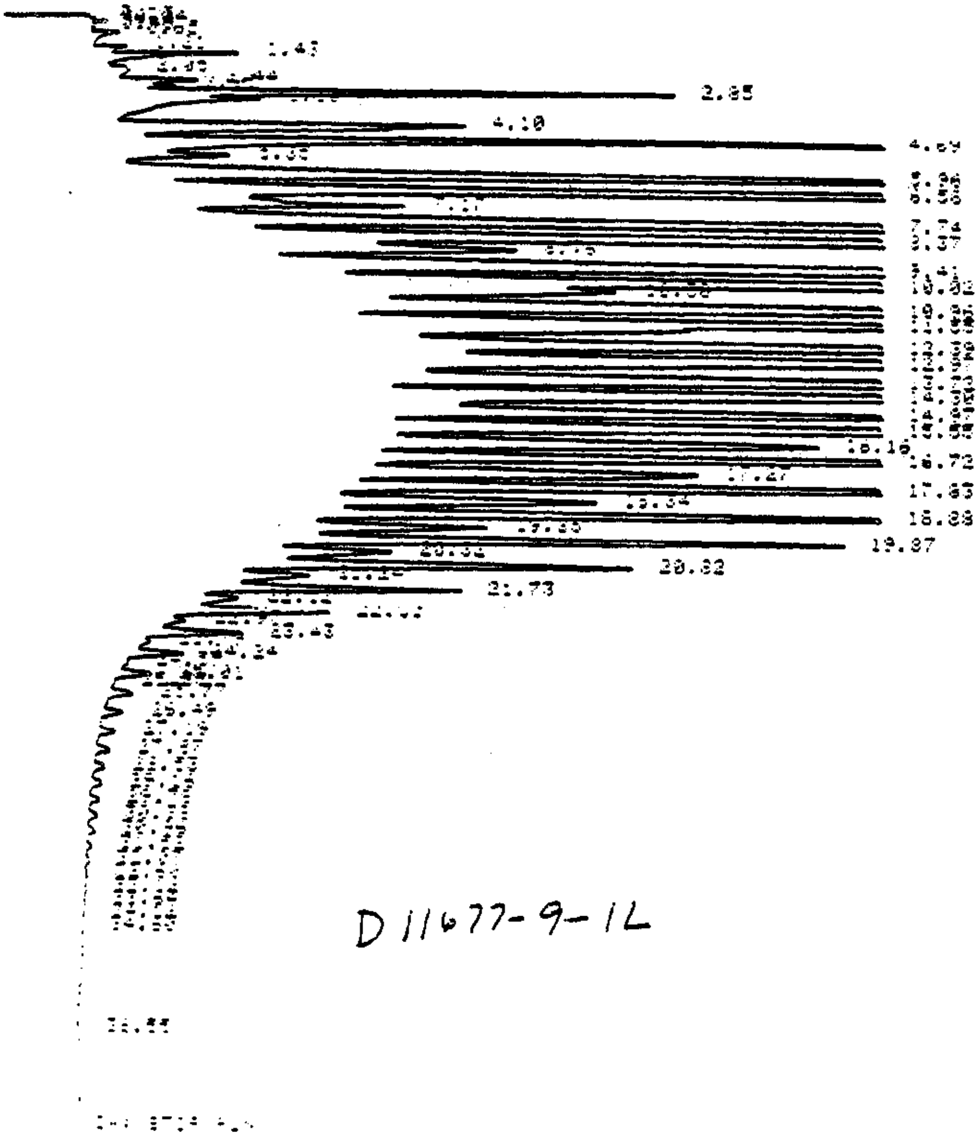
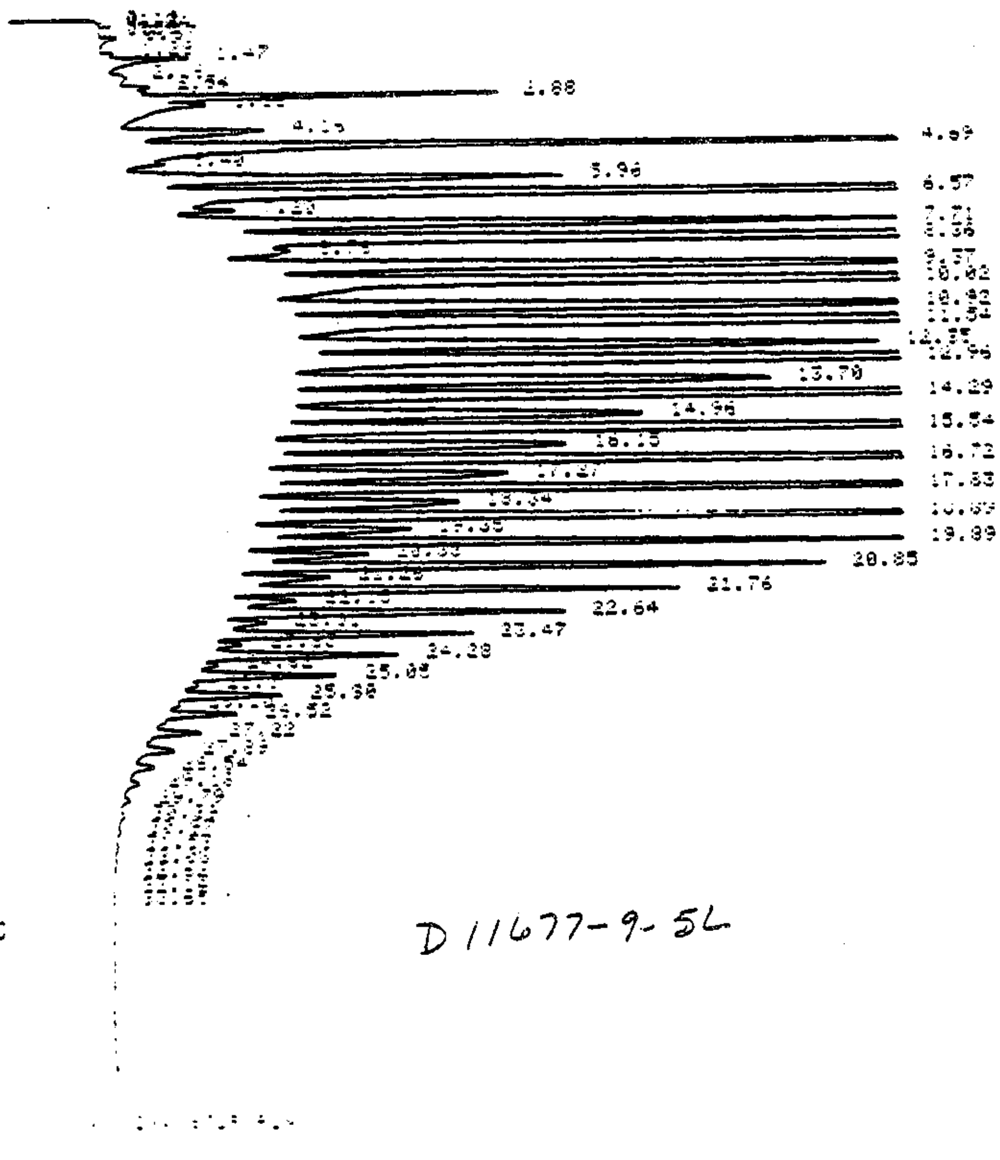
Fig. 44



