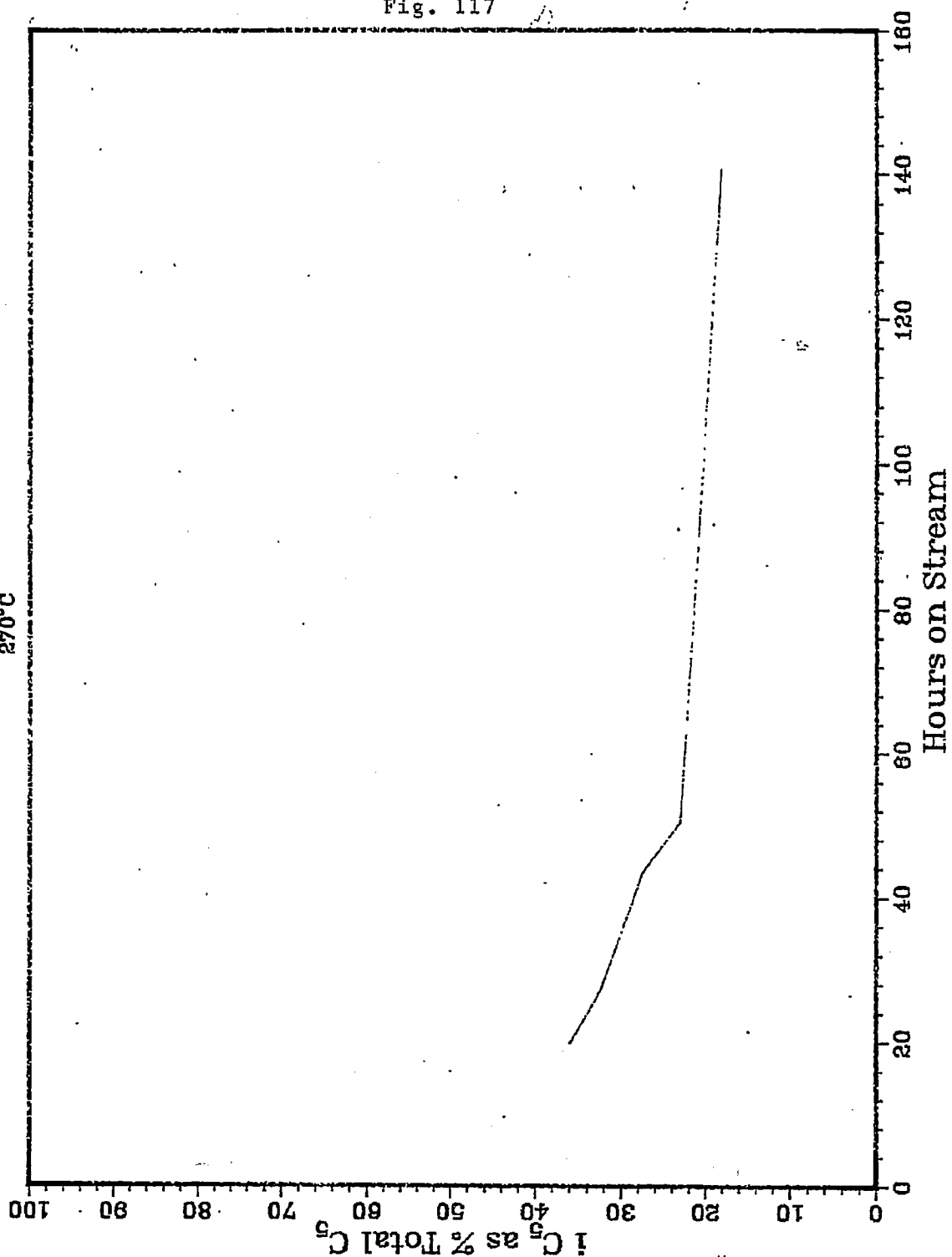


RUN 10112-17

1:1 H₂:CO
290 PSIG
270°C



RUN 10112-17

1:1 H₂:CO
290 PSIG
270°C

Fig. 118

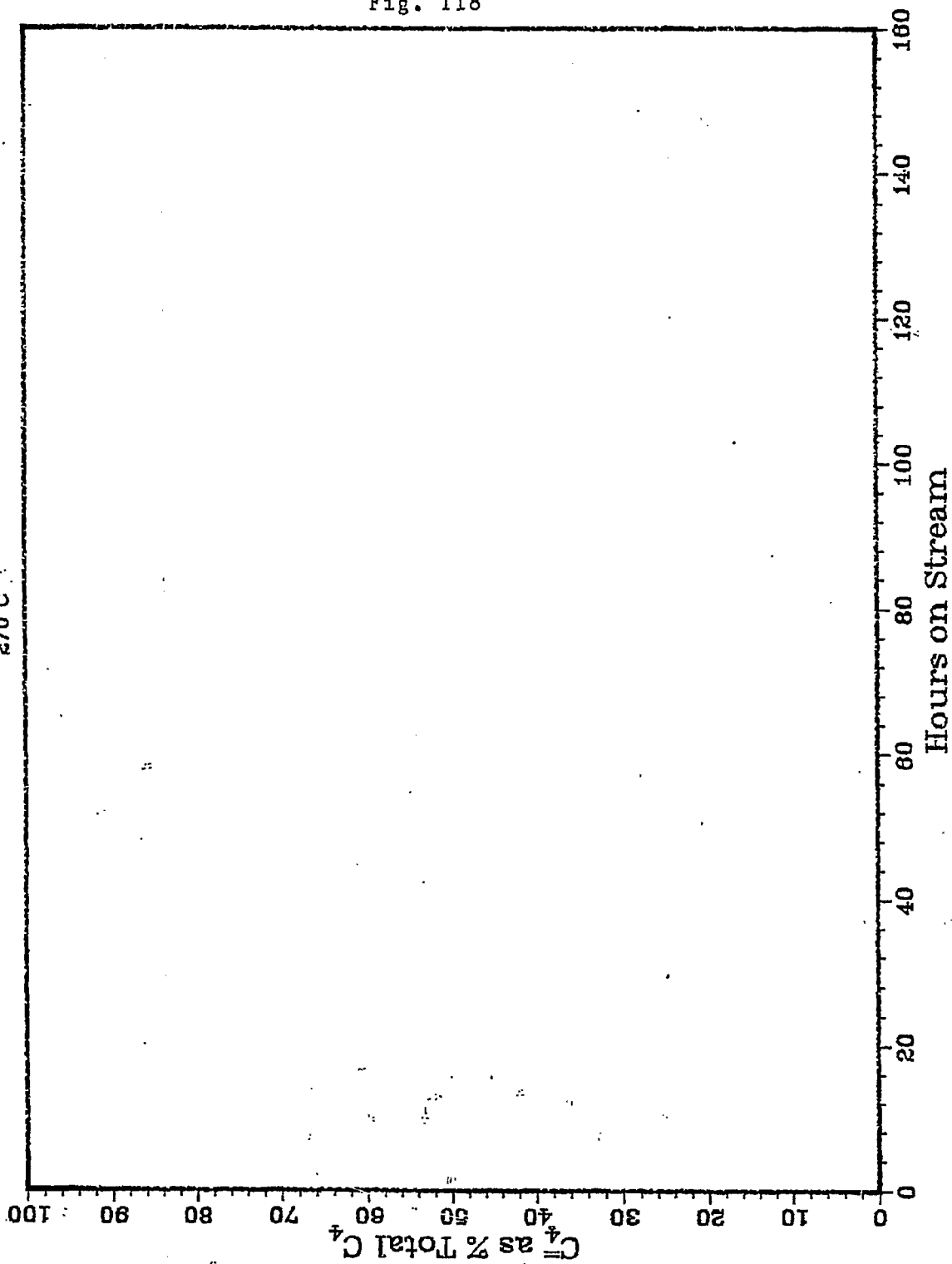


Fig. 119

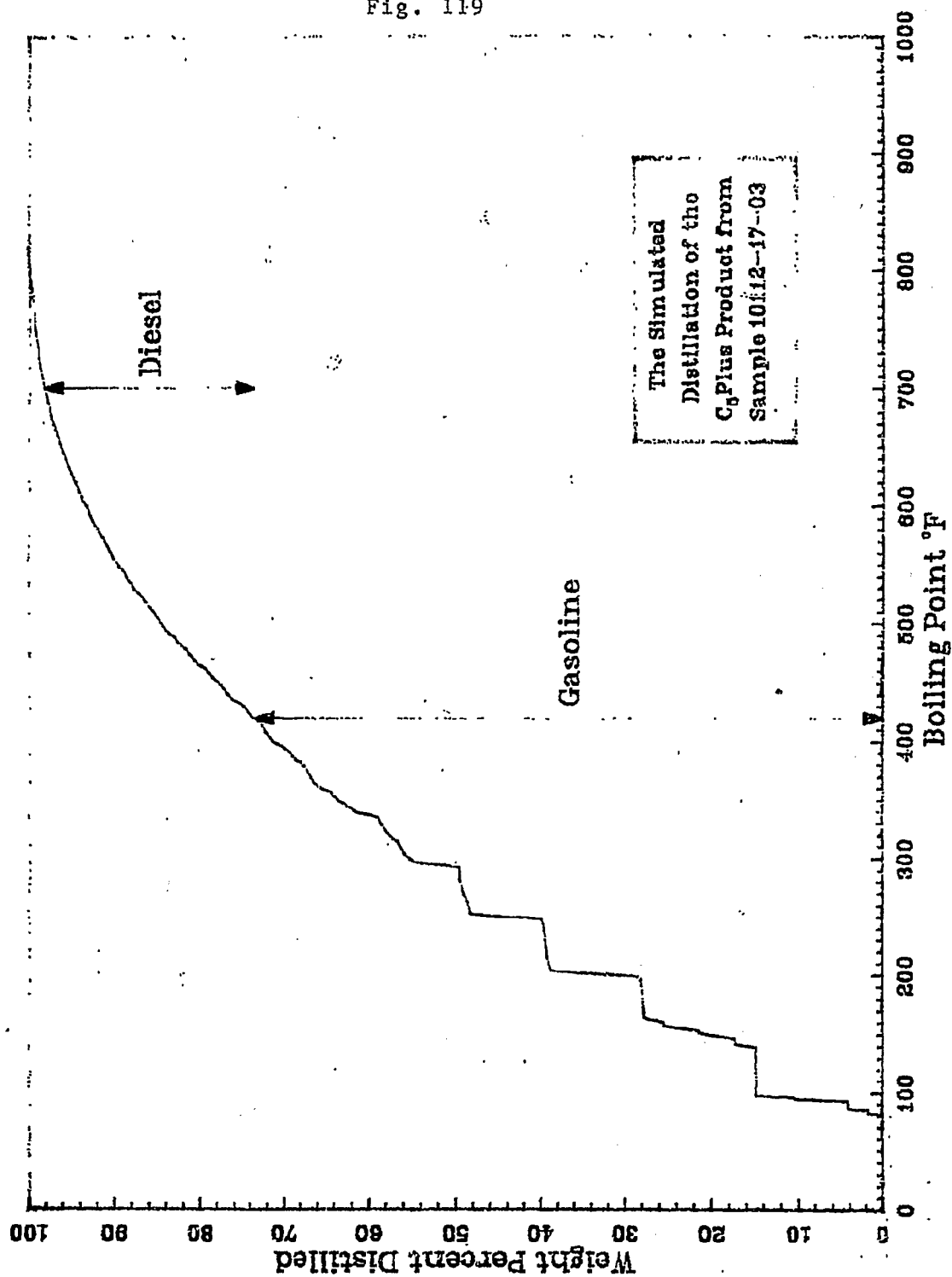


Fig. 120

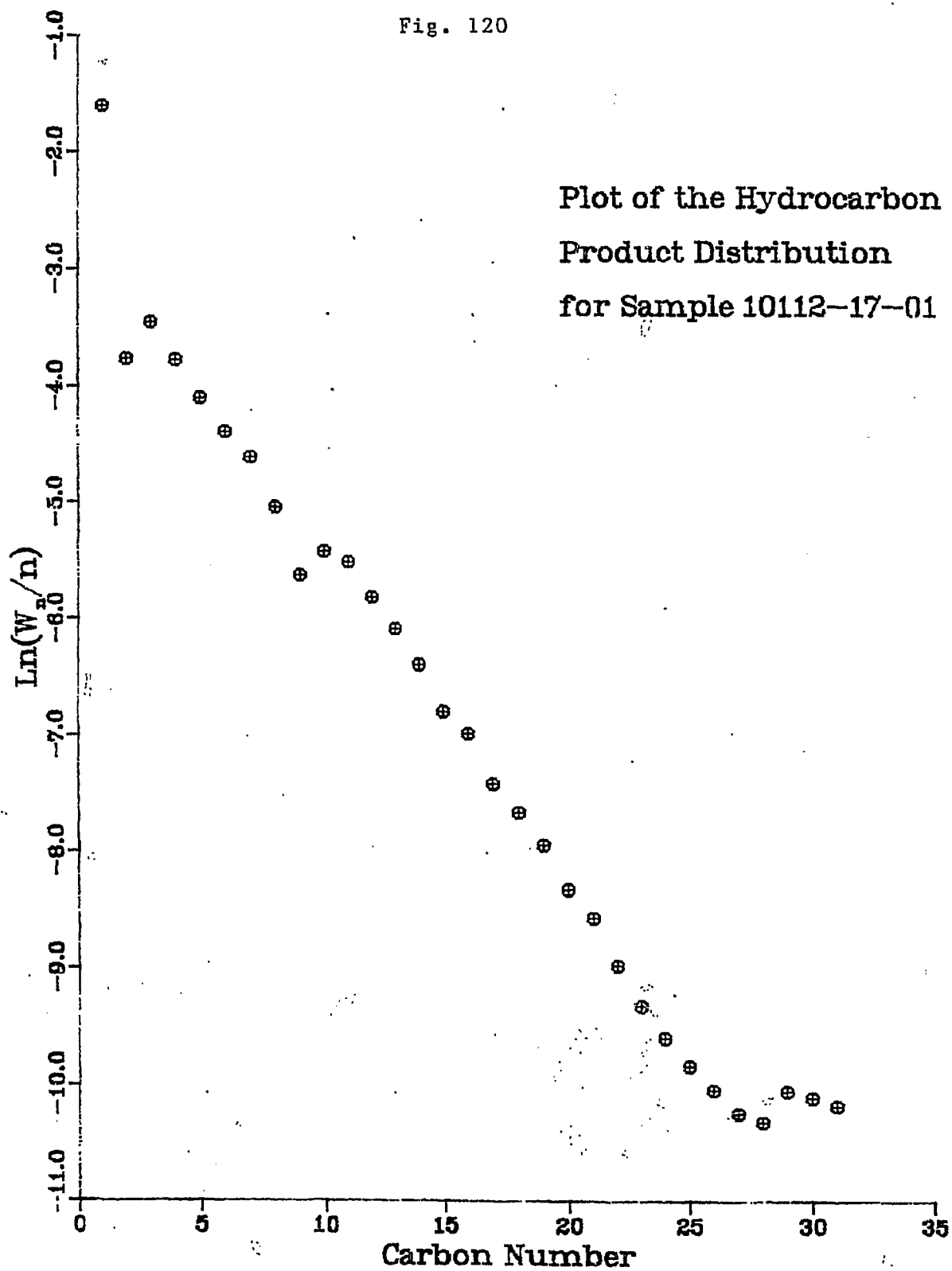


Fig. 121

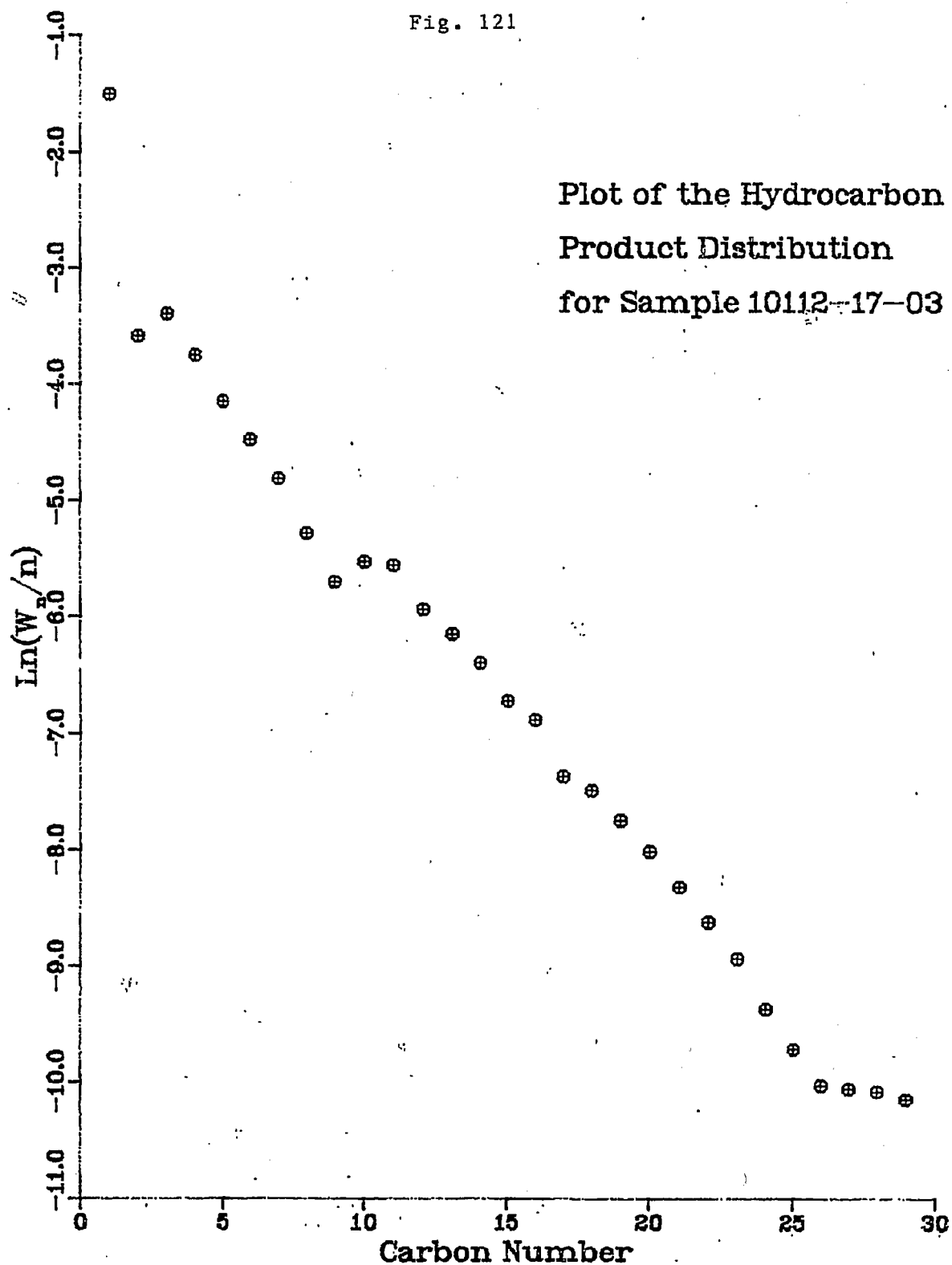
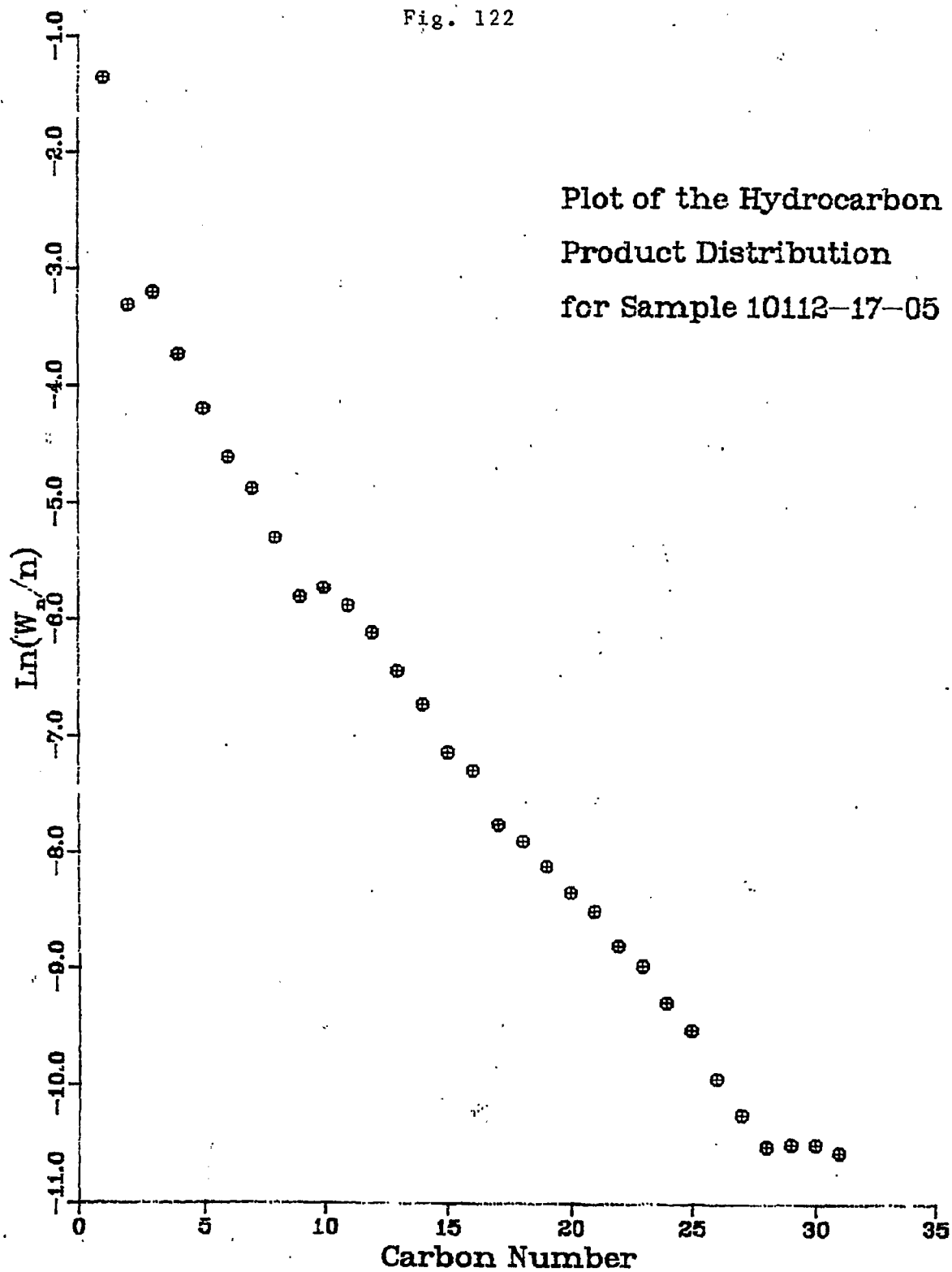


Fig. 122



RT: 8.1023 0.20

Fig. 123

RT: OVEN TEMP=25°C SETPT=25°C LIMIT=405°C

RT: OVEN TEMP=75°C SETPT=75°C LIMIT=405°C

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

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

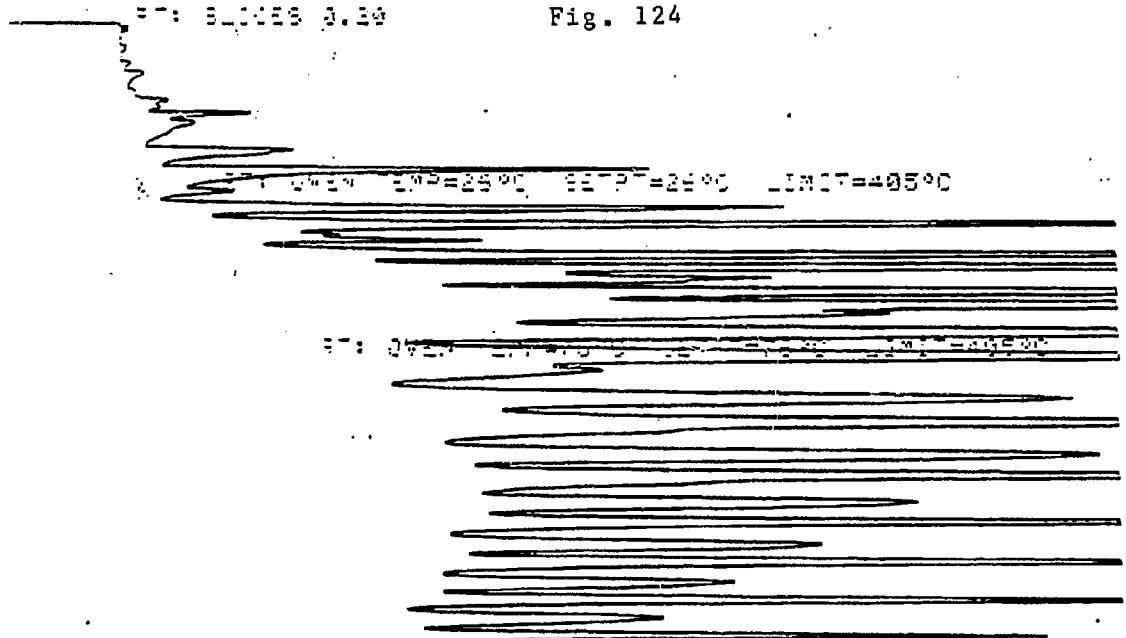
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE: 10112-17-1L

RT: 8-10-68 9.30

Fig. 124



RT: OVEN TEMP=25°C SETPT=25°C LIMIT=405°C

RT: OVEN TEMP=25°C SETPT=25°C LIMIT=405°C

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

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

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

RT: STOP RUN

SAMPLE:10112-17-3L

RT: SLICES 3.20

Fig. 125

RT: OVEN TEMP=25°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:10112-17-SL

TABLE 18 RESULT OF SYNGAS OPERATION

RUN NO. 10112-17
 CATALYST CO/TH/X2+UCC-101 #10252-61C 80 CC 35.0 CM (33.9 AFTER RUN -1.1G)
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-17-01	112-17-02	112-17-03	112-17-04	112-17-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	20.0	27.5	43.5	50.5	140.5
PRESSURE, PSIG	302	290	294	293	293
TEMP. C	271	271	271	266	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	20.00	7.50	23.50	7.00	97.00
EFFLNT GAS LITER	261.20	109.50	350.50	107.08	1584.10
GM AQUEOUS LAYER	40.00	14.28	44.75	10.30	142.77
GM OIL	9.47	3.64	11.42	1.86	25.78
MATERIAL BALANCE					
GM ATOM CARBON %	90.82	99.96	99.83	96.97	100.27
GM ATOM HYDROGEN %	91.79	98.17	99.72	93.08	98.79
GM ATOM OXYGEN %	94.96	101.91	102.16	96.97	101.03
RATIO CHX/(H2O+CO2)	0.8662	0.9367	0.9236	1.0000	0.9696
RATIO X IN CHX	2.4780	2.5043	2.5262	2.5664	2.6211
USAGE H2/CO PRODT	1.6369	1.6234	1.6475	1.6948	1.6613
RATIO CO2/(H2O+CO2)	0.2070	0.2290	0.2198	0.2183	0.2385
K SHIFT IN EFFLNT	0.15	0.18	0.18	0.18	0.21
CONVERSION					
ON CO %	36.58	35.87	34.90	30.48	30.27
ON H2 %	62.95	60.91	59.48	53.82	51.68
ON CO+H2 %	49.83	48.28	47.18	41.91	40.90
PRDT SELECTIVITY, WT %					
CH4	20.07	21.21	22.28	23.83	25.78
C2 HC'S	4.62	4.96	5.52	5.72	7.30
C3H8	4.38	4.74	4.79	5.53	6.50
C3H6=	5.03	5.37	5.25	7.00	5.76
C4H10	3.31	3.43	3.35	3.94	3.76
C4H8=	5.87	6.27	6.04	7.24	5.84
C5H12	3.57	3.51	3.19	3.34	3.05
C5H10=	4.71	4.95	4.67	5.61	4.49
C6H14	4.13	3.92	3.45	3.35	3.02
C6H12= & CYCLO'S	3.30	3.47	3.32	3.50	2.95
C7+ IN GAS	16.36	14.70	14.12	15.73	16.48
LIQ HC'S	24.65	23.47	24.03	15.20	15.08
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	43.29	45.99	47.23	53.25	54.94
C5 -420 F	43.65	40.40	38.84	36.71	35.11
420-700 F	12.06	12.64	12.94	8.92	8.85
700-END PT	1.00	0.97	0.99	1.11	1.11
C5+-END PT	56.71	54.01	52.77	46.74	45.06
ISO/NORMAL MOLE RATIO					
C4	0.2356	0.2166	0.1852	0.2085	0.1320
C5	0.5599	0.4770	0.3814	0.3018	0.2249
C6	0.8712	0.7211	0.5716	0.5007	0.3571
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.8311	0.8413	0.8717	0.7541	1.0763
C4	0.5454	0.5280	0.5350	0.5252	0.6212
C5	0.7368	0.6885	0.6651	0.5790	0.6607
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY BL OIL		CLDY BL OIL		CLR GR OIL
DENSITY	0.760		0.765		0.768
N, REFRACTIVE INDEX	1.4290		1.4308		1.4329
SIMULT'D DISTILATN					
10 WT % @ DEG F	300		309		329
16	323		335		360
50	428		445		466
84	569		591		627
90	617		634		674
RANGE(16-84 %)					
	246		256		267
WT % @ 420 F					
	47.00	42.00	42.00	34.00	34.00
WT % @ 700 F					
	95.95	95.86	95.86	92.67	92.67

IX. RUN 8 (10112-18) with Catalyst 8 (Co/X₃ + UCC-101)

This catalyst, the third of five treated with a metal additive, was prepared by a different technique than Catalyst 7. The metal component was prepared by impregnating a precipitate of cobalt oxide $\cdot XH_2O$ with a salt of the additive to give 4 percent additive on the cobalt. This was physically mixed with UCC-101 in a MC:SSC ratio of 3:14, bonded with 15 percent SiO_2 , and formed as an extrudate.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4 's are plotted against time on stream in Figs. 126-129. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 130-131. Carbon number product distributions are plotted in Figs. 132-138. Chromatograms from simulated distillations are reproduced in Figs. 139-145. Detailed material balances appear in Tables 19-20.

The conversion was only 75 percent of that of Catalyst 3, even though this catalyst, lacking any thorium, contained more cobalt. Cobalt catalysts normally have low water gas shift activity at best; with this catalyst it was lower still, only 7 percent of the oxygen having been rejected as CO_2 . The usage ratio, 2:1, is an inefficient use of a 1:1 syngas. The additive, although present in such small quantity, seems to have inhibited the activity of the cobalt, and to a degree which cannot be ac-

counted for by the absence of thorium.

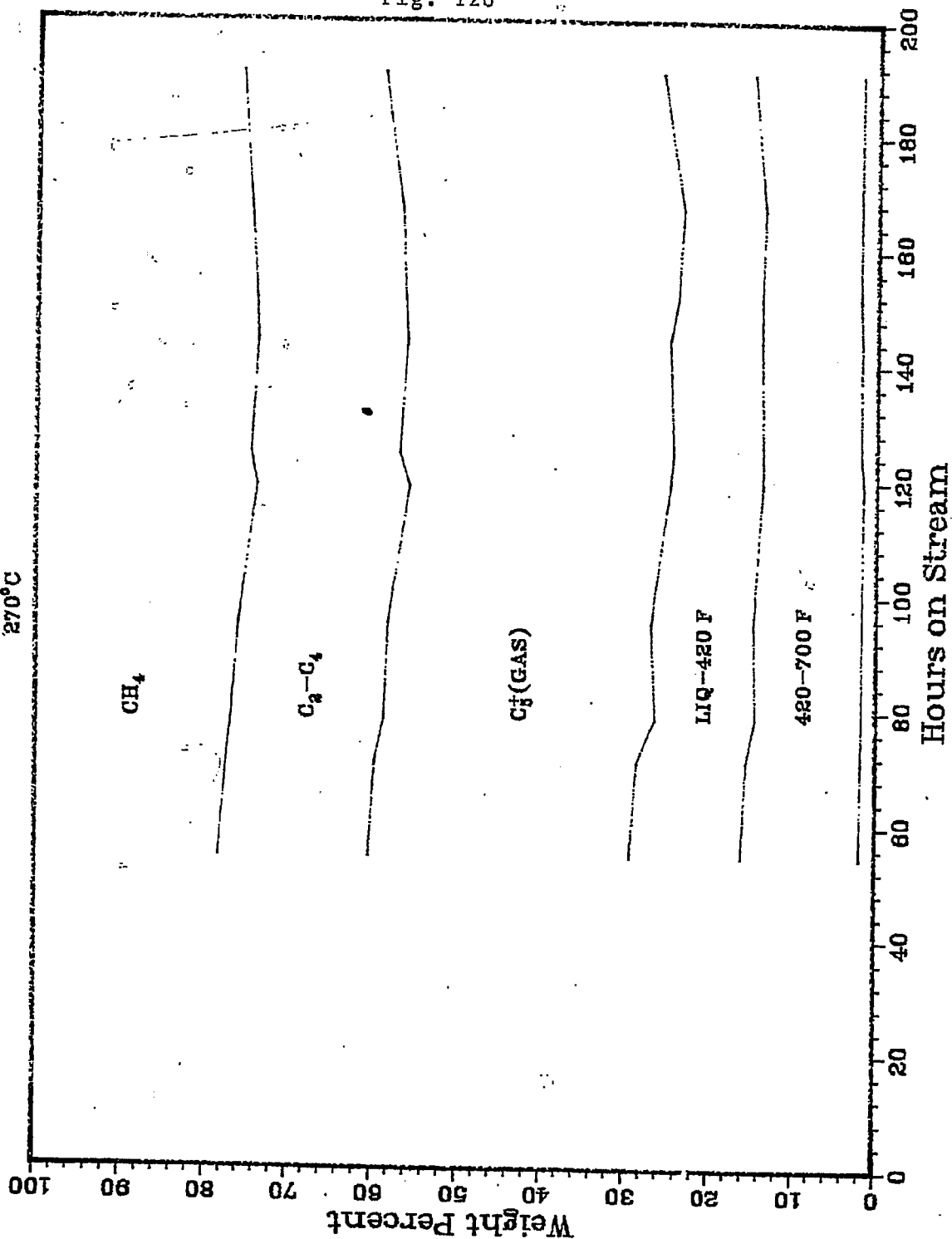
The product selectivity remained constant throughout the run. The methane yield, initially higher than usual, declined with hours on stream to a fairly typical level at the end of the run. The products were predominantly in the lighter end of the range, with more C_5^+ than usual in the gas phase, fewer liquids, especially diesel oil and wax, and a lower yield of total motor fuels. Percent olefins of the C_4 's was normal. Isomerization of the pentanes was below normal. The chromatograms of the simulated distillations show that the liquid was mostly straight chain hydrocarbons. The Schulz-Flory plots show the usual excess methane, and no carbon number cut-off.

This catalyst shows no advantage over the usual Co/Th catalysts.

RUN 10112-18

1:1 H₂:CO
290 PSIG
270°C

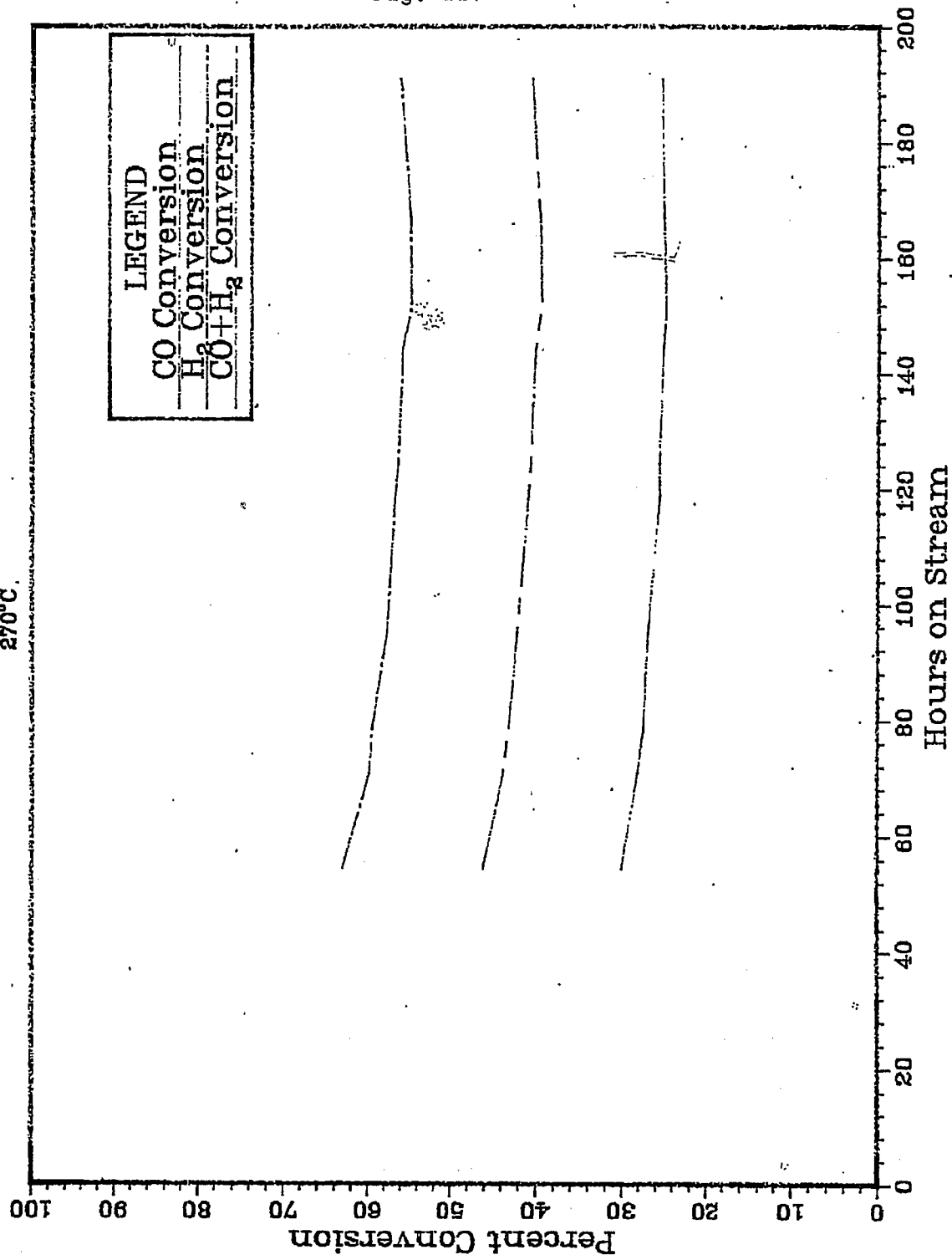
Fig. 126



RUN 10112-18

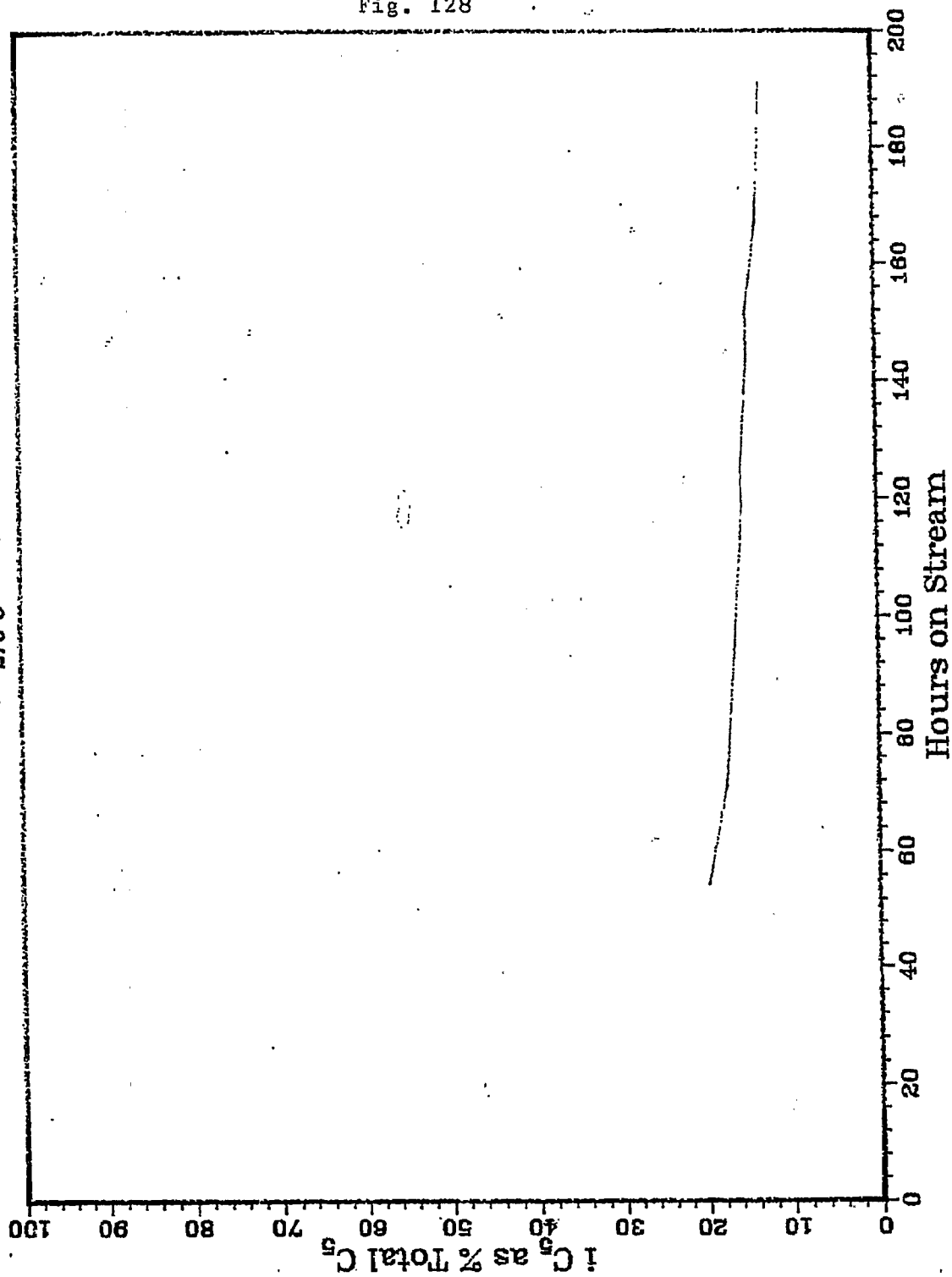
1:1 H₂:CO
290 PSIG
270°C

Fig. 127



RUN 10112-18

1:1 H₂:CO
290 PSIG
270°C



RUN 10112-18

1:1 H₂:CO
290 PSIG
270°C

Fig. 129

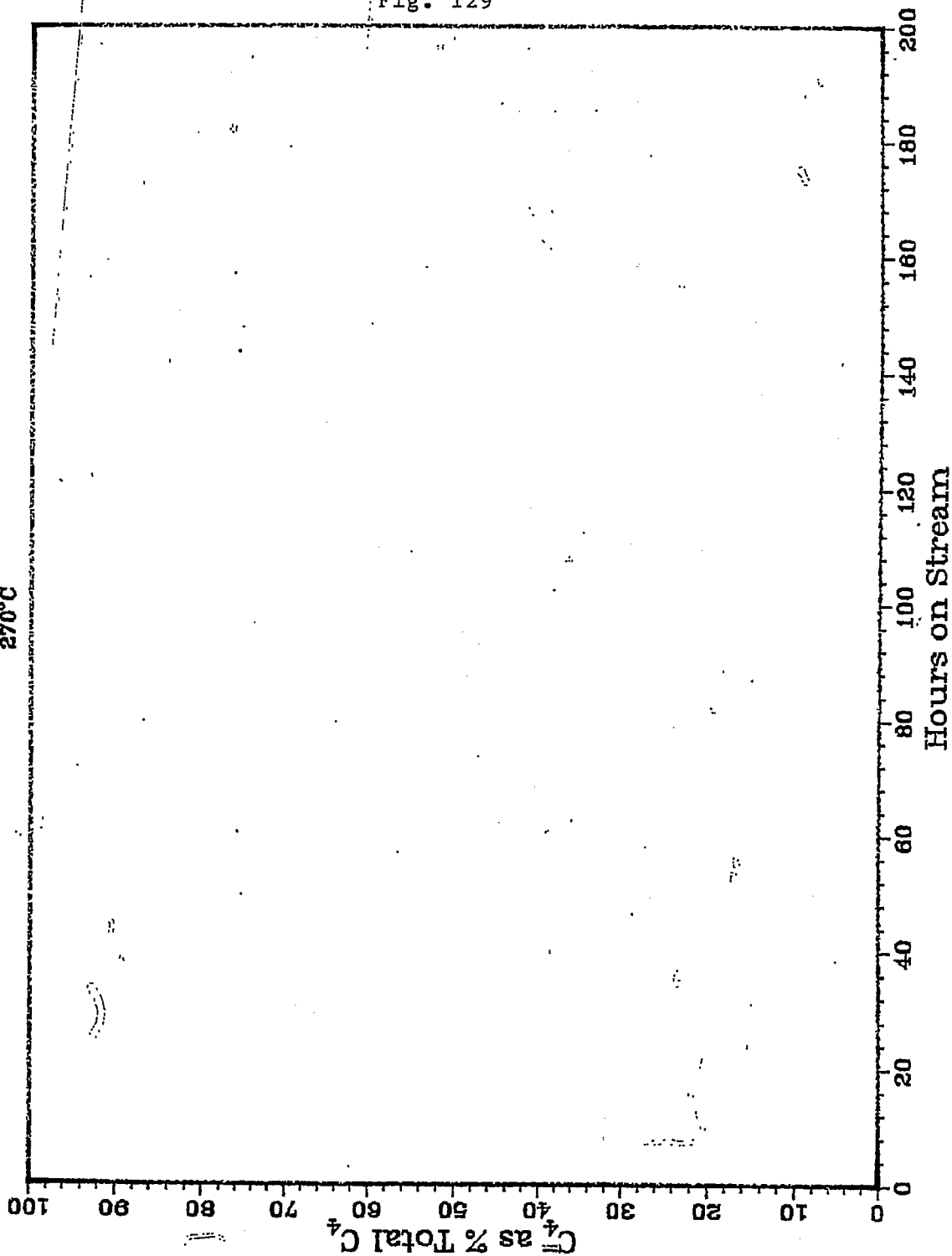


Fig. 130

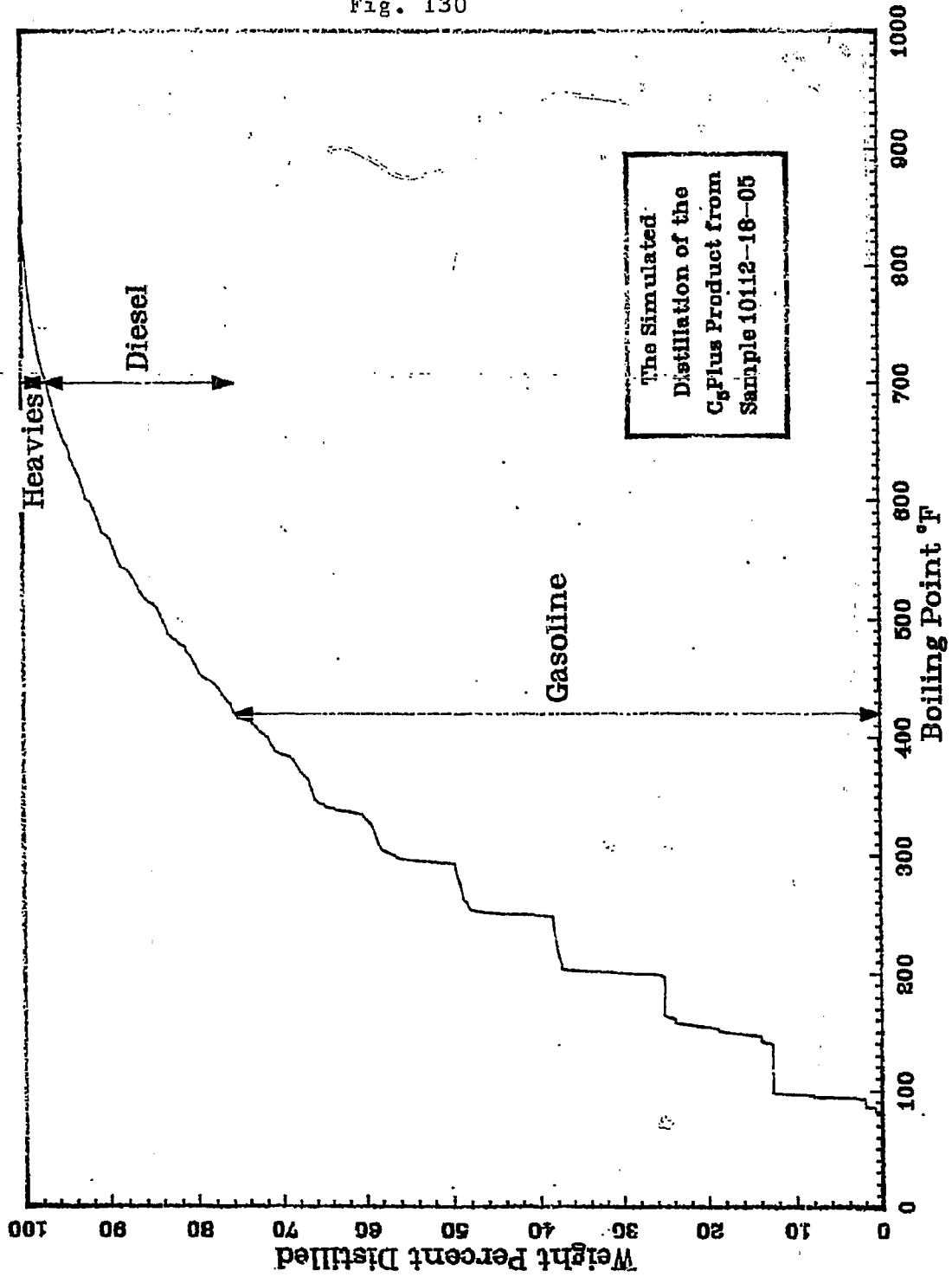


Fig. 131

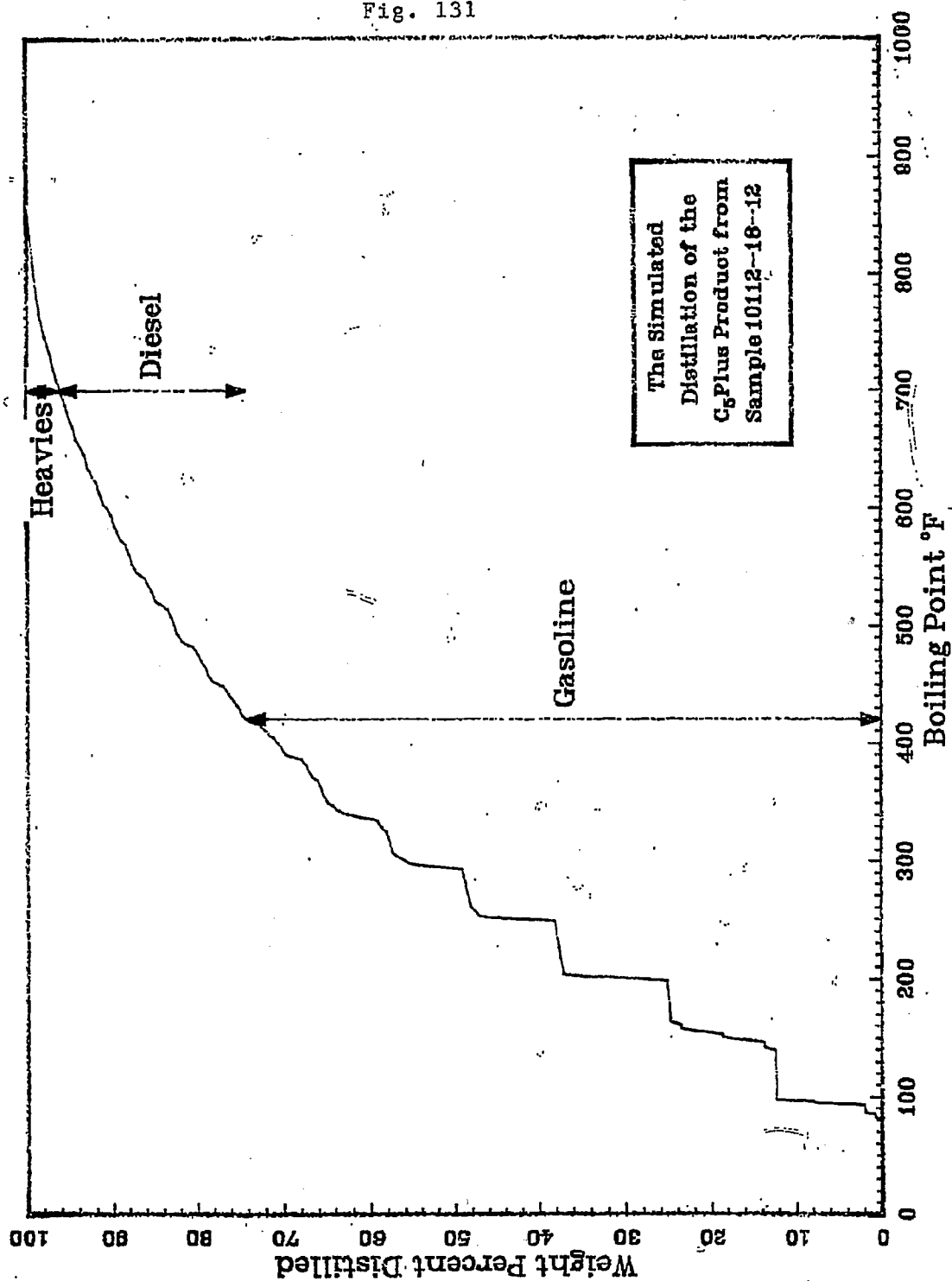


Fig. 132

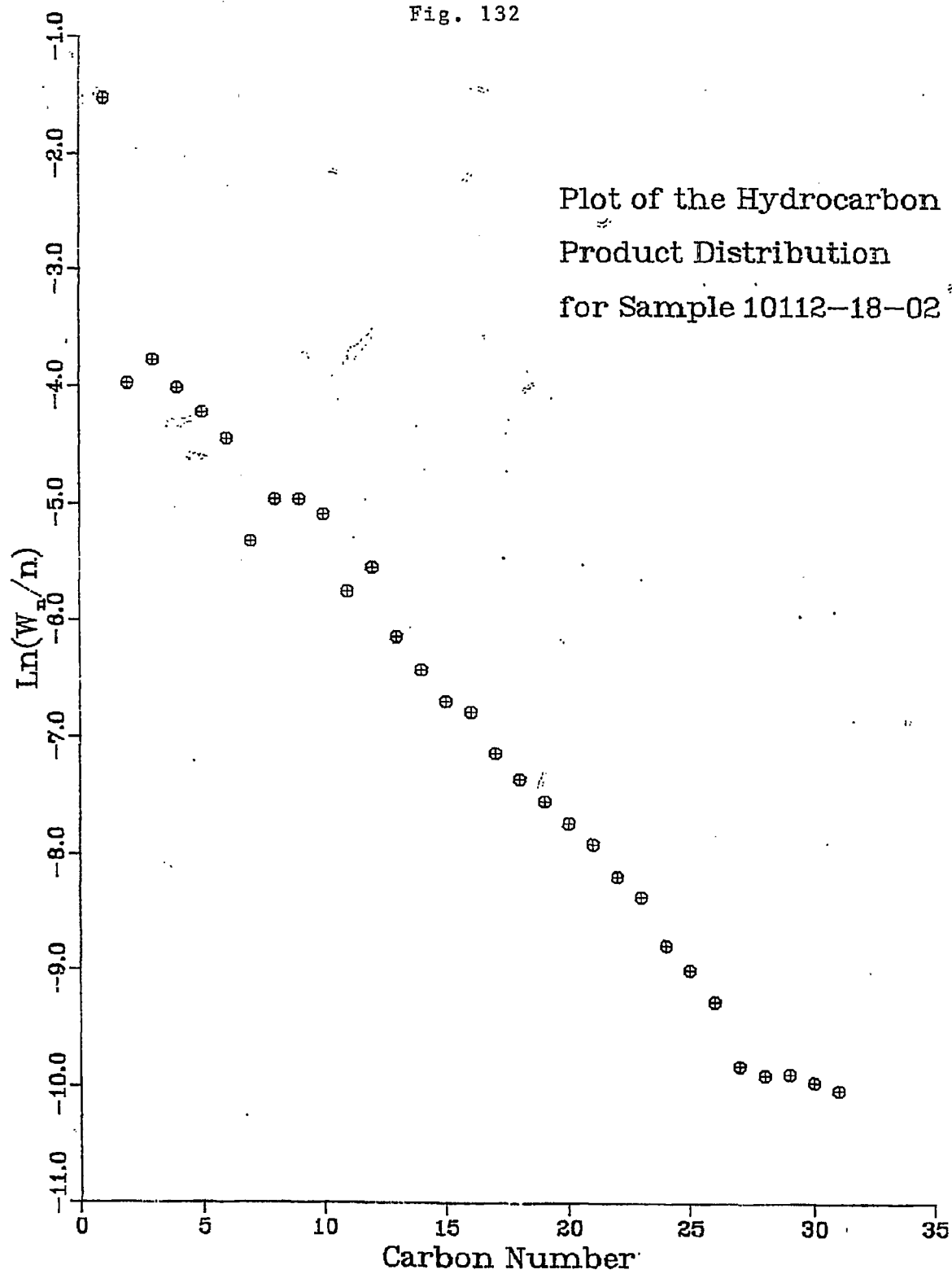


Fig. 133

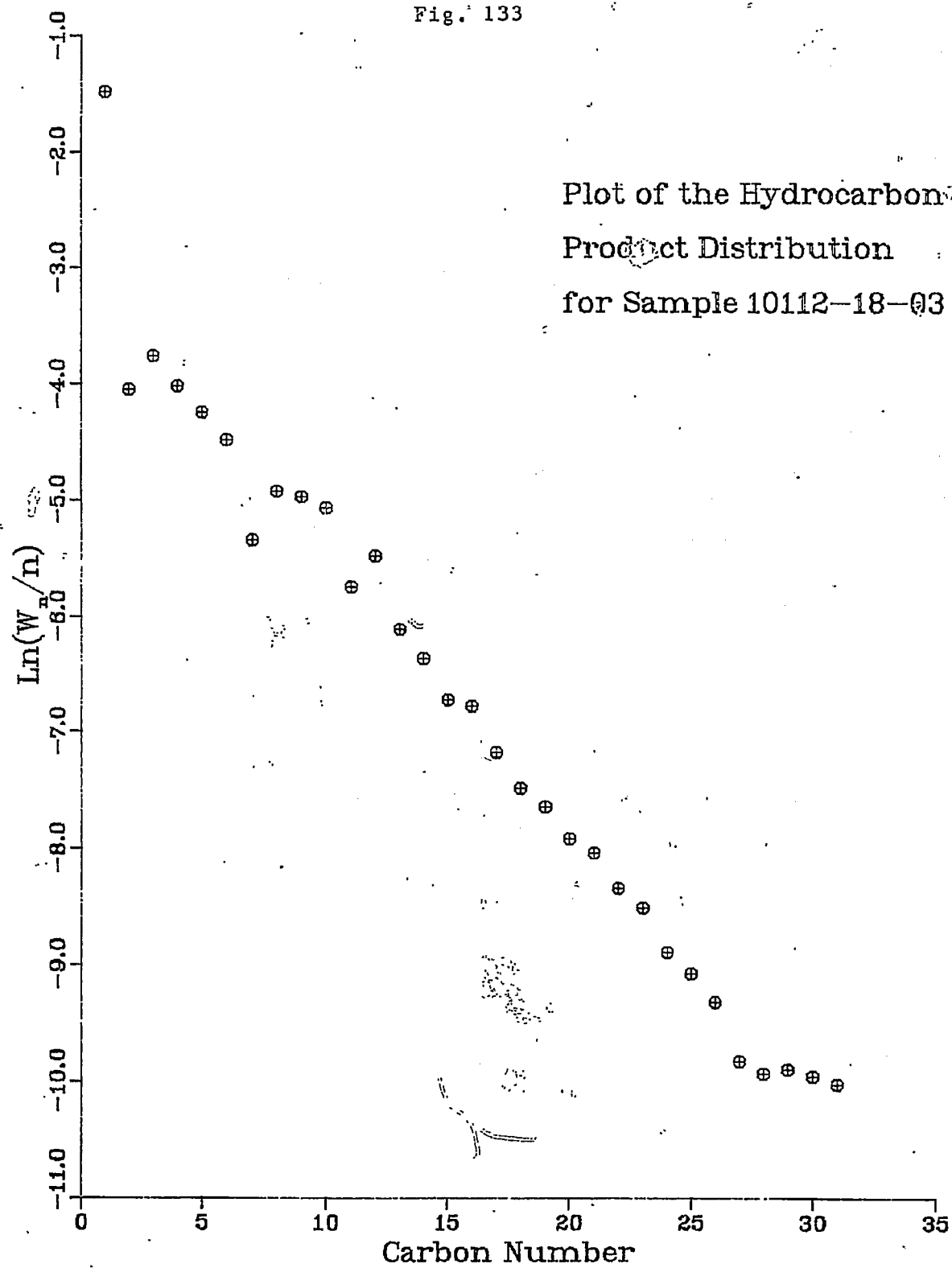
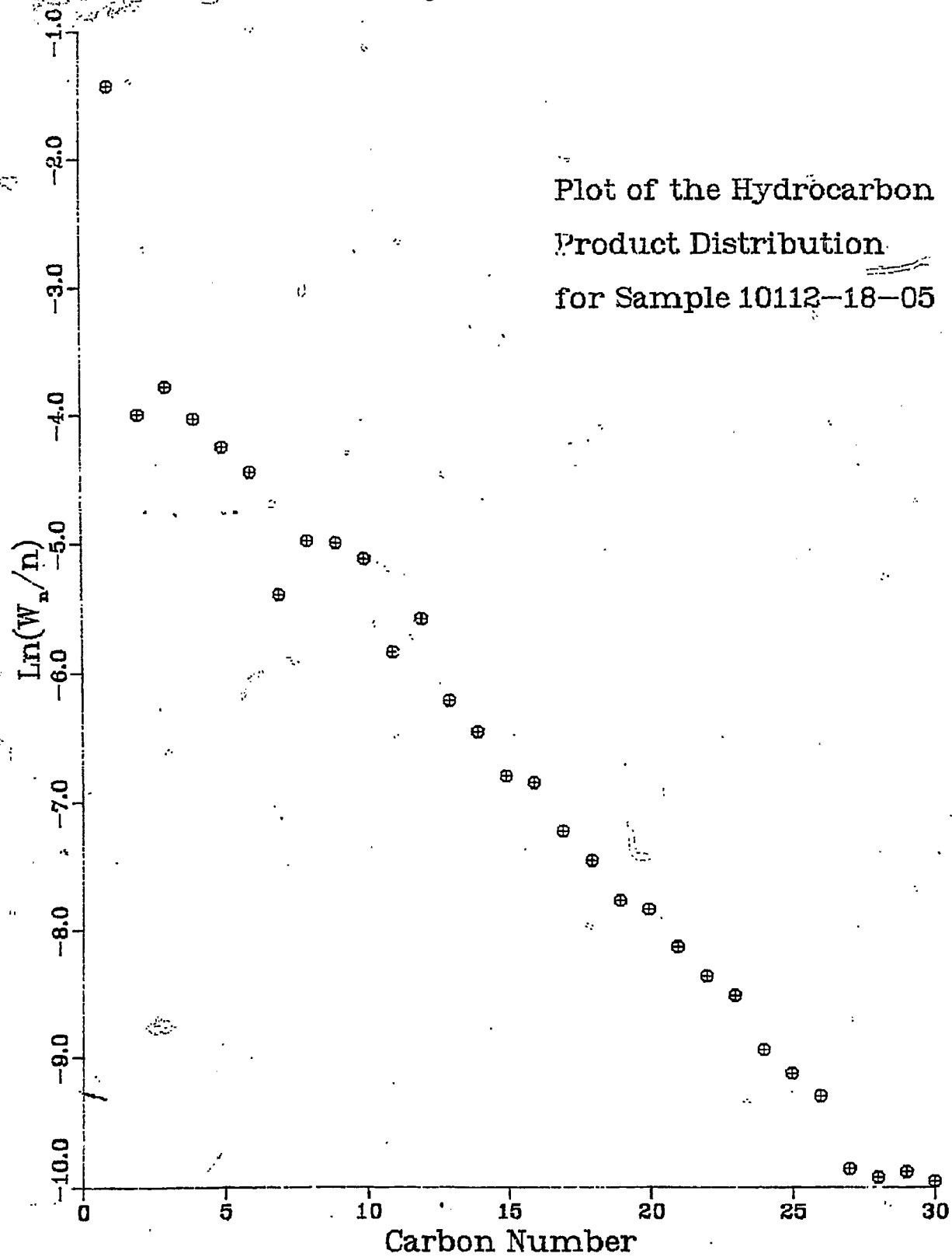


