

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	52.56	54.74	55.67	13.05	54.37
C5 - 420 F	47.44	45.26	44.33	25.64	45.63
420-700 F	0.00	0.00	0.00	52.22	0.00
700-END PT	0.00	0.00	0.00	9.08	0.00
C5+--END PT	47.44	45.26	44.33	86.95	45.63
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0000	0.0000	0.0000	0.0000
C5	0.0000	0.0000	0.0000	0.0000	0.0000
C6	0.7609	0.5581	1.0465	0.3962	1.0192
C4=	0.0808	0.1042	0.0717	0.0664	0.0577
PARAFFIN/OLEFIN RATIO					
C3	0.2617	0.2702	0.2647	0.2759	0.2863
C4	0.2135	0.1824	0.2325	0.2131	0.2273
C5	0.7018	0.9412	1.0182	1.1321	0.9118
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	---	---	YLW OIL	---
DENSITY	---	---	---	0.778	---
N, REFRACTIVE INDEX	---	---	---	1.4371	---
SIMULT'D DISTILATN					
10 WT % @ DEG F	---	---	---	369	---
16	---	---	---	403	---
50	---	---	---	540	---
84	---	---	---	681	---
90	---	---	---	715	---
RANGE(16-84 %)	---	---	---	278	---
WT % @ 420 F	---	---	---	19.00	---
WT % @ 700 F	---	---	---	88.00	---

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Potassium Promoted Iron Precipitated on UCC-108, Run 10011-16

UCC-108 was clearly the outstanding catalyst during Task 1 testing. The physical mixture of promoted iron and UCC-104, a less active modification of UCC-108, produced an excellent gasoline product in Run 10011-10. For these reasons, a precipitation catalyst was prepared from UCC-108, using the same procedure as with UCC-104 in Run 10011-11.

The conversion and product selectivity are presented in Figures 80 and 81. Tables 13A and 13B contain the detailed material balance data.

This catalyst was completely inactive for F-T synthesis. There may be something in the catalyst poisoning the metal component, although the nature of the poisoning is unknown at this time. Further testing is warranted to see if the poisoning is a general phenomenon for UCC-108 or only a problem with this particular preparation technique.

