Table B17 (continued)

FILE: 1256102D DATA A1

C5+-END PT	73.85	73.77	74.20	74.59	73.80
ISO/NORMAL MOLE RATIO					
C4	0.0219	0.0220	0.0214	0.0218	0.0223
C5	0.0364	0.0361	0.0376	0.0364	0.0334
C6	0.1134	0.1186	0.1185	0.1207	0.1201
C4=	0.0743	0.0733	0.0741	0.0744	0.0752
PARAFFIN/OLEFIN RATIC					
C3	3.3004	3.4610	3.4624	3.4411	3.5250
C4	2.5612	2.6429	2.6021	2.5870	2.6087
C5	5.1179	5.1539	5.1720	5.0221	5.1048
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7943	0.8024	0.8512	0.8086	0.8535
RATIO CH4/(1-A)**2	3.4843	3.7642	6.6350	3.8823	7.0010
ALPHA FRM CORRELATION			0.7901		0.7916
ALPHA (EXPTL/CORR)			1.0774		1.0782
W%CH4 FRM CORRELATION			28.7817		28.5474
W%CH4 (EXPTL/CORR)			0.5102		0.5265
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F			290		291
16			301		305
50			492		510
84			744		791
90			826		877
RANGE(16-84 %)			443		486
WT % @ 420 F			38.10		36.10
WT % @ 700 F			79.50		75.80

V. Run 47 (11617-06) with Catalyst 47 ($Co/X_9/X_{10}$/TC-103)

This run continued the attempt, begun with Run 44, to replicate the carbon number cut-off at the heavy end of the diesel range, which was first observed with Catalyst 20 and later with Catalyst 31. Formulation of the catalyst was similar to that of Catalyst 31 but with one added step. Both catalysts were activated under hydrogen at 350C, but the hydrogen treatment of this catalyst was followed first by exposure to 350C air, then by a second exposure to 350C hydrogen. The theoretical content of cobalt, X_9 and X_{10} was, respectively, 7.8, 0.35 and 0.47 percent.

Simulated distillations of the C_5^+ product are plotted in Figs. B130-131. Carbon number product distributions are plotted in Figs. B132-133. Chromatograms from simulated distillations are reproduced in Figs. B134-135. Detailed material balances appear in Table B18.

The initial activity was extremely low at only 8 percent conversion of the syngas—far lower even than the poor (27 percent) conversion of Catalyst 31 under similar conditions. The run was accordingly terminated after only two samples and 72.5 hours on stream.

Apparently the exposure to air during preparation, which was attempted on the possibility that it might improve the catalyst's activity, had exactly the opposite effect. As to the carbon number cut-off which was the subject of the test, the run was too short to provide any indication whether or not the result with Catalyst 31 was real.

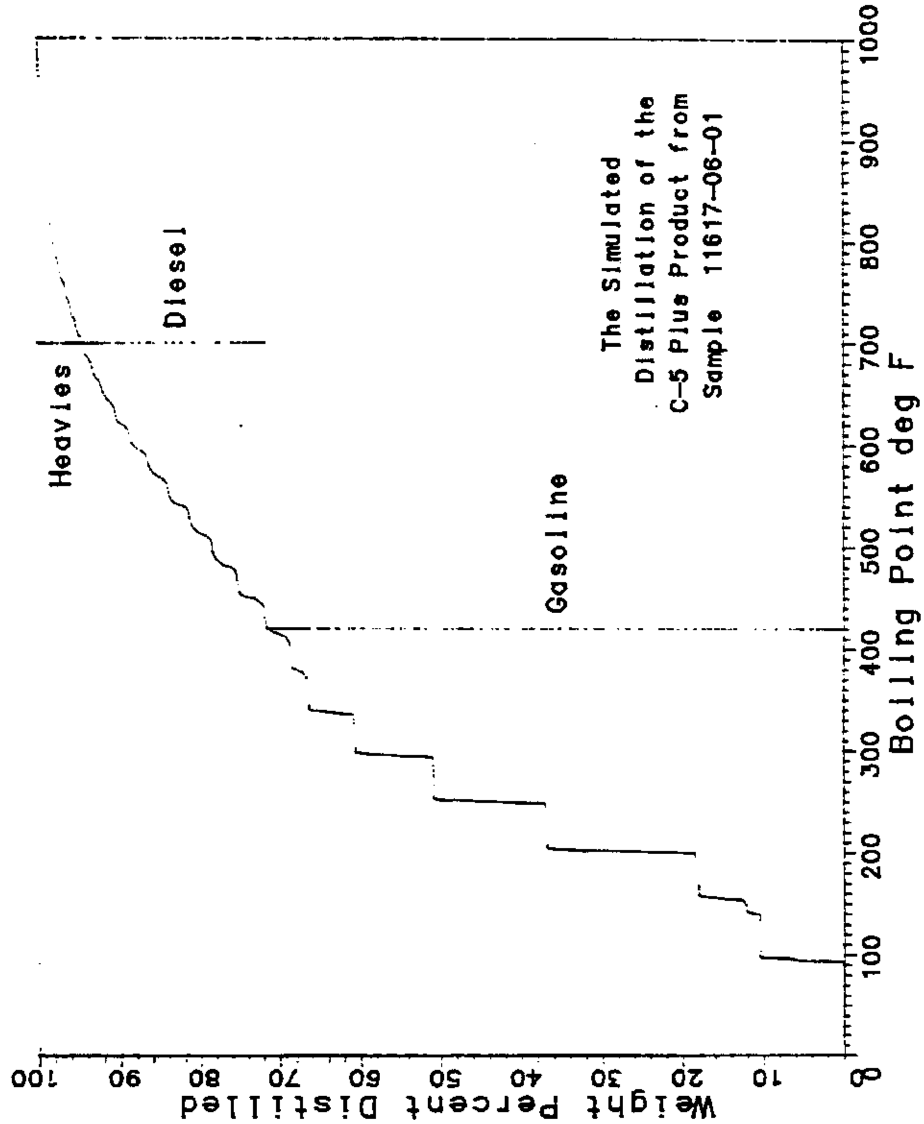

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-06-01
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B130

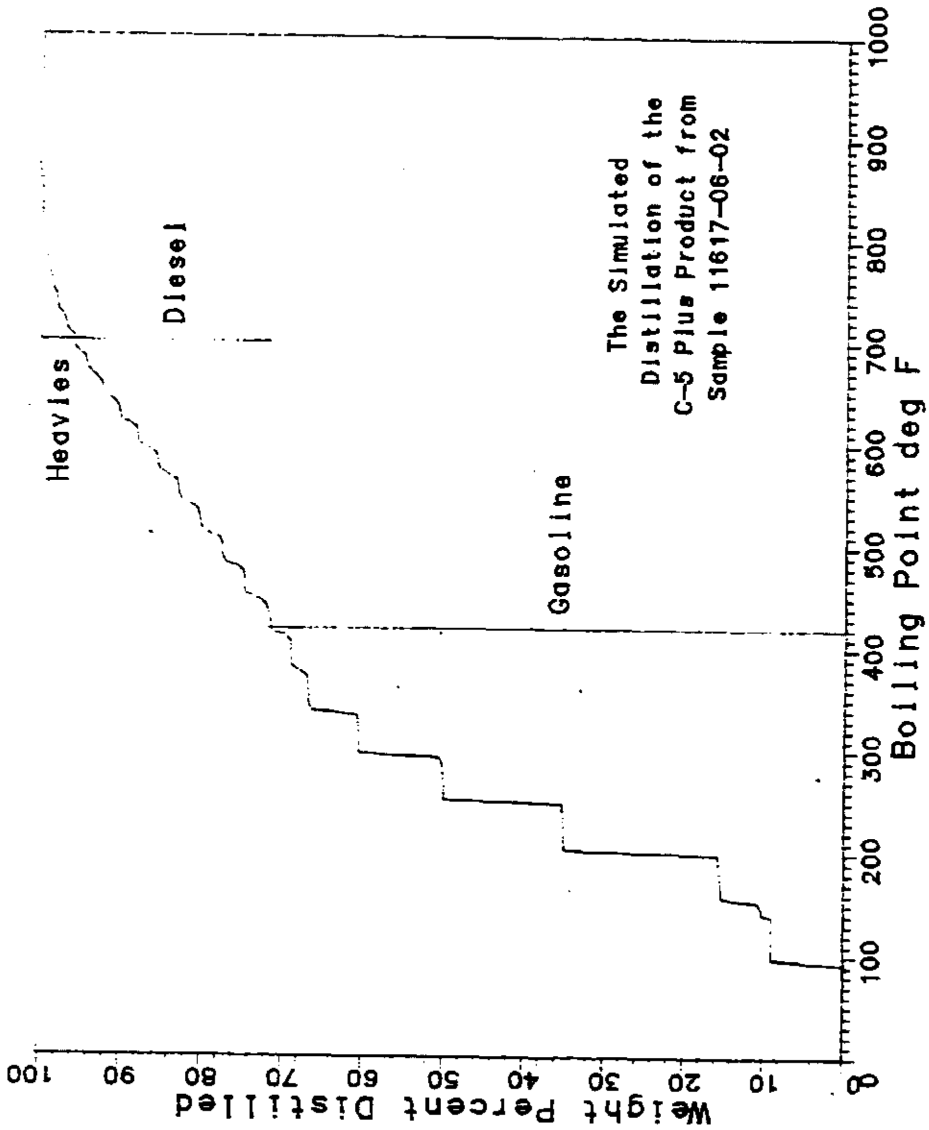

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-06-02
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B131

