

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	64.55	65.32	64.77	66.29
C5 - 420 F	32.14	29.88	31.02	29.96
420-700 F	2.71	3.73	3.56	3.23
700-END PT	0.60	1.07	0.64	0.52
C5+-END PT	35.45	35.68	35.23	33.71
ISO/NORMAL MOLE RATIO				
C4	0.1059	0.1029	0.1037	0.1101
C5	0.5871	0.5753	0.5699	0.5485
C6	2.3216	2.3079	2.2315	2.2246
C4=	0.1712	0.1709	0.1727	0.1753
PARAFFIN/OLEFIN RATIO				
C3	5.7670	5.7780	5.9220	5.6236
C4	1.7020	1.6979	1.7205	1.7486
C5	26.1179	26.4316	27.2000	27.7363
LIQ HC COLLECTION				
PHYS. APPEARANCE	GREEN OIL	---	GREEN OIL	GREEN OIL
DENSITY	0.763	---	0.760	0.758
N, REFRACTIVE INDEX	1.4310	- -	1.4305	1.4306
SIMULT'D DISTILATN				
10 WT % @ DEG F	254	- -	254	253
16	286	- -	285	284
50	363	- -	393	391
84	544	- -	564	556
90	621	- -	635	626
RANGE(16-84 %)	258	---	279	272
WT % @ 420 F	69.80	---	59.70	60.30
WT % @ 700 F	94.50	- -	93.90	94.50

Potassium Promoted Iron Precipitated on UCC-101, Run 10011-11

The iron was precipitated by the addition of aqueous ammonia to a boiling slurry of ferric nitrate and UCC-101. The dried metal loaded molecular sieve was impregnated with potassium carbonate solution, dried, pressed into pellets and air-calcined at 250°C. The effect of promotion can be determined by comparison of this catalyst to the one used in Run 10011-7, reported last quarter, since the major difference is the addition of promoter. The effects of the method of metal incorporation can be determined by comparison of this run with Run 10011-9. The two catalysts involved have the same elements present. The difference is that one was a physical mixture of the MC and SSC, the other had the MC precipitated on the SSC.

The conversion, product selectivity, percent iso- of the pentanes, and percent olefins of the C₄'s are presented in Figures 67 to 70. Figures 71 to 75 contain the carbon number product distribution, S-F plots. The detailed material balances are given in Tables 11A and 11B.

The conversion of syngas is much lower than in the physical mixture catalysts. There are a number of factors contributing to this lower activity. The first is that less iron is present in this precipitation catalyst than in the physical mixture catalysts. This catalyst contains only 75% as much iron as the catalyst used in the corresponding physical mixture, Run 10011-9. Another possible factor is the difference in the iron surface area in the reduced catalysts. This difference is not adequately determined yet. The other possible cause for a lower activity is a metal support effect with the molecular sieve. The syngas conversion activity which was present was quite constant. It showed essentially no deactivation.

The H₂/CO usage ratio was much higher than with the physical mixture catalysts. Much of the oxygen from the carbon monoxide went into water production instead of carbon dioxide. This means the catalyst has lower water gas shift (WGS) activity. Introduction

of WGS activity is one of the effects of potassium promotion. This catalyst has an 80% higher potassium to iron ratio than the physical mixture catalyst. It is obvious that most of the potassium added to the catalyst is not going into promotion of the iron. It is probably being tied up by the molecular sieve. This has an effect not just on the lower WGS activity but also should affect the molecular sieves ability to isomerize the F-T products.

As with the conversion, the product selectivity does not show gradual changes due to deactivation. The methane yield is high, similar to what was seen in Run 10011-10, the physical mixture of iron plus UCC-104. The total C_5^+ yield from this catalyst is generally higher than that of Run 10011-10. The carbon number product distribution plots, Figures 71 to 75, show deviation from S-F behavior. This is not a double α deviation. There seems to be a carbon number cutoff above C_{25} caused by UCC-101. While it is possible that these deviations are due to errors in the analyses, comparable samples from other runs do not show such large deviations.

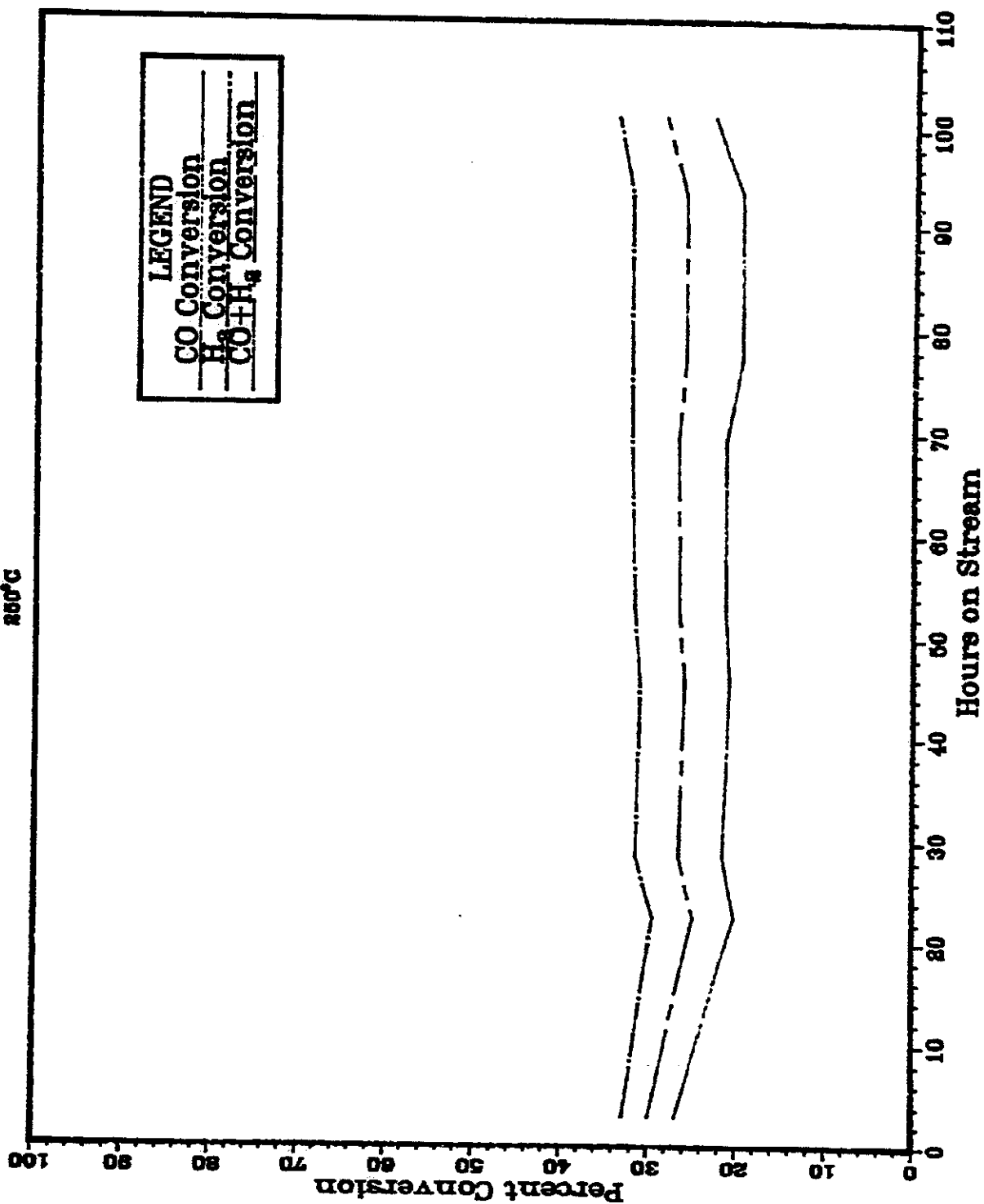
Up to 55% of the hydrocarbons produced boil in the gasoline or diesel range. This is better than the physical mixture with UCC-104, Run 10011-10. It is comparable to the amount produced by a physical mixture with UCC-101 or the unpromoted iron precipitated on UCC-101. The quality of this product is an important aspect of this catalyst's chemistry. The C_4 's are olefinic as is the liquid product, based on the density and refractive index. The condensed product is liquid at room temperature while a comparably heavy sample from the reference iron catalyst was a solid. The product must therefore be more isomerized than that of the reference catalyst, even though pentanes are isomerized only to the same extent as with the reference catalyst. The chromatogram from the simulated distillation of the condensed product, Figure 76, shows the liquid product is dominated by normals. It is somewhat isomerized but is not even close to what was seen in Run 10011-10 or even what was seen in the corresponding unpromoted Fe on UCC-101 catalyst used in Run 10011-7, Figure 77.