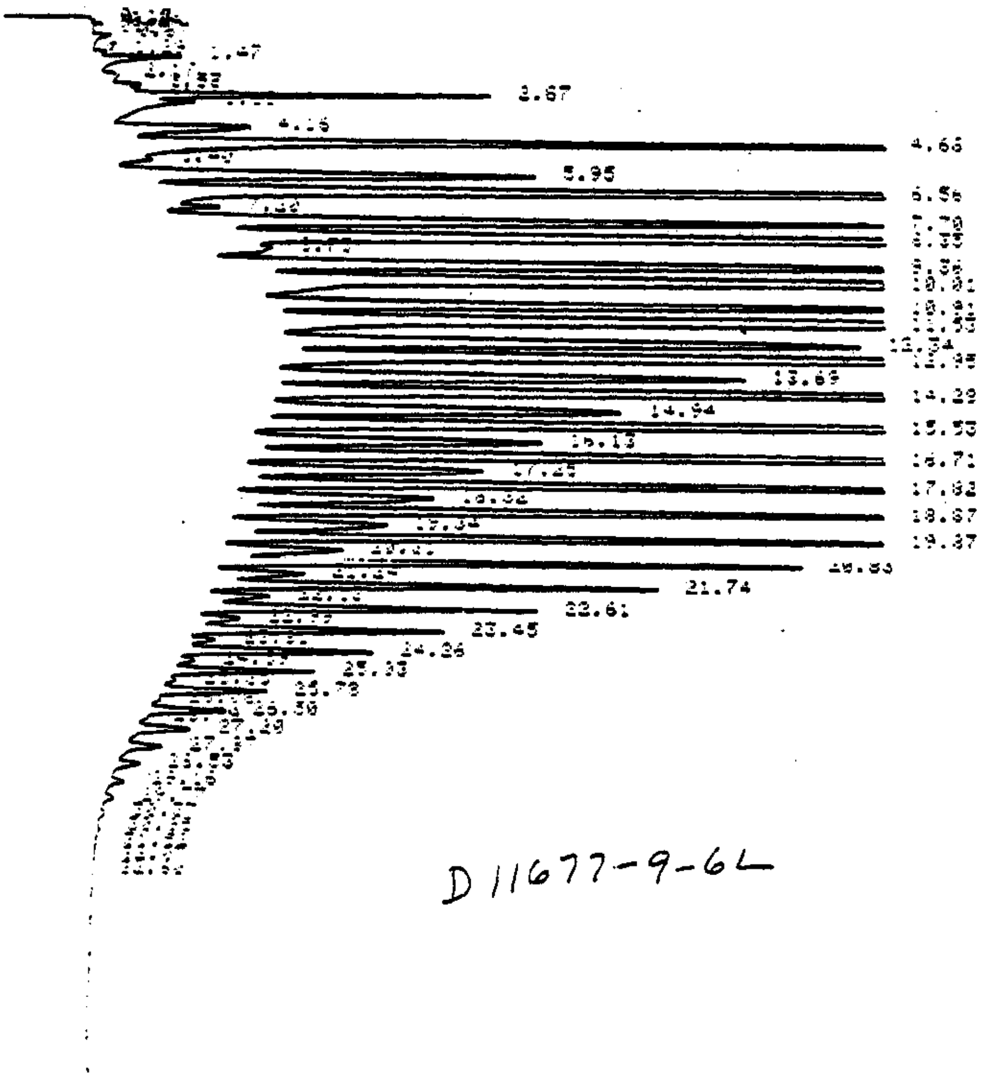
D 11677-9-1L

Fig. 45



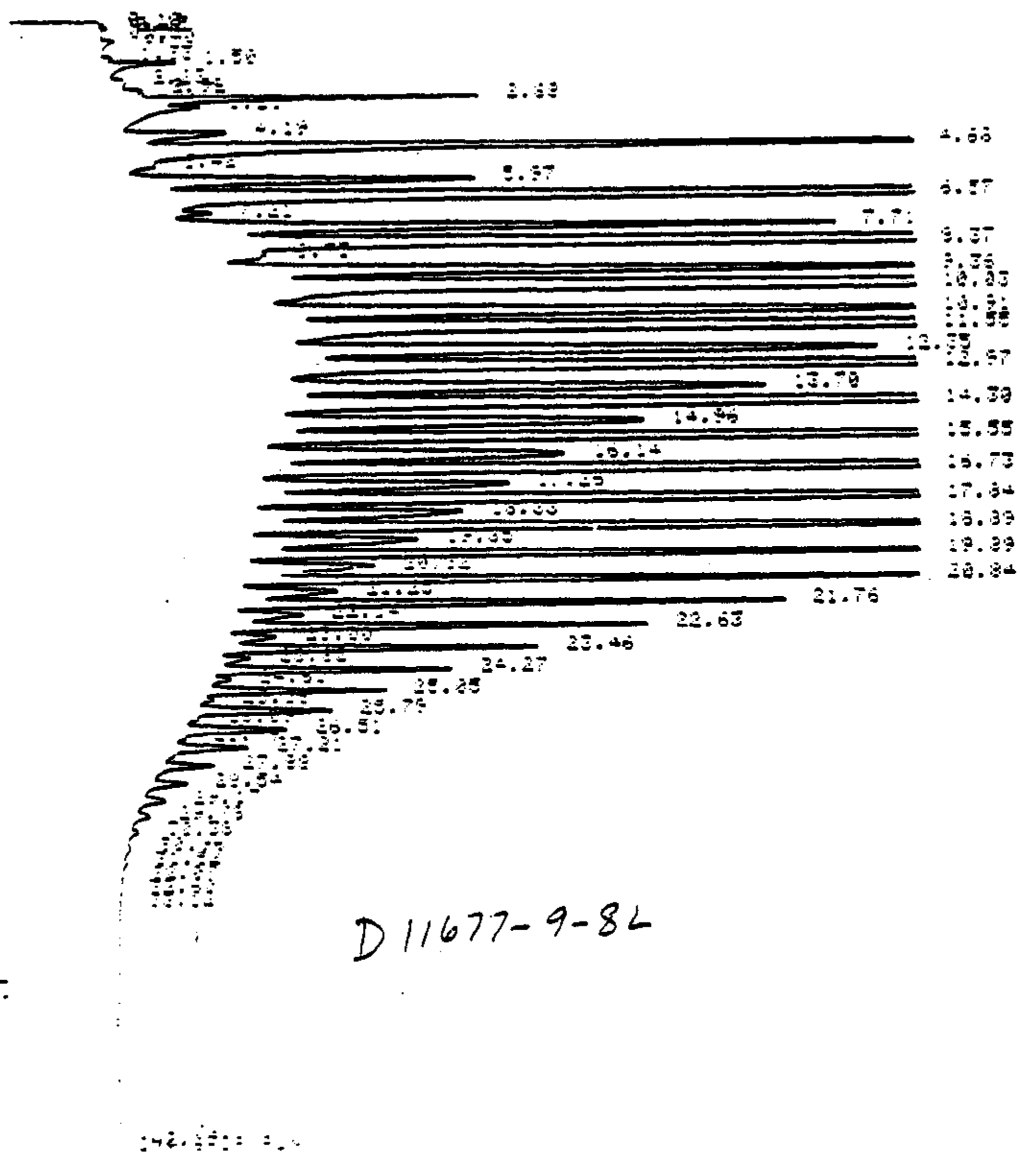
1.47
5.96
6.57
10.02
13.70
14.29
14.96
15.54
16.72
17.83
19.89
20.85
21.76
22.64
23.47
24.28
25.08
25.98
D11677-9-5L

