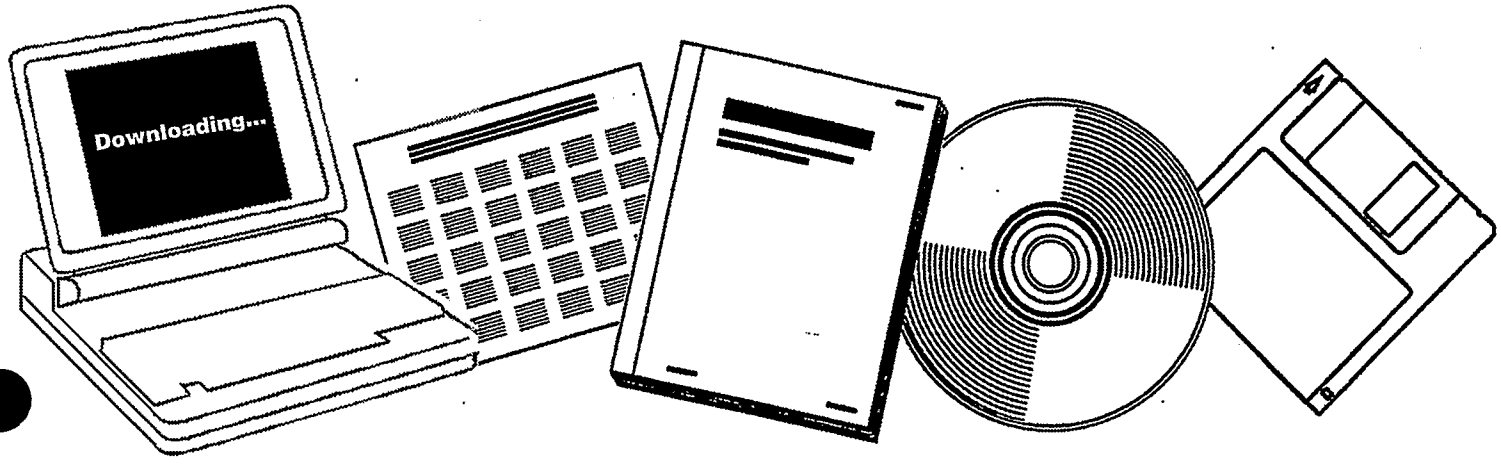
IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. FIFTH QUARTERLY TECHNICAL PROGRESS REPORT, OCTOBER-DECEMBER 1985

UNION CARBIDE CORP., TARRYTOWN, NY.
TARRYTOWN TECHNICAL CENTER

1985



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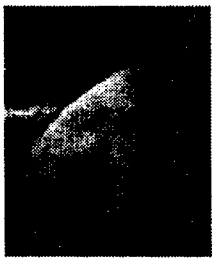

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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

Fifth Quarterly Report
October - December 1985

IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS

DOE-CH Form 383 (Rev. 6-78)

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

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Contents

Appendixes

I. CONTRACT OBJECTIVE

The objective of the contract is to consolidate the advances made during the previous contract in the conversion of syngas to motor fuels using Molecular Sieve-containing catalysts and to demonstrate the practical utility and economic value of the new catalyst/process systems with appropriate laboratory runs.

II. SCHEDULE

The contract work was planned for the twenty-eight month period beginning September 18, 1984.

Work on the program is divided into six tasks.

Task 1 consists of the preparation of a detailed, non-proprietary work plan covering the entire performance of the contract. This work plan was completed in November, 1984.

Task 2 consists of a preliminary techno-economic assessment of the UCC catalyst/process system. This assessment, as well as the final techno-economic evaluation planned for Task 6, will be based on a sensitivity analysis which MITRE will conduct on their recently completed economic evaluation of the Union Carbide Corporation (UCC) system.

Task 3 consists of the optimization of the most promising catalysts developed under prior contract DE-AC22-81PC40077 toward goals defined by the MITRE and Task 2 studies. This work will run through the first 24 months of the contract.

Task 4 consists of the optimization of the UCC catalyst system in a manner which will give it the longest possible service life. This work will run through the first 24 months of the contract.

Task 5 consists of the optimization of a UCC process/catalyst system based upon a tubular reactor with a recycle loop

(i.e., the Arge reactor) containing the most promising catalysts developed under the Tasks 3 and 4 studies. This optimal performance will be estimated from a mathematical model of the tubular reactor which incorporates reaction rate constants determined from appropriate Berty reactor runs. This effort will run through the first 24 months of the contract.

Task 6 consists of an economic evaluation of the optimal performance found under Task 5 for the UCC process/catalyst system. This effort will be based on the MITRE sensitivity analysis referred to in the description of Task 2.

The final four months of the contract will be devoted exclusively to the writing of the Eighth Quarterly Report and the Final Technical Report.

III. ORGANIZATION

This contract is being carried out by the Catalyst Research and Development Group of the Molecular Sieve Technology Department, Catalysts and Process Systems Division, Union Carbide Corporation, Tarrytown, New York.

The principal investigator is Dr. Jule A. Rabo.

The program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

Task 1, a detailing of the work planned for the other tasks in the contract, has been completed.

B. Task 2

Task 2, a preliminary techno-economic assessment of the UCC catalyst/process system, will be based on a sensitivity analysis which MITRE is conducting on their recently completed economic evaluation of the UCC system.

This sensitivity study is expected to graphically show the differential cost (around the base case cost), expressed as differential cents per gallon of motor fuels, for changes in each of the operating parameters of space velocity, catalyst life, methane make, alpha, C_{25}-C_{30} carbon cutoff, overall conversion, feed H_2:CO ratio, reactor temperature, and reactor pressure.

These differential cost-operating parameter curves will not only strikingly illuminate which of those operating parameters have the greatest effect on product cost (for Task 2), but they will also be used with catalyst performance data and the existing tubular reactor design curves to readily obtain an economic worth for each tested catalyst for any set of envisioned process conditions (for Task 6).

C. Tasks 3 and 4

The focus of the quarter's catalyst testing revolved around establishing the validity of previously observed deviations from normal Schulz-Flory kinetics and around further improving the X_{11} promoted Catalyst 32 (Run 12200-19), which demonstrated promising product quality and selectivity.

Attempts to reproduce the potential "carbon number cut-off" observed with two previous X_9 and X_{10} promoted catalysts were unsuccessful.

Significant improvement was made on the promising X_{11} promoted Catalyst 32 by using newly developed Molecular Sieves, TC-123 and TC-133, as the catalyst supports in place of TC-103.

At 240C the TC-123 catalyst (Run 45) demonstrated superior selectivity to comparable TC-103 catalysts. This was evidenced by reduced methane make, high C_5^+ yield and high olefin content. The catalyst's inherently low methane production rate permitted it to be operated with a higher H_2:CO feed ratio to achieve a higher conversion rate.

The preliminary test results for these catalysts are summarized in Appendix A. The detailed test results for the catalysts first reported in last quarter's report (Appendix A of that report) are given in Appendix B.

D. Task 5

A dual capillary gas chromatographic method for the characterization of Fischer-Tropsch reaction products, developed by the Pittsburgh Energy Technology Center (PETC), has been successfully

implemented by Union Carbide Corporation's Tarrytown, N.Y., Central Scientific Laboratory.

Appendix C details the quantitative results obtained by this method for a sample of the hydrocarbon product produced during Run 11677-11 of the previous contract, and reported as Run 6 in the Third Annual Report of that contract.

This comprehensive analysis verifies earlier, less vigorous analyses which indicated that the C_5-C_{11} gasoline cut lacks aromatics and naphthenes (desirable for high yield reforming), and that the C_{12}-C_{18} distillate range contains predominantly normal paraffins (giving it a high cetane number).

Work was completed on the conversion of all of the DTSS programs (Dartmouth Time Sharing System, an outside computer system) over to CAS (Catalysts and Services, an inside computer system) before the January 1st termination of DTSS.

E. Task 6

The final techno-economic evaluation will begin with the promising performance of Catalyst 45 (described in Appendix A). Its Berty (CSTR) rate data will be used with our mathematical simulation of the tubular reactor to generate a wide range of possible process operating conditions. These conditions, in turn, will be costed with the forthcoming results of MITRE sensitivity studies to define the optimum set of conditions that will give the lowest cost/bbl of F-T product.

This effort will begin in February, after the ongoing conversions of computer programs are completed.

V. CHANGES

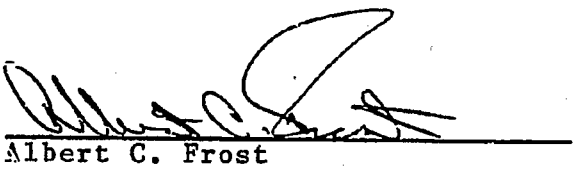
There were no contract changes during the Fourth Quarter.

The nomenclature of the shape-selective components of our catalysts has been amended, in keeping with the desires of our Law Department, to change the prefix letters from "UCC-" to "TC-". This new prefix will also be used when describing old catalysts previously described with the "UCC-" prefix. However, the headings of the tables in Appendix B, prepared some months ago, are presented with the zeolite components prefixed with "U", a short-hand version of the old "UCC" prefix.

VI. FUTURE WORK

Tasks 3 and 4 will continue to be devoted to developing new, stable catalyst formulations which will have higher specific activities and lower methane makes than do our present catalysts.

Task 5 will be devoted to examining the space velocity-methane make trade-off with correlated data for the $Co/X_{11}/TC-103$ and $Co/X_{11}/TC-123$ catalyst systems.



Albert C. Frost

APPENDIX A. CATALYST TESTING: SUMMARY OF RUNS REPORTED DURING THIS QUARTER

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J. G. Miller, L. F. Elek, C-L Yang and K. N. Beale

This report is organized around the five catalytic tests conducted from October through December 1985, the fifth quarter of this contract.

A list of the catalysts tested, a description of their preparation, and a brief statement of each test's objective, are shown in Table A1. All of the catalysts tested involved cobalt oxide intimately contacted with one of three Molecular Sieve supports: TC-103, TC-123 or TC-133. Two of the catalysts (Runs 44 and 47) looked at establishing the validity of the deviations from the Schulz-Flory kinetics observed previously in Runs 20 and 31. The remainder of the runs probed the use of the newly developed Molecular Sieves TC-123 and TC-133.

An abbreviated table of results for these catalyst runs is shown in Table A2. The conversion, weight percent CH_4, weight percent C_5^+, specific activity and methane factor, as well as a qualitative estimate of stability, are listed for each catalyst. A more complete report of results and analyses of these runs will be presented in the Sixth Quarterly Report.

Table A1. Description of most of the catalysts tested during the fifth quarter.

Run	Catalyst	Catalyst preparation	Objective of test
44	Co/X_9/X_{10}/TC-103 (12561-01)	The X_9 and X_{10} promoted cobalt oxide catalyst was formulated similarly to Catalyst 20. Theoretical pct Co=11.9, pct X_9=0.5, pct X_{10}=0.7.	To reproduce the carbon number cut-off observed in Run 20.
45	Co/X_{11}/TC-123 (12570-02)	The X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 32, except that TC-123 was substituted for TC-103 and a slightly different catalyst pretreatment method was used. Theoretical pct Co=8.2, pct X_{11}=1.6.	To test the use of TC-123 as the catalyst support.
46	Co/X_{11}/TC-133 (12561-02)	The X_{11} promoted cobalt oxide catalyst was formulated similarly to Run 45, except that TC-133 was substituted for TC-103. Theoretical pct Co=8.2, pct X_{11}=1.6.	To test the use of TC-133 in the catalyst.
47	Co/X_9/X_{10}/TC-103 (11617-06)	The X_9 and X_{10} promoted cobalt oxide catalyst was formulated similarly to Run 31. Theoretical pct Co=7.8, pct X_9=0.35, pct X_{10}=0.47.	To reproduce the carbon number cutoff observed for Run 31 and to test a new activation procedure.
48	Co/X_{11}/X_{12}/TC-123 (11617-07)	The X_{11} and X_{12} cobalt oxide catalyst was formulated similarly to Run 39, except that TC-123 was substituted for TC-103. Theoretical pct Co=7.6, pct X_{11}=1.4, pct X_{12}=5.0.	To test the use of X_{12} to improve the activity of Run 45, while maintaining its good activity.

Table A2. Preliminary catalyst test results for most of the runs made during the fifth quarter.

Run	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Methane factor[a]	Stability
44	$Co/X_9/X_{10}/TC-103$ (12561-01)	47.5	44.7	10.8	77.4	2.45	2.36	Fair[b]
		235.0	41.3	10.6	78.3	2.14	0.73	
45	$Co/X_{11}/TC-123$ (12570-02)	45.3	48.0	3.6	91.7	3.36	1.17	Excellent[b]
		259.3	46.2	3.4	90.3	2.95	0.65	
		282.7	57.7	7.3	85.2	2.32	1.96	Excellent[c]
		475.7	57.7	6.1	86.3	2.37	1.84	
		499.8	62.6	11.2	80.7	3.16	17.7	Excellent[f]
		571.8	62.2	11.5	80.0	2.05	4.61	
		595.8	70.1	7.2	85.7	1.84	2.67	Good[e]
		740.8	66.7	7.8	84.9	1.51	2.11	
		(Catalyst was tested a total of 1500 hrs.)						
46	$Co/X_{11}/TC-133$ (12561-02)	48.0	49.6	6.3	83.7	2.44	2.02	Excellent[b]
		170.0	50.3	5.3	85.6	2.64	1.35	
		194.5	64.3	13.5	74.8	2.22	4.28	Excellent[c]
		336.0	63.6	11.5	78.3	2.19	4.03	
		360.0	67.3	8.3	82.2	1.49	1.67	Good[d]
		459.0	66.8	10.7	79.0	1.22	2.62	
		480.5	67.9	14.5	74.6	0.97	3.85	Excellent[e]
		646.5	66.7	15.0	73.8	0.96	3.93	
47	$Co/X_9/X_{10}/TC-103$ (11617-06)	26.5	8.2	21.9	62.4	0.17	2.23	___[b]
		72.5	8.3	21.0	65.0	0.17	2.12	

Conditions:

a. The ratio of the quantity of CH_4 actually produced to the quantity of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.
b. 240C, 300 psig, 300 GHSV, 1:1 H_2:CO.
c. " " " " " 1.5:1 H_2:CO.
d. " 500 psig " " " "
e. " " " " " 1.75:1 H_2:CO.
f. " 300 psig " " " "

continued

Table A2, continued.

Run	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Methane factor[a]	Stability
48	$Co/X_{11}/X_{12}$/TC-103 (11617-07)	43.5	49.6	3.7	87.4	6.50	2.48	Excellent[b]
		189.0	51.8	4.3	87.3	3.75	0.72	
		236.0	65.5	19.2	68.8	2.84	4.15	Excellent[c]
		333.0	68.1	17.5	71.4	3.01	3.52	
		357.0	69.2	8.4	80.1	2.00	1.02	Good[d]
		501.0	65.2	8.5	78.8	1.65	0.88	

Conditions:

a. The ratio of the quantity of CH_4 actually produced to the quantity of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.

b. 240C, 300 psig, 300 GHSV, 1:1 H_2:CO.

c. " " " " " 1.5:1 H_2:CO.

d. " 500 psig " " " "

APPENDIX B. CATALYST TESTING: DETAILS OF RUNS REPORTED DURING LAST QUARTER

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J. G. Miller, L. F. Elek, C-L Yang and K. N. Beale

Contents

I. INTRODUCTION

Presented in this report are detailed analyses of ten catalyst test runs summarized in Appendix A of the Fourth Quarterly Report, which constituted the major thrust of the work during that quarter.

All ten catalysts contained X_{11}-promoted cobalt oxide, in intimate contact with a Molecular Sieve. In Catalysts 34 and 35 the Molecular Sieves were, respectively, TC-114 and TC-115; in the eight remaining catalysts it was TC-103. Catalysts 40 and 41 were formulated by the method developed in the previous contract, and the eight remaining catalysts by the method first used for Catalyst 11 of the Third Quarterly Report.

The purpose of all these tests was to explore a number of variations on Fourth Quarterly Report Catalyst 32 (Run 12200-19, $Co/X_{11}/TC-103$), a promising formulation with superior activity and selectivity. Among the variations tested were methods of pretreating the catalyst, new Molecular Sieve supports, higher concentrations of Co and X_{11}, and use of a new additive, X_{12}. In addition, an attempt was made to replicate the results of Run 12200-19.

II. Run 34 (12200-20) with Catalyst 34 ($Co/X_{11}/TC-114$)

The purpose of this run was to test a variation on the highly promising Catalyst 32 of the Fourth Quarterly Report (Run 12200-19, $Co/X_{11}/TC-103$)--namely, the substitution for TC-103 of a newly developed Molecular Sieve, TC-114. The formulation was similar to that of Catalyst 32, with the X_{11}-promoted cobalt oxide formed in close contact with TC-114 by the method developed for Catalyst 11 of the Third Quarterly Report. The theoretical concentrations of cobalt and X_{11}, 8.2 and 1.6 percent respectively, were the same as in Catalyst 32.

Only one sample was taken, at 19.5 hours on stream, after which the run was terminated. The simulated distillation of the C_5^+ product in that sample is plotted in Fig. B1, the carbon number product distribution in Fig. B2, and the chromatogram from a simulated distillation in Fig. B1. Detailed material balances appear in Table B1.

The initial syngas conversion was about 9 percent, only 20 percent as good as with Catalyst 32. Due to the high residual H_2:CO ratio in the Berty reactor resulting from the low conversion, the product selectivity was equally poor.

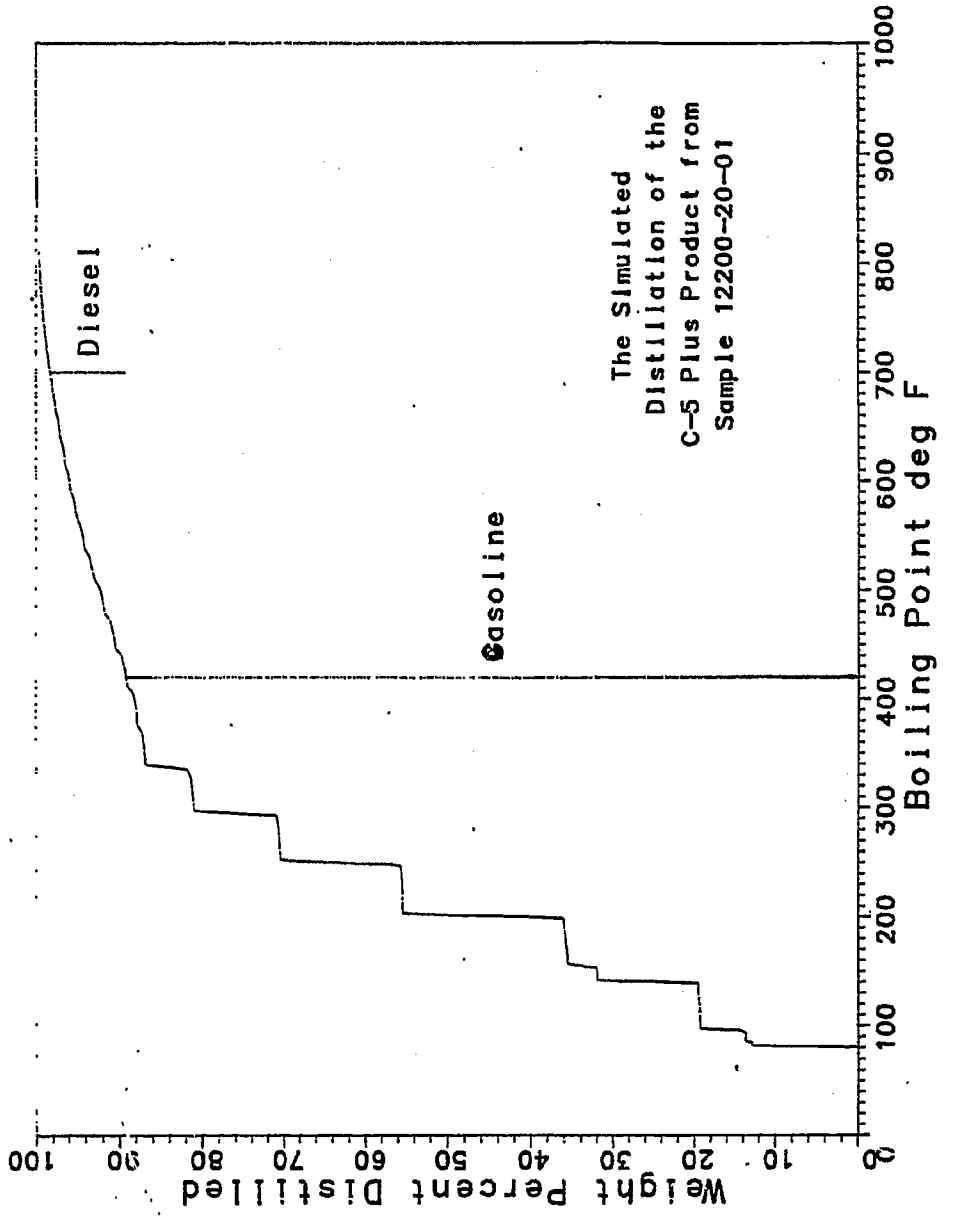

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-20-01
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B1

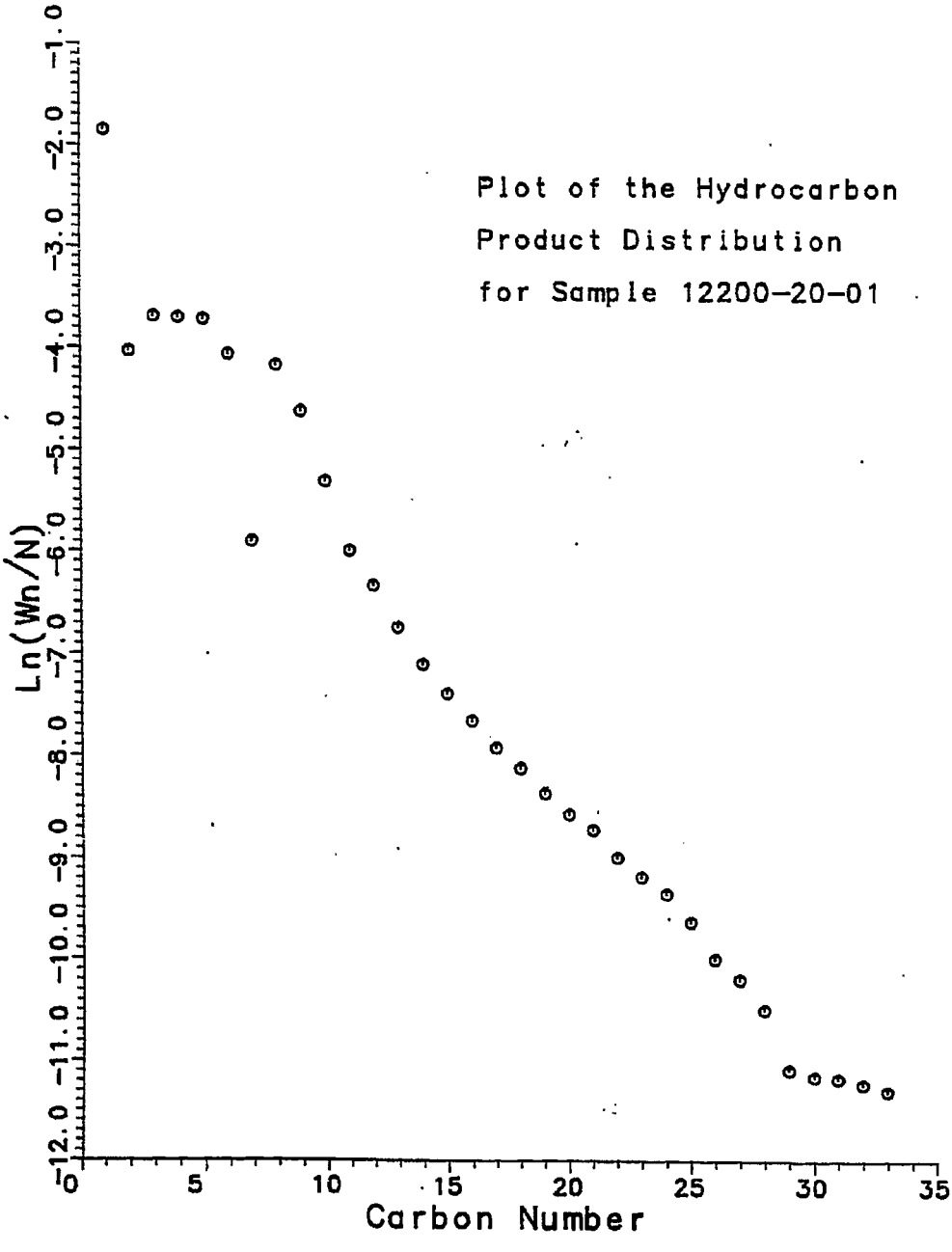

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-20-01
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B2

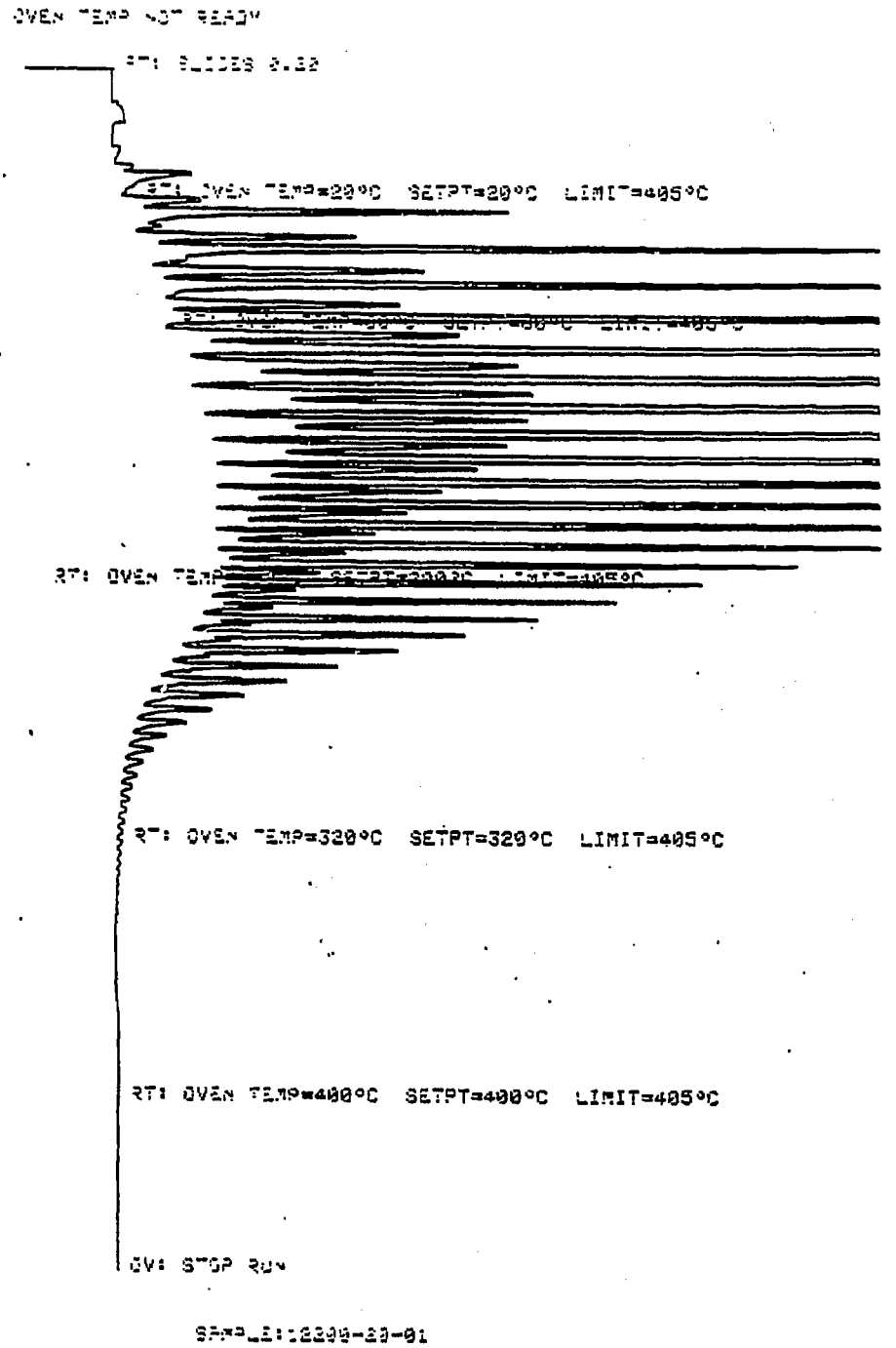

OVEN TEMP NOT READY
RT: SLICES 0.32
RT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
OV: STOP RUN

Fig. B3

Table B1

FILE: 1220020A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-20
CATALYST CO/K11-U114 80 CC 46.2 G AFTER USE:44.6 G (-1.6 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-93-6)

RUN & SAMPLE NO.	12200-20-01
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	19.5
PRESSURE,PSIG	300
TEMP. C	241
FEED CC/MIN	400
HOURS FEEDING	19.50
EFFLNT GAS LITER	410.05
GM AQUEOUS LAYER	4.63
GM OIL	0.62
MATERIAL BALANCE	
GM ATOM CARBON %	94.75
GM ATOM HYDROGEN %	91.80
GM ATOM OXYGEN %	96.17
RATIO CHX/(H2O+CO2)	0.7678
RATIO X IN CHX	2.4915
USAGE H2/CO PRODT	2.4596
FEED H2/CO FRM EFFLNT	0.9688
RESIDUAL H2/CO RATIO	0.8890
RATIO CO2/(H2O+CO2)	0.0197
K SHIFT IN EFFLNT	0.0178
SPECIFIC ACTIVITY SA	0.1756
CONVERSION	
ON CO %	5.09
ON H2 %	12.91
ON CO+H2 %	8.94
PRDT SELECTIVITY,WT %	
CH4	15.75
C2 HC'S	3.55
C3H8	5.69
C3H6=	1.78
C4H10	8.37
C4H8=	1.51
C5H12	11.44
C5H10=	0.71
C6H14	10.32
C6H12= & CYCLO'S	0.00
C7+ IN GAS	31.44
LIQ HC'S	9.44
TOTAL	100.00
SUB-GROUPING	
C1 -C4	36.66
C5 -420 F	56.48
420-700 F	5.82
700-END PT	1.04

Table B1 (continued)

FILE: 1220020A TSS4Q1 A1

C5+-END PT	63.34
ISO/NORMAL MOLE RATIO	
C4	1.0882
C5	2.4722
C6	3.4526
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	3.0479
C4	5.3585
C5	15.6250
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.7462
RATIO CH4/(1-A)**2	2.4454
ALPHA FRM CORRELATION	0.8176
ALPHA (EXPTL/CORR)	0.9127
W%CH4 FRM CORRELATION	20.2497
W%CH4 (EXPTL/CORR)	0.7776
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLR OIL
DENSITY	N/A
N, REFRACTIVE INDEX	N/A
SIMULT'D DISTILATN	
10 WT % @ DEG F	331
16	372
50	505
84	661
90	706
RANGE(16-84 %)	289
WT % @ 420 F	27.30
WT % @ 700 F	89.00

III. Run 35 (12185-20) with Catalyst 35 ($Co/X_{11}/TC-115$)

This run tested a second variation on Catalyst 32, the substitution of the Molecular Sieve TC-115 for TC-103. The formulation was similar to that of Catalyst 34 except with lower levels of cobalt and X_{11}, the theoretical concentrations of which were 4.1 and 0.8 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B4-7. Simulated distillations of the C_5^+ product are plotted in Figs. B8-9. Carbon number product distributions are plotted in Figs. B10-11. Chromatograms from simulated distillations are reproduced in Figs. B12-13. Detailed material balances appear in Table B2.

The performance of this catalyst was little better than that of Catalyst 34. Initial syngas conversion was only 13 percent, and methane production was unacceptably high at about 30 percent.

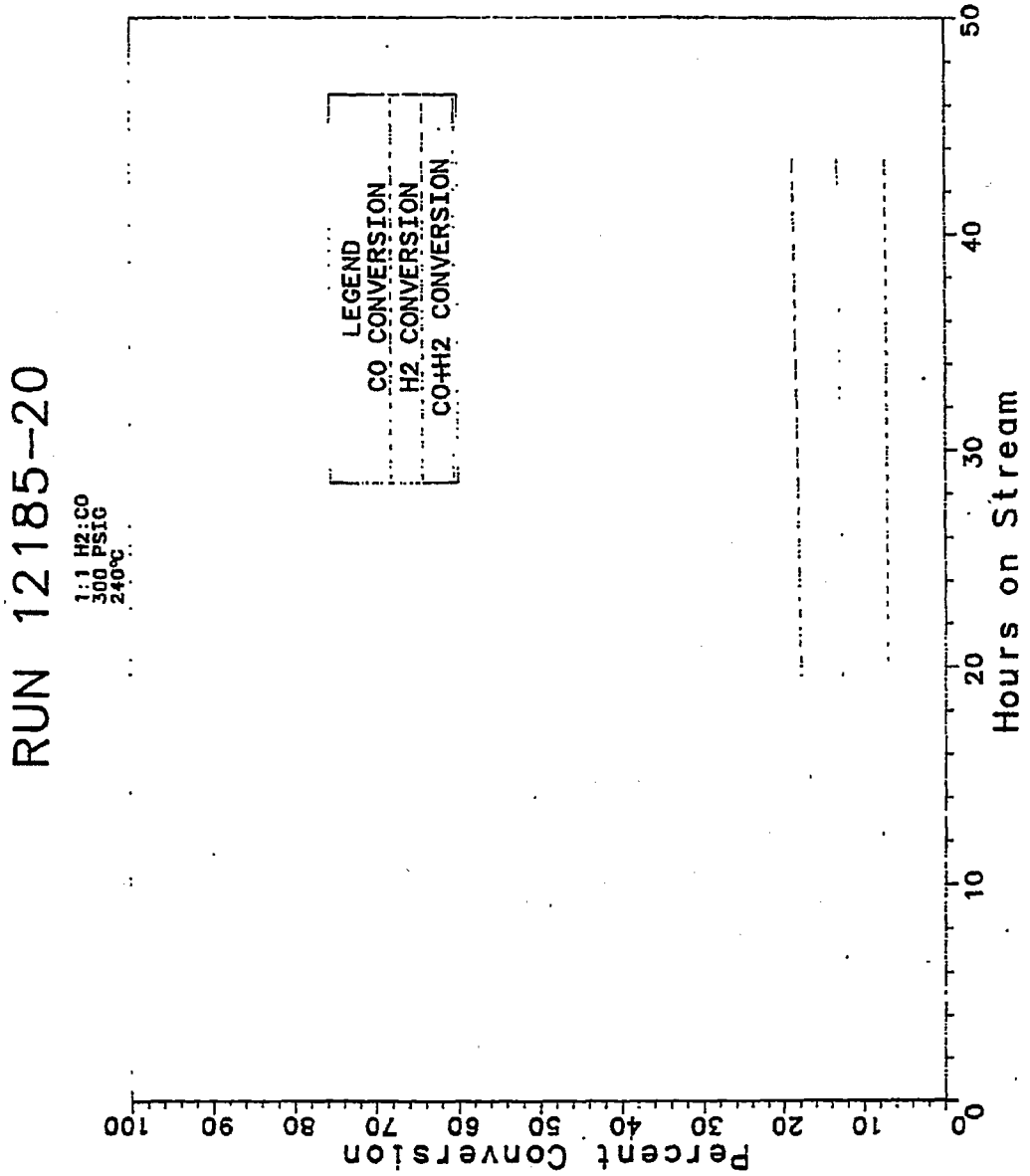

RUN 12185-20
1:1 H2:CO
300 PSIG
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50

Fig. B4

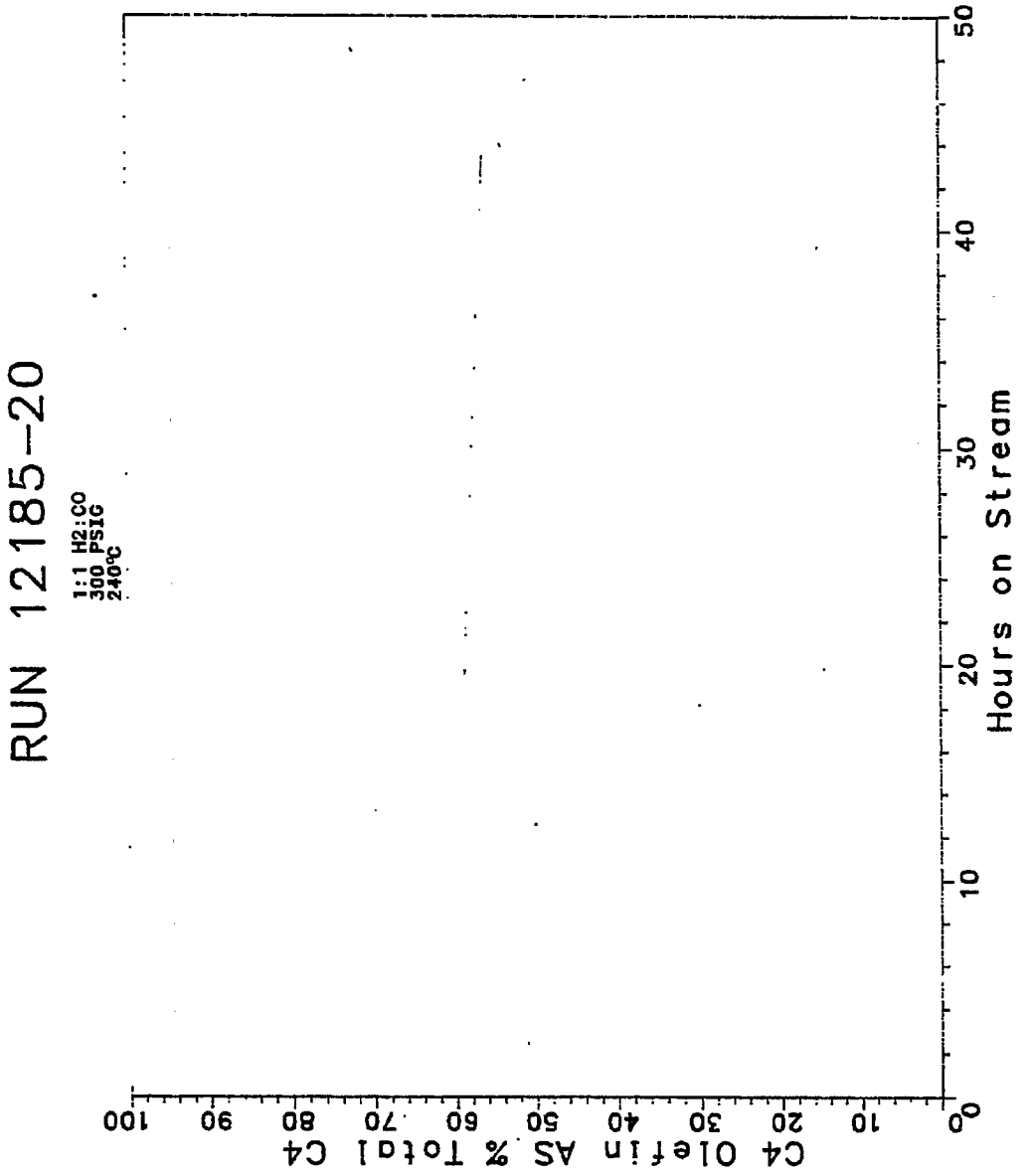

RUN 12185-20
1:1 H2:CO
300 PSIG
240°C
C4 Olefin As % Total C4
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
Hours on Stream

Fig. B5

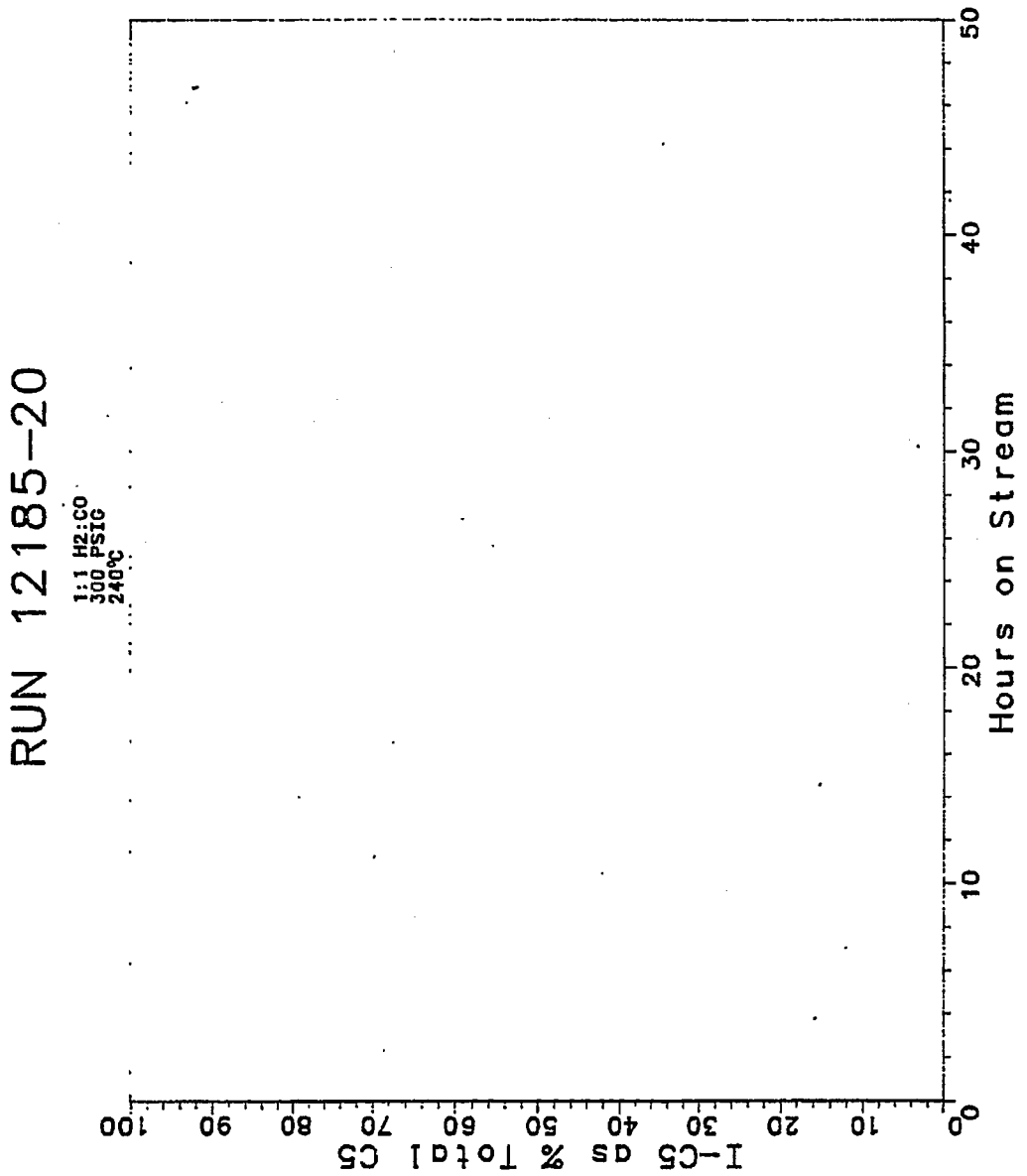

RUN 12185-20
1:1 H2:CO
300 PSIG
240°C
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
Hours on Stream

Fig. B6

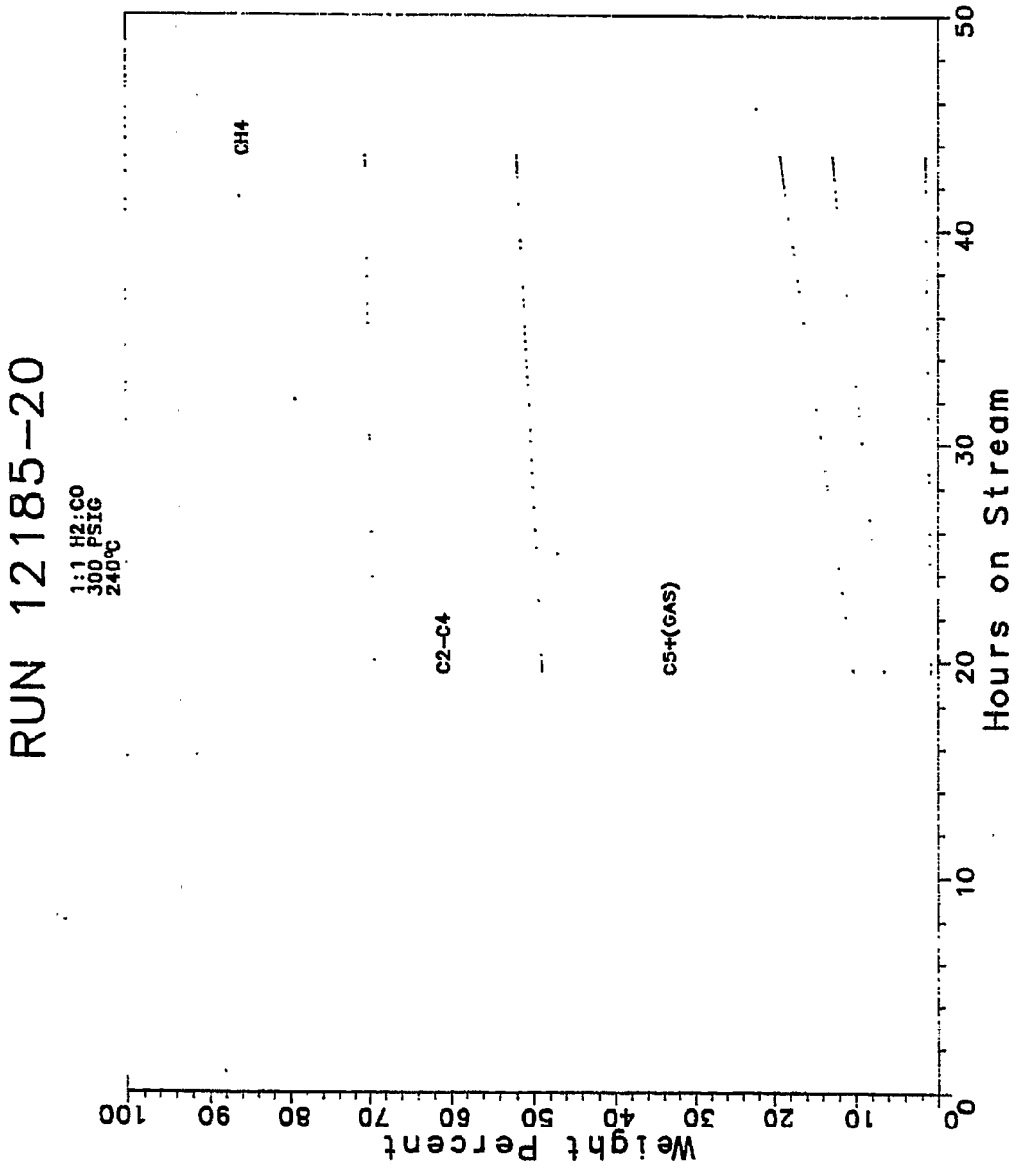

RUN 12185-20
1:1 H2:CO
300 PSIG
240°C
CH4
C2-C4
C5+(GAS)
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50

