FIGURE 22

997219

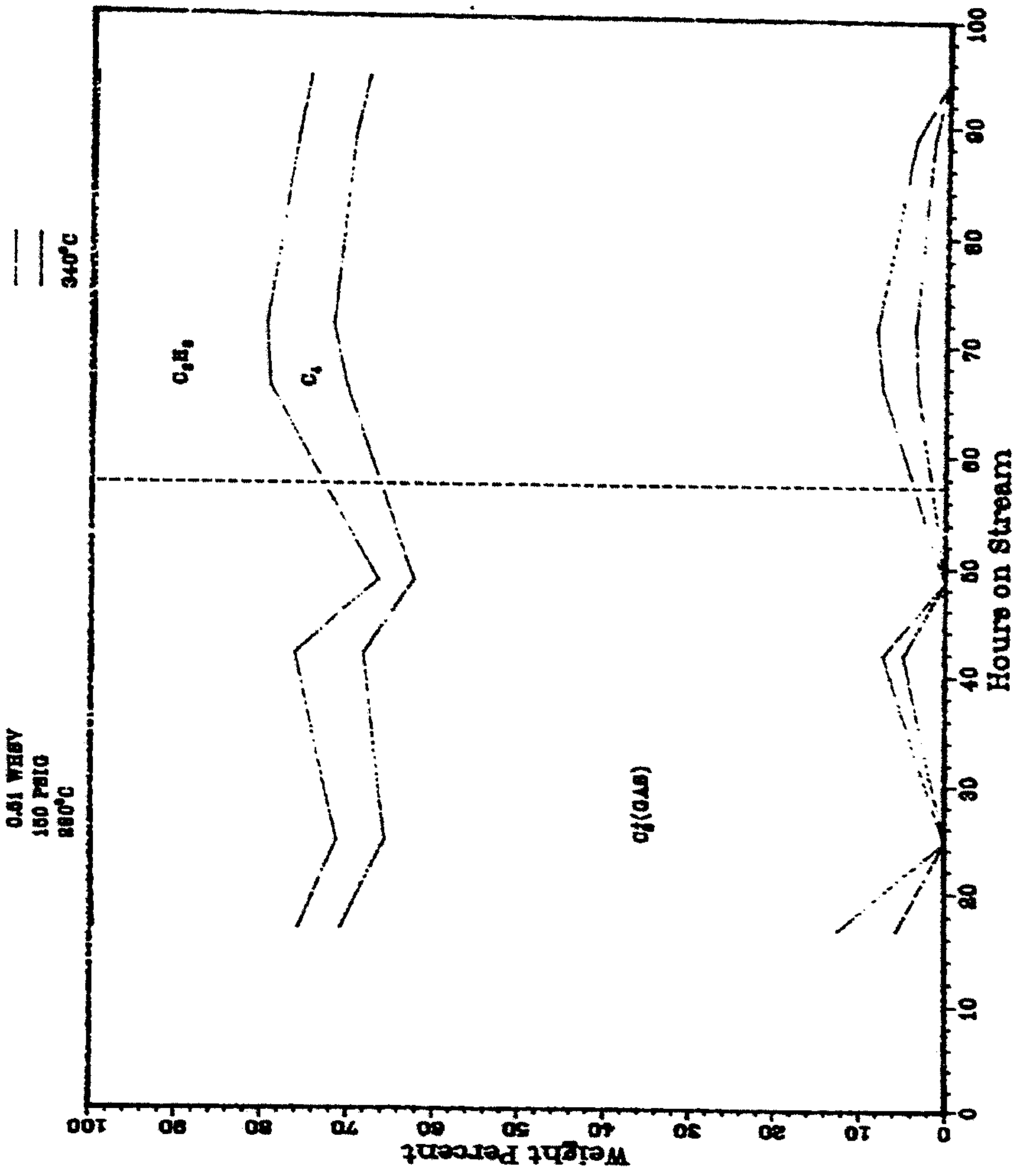


TABLE 6A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-19
CATALYST LZ-Y82 #10042-25 55CC 35.00GM (35.53G AFTER THE RUN, +0.53G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 35.4 CC/HR EFFLUENT 19.1 L/HR AQ LAYR 14.6 CC/HR

RUN & SAMPLE NO.	9972-19-01	972-19-02	972-19-03	972-19-04	972-19-05
C3H6 WHSV	0.52	0.50	0.52	0.49	0.53
HRS ON STREAM	16.67	24.67	41.84	48.67	65.92
PRESSURE,PSIG	152	146	147	145	153
TEMP. C	279	280	279	277	338
FEED C3H6 CC	598.42	276.87	609.75	232.20	673.59
HOURS FEEDING	16.67	8.00	17.17	6.83	17.25
EFFLNT GAS LITER	313.11	149.98	329.20	130.66	330.87
GM AQUEOUS LAYER	238.4	117.21	251.5	98.62	252.05
GM LIQ HYDROCARBON	2.70	0.00	1.10	0.00	2.70
WT FR. LIQ HC/FEED	0.0072	0.0000	0.0035	0.0000	0.0069
MATERIAL BALANCE WT %	94.86	101.08	97.09	110.27	100.84
C3H6 CONVERSION %	6.12	4.73	5.01	3.23	9.38
PRDT SELECTIVITY,WT %					
CH4	0.18	0.00	0.12	0.00	0.15
C2 HC'S	0.19	0.21	0.16	0.15	0.23
C3H8	23.96	28.62	23.58	33.48	20.59
C4H10	1.41	1.49	2.45	1.12	1.41
C4H8=	3.56	4.11	5.59	3.00	7.67
C5H12	1.31	1.48	1.84	0.88	1.03
C5H10=	0.10	0.00	0.18	0.00	0.21
C6H14	7.93	8.86	7.18	6.83	8.41
C6H12= & CYCLO'S	20.99	26.69	25.67	27.43	26.68
C7+ IN GAS	27.94	28.54	25.97	27.11	26.35
LIQ HC'S	12.44	0.00	7.28	0.00	7.33
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	29.30	34.43	31.89	37.75	29.99
C5 -420 F	65.04	65.57	63.24	62.25	66.76
420-700 F	5.18	0.00	4.36	0.00	3.04
700-END PT	0.49	0.00	0.52	0.00	0.21
C5+-END PT	70.70	65.57	68.11	62.25	70.01
ISO/NORMAL MOLE RATIO					
C4	6.1395	5.0714	0.5688	7.0588	1.1116
C5	4.8718	4.2308	4.1569	1000.0000	1.7453
C6	5.1263	4.2245	3.5879	3.1241	3.6116
C4=	0.6085	0.6274	0.5146	0.6745	0.6079

[redacted]

PARAFFIN/OLEFIN RATIO					
C3	0.0151	0.0138	0.0120	0.0109	0.0206
C4	0.3828	0.3493	0.4220	0.3596	0.1781
C5	12.7222	0.0000	9.7407	0.0000	4.7705
1.10 HC COLLECTION					
PHYS. APPEARANCE	GREEN OIL	GREEN OIL	GREEN OIL	GREEN OIL	GREEN OIL
DENSITY	-				
N, REFRACTIVE INDEX	1.4608				
SIMULT'D DISTILATN					
10 WT % @ DEG F	289	---	352	--	286
16	324	- -	378	--	303
50	409	---	467	---	407
84	540	---	616	--	534
90	606	---	665	--	592
RANGE(16-84 %)	216	--	238	---	231
WT % @ 420 F	54.5	- -	33.0	--	55.7
WT % @ 700 F	96.1	- -	92.9	--	97.1

TABLE 6B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-19
CATALYST LZ-Y82 #10042-25 55CC 35.00GM (35.53GM AFTER THE RUN,+0.53G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 35.4 CC/HR EFFLUENT 19.1 L/HR AQ LAYR 14.6 CC/HR