Fig. 46



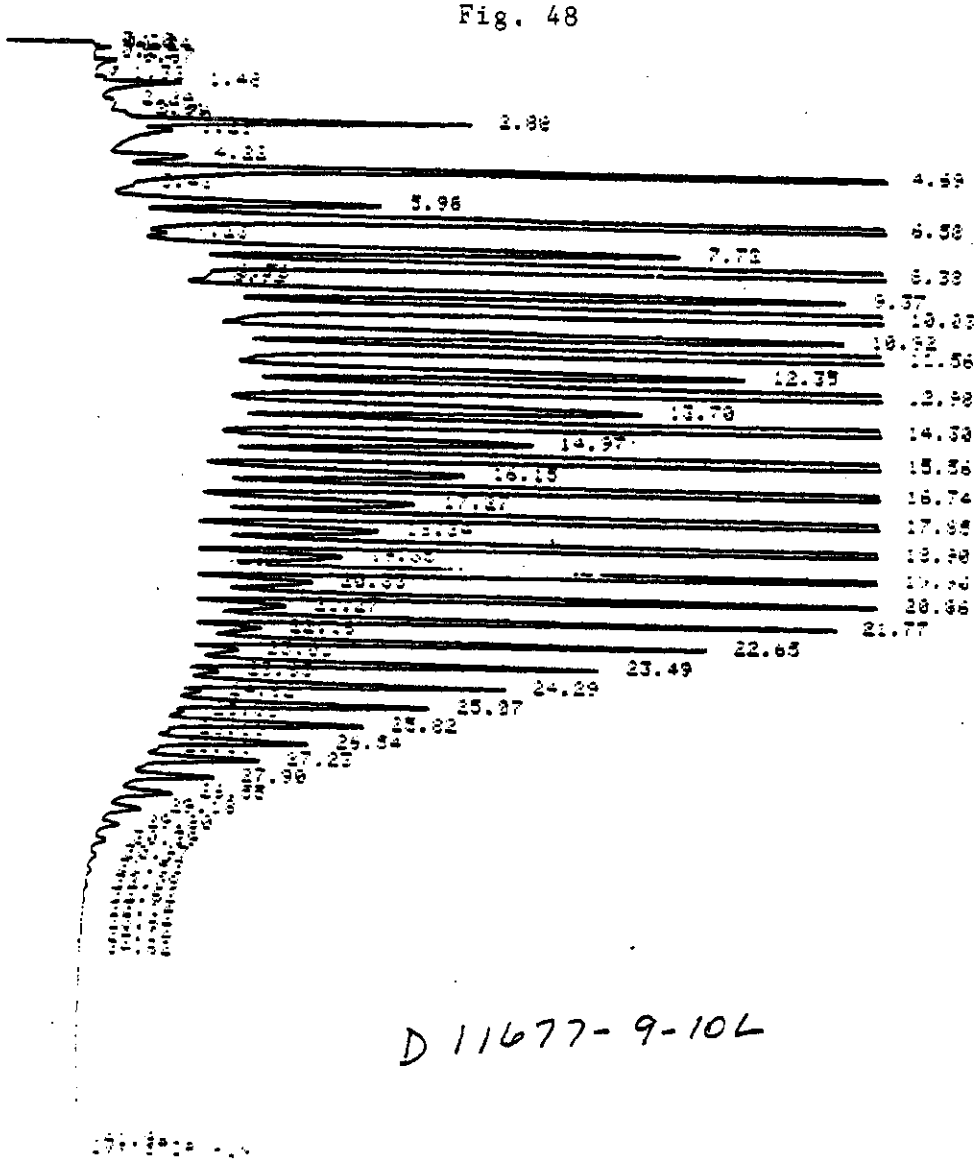
D 11677-9-6L

Fig. 47



D 11677-9-8L

Fig. 48



D 11677-9-10L

TABLE 10 RESULT OF SYNGAS OPERATION

RUN NO. 11677-09
CATALYST CO/TH+UCC-103+UCC-101 #11684-39C 80 CC 39.33 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	11677-09-04	677-09-05	677-09-06	677-09-07	677-09-08
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	48.0	67.0	90.0	97.5	114.0
PRESSURE,PSIG	296	294	290	311	311
TEMP. C	267	267	269	264	264
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.00	25.00	23.00	7.50	24.00
EFFLNT GAS LITER	67.70	291.00	260.20	86.20	286.00
GM AQUEOUS LAYER	14.90	62.09	58.58	18.30	58.57
GM OIL	5.28	22.00	19.50	6.09	19.49
MATERIAL BALANCE					
GM ATOM CARBON %	92.21	93.63	91.49	89.55	90.97
GM ATOM HYDROGEN %	90.45	92.40	91.17	91.11	92.13
GM ATOM OXYGEN %	93.74	94.91	94.33	91.47	93.37
RATIO CHX/(H2O+CO2)	0.9533	0.9608	0.9152	0.9389	0.9238
RATIO X IN CHX	2.4229	2.4329	2.4550	2.4253	2.4153
USAGE H2/CO PRODT	1.9286	1.9438	1.9340	1.9861	1.9907
RATIO CO2/(H2O+CO2)	0.0927	0.0894	0.0925	0.0714	0.0671
K SHIFT IN EFFLNT	0.04	0.04	0.04	0.03	0.03
CONVERSION					
ON CO %	37.13	36.66	36.92	35.54	34.23
ON H2 %	74.64	73.55	74.68	71.47	69.88
ON CO+H2 %	55.70	54.98	55.77	53.66	52.17
PRDT SELECTIVITY,WT %					
CH4	17.18	17.66	18.75	17.47	16.90
C2 HC'S	3.29	3.33	3.46	3.34	3.58
C3H8	4.63	4.56	4.67	4.49	4.62
C3H6=	1.89	1.91	1.87	1.93	2.02
C4H10	4.01	4.05	4.13	3.98	3.96
C4H8=	3.66	3.69	3.59	3.71	3.62
C5H12	4.20	4.22	4.23	4.21	4.26
C5H10=	3.50	3.56	3.39	3.57	3.55
C6H14	4.65	4.73	4.45	4.78	4.63
C6H12= & CYCLO'S	2.59	2.53	2.12	2.69	2.70
C7+ IN GAS	10.90	10.51	10.70	11.36	10.96
LIQ HC'S	39.51	39.24	38.63	38.47	39.21
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.65	35.20	36.47	34.92	34.69
C5 -420 F	46.88	46.45	45.61	46.70	46.57
420-700 F	16.72	16.61	16.21	16.46	16.77
700-END PT	1.75	1.74	1.72	1.92	1.96
C5+-END PT	65.35	64.80	63.53	65.08	65.31
ISO/NORMAL MOLE RATIO					
C4	0.1011	0.0917	0.0851	0.0796	0.0795
C5	0.1441	0.1241	0.1220	0.1181	0.1113
C6	0.2626	0.2450	0.2324	0.2044	0.1826
C4=	0.0835	0.0899	0.0952	0.0887	0.0902
PARAFFIN/OLEFIN RATIO					
C3	2.3394	2.2785	2.3799	2.2228	2.1856
C4	1.0573	1.0583	1.1090	1.0368	1.0547
C5	1.1651	1.1527	1.2141	1.1448	1.1679
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.7954	0.7938		0.7968
RATIO CH4/(1-A)**2		4.2187	4.4094		4.0930
LIQ HC COLLECTION					
PHYS. APPEARANCE		LT BL OIL	LT BL OIL		LT BL OIL
DENSITY		0.698	0.699		0.698
N, REFRACTIVE INDEX		1.4241	1.4235		1.4238
SIMULT'D DISTILATN					
10 WT % @ DEG F		260	259		270
16		299	299		301
50		413	412		414
84		581	578		591
90		631	628		642
RANGE(16-84 %)		282	279		290
WT % @ 420 F	53.25	53.25	53.60	52.22	52.22
WT % @ 700 F	95.57	95.57	95.56	95.00	95.00

TABLE 11 RESULT OF SYNGAS OPERATION

RUN NO. 11677-09
CATALYST CO/TH+UCC-103+UCC-101 #11684-39C 80 CC 39.33 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	11677-09-09	677-09-10
	=========	=========
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	121.5	234.0
PRESSURE,PSIG	295	294
TEMP. C	263	263
FEED CC/MIN	400	400
HOURS FEEDING	7.50	120.00
EFFLNT GAS LITER	89.60	1539.45
GM AQUEOUS LAYER	17.66	282.49
GM OIL	5.47	87.53
MATERIAL BALANCE		
GM ATOM CARBON %	89.06	93.66
GM ATOM HYDROGEN %	89.76	94.71
GM ATOM OXYGEN %	92.24	95.59
RATIO CHX/(H2O+CO2)	0.8954	0.9363
RATIO X IN CHX	2.4390	2.4444
USAGE H2/CO PRODT	1.9982	2.0298
RATIO CO2/(H2O+CO2)	0.0661	0.0591
K SHIFT IN EFFLNT	0.03	0.03
CONVERSION		
ON CO %	32.78	32.19
ON H2 %	68.53	66.68
ON CO+H2 %	50.72	49.53
PRDT SELECTIVITY,WT %		
CH4	17.92	17.98
C2 HC'S	3.38	3.82
C3H8	4.80	4.90
C3H6=	1.98	1.91
C4H10	4.15	4.34
C4H8=	3.84	3.68
C5H12	4.40	4.75
C5H10=	3.57	3.37
C6H14	4.79	5.02
C6H12= & CYCLO'S	2.66	2.62
C7+ IN GAS	10.97	11.61
LIQ HC'S	37.55	35.99
TOTAL	100.00	100.00

SUB-GROUPING		
C1 -C4	36.05	36.63
C5 -420 F	45.62	45.80
420-700 F	15.95	15.29
700-END PT	2.38	2.28
C5+-END PT	63.95	63.37
ISO/NORMAL MOLE RATIO		
C4	0.0744	0.0588
C5	0.1101	0.0928
C6	0.1771	0.1469
C4=	0.0918	0.1016
PARAFFIN/OLEFIN RATIO		
C3	2.3098	2.4439
C4	1.0435	1.1395
C5	1.1957	1.3683
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))		0.7990
RATIO CH4/(1-A)**2		4.4481
LIQ HC COLLECTION		
PHYS. APPEARANCE		LT BL OIL
DENSITY		0.680
N, REFRACTIVE INDEX		1.4231
SIMULT'D DISTILATN		
10 WT % @ DEG F		282
16		302
50		417
84		601
90		655
RANGE(16-84 %)		299
WT % @ 420 F	51.20	51.20
WT % @ 700 F	93.67	93.67

IV. Run 3 (11723-03) with Catalyst 3 (Co/Th+UCC-103+UCC-108)

This catalyst is identical in formulation and preparation to Catalyst 2 except with UCC-108 in place of UCC-101. This catalyst is also related to Run 10225-7, reported as Run 5 in the Tenth Quarterly Report.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 49-52 for this run and in Figs. 53-56 for Run 10225-7. Simulated distillations of the C_5^+ product are plotted in Figs. 57-60. Carbon number product distributions are plotted in Figs. 61-70. Chromatograms from simulated distillations are reproduced in Figs. 71-80. Detailed material balances appear in Tables 12-15 for this run and in Tables 16-18 for Run 10225-7.

As with Catalysts 1 and 2, the conversion of this catalyst was fairly stable. There was no abrupt initial deactivation, and deactivation was gradual and steady over the 240 hour test. From an initial level of 70 percent, conversion of syngas declined by 1.1 percentage points each 24 hours on stream. With the same cobalt loading as Catalyst 2, but at 7C higher temperature, the initial conversion was 22 percent higher. Catalyst 2, however, deactivated less rapidly at the end of the run--1.2 percentage points in the last 100 hours, versus about 25 hours for this catalyst. Tenth Quarter Catalyst 5 (Run 10225-07), with Co/Th and UCC-108 but with no UCC-103 in close contact with the cobalt, deactivated more than twice as rapidly as this catalyst, losing one percentage point of syngas conversion in less than 10 hours.

The water gas shift activity of this catalyst was better than with Catalysts 1 and 2 but still on the low side, with 12-19 percent of the oxygen rejected as CO_2 and a high H_2:CO usage ratio of 1.7-1.9:1. The corresponding values for Tenth Quarter Catalyst 5, about 21 percent and 1.6-1.7:1 respectively, were more nearly representative of the cobalt catalysts tested to date.

The selectivity, although again stable, was not as good as with Catalysts 1 and 2 and not up to the best obtained with other cobalt catalysts. Methane production was a high 19 percent to begin with, rose still further to 21 percent at 100 hours on stream, and remained absolutely constant thereafter. With Catalyst 2, methane production was 17.1 percent initially and averaged 17.7 percent for all samples after 48 hours on stream, the difference possibly due to the 7C lower reaction temperature of Catalyst 2. The methane production of Tenth Quarter Catalyst 5 was much less stable; although initially lower at 14 percent, it was up to 21 percent by 120 hours on stream and over 24 percent by the end of the 190-hour run. Production of C_2-C_4 hydrocarbons was constant, about the same level as with Catalyst 2, somewhat higher than with Catalyst 1 (which also produced less methane), and also higher than with Tenth Quarter Catalyst 5 (whose methane production was high).