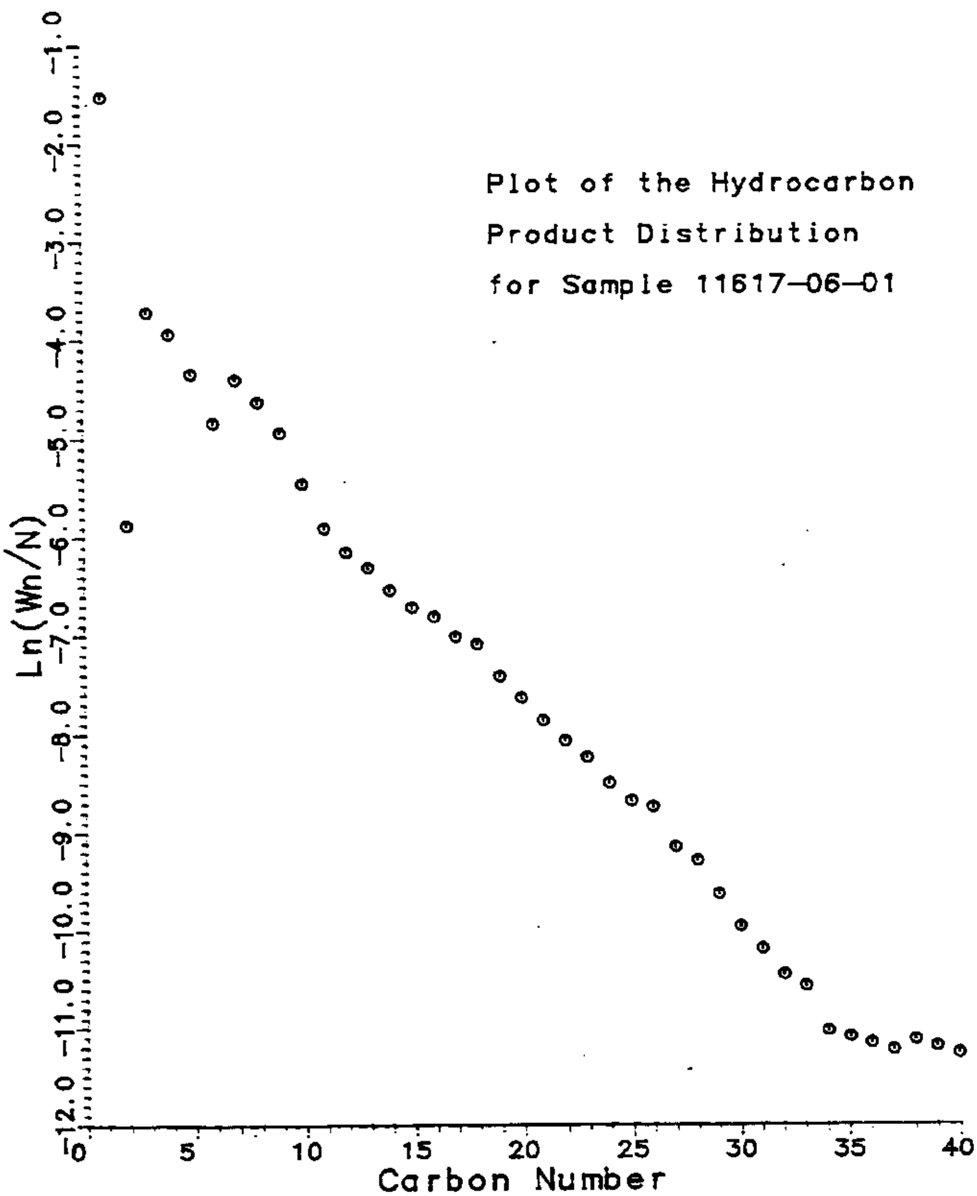
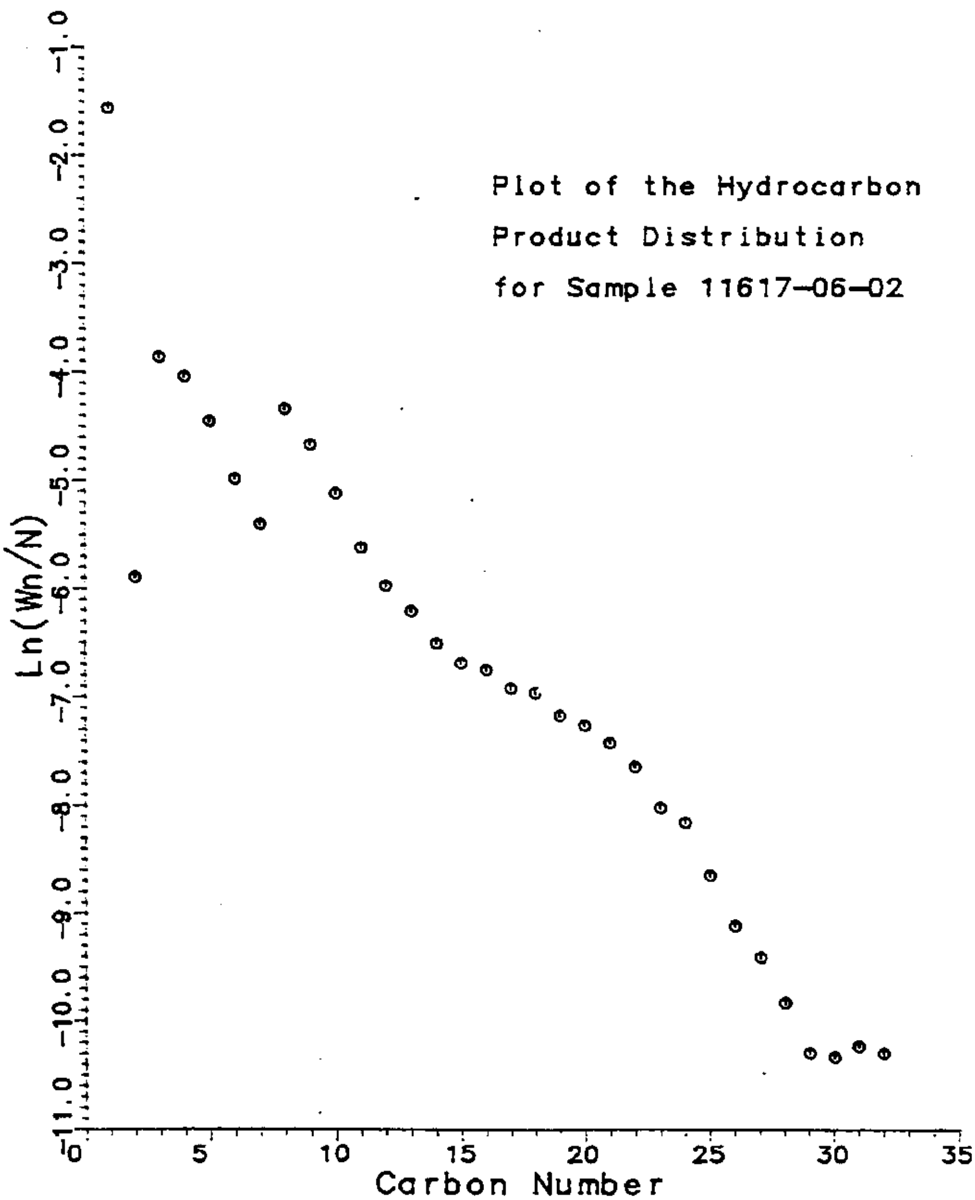

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-06-01
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B132



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-06-02
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
35
Carbon Number

