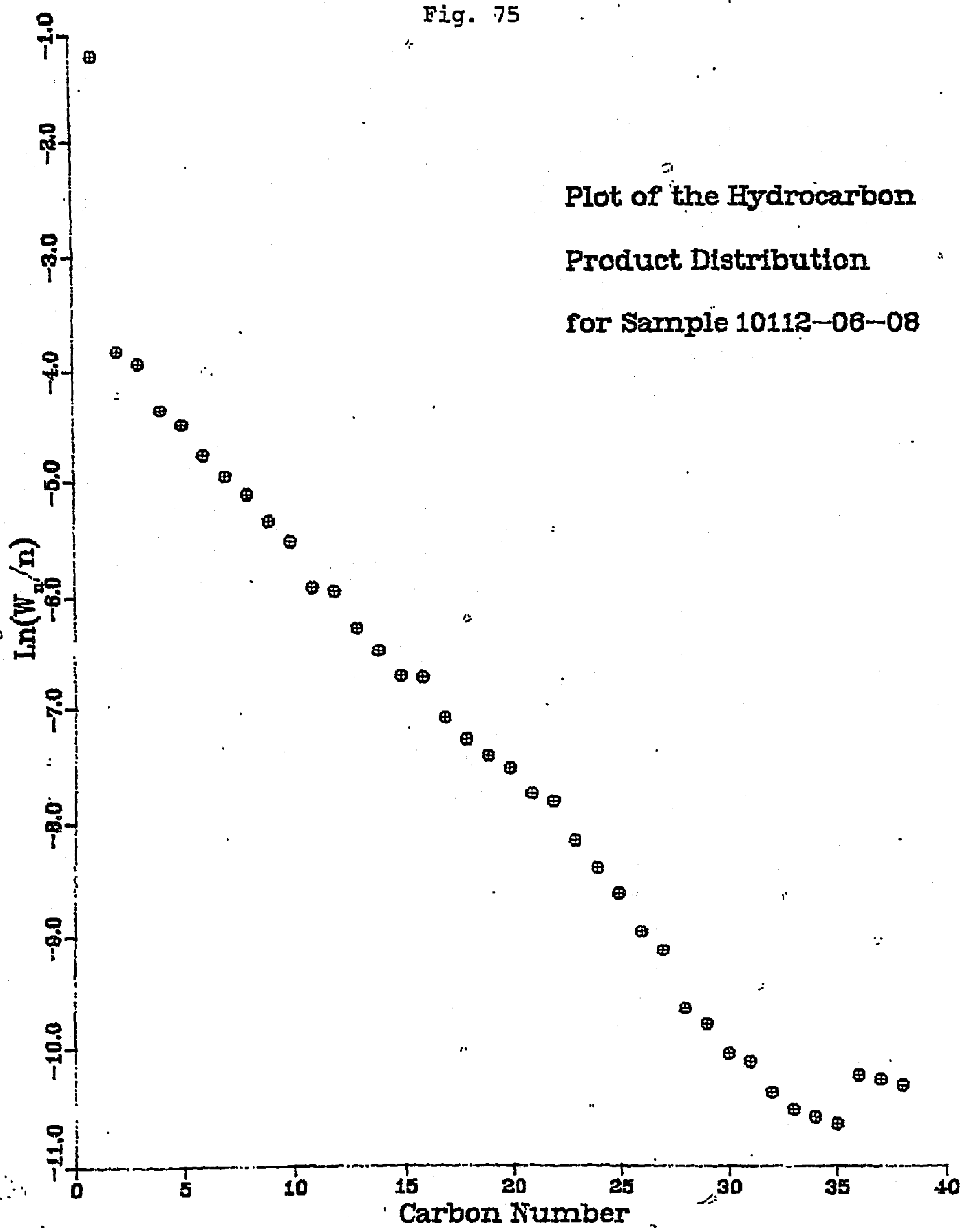

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-06-08
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 76

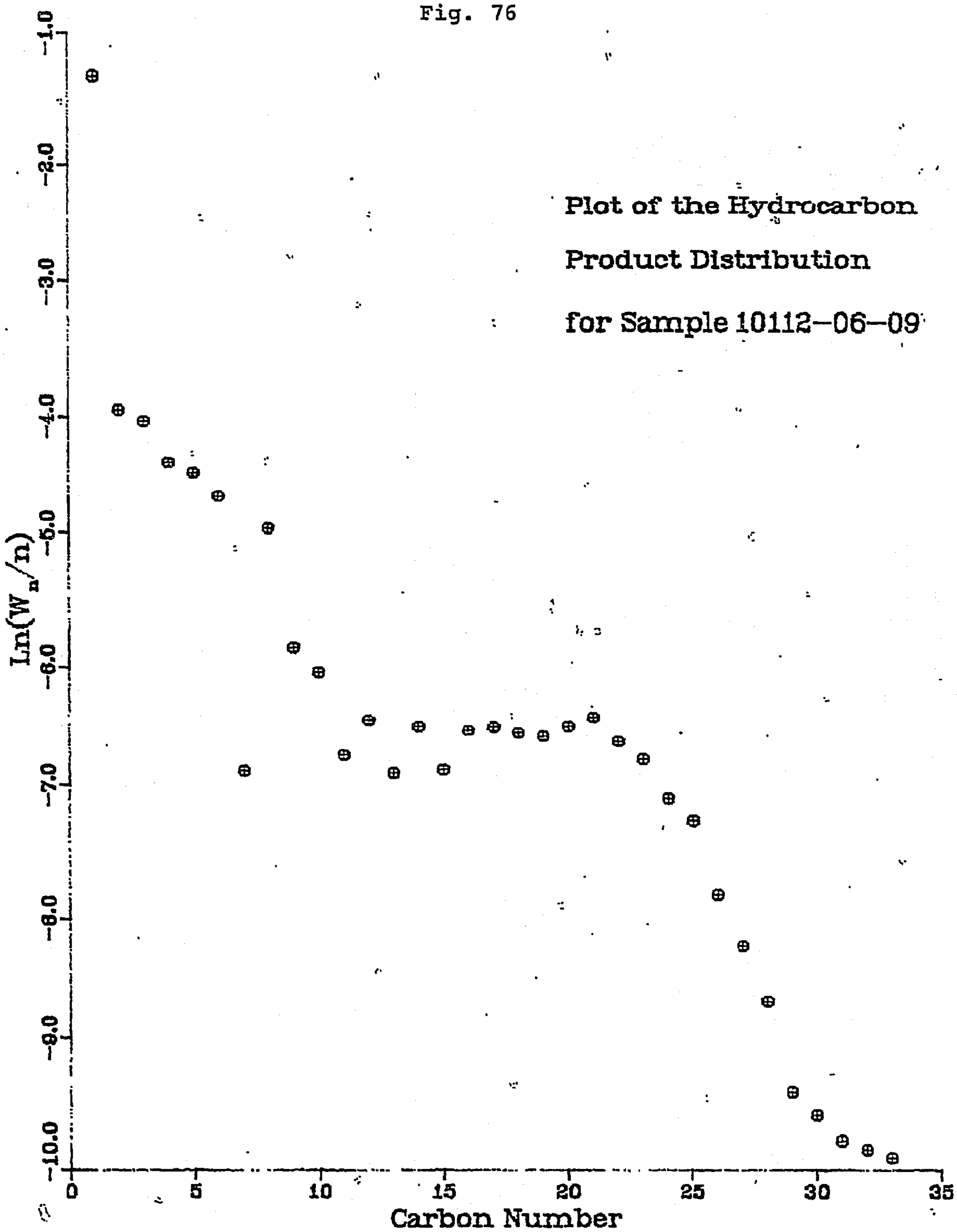

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-06-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 77

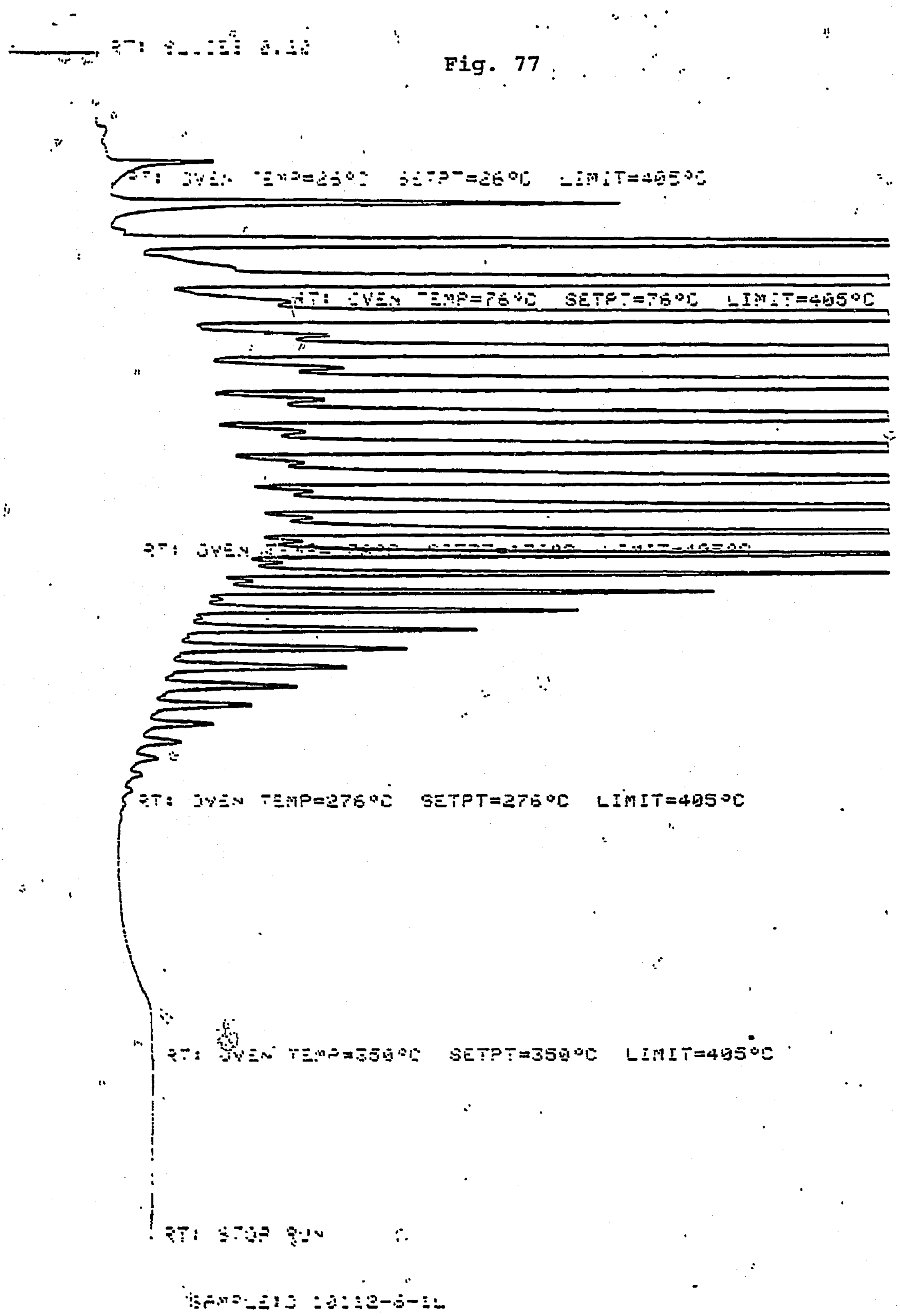
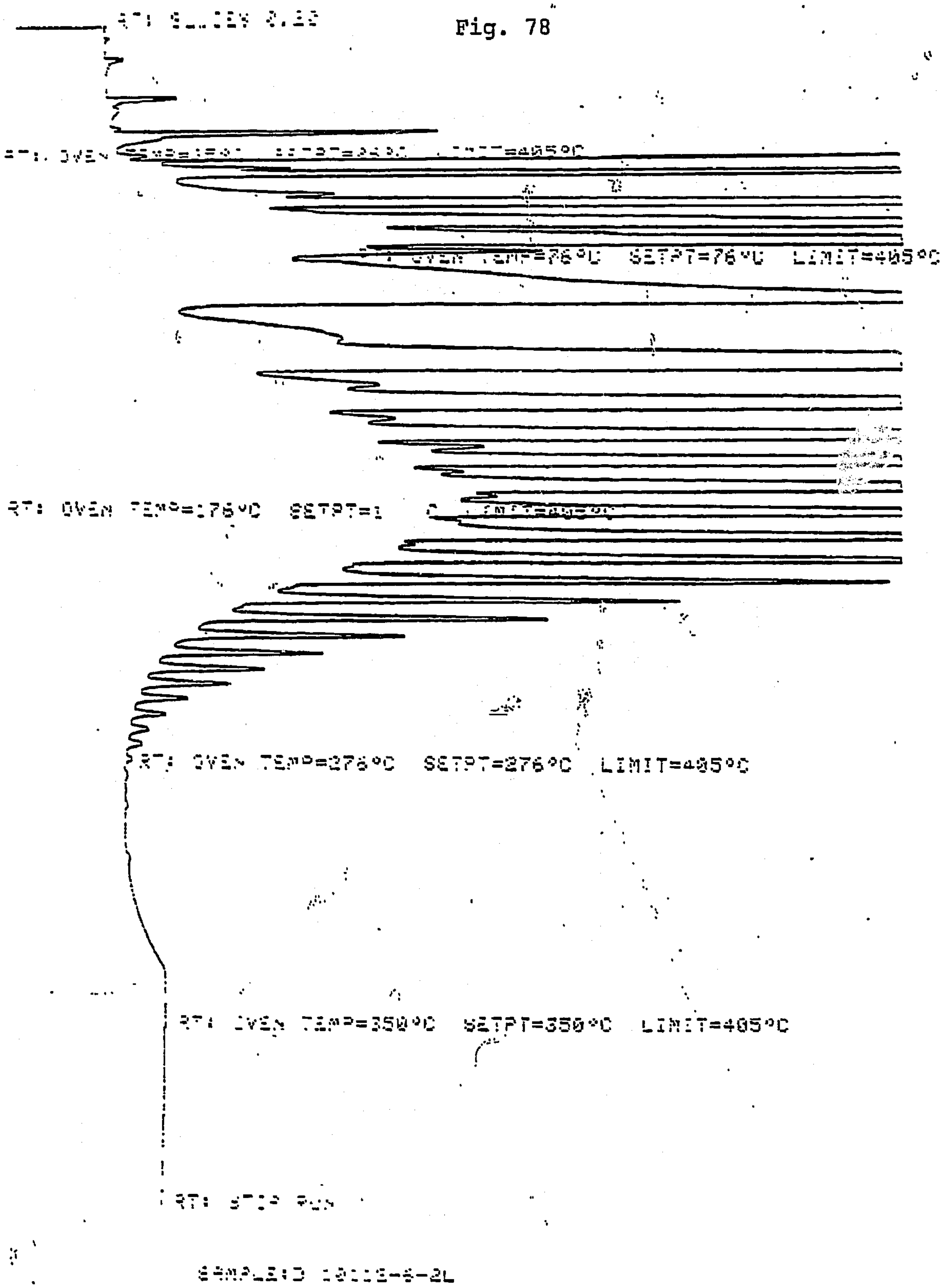

RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 78



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

Fig. 79

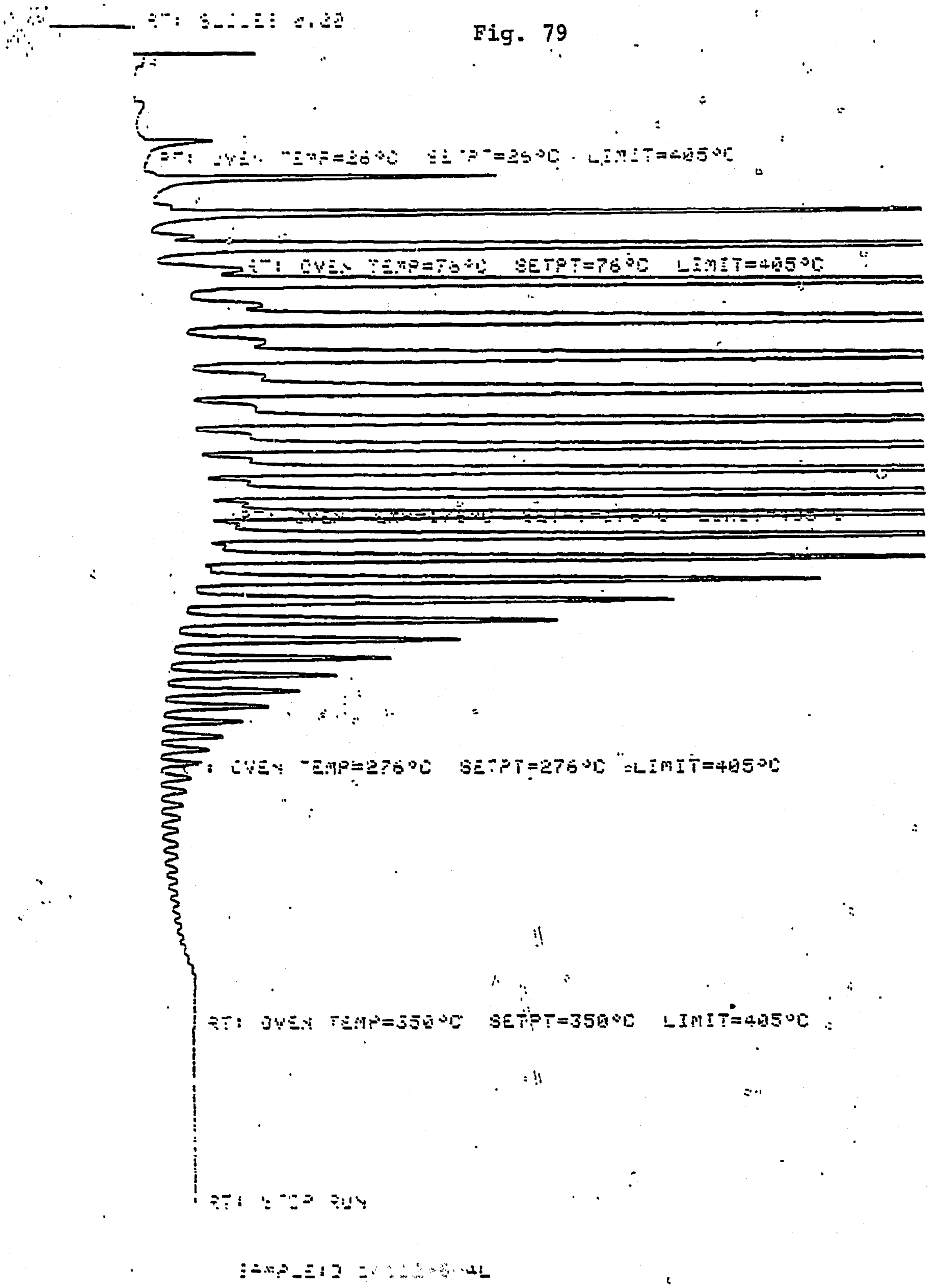

RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 80

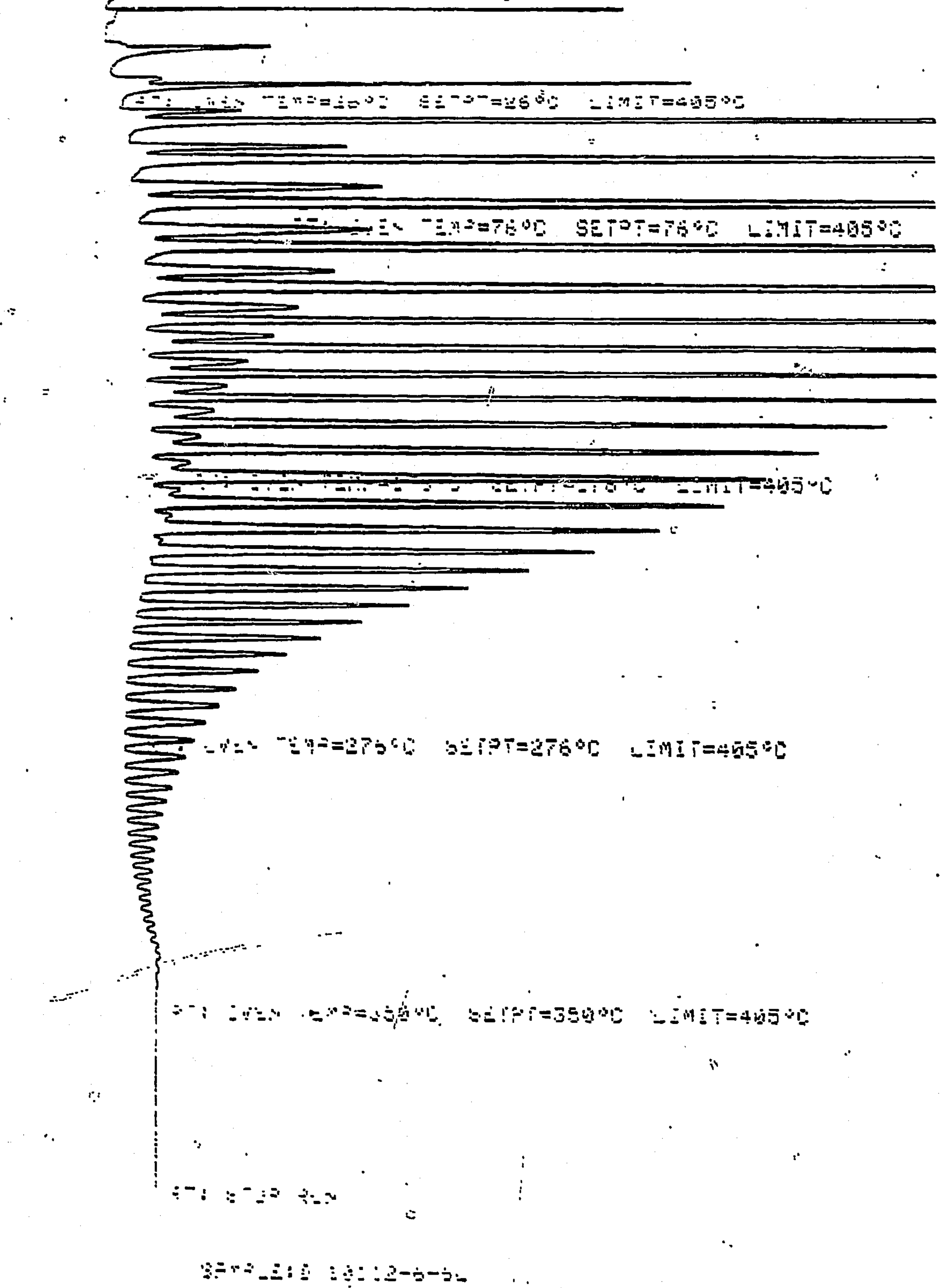

LIMIT=405°C
TEMP=76°C SETPT=76°C LIMIT=405°C
LIMIT=405°C
TEMP=276°C SETPT=276°C LIMIT=405°C
SETPT=350°C LIMIT=405°C

Fig. 81

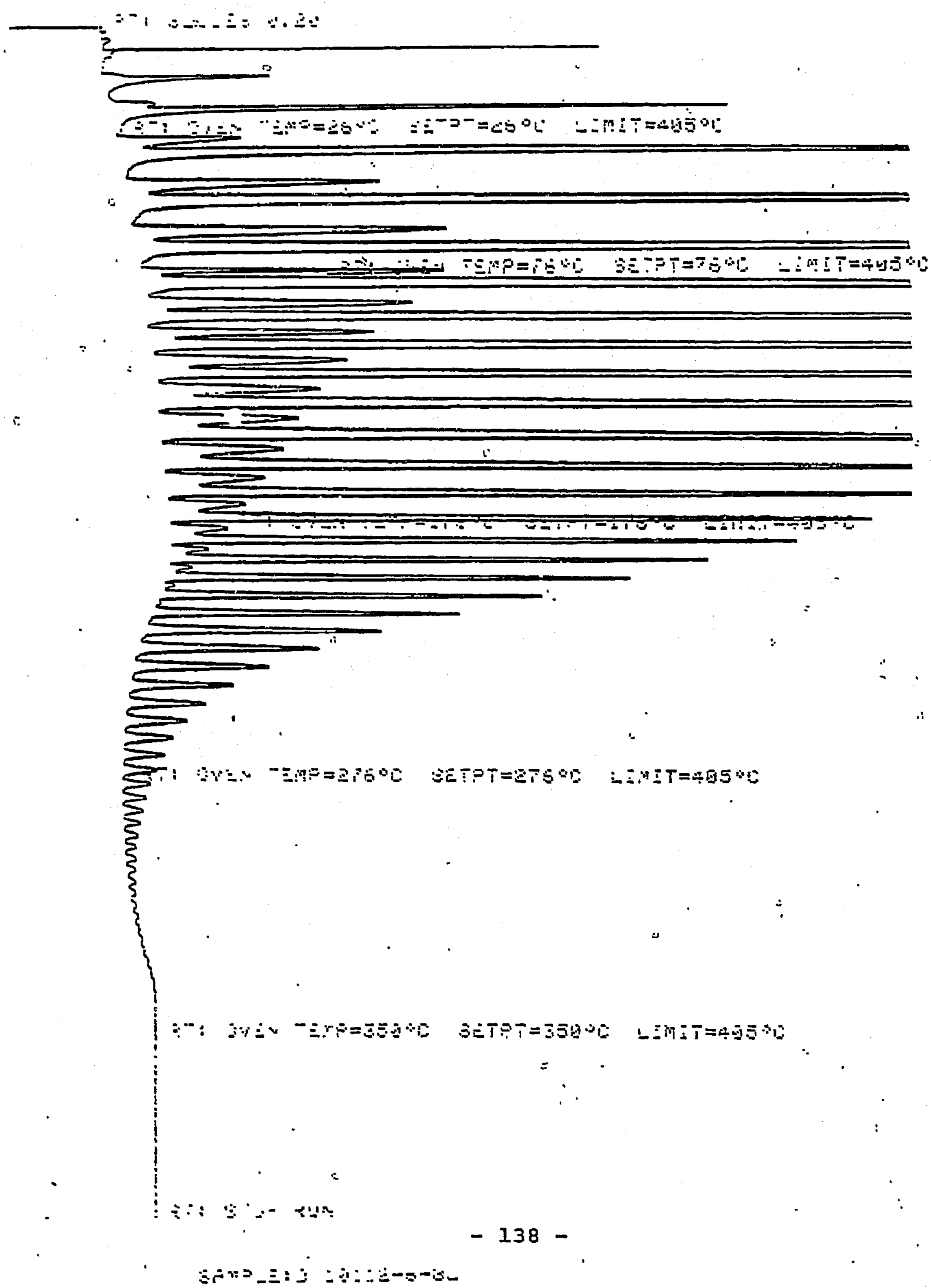

LIMIT=405°C
TEMP=76°C SETPT=76°C LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
TEMP=350°C SETPT=350°C LIMIT=405°C
RUN

Fig. 82

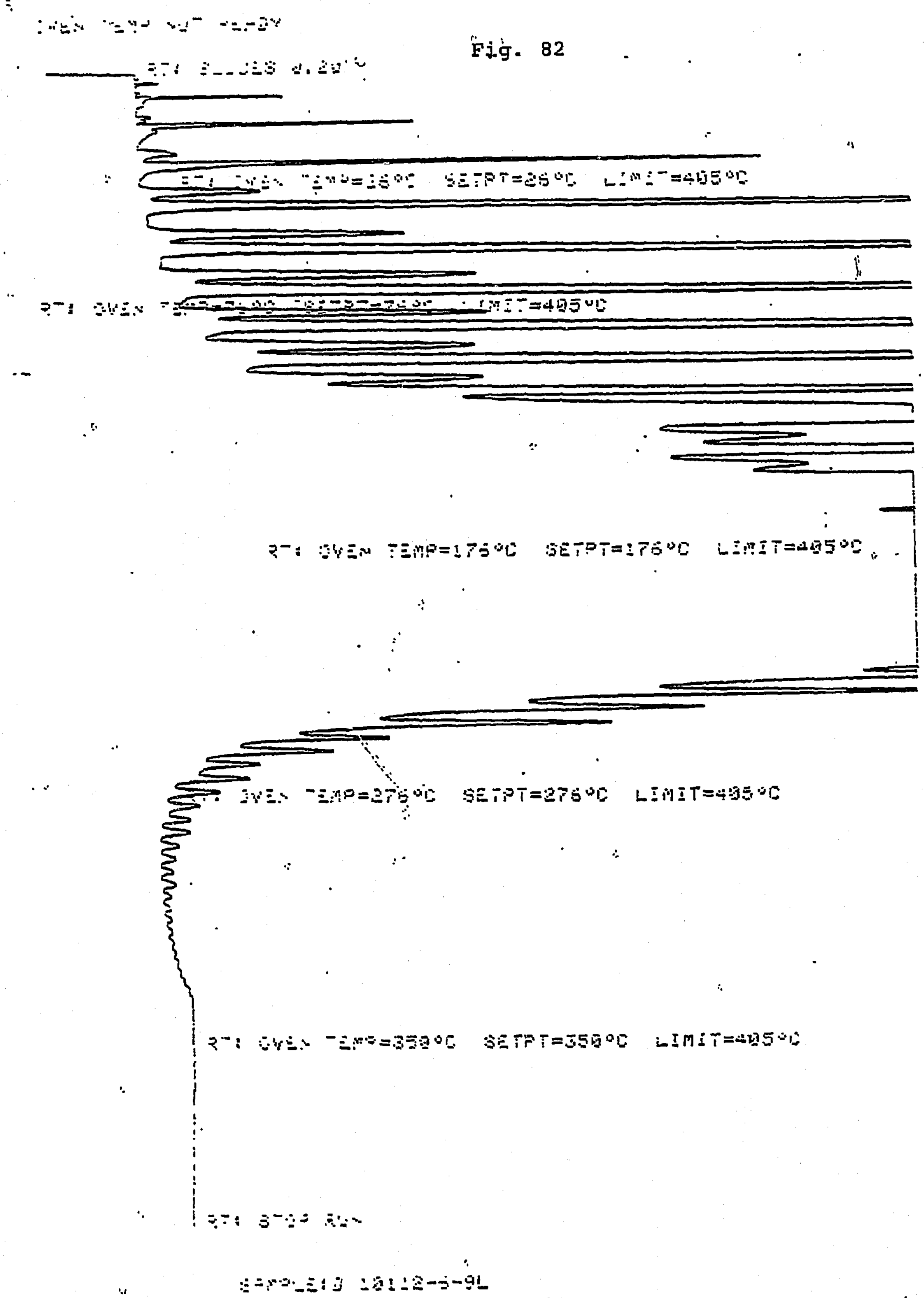

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

TABLE 6A RESULT OF SYNGAS OPERATION

RUN NO. 10112-06
CATALYST COBALT-LZ-105-6 #10042-86 80 CC 40.1GM (55.8 AFTER RUN 16 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-06-01	112-06-02	112-06-03	112-06-04	112-06-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.0	43.0	47.92	64.75	74.08
PRESSURE,PSIG	301	296	298	293	292
TEMP. C	220	220	220	220	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.00	21.00	4.92	21.75	7.25
EFFLNT GAS LITER	390.47	344.89	88.29	406.93	113.24
GM AQUEOUS LAYER	31.62	18.17	3.81	16.86	3.77
GM OIL	6.98	6.91	1.91	8.44	12.24
MATERIAL BALANCE					
GM ATOM CARBON %	88.96	82.83	89.43	91.80	126.31
GM ATOM HYDROGEN %	95.92	84.04	91.98	94.82	118.04
GM ATOM OXYGEN %	102.35	89.48	94.26	96.83	109.54
RATIO CHX/(H2O+CO2)	0.4481	0.6136	0.7133	0.6955	1.4419
RATIO X IN CHX	2.3816	2.3632	2.3373	2.3214	2.7045
USAGE H2/CO PRODT	1.3958	1.3201	1.2987	1.3289	1.0837
RATIO CO2/(H2O+CO2)	0.2183	0.2845	0.3137	0.2923	0.7807
K SHIFT IN EFFLNT	0.25	0.35	0.42	0.38	3.03
CONVERSION					
ON CO %	18.17	18.68	19.34	17.75	66.75
ON H2 %	33.27	29.53	27.83	26.36	69.70
ON CO+H2 %	26.01	24.14	23.64	22.13	68.17
PRDT SELECTIVITY,WT %					
CH4	16.57	15.79	14.67	13.94	32.10
C2 HC'S	2.48	2.37	2.03	2.06	4.26
C3H8	3.09	2.94	2.80	2.59	4.46
C3H6=	1.93	1.84	1.93	2.10	0.44
C4H10	2.69	2.56	2.48	2.41	3.22
C4H8=	2.23	2.13	2.42	2.72	0.58
C5H12	3.57	3.40	3.31	3.09	3.81
C5H10=	2.64	2.51	2.94	2.85	0.60
C6H14	3.45	3.29	3.20	3.18	3.12
C6H12= & CYCLO'S	2.25	2.15	2.14	1.30	0.40
C7+ IN GAS	18.08	17.23	16.54	16.06	4.58
LIQ HC'S	41.01	43.80	45.53	47.72	42.42

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	28.99	27.63	26.33	25.81	45.06
C5 -420 F	45.11	46.34	43.61	39.69	18.80
420-700 F	22.71	23.47	24.13	28.82	16.06
700-END PT	3.18	2.57	5.92	5.69	20.08
C5+-END PT	71.01	72.37	73.67	74.19	54.94
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0000	0.0224	0.0364	0.0674
C5	0.0000	0.0000	0.0285	0.0563	0.1461
C6	0.0000	0.0000	0.0282	0.0831	0.1879
C4=	0.0000	0.0000	0.0000	0.0000	0.1466
PARAFFIN/OLEFIN RATIO					
C3	1.5287	1.5287	1.3852	1.1777	9.6493
C4	1.1621	1.1621	0.9862	0.8569	5.3549
C5	1.3164	1.3164	1.0974	1.0516	6.1266
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLR OIL		OIL & SLD	CLDY SLD
DENSITY	0.765	0.778	-	-	
N, REFRACTIVE INDEX	1.4311	1.4292	-	1.4321	
SIMULT'D DISTILATN					
10 WT % @ DEG F	334	303		339	391
16	357	325		380	436
50	476	469		515	683
84	629	630		673	1033
90	675	669		717	1110
RANGE(16-84 %)	272	305		293	597
WT % @ 420 F	36.86	40.55		27.70	14.80
WT % @ 700 F	92.24	94.13		88.08	52.67

p

TABLE 6B RESULT OF SYNGAS OPERATION

RUN NO. 10112-06
CATALYST COBALT-LZ-105-6 #10042-86 80 CC 40.1GM (55.8 AFTER RUN +16 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-06-06	112-06-07	112-06-08	112-06-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	88.75	95.83	113.0	119.58
PRESSURE,PSIG	294	292	292	292
TEMP. C	249	249	249	249
FEED CC/MIN	400	400	400	400
HOURS FEEDING	16.75	7.08	24.25	6.58
EFFLNT GAS LITER	208.49	94.35	333.00	93.55
GM AQUEOUS LAYER	15.41	7.36	25.20	6.87
GM OIL	14.01	5.31	18.20	7.01
MATERIAL BALANCE				
GM ATOM CARBON %	94.44	93.95	92.92	101.05
GM ATOM HYDROGEN %	93.49	96.19	95.62	103.65
GM ATOM OXYGEN %	94.93	95.75	94.41	97.13
RATIO CHX/(H2O+CO2)	0.9869	0.9501	0.9554	1.1154
RATIO X IN CHX	2.7479	2.7615	2.7007	2.6096
USAGE H2/CO PRODT	1.0064	1.0642	1.0932	1.1346
RATIO CO2/(H2O+CO2)	0.6759	0.6173	0.5835	0.5880
K SHIFT IN EFFLNT	1.98	1.51	1.30	1.33
CONVERSION				
ON CO %	66.89	60.14	55.09	57.24
ON H2 %	68.27	63.50	59.37	61.17
ON CO+H2 %	67.58	61.84	57.26	59.23
PRDT SELECTIVITY,WT %				
CH4	32.74	33.50	30.87	26.76
C2 HC'S	4.78	4.78	4.41	3.87
C3H8	5.59	5.63	5.21	4.63
C3H6=	0.53	0.60	0.69	0.67
C4H10	4.23	4.39	4.15	3.86
C4H8=	0.74	0.81	0.93	1.08
C5H12	5.36	4.88	4.64	4.16
C5H10=	0.84	0.84	0.92	1.47
C6H14	4.70	4.64	4.41	4.70
C6H12= & CYCLO'S	0.60	0.57	0.69	0.76
C7+ IN GAS	9.32	9.40	10.63	9.14
LIQ HC'S	30.56	29.98	32.46	38.91

p

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	48.61	49.70	46.26	40.87
C5 -420 F	33.27	30.51	35.12	25.73
420-700 F	13.00	15.89	15.16	24.58
700-END PT	5.11	3.90	3.45	8.82
C5+-END PT	51.39	50.30	53.74	59.13
ISO/NORMAL MOLE RATIO				
C4	0.0475	0.0516	0.0421	0.0637
C5	0.1101	0.0962	0.0857	0.0797
C6	0.1444	0.1452	0.1260	0.1613
C4=	0.1375	0.1490	0.1275	0.1412
PARAFFIN/OLEFIN RATIO				
C3	10.0895	9.0183	7.2191	6.5984
C4	5.5151	5.2564	4.3029	3.4567
C5	6.2030	5.6558	4.9208	2.7435
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLDY SLD		OIL & SLD	OIL & SLD
DENSITY	-	-	0.752	0.756
N, REFRACTIVE INDEX	1.4301	-	1.4255	1.4258
SIMULT'D DISTILATN				
10 WT % @ DEG F	288		295	385
16	304		310	447
50	474		454	618
84	711		654	722
90	772		709	745
RANGE(16-84 %)	407		344	275
WT % @ 420 F	40.73		42.64	14.15
WT % @ 700 F	87.00		89.36	77.33

VIII. RUN 10112-10, Co/Th/K on LZ-Y-82

LZ-Y-82 is the acid form of steam-stabilized Y zeolite. This catalyst was prepared by precipitating cobalt oxide with sodium carbonate from a slurry of LZ-Y-82 and cobalt nitrate. The metal-loaded zeolite was promoted by impregnation with potassium and thorium nitrates. The dried powder was formed in pellets and calcined for two hours at 250C.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 83-86. Simulated distillations of the pentane+ product for two samples are given in Figs. 87 and 88. Carbon number product distributions are given in Figs. 89-93. Chromatograms from simulated distillations are reproduced in Figs. 94-98. Detailed material balances appear in Tables 7A and 7B.

Unlike the previous catalyst, this one was not tested at 220C but only at 250C; the hope was that promotion would allow it to operate at 250C with a reasonable product distribution. Activity at 250C was good (Fig. 83), but the catalyst did deactivate, particularly in its hydrogen conversion. Also, conversion of hydrogen was twice that of carbon monoxide. Despite its promotion this catalyst had almost no WGS activity, as indicated by the fact that less than 10 percent of the by-product oxygenate was carbon dioxide and more than 90 percent was water.

Product selectivity is good (Fig. 84). Methane yield is only

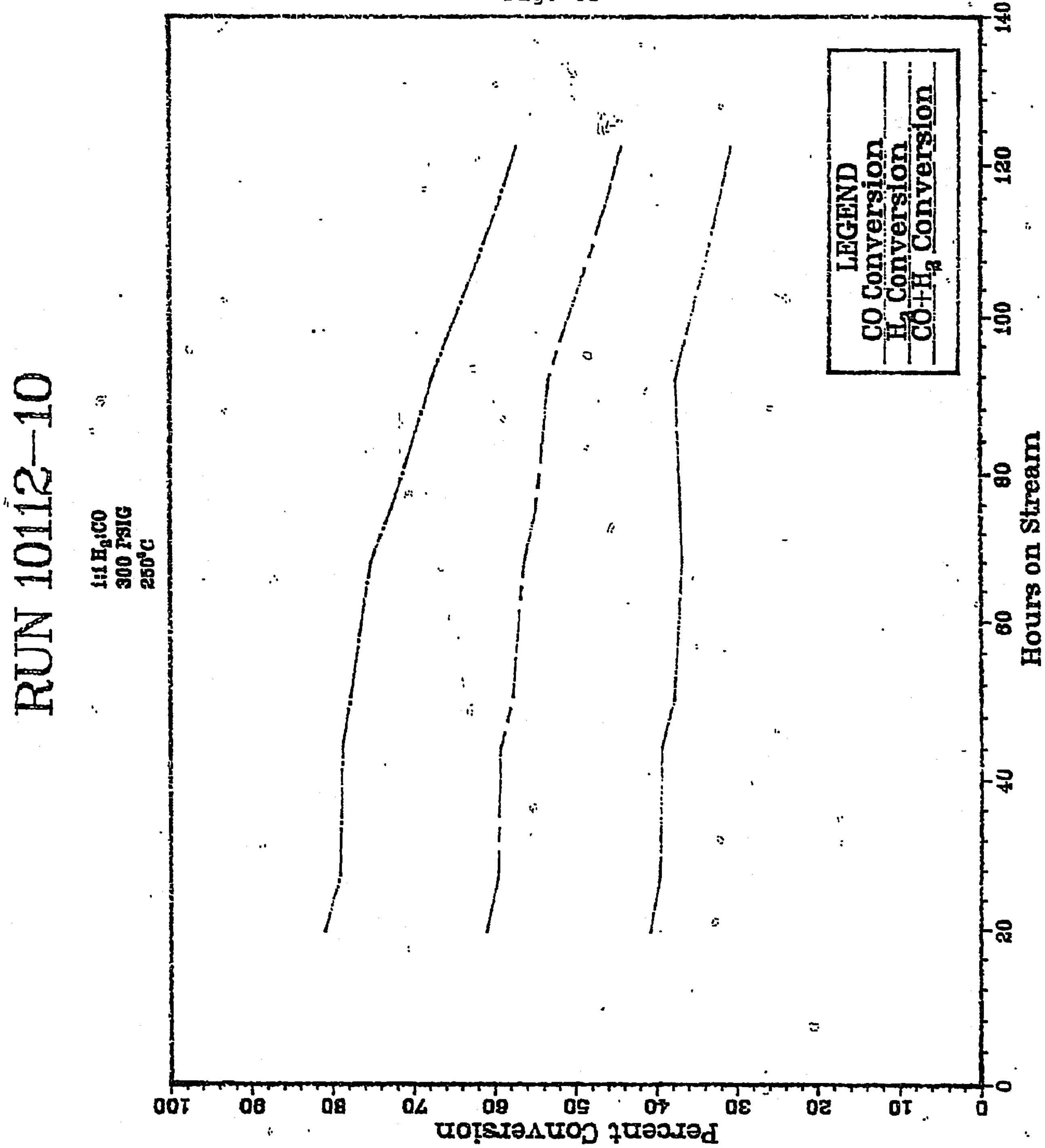
12 percent, against more than 30 percent with the cobalt-on-LZ-105 catalyst at similar process conditions. That this methane yield, which is more typical of the iron and Molecular Sieve-containing F-T catalysts, can nevertheless be obtained from cobalt-containing catalysts is shown in Figs. 89-93. As usual, the methane yield differs markedly from those of the other hydrocarbons, suggesting a separate mechanism for methane formation, possibly a separate methanation site.

Again, C_2-C_4 hydrocarbons are produced with poor selectivity, but yields of total motor fuels are excellent. A theoretical catalyst following a Schulz-Flory distribution could be optimized to produce 71.9 percent of its product in the pentane-700F (total motor fuel) range. This catalyst does even better, especially if the methane is disregarded. The theoretical catalyst could produce 74 percent of non-methane product in the motor fuel range; the corresponding yield for this catalyst is 83 percent. Methane being an undesirable product, the excellent carbon number product distribution of this catalyst could be improved still further if the methane-producing mechanism could be blocked. The superior selectivity for motor fuels can be explained in two ways: first, the low yield of lights other than methane, and second, an apparent carbon number cut-off just above the diesel oil range. Both effects can be seen in the carbon number product distributions (Figs. 89-93). Most of the pentane+ product boils in the gasoline range (Figs. 87 and 88).

The C_4's are about half olefins (Fig. 86). The refractive intercept of the condensed product suggests that the liquid is 45 percent olefins, the rest paraffins. The pentane is well isomerized (Fig. 85), although not to its equilibrium level. Initial samples of the condensed products are quite isomerized, as illustrated by the chromatograms of simulated distillations (Figs. 94-98). Later samples are clearly dominated by straight-chain products. Loss of isomerizing activity is less evident with pentane than with the liquid product, but is shown by the ratio of 3-methyl-pentane to n-hexane; this ratio drops by a factor of 2.4 over the course of the run.

During the run this catalyst showed little deactivation of the conversion or general product selectivity, but acid activity did deactivate significantly.

Fig. 83


RUN 10112—10
1:1 H2:CO
300 PSIG
250°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140

intercept of the condensed product suggests that the liquid is 45 percent olefins, the rest paraffins. The pentane is well isomerized (Fig. 85), although not to its equilibrium level. Initial samples of the condensed products are quite isomerized, as illustrated by the chromatograms of simulated distillations (Figs. 94-98). Later samples are clearly dominated by straight-chain products. Loss of isomerizing activity is less evident with pentane than with the liquid product, but is shown by the ratio of 3-methyl-pentane to n-hexane; this ratio drops by a factor of 2.4 over the course of the run.

During the run this catalyst showed little deactivation of the conversion or general product selectivity, but acid activity did deactivate significantly.

Fig. 83

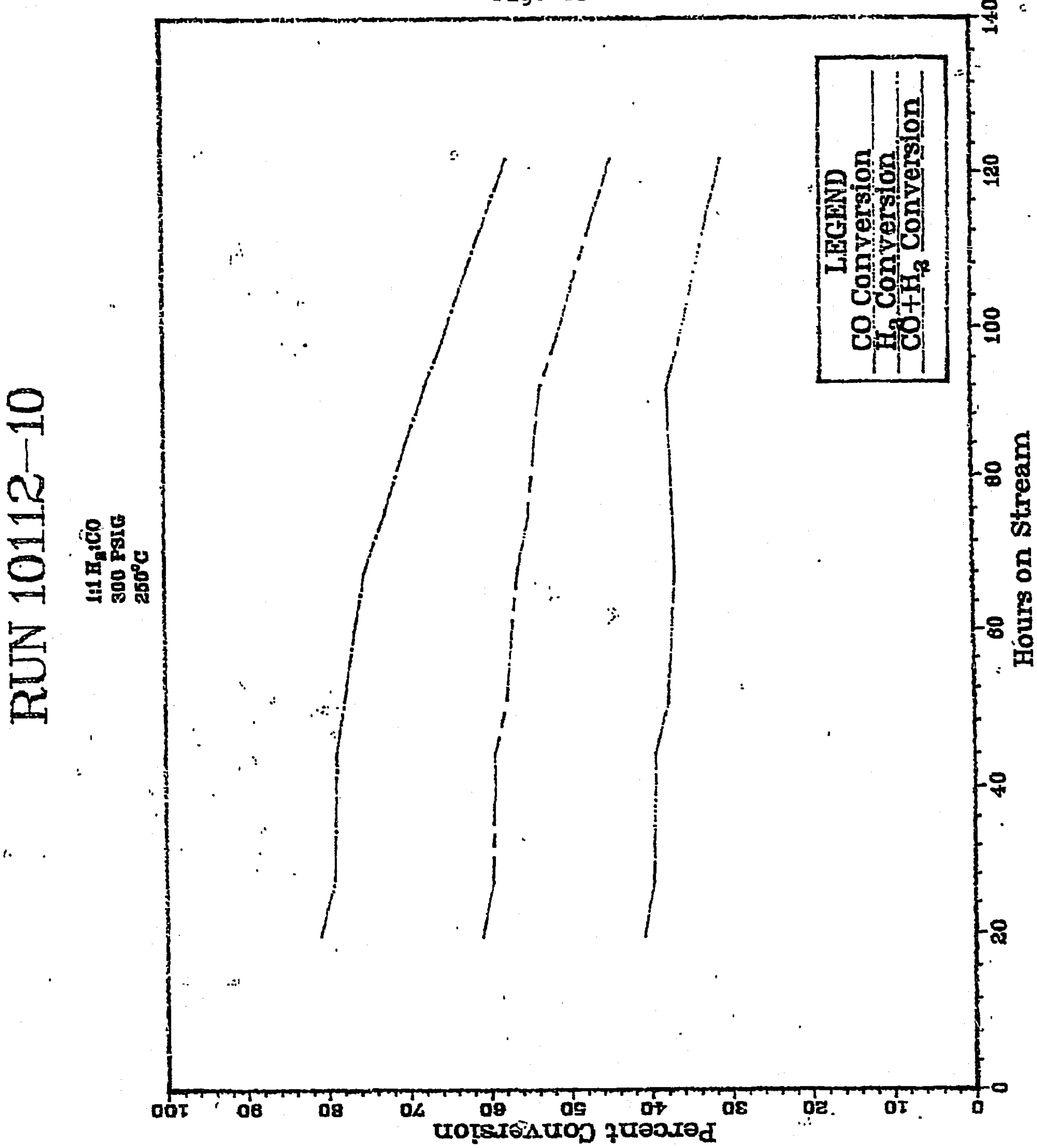

RUN 10112—10
1:1 H2:CO
300 PSIG
250°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
140

Fig. 84

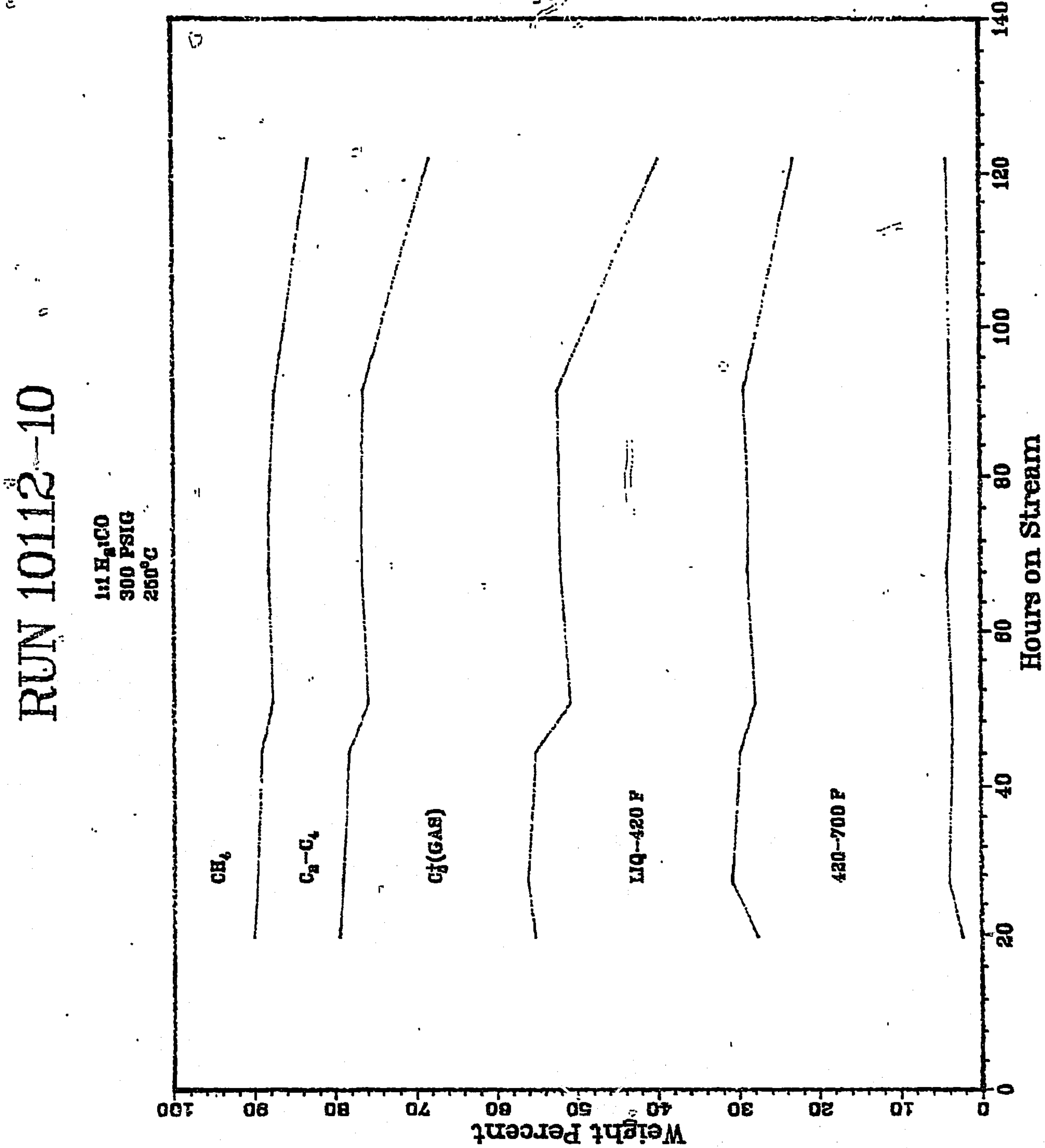
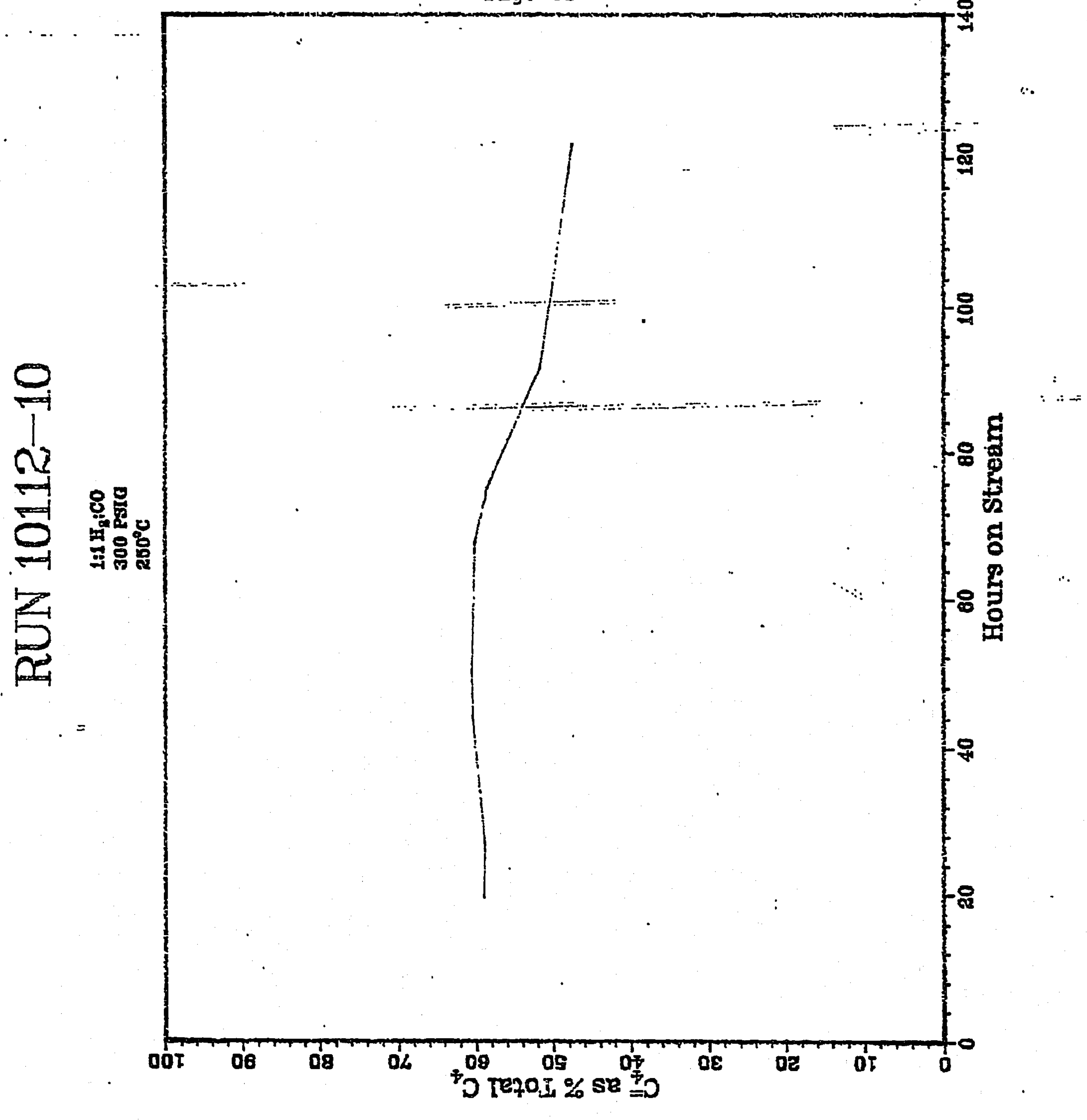
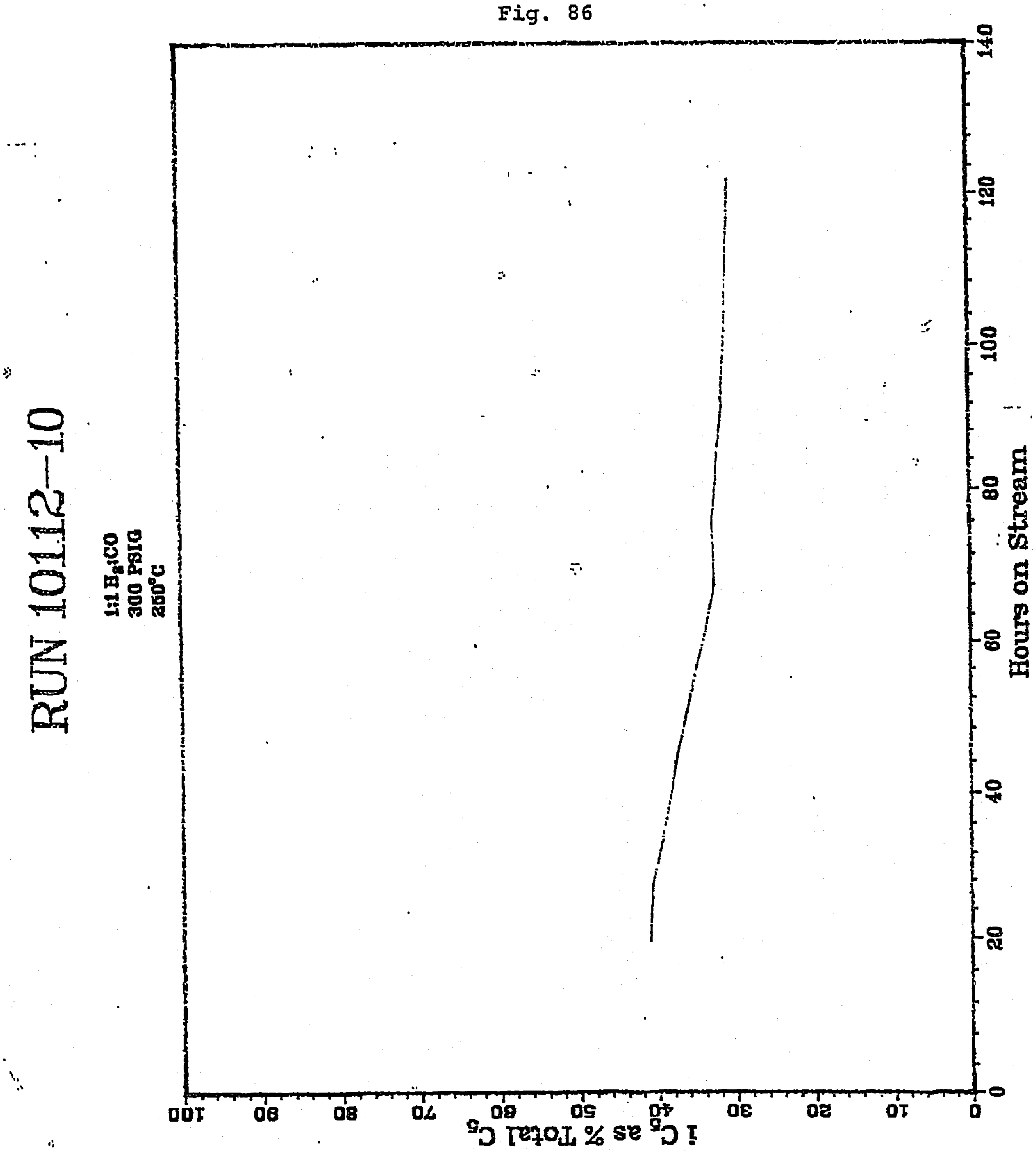