RUN & SAMPLE NO.	9972-19-06	972-19-07	972-19-08
C3H6 WHSV	0.53	0.52	0.49
HRS ON STREAM	71.67	88.79	94.29
PRESSURE,PSIG	144	145	145
TEMP. C	338	338	338
FEED C3H6 CC	207.88	612.90	185.63
HOURS FEEDING	5.75	17.12	5.50
EFFLNT GAS LITER	109.36	334.28	106.22
GM AQUEOUS LAYER	83.08	250.11	80.30
GM LIQ HYDROCARBON	0.71	0.70	0.00
WT FR. LIQ HC/FEED	0.0067	0.0022	0.0000
MATERIAL BALANCE WT %	100.98	105.49	112.99
C3H6 CONVERSION %	8.42	5.62	5.52
PRDT SELECTIVITY,WT %			
CH4	0.21	0.16	0.26
C2 HC'S	0.78	0.78	0.30
C3H8	20.10	23.74	24.90
C4H10	0.68	0.60	0.68
C4H8=	7.20	6.02	6.21
C5H12	0.48	0.67	0.75
C5H10=	0.00	0.20	0.25
C6H14	8.73	7.67	7.89
C6H12= & CYCLO'S	30.03	32.33	34.51
C7+ IN GAS	24.24	24.55	24.26
LIQ HC'S	8.07	3.78	0.00
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 - C4	28.46	30.81	32.34
C5 -420 F	67.91	67.49	67.66
420-700 F	3.23	1.51	0.00
700-END PT	0.40	0.19	0.00
C5+ END PT	71.54	69.19	67.66
ISO/NORMAL MOLE RATIO			
C4	0.0000	5.4500	5.1739
C5	1000.0000	1.1296	1.2909
C6	3.3732	2.6382	2.3524
C4=	0.6430	0.6432	0.6407

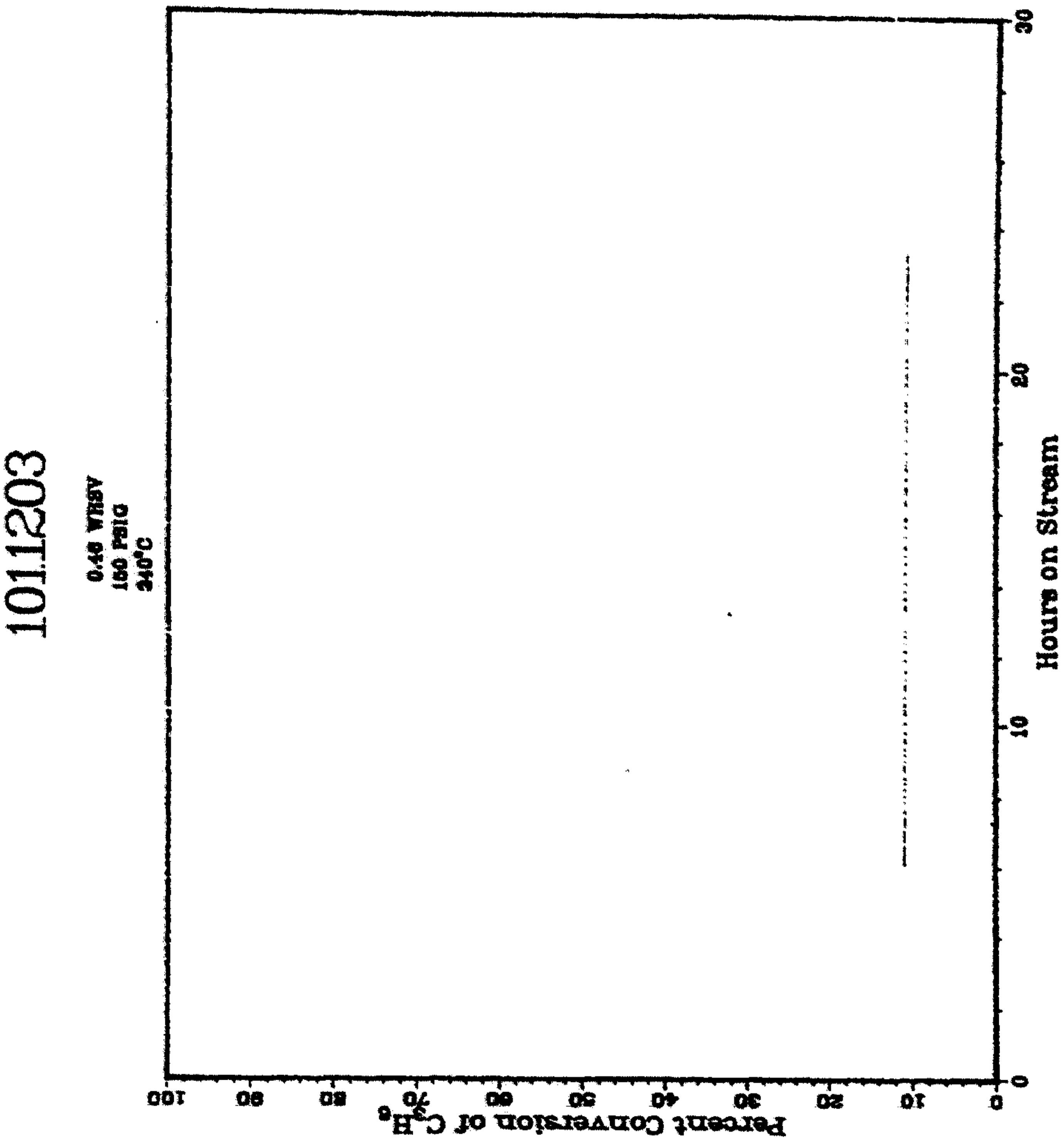
PARAFFIN/OLEFIN RATIO			
C3	0.0178	0.0137	0.0141
C4	0.0908	0.0967	0.1054
C5	0.0000	3.2857	2.8636
LIQ HC COLLECTION			
PHYS. APPEARANCE	YL-GR OIL	YL-GR OIL	YL-GR OIL
DENSITY			
N. REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F			---
16			---
50			---
84			---
90			---
RANGE(16-84 %)			---
WT % @ 420 F			---
WT % @ 700 F			---

97% H-Y-62, Run 10112-3

97% H-Y-62 is the completely acid form of non-stabilized zeolite. It is synthesized by extensive exchange of sodium Y with ammonium cation. This is followed by calcination to remove the ammonia. X-ray diffraction showed the structure still to be intact after calcination.

Figure 23 shows the conversion of propylene to be low. The product selectivity is shown in Figure 24. The detailed material balances are shown in Table 7. This catalyst is also not significant for Task 1 due to its low activity.

FIGURE 23


1011203
0.46 WHSV
150 PSIG
240°C
Percent Conversion of C_3H_6
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30