Migration of the potassium to the molecular sieve would explain both the low WGS activity of this catalyst and its decreased isomerization ability.

The potassium did have some effect on the metal component. Without the promotion the catalyst did not produce any diesel range product. With this catalyst, over 12% of the hydrocarbons produced boils above the gasoline range. As is obvious from the WGS activity, the product isomerization and chain growth probability, the potassium promoter is added to both the MC and SSC and has its effect on both of these components. This catalyst has definite tradeoffs. Increasing the chain growth probability and WGS activity of the MC through potassium promotion is accompanied by a decrease in the molecular sieve activity.

For a specific application, the level of promotion selected will be as high as possible (for WGS and chain growth) without reducing product quality (achieved by the isomerization activity of the molecular) below an acceptable level.

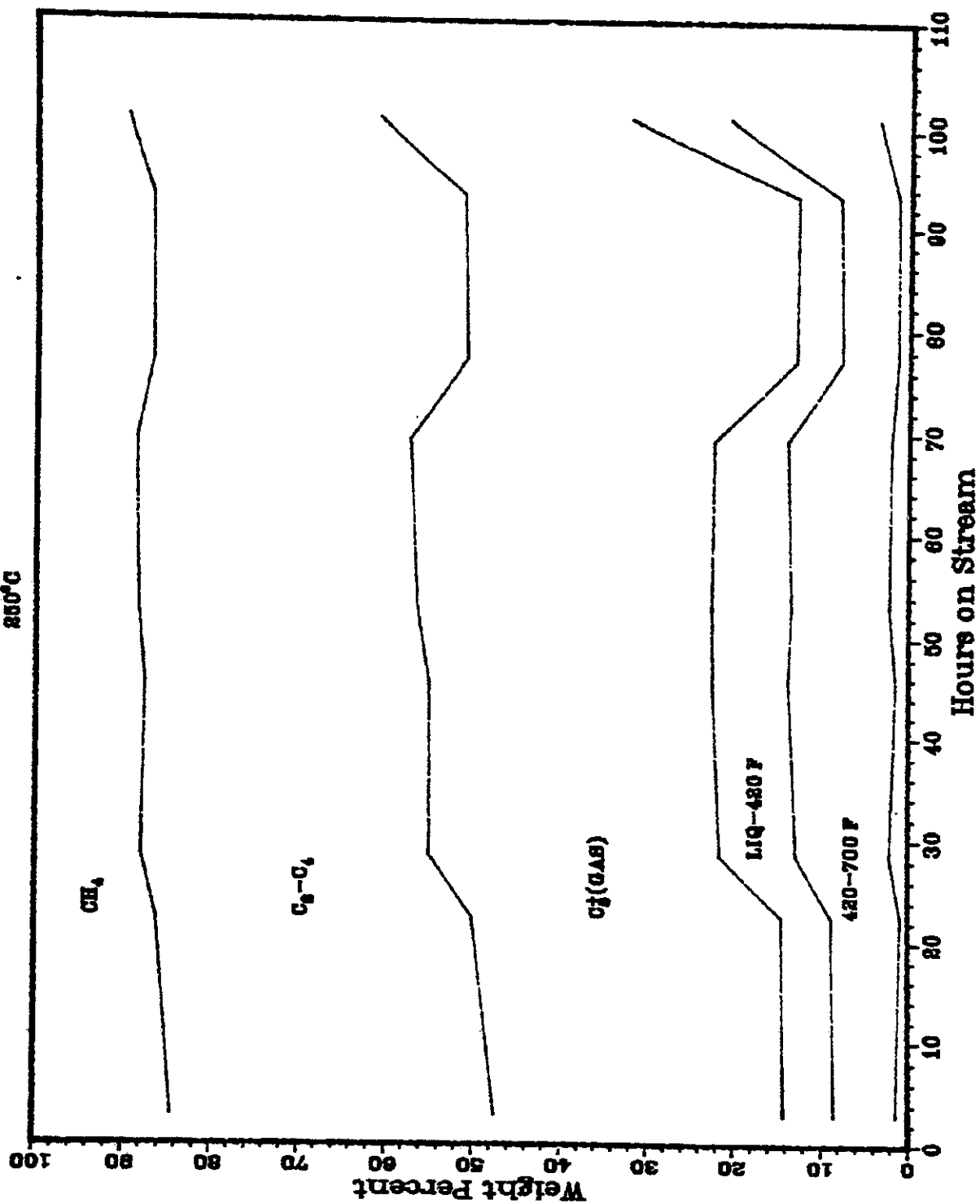
FIGURE 67



1001111

144 H₂CO
300 PSIG
250°C

FIGURE 68



1001111

111 H₂CO
300 FBIG
250°C

