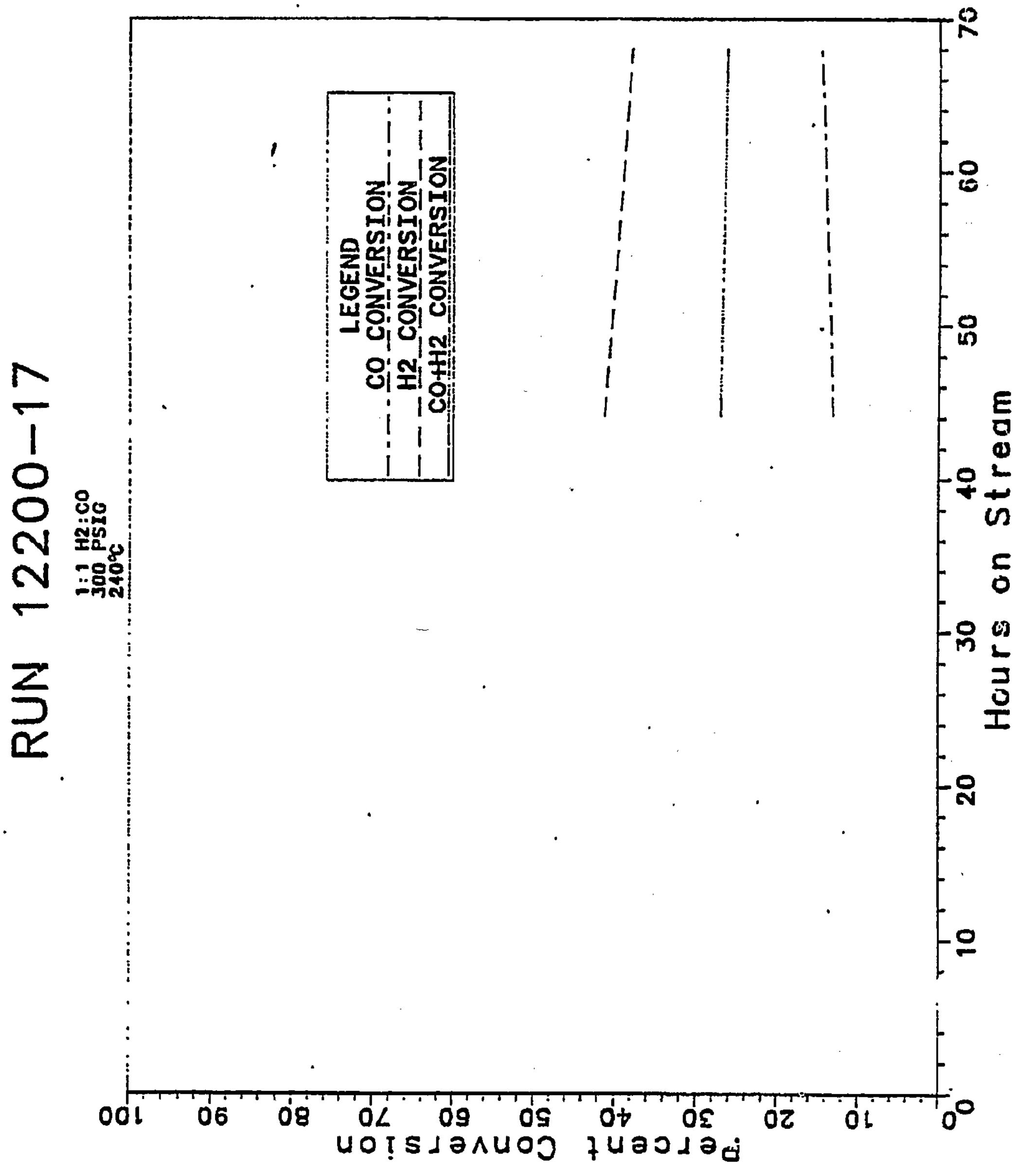

RUN 12200-17
1:1 H2:CO
300 PSIG
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Hours on Stream
Percent Conversion

Fig. B117

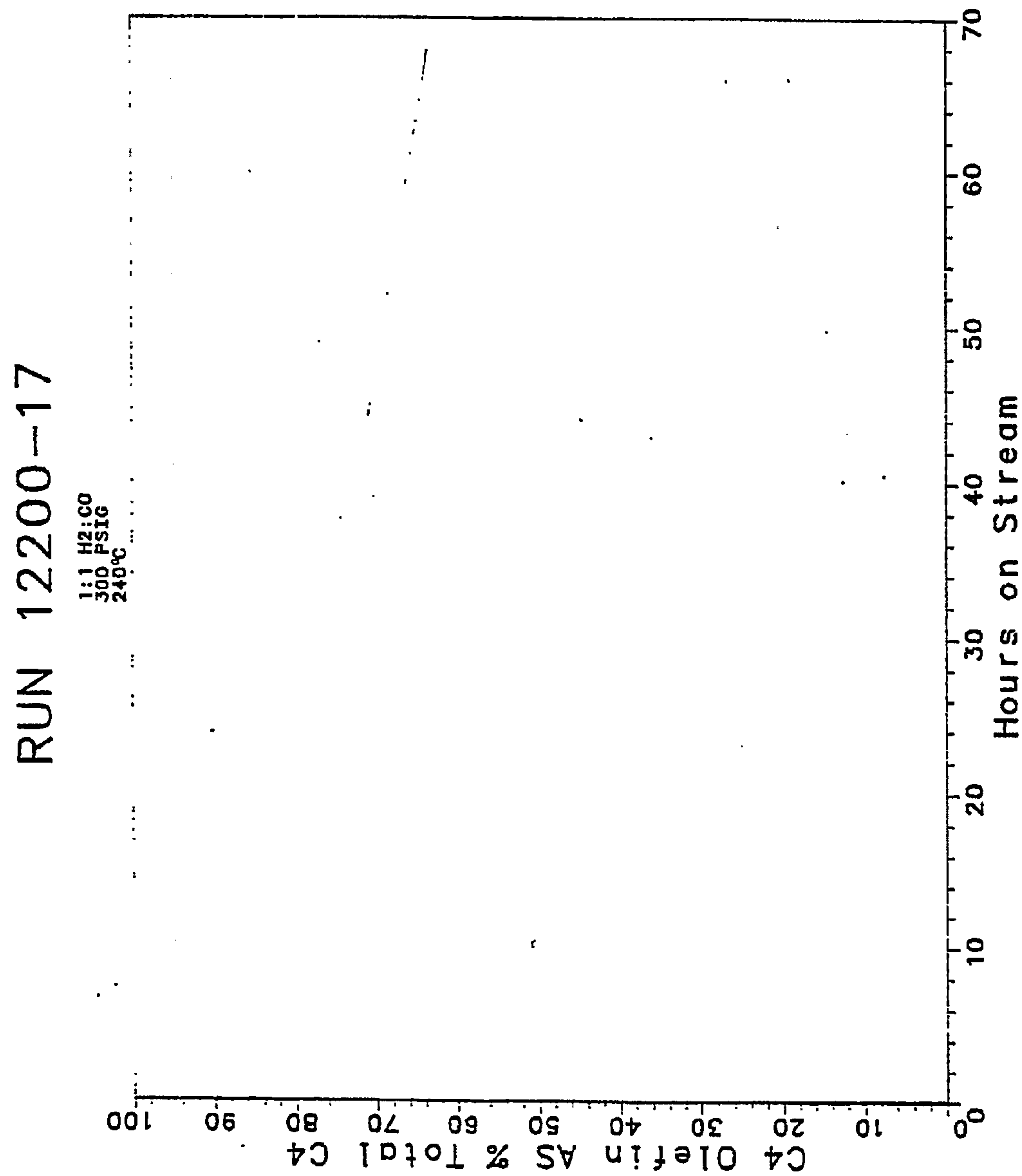

RUN 12200–17
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100

Fig. B118

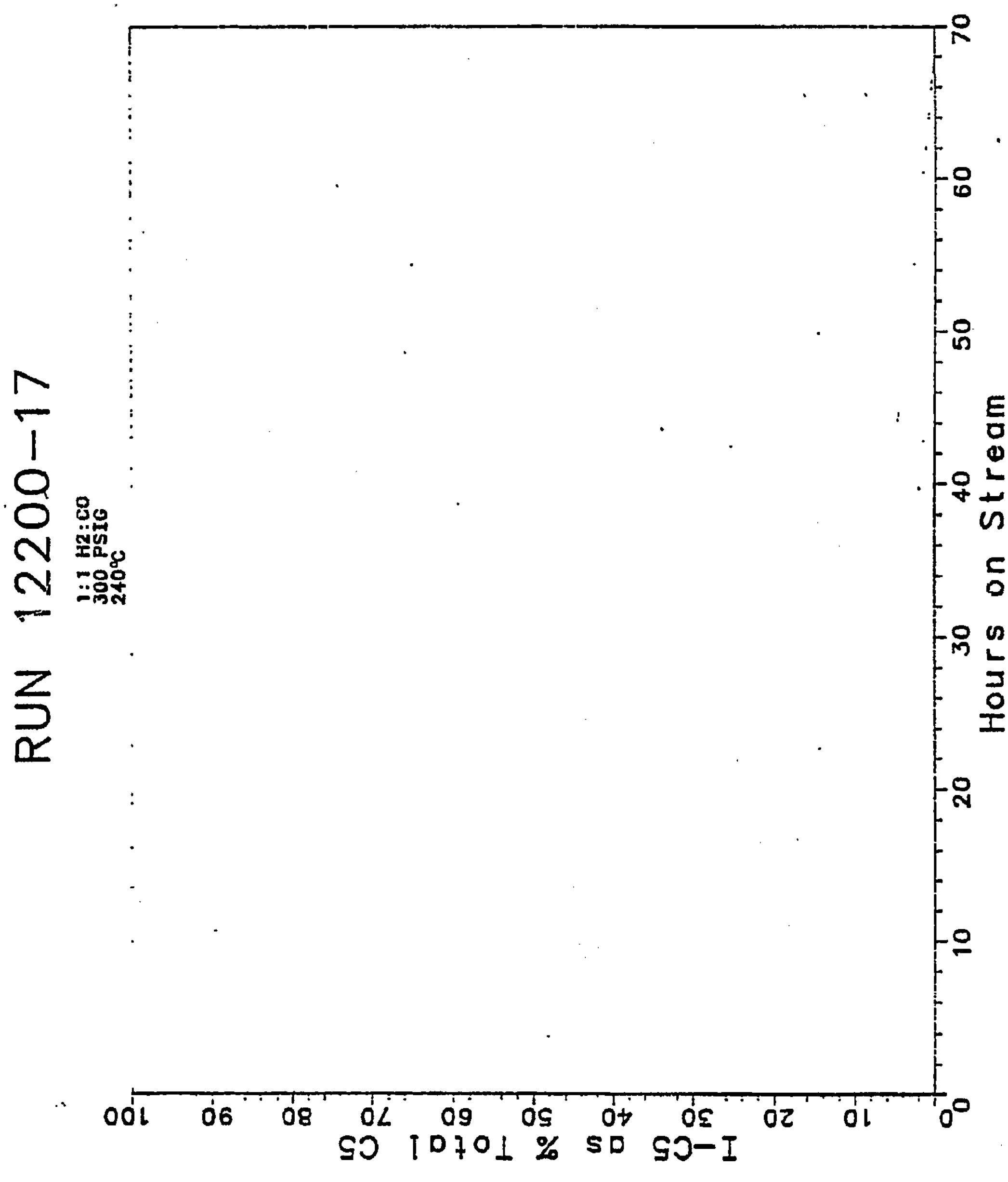

RUN 12200-17
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
0 10 20 30 40 50 60 70
I-C5 as % Total C5
0 10 20 30 40 50 60 70 80 90 100

Fig. B119

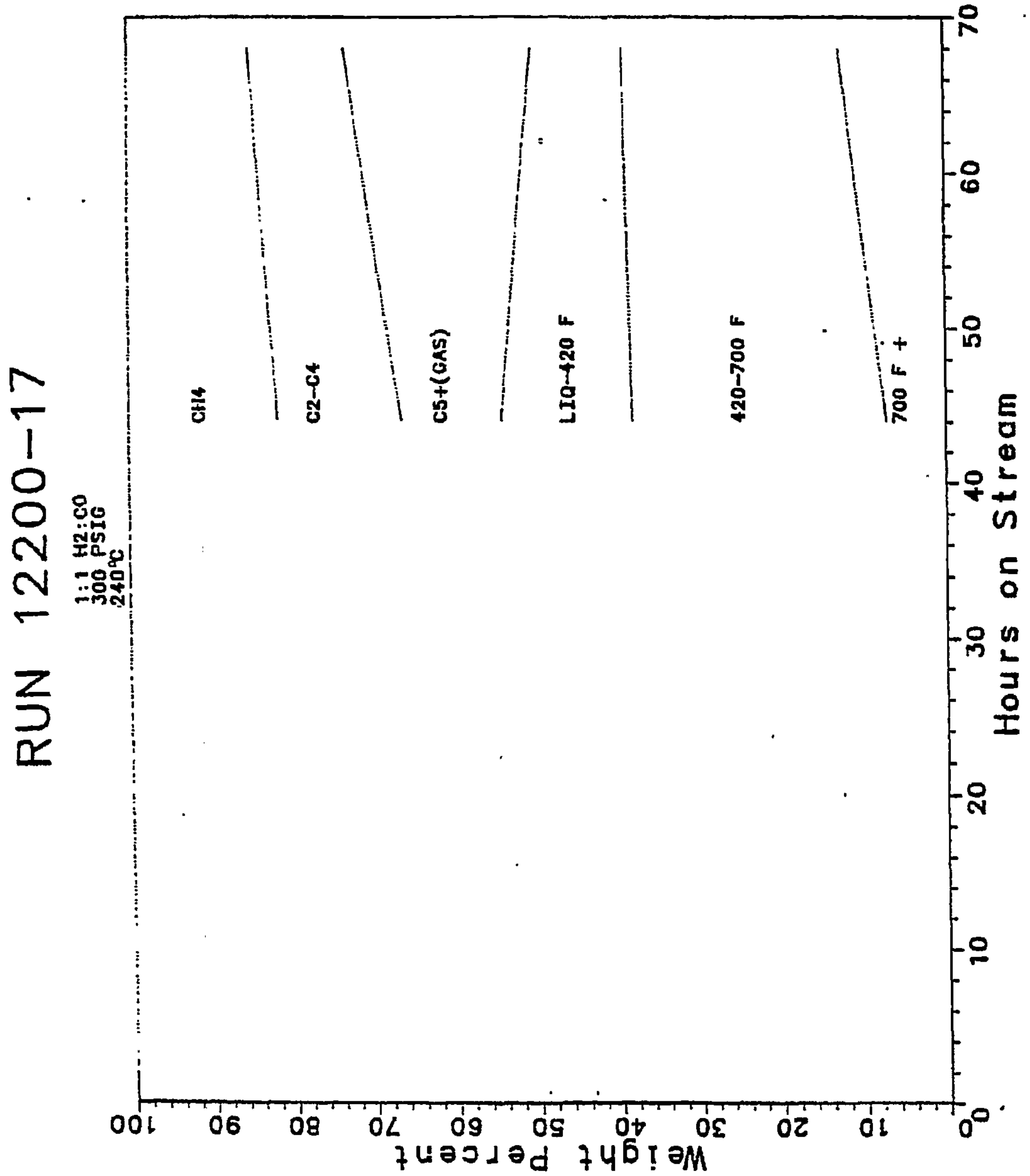

RUN 12200-17
1:1 H2:CO
300 PSIG
240°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B120

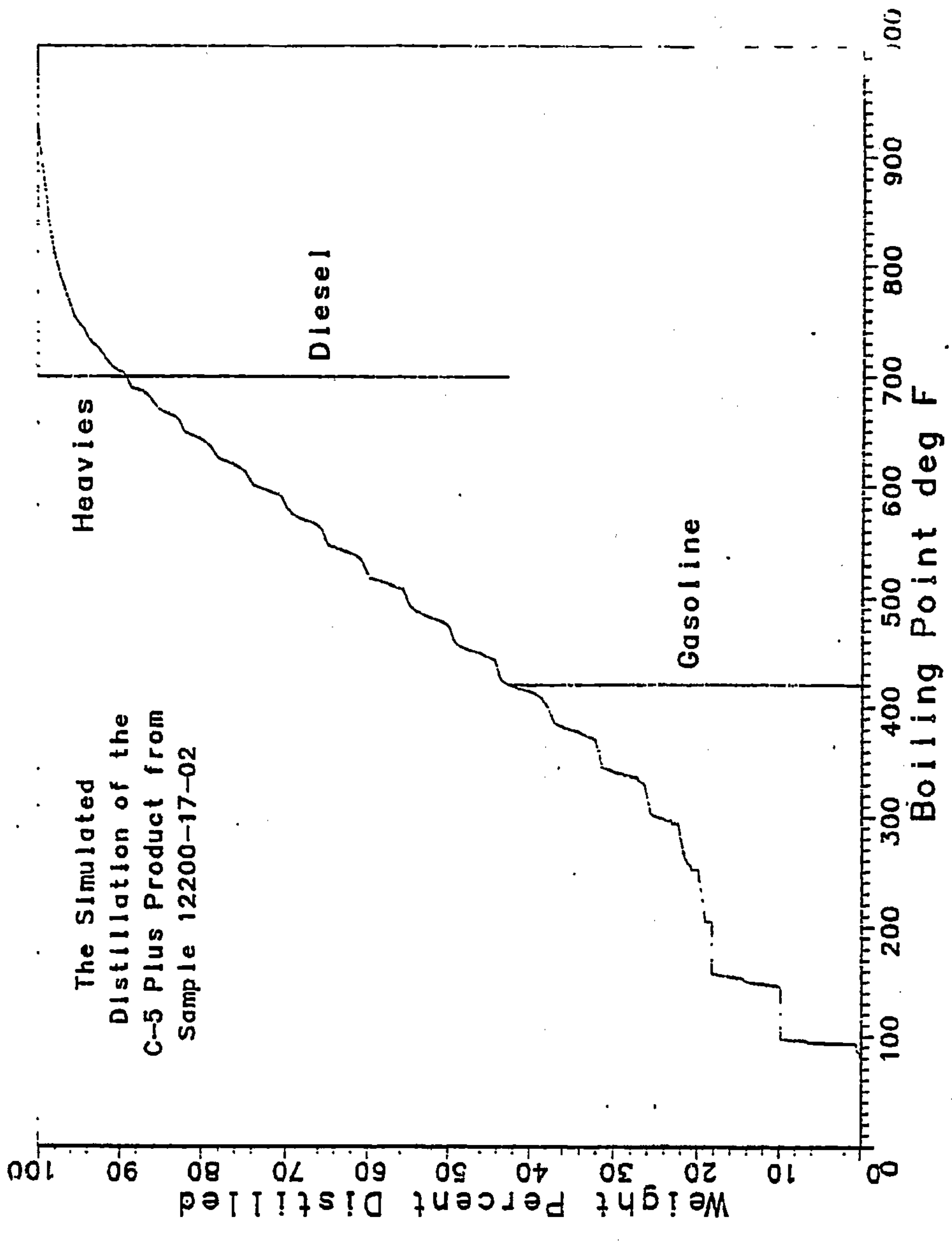
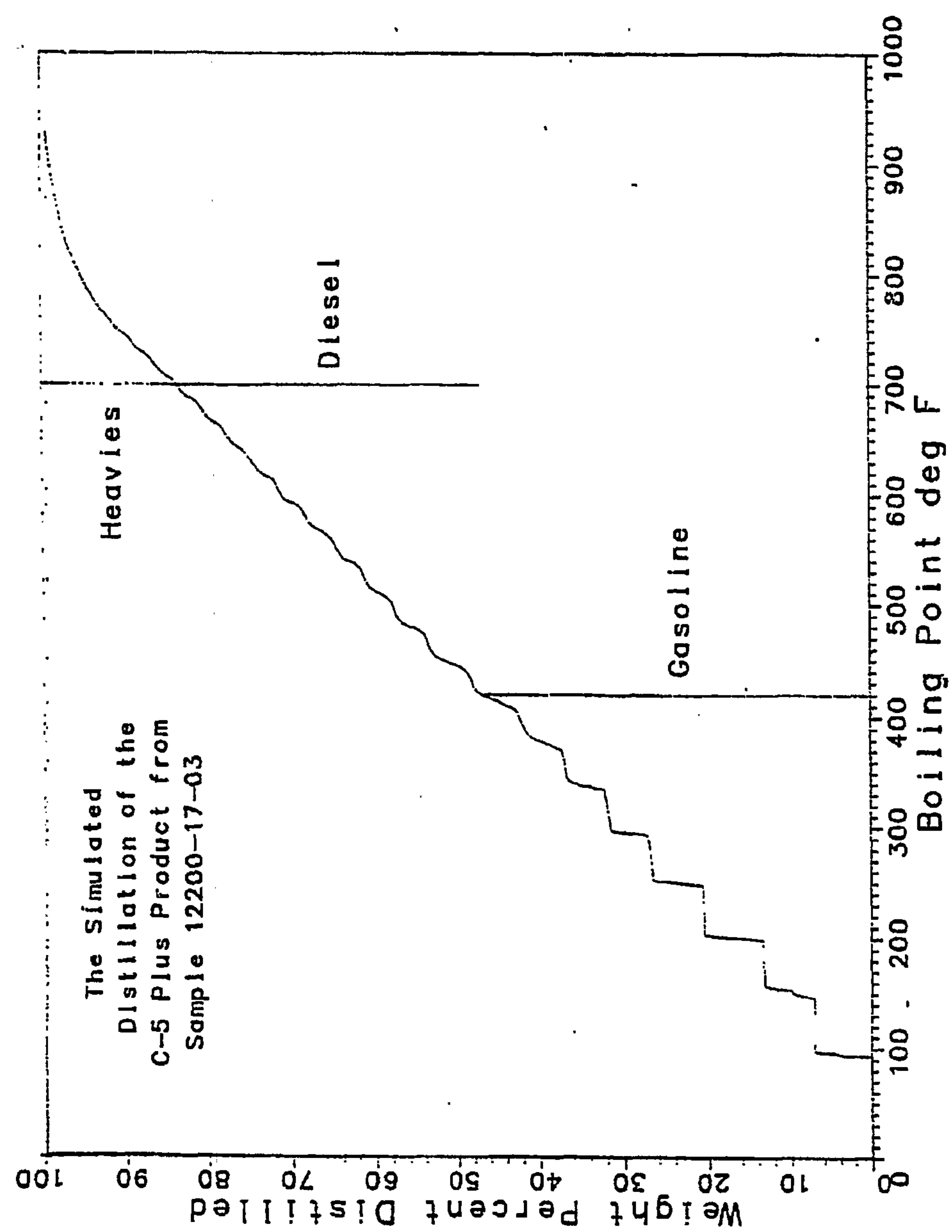

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-17-02
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900

Fig. B121



The Simulated Distillation of the C-5 Plus Product from Sample 12200-17-03
Heavies
Diesel
Gasoline
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point deg F
100
200
300
400
500
600
700
800
900
1000

Fig. B122

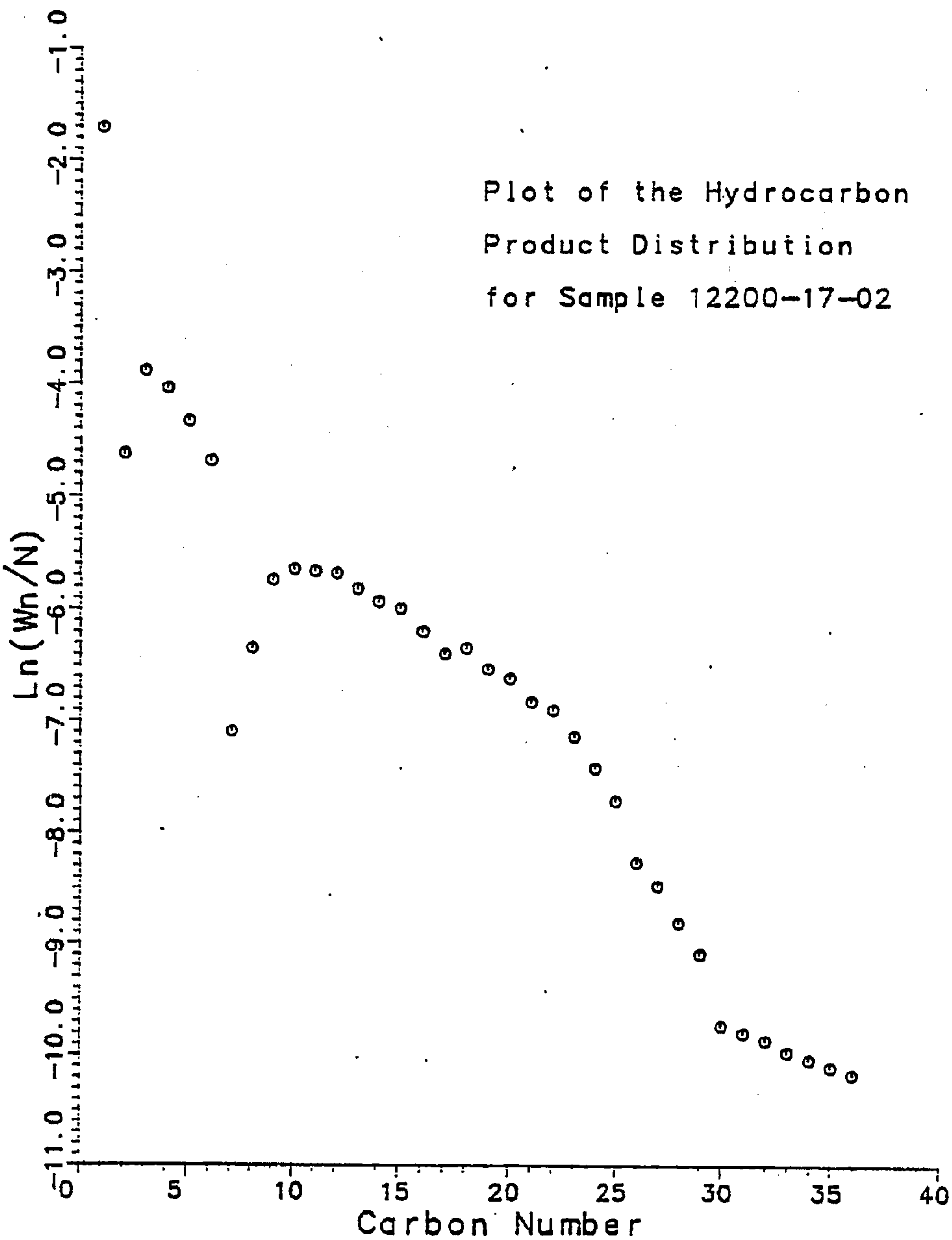

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-17-02
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B123

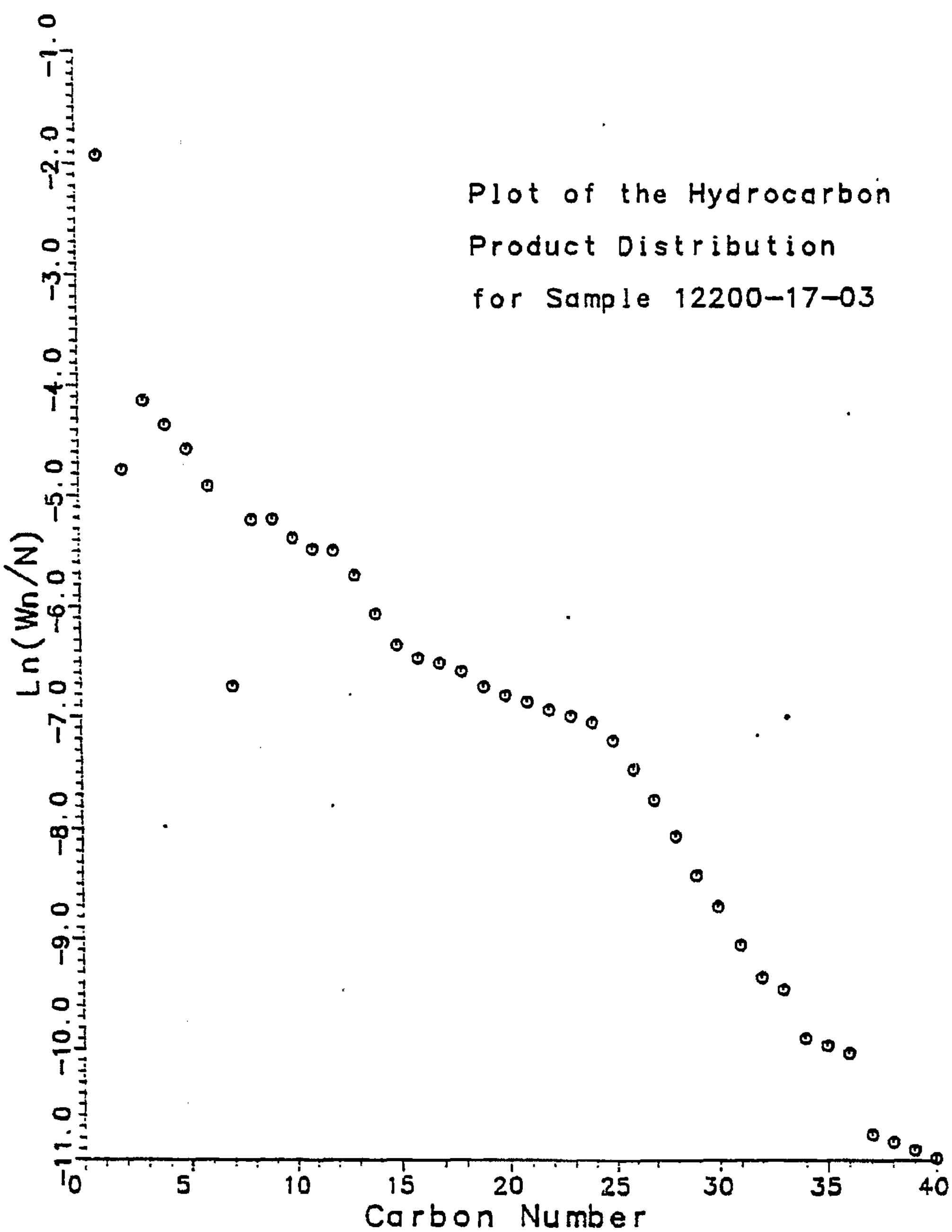

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-17-03
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B124

T141

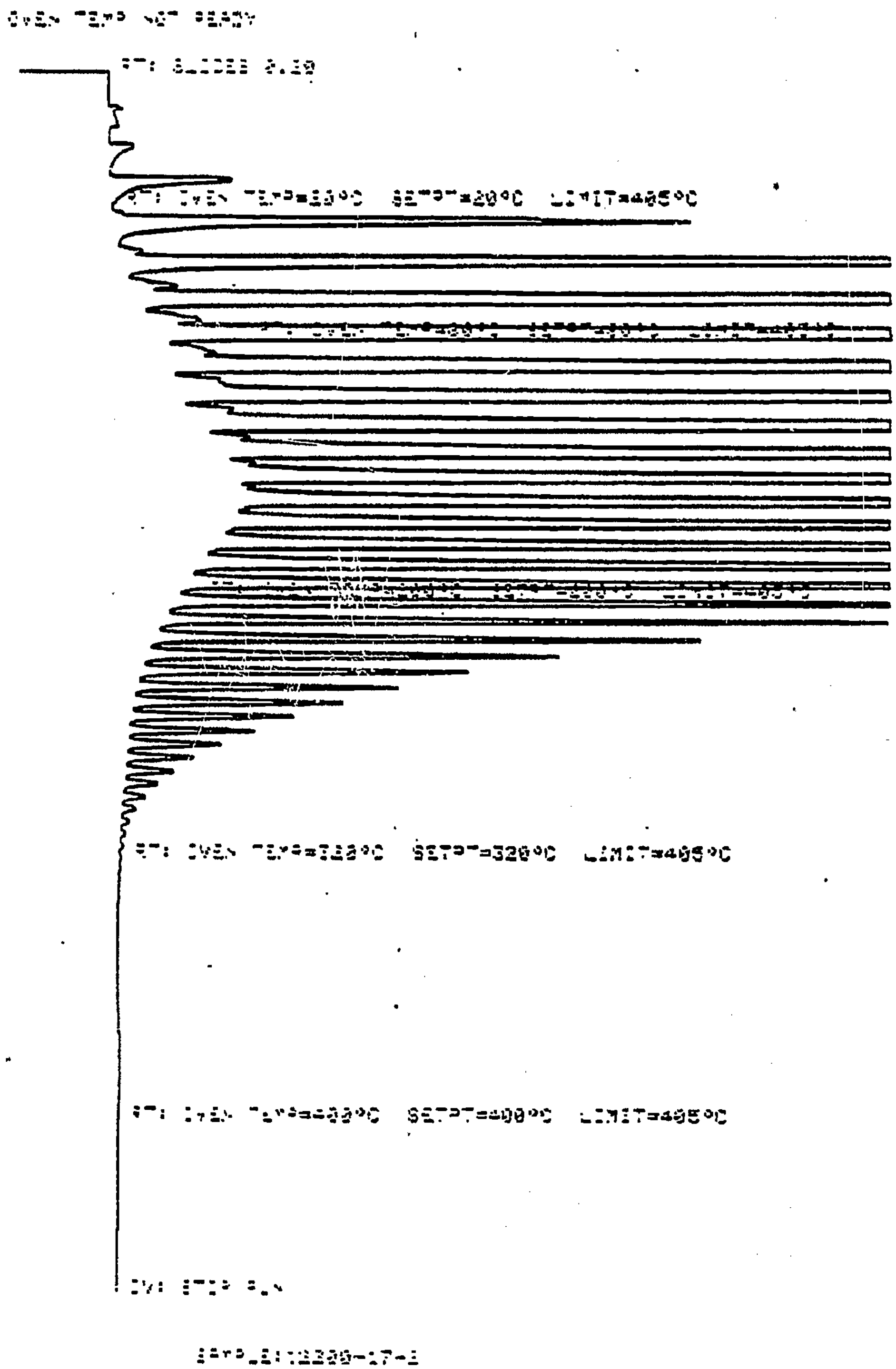


Fig. B125

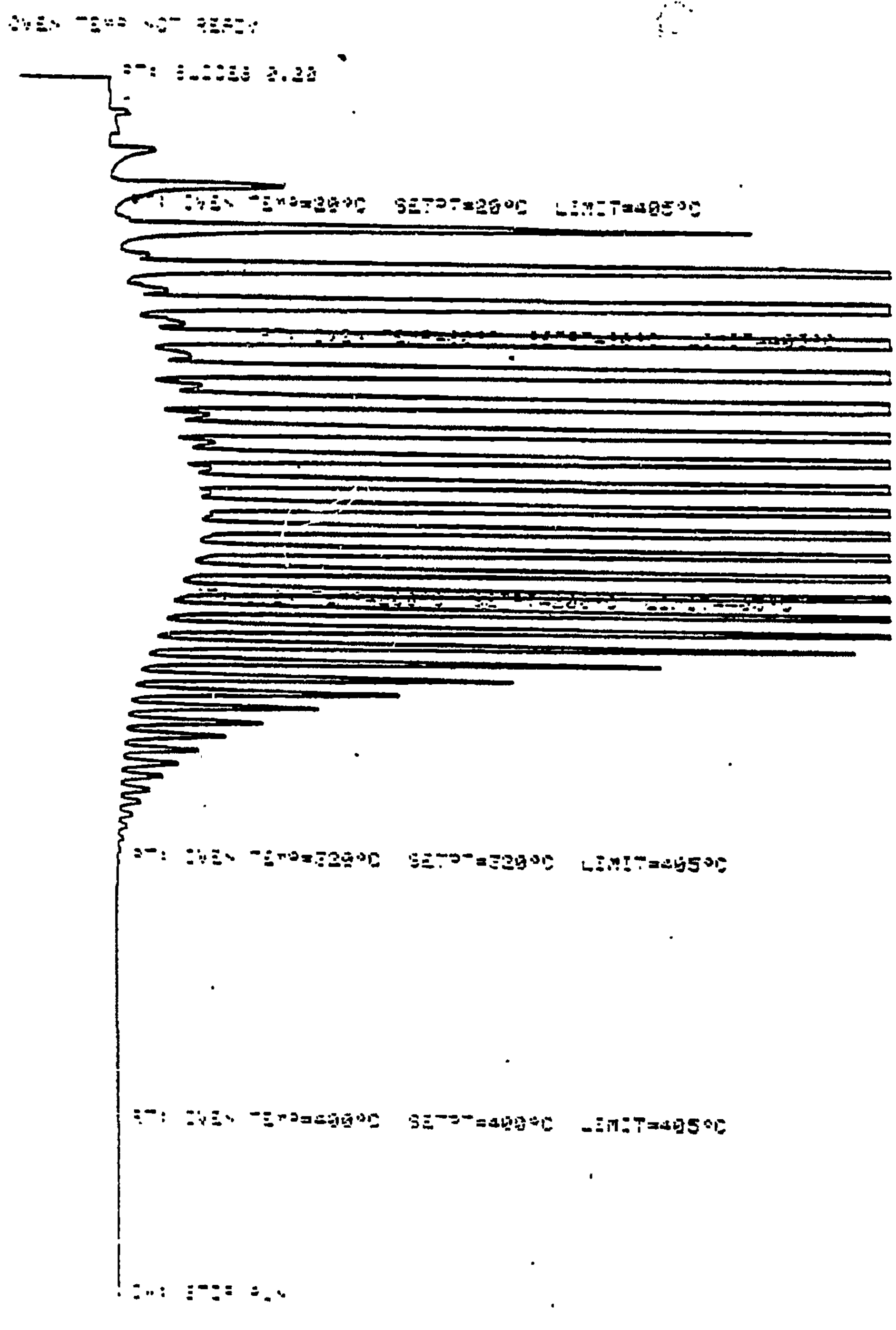


Fig. B126

Table B9

FILE: 1220017A TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-17
CATALYST CO/X9/X10/X4-U103 80 CC 34.1 G AFTER USE:52.3 G (+18.2 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-50-31)

RUN & SAMPLE NO.	12200-17-02	200-17-03
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	44.0	68.0
PRESSURE,PSIG	300	300
TEMP. C	239	240
FEED CC/MIN	400	400
HOURS FEEDING	24.00	24.00
EFFLNT GAS LITER	360.60	392.35
GM AQUEOUS LAYER	39.98	35.71
GM OIL	9.40	10.41
MATERIAL BALANCE		
GM ATOM CARBON %	82.36	87.68
GM ATOM HYDROGEN %	81.27	88.76
GM ATOM OXYGEN %	94.03	95.71
RATIO CHX/(H2O+CO2)	0.4634	0.5998
RATIO X IN CHX	2.4546	2.3829
USAGE H2/CO PRODT	3.1266	2.6265
FEED H2/CO FRM EFFLNT	0.9868	1.0124
RESIDUAL H2/CO RATIO	0.6671	0.7360
RATIO CO2/(H2O+CO2)	0.0291	0.0384
K SHIFT IN EFFLNT	0.0200	0.0294
SPECIFIC ACTIVITY SA	1.0313	0.9627
CONVERSION		
ON CO %	13.00	14.62
ON H2 %	41.18	37.93
ON CO+H2 %	26.99	26.35
PRDT SELECTIVITY,WT %		
CH4	18.23	14.80
C2 HC'S	1.97	1.73
C3H8	1.75	1.85
C3H6=	4.46	3.00
C4H10	2.12	1.94
C4H8=	4.98	3.26
C5H12	2.27	2.12
C5H10=	4.31	3.07
C6H14	2.59	2.45
C6H12= & CYCLO'S	2.96	1.99
C7+ IN GAS	0.00	13.21
LIQ HC'S	54.36	50.59
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	33.51	26.57
C5 -420 F	28.17	33.97
420-700 F	31.10	26.66
700-END PT	7.23	12.80

Table B9 (continued)

FILE: 1220017A TSS3Q1   A1

C5+-END PT	66.49	73.43
ISO/NORMAL MOLE RATIO		
C4	0.0000	0.0000
C5	0.0486	0.0000
C6	0.0000	0.0000
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	0.3735	0.5879
C4	0.4110	0.5749
C5	0.5119	0.6708
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8487	0.8691
RATIO CH4/(1-A)**2	7.9586	8.6411
ALPHA FRM CORRELATION	0.8317	0.8269
ALPHA (EXPTL/CORR)	1.0204	1.0511
W%CH4 FRM CORRELATION	15.4198	17.1499
W%CH4 (EXPTL/CORR)	1.1822	0.8628
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLD OIL	CLD OIL
DENSITY	0.7737	0.7742
N, REFRACTIVE INDEX	1.4300	1.4303
SIMULT'D DISTILATN		
10 WT % @ DEG F	330	376
16	346	407
50	517	569
84	686	746
90	718	782
RANGE(16-84 %)	340	339
WT % @ 420 F	29.50	22.00
WT % @ 700 F	86.70	74.70

V. Run 29 (12200-18) with Catalyst 29 ($Co/X_9/X_{10}$/UCC-113

The purpose of this short run was to test the effect of reducing the cobalt concentration in a cobalt/X_9/X_{10} catalyst formulated by the method used for Catalyst 11. The results are to be compared with those of Catalyst 26 (Run 12185-14). The theoretical concentrations of cobalt, X_9 and X_{10} were 7.8, 0.35 and 0.47 percent respectively, as against 11.9, 0.5 and 0.7 percent respectively in Catalyst 26.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B127-130. Simulated distillations of the C_5^+ product are plotted in Figs. B131-133. Carbon number product distributions are plotted in Figs. B134-136. Chromatograms from simulated distillations are reproduced in Figs. B137-139. Detailed material balances appear in Table B10.

The syngas conversion, specific activity, and specific activity per unit cobalt concentration compare as follows with those for Catalyst 26 (all at 250C reaction temperature):

	Pct. Co	Syngas conversion, pct	Specific activity	S.A. per pct cobalt
Catalyst 29	7.8	38.0	1.5	0.19
Catalyst 26	11.9	50.6	2.4	0.20

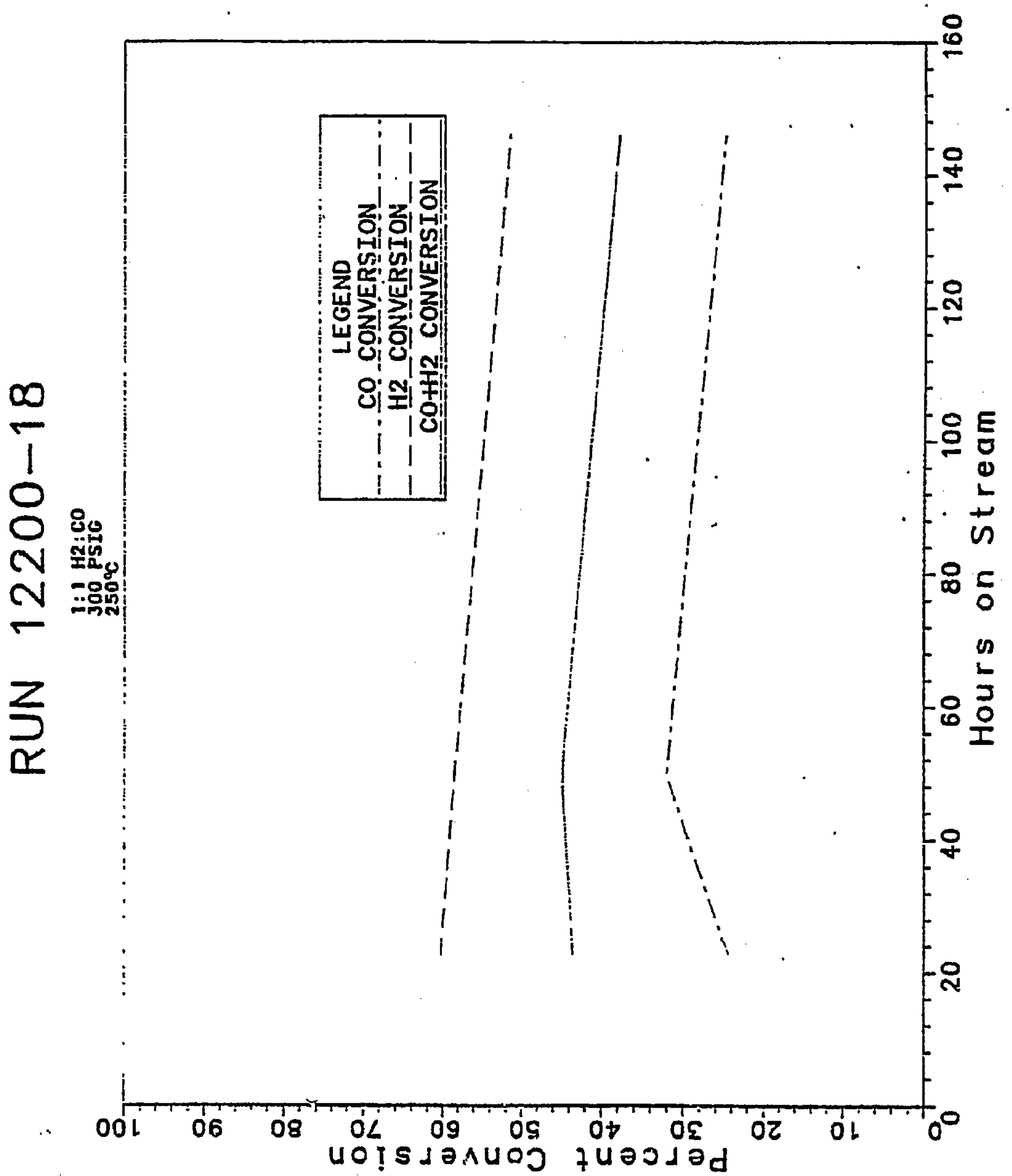
(Values for Catalyst 29 were calculated from a sample taken at 146.0 hours on stream, those for Catalyst 26 from averages over the period tested at 250C.)

Although the syngas conversion was lower than that of Catalyst 26, from the specific activities per unit cobalt concentration the two catalysts are about equally efficient in their use of the cobalt.

The run was too short for any reliable comparisons of stability.

There were slight differences in selectivity between the two catalysts, most of which can be attributed to the differences in residual H_2:CO ratios in the reactor resulting from the differences in syngas conversion.

Results of this run demonstrate that in the cobalt/X_9/X_{10} catalyst, the efficacy of the cobalt in the Fischer-Tropsch reaction is relatively uniform across the concentration range of 7.8 to 11.9 percent.



RUN 12200—18
1:1 H2:CO
300 PSIG
250°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
140
160

Fig. B127

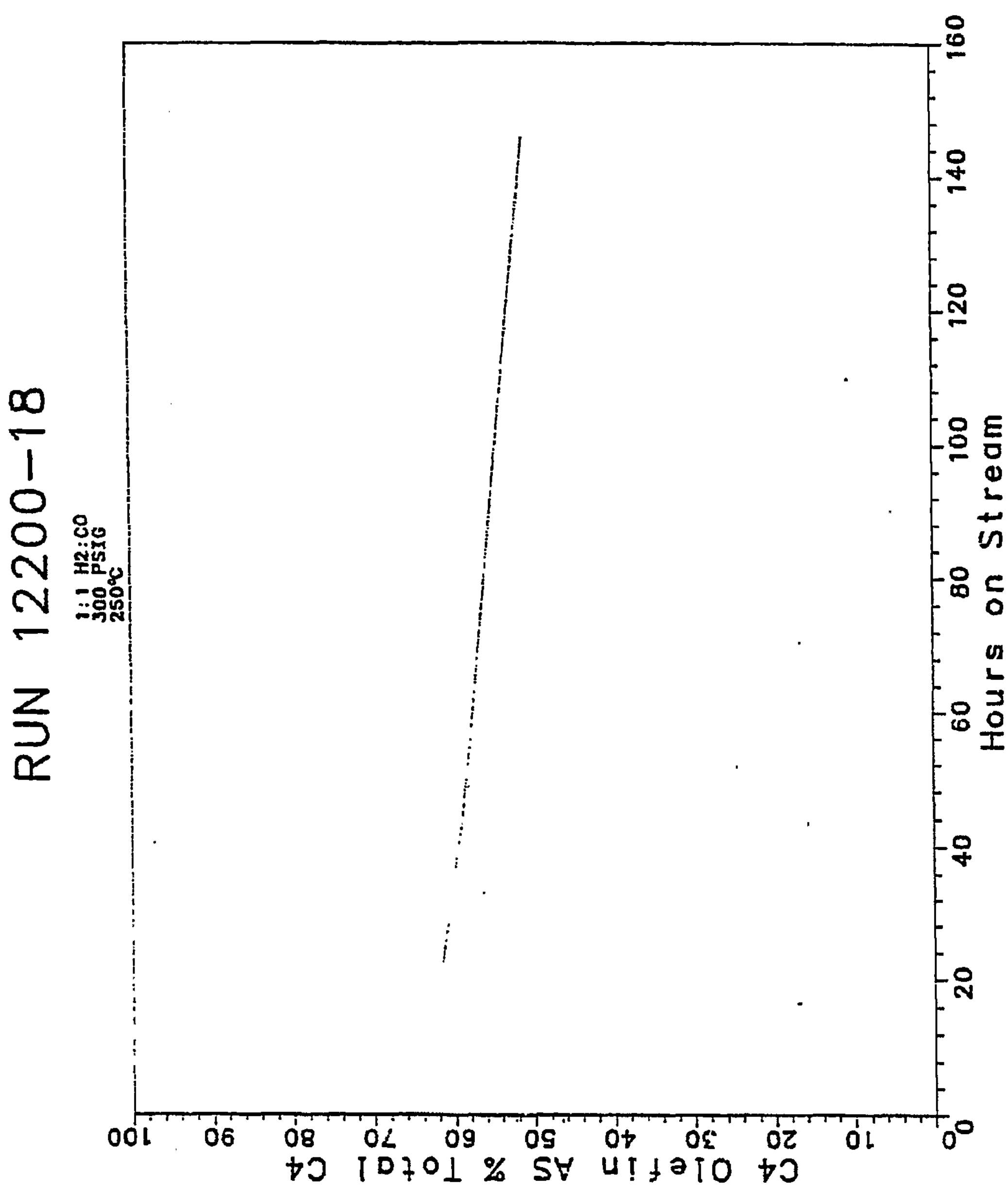

RUN 12200-18
1:1 H2:CO
300 PSIG
250°C
Hours on Stream
0
20
40
60
80
100
120
140
160
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100

Fig. B128

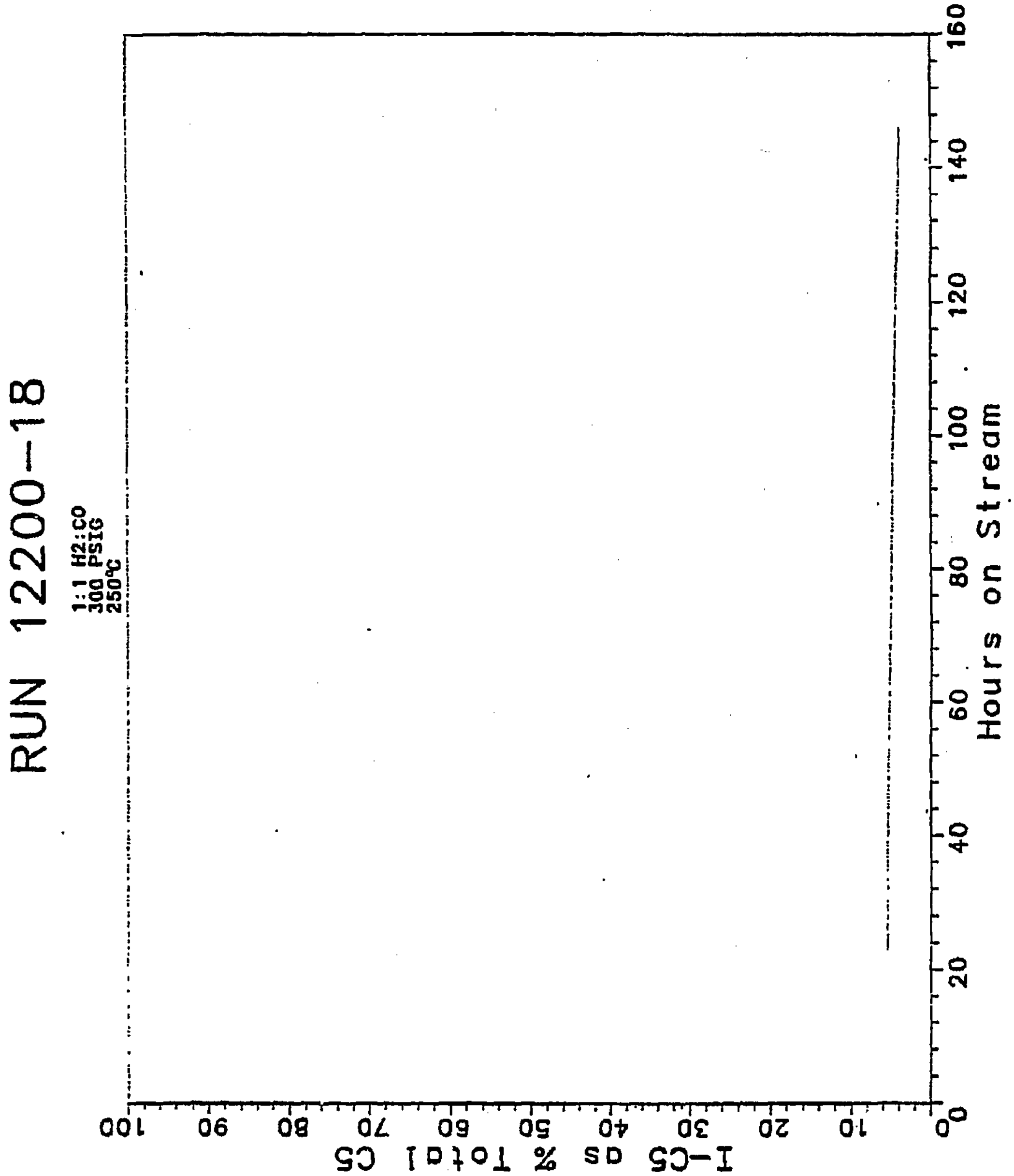

RUN 12200-18
1:1 H2:CO
300 PSIG
250°C
Hours on Stream
I-C5 as % Total C5
0
20
40
60
80
100
120
140
160
10
30
50
70
90

Fig. B129

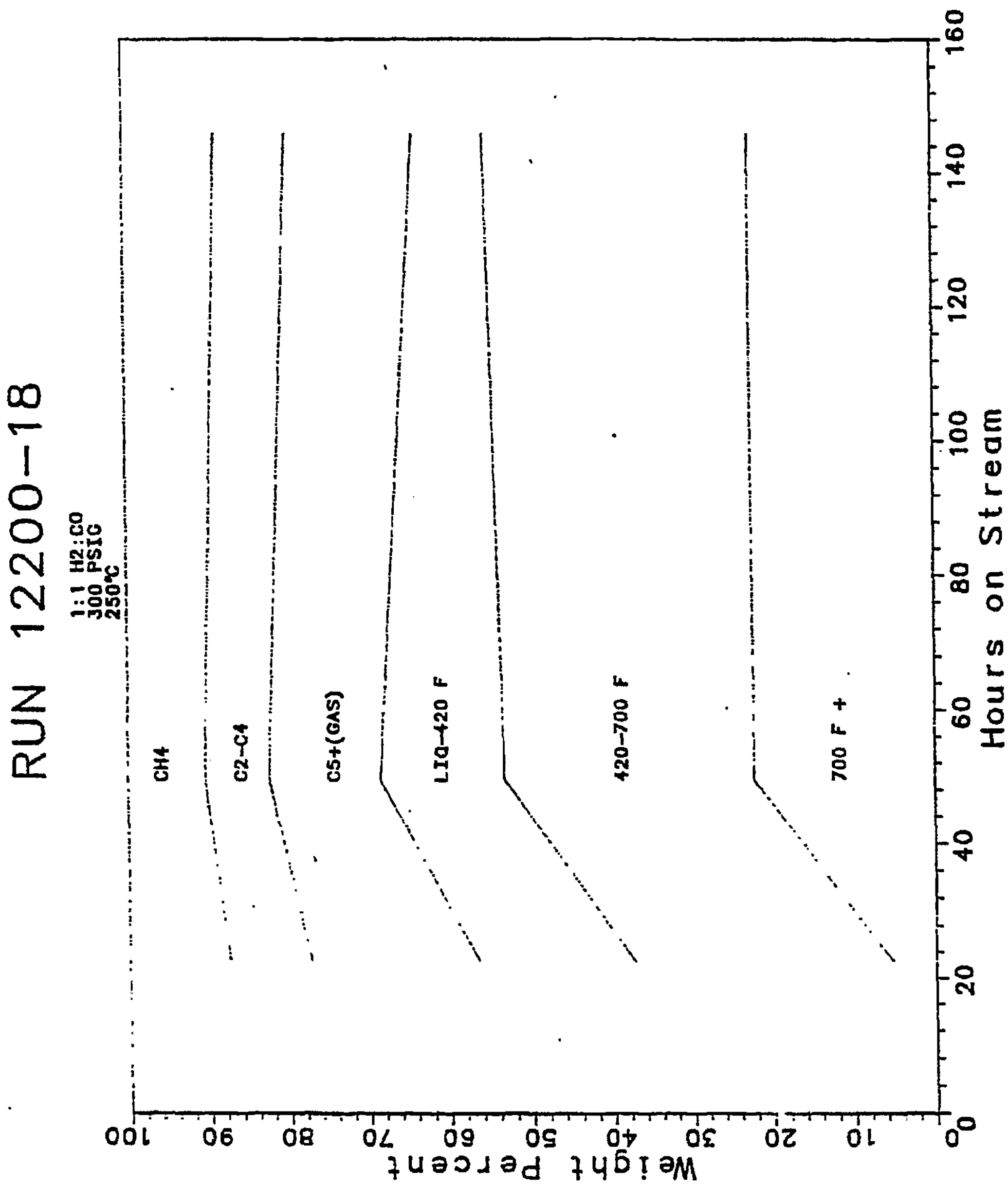

RUN 12200-18
1:1 H2:CO
300 PSIG
250°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
120
140
160

Fig. B130

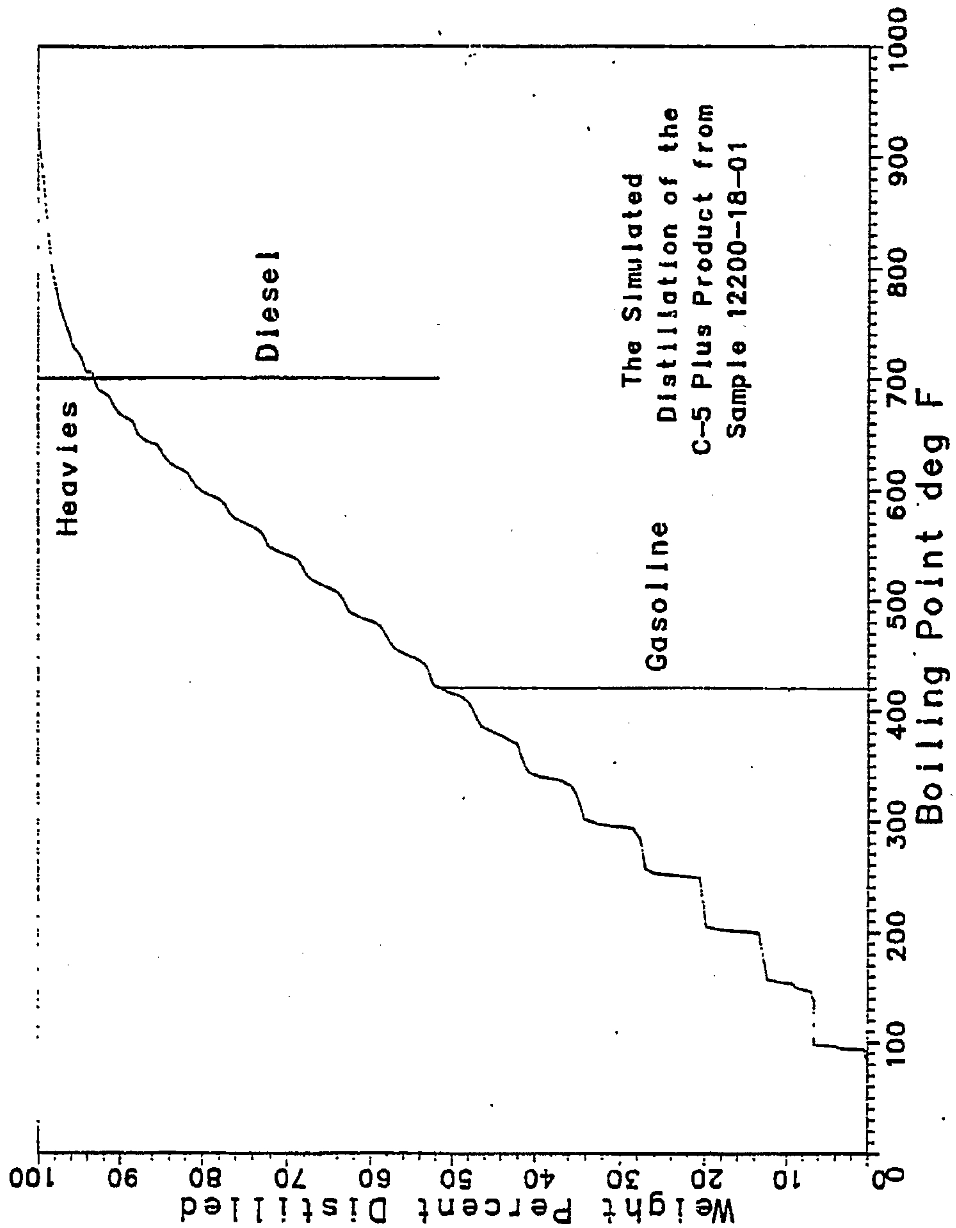

The Simulated Distillation of the C-5 Plus Product from Sample 12200-18-01
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B131