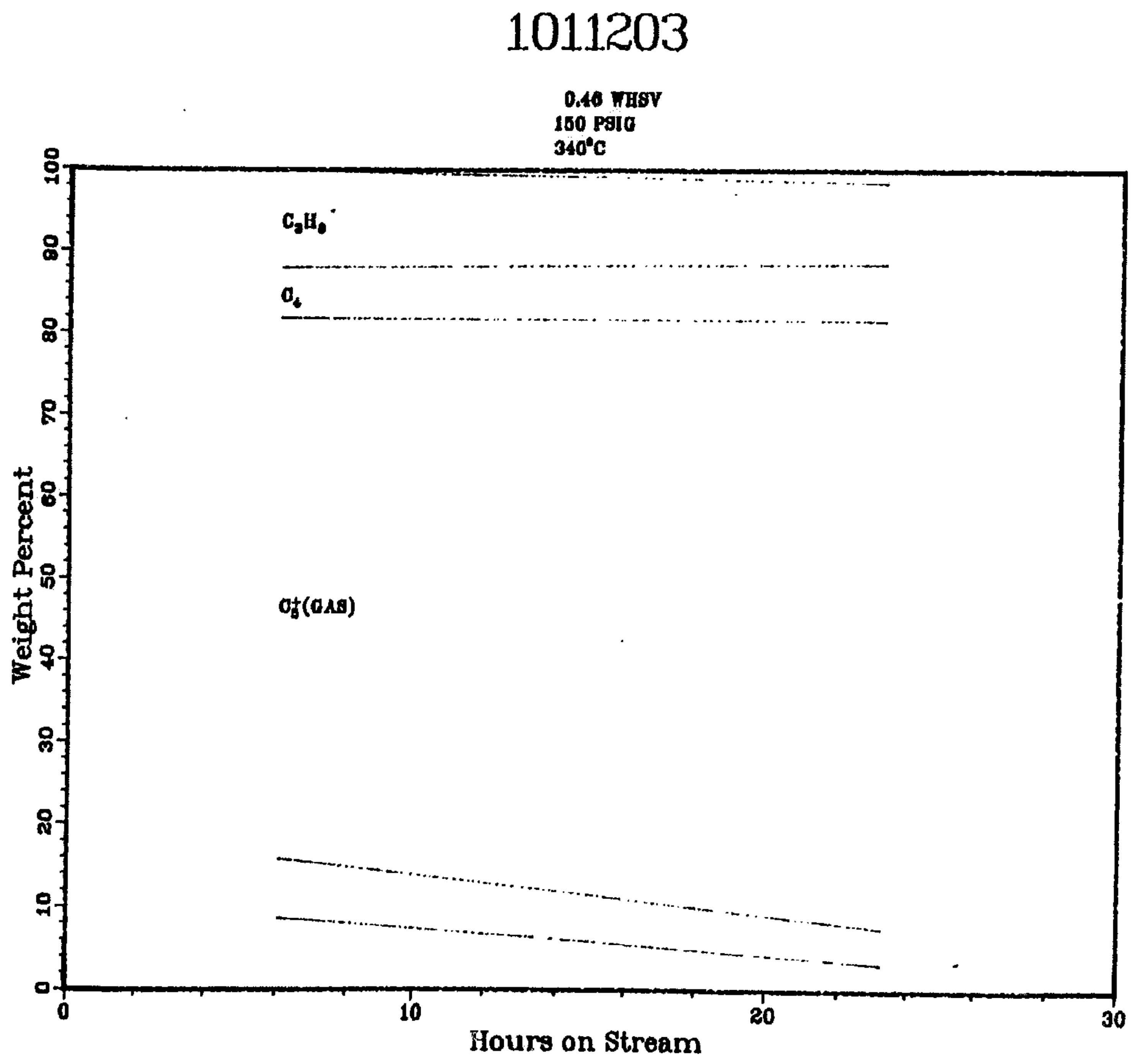

1011203
0.46 WHSV
150 PSIG
340°C
C_3H_8
C_4
C_5^+(GAS)
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30

FIGURE 24

TABLE 7 RESULT OF PROPYLENE OPERATION

RUN NO. 10112-03
CATALYST 97% H Y62 #9530-88 65CC 35.0GM (29.04GM AFTER THE RUN,-5.96G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 33.5 CC/HR EFFLUENT 17.4 L/HR AQ LAYR 12.3 CC/HR

RUN & SAMPLE NO.	10112-03-01	011203-02
C3H6 WHSV	0.42	0.51
HRS ON STREAM	6.08	23.25
PRESSURE,PSIG	157	138
TEMP. C	340	342
FEED C3H6 CC	177.45	600.31
HOURS FEEDING	6.08	17.17
EFFLNT GAS LITER	90.53	312.87
GM AQUEOUS LAYER	50.31	235.51
GM LIQ HYDROCARBON	1.50	2.45
WT FR. LIQ HC/FEED	0.0166	0.0080
MATERIAL BALANCE WT %	99.27	99.58
C3H6 CONVERSION %	10.92	10.71
PRDT SELECTIVITY,WT %		
CH4	0.06	0.79
C2 HC'S	0.11	0.78
C3H8	11.77	9.95
C4H10	0.57	3.80
C4H8=	5.62	3.12
C5H12	0.54	0.37
C5H10=	1.39	0.91
C6H14	8.05	4.95
C6H12= & CYCLO'S	32.46	48.31
C7+ IN GAS	23.64	19.47
LIQ HC'S	15.77	7.54
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	18.12	18.44
C5 -420 F	73.23	78.36
420-700 F	5.96	2.01
700-END PT	2.68	1.18
C5+-END PT	81.88	81.56
ISO/NORMAL MOLE RATIO		
C4	2.5000	21.4697
C5	1.0000	1.0172
C6	2.7641	3.4054
C4=	0.6975	0.6458

PARAFFIN/OLEFIN RATIO		
C3	0.0139	0.0115
C4	0.0978	1.1751
C5	0.3789	0.3953
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLEAR OIL	CLEAR OIL
DENSITY		
N, REFRACTIVE INDEX		
SIMULT'D DISTILATN		
10 WT % @ DEG F	279	279
16	292	288
50	463	394
84	702	697
90	740	743
RANGE(16-84 %)	410	409
WT % @ 420 F	45.2	57.6
WT % @ 700 F	83.0	84.3

Summary of Task 1 testing

Task 1 testing has been very successful. All the milestones were achieved and information learned in Task 1 has been put to use in Task 2. In the process of this testing, a superior Task 1 catalyst was identified, UCC-108.

A comparison of the ZSM-5 type catalysts and UCC-108 is given in Table 8. The data are all at 280°C. All the catalysts have high conversion. The high silica/alumina ratio ZSM-5 shows the greatest deactivation. None of the catalysts produced much propane at these conditions. LZ-105 produces the most initially. UCC-108 produces the least and shows the most consistent selectivity over the course of the run. The catalysts all produce mostly C_5^+ hydrocarbons. Here again UCC-108 produces the most and shows the least signs of deactivation. The refractive index shows the liquid products are olefinic although the LZ-105 and ZSM-5 did produce some aromatics initially. These data show a clear superiority for UCC-108.

There are other considerations which are also important when analyzing Task 1 results. The testing revealed aspects of molecular sieve activity which show that some SSC's, while inferior in Task 1 tests, may deserve consideration in task 2 when certain types of chemistry are desired. UCC-101, one of the first molecular sieves tested in Task 1 was not highly active, but did produce both gasoline and diesel range materials. UCC-103, a modification of UCC-101, had activity similar to UCC-101 but showed slightly lower deactivation. UCC-109 could be useful when a very acidic catalyst is desired, such as when paraffinic hydrocarbons are produced by the metal component. LZ-Y-82 could possibly be useful in such a situation although coking is likely to be an even worse problem with LZ-Y-82 than with UCC-109. $AlPO_4$-11 might be useful to see the effects of a pore system with no acid activity. There are many molecular sieves which can be useful in Task 2 depending upon the desired properties, but UCC-104 and its active modification UCC-108 appear overall the most promising candidates.

TABLE 8

PROPYLENE OLIGOMERIZATION

280°C $H_2:C_3H_6:H_2O$ 1:1:2

Catalyst	LZ-105	ZSM-5 $SiO_2/Al_2O_3=35$	H-ZSM-5 $SiO_2/Al_2O_3=85$	UCC-108
Conversion	97-90%	90-85	84-44	74-60
C_3H_8	10-2	6-2	6-3	2.5-2.3
C_5+	72-89	79-90	81-87	95.5-96.5
Ref. Index	1.454-1.425	1.441-1.423	1.436-1.428	1.421-1.419

INTRODUCTION TO TASK 2 TESTING

Task 2 (syngas) testing began with shakedown runs in July. The first successful test was in August. Since then, Task 2 testing has been in a screening mode, developing information about the metal component and relating Task 2 results to those obtained in Task 1. This syngas testing has received more emphasis as the year continued until at the present time, Task 1 testing has been suspended so that all the facilities can be used for Task 2 testing.

The testing began with a state-of-the-art Fischer-Tropsch catalyst without a shape selective component (SSC). This catalyst was used to establish conditions appropriate for testing the SSC containing catalysts This catalyst also gave results (conversion and product selectivity) against which the SSC containing catalysts could be compared.

Results of test runs in the most recent quarter are discussed in detail, followed by a summary of what has been learned thus far in Task 2 testing.

Two metal components (MC), iron and cobalt, have been studied with and without promoters. These MC's have been combined with SSC's in a number of ways; precipitation, impregnation, physical mixture, and carbonyl adsorption. Physical mixture has been an especially useful technique for screening new shape selective components. A physical mixture with α-Al_2O_3 as the "SSC" was tested to act as a more realistic reference catalyst. This catalyst has all the characteristics of the molecular sieve containing physical mixture catalysts (particle size of the MC, dilution, particle size of the SSC) except for the pore system and catalytic activity of the sieve. Test results with this catalyst are presented in the next section.

