Fig. 176

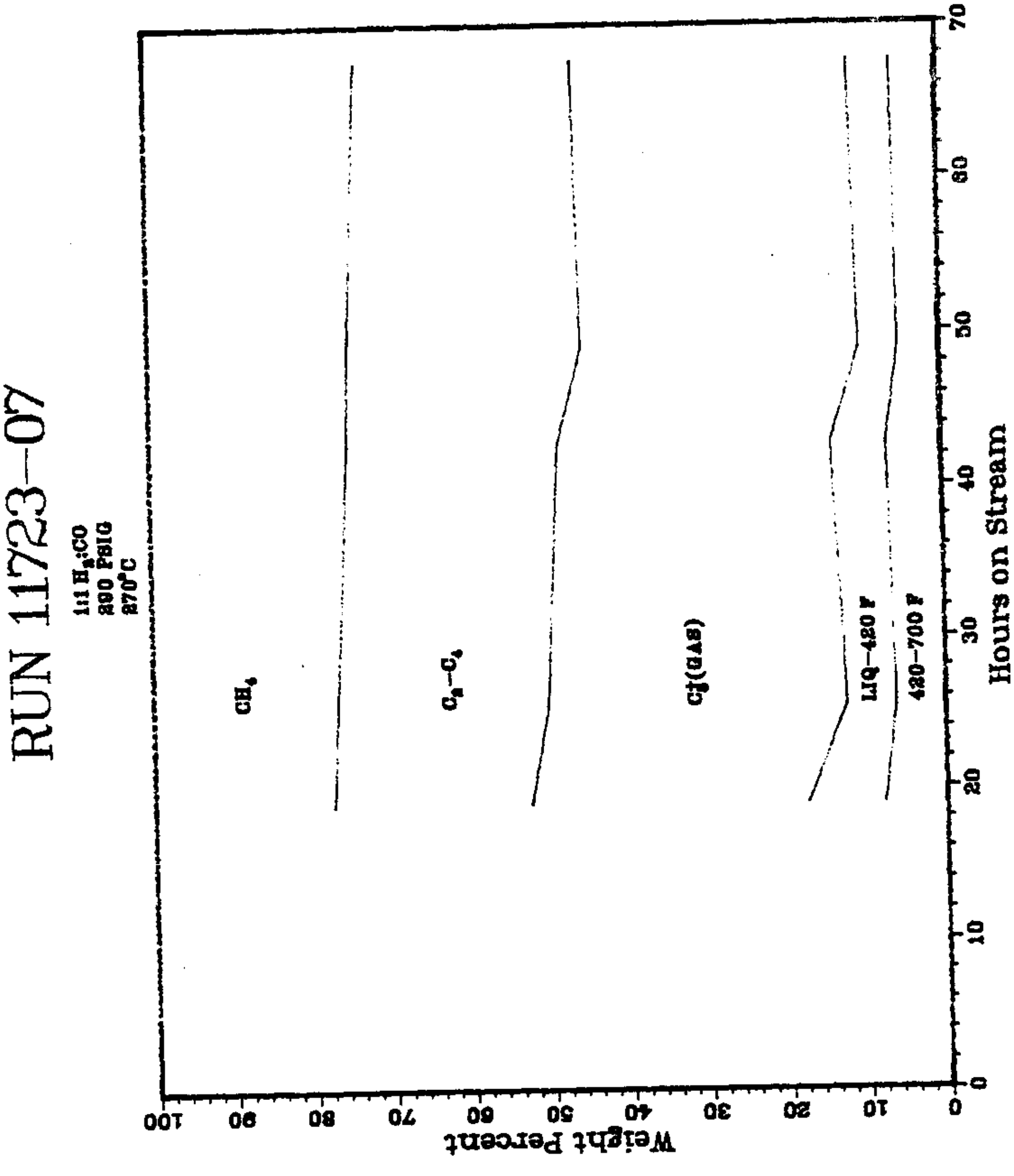

RUN 11723-07
1:1 H_2:CO
390 PSIG
270°C
CH_4
C_2–C_4
C_5^+(GAS)
LIQ–420 F
420–700 F
Hours on Stream
Weight Percent
0
10
20
30
40
50
60
70
80
90
100

Fig. 177

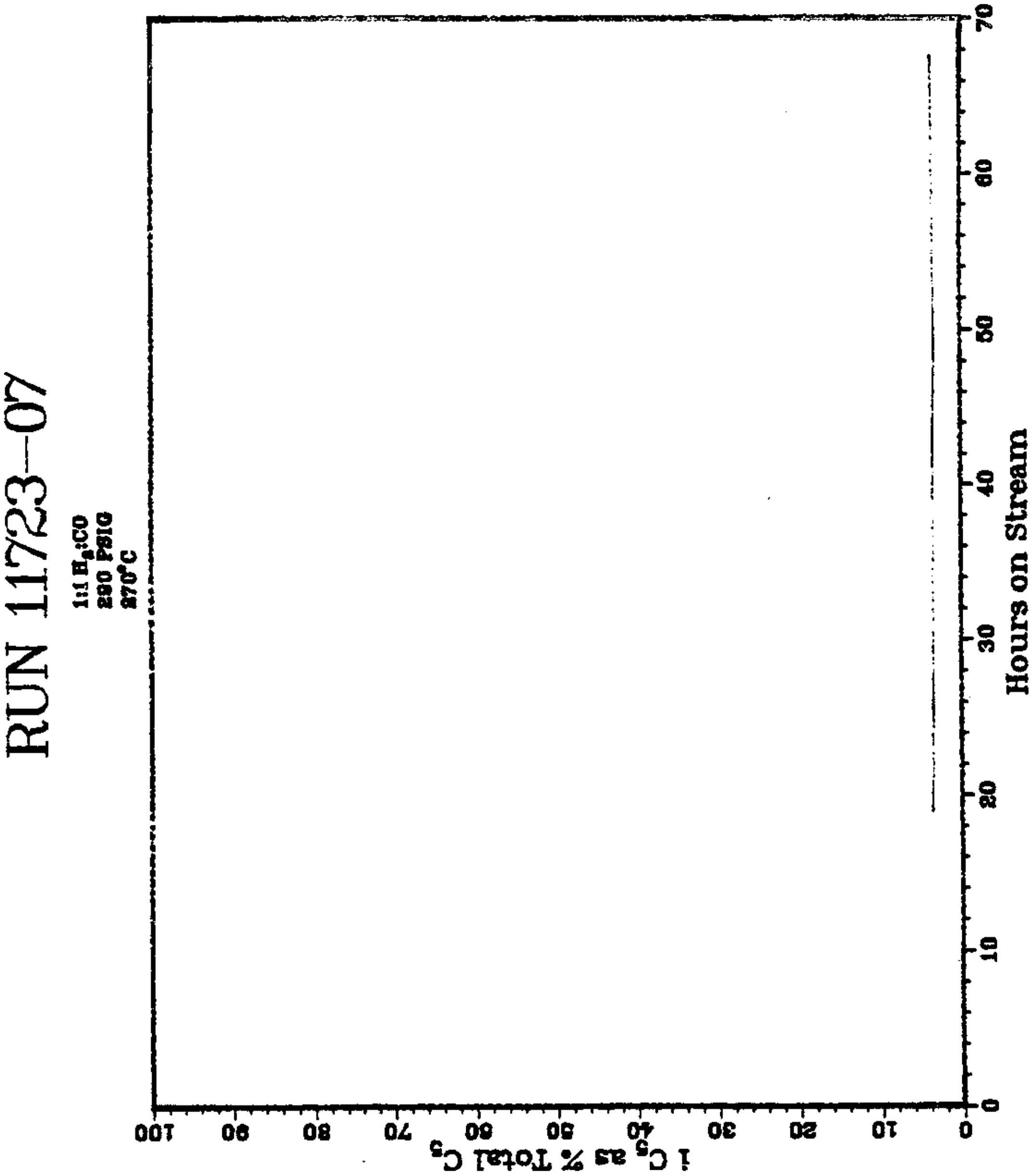

RUN 11723–07
1:1 H2:CO
290 PSIG
270°C
Hours on Stream
0
10
20
30
40
50
60
70
i C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100