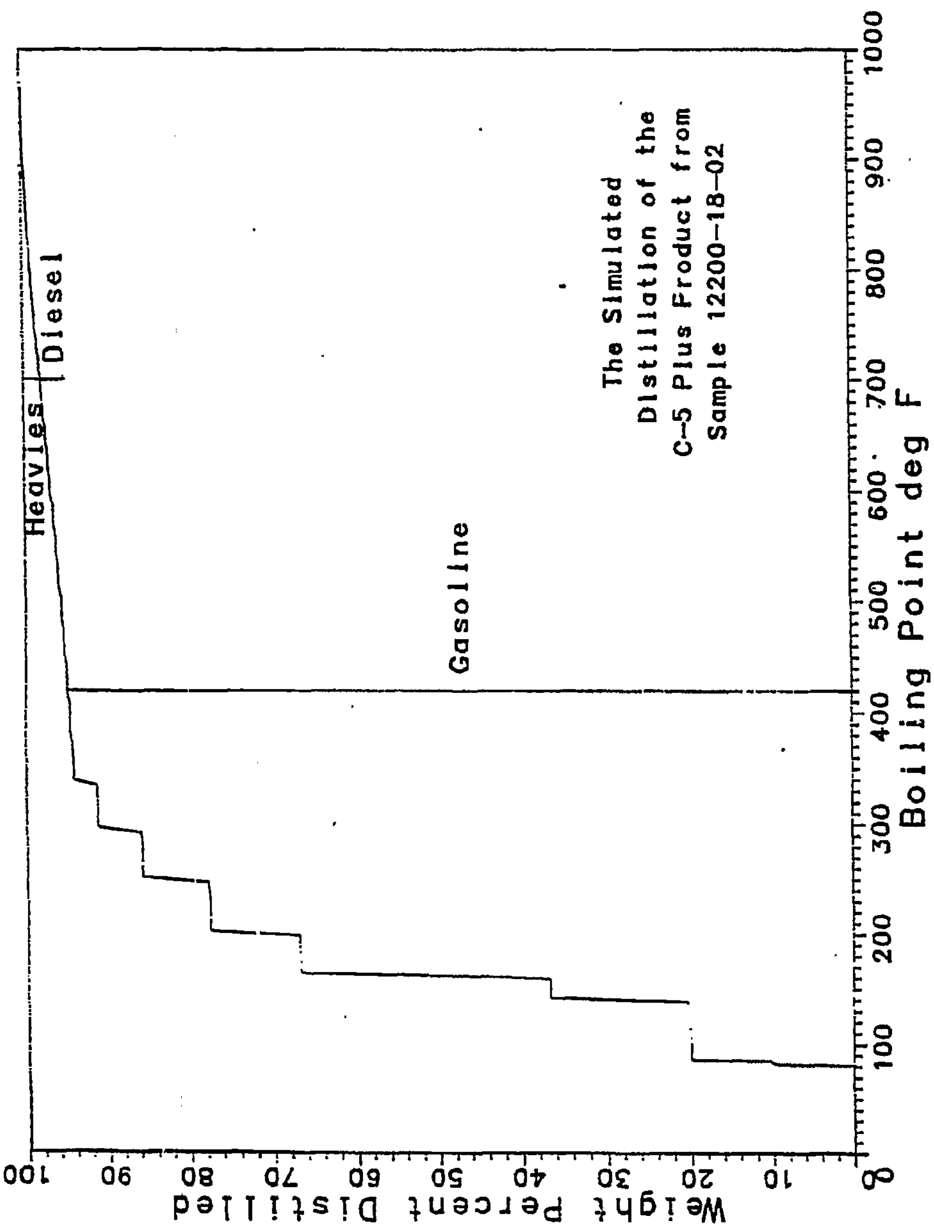

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-18-02
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B132

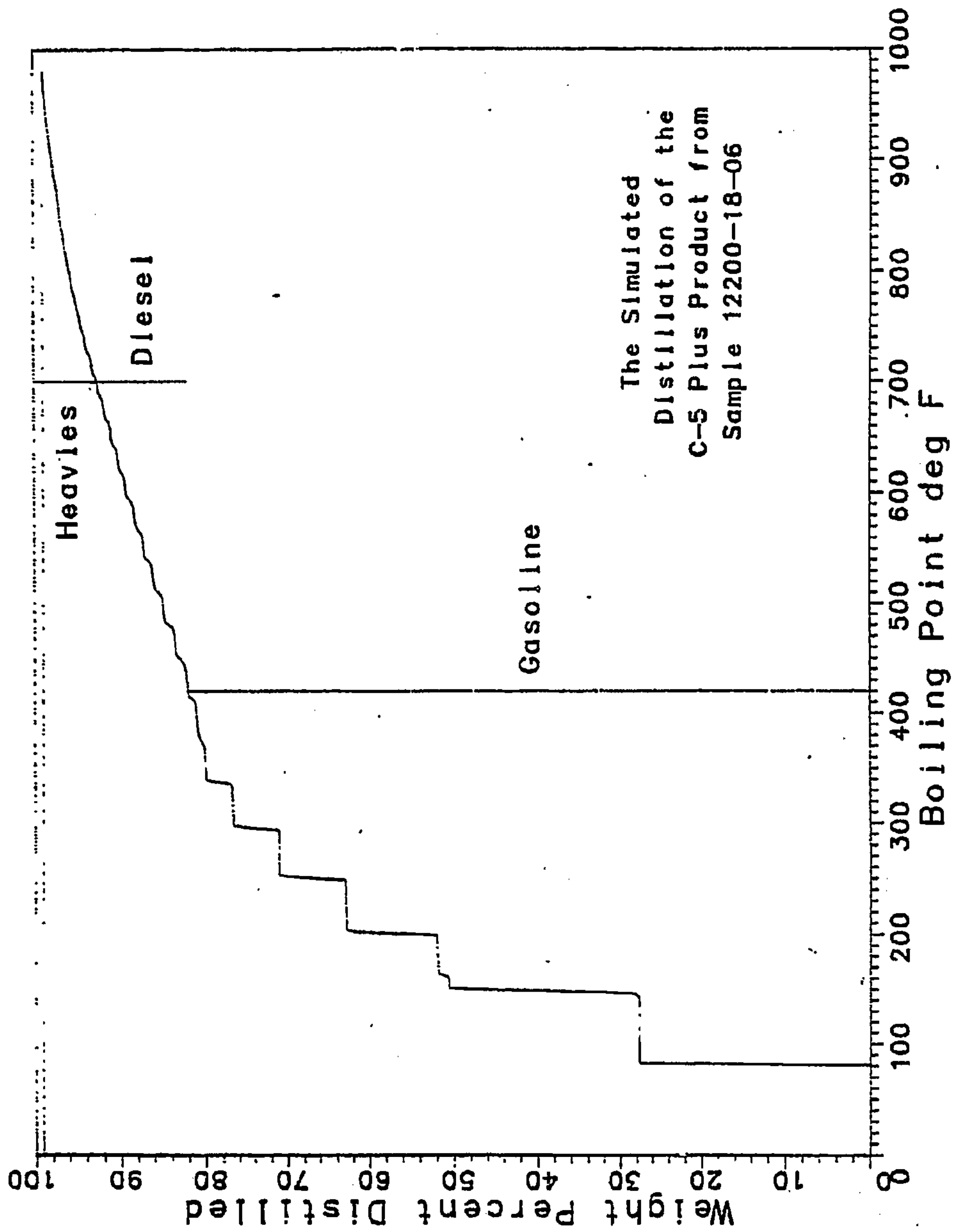
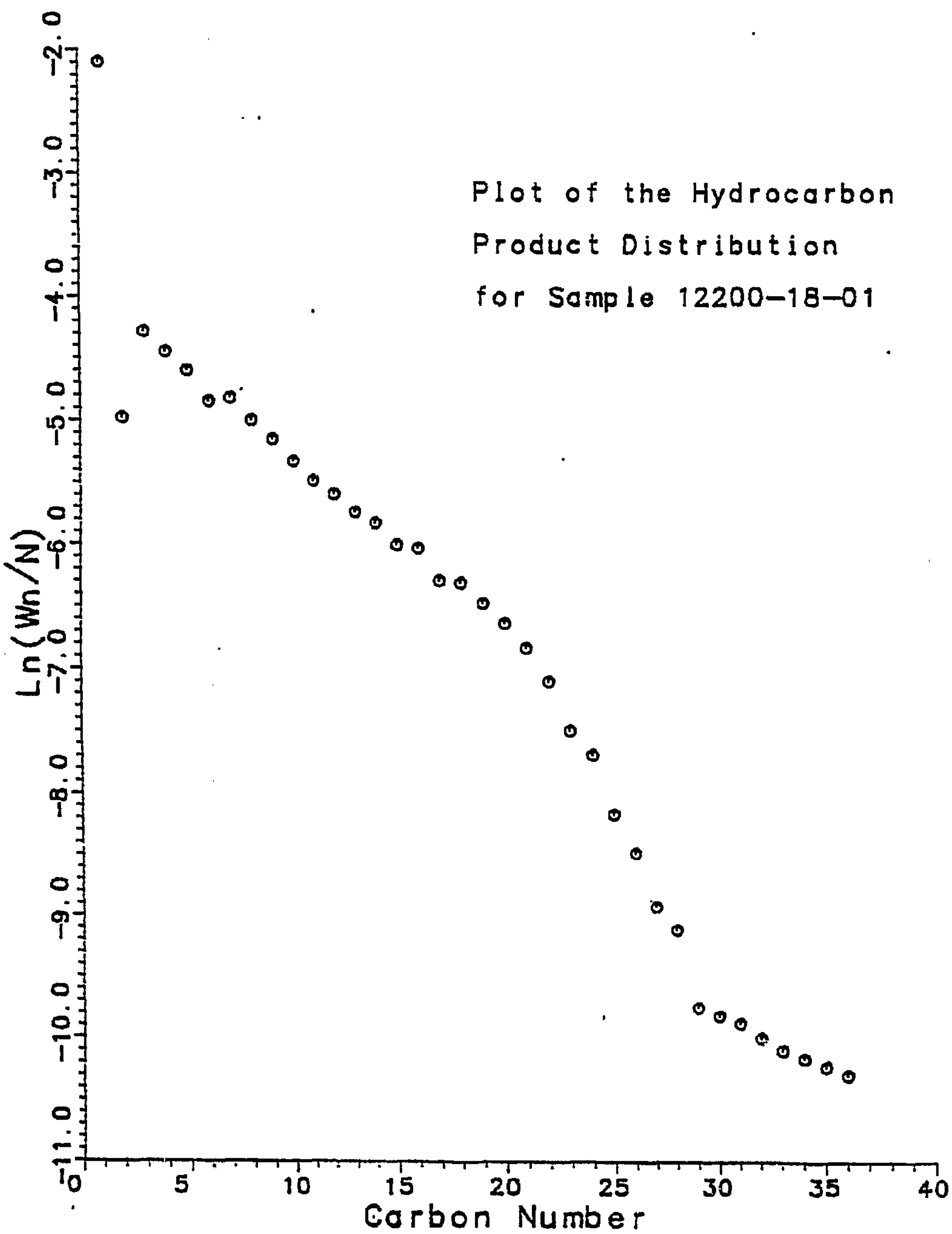

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-18-06
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B133



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-18-01
Ln(Wn/N)
-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. B134

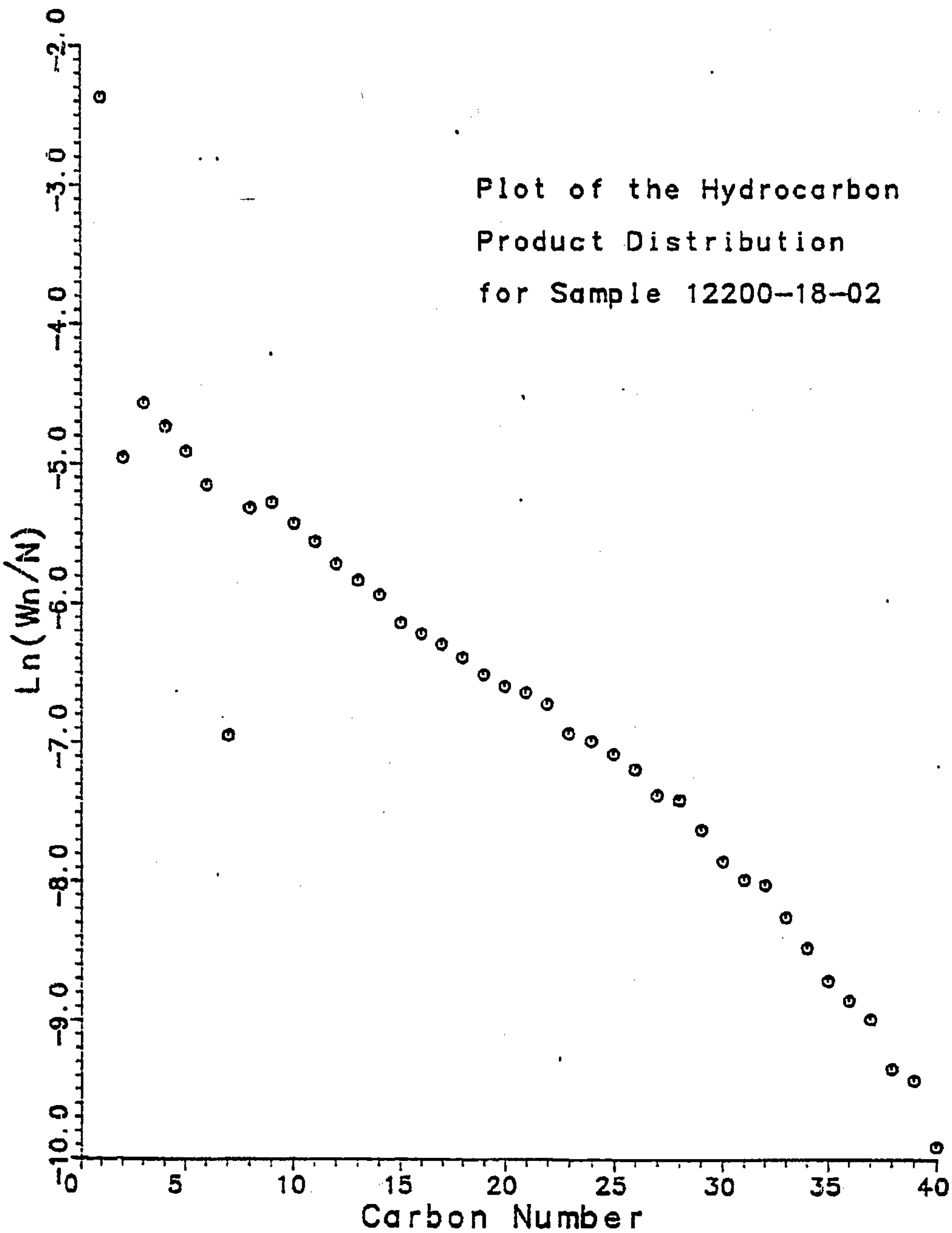

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-18-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B135

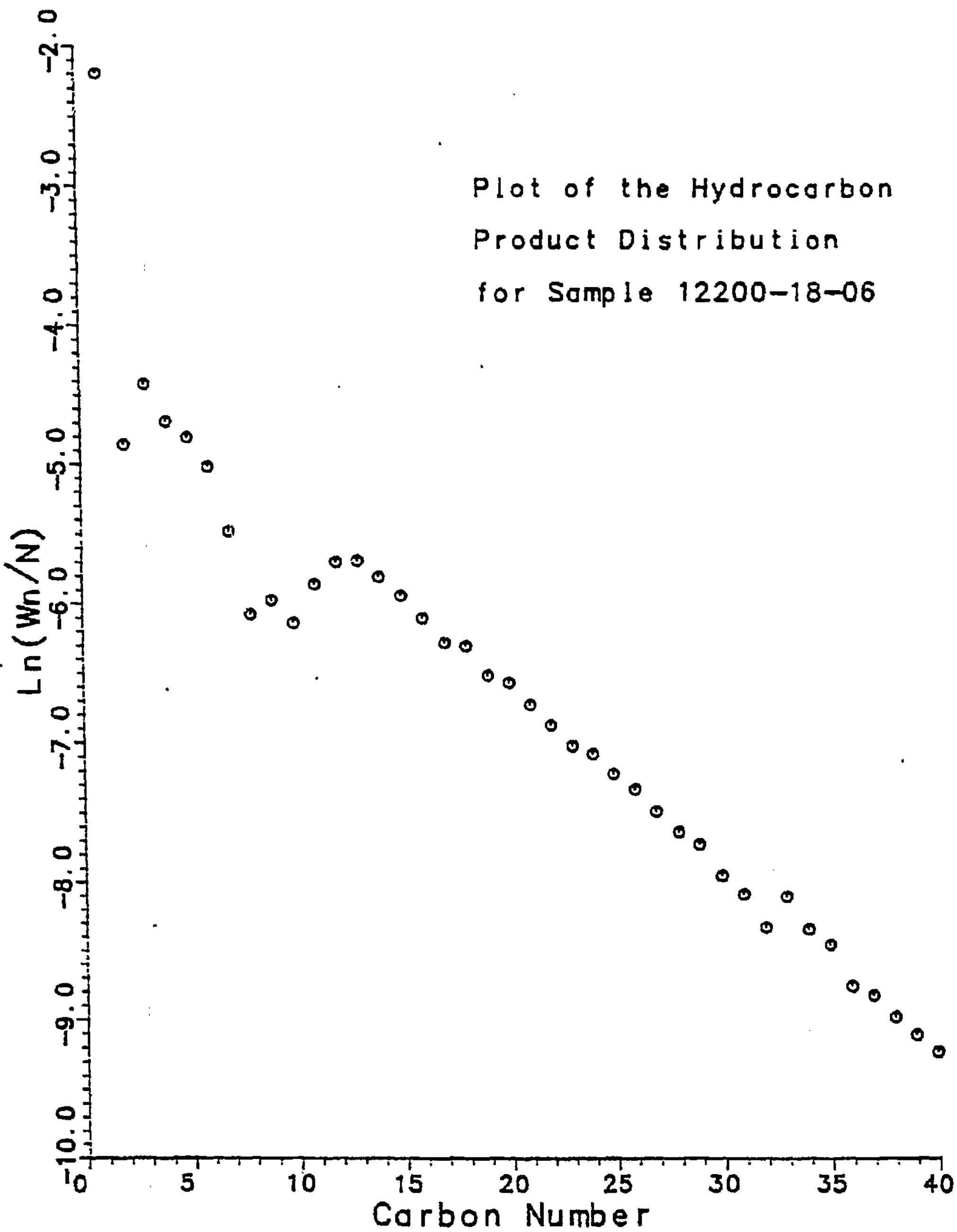

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-18-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B136

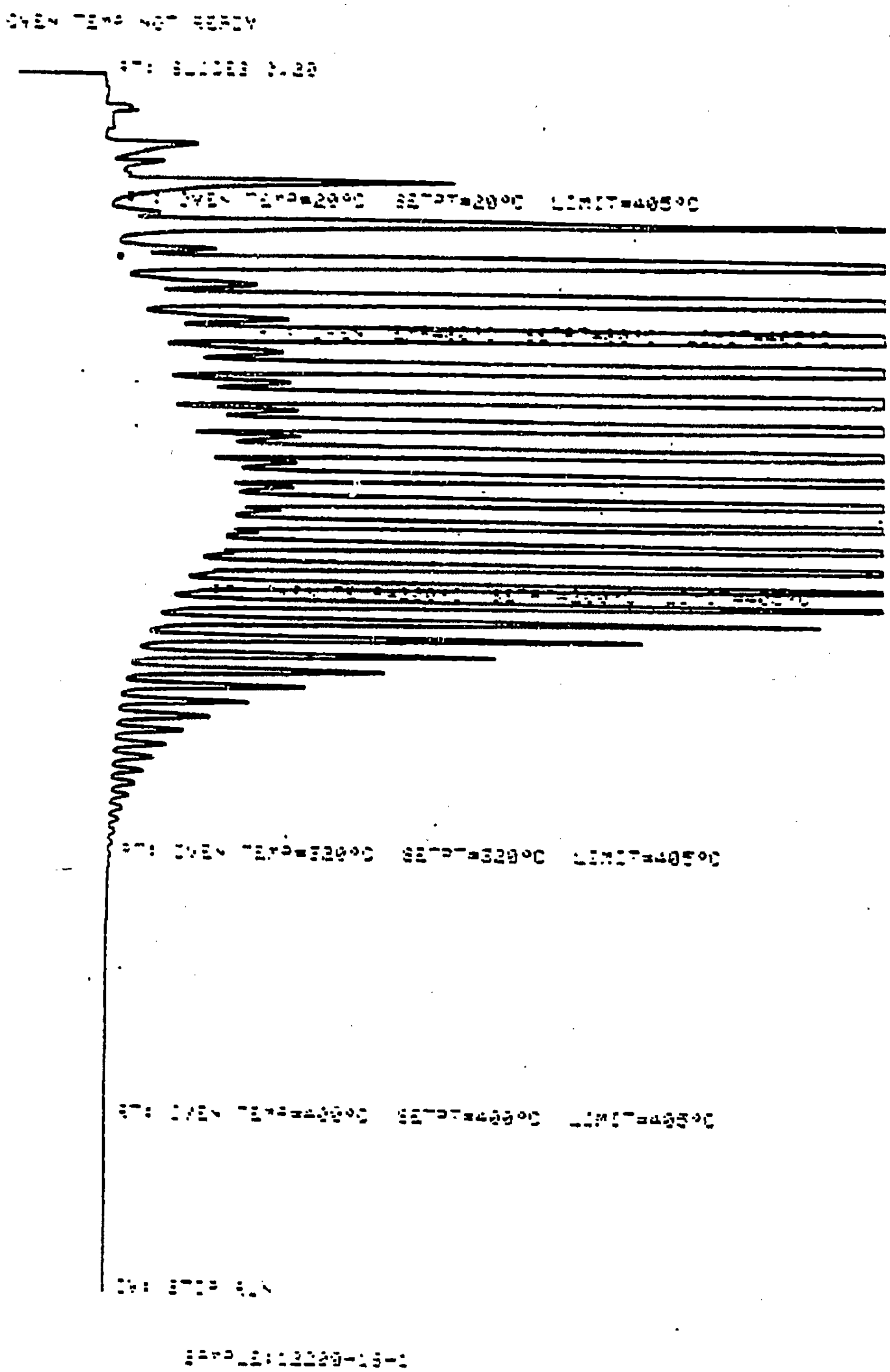


Fig. B137

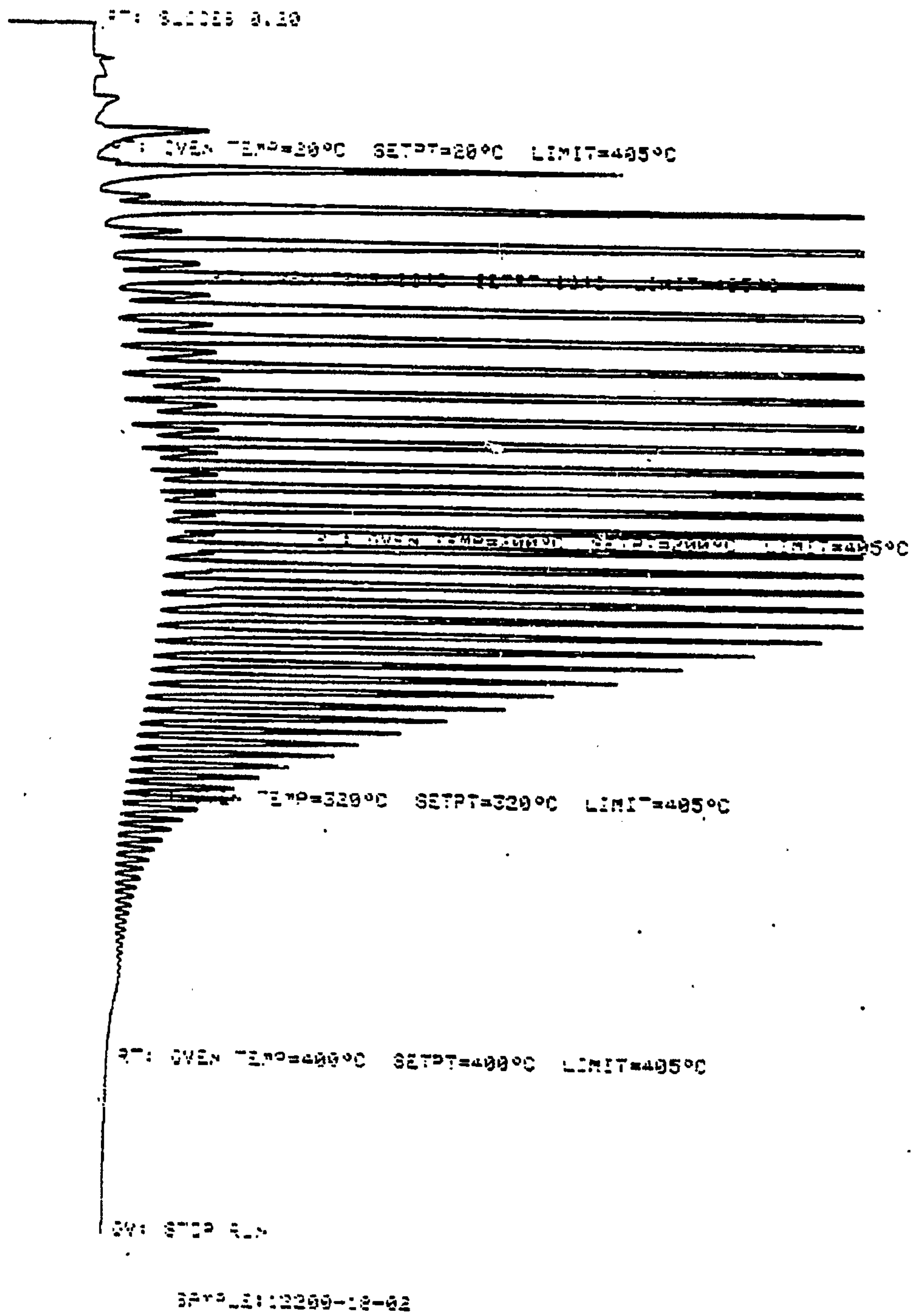
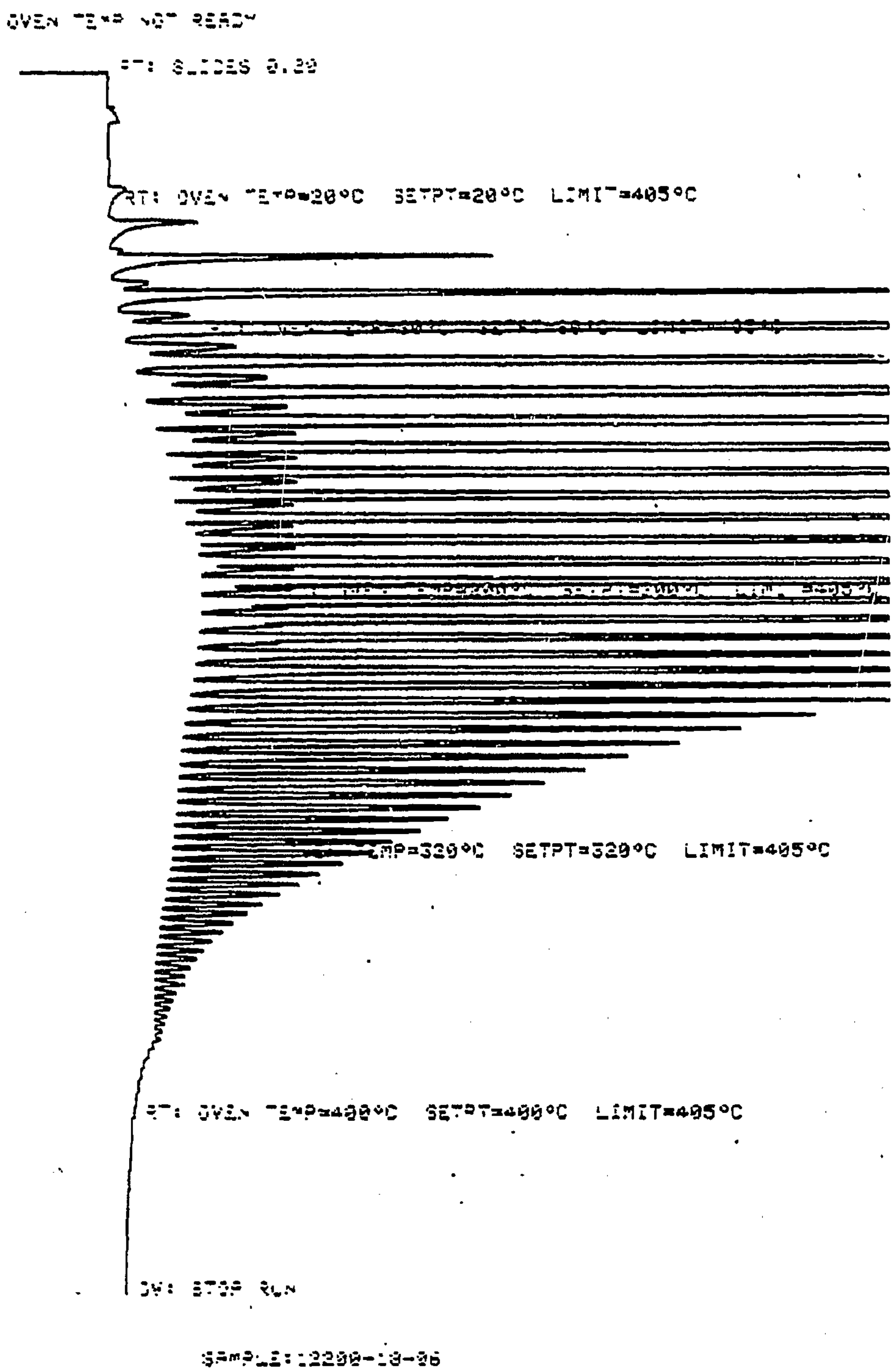

SETPT=20°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B138



RT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
MP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B139

Table B10

FILE: 1220018A TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-18
CATALYST CO/X9/X10-U103 80 CC 35.2 G AFTER USE:53.1 G (+17.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-71-23)

RUN & SAMPLE NO.	12200-18-01	200-18-02	200-18-06
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.5	49.5	146.0
PRESSURE,PSIG	300	300	300
TEMP. C	242	247	247
FEED CC/MIN	400	400	400
HOURS FEEDING	22.50	27.00	27.00
EFFLNT GAS LITER	255.98	368.70	396.50
GM AQUEOUS LAYER	59.75	48.44	44.29
GM OIL	14.10	37.67	27.50
MATERIAL BALANCE			
GM ATOM CARBON %	72.59	96.89	94.77
GM ATOM HYDROGEN %	83.02	94.69	90.78
GM ATOM OXYGEN %	90.59	92.65	94.32
RATIO CHX/(H2O+CO2)	0.4655	1.1728	1.0202
RATIO X IN CHX	2.3472	2.2987	2.3340
USAGE H2/CO PRODT	2.8291	1.7891	1.9854
FEED H2/CO FRM EFFLNT	1.1436	0.9773	0.9579
RESIDUAL H2/CO RATIO	0.6005	0.5961	0.6165
RATIO CO2/(H2O+CO2)	0.0599	0.0895	0.0553
K SHIFT IN EFFLNT	0.0382	0.0586	0.0361
SPECIFIC ACTIVITY SA	1.9052	2.0852	1.4785
CONVERSION			
ON CO %	24.37	31.95	24.94
ON H2 %	60.29	58.50	51.70
ON CO+H2 %	43.53	45.07	38.03
PRDT SELECTIVITY,WT %			
CH4	12.44	9.41	11.20
C2 HC'S	1.39	1.42	1.55
C3H8	1.87	1.50	1.82
C3H6=	2.29	1.64	1.81
C4H10	1.85	1.50	1.84
C4H8=	2.86	2.03	1.84
C5H12	2.33	1.88	2.26
C5H10=	2.73	1.80	1.84
C6H14	2.85	2.20	2.64
C6H12= & CYCLO'S	1.89	1.27	1.32
C7+ IN GAS	11.18	6.78	7.85
LIQ HC'S	56.32	68.56	64.04
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	22.70	17.51	20.05
C5 -420 F	39.96	29.16	24.42
420-700 F	32.04	31.19	33.11
700-END PT	5.29	22.14	22.41

Table B10 (continued)

FILE: 1220018A TSS3Q1 A1

C5+-END PT	77.30	82.49	79.95
ISO/NORMAL MOLE RATIO			
C4	0.0000	0.0000	0.0000
C5	0.0576	0.0557	0.0416
C6	0.0807	0.0820	0.0544
C4=	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO			
C3	0.7809	0.8747	0.9614
C4	0.6253	0.7128	0.9652
C5	0.8317	1.0120	1.1966
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))	0.8385	0.8951	0.8946
RATIO CH4/(1-A)**2	4.7666	8.5521	10.0774
ALPHA FRM CORRELATION	0.8367	0.8367	0.8351
ALPHA (EXPTL/CORR)	1.0022	1.0697	1.0712
W%CH4 FRM CORRELATION	14.5642	15.6594	16.1677
W%CH4 (EXPTL/CORR)	0.8539	0.6012	0.6929
LIQ HC COLLECTION			
PHYS. APPEARANCE	CLD OIL	CLD OIL	OIL WAX
DENSITY	0.761	0.805	0.803
N, REFRACTIVE INDEX	N/A	N/A	N/A
SIMULT'D DISTILATN			
10 WT % @ DEG F	297	338	412
16	338	380	445
50	501	594	616
84	661	802	839
90	690	858	904
RANGE(16-84 %)	323	422	394
WT % @ 420 F	33.70	22.20	13.30
WT % @ 700 F	90.60	67.70	65.00

VI. <u>Run 30 (12185-16) with Catalyst 30 (Co/X_9/X_{10}/X_3/UCC-103</u>

The purpose of this run was to test the effect of a small concentration of additive X_3 on the activity, stability and selectivity of a cobalt/X_9/X_{10} catalyst. Aside from the addition of X_3, and slight differences in the concentrations of the other constituents, the formulation of the catalyst was the same as that of Catalyst 26; the theoretical concentrations of cobalt, X_9, X_{10} and X_3 were, respectively, 7.8, 0.35, 0.47 and 0.06 percent.

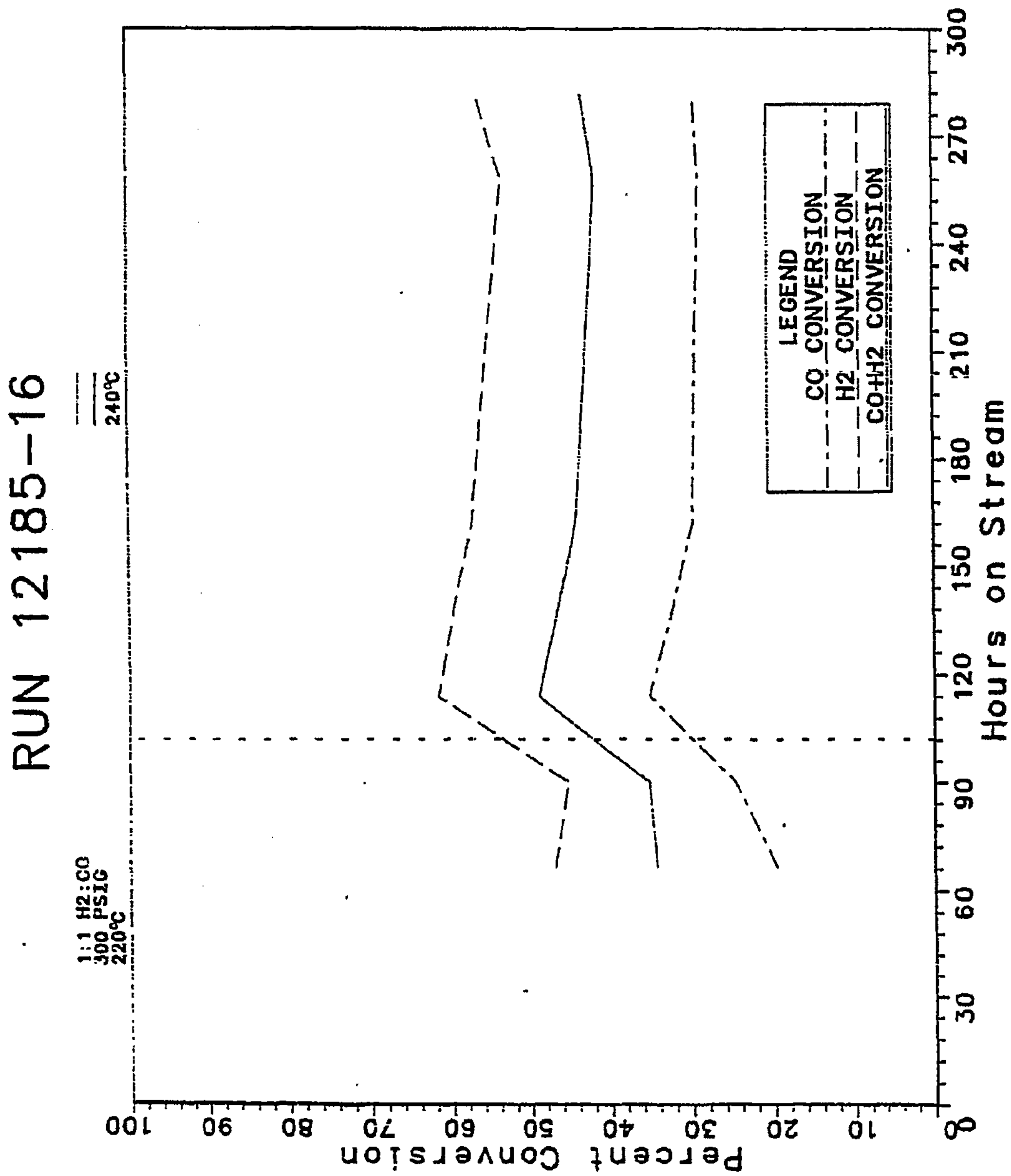
Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B140-143. Simulated distillations of the C_5^+ product are plotted in Figs. B144-150. Carbon number product distributions are plotted in Figs. B151-157. Chromatograms from simulated distillations are reproduced in Figs. B158-164. Detailed material balances appear in Tables B11-12.

For the first two samples, at 220C and 90 hours on stream, the syngas conversion was about 35 percent, as against 30 percent for Catalyst 26. When the reaction temperature was raised to 240C at 114 hours on stream, the conversion increased to 45 percent, with a specific activity of 3.1--both approximately the same as for Catalyst 26.

Thereafter, however, the stability of this catalyst was inferior to that of Catalyst 26. By linear least squares analysis, the conversion decreased by one percentage point every 23 hours and the specific activity by one specific activity unit every 165 hours.

The initial product selectivity at 240C was similar to that of Catalyst 26--about 8 percent methane, C_4's with a paraffin:olefin ratio of about 0.7:1, and about 81 percent C_5^+. As the activity declined with time on stream, the proportion of methane increased and that of C_5^+ decreased. Except for the usual excess of methane, the Schulz-Flory plots were linear throughout the run.

The addition of X_3, even in the minute concentration used in this test, enhanced the initial activity and had little efect on the selectivity. But it substantially impaired the catalyst's stability.



RUN 12185-16
1:1 H2:CO
300 PSIG
220°C
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
30
60
90
120
150
180
210
240
270
300

Fig. B140

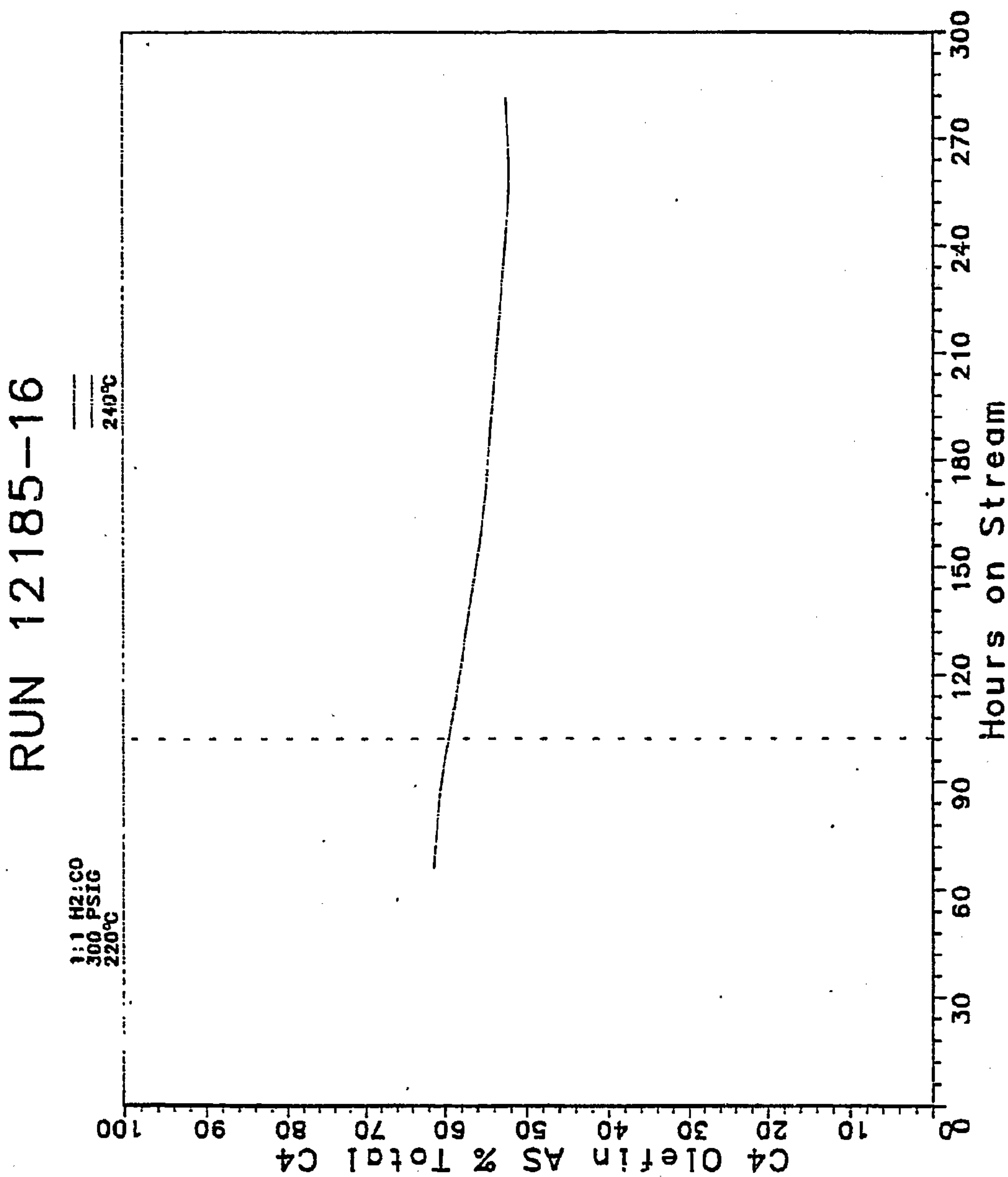

RUN 12185-16
1:1 H2:CO
300 PSIG
220°C
240°C
Hours on Stream
0
30
60
90
120
150
180
210
240
270
300
C4 Olefin AS % Total C4
10
20
30
40
50
60
70
80
90
100

Fig. B141

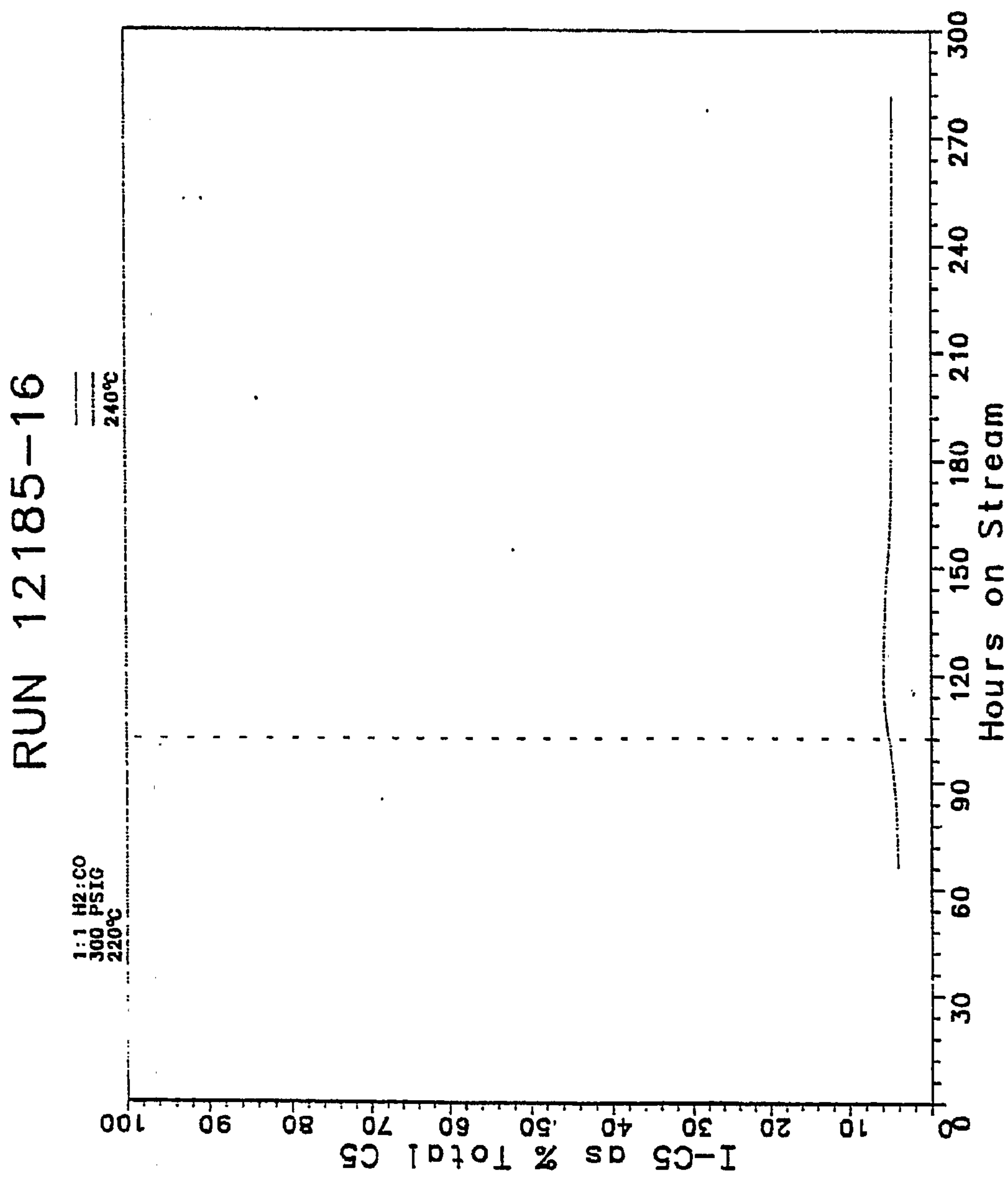

RUN 12185-16
1:1 H2:CO
300 PSIG
220°C
240°C
Hours on Stream
I-C5 as % Total C5

Fig. B142

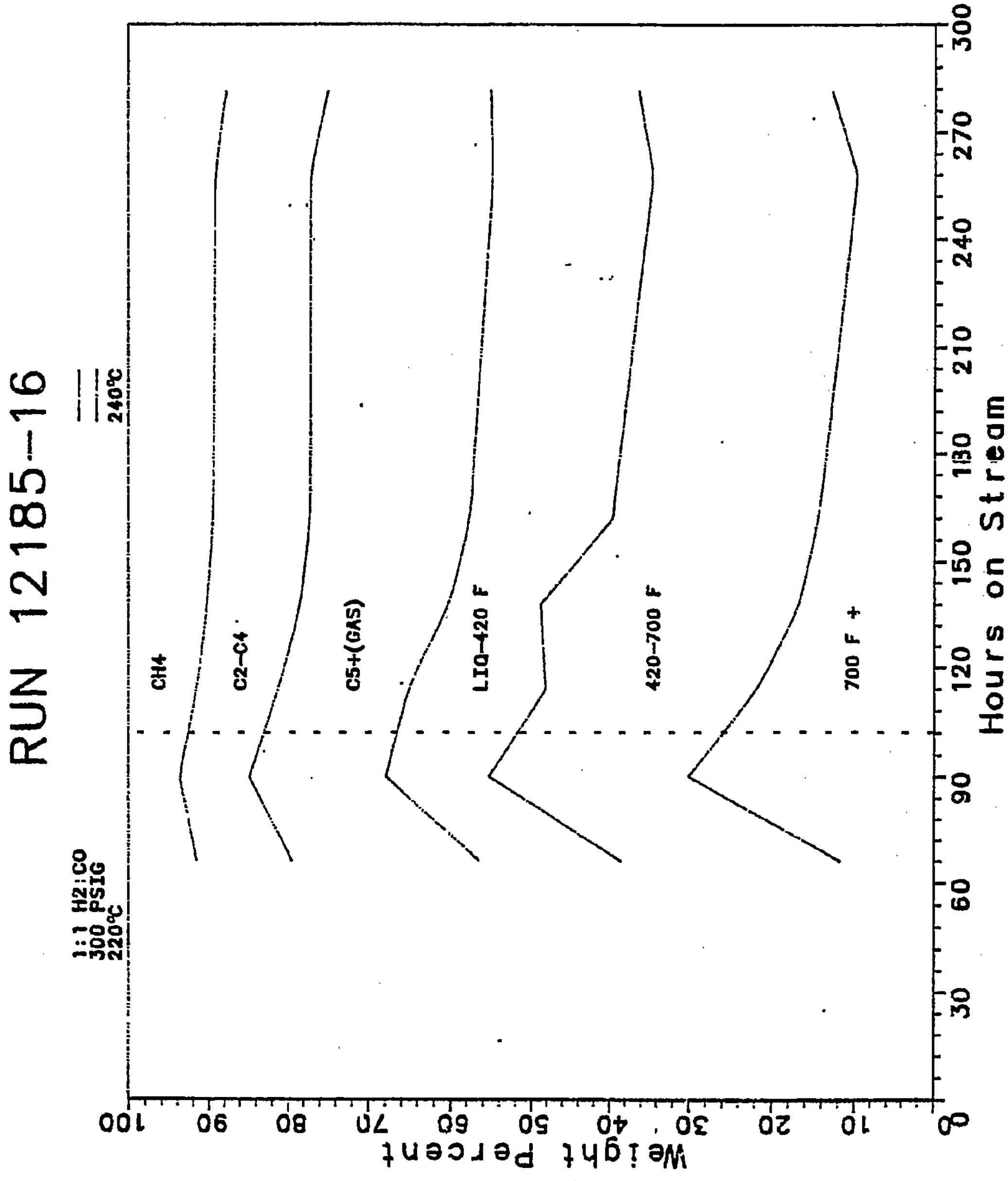
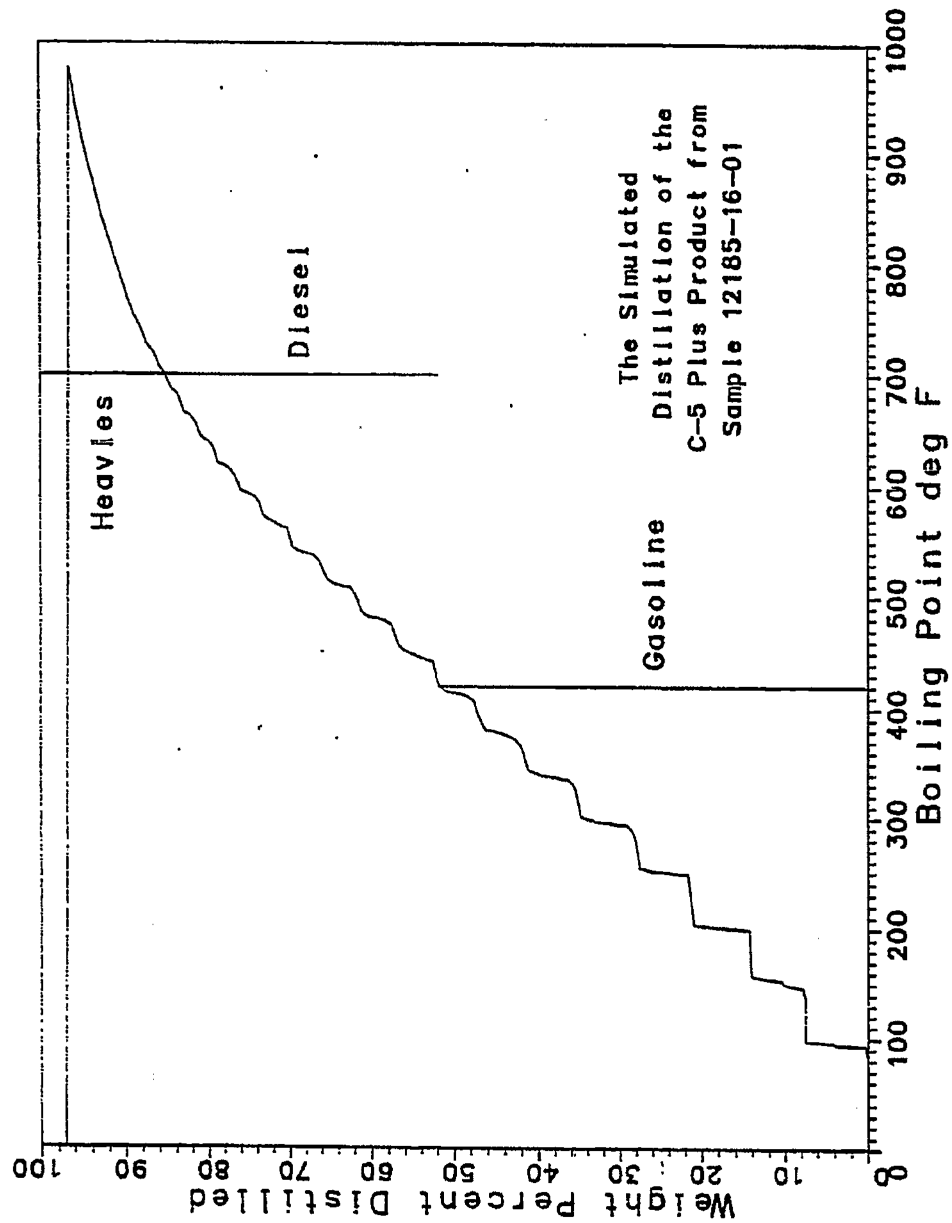

RUN 12185-16
1:1 H2:CO
300 PSIG
220°C
240°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
Weight Percent
0
30
60
90
120
150
180
210
240
270
300
10
20
30
40
50
60
70
80
90
100

Fig. B143



Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-16-01
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

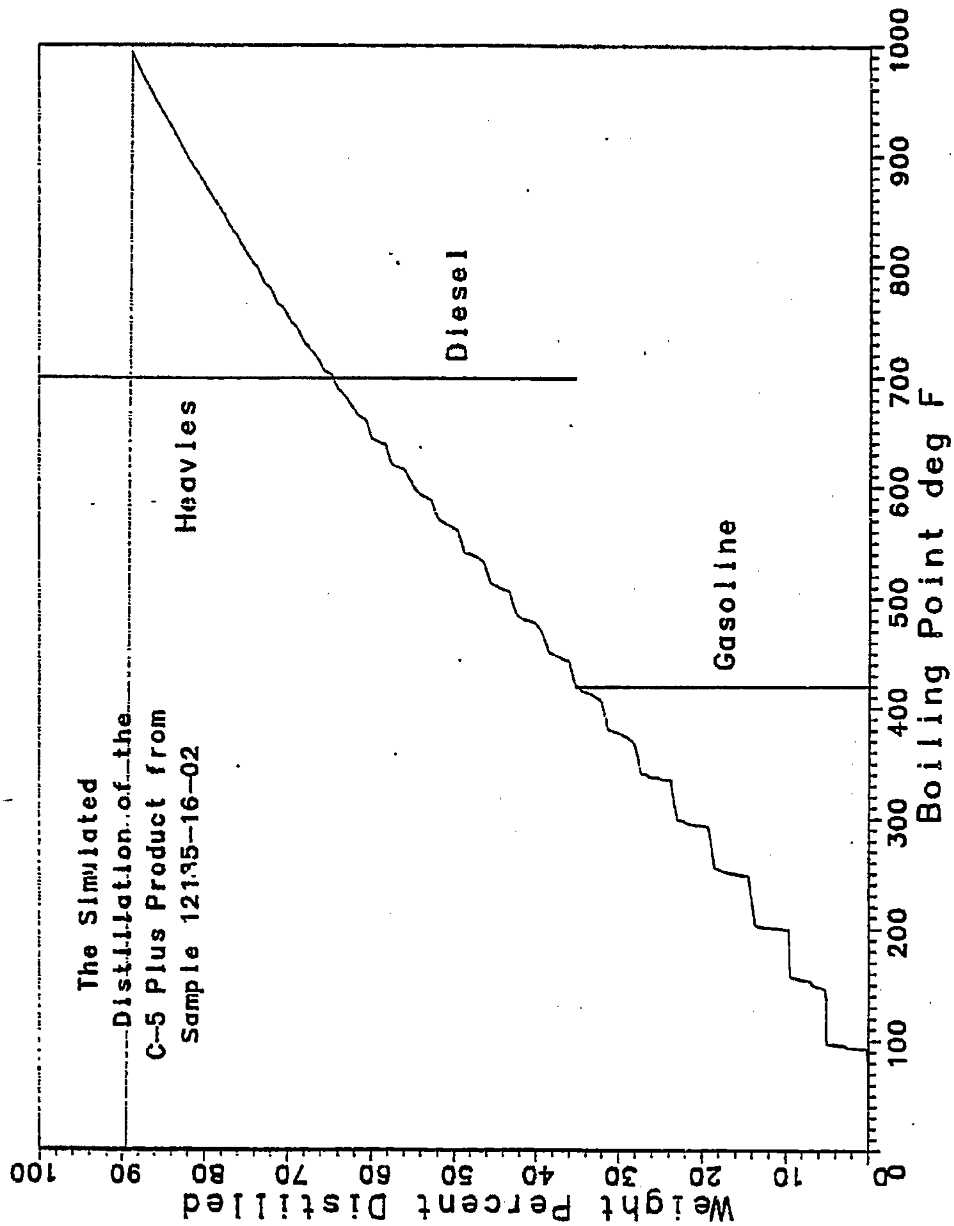
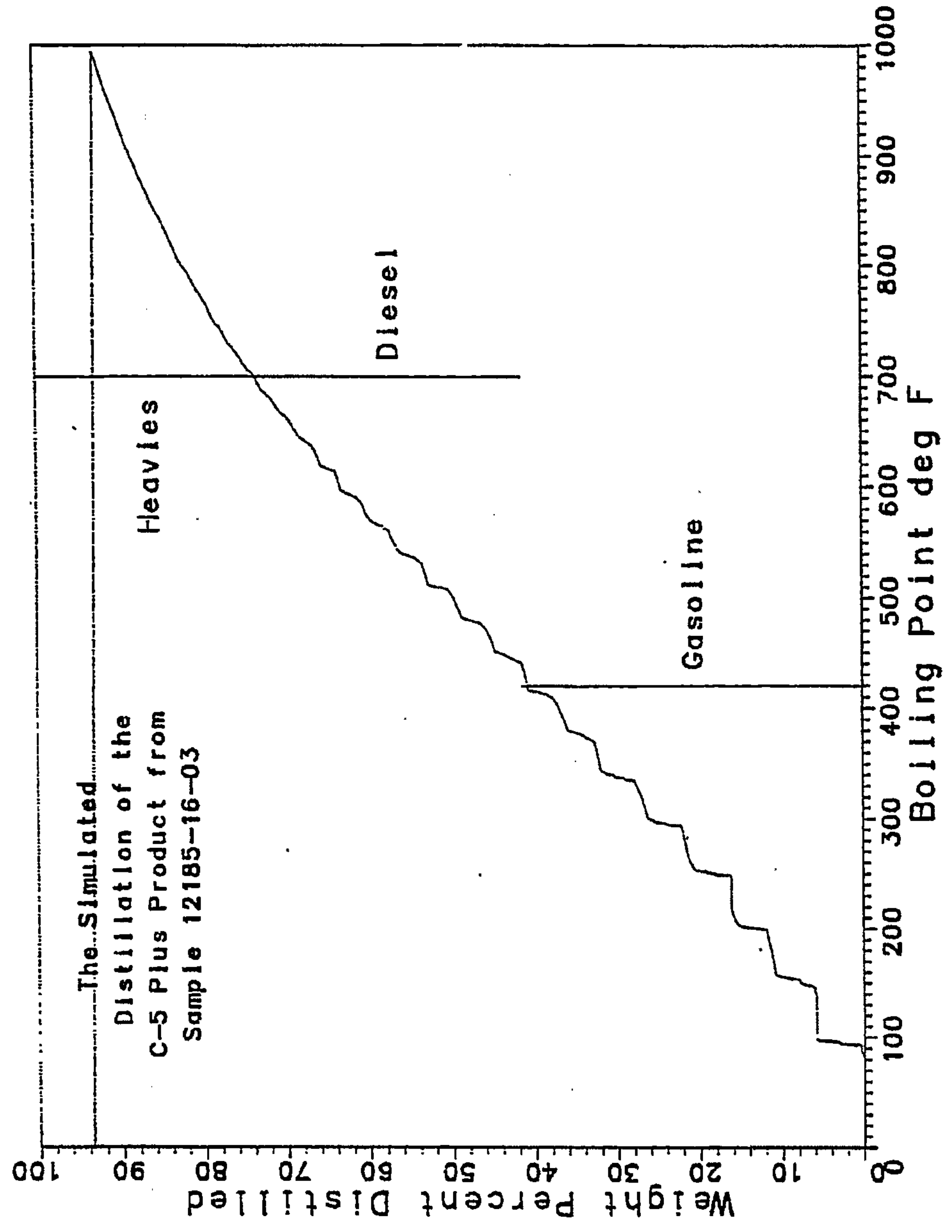
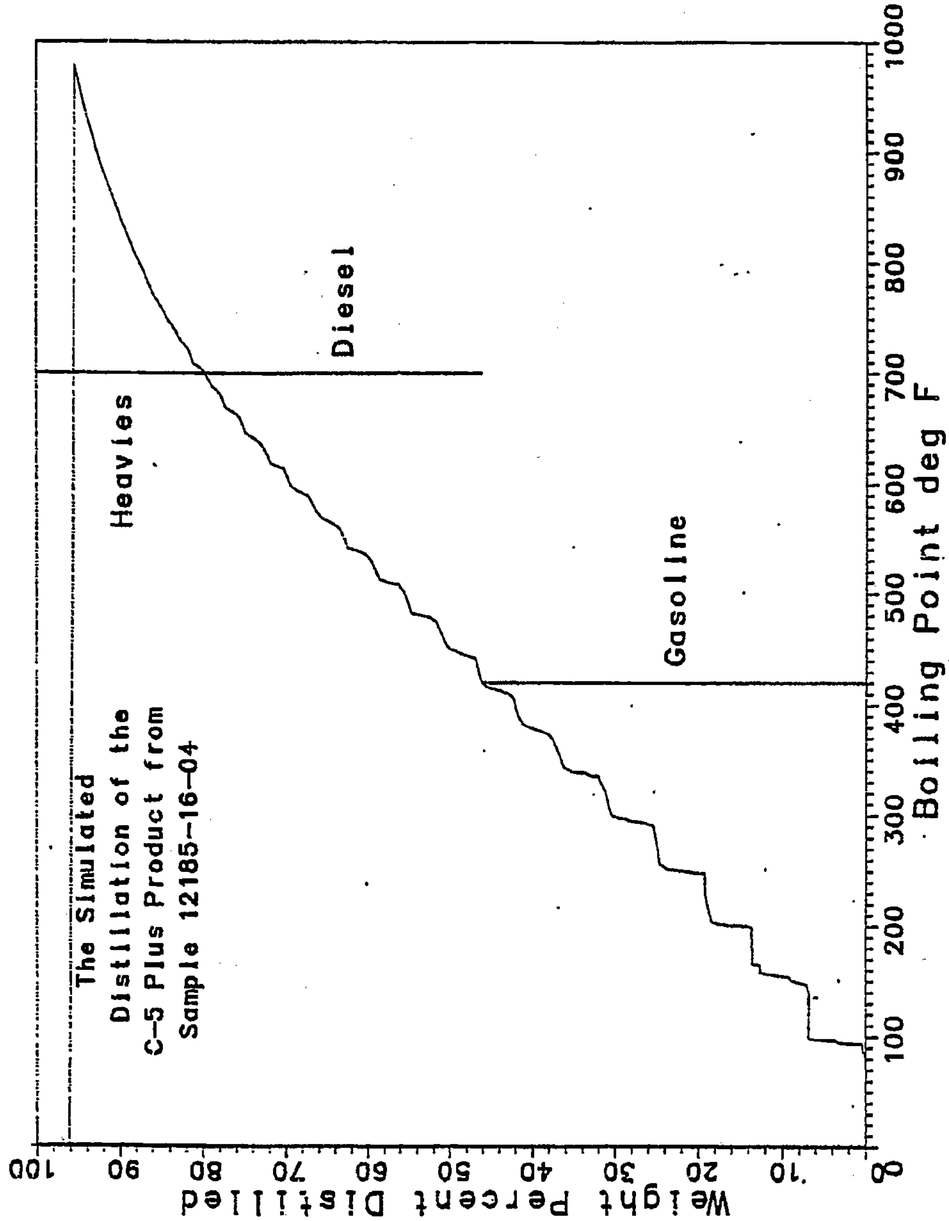