The data from this quarter is presented substantially as in the previous quarter. The simulated distillations are of the entire C_5^+ product as explained in the introduction to Task 1 testing. The carbon number product distributions now include the C_7 to C_{12} hydrocarbons. This data was absent in previous plots. Major portions of these species were analyzed in an unresolved backflush peak. This heavies peak is divided into the proper components by an "equilibrium flash" calculation. As will be seen in the plots, this calculation was quite effective in supplying the missing data.

Physical Mixture of Potassium Promoted Iron and α-Al_2O_3, Run 10011-15

The metal component of this catalyst is iron precipitated with aqueous ammonia from a boiling solution of the nitrate salt. The $Fe_2O_3 \cdot xH_2O$ was then impregnated with potassium carbonate. The MC was physically mixed with 1μ particle size α-Al_2O_3 polishing powder and pressed into pellets. This same synthesis procedure has been used in many physical mixture catalysts with the molecular sieve replacing the α-Al_2O_3. This catalyst should be a good reference for those other physical mixture catalysts.

The syngas conversion, product selectivity, percent iso- of the pentanes, and percent olefins of the C_4's are shown in Figures 25 to 28. The Schultz-Flory distributions of the samples are shown in Figures 29 to 34. The C_5^+ simulated distillation of selected samples are shown in Figures 35 to 37. The detailed data for material balances are presented in Tables 9A to 9C.

The metal component achieved high conversion of syngas at 250°C. The H_2/CO usage ratio of 0.6 indicates the catalyst could effectively use an even lower H_2/CO ratio syngas. (This does not guarantee that the catalyst would not deactivate too rapidly under those conditions; it only means that initially the H_2 and CO conversions would be similar.) The usage ratio increased, as expected, when the feed was switched from 1:1 to 2:1 syngas. These conversion results stem entirely from the metal component and therefore are fairly consistent among all the iron physical mixture catalysts.

The major effect of the shape selective component is exhibited in the detailed nature of the product selectivity. The methane yield is low but still higher than was seen with the reference iron catalyst under comparable process conditions. The difference is probably due to the preparation of the MC, the synthesis conditions and/or possibly the grinding necessary to form the physical mixture catalysts reported last quarter. The C_5^+ yield is quite good, accounting for almost 70% of the hydrocarbons produced by weight. The plots of the hydrocarbon distribution by carbon numbers, Figures 29 to 34, show the initial samples have excellent adherence to a Schulz-Flory distribution: that is, the plot of ln(Wn/n) vs n (where n is the carbon number) is linear. The later samples show more deviation, but not the two α's with a distinct break at C_{20} which was evident in the reference iron catalyst performance. An example of this behavior is presented in Figure 38. The major deviation occures in samples 10 and 12. It appears that the gas phase product (C_1-C_7) has a lower α (higher slope) than the liquid product (C_8-C_{40}). This is due to the longer time it takes for the wax produced at 250°C and 1:1H_2:CO feed (samples 1-8) to completely leave the reactor and have the heavy hydrocarbon distribution accurately reflect the products produced at the new reaction conditions, 280°C and 2:1 H_2:CO feed. The initial buildup of this wax in the reactor can be observed by looking at the increase in the 700°F+ product in the initial samples. These products build up in the reactor and only gradually reach their true levels in the collected products. This was very evident in the reference iron catalyst where the 700°F+ product was less than 1% in the first sample and was over 25% two days later with no process condition changes. Some of this may have been due to initial changes in the catalyst but most of it is due to buildup of the product inside the reactor. Due to this phenomenon samples 5 to 8 are more indicative of the true product distribution at 250°C than are the initial samples in this run. Samples 11 to 13 are also more indicative of the products produced at 280°C than are samples 9 and 10.

The quality of the C_5^+ product, gasoline octane number, is important to the analysis of the effect of the molecular sieve in this type of catalyst. The simulated distillation of C_5^+ product from sample 8 is presented in Figure 36. The distillation is smooth except where gas phase products have been included, showing that no single hydrocarbon is predominant in the product. Figure 28 shows the C_4's are mainly olefinic. The refractive index and density suggest the condensed product is also olefinic.

Figure 27 shows the C_5 paraffins are mainly n-pentane with little iso-pentane. The iso/normal ratio is similar to what was seen with the reference catalyst. The actual chromatogram from the ASTM simulated distillation, seen in Figure 39, shows that not only are the C_5 paraffins dominated by the normal but the entire liquid product is also dominated by normals. These are recognizable by the regular spacing of the individual peaks. This dominance of normals was also seen with the reference iron catalyst as is obvious from Figure 40.

The high percentage of normals has two important effects on the quality of this C_5^+ product. The first is that the gasoline produced has a very poor octane number, 55. The gasoline boiling range product needs extensive upgrading before it is usable as gasoline. The second effect is on the heavier product, the diesel oil. Straight chain products pack well together and therefore are solids at fairly high temperatures. The pour point of the C_5^+ product was above room temperature. It was a solid coming out of the reactor. While the cetane index of the normals may be very high, the diesel oil must be dewaxed to lower the pour point before it can be used as fuel.

This hydrocarbon product is very similar to what was produced by the reference iron catalyst. This catalyst had a somewhat lower α, that is a tendency to produce lighter products. This is probably a particle size effect. The much greater changes seen with the molecular sieve containing catalysts, reported last quarter, are due to the catalytic action of the molecular sieve and not due to changes in the metal component during catalyst preparation.