Fig. 178

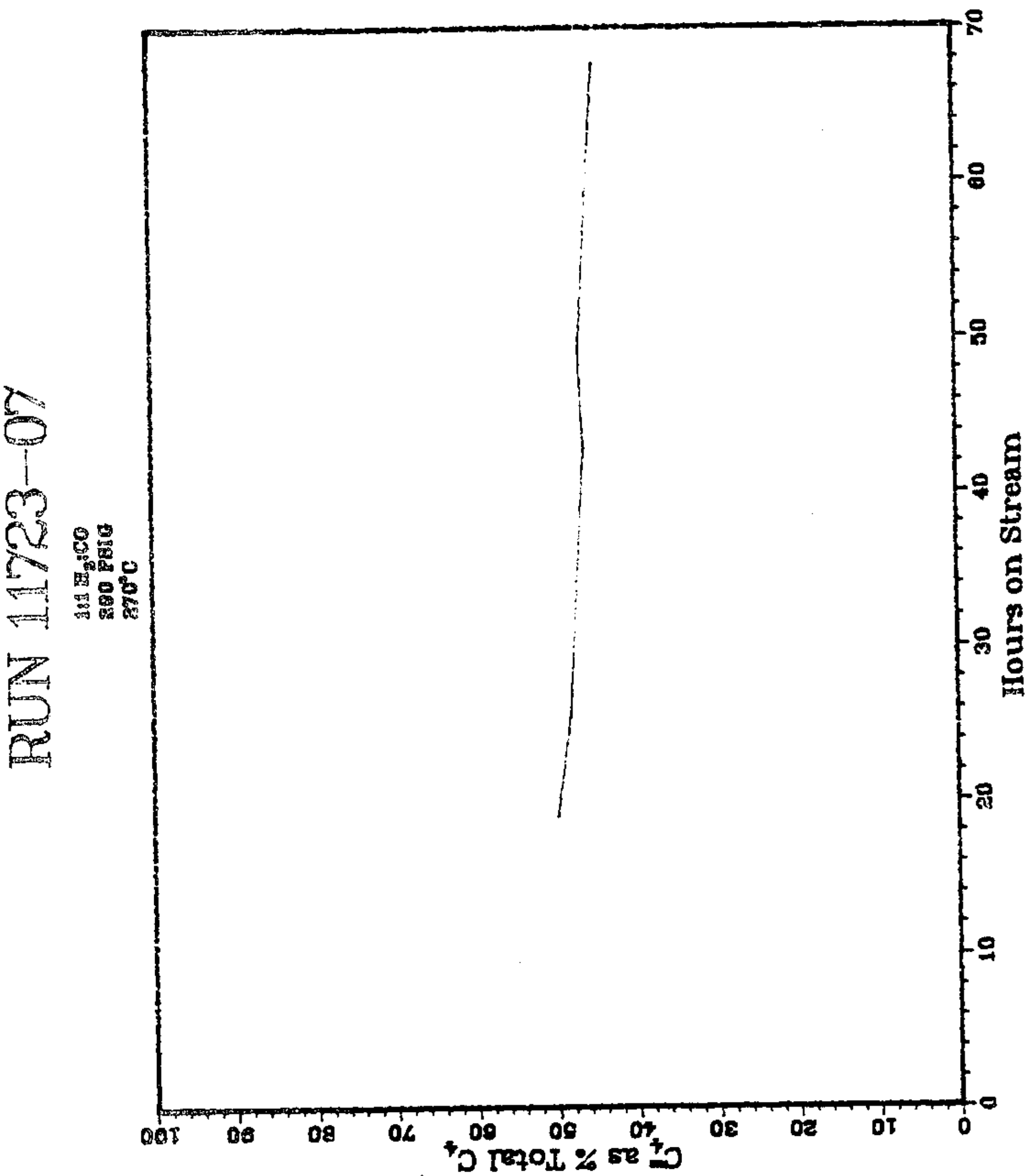

RUN 11723-07
Hours on Stream
0
10
20
30
40
50
60
70
$C_4^=$ as % Total C_4
0
10
20
30
40
50
60
70
80
90
100

Fig. 179

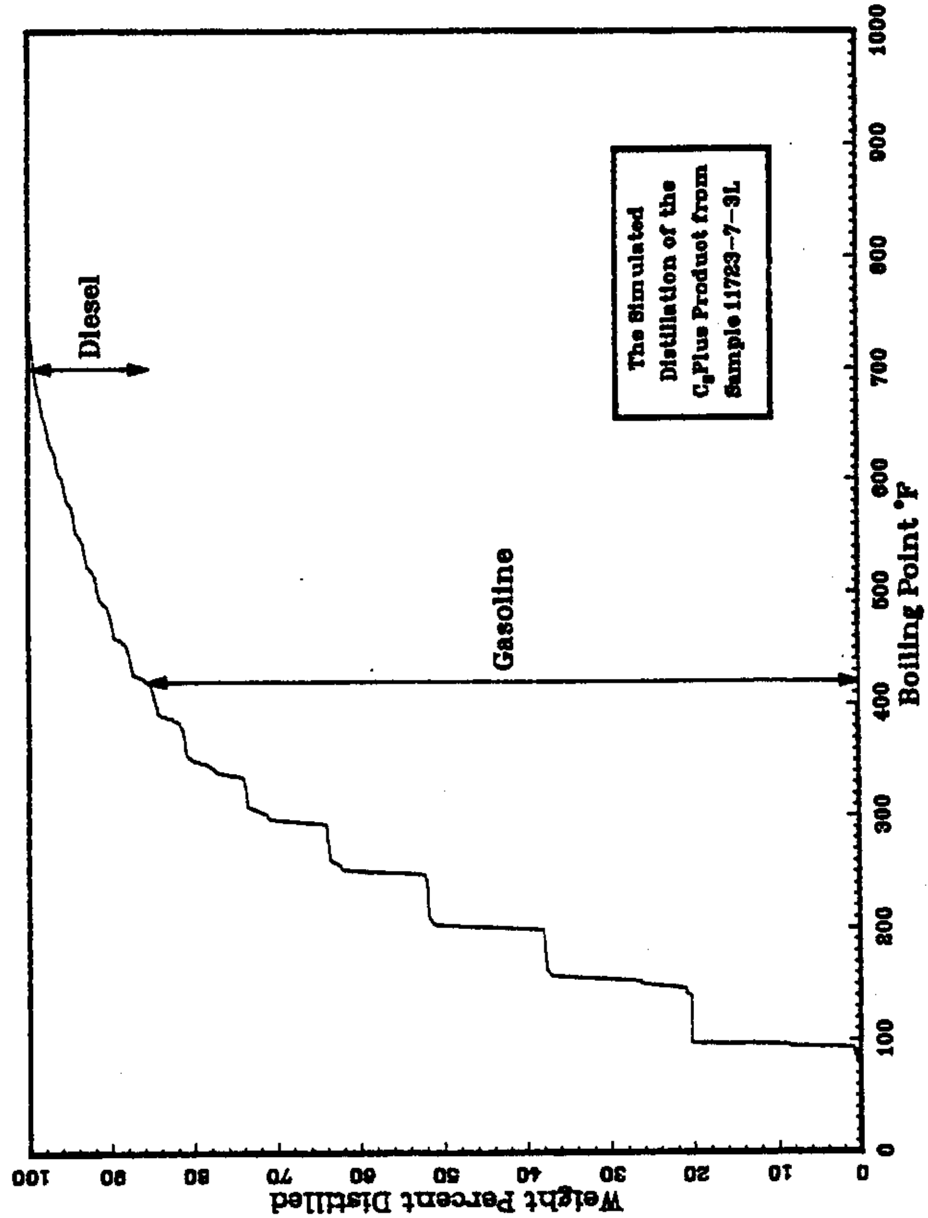
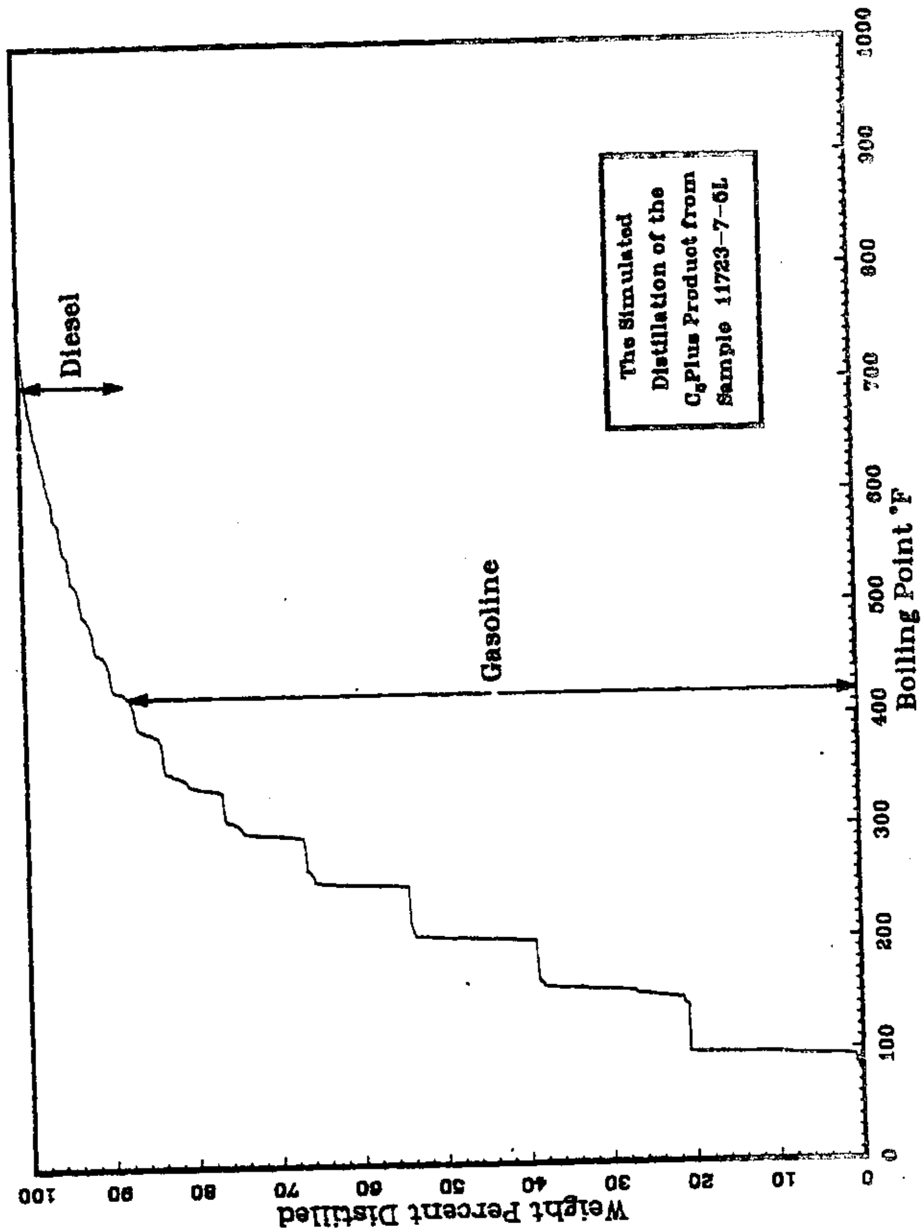
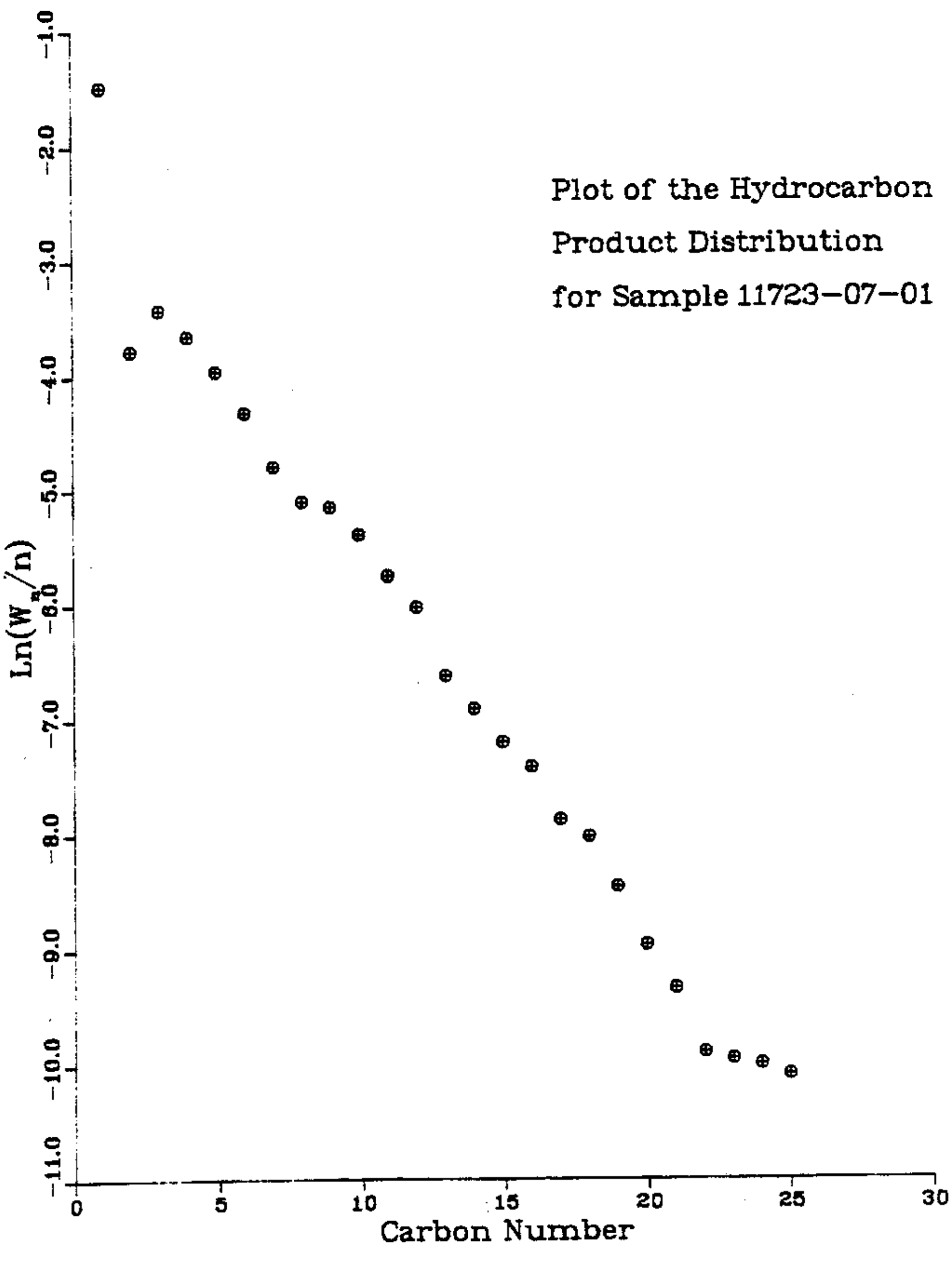