1001116

1:1 H₂:CO
300 PSIG
250°C

2:1 H₂:CO
250°C

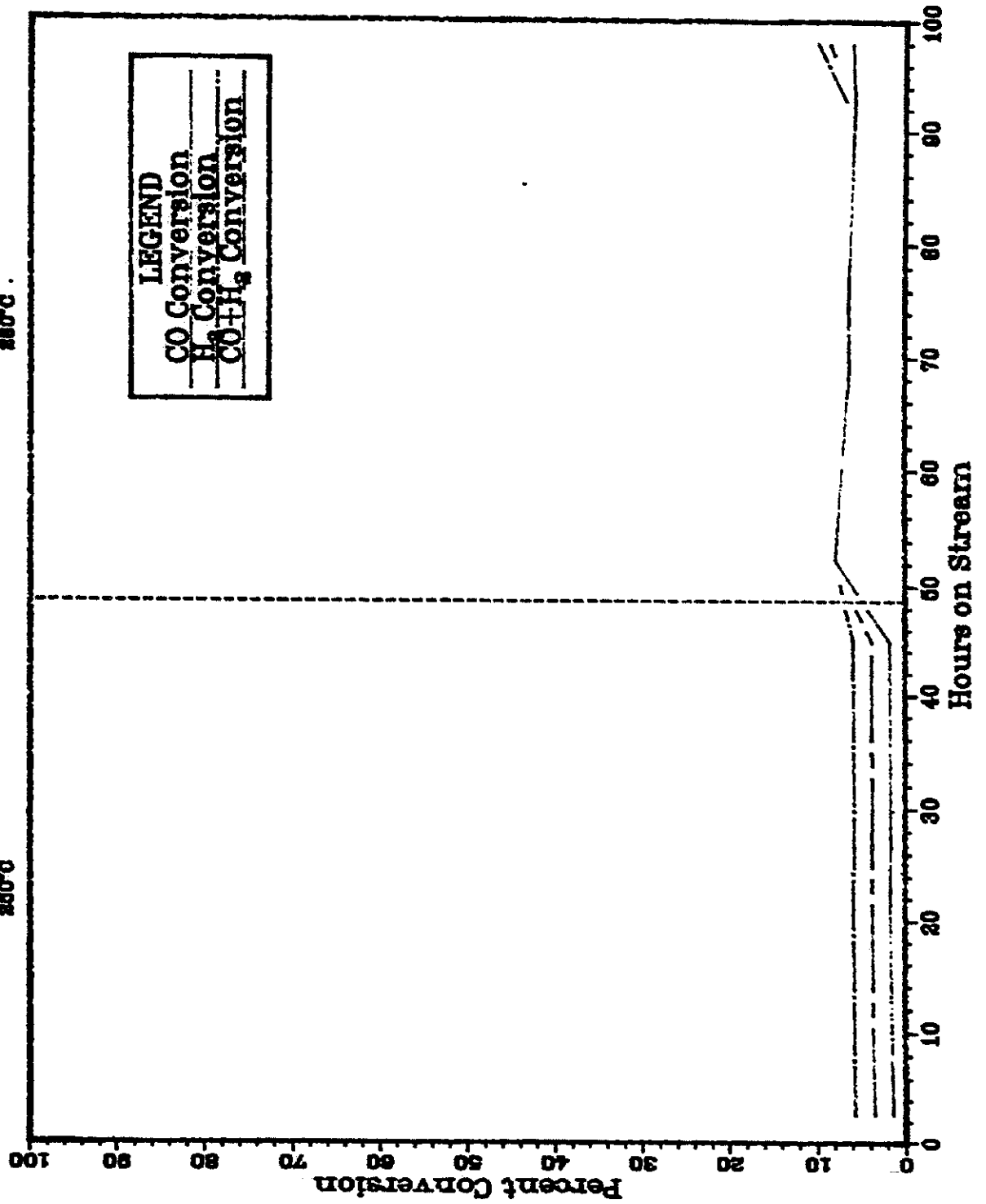


FIGURE 80

1001116

FIGURE 81

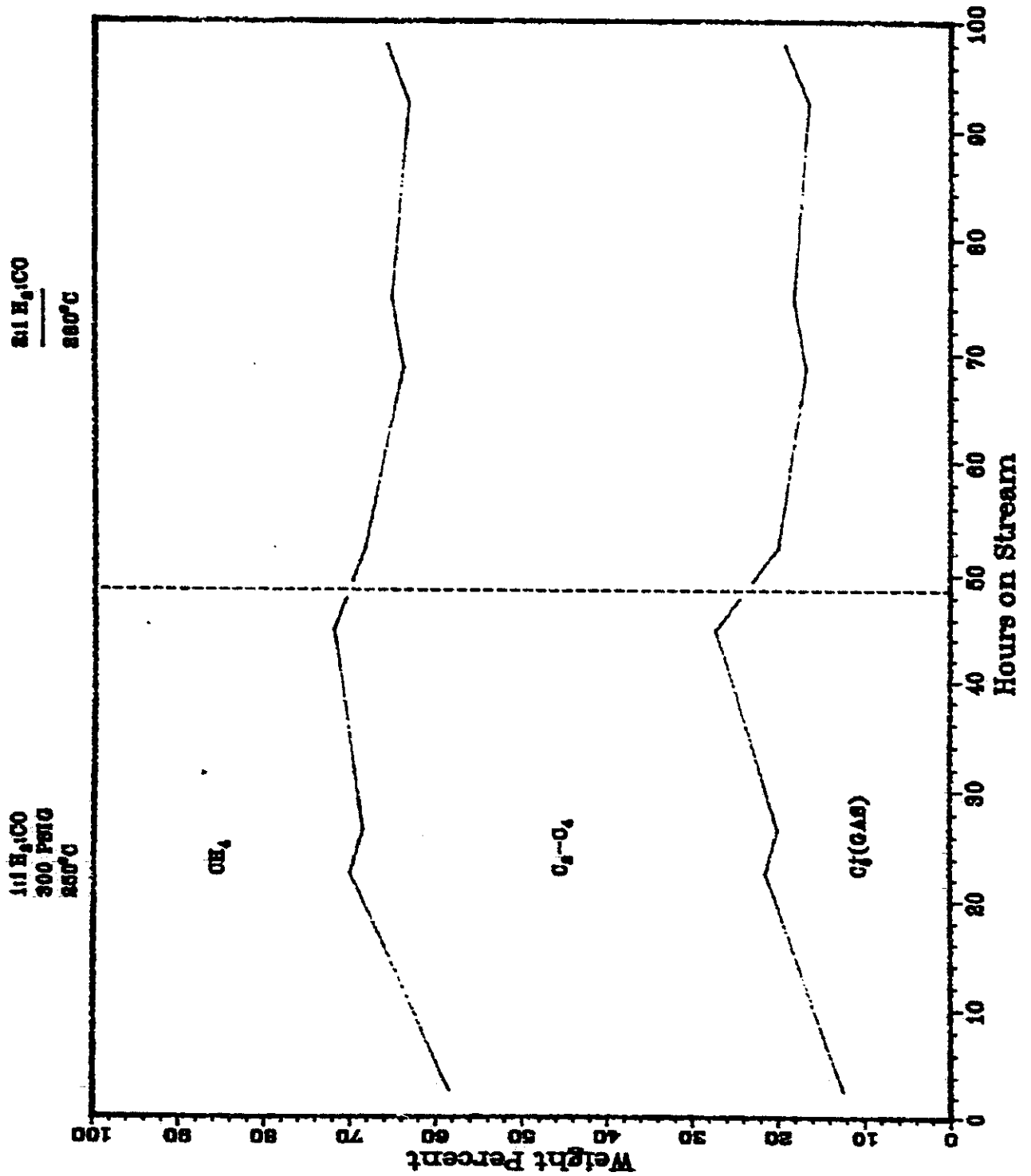


TABLE 13A

RESULT OF SYNGAS OPERATION

RUN NO. 10011-16
 CATALYST FE-UCC-108, #10042-79 80 CC 61.8GM (61.6 AFTER RUN - .2 G)
 FEED H₂:CO OF 50:50 @ 400 CC/MN & 67:33 @ 600 CC/MN FOR 300/450 SV

RUN & SAMPLE NO. 10011-16-01 011-16-02 011-16-03 011-16-04 011-16-05
 =====

FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	67:33: 0
HRS ON STREAM	2.63	22.55	26.58	44.91	52.41
PRESSURE, PSIG	299	301	300	301	295
TEMP. C	248	248	249	249	280
FEED CC/MIN	400	400	400	400	600
HOURS FEEDING	2.63	19.92	4.03	18.33	7.50
EFFLNT GAS LITER	66.97	514.70	104.90	472.56	265.00
GM AQUEOUS LAYER	0.00	0.00	0.00	0.00	0.00
GM OIL	0.00	0.00	0.00	0.00	0.00

MATERIAL BALANCE

GM ATOM CARBON %	107.78	108.84	109.60	108.77	106.49
GM ATOM HYDROGEN %	106.55	109.06	109.78	108.82	100.73
GM ATOM OXYGEN %	110.66	111.50	112.32	111.33	106.06
RATIO CHX/(H ₂ O+CO ₂)	0.3178	0.3779	0.3691	0.4024	1.0626
RATIO X IN CHX	3.0744	2.7981	2.7440	2.7256	2.8988
USAGE H ₂ /CO PRODT	2.0513	2.0289	2.0045	2.0163	1.9497
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0449	0.0432	0.0447	0.0446	0.1793
K SHIFT IN EFFLNT	0.04	0.04	0.04	0.04	0.41

CONVERSION

ON CO %	1.42	1.65	1.63	1.76	7.95
ON H ₂ %	5.72	5.82	5.74	5.90	7.99
ON CO+H ₂ %	3.56	3.74	3.69	3.83	7.98

PRDT SELECTIVITY, WT %

CH ₄	41.54	29.98	31.41	27.95	31.60
C ₂ HC'S	19.13	15.88	15.03	13.93	17.23
C ₃ H ₈	6.66	7.36	7.29	6.60	11.39
C ₃ H ₆ =	8.05	11.27	11.18	11.03	6.10
C ₄ H ₁₀	7.57	4.90	4.85	3.78	7.63
C ₄ H ₈ =	4.52	9.12	10.12	9.13	5.80
C ₅ H ₁₂	5.97	3.14	2.31	3.17	4.67
C ₅ H ₁₀ =	0.00	2.19	3.43	3.99	1.71
C ₆ H ₁₄	1.43	5.92	4.36	6.10	5.38
C ₆ H ₁₂ = & CYCLO'S	0.00	0.66	0.00	2.74	1.78
C ₇ + IN GAS	5.13	9.58	10.02	11.57	6.71
LIQ HC'S	0.00	0.00	0.00	0.00	0.00

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	87.47	78.51	79.88	77.42	79.75
C5 -420 F	12.53	21.49	20.12	27.58	20.25
420-700 F	0.00	0.00	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00	0.00	0.00
C5+ -END PT	12.53	21.49	20.12	27.58	20.25
ISO/NORMAL MOLE RATIO					
C4	1.5700	0.3662	0.4030	0.7500	0.4370
C5	3.7059	1.6316	1.2500	0.6364	0.8760
C6	0.0000	3.6471	3.0714	3.8333	2.3786
C4=	0.1818	0.1615	0.1469	0.1429	0.2372
PARAFFIN/OLEFIN RATIO					
C3	0.7892	0.6234	0.6221	0.5714	1.7837
C4	1.6154	0.5187	0.4631	0.4000	1.2694
C5	0.0000	1.3889	0.6545	0.7714	2.6593
LIO HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N. REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F					
16					
50					
84					
90					
RANGE(16-84 %)					
WT % @ 420 F					
WT % @ 700 F					

TABLE 13B RESULT OF SYNGAS OPERATION

RUN NO. 10011 16
 CATALYST FE UCC 108, #10042-79 80 CC 61.8GM (61.6 AFTER RUN 12 G)
 FEED H₂:CO OF 66:33 @ 600 CC/MN OR 450 GHSV

RUN & SAMPLE NO. 10011 16 06 011-16 07 011-16-08 011 16-09

	66:33: 0	66:33: 0	66:33: 0	66:33: 0
FEED H ₂ :CO:AR	66:33: 0	66:33: 0	66:33: 0	66:33: 0
HRS ON STREAM	68.58	74.75	92.58	97.99
PRESSURE, PSIG	293	300	300	301
TEMP., C	280	280	280	280

FEED CC/MIN	600	600	600	600
HOURS FEEDING	16.17	6.17	17.83	5.41
EFFLNT GAS LITER	574.70	220.51	643.12	197.13
GM AQUEOUS LAYER	0.00	0.00	0.00	3.47
GM OIL	0.00	0.00	0.00	0.00

MATERIAL BALANCE

GM ATOM CARBON %	105.53	106.54	106.88	108.47
GM ATOM HYDROGEN %	100.61	101.08	101.63	106.37
GM ATOM OXYGEN %	106.48	107.31	108.32	116.78
RATIO CHX/(H ₂ O+CO ₂)	0.8571	0.8844	0.7812	0.4010
RATIO X IN CHX	2.9984	2.9718	3.0077	2.9557
USAGE H ₂ /CO PRODT	1.9772	1.9835	1.9804	1.9956
RATIO CO ₂ /(H ₂ O+CO ₂)	0.1508	0.1493	0.1379	0.0650
K SHIFT IN EFFLNT	0.34	0.33	0.30	0.13

CONVERSION

ON CO %	6.33	6.45	5.70	5.97
ON H ₂ %	7.03	7.12	6.64	9.97
ON CO+H ₂ %	6.79	6.89	6.31	8.62

PRDT SELECTIVITY, WT %

CH ₄	36.07	34.79	36.73	34.22
C ₂ HC'S	18.60	19.16	18.27	17.98
C ₃ H ₈	12.07	11.84	12.44	11.86
C ₃ H ₆	5.27	5.47	5.46	5.34
C ₄ H ₁₀	6.71	5.67	5.82	5.95
C ₄ H ₈	4.96	4.72	4.61	5.21
C ₅ H ₁₂	4.05	4.51	4.35	4.08
C ₅ H ₁₀	1.70	1.62	0.62	1.60
C ₆ H ₁₄	4.54	4.37	4.23	4.18
C ₆ H ₁₂ & CYCLO'S	0.00	0.73	0.29	1.27
C ₇ + IN GAS	6.63	7.14	7.17	8.31
LIQ HC'S	0.00	0.00	0.00	0.00