FIGURE 25

1001115

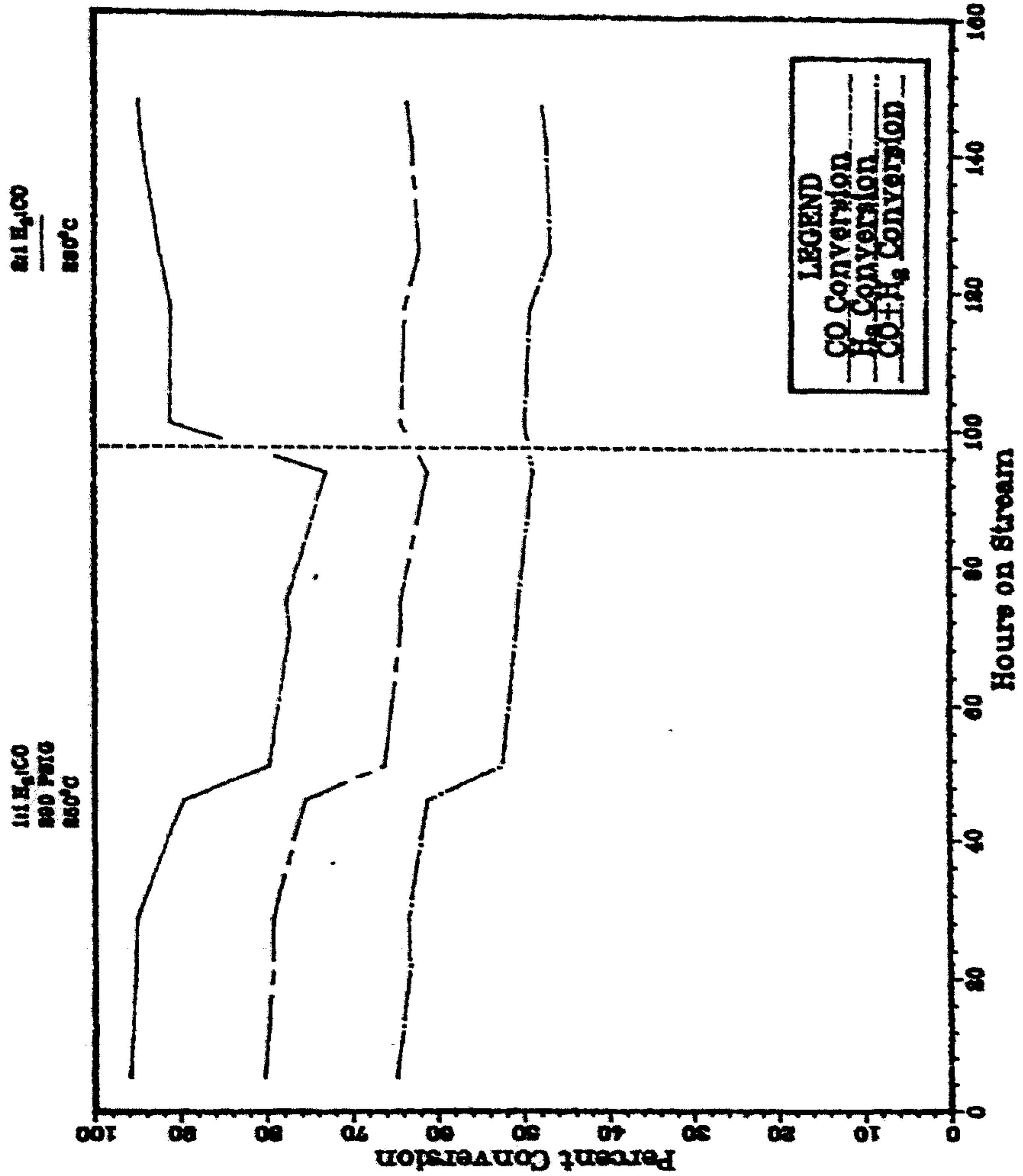
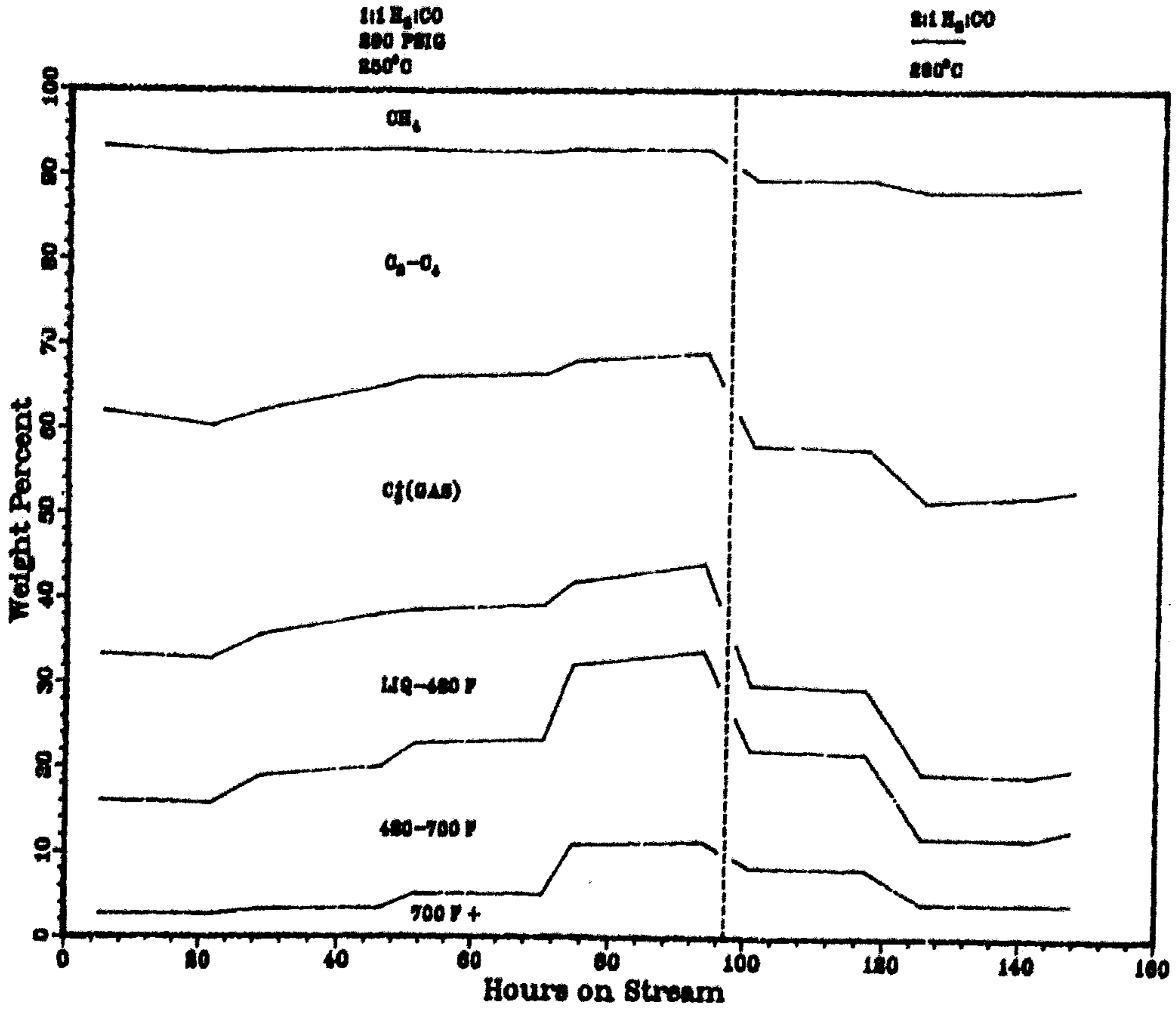


FIGURE 26


1:1 H2:CO
300 PSIG
250°C
2:1 H2:CO
260°C
CH4
C2-C4
C5+(GAS)
LIQ-480 F
480-700 F
700 F +
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160

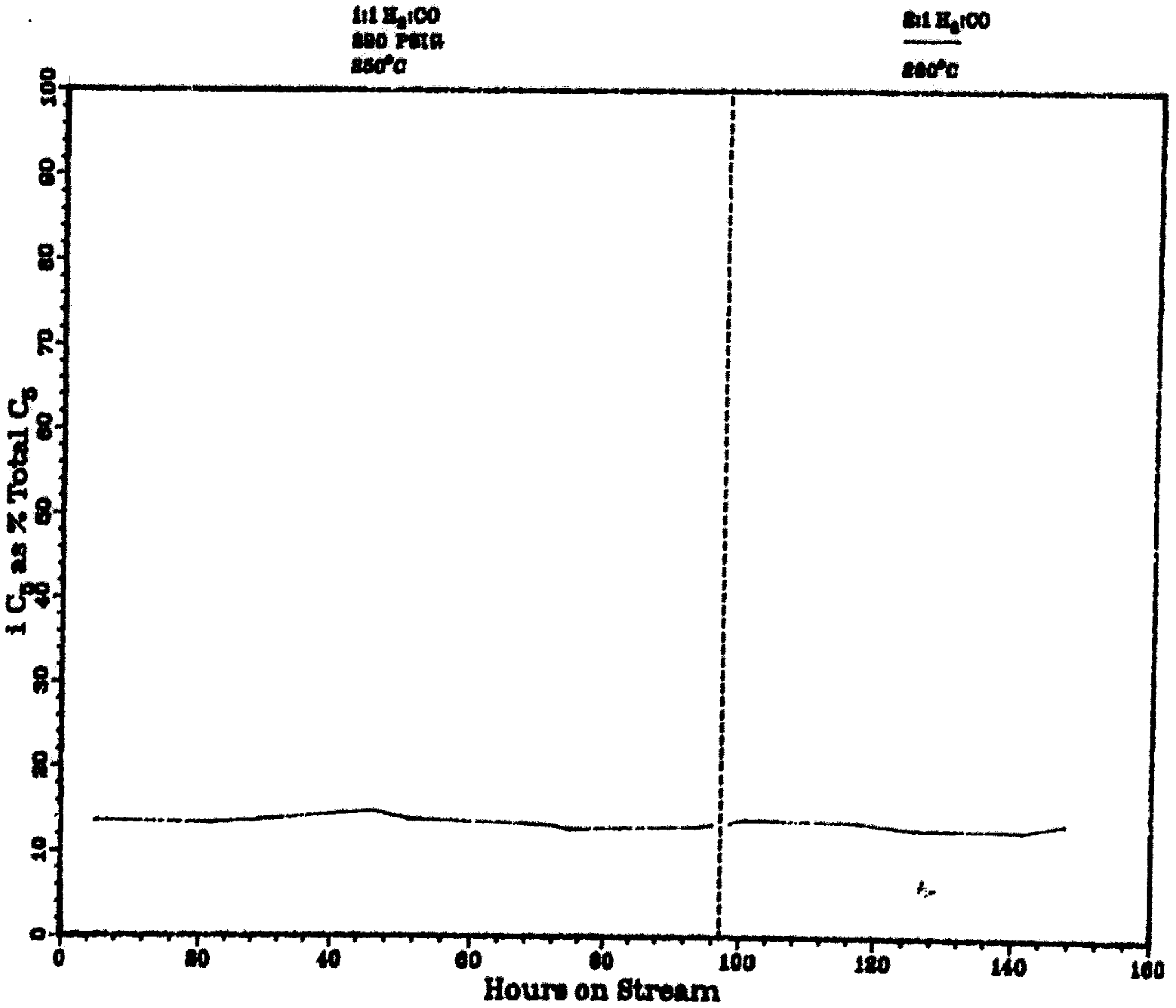

1:1 H_2:CO
280 PSIG
250°C
2:1 H_2:CO
250°C
1 C_5 as % Total C_5
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160