Production of C_5^+, initially 63 percent, deactivated slightly to about 60 percent and remained constant at 59.4 percent during the last 140 hours on stream. Since the yield of heavies was low and steady, the production of motor fuels also remained constant during the last 140 hours at 58.3 percent. The motor fuels boiled mostly below 420F; 48 percent of the total product boiled in the gasoline range, 10 percent in the diesel range. During the run the balance shifted slightly from gasoline to diesel. In comparison with Tenth Quarter Catalyst 5 (Run 10225-07), for which the initial selectivity for gasoline and diesel was 49 and 22 percent respectively, this catalyst produced about the same proportion of gasoline but a smaller proportion of diesel fuel. Catalyst 2, with UCC-101 in place of UCC-108, produced 45 percent gasoline and 17 percent diesel. Even if the gasoline/diesel cut is taken at 300F, this catalyst still produced 45 percent more gasoline than diesel. Overall, the product distribution was rather on the light side.

Isomerization of the pentane was no more extensive than with cobalt alone. The same result was also obtained with Tenth Quarter Catalyst 5, in contrast to the results from the iron UCC-108 catalysts reported earlier.

The C_4 hydrocarbons were slightly less than 50 percent butenes, as with Catalyst 2, and relatively stable. This was more olefinic than the C_4's from Eleventh Quarter Catalyst 7 (Run 10225-16), and less than those from Catalyst 1 or Tenth Quarter Catalyst 5 (Run 10225-07).

The Schulz-Flory plots show excess methane, but no carbon number cut-off. The liquid product, as with Catalysts 1 and 2, was a clear oil without wax.

This catalyst demonstrates once again the stabilizing effect of an intimate physical contact between metal component and Molecular Sieve. The effects of the UCC-108 seem to be subordinated to those of the UCC-103.

Fig. 49

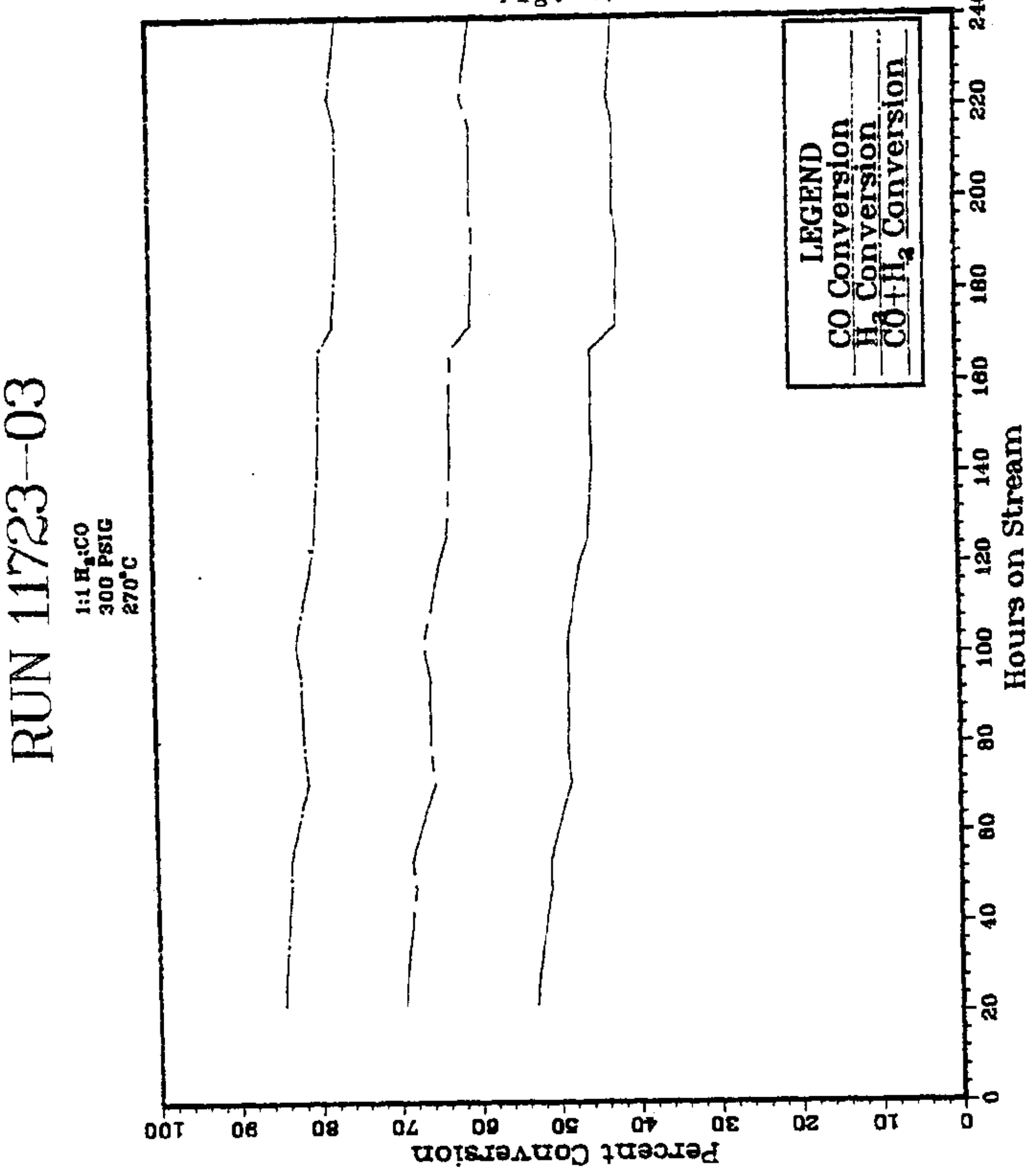
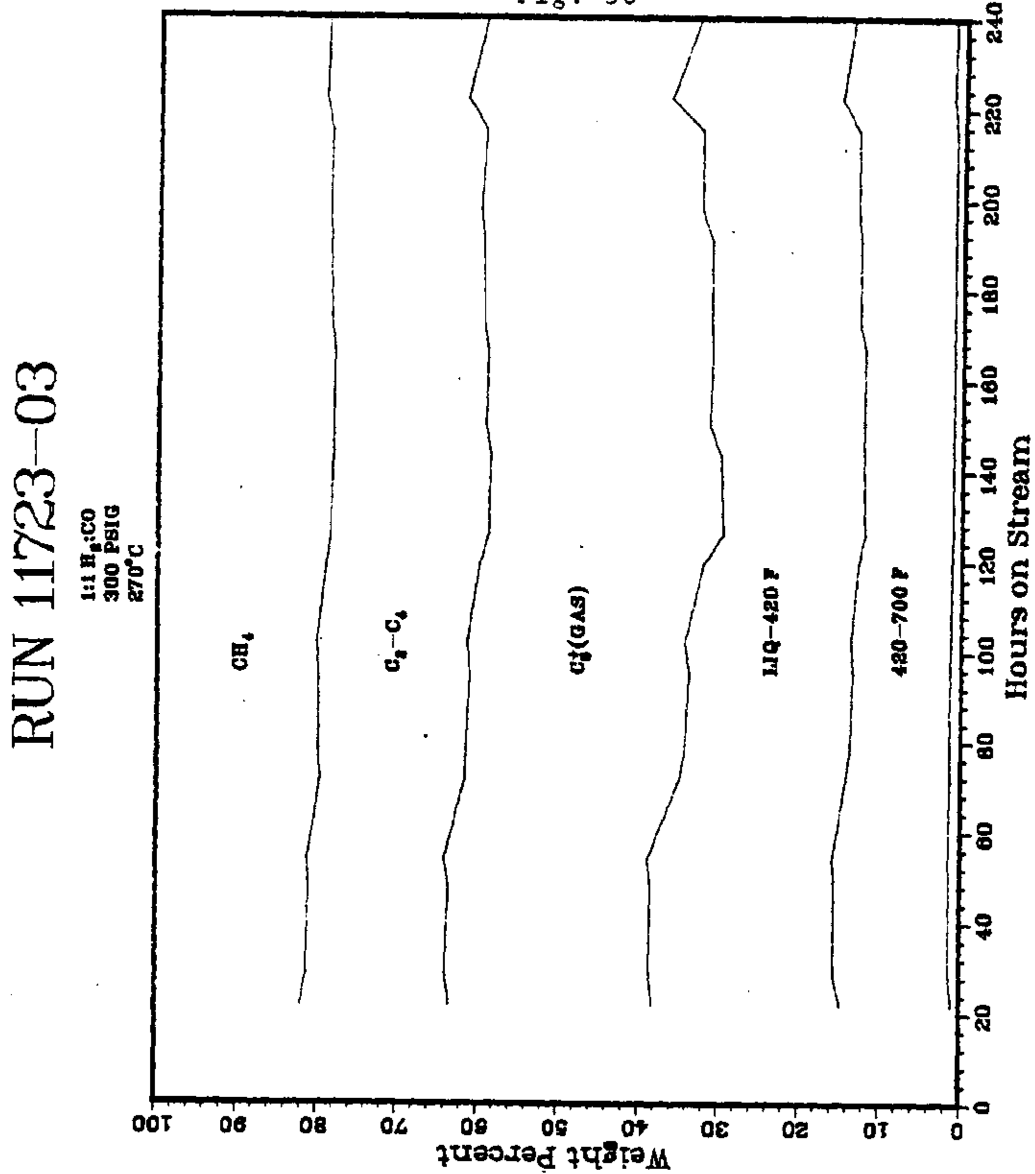

RUN 11723-03
1:1 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion

Fig. 50



RUN 11723-03
1:1 H2:CO
300 PSIG
270°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
Hours on Stream
Weight Percent
0
20
40
60
80
100
120
140
160
180
200
220
240
0
10
20
30
40
50
60
70
80
90
100