TOTAL	100.00	100.00	100.00	100.00
SUB GROUPING				
C1 - C4	83.07	81.64	83.34	80.57
C5 - 420 F	16.93	18.36	16.66	19.43
420- 700 F	0.00	0.00	0.00	0.00
700- END PT	0.00	0.00	0.00	0.00
C5+ - END PT	16.93	18.36	16.66	19.43
ISO/NORMAL MOLE RATIO				
C4	0.2581	0.2586	0.1918	0.2130
C5	0.6400	0.6404	0.4537	0.4528
C6	2.2766	1.9804	1.6667	2.0698
C4+	0.2727	0.2414	0.1323	0.2222
PARAFFIN/OLEFIN RATIO				
C3	2.1749	2.0668	2.1746	2.1185
C4	1.7093	1.1587	1.2196	1.1078
C5	2.3099	2.7101	6.8261	2.4839
LIQ HC COLLECTION				
PHYS. APPEARANCE				
DENSITY				
N. REFRACTIVE INDEX				
SIMULT'D DISTILATN				
10 WT % @ DEG F				
16				
50				
84				
90				
RANGE(16-84 %)				
WT % @ 420 F				
WT % @ 700 F				

Cobalt Pore-Filled on Silica Alumina, Run 10112-2

Aerocat 8020 silica-alumina was formed as 20% alumina-bonded extrudate which was pore-filled with a cobalt nitrate solution, dried, and air calcined. This catalyst contains 10% cobalt, a much lower percentage of metal component than the iron based catalysts. This catalyst was prepared to act as a reference for a catalyst using a molecular sieve extrudate instead of the silica alumina extrudate. The silica alumina is acidic like the molecular sieve but does not have the molecular sieve's shape selective control.

The conversion, product selectivity, percent iso- of the pentanes and percent olefins in the C₄'s are presented in Figures 82 to 85. The carbon number product distributions are shown in Figures 86 to 92. Tables 14A to 14D contain the detailed material balances.

This catalyst had essentially no activity at 220°C. While this reaction temperature is lower than any used for the iron catalysts, it was used for the cobalt catalyst because cobalt is expected to be more active than iron and to have a carbon number product distribution inferior to iron tested at the same temperature. Since the catalyst is unpromoted, 220°C was chosen as a good starting temperature. Actually the cobalt on UCC-101, Run 10011-14, was tested first and it was active at 220°C. Considering the low metal loading level, this catalyst had reasonable activity at 250°C. Cobalt has little intrinsic water gas shift activity so it could not effectively use the 1:1 syngas feed. This lack of WGS activity is most easily seen in the H₂/CO usage ratio, which is above 2. The physical mixture, promoted iron catalysts with good WGS activity had usage ratios of 0.65. The 1:1 syngas was still used in spite of this high usage ratio to obtain the most favorable product distribution. The catalyst did not show signs of significant deactivation in spite of this CO rich syngas feed.

The product selectivity is good at 250°C except that the methane yield is quite high compared to the yield of the other hydrocarbons. This is best illustrated in the S-F product distribution plots shown in Figures 86 to 92. The yield of methane is significantly above

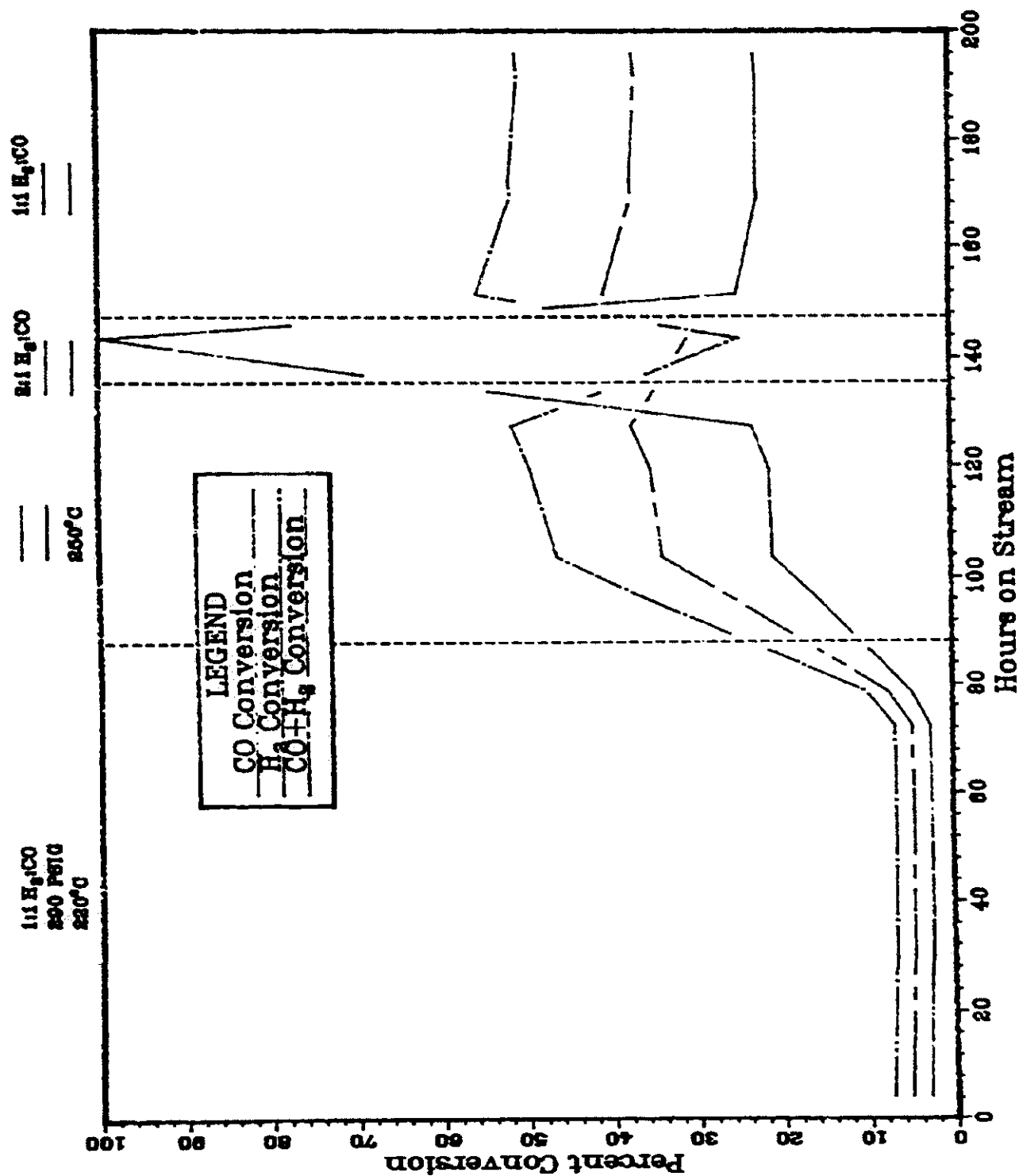
the line of all the other carbon number yields. This was not seen in any of the iron catalysts. This means the probability of forming the first C-C bond is significantly less than the probability of forming any other C-C bond. The change in probability is not a gradual change as would be expected from other properties of the hydrocarbons. This implies that there is a separate mechanism for methanation which does not lead to F-T synthesis, i.e. not only does the methane arise from the F-T synthesis as part of the S-F product distribution but also from a separate methanation mechanism.

This high methane yield could be acceptable if the gasoline and diesel oil yields were also high. The gasoline and diesel oil yields are superior, being consistently over 50% of the total hydrocarbon production. The hydrocarbons except for methane generally followed a straight line S-F product distribution. This means a significant amount of heavy hydrocarbons are also produced. The C_{13} 's being olefinic suggested the liquid product is also olefinic. The pentanes were hardly isomerized as shown in Figure 84. In spite of this lack of isomerization of the pentanes, the condensed product was liquid at room temperature. The chromatograms of the simulated distillation, Figures 93 to 95, show why this is so. The initial liquid samples were quite isomerized but this activity deactivated rapidly probably due to coking of the silica-alumina. The later samples were quite dominated by the normals. Toward the end of the run, the catalyst was probably producing wax. It was not seen in the product because it was still in the process of filling the reactor with this wax. The initial samples were probably high quality gasoline but because of the rapid deactivation of the isomerization activity, the catalyst is probably not useful without frequent regenerations.