FIGURE 27

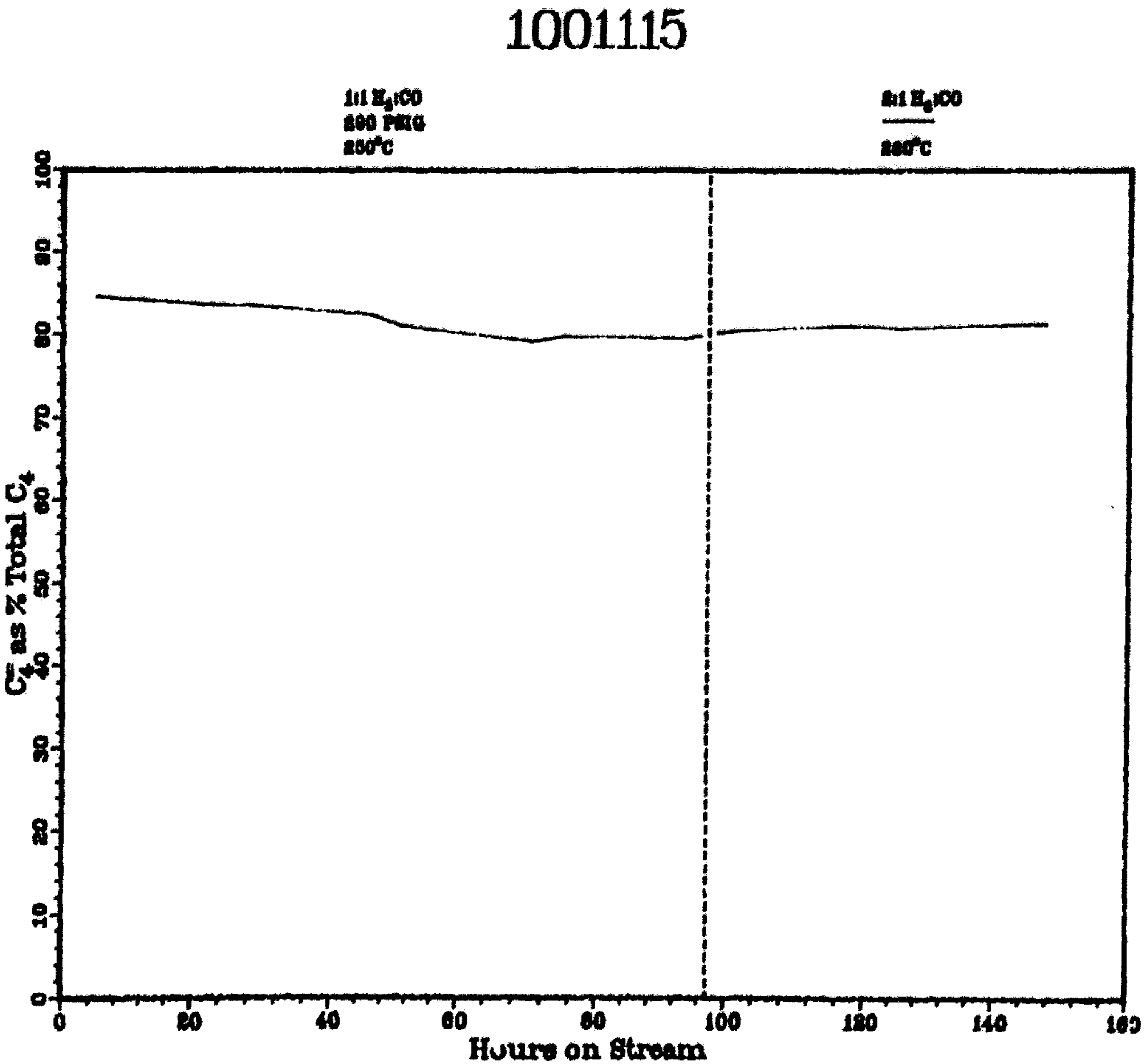

1001115
1:1 H_2:CO
300 PSIG
250°C
2:1 H_2:CO
250°C
$C_4^=$ as % Total C_4
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160