Fig. B133

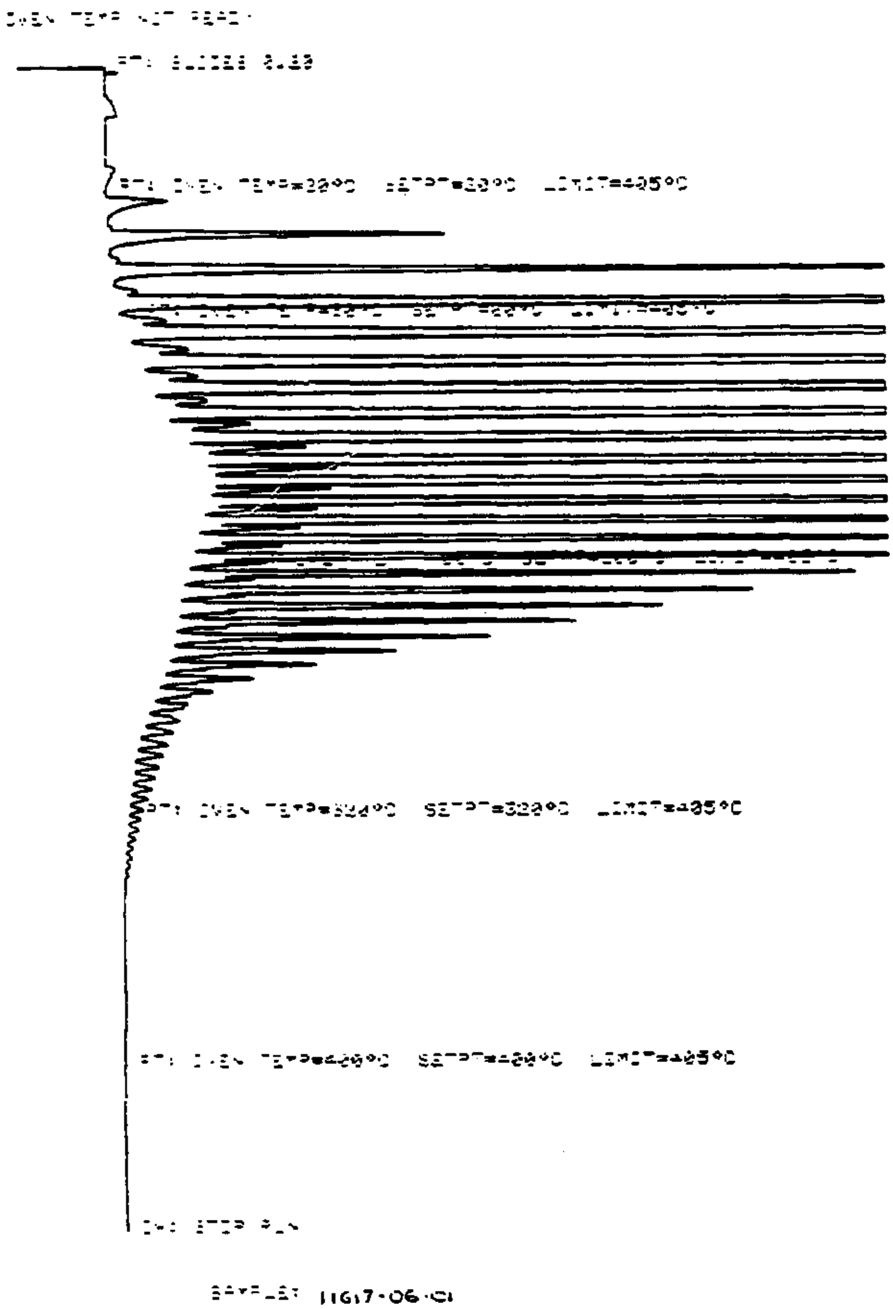


Fig. B134

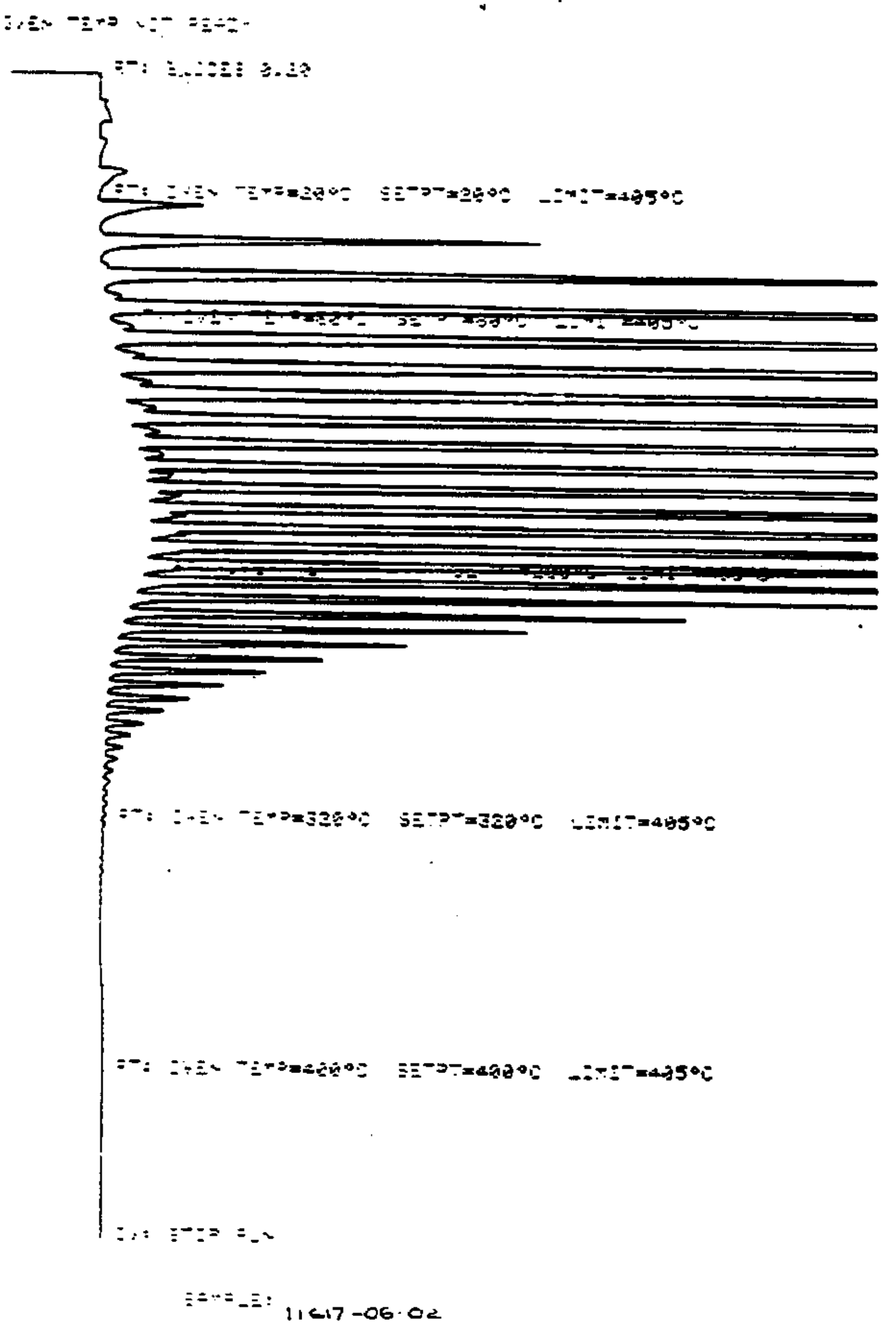

LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C
1147-06-02

Fig. B135

Table B18

FILE: 1161706A T5Q4 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-06
CATALYST CO/X9/X10-TC103 250 CC 124.6 G AFTER USE:150.2 G (+25.6 G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12524-17)

RUN & SAMPLE NO.	11617-06-01	617-06-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	26.5	72.5
PRESSURE,PSIG	300.00	300.00
TEMP. C	239.00	239.00
FEED CC/MIN	1260.00	1260.00
HOURS FEEDING	26.50	46.00
EFFLNT GAS LITER	1767.29	3068.20
GM AQUEOUS LAYER	27.52	45.22
GM OIL	4.77	9.26
MATERIAL BALANCE		
GM ATOM CARBON %	91.39	91.20
GM ATOM HYDROGEN %	95.35	95.70
GM ATOM OXYGEN %	94.87	94.31
RATIO CHX/(H2O+CO2)	0.5116	0.5519
RATIO X IN CHX	2.4846	2.4629
USAGE H2/CO PRODT	3.1194	2.9759
FEED H2/CO FRM EFFLNT	1.0433	1.0493
RESIDUAL H2/CO RATIO	0.9554	0.9635
RATIO CO2/(H2O+CO2)	0.0096	0.0093
K SHIFT IN EFFLNT	0.0093	0.0091
SPECIFIC ACTIVITY SA	0.1608	0.1721
CONVERSION		
ON CO %	4.06	4.26
ON H2 %	12.15	12.09
ON CO+H2 %	8.19	8.27
PRDT SELECTIVITY,WT %		
CH4	21.93	21.02
C2 HC'S	0.56	0.55
C3H8	2.25	1.96
C3H6=	5.06	4.36
C4H10	2.76	2.53
C4H8=	5.07	4.53
C5H12	2.68	2.39
C5H10=	3.85	3.46
C6H14	4.48	3.83
C6H12= & CYCLO'S	0.27	0.28
C7+ IN GAS	29.22	31.71
LIQ HC'S	21.86	23.36
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	37.63	34.96
C5 -420 F	44.55	45.93
420-700 F	14.36	16.26
700-END PT	3.45	2.85