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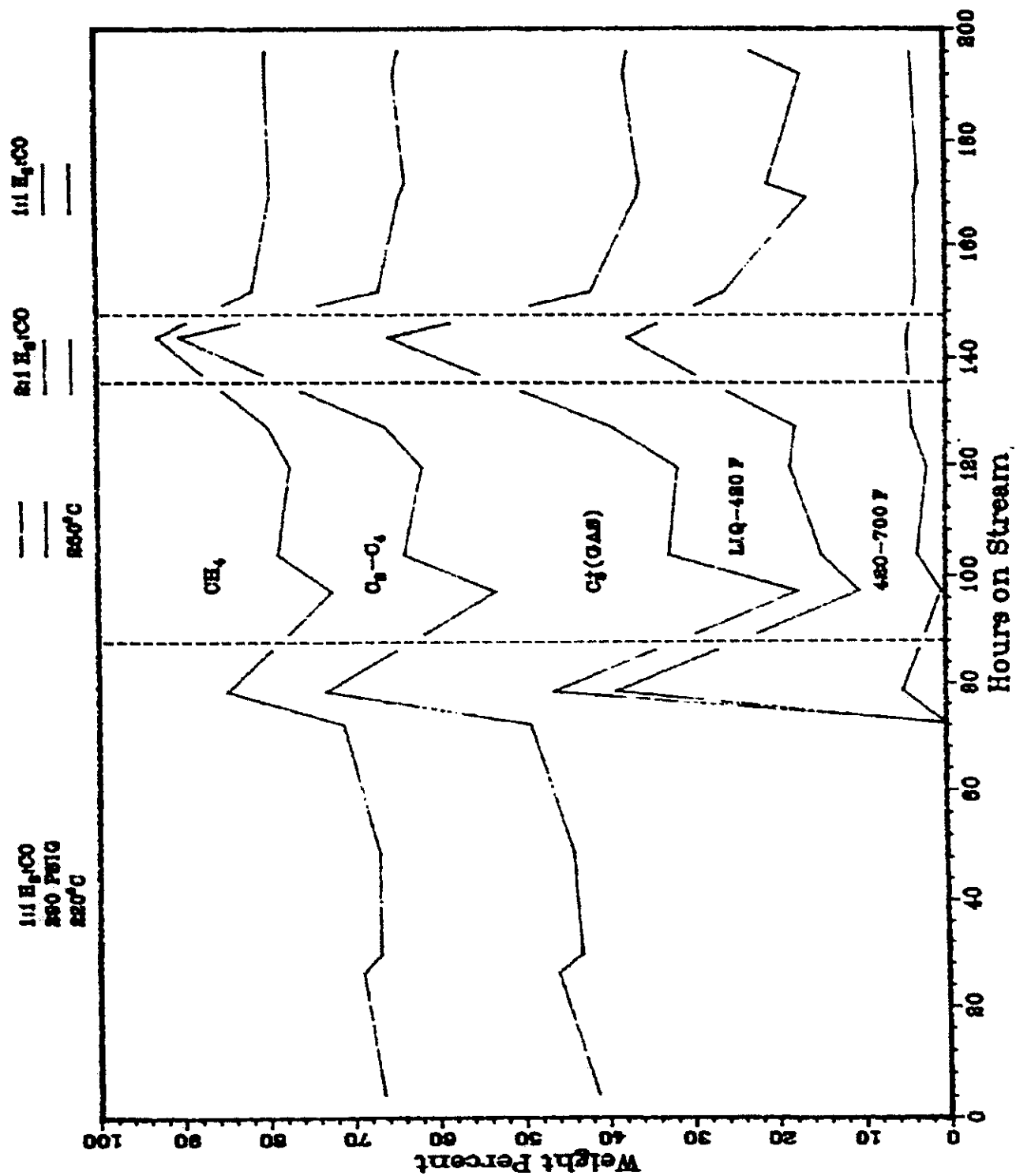
1011202