Fig. 134



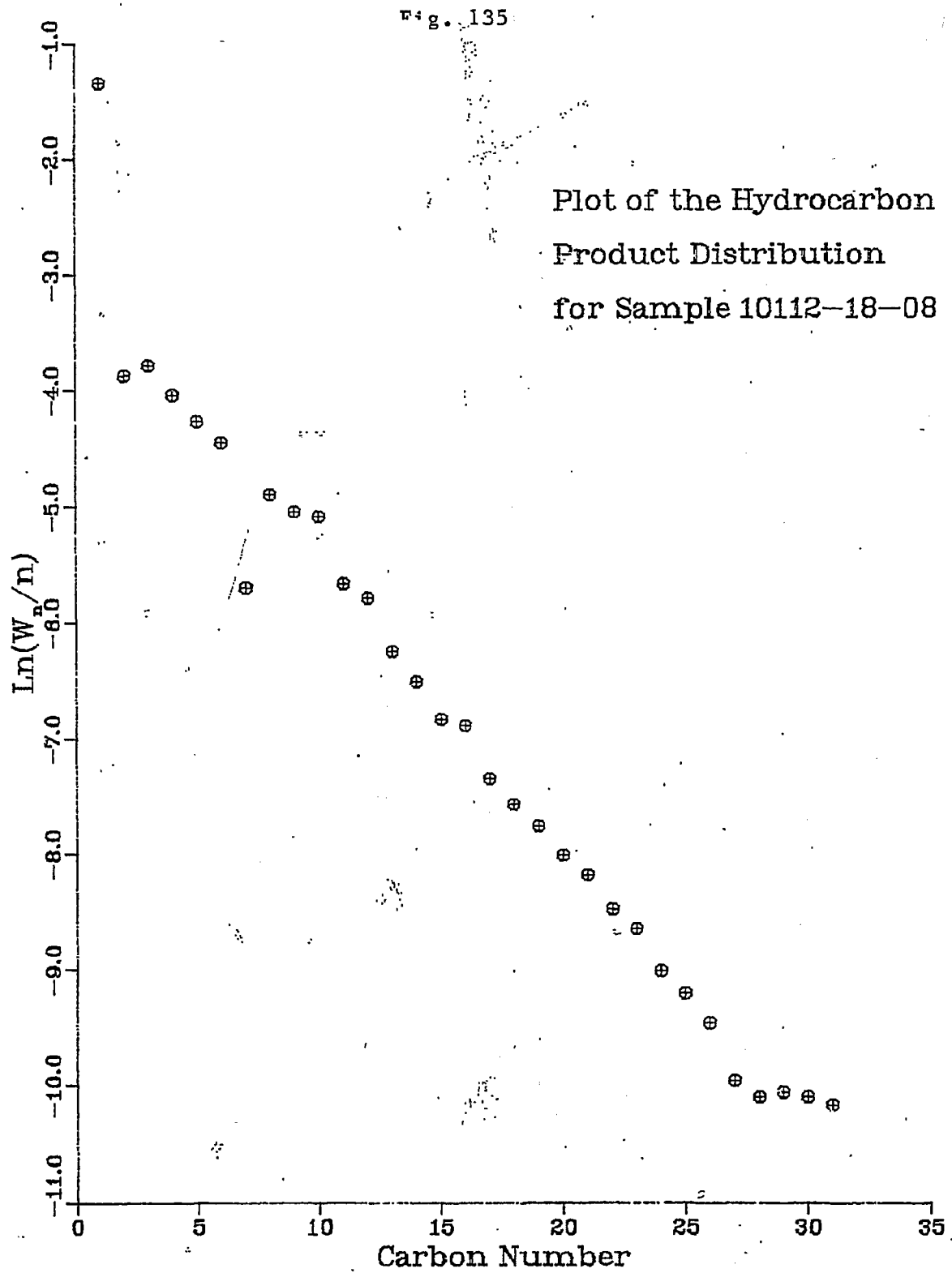


Fig. 136

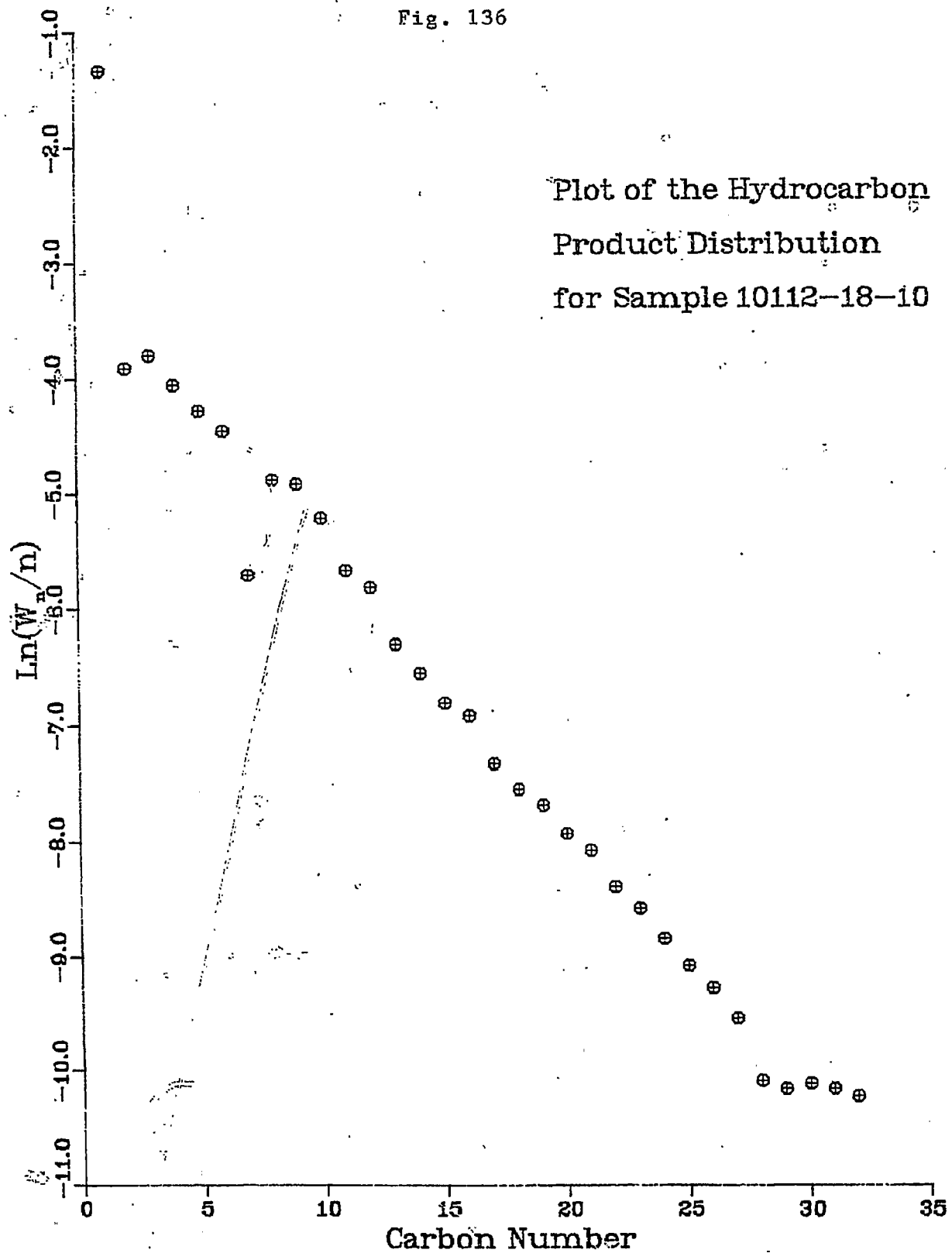


Fig. 137

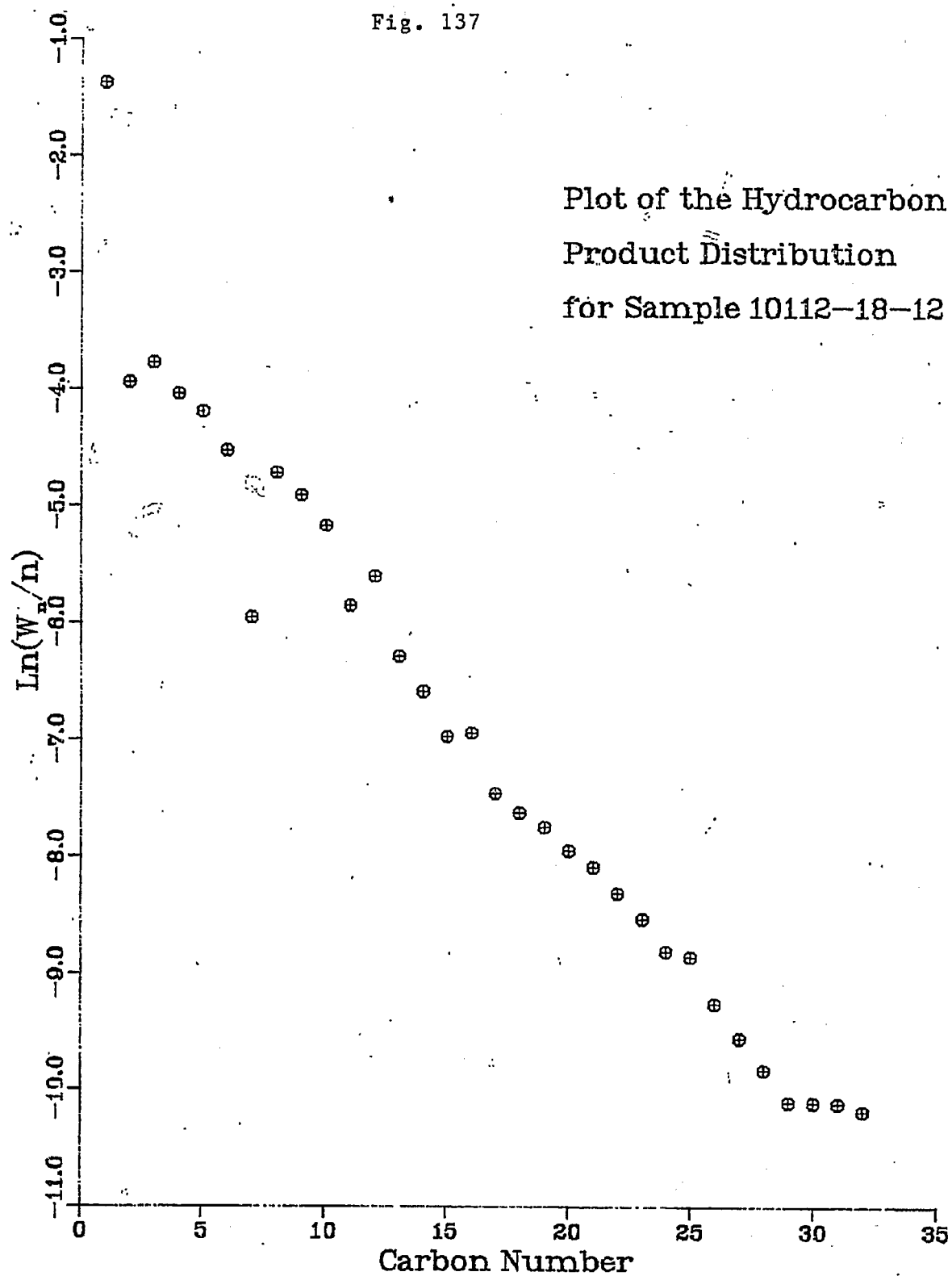


Fig. 138

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-18-14

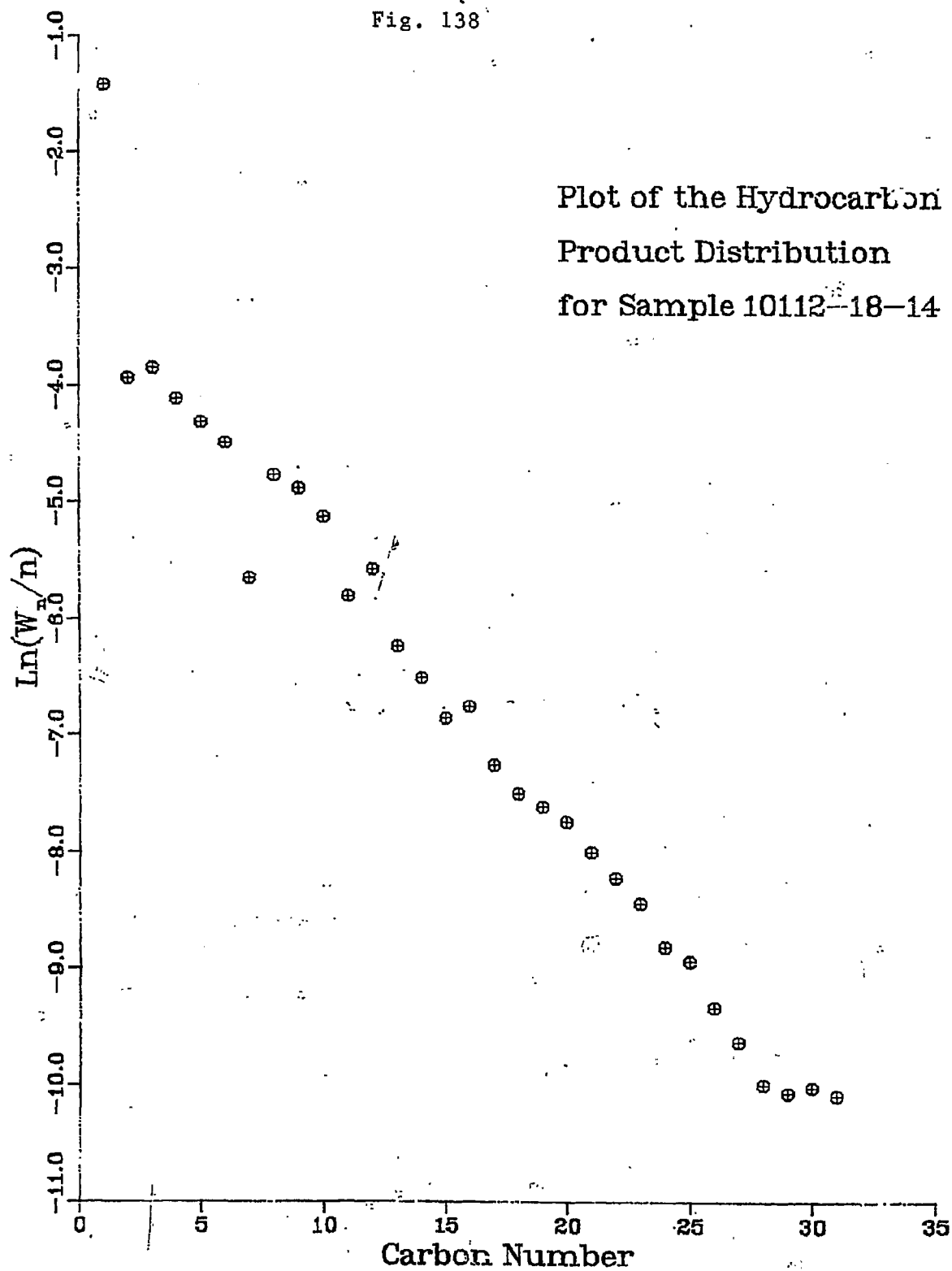


Fig. 139

2-1: 1414 - 170 = 1244 33-10-1 = 22 11017 = 4950

TEMP=178°C SETPT=178°C LIMIT=405°C

2-1: 0.5% Zn=276°C 0.5% Zn=276°C LIMIT=495°C

RT: GIVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

527915:J:2-19-21

OVEN TEMP NOT STABLE

Fig. 140

RT: 3.1023 3.23

RT: OVEN TEMP=24°C SETPT=26°C LIMIT=405°C

RT: OVEN TEMP=24°C SETPT=26°C LIMIT=405°C

RT: OVEN TEMP=175°C SETPT=176°C LIMIT=405°C

RT: OVEN TEMP=275°C SETPT=276°C LIMIT=405°C

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

RT: STOP RUN

SAMPLE: 010112-10-3L

OVEN TEMP NOT READY

Fig. 141

RT: 811015 8.22

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

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

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

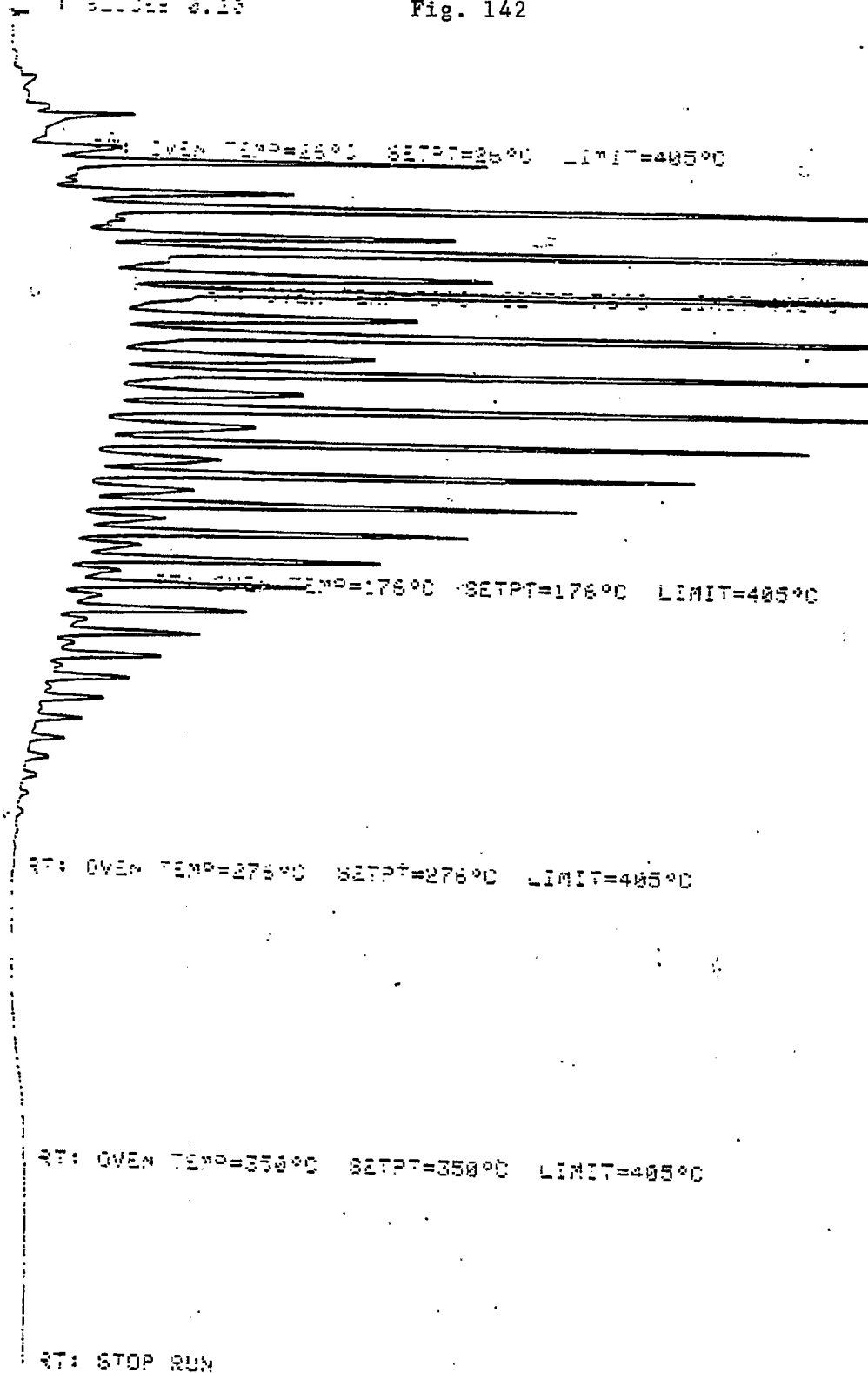
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE: D10112-16-5L

71 SLIDE: 8.18

Fig. 142



SAMPLE: J19112-18-81

OVEN TEMP NOT READY

Fig. 143

RT: SLICES 0.30

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

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

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

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

RT: STOP RUN

SAMPLE: D10112-10-10

QVI START 5/20/68 12 20

Fig. 144

RT: OVEN TEMP=76°C

RT: OVEN TEMP=240°C SETPT=240°C LIMIT=405°C

RT: OVEN TEMP=178°C SETPT=178°C LIMIT=405°C

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

QVI START FINAL TIME 1

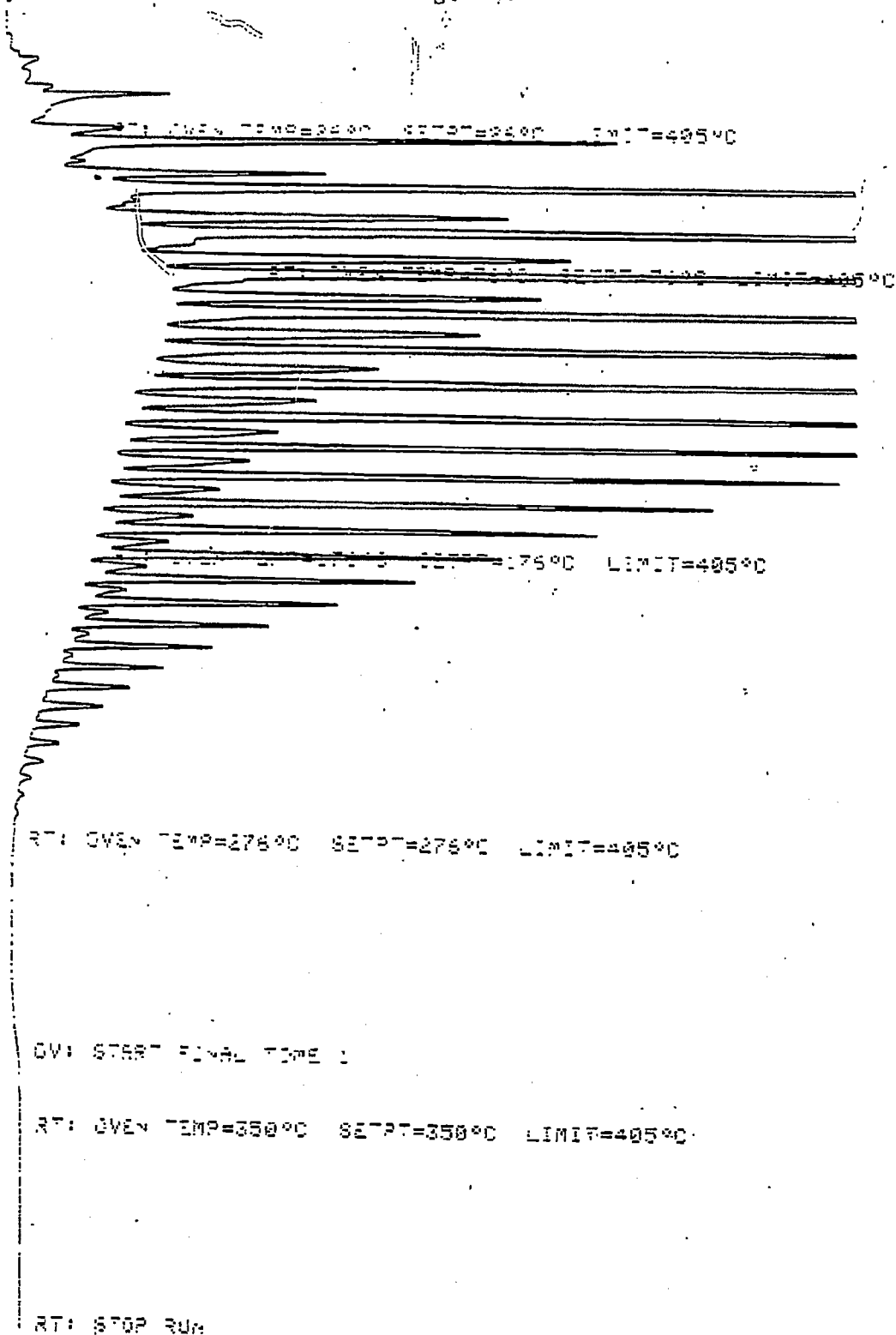
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLES: 310:12-13-12

DATA START RUN

Fig. 145



SAMPLE: D10112-18-12

TABLE 19 RESULT OF SYNGAS OPERATION

RUN NO.	10112-18				
CATALYST	CO/X3+UCC-101 #10252-75C 80 CC 36.0 GM (37.8 AFTER RUN +1.8G)				
FEED	H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10112-18-02	112-18-03	112-18-04	112-18-05	112-18-08
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	54.5	71.0	78.5	95.0	118.9
PRESSURE, PSIG	301	294	302	290	289
TEMP. C	272	271	271	271	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	30.50	16.50	7.50	24.00	23.92
EFFLNT GAS LITER	442.50	246.50	111.40	365.15	368.11
GM AQUEOUS LAYER	64.28	33.37	14.76	47.23	46.94
GM OIL	18.33	9.02	3.65	11.69	10.15
MATERIAL BALANCE					
GM ATOM CARBON %	101.97	100.79	99.83	99.74	99.00
GM ATOM HYDROGEN %	97.54	97.61	95.38	97.55	96.86
GM ATOM OXYGEN %	101.58	101.14	100.46	100.87	101.57
RATIO CHX/(H2O+CO2)	1.0138	0.9871	0.9760	0.9572	0.9024
RATIO X IN CHX	2.4964	2.5066	2.5209	2.5331	2.5774
USAGE H2/CO PRODT	2.0219	2.0387	2.0411	2.0492	2.0561
RATIO CO2/(H2O+CO2)	0.0760	0.0696	0.0702	0.0679	0.0678
K SHIFT IN EFFLNT	0.04	0.04	0.04	0.04	0.04
CONVERSION					
ON CO %	30.06	28.28	27.59	27.05	25.75
ON H2 %	63.13	59.91	59.61	57.85	56.84
ON CO+H2 %	46.23	43.84	43.23	42.28	41.13
PRDT SELECTIVITY, WT %					
CH4	21.80	22.67	23.20	24.05	26.17
C2 HC'S	3.75	3.47	3.64	3.68	4.17
C3H8	3.79	3.67	3.76	3.62	3.58
C3H6=	3.08	3.28	3.28	3.27	3.22
C4H10	2.99	2.87	2.96	2.81	2.76
C4H8=	4.19	4.26	4.49	4.33	4.27
C5H12	3.33	3.14	3.24	3.09	3.02
C5H10=	3.97	4.04	4.14	4.12	3.99
C6H14	3.93	3.65	3.83	3.68	3.59
C6H12= & CYCLO'S	3.10	3.14	3.44	3.44	3.43
C7+ IN GAS	16.70	17.21	17.64	17.03	16.99
LIQ HC'S	29.38	28.60	26.38	26.89	24.81
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	39.59	40.23	41.33	41.76	44.17
C5 -420 F	44.18	44.16	44.10	43.39	42.09
420-700 F	14.34	13.85	12.88	13.13	12.19
700-END PT	1.90	1.77	1.69	1.73	1.56
C5+END PT	60.41	59.77	58.67	58.24	55.83
ISO/NORMAL MOLE RATIO					
C4	0.1347	0.1246	0.1190	0.1075	0.1034
C5	0.2460	0.2134	0.2082	0.1971	0.1836
C6	0.3662	0.3108	0.3127	0.2856	0.2732
C4+	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1761	1.0664	1.0941	1.0573	1.0616
C4	0.6889	0.6509	0.6358	0.6267	0.6244
C5	0.8144	0.7569	0.7612	0.7272	0.7353
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY L BL	CLDY L BL		CLDY L BL	CLR LT BL
DENSITY	0.759	0.761		0.762	0.762
N, REFRACTIVE INDEX	1.4279	1.4276		1.4279	1.4280
SIMULT'D DISTILLATN					
10 WT % @ DEG F	301	302		302	303
16	328	328		330	331
50	445	443		445	445
84	618	604		612	608
90	665	657		661	659
RANGE(16-84 %)	290	276		282	277
WT % @ 420 F	44.75	45.40		44.75	44.60
WT % @ 700 F	93.55	93.82		93.58	93.73

TABLE 20

RESULT OF SYNGAS OPERATION

RUN NO. 10112-18

CATALYST CO/X3+UCC-101 #10252-75C 80 CC 36.0 GM (37.8 AFTER RUN +1.8G)

FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10112-18-09	112-18-10	112-18-11	112-18-12	112-18-14
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	124.5	144.3	151.3	167.0	191.0
PRESSURE, PSIG	299	288	289	289	294
TEMP. C	271	271	271	271	271
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.58	25.33	7.00	22.75	24.00
EFFLNT GAS LITER	86.53	396.47	110.19	361.67	374.70
GM AQUEOUS LAYER	10.47	47.52	12.63	41.06	48.19
GM OIL	2.38	10.79	2.83	9.21	10.68
MATERIAL BALANCE					
GM ATOM CARBON %	100.14	100.32	100.07	101.30	100.06
GM ATOM HYDROGEN %	96.37	96.60	96.09	97.28	98.28
GM ATOM OXYGEN %	101.33	101.97	101.23	101.91	102.97
RATIO CHX/(H ₂ O+CO ₂)	0.9533	0.9347	0.9527	0.9754	0.8913
RATIO X IN CHX	2.5593	2.5738	2.5711	2.5635	2.5309
USAGE H ₂ /CO PRD	2.0551	2.0605	2.0630	2.0647	2.0473
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0696	0.0685	0.0687	0.0688	0.0630
K SHIFT IN EFFLNT	0.04	0.04	0.04	0.04	0.04
CONVERSION					
ON CO %	25.85	25.30	24.97	25.25	25.49
ON H ₂ %	56.46	55.90	54.89	54.92	56.16
ON CO+H ₂ %	40.86	40.31	39.62	39.78	40.68
PRDT SELECTIVITY, WT %					
CH ₄	25.43	26.18	26.05	25.41	24.17
C ₂ HC'S	3.86	4.01	4.01	3.89	3.90
C ₃ H ₈	3.51	3.47	3.42	3.46	3.25
C ₃ H ₆ =	3.23	3.26	3.21	3.42	3.13
C ₄ H ₁₀	2.72	2.70	2.68	2.64	2.49
C ₄ H ₈ =	4.27	4.23	4.22	4.37	4.06
C ₅ H ₁₂	2.98	2.95	2.94	3.00	2.84
C ₅ H ₁₀ =	3.97	4.00	4.02	4.54	3.89
C ₆ H ₁₄	3.57	3.56	3.54	5.03	3.34
C ₆ H ₁₂ = & CYCLO'S	3.38	3.47	3.44	1.47	3.39
C ₇ + IN GAS	18.58	17.19	18.38	19.27	19.56
LIQ HC'S	24.51	24.98	24.09	23.51	25.98
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING

C1 -C4	43.01	43.85	43.59	43.17	41.00
C5 -420 F	43.23	42.13	42.44	43.19	43.80
420-700 F	11.89	12.12	11.87	11.59	13.22
700-END PT	1.87	1.90	2.10	2.05	1.97
C5+-END PT	56.99	56.15	56.41	56.83	59.00

ISO/NORMAL MOLE RATIO

C4	0.0966	0.1067	0.1005	0.0936	0.0869
C5	0.1848	0.1732	0.1735	0.1569	0.1493
C6	0.2723	0.2535	0.2491	1.2749	0.2350
C4=	0.0000	0.0000	0.0000	0.0000	0.0000

PARAFFIN/OLEFIN RATIO

C3	1.0369	1.0162	1.0187	0.9653	0.9939
C4	0.6154	0.6163	0.6133	0.5832	0.5915
C5	0.7286	0.7166	0.7109	0.6421	0.7098

LIQ HC COLLECTION

PHYS. APPEARANCE

DENSITY

N, REFRACTIVE INDEX

SIMULT'D DISTILLATN

10 WT % @ DEG F

16

50

84

90

RANGE(16-84 %)

WT % @ 420 F

WT % @ 700 F

CLDY L BL

0.762

1.4285

300

332

443

624

673

292

43.86

92.38

42.00

91.27

CLDY L BL

0.763

1.4290

304

340

452

634

688

294

42.00

91.27

CLDY L BL

0.762

1.4286

304

340

453

629

676

289

41.50

92.40

X. RUN 9 (10225-8) with Catalyst 9 (Co/Th/X₄ + UCC-101)

This is the fourth of five catalysts treated with a metal additive. The metal component was composed of cobalt with 15 percent thorium, impregnated with 15 percent of a metal additive. This was physically mixed with UCC-101 in a MC:SSC ratio of 3:14, bonded with 15 percent SiO₂, and formed as an extrudate.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 146-149. Simulated distillations of the C₅⁺ product for four samples are plotted in Figs. 150-153. Carbon number product distributions are plotted in Figs. 154-173. Chromatograms from simulated distillations are reproduced in Figs. 174-180. Detailed material balances appear in Tables 21-28.

This catalyst shows certain important advantages over the standard cobalt/thorium catalysts tested heretofore. The most notable result of this test is the unusually long run of 480 hours on stream. Initially the conversion was 75.2 percent, about the same as the 75.7 percent of Catalyst 3. But since it deactivated only one-quarter as rapidly as Catalyst 3, the activity of this catalyst was still as high after 480 hours (even in the face of two power failures, evident in the plots) as that of Catalyst 3 was after 122 hours. The additive in this catalyst has endowed it with far greater stability than that of any other

cobalt catalyst tested to date. The water gas shift activity, however, is still low: 37 percent initially, falling to 22 percent for most of the run, again about the same as for Catalyst 3 (37 and 20 percent).

The selectivity was also far more stable than with other cobalt catalysts. Initially the selectivity to methane was the same as that of Catalyst 3; but since it increased less than 40 percent as fast this catalyst produced no more methane at 480 hours on stream than Catalyst 3 did at 180 hours. The production of C₂-C₄ was also the same initially as for Catalyst 3, but it increased at a higher rate; after 180 hours on stream this catalyst produced about 33 percent more C₂-C₄ than did Catalyst 3. These two trends offset each other, so that the yields of total C₁-C₄, and of C₅⁺ as well, were about the same.

Similarly, the gasoline selectivity was initially about the same as for Catalyst 3, but it dropped so much more slowly that it was better for this catalyst after 480 hours on stream than for Catalyst 3 after 24 hours. Selectivities for both diesel oil and heavies were initially about 15 percent lower than those of Catalyst 3, and remained lower throughout the run.

One clue to some of this catalyst's activities is the olefinic content of the C₄'s. Initially this was a little lower than for Catalyst 3; but instead of falling off, as usually happens, it increased slightly, then held steady for the rest of the run. After 60 hours on stream the C₄ fraction of this catalyst was more olefinic than that of Catalyst 3.

Isomerization of the pentane was lower than that of Catalyst 3, and the chromatograms of the simulated distillations show that this was also true of the liquid product.

Initial production of total motor fuels was a high 67 percent, and though it dropped to 52 percent by 480 hours on stream it was still an improvement over Catalyst 3.

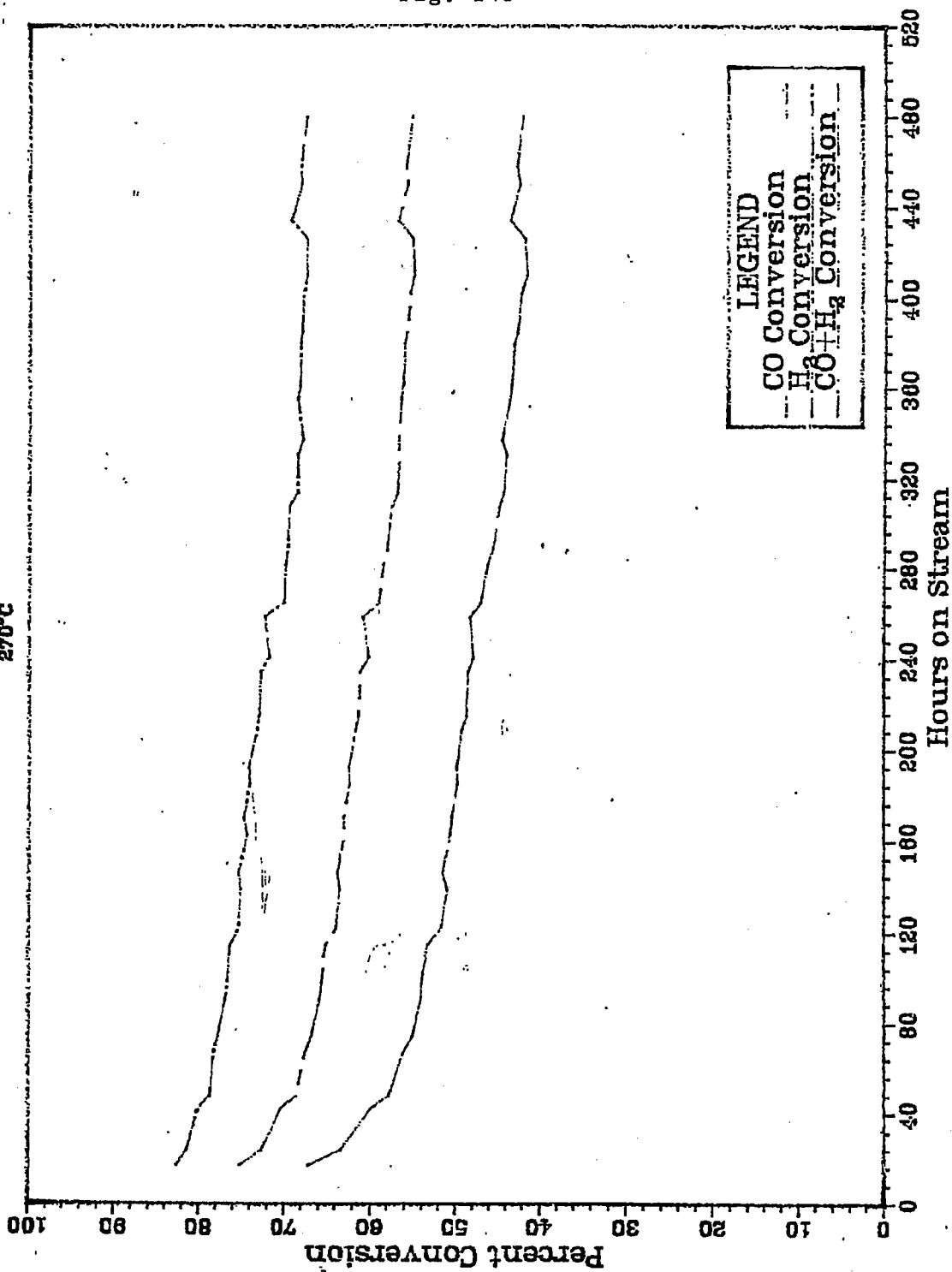
The liquid product contained no wax, the first time that this has happened with a Co+UCC-101 catalyst. The absence of wax is reflected in the lower pour point of the heavier fuel fractions: the pour points of the jet fuel and diesel oil were -10F and 20F respectively, as against 0F and 50F for Catalyst 3. In light of the low isomerization, and the lack of carbon number cut-off shown in the Schulz-Flory plots, this finding is hard to explain. Possibly it is due to the higher olefin content: 48 and 36 percent respectively in the gasoline and jet fuel fractions, as against 36 and 32 percent for Catalyst 3.

This formulation is a major improvement in cobalt F-T catalysts. The additive used has improved the quality of the catalyst's product, and significantly extended the catalyst's life and stability.

