Table A16

RESULT OF SYNGAS OPERATION

RUN NO. 11885-05
CATALYST Co/Th/X4/X8-U103+U101 1186427 250 CC 110.1G(138.4 @END +28.4)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-05-21
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	259.5
PRESSURE,PSIG	299
TEMP. C	261
FEED CC/MIN	1260
HOURS FEEDING	24.00
EFFLNT GAS LITER	1112.75
GM AQUEOUS LAYER	174.09
GM OIL	69.20
MATERIAL BALANCE	
GM ATOM CARBON %	98.65
GM ATOM HYDROGEN %	100.65
GM ATOM OXYGEN %	102.42
RATIO CHX/(H2O+CO2)	0.8725
RATIO X IN CHX	2.3733
USAGE H2/CO PRODT	2.1643
FEED H2/CO FRM EFFLNT	1.0202
RESIDUAL H2/CO RATIO	0.5848
RATIO CO2/(H2O+CO2)	0.0465
K SHIFT IN EFFLNT	0.0285
SPECIFIC ACTIVITY SA	0.8366
CONVERSION	
ON CO %	27.57
ON H2 %	58.48
ON CO+H2 %	43.18
PRDT SELECTIVITY,WT %	
CH4	14.12
C2 HC'S	1.92
C3H8	2.23
C3H6=	2.77
C4H10	1.76
C4H8=	3.46
C5H12	2.08
C5H10=	3.25
C6H14	2.55
C6H12= & CYCLO'S	2.76
C7+ IN GAS	13.25
LIQ HC'S	49.85
TOTAL	100.00

Table A16 (continued)

SUB-GROUPING	
C1 -C4	26.26
C5 -420 F	43.58
420-700 F	23.52
700-END PT	6.63
C5+-END PT	73.74
ISO/NORMAL MOLE RATIO	
C4	0.0427
C5	0.0550
C6	0.2692
C4=	0.0441
PARAFFIN/OLEFIN RATIO	
C3	0.7693
C4	0.4897
C5	0.6201
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8308
RATIO CH4/(1-A)**2	4.9347
ALPHA FRM CORRELATION	0.8369
ALPHA (EXPTL/CORR)	0.9928
W%CH4 FRM CORRELATION	18.6301
W%CH4 (EXPTL/CORR)	0.7581
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLDY WAXY
DENSITY	0.749
N, REFRACTIVE INDEX	1.4300
SIMULT'D DISTILATN	
10 WT % @ DEG F	296
16	332
50	474
84	674
90	734
RANGE(16-84 %)	342
WT % @ 420 F	39.50
WT % @ 700 F	86.69

NEW FORMAT JAN 25,85

VII. Run 6 (11723-18) with Catalyst 6 (Co/Th/X_4/K/UCC-103+UCC-101

The X_4 in this catalyst was obtained from the source containing catalyst poisons, which were removed before the catalyst was formulated. The cobalt content was about 7 percent, and the levels of X_4, thorium and potassium were each 15 percent of the cobalt content. Catalyst 5 has shown that X_8, which increased the water gas shift activity of Catalyst 2, impairs the effectiveness of a catalyst containing X_4; the potassium was substituted in an attempt to raise the water gas shift activity without interfering with the beneficial effects of the X_4.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. A125-128. Simulated distillations of the C_5^+ product are plotted in Figs. A129-131. Carbon number product distributions are plotted in Figs. A132-141. Chromatograms from simulated distillations are reproduced in Figs. A142-144. Detailed material balances appear in Tables A17-18.

The initial activity was unusally high, with 80 percent of the syngas converted at 269C for a specific activity of nearly 5. The H_2:CO usage ratio was a little low at 1.67:1, and with 22 percent of the oxygen rejected as CO_2 the potassium appeared to be stimulating the water gas shift activity. With the high rate of conversion, and a usage ratio higher than the feed ratio, the

ratio of H_2 to CO in the reactor was very low at 0.285:1.

Despite the higher reaction temperature going from Sample 1 to Sample 2, the conversion dropped due to rapid catalyst deactivation; contrary to usual experience, it was the conversion of CO which deactivated most rapidly at first. Until the temperature was reduced to less than 265C the conversion deactivated at a rate of one percentage point every 7.6 hours for the CO and every 17.7 hours for the H_2. By 113 hours on stream the specific activity had fallen from nearly 5 to 1.8, which is within the usual range for catalysts with this level of cobalt; the specific activity of catalyst 3, for example, initially about 3, was down to about 2 by 119 hours on stream. With continuing deactivation the specific activity at 233 hours on stream was less than 0.9, and during the time when the reactor temperature was maintained at 261C the deactivation rate was one percentage point every 17 hours. This is a poorer stability than with the first intimately mixed cobalt/thorium UCC-103 catalyst in Run 10225-16 (Eleventh Quarterly Report Catalyst 7).

The water gas shift activity, however, was higher than for catalysts without potassium. The H_2:CO usage ratio was as low as 1.55:1, in Sample 2, with 27 percent of the oxygen rejected as CO_2. The average usage ratio was about 1.85:1, with 15 percent of the oxygen rejected as CO_2. This compares with usage ratios above 2.0:1, and less than 10 percent of the oxygen rejected as CO_2, for the average intimately mixed catalysts.

When the conversion deactivates so rapidly it is reasonable

to expect the selectivity to deteriorate as well. Despite the low H_2:CO ratio in the reactor, the production of methane was initially high at about 15 percent. During the high temperature portion of the run, the methane production was 30 percent higher than the model predicted. During the low temperature period it was less than 90 percent of the model prediction at first, then rose at a rate of one percentage point every 27 hours to reach 100 percent of the predicted value.

The production of C_5^+'s was fairly high early in the run, above 76 percent at 113 hours on stream, but dropped 10 percentage points during the next five days. The production of gasoline and heavies was fairly constant. Production of diesel fuel dropped at a rate of one percentage point every 17 hours, bringing down the production both of total C_5^+'s and of total motor fuels.

The percentage of olefins in the C_4's seems to have been temperature dependent, with the highest percentages at the highest temperatures, and also to fall off with deactivation. Aside from the usual excess of methane the hydrocarbon distribution departs somewhat from the Schulz-Flory model, with a curve at the end of the diesel range which, though slight, has not been seen in these catalysts recently.

The potassium did contribute something to the catalyst's water gas shift activity. But it also lowered its stability, and it failed to stimulate either the chain growth of the Fischer-Tropsch hydrocarbons, or the olefinic content of the products, as it does with iron catalysts.

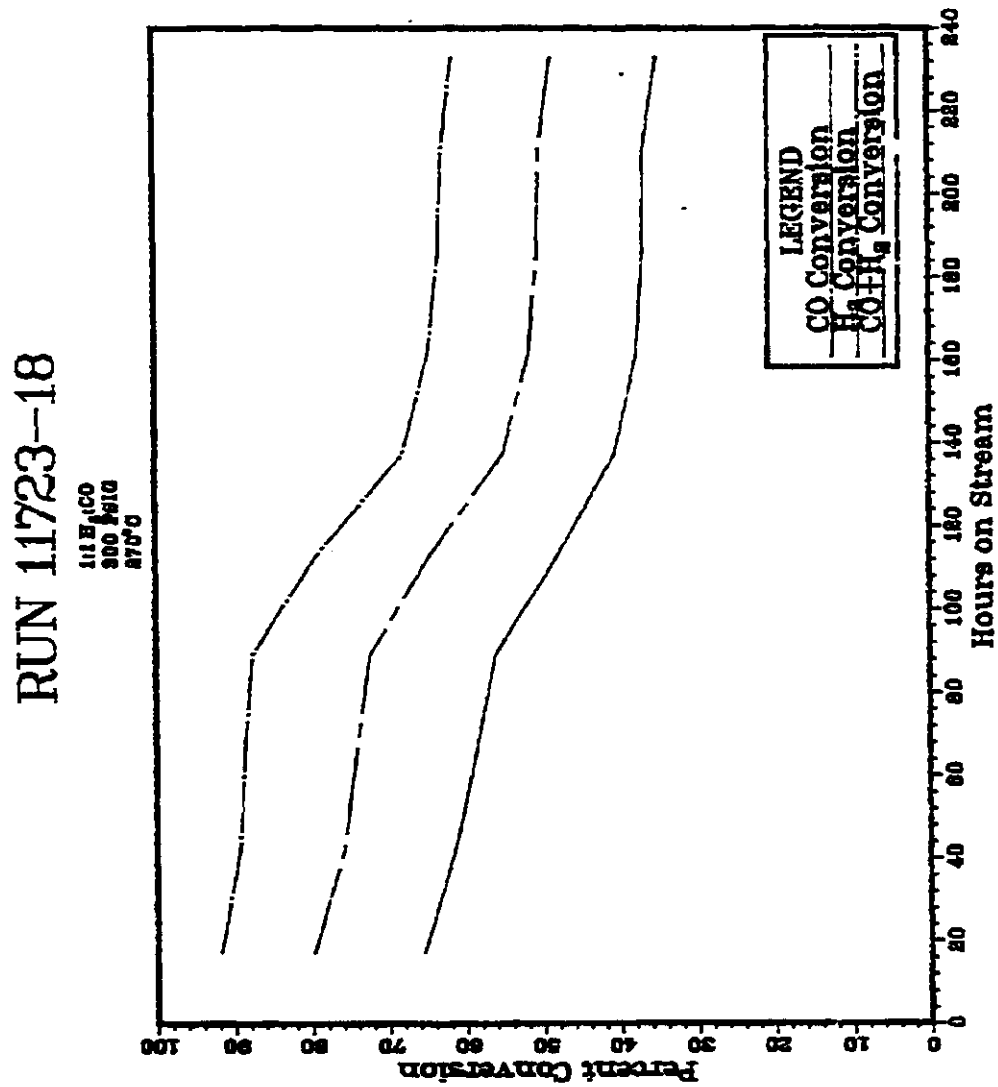

RUN 11723-18
LEGEND
CO Conversion
H_2 Conversion
$CO+H_2$ Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. A125