Table B18 (continued)

FILE: 1161706A T5Q4 A1

C5+-END PT	62.37	65.04
ISO/NORMAL MOLE RATIO		
C4	0.0000	0.0000
C5	0.0000	0.0000
C6	0.2984	0.2832
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	0.4247	0.4290
C4	0.5250	0.5399
C5	0.6765	0.6708
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8056	0.8044
RATIO CH4/(1-A)**2	5.8027	5.4936
ALPHA FRM CORRELATION	0.8142	0.8138
ALPHA (EXPTL/CORR)	0.9894	0.9884
W%CH4 FRM CORRELATION	20.8474	20.9753
W%CH4 (EXPTL/CORR)	1.0520	1.0024
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLD OIL	CLD OIL
DENSITY		
N, REFRACTIVE INDEX		
SIMULT'D DISTILATN		
10 WT % @ DEG F	381.00	379.00
16	416.00	414.00
50	541.00	543.00
84	699.00	684.00
90	745.00	710.00
RANGE(16-84 %)	283.00	270.00
WT % @ 420 F	18.50	19.20
WT % @ 700 F	84.20	87.80

VI. Run 48 (11617-07) with Catalyst 48 ($Co/X_{11}/X_{12}/TC-123$)

The purpose of this run was to assess the effect of adding a second promoter, X_{12}, to the $Co/X_{11}/TC-123$ type of catalyst. When combined with a $Co/X_{11}/TC-103$ formulation in Catalyst 39, X_{12} had demonstrated certain desirable properties such as improved activity and lower methane production. The results are to be compared with those of both Catalyst 39 ($Co/X_{11}/X_{12}/TC-103$) and Catalyst 45 ($Co/X_{11}/TC-123$).

Formulation of the catalyst was by the same method as for Catalyst 39 except for the replacement of TC-103 by TC-123. The theoretical content of cobalt, X_{11} and X_{12} was 7.6, 1.4 and 5.0 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B136-139. Simulated distillations of the C_5^+ product are plotted in Figs. B140-148. Carbon number product distributions are plotted in Figs. B149-157. Chromatograms from simulated distillations are reproduced in Figs. B158-165. Detailed material balances appear in Tables B19-22.

The catalyst's initial conversion, selectivity, and product quality compared as follows with those of Catalysts 39 and 45. Test conditions were the same for all three: H_2:CO feed ratio 1:1, 300 psig, 240C.

	Catalyst 48 $Co/X_{11}/X_{12}/TC-123$	Catalyst 39 $Co/X_{11}/X_{12}/TC-103$	Catalyst 45 $Co/X_{11}/TC-123$
Conversion, pct	51	51	47
CH_4, pct	4.5	4.5	3.5
C_5^+, pct	87	87	91
C_4 olefin/paraffin	1.4	1.8	2.7

Adding X_{12} to the formulation of Catalyst 45 improved conversion by 4 percentage points, but at the cost of substantially poorer selectivity: higher methane production, lower production of C_5^+, and much lower olefin content of the C_4 fraction. As compared with Catalyst 39, conversion and selectivity were essentially the same and C_4 olefin content again much lower. All three catalysts showed excellent stability under the test conditions noted.

When the H_2:CO feed ratio was raised to 1.5:1 at 217 hours on stream the conversion rose sharply to about 67 percent, as against about 58 percent with Catalyst 45, and remained essentially unchanged during the 150 hours on stream at this feed ratio. Again, however, the improved conversion and stability were offset by losses in selectivity: methane production rose to about 17 percent and C_5^+ production dropped to about 70 percent, as against 7 and 86 percent respectively with Catalyst 45. Evidently the X_{12} additive increases the catalyst's sensitivity in an undesirable fashion to the H_2:CO ratio of the syngas feed.

During the last 150 hours on stream, at an increased pressure of 500 psig, the conversion improved somewhat to about 69 percent, the methane production dropped to about 9 percent, and the selectivity remained essentially constant. There was, however, a significant loss of stability. Catalyst 45, at the same high pressure, performed in much the same way.

These results demonstrate once again that X_{12}, when added to a formulation promoted with X_{11}, improves the catalyst's activity but also makes it more sensitive, in terms of product selectivity, to the H_2:CO ratio of the feed.

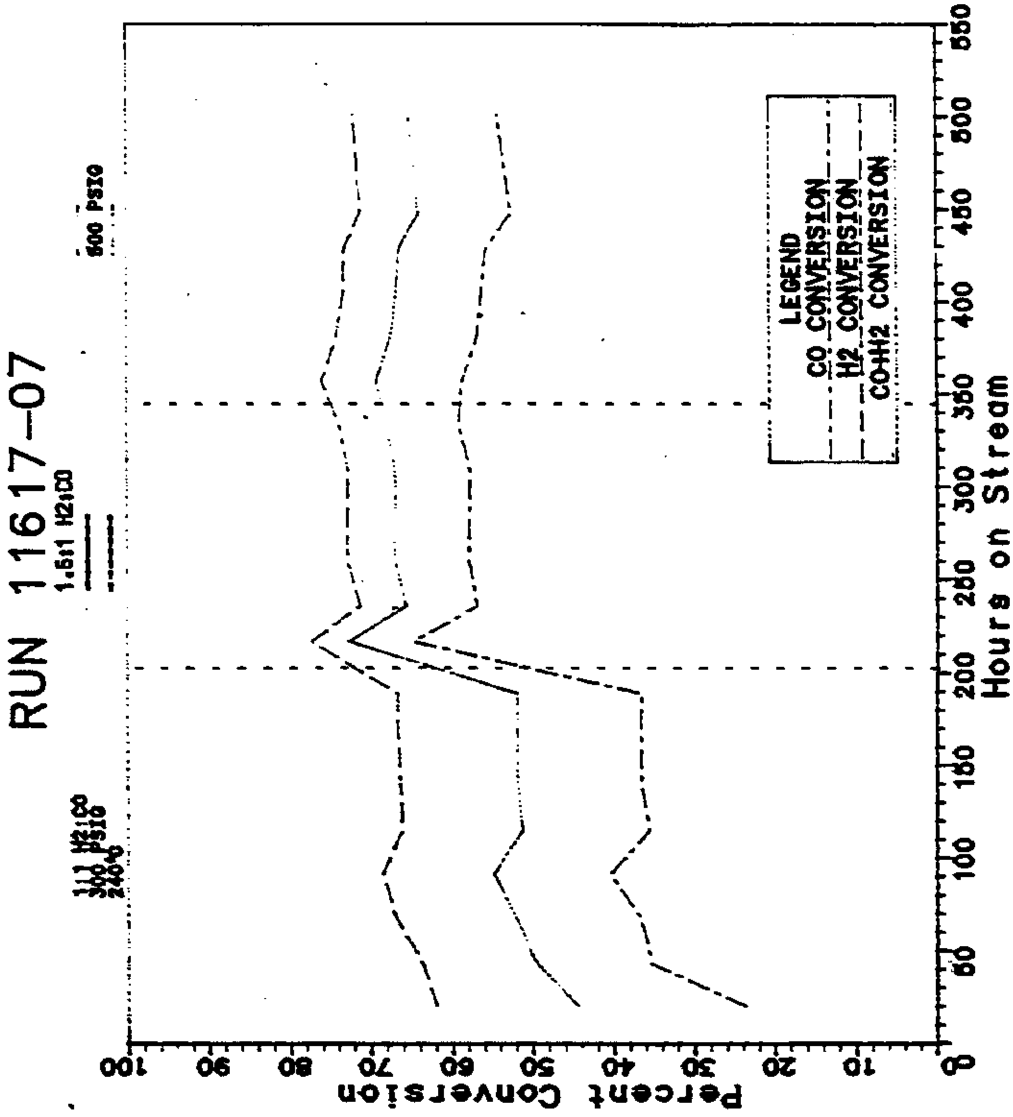

RUN 11617-07
1:1 H2:CO
300 PSIG
1.5:1 H2:CO
500 PSIG
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550