RUN 10112-10
1:1 H_2:CO
300 PSIG
250°C
CH_4
C_2–C_4
C_5^+(GAS)
LIQ–420 F
420–700 F
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140

Fig. 85



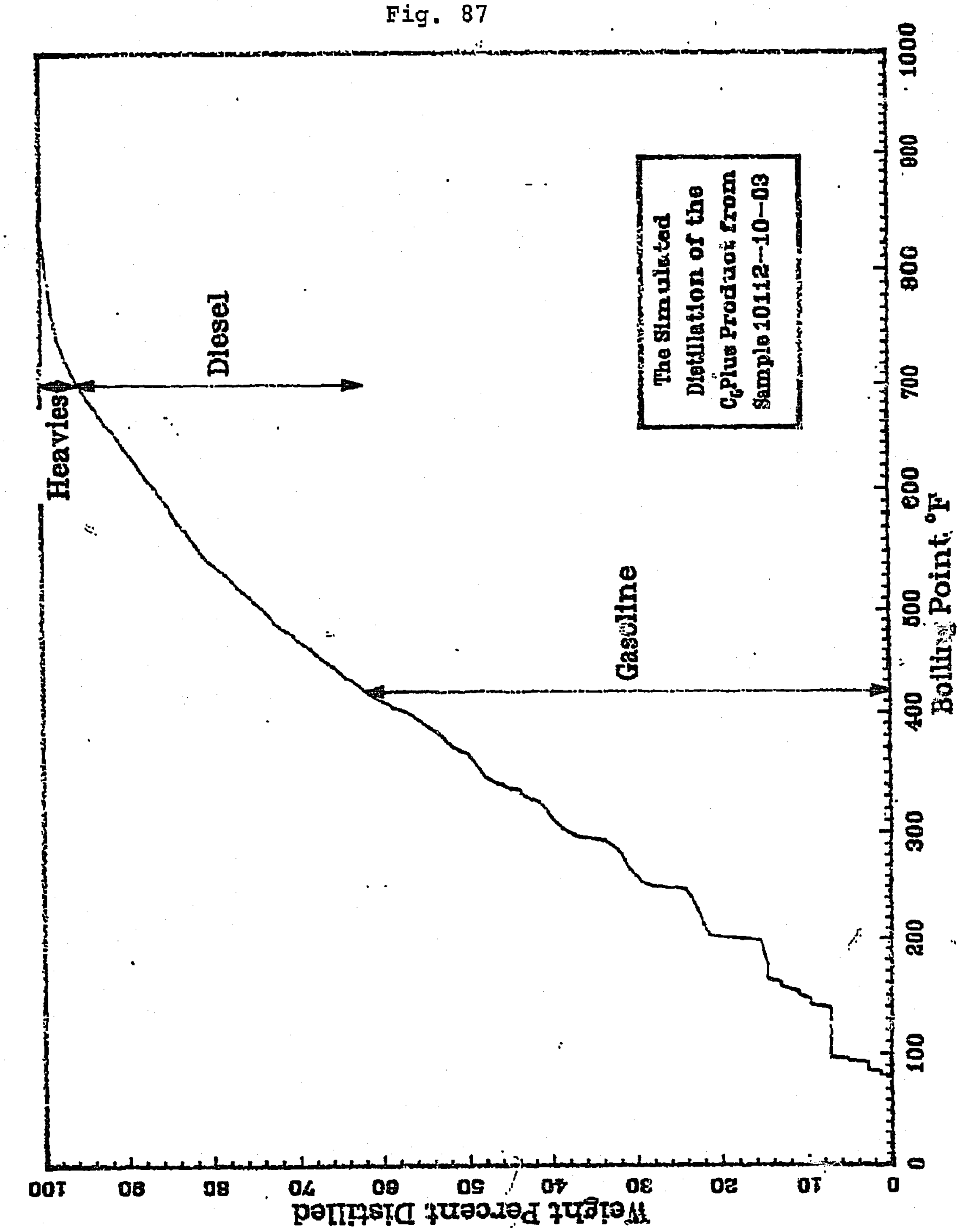
RUN 10112—10
1:1 H_2:CO
300 PSIG
250°C
Hours on Stream
0
20
40
60
80
100
120
140
$C_4^=$ as % Total C_4
0
10
20
30
40
50
60
70
80
90
100

Fig. 86


RUN 10112—10
1:1 H2:CO
300 PSIG
250°C
Hours on Stream
i C5 as % Total C5
0
20
40
60
80
100
120
140
0
10
20
30
40
50
60
70
80
90
100

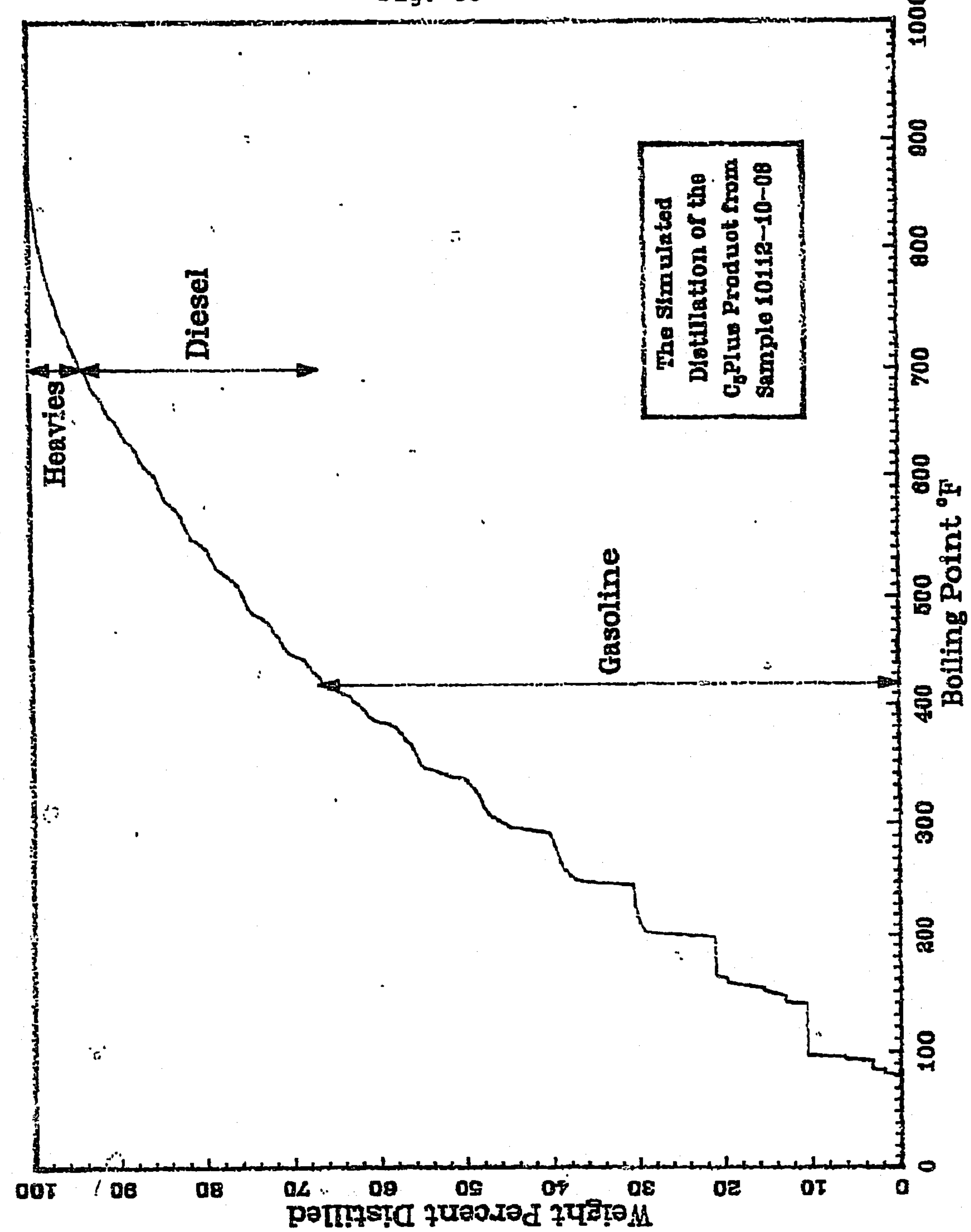
p

Fig. 87



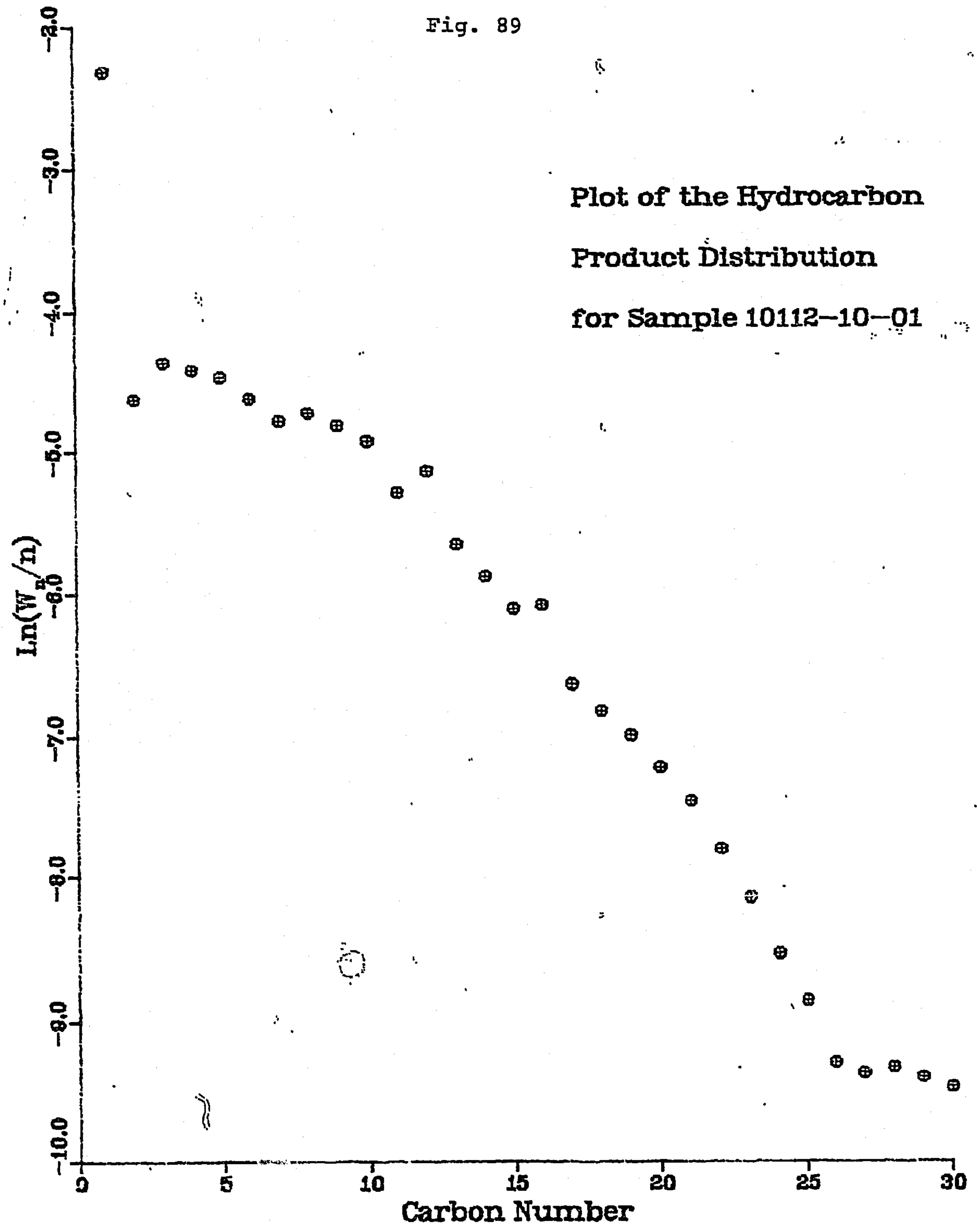
The Simulated Distillation of the C_6Plus Product from Sample 10112-10-03
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 88


Heavies
Diesel
Gasoline
The Simulated Distillation of the C5Plus Product from Sample 10112-10-08
Boiling Point °F
Weight Percent Distilled

p

Fig. 89



Plot of the Hydrocarbon
Product Distribution
for Sample 10112-10-01
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. 90

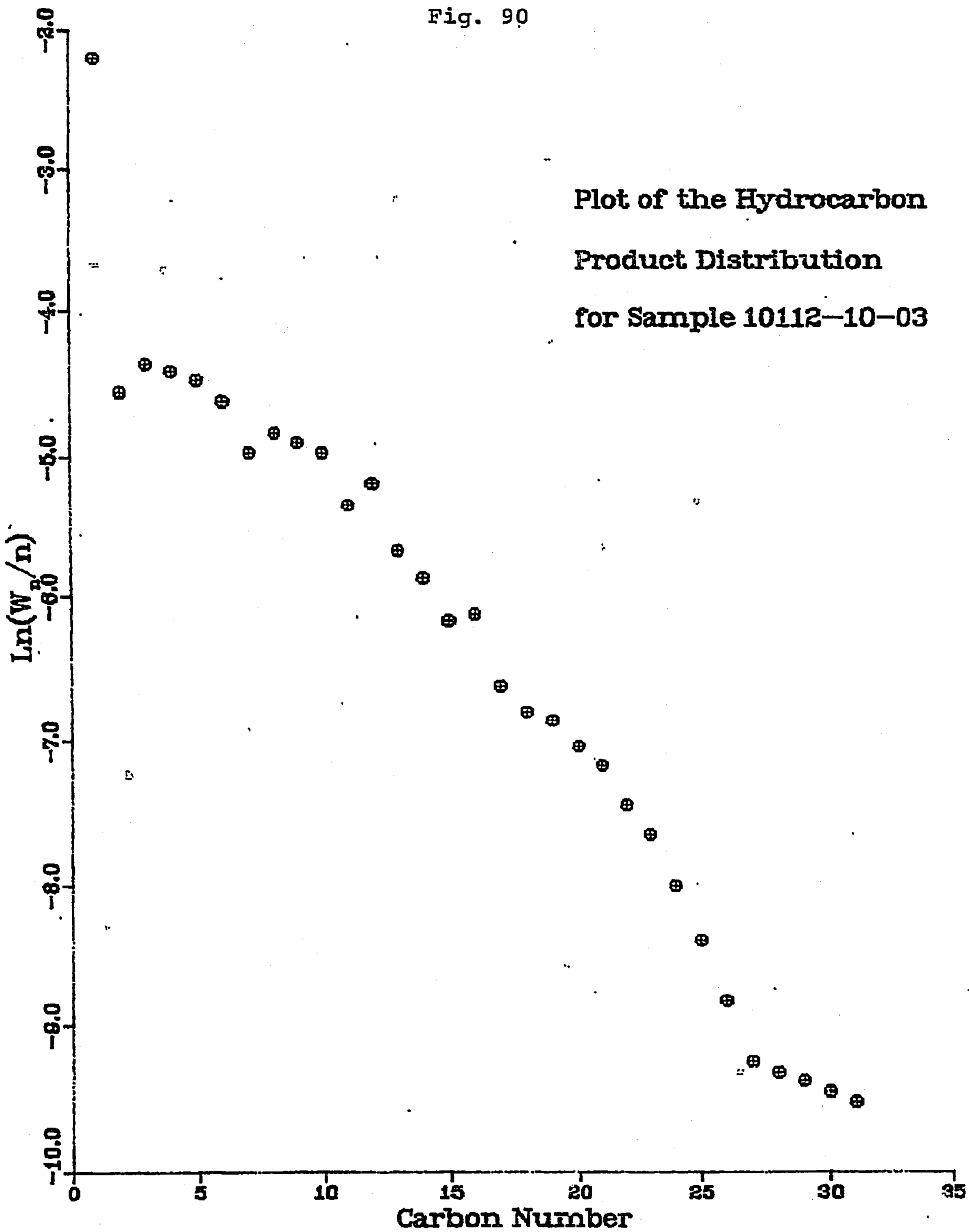

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–10–03
Ln(Wn/n)
–2.0
–3.0
–4.0
–5.0
–6.0
–7.0
–8.0
–9.0
–10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 91

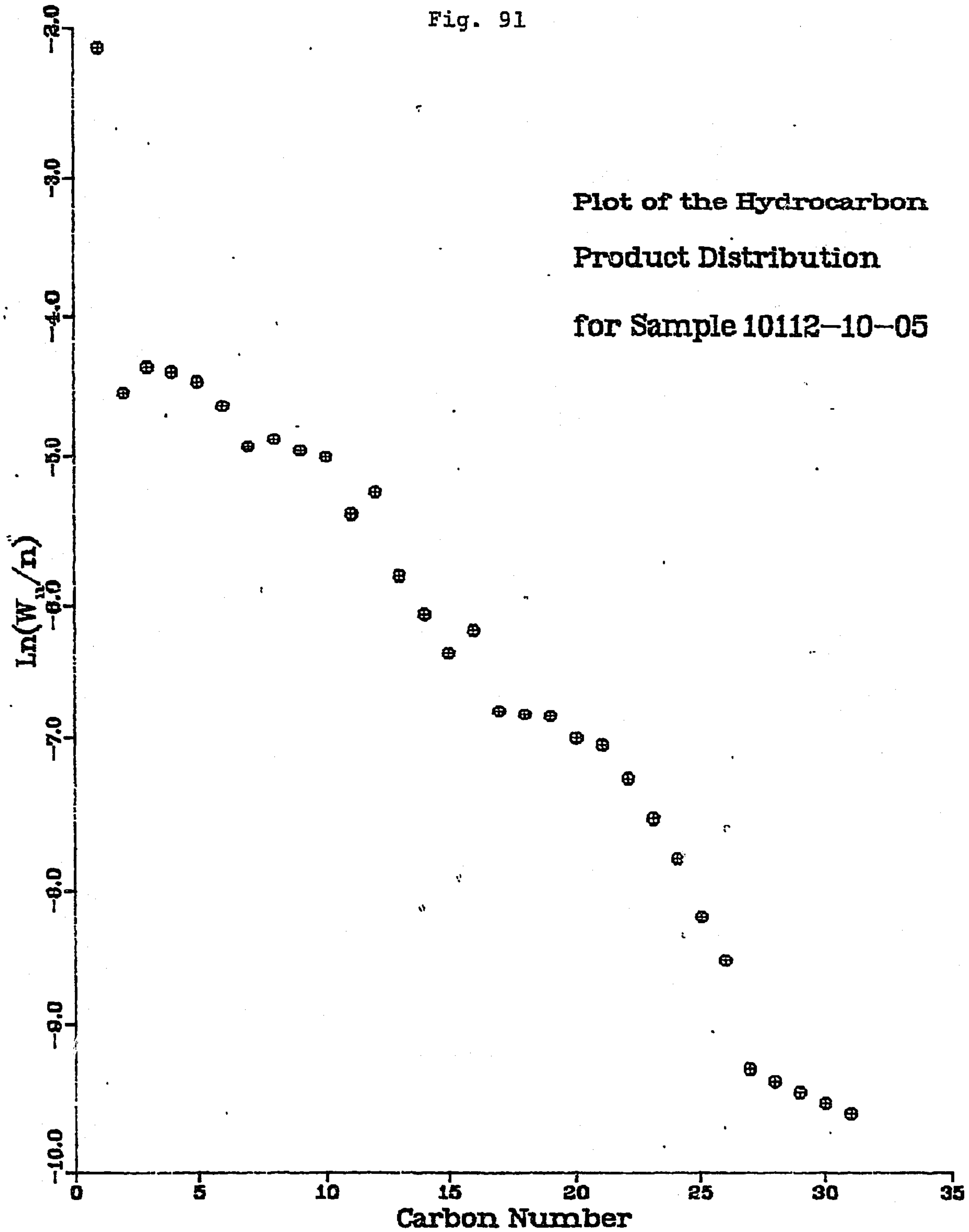

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-10-05
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 92

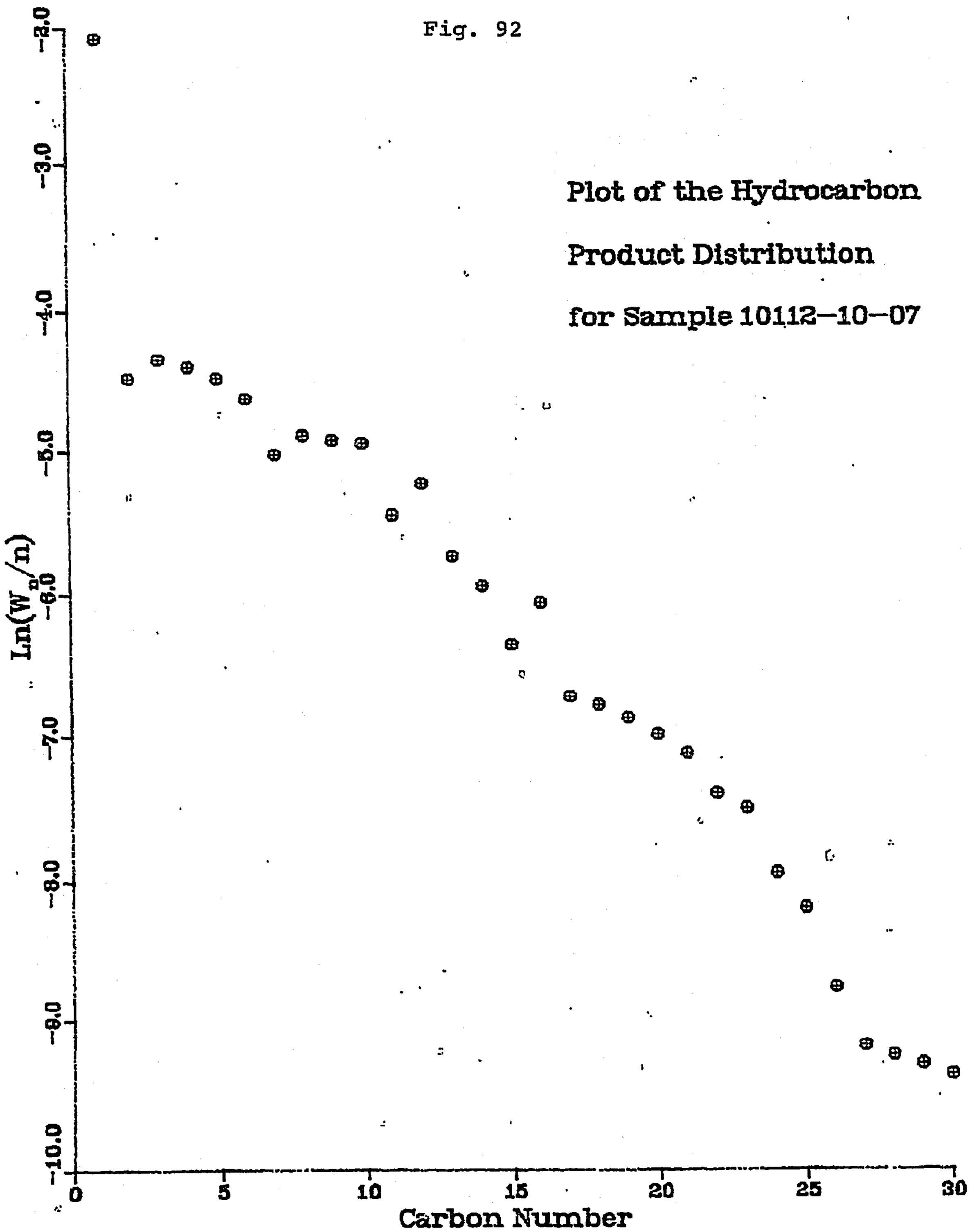

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-10-07
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 93

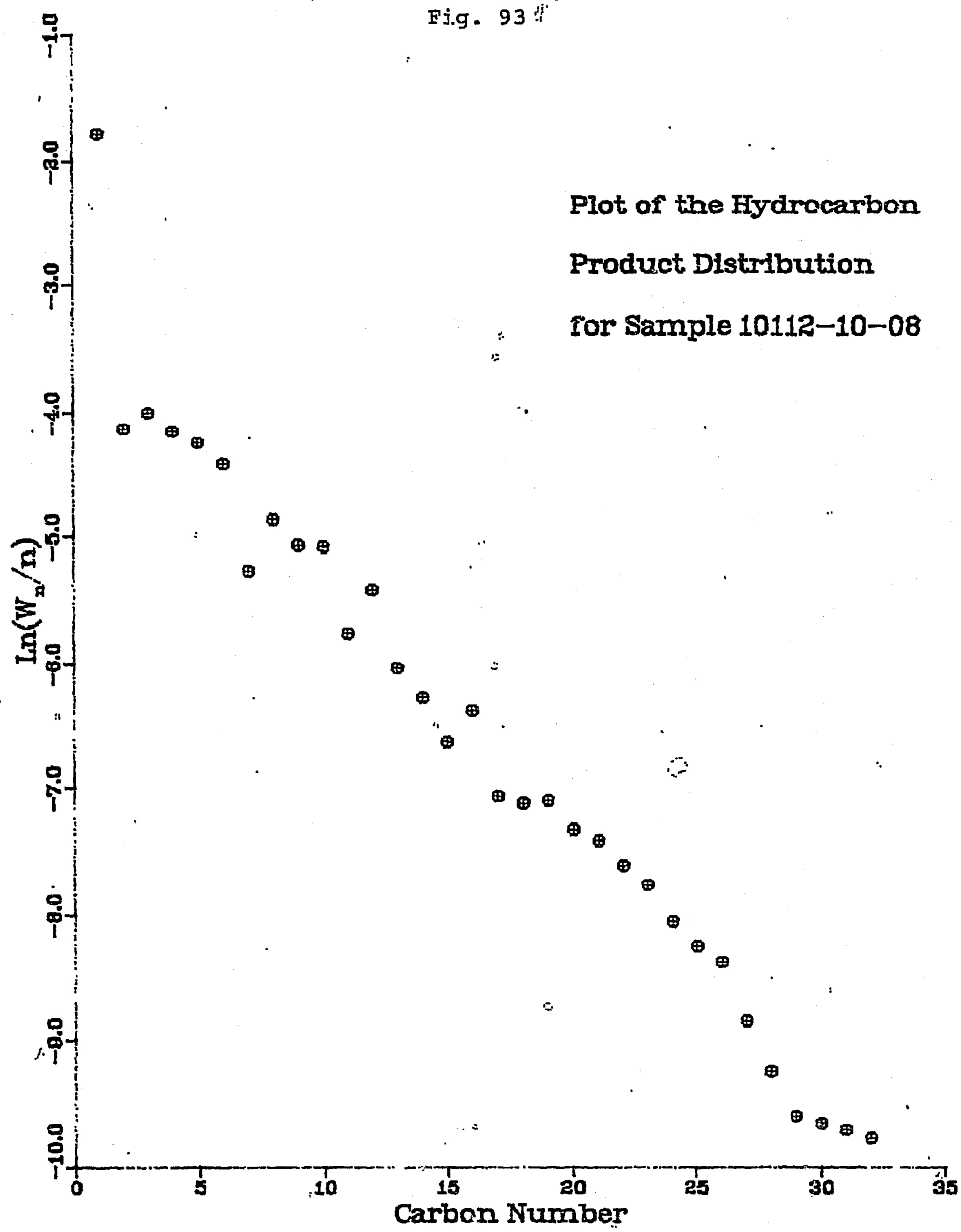
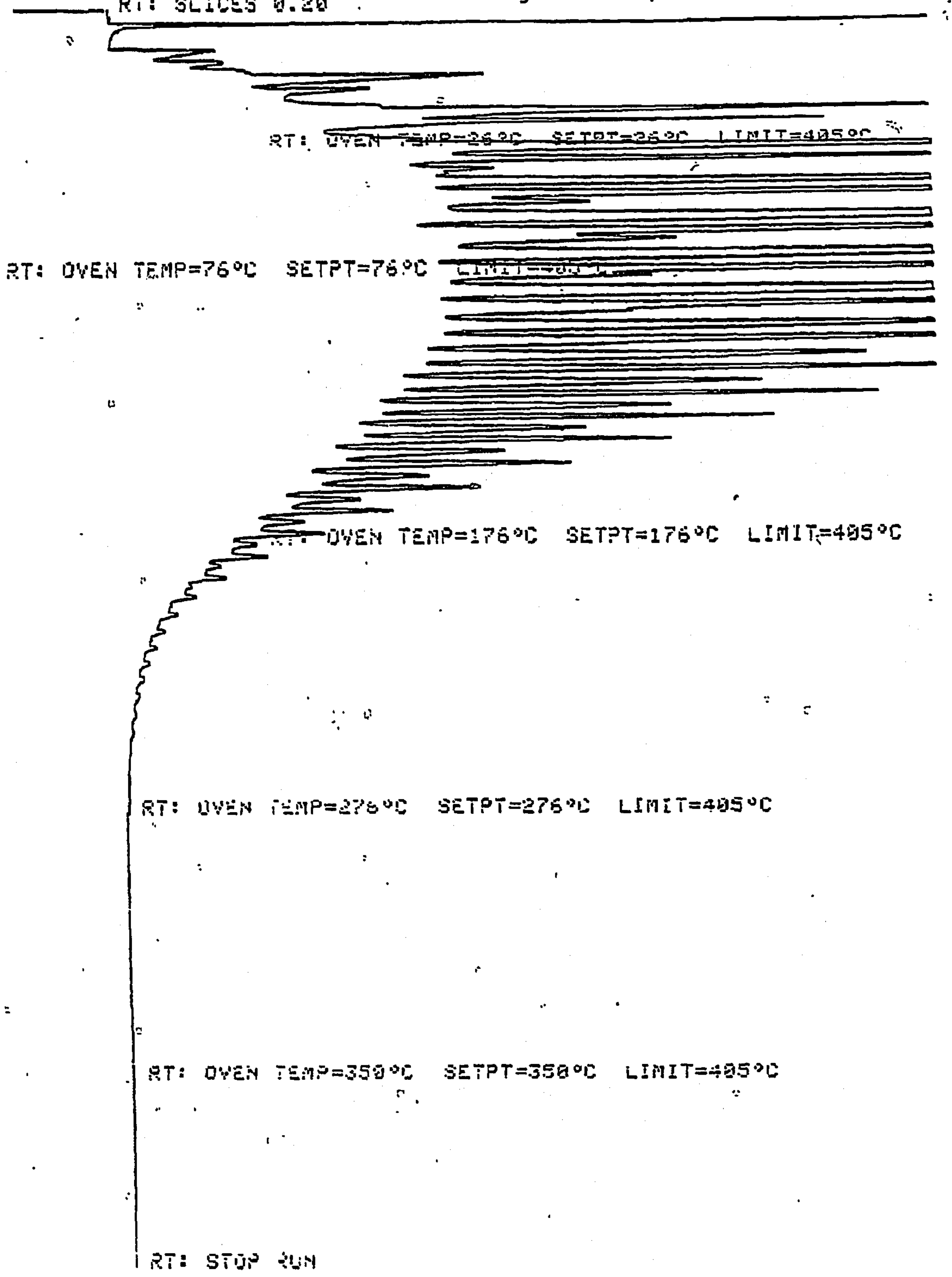
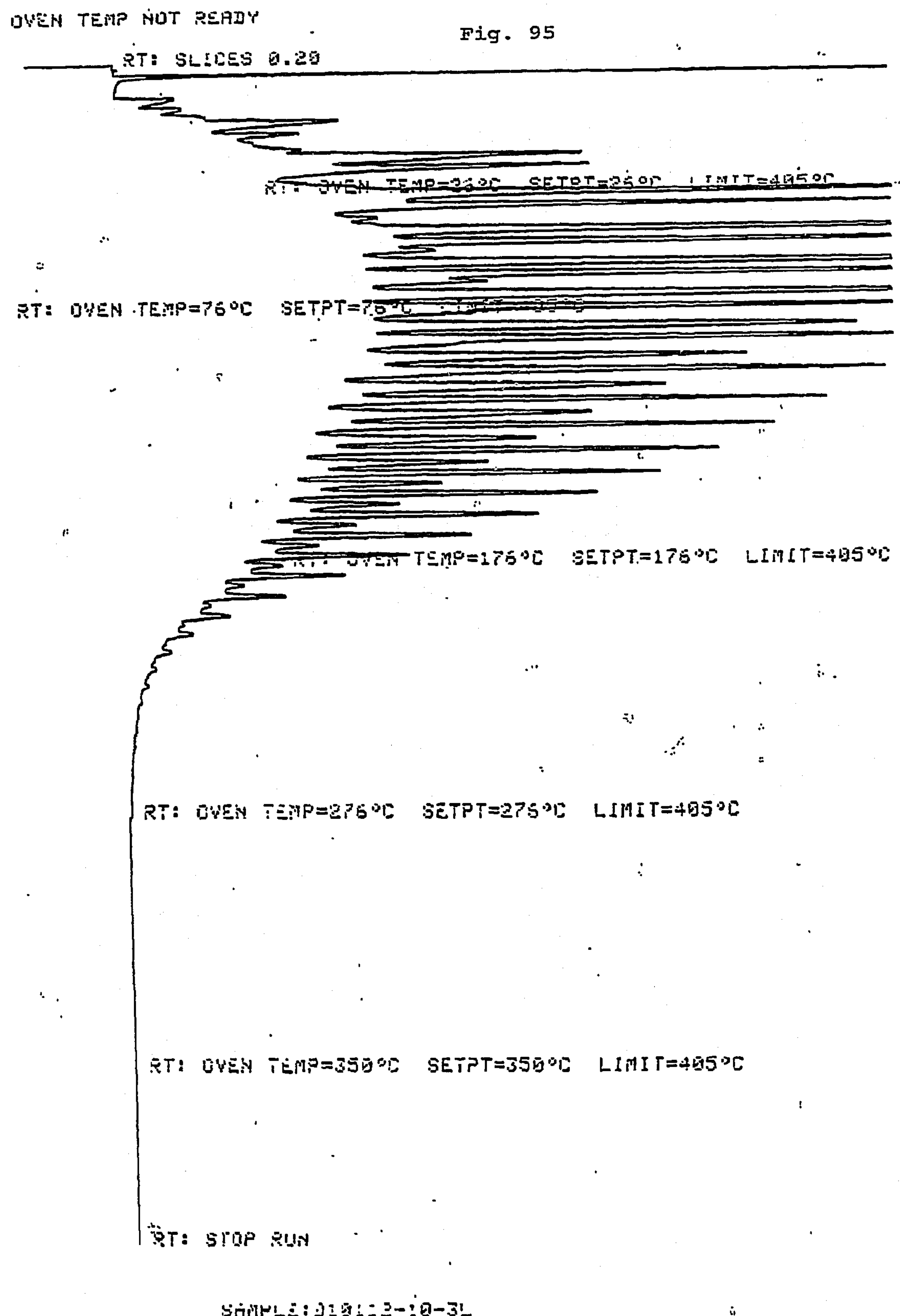

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-10-08
ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 94



SAMPLE:D10112-10-1L

Fig. 95


OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=76°C SETPT=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

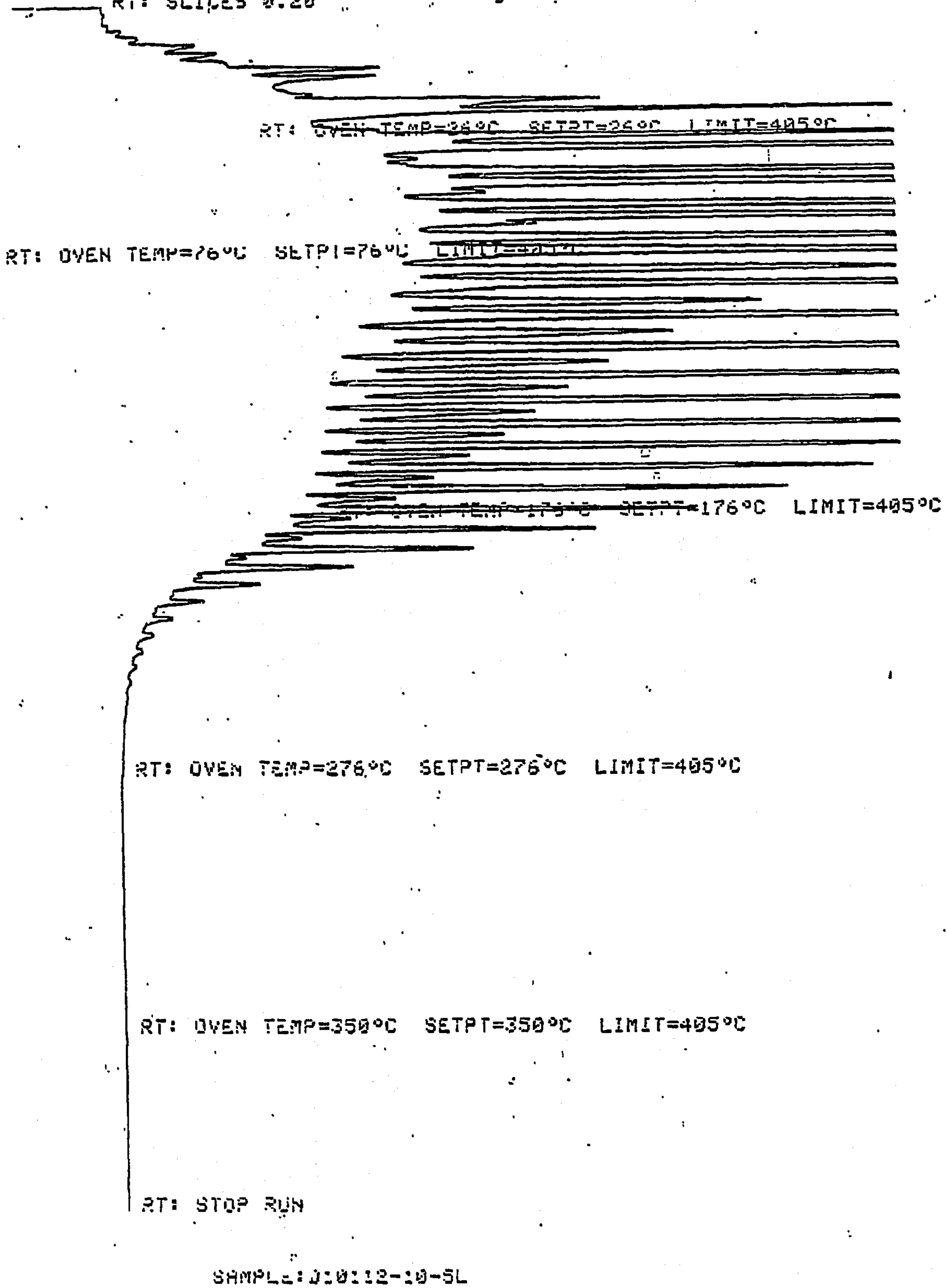
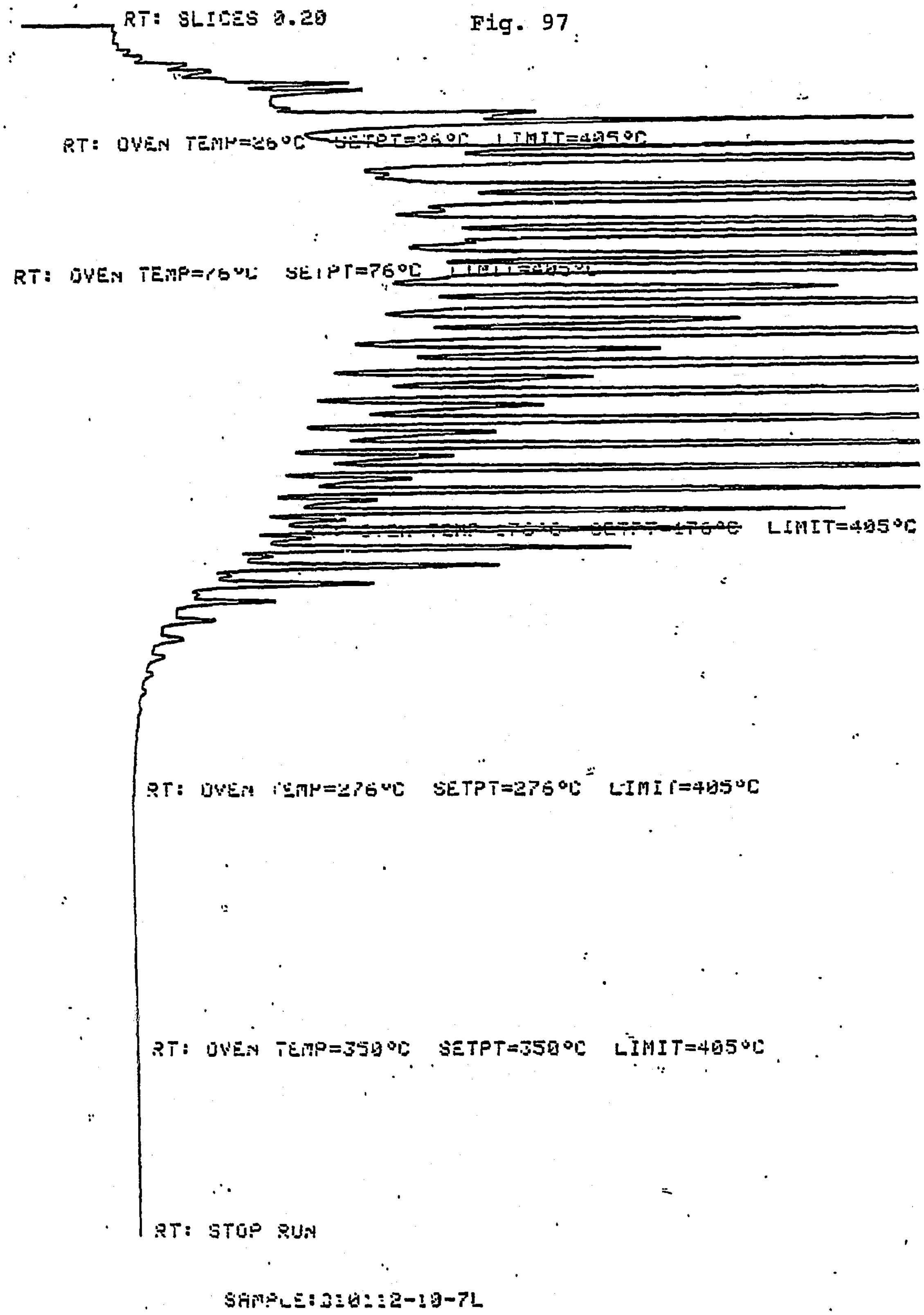

RT: SLICES 0.20
RT: OVEN TEMP=76°C SETPT=76°C
SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

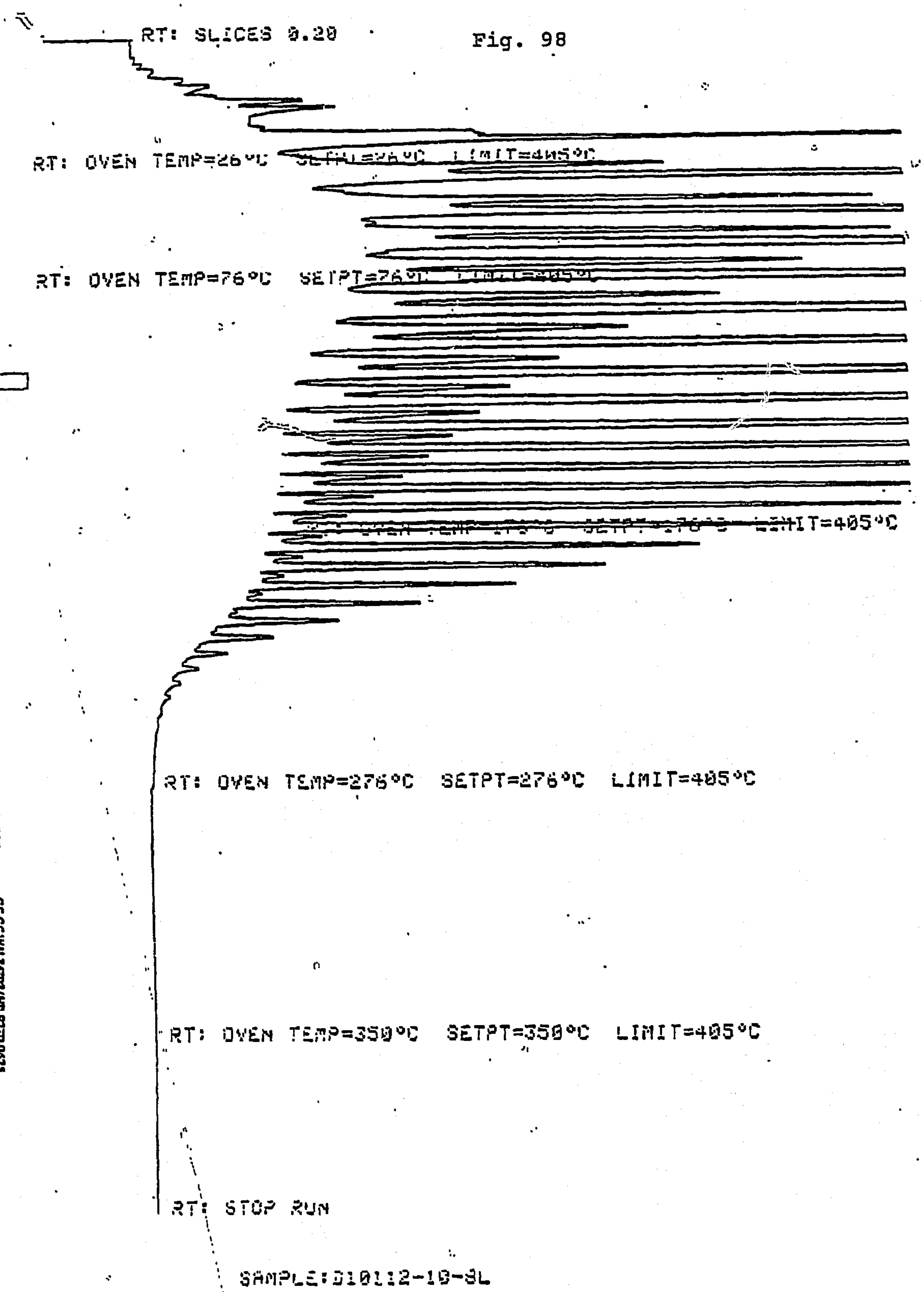
Fig. 96

Fig. 97



RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°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:310112-10-7L

Fig. 98



RT: SLICES 0.20
RT: OVEN TEMP=26°C
RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°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:D10112-10-8L

p

TABLE 7A RESULT OF SYNGAS OPERATION

RUN NO. 10112-10
CATALYST CO-PPT,THO2,K-Y-82 #10252-17C CC 31.0GM (48.8 AFTER RUN +18G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-10-01	112-10-02	112-10-03	112-10-04	112-10-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.67	27.0	44.0	50.25	67.92
PRESSURE,PSIG	312	294	305	305	309
TEMP. C	252	250	251	252	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.67	7.33	24.33	6.25	23.92
EFFLNT GAS LITER	179.50	74.85	257.47	67.24	264.38
GM AQUEOUS LAYER	56.78	22.60	75.02	18.80	71.94
GM OIL	23.73	9.62	31.94	7.07	27.07
MATERIAL BALANCE					
GM ATOM CARBON %	84.10	91.35	93.96	92.52	91.68
GM ATOM HYDROGEN %	84.78	93.17	94.81	92.26	94.19
GM ATOM OXYGEN %	90.39	97.54	99.66	99.88	99.30
RATIO CHX/(H2O+CO2)	0.8314	0.8429	0.8556	0.8107	0.8018
RATIO X IN CHX	2.2449	2.2523	2.2627	2.2928	2.2838
USAGE H2/CO PRODT	1.8322	1.8707	1.8726	1.8578	1.8868
RATIO CO2/(H2O+CO2)	0.0902	0.0786	0.0803	0.0866	0.0747
K SHIFT IN EFFLNT	0.03	0.03	0.03	0.03	0.03
CONVERSION					
ON CO %	40.82	39.71	39.36	37.71	36.74
ON H2 %	80.99	79.05	78.67	77.67	75.11
ON CO+H2 %	60.98	59.57	59.10	57.66	56.18
PRDT SELECTIVITY,WT %					
CH4	10.00	10.37	11.03	12.31	11.96
C2 HC'S	1.94	1.99	2.10	2.38	2.26
C3H8	2.26	2.26	2.24	2.47	2.46
C3H6=	1.54	1.54	1.56	1.68	1.57
C4H10	2.01	2.02	1.94	2.15	2.12
C4H8=	2.80	2.79	2.88	3.19	3.09
C5H12	2.73	2.74	2.57	2.81	2.68
C5H10=	2.98	3.02	3.12	3.49	3.43
C6H14	3.70	3.81	3.47	3.71	3.36
C6H12= & CYCLO'S	2.17	2.22	2.45	2.81	2.80
C7+ IN GAS	12.59	11.15	11.62	12.26	12.30
LIQ HC'S	55.26	56.08	55.03	50.74	51.97

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	20.56	20.97	21.74	24.19	23.47
C5 -420 F	51.67	48.18	48.41	47.91	47.69
420-700 F	25.41	26.92	26.31	24.35	24.68
700-END PT	2.36	3.93	3.54	3.55	4.16
C5+-END PT	79.44	79.03	78.26	75.81	76.53
ISO/NORMAL MOLE RATIO					
C4	0.3643	0.3660	0.3197	0.3236	0.2759
C5	0.6929	0.6841	0.5958	0.5584	0.4772
C6	1.3797	1.3400	1.1176	1.0271	0.8758
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.3991	1.3982	1.3717	1.4034	1.4964
C4	0.6928	0.6965	0.6523	0.6501	0.6616
C5	0.8925	0.8834	0.8011	0.7832	0.7587
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.757		0.760		0.762
N, REFRACTIVE INDEX	1.4264	-	1.4278	-	1.4289
SIMULT'D DISTILATN					
10 WT % @ DEG F	273		285		287
16	300		308		309
50	421		438		448
84	589		623		643
90	635		667		684
RANGE(16-84 %)	289		315		334
WT % @ 420 F	49.75		45.75		44.50
WT % @ 700 F	95.73		93.56		92.00

TABLE 7B RESULT OF SYNGAS OPERATION

RUN NO. 10112-10
CATALYST CO-PPT,THO2,K-Y-82 #10252-17C CC 31.0GM (48.8 AFTER RUN+18 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-10-06	112-10-07	112-10-08
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	75.42	91.50	122.0
PRESSURE,PSIG	307	304	304
TEMP. C	251	250	250
FEED CC/MIN	400	400	400
HOURS FEEDING	7.50	23.58	30.50
EFFLNT GAS LITER	87.86	294.60	451.65
GM AQUEOUS LAYER	20.35	63.99	64.34
GM OIL	8.92	28.03	22.97
MATERIAL BALANCE			
GM ATOM CARBON %	95.63	94.50	96.98
GM ATOM HYDROGEN %	95.35	102.84	101.73
GM ATOM OXYGEN %	98.75	98.15	99.60
RATIO CHX/(H2O+CO2)	0.9118	0.8980	0.9102
RATIO X IN CHX	2.2854	2.3017	2.4095
USAGE H2/CO PRODT	1.8772	1.8626	1.8695
RATIO CO2/(H2O+CO2)	0.0860	0.0929	0.1084
K SHIFT IN EFFLNT	0.04	0.06	0.08
CONVERSION			
ON CO %	36.94	37.55	30.70
ON H2 %	72.62	67.57	57.12
ON CO+H2 %	54.75	53.19	44.22
PRDT SELECTIVITY,WT %			
CH4	11.94	12.66	16.98
C2 HC'S	2.24	2.26	3.20
C3H8	2.53	2.72	3.83
C3H6=	1.51	1.17	1.67
C4H10	2.21	2.42	3.35
C4H8=	3.01	2.49	2.93
C5H12	2.79	2.96	4.13
C5H10=	3.34	2.69	3.00
C6H14	3.57	3.57	4.63
C6H12= & CYCLO'S	2.87	2.29	2.55
C7+ IN GAS	11.88	12.54	14.02
LIQ HC'S	52.12	52.24	39.70

TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	23.44	23.71	31.96
C5 -420 F	47.90	47.03	45.09
420-700 F	25.02	25.51	18.90
700-END PT	3.65	3.75	4.05
C5+-END PT	76.56	76.29	68.04
ISO/NORMAL MOLE RATIO			
C4	0.2758	0.2566	0.2110
C5	0.4824	0.4562	0.4325
C6	0.8329	0.7872	0.5783
C4=	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO			
C3	1.6001	2.2107	2.1917
C4	0.7073	0.9363	1.1021
C5	0.8105	1.0684	1.3375
LIQ HC COLLECTION			
PHYS. APPEARANCE		CLR OIL	CLR OIL
DENSITY		0.760	0.761
N, REFRACTIVE INDEX		1.4278	1.4278
SIMULT'D DISTILATN			
10 WT % @ DEG F		292	301
16		316	329
50		448	456
84		632	656
90		677	701
RANGE(16-84 %)		316	327
WT % @ 420 F		44.00	42.20
WT % @ 700 F		92.83	89.80

IX. RUN 10112-9, Co/Th/K on LZ-Y-82

This catalyst came from the same batch of metal-loaded Molecular Sieve used in Run 10112-10, but the pellets were calcined for two hours at 500C, instead of 250C.

Calcination at 500C resulted in a very low activity (Fig. 99). Product selectivity is given in Fig. 100. Detailed material balances are given in Table 8.

Comparison of Runs 100112-9 and 100112-10 shows that calcination at 500C has a disastrous effect on the catalyst's activity. An explanation for this will have to await analysis of the two catalysts. A prime suspect is sintering of the metal component.