The Simulated Distillation of the C-5 Plus Product from Sample 12135-16-02
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B145



The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-16-03
Heavies
Diesel
Gasoline
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. B146



The Simulated Distillation of the C-5 Plus Product from Sample 12185-16-04
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

Fig. B147

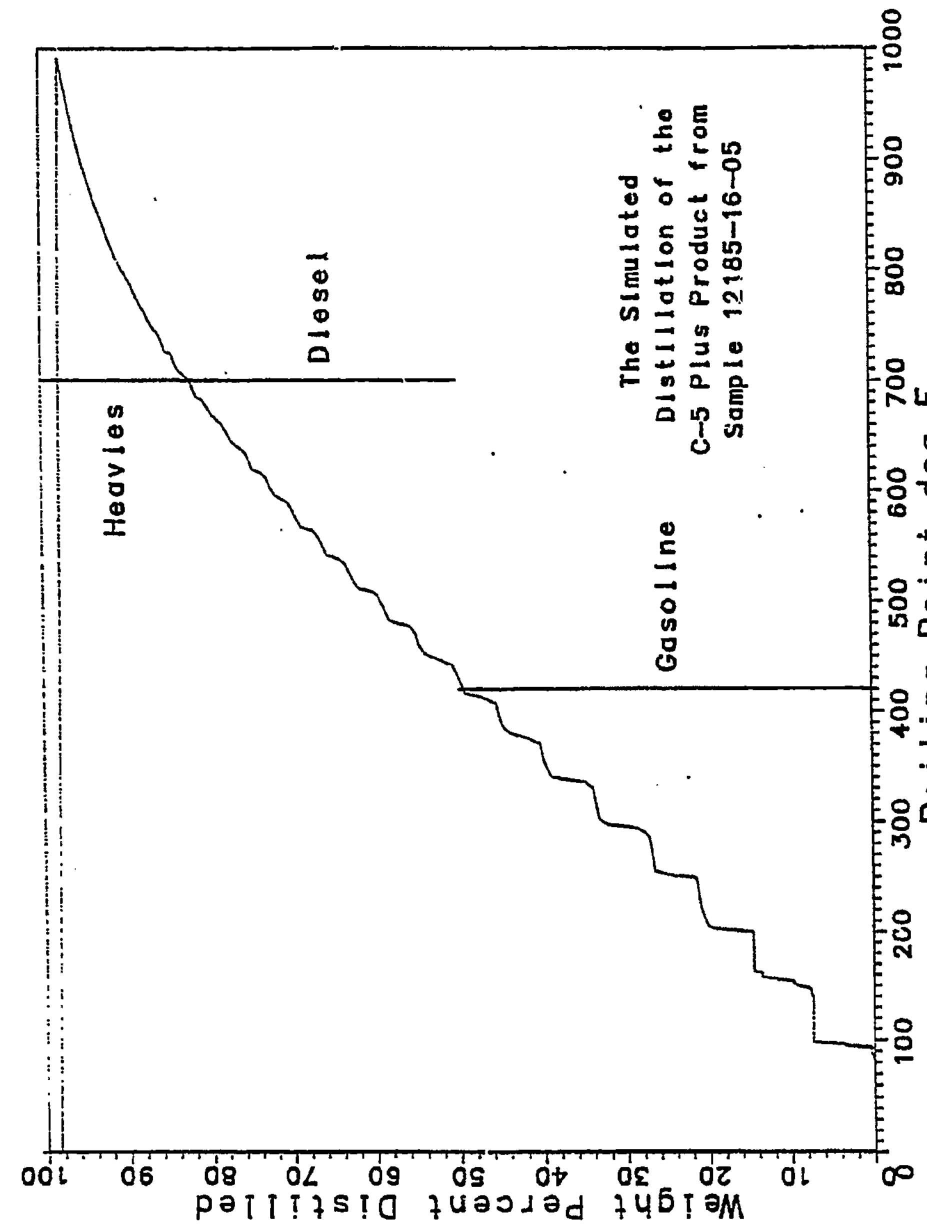

Heavies
Diesel
Gasoline
The Simulated Distillation of the C-5 Plus Product from Sample 12185-16-05
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
1000

Fig. B148

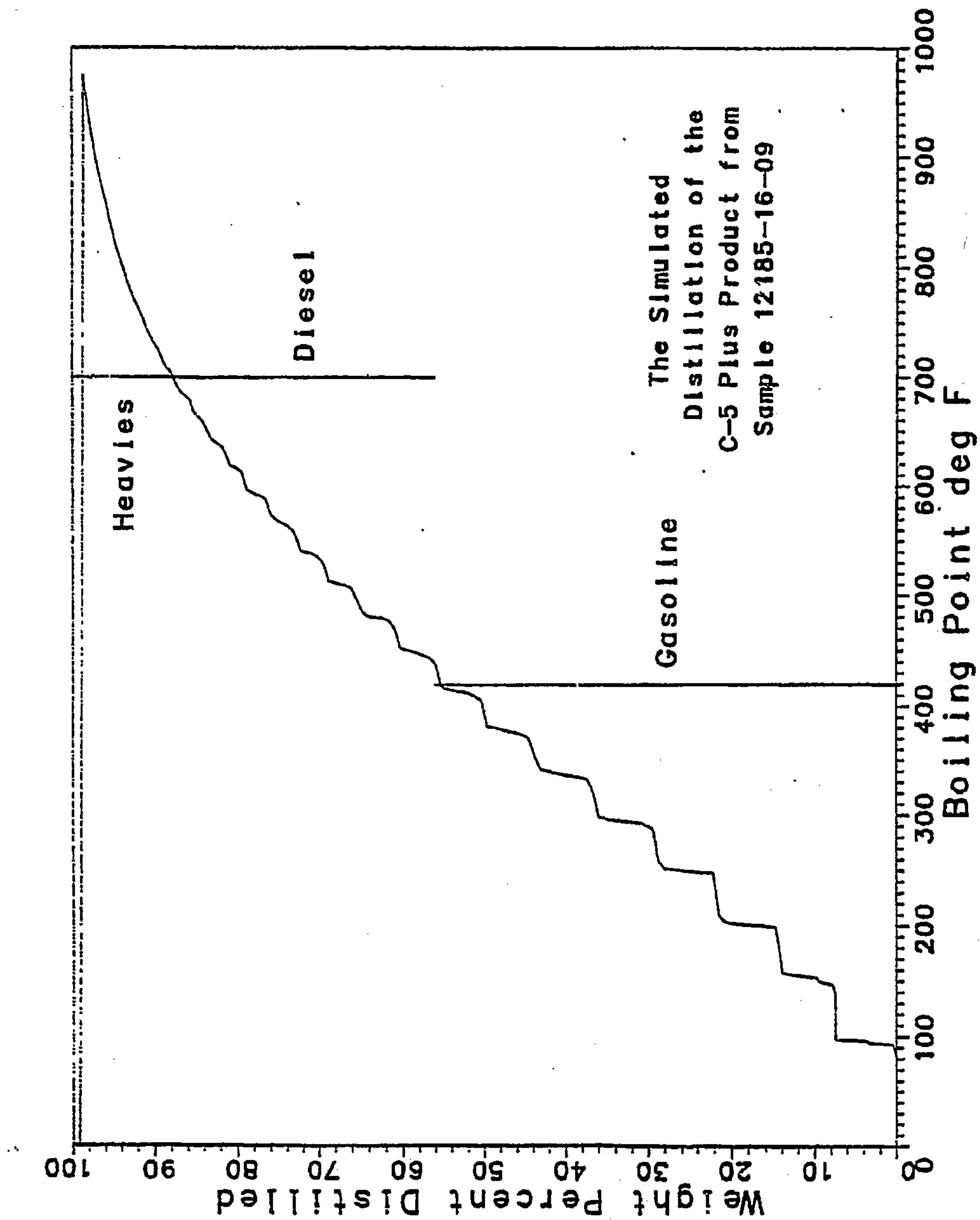

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-16-09
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B149

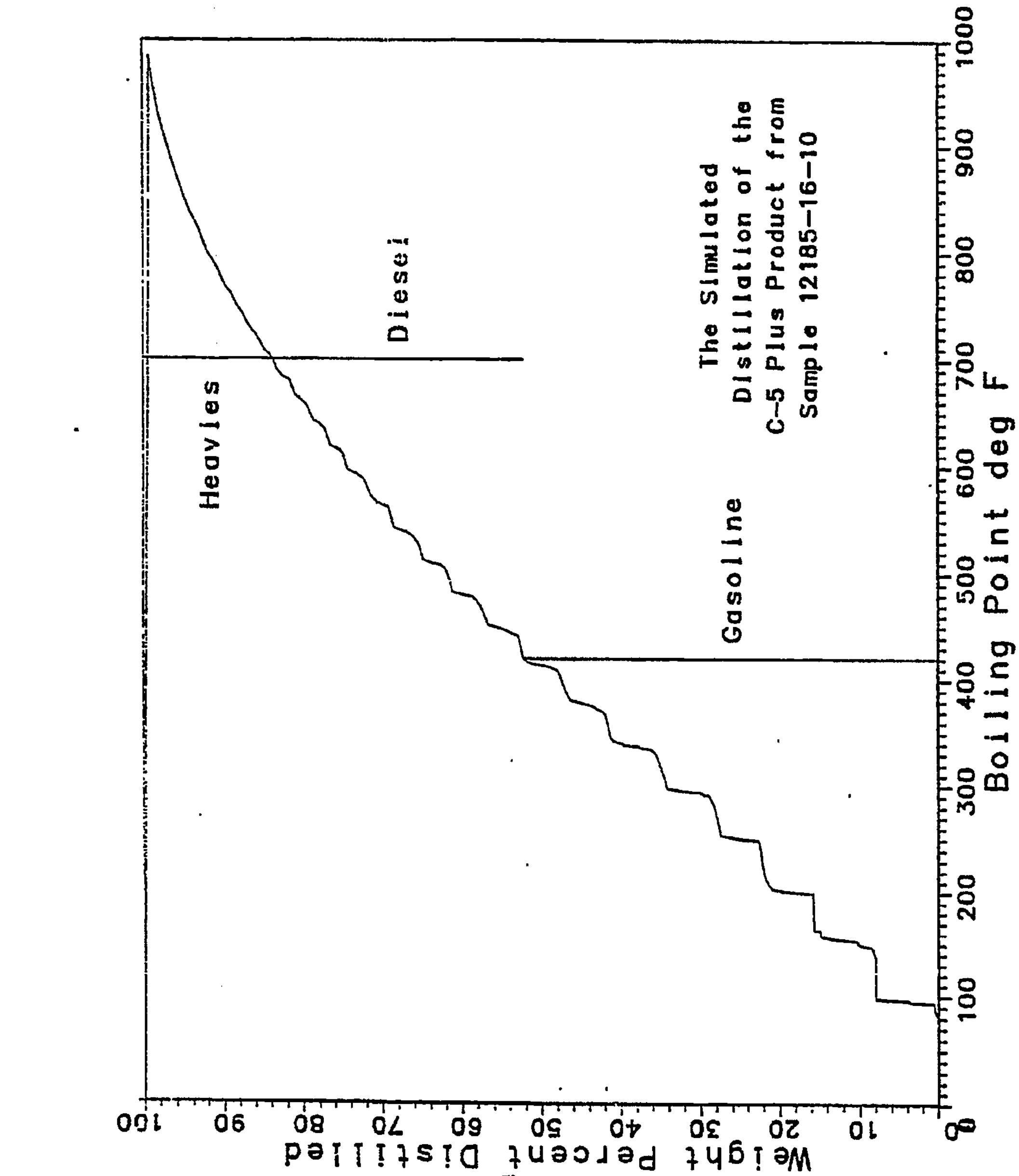

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-16-10
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000
0 10 20 30 40 50 60 70 80 90 100

Fig. B150

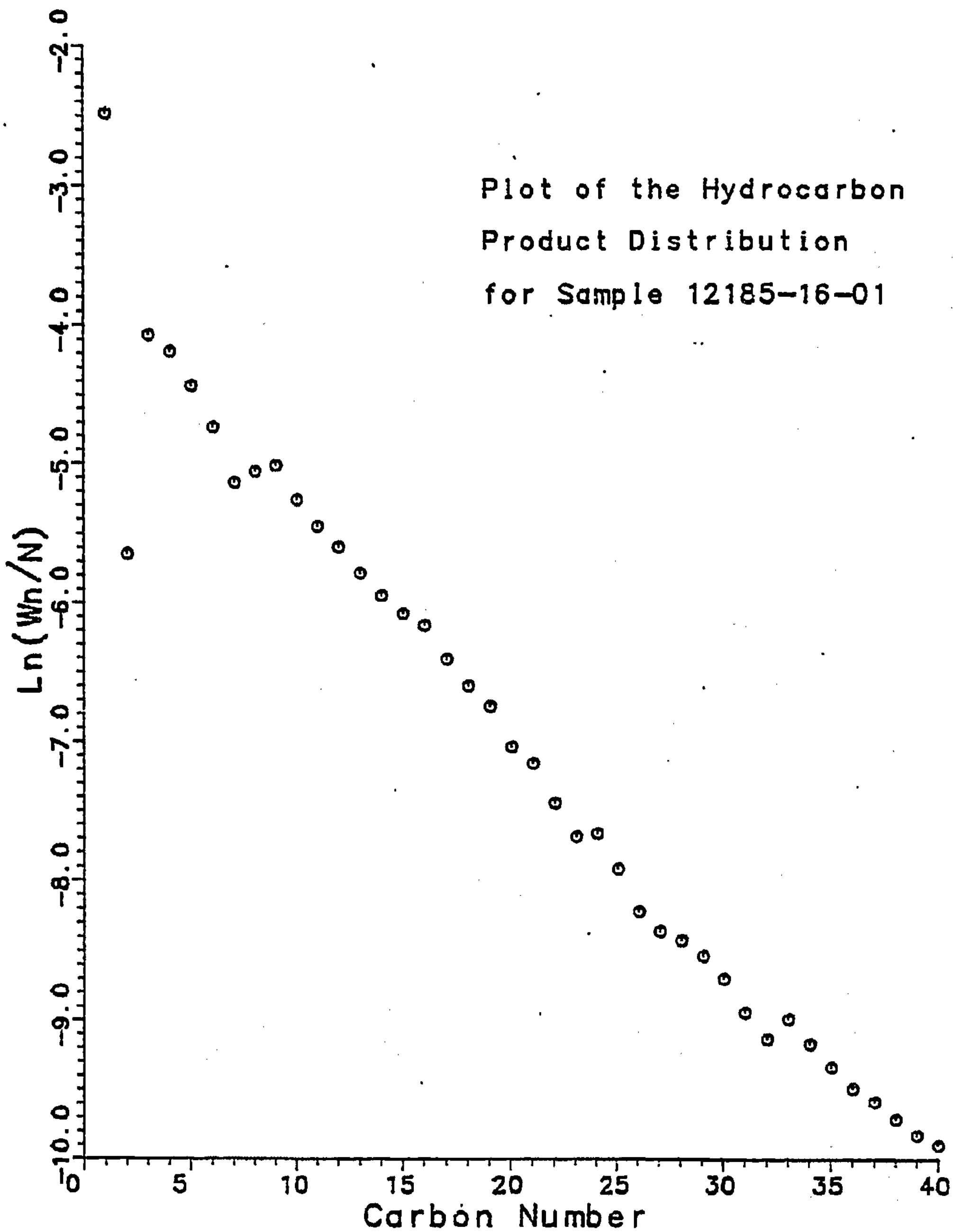
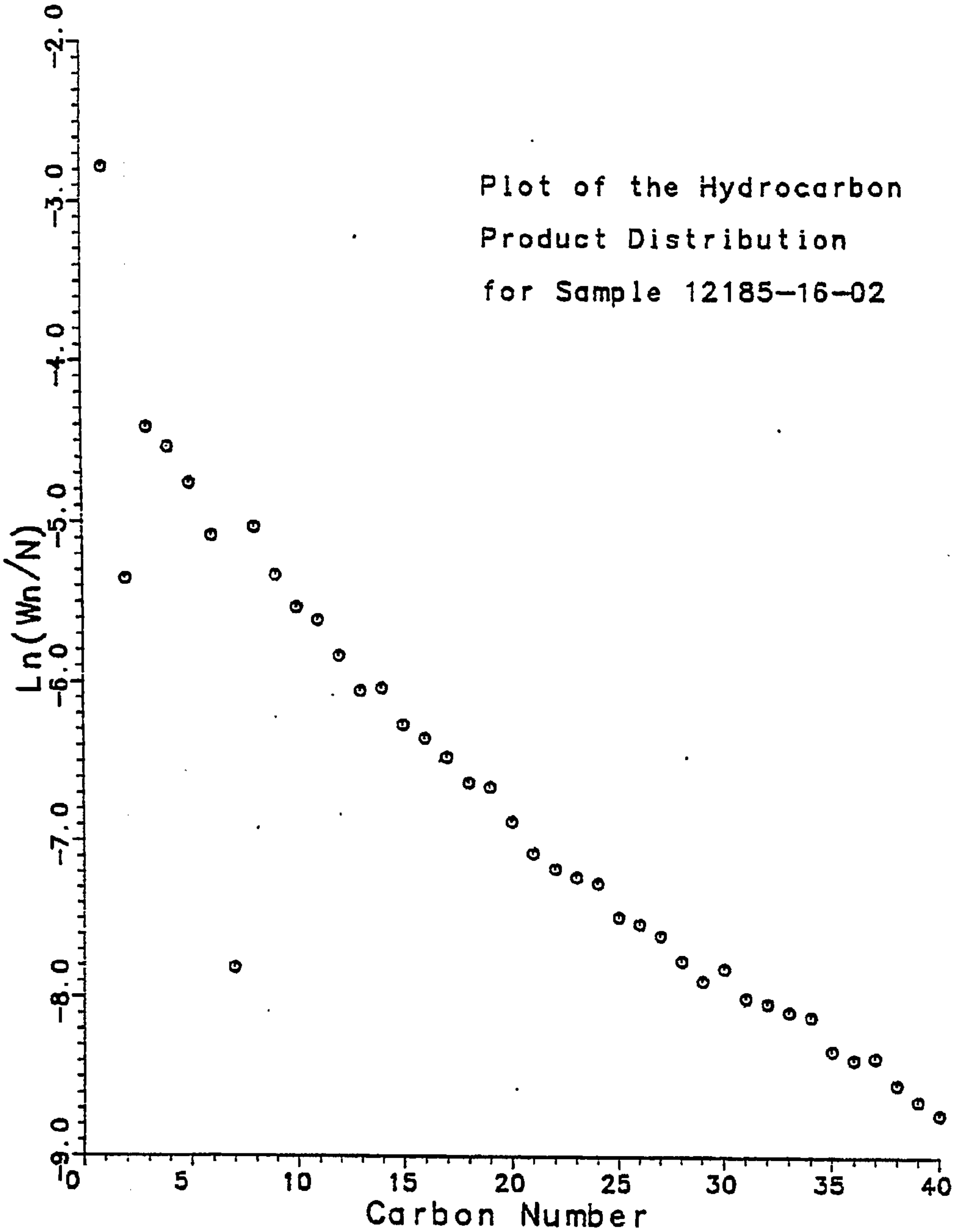
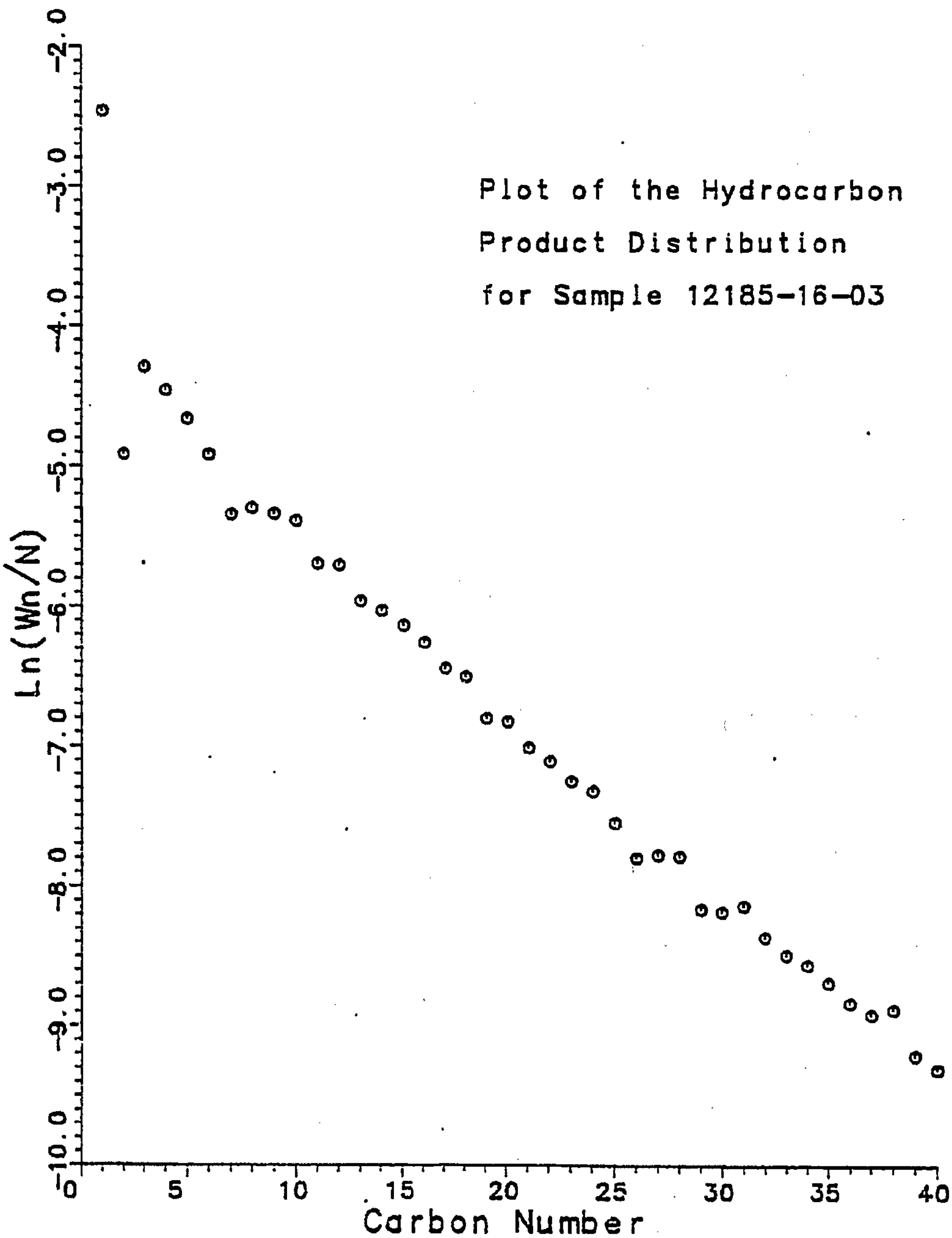
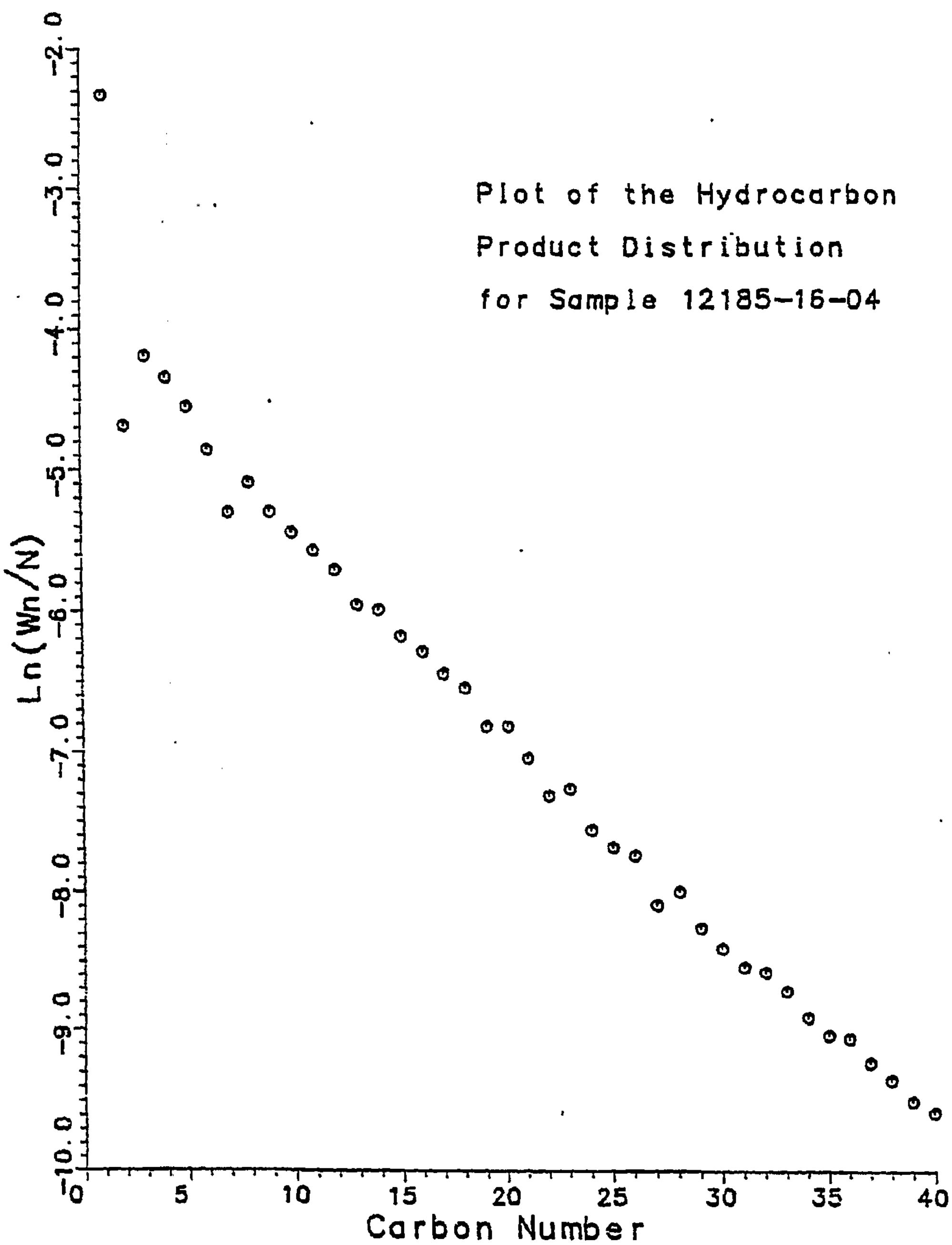

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B151


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B152


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-03
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. B153



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-04
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. B154

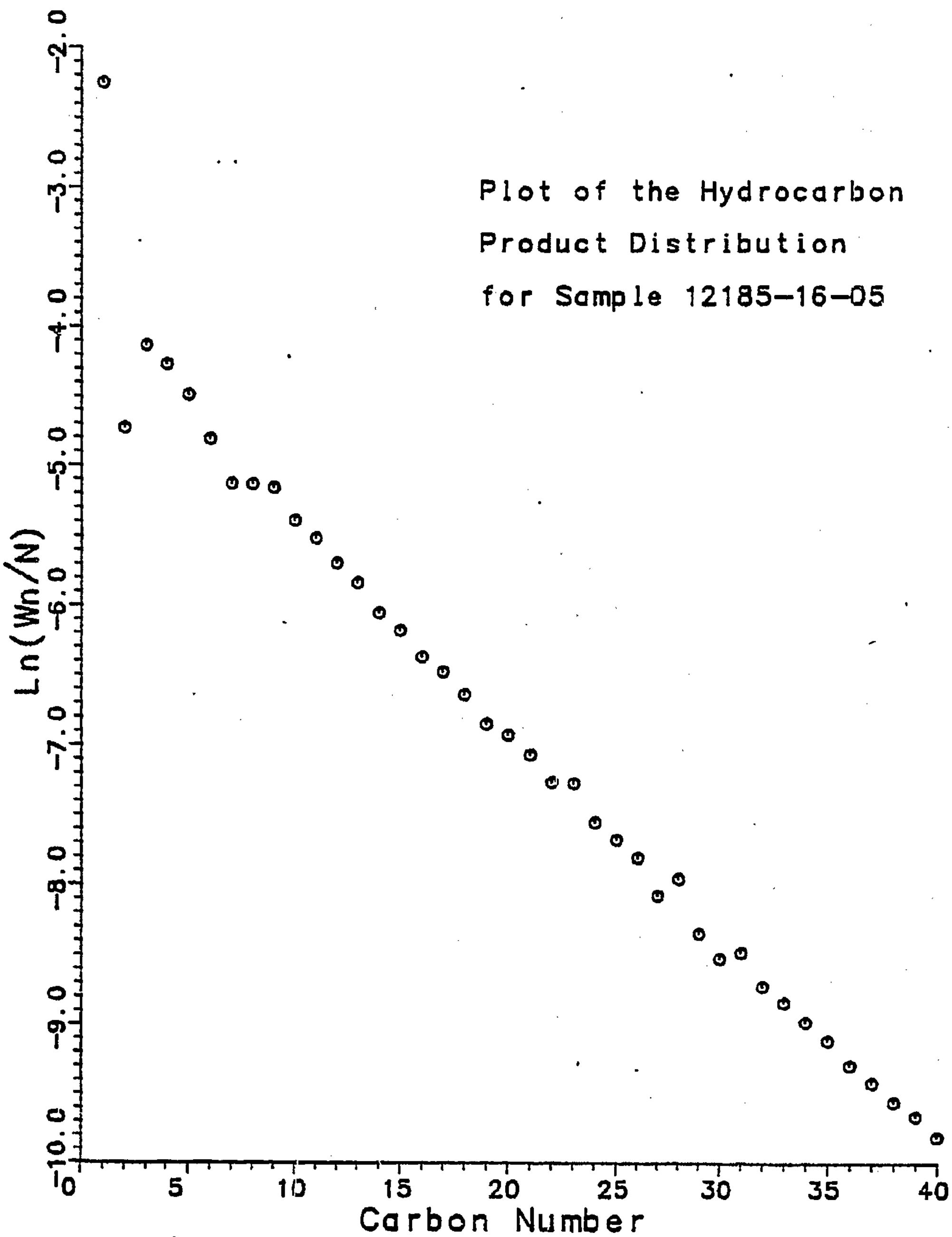

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-05
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B155

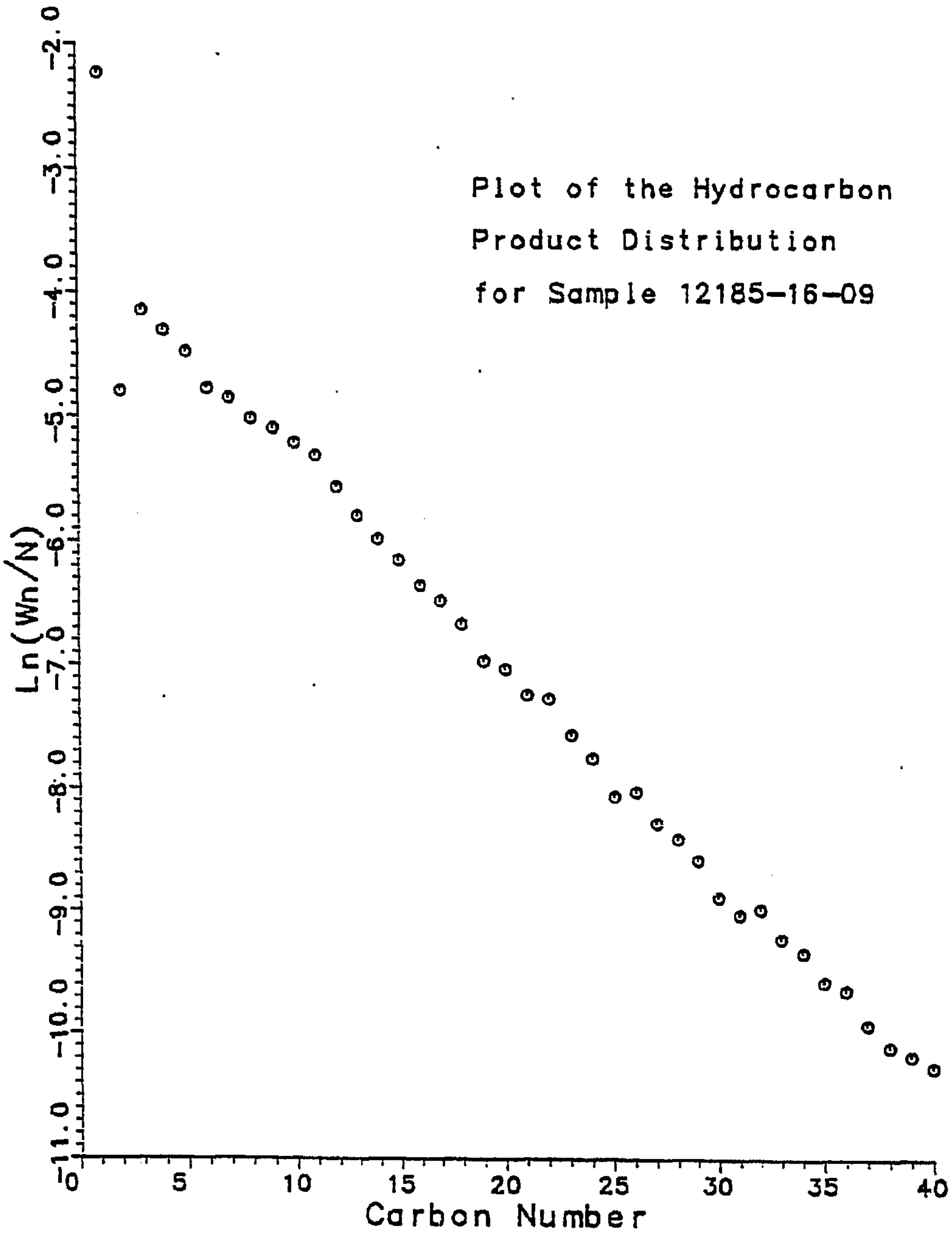
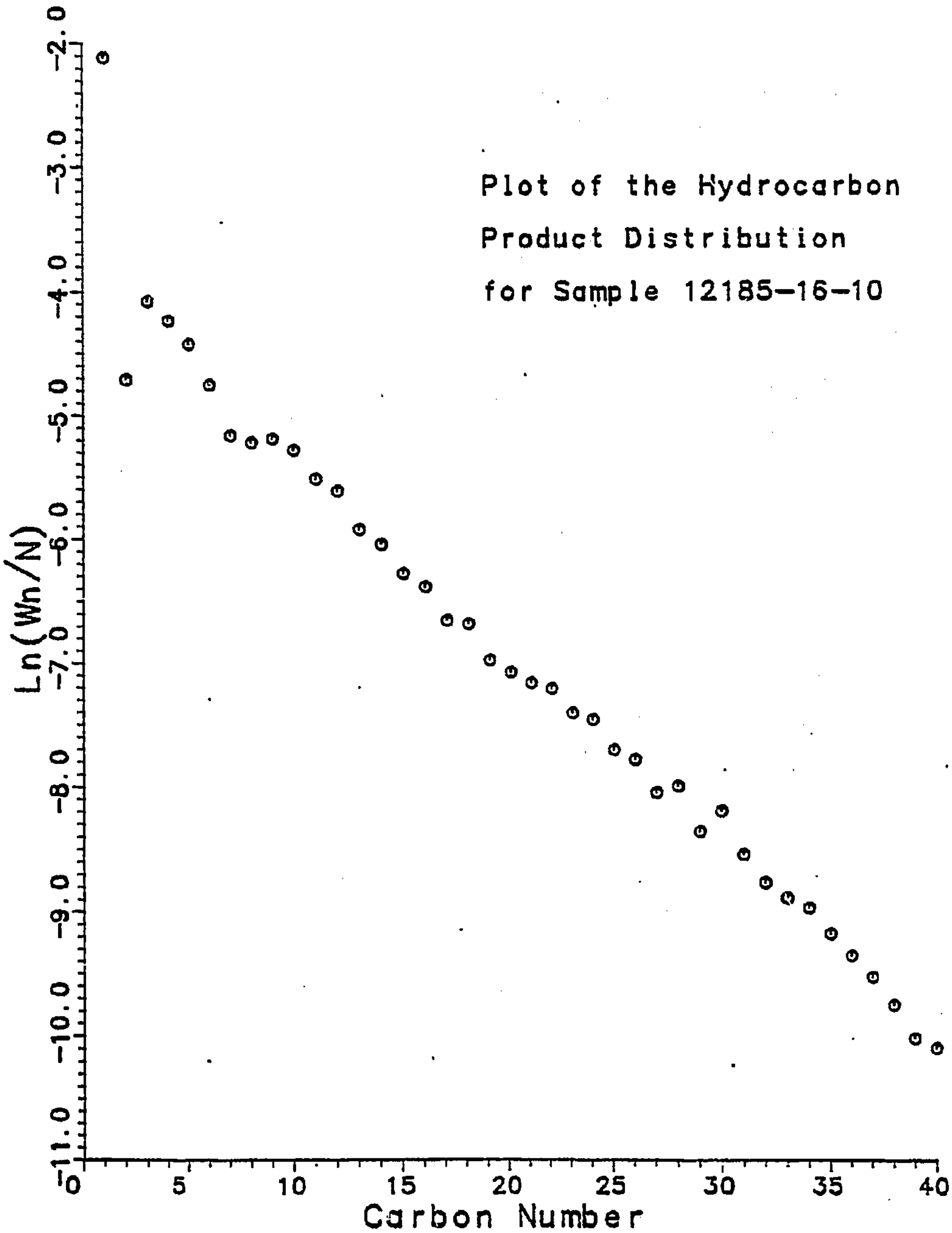

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-09
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B156


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-16-10
Ln(Wn/N)
-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. B157

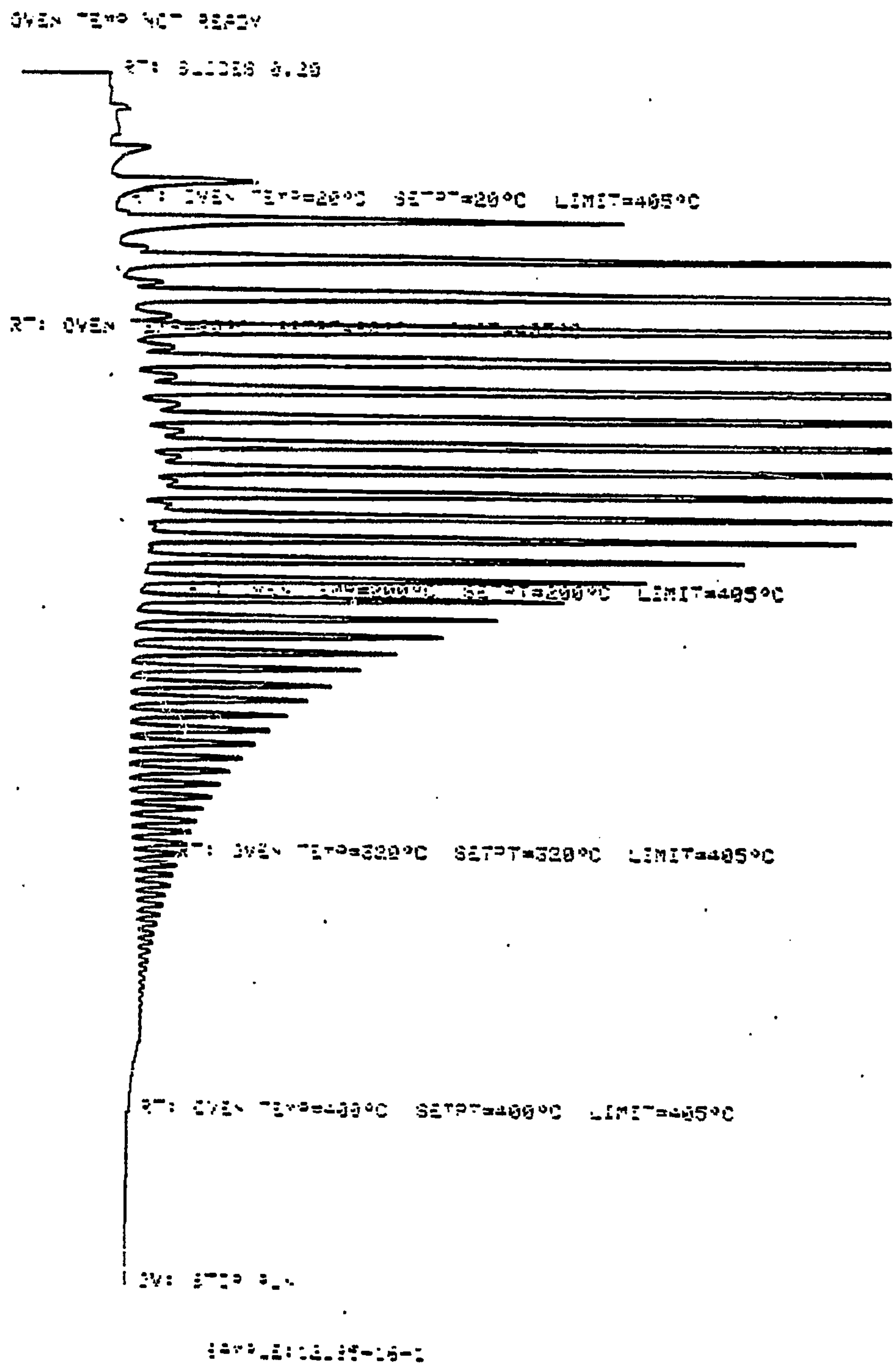


Fig. B158

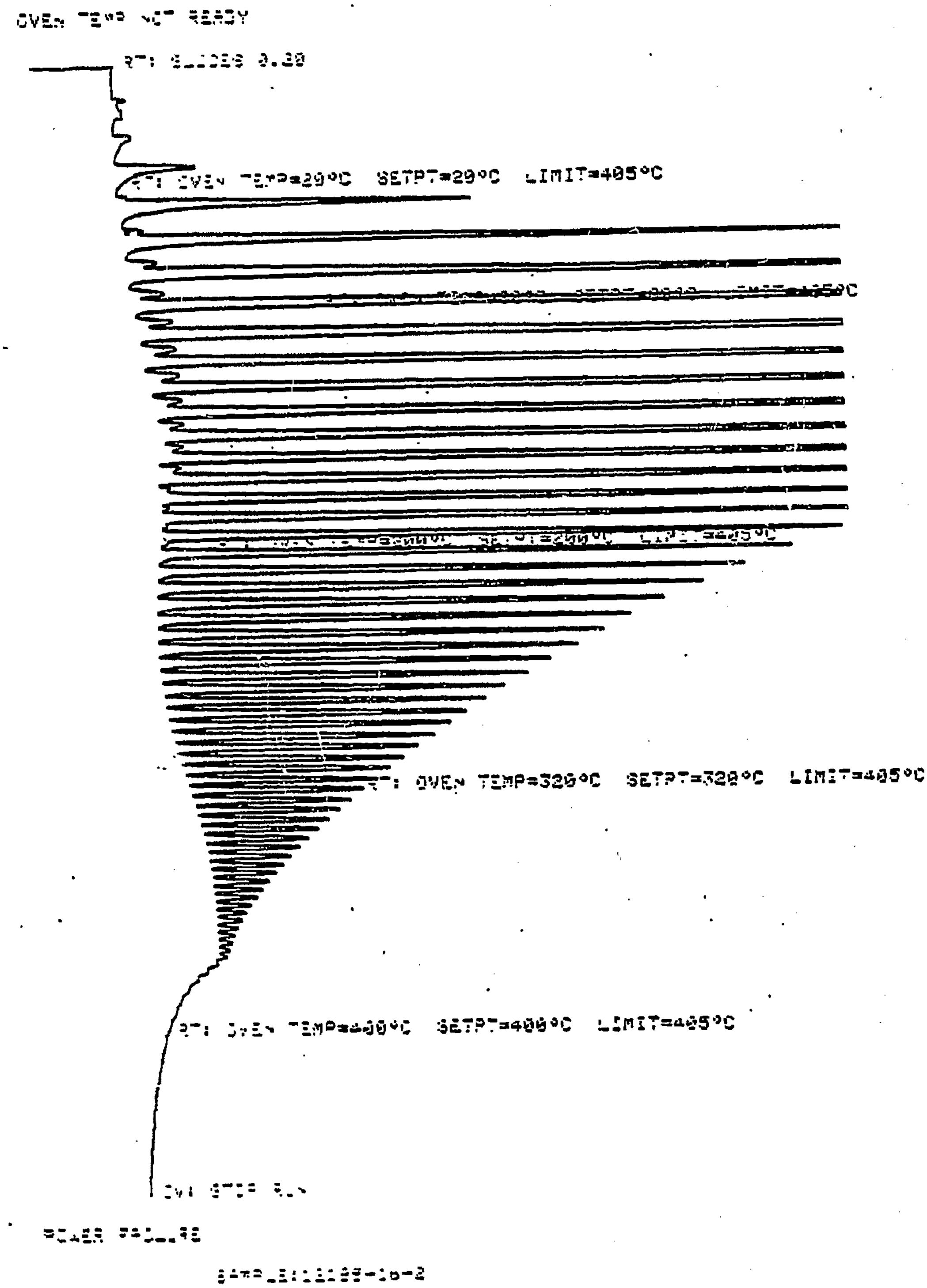

OVEN TEMP NOT READY
RT: OVEN TEMP=29°C SETPT=29°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
LIMIT=405°C

Fig. B159

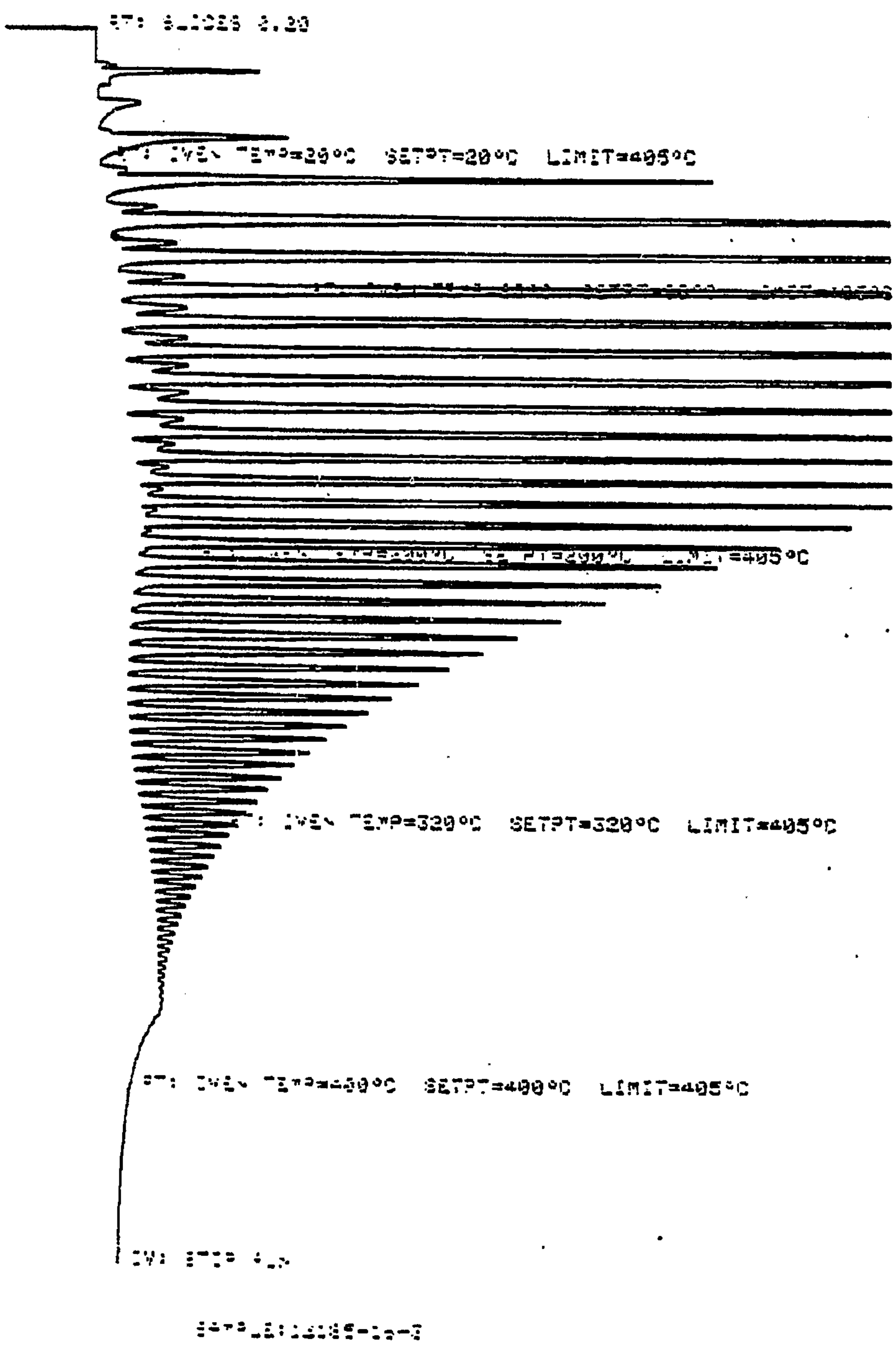


Fig. B160

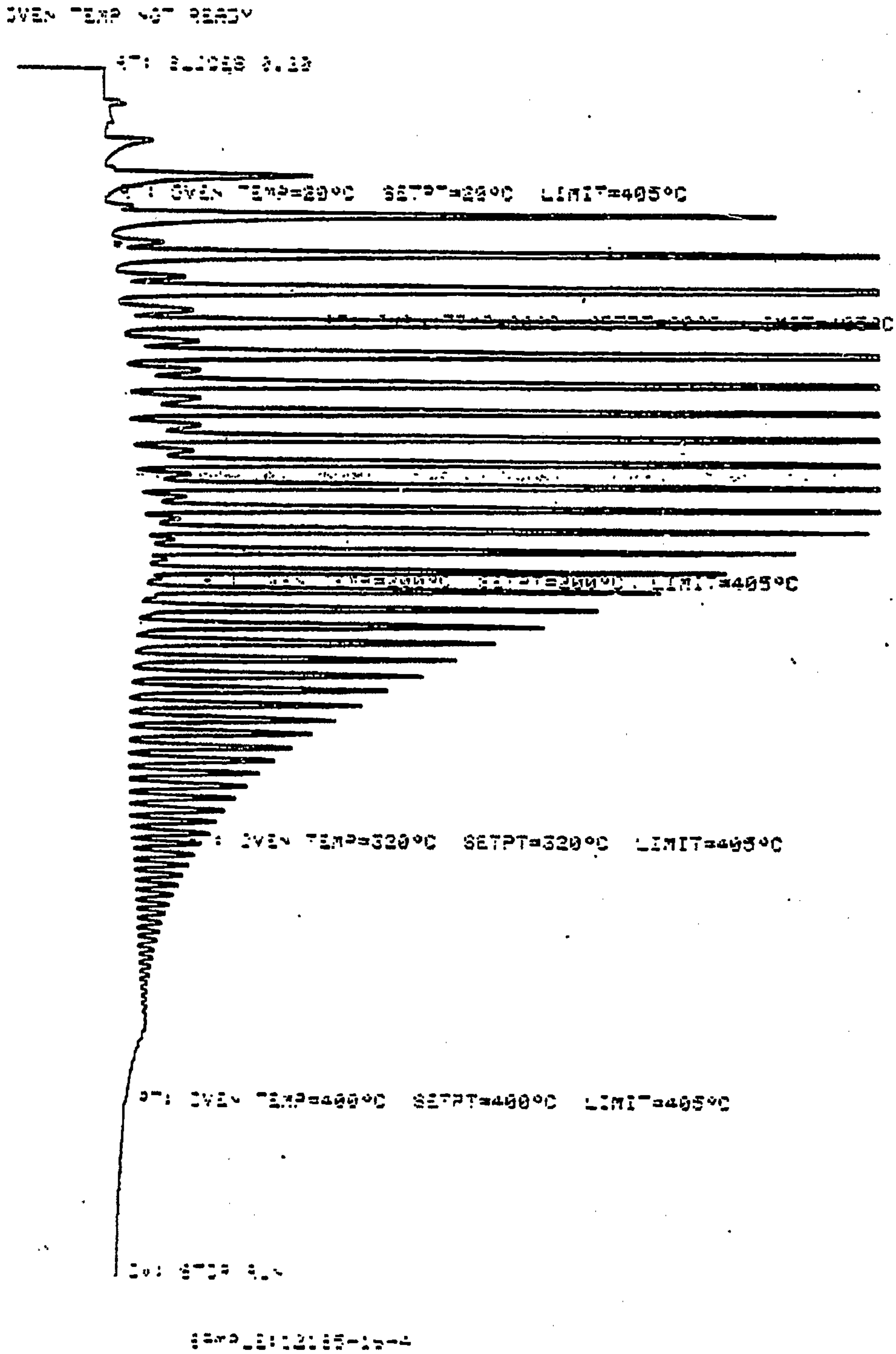

OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B161

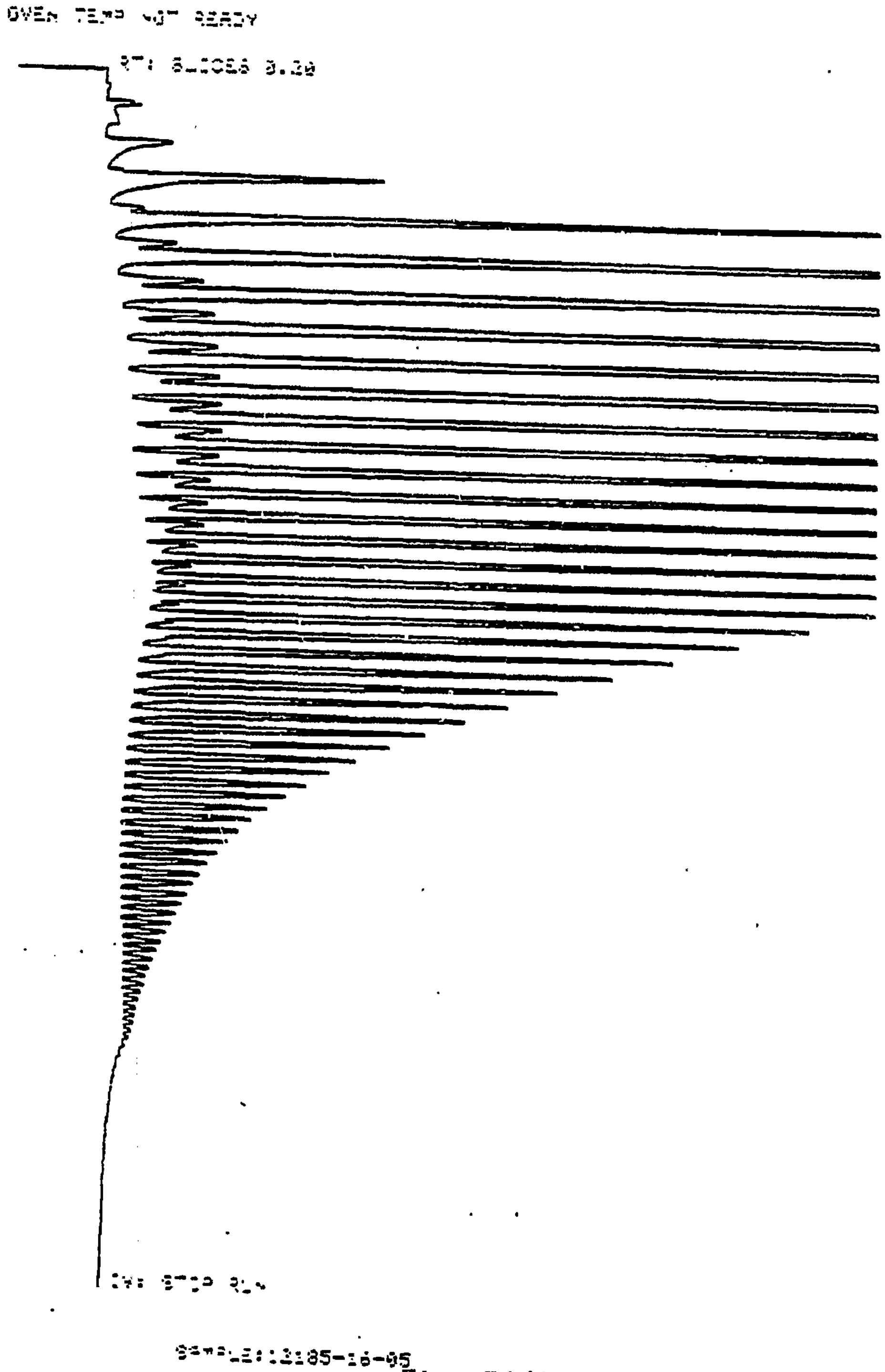
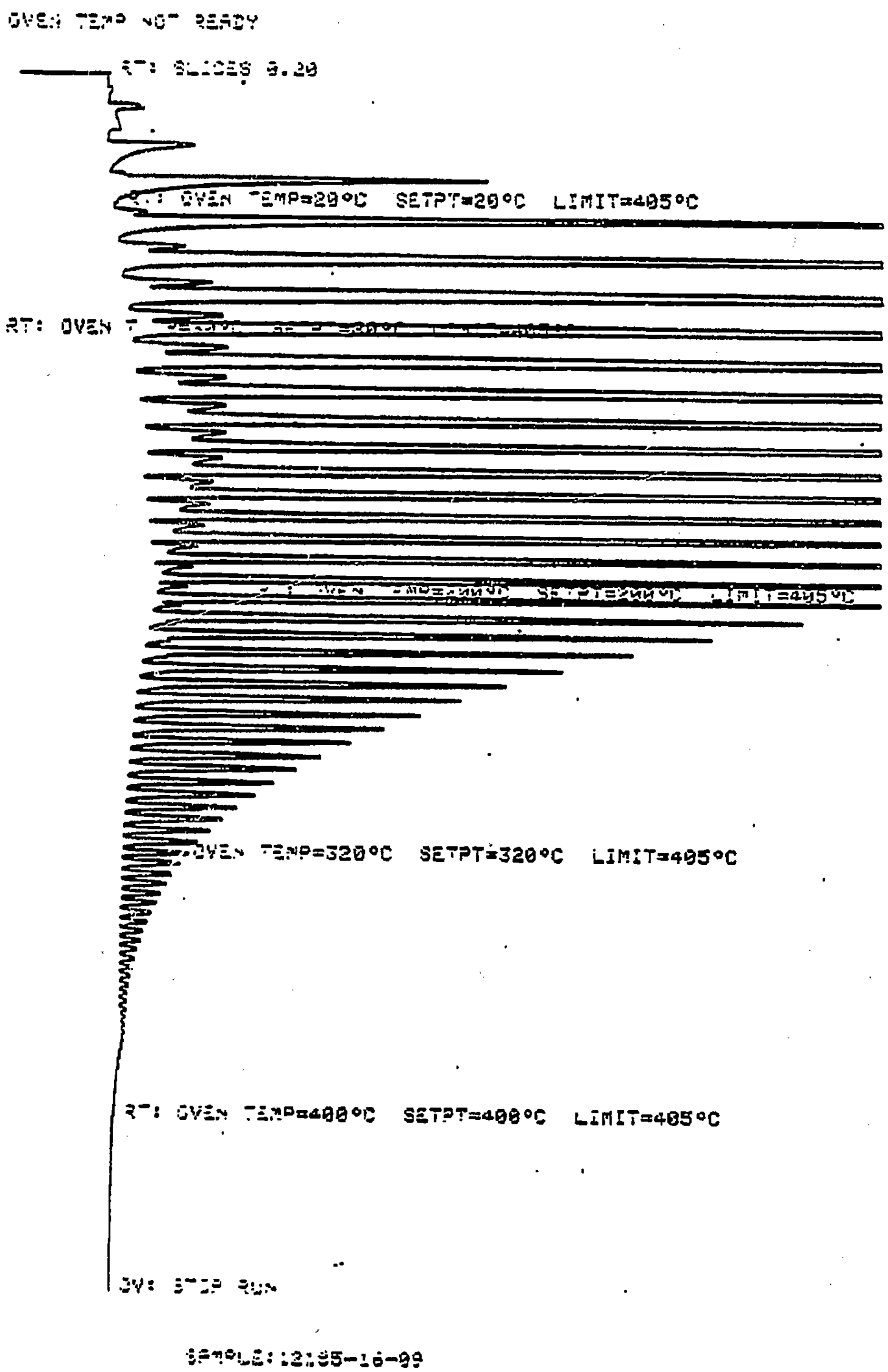