Fig. 51

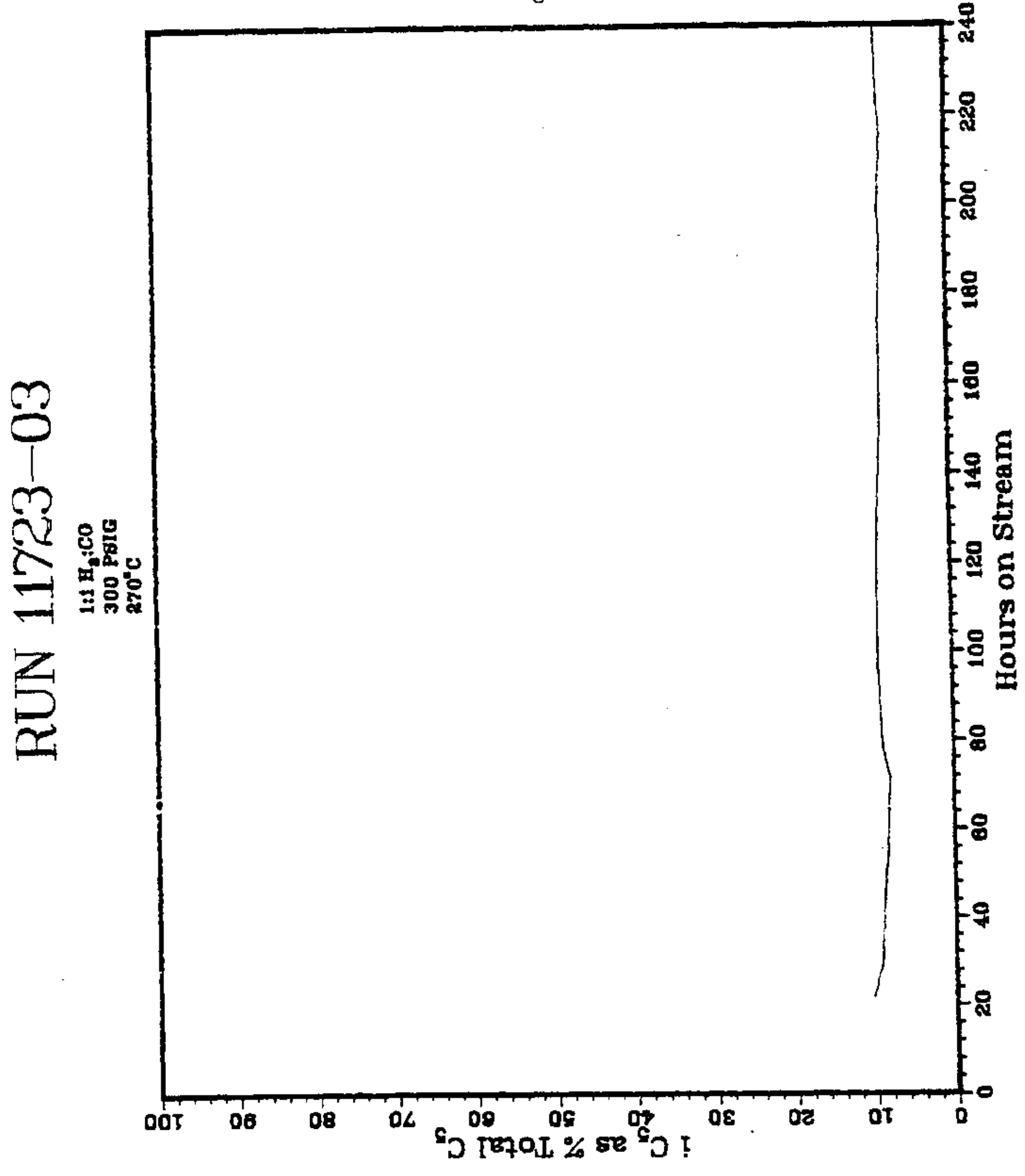
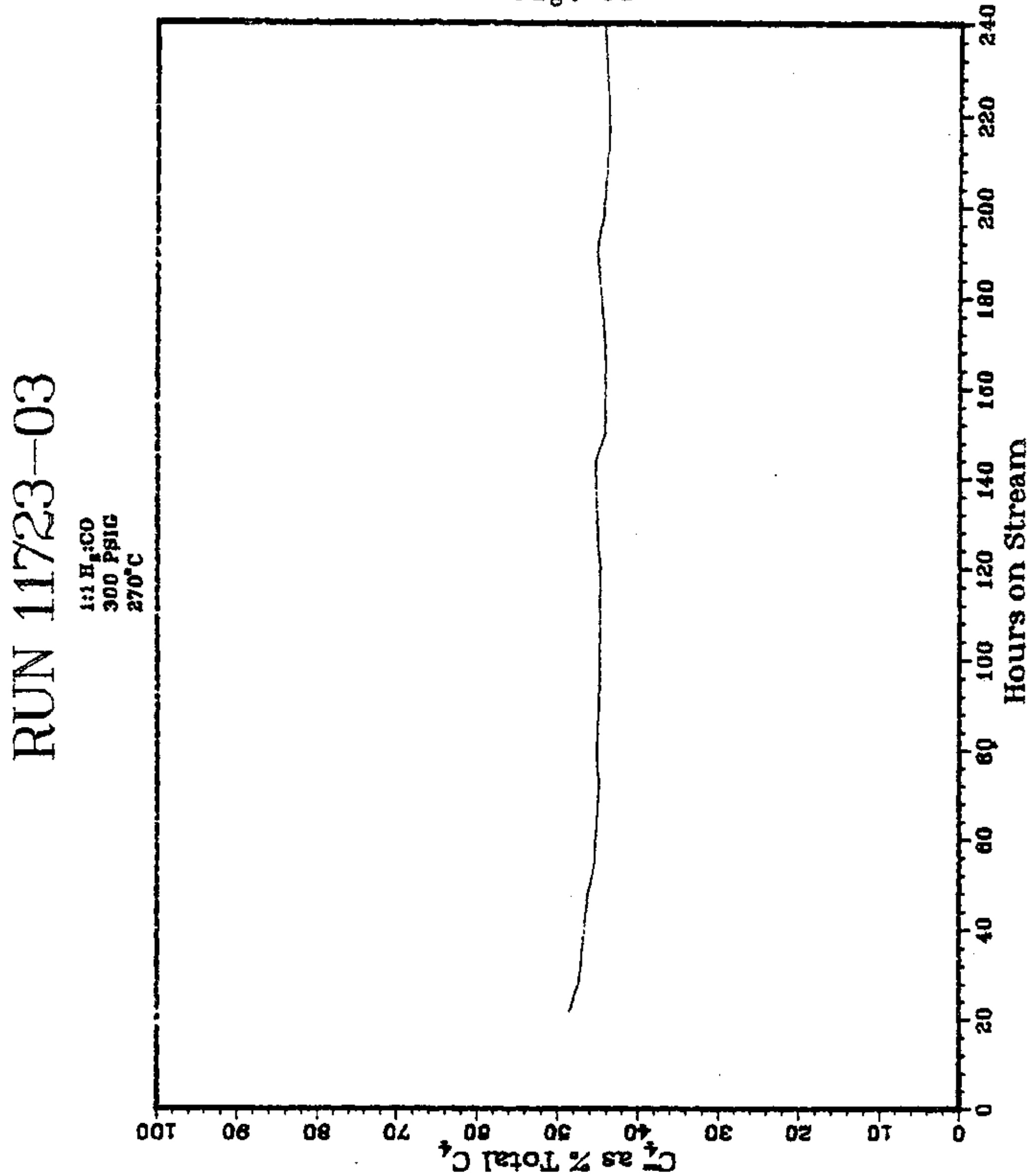

RUN 11723—03
1:1 H_2:CO
300 PSIG
270°C
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
240
i C_5 as % Total C_5
0
10
20
30
40
50
60
70
80
90
100

Fig. 52



RUN 11723-03
1:1 H_2:CO
300 PSIG
270°C
Hours on Stream
$C_4^=$ as % Total C_4
0
20
40
60
80
100
120
140
160
180
200
220
240
0
10
20
30
40
50
60
70
80
90
100