Fig. B7

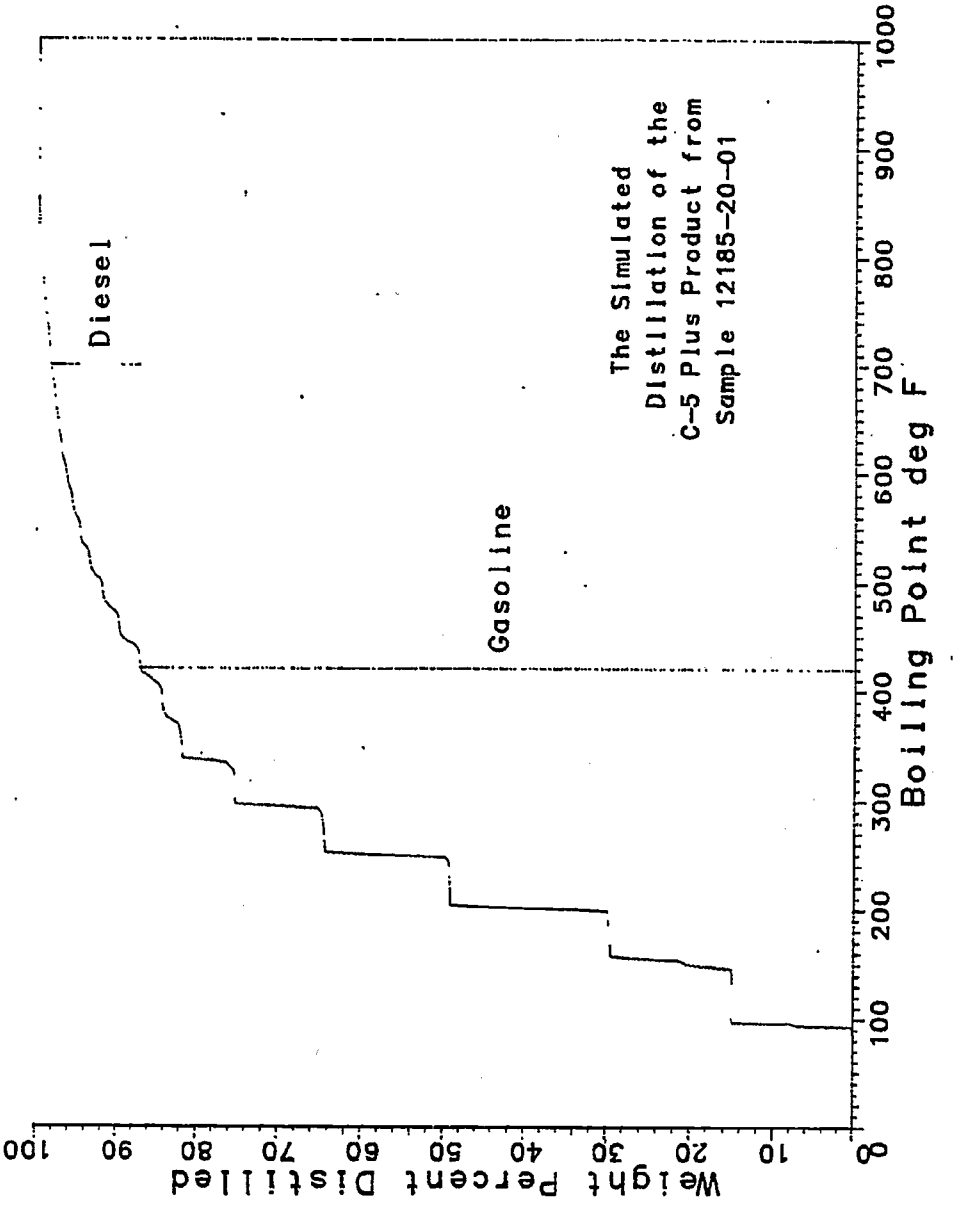

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-20-01
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B8

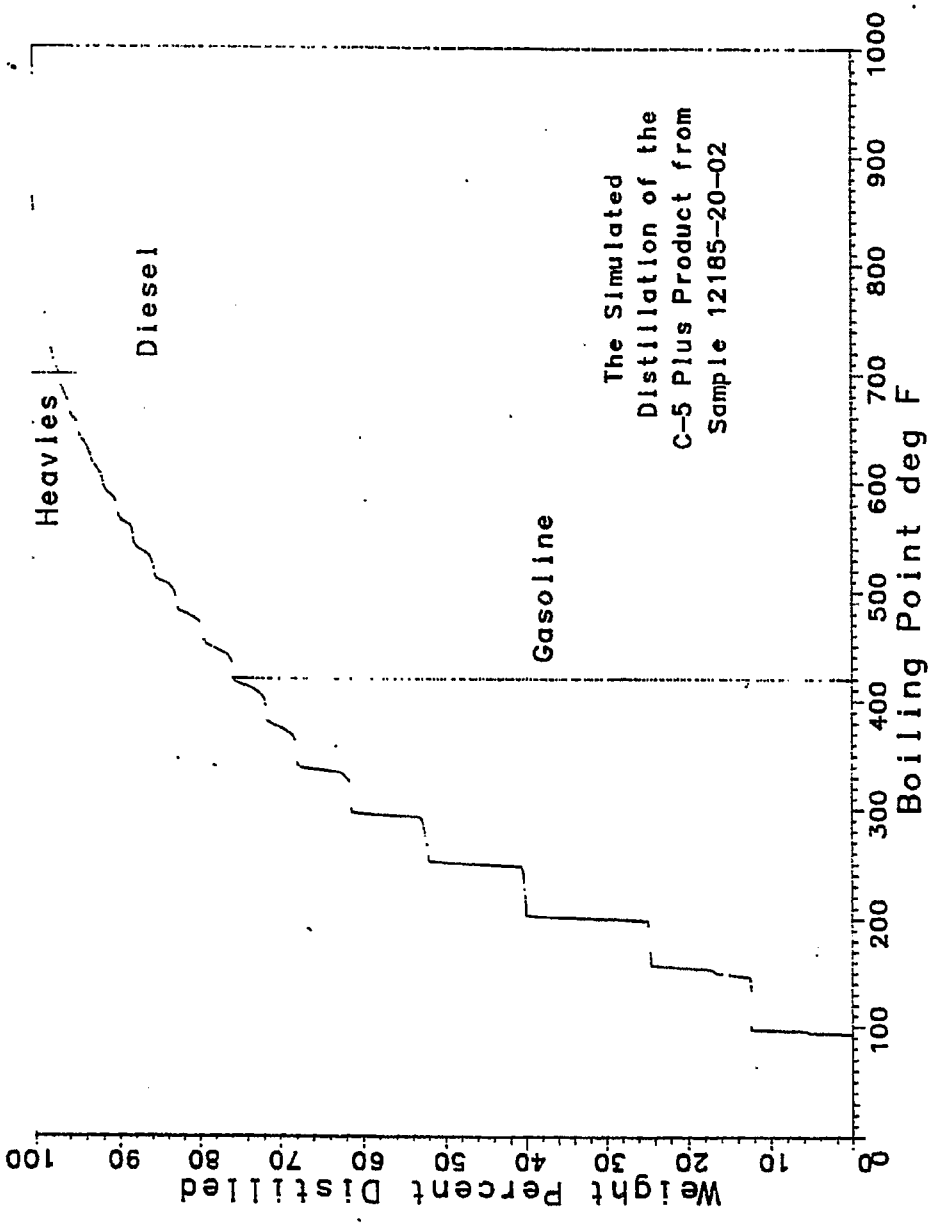

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-20-02
Gasoline
Diesel
Heavies
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B9

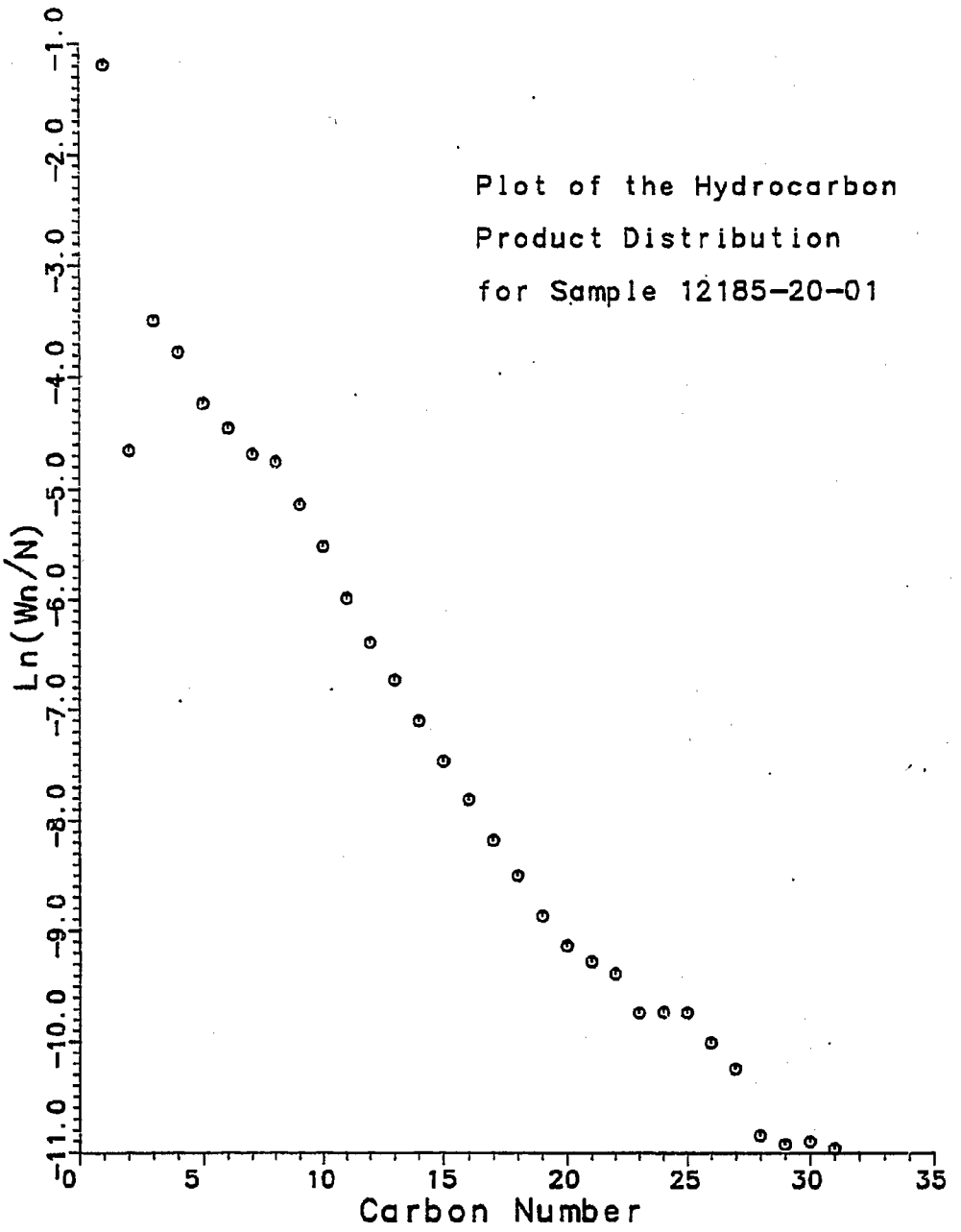

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-20-01
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B10

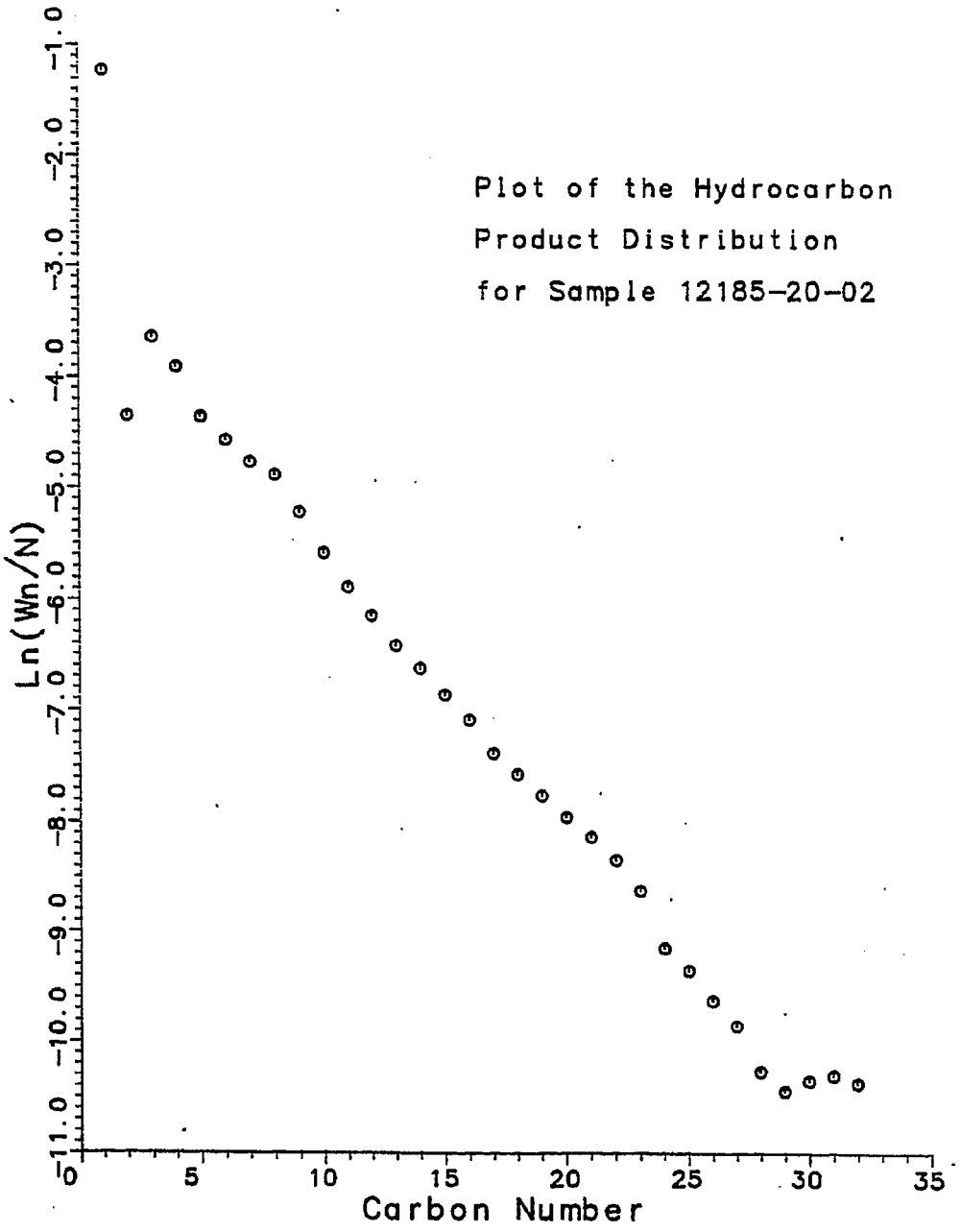

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-20-02
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B11

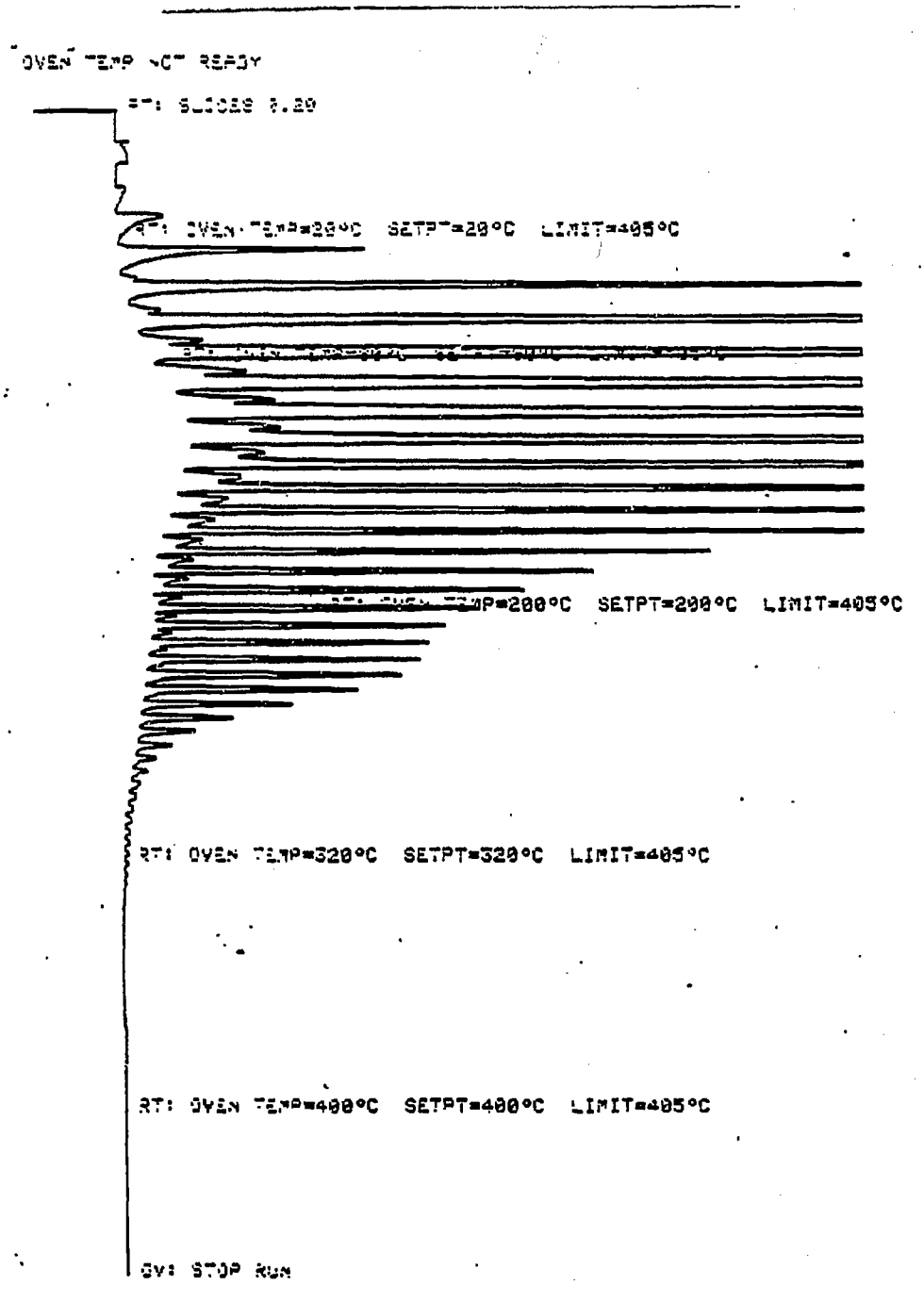

OVEN TEMP >C" READY
RT: OVEN TEMP=200°C SETPT=200°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
SV: STOP RUN

Fig. B12

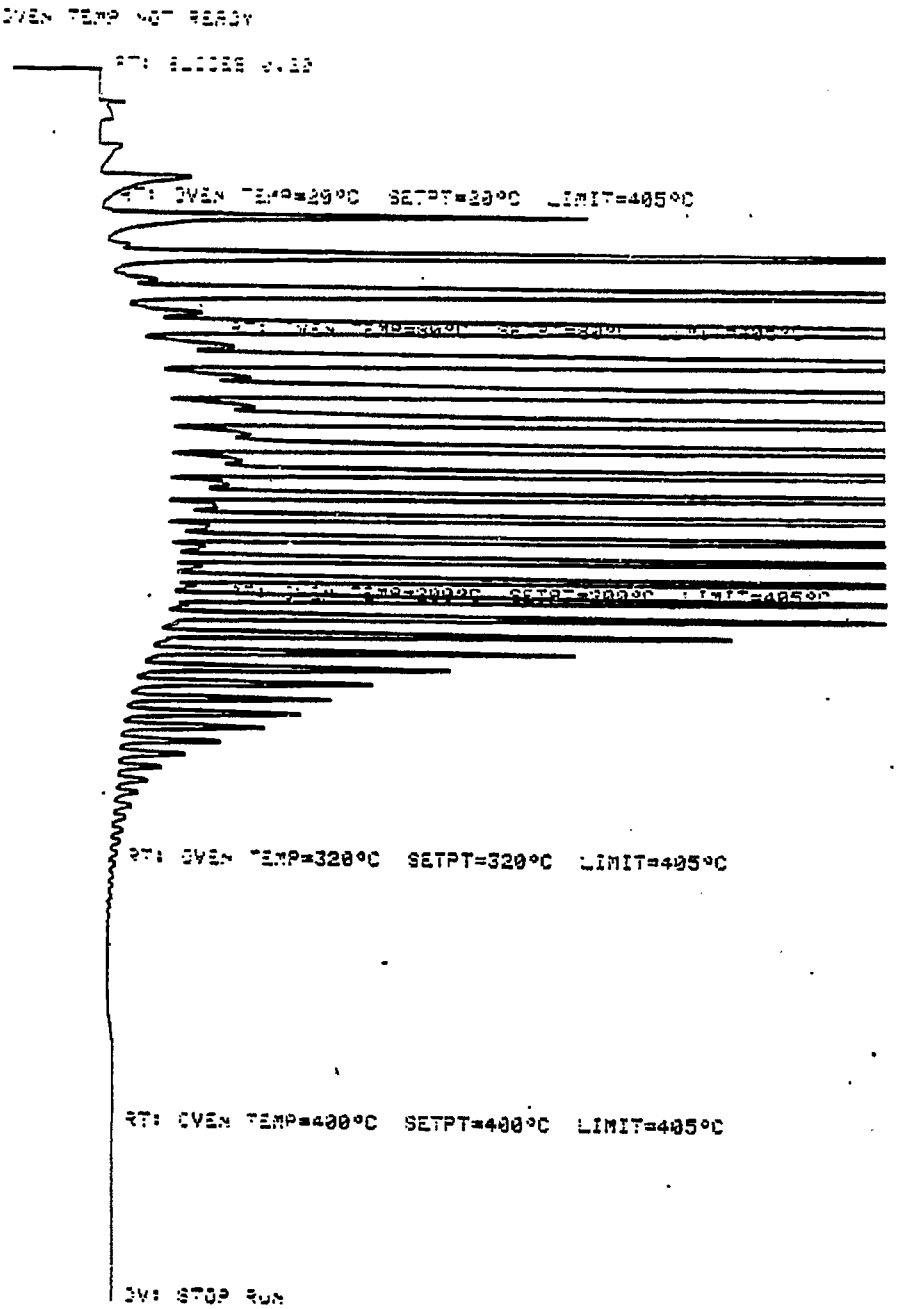

OVEN TEMP NOT READY
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
SV: STOP RUN

Fig. B13

Table B2

FILE: 1218520A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-20
CATALYST CO/X11-U115 80 CC 45.9 G AFTER USE:44.6 (-1.3 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-94)

RUN & SAMPLE NO.	12185-20-01	185-20-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	19.5	43.5
PRESSURE,PSIG	300	300
TEMP. C	242	242
FEED CC/MIN	400	400
HOURS FEEDING	19.50	24.00
EFFLNT GAS LITER	408.30	497.70
GM AQUEOUS LAYER	9.88	13.46
GM OIL	0.93	2.21
MATERIAL BALANCE		
GM ATOM CARBON %	93.24	92.72
GM ATOM HYDROGEN %	98.85	98.88
GM ATOM OXYGEN %	95.92	95.76
RATIO CHX/(H2O+CO2)	0.7053	0.6868
RATIO X IN CHX	2.6702	2.6623
USAGE H2/CO PRODT	2.6958	2.7348
FEED H2/CO FRM EFFLNT	1.0602	1.0664
RESIDUAL H2/CO RATIO	0.9372	0.9356
RATIO CO2/(H2O+CO2)	0.0109	0.0096
K SHIFT IN EFFLNT	0.0103	0.0091
SPECIFIC ACTIVITY SA	0.2129	0.2215
CONVERSION		
ON CO %	7.00	7.27
ON H2 %	17.79	18.65
ON CO+H2 %	12.55	13.14
PRDT SELECTIVITY,WT %		
CH4	30.75	29.53
C2 HC'S	1.92	2.61
C3H8	4.06	3.73
C3H6=	5.20	4.19
C4H10	3.91	3.59
C4H8=	5.38	4.45
C5H12	3.72	3.61
C5H10=	3.61	2.81
C6H14	4.29	3.97
C6H12= & CYCLO'S	2.74	2.26
C7+ IN GAS	24.20	20.16
LIQ HC'S	10.22	19.09
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	51.20	48.09
C5 -420 F	42.38	39.14
420-700 F	5.59	11.24
700-END PT	0.82	1.53

Table B2 (continued)

FILE: 1218520A TSS4Q1 A1

C5+-END PT	48.80	51.91
ISO/NORMAL MOLE RATIO		
C4	0.0000	0.0000
C5	0.0000	0.0000
C6	0.0000	0.0000
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	0.7449	0.8502
C4	0.7013	0.7773
C5	1.0035	1.2511
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.7433	0.7767
RATIO CH4/(1-A)**2	4.6662	5.9220
ALPHA FRM CORRELATION	0.8150	0.8151
ALPHA (EXPTL/CORR)	0.9121	0.9529
W%CH4 FRM CORRELATION	21.2919	21.2662
W%CH4 (EXPTL/CORR)	1.4440	1.3886
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLR OIL	CLD OIL
DENSITY	N/A	N/A
N, REFRACTIVE INDEX	N/A	N/A
SIMULT'D DISTILATN		
10 WT % @ DEG F	335	337
16	371	374
50	453	481
84	610	638
90	676	682
RANGE(16-84 %)	239	264
WT % @ 420 F	37.30	33.10
WT % @ 700 F	92.00	92.00

IV. Run 36 (12200-21) with Catalyst 36 (Co/X_{11}/TC-103)

The variation on Catalyst 32 tested in this run was made up of the same constituents as Catalyst 32 but with a higher concentration of cobalt oxide. As in Catalyst 32, the X_{11}-promoted cobalt oxide was formed in close contact with TC-103 by the method first developed for Catalyst 11 of the Third Quarterly Report. Pretreatment of the catalyst, however, was by the method used for Catalysts 20 and 31, both of which showed potential carbon number cut-offs. The theoretical concentrations of cobalt and X_{11} were 12.3 and 2.4 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B14-17. Simulated distillations of the C_5^+ product are plotted in Figs. B18-19. Carbon number product distributions are plotted in Figs. B20-21. A chromatogram, from the simulated distillation of one sample, is reproduced in Fig. B22. Detailed material balances appear in Table B3.

The initial conversion of $CO+H_2$ (after obtaining a good material balance), nearly 55 percent, was substantially higher than with any other catalyst of this type tested at 240C to date--not excluding Catalyst 32, for which the corresponding initial conversion was about 42 percent. The calculated specific activity, at 5.9, was nearly twice the value of 3.0 for Catalyst 32. Un-

fortunately for these auspicious beginnings, the run was involuntarily aborted by a power failure after only 50 hours on stream, not enough time for any measure of stability.

The selectivity, as far as it went, was equally superior to that of Catalyst 32:

	Percent of total product (240C, 300 GHSV, 1:1 H_2:CO)	
	Catalyst 36	Catalyst 32
CH_4	3.4	5.3
C_5^+	88.6	85.0
Schulz-Flory alpha, calculated	0.84	0.89
C_4 olefin/paraffin	3.73	2.05

The Schulz-Flory plots, like those of Catalyst 32, are linear except for the excess methane, and show no potential carbon number cut-off such as has been seen with two previous catalysts.

Despite the short duration of its run, this catalyst has demonstrated a potentially substantial benefit, in both activity and selectivity, of raising the cobalt concentration of the X_{11}-promoted catalyst. The same formulation was accordingly re-tested, and is reported as Catalyst 38.

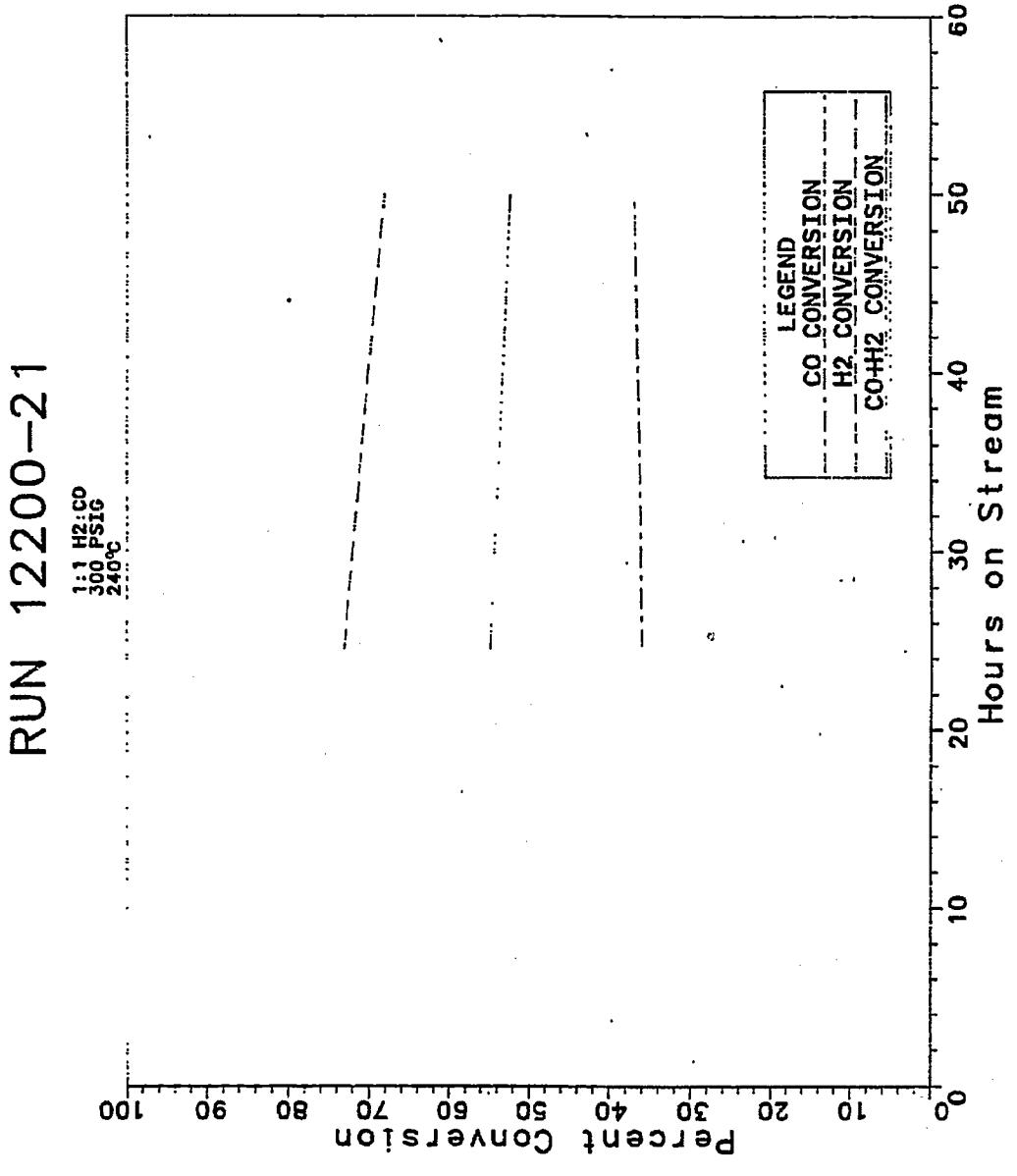
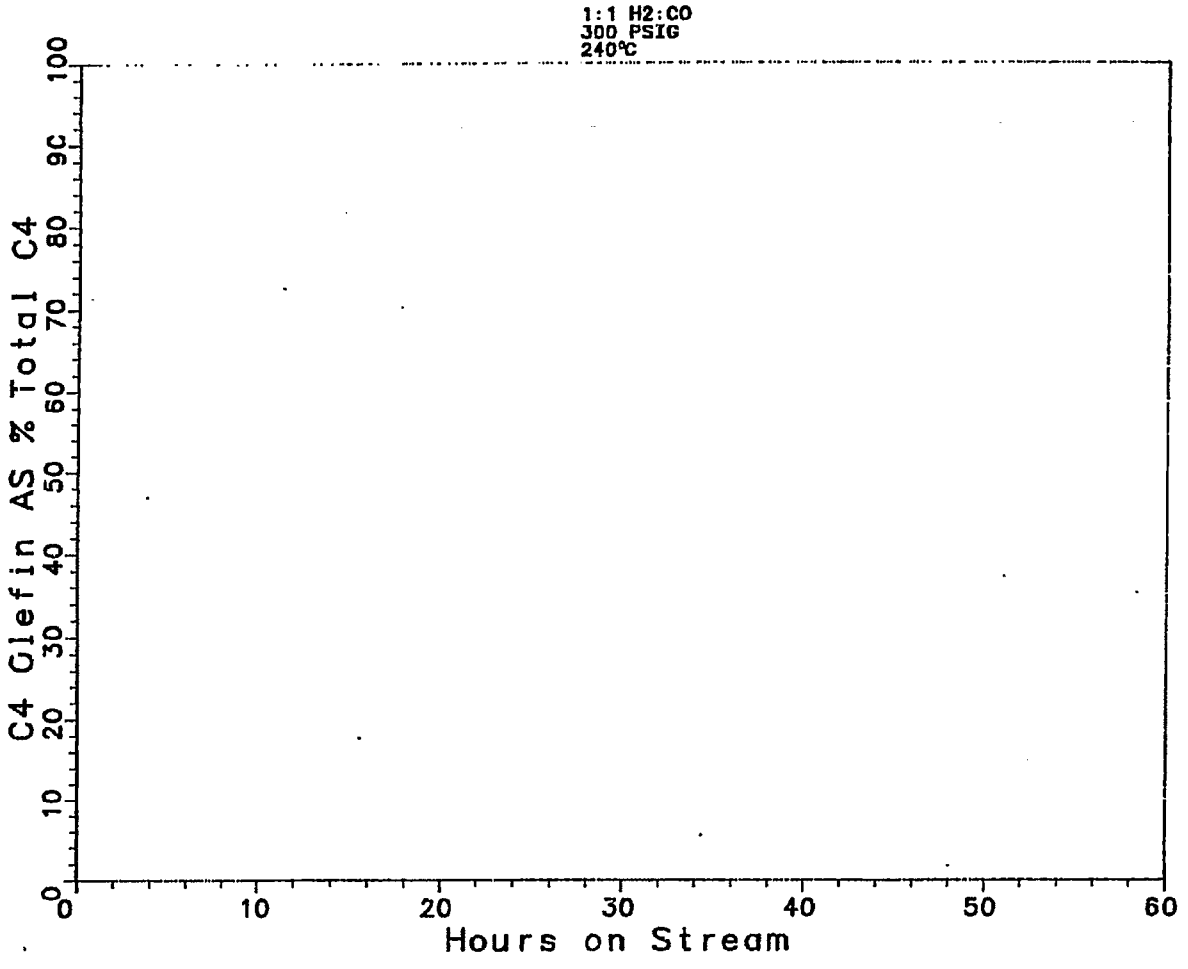

RUN 12200-21
1:1 H2:CO
300 PSIG
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B14

Fig. B15

RUN 12200-21



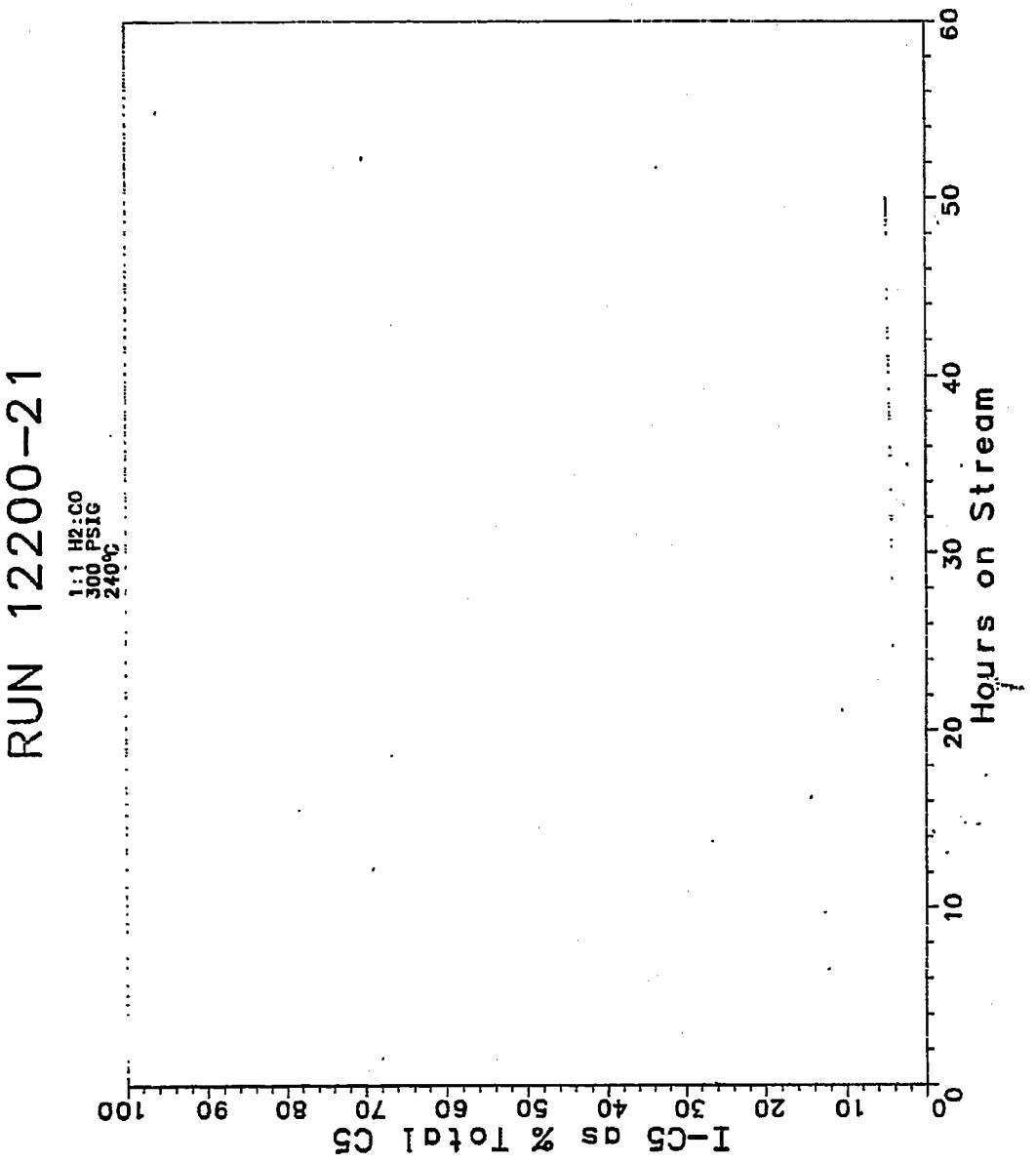

RUN 12200-21
1:1 H2:CO
300 PSIG
240°C
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
Hours on Stream

Fig. B16

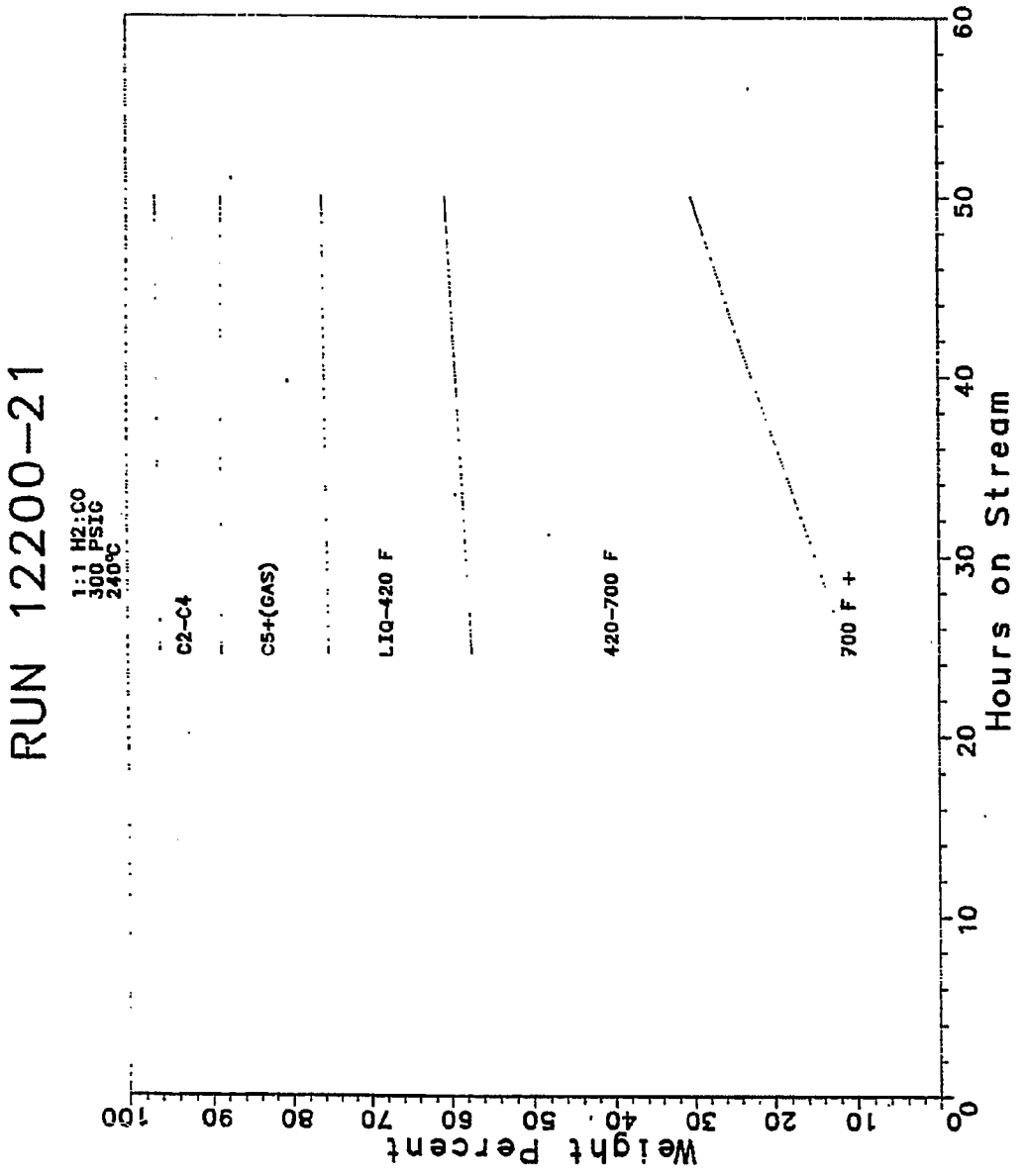

RUN 12200-21
1:1 H2:CO
300 PSIG
240°C
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B17

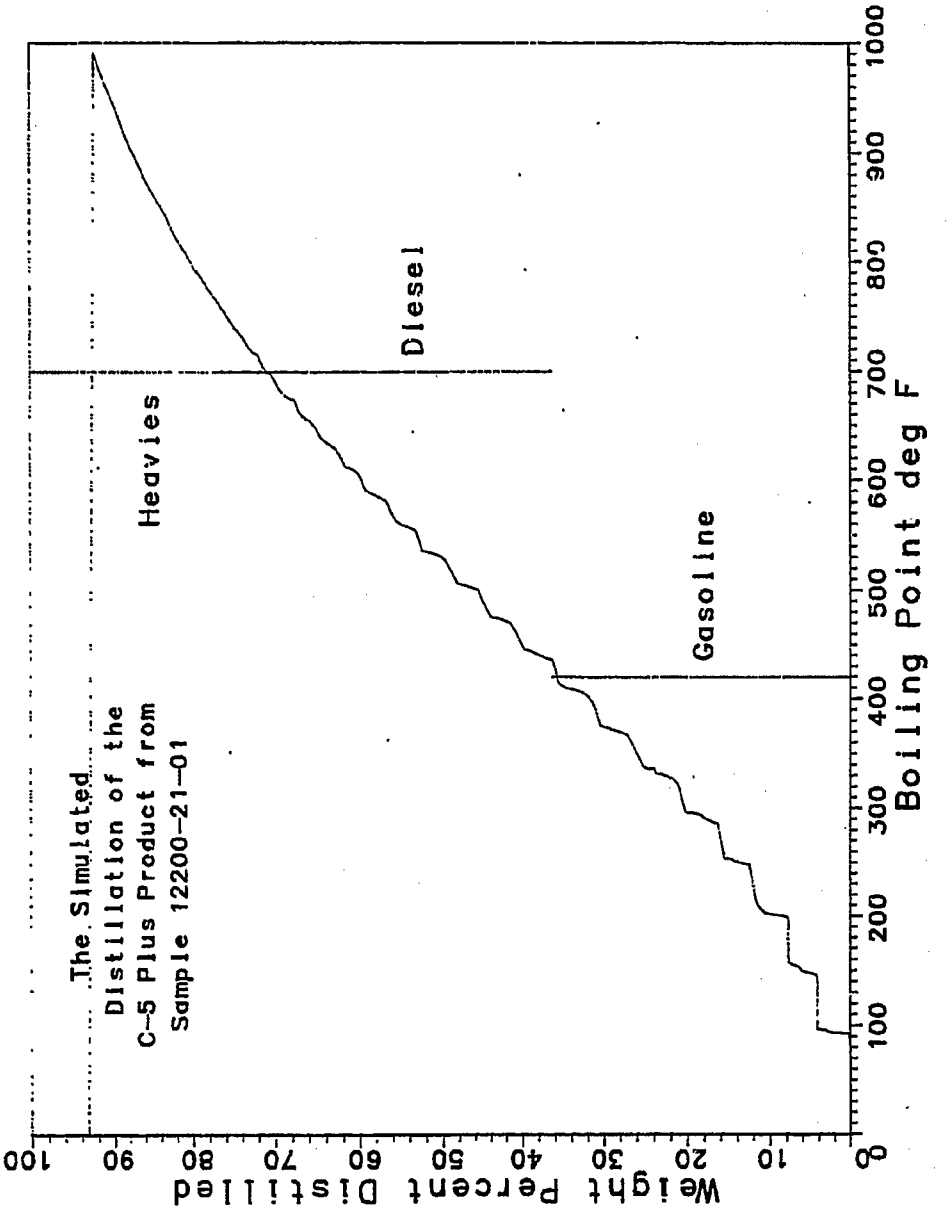

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-21-01
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B18

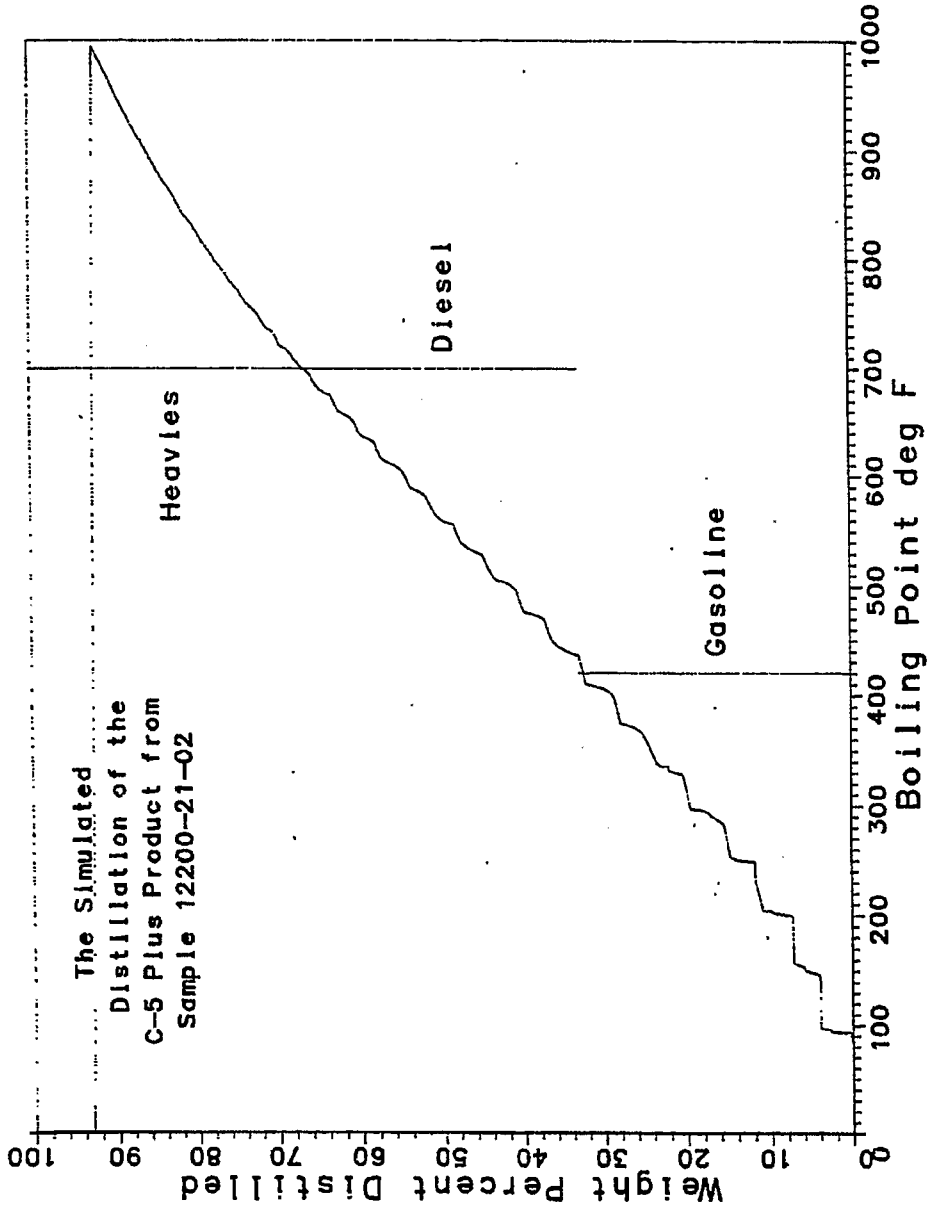

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-21-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B19