Diesel
Gasoline
The Simulated
Distillation of the
C_5Plus Product from
Sample 11723-7-3L
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000

Fig. 180



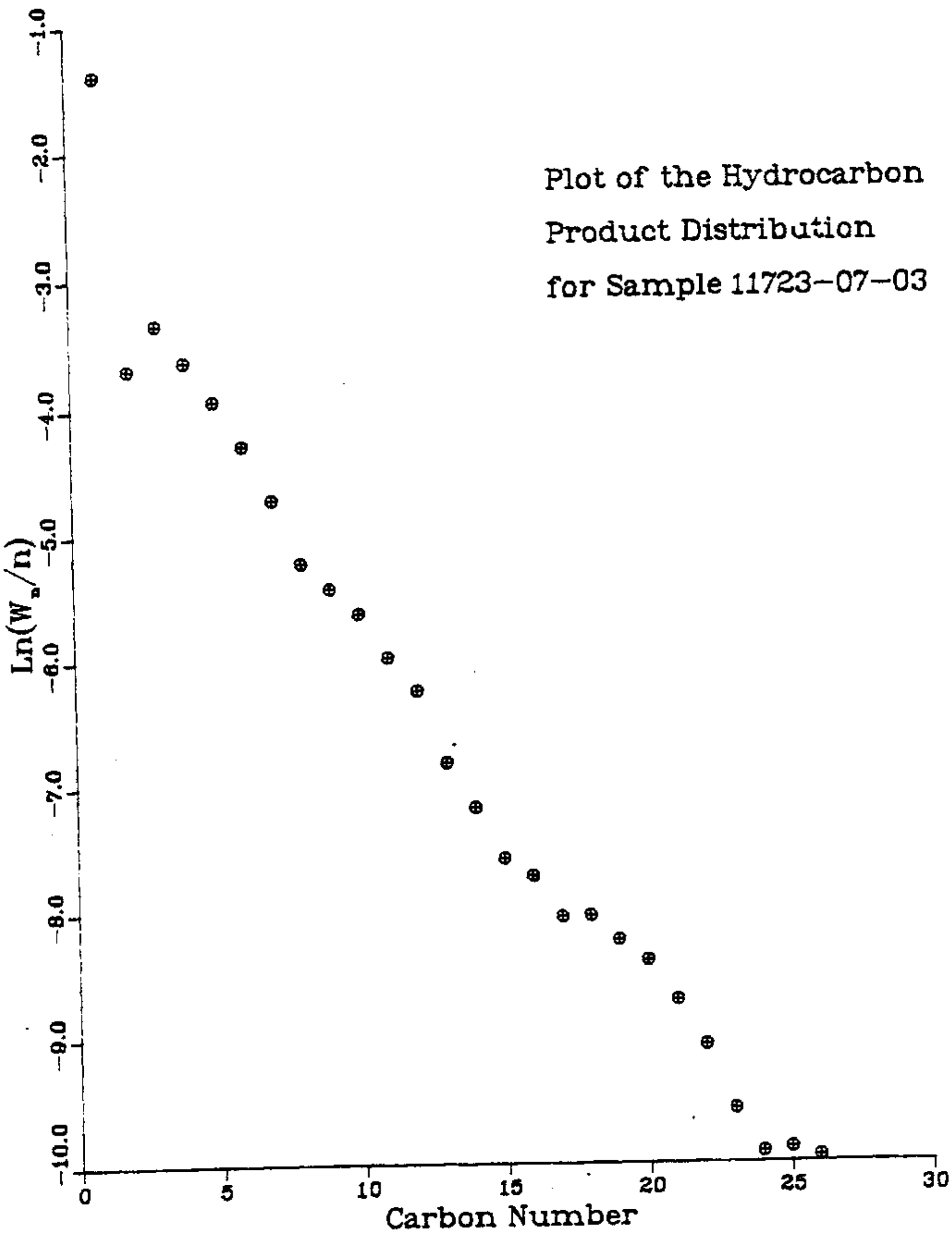
The Simulated
Distillation of the
C_5Plus Product from
Sample 11723-7-5L
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
1000

Fig. 181



Plot of the Hydrocarbon
Product Distribution
for Sample 11723-07-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 182



Plot of the Hydrocarbon
Product Distribution
for Sample 11723-07-03
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 183

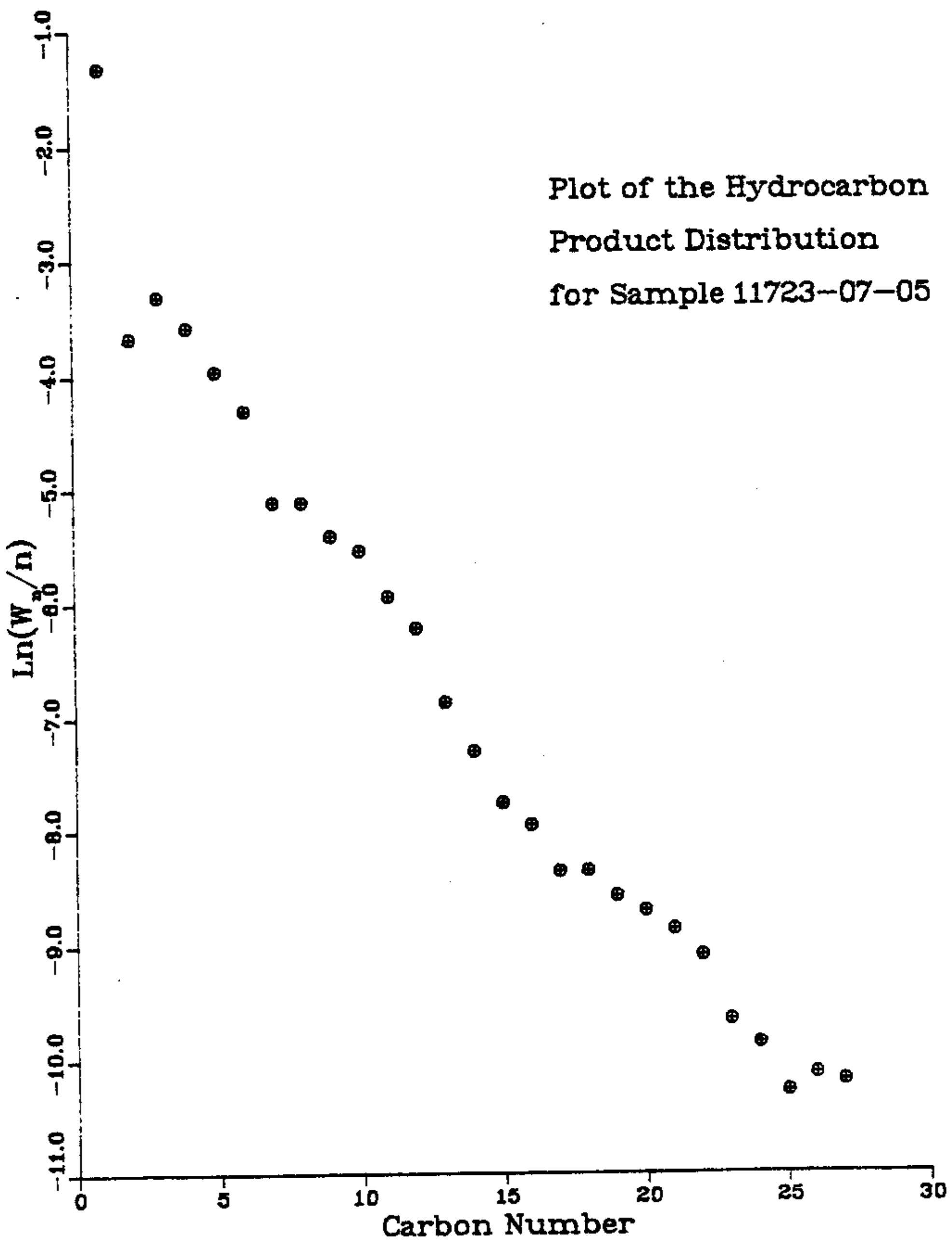

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-07-05
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