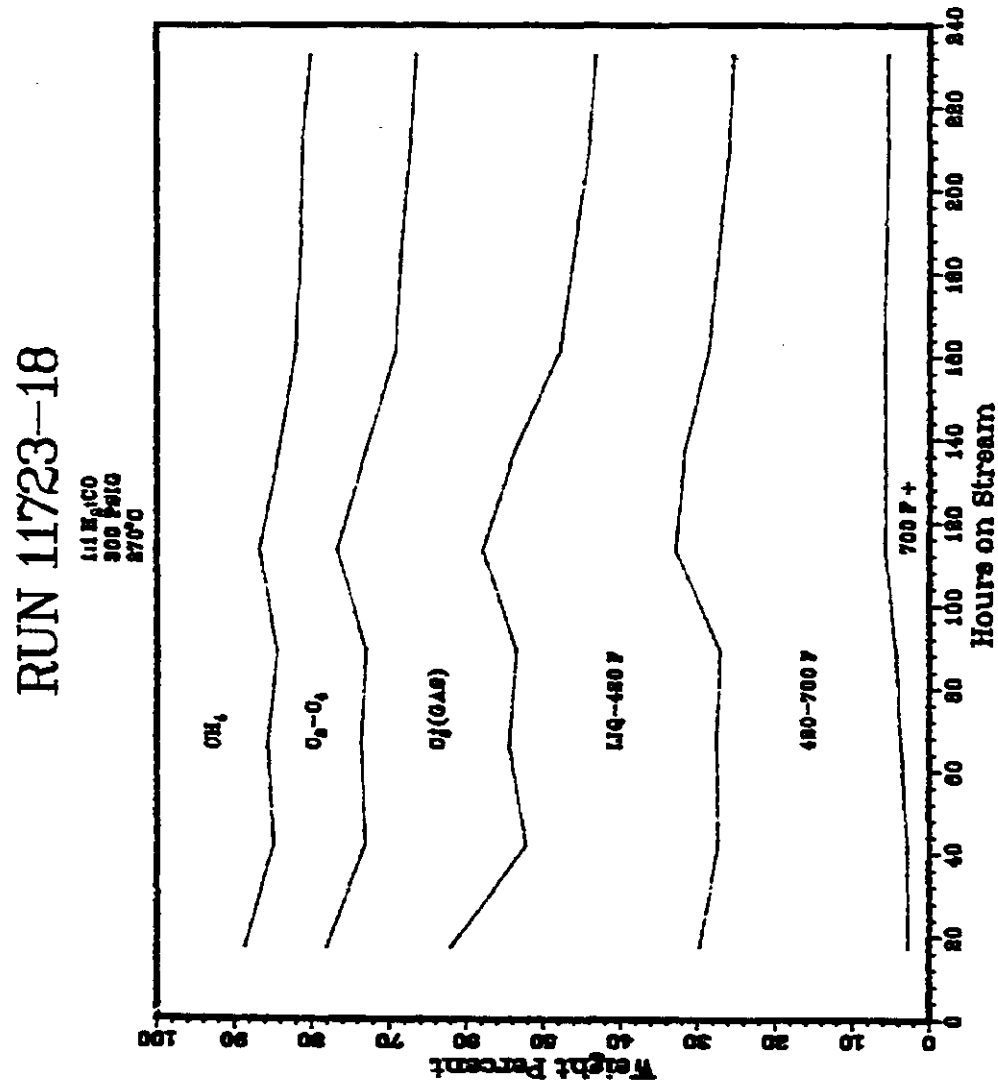


Fig. A126

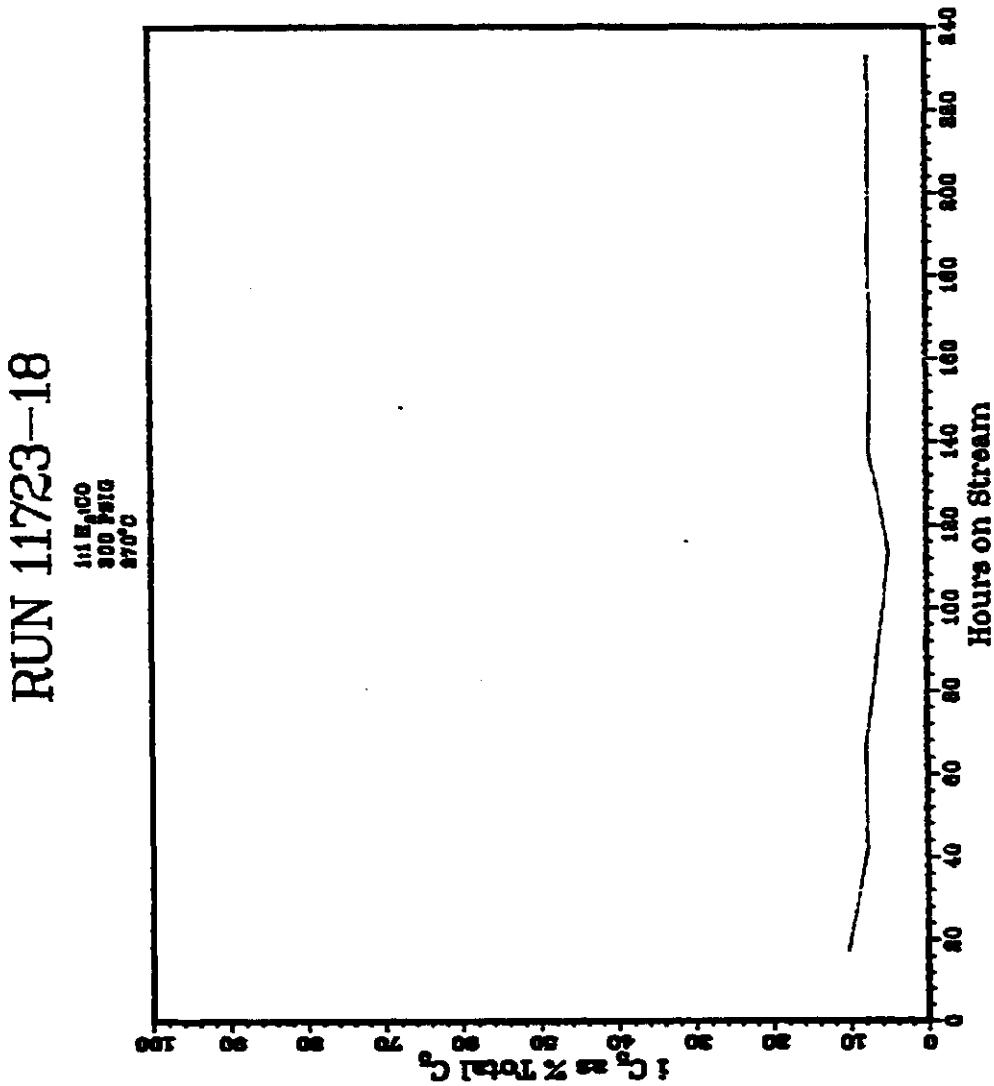

RUN 11723-18
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
240
0
10
20
30
40
50
60
70
80
90
100