Fig. 5

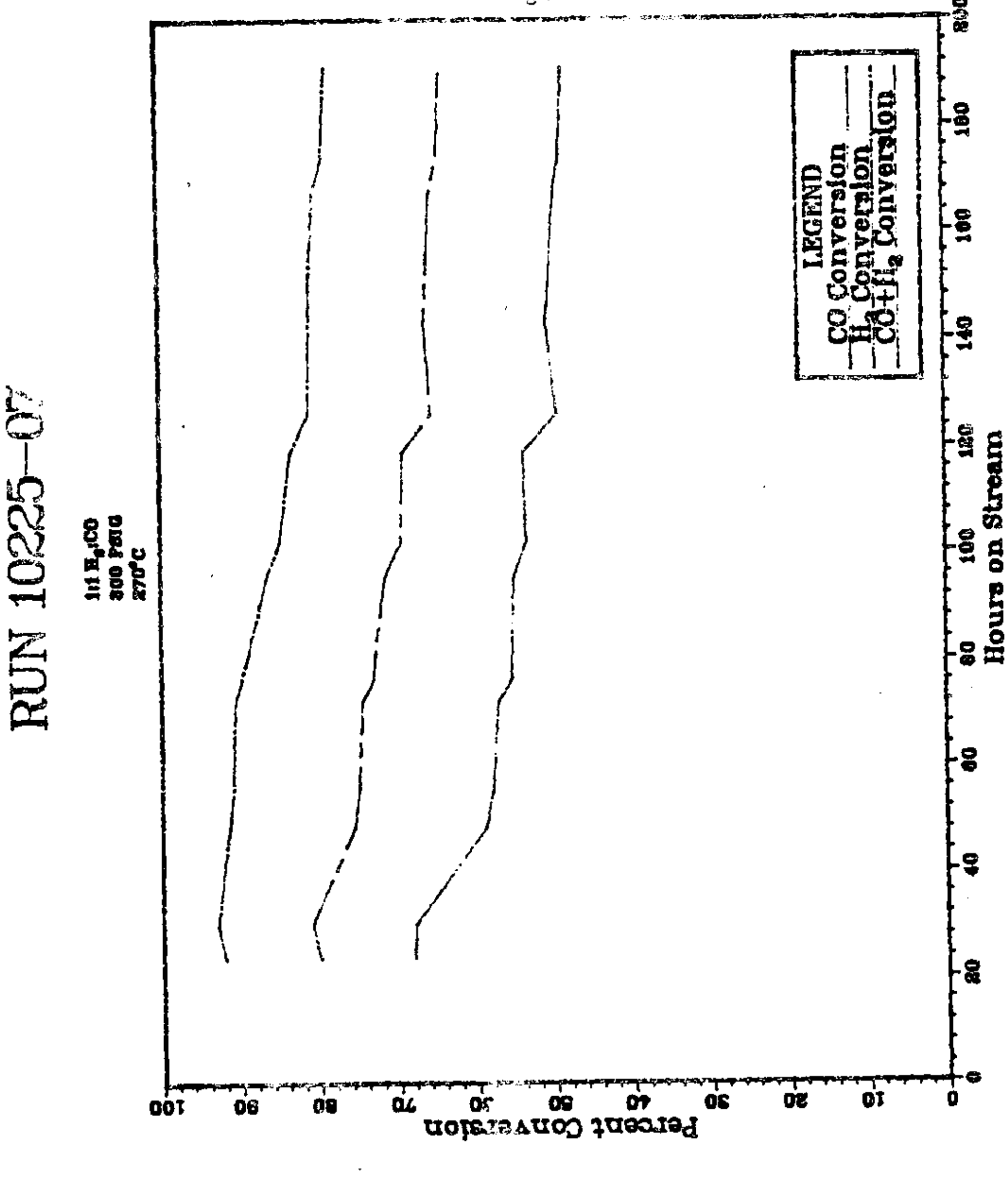

RUN 10225–07
1:1 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion
0
20
40
60
80
100
120
140
160
180
200
0
10
20
30
40
50
60
70
80
90
100

Fig. 54

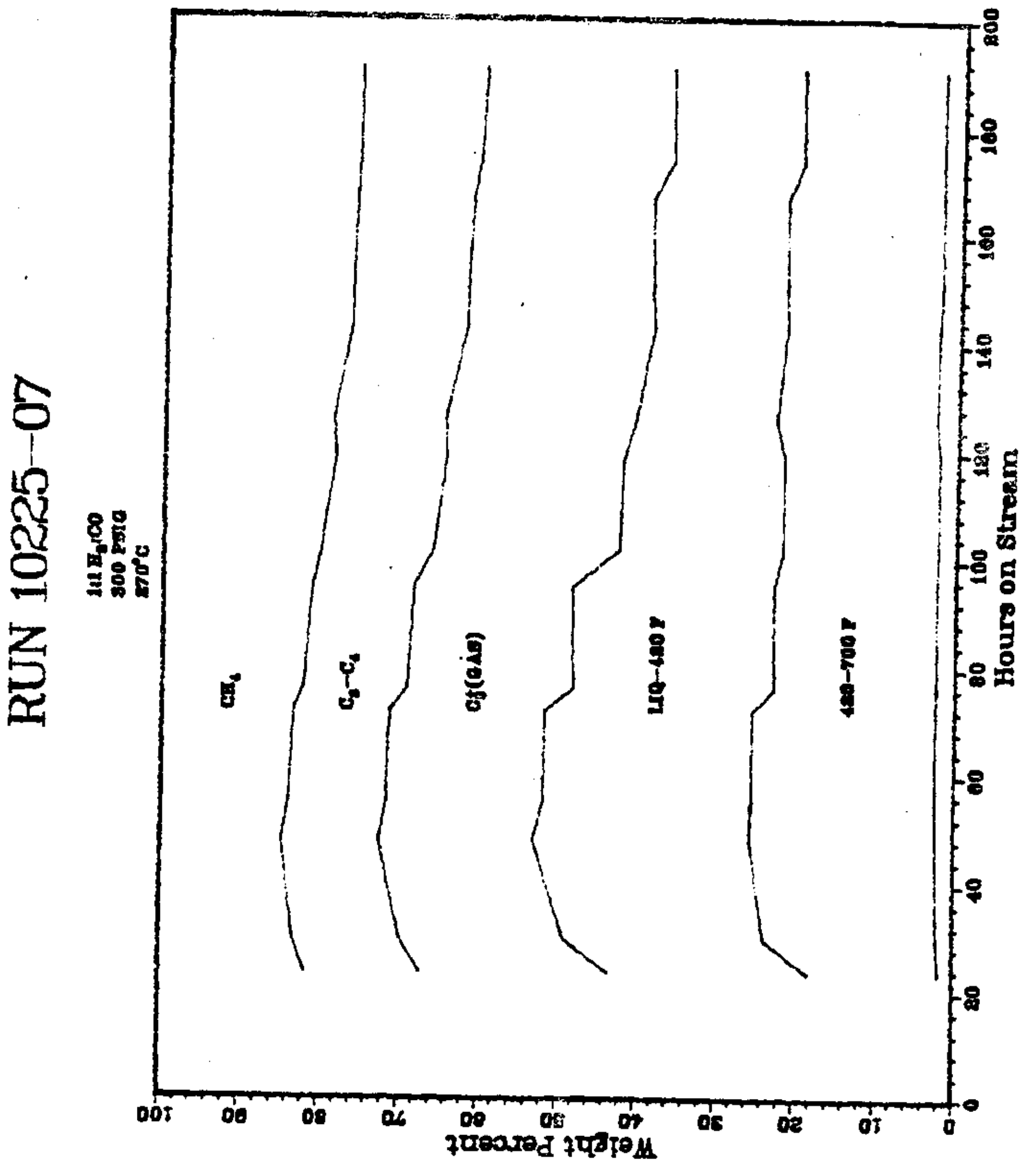

RUN 10225-07
1:1 H_2:CO
300 PSIG
270°C
CH_4
C_2-C_4
C_5^+(GAS)
LIQ-480 F
480-700 F
Hours on Stream
Weight Percent
0
20
40
60
80
100
120
140
160
180
200
10
30
50
70
90

Fig. 55

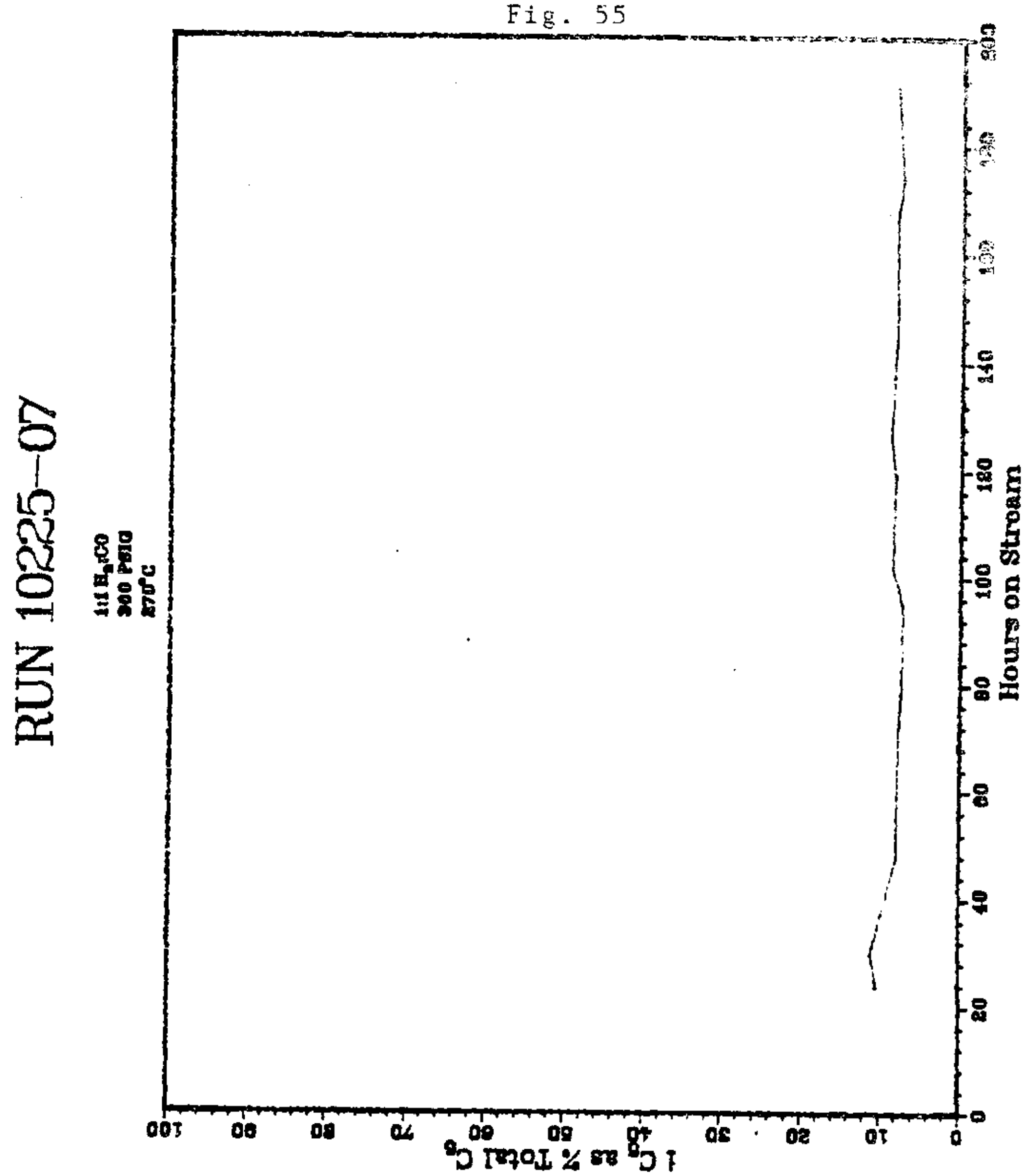

RUN 10225—07
1:1 H2:CO
300 PSIG
270°C
Hours on Stream
0
20
40
60
80
100
120
140
10
20
30
40
50
60
70
80
90
100