TABLE 47 RESULT OF SYNGAS OPERATION

RUN NO. 11723-07
CATALYST CO/TH+UCC-103+UCC-101+CU/ZN-WGSC #11684-55C 250 CC 112.0 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 302 GHSV

	11723-07-01	723-07-02	723-07-03	723-07-04	723-07-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.0	25.5	42.8	48.9	67.6
PRESSURE,PSIG	301	291	293	292	294
TEMP. C	273	273	273	272	272
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	19.00	6.50	23.75	6.17	24.88
EFFLNT GAS LITER	805.15	306.40	1168.80	320.75	1311.70
GM AQUEOUS LAYER	141.18	40.39	147.58	32.84	132.51
GM OIL	18.28	4.63	16.92	3.09	12.47
MATERIAL BALANCE					
GM ATOM CARBON %	89.09	96.47	94.55	96.91	95.73
GM ATOM HYDROGEN %	96.06	98.54	100.45	100.62	99.99
GM ATOM OXYGEN %	94.82	97.13	97.95	97.94	98.67
RATIO CHX/(H2O+CO2)	0.8088	0.9744	0.8676	0.9541	0.8688
RATIO X IN CHX	2.5615	2.5845	2.6181	2.6298	2.6544
USAGE H2/CO PRODT	2.0962	2.1297	2.1553	2.1813	2.1851
RATIO CO2/(H2O+CO2)	0.0452	0.0501	0.0390	0.0388	0.0349
K SHIFT IN EFFLNT	0.03	0.03	0.03	0.03	0.03
CONVERSION					
ON CO %	28.76	27.44	24.60	23.04	21.18
ON H2 %	62.18	57.92	53.54	49.52	47.53
ON CO+H2 %	46.10	42.84	39.51	36.53	34.64
PRDT SELECTIVITY,WT %					
CH4	22.68	23.32	24.94	25.18	26.64
C2 HC'S	4.60	4.58	5.05	4.99	5.11
C3H8	6.09	6.63	6.72	7.14	6.82
C3H6=	3.75	4.16	3.97	5.15	4.17
C4H10	5.31	5.82	5.84	6.52	6.28
C4H8=	5.10	5.22	4.87	5.56	4.91
C5H12	5.30	5.73	5.84	6.15	5.79
C5H10=	4.34	4.65	4.01	4.39	3.77
C6H14	5.42	5.85	5.41	5.32	5.47
C6H12= & CYCLO'S	2.63	3.27	2.85	2.39	2.69
C7+ IN GAS	17.33	18.32	16.45	16.96	17.10
LIQ HC'S	17.47	12.45	14.05	10.24	11.25
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	47.52	49.72	51.39	54.55	53.92
C5 -420 F	44.79	44.06	41.59	40.13	40.23
420-700 F	7.48	5.89	6.65	4.93	5.42
700-END PT	0.21	0.33	0.37	0.39	0.43
C5+-END PT	52.48	50.28	48.61	45.45	46.08
ISO/NORMAL MOLE RATIO					
C4	0.0252	0.0252	0.0234	0.0236	0.0224
C5	0.0375	0.0364	0.0356	0.0346	0.0374
C6	0.0607	0.0660	0.0574	0.0632	0.0494
C4=	0.0836	0.0847	0.0881	0.1017	0.0869
PARAFFIN/OLEFIN RATIO					
C3	1.5511	1.5226	1.6123	1.3226	1.5626
C4	1.0049	1.0752	1.1578	1.1324	1.2348
C5	1.1873	1.1995	1.4140	1.3604	1.4910
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7293		0.7463		0.7434
RATIO CH4/(1-A)**2	3.0953		3.8762		4.0449
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY		CLR OIL		CLR OIL
DENSITY	.733 .735		0.748		0.754
N, REFRACTIVE INDEX	1.4205		1.4219		1.4232
SIMULT'D DISTILATN					
10 WT % @ DEG F	263		280		304
16	304		306		309
50	391		420		423
84	535		582		597
90	577		629		642
RANGE(16-84 %)	231		276		288
WT % @ 420 F	56.00	50.00	50.00	48.00	48.00
WT % @ 700 F	98.82	97.35	97.35	96.18	96.18

XI. Run 10 (11723-08) with Catalyst 10 ($Co/Th+UCC-103+UCC-101+Cu/Zn/Al_2O_3$)

This catalyst is the same as Catalyst 8 except that the copper/zinc water gas shift component was replaced with the copper/zinc/alumina component used in Catalyst 7.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 184-187. Simulated distillations of the C_5^+ product are plotted in Figs. 188-189. Carbon number product distributions are plotted in Figs. 190-192. Detailed material balances appear in Tables 48-49.

The conversion and stability of this catalyst were a little better than those of Catalysts 8 and 9. The initial syngas conversion of 58 percent was close to the 57 percent initial conversion value of Catalyst 2. The deactivation rate, a steady one percentage point every 12 hours on stream, was twice that of Catalyst 2, 60 percent of that of Catalyst 8, and only one third of that of Catalyst 9. The water gas shift activity was still low, however, with only 6-8 percent of the oxygen rejected as CO_2. The H_2:CO usage ratio was 2.0:1. Both of these values are similar to those of Catalyst 2.

The initial production of methane was 17 percent, similar to that of Catalyst 2, but the stability was poorer, increasing at the rate of one percentage point every 18 hours on stream. Initial production of C_5^+ was 61.2 percent, and of motor fuels 60.8 percent, lower than those of Catalyst 2 which were 65.5 and 63.9 percent respectively. Gasoline production was 52.5 percent, as against 46.7 percent with Catalyst 2. There was no appreciable isomerization of the pentane. A little more than half of the C_4 hydrocarbon product was butenes. The Schulz-Flory plots are fairly straight except for the excess methane.

In general, except for its poorer stability, the action of this catalyst is much like that of Catalyst 2. The copper/zinc/alumina water gas shift component appears to make little or no positive contribution, and may be responsible for the impaired stability. Why this should happen is not clear from the data; the component itself was active when tested without a Fischer-Tropsch co-actor.