RUN 10225-08

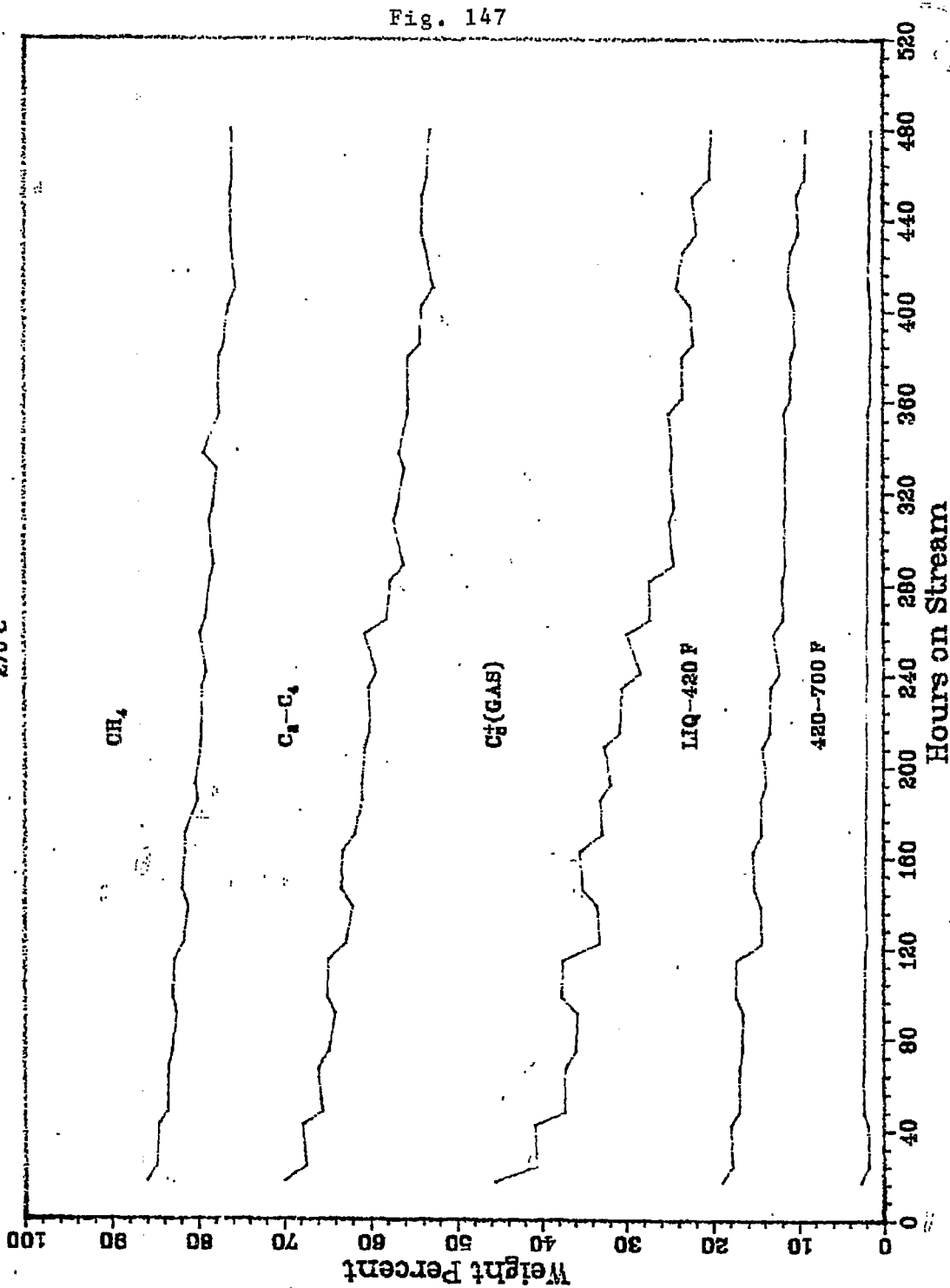
1:1 H₂:CO
300 PSIG
270°C

Fig. 146



RUN 10225-08

1:1 H₂:CO
300 PSIG
270°C



RUN 10225-08

1:1 H₂:CO
300 PSIG
270°C

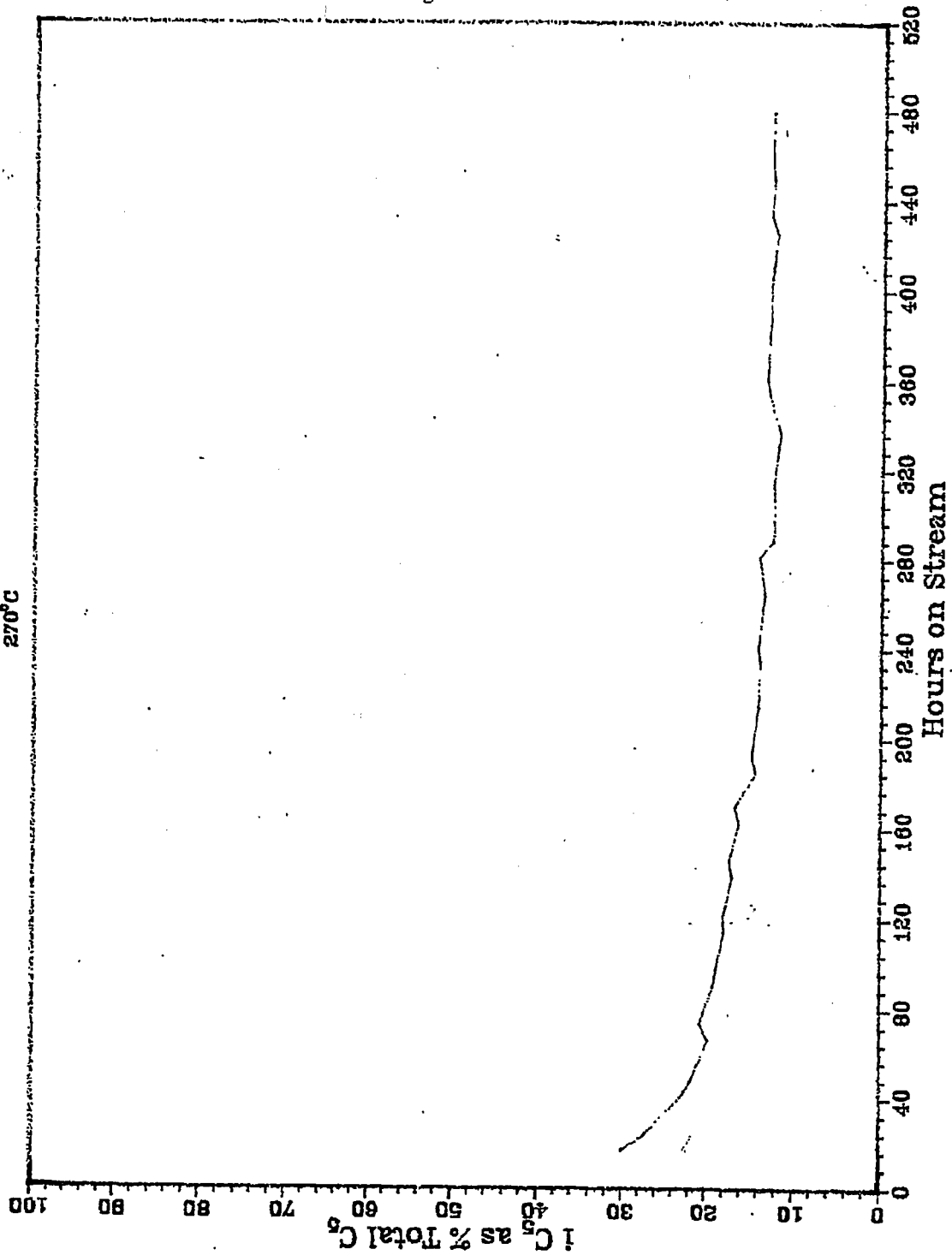


Fig. 148

RUN 10225-08

1:1 H₂:CO
300 PSIG
270°C

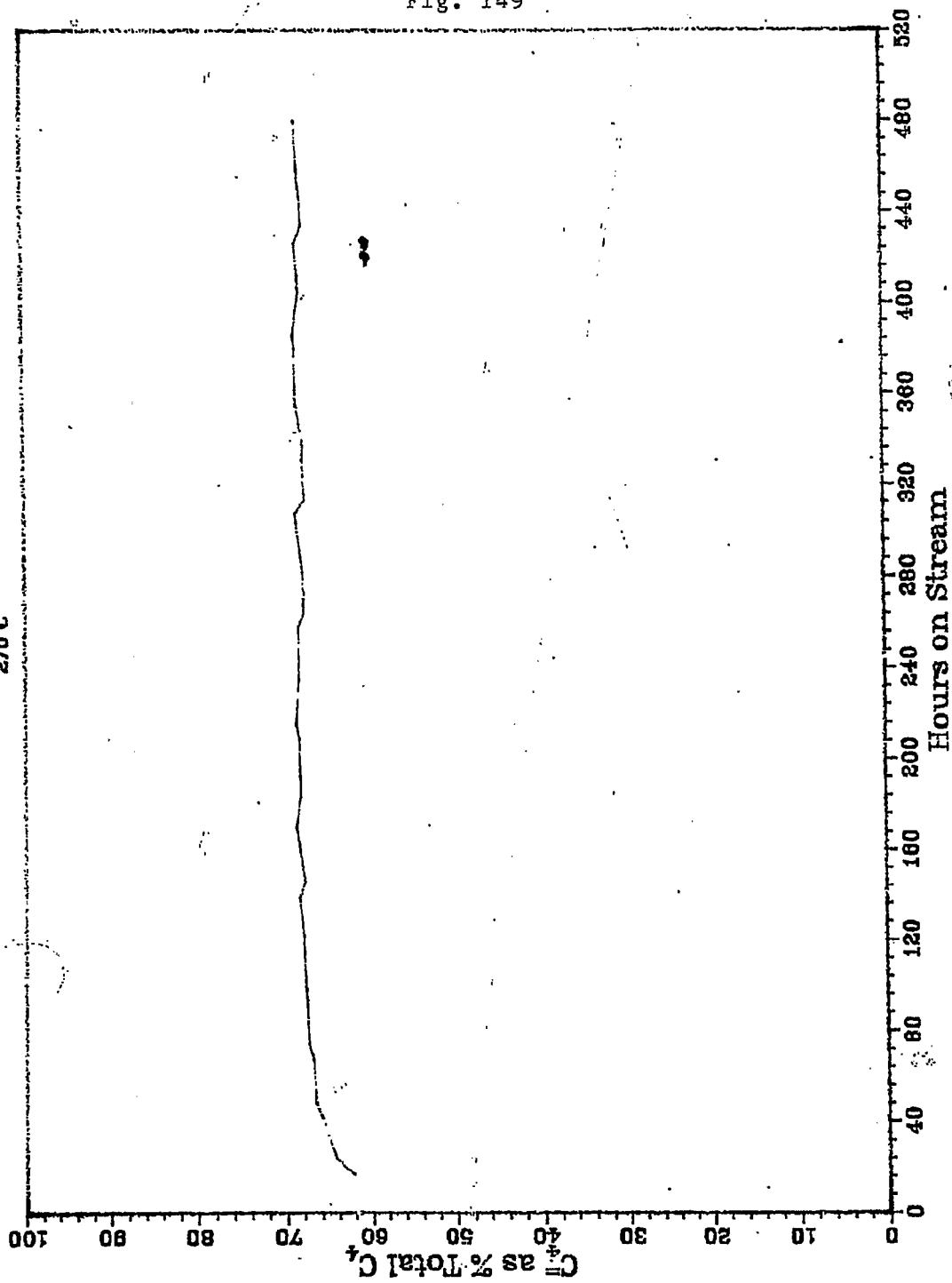


Fig. 150

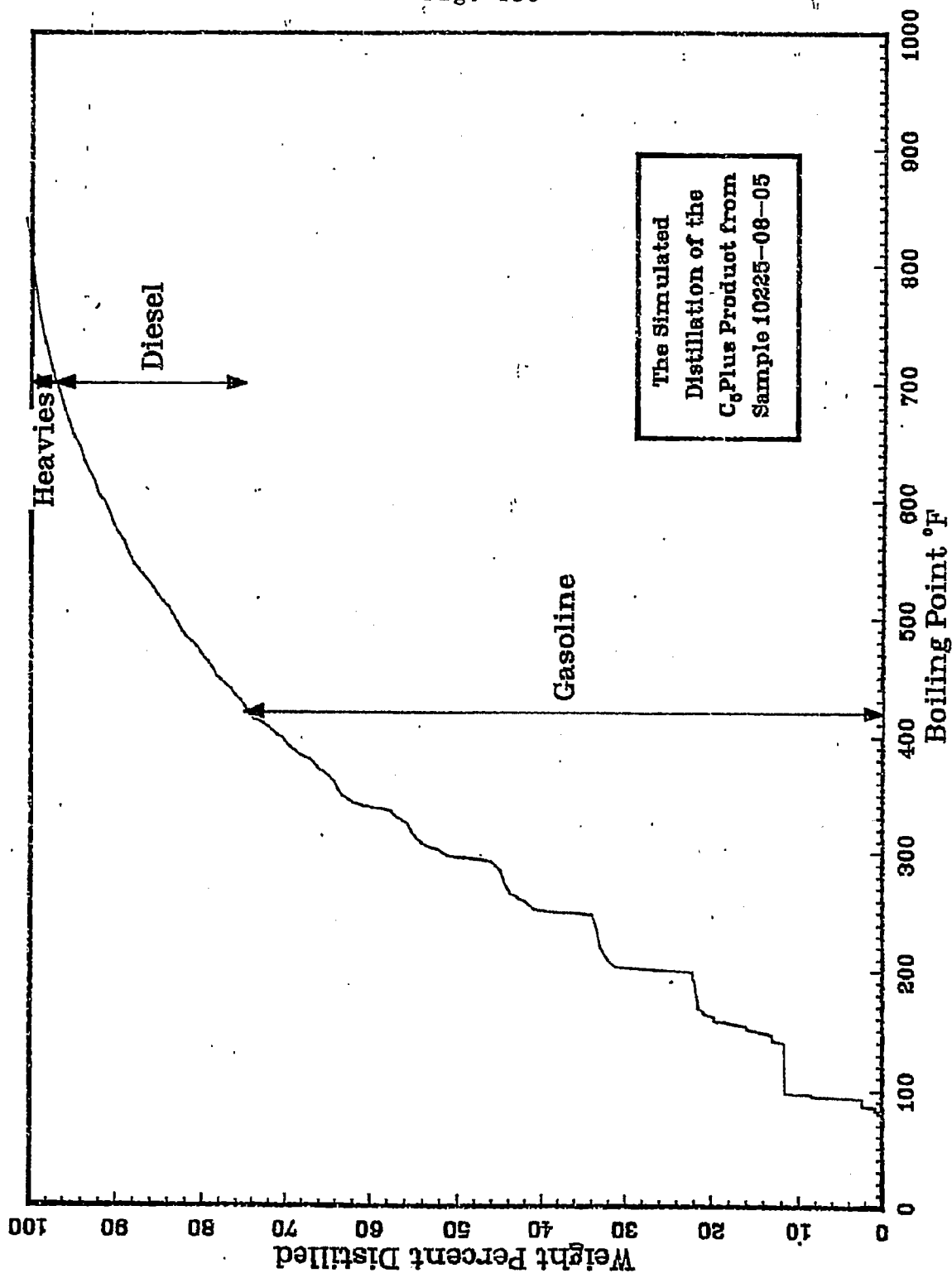


Fig. 151

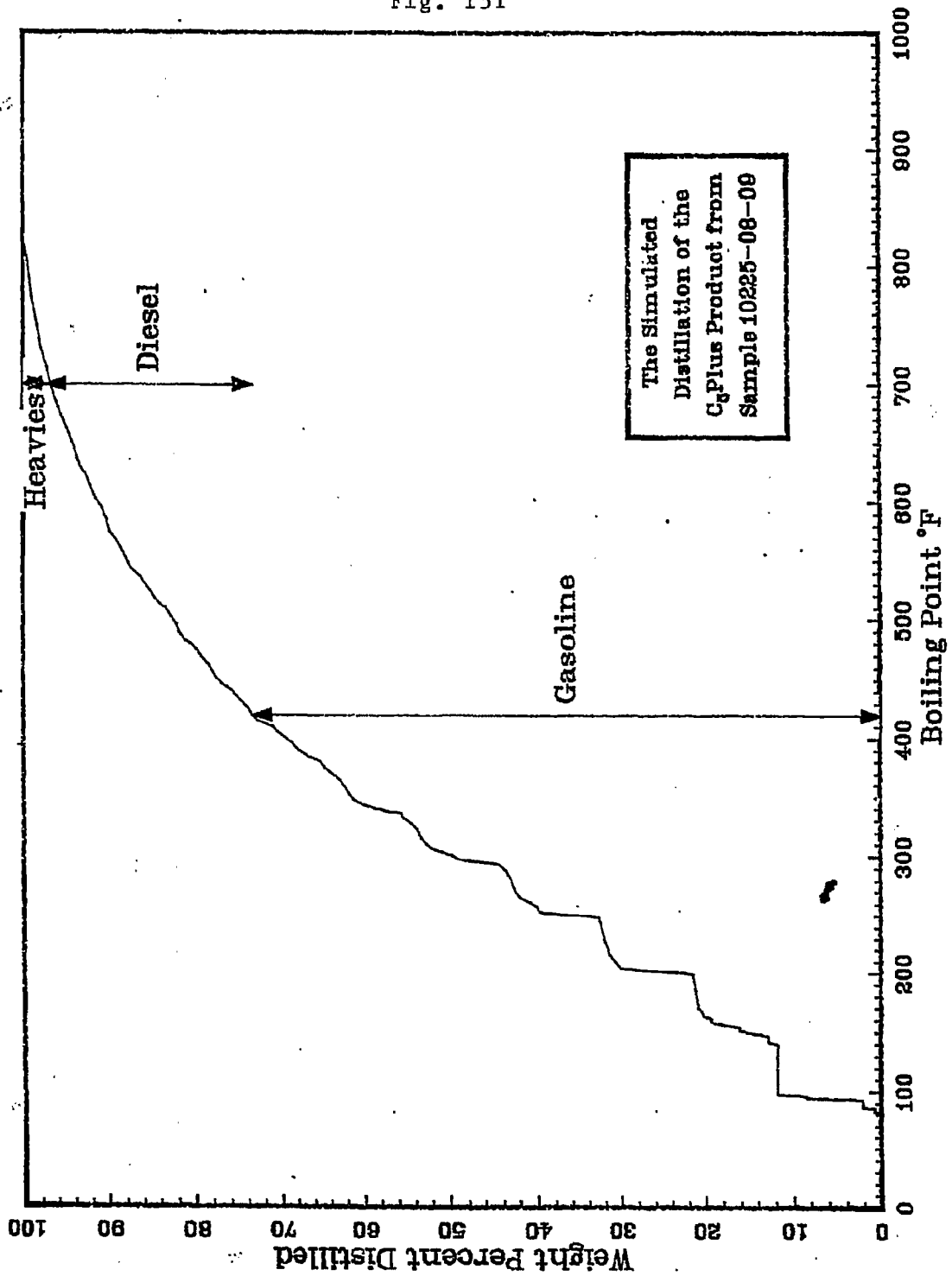


Fig. 152

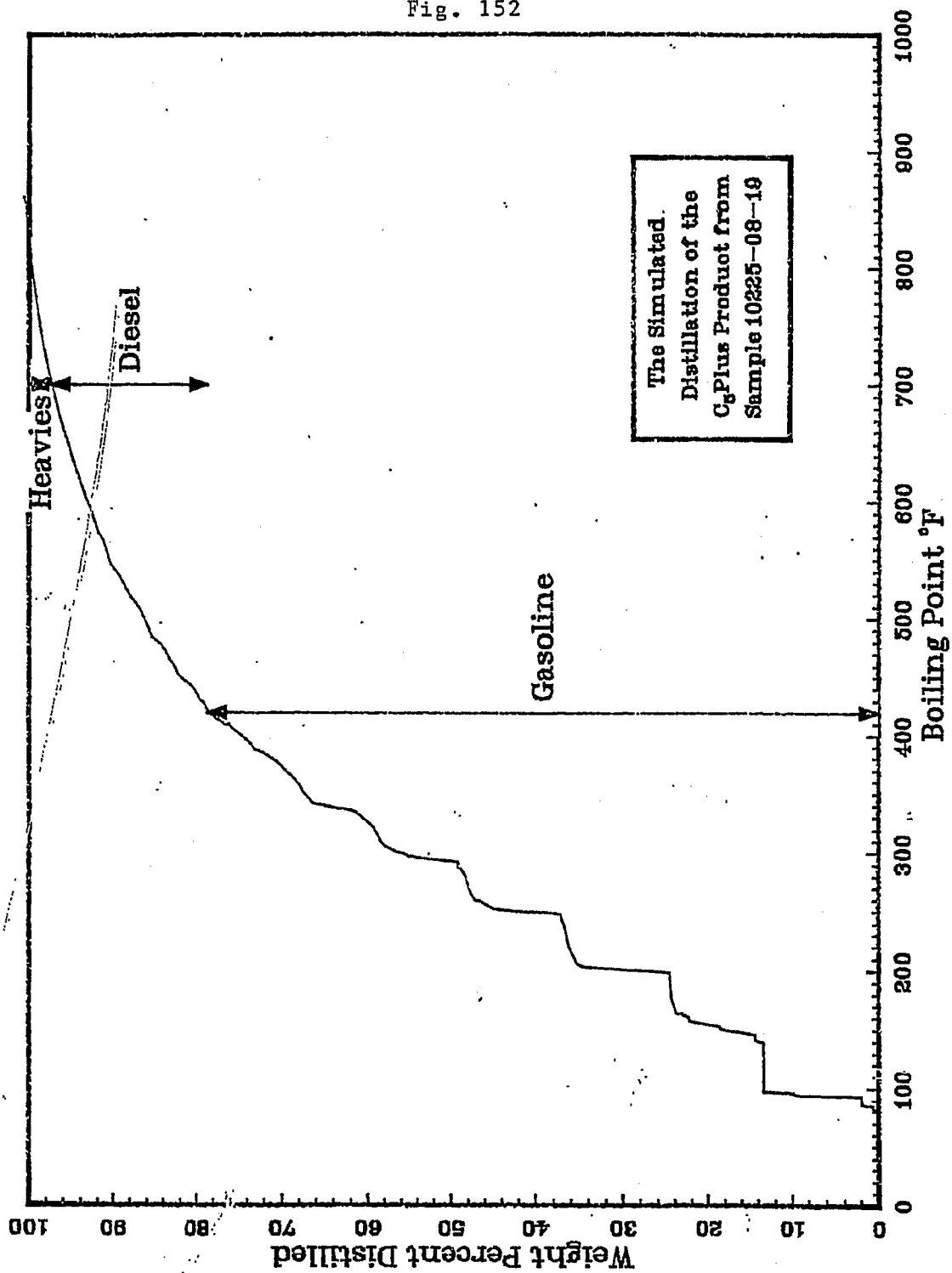


Fig. 153

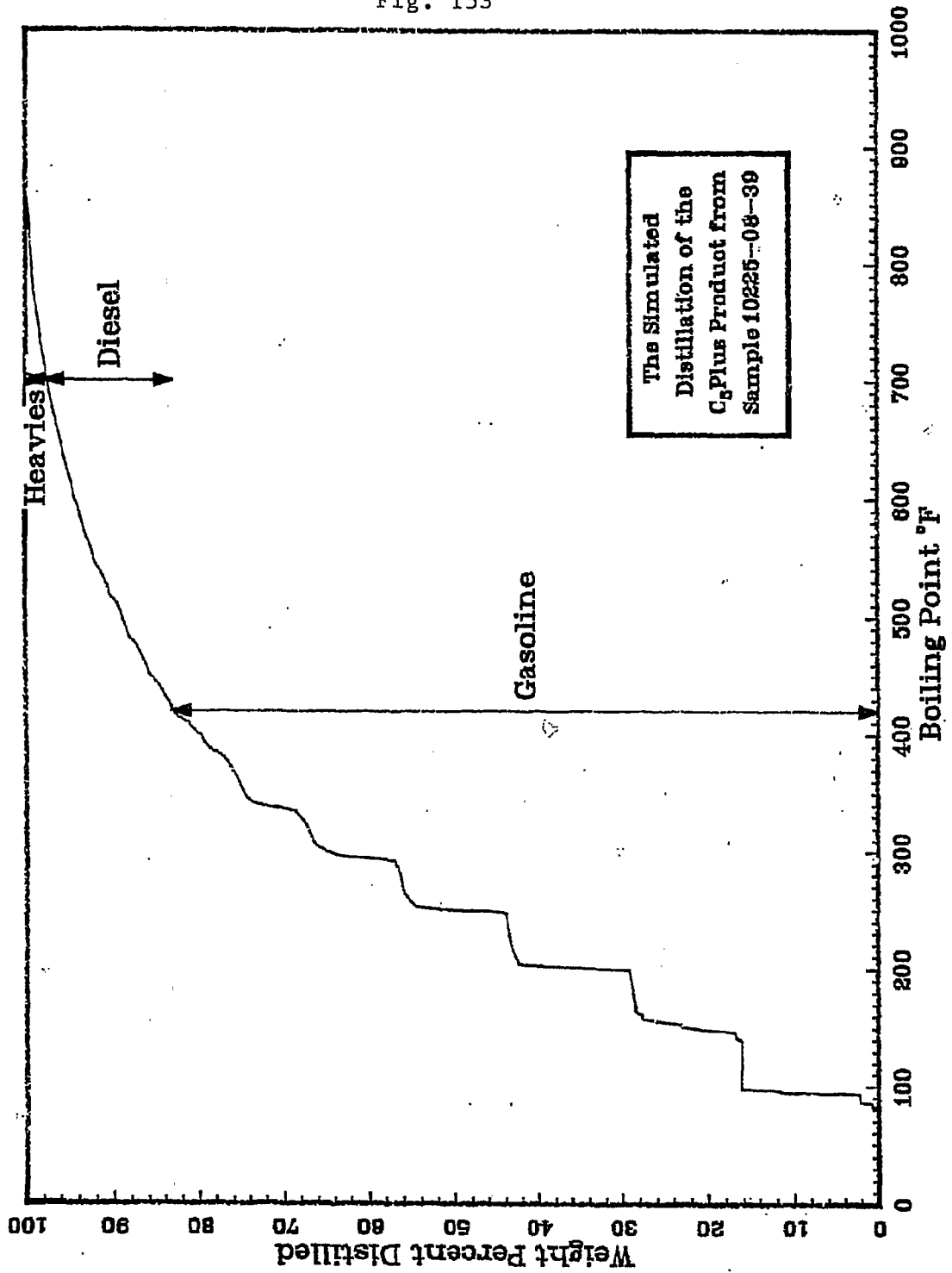


Fig. 154

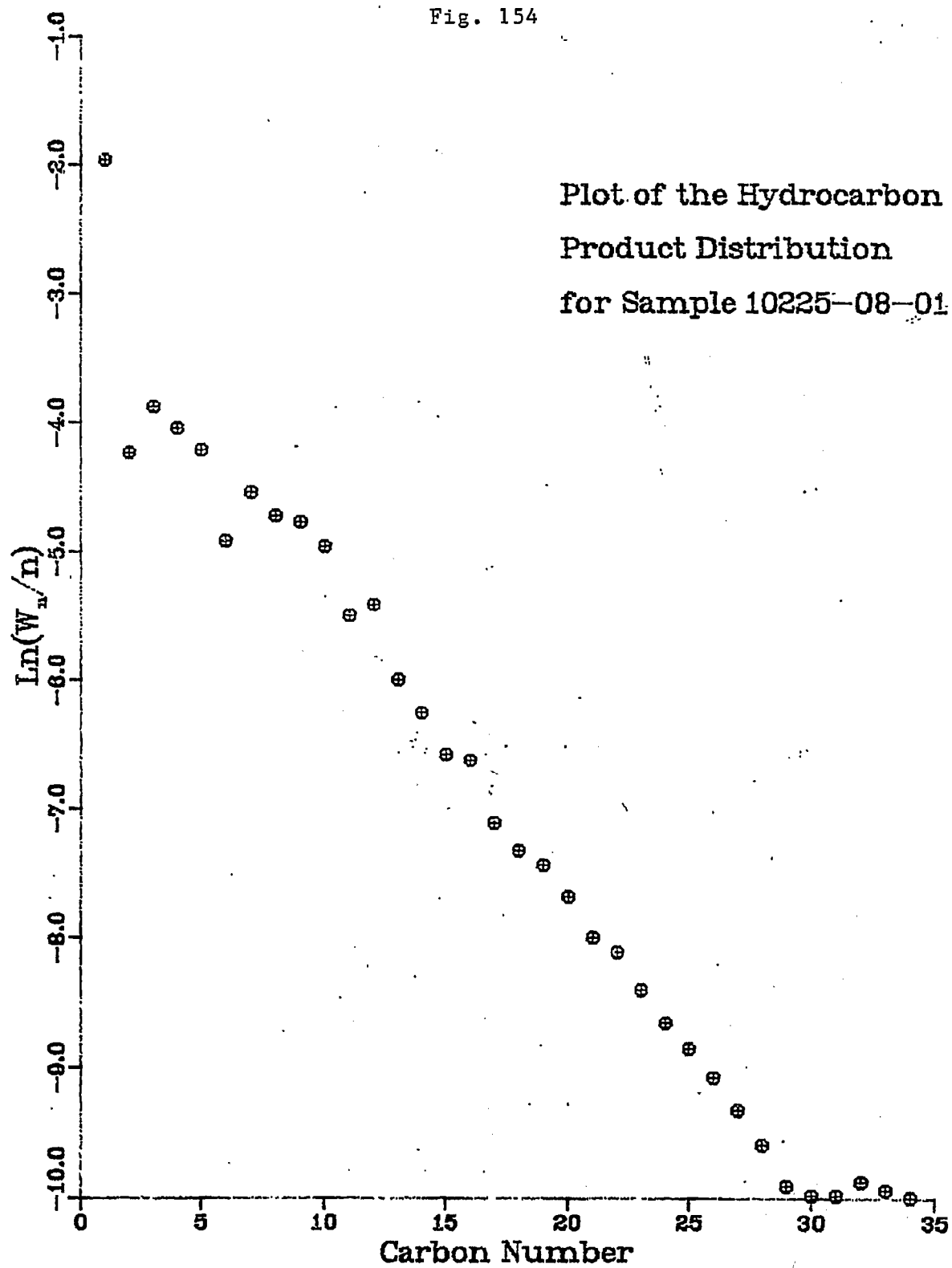


Fig. 155

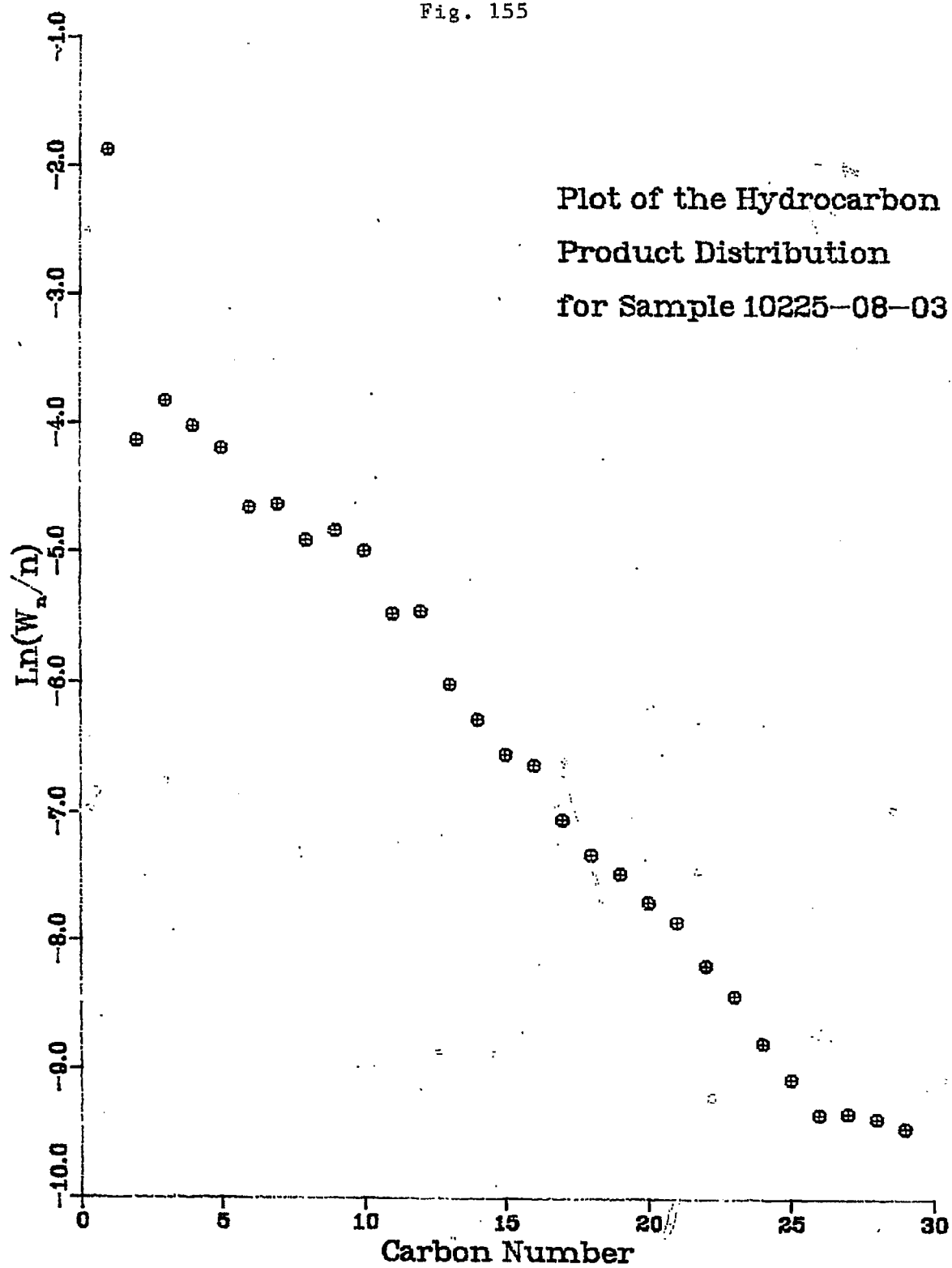


Fig. 156

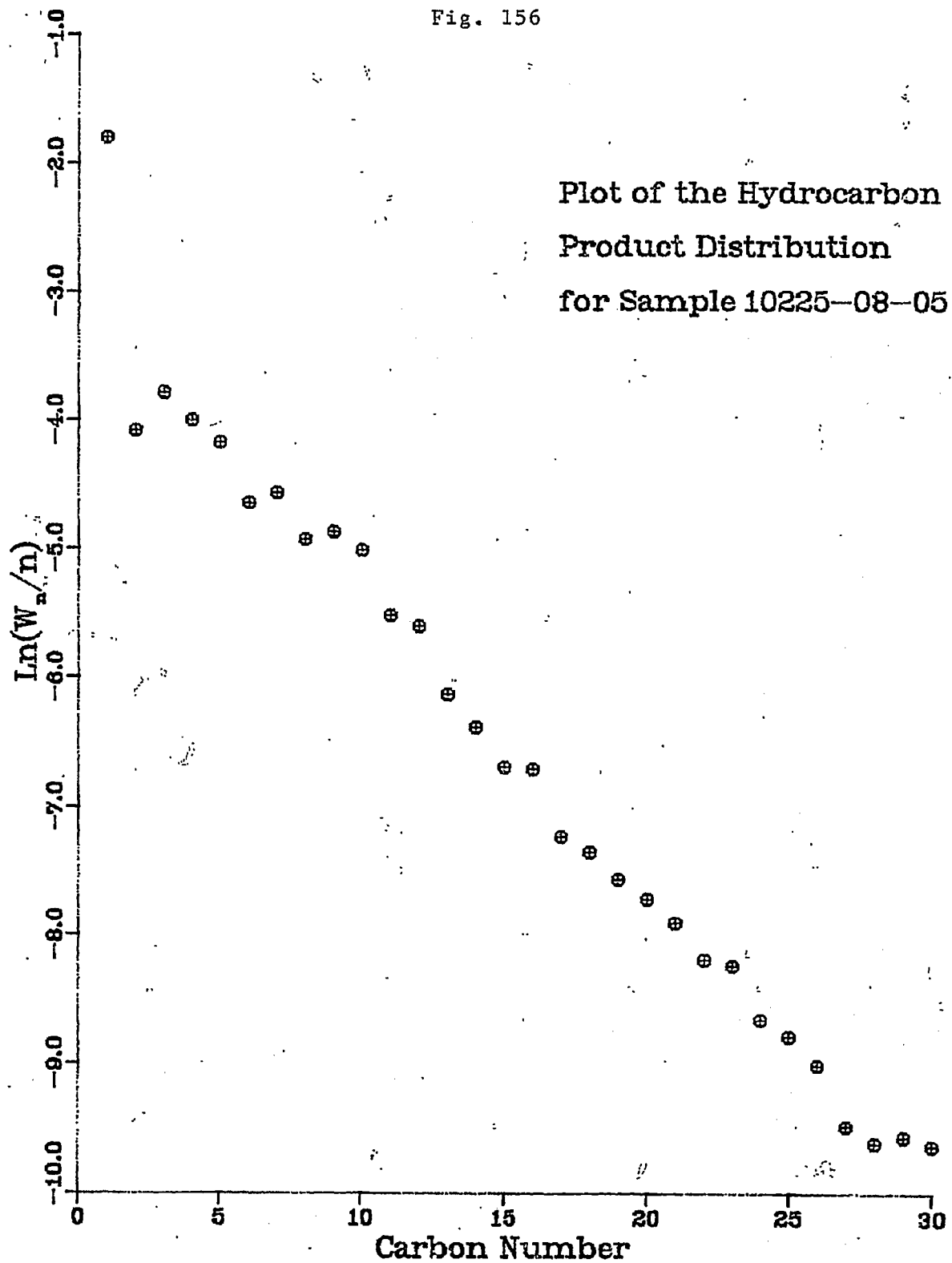


Fig. 157

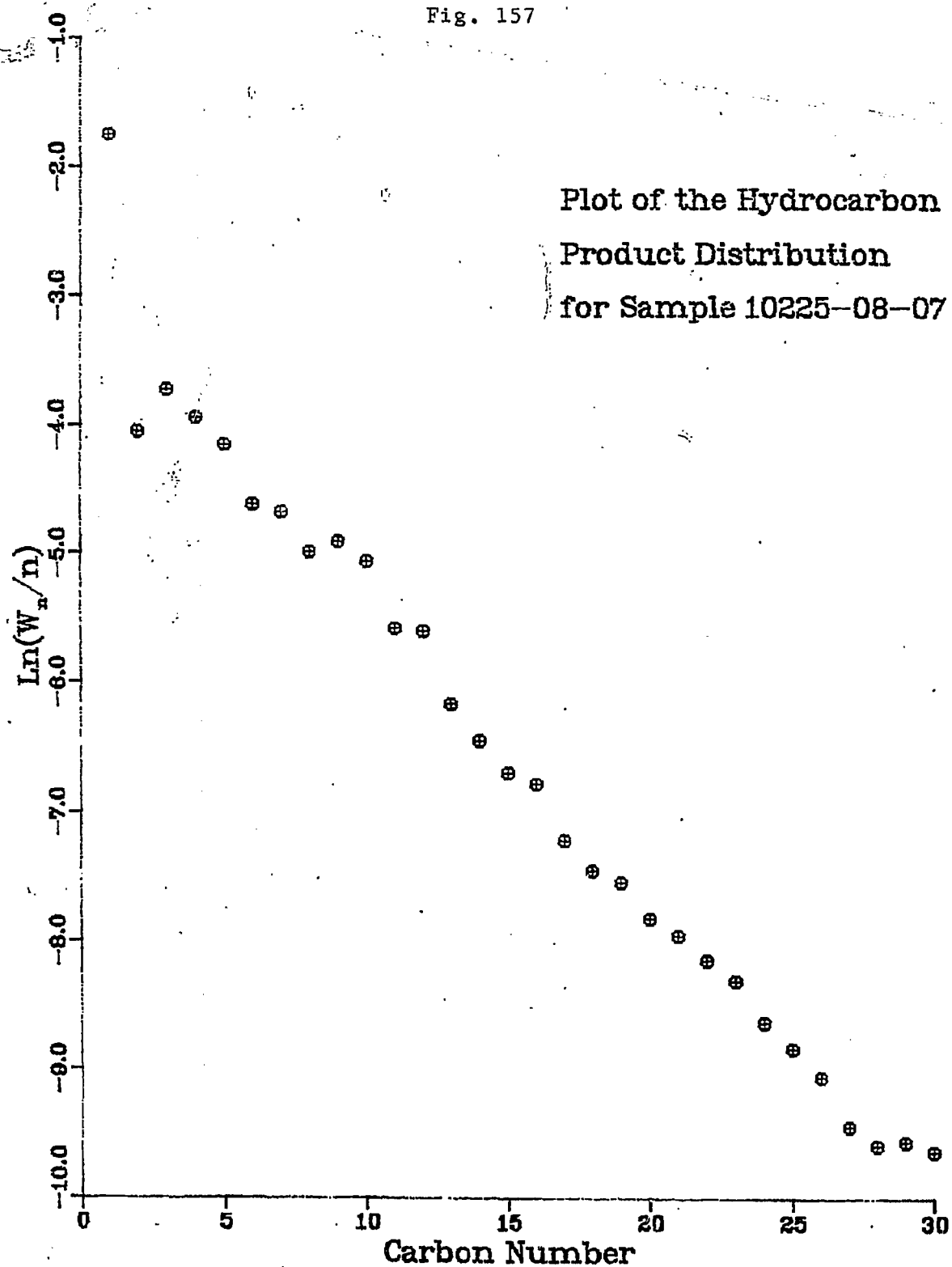


Fig.. 158

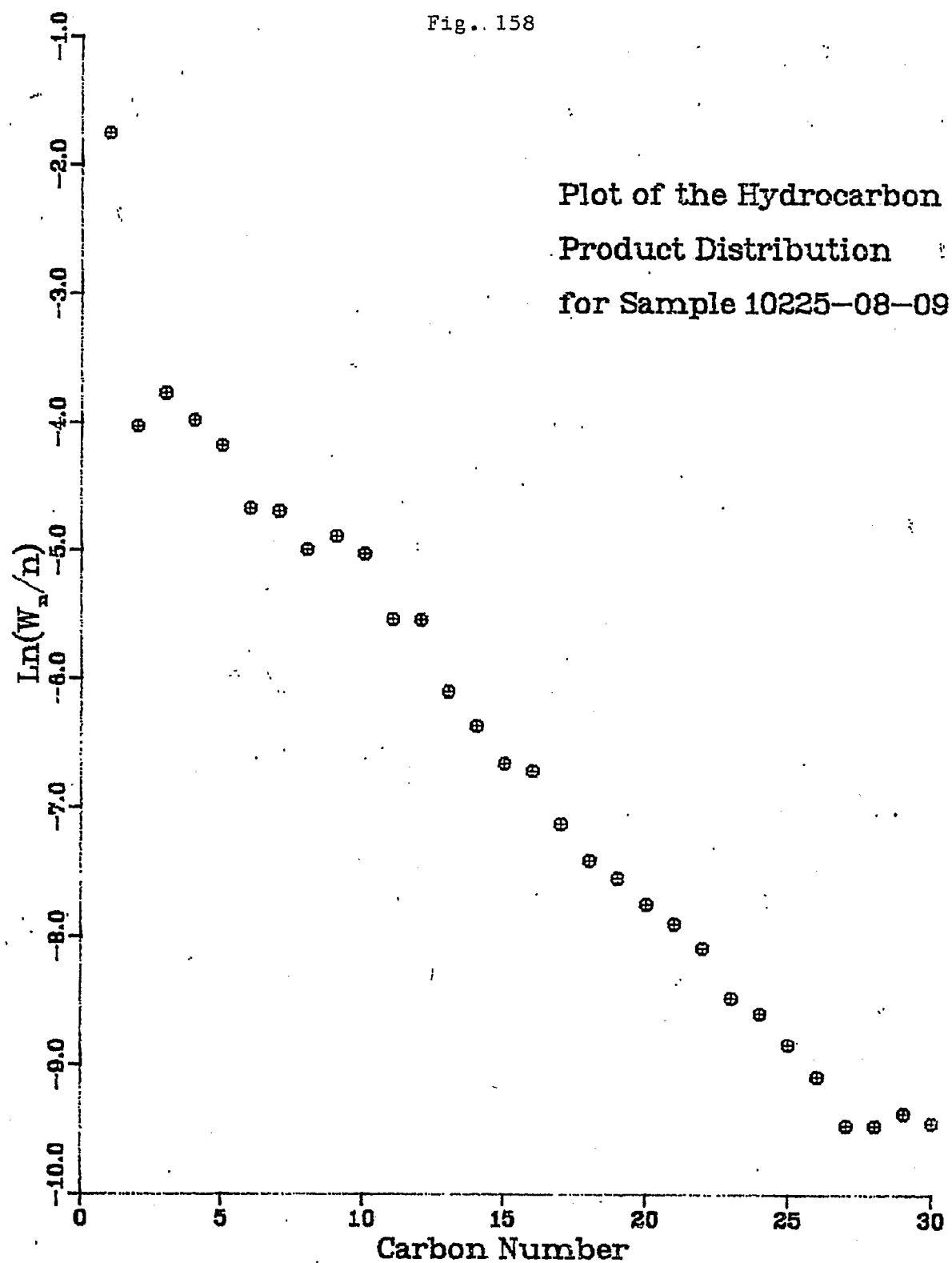


Fig. 159

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-08-11

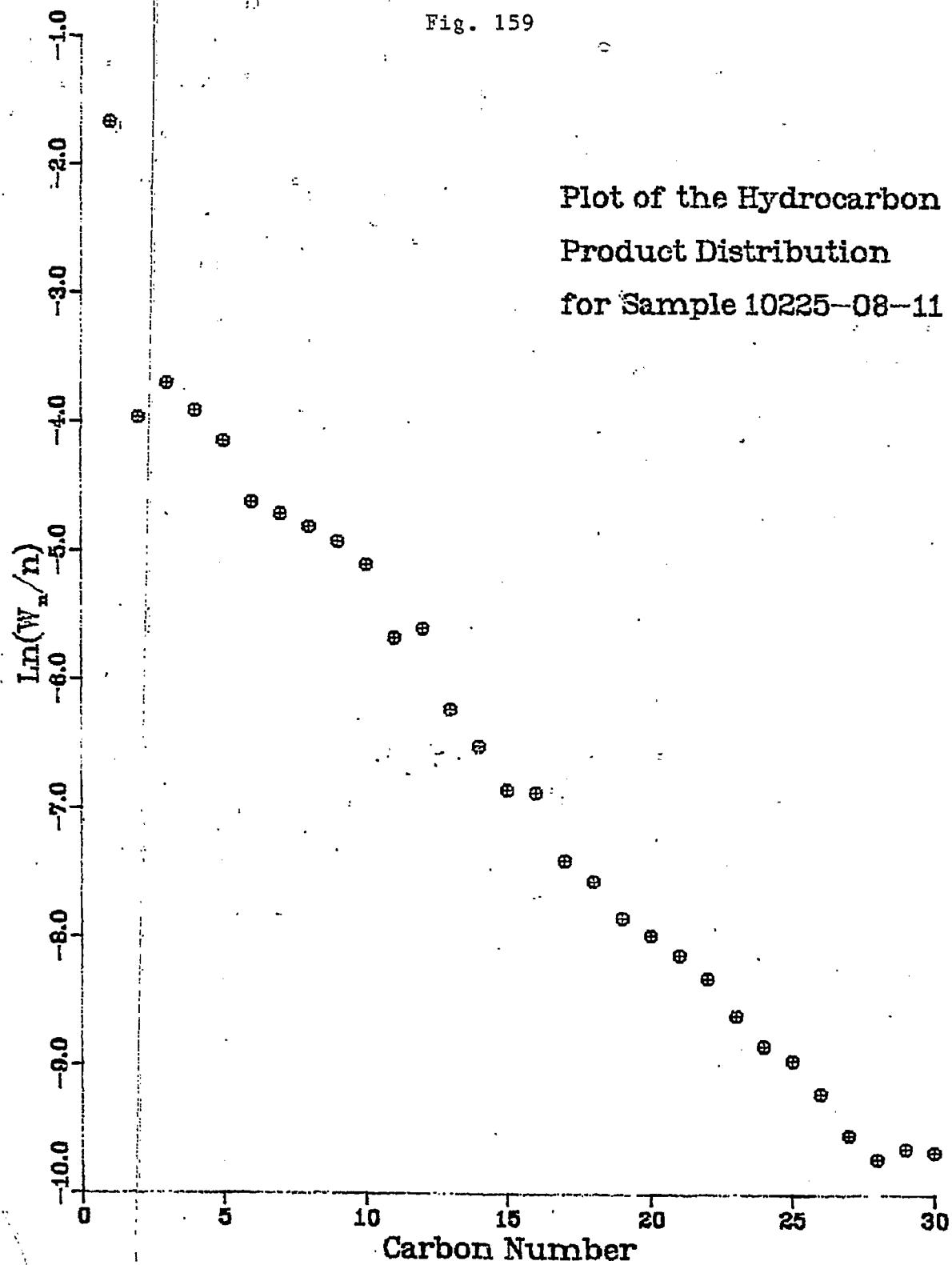


Fig. 160

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-08-13

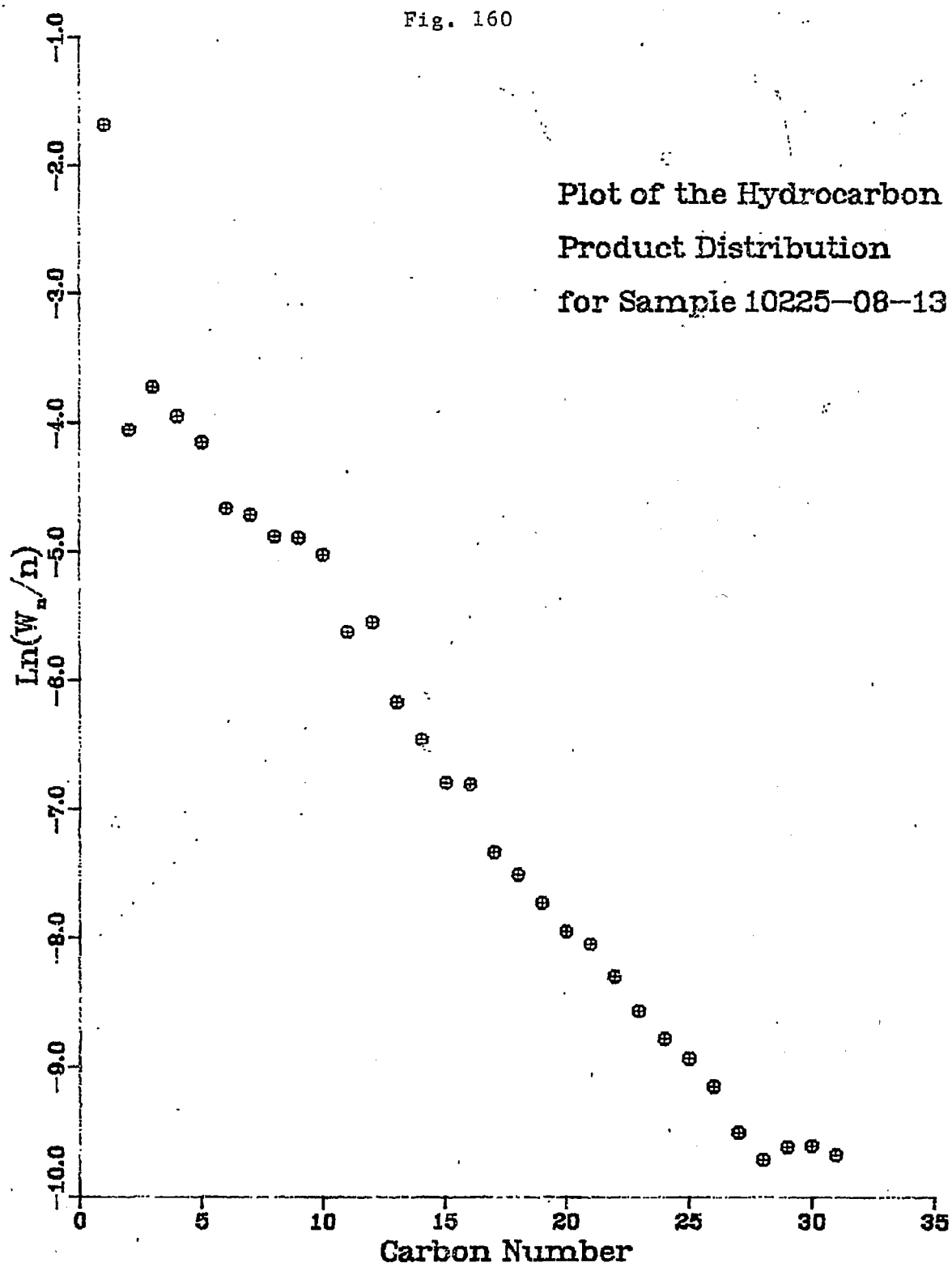


Fig. 161

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-08-15

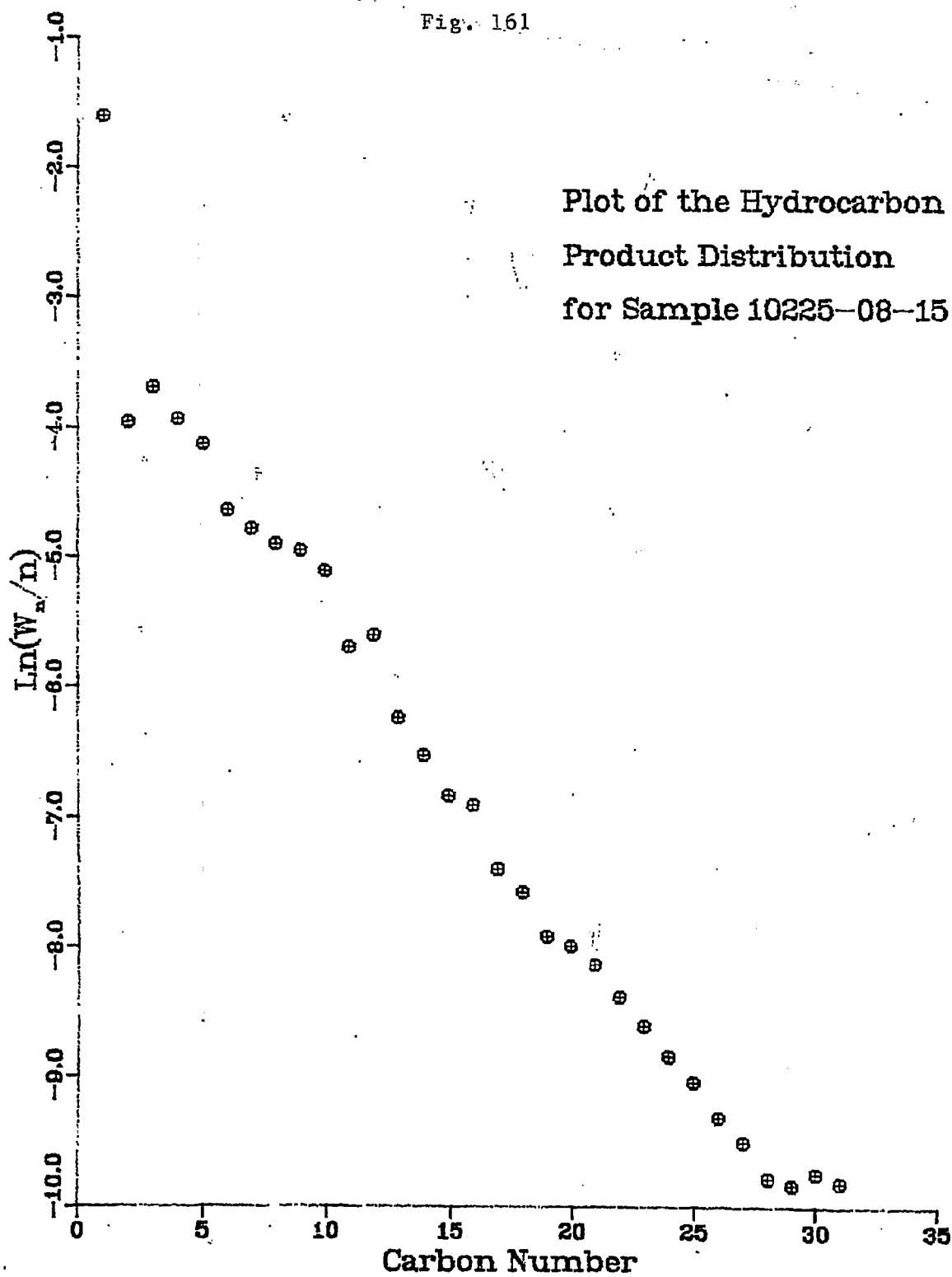


Fig. 162

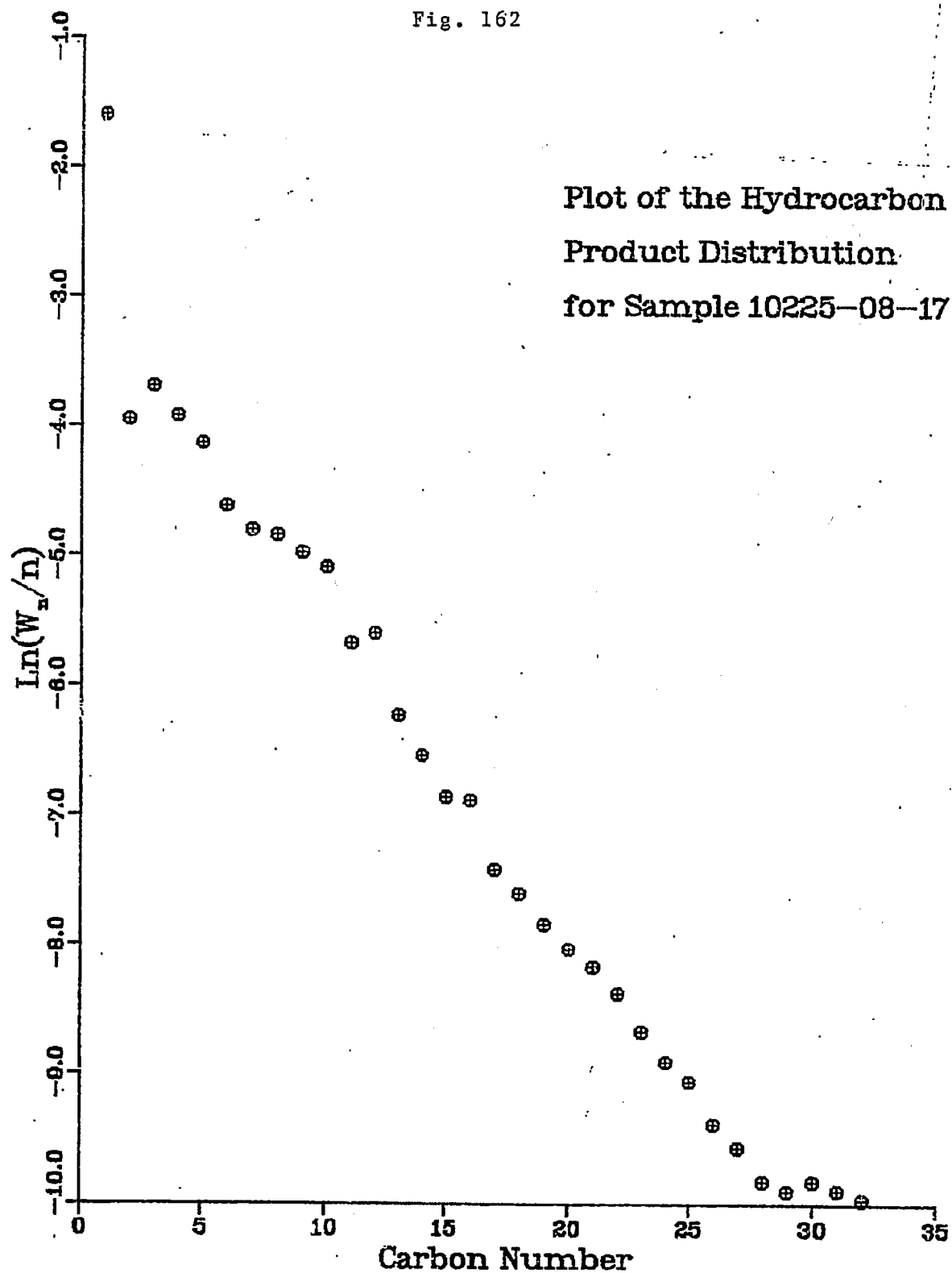


Fig. 163

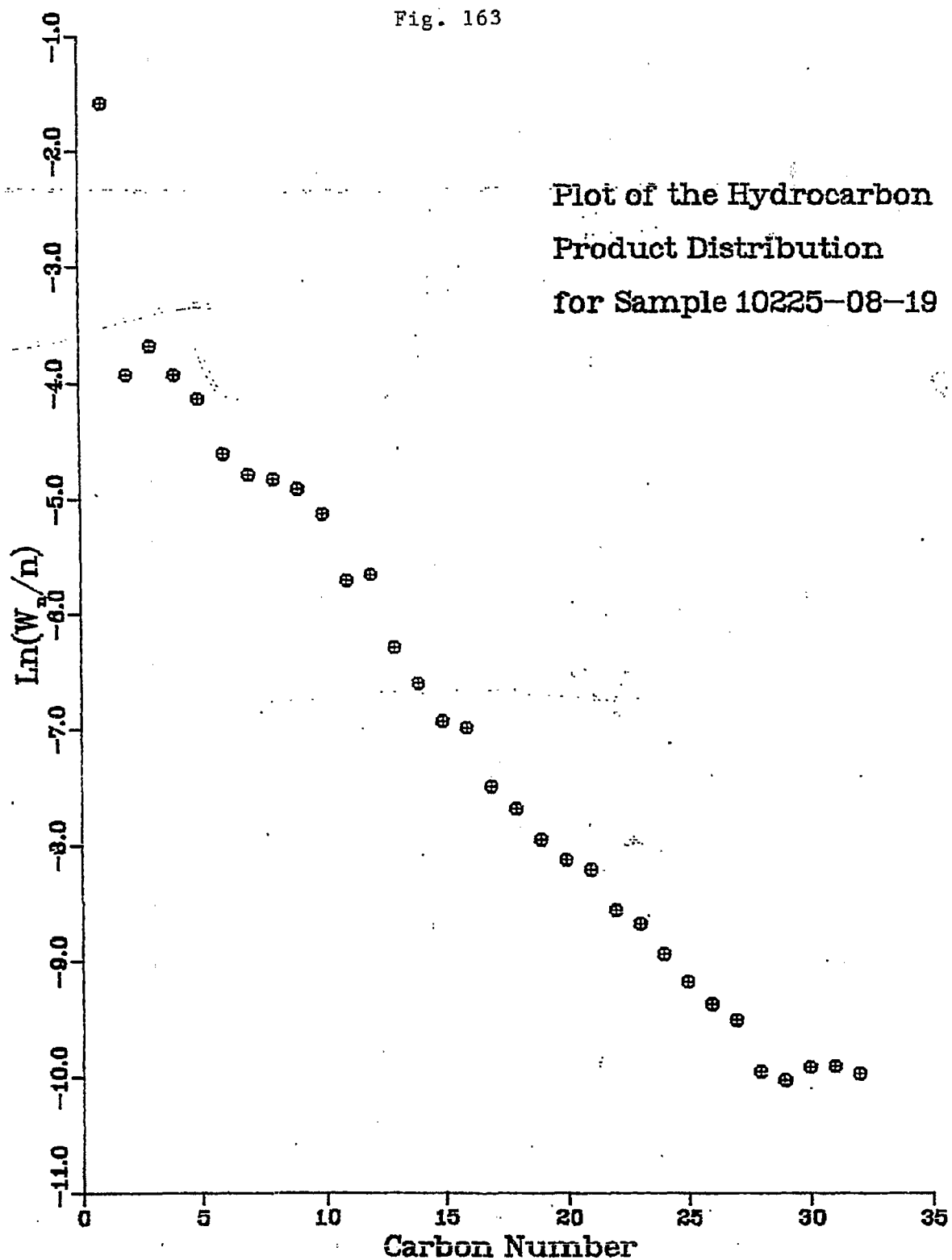


Fig. 164

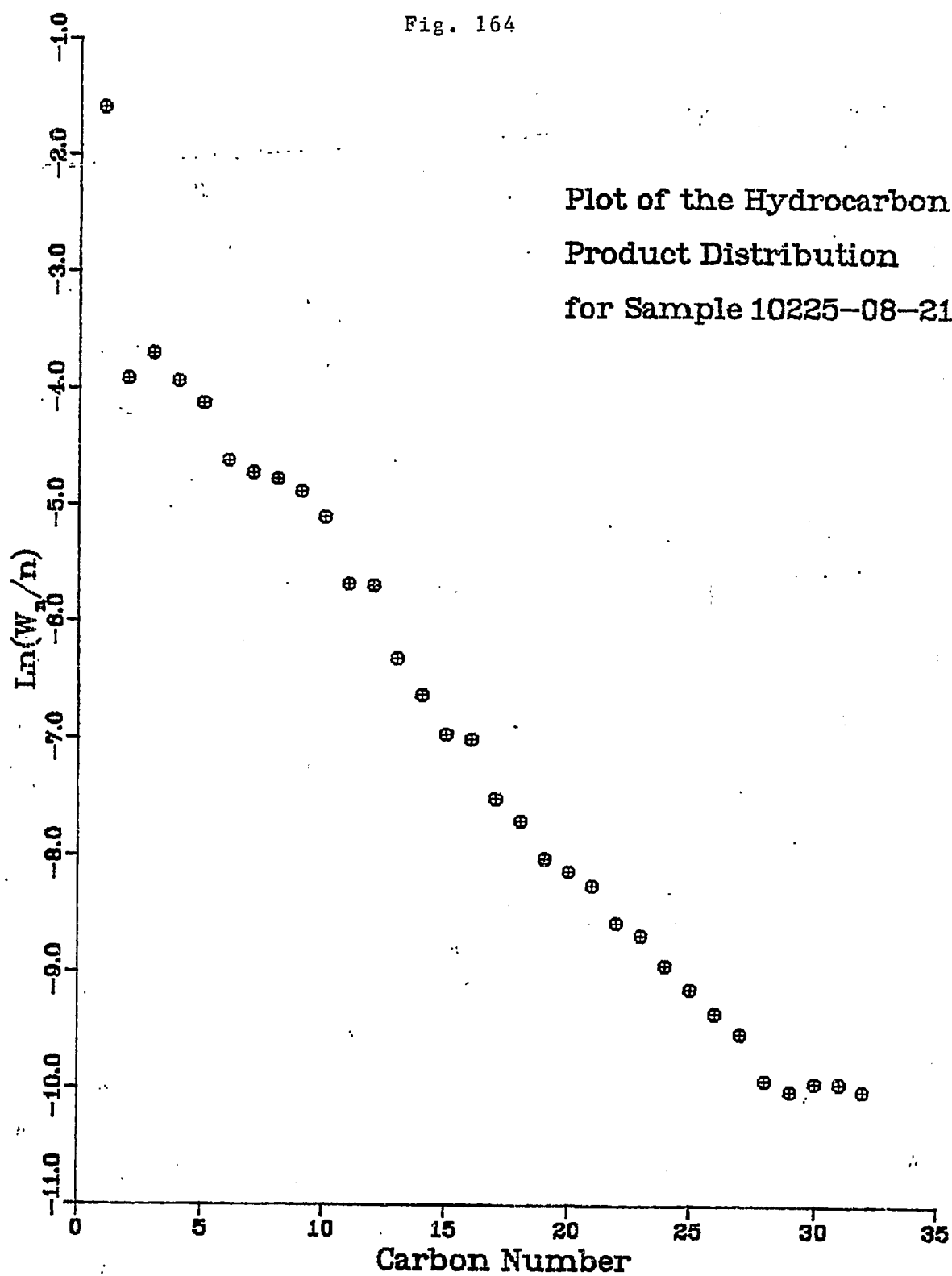


Fig. 165

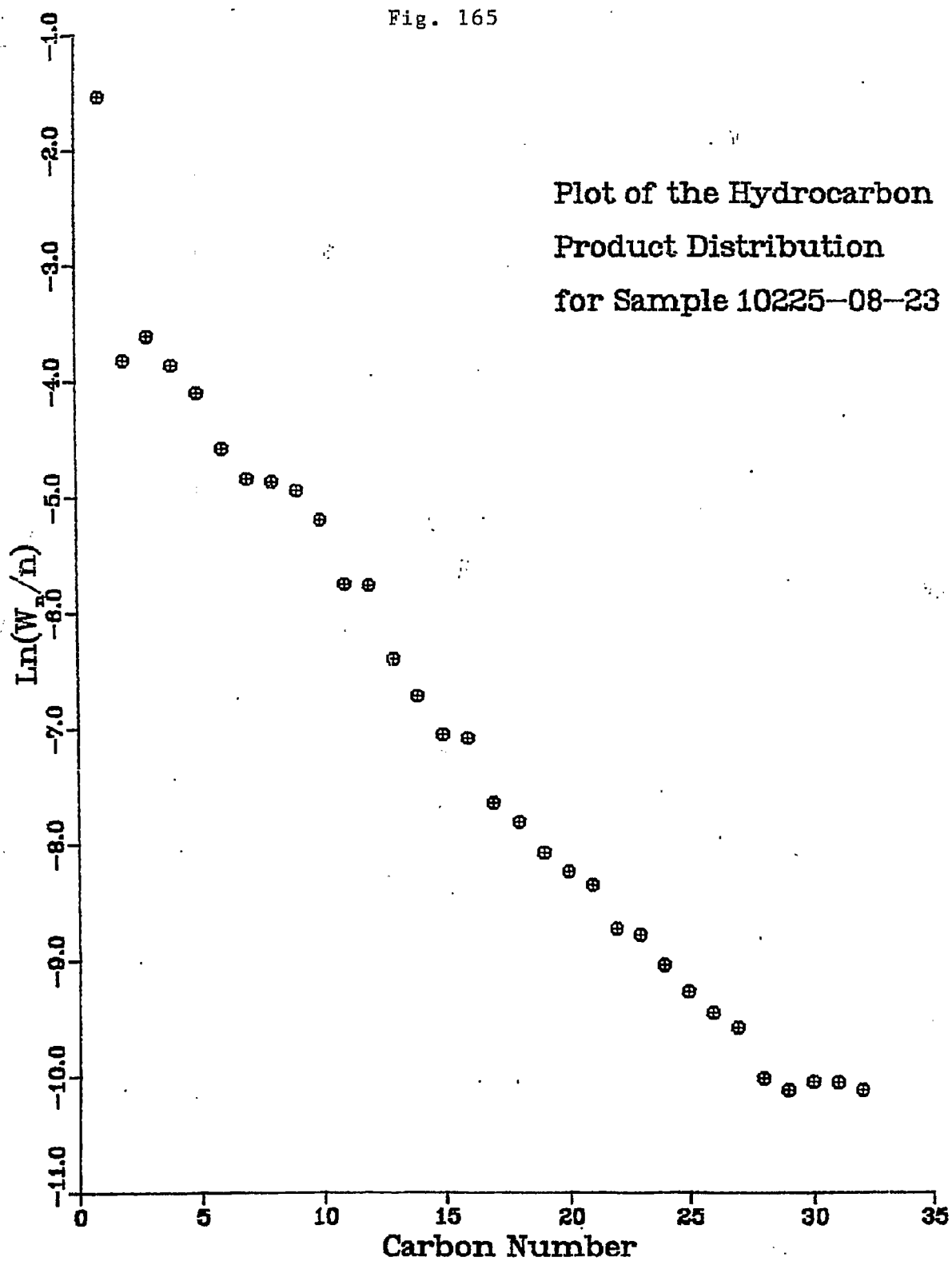


Fig. 166

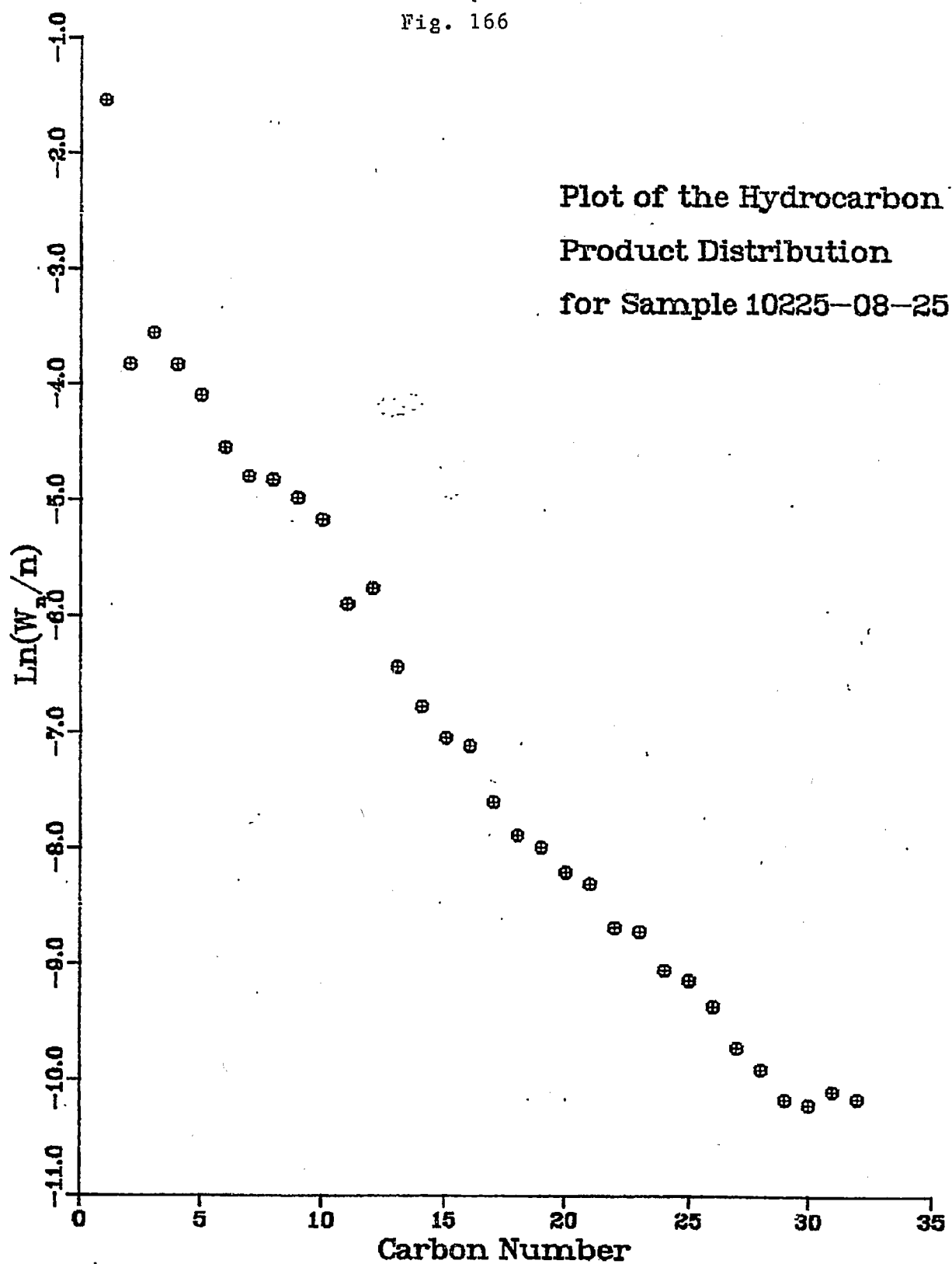


Fig. 167

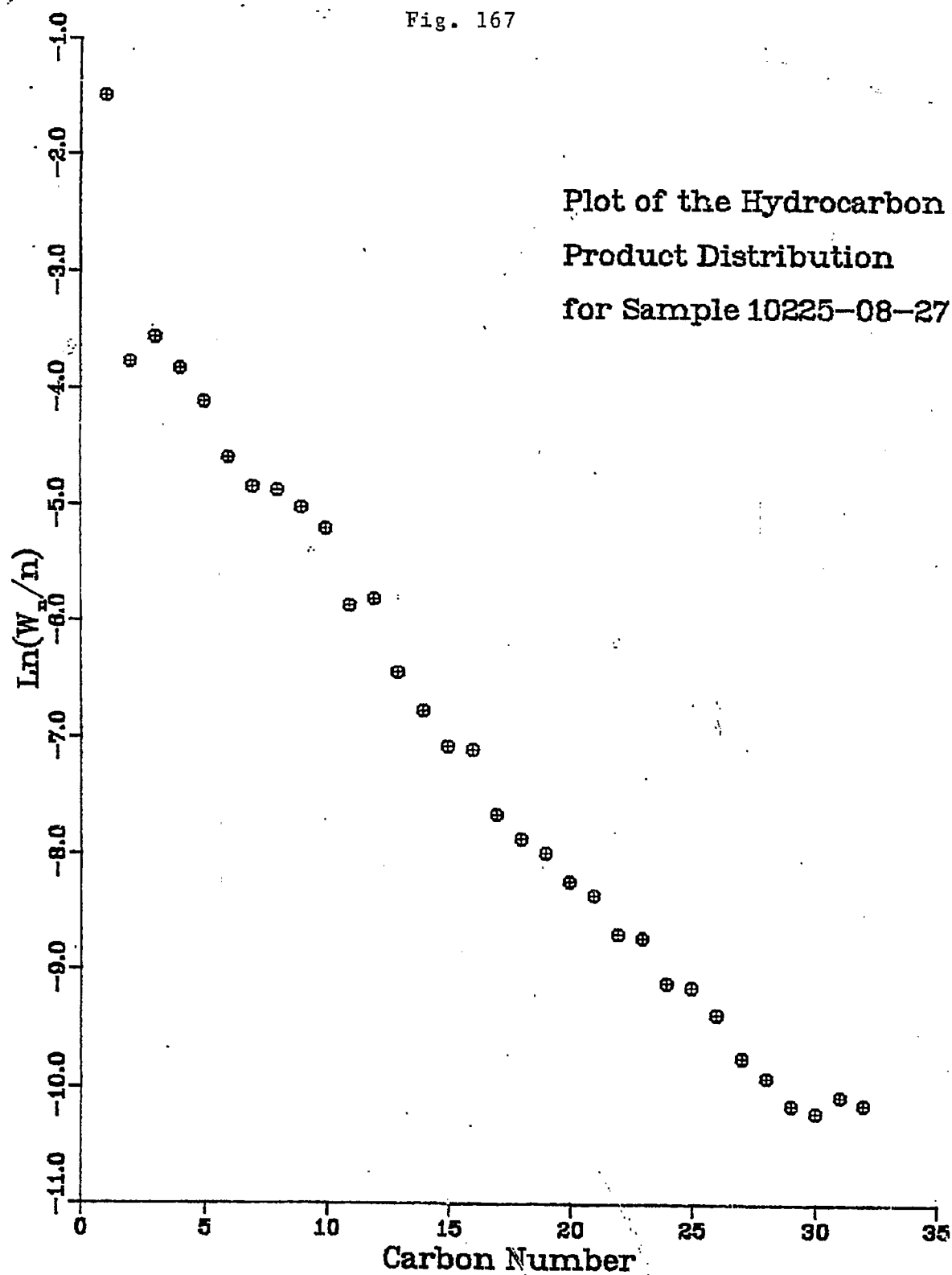


Fig. 168

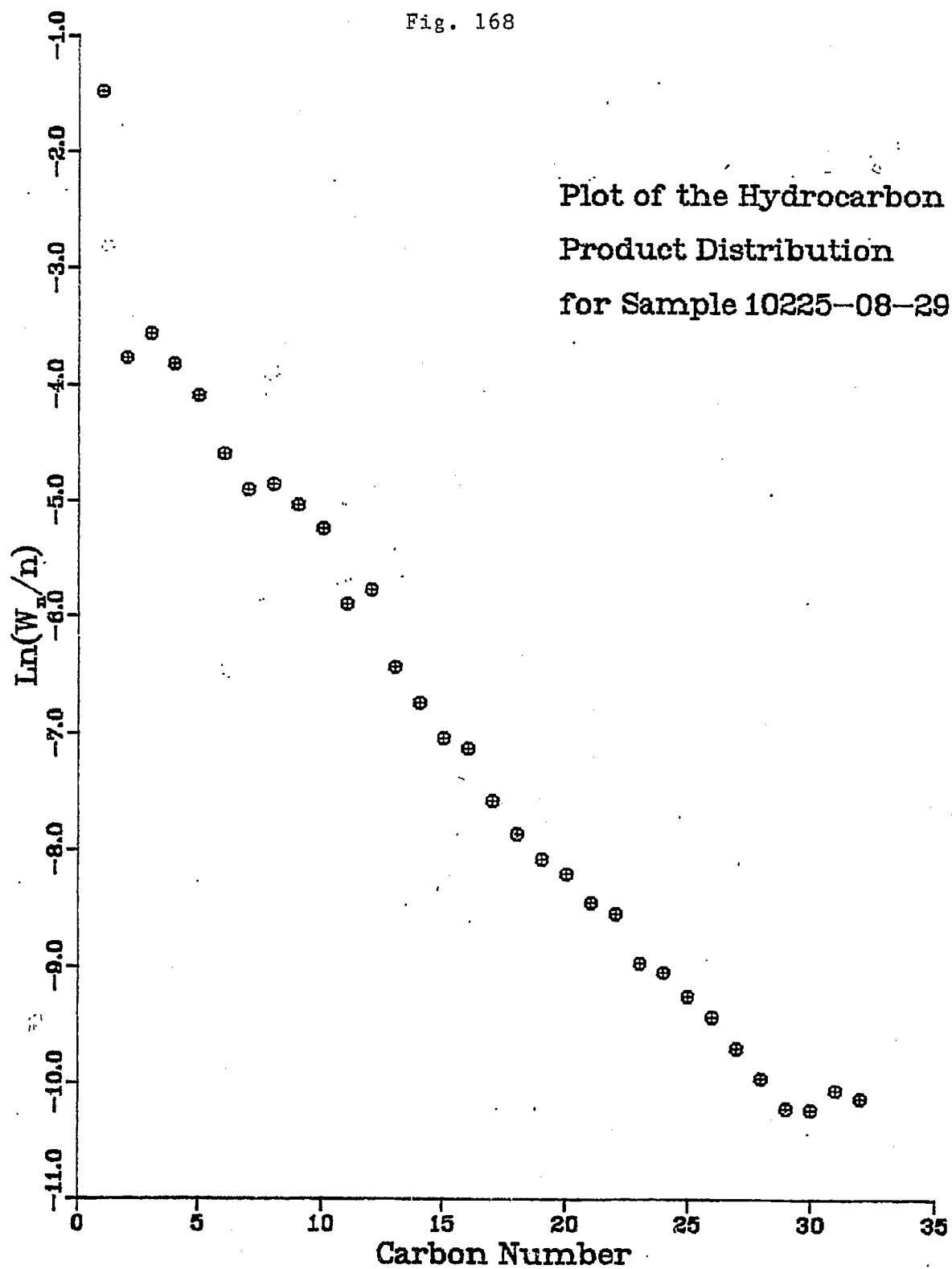


Fig. 169

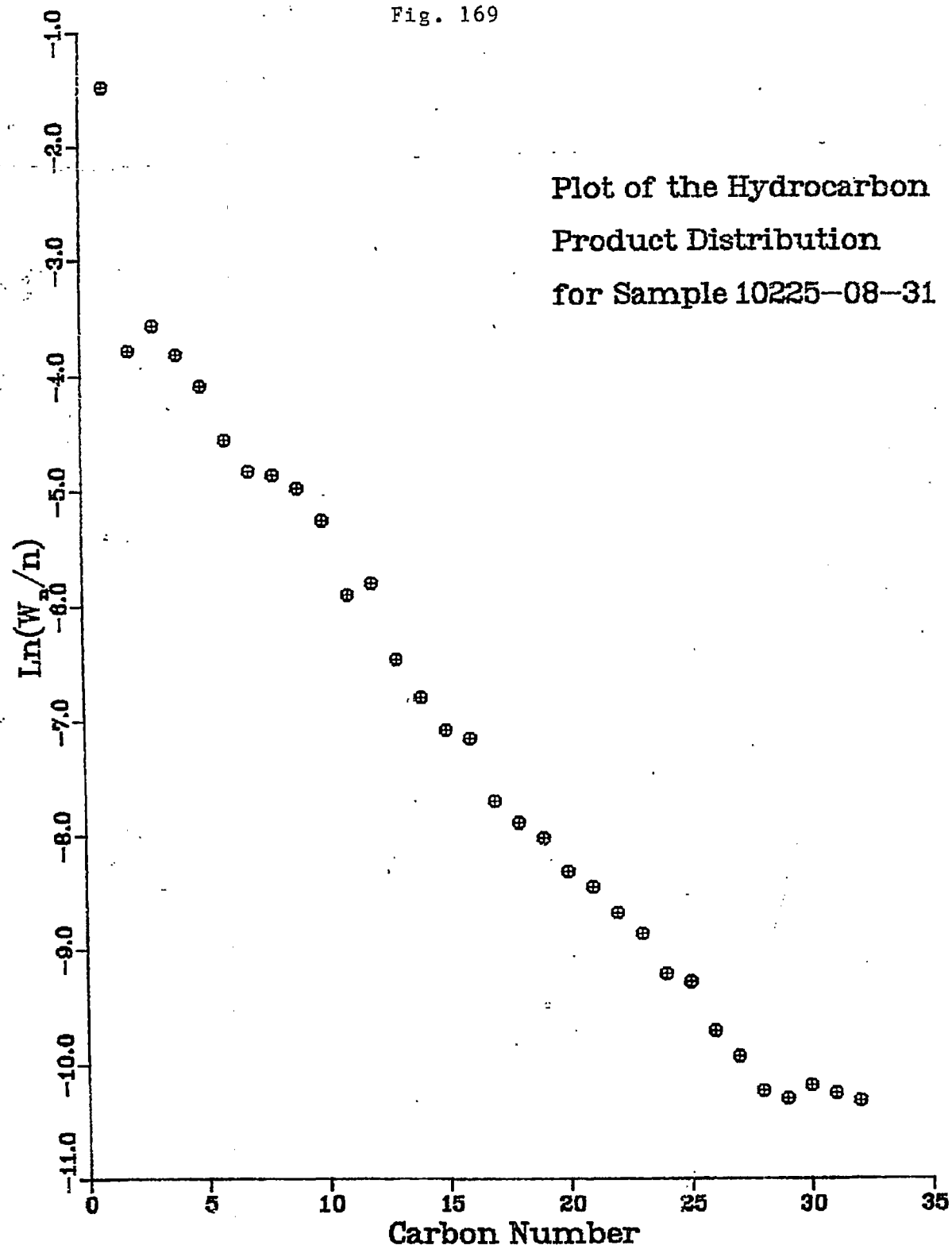


Fig. 170

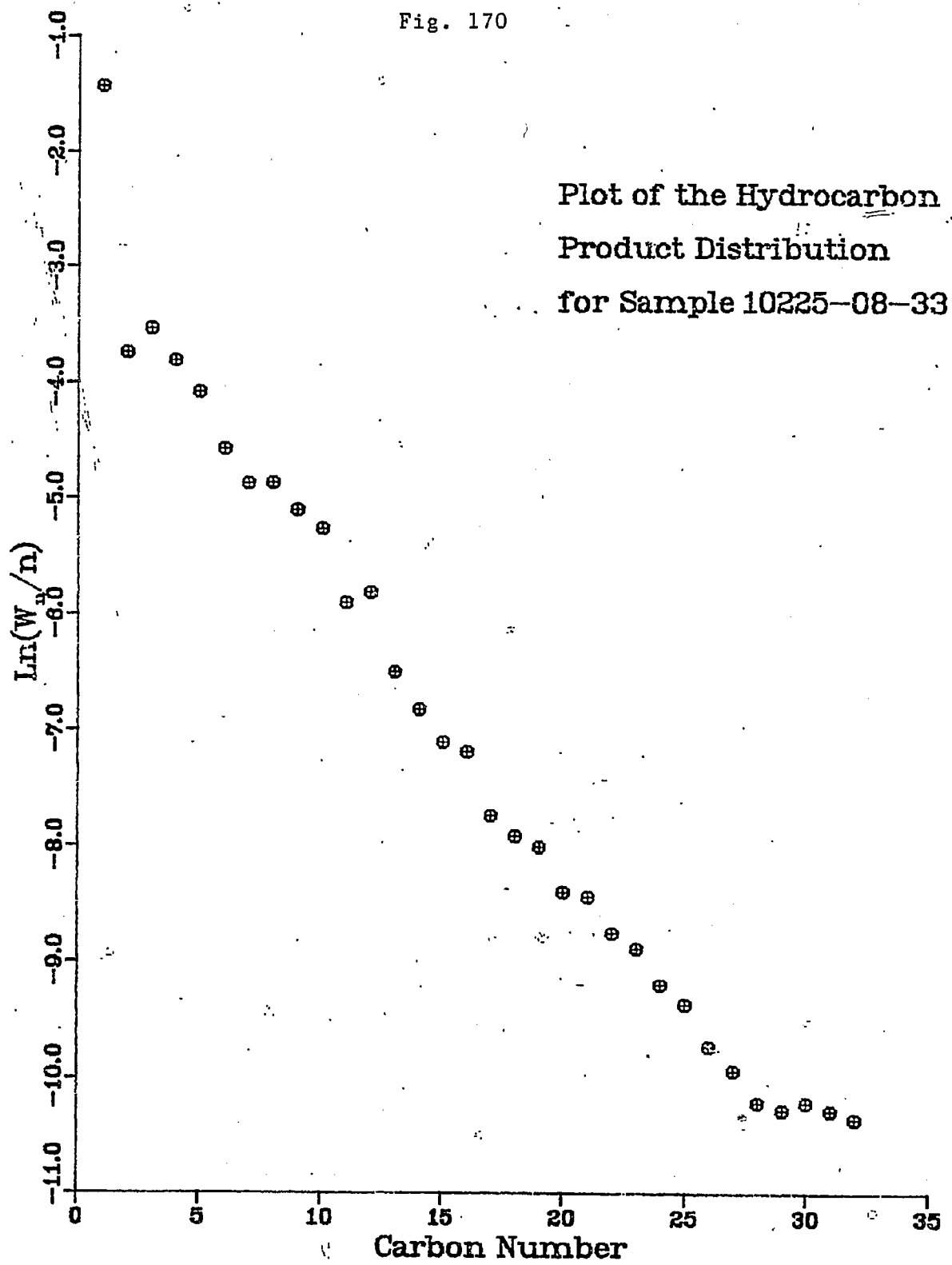


Fig. 171

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-08-35

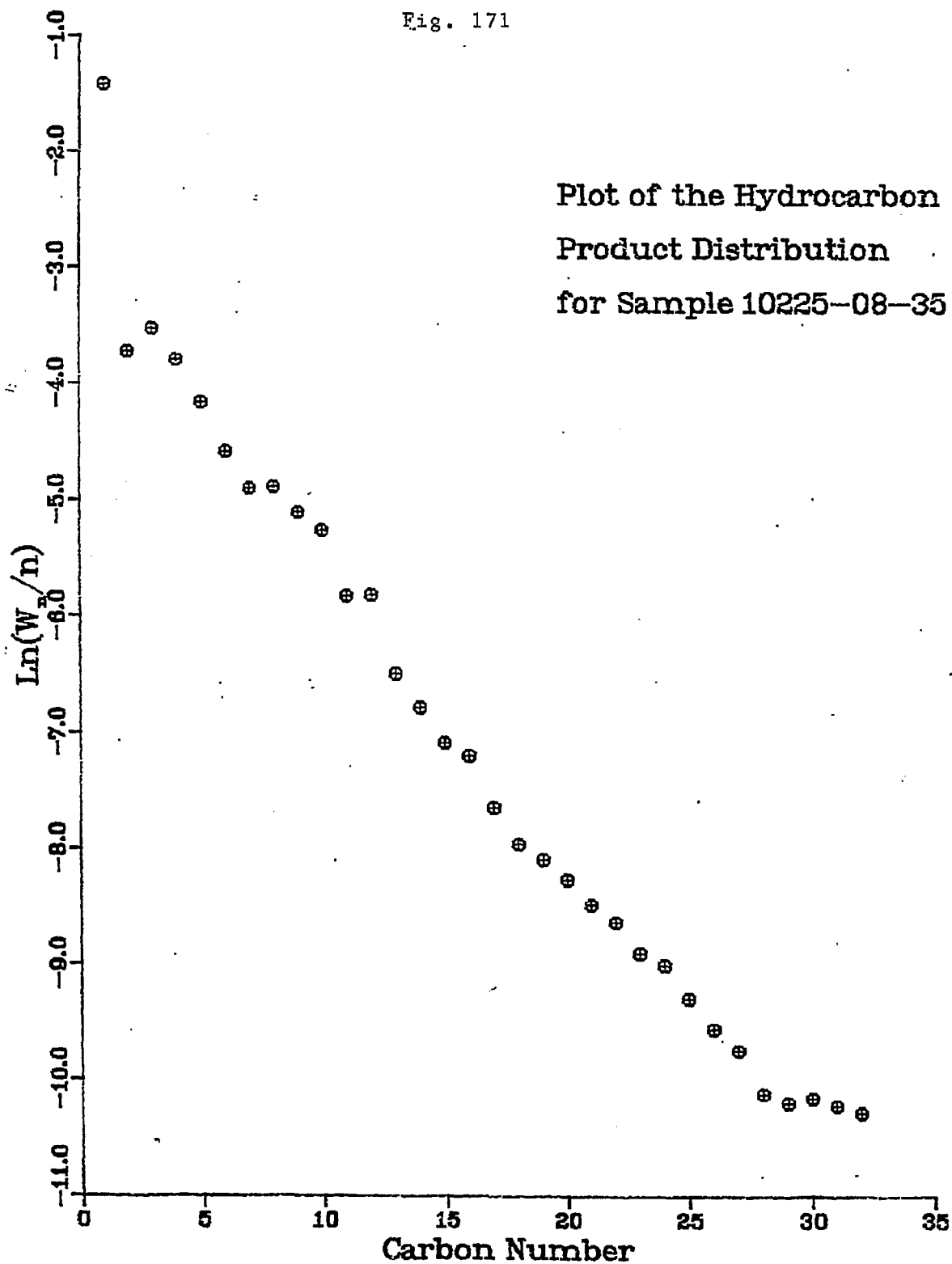


Fig. 172

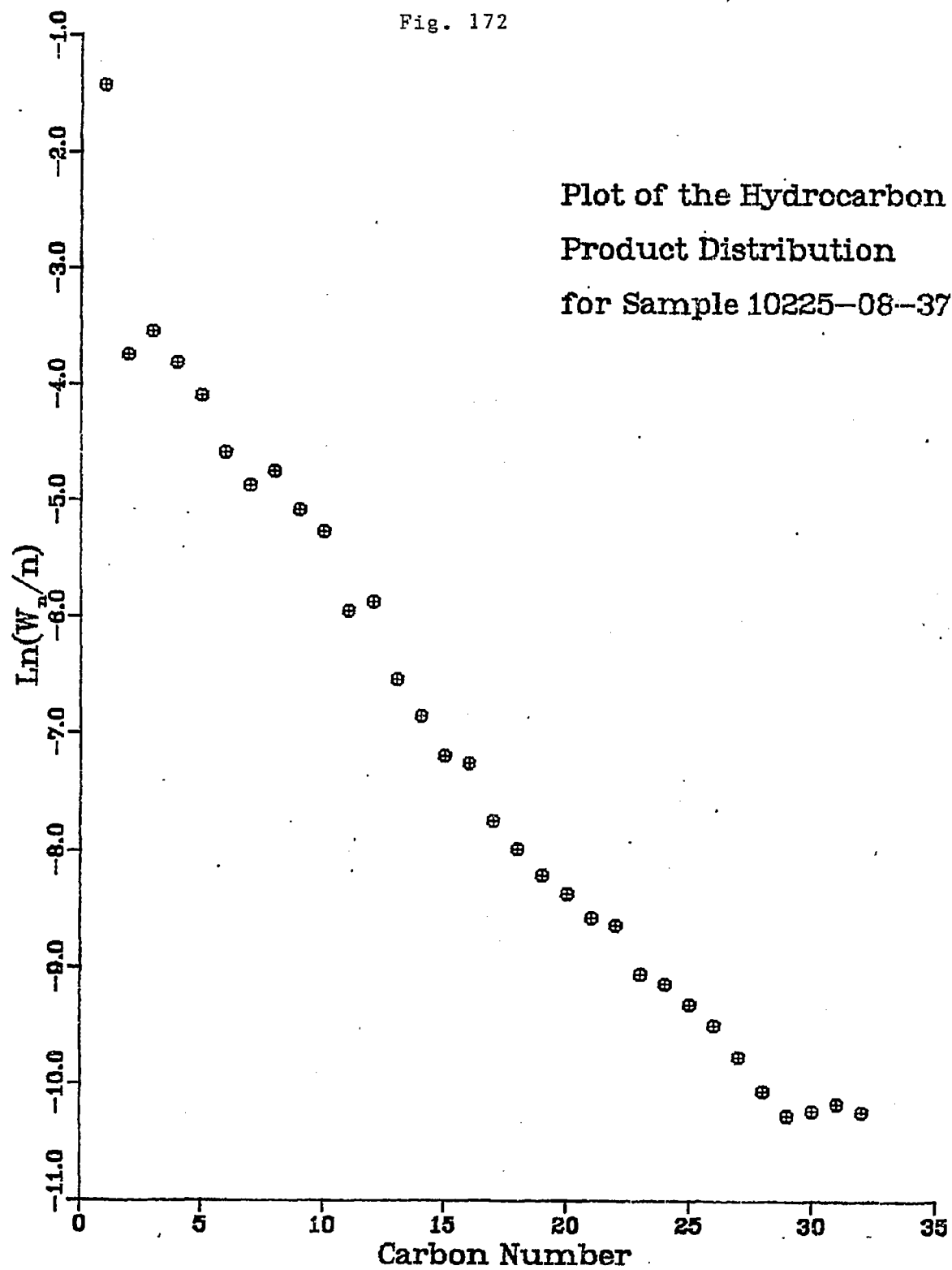


Fig. 173

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-08-39

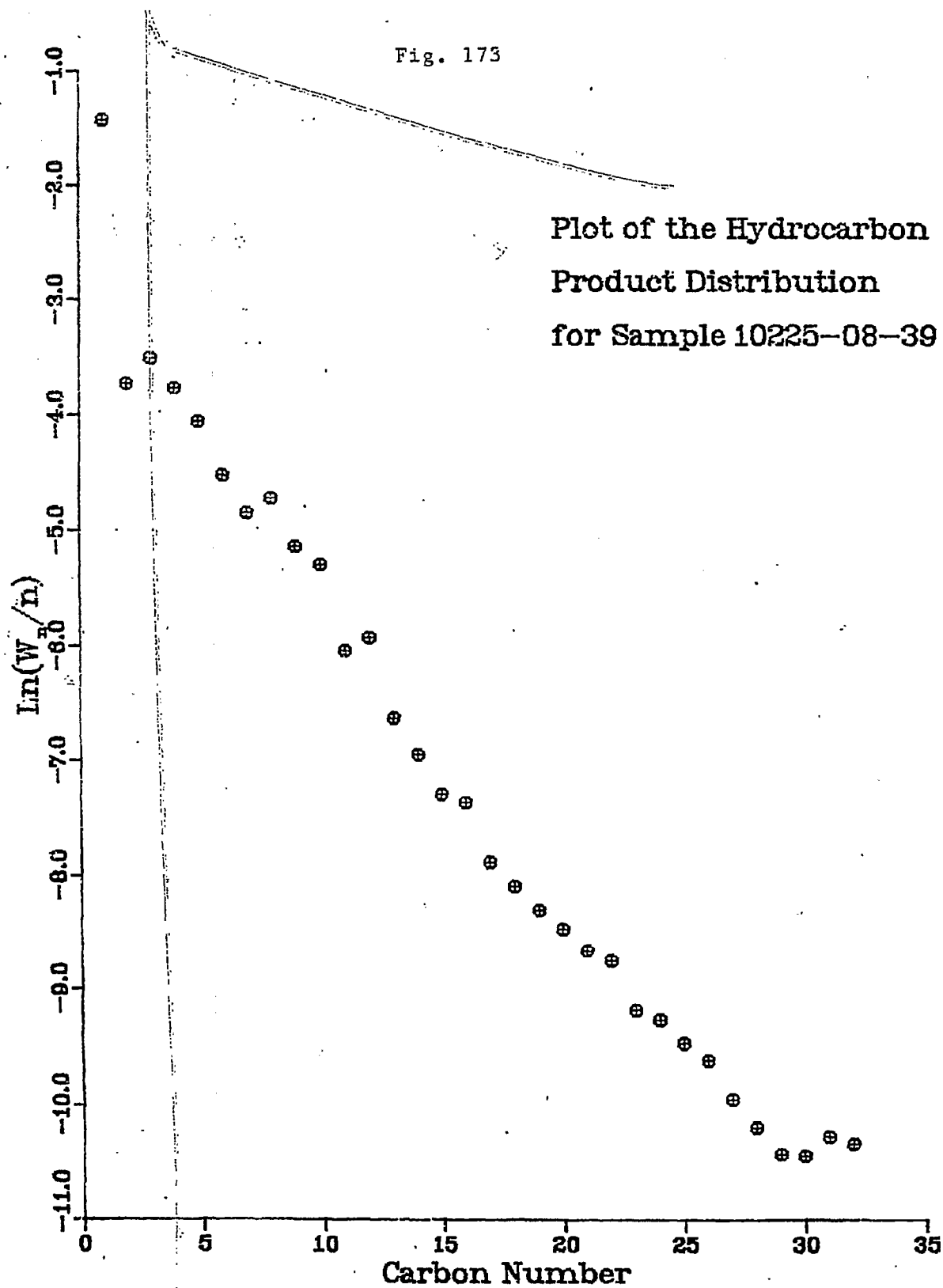
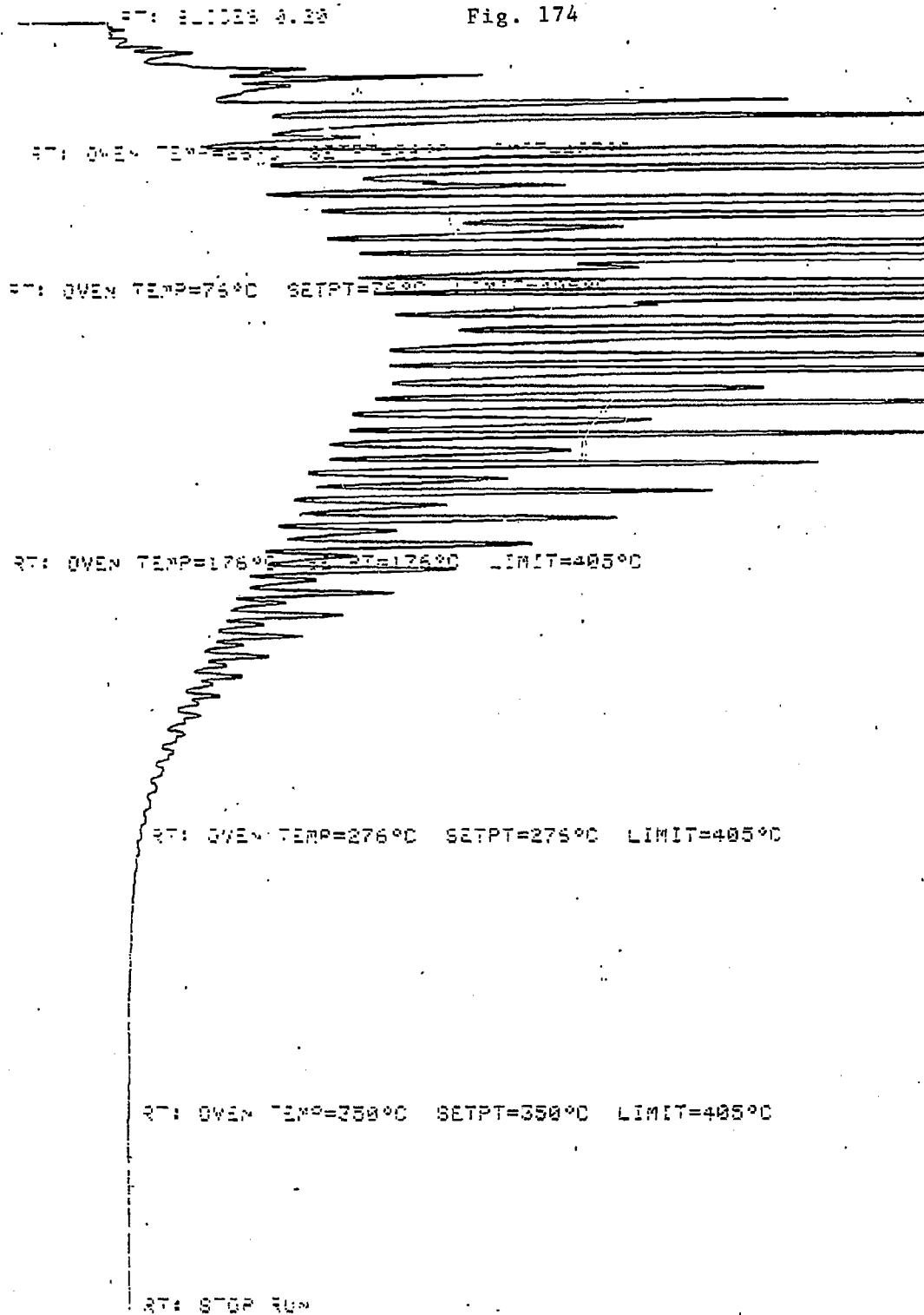


Fig. 174



SAMPLE: 10225-8-11

1.20

Fig. 175

RT: OVEN TEMP=25°C SETPT=25°C LIMIT=350°C

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

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

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

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

RT: STOP RUN

SAMPLE: 10225-3-7L

0.20

Fig. 176

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

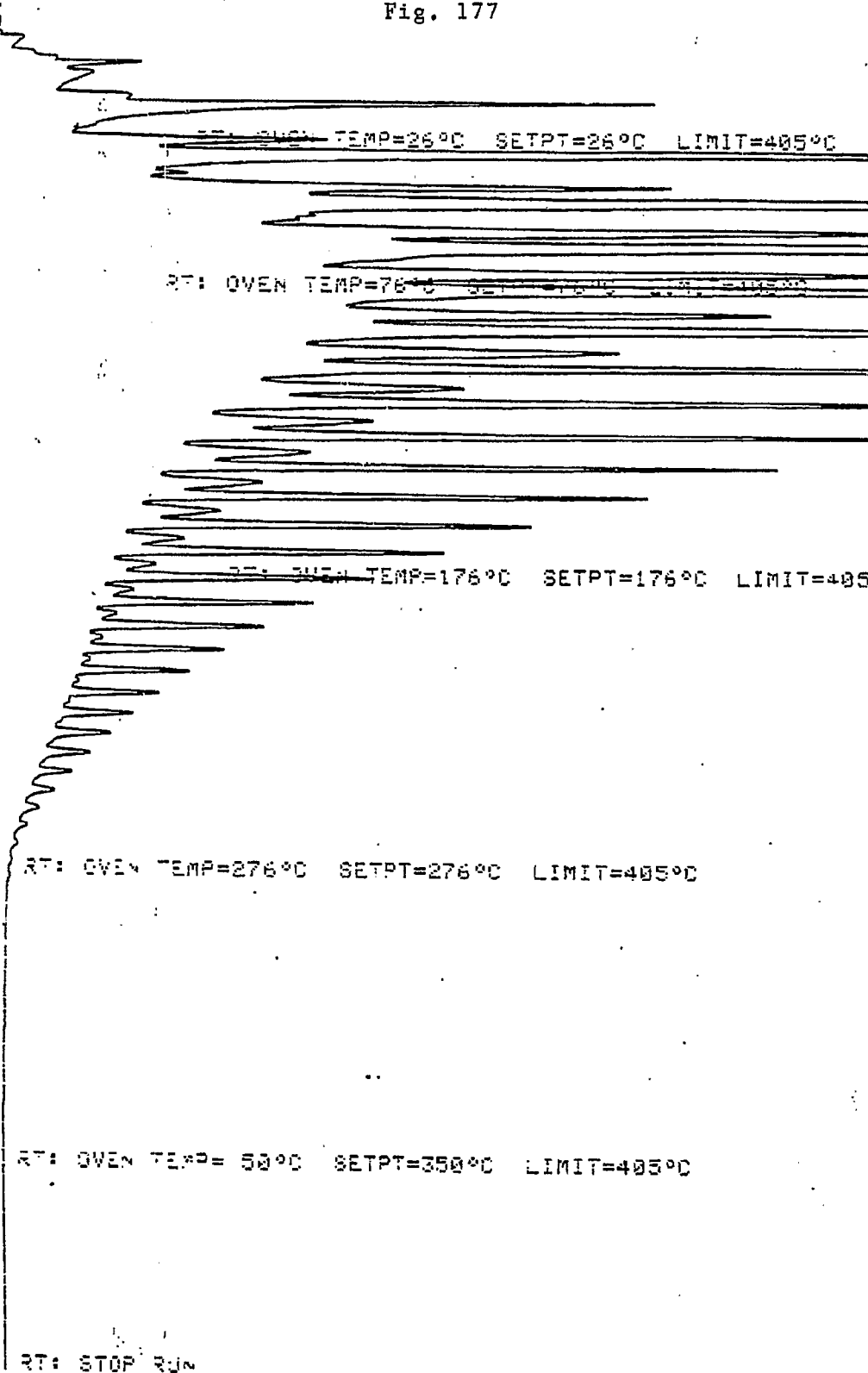
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE:10225-8-19L

RT: SLICES 9.20

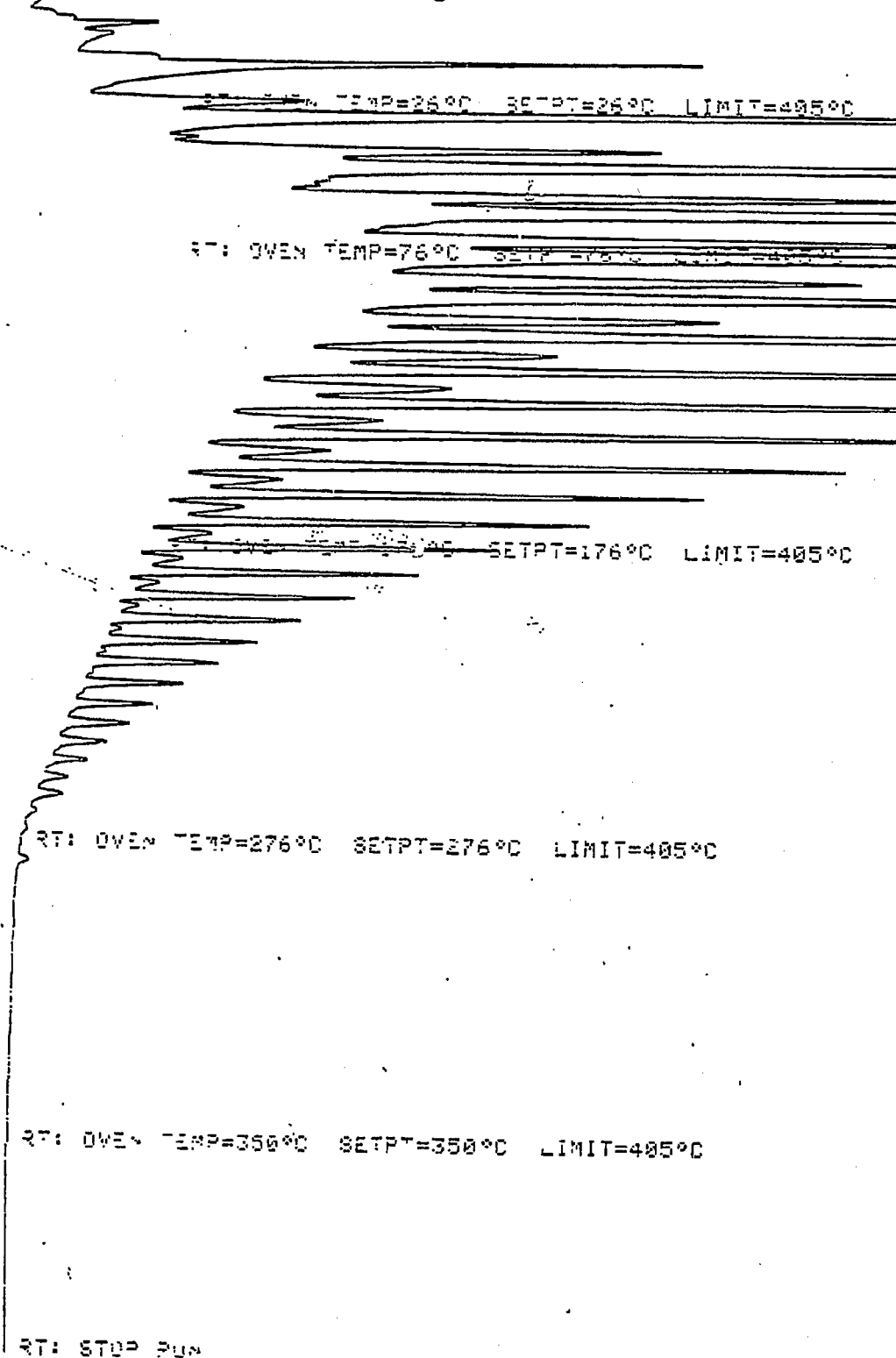
Fig. 177



SAMPLE: 10225-8-23L

RT: SLICES 0.20

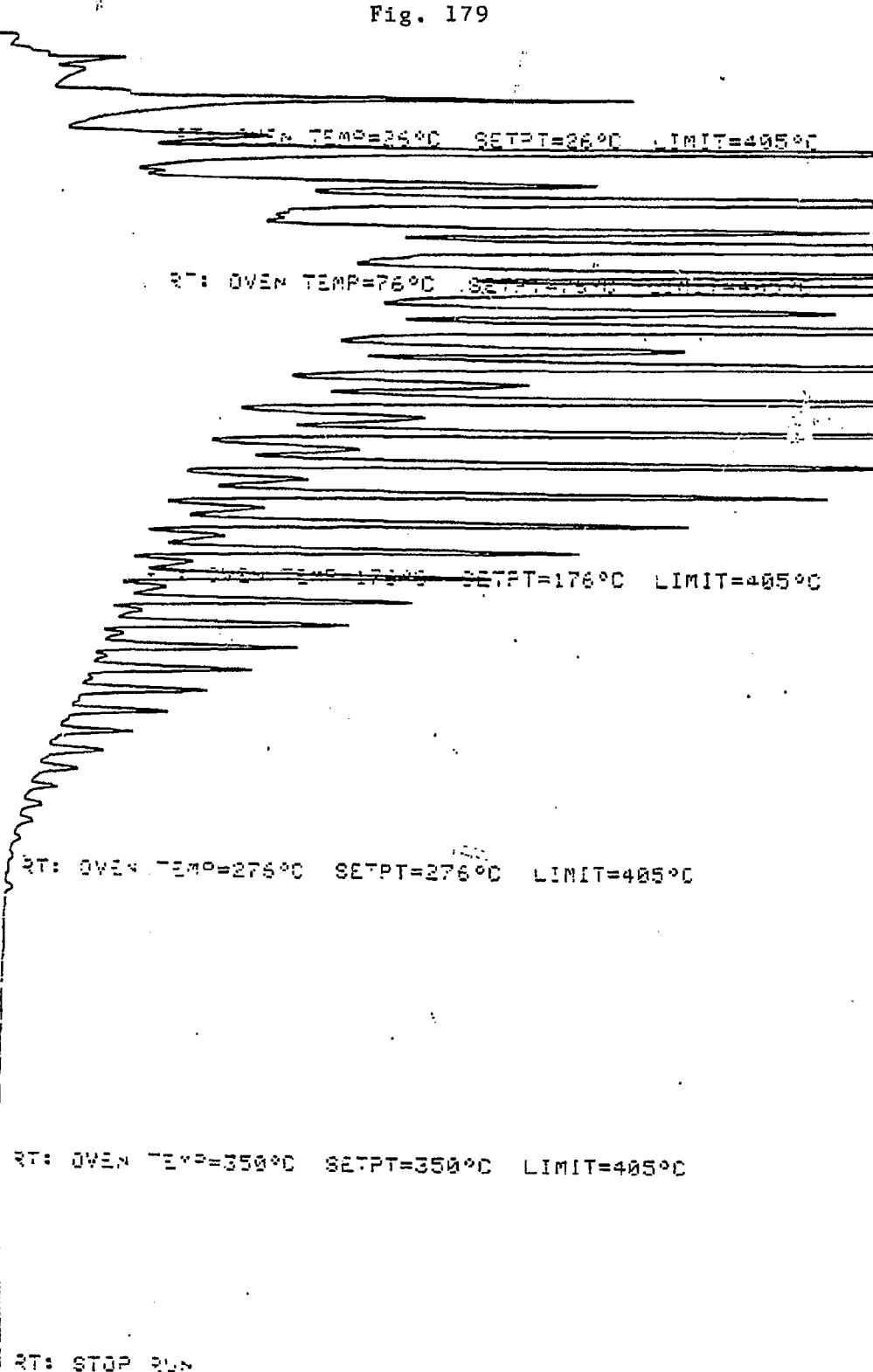
Fig. 178



SAMPLE: D10225-8-29L

RT: 8/10/83 0.20

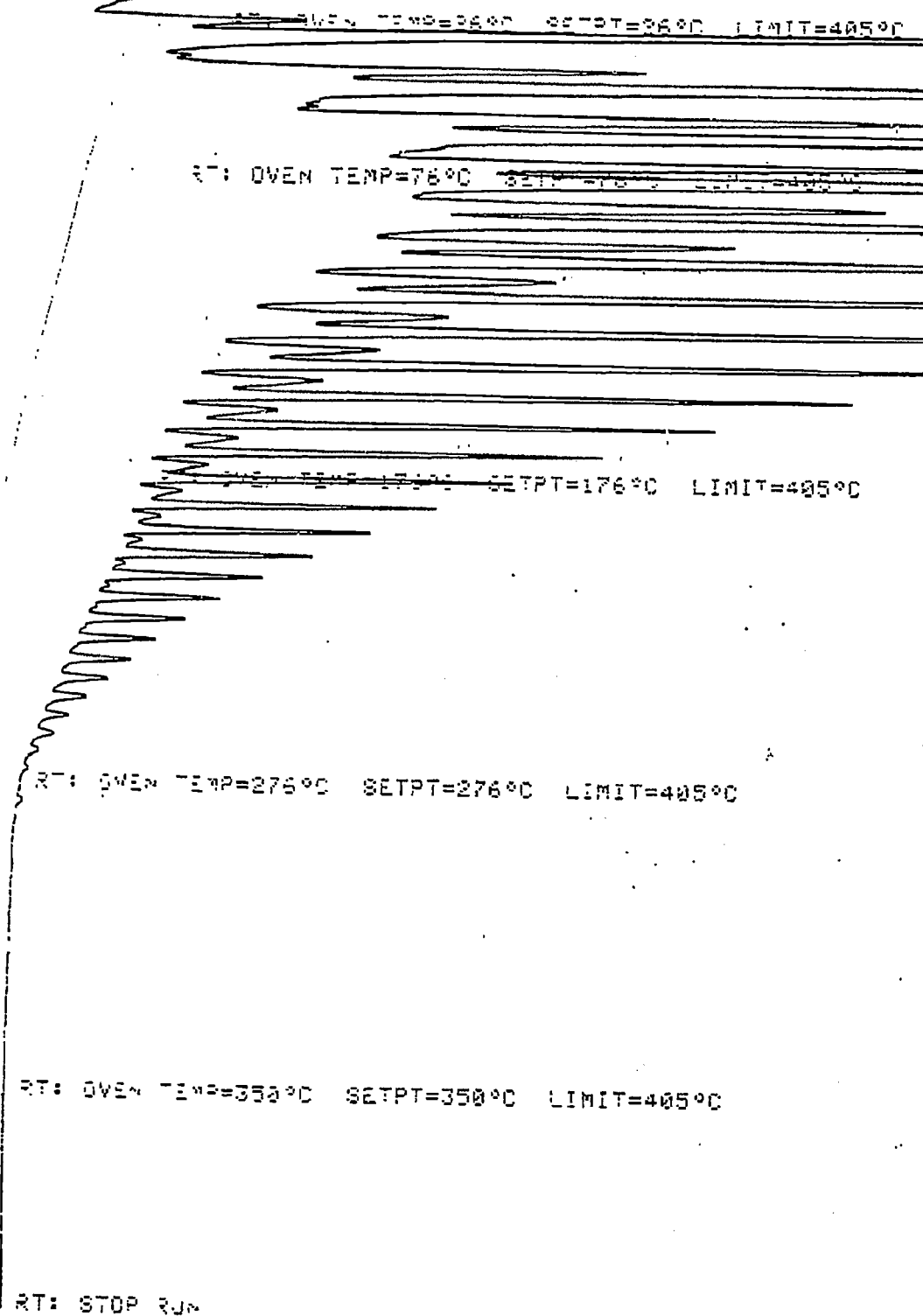
Fig. 179



SAMPLE: D10225-8-35L

RT: 8-1015 9.20

Fig. 180



SAMPLE: 10225-8-39L

TABLE 21 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-08-01	225-08-02	225-08-03	225-08-04	225-08-05
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	17.0	24.0	42.5	48.0	66.5
PRESSURE, PSIG	299	301	304	303	305
TEMP. C	270	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.00	7.00	25.50	5.50	24.00
EFFLNT GAS LITER	149.15	67.50	254.92	57.93	255.03
GM AQUEOUS LAYER	40.72	18.20	66.30	14.38	62.74
GM OIL	23.54	8.55	31.15	5.95	25.95
MATERIAL BALANCE					
GM ATOM CARBON %	88.40	92.22	93.38	94.53	94.76
GM ATOM HYDROGEN %	95.03	99.12	100.49	101.36	101.85
GM ATOM OXYGEN %	90.30	96.94	95.94	98.54	97.44
RATIO CHX/(H2O+CO2)	0.9576	0.8996	0.9427	0.9105	0.9384
RATIO X IN CHX	2.3387	2.3622	2.3601	2.3854	2.3837
USAGE H2/CO PRODT	1.3004	1.3261	1.4072	1.4092	1.4609
RATIO CO2/(H2O+CO2)	0.3682	0.3452	0.3097	0.3071	0.2855
K SHIFT IN EFFLNT	0.33	0.29	0.24	0.24	0.21
CONVERSION					
ON CO %	67.21	63.39	59.86	57.74	56.16
ON H2 %	82.61	81.37	80.07	78.66	78.25
ON CO+H2 %	75.19	72.71	70.34	68.57	67.60