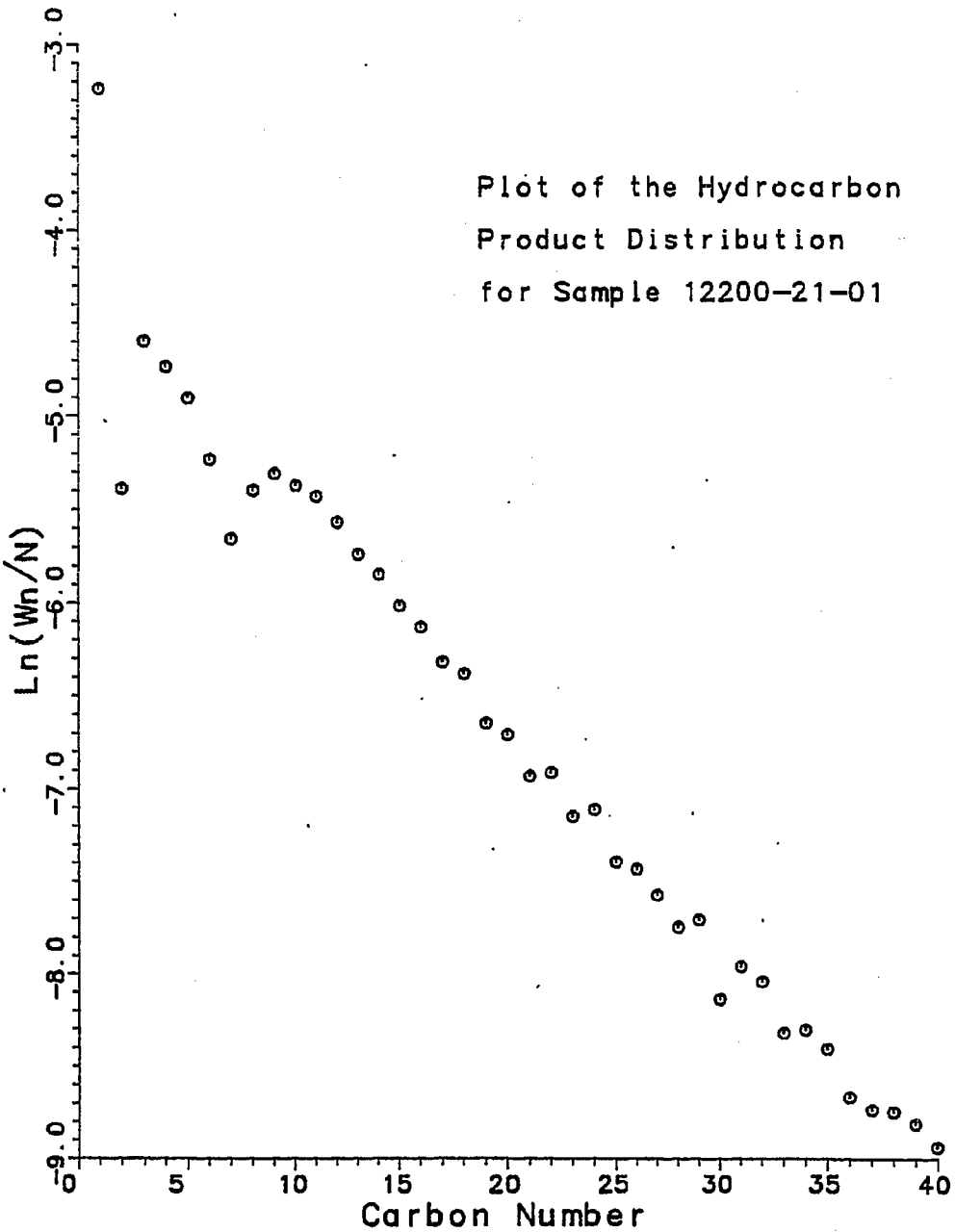

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-21-01
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B20

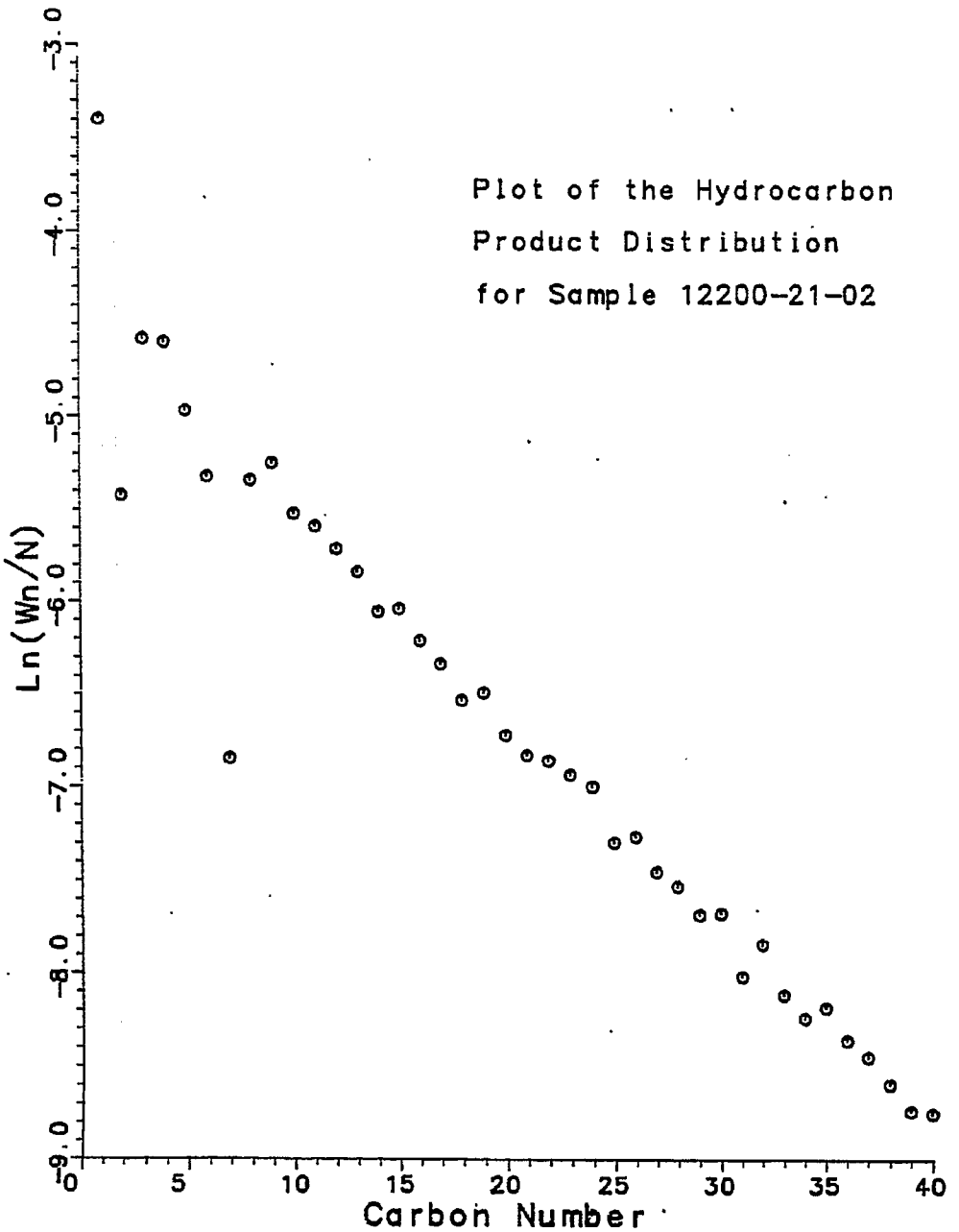
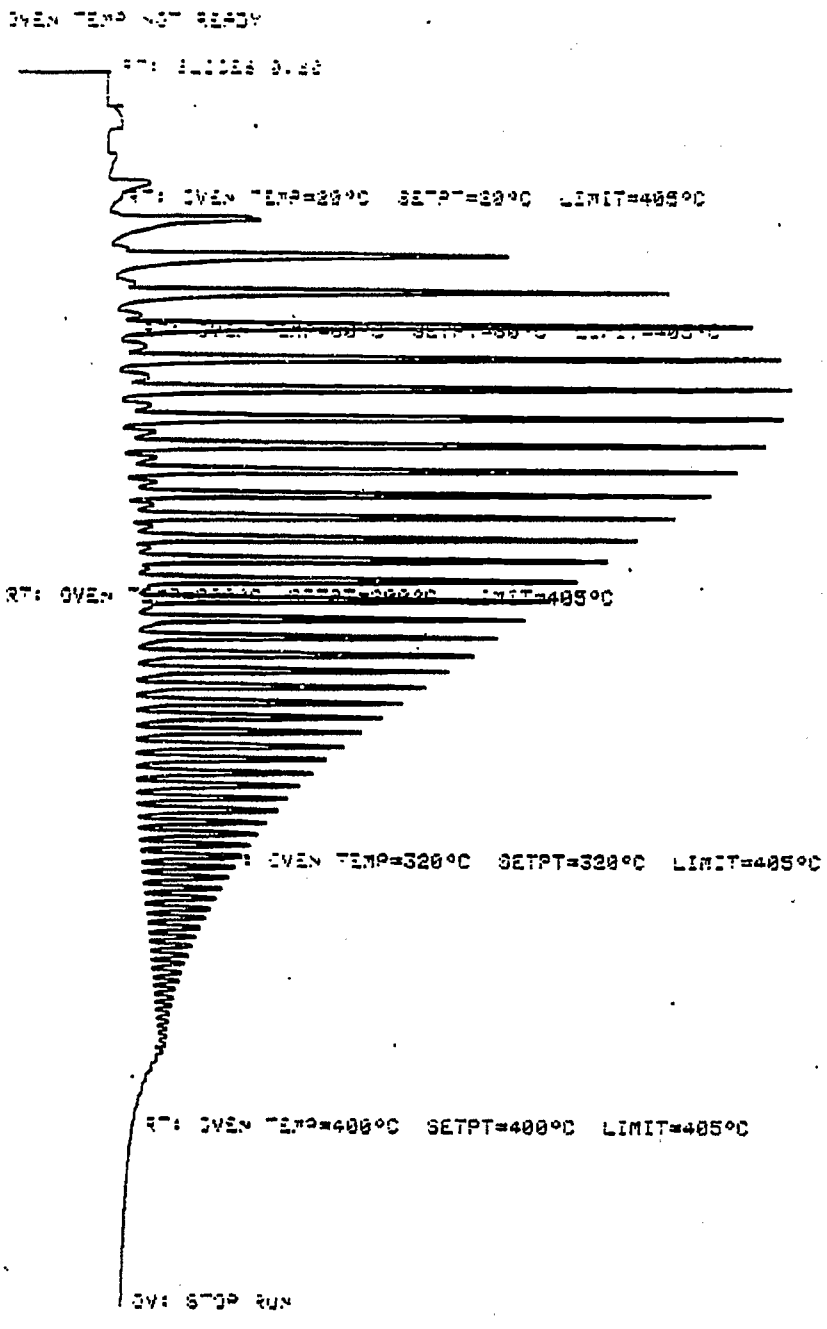

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-21-02
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B21



SAMPLE:12200-21-02

Fig. B22

Table B3

FILE: 1220021A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-21
CATALYST CO/X11-U103 80 CC 35.2 G AFTER USE:53.2G (+18.0 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT #12541-1)

RUN & SAMPLE NO.	12200-21-01	200-21-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	24.5	50.0
PRESSURE,PSIG	300	300
TEMP. C	238	237
FEED CC/MIN	400	400
HOURS FEEDING	24.50	25.50
EFFLNT GAS LITER	230.01	306.49
GM AQUEOUS LAYER	64.19	57.95
GM OIL	32.81	47.53
MATERIAL BALANCE		
GM ATOM CARBON %	78.04	99.43
GM ATOM HYDROGEN %	80.38	96.27
GM ATOM OXYGEN %	86.34	93.72
RATIO CHX/(H2O+CO2)	0.7531	1.1955
RATIO X IN CHX	2.1894	2.1787
USAGE H2/CO PRODT	2.0949	1.7853
FEED H2/CO FRM EFFLNT	1.0300	0.9682
RESIDUAL H2/CO RATIO	0.4341	0.4905
RATIO CO2/(H2O+CO2)	0.0797	0.0603
K SHIFT IN EFFLNT	0.0376	0.0315
SPECIFIC ACTIVITY SA	6.3050	5.9101
CONVERSION		
ON CO %	35.88	36.89
ON H2 %	72.97	68.03
ON CO+H2 %	54.70	52.21
PRDT SELECTIVITY,WT %		
CH4	3.94	3.37
C2 HC'S	0.91	0.89
C3H8	0.83	0.76
C3H6=	2.21	2.33
C4H10	0.93	0.88
C4H8=	2.60	3.17
C5H12	1.16	1.08
C5H10=	2.56	2.42
C6H14	1.36	1.25
C6H12= & CYCLO'S	1.84	1.69
C7+ IN GAS	6.32	6.08
LIQ HC'S	75.34	76.08
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	11.41	11.40
C5 -420 F	31.33	28.03
420-700 F	46.41	30.13
700-END PT	10.85	30.43

Table B3 (continued)

FILE: 1220021A TSS4Q1 A1

C5+-END PT	88.59	88.60
ISO/NORMAL MOLE RATIO		
C4	0.0000	0.0000
C5	0.0434	0.0518
C6	0.0546	0.0255
C4=	0.0000	5.3528
PARAFFIN/OLEFIN RATIO		
C3	0.3586	0.3131
C4	0.3443	0.2681
C5	0.4412	0.4364
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8842	0.8919
RATIO CH4/(1-A)**2	2.9386	2.8842
ALPHA FRM CORRELATION	0.8527	0.8468
ALPHA (EXPTL/CORR)	1.0370	1.0533
W%CH4 FRM CORRELATION	8.6792	10.2773
W%CH4 (EXPTL/CORR)	0.4538	0.3277
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	OIL WAX
DENSITY	N/A	N/A
N, REFRACTIVE INDEX	N/A	N/A
SIMULT'D DISTILATN		
10 WT % @ DEG F	331	336
16	372	399
50	585	631
84	886	917
90	973	995
RANGE(16-84 %)	514	518
WT % @ 420 F	24.00	20.40
WT % @ 700 F	85.60	60.00

V. Run 37 (12185-21) with Catalyst 37 ($Co/X_{11}/TC-103$)

The purpose of this run was to test the effect of pretreatment on the catalyst's performance, the pretreatment in this instance being the same as for Catalysts 20 and 31, both of which showed potential carbon number cut-offs. In all other respects of composition and preparation this catalyst was identical to Catalyst 32. The theoretical concentrations of cobalt and X_{11} were 8.2 and 1.6 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B23-26. Simulated distillations of the C_5^+ product are plotted in Figs. B27-35. Carbon number product distributions are plotted in Figs. B36-44. Chromatograms from simulated distillations are reproduced in Figs. B45-51. Detailed material balances appear in Tables B4-6.

The initial conversion (at 240C, after obtaining a good material balance) was about 49 percent, somewhat better than the corresponding value of about 46 percent for Catalyst 32. Stability was only fair, with an estimated loss of conversion of one percentage point every 24 hours.

At 260C the conversion rose to 62 percent, again higher than the corresponding value of 56 percent for Catalyst 32. Stability was somewhat better than at 240C, with an estimated loss of con-

version of one percentage point every 60-100 hours.

In selectivity, however, this catalyst was significantly poorer than Catalyst 32:

	Percent of total product (260C, 300 GHSV, 1:1 H_2:CO)	
	Catalyst 37	Catalyst 32
CH_4	10.7	7.6
C_5^+	77.4	82.1
C_4 olefin/paraffin	1.1	1.8

With three percentage points more methane and five percentage points less C_5^+, the product was substantially lighter than that of Catalyst 32. And with a lower ratio of olefin to paraffin in the C_4 fraction, the hydrogenation activity was higher.

The Schulz-Flory plots showed no deviation from normal kinetics except for the usual high methane. And although it had been thought that a carbon number cut-off is associated with the pretreatment used with this catalyst, no such cut-off was present.

This run has developed some useful information on the effects of pretreatment. Although it seems to have significantly improved the catalyst's activity, the stability was only fair and the selectivity was inferior.

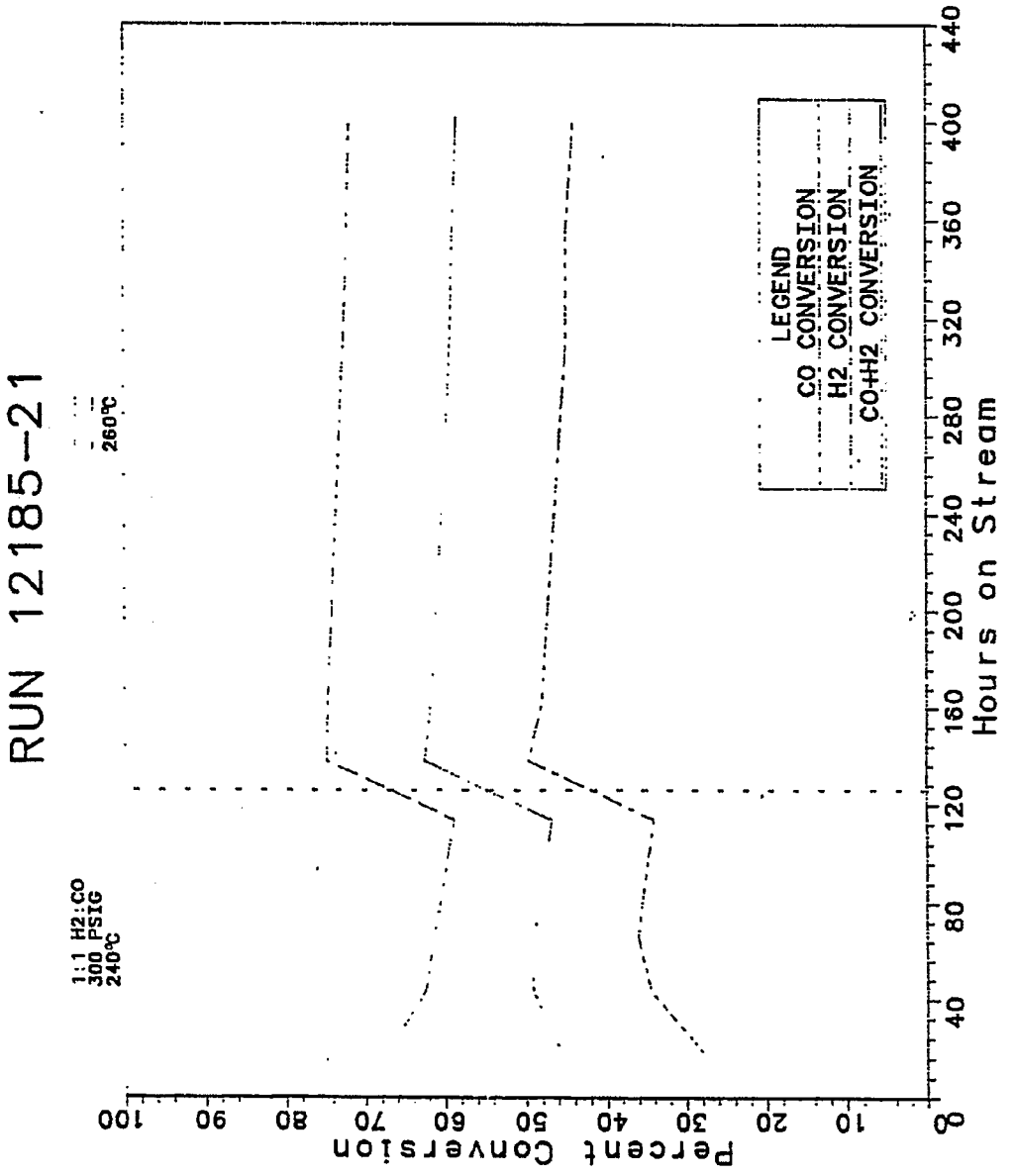

RUN 12185-21
1:1 H2:CO
300 PSIG
240°C
260°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B23

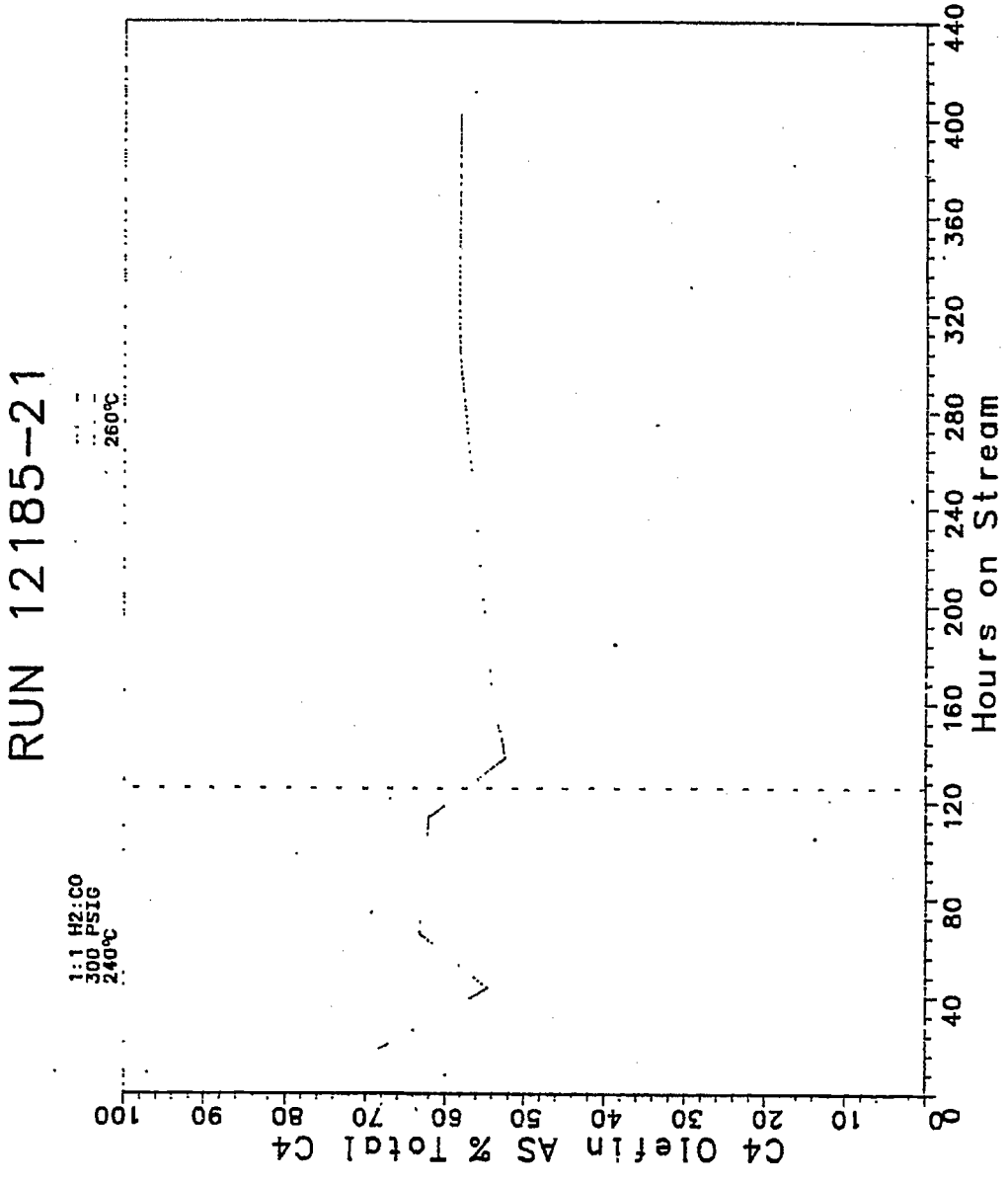

RUN 12185-21
260°C
1:1 H2:CO
300 PSIG
240°C
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440
Hours on Stream

Fig. B24

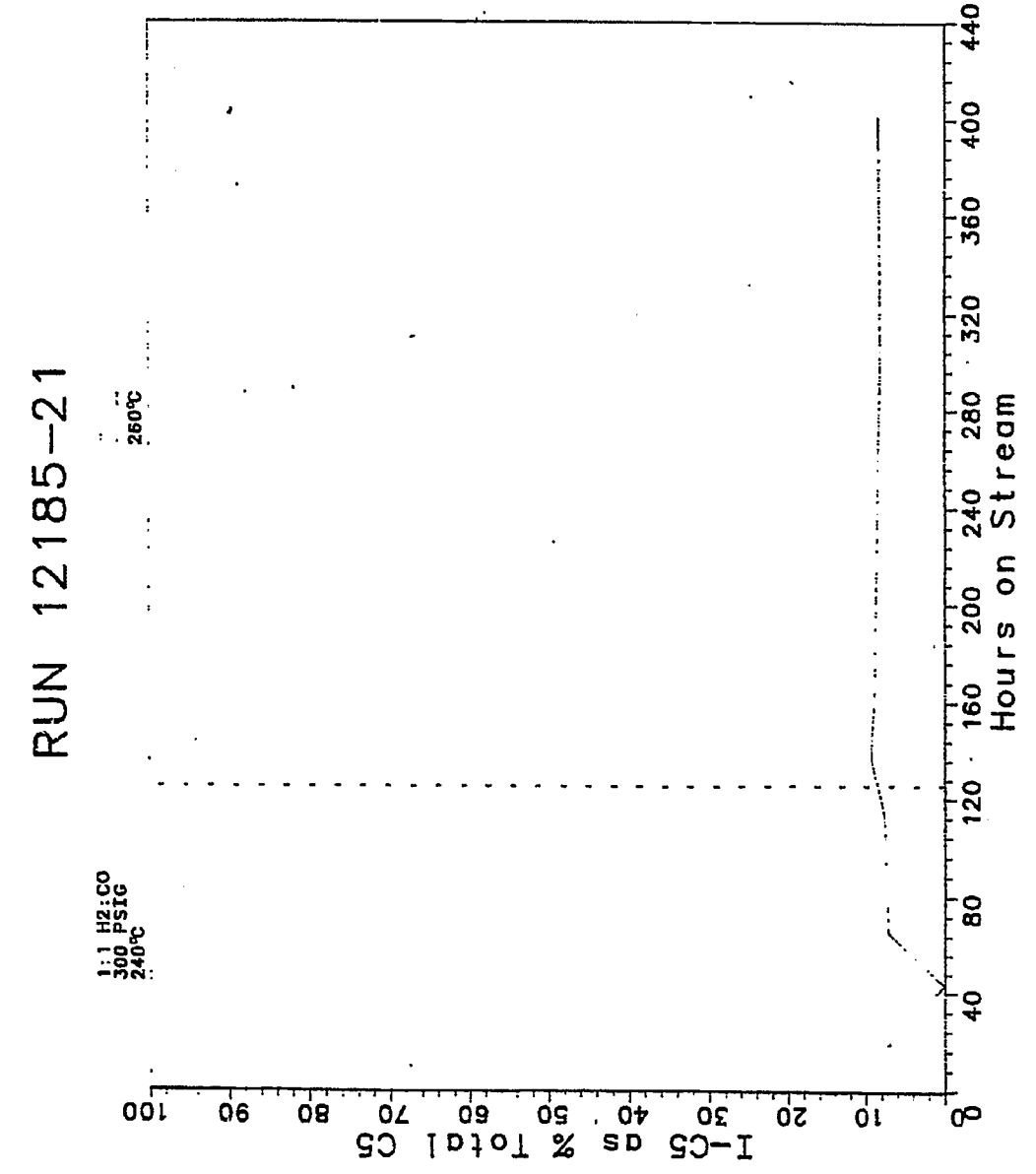

RUN 12185-21
1:1 H2:CO
300 PSIG
240°C
260°C
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
40
80
120
160
200
240
280
320
360
400
440

Fig. B25

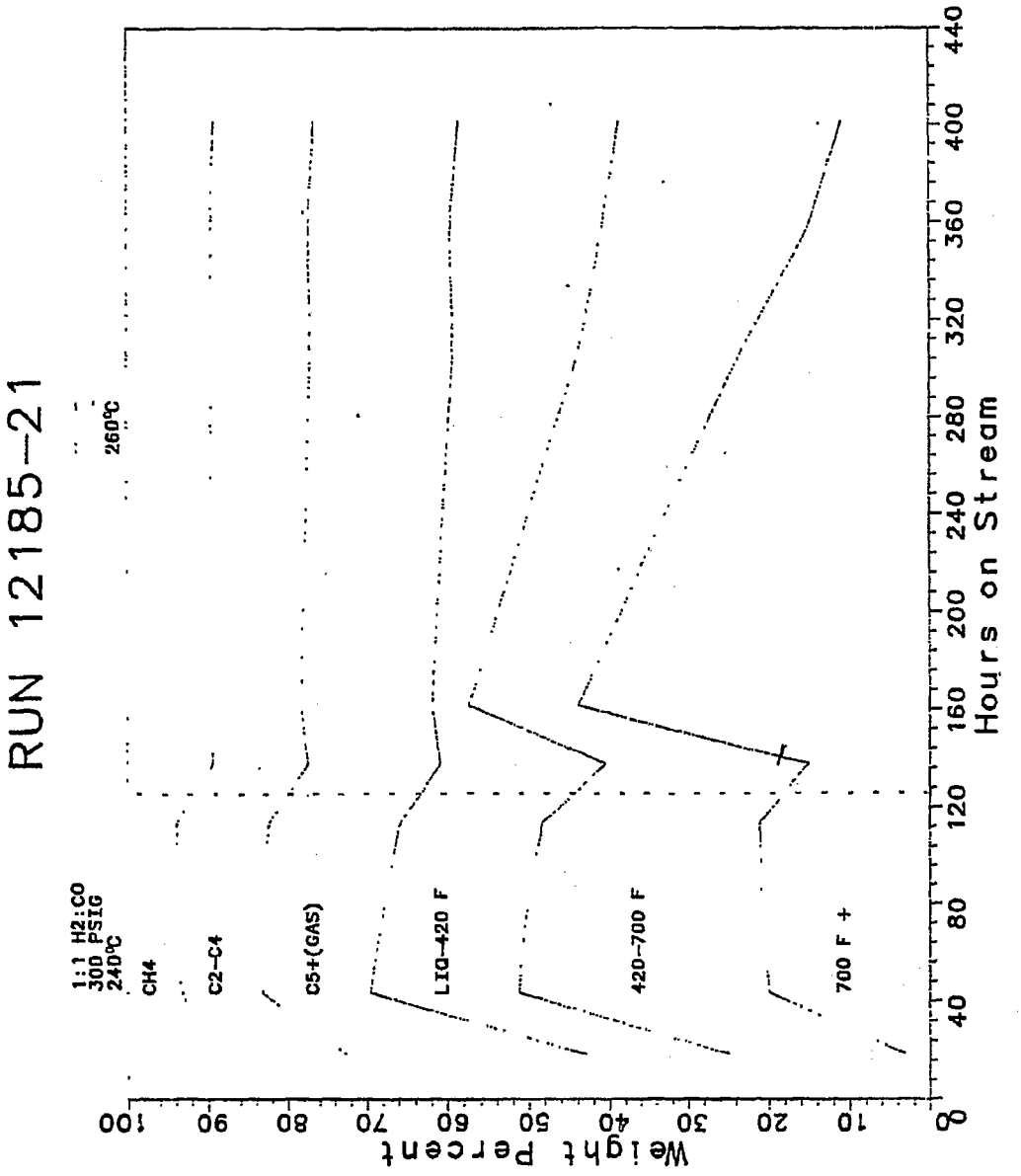

RUN 12185-21
1:1 H2:CO
300 PSIG
240°C
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B26

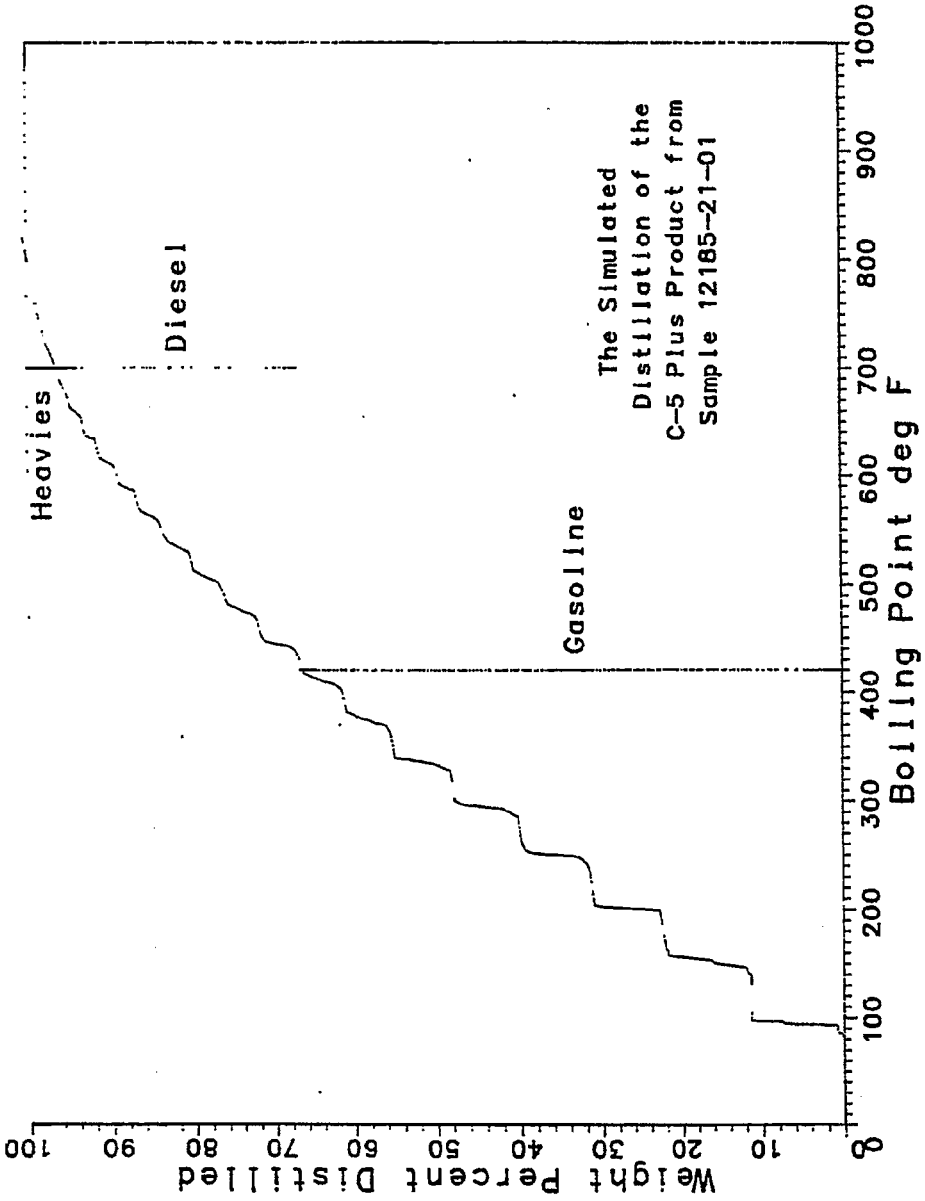

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-01
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B27

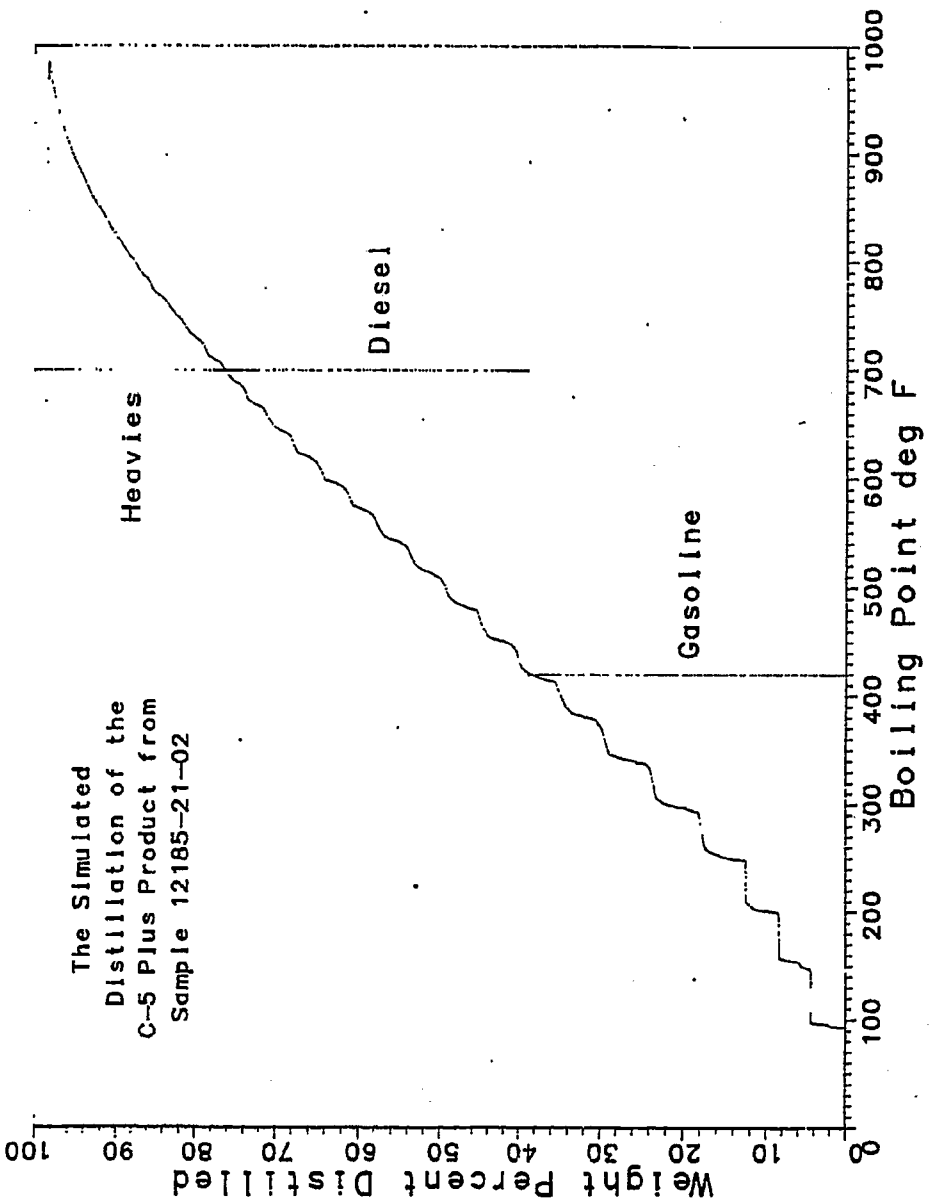

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B28

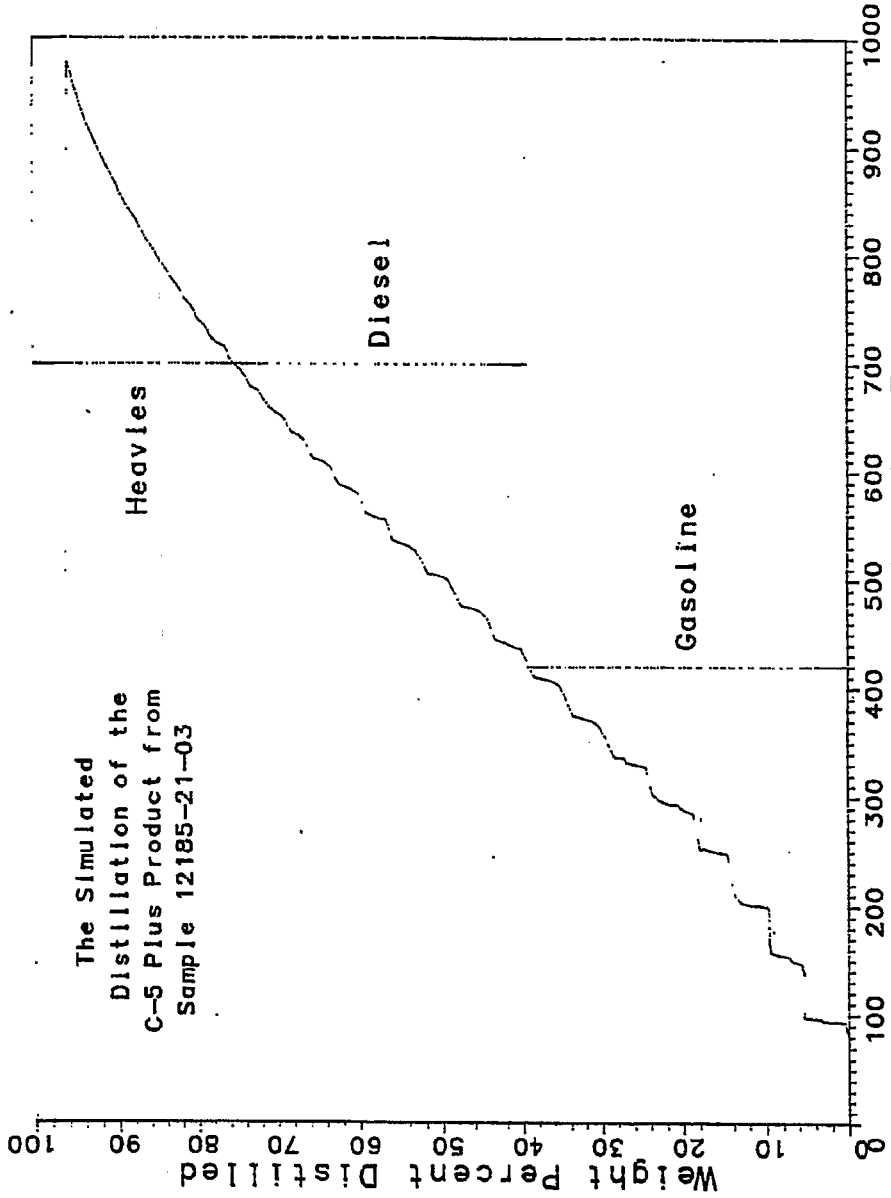

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-03
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B29

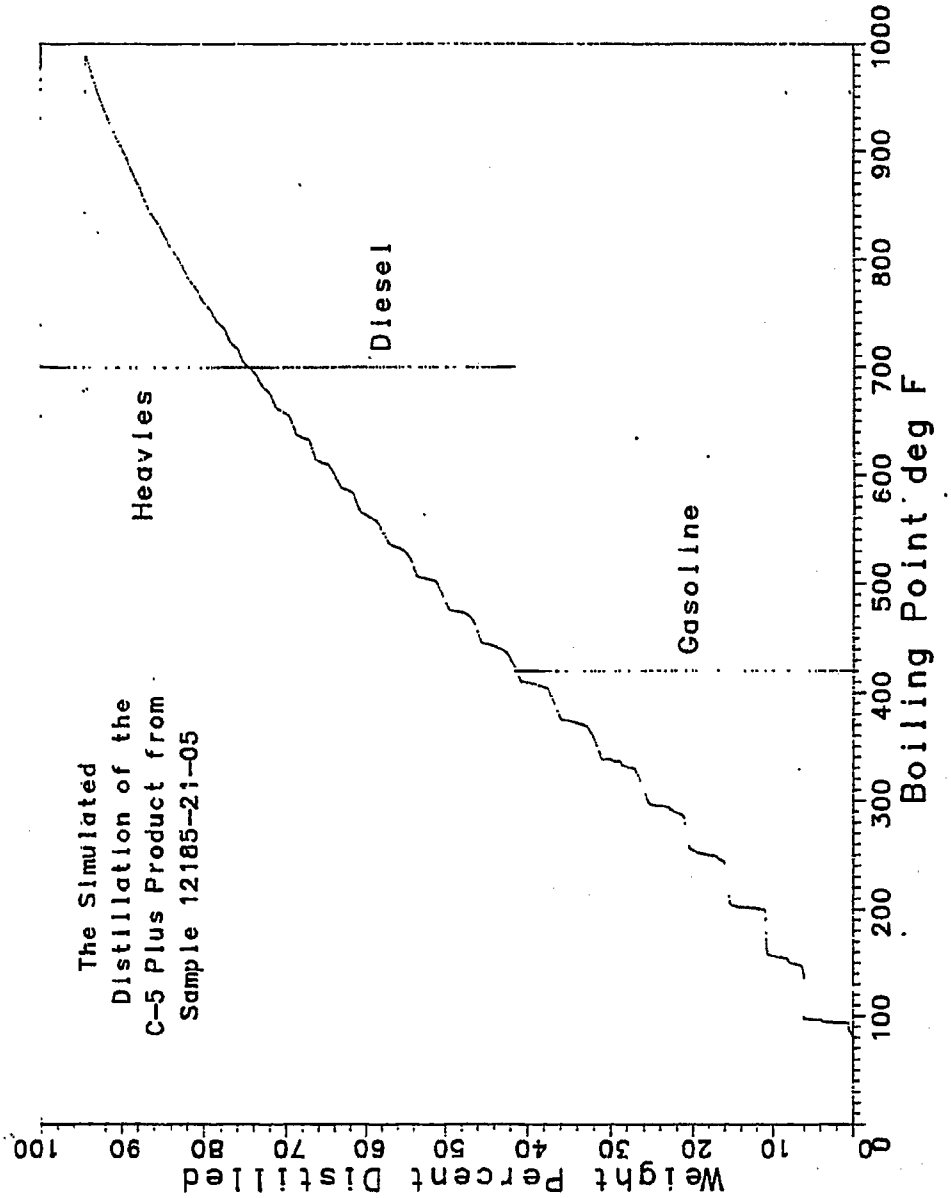

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-05
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B30

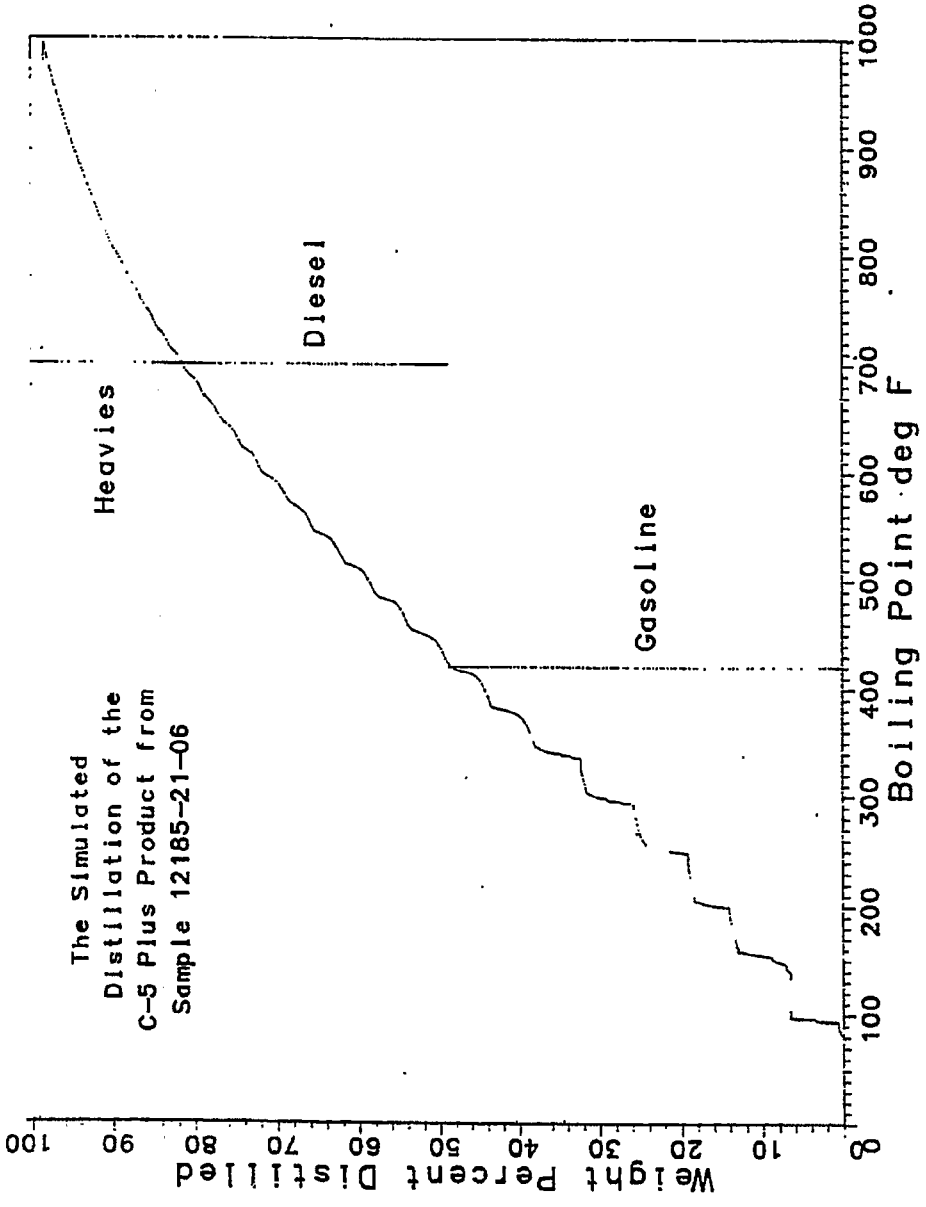

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-06
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B31