Fig. B162



OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B163

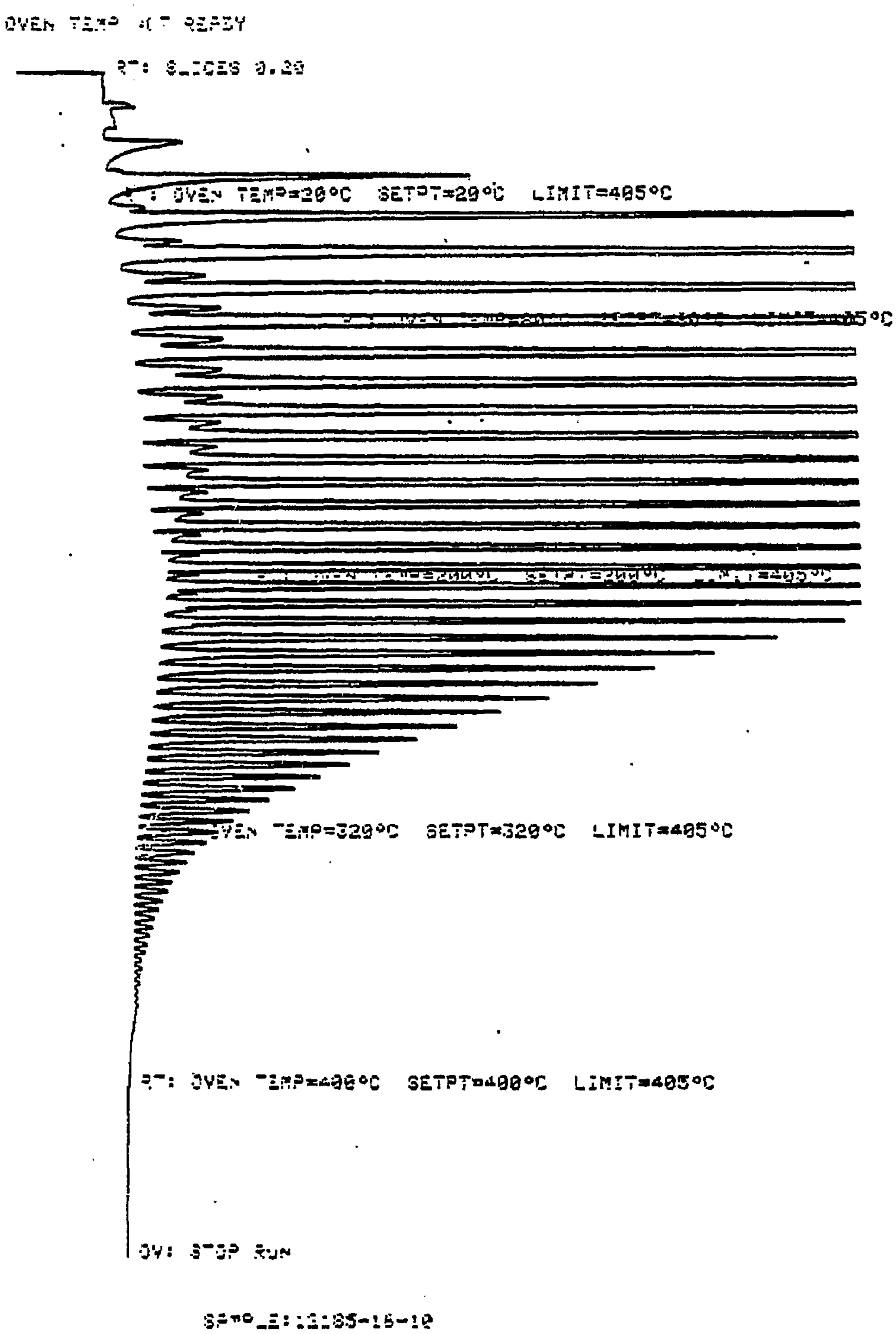

OVEN TEMP NOT READY
RT: SLICES 0.20
OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
OV: STOP RUN

Fig. B164

Table B11

FILE: 1218516A TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-16
CATALYST CO/X9/X10/X3-U103 80 CC 35.0 G AFTER USE:51.0 G (+16.0 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-66-11)

RUN & SAMPLE NO.	12185-16-01	185-16-02	185-16-03	185-16-04	185-16-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	66.0	90.0	114.0	138.0	162.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	218	218	241	241	241
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	66.00	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	992.90	398.54	331.90	340.55	349.40
GM AQUEOUS LAYER	146.94	37.68	53.99	53.65	53.96
GM OIL	42.22	27.70	36.94	30.90	27.12
MATERIAL BALANCE					
GM ATOM CARBON %	84.17	99.18	100.54	98.56	96.99
GM ATOM HYDROGEN %	97.74	104.87	106.69	104.84	104.49
GM ATOM OXYGEN %	95.95	95.78	96.40	97.26	98.10
RATIO CHX/(H2O+CO2)	0.5766	1.1644	1.1415	1.0448	0.9613
RATIO X IN CHX	2.2755	2.2379	2.2879	2.3150	2.3294
USAGE H2/CO PRODT	2.7721	1.9235	1.8664	1.9654	2.0710
FEED H2/CO FRM EFFLNT	1.1613	1.0573	1.0611	1.0637	1.0774
RESIDUAL H2/CO RATIO	0.7692	0.7719	0.6273	0.6360	0.6561
RATIO CO2/(H2O+CO2)	0.0153	0.0216	0.0611	0.0526	0.0419
K SHIFT IN EFFLNT	0.0119	0.0170	0.0409	0.0353	0.0287
SPECIFIC ACTIVITY SA	4.4710	5.9678	3.0478	2.6795	2.3218
CONVERSION					
ON CO %	19.57	24.78	35.01	32.17	29.78
ON H2 %	46.73	45.09	61.58	59.44	57.24
ON CO+H2 %	34.16	35.22	48.69	46.23	44.02
PRDT SELECTIVITY,WT %					
CH4	8.44	6.23	8.55	9.83	10.59
C2 HC'S	0.71	0.95	1.47	1.66	1.77
C3H8	2.09	1.47	1.88	2.16	2.39
C3H6=	3.09	2.19	2.25	2.42	2.45
C4H10	2.42	1.74	1.97	2.31	2.56
C4H8=	3.70	2.57	2.68	2.95	3.05
C5H12	2.91	2.10	2.43	2.87	3.09
C5H10=	3.07	2.23	2.29	2.45	2.54
C6H14	3.15	2.34	2.56	3.03	3.24
C6H12= & CYCLO'S	2.13	1.41	1.53	1.68	1.64
C7+ IN GAS	11.84	8.88	7.23	8.23	9.09
LIQ HC'S	56.43	67.89	65.17	60.21	57.59
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	20.47	15.16	18.80	21.53	22.82
C5 -420 F	40.94	29.65	33.04	29.58	37.56
420-700 F	26.92	25.19	26.59	32.27	25.34
700-END PT	11.68	30.01	21.57	16.62	14.28

Table B11 (continued)

FILE: 1218516A TSS3Q1 A1

C5+-END PT	79.53	84.84	81.20	78.47	77.18
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0000	0.0210	0.0160	0.0148
C5	0.0421	0.0461	0.0622	0.0603	0.0511
C6	0.0499	0.0478	0.0647	0.0636	0.0513
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.6435	0.6415	0.8006	0.8520	0.9303
C4	0.6318	0.6550	0.7105	0.7549	0.8110
C5	0.9206	0.9132	1.0332	1.1397	1.1794
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8384	0.8762	0.8685	0.8588	0.8550
RATIO CH4/(1-A)**2	3.2353	4.0676	4.9383	4.9316	5.0395
ALPHA FRM CORRELATION	0.8261	0.8259	0.8346	0.8339	0.8324
ALPHA (EXPTL/CORR)	1.0149	1.0609	1.0406	1.0299	1.0271
W%CH4 FRM CORRELATION	12.1739	12.2269	14.9807	15.1896	15.6586
W%CH4 (EXPTL/CORR)	0.6936	0.5095	0.5704	0.6469	0.6766
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY	0.779	0.831	0.808	0.811	0.789
N, REFRACTIVE INDEX	N/A	N/A	N/A	N/A	N/A
SIMULT'D DISTILATN					
10 WT % @ DEG F	302	368	321	301	296
16	342	412	370	343	338
50	512	645	573	542	533
84	751	970	878	817	780
90	849	1046	975	914	858
RANGE(16-84 %)	409	558	508	474	442
WT % @ 420 F	31.60	18.70	26.10	18.80	31.20
WT % @ 700 F	79.30	55.80	66.90	72.40	75.20

Table B12

FILE: 1218516B TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-16
CATALYST CO/X9/X10/X3-U103 80 CC 35.0 G AFTER USE:51.0 G (+16.0 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-66-11)

RUN & SAMPLE NO.	12185-16-09	185-16-10
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	258.0	281.5
PRESSURE,PSIG	300	300
TEMP. C	241	245
FEED CC/MIN	400	400
HOURS FEEDING	22.00	23.50
EFFLNT GAS LITER	336.20	351.20
GM AQUEOUS LAYER	42.33	47.59
GM OIL	23.71	26.15
MATERIAL BALANCE		
GM ATOM CARBON %	98.53	99.94
GM ATOM HYDROGEN %	105.22	103.58
GM ATOM OXYGEN %	95.81	98.00
RATIO CHX/(H2O+CO2)	1.1089	1.0735
RATIO X IN CHX	2.3322	2.3626
USAGE H2/CO PRODT	1.9700	1.9799
FEED H2/CO FRM EFFLNT	1.0680	1.0365
RESIDUAL H2/CO RATIO	0.6992	0.6395
RATIO CO2/(H2O+CO2)	0.0366	0.0479
K SHIFT IN EFFLNT	0.0265	0.0322
SPECIFIC ACTIVITY SA	2.0709	1.9191
CONVERSION		
ON CO %	29.02	29.62
ON H2 %	53.53	56.58
ON CO+H2 %	41.68	43.34
PRDT SELECTIVITY,WT %		
CH4	10.81	12.16
C2 HC'S	1.67	1.81
C3H8	2.47	2.73
C3H6=	2.32	2.38
C4H10	2.66	2.82
C4H8=	2.78	3.01
C5H12	3.22	3.37
C5H10=	2.51	2.65
C6H14	3.48	3.64
C6H12= & CYCLO'S	1.61	1.56
C7+ IN GAS	11.57	9.61
LIQ HC'S	54.90	55.26
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	22.70	24.92
C5 -420 F	42.71	38.61
420-700 F	24.87	23.71
700-END PT	9.72	12.76

Table B12 (continued)

FILE: 1218516B TSS3Q1 A1

C5+-END PT	77.30	75.08
ISO/NORMAL MOLE RATIO		
C4	0.0114	0.0137
C5	0.0495	0.0495
C6	0.0461	0.0567
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	1.0165	1.0910
C4	0.9242	0.9028
C5	1.2480	1.2356
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8413	0.8520
RATIO CH4/(1-A)**2	4.2939	5.5540
ALPHA FRM CORRELATION	0.8293	0.8334
ALPHA (EXPTL/CORR)	1.0145	1.0223
W%CH4 FRM CORRELATION	16.6199	16.2418
W%CH4 (EXPTL/CORR)	0.6507	0.7490
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	OIL WAX
DENSITY	0.781	0.776
N, REFRACTIVE INDEX	N/A	N/A
SIMULT'D DISTILATN		
10 WT % @ DEG F	295	295
16	336	338
50	483	511
84	709	761
90	782	826
RANGE(16-84 %)	373	423
WT % @ 420 F	37.00	34.00
WT % @ 700 F	82.30	76.90

VII. Run 31 (12185-17) with Catalyst 31 ($Co/X_9/X_{10}$/UCC-103

This run was a further test of the effect of calcination pretreatment on a catalyst's activity and selectivity. The catalyst was prepared in the same way as Catalyst 20 of the Third Quarterly Report and Catalysts 26 and 29, with all of which it is to be compared, except that it was not calcined before it was activated. Catalyst 20 was calcined after bonding with silica, Catalyst 26 and 29 both before and after bonding. The theoretical content of cobalt, X_9 and X_{10} were, respectively, 7.8, 0.35 and 0.47 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B165-168. Simulated distillations of the C_5^+ product are plotted in Figs. B169-172. Carbon number product distributions are plotted in Figs. B173-176. Chromatograms from simulated distillations are reproduced in Figs. B177-180. Detailed material balances appear in Table B13.

The syngas conversion at 240C was about 27 percent, with specific activity of about 0.9--much lower than the specific activities of Catalysts 26 and 29, which were about 3.1 and 1.9 respectively.

The run was too short for any reliable measure of stability.

Some interesting selectivity effects were observed for this catalyst as evidenced by the Schulz-Flory plots. Even after good material balances were obtained there were deviations from the normal linear distribution predicted by Schulz-Flory kinetics, notably an apparent carbon number cut-off at about C_{25}. In this respect it was like Catalyst 20, which also was not calcined before bonding, and unlike Catalysts 26 and 29, which were.

These preliminary results suggest that calcination before bonding may introduce novel selectivity effects, possibly by altering the molecular sieve component crystallinity. But again the run was too short for reliable conclusions, and more definitive tests are to be undertaken.

Of the catalysts formulated by the method for intimately contacting cobalt with UCC-103, first used for Catalyst 11, only this one and Catalyst 20 have substantially deviated from normal Schulz-Flory kinetics. These results point up the potential importance of pretreatment for both activity and selectivity.

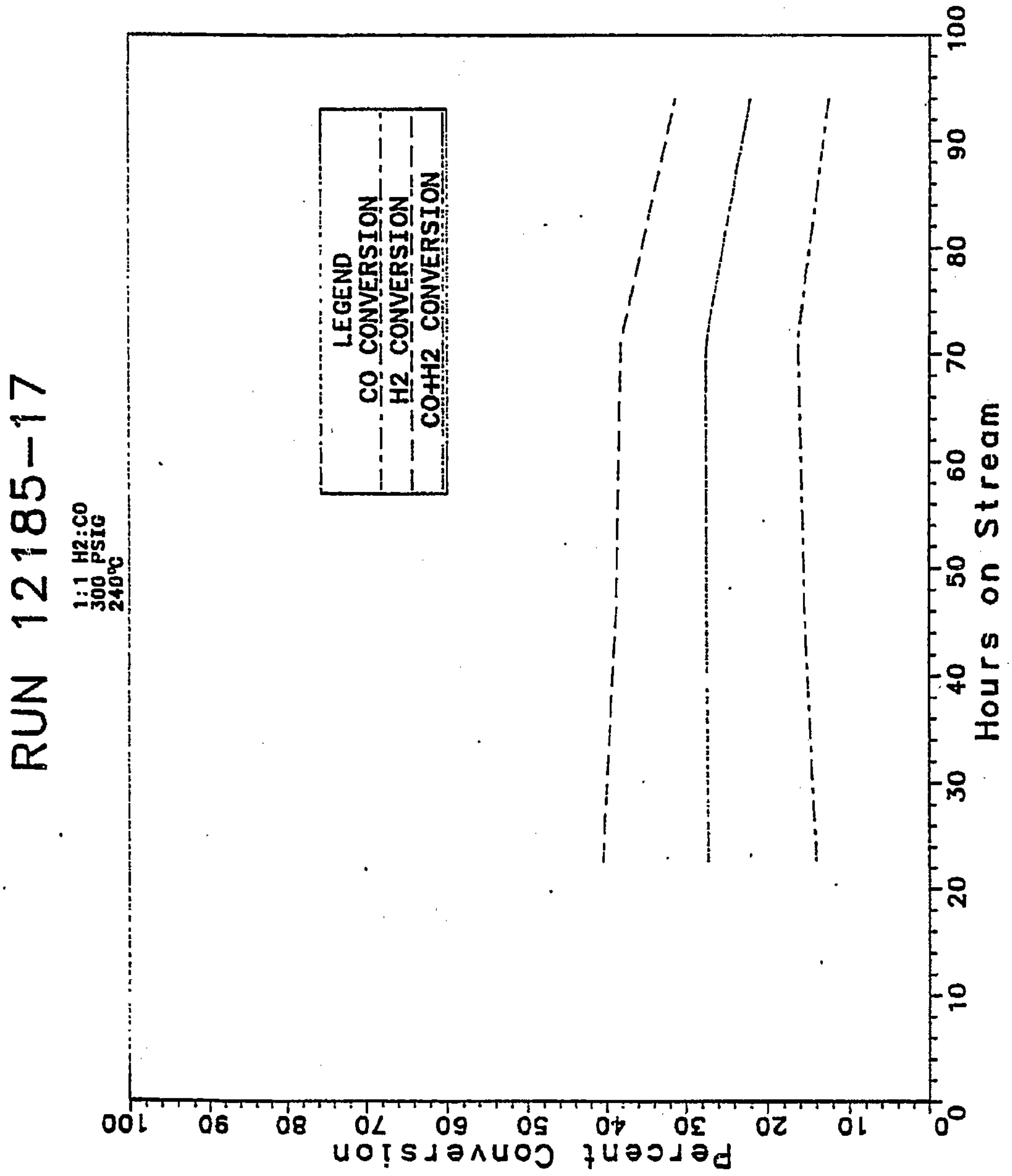

RUN 12185-17
1:1 H2:CO
300 PSIG
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B165

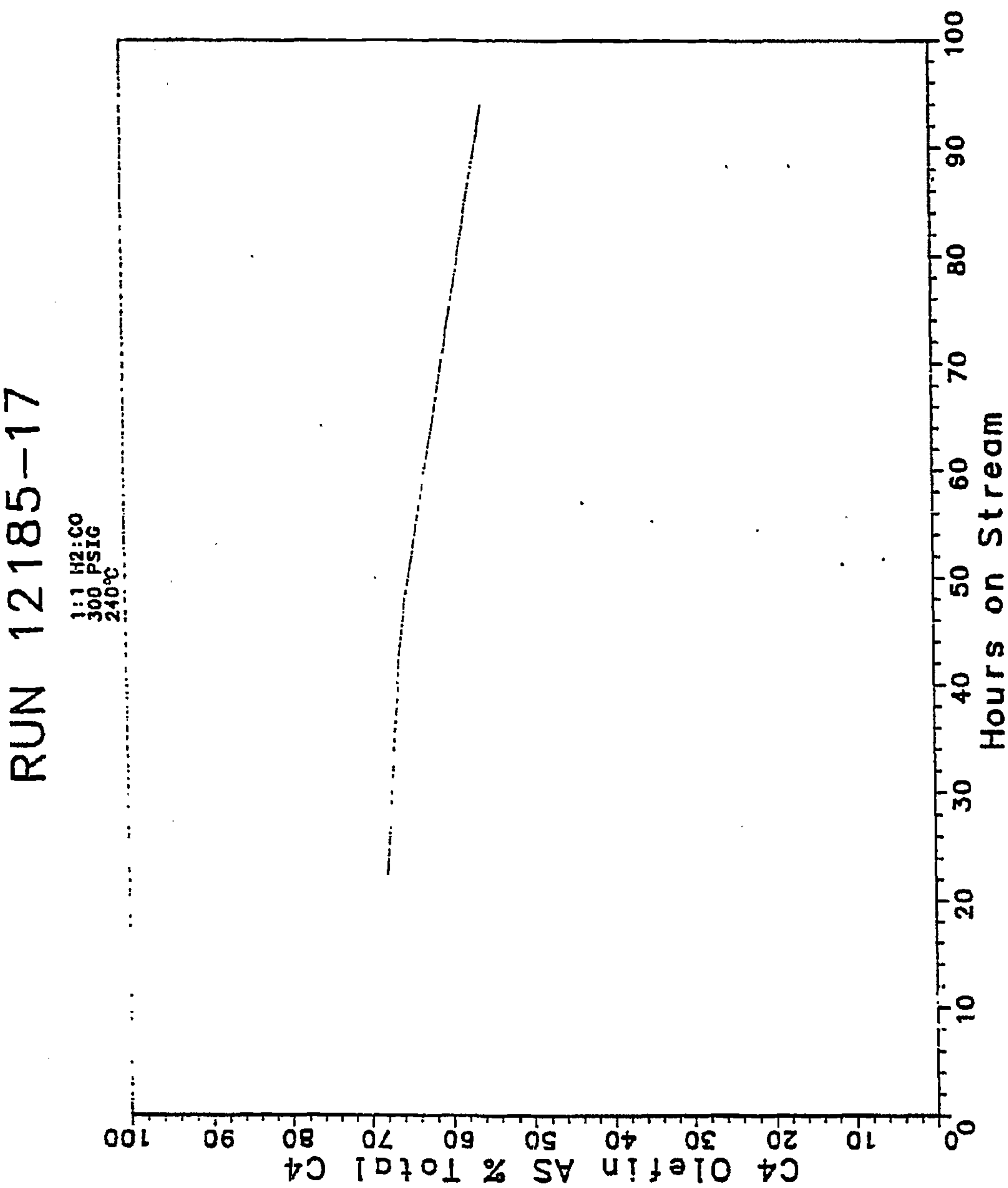

RUN 12185-17
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100

Fig. B166

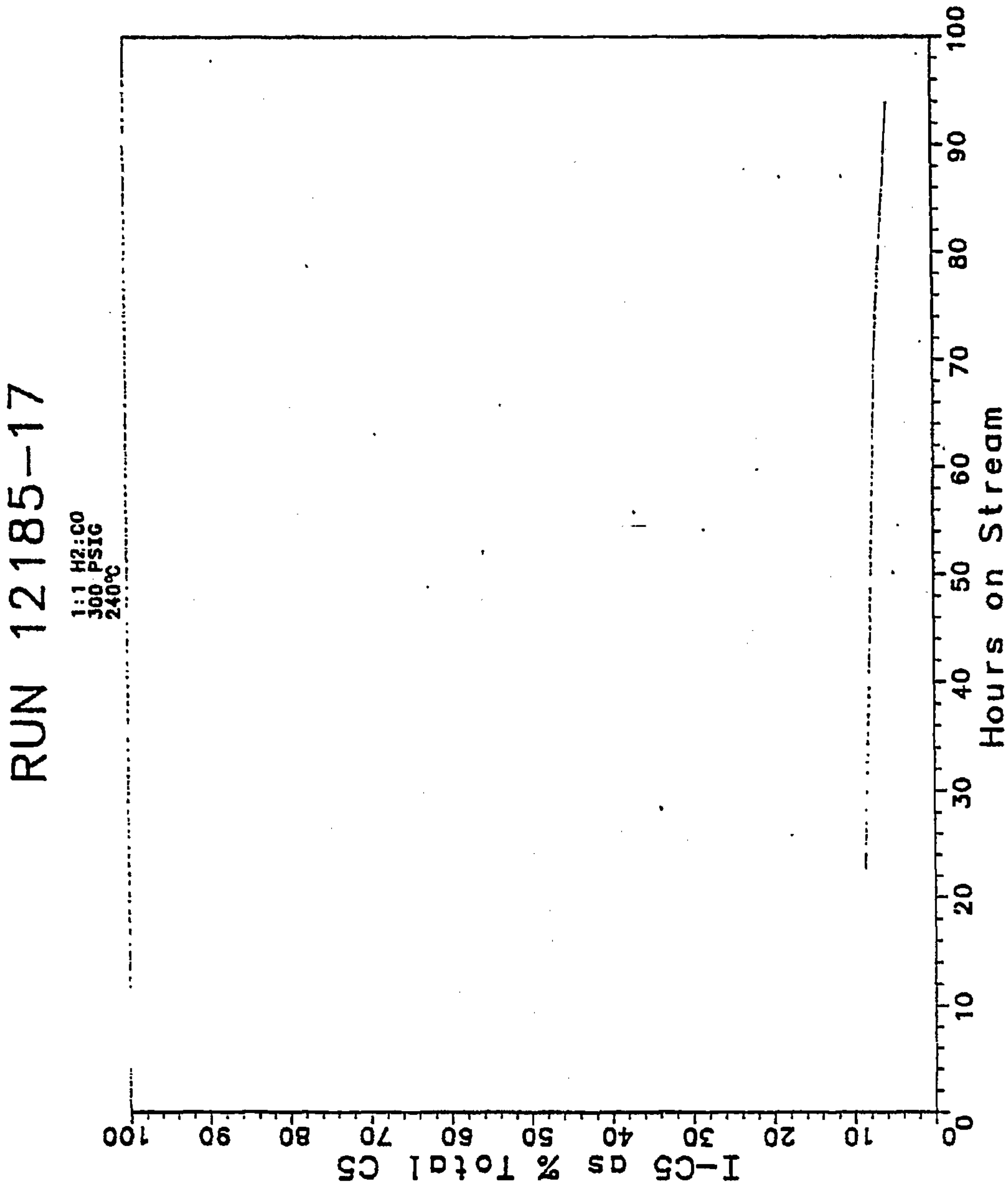

RUN 12185-17
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100

Fig. B167

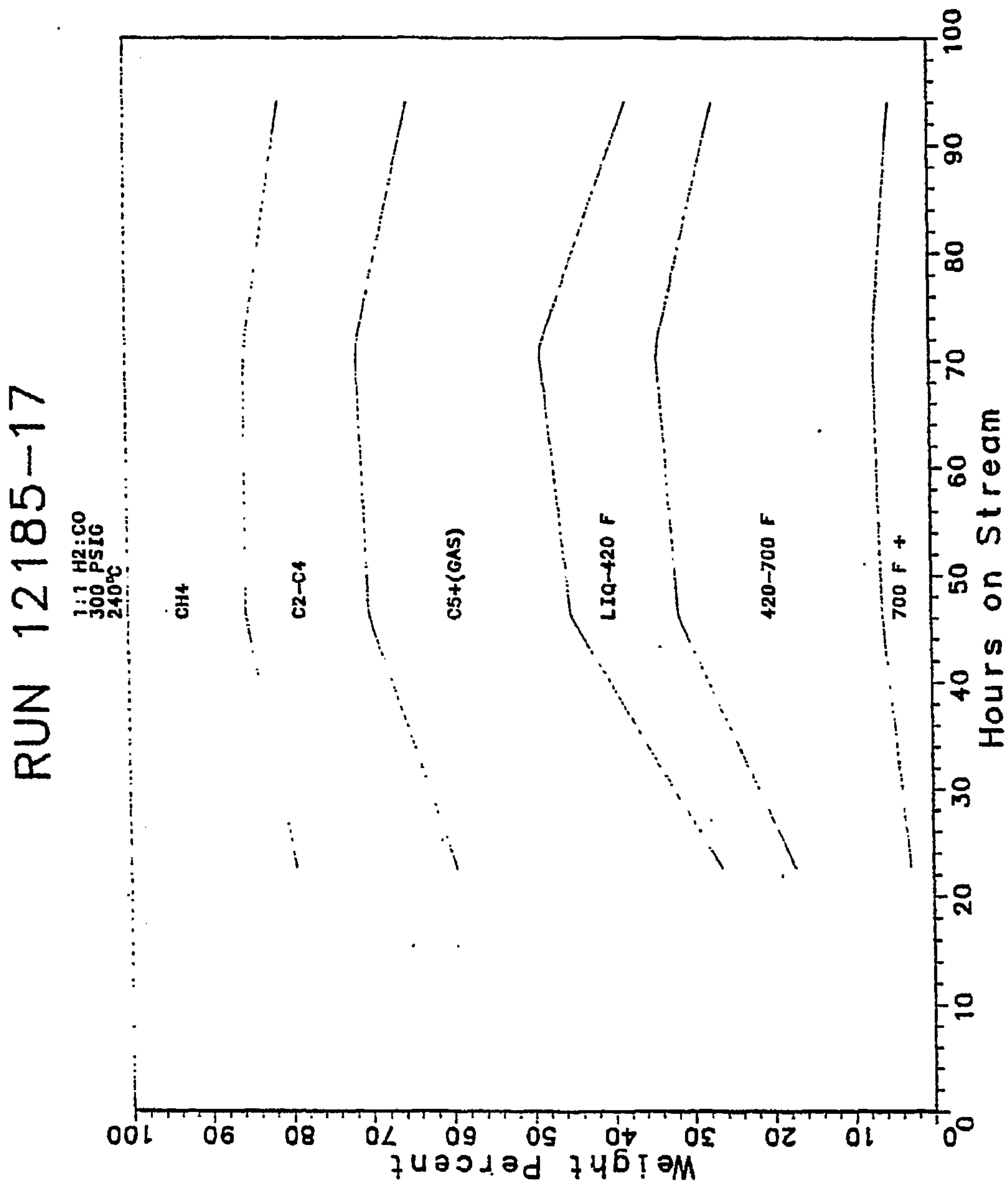

RUN 12185—17
1:1 H2:CO
300 PSIG
240°C
CH4
C2—C4
C5+(GAS)
LIQ—420 F
420—700 F
700 F +
Hours on Stream
Weight Percent
0
10
20
30
40
50
60
70
80
90
100

Fig. B168

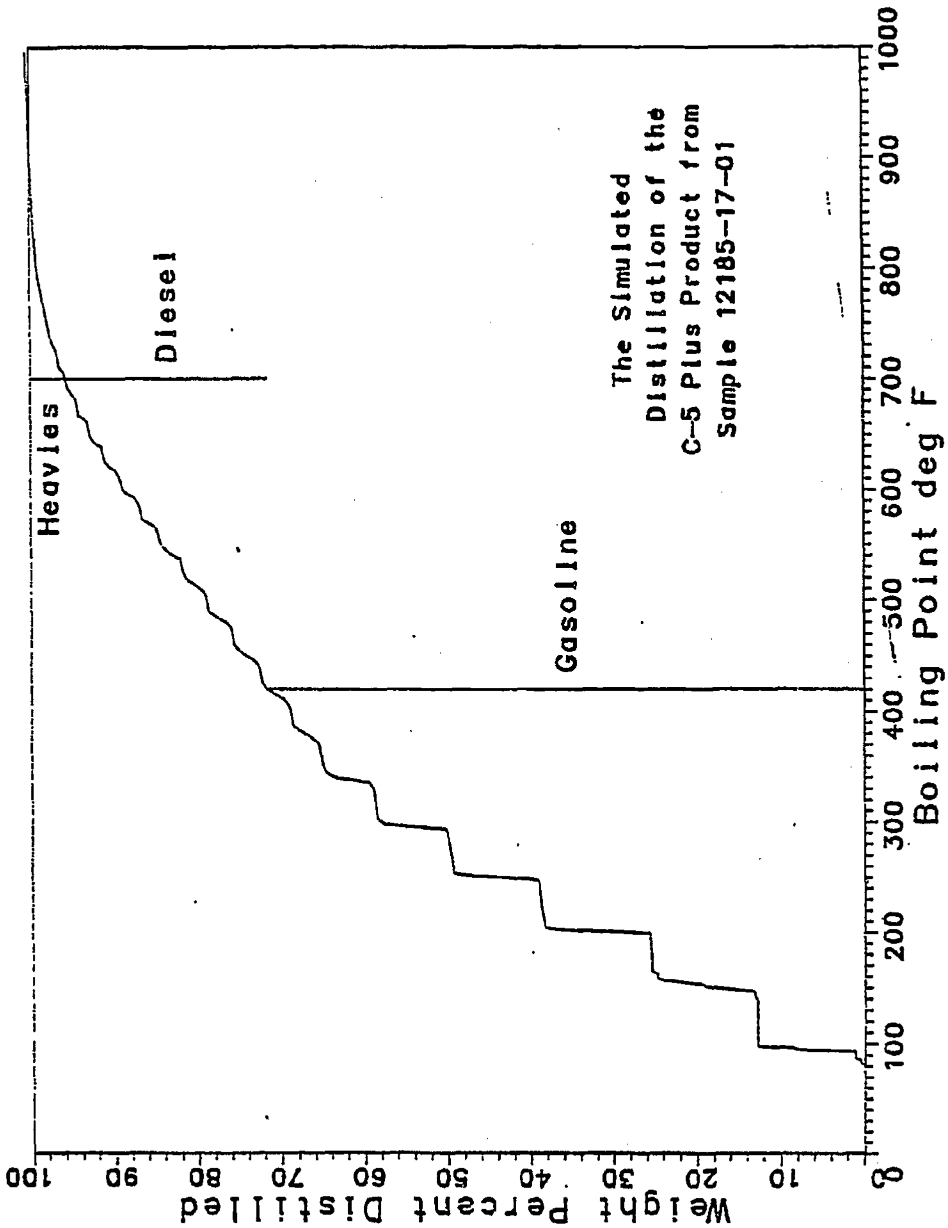
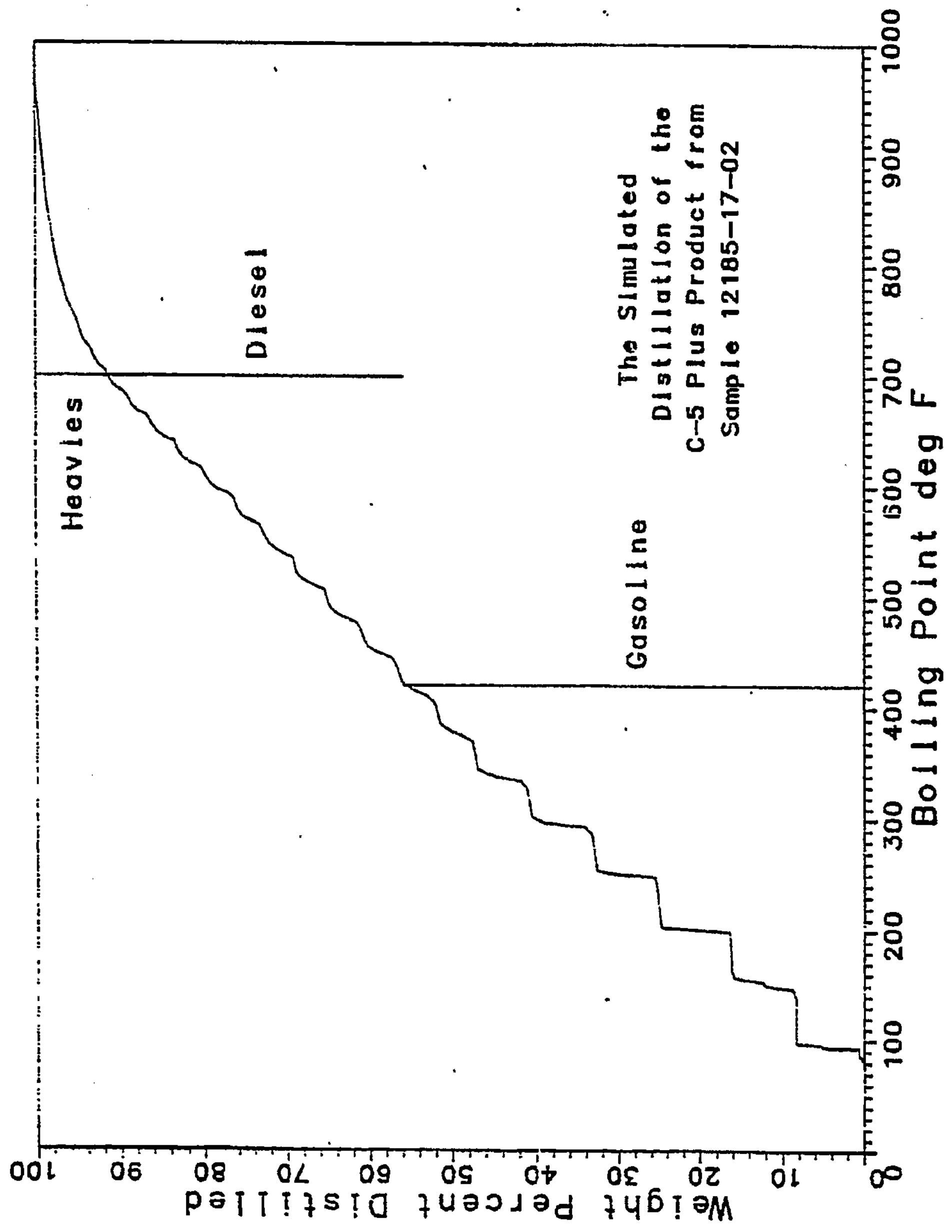
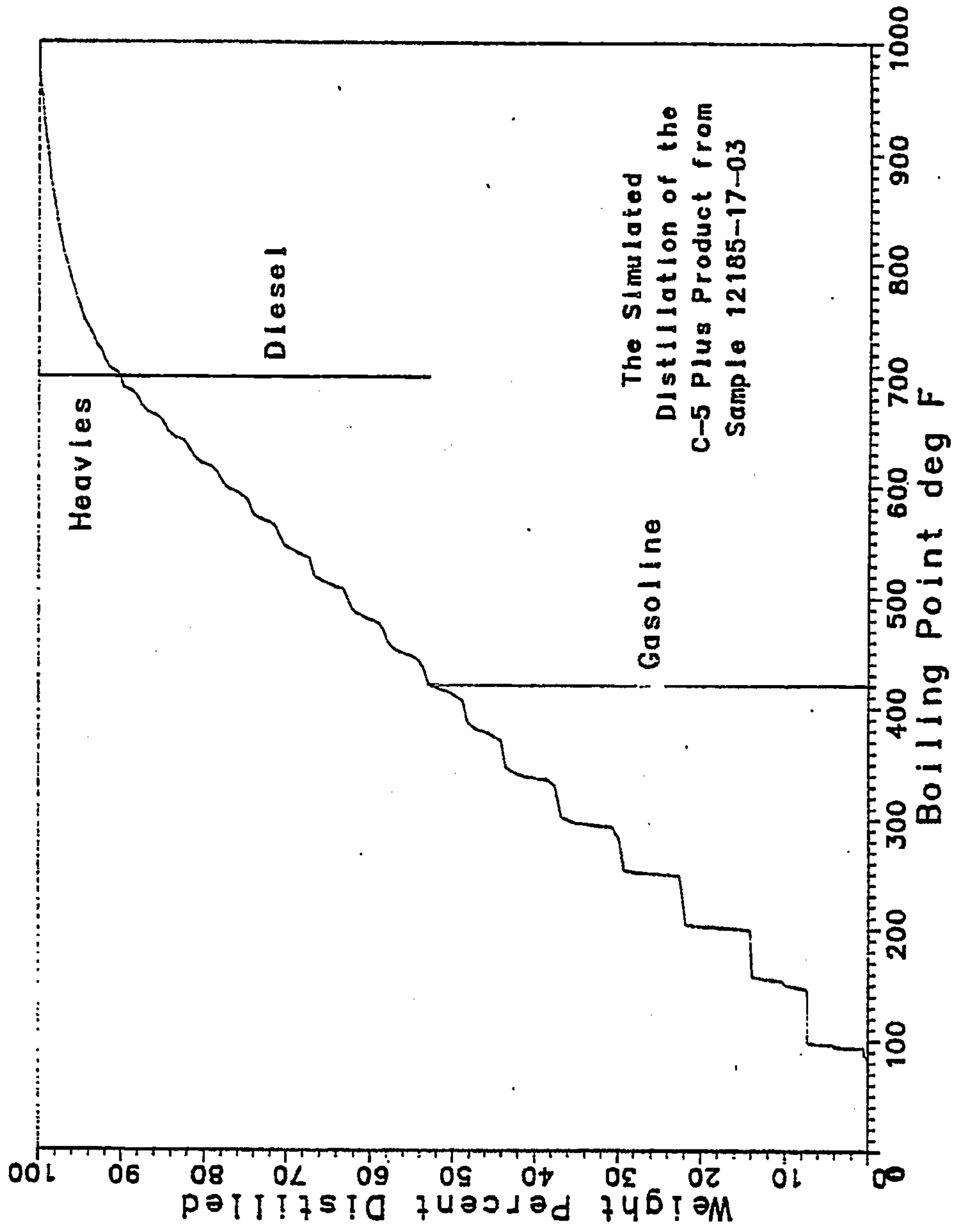

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-17-01
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B169



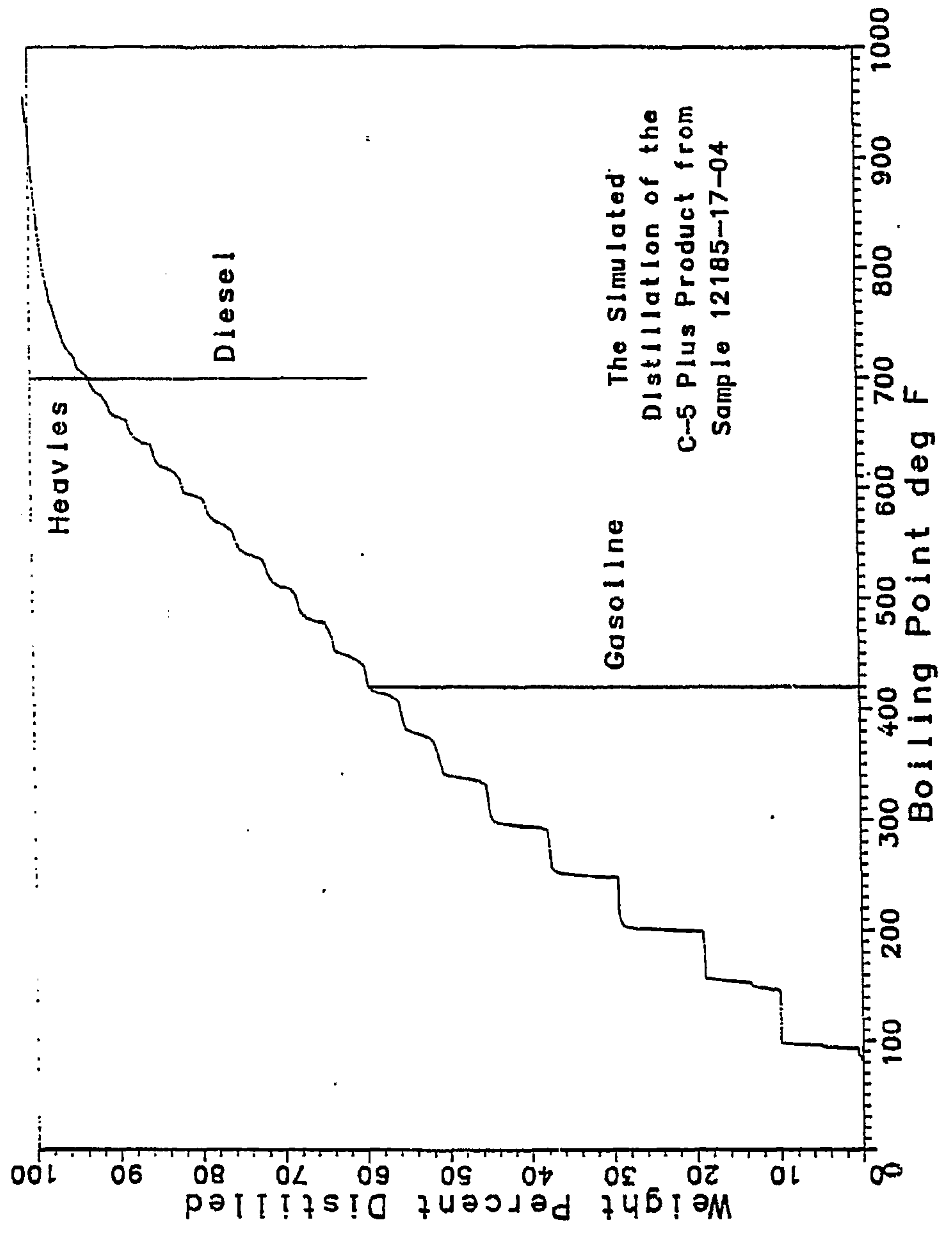
Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-17-02
Boiling Point deg F
100 200 300 400 500 600 700 800 900 1000
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B170



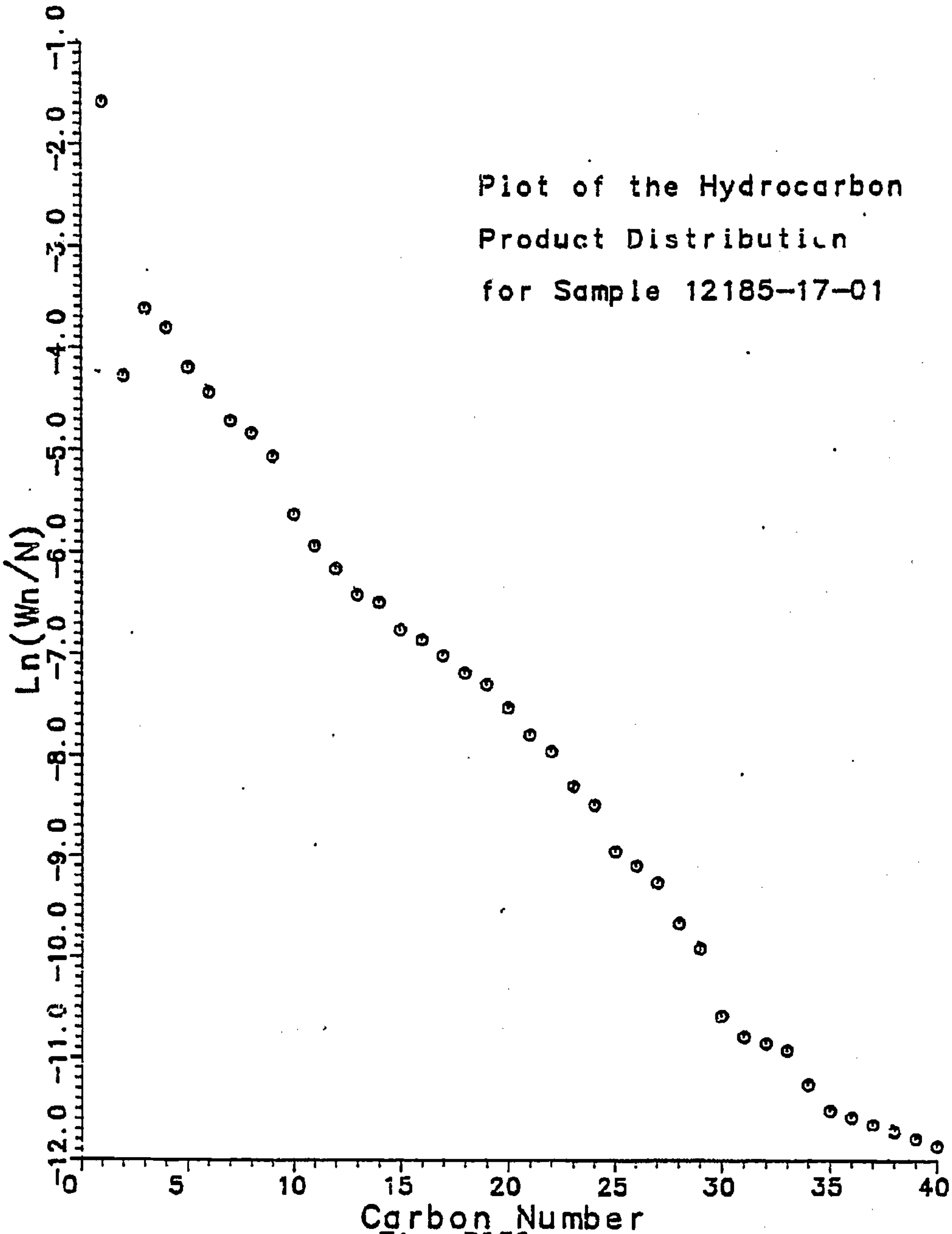
Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-17-03
Boiling Point deg F
Weight Percent Distilled

Fig. B171



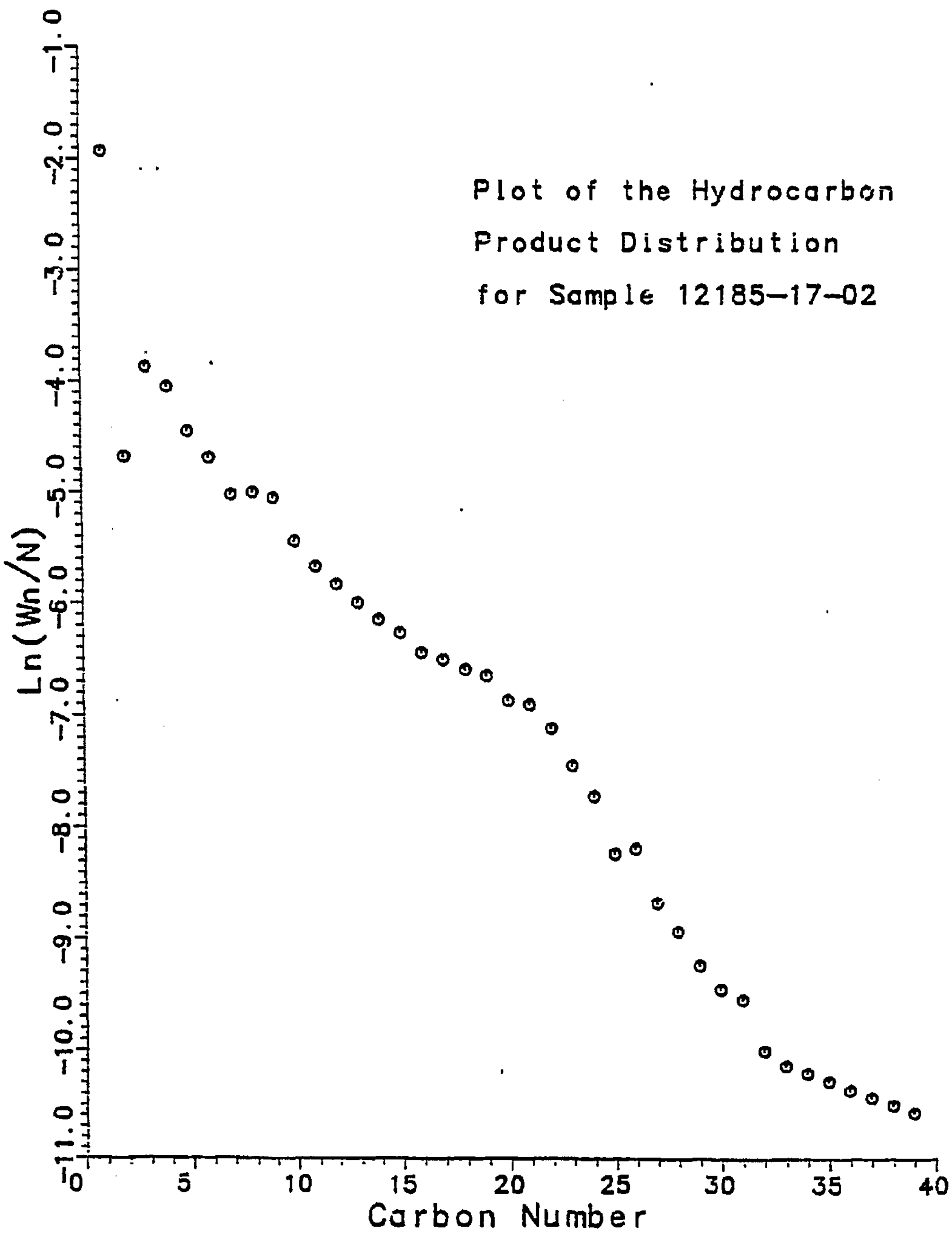
Heavies
Diesel
Gasoline
The Simulated Distillation of the C-5 Plus Product from Sample 12185-17-04
Boiling Point deg F
0 100 200 300 400 500 600 700 800 900 1000
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B172



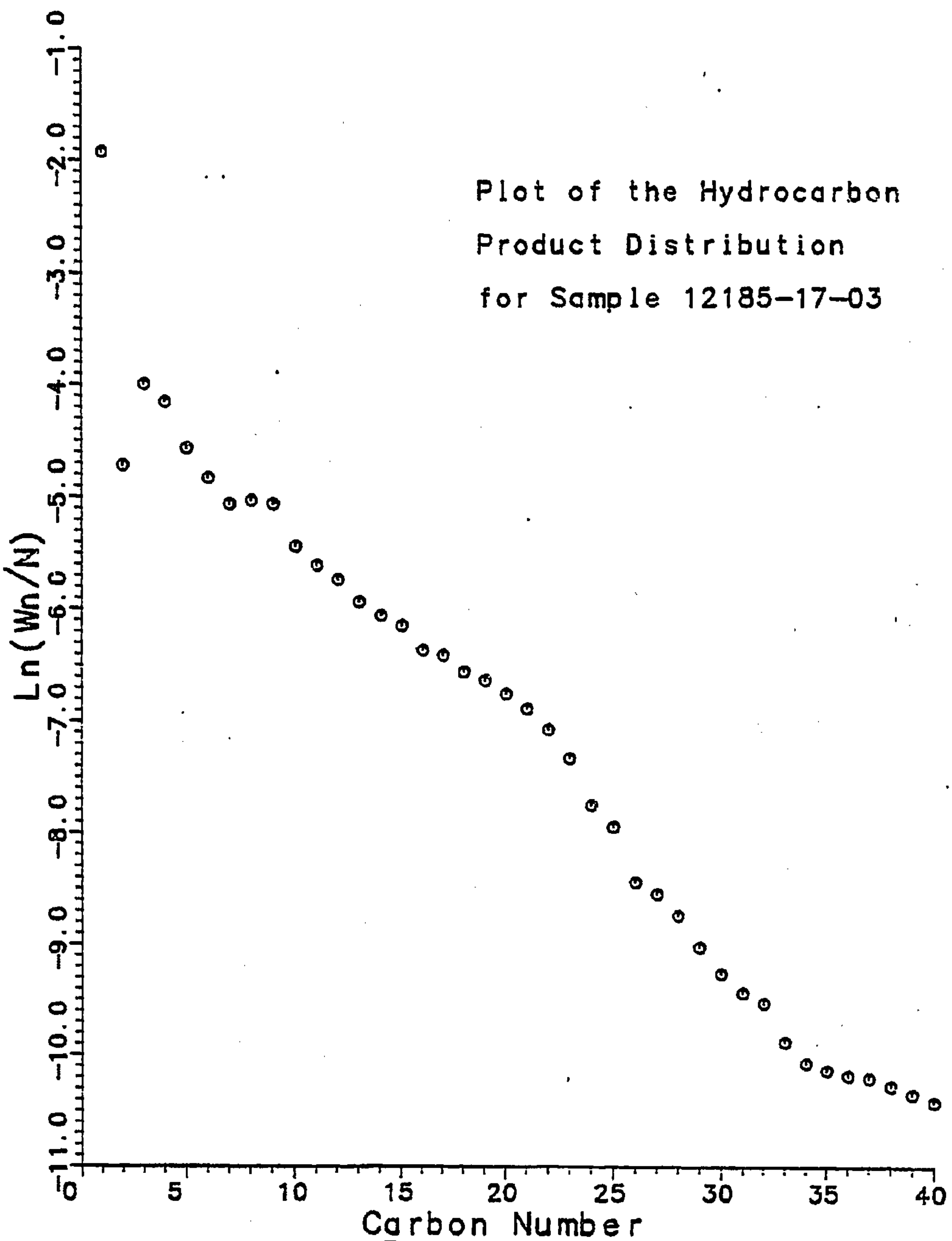
Plot of the Hydrocarbon
Product Distribution
for Sample 12185-17-01
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