Fig. 56

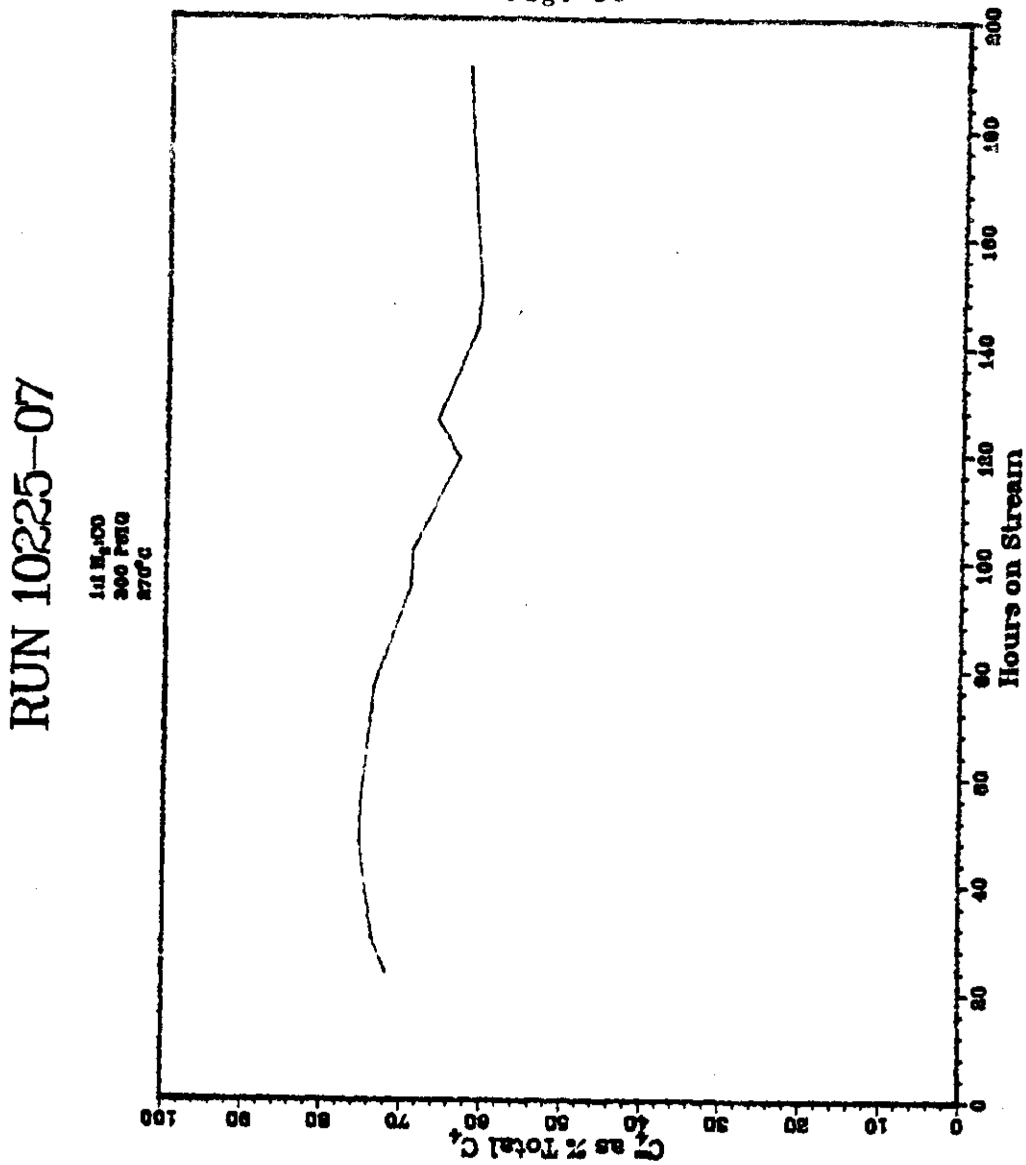

RUN 10225–07
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
0
10
20
30
40
50
60
70
80
90
100

Fig. 57

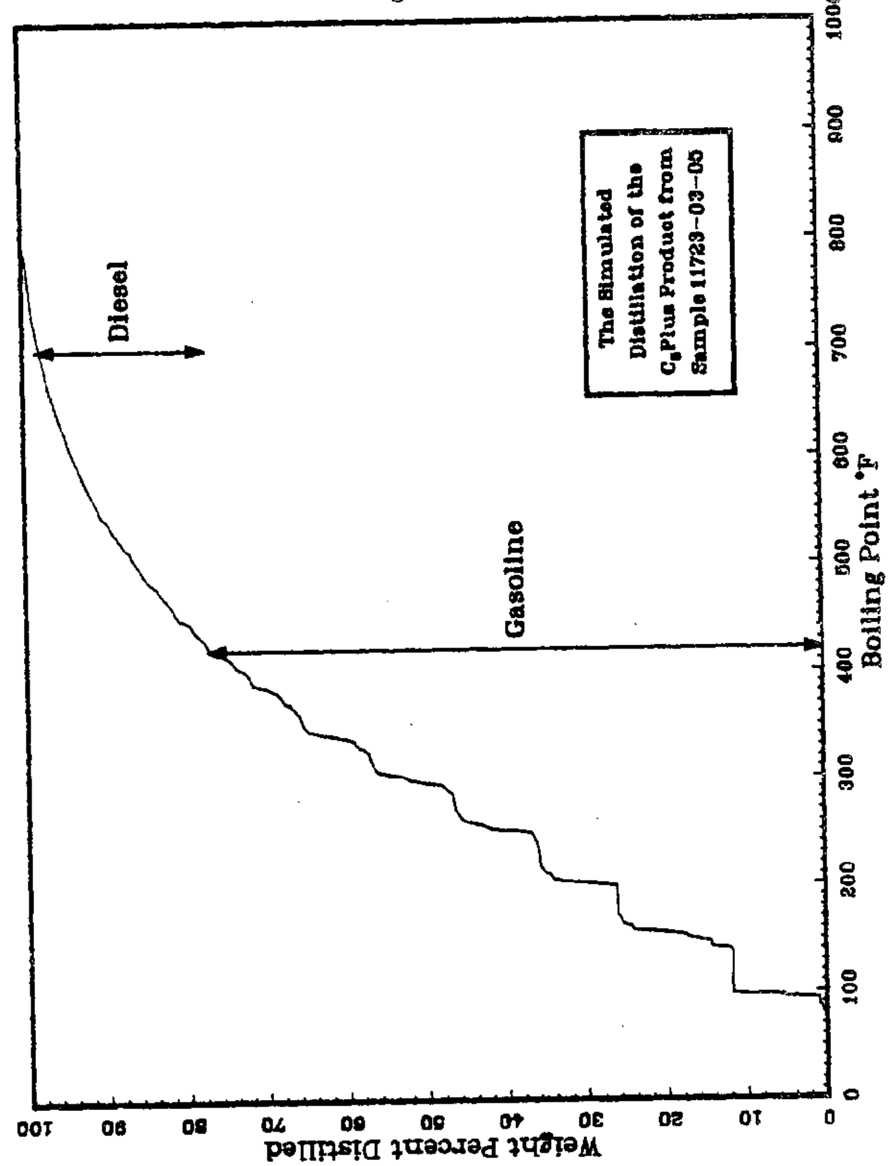
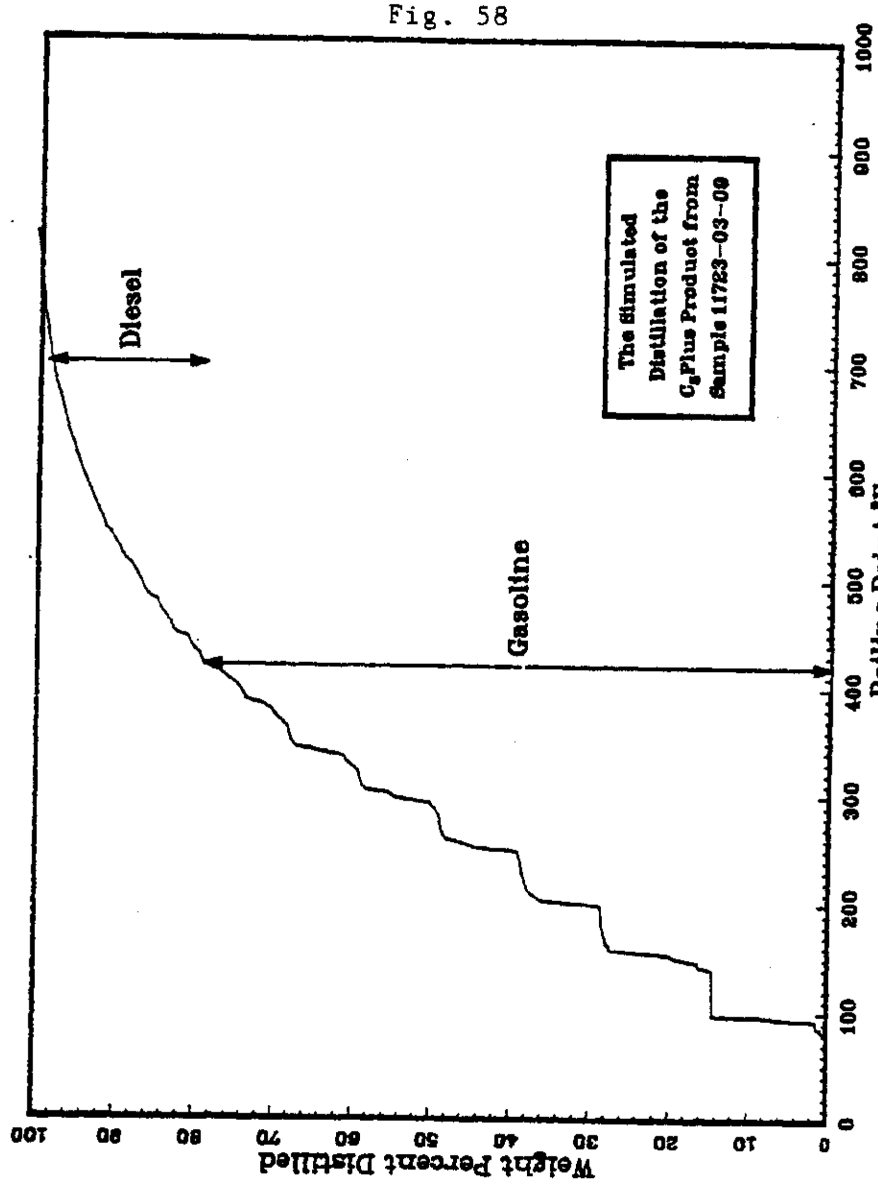