Fig. A127

RUN 11723-18

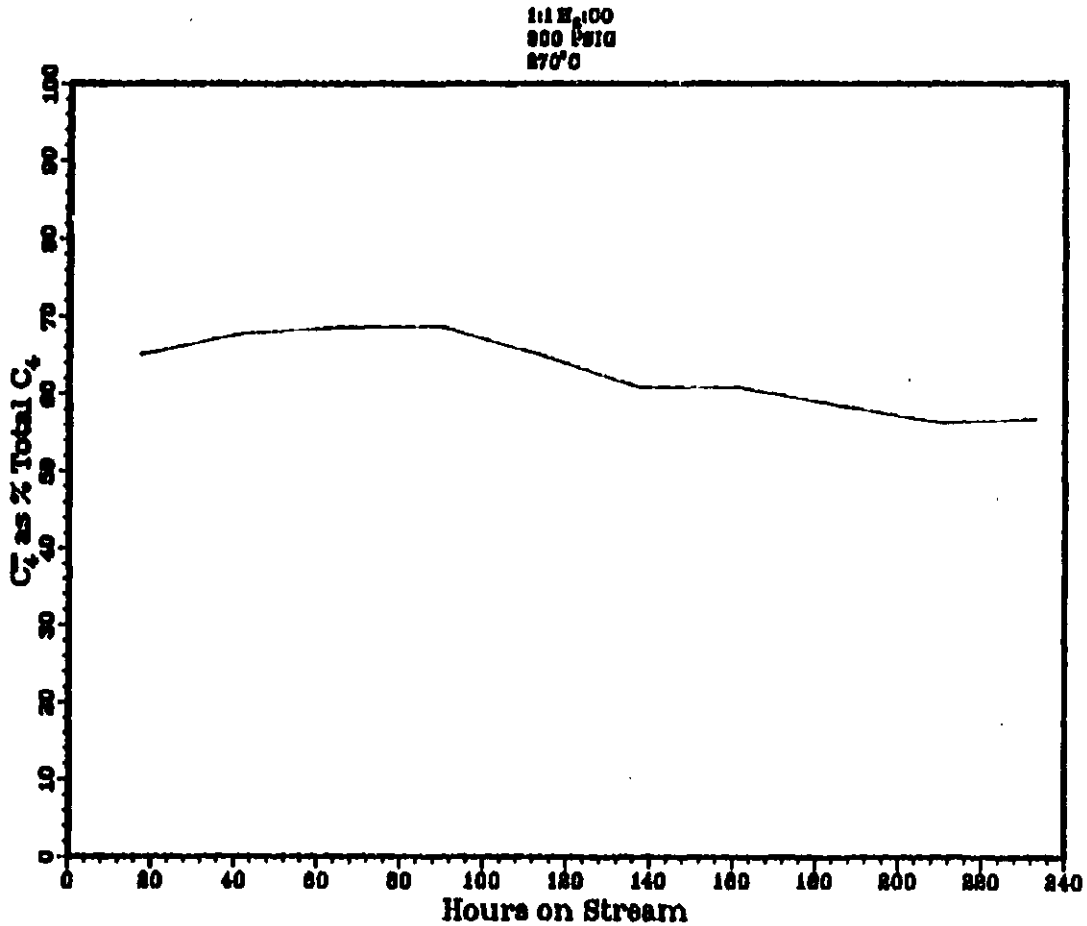


Fig. A128

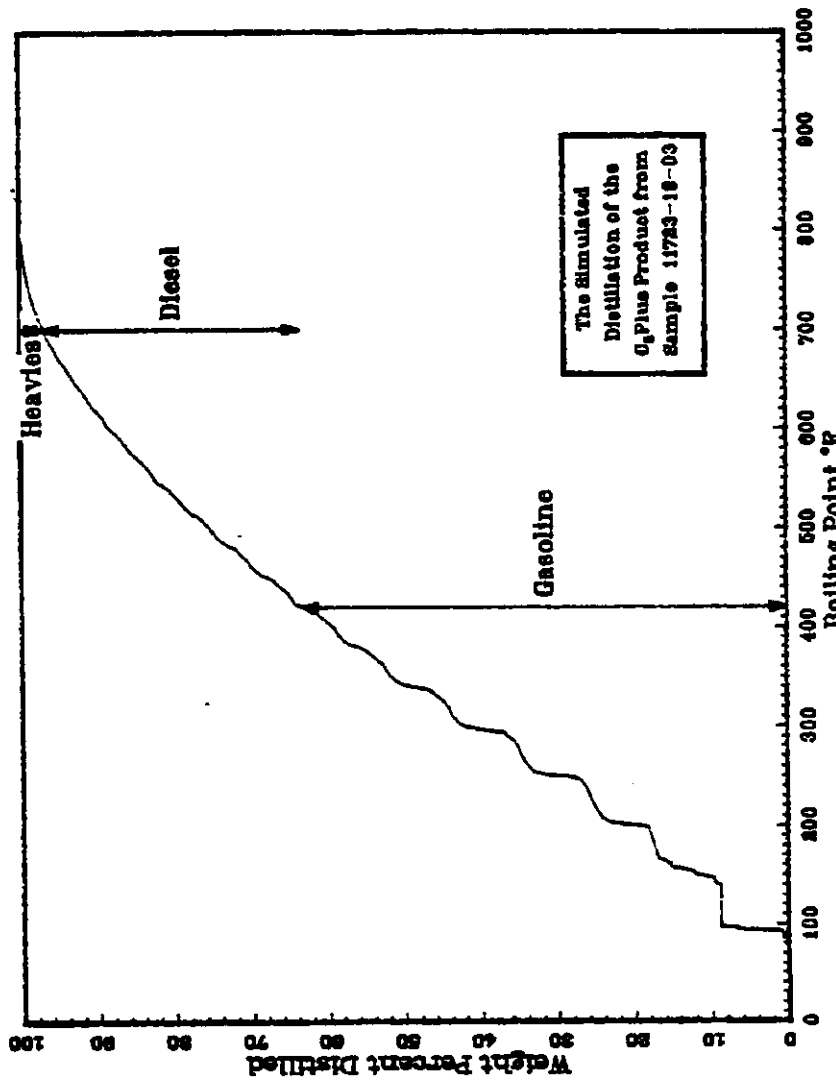

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heaviest
The Simulated Distillation of the C5 Plus Product from Sample 11723-18-03

Fig. A129

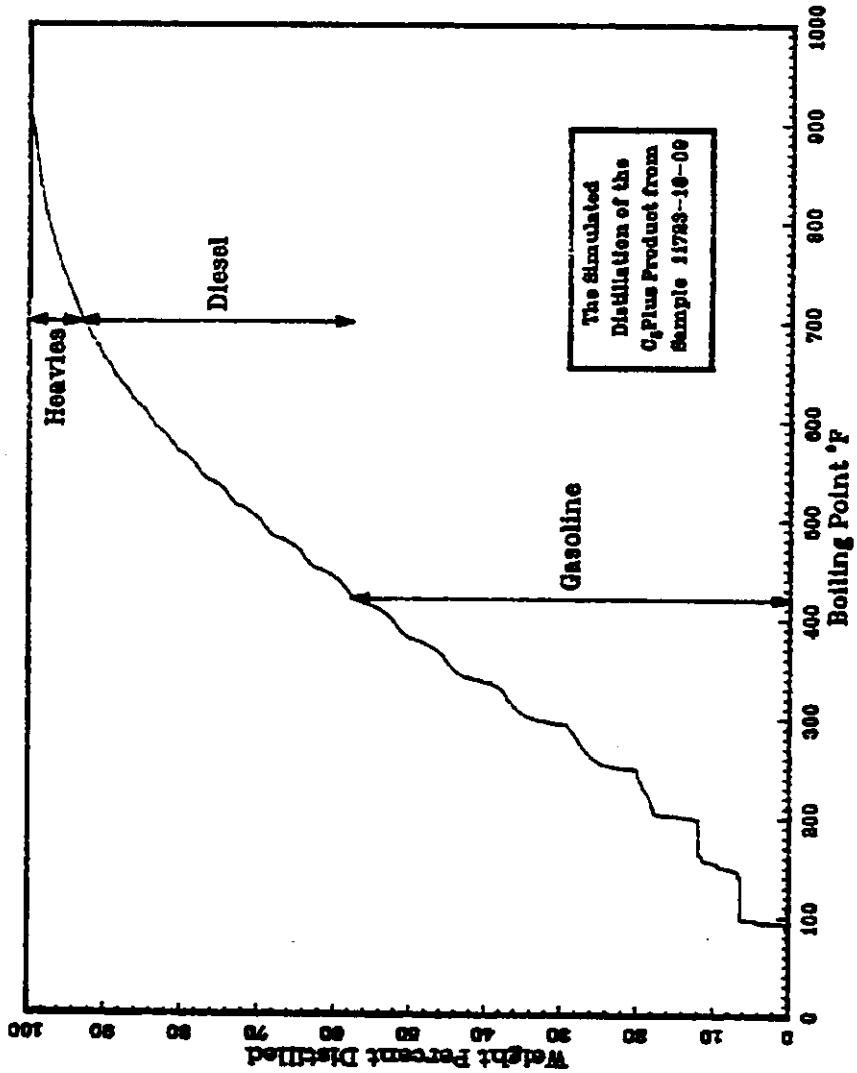

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11723-10-09
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000