FIGURE 82



1011202

FIGURE 83



1011202

FIGURE 84

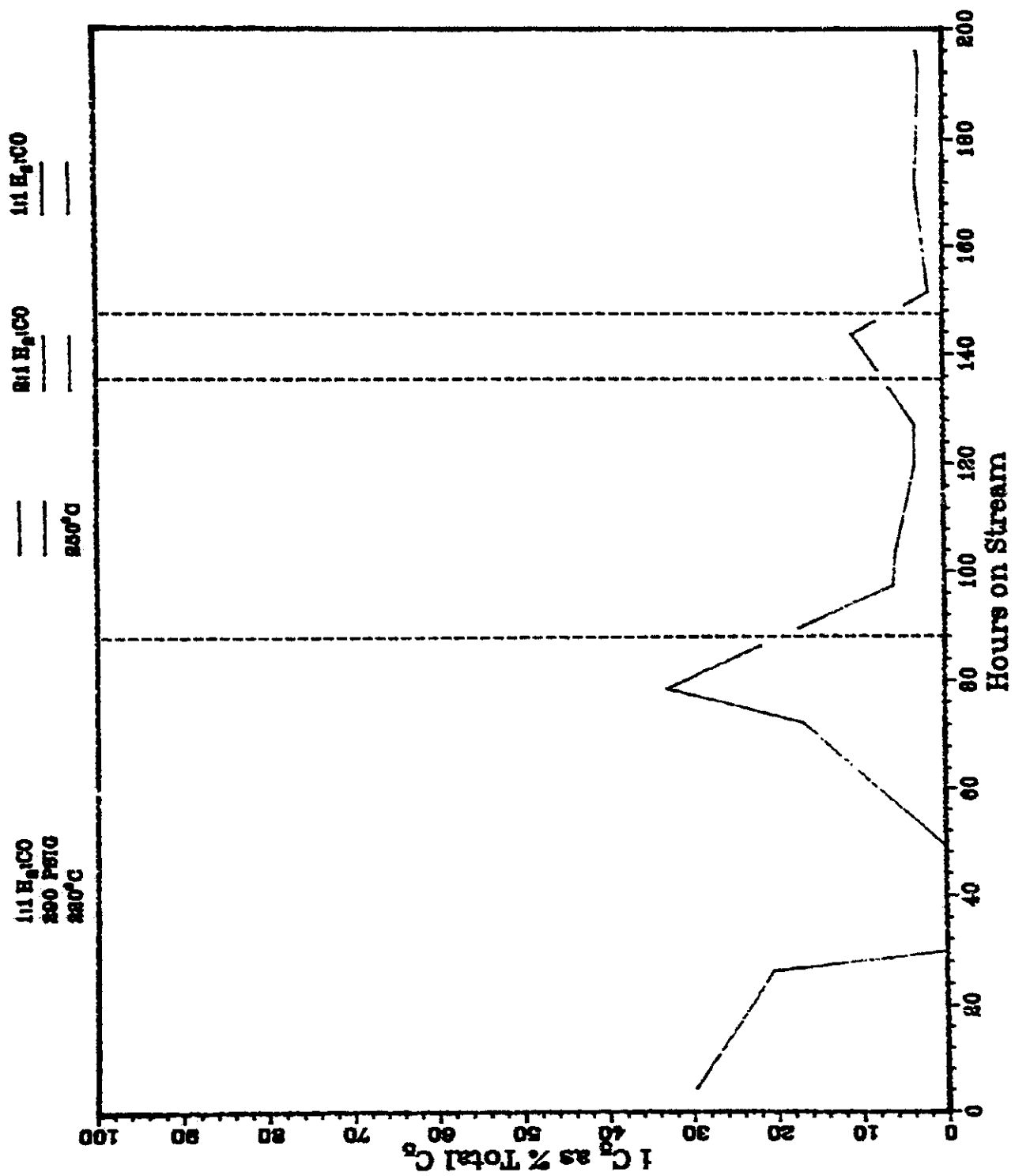


FIGURE 85

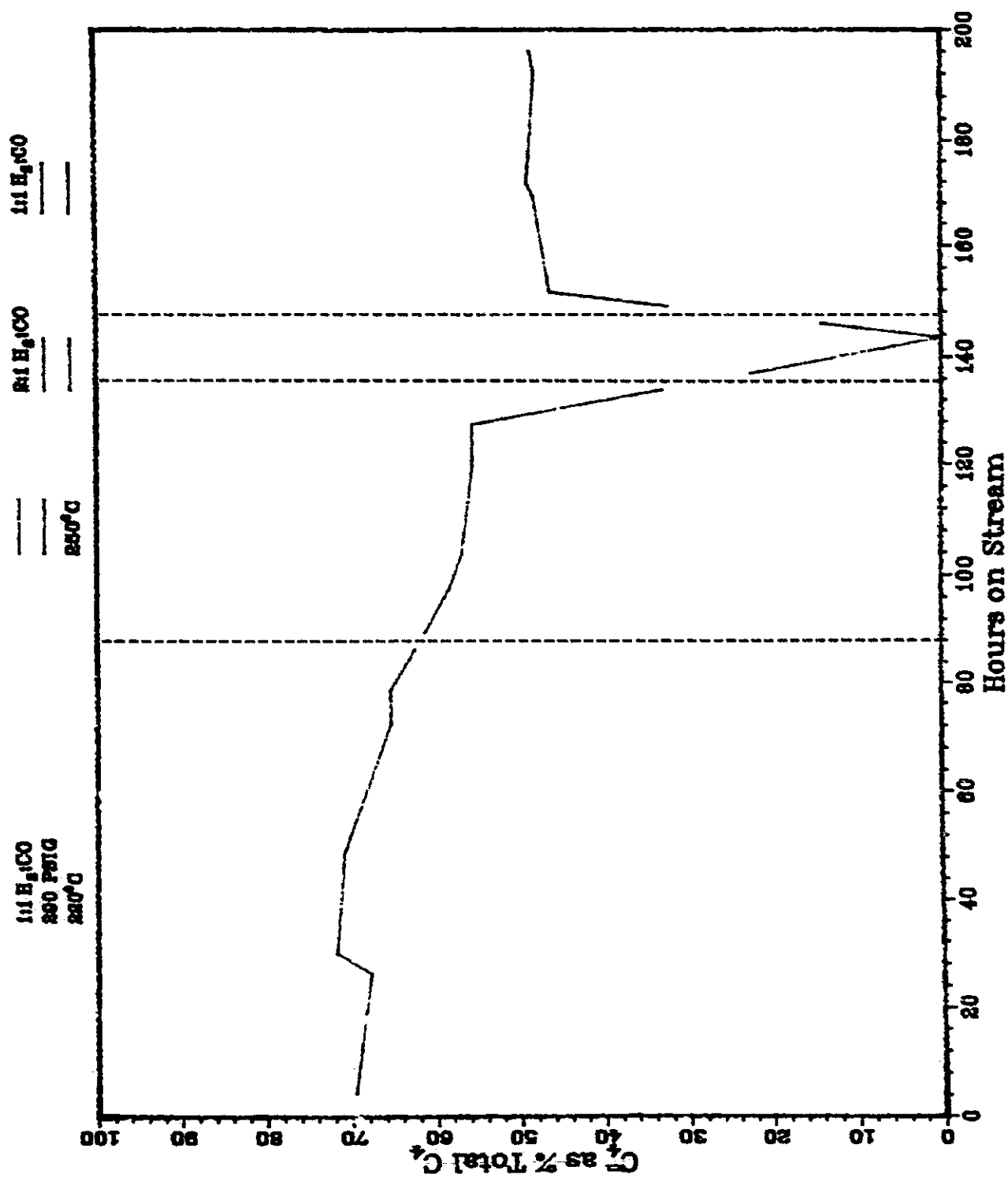


FIGURE 86

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-02-06

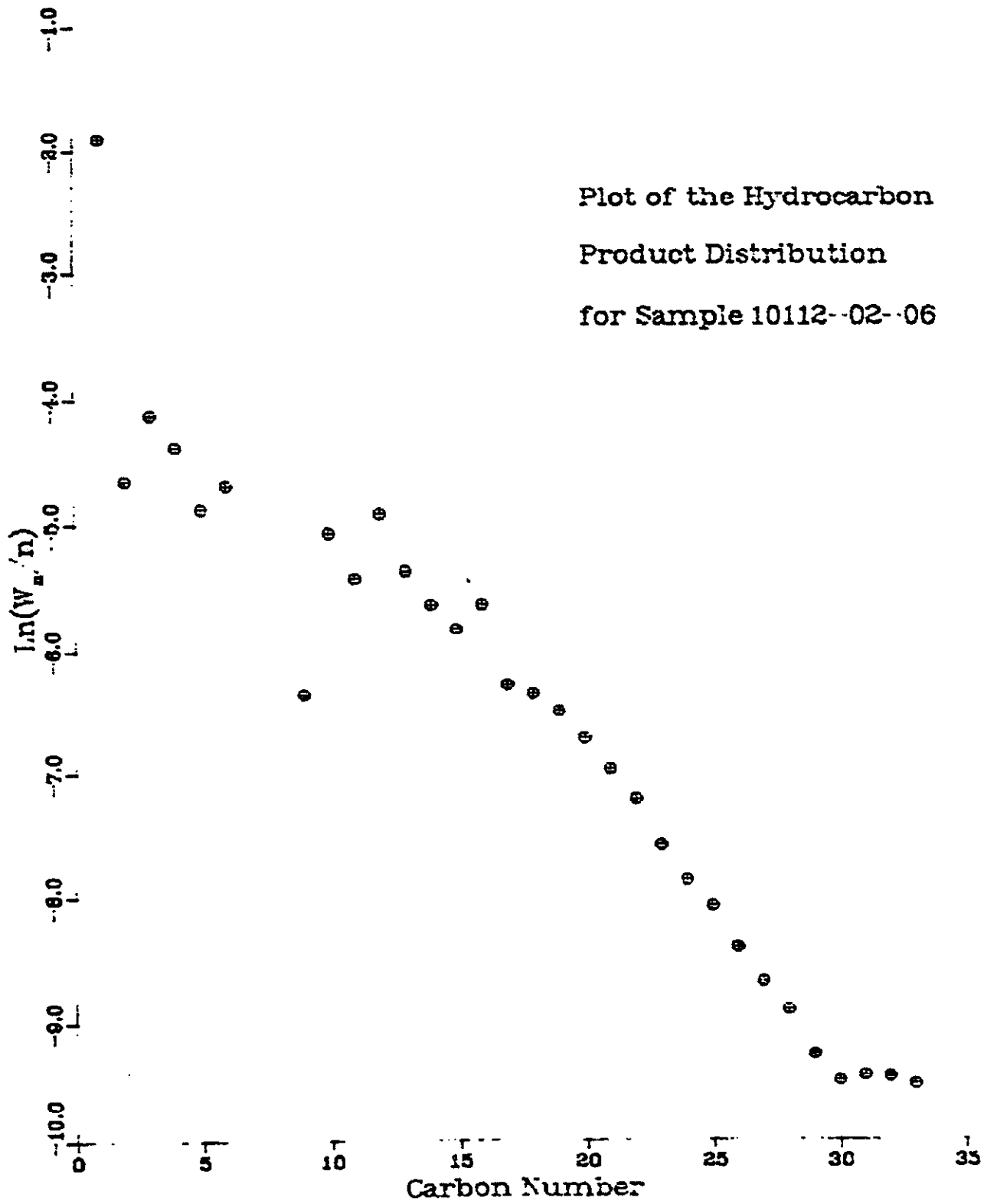


FIGURE 87

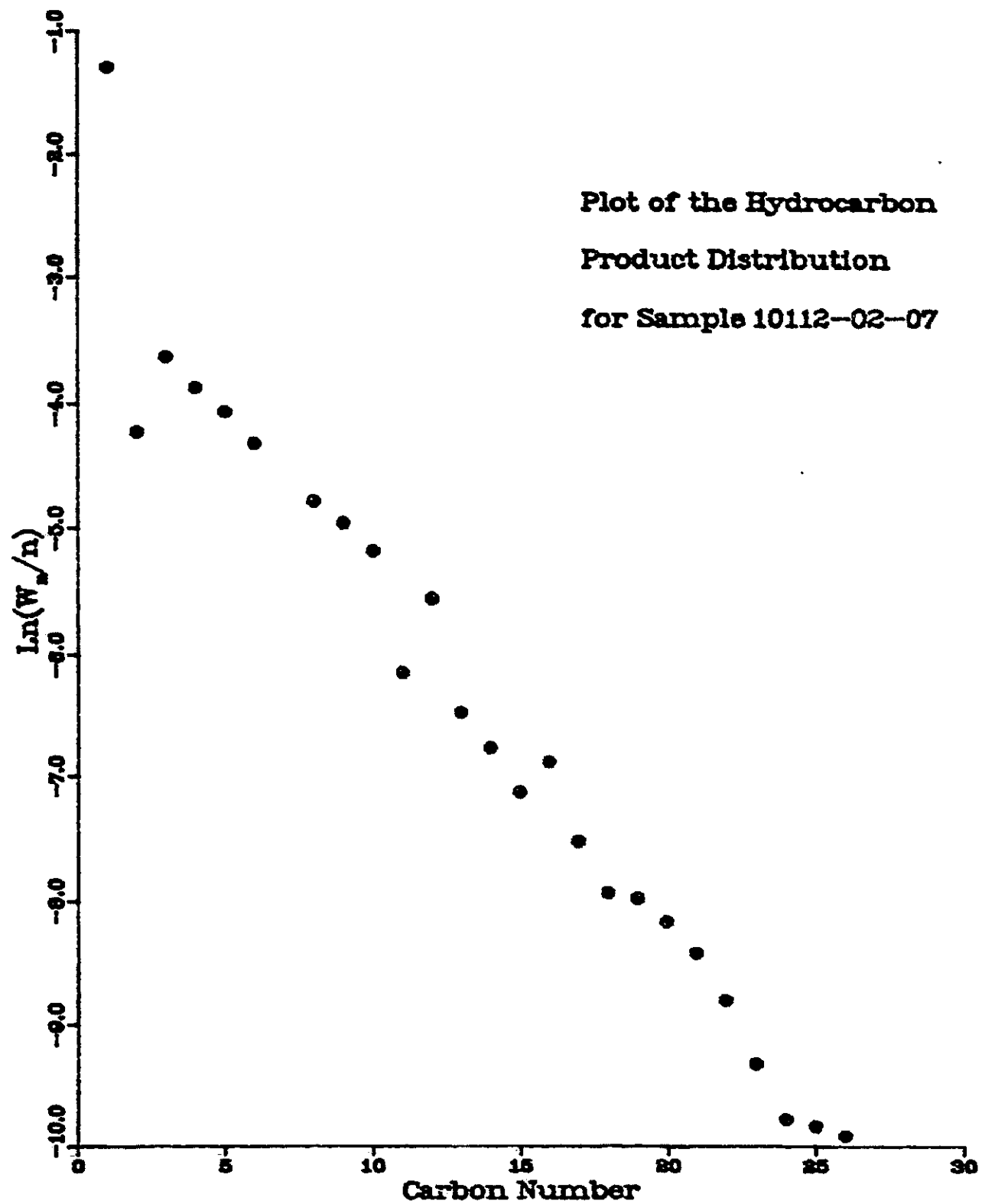


FIGURE 88

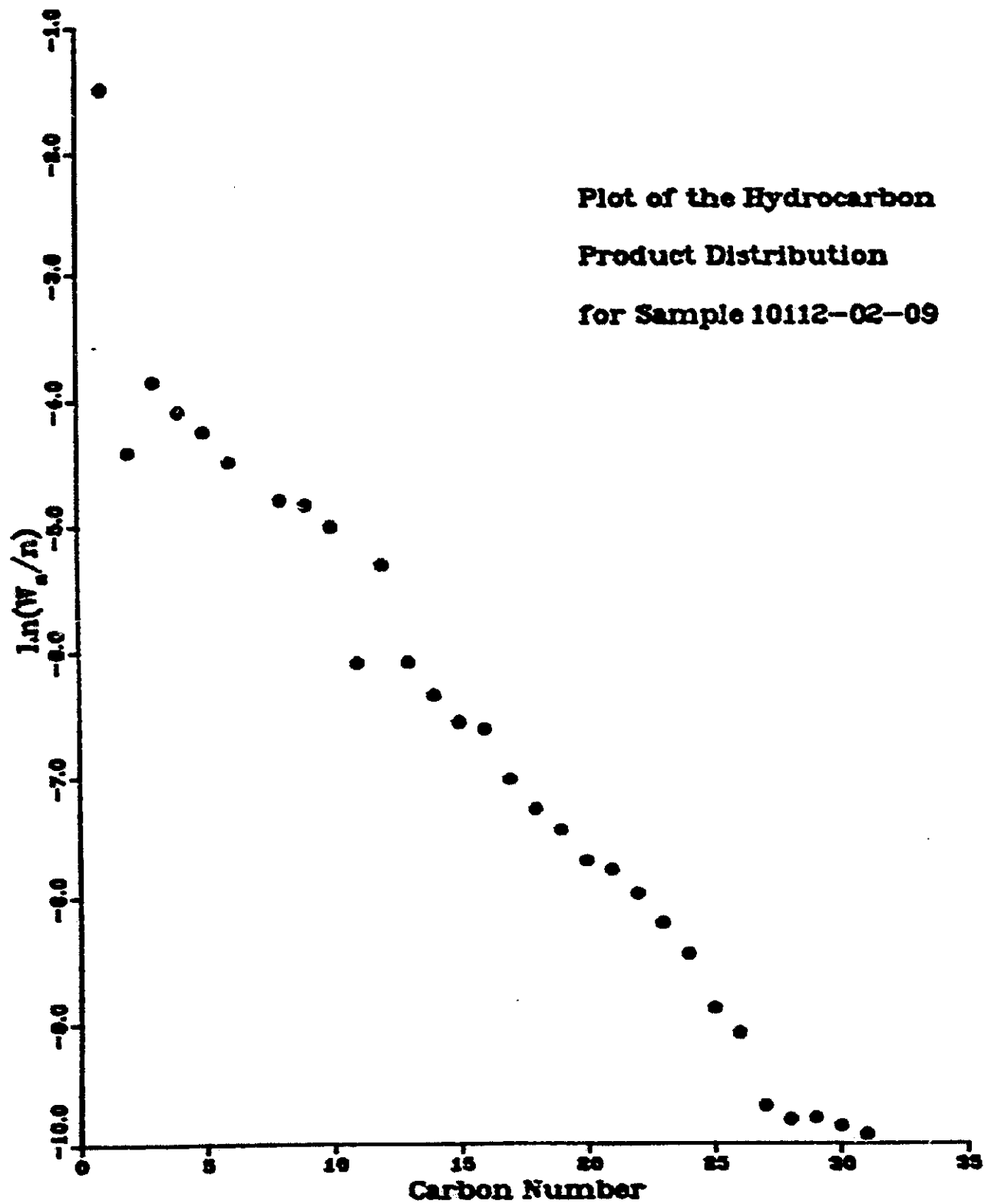


FIGURE 89

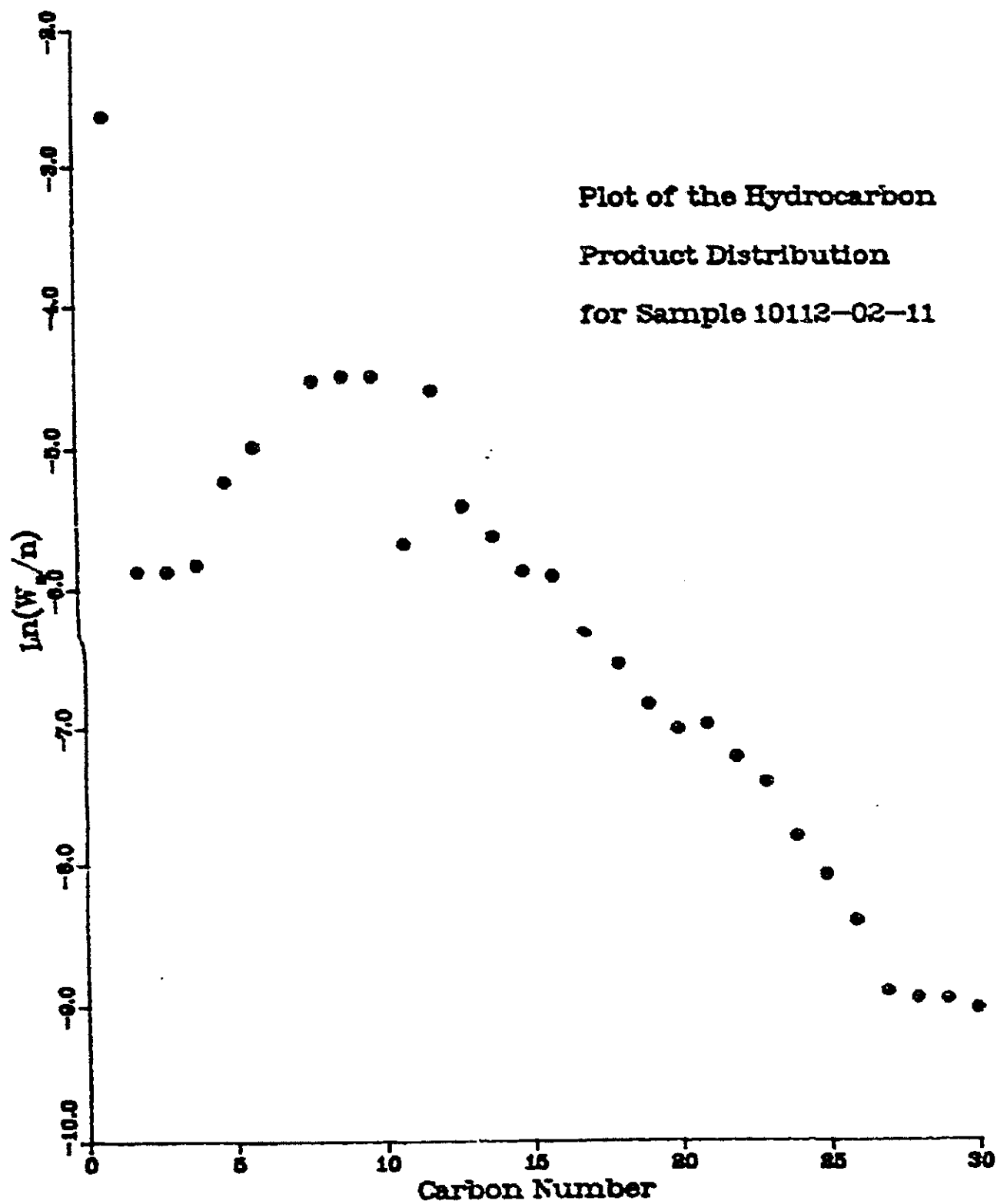


FIGURE 90

Plot of the Hydrocarbon
Product Distribution
for Sample 10112-02-12

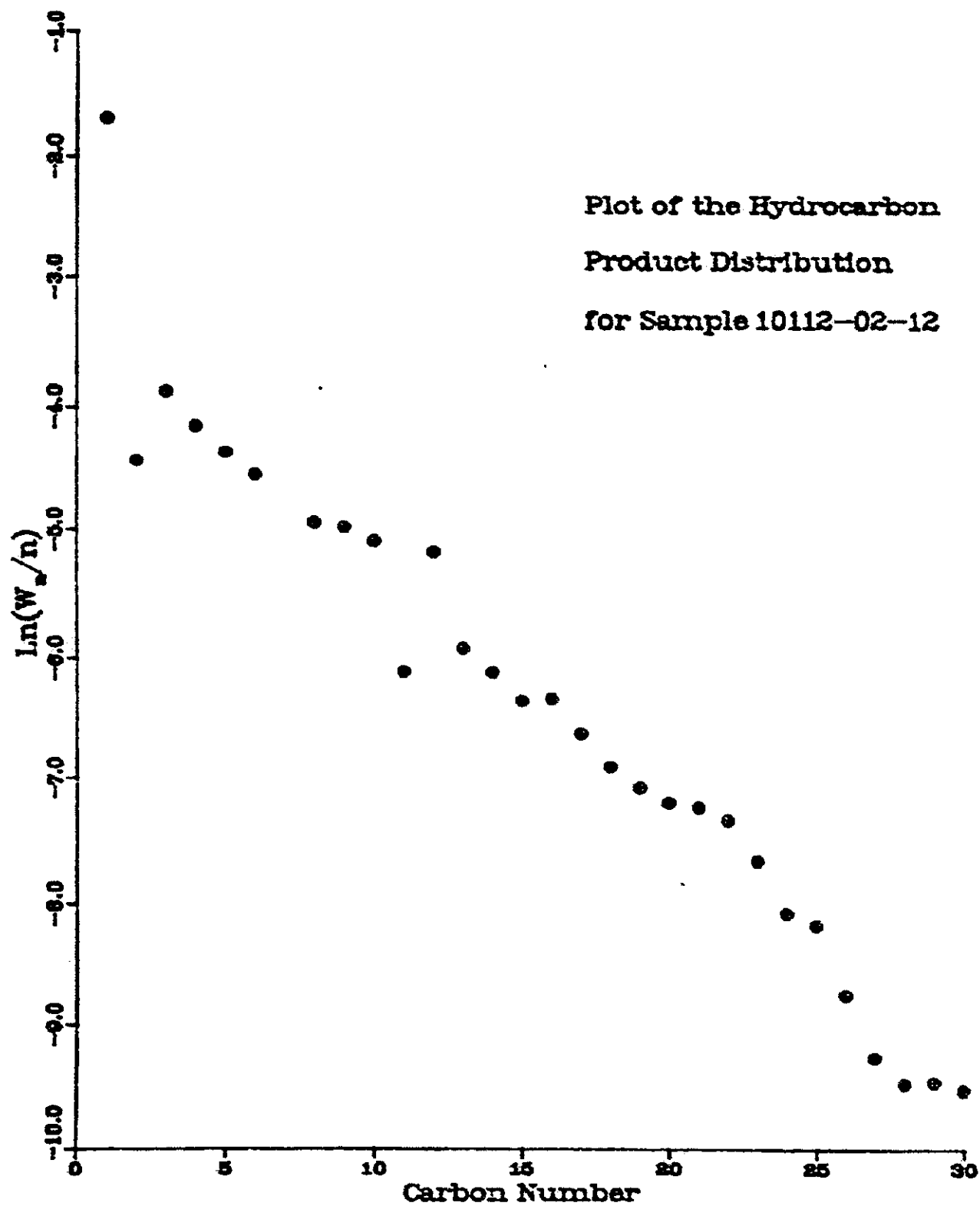


FIGURE 91

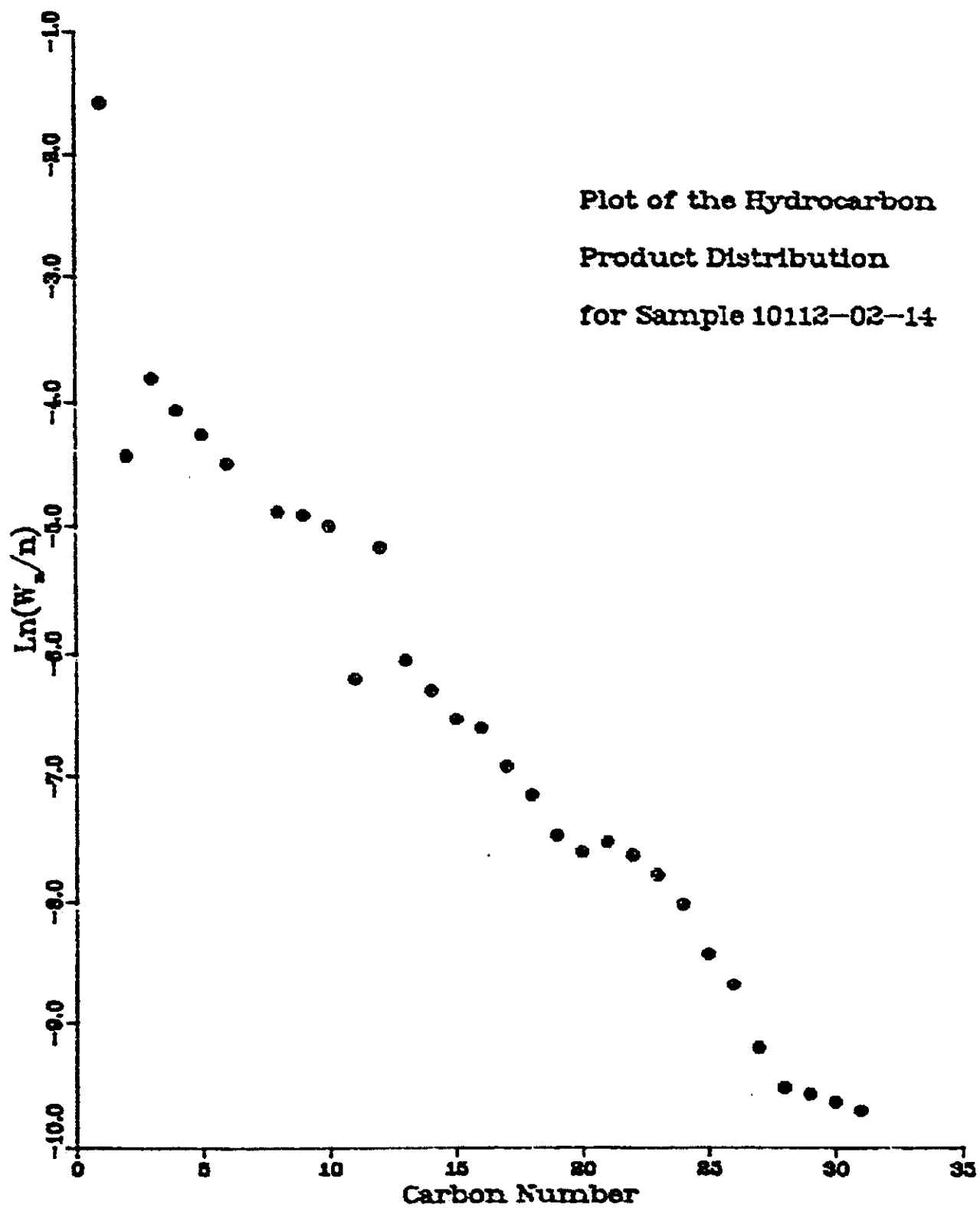
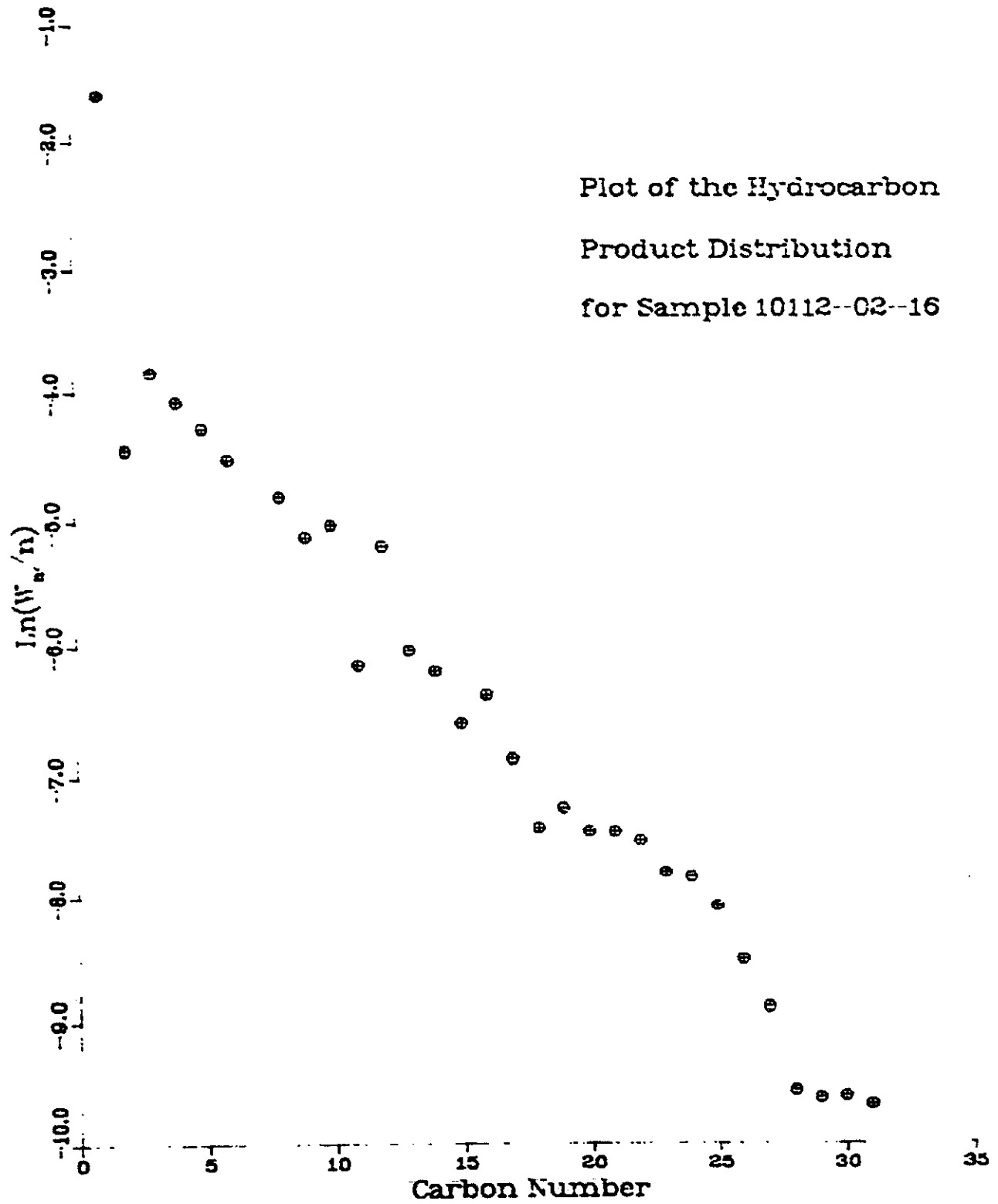


FIGURE 92



RT: SLICES 9.20

FIGURE 93

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=176°C SETPT=176°C LIMIT=405°C