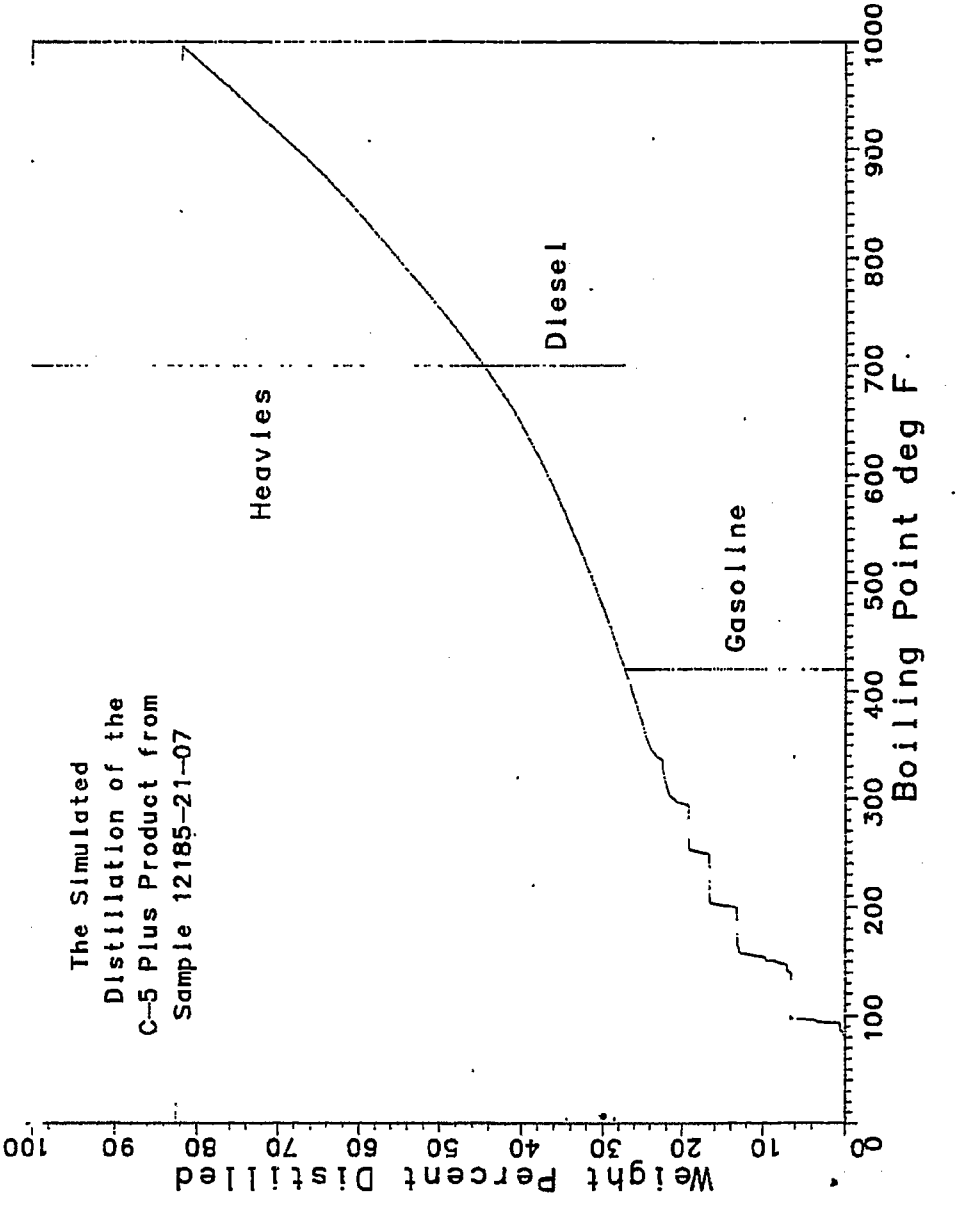

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-07
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B32

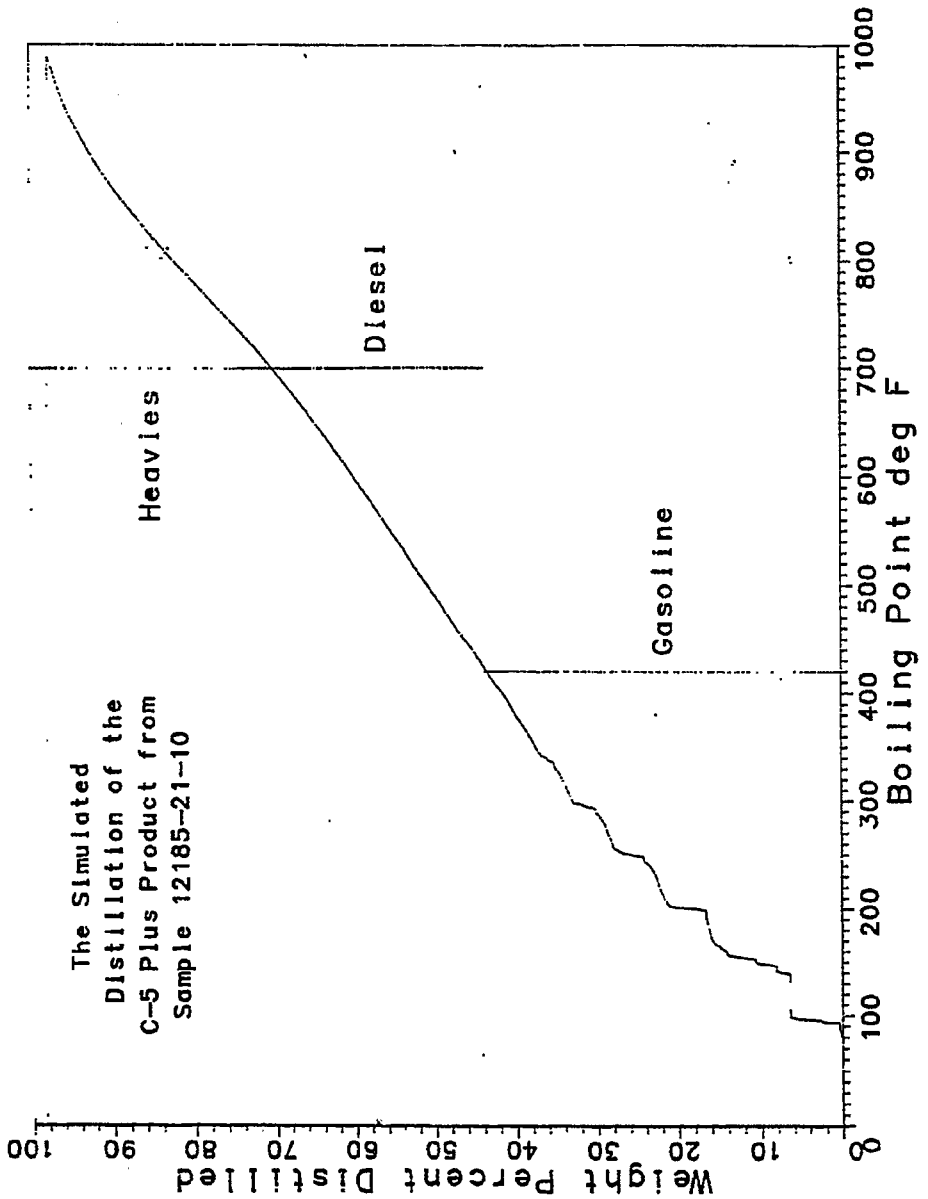

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-10
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B33

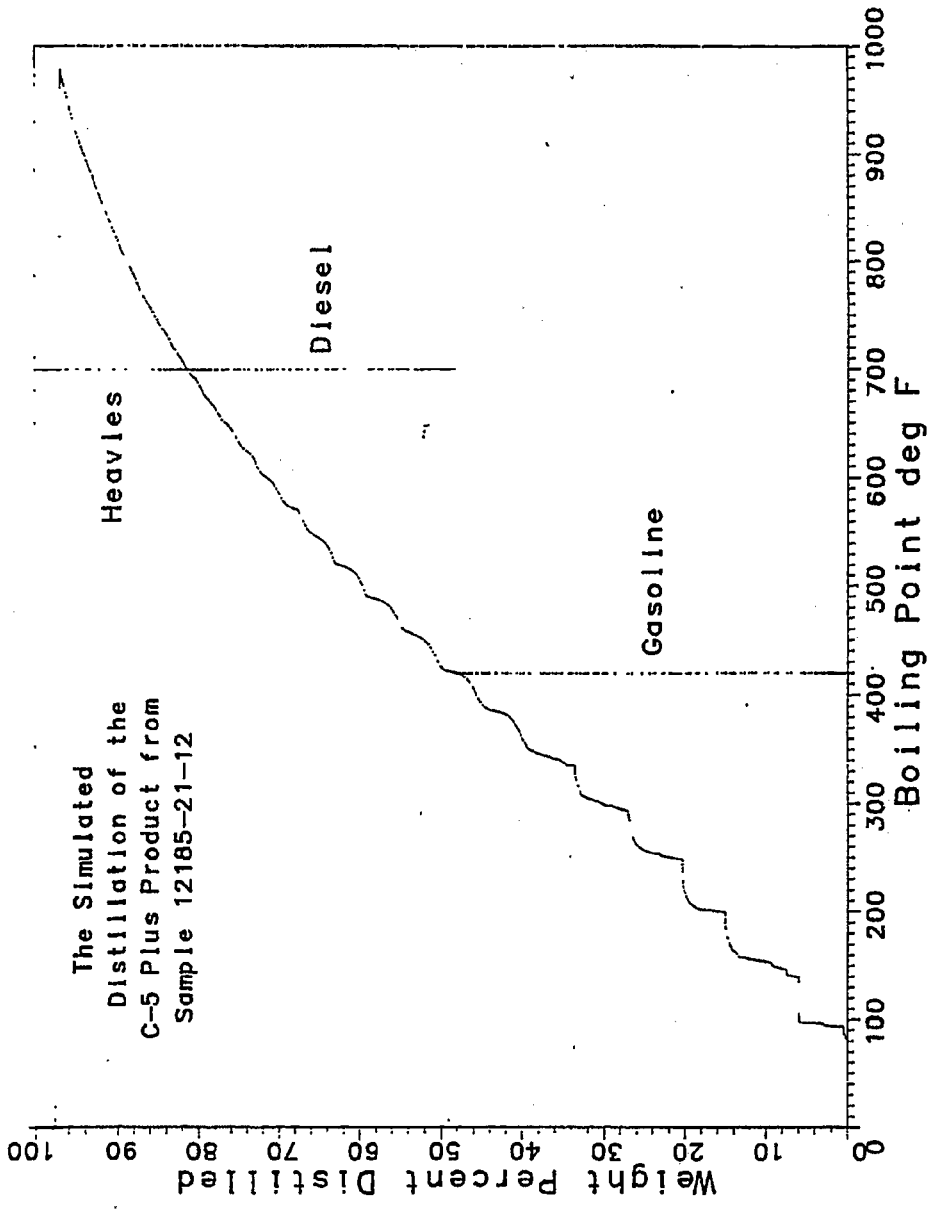

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12185-21-12
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B34

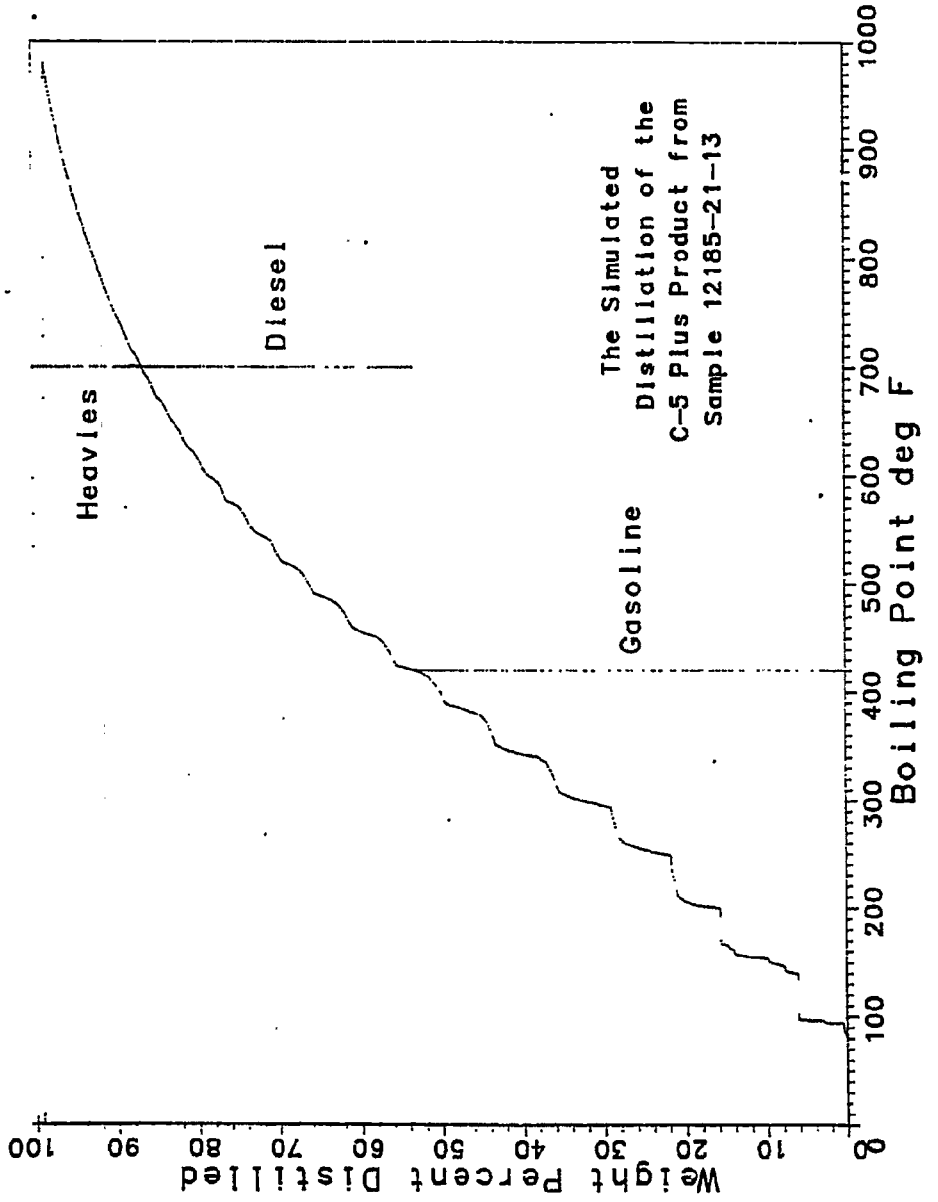

The Simulated Distillation of the C-5 Plus Product from Sample 12185-21-13
Gasoline
Diesel
Heavies
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B35

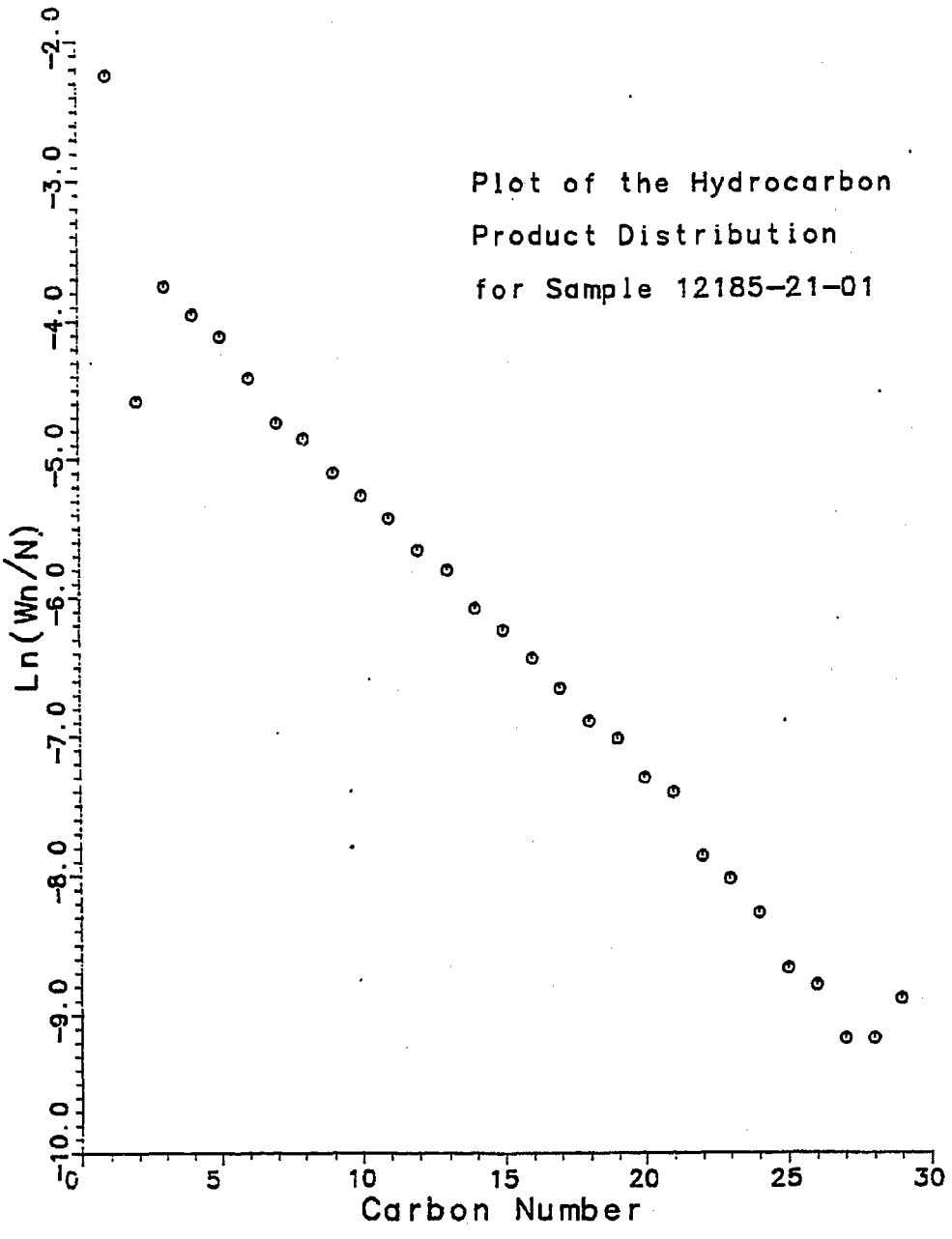

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B36

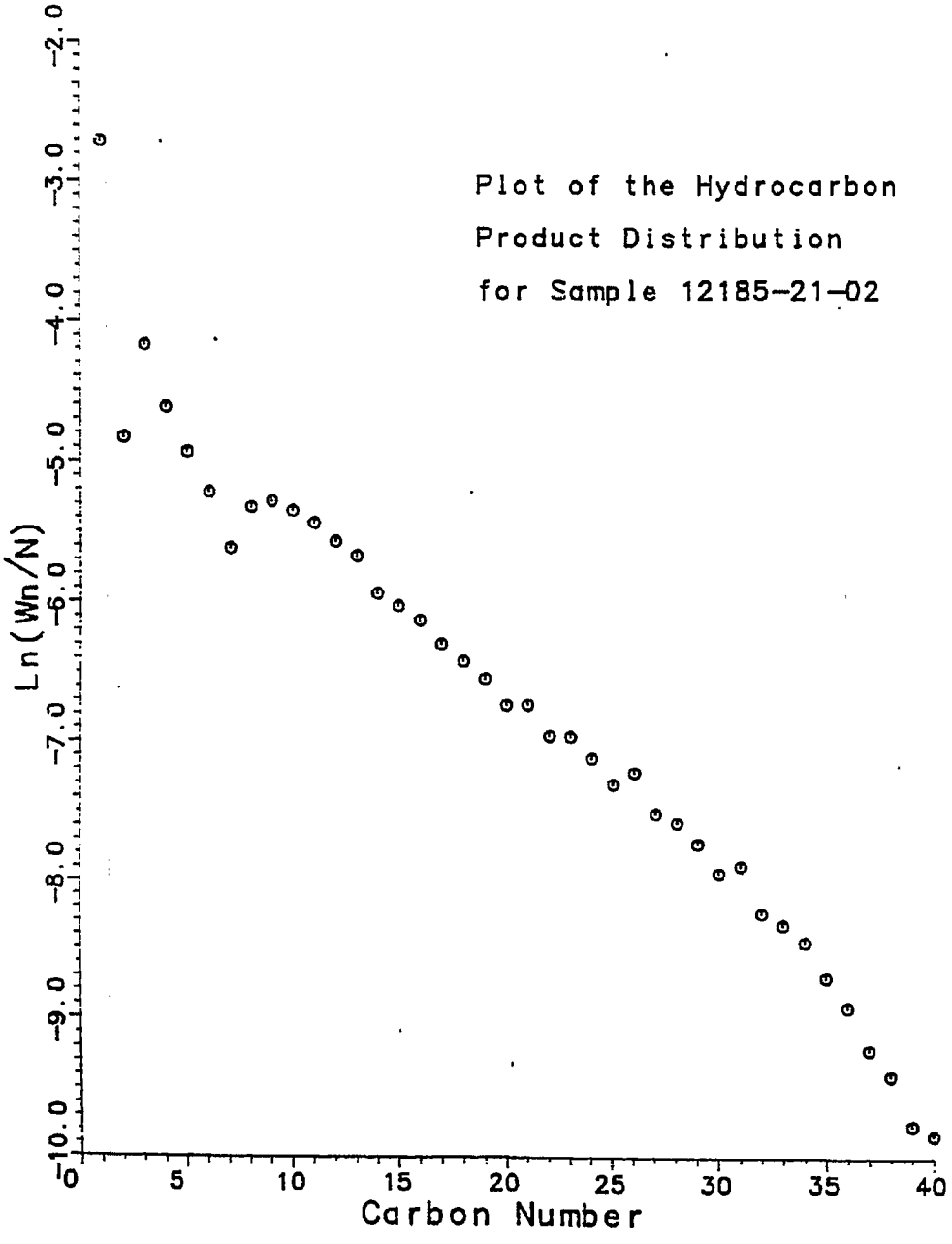

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B37

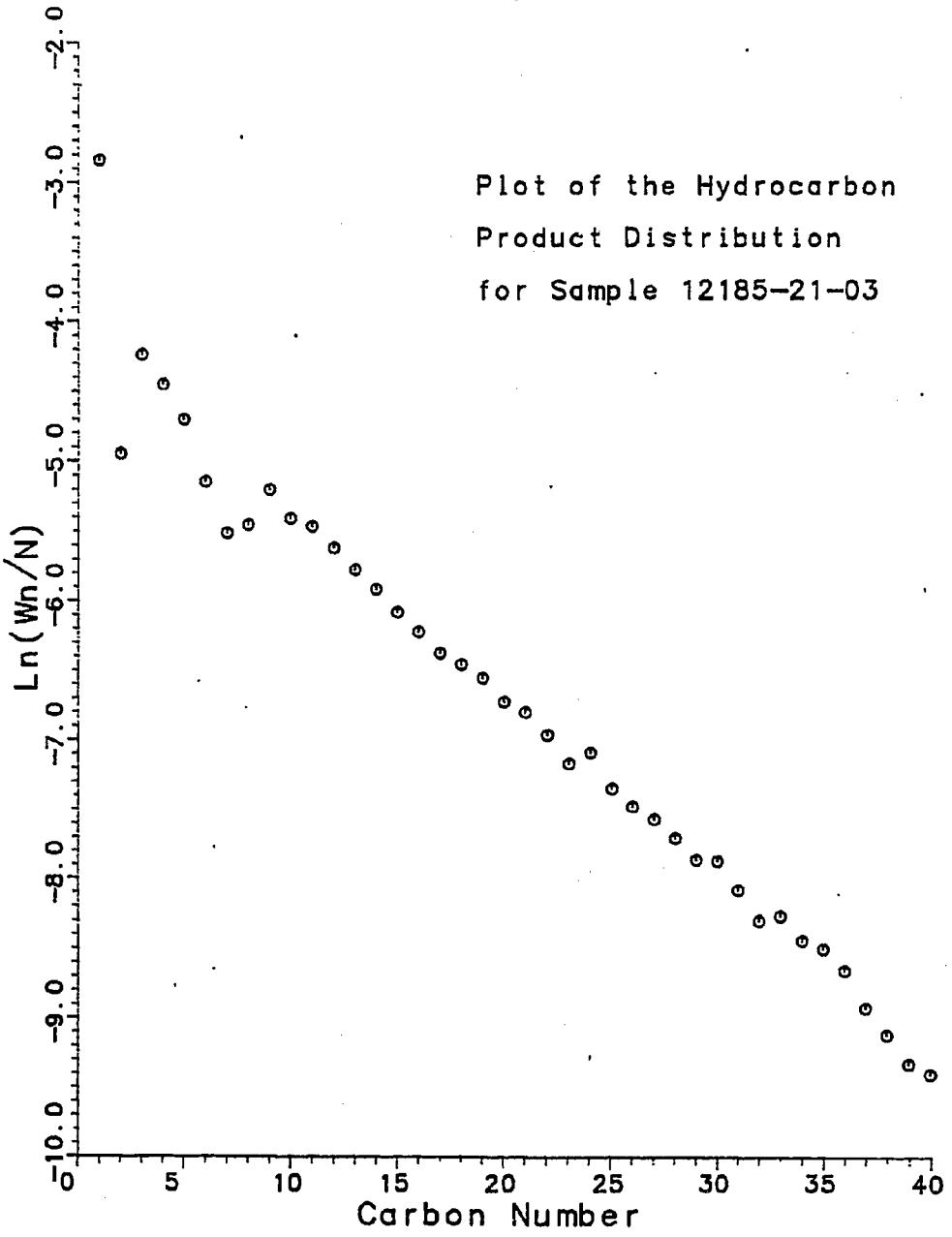

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-03
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B38

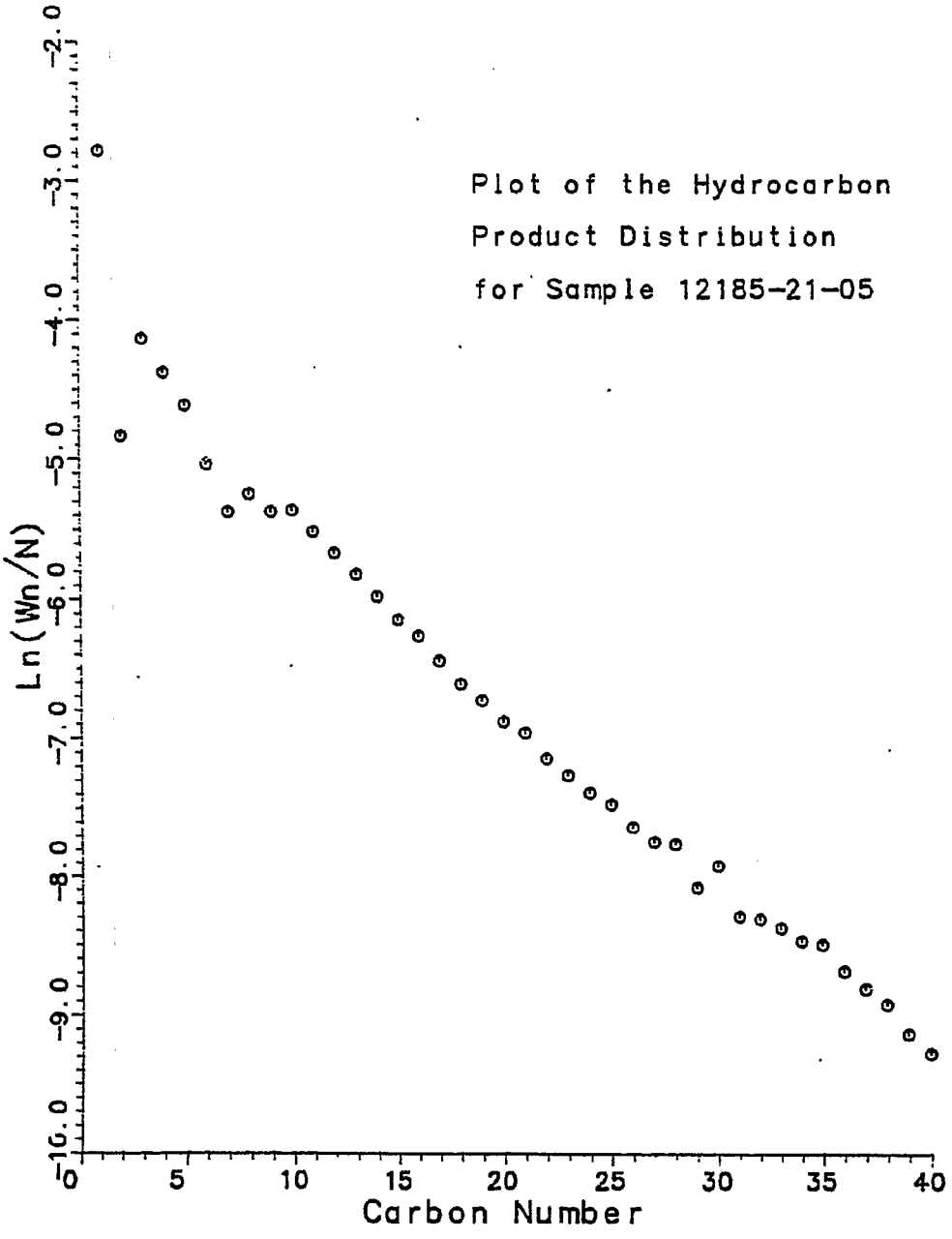

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-05
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B39

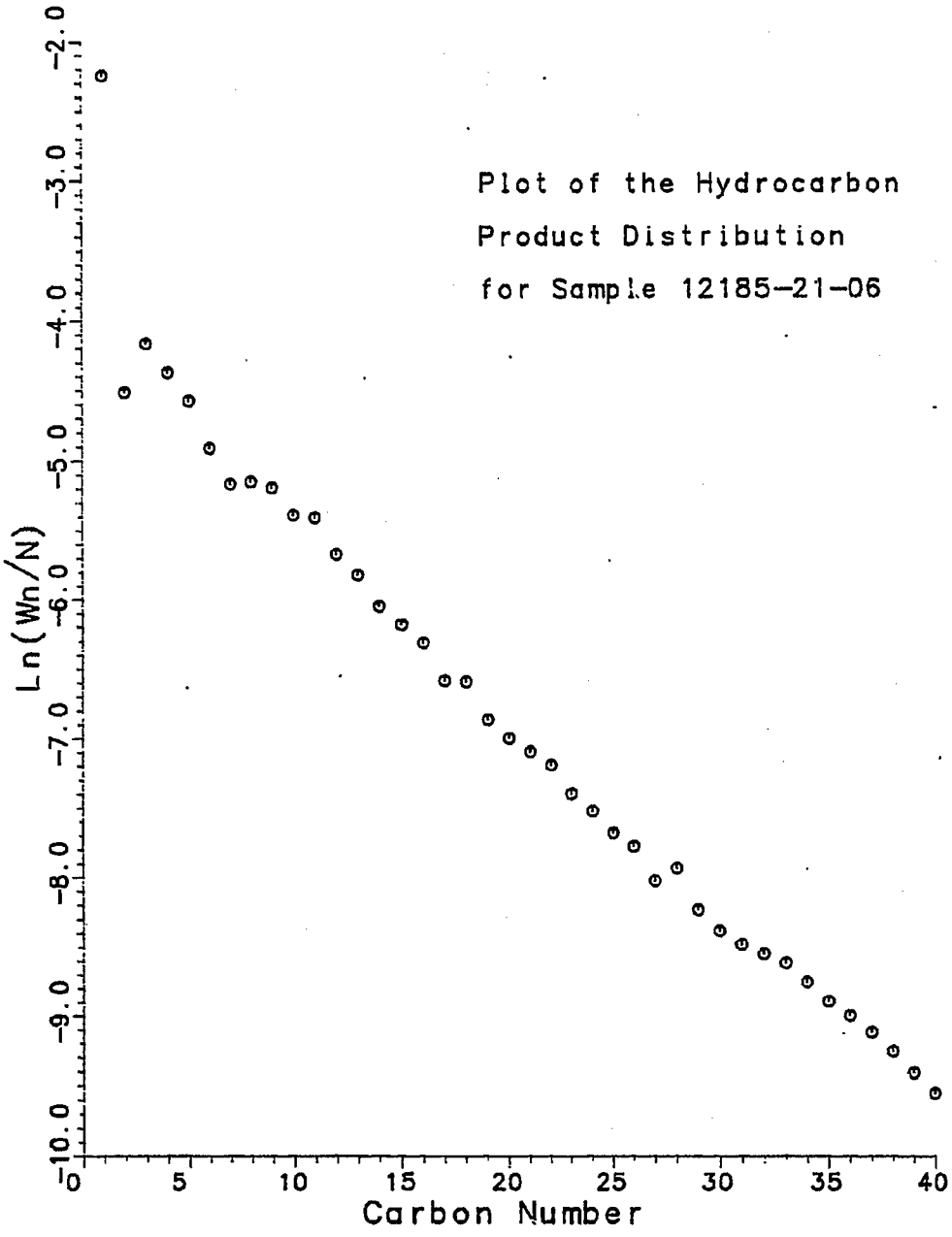

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B40

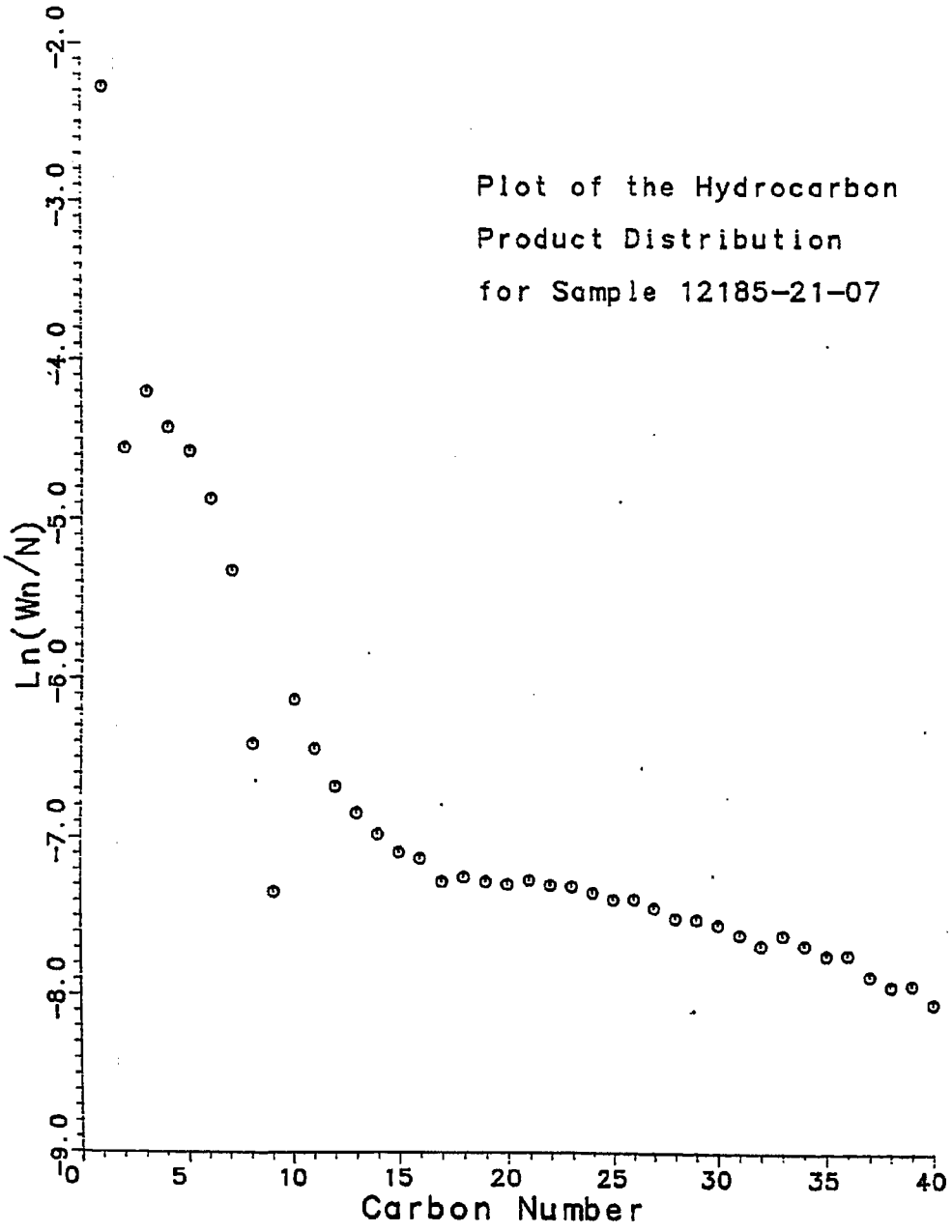

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-07
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B41

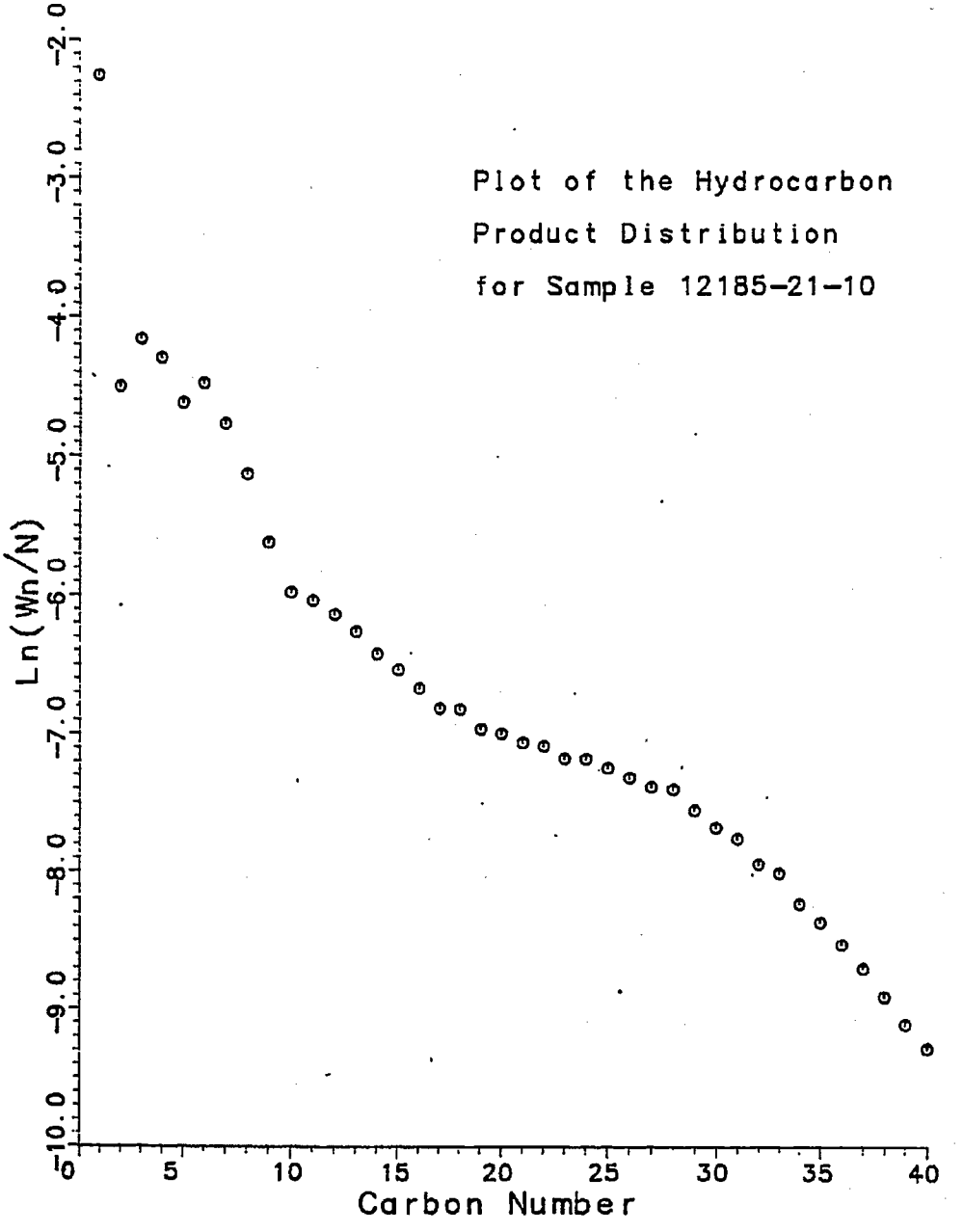

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-10
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B42

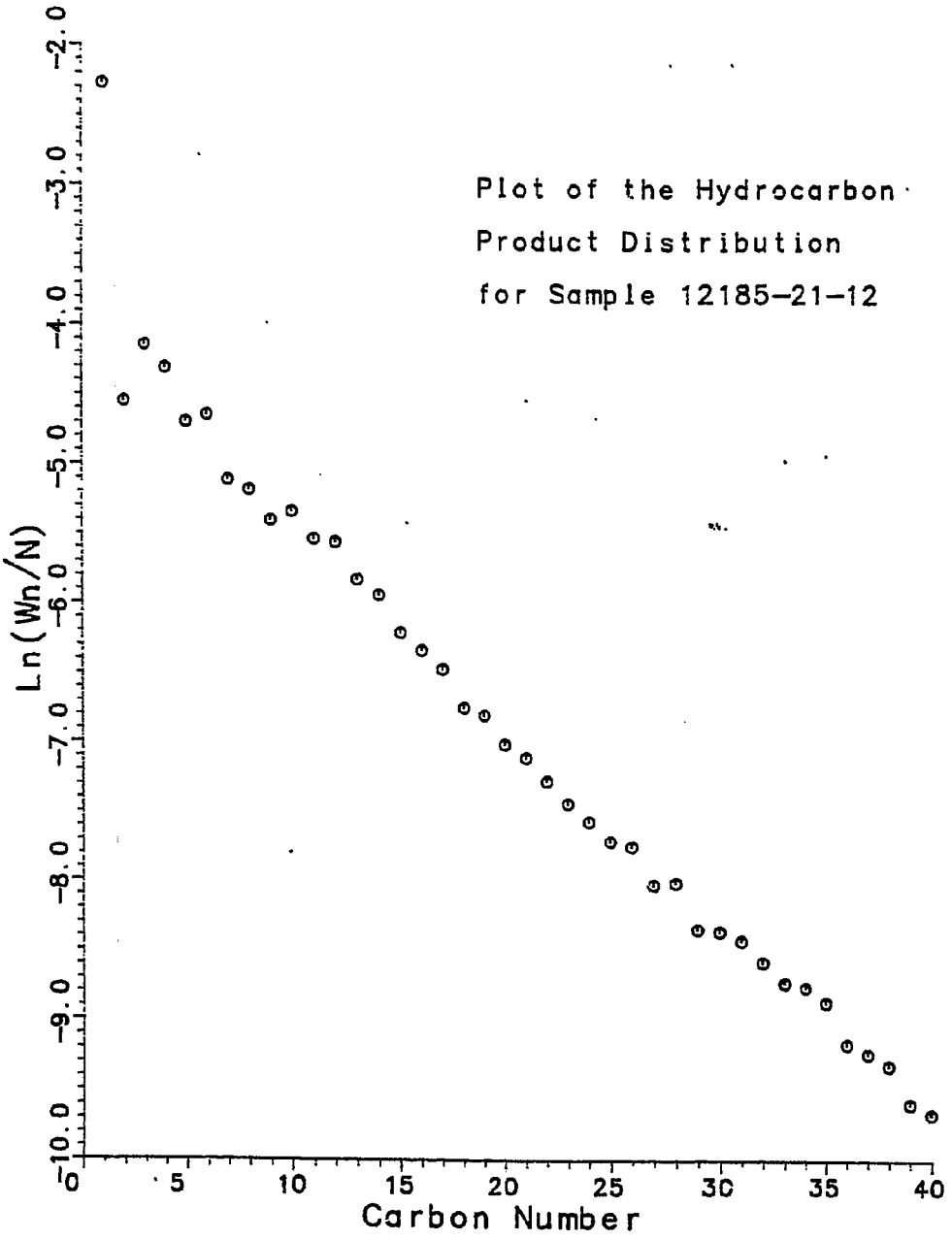

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-12
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B43

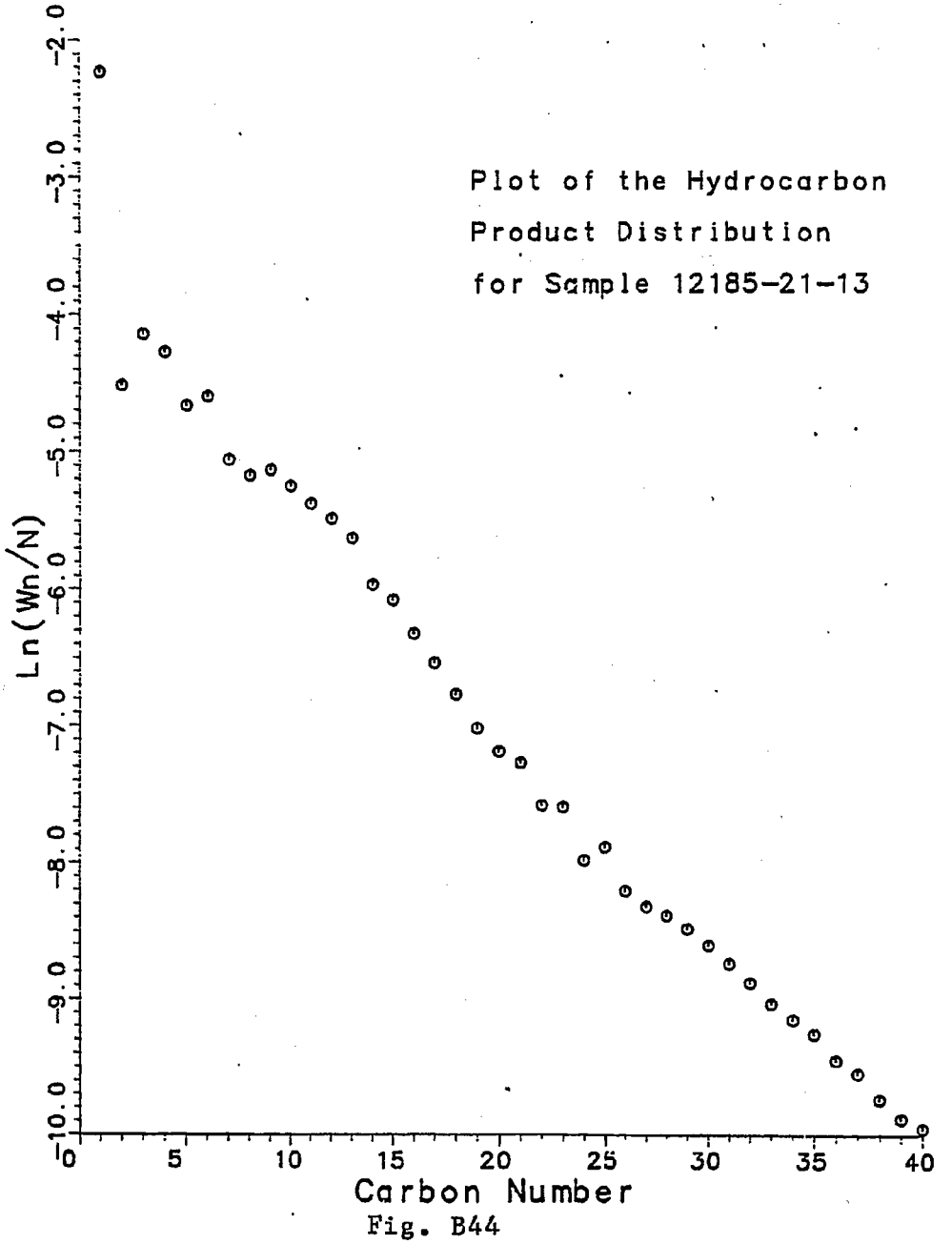

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-21-13
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B44