PRDT SELECTIVITY, WT %					
CH4	14.00	15.13	15.36	16.44	16.53
C2 HC'S	2.89	3.21	3.20	3.41	3.37
C3H8	3.43	3.55	3.35	3.55	3.41
C3H6=	2.75	3.15	3.20	3.41	3.38
C4H10	2.70	2.73	2.49	2.63	2.47
C4H8=	4.30	4.77	4.66	5.05	4.82
C5H12	3.13	3.08	2.70	2.88	2.68
C5H10=	4.26	4.76	4.85	5.20	5.03
C6H14	3.69	3.59	3.06	3.22	3.02
C6H12= & CYCLO'S	0.28	0.35	2.56	2.77	2.75
C7+ IN GAS	13.10	15.00	13.71	14.20	15.29
LIQ HC'S	45.48	40.68	40.86	37.24	37.23
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	30.08	32.54	32.26	34.48	33.99
C5 -420 F	50.88	49.62	49.82	48.50	48.99
420-700 F	16.31	16.13	16.20	14.69	14.68
700-END PT	2.73	1.72	1.72	2.33	2.33
C5+-END PT	69.92	67.46	67.74	65.52	66.01
ISO/NORMAL MOLE RATIO					
C4	0.2051	0.1861	0.1585	0.1514	0.1381
C5	0.4293	0.3759	0.2930	0.2795	0.2473
C6	0.8211	0.6734	0.5049	0.4829	0.4246
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1915	1.0750	0.9995	0.9944	0.9633
C4	0.6064	0.5527	0.5159	0.5020	0.4953
C5	0.7138	0.6296	0.5412	0.5391	0.5182
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	-	CLR OIL	-	CLR OIL
DENSITY	0.748		0.756		0.757
N, REFRACTIVE INDEX	1.4234		1.4255		1.4268
SIMULT'D DISTILATN					
10 WT % @ DEG F	246		261		262
16	267		289		293
50	394		403		408
84	579		573		599
90	643		629		654
RANGE(16-84 %)	312		284		306
WT % @ 420 F	58.14	56.14	56.14	54.29	54.29
WT % @ 700 F	94.00	95.78	95.78	93.73	93.73

TABLE 22

RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-08-06	225-08-07	225-08.03	225-08-09	225-08-10
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	74.0	90.5	98.0	114.5	122.0
PRESSURE, PSIG	297	305	297	300	301
TEMP. C	269	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.50	24.00	7.50	24.00	7.50
EFFLNT GAS LITER	79.75	263.30	84.90	273.70	86.45
GM AQUEOUS LAYER	19.61	62.74	19.46	62.26	19.34
GM OIL	7.56	24.19	8.31	26.60	6.90
MATERIAL BALANCE					
GM ATOM CARBON %	93.21	94.65	98.13	98.43	96.41
GM ATOM HYDROGEN %	100.57	102.34	105.12	105.58	103.48
GM ATOM OXYGEN %	96.98	97.84	99.36	99.15	99.23
RATIO CHX/(H ₂ O+CO ₂)	0.9125	0.9253	0.9711	0.9827	0.9324
RATIO X IN CHX	2.3949	2.4039	2.3948	2.3978	2.4215
USAGE H ₂ /CO PRDNT	1.4684	1.4913	1.5017	1.5236	1.5203
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2790	0.2716	0.2729	0.2646	0.2619
K SHIFT IN EFFLNT	0.21	0.20	0.20	0.20	0.19
CONVERSION					
ON CO %	55.09	54.03	53.97	53.37	51.71
ON H ₂ %	77.73	76.85	76.54	76.32	75.32
ON CO+H ₂ %	66.84	65.88	65.64	65.25	63.93
PRDNT SELECTIVITY, WT %					
CH ₄	17.04	17.47	17.10	17.28	18.34
C ₂ HC'S	3.37	3.50	3.39	3.56	3.66
C ₃ H ₈	3.59	3.60	3.50	3.46	3.67
C ₃ H ₆ =	3.52	3.60	3.49	3.44	3.69
C ₄ H ₁₀	2.58	2.59	2.52	2.46	2.60
C ₄ H ₈ =	5.14	5.20	5.07	5.00	5.27
C ₅ H ₁₂	2.71	2.72	2.68	2.60	2.70
C ₅ H ₁₀ =	5.07	5.20	5.17	5.04	5.42
C ₆ H ₁₄	3.04	3.02	2.94	2.79	2.96
C ₆ H ₁₂ = & CYCLO'S	2.82	2.91	2.87	2.80	3.22
C ₇ + IN GAS	15.14	14.42	13.63	13.98	15.35
LIQ HC'S	35.98	35.77	37.63	37.59	33.12
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	35.24	35.96	35.08	35.20	37.23
C5 -420 F	48.12	47.50	47.61	47.51	48.39
420-700 F	14.33	14.25	15.12	15.10	12.41
700-END PT	2.31	2.30	2.19	2.19	1.97
C5+ -END PT	64.76	64.04	64.92	64.80	62.77
ISO/NORMAL MOLE RATIO					
C4	0.1383	0.1285	0.1262	0.1210	0.1154
C5	0.2618	0.2376	0.2325	0.2182	0.2199
C6	0.4066	0.3654	0.3565	0.3338	0.3208
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.9740	0.9566	0.9565	0.9582	0.9481
C4	0.4851	0.4814	0.4798	0.4758	0.4752
C5	0.5197	0.5081	0.5036	0.5013	0.4852
LIQ HC COLLECTION					
PHYS. APPEARANCE	-	CLR OIL	-	CLR OIL	-
DENSITY		0.758		0.756	
N, REFRACTIVE INDEX		1.4267		1.4265	
SIMULT'D DISTILATN					
10 WT % @ DEG F		263		263	
16		296		296	
50		410		410	
84		600		596	
90		656		651	
RANGE(16-84 %)		304		300	
WT % @ 420 F	53.75	53.75	54.00	54.00	56.60
WT % @ 700 F	93.58	93.58	94.18	94.18	94.06