Fig. A130

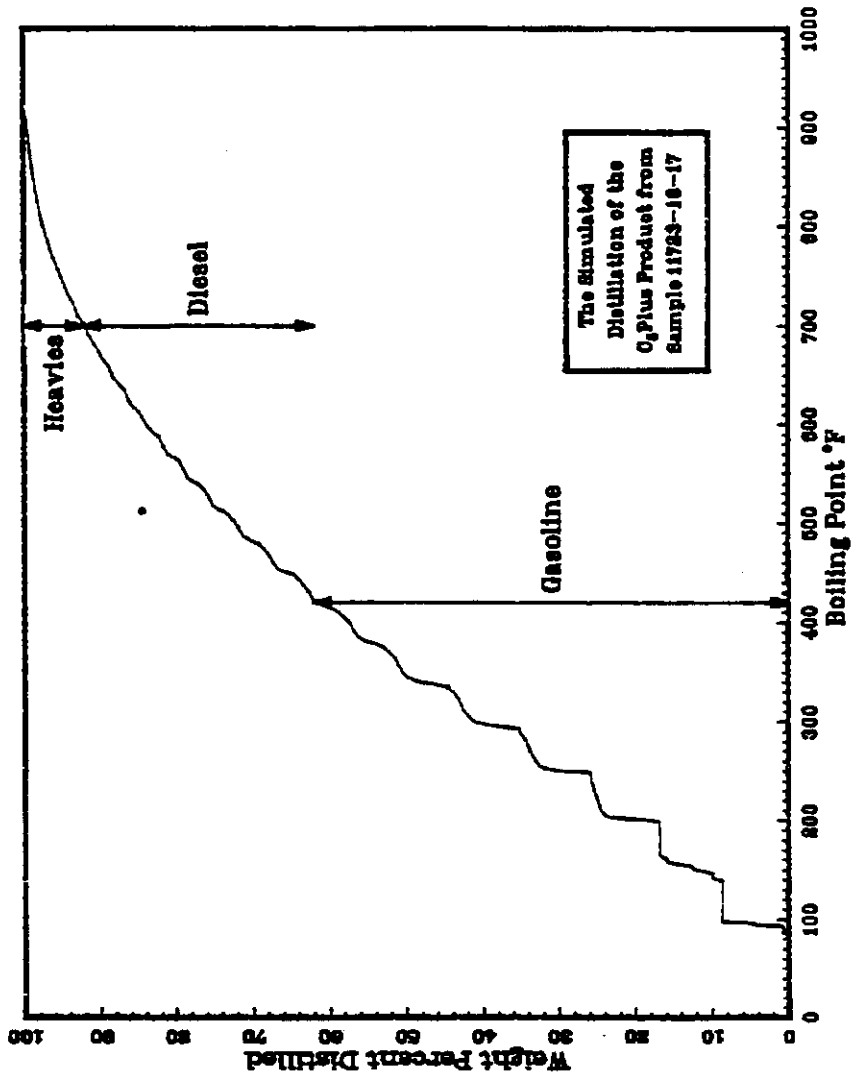
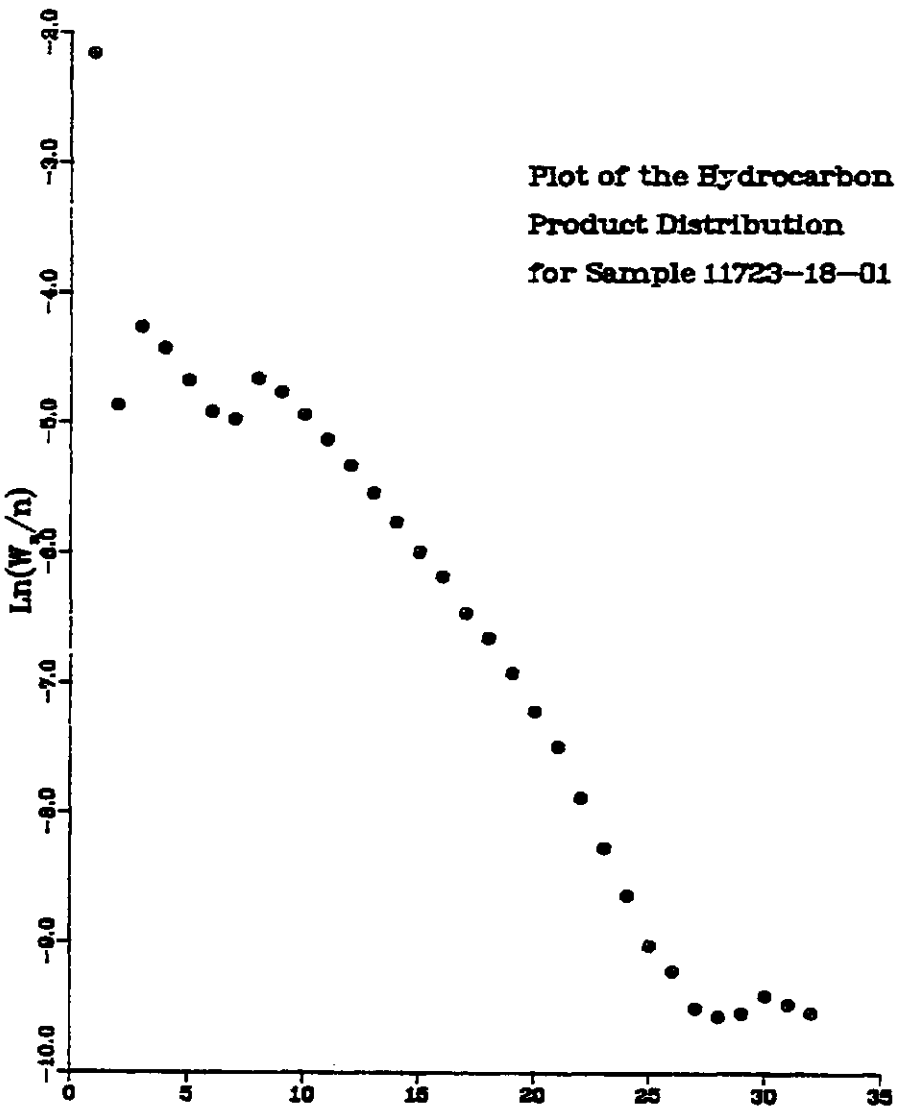

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11763-16-17

Fig. A131


Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-01
Ln(W_n/n)
-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
35
Carbon Number
Fig. A132