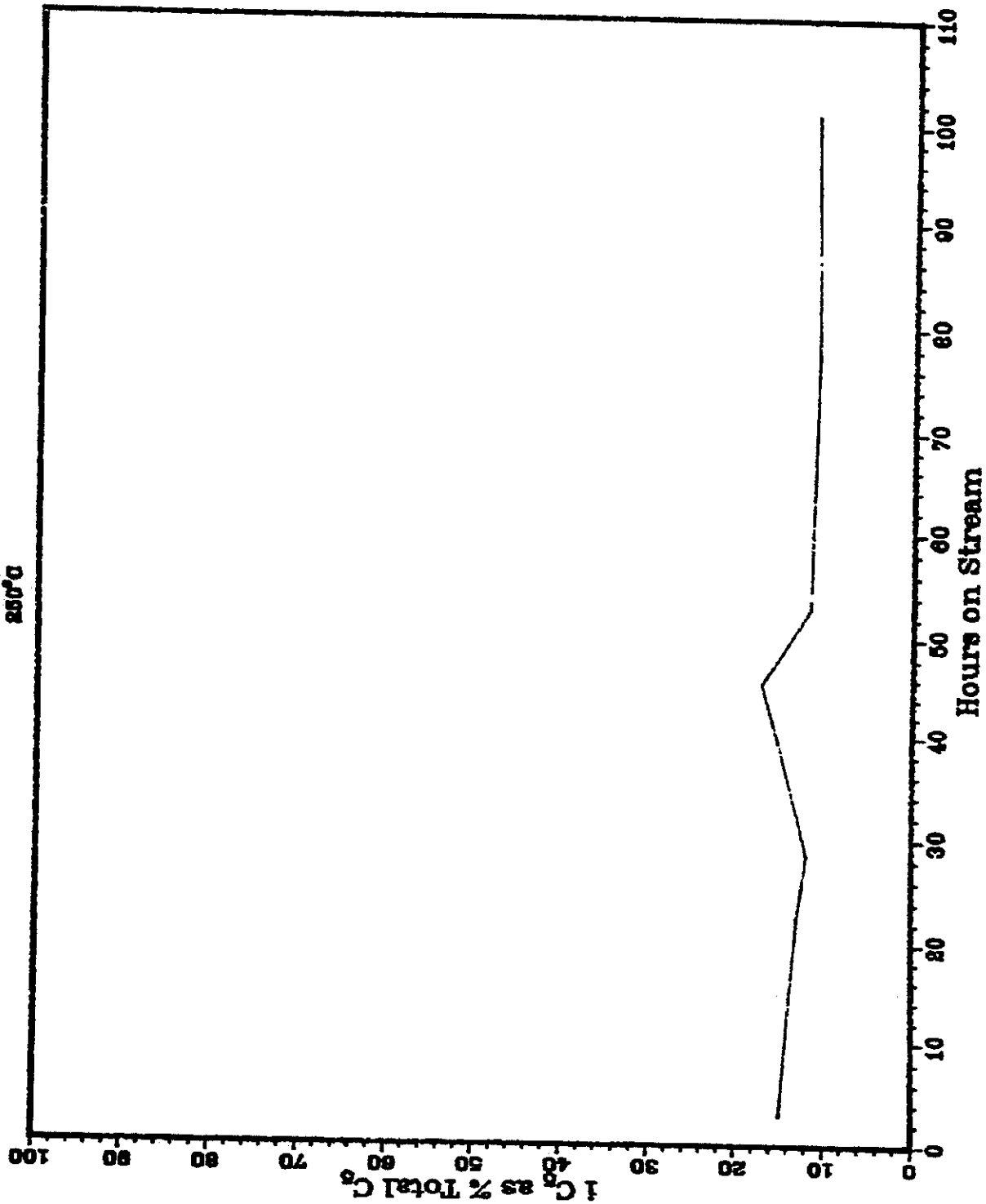


FIGURE 69

FIGURE 70

1001111

111 H₂CO
300 PSIG
250°C

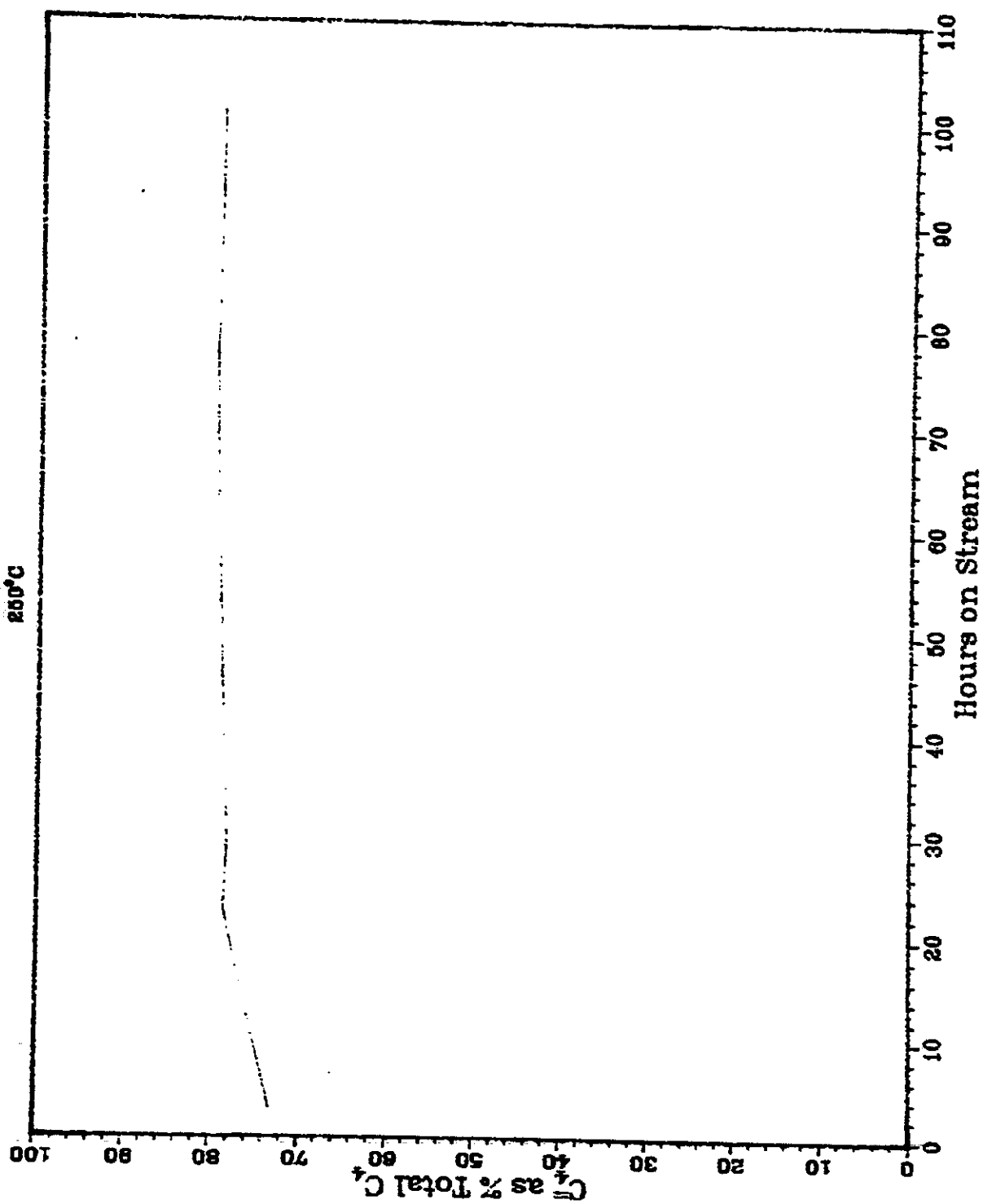


FIGURE 71

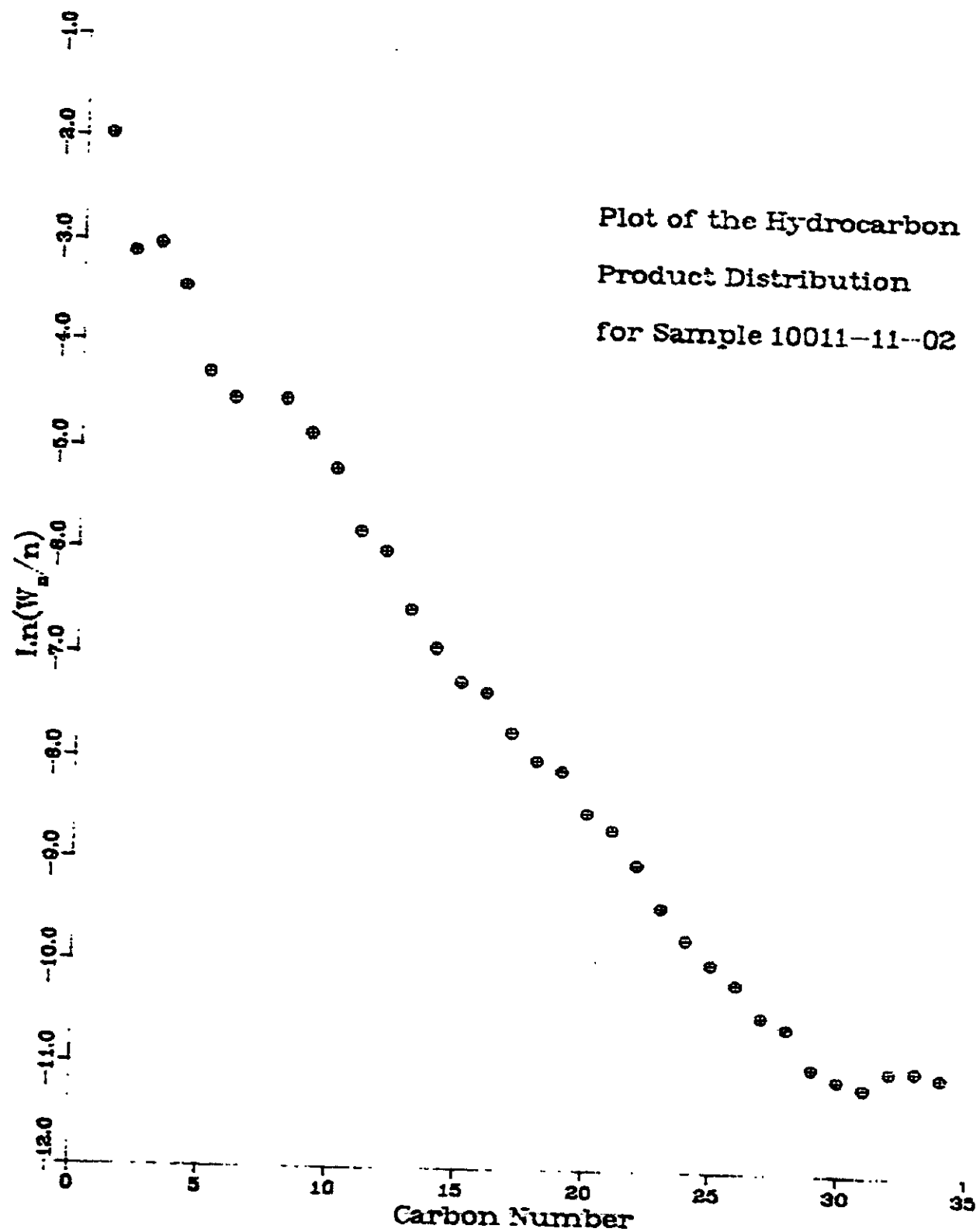


FIGURE 72

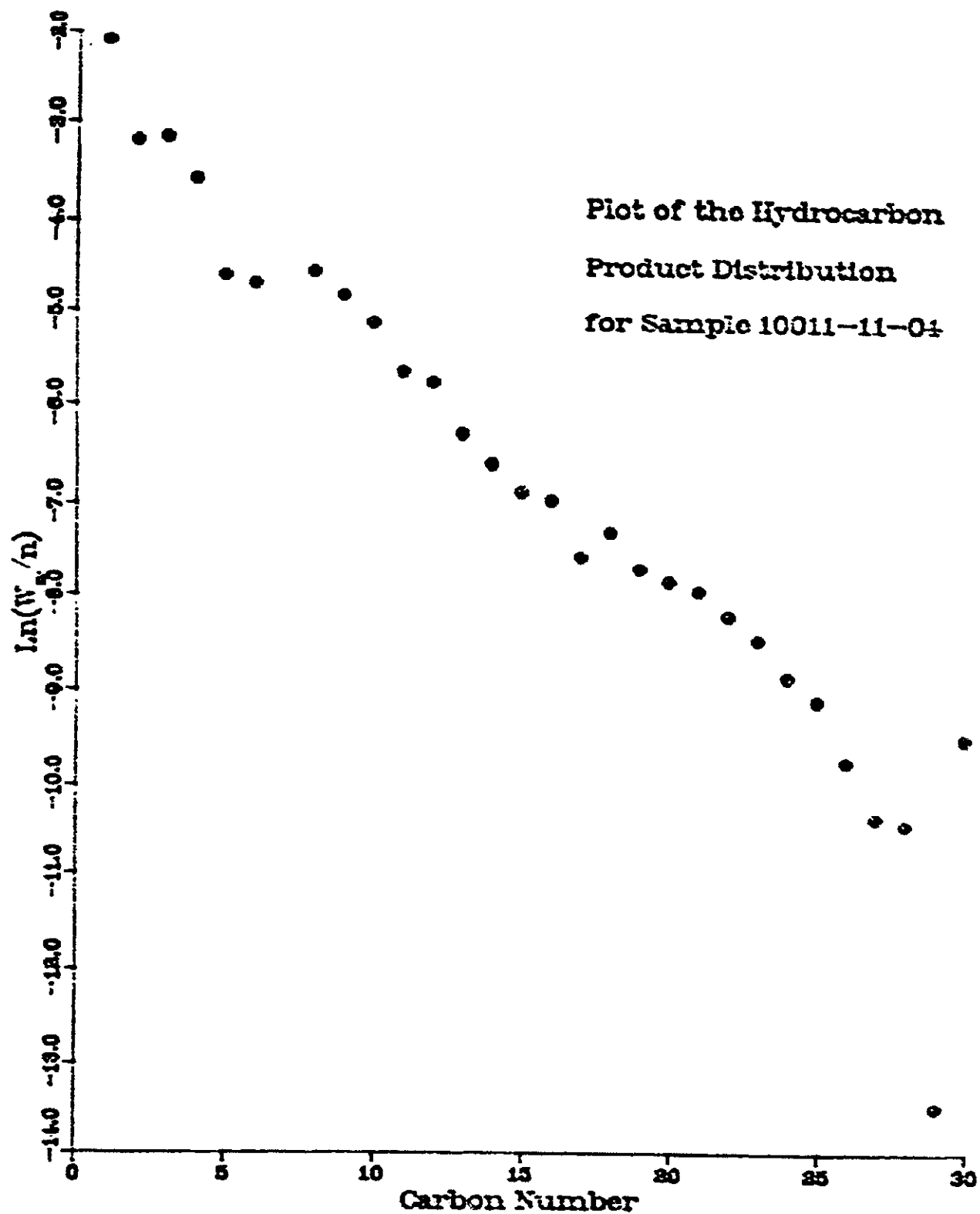


FIGURE 73

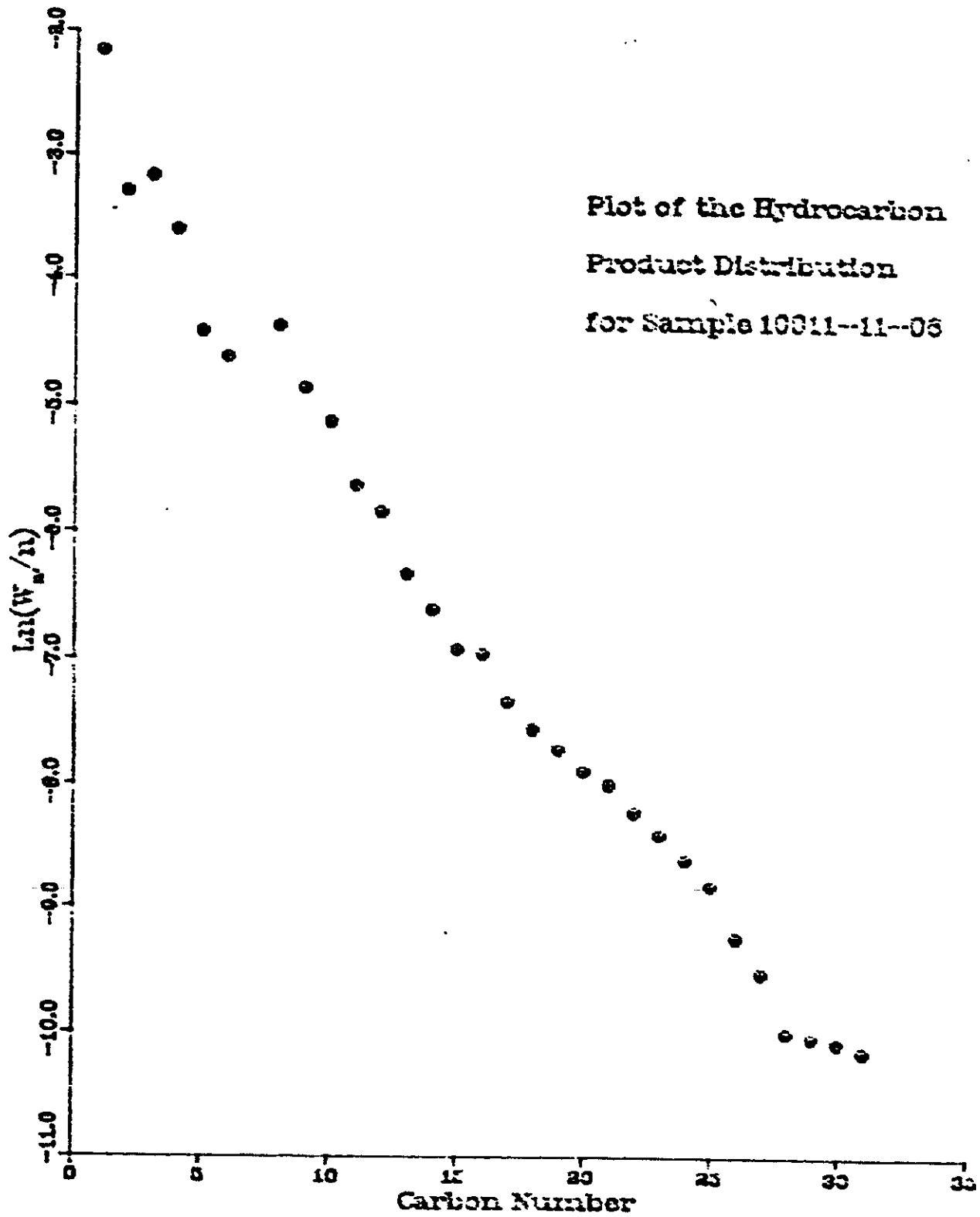


FIGURE 74

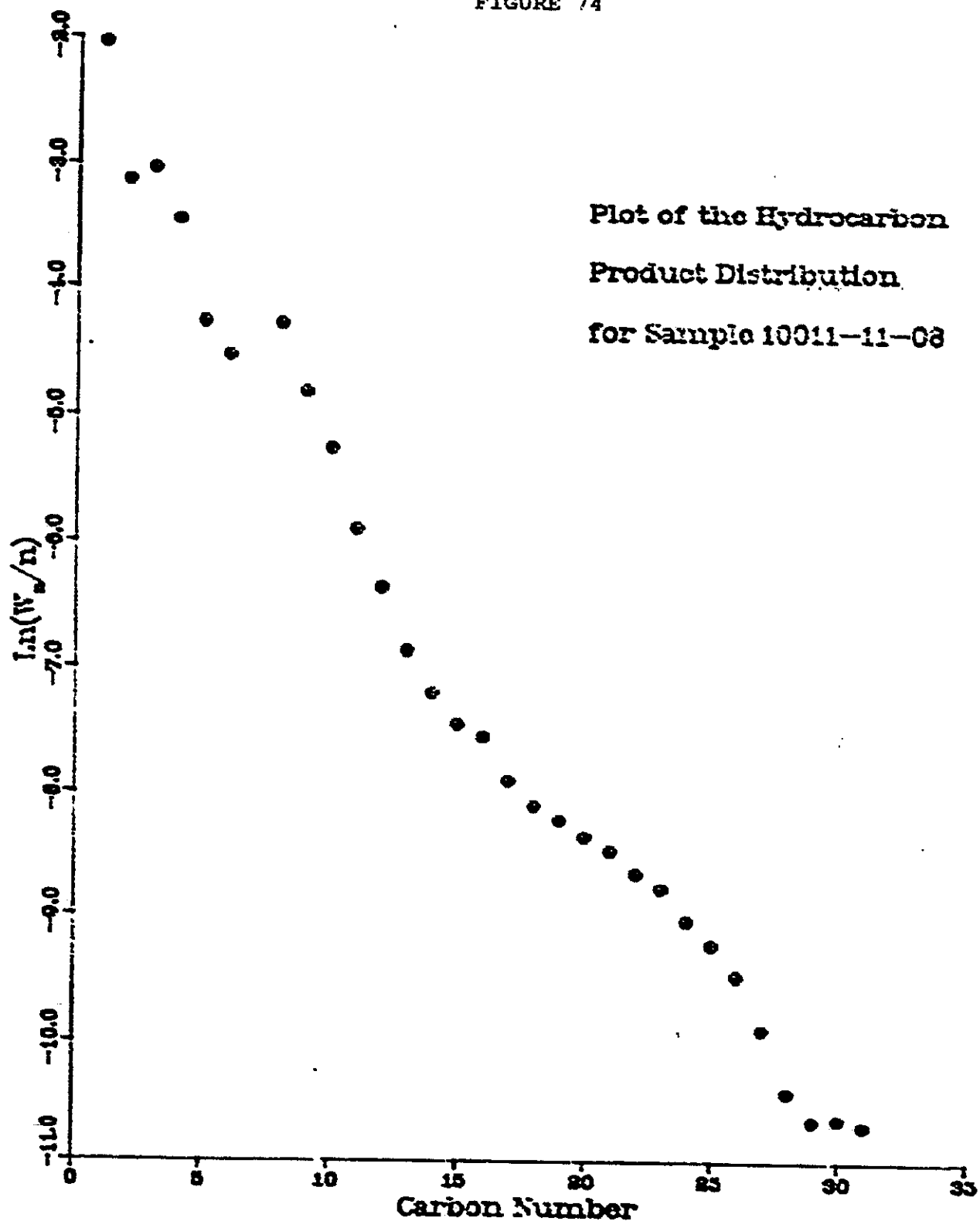
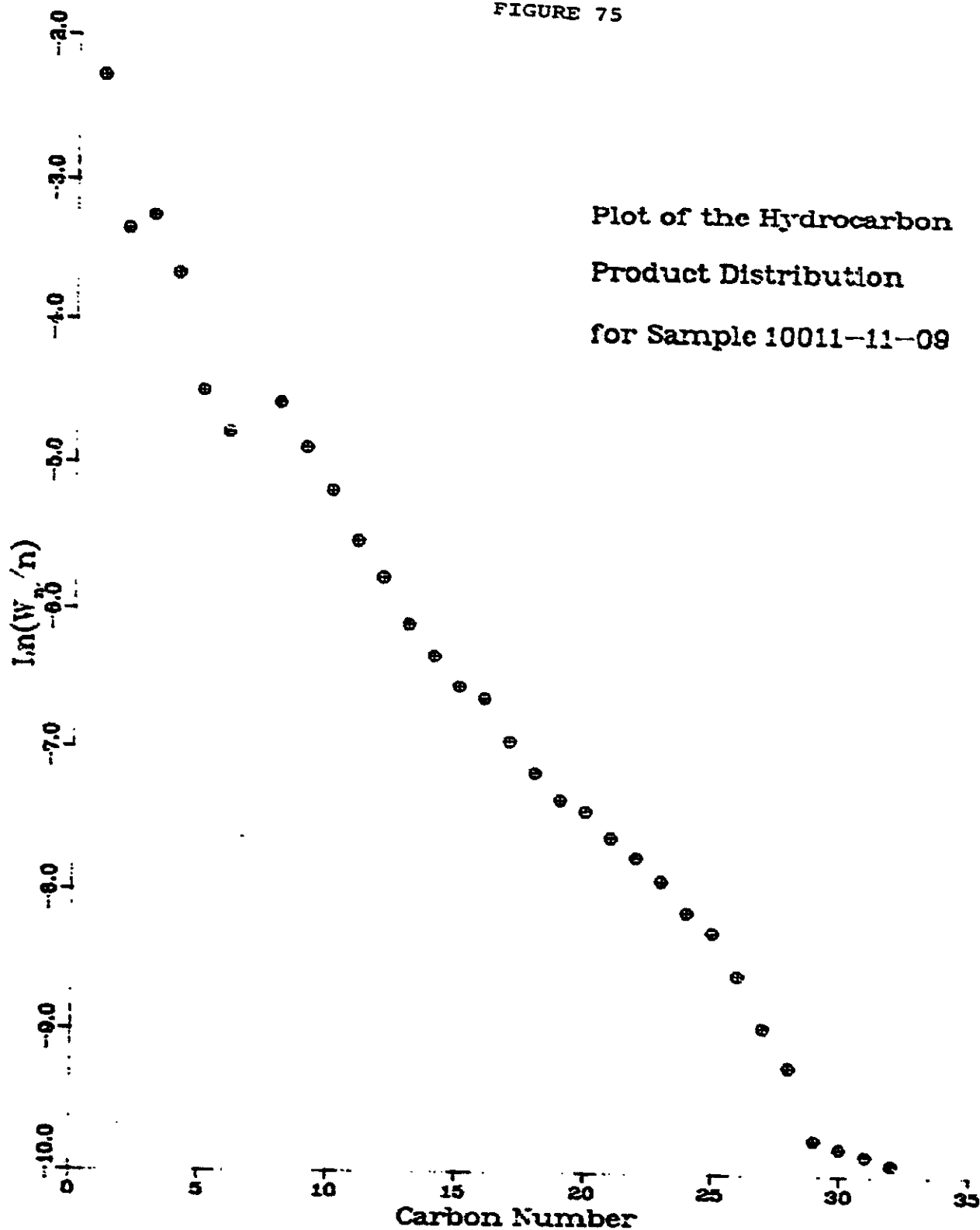