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

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

RT: STOP RUN

SAMPLE D 10112-2-7L

RT: SLICES 9.20

FIGURE 94

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: 110112-2-121

RT: SLICES 0.20

FIGURE 95

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=26°C SETPT=26°C LIMIT=405°C

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

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

RT: STOP RUN

SAMPLE: D10112-2-16L

TABLE 14A RESULT OF SYNGAS OPERATION

RUN NO. 10112 02

CATALYST CO SIO₂·AL₂O₃ #10042 15 80 CC 40.2GM (48.4 AFTER RUN -8.1%)FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MIN OR 300 CHCV

RUN & SAMPLE NO. 10112 02 01 112 02 02 112 02-03 112 02-04 112 02 05

FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	4.16	26.33	29.91	48.91	77.41
PRESSURE, PSIG	289	288	289	291	289
TEMP. C	720	220	270	720	720

FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	4.16	22.17	3.58	19.00	23.50
EFFLUENT GAS LITER	95.26	514.89	84.22	443.86	560.08
GM AQUEOUS LAYER	0.00	0.00	0.00	0.00	0.00
GM OIL	0.00	0.00	0.00	0.00	0.00

MATERIAL BALANCE

GM ATOM CARBON %	97.00	97.59	98.63	97.79	99.04
GM ATOM HYDROGEN %	98.45	100.08	101.35	100.67	103.75
GM ATOM OXYGEN %	98.71	99.03	100.22	99.41	100.52
RATIO CH ₄ /(H ₂ O+CO ₂)	0.6890	0.6288	0.5918	0.5811	0.6230
RATIO X IN CH ₄	2.7149	2.6465	2.6914	2.6854	2.6097
