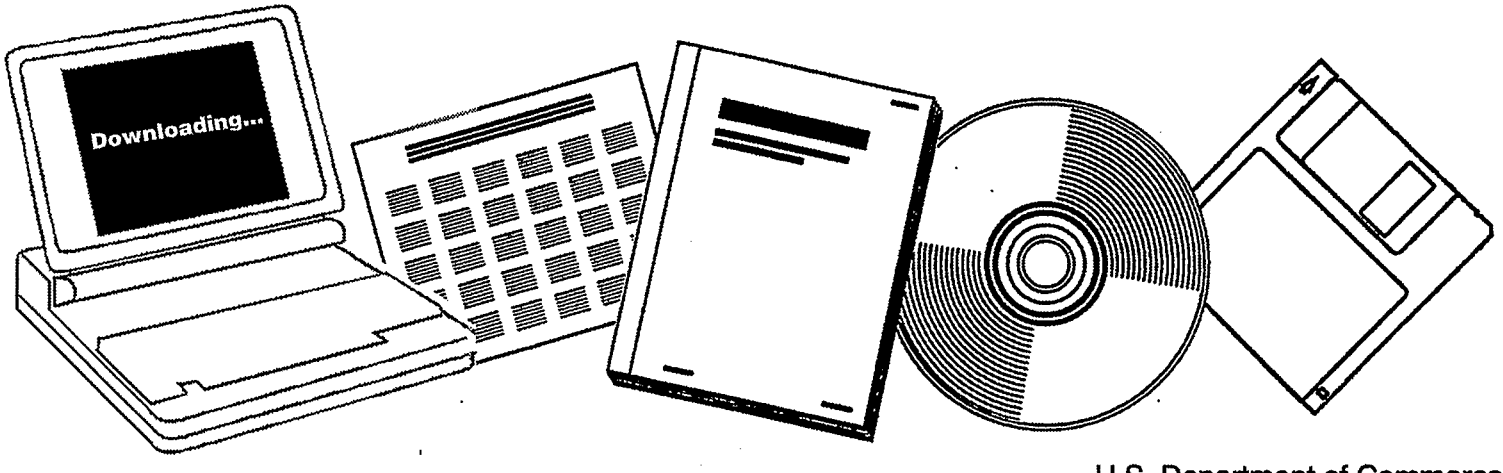
IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. SECOND QUARTER TECHNICAL PROGRESS REPORT, JANUARY-MARCH 1984

UNION CARBIDE CORP., TARRYTOWN, NY.
MOLECULAR SIEVE DEPT

1984



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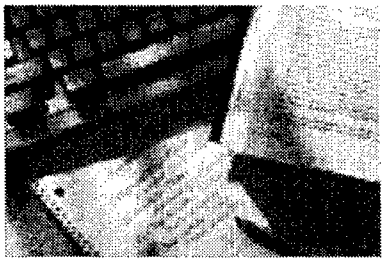

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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

Second Quarterly Report
January - March 1985

IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

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 techno-economic studies that will supplement those that are presently being carried out by MITRE. These studies are tentatively scheduled to be completed by April, 1985.

Task 3 consists of the optimization of the most promising catalysts developed under prior contract DE-AC22-81PC40077 towards 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 that 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 catalyst 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 run from the eighteenth through the twenty-fourth month of the contract.

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, in 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, is being delayed until the MITRE study is completed.

It was recommended that both Tasks 2 and 6 (the final techno-economic study) be replaced by a sequential sensitivity study carried out by MITRE. This sensitivity study would graphically represent 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, α, C_{25}-C_{30} carbon cutoff, overall conversion, feed H_2/CO ratio, reactor temperature, and reactor pressure.

These differential cost-operating curves would not only strikingly illuminate which of those operating parameters have the greatest effect on product cost, but they would 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.

C. Tasks 3 and 4

The three most important runs reported for this quarter were Runs 15, 11 and 17.

In Run 15 replacement of slightly radioactive thoria with a combination of additives, X_9 and X_{10}, was very successful. This catalyst demonstrated the excellent stability found in Run 6 (11677-11) of the Third Annual Report of the previous contract, as well as a slightly higher specific activity and a lower methane make.

Run 11 demonstrated the potential use of a new catalyst formulating procedure to produce catalysts with superior specific activities. This catalyst showed a high initial specific activity, but lacked stability. A number of subsequent runs this quarter were geared toward incorporating the stabilizing additives developed previously.

In Run 17 iron, instead of cobalt as the Fischer-Tropsch active component, was intimately mixed into the catalyst with the new formulating procedure. Unfortunately the catalyst showed poor activity.

The preliminary test results of these three runs, as well as thirteen other runs reported for this quarter, are listed in Appendix A as Runs 10-25. Additional, detailed analyses of these runs will be presented in the next quarterly report.

Such detailed analyses for the runs (1-9) reported for the first quarter in a preliminary manner are listed in Appendix B.

D. Task 5

The Task 5 process/catalyst optimization work was temporarily interrupted by the data preparation work required for the Fourteenth and Fifteenth Quarterly Reports of the previous contract.

E. Task 6

Since this final techno-economic evaluation is scheduled to begin in Fiscal Year 1986, no work was done on it this quarter.

Additionally, the proposed sequential sensitivity studies recommended for MITRE would satisfy the objectives of this task as well as those of Task 2 (see B. Task 2).

V. CHANGES

There were no contract changes during the Second Quarter.

VI. FUTURE WORK

Task 2 will be initiated at the completion of the outstanding MITRE study. Hopefully, our recommendation that MITRE fulfill the requirements of both Tasks 2 and 6 with a sequential sensitivity study will be accepted by the DOE.

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

Task 5 will be devoted to a rough technical comparison between the UCC and Gulf-Badger (as sketchily described in a 1983 Hydrocarbon Processing article) catalyst/process systems, and to incorporating heat generation and heat transfer terms into the presently isothermal mathematical model, so that upper space velocity limits can be defined for different operating pressures.

A. C. Frost

APPENDIX A

Appendix A. CATALYST TESTING

J. G. Miller, L. F. Elek, C-L Yang and P. K. Coughlin

This report is organized around sixteen catalyst tests reported from January through March 1985, the second quarter of this contract.

A list of the catalysts tested and a description of their preparation are shown in Table A1. All but one of the runs (Run 24) involved catalysts which have cobalt oxide or iron oxide intimately contacted with UCC-103. The catalyst used in Run 24 used a newly developed shape selective component, UCC-113, in intimate contact with cobalt oxide.

Seven of the catalysts were prepared by the method developed in the previous three-year contract (DE-AC22-81PC40077); the remainder were prepared by a newly developed method.

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, the methane factor and a qualitative estimate of stability are listed for each catalyst. A more complete report of results and analyses for these runs will be presented in the Third Quarterly Report.

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

Run	Catalyst	Catalyst preparation
10	Co/Th/X_4/UCC-103 (12185-06)	The thorium-promoted cobalt oxide was formed in close contact with UCC-103, then further promoted with X_4. The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Pct Co=18.8, pct Th=2.9, pct X_4=1.7.
11	Co/UCC-103 (12200-06)	Cobalt oxide was formed in close contact with UCC-103 by a new method. The resulting powder was bonded with 15% silica and extruded to 1/8" pellets. Pct Co=12.8.
12	Co/Th/X_4/UCC-103 +UCC-101	The thorium/X_4 promoted cobalt oxide was formed in close contact with UCC-103 as described in Run 10. The resulting powder was mixed with UCC-101 in a weight ratio of 1.125:1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Pct Co=4.4, pct Th=0.6, pct X_4=0.4.
13	Co/Th/X_4/UCC-103 (12200-07)	The catalyst was prepared by the method described in Run 10 (12185-06). Pct Co=8.3, pct Th=1.1, pct X_4=0.8.
14	Co/Th/X_4/UCC-103 (12200-08)	Same catalyst as Run 3 (12200-07) after attempted regeneration using H_2.
15	Co/X_9/X_{10}/X_4/UCC-103 (12185-08)	X_9 and X_{10}-promoted cobalt oxide was formed in close contact with UCC-103, then further promoted with X_4. The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Pct Co=8.4, pct X_9=0.4, pct X_{10}=0.5, pct X_4=0.8.
16	Co/X_9/X_{10}/X_4/UCC-103 (12200-09)	X_9, X_{10}, X_4-promoted cobalt oxide catalyst was prepared by the method used for Run 11 (12200-06). Pct Co=8.4, pct X_9=0.4, pct X_{10}=0.5, pct X_4=0.8.
17	Fe/K/UCC-103 (12200-10)	Potassium promoted iron oxide was formed in close contact with UCC-103 by the method used in Run 11 (12200-06). The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Theoretical pct Fe=8.5, pct K=0.2.
18	Fe/K/UCC-103 (12200-11)	This catalyst was prepared by the method described in Run 17, except that it was calcined at a lower temperature. Theoretical pct Fe=8.5, pct K=0.3.

continued

Table A1, continued.

Run	Catalyst	Catalyst preparation
19	Co/X_9/X_{10}/X_4/UCC-103 (12185-09)	Cobalt oxide was formed in close contact with UCC-103 by the method used in Run 11, then further promoted with X_9, X_{10} and X_4. The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Theoretical pct Co=11.3, pct X_9=0.5, pct X_{10}=0.7, pct X_4=1.3.
20	Co/X_9/X_{10}/UCC-103 (12185-11)	The X_9 and X_{10} promoted cobalt oxide was formed in close contact with UCC-103 by the method used in Run 11. The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Theoretical pct Co=11.9, pct X_9=0.5, pct X_{10}=0.7.
21	Co/X_9/X_{10}/X_4/UCC-103+UCC-112 (12200-12)	The X_9, X_{10} and X_4 promoted cobalt oxide was formed in close contact with UCC-103 as described in Run 15. The resulting powder was mixed with UCC-112 in a weight ratio of 1.125:1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Theoretical pct Co=5.84, pct X_9=0.26, pct X_{10}=0.29, pct X_4=1.34.
22	Co/X_9/X_{10}/X_4/UCC-103 (12185-12)	This catalyst was formulated similarly to Run 21, except that UCC-112 was omitted. Theoretical pct Co=11.0, pct X_9=0.49, pct X_{10}=0.54, pct X_4=2.54.
23	Co/X_9/X_{10}/X_4/UCC-103 (12200-13)	The UCC-103 was combined with X_4 before forming in close contact with X_9 and X_{10} promoted cobalt oxide by the method used in Run 11. The resulting powder, after bonding with 15% silica, was extruded to 1/8" pellets. Theoretical Pct Co=11.5, pct X_9=0.50, pct X_{10}=0.66, pct X_4=2.21.
24	Co/X_9/X_{10}/UCC-113 (12185-13)	This catalyst was formulated similarly to Run 20 except that UCC-113 was substituted for UCC-103. Theoretical pct Co=7.9, pct X_9=0.37, pct X_{10}=0.50.
25	Co/X_9/X_{10}/X_4/UCC-103 (12200-14)	This catalyst was formulated similarly to Run 23, except that a different X_4 source was used. Theoretical pct Co=7.2, pct X_9=0.32, pct X_{10}=0.43, pct X_4=0.33.

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

Catalyst run no.	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Methane factor(1)	Stability
10	Co/Th/X_4/UCC-103 (12185-06)	43.0 187.5	61.6 54.2	11.2 10.6	78.1 78.2	1.99 1.53	2.80 1.92	Fair
11	Co/UCC-103 (12200-06)	71.0 165.5	77.8 68.5	10.1 16.1	80.3 73.1	12.54 4.01	3.42 6.47	Poor
12	Co/Th/X_4/UCC-103+UCC-101 (12185-07)	43.0 499.5	48.6 43.3	14.2 13.2	67.7 69.9	1.08 0.50	3.46 2.58	Good
13	Co/Th/X_4/UCC-103 (12200-07)	43.5 236.5	54.5 44.6	9.22 11.2	77.9 73.2	2.23 1.29	1.88 2.60	Fair
14	Co/Th/X_4/UCC-103 (12200-08)	19.5 67.8	48.6 45.6	8.02 11.3	78.3 71.7	1.70 1.28	1.80 2.44	Fair
15	Co/X_9/X_{10}/X_4/UCC-103 (12185-08)	45.0 139.5 358.0	60.5 56.5 55.7	11.2 12.6 12.5	74.3 73.7 71.4	2.44 2.13 1.87	2.65 1.55 2.91	Excellent
16	Co/X_9/X_{10}/X_4/UCC-103 (12200-09)	Inactive						
17	Fe/K/UCC-103 (12200-10)	92.7 116.7	21.9 23.7	7.9 8.8	58.8 61.0	0.47 0.51	0.52 0.51	—
18	Fe/K/UCC-103 (12200-11)	19.5 43.0	18.0 16.9	17.6 18.6	39.6 40.1	0.47 0.40	1.12 1.03	—
19	Co/X_9/X_{10}/X_4/UCC-103 (12185-09)	24.5 48.5	44.8 42.8	18.5 18.1	58.1 61.6	0.74 0.56	2.45 2.11	—
20	Co/X_9/X_{10}/UCC-103 (12185-11)	42.5 115.5	85.7 62.1	12.9 17.9	75.2 66.3	12.5 2.31	5.91 6.14	Poor
21	Co/X_9/X_{10}/X_4/UCC-103 +UCC-112 (12200-12)	42.5 163.5	44.0 37.9	12.6 18.4	66.7 63.4	1.04 0.61	1.28 3.91	Fair

Conditions: 300 psig, 260C, 300 GHSV.

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

continued

Table A2, continued.

Catalyst run no.	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Methane factor(1)	Stability
22	$Co/X_9/X_{10}/X_4$/UCC-103 (12185-12)	45.5	60.6	12.4	75.6	2.51	4.27	Fair
		93.5	58.9	12.2	74.8	2.16	3.72	
23	$Co/X_9/X_{10}/X_4$/UCC-103 (12200-13)	20.0	52.0	15.2	72.7	1.10	5.68	Poor
		44.0	41.9	17.4	69.9	0.85	5.92	
24	$Co/X_9/X_{10}$/UCC-113 (12185-13)	42.5	88.4	18.4	68.6	14.59	6.91	Poor
		186.5	54.0	18.4	67.1	1.51	5.60	
25	$Co/X_9/X_{10}/X_4$/UCC-103 (12200-14)	44.0	62.6	9.72	79.6	3.72	0.76	Poor
		140.0	52.6	17.1	67.7	1.54	3.34	

Conditions: 300 psig, 260C, 300 GHSV.

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

APPENDIX B

Appendix B. CATALYST TESTING

J. G. Miller, L. F. Elek, C-L Yang and P. K. Coughlin

Contents

I. INTRODUCTION

This report presents detailed analyses of the nine catalyst test runs which were summarized in the First Quarterly Report, and which constituted the major thrust of the work during that quarter.

Seven of the nine catalysts tested were based on intimate mixtures of cobalt and UCC-103, and two on intimate mixtures of X_3 and UCC-103. Results of each run are compared, as appropriate, with those of runs reported earlier.

Several lines of investigation were explored. Two of the catalyst runs tested the effectiveness of the shape-selective components UCC-107 and S115 on improving product quality. In other runs the Fischer-Tropsch active metal X_3 was tested for its beneficial replacement of cobalt, X_7 was used as an additive in the cobalt system for the potential reduction of excess methane production, and a catalyst with a high level of cobalt was screened for improving the specific activity. This report also describes the first attempted regeneration of an intimately mixed cobalt and UCC-103 catalyst.

II. Run 1 (12185-01) with Catalyst 1 (Co/UCC-103+UCC-107)

The purpose of this run was to test the effect of the shape selective component UCC-107 on the quality of the Fischer-Tropsch product. The catalyst was to be compared with a Co/UCC-103+UCC-101 catalyst (Run 12064-02) from the Fifteenth Quarterly Report of Contract DE-AC22-84PC70028.

The cobalt oxide was formed in close contact with UCC-103. The resulting powder was mixed with UCC-107 in a weight ratio of 1.125:1, and the mixture, after bonding with 15 weight percent silica, was extruded as 1/8-inch pellets. The final catalyst contained 6.75 percent Co.

The catalyst was totally inactive. It is not clear whether this was due to the method of its preparation, or to problems encountered during the activation procedure.

III. Run 2 (12200-01) with Catalyst 2 (X_3/K/UCC-103+UCC-101)

This run continues the search, begun in the Thirteenth Quarter of the previous contract, for improvements over the Third Annual Report Catalyst 6 (Co/Th/X_4/UCC-103+UCC-101), which was one of the most effective catalysts developed in this program to date. The purpose was to test the effect of replacing the cobalt with a different Fischer-Tropsch-active metal, X_3.

The X_3 and potassium were formed in close contact with UCC-103. The resulting powder was mixed with UCC-101 in a weight ratio of 1.125:1, and the mixture, after bonding with 15 weight percent silica, was extruded as 1/8-inch pellets. The final catalyst contained 1.1 percent X_3 and 0.45 percent potassium.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B1-4. Simulated distillations of the C_5^+ product are plotted in Figs. B5-9. Carbon number product distributions are plotted in Figs. B10-14. Chromatograms from simulated distillations are reproduced in Figs. B15-19. Detailed material balances appear in Table B1.

During the first 43.5 hours of the run, when the reactor pressure was 100 psig, the conversion of $CO+H_2$ dropped sharply from 42.06 percent at 19.5 hours to 15.56 percent at 43.5 hours. (From the results of a repeat run--see Run 9--this was apparently

due to a material balance discrepancy resulting from a gas chromatography error.) After 43.5 hours, when the pressure was raised to 300 psig, the conversion increased to 31.87 percent at 69.5 hours, then declined to 20.30 percent at the end of the run. During the last 48 hours on stream the conversion deactivated at a rate of 1 percentage point every 26 hours. These anomalies, coupled with the relatively short duration of the run (164.5 hours), make it impossible to form any reliable conclusions about the catalyst's stability.

The specific activity at 69.5 hours on stream was 0.37, as against 0.9 for Third Annual Report Catalyst 6 at approximately the same time. On the basis of weight percent Fischer-Tropsch metal, however, the X_3 in this catalyst was substantially more active than the cobalt in Third Annual Report Catalyst 6--0.34 units of specific activity per weight percent of metal as against 0.20 units.

The water gas shift activity was very low, with only about 0.5 percent of the oxygen converted to CO_2; the resulting H_2/CO usage ratio, 2.79:1, was one of the highest observed in this study.

The product selectivity observed for Sample 1, showing a product balance of 3.84 percent CH_4 and 93.2 percent C_5^+, was probably due to errors in gas chromatography analysis. After 69.5 hours on stream the selectivity was not much different from that of a cobalt catalyst.

As with cobalt catalysts, the production of methane was ex-

cessive. From C_3 to about C_{25} the Schulz-Flory distribution plot was almost straight (see, for example, Sample 10, Fig. B14), after which there was an apparent carbon number cut-off.

The C_4 product was 80 percent olefins as against 60 percent for Third Annual Report Catalyst 6. Isomerization of the pentane, however, was much lower, decreasing from about 20 percent at 69.5 hours on stream to almost zero at the end of the run. With Third Annual Report Catalyst 6, production of isopentane was almost steady at about 10 percent of total pentane.

This catalyst has two desirable properties in its highly olefinic product and its high relative activity per weight percent of metal. Judging from this run, however, its product was excessively high in methane and its stability, except during the last 48 hours of the run, was poor.

Fig. B1

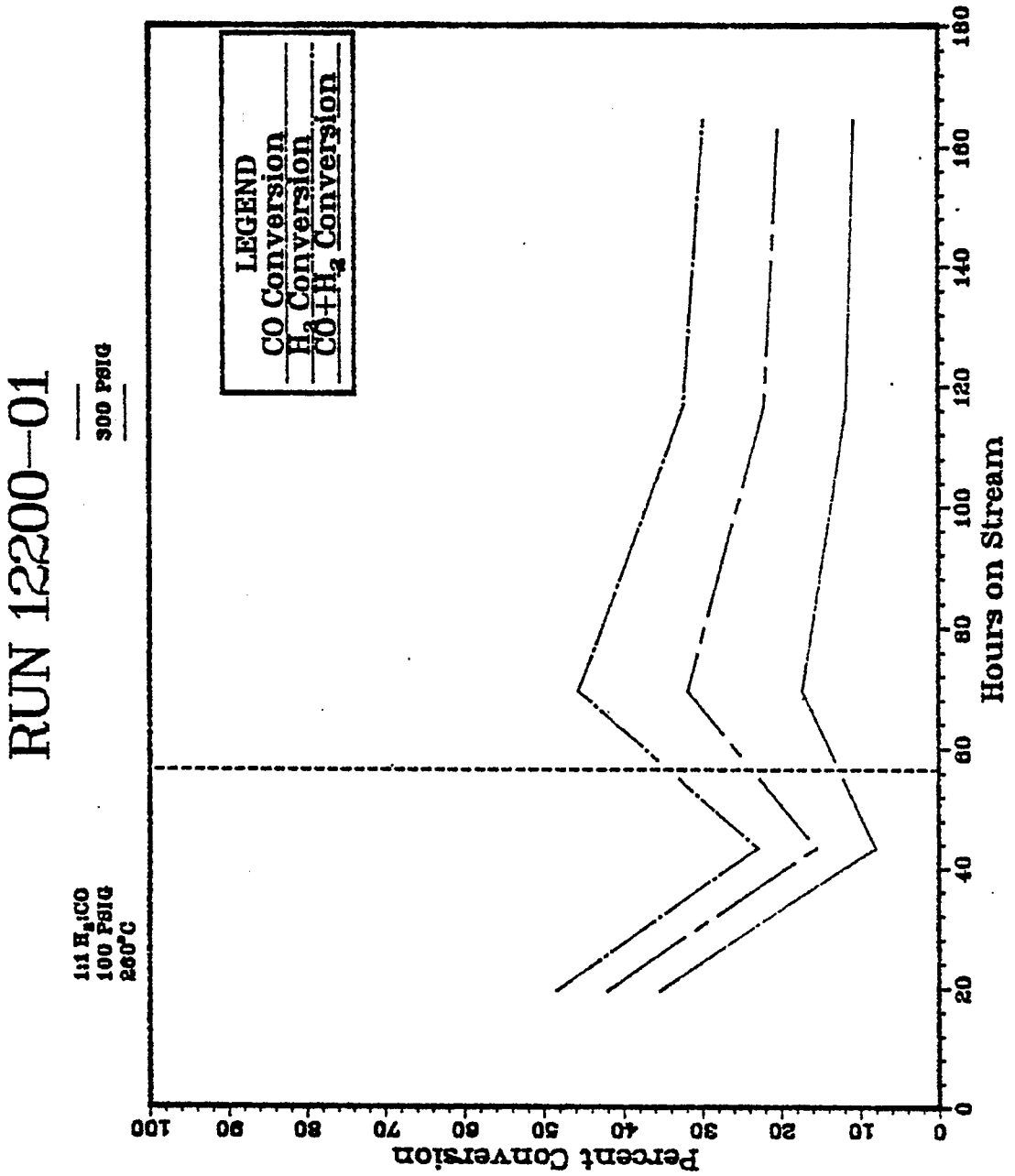

RUN 12200-01
300 PSIG
1:1 H2:CO
100 PSIG
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. B2

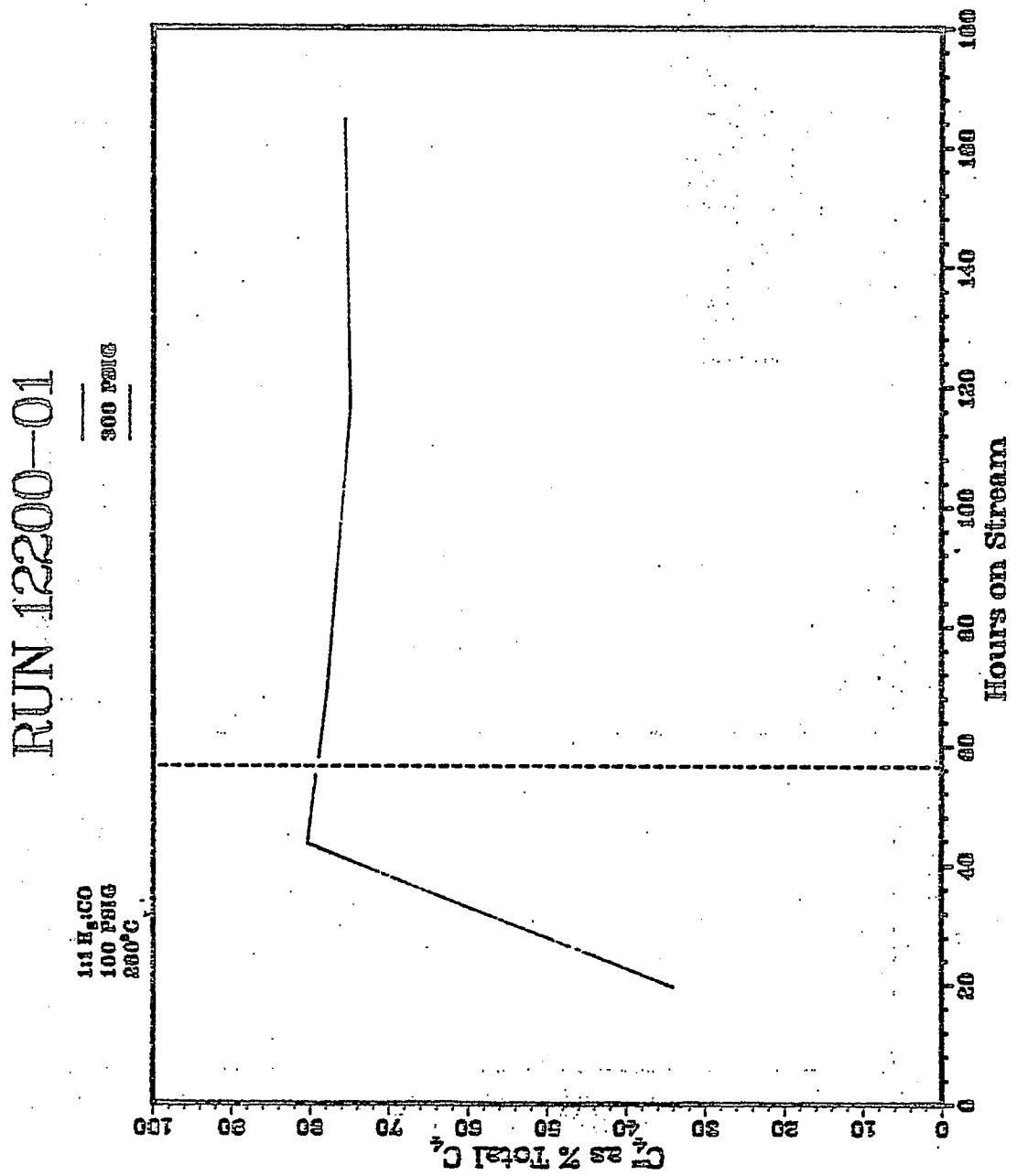

RUN 12200-01
300 PSIG
1:1 H2:CO
100 PSIG
280°C
C4 as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200

Fig. B3

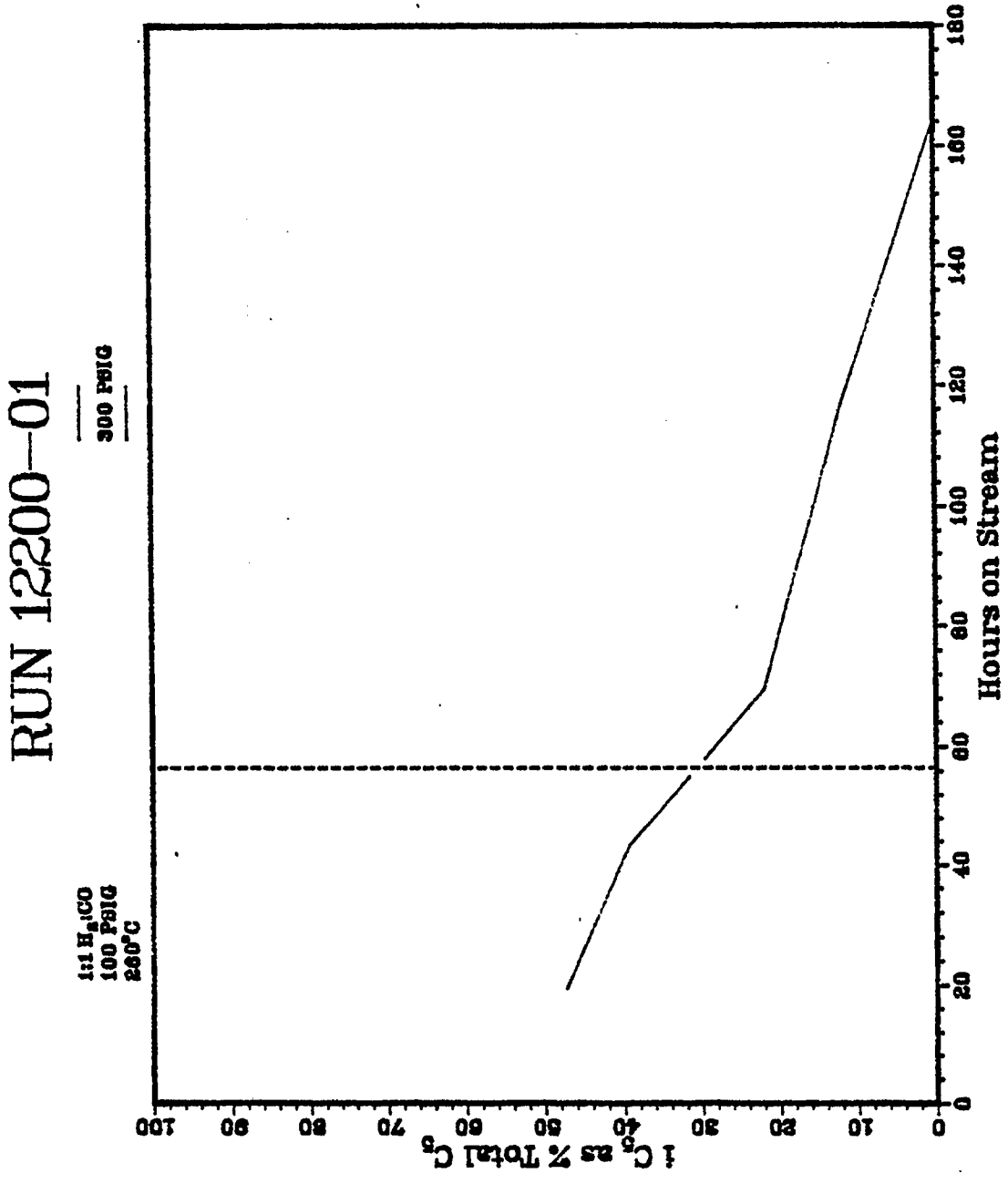

RUN 12200-01
300 PSIG
1:1 H2:CO
100 PSIG
260°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. B4

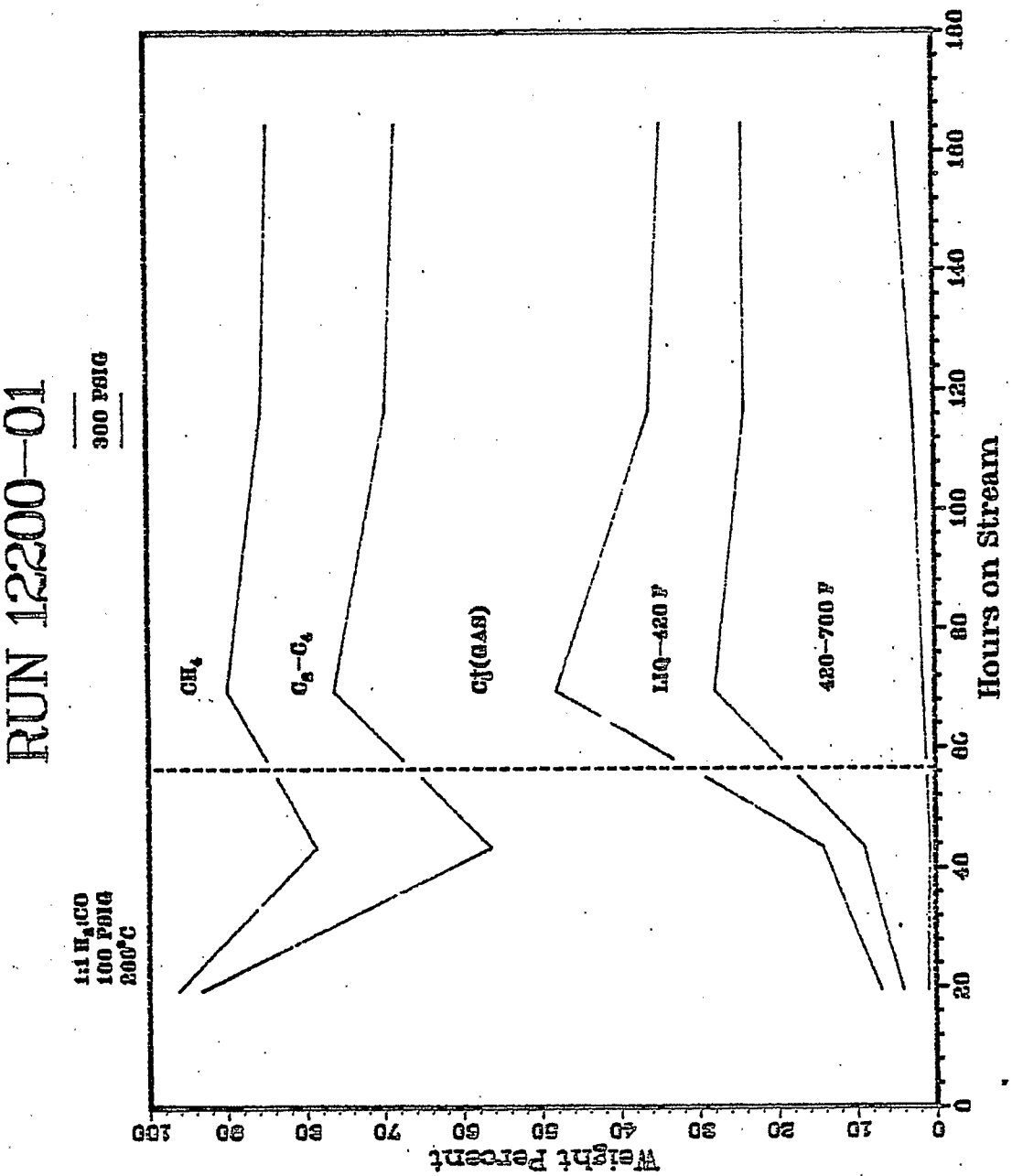

RUN 12200-01
300 PSIG
1:1 H2:CO
100 PSIG
200°C
CH4
C2-C4
C5(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
20
40
60
80
100
120
140
160
180
0
20
30
40
50
60
70
80
100

Fig. B5

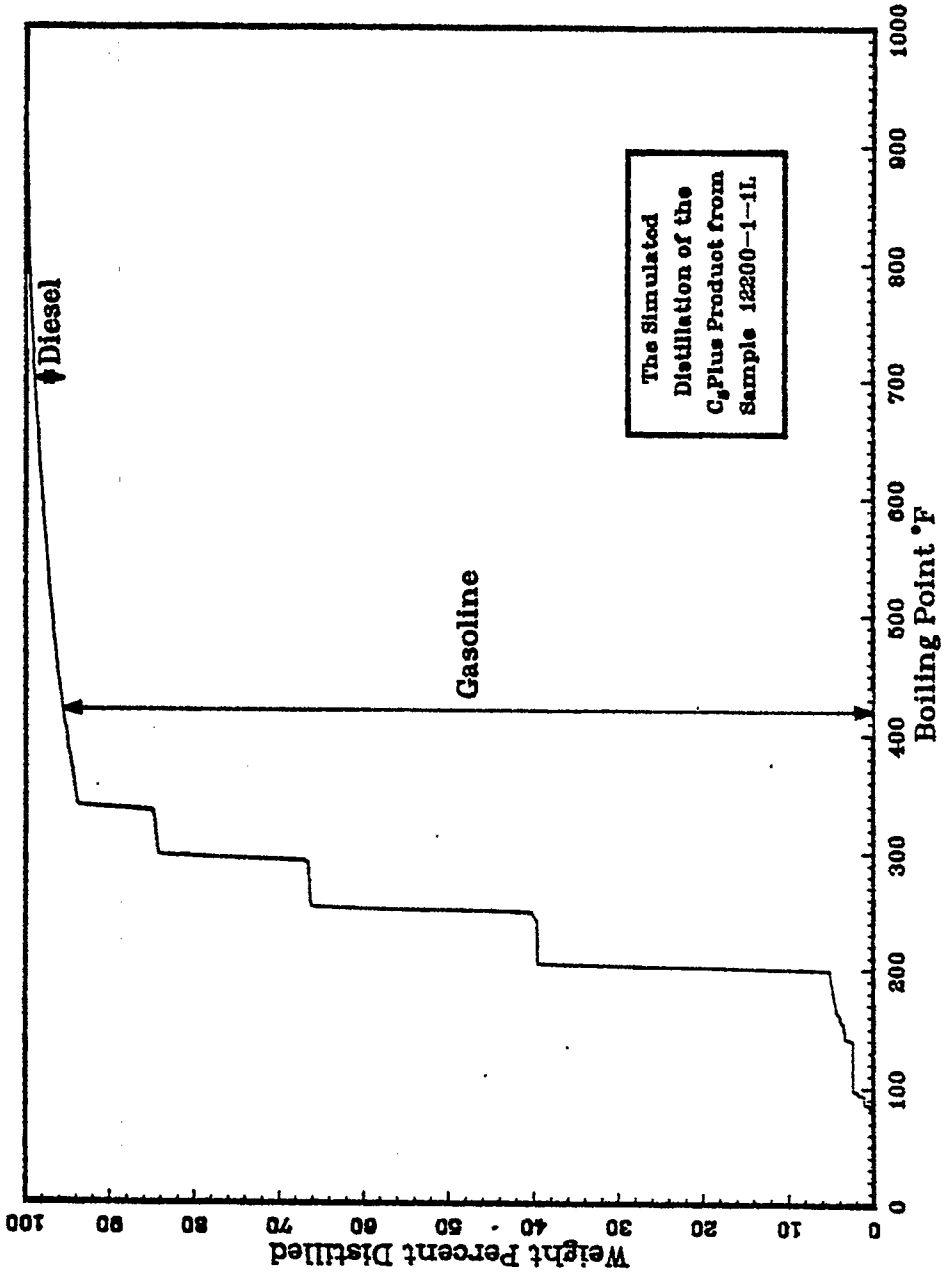
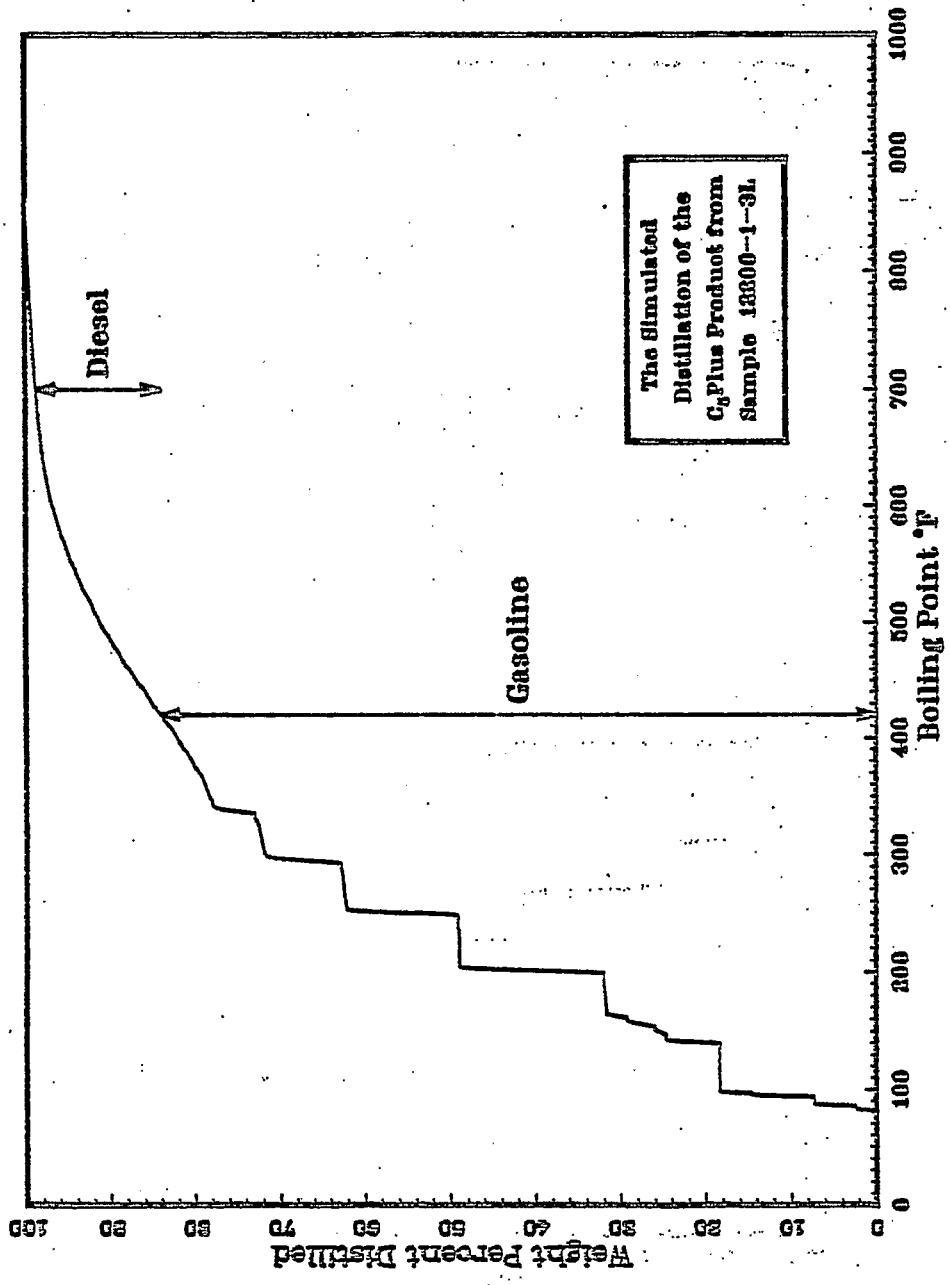

Diesel
Gasoline
The Simulated Distillation of the C5Plus Product from Sample 12200-1-1L
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000

Fig. B6


Weight Percent Distilled
0
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20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
The Simulated Distillation of the C5 Plus Product from Sample 13300--1--3L

Fig. B7

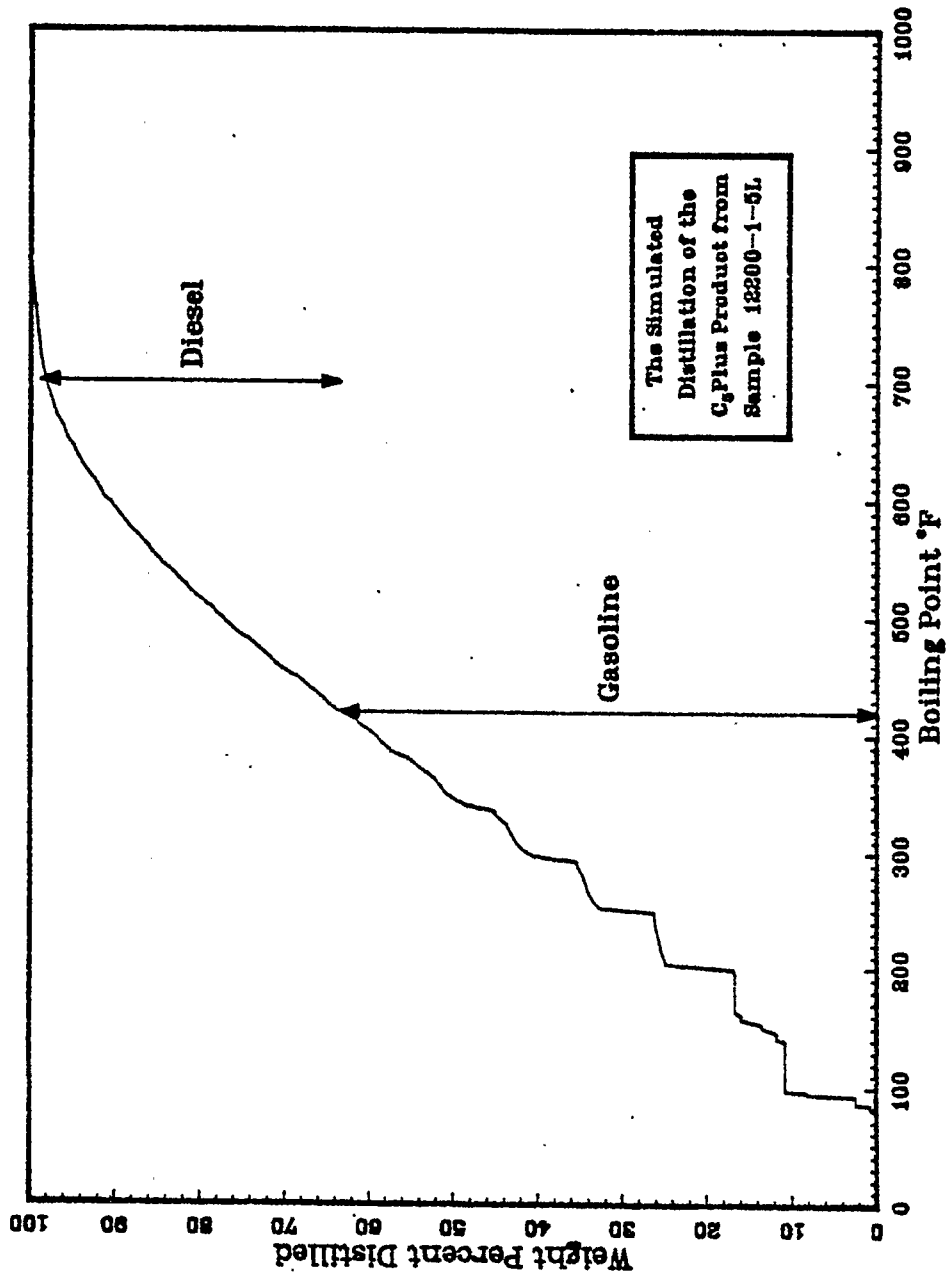

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
The Simulated Distillation of the C5 Plus Product from Sample 12200-1-5L

Fig. B8

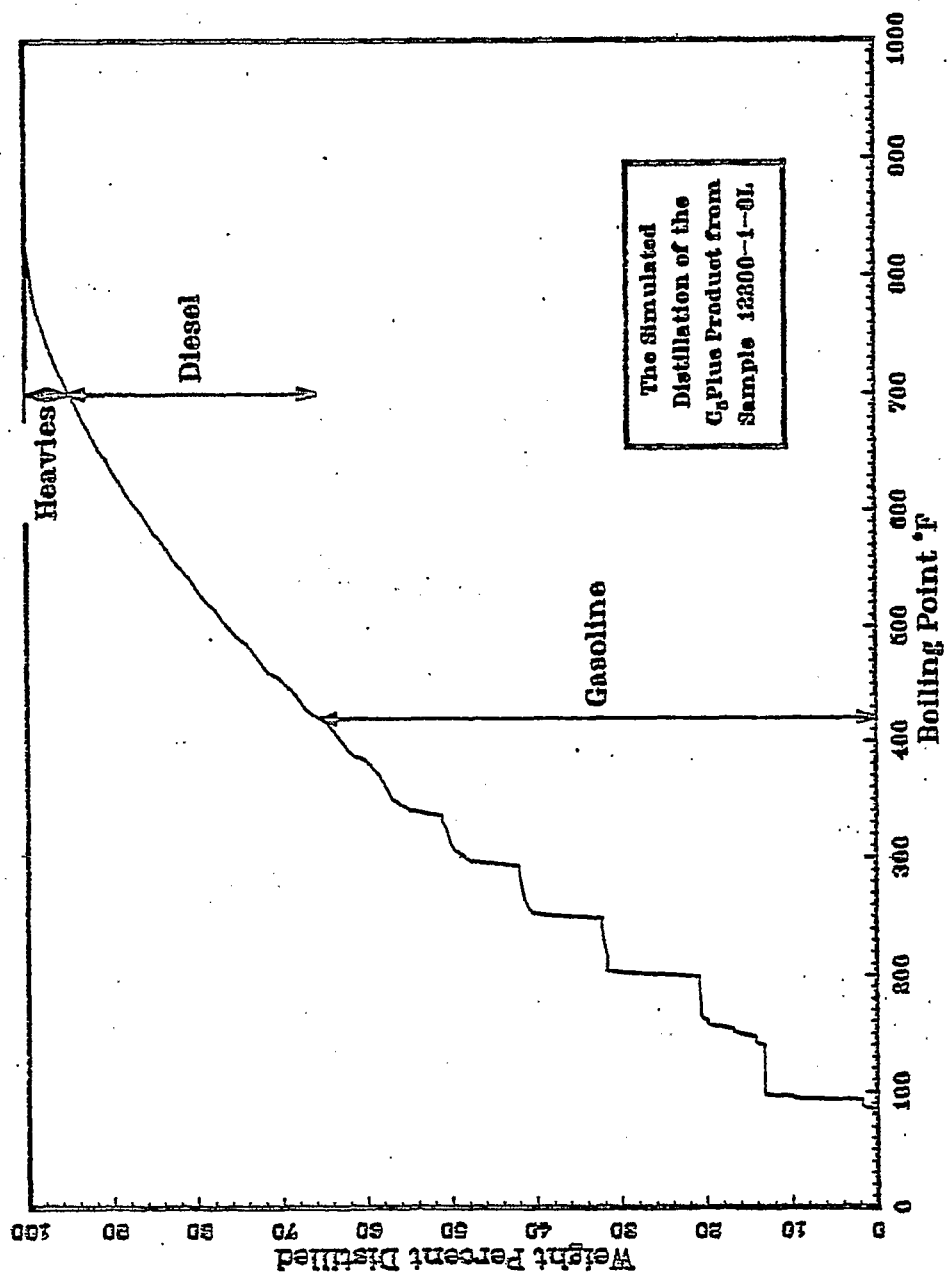

The Simulated Distillation of the C_5Plus Product from Sample 12300-1-01
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B9

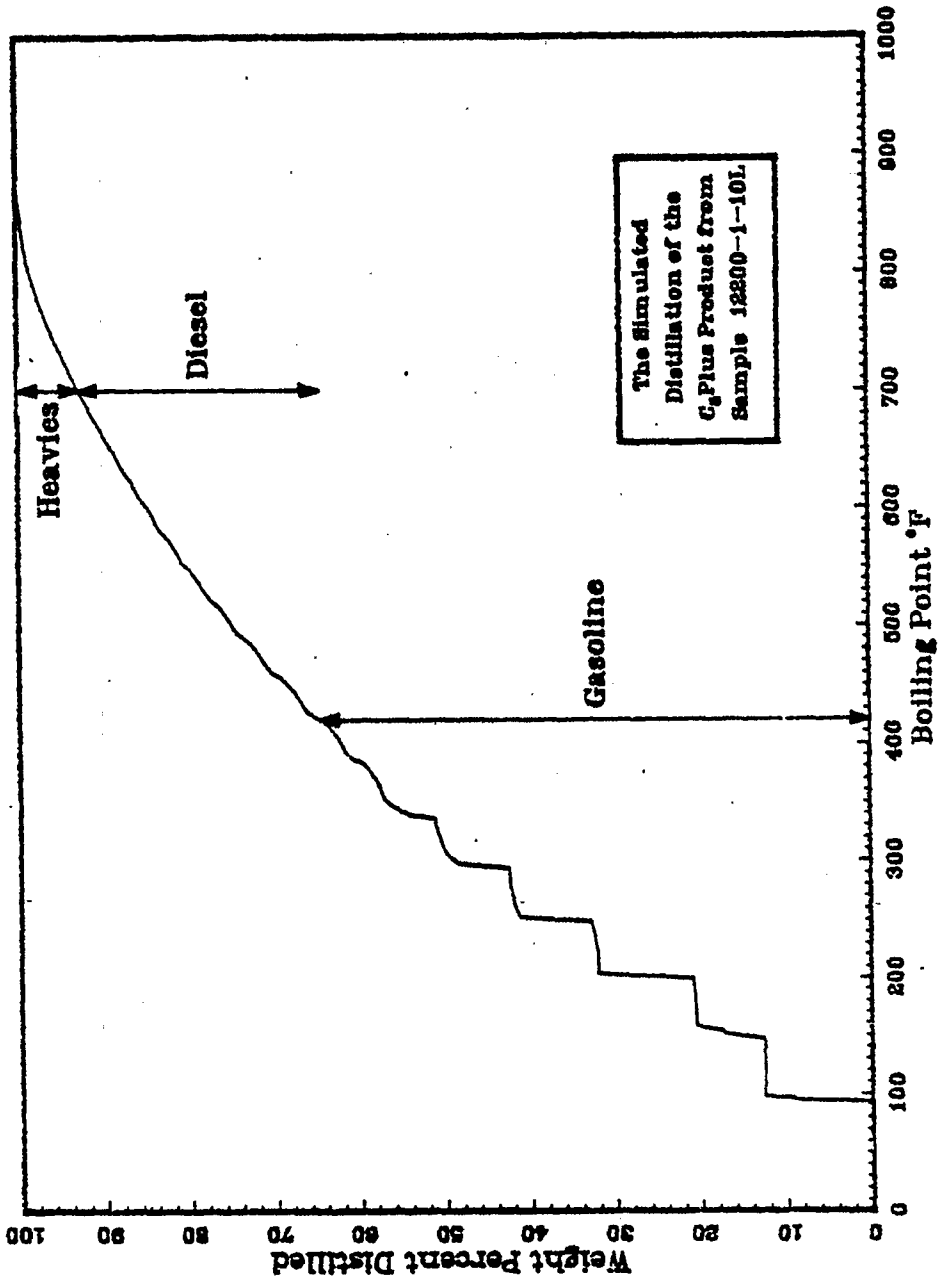

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12200-1-10L

Fig. B10

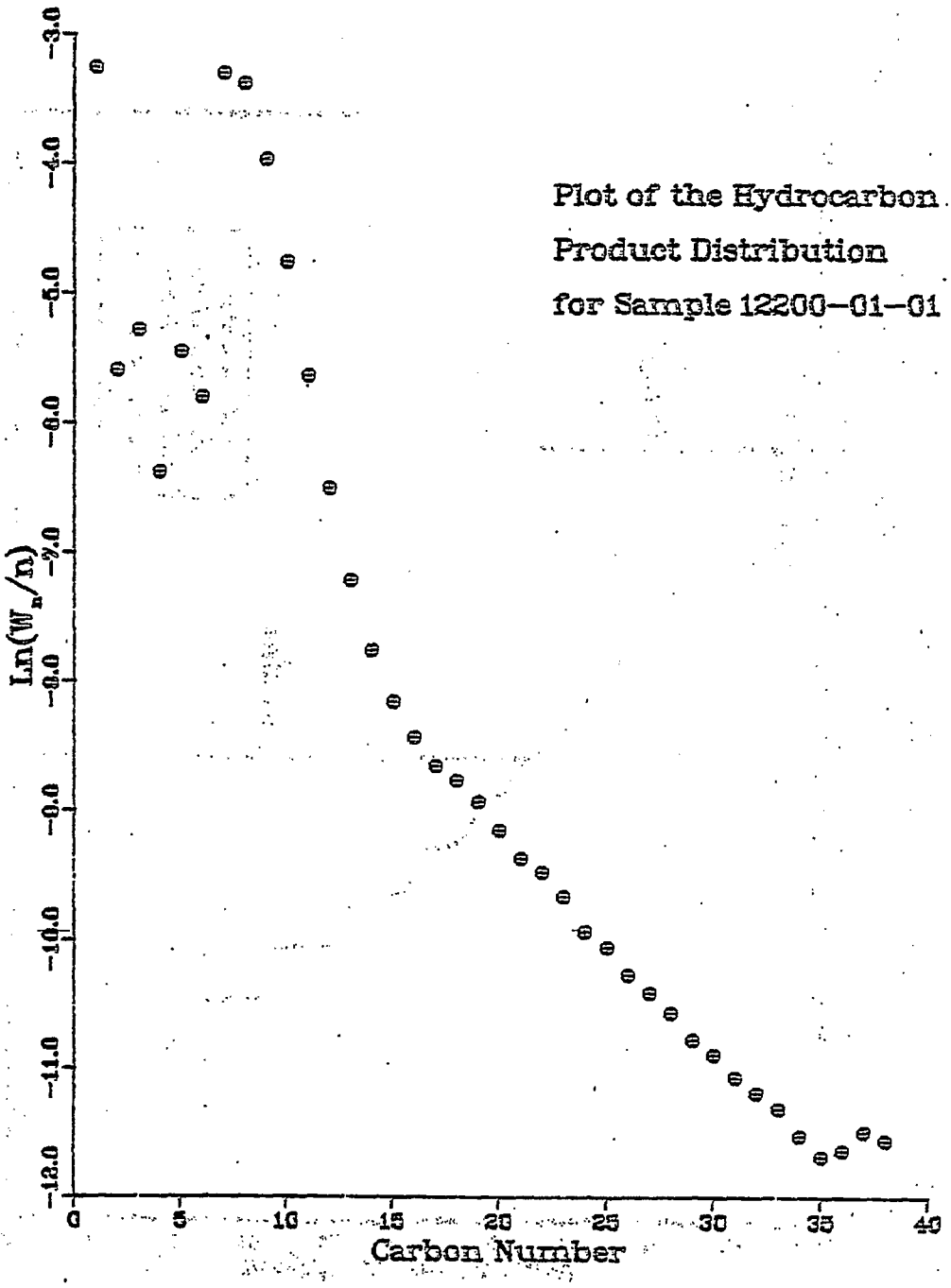

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-01-01
Ln(W_n/n)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B11

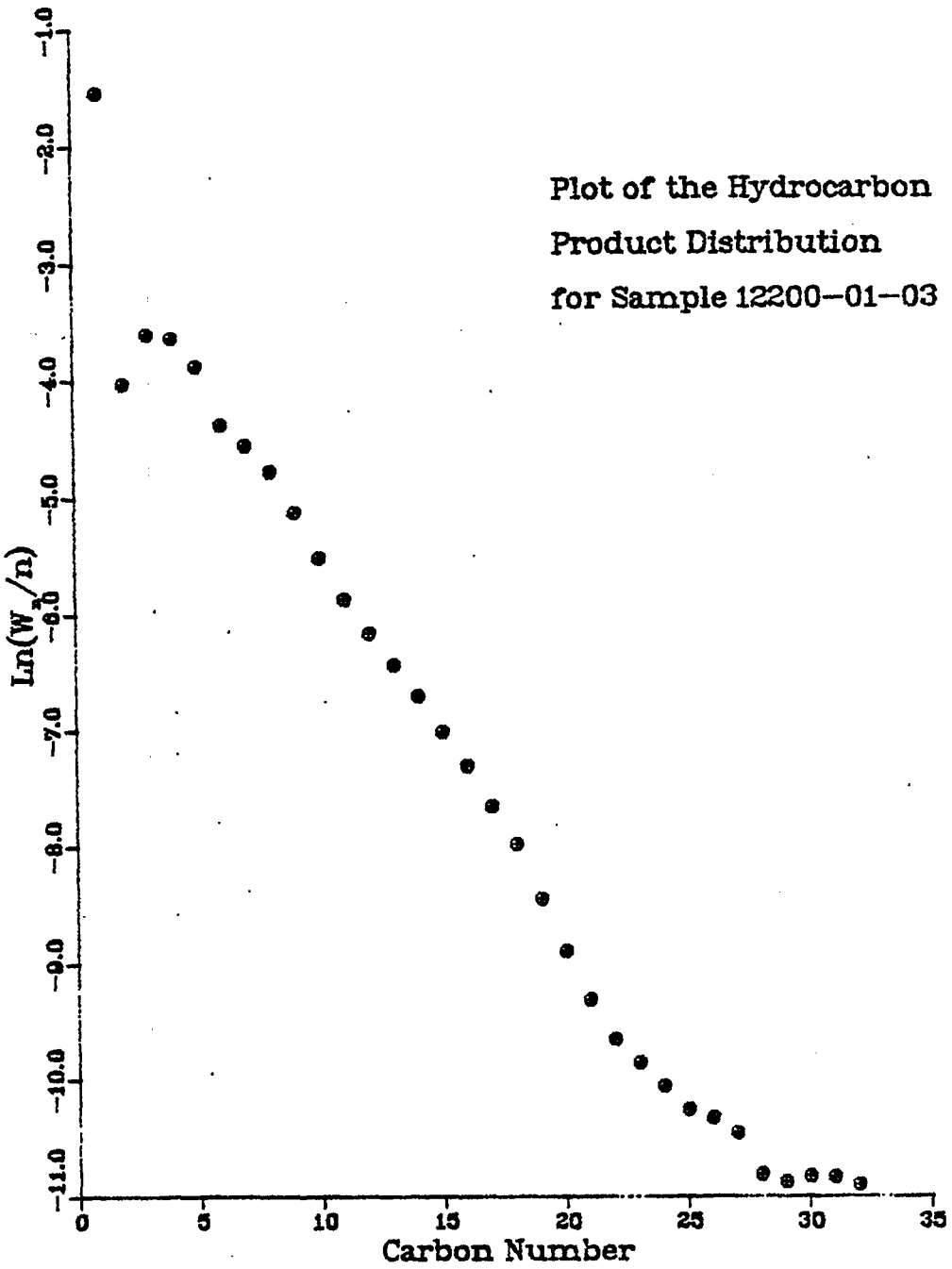

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-01-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B12

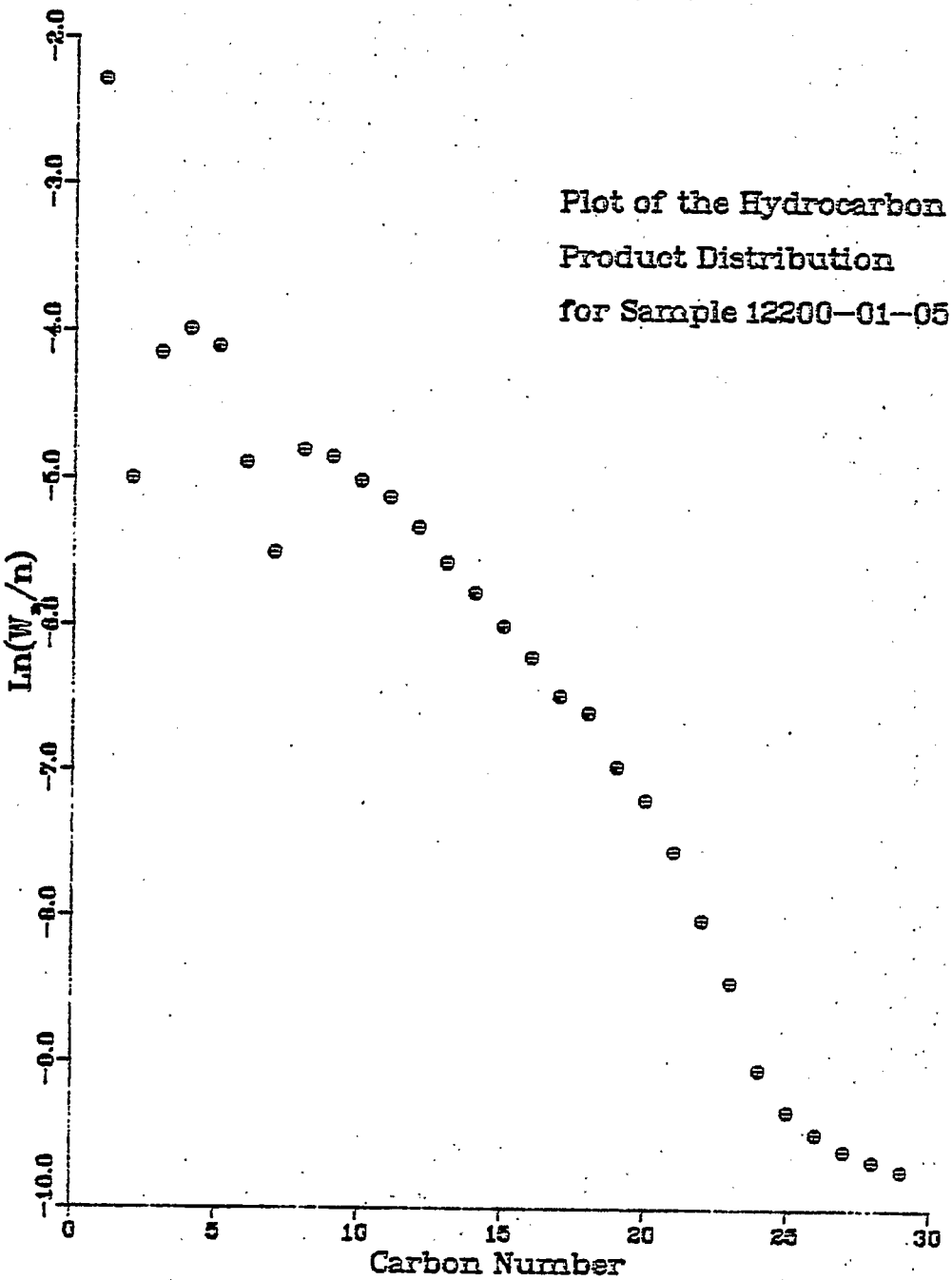

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-01-05
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B13

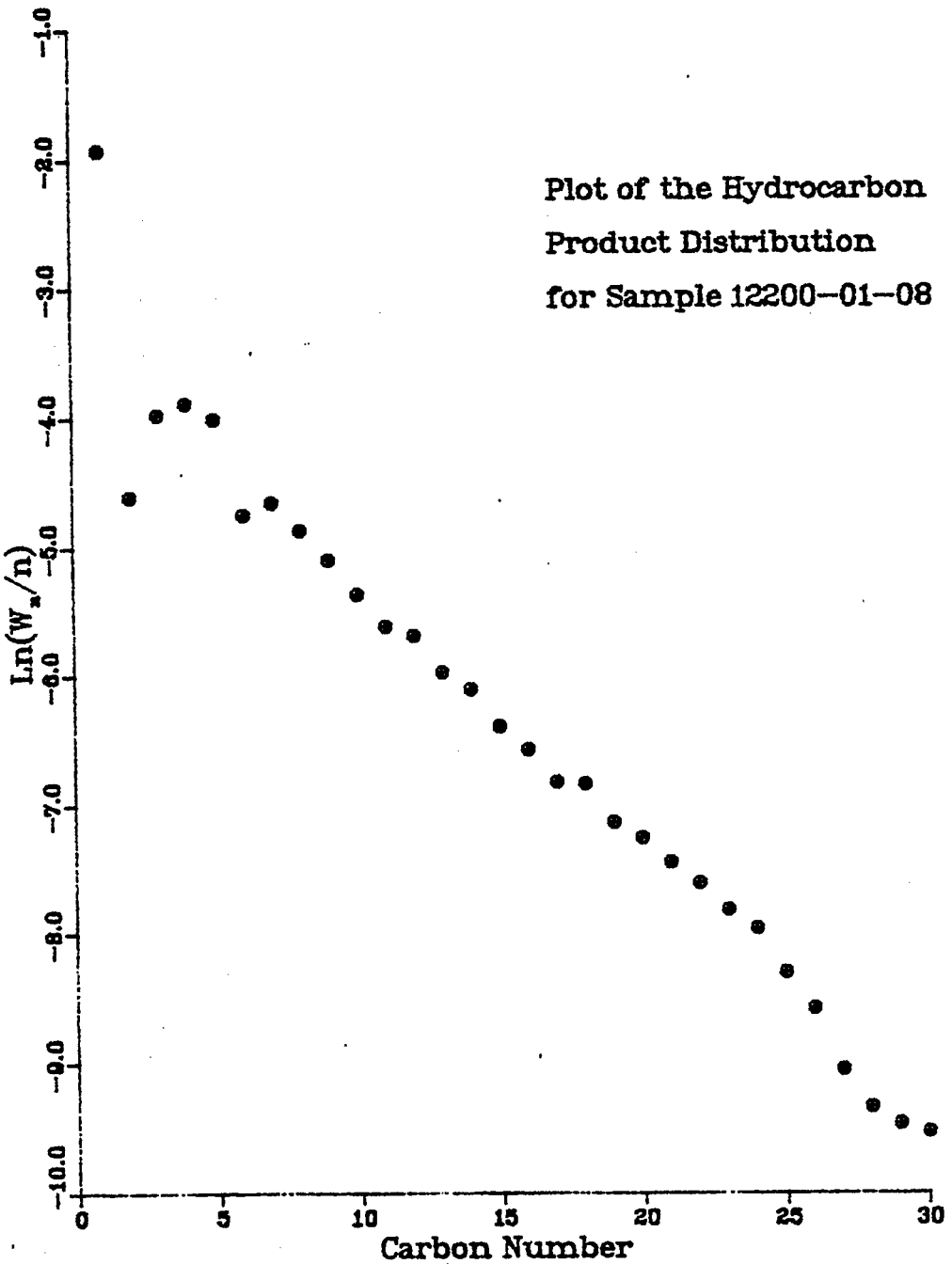

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-01-08
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B14

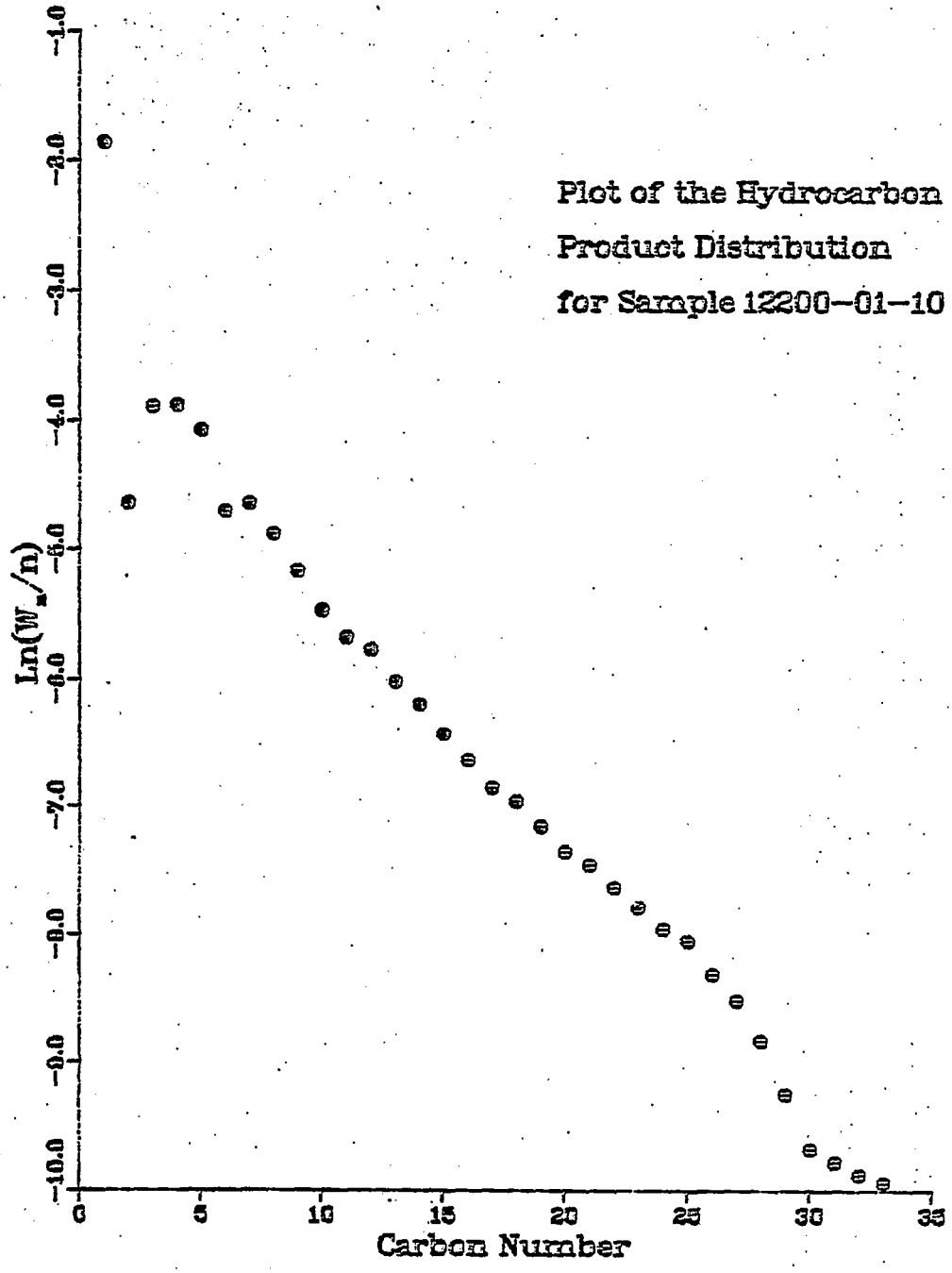

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-01-10
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B15

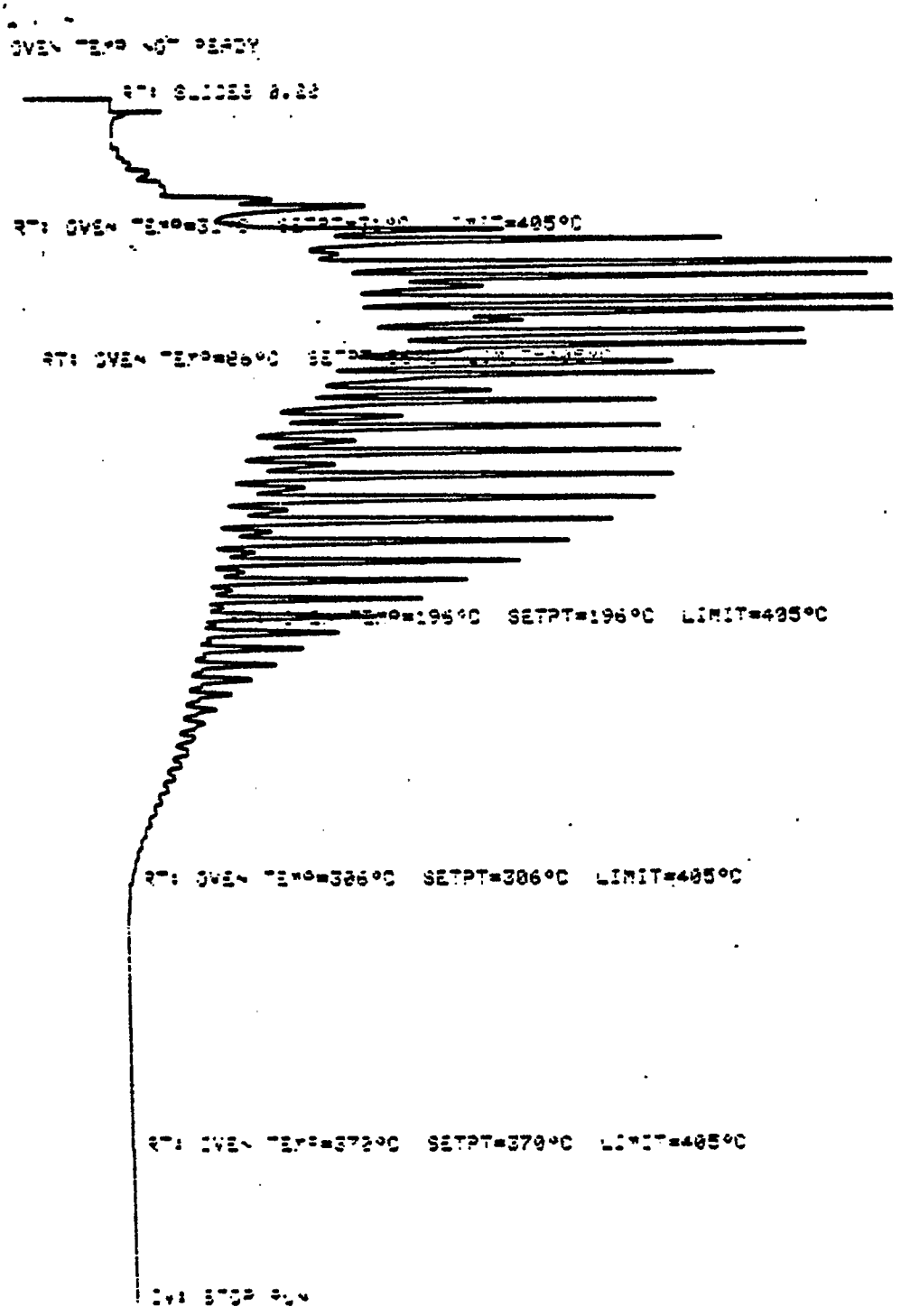
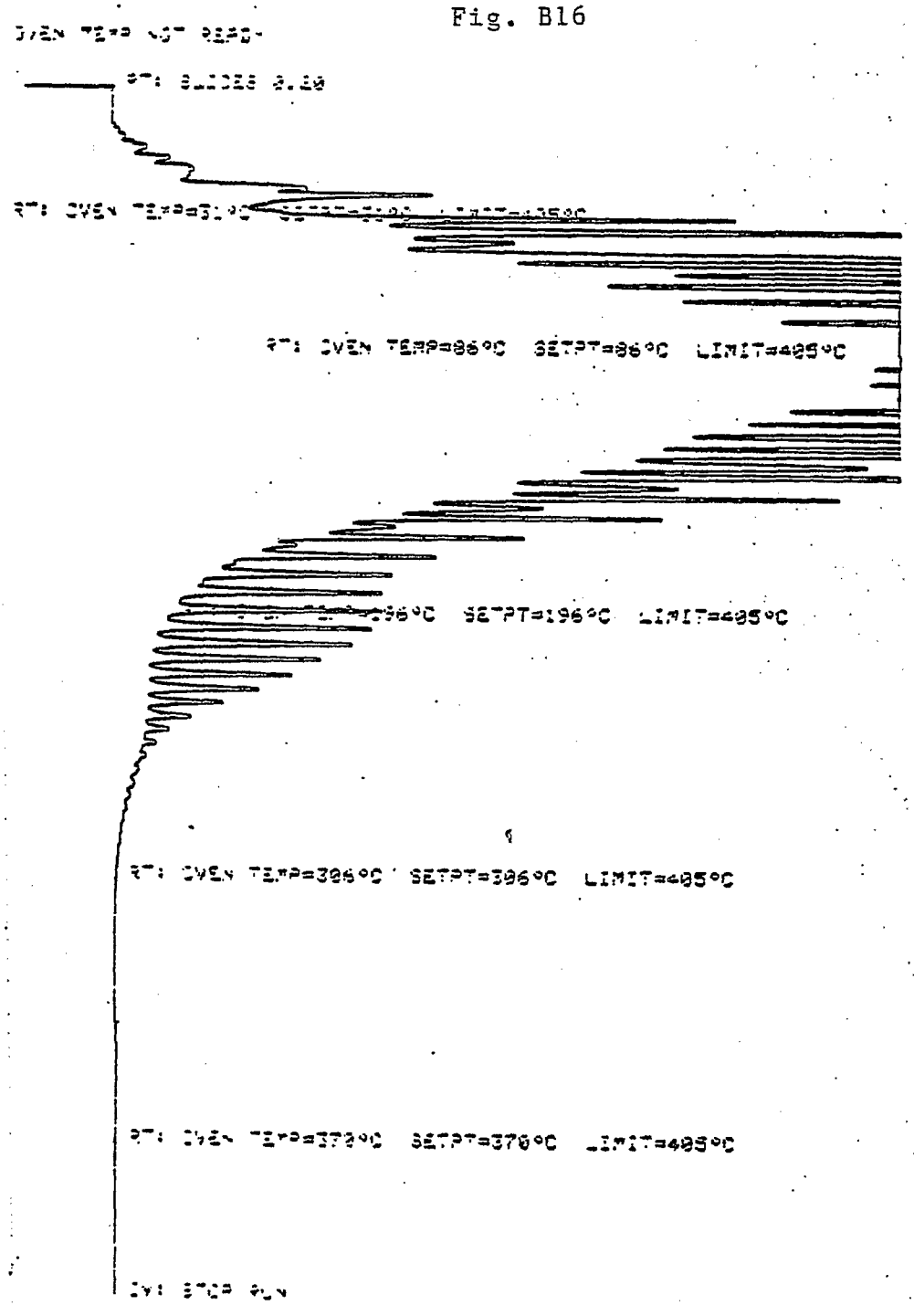
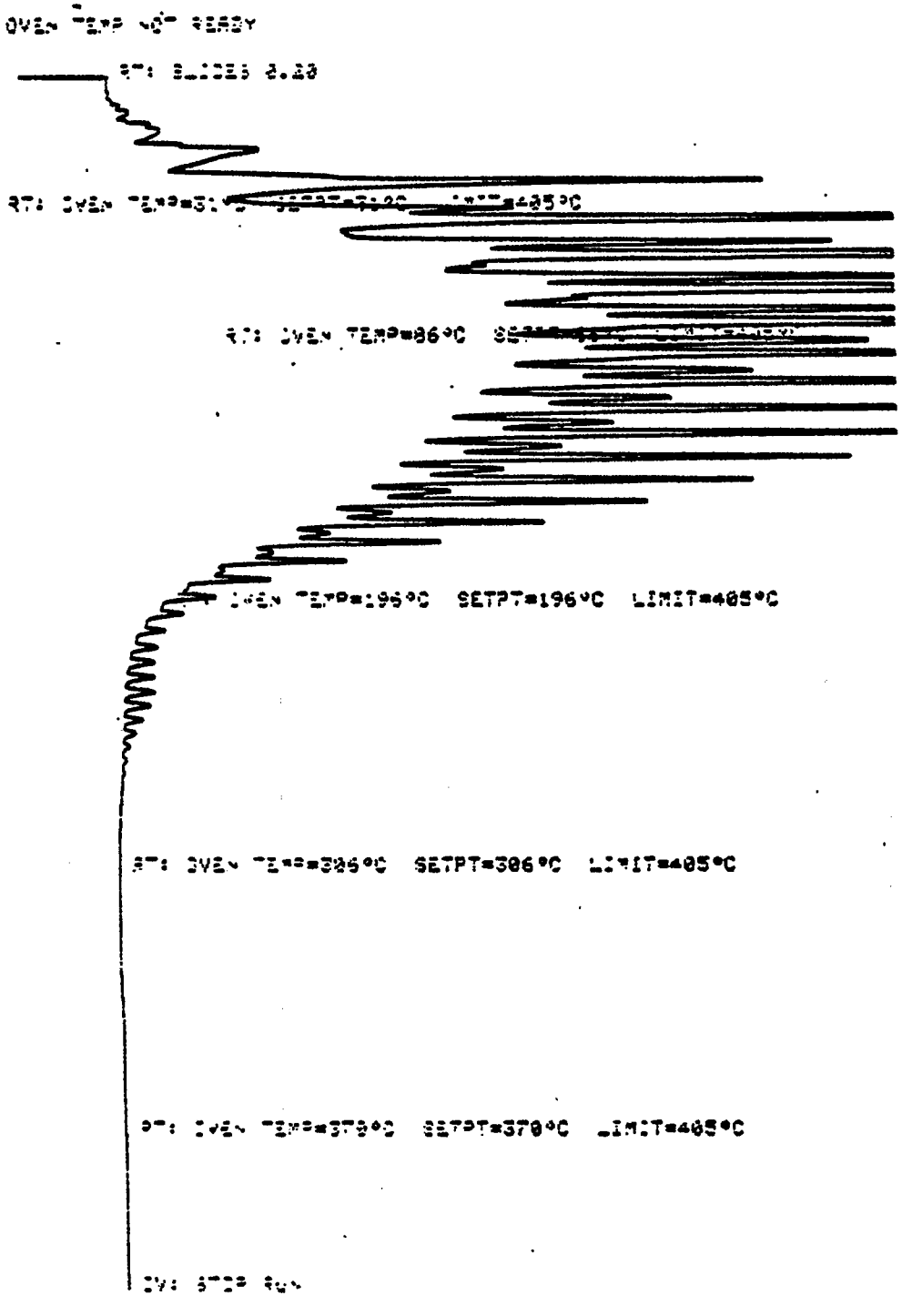

SETPT=196°C LIMIT=405°C
SETPT=306°C LIMIT=405°C
SETPT=370°C
12200-01-01

Fig. B16



12200-01-03

Fig. B17



12200-01-05

Fig. B18

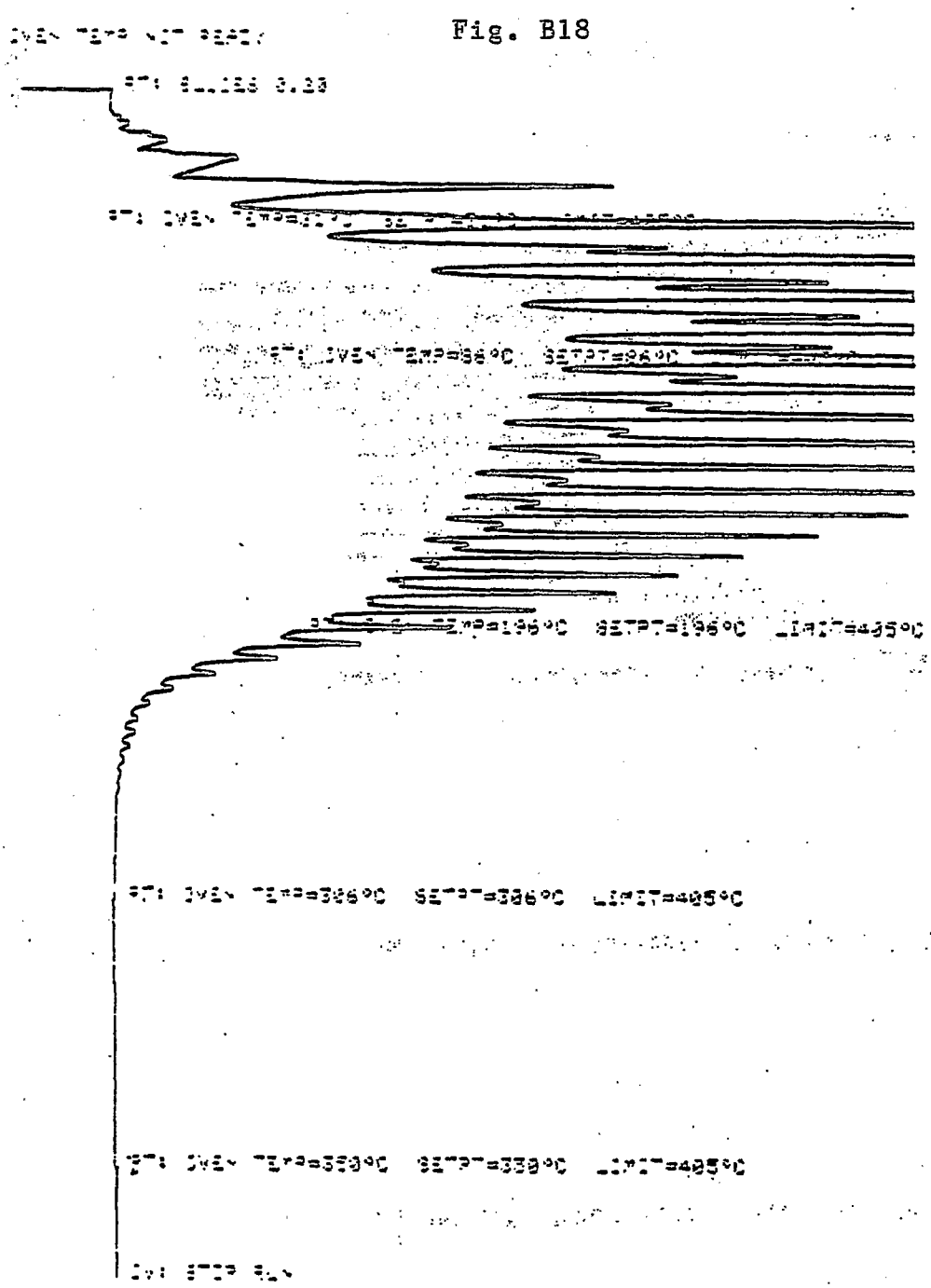


Fig. B19

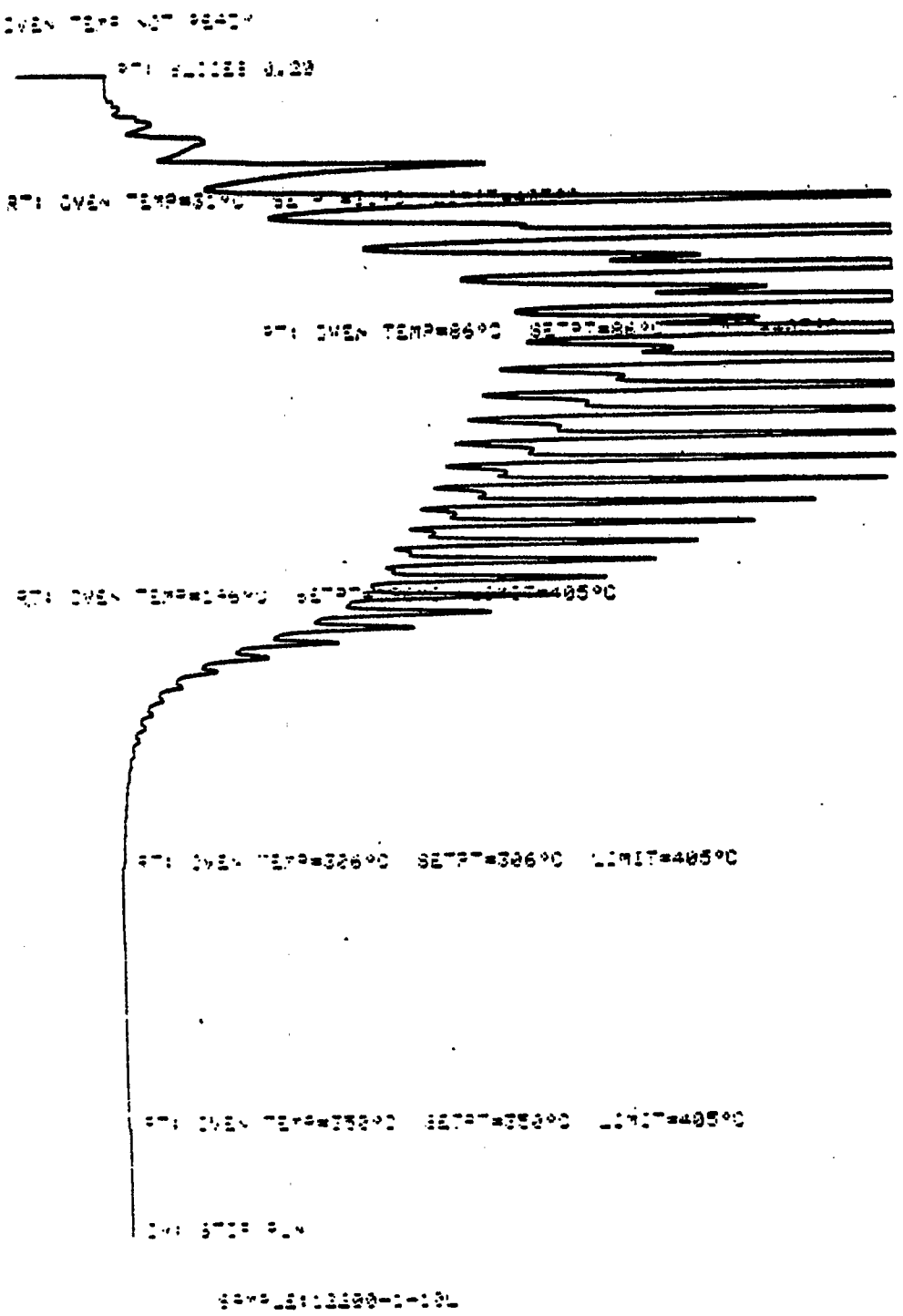


Table B1

RESULT OF SYNGAS OPERATION

RUN NO. 12200-01
CATALYST X3/K-U103+U101 12006-7 80 CC 40.8 GM (46.9 AFTER RUN +6.1G)
FEED H2:CO OF 50:50 @400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-01-01	200-01-03	200-01-05	200-01-08	200-01-10
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	69.5	116.5	164.5
PRESSURE,PSIG	100	100	300	300	300
TEMP. C	259	261	259	259	259
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.50	24.00	24.00	24.50	48.00
EFFLNT GAS LITER	351.10	473.05	365.40	431.35	860.95
GM AQUEOUS LAYER	21.95	19.79	47.55	31.16	54.49
GM OIL	3.90	1.82	12.16	6.59	11.25
MATERIAL BALANCE					
GM ATOM CARBON %	117.74	93.36	86.52	89.95	89.85
GM ATOM HYDROGEN %	121.92	93.87	91.54	90.94	90.47
GM ATOM OXYGEN %	91.65	98.38	96.37	96.64	95.97
RATIO CHX/(H2O+CO2)	2.6761	0.5971	0.6026	0.6106	0.6099
RATIO X IN CHX	2.0936	2.4804	2.2846	2.3598	2.3736
USAGE H2/CO PRODT	1.4172	2.8779	2.7788	2.7893	2.7946
FEED H2/CO FRM EFFLNT	1.0355	1.0054	1.0580	1.0110	1.0069
RESIDUAL H2/CO RATIO	0.8262	0.8415	0.6965	0.7745	0.7919
RATIO CO2/(H2O+CO2)	0.0037	0.0057	0.0037	0.0046	0.0051
K SHIFT IN EFFLNT	0.0031	0.0048	0.0026	0.0035	0.0041
SPECIFIC ACTIVITY SA	2.2950	0.3761	0.3658	0.2093	0.1849
CONVERSION					
ON CO %	35.42	8.05	17.36	11.74	10.73
ON H2 %	48.47	23.03	45.59	32.38	29.79
ON CO+H2 %	42.06	15.56	31.87	22.12	20.30
PRDT SELECTIVITY,WT %					
CH4	3.84	21.39	10.20	14.58	15.58
C2 HC'S	0.75	3.56	1.34	2.00	1.95
C3H8	0.34	1.72	1.15	1.52	1.60
C3H6=	1.18	6.43	3.58	4.13	4.54
C4H10	0.45	2.14	1.70	2.13	2.07
C4H8=	0.23	8.42	5.73	6.11	6.19
C5H12	0.89	3.40	2.48	2.57	2.35
C5H10=	1.27	6.92	5.76	6.56	6.23
C6H14	1.30	5.42	2.65	2.84	2.23
C6H12= & CYCLO'S	0.52	2.10	1.87	2.39	3.25
C7+ IN GAS	82.35	24.29	15.53	19.04	19.56
LIQ HC'S	6.89	14.22	48.02	36.12	34.45
TOTAL	100.00	100.00	100.00	100.00	100.00

Table B1 (continued)

SUB-GROUPING					
C1 -C4	6.79	43.64	23.70	30.47	31.92
C5 -420 F	89.09	47.35	48.45	45.51	43.96
420-700 F	3.13	8.28	26.41	21.38	19.29
700-END PT	0.98	0.73	1.44	2.64	4.82
C5+-END PT	93.21	56.36	76.30	69.53	68.08
ISO/NORMAL MOLE RATIO					
C4	0.3550	0.2656	0.1396	0.1056	0.0000
C5	0.8962	0.6455	0.2817	0.1362	0.0000
C6	2.1905	1.9643	0.4187	0.3089	0.0000
C4=	0.4727	0.0566	0.0455	0.0437	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.2768	0.2550	0.3075	0.3515	0.3360
C4	1.9321	0.2455	0.2859	0.3360	0.3228
C5	0.6819	0.4777	0.4185	0.3807	0.3664
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7722	0.7385	0.8013	0.8197	0.8290
RATIO CH4/(1-A)**2	0.7401	3.1273	2.5825	4.4877	5.3259
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	311	332	301	324	338
16	337	359	333	348	363
50	461	456	450	485	497
84	685	579	592	656	687
90	747	622	628	698	733
RANGE(16-84 %)	348	220	259	308	324
WT % @ 420 F	40.20	36.70	42.00	33.50	30.00
WT % @ 700 F	85.70	94.90	97.00	92.70	86.00

IV. Run 3 (12185-02) with Catalyst 3 (Co/X_7/UCC-103+UCC-101)

The purpose of this run was to test whether it is possible to reduce the production of methane, which has been unacceptably high with the cobalt catalysts tested to date, by the use of a metal additive, in this case X_7. The catalyst is to be compared with Third Annual Report Catalyst 2, (Co/Th/UCC-103+UCC-101, Run 11677-09).

The X_7-promoted cobalt oxide was formed in close contact with UCC-103. The resulting powder was mixed with UCC-101 in a weight ratio of 1.125:1, and the mixture, after bonding with 15 weight percent silica, was extruded as 1/8-inch pellets. The final catalyst contained 6.5 percent cobalt and 1.3 percent X_7.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B20-23. Simulated distillations of the C_5^+ product are plotted in Figs. B24-27. Carbon number product distributions are plotted in Figs. B28-31. Chromatograms from simulated distillations are reproduced in Figs. B32-35. Detailed material balances appear in Table B2.

The specific activity peaked at 0.40 after 41.1 hours on stream; the specific activity of Third Annual Report Catalyst 2, at approximately the same time on stream, was 1.3. The duration of the run was too short for reliable conclusions as to long term

stability. From an approximation based on a linear least squares analysis of the last 48 hours of the run, the catalyst deactivated at a rate of one percentage point every 14 hours; Third Annual Report Catalyst 2, during the first 120 hours, deactivated at a rate of one percentage point every 24 hours.

The water gas shift activity was extremely low, with only about 1.3 percent of the oxygen rejected as CO_2 and the remainder as H_2O, for an unusually high usage ratio of 2.6:1. With Third Annual Report Catalyst 2, 9 percent of the oxygen was rejected as CO_2, and the usage ratio was about 2.0:1.

The selectivity was fairly constant, although again the short duration of the run rules out any firm conclusions. The product in general was much lighter than that of Third Annual Report Catalyst 2: 43.6 percent C_1-C_4 as against 34.7 percent, 10.7 percent diesel fuel as against 16.7 percent, and gasoline nearly the same at about 45 percent. The differences appear to be due primarily to a depressing effect by X_7 on the catalyst's conversion of syngas, elevating the ratio of hydrogen to carbon monoxide in the reactor to 0.73:1, as against 0.41:1 for Third Annual Report Catalyst 2, leading to α values of 0.769 and 0.789 respectively.

To assess the effect of the additive X_7 on methane production, the mathematical model reported in Contract DE-AC22-81PC-4007 was applied. The ratio of weight percent CH_4 was calculated as

$$\text{exp/corr} = 0.875:1$$

where "exp" is the weight percent CH_4 actually produced and

"corr" is the weight percent predicted by the model. This is slightly less than the value of 1.176 calculated for Third Annual Report Catalyst 2.

Both the isomerization of the pentane and the olefin content of the C_4 were about the same as with Third Annual Report Catalyst 2. Aside from the high methane production, the Schulz-Flory plots show a fairly linear product distribution.

In this catalyst the additive X_7 did reduce the methane production slightly--an effect which was, however, nullified by a drastic loss of activity.

Fig. B20

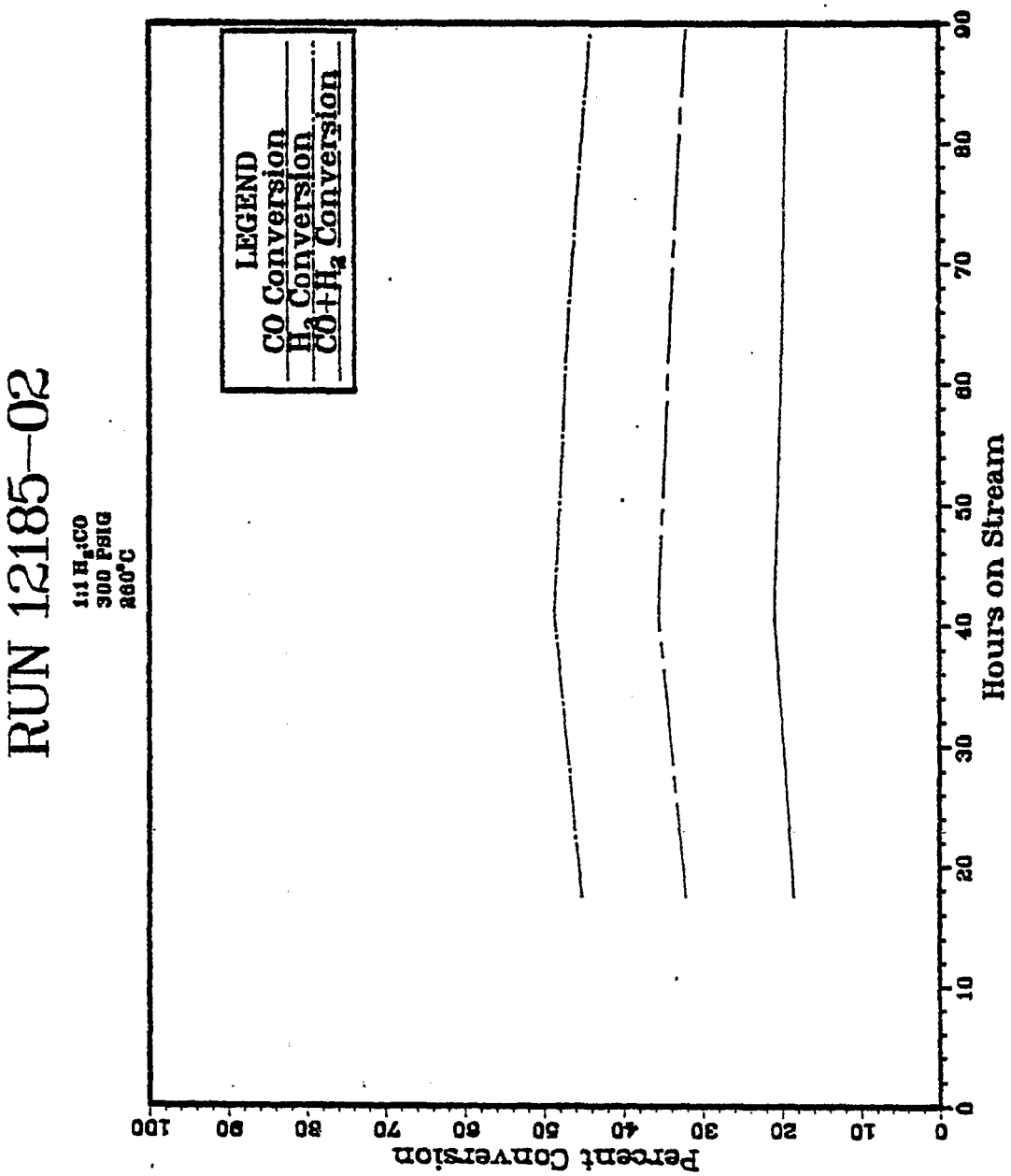

RUN 12185-02
1:1 H2:CO
300 PSIG
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B21

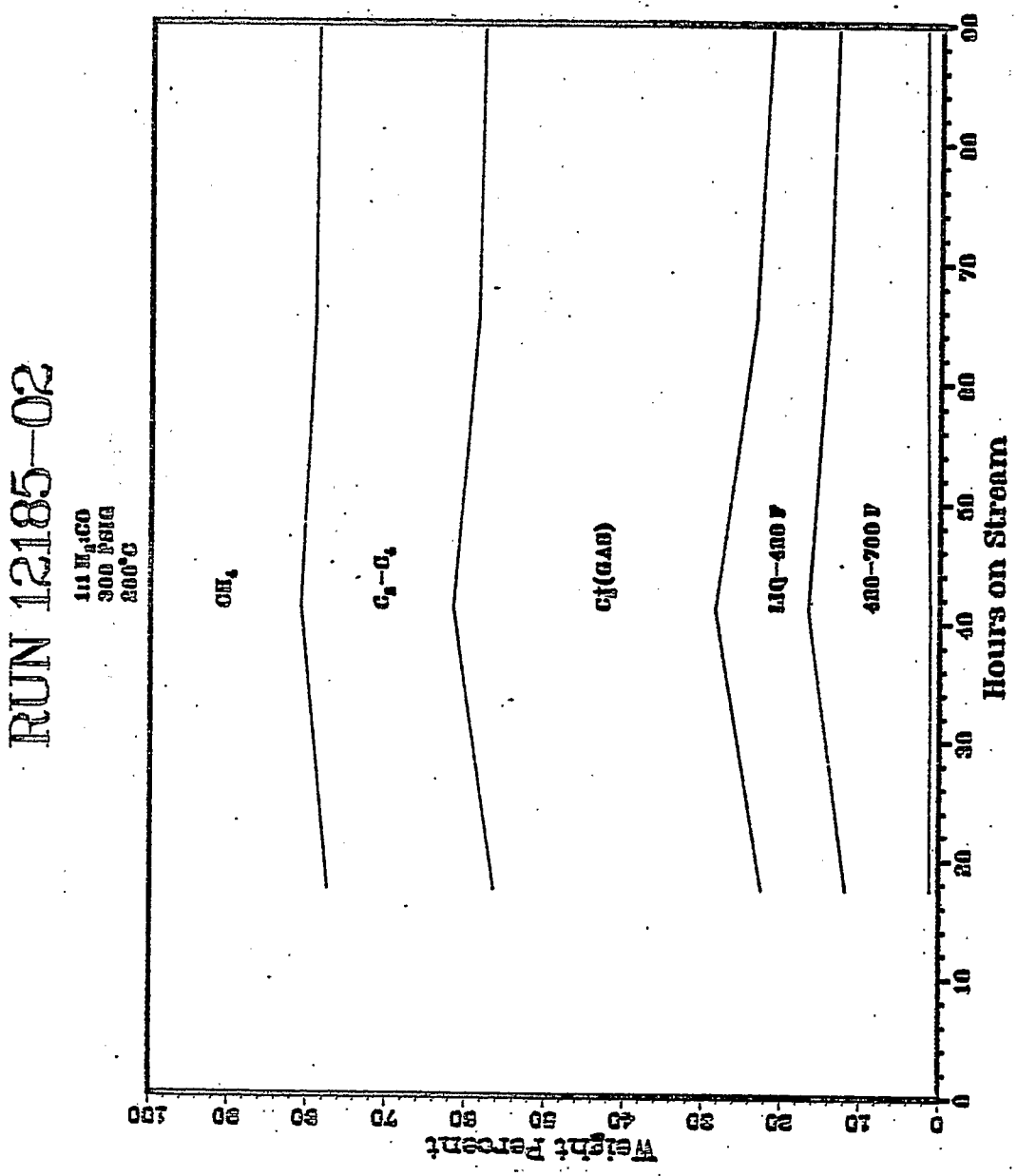

RUN 12185-02
1:1 H2:CO
300 PSIG
200°C
CH4
C2-C4
C5+(GAS)
LIQ-400 F
400-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B22

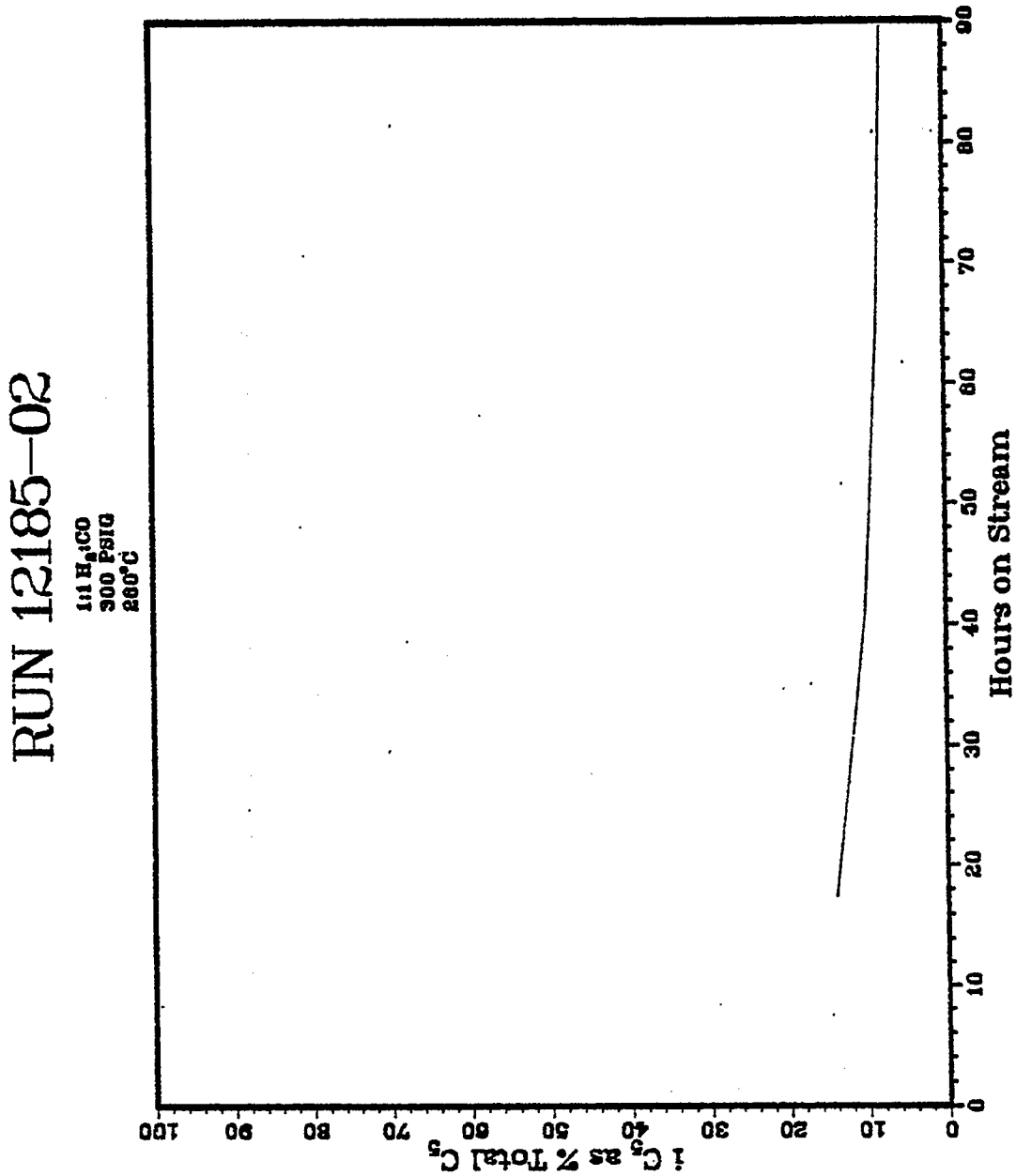

RUN 12185-02
1:1 H2:CO
300 PSIG
260°C
i C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
10
20
30
40
50
60
70
80
90

Fig. B23

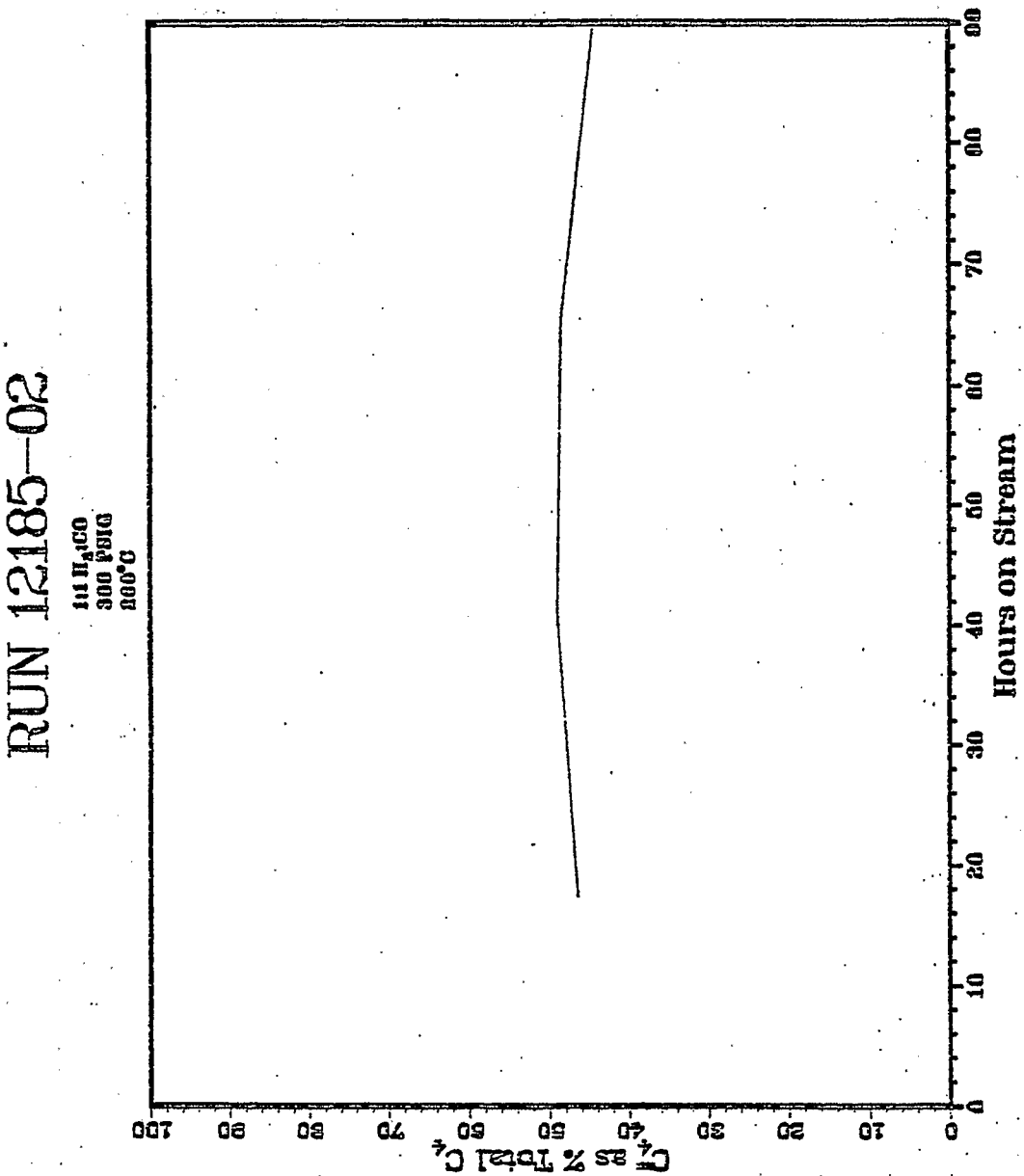

RUN 12185-02
111 H2CO
300 PSIG
800°C
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
C4 as % Total C4

Fig. B24

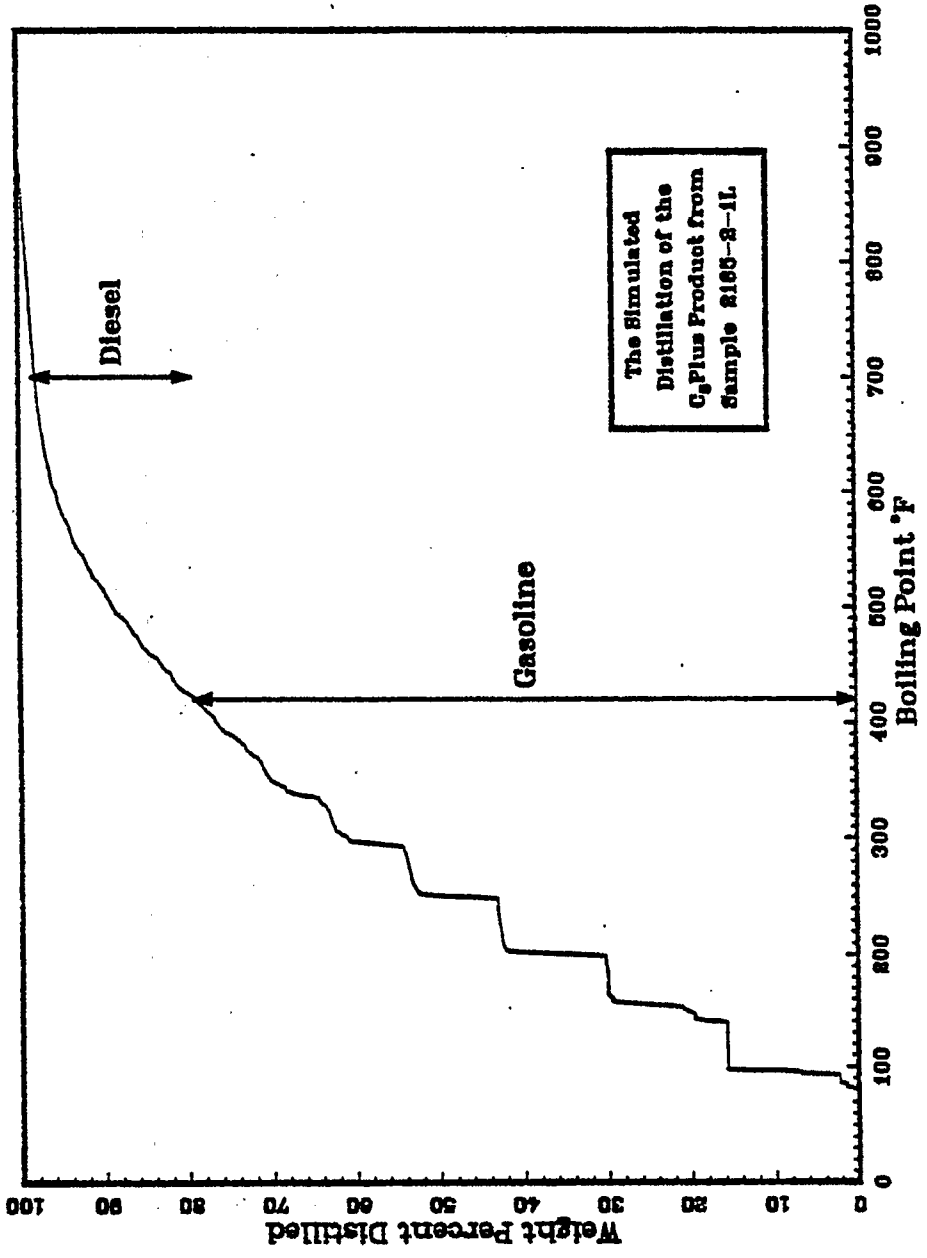

The Simulated Distillation of the C5 Plus Product from Sample 8186-3-1L
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B25

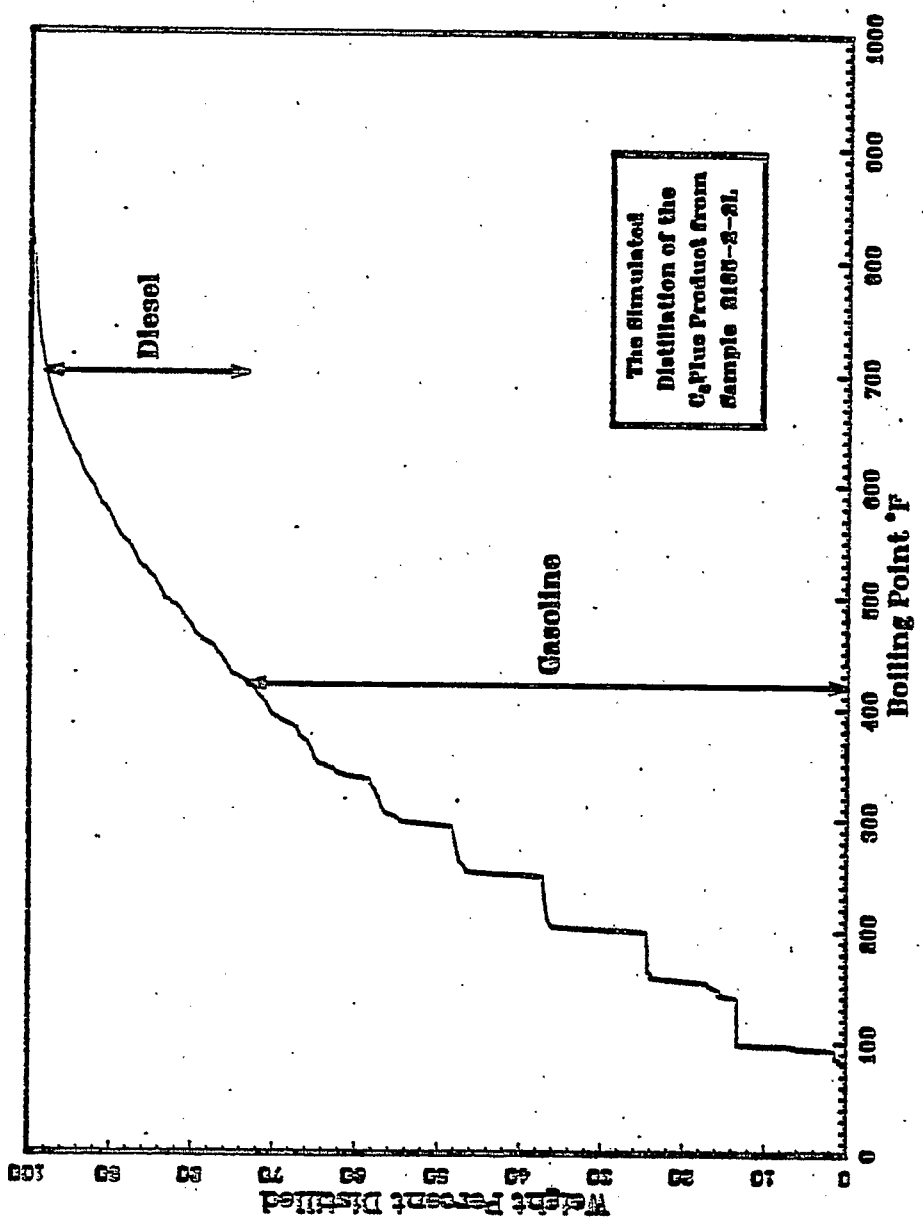

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 8160-2-2L
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B26

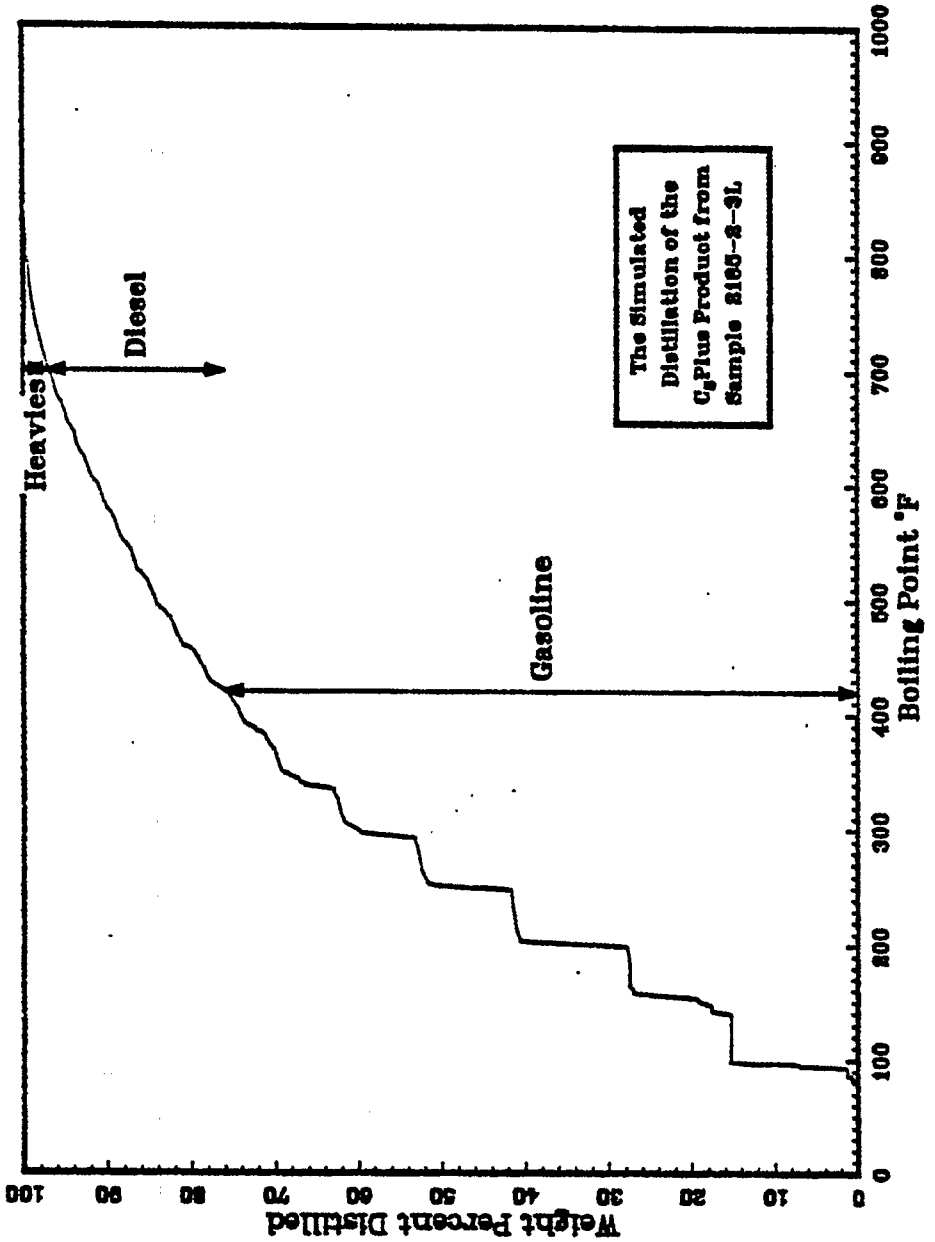

The Simulated Distillation of the C5Plus Product from Sample 8185-2-3L
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B27

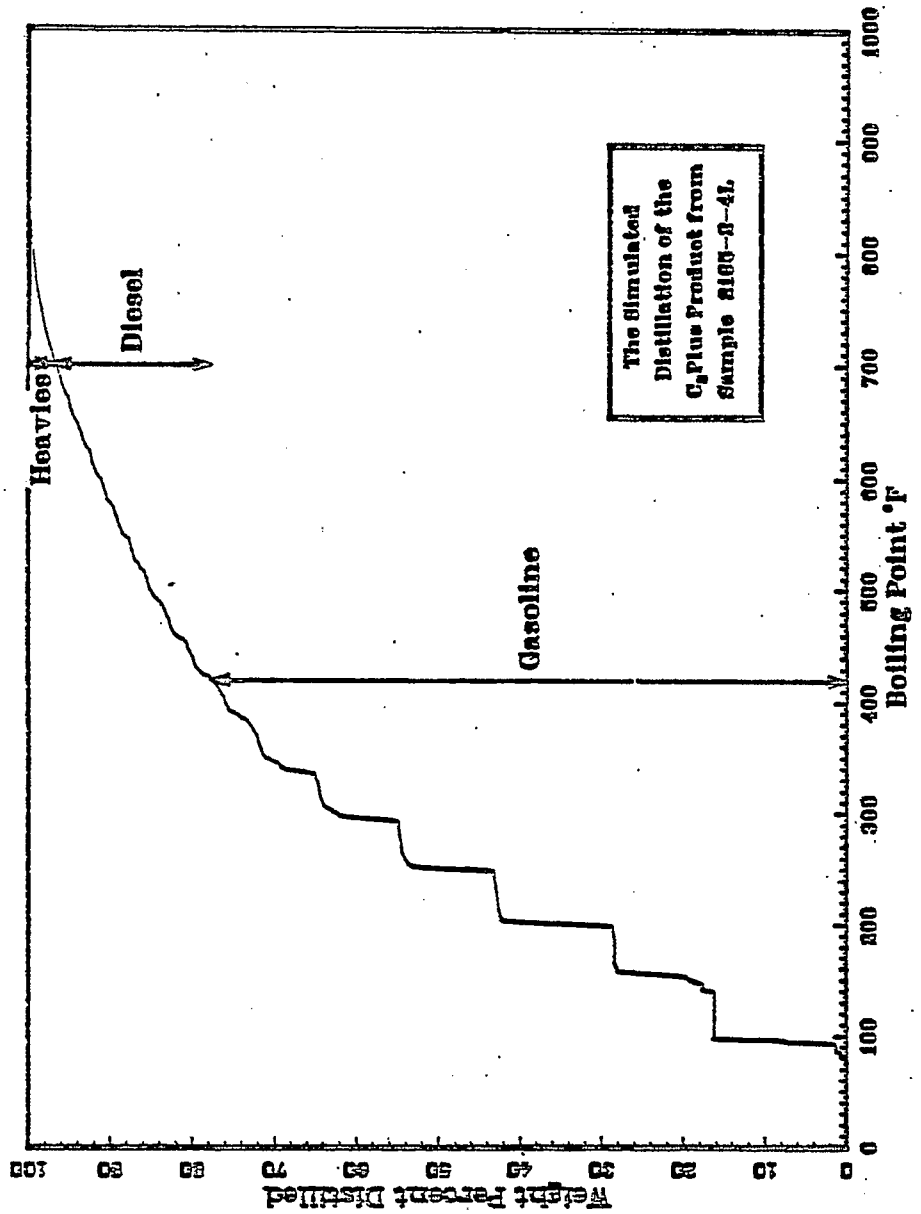

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 8108-3-41.
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B28

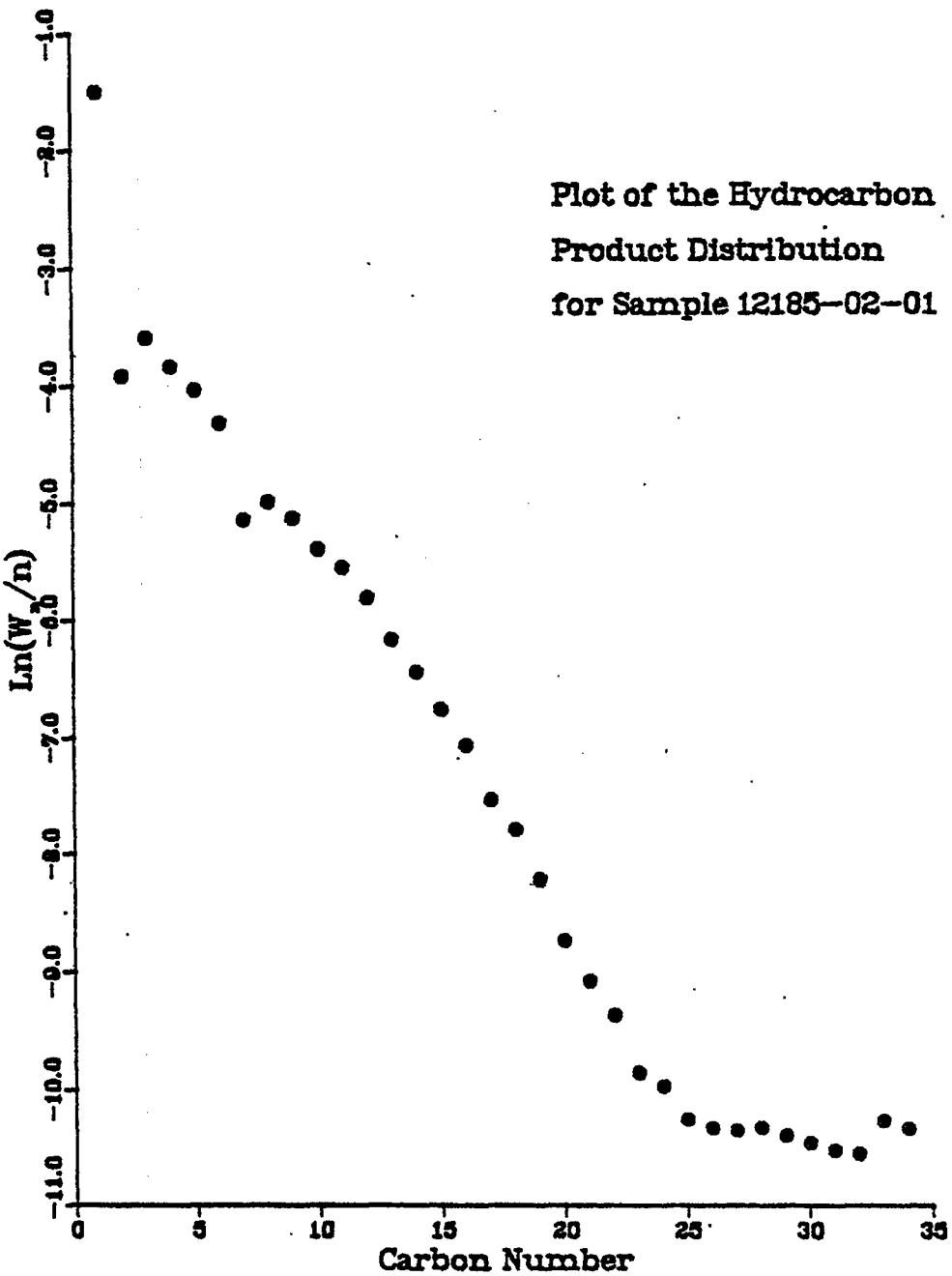

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-02-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B29

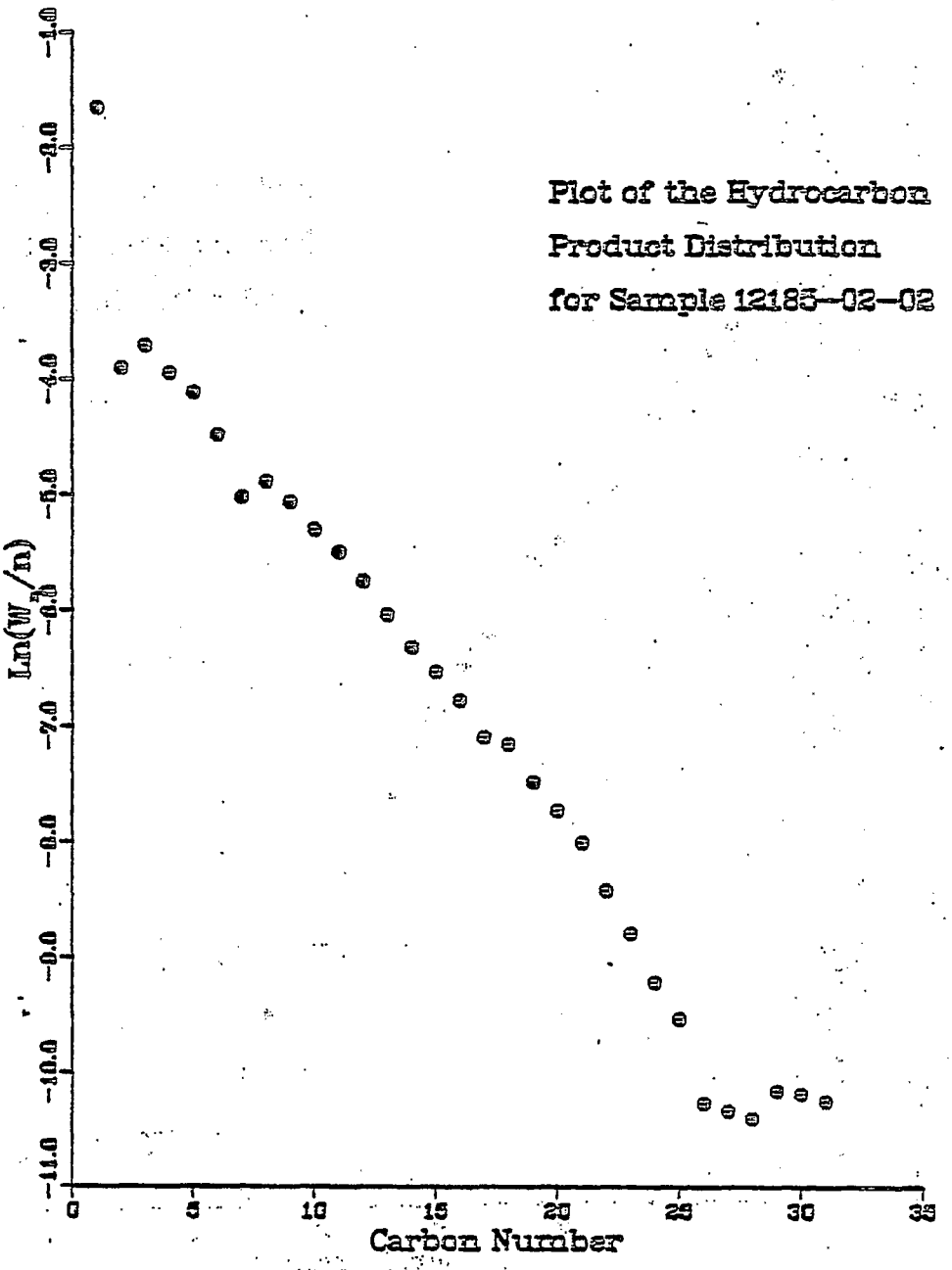

Plot of the Hydrocarbon
Product Distribution
for Sample 12183-02-02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B30

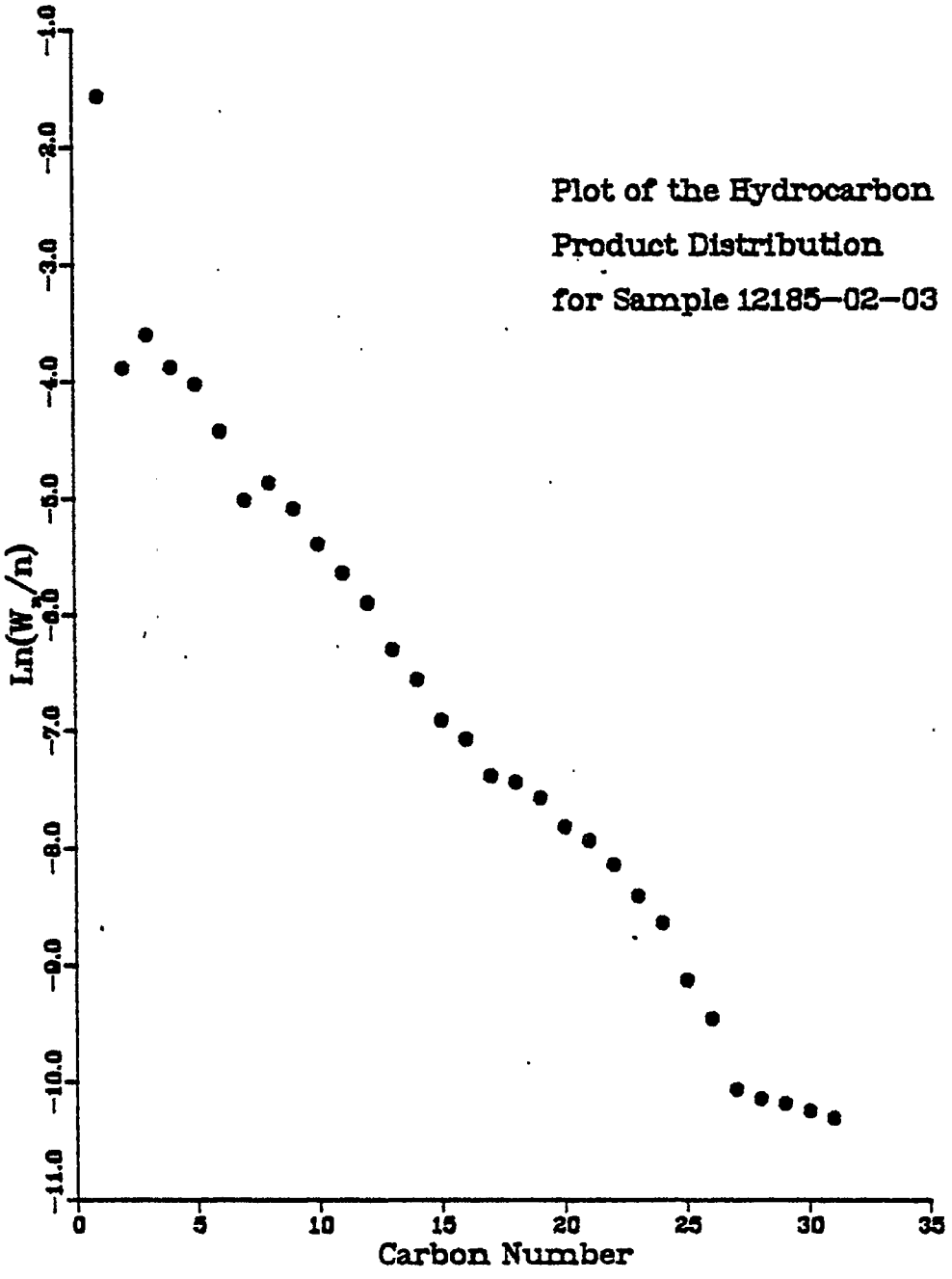
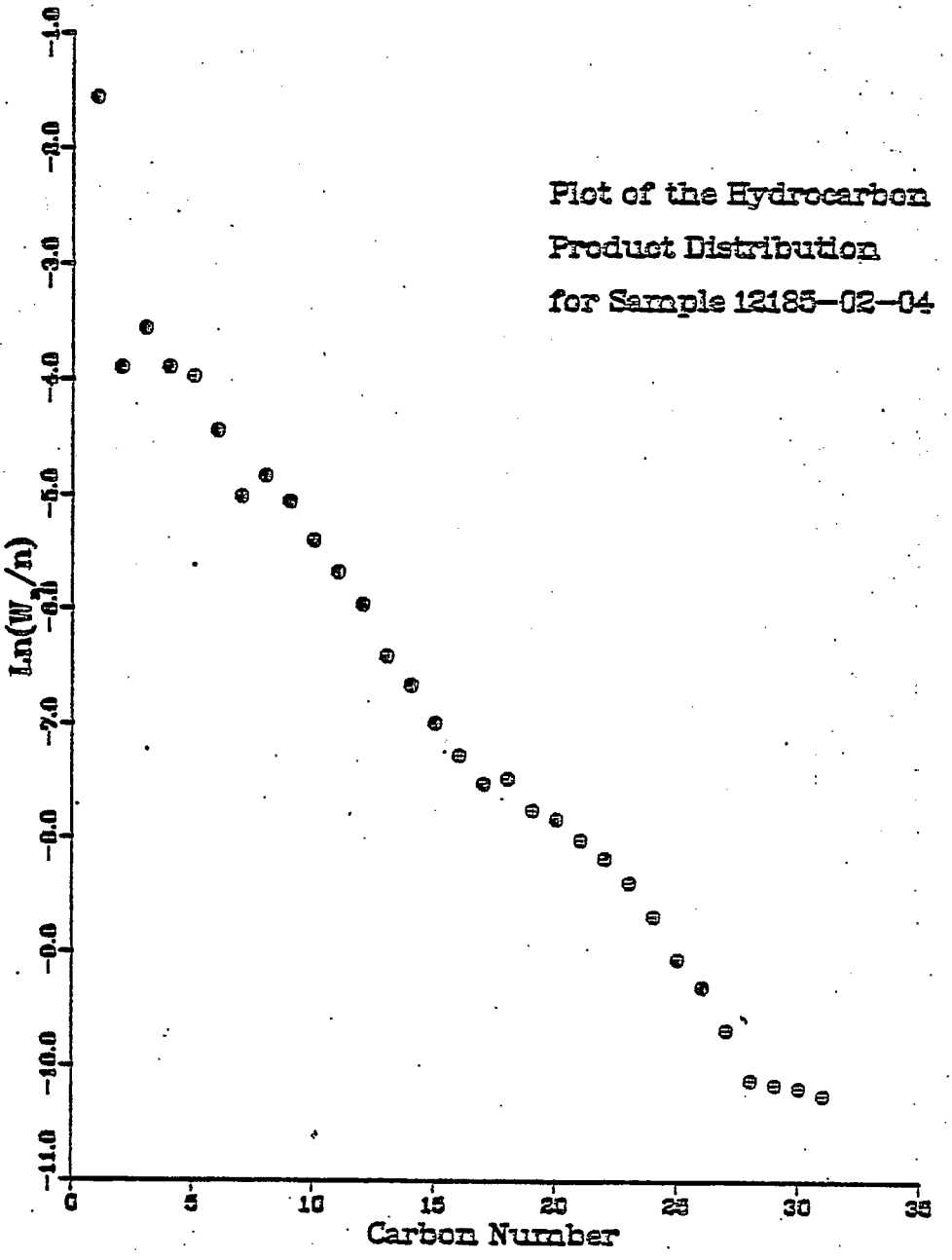

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-02-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B31


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-02-04
Ln(Wn/n)
-1.0
-3.0
-5.0
-7.0
-9.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

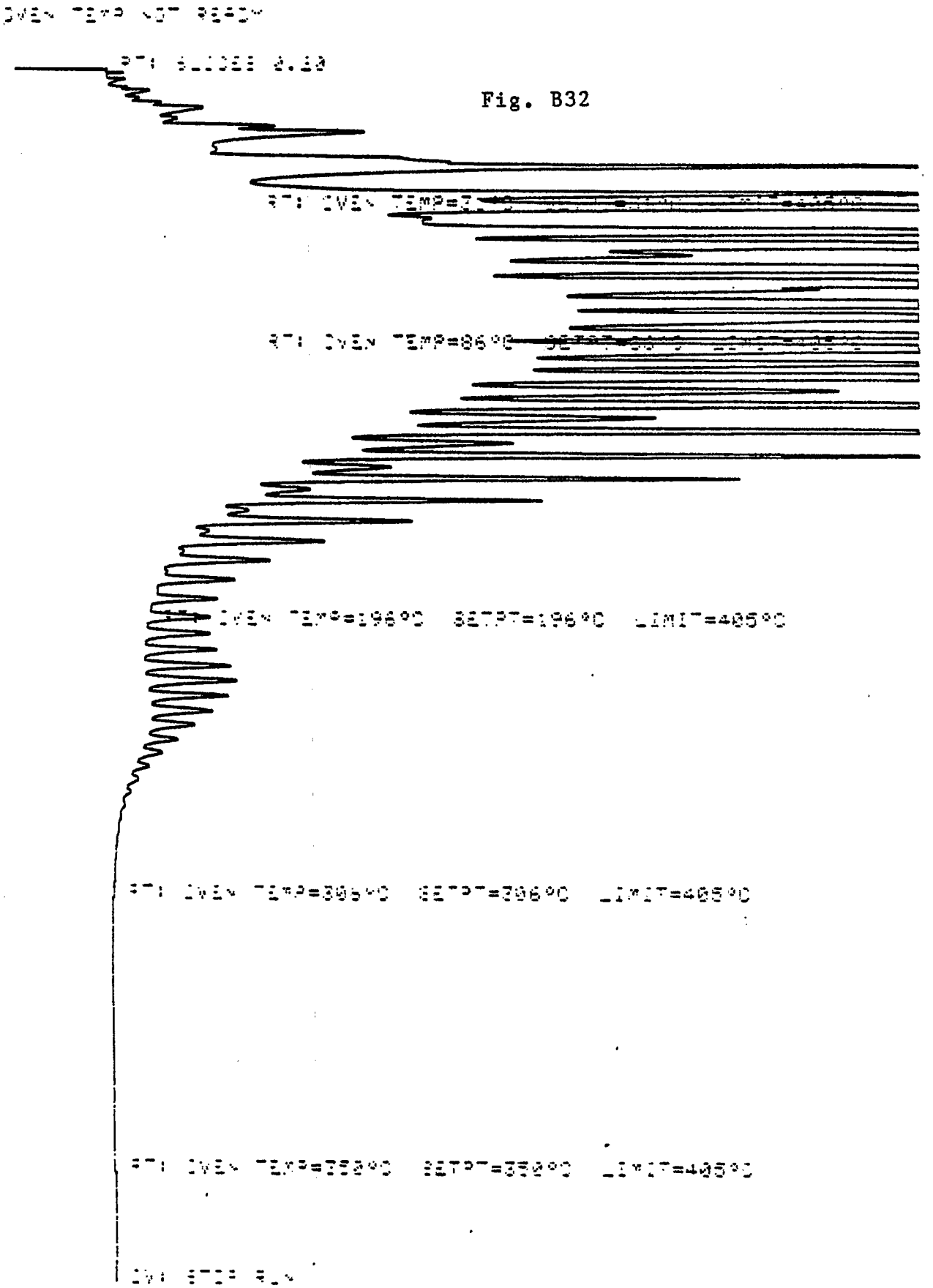

OVEN TEMP NOT READY
PT: 01:00:00 0.00
PT: OVEN TEMP=7
PT: OVEN TEMP=86°C
OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
PT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
OVEN PT: R_N

Fig. B32

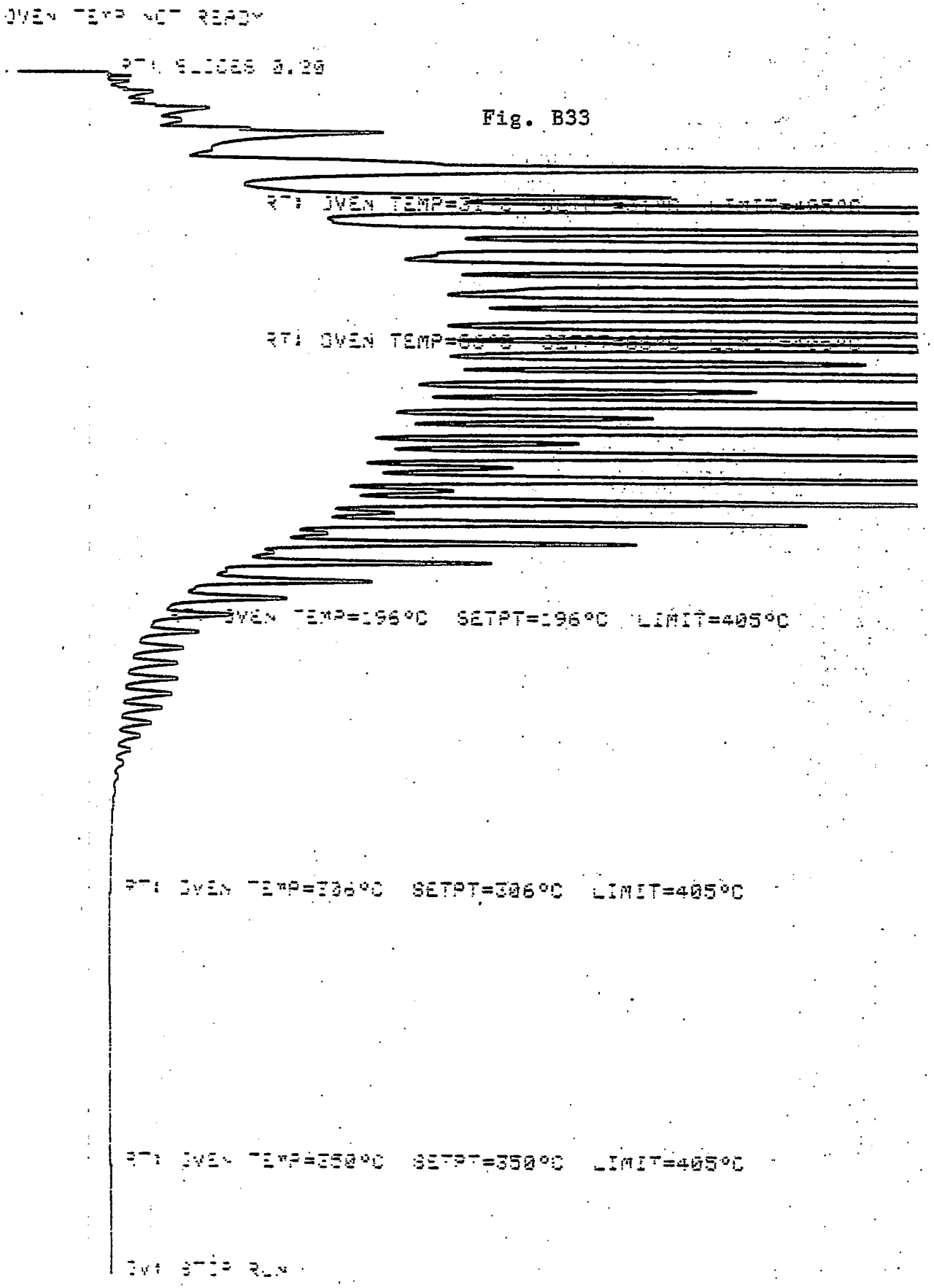
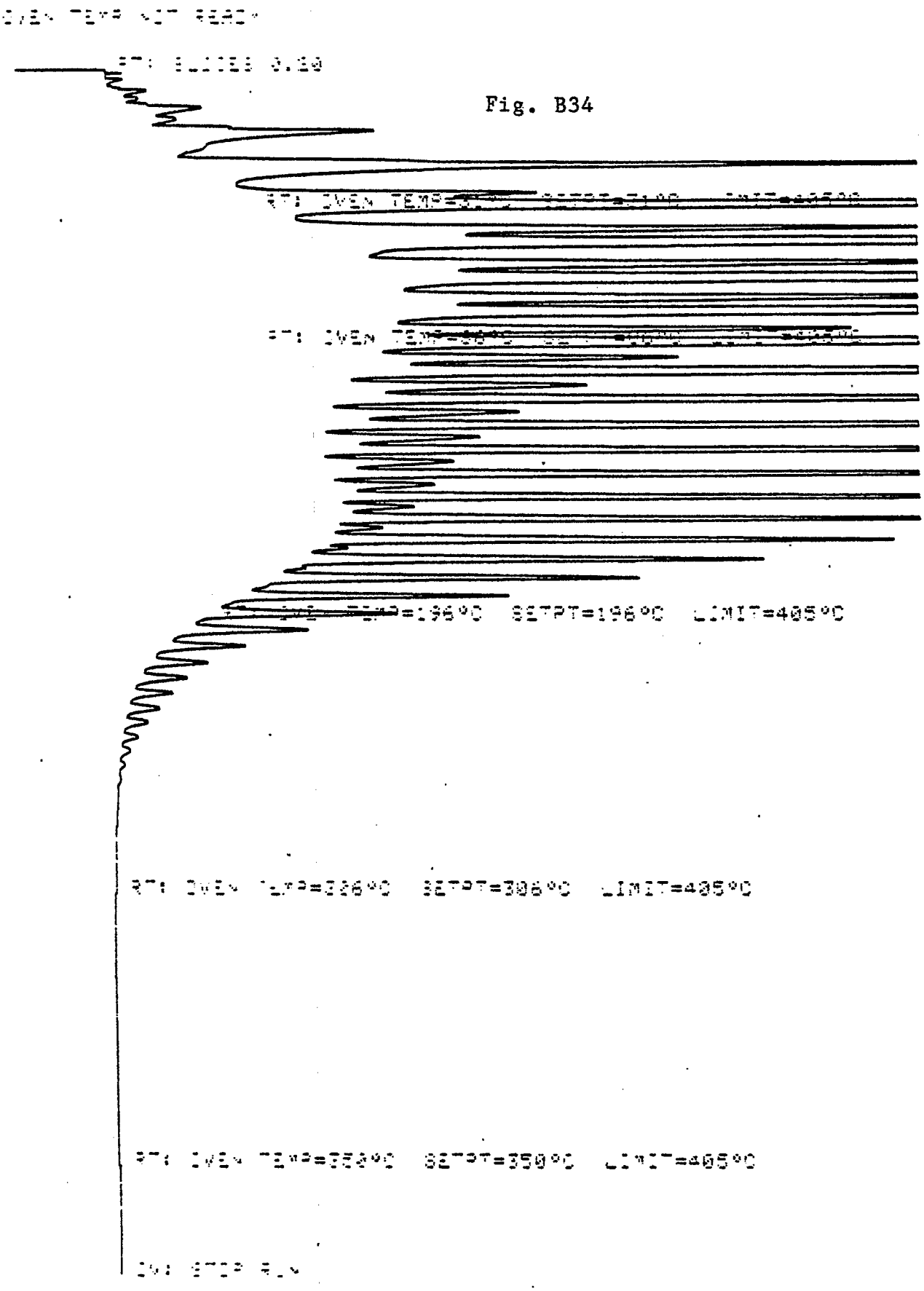

OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. B33

Fig. B34



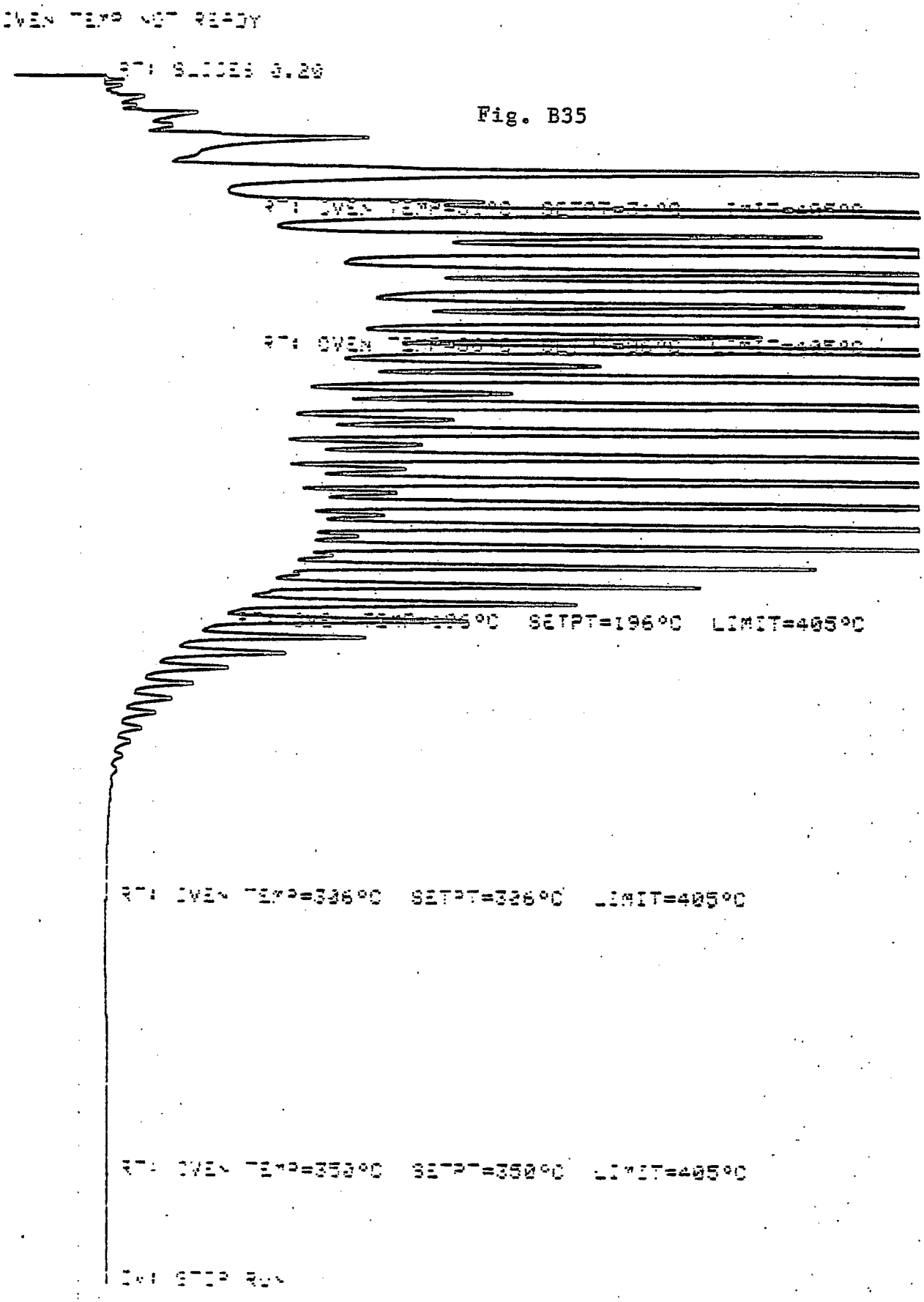

SETPT=196°C LIMIT=405°C
T=336°C SETPT=336°C LIMIT=405°C
T=350°C SETPT=350°C LIMIT=405°C

Fig. B35

Table B2

RESULT OF SYNGAS OPERATION

RUN NO. 12185-02
CATALYST CO/X7-U103+U101 12006-34 250 CC 119.GM (115. AFTER RUN -4. G)
FEED H2:CO OF 50:50 @1260 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-02-01	185-02-02	185-02-03	185-02-04
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	17.5	41.1	65.4	89.5
PRESSURE,PSIG	300	300	300	300
TEMP. C	261	261	261	261
FEED CC/MIN	1260	1260	1260	1260
HOURS FEEDING	17.50	23.51	24.30	24.10
EFFLNT GAS LITER	874.30	1178.90	1217.55	1239.25
GM AQUEOUS LAYER	92.94	155.57	149.34	122.77
GM OIL	14.40	28.07	22.11	20.05
MATERIAL BALANCE				
GM ATOM CARBON %	88.88	90.64	88.85	90.51
GM ATOM HYDROGEN %	93.43	101.65	98.90	96.58
GM ATOM OXYGEN %	94.63	98.66	96.56	94.71
RATIO CHX/(H2O+CO2)	0.7368	0.6983	0.6907	0.8020
RATIO X IN CHX	2.5879	2.5117	2.5479	2.5557
USAGE H2/CO PRODT	2.5613	2.6005	2.6232	2.4307
FEED H2/CO FRM EFFLNT	1.0512	1.1214	1.1131	1.0671
RESIDUAL H2/CO RATIO	0.7064	0.7288	0.7380	0.7404
RATIO CO2/(H2O+CO2)	0.0186	0.0170	0.0188	0.0220
K SHIFT IN EFFLNT	0.0134	0.0126	0.0141	0.0166
SPECIFIC ACTIVITY SA	0.3732	0.4037	0.3736	0.3641
CONVERSION				
ON CO %	18.59	20.98	19.90	19.33
ON H2 %	45.29	48.65	46.89	44.03
ON CO+H2 %	32.27	35.61	34.12	32.08
PRDT SELECTIVITY,WT %				
CH4	22.61	19.21	20.86	21.11
C2 HC'S	4.00	4.03	4.10	4.07
C3H8	5.87	5.16	5.77	6.12
C3H6=	2.41	2.20	2.44	2.48
C4H10	4.71	4.01	4.34	4.62
C4H8=	3.95	3.73	3.95	3.57
C5H12	5.71	4.80	5.16	5.50
C5H10=	3.17	3.38	3.78	3.90
C6H14	6.99	5.72	5.97	5.86
C6H12= & CYCLO'S	1.08	1.11	1.24	1.22
C7+ IN GAS	17.04	18.22	19.10	20.01
LIQ HC'S	22.46	28.43	23.31	21.53
TOTAL	100.00	100.00	100.00	100.00

Table B2 (continued)

SUB-GROUPING				
C1 -C4	43.55	38.35	41.45	41.98
C5 -420 F	44.62	44.96	44.45	45.00
420-700 F	10.71	15.44	12.36	11.13
700-END PT	1.12	1.25	1.75	1.90
C5+-END PT	56.45	61.65	58.55	58.02
ISO/NORMAL MOLE RATIO				
C4	0.1176	0.0896	0.0798	0.0745
C5	0.1624	0.1131	0.0923	0.0846
C6	0.4511	0.3271	0.2953	0.1697
C4=	0.0331	0.0471	0.0515	0.0664
PARAFFIN/OLEFIN RATIO				
C3	2.3219	2.2367	2.2571	2.3542
C4	1.1508	1.0398	1.0602	1.2483
C5	1.7516	1.3787	1.3265	1.3703
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.7468	0.7693	0.7816	0.7839
RATIO CH4/(1-A)**2	3.5261	3.6114	4.3738	4.5196
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLD OIL	CLD OIL	CLR OIL	CLR OIL
DENSITY	0.7554	0.7570	0.7580	0.7578
N, REFRACTIVE INDEX	1.4259	1.4269	1.4270	1.4269
SIMULT'D DISTILATN				
10 WT % @ DEG F	302	303	304	304
16	328	332	338	339
50	426	448	457	457
84	559	601	635	649
90	606	642	677	692
RANGE(16-84 %)	231	269	297	310
WT % @ 420 F	47.30	41.30	39.50	39.50
WT % @ 700 F	95.00	95.60	92.50	91.20

V. Run 4 (12185-03) with Catalyst 4 (Co/UCC-103)

The purpose of this run was to test the effect on catalytic activity of a relatively high concentration of cobalt in intimate contact with UCC-103 alone, omitting any other metal additives or Molecular Sieves.

The cobalt oxide was formed in close contact with UCC-103, and after bonding with 15 weight percent silica the mixture was extruded as 1/8-inch pellets. The final catalyst contained 17.0 percent cobalt.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B36-39. Simulated distillations of the C_5^+ product are plotted in Figs. B40-49. Carbon number product distributions are plotted in Figs. B50-59. Chromatograms from simulated distillations are reproduced in Figs. B60-69. Detailed material balances appear in Tables B3-4.

The catalyst was activated and run at an initial reactor pressure of 100 psig, which was raised to 300 psig about half-way through the run. During the first half, at 100 psig, the calculated specific activity was extraordinarily high, as much as 15.3, and calculated conversion at 19.25 hours on stream was 71.9 percent. The mathematical model used to determine specific activity, however, is based mainly on 300 psig pressure tests and

breaks down under large changes of pressure. A more realistic value was obtained during the last half of the run at 300 psig: at 138.5 hours on stream, after 24 hours at 300 psig, the specific activity was 8.0.

In agreement with previous tests of catalysts lacking the stabilizing additives thorium and X_4, the stability was poor. As estimated by least squares analysis, the rate of deactivation during the first 114 hours on stream, at 100 psig, was one percentage point every 31.8 hours. During the rest of the run, at 300 psig, it accelerated sharply to one percentage point every 6 hours, while the specific activity plummeted from 8.0 at 138.5 hours to 1.8 at 234.5 hours. The greatly accelerated deactivation at 300 psig may have been due to the lower residual ratios of hydrogen to carbon monoxide resulting from the observed increase in conversion.

The product selectivity also deteriorated rapidly with time on stream. During the first 114.5 hours, at 100 psig, methane production rose from 18.8 to 21.4 percent, equivalent, by linear least squares analysis, to a rate of increase of one percentage point every 40.5 hours. When the pressure was raised to 300 psig the methane production dropped to 8.0 percent, then rose again to 20.2 percent at the end of the run--an estimated rate of increase of one percentage point every 6.8 hours.

Production of C_5^+ followed a similar (complementary) pattern. During the first 114.5 hours on stream the C_5^+ portion of total product decreased from 66.1 to 62.7 percent, an estimated rate of

decrease of one percentage point every 30 hours. When the pressure was raised to 300 psig it jumped to 81.2 percent, then decreased to 66.4 percent at the end of the run, an estimated rate of decrease of one percentage point every 6.0 hours.

Approximately 20 percent of the oxygen was rejected as CO_2, roughly twice as high as usual for catalysts of this type. The H_2/CO usage ratio was correspondingly low, in the range of 1.6 to 1.9.

The olefin content of the C_4's fell from 56 percent butene initially to 50 percent after 114.8 hours. When the pressure was raised to 300 psig the butene content increased to 60 percent, then declined during the rest of the run to about 42 percent at the end. Isomerization of the pentane at 100 psig was constant at about 10 percent, and at 300 psig dropped to about 5 percent. Aside from the excess methane, the Schulz-Flory plots once again show a fairly straight line product distribution.

This test has demonstrated that substantially higher activity may be obtained by confining the catalyst to a single Molecular Sieve and raising the concentration of the metal component. But additives are still needed to improve the catalyst's stability.

Fig. B36

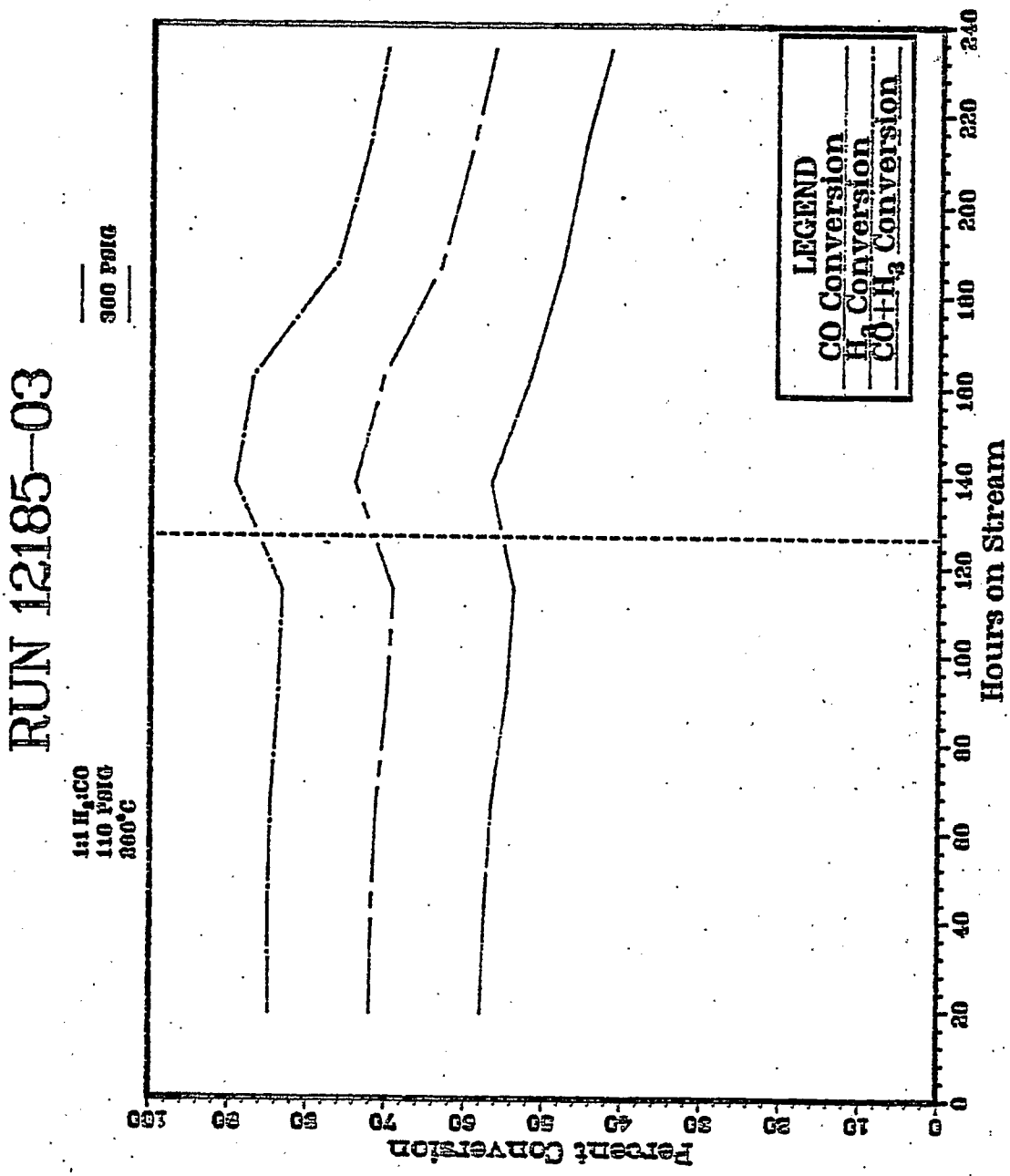

RUN 12185-03
1:1 H2:CO
110 PSIG
260°C
300 PSIG
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. B37

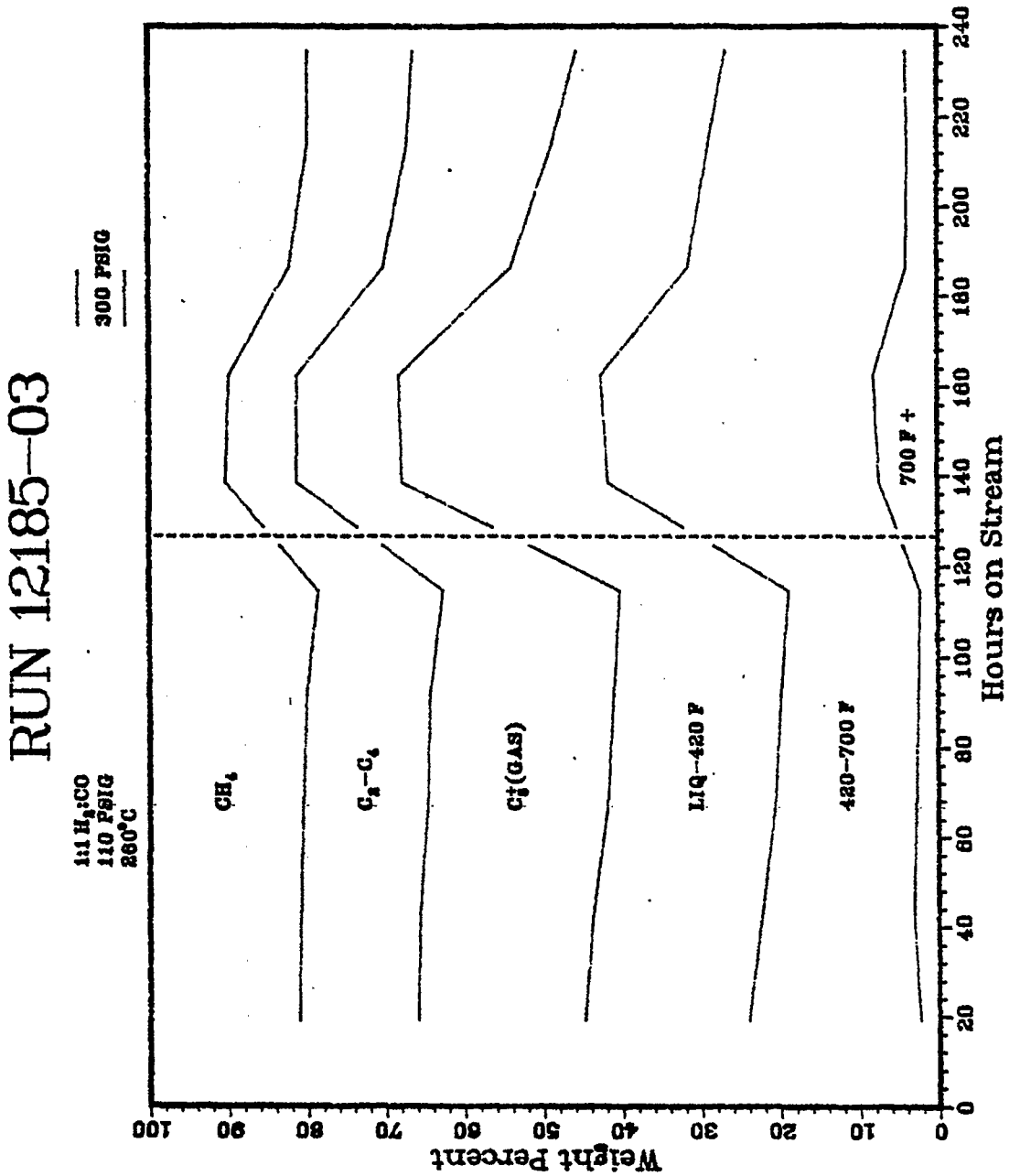

RUN 12185-03
1:1 H2:CO
110 PSIG
260°C
300 PSIG
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. B38

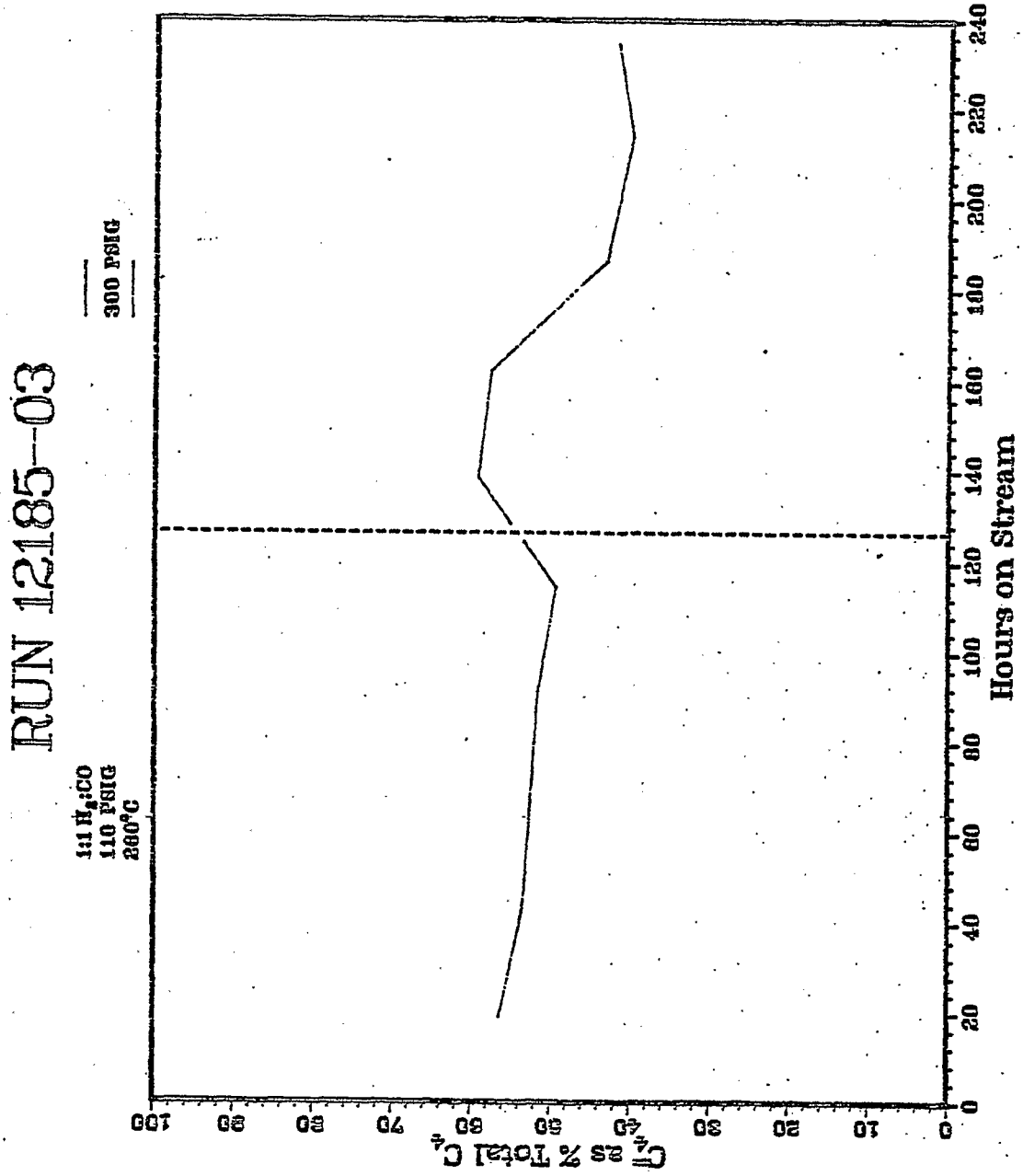

RUN 12185-03
1:1 H2:CO
110 PSIG
280°C
300 PSIG
C4= as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
220
240
10
20
30
40
50
60
70
80
90
100

Fig. B39

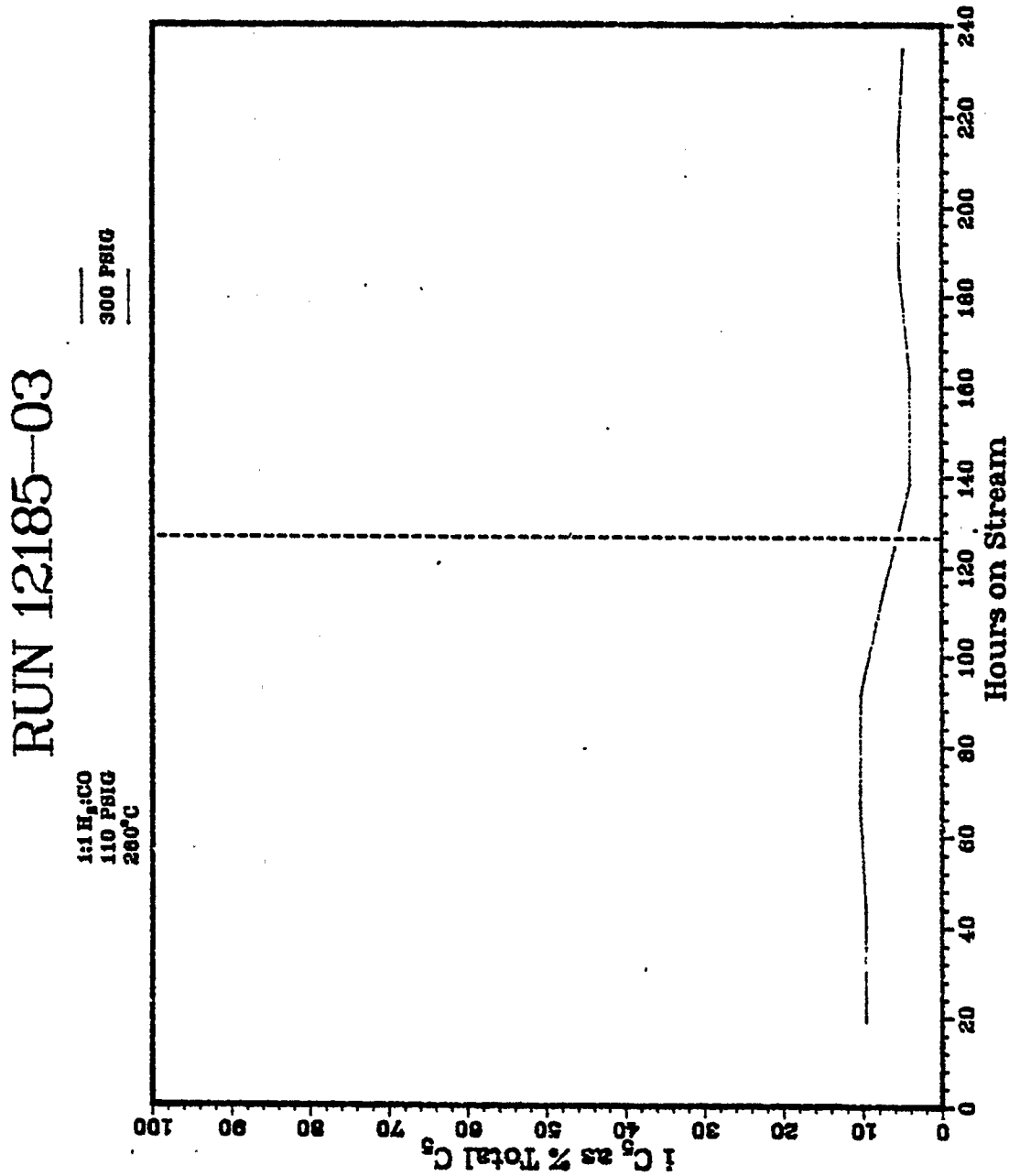

RUN 12185-03
300 PSIG
1:1 H2:CO
110 PSIG
280°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. B40

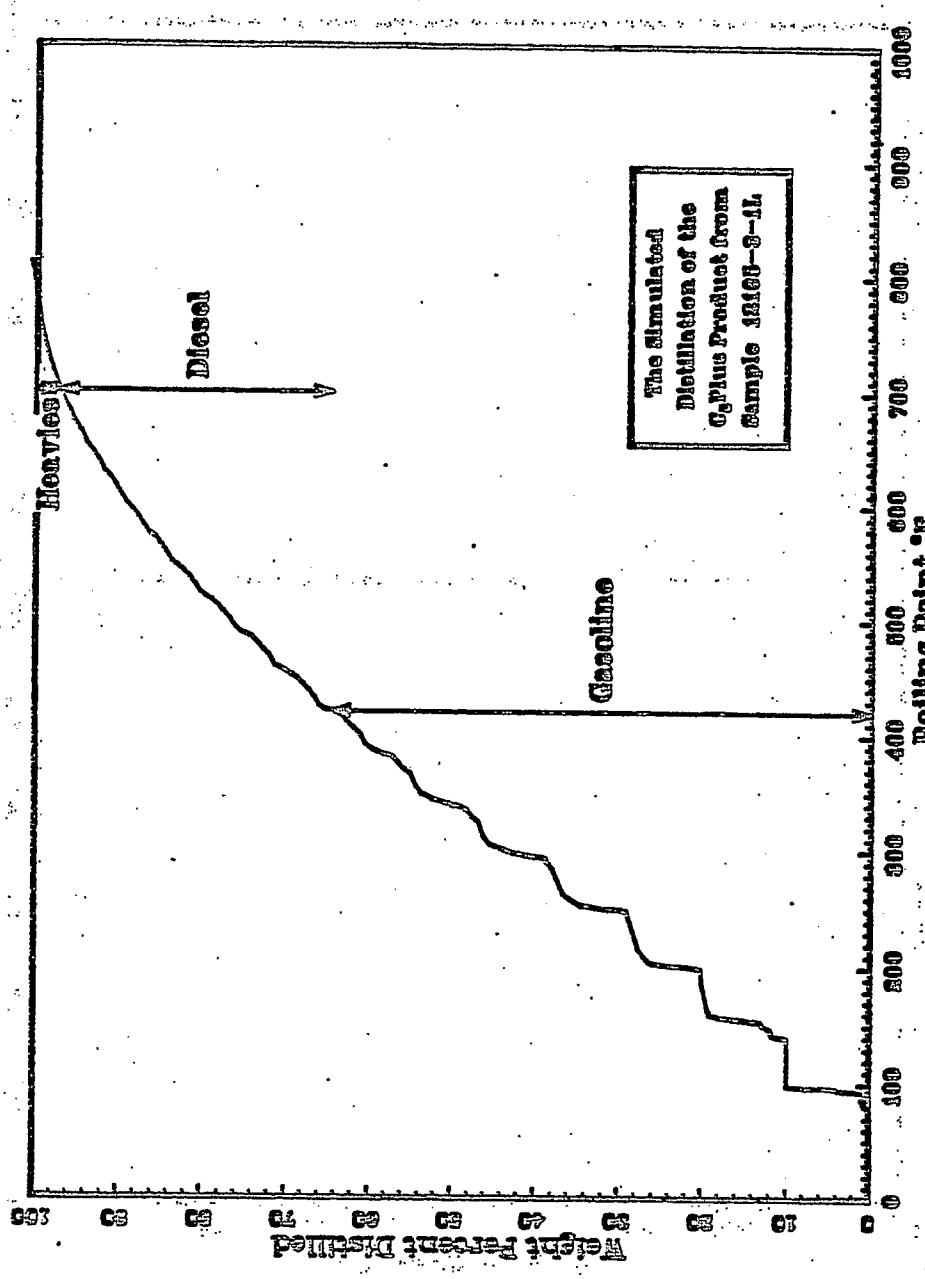

Weight Percent Distilled
Boiling Point °F
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12166-3-11

Fig. B41

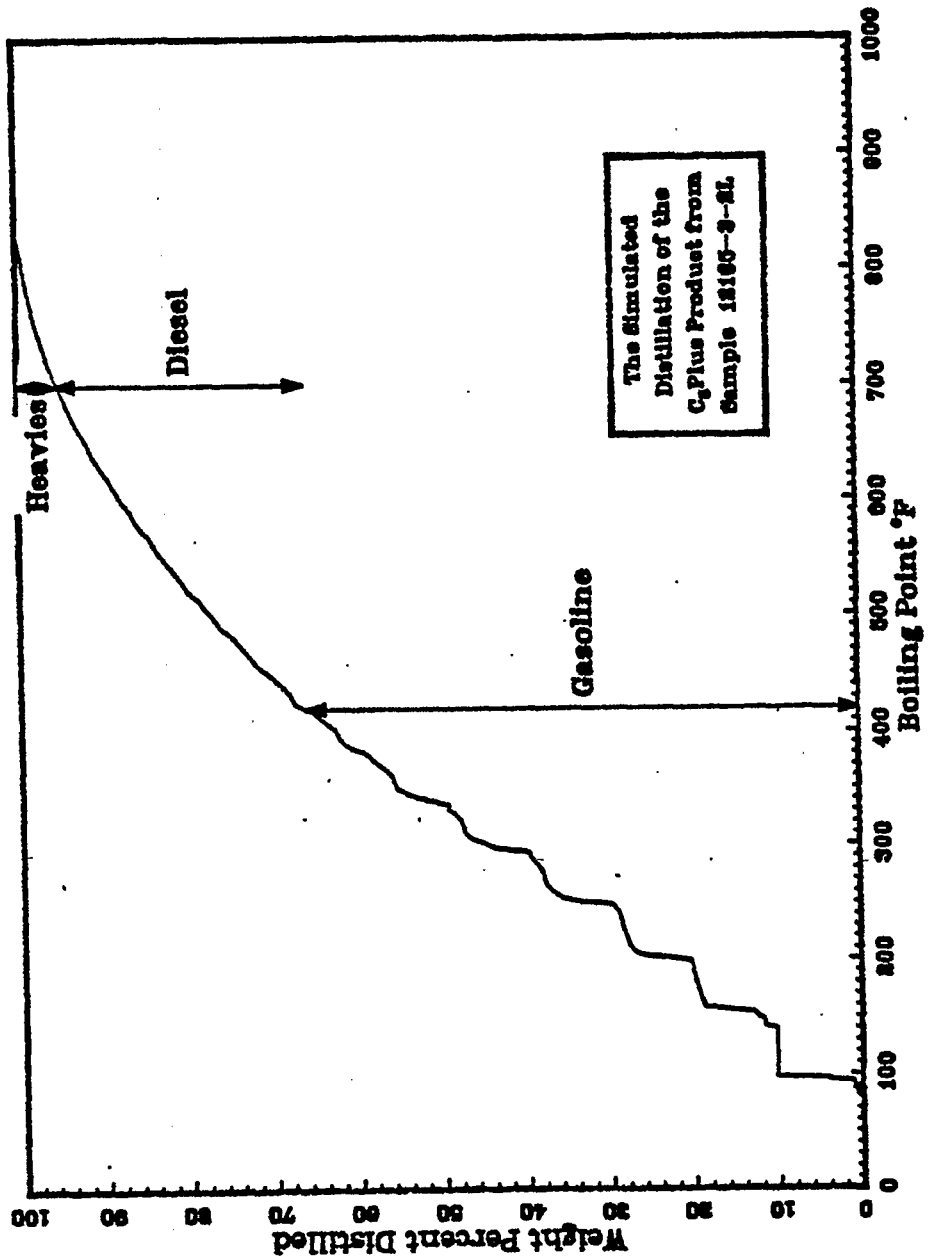

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12105-2-4L
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B42

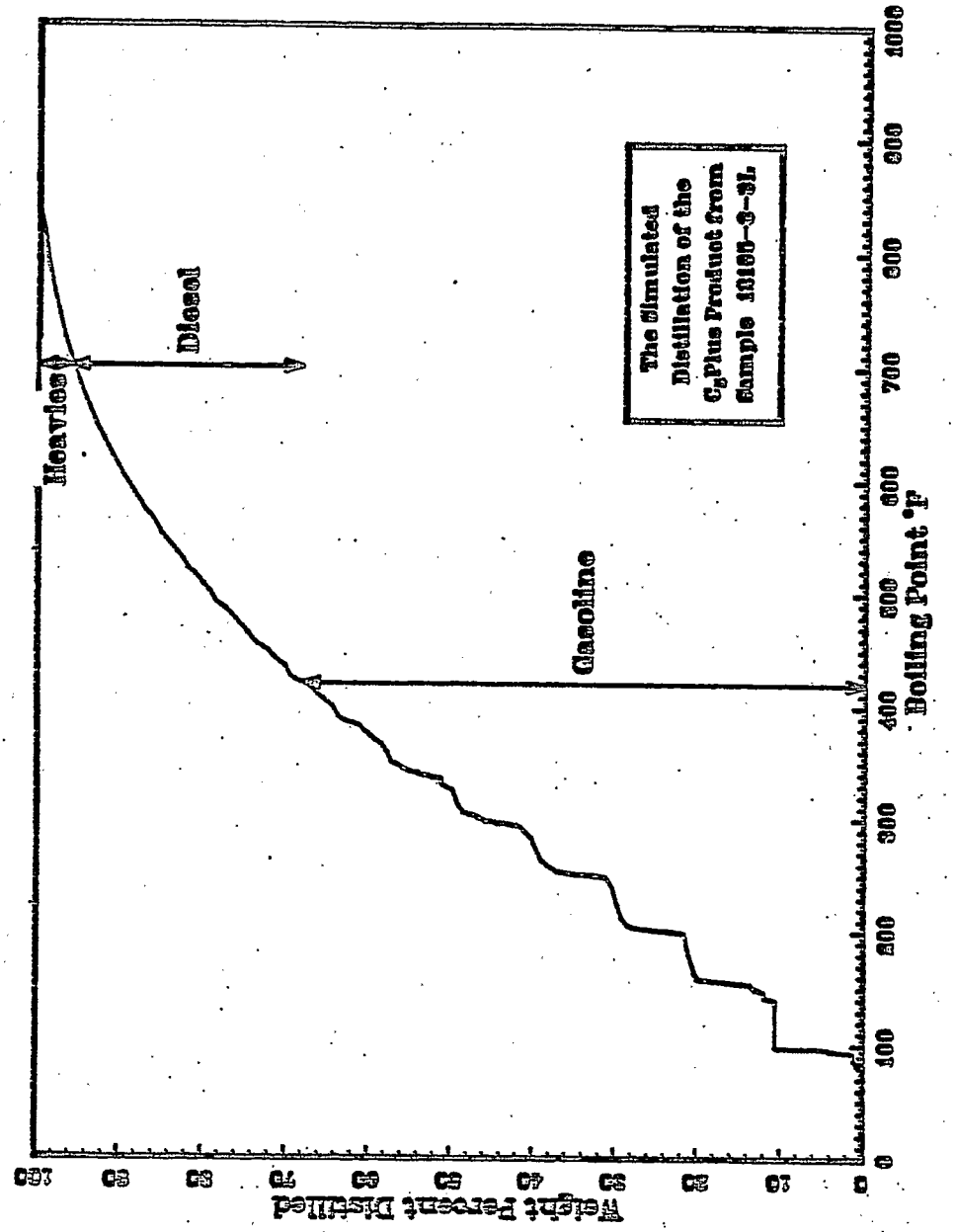

The Simulated Distillation of the C5 Plus Product from Sample 13165-3-3L
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B43

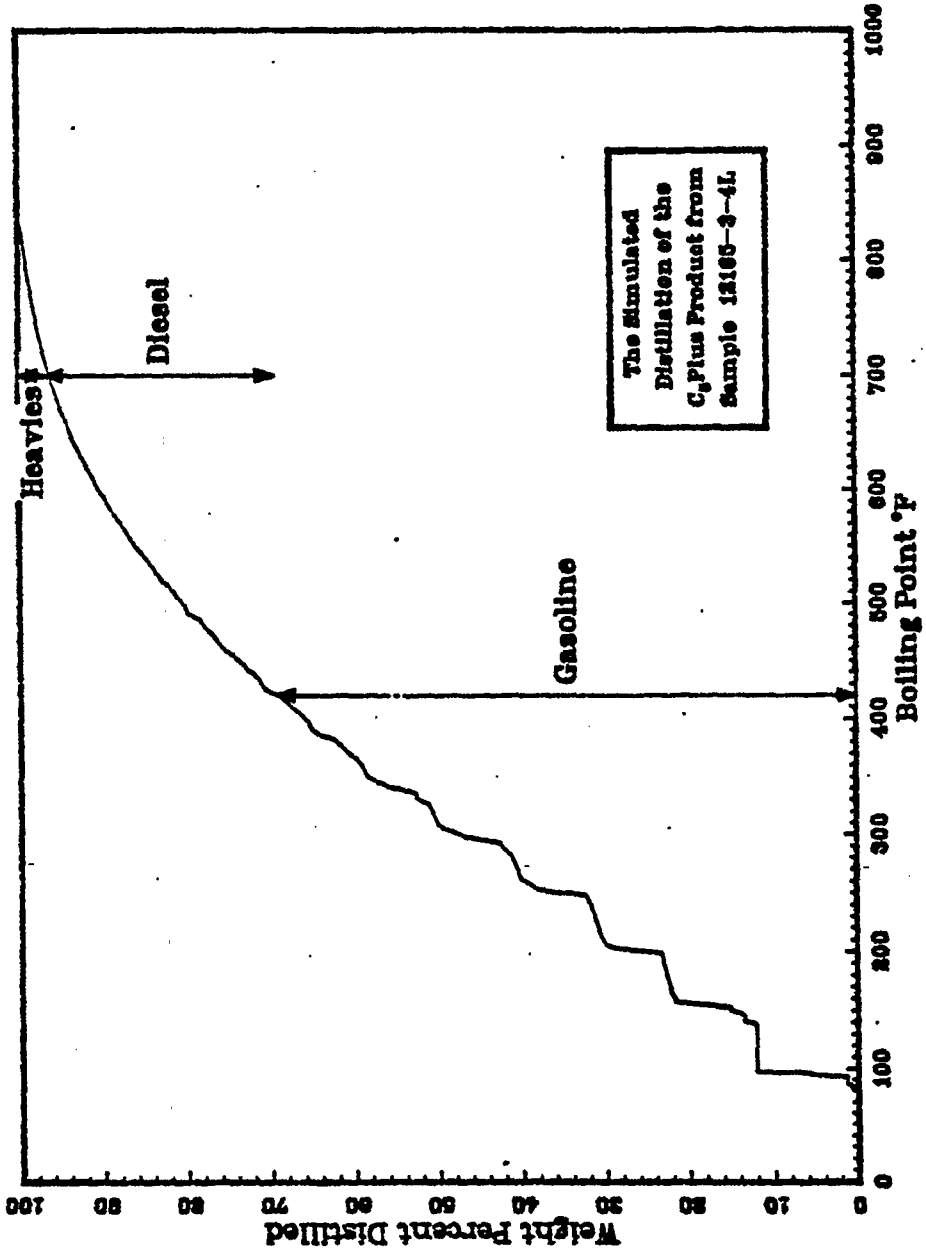

Weight Percent Distilled
0
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12165-3-4L

Fig. B44

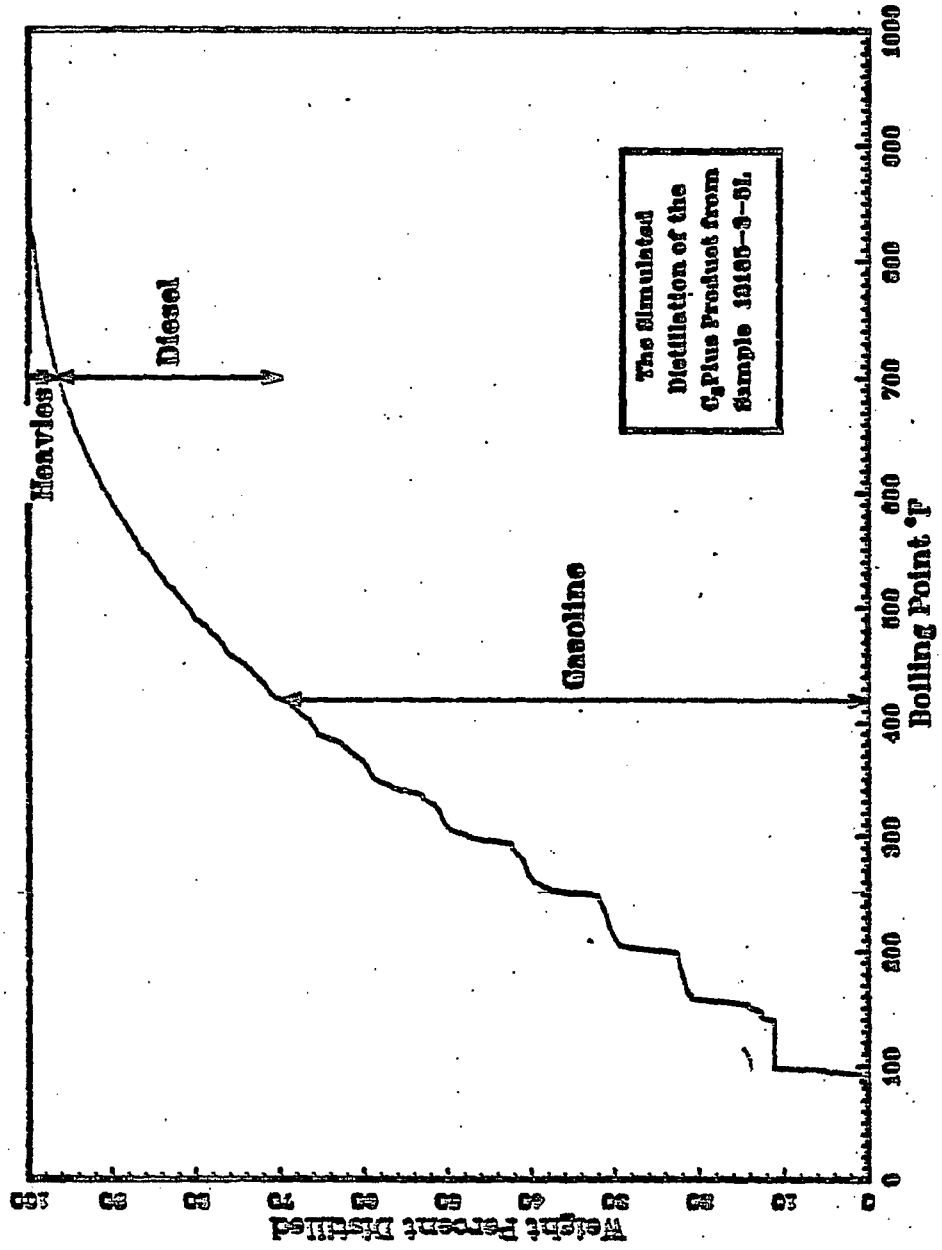

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 19185-3-61.

Fig. B45

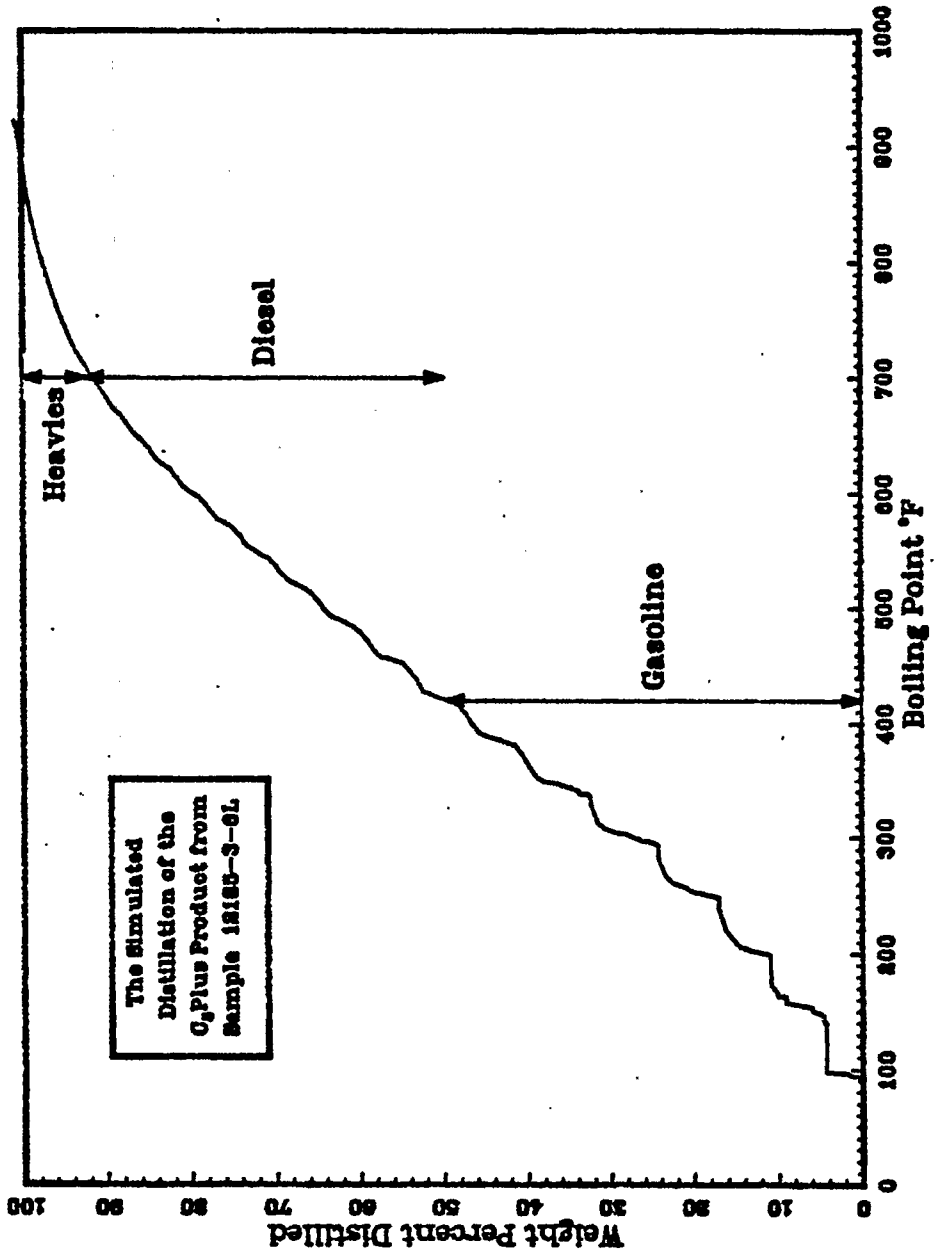

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 18185-3-61
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B46

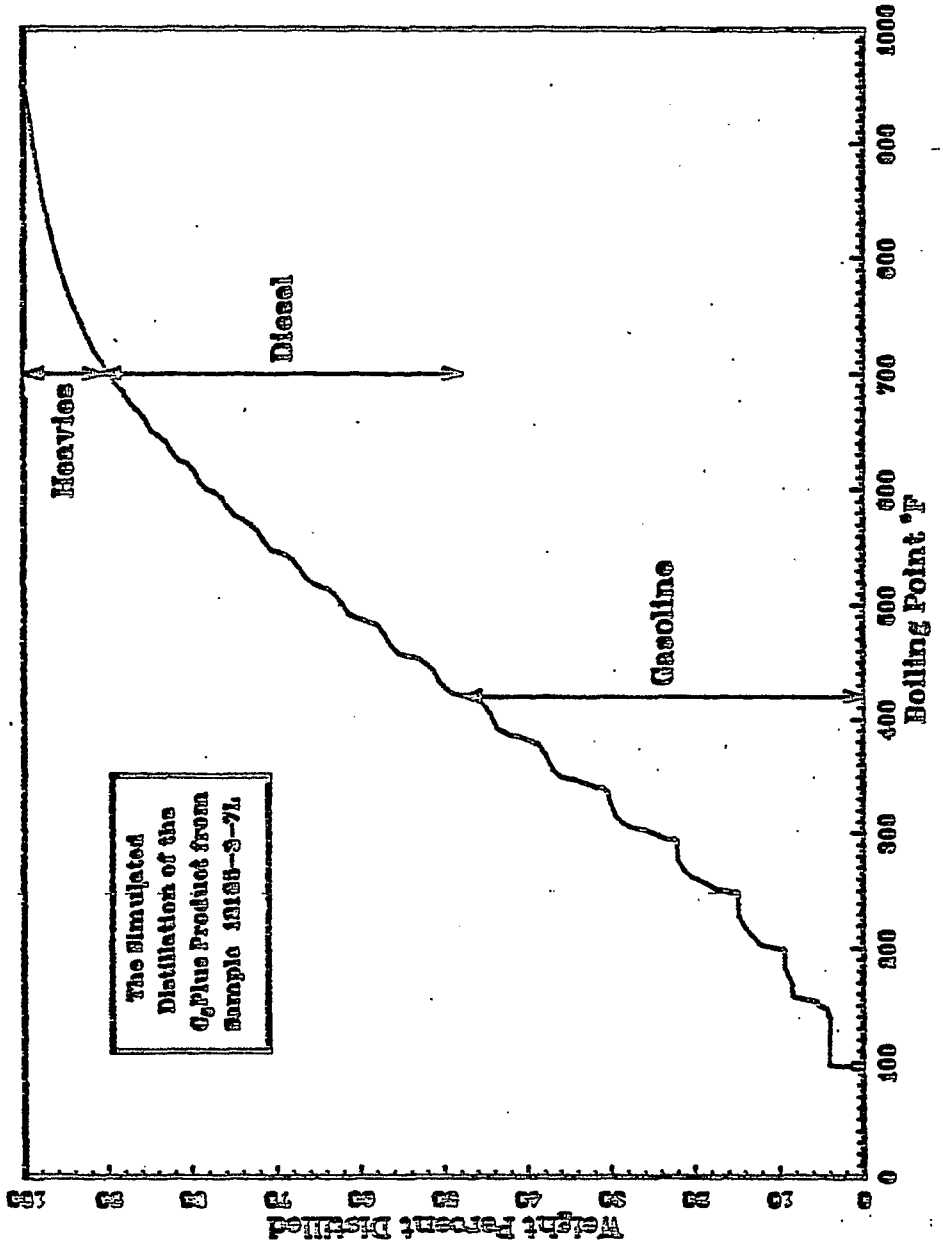

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000
Boiling Point °F
Heavies
Diesel
Gasoline
The Simulated Distillation of the C6 Plus Product from Sample 12168-3-7L

Fig. B47

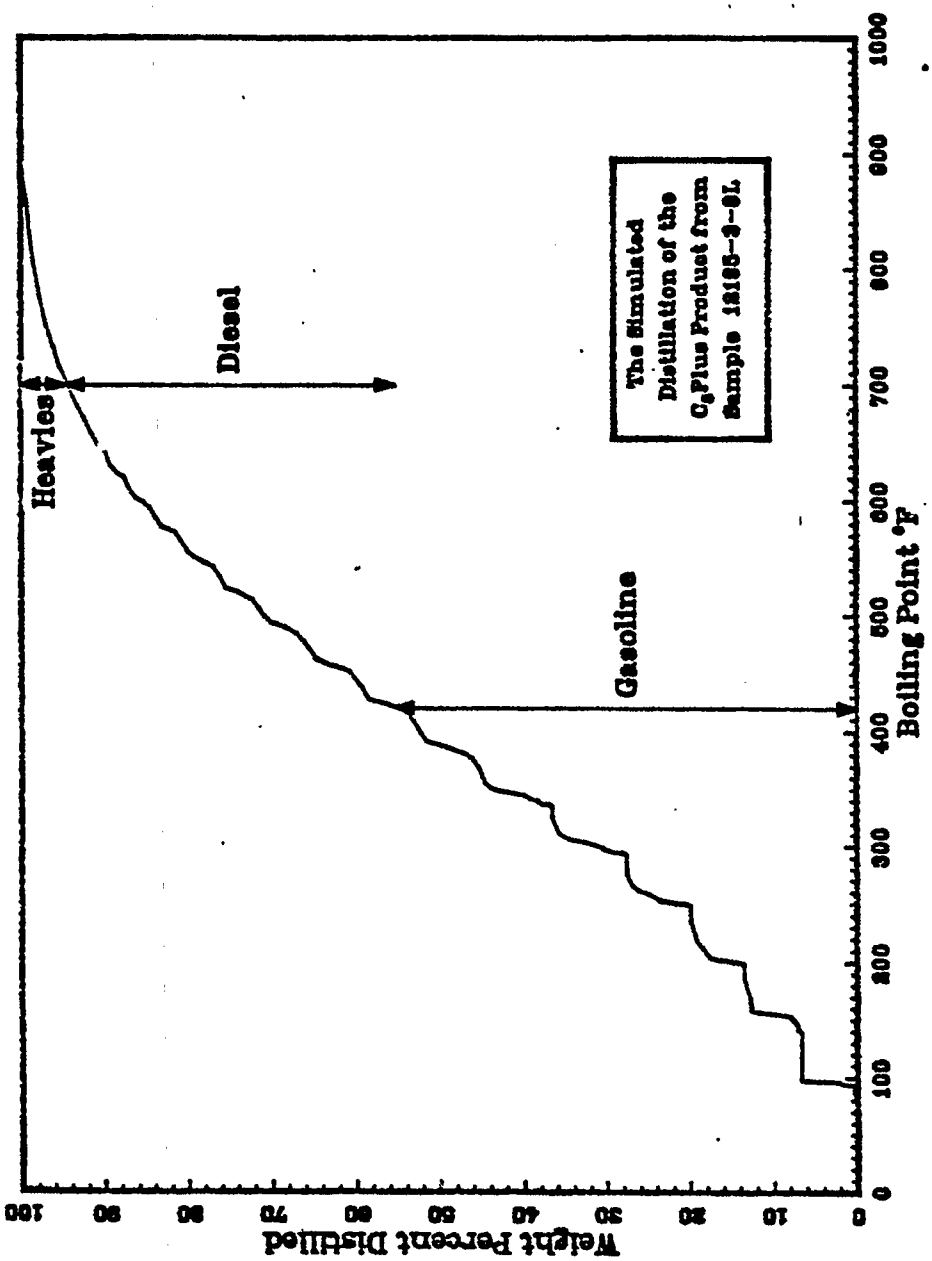
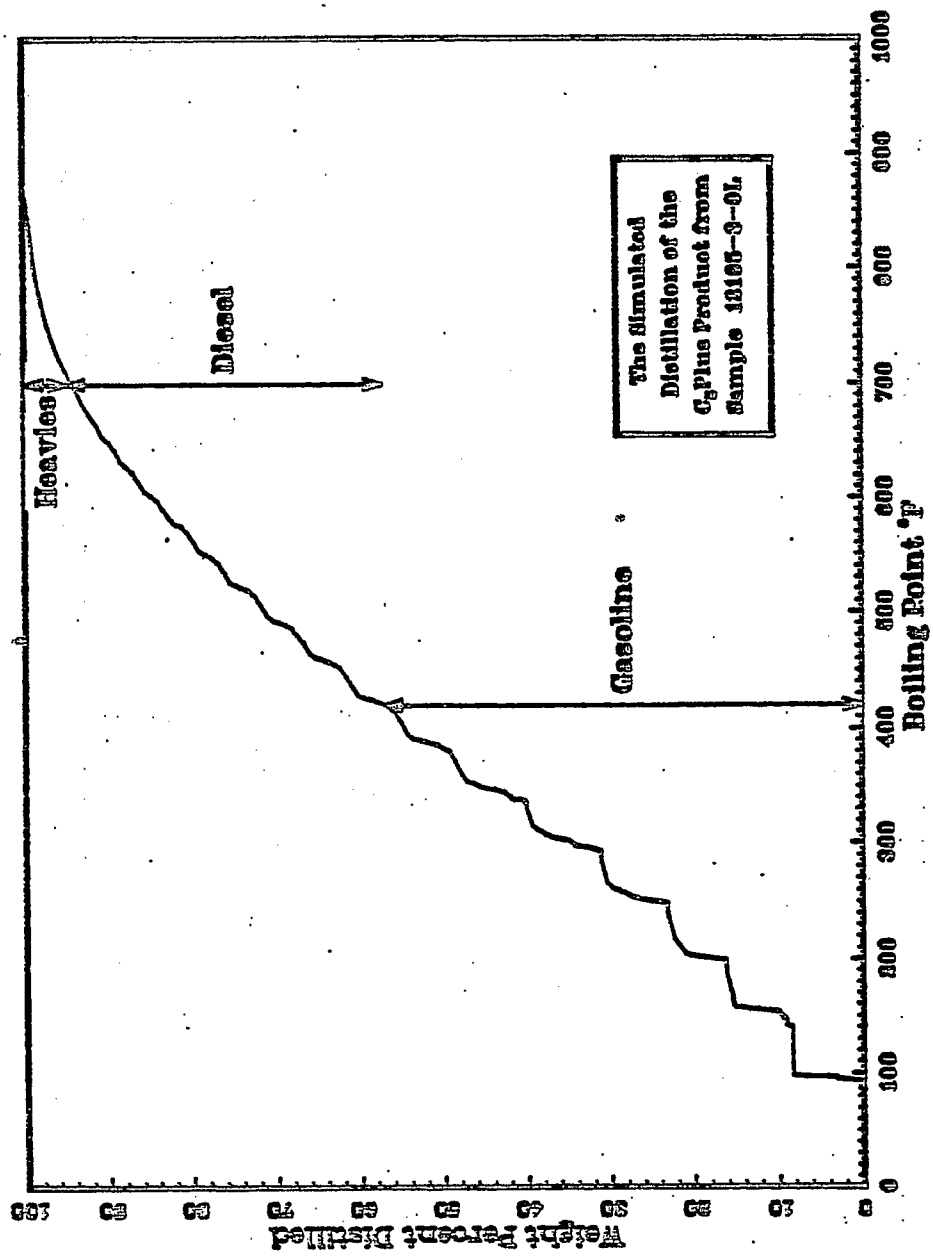

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 18185-2-8L

Fig. B48


Weight Percent Distilled
Boiling Point °F
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12165-3-01.

Eig. B49

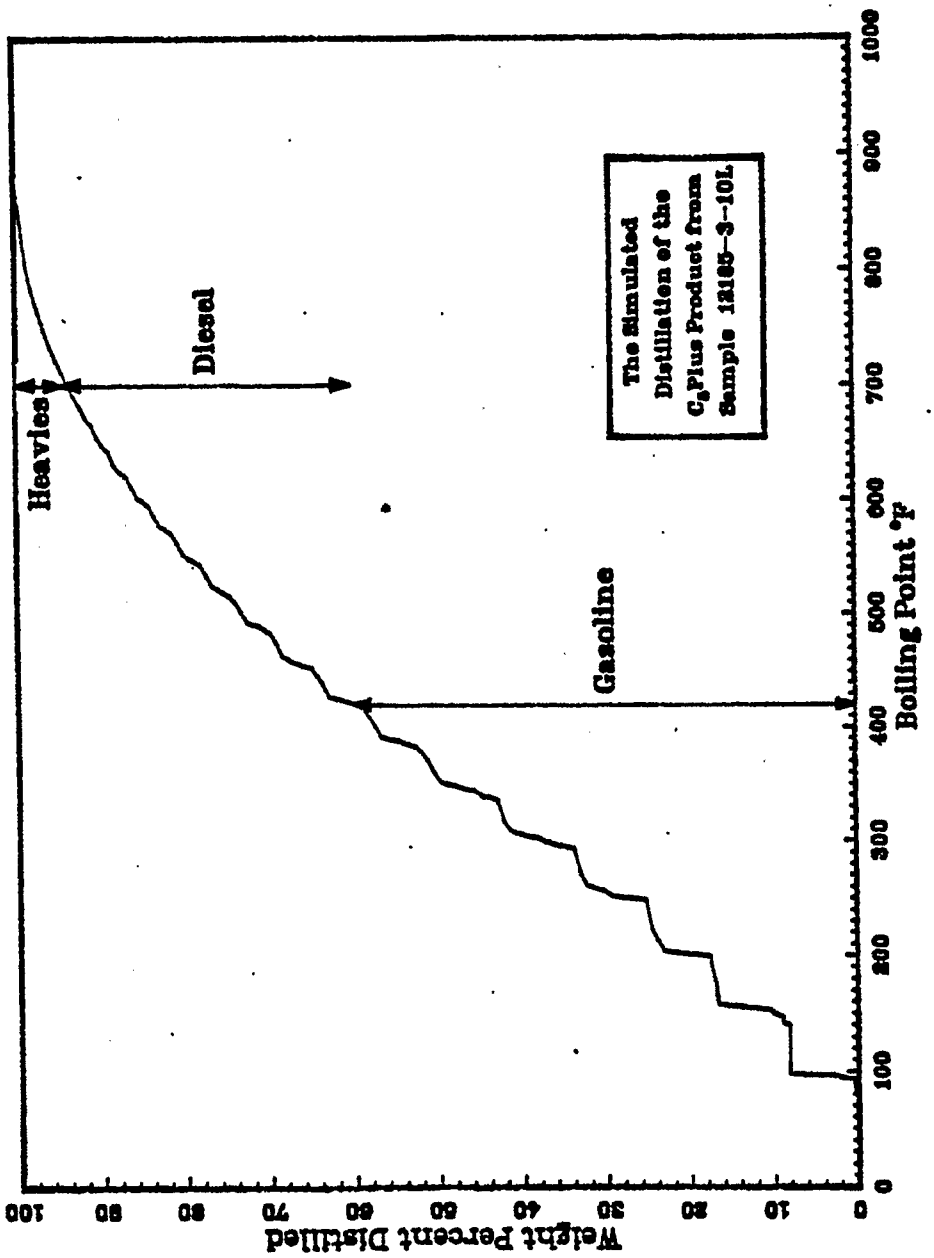

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12185-3-10L

Fig. B50

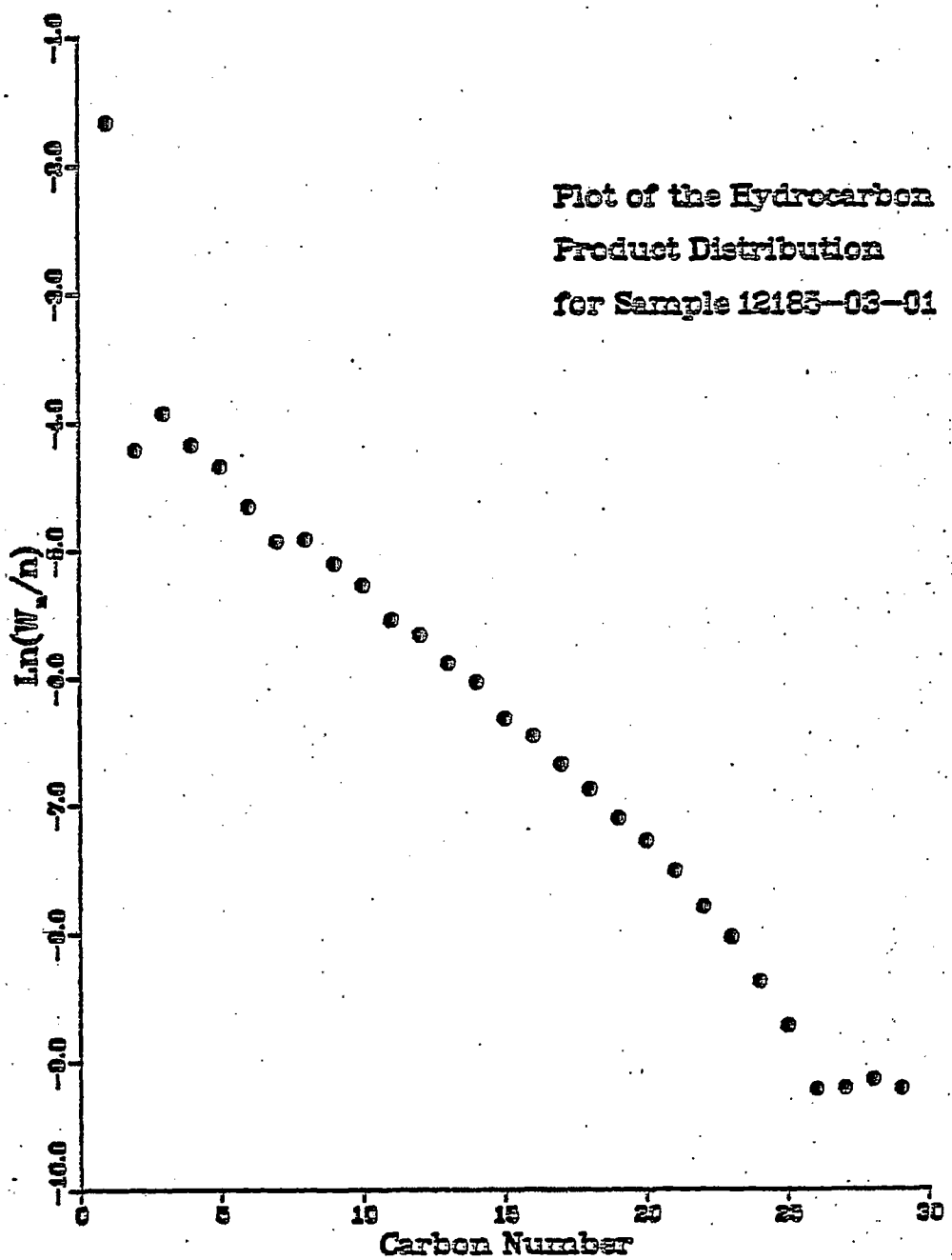

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-01
Ln(Wn/n)
-1.0
-3.0
-5.0
-7.0
-9.0
-0.0
-0.0
-0.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B51

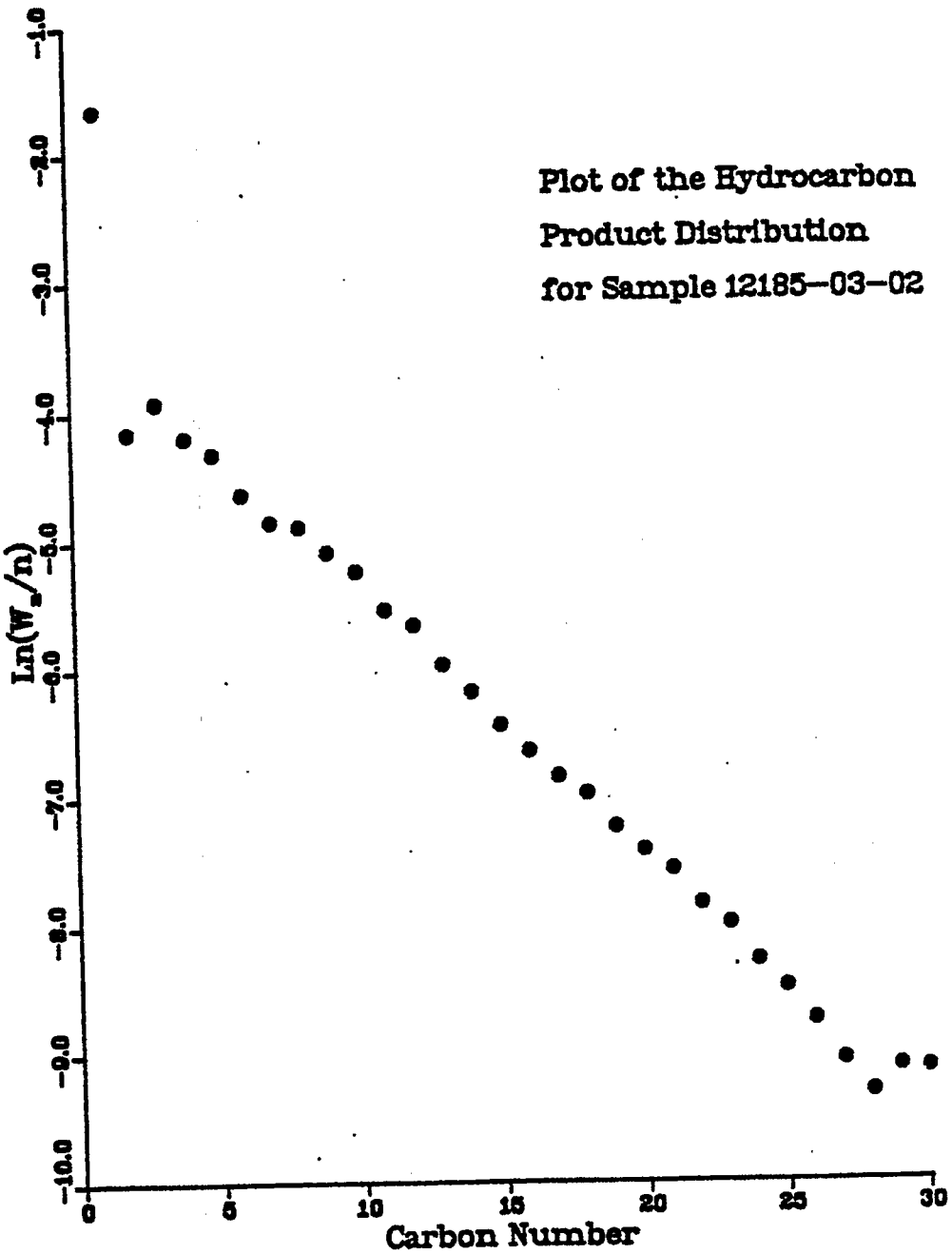

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B52

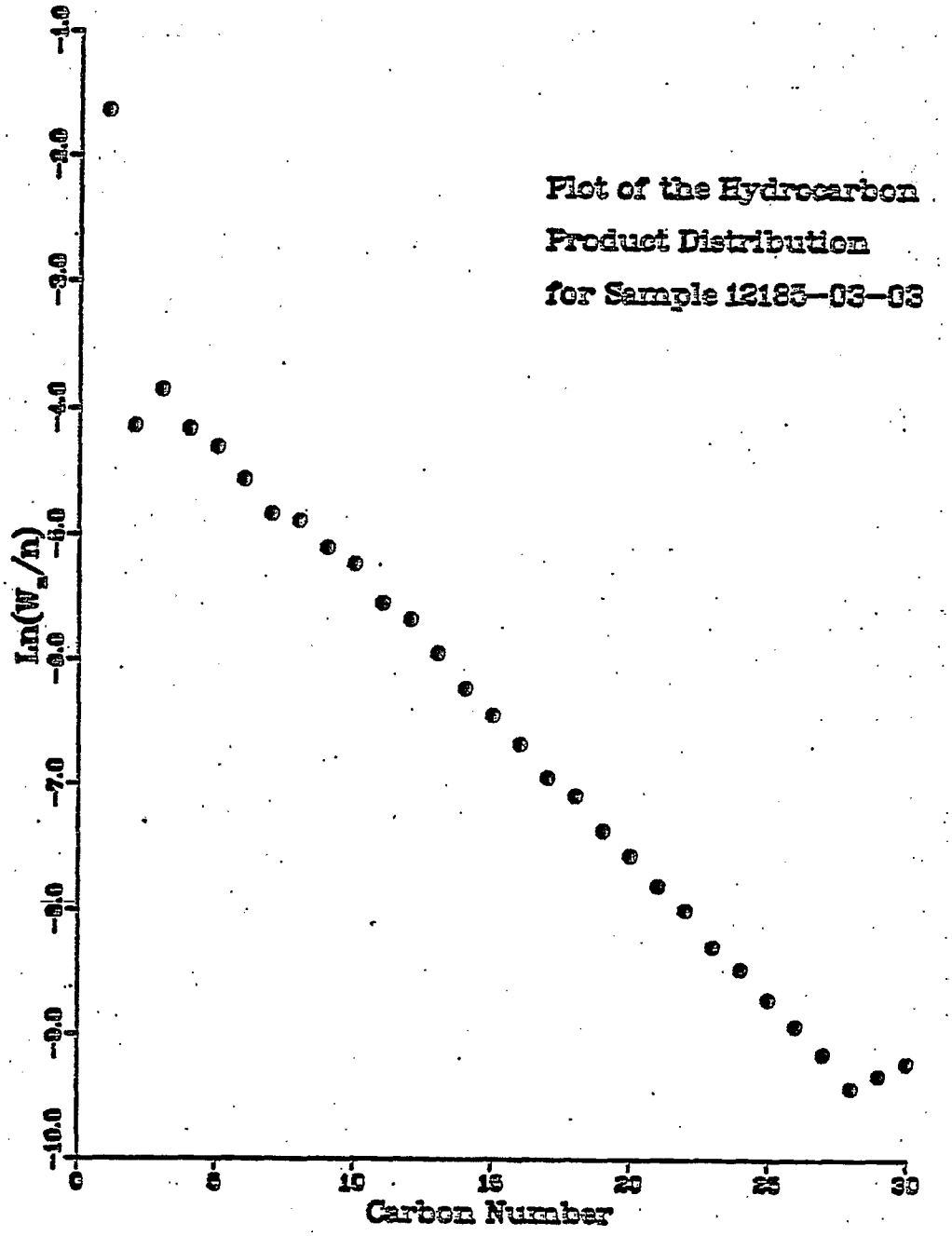

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-03
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B53

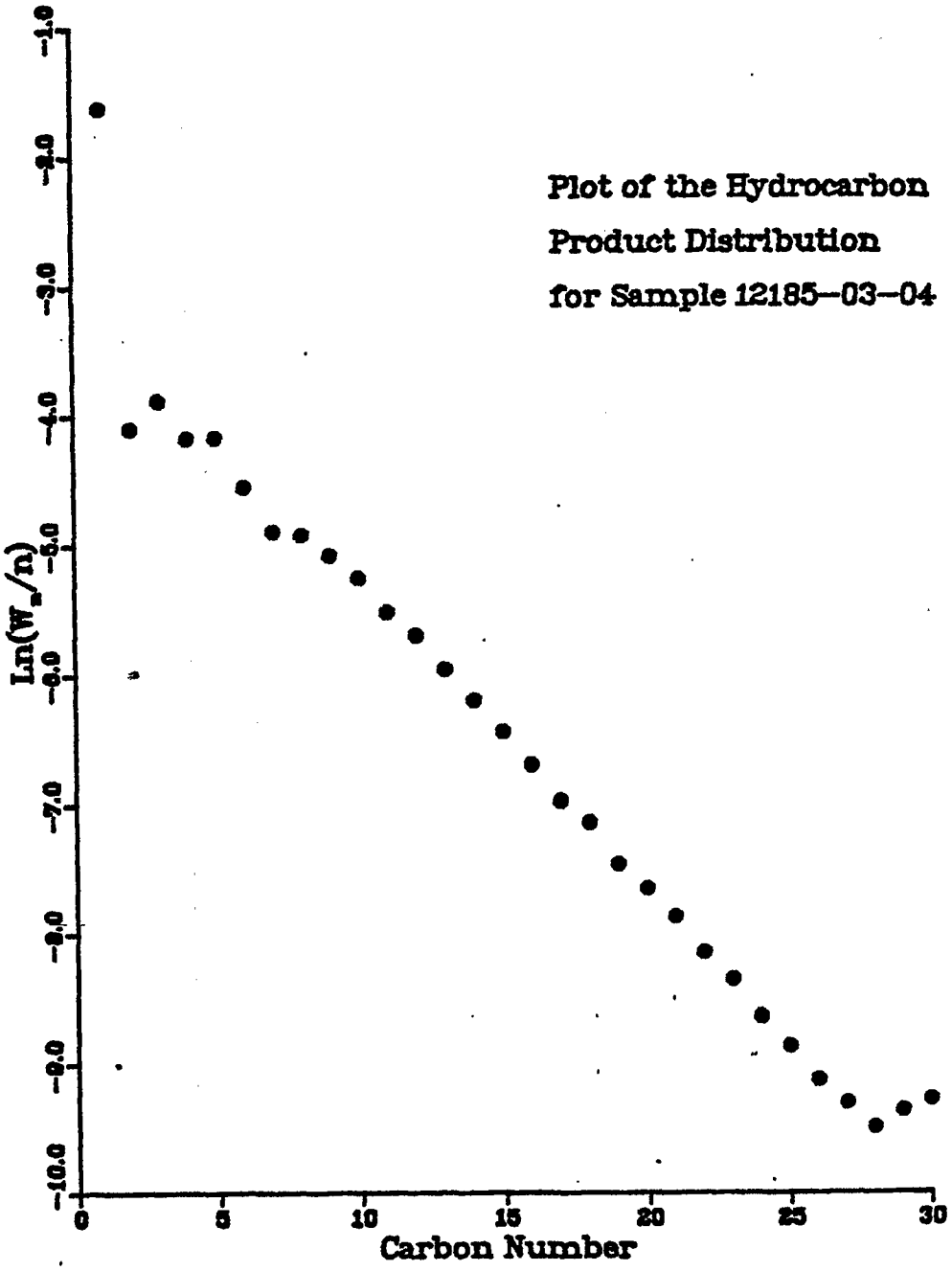

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-04
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B54

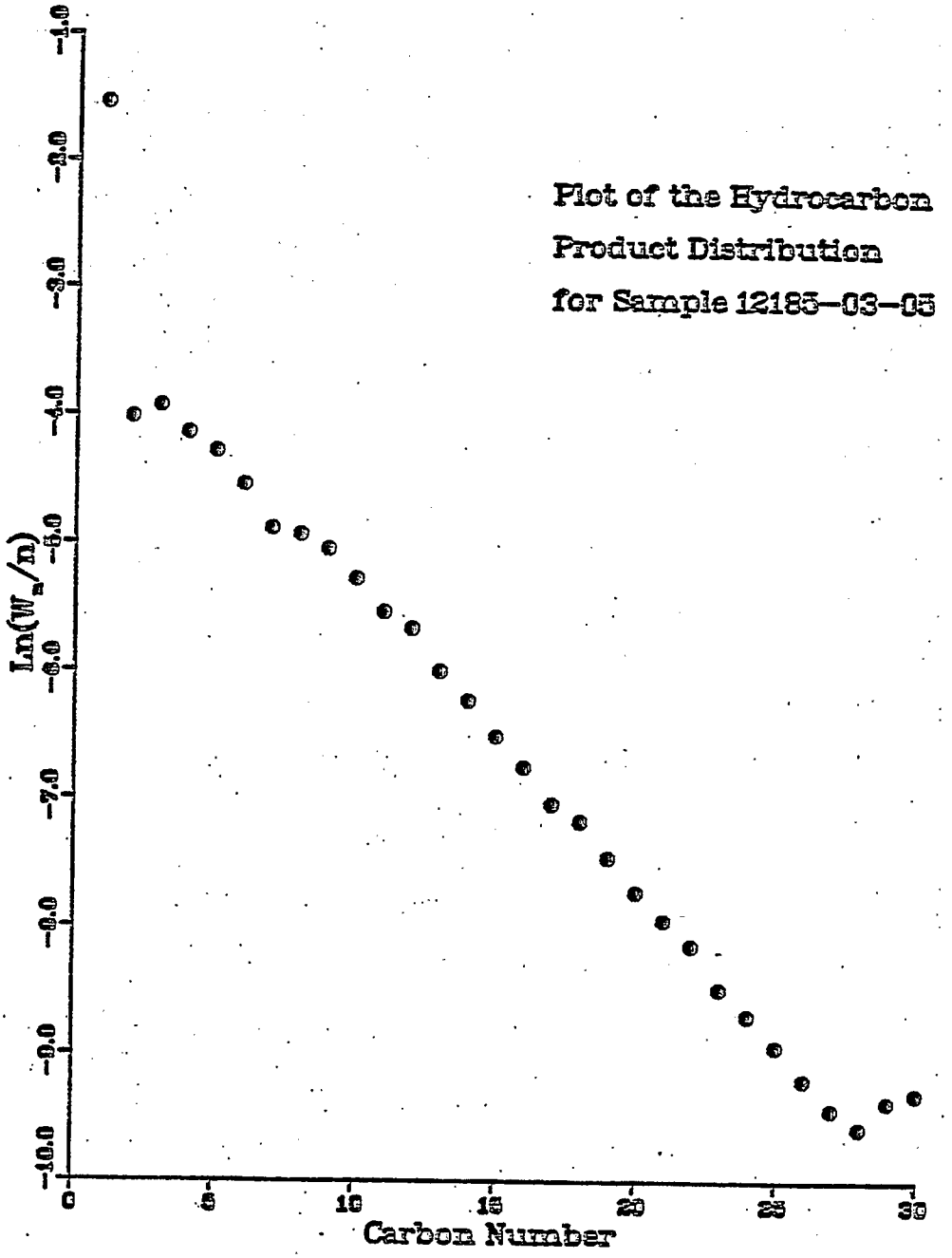

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-05
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B55

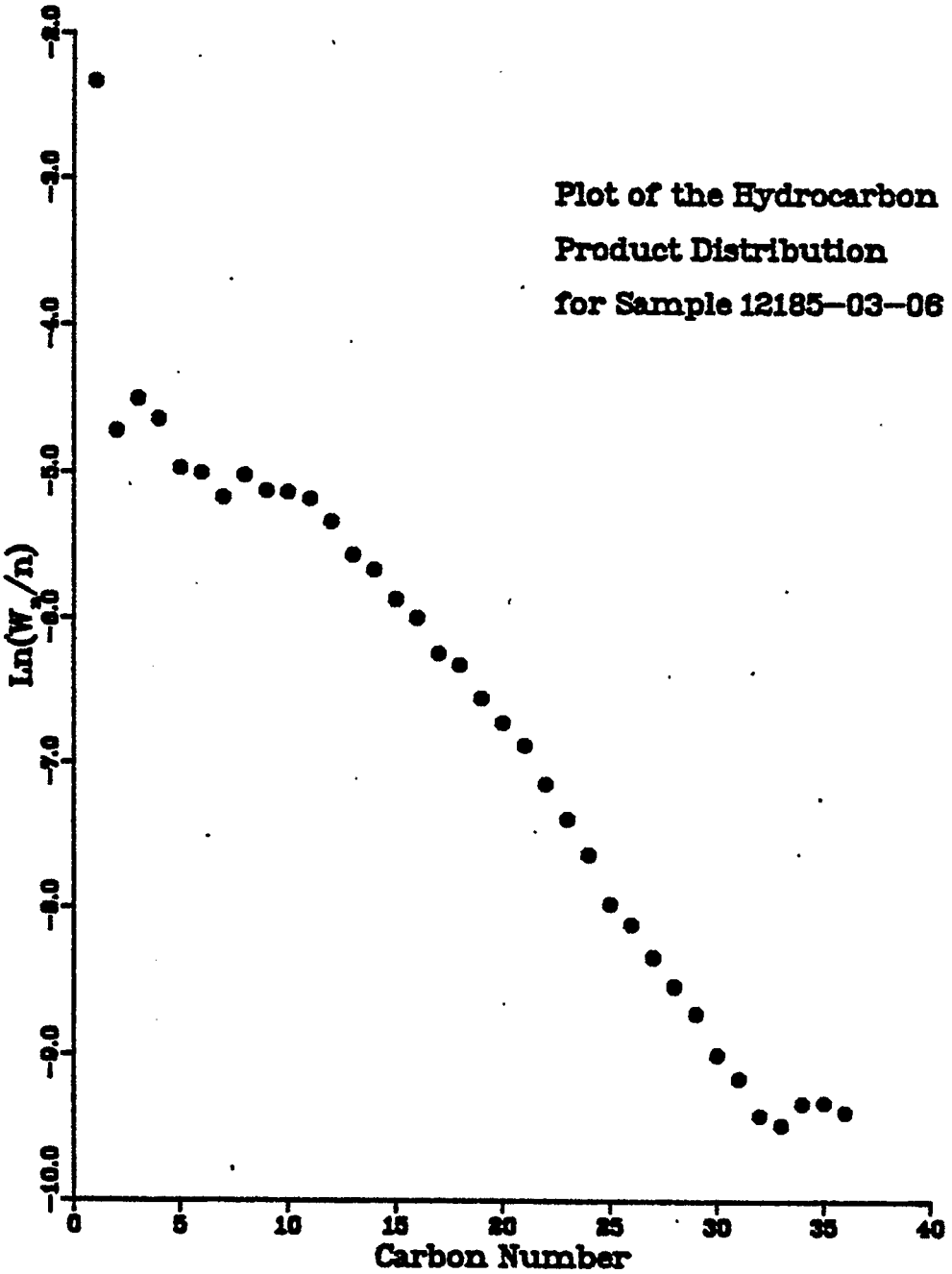

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-06
Ln(W_n/n)
-2.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B56

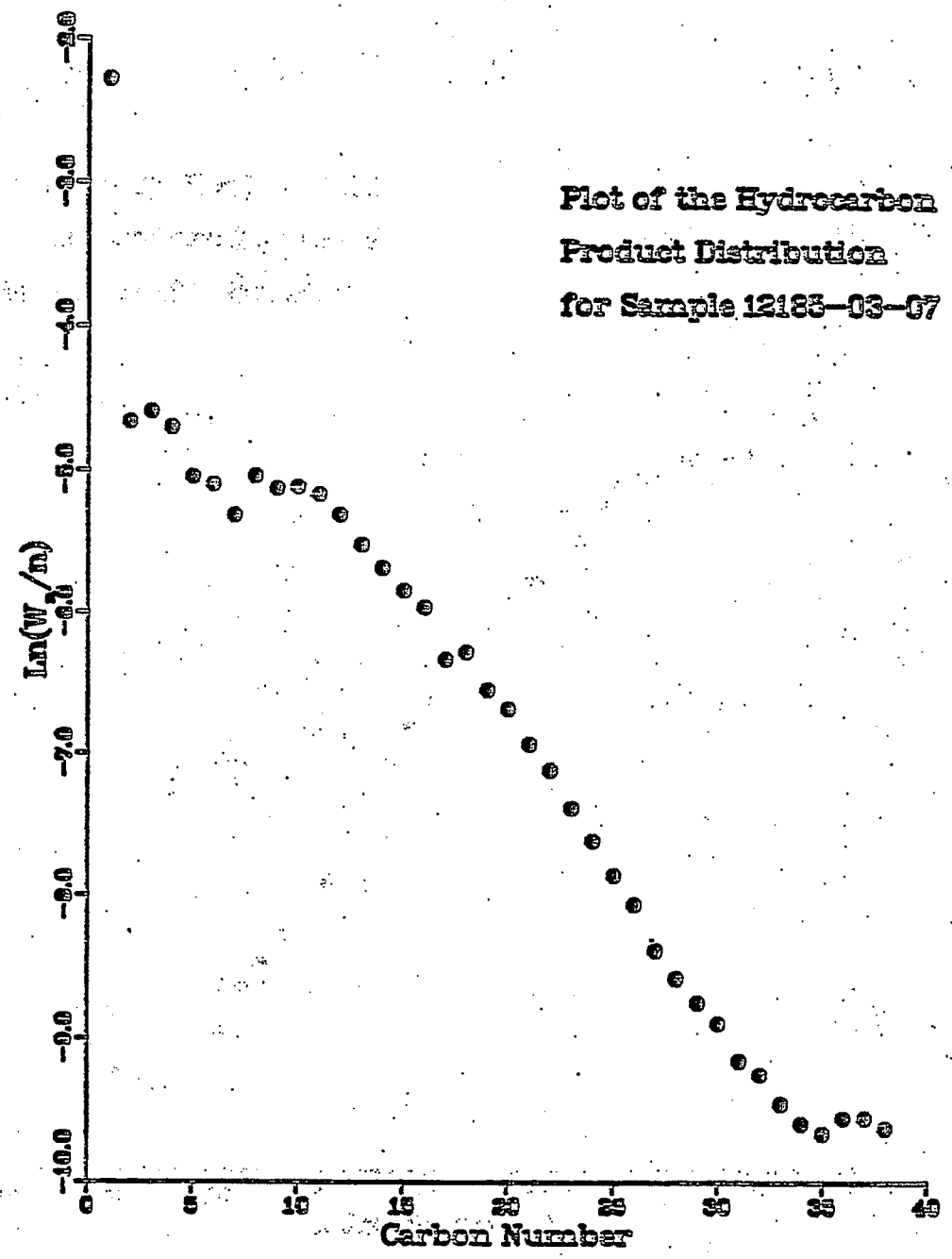
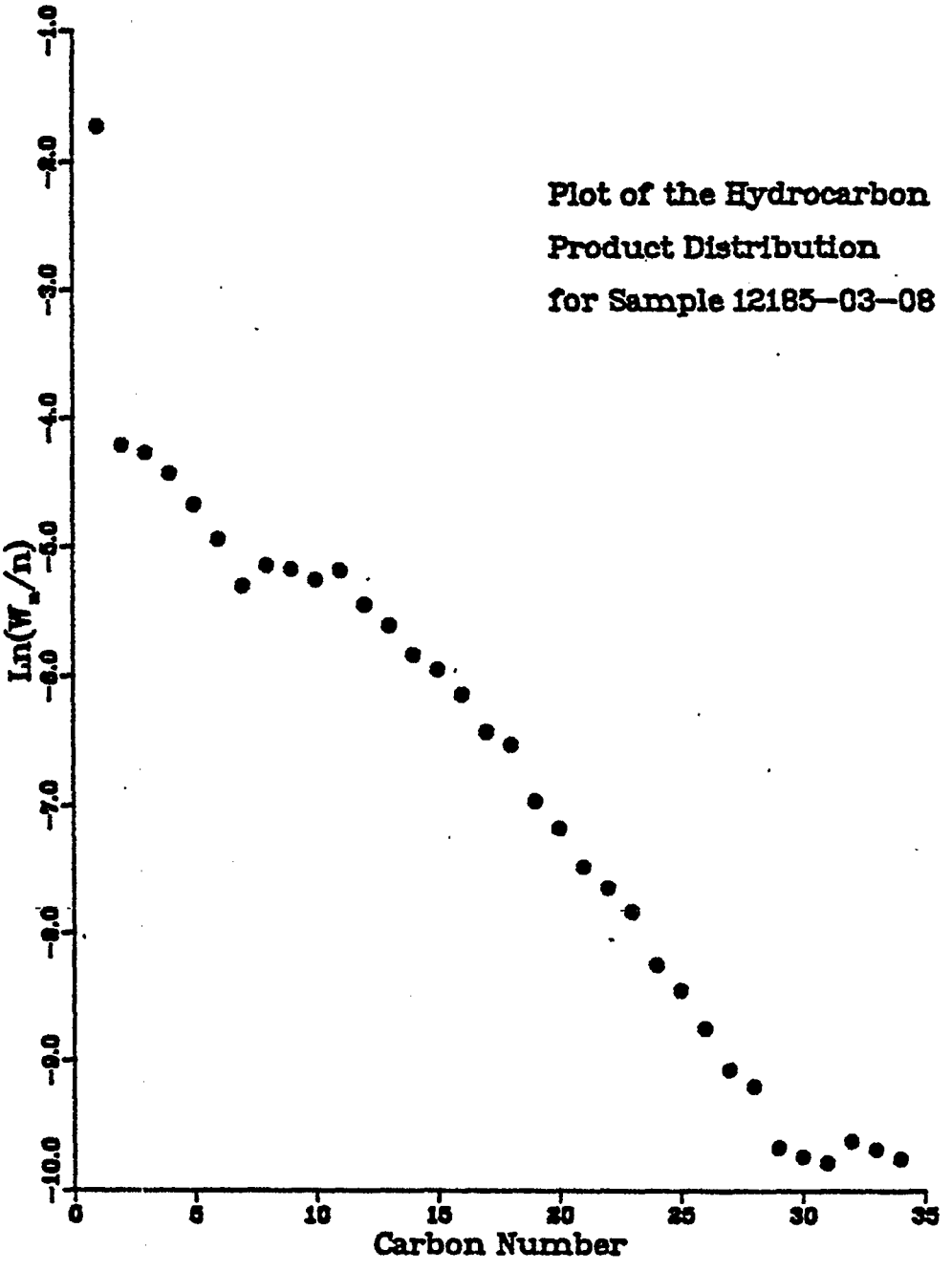

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-07
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B57


Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-08
Ln(Wn/n)
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-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. B58

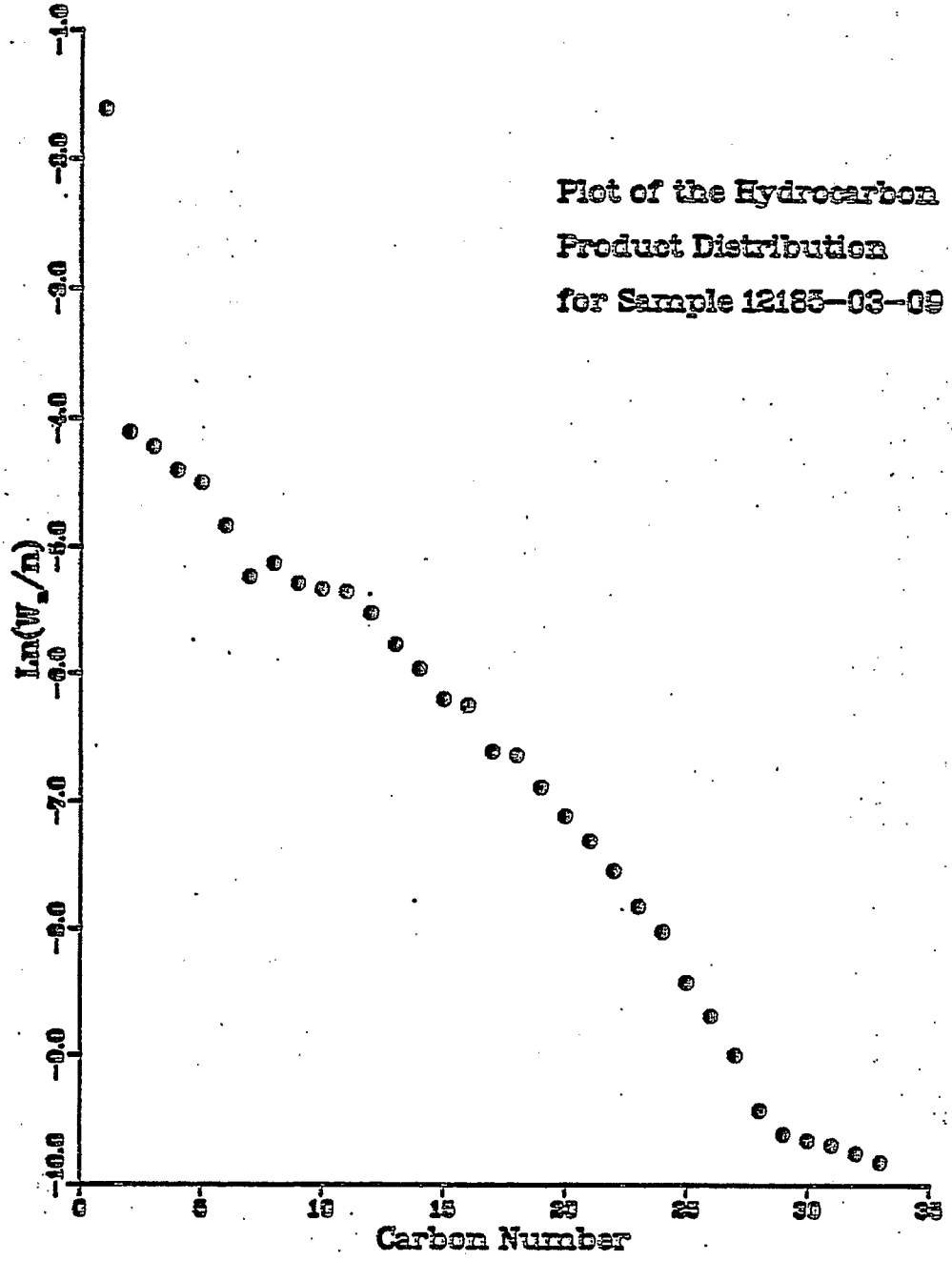

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B59

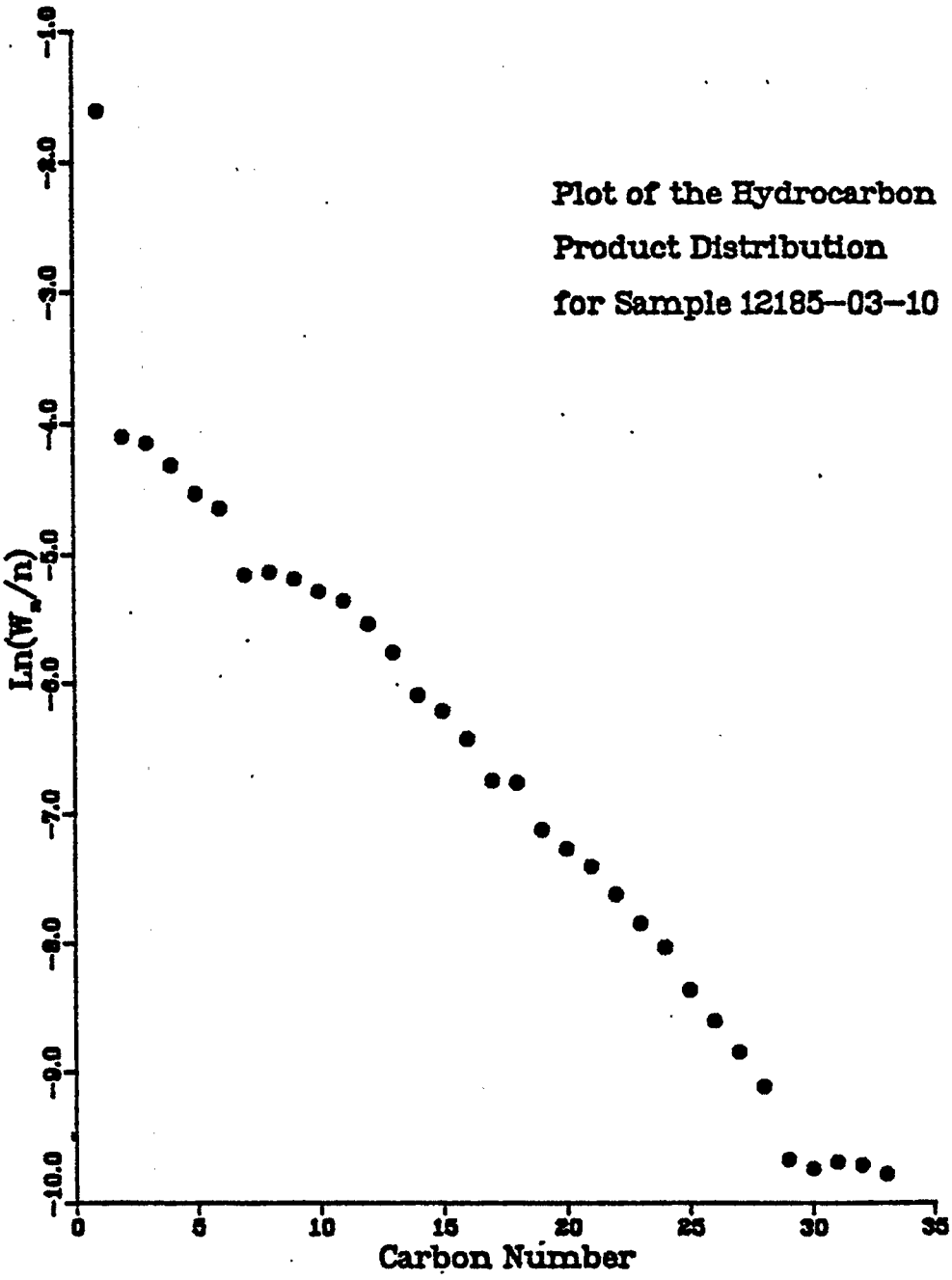

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-03-10
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B60

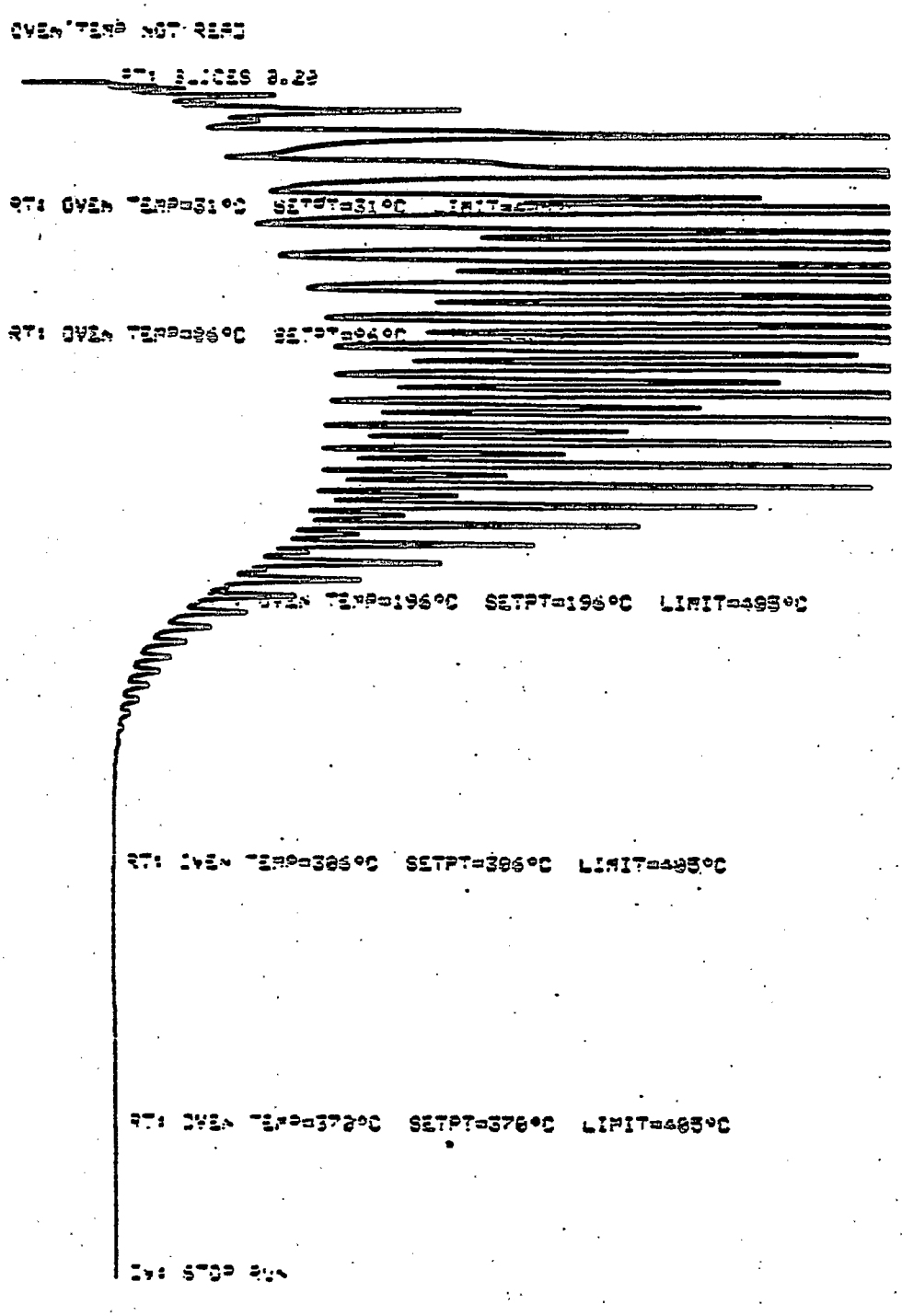

RT: OVEN TEMP=196°C SETPT=196°C LIMIT=493°C
RT: OVEN TEMP=386°C SETPT=386°C LIMIT=493°C
RT: OVEN TEMP=372°C SETPT=376°C LIMIT=485°C

Fig. B61

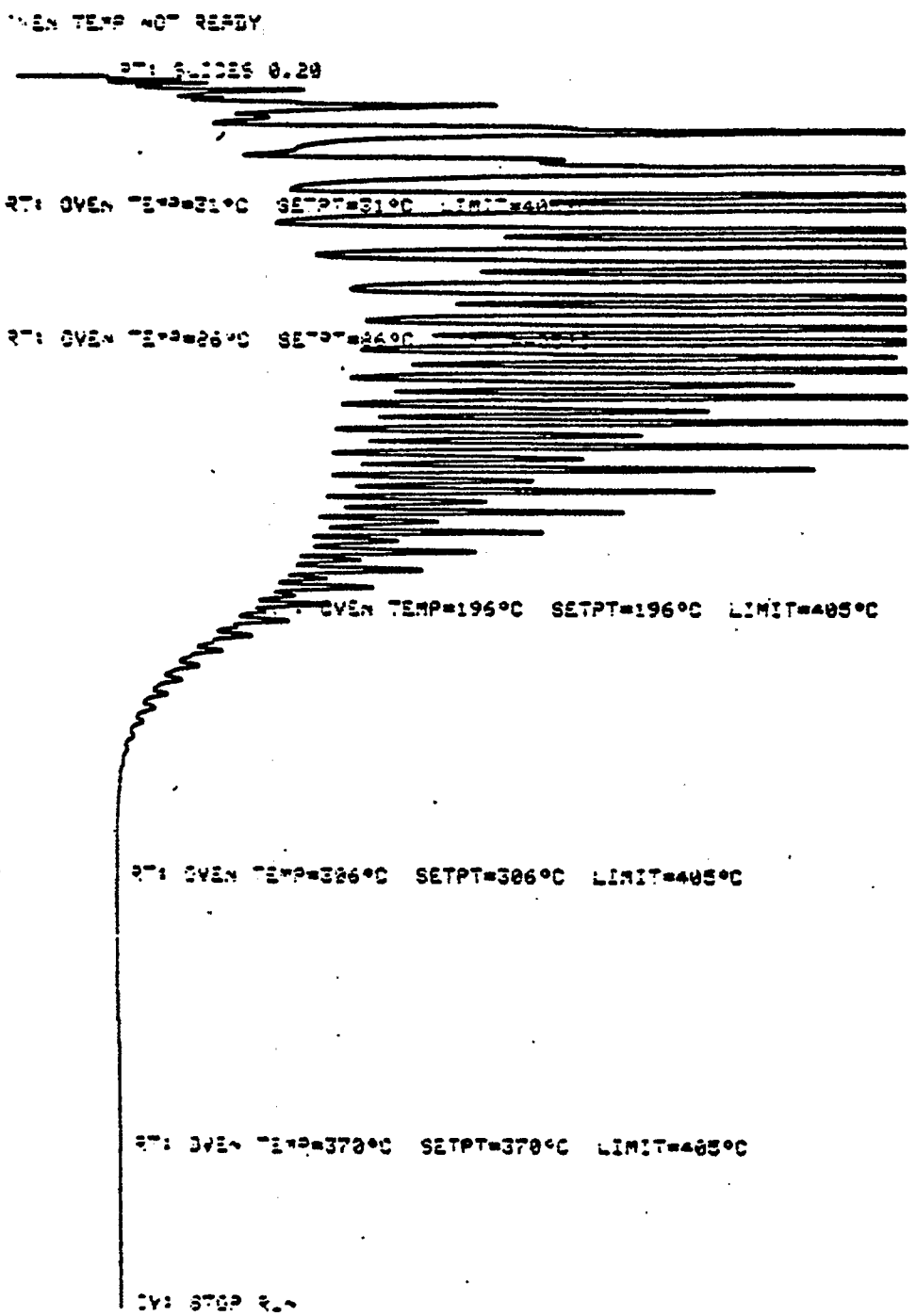

OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
OVEN TEMP=370°C SETPT=370°C LIMIT=405°C

Fig. B62

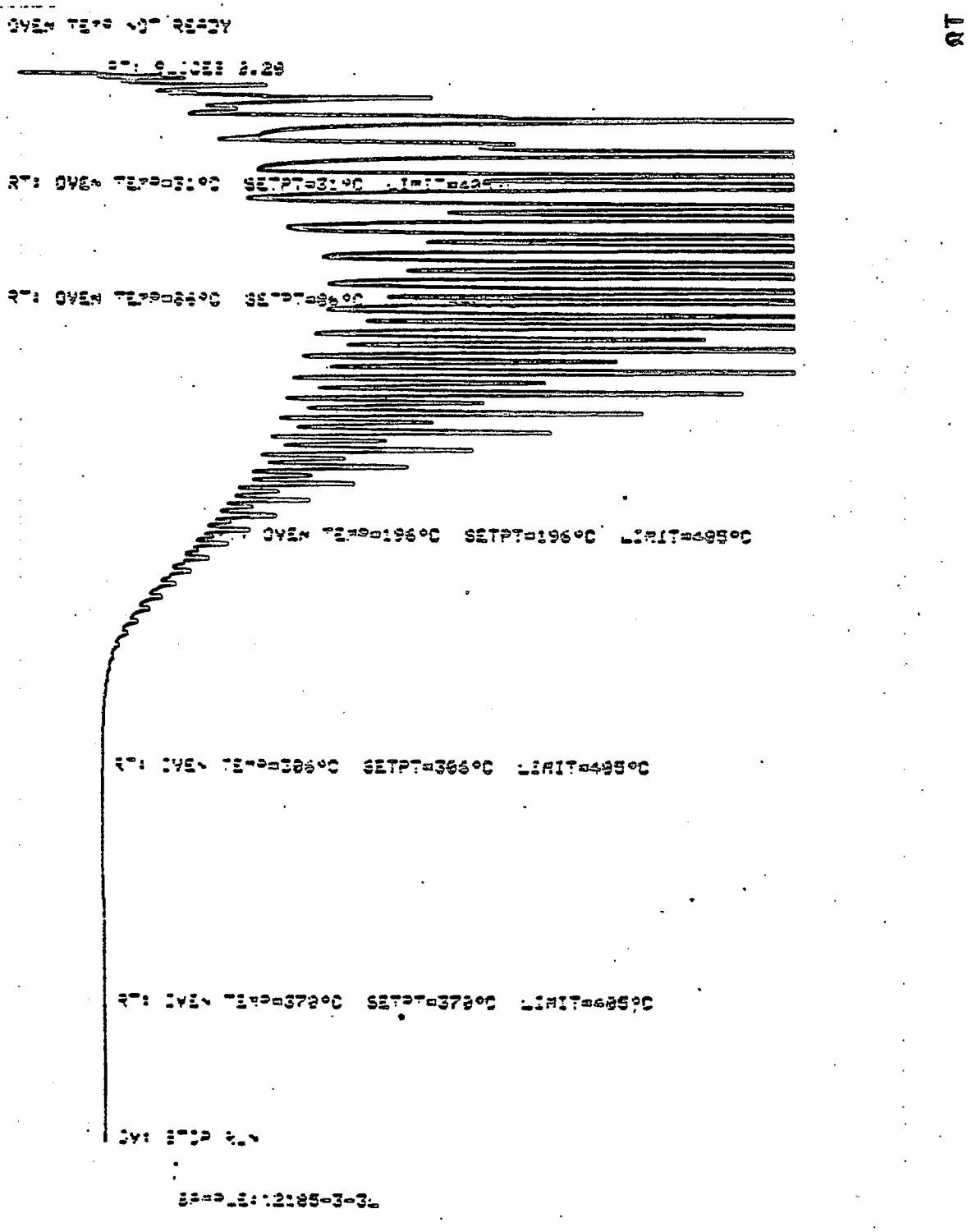

OVEN TEMP NOT READY
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=495°C
RT: OVEN TEMP=366°C SETPT=366°C LIMIT=495°C
RT: OVEN TEMP=372°C SETPT=372°C LIMIT=495°C

Fig. B63

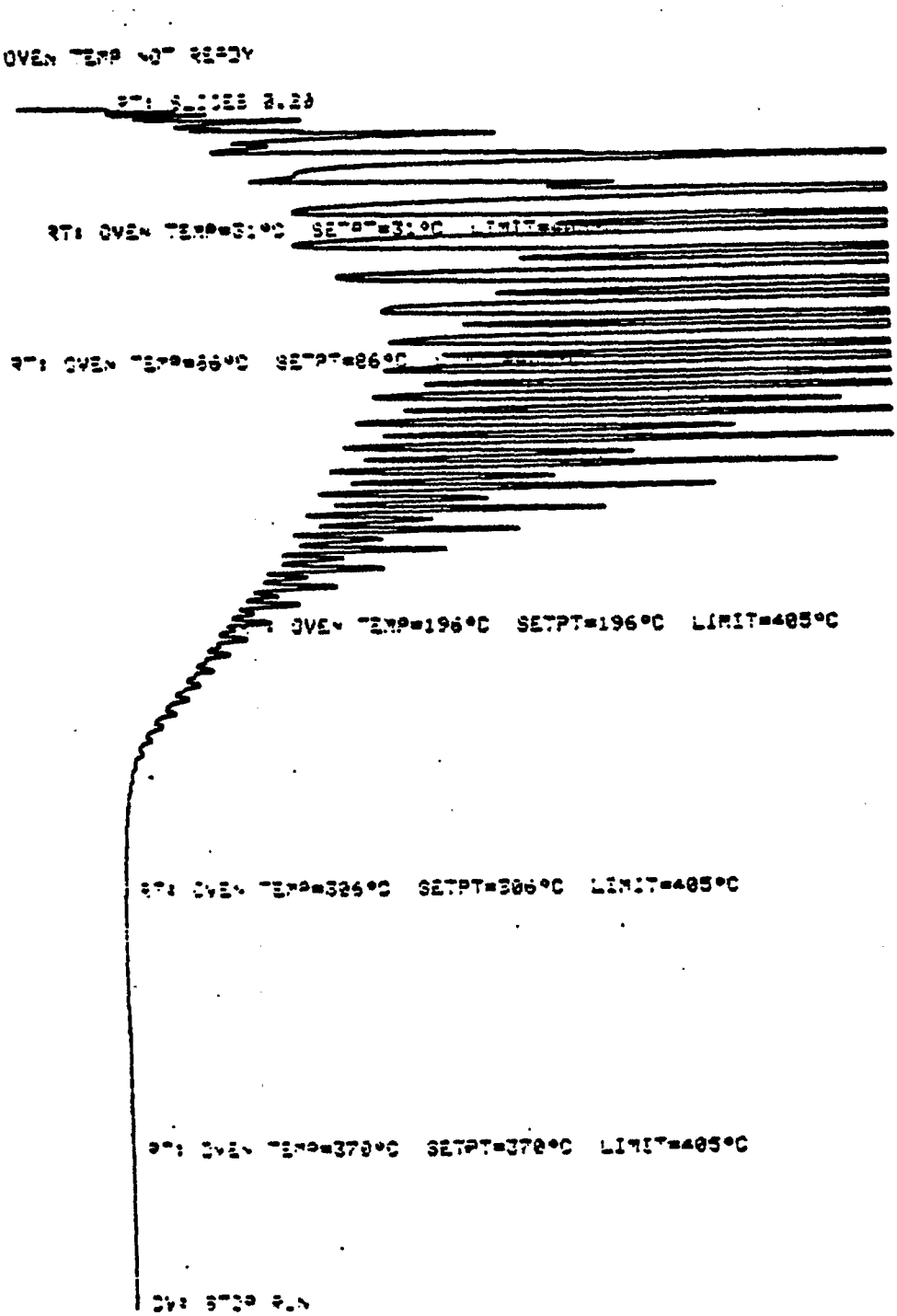

OVEN TEMP ADJ READY
OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
OVEN TEMP=326°C SETPT=306°C LIMIT=405°C
OVEN TEMP=370°C SETPT=370°C LIMIT=405°C

Fig. B64

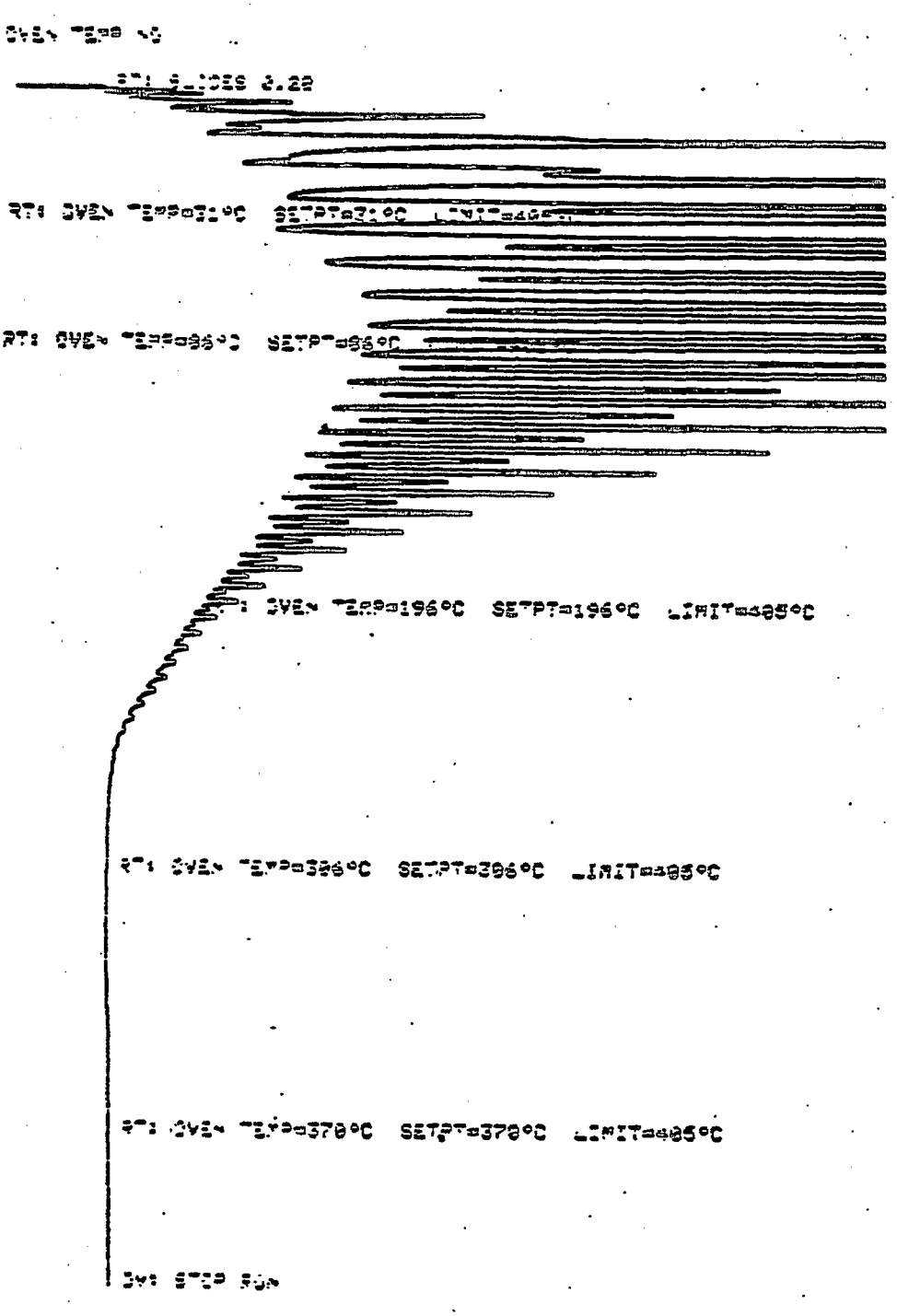


Fig. B65

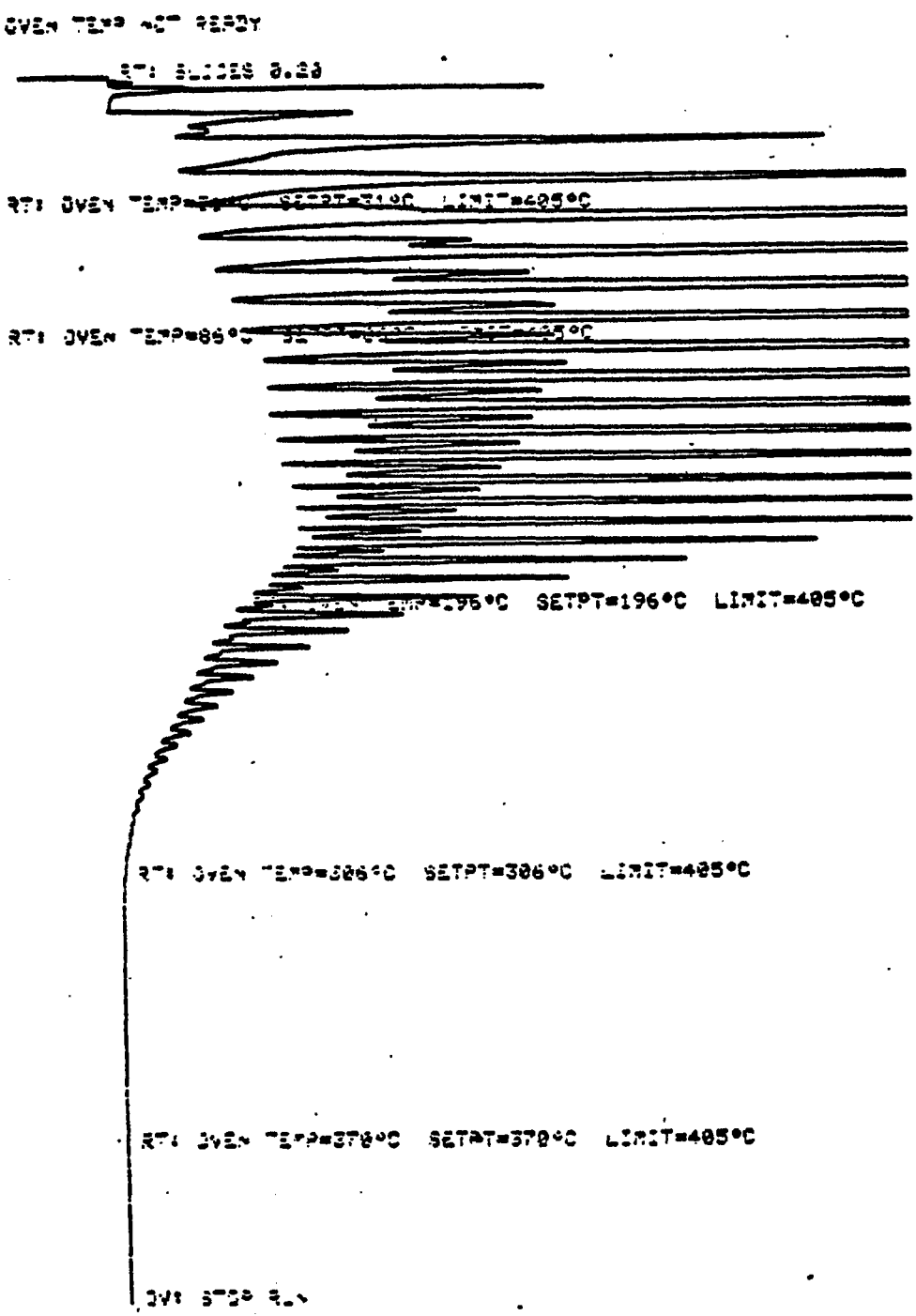

SETPT=196°C LIMIT=405°C
SETPT=306°C LIMIT=405°C
SETPT=370°C LIMIT=405°C

Fig. B66

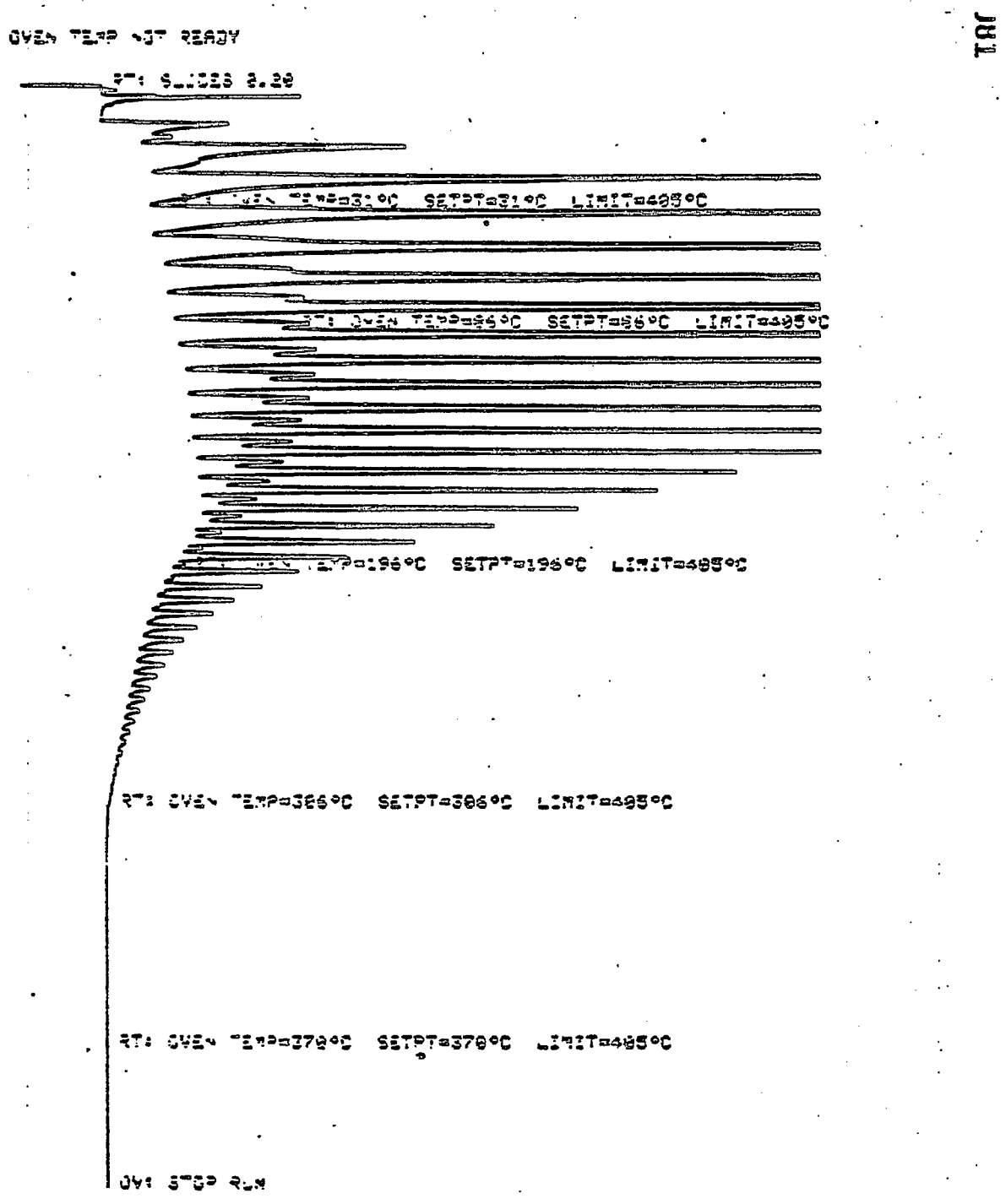

OVEN TEMP NOT READY
RT: 5.1035 2.20
SETPT=310°C LIMIT=405°C
RT: OVEN TEMP=356°C SETPT=356°C LIMIT=405°C
TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=370°C SETPT=370°C LIMIT=405°C
OVT STOP RUN
SAMPLE:12:85-3-7L

Fig. B67

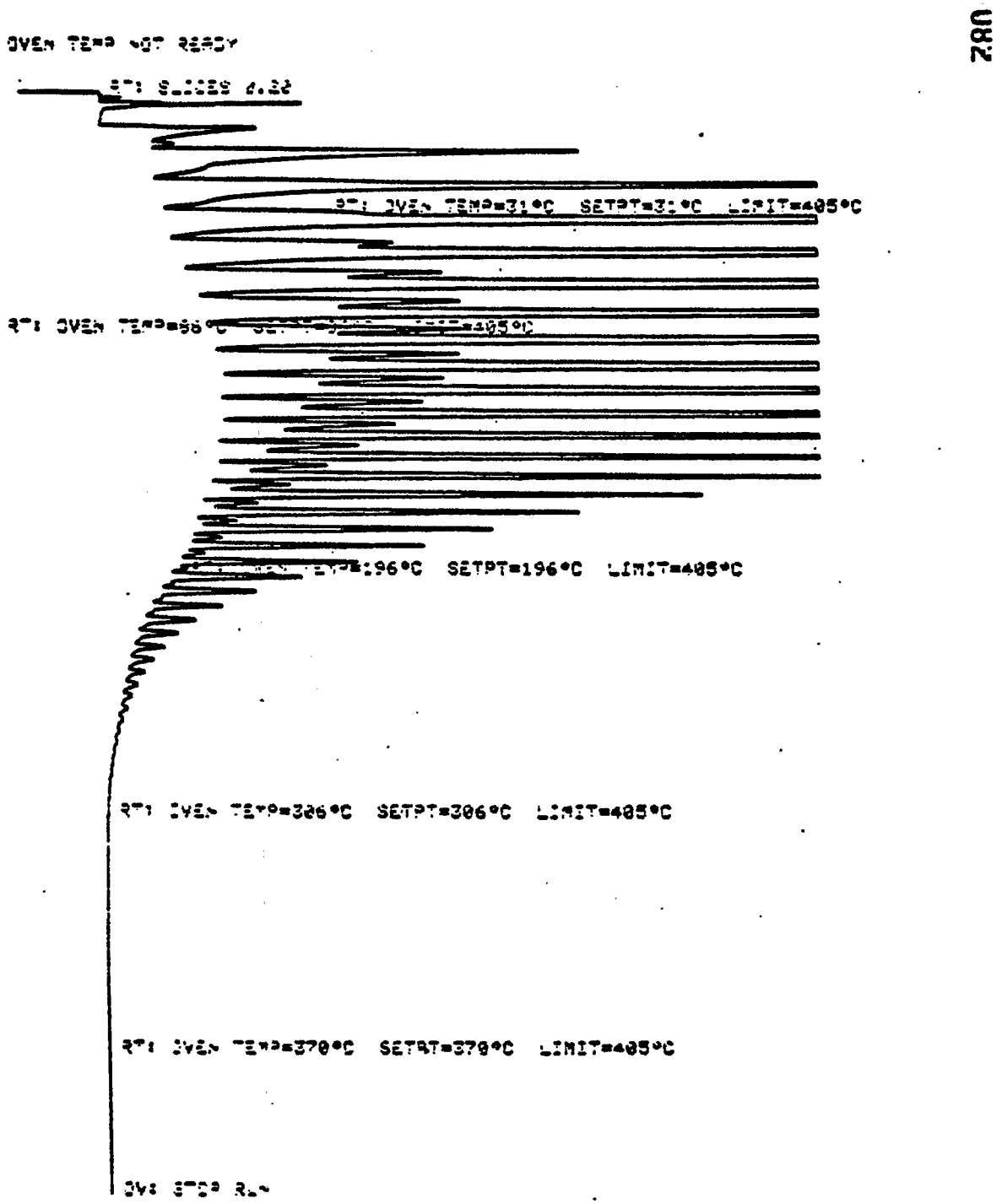

OVEN TEMP NOT READY
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=370°C SETPT=370°C LIMIT=405°C

Fig. B68

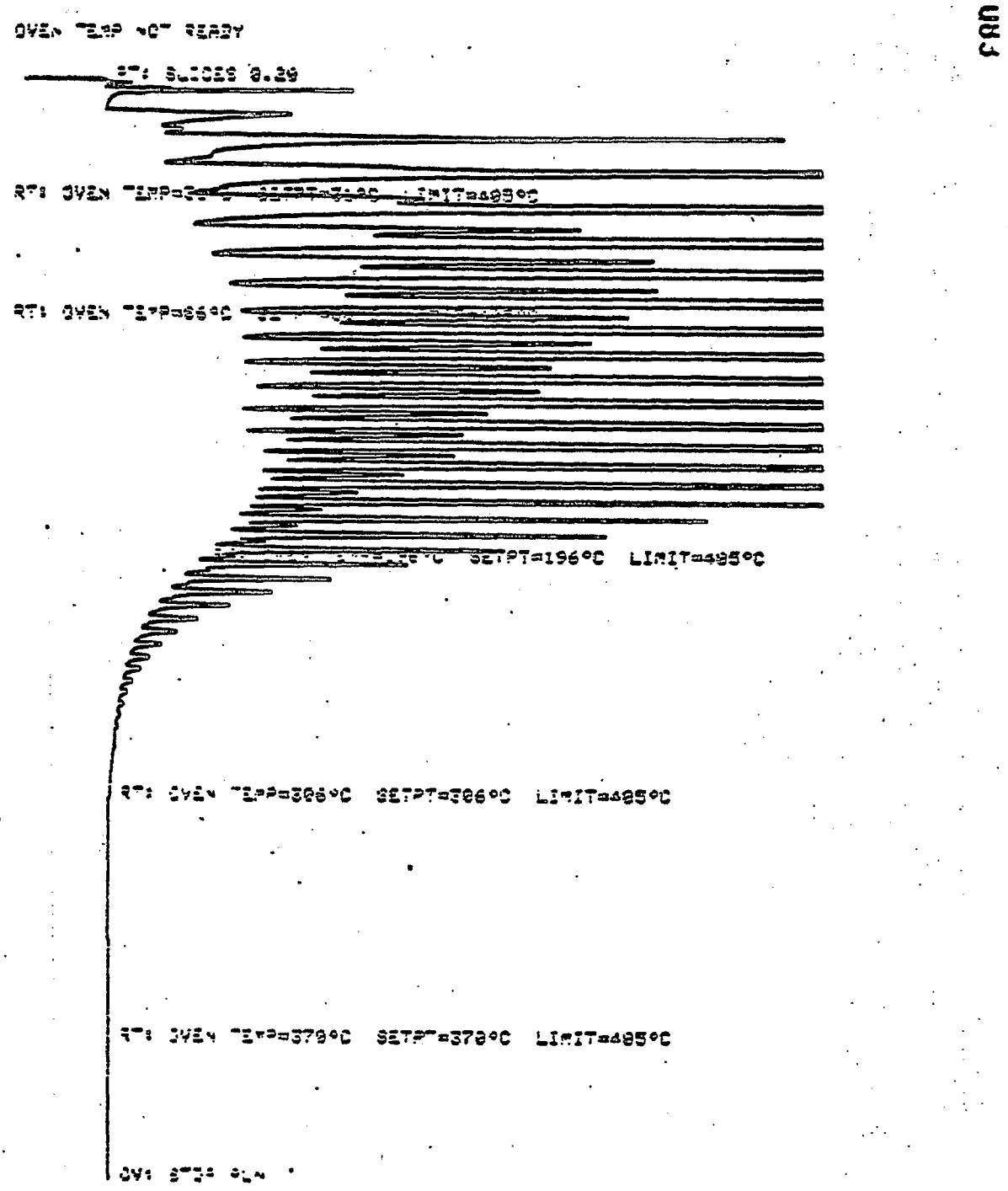
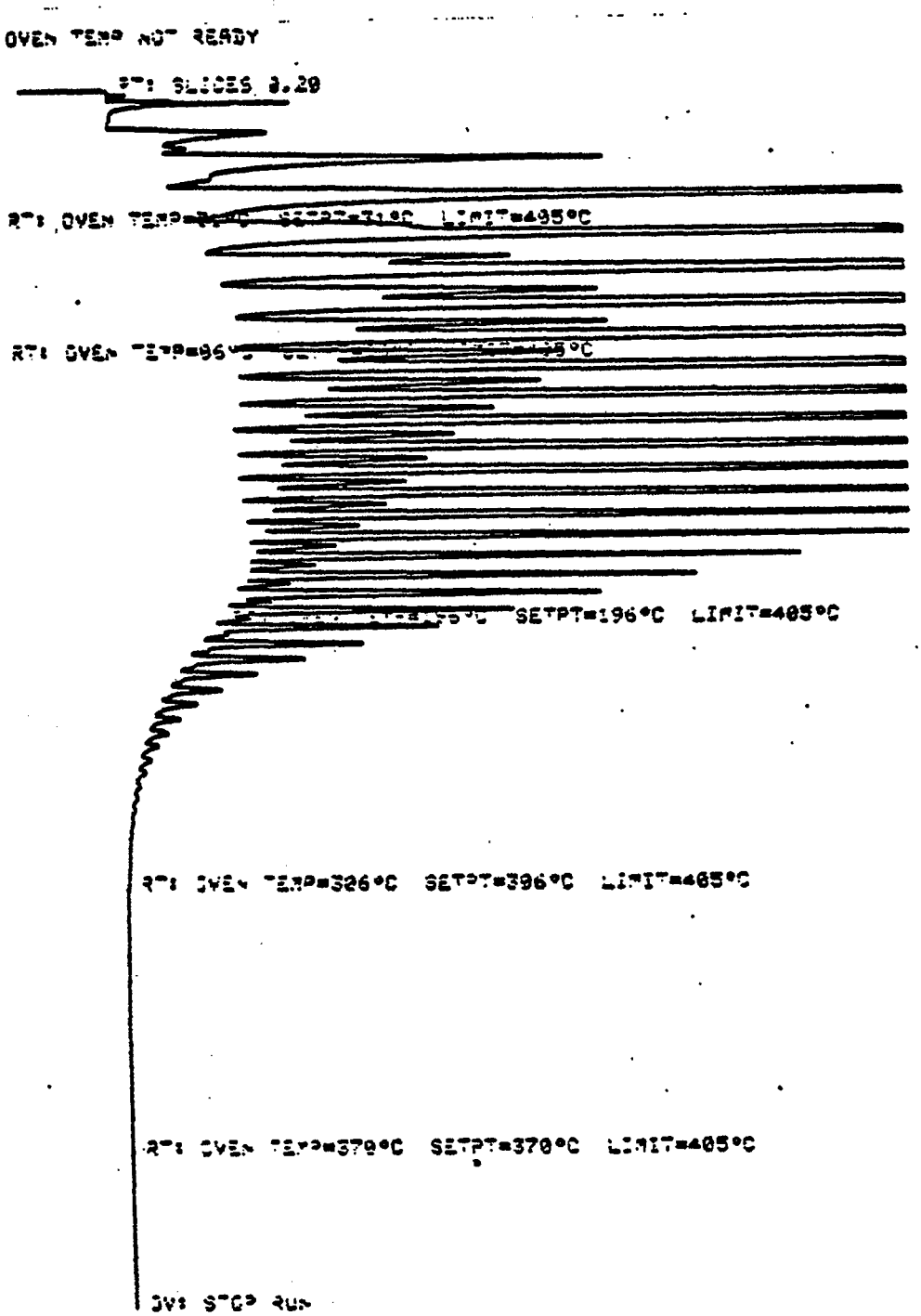

SETPT=196°C LIMIT=485°C
SETPT=306°C LIMIT=485°C
SETPT=378°C LIMIT=485°C

Fig. B69


OVEN TEMP NOT READY
RT: SLICES 8.29
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SETPT=396°C LIMIT=405°C
SETPT=370°C LIMIT=405°C

Table B3

RESULT OF SYNGAS OPERATION

RUN NO. 12185-03
CATALYST CO/U103 12006-38 80 CC 32.36 GM (31.92 G AFTER RUN -.4G)
FEED H2:CO OF 50:50 @400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-03-01	185-03-02	185-03-03	185-03-04	185-03-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.25	43.25	66.50	91.50	114.50
PRESSURE,PSIG	100	100	100	100	100
TEMP. C	262	261	261	261	261
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	19.25	24.00	23.50	25.00	23.00
EFFLNT GAS LITER	180.96	226.43	227.11	247.45	229.35
GM AQUEOUS LAYER	55.29	67.72	65.41	70.48	65.25
GM OIL	25.42	31.54	30.00	30.51	26.67
MATERIAL BALANCE					
GM ATOM CARBON %	91.76	92.44	94.08	93.93	92.66
GM ATOM HYDROGEN %	100.07	100.87	101.71	102.04	101.53
GM ATOM OXYGEN %	96.74	94.94	95.26	95.79	95.95
RATIO CHX/(H2O+CO2)	0.8917	0.9435	0.9729	0.9568	0.9241
RATIO X IN CHX	2.4949	2.5039	2.5111	2.5210	2.5492
USAGE H2/CO PRODT	1.5979	1.6154	1.6185	1.6640	1.6948
FEED H2/CO FRM EFFLNT	1.0905	1.0912	1.0811	1.0863	1.0957
RESIDUAL H2/CO RATIO	0.3933	0.3869	0.3825	0.3908	0.3984
RATIO CO2/(H2O+CO2)	0.2646	0.2513	0.2470	0.2304	0.2270
K SHIFT IN EFFLNT	0.1415	0.1298	0.1255	0.1170	0.1170
SPECIFIC ACTIVITY SA	14.5010	15.3414	15.2251	13.8321	13.0229
CONVERSION					
ON CO %	57.88	57.33	56.52	54.63	53.78
ON H2 %	84.81	84.87	84.62	83.68	83.20
ON CO+H2 %	71.93	71.70	71.12	69.75	69.16
PRDT SELECTIVITY,WT %					
CH4	18.87	19.17	19.43	19.95	21.43
C2 HC'S	2.97	3.15	3.20	3.33	3.60
C3H8	3.33	3.54	3.83	3.78	3.81
C3H6=	2.61	2.42	2.56	2.40	2.09
C4H10	2.75	2.88	3.03	3.06	3.29
C4H8=	3.42	3.19	3.24	3.15	3.10
C5H12	4.30	4.55	4.63	4.69	4.10
C5H10=	2.21	2.14	2.18	3.10	2.84
C6H14	4.41	4.57	4.72	4.78	4.84
C6H12= & CYCLO'S	0.96	0.88	1.24	1.25	1.22
C7+ IN GAS	9.21	9.78	10.01	9.46	9.43
LIQ HC'S	44.95	43.75	41.92	41.07	40.25
TOTAL	100.00	100.00	100.00	100.00	100.00

Table B3 (continued)

SUB-GROUPING					
C1 -C4	33.95	34.34	35.29	35.66	37.32
C5 -420 F	42.00	43.35	43.95	44.42	43.76
420-700 F	21.62	19.16	17.98	17.46	16.66
700-END PT	2.43	3.15	2.77	2.46	2.25
C5+-END PT	66.05	65.66	64.71	64.34	62.68
ISO/NORMAL MOLE RATIO					
C4	0.0144	0.0166	0.0170	0.0177	0.0181
C5	0.1069	0.1073	0.1160	0.1153	0.0796
C6	0.2147	0.2573	0.2258	0.2347	0.2433
C4=	0.1090	0.1175	0.1268	0.1270	0.1376
PARAFFIN/OLEFIN RATIO					
C3	1.2155	1.3975	1.4298	1.5050	1.7417
C4	0.7754	0.8713	0.9025	0.9379	1.0252
C5	1.8884	2.0630	2.0709	1.4702	1.4043
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8118	0.8134	0.8050	0.7991	0.7961
RATIO CH4/(1-A)**2	5.3268	5.5086	5.1102	4.9445	5.1531
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL	CLR OIL	CLR OIL	CLR OIL
DENSITY	0.7518	0.7500	0.7487	0.7480	0.7473
N, REFRACTIVE INDEX	1.4226	1.4225	1.4220	1.4223	1.4214
SIMULT'D DISTILATN					
10 WT % @ DEG F	256	254	253	253	252
16	295	290	288	287	284
50	433	422	419	415	410
84	608	619	603	594	588
90	653	670	659	648	643
RANGE(16-84 %)	313	329	315	307	304
WT % @ 420 F	46.50	49.00	50.50	51.50	53.00
WT % @ 700 F	94.60	92.80	93.40	94.00	94.40

Table B4

RESULT OF SYNGAS OPERATION

RUN NO. 12185-03
CATALYST CO/U103 12006-38 80 CC 32.36 GM (31.92 G AFTER RUN -.4G)
FEED H2:CO OF 50:50 @400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-03-06	185-03-07	185-03-08	185-03-09	185-03-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	138.50	162.50	186.50	214.00	234.50
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	259	258	259	259	259
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	22.00	24.00	24.00	27.50	20.50
EFFLNT GAS LITER	166.90	194.50	244.35	323.35	259.10
GM AQUEOUS LAYER	77.00	81.64	70.56	69.03	53.44
GM OIL	41.07	42.76	30.76	32.69	22.08
MATERIAL BALANCE					
GM ATOM CARBON %	84.89	85.27	85.04	92.90	96.12
GM ATOM HYDROGEN %	95.80	94.59	99.09	101.04	103.71
GM ATOM OXYGEN %	95.87	95.28	94.17	96.67	102.02
RATIO CHX/(H2O+CO2)	0.7796	0.7862	0.7836	0.9001	0.8473
RATIO X IN CHX	2.3132	2.3212	2.4791	2.5252	2.5272
USAGE H2/CO PRODT	1.7759	1.8639	1.8615	1.7538	1.8110
FEED H2/CO FRM EFFLNT	1.1286	1.1093	1.1653	1.0877	1.0791
RESIDUAL H2/CO RATIO	0.2809	0.2997	0.5275	0.5476	0.5538
RATIO CO2/(H2O+CO2)	0.1863	0.1561	0.1791	0.2026	0.1907
K SHIFT IN EFFLNT	0.0643	0.0554	0.1151	0.1391	0.1305
SPECIFIC ACTIVITY SA	7.9890	6.5128	2.3665	2.0494	1.8239
CONVERSION					
ON CO %	56.70	51.76	47.81	44.77	41.78
ON H2 %	89.22	86.96	76.37	72.20	70.12
ON CO+H2 %	73.94	70.27	63.18	59.06	56.49
PRDT SELECTIVITY,WT %					
CH4	9.77	10.22	17.87	20.18	20.19
C2 HC'S	1.79	1.89	2.95	3.29	3.32
C3H8	1.60	1.54	2.93	3.28	3.43
C3H6=	1.72	1.50	1.25	1.15	1.31
C4H10	1.61	1.57	2.74	2.98	3.14
C4H8=	2.26	2.07	2.01	1.91	2.18
C5H12	2.33	2.20	3.48	3.67	4.05
C5H10=	1.14	1.01	1.19	1.92	1.31
C6H14	2.78	2.59	3.72	4.20	4.78
C6H12= & CYCLO'S	1.23	1.07	0.57	0.59	1.01
C7+ IN GAS	5.91	6.06	7.22	8.12	9.57
LIQ HC'S	67.86	68.29	54.06	48.71	45.71
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	18.76	18.78	29.76	32.80	33.58
C5 -420 F	39.51	38.54	38.62	38.32	39.68
420-700 F	34.33	34.55	27.62	25.04	22.67
700-END PT	7.40	8.13	4.00	3.85	4.07

Table B4 (continued)

C5+-END PT	81.24	81.22	70.24	67.20	66.42
ISO/NORMAL MOLE RATIO					
C4	0.0154	0.0154	0.0215	0.0194	0.0188
C5	0.0421	0.0421	0.0582	0.0593	0.0525
C6	0.0959	0.0805	0.0873	0.1343	0.1244
C4=	0.0683	0.0659	0.1208	0.1256	0.1180
PARAFFIN/OLEFIN RATIO					
C3	0.8900	0.9834	2.2342	2.7102	2.5029
C4	0.6871	0.7328	1.3165	1.5053	1.3890
C5	1.9951	2.1091	2.8506	1.8608	3.0048
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8589	0.8614	0.8272	0.8267	0.8264
RATIO CH4/(1-A)**2	4.9114	5.3161	5.9829	6.7189	6.6978
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	CLD OIL	CLD OIL	OIL WAX	OIL WAX
DENSITY (@40 C)	0.7020	0.6655	0.7211	0.6541	0.6499
N, REFRACTIVE INDEX	1.4620	1.4270	1.4239	1.4236	1.4240
SIMULT'D DISTILATN					
10 WT % @ DEG F	267	277	275	284	289
16	306	309	306	308	307
50	472	483	454	457	454
84	660	669	621	632	643
90	711	719	670	679	691
RANGE(16-84 %)	354	360	315	324	336
WT % @ 420 F	38.50	37.50	41.50	40.70	41.50
WT % @ 700 F	89.10	88.10	92.60	92.10	91.10

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VI. Run 5 (12200-02) with Catalyst 5 (CO/UCC-103)

This catalyst is the same as Catalyst 4 in all respects except that it was activated at 300 psig H_2 instead of 100 psig. Temperature (260C) and H_2:CO ratio (1:1) were the same as in the previous run.

Possibly due to equipment malfunction during the activation procedure, in this run the catalyst was totally inactive. It was retested in Run 6.

VII. Run 6 (12200-03) with Catalyst 6 (Co/UCC-103)

This catalyst is identical to Catalysts 4 and 5, and it was activated under conditions identical to those in Run 5 (260C, 1:1 H_2:CO, 300 psig H_2).

These are the same conditions under which cobalt catalysts are normally activated; and the same catalyst, when activated at 100 psig H_2 in Run 4, was highly active initially.

Yet once more, as in Run 5, in this run it was totally inactive. There is no readily apparent explanation for this anomalous result.

VIII. Run 7 (12185-04) with Catalyst 7 (Co/UCC-103)

This run constitutes the first attempt in the present program to regenerate a cobalt catalyst which has been tested and deactivated in another run. The catalyst used is the spent catalyst remaining from Run 4 (12185-03), which was regenerated under 5 percent oxygen in nitrogen, reactivated under 100 psi hydrogen, and placed on stream under a reactor pressure of 300 psig.

Simulated distillations of the C_5^+ product are plotted in Figs. B70-71. Carbon number product distributions are plotted in Figs. B72-73. Chromatograms from simulated distillations are reproduced in Figs. B74-75. Detailed material balances appear in Table B5.

The conversion of the original catalyst in Run 4, after 234.5 hours on stream, was only 56.49 percent. In this run the initial conversion was substantially lower still, at 43.16 percent. This attempted regeneration failed to improve the catalyst's conversion, and based on the calculated specific activity it was only one-third as active as in its original state.

In one respect only, the production of methane, did regeneration improve the catalyst's performance. Comparison of the methane make by the method described in the report of Run 3, the "exp/corr" ratio of weight percent methane was 0.80:1, as against a ratio of 1.16:1 in the catalyst's original state. The produc-

tion of C_5^+ was about the same initially as in the catalyst's original state, but decreased with time on stream; and the butene content of the C_4 was less than 5 percent, as against about 42 percent in the catalyst's original state.

Aside from the useful reduction of the methane product, this first attempt at regenerating a spent cobalt catalyst with oxygen has been unsuccessful.

Fig. B70

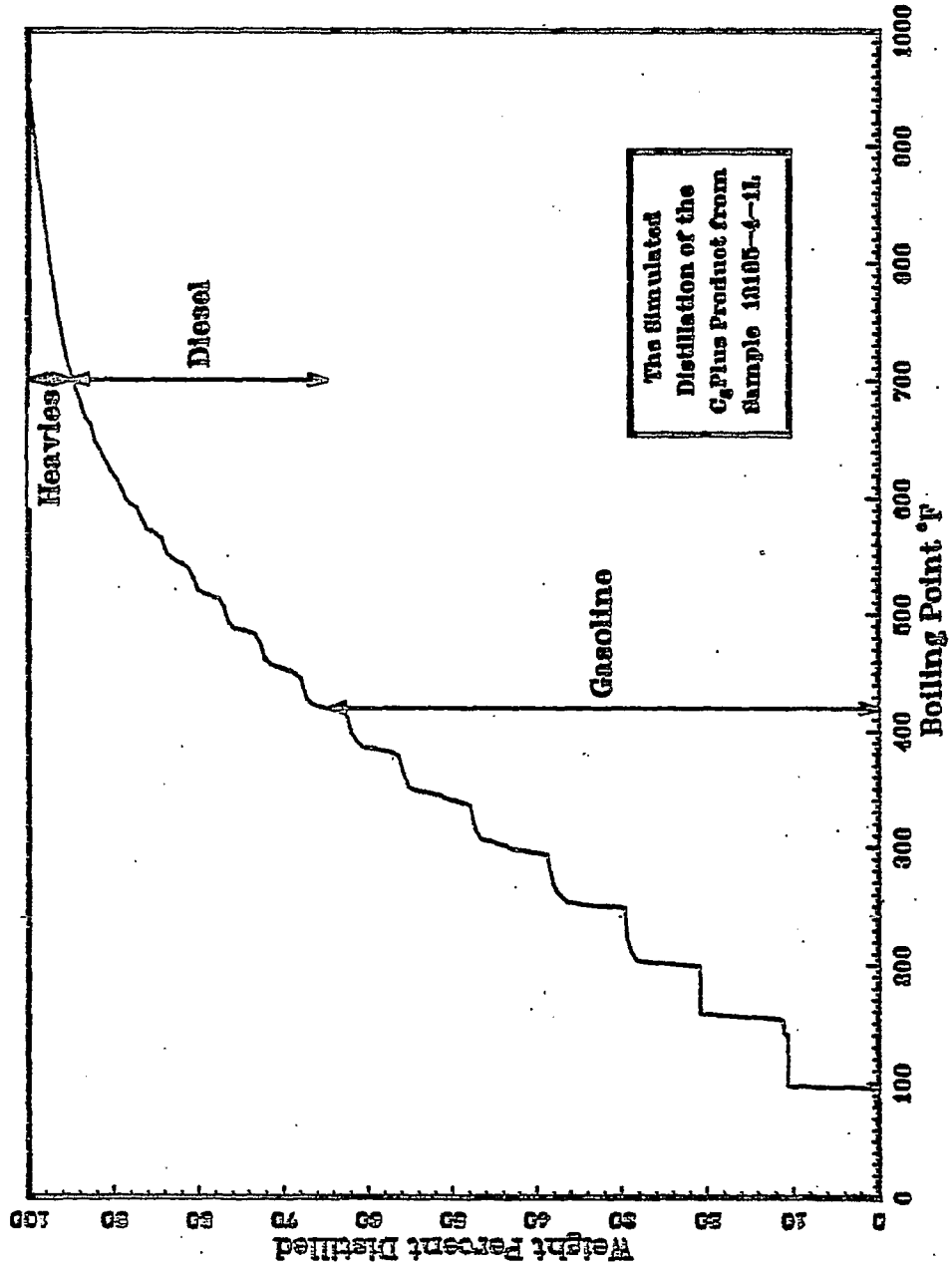

The Simulated Distillation of the C5 Plus Product from Sample 18105-4-11.
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B71

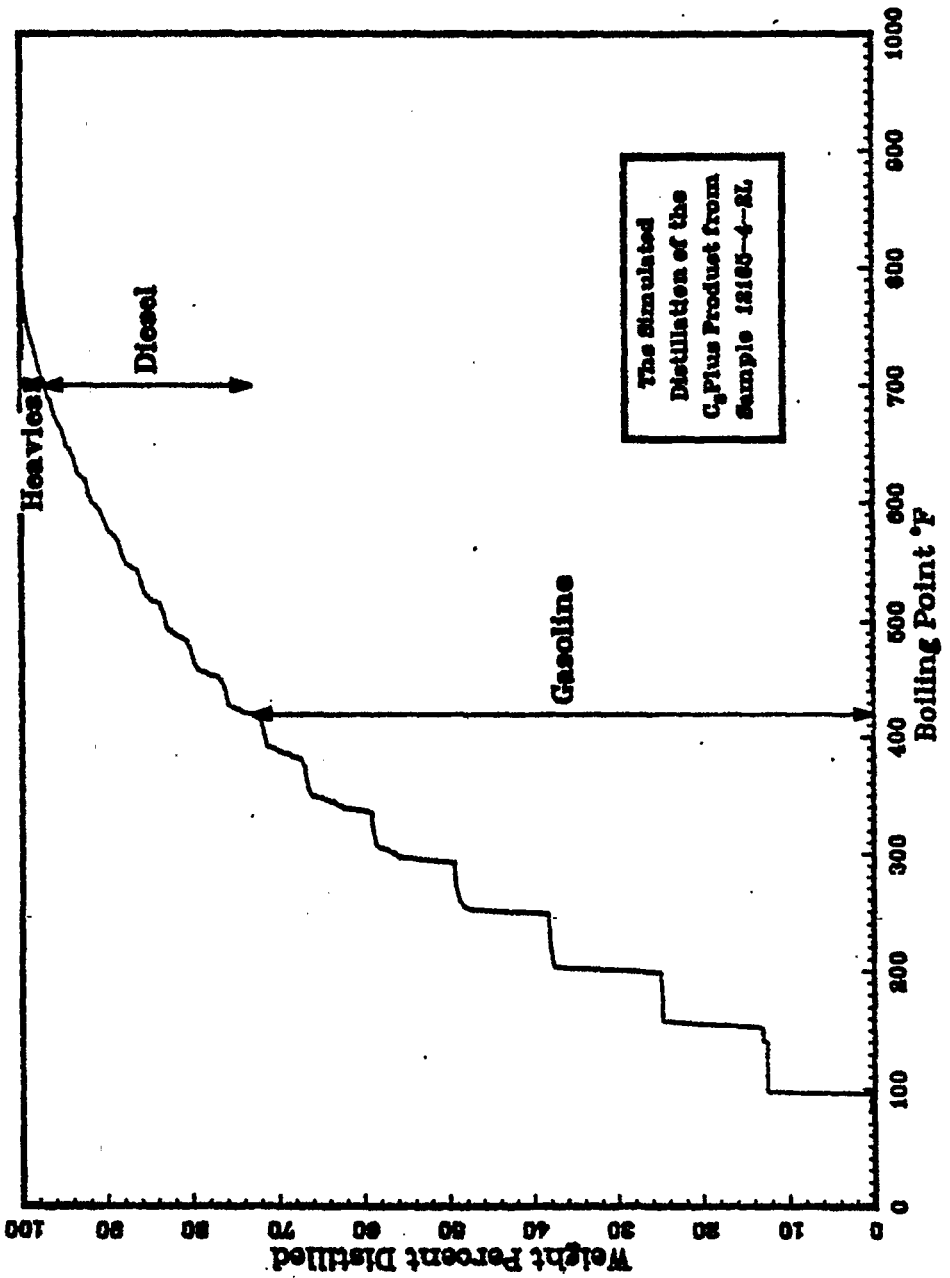

The Simulated Distillation of the C5 Plus Product from Sample 12185-4-2L
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B72

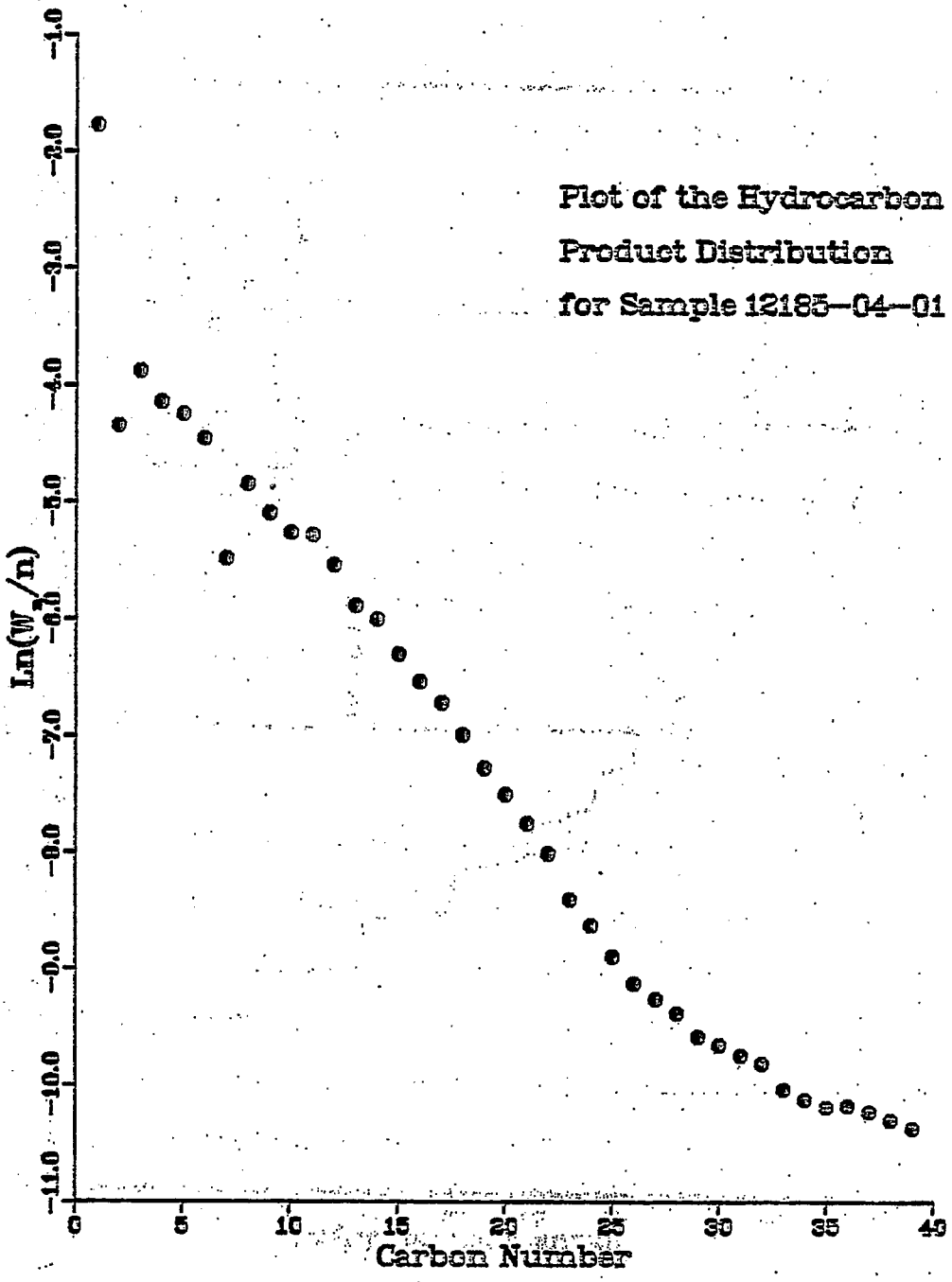

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-04-01
Ln(W_n/n)
-1.0
-3.0
-5.0
-7.0
-9.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B73

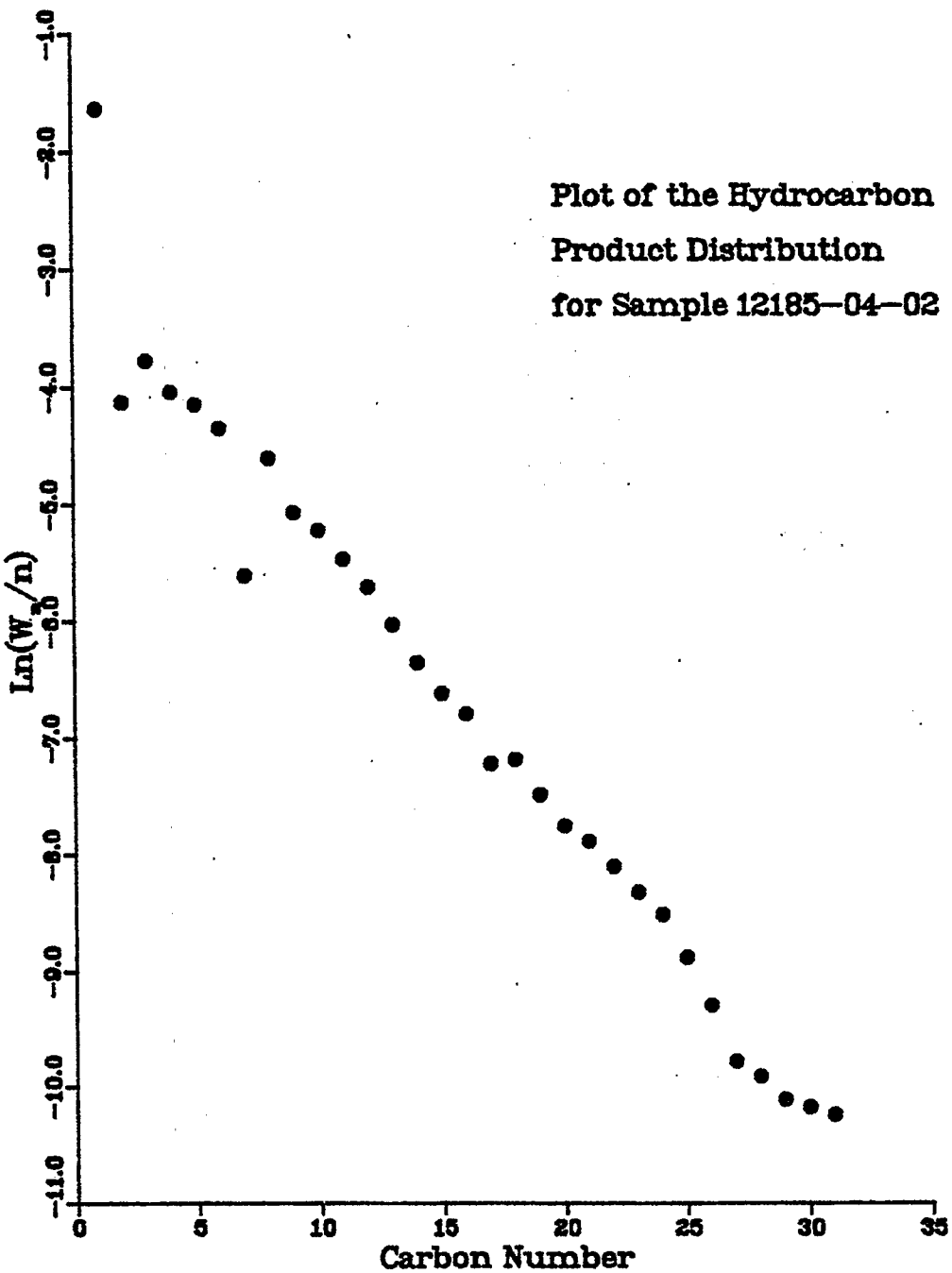

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-04-02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B74

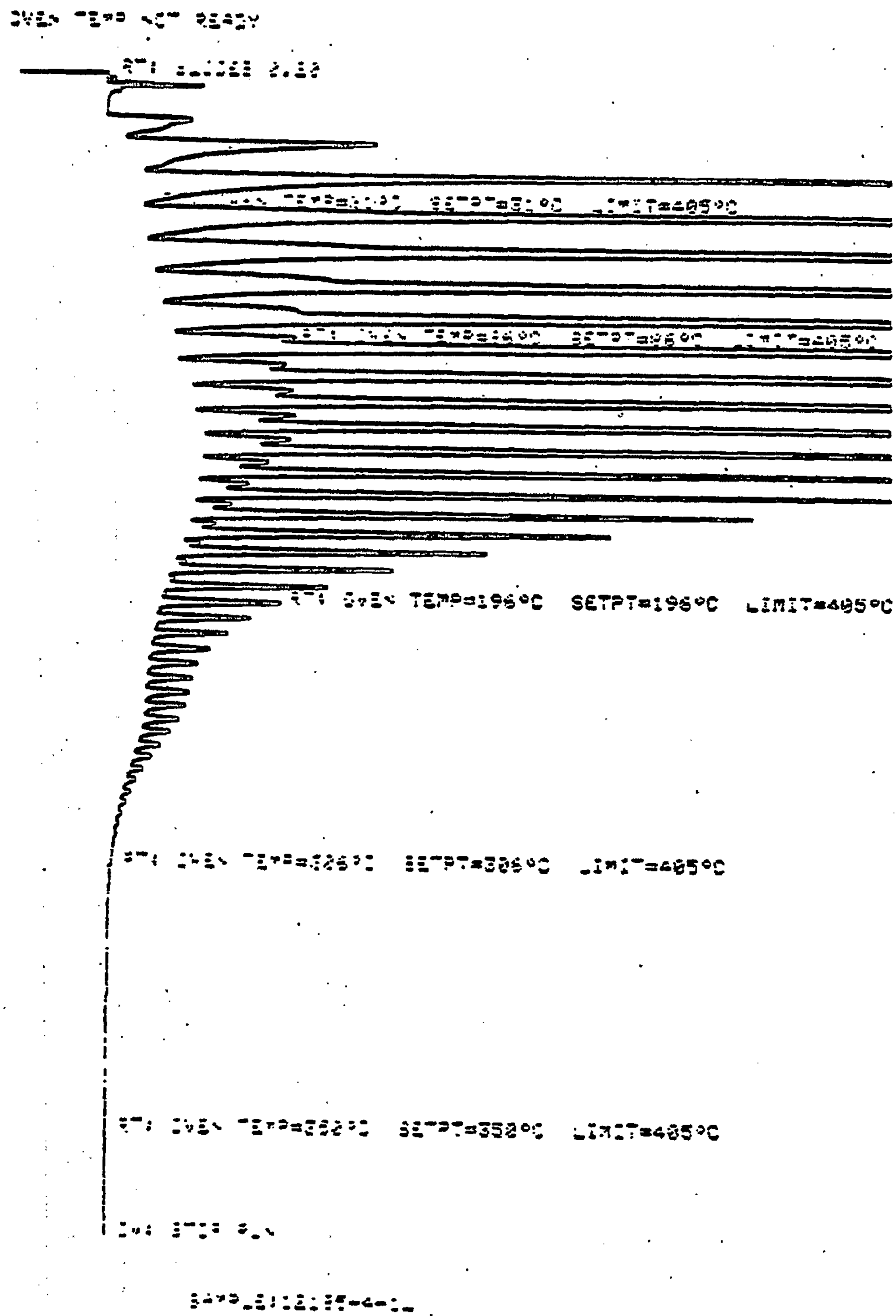


Fig. B75

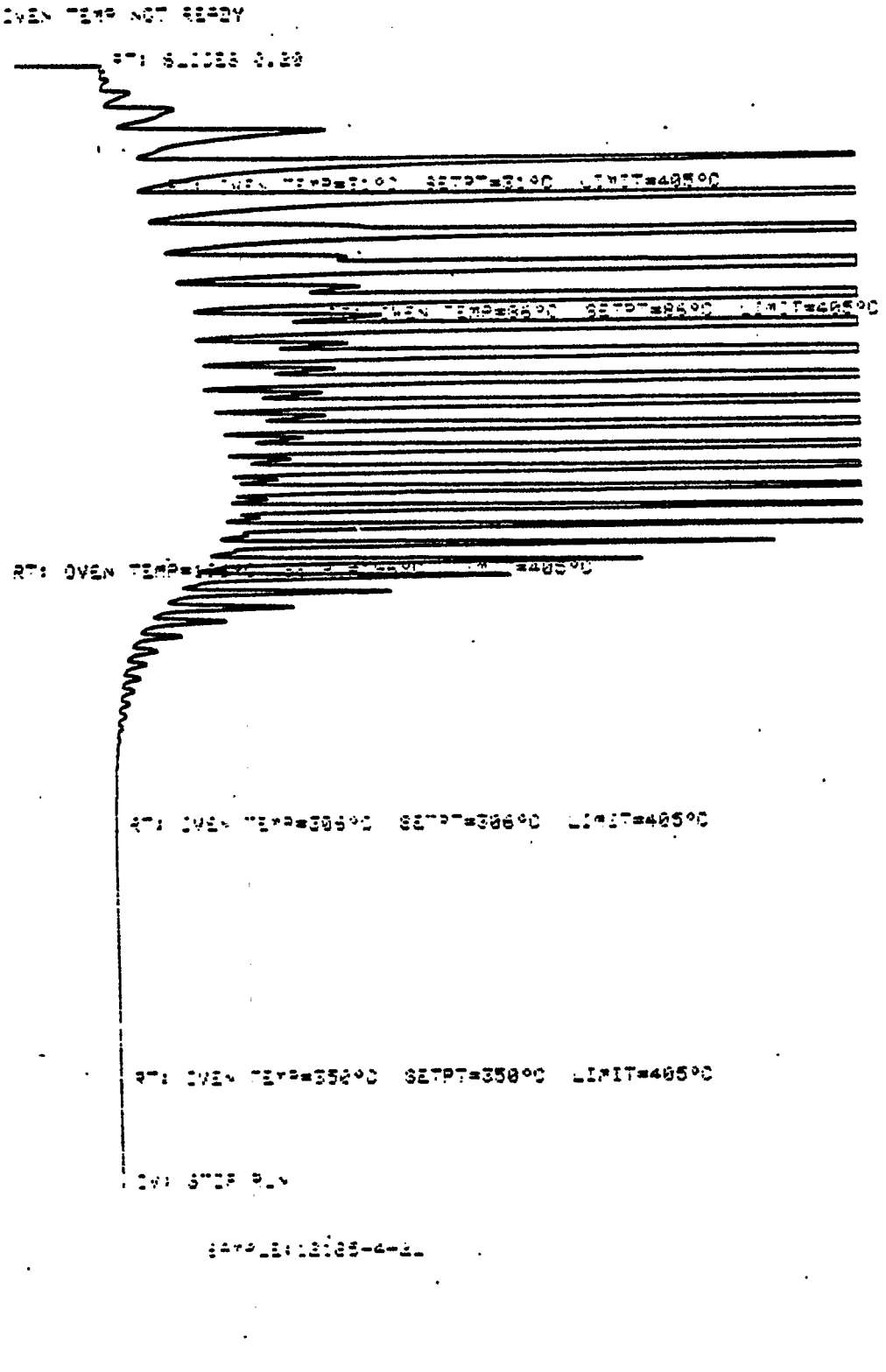

OVEN TEMP NOT READY
RT: OVEN TEMP=356°C SETPT=356°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
OV: STOP RUN

Table B5

RESULT OF SYNGAS OPERATION

RUN NO. 12185-04
CATALYST CO-U103 12006-38 80 CC 32.36 GM (31.92 G AFTER RUN -.4G)
FEED H2:CO OF 50:50 @400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-04-01	185-04-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	22.00	46.00
PRESSURE,PSIG	300	300
TEMP. C	260	262
FEED CC/MIN	400	400
HOURS FEEDING	22.00	24.00
EFFLNT GAS LITER	300.30	408.20
GM AQUEOUS LAYER	52.48	40.97
GM OIL	14.61	8.46
MATERIAL BALANCE		
GM ATOM CARBON %	84.82	90.74
GM ATOM HYDROGEN %	100.47	104.57
GM ATOM OXYGEN %	91.66	95.31
RATIO CHX/(H2O+CO2)	0.7667	0.7933
RATIO X IN CHX	2.5055	2.5567
USAGE H2/CO PRODT	2.5034	2.4950
FEED H2/CO FRM EFFLNT	1.1845	1.1524
RESIDUAL H2/CO RATIO	0.6990	0.8258
RATIO CO2/(H2O+CO2)	0.0117	0.0100
K SHIFT IN EFFLNT	0.0083	0.0083
SPECIFIC ACTIVITY SA	0.6933	0.3465
CONVERSION		
ON CO %	26.91	19.57
ON H2 %	56.87	42.36
ON CO+H2 %	43.16	31.77
PRDT SELECTIVITY,WT %		
CH4	16.93	19.52
C2 HC'S	2.60	3.23
C3H8	5.98	6.61
C3H6=	0.21	0.26
C4H10	6.07	6.81
C4H8=	0.30	0.23
C5H12	6.96	7.85
C5H10=	0.21	0.06
C6H14	6.93	7.76
C6H12= & CYCLO'S	0.03	0.00
C7+ IN GAS	12.63	19.76
LIQ HC'S	41.15	27.91
TOTAL	100.00	100.00

Table B5 (continued)

SUB-GROUPING		
C1 -C4	32.09	36.66
C5 -420 F	44.04	46.04
420-700 F	20.37	15.24
700-END PT	3.50	2.07
C5+-END PT	67.91	63.34
ISO/NORMAL MOLE RATIO		
C4	0.0254	0.0259
C5	0.0327	0.0312
C6	0.0551	0.0477
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	27.3551	23.9636
C4	19.3933	28.5972
C5	31.9762	127.6000
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8044	0.7923
RATIO CH4/(1-A)**2	4.4272	4.5246
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	CLD OIL
DENSITY	0.7518	0.7415
N, REFRACTIVE INDEX	1.4232	1.4235
SIMULT'D DISTILATN		
10 WT % @ DEG F	301	305
16	313	344
50	453	457
84	622	626
90	683	674
RANGE(16-84 %)	309	282
WT % @ 420 F	42.00	38.00
WT % @ 700 F	91.50	92.60

IX. Run 8 (12200-04) with Catalyst 8 (Co/Th/X_4/UCC-103+S115)

This catalyst was prepared to test the effect of S115 (silicalite) as a second Molecular Sieve. This is essentially the same catalyst as the Third Annual Report Catalyst 6 (Run 11677-11) of the previous contract DE-AC22-81PC40077, except that the UCC-101 has been replaced by S115.

The thorium-promoted cobalt oxide was formed in close contact with UCC-103, then further promoted with X_4. The resulting powder was mixed with S115 in a weight ratio of 1.125:1, and the mixture, after bonding with 15 weight percent silica, was extruded as 1/8-inch pellets. The final catalyst contained 4.4 percent cobalt, 0.6 percent thorium, and 0.4 percent X_4.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B76-79. Simulated distillations of the C_5^+ product are plotted in Figs. B80-88. Carbon number product distributions are plotted in Figs. B89-97. Chromatograms from simulated distillations are reproduced in Figs. B98-106. Detailed material balances appear in Tables B6-7.

Excluding the first data point, at 18.5 hours on stream, the catalyst deactivated during the remaining 288 hours of the run at a rate of one percentage point every 52.6 hours. With Third Annual Report Catalyst 6, in contrast, there was no measurable loss

of activity after the first 115.5 hours on stream. The difference is believed to be due, not to the substitution of S115 for UCC-101, but to differences in intimately combining the metal-UCC-103 component.

The specific activity, initially 1.12, declined to 0.75 at the end of the 306.5 hour run. These levels are comparable to those calculated for Third Annual Report Catalyst 6, which were 0.97 after 115.5 hours on stream, and 0.89 at the end of the run, 284.5 hours.

About 6 percent of the oxygen was converted to CO_2, as against about 9 percent for Third Annual Report Catalyst 6. The usage ratio of this catalyst was a little higher.

Like the conversion, the product selectivity failed to match that of Third Annual Report Catalyst 6 in stability. Methane production rose from 10.1 percent after 42.5 hours to 13.4 percent after 306.5 hours. Fluctuations in the reactor temperature make it difficult to calculate the rate of increase precisely, but it can be estimated, from a linear least squares analysis, at about one percentage point every 140 hours. For the Third Annual Report Catalyst 6 the rate of increase was estimated at one percentage point every 3700 hours, although the quantities actually produced during the run were a little higher than those of the present catalyst. Production of C_5^+ was likewise a little less stable than with Third Annual Report Catalyst 6.

When the two catalysts are compared at about 115 hours on stream, the product of this catalyst was slightly heavier, with

an α of 0.826 as against 0.806. The C_5^+ was 72.2 percent of total product and the heavies 5.9 percent, as against 69.3 and 2.9 percent respectively for Third Annual Report Catalyst 6. The product from C_5 to 700F, however, was essentially the same for both at about 66 percent.

One encouraging result of this run is the lower methane production. Again comparing the two catalysts at about 115 hours on stream, the "exp/corr" ratio of weight percent methane produced by this catalyst (as calculated by the method described in the report of Run 3) was 0.69:1 as against 0.92:1 for Third Annual Report Catalyst 6. In the product of this catalyst, therefore, the excess of methane, over and above that which would be expected from a linear extrapolation of the Schulz-Flory plot, has been substantially reduced.

Otherwise there are no noteworthy differences between the products of the two catalysts. They were alike in butene content of the C_4's (about 60 percent), in isomerization of the pentane, and in aromatic content of the C_5-350C gasoline fraction (less than one percent); and aside from the excess of methane the Schulz-Flory plots show fairly linear product distributions for both.

The substitution of S115 for UCC-101 in the formulation of this catalyst had no significant effect on motor fuel quality. The catalyst did show improvement in reducing the methane make but lacked good stability.

Fig. B76

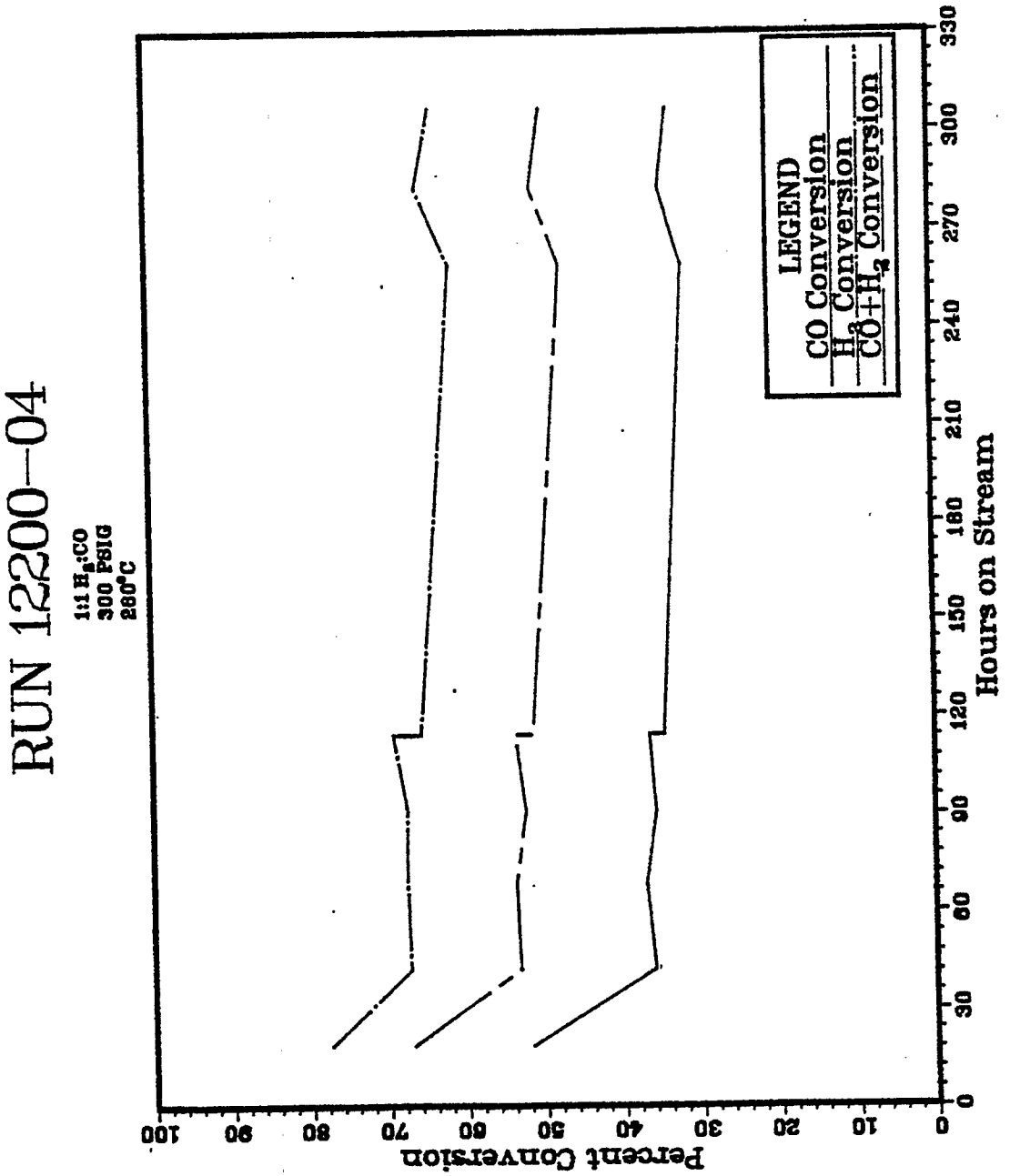

RUN 12200-04
1:1 H2:CO
300 PSIG
280°C
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
30
60
90
120
150
180
210
240
270
300
330
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion

Fig. B77

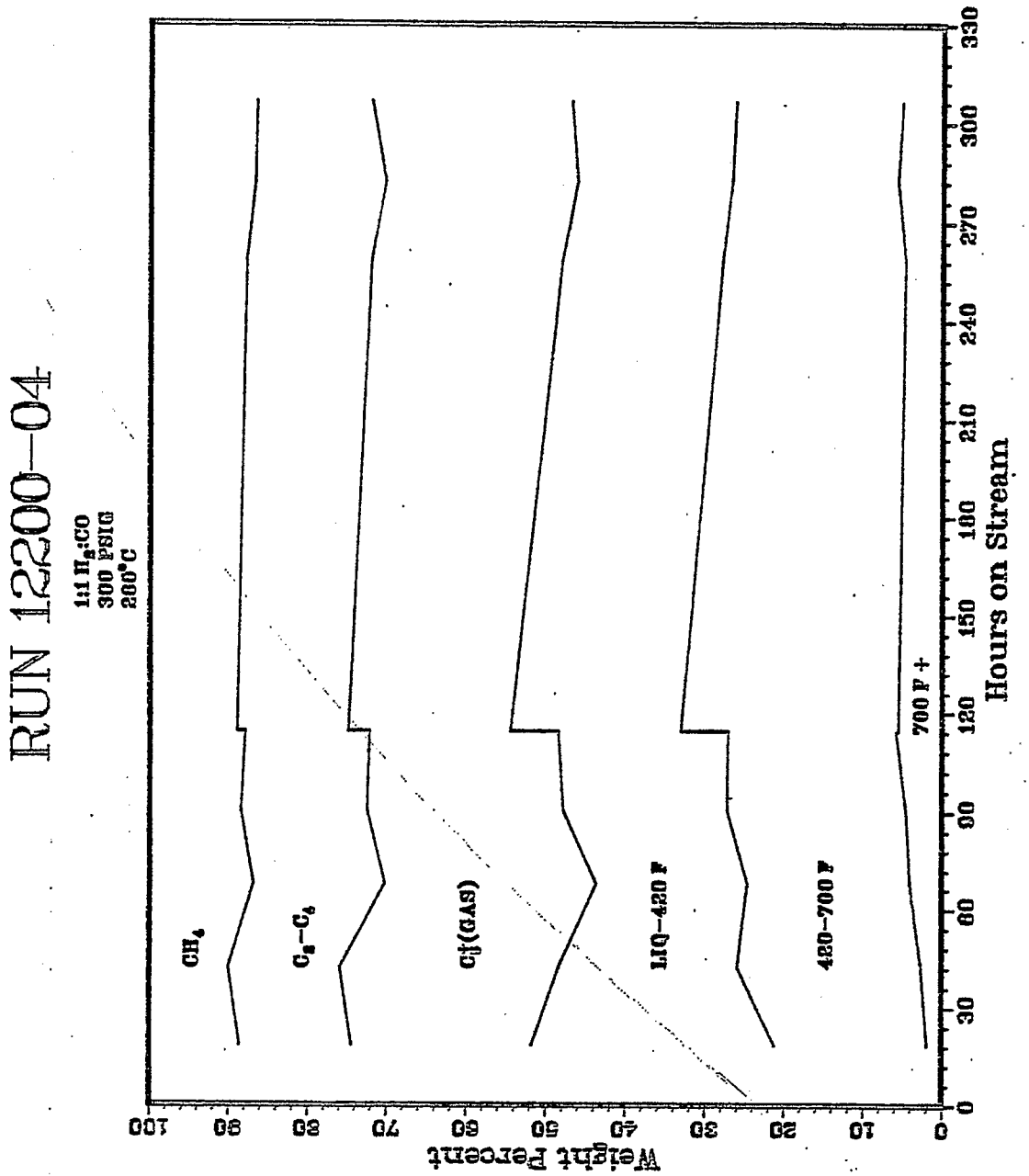
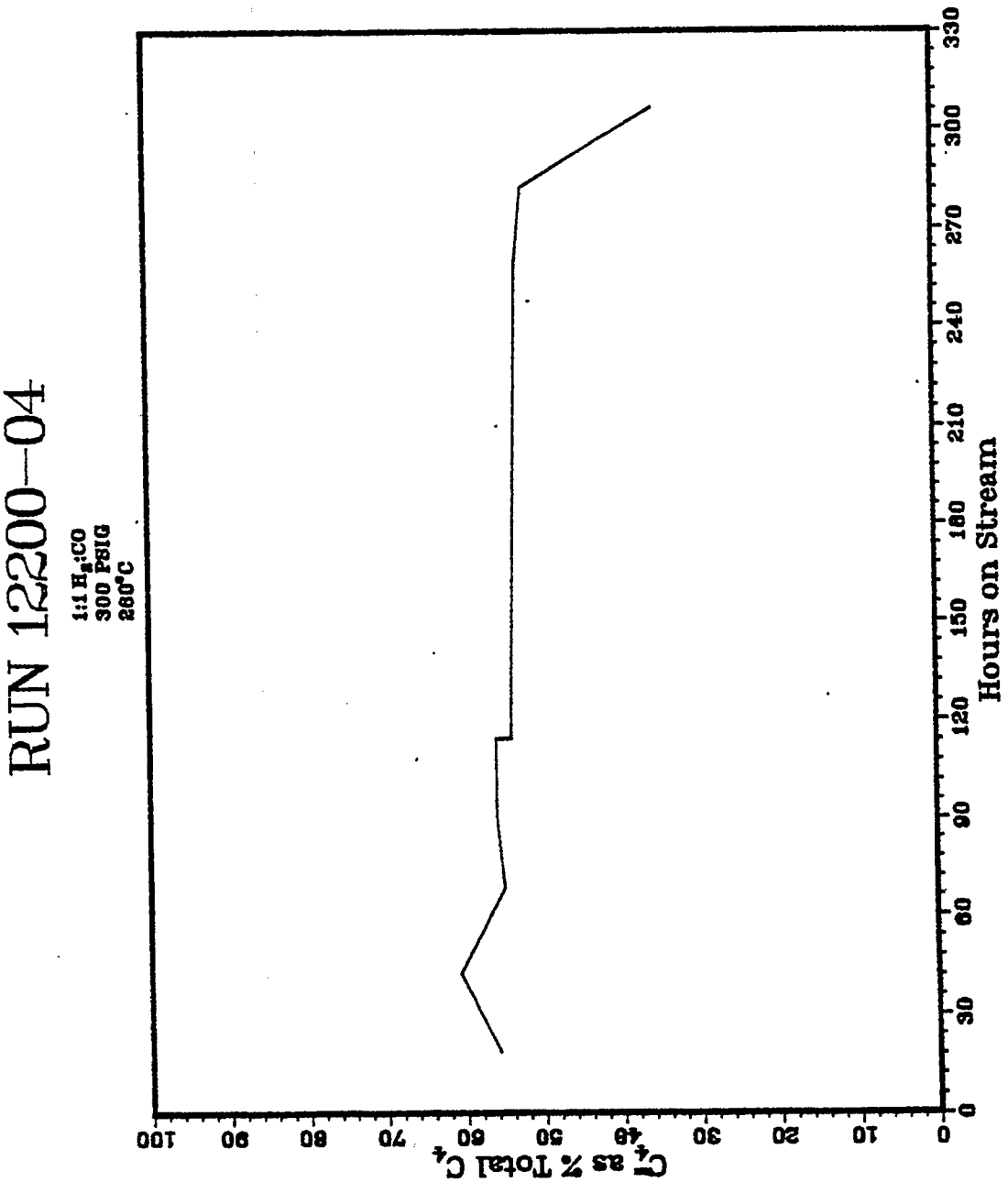

RUN 12200-04
1:1 H2:CO
300 PSIG
200°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F+
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
300
330

Fig. B78


RUN 12200-04
1:1 H2:CO
300 PSIG
280°C
C4 as % Total C4
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
300
330
Hours on Stream

RUN 12200-04

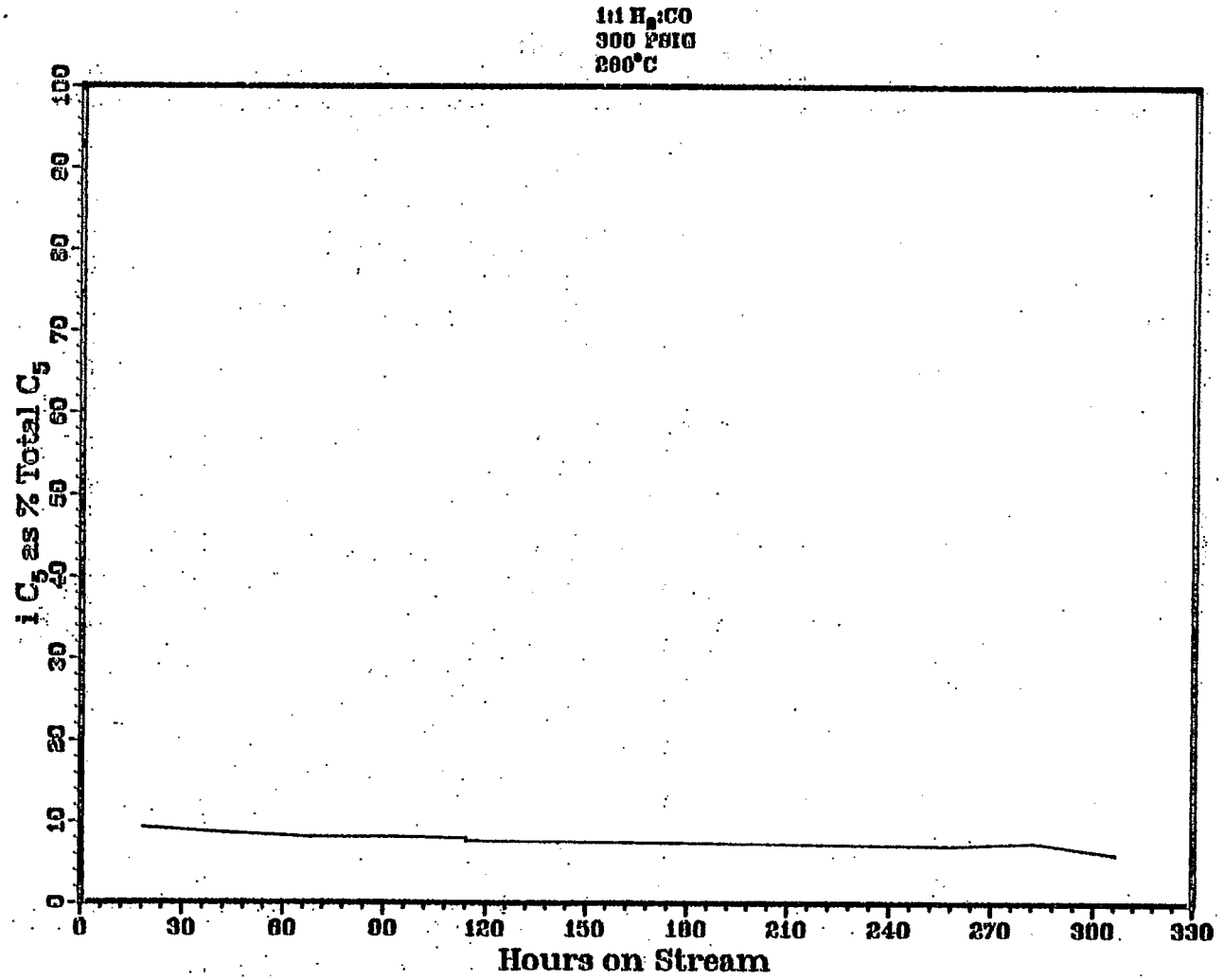


Fig. B79

Fig. B80

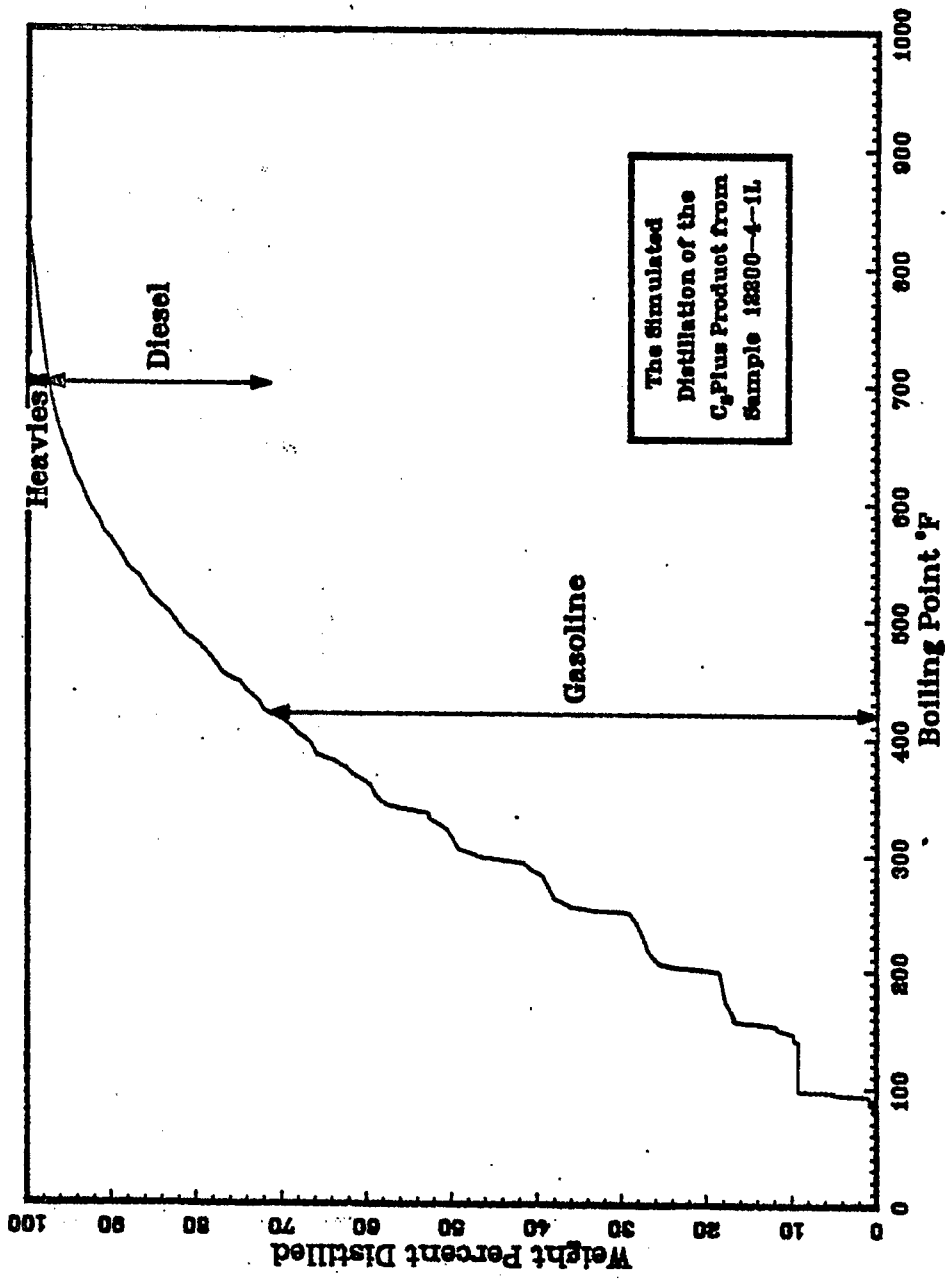

The Simulated Distillation of the C5Plus Product from Sample 12300—4—1L
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B81

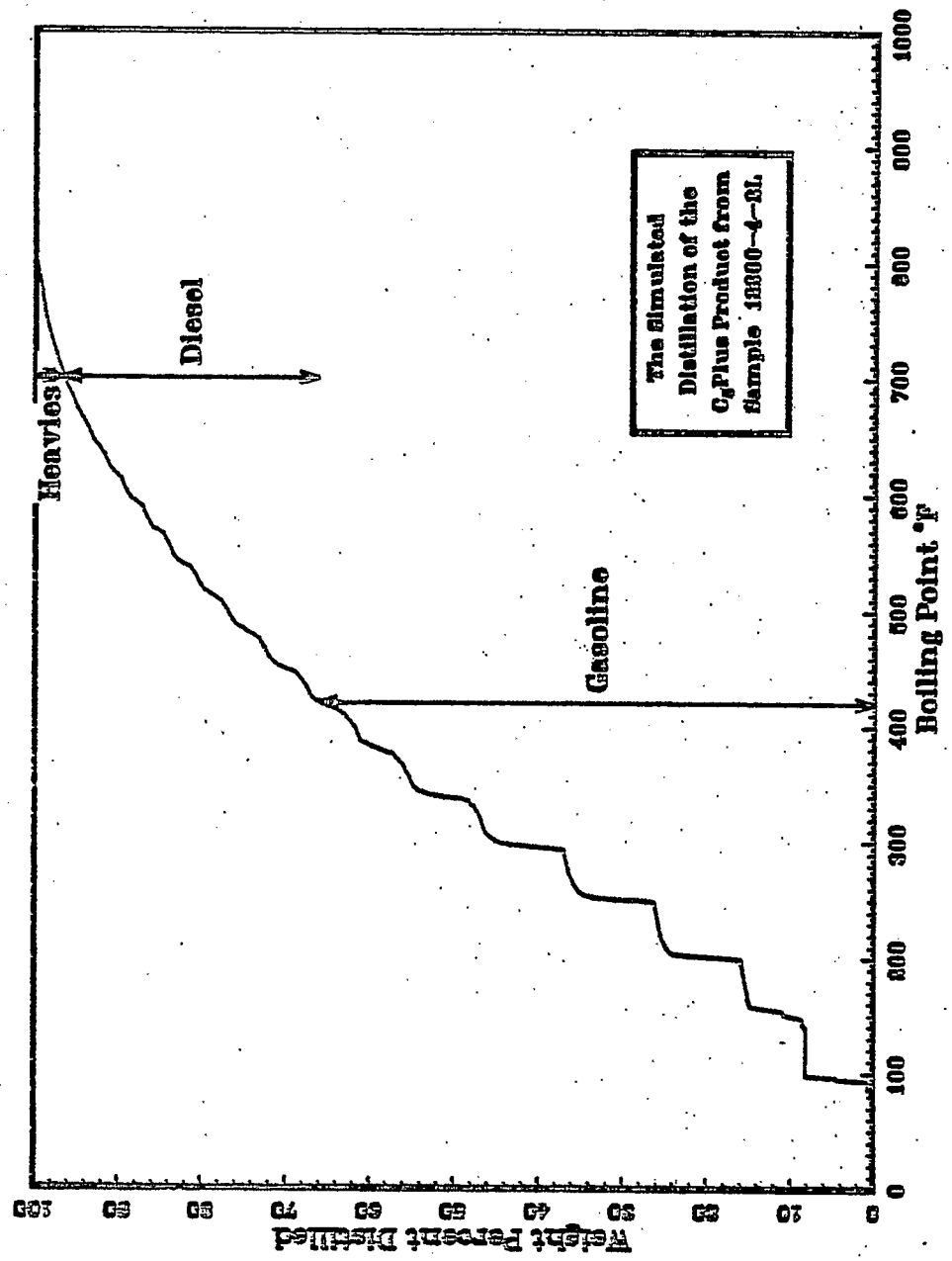

Heavies
Diesel
Gasoline
The Simulated Distillation of the C_5Plus Product from Sample 13300-4-31.
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. B82

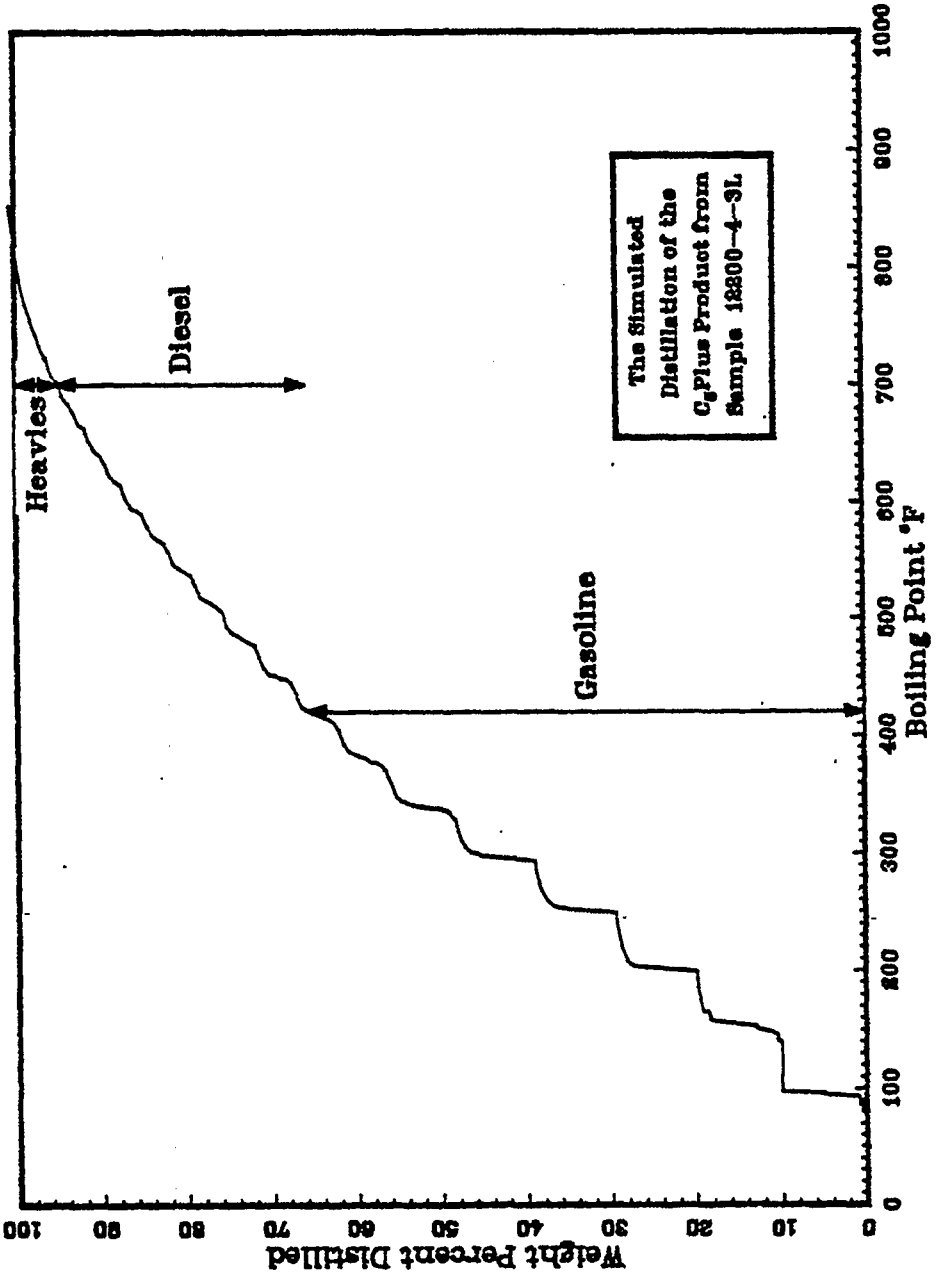

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12800-4-3L

Fig. B83

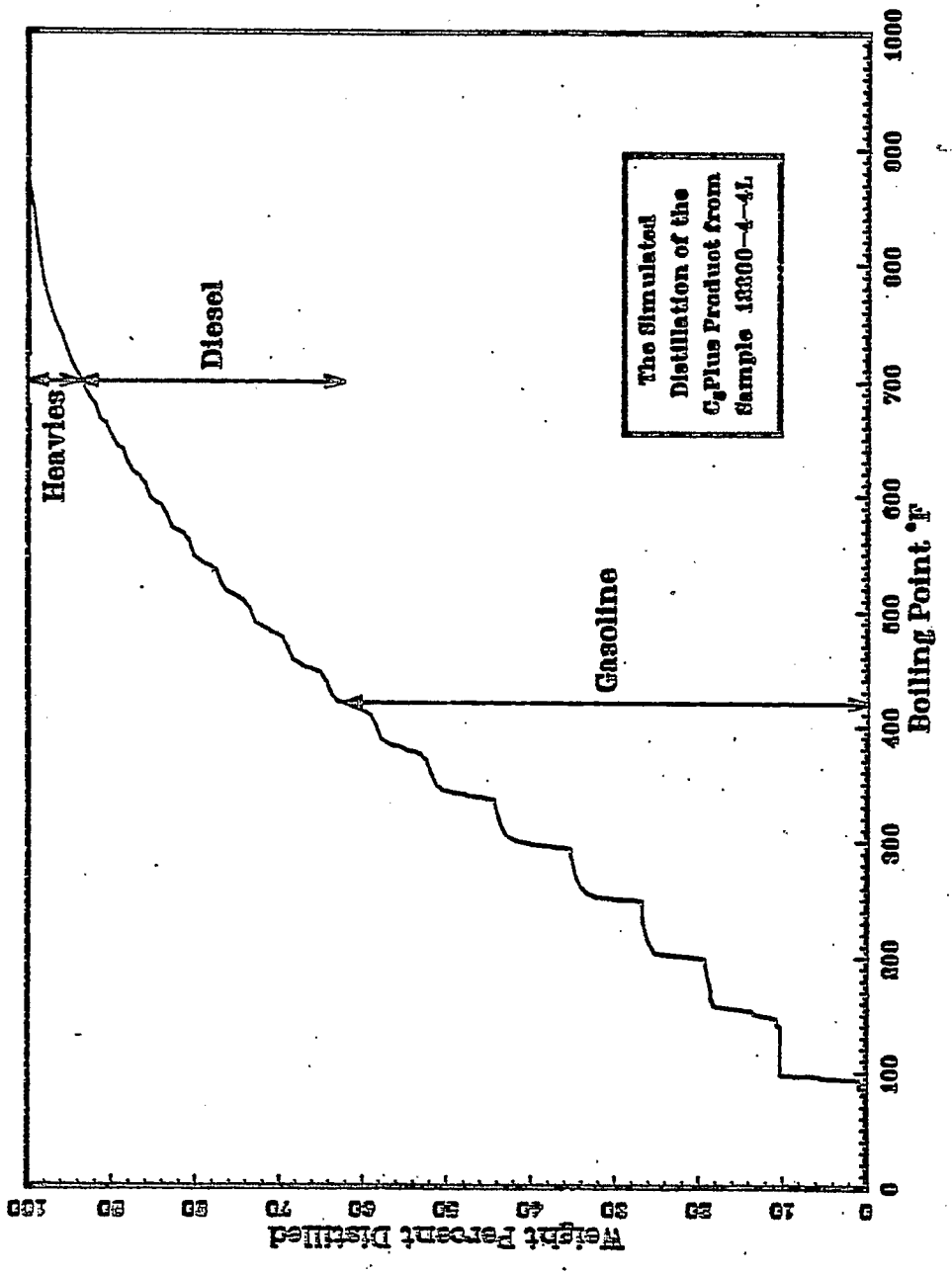

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point, °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 13300-4-4L

Fig. B84

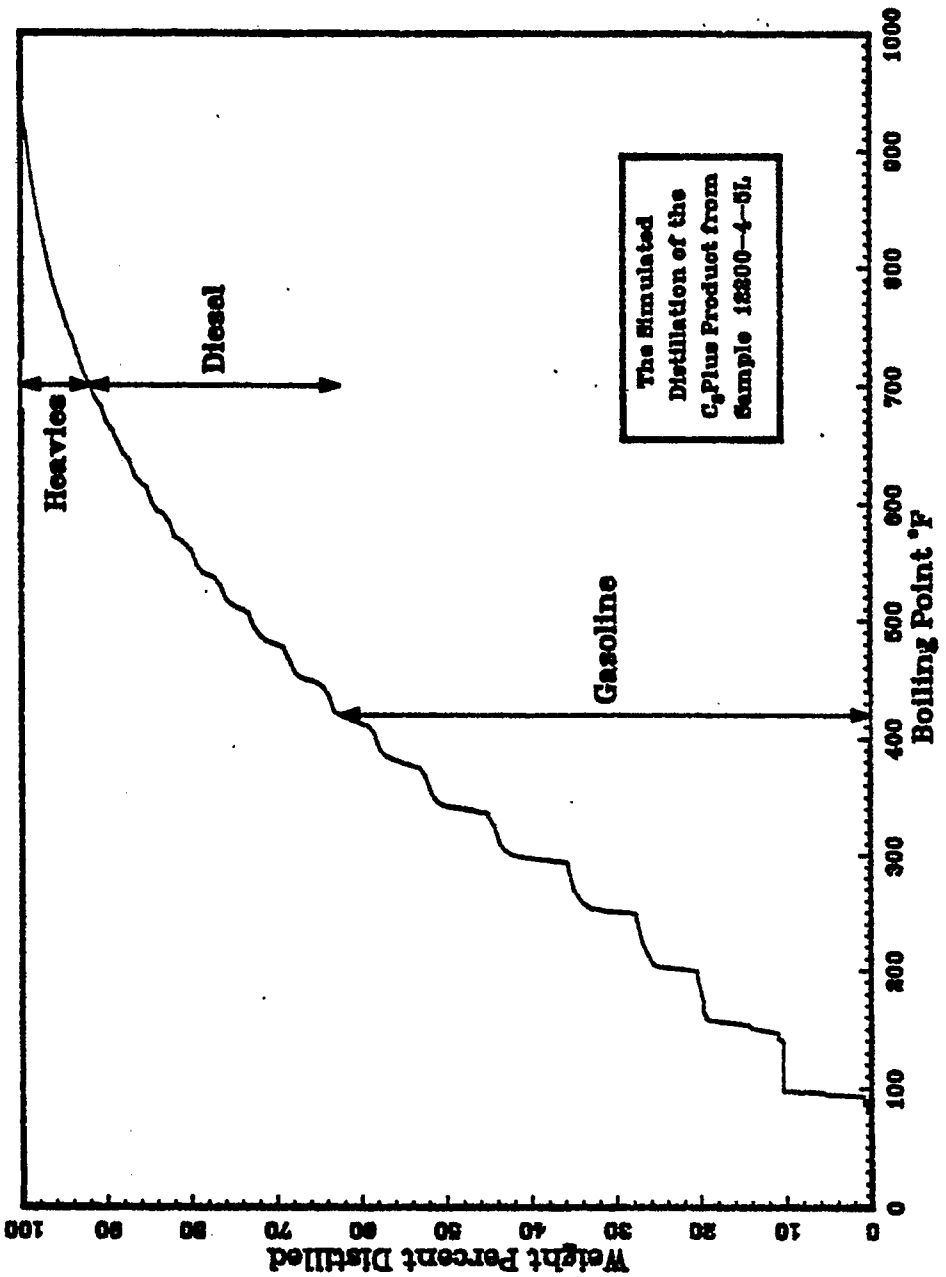

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12800-4-5L
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B85

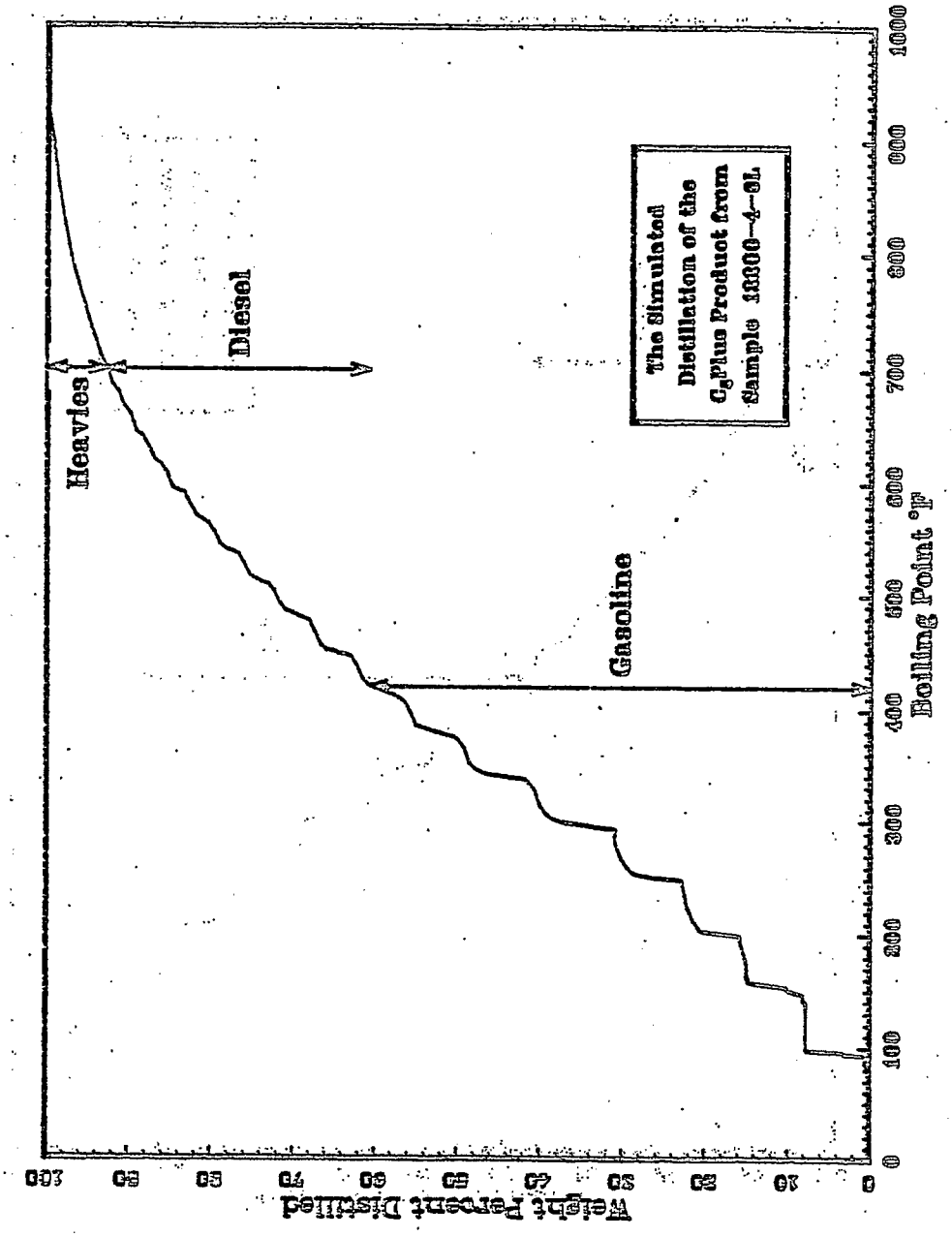

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12300-4-81

Fig. B86

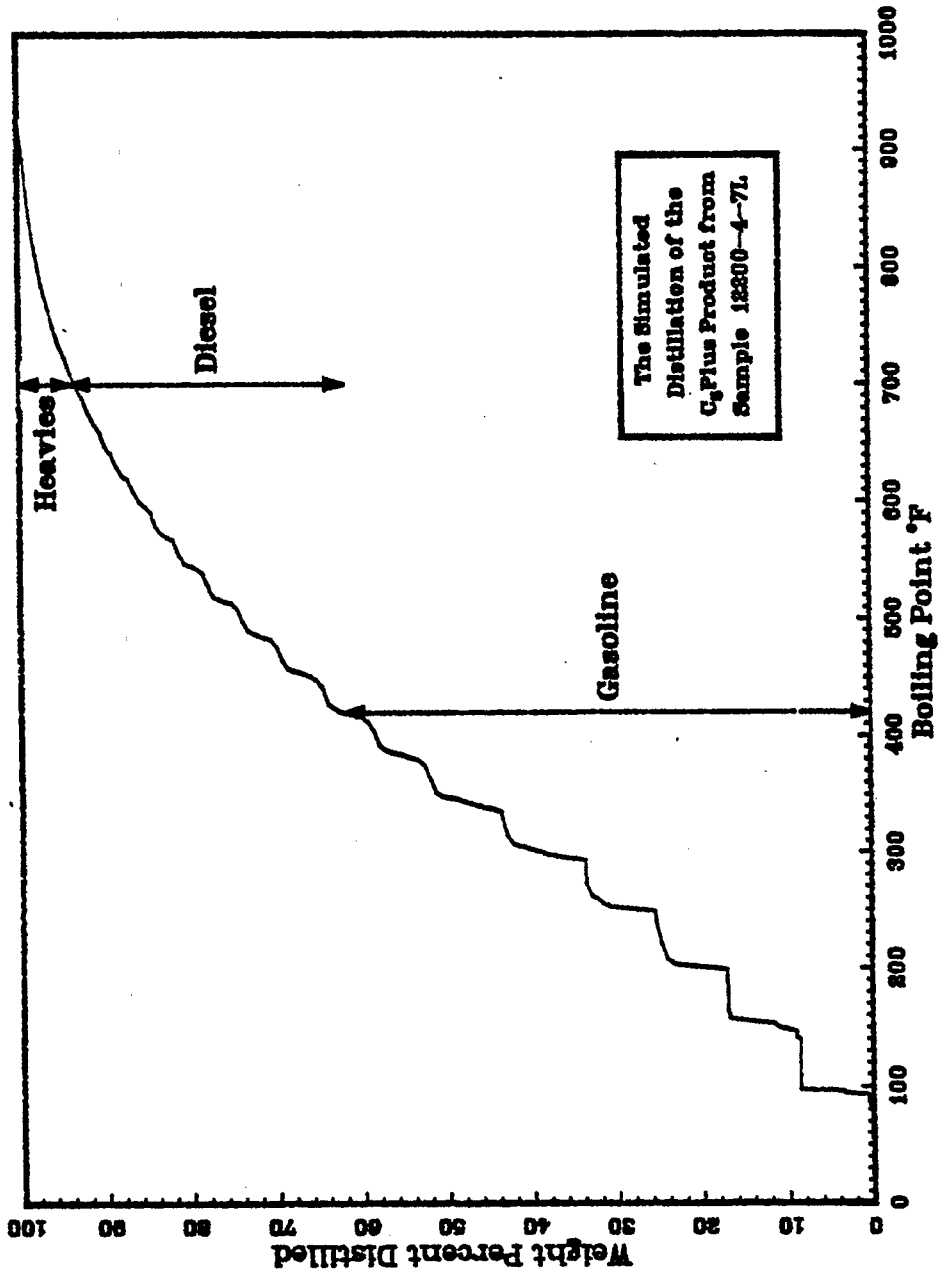

The Simulated Distillation of the C5 Plus Product from Sample 12300-4-71.
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B87

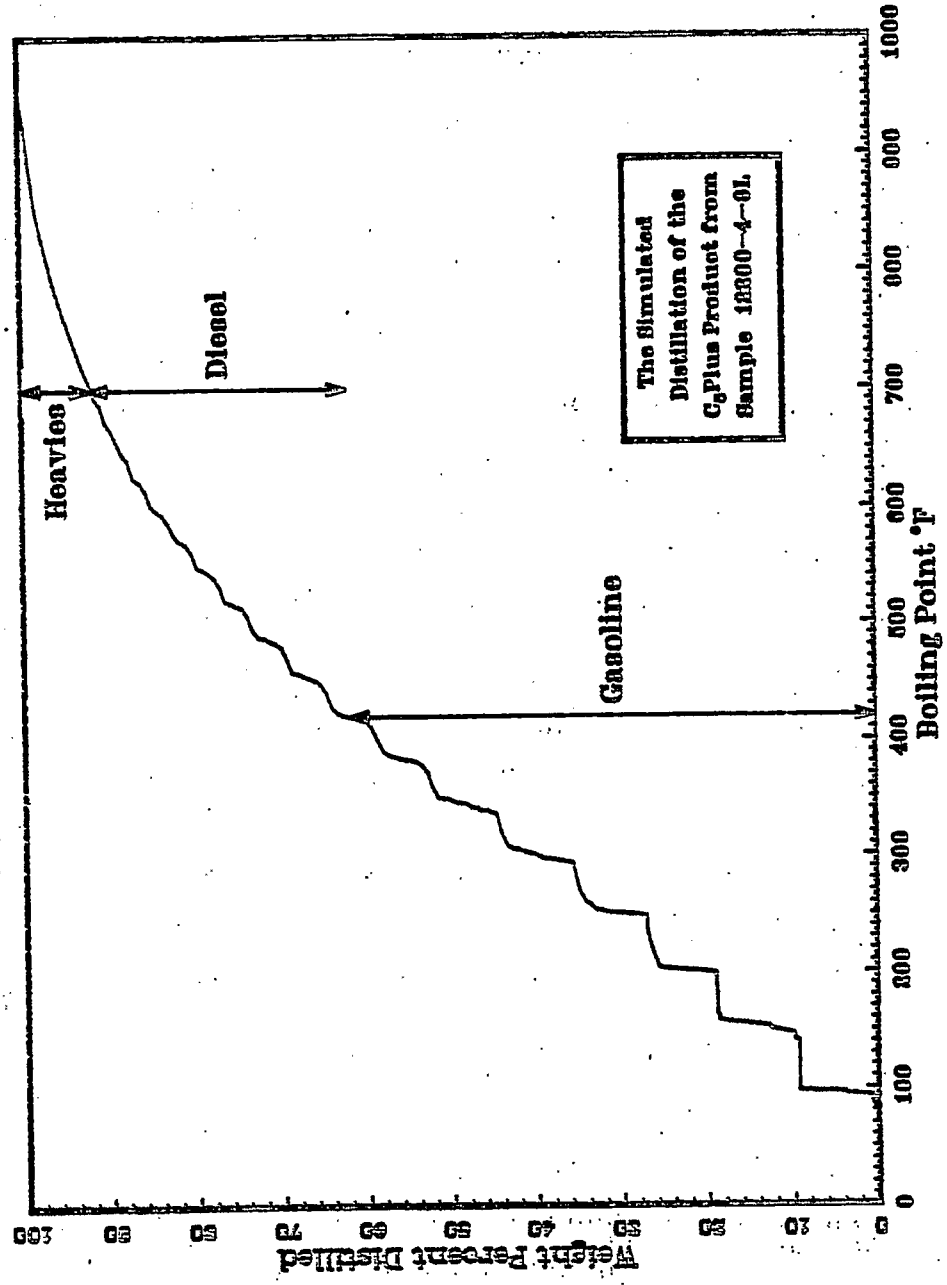

The Simulated Distillation of the C_5 Plus Product from Sample 12300-4-01.
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
0
20
30
40
50
60
70
80
90
100

Fig. B88

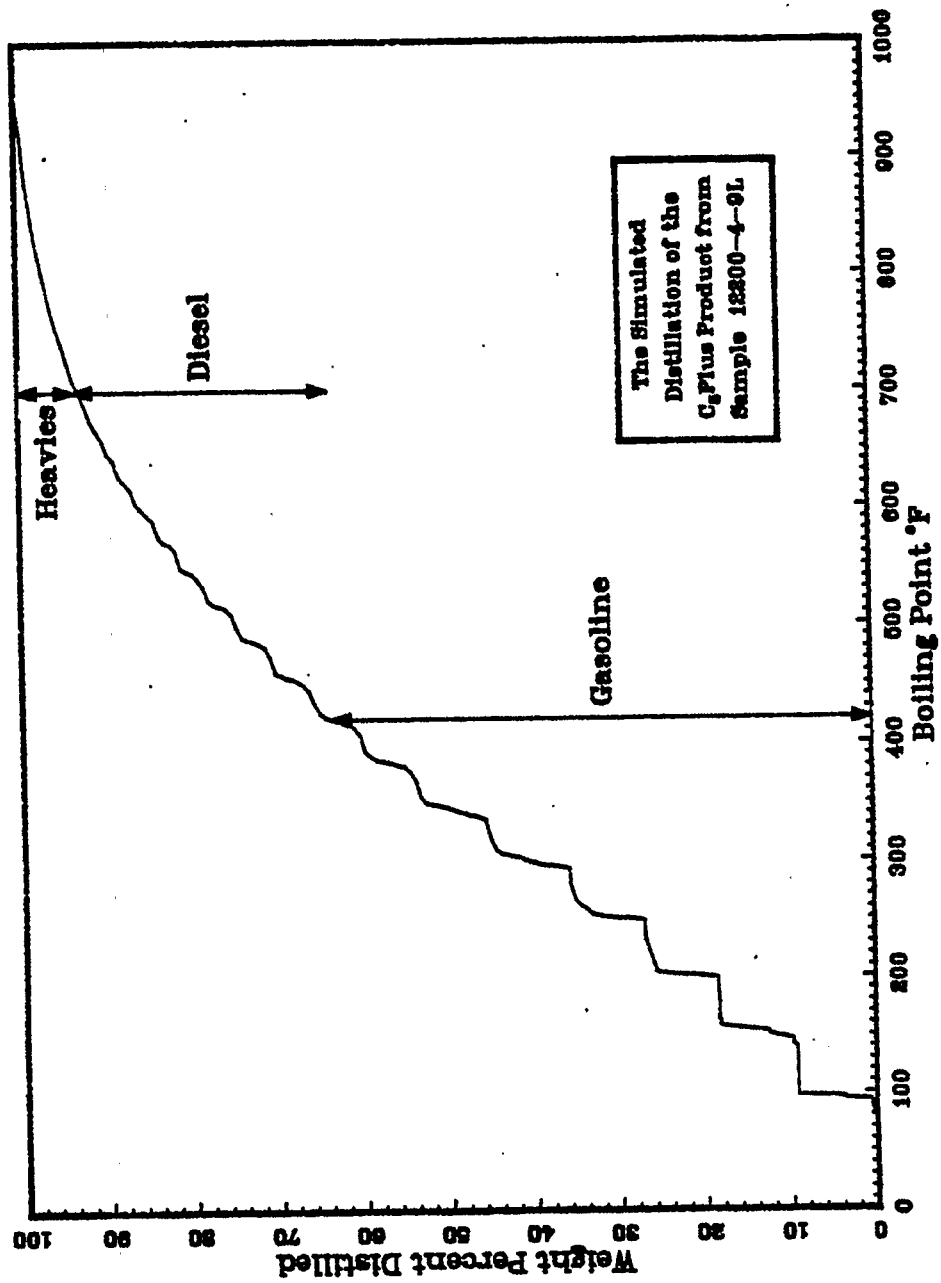

The Simulated Distillation of the C5 Plus Product from Sample 12800-4-9L
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B89

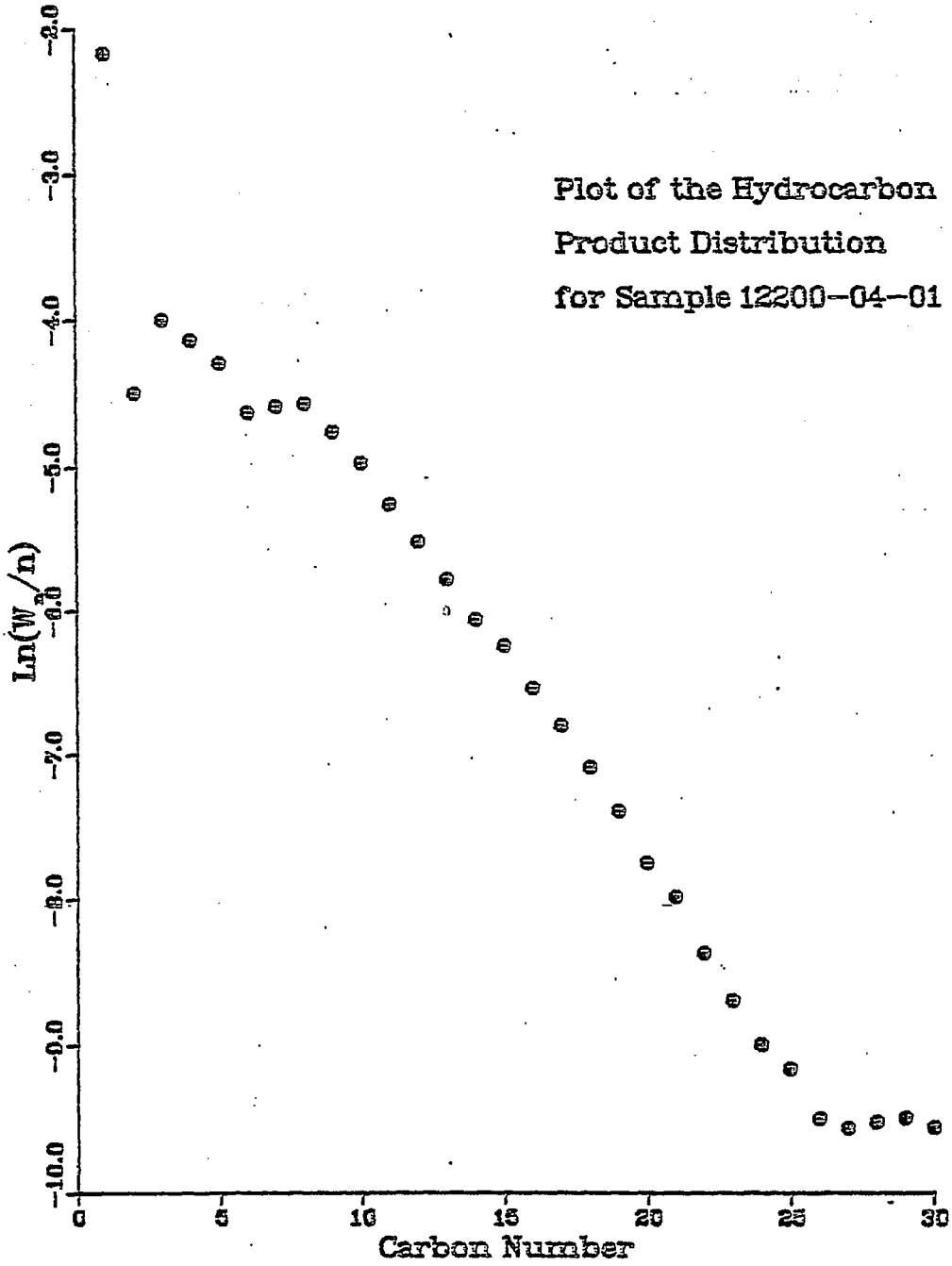

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-01
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B90

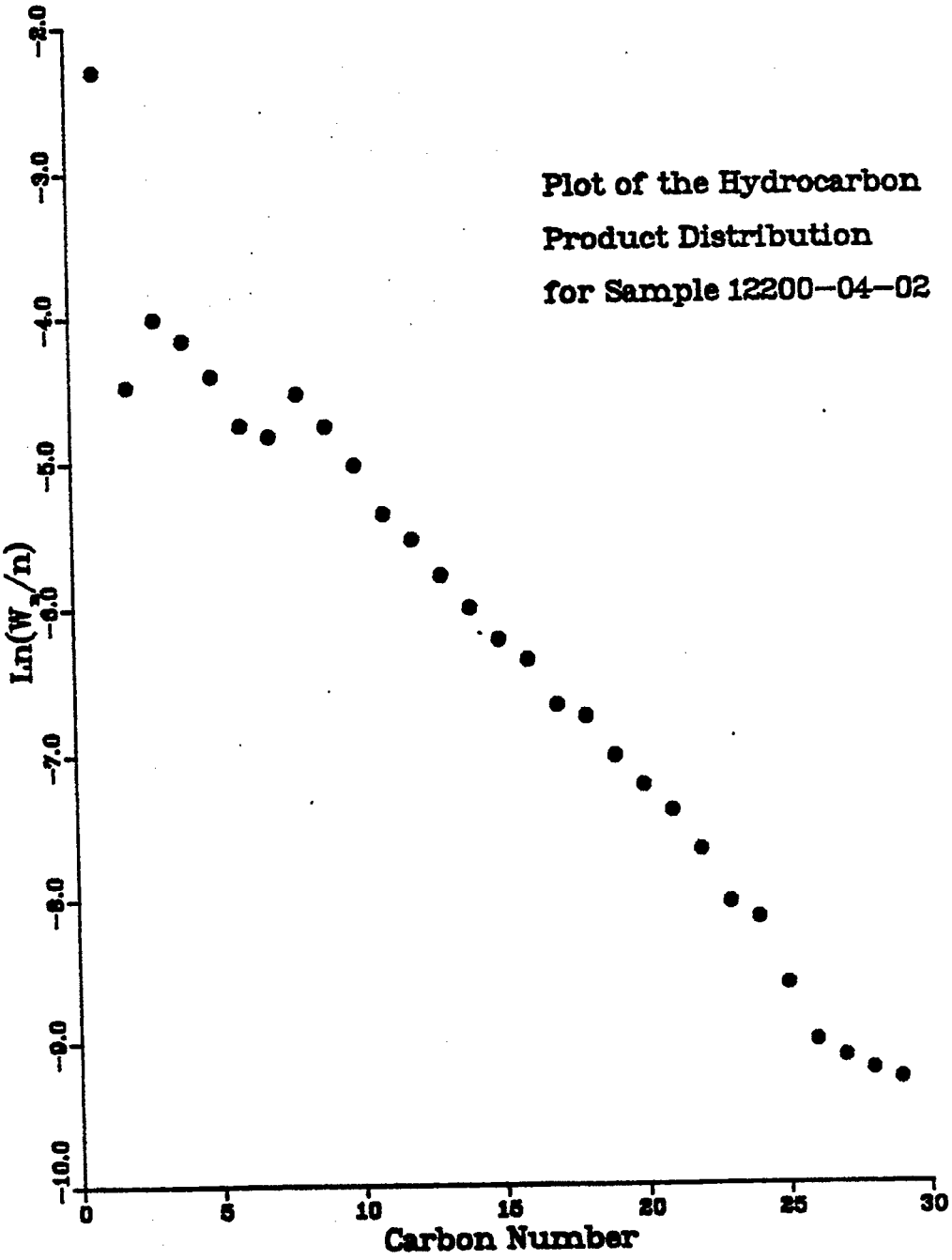

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-02
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B91

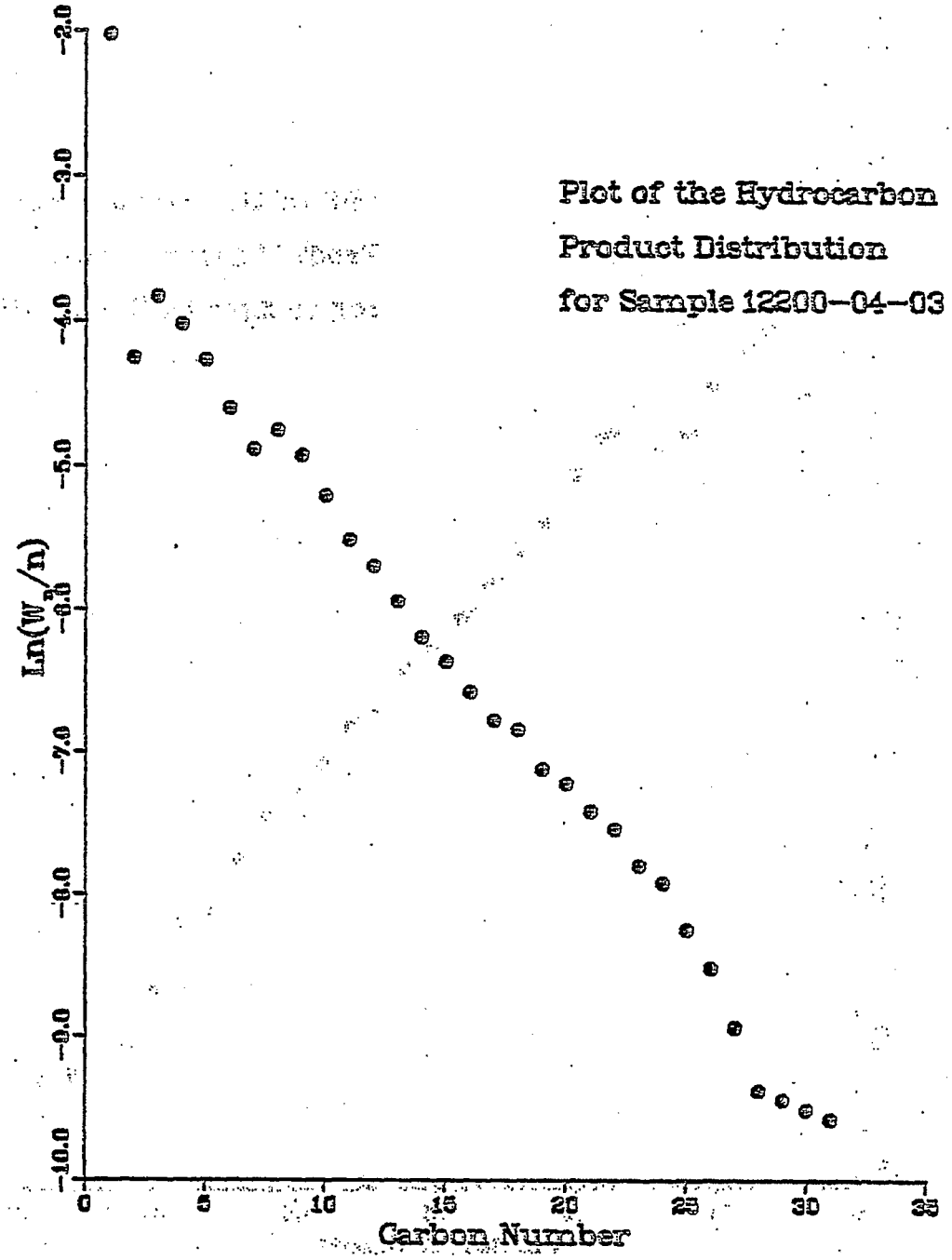

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-03
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B92

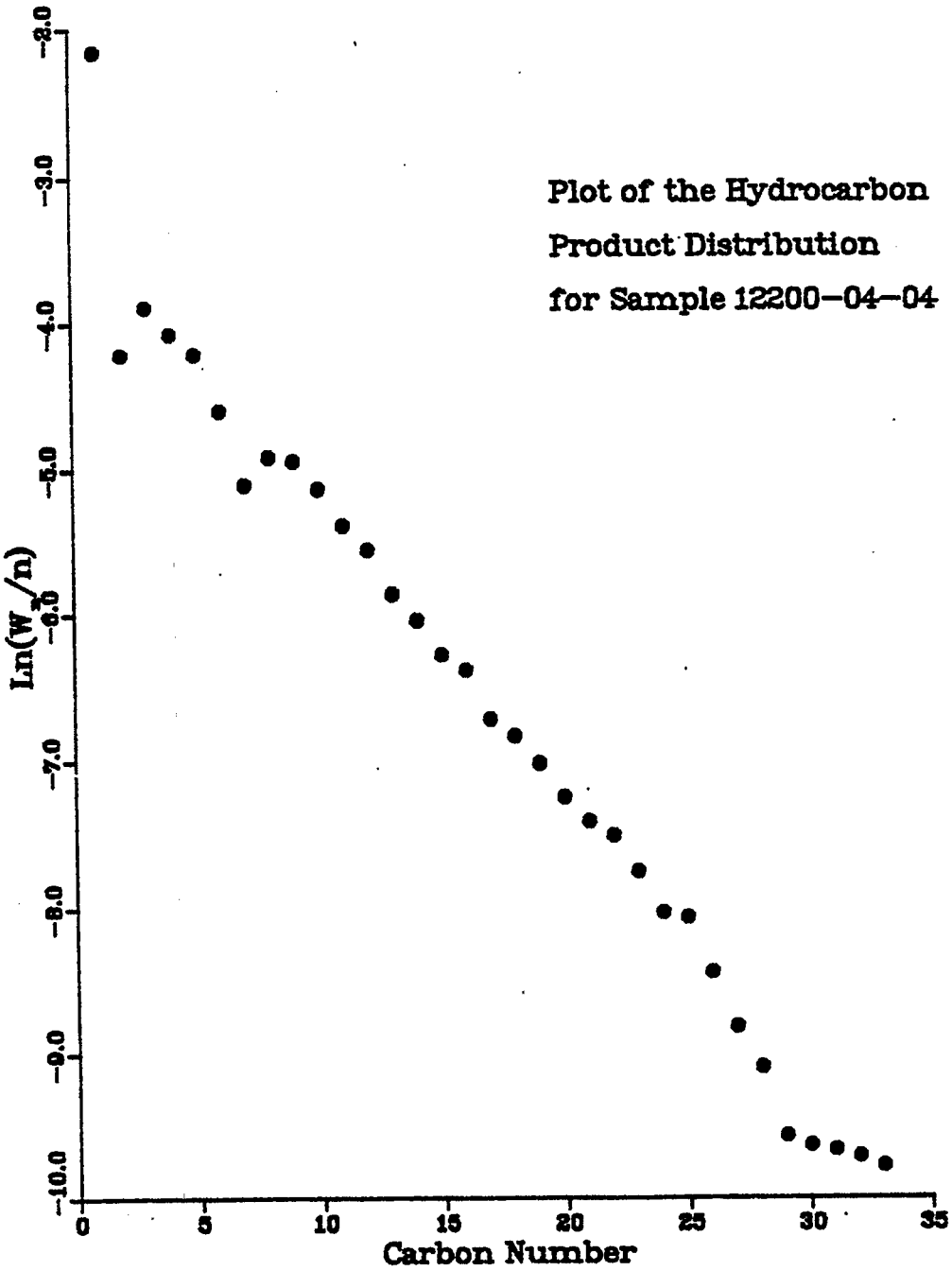

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-04
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B93

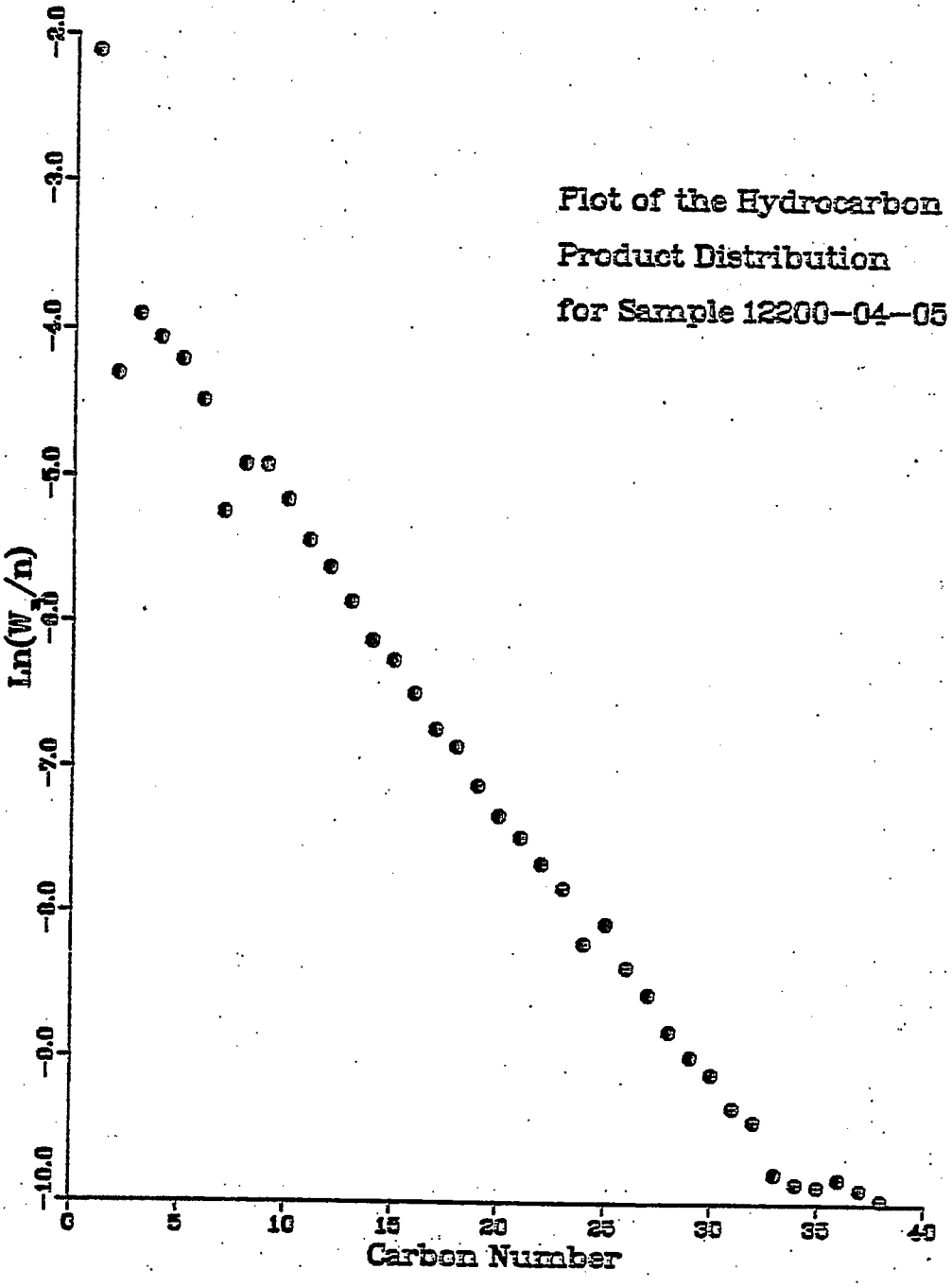

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-05
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B94

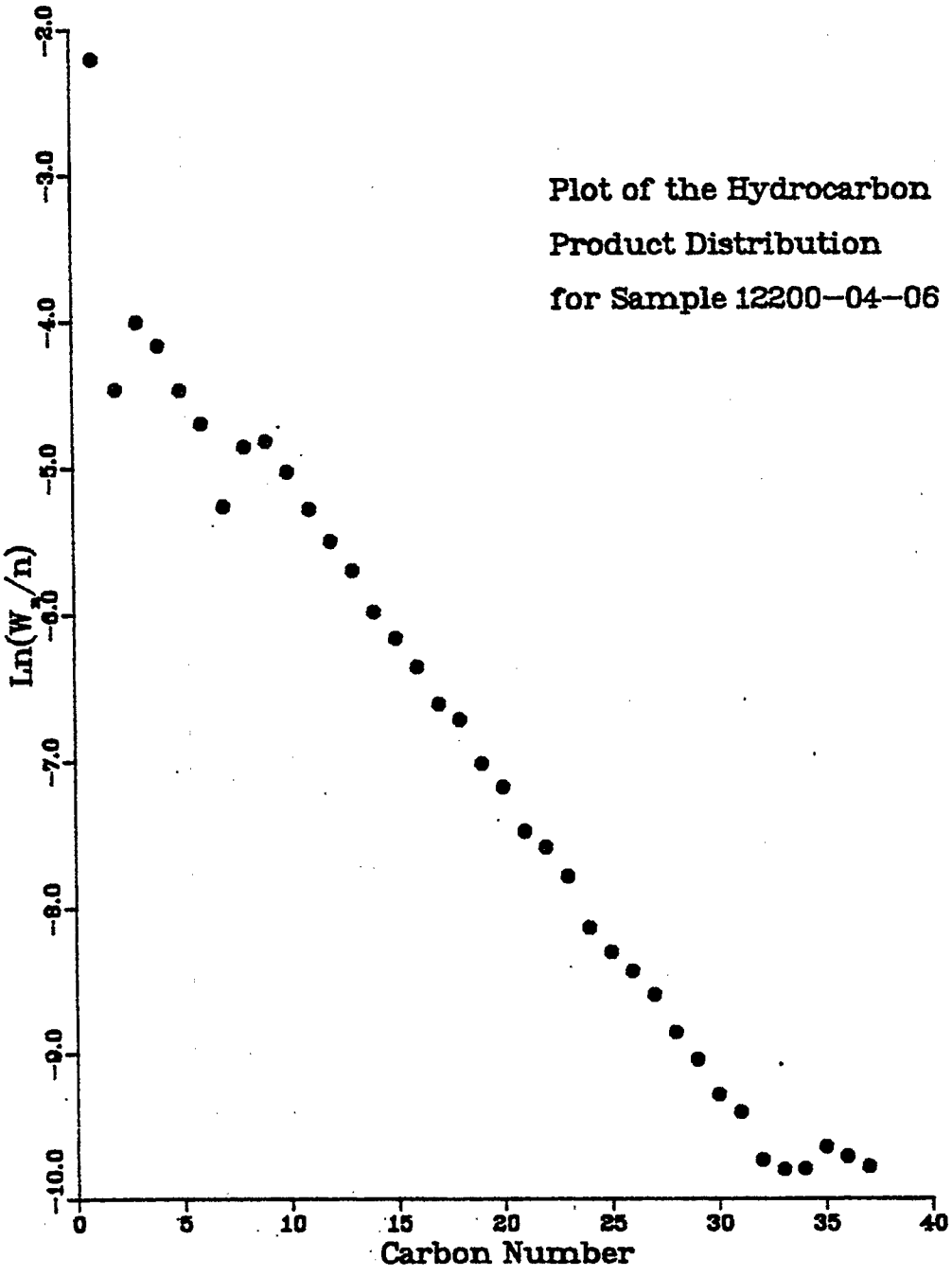

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-06
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B95