FIGURE 75

Plot of the Hydrocarbon
Product Distribution
for Sample 10011-11-09



RT: SLICES 0.20

FIGURE 76

IN ORDER TO OBTAIN A CORRELATION OF THE DATA

A CORRELATION OF THE DATA

RT: STOP 1.00

DATE: 11-11-66

RT: 3.1CES 0.20

FIGURE 77

D10011-7-166

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

TABLE 11A RESULT OF SYNGAS OPERATION

RUN NO.	10011-11				
CATALYST	FE-PPT-UCC-101+K #10042-63 80CC 48.3GM(55.6G AFTER RUN,+7.3G)				
FEED	H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10011-11-01	011-11-02	011-11-03	011-11-04	011-11-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	3.0	22.58	28.58	45.58	53.0
PRESSURE,PSIG	299	298	300	290	293
TEMP. C	248	248	248	248	248
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	3.00	22.58	6.00	23.00	7.42
EFFLNT GAS LITER	51.85	439.49	119.92	458.63	147.92
GM AQUEOUS LAYER	2.73	20.53	5.99	22.98	7.74
GM OIL	0.43	3.25	1.49	5.70	1.93
MATERIAL BALANCE					
GM ATOM CARBON %	88.97	97.37	102.60	102.33	102.43
GM ATOM HYDROGEN %	91.50	100.63	105.25	103.92	105.65
GM ATOM OXYGEN %	97.64	102.68	106.79	107.15	106.78
RATIO CHX/(H2O+CO2)	0.6192	0.7232	0.7946	0.7635	0.7892
RATIO X IN CHX	2.4213	2.3615	2.3194	2.3217	2.3116
USAGE H2/CO PRODT	1.0641	1.3232	1.3646	1.3549	1.3929
RATIO CO2/(H2O+CO2)	0.4303	0.3073	0.2948	0.2937	0.2783
K SHIFT IN EFFLNT	0.71	0.41	0.37	0.37	0.35
CONVERSION					
ON CO %	26.84	20.32	21.66	21.05	21.49
ON H2 %	32.82	29.51	31.53	31.22	31.89
ON CO+H2 %	29.87	24.99	26.66	26.17	26.77
PRDT SELECTIVITY,WT %					
CH4	15.55	13.77	12.08	12.40	11.73
C2 HC'S	8.92	8.92	7.95	8.29	7.99
C3H8	4.53	3.34	3.00	2.93	2.91
C3H6=	10.43	11.20	10.49	9.99	9.91
C4H10	3.62	2.78	2.57	2.47	2.40
C4H8=	9.53	9.84	8.93	8.92	8.74
C5H12	4.05	3.33	2.89	1.94	2.89
C5H10=	1.83	3.50	3.10	3.18	3.31
C6H14	4.54	3.27	3.17	2.87	3.11
C6H12= & CYCLO'S	4.14	3.17	2.92	2.76	2.97
C7+ 1N GAS	18.62	22.29	21.28	21.77	21.47
L1Q HC'S	14.25	14.58	21.62	22.48	22.57

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	52.57	49.85	45.02	44.99	43.67
C5 -420 F	38.88	41.33	42.00	41.16	42.79
420-700 F	7.13	7.88	10.81	12.32	11.28
700-END PT	1.43	0.95	2.16	1.53	2.26
C5+-END PT	47.43	50.15	54.98	55.01	56.33
ISO/NORMAL MOLE RATIO					
C4	0.0844	0.0685	0.0800	0.0878	0.0849
C5	0.1750	0.1483	0.1354	0.2067	0.1318
C6	0.4639	0.3732	0.3908	0.3505	0.2956
C4±	0.0760	0.0746	0.0761	0.0718	0.0694
PARAFFIN/OLEFIN RATIO					
C3	0.4142	0.2849	0.2732	0.2802	0.2805
C4	0.3665	0.2726	0.2779	0.2671	0.2646
C5	2.1536	0.9272	0.9065	0.5944	0.8467
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	YL-BR OIL	---	YL-BR OIL	--
DENSITY	---	0.772	---	0.768	---
N, REFRACTIVE INDEX	---	1.4326	---	1.4328	--
SIMULT'D DISTILLATION					
10 WT % @ DEG F	---	332	---	332	--
16	---	343	---	344	---
50	---	456	---	470	---
84	---	618	---	633	---
90	---	661	---	674	---
RANGE(16-84 %)	---	275	---	289	--
WT % @ 420 F	---	39.50	---	38.40	---
WT % @ 700 F	---	93.50	---	93.20	---

TABLE 11B

RESULT OF SYNGAS OPERATION

RUN NO. 10011-11
 CATALYST FE-PPT-UCC-101+K #10042-63 80CC 48.3G (55.6G AFTER RUN.+7.3G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-11-06 011-11-07 011-11-08 011-11-09

FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	69.33	77.16	93.33	101.08
PRESSURE, PSIG	294	295	295	296
TEMP. C	248	248	248	248

FEED CC/MIN	400	400	400	400
HOURS FEEDING	23.75	7.83	24.00	7.75
EFFLNT GAS LITER	471.74	156.05	478.30	153.78
GM AQUEOUS LAYER	24.76	9.75	29.88	8.46
GM OIL	6.17	1.04	3.20	3.26

MATERIAL BALANCE

GM ATOM CARBON %	103.26	101.41	101.54	105.29
GM ATOM HYDROGEN %	104.47	105.16	105.27	107.04
GM ATOM OXYGEN %	107.47	109.84	109.87	108.00
RATIO CHX/(H ₂ O+CO ₂)	0.7959	0.6310	0.6357	0.8723
RATIO X IN CHX	2.3032	2.3504	2.3462	2.2731
USAGE H ₂ /CO PRODT	1.3900	1.4023	1.3994	1.4195
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2797	0.2489	0.2506	0.2738
K SHIFT IN EFFLNT	0.34	0.29	0.29	0.33

CONVERSION

ON CO %	21.50	19.82	19.98	23.11
ON H ₂ %	32.33	32.42	32.50	34.06
ON CO+H ₂ %	26.95	26.23	26.35	28.63

PRDT SELECTIVITY, WT %

CH ₄	11.51	13.32	13.08	10.34
C ₂ HC'S	7.50	8.78	8.72	6.96
C ₃ H ₈	2.84	3.18	3.20	2.55
C ₃ H ₆	9.92	11.28	11.26	9.00
C ₄ H ₁₀	2.30	2.62	2.66	2.15
C ₄ H ₈	8.75	10.04	9.94	7.99
C ₅ H ₁₂	2.79	3.07	3.17	2.55
C ₅ H ₁₀	3.27	3.87	3.87	3.14
C ₆ H ₁₄	3.11	3.39	3.38	2.57
C ₆ H ₁₂ & CYCLO'S	2.87	2.94	3.17	2.53
C ₇ + IN GAS	22.79	24.52	24.64	18.05
LIQ HC'S	22.35	12.98	12.91	32.17

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	42.82	49.23	48.86	39.00
C5 -420 F	43.26	42.99	42.99	40.19
420-700 F	11.89	6.49	6.74	17.11
700-END PT	2.03	1.30	1.41	3.70
C5+ -END PT	57.18	50.77	51.14	61.00
ISO/NORMAL MOLE RATIO				
C4	0.0706	0.0729	0.0791	0.0729
C5	0.1253	0.1234	0.1270	0.1280
C6	0.3747	0.2847	0.3920	0.2526
C4=	0.0713	0.0715	0.0710	0.0702
PARAFFIN/OLEFIN RATIO				
C3	0.2729	0.2690	0.2716	0.2706
C4	0.2541	0.2520	0.2585	0.2595
C5	0.8303	0.7719	0.7959	0.7910
LIQ HC COLLECTION				
PHYS. APPEARANCE	YL-BR OIL	- -	YL BR OIL	CLEAR OIL
DENSITY	0.773	--	0.774	0.773
N. REFRACTIVE INDEX	1.4331	---	1.4340	1.4346
SIMULT'D DISTILATN				
10 WT % @ DEG F	331	-	321	324
16	343	-	332	343
50	474	-	476	479
84	649	---	668	669
90	694	---	711	713
RANGE(16-84 %)	306	- -	336	376
WT % @ 420 F	37.70	-	36.90	35.30
WT % @ 700 F	90.90	-	89.10	88.50