Fig. 99

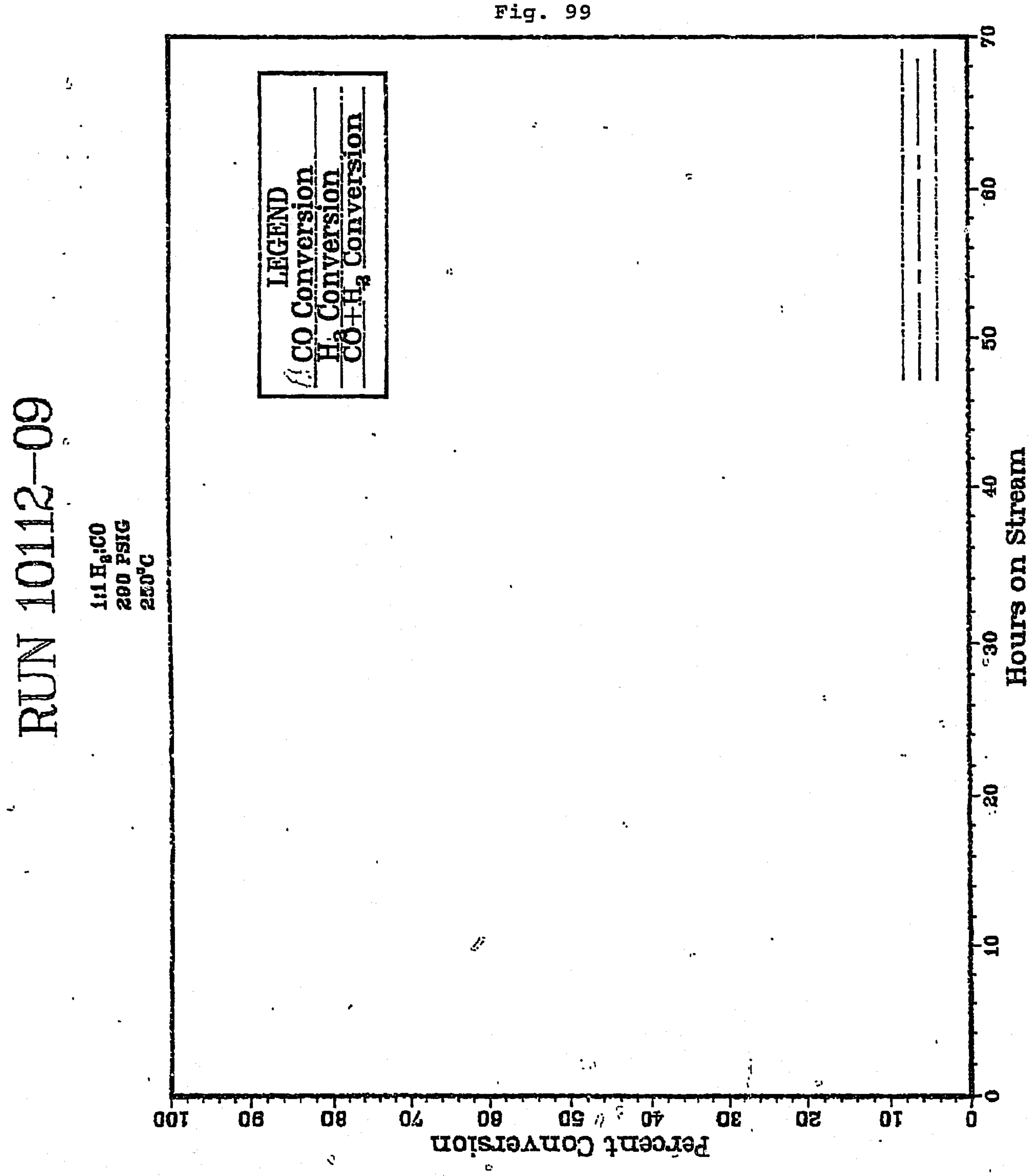
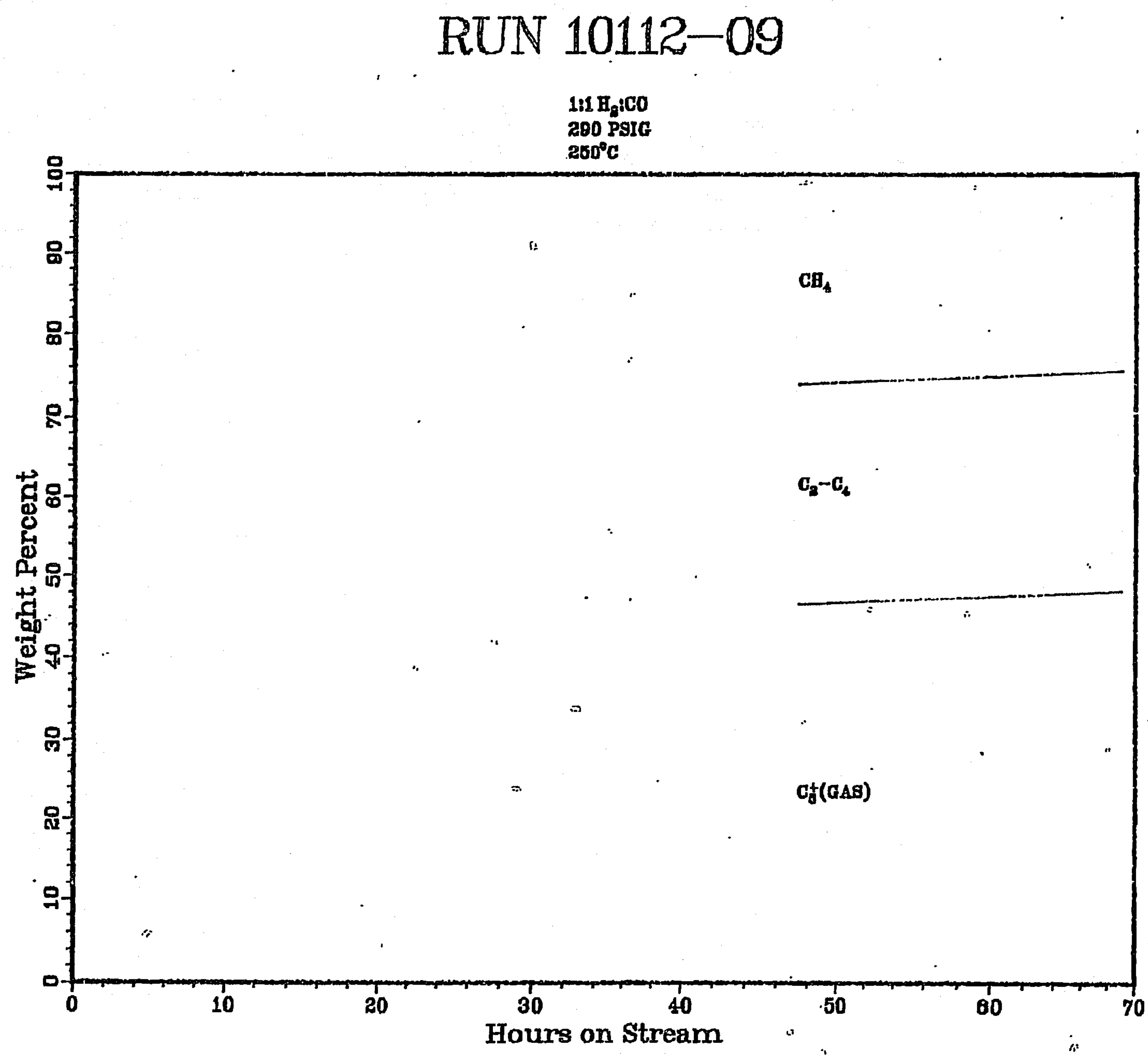

RUN 10112-09
1:1 H2:CO
290 PSIG
250°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50
60
70

Fig. 100



RUN 10112–09
1:1 H2:CO
290 PSIG
250°C
CH4
C2–C4
C5+(GAS)
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50
60
70

p

TABLE 8 RESULT OF SYNGAS OPERATION

RUN NO. 10112-09
CATALYST CO-PPT-Y-82 10252-05-C 80CC 31.0 GM (33.0 AFTER RUN +2.0G)
FEED H2:CO:ARGON OF 50:50: 0 @ 800 CC/MN OR 600 GHSV

RUN & SAMPLE NO.	10112-09-01	112-09-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	47.38	69.00
PRESSURE,PSIG	291	292
TEMP. C	250	250
FEED CC/MIN	800	800
HOURS FEEDING	47.38	21.62
EFFLNT GAS LITER	2120.95	985.53
GM AQUEOUS LAYER	0.00	0.00
GM OIL	0.00	0.00
MATERIAL BALANCE		
GM ATOM CARBON %	94.88	95.22
GM ATOM HYDROGEN %	97.43	100.90
GM ATOM OXYGEN %	95.75	95.99
RATIO CHX/(H2O+CO2)	0.7898	0.8182
RATIO X IN CHX	2.7156	2.6755
USAGE H2/CO PRODT	1.8642	1.8624
RATIO CO2/(H2O+CO2)	0.1411	0.1402
K SHIFT IN EFFLNT	0.16	0.17
CONVERSION		
ON CO %	4.05	4.22
ON H2 %	8.18	8.13
ON CO+H2 %	6.14	6.23
PRDT SELECTIVITY,WT %		
CH4	26.06	24.41
C2 HC'S	6.16	5.87
C3H8	8.44	8.20
C3H6=	1.89	2.22
C4H10	9.01	8.84
C4H8=	1.81	2.26
C5H12	10.17	9.43
C5H10=	0.27	0.85
C6H14	9.43	9.70
C6H12= & CYCLO'S	0.00	0.00
C7+ IN GAS	26.76	28.21
LIQ HC'S	0.00	0.00

TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	53.37	51.80
C5 -420 F	46.63	48.20
420-700 F	0.00	0.00
700-END PT	0.00	0.00
C5+-END PT	46.63	48.20
ISO/NORMAL MOLE RATIO		
C4	0.4366	0.4014
C5	1.1445	1.0229
C6	1.6422	1.5000
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	4.2712	3.5245
C4	4.8000	3.7798
C5	37.1000	10.7273
LIQ HC COLLECTION		
PHYS. APPEARANCE	---	---
DENSITY	---	---
N, REFRACTIVE INDEX	---	---
SIMULT'D DISTILATN		
10 WT % @ DEG F	---	---
16	---	---
50	---	---
84	---	---
90	---	---
RANGE(16-84 %)	---	---
WT % @ 420 F	---	---
WT % @ 700 F	---	---

X. RUN 10112-4, 20 Percent Co on UCC-101

This catalyst was prepared by precipitating cobalt oxide from an aqueous zeolite slurry, the same method used for the previous cobalt catalysts. It was not promoted with either potassium or thorium, but was calcined in air at 250C.

Conversion, product selectivity, isomerization of the pentane, and percent olefins in the C_4's are plotted against time on stream in Figs. 101-104. Simulated distillations for three samples are given in Figs. 105-107. Carbon number product distributions are given in Figs. 108-116. Chromatograms of the simulated distillations are illustrated in Figs. 117-124. Detailed material balances are given in Tables 9A-9D.

This catalyst was not very active at 220C (Fig. 101). The cobalt-on-LZ-105 catalyst (Run 10112-6) was slightly more active at comparable reaction conditions. The LZ-105 catalyst also had higher WGS activity and used the 1:1 syngas more efficiently. At 250C, this catalyst was again less active than 10112-6. Furthermore, at 250C its WGS activity improved slightly relative to the F-T activity--a behavior which is common for this type of F-T catalyst and which implies a lower activation energy for the WGS reaction than for the F-T reaction. The catalyst was still not using the 1:1 syngas efficiently, although the usage ratio did drop from 1.9 to 1.6. While it is preferable to have the feed and usage ratios equal, tests of catalysts with inadequate WGS activity do show catalyst stability with low hydrogen:carbon monoxide feed. In a Berty reactor the catalyst sees only the product composition, not the feed composition. At 250C this catalyst maintained activity despite seeing a syngas with a hydrogen:carbon monoxide ratio lower than 0.6.

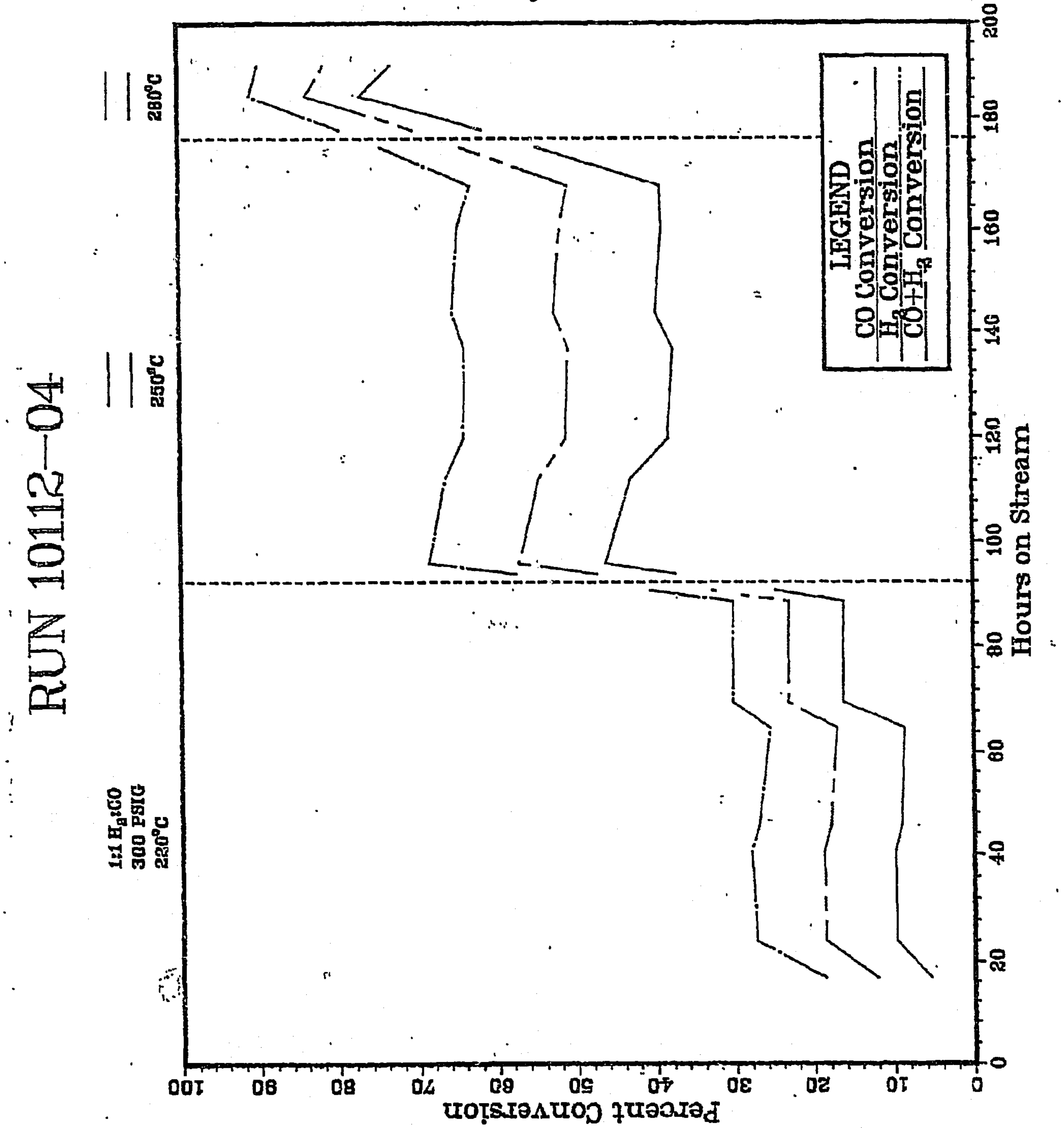
Product selectivity at 220C was changing constantly (Fig. 102), mostly due to increasing quantities of heavies in the effluent. Also, the material balances show that only the last samples taken at 220C truly represent the products produced at steady-state condition. However, the measured product selectivity at 250C is much more stable, and yields are typical for cobalt catalysts. The selectivity of this catalyst at 250C is similar to that of the cobalt-on-LZ-105 catalyst at 220C, even though the conversion of this catalyst is much higher. The methane yield is high, but low yields of the C_2-C_4 fraction allow for the high selectivity to gasoline and diesel oil. The 70 percent yield of gasoline and diesel oil compares well with that of the best catalysts tested.

The carbon number distributions again show the methane yield to be out of line with those of the other hydrocarbons (Figs. 108-116). High yields of gasoline and diesel oil are mostly due to low C_2-C_4 yields. While some samples seem to show oligomerization and/or possible carbon-number cut-offs, there does not seem to be a general trend with this catalyst. The 70 percent motor fuel is roughly 40 percent gasoline and 30 percent diesel oil. The $C_5{}^+$ product also contains 6 percent heavies.

It is not the quantity of heavies alone which contributes to the waxy nature of the condensed product. The refractive intercept for the liquid product, the chromatograms of the simulated distillations (Figs. 117-124), and the low degree of pentane isomerization (Fig. 103), all show that the liquid product is primarily straight-chain hydrocarbons. Such a product composition, typical of cobalt catalysts, produces a solid condensed product. UCC-101, while not a strong acid, generally isomerizes hydrocarbons better than it did in this test. Possibly the Molecular Sieve was not able to recover during the test from its deactivation at 220C.

The activity of this catalyst is similar to those of other cobalt catalysts. The cobalt-on-LZ-Y-82 (Run 10112-10) had an initial acid activity which during the run decreased to a level similar to that of UCC-101. The cobalt-on-LC-105-6 (Run 10112-6) had a lower conversion but similar product selectivity; however, at both 220C and 250C it was a poor F-T catalyst. The 20 percent cobalt-on-UCC-101 catalyst reported in this section could profit from more acid activity to prevent it from producing so waxy a product.

Fig. 101



RUN 10112-04
1:1 H_2:CO
300 PSIG
220°C
250°C
280°C
Percent Conversion
Hours on Stream
LEGEND
CO Conversion
H_2 Conversion
CO+H_2 Conversion
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 102

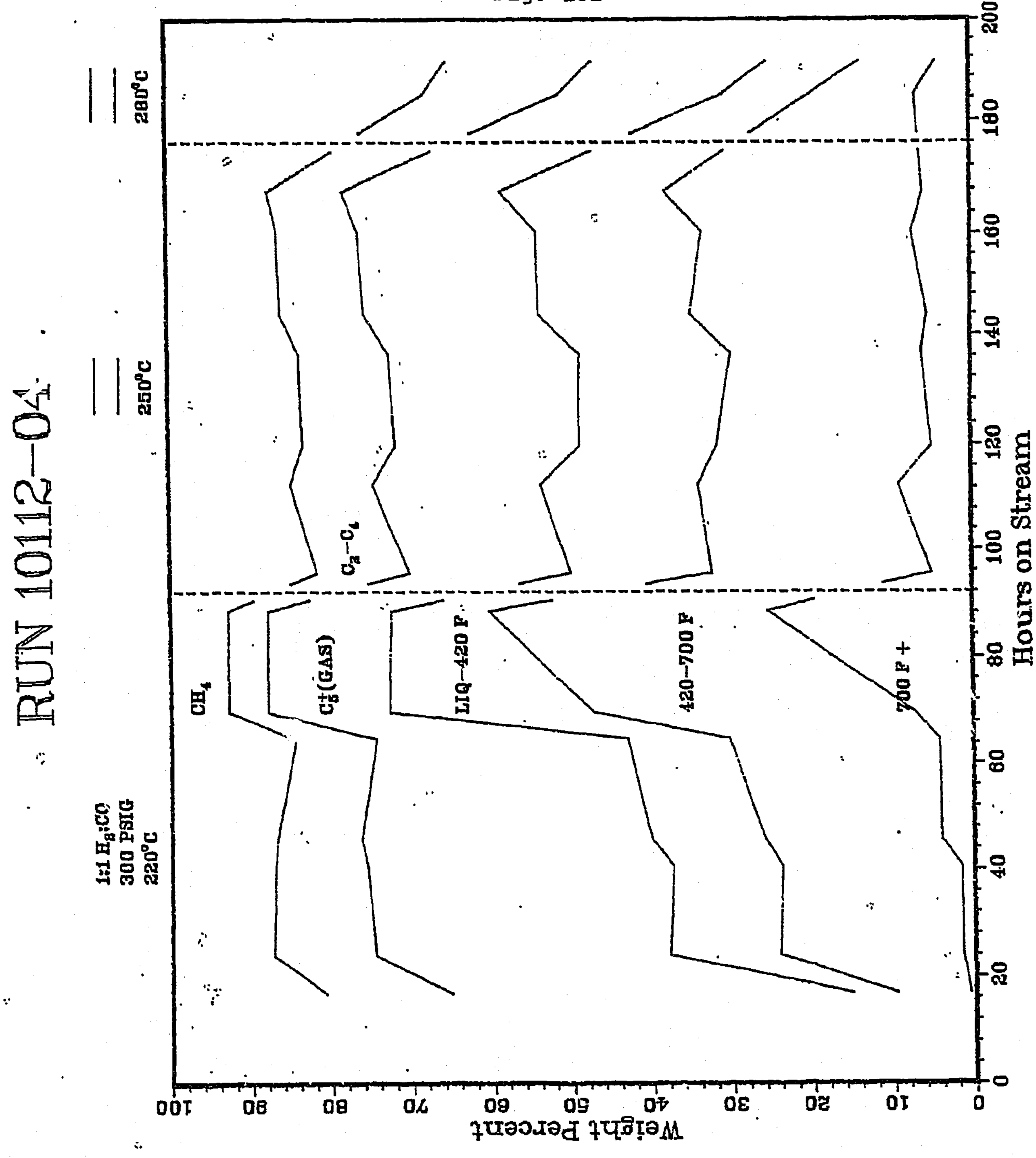

RUN 10112-04
1:1 H2:CO
300 PSIG
220°C
250°C
280°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200

Fig. 103

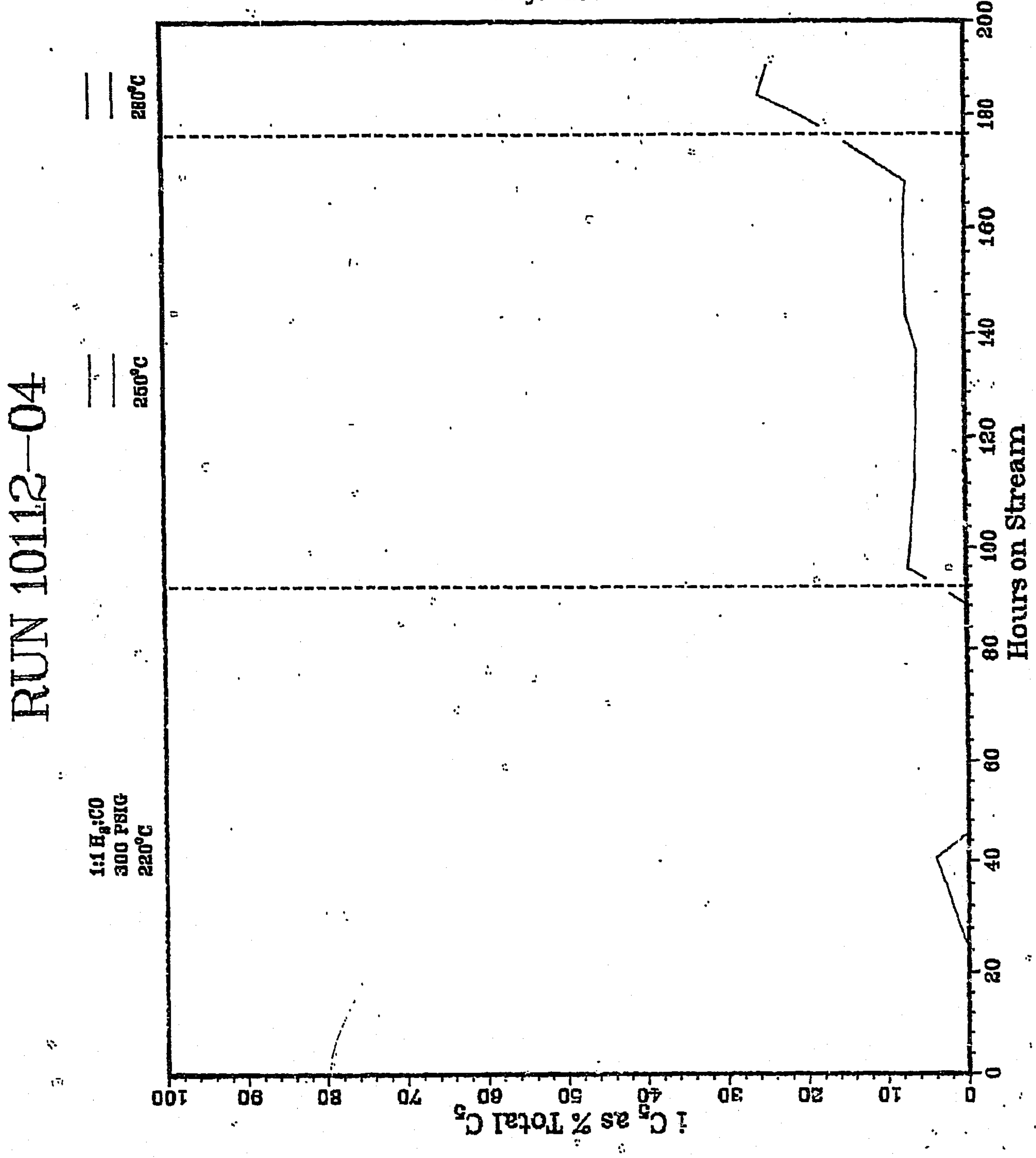

RUN 10112—04
1:1 H_2:CO
300 PSIG
220°C
250°C
280°C
Hours on Stream
i C_5 as % Total C_5
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 104

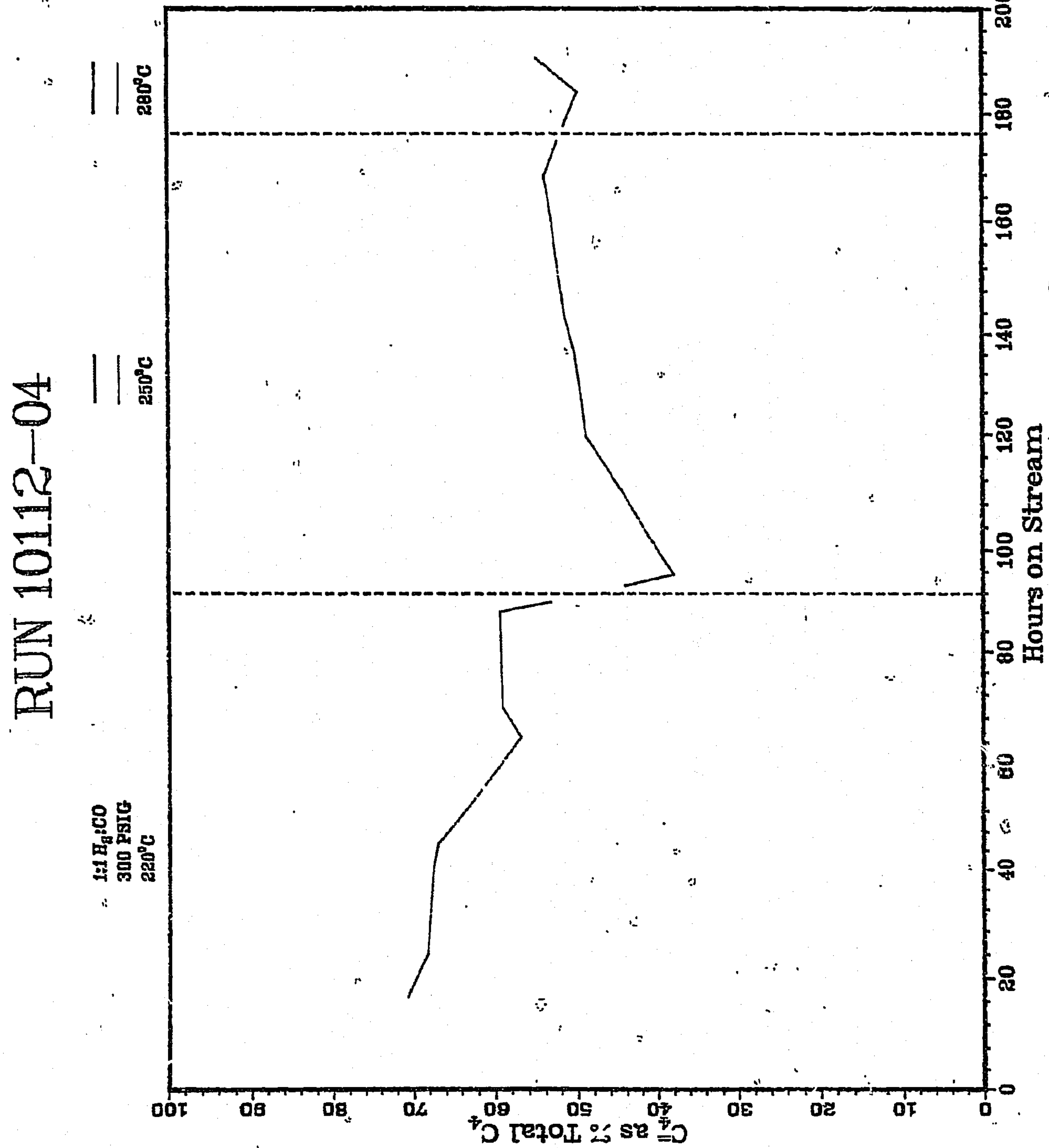
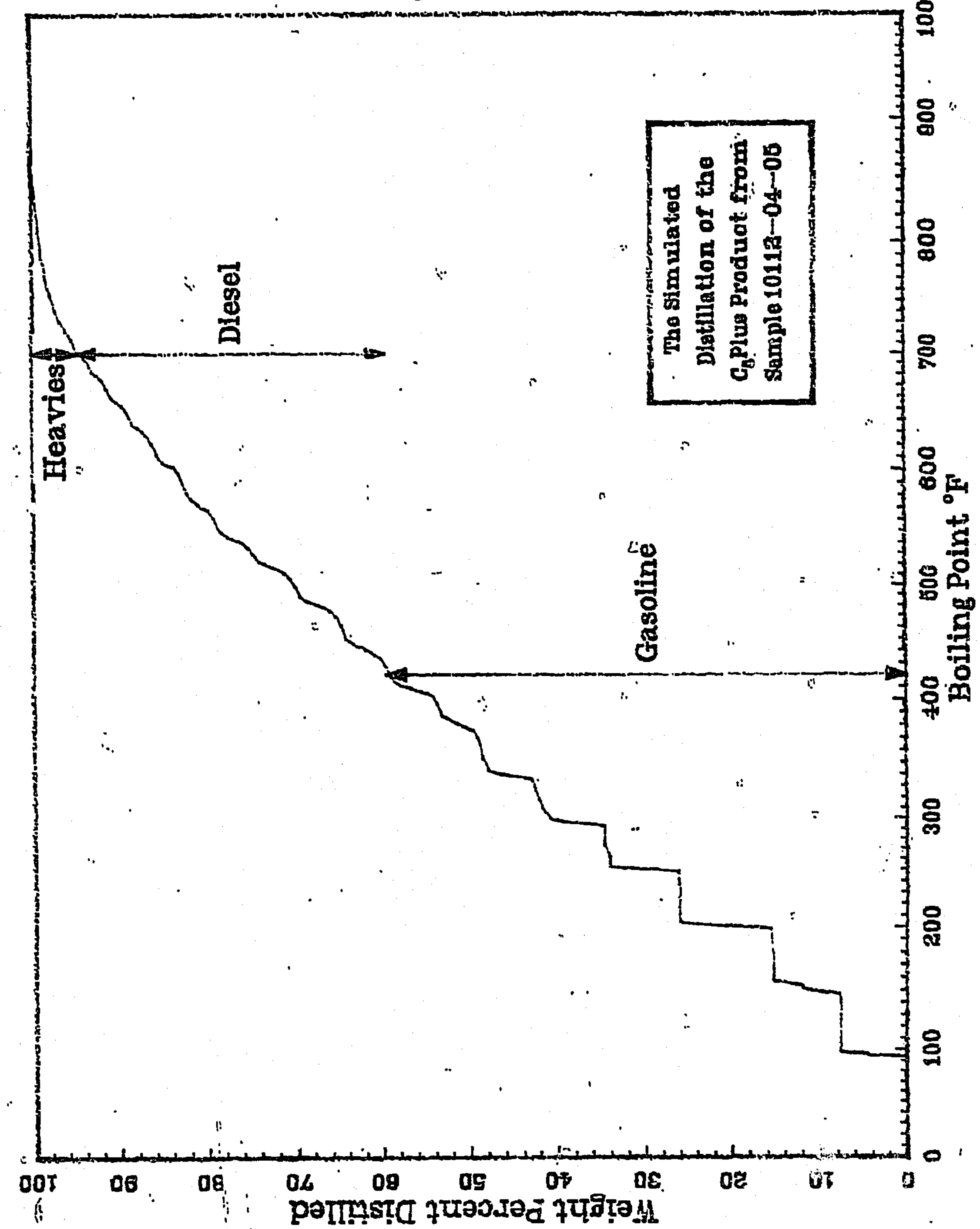

RUN 10112-04
1:1 H_2:CO
300 PSIG
220°C
250°C
280°C
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
$C_4^=$ as % Total C_4
0
10
20
30
40
50
60
70
80
90
100

Fig. 105



Weight Percent Distilled
Boiling Point °F
Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C_5 Plus Product from
Sample 10112-04-05

Fig. 106

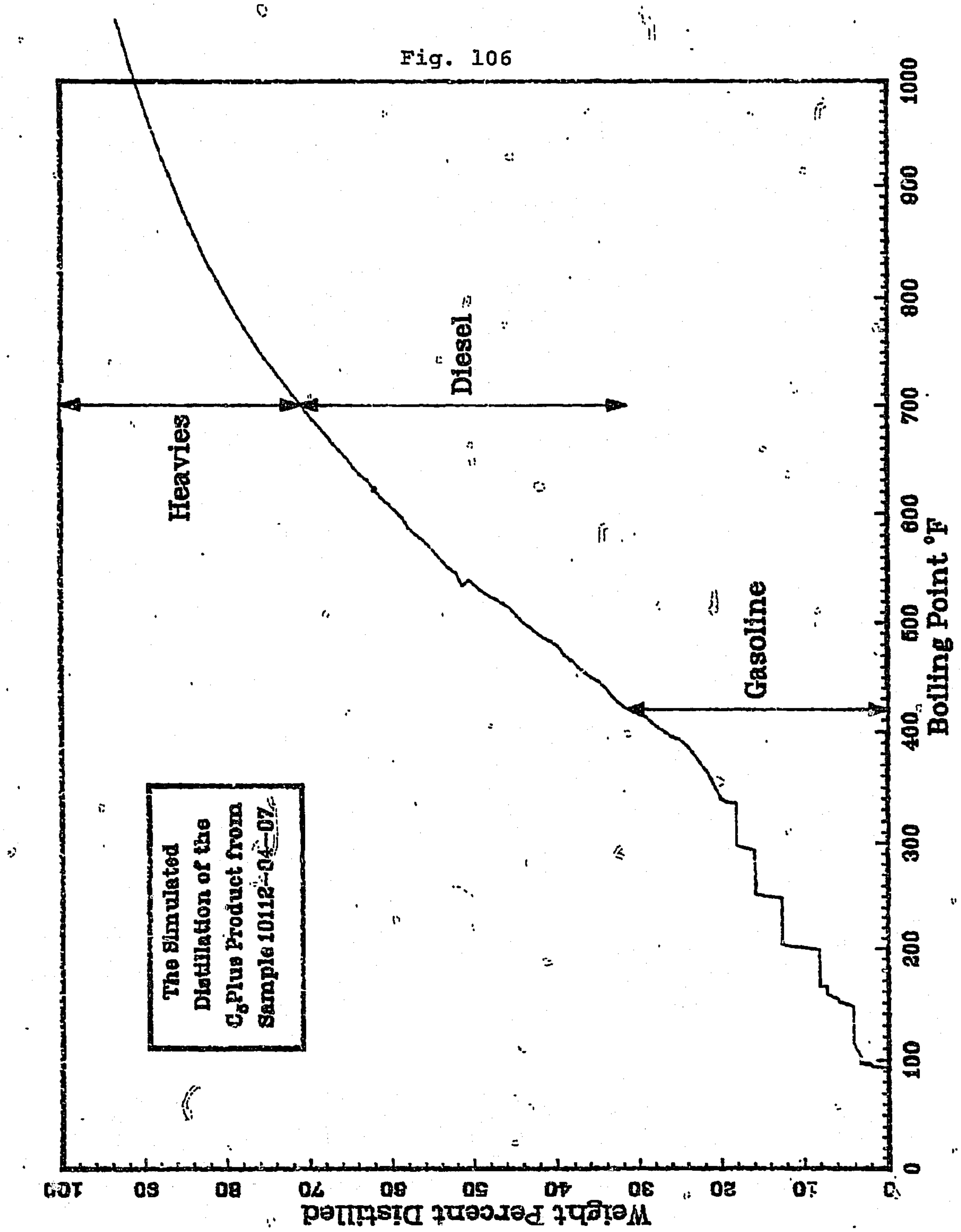

The Simulated
Distillation of the
C_6Plus Product from
Sample 10112-04-07
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 107

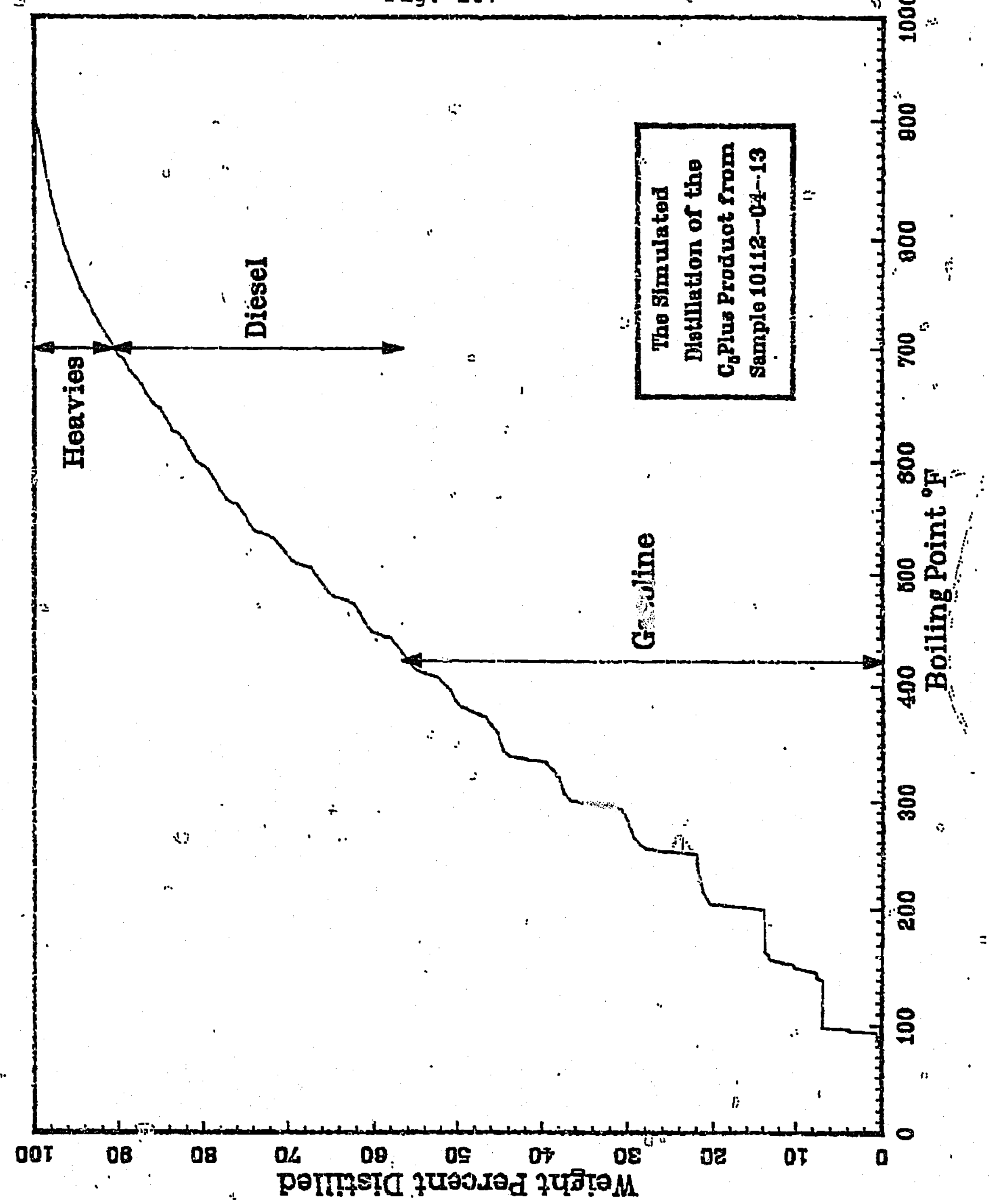

The Simulated Distillation of the C_5Plus Product from Sample 10112-04-13
Heavies
Diesel
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 108

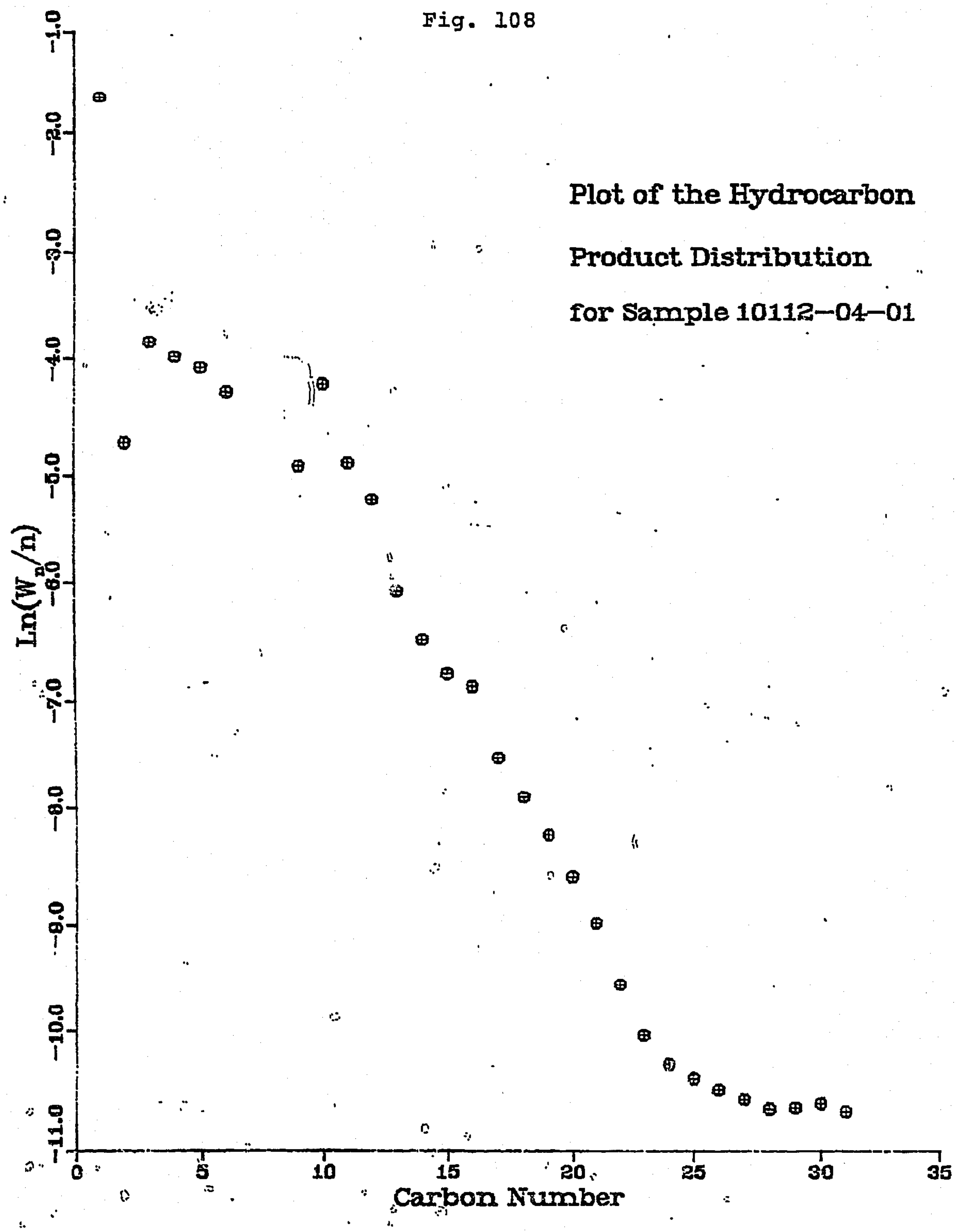
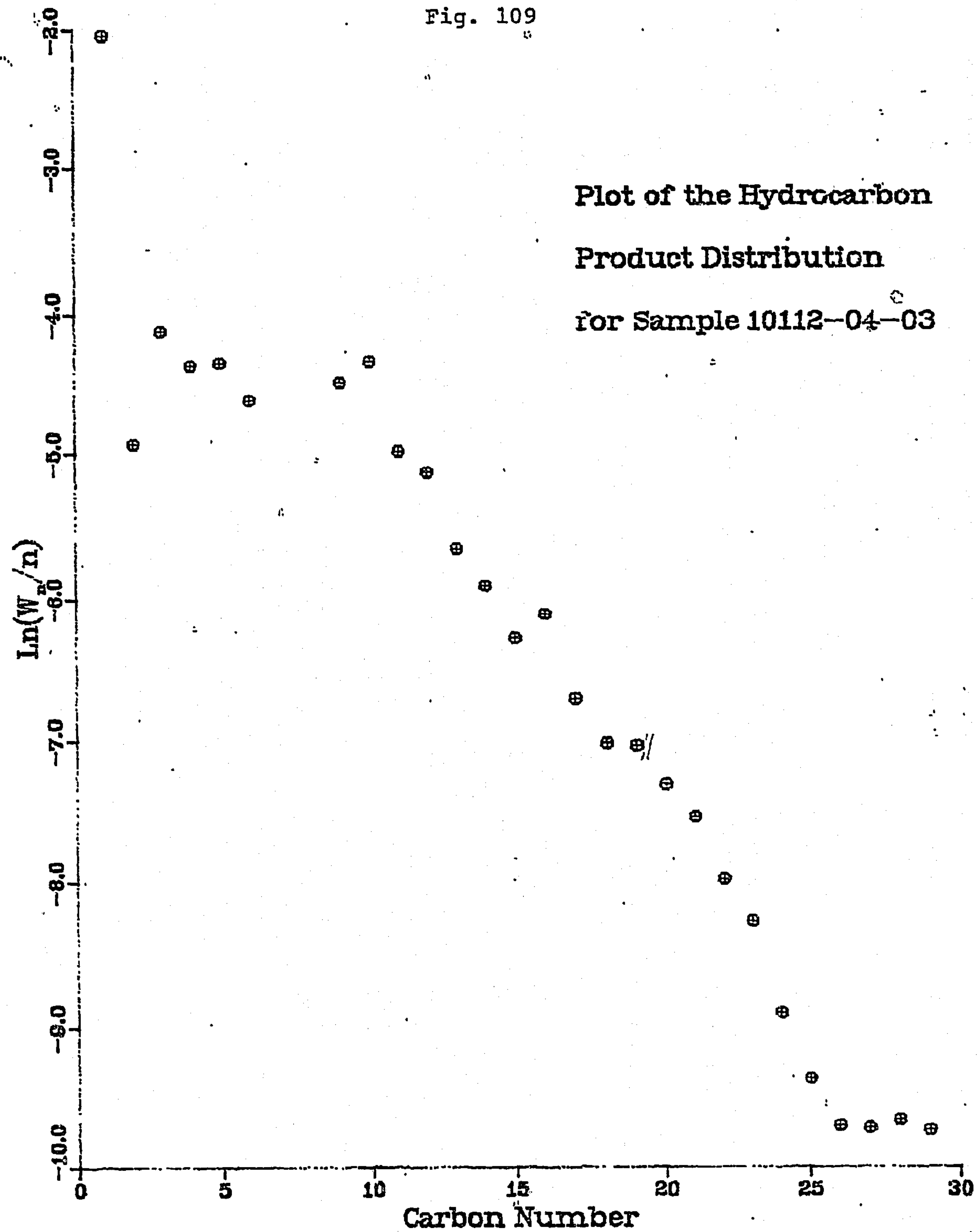
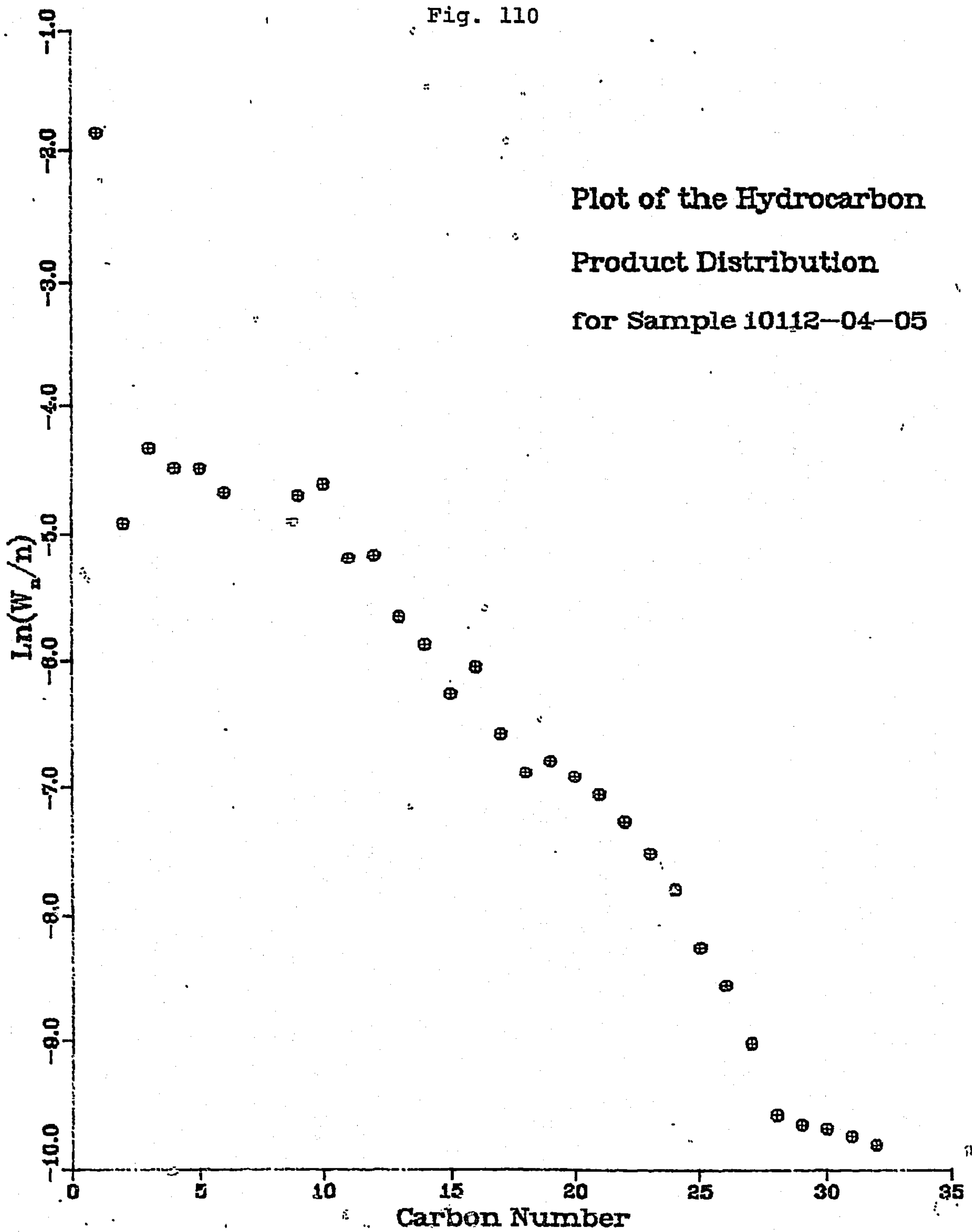

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–04–01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 109



Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-03
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. 110



Plot of the Hydrocarbon
Product Distribution
for Sample 10112–04–05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 111

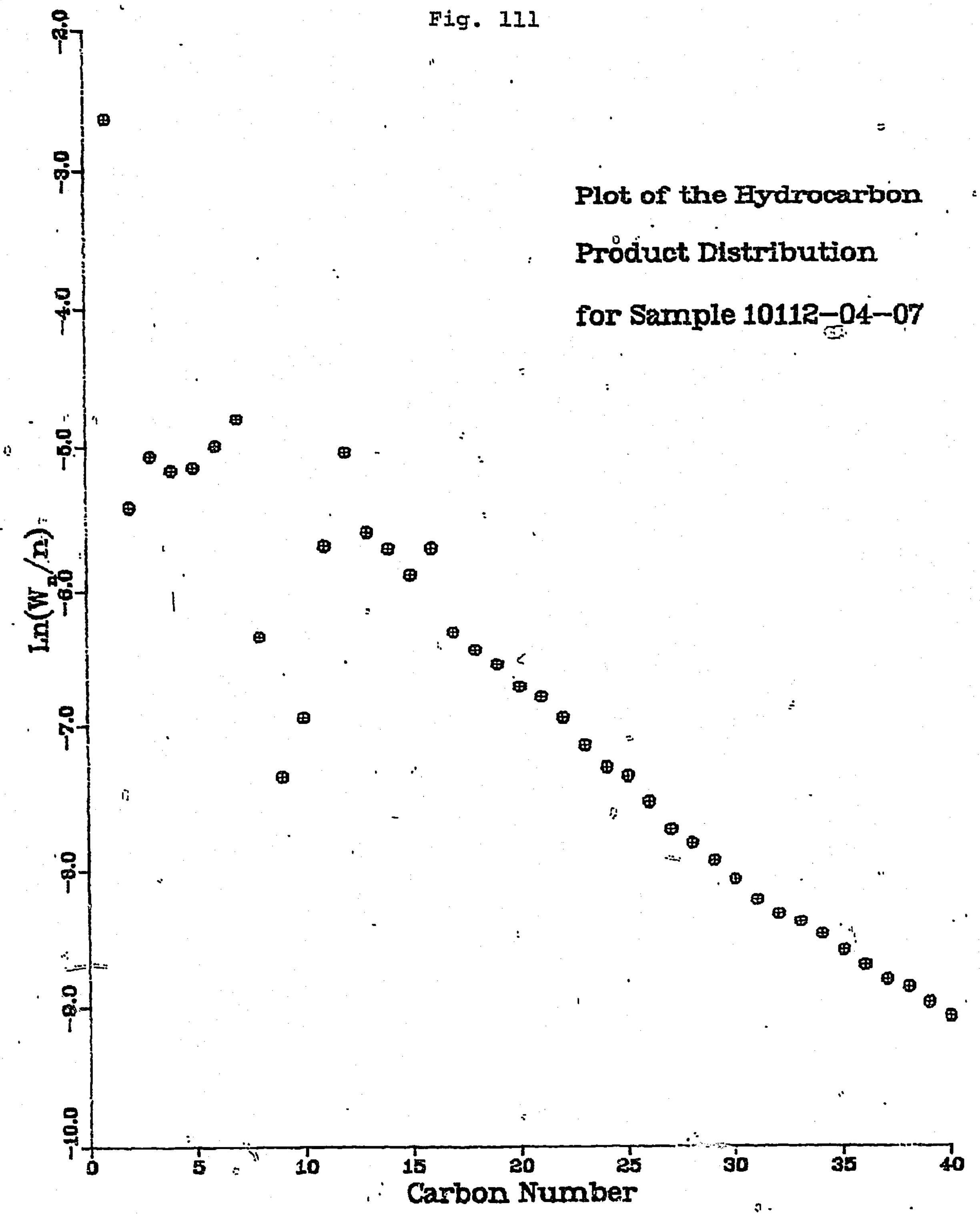

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-07
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 112

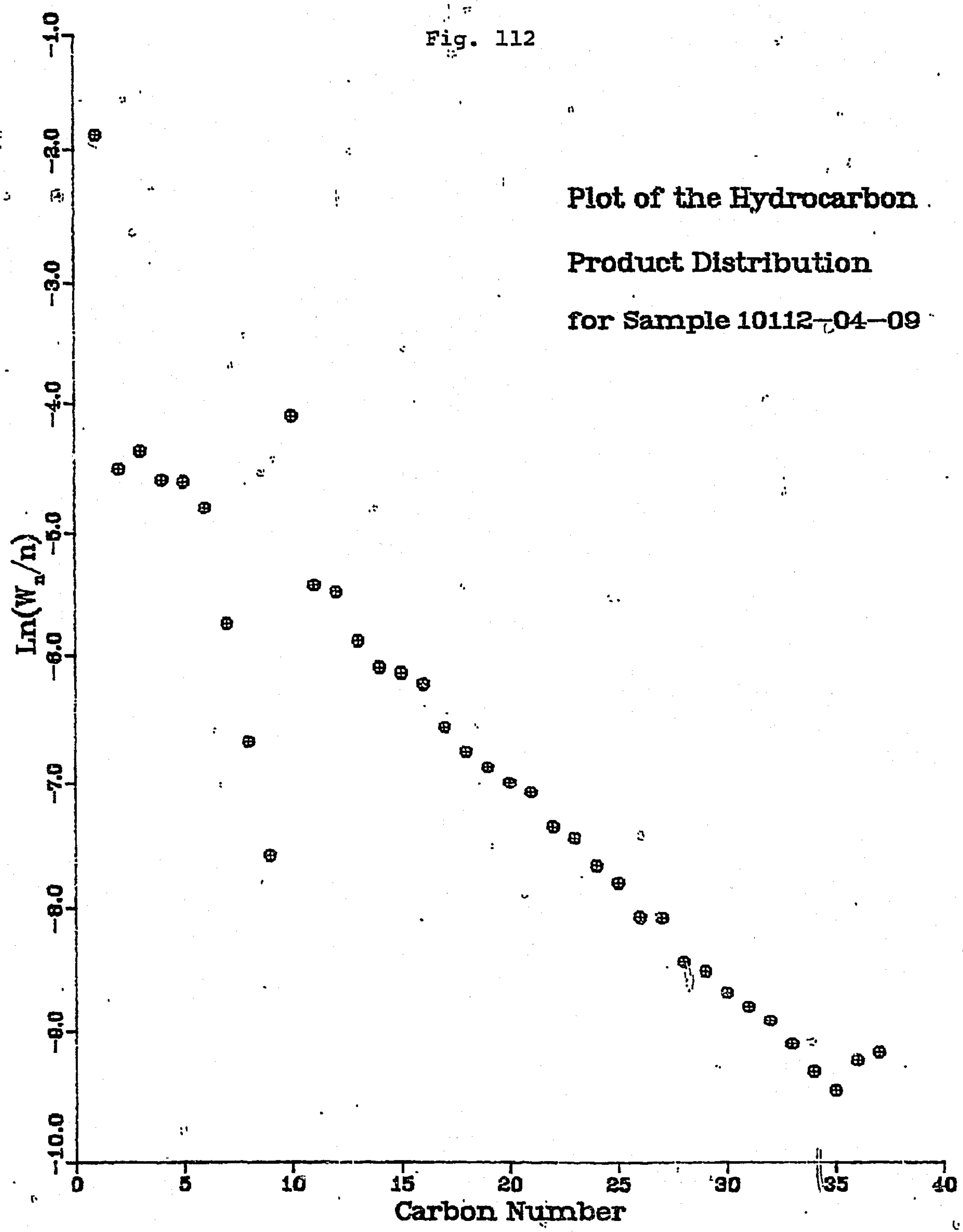

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-09
$Ln(W_n/n)$
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 113