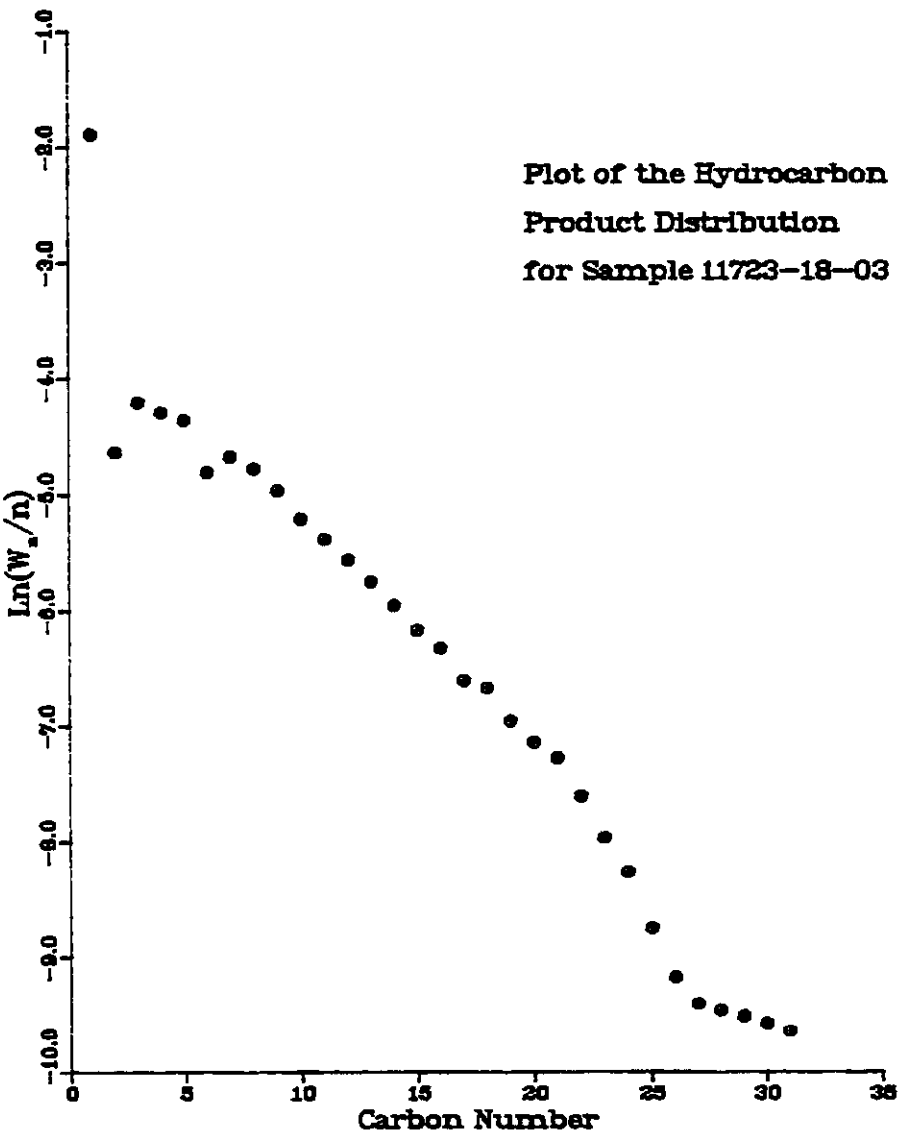

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A133

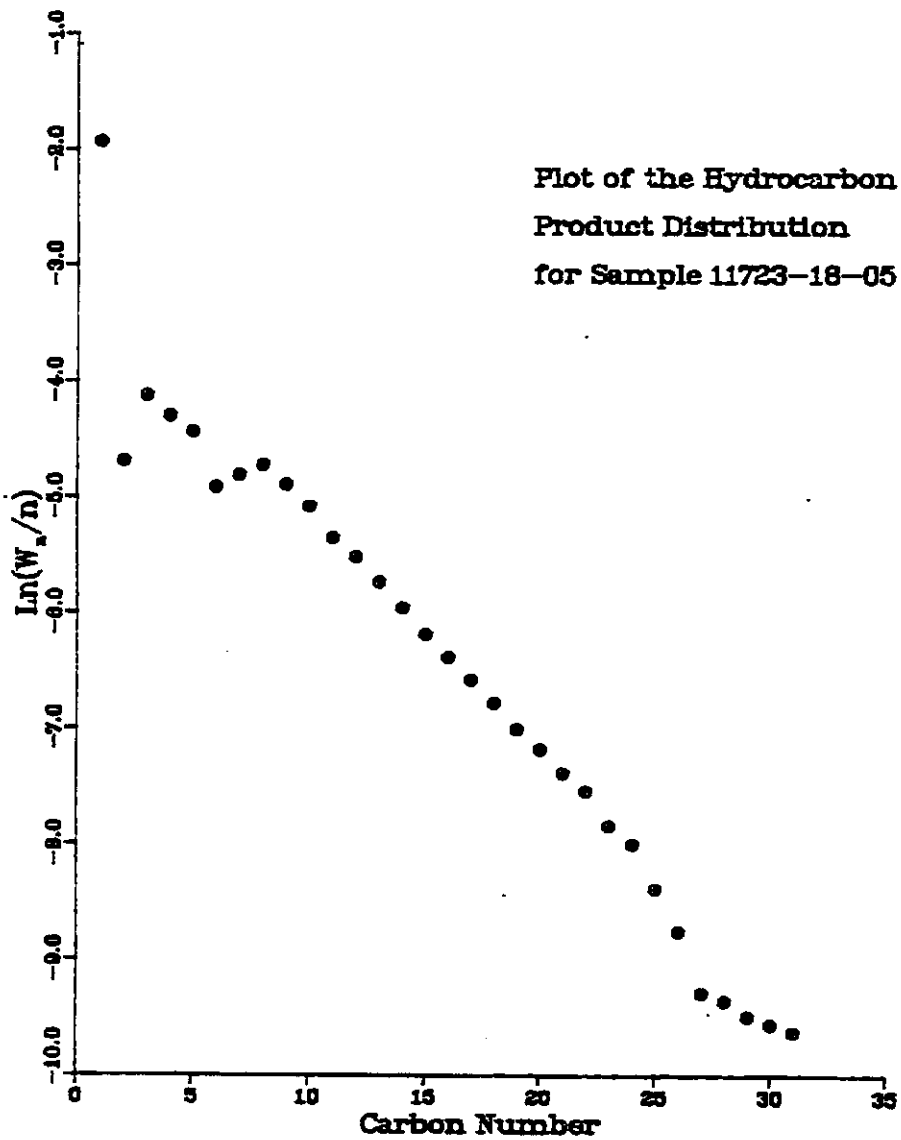

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A134

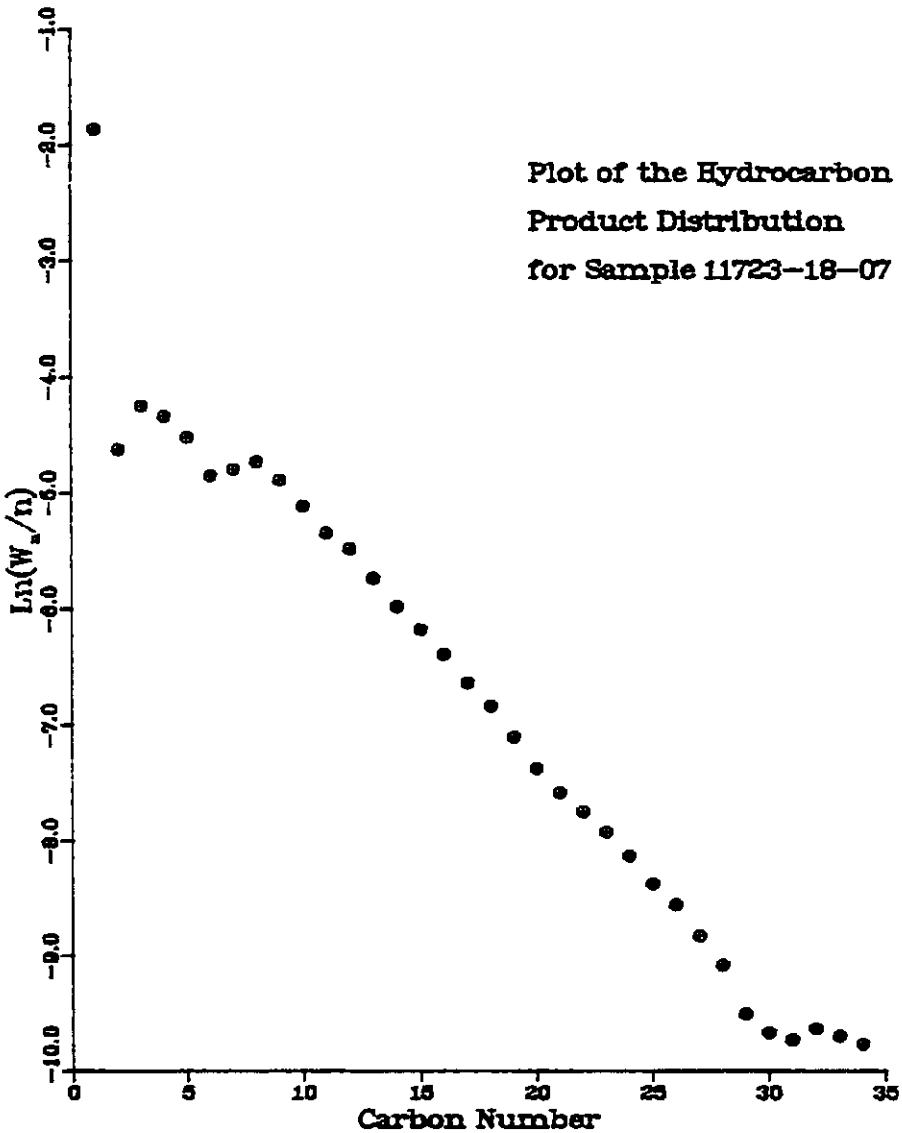

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A135

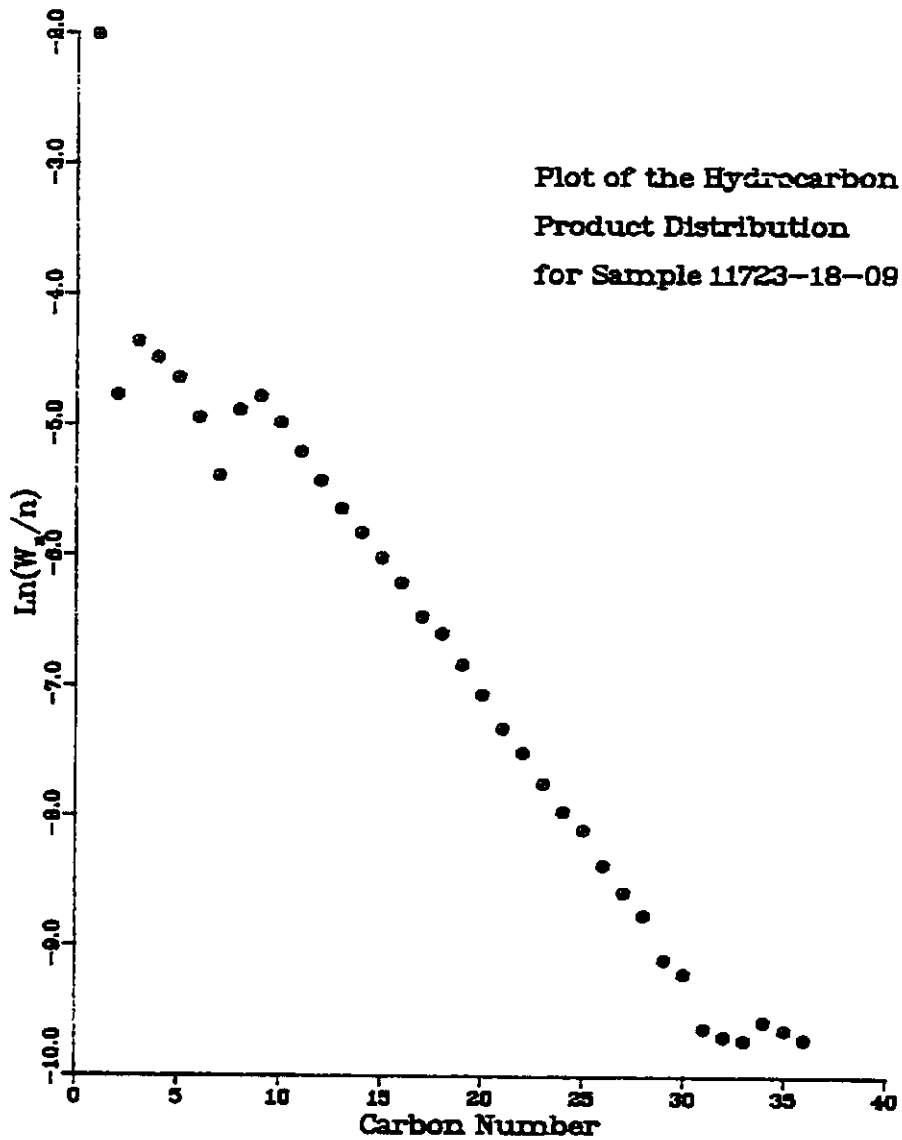

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-09
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A136