Fig. 184

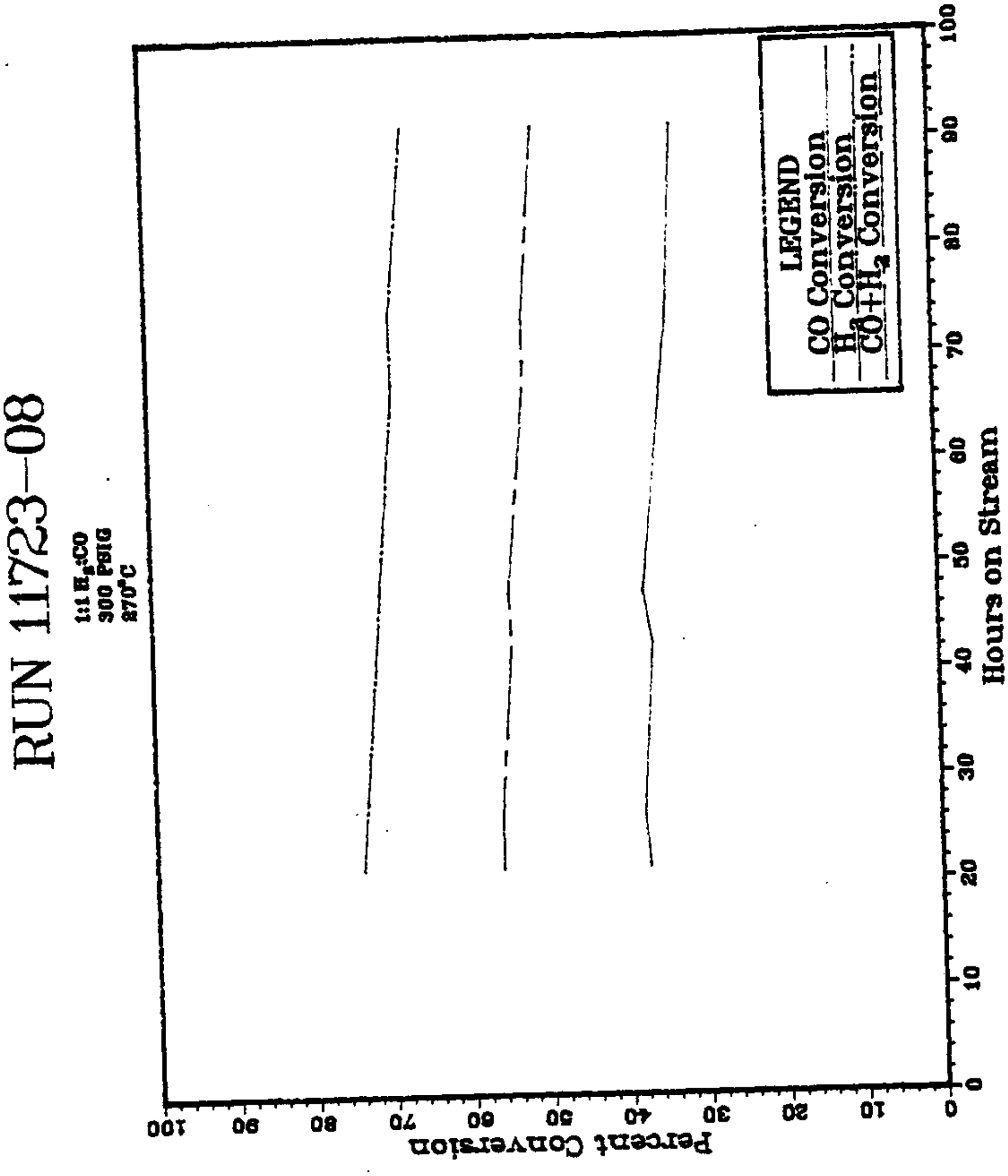
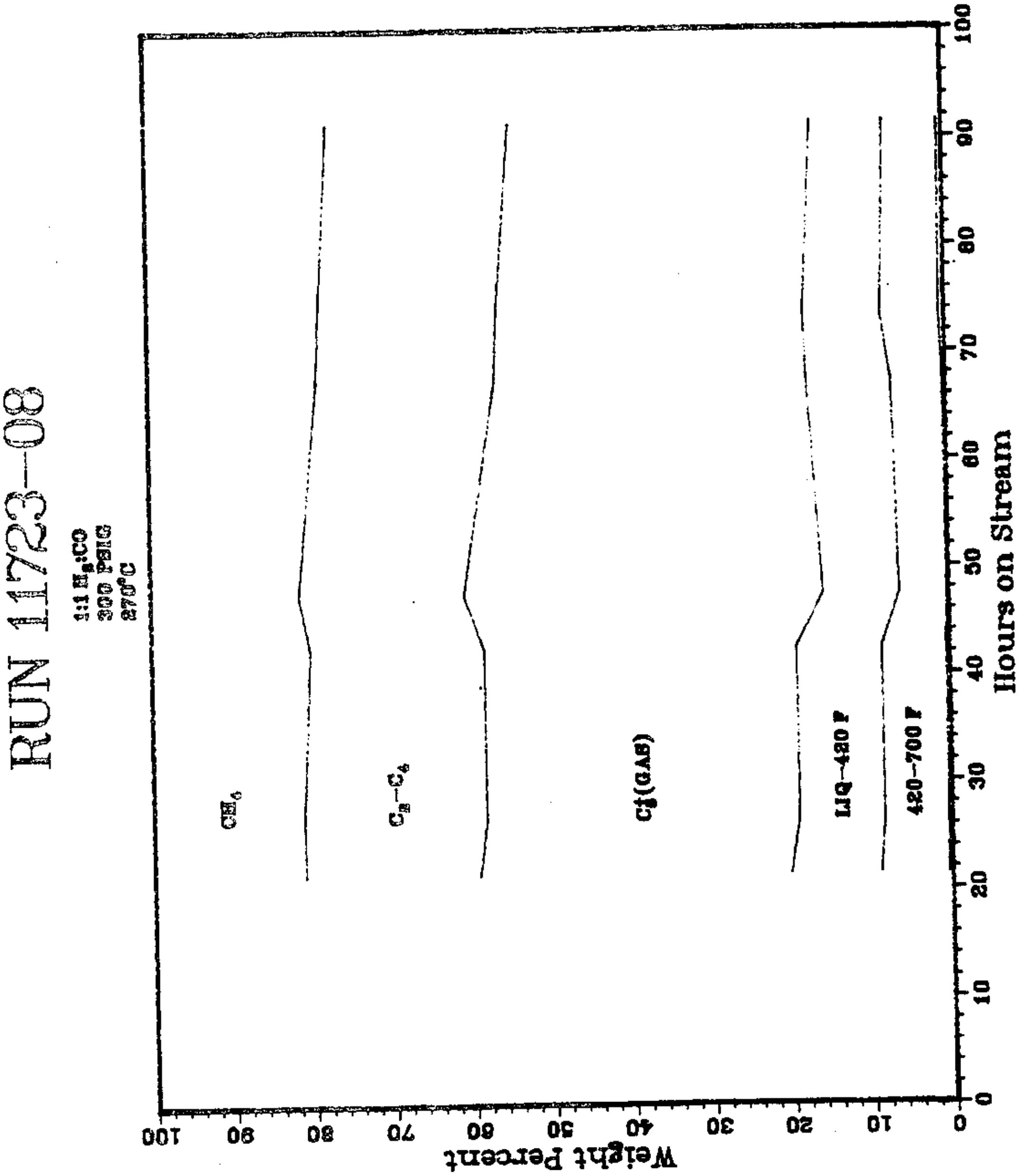
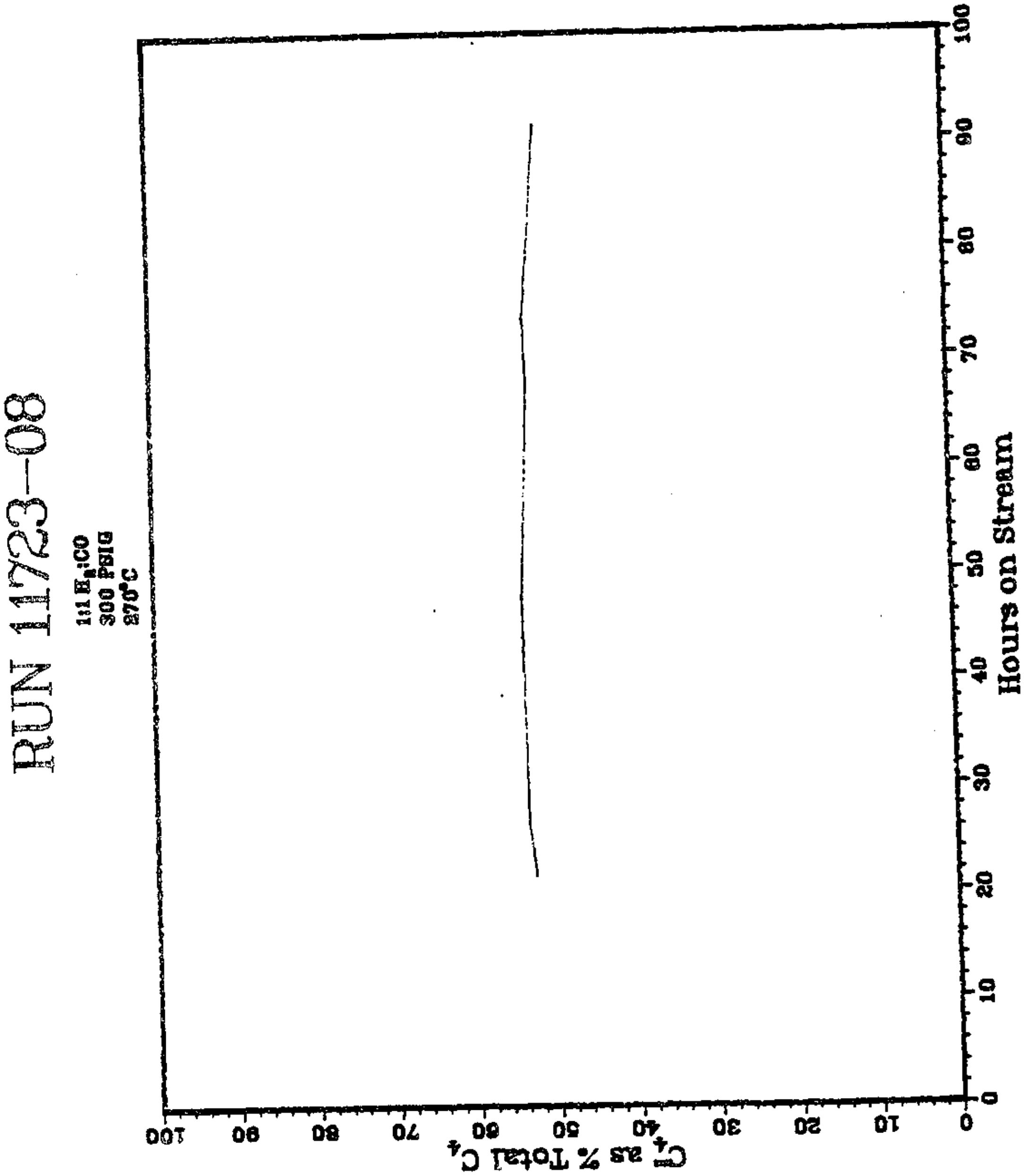

RUN 11723-08
1:1 H_2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H_2 Conversion
CO+H_2 Conversion
Hours on Stream
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100

Fig. 185



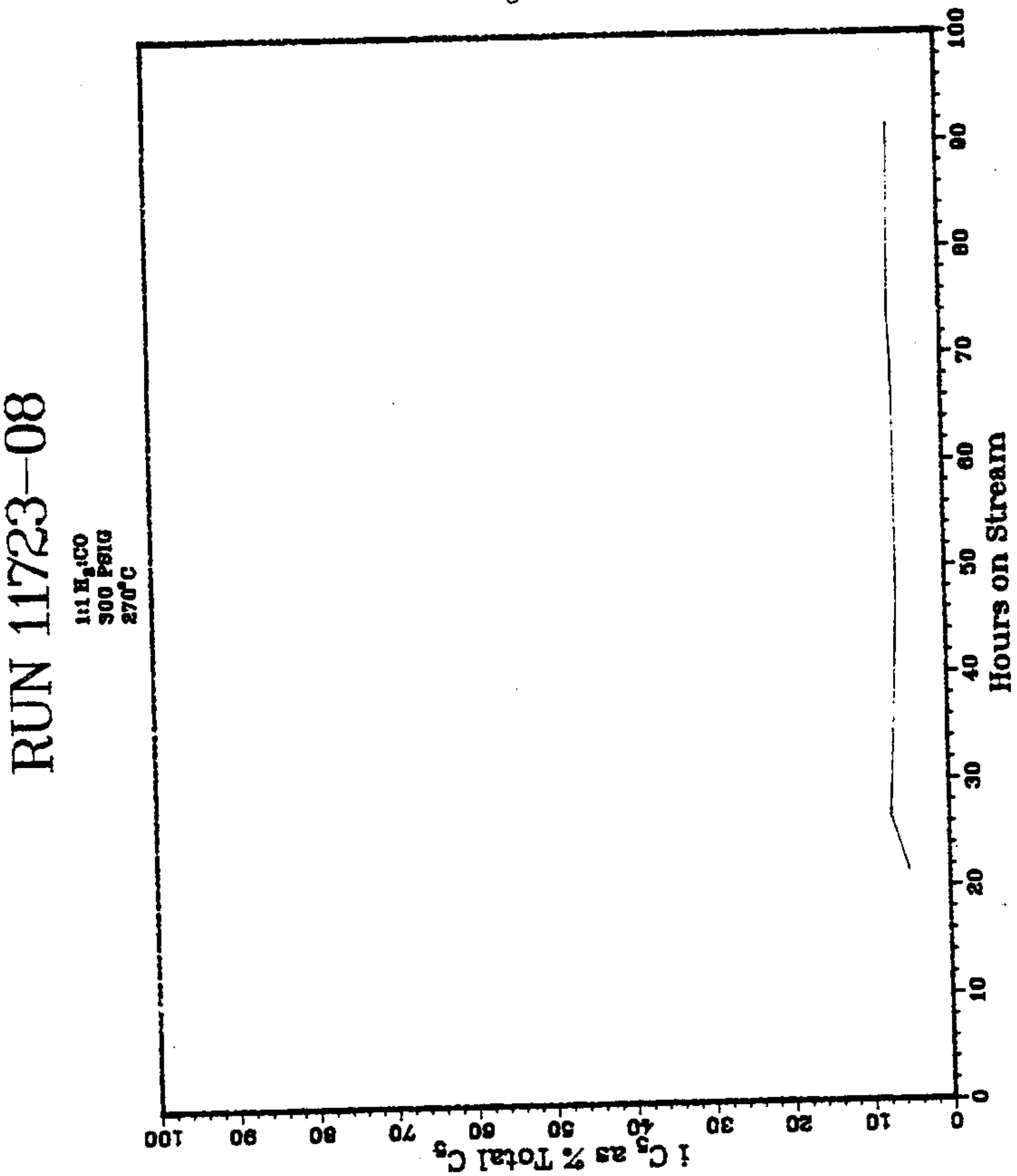
RUN 11723-08
1:1 H_2:CO
300 PSIG
270°C
CH_4
C_2-C_4
C_5^+(GAS)
LIQ-420 F
420-700 F
Hours on Stream
Weight Percent