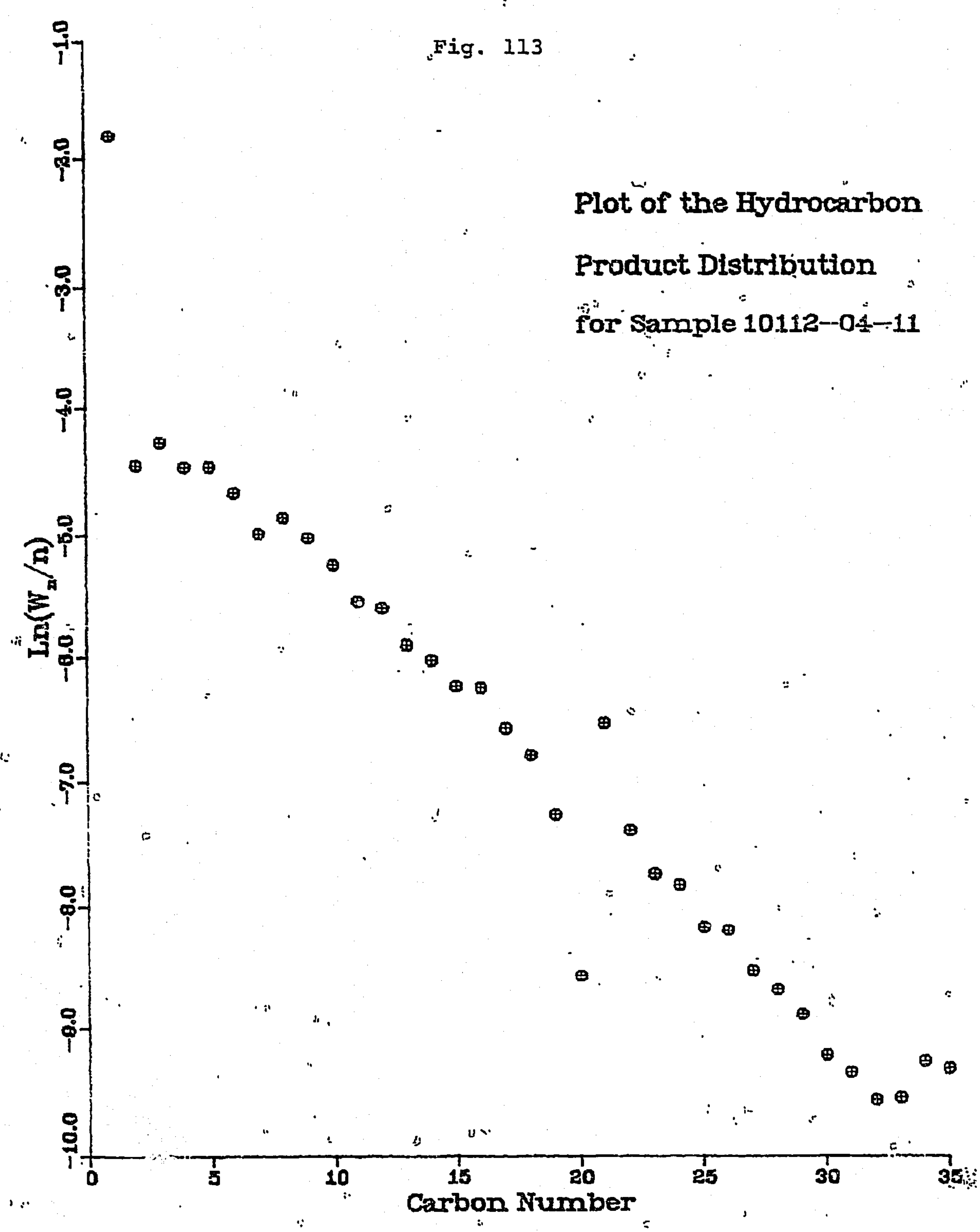

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--04--11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 114

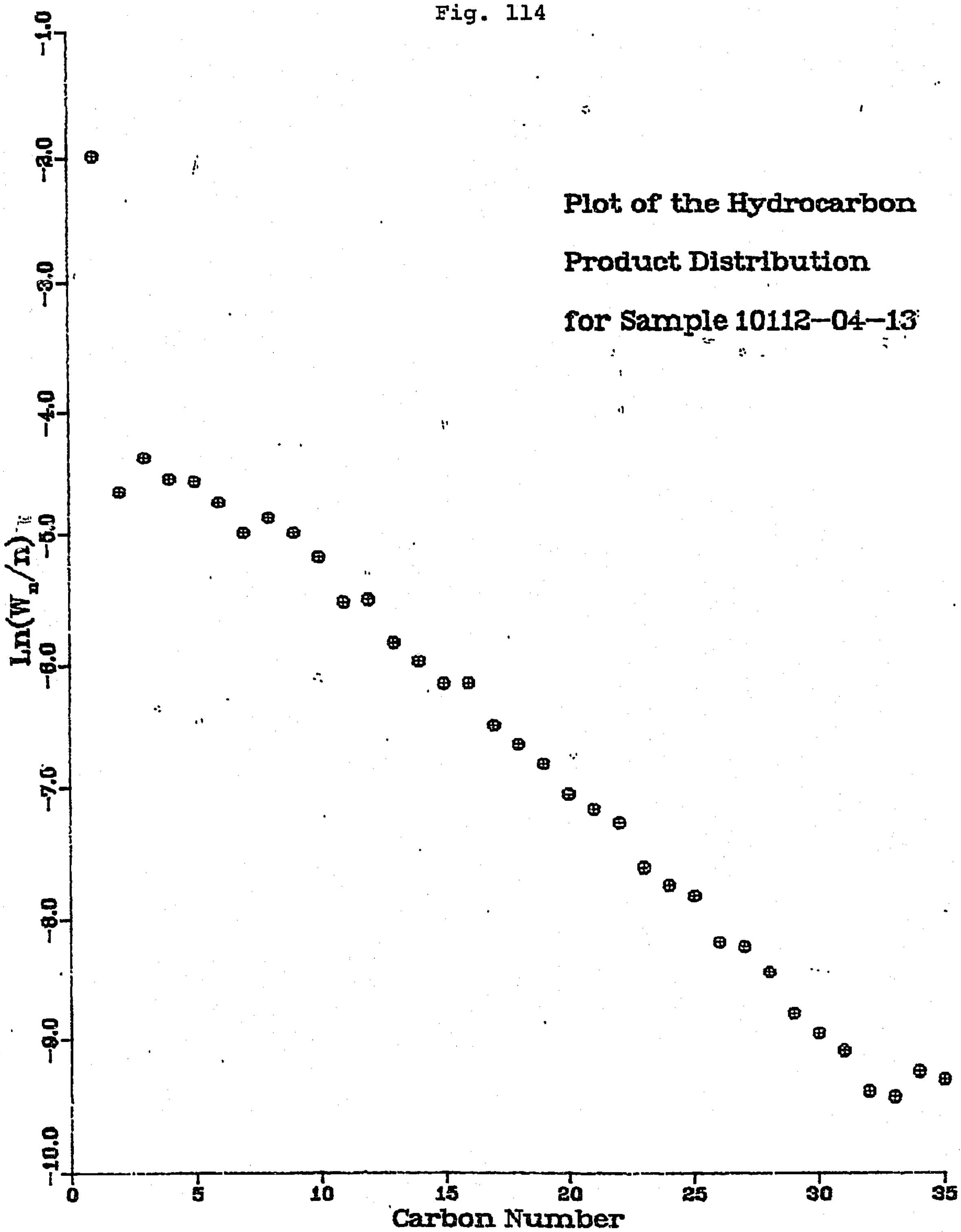

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-13
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 115

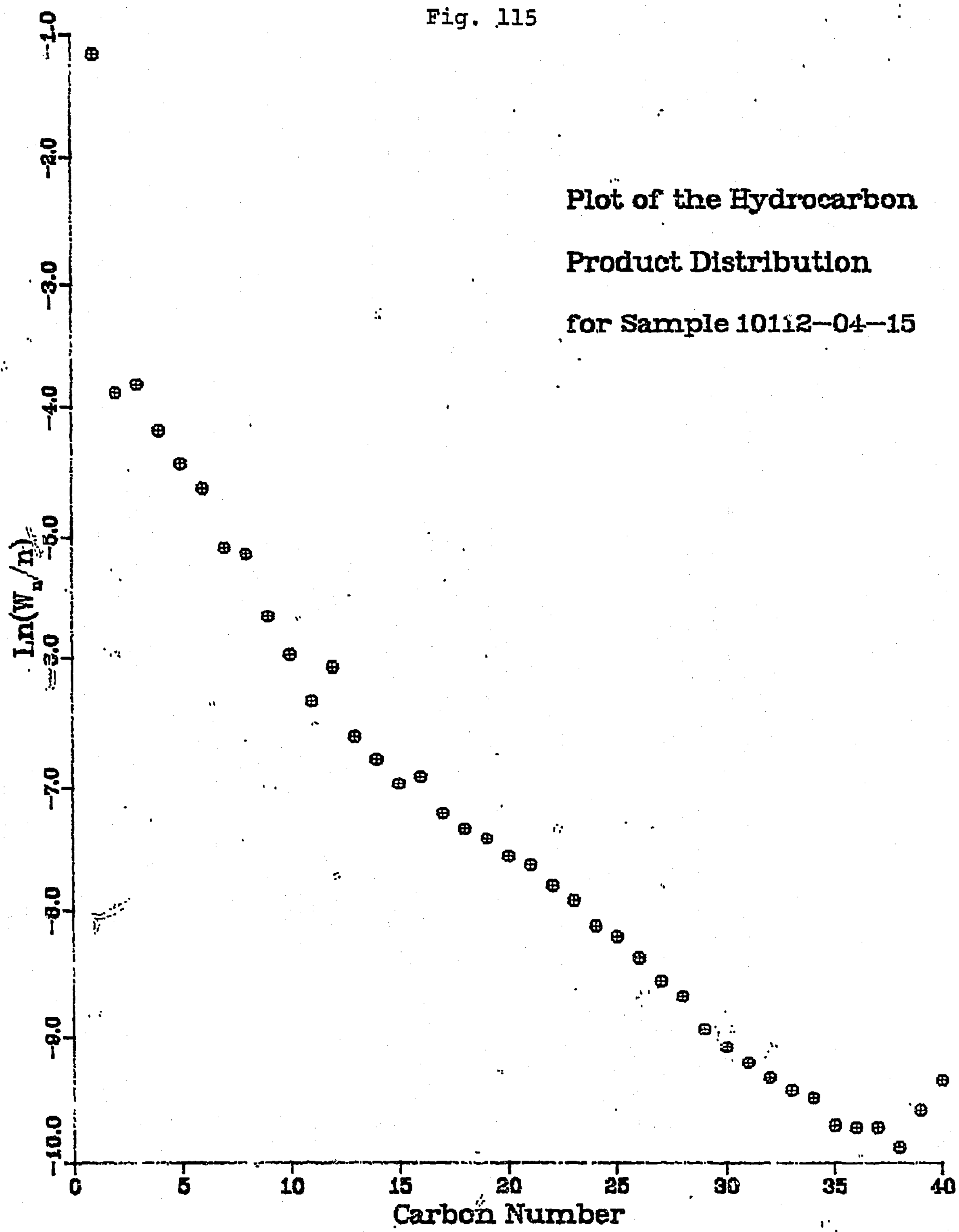
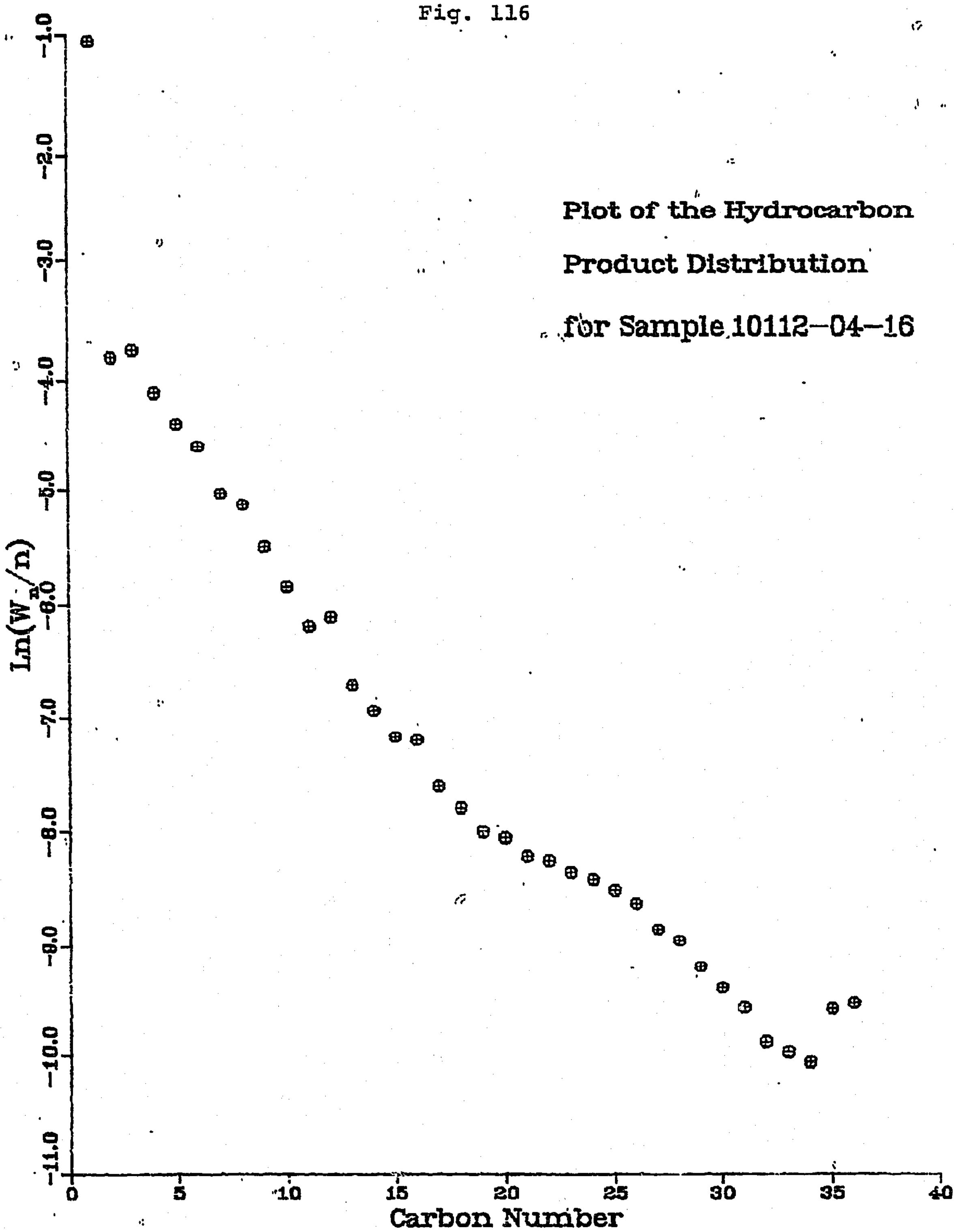
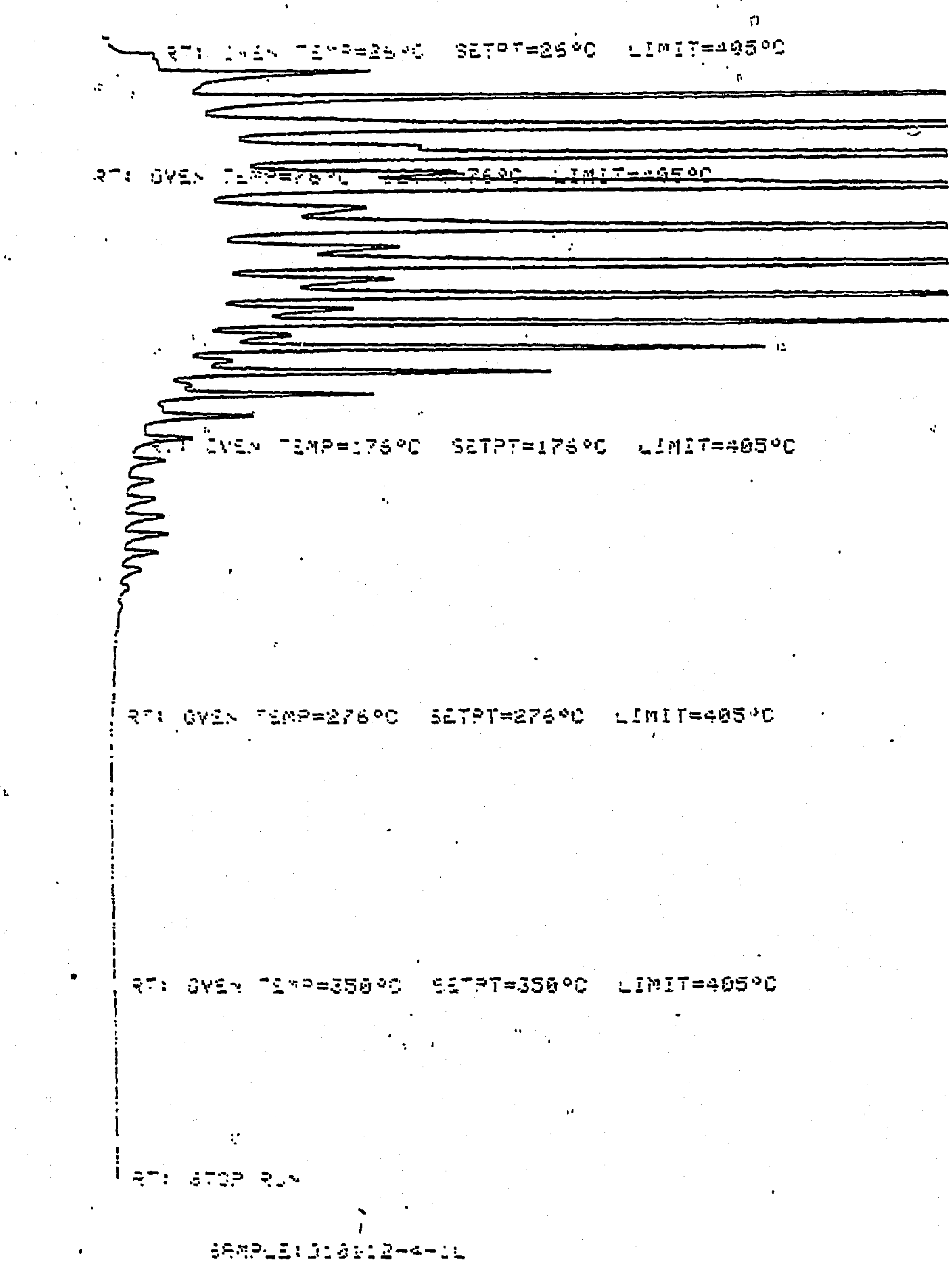

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-15
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 116



Plot of the Hydrocarbon
Product Distribution
for Sample 10112-04-16
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 117



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
SETPT=350°C LIMIT=405°C

Fig. 118

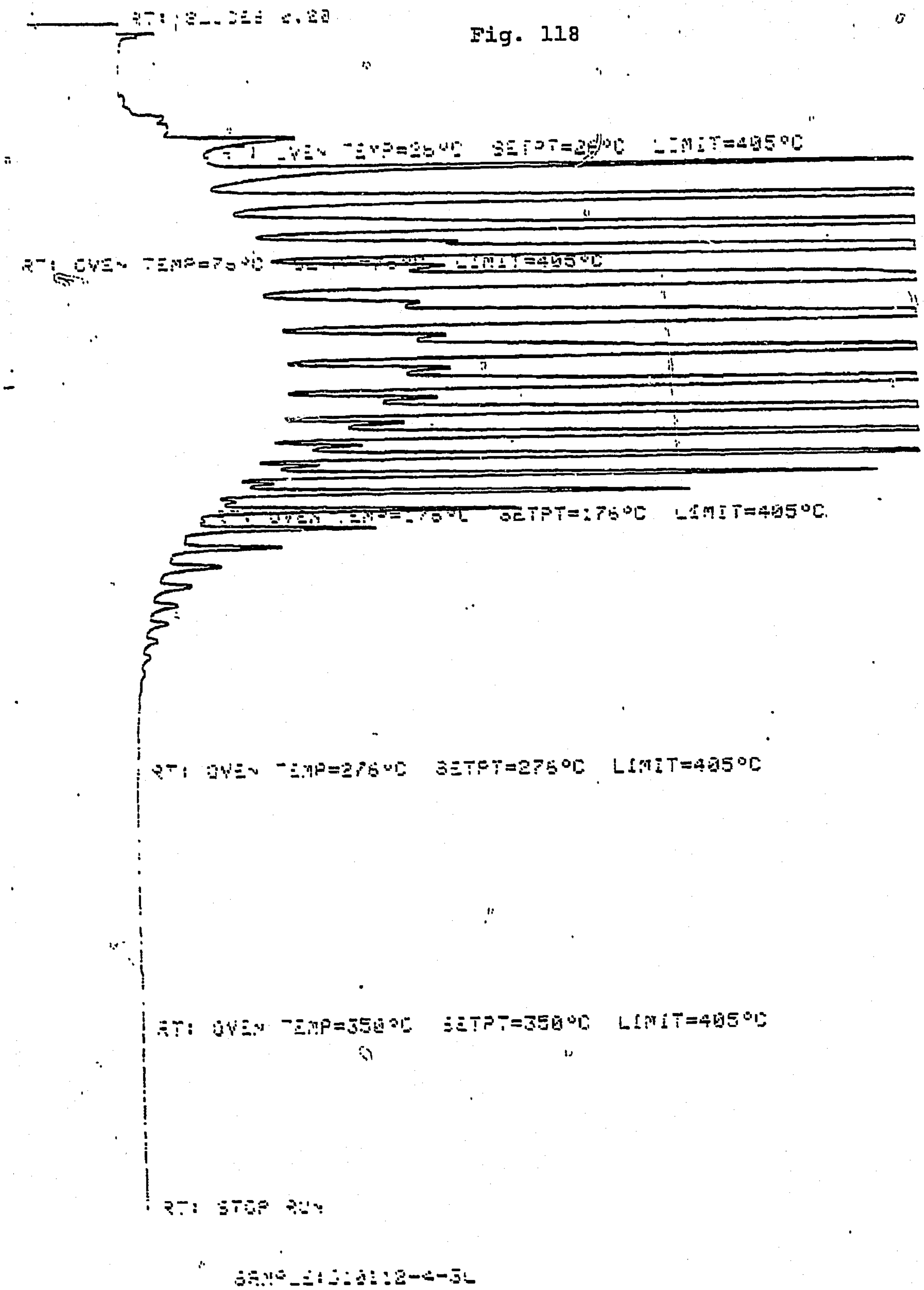

LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 119

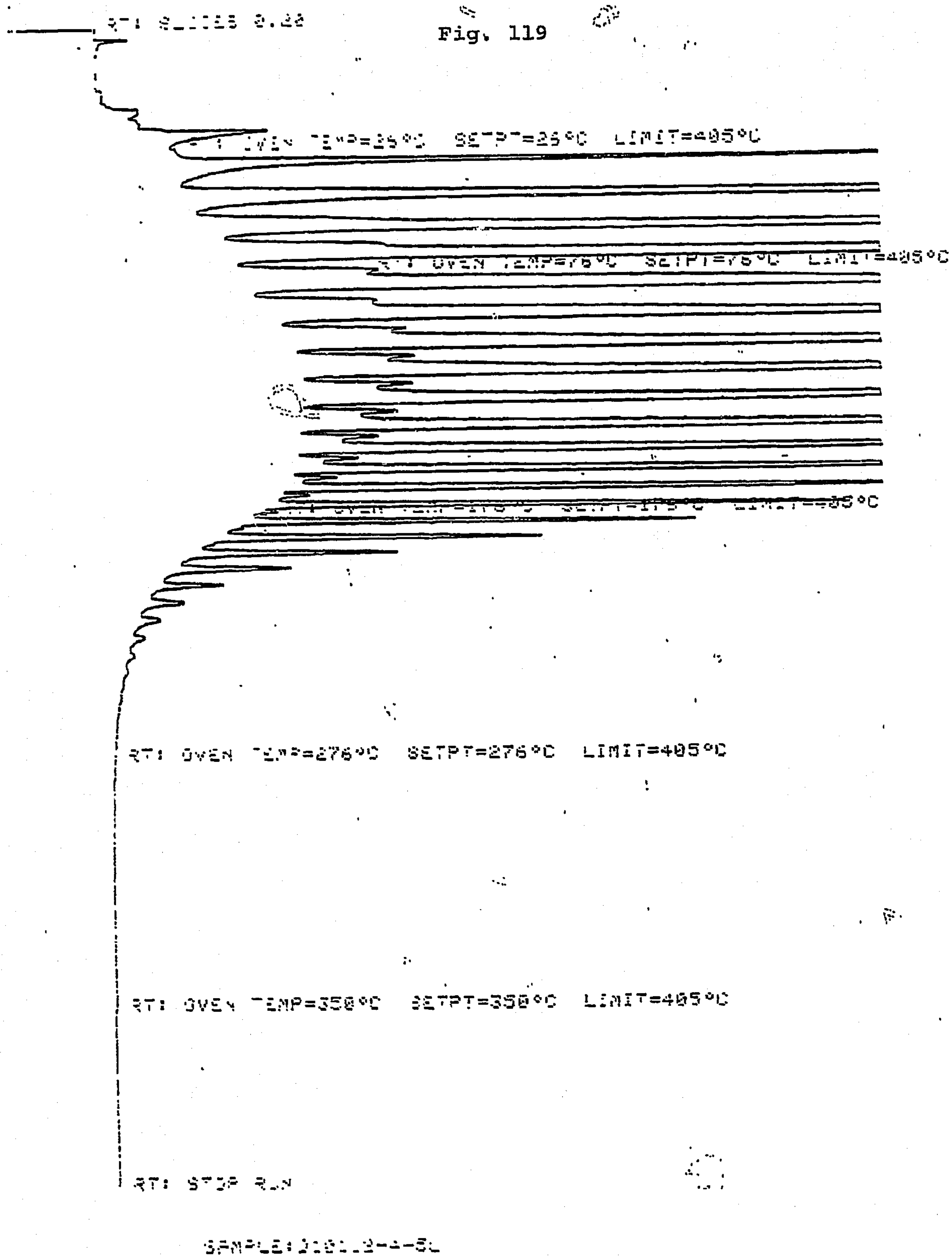
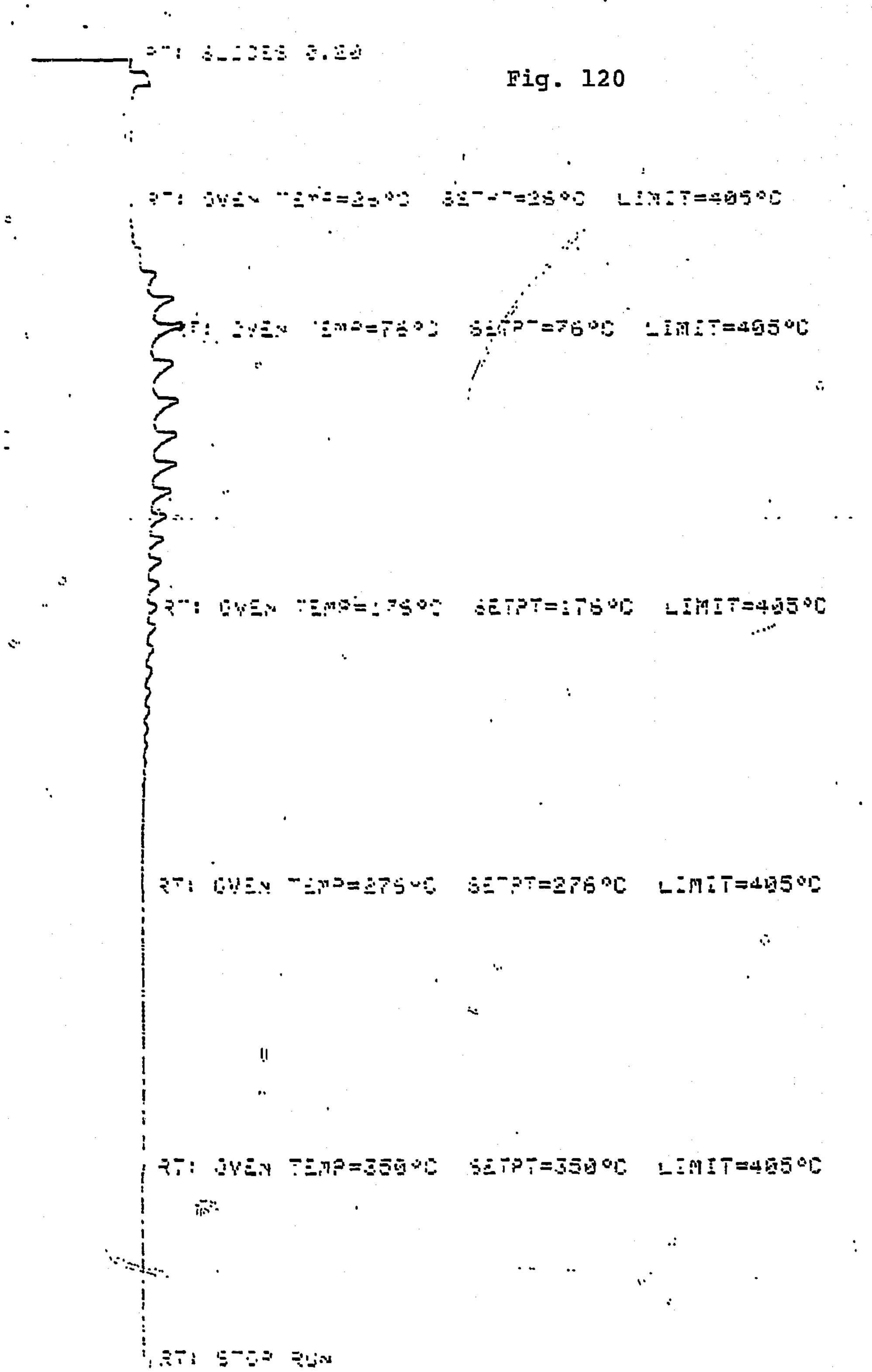

RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 120



SAMPLE:D10112-4-7L

Fig. 121

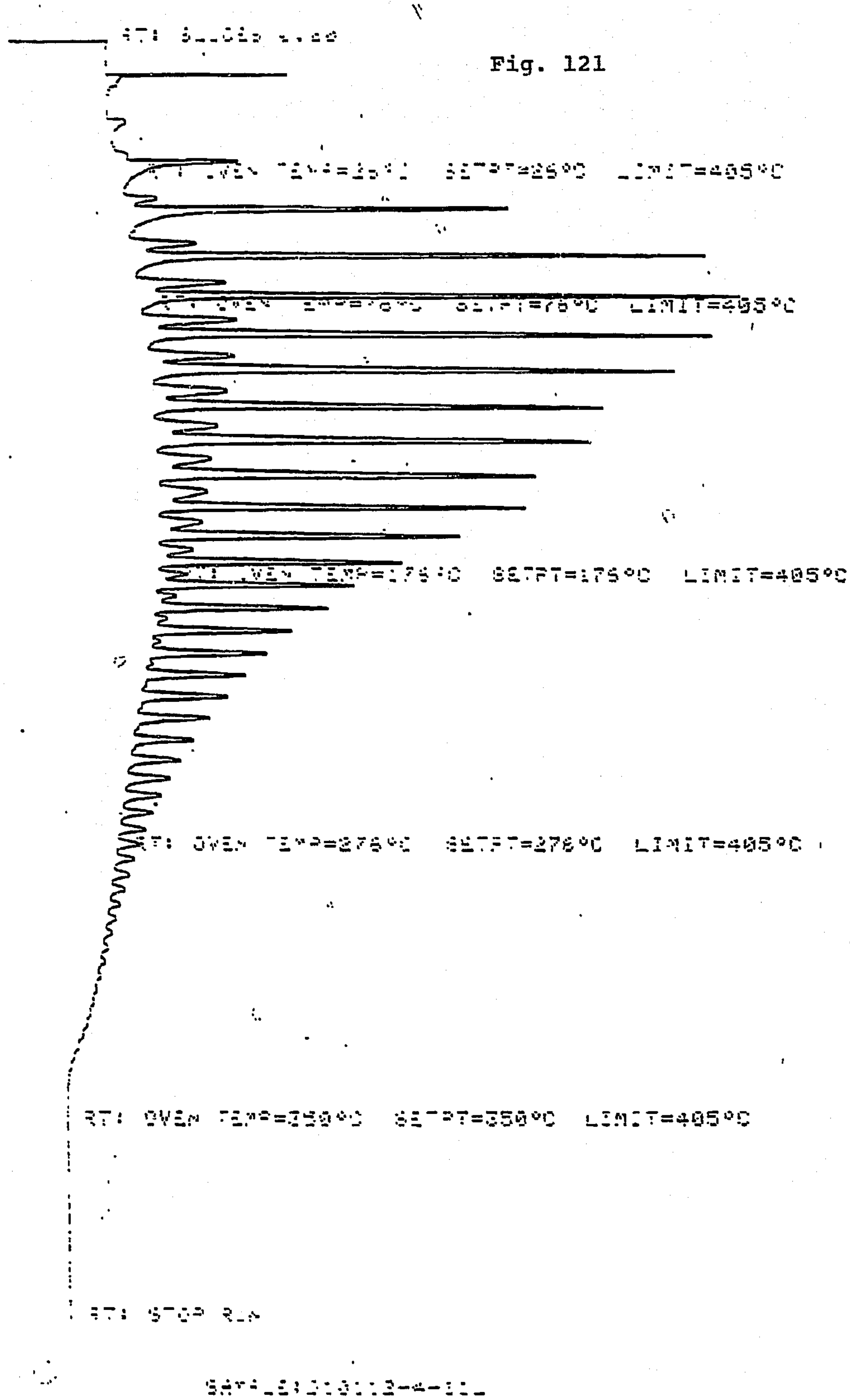

LIMIT=405°C
SETPT=175°C LIMIT=405°C
SETPT=275°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 122

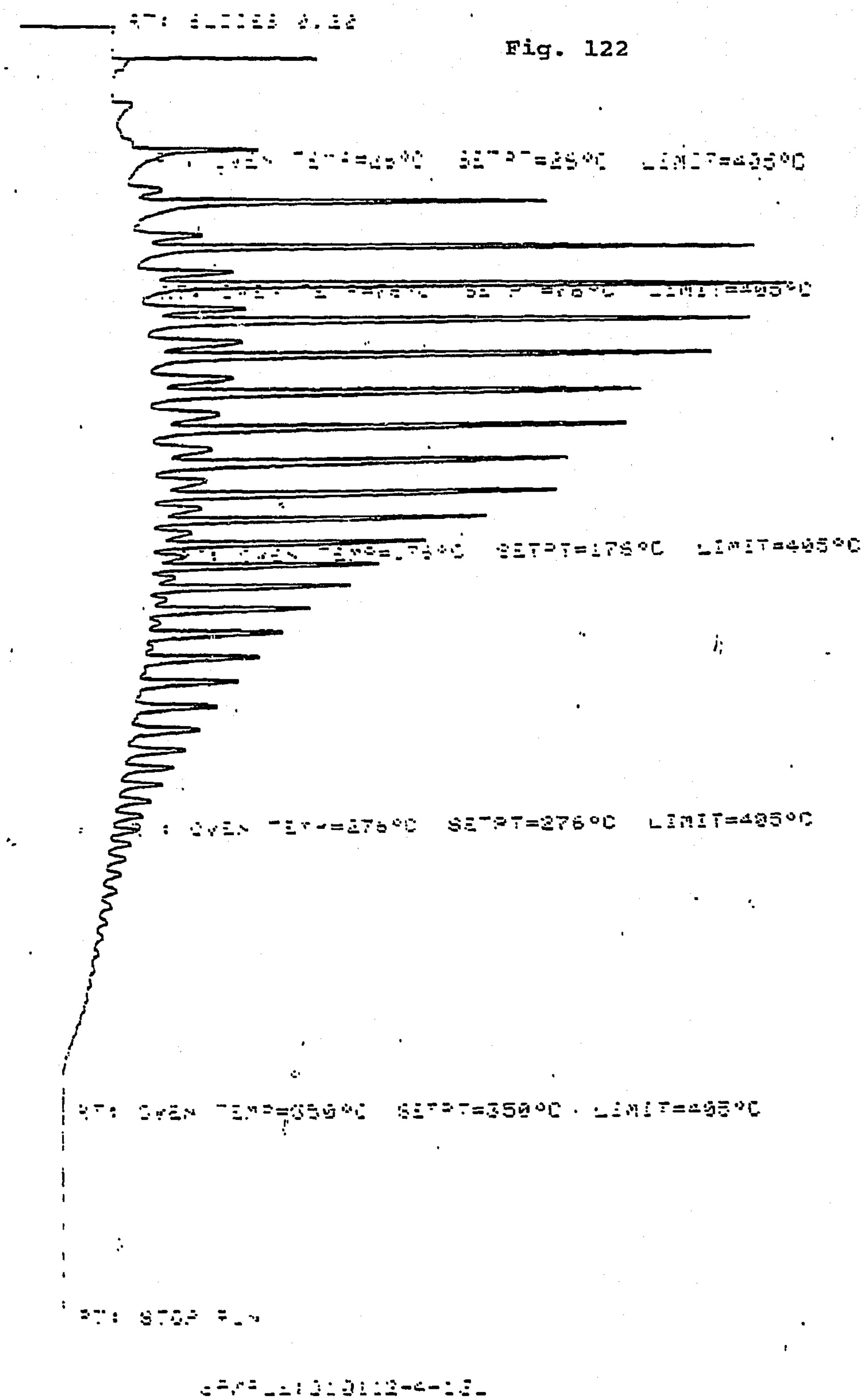

SETPT=175°C LIMIT=405°C
OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
SETPT=350°C LIMIT=405°C

Fig. 123

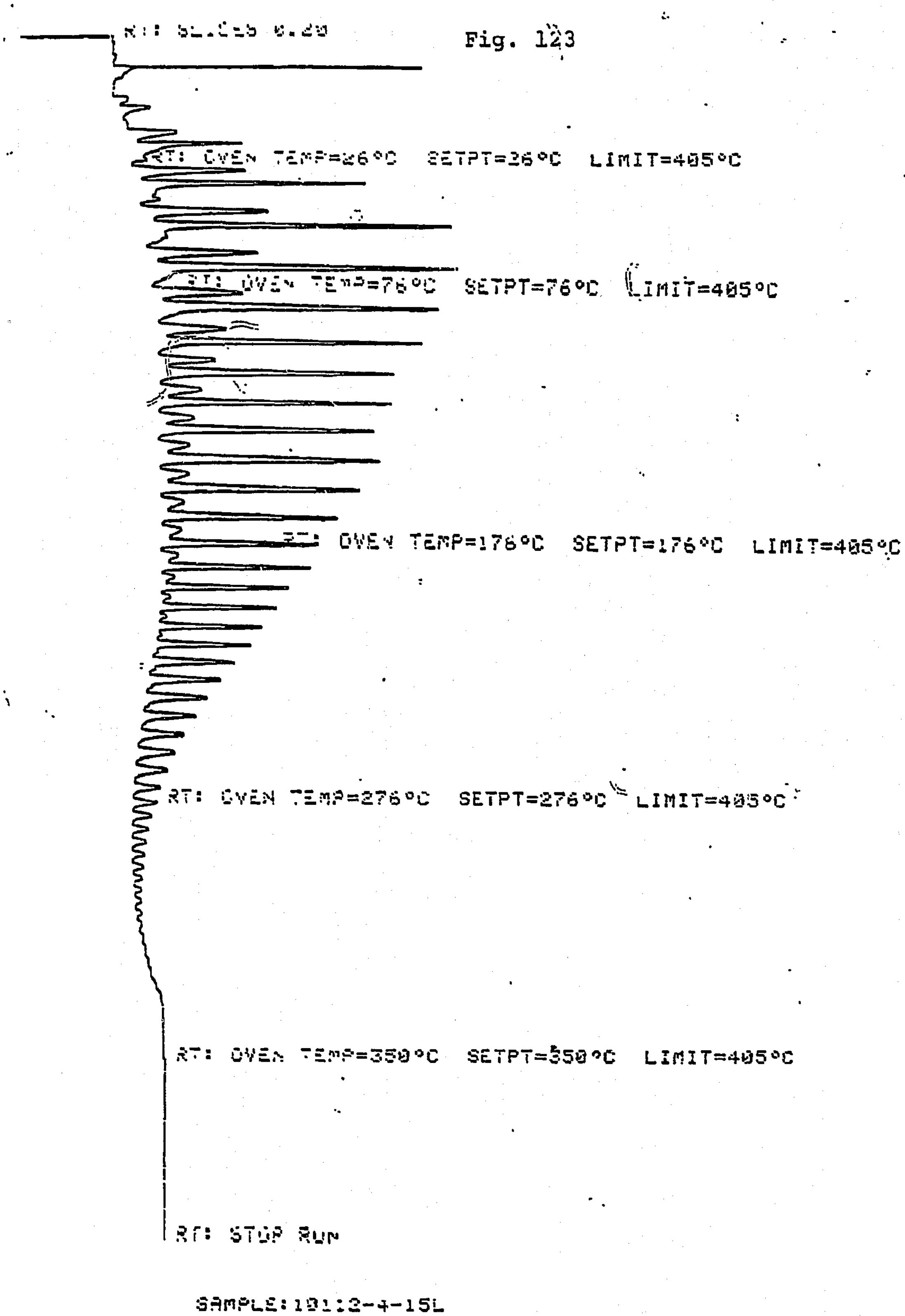
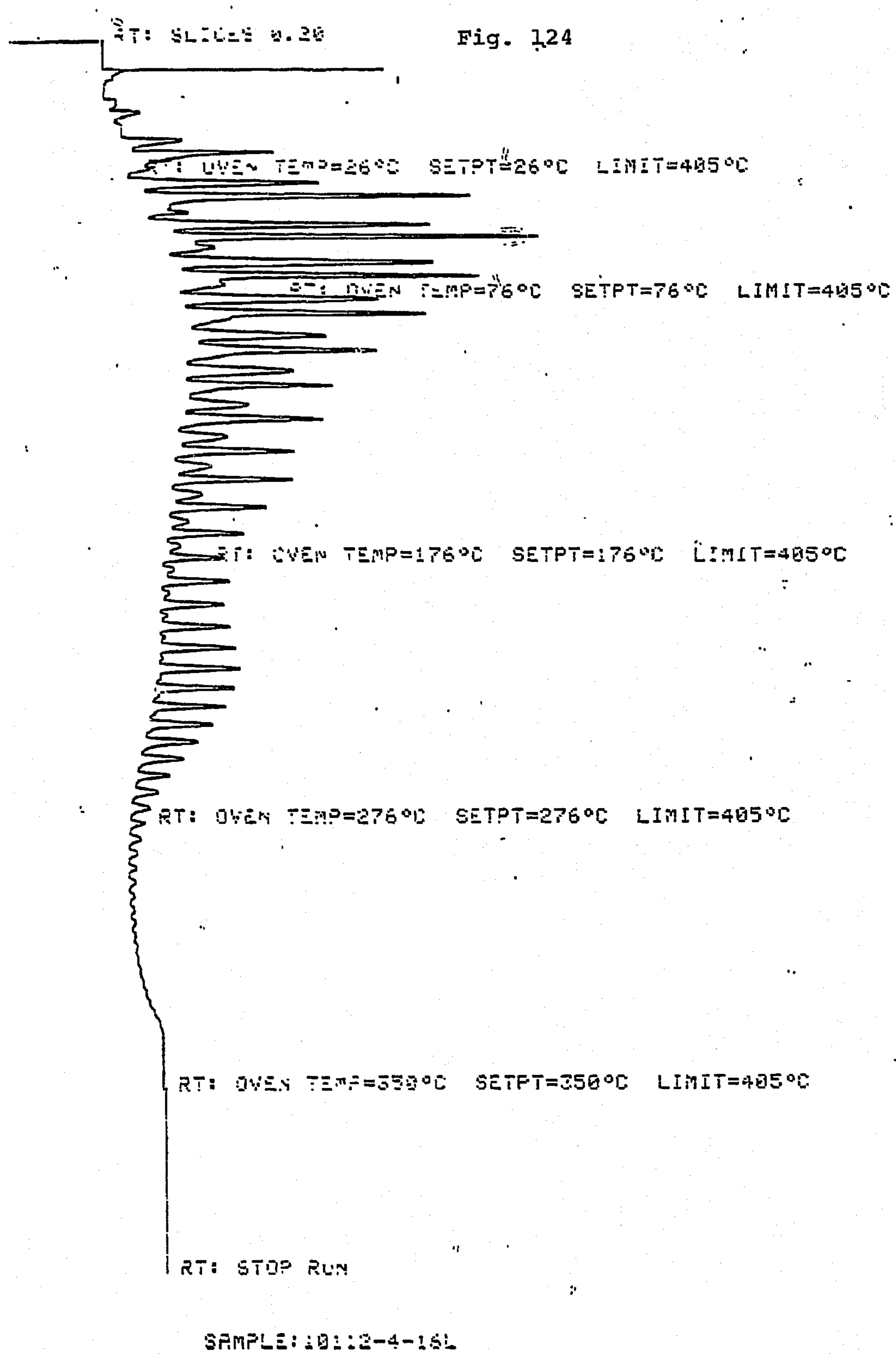

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C
RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP Run
SAMPLE:101:2-4-15L

Fig. 124



RT: SLICES 0.20
RT: OVEN TEMP=26°C SETPT=26°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:101:2-4-16L

TABLE 9A RESULT OF SYNGAS OPERATION

RUN NO. 10112-04
CATALYST COBALT-UCC-101 #10042-84 80CC 31.4GM (39.3G AFTER RUN +8.0 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-04-01	112-04-02	112-04-03	112-04-04	112-04-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	16.83	23.99	40.49	45.49	64.74
PRESSURE,PSIG	297	300	300	302	299
TEMP. C	216	220	220	219	219
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	16.83	7.50	24.00	5.00	24.25
EFFLNT GAS LITER	331.30	137.60	438.25	89.82	452.13
GM AQUEOUS LAYER	12.50	8.53	27.28	5.48	26.56
GM OIL	0.86	1.68	5.39	1.08	5.23
MATERIAL BALANCE					
GM ATOM CARBON %	89.77	89.80	90.80	88.61	89.50
GM ATOM HYDROGEN %	91.06	91.58	91.11	87.71	91.51
GM ATOM OXYGEN %	96.83	97.49	98.40	96.59	98.39
RATIO CHX/(H2O+CO2)	0.3986	0.5219	0.5281	0.4881	0.4431
RATIO X IN CHX	2.4041	2.2702	2.2801	2.2835	2.3322
USAGE H2/CO PRODT	2.0184	1.9945	1.9898	1.9808	1.9252
RATIO CO2/(H2O+CO2)	0.0224	0.0249	0.0273	0.0280	0.0436
K SHIFT IN EFFLNT	0.02	0.02	0.02	0.02	0.04
CONVERSION					
ON CO %	5.50	9.79	9.86	9.09	8.68
ON H2 %	18.76	27.53	28.15	27.20	25.69
ON CO+H2 %	12.18	18.75	18.97	18.10	17.28
PRDT SELECTIVITY,WT %					
CH4	19.16	12.80	13.02	13.31	15.66
C2 HC'S	1.79	1.40	1.44	1.44	1.48
C3H8	1.83	1.60	1.52	1.37	1.98
C3H6=	4.56	3.93	3.37	2.74	2.02
C4H10	2.23	1.84	1.70	1.68	2.02
C4H8=	5.22	3.83	3.40	3.29	2.56
C5H12	2.56	1.91	2.16	1.96	2.40
C5H10=	5.93	4.63	4.35	3.98	3.31
C6H14	2.57	2.40	2.22	2.03	2.54
C6H12= & CYCLO'S	5.70	4.06	3.67	3.62	3.14
C7+ IN GAS	33.12	23.71	25.78	24.47	19.87
LIQ HC'S	15.34	37.88	37.36	40.13	43.01

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	34.79	25.40	24.45	23.81	25.72
C5 -420 F	55.45	50.36	51.64	50.10	43.87
420-700 F	9.14	22.73	22.33	22.07	26.21
700-END PT	0.63	1.52	1.58	4.01	4.19
C5+-END PT	65.21	74.60	75.55	76.19	74.28
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0449	0.0529	0.0000	0.0000
C5	0.0000	0.0000	0.0426	0.0000	0.0000
C6	0.0598	0.1780	0.1047	0.0000	0.0000
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.3822	0.3878	0.4305	0.4762	0.3350
C4	0.4119	0.4655	0.4819	0.4920	0.7590
C5	0.4188	0.4015	0.4832	0.4798	0.7066
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLEAR OIL	---	GR-BR OIL	---	GR-BR OIL
DENSITY		---	0.766	---	0.770
N, REFRACTIVE INDEX		---	1.4319	---	1.4334
SIMULT'D DISTILATN					
10 WT % @ DEG F	345	---	339	---	343
16	372	---	372	---	381
50	464	---	475	---	511
84	582	---	607	---	659
90	624	---	650	---	699
RANGE(16-84 %)	210	---	235	---	278
WT % @ 420 F	36.33	---	36.00	---	29.30
WT % @ 700 F	95.92	---	95.78	---	90.25

TABLE 9B RESULT OF SYNGAS OPERATION

RUN NO. 10112-04
CATALYST COBALT-UCC-101 #10042-84 80CC 31.4GM (39.3G AFTER RUN +8.0 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-04-06	112-04-07	112-04-08	112-04-09	112-04-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	69.66	88.16	95.49	112.49	119.74
PRESSURE,PSIG	300	299	302	304	300
TEMP. C	219	220	253	253	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	4.92	23.42	7.33	24.33	7.25
EFFLNT GAS LITER	91.66	441.10	96.82	314.21	93.59
GM AQUEOUS LAYER	4.38	20.86	14.01	46.51	15.34
GM OIL	3.84	18.30	9.71	32.22	7.24
MATERIAL BALANCE					
GM ATOM CARBON %	97.93	99.04	104.40	100.21	93.73
GM ATOM HYDROGEN %	97.21	97.98	100.15	96.98	93.68
GM ATOM OXYGEN %	96.24	97.33	101.89	97.38	98.15
RATIO CHX/(H2O+CO2)	1.1237	1.1247	1.0725	1.0886	0.8667
RATIO X IN CHX	2.1567	2.1571	2.4217	2.3485	2.3831
USAGE H2/CO PRODT	1.9409	1.9354	1.4582	1.5410	1.5702
RATIO CO2/(H2O+CO2)	0.0513	0.0535	0.3204	0.2633	0.2207
K SHIFT IN EFFLNT	0.04	0.05	0.26	0.20	0.17
CONVERSION					
ON CO %	16.39	16.33	46.28	43.09	38.45
ON H2 %	30.35	30.26	68.52	66.38	64.11
ON CO+H2 %	23.34	23.26	57.17	54.54	51.28
PRDT SELECTIVITY,WT %					
CH4	7.27	7.27	18.41	15.35	16.80
C2 HC'S	0.79	0.87	2.76	2.25	2.56
C3H8	0.93	0.93	3.49	2.83	3.07
C3H6=	0.92	0.95	0.89	1.00	1.27
C4H10	0.95	0.94	2.85	2.29	2.45
C4H8=	1.32	1.32	1.68	1.85	2.26
C5H12	1.16	1.17	3.44	2.81	3.12
C5H10=	1.62	1.72	2.04	2.29	2.77
C6H14	1.30	1.24	3.57	3.03	3.34
C6H12= & CYCLO'S	1.47	1.51	1.72	1.95	2.31
C7+ IN GAS	9.65	9.83	9.27	10.71	11.22
LIQ HC'S	72.61	72.25	49.89	53.64	48.82

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	12.19	12.28	30.07	25.57	28.41
C5 -420 F	40.61	27.51	37.50	40.34	39.85
420-700 F	39.93	34.74	27.44	25.06	26.85
700-END PT	7.26	25.47	4.99	9.03	4.88
C5+-END PT	87.81	87.72	69.93	74.43	71.59
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0000	0.0432	0.0406	0.0401
C5	0.0000	0.0000	0.0784	0.0675	0.0657
C6	0.0854	0.0000	0.2313	0.2247	0.2234
C4=	0.0369	0.0000	0.0725	0.0595	0.0560
PARAFFIN/OLEFIN RATIO					
C3	0.9618	0.9379	3.7512	2.6949	2.3003
C4	0.6944	0.6866	1.6335	1.1940	1.0492
C5	0.6949	0.6600	1.6397	1.1920	1.0924
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	WHITE SLD	---	WHITE SLD	---
DENSITY	---		---		---
N, REFRACTIVE INDEX	---		---		---
SIMULT'D DISTILATN					
10 WT % @ DEG F	---	395	---	298	---
16	---	418	---	332	---
50	---	596	---	494	---
84	---	908	---	710	---
90	---	1015	---	768	---
RANGE(16-84 %)	---	490	---	378	---
WT % @ 420 F	---	16.66	---	36.44	---
WT % @ 700 F	---	64.75	---	83.17	---

TABLE 9C RESULT OF SYNGAS OPERATION

RUN NO. 10112-04
CATALYST COBALT-UCC-101 #10042-84 80CC 31.4GM (39.3G AFTER RUN +8.0 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-04-11	112-04-12	112-04-13	112-04-14	112-04-15
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	136.32	143.90	160.40	167.57	184.49
PRESSURE,PSIG	302	300	301	302	302
TEMP. C	252	252	252	251	284
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	23.83	7.58	24.08	7.17	24.08
EFFLNT GAS LITER	309.67	99.55	320.07	94.79	272.47
GM AQUEOUS LAYER	50.42	16.18	51.41	12.13	40.74
GM OIL	23.79	9.53	30.27	10.02	33.68
MATERIAL BALANCE					
GM ATOM CARBON %	94.38	99.43	99.87	100.64	119.69
GM ATOM HYDROGEN %	93.80	98.45	99.01	94.70	116.05
GM ATOM OXYGEN %	98.34	99.24	99.36	93.73	107.43
RATIO CHX/(H2O+CO2)	0.8791	1.0057	1.0157	1.2565	1.2434
RATIO X IN CHX	2.3720	2.3238	2.3130	2.2868	2.7031
USAGE H2/CO PRODT	1.5926	1.6257	1.6508	1.6532	1.2256
RATIO CO2/(H2O+CO2)	0.2107	0.2050	0.1928	0.2154	0.5867
K SHIFT IN EFFLNT	0.15	0.15	0.14	0.16	0.55
CONVERSION					
ON CO %	37.80	39.93	39.13	39.35	76.96
ON H2 %	63.94	65.41	64.73	63.11	90.81
ON CO+H2 %	50.83	52.61	51.87	50.87	83.78
PRDT SELECTIVITY,WT %					
CH4	16.43	14.20	13.82	12.72	32.05
C2 HC'S	2.36	2.07	1.93	1.79	4.13
C3H8	2.95	2.65	2.53	2.29	4.86
C3H6=	1.27	1.31	1.31	1.24	1.75
C4H10	2.35	2.15	2.05	1.87	3.12
C4H8=	2.29	2.20	2.23	2.10	2.98
C5H12	2.96	2.82	2.62	2.36	3.31
C5H10=	2.85	2.63	2.66	2.43	2.63
C6H14	3.29	3.02	2.90	2.53	3.55
C6H12= & CYCLO'S	2.39	2.36	2.40	2.21	2.10
C7+ IN GAS	12.09	10.80	11.51	9.99	8.82
LIQ HC'S	48.78	53.78	54.04	58.47	30.70

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	27.65	24.58	23.88	22.01	48.89
C5 -420 F	42.40	40.46	42.69	39.98	31.29
420-700 F	23.83	29.58	26.18	32.16	13.03
700-END PT	6.12	5.38	7.25	5.85	6.79
C5+-END PT	72.35	75.42	76.12	77.99	51.11
ISO/NORMAL MOLE RATIO					
C4	0.0319	0.0358	0.0374	0.0364	0.1202
C5	0.0634	0.0794	0.0829	0.0797	0.3455
C6	0.2234	0.2338	0.2108	0.1993	0.8357
C4=	0.0541	0.0493	0.0450	0.0427	0.0714
PARAFFIN/OLEFIN RATIO					
C3	2.2156	1.9307	1.8464	1.7649	2.6530
C4	0.9925	0.9455	0.8866	0.8568	1.0107
C5	1.0107	1.0425	0.9578	0.9434	1.2208
LIQ HC COLLECTION					
PHYS. APPEARANCE	WHITE OIL	---	WHITE OIL	---	GREEN OIL
DENSITY	0.774	---	0.763	---	0.767
N, REFRACTIVE INDEX	1.4302	---	1.4305	---	1.4330
SIMULT'D DISTILATN					
10 WT % @ DEG F	297	---	297	---	279
16	328	---	329	---	315
50	476	---	477	---	511
84	671	---	678	---	750
90	727	---	733	---	809
RANGE(16-84 %)	343	---	349	---	435
WT % @ 420 F	38.60	---	38.13	---	35.44
WT % @ 700 F	87.46	---	86.58	---	77.89

TABLE 9D RESULT OF SYNGAS OPERATION

RUN NO. 10112-04
CATALYST COBALT-UCC-101 #10042-84 80CC 31.4GM (39.3G AFTER RUN +8.0G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-04-16
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	191.07
PRESSURE,PSIG	301
TEMP. C	284
FEED CC/MIN	400
HOURS FEEDING	6.58
EFFLNT GAS LITER	67.67
GM AQUEOUS LAYER	11.67
GM OIL	6.08
MATERIAL BALANCE	
GM ATOM CARBON %	102.29
GM ATOM HYDROGEN %	101.11
GM ATOM OXYGEN %	98.49
RATIO CHX/(H2O+CO2)	1.0819
RATIO X IN CHX	2.7628
USAGE H2/CO PRODT	1.2443
RATIO CO2/(H2O+CO2)	0.5344
K SHIFT IN EFFLNT	0.43
CONVERSION	
ON CO %	73.19
ON H2 %	89.79
ON CO+H2 %	81.44
PRDT SELECTIVITY,WT %	
CH4	34.98
C2 HC'S	4.42
C3H8	4.89
C3H6=	2.13
C4H10	3.06
C4H8=	3.58
C5H12	3.31
C5H10=	3.06
C6H14	3.70
C6H12= & CYCLO'S	2.50
C7+ IN GAS	9.14
LIQ HC'S	25.24

p

TOTAL	100.00
SUB-GROUPING	
C1 -C4	53.07
C5 -420 F	33.30
420-700 F	9.41
700-END PT	4.22
C5+-END PT	46.93
ISO/NORMAL MOLE RATIO	
C4	0.1233
C5	0.3264
C6	0.8412
C4=	0.0677
PARAFFIN/OLEFIN RATIO	
C3	2.1902
C4	0.8246
C5	1.0501
LIQ HC COLLECTION	
PHYS. APPEARANCE	GREEN OIL
DENSITY	0.763
N, REFRACTIVE INDEX	1.4425
SIMULT'D DISTILATN	
10 WT % @ DEG F	261
16	296
50	441
84	708
90	765
RANGE(16-84 %)	412
WT % @ 420 F	46.00
WT % @ 700 F	83.27

XI. RUN 10112-7, Co/Th on UCC-101

The same lot of metal-loaded Molecular Sieve used to prepare the 20 percent cobalt-on-UCC-101 catalyst (Run 10112-4) was impregnated with thorium to give 1 percent thorium, equivalent to 5 percent thorium on a cobalt basis. The promoted powder was dried, formed into pellets, and calcined at 250C.