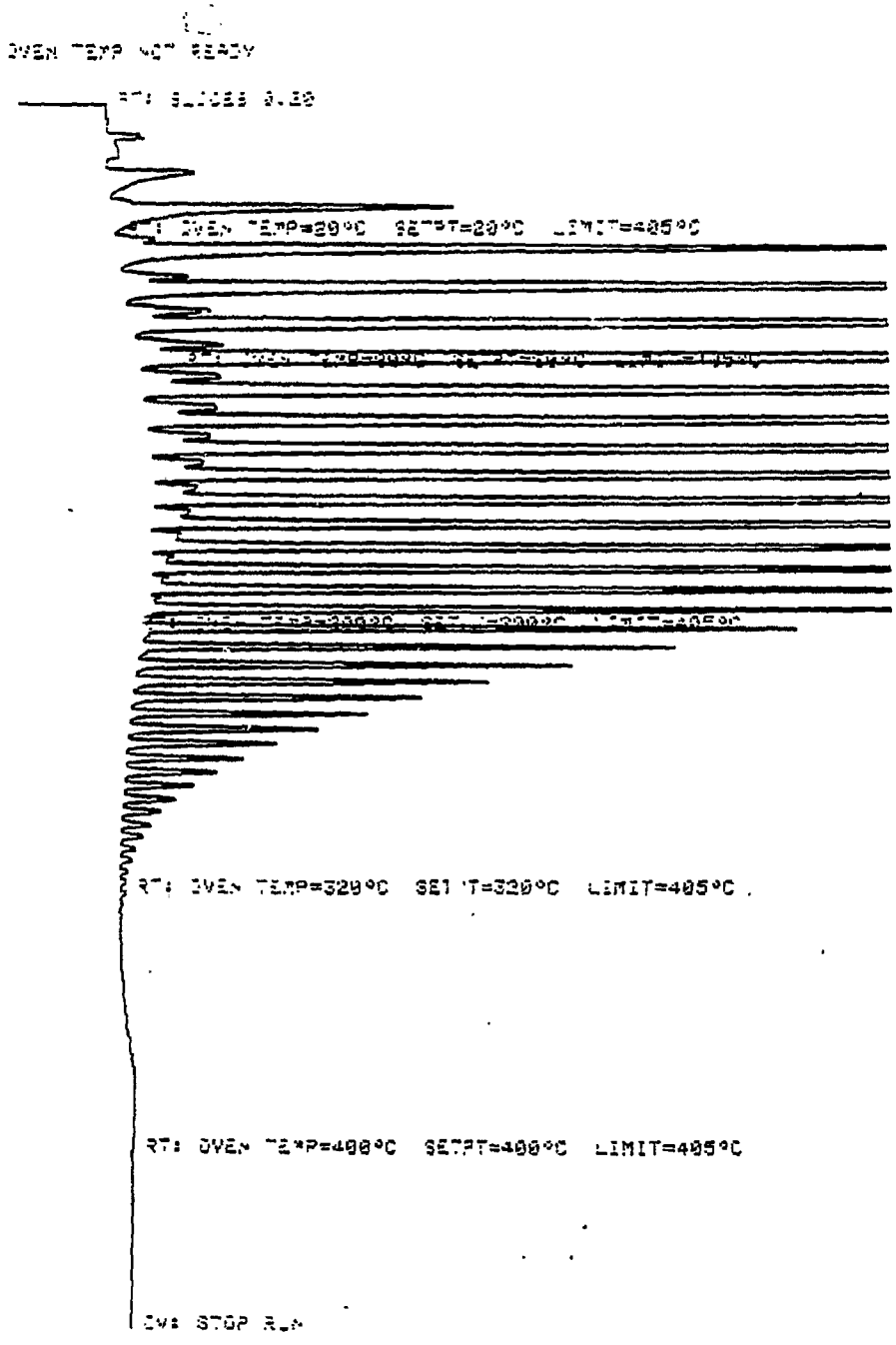

OVEN TEMP OK READY
RT: SLICES 0.30
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
CW: STOP RUN

Fig. B45

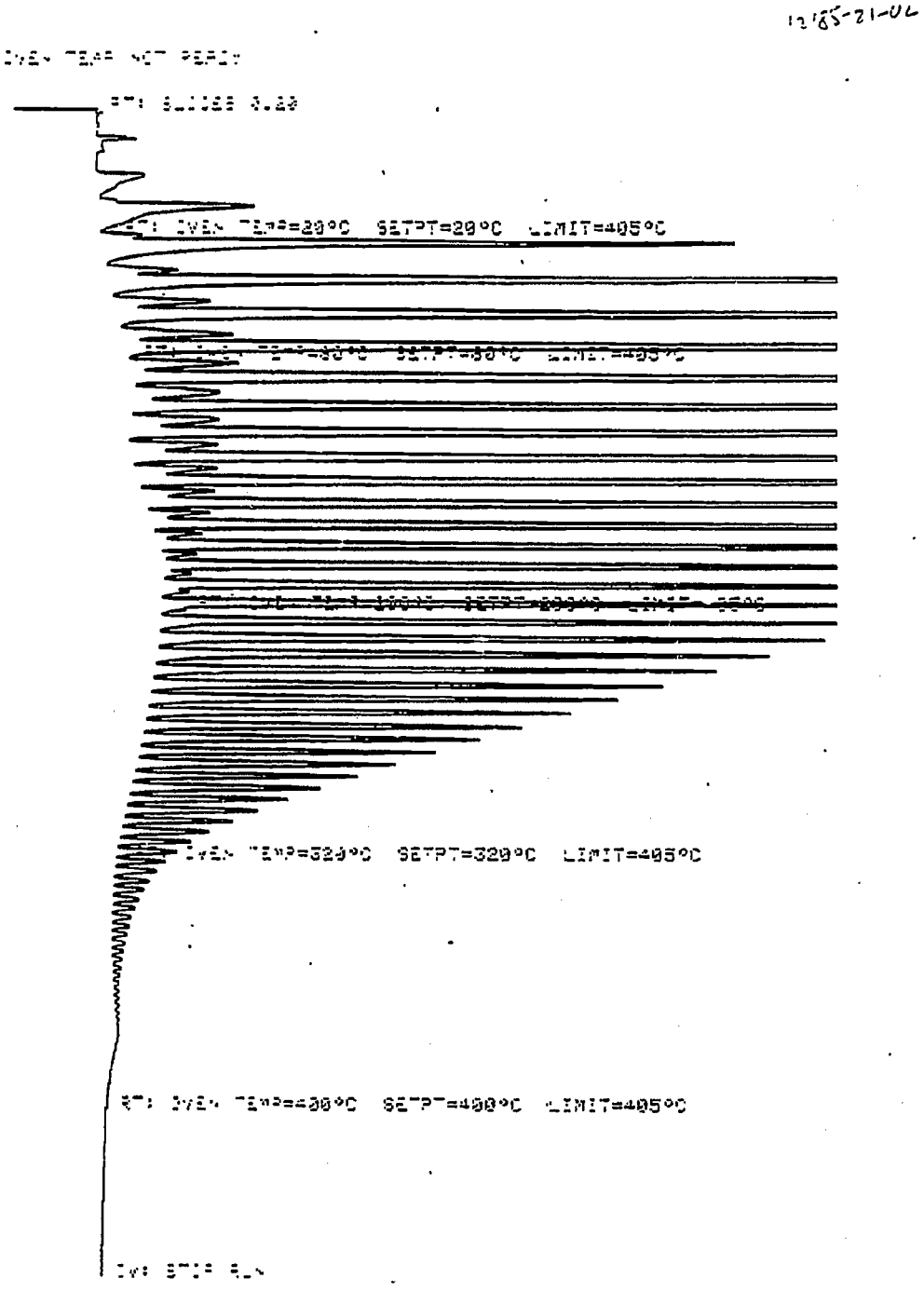

SETPT=20°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B46

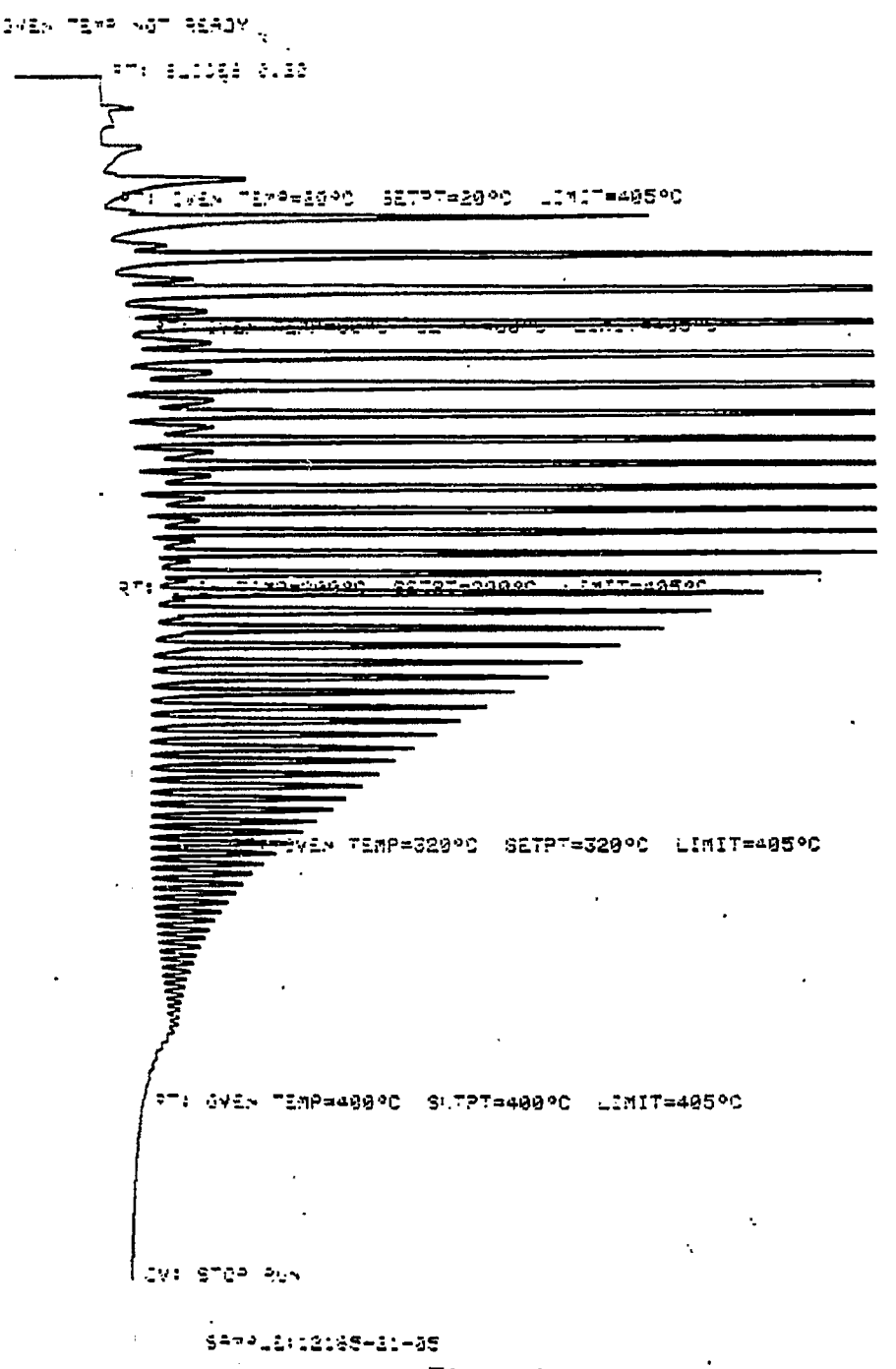

OVEN TEMP NOT READY
PT: 0.1000 0.00
PT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
PT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
PT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
CW: STOP RUN

Fig. B47

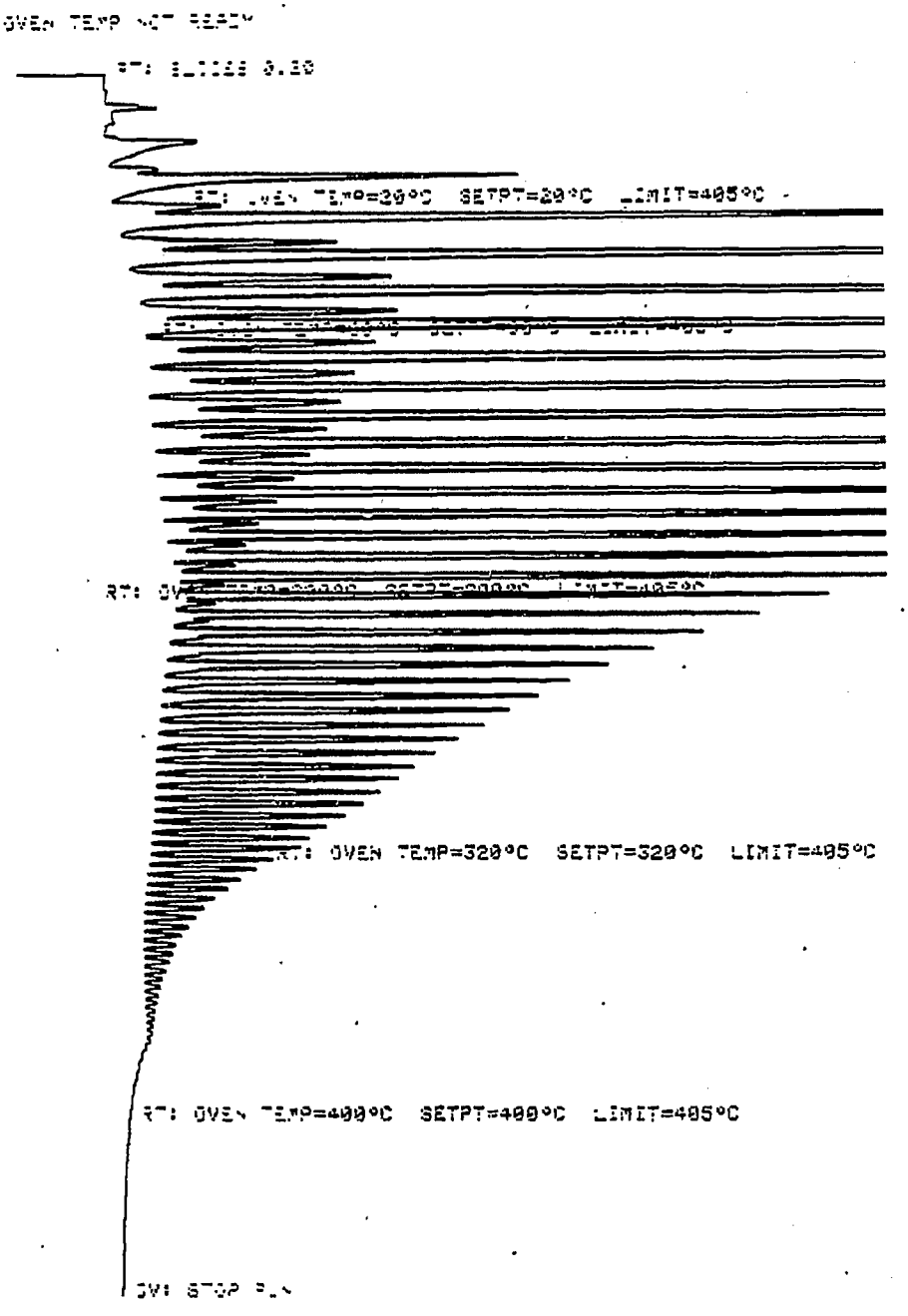

RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B48

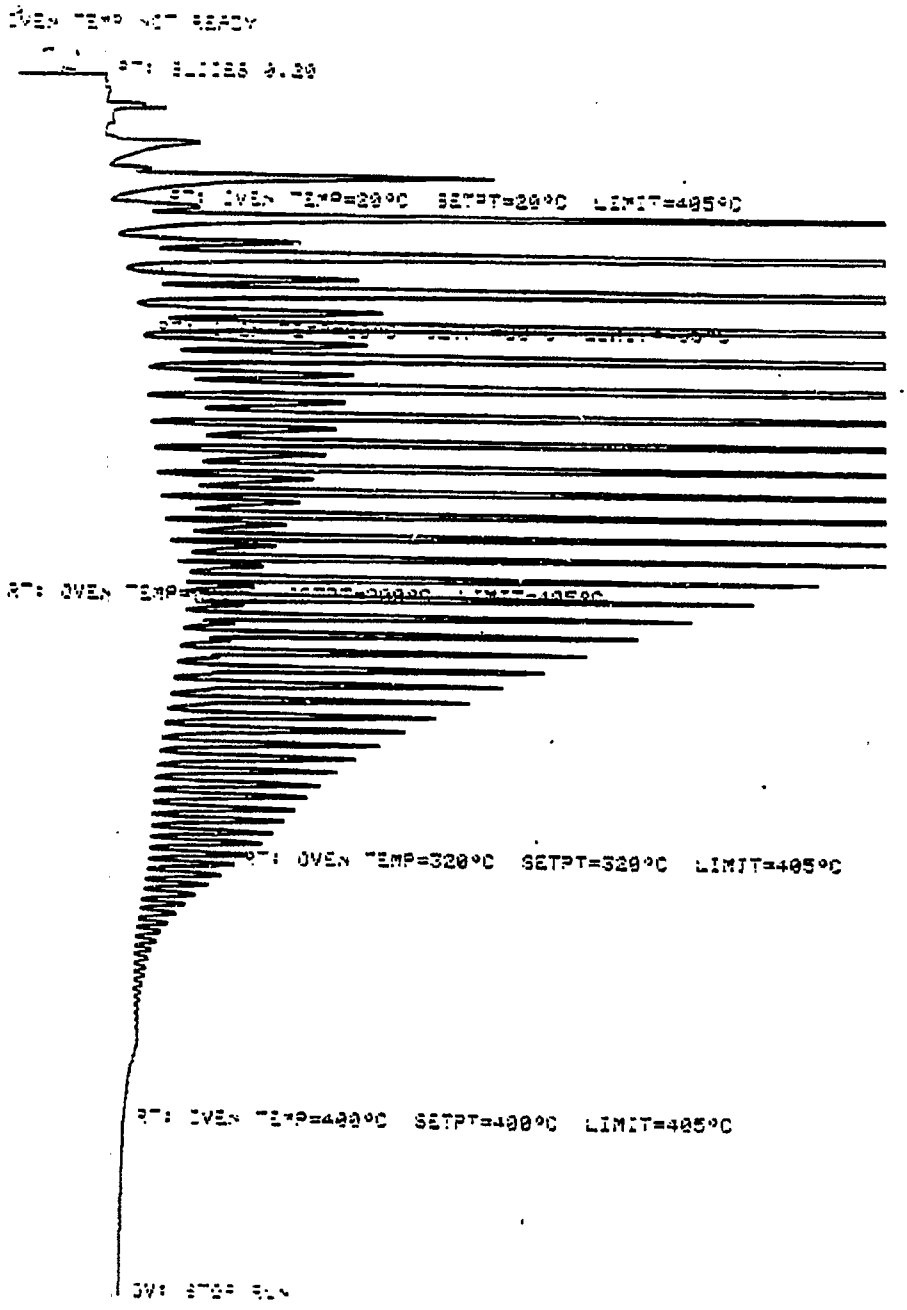

OVEN TEMP NOT READY
ST: ELIIES 0.30
ST: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
ST: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
ST: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B49

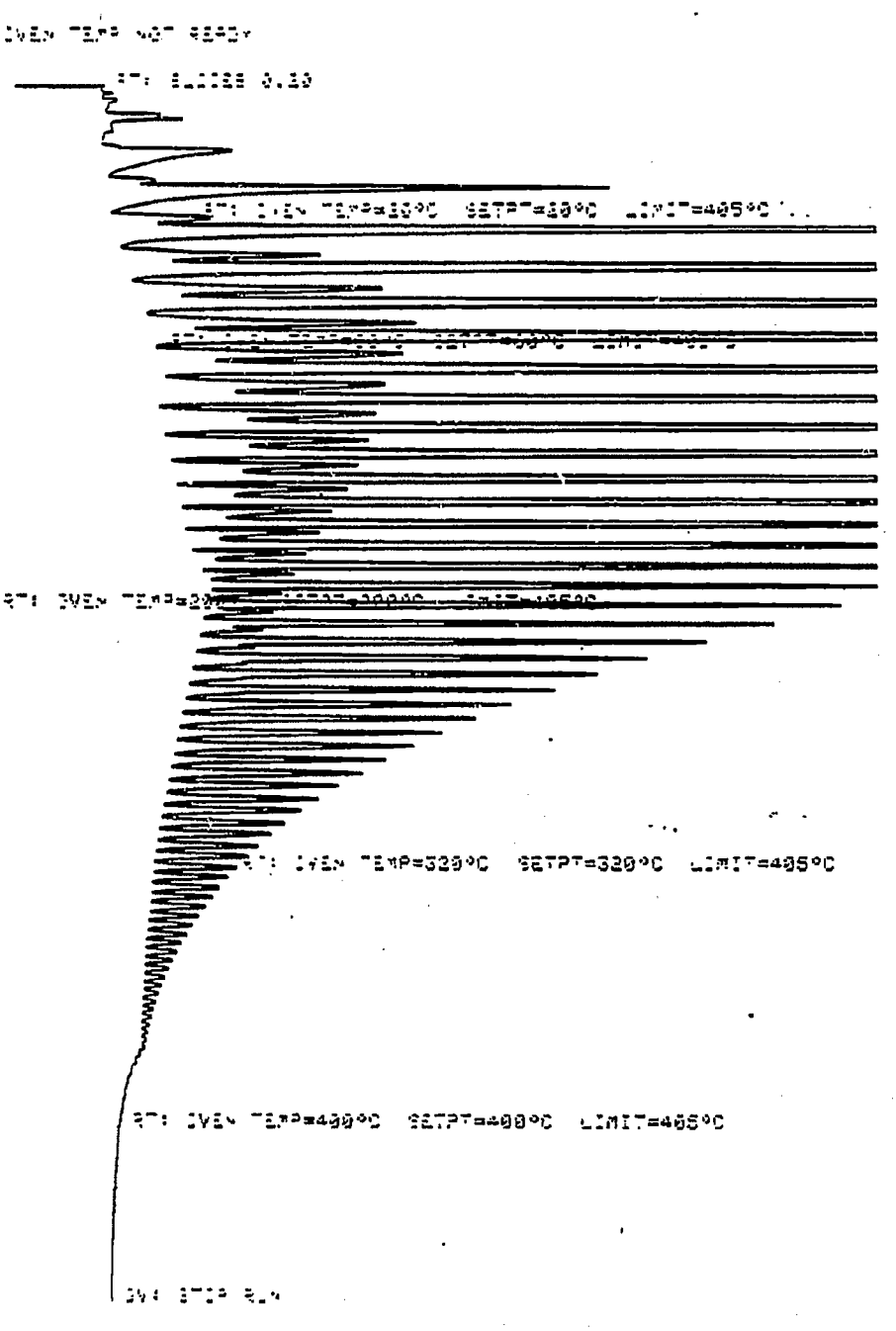

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
PT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B50

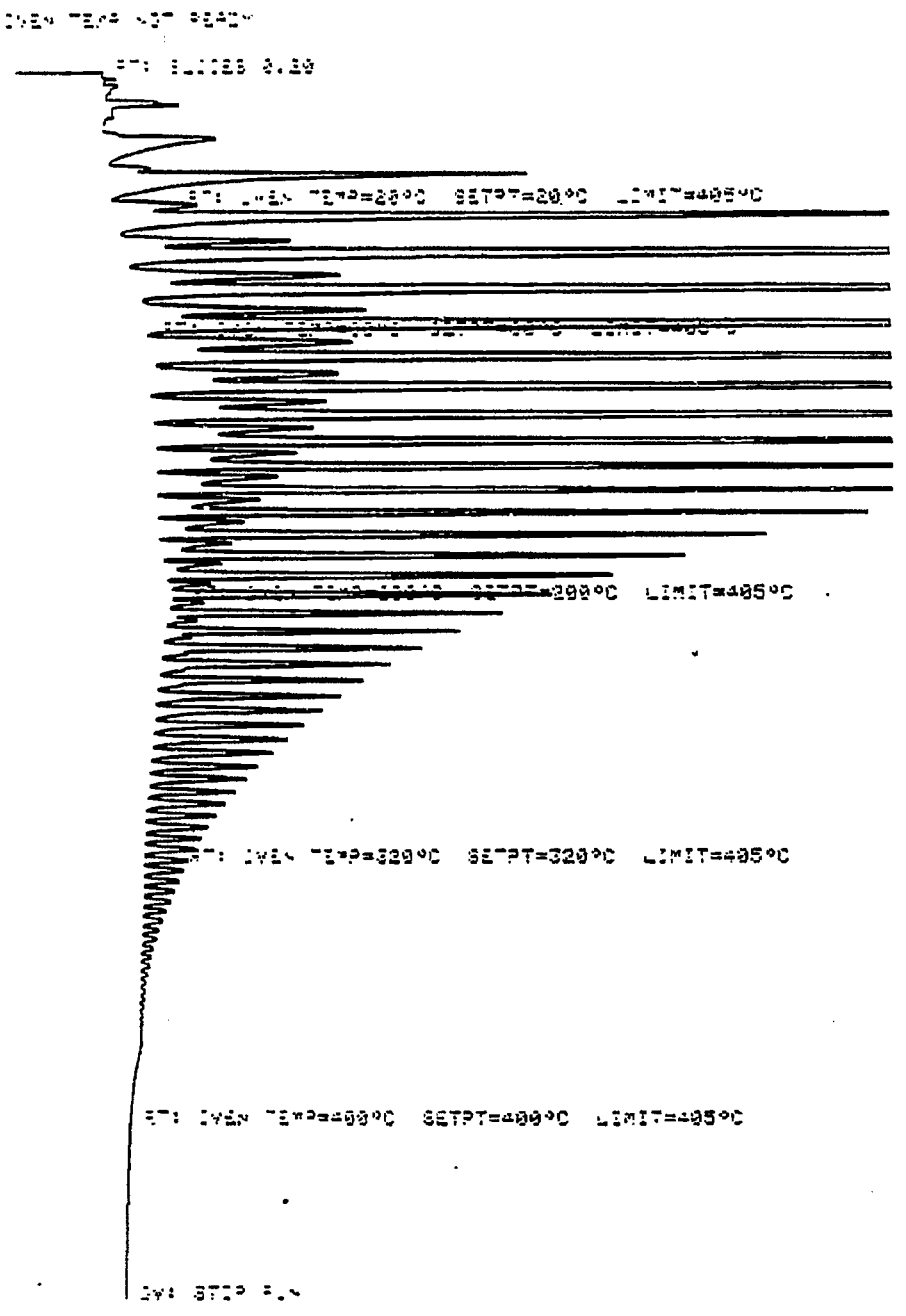

OVEN TEMP NOT READY
ST: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
ST: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
ST: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
SAMPLE:12:85-21-13

Fig. B51

Table B4

FILE: 1218521A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-21
CATALYST CO/X11-U103 80 CC 31.3 G AFTER USE:48.2 G (+16.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT312251-100)

RUN & SAMPLE NO.	12185-21-01	185-21-02	185-21-03	185-21-04	185-21-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.7	43.7	66.0	90.0	114.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	240	240	240	240	240
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	18.75	25.00	22.25	24.00	24.00
EFFLNT GAS LITER	221.08	306.55	296.42	325.30	334.60
GM AQUEOUS LAYER	43.91	60.36	47.59	48.62	48.49
GM OIL	9.60	34.67	35.98	35.43	35.73
MATERIAL BALANCE					
GM ATOM CARBON %	86.20	88.15	98.11	96.42	99.00
GM ATOM HYDROGEN %	71.05	97.66	103.86	101.67	103.77
GM ATOM OXYGEN %	104.78	91.19	92.70	91.81	93.53
RATIO CHX/(H2O+CO2)	0.4756	0.9029	1.1923	1.1727	1.2056
RATIO X IN CHX	2.3169	2.2562	2.2375	2.2453	2.2457
USAGE H2/CO PRODT	1.9805	2.0041	1.7954	1.8187	1.8053
FEED H2/CO FRM EFFLNT	0.8242	1.1079	1.0587	1.0545	1.0481
RESIDUAL H2/CO RATIO	0.3757	0.6362	0.6420	0.6569	0.6565
RATIO CO2/(H2O+CO2)	0.2044	0.0696	0.0691	0.0652	0.0632
K SHIFT IN EFFLNT	0.0965	0.0476	0.0477	0.0458	0.0443
SPECIFIC ACTIVITY SA	5.9900	3.4261	3.6485	3.3732	3.2900
CONVERSION					
ON CO %	27.95	34.48	36.12	34.23	34.09
ON H2 %	67.16	62.38	61.26	59.03	58.72
ON CO+H2 %	45.66	49.15	49.05	46.96	46.69
PRDT SELECTIVITY,WT %					
CH4	10.66	6.69	5.87	6.17	6.21
C2 HC'S	2.06	1.60	1.43	1.49	1.60
C3H8	2.22	1.91	1.78	1.91	1.96
C3H6=	4.84	2.71	2.58	2.71	2.87
C4H10	2.50	1.83	1.76	1.87	1.96
C4H8=	5.22	2.12	2.91	2.93	3.08
C5H12	3.17	1.87	1.97	2.11	2.15
C5H10=	5.06	1.74	2.57	2.59	2.83
C6H14	3.98	2.17	2.16	2.33	2.30
C6H12= & CYCLO'S	3.31	1.09	1.34	1.37	1.62
C7+ IN GAS	14.08	6.61	7.11	7.52	7.56
LIQ HC'S	42.89	69.66	68.53	67.00	65.86
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	27.51	16.87	16.32	17.07	17.69
C5 -420 F	47.70	31.80	32.77	49.43	33.97
420-700 F	21.79	31.49	30.15	26.80	27.40
700-END PT	3.00	19.85	20.76	6.70	20.94

Table B4 (continued)

FILE: 1218521A TSS4Q1 A1

C5+-END PT	72.49	83.13	83.68	82.93	82.31
ISO/NORMAL MOLE RATIO					
C4	0.0200	0.0000	0.0200	0.0254	0.0242
C5	0.0780	0.0000	0.0767	0.0810	0.0814
C6	0.0699	0.0000	0.0767	0.0795	0.0810
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.4385	0.6726	0.6599	0.6743	0.6532
C4	0.4618	0.8348	0.5840	0.6158	0.6149
C5	0.6084	1.0463	0.7438	0.7912	0.7406
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8043	0.8847	0.8773	0.7418	0.8686
RATIO CH4/(1-A)**2	2.7853	5.0260	3.8943	0.9253	3.5951
ALPHA FRM CORRELATION	0.8596	0.8340	0.8335		0.8324
ALPHA (EXPTL/CORR)	0.9357	1.0608	1.0525		1.0434
W%CH4 FRM CORRELATION	6.9866	14.9473	15.0857		15.4238
W%CH4 (EXPTL/CORR)	1.5264	0.4473	0.3888		0.4026
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	291	335	330		329
16	330	369	370		368
50	447	566	562		563
84	616	789	823		857
90	662	847	892		936
RANGE(16-84 %)	286	420	453		489
WT % @ 420 F	42.20	26.30	25.70	50.00	26.60
WT % @ 700 F	93.00	71.50	69.70	90.00	68.20

Table B5

FILE: 1218521B TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-21
CATALYST CO/X11-U103 80 CC 31.3 G AFTER USE:48.2 G (+16.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-100)

RUN & SAMPLE NO.	12185-21-06	185-21-07	185-21-09	185-21-10	185-21-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	138.0	162.0	281.7	309.7	331.7
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	259	259	260	260	260
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	24.00	71.67	28.00	22.00
EFFLNT GAS LITER	266.10	265.50	833.52	328.45	260.50
GM AQUEOUS LAYER	57.57	60.03	185.20	71.37	55.08
GM OIL	42.44	41.76	119.52	45.51	36.33
MATERIAL BALANCE					
GM ATOM CARBON %	98.58	97.55	98.67	98.97	100.09
GM ATOM HYDROGEN %	102.71	102.07	104.79	104.54	105.40
GM ATOM OXYGEN %	94.26	94.89	96.75	96.54	96.23
RATIO CHX/(H2O+CO2)	1.1178	1.0719	1.0523	1.0670	1.1083
RATIO X IN CHX	2.3407	2.3317	2.3340	2.3367	2.3308
USAGE H2/CO PRODT	1.5677	1.6268	1.6992	1.7046	1.6863
FEED H2/CO FRM EFFLNT	1.0419	1.0463	1.0620	1.0563	1.0530
RESIDUAL H2/CO RATIO	0.5242	0.5114	0.5310	0.5287	0.5339
RATIO CO2/(H2O+CO2)	0.2165	0.1928	0.1630	0.1582	0.1574
K SHIFT IN EFFLNT	0.1448	0.1220	0.1034	0.0993	0.0997
SPECIFIC ACTIVITY SA	2.7000	2.6132	2.2117	2.1370	2.1386
CONVERSION					
ON CO %	49.62	47.96	45.45	44.87	45.05
ON H2 %	74.65	74.56	72.72	72.41	72.14
ON CO+H2 %	62.39	61.56	59.50	59.02	58.95
PRDT SELECTIVITY,WT %					
CH4	10.67	10.33	10.56	10.56	10.31
C2 HC'S	2.20	2.11	2.18	2.23	2.18
C3H8	2.88	2.66	2.59	2.63	2.57
C3H6=	1.81	1.84	2.08	2.09	2.08
C4H10	2.46	2.25	2.32	2.33	2.30
C4H8=	2.61	2.55	3.13	3.15	3.12
C5H12	2.76	2.66	2.66	2.66	2.67
C5H10=	2.40	2.52	1.74	1.73	1.98
C6H14	3.00	2.96	3.04	3.91	3.97
C6H12= & CYCLO'S	1.44	1.62	1.98	2.08	2.24
C7+ IN GAS	6.93	6.62	7.19	7.38	7.60
LIQ HC'S	60.82	61.88	60.54	59.24	58.98
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	22.64	21.74	22.85	22.99	22.57
C5 -420 F	36.91	20.72	46.88	33.47	47.94
420-700 F	25.42	13.61	24.22	20.56	23.59
700-END PT	15.02	43.93	6.05	22.99	5.90

Table B5 (continued)

FILE: 1218521B TSS4Q1 A1

C5+-END PT	77.36	78.26	77.15	77.01	77.43
ISO/NORMAL MOLE RATIO					
C4	0.0179	0.0181	0.0201	0.0198	0.0212
C5	0.1036	0.0969	0.0843	0.0872	0.0869
C6	0.1397	0.1304	0.1355	0.4624	0.4599
C4=	0.0000	0.0000	0.1019	0.1014	0.1031
PARAFFIN/OLEFIN RATIO					
C3	1.5181	1.3757	1.1903	1.1985	1.1800
C4	0.9107	0.8524	0.7140	0.7127	0.7120
C5	1.1187	1.0282	1.4886	1.4958	1.3101
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8576	0.8946	0.7945	0.8780	0.8525
RATIO CH4/(1-A)**2	5.2625	9.2978	2.5005	7.0997	4.7408
ALPHA FRM CORRELATION	0.8423	0.8435		0.8418	
ALPHA (EXPTL/CORR)	1.0181	1.0606		1.0430	
W%CH4 FRM CORRELATION	16.5194	16.1482		16.8770	
W%CH4 (EXPTL/CORR)	0.6460	0.6395		0.6257	
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	296	471		256	
16	338	561		324	
50	515	852		617	
84	785	1038		849	
90	864	1070		897	
RANGE(16-84 %)	447	477		525	
WT % @ 420 F	33.50	7.00	50.00	26.50	50.00
WT % @ 700 F	75.30	29.00	90.00	61.20	90.00

Table B6

FILE: 1218521C TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12185-21
CATALYST CO/X11-U103 80 CC 31.3 G AFTER USE:48.2 G (+16.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12251-100)

RUN & SAMPLE NO.	12185-21-12	185-21-13
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	356.5	401.7
PRESSURE,PSIG	300	300
TEMP. C	260	260
FEED CC/MIN	400	400
HOURS FEEDING	24.75	45.25
EFFLNT GAS LITER	291.85	534.70
GM AQUEOUS LAYER	61.12	113.90
GM OIL	41.18	71.84
MATERIAL BALANCE		
GM ATOM CARBON %	99.62	98.41
GM ATOM HYDROGEN %	104.72	104.44
GM ATOM OXYGEN %	95.38	95.45
RATIO CHX/(H2O+CO2)	1.1210	1.0843
RATIO X IN CHX	2.3317	2.3410
USAGE H2/CO PRODT	1.6884	1.7323
FEED H2/CO FRM EFFLNT	1.0512	1.0613
RESIDUAL H2/CO RATIO	0.5335	0.5361
RATIO CO2/(H2O+CO2)	0.1541	0.1430
K SHIFT IN EFFLNT	0.0972	0.0895
SPECIFIC ACTIVITY SA	2.1239	2.0474
CONVERSION		
ON CO %	44.83	43.90
ON H2 %	72.00	71.66
ON CO+H2 %	58.76	58.19
PRDT SELECTIVITY,WT %		
CH4	10.38	10.83
C2 HC'S	2.12	2.20
C3H8	2.60	2.63
C3H6=	2.18	2.17
C4H10	2.29	2.40
C4H8=	3.09	3.22
C5H12	2.59	2.71
C5H10=	1.98	2.01
C6H14	3.74	3.93
C6H12= & CYCLO'S	2.03	2.10
C7+ IN GAS	7.25	7.19
LIQ HC'S	58.76	58.61
TOTAL	100.00	100.00
SUB-GROUPING		
C1 -C4	22.65	23.45
C5 -420 F	36.41	37.87
420-700 F	25.76	27.78
700-END PT	15.18	10.90

Table B6 (continued)

FILE: 1218521C TSS4Q1 A1

C5+-END PT	77.35	76.55
ISO/NORMAL MOLE RATIO		
C4	0.0212	0.0202
C5	0.0889	0.0906
C6	0.4615	0.4501
C4=	0.1037	0.1084
PARAFFIN/OLEFIN RATIO		
C3	1.1405	1.1557
C4	0.7167	0.7191
C5	1.2717	1.3106
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8552	0.8372
RATIO CH4/(1-A)**2	4.9510	4.0857
ALPHA FRM CORRELATION	0.8414	0.8412
ALPHA (EXPTL/CORR)	1.0164	0.9953
W%CH4 FRM CORRELATION	17.0146	17.0873
W%CH4 (EXPTL/CORR)	0.6100	0.6337
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	OIL WAX
DENSITY		
N, REFRACTIVE INDEX		
SIMULT'D DISTILATN		
10 WT % @ DEG F	301	291
16	342	308
50	520	480
84	795	730
90	879	817
RANGE(16-84 %)	453	422
WT % @ 420 F	31.50	34.00
WT % @ 700 F	74.60	81.40

VI. Run 38 (12200-22) with Catalyst 38 ($Co/X_{11}/TC-103$)

This was a repeat of Run 36 which, in the short 50 hours on stream before it was cut off by a power failure, produced promising results both in activity and selectivity. The catalyst was identical in composition and preparation to Catalyst 36, including the same concentrations of cobalt and X_{11}, 12.3 and 2.4 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B52-55. Simulated distillations of the C_5+ product are plotted in Figs. B56-64. Carbon number product distributions are plotted in Figs. B65-73. Chromatograms from simulated distillations are reproduced in Figs. B74-82. Detailed material balances appear in Tables B7-10.

During the first stage of the run, at 240C, the activity of this catalyst was somewhat lower than in Run 36. At about 50 hours on stream the conversion of $CO+H_2$ was about 50 percent, as against 52 percent in Run 36. The difference may be due, wholly or in part, to a temperature control failure early in the run which exposed the catalyst to a temperature of 248C (eight degrees above specification) for some part of the time until the first sample was taken.

The selectivity was essentially the same as in Run 36, with

methane content less than 4 percent, C_{5+} content about 88 percent, and high olefin content in the C_4 fraction.

The stability at 240C was fairly poor, with conversion falling from 50 percent initially to 44 percent after 100 hours. At the same time the methane production, as usual during deactivation, was increasing.

When the reactor temperature was raised to 260C the conversion increased to about 54 percent, approximately the same as with Catalyst 32. On a basis of weight percent cobalt, however, Catalyst 32, with only 8.2 percent cobalt, was substantially more active.

In selectivity, this catalyst was somewhat better than Catalyst 32:

	Percent of total product (260C, 300 GHSV, 1:1 H_2:CO)	
	Catalyst 38	Catalyst 32
CH_4	6.5	7.6
C_5^+	82.8	82.1
C_4 olefin/paraffin	2.2	1.8

The stability, however, was poorer than that of Catalyst 32, with a loss of conversion, as estimated by linear least squares, of one percentage point every 70 hours. An interesting feature of this process was the fact that the methane production remained stable throughout, with an estimated increase of only one percentage point every 2000 hours.

The Schulz-Flory plots, as in Run 36, were linear, with no

evidence of a carbon number cut-off.

Near the end of the run the H_2:CO ratio was increased to test the effect on conversion and methane make. When the ratio was raised from 1:1 to 2:1 the methane production increased sharply to more than 30 percent and the conversion to 90 percent. Upon lowering the ratio to 1.5:1, methane production dropped to about 18 percent and conversion to about 70 percent. In each of these stages the time on stream was too short for any conclusions as to stability.

From this test it appears that a substantial increase in the cobalt concentration of this type of catalyst has mixed effects, improving activity but impairing stability. The results from manipulating the H_2:CO ratio suggest that raising this ratio may enhance the activity of a catalyst which has an inherently low production of methane.

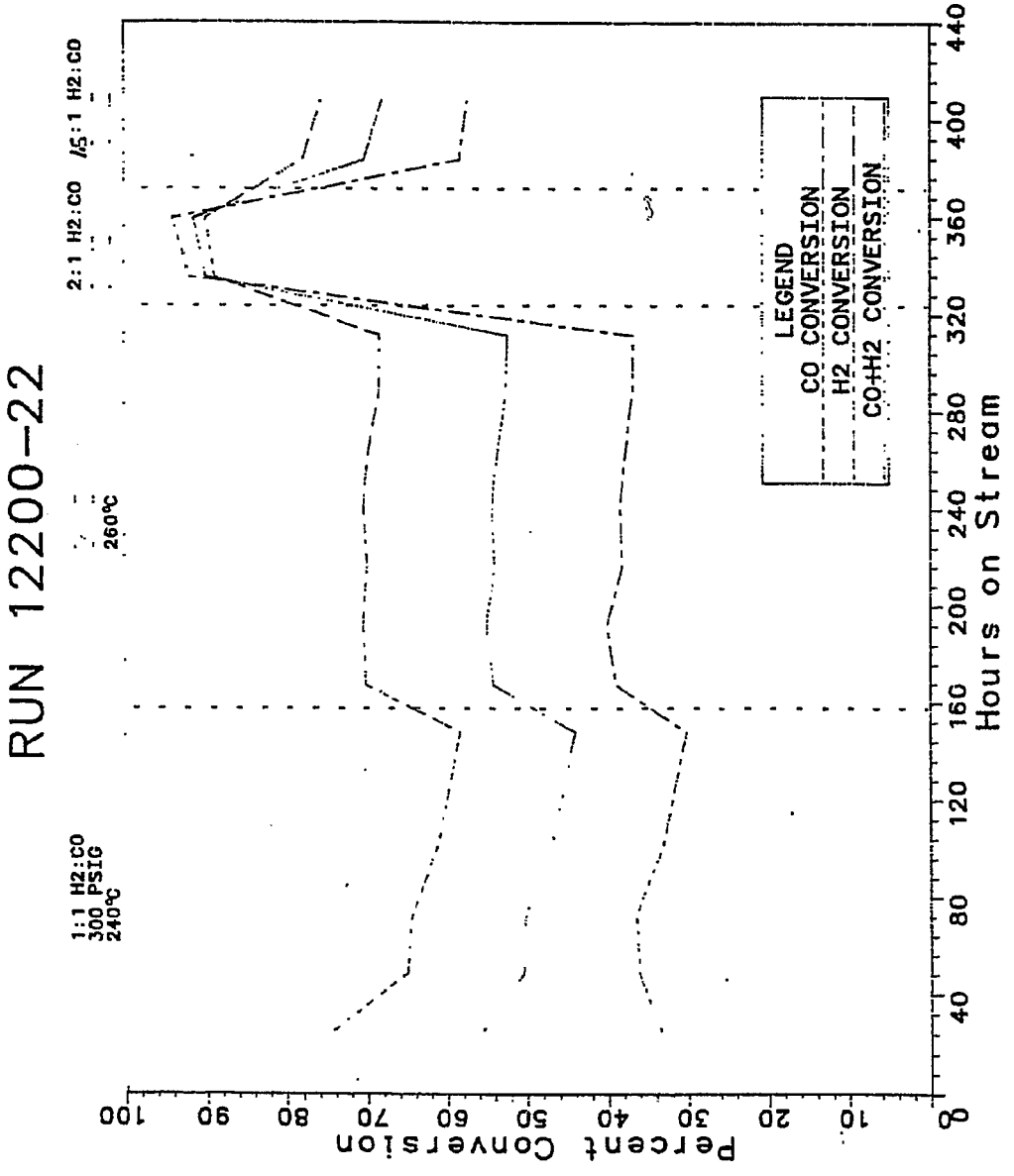

RUN 12200-22
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
260°C
.5:1 H2:CO
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B52

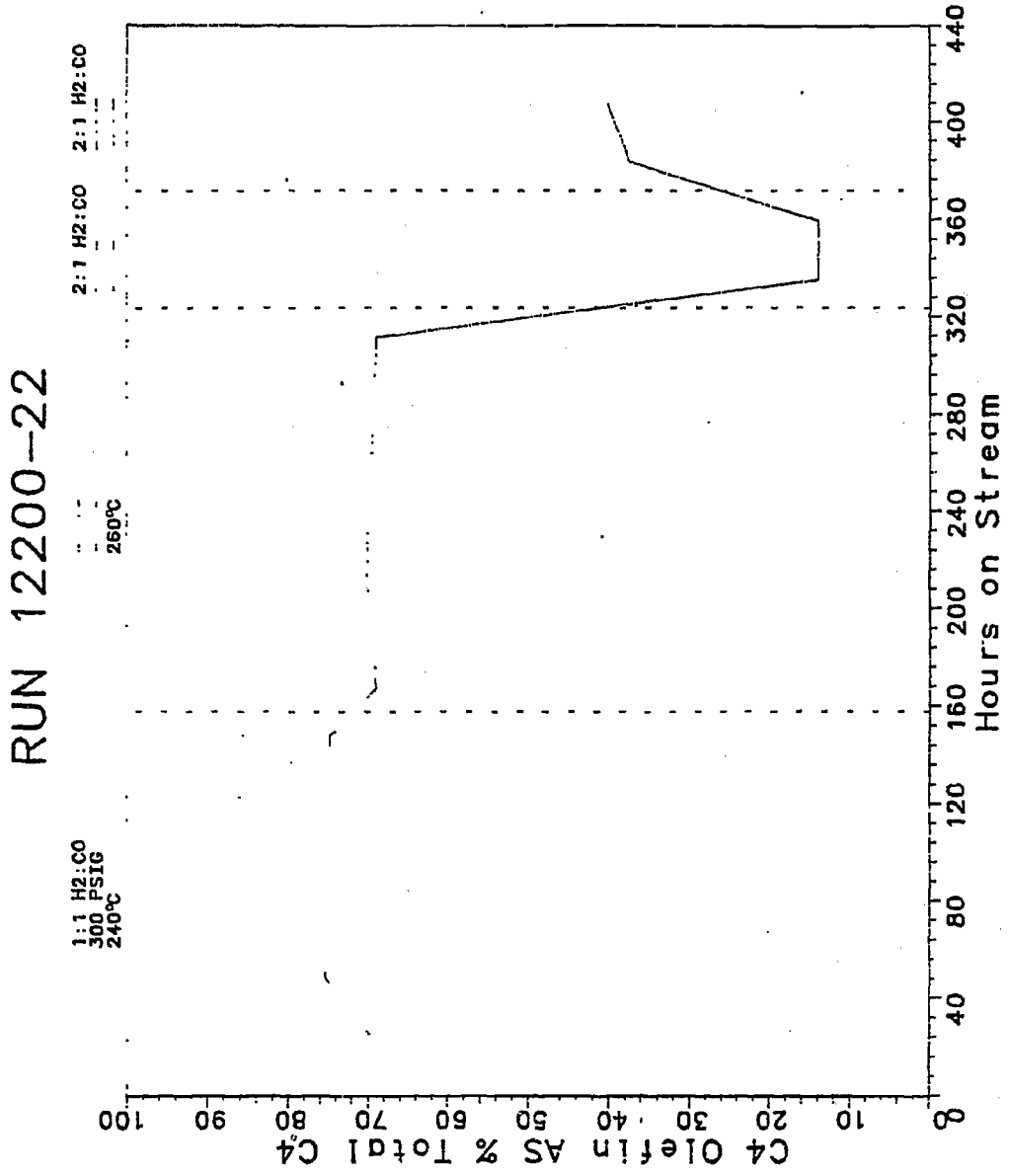

RUN 12200-22
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
260°C
2:1 H2:CO
C4 Olefin As % Total C4
Hours on Stream
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B53