Fig. 186



RUN 11723-08
1:1 H2:CO
300 PSIG
270°C
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
C4= as % Total C4

Fig. 187



RUN 11723-08
1:1 H2:CO
300 PSIG
270°C
Hours on Stream
i C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100

Fig. 188

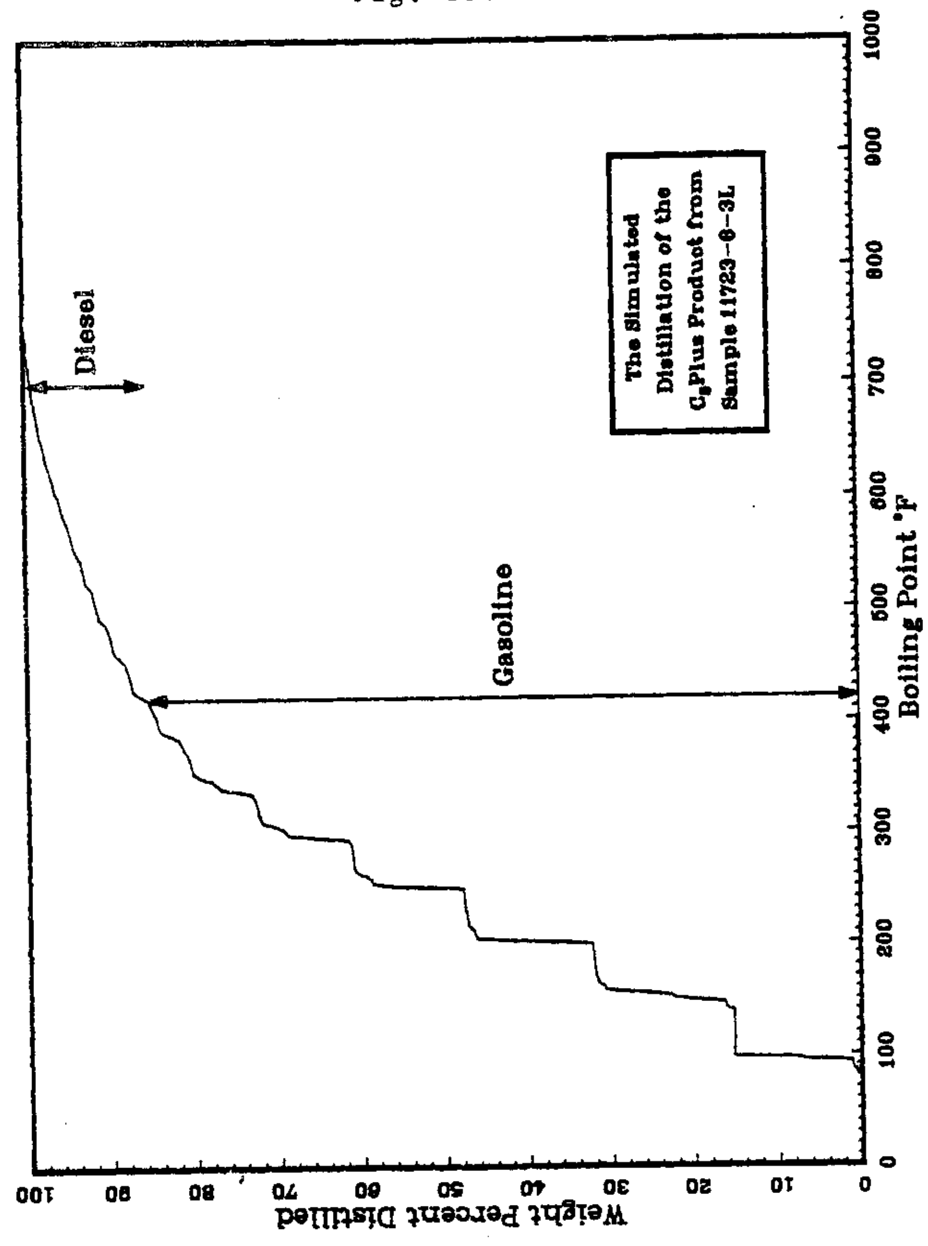
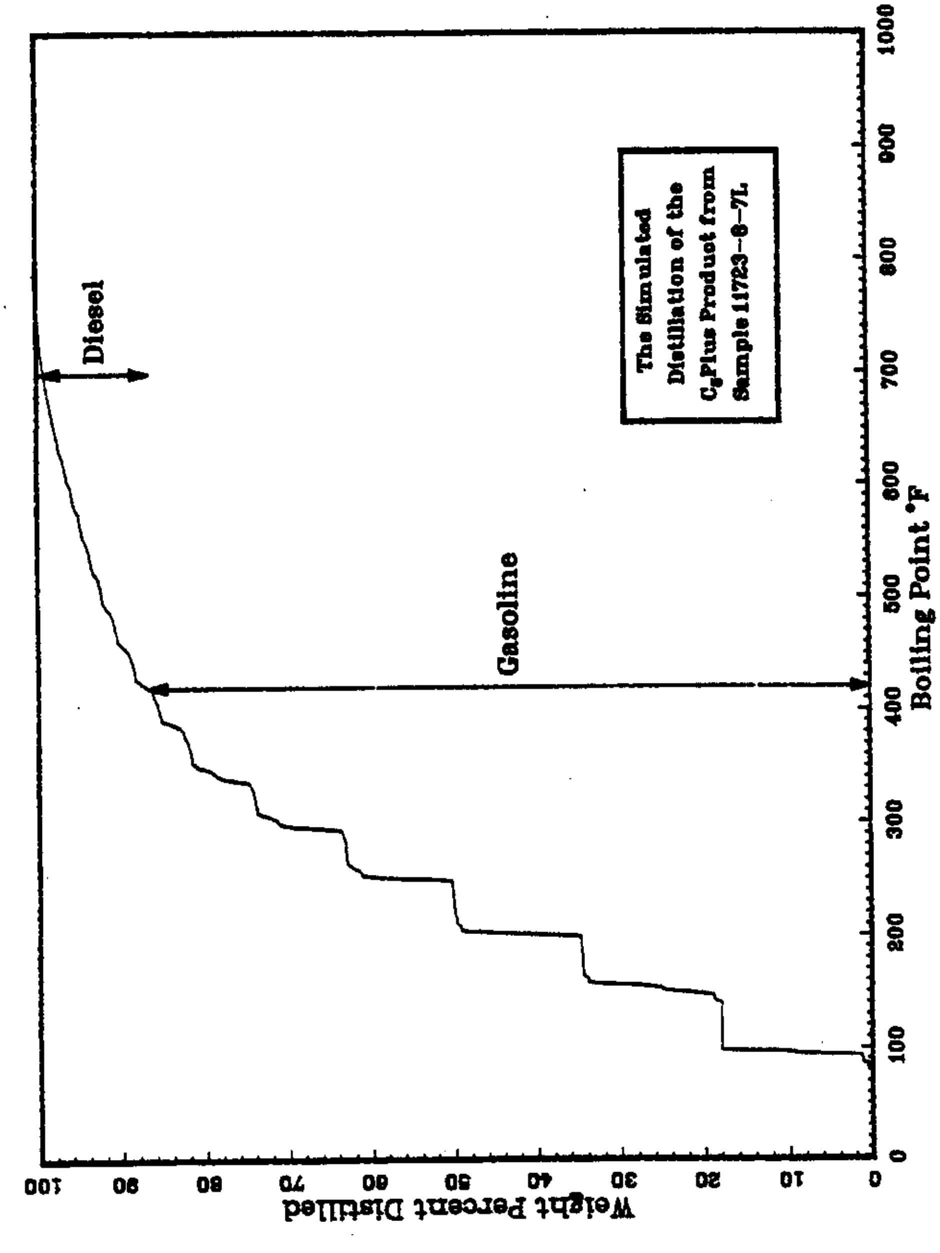
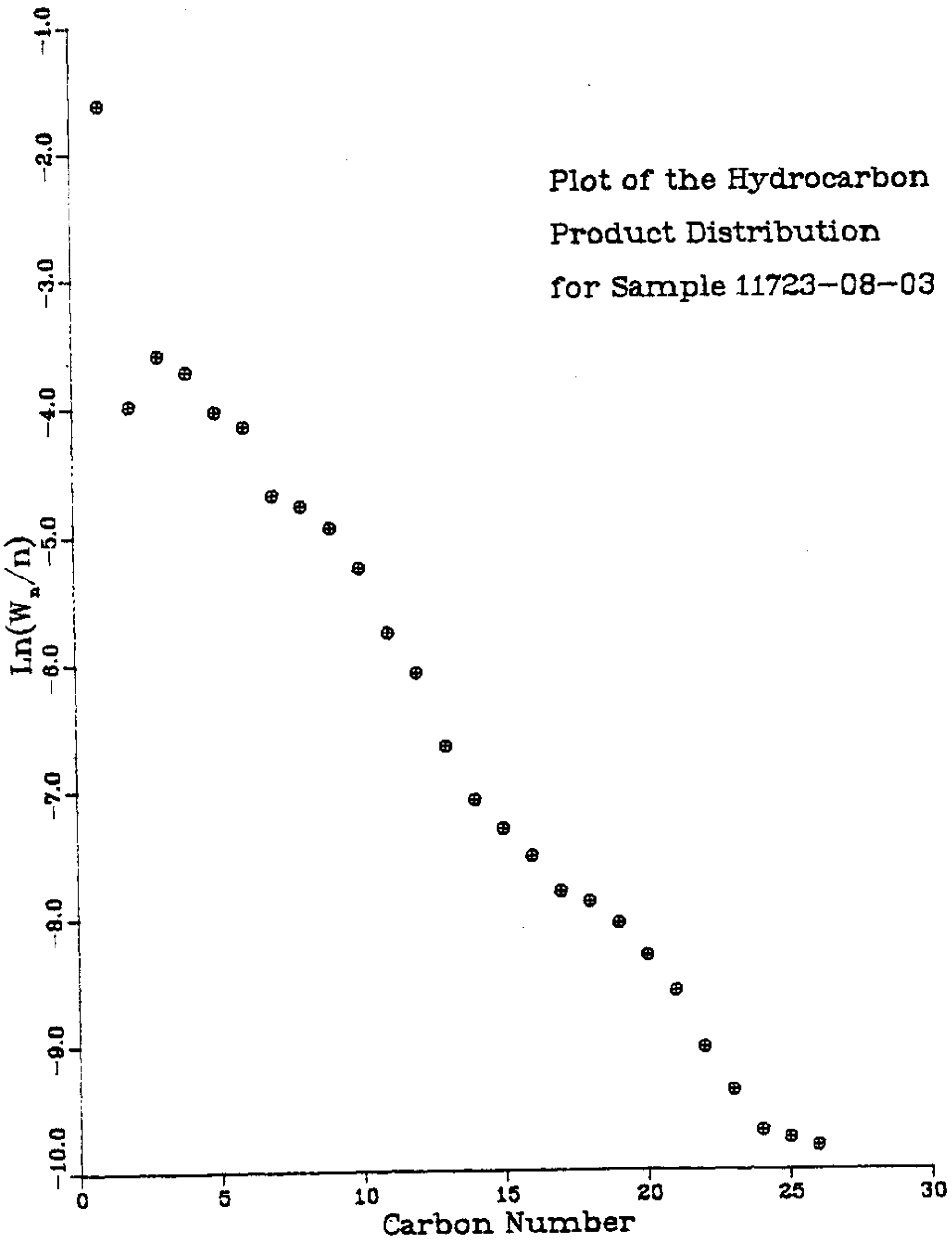