Conversion, product selectivity, isomerization of the pentane, and percent olefins in the C_4's are presented in Figs. 125-128. Carbon number product distributions are given in Figs. 133-144. Simulated distillations of representative samples are shown in Figs. 129-132. Chromatograms of the simulated distillations are illustrated in Figs. 145-156. Material balances are detailed in Tables 10A-10E.

The activity and selectivity of this catalyst differ very little from those of its unpromoted form (Run 10112-4). The addition of thorium lowered its activity slightly, but the products are almost identical (Fig. 133). The pentane+ products from the two catalysts may be slightly different. The pentane is no more isomerized, but the liquid product may be a little more so, which could be due to the absence of the preliminary, possibly debilitating period when the unpromoted catalyst was run at 220C.

Thorium had little effect on this catalyst at this level of promotion.

Fig. 125

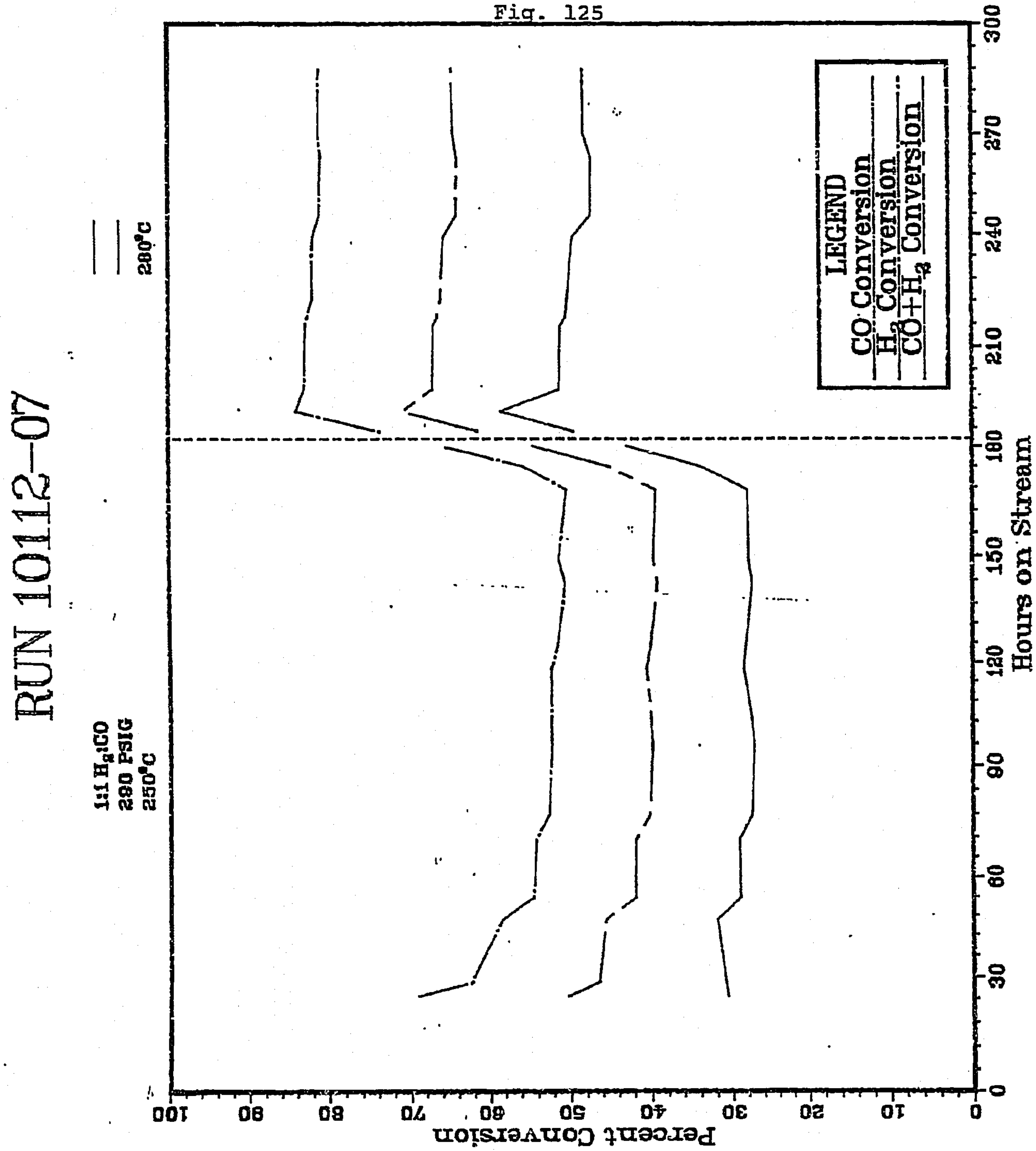

RUN 10112-07
1:1 H_2:CO
290 PSIG
250°C
280°C
LEGEND
CO Conversion
H_2 Conversion
CO+H_2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
300

Fig. 126

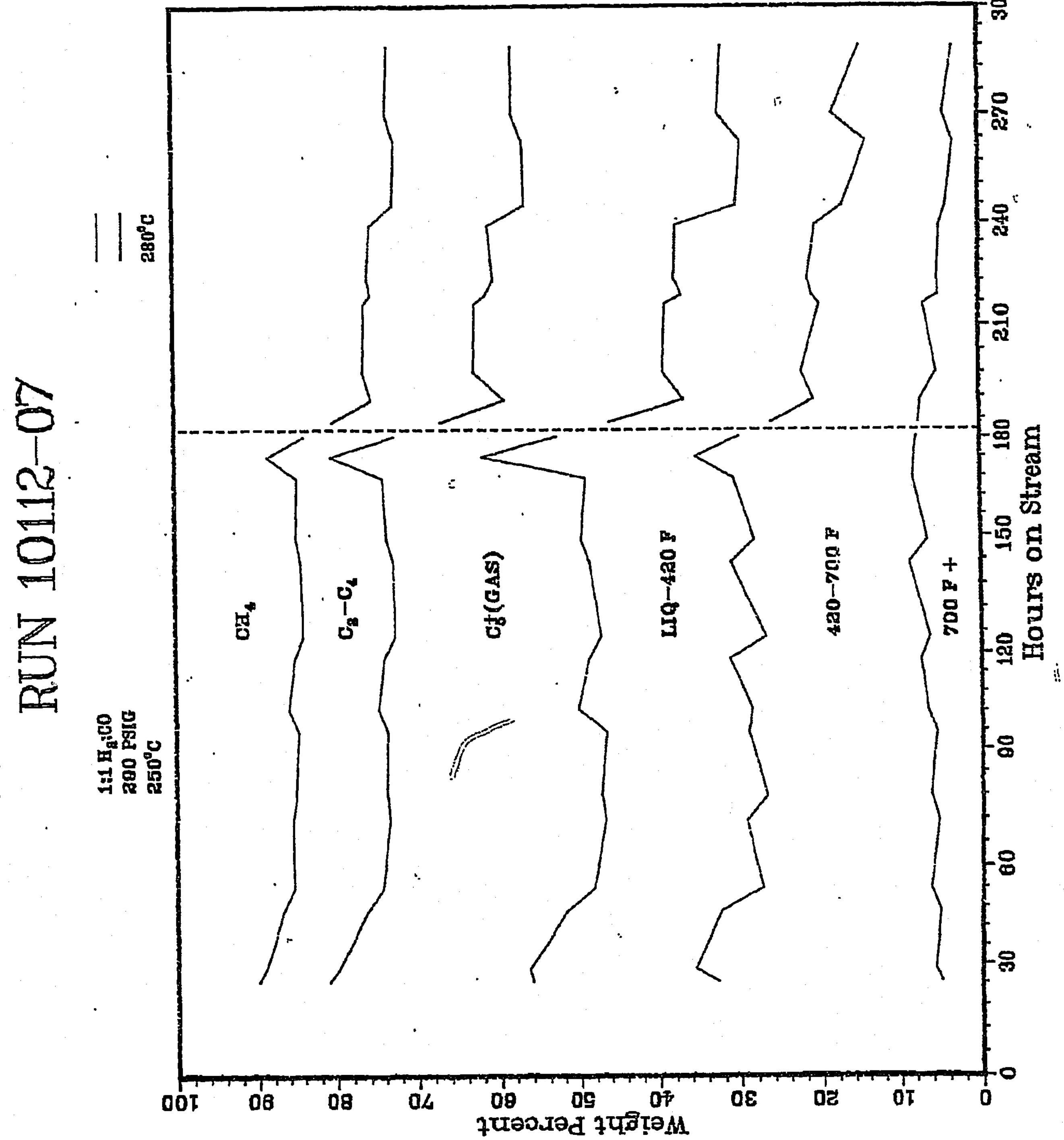

RUN 10112-07
1:1 H_2:CO
290 PSIG
250°C
280°C
CH_4
C_2-C_4
C_5^+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
0
30
60
90
120
150
180
210
240
270
300
Weight Percent
0
10
20
30
40
50
60
70
80
90
100

Fig. 127

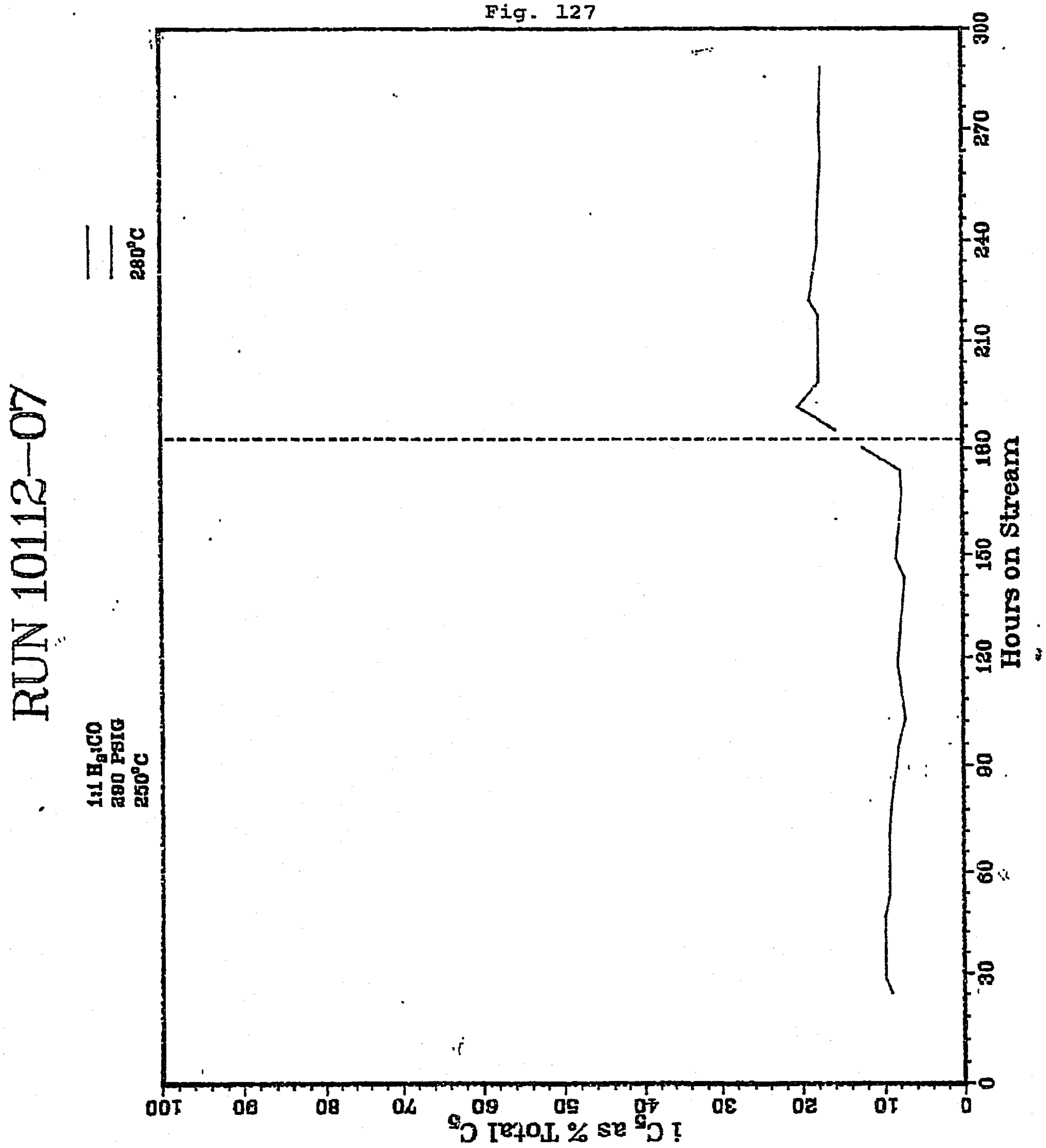
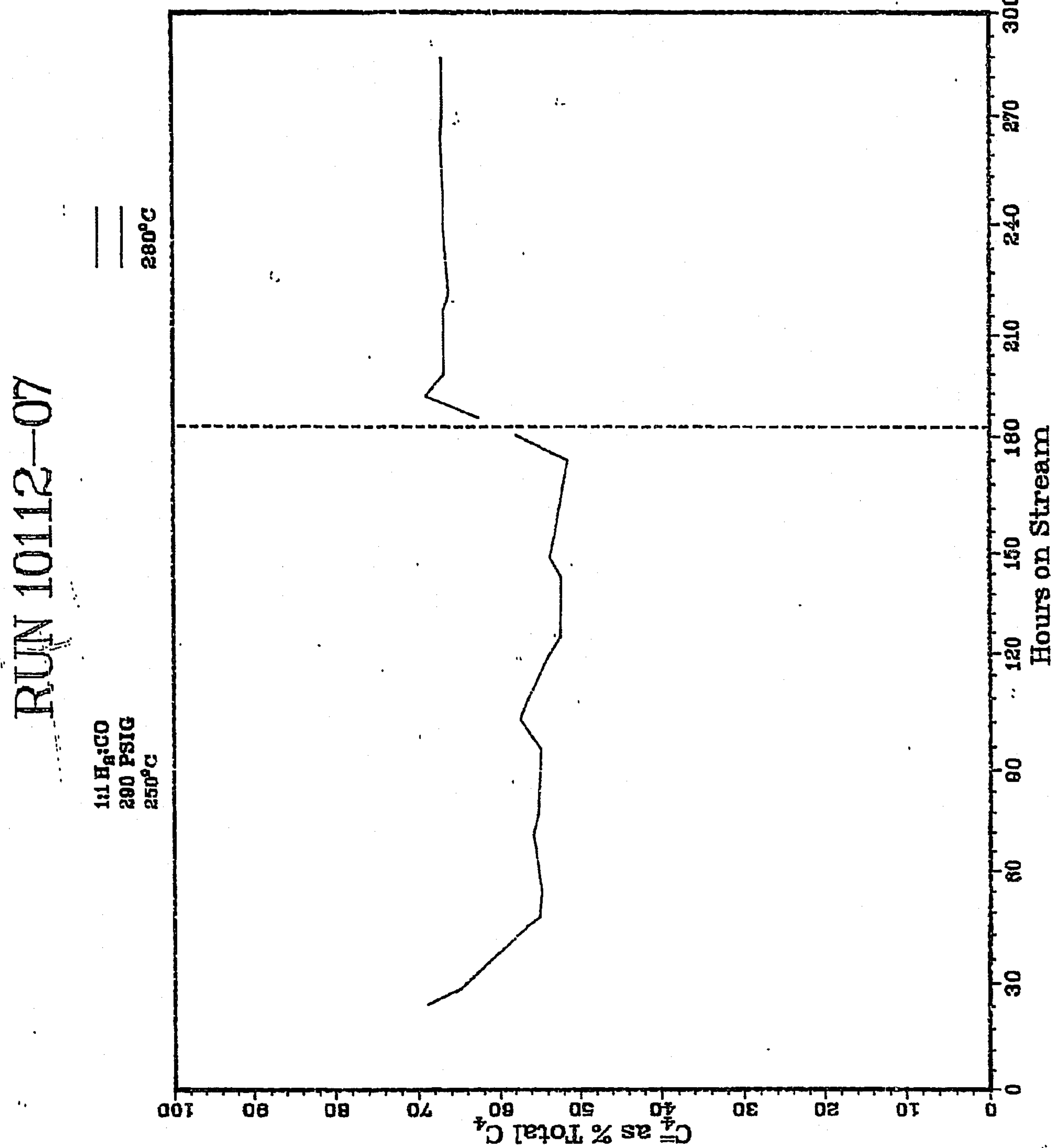
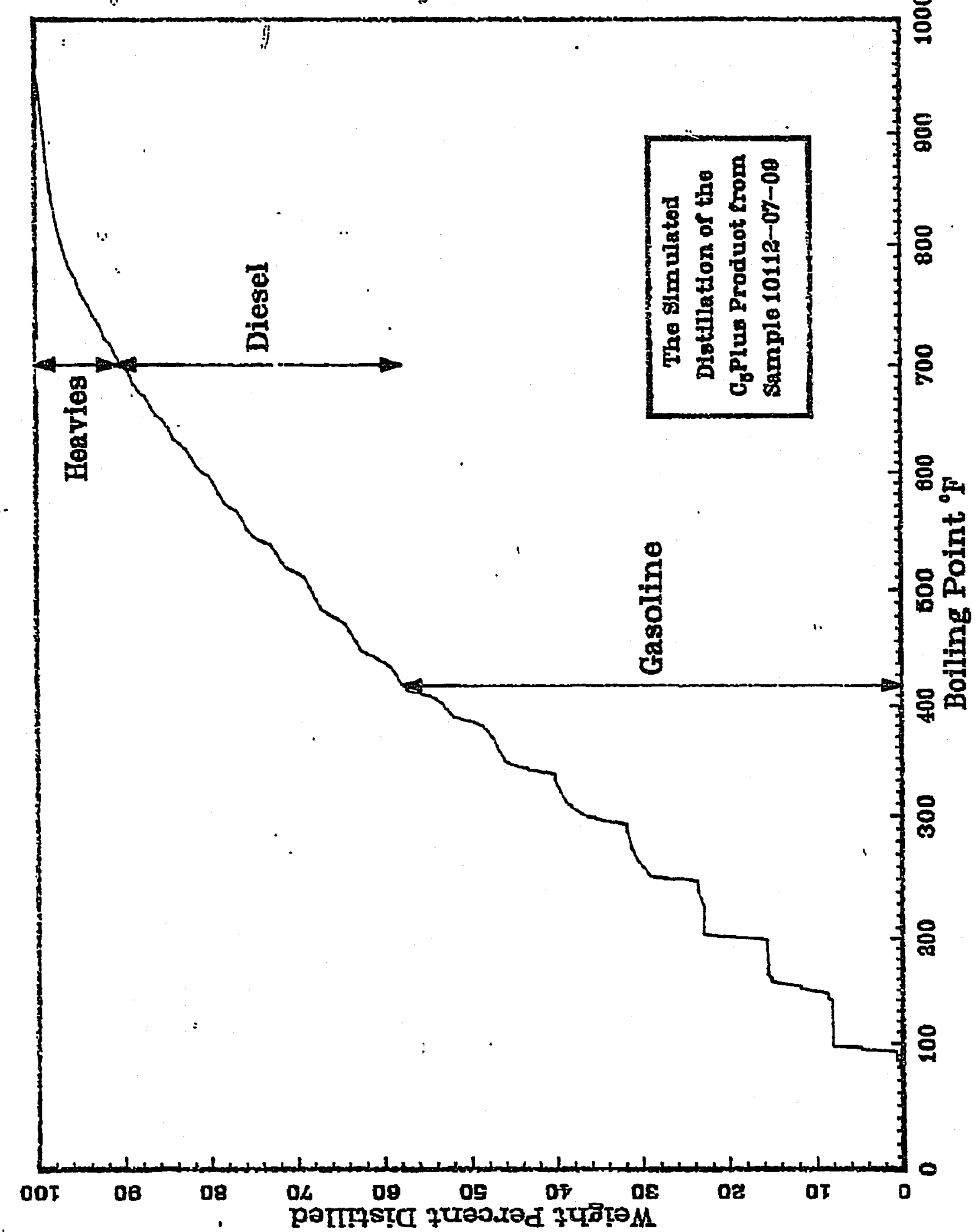

RUN 10112-07
1:1 H2:CO
390 PSIG
250°C
280°C
Hours on Stream
i C5 as % Total C5

Fig. 128



RUN 10112-07
1:1 H2:CO
290 PSIG
250°C
280°C
Hours on Stream
C4= as % Total C4

Fig. 129



Heavies
Diesel
Gasoline
The Simulated Distillation of the C_5Plus Product from Sample 10112-07-09
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 130

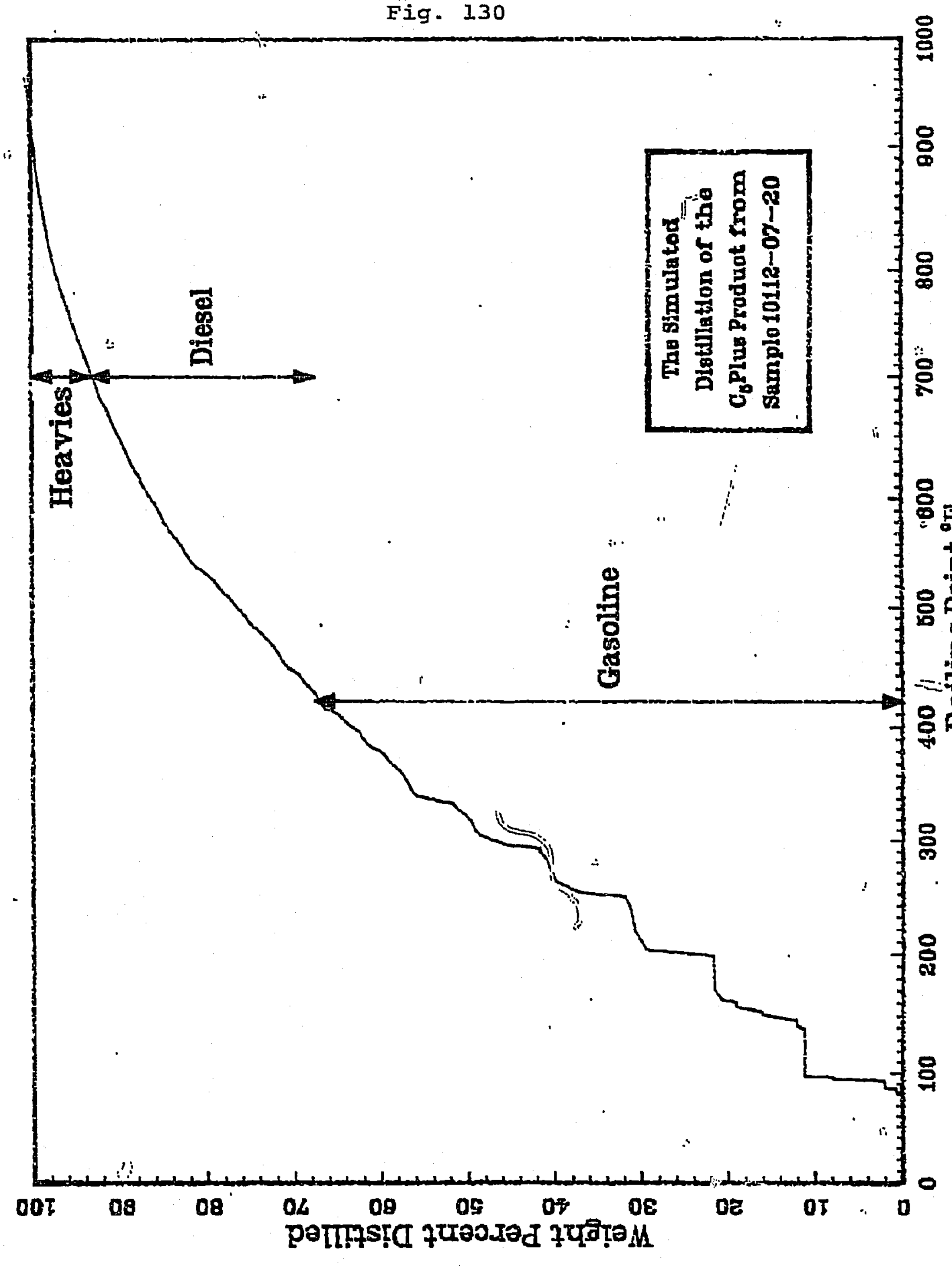

The Simulated
Distillation of the
C_5Plus Product from
Sample 10112-07-20
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 131

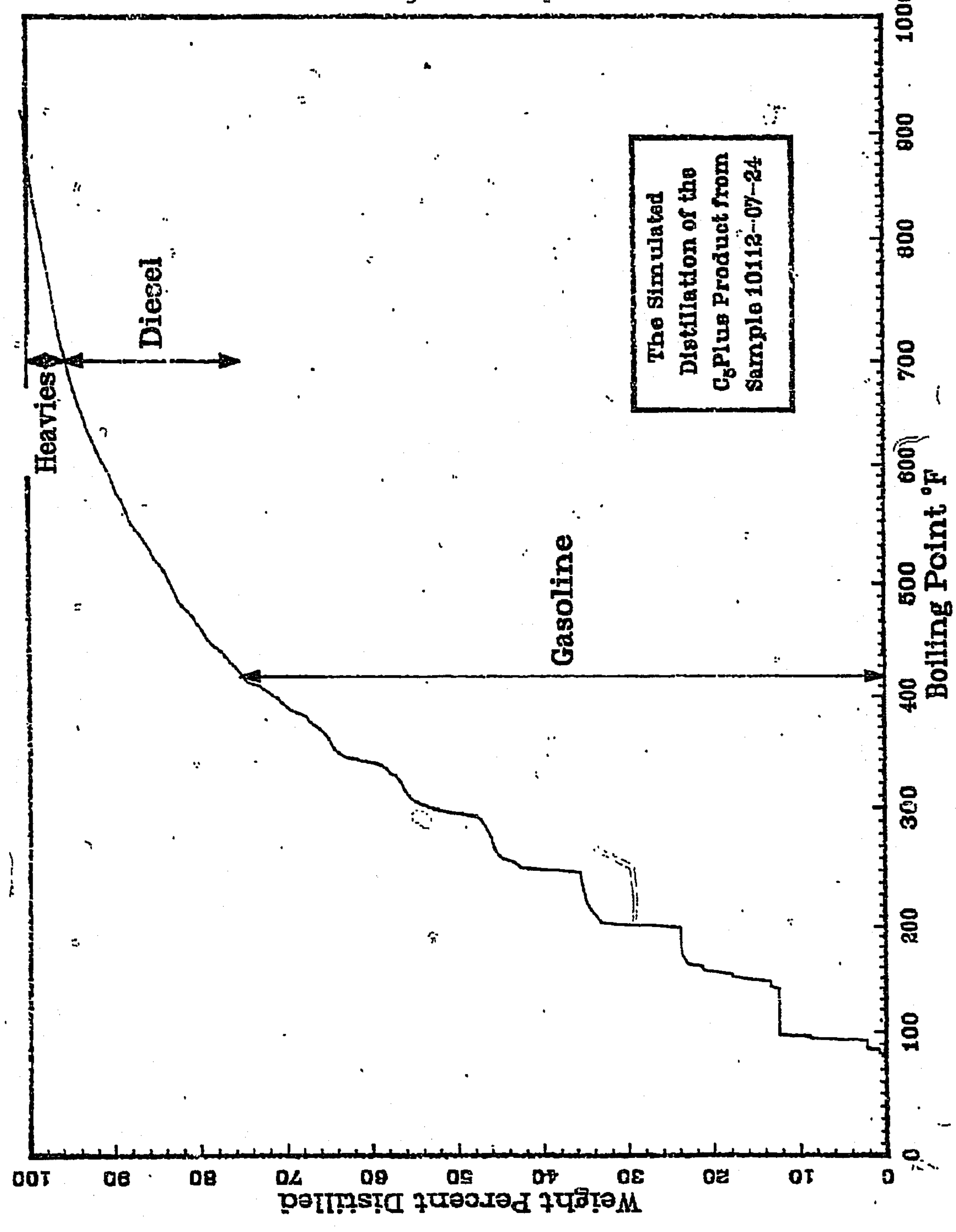

The Simulated
Distillation of the
C_5Plus Product from
Sample 10112-07-24
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 132

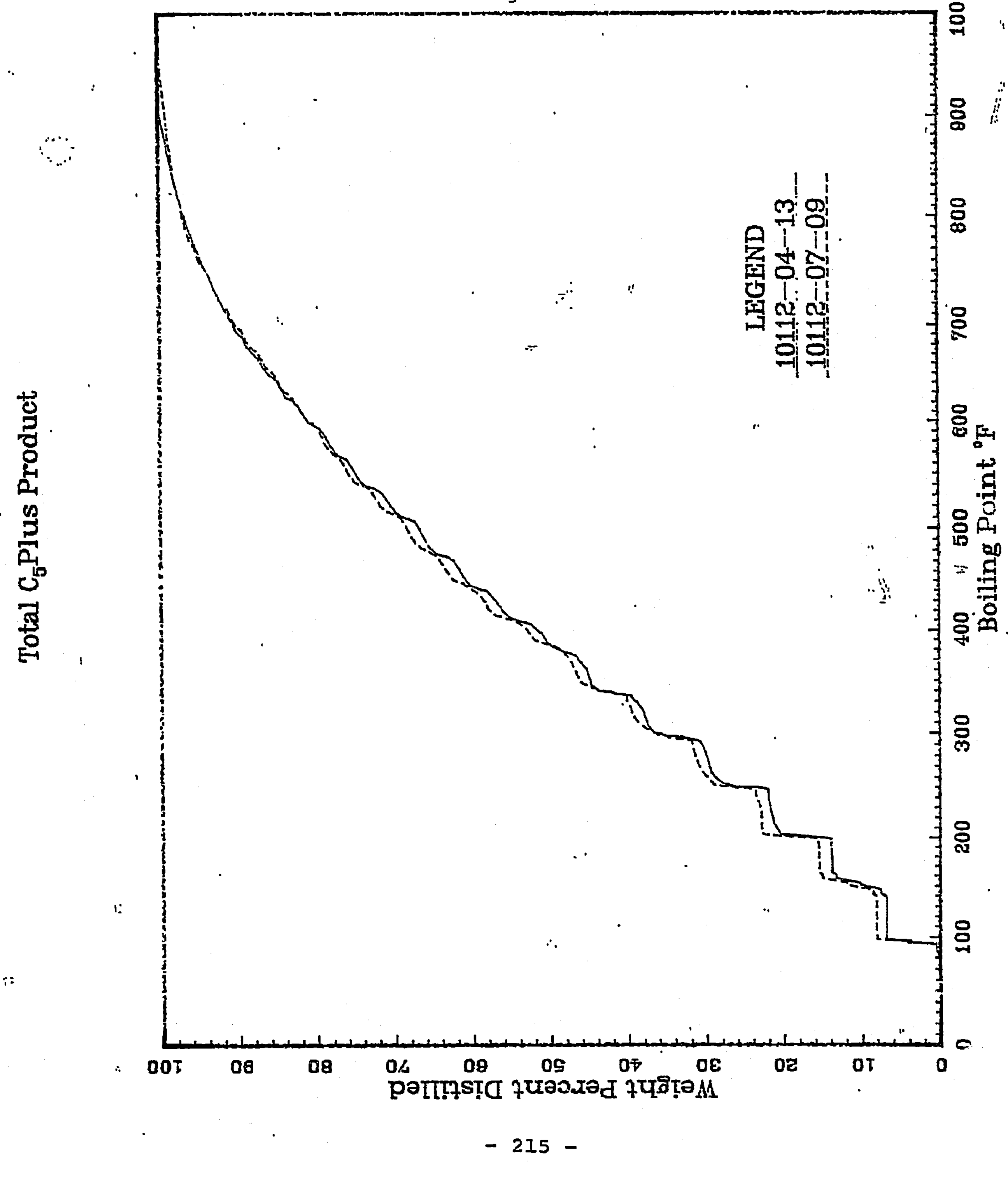

Total C_5Plus Product
LEGEND
10112--04--13
10112--07--09
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 133

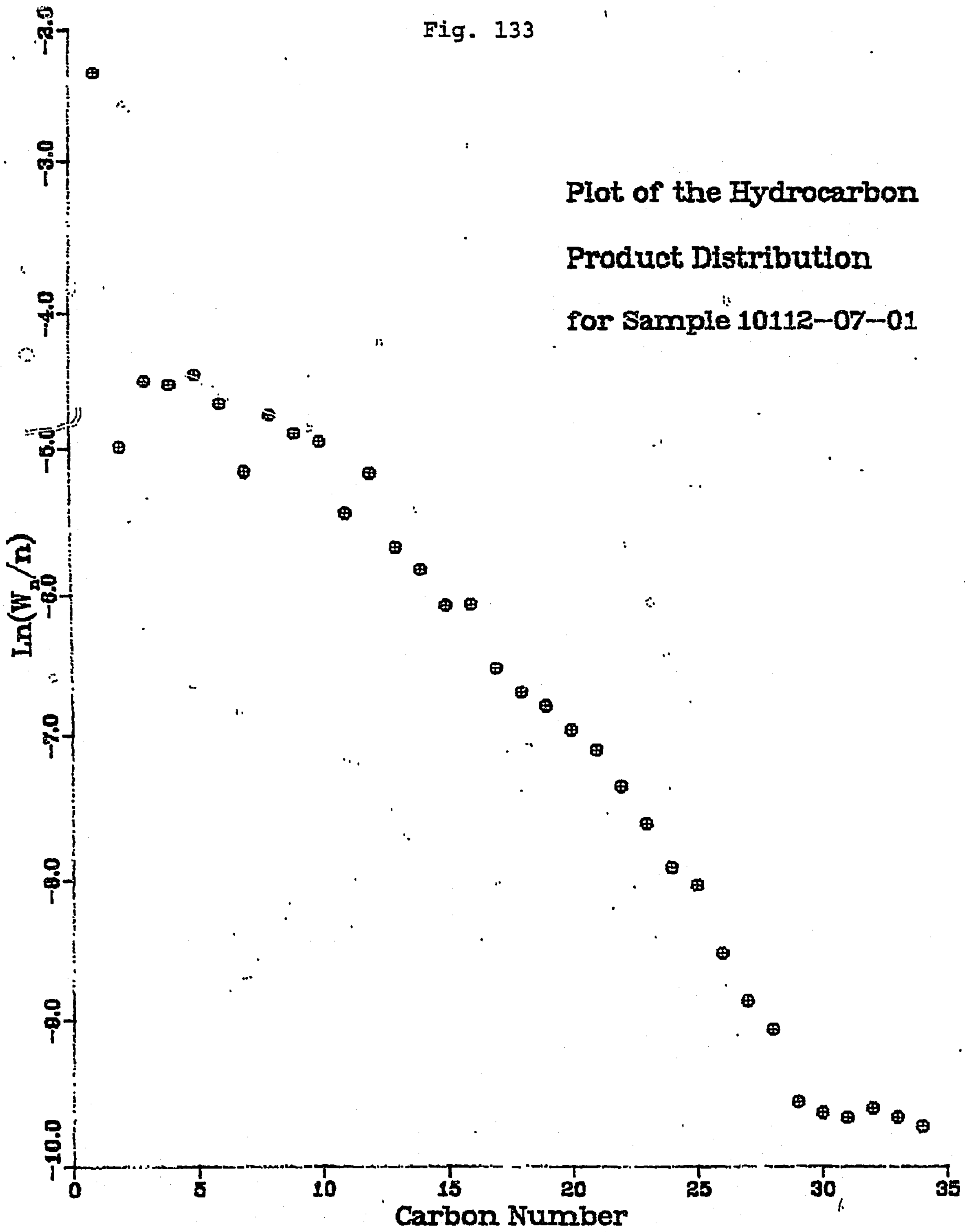

Plot of the Hydrocarbon
Product Distribution
for Sample 10112--07--01
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 134

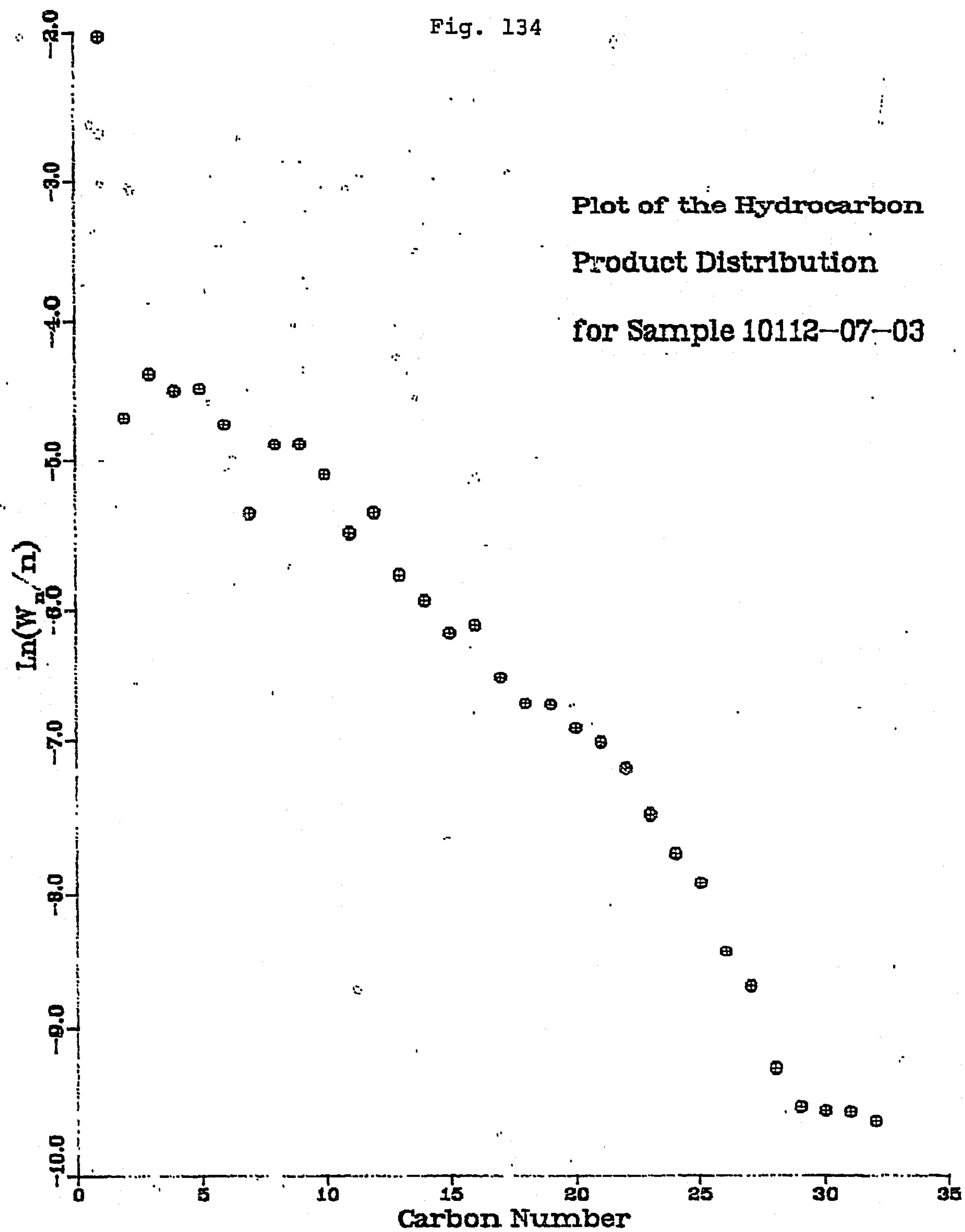

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–07–03
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 135

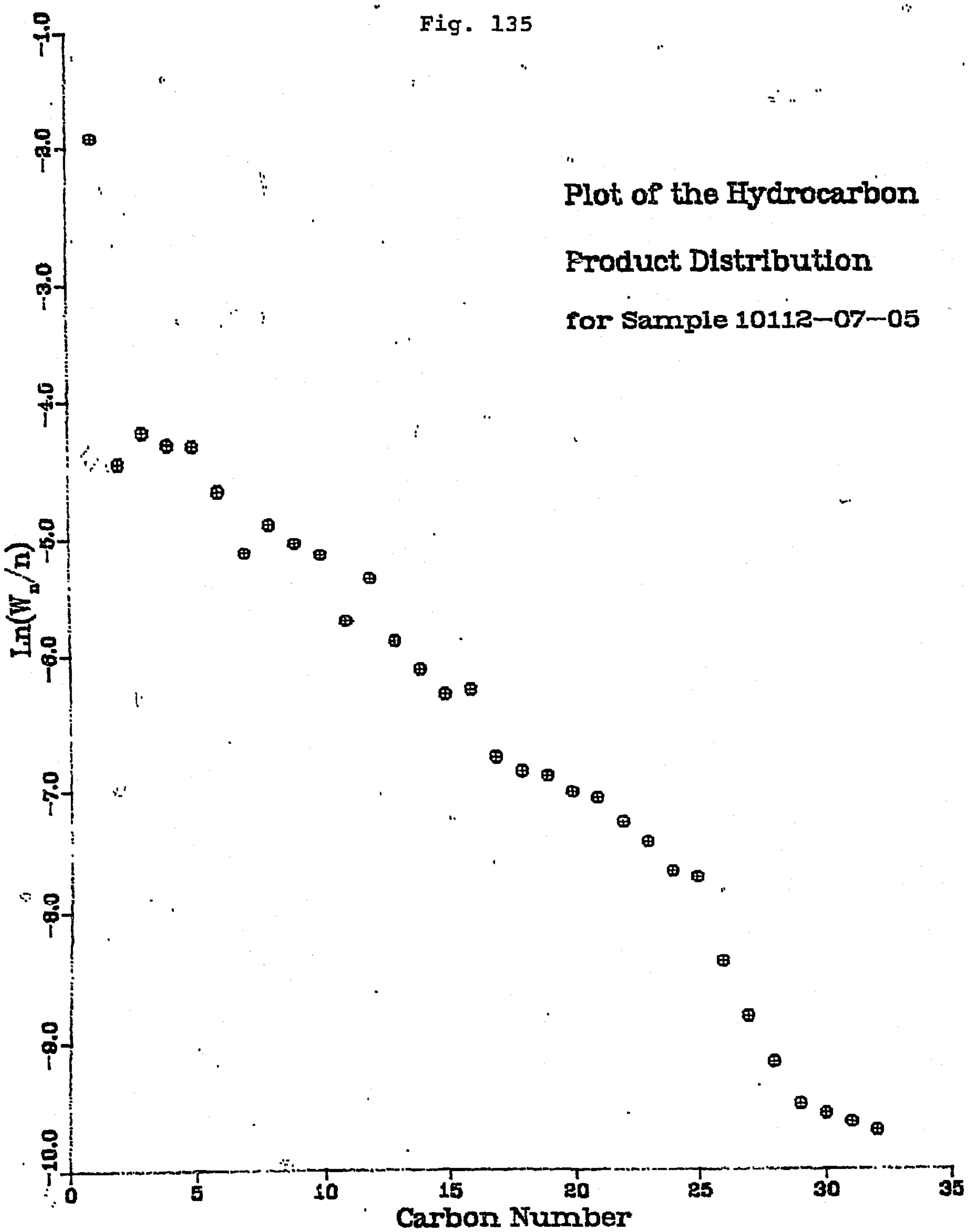

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 136

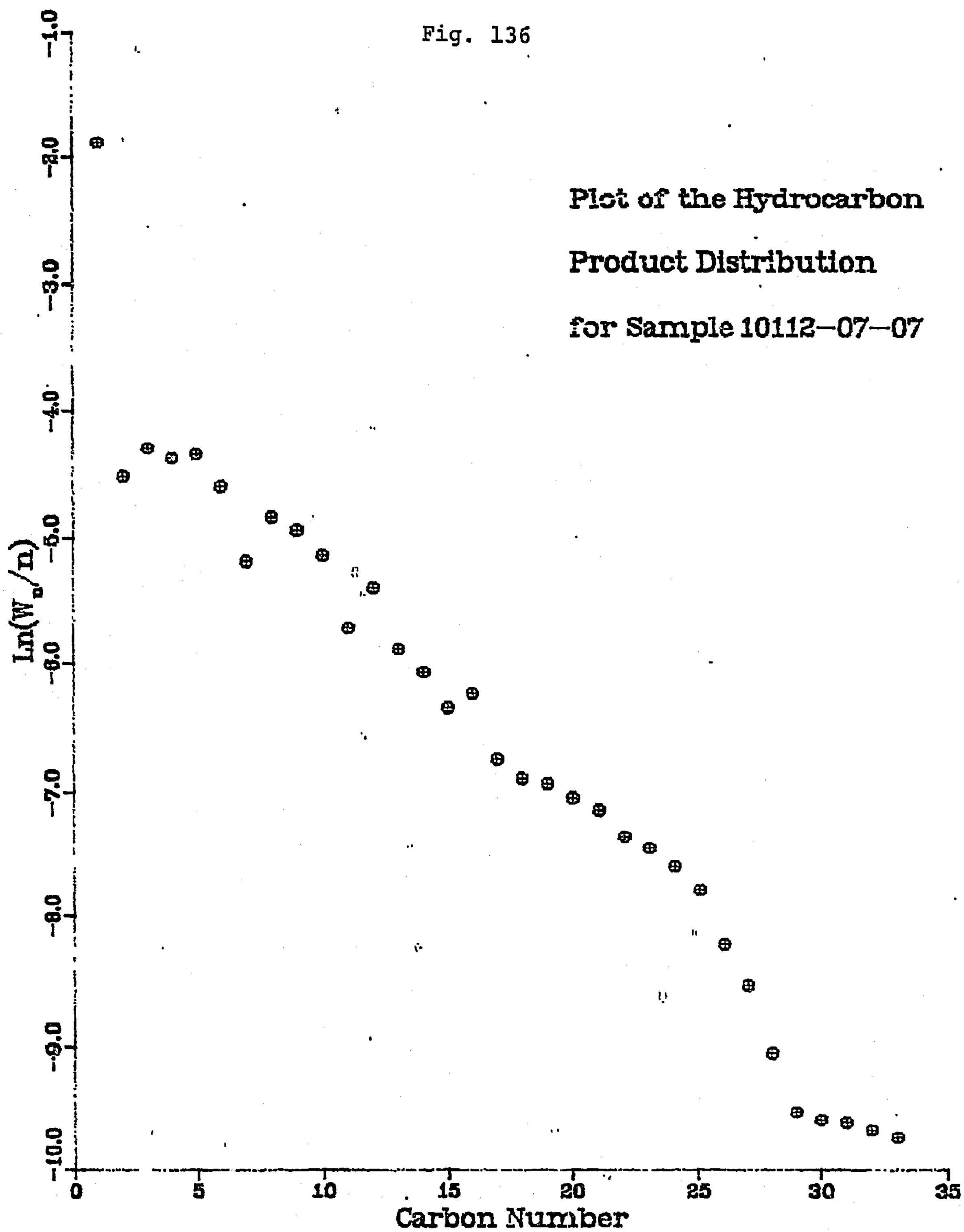

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 137

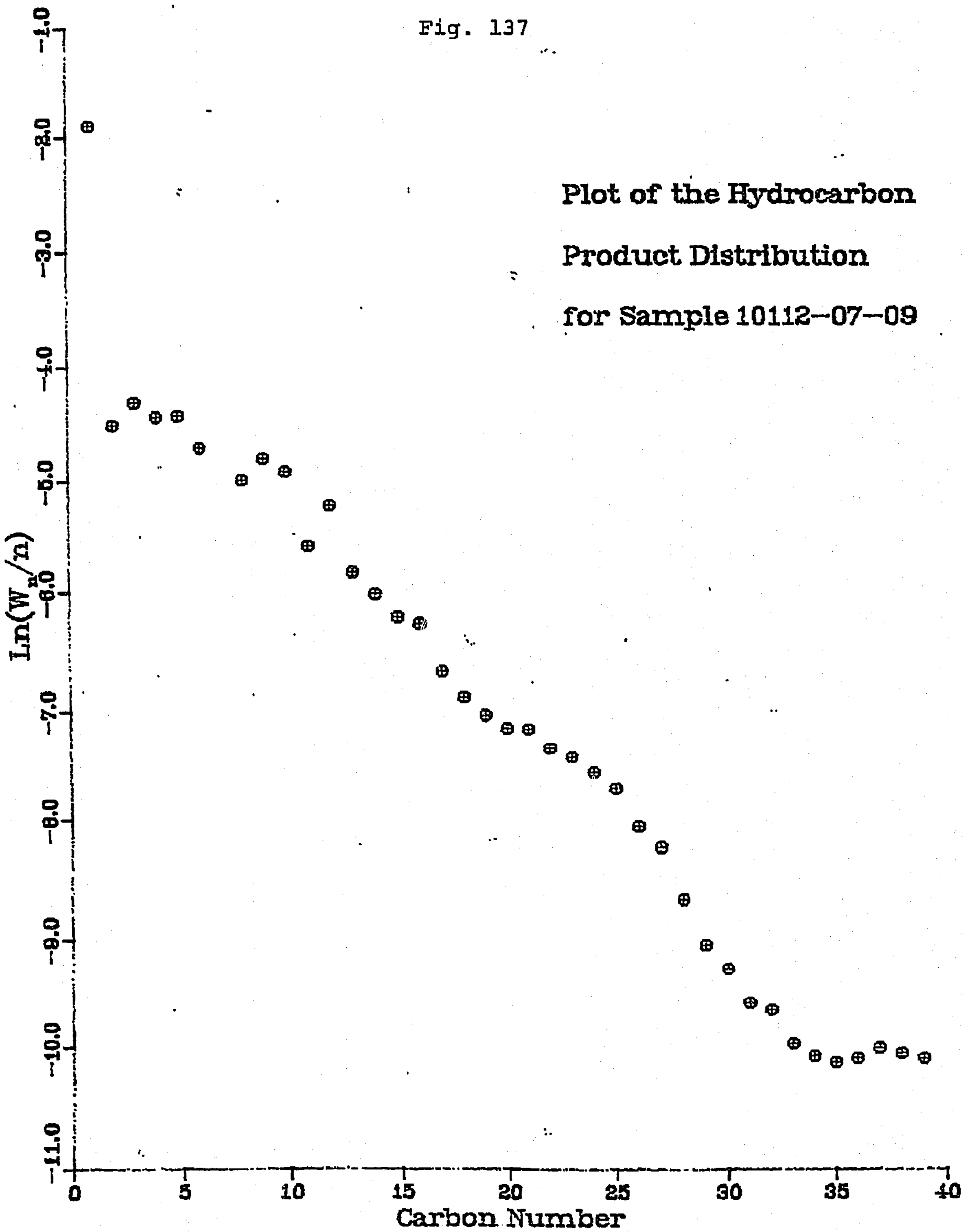

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 138

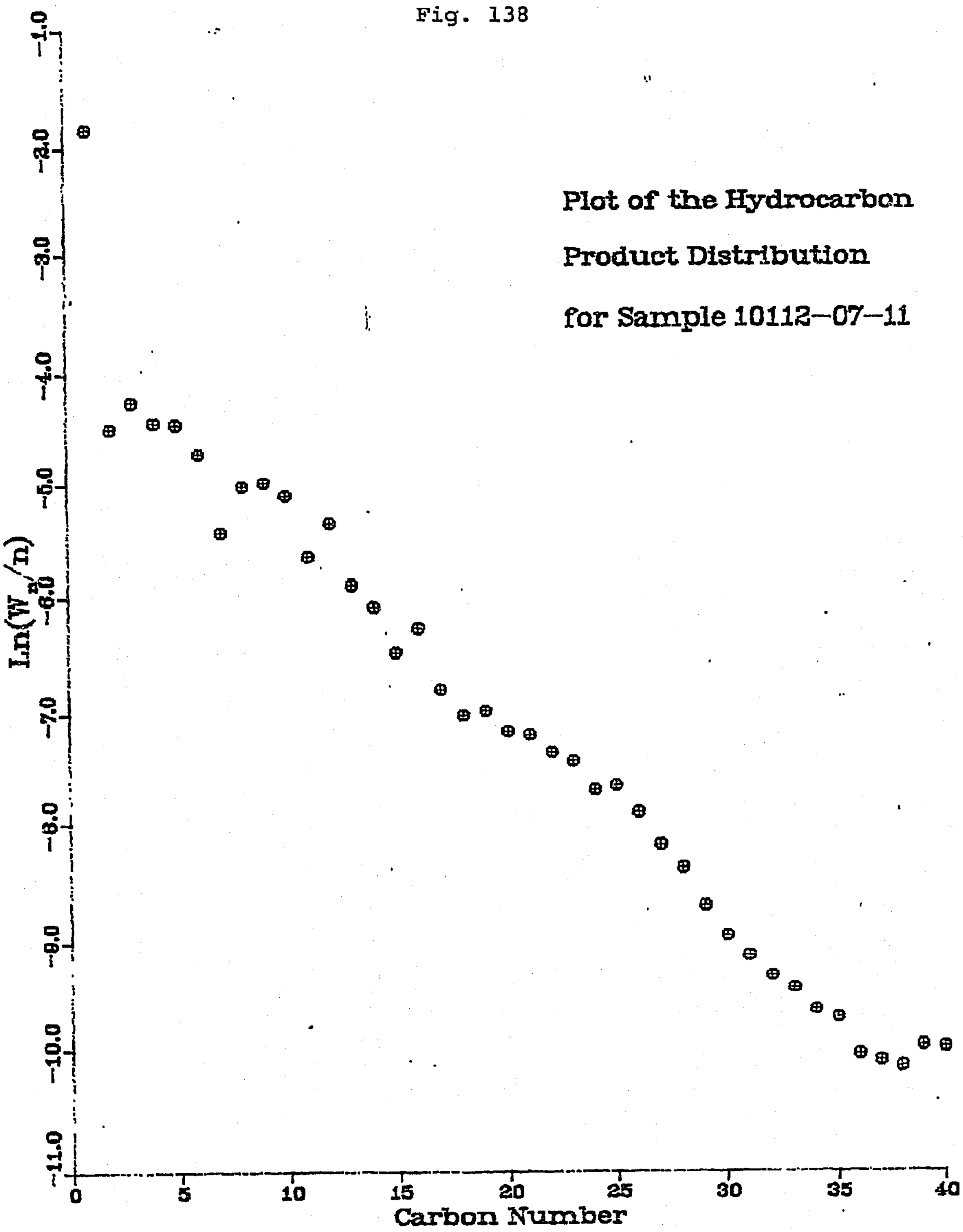

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 139

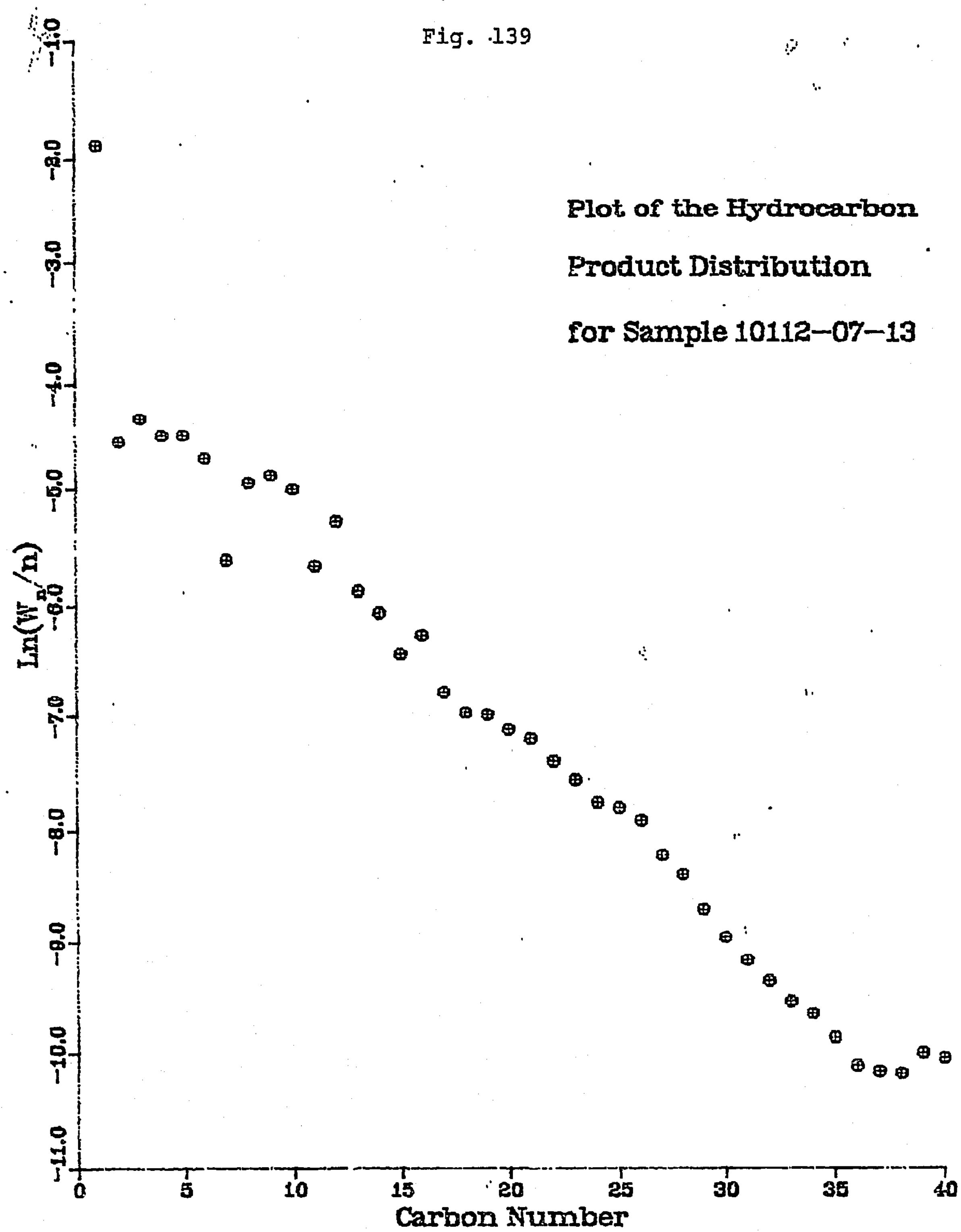

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 140

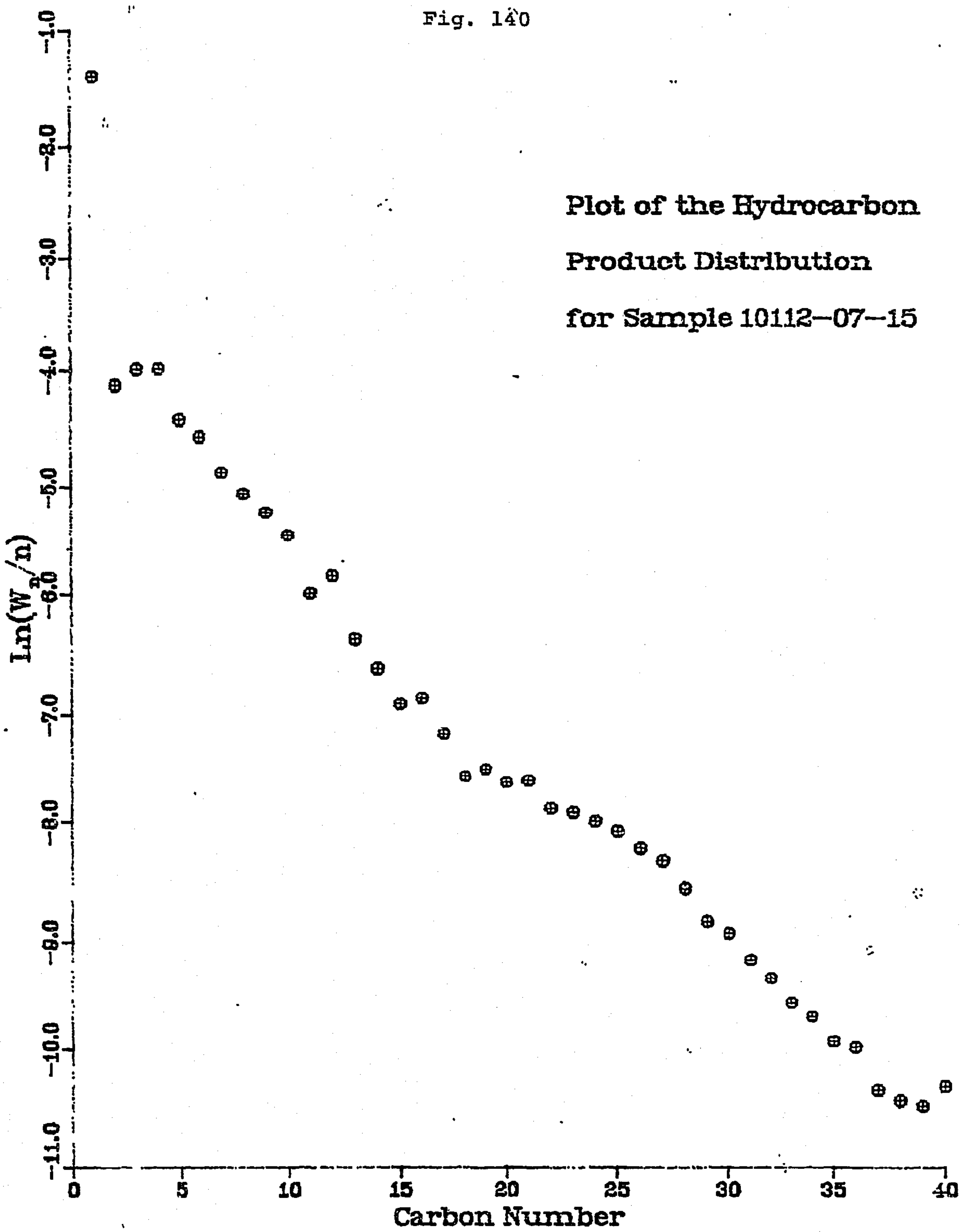

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–07–15
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 141