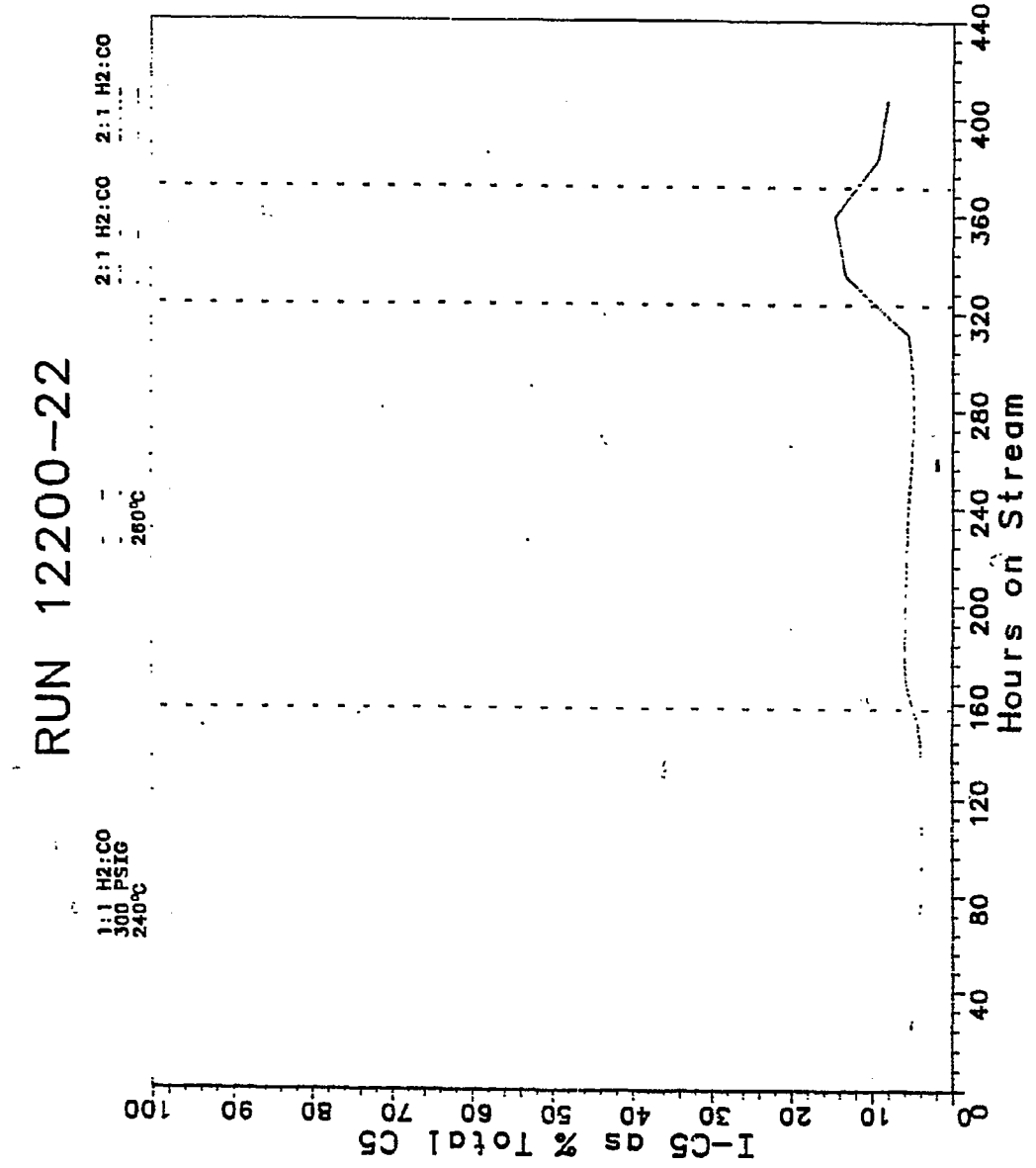

RUN 12200-22
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
260°C
2:1 H2:CO
I-C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B54

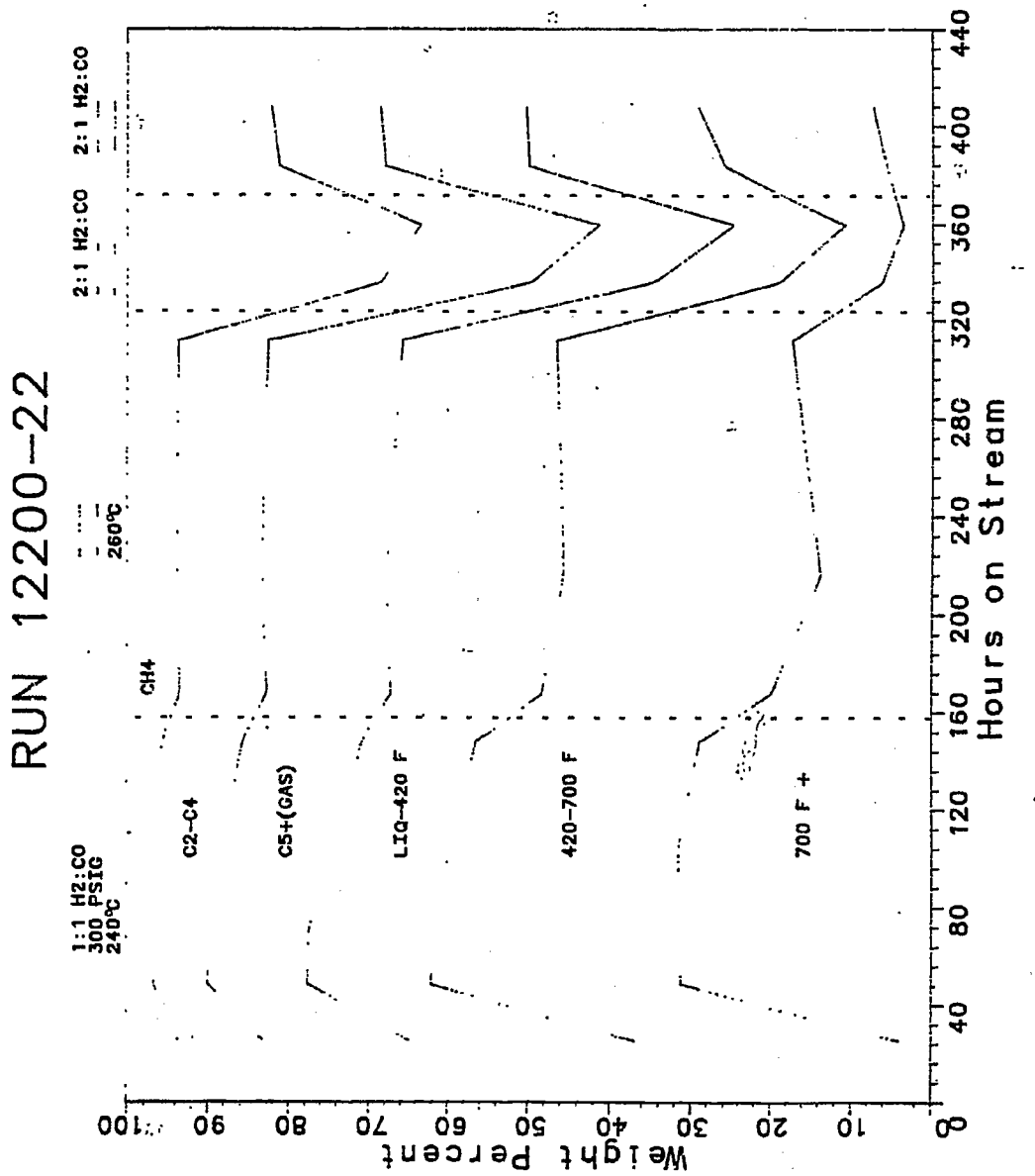

RUN 12200-22
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
260°C
2:1 H2:CO
2:1 H2:CO
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. B55

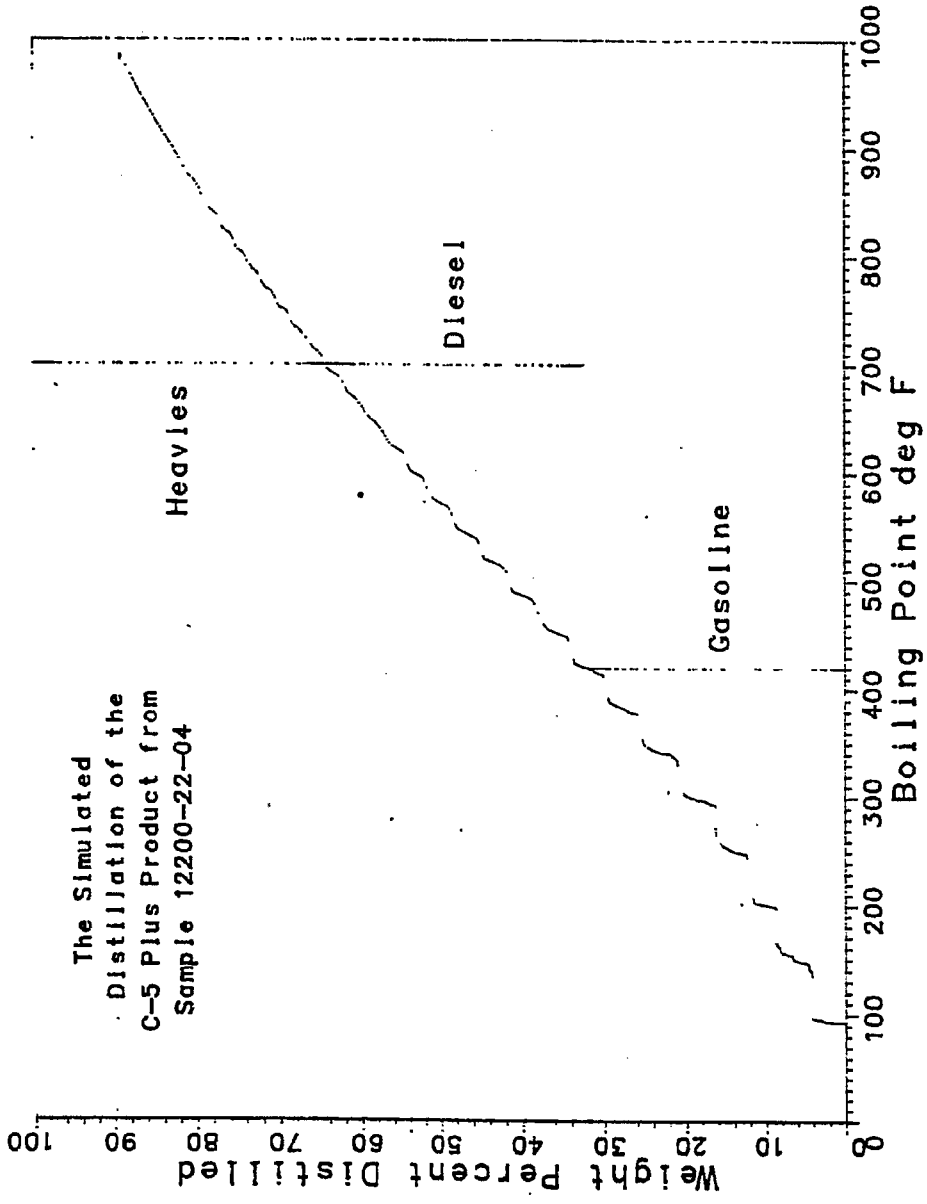

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-04
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B56

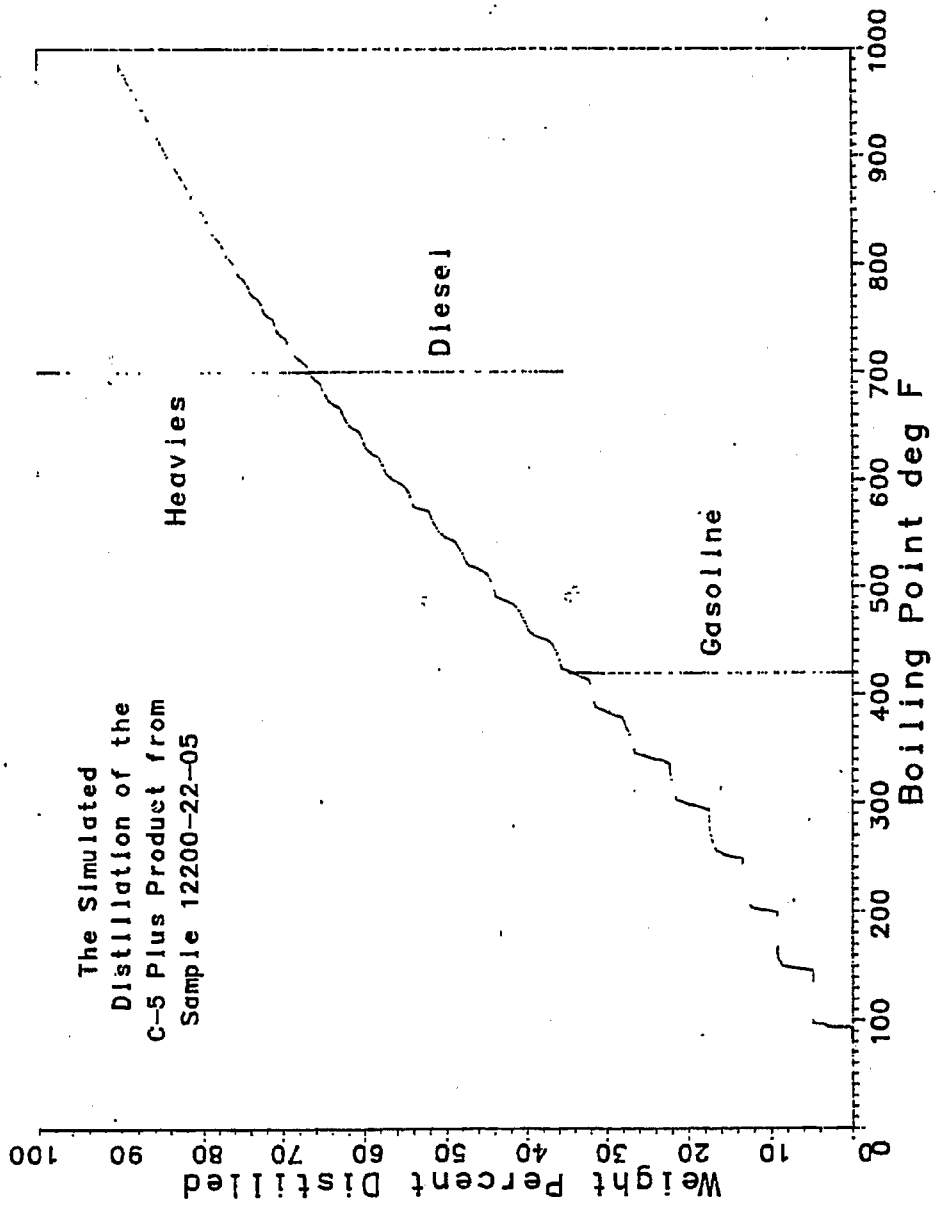
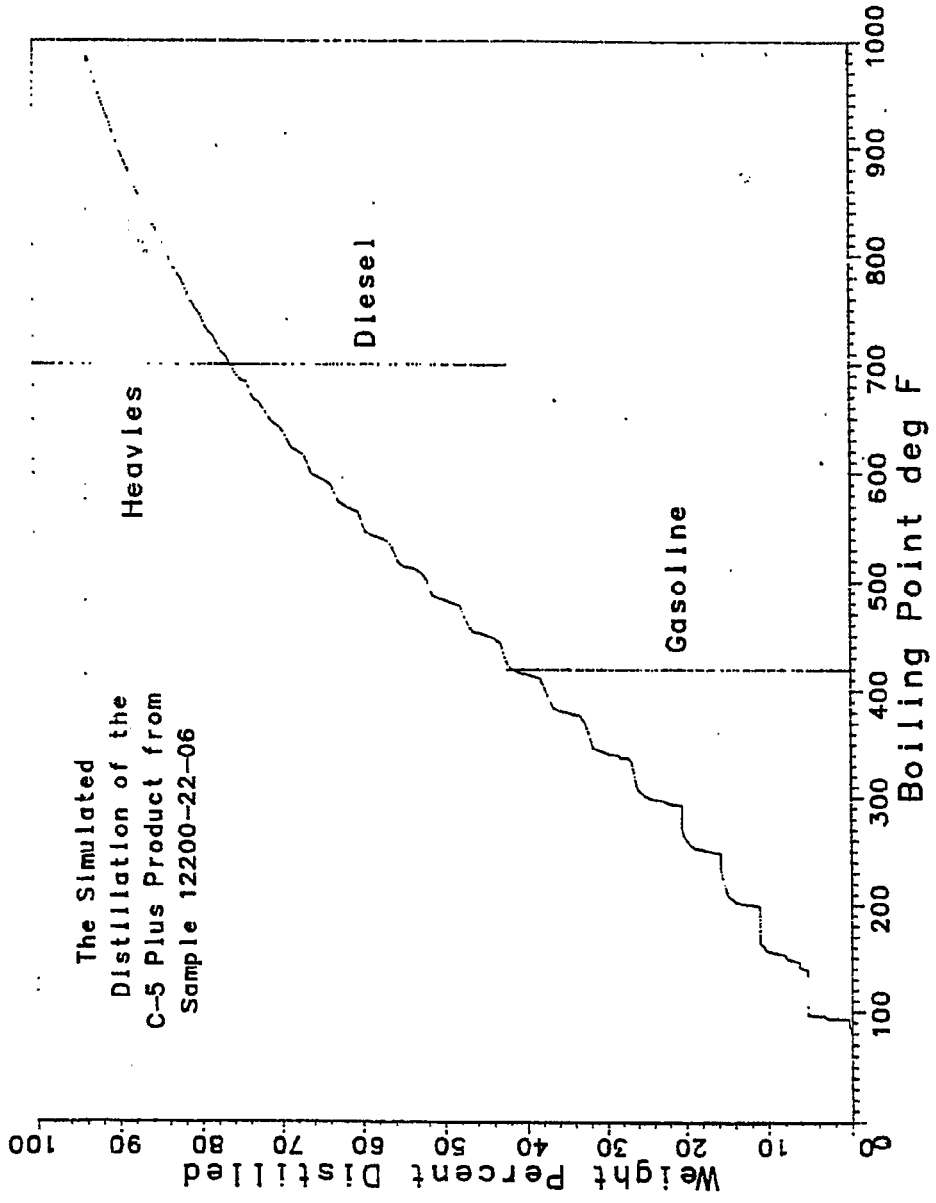

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-05
Heavies
Diesel
Gasoline
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point deg F
100
200
300
400
500
600
700
800
900
1000

Fig. B57


The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-06
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
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100
100
200
300
400
500
600
700
800
900
1000

Fig. B58

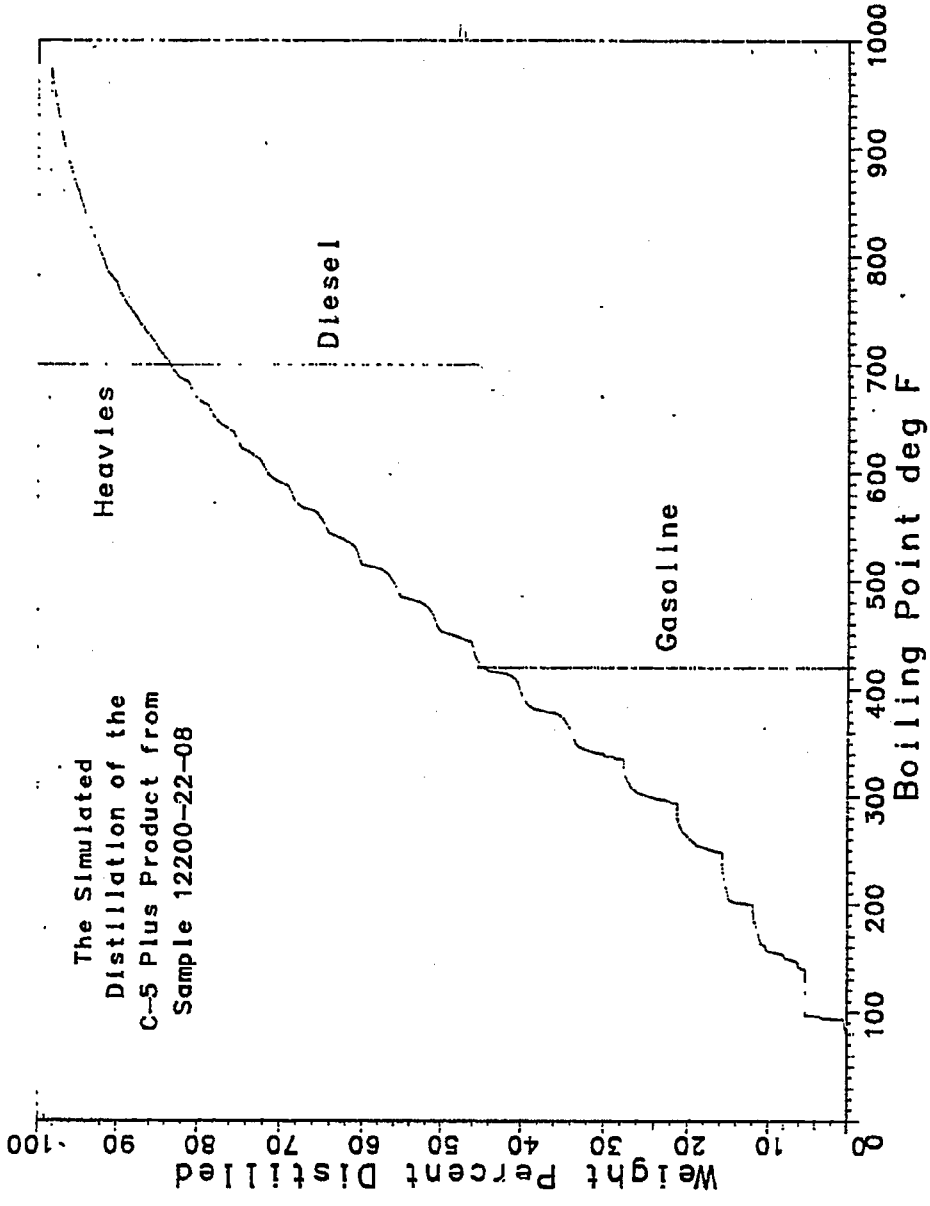

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-08
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B59

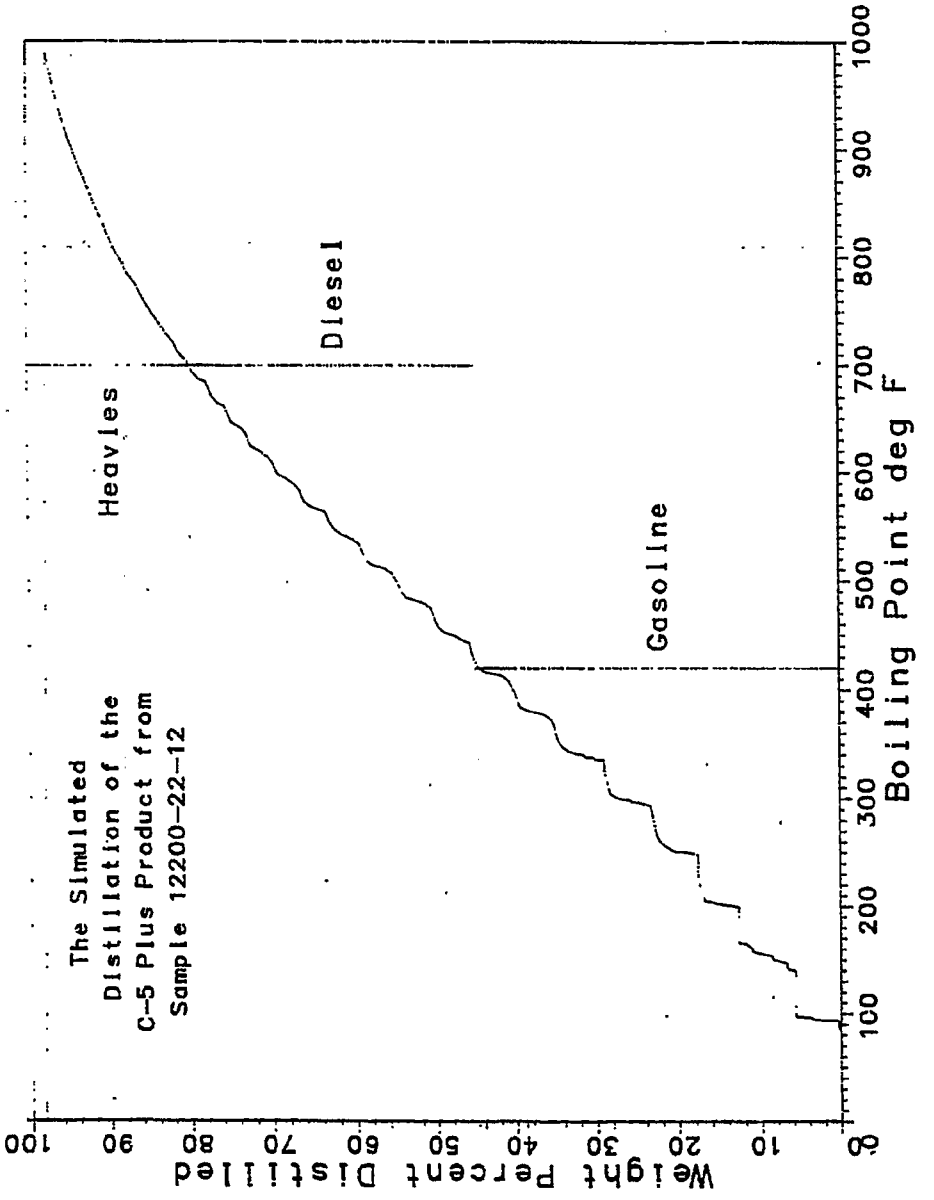

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-12
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B60

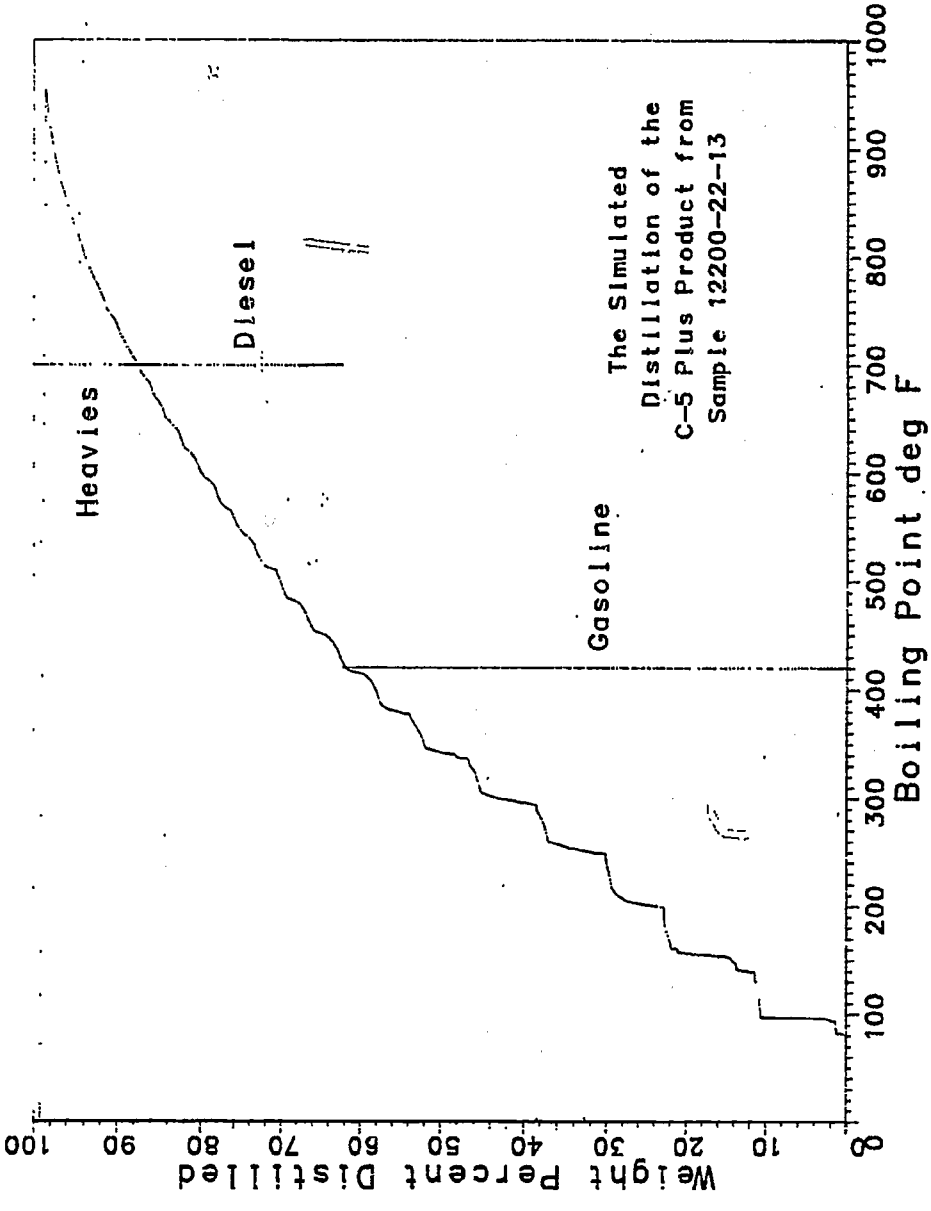

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-13
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B61

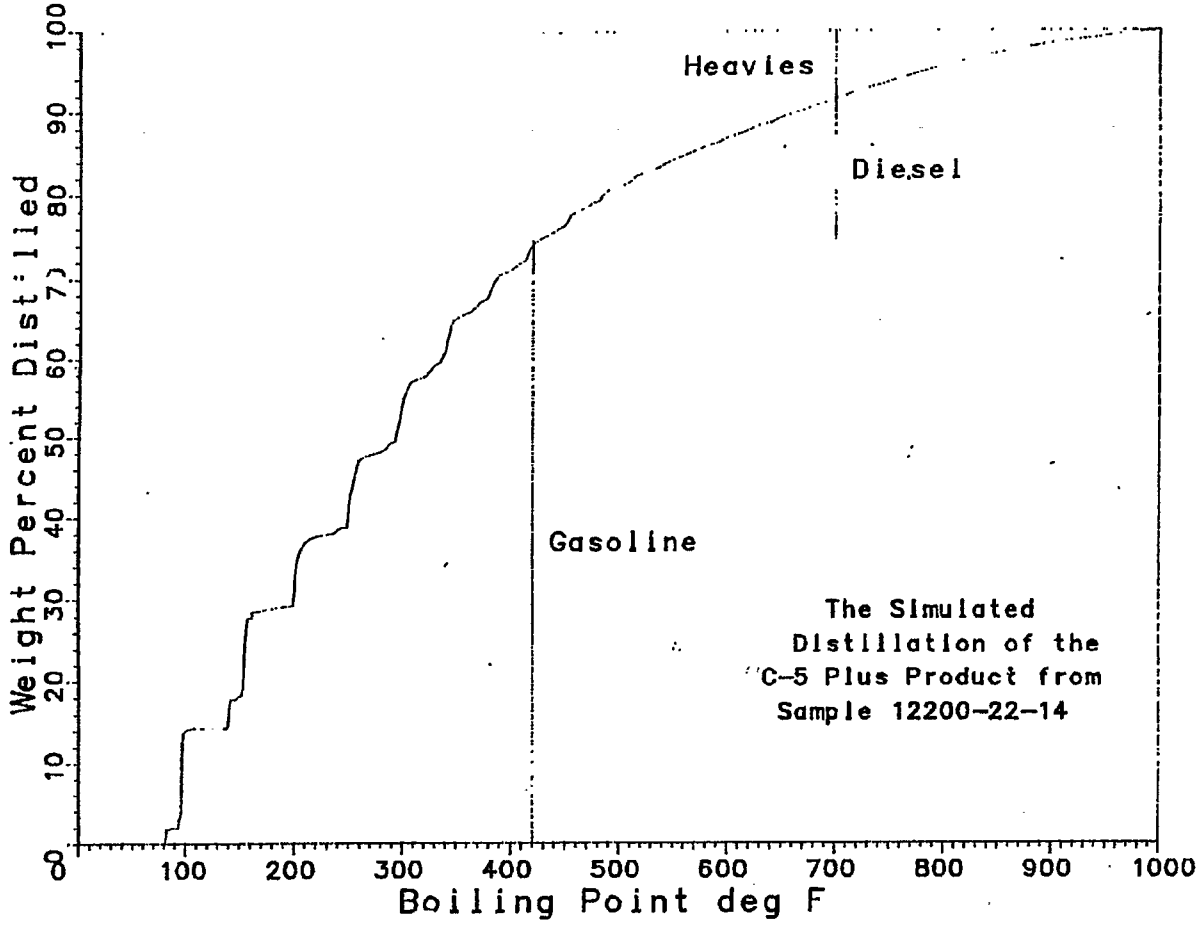

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
Boiling Point deg F
Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-14

Fig. 862

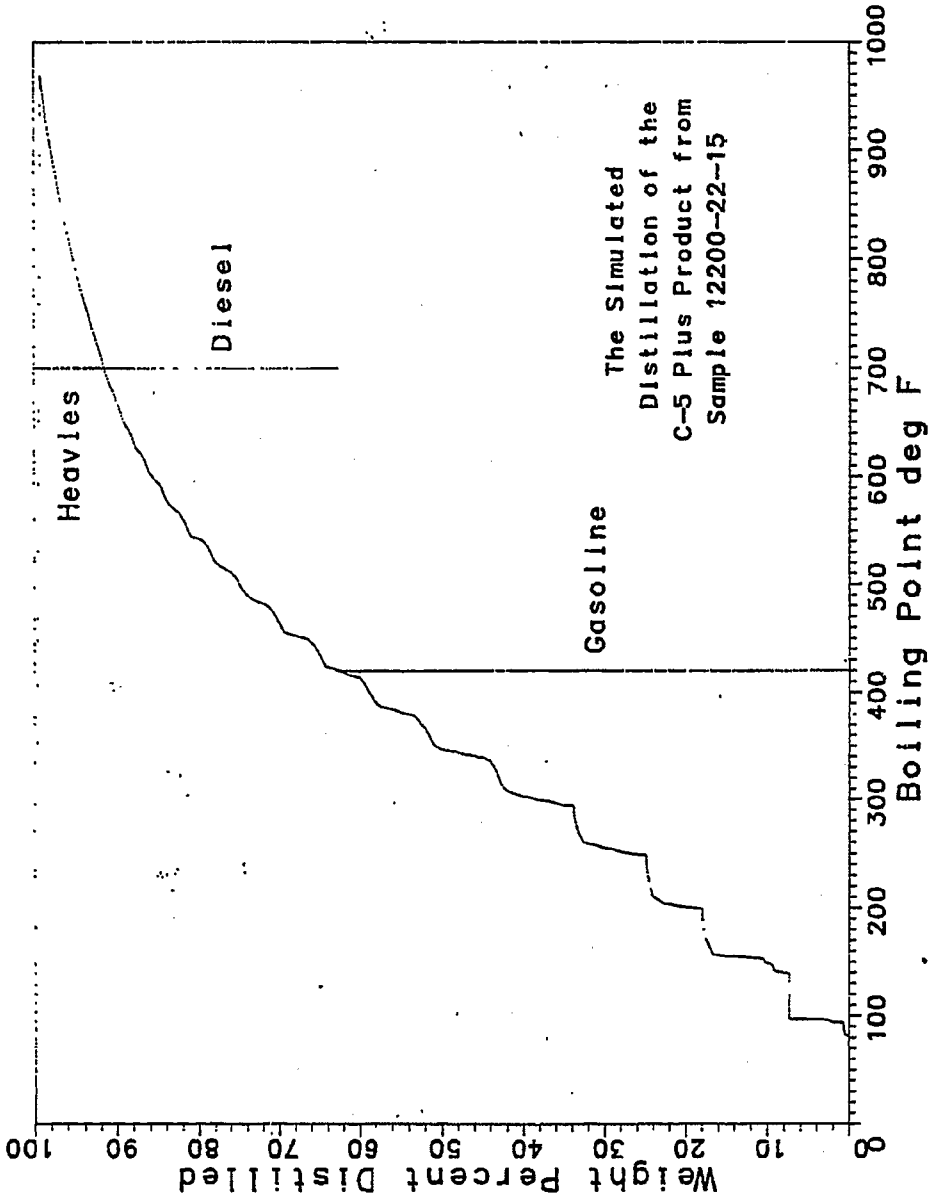

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-15
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B63

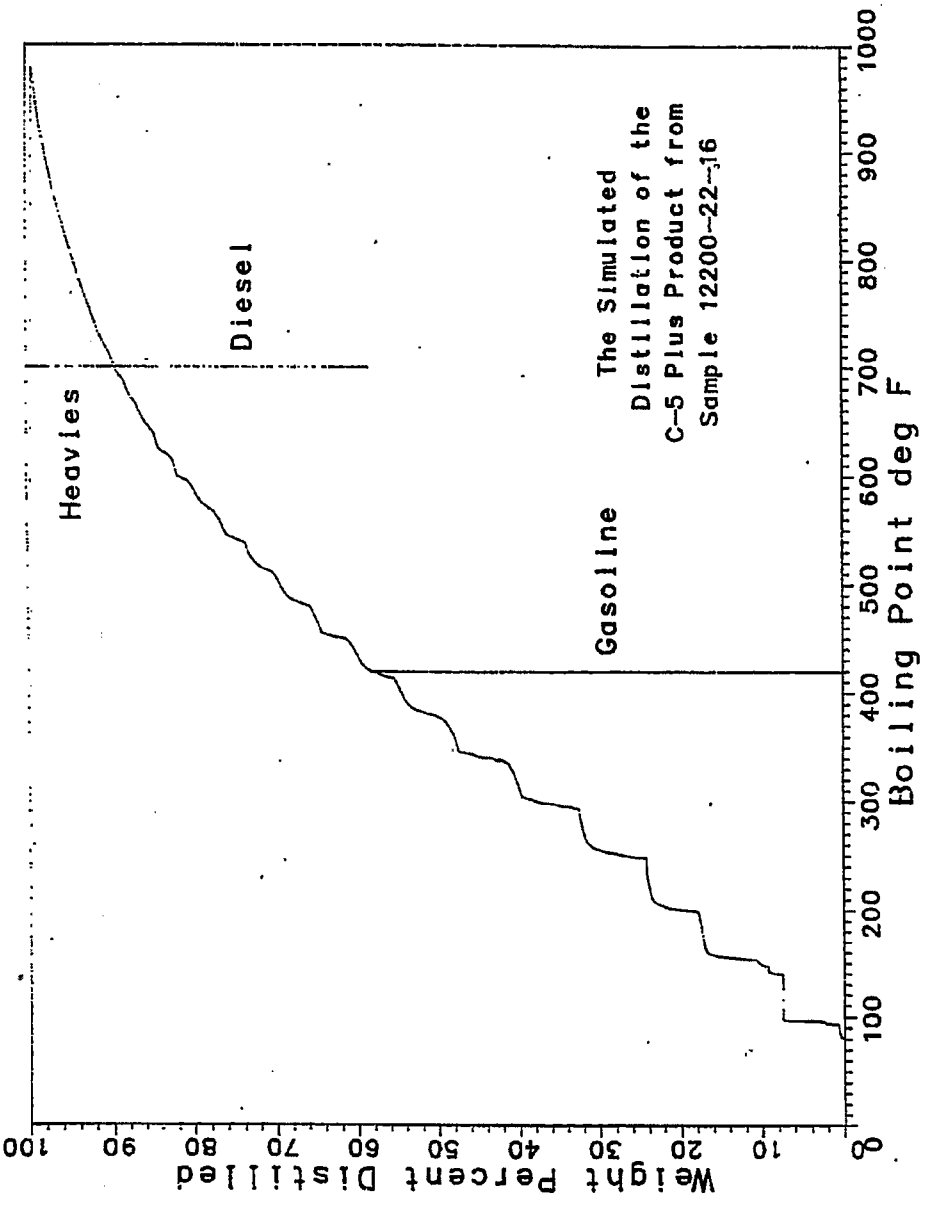

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12200-22-16
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B64

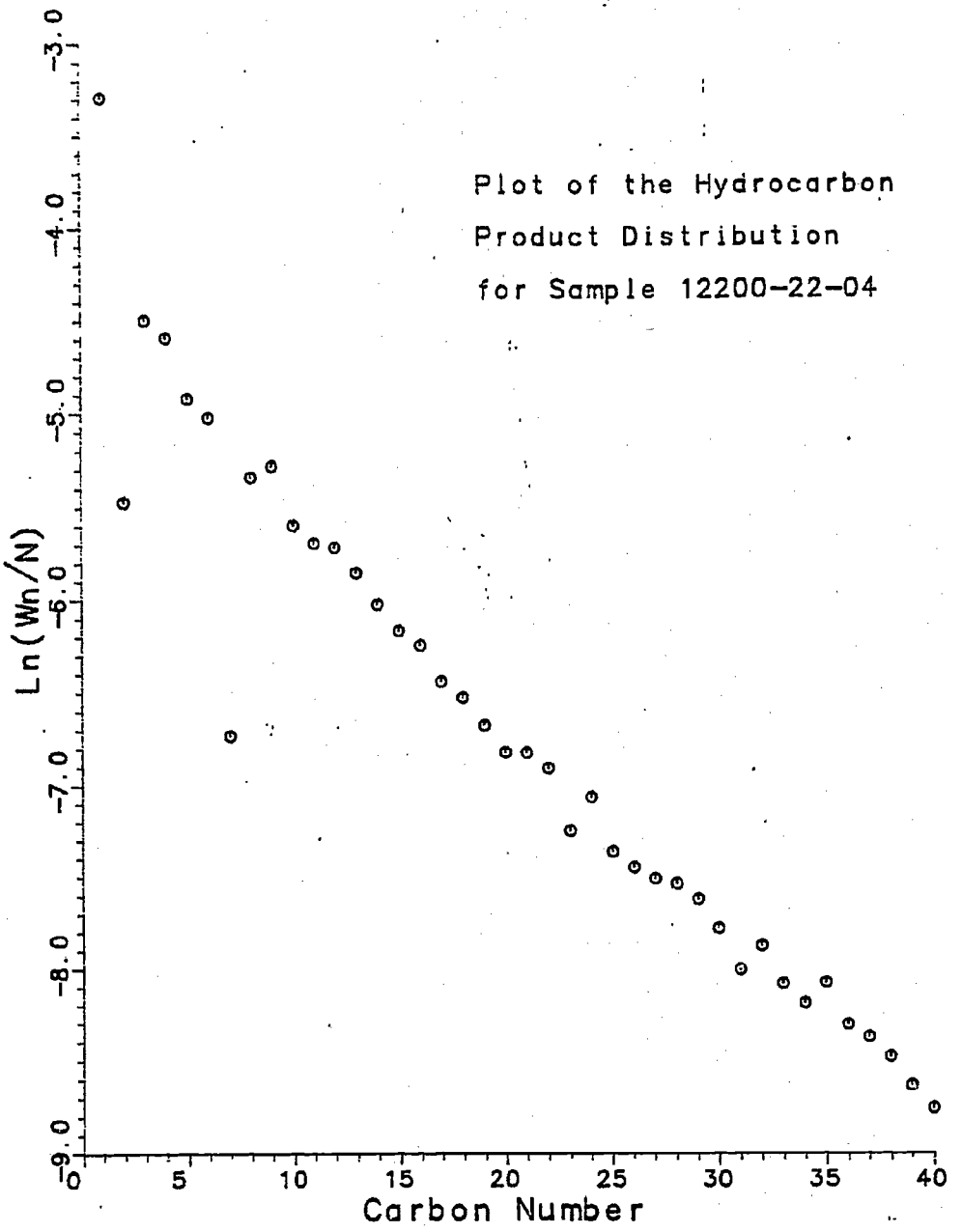

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-04
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B65

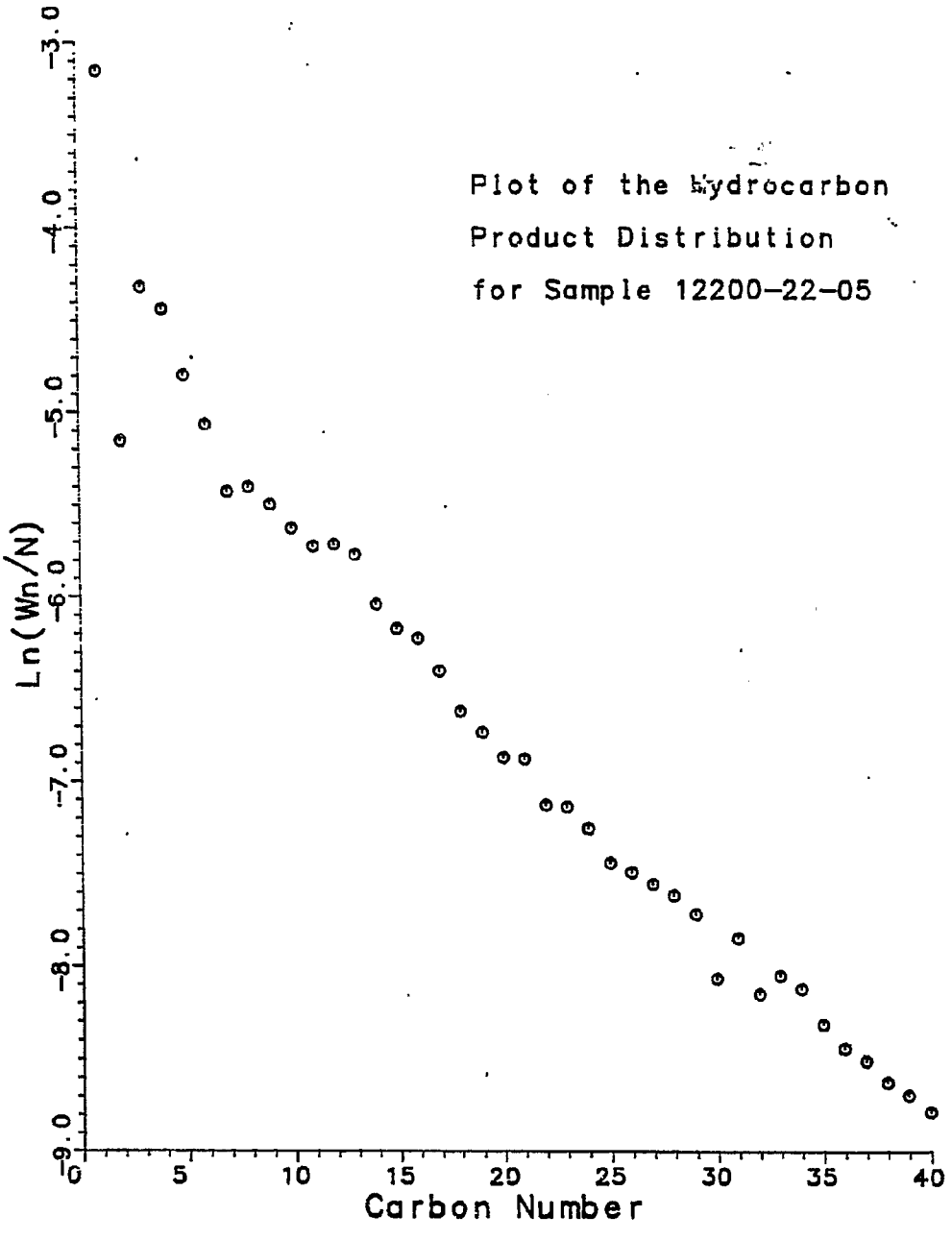

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-05
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B66