The Simulated Distillation of the C_5Plus Product from Sample 11723-6-3L
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 189



Diesel
Gasoline
The Simulated
Distillation of the
C_5Plus Product from
Sample 11723-6-7L
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. 190



Plot of the Hydrocarbon
Product Distribution
for Sample 11723-08-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. 191

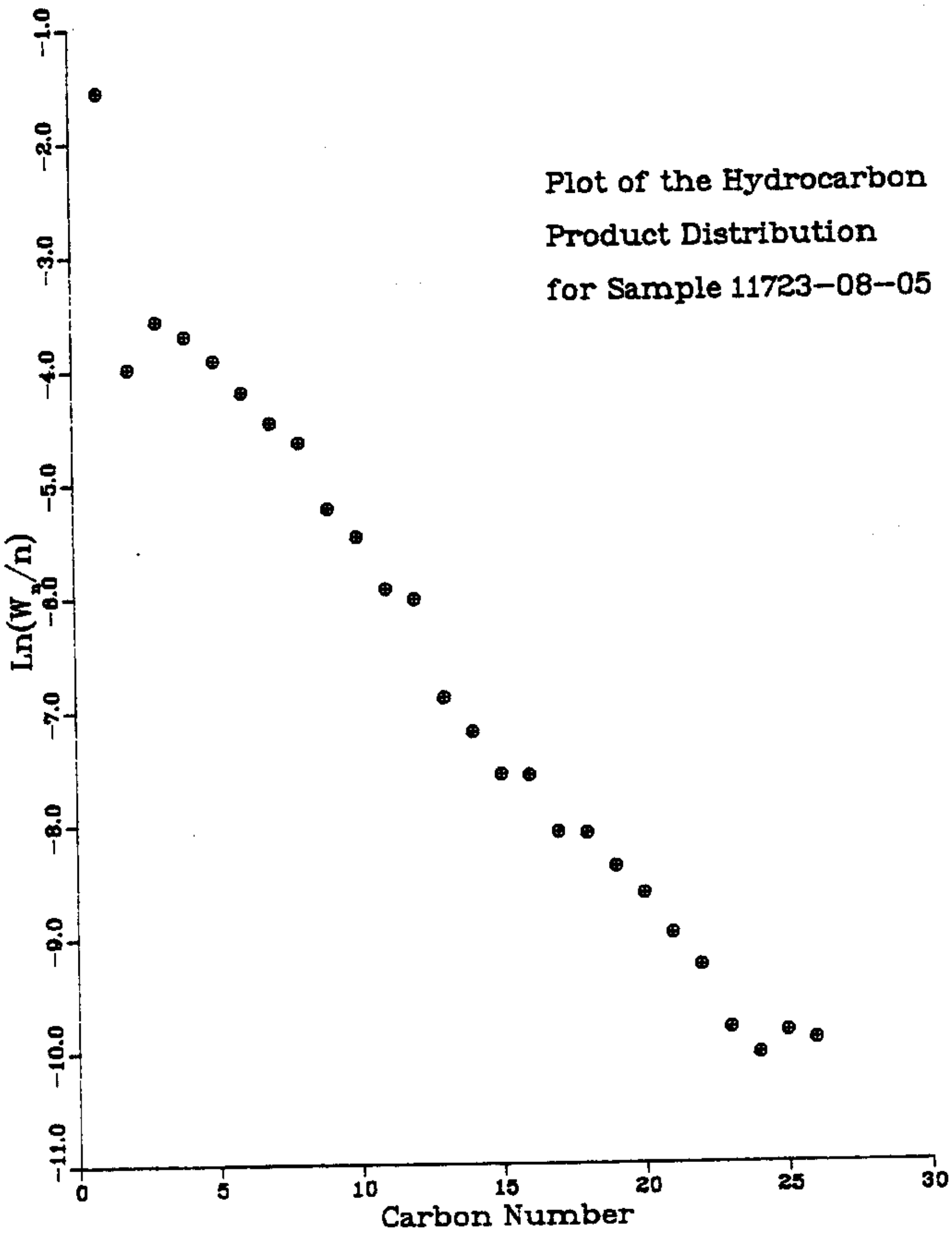
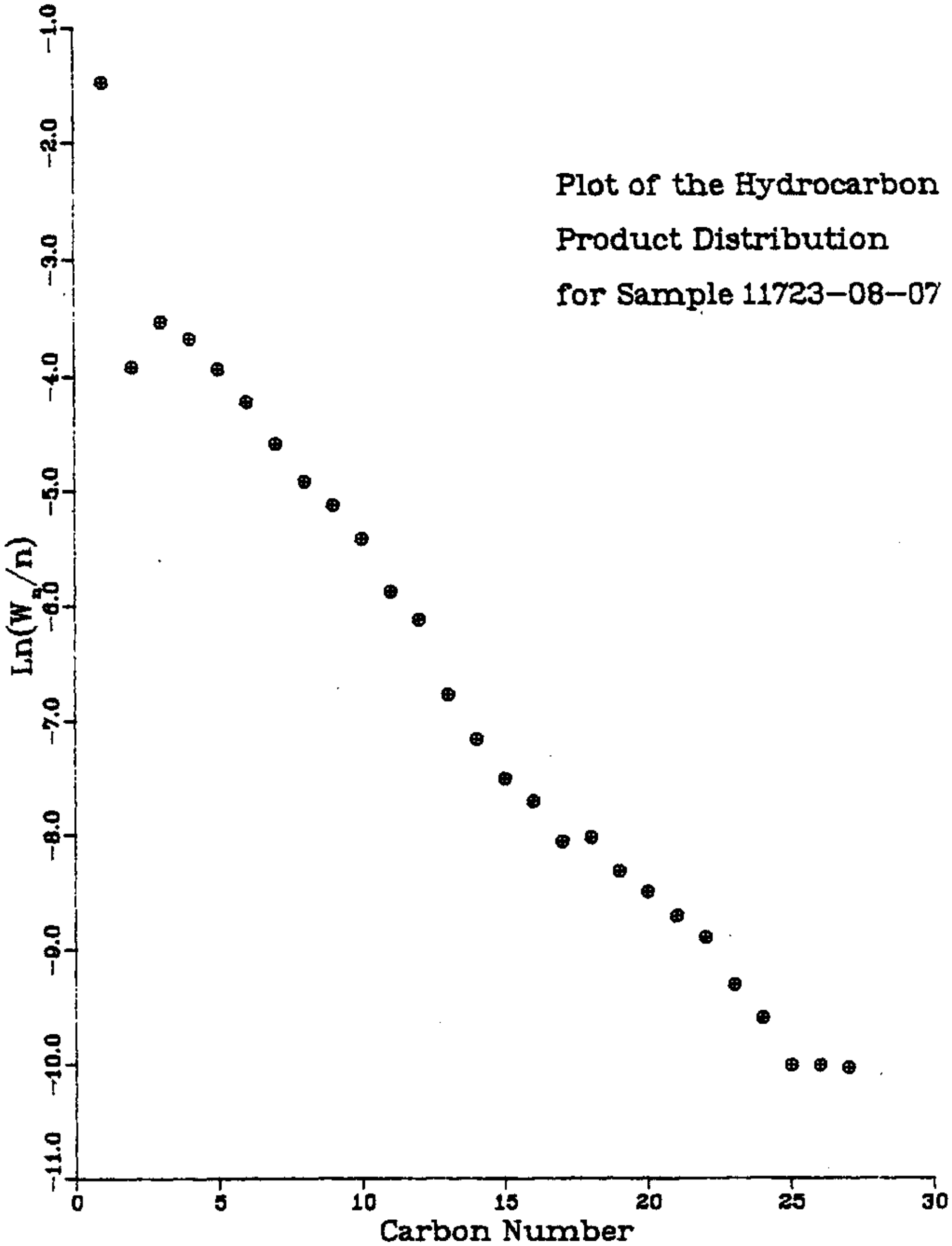