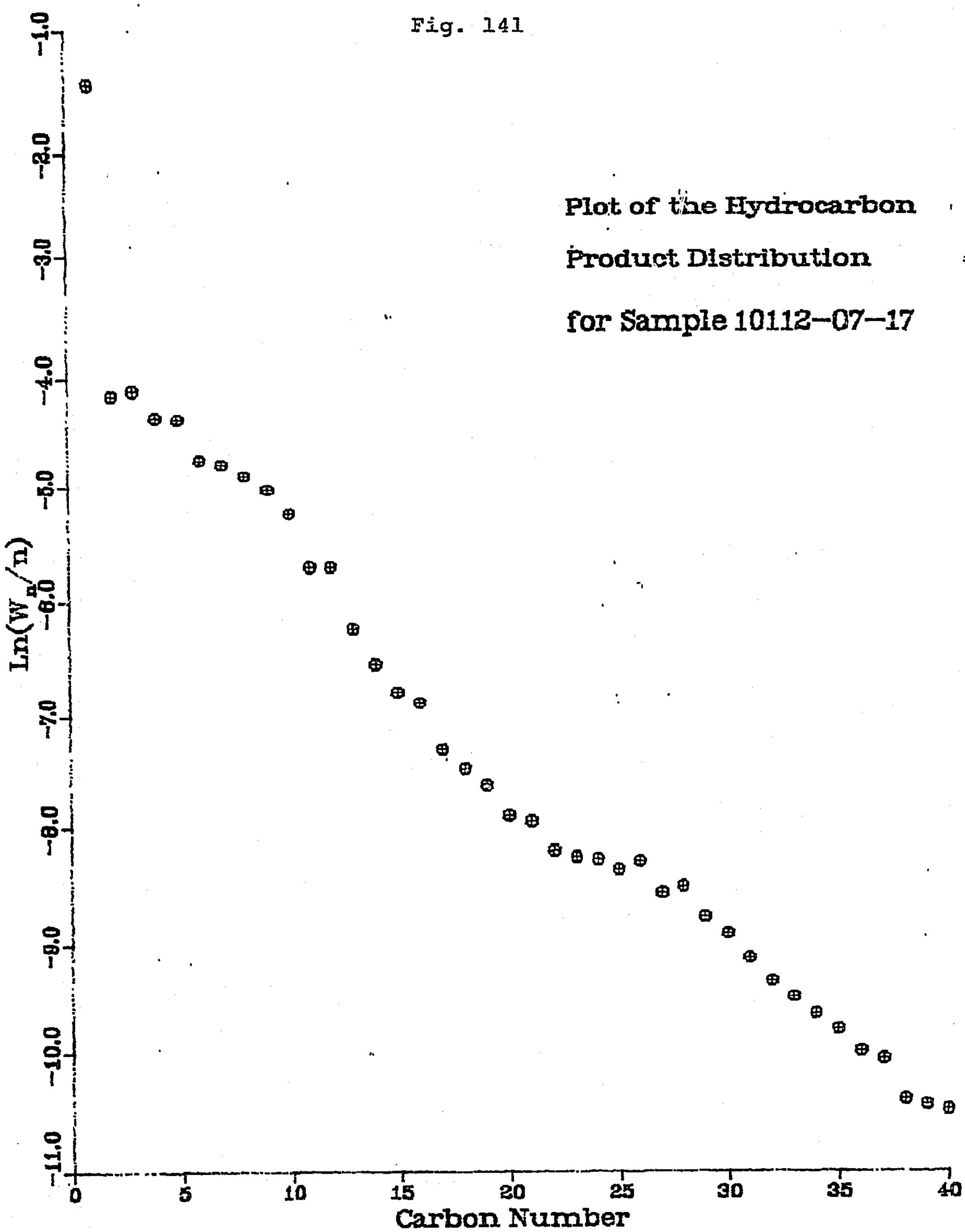
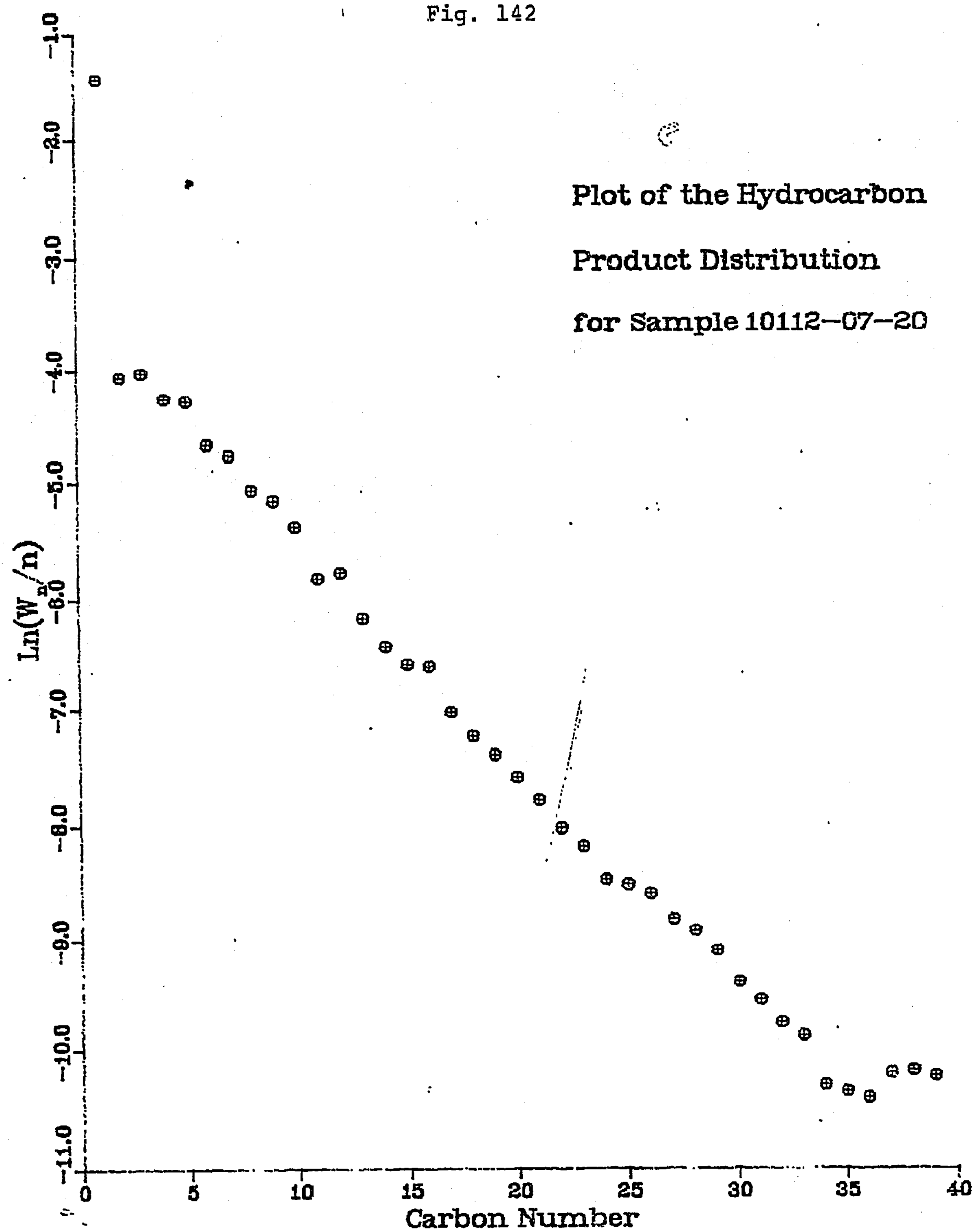

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-17
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 142



Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-20
$Ln(W_n/n)$
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 143

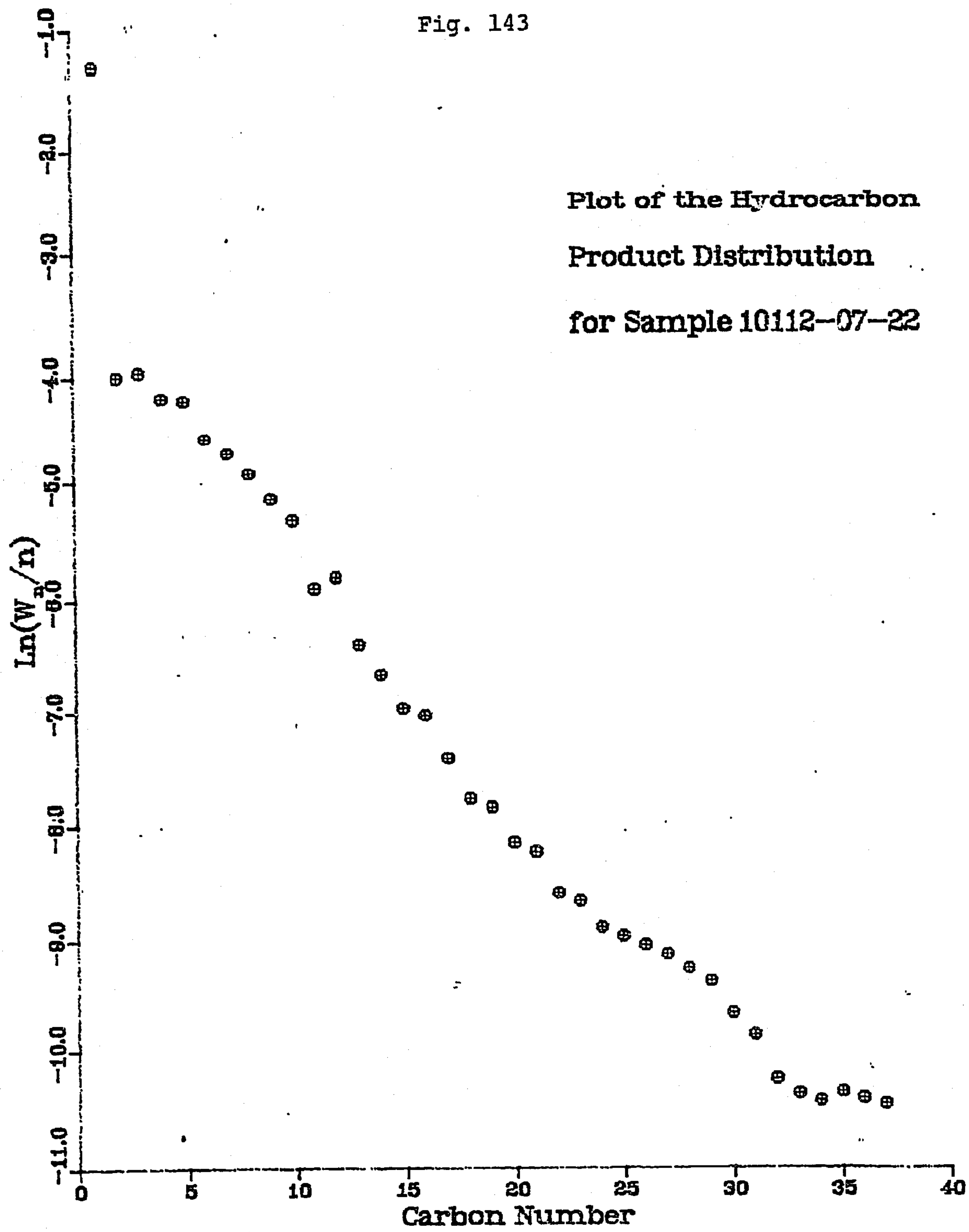
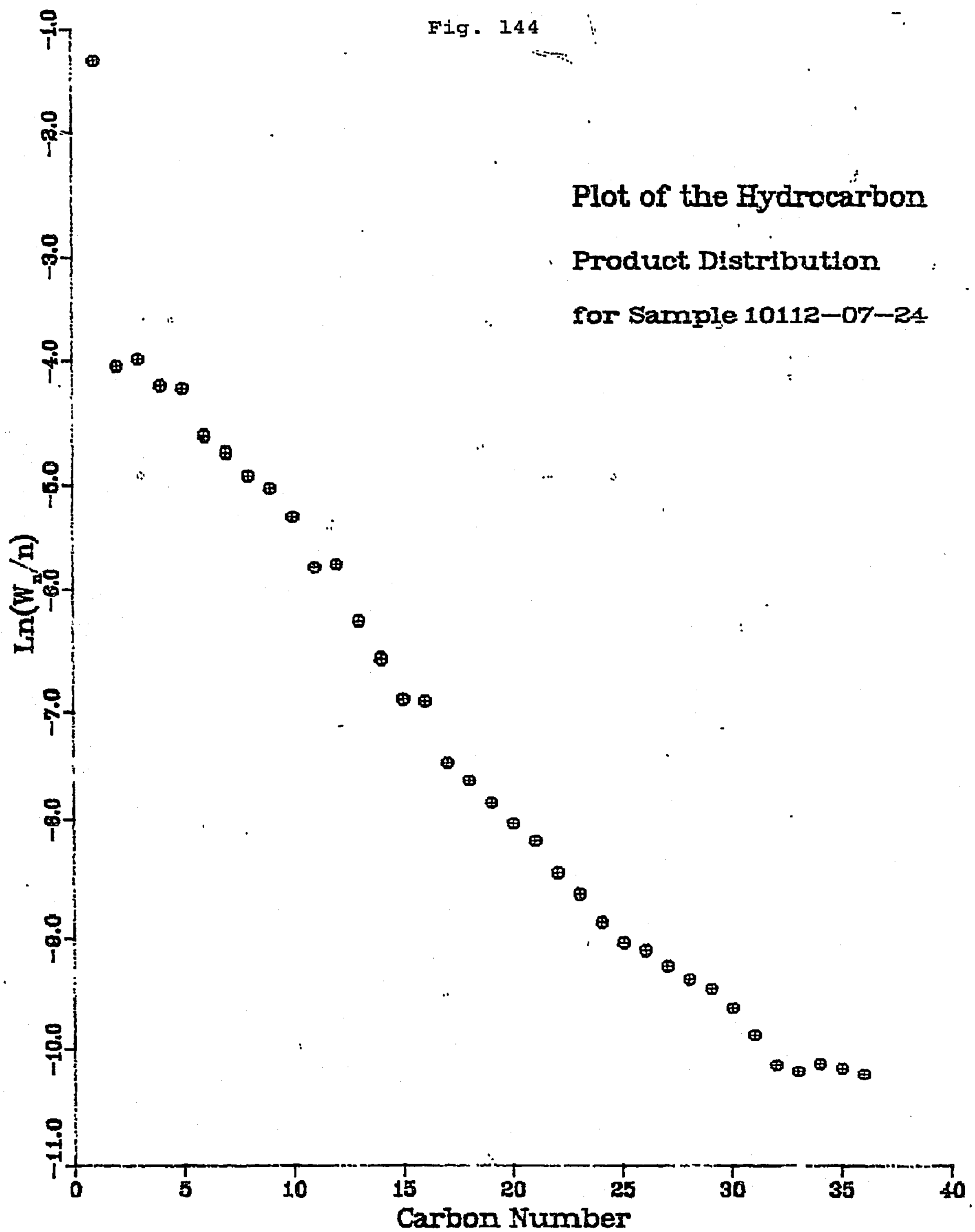

Plot of the Hydrocarbon
Product Distribution
for Sample 10112–07–22
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 144



Plot of the Hydrocarbon
Product Distribution
for Sample 10112-07-24
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. 145

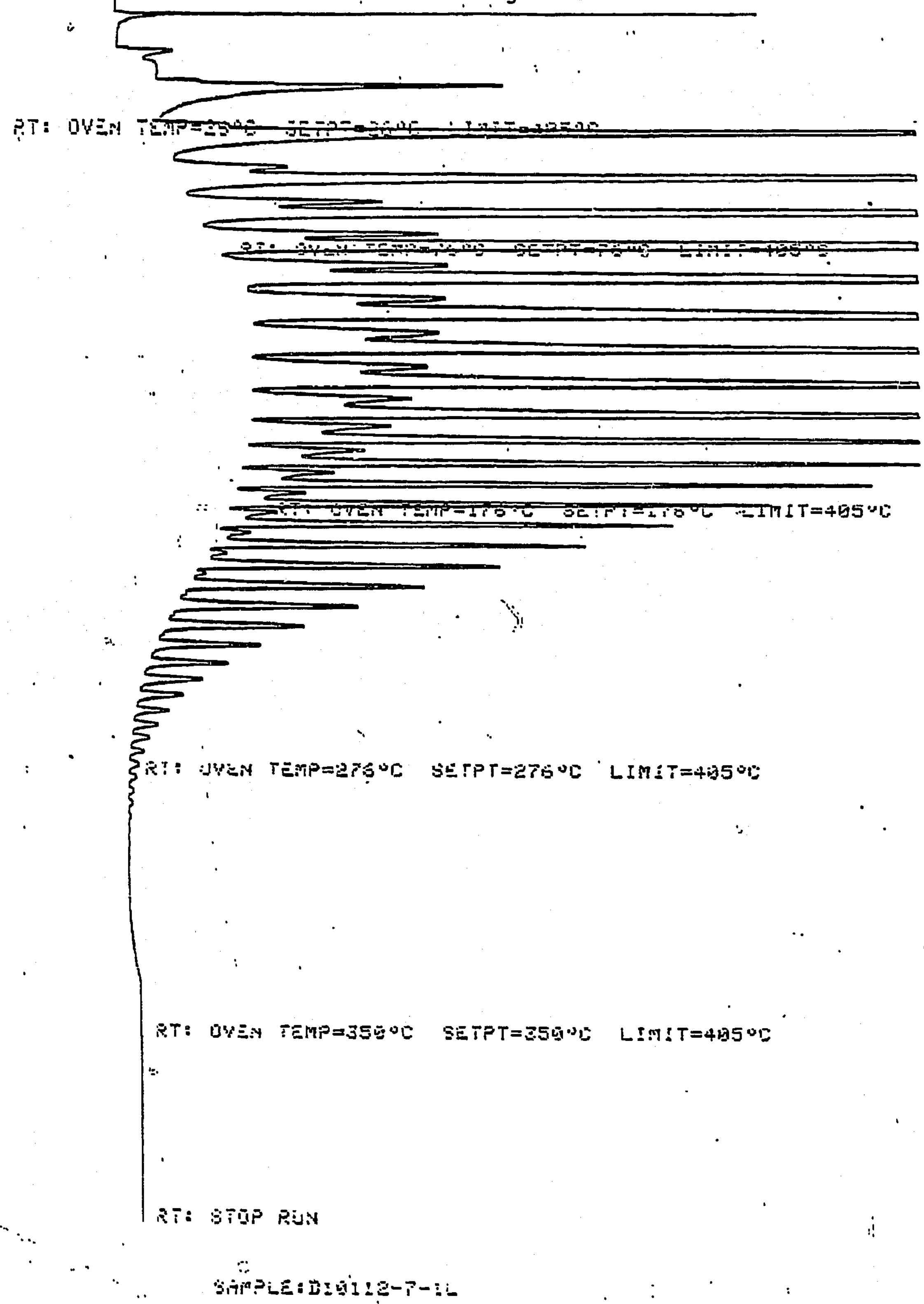

RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:D10112-7-1L

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Fig. 146

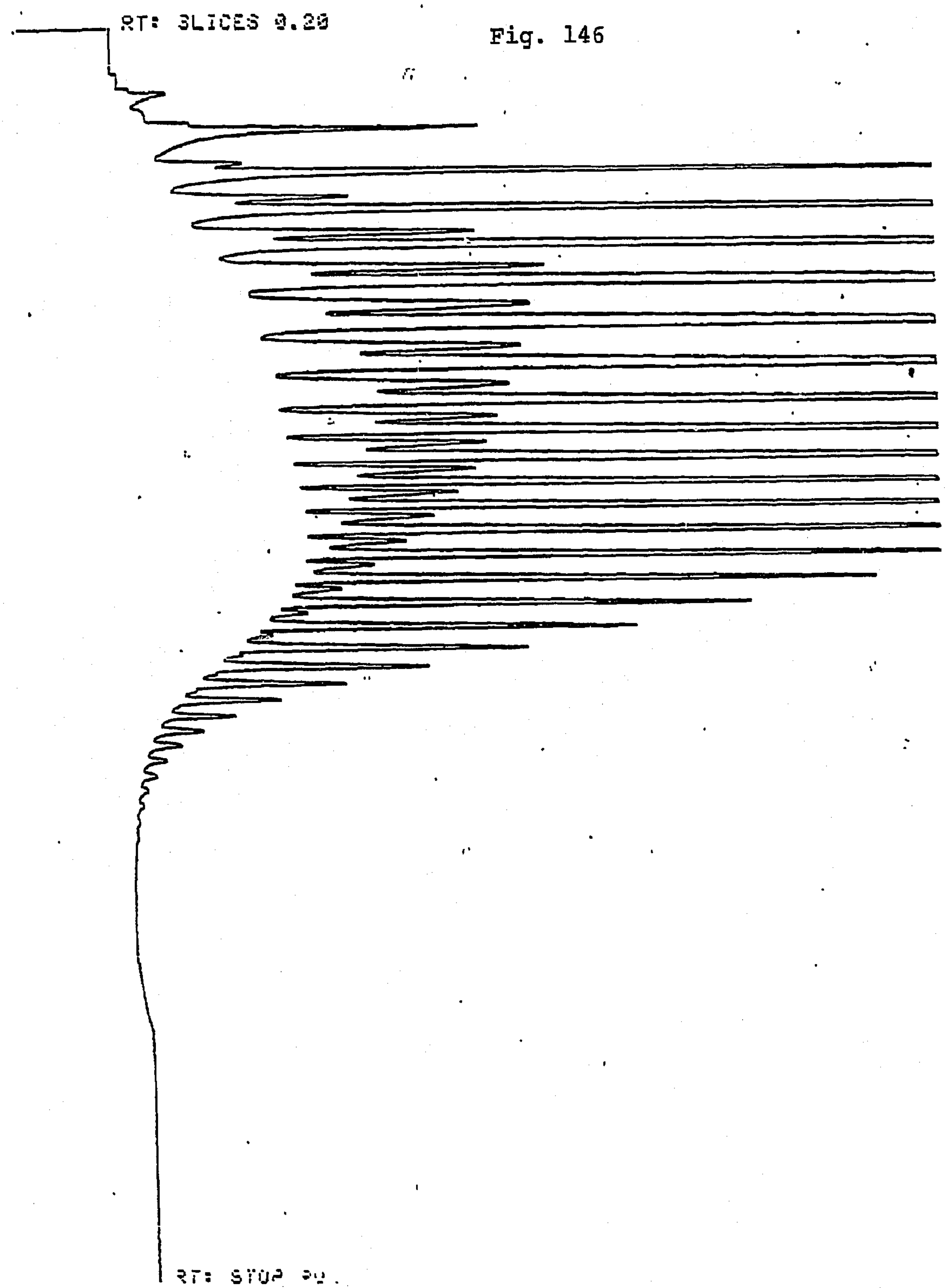


Fig. 147

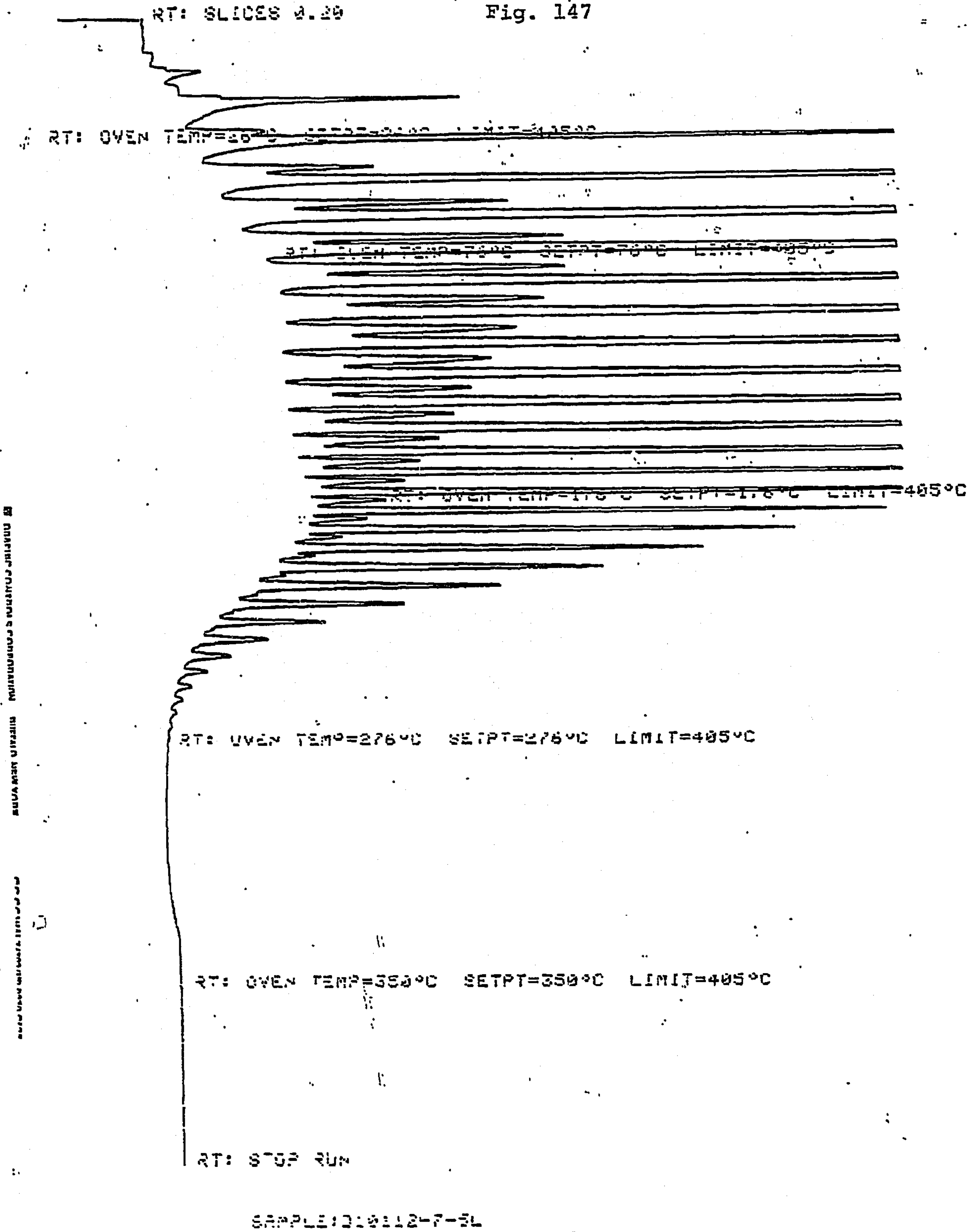

RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:310112-7-5L

Fig. 148

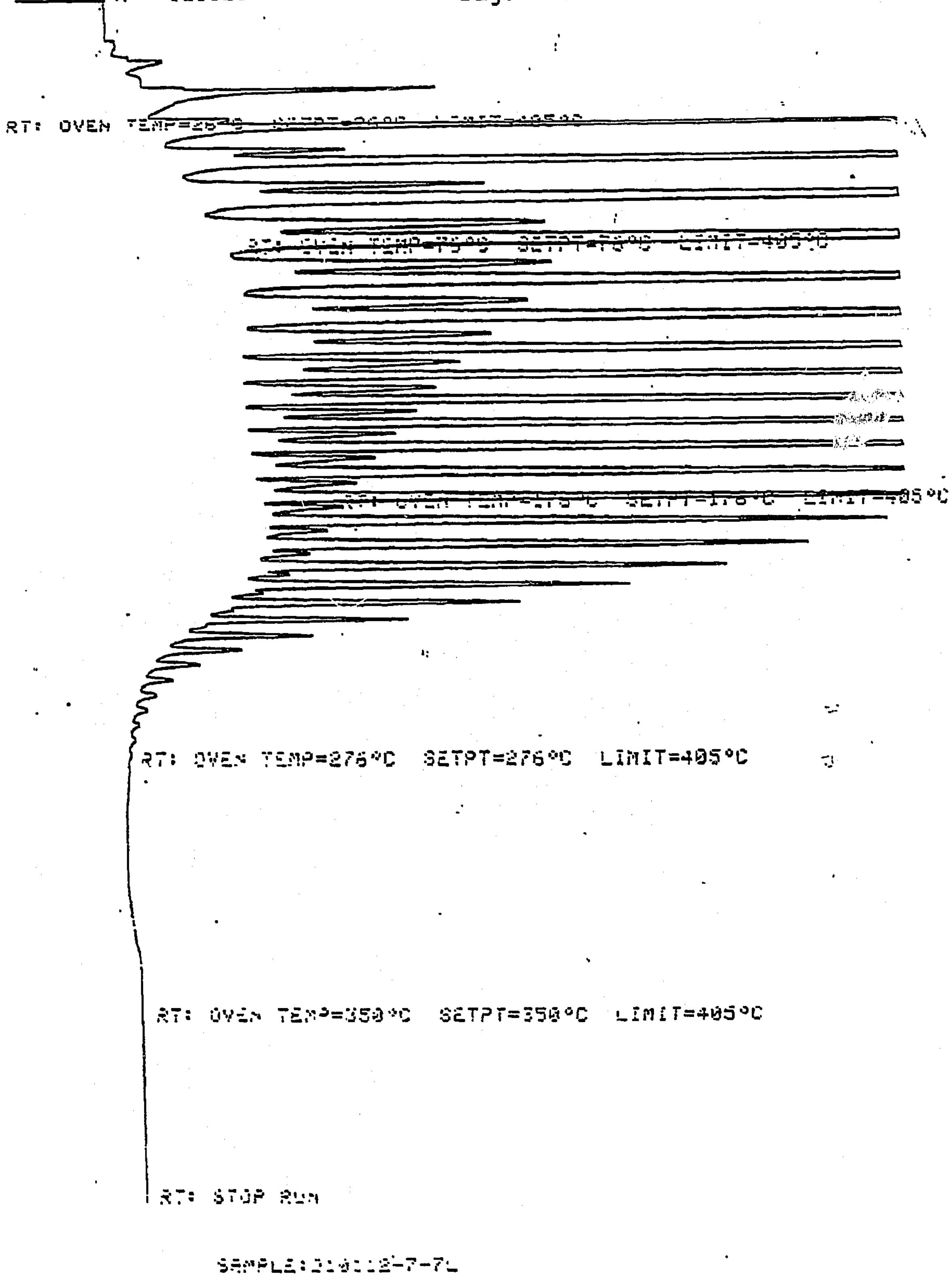
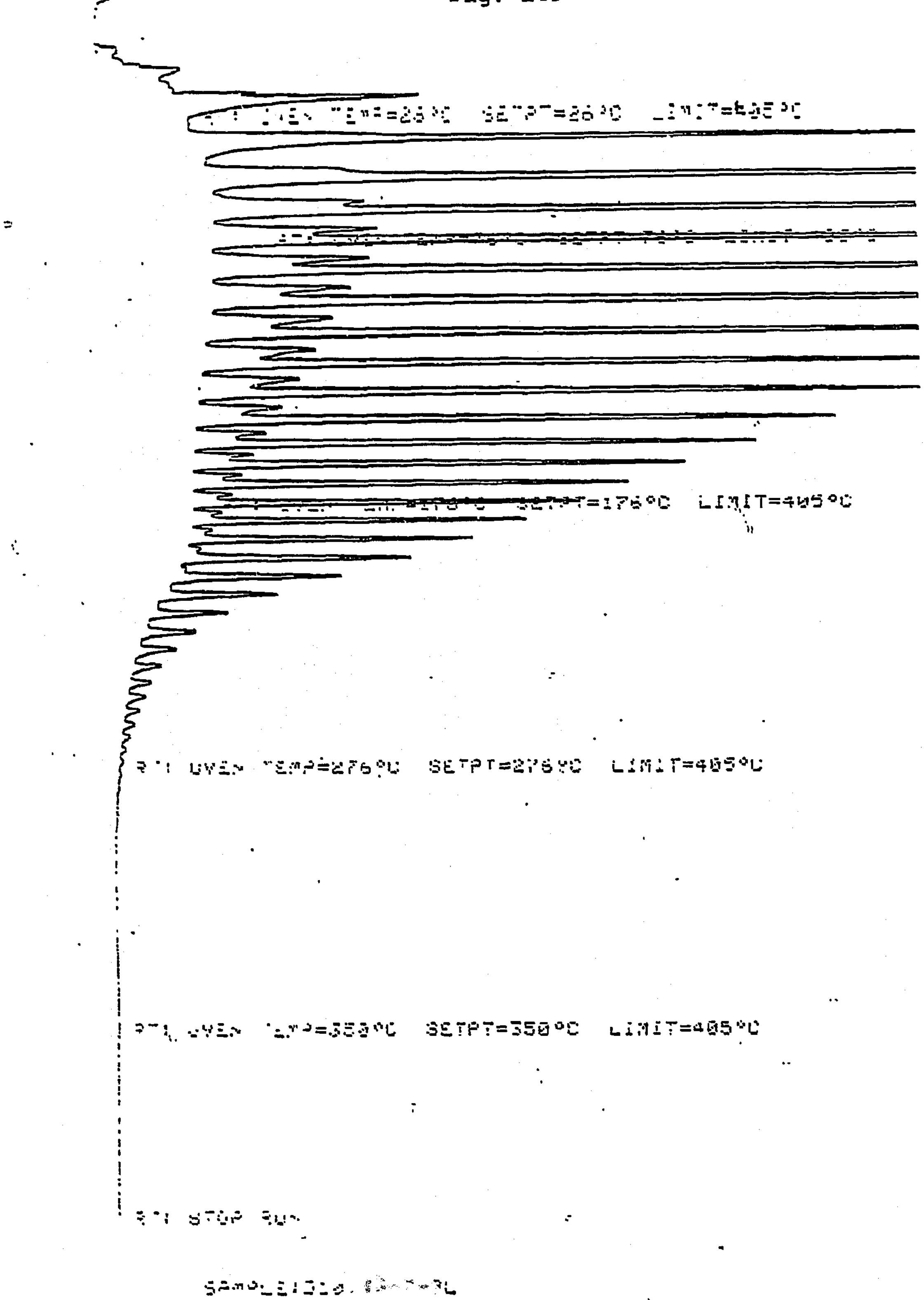

RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 149


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

p

Fig. 150

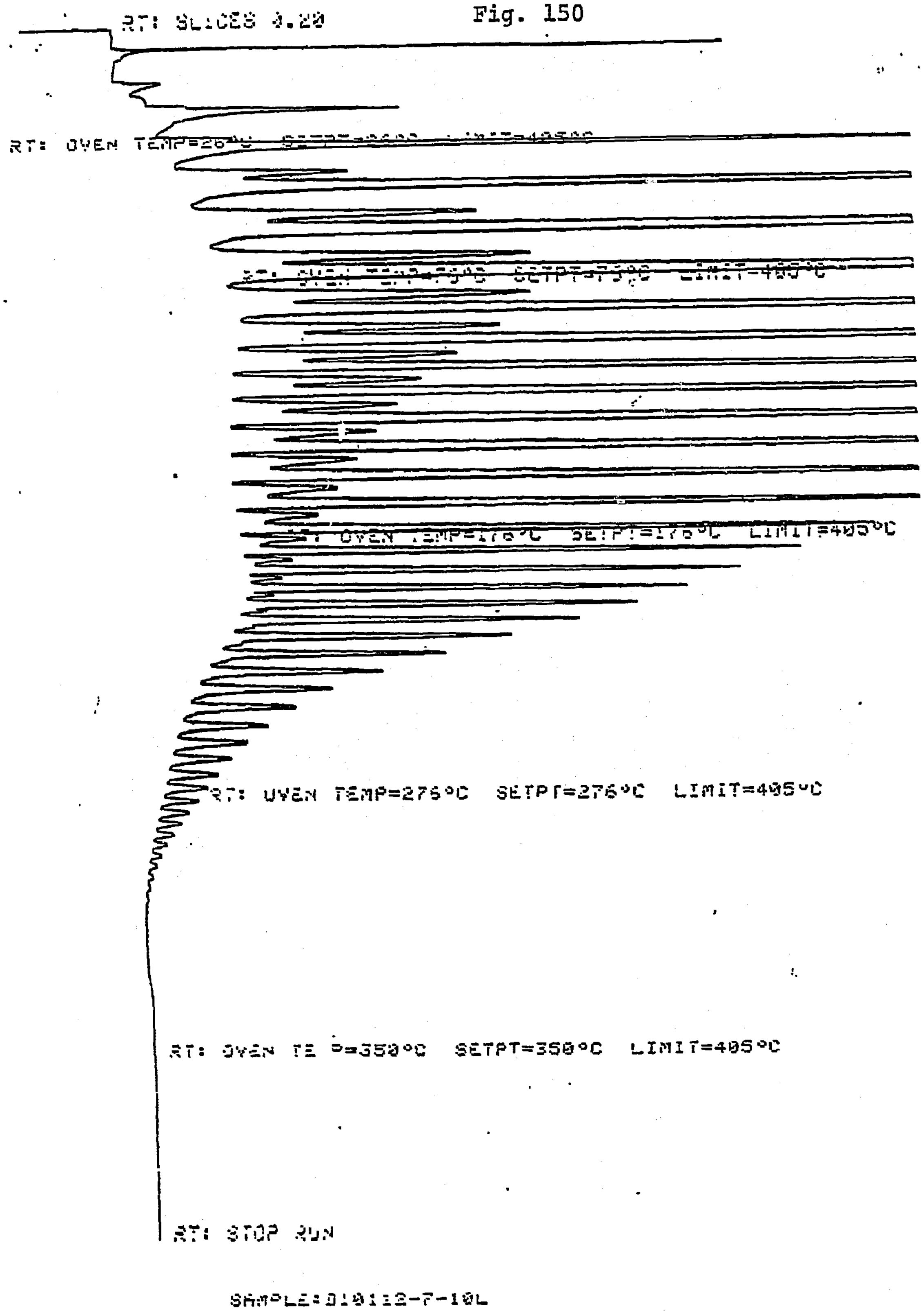

RT: SLICES 0.20
RT: OVEN TEMP=26°C
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TE P=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN
SAMPLE:B10112-7-10L

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Fig. 151

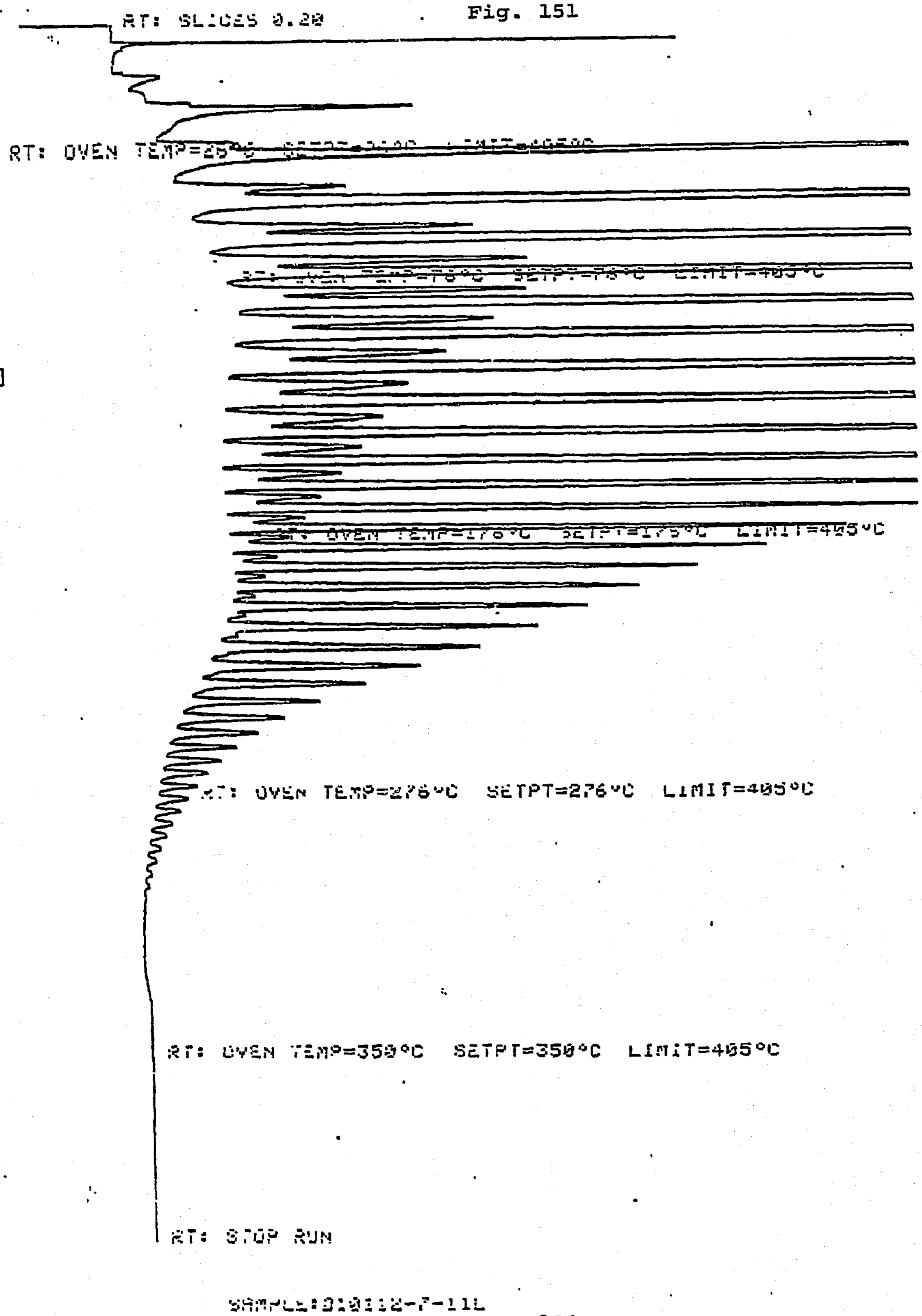
RT: SLICES 0.20
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 152

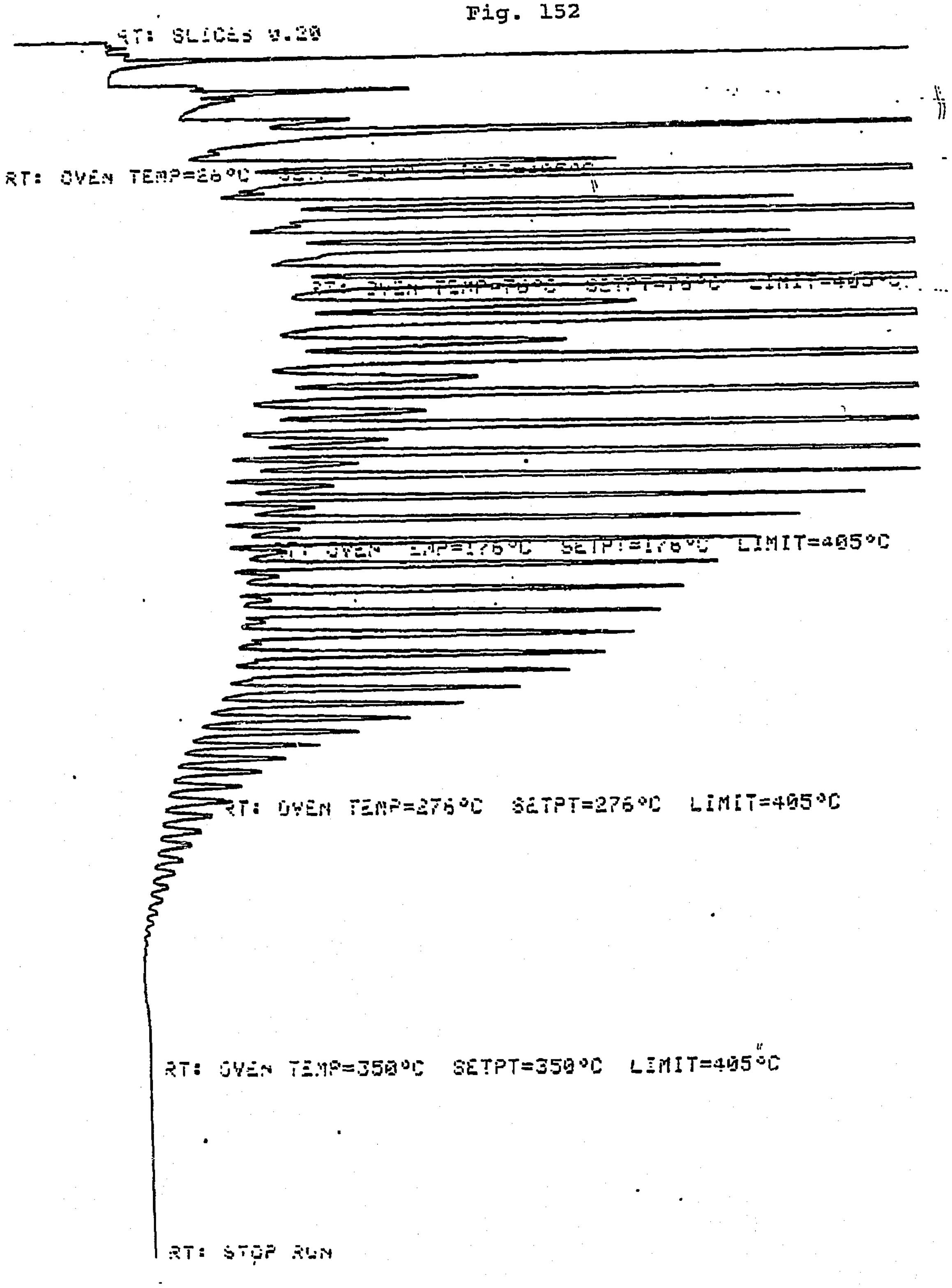
RT: SLICES 0.20
RT: OVEN TEMP=26°C
LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 153

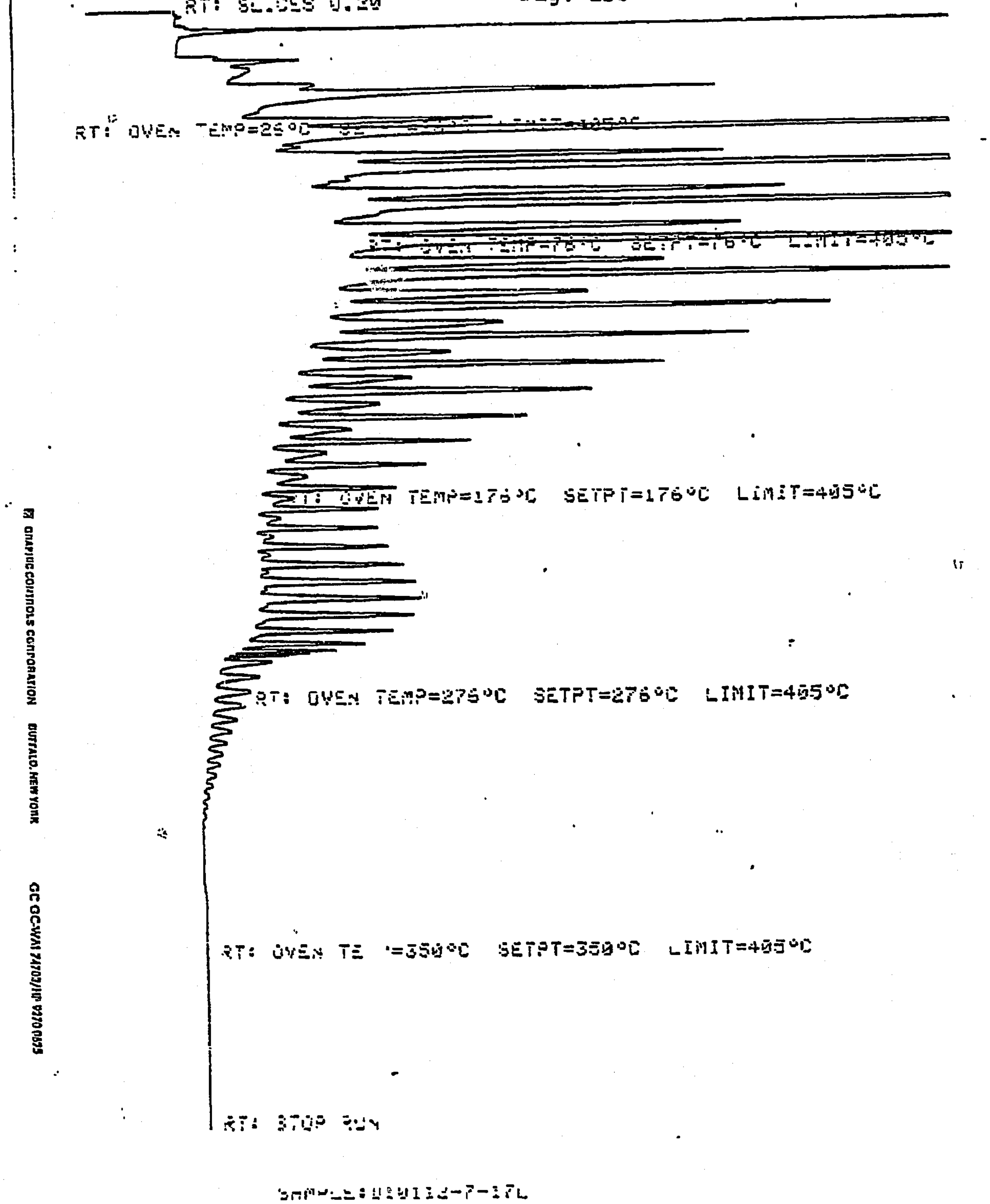
RT: SLICES 0.20
RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TE =350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