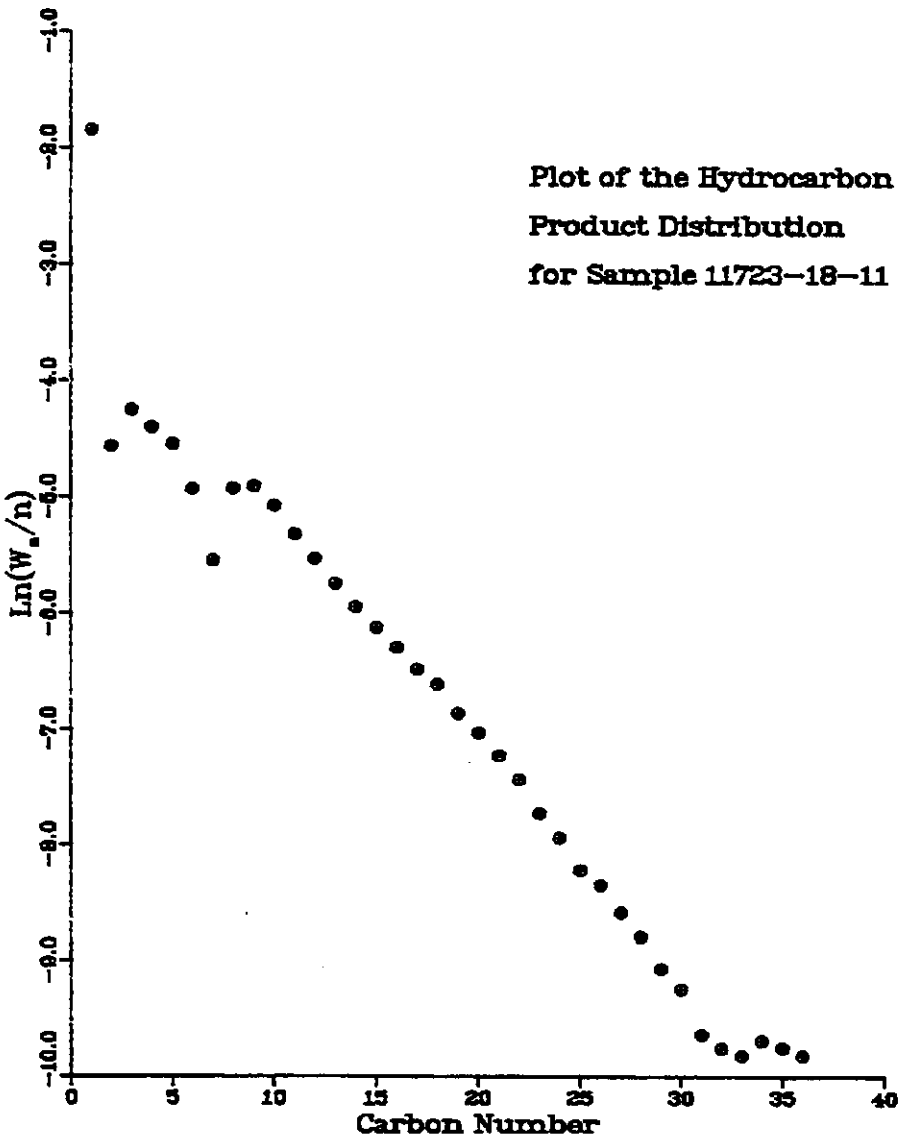

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A137

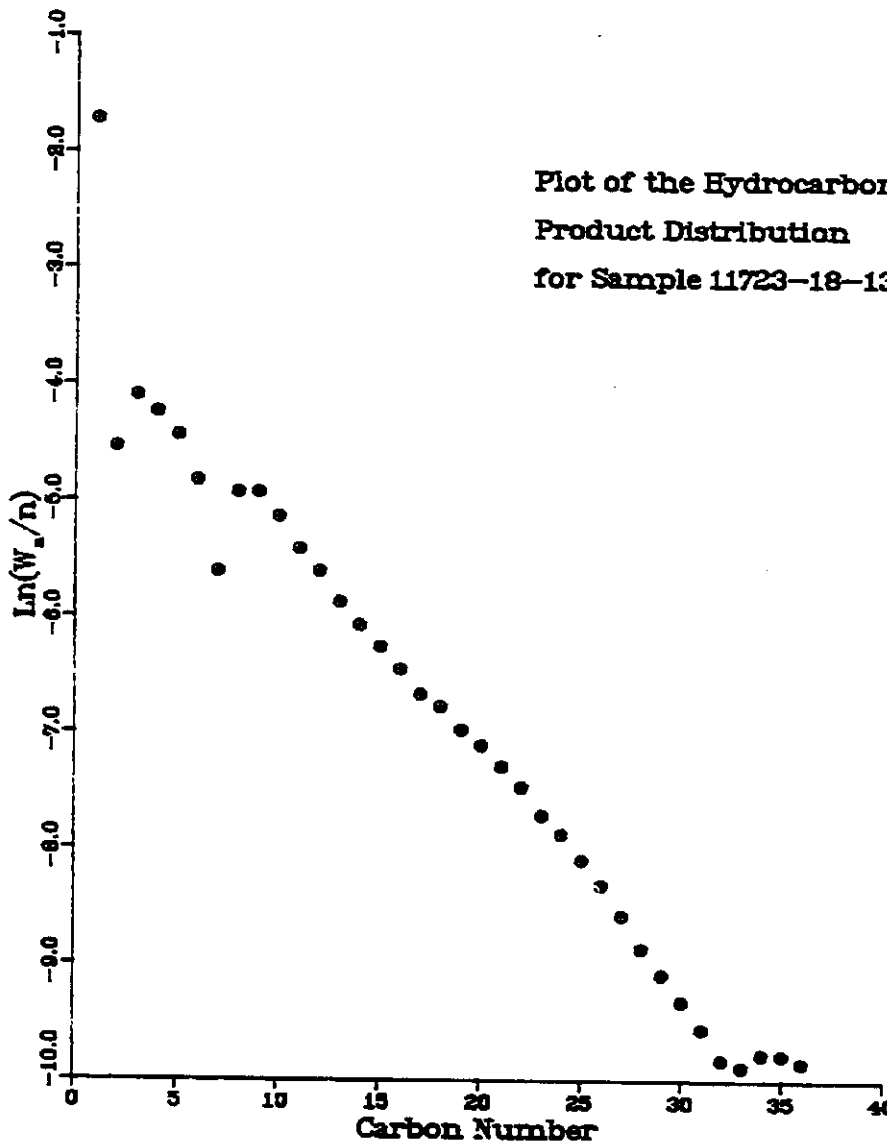

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A138

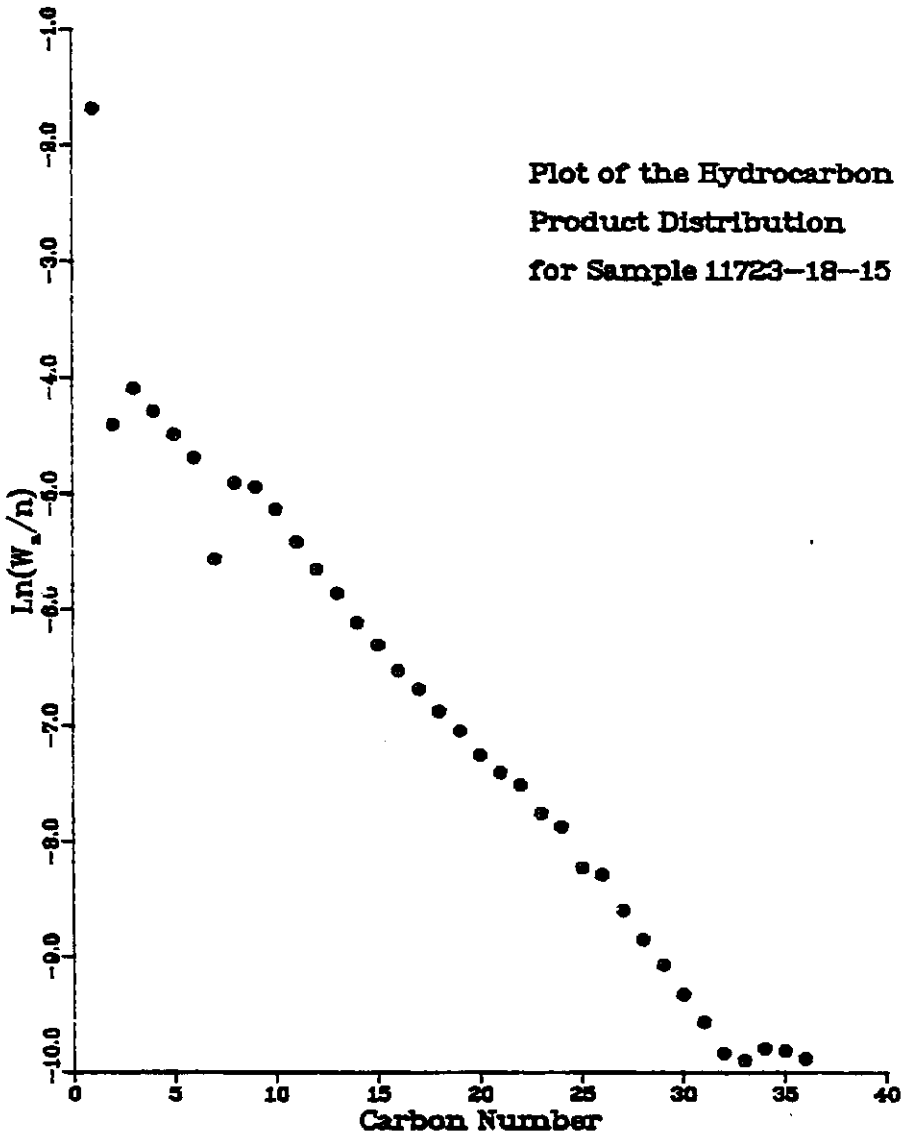

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-15
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A139