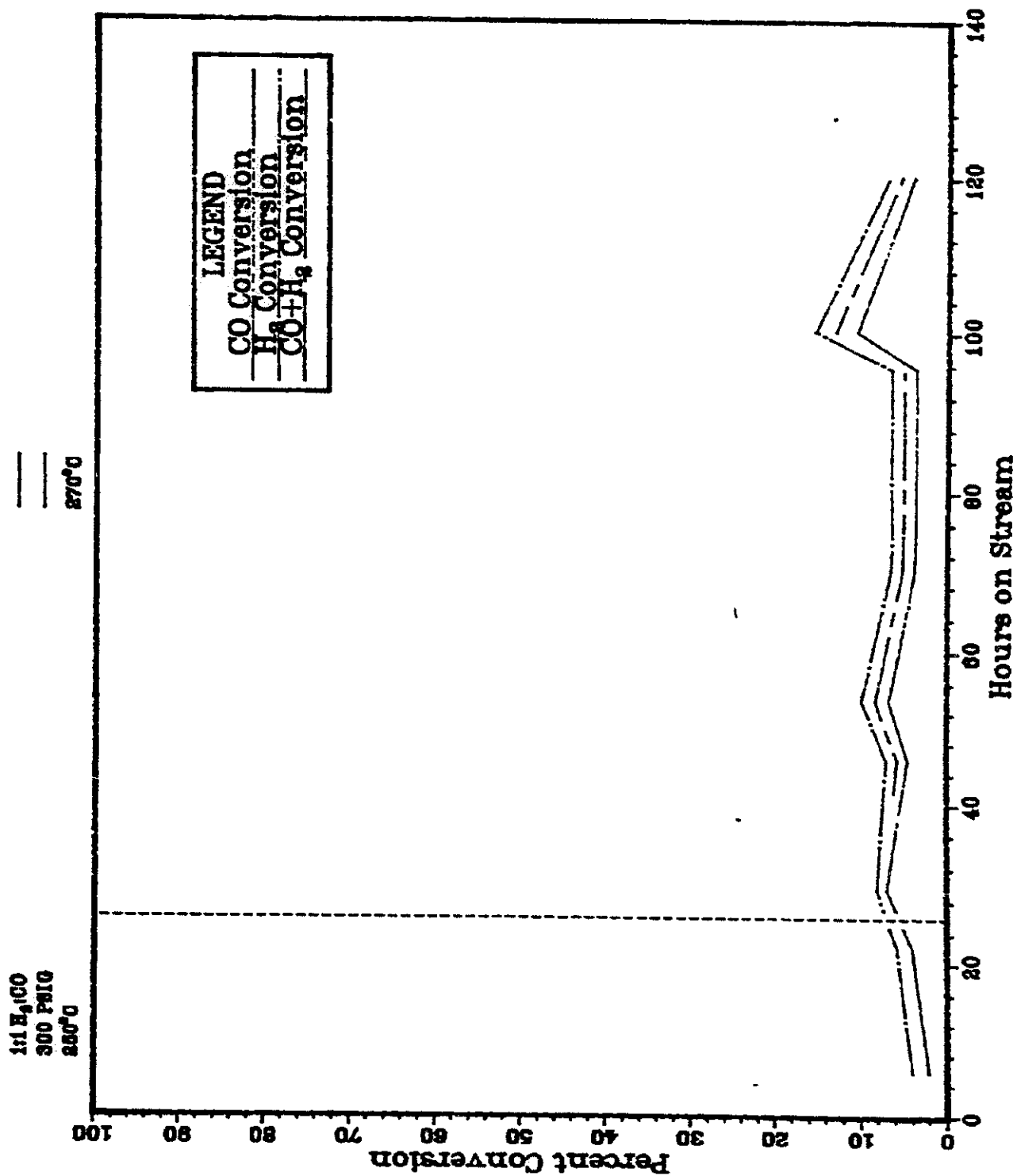
Potassium Promoted Iron Precipitated on UCC-101, Run 10011-12

Catalyst from the same batch as used in Run 10011-11 was tested in Run 10011-12, without activation. The conversion and product selectivity are presented in Figures 78 and 79. The detailed material balances are shown in Tables 12A and 12B.

Iron oxide is supposed to be a non-deactivating component of a F-T catalyst. Superior results should be obtained if the catalyst is not reduced or carbided prior to F-T catalysts. To see if this idea was applicable to these molecular sieve containing catalysts, the catalyst used in Run-10011-11 with known catalytic activity was tested with no preactivation procedures.

This catalyst without activation was almost completely inactive for syngas conversion. The product selectivity was poor. The idea of an unreduced F-T catalyst does not seem to be applicable to this type of catalyst. Further discussion of the activity of this catalyst is not warranted.