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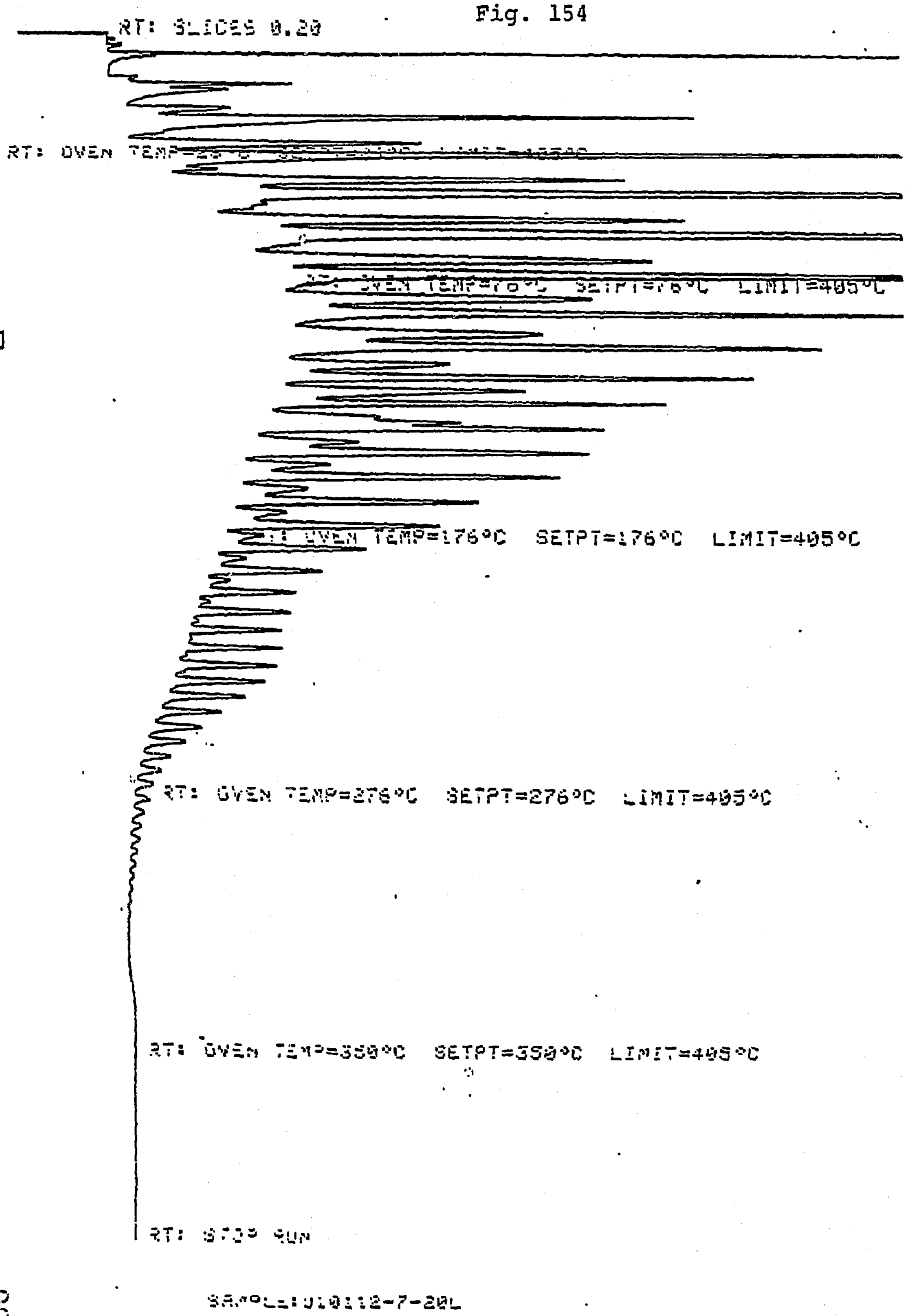
Fig. 154


RT: SLICES 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

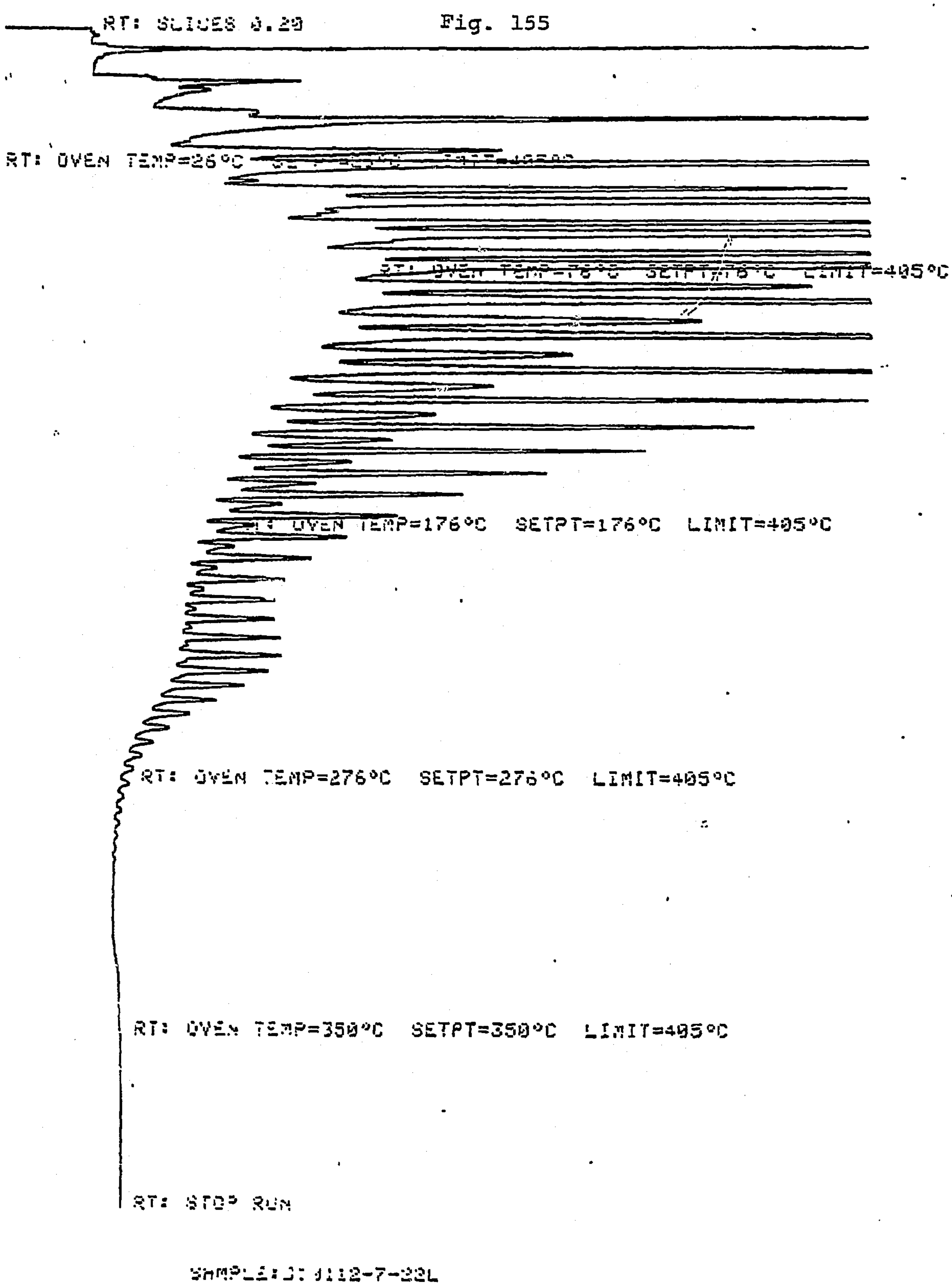
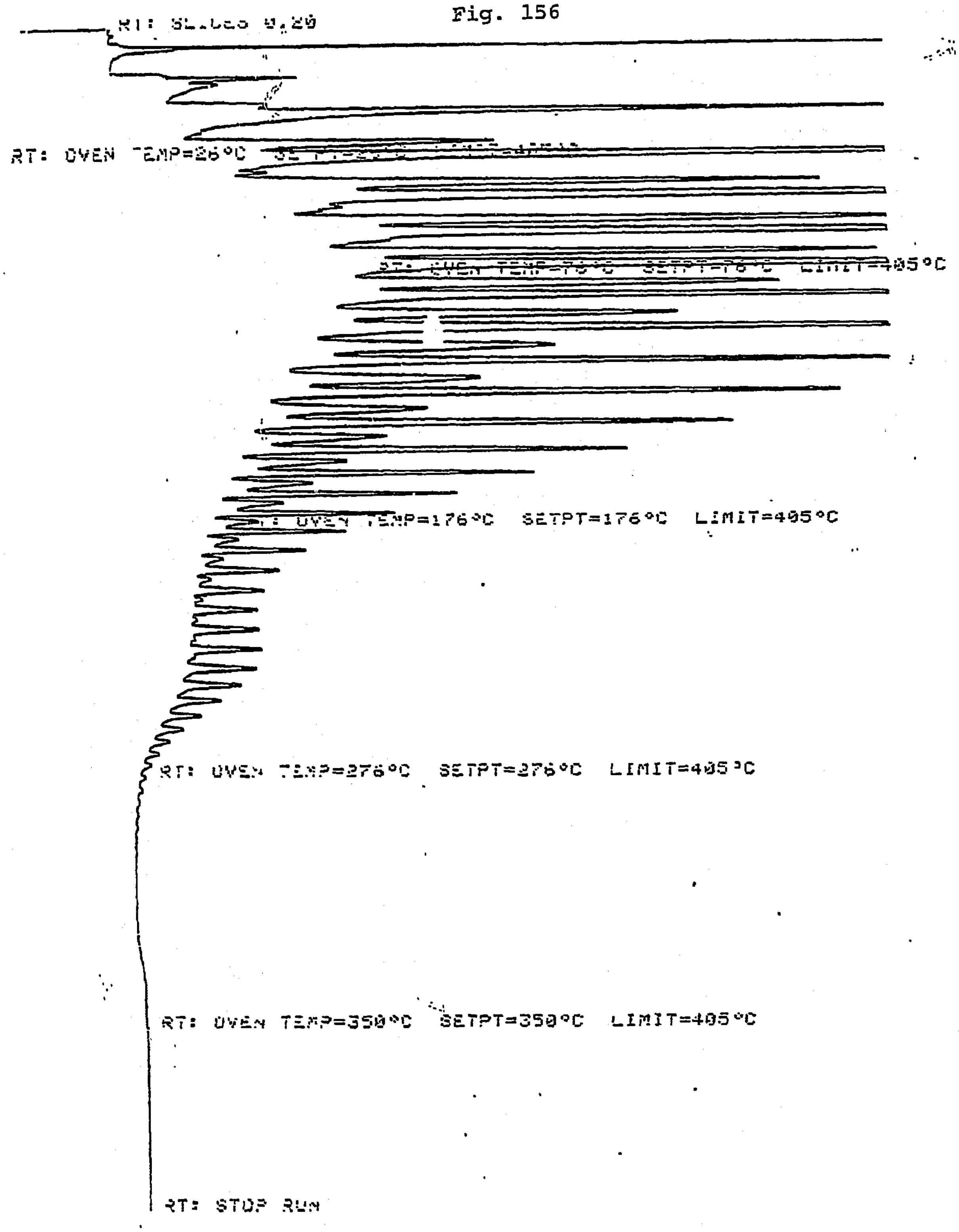

RT: OVEN TEMP=26°C
LIMIT=405°C
OVEN TEMP=176°C SETPT=176°C LIMIT=405°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 155

Fig. 156



SAMPLE#310112-7-24L

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TABLE 10A RESULT OF SYNGAS OPERATION

RUN NO. 10112-07
CATALYST CO-THO2-UCC-101 #10042-93 80 CC 30.5GM (38.4 AFTER RUN +7.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-07-01	112-07-02	112-07-03	112-07-04	112-07-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	24.52	28.43	46.85	53.85	71.27
PRESSURE,PSIG	302	298	296	295	294
TEMP. C	252	252	252	252	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.60	3.91	22.33	7.00	24.42
EFFLNT GAS LITER	267.75	49.22	313.35	102.90	366.82
GM AQUEOUS LAYER	69.72	8.78	50.12	13.70	47.78
GM OIL	21.83	3.84	21.92	5.79	20.20
MATERIAL BALANCE					
GM ATOM CARBON %	81.39	90.07	94.35	95.00	96.71
GM ATOM HYDROGEN %	84.73	87.89	99.89	96.35	98.75
GM ATOM OXYGEN %	95.00	95.87	98.35	98.54	99.33
RATIO CHX/(H2O+CO2)	0.6227	0.8093	0.8699	0.8722	0.9050
RATIO X IN CHX	2.2217	2.2410	2.2998	2.3328	2.3324
USAGE H2/CO PRODT	1.8420	1.7831	1.8118	1.7922	1.8155
RATIO CO2/(H2O+CO2)	0.0694	0.1056	0.1090	0.1216	0.1158
K SHIFT IN EFFLNT	0.03	0.06	0.08	0.09	0.09
CONVERSION					
ON CO %	30.69	30.92	31.97	28.98	29.10
ON H2 %	69.10	62.38	58.34	54.50	54.15
ON CO+H2 %	50.28	46.46	45.53	41.83	41.75
PRDT SELECTIVITY,WT %					
CH4	10.07	10.89	13.26	14.75	14.67
C2 HC'S	1.39	1.58	1.90	2.04	2.32
C3H8	1.35	1.56	2.21	2.43	2.48
C3H6=	1.97	1.83	1.74	1.58	1.88
C4H10	1.37	1.55	2.15	2.27	2.40
C4H8=	2.93	2.77	2.54	2.66	2.92
C5H12	1.90	2.02	2.68	2.90	2.95
C5H10=	3.91	3.75	3.27	3.47	3.65
C6H14	2.02	2.06	2.68	2.94	2.93
C6H12= & CYCLO'S	3.60	3.22	2.74	2.89	2.81
C7+ IN GAS	13.41	12.22	13.05	13.79	14.21
LIQ HC'S	56.12	56.55	51.76	48.28	46.75

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	19.05	20.18	23.81	25.74	26.69
C5 -420 F	48.06	44.20	43.70	46.75	43.98
420-700 F	28.01	29.97	27.45	21.24	24.07
700-END PT	4.88	5.65	5.05	6.28	5.26
C5+-END PT	80.95	79.82	76.19	74.26	73.31
ISO/NORMAL MOLE RATIO					
C4	0.0544	0.0716	0.0793	0.0514	0.0802
C5	0.1007	0.1097	0.1101	0.1023	0.1027
C6	0.1189	0.1156	0.1494	0.1587	0.1438
C4=	0.0000	0.0000	0.0000	0.0396	0.0510
PARAFFIN/OLEFIN RATIO					
C3	0.6540	0.8108	1.2127	1.4731	1.2566
C4	0.4525	0.5393	0.8156	0.8237	0.7925
C5	0.4731	0.5229	0.7975	0.8120	0.7861
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	-	CLDY OIL	-	CLDY OIL
DENSITY	0.759	-	0.760	-	0.764
N, REFRACTIVE INDEX	1.4290	-	1.4300		1.4296
SIMULT'D DISTILATN					
10 WT % @ DEG F	300		302		303
16	329		338		340
50	460		480		483
84	641		656		672
90	689		698		711
RANGE(16-84 %)	312		318		332
WT % @ 420 F	41.38		37.22		37.27
WT % @ 700 F	91.30		90.25		88.75

p

TABLE 10B RESULT OF SYNGAS OPERATION

RUN NO. 10112-07
CATALYST CO-THO2-UCC-101 #10042-93 80CC 30.5G (38.4G AFTER RUN +7.8 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-07-06	112-07-07	112-07-08	112-07-09	112-07-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	77.68	95.27	102.60	118.03	124.52
PRESSURE,PSIG	294	294	291	293	293
TEMP. C	252	252	251	251	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.42	24.02	7.33	22.76	6.48
EFFLNT GAS LITER	94.80	363.62	111.18	346.16	99.91
GM AQUEOUS LAYER	11.79	44.13	13.61	42.26	11.63
GM OIL	4.87	18.21	6.14	19.06	5.20
MATERIAL BALANCE					
GM ATOM CARBON %	93.34	95.54	96.00	95.63	96.13
GM ATOM HYDROGEN %	94.20	95.76	97.04	99.03	99.01
GM ATOM OXYGEN %	96.71	98.62	98.48	97.66	97.98
RATIO CHX/(H2O+CO2)	0.8703	0.8816	0.9050	0.9228	0.9283
RATIO X IN CHX	2.3418	2.3471	2.3195	2.3405	2.3638
USAGE H2/CO PRODT	1.8101	1.8172	1.8316	1.8284	1.8151
RATIO CO2/(H2O+CO2)	0.1161	0.1154	0.1077	0.1139	0.1233
K SHIFT IN EFFLNT	0.09	0.09	0.08	0.09	0.10
CONVERSION					
ON CO %	27.48	27.19	27.52	28.48	28.22
ON H2 %	52.52	52.22	52.20	52.16	51.43
ON CO+H2 %	40.06	39.72	39.92	40.52	40.00
PRDT SELECTIVITY,WT %					
CH4	15.16	15.46	14.17	15.08	16.16
C2 HC'S	2.18	2.12	2.06	2.22	2.25
C3H8	2.48	2.45	2.54	2.60	2.82
C3H6=	1.62	1.56	1.73	1.45	1.46
C4H10	2.28	2.27	2.11	2.24	2.34
C4H8=	2.71	2.66	2.74	2.54	2.48
C5H12	2.98	2.98	2.61	2.78	2.87
C5H10=	3.52	3.39	3.34	3.24	3.08
C6H14	2.93	2.97	2.71	2.84	2.99
C6H12= & CYCLO'S	2.96	2.94	2.81	2.62	2.59
C7+ IN GAS	13.93	14.72	13.08	13.71	13.80
LIQ HC'S	47.24	46.49	50.08	48.68	47.15

p

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	26.43	26.51	25.37	26.13	27.51
C5 -420 F	46.64	44.40	46.09	42.61	45.61
420-700 F	20.79	23.57	22.04	24.00	20.75
700-END PT	6.14	5.52	6.51	7.25	6.13
C5+-END PT	73.57	73.49	74.63	73.87	72.49
ISO/NORMAL MOLE RATIO					
C4	0.0494	0.0389	0.0424	0.0451	0.0418
C5	0.1002	0.0885	0.0782	0.0889	0.0861
C6	0.1378	0.1263	0.1335	0.1280	0.1373
C4=	0.0000	0.0000	0.0000	0.0000	0.0543
PARAFFIN/OLEFIN RATIO					
C3	1.4578	1.4990	1.4070	1.7156	1.8383
C4	0.8120	0.8236	0.7447	0.8501	0.9103
C5	0.8240	0.8529	0.7613	0.8327	0.9057
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	CLDY OIL	---	CLDY OIL	---
DENSITY	---	0.763	---	0.752	---
N, REFRACTIVE INDEX	---	1.4291	---	1.4305	---
SIMULT'D DISTILATN					
10 WT % @ DEG F	---	302	---	311	---
16	---	339	---	343	---
50	---	482	---	485	---
84	---	675	---	695	---
90	---	717	---	740	---
RANGE(16-84 %)	---	336	---	352	---
WT % @ 420 F	---	37.43	---	35.80	---
WT % @ 700 F	---	88.13	---	85.11	---

TABLE 10C RESULT OF SYNGAS OPERATION

RUN NO. 10112-07
CATALYST CO-THO2-UCC-101 #10042-93 80CC 30.5G (38.4G AFTER RUN +7.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-07-11	112-07-12	112-07-13	112-07-14	112-07-15
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	143.02	148.77	167.19	173.93	191.1
PRESSURE,PSIG	294	292	290	293	294
TEMP. C	251	252	251	252	280
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.98	5.75	24.17	6.75	23.92
EFFLNT GAS LITER	387.60	89.13	381.42	106.93	293.87
GM AQUEOUS LAYER	44.82	10.07	42.31	14.11	49.99
GM OIL	20.06	4.90	20.60	9.76	34.59
MATERIAL BALANCE					
GM ATOM CARBON %	95.57	97.30	97.59	106.44	119.32
GM ATOM HYDROGEN %	99.12	98.58	101.25	113.85	113.21
GM ATOM OXYGEN %	97.79	98.14	97.98	102.27	104.83
RATIO CHX/(H2O+CO2)	0.9128	0.9664	0.9841	1.1443	1.3590
RATIO X IN CHX	2.3600	2.3463	2.3468	2.2611	2.5371
USAGE H2/CO PRODT	1.8371	1.8363	1.8542	1.8703	1.5195
RATIO CO2/(H2O+CO2)	0.1128	0.1157	0.1105	0.1005	0.3698
K SHIFT IN EFFLNT	0.09	0.09	0.09	0.08	0.22
CONVERSION					
ON CO %	27.37	27.85	27.96	33.81	58.48
ON H2 %	50.54	51.25	50.34	55.69	83.94
ON CO+H2 %	39.17	39.63	39.36	45.12	70.88
PRDT SELECTIVITY,WT %					
CH4	15.94	15.32	15.45	11.61	24.77
C2 HC'S	2.29	2.17	2.12	1.71	3.23
C3H8	2.83	2.73	2.64	2.01	3.37
C3H6=	1.48	1.50	1.35	1.05	2.16
C4H10	2.34	2.26	2.20	1.66	2.36
C4H8=	2.48	2.53	2.31	1.70	5.04
C5H12	2.89	2.92	2.76	2.02	2.76
C5H10=	3.05	3.11	2.89	1.97	3.35
C6H14	2.93	2.88	2.88	2.37	3.35
C6H12= & CYCLO'S	2.54	2.61	2.55	1.80	2.73
C7+ IN GAS	12.68	12.36	13.92	10.15	10.24
LIQ HC'S	48.55	49.61	48.94	61.94	36.64

p

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	27.36	26.51	26.07	19.74	40.93
C5 -420 F	41.61	45.21	43.19	44.95	38.27
420-700 F	22.35	21.83	22.52	27.25	13.73
700-END PT	8.68	6.45	8.21	8.05	7.07
C5+-END PT	72.64	73.49	73.93	80.26	59.07
ISO/NORMAL MOLE RATIO					
C4	0.0387	0.0377	0.0396	0.0393	0.1138
C5	0.0788	0.0910	0.0827	0.0846	0.2540
C6	0.1227	0.1311	0.1252	0.2364	0.6992
C4=	0.0407	0.0000	0.0000	0.0000	0.6143
PARAFFIN/OLEFIN RATIO					
C3	1.8232	1.7312	1.8661	1.8259	1.4909
C4	0.9133	0.8639	0.9219	0.9447	0.4523
C5	0.9231	0.9109	0.9298	0.9962	0.8005
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	---	CLDY OIL	---	CLDY OIL
DENSITY	0.757	---	0.758	---	0.758
N, REFRACTIVE INDEX	1.4306	---	1.4305	---	1.4304
SIMULT'D DISTILATN					
10 WT % @ DEG F	304	---	303	---	260
16	341	---	340	---	300
50	489	---	485	---	460
84	716	---	707	---	732
90	770	---	762	---	789
RANGE(16-84 %)	375	---	367	---	432
WT % @ 420 F	36.09	---	37.20	---	43.25
WT % @ 700 F	82.13	---	83.22	---	80.71

TABLE 10D RESULT OF SYNGAS OPERATION

RUN NO. 10112-07
CATALYST CO-THO2-UCC-101 #10042-93 80CC 30.5G (38.4G AFTER RUN +7.8 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-07-16	112-07-17	112-07-18	112-07-19	112-07-20
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	198.1	215.27	217.6	222.27	239.1
PRESSURE,PSIG	294	295	292	292	297
TEMP. C	278	279	278	278	278
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.00	24.17	2.33	7.00	23.83
EFFLNT GAS LITER	74.50	260.88	25.33	76.38	262.51
GM AQUEOUS LAYER	18.06	62.35	6.06	18.22	62.01
GM OIL	8.20	28.30	2.52	7.56	25.75
MATERIAL BALANCE					
GM ATOM CARBON %	98.61	99.76	99.07	98.32	99.16
GM ATOM HYDROGEN %	99.97	100.73	100.07	99.37	99.85
GM ATOM OXYGEN %	96.47	97.42	98.15	98.79	98.90
RATIO CHX/(H2O+CO2)	1.0543	1.0591	1.0230	0.9884	1.0064
RATIO X IN CHX	2.5050	2.5079	2.5254	2.5249	2.5264
USAGE H2/CO PRODT	1.6775	1.6754	1.6708	1.6426	1.6698
RATIO CO2/(H2O+CO2)	0.2231	0.2255	0.2253	0.2327	0.2233
K SHIFT IN EFFLNT	0.10	0.10	0.10	0.11	0.10
CONVERSION					
ON CO %	51.17	51.05	50.35	50.15	49.49
ON H2 %	82.87	82.76	82.52	81.89	81.85
ON CO+H2 %	67.13	66.98	66.52	66.11	65.73
PRDT SELECTIVITY,WT %					
CH4	23.80	23.94	24.74	24.38	24.69
C2 HC'S	3.18	3.20	3.30	3.39	3.43
C3H8	2.64	2.65	2.74	3.05	2.81
C3H6=	2.32	2.33	2.41	2.67	2.51
C4H10	1.80	1.81	1.87	2.15	1.91
C4H8=	3.47	3.49	3.61	4.04	3.69
C5H12	2.35	2.36	2.44	2.67	2.46
C5H10=	4.14	4.16	4.30	4.64	4.41
C6H14	2.31	2.33	2.40	2.62	2.42
C6H12= & CYCLO'S	2.99	3.00	3.10	3.19	3.14
C7+ IN GAS	11.82	11.88	12.28	9.56	11.11
LIQ HC'S	39.19	38.84	36.81	37.65	37.43

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	37.21	37.42	38.67	39.69	39.03
C5 -420 F	40.45	42.55	40.35	38.85	40.43
420-700 F	17.24	13.36	16.20	16.56	15.87
700-END PT	5.09	6.67	4.78	4.89	4.66
C5+-END PT	62.79	62.58	61.33	60.31	60.97
ISO/NORMAL MOLE RATIO					
C4	0.0895	0.0895	0.0895	0.1009	0.0914
C5	0.2154	0.2154	0.2154	0.2324	0.2170
C6	0.3093	0.3093	0.3093	0.3370	0.3011
C4=	0.0552	0.0552	0.0552	0.0575	0.0560
PARAFFIN/OLEFIN RATIO					
C3	1.0858	1.0858	1.0858	1.0889	1.0695
C4	0.4995	0.4995	0.4995	0.5133	0.5009
C5	0.5521	0.5521	0.5521	0.5585	0.5434
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	WHITE WAX	---	---	GREEN WAX
DENSITY	---	0.754	---	---	0.758
N, REFRACTIVE INDEX	---	1.4322	---	---	1.4288
SIMULT'D DISTILATN					
10 WT % @ DEG F	---	260	---	---	263
16	---	298	---	---	301
50	---	430	---	---	444
84	---	716	---	---	661
90	---	790	---	---	733
RANGE(16-84 %)	---	418	---	---	360
WT % @ 420 F	---	48.43	---	---	45.14
WT % @ 700 F	---	82.83	---	---	87.55

TABLE 10E RESULT OF SYNGAS OPERATION

RUN NO. 10112-07
CATALYST CO-THO2-UCC-101 #10042-93 80CC 30.5G (38.4G AFTER RUN +7.8G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-07-21	112-07-22	112-07-23	112-07-24
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	245.6	263.1	270.1	287.68
PRESSURE,PSIG	292	291	299	295
TEMP. C	278	278	278	278
FEED CC/MIN	400	400	400	400
HOURS FEEDING	6.50	23.99	7.00	24.58
EFFLNT GAS LITER	72.47	269.67	79.60	279.51
GM AQUEOUS LAYER	16.99	62.70	18.06	63.41
GM OIL	5.12	18.90	6.30	22.11
MATERIAL BALANCE				
GM ATOM CARBON %	95.94	96.69	99.33	99.31
GM ATOM HYDROGEN %	96.41	97.62	99.26	100.30
GM ATOM OXYGEN %	99.88	99.69	100.51	99.54
RATIO CHX/(H2O+CO2)	0.9020	0.9245	0.9705	0.9942
RATIO X IN CHX	2.5904	2.5908	2.5695	2.5748
USAGE H2/CO PRODT	1.6535	1.6762	1.6669	1.6958
RATIO CO2/(H2O+CO2)	0.2245	0.2185	0.2267	0.2185
K SHIFT IN EFFLNT	0.10	0.10	0.11	0.10
CONVERSION				
ON CO %	47.17	47.14	48.01	48.12
ON H2 %	80.98	80.83	81.07	81.00
ON CO+H2 %	64.11	64.07	64.53	64.64
PRDT SELECTIVITY,WT %				
CH4	27.57	27.71	26.70	27.07
C2 HC'S	3.83	3.69	3.61	3.48
C3H8	3.14	3.04	2.97	2.92
C3H6=	2.80	2.73	2.67	2.64
C4H10	2.14	2.07	2.07	2.00
C4H8=	4.12	4.05	4.03	3.90
C5H12	2.75	2.71	2.67	2.59
C5H10=	4.92	4.79	4.75	4.58
C6H14	2.71	2.74	2.55	2.59
C6H12= & CYCLO'S	3.50	3.50	3.35	3.36
C7+ IN GAS	12.40	13.38	12.35	13.04
LIQ HC'S	30.11	29.60	32.29	31.83

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	43.60	43.29	42.04	42.01
C5 -420 F	39.24	42.60	39.55	43.19
420-700 F	13.25	11.06	14.21	11.87
700-END PT	3.91	3.05	4.20	2.93
C5+-END PT	56.40	56.71	57.96	57.99
ISO/NORMAL MOLE RATIO				
C4	0.0914	0.0844	0.0885	0.0850
C5	0.2170	0.2113	0.2139	0.2098
C6	0.3011	0.2916	0.2875	0.2831
C4=	0.0560	0.0560	0.0582	0.0580
PARAFFIN/OLEFIN RATIO				
C3	1.0695	1.0658	1.0641	1.0557
C4	0.5009	0.4930	0.4962	0.4942
C5	0.5434	0.5493	0.5468	0.5504
LIQ HC COLLECTION				
PHYS. APPEARANCE	---	GREEN OIL	---	GREEN OIL
DENSITY	---	0.756	---	0.757
N, REFRACTIVE INDEX	---	1.4282	---	1.4275
SIMULT'D DISTILATN				
10 WT % @ DEG F	---	260	---	259
16	---	297	---	293
50	---	413	---	411
84	---	626	---	614
90	---	704	---	688
RANGE(16-84 %)	---	329	---	321
WT % @ 420 F	---	52.33	---	53.50
WT % @ 700 F	---	89.71	---	90.80

XII. RUN 10225-2, Co/Th on UCC-107

This catalyst was prepared by the same method used for the previous catalyst (Run 10112-7), except that UCC-107 was substituted for UCC-101. The catalyst was thorium-loaded to 1 percent thorium, and calcined at 250C.

Conversion, product selectivity, isomerization of the pentane, and percent olefins in the C_4's are presented in Figs. 157-160. Simulated distillations of two samples are given in Figs. 161 and 162. Carbon number product distributions are shown in Figs. 163-168. Chromatograms of the simulated distillations are reproduced in Figs. 169-174. Detailed material balances are given in Tables 11A-11C.

The catalyst was initially contacted with syngas at 270C. After 24 hours on stream, it was determined that the catalyst was producing too much methane. The temperature was then lowered to 250C, where it was maintained for the remainder of the test. After 95 hours on stream, the selectivity shifted toward the production of lighter products. As in Run 10225-3 (reported earlier in this report, but chronologically following this run) there was no recorded malfunction to explain the sudden change. Also, the selectivity recovered in part during the rest of the run. This again was probably a mechanical rather than a catalyst problem.

The catalyst maintained high conversion at 250C (Fig. 157).

As with all but one of the other cobalt catalysts, this one evinced little WGS activity compared with its F-T synthesis activity; at 270C, however, it did show good WGS activity. If the 96 and 119 hour samples are disregarded, it did produce more lights at the end of the test. Also, its selectivity was generally like that of the cobalt catalysts. Carbon number product distributions (Figs. 163-168) show not only the usual high methane yields but also an apparent carbon number cut-off, illustrated most dramatically in Sample 5. Initial samples contained 70 percent motor fuel, later samples only 62 percent. All samples contained 5 percent heavies.

The condensed product was not as waxy as those from earlier runs. Only the last two samples contained some wax. The C_4's were more olefinic and the pentanes (except the last sample) more isomerized than those from other catalysts (Figs. 159, 160). Also, the refractive intercept of the liquid product corresponded to 50 percent olefins, and the chromatograms of the simulated distillations showed the initial liquid products to be quite isomerized, although this dropped off significantly about halfway through the run. Both the olefinic and isomeric contents of the liquid contributed to its lower wax content.

UCC-107 seems to be an acidic Molecular Sieve, but as with LZ-Y-82 the acid activity seems to deactivate over the test period. The LZ-Y-82 seems, however, to deactivate more rapidly than the UCC-107.

p

Fig. 157

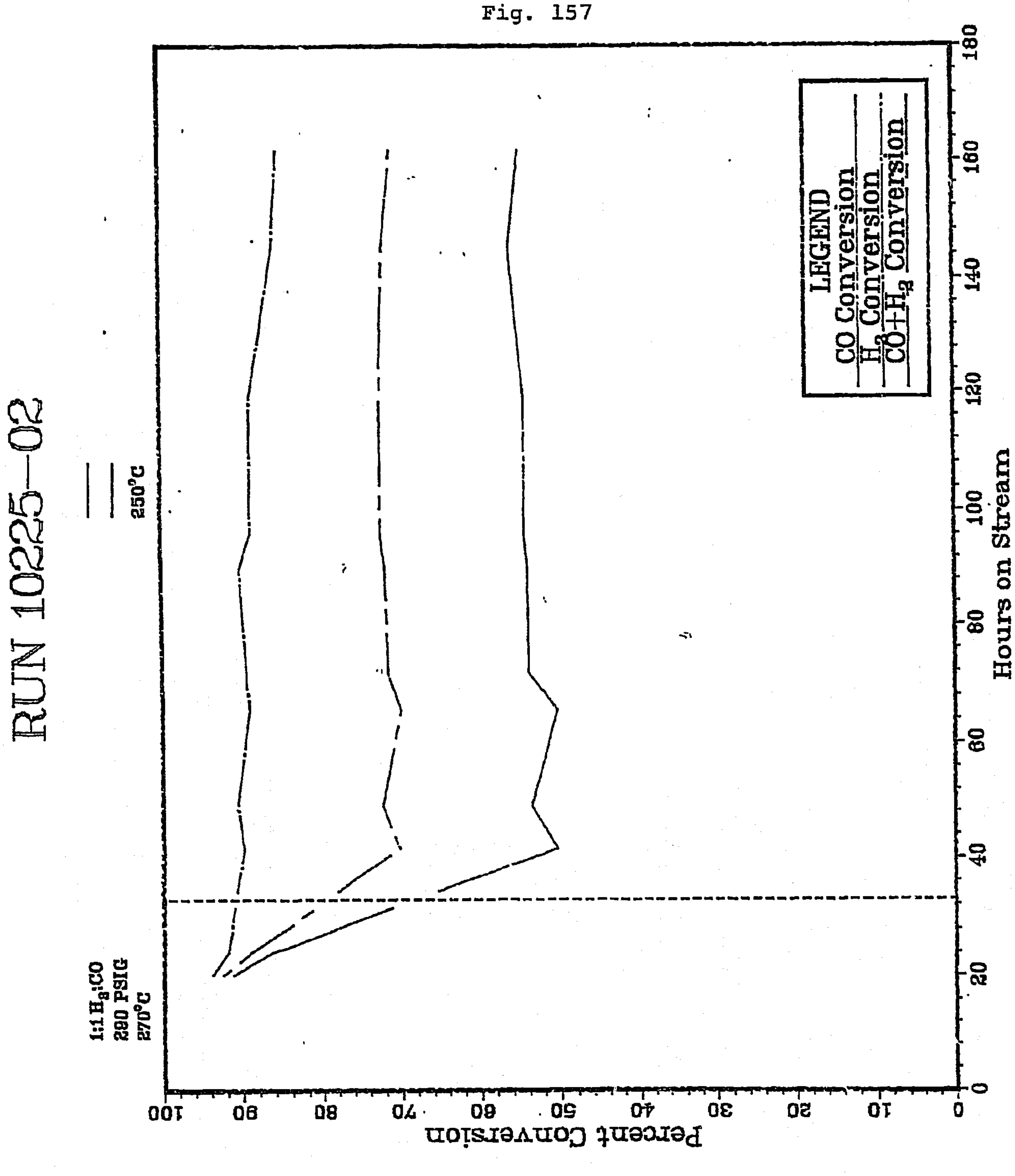

RUN 10225-02
1:1 H_2:CO
290 PSIG
270°C
250°C
LEGEND
CO Conversion
H_2 Conversion
CO+H_2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
140
160
180

Fig. 158

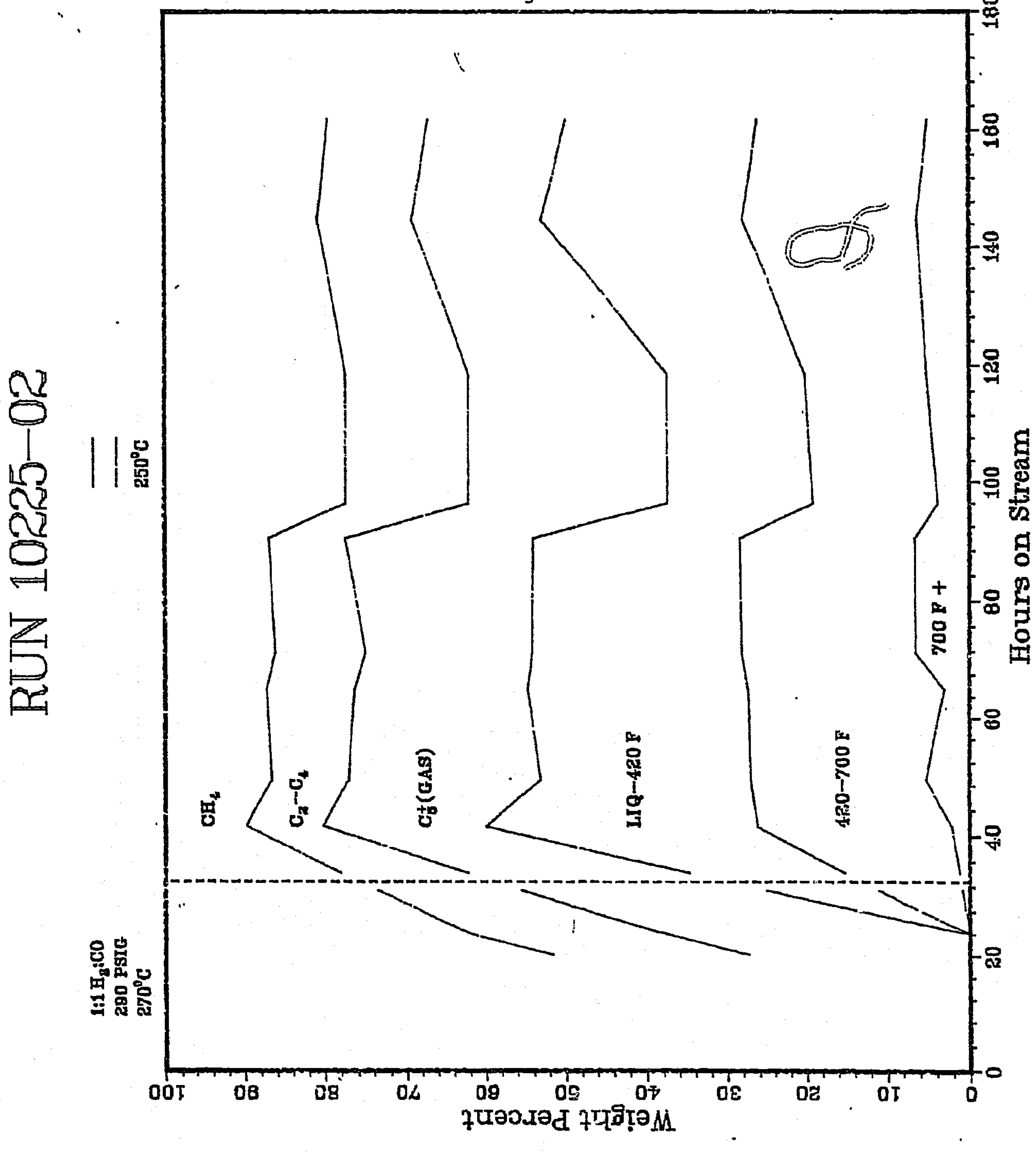

RUN 10225-02
1:1 H2:CO
290 PSIG
270°C
250°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
120
140
160
180

Fig. 159

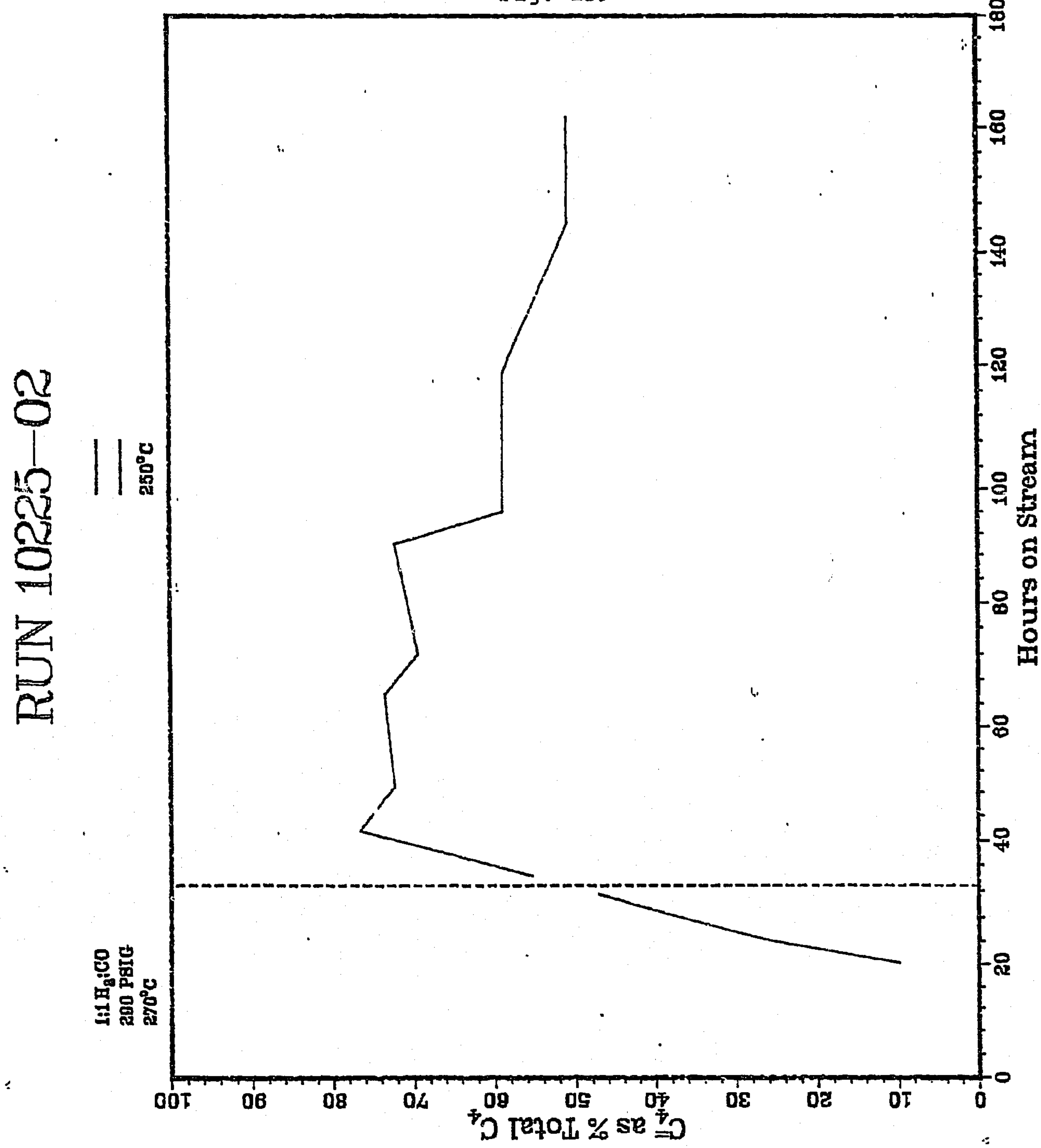

RUN 10225—02
1:1 H_2:CO
200 PSIG
270°C
250°C
$C_4^=$ as % Total C_4
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160
180

Fig. 160

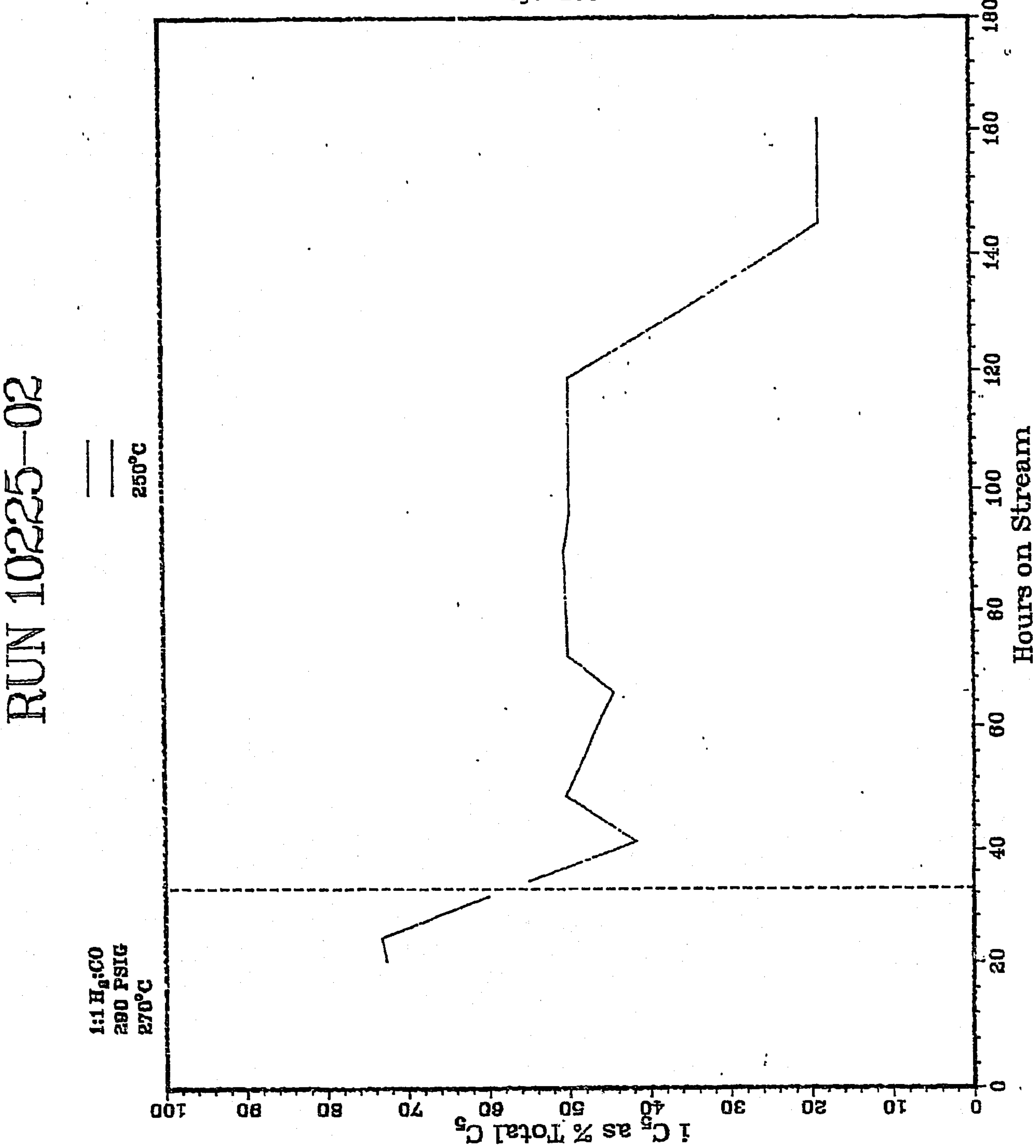
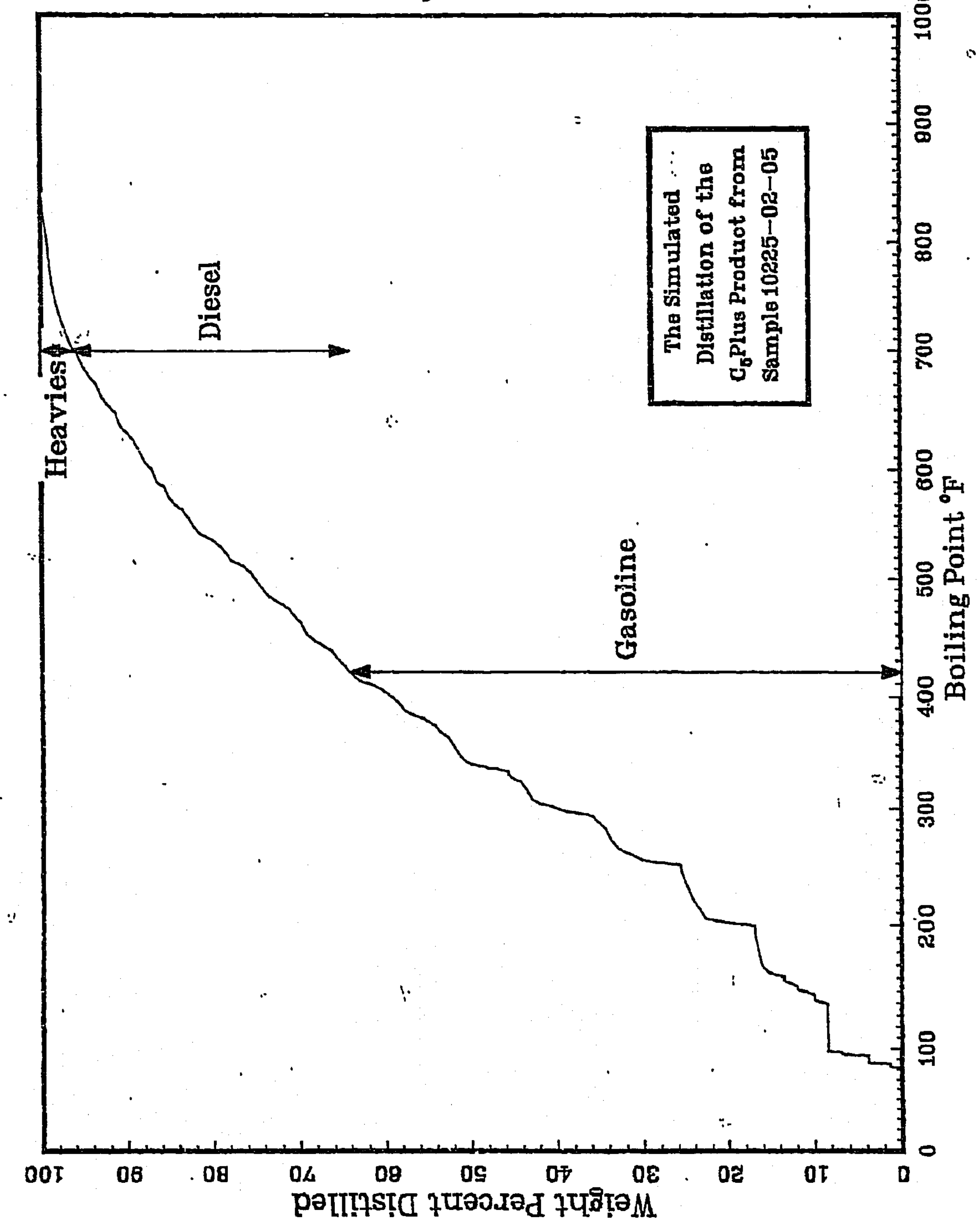
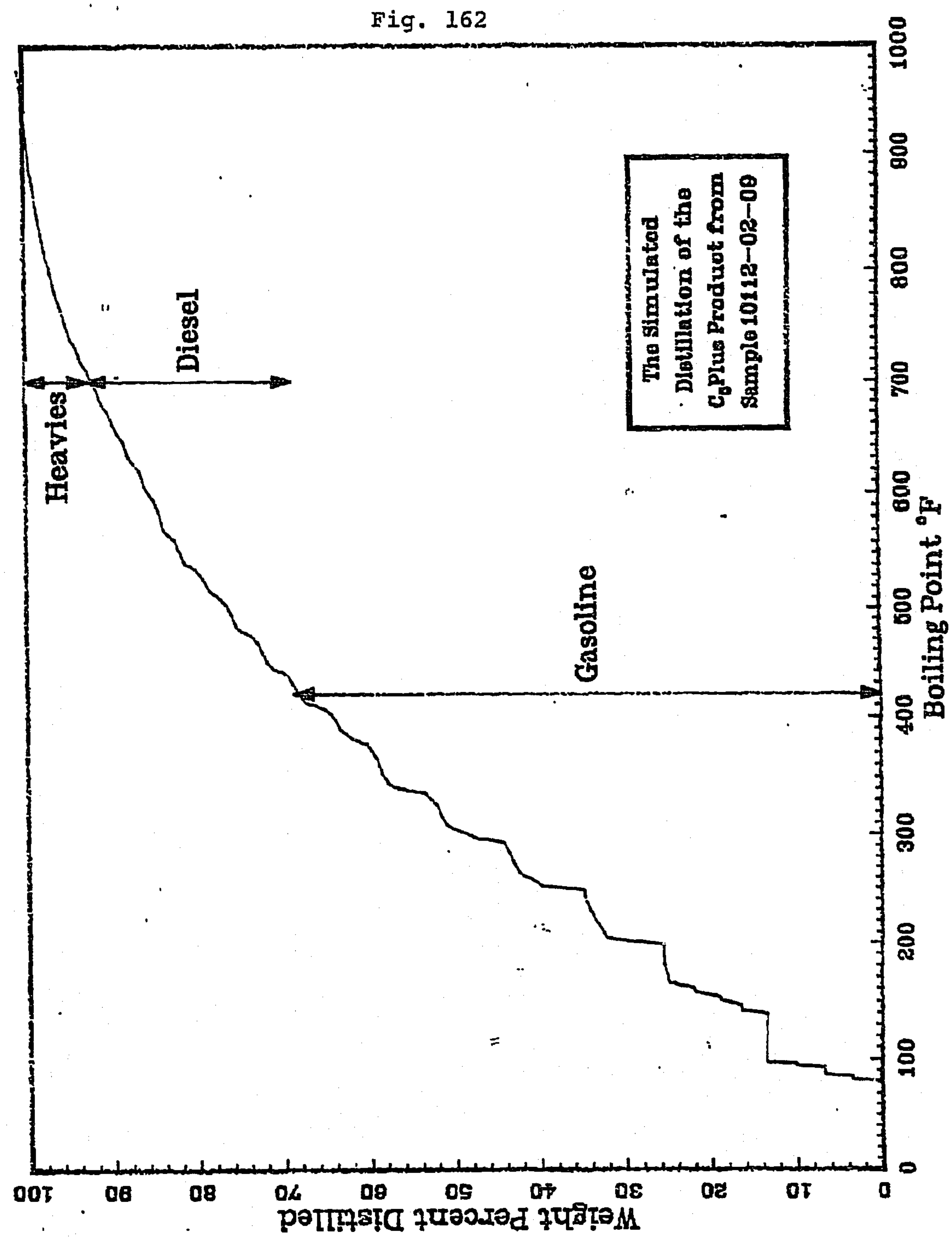

RUN 10225-02
1:1 H2:CO
290 PSIG
270°C
250°C
Hours on Stream
0
20
40
60
80
100
120
140
160
180
i C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100

Fig. 161



The Simulated
Distillation of the
C_6Plus Product from
Sample 10225-02-05
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 162



Heavies
Diesel
Gasoline
The Simulated Distillation of the C_5Plus Product from Sample 10112-02-09
Boiling Point °F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
1000

Fig. 163

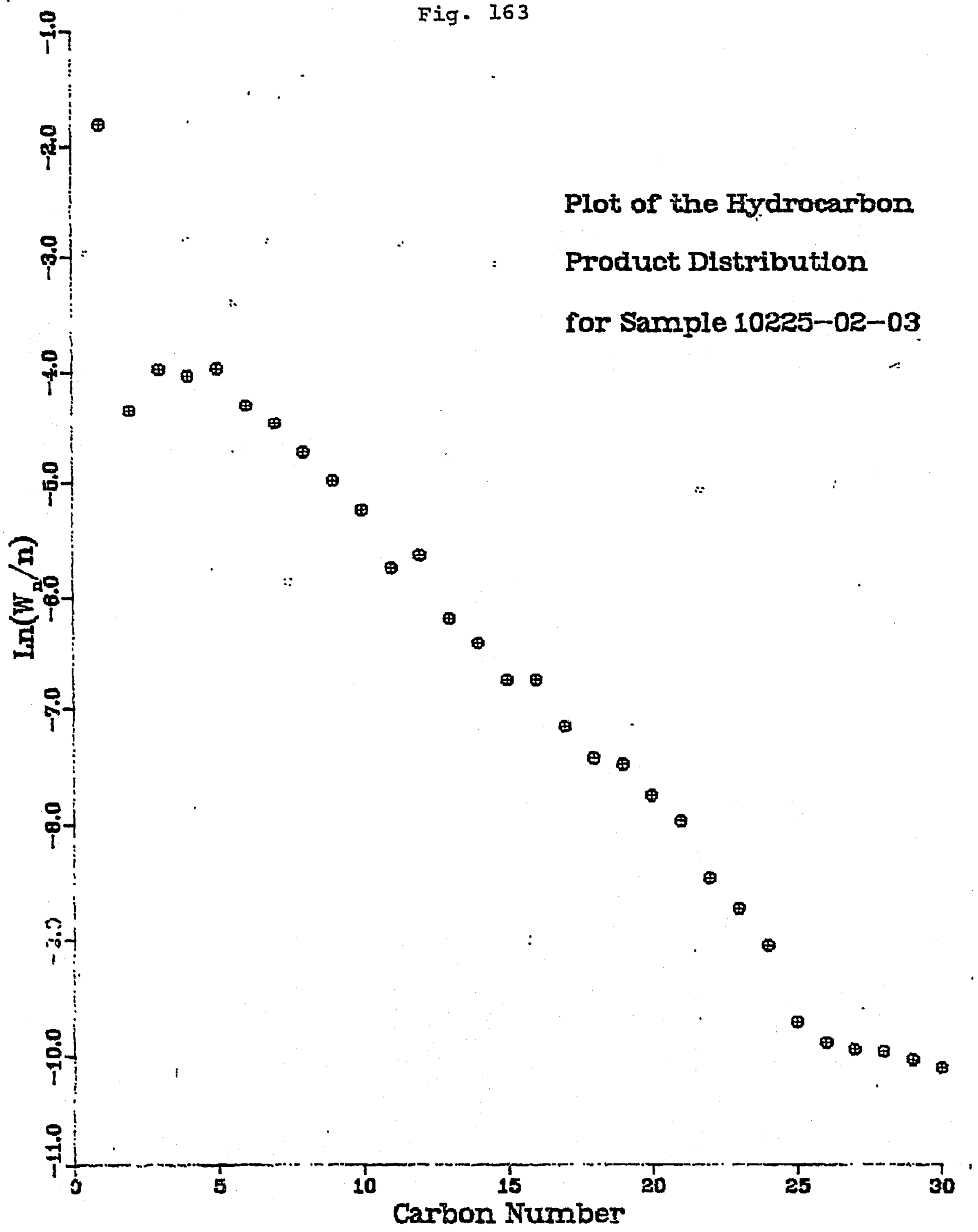

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-02-03
$Ln(W_n/n)$
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 164