The Simulated
Distillation of the
Sample 11723-03-05
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. 58



The Simulated Distillation of the C_5Plus Product from Sample 11723-03-09
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. 59

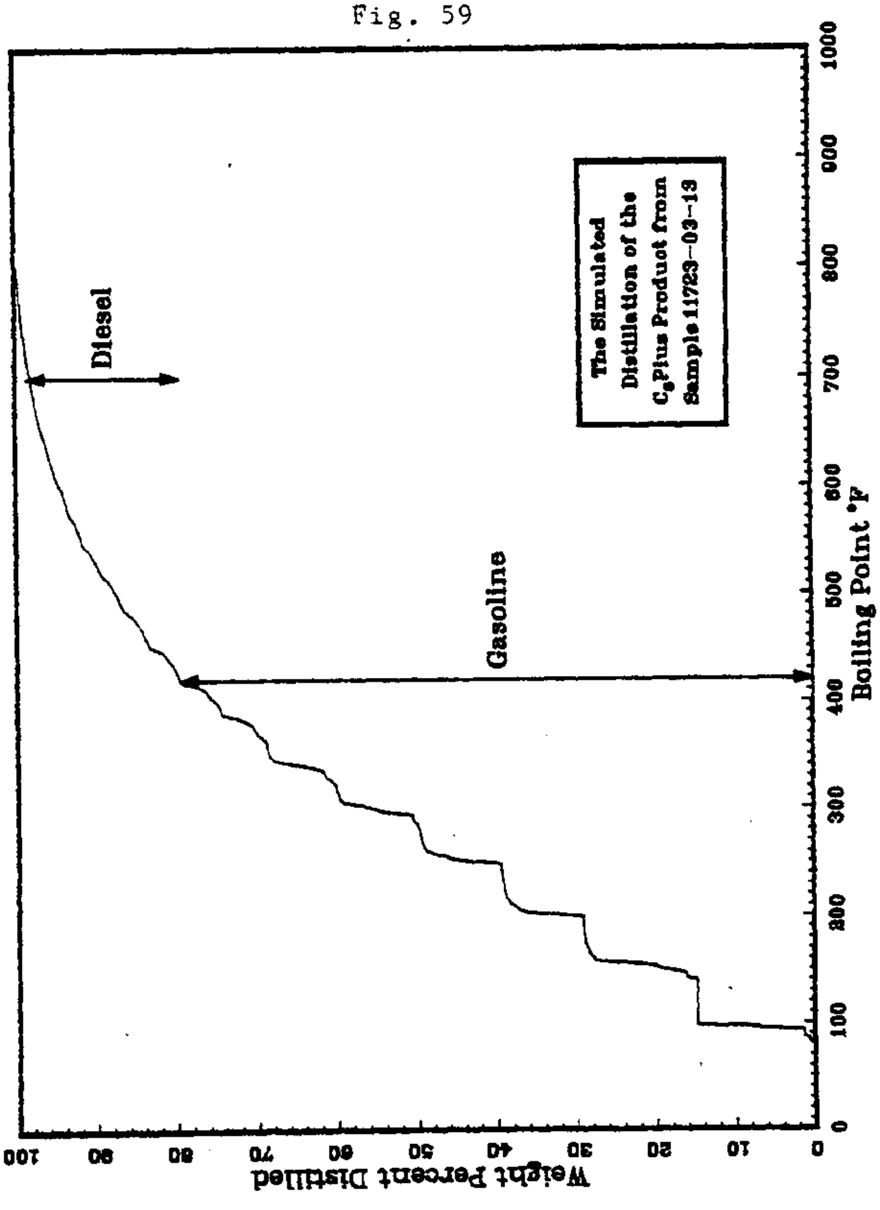
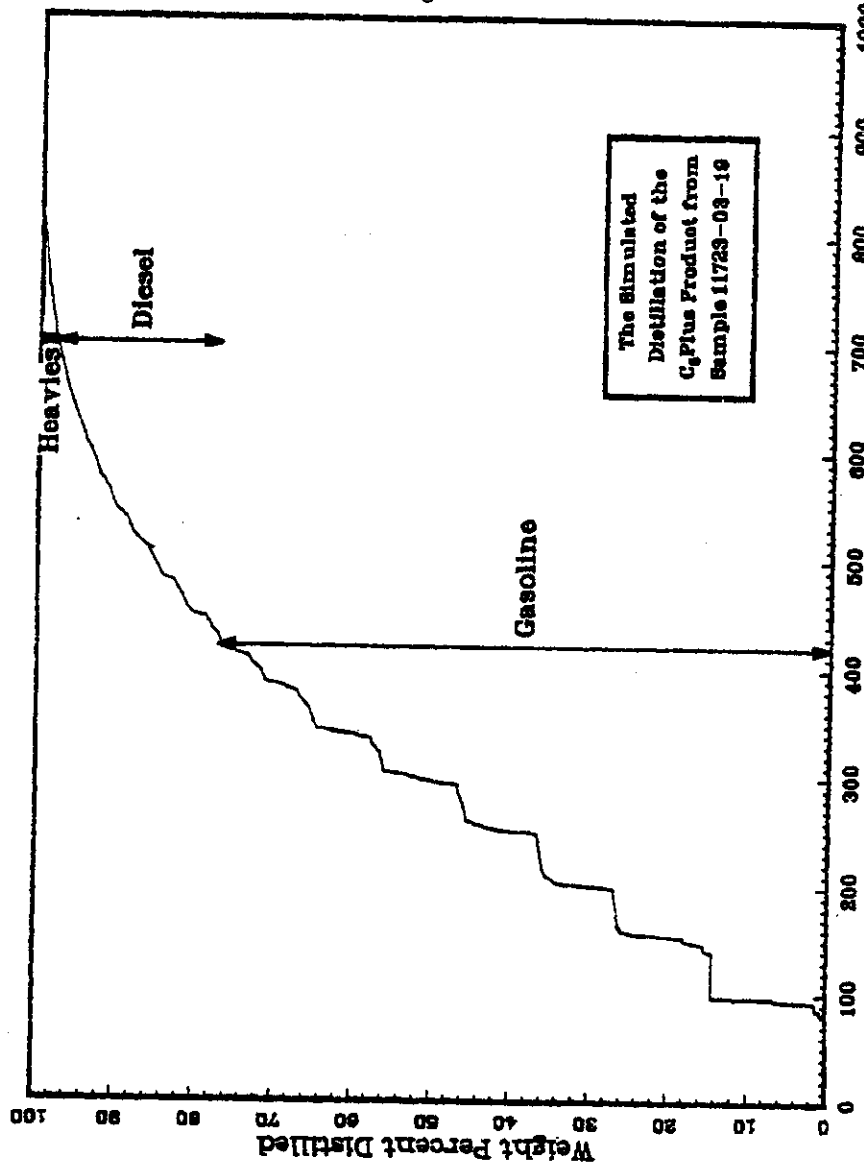

Diesel
Gasoline
The Simulated
Distillation of the
Sample 11723-03-13
Boiling Point °F
Weight Percent Distilled

Fig. 60


The Simulated
Distillation of the
Sample 11723-03-19
Diesel
Gasoline
Heavies
Boiling Point °F
Weight Percent Distilled