TABLE 23 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-08-11	225-08-12	225-08-13	225-08-14	225-08-15
	=====	=====	=====	=====	=====
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	138.5	146.0	162.5	170.0	185.0
PRESSURE, PSIG	302	302	299	299	299
TEMP. °C	270	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	7.50	24.00	7.50	22.50
EFFLNT GAS LITER	278.80	86.60	282.00	87.10	268.15
GM AQUEOUS LAYER	61.90	19.10	61.13	19.20	57.59
GM OIL	22.09	7.46	23.87	6.82	20.47
MATERIAL BALANCE					
GM ATOM CARBON %	96.60	97.18	97.21	96.20	96.91
GM ATOM HYDROGEN %	103.52	103.95	104.88	103.91	105.03
GM ATOM OXYGEN %	99.48	98.44	98.61	97.80	99.01
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9304	0.9693	0.9654	0.9604	0.9481
RATIO X IN CH ₄	2.4317	2.4168	2.4226	2.4258	2.4537
USAGE H ₂ /CO PRODT	1.5331	1.5462	1.5594	1.5724	1.5772
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2572	0.2548	0.2489	0.2424	0.2433
K SHIFT IN EFFLNT	0.19	0.19	0.19	0.18	0.18
CONVERSION					
ON CO %	51.04	51.48	50.71	50.53	49.81
ON H ₂ %	75.15	75.35	74.34	74.77	74.06
ON CO+H ₂ %	63.51	63.82	62.98	63.12	62.42
PRDT SELECTIVITY, WT %					
CH ₄	18.83	18.20	18.53	18.49	19.99
C ₂ HC'S	3.79	3.60	3.47	3.69	3.83
C ₃ H ₈	3.67	3.64	3.56	3.69	3.70
C ₃ H ₆ =	3.75	3.65	3.65	4.06	3.84
C ₄ H ₁₀	2.60	2.53	2.51	2.72	2.57
C ₄ H ₈ =	5.41	5.10	5.19	5.70	5.26
C ₅ H ₁₂	2.69	2.55	2.58	2.81	2.63
C ₅ H ₁₀ =	5.21	5.19	5.24	5.74	5.46
C ₆ H ₁₄	2.90	2.77	2.71	2.91	2.81
C ₆ H ₁₂ = & CYCLO'S	3.01	2.88	2.92	3.08	2.98
C ₇ + IN GAS	14.78	14.70	14.08	14.29	13.80
LIQ HC'S	33.37	35.20	35.56	32.82	33.11
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	38.05	36.71	36.91	38.35	39.20
C5 -420 F	47.47	48.01	47.66	47.32	46.34
420-700 F	12.50	13.20	13.34	12.34	12.45
700-END PT	1.98	2.07	2.09	2.00	2.01
C5+-END PT	61.95	63.29	63.09	61.65	60.80
ISO/NORMAL MOLE RATIO					
C4	0.1091	0.1083	0.1088	0.1339	0.0963
C5	0.2044	0.2101	0.1939	0.1996	0.1680
C6	0.3098	0.2929	0.2918	0.2973	0.2642
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.9338	0.9506	0.9323	0.8663	0.9195
C4	0.4651	0.4787	0.4663	0.4600	0.4719
C5	0.5019	0.4779	0.4785	0.4760	0.4687
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	-	CLR OIL	-	CLR OIL
DENSITY	0.757		0.757		0.752
N, REFRACTIVE INDEX	1.4266		1.4267		1.4269
SIMULT'D DISTILLATN					
10 WT % @ DEG F	259		259		259
16	291		292		295
50	402		402		403
84	584		582		585
90	648		647		649
RANGE(16-84 %)	293		290		290
WT % @ 420 F	56.60	56.60	56.60	56.33	56.33
WT % @ 700 F	94.06	94.11	94.11	93.92	93.92

TABLE 24 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-08-16	225-08-17	225-08-18	225-08-19	225-08-20
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	192.0	209.0	215.0	234.5	241.0
PRESSURE, PSIG	302	296	305	304	300
TEMP. C	270	270	270	270	270
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.00	24.00	6.00	25.50	6.50
EFFLNT GAS LITER	83.95	290.25	72.70	311.95	87.10
GM AQUEOUS LAYER	17.72	60.74	15.08	64.09	16.34
M OIL	6.23	21.37	4.97	21.11	5.34
MATERIAL BALANCE					
GM ATOM CARBON %	98.08	96.96	96.64	97.38	105.42
GM ATOM HYDROGEN %	105.40	105.74	104.95	105.83	112.14
GM ATOM OXYGEN %	99.14	98.68	98.53	98.86	105.42
RATIO CHX/(H2O+CO2)	0.9735	0.9571	0.9512	0.9627	0.9999
RATIO X IN CHX	2.4492	2.4589	2.4631	2.4640	2.4752
USAGE H2/CO PRODT	1.5822	1.5897	1.5912	1.6010	1.5893
RATIO CO2/(H2O+CO2)	0.2443	0.2398	0.2389	0.2364	0.2504
K SHIFT IN EFFLNT	0.18	0.18	0.18	0.18	0.19
CONVERSION					
ON CO %	49.88	49.31	48.82	48.68	48.07
ON H2 %	74.23	73.17	73.00	72.83	71.81
ON CO+H2 %	62.49	61.75	61.41	61.26	60.31
PRDT SELECTIVITY, WT %					
CH4	19.75	20.27	20.41	20.50	20.99
C2 HC'S	3.82	3.85	3.93	3.94	3.98
C3H8	3.77	3.71	3.75	3.73	3.81
C3H6=	3.79	3.76	3.84	3.88	3.90
C4H10	2.63	2.58	2.62	2.58	2.65
C4H8=	5.40	5.31	5.47	5.31	5.47
C5H12	2.66	2.63	2.68	2.61	2.69
C5H10=	5.44	5.35	5.61	5.46	5.62
C6H14	2.79	2.83	2.86	2.85	2.91
C6H12= & CYCLO'S	2.99	3.04	3.13	3.13	3.20
C7+ IN GAS	15.12	14.13	15.03	15.62	16.48
LIQ HC'S	31.83	32.55	30.67	30.39	28.30
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	39.16	39.47	40.02	39.93	40.80
C5 -420 F	46.94	46.31	46.61	46.82	46.92
420-700 F	12.01	12.28	11.45	11.34	10.47
700-END PT	1.89	1.93	1.92	1.91	1.81
C5+-END PT	60.84	60.53	59.98	60.07	59.20
ISO/NORMAL MOLE RATIO					
C4	0.1001	0.0960	0.1000	0.0910	0.0941
C5	0.1740	0.1672	0.1634	0.1613	0.1648
C6	0.2529	0.2579	0.2527	0.2502	0.2486
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.9508	0.9406	0.9303	0.9188	0.9317
C4	0.4695	0.4679	0.4615	0.4679	0.4680
C5	0.4752	0.4789	0.4648	0.4653	0.4660
LIQ HC COLLECTION					
PHYS. APPEARANCE	-	CLR OIL	-	CLR OIL	-
DENSITY		0.757		0.758	
N, REFRACTIVE INDEX		1.4268		1.4270	
SIMULT'D DISTILLTN					
10 WT % @ DEG F		260		260	
16		298		298	
50		403		403	
84		582		583	
90		647		649	
RANGE(16-84 %)					
		284		285	
WT % @ 420 F	56.33	56.33	56.40	56.40	56.60
WT % @ 700 F	94.06	94.06	93.73	93.73	93.60

TABLE 25

RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10225-08-21 225-08-22 225-08-23 225-08-24 225-08-25
 =====

	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	258.5	264.5	281.5	288.5	307.5
PRESSURE, PSIG	297	300	301	304	305
TEMP. C	270	270	270	269	269

FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	6.00	24.00	6.00	25.00
EFFLNT GAS LITER	297.65	76.20	308.15	78.65	325.20
GM AQUEOUS LAYER	60.34	14.32	57.28	14.26	59.43
GM OIL	19.72	4.23	16.90	3.81	15.89

MATERIAL BALANCE

GM ATOM CARBON %	98.38	96.72	97.23	98.69	97.96
GM ATOM HYDROGEN %	107.24	105.31	105.94	106.42	105.28
GM ATOM OXYGEN %	99.08	98.79	98.82	100.26	99.65
RATIO CHX/(H2O+CO2)	0.9821	0.9459	0.9579	0.9584	0.9548
RATIO X IN CHX	2.4603	2.4805	2.4927	2.5032	2.4909
USAGE H2/CO PRODT	1.6179	1.5785	1.6105	1.6116	1.6277
RATIO CO2/(H2O+CO2)	0.2310	0.2472	0.2365	0.2380	0.2277
K SHIFT IN EFFLNT	0.17	0.20	0.19	0.19	0.18

CONVERSION

ON CO %	48.47	47.25	46.43	45.81	44.98
ON H2 %	72.46	70.06	69.84	69.64	69.44
ON CO+H2 %	60.98	59.14	58.64	58.17	57.65

PRDT SELECTIVITY, WT %

CH4	20.34	20.89	21.55	21.96	21.47
C2 HC'S	3.96	4.35	4.42	4.45	4.34
C3H8	3.65	4.16	4.09	4.37	4.24
C3H6=	3.75	4.17	4.04	4.32	4.22
C4H10	2.54	2.84	2.81	2.95	2.78
C4H8=	5.23	5.66	5.66	6.00	5.82
C5H12	2.61	2.71	2.71	2.80	2.68
C5H10=	5.43	5.42	5.59	5.60	5.59
C6H14	2.78	3.03	2.92	2.98	2.92
C6H12= & CYCLO'S	3.12	3.23	3.21	3.25	3.42
C7+ IN GAS	16.84	16.43	15.87	16.85	17.60
LIQ HC'S	29.75	27.12	27.12	24.46	24.91

TOTAL	100.00	100.00	100.00	100.00	100.00
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SUB-GROUPING					
C1 -C4	39.47	42.07	42.58	44.05	42.88
C5 -420 F	47.62	46.11	45.60	44.48	45.44
420-700 F	11.01	10.09	10.09	9.71	9.89
700-END PT	1.90	1.74	1.74	1.76	1.79
C5+-END PT	60.53	57.93	57.42	55.95	57.12
ISO/NORMAL MOLE RATIO					
C4	0.0914	0.0965	0.0872	0.0915	0.0448
C5	0.1573	0.1555	0.1631	0.1426	0.1414
C6	0.2294	0.2534	0.2323	0.2370	0.2181
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.9297	0.9526	0.9664	0.9640	0.9590
C4	0.4685	0.4836	0.4801	0.4746	0.4617
C5	0.4672	0.4868	0.4702	0.4863	0.4665
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.756		0.755		0.755
N, REFRACTIVE INDEX	1.4271		1.4276		1.4277
SIMULT'D DISTILATN					
10 WT % @ DEG F	260		262		273
16	299		299		302
50	403		403		413
84	583		583		602
90	650		649		665
RANGE(16-84 %)					
	284		284		300
WT % @ 420 F					
	56.60	56.40	56.40	53.10	53.10
WT % @ 700 F					
	93.60	93.60	93.60	92.80	92.80

TABLE 26 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10225-08-26 225-08-27 225-08-28 225-08-29 225-08-30..

	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	313.5	330.5	337.0	354.8	361.5
PRESSURE, PSIG	302	295	297	299	296
TEMP. C	269	269	269	269	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.00	23.00	6.50	24.25	6.75
EFFLNT GAS LITER	78.85	300.75	85.10	318.15	89.32
GM AQUEOUS LAYER	14.15	54.26	15.12	56.39	15.73
GM OIL	3.66	14.02	4.01	14.96	3.92

MATERIAL BALANCE

GM ATOM CARBON %	97.39	96.57	96.73	97.05	97.47
GM ATOM HYDROGEN %	105.36	104.62	105.40	104.19	104.64
GM ATOM OXYGEN %	99.64	99.21	98.31	99.18	99.61
RATIO CHX/(H2O+CO2)	0.9395	0.9286	0.9568	0.9415	0.9412
RATIO X IN CHX	2.5022	2.5118	2.4835	2.5167	2.5147
USAGE H2/CO PRODT	1.6229	1.6301	1.6245	1.6368	1.6413
RATIO CO2/(H2O+CO2)	0.2294	0.2260	0.2281	0.2259	0.2235
K SHIFT IN EFFLNT	0.18	0.18	0.19	0.18	0.17

CONVERSION

ON CO %	44.53	44.16	44.77	43.85	43.55
ON H2 %	68.53	68.50	67.96	68.54	68.25
ON CO+H2 %	57.00	56.82	56.86	56.63	56.34

PRDT SELECTIVITY, WT %

CH4	22.01	22.45	20.78	22.74	22.60
C2 HC'S	4.48	4.60	4.51	4.62	4.51
C3H8	4.18	4.22	4.32	4.15	4.19
C3H6=	4.17	4.27	4.35	4.37	4.38
C4H10	2.84	2.87	3.20	2.84	2.88
C4H8=	5.67	5.77	6.41	5.90	6.00
C5H12	2.69	2.66	2.68	2.80	2.82
C5H10=	5.60	5.53	5.72	5.53	5.60
C6H14	2.94	2.85	3.27	2.83	2.95
C6H12= & CYCLO'S	3.35	3.23	3.38	3.19	3.40
C7+ IN GAS	17.69	16.80	16.77	16.01	17.11
LIQ HC'S	24.37	24.75	24.62	25.02	23.55

TOTAL	100.00	100.00	100.00	100.00	100.00
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SUB-GROUPING						
C1 -C4	43.35	44.18	43.57	44.62	44.57	
C5 -420 F	45.24	44.24	44.98	43.74	44.55	
420-700 F	9.65	9.80	9.77	9.93	9.44	
700-END PT	1.75	1.78	1.67	1.70	1.44	
C5+-END PT	56.65	55.82	56.43	55.38	55.43	
ISO/NORMAL MOLE RATIO						
C4	0.0871	0.0853	0.1376	0.0815	0.0795	
C5	0.1433	0.1379	0.1345	0.1522	0.1550	
C6	0.2223	0.2176	0.2912	0.2079	0.2065	
C4=	0.0000	0.0000	0.0000	0.0000	0.0000	
PARAFFIN/OLEFIN RATIO						
C3	0.9560	0.9423	0.9475	0.9077	0.9137	
C4	0.4841	0.4801	0.4813	0.4648	0.4636	
C5	0.4674	0.4683	0.4560	0.4918	0.4894	
LIQ HC COLLECTION						
PHYS. APPEARANCE		CLR OIL		CLR OIL		
DENSITY		0.757		0.755		
N, REFRACTIVE INDEX		1.4273		1.4274		
SIMULT'D DISTILATN						
10 WT % @ DEG F		273		271		
16		302		302		
50		412		412		
84		601		596		
90		665		656		
RANGE(16-84 %)		299		294		
WT % @ 420 F	53.20	53.20	53.50	53.50	53.80	
WT % @ 700 F	92.80	92.80	93.20	93.20	93.90	

TABLE 27 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/Z440X1-101 #10252-684 RD CR 35.4 GR (40.6 AFTER RUN 14,000)
 FEED H2(CO):ARCOH OF 50:50: 0 @ 400 C/HR OR 300 C/HR

RUN & SAMPLE NO.	10225-08-31	225-08-32	225-08-33	225-08-34	225-08-35
FEED H2(CO):AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HR3 ON PURFAN	379.9	394.8	402.0	410.0	426.0
PRESSURE, PSIG	399	304	295	301	303
TEMP. C	269	269	269	269	269
FEED C2/HR	400	400	400	400	400
MOLES FEED H2	25.17	4.83	22.08	8.00	24.00
FEED H2 GAS LITERS	335.38	64.39	294.52	105.20	319.20
GR ACIDFAS LAYER	38.66	11.34	24.83	18.47	55.60
GR OIL	14.60	2.61	35.94	4.40	13.23
MATERIAL BALANCE					
GR ATOM CARBON %	98.05	97.33	96.90	94.66	96.26
GR ATOM HYDROGEN %	105.03	104.48	104.01	101.65	103.05
GR ATOM OXYGEN %	100.04	100.20	100.26	98.83	99.48
RATIO GR/ (H2O)(O2)	0.9454	0.9216	0.9078	0.8837	0.9102
RATIO X H GR	2.5162	2.5291	2.5382	2.5554	2.5444
WEIGHT H2(O) FEED	1.6469	1.6468	1.6481	1.6469	1.6545
RATIO GR/ (H2O)(O2)	0.2219	0.2203	0.2190	0.2194	0.2177
R FEED OF FEED	0.17	0.17	0.17	0.17	0.17
COMPOSITION					
GR O2 %	43.32	42.87	42.43	41.75	42.02
GR H2 %	68.16	68.03	67.81	67.41	67.52
GR CO H2 %	56.17	55.90	55.57	55.04	55.20
PRODUCT SELECTIVITY, WT %					
CH4	22.70	23.20	23.71	24.51	24.00
C2 H6	4.55	4.74	4.77	4.86	4.82
C3 H8	4.17	4.30	4.31	4.44	4.34
C4 H10	4.32	4.49	4.41	4.54	4.45
C5 H12	2.86	2.94	2.92	2.99	2.91
C6 H14	5.95	6.18	5.97	6.12	6.04
C7 H16	2.79	2.88	2.80	2.84	2.79
C8 H18	5.60	5.74	5.64	5.00	4.96
C9 H20	2.90	2.96	2.85	2.67	2.74
C10 H22	3.36	3.42	3.33	3.41	3.38
C7+ IN GAS	17.31	16.82	16.62	14.61	16.13
LQ OIL	23.48	22.33	22.69	24.11	23.43
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING

CL -C4	44.56	45.85	46.07	47.46	46.57
C5 -420 F	44.59	43.76	43.37	41.35	42.56
420-700 F	9.41	9.00	9.14	9.37	9.30
700-1500 FT	1.43	1.38	1.41	1.62	1.57
C51-1500 FT	55.44	54.15	53.93	52.54	53.43
ISO/NORMAL MOLE RATIO					
C4	0.0759	0.0783	0.0789	0.0790	0.0771
C5	0.1518	0.1501	0.1501	0.1467	0.1412
C6	0.1908	0.2008	0.1892	0.1176	0.1174
C7-	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C4	0.9219	0.9140	0.9313	0.9336	0.9321
C5	0.4635	0.4594	0.4719	0.4714	0.4650
C6	0.4831	0.4878	0.4823	0.5529	0.5468
LIQ HC COLLECTION					
PTCH. APPARATUS	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.758		0.756		0.757
N. REFRACTIVE INDEX	1.4272		1.4274		1.4276
MINORITY DISTILLATE					
10 WT % @ 100 F	274		278		276
16	302		303		301
50	412		412		412
84	591		593		596
90	650		651		655
RANKS(16-84 %)	289		290		293
WT % @ 420 F	53.80	53.50	53.50	53.60	53.60
WT % @ 700 F	93.90	93.80	93.80	93.80	93.30

TABLE 28 RESULT OF SYNGAS OPERATION

RUN NO. 10225-08
 CATALYST CO/TH/X4+UCC-101 #10252-48C 80 CC 35.8 GM (40.6 AFTER RUN +4.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-08-36	225-08-37	225-08-38	225-08-39
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	434.0	450.0	458.0	480.0
PRESSURE, PSIG	302	295	306	297
TEMP. C	270	270	270	270
FEED CC/MIN	400	400	400	400
HOURS FEEDING	8.00	24.00	8.00	30.00
EFFLNT GAS LITER	104.40	317.00	106.20	410.80
GM AQUEOUS LAYER	18.69	56.06	18.54	69.51
GM OIL	4.29	12.88	3.94	14.79
MATERIAL BALANCE				
GM ATOM CARBON %	96.79	96.32	96.93	99.22
GM ATOM HYDROGEN %	103.40	103.68	104.02	106.04
GM ATOM OXYGEN %	99.31	99.20	99.43	101.22
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9312	0.9202	0.9309	0.9444
RATIO X IN CH ₄	2.5430	2.5410	2.5452	2.5429
USAGE H ₂ /CO PRODT	1.6440	1.6612	1.6553	1.6645
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2256	0.2158	0.2209	0.2186
K SHIFT IN EFFLNT	0.17	0.16	0.17	0.17
CONVERSION				
ON CO %	43.71	42.63	42.93	42.32
ON H ₂ %	69.28	68.11	68.21	67.49
ON CO+H ₂ %	56.92	55.84	56.02	55.33
PRDT SELECTIVITY, WT %				
CH ₄	23.90	23.85	24.00	23.91
C ₂ HC'S	4.91	4.73	4.81	4.80
C ₃ H ₈	4.27	4.31	4.37	4.44
C ₃ H ₆ =	4.23	4.39	4.38	4.55
C ₄ H ₁₀	2.89	2.91	2.94	3.01
C ₄ H ₈ =	5.80	5.91	6.03	6.23
C ₅ H ₁₂	2.76	2.81	2.83	2.87
C ₅ H ₁₀ =	5.45	5.46	5.29	5.75
C ₆ H ₁₄	2.82	2.83	2.93	2.85
C ₆ H ₁₂ = & CYCLO'S	3.27	3.27	3.39	3.64
C ₇ + IN GAS	17.81	17.11	18.65	17.86
LIQ HC'S	21.89	22.42	20.37	20.09
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	46.00	46.10	46.53	46.95
C5 -420 F	44.01	43.67	44.18	43.89
420-700 F	8.49	8.70	7.90	7.79
700-END PT	1.49	1.52	1.38	1.37
C5+-END PT	54.00	53.90	53.47	53.05
ISO/NORMAL MOLE RATIO				
C4	0.0792	0.0761	0.0788	0.0746
C5	0.1491	0.1463	0.1489	0.1459
C6	0.1935	0.1968	0.1838	0.1293
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	0.9634	0.9367	0.9517	0.9329
C4	0.4818	0.4759	0.4716	0.4669
C5	0.4916	0.5008	0.5208	0.4844
LIQ HC COLLECTION				
PHYS. APPEARANCE		CLR OIL		CLR OIL
DENSITY		0.755		0.758
N, REFRACTIVE INDEX		1.4272		1.4274
SIMULT'D DISTILATN				
10 WT % @ DEG F		265		267
16		301		301
50		410		411
84		595		595
90		657		656
RANGE(16-84 %)				
		294		294
WT % @ 420 F	54.40	54.40	54.40	54.40
WT % @ 700 F	93.20	93.20	93.20	93.20

XI. RUN 10 (10225-9) with Catalyst 10 (Co/X₄ + UCC-101)

This catalyst is similar to Catalyst 9 except that the metal component was formulated differently. An extrudate of UCC-101, bonded with 20 percent Al₂O₃, was pore filled with a solution of cobalt and the additive, to give 10 percent total metal on the extrudate. Although the metal component contained no thorium, it did contain 15 percent additive--the same additive as in Catalyst 9, this time pore filled instead of physically mixed.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 181-184. Simulated distillations of the C₅⁺ product for two samples are plotted in Figs. 185-186. Carbon number product distributions are plotted in Figs. 187-195. Chromatograms from simulated distillations are reproduced in Figs. 196-200. Detailed material balances appear in Tables 29-32.

The conversion was lower than normal, but remained steady after an initial deactivation. With its low cobalt loading this catalyst contains only two-thirds as much cobalt as Catalyst 3, yet at 170 hours on stream its activity per cobalt atom was 93 percent of that of Catalyst 3, a fairly efficient use of the cobalt. The water gas shift activity was lower than usual, only 10 percent of the oxygen having been rejected as CO₂.

The selectivity remained steady throughout the run, although

it was never very good. Methane production was high, higher than for Catalyst 9. Production of C_2-C_4 was also high, about the same as for Catalyst 9. The gasoline yield was about as high as for Catalyst 9, and higher than for Catalyst 3. The diesel oil production was much lower than for Catalyst 3, and there were almost no heavies. In contrast to Catalyst 9's steady high production of olefins, the olefin production of this catalyst was low to start with, and fell off with hours on stream. Isomerization of the pentane was highly isomerized at first, but deactivated rapidly to a level below that of Catalyst 3. The chromatograms of the simulated distillations show a decrease of isomerization with time; at all times the liquid was predominantly straight chain hydrocarbons. The Schulz-Flory plots show the usual excess methane and no carbon number cut-off.

This catalyst is inferior to Catalyst 9.

RUN 10225-09

1:1 H₂:CO
300 PSIG
270°C

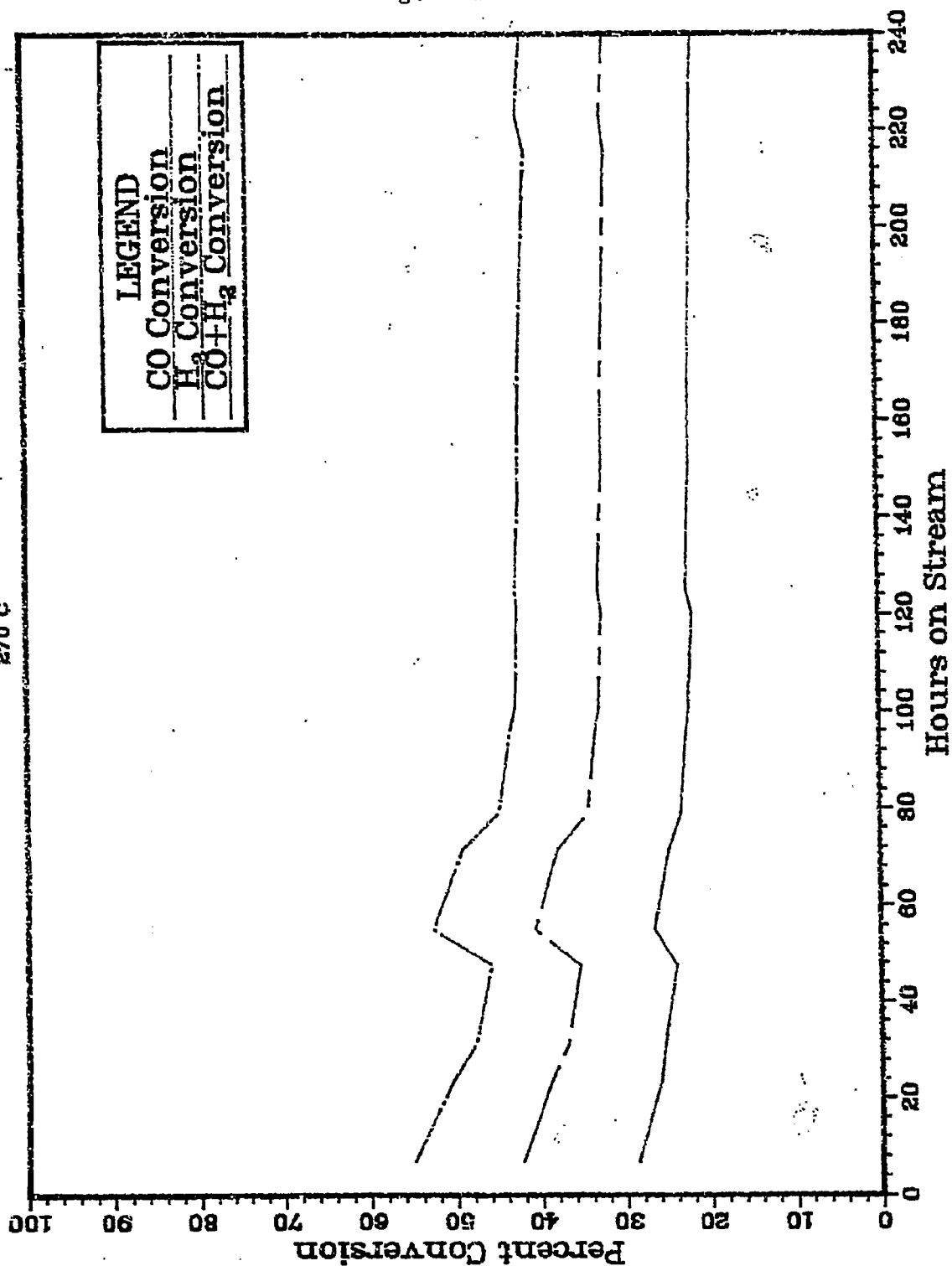
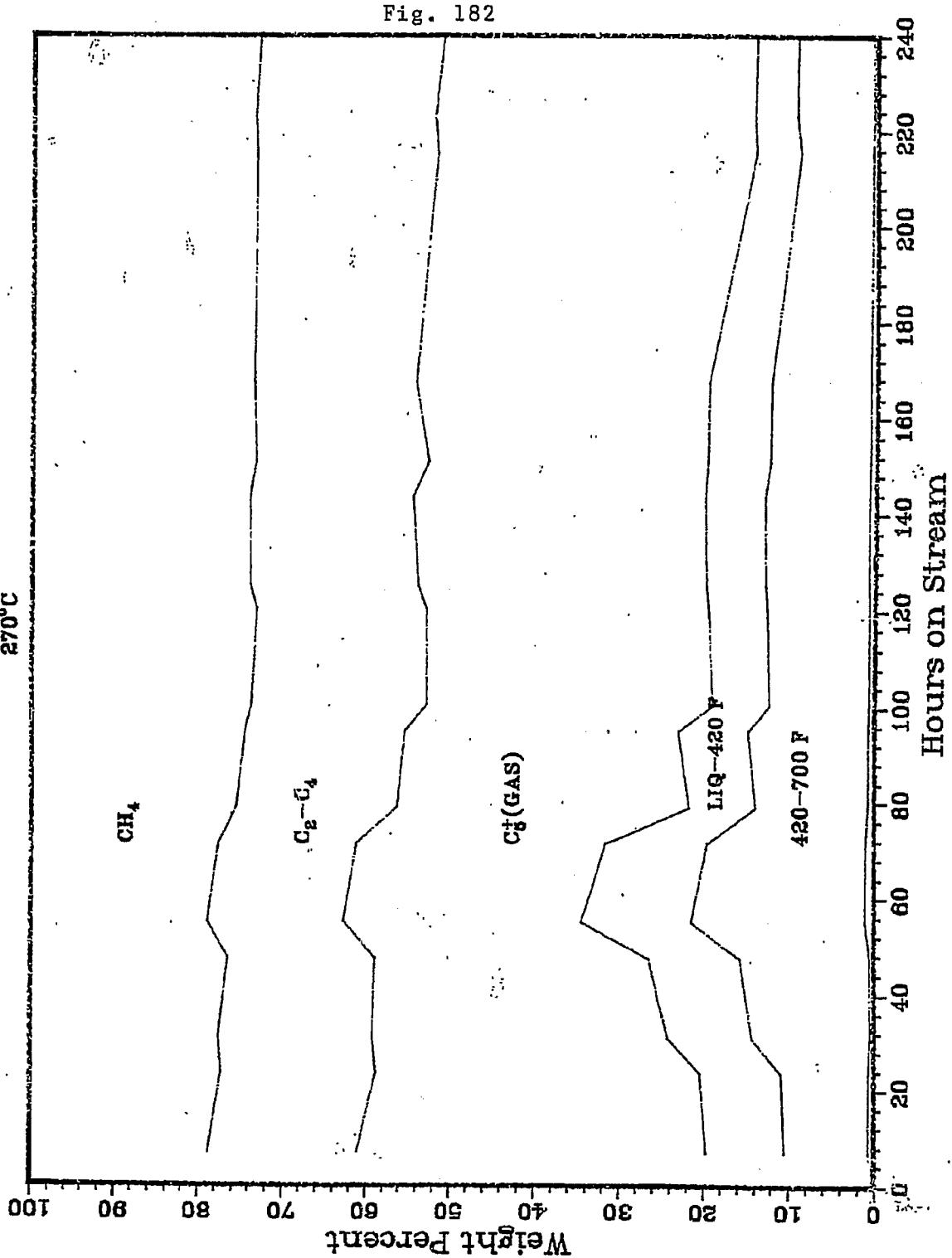


Fig. 181

RUN 10225-09

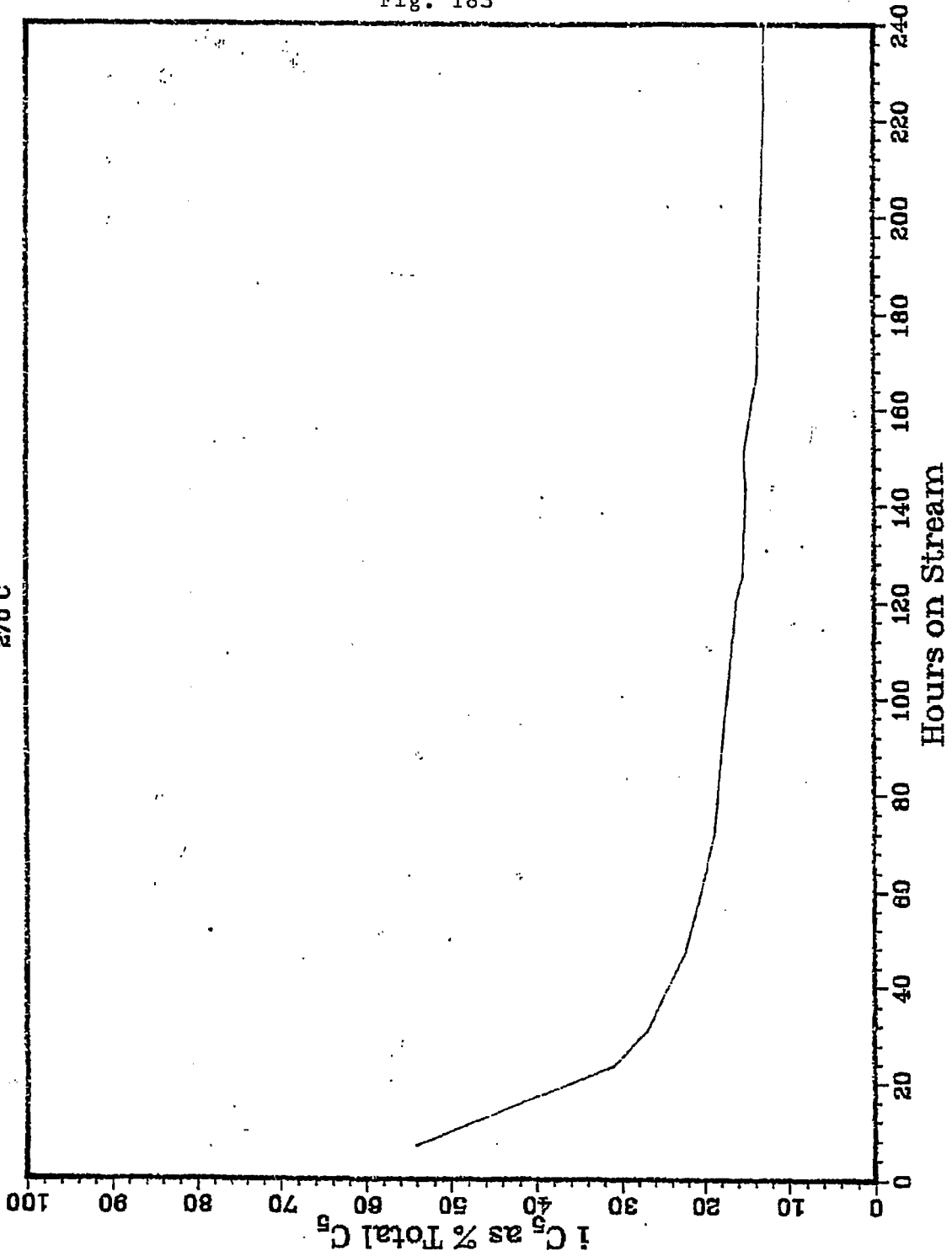
1:1 H₂:CO
300 PSIG
270°C



RUN 10225-09

1:1 H₂:CO
300 PSIG
270°C

Fig. 183



RUN 10225-09

1:1 H₂:CO
300 PSIG
270°C

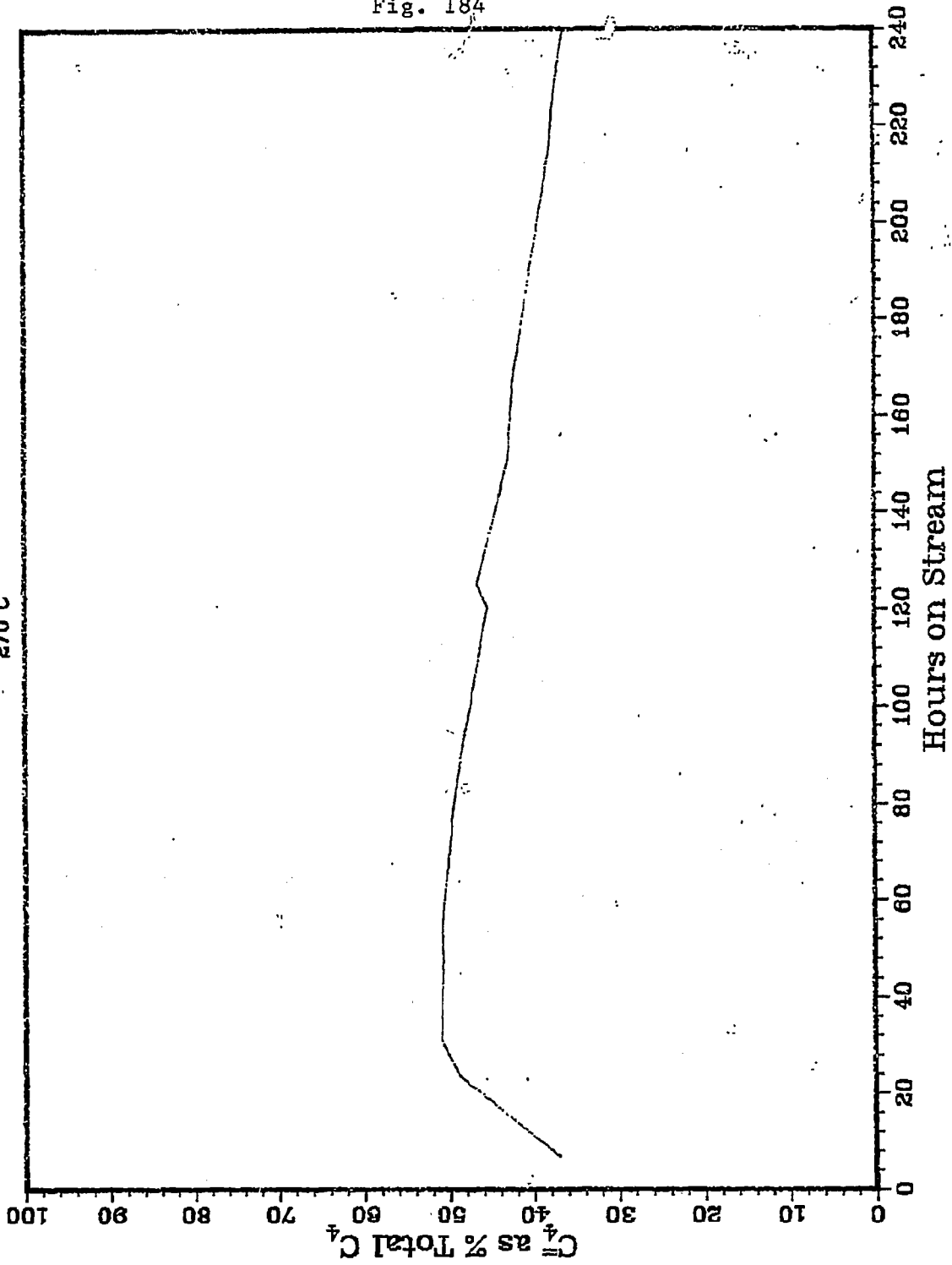


Fig. 185

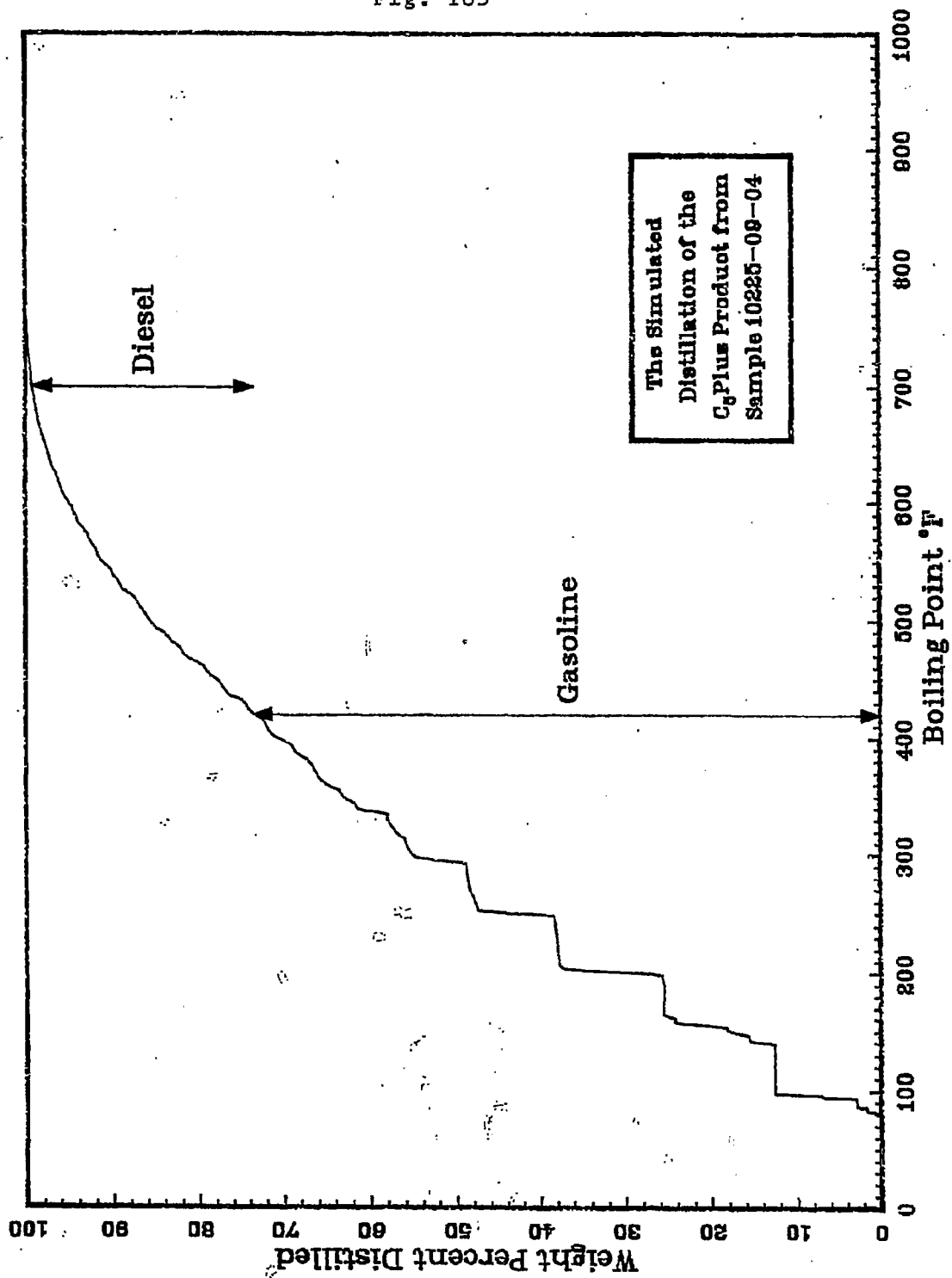


Fig. 186

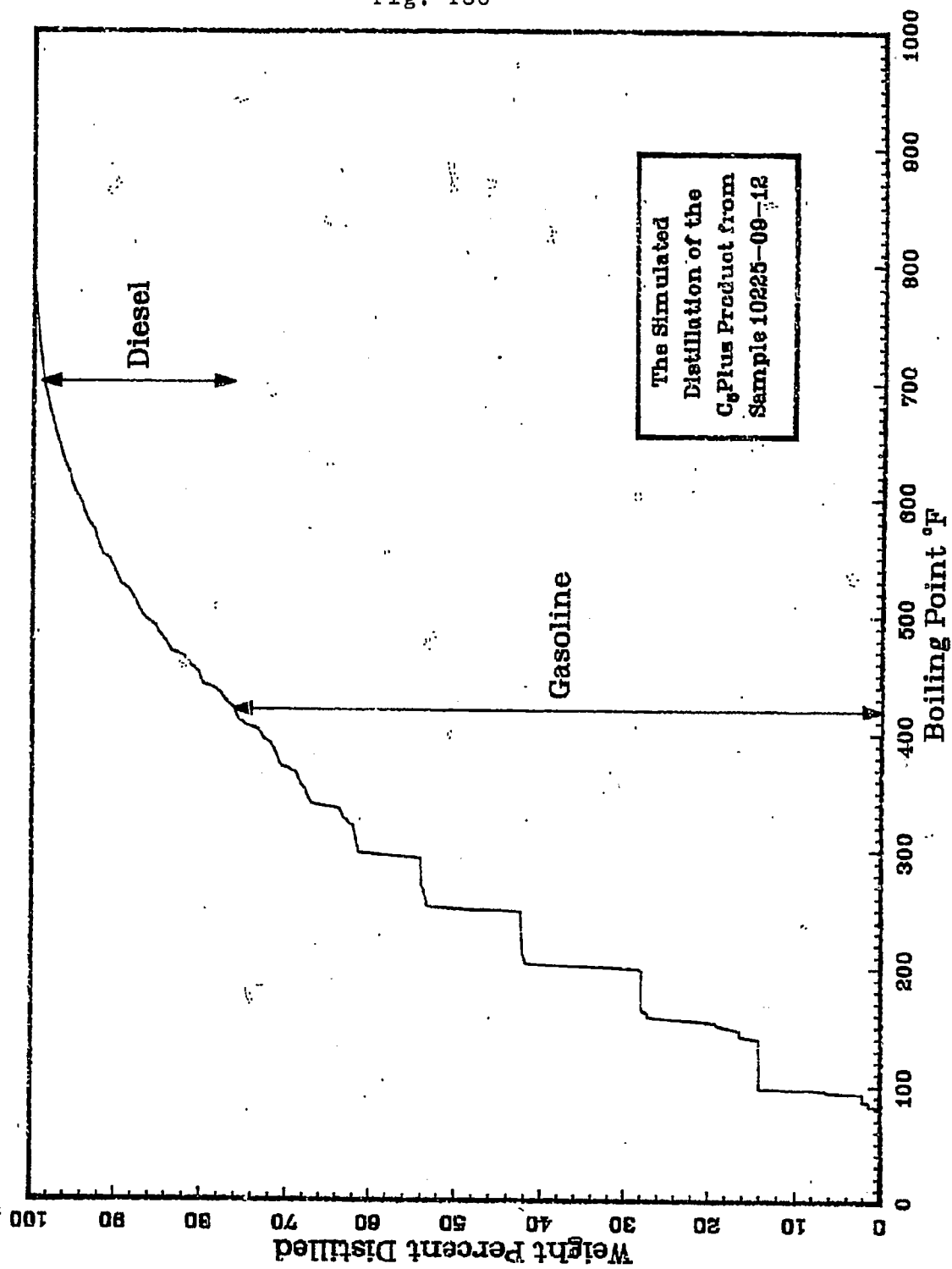


Fig. 187

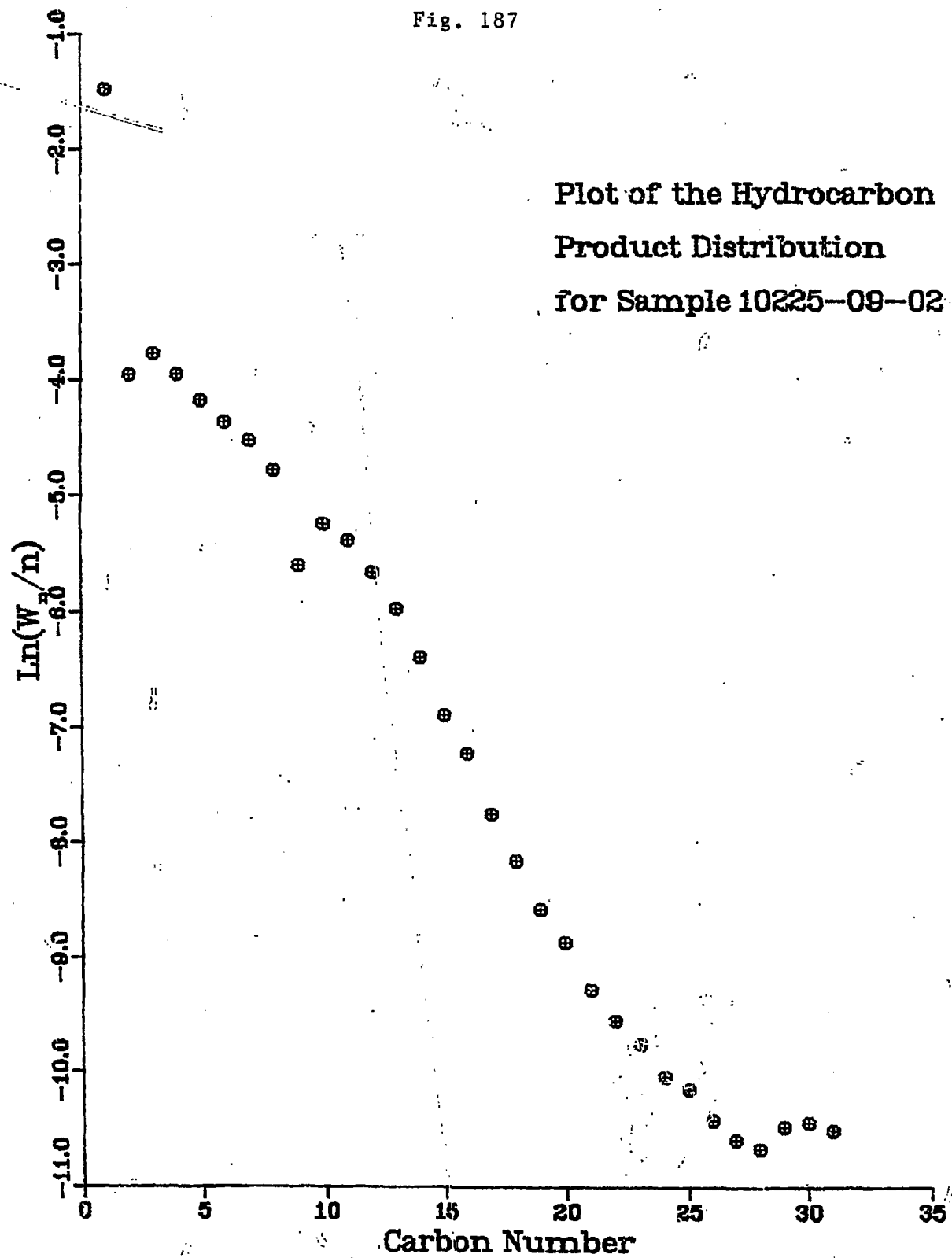


Fig. 188

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-09-04

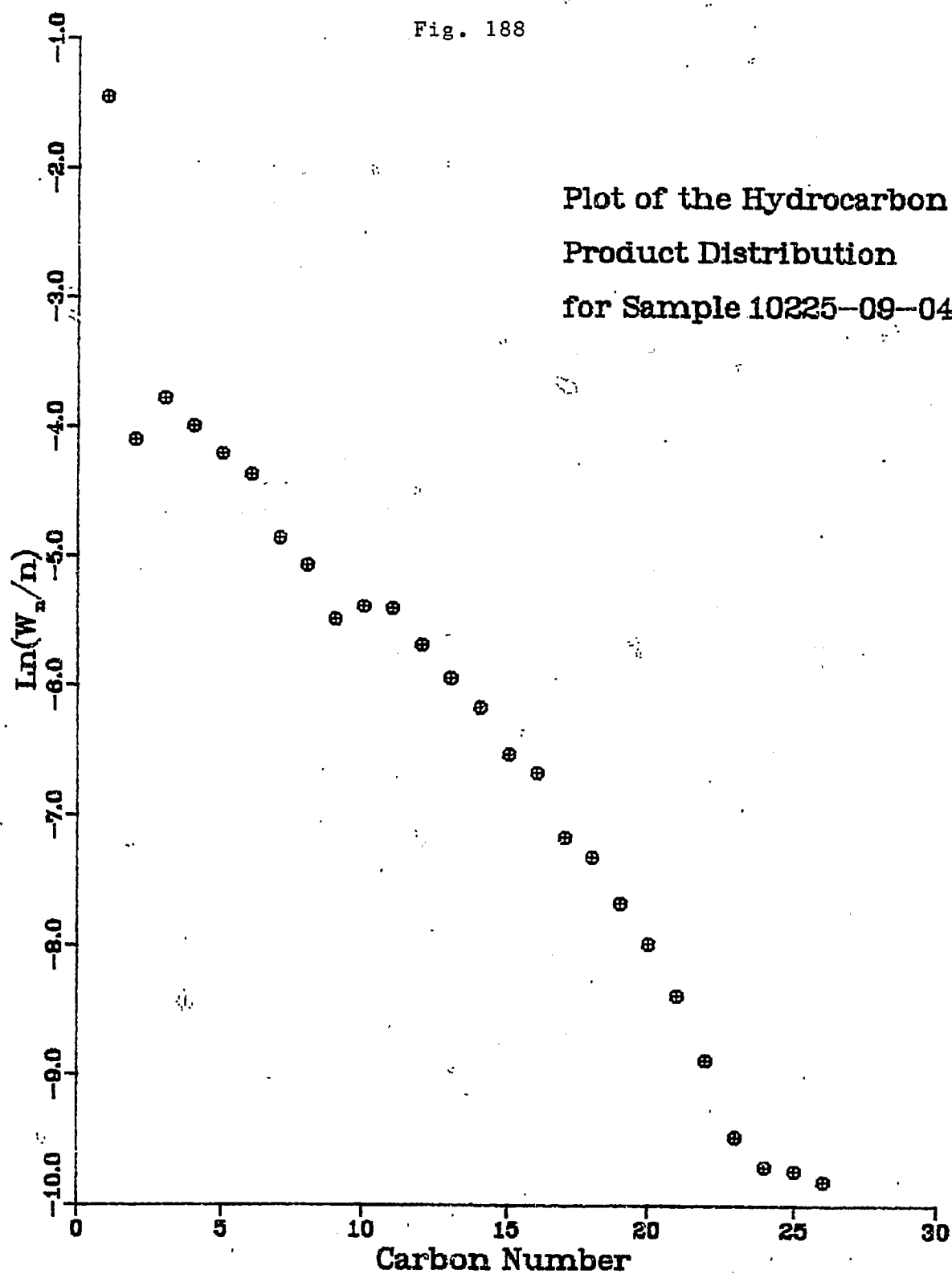


Fig. 189

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-09-06

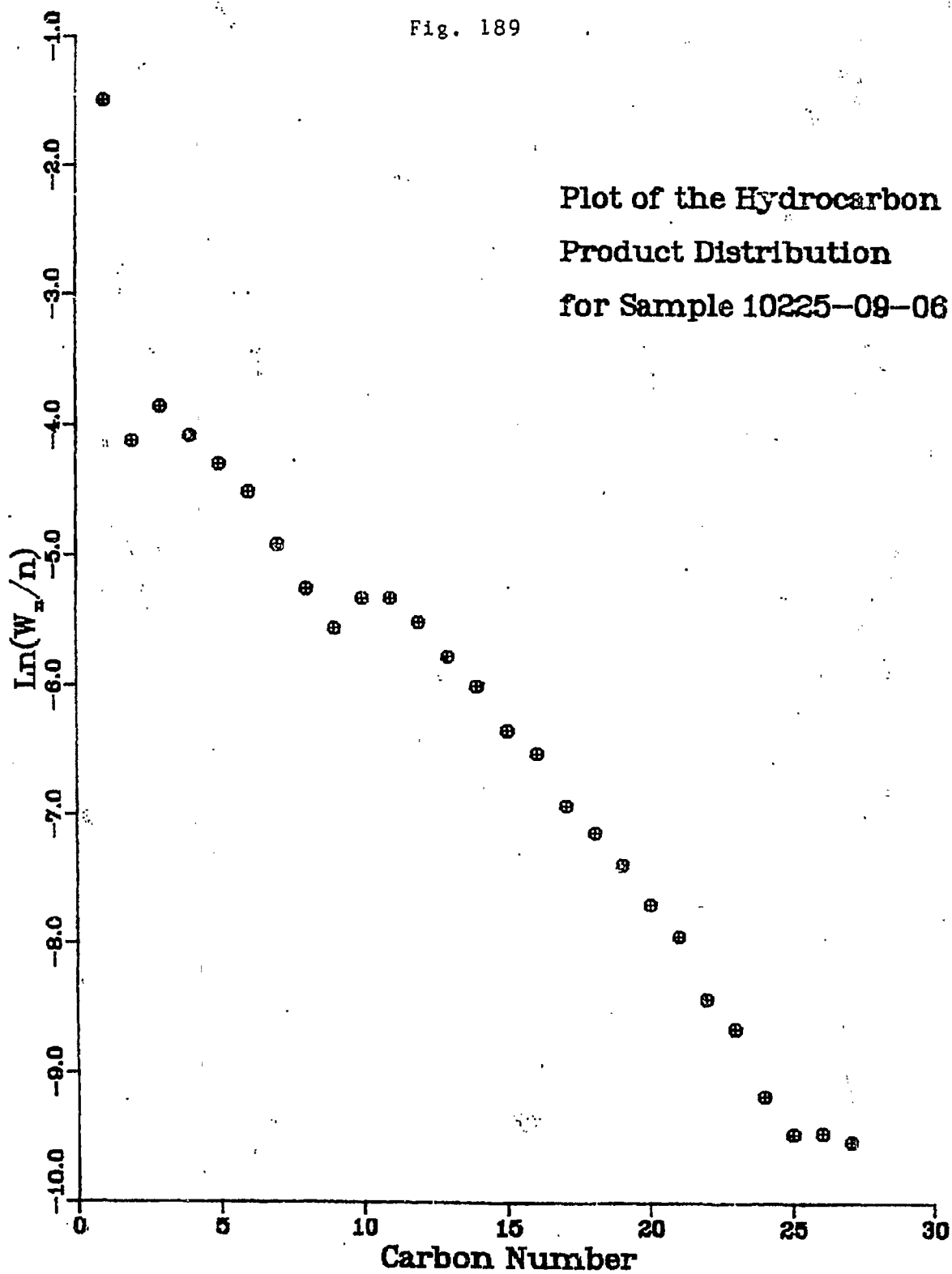
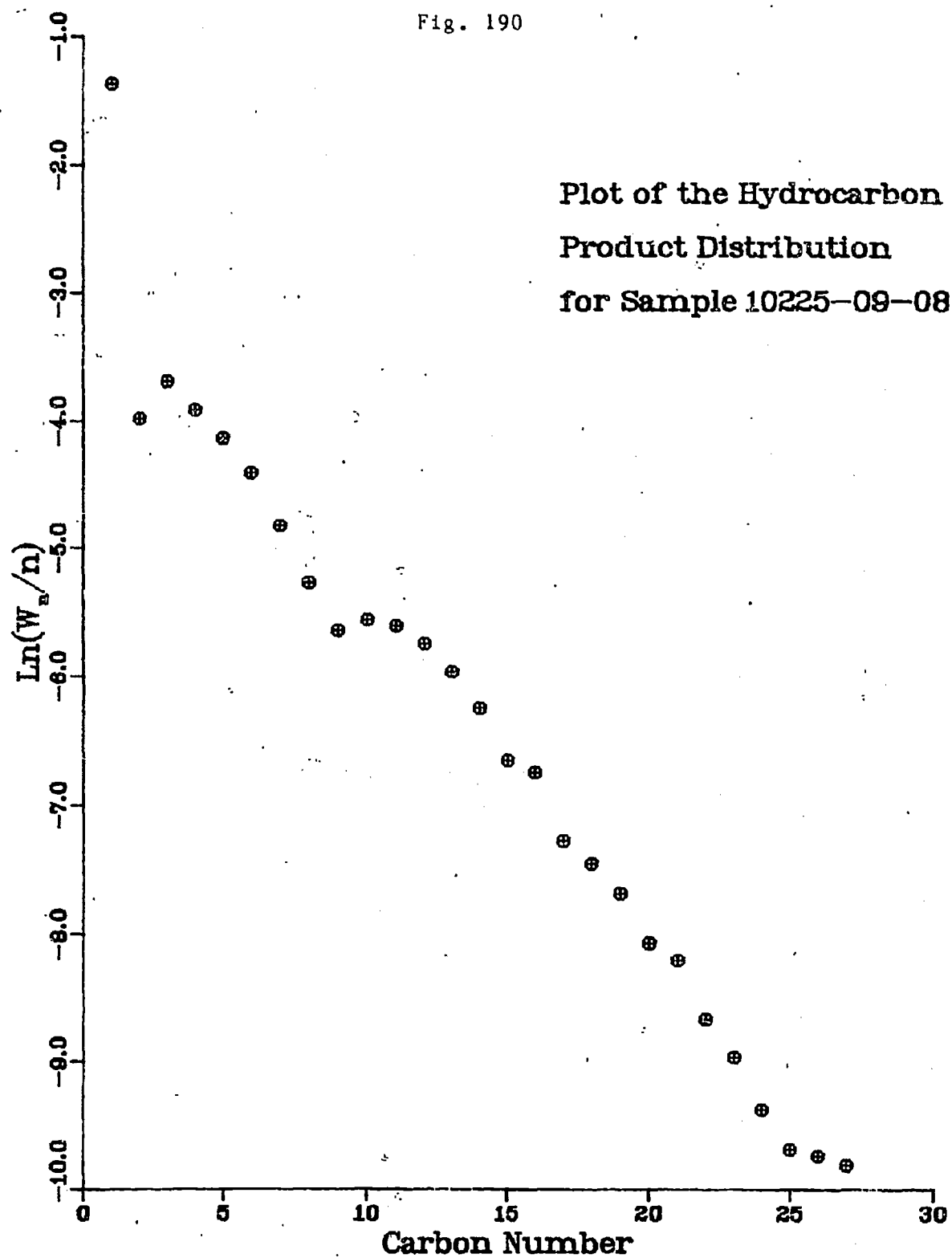