USAGE H ₂ /CO PRODT	2.0565	2.0657	2.0694	2.0897	2.0779
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0650	0.0489	0.0487	0.0415	0.0417
K SHIFT IN EFFLUENT	0.07	0.05	0.05	0.04	0.04

CONVERSION

ON CO %	3.01	2.68	2.54	2.46	2.64
ON H ₂ %	7.37	6.89	6.75	6.67	6.72
ON CO+H ₂ %	5.21	4.81	4.68	4.59	4.73

PRDT SELECTIVITY, WT %

CH ₄	33.39	31.15	33.13	33.05	28.85
C ₂ HC'S	3.35	2.97	3.23	3.19	3.13
C ₃ H ₈	3.50	3.28	3.50	3.30	3.32
C ₃ H ₆ =	6.59	6.41	6.68	6.69	6.30
C ₄ H ₁₀	3.69	3.36	2.97	2.90	3.29
C ₄ H ₈ =	8.14	6.81	7.75	6.77	5.96
C ₅ H ₁₂	3.85	3.20	2.86	2.30	2.62
C ₅ H ₁₀ =	5.12	4.57	4.85	3.70	4.75
C ₆ H ₁₄	4.89	4.05	3.86	3.35	3.84
C ₆ H ₁₂ = & CYCLO'S	3.15	2.88	0.00	2.44	5.51
C ₇ + IN GAS	24.34	31.32	31.68	32.29	32.42
LIQ HC'S	0.00	0.00	0.00	0.00	0.00