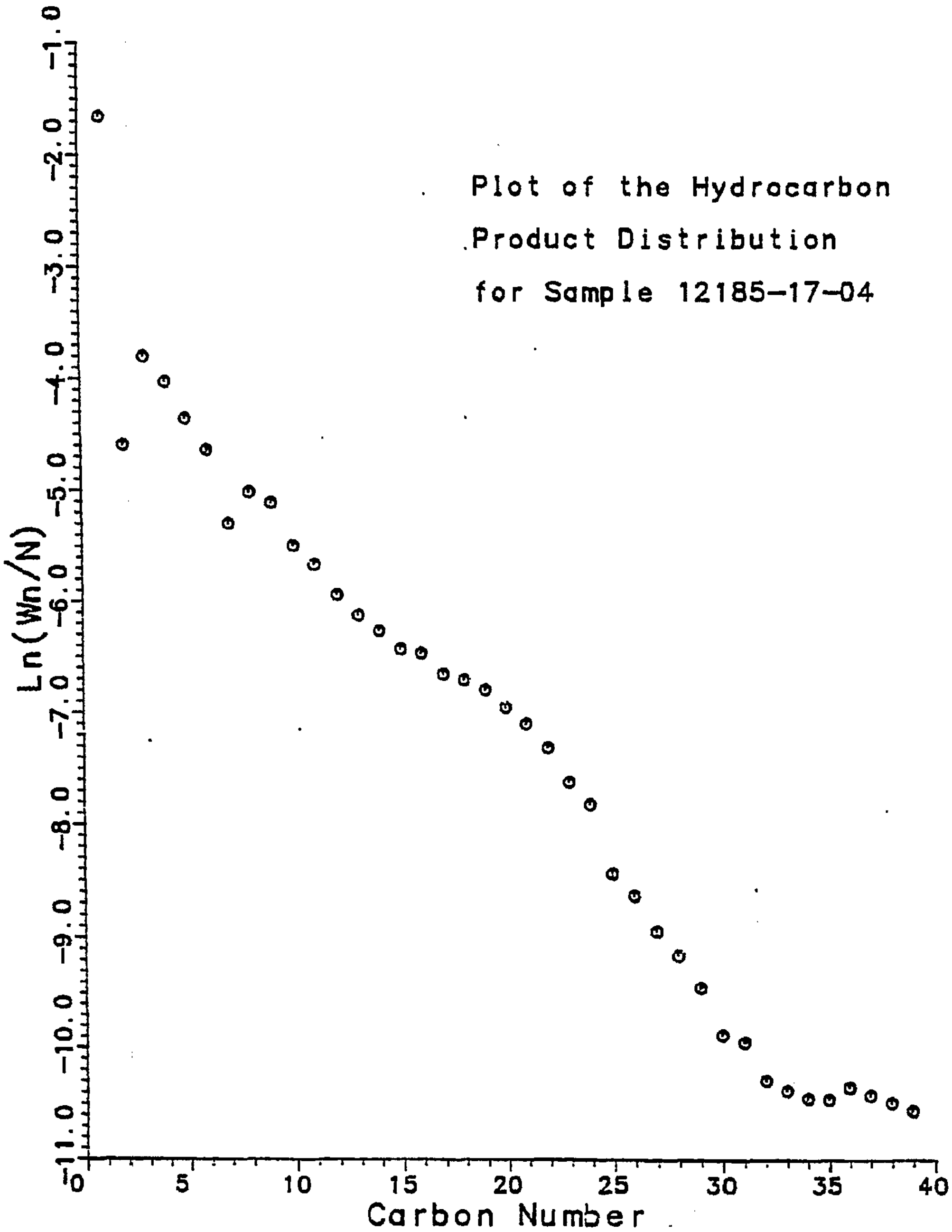
Fig. B173



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-17-02
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
40
Carbon Number

Fig. B174


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-17-03
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
40
Carbon Number
Fig. B175



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-17-04
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
40
Carbon Number

Fig. B176

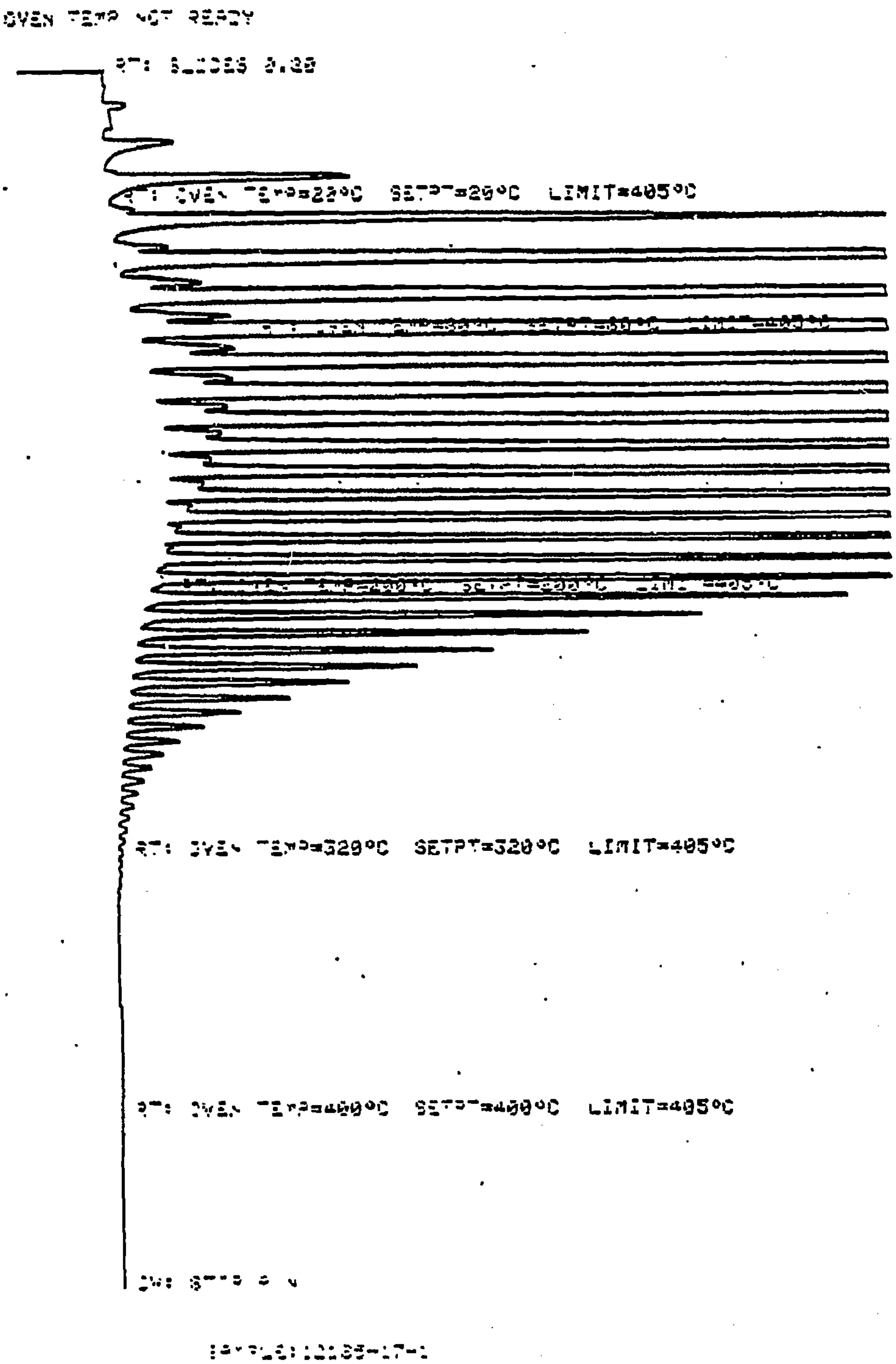


Fig. B177

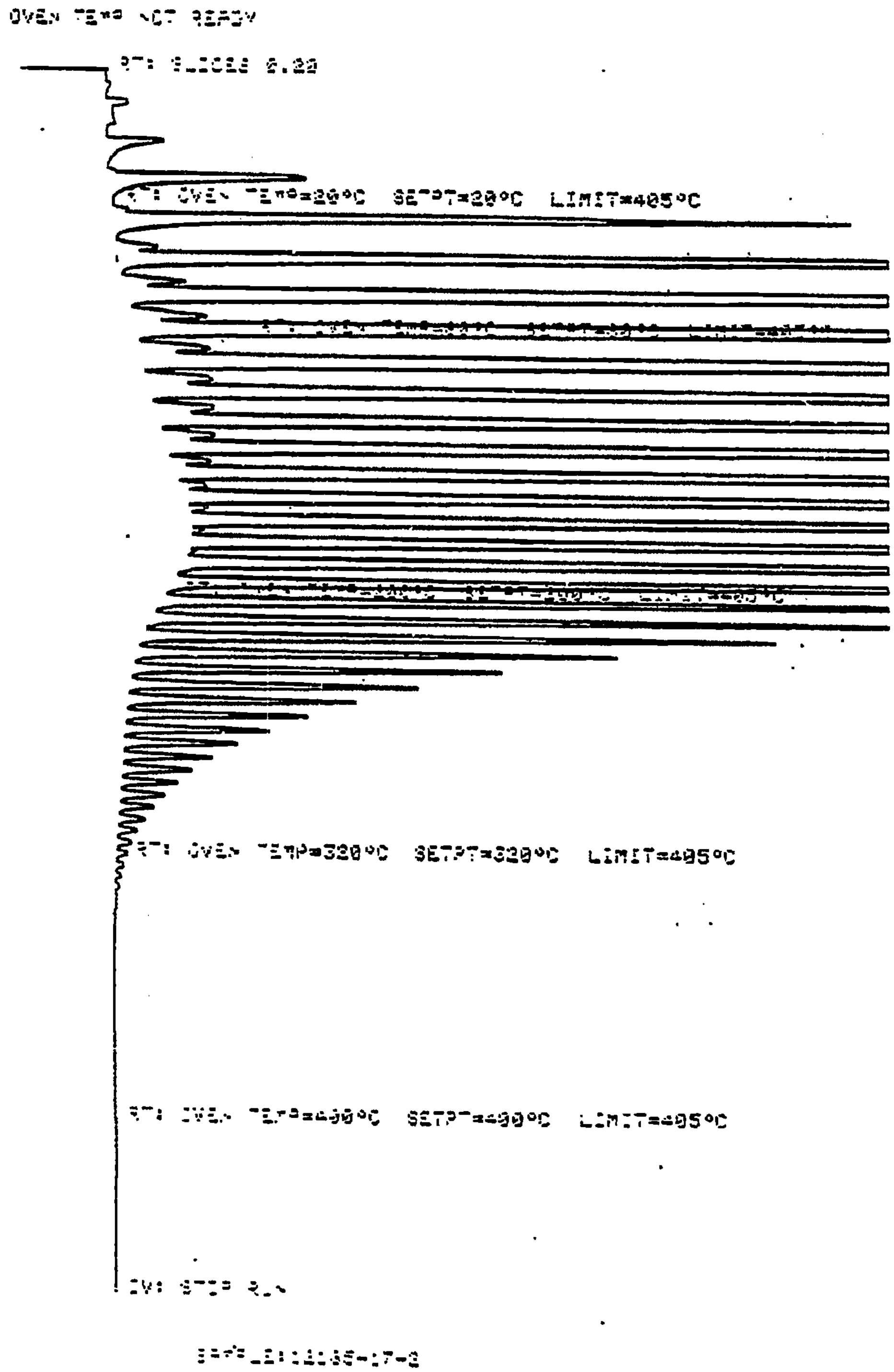

OVEN TEMP NOT READY
OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
STOP RUN

Fig. B178

T/T

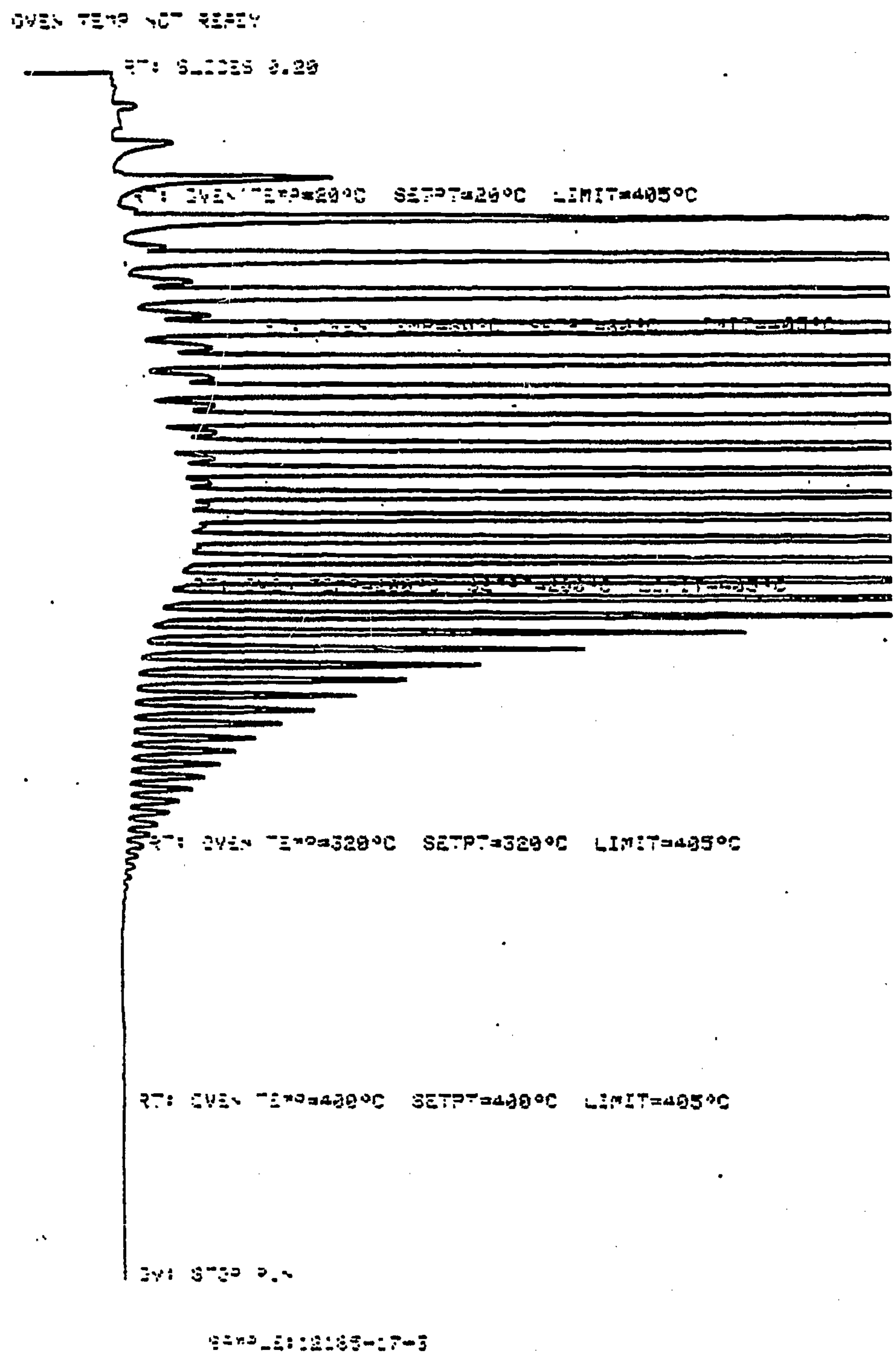
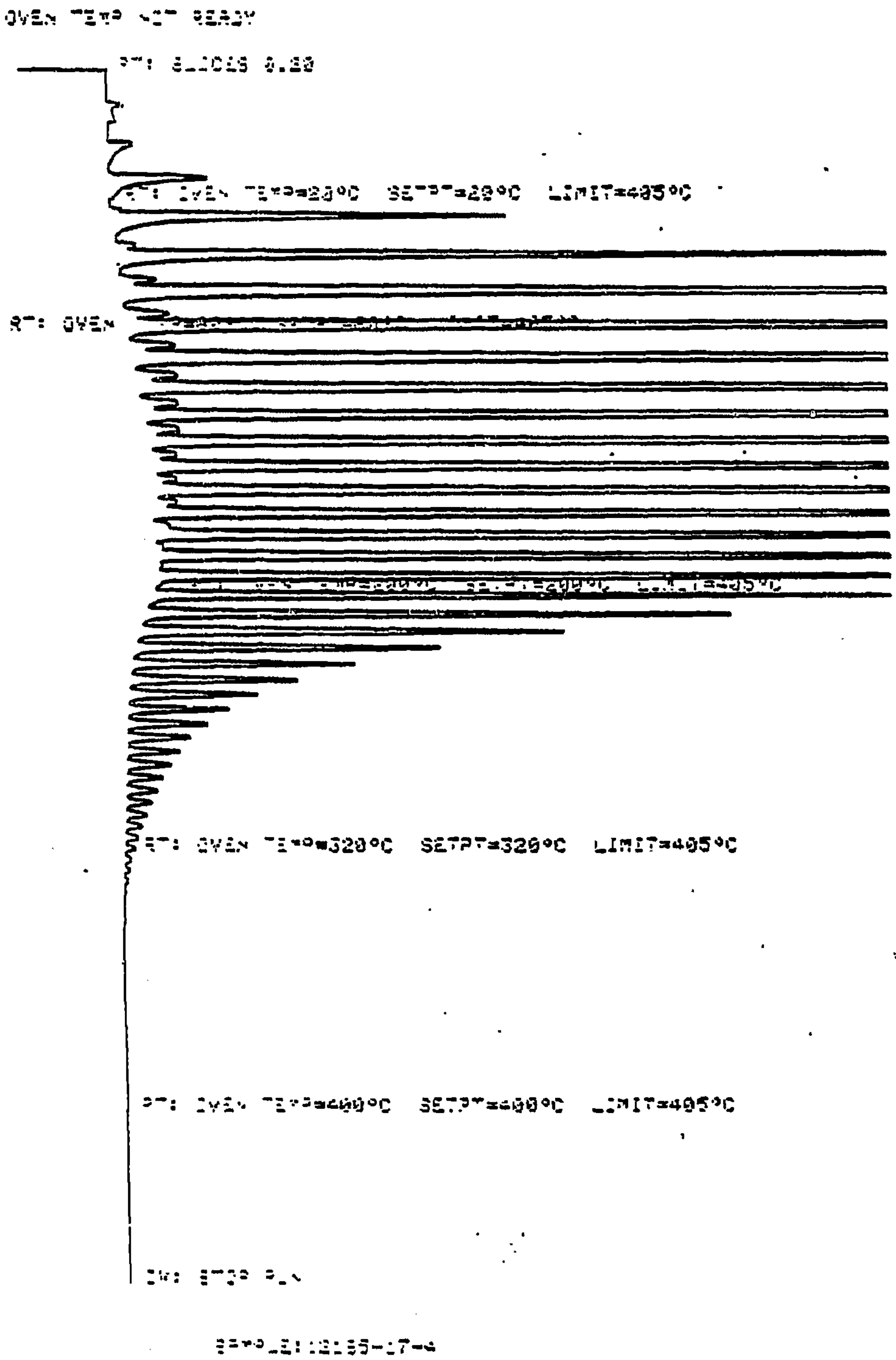

OVEN TEMP NOT READY
RT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B179



OVEN TEMP NOT READY
OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
SETPT=400°C

Fig. B180

Table B13

FILE: 1218517A TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-17
CATALYST CO/X9/X10-U103 80 CC 37.1 G AFTER USE:49.1 G (+ 12.0 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-78-24)

RUN & SAMPLE NO.	12185-17-01	185-17-02	185-17-03	185-17-04
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.5	46.0	71.0	94.0
PRESSURE,PSIG	300	300	300	300
TEMP. C	240	241	241	241
FEED CC/MIN	400	400	400	400
HOURS FEEDING	22.50	23.50	25.00	23.00
EFFLNT GAS LITER	374.05	409.20	439.85	437.50
GM AQUEOUS LAYER	37.52	38.82	39.13	28.50
GM OIL	5.12	10.56	12.77	7.10
MATERIAL BALANCE				
GM ATOM CARBON %	90.19	92.83	93.55	95.34
GM ATOM HYDROGEN %	90.00	98.07	99.40	99.11
GM ATOM OXYGEN %	100.11	100.44	99.71	101.36
RATIO CHX/(H2O+CO2)	0.5485	0.6486	0.7050	0.6551
RATIO X IN CHX	2.4868	2.3815	2.3890	2.4772
USAGE H2/CO PRODT	2.8727	2.6438	2.4910	2.6103
FEED H2/CO FRM EFFLNT	0.9979	1.0565	1.0625	1.0395
RESIDUAL H2/CO RATIO	0.6917	0.7651	0.7844	0.8154
RATIO CO2/(H2O+CO2)	0.0275	0.0158	0.0246	0.0281
K SHIFT IN EFFLNT	0.0195	0.0123	0.0198	0.0236
SPECIFIC ACTIVITY SA	0.9322	0.8442	0.8603	0.6164
CONVERSION				
ON CO %	14.04	15.51	16.30	12.49
ON H2 %	40.41	38.81	38.21	31.36
ON CO+H2 %	27.21	27.48	27.58	22.11
PRDT SELECTIVITY,WT %				
CH4	20.76	14.71	14.75	19.18
C2 HC'S	2.83	1.87	1.80	2.04
C3H8	2.48	1.97	2.21	3.10
C3H6=	5.60	4.32	3.35	3.66
C4H10	2.95	2.46	2.55	3.26
C4H8=	5.99	4.55	3.76	3.93
C5H12	2.98	2.46	2.44	3.44
C5H10=	4.62	3.39	2.77	3.02
C6H14	3.41	2.81	2.79	3.64
C6H12= & CYCLO'S	3.75	2.70	2.02	2.20
C7+ IN GAS	18.29	13.82	12.86	14.79
LIQ HC'S	26.33	44.93	48.70	37.74
TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	40.61	29.88	28.42	35.17
C5 -420 F	42.27	38.80	37.64	38.04
420-700 F	14.38	25.25	26.93	21.96
700-END PT	2.74	6.07	7.01	4.83

Table B13 (continued)

FILE: 1218517A TSS3Q1 A1

C5+-END PT	59.39	70.12	71.58	64.83
ISO/NORMAL MOLE RATIO				
C4	0.0445	0.0403	0.0326	0.0285
C5	0.0929	0.0846	0.0777	0.0589
C6	0.0352	0.0670	0.0294	0.0000
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	0.4222	0.4346	0.6281	0.8078
C4	0.4762	0.5219	0.6542	0.8026
C5	0.6270	0.7062	0.8550	1.1062
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.7945	0.8341	0.8408	0.8231
RATIO CH4/(1-A)**2	4.9183	5.3496	5.8176	6.1315
ALPHA FRM CORRELATION	0.8299	0.8249	0.8237	0.8218
ALPHA (EXPTL/CORR)	0.9574	1.0112	1.0207	1.0016
W%CH4 FRM CORRELATION	16.2130	17.9825	18.3584	18.9434
W%CH4 (EXPTL/CORR)	1.2807	0.8183	0.8034	1.0124
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLD OIL	CLD OIL	CLD OIL	CLD OIL
DENSITY (* 40 C)	0.765	0.742	0.757	0.998
N, REFRACTIVE INDEX	1.4208*	1.4231*	1.4229*	1.3314*
SIMULT'D DISTILATN				
10 WT % @ DEG F	298	303	303	335
16	338	344	344	372
50	487	517	517	525
84	662	687	688	683
90	704	726	728	721
RANGE(16-84 %)	324	343	344	311
WT % @ 420 F	35.00	30.30	30.30	29.00
WT % @ 700 F	89.60	86.50	85.60	87.20

VIII. Run 32 (12200-19) with Catalyst 32 (Co/X_{11}/UCC-103

The purpose of this run was to test the effectiveness of a new additive, X_{11}, in an intimately contacted cobalt/UCC-103 catalyst formulated by the method developed for Catalyst 11. It is to be compared with a similar catalyst promoted with X_9 and X_{10}, and with Catalyst 15 (Run 12185-08, cobalt/X_9/X_{10}/X_4/UCC-103), formulated by the method developed in the previous contract and one of the most effective catalysts developed to date. The theoretical concentration of cobalt and X_{11} were, respectively, 8.2 and 1.6 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B181-184. Simulated distillations of the C_5^+ product are plotted in Figs. B185-194. Carbon number product distributions are plotted in Figs. B195-204. Chromatograms from simulated distillations are reproduced in Figs. B205-214. Detailed material balances appear in Tables B14-15.

The run was conducted at temperatures of 240C, 260C and 270C successively. During the first 163 hours on stream at 240C the activity was similar to that of Catalyst 26 (cobalt/X_9/X_{10}), the syngas conversion ranging from 46.7 to 41.7 percent, the specific activity from 3.1 to 2.1. (An unusually large scatter of the data is probably due to error generated in handling the large quantity of wax produced.) By linear least squares analysis the loss of syngas conversion was estimated at one percentage point every 36.5 hours, the loss of specific activity at one specific activity unit every 4340 hours. The errors associated with these calculations suggest that longer runs are needed for reliable determinations of stability.

At 260C the conversion rose to 56.5 percent, with specific activity of 2.07. After 216 hours at this reaction temperature the conversion was 57.6 percent and the specific activity 1.8. By linear least squares this was equivalent to an estimated gain in conversion of one percentage point every 370 hours, and a loss in specific activity of one specific activity unit every 1065 hours. Unlike Catalyst 26, the stability at 260C was excellent and the activity was comparable to that of Catalyst 15, one of the most effective developed to date.

At 270C, however, both the activity and selectivity deteriorated. After 73 hours at this reaction temperature the conversion had decreased to 56.4 percent.

The catalyst compares with Catalyst 15 in detail as follows:

	Catalyst 32 $Co/X_{11}/UCC\text{-}103$	Catalyst 15 $Co/X_4/X_{10}/X_4/UCC\text{-}103$
Syngas conversion, pct	56.5	56.0
Specific activity	2.1	2.0
Methane, pct	7.95	11.68
C_2-C_4, pct	11.00	15.61
C_5-420F, pct	36.73	44.20
420-700F, pct	26.10	22.96
700F+, pct	18.22	5.55
C_4 olefins/paraffins	1.78	0.93

- more -

	Catalyst 32 $Co/X_{11}/UCC-103$	Catalyst 15 $Co/X_4/X_{10}/X_4/UCC-103$
Total motor fuels, pct	62.83	67.16
C_5^+, pct	81.05	72.71

Total motor fuels, which was below that of Catalyst 15, was depressed by a combination of reduced production of low-grade gasoline and elevated production of wax.

This was more than offset, however, by four notably useful properties. Production of methane was unusually low at about 8 percent as against nearly 12 percent for Catalyst 15. Total C_5^+ was more than 80 percent as against approximately 70 percent usually obtained. Production of 420-700F diesel fuel was more than 26 percent as against 23 percent for Catalyst 15. And the olefin content of the C_4's was 64 percent as against 48 percent for Catalyst 15.

The Schulz-Flory plots were linear except for the excess methane. Isomerization of the pentanes was at the customarily low level of less than 10 percent.

For its demonstration of X_{11}'s contribution to both selectivity and stability, this is one of the most valuable catalysts developed thus far.

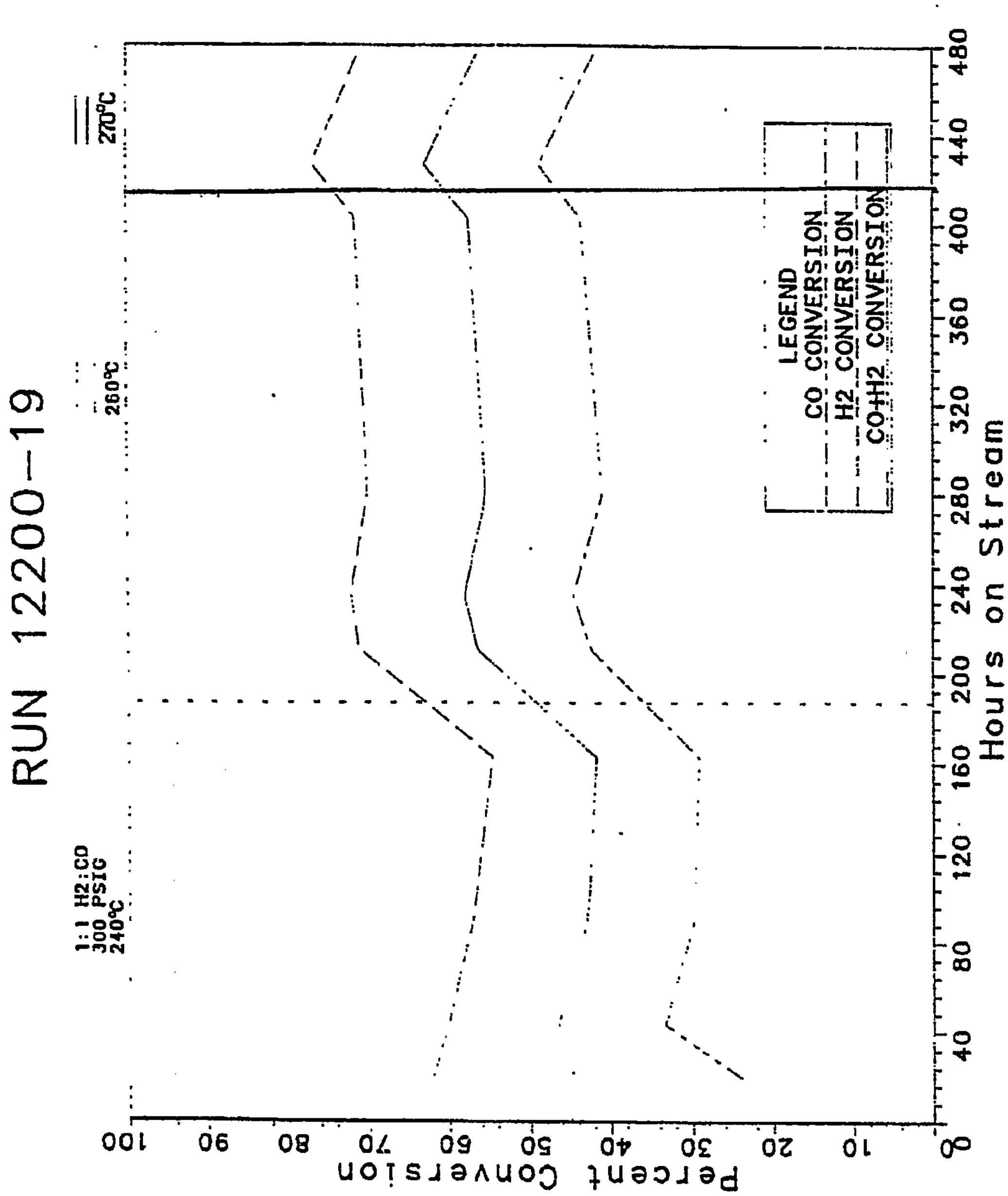

RUN 12200-19
1:1 H2:CO
300 PSIG
240°C
260°C
270°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440
480

Fig. B181

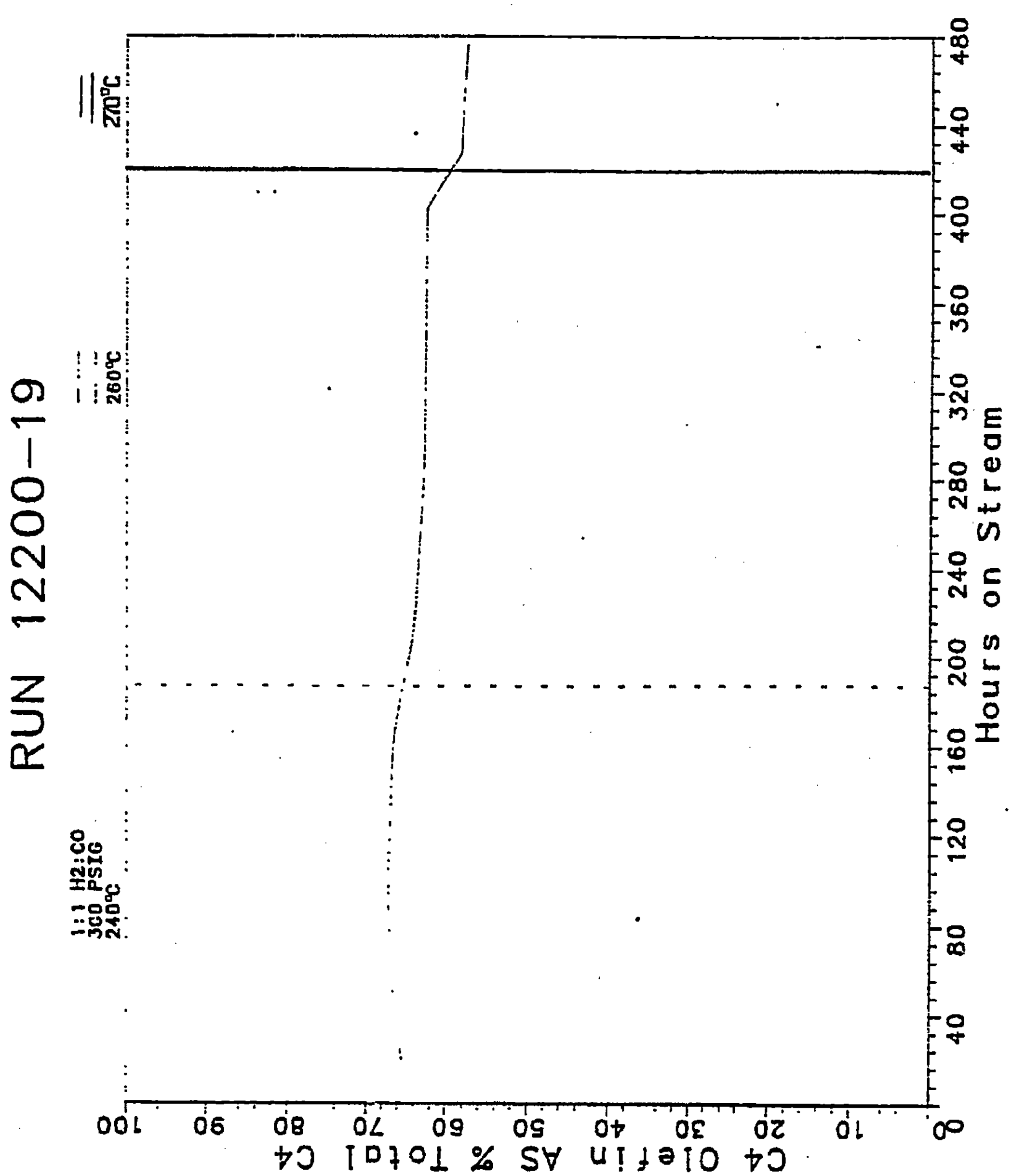
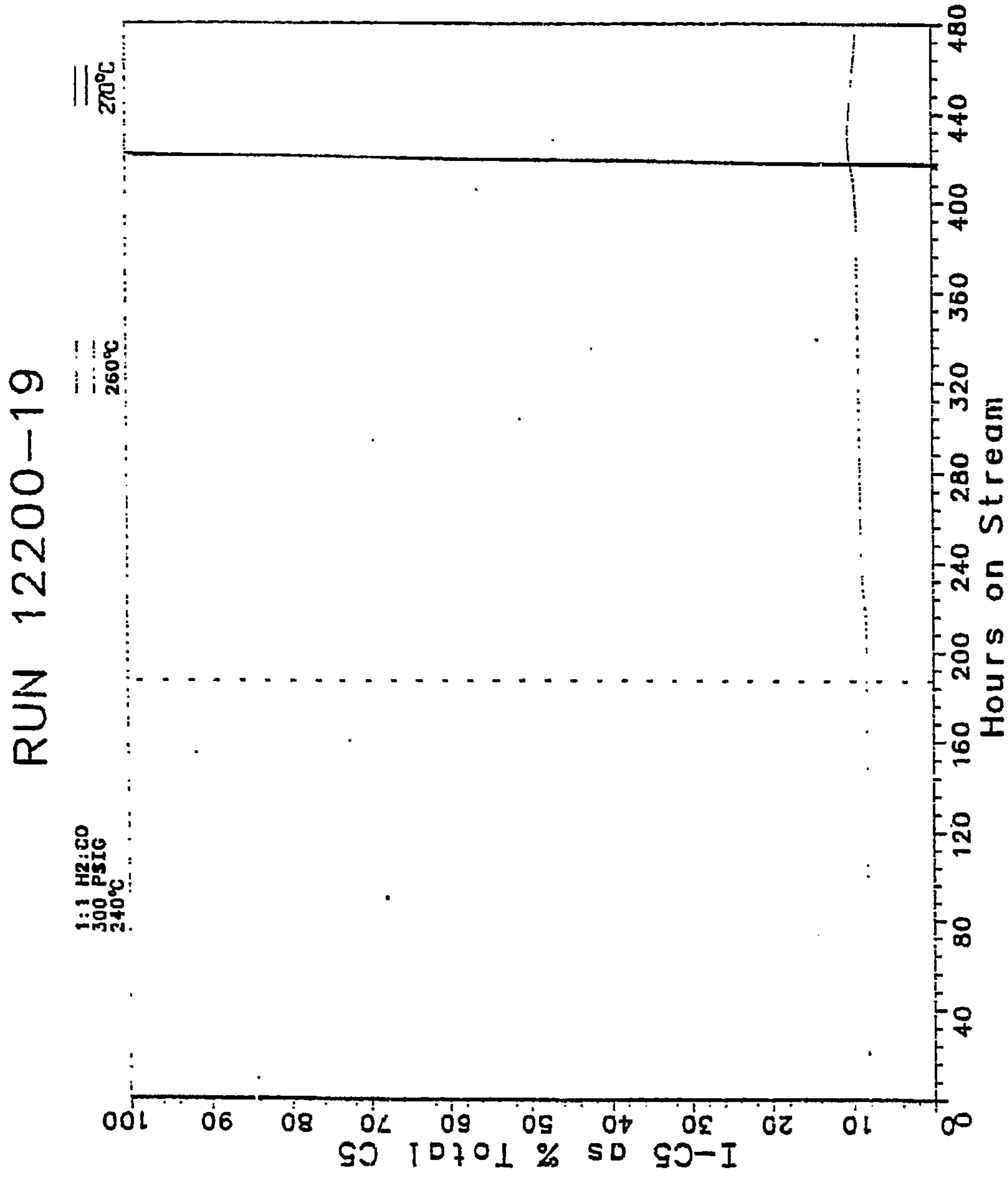

RUN 12200-19
1:1 H2:CO
300 PSIG
240°C
260°C
270°C
Hours on Stream
0
40
80
120
160
200
240
280
320
360
400
440
480
C4 Olefin AS % Total C4
10
20
30
40
50
60
70
80
90
100

Fig. B182



RUN 12200-19
1:1 H2:CO
300 PSIG
240°C
260°C
270°C
Hours on Stream
0
40
80
120
160
200
240
280
320
360
400
440
480
I-C5 as % Total C5
10
20
30
40
50
60
70
80
90
100

Fig. B183

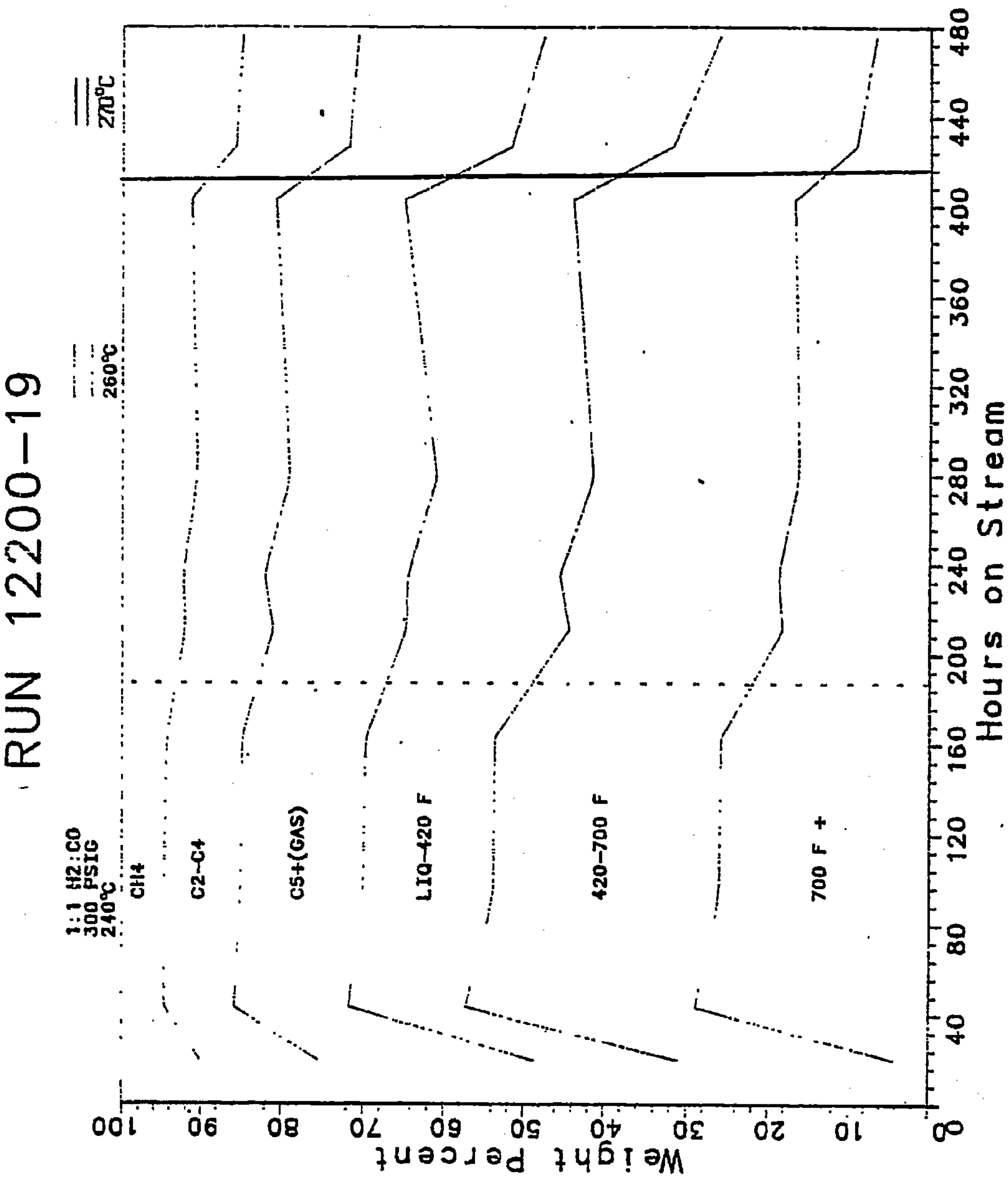

RUN 12200-19
1:1 H2:CO
300 PSIG
240°C
260°C
270°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0 10 20 30 40 50 60 70 80 90 100
40 80 120 160 200 240 280 320 360 400 440 480

Fig. B184

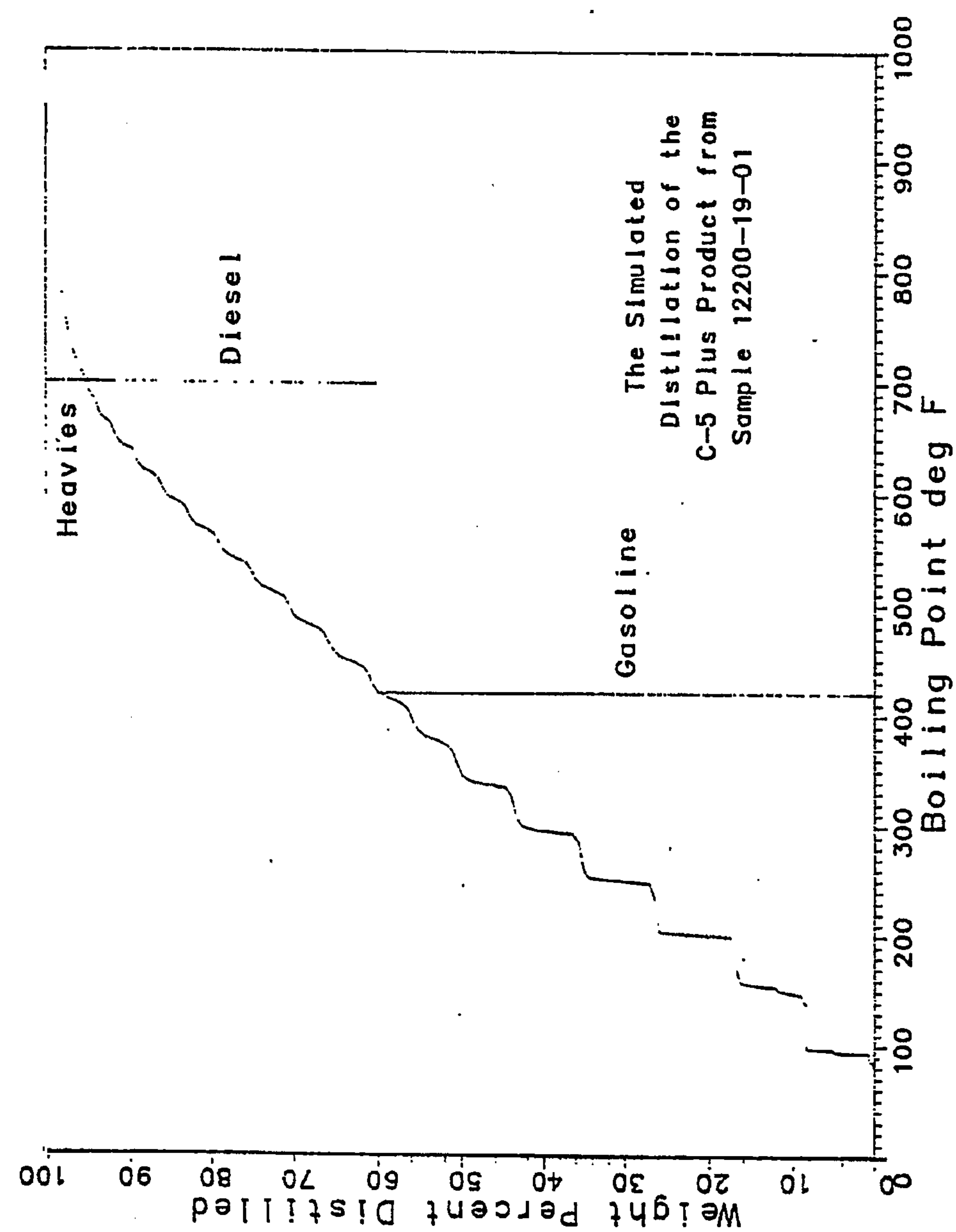
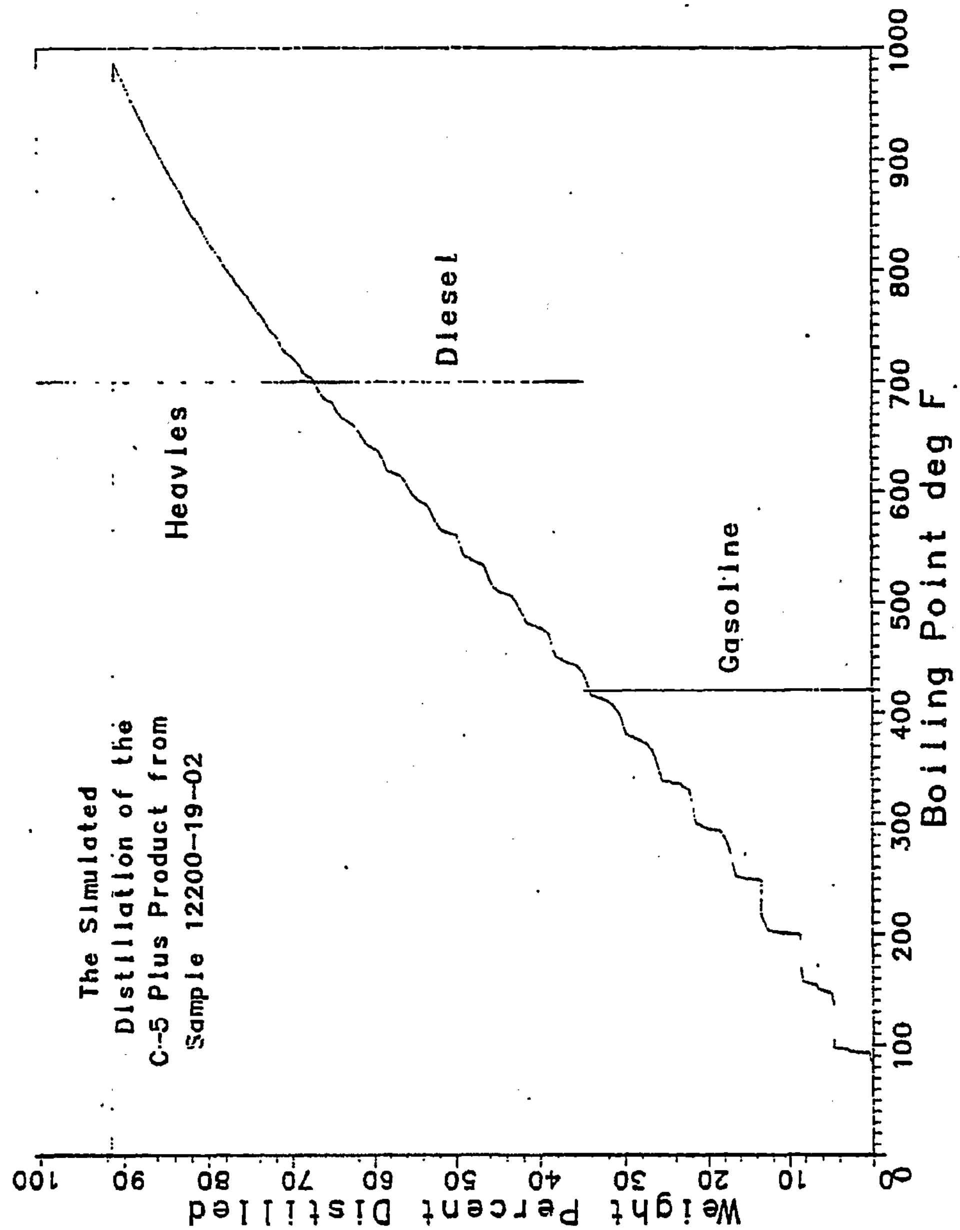
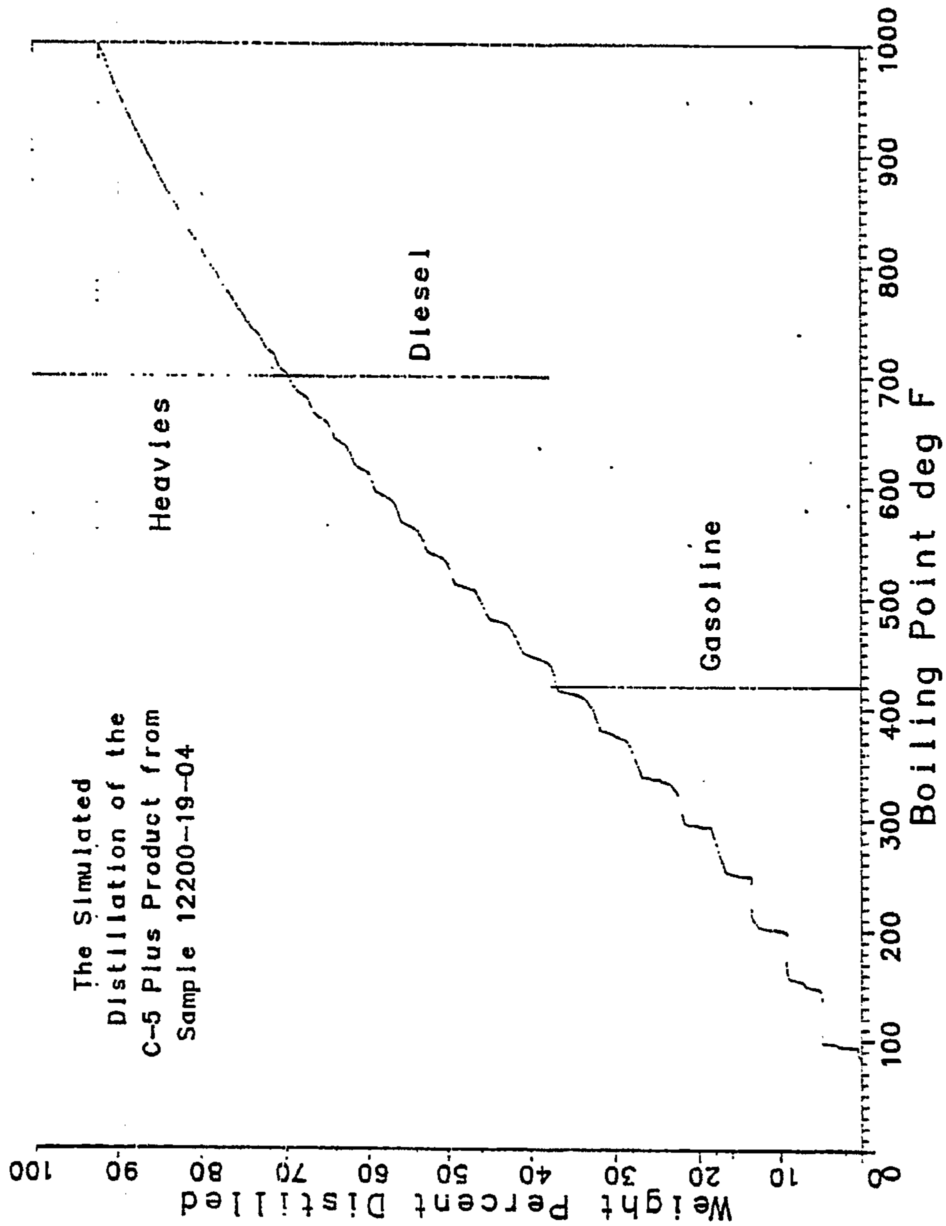

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-19-01
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B185



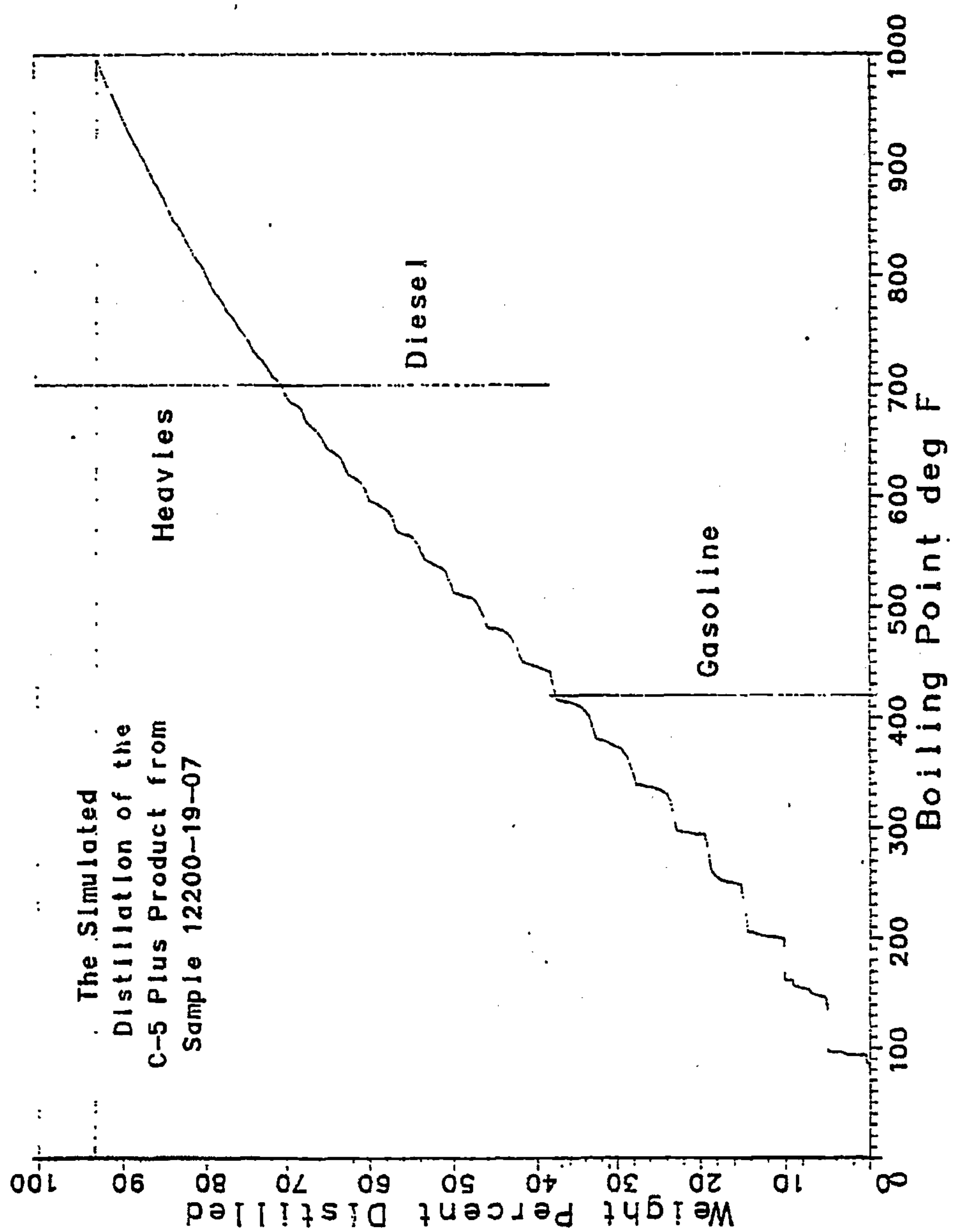
The Simulated Distillation of the C-5 Plus Product from Sample 12200-19-02
Heavies
Diesel
Gasoline
Boiling Point deg F
0 100 200 300 400 500 600 700 800 900 1000
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B186



The Simulated Distillation of the C-5 Plus Product from Sample 12200-19-04
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. B187



The Simulated Distillation of the C-5 Plus Product from Sample 12200-19-07
Heavies
Diesel
Gasoline
Boiling Point deg 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. B188

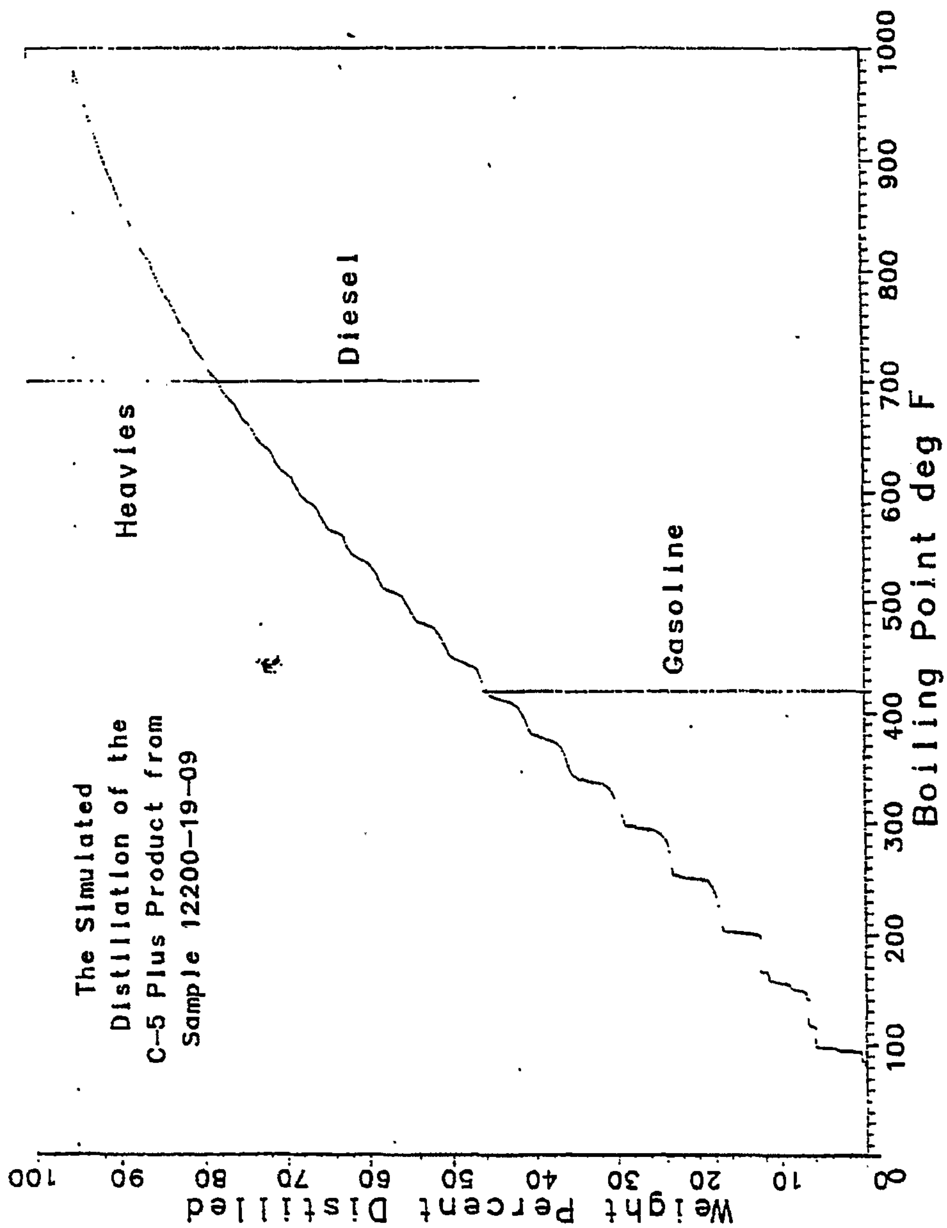

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-19-09
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B189