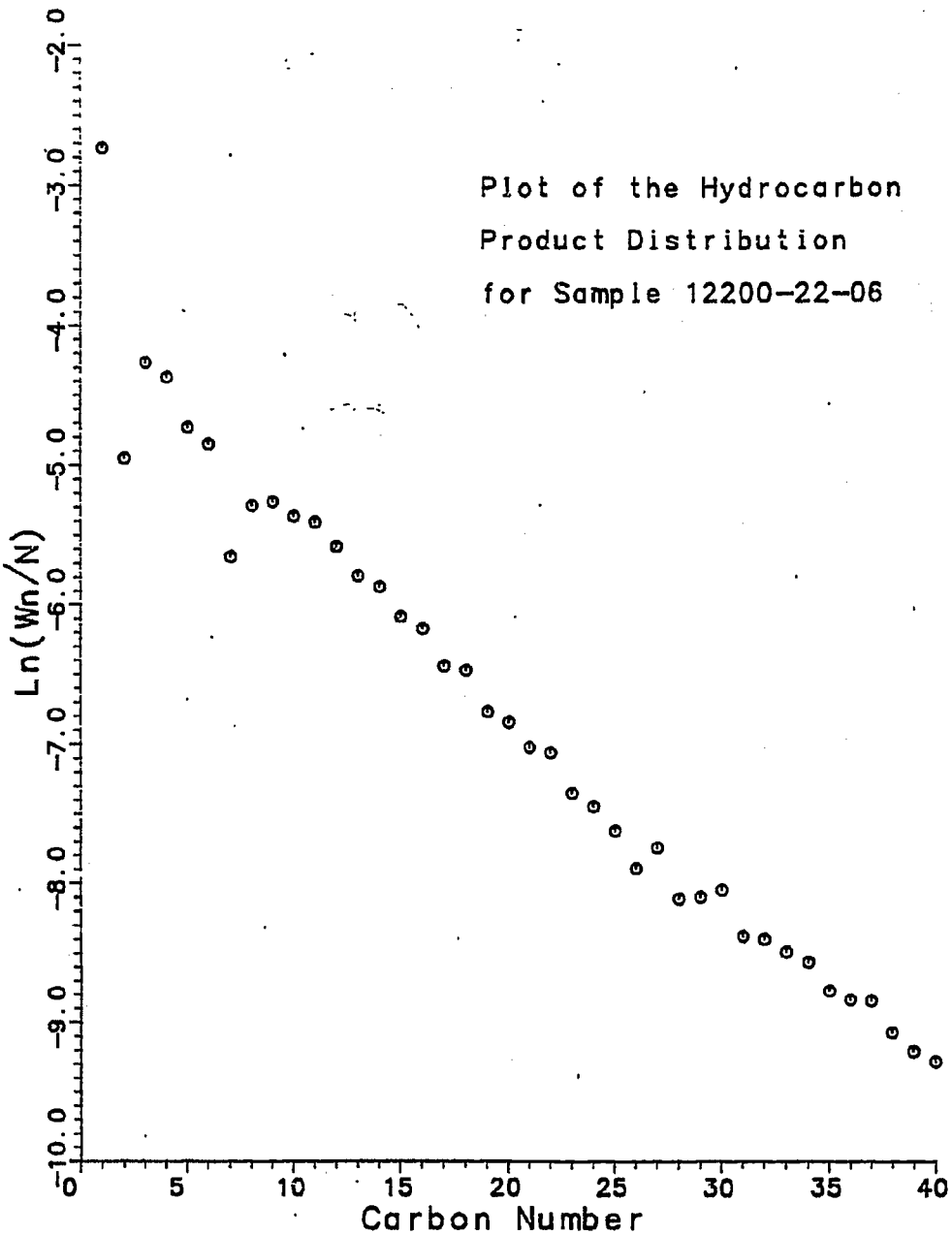

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B67

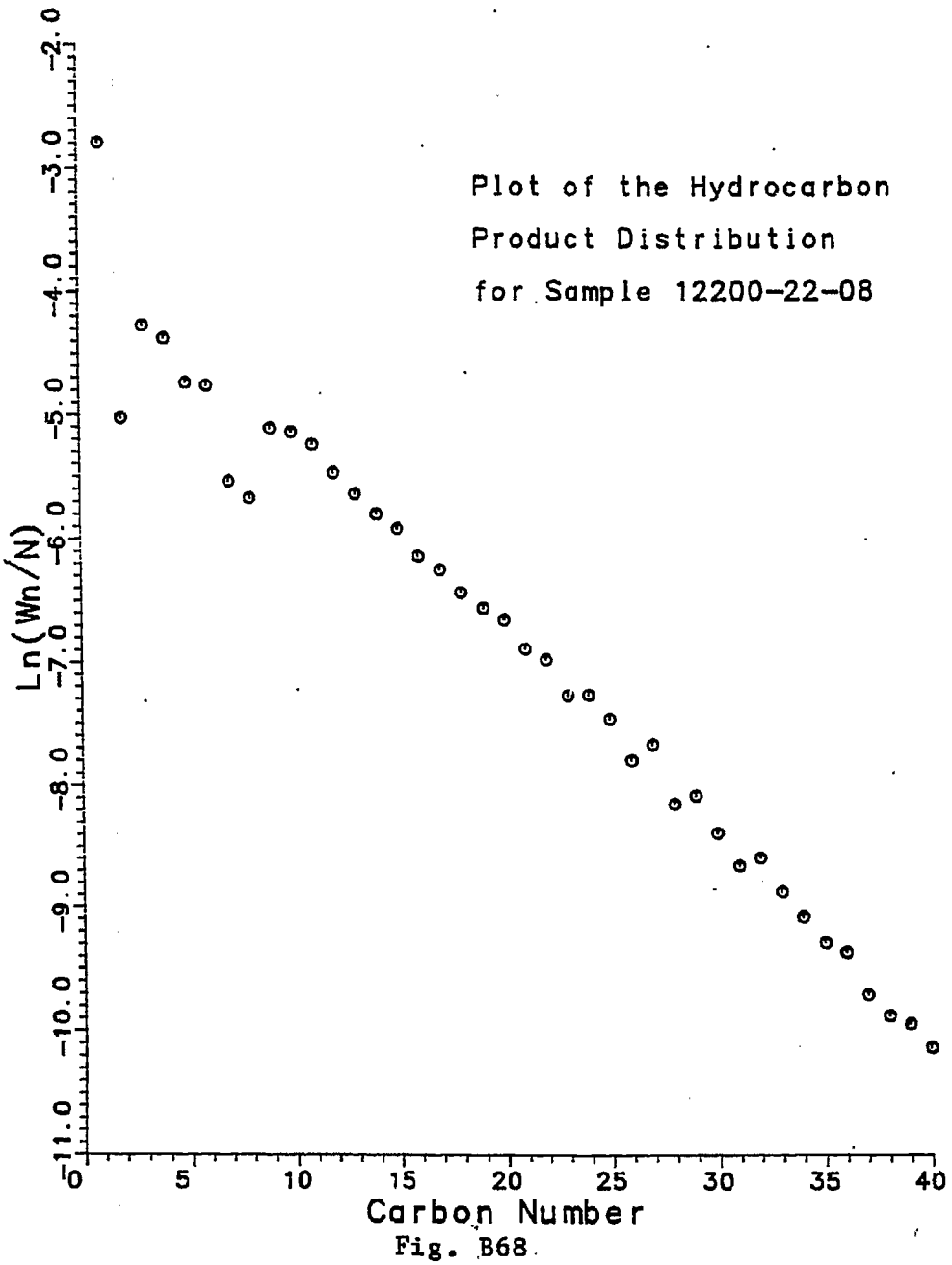

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-08
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B68

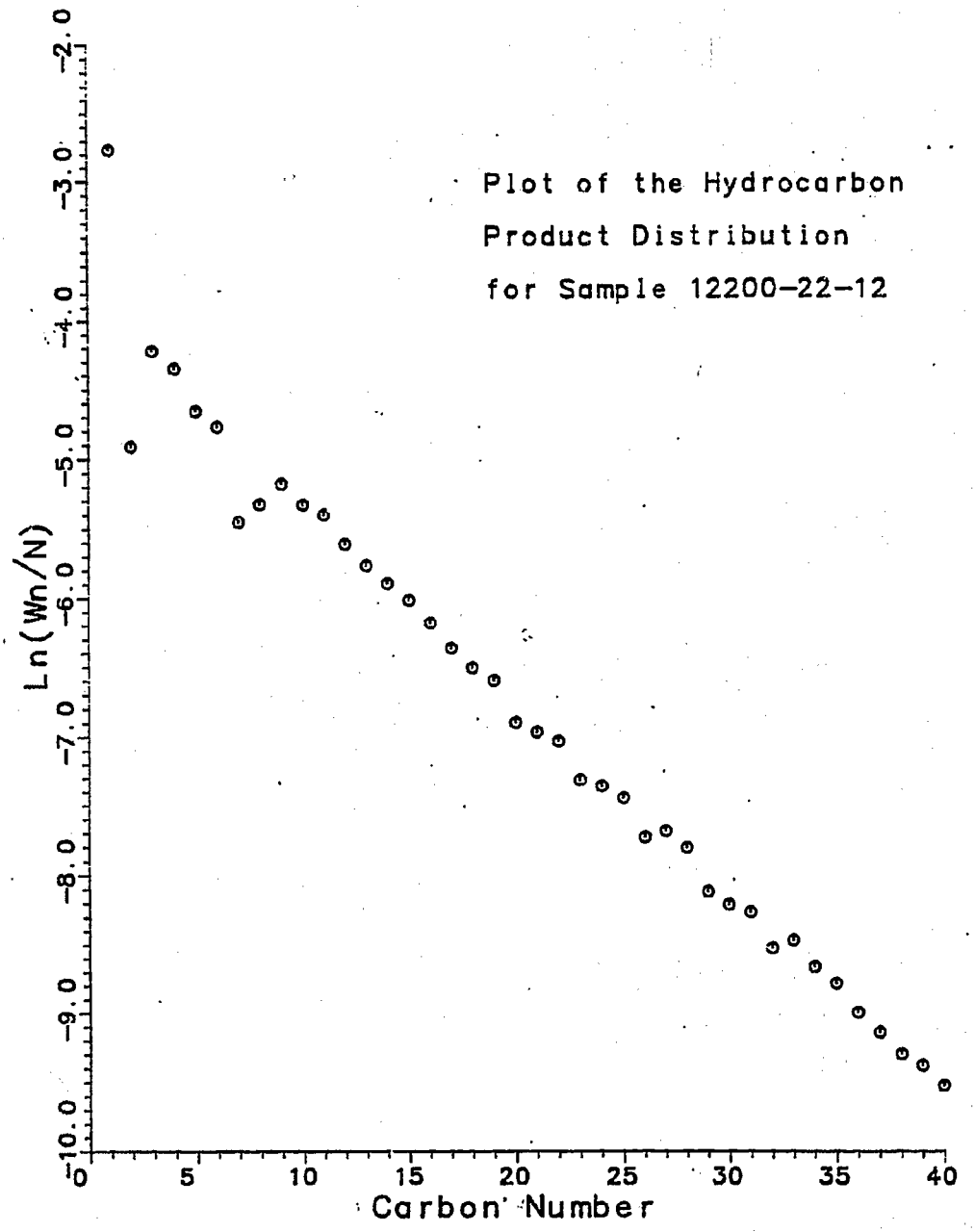

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-12
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B69

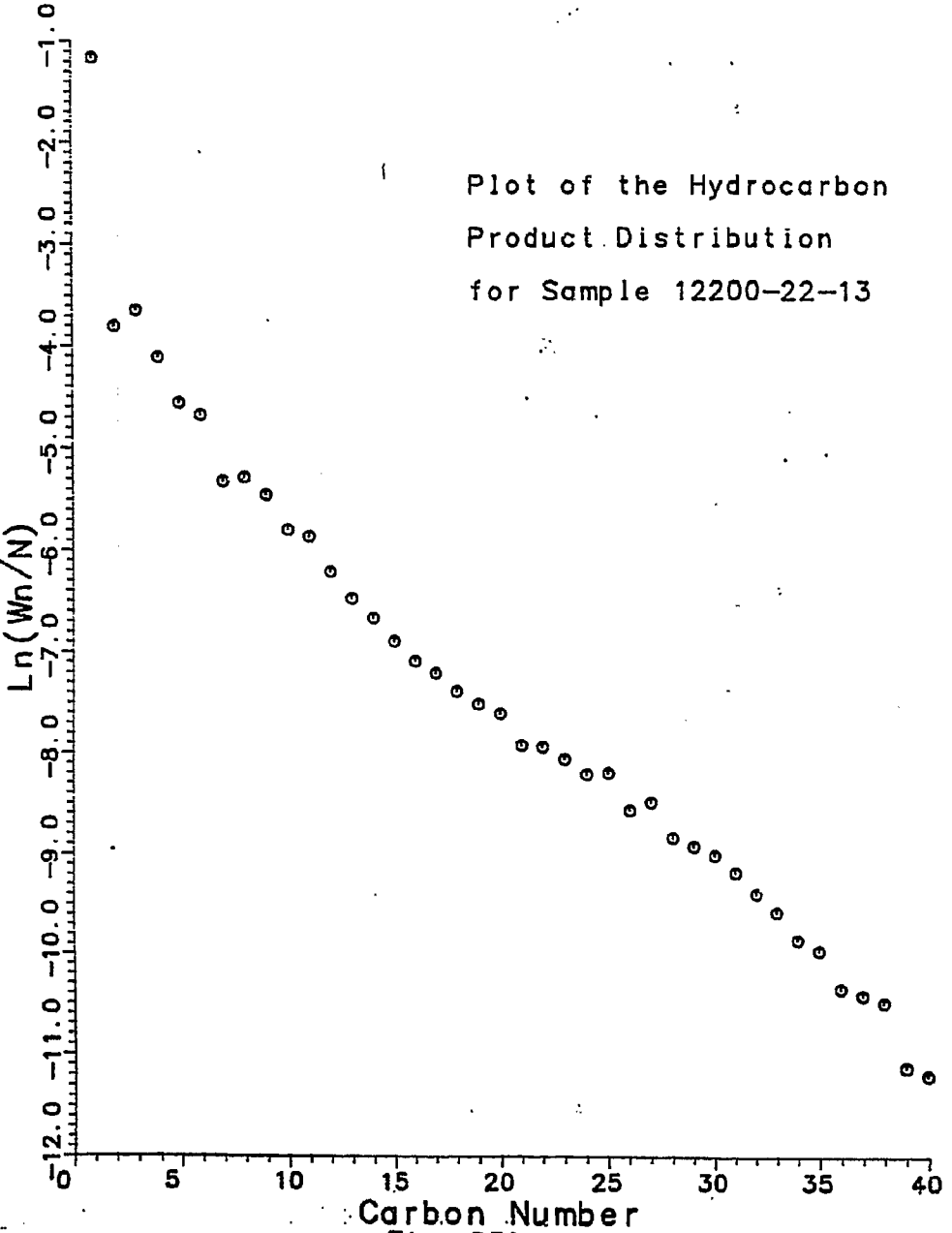

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-13
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B70

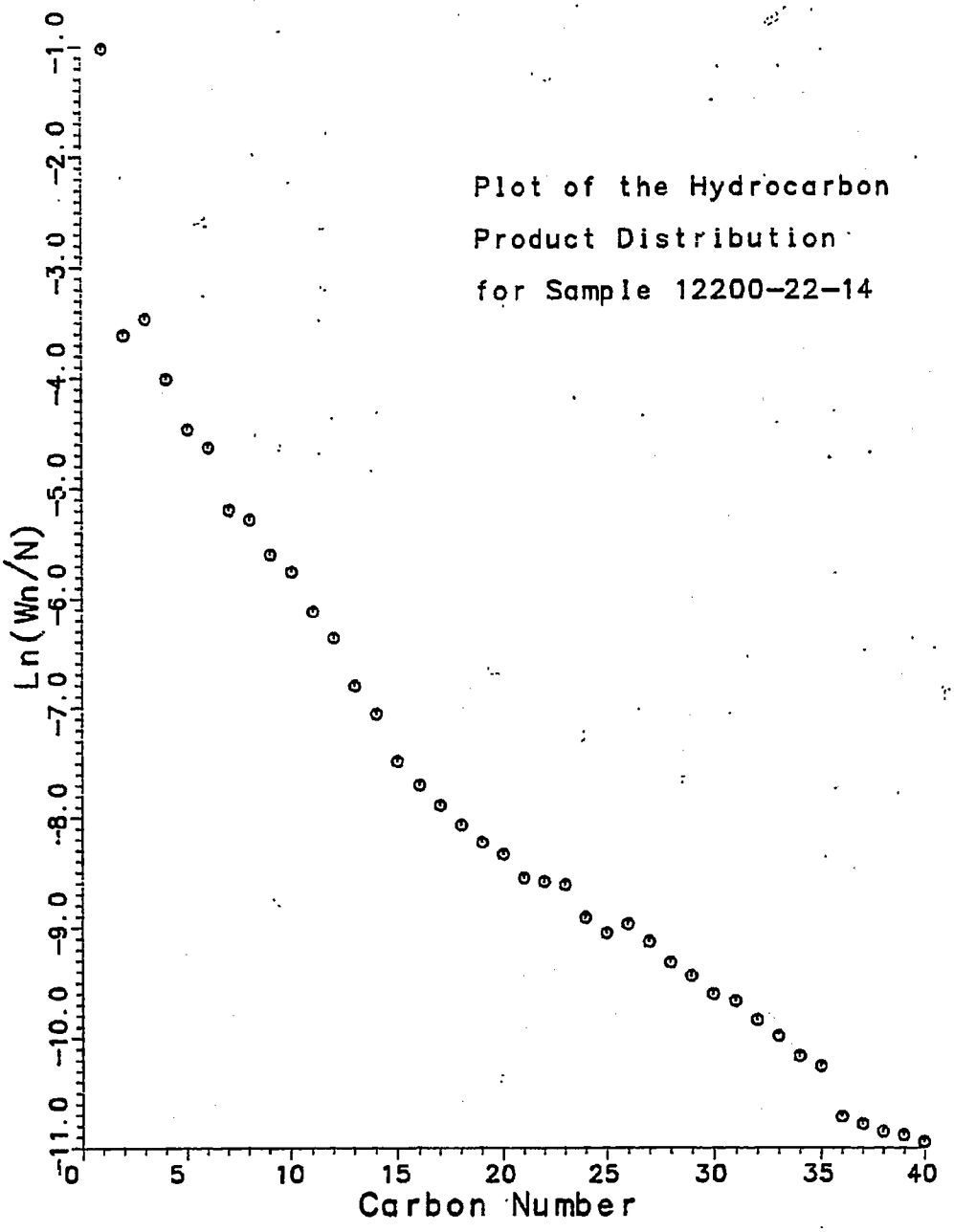

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-14
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B71

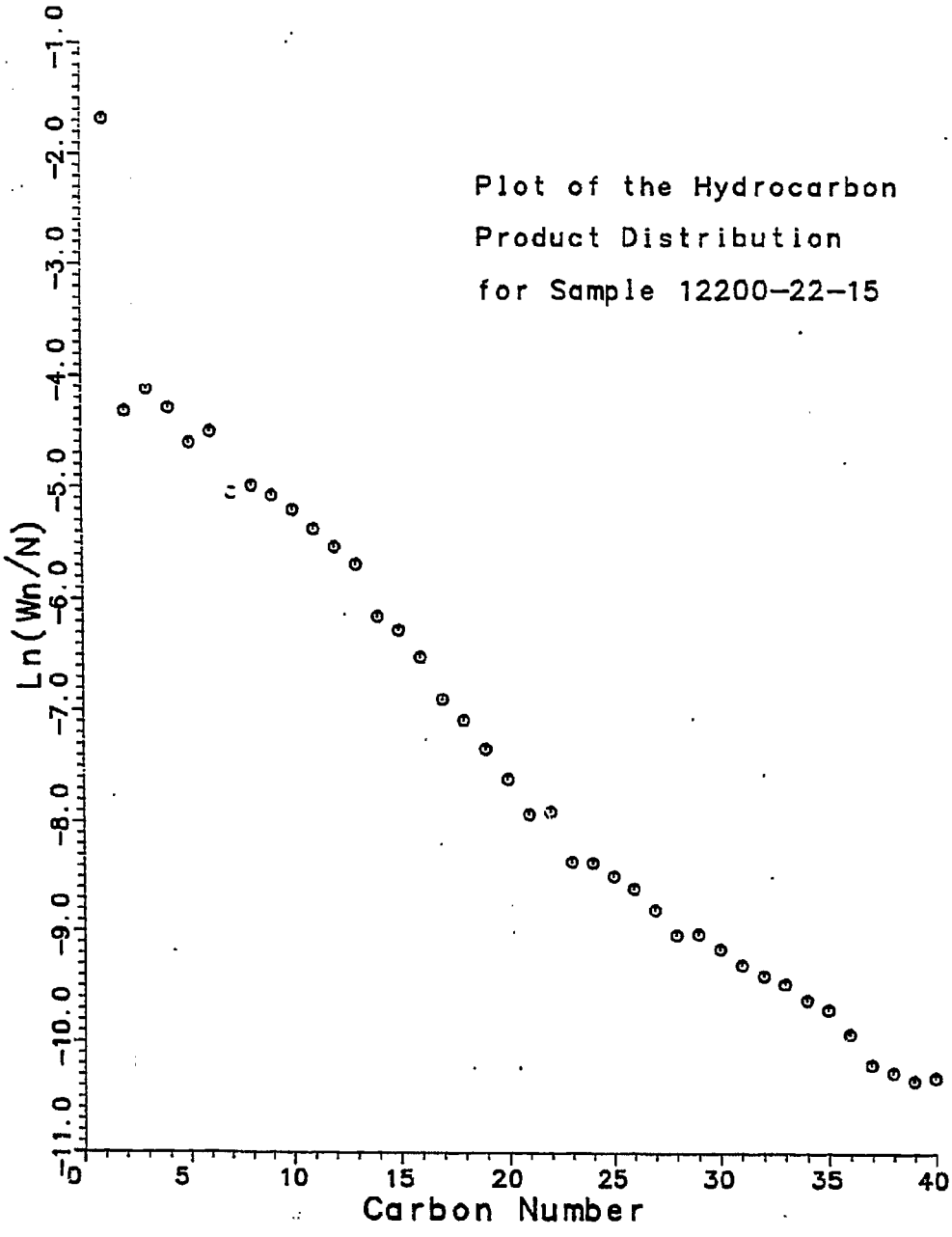

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-15
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B72

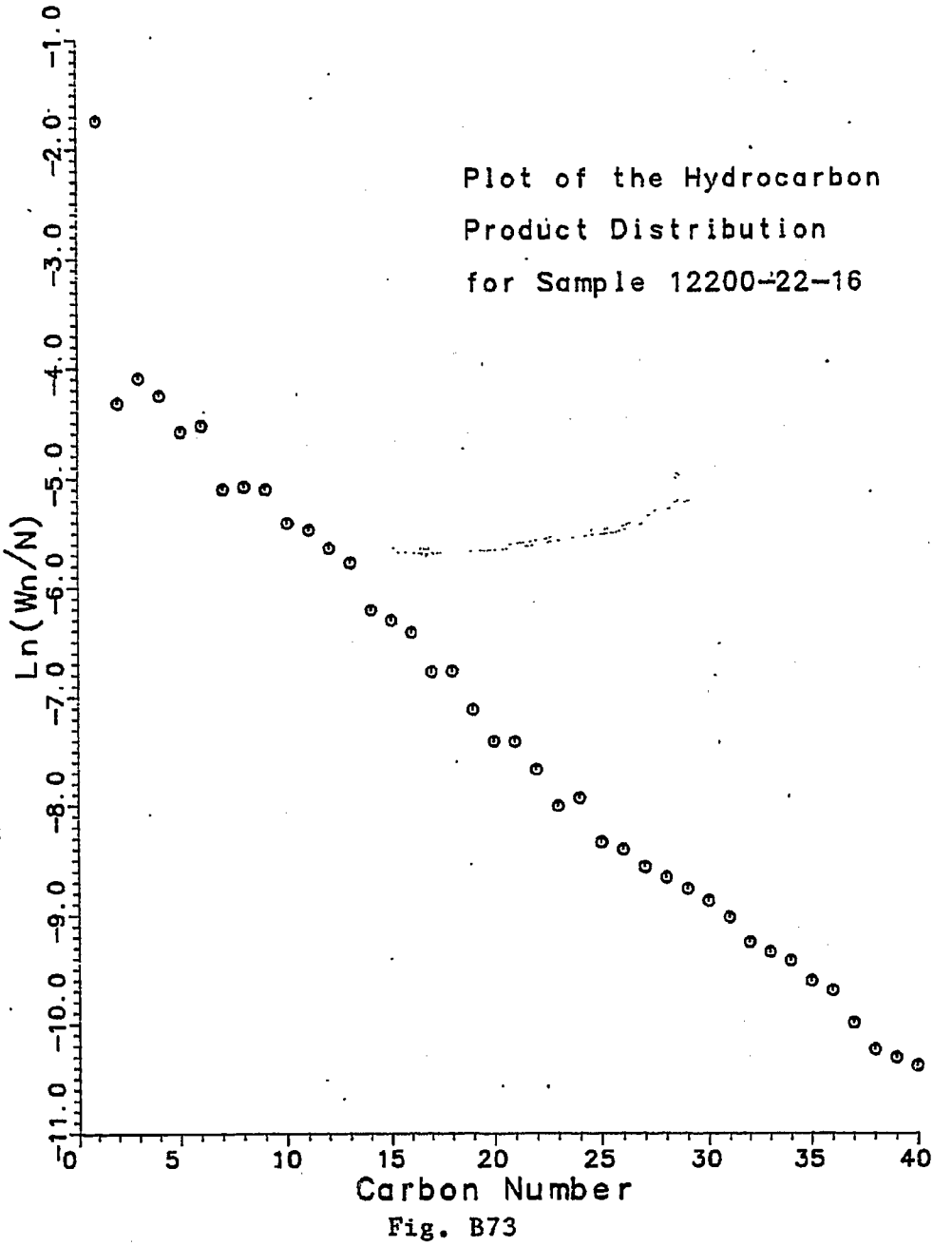

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-22-16
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B73

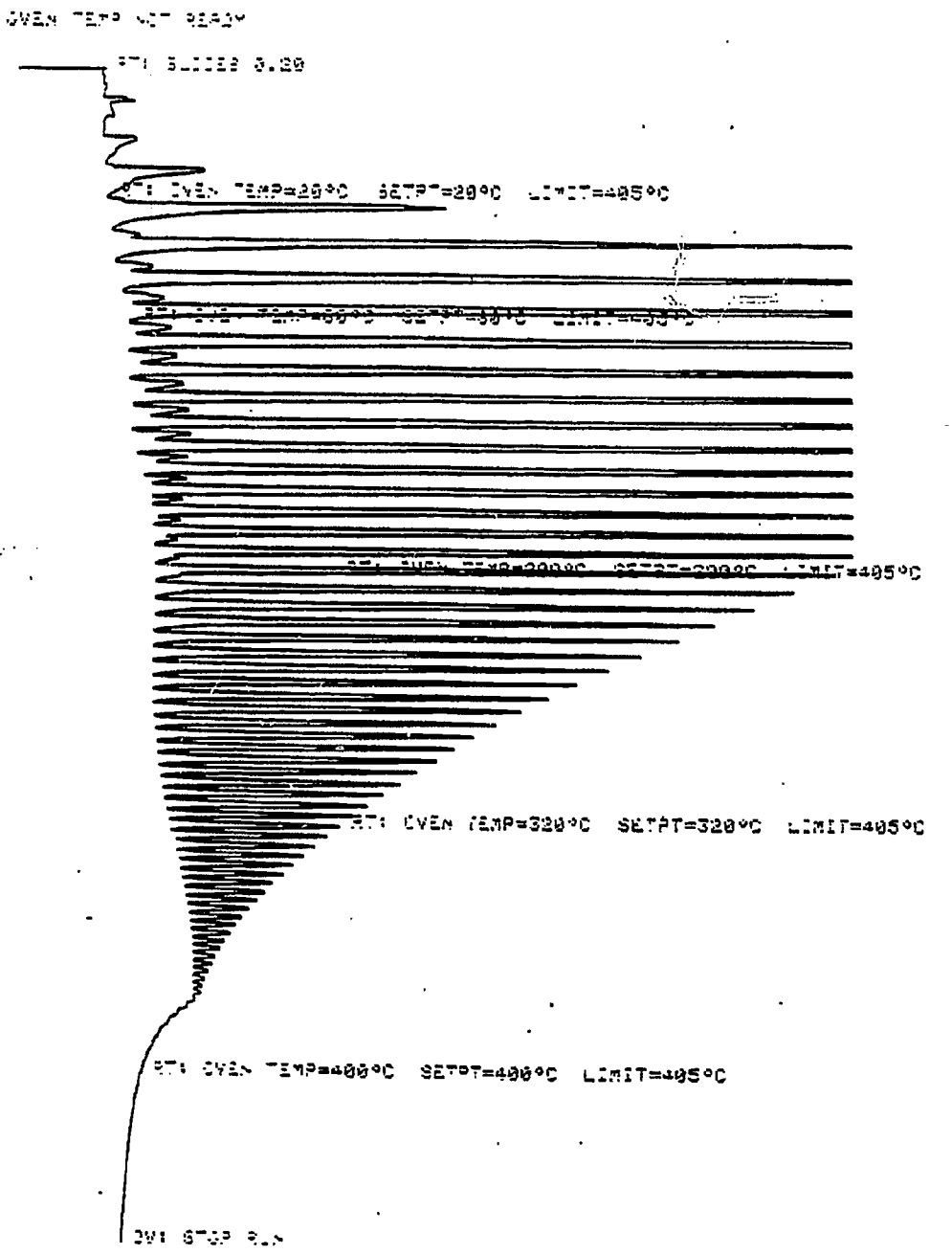

OVEN TEMP SET READY
PT: SLIDE 0.20
PT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
PT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
PT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
OVEN STOP RUN
TEMP_12:12200-22-04

Fig. B74

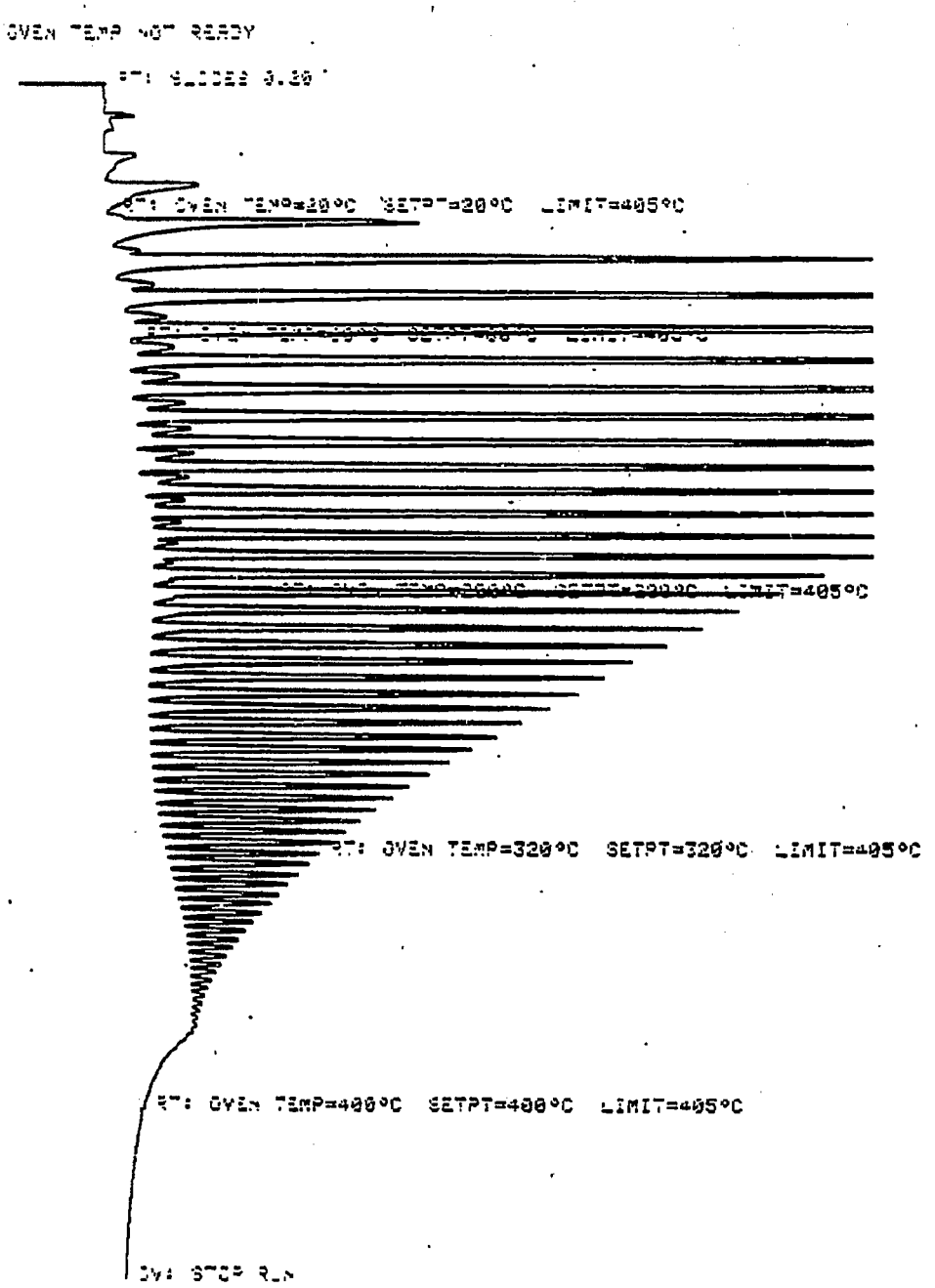
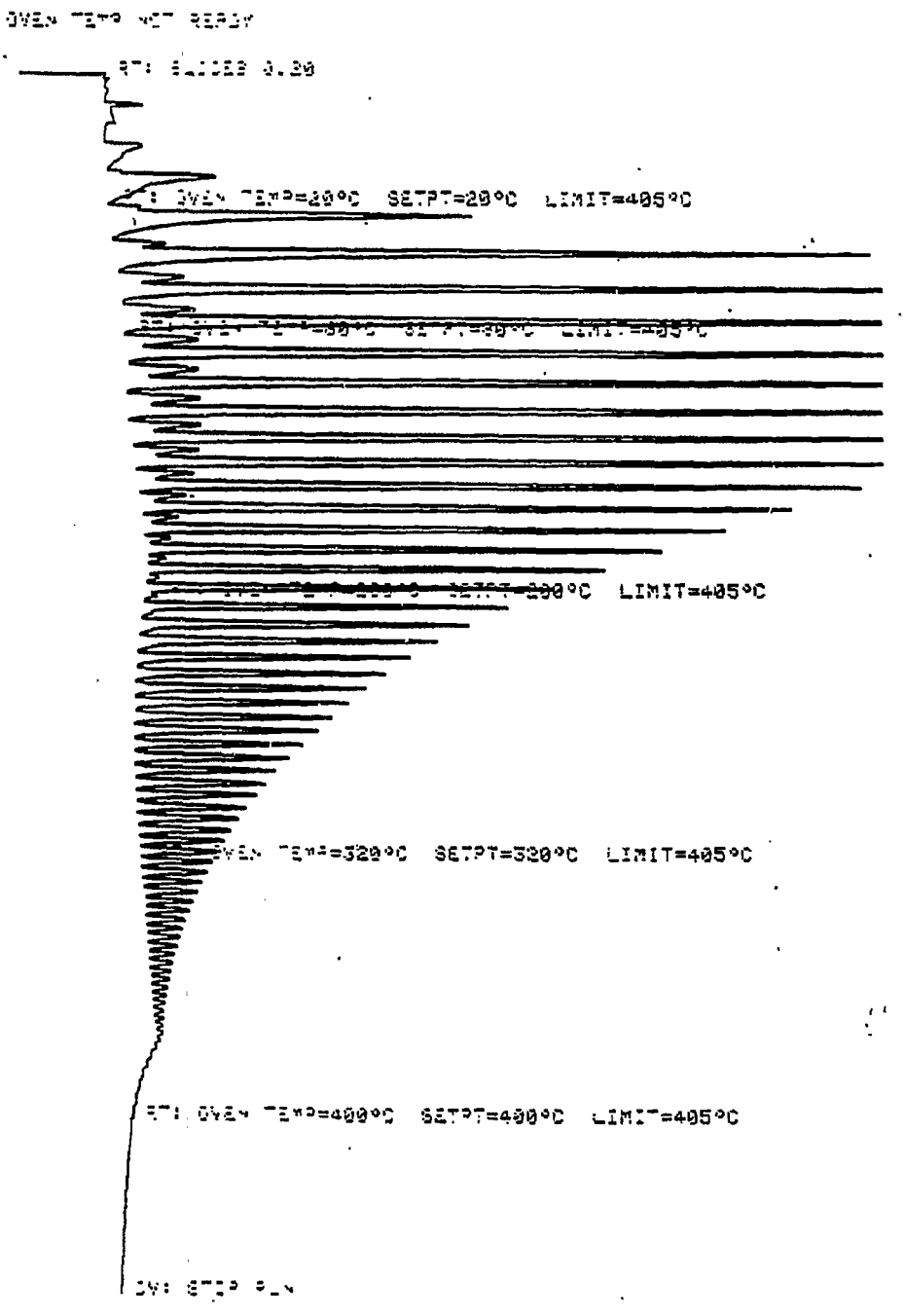
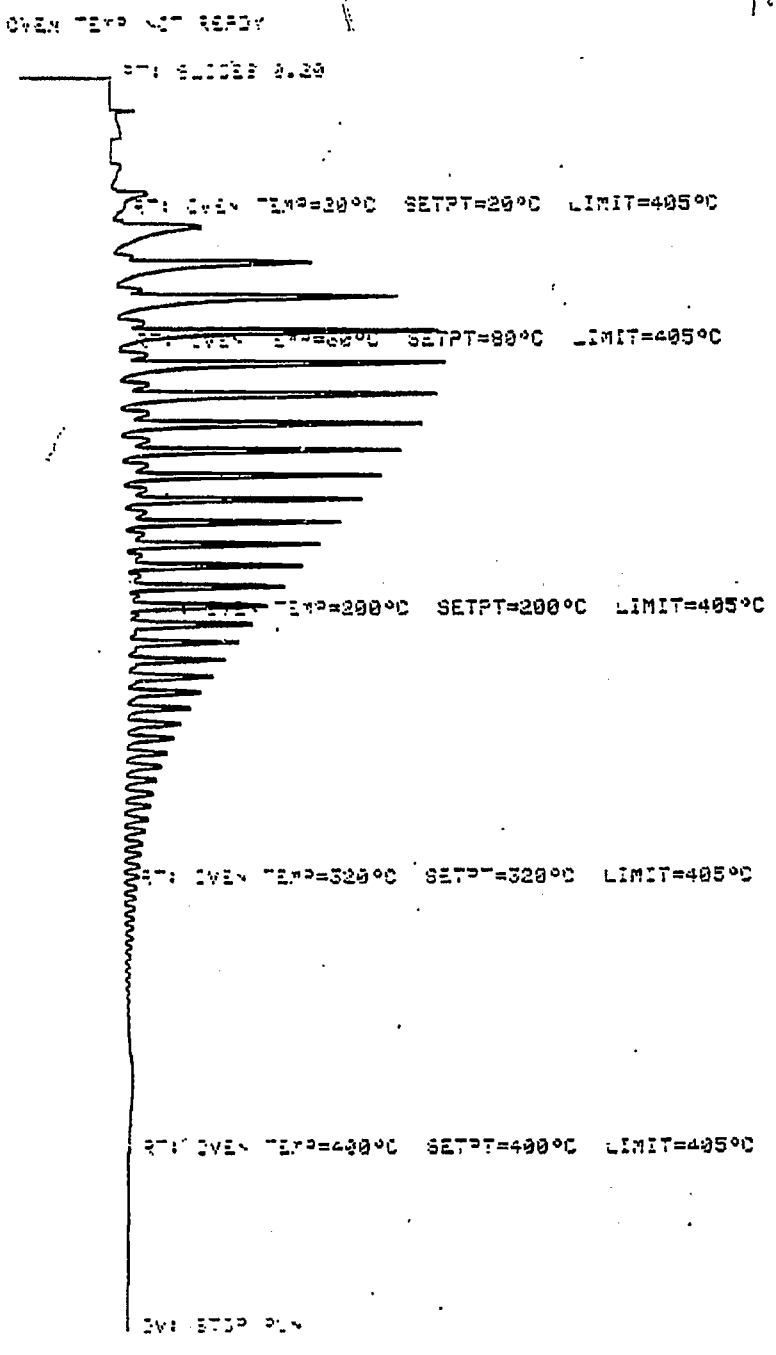

OVEN TEMP NOT READY
PT: CLOSED 0.20
PT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
PT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
PT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
DV: STOP RUN
SAMPLE:18220-22-05

Fig. B75



SAMPLE: 12200-22-06

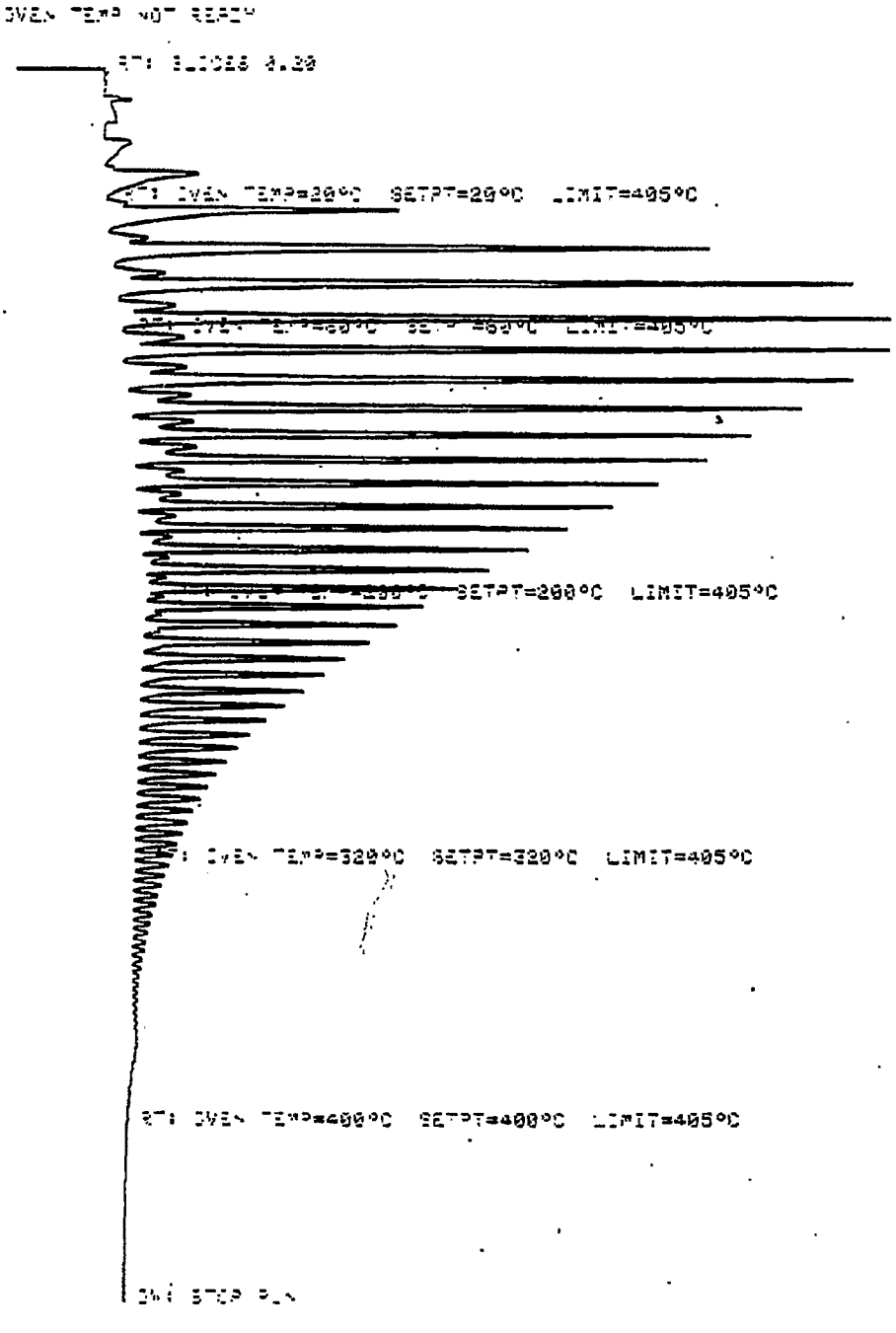
Fig. B76



SAMPLE: 12200-22-08

Fig. B77

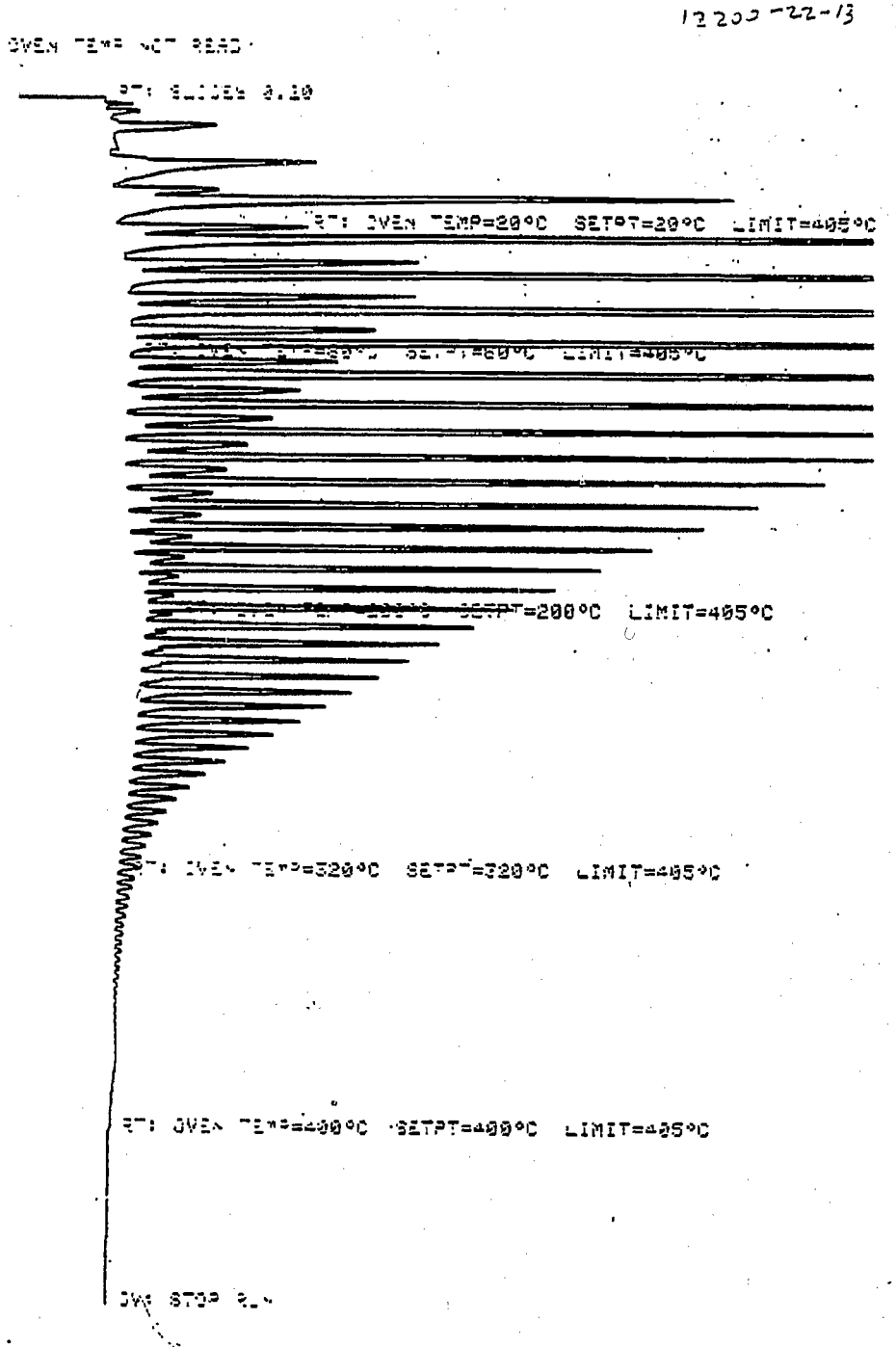
12200-22-12



SAMPLE: 12200-20-12

Fig. B78

12200-22-13



12200-22-13

Fig. B79

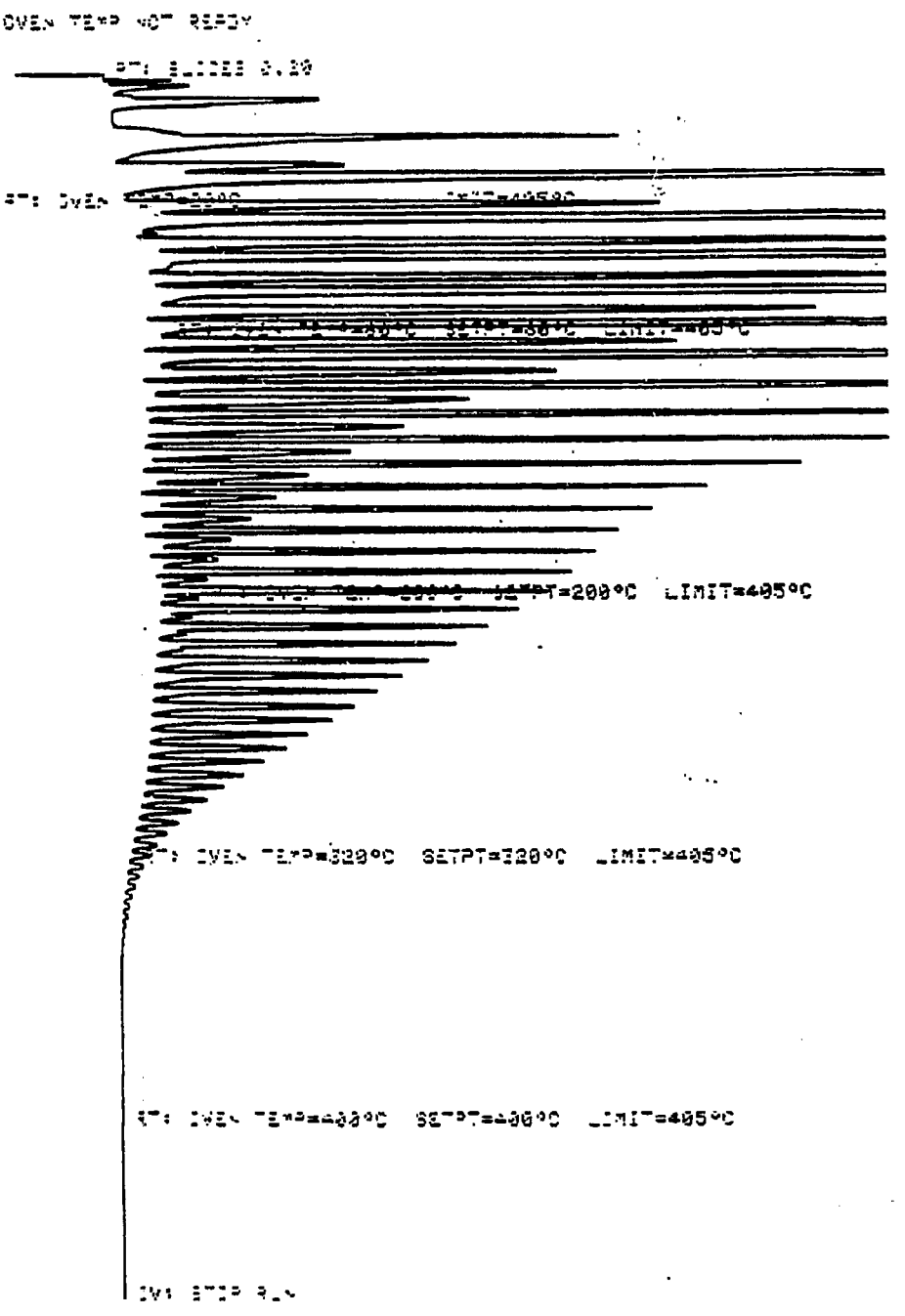


Fig. B80

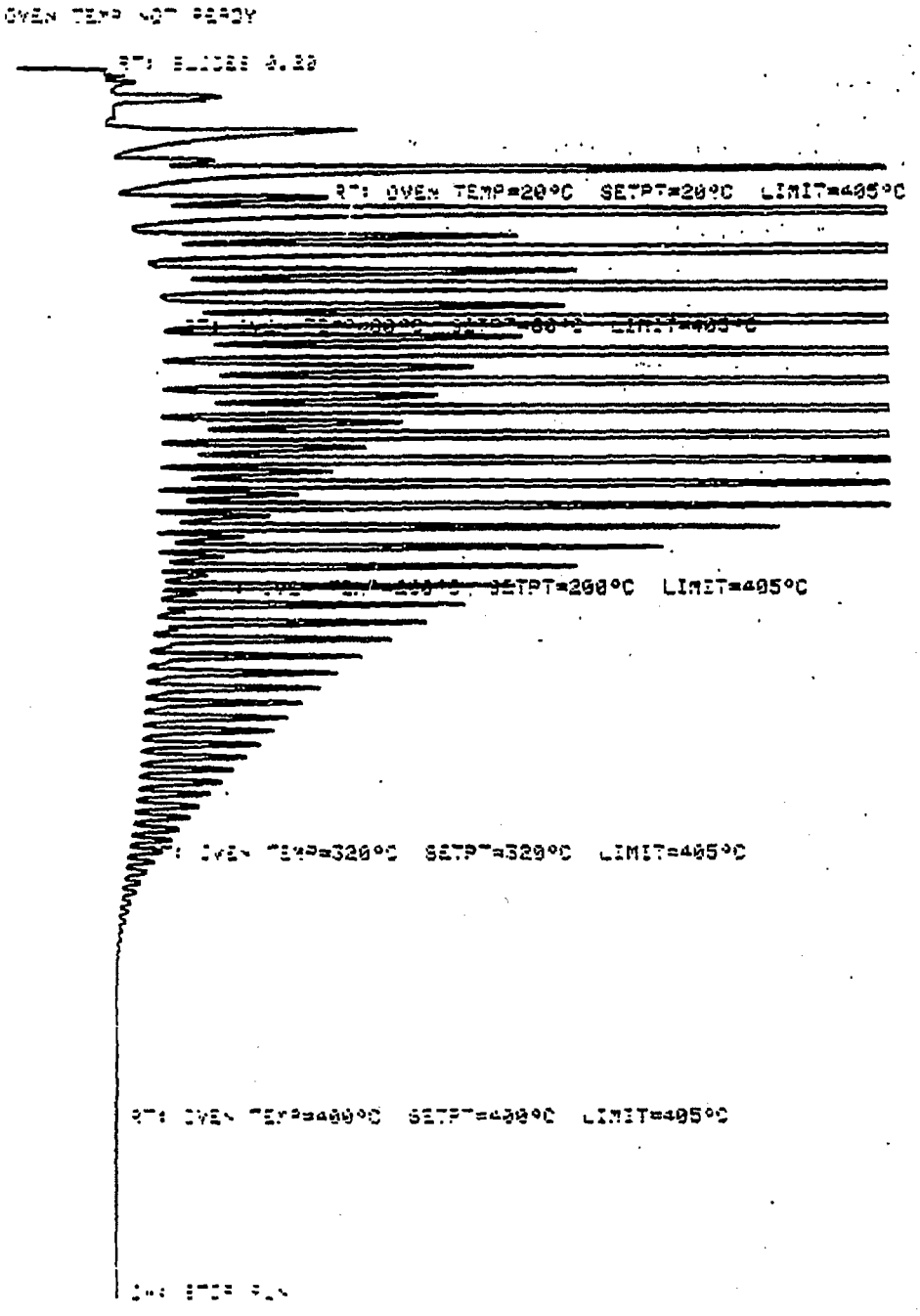

OVEN TEMP NOT READY
RT: OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
SETPT=200°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B81