Fig. B136

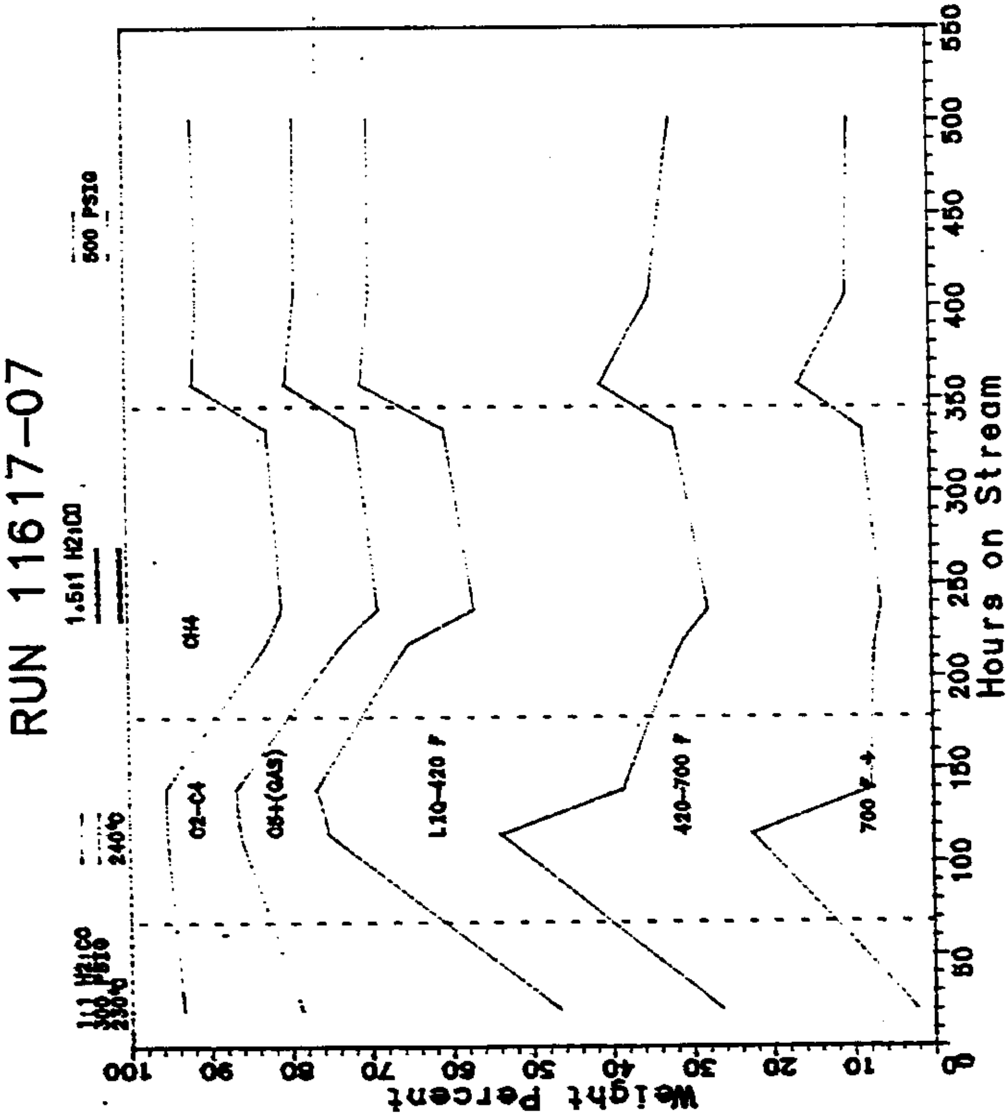
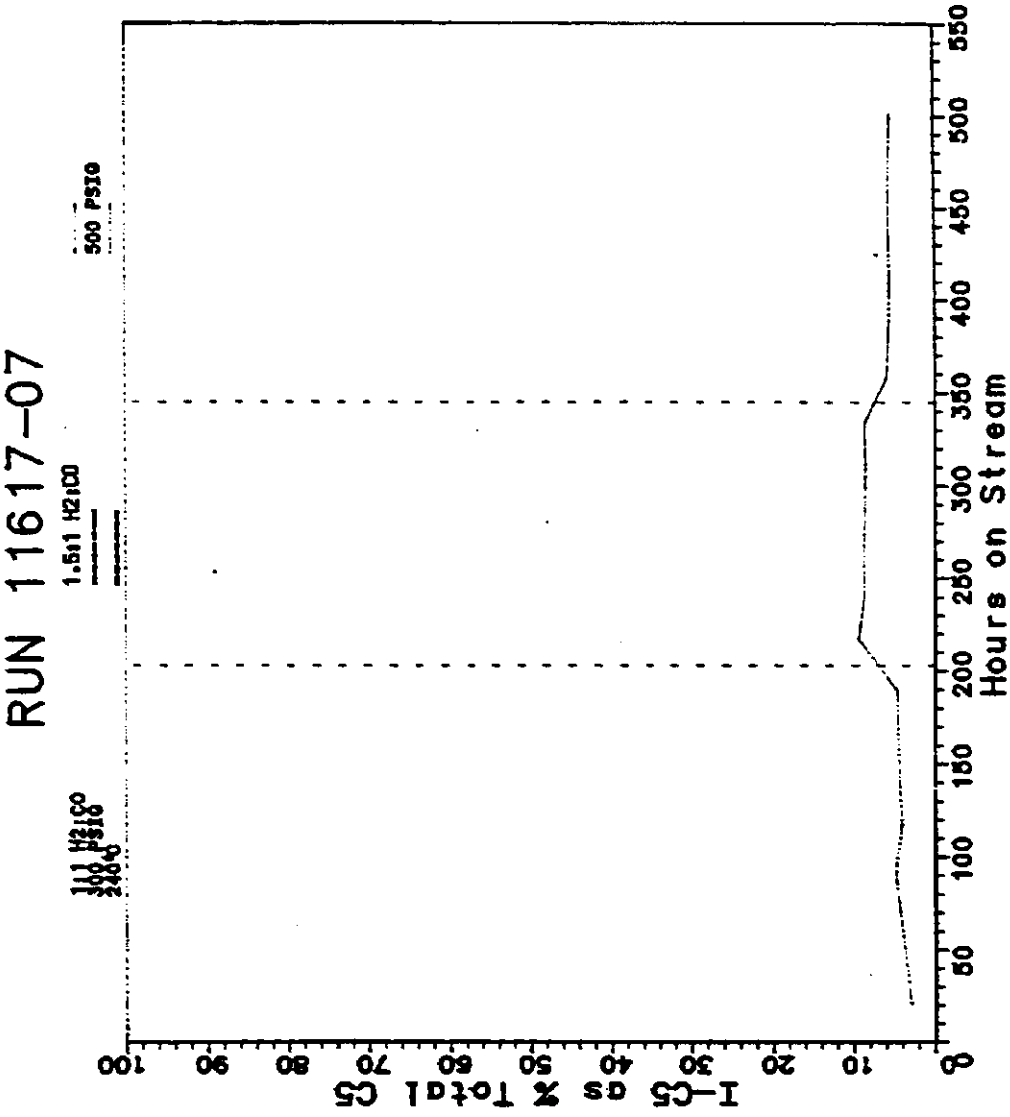

RUN 11617-07
Hours on Stream
Weight Percent
CH4
C2-C4
C5+(GAS)
420-700 F
500 PSIG
1.5:1 H2:CO
240°C

Fig. B137



RUN 11617-07
Hours on Stream
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550