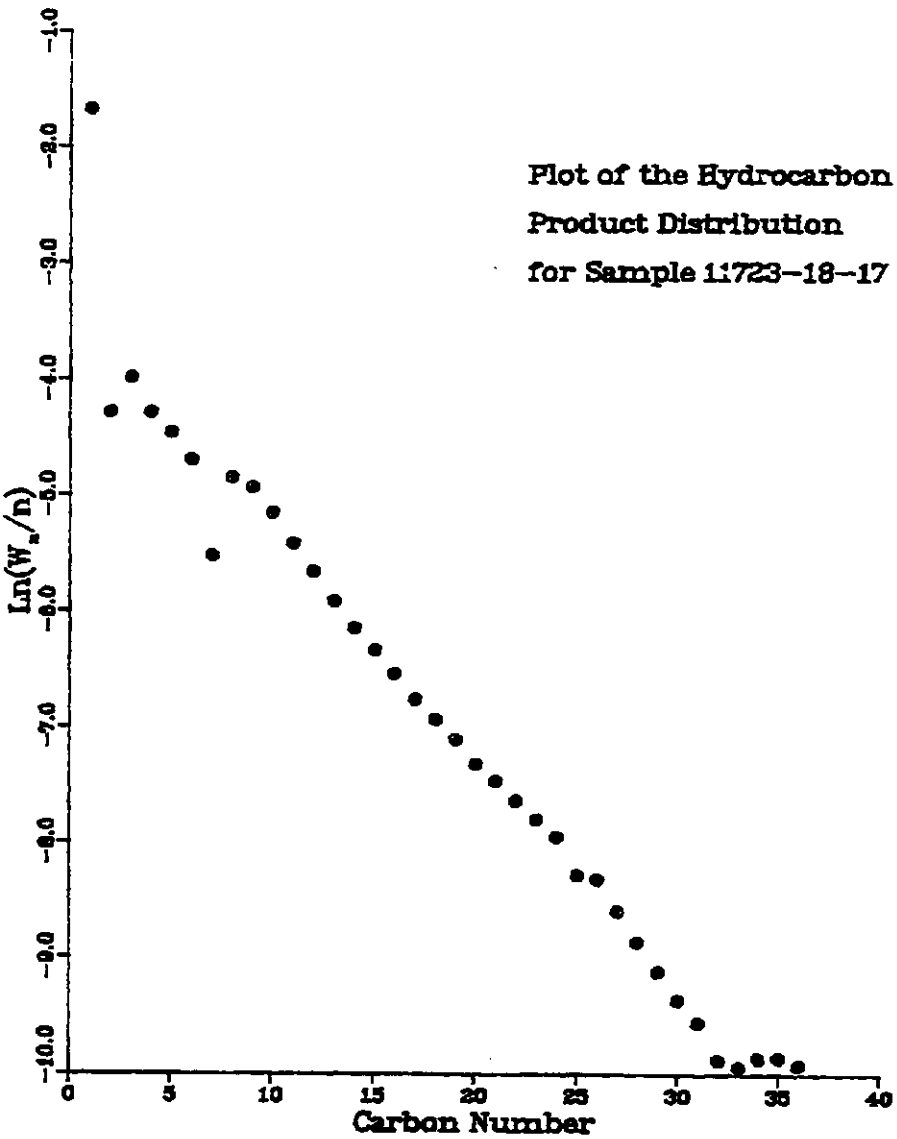

Plot of the Hydrocarbon
Product Distribution
for Sample 1:723-18-17
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A140

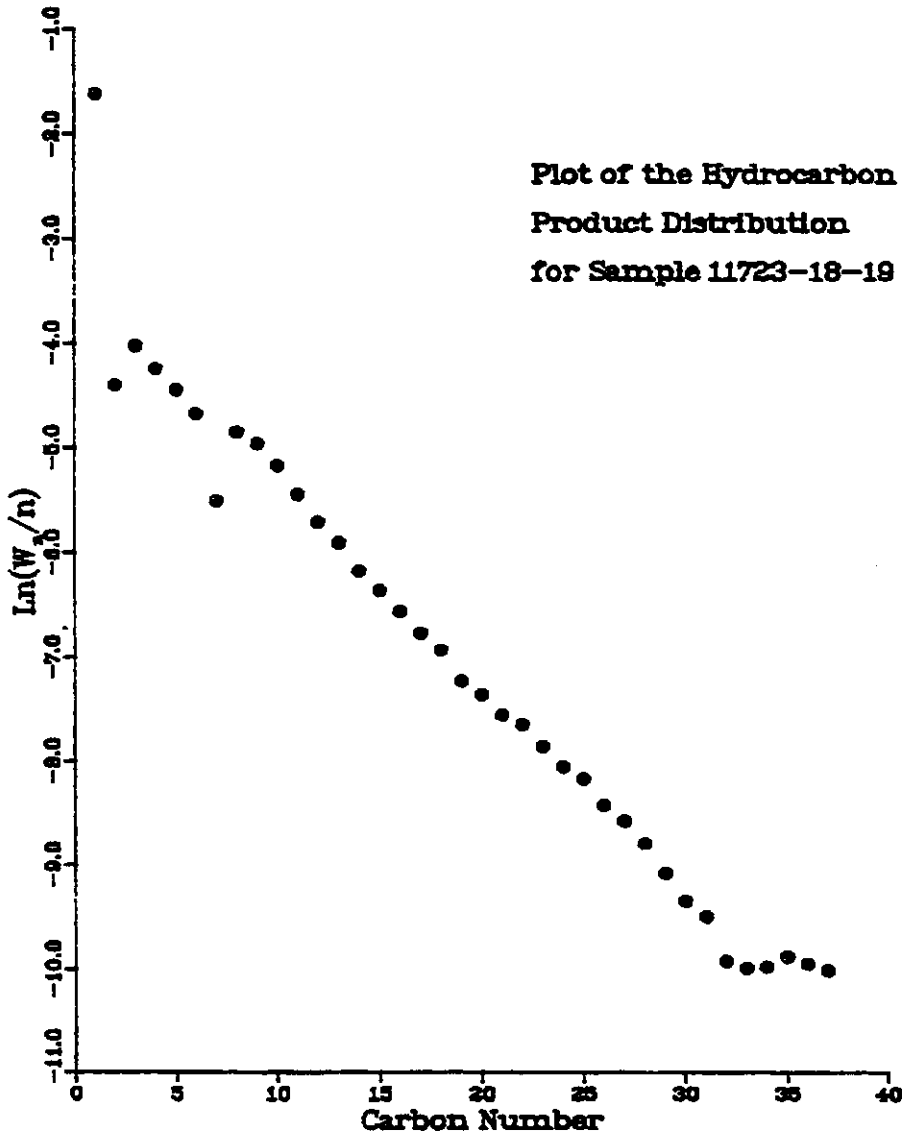

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-18-19
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A141