FIGURE 78



1001112

FIGURE 79

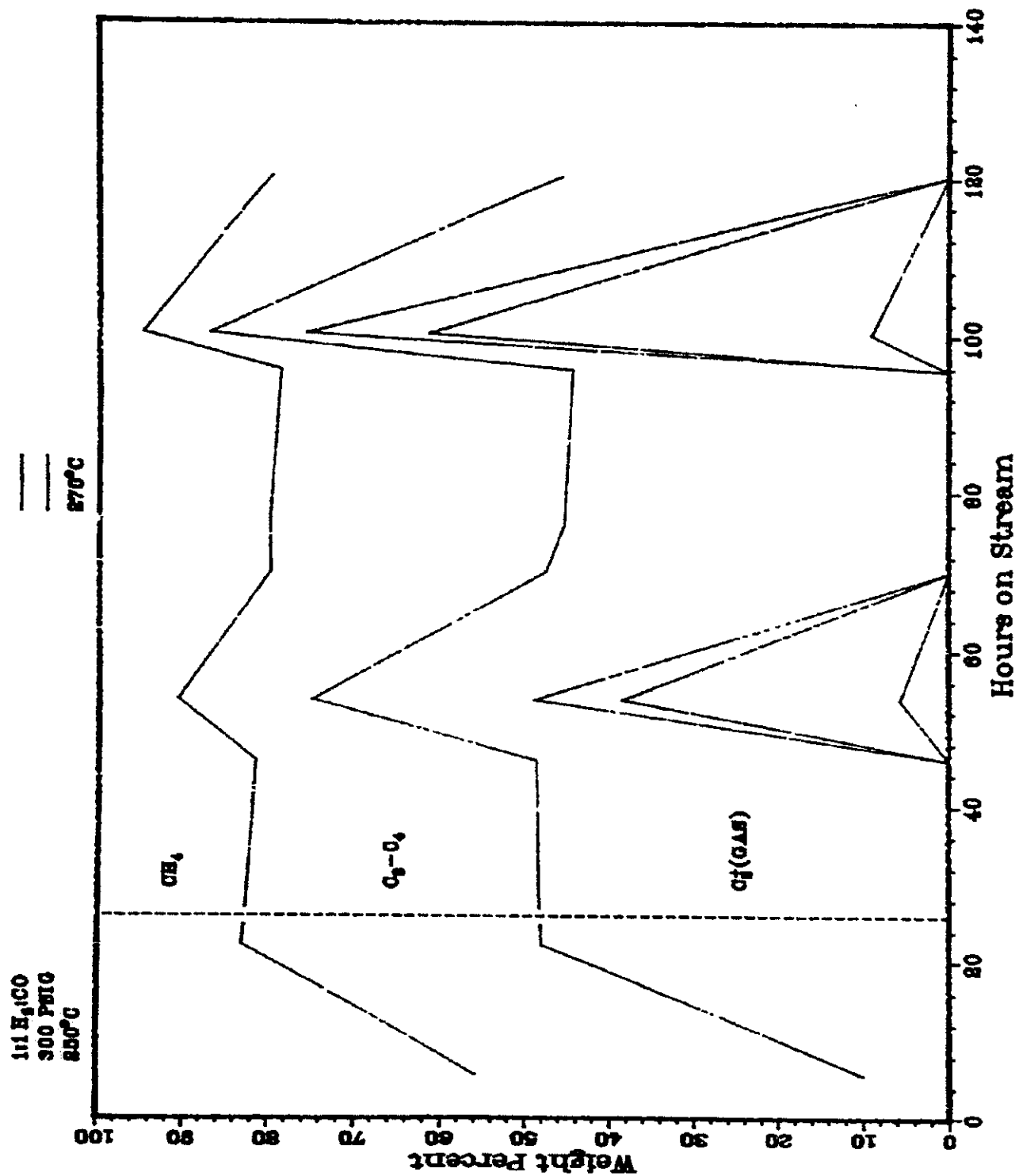


TABLE 12A RESULT OF SYNGAS OPERATION

RUN NO. 10011-12 (NO PRIOR ACTIVATION)
 CATALYST PPT-FE-UCC 101+K 10042-63 80CC 48.3GM (49.1G AFTER RUN, +0.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-12-01	011-12-02	011-12-03	011-12-04	011 12-05
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	5.75	22.25	29.58	46.00	53.75
PRESSURE, PSIG	294	300	297	296	297
TEMP. C	249	249	270	270	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.75	16.50	7.33	16.42	7.75
EFFLNT GAS LITER	148.00	417.05	176.86	397.86	190.91
GM AQUEOUS LAYER	0.00	0.00	0.00	0.00	0.61
GM OIL	0.00	0.00	0.00	0.00	1.48
MATERIAL BALANCE					
GM ATOM CARBON %	103.13	105.56	102.86	102.98	106.14
GM ATOM HYDROGEN %	111.48	108.16	104.84	103.87	110.29
GM ATOM OXYGEN %	108.73	109.96	106.17	105.71	106.99
RATIO CH ₄ /(H ₂ O+CO ₂)	0.0531	0.3034	0.5400	0.5159	0.8676
RATIO X IN CH ₄	2.9847	2.4309	2.4344	2.4342	2.2179
USAGE H ₂ /CO PRDCT	0.9162	0.9835	0.9716	1.2756	1.4384
RATIO CO ₂ /(H ₂ O+CO ₂)	0.3115	0.3670	0.4611	0.3189	0.2539
K SHIFT IN EFFLNT	0.48	0.58	0.86	0.46	0.34
CONVERSION					
ON CO %	2.09	4.07	6.90	4.57	6.78
ON H ₂ %	4.08	5.86	8.09	7.10	9.93
ON CO+H ₂ %	3.12	4.95	7.50	5.84	8.39
PRDCT SELECTIVITY, WT %					
CH ₄	44.18	16.84	17.43	18.42	9.27
C ₂ HC'S	14.24	9.25	10.44	9.23	4.14
C ₃ H ₈	6.07	3.57	2.97	2.68	1.33
C ₃ H ₆	17.57	9.17	9.21	9.28	4.70
C ₄ H ₁₀	3.61	2.87	2.77	1.92	1.03
C ₄ H ₈ =	4.24	10.34	9.42	9.98	4.56
C ₅ H ₁₂	0.00	2.76	2.80	2.31	1.20
C ₅ H ₁₀ =	0.00	1.89	1.94	2.31	1.22
C ₆ H ₁₄	0.00	5.23	3.59	3.21	3.17
C ₆ H ₁₂ = & CYCLO'S	0.00	3.85	5.86	5.20	3.34
C/+ IN GAS	10.09	34.23	34.06	34.86	17.26
LIQ HC'S	0.00	0.00	0.00	0.00	48.79

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	89.91	52.04	51.76	51.50	25.02
C5 -420 F	10.09	47.96	48.24	48.50	36.53
420-700 F	0.00	0.00	0.00	0.00	32.69
700-END PT	0.00	0.00	0.00	0.00	5.76
C5+ -END PT	10.09	47.96	48.24	48.50	74.98
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	0.0000	0.6200	0.3182	0.2000	0.9200
C4+	0.0000	0.0933	0.0960	0.0909	0.0461
PARAFFIN/OLEFIN RATIO					
C3	0.3298	0.3711	0.3082	0.2755	0.2700
C4	0.8235	0.2683	0.2329	0.1855	0.2170
C5	0.0000	1.4167	1.4026	0.9710	0.9559
ULO HC COLLECTION					
PHYS. APPEARANCE	---	---	-	---	YLW OIL
DENSITY	---	---	---	---	
N, REFRACTIVE INDEX	---	---	---	---	
SIMULT'D DISTILATN					
10 WT % @ DEG F	--	---	---	-	348
16	--	---	---	---	392
50	--	---	---	---	533
84	--	---	---	---	674
90	--	---	---	---	715
RANGE(16-84 %)	--	---	---	---	282
WT % @ 420 F	--	---	---	---	21.20
WT % @ 700 F	---	---	-	---	88.20

TABLE 12B RESULT OF SYNGAS OPERATION

RUN NO. 10011-12 (NO PRIOR ACTIVATION)
 CATALYST PPT-FE-UCC-101+K 10042-63 80CC 48.3GM (49.1G AFTER RUN,+0.8G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-12-06	011-12-07	011-12-08	011-12-09	011-12-10
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	70.17	76.00	95.75	100.33	120.24
PRESSURE, PSIG	295	294	292	294	293
TEMP. C	269	268	269	269	269
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	16.42	5.83	19.75	4.58	19.91
EFFLNT GAS LITER	410.20	148.25	492.51	115.14	468.80
GM AQUEOUS LAYER	0.00	0.00	0.00	1.28	0.00
GM OIL	0.00	0.00	0.00	2.62	0.00
MATERIAL BALANCE					
GM ATOM CARBON %	104.68	106.37	104.50	113.91	99.09
GM ATOM HYDROGEN %	107.73	109.80	107.53	119.56	101.83
GM ATOM OXYGEN %	107.56	109.25	107.27	111.53	101.27
RATIO CHX/(H ₂ O+CO ₂)	0.4668	0.4694	0.4757	1.2826	0.5579
RATIO X IN CHX	2.4585	2.4641	2.5007	2.1119	2.4816
USAGE H ₂ /CO PRODT	1.3053	1.3278	1.3569	1.6942	1.4117
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2674	0.2589	0.2519	0.1562	0.2457
K SHIFT IN EFFLNT	0.36	0.35	0.34	0.18	0.32
CONVERSION					
ON CO %	3.79	3.72	3.67	10.66	4.01
ON H ₂ %	6.55	6.53	6.59	15.52	7.02
ON CO+H ₂ %	5.19	5.15	5.15	13.15	5.54
PRDT SELECTIVITY, WT %					
CH ₄	20.11	20.08	21.28	5.12	20.30
C ₂ HC'S	9.16	10.38	8.49	1.88	9.86
C ₃ H ₈	2.66	2.69	2.93	0.72	3.01
C ₃ H ₆ =	9.69	9.50	10.56	2.49	10.04
C ₄ H ₁₀	1.98	1.92	2.41	0.51	2.13
C ₄ H ₈ =	8.96	10.17	10.00	2.33	9.03
C ₅ H ₁₂	1.64	1.97	2.29	0.59	2.18
C ₅ H ₁₀ =	2.27	2.04	2.19	0.51	2.33
C ₆ H ₁₄	3.97	3.29	4.30	0.87	4.41
C ₆ H ₁₂ = & CYCLO'S	5.64	6.09	6.35	1.61	7.27
C ₇ IN GAS	33.91	31.86	29.19	7.68	29.44
LIQ HC'S	0.00	0.00	0.00	75.68	0.00