Fig. B138

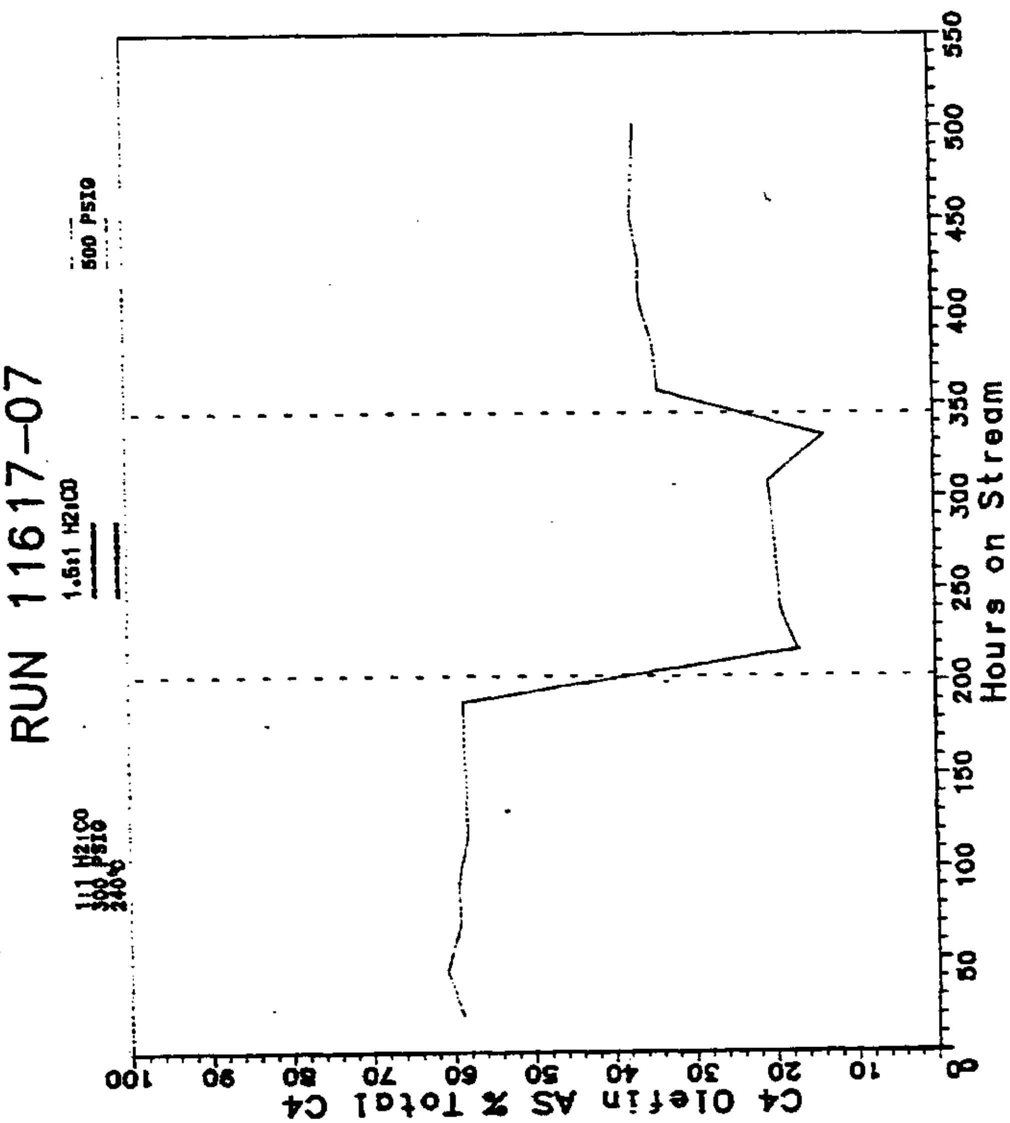

RUN 11617-07
1:1 H2:CO
300 PSIG
240°C
1.5:1 H2:CO
500 PSIG
Hours on Stream
C4 Olefin AS % Total C4

Fig. B139

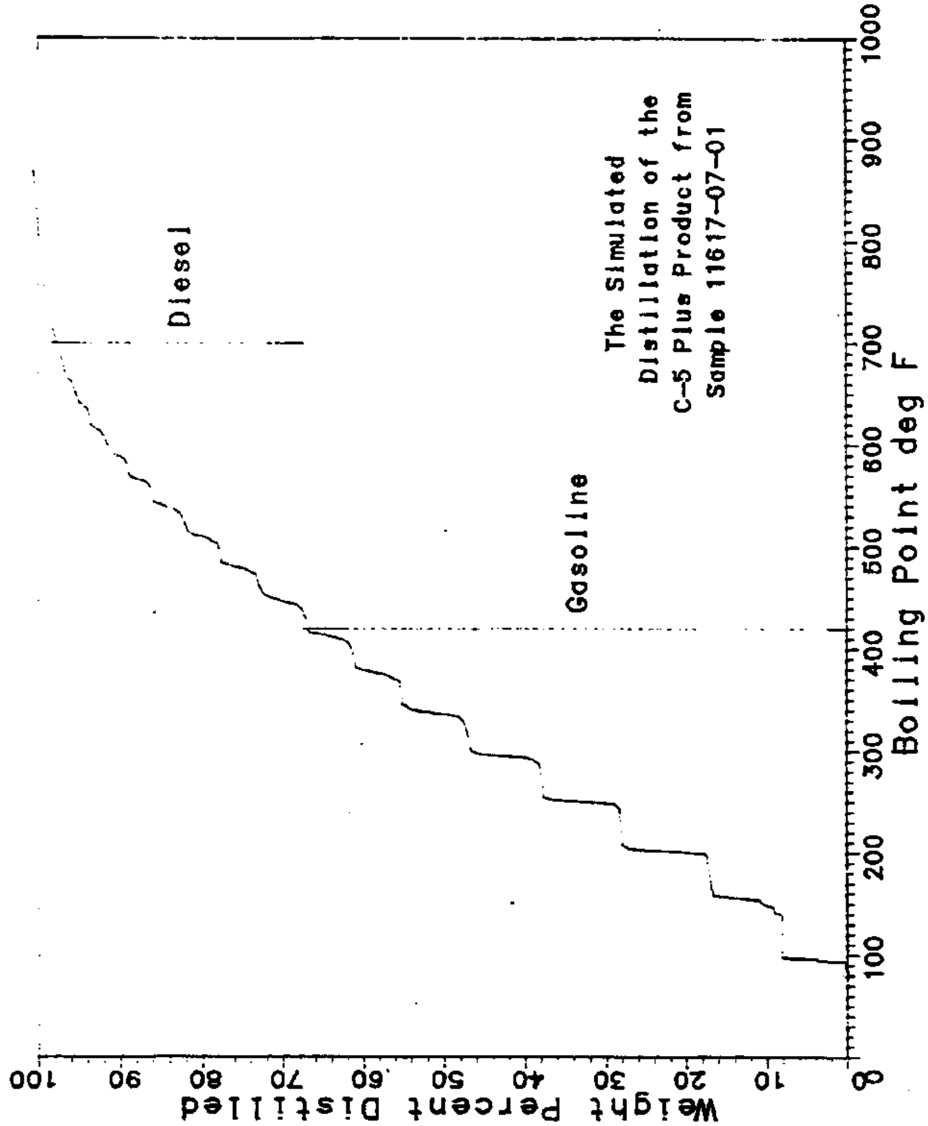

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-01
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B140

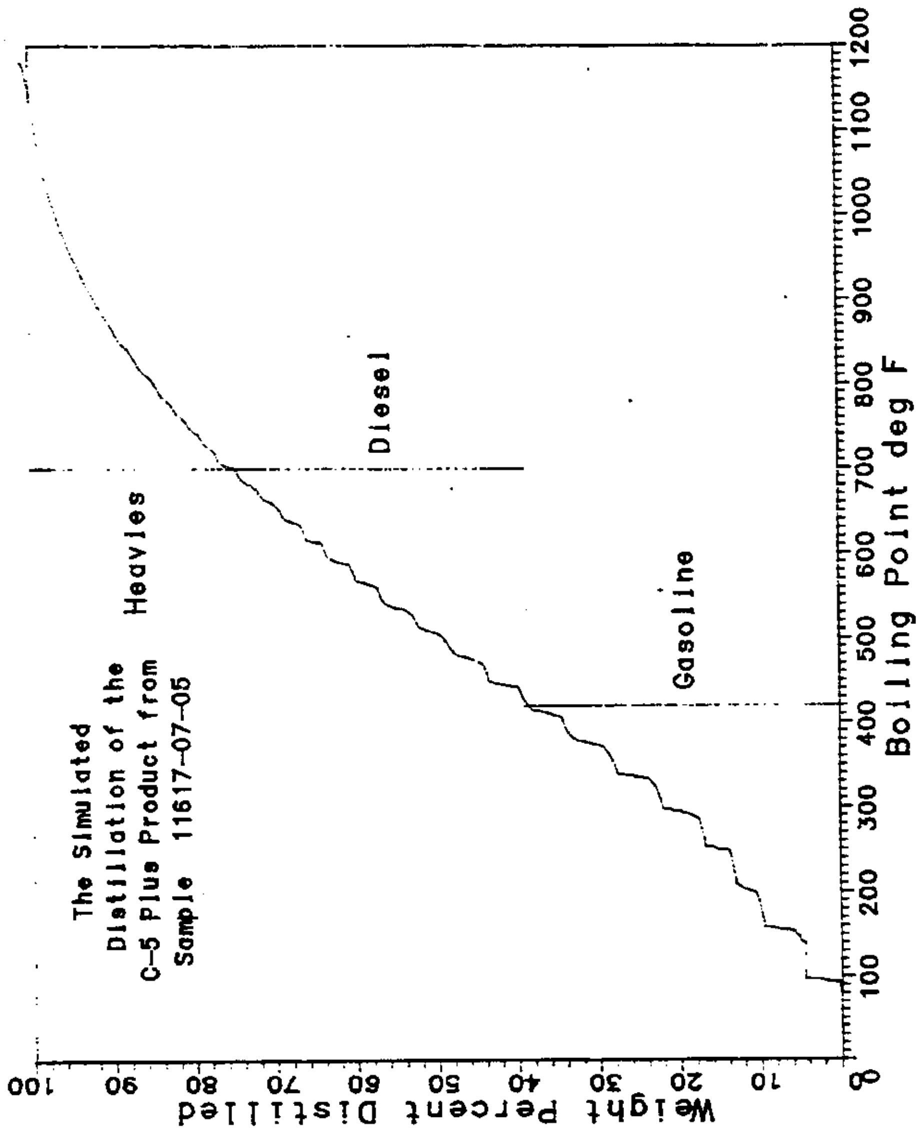

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-05
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
10
20
30
40
50
60
70
80
90
100