FIGURE 28

FIGURE 29

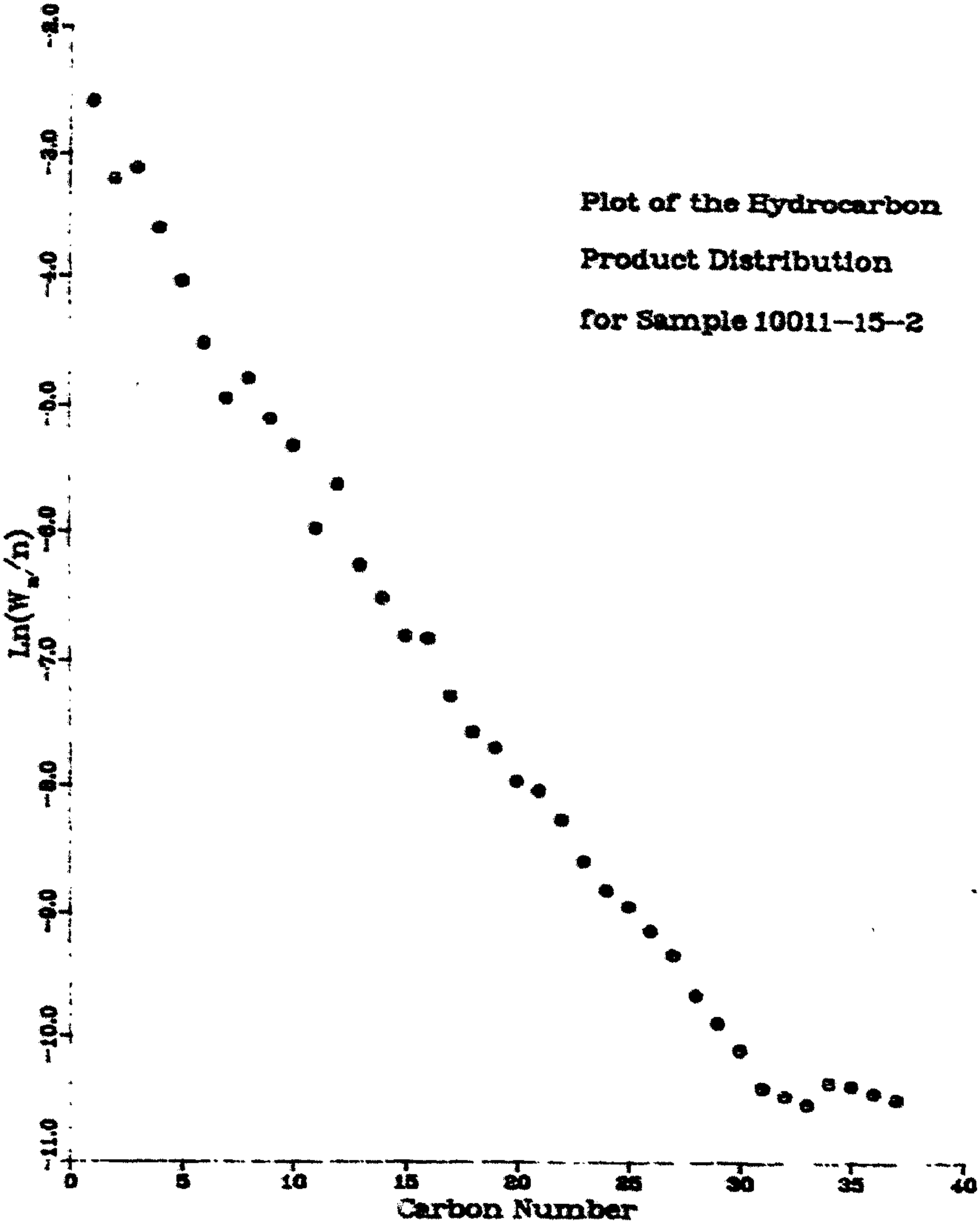

Plot of the Hydrocarbon Product Distribution for Sample 10011-15-2

FIGURE 30

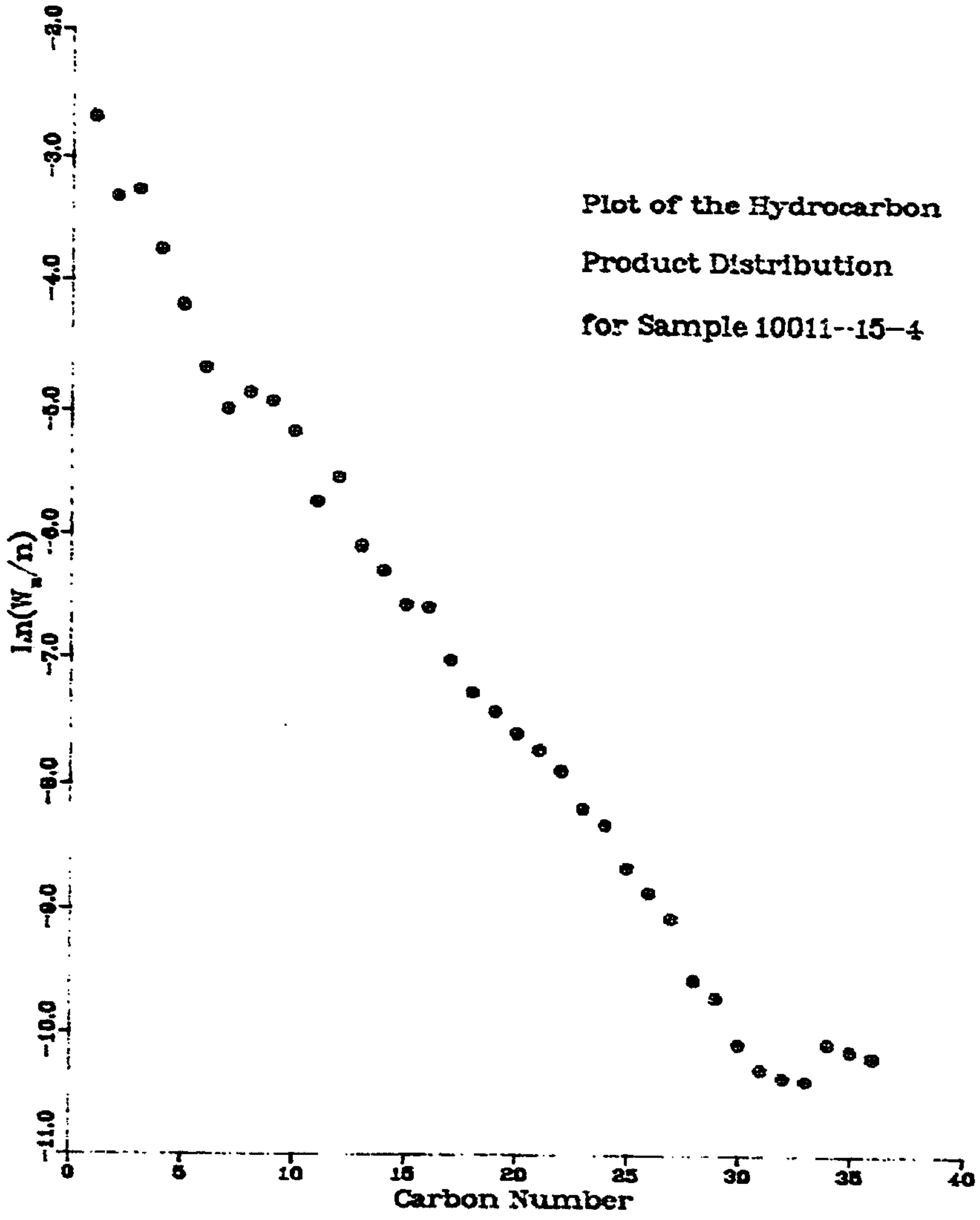
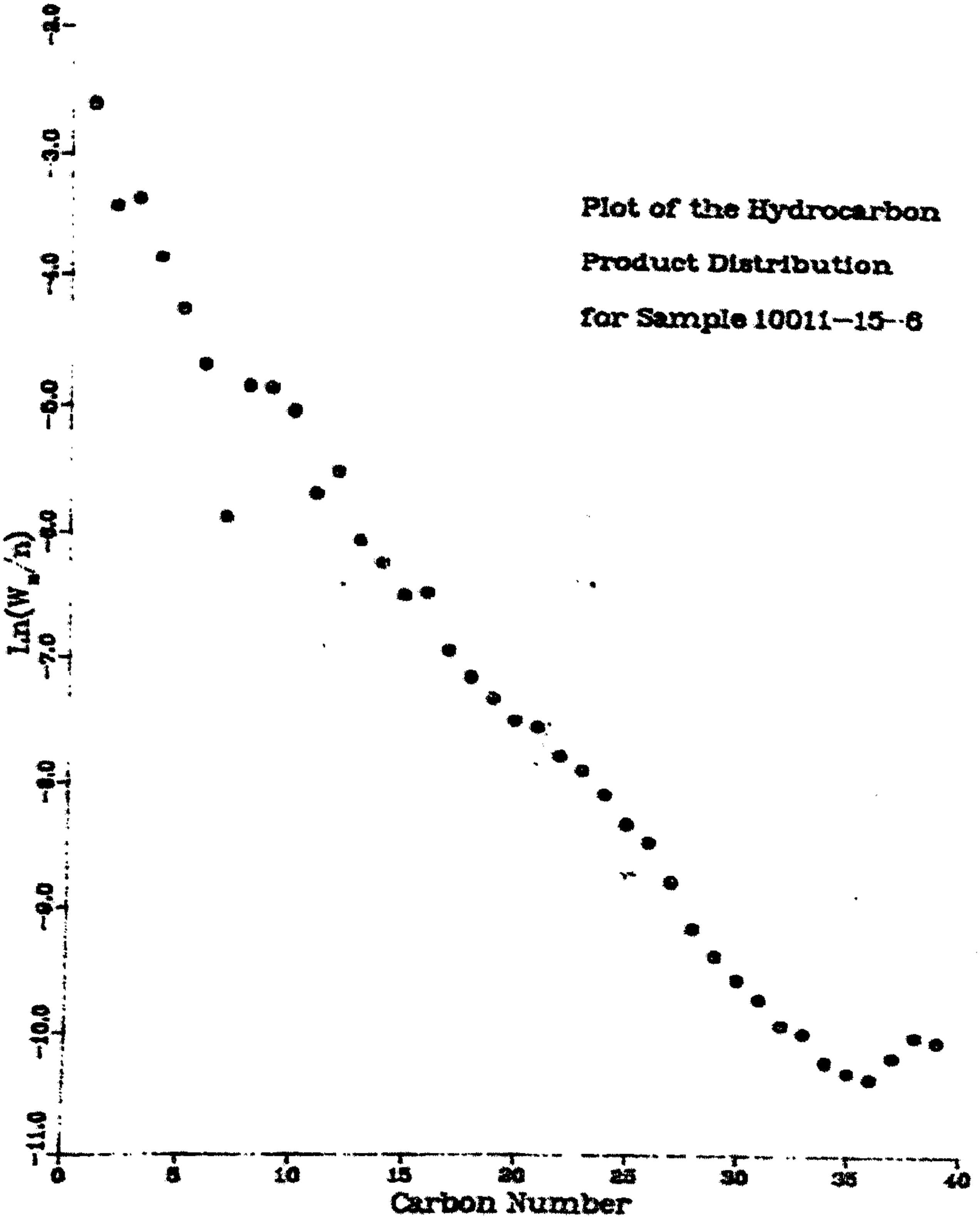