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-08-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

Fig. 192



Plot of the Hydrocarbon
Product Distribution
for Sample 11723-08-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
Carbon Number

TABLE 48 RESULT OF SYNGAS OPERATION

RUN NO. 11723-08
CATALYST CO/TH+UCC-103+UCC-101+CU/ZN-WGSC #11684-61C 250 CC 111.5 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 302 GHSV

	11723-08-01	723-08-02	723-08-03	723-08-04	723-08-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	21.5	26.5	42.5	47.5	67.5
PRESSURE,PSIG	301	290	290	299	293
TEMP. C	272	273	273	273	273
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	21.50	5.00	21.00	5.00	25.00
EFFLNT GAS LITER	622.60	183.40	809.50	197.15	1005.40
GM AQUEOUS LAYER	142.90	40.51	170.14	38.68	193.41
GM OIL	24.06	6.82	28.64	5.97	29.87
MATERIAL BALANCE					
GM ATOM CARBON %	72.06	90.97	93.16	96.21	93.58
GM ATOM HYDROGEN %	75.51	95.57	97.91	99.96	98.47
GM ATOM OXYGEN %	74.82	92.91	95.15	94.50	95.12
RATIO CHX/(H20+CO2)	0.8995	0.9420	0.9402	1.0535	0.9517
RATIO X IN CHX	2.4736	2.4767	2.4908	2.4574	2.5190
USAGE H2/CO PRODT	1.9702	1.9743	2.0024	2.0146	2.0378
RATIO CO2/(H20+CO2)	0.0812	0.0839	0.0761	0.0749	0.0692
K SHIFT IN EFFLNT	0.04	0.04	0.04	0.04	0.04
CONVERSION					
ON CO %	37.29	37.86	36.43	37.52	34.72
ON H2 %	73.71	73.16	71.44	71.03	68.84
ON CO+H2 %	55.92	55.95	54.37	54.59	52.22
PRDT SELECTIVITY,WT %					
CH4	18.94	18.91	19.86	18.51	21.16
C2 HC'S	3.79	3.75	3.74	3.53	3.75
C3H8	5.57	5.78	5.41	5.16	5.43
C3H6=	2.76	3.02	2.91	2.80	3.09
C4H10	4.68	4.85	4.59	4.36	4.79
C4H8=	5.00	5.35	5.14	4.90	5.17
C5H12	4.49	5.12	5.08	4.71	5.23
C5H10=	4.61	4.86	3.83	4.44	4.82
C6H14	5.20	5.03	5.20	4.76	5.29
C6H12= & CYCLO'S	3.83	3.83	4.16	3.48	3.60
C7+ IN GAS	21.01	20.39	20.84	27.61	20.25
LIQ HC'S	20.13	19.11	19.23	15.73	17.43
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	40.74	41.65	41.65	39.26	43.38
C5 -420 F	50.41	49.94	49.88	54.60	49.83
420-700 F	8.34	7.92	7.97	5.81	6.44
700-END PT	0.52	0.49	0.50	0.32	0.36
C5+-END PT	59.26	58.35	58.35	60.74	56.62
ISO/NORMAL MOLE RATIO					
C4	0.0552	0.0495	0.0456	0.0429	0.0406
C5	0.0555	0.0800	0.0689	0.0668	0.0678
C6	0.1496	0.1276	0.1252	0.1029	0.1125
C4=	0.0593	0.0598	0.0613	0.0638	0.0684
PARAFFIN/OLEFIN RATIO					
C3	1.9293	1.8296	1.7740	1.7592	1.6754
C4	0.9036	0.8743	0.8615	0.8590	0.8937
C5	0.9477	1.0248	1.2886	1.0326	1.0539
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))			0.7528		0.7411
RATIO CH4/(1-A)**2			3.2494		3.1574
LIQ HC COLLECTION					
PHYS. APPEARANCE			CLDY LT BL		CLDY LT BL
DENSITY			0.747		0.746
N, REFRACTIVE INDEX			1.4226		1.4226
SIMULT'D DISTILATN					
10 WT % @ DEG F			261		255
16			293		284
50			390		387
84			573		547
90			616		600
RANGE(16-84 %)			280		263
WT % @ 420 F	56.00	56.00	56.00	61.00	61.00
WT % @ 700 F	97.42	97.42	97.42	97.95	97.95

TABLE 49 RESULT OF SYNGAS OPERATION

RUN NO. 11723-08
CATALYST CO/TH+UCC-103+UCC-101+CU/ZN-WGSC #11684-61C 250 CC 111.5 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 302 GHSV

	11723-08-06	723-08-07
	=========	=========
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	73.5	91.5
PRESSURE,PSIG	297	297
TEMP. C	273	273
FEED CC/MIN	1260	1260
HOURS FEEDING	6.00	24.00
EFFLNT GAS LITER	209.20	951.45
GM AQUEOUS LAYER	44.87	179.49
GM OIL	6.08	24.32
MATERIAL BALANCE		
GM ATOM CARBON %	80.00	89.08
GM ATOM HYDROGEN %	87.28	94.57
GM ATOM OXYGEN %	85.02	92.64
RATIO CHX/(H2O+CO2)	0.8339	0.8837
RATIO X IN CHX	2.5233	2.5545
USAGE H2/CO PRODT	2.0391	2.0547
RATIO CO2/(H2O+CO2)	0.0600	0.0633
K SHIFT IN EFFLNT	0.03	0.04
CONVERSION		
ON CO %	33.81	32.56
ON H2 %	69.06	66.88
ON CO+H2 %	52.20	50.23
PRDT SELECTIVITY,WT %		
CH4	21.48	22.77
C2 HC'S	3.86	3.98
C3H8	5.54	5.82
C3H6=	2.94	2.97
C4H10	4.72	5.03
C4H8=	5.16	5.09
C5H12	5.00	5.07
C5H10=	4.55	4.67
C6H14	4.91	5.15
C6H12= & CYCLO'S	4.26	3.48
C7+ IN GAS	19.85	19.47
LIQ HC'S	17.74	16.51
TOTAL	100.00	100.00

SUB-GROUPING		
C1 -C4	43.70	45.65
C5 -420 F	48.32	46.92
420-700 F	7.29	6.79
700-END PT	0.69	0.64
C5+-END PT	56.30	54.35
ISO/NORMAL MOLE RATIO		
C4	0.0406	0.0413
C5	0.0716	0.0667
C6	0.0983	0.0955
C4=	0.0650	0.0663
PARAFFIN/OLEFIN RATIO		
C3	1.7962	1.8716
C4	0.8820	0.9533
C5	1.0692	1.0563
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))		0.7519
RATIO CH4/(1-A)**2		3.6983
LIQ HC COLLECTION		
PHYS. APPEARANCE		CLDY LT BL
DENSITY		0.752
N, REFRACTIVE INDEX		1.4225
SIMULT'D DISTILATN		
10 WT % @ DEG F		260
16		302
50		391
84		579
90		630
RANGE(16-84 %)		277
WT % @ 420 F	55.00	55.00
WT % @ 700 F	96.12	96.12

XII. Summary

The catalysts tested this past year have shown consistent improvements in both stability and selectivity. The catalytic testing seems to be converging toward a single type of catalyst as being superior to the rest. The close contact between the cobalt metal component and the shape selective component, either UCC-101 or UCC-103, is a key component to the improvements in the present catalysts.

The nine Fischer-Tropsch catalysts reported for the Twelfth Quarter all have close contact between the metal component and the shape selective component. When these catalysts are compared to like catalysts without the close contact of metal component and shape selective component, the current catalysts have a number of properties in common which are the result of this improved method of catalyst preparation. Enhanced stability is the most noticeable property which the current catalysts have in common. The catalyst is more stable than a like catalyst without close contact when the cobalt is in contact with either UCC-101 or UCC-103. This synergism between metal component and shape selective component emphasizes the advantages of the one-bed system. A two-bed system, separating the metal component and shape selective component, would not allow this interaction to occur.

These catalysts also have other properties in common. The catalysts with this interaction generally produce a less olefinic product than do similar physical mixture catalysts. The amount of olefins in the product can still be increased by the addition of an additive like X_4, which was known to increase the olefins in the product of physical mixture catalysts. The current catalysts also seem to produce a less waxy product than the corresponding physical mixture catalysts. These current catalysts also have lower water gas shift activity, usually with less than 10 percent of the oxygen being rejected as CO_2. In the physical mixture catalysts over 20 percent of the oxygen is rejected as CO_2.

The addition of a second shape selective component, not in close contact with the cobalt, may have some effect on the activity of the catalyst. However, the effect of this second shape selective component is much less than that of the first shape selective component which is in close contact with the cobalt. More detailed analysis of product may show the more subtle effects of the second shape selective component.

The additive X_6 gave very different results with Catalyst 5 than it had previously in Run 11677-3. The water gas shift activity was also not reduced as it had been in Run 11677-3. The best explanation for the lack of activity of X_6 is that it may be acting more strongly with the shape selective component than it is with the cobalt.

Previously, X_4 was shown to increase the stability of a physical mixture catalyst by a factor of 4 compared to a like catalyst without X_4. This additive also increases the stability of current catalysts as well. Catalyst 6 showed no measurable deactivation over the last eight days on stream. The selectivity was also stable over this time period. This catalyst produced just 13 percent methane and 67 percent motor fuels with 3 percent heavies. This catalyst is the most important catalyst reported to date.

The water gas shift catalysts reported were particularly poor. While the water gas shift component was active on its own, it would not work at all in combination with a Fischer-Tropsch component. For Catalysts 8 and 9, not only did the water gas shift component have no activity, but the Fischer-Tropsch component was also badly deactivated in those catalysts.

The catalysts reported since the Second Annual Report have shown that cobalt catalysts are more active and selective for motor fuels than iron catalysts. The waxiness of the liquid product from cobalt catalysts can be lowered or eliminated by proper control of process conditions and catalyst formulation. The close contact of metal component and shape selective component and the use of X_4 as an additive are the most important factors in the synthesis of stable, selective Fischer-Tropsch catalysts.