Fig. B141

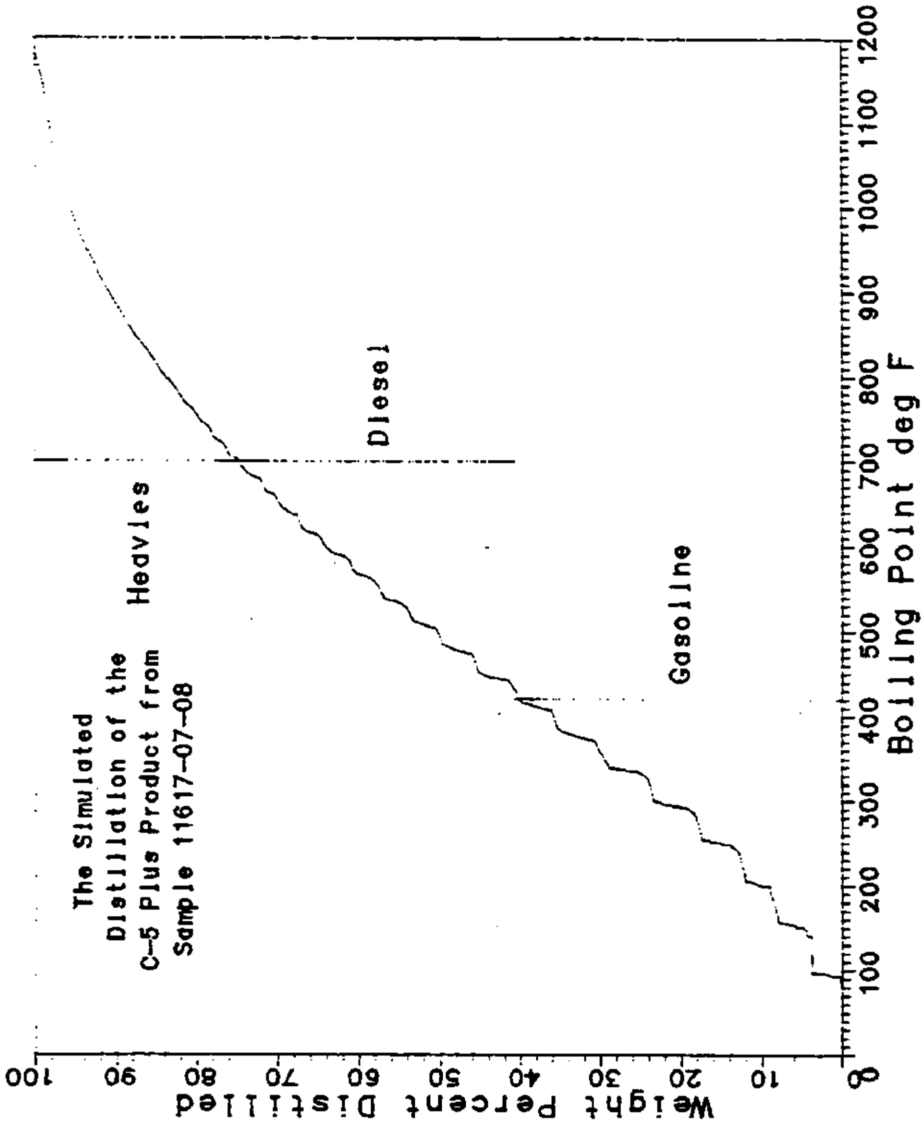
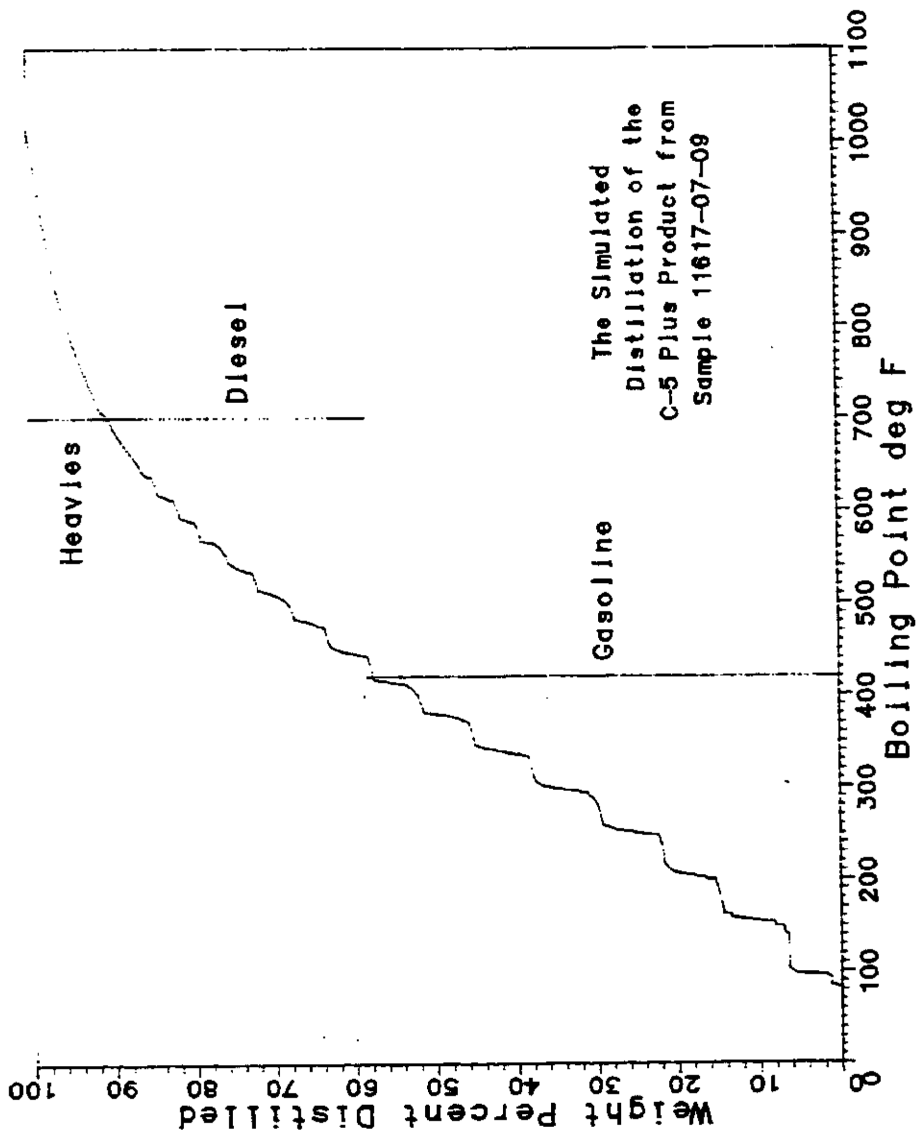

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-08
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Fig. B142



Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-09
Boiling Point deg F
Weight Percent Distilled