Fig. 190



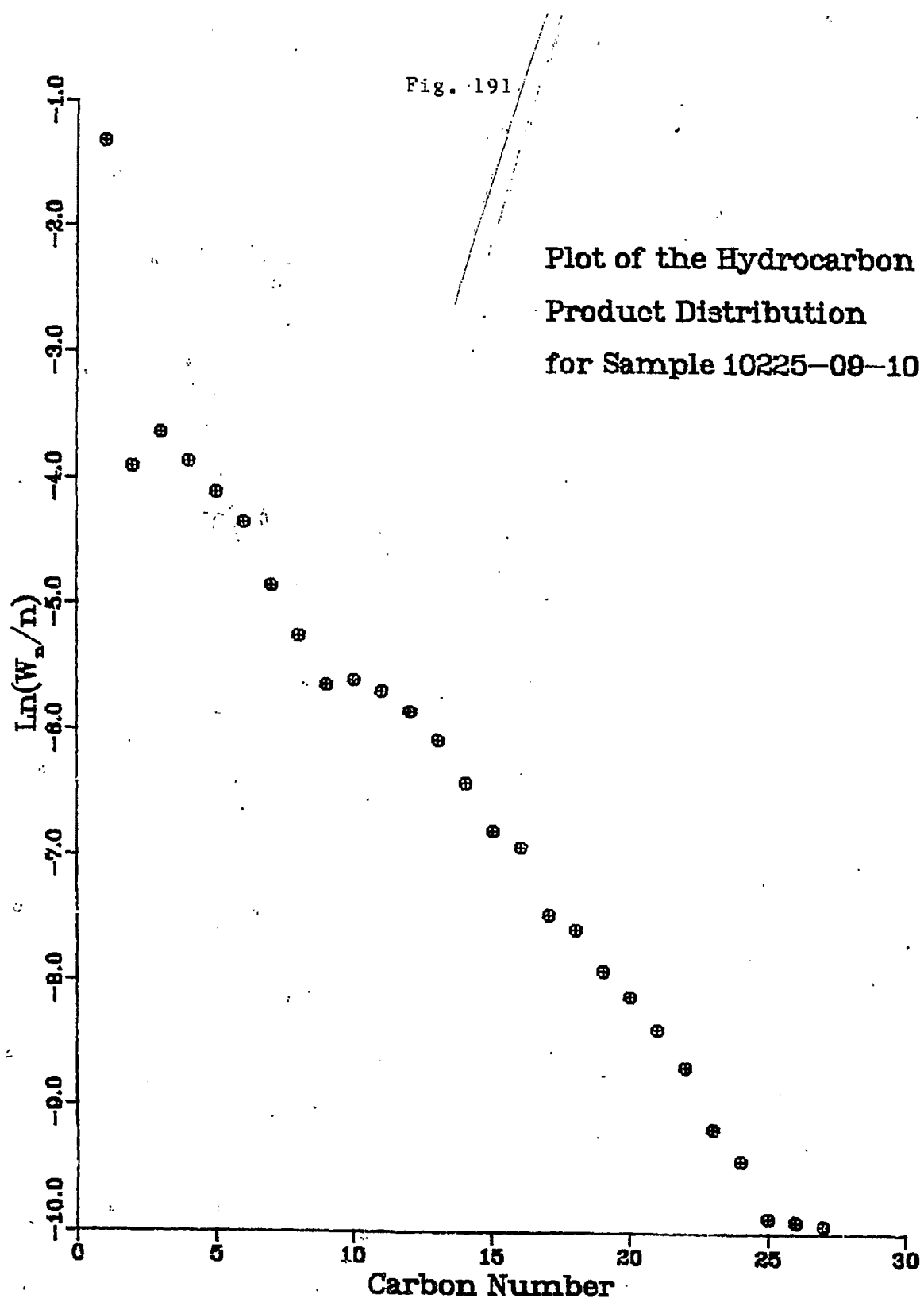


Fig. 192

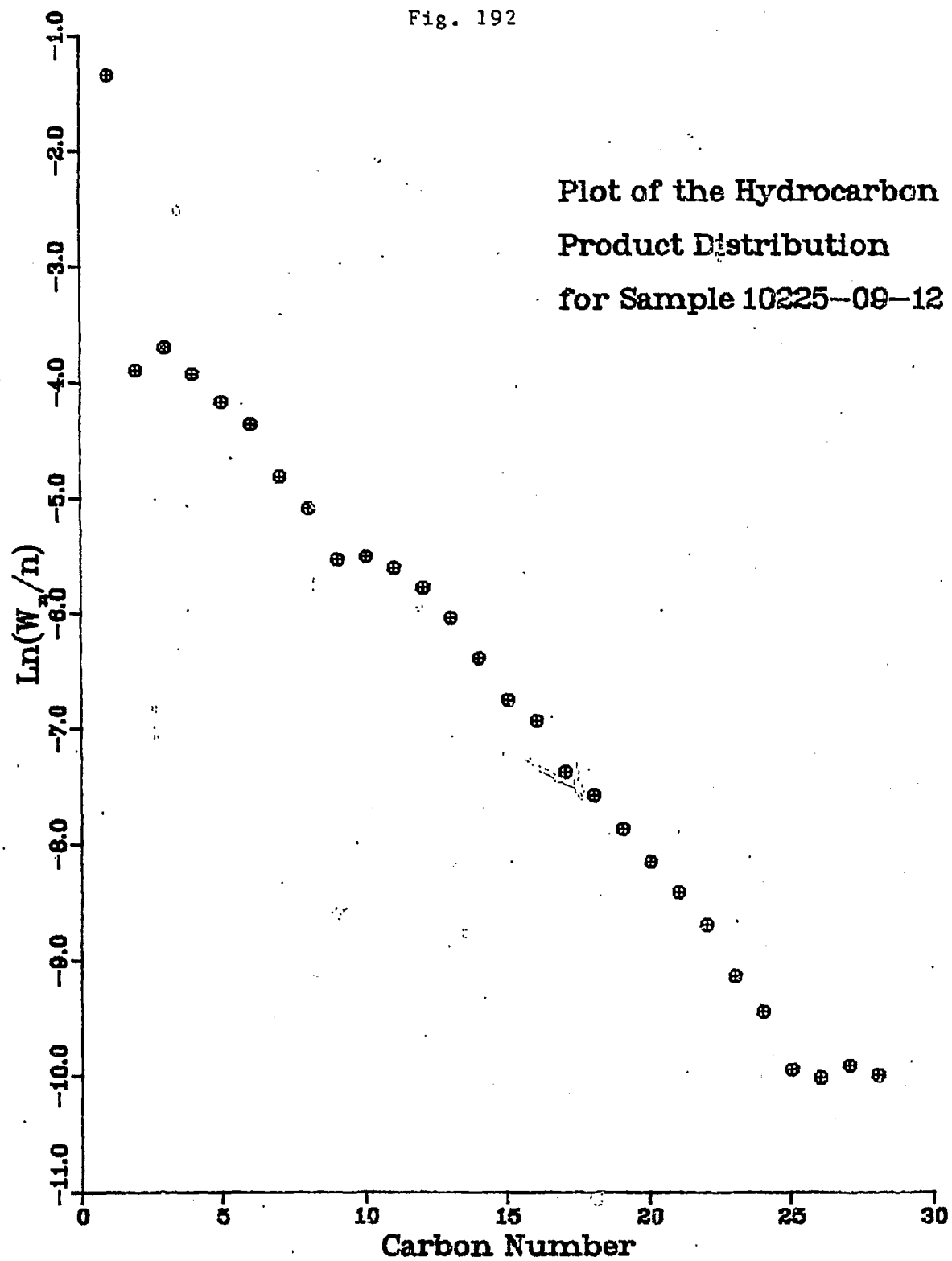


Fig. 193

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-09-14

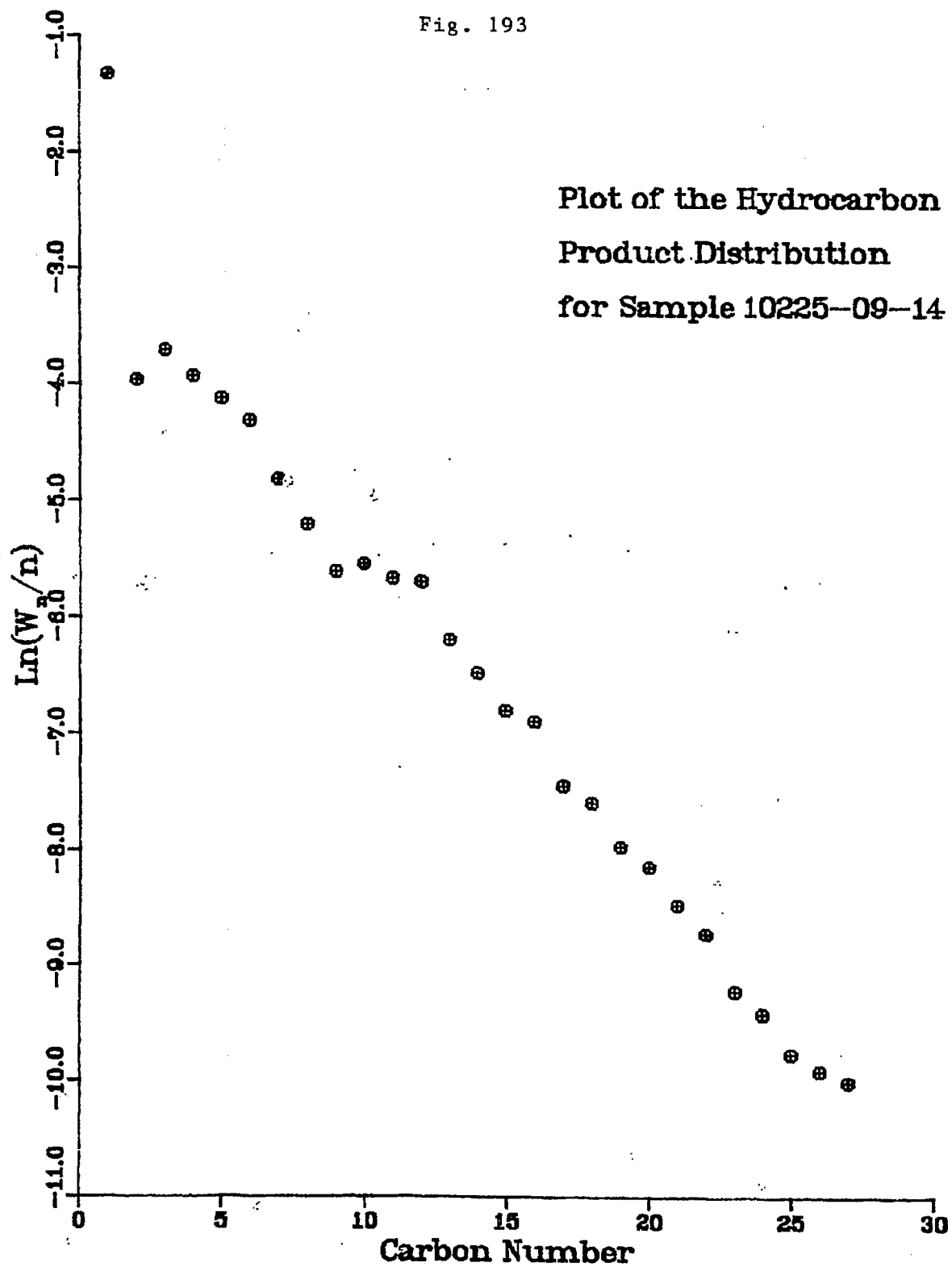


Fig. 194

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-09-16

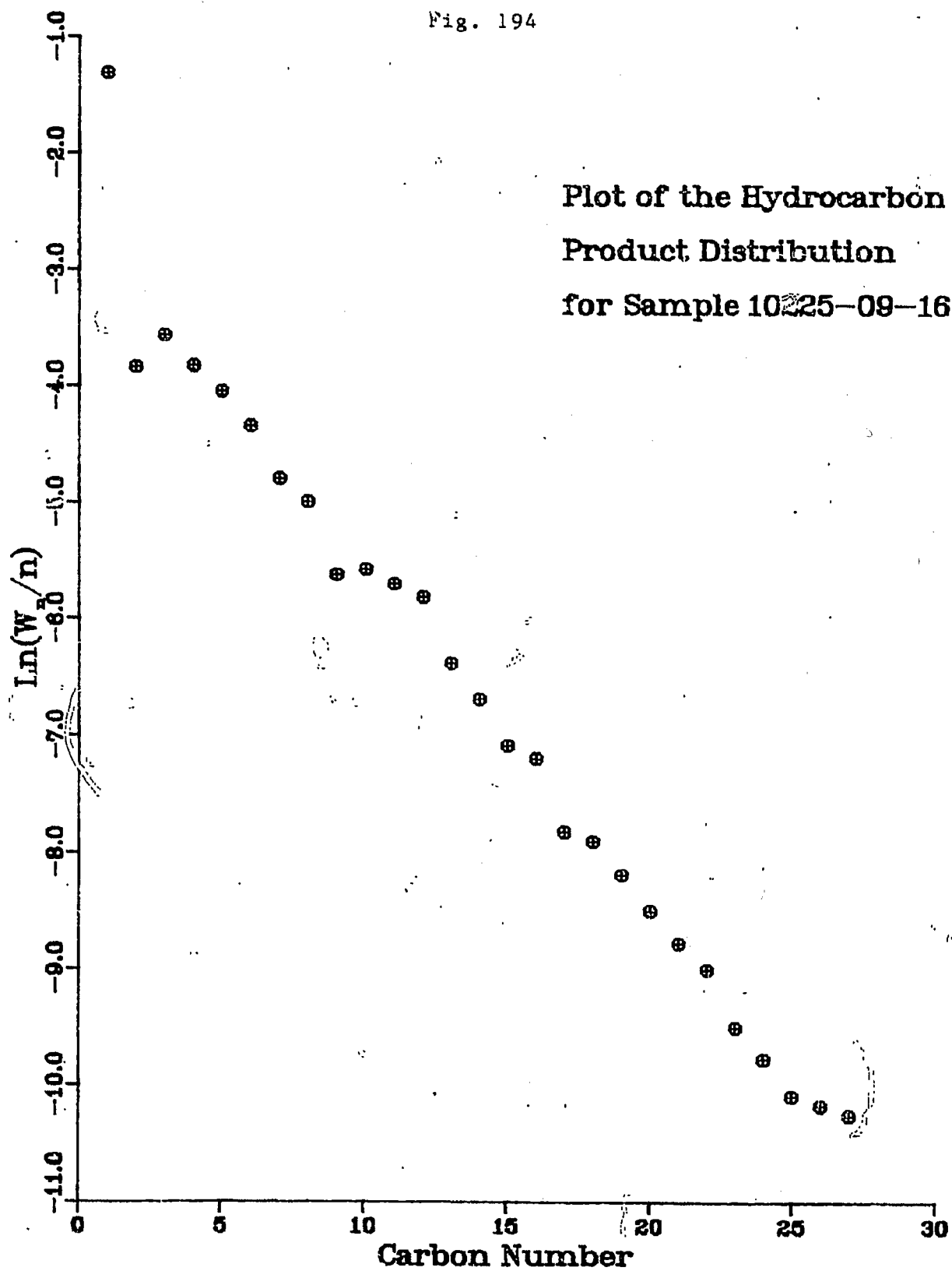
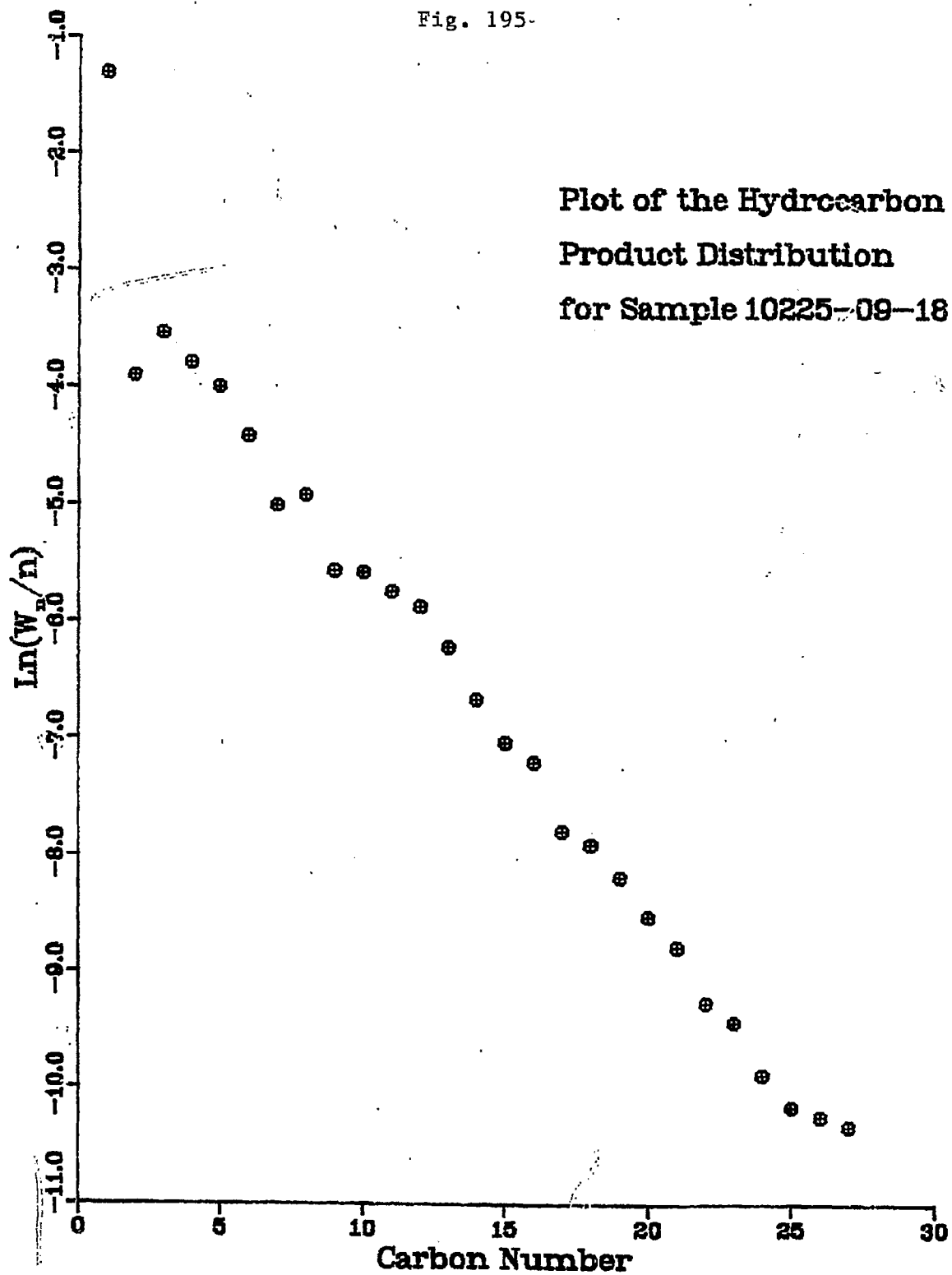
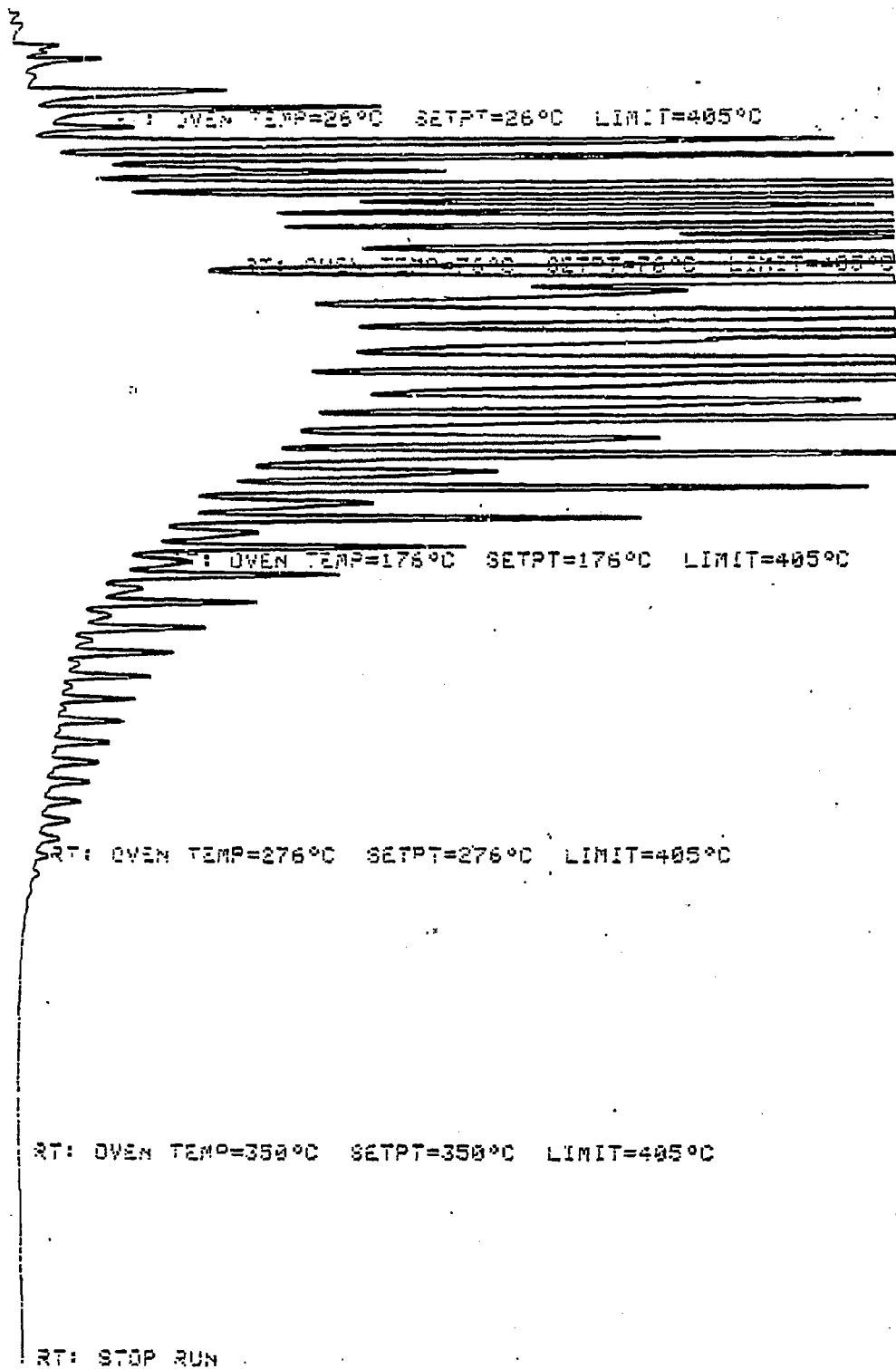


Fig. 195-



RT: 8.1038 0.20

Fig. 196



SAMPLE: 10225-9-2L

RT: SLICES 9.20

Fig. 197

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:10225-9-6L

RT: SLICES 0.20

Fig. 198

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: 10225-9-10L

RT: SLICES 0.20

Fig. 199

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

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

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

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

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

RT: STOP RUN

SAMPLE:10225-9-14L

RT: SLICES 0.20

Fig. 200

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:10225-9-18L

TABLE 29 RESULT OF SYNGAS OPERATION

RUN NO.	10225-09				
CATALYST	CO/X4+UCC-101 #10252-63C 80 CC 36.0 GM (38 AFTER RUN +2.0G)				
FEED	H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10225-09-01	225-09-02	225-09-03	225-09-04	225-09-05
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	7.0	23.5	31.0	47.5	55.0
PRESSURE, PSIG	292	303	299	301	303
TEMP. C	271	271	271	271	271
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.00	23.50	7.50	24.00	7.50
EFFLNT GAS LITER	96.00	361.10	126.50	404.70	73.90
GM AQUEOUS LAYER	13.20	44.33	12.43	39.76	11.63
GM OIL	2.15	7.21	2.94	9.42	2.59
MATERIAL BALANCE					
GM ATOM CARBON %	85.03	90.13	98.50	95.34	57.65
GM ATOM HYDROGEN %	92.11	99.12	104.06	103.47	68.82
GM ATOM OXYGEN %	89.55	95.39	99.69	98.33	64.11
RATIO CHX/(H2O+CO2)	0.8272	0.7988	0.9500	0.8733	0.6829
RATIO X IN CHX	2.5258	2.5366	2.5241	2.5395	2.4830
USAGE H2/CO PRODT	1.9019	1.9288	1.9425	1.9446	1.9557
RATIO CO2/(H2O+CO2)	0.1058	0.0950	0.1036	0.0976	0.0684
K SHIFT IN EFFLNT	0.08	0.08	0.09	0.08	0.06
CONVERSION					
ON CO %	28.68	25.90	25.42	24.03	26.57
ON H2 %	55.01	50.54	47.85	45.87	52.71
ON CO+H2 %	42.37	38.81	36.94	35.39	40.80
PRDT SELECTIVITY, WT %					
CH4	21.30	22.83	22.46	23.50	21.09
C2 HC'S	3.04	3.84	3.20	3.31	2.97
C3H8	4.46	4.22	4.23	4.15	3.87
C3H6=	2.21	2.66	2.96	2.69	2.44
C4H10	5.05	3.98	3.98	3.70	3.43
C4H8=	2.87	3.67	4.00	3.68	3.44
C5H12	6.83	4.77	4.79	4.29	3.88
C5H10=	1.57	2.89	3.35	3.15	2.84
C6H14	8.50	5.77	5.82	5.31	4.52
C6H12= & CYCLO'S	0.77	1.88	2.36	2.29	1.93
C7+ IN GAS	23.63	23.06	18.70	17.47	14.99
LIQ HC'S	19.76	20.44	24.16	26.47	34.61
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	38.94	41.19	40.82	41.02	37.24
C5 -420 F	50.58	47.98	44.84	43.27	41.31
420-700 F	9.76	10.09	13.85	15.18	20.29
700-END PT	0.72	0.74	0.48	0.53	1.17
C5+END PT	61.06	58.81	59.18	58.98	62.76
ISO/NORMAL MOLE RATIO					
C4	0.3843	0.1845	0.1775	0.1321	0.1312
C5	1.1817	0.4485	0.3695	0.2877	0.2683
C6	2.0952	0.8054	0.6420	0.4861	0.4461
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.9253	1.5153	1.3652	1.4701	1.5146
C4	1.6969	1.0462	0.9604	0.9705	0.9645
C5	4.2245	1.6016	1.3916	1.3248	1.3277
LIQ HC COLLECTION					
PHYS. APPEARANCE		LT BL OIL		LT BL OIL	
DENSITY		0.756		0.760	
N, REFRACTIVE INDEX		1.4255		1.4275	
SIMULT'D DISTILLATN					
10 WT % @ DEG F		312		317	
16		339		346	
50		425		449	
84		540		574	
90		585		608	
RANGE(16-84 %)		201		228	
WT % @ 420 F	47.00	47.00	40.67	40.67	38.00
WT % @ 700 F	96.38	96.38	98.00	98.00	96.62

TABLE 30

RESULT OF SYNGAS OPERATION

RUN NO. 10225-09

CATALYST CO/X4+JCC-101 #10252-63C 80 CC 36.0 GM (38 AFTER RUN +2.0G)

FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-09-06	225-09-07	225-09-08	225-09-09	225-09-10
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	71.5	79.0	95.2	100.5	120.2
PRESSURE, PSIG	296	298	298	300	296
TEMP. C	271	271	271	271	271
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	7.50	23.67	5.33	25.00
EFFLNT GAS LITER	283.75	129.15	406.95	93.64	438.70
GM AQUEOUS LAYER	37.21	11.11	35.05	7.65	35.88
GM OIL	8.29	2.42	7.65	1.42	6.65
MATERIAL BALANCE					
GM ATOM CARBON %	67.34	97.68	95.21	96.62	96.14
GM ATOM HYDROGEN %	77.91	101.85	101.86	102.85	102.17
GM ATOM OXYGEN %	73.04	98.91	97.56	98.63	98.72
RATIO CH ₄ /(H ₂ O+CO ₂)	0.7272	0.9437	0.8914	0.9056	0.8791
RATIO X IN CH ₄	2.5093	2.5670	2.5870	2.6029	2.6241
USAGE H ₂ /CO PRDNT	1.9566	1.9446	1.9452	1.9400	1.9435
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0753	0.1091	0.1064	0.1123	0.1112
K SHIFT IN EFFLNT	0.06	0.09	0.09	0.10	0.10
CONVERSION					
ON CO %	24.87	23.44	22.72	22.45	21.92
ON H ₂ %	49.22	44.90	43.55	42.81	42.53
ON CO+H ₂ %	37.93	34.39	33.48	32.95	32.54
PRDT SELECTIVITY, WT %					
CH ₄	22.35	24.42	25.44	26.20	26.81
C ₂ HC'S	3.26	3.60	3.72	4.25	4.00
C ₃ H ₈	3.93	4.70	4.76	5.07	5.17
C ₃ H ₆ =	2.43	2.79	2.70	3.34	2.67
C ₄ H ₁₀	3.45	4.18	4.19	4.39	4.61
C ₄ H ₈ =	3.32	3.96	3.76	3.84	3.73
C ₅ H ₁₂	3.88	4.69	4.64	4.59	5.08
C ₅ H ₁₀ =	2.91	3.28	3.34	3.12	3.14
C ₆ H ₁₄	4.61	5.46	5.09	5.27	5.61
C ₆ H ₁₂ = & CYCLO'S	1.98	2.49	2.23	2.13	2.12
C ₇ + IN GAS	16.19	18.61	16.95	18.72	17.41
LIQ HC'S	31.69	21.81	23.17	19.08	19.65
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	38.73	43.66	44.57	47.09	47.00
C5 -420 F	41.62	42.34	40.55	40.62	40.35
420-700 F	18.58	13.21	14.04	11.56	11.90
700-END PT	1.07	0.79	0.83	0.73	0.75
C5+-END PT	61.27	56.34	55.43	52.91	53.00
ISO/NORMAL MOLE RATIO					
C4	0.1222	0.1187	0.1089	0.1380	0.1034
C5	0.2314	0.2259	0.2131	0.2087	0.1924
C6	0.3989	0.3778	0.3422	0.3417	0.3005
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.5450	1.6054	1.6812	1.4511	1.8458
C4	1.0022	1.0171	1.0736	1.1051	1.1950
C5	1.2952	1.3876	1.3490	1.4309	1.5737
LIQ HC COLLECTION					
PHYS. APPEARANCE	LT BL OIL		LT BL OIL		LT BL OIL
DENSITY	0.761		0.760		0.759
N, REFRACTIVE INDEX	1.4280		1.4275		1.4274
SIMULT'D DISTILATN					
10 WT % @ DEG F	325		331		330
16	353		362		366
50	455		459		460
84	590		591		597
90	629		630		636
RANGE(16-84 %)	237		229		231
WT % @ 420 F	38.00	35.80	35.80	35.60	35.60
WT % @ 700 F	96.62	96.40	96.40	96.17	96.17

TABLE 31

RESULT OF SYNGAS OPERATION

RUN NO. 10225-09
 CATALYST CO/X4+UCC-101 #10252-63C 80 CC 36.0 GM (38 AFTER RUN +2.0G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-09-11	225-09-12	225-09-13	225-09-14
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	125.1	143.5	151.0	167.5
PRESSURE, PSIG	300	297	301	295
TEMP. C	271	271	271	271
FEED CC/MIN	400	400	400	400
HOURS FEEDING	4.92	23.33	7.50	24.00
EFFLNT GAS LITER	86.20	412.15	131.90	423.50
GM AQUEOUS LAYER	6.84	32.48	10.15	32.47
GM OIL	1.37	6.52	2.05	6.57
MATERIAL BALANCE				
GM ATOM CARBON %	96.67	96.83	96.74	97.09
GM ATOM HYDROGEN %	102.34	102.94	101.55	101.90
GM ATOM OXYGEN %	98.11	98.45	98.21	98.42
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9308	0.9225	0.9279	0.9347
RATIO X IN CH ₄	2.6069	2.6071	2.6279	2.6195
USAGE H ₂ /CO PRODT	1.9392	1.9421	1.9383	1.9390
RATIO CO ₂ /(H ₂ O+CO ₂)	0.1161	0.1141	0.1194	0.1186
K SHIFT IN EFFLNT	0.10	0.10	0.11	0.10
CONVERSION				
ON CO %	22.57	22.29	22.12	22.16
ON H ₂ %	42.71	42.24	42.25	42.20
ON CO+H ₂ %	32.93	32.57	32.43	32.42
PRDT SELECTIVITY, WT %				
CH ₄	26.06	26.02	26.75	26.47
C ₂ HC'S	3.73	4.05	3.93	3.81
C ₃ H ₈	5.14	5.03	5.53	5.15
C ₃ H ₆ =	2.71	2.41	2.59	2.30
C ₄ H ₁₀	4.53	4.45	4.81	4.61
C ₄ H ₈ =	3.85	3.39	3.52	3.28
C ₅ H ₁₂	4.97	4.94	5.32	5.27
C ₅ H ₁₀ =	3.14	2.73	2.37	2.86
C ₆ H ₁₄	5.48	5.65	5.96	6.03
C ₆ H ₁₂ = & CYCLO'S	2.09	1.92	1.34	2.04
C ₇ + IN GAS	18.37	19.28	17.92	18.37
LIQ HC'S	19.93	20.13	19.95	19.82
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	46.01	45.35	47.14	45.62
C5 -420 F	41.15	41.69	40.43	42.03
420-700 F	12.06	12.18	11.69	11.62
700-END PT	0.78	0.78	0.74	0.74
C5+-END PT	53.99	54.65	52.86	54.38
ISO/NORMAL MOLE RATIO				
C4	0.0963	0.0896	0.0920	0.0932
C5	0.1818	0.1760	0.1799	0.1580
C6	0.2997	0.2777	0.2988	0.2688
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	1.8135	1.9915	2.0369	2.1368
C4	1.1366	1.2666	1.3187	1.3560
C5	1.5373	1.7615	2.1824	1.7892
LIQ HC COLLECTION				
PHYS. APPEARANCE		LT HL OIL		LT HL OIL
DENSITY		0.758		0.759
N, REFRACTIVE INDEX		1.4271		1.4265
SIMULT'D DISTILAIN				
10 WT % @ DEG F		328		327
16		367		363
50		460		457
84		595		591
90		634		630
RANGE(16-84 %)		228		228
WT % @ 420 F	35.60	35.60	37.67	37.67
WT % @ 700 F	96.11	96.11	96.28	96.28

TABLE 32 RESULT OF SYNGAS OPERATION

RUN NO. 10225-09
 CATALYST CO/X4+UCC-101 #10252-63C 80 CC 36.0 GM (38 AFTER RUN +2.0G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10225-09-16 225-09-17 225-09-18

FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	215.5	223.0	239.5
PRESSURE, PSIG	302	298	300
TEMP. C	271	271	271
FEED CC/MIN	400	400	400
HOURS FEEDING	17.00	7.50	24.00
EFFLNT GAS LITER	307.22	119.28	396.08
GM AQUEOUS LAYER	22.91	9.59	30.70
GM OIL	3.31	1.31	4.19
MATERIAL BALANCE			
GM ATOM CARBON %	98.08	86.80	89.61
GM ATOM HYDROGEN %	103.71	92.12	94.81
GM ATOM OXYGEN %	99.75	89.19	91.93
RATIO CH _x /(H ₂ O+CO ₂)	0.9186	0.8743	0.8794
RATIO X IN CH _x	2.6384	2.6386	2.6494
USAGE H ₂ /CO PRDNT	1.9383	1.9413	1.9357
RATIO CO ₂ /(H ₂ O+CO ₂)	0.1200	0.1136	0.1179
K SHIFT IN EFFLNT	0.11	0.10	0.11
CONVERSION			
ON CO %	21.67	21.70	21.44
ON H ₂ %	41.28	42.22	41.59
ON CO+H ₂ %	31.75	32.26	31.80
PRDNT SELECTIVITY, WT %			
CH ₄	26.67	26.56	27.08
C ₂ HC'S	4.31	3.86	4.04
C ₃ H ₈	6.10	6.22	6.41
C ₃ H ₆ =	2.38	2.31	2.29
C ₄ H ₁₀	5.47	5.62	5.79
C ₄ H ₈ =	3.24	3.28	3.19
C ₅ H ₁₂	6.17	5.99	6.10
C ₅ H ₁₀ =	2.54	2.29	3.02
C ₆ H ₁₄	6.27	6.69	5.89
C ₆ H ₁₂ = & CYCLO'S	1.54	1.49	1.39
C ₇ + IN GAS	21.01	21.24	20.58
LIQ HC'S	14.30	14.45	14.22
TOTAL	100.00	100.00	100.00

SUB-GROUPING			
C1 -C4	48.17	47.84	48.80
C5 -420 F	42.77	42.72	41.91
420-700 F	8.52	8.94	8.79
700-END PT	0.54	0.51	0.50
C5+-END PT	51.83	52.16	51.20
ISO/NORMAL MOLE RATIO			
C4	0.0866	0.0825	0.0827
C5	0.1491	0.1473	0.1460
C6	0.2181	0.2551	0.0744
C4=	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO			
C3	2.4431	2.5757	2.6743
C4	1.6325	1.6554	1.7512
C5	2.3613	2.5395	1.9595
LIQ HC COLLECTION			
PHYS. APPEARANCE	CLR OIL		CLR OIL
DENSITY	0.757		0.756
N, REFRACTIVE INDEX	1.4262		1.4260
SIMULT'D DISTILLATN			
10 WT % @ DEG F	334		336
16	370		375
50	461		461
84	594		588
90	632		628
RANGE(16-84 %)	224		213
WT % @ 420 F	36.67	34.67	34.67
WT % @ 700 F	96.24	96.50	96.50

XII. RUN 11 (10225-5) with Catalyst 11 (Fe/K + UCC-108)

This catalyst was run to collect samples for a research octane measurement. It was prepared by precipitating $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ from a refluxing solution of ferric nitrate upon the addition of a stoichiometric quantity of aqueous ammonia. The washed and dried precipitate was impregnated with K_2CO_3 solution to give one percent K_2O on the iron oxide. This metal component was then physically mixed with an equal weight of UCC-108, and pressed into tablets without a binder.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4 's are plotted against time on stream in Figs. 201-204. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 205-206. Carbon number product distributions are plotted in Figs. 207-210. Chromatograms from simulated distillations are reproduced in Figs. 211-214. Detailed material balances appear in Tables 33-34.

The samples from the first 260 hours on stream were combined, and material balanced as a single sample. At 270 hours on stream the conversion was high. So also was the water gas shift activity; 85 percent of the oxygen was rejected as CO_2 . The $\text{H}_2:\text{CO}$ usage ratio was $\sim 0.73:1$, which is desirable if a syngas feed with a $\text{H}_2:\text{CO}$ ratio lower than $1:1$ is to be used.

Unlike cobalt catalysts, there was no excess production of

methane. The C₂-C₄ fraction, however, was much higher than for cobalt. The yield of C₅⁺ was low, but this was far into the run; by 270 hours on stream much of the catalyst may have been deactivated. There was little diesel oil, and almost no heavies. The percent olefins of the C₄ was unusually low for an iron catalyst, and may be a sign of deactivation.

The isomerization of the pentane was also unusually low. The gas analyses of the early samples (for which there is only one combined material balance) show a progressive deactivation. Initially, 61 percent of the pentanes was isopentane. By 40 hours on stream this was down to 56 percent; by 130 hours, 30 percent; and by 250 hours, 26.5 percent. The loss of isomerizing activity during collection of the sample for RON would significantly lower the measured RON from its initial value. The chromatograms of the simulated distillations show the RON sample to have been somewhat isomerized; by the next sample, however, the value was much lower, which paralleled the isomerization of the pentane.

The RON clear of the distilled gasoline fraction (which, due to poor condensation, lacked many lights) was only 57.6. The gasoline did contain 47 percent olefins, and the pour point of the diesel oil was 20F.

This catalyst deactivated so quickly that the quality of the gasoline it produced initially could not be reliably measured. A probable reason for the deactivation is migration of alkali from the iron component to the UCC-108, deactivating the Molecular Sieve.

RUN 10225-05

1:1 H₂:CO
280 PSIG
250°C

250 PSIG

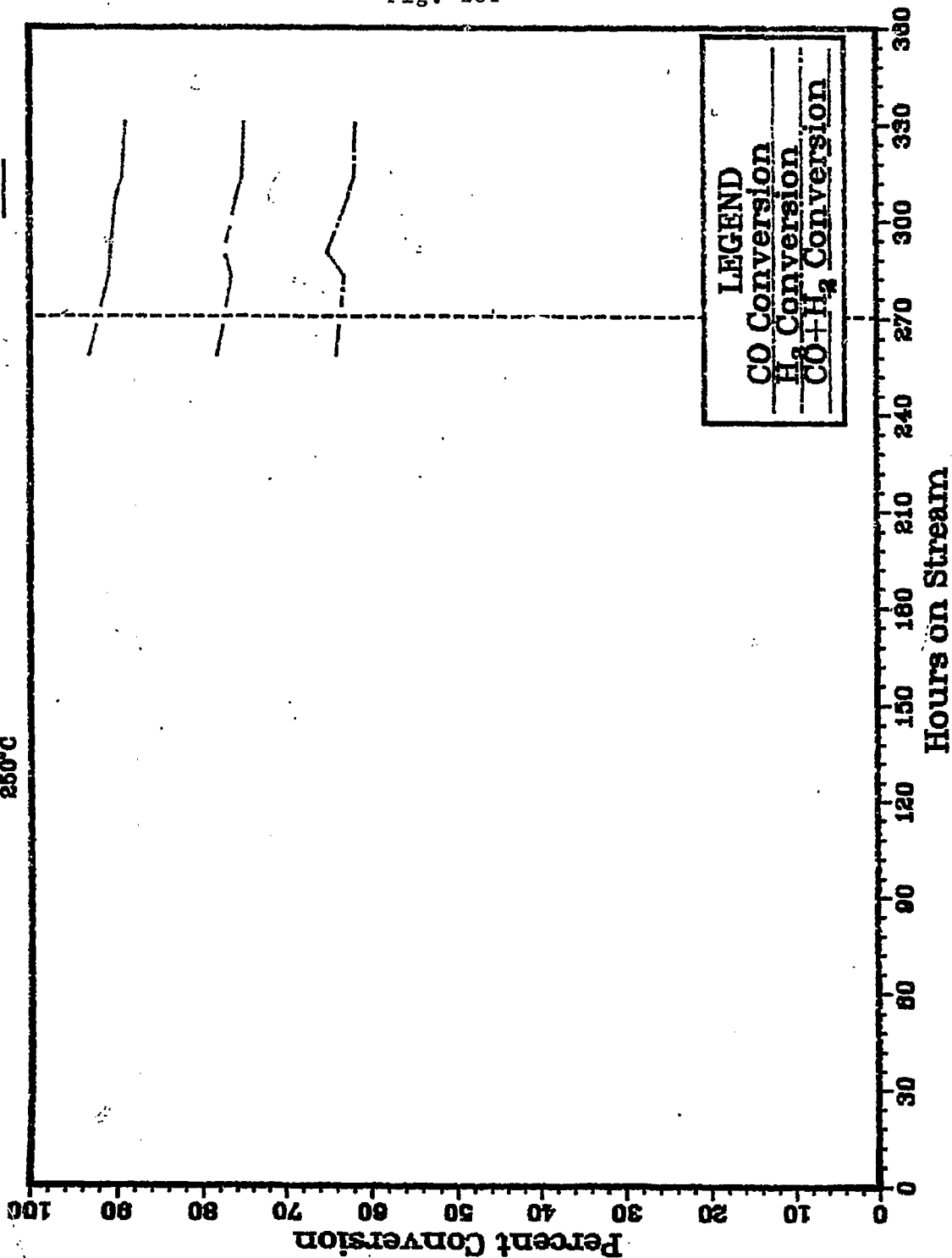
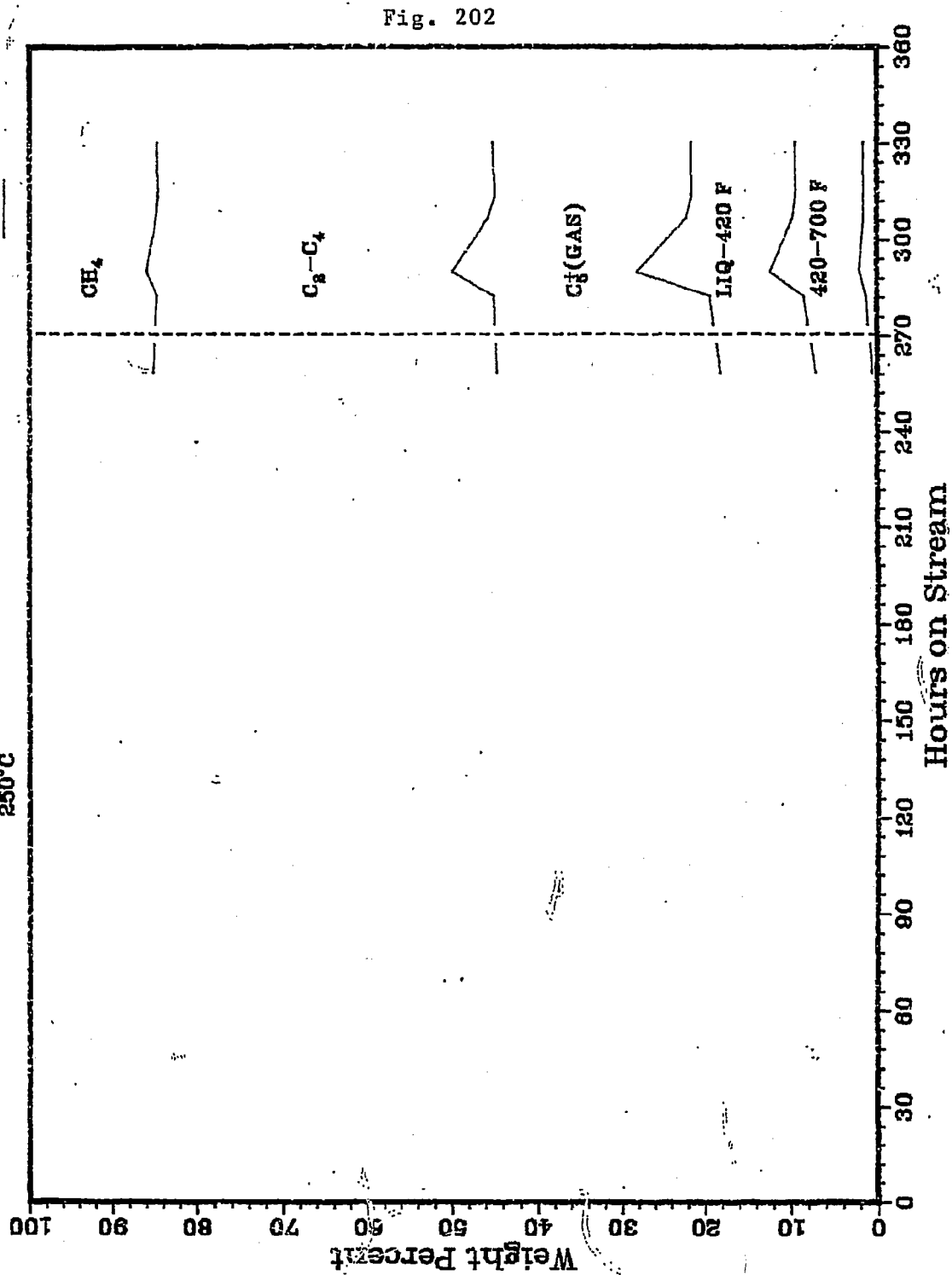