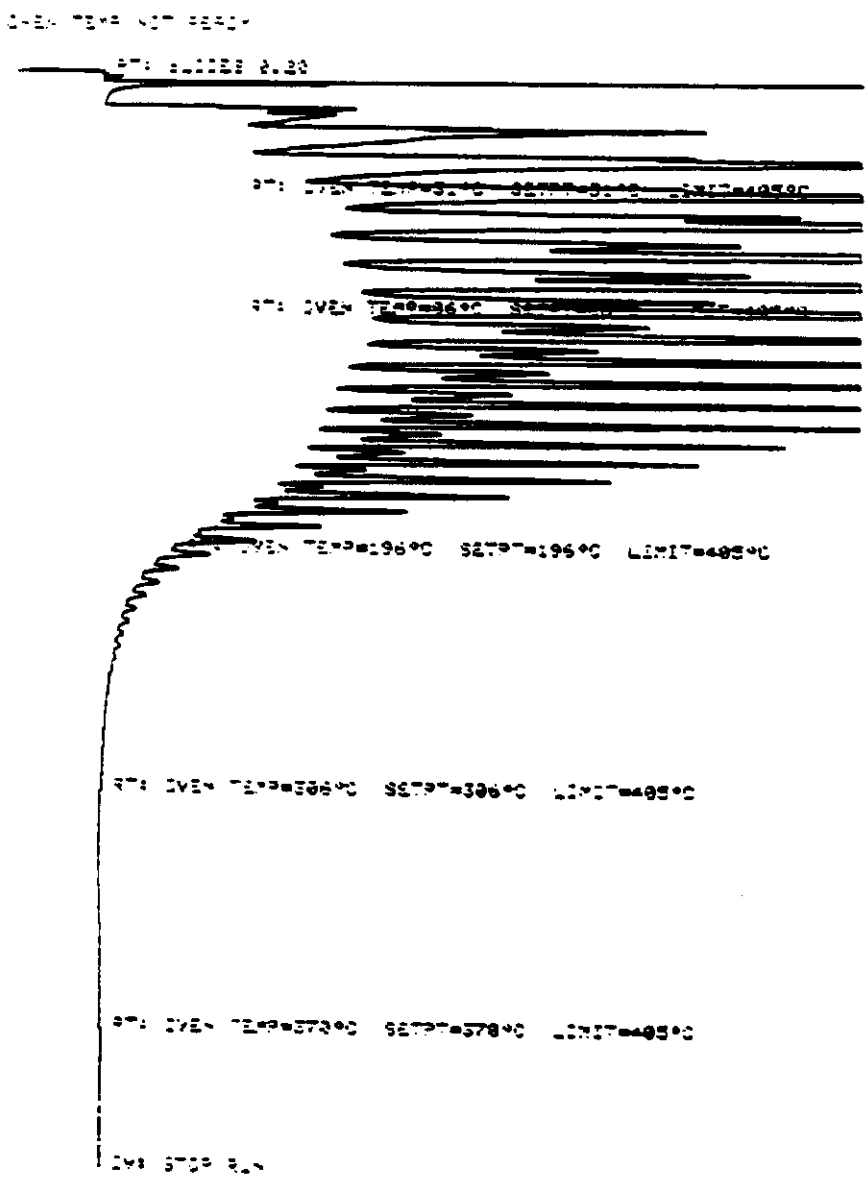


Fig. A142

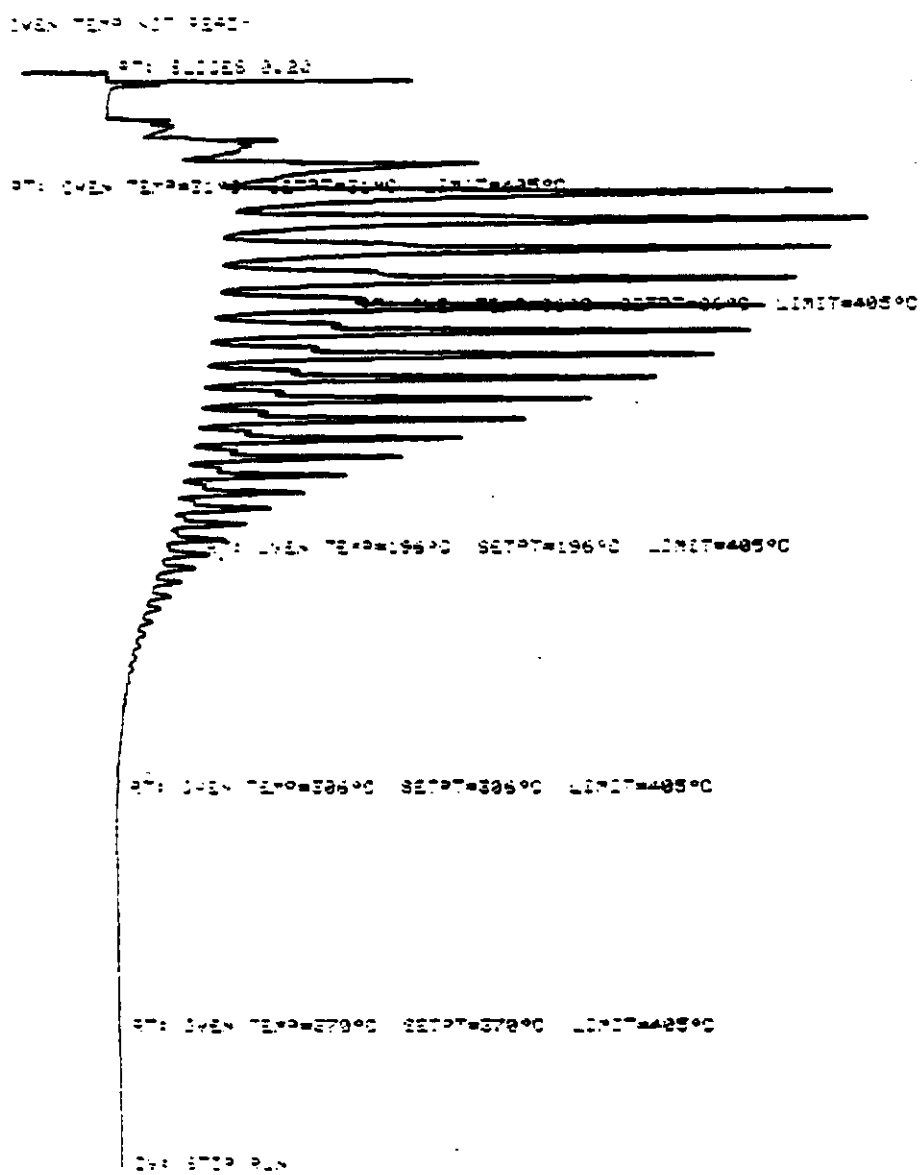
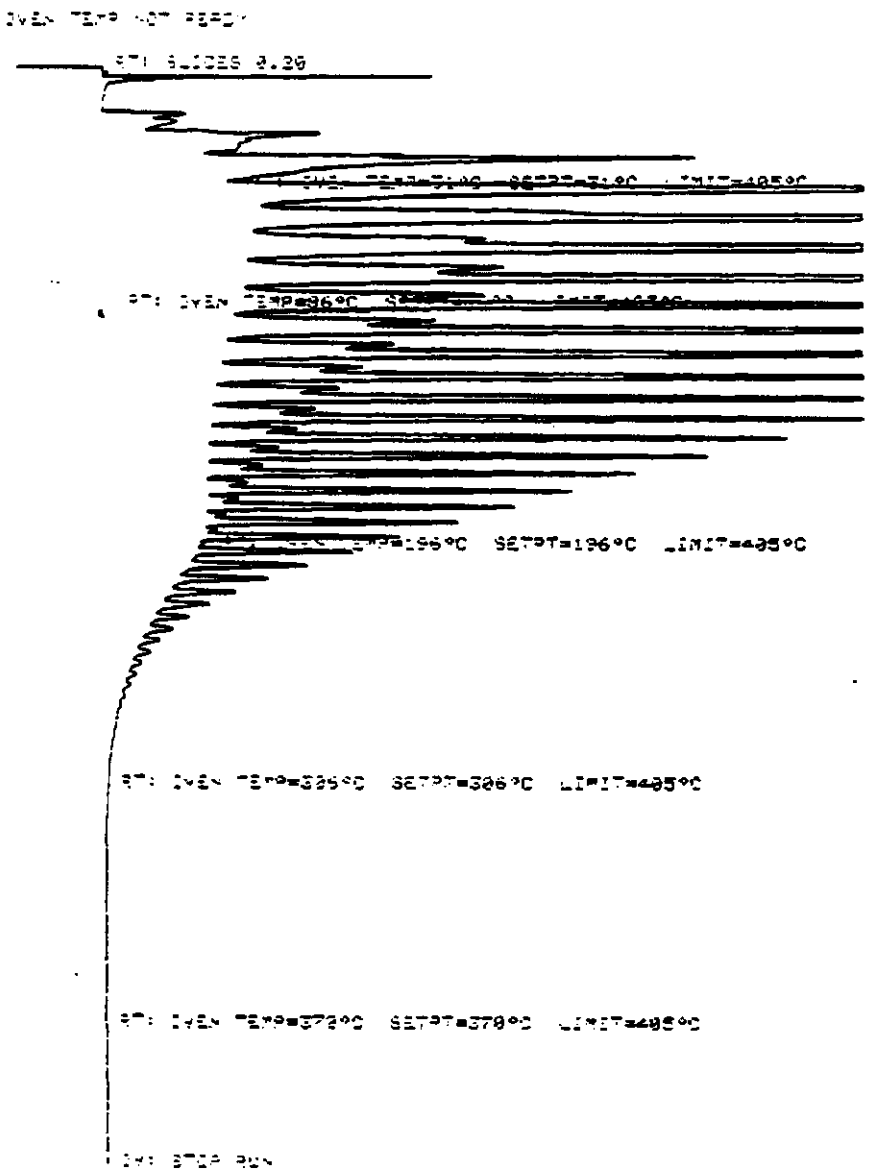


Fig. A143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SET: OVEN TEMP=326°C SETPT=326°C LIMIT=405°C
SET: OVEN TEMP=370°C SETPT=370°C LIMIT=405°C
SET: STOP RUN

Fig. A144