Plot of the Hydrocarbon
Product Distribution
for Sample 10011--15-4
ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

FIGURE 31



Plot of the Hydrocarbon
Product Distribution
for Sample 10011-15-6
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
Ln(W_n/n)
0
5
10
15
20
25
30
35
40
Carbon Number

FIGURE 32

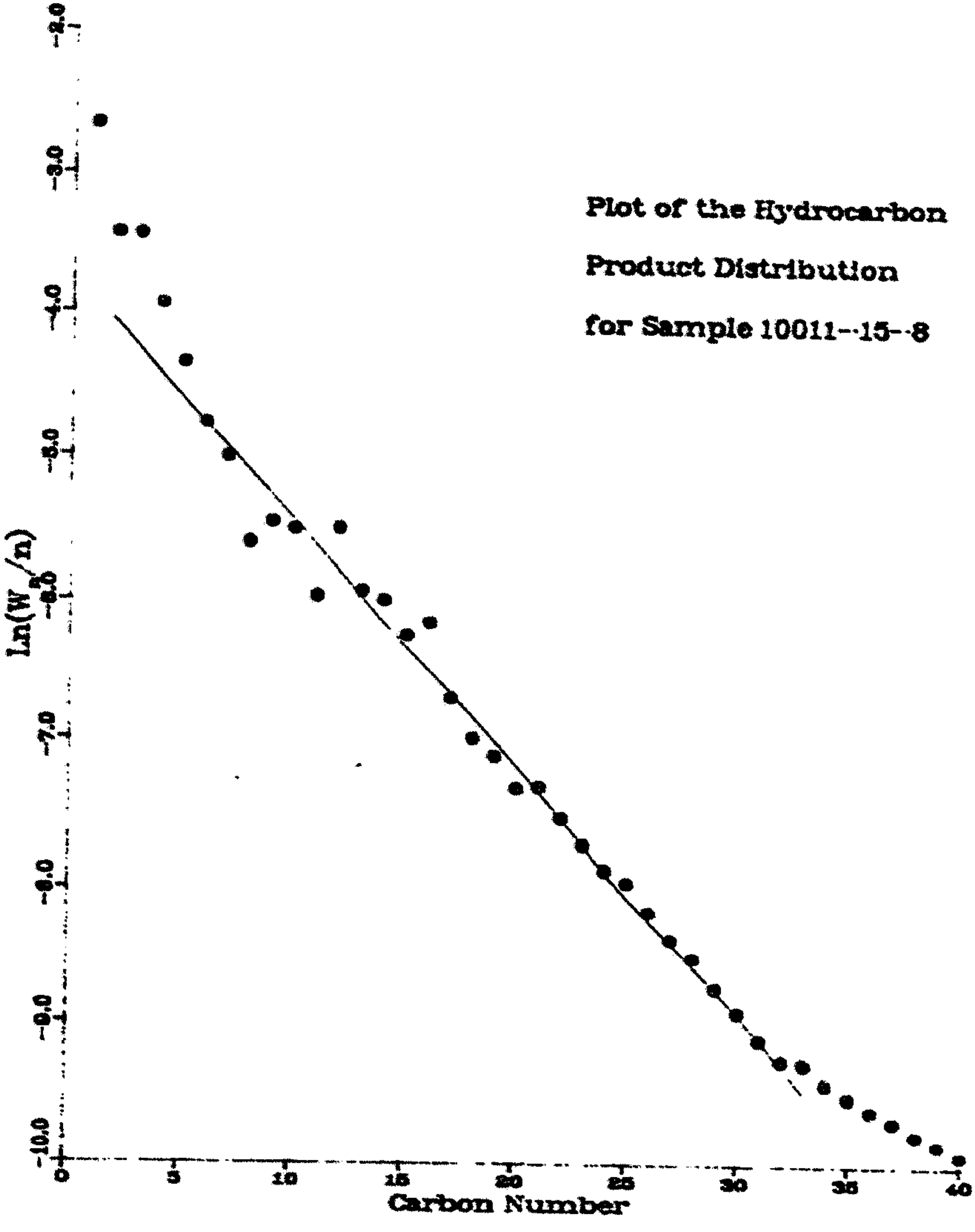
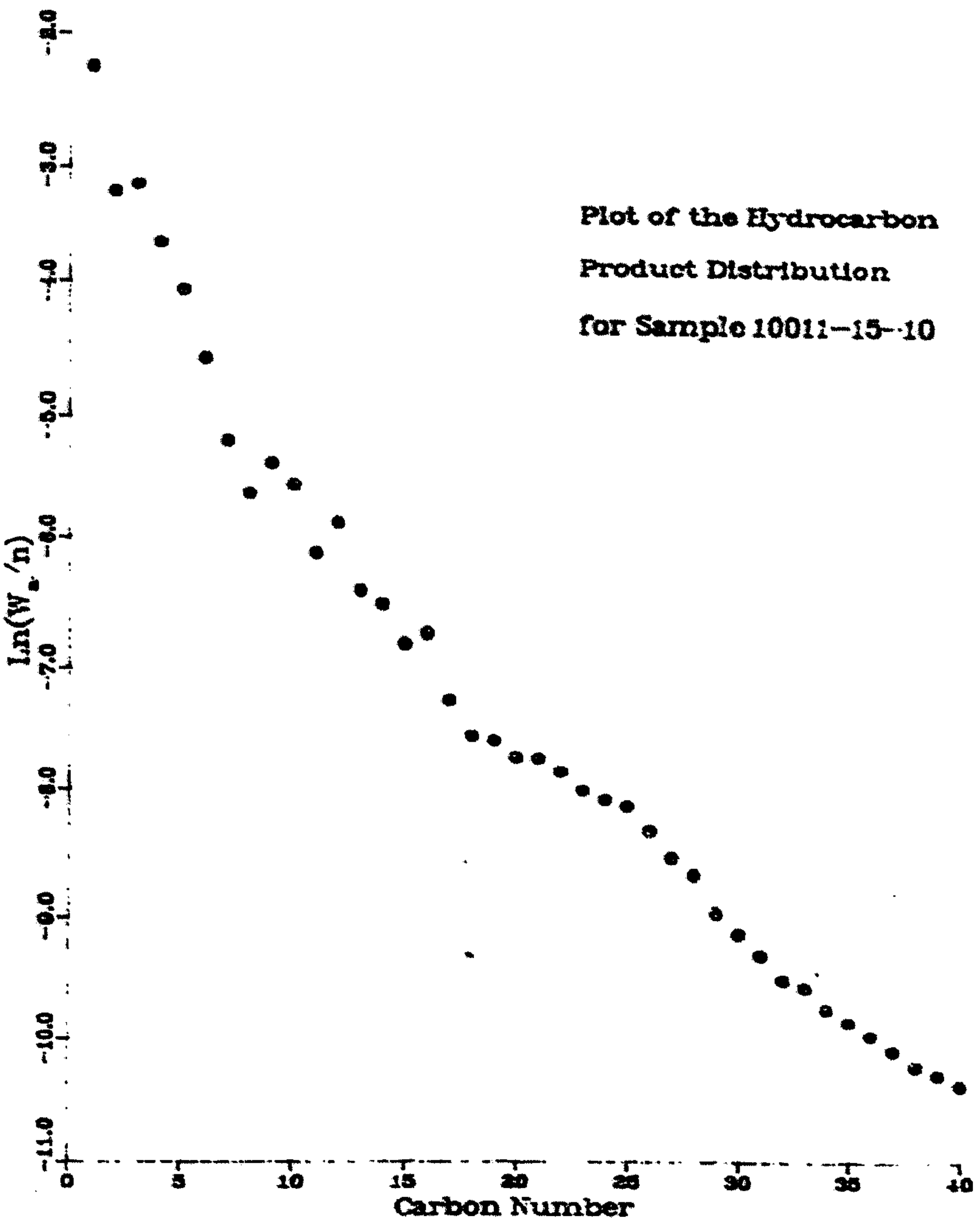

Plot of the Hydrocarbon
Product Distribution
for Sample 10011--15--8
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
Ln(W_n/n)
0
5
10
15
20
25
30
35
40
Carbon Number

FIGURE 33



Plot of the Hydrocarbon
Product Distribution
for Sample 10011-15-10