Fig. 201

RUN 10225-05

1:1 H₂:CO
280 PSIG
250°C

250 PSIG



RUN 10225-05

1:1 H₂:CO
260 PSIG
250°C

250 PSIG

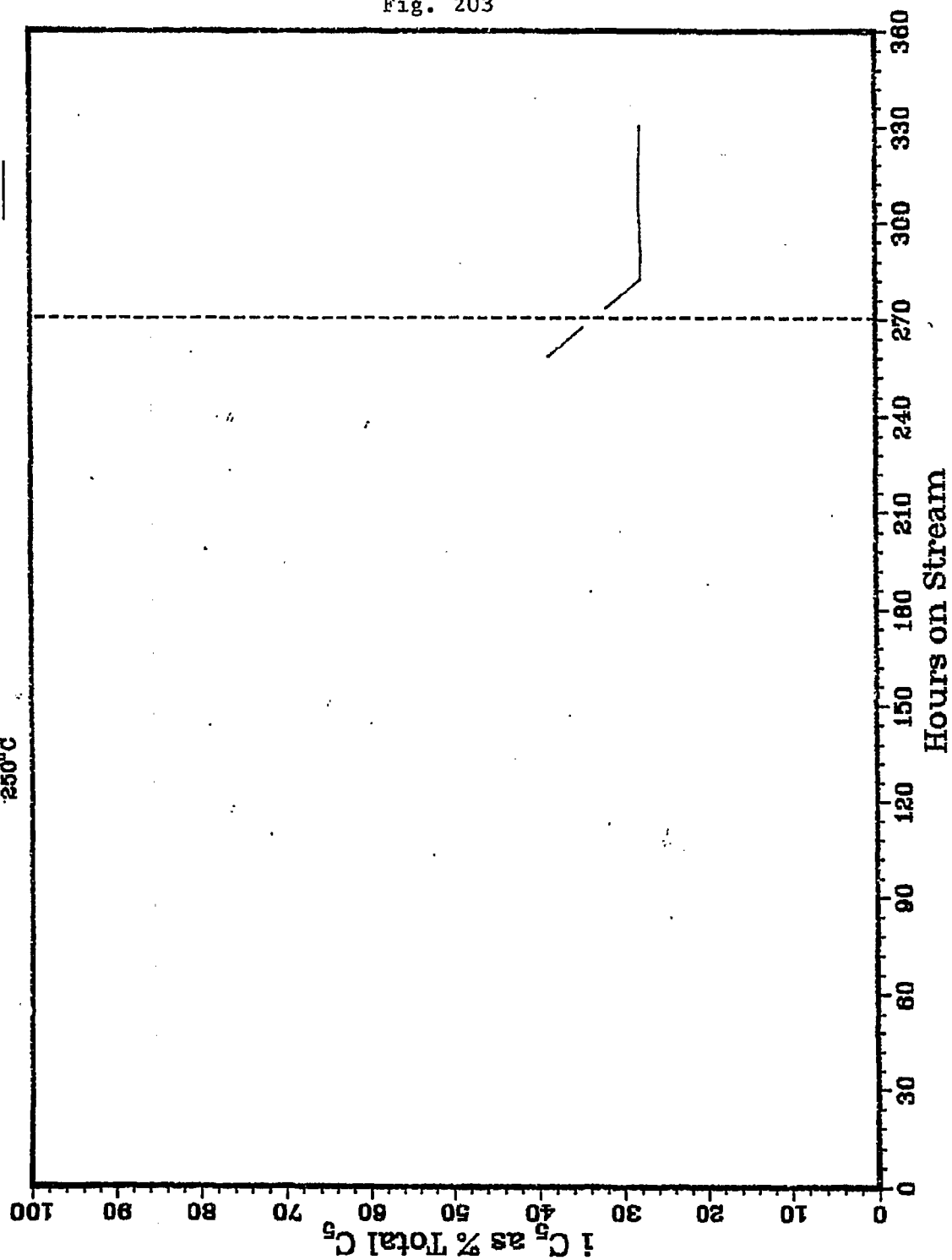


Fig. 203

RUN 10225-05

1:1 H₂:CO
280 PSIG
250°C

250 PSIG

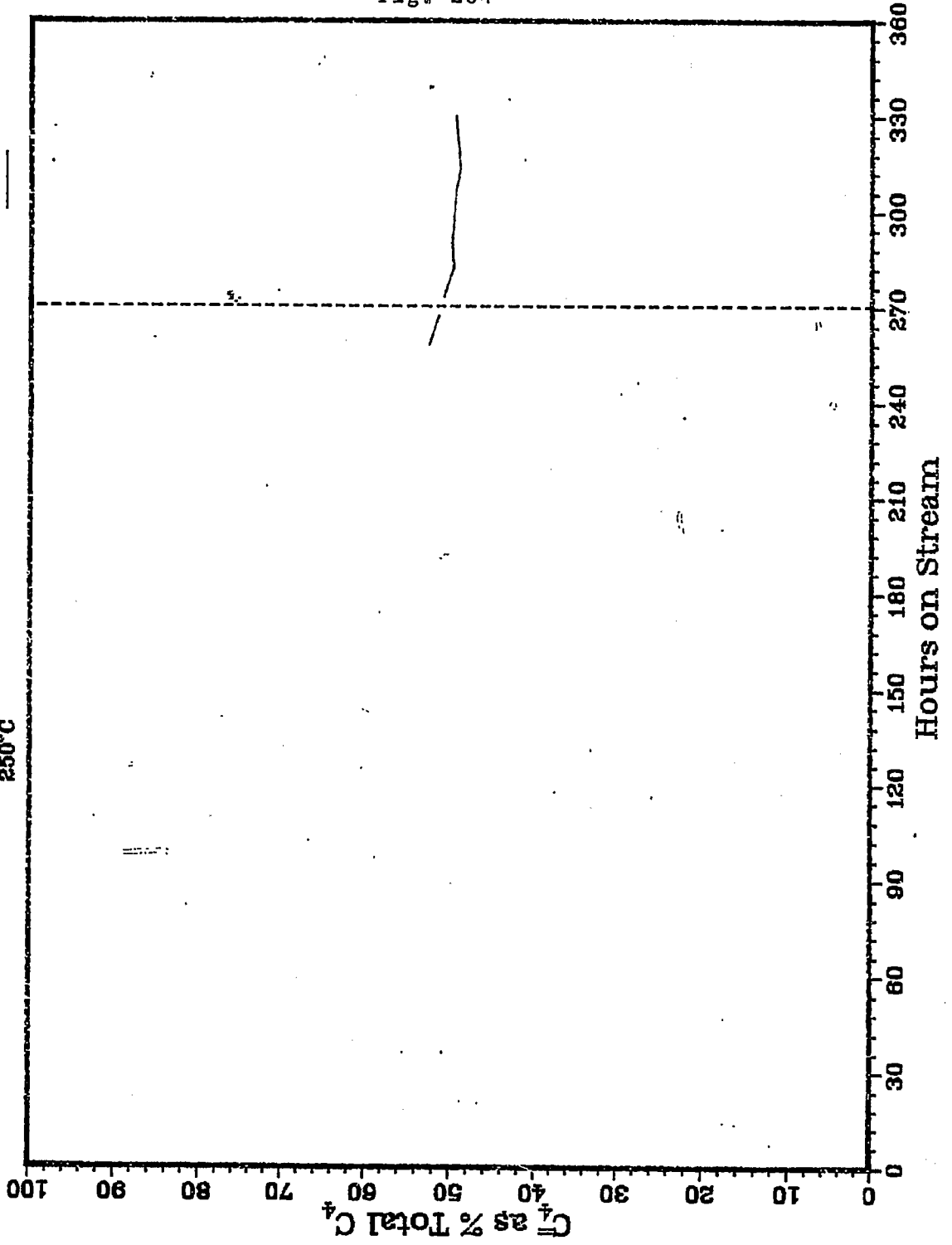


Fig. 205

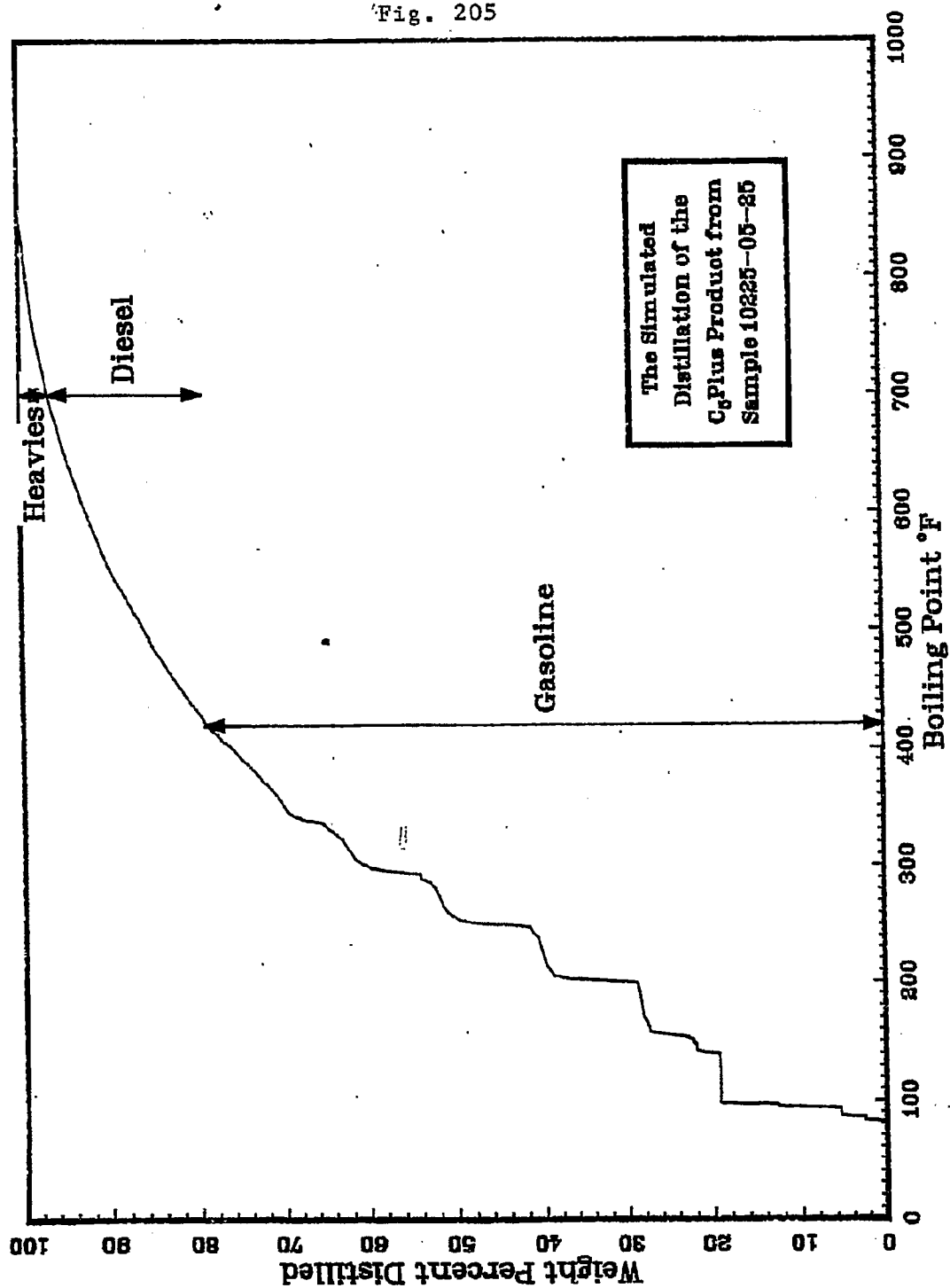


Fig. 206

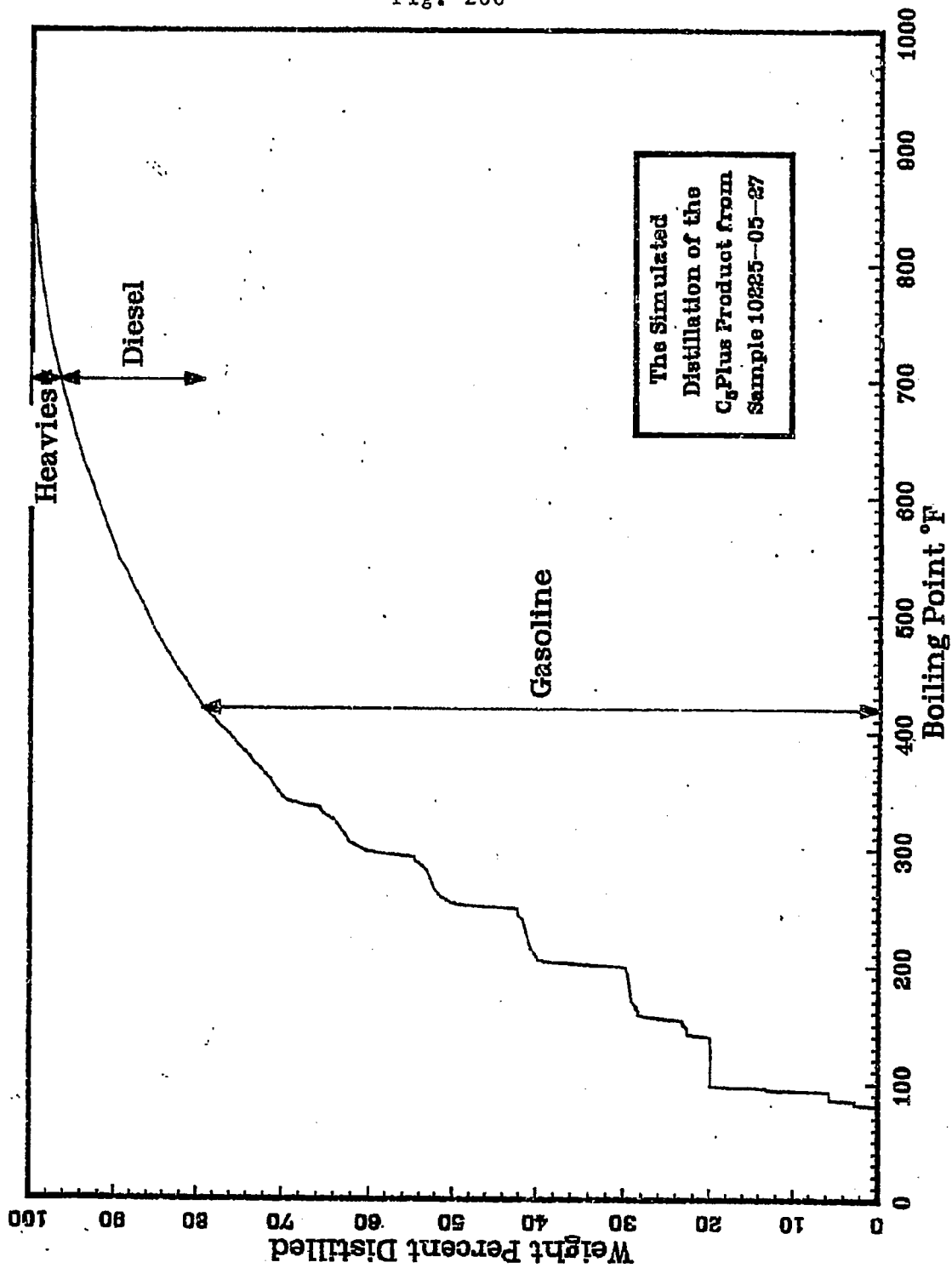


Fig. 207

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-05-22

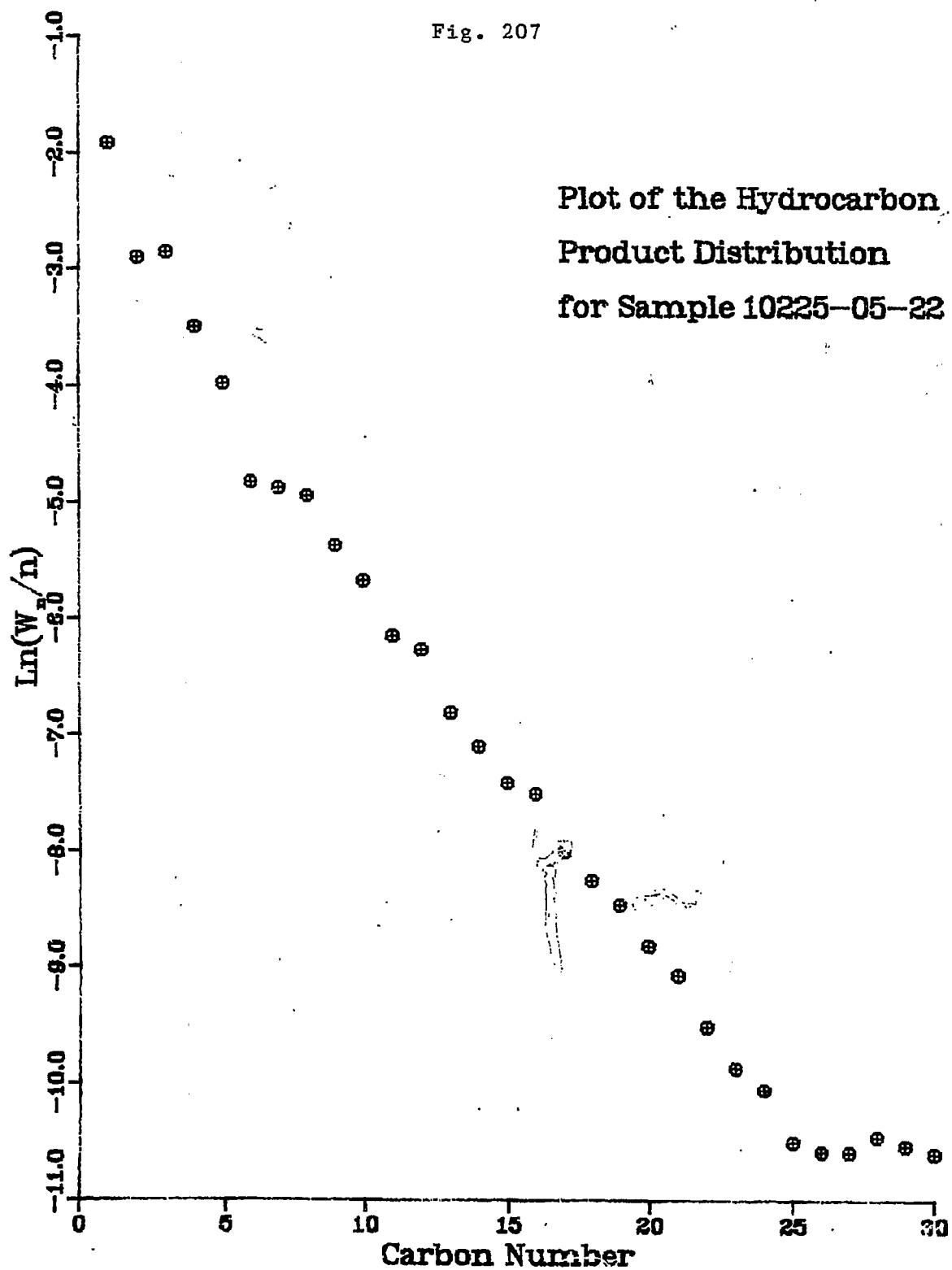


Fig. 208

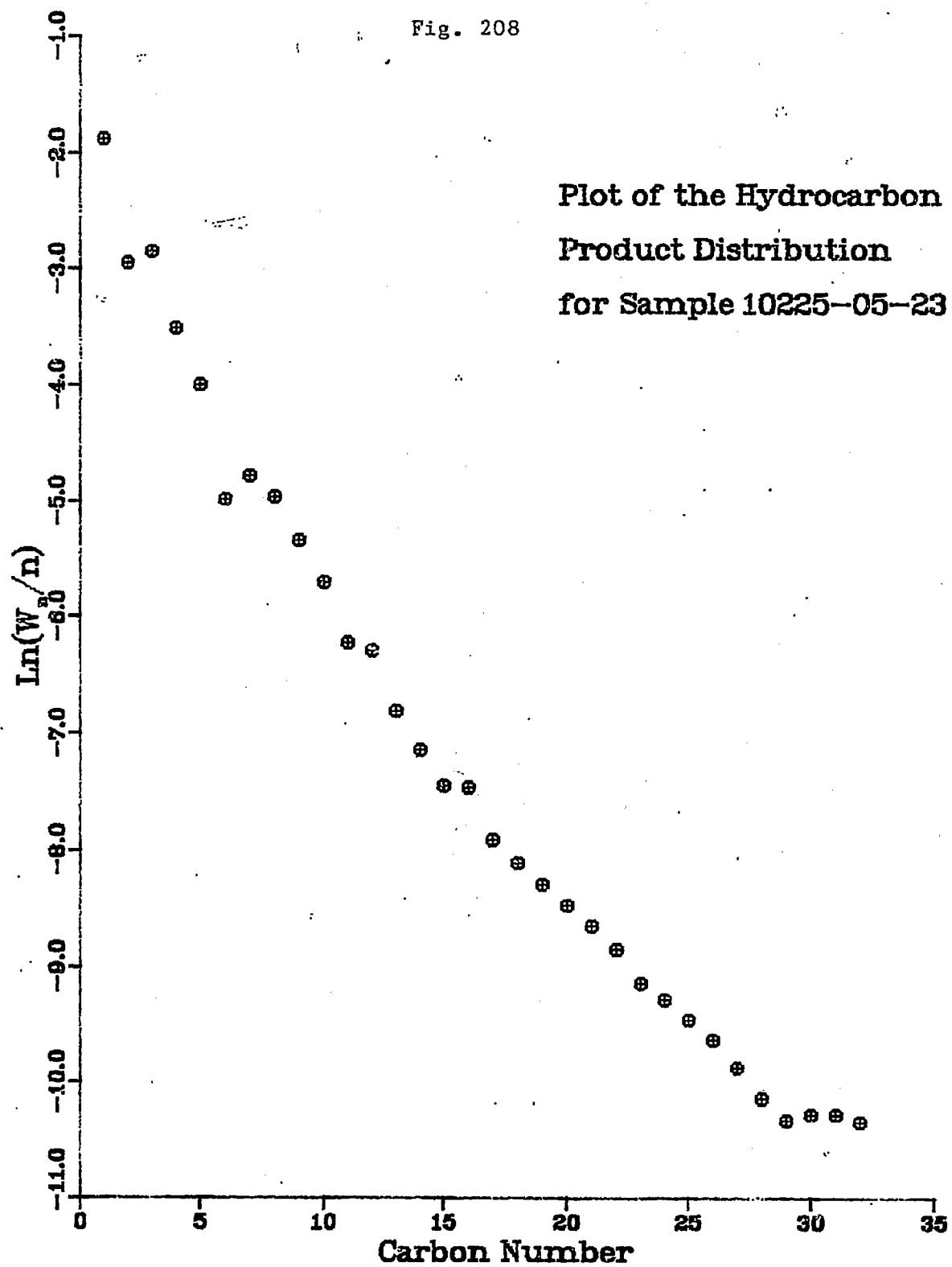


Fig. 209

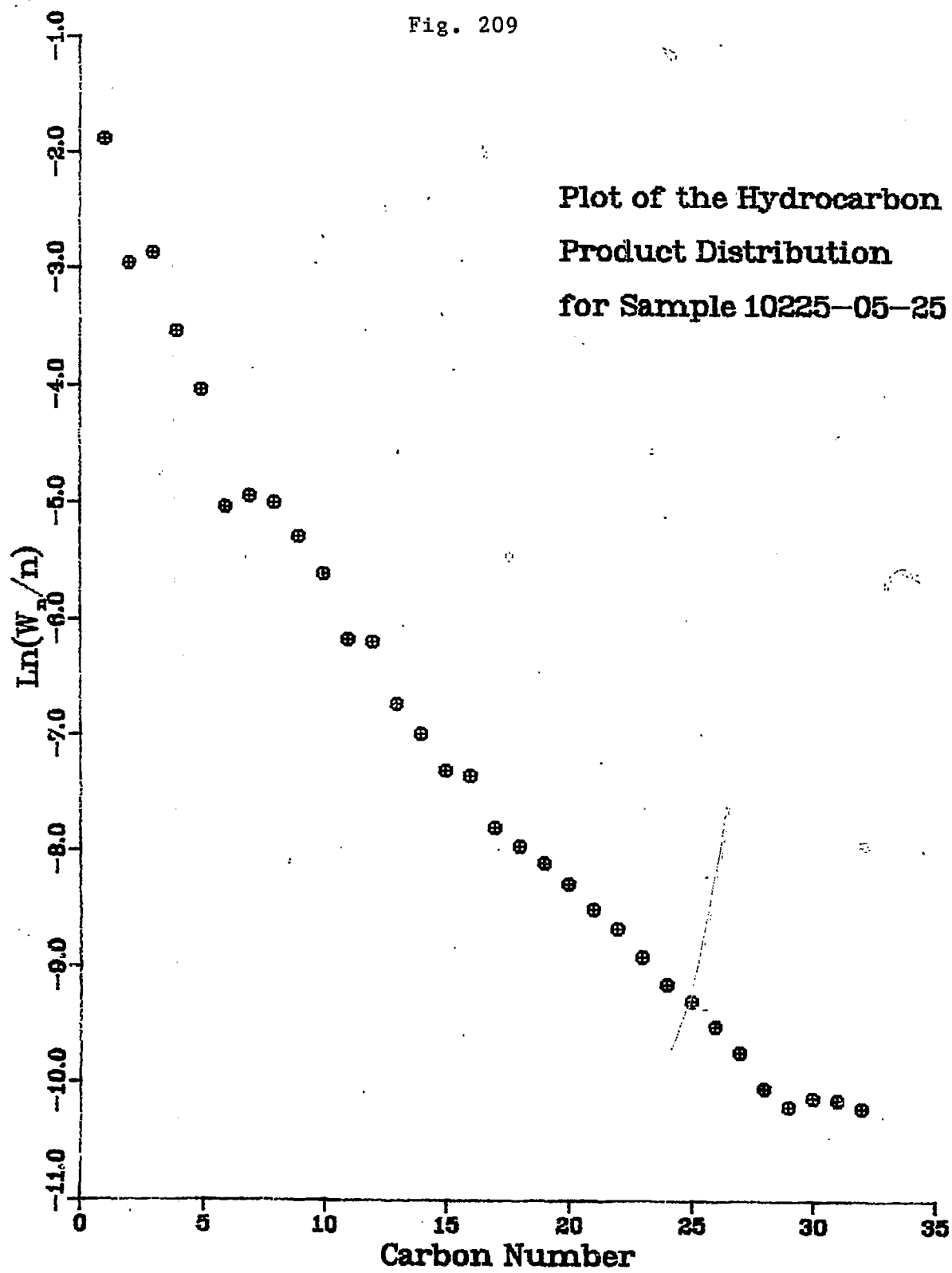
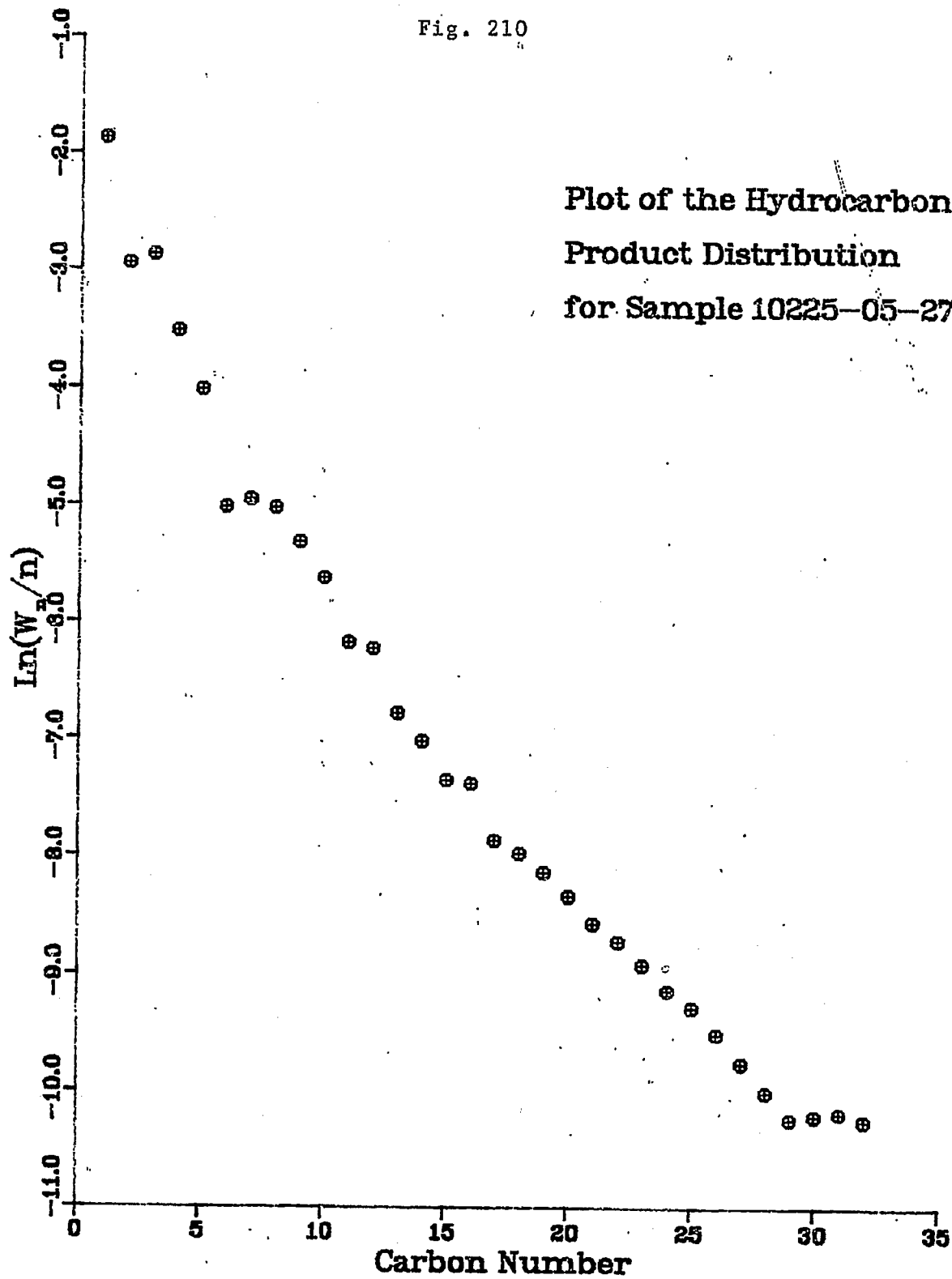


Fig. 210

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-05-27



RT: SLICES 0.20

Fig. 211

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

OUT OF PAPER

10225-S-HIX

RT: SLICES 0.20

Fig. 212

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: D10225-5-23L

RT: SLICES 0.20

Fig. 213

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=300°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE: D10225-5-25L

RT: SLICES .20

Fig. 214

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: D10225 -5-27L

TABLE 33 RESULT OF SYNGAS OPERATION

RUN NO. 10225-05
 CATALYST FE/K +UCC-108 #10252-18-5 80 CC 59.7GM (72.9 AFTER RUN +13 G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-05-22	225-05-23	225-05-24	225-05-25
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	258.5	282.5	290.0	306.5
PRESSURE, PSIG	281	240	258	256
TEMP. C	250	250	250	250
FEED CC/MIN	400	400	400	400
HOURS FEEDING	258.50	24.00	7.50	24.00
EFFLNT GAS LITER	3142.47	275.31	61.45	273.75
GM AQUEOUS LAYER	122.27	10.10	3.30	10.57
GM OIL	152.58	13.69	4.84	15.50
MATERIAL BALANCE				
GM ATOM CARBON %	93.31	86.68	64.62	85.96
GM ATOM HYDROGEN %	100.13	92.52	70.47	92.13
GM ATOM OXYGEN %	97.19	89.98	65.48	89.15
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9210	0.9253	0.9738	0.9268
RATIO X IN CH ₄	2.5107	2.5200	2.4726	2.5144
USAGE H ₂ /CO PRDNT	0.7194	0.7242	0.7762	0.7301
RATIO CO ₂ /(H ₂ O+CO ₂)	0.8522	0.8518	0.8096	0.8450
K SHIFT IN EFFLNT	32.43	24.30	17.11	21.62
CONVERSION				
ON CO %	93.09	90.60	90.48	89.86
ON H ₂ %	63.80	62.76	64.86	62.47
ON CO+H ₂ %	77.93	76.23	77.12	75.69
PRDNT SELECTIVITY, WT %				
CH ₄	14.79	15.31	14.06	15.23
C ₂ HC'S	11.00	10.43	9.51	10.37
C ₃ H ₈	12.25	12.87	11.66	12.68
C ₃ H ₆ =	5.05	4.39	3.98	4.29
C ₄ H ₁₀	5.89	6.09	5.53	6.00
C ₄ H ₈ =	6.30	5.83	5.31	5.68
C ₅ H ₁₂	4.38	4.38	3.90	4.20
C ₅ H ₁₀ =	4.97	4.77	4.29	4.62
C ₆ H ₁₄	4.11	3.46	3.08	3.31
C ₆ H ₁₂ = & CYCLO'S	0.44	0.38	0.29	0.33
C ₇ + IN GAS	12.61	12.68	10.18	11.04
LIQ HC'S	18.22	19.42	28.23	22.26
TOTAL	100.00	100.00	100.00	100.00

SUB-GROUPING				
C1 -C4	55.28	54.92	50.04	54.25
C5 -420 F	37.61	36.63	37.66	36.05
420-700 F	6.56	7.10	10.33	8.15
700-END PT	0.55	1.35	1.98	1.56
C5+-END PT	44.72	45.08	49.96	45.75
ISO/NORMAL MOLE RATIO				
C4	0.1524	0.1018	0.1022	0.1006
C5	0.6290	0.3863	0.3836	0.3881
C6	1.0989	0.6075	0.6035	0.6070
C4=	0.0834	0.0693	0.0703	0.0705
PARAFFIN/OLEFIN RATIO				
C3	2.3150	2.7947	2.7985	2.8226
C4	0.9018	1.0092	1.0041	1.0199
C5	0.8576	0.8923	0.8832	0.8827
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLR OIL	CLR OIL	-	CLR OIL
DENSITY	0.759	0.759		0.758
N, REFRACTIVE INDEX	1.4283	1.4284		1.4280
SIMULT'D DISTILATN				
10 WT % @ DEG F	242	246		248
16	270	273		275
50	386	398		399
84	542	596		600
90	595	659		661
RANGE(16-84 %)	272	323		325
WT % @ 420 F	61.00	56.50	56.40	56.40
WT % @ 700 F	97.00	93.06	93.00	93.00

TABLE 34 RESULT OF SYNGAS OPERATION

RUN NO. 10225-05
 CATALYST FE/K +UCC-108 #10252-18-5 80 CC 59.7GM (72.9 AFTER RUN +13 G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10225-05-26 225-05-27
 =====

FEED H ₂ :CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	313.5	330.5
PRESSURE, PSIG	258	256
TEMP. C	250	250

FEED CC/MIN	400	400
HOURS FEEDING	7.00	24.00
EFFLNT GAS LITER	89.40	308.90
GM AQUEOUS LAYER	3.21	11.01
GM OIL	4.77	16.37

MATERIAL BALANCE

GM ATOM CARBON %	95.14	95.69
GM ATOM HYDROGEN %	101.30	101.79
GM ATOM OXYGEN %	99.29	99.64
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9138	0.9177
RATIO X IN CH ₄	2.5226	2.5206
USAGE H ₂ /CO PRDNT	0.7203	0.7223
RATIO CO ₂ /(H ₂ O+CO ₂)	0.8507	0.8500
K SHIFT IN EFFLNT	21.33	20.34

CONVERSION

ON CO %	89.13	88.61
ON H ₂ %	61.76	61.57
ON CO+H ₂ %	75.02	74.68

PRDNT SELECTIVITY, WT %

CH ₄	15.46	15.36
C ₂ HC'S	10.52	10.56
C ₃ H ₈	12.80	12.74
C ₃ H ₆ =	4.32	4.35
C ₄ H ₁₀	6.19	6.10
C ₄ H ₈ =	5.75	5.76
C ₅ H ₁₂	4.27	4.31
C ₅ H ₁₀ =	4.66	4.70
C ₆ H ₁₄	3.37	3.36
C ₆ H ₁₂ = & CYCLO'S	0.35	0.36
C ₇ + IN GAS	10.72	10.85
LIQ HC'S	21.59	21.56

TOTAL	100.00	100.00
-------	--------	--------

SUB-GROUPING		
C1 -C4	55.03	54.86
C5 -420 F	35.57	35.76
420-700 F	7.82	7.81
700-END PT	1.58	1.57
C5+END PT	44.97	45.14
ISO/NORMAL MOLE RATIO		
C4	0.1154	0.1046
C5	0.3878	0.3849
C6	0.5965	0.5992
C4=	0.0864	0.0759
PARAFFIN/OLEFIN RATIO		
C3	2.8246	2.7937
C4	1.0398	1.0208
C5	0.8921	0.8918
LIQ HC COLLECTION		
PHYS. APPEARANCE	-	CLR OIL
DENSITY		0.758
N, REFRACTIVE INDEX		1.4277
SIMULT'D DISTILLAIN		
10 WT % @ DEG F		249
16		275
50		398
84		601
90		665
RANGE(16-84 %)		326
WT % @ 420 F	56.50	56.50
WT % @ 700 F	92.70	92.70

XIII. RUN 12 (10225-10) with Catalyst 12 (Fe/Rh + UCC-108)

According to UK Patent Application GB2099716A, a catalyst with Fe/Rh and ZSM-5 has very high selectivity for gasoline; the purpose of this catalyst was to test the properties of the same metal component in combination with UCC-108. A precipitate of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ was prepared in the same way as for Catalyst 11, and impregnated with a solution of RhCl_3 to give 2 percent rhodium on the catalyst. This metal component was then physically mixed with an equal quantity of UCC-108, bonded with 15 percent SiO_2 , and formed as an extrudate.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4 's are plotted against time on stream in Figs. 215-218. Simulated distillations of the C_5^+ product for two samples are plotted in Figs. 219-220. Carbon number product distributions are plotted in Figs. 221-227. Chromatograms from simulated distillations are reproduced in Figs. 228-234. Detailed material balances appear in Tables 35-37.

The conversion of this catalyst was low, and did not significantly improve with increasing temperature. At 250C the water gas shift activity was also low, with 15 percent of oxygen rejected as CO_2 , but at 280C it was up to 35 percent of oxygen rejected as CO_2 . The $\text{H}_2:\text{CO}$ usage ratio, however, was still ~1.5:1, not a good usage for 1:1 syngas.

The selectivity was poor, with high levels of methane and C₂-C₄, low C₅⁺, and almost no diesel oil or heavies. The percent olefin of the C₄'s was not particularly good for an iron catalyst. The isomerization of the pentane, while initially high, lessened with time, although the chromatograms of the liquid distillations show that the liquid remained highly isomerized. The Schulz-Flory plots suggest a possible double with the change at C₁₃-C₁₅.

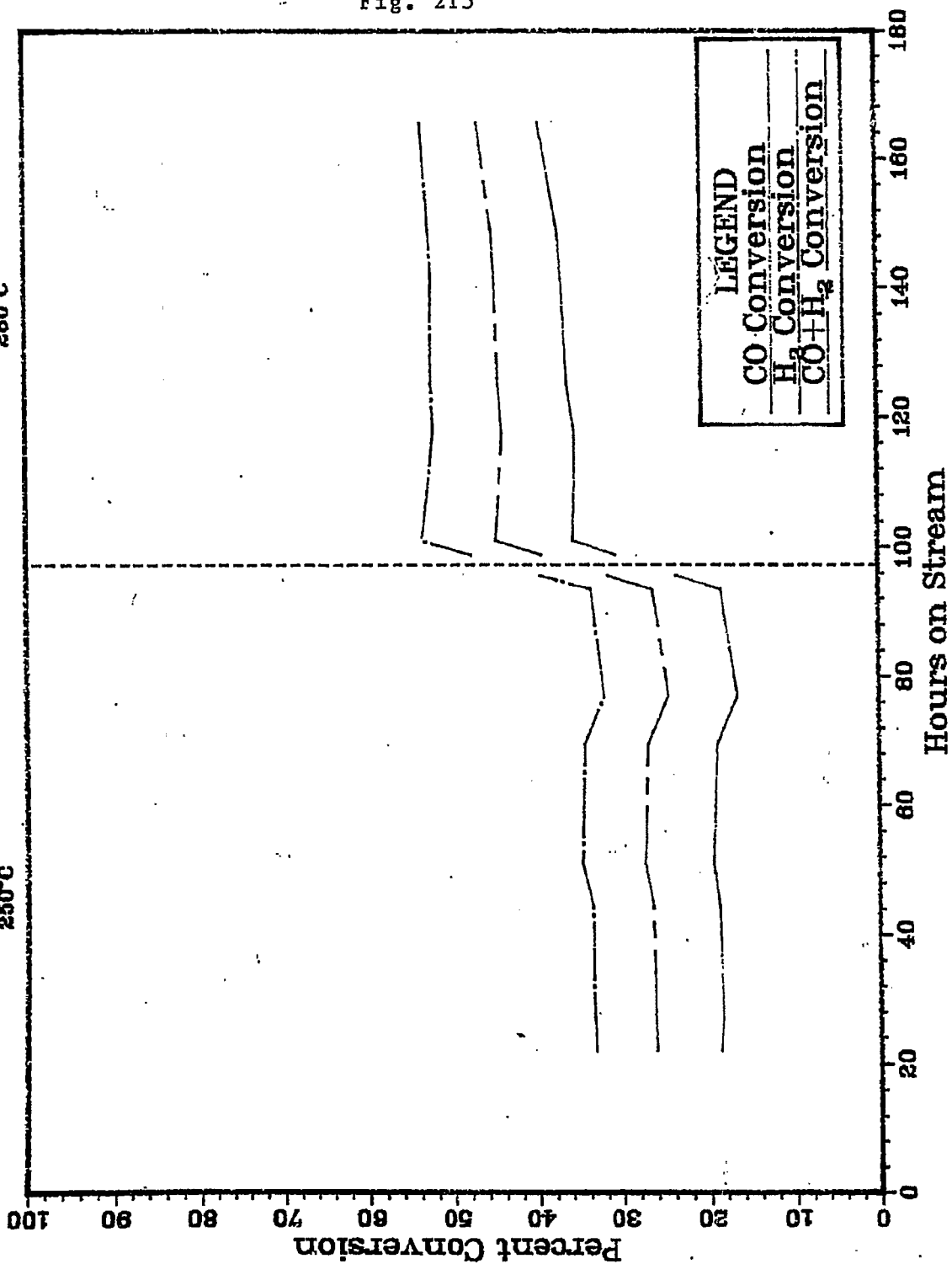
This is not a promising catalyst, with its low activity and poor selectivity.