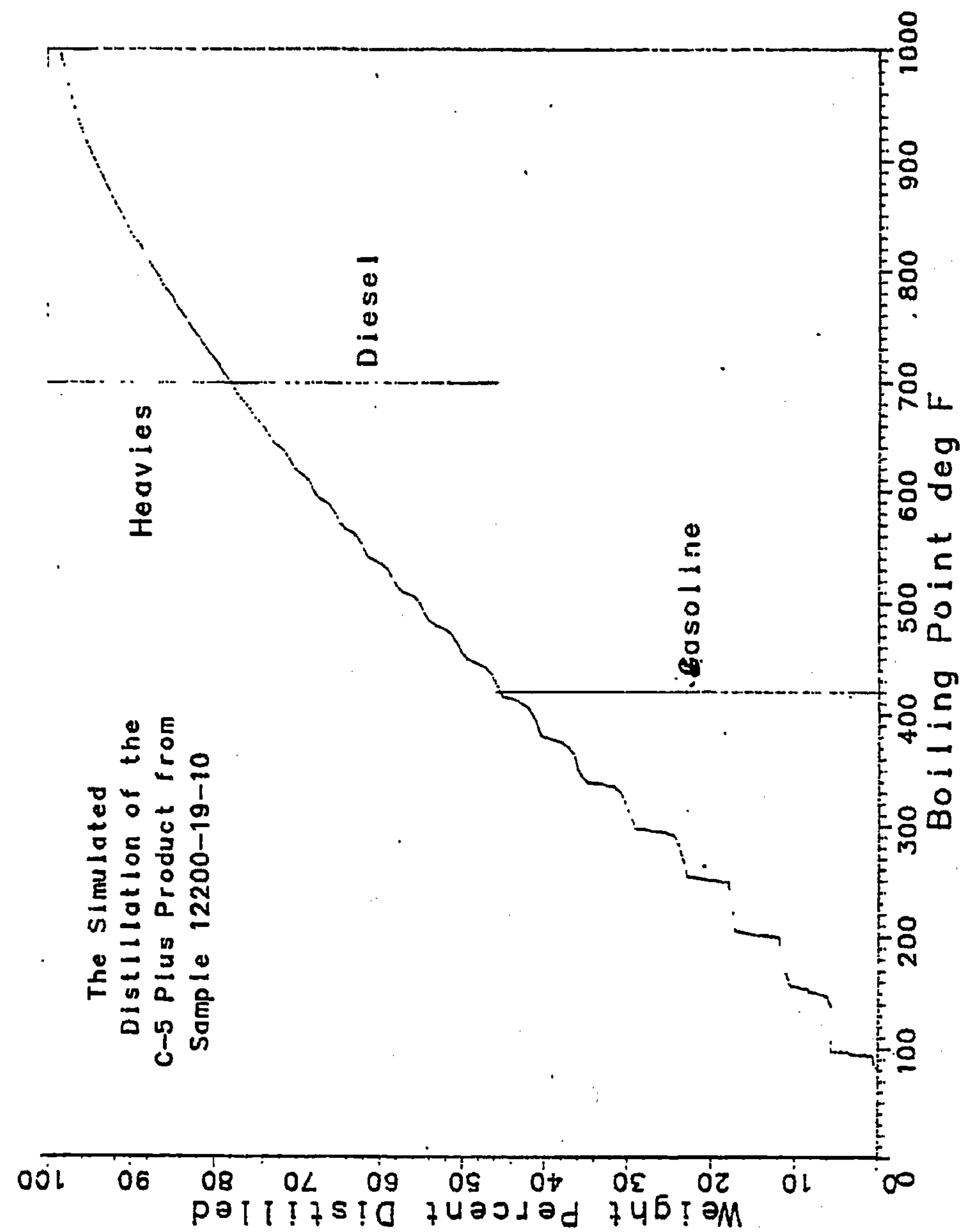

The Simulated Distillation of the C-5 Plus Product from Sample 12200-19-10
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B190

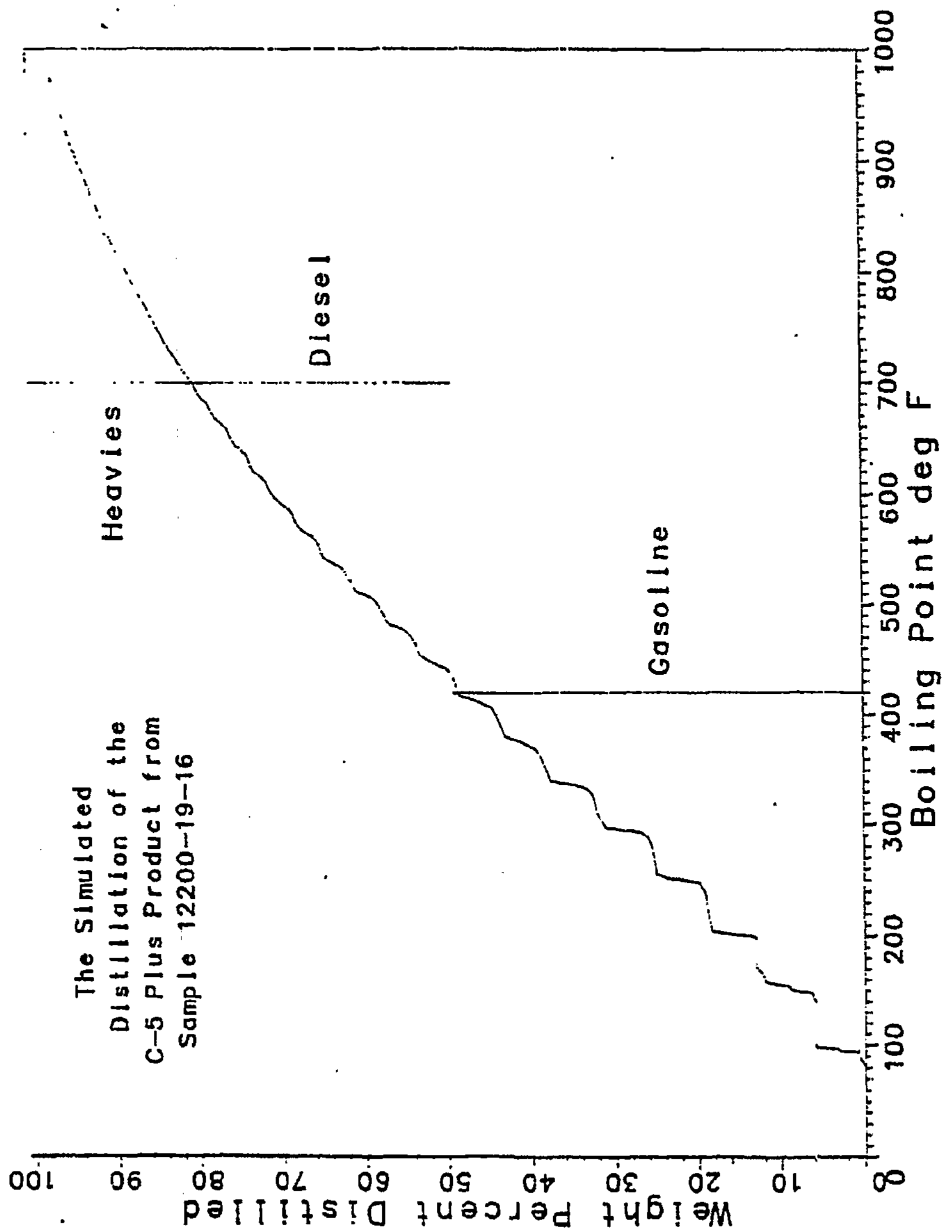

The Simulated Distillation of the C-5 Plus Product from Sample 12200-19-16
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B191

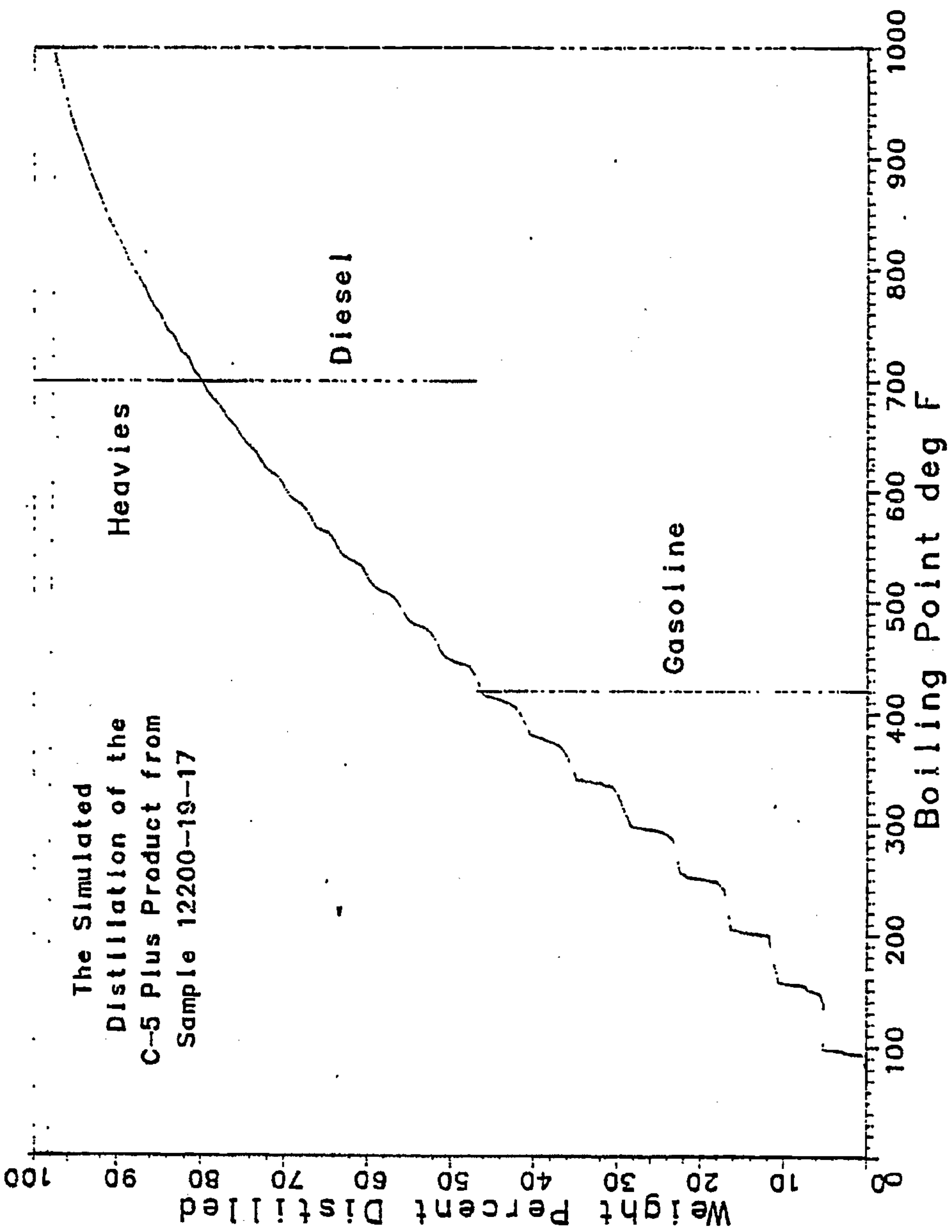

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-19-17
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B192

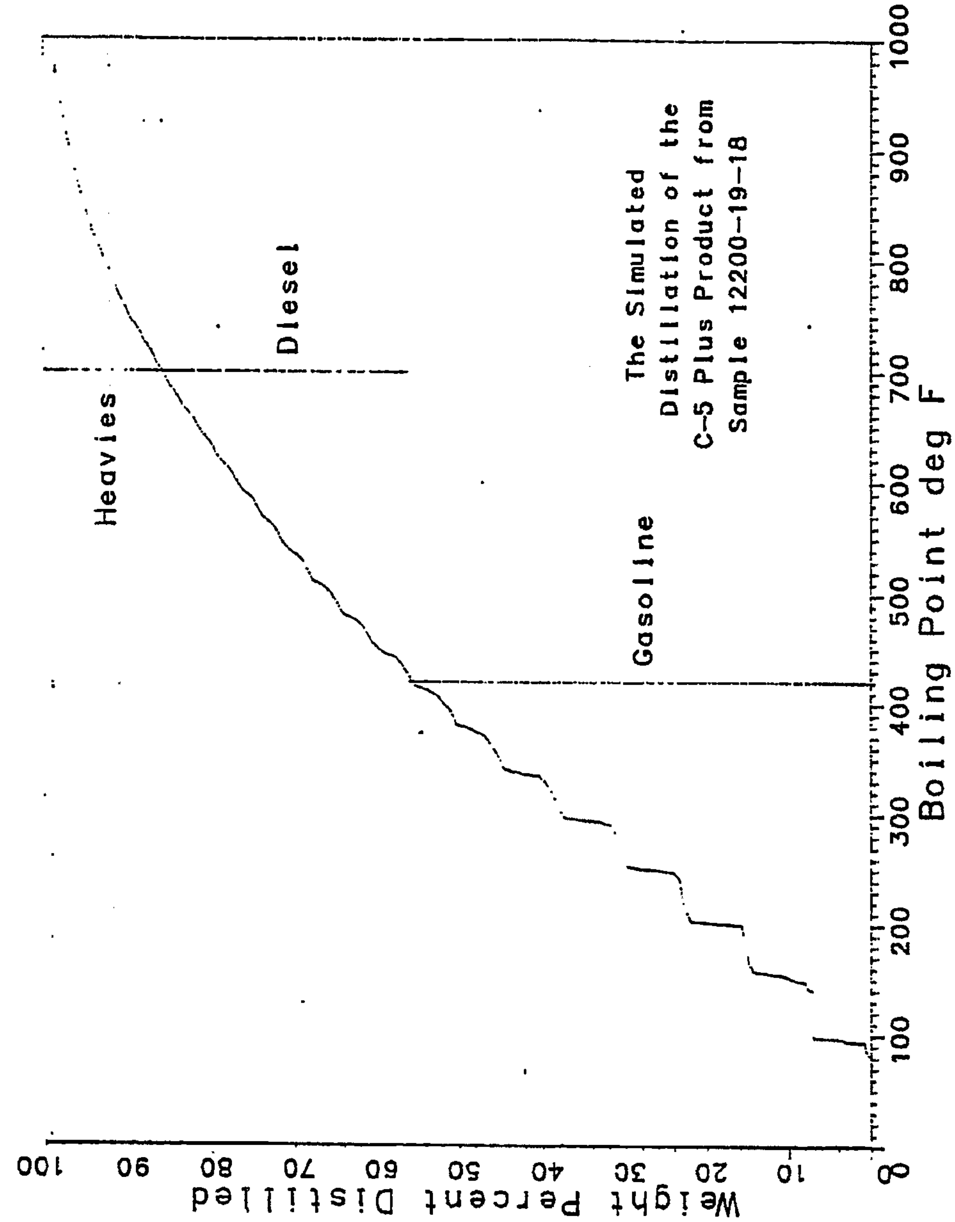

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-19-18
Boiling Point deg F
0 100 200 300 400 500 600 700 800 900 1000
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B193

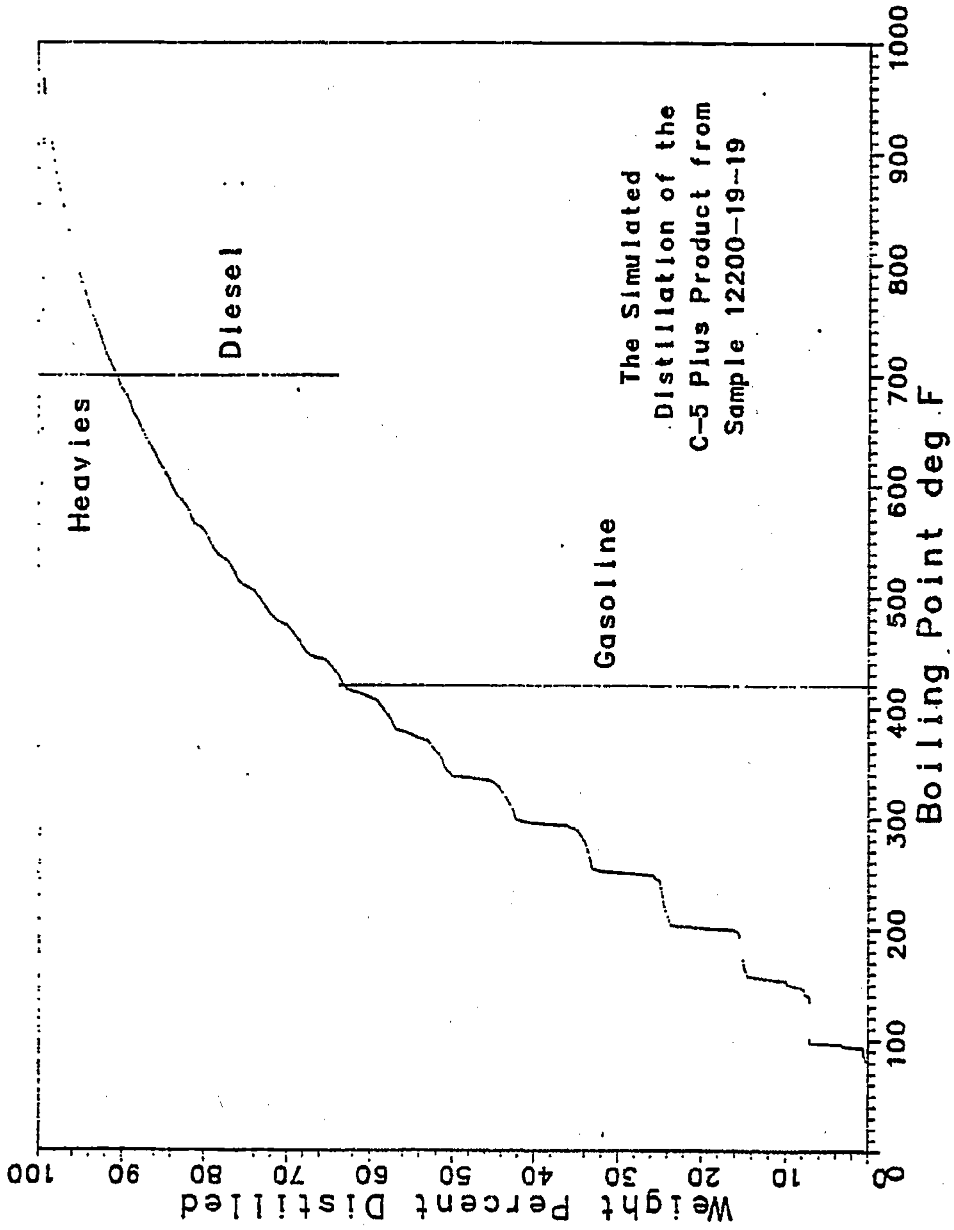

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-19-19
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B194

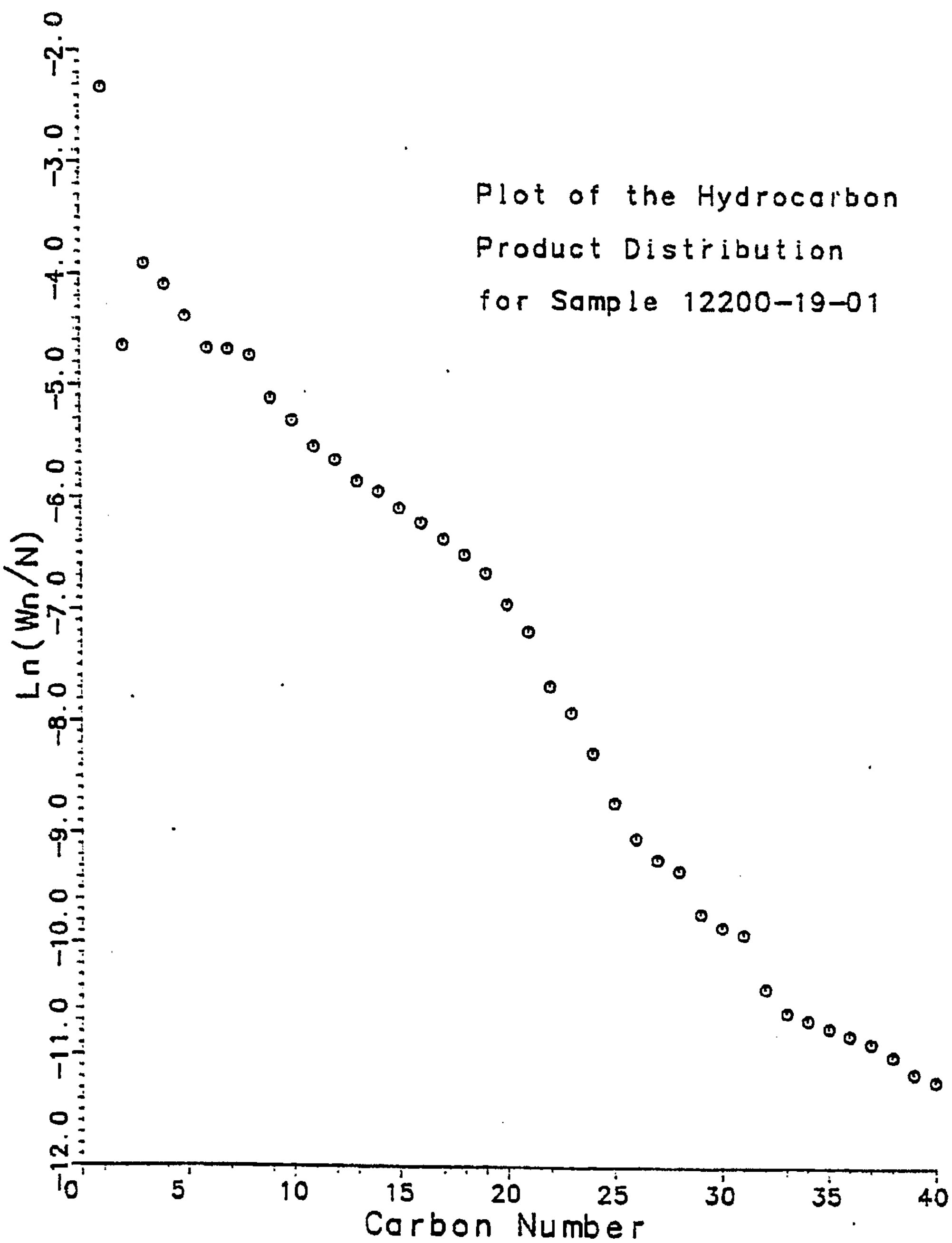
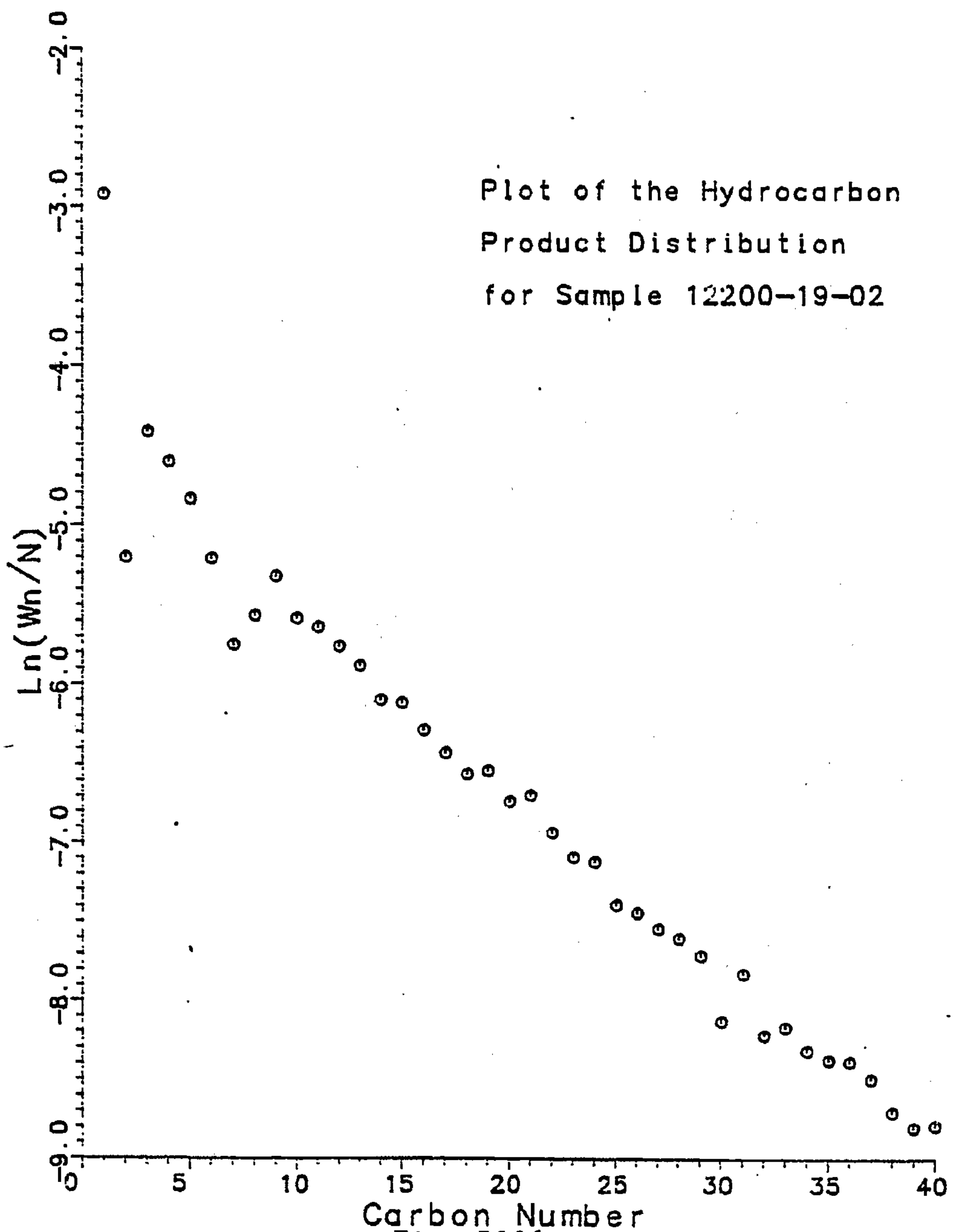

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B195


Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B196

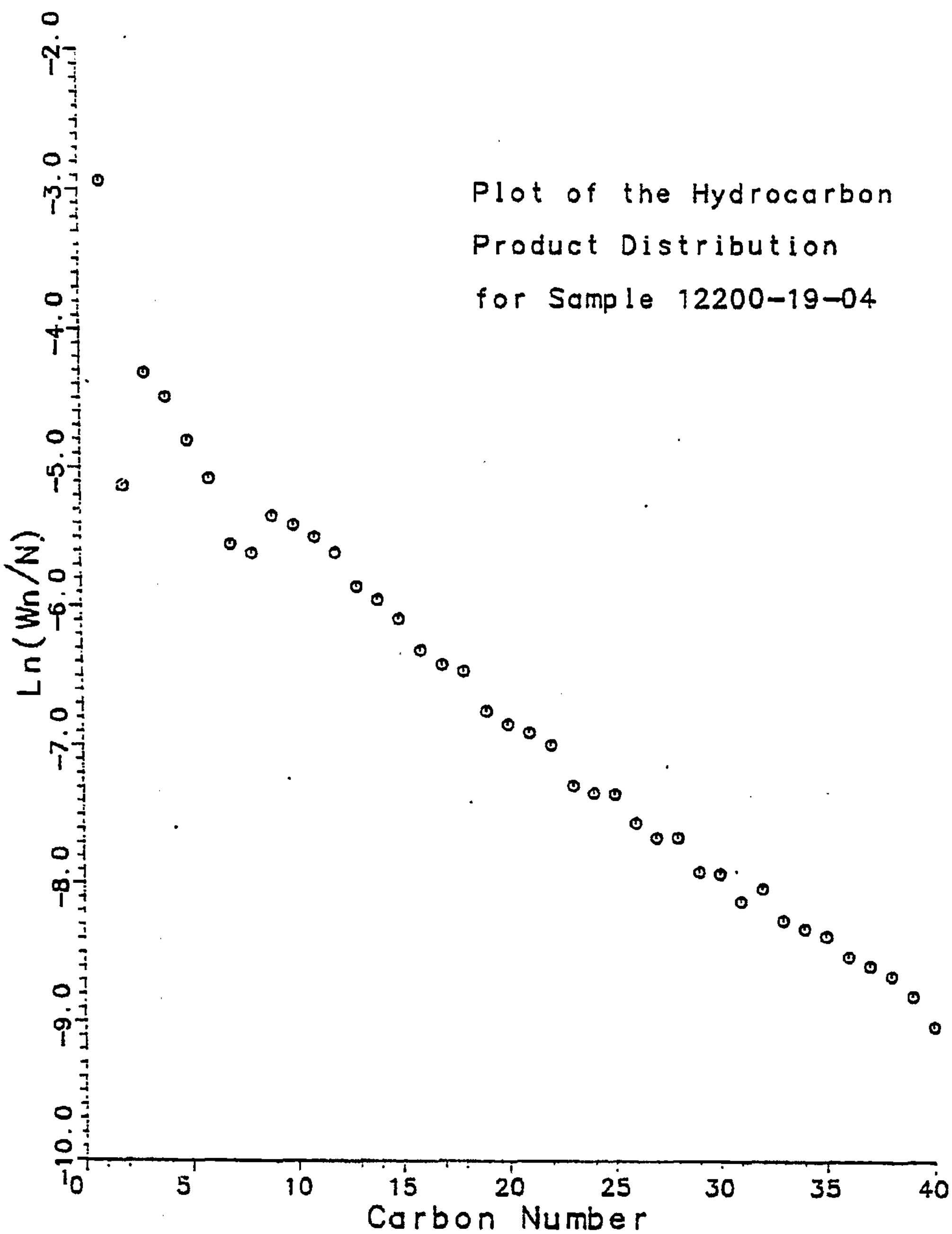
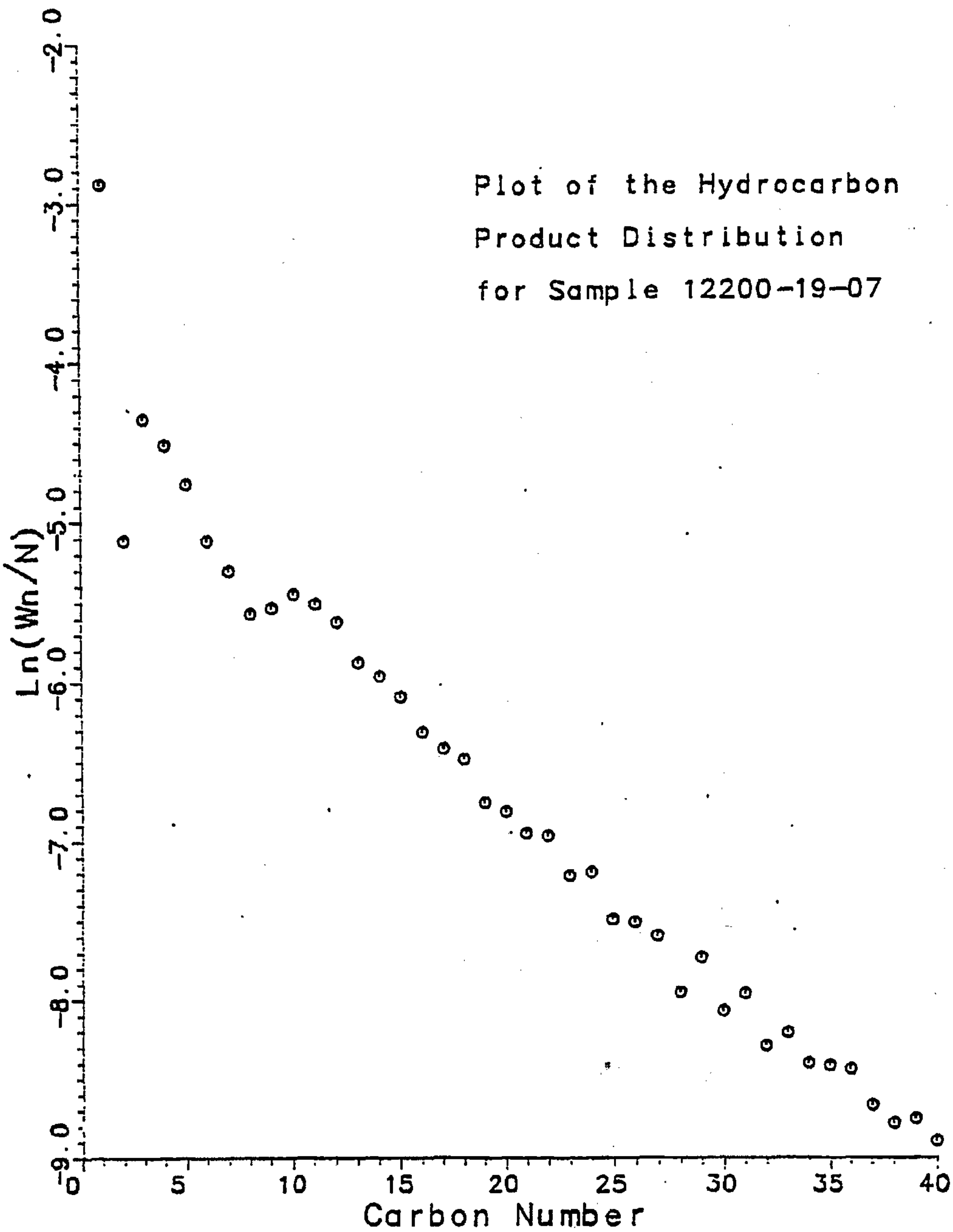

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-04
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B197



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-07
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B198

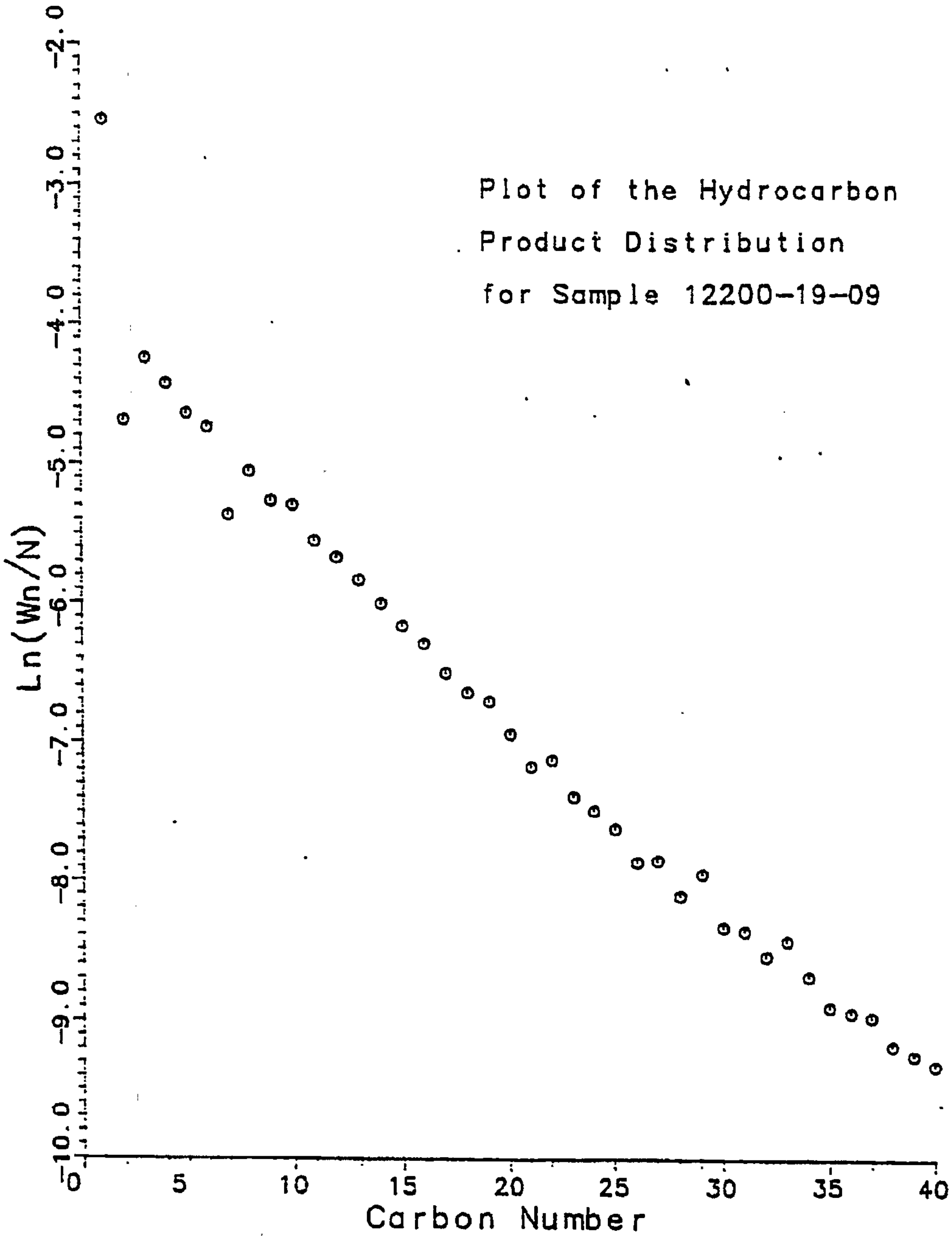
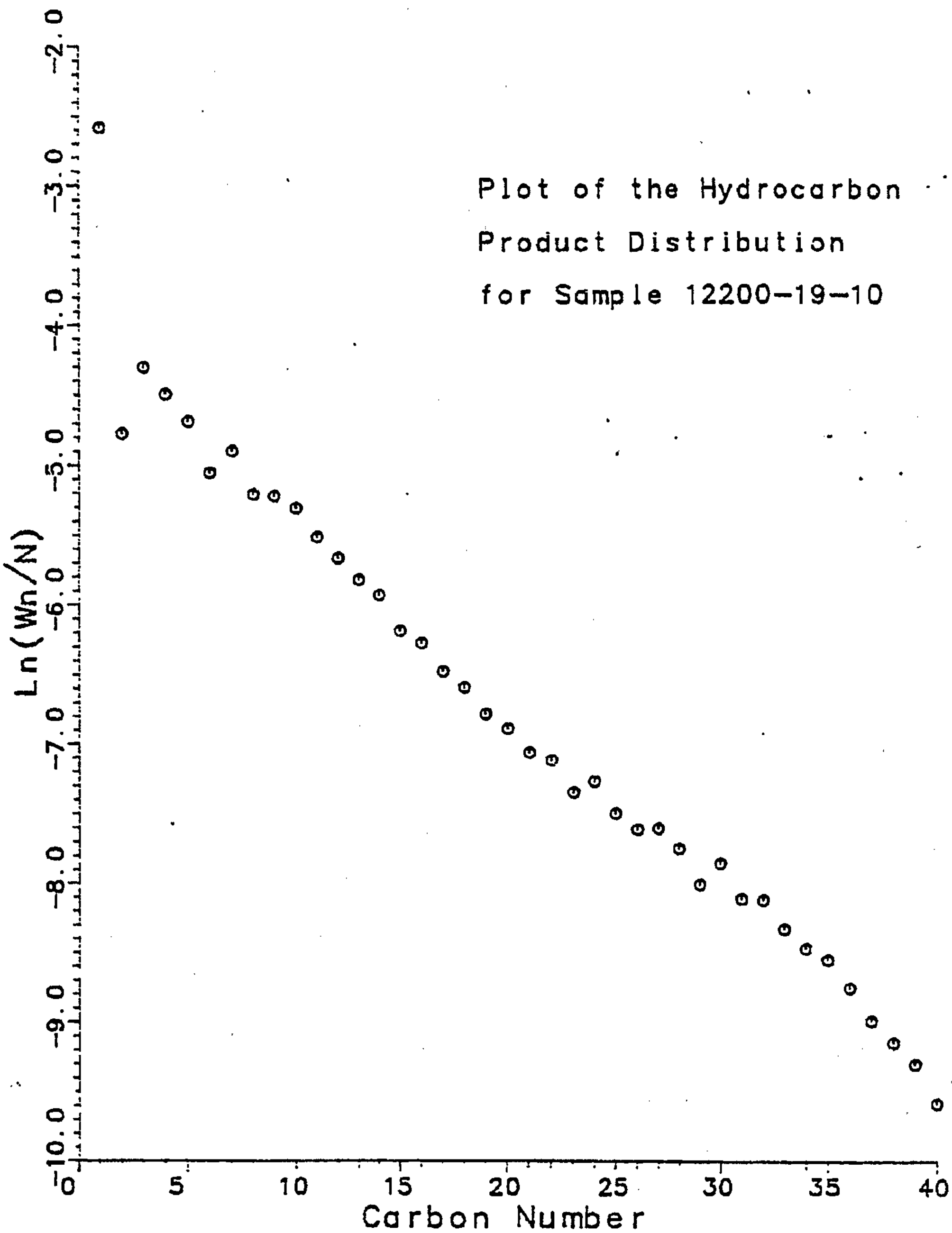
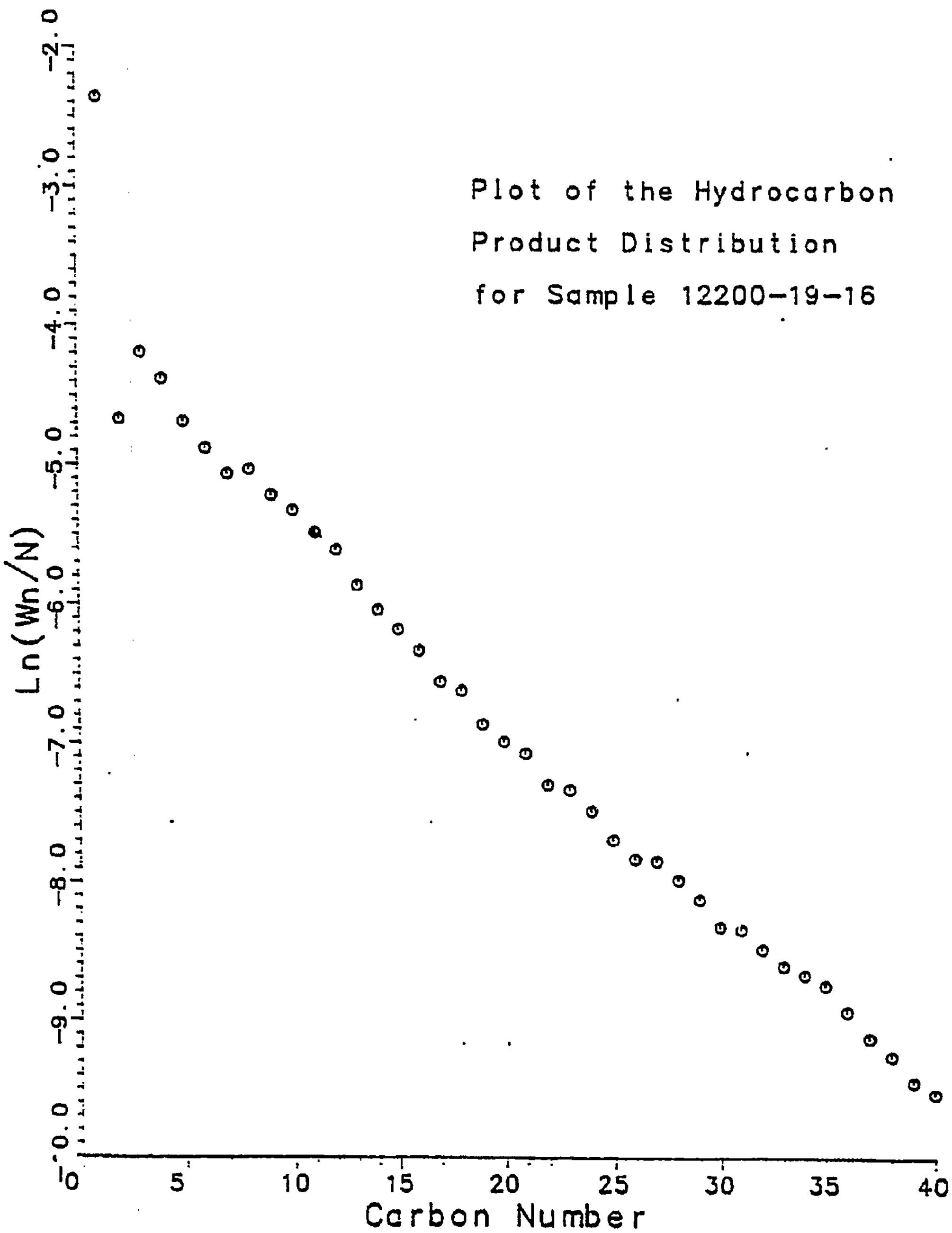

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-09
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

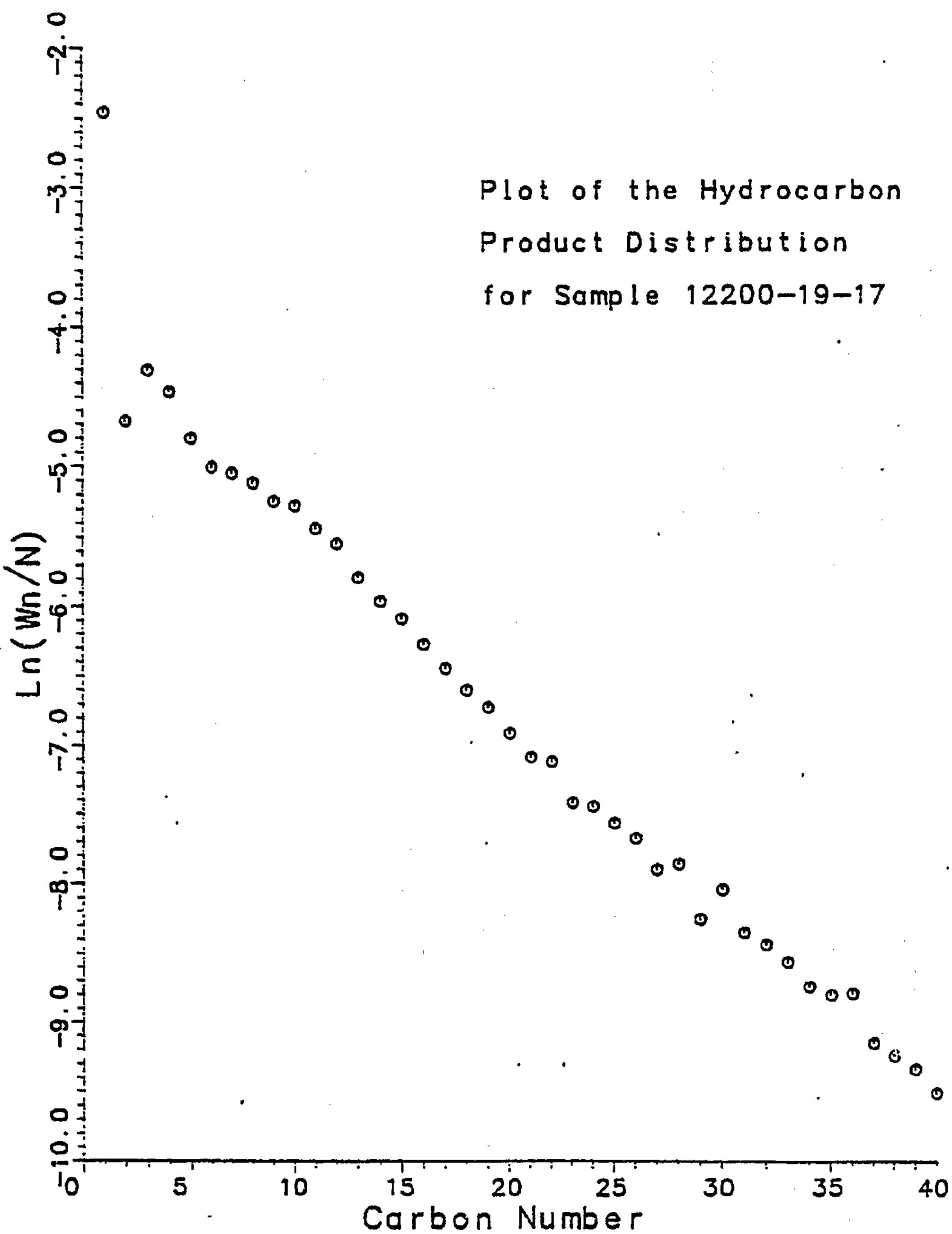
Fig. B199



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-10
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

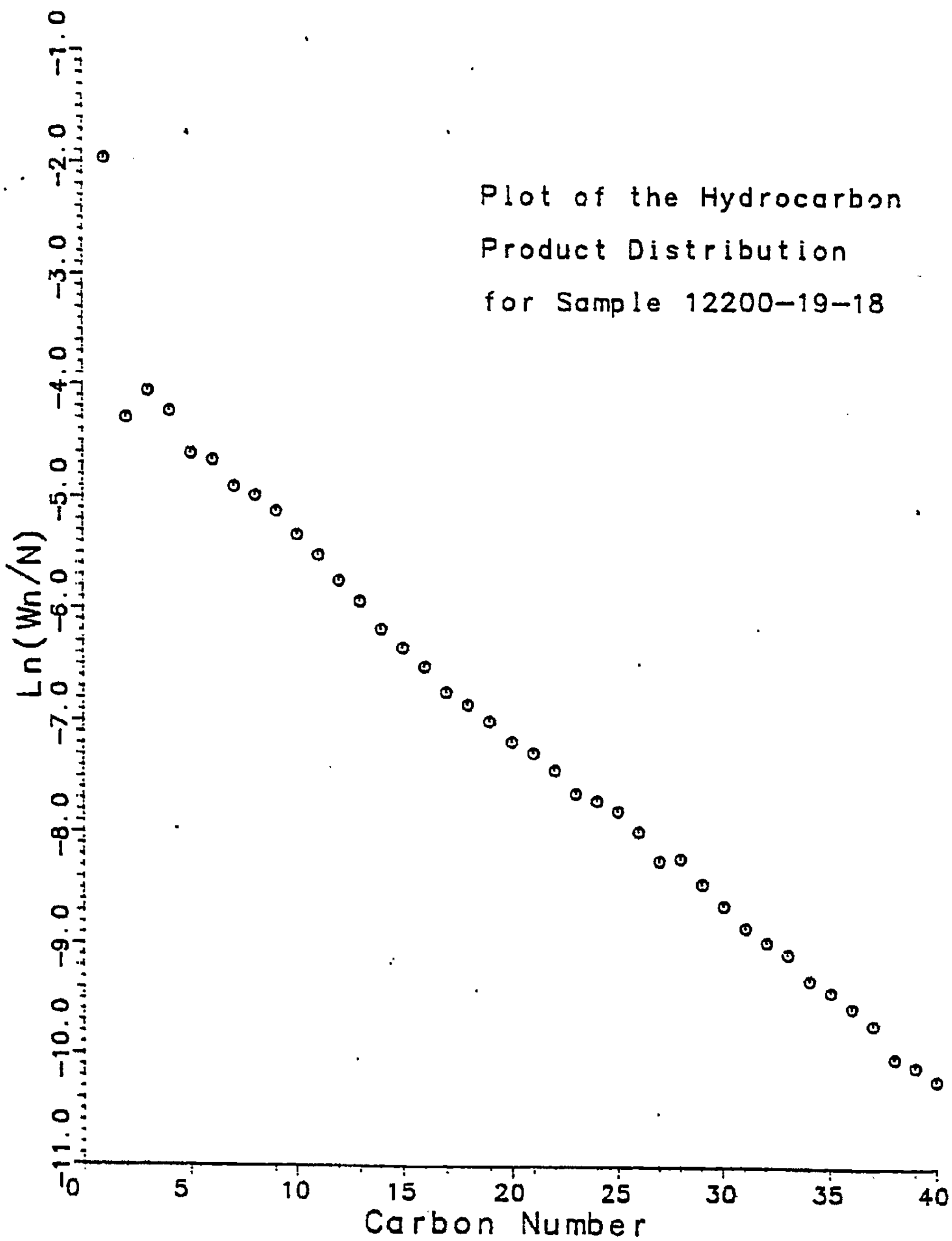
Fig. B200


Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-16
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. B201



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-17
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. B202



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-18
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
40
Carbon Number

Fig. B203

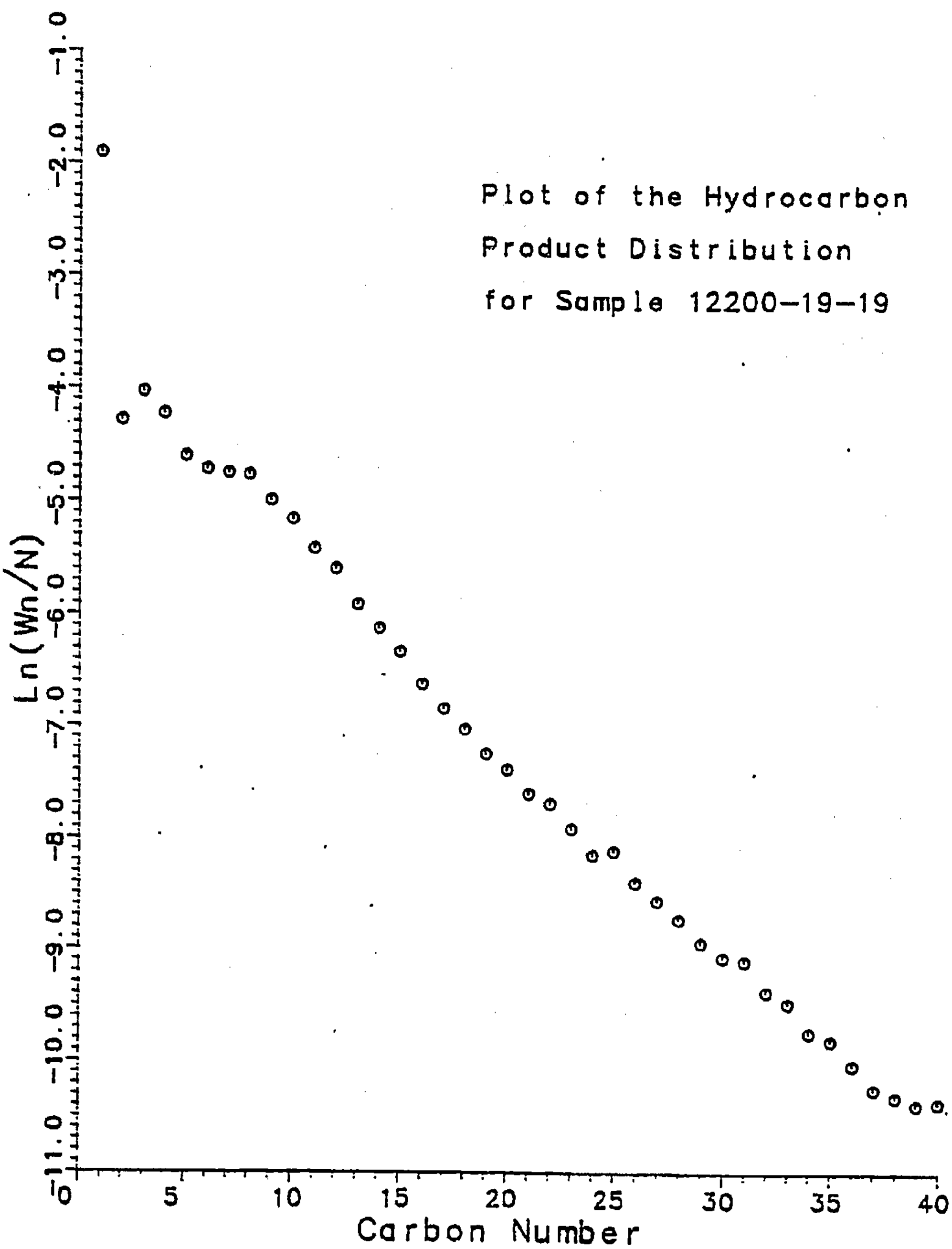

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-19-19
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B204

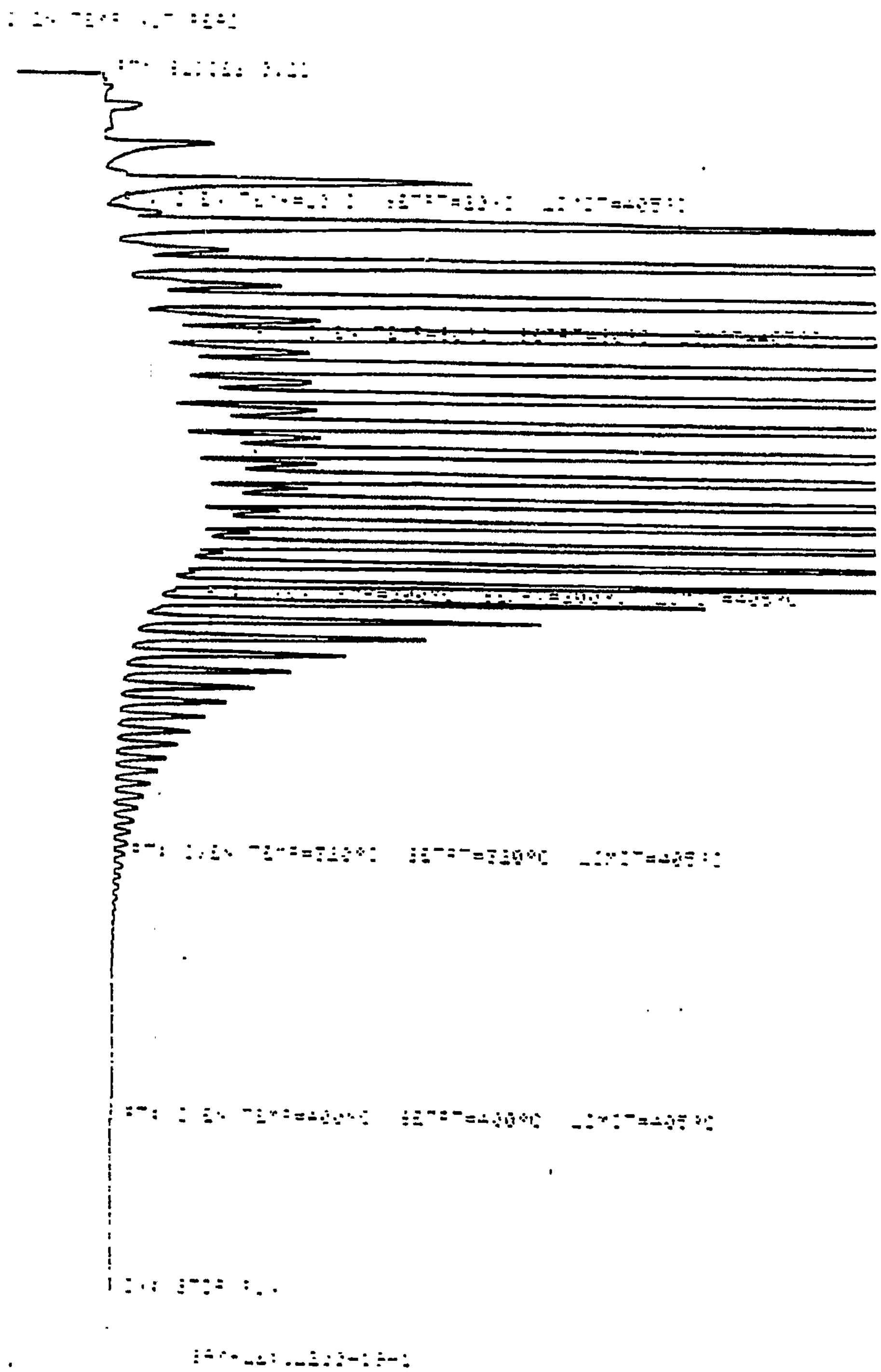


Fig. B205

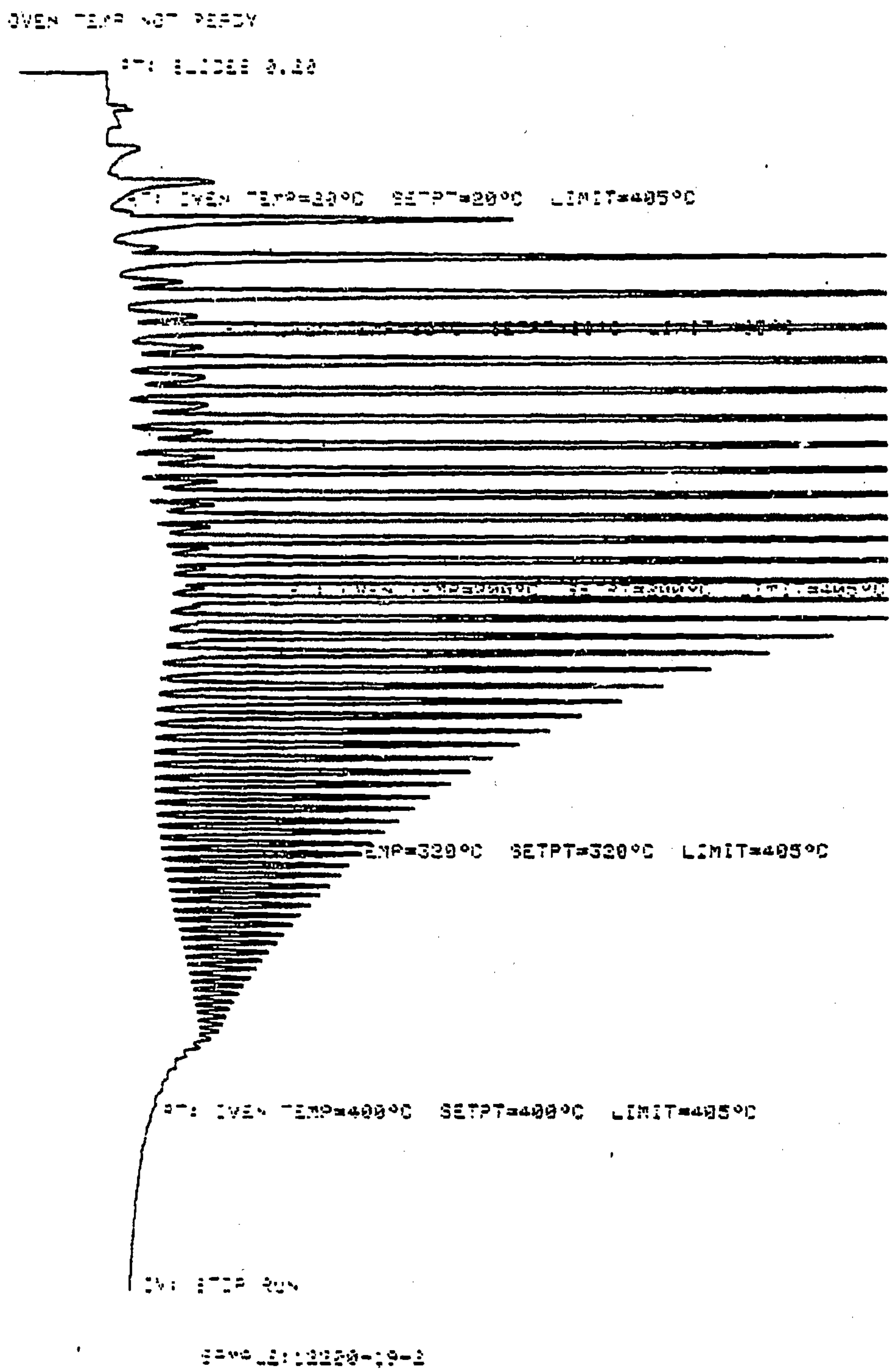

ST: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
EMP=320°C SETPT=320°C LIMIT=405°C