Fig. B143

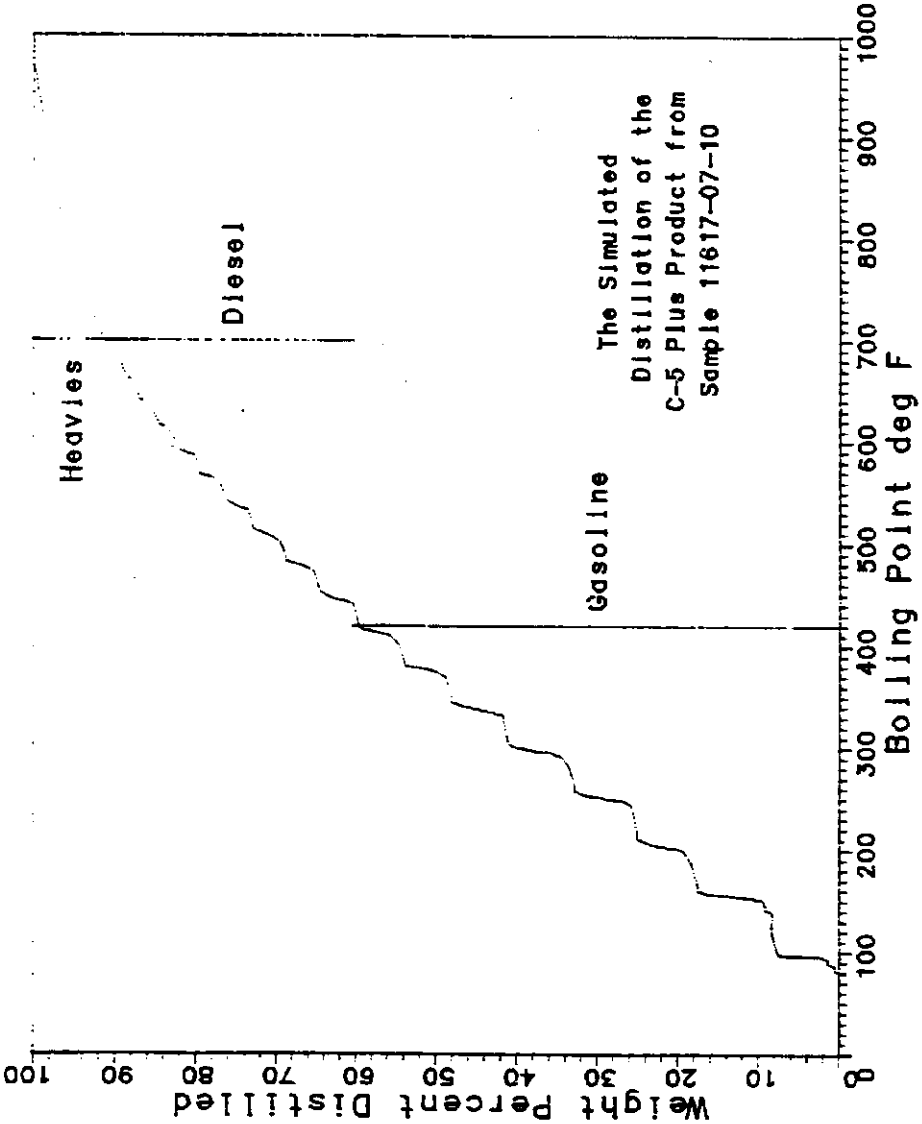
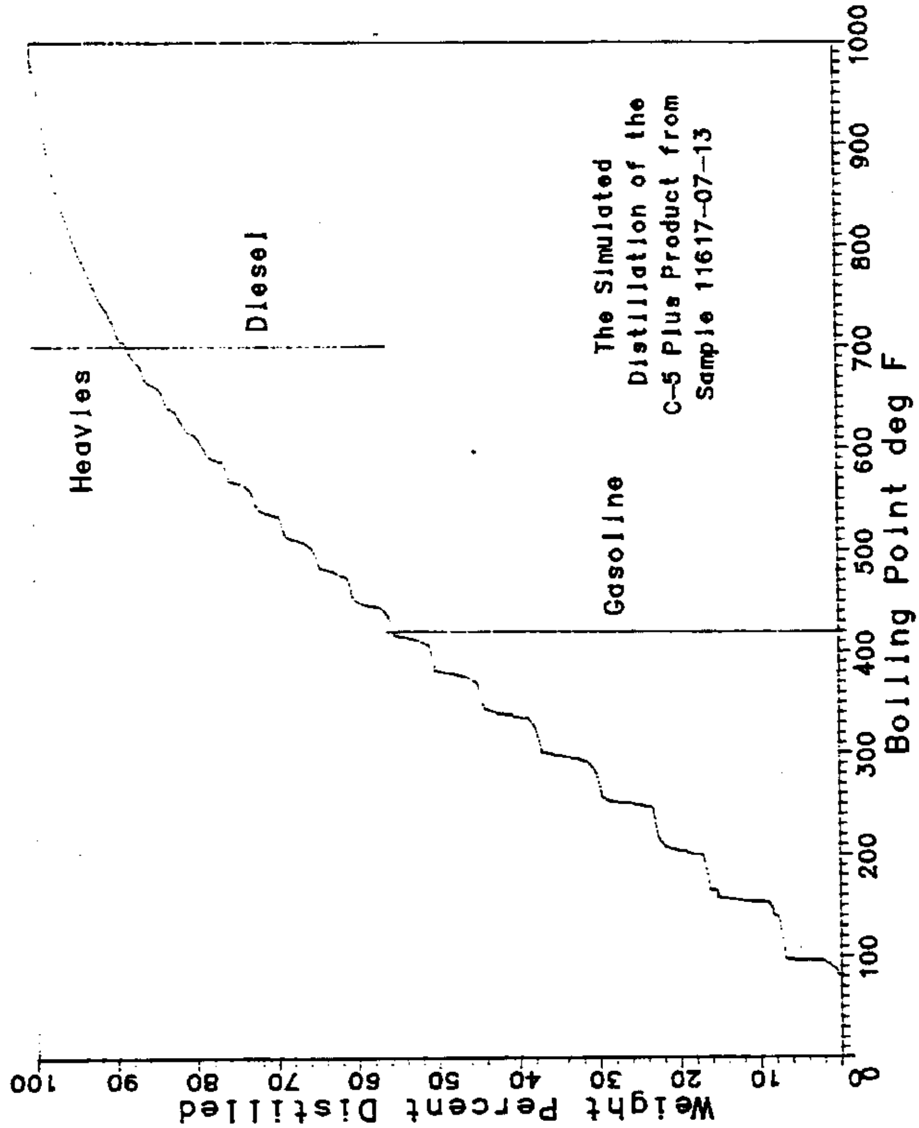

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-10
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B144



The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-13
Heavies
Diesel
Gasoline
Boiling Point deg 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. B145

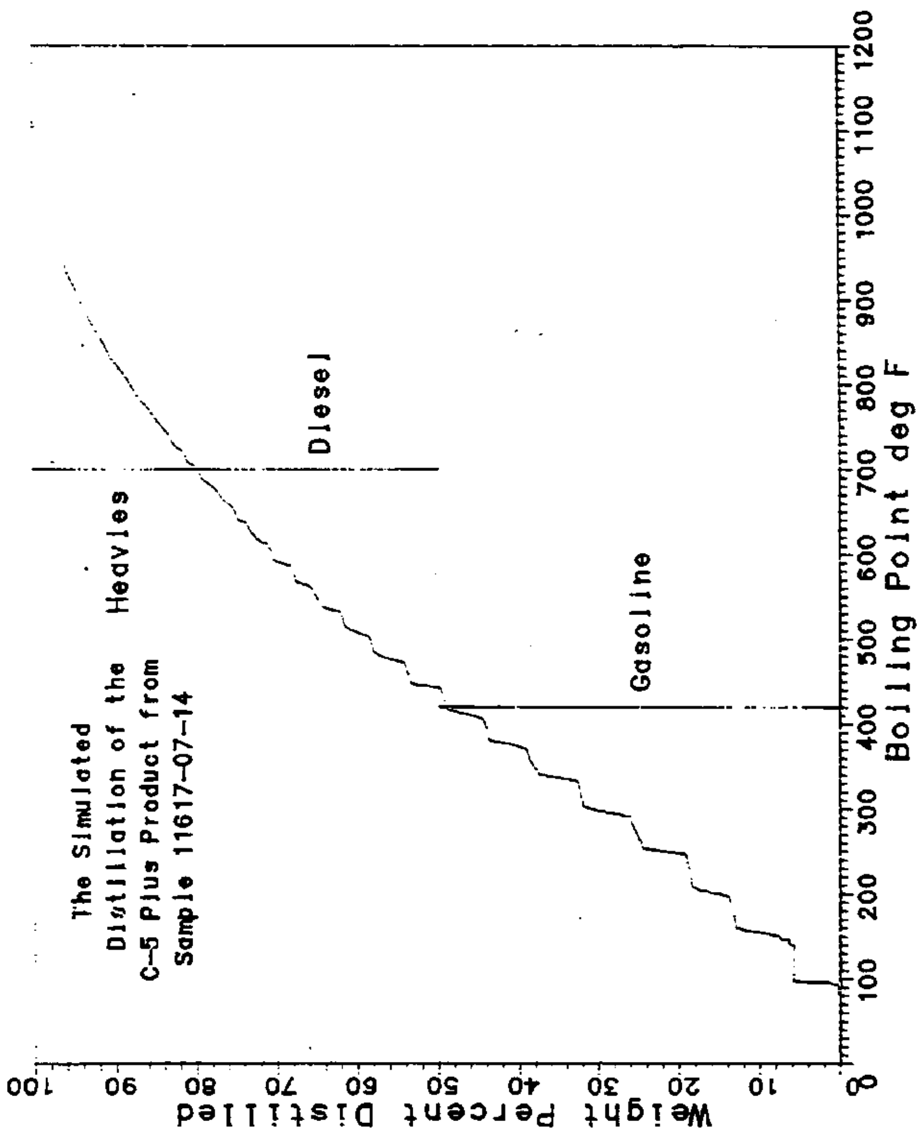

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-07-14
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Fig. B146