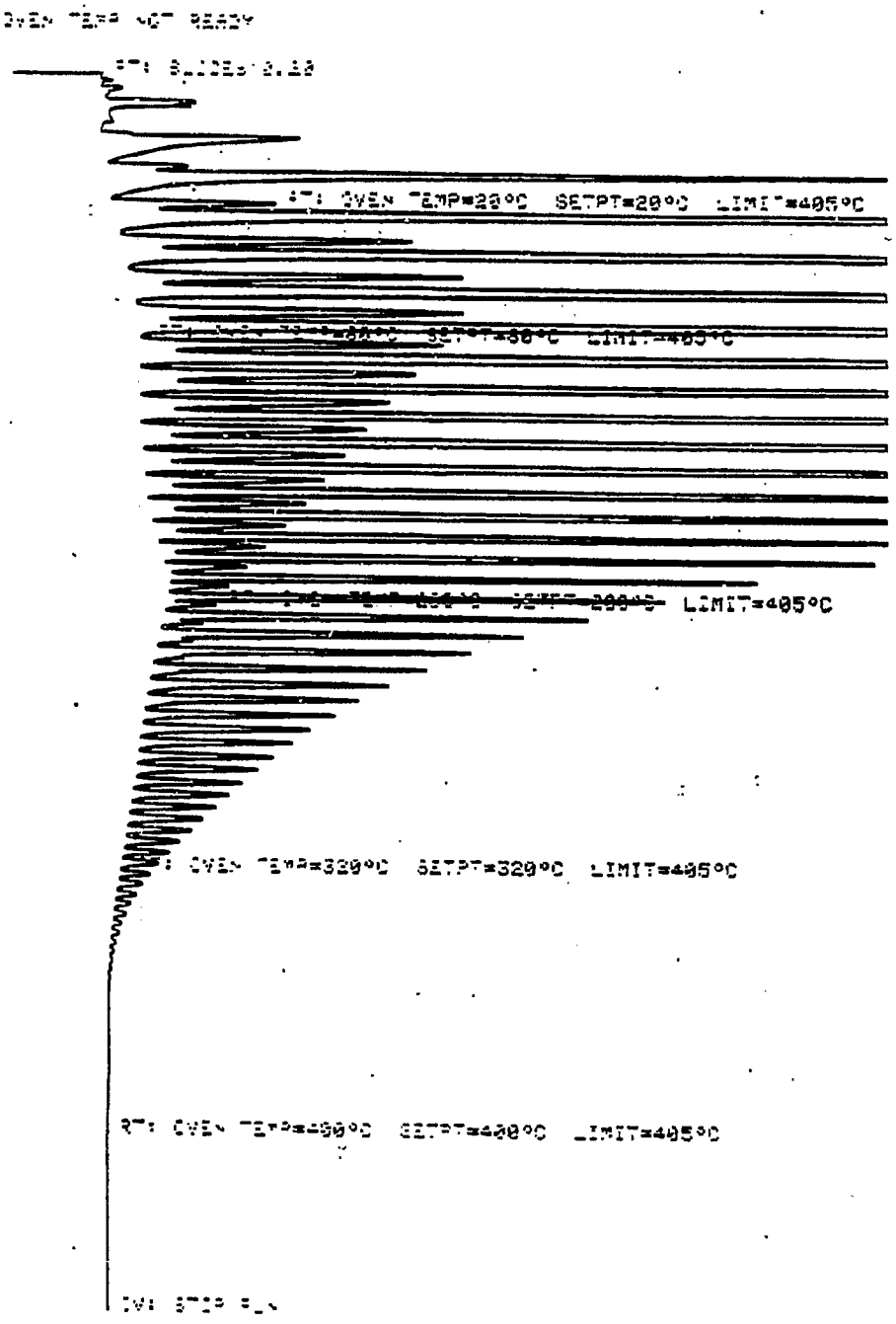

OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C

Fig. B82

Table B7

FILE: 1220022A TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-22
CATALYST CO/X11-U103 80 CC 33.1 G AFTER USE:49.2 G (+16.1 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-5)

RUN & SAMPLE NO.	12200-22-01	200-22-02	200-22-03	200-22-04	200-22-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	25.0	48.5	72.5	101.0	148.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	248	240	240	240	240
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	25.00	23.50	24.00	28.50	47.00
EFFLNT GAS LITER	194.50	284.70	301.85	366.07	641.08
GM AQUEOUS LAYER	71.61	48.40	47.37	54.26	91.91
GM OIL	19.66	42.50	45.78	45.42	65.70
MATERIAL BALANCE					
GM ATOM CARBON %	60.33	96.60	100.58	96.58	97.29
GM ATOM HYDROGEN %	70.92	94.21	96.99	93.23	94.17
GM ATOM OXYGEN %	79.46	90.11	91.15	90.65	94.56
RATIO CHX/(H2O+CO2)	0.4740	1.2429	1.3669	1.2397	1.1075
RATIO X IN CHX	2.2393	2.1776	2.1772	2.1866	2.1929
USAGE H2/CO PRODT	2.6144	1.7557	1.7021	1.7804	1.8769
FEED H2/CO FRM EFFLNT	1.1755	0.9752	0.9642	0.9654	0.9680
RESIDUAL H2/CO RATIO	0.4528	0.5341	0.5406	0.5613	0.5771
RATIO CO2/(H2O+CO2)	0.0806	0.0621	0.0597	0.0533	0.0471
K SHIFT IN EFFLNT	0.0397	0.0353	0.0343	0.0316	0.0285
SPECIFIC ACTIVITY SA	3.1689	4.6006	4.6112	3.8048	3.2358
CONVERSION					
ON CO %	33.43	36.11	36.47	33.14	30.07
ON H2 %	74.36	65.01	64.38	61.12	58.31
ON CO+H2 %	55.55	50.38	50.17	46.89	43.96
PRDT SELECTIVITY,WT %					
CH4	6.40	3.26	3.20	3.75	4.30
C2 HC'S	1.36	0.71	0.84	0.85	1.16
C3H8	1.47	0.73	0.75	0.90	1.09
C3H6=	2.67	2.04	2.12	2.47	2.93
C4H10	1.56	0.86	0.88	1.05	1.23
C4H8=	3.47	2.53	2.59	3.04	3.51
C5H12	1.84	1.05	1.06	1.22	1.40
C5H10=	2.72	2.07	2.14	2.45	2.74
C6H14	2.84	1.55	1.54	1.78	0.43
C6H12= & CYCLO'S	2.64	1.98	1.91	2.19	3.37
C7+ IN GAS	8.29	5.63	5.61	6.32	6.91
LIQ HC'S	64.75	77.60	77.36	73.98	70.94
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	16.91	10.13	10.38	12.06	14.21
C5 -420 F	46.37	27.79	27.73	28.02	29.27
420-700 F	32.89	31.04	30.95	28.38	27.76
700-END PT	3.82	31.04	30.95	31.55	28.76

Table B7 (continued)

FILE: 1220022A TSS4Q1 A1

C5+-END PT	83.09	89.87	89.62	87.94	85.79
ISO/NORMAL MOLE RATIO					
C4	0.0218	0.0000	0.0000	0.0000	0.0000
C5	0.0546	0.0470	0.0425	0.0396	0.0420
C6	0.3264	0.2610	0.2525	0.2536	0.0000
C4=	0.0530	0.0272	0.0262	0.0272	0.0280
PARAFFIN/OLEFIN RATIO					
C3	0.5244	0.3414	0.3402	0.3457	0.3546
C4	0.4327	0.3276	0.3292	0.3325	0.3396
C5	0.6593	0.4915	0.4804	0.4866	0.4957
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8561	0.8466	0.8321	0.8836	0.8795
RATIO CH4/(1-A)**2	3.0910	1.3835	1.1354	2.7659	2.9605
ALPHA FRM CORRELATION				0.8401	0.8387
ALPHA (EXPTL/CORR)				1.0518	1.0487
W%CH4 FRM CORRELATION				13.0561	13.4749
W%CH4 (EXPTL/CORR)				0.2871	0.3188
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F				345	344
16				389	386
50				646	624
84				949	935
90				1029	1015
RANGE(16-84 %)				560	549
WT % @ 420 F	43.30	20.00	20.00	19.00	20.33
WT % @ 700 F	94.10	60.00	60.00	57.36	59.46

Table B8

FILE: 1220022B TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-22
CATALYST CO/X11-U103 80 CC 33.1 G WATER USE:49.2 G (+16.1 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-5)

RUN & SAMPLE NO.	12200-22-06	200-22-07	200-22-08	200-22-09	200-22-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	167.5	191.5	215.5	239.5	263.5
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	256	257	256	258	258
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.50	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	231.90	278.70	283.05	280.15	281.20
GM AQUEOUS LAYER	43.47	53.75	56.55	58.88	57.05
GM OIL	31.97	40.64	38.73	37.68	36.87
MATERIAL BALANCE					
GM ATOM CARBON %	99.24	97.93	97.45	96.33	95.96
GM ATOM HYDROGEN %	93.89	94.49	94.66	95.23	93.72
GM ATOM OXYGEN %	95.71	93.56	95.45	95.79	95.08
RATIO CHX/(H2O+CO2)	1.1139	1.1414	1.0633	1.0166	1.0273
RATIO X IN CHX	2.2479	2.2411	2.2390	2.2471	2.2444
USAGE H2/CO PRODT	1.7037	1.6985	1.7821	1.8143	1.8120
FEED H2/CO FRM EFFLNT	0.9461	0.9649	0.9713	0.9885	0.9767
RESIDUAL H2/CO RATIO	0.4639	0.4756	0.4730	0.4750	0.4740
RATIO CO2/(H2O+CO2)	0.1310	0.1261	0.1062	0.1058	0.1036
K SHIFT IN EFFLNT	0.0699	0.0686	0.0562	0.0562	0.0548
SPECIFIC ACTIVITY SA	2.5421	2.4279	2.3870	2.1653	2.1193
CONVERSION					
ON CO %	38.89	40.01	38.07	38.34	37.57
ON H2 %	70.04	70.43	69.85	70.37	69.71
ON CO+H2 %	54.04	54.95	53.73	54.27	53.45
PRDT SELECTIVITY,WT %					
CH4	6.53	6.17	6.14	6.53	6.39
C2 HC'S	1.42	1.49	1.32	1.48	1.38
C3H8	1.58	1.49	1.48	1.54	1.57
C3H6=	2.64	2.55	2.72	2.73	2.80
C4H10	1.61	1.52	1.53	1.60	1.62
C4H8=	3.45	3.37	3.50	3.58	3.57
C5H12	1.87	1.81	1.81	1.91	1.91
C5H10=	2.54	2.49	2.57	2.58	2.72
C6H14	2.83	2.84	2.73	2.97	2.98
C6H12= & CYCLO'S	1.89	2.09	2.10	1.95	1.93
C7+ IN GAS	6.31	6.07	6.21	6.55	6.59
LIQ HC'S	67.34	68.11	67.90	66.57	66.55
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	17.23	16.60	16.68	17.47	17.32
C5 -420 F	34.42	49.35	37.69	49.25	49.41
420-700 F	28.48	27.24	31.85	26.63	26.62
700-END PT	19.86	6.81	13.78	6.66	6.66

Table B8 (continued)

FILE: 1220022B TSS4Q1 A1

C5+-END PT	82.77	83.40	83.32	82.53	82.68
ISO/NORMAL MOLE RATIO					
C4	0.0169	0.0168	0.0171	0.0161	0.0174
C5	0.0624	0.0647	0.0611	0.0595	0.0527
C6	0.3890	0.4354	0.3996	0.4143	0.4163
C4=	0.0560	0.0551	0.0540	0.0571	0.0550
PARAFFIN/OLEFIN RATIO					
C3	0.5712	0.5573	0.5184	0.5386	0.5354
C4	0.4493	0.4355	0.4231	0.4303	0.4376
C5	0.7145	0.7072	0.6868	0.7185	0.6827
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8613	0.8322	0.8623	0.8171	0.8136
RATIO CH4/(1-A)**2	3.3918	2.1918	3.2389	1.9542	1.8372
ALPHA FRM CORRELATION	0.8484		0.8475		
ALPHA (EXPTL/CORR)	1.0151		1.0175		
W%CH4 FRM CORRELATION	13.9839		14.2772		
W%CH4 (EXPTL/CORR)	0.4668		0.4299		
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	309		304		
16	348		343		
50	548		514		
84	853		736		
90	945		798		
RANGE(16-84 %)	505		393		
WT % @ 420 F	28.20	50.00	32.80	50.00	50.00
WT % @ 700 F	70.50	90.00	79.70	90.00	90.00

Table B9.

FILE: 1220022C TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-22
CATALYST CO/X11-U103 80 CC 33.1 G AFTER USE:49.2 G (+16.1 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-5)

RUN & SAMPLE NO.	12200-22-11	200-22-12	200-22-13	200-22-14	200-22-15
FEED H2:CO:AR	50:50: 0	50:50: 0	66:33: 0	66:33: 0	60:40: 0
HRS ON STREAM	287.5	311.5	335.5	359.5	383.5
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	257	257	259	258	258
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	24.00	22.50	24.00	22.50
EFFLNT GAS LITER	290.50	293.20	156.90	154.80	184.75
GM AQUEOUS LAYER	56.25	55.58	74.22	76.56	76.29
GM OIL	37.35	36.98	35.05	23.29	29.41
MATERIAL BALANCE					
GM ATOM CARBON %	97.53	98.44	119.04	104.07	87.68
GM ATOM HYDROGEN %	95.18	95.45	103.94	94.66	90.96
GM ATOM OXYGEN %	95.90	96.17	102.01	97.97	97.18
RATIO CHX/(H2O+CO2)	1.0522	1.0735	1.2275	1.0829	0.8271
RATIO X IN CHX	2.2406	2.2428	2.7814	2.8967	2.5036
USAGE H2/CO PRODT	1.8179	1.8064	1.6922	1.7453	2.0770
FEED H2/CO FRM EFFLNT	0.9759	0.9696	1.7490	1.8220	1.5562
RESIDUAL H2/CO RATIO	0.4879	0.4858	2.3925	3.0243	0.8283
RATIO CO2/(H2O+CO2)	0.0944	0.0943	0.2340	0.2471	0.1032
K SHIFT IN EFFLNT	0.0509	0.0506	0.7307	0.9926	0.0953
SPECIFIC ACTIVITY SA	2.0878	2.0645	2.1748	2.2070	1.7389
CONVERSION					
ON CO %	36.69	36.63	91.89	94.00	58.29
ON H2 %	68.35	68.25	88.91	90.05	77.80
ON CO+H2 %	52.33	52.20	89.99	91.45	70.17
PRDT SELECTIVITY,WT %					
CH4	6.23	6.32	31.26	36.40	18.71
C2 HC'S	1.38	1.48	4.47	5.43	2.67
C3H8	1.55	1.54	7.54	9.03	3.74
C3H6=	2.84	2.88	0.36	0.38	1.16
C4H10	1.57	1.64	5.68	6.33	3.49
C4H8=	3.60	3.53	0.89	0.99	2.02
C5H12	1.86	1.88	4.80	5.16	3.87
C5H10=	2.67	2.88	0.45	0.51	1.16
C6H14	2.69	2.93	4.51	5.13	5.16
C6H12= & CYCLO'S	1.81	2.16	0.44	0.30	1.00
C7+ IN GAS	6.54	6.80	4.80	5.53	6.92
LIQ HC'S	67.26	65.96	34.80	24.81	50.10
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	17.16	17.39	50.19	58.55	31.78
C5 -420 F	49.21	35.98	30.77	30.58	42.42
420-700 F	26.90	29.35	12.77	7.32	20.04
700-END PT	6.73	17.28	6.26	3.55	5.76

Table B9 (continued)

FILE: 1220022C TSS4Q1 A1

C5+-END PT	82.84	82.61	49.81	41.45	68.22
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0170	0.0676	0.0705	0.0332
C5	0.0507	0.0602	0.1531	0.1717	0.1027
C6	0.4459	0.4471	0.3413	0.3843	0.3231
C4=	0.0532	0.0561	0.3281	0.3751	0.1491
PARAFFIN/OLEFIN RATIO					
C3	0.5201	0.5095	20.1335	22.7590	3.0769
C4	0.4204	0.4491	6.1915	6.1909	1.6642
C5	0.6757	0.6338	10.3663	9.7532	3.2406
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7897	0.8644	0.8234	0.7947	0.8116
RATIO CH4/(1-A)**2	1.4097	3.4343	10.0198	8.6368	5.2719
ALPHA FRM CORRELATION		0.8461	0.7683	0.7570	0.8201
ALPHA (EXPTL/CORR)		1.0216	1.0716	1.0498	0.9897
W%CH4 FRM CORRELATION		14.9137	39.4675	42.7805	23.2060
W%CH4 (EXPTL/CORR)		0.4235	0.7921	0.8509	0.8061
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F		304	253	237	257
16		345	288	257	298
50		541	452	389	423
84		797	720	676	640
90		873	785	761	727
RANGE(16-84 %)		452	432	419	342
WT % @ 420 F	50.00	29.30	45.30	56.20	48.50
WT % @ 700 F	90.00	73.80	82.00	85.70	88.50

Table B10

FILE: 1220022D TSS4Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-22
CATALYST CO/X11-U103 80 CC 33.1 G AFTER USE:49.2 G (+16.1 G)
FEED H2:CO OF 60:40 @ 400 CC/MN OR 300 GHSV (CAT#12424-5)

RUN & SAMPLE NO.	12200-22-16
FEED H2:CO:AR	60:40: 0
HRS ON STREAM	407.5
PRESSURE,PSIG	300
TEMP. C	258
FEED CC/MIN	400
HOURS FEEDING	24.00
EFFLNT GAS LITER	220.00
GM AQUEOUS LAYER	70.71
GM OIL	34.22
MATERIAL BALANCE	
GM ATOM CARBON %	97.35
GM ATOM HYDROGEN %	92.01
GM ATOM OXYGEN %	97.84
RATIO CHX/(H2O+CO2)	0.9902
RATIO X IN CHX	2.4847
USAGE H2/CO PRODT	1.8717
FEED H2/CO FRM EFFLNT	1.4177
RESIDUAL H2/CO RATIO	0.8084
RATIO CO2/(H2O+CO2)	0.1312
K SHIFT IN EFFLNT	0.1221
SPECIFIC ACTIVITY SA	1.7690
CONVERSION	
ON CO %	57.30
ON H2 %	75.65
ON CO+H2 %	68.06
PRDT SELECTIVITY,WT %	
CH4	17.73
C2 HC'S	2.67
C3H8	3.72
C3H6=	1.32
C4H10	3.48
C4H8=	2.25
C5H12	3.86
C5H10=	1.29
C6H14	4.99
C6H12= & CYCLO'S	1.12
C7+ IN GAS	7.08
LIQ HC'S	50.48
TOTAL	100.00
SUB-GROUPING	
C1 -C4	31.18
C5 -420 F	39.80
420-700 F	21.71
700-END PT	7.32

Table B10 (continued)

FILE: 1220022D TSS4Q1 A1

C5+-END PT	68.82
ISO/NORMAL MOLE RATIO	
C4	0.0276
C5	0.0890
C6	0.3179
C4=	0.1306
PARAFFIN/OLEFIN RATIO	
C3	2.6881
C4	1.4902
C5	2.9028
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8264
RATIO CH4/(1-A)**2	5.8804
ALPHA FRM CORRELATION	0.8213
ALPHA (EXPTL/CORR)	1.0062
W%CH4 FRM CORRELATION	22.8392
W%CH4 (EXPTL/CORR)	0.7763
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL WAX
DENSITY	
N, REFRACTIVE INDEX	
SIMULT'D DISTILATN	
10 WT % @ DEG F	259
16	300
50	454
84	686
90	762
RANGE(16-84 %)	386
WT % @ 420 F	42.50
WT % @ 700 F	85.50

VII. Run 39 (11617-04) with Catalyst 39 ($Co/X_{11}/X_{12}/TC-103$)

This catalyst is a variation on Catalyst 32 with the addition of a new promoter, X_{12}. The object of the run was to investigate whether the presence of X_{12} will improve the catalyst's activity while maintaining the superior selectivity and stability of Catalyst 32.

Aside from the addition of X_{12}, and the same pretreatment as with Catalyst 37, the composition and preparation were similar to those of Catalyst 32. The theoretical concentrations of cobalt, X_{11} and X_{12} were 7.6, 1.4 and 5.0 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B83-86. Simulated distillations of the C_5^+ product are plotted in Figs. B87-96. Carbon number product distributions are plotted in Figs. B97-106. Chromatograms from simulated distillations are reproduced in Figs. B107-115. Detailed material balances appear in Tables B11-13.

To provide a fair measure of stability, the run was conducted for more than 200 hours at each of two temperatures, 240C and 260C. At 240C the initial conversion was more than 50 percent, substantially higher than the 45 percent obtained with Catalyst 32. Stability over this period was excellent, with a gain of activity, as estimated by linear least squares analysis, of one

percentage point every 100 hours. Due to the large quantities of wax produced, however, there was a large scatter in the data.

The selectivity at 240C was comparable to, or better than, that of Catalyst 32. The methane production fluctuated around 4 percent, and production of C_5^+ was more than 85 percent; the corresponding levels for Catalyst 32 were 5 percent and about 85 percent. Some part of the improvement in selectivity can perhaps be attributed to the reduced residual H_2:CO ratio in the reactor due to the catalyst's higher activity; however, such parameters as the weight percent methane (experimental/correlation, as described in previous reports) show a real reduction in methane make. This formulation has produced the highest activity to date for the TC-103 catalysts of its type.

At 260C the catalyst was also more active than Catalyst 32, with 60 percent syngas conversion as against 56 percent. The stability, however, was poorer than at 240C, with conversion deactivating at an estimated rate of one percentage point every 40 hours. The selectivity at 260C was approximately the same as that of Catalyst 32, with initial methane production of about 8 percent and up to about 11 percent after some 220 hours on stream.

The Schulz-Flory plots at both 240C and 260C were linear, again except for the usual high methane. The olefin content of the light gas fraction was lower than for Catalyst 32; the olefin:paraffin ratio of the C_4 fraction was about 1.5 at 260C, as against about 1.75 for Catalyst 32.

This run has demonstrated several potentially valuable functions of X_{12} in enhancing the performance of X_{11}-promoted catalysts, among them improved activity, lower methane production, higher production of C_5^+, and better stability at 240C. At 260C, however, X_{11} appears from this test to impair the stability of these catalysts.

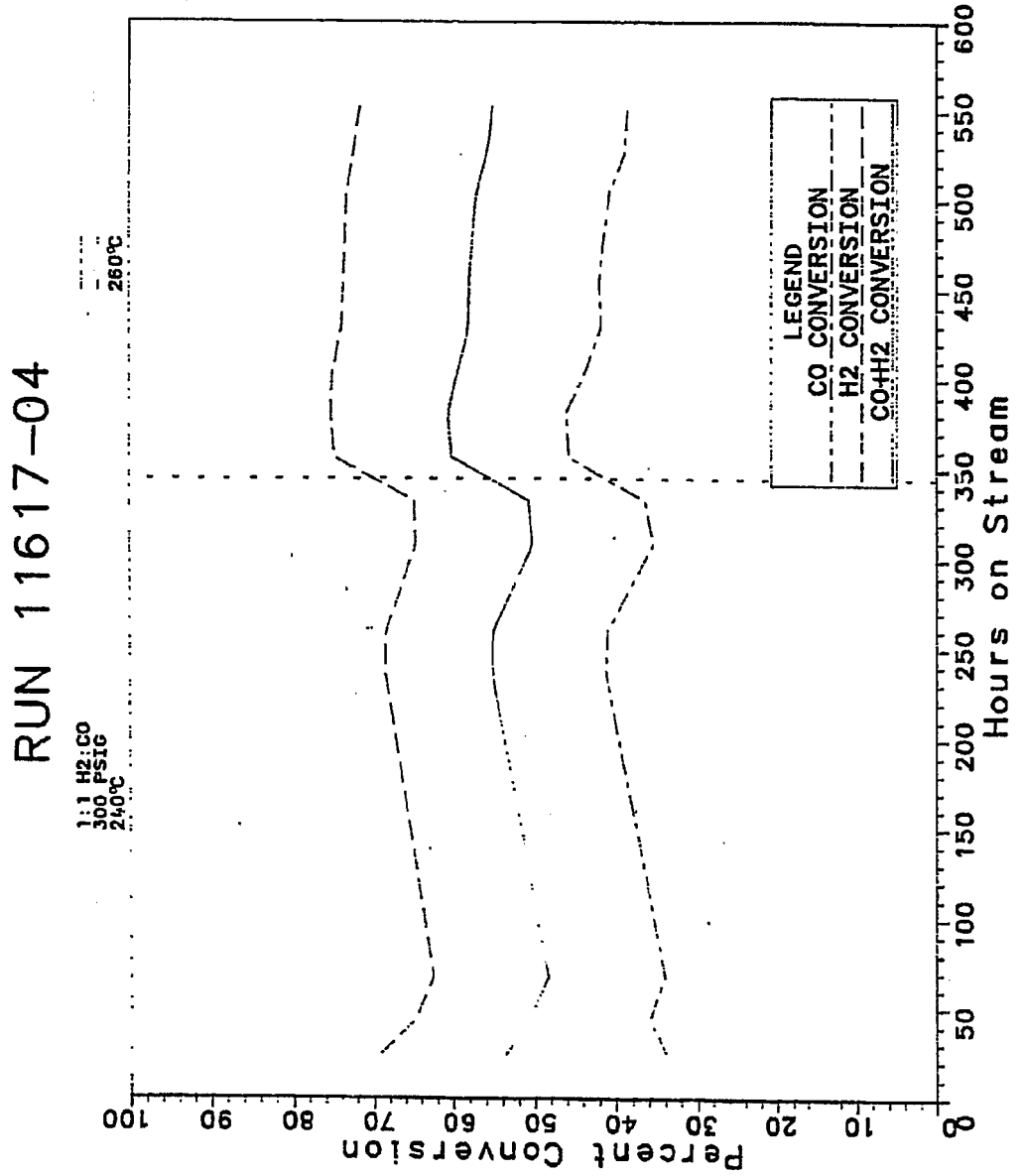

RUN 11617-04
1:1 H2:CO
300 PSIG
240°C
260°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550
600

Fig. B83

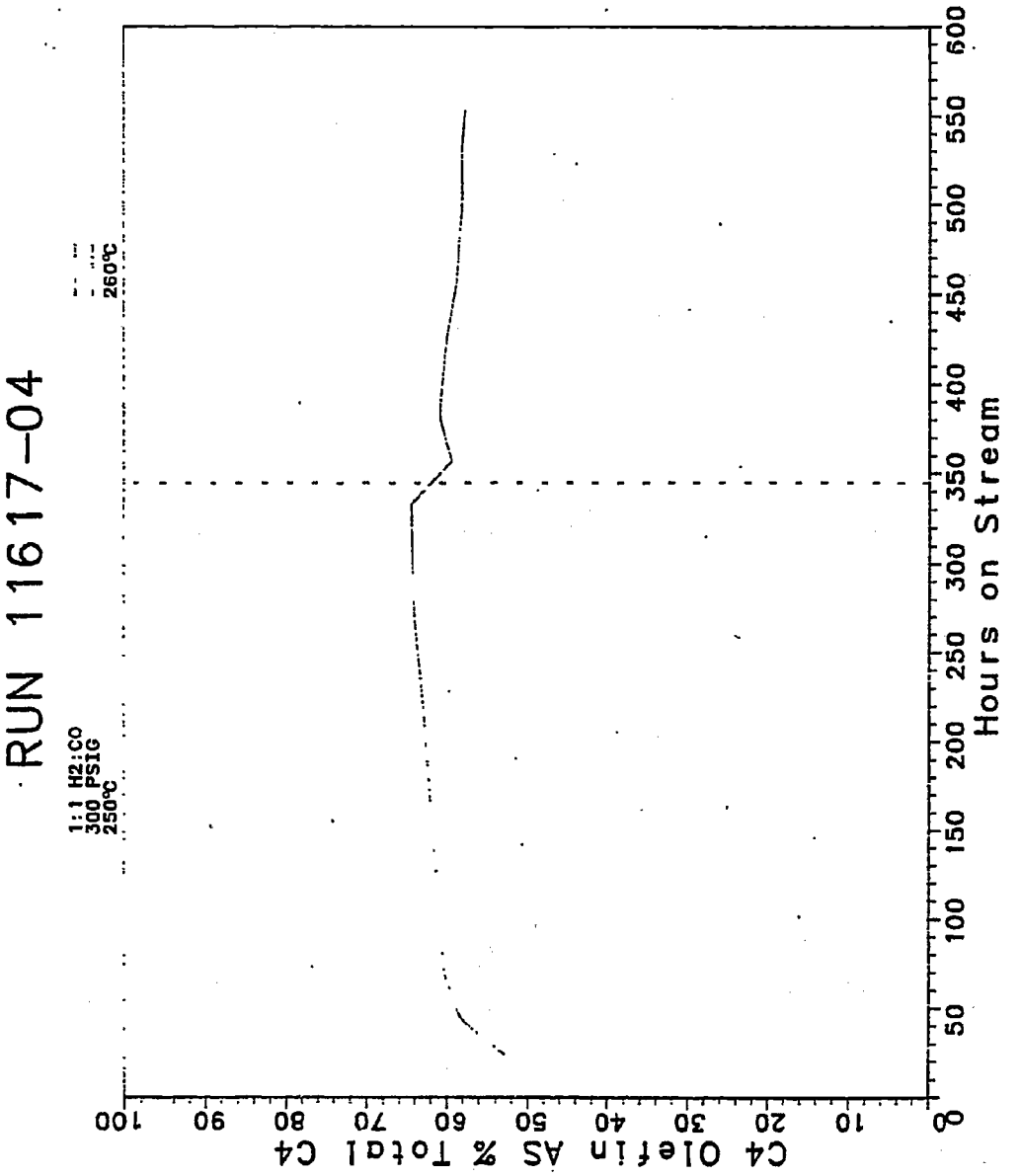

RUN 11617-04
1:1 H2:CO
300 PSIG
250°C
260°C
C4 Olefin As % Total C4
Hours on Stream
0
50
100
150
200
250
300
350
400
450
500
550
600
10
20
30
40
50
60
70
80
90
100

Fig. B84

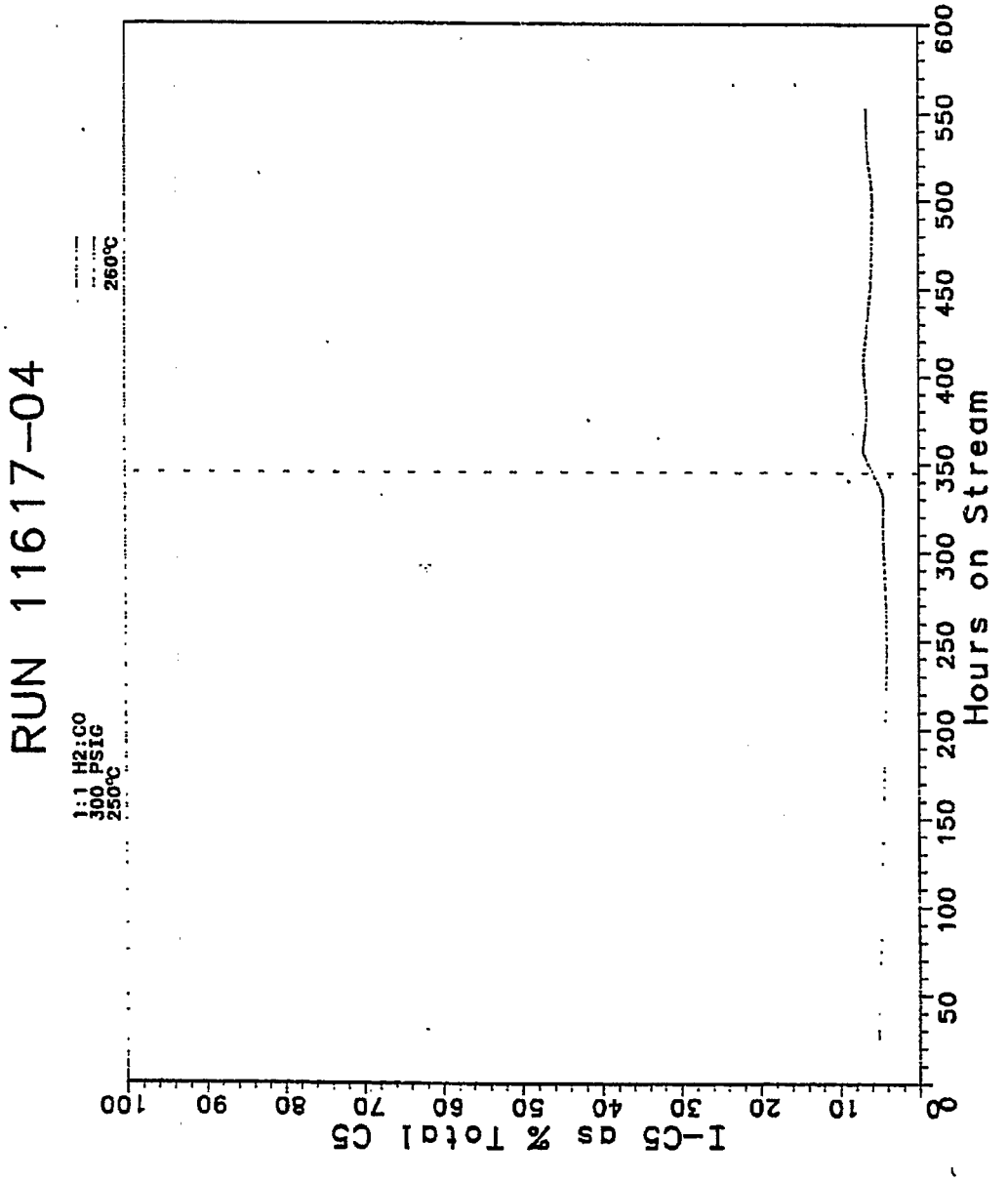

RUN 11617-04
1:1 H2:CO
300 PSIG
250°C
260°C
I-C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550
600

Fig. B85

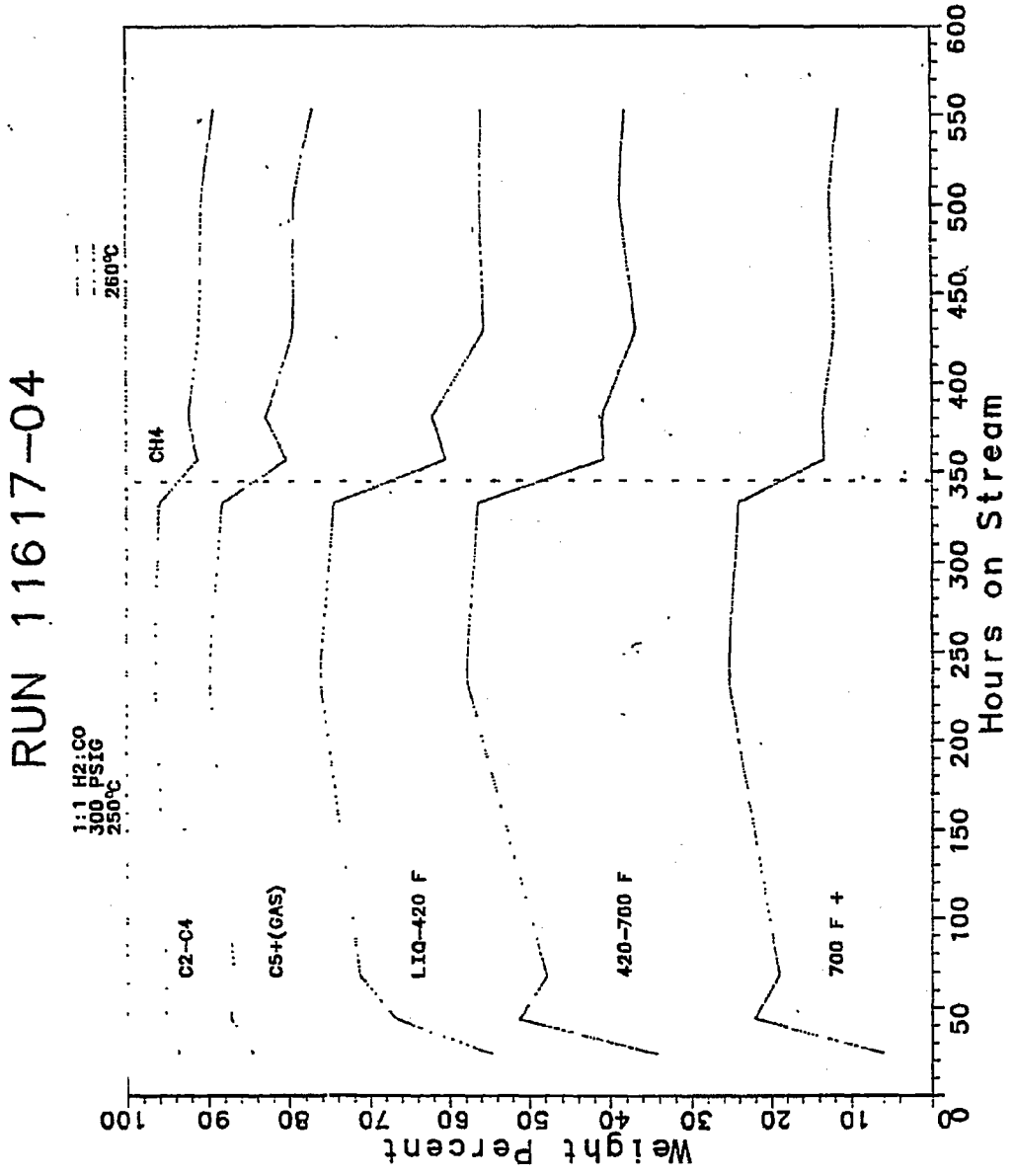

RUN 11617-04
1:1 H2:CO
300 PSIG
250°C
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
50
100
150
200
250
300
350
400
450
500
550
600
10
20
30
40
50
60
70
80
90
100

Fig. B86

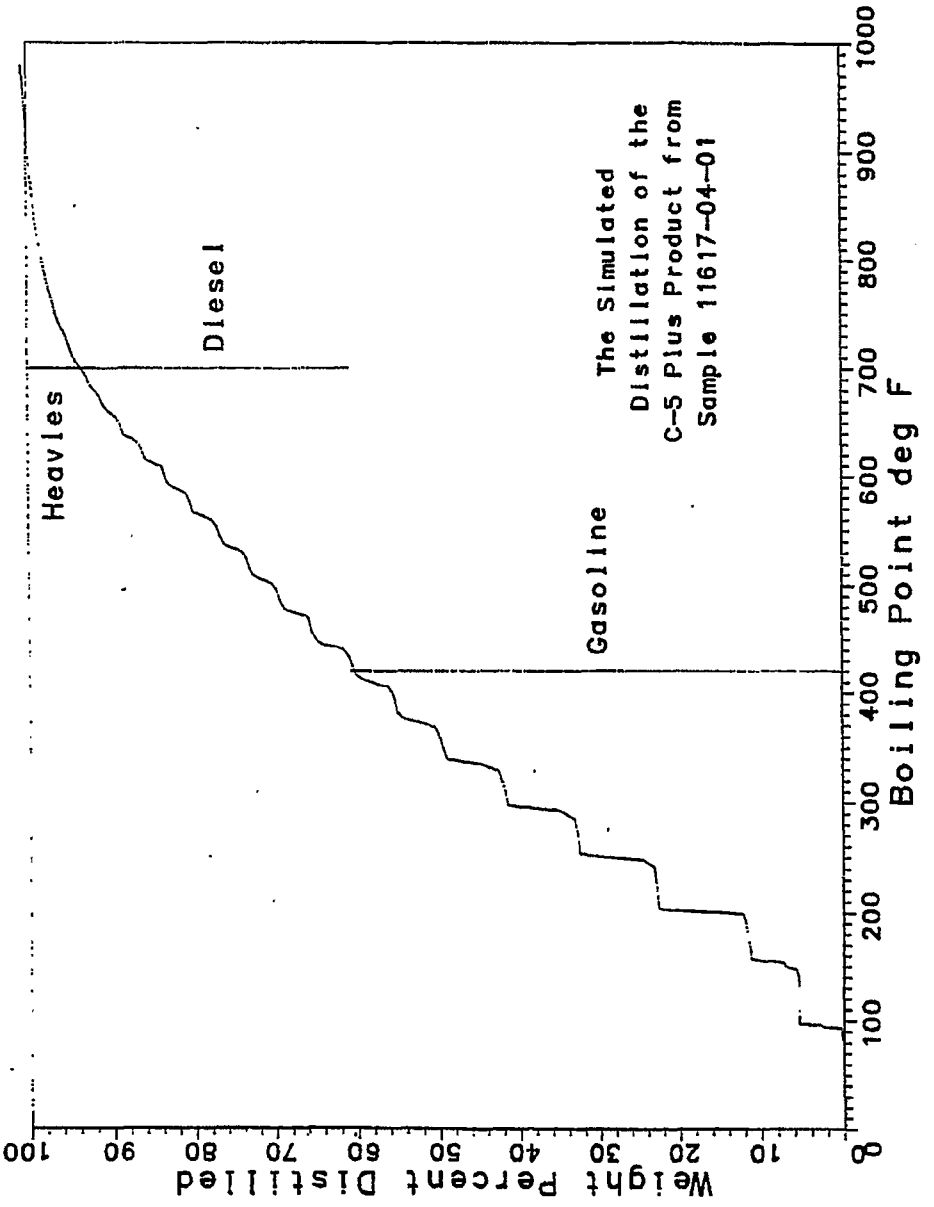

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-04-01
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B87

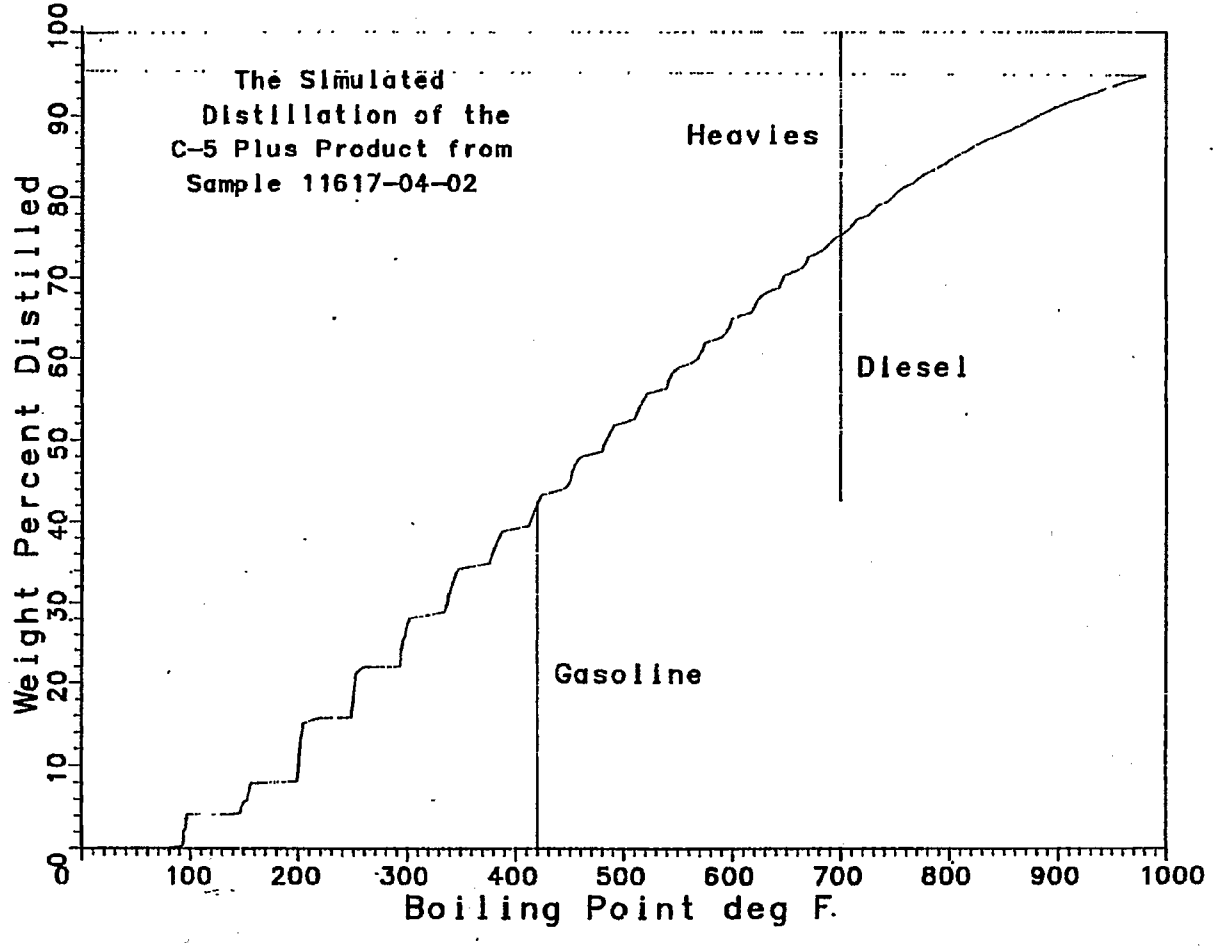

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-04-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F.
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B88