RUN 10225-10

1:1 H₂:CO
300 PSIG
250°C

280°C

Fig. 215



RUN 10225-10

1:1 H₂:CO
300 PSIG
250°C

280°C

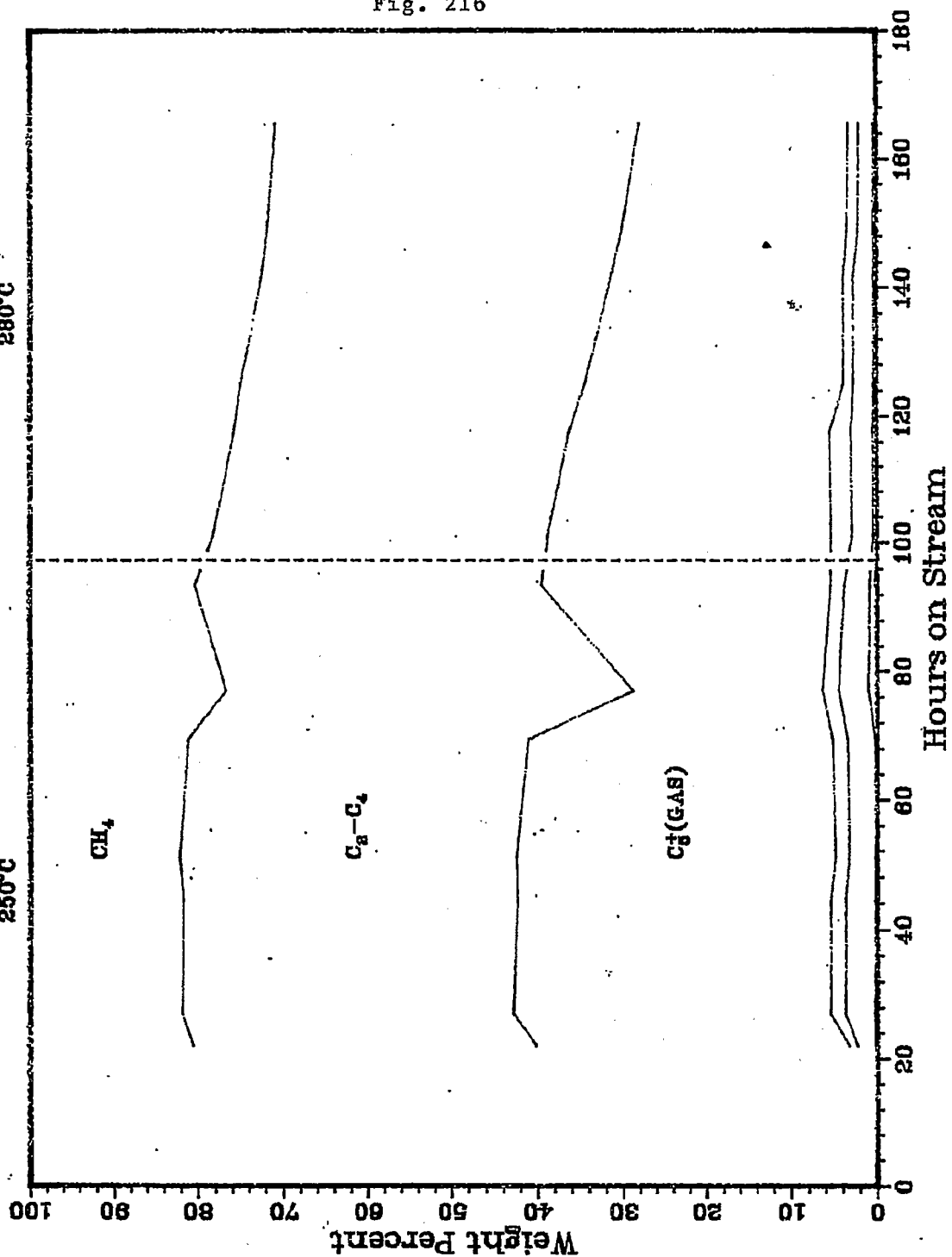


Fig. 216

RUN 10225-10

1:1 H₂:CO
300 PSIG
250°C

—
—
280°C

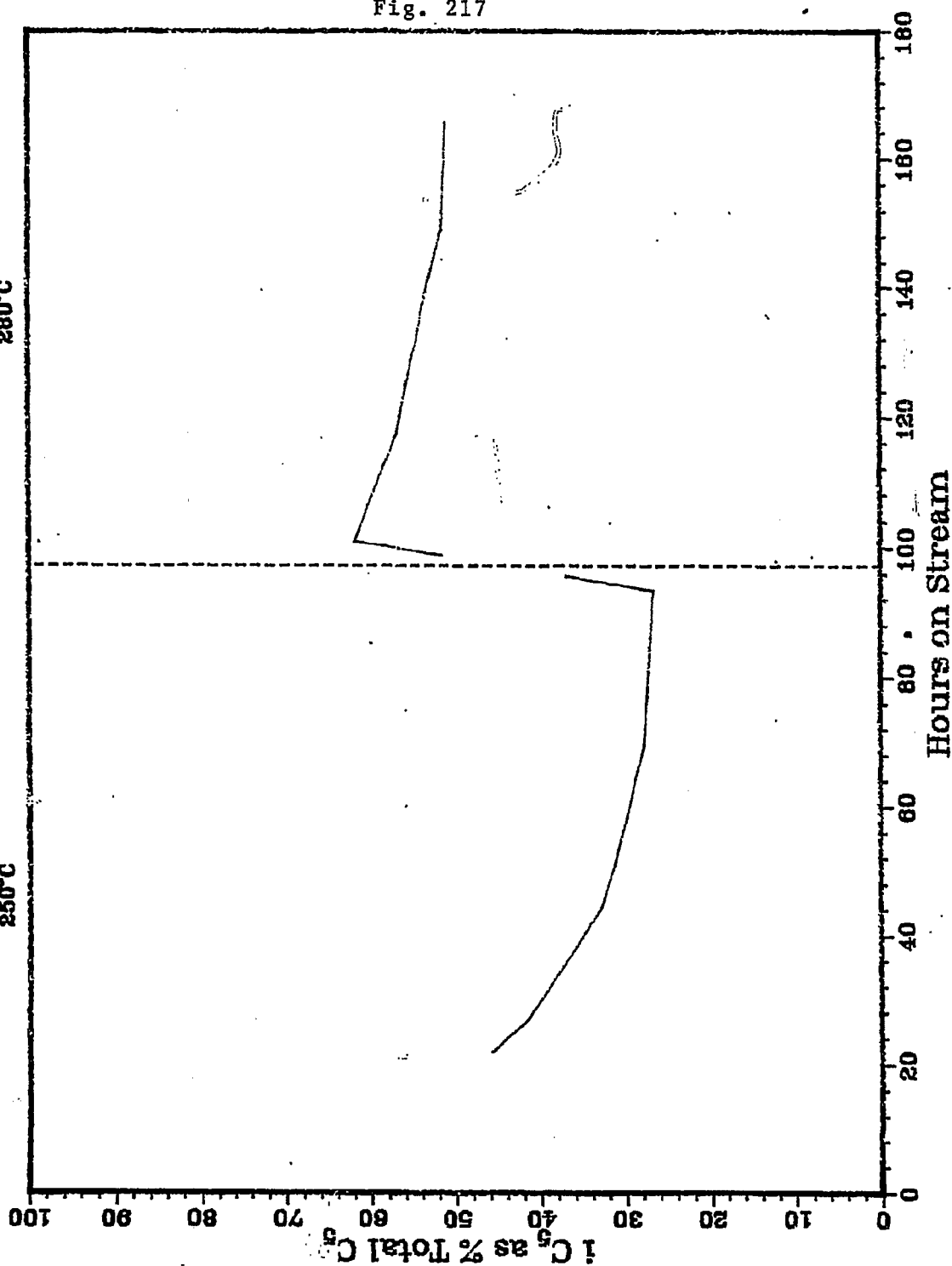


Fig. 217

RUN 10225-10

1:1 H₂:CO
300 PSIG
250°C

280°C

Fig. 218

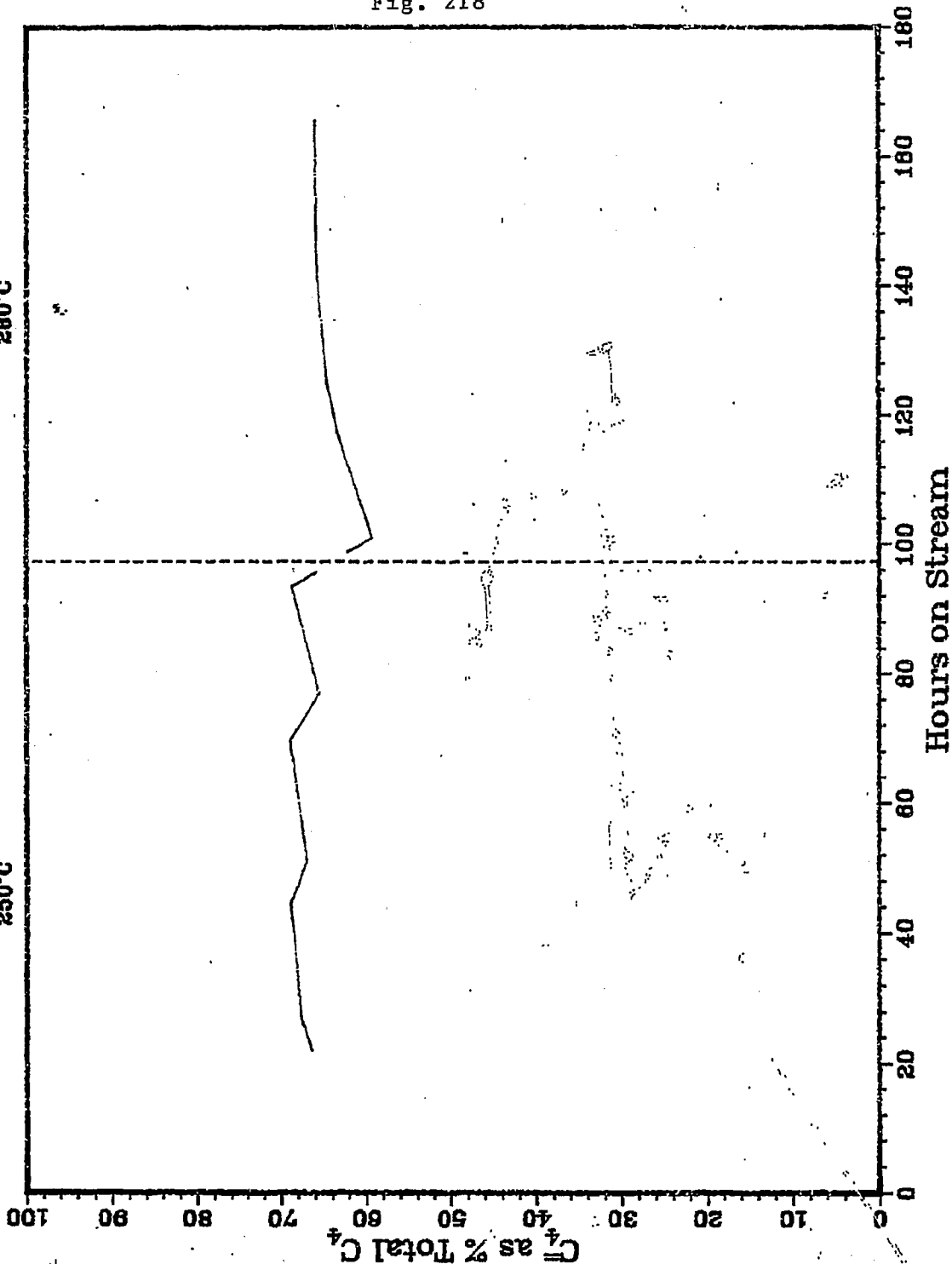


Fig. 219

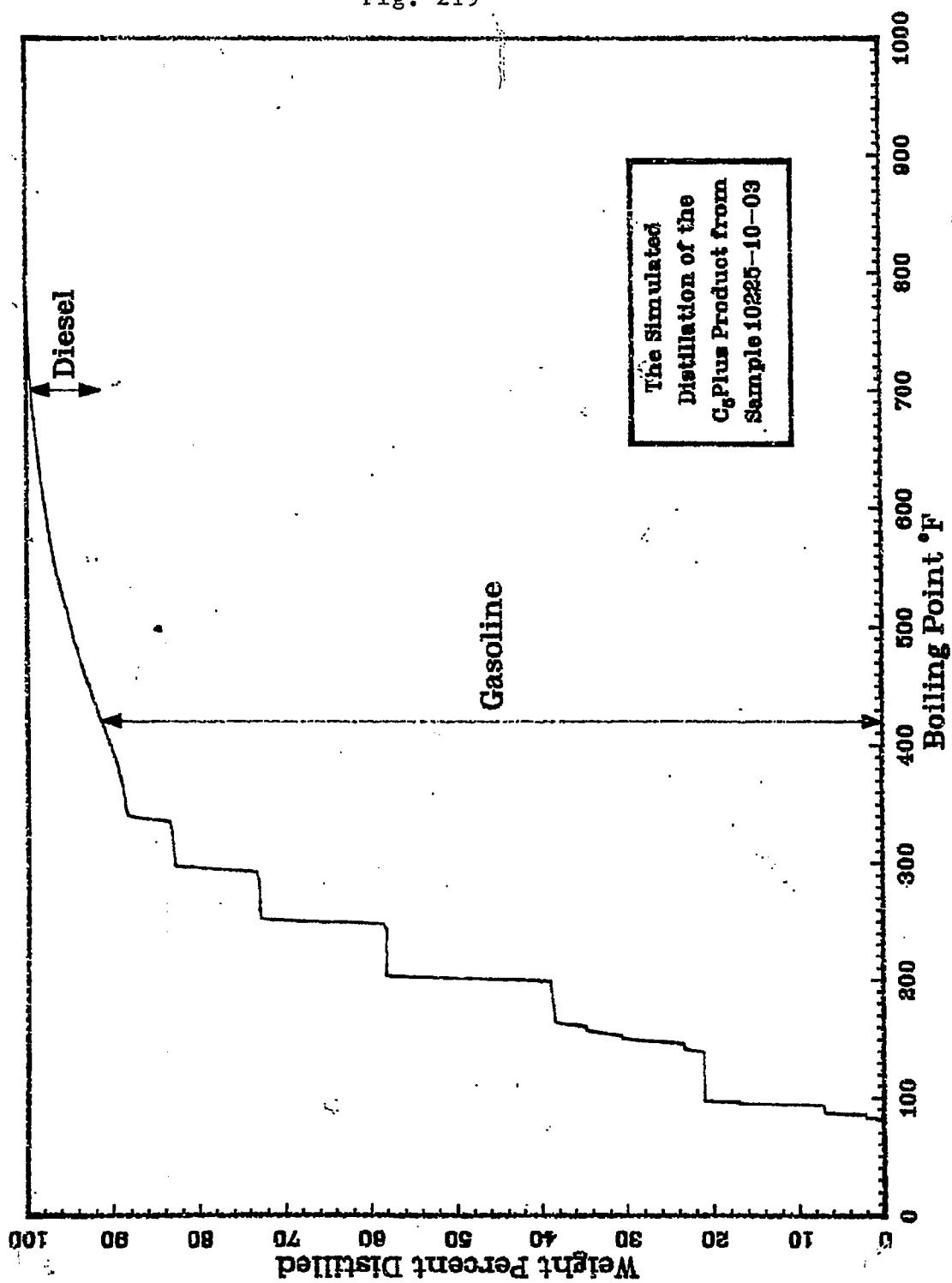


Fig.: 220

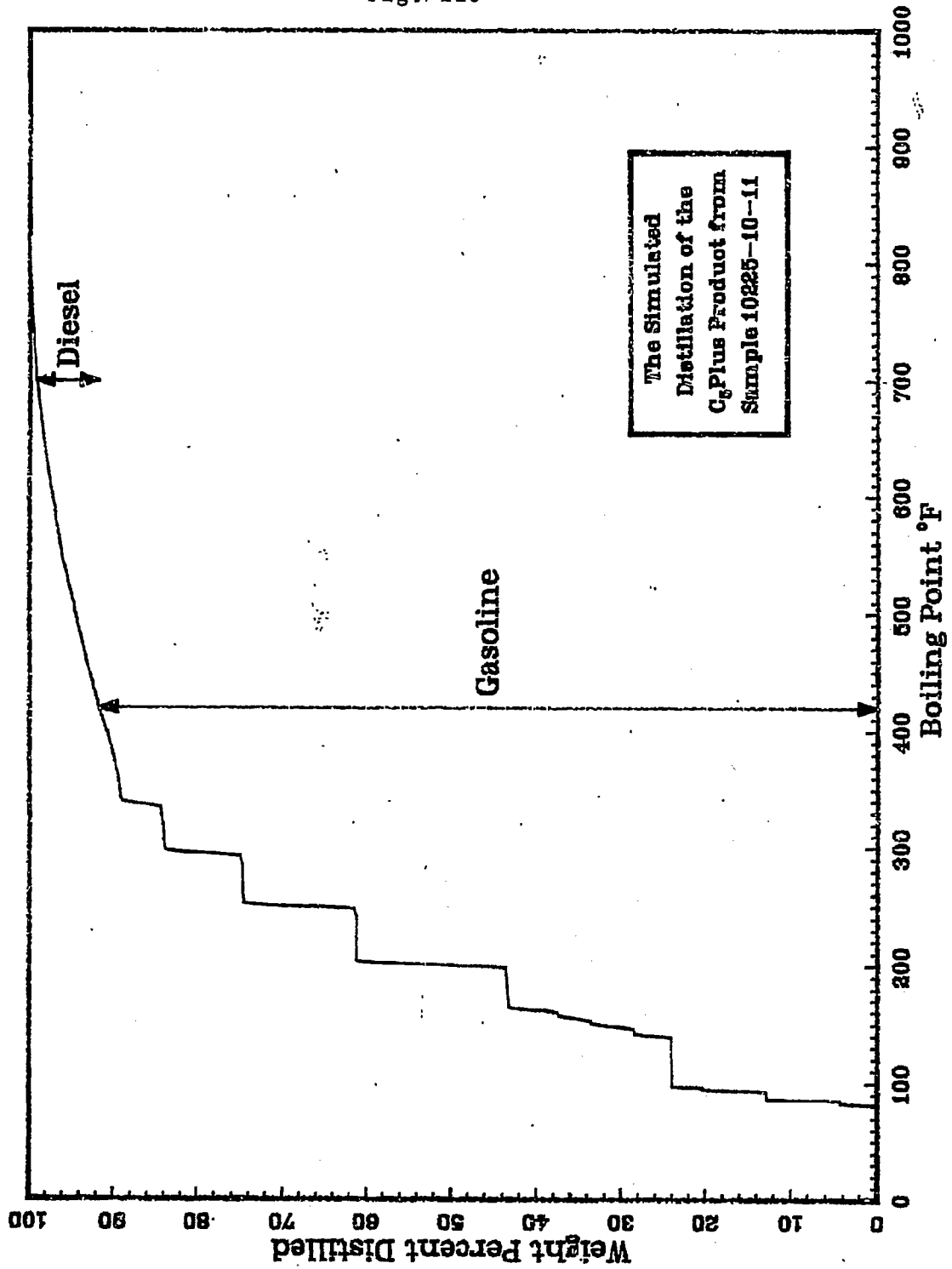


Fig. 221

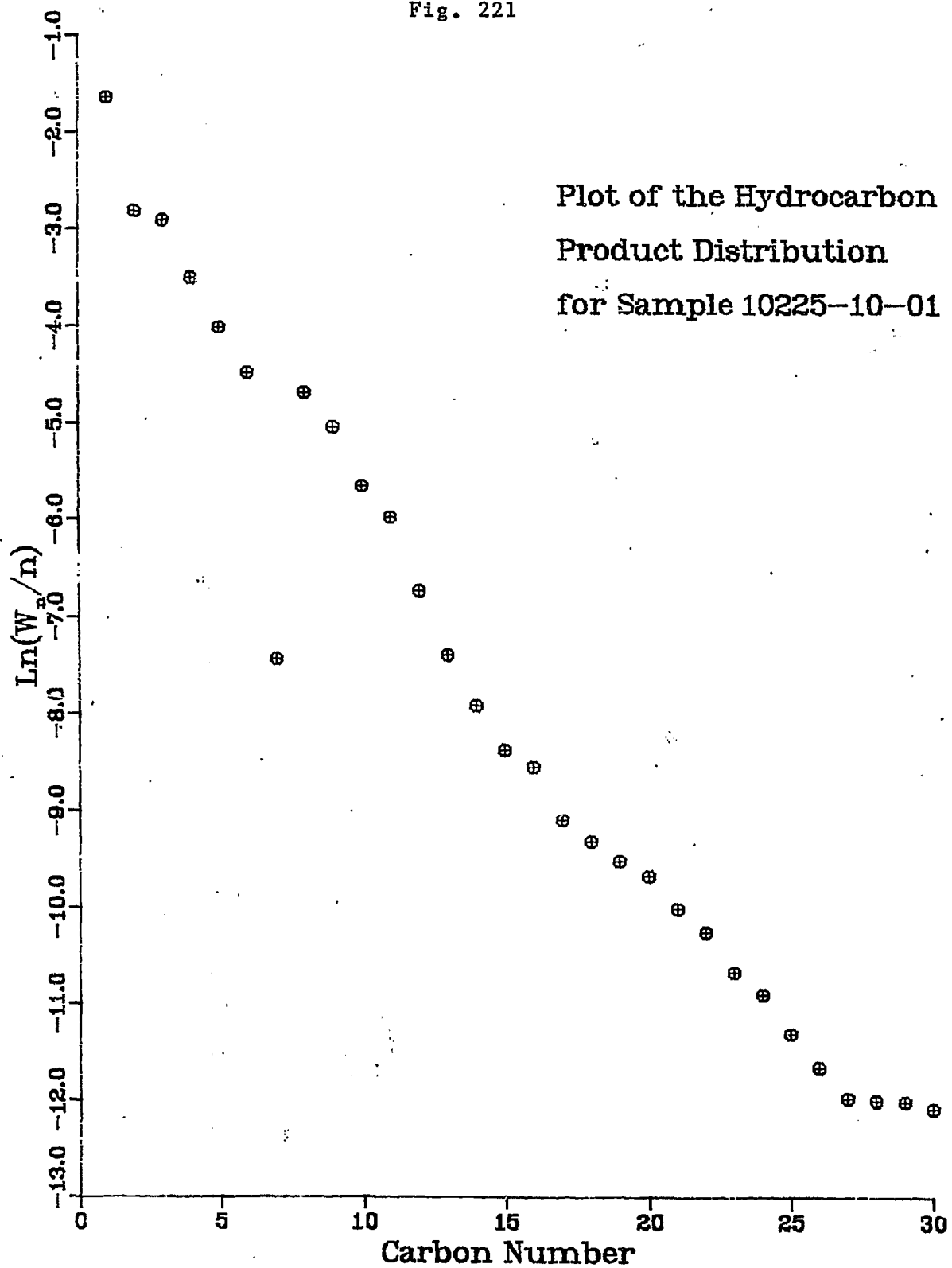


Fig. 222

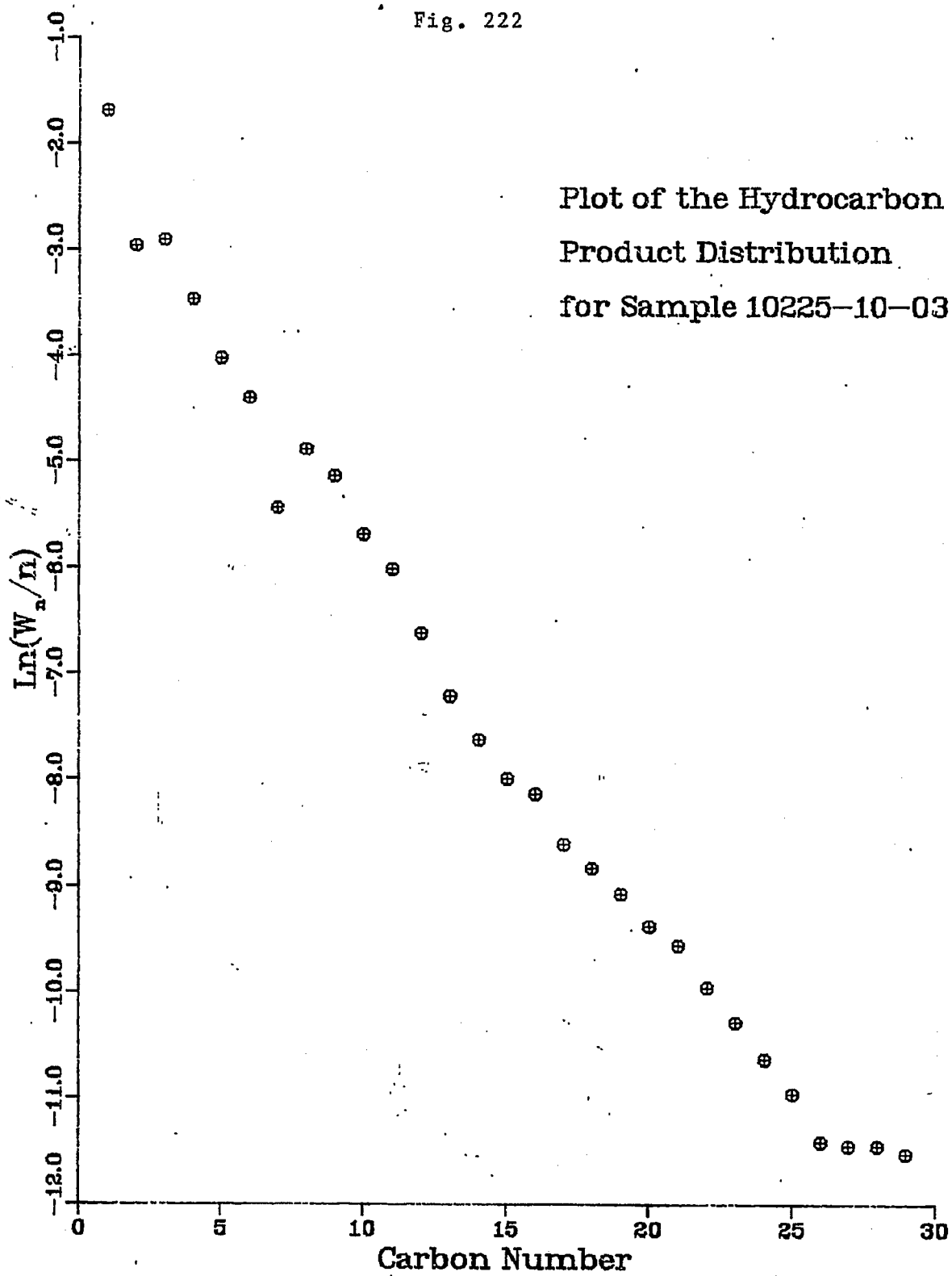


Fig. 223

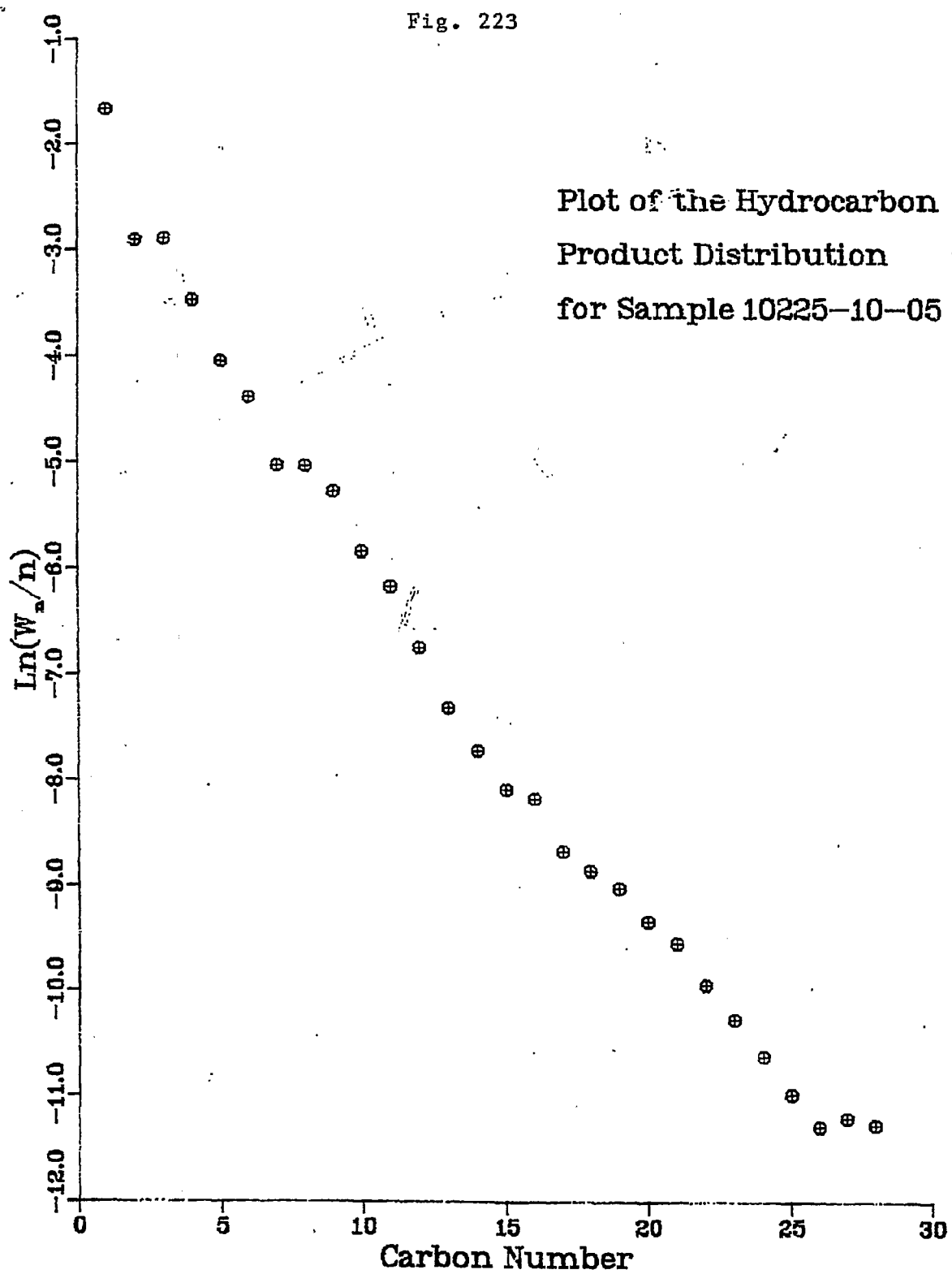


Fig. 224

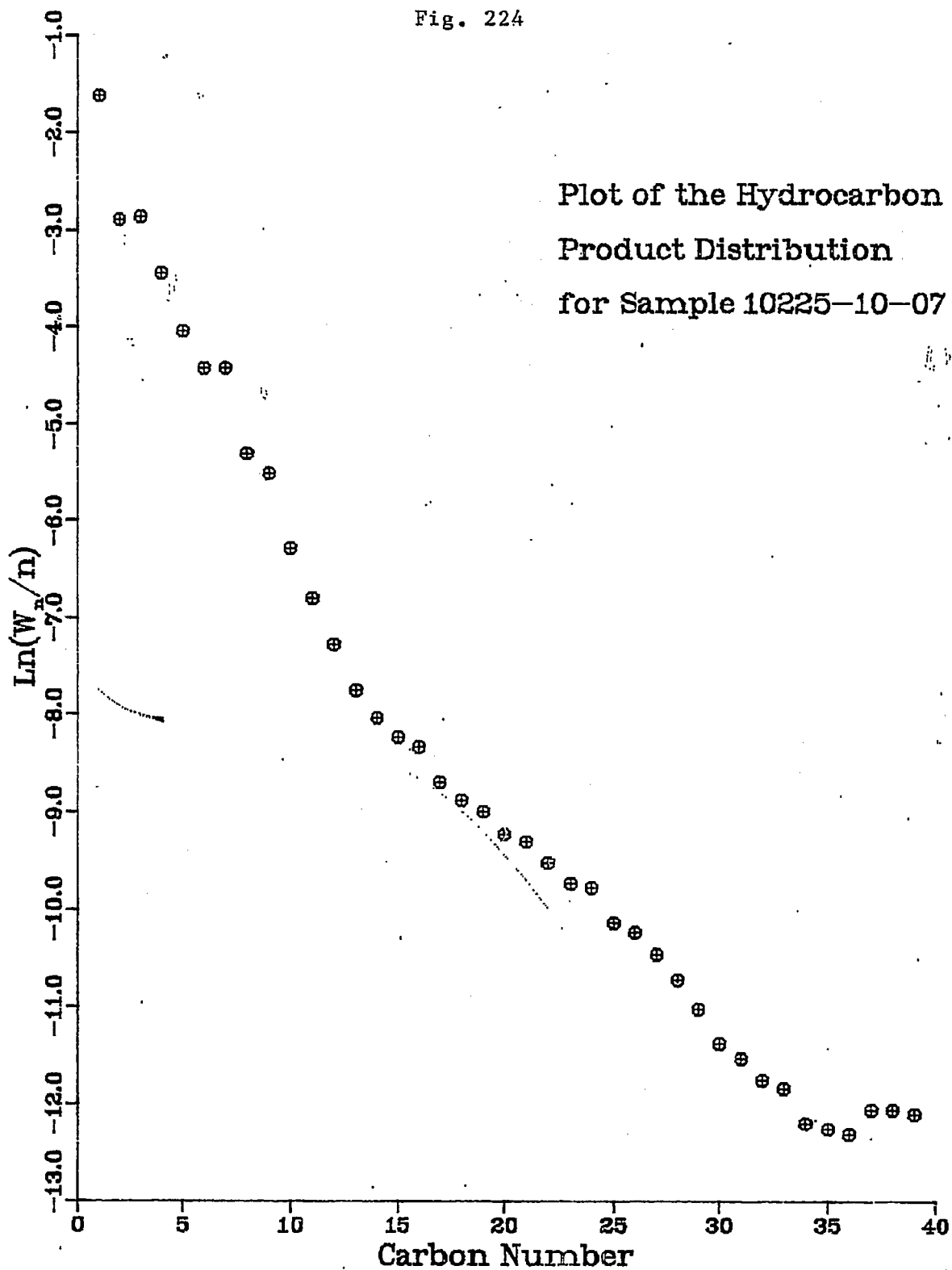


Fig. 225

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-10-09

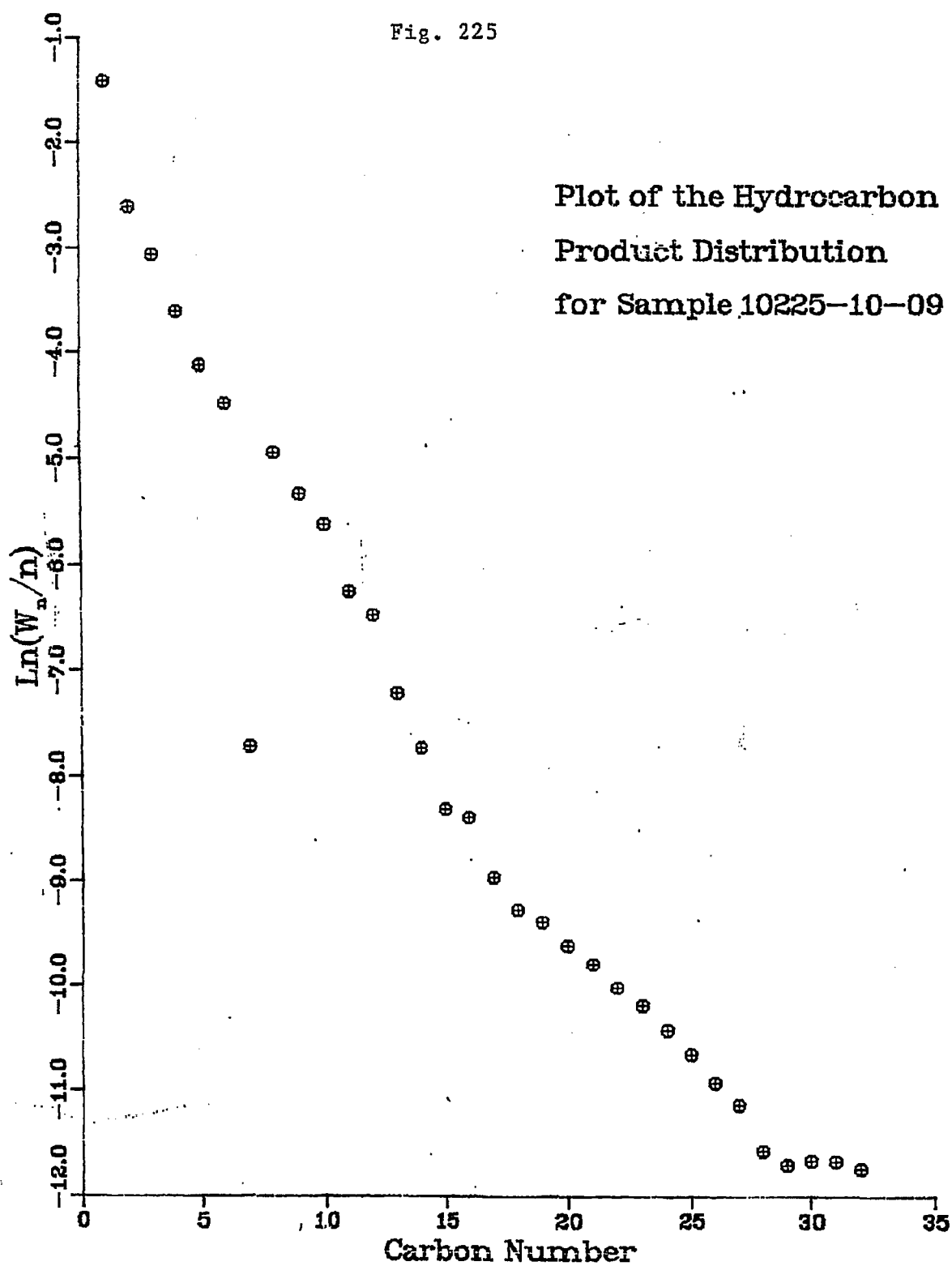


Fig. 226

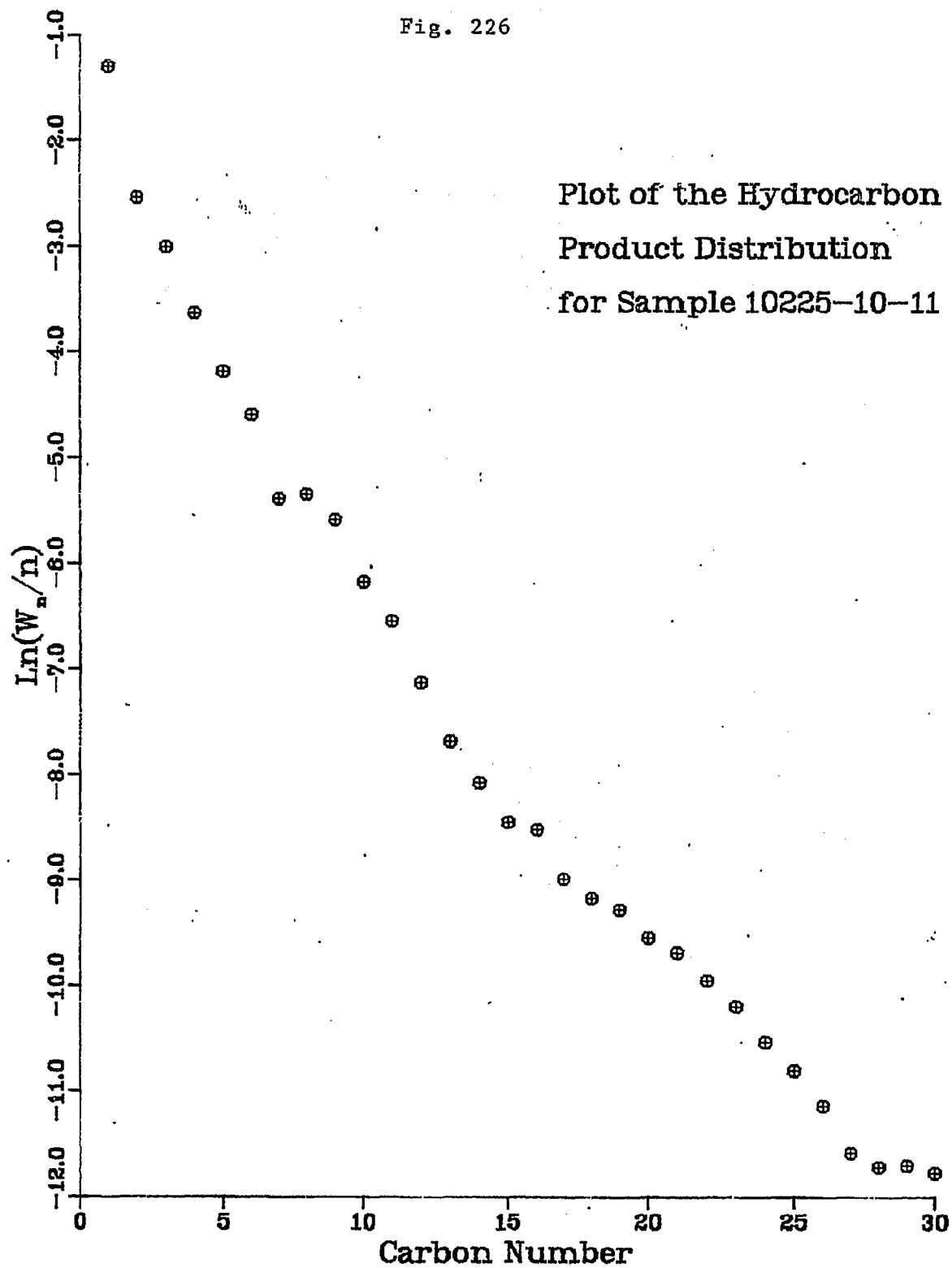
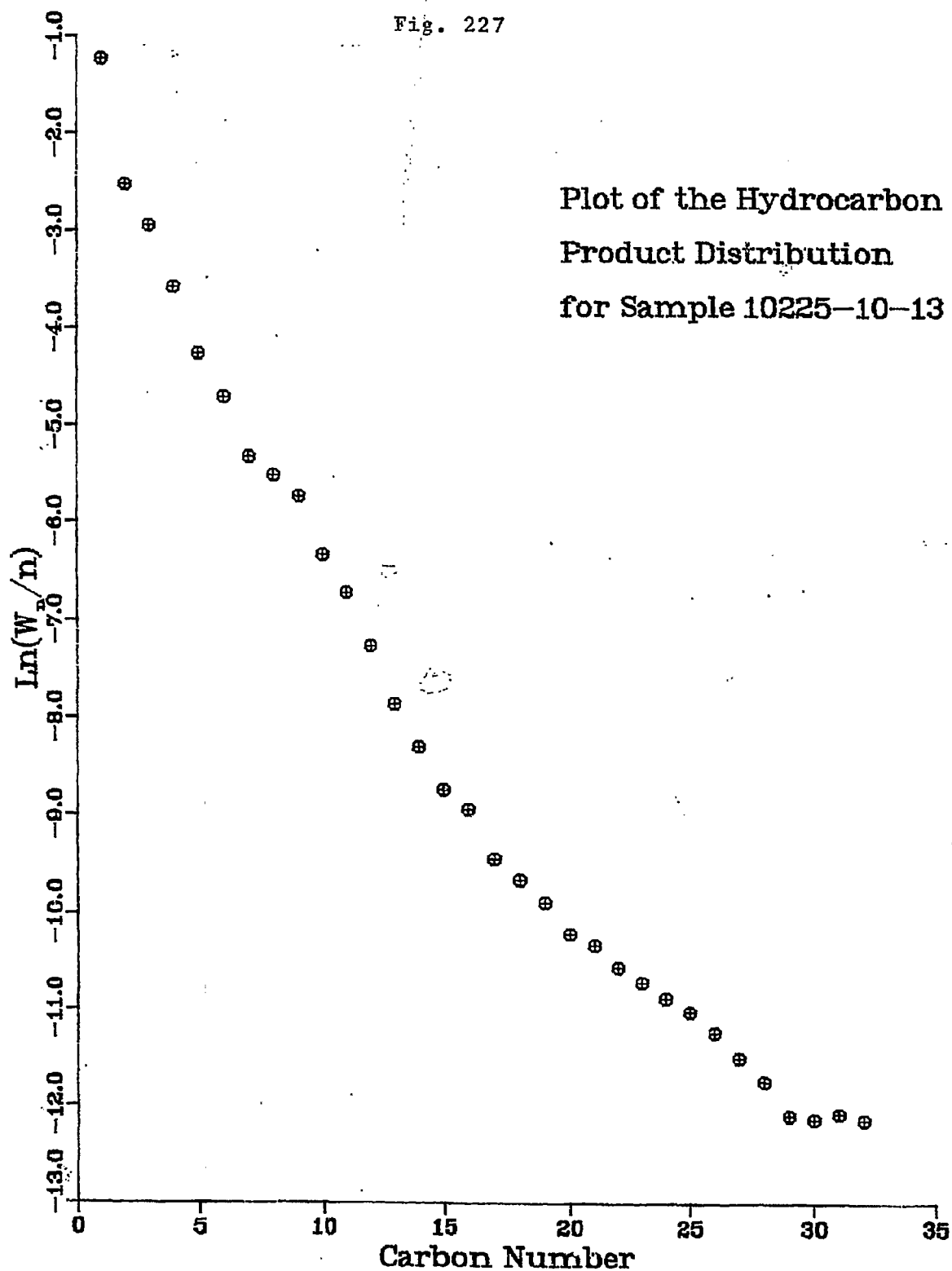


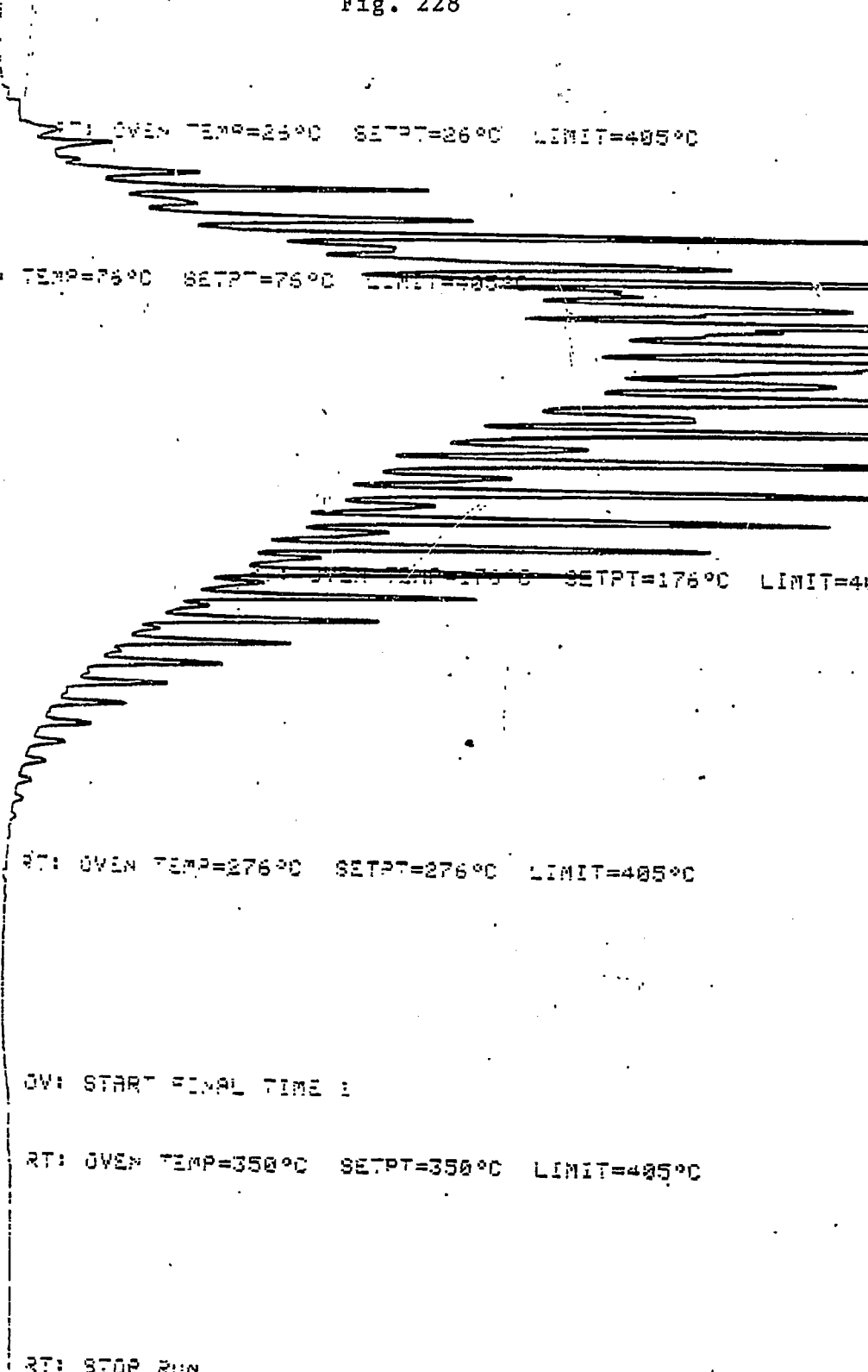
Fig. 227

Plot of the Hydrocarbon
Product Distribution
for Sample 10225-10-13



LOW TEMPERATURE PROCEDURE 20

Fig. 228



RT: OVEN TEMP=25°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

OV: START FINAL TIME :

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

RT: STOP RUN

SAMPLE: D19225-10-11

RT: SLICES 0.20

Fig. 229

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:D10225-10-3L

OVEN TEMP NOT READY

Fig. 230

JV: START PREHEAT 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

JV: START FINAL TIME 1

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

RT: STOP RUN

SAMPLE: D10225-10-5L

RT: SLICES 0.20

Fig. 231

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:D10225-10-7L

RT: SLICES 9.20

Fig. 232

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: 010225-10-9L

OVEN TEMP NOT READY

Fig. 233

OV: START PROCE W 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

OV: START FINAL TIME :

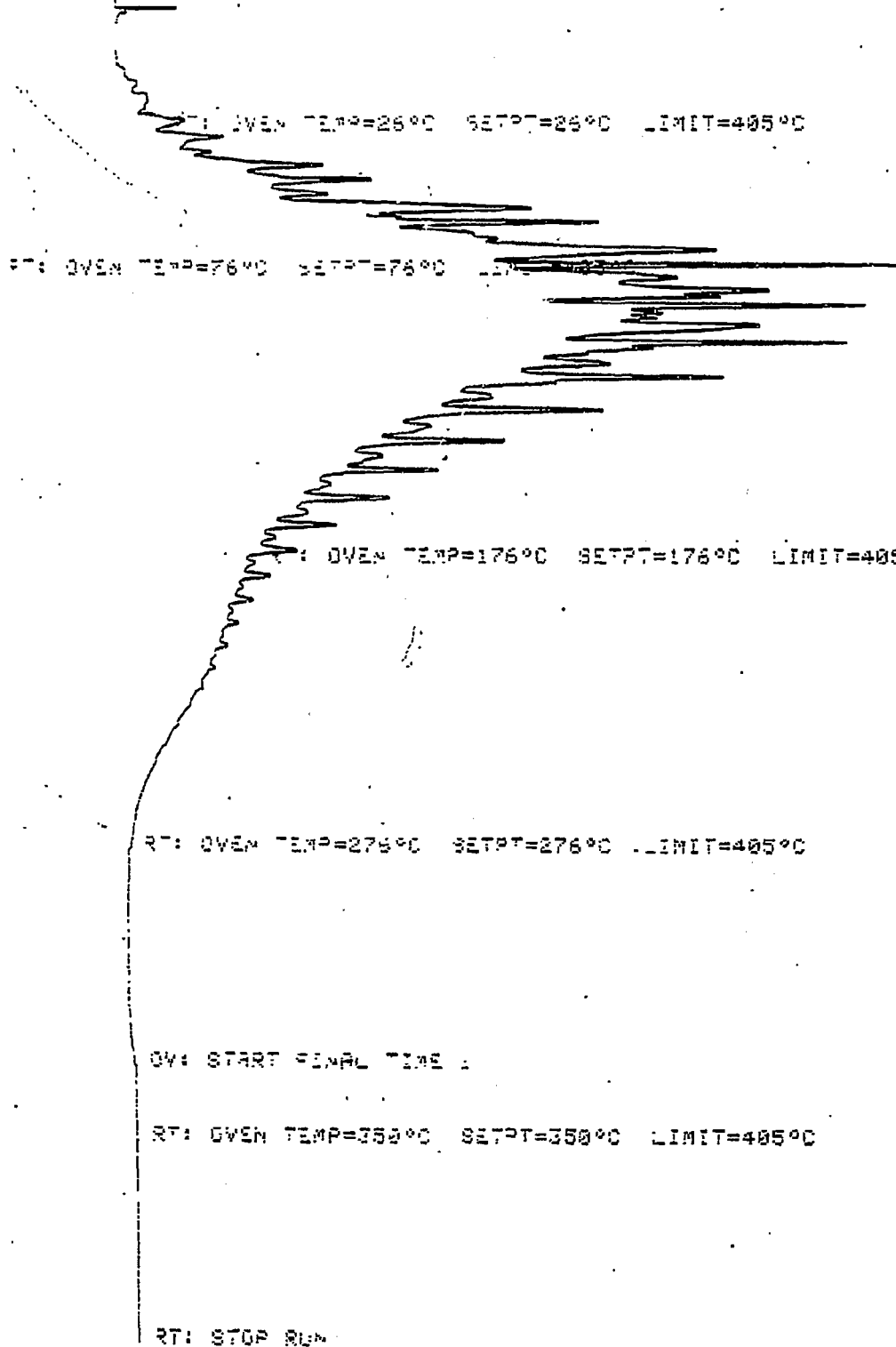
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

OVEN TEMP NOT READY

Fig. 234

RT: START RUN



SAMPLE: D10225-10-13

TABLE 35

RESULT OF SYNGAS OPERATION

RUN NO. 10225-10
 CATALYST FE/RH +HCC-108 #10252-78C 80 CC 43.9GM (42.1 AFTE; RUN -1.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-10-01	225-10-02	225-10-03	225-10-04	225-10-05
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.0	27.0	44.5	51.0	69.5
PRESSURE, PSIG	306	305	299	303	303
TEMP. C	253	251	251	251	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.00	5.00	22.50	6.50	25.00
EFFLNT GAS LITER	427.25	95.55	433.00	125.55	474.50
GM AQUEOUS LAYER	20.32	4.93	22.18	6.73	25.89
GM OIL	0.86	0.32	1.42	0.39	1.51
MATERIAL BALANCE					
GM ATOM CARBON %	99.79	98.10	98.85	100.26	97.83
GM ATOM HYDROGEN %	102.83	102.08	102.95	104.36	102.18
GM ATOM OXYGEN %	99.47	98.51	99.16	100.30	98.78
RATIO CH ₄ /(H ₂ O+CO ₂)	1.0200	0.9749	0.9816	0.9976	0.9446
RATIO X IN CH ₄	2.5571	2.5210	2.5196	2.5124	2.5348
USAGE H ₂ /CO PRDCT	1.8412	1.8559	1.8363	1.8422	1.8379
RATIO CO ₂ /(H ₂ O+CO ₂)	0.1565	0.1388	0.1471	0.1454	0.1445
K SHIFT IN EFFLNT	0.16	0.14	0.15	0.14	0.14
CONVERSION					
ON CO %	18.81	18.60	18.91	19.60	19.06
ON H ₂ %	33.32	33.54	33.62	34.74	34.39
ON CO+H ₂ %	26.17	26.22	26.42	27.32	26.89
PRDCT SELECTIVITY, WT %					
CH ₄	19.42	18.21	18.38	17.89	18.94
C ₂ HC'S	11.92	10.65	10.35	10.12	10.90
C ₃ H ₈	8.54	8.26	8.22	8.58	8.34
C ₃ H ₆ =	7.80	7.82	8.15	8.56	8.24
C ₄ H ₁₀	4.17	4.04	3.97	4.17	3.96
C ₄ H ₈ =	7.97	8.18	8.50	8.17	8.50
C ₅ H ₁₂	2.77	2.63	2.64	2.77	2.63
C ₅ H ₁₀ =	6.23	6.00	6.29	6.66	6.12
C ₆ H ₁₄	2.97	2.86	2.71	2.82	2.48
C ₆ H ₁₂ = & CYCLO'S	3.83	4.60	4.67	5.16	4.93
C ₇ + IN GAS	21.06	21.24	20.72	20.19	19.77
LIQ HC'S	3.33	5.51	5.40	4.91	5.19
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	59.81	57.16	57.56	57.49	58.87
C5 -420 F	37.85	39.15	38.82	39.23	37.67
420-700 F	2.14	3.42	3.36	3.04	3.21
700-END PT	0.20	0.27	0.26	0.23	0.25
C5+-END PT	40.19	42.84	42.44	42.51	41.13
ISO/NORMAL MOLE RATIO					
C4	0.2182	0.1965	0.1550	0.1538	0.1440
C5	0.8431	0.7075	0.4890	0.4539	0.3842
C6	0.8571	0.7187	0.5180	0.5029	0.4238
C4=	0.1789	0.1485	0.1057	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.0440	1.0072	0.9631	0.9564	0.9648
C4	0.5050	0.4763	0.4515	0.4925	0.4496
C5	0.4315	0.4255	0.4086	0.4043	0.4172
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILLATN					
10 WT % @ DEG F	356		348		345
16	384		376		374
50	479		470		470
84	622		608		611
90	662		650		651
RANGE(16-84 %)	238		232		237
WT % @ 420 F	30.00	33.00	33.00	33.33	33.33
WT % @ 700 F	94.14	95.14	95.14	95.23	95.23

TABLE 36

RESULT OF SYNGAS OPERATION

RUN NO. 10225-10
 CATALYST FE/RH +UCC-108 #10252-78C 80 CC 43.9GM (42.1 AFTER RUN -1.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-10-06	225-10-07	225-10-08	225-10-09	225-10-10
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	77.0	93.5	101.0	117.5	125.0
PRESSURE, PSIG	305	297	302	300	306
TEMP. C	251	251	281	281	281
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.50	24.00	7.50	24.00	7.50
EFFLNT GAS LITER	142.10	458.95	117.15	385.55	118.95
GM AQUEOUS LAYER	7.44	23.82	11.03	35.31	10.16
GM OIL	0.46	1.48	0.78	2.49	0.54
MATERIAL BALANCE					
GM ATOM CARBON %	94.91	98.12	96.10	96.58	95.83
GM ATOM HYDROGEN %	99.05	101.88	101.72	103.30	101.26
GM ATOM OXYGEN %	98.29	99.01	95.49	97.71	95.90
RATIO CH ₄ /(H ₂ O+CO ₂)	0.7972	0.9465	1.0229	0.9584	0.9975
RATIO X IN CH ₄	2.6633	2.5552	2.6244	2.6703	2.6887
USAGE H ₂ /CO PRODT	1.8232	1.8364	1.5999	1.5506	1.5227
RATIO CO ₂ /(H ₂ O+CO ₂)	0.1499	0.1488	0.2785	0.2985	0.3251
K SHIFT IN EFFLNT	0.15	0.15	0.30	0.34	0.38
CONVERSION					
ON CO %	16.62	18.60	35.68	35.40	36.28
ON H ₂ %	32.14	33.70	53.45	52.17	52.33
ON CO+H ₂ %	24.55	26.29	44.81	44.07	44.52
PRDT SELECTIVITY, WT %					
CH ₄	23.29	19.74	21.83	24.26	25.04
C ₂ HC'S	13.32	11.00	13.17	14.58	14.80
C ₃ H ₈	10.29	8.60	8.13	7.53	7.87
C ₃ H ₆ =	10.43	8.34	6.38	6.46	6.74
C ₄ H ₁₀	4.87	4.06	4.86	4.02	4.00
C ₄ H ₈ =	8.98	8.64	6.84	6.74	7.04
C ₅ H ₁₂	3.35	2.69	3.46	2.88	2.81
C ₅ H ₁₀ =	7.65	6.04	5.09	5.20	5.36
C ₆ H ₁₄	3.12	2.49	3.65	3.22	3.03
C ₆ H ₁₂ = & CYCLO'S	5.87	4.61	3.39	3.57	3.51
C ₇ + IN GAS	2.42	18.37	17.90	16.05	15.98
LIQ HC'S	6.41	5.43	5.32	5.48	3.81
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	71.18	60.37	61.19	63.59	65.49
C5 -420 F	24.38	35.86	35.90	33.42	31.85
420-700 F	3.45	2.93	2.54	2.62	2.35
700-END PT	0.99	0.84	0.37	0.38	0.30
C5+-END PT	28.82	39.63	38.81	36.41	34.51
ISO/NORMAL MOLE RATIO					
C4	0.1400	0.1336	0.5481	0.4307	0.3921
C5	0.3783	0.3636	1.6182	1.3152	1.2624
C6	0.4146	0.4027	1.5502	1.3428	1.2721
C4=	0.0000	0.0000	0.0000	0.5948	0.5814
PARAFFIN/OLEFIN RATIO					
C3	0.9421	0.9847	1.2168	1.1116	1.1144
C4	0.5238	0.4531	0.6854	0.5751	0.5479
C5	0.4250	0.4330	0.6602	0.5383	0.5103
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLR OIL		CLR LT BL	
DENSITY				0.808	
N, REFRACTIVE INDEX				1.4542	
SIMULT'D DISTILATN					
10 WT % @ DEG F		335		317	
16		368		341	
50		511		439	
84		695		608	
90		749		667	
RANGE(16-84 %)		327		267	
WT % @ 420 F	30.67	30.67	45.33	45.33	30.33
WT % @ 700 F	84.56	84.56	93.07	93.07	92.11

TABLE 37

RESULT OF SYNGAS OPERATION

RUN NO. 10225-10
 CATALYST FE/RH +UCC-108 #10252-78C 80 CC 43.9GM (42.1 AFTER RUN -1.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10225-10-11 225-10-12 225-10-13

FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	141.5	149.0	165.5
PRESSURE, PSIG	301	299	304
TEMP. C	281	280	280

FEED CC/MIN	400	400	400
HOURS FEEDING	24.00	7.50	24.00
EFFLNT GAS LITER	388.55	107.65	345.85
GM AQUEOUS LAYER	32.52	9.35	29.91
GM OIL	1.74	0.43	1.37

MATERIAL BALANCE

GM ATOM CARBON %	97.15	85.84	86.63
GM ATOM HYDROGEN %	102.98	91.96	93.71
GM ATOM OXYGEN %	98.19	87.67	88.51
RATIO CH ₄ /(H ₂ O+CO ₂)	0.9620	0.9272	0.9282
RATIO X IN CH ₄	2.7406	2.7577	2.7785
USAGE H ₂ /CO PRODT	1.4794	1.4664	1.4238
RATIO CO ₂ /(H ₂ O+CO ₂)	0.3496	0.3509	0.3783
K SHIFT IN EFFLNT	0.43	0.44	0.51

CONVERSION

ON CO %	36.94	37.35	39.52
ON H ₂ %	52.31	52.58	53.44
ON CO+H ₂ %	44.85	45.22	46.76

PRDT SELECTIVITY, WT %

CH ₄	27.47	28.18	29.14
C ₂ HC'S	15.73	15.95	15.93
C ₃ H ₈	7.87	8.09	8.27
C ₃ H ₆ =	6.96	7.10	7.48
C ₄ H ₁₀	3.68	3.69	3.86
C ₄ H ₈ =	6.85	6.90	7.24
C ₅ H ₁₂	2.50	2.46	2.30
C ₅ H ₁₀ =	5.06	4.85	4.77
C ₆ H ₁₄	2.62	2.54	2.38
C ₆ H ₁₂ = & CYCLO'S	3.42	3.27	3.05
C ₇ + IN GAS	14.07	13.63	12.38
LIQ HC'S	3.78	3.36	3.21

TOTAL	100.00	100.00	100.00
-------	--------	--------	--------

SUB-GROUPING			
C1 -C4	68.55	69.90	71.93
C5 -420 F	28.81	28.05	26.12
420-700 F	2.33	1.77	1.69
700-END PT	0.30	0.28	0.27
C5+-END PT	31.45	30.10	28.07
ISO/NORMAL MOLE RATIO			
C4	0.3316	0.3184	0.3199
C5	1.1253	1.0632	1.0404
C6	1.1208	1.0607	1.0800
C4=	0.5533	0.5387	0.5085
PARAFFIN/OLEFIN RATIO			
C3	1.0795	1.0869	1.0547
C4	0.5193	0.5160	0.5145
C5	0.4801	0.4927	0.4683
LIQ HC COLLECTION			
PHYS. APPEARANCE	CLR L BL		CLR L BL
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F	349		334
16	380		360
50	484		451
84	642		618
90	683		679
RANGE(16-84 %)	262		258
WT % @ 420 F	30.33	39.00	39.00
WT % @ 700 F	92.11	91.67	91.67

XIV. SUMMARY

Considerable knowledge was gained this quarter about cobalt-containing F-T catalysts. The first series of runs established that for cobalt catalysts a far lower percentage of the F-T active metal was desirable in the catalyst than had been the case for iron F-T catalysts. There are two reasons for this difference. The first is that with the cobalt being more active than iron on a per gram basis, a lower percentage of metal allows an equivalent conversion at the same process conditions. The second reason is that at a 1:1 MC:SSC ratio the primary products of the cobalt overwhelm the SSC, which has insufficient activity to properly upgrade the product. This is not just another manifestation of the higher activity, but is also a result of the lower product quality (i.e., higher wax content) of the product of cobalt F-T catalysts.

The many experiments with the cobalt-containing catalysts have established general trends for their hydrocarbon products. The most obvious difference in cobalt and iron catalysts is the excessive methane produced by cobalt catalysts. Every Schulz-Flory plot shows that the amount of methane produced is completely out of line with the amounts of other hydrocarbons produced, that is, there is a second mechanism which produces primarily methane. The yield of the C₂-C₄ hydrocarbons is often low and is

a function of the additives to the metal component. The amount of total motor fuel is generally higher than that from iron catalysts, but the distribution between gasoline and diesel oil is a function of the composition of the catalyst. In general the hydrocarbons produced by the cobalt are more paraffinic and less isomerized than those produced by iron. This leads to a more waxy product being produced by the cobalt catalyst.

This quarter's runs have also shown that while UCC-101 and UCC-108 had dramatically different effects on the isomerization activity and selectivity of catalysts containing iron as their metal component, these two Molecular Sieves had only slightly different effects on the isomerization activity and selectivity of catalysts containing cobalt as their metal component. More specifically, while the Fe/UCC-108 catalysts produced a highly isomerized product containing mostly gasoline with only a small amount of diesel oil, and the Fe/UCC-101 catalysts produced a higher yield of motor fuels that had fewer isomers and more diesel oil, such differences were far less between the products produced by the Co/UCC-108 and the Co/UCC-101 catalysts.

There was, however, a significant difference between the olefin contents of the products produced by these two cobalt containing catalysts; the Co/UCC-108 catalyst yielded a far more olefinic, less waxy product than did the Co/UCC-101 catalyst.

The last and most important information discovered from this quarter's runs was the great effect which additives can have on cobalt catalysts. The additive used in experiment 10225-8 (Run

9 in this report) not only improved the product quality significantly, but greatly improved the catalyst's stability. This was the first cobalt and UCC-101 catalyst which did not produce a waxy liquid product. The catalyst deactivated at a rate 4 times lower than did similar catalysts without the additive. The liquid product was more olefinic and had a lower pour point than that from the reference catalyst.

Generally the cobalt catalysts have been very successful. The aspect that needs the most improvement is the excessive methane production.

APPENDIX B. SURFACE STUDIES

By G. A. Somorjai

Our study of the catalytic hydrogenation of carbon monoxide has moved into a new direction this quarter. We have recently begun a study of the clean and sulfided Mo(100) surface as a Fischer-Tropsch catalyst. Also we have continued our work on potassium and oxygen promoters in Rhenium Fischer-Tropsch. Molybdenum appears to have some interesting properties as a Fischer-Tropsch catalyst, in that it produces a high turnover of ethylene. The following are turnover frequencies found for two different reaction conditions.

T	P	H ₂ :CO	CH ₄	CH ₂ =CH ₂	CH ₃ -CH ₃	CH ₂ =CH-CH ₃
550K	1.7 ATM	5:1	.25	1.4X10 ⁻²	5X10 ⁻³	0
580K	1.0 ATM	1:1	.16	5X10 ⁻³	1.6X10 ⁻³	1.5X10 ⁻³

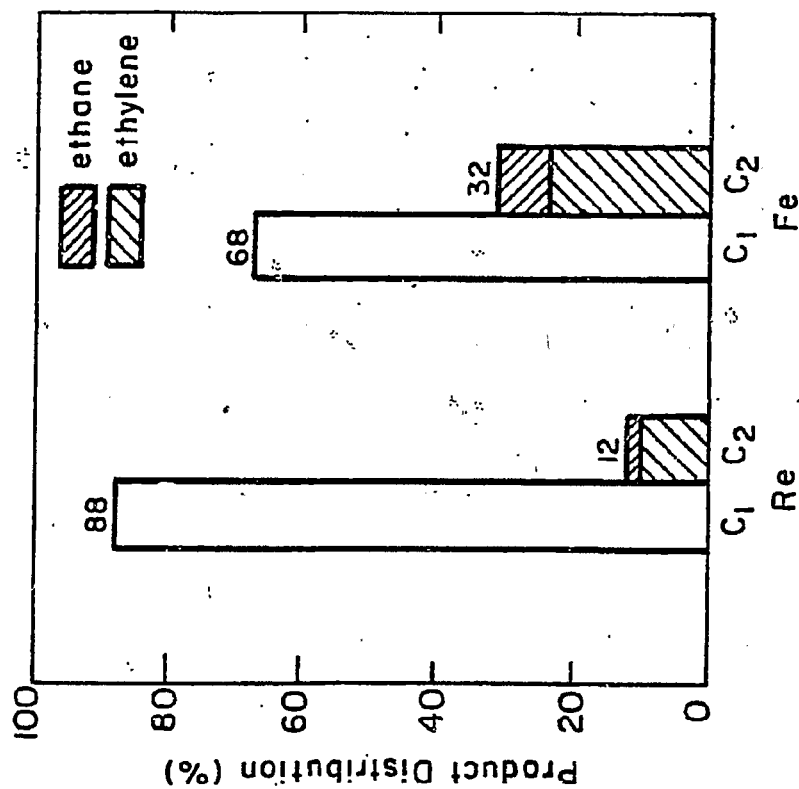
As can be seen, the production of ethylene was about three times that of ethane. The catalyst has not been observed to poison over the 6 hour period for which most reactions have been run. Furthermore, submonolayer amounts of sulfur on the surface tend to inhibit methane formation but not affect the rate of ethane and ethylene formation.

CO Hydrogenation on Promoted (Unsupported) Fe, Re and Pt Samples

Our work in this area since our last report has focused on Fe and Re samples. We have concentrated on the effects of dosing these samples with K, O, and S. We have found, as shown in Figures B1 and B2, that the addition of an alkali to the surface of either Re or Fe before a CO hydrogenation reaction changes the selectivity of the catalyst. For alkali addition this selectivity change is a shift toward higher molecular weight products. Conversely, as seen in Figures B1 and B3, the addition of oxygen to the surface shifts the product distribution to methane.

We have also noted that added oxygen increases activity maintenance of the catalyst. This seems to be due to the decreased build-up of graphitic type carbon, as noted in Auger spectroscopy. Our current and planned interests are to further characterize the effect of S on this system and to try to further characterize the surfaces before and after reaction with the aid of an XPS system we are about to bring on line.

Figure B1



CO Hydrogenation
540K CO/H₂=1/4
32 psi

	Re	Fe
Turnover Number (molecules/site/sec)	2	5
E _a (CH ₄)	28	24
E _a (C ₂ H ₄)	21	17

Figure B2

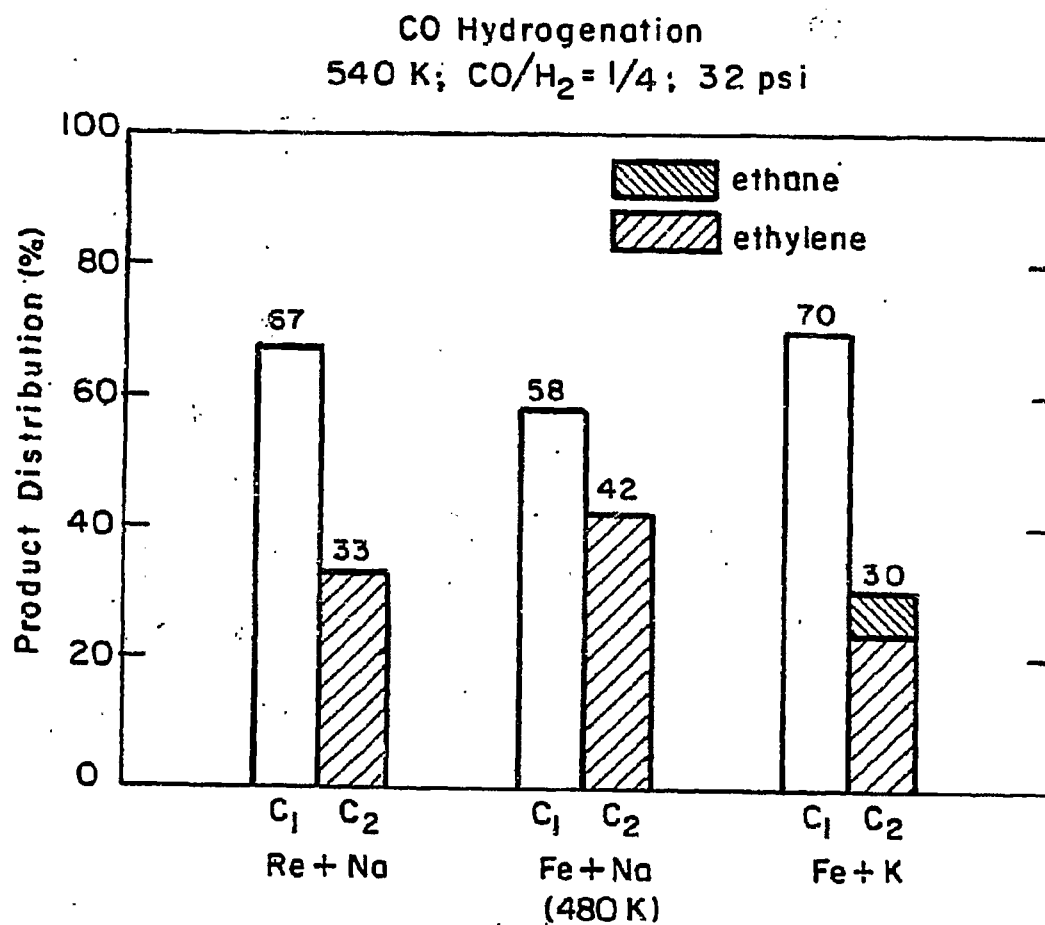
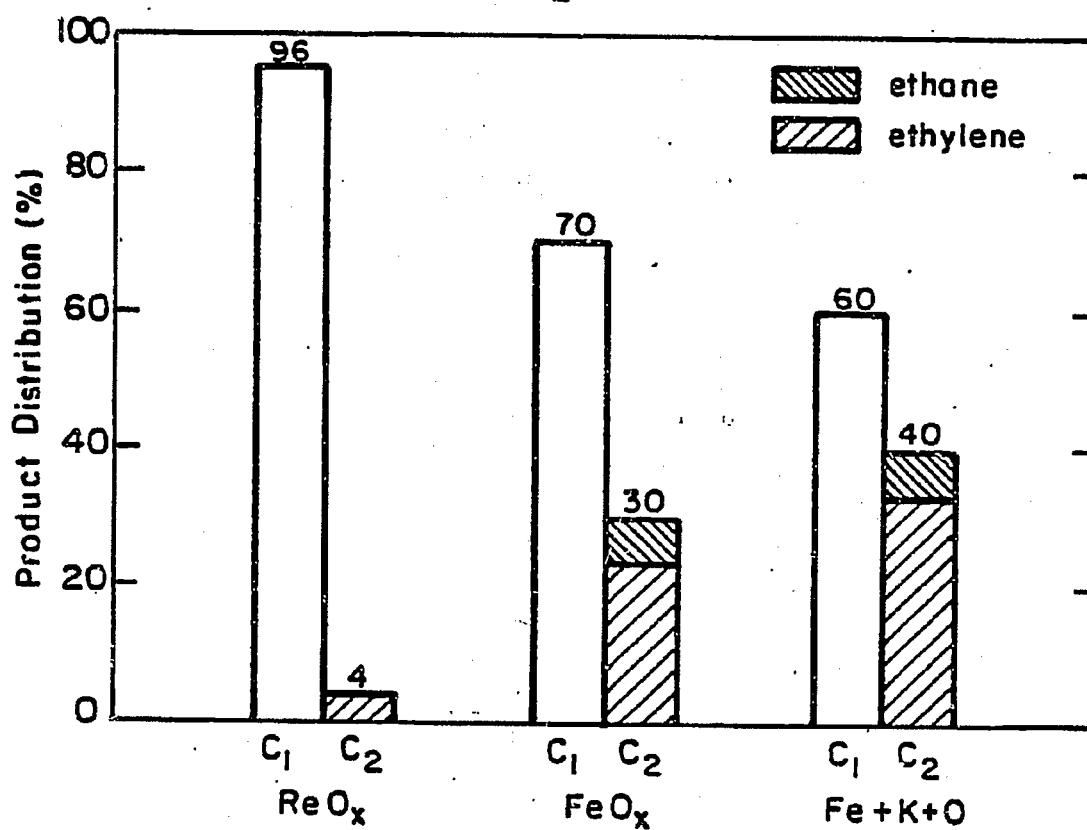


Figure B3

CO Hydrogenation
540 K; CO/H₂ = 1/4; 32 psi



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