Fig. B206

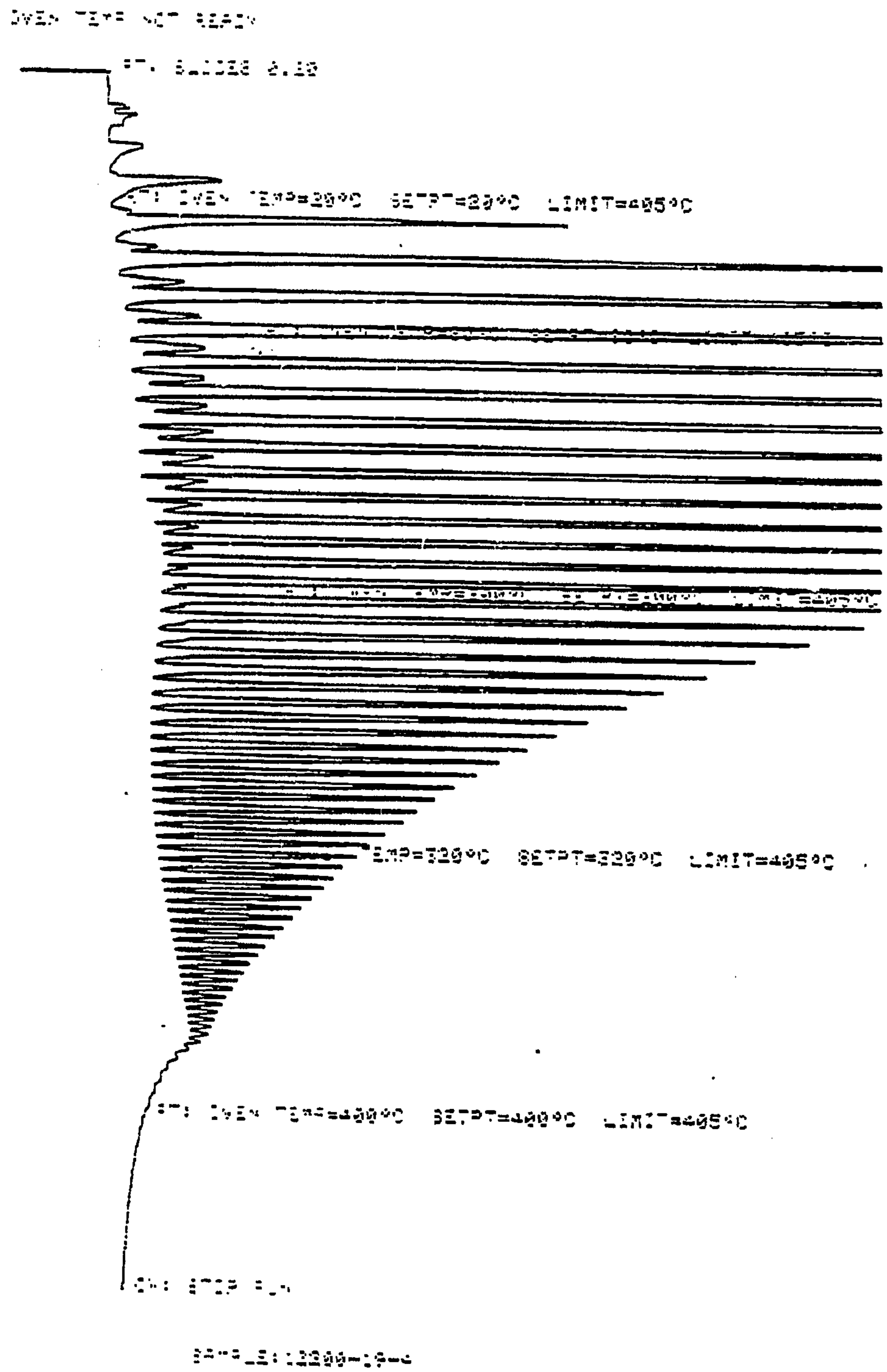


Fig. B207

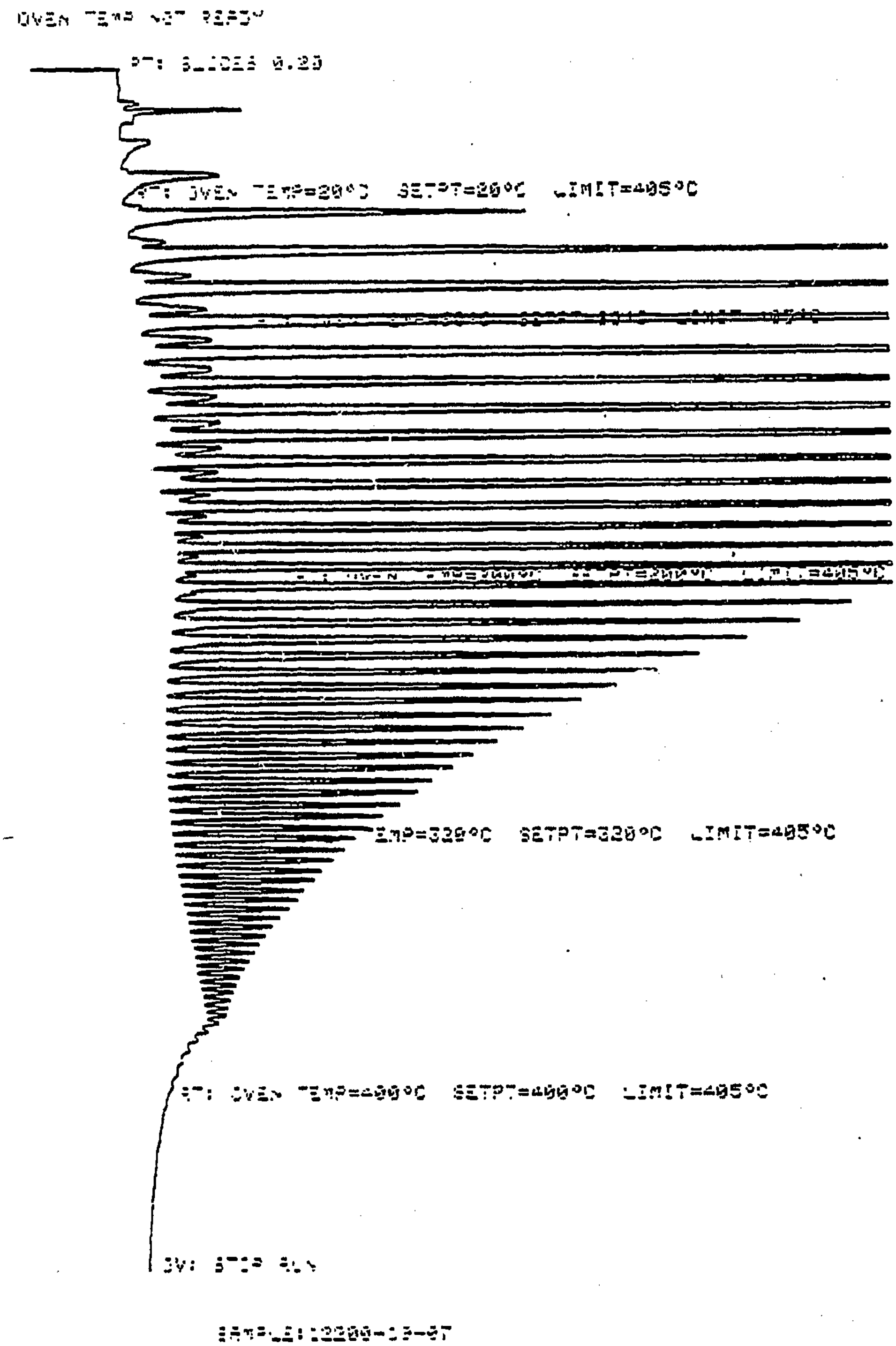


Fig. B208

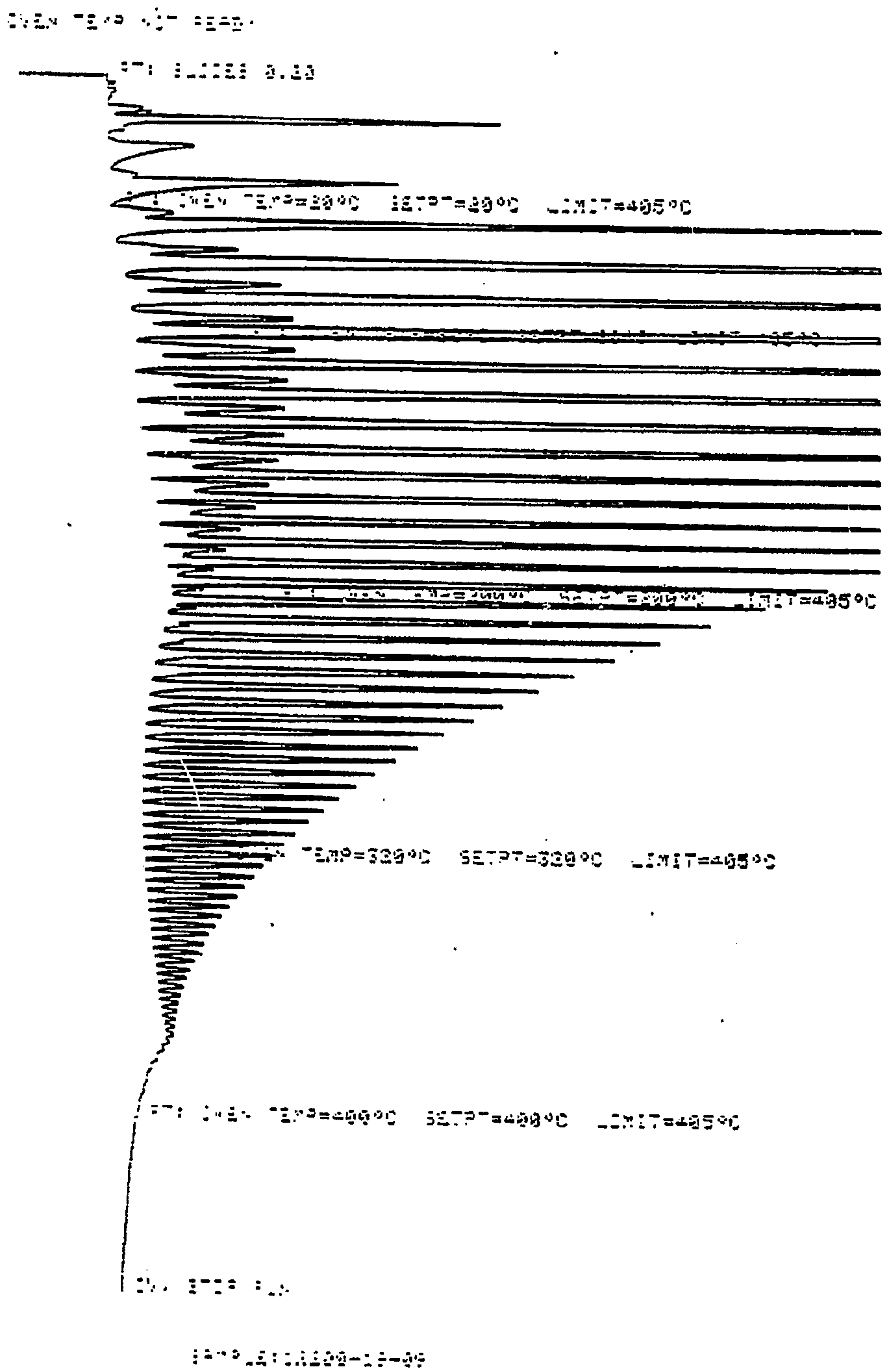


Fig. B209

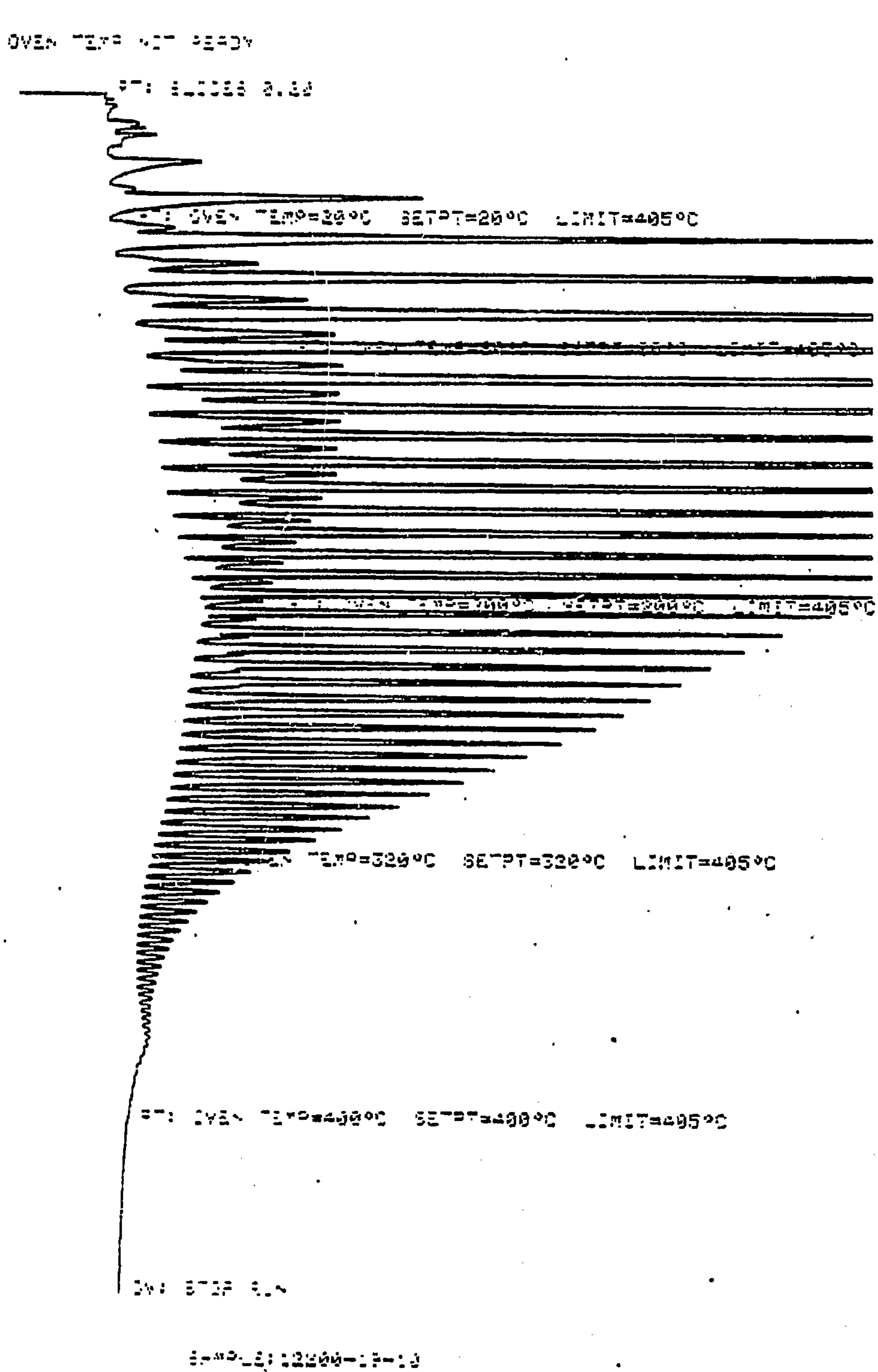


Fig. B210

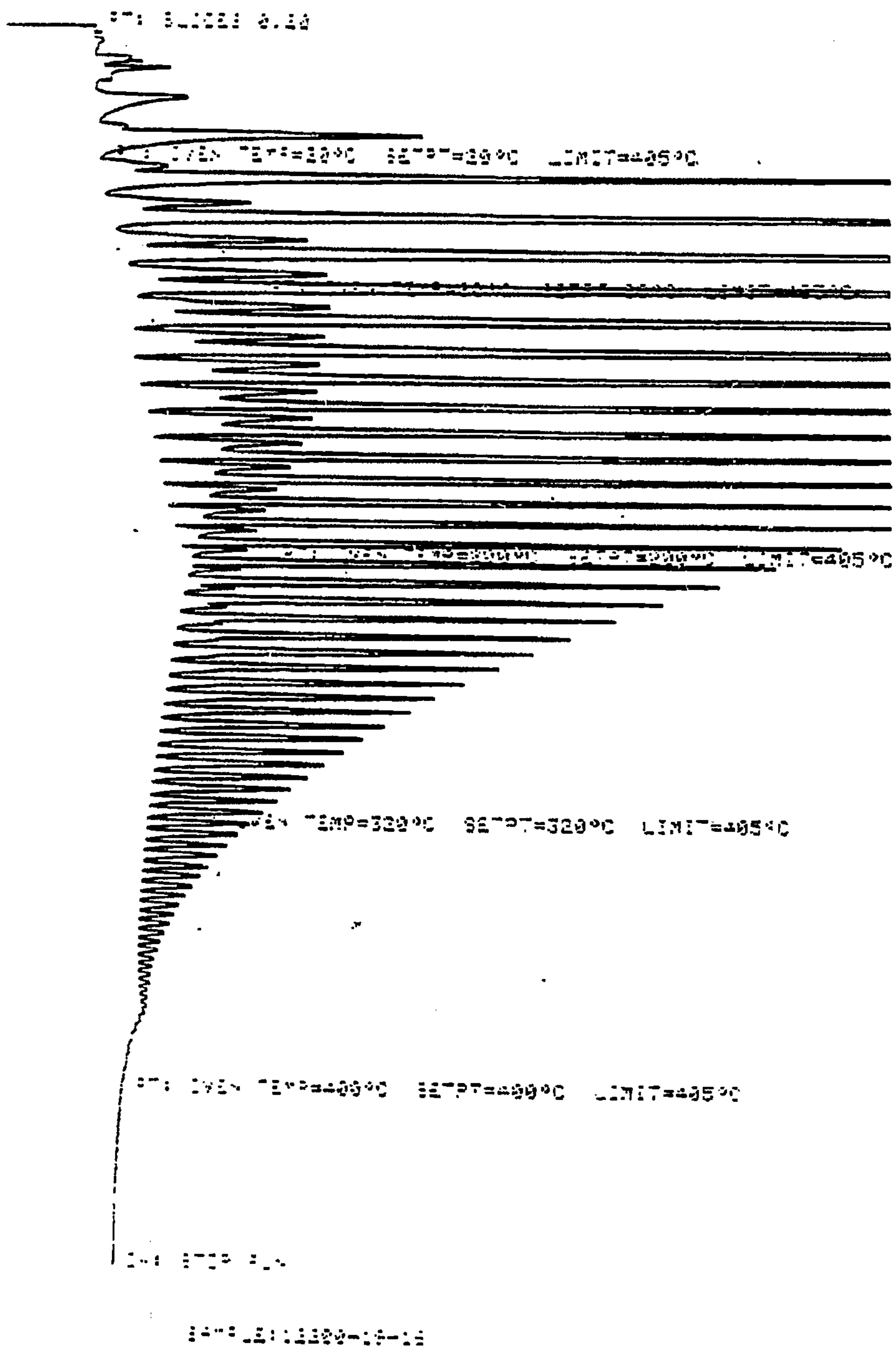
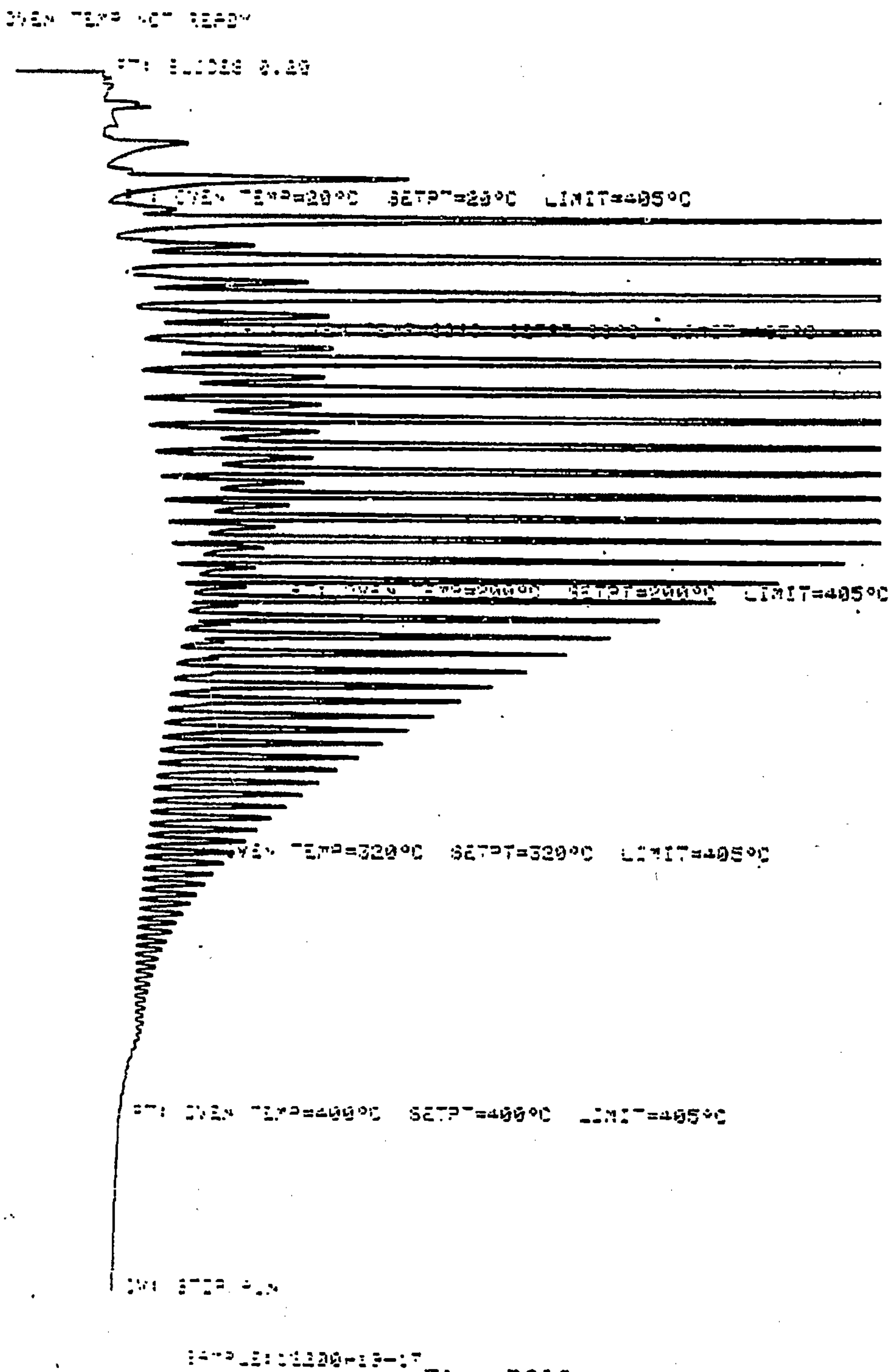


Fig. B211



OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
LIMIT=405°C
TEMP=320°C SETPT=320°C LIMIT=405°C
OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

.Fig. B212

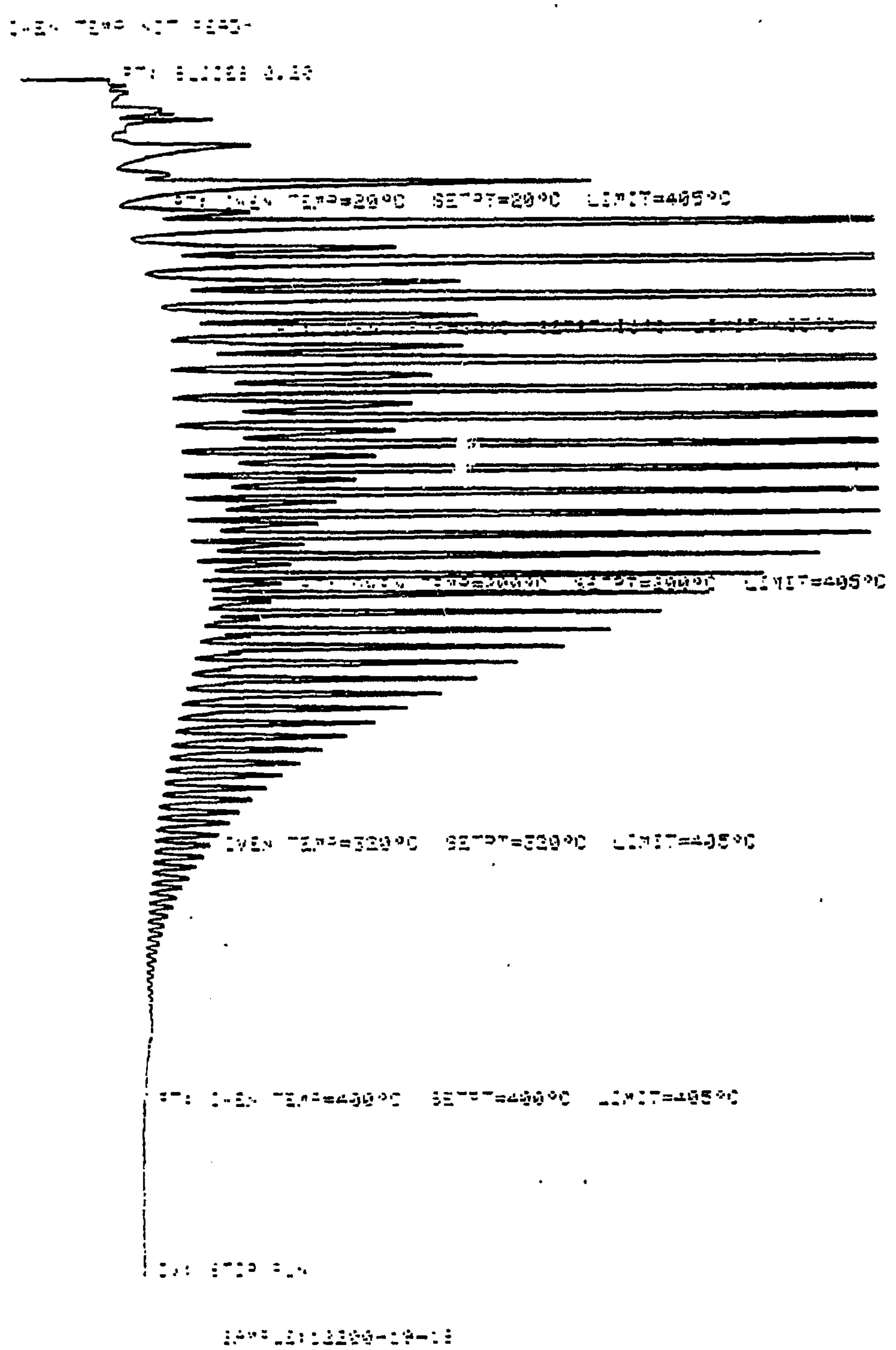


Fig. B213

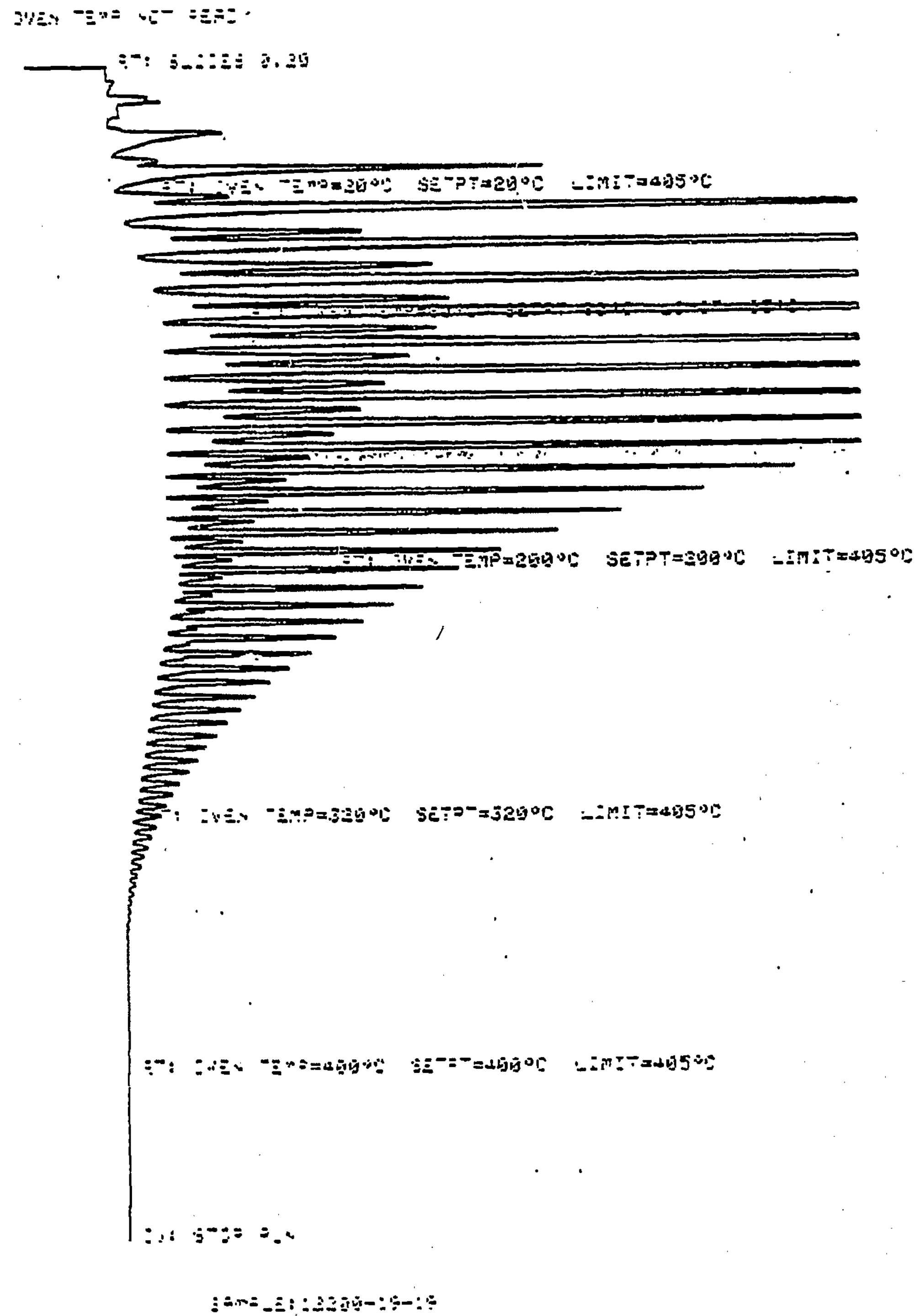

TEMP=20°C SETPT=20°C LIMIT=405°C
TEMP=200°C SETPT=200°C LIMIT=405°C
TEMP=320°C SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B214

Table B14

FILE: 1220019A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-19
CATALYST CO/X11-U103 250 CC 104.3 G AFTER RUN:153.9 G (+49.6 G)
FEED H2:CO OF 50:50 @1260 CC/MN OR 300 GHSV (CAT#12006-64)

RUN & SAMPLE NO.	12200-19-01	200-19-02	200-19-04	200-19-07	200-19-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.5	43.5	91.5	163.0	211.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	241	243	241	242	261
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	19.50	24.00	24.00	21.50	24.00
EFFLNT GAS LITER	642.50	1078.55	1142.30	1025.60	922.15
GM AQUEOUS LAYER	171.63	154.42	140.32	126.86	174.59
GM OIL	28.85	123.79	112.82	95.05	129.37
MATERIAL BALANCE					
GM ATOM CARBON %	66.65	104.75	107.31	102.89	103.17
GM ATOM HYDROGEN %	78.63	101.98	99.98	101.41	99.21
GM ATOM OXYGEN %	88.20	99.94	101.66	99.00	99.79
RATIO CHX/(H2O+CO2)	0.3884	1.1743	1.2289	1.1571	1.0991
RATIO X IN CHX	2.3043	2.2236	2.2226	2.2279	2.2775
USAGE H2/CO PRODT	3.0781	1.7591	1.7944	1.8520	1.6149
FEED H2/CO FRM EFFLNT	1.1797	0.9736	0.9317	0.9856	0.9617
RESIDUAL H2/CO RATIO	0.5866	0.5821	0.5693	0.6312	0.4815
RATIO CO2/(H2O+CO2)	0.0618	0.0869	0.0574	0.0512	0.1823
K SHIFT IN EFFLNT	0.0386	0.0554	0.0347	0.0341	0.1073
SPECIFIC ACTIVITY SA	2.1516	3.0419	3.0719	2.4235	2.0702
CONVERSION					
ON CO %	23.81	33.26	29.58	29.03	42.37
ON H2 %	62.11	60.09	56.97	54.55	71.14
ON CO+H2 %	44.54	46.50	42.79	41.70	56.47
PRDT SELECTIVITY,WT %					
CH4	9.91	5.43	5.34	5.65	7.95
C2 HC'S	1.94	1.11	1.19	1.21	1.85
C3H8	2.30	1.27	1.33	1.31	1.92
C3H6=	3.80	2.38	2.70	2.58	2.41
C4H10	2.39	1.38	1.50	1.50	1.77
C4H8=	4.36	2.63	2.98	2.90	3.04
C5H12	2.78	1.61	1.74	1.74	2.29
C5H10=	3.54	2.36	2.36	2.55	2.56
C6H14	3.17	1.75	1.93	1.92	2.43
C6H12= & CYCLO'S	2.48	1.55	1.82	1.69	1.69
C7+ IN GAS	14.85	6.80	7.17	7.24	7.47
LIQ HC'S	48.48	71.73	69.94	69.70	64.61
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	24.70	14.20	15.04	15.15	18.95
C5 -420 F	44.51	28.56	31.18	31.25	36.73
420-700 F	26.76	28.33	27.76	27.81	26.10
700-END PT	4.02	28.91	26.02	25.79	18.22

Table B14 (continued)

FILE: 1220019A TSS4Q1 A1

C5+-END PT	75.30	85.80	84.96	84.85	81.05
ISO/NORMAL MOLE RATIO					
C4	0.0239	0.0322	0.0328	0.0352	0.0239
C5	0.0888	0.0896	0.0901	0.0903	0.0900
C6	0.0906	0.0859	0.0807	0.0775	0.1140
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.5770	0.5108	0.4700	0.4847	0.7617
C4	0.5300	0.5054	0.4867	0.5009	0.5616
C5	0.7625	0.6636	0.7188	0.6636	0.8688
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8113	0.8852	0.8755	0.8769	0.8582
RATIO CH4/(1-A)**2	2.7842	4.1216	3.4426	3.7244	3.9554
ALPHA FRM CORRELATION	0.8379	0.8381	0.8393	0.8342	0.8463
ALPHA (EXPTL/CORR)	0.9683	1.0562	1.0431	1.0511	1.0140
W%CH4 FRM CORRELATION	13.9666	14.3384	13.5150	15.3183	15.6910
W%CH4 (EXPTL/CORR)	0.7098	0.3787	0.3949	0.3687	0.5066
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.789	0.785	0.789	0.797	0.810
N, REFRACTIVE INDEX	1.4209*	N/A	N/A	N/A	N/A
SIMULT'D DISTILATN					
10 WT % @ DEG F	294	339	337	337	293
16	334	399	379	379	336
50	483	635	596	596	538
84	641	934	915	912	830
90	683	1017	999	996	923
RANGE(16-84 %)	307	535	536	533	494
WT % @ 420 F	36.50	20.20	23.10	23.10	31.40
WT % @ 700 F	91.70	59.70	62.80	63.00	71.80

Table B15

FILE: 1220019B TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-19
CATALYST CO/X11-U103 250 CC 104.3 G AFTER USE:153.9 G (+49.6 G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12006-64)

RUN & SAMPLE NO.	12200-19-10	200-19-16	200-19-17	200-19-18	200-19-19
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	235.0	279.0	403.0	427.0	476.0
PRESSURE.PSIG	300	300	300	300	300
TEMP. C	264	263	263	272	267
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	24.00	24.00	24.00	24.00	49.00
EFFLNT GAS LITER	908.85	930.75	931.10	772.85	1972.35
GM AQUEOUS LAYER	169.54	175.73	176.82	176.69	370.70
GM OIL	139.07	117.66	141.81	98.32	186.55
MATERIAL BALANCE					
GM ATOM CARBON %	104.72	100.96	105.70	89.98	102.42
GM ATOM HYDROGEN %	101.25	99.51	104.79	91.46	101.12
GM ATOM OXYGEN %	97.71	98.33	98.47	91.27	103.48
RATIO CHX/(H2O+CO2)	1.2099	1.0787	1.2151	0.9647	0.9709
RATIO X IN CHX	2.2674	2.3058	2.2897	2.4017	2.4142
USAGE H2/CO PRODT	1.5616	1.6825	1.6240	1.5986	1.6712
FEED H2/CO FRM EFFLNT	0.9669	0.9856	0.9914	1.0165	0.9874
RESIDUAL H2/CO RATIO	0.4882	0.5014	0.5009	0.4608	0.4927
RATIO CO2/(H2O+CO2)	0.1882	0.1598	0.1592	0.2371	0.2057
K SHIFT IN EFFLNT	0.1132	0.0954	0.0948	0.1433	0.1276
SPECIFIC ACTIVITY SA	1.8631	1.6635	1.8239	1.5200	1.4227
CONVERSION					
ON CO %	44.60	41.00	43.67	48.84	41.97
ON H2 %	72.03	69.99	71.54	76.81	71.04
ON CO+H2 %	58.08	55.39	57.55	62.94	56.42
PRDT SELECTIVITY,WT %					
CH4	7.61	9.51	8.63	14.21	15.04
C2 HC'S	1.70	1.89	1.97	2.76	2.80
C3H8	1.91	2.10	1.90	3.00	3.02
C3H6=	2.27	2.47	2.17	2.27	2.37
C4H10	1.67	1.91	1.77	2.48	2.56
C4H8=	2.82	3.12	2.86	3.36	3.34
C5H12	2.08	2.35	2.09	2.96	3.11
C5H10=	2.55	2.28	2.02	2.07	1.94
C6H14	2.25	2.65	2.42	3.34	3.31
C6H12= & CYCLO'S	1.51	1.70	1.58	1.79	1.68
C7+ IN GAS	9.26	9.03	7.69	10.03	13.07
LIQ HC'S	64.48	60.99	65.00	51.74	47.77
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	17.97	21.00	19.20	28.07	29.13
C5 -420 F	36.61	37.59	36.73	40.06	44.70
420-700 F	26.82	25.19	27.17	22.66	19.49
700-END PT	18.70	16.22	16.90	9.21	6.69

Table B15 (continued)

FILE: 1220019B TSS3Q1 A1

C5+-END PT	82.13	79.00	80.80	71.93	70.87
ISO/NORMAL MOLE RATIO					
C4	0.0194	0.0200	0.0202	0.0225	0.0199
C5	0.0979	0.0997	0.1039	0.1171	0.1033
C6	0.1238	0.1127	0.1162	0.1732	0.1489
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.7623	0.8138	0.8368	1.2612	1.2144
C4	0.5710	0.5912	0.5991	0.7138	0.7374
C5	0.7926	1.0054	1.0090	1.3872	1.5643
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8705	0.8589	0.8654	0.8435	0.8245
RATIO CH4/(1-A)**2	4.5394	4.7775	4.7653	5.8023	4.9833
ALPHA FRM CORRELATION	0.8455	0.8443	0.8443	0.8479	0.8449
ALPHA (EXPTL/CORR)	1.0296	1.0173	1.0250	0.9949	0.9759
W%CH4 FRM CORRELATION	16.5747	16.7535	16.7399	17.4703	17.3840
W%CH4 (EXPTL/CORR)	0.4592	0.5678	0.5155	0.8131	0.8652
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY	N/A	N/A	N/A	N/A	N/A
N. REFRACTIVE INDEX	N/A	N/A	N/A	N/A	N/A
SIMULT'D DISTILATN					
10 WT % @ DEG F	297	295	295	282	275
16	339	337	337	310	296
50	542	533	531	482	445
84	814	805	799	738	680
90	877	885	878	803	749
RANGE(16-84 %)	475	468	462	428	384
WT % @ 420 F	29.40	32.10	32.20	38.40	45.20
WT % @ 700 F	71.00	73.40	74.00	82.20	86.00

IX. Run 33 (12185-18) with Catalyst 33 ($Co/X_9/X_{10}/X_4/X_3$/UCC-113)

The purpose of this run, as of Run 30, was to test the effect of a small quantity of the additive X_3 on activity, stability and selectivity. The X_3 was incorporated this time in a catalyst formulated in the same way as Catalyst 15 ($Co/X_9/X_{10}/X_4$/UCC-103), which was highly stable, with excellent selectivity, when tested in Run 12185-08. The theoretical concentrations of cobalt, X_9, X_{10}, X_4 and X_3 were, respectively, 8.2, 0.37, 0.49, 0.48 and 0.06 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B215-218. Simulated distillations of the C_5^+ product are plotted in Figs. B219-223. Carbon number product distributions are plotted in Figs. B224-228. Chromatograms from simulated distillations are reproduced in Figs. B229-233. Detailed material balances appear in Table B16.

The results were similar to those of Run 30, which tested X_3 in a catalyst of different composition and prepared by a different method. The initial activity, 63 percent syngas conversion, was about the same as in Run 15, but after 116.5 hours on stream it had dropped to 52 percent as against 58.3 percent in Run 30. In the same period the specific activity dropped from the initial 2.9 to 1.3, as against 2.6 to 2.3 in Run 30.

The selectivity was similar to that of Catalyst 15 initially, but deteriorated with the steady loss of activity.

As in Run 30, adding X_3 failed to improve this catalyst's activity or selectivity under the conditions of the test, and significantly reduced its stability.

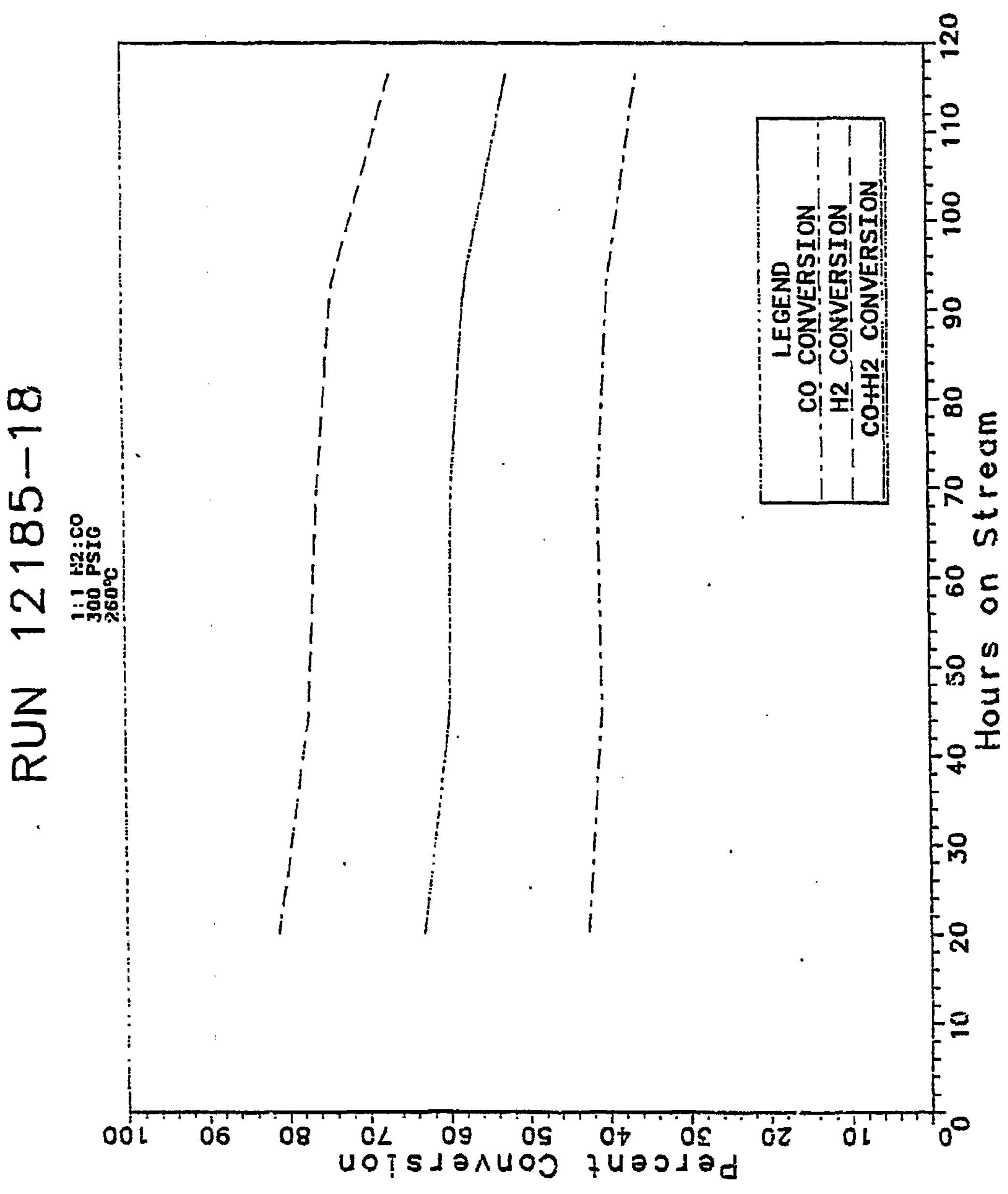

RUN 12185-18
1:1 H2:CO
300 PSIG
260°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Hours on Stream
Percent Conversion

Fig. B215

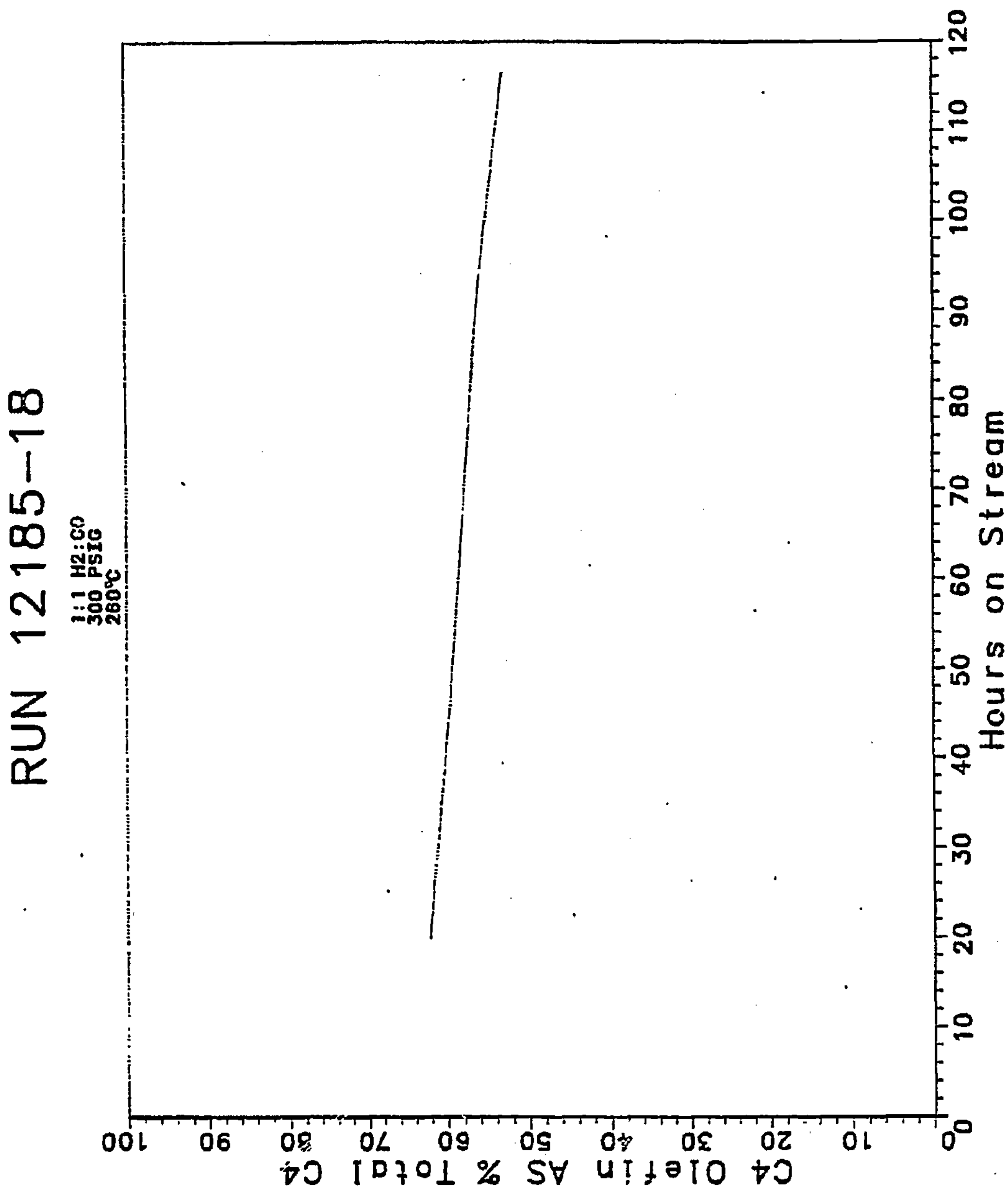

RUN 12185-18
1:1 H2:CO
300 PSIG
280°C
Hours on Stream
C4 Olefin AS % Total C4

Fig. B216

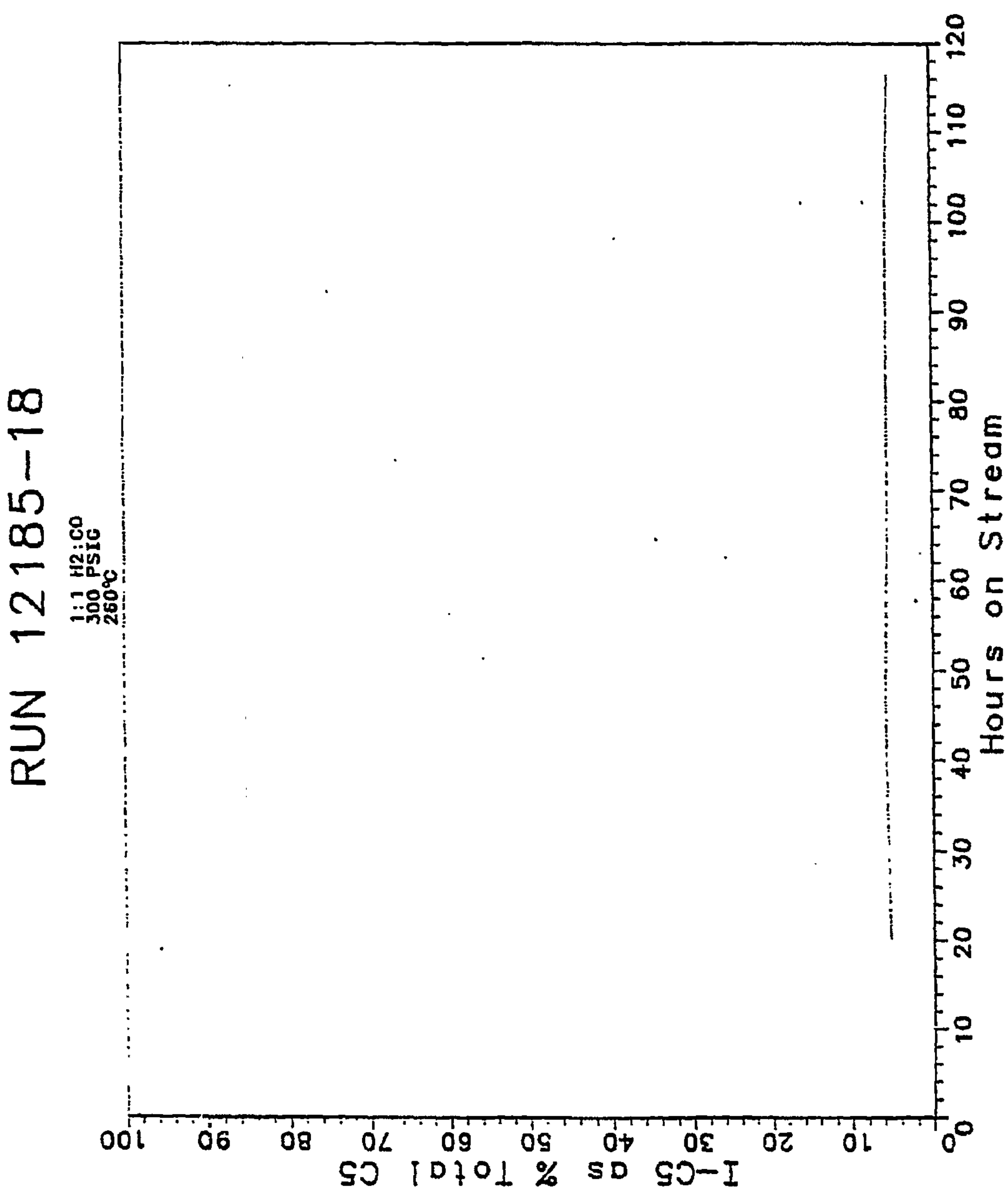
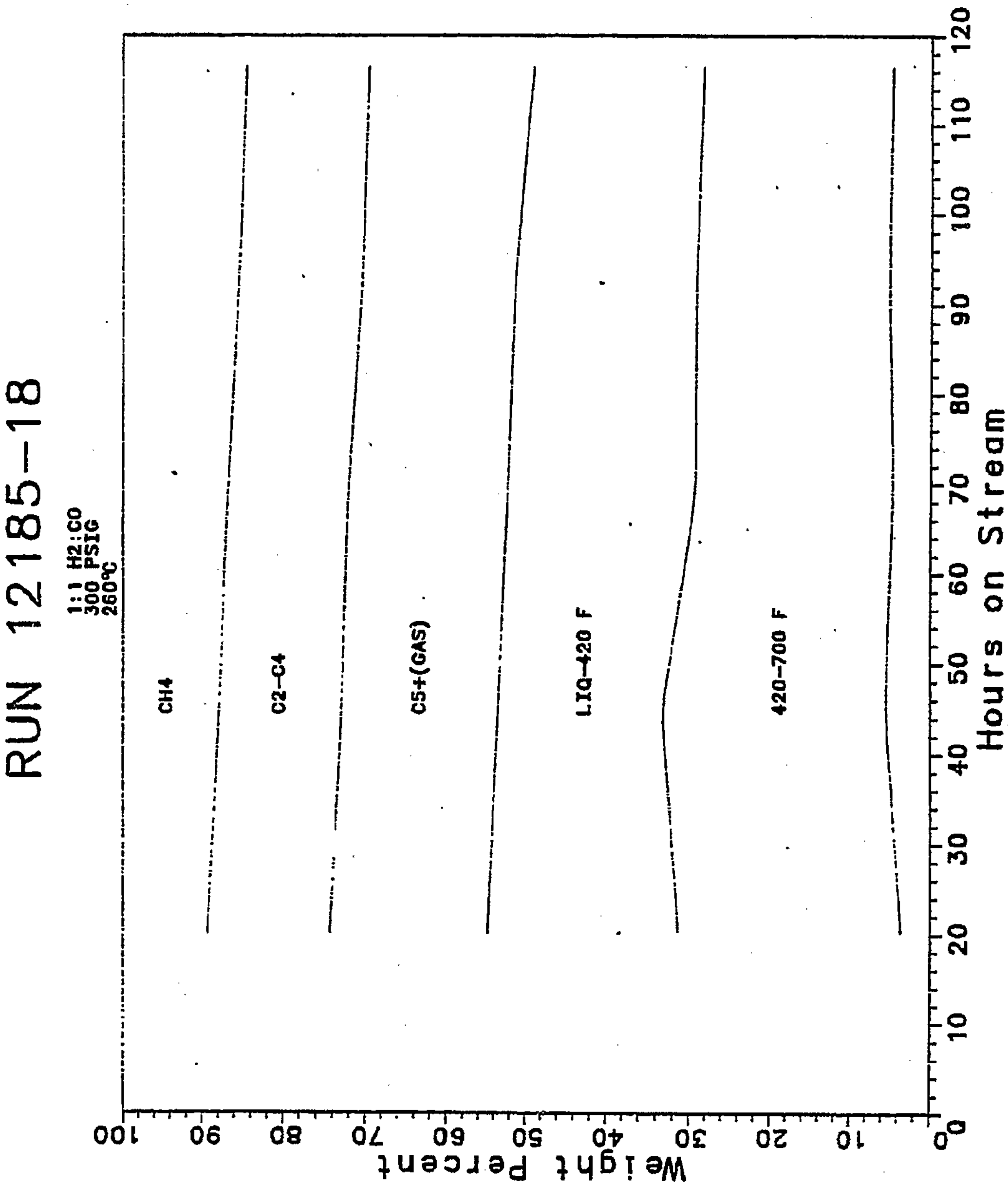

RUN 12185-18
1:1 H2:CO
300 PSIG
260°C
Hours on Stream
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
110
120

Fig. B217



RUN 12185-18
1:1 H2:CO
300 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
Hours on Stream
Weight Percent
0 10 20 30 40 50 60 70 80 90 100 110 120
0 10 20 30 40 50 60 70 80 90 100

Fig. B218

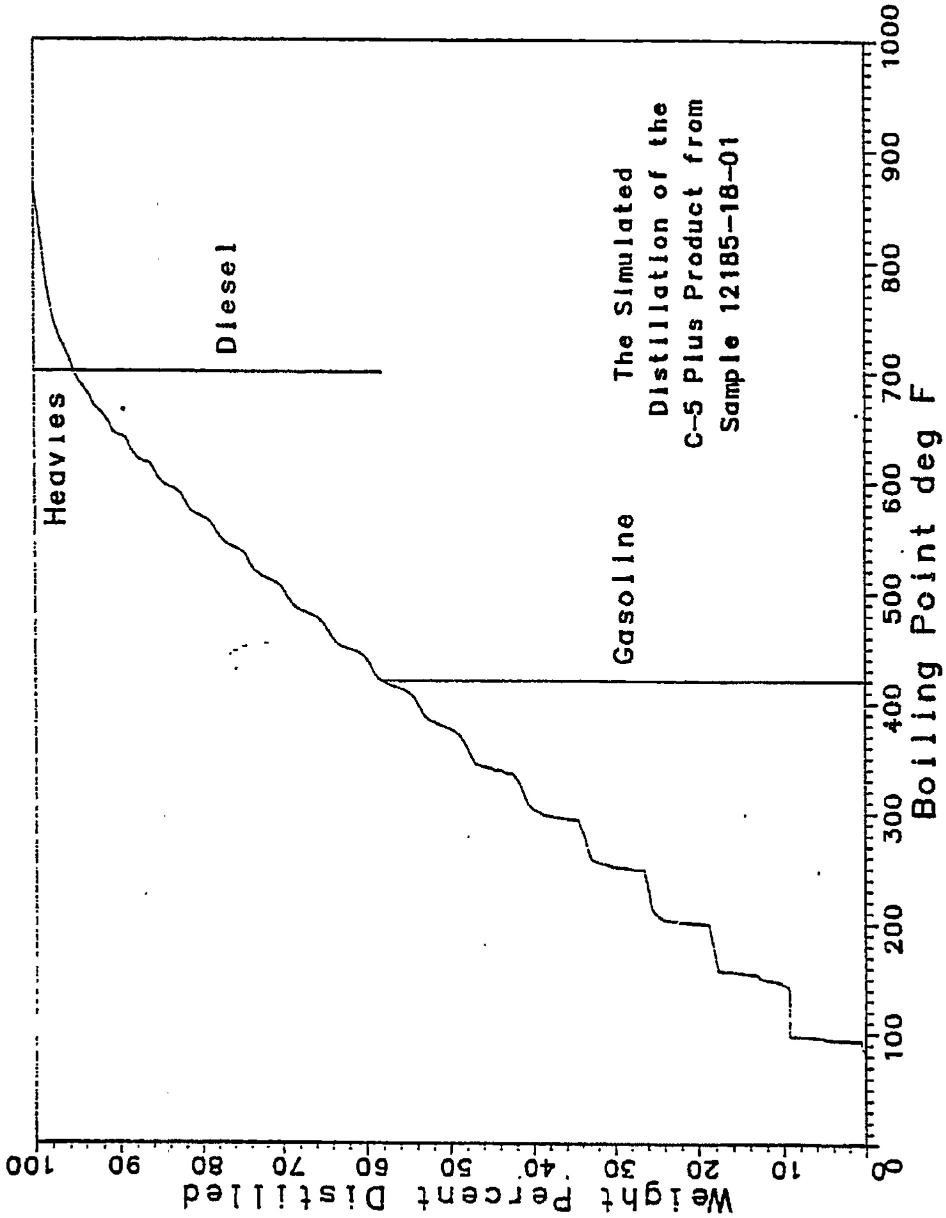

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-18-01
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B219

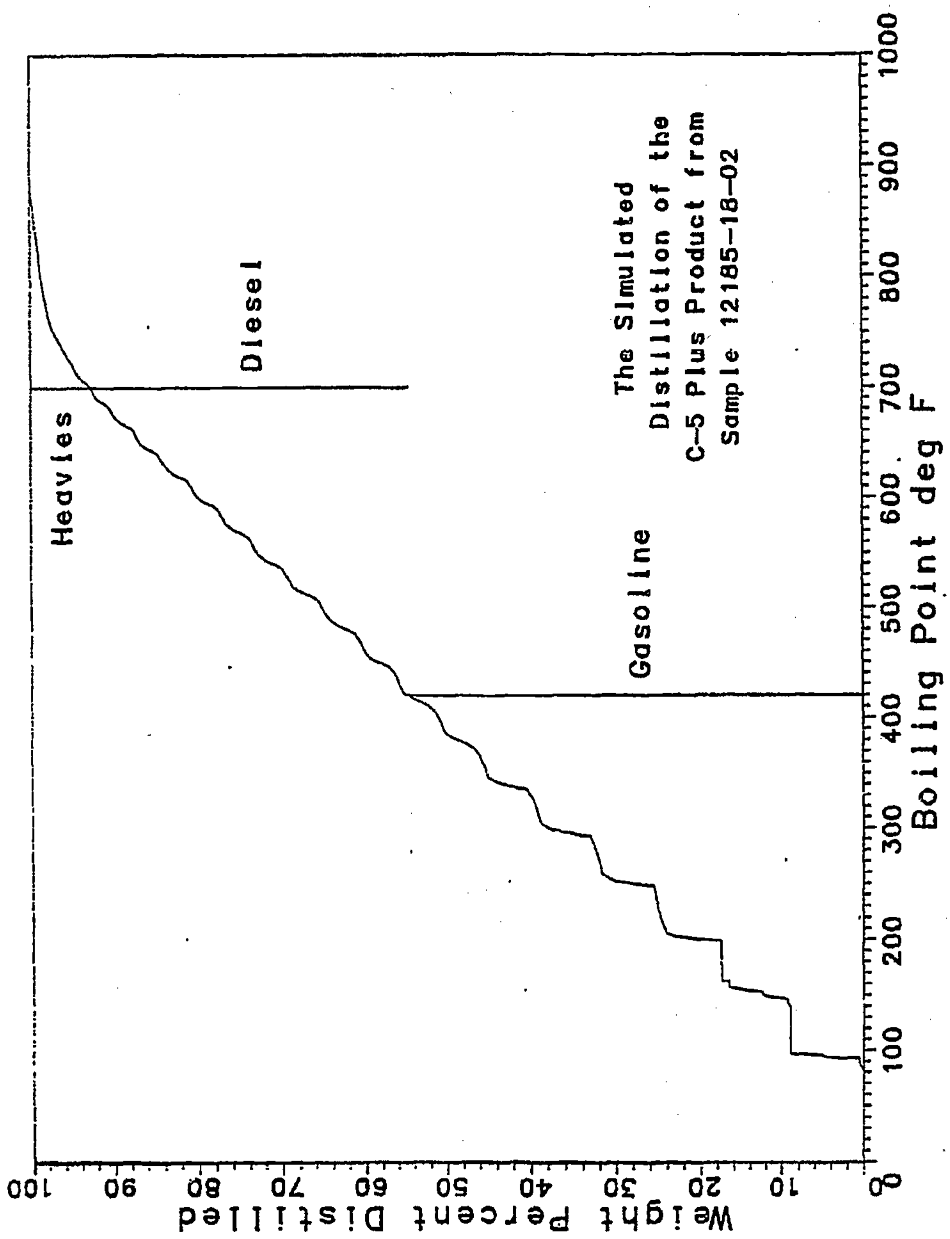
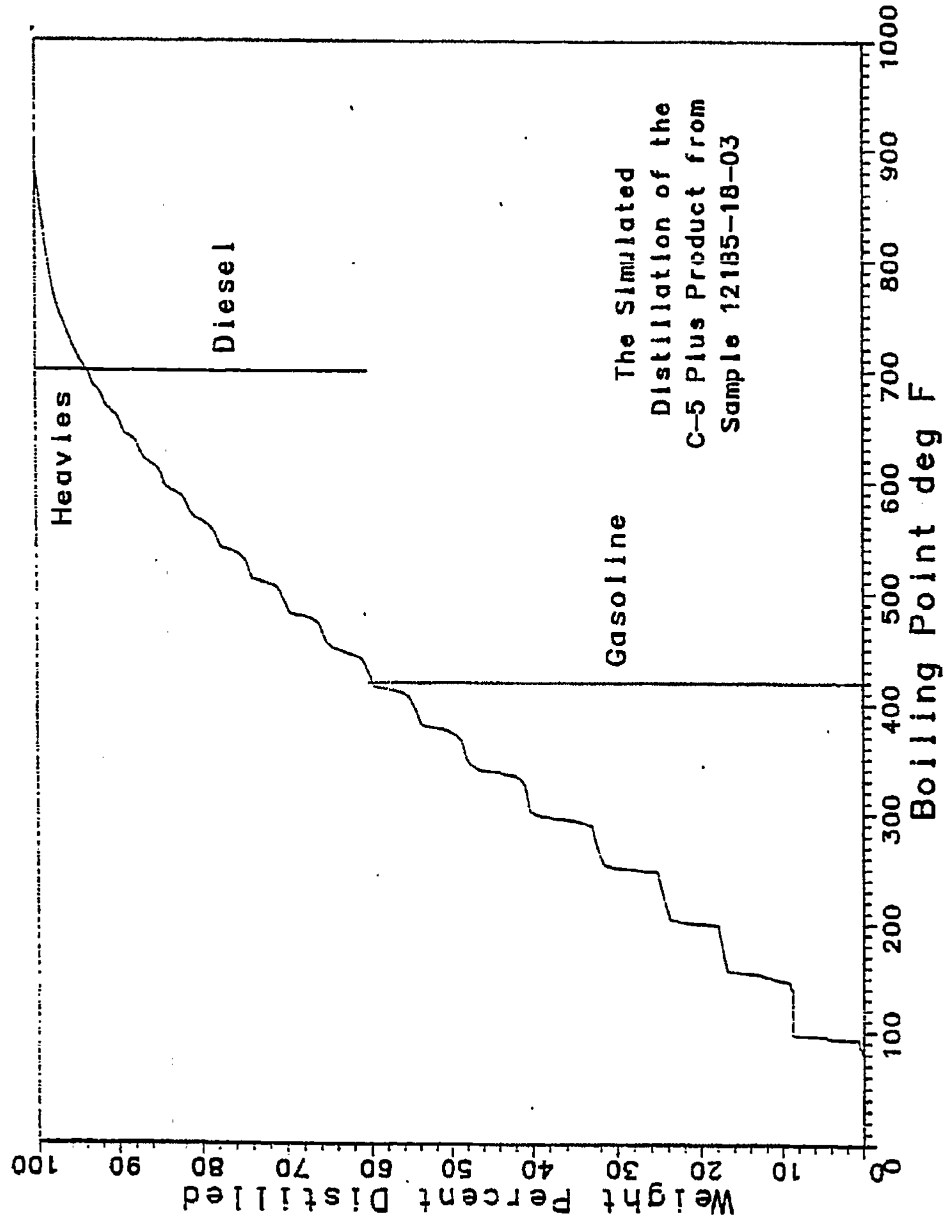
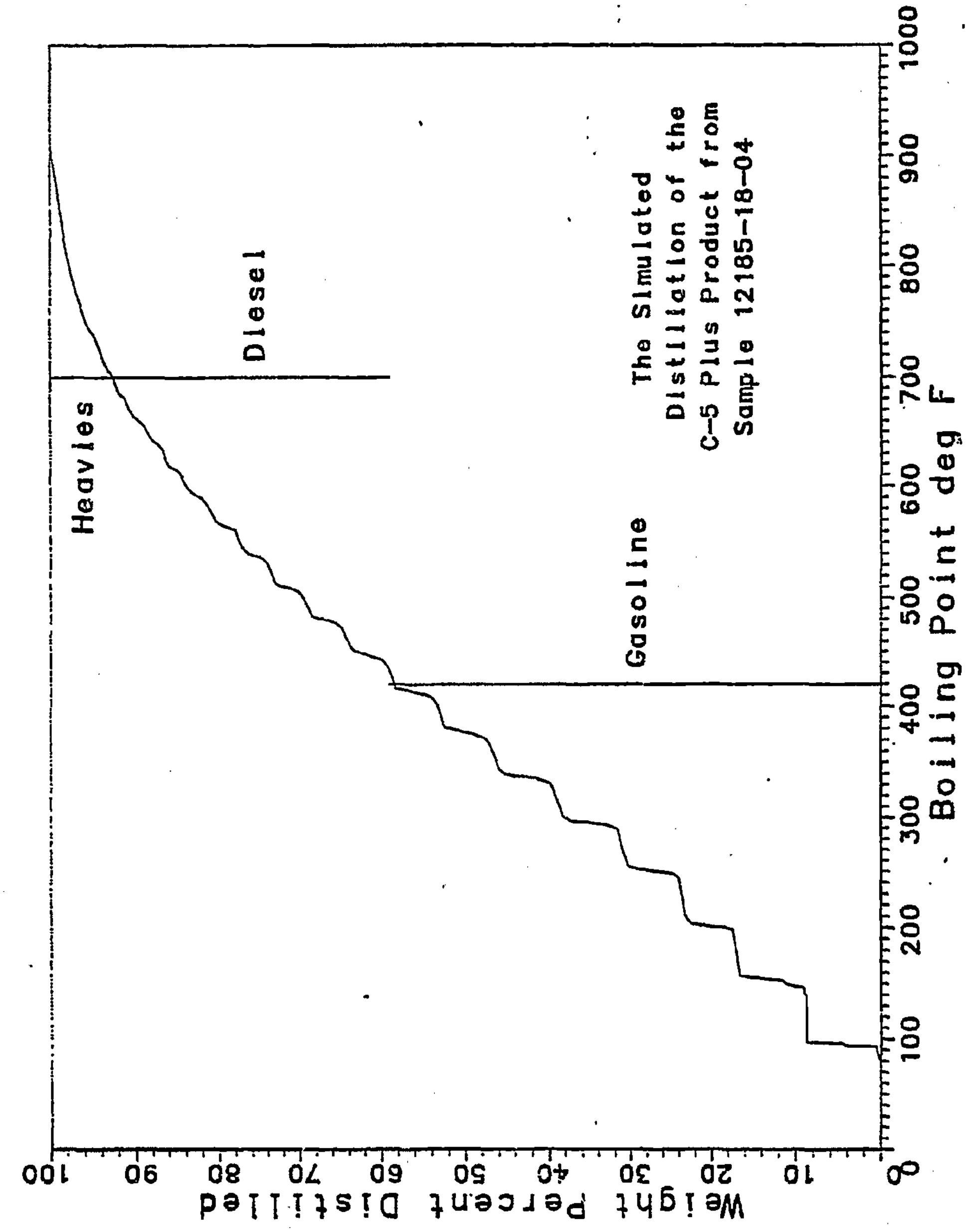

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-18-02
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig B220



Heavies
Diesel
Gasoline
The Simulated Distillation of the C-5 Plus Product from Sample 121B5-18-03
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. B221



The Simulated Distillation of the C-5 Plus Product from Sample 12185-18-04
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

Fig. B222

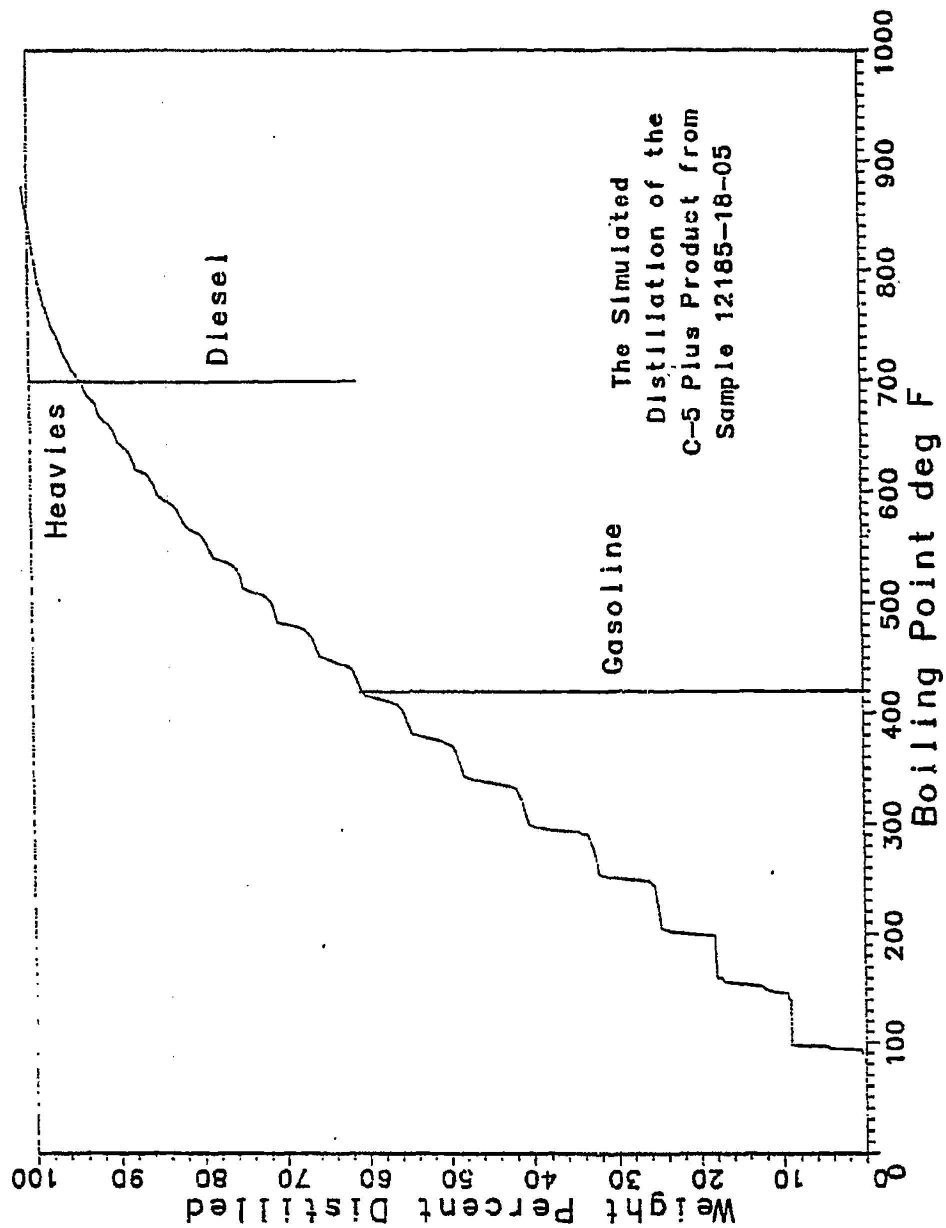
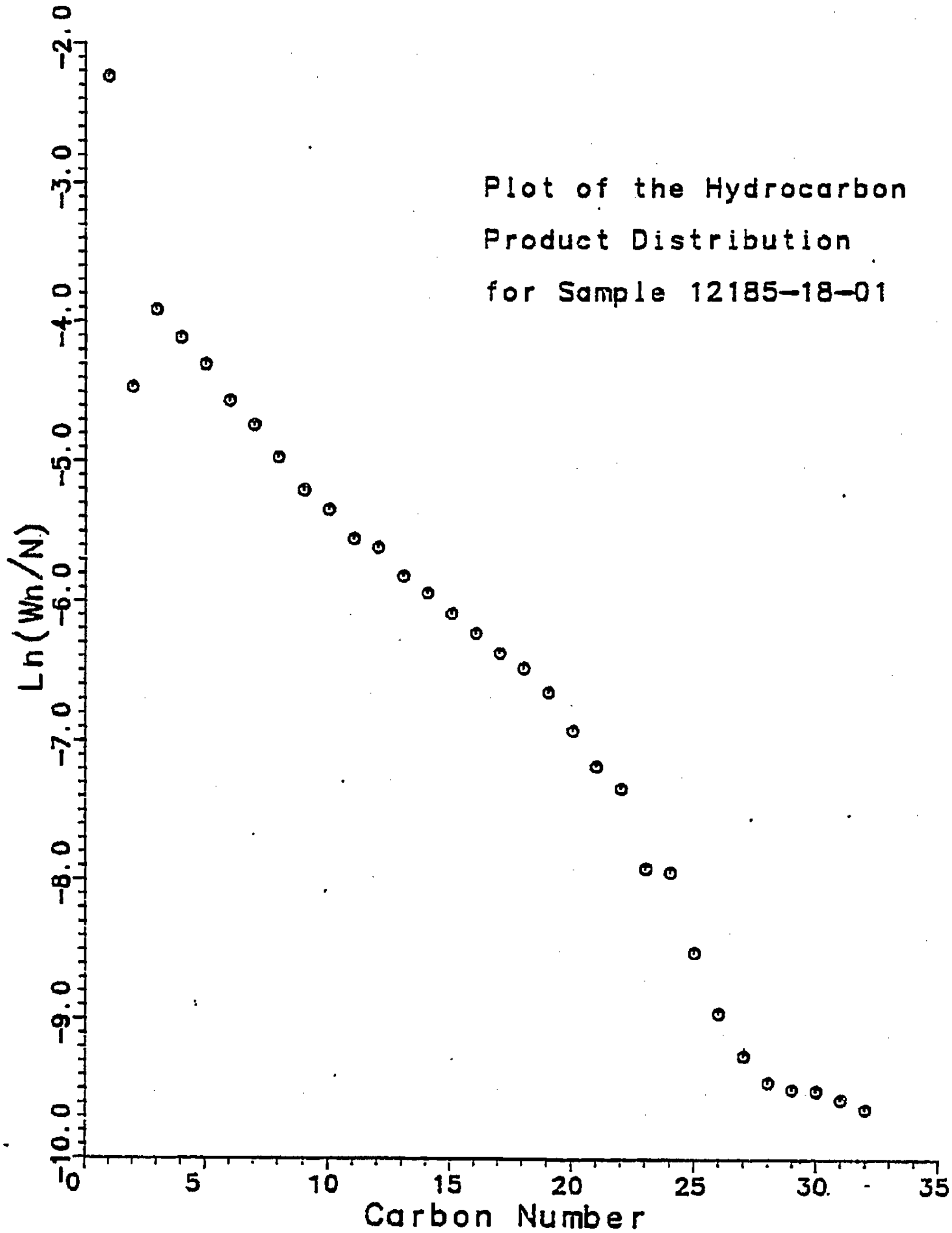
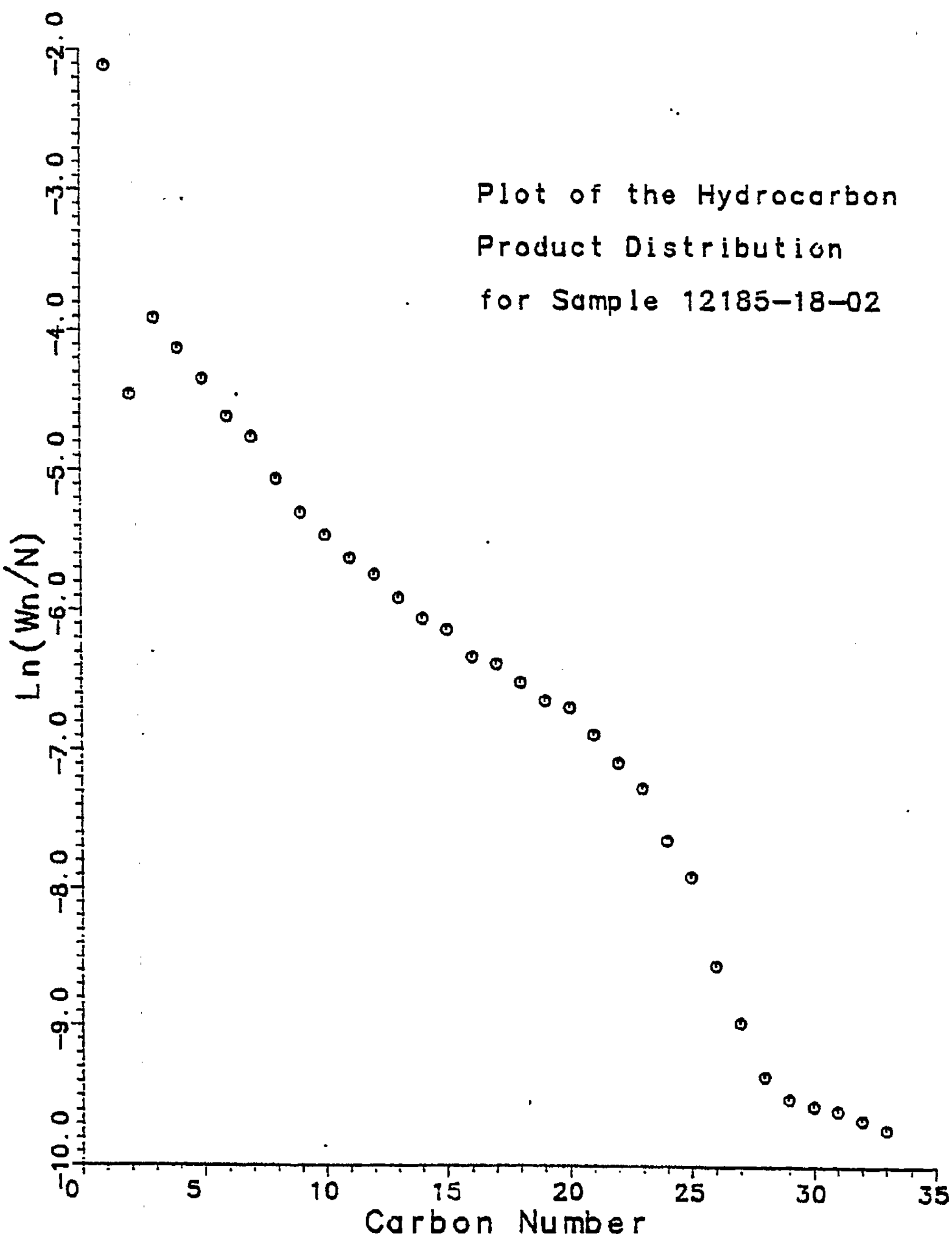

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-18-05
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B223



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-18-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-10
0
5
10
15
20
25
30
35
Carbon Number

Fig. B224



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-18-02
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
Carbon Number

Fig. B225

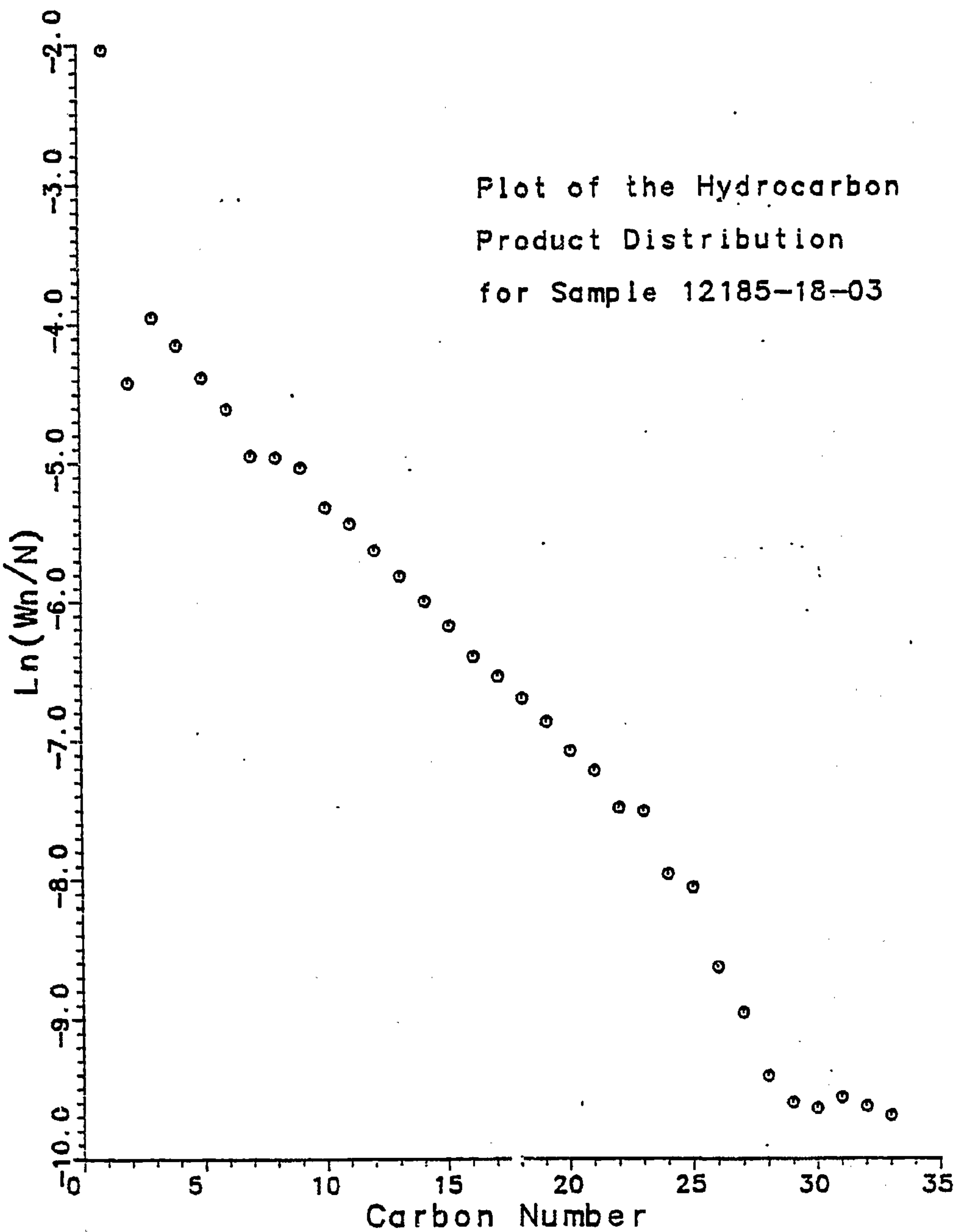

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-18-03
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B226

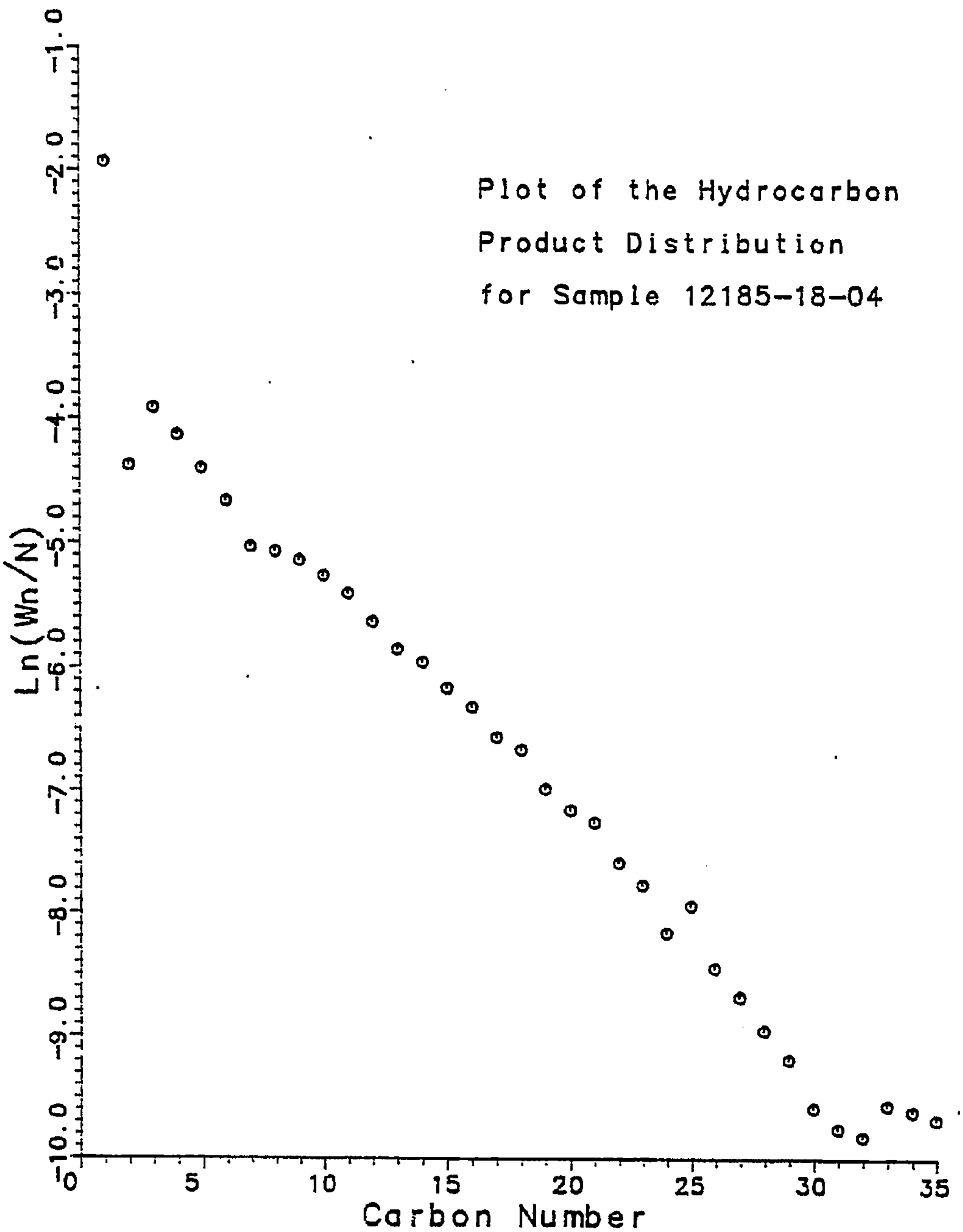
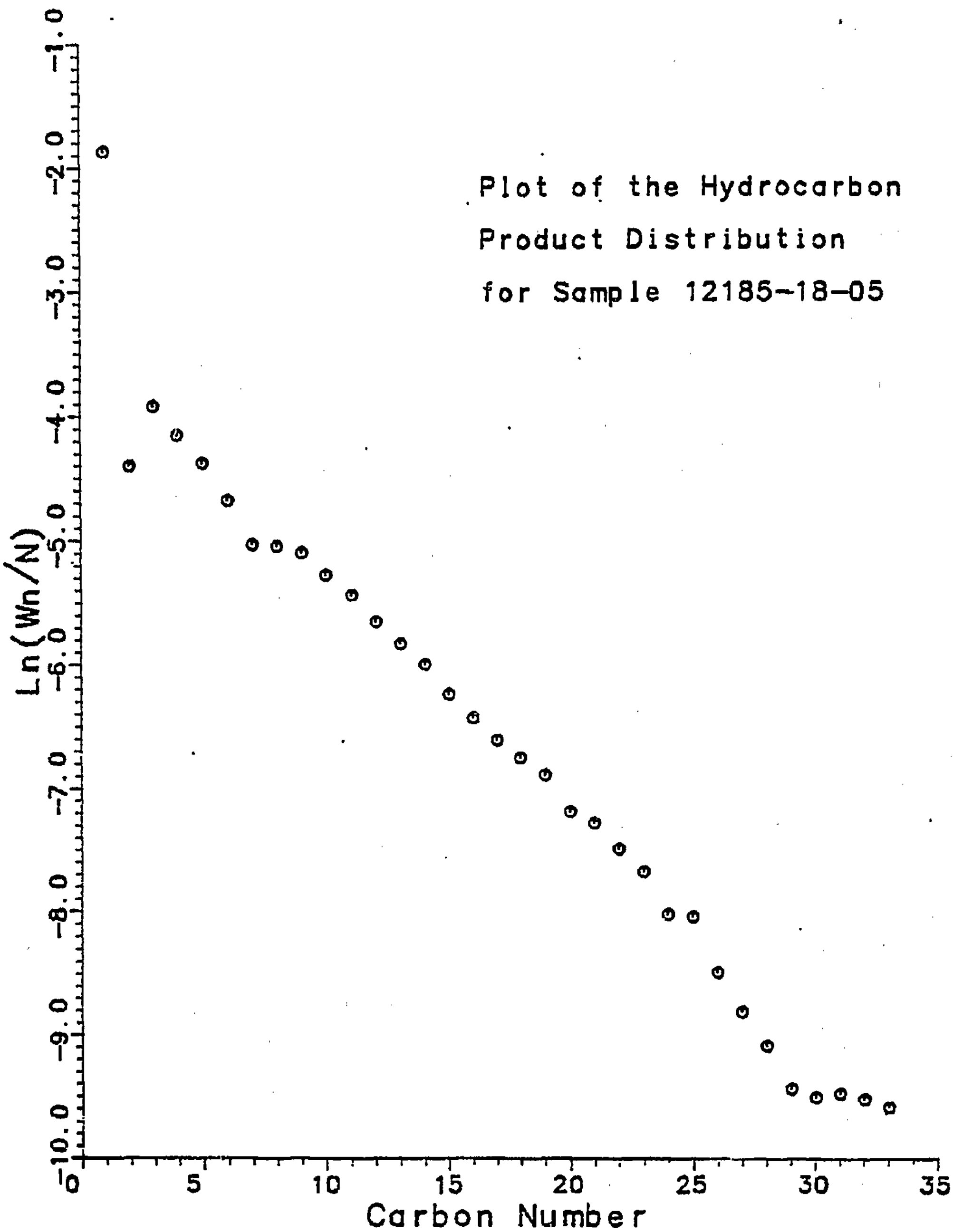

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-18-04
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

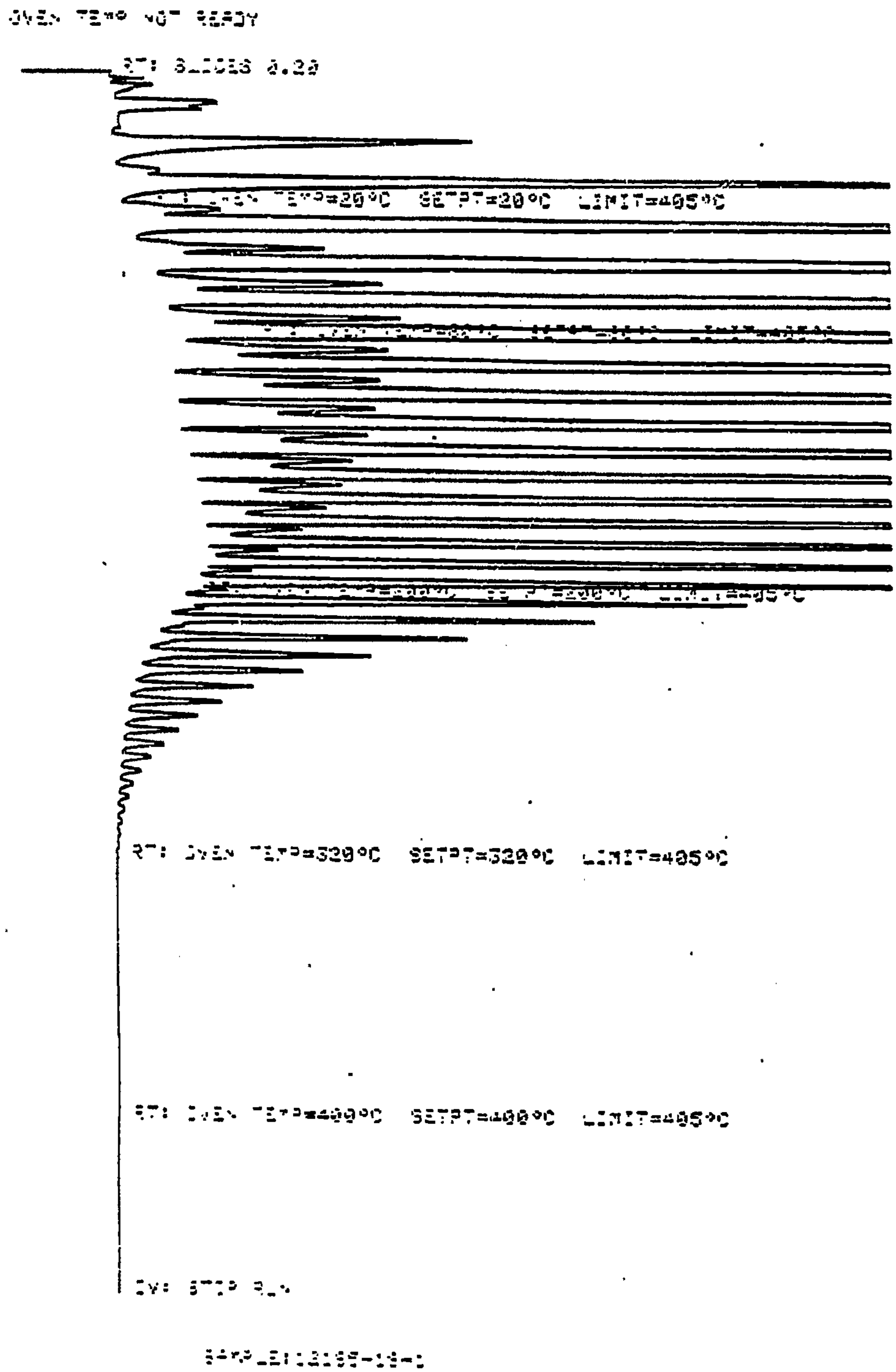
Fig. B227



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-18-05
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
35
Carbon Number

Fig. B228

1/3


OVEN TEMP NOT READY
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RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B229

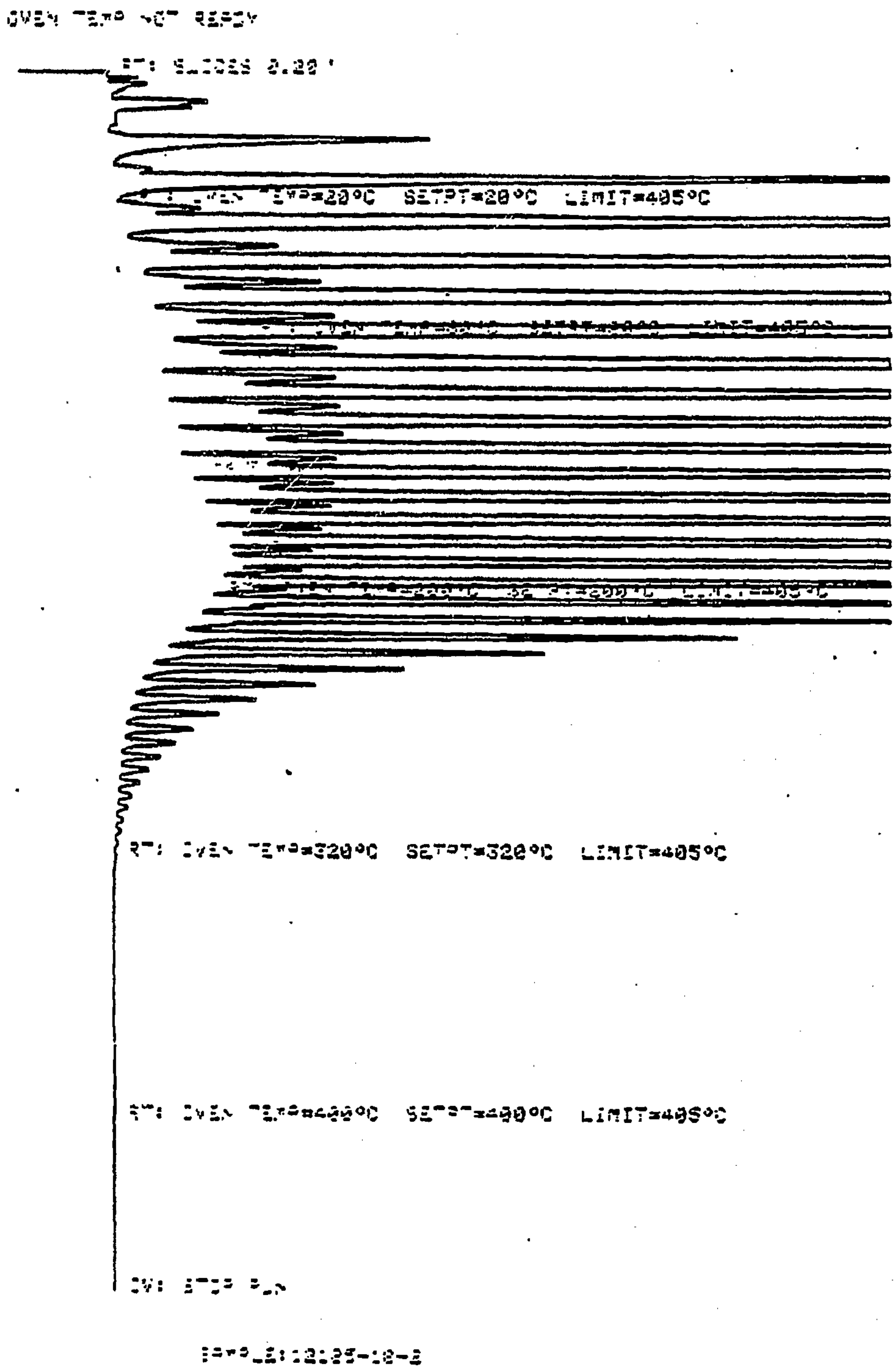

SETPT=20°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B230

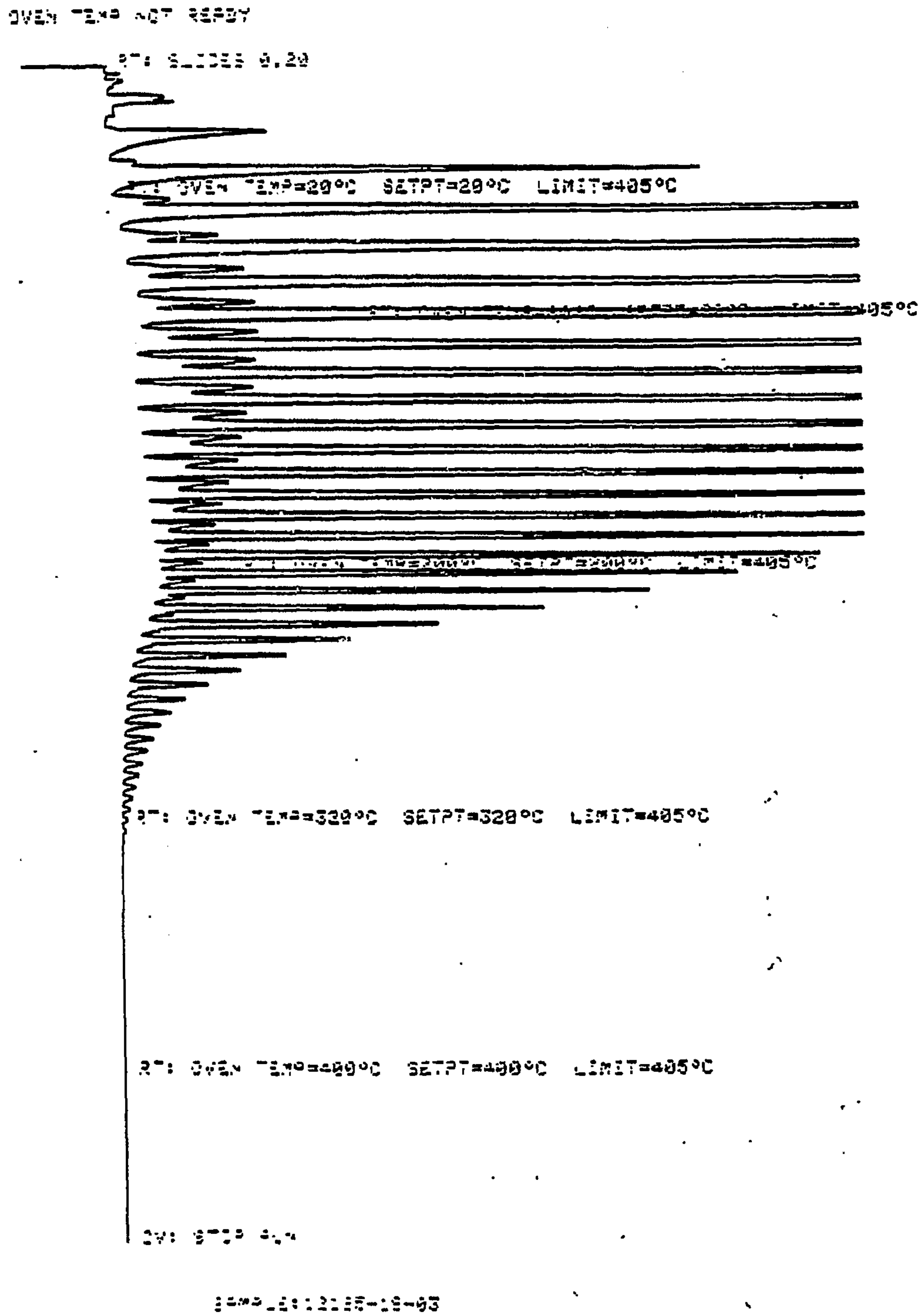
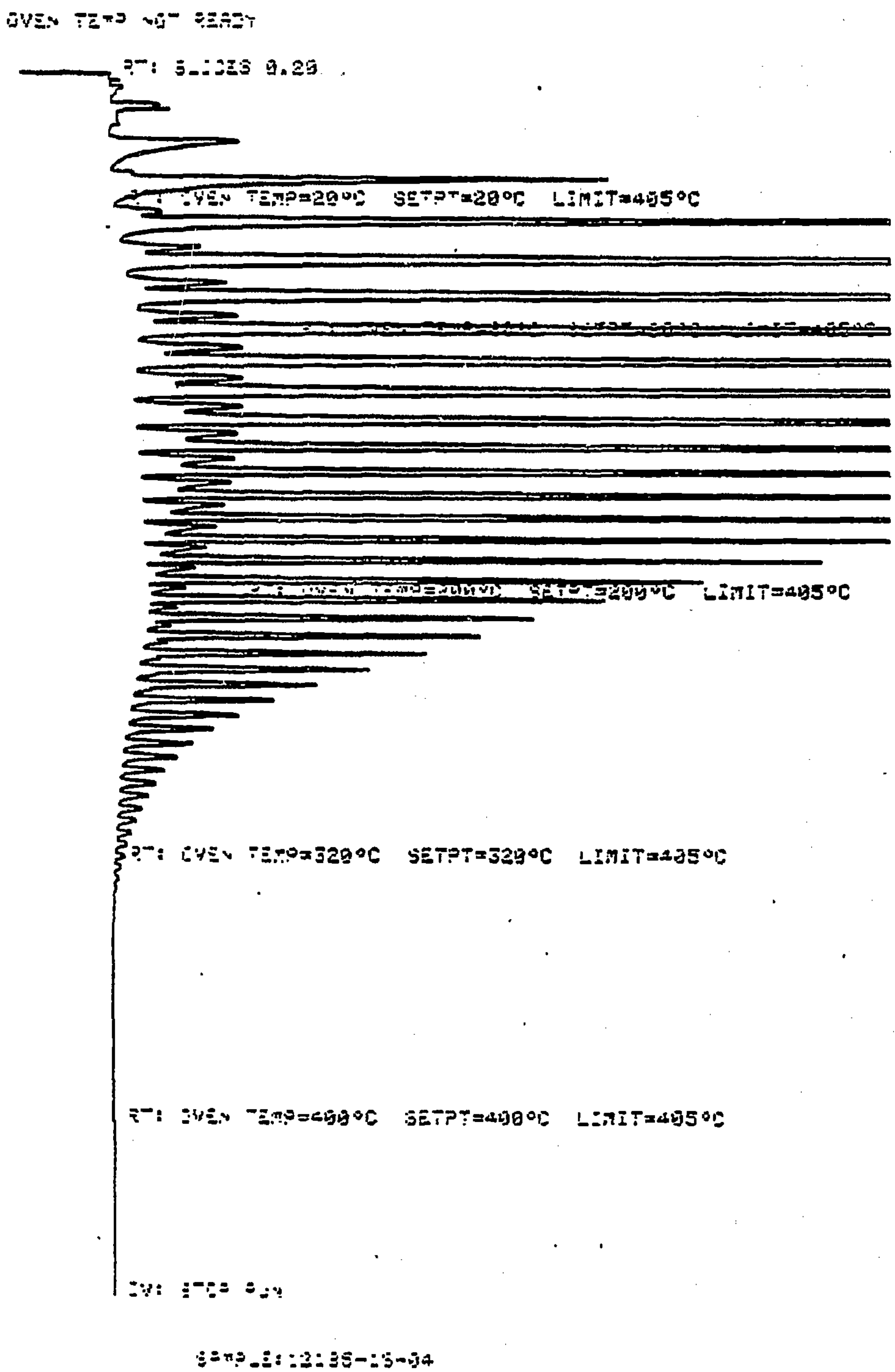

OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B231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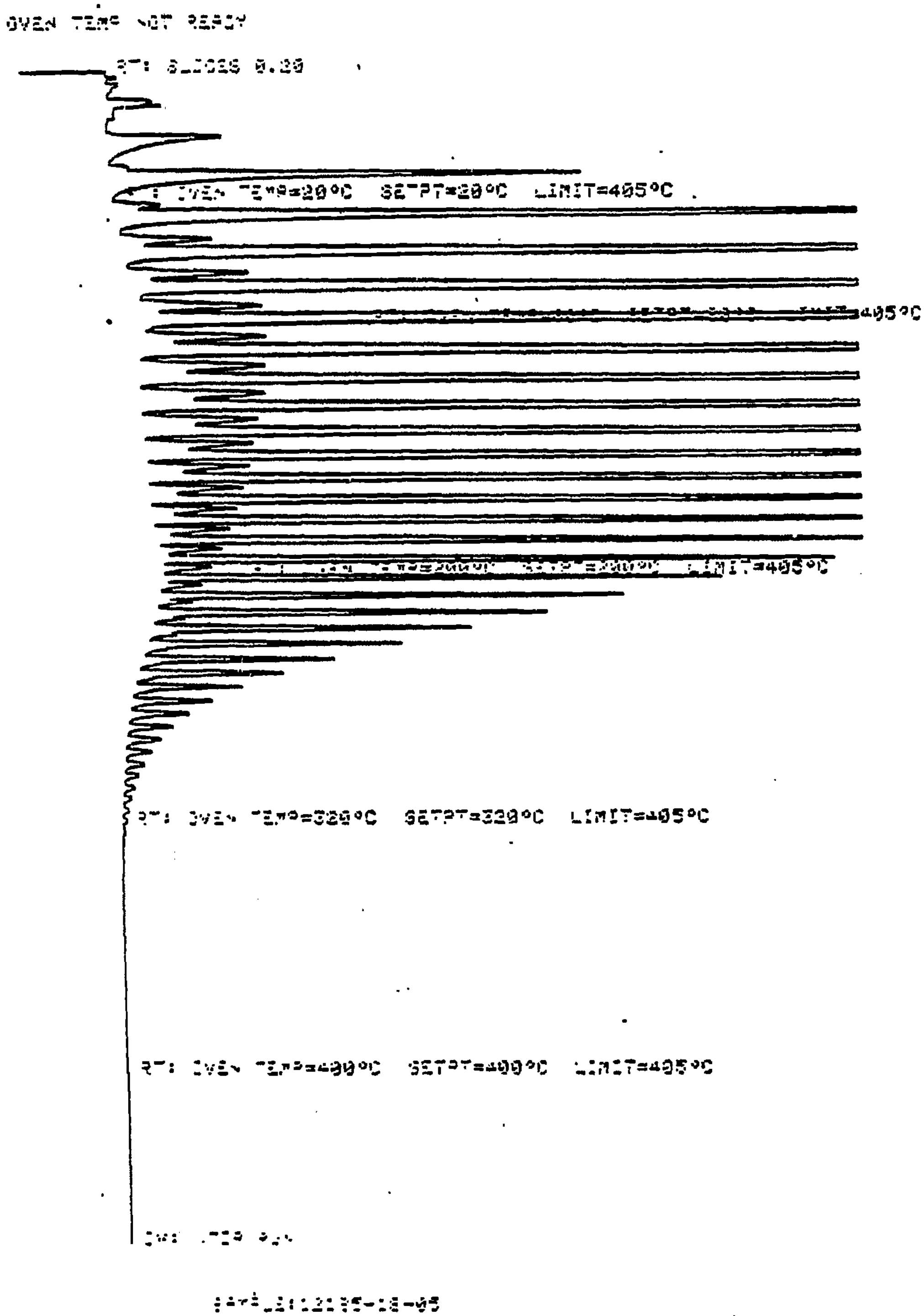
LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B232

ITT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RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B233

Table B16

FILE: 1218518A TSS3Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-18
CATALYST CO/X9/X10/X4/X3-U103 80 CC 34,5 G AFTER USE:47.9 G (+13.4 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-84-27)

RUN & SAMPLE NO.	12185-18-01	185-18-02	185-18-03	185-18-04	185-18-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	20.0	44.5	68.5	92.5	116.5
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	260	259	257	262	259
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	20.00	24.50	24.00	24.00	24.00
EFFLNT GAS LITER	175.50	255.50	256.90	274.55	301.45
GM AQUEOUS LAYER	64.79	75.39	74.17	70.84	63.42
GM OIL	23.46	30.69	29.59	28.94	24.94
MATERIAL BALANCE					
GM ATOM CARBON %	79.15	89.23	89.57	92.58	91.28
GM ATOM HYDROGEN %	90.25	97.50	99.95	101.02	101.78
GM ATOM OXYGEN %	90.13	95.87	96.54	98.49	96.28
RATIO CHX/(H2O+CO2)	0.7336	0.8324	0.8261	0.8474	0.8556
RATIO X IN CHX	2.3360	2.3628	2.3823	2.4101	2.4278
USAGE H2/CO PRODT	2.1743	2.0708	2.0647	2.0361	2.0753
FEED H2/CO FRM EFFLNT	1.1402	1.0927	1.1159	1.0912	1.1150
RESIDUAL H2/CO RATIO	0.3764	0.4218	0.4559	0.4725	0.5811
RATIO CO2/(H2O+CO2)	0.0825	0.0846	0.0908	0.0974	0.0855
K SHIFT IN EFFLNT	0.0338	0.0390	0.0455	0.0510	0.0543
SPECIFIC ACTIVITY SA	2.8966	2.4422	2.4544	1.6981	1.2861
CONVERSION					
ON CO %	42.48	40.68	41.02	39.57	35.73
ON H2 %	81.01	77.10	75.91	73.83	66.51
ON CO+H2 %	63.01	59.70	59.42	57.44	51.96
PRDT SELECTIVITY,WT %					
CH4	10.76	12.18	13.18	14.53	15.51
C2 HC'S	2.32	2.33	2.44	2.52	2.47
C3H8	2.73	2.85	2.93	3.17	3.35
C3H6=	3.29	3.19	2.88	2.86	2.65
C4H10	2.55	2.66	2.73	2.89	3.04
C4H8=	4.04	3.81	3.63	3.56	3.30
C5H12	3.28	3.20	3.27	3.29	3.40
C5H10=	3.55	3.29	3.04	2.86	2.89
C6H14	3.16	3.28	3.53	3.44	3.65
C6H12= & CYCLO'S	2.10	1.84	1.93	1.74	1.64
C7+ IN GAS	7.51	7.89	8.11	7.66	9.01
LIQ HC'S	54.71	53.49	52.33	51.47	49.08
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	25.69	27.02	27.78	29.54	30.33
C5 -420 F	43.13	39.82	43.01	41.27	41.40
420-700 F	27.63	27.76	24.65	24.04	23.61
700-END PT	3.56	5.40	4.55	5.15	4.66

Table B16 (continued)

FILE: 1218518A TSS3Q1 A1

C5+-END PT	74.31	72.98	72.22	70.46	69.67
ISO/NORMAL MOLE RATIO					
C4	0.0162	0.0169	0.0163	0.0156	0.0173
C5	0.0549	0.0610	0.0569	0.0580	0.0545
C6	0.0616	0.0637	0.0634	0.0619	0.0630
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.7911	0.8546	0.9734	1.0564	1.2079
C4	0.6081	0.6731	0.7260	0.7826	0.8883
C5	0.8971	0.9474	1.0457	1.1210	1.1426
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8145	0.8318	0.8203	0.8254	0.8238
RATIO CH4/(1-A)**2	3.1271	4.3066	4.0812	4.7659	4.9942
ALPHA FRM CORRELATION	0.8584	0.8529	0.8492	0.8472	0.8373
ALPHA (EXPTL/CORR)	0.9489	0.9753	0.9659	0.9742	0.9838
W%CH4 FRM CORRELATION	11.7435	13.2373	13.9524	15.6338	18.0769
W%CH4 (EXPTL/CORR)	0.9158	0.9202	0.9447	0.9297	0.8581
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	CLD OIL	CLD OIL	CLD OIL	OIL WAX
DENSITY (* 40 C)	0.757	0.763	0.745	0.746	0.747
N, REFRACTIVE INDEX	1.4171*	1.4192*	1.4194*	1.4200*	1.4200*
SIMULT'D DISTILATN					
10 WT % @ DEG F	251	255	254	267	291
16	294	299	296	297	301
50	453	484	450	452	453
84	627	665	641	643	643
90	667	701	685	701	695
RANGE(16-84 %)	333	366	345	346	342
WT % @ 420 F	43.00	38.00	44.20	43.30	42.40
WT % @ 700 F	93.50	89.90	91.30	90.00	90.50

X. Summary

The work reported this Quarter was directed toward exploring the most promising developments of the Third Quarter, and centered mostly on catalysts prepared by the new method first used for Catalyst 11. Catalysts of this type have shown a potential for high activity and selectivity.

Three of the eight runs investigated the stability of these catalysts as a function of reaction temperature.

Catalysts which had performed well at 260C were less effective at initial temperatures of 250C and below, suffering losses both in initial conversion and in initial water gas shift activity.

A cobalt/X_9/X_{10}/UCC-103 catalyst was found to have good to excellent stability at reaction temperatures of 250C and below.

A similar catalyst, with UCC-113 in place of UCC-103, was less stable at all temperatures tested.

The new additive X_{11}, tested in a UCC-103 catalyst, contributed excellent stability at temperatures up to 260C, as well as interesting selectivity effects. These included a significant shift toward a heavier product, with C_5^+ production more than 80 percent at 260C, methane production less than 8 percent, and the light gasoline fraction significantly higher in olefins. Total motor fuels were reduced because of high wax production, but the

valuable high-quality diesel fraction (420-700F) was substantially higher.

Two other additives, X_4 and X_3, proved ineffective.

Finally, tests of pretreatment methods disclosed a possible correlation between the Molecular Sieve component crystallinity and a carbon number cut-off, which is to be subjected to further study.

APPENDIX C. TABULATION OF PREVIOUS IRON CATALYST RUNS AND THEIR SPECIFIC ACTIVITIES

Table C1

TESTS ON IRON CATALYST SYSTEMS
Comparison against a rate expression for cobalt catalyst
in terms of SA at 50:50 feed, 300 psig, 250 C

Shape Select -ive Componnt	METAL COMPONENTS & PREPARATION: Precipitation		Physical Mixture			Intimate Contact
	Fe-ppt-_	Fe-ppt- +K	ref Fe,K +	ucc Fe,K +	Fe,Rh +	Fe,K-
No molsv			10011-6,Q7 *			
Alumina				10011-15,Q8 (0.649)		
Y-52,NaY	9972-12,Q7 *					
UCC-101	9710-18,Q6 * -19, " * 10011- 1, " * - 2, " (<.50) - 4, " (<.34) - 5, " (<.13) 9972-11,Q7 (<.64) 10011- 7, " *	10011-11,Q8 (.534) -12, " (.072)	10011-8,Q7(.904)	10011- 9,Q7 (0.555)		
UCC-103						12200-10,R3 (0.514) -11,R3 (0.413)
UCC-107		10112-11,Q9 (.070)				
UCC-111				10225-03,Q9 (0.995)		
UCC-109				10011-17,Q9 (0.954)		
UCC-104		10225-4,Q9 (.030)		10011-10,Q8 (0.604)		
UCC-108		10011-16,Q8 (.025)		10225-5,Q10(1.02)	10225-10,Q10 (0.431) 10225-11,Q11 *	
LZ-105-6		10225-1,Q9 (.621)				

Note: Q - quarterly report, 1st contract. R - quarterly report, 2nd contract
* - experimental condition not conducive for such comparison
( ) - Specific Activity of the catalyst

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