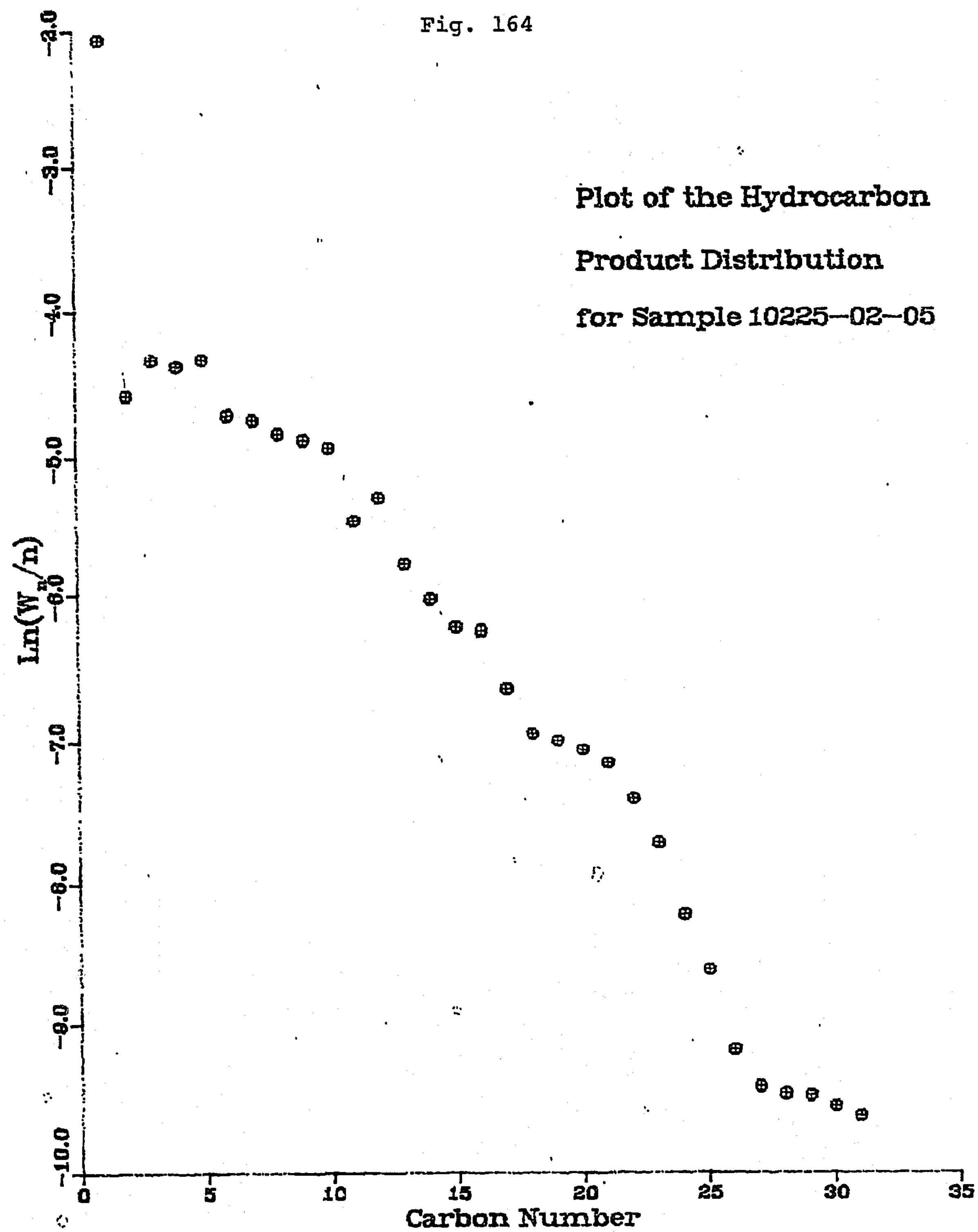

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-02-05
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 165

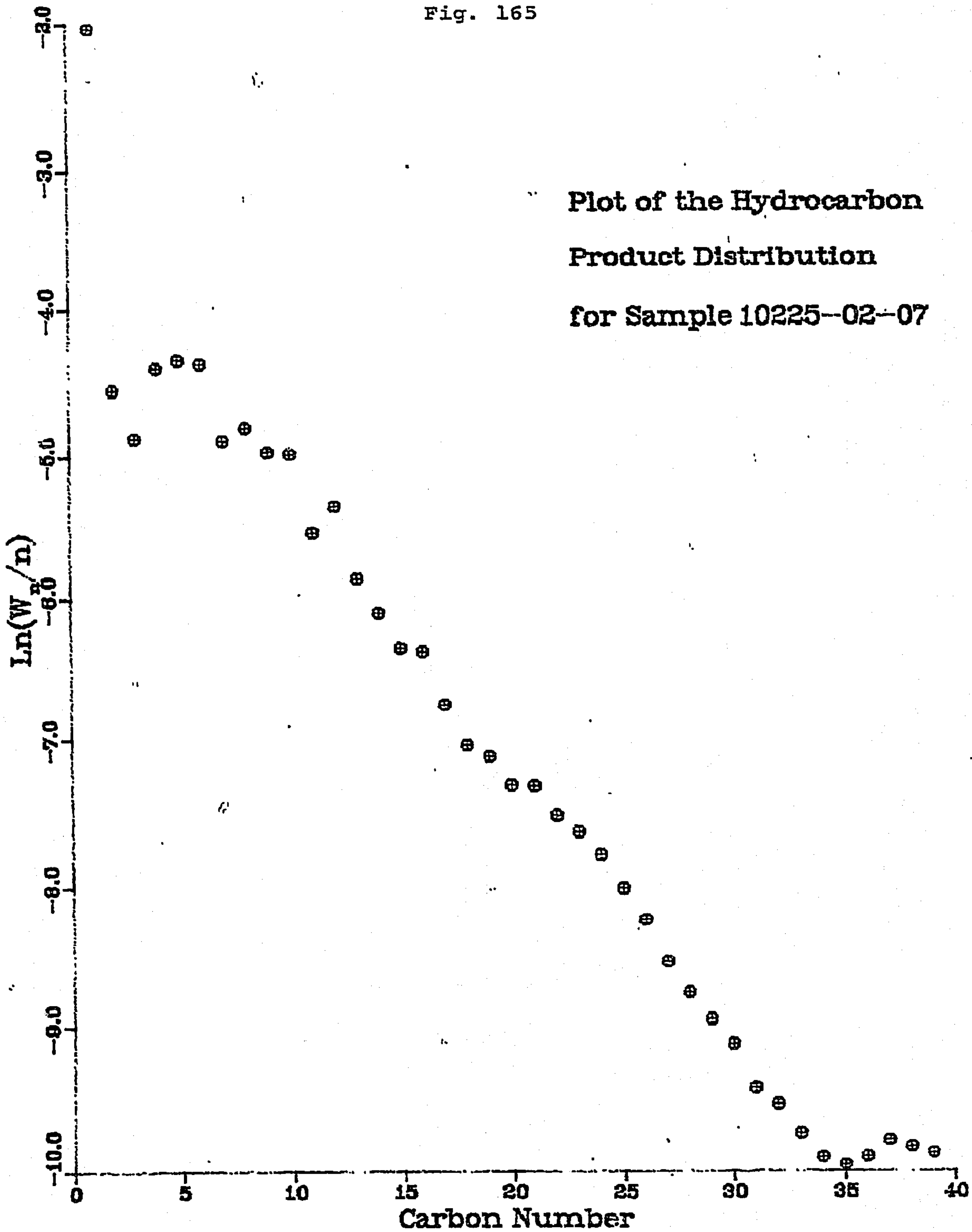

Plot of the Hydrocarbon
Product Distribution
for Sample 10225--02--07
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 166

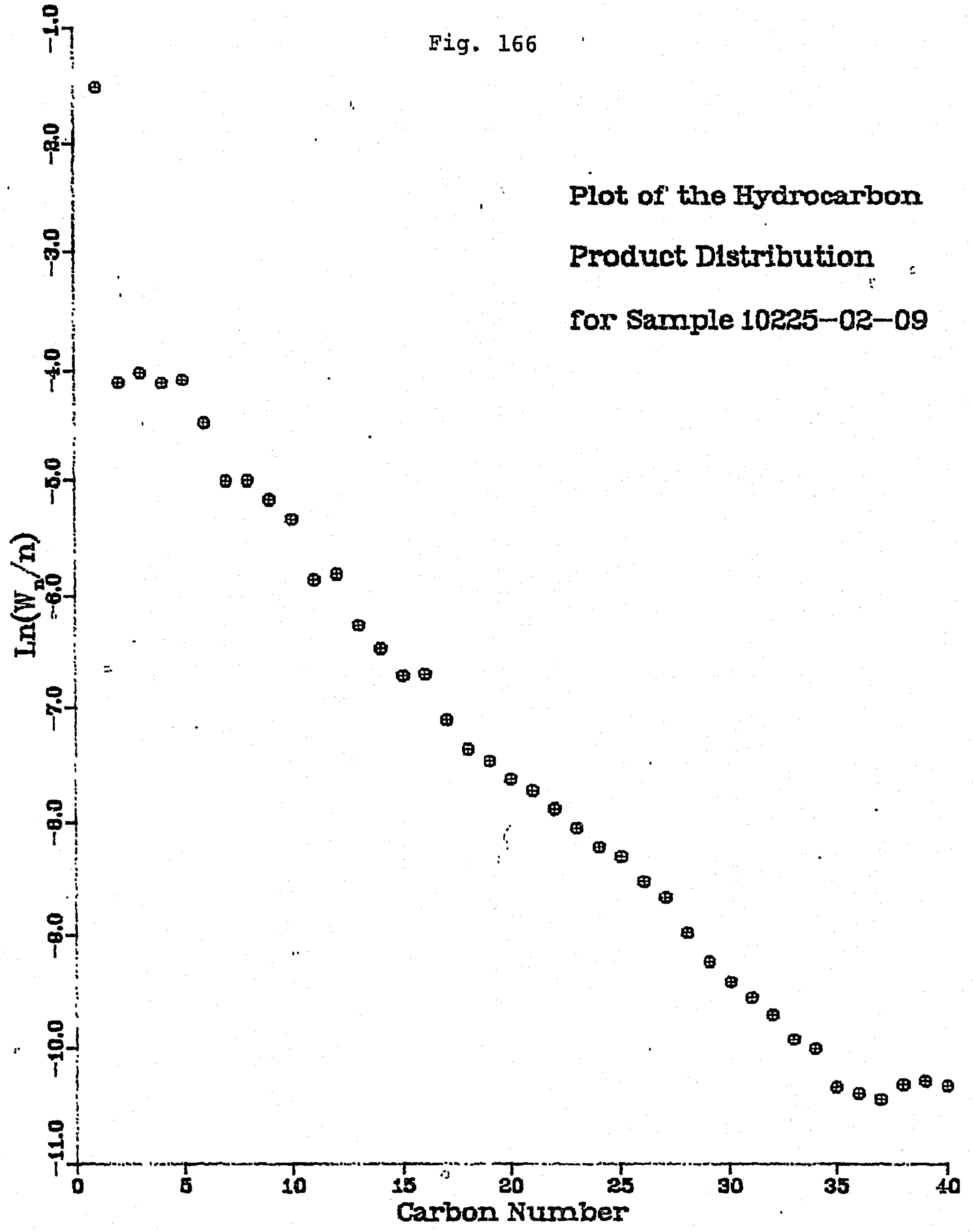
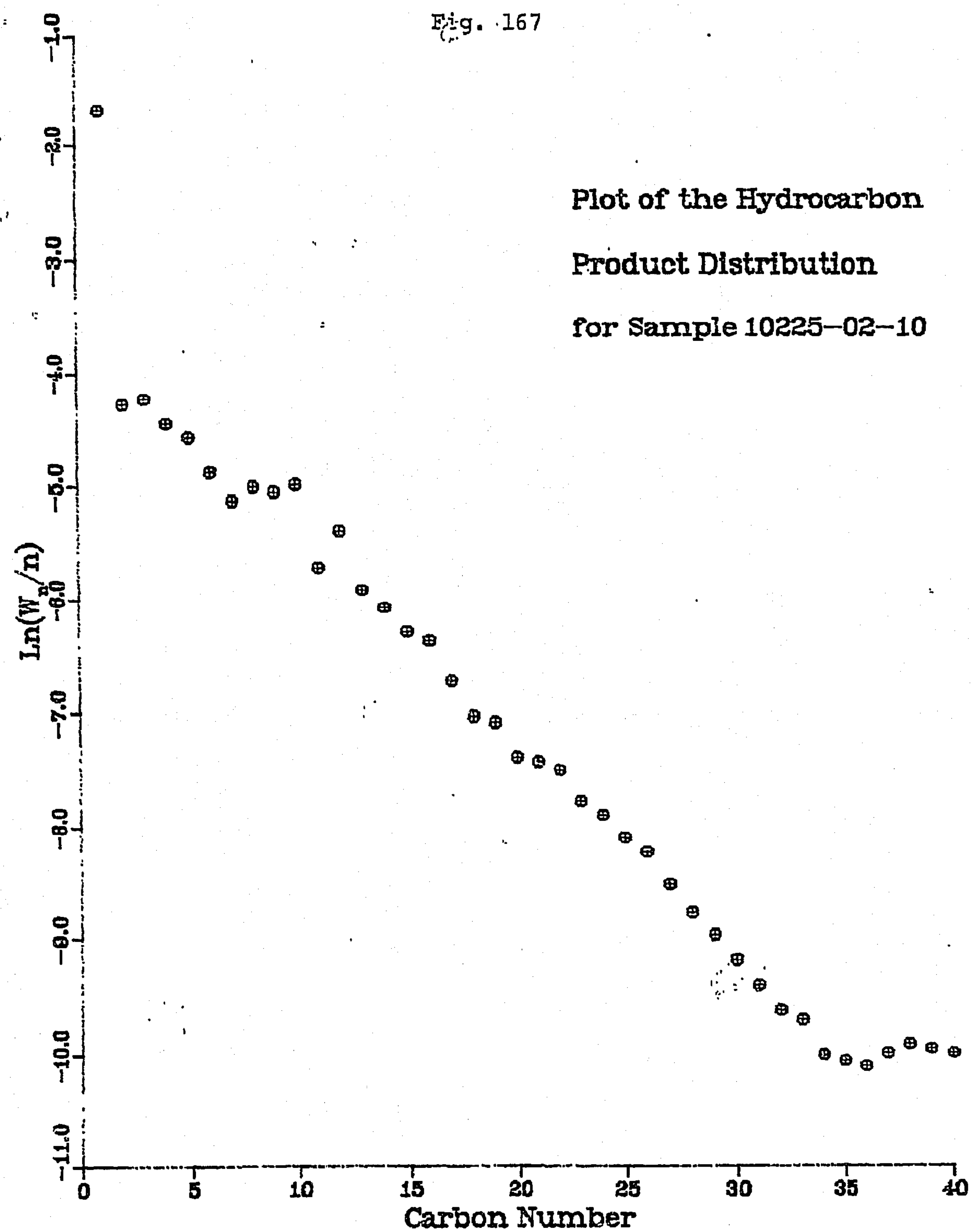
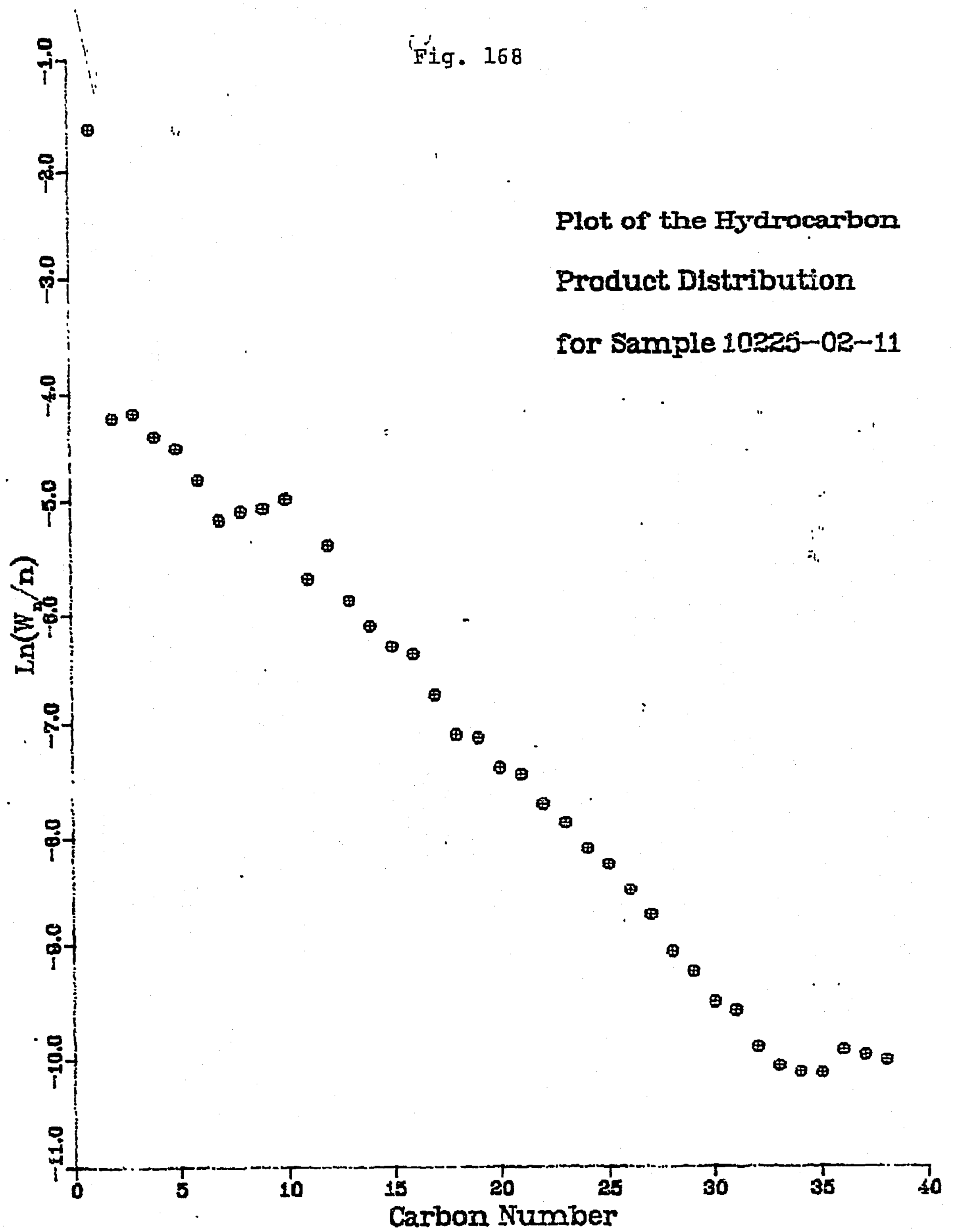

Plot of the Hydrocarbon
Product Distribution
for Sample 10225–02–09
$Ln(W_n/n)$
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 167



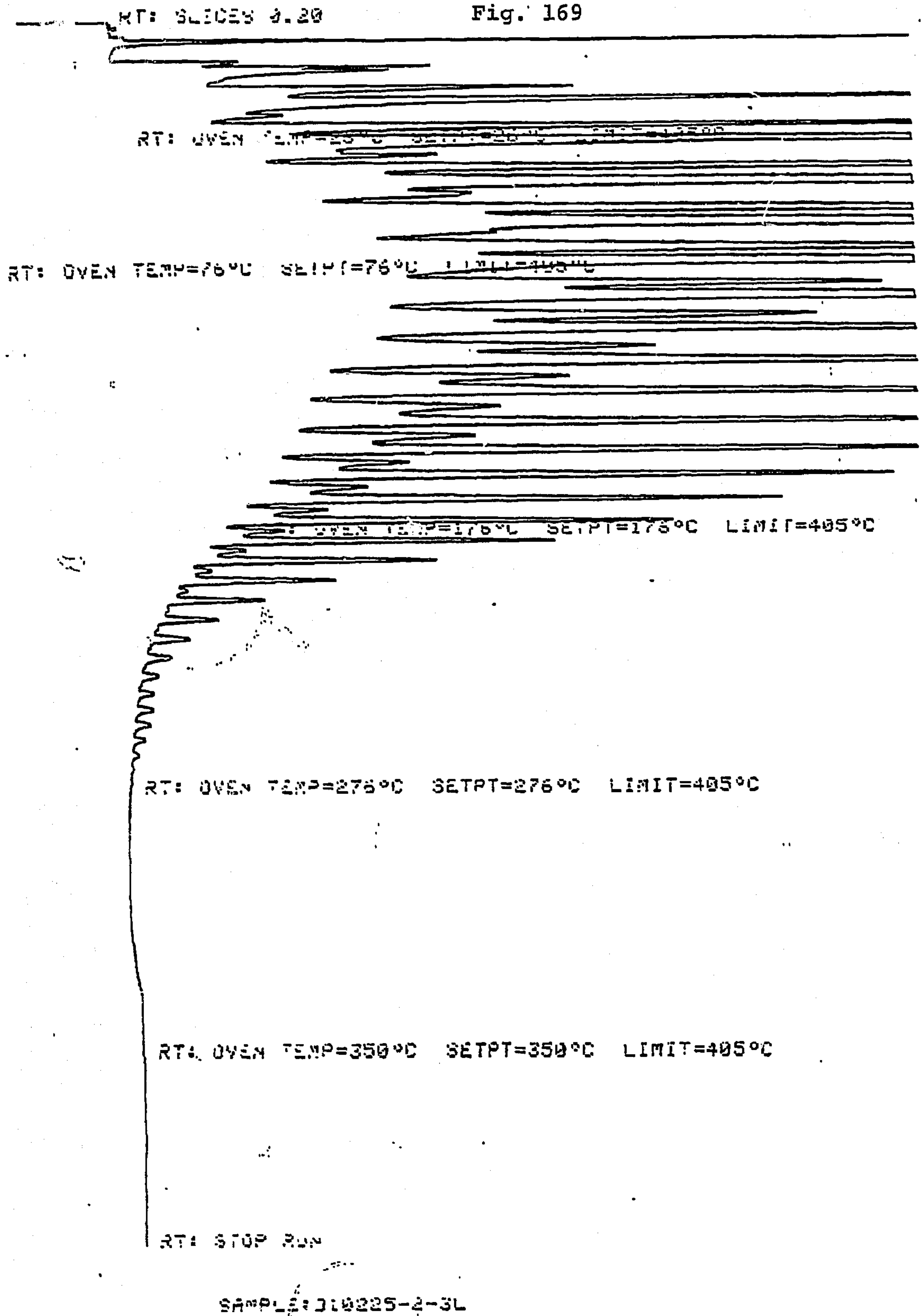
Plot of the Hydrocarbon
Product Distribution
for Sample 10225-02-10
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 168



Plot of the Hydrocarbon
Product Distribution
for Sample 10225-02-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. 169


RT: SLICES 0.20
RT: OVEN TEMP=76°C SETPT=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:310225-2-3L

017

Fig. 170

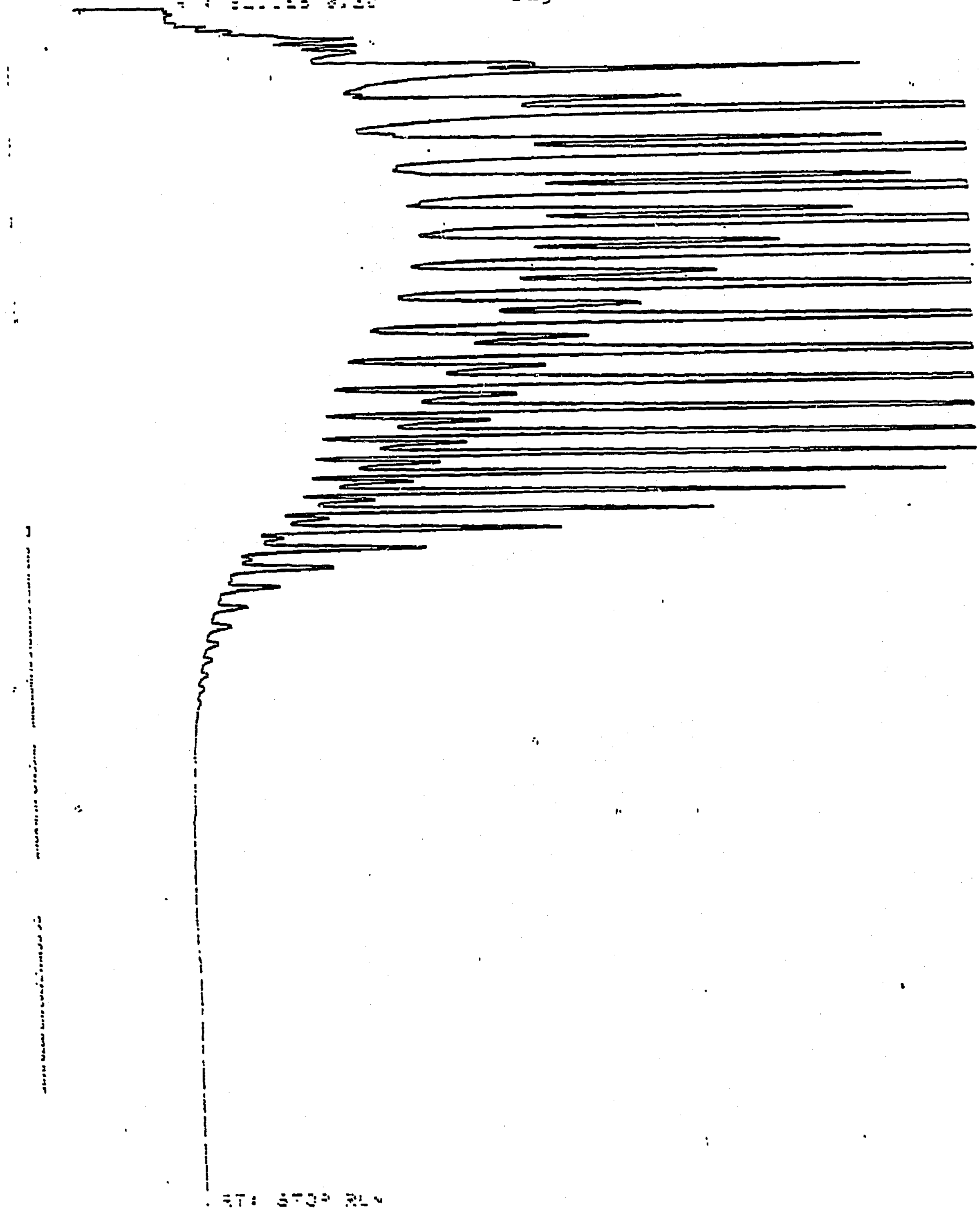


Fig. 171

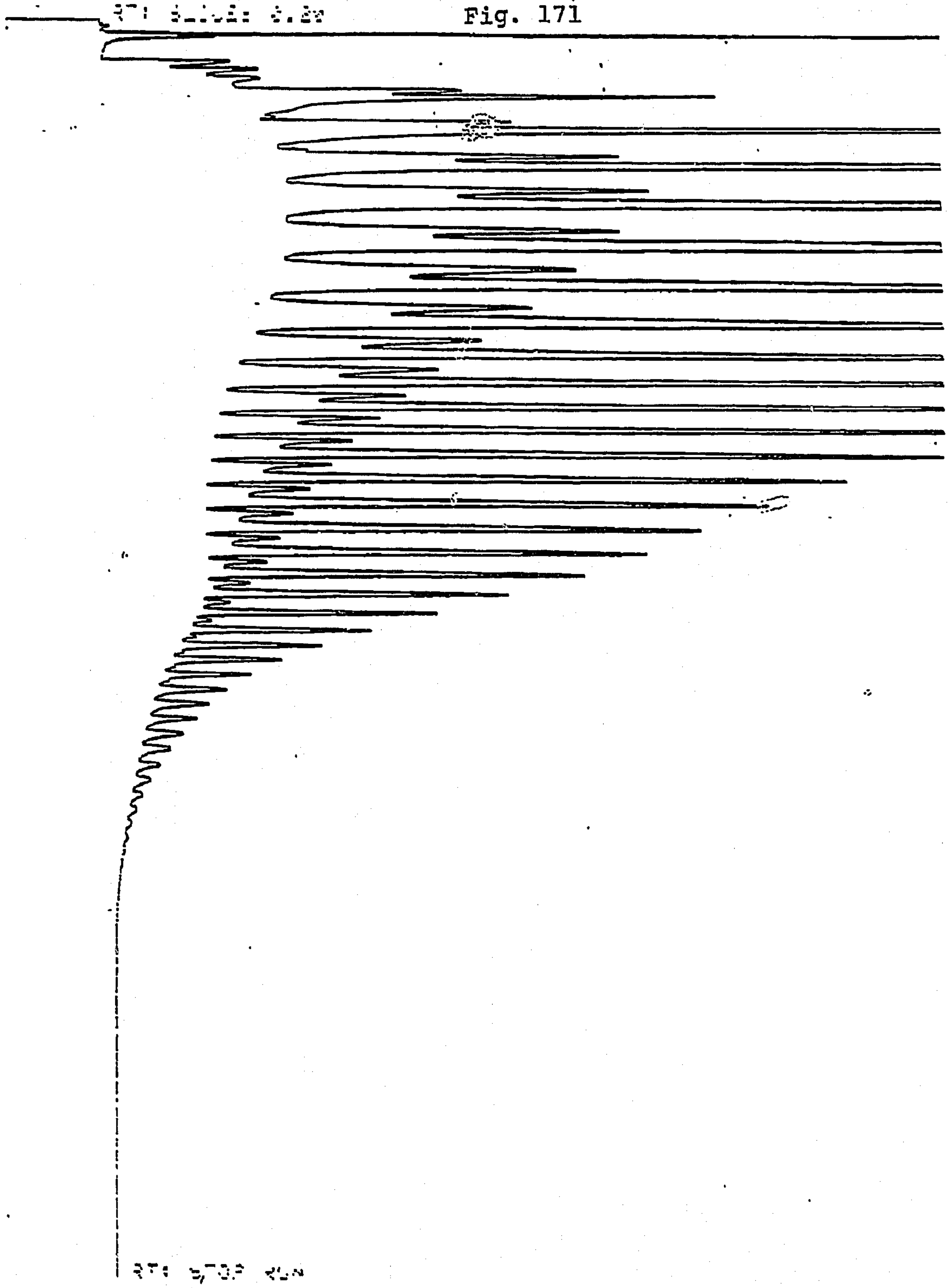


Fig. 172

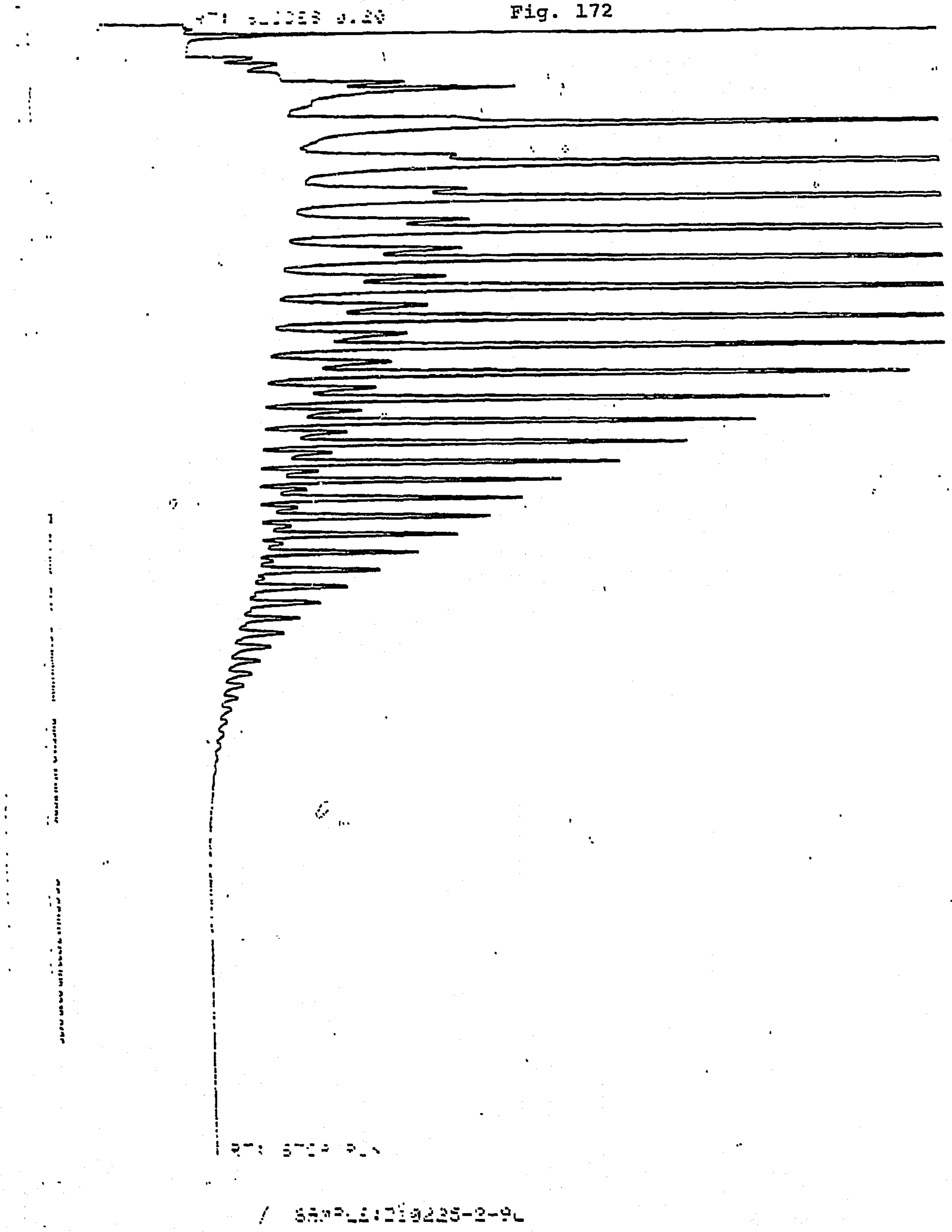


Fig. 173

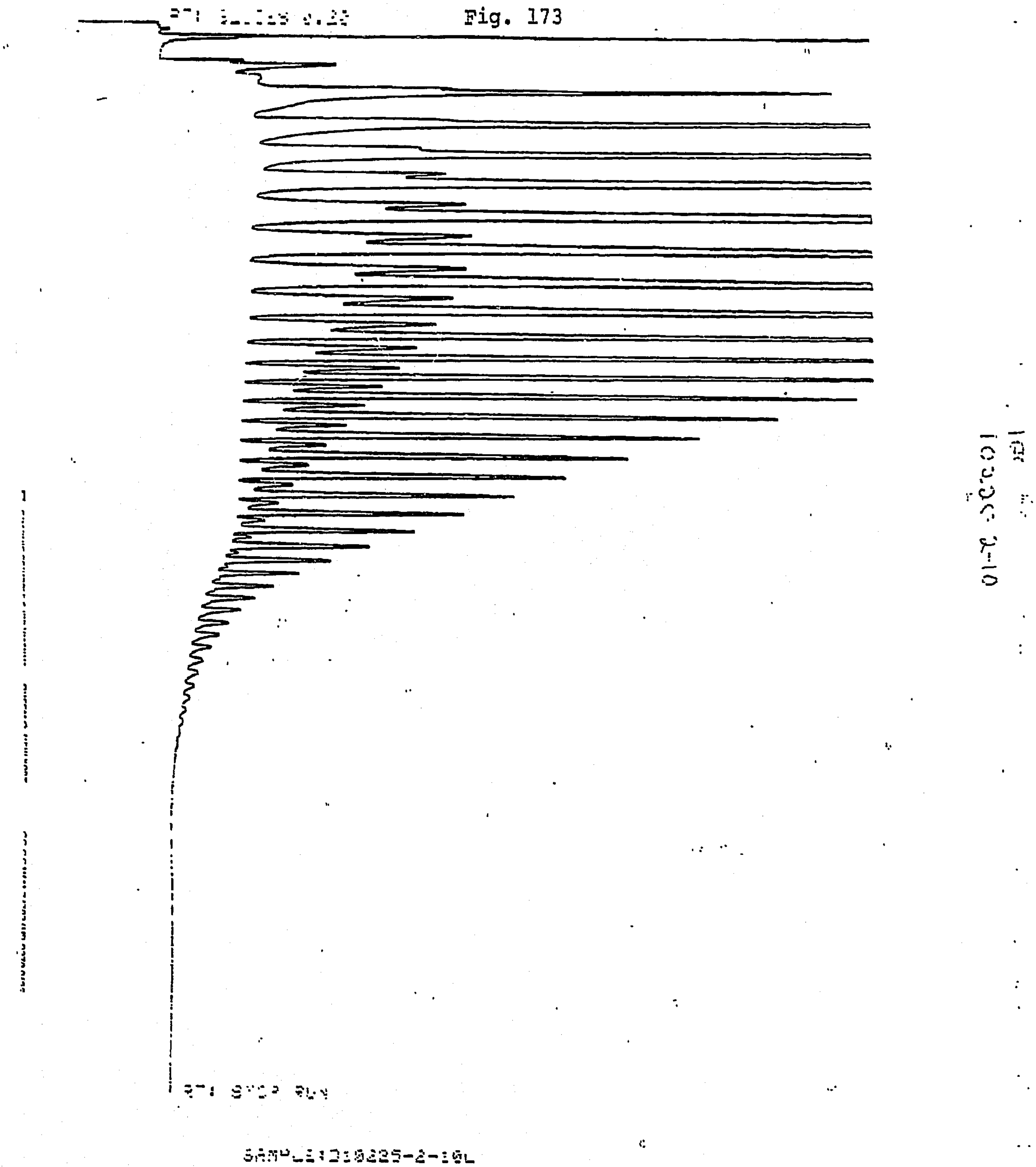


Fig. 174

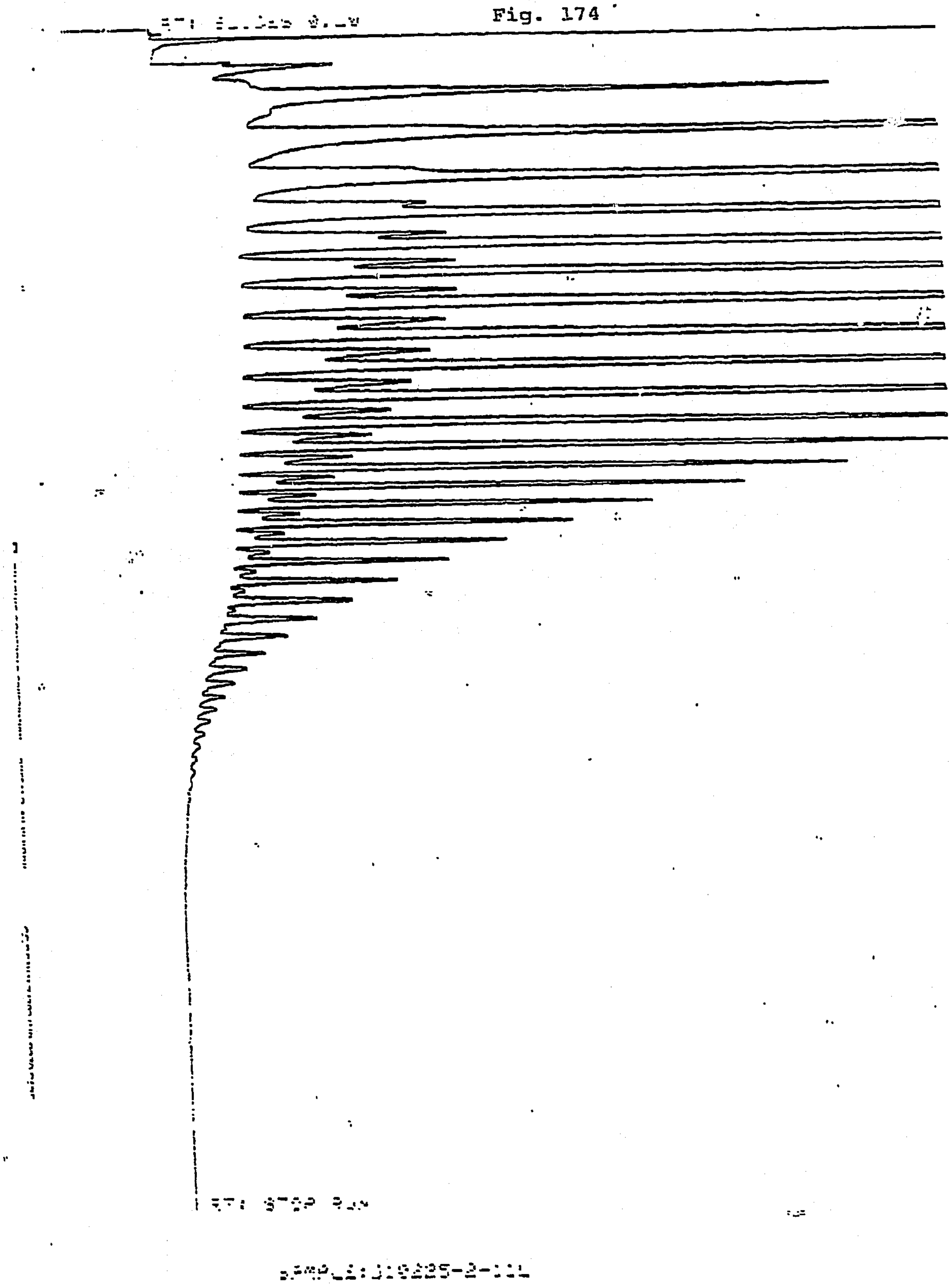


TABLE 11A RESULT OF SYNGAS OPERATION

RUN NO. 10225-02
CATALYST CO-THO2-UCC-107 #10042-97 80 CC 35.6GM (53.1 AFTER RUN +17 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-02-01	225-02-02	225-02-03	225-02-04	225-02-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	20.25	24.17	41.50	49.0	65.5
PRESSURE,PSIG	293	293	299	303	306
TEMP. C	266	266	247	251	249
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	20.25	24.17	17.33	7.50	24.00
EFFLNT GAS LITER	216.33	251.15	147.62	65.04	213.47
GM AQUEOUS LAYER	18.57	22.16	60.24	26.35	84.33
GM OIL	0.00	0.00	29.88	11.70	37.44
MATERIAL BALANCE					
GM ATOM CARBON %	102.07	100.98	94.02	94.96	94.55
GM ATOM HYDROGEN %	101.52	89.82	95.60	97.44	97.61
GM ATOM OXYGEN %	101.30	103.87	100.00	103.67	102.12
RATIO CHX/(H2O+CO2)	1.0149	0.9433	0.8724	0.8265	0.8421
RATIO X IN CHX	3.1438	2.9352	2.2244	2.2850	2.2806
USAGE H2/CO PRODT	1.0270	0.9318	1.7098	1.6005	1.7003
RATIO CO2/(H2O+CO2)	0.7699	0.7656	0.1364	0.1856	0.1460
K SHIFT IN EFFLNT	2.35	1.72	0.03	0.05	0.04
CONVERSION					
ON CO %	91.21	86.29	50.21	53.48	50.06
ON H2 %	93.79	91.91	89.77	90.57	89.03
ON CO+H2 %	92.49	88.94	70.16	72.26	69.85
PRDT SELECTIVITY,WT %					
CH4	48.28	38.09	10.25	13.35	12.74
C2 HC'S	7.11	5.90	1.61	2.17	2.04
C3H8	8.70	7.52	1.33	0.18	1.69
C3H6=	0.63	1.52	2.18	2.17	2.18
C4H10	7.08	6.88	1.07	1.44	1.35
C4H8=	0.75	2.34	3.36	3.61	3.60
C5H12	9.18	11.36	1.79	2.46	2.24
C5H10=	0.28	1.34	4.10	4.21	4.24
C6H14	6.45	9.34	1.89	2.56	2.32
C6H12= & CYCLO'S	0.21	0.79	3.05	5.24	3.06
C7+ IN GAS	11.30	14.92	9.36	9.40	9.82
LIQ HC'S	0.00	0.00	59.99	53.21	54.73

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TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	72.56	62.25	19.80	22.92	23.59
C5 -420 F	27.44	37.75	53.88	49.94	49.04
420-700 F	0.00	0.00	24.11	21.82	24.32
700-END PT	0.00	0.00	2.21	5.32	3.04
C5+-END PT	27.44	37.75	80.20	77.08	76.41
ISO/NORMAL MOLE RATIO					
C4	0.4331	0.5054	0.2359	0.3379	0.2623
C5	2.6647	2.7395	0.7188	1.0135	0.7997
C6	3.9118	3.8977	0.8980	1.1832	0.9537
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	13.1751	4.7212	0.5841	0.0775	0.7409
C4	9.0609	2.8376	0.3078	0.3857	0.3618
C5	31.4016	8.2168	0.4252	0.5681	0.5144
LIQ HC COLLECTION					
PHYS. APPEARANCE			GREEN OIL		GREEN OIL
DENSITY	-	-	0.756	-	0.755
N, REFRACTIVE INDEX	-	-	1.4275	-	1.4266
SIMULT'D DISTILATN					
10 WT % @ DEG F	-	-	249	-	258
16	-	-	279	-	292
50	-	-	403	-	420
84	-	-	573	-	616
90	-	-	625	-	659
RANGE(16-84 %)	-	-	294	-	324
WT % @ 420 F	-	-	56.14	-	50.00
WT % @ 700 F	-	-	96.32	-	94.44

TABLE 11B RESULT OF SYNGAS OPERATION

RUN NO. 10225-02
CATALYST CO-THO2-UCC-107 #10042-97 80 CC 35.6GM (53.1 AFTER RUN +17 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-02-06	225-02-07	225-02-08	225-02-09	225-02-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	71.75	90.0	96.0	118.75	144.75
PRESSURE,PSIG	299	292	291	303	301
TEMP. C	250	252	255	255	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.25	24.50	6.00	28.75	26.00
EFFLNT GAS LITER	59.44	232.99	58.62	280.62	234.70
GM AQUEOUS LAYER	20.89	81.90	22.51	107.86	82.90
GM OIL	11.02	43.21	6.29	30.13	41.70
MATERIAL BALANCE					
GM ATOM CARBON %	103.48	104.90	95.07	94.98	91.09
GM ATOM HYDROGEN %	103.13	101.89	104.49	104.44	103.31
GM ATOM OXYGEN %	106.08	107.95	112.18	112.12	94.48
RATIO CHX/(H2O+CO2)	0.9464	0.9381	0.6951	0.6948	0.9260
RATIO X IN CHX	2.3073	2.2803	2.5081	2.5079	2.4226
USAGE H2/CO PRODT	1.6209	1.5834	1.5441	1.5443	1.6837
RATIO CO2/(H2O+CO2)	0.1962	0.2072	0.2213	0.2211	0.1864
K SHIFT IN EFFLNT	0.06	0.05	0.08	0.08	0.08
CONVERSION					
ON CO %	53.70	53.82	54.12	54.13	55.94
ON H2 %	89.38	90.11	88.68	88.69	85.81
ON CO+H2 %	71.51	71.70	72.22	72.23	71.81
PRDT SELECTIVITY,WT %					
CH4	13.89	13.13	22.70	22.70	19.23
C2 HC'S	2.17	2.14	3.28	3.28	2.71
C3H8	1.87	0.17	3.26	3.26	2.81
C3H6=	2.03	2.14	2.12	2.11	1.46
C4H10	1.56	1.42	2.75	2.75	2.29
C4H8=	3.42	3.55	3.79	3.79	2.28
C5H12	2.62	2.42	4.26	4.26	2.68
C5H10=	3.98	4.14	4.12	4.12	2.39
C6H14	2.47	2.52	3.80	3.79	2.70
C6H12= & CYCLO'S	2.71	5.15	2.98	2.98	1.85
C7+ IN GAS	9.15	9.25	9.54	9.53	6.61
LIQ HC'S	54.13	53.97	37.42	37.43	52.98

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TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	24.94	22.55	37.90	37.89	30.79
C5 -420 F	46.91	49.11	43.02	41.94	41.23
420-700 F	21.65	21.77	15.34	14.99	21.63
700-END PT	6.50	6.57	3.74	5.18	6.36
C5+-END PT	75.06	77.45	62.10	62.11	69.21
ISO/NORMAL MOLE RATIO					
C4	0.3341	0.3379	0.2963	0.2963	0.1326
C5	0.9993	1.0135	0.9858	0.9858	0.2303
C6	1.1377	1.1832	0.9785	0.9785	0.2259
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.8812	0.0775	1.4724	1.4724	1.8349
C4	0.4421	0.3857	0.6996	0.6996	0.9698
C5	0.6387	0.5681	1.0057	1.0057	1.0906
LIQ HC COLLECTION					
PHYS. APPEARANCE	-	GREEN OIL	-	GREEN OIL	MILKY OIL
DENSITY	-	0.758	-	0.755	0.757
N, REFRACTIVE INDEX	-	1.4274	-	1.4266	1.4264
SIMULT'D DISTILATN					
10 WT % @ DEG.F	-	259	-	261	260
16	-	297	-	300	300
50	-	438	-	441	440
84	-	666	-	677	663
90	-	723	-	741	724
RANGE(16-84 %)	-	369	-	377	363
WT % @ 420 F	-	47.50	-	46.11	47.18
WT % @ 700 F	-	87.83	-	86.15	88.00

TABLE 11C RESULT OF SYNGAS OPERATION

RUN NO. 10225-02
CATALYST CO-THO2-UCC-107 #10042-97 80 CC 35.6GM (53.1 AFTER RUN +17 G)
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 400 GHSV

RUN & SAMPLE NO.	10225-02-11
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	161.75
PRESSURE,PSIG	298
TEMP. C	251
FEED CC/MIN	400
HOURS FEEDING	17.00
EFFLNT GAS LITER	183.20
GM AQUEOUS LAYER	61.74
GM OIL	28.80
MATERIAL BALANCE	
GM ATOM CARBON %	105.56
GM ATOM HYDROGEN %	118.19
GM ATOM OXYGEN %	110.83
RATIO CHX/(H2O+CO2)	0.9001
RATIO X IN CHX	2.4508
USAGE H2/CO PRODT	1.6702
RATIO CO2/(H2O+CO2)	0.1933
K SHIFT IN EFFLNT	0.09
CONVERSION	
ON CO %	54.61
ON H2 %	85.19
ON CO+H2 %	70.77
PRDT SELECTIVITY,WT %	
CH4	20.49
C2 HC'S	2.90
C3H8	2.99
C3H6=	1.56
C4H10	2.44
C4H8=	2.43
C5H12	2.86
C5H10=	2.55
C6H14	2.88
C6H12= & CYCLO'S	1.97
C7+ IN GAS	7.04
LIQ HC'S	49.92

TOTAL	100.00
SUB-GROUPING	
C1 -C4	32.79
C5 -420 F	41.03
420-700 F	21.13
700-END PT	5.05
C5+-END PT	67.21
ISO/NORMAL MOLE RATIO	
C4	0.1326
C5	0.2303
C6	0.2259
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	1.8349
C4	0.9698
C5	1.0906
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLDY-GR OIL
DENSITY	0.753
N, REFRACTIVE INDEX	1.4244
SIMULT'D DISTILATN	
10 WT % @ DEG F	261
16	302
50	439
84	646
90	701
RANGE(16-84 %)	344
WT % @ 420 F	47.56
WT % @ 700 F	89.88

XIII. SUMMARY

Results of the last two quarters' investigations show some general trends in performance for the Task 2 catalysts.

The metal component has the largest effect on the activity and on the general distribution of hydrocarbon products (methane, C_2-C_4 hydrocarbons, gasoline, diesel, and heavies) (Table 12). All the cobalt catalysts produce significant quantities of methane, but only small amouants of the C_2-C_4 hydrocarbons. The low C_2 production gives cobalt catalysts a lower C_1-C_2 yield than those of the iron catalysts, despite the high production of methane. Yields of motor fuels (gasoline and diesel oil) are also much higher with cobalt catalysts, many of which, despite high methane production, yielded more than 70 percent gasoline and diesel oil. The iron catalysts tested in this quarter yielded 45-50 percent hydrocarbons in the motor fuel range, but some iron catalysts tested previously produced more than 55 percent. The principal difference in motor fuel production between iron and cobalt catalysts is in the amount of the diesel oil cut; both produced similar quantities of gasoline.

The Molecular Sieve strongly affects the type, if not the carbon number, of the hydrocarbon product. Highly acidic Sieves like UCC-109 and LZ-Y-82 initially produce highly isomerized hydrocarbons. Formation of the hydrogen-deficient coke results in simultaneous formation of hydrogen-rich paraffinic effluent.

Such coking quickly deactivates the acidity of these Molecular Sieves, thereby lessening their influence on the hydrocarbon products.

UCC-111 has only a minor chemical effect on product hydrocarbons, simply isomerizing the olefinic double bond and leaving the carbon skeleton unchanged. Small as this chemical effect may be, the resulting changes in pour point and octane number of the liquid are significant and important. Furthermore, this activity does not lead to coking or deactivation of the Molecular Sieve.

The activity of UCC-101 falls between the two extremes. Its acid activity is not so great as to induce rapid coking, but it is able to effect more than a simple double-bond migration. Also, some UCC-101 catalysts seem to show a carbon number cut-off in the product which lies just above the upper boiling range of diesel oil.

Based on yield of liquid hydrocarbon fuels, cobalt catalysts seem to be the most promising. They still need modification, however, to improve product quality, and to make a less waxy heavy product.

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TABLE 12

a) Iron based catalysts

	Fe/K + UCC-109	Fe/K + $AlPO_4$-11	Fe/K on LZ-105-6
Conversion	50	77	36
C_1-C_2	22.1	22.1	24.8
C_3-C_4	28.5	27.4	30.4
gasoline (C_5 - 420°F)	43.0	38.5	41.4
diesel oil (420-700°F)	5.5	11.0	2.9
heavies (700°F+)	0.9	1.7	0.4
motor fuel (C_5-700°F)	48.5	49.4	44.3

TABLE 12 continued

b) Cobalt based catalysts

	Co on LZ-105	Co/Th/K on LZ-Y82	Co on UCC-101	Co/Th/K on UCC-101	Co/Th on UCC-107
Conversion	28	55	53	52	70
C_1-C_2	16.7	14.2	14.5	16.2	14.8
C_3-C_4	9.6	9.3	7.5	9.1	8.8
gasoline (C_5-420°F)	43.6	47.9	40.0	46.1	49.0
diesel oil (420-700°F)	24.1	25.0	32.2	22.0	23.3
heavies (700°F+)	5.9	3.7	5.9	6.5	3.0
motor fuel (C_5-700°F)	67.7	72.9	72.1	68.1	73.4

Appendix C. ANALYTICAL TECHNIQUES

By J. M. Basile

Efforts to evaluate liquid chromatography as a viable alternative to FIA for the separation of hydrocarbon group types from the total C_5^+ liquid product have been concluded.

Samples received from the one remaining LC manufacturer, IBM, were evaluated with the Envirochem gas chromatograph.

Results were consistent with those of samples tested previously. Separation of group types was again incomplete, due to the inability of present LC column technology to handle the wide boiling range of the samples under investigation.

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Appendix D. SURFACE STUDIES

By G. A. Somorjai

Examination of the catalytic hydrogenation of carbon monoxide has progressed in two major directions during the past three months. We have continued the study of the thorium oxide catalysts, and have characterized several new rhodium catalysts.

1. Thorium Oxide Catalysts

Thorium dioxide has been shown to be an active catalyst in synthesizing methanol. At a space velocity of 5000 Hr^{-1}, a total pressure of 50 atmospheres (carbon monoxide:hydrogen ratio = 1), and a temperature of 320C, carbon conversions of 3 percent can be obtained. This yield is comparable to that obtained with zinc oxide-chroma catalysts. The measured activation energy for the methanol synthesis is 11 kilocalories per mole.

These thorium catalysts, which were prepared by low-temperature calcination on thorium oxycarbonate, show very even activity over long periods of time. Unlike catalysts based on copper oxide, they require no carbon dioxide to maintain the methanol synthesis.

Product distributions can be varied by changing the acid-base properties of the thoria catalysts. Alkali metal-promoted thorias produce more isobutanol and less gaseous hydrocarbons as side products than do the more acidic thorias. However, the intrinsic activity for methanol synthesis does not appear to be a function of the alkali metal concentration.

2. <u>Rhodium Catalysts</u>

We have prepared a number of rhodium compounds and have characterized them by scanning electron microscopy, X-ray powder diffraction, AES and XPS. $CuRh_2O_4$ has been shown to be catalytically inactive. Compounds to be tested for catalytic activity in the future include Na_2RhO_3, K_2RhO_3, and Cs_2RhO_3. The X-ray photo-electron spectrometer for the new UHV system is being built and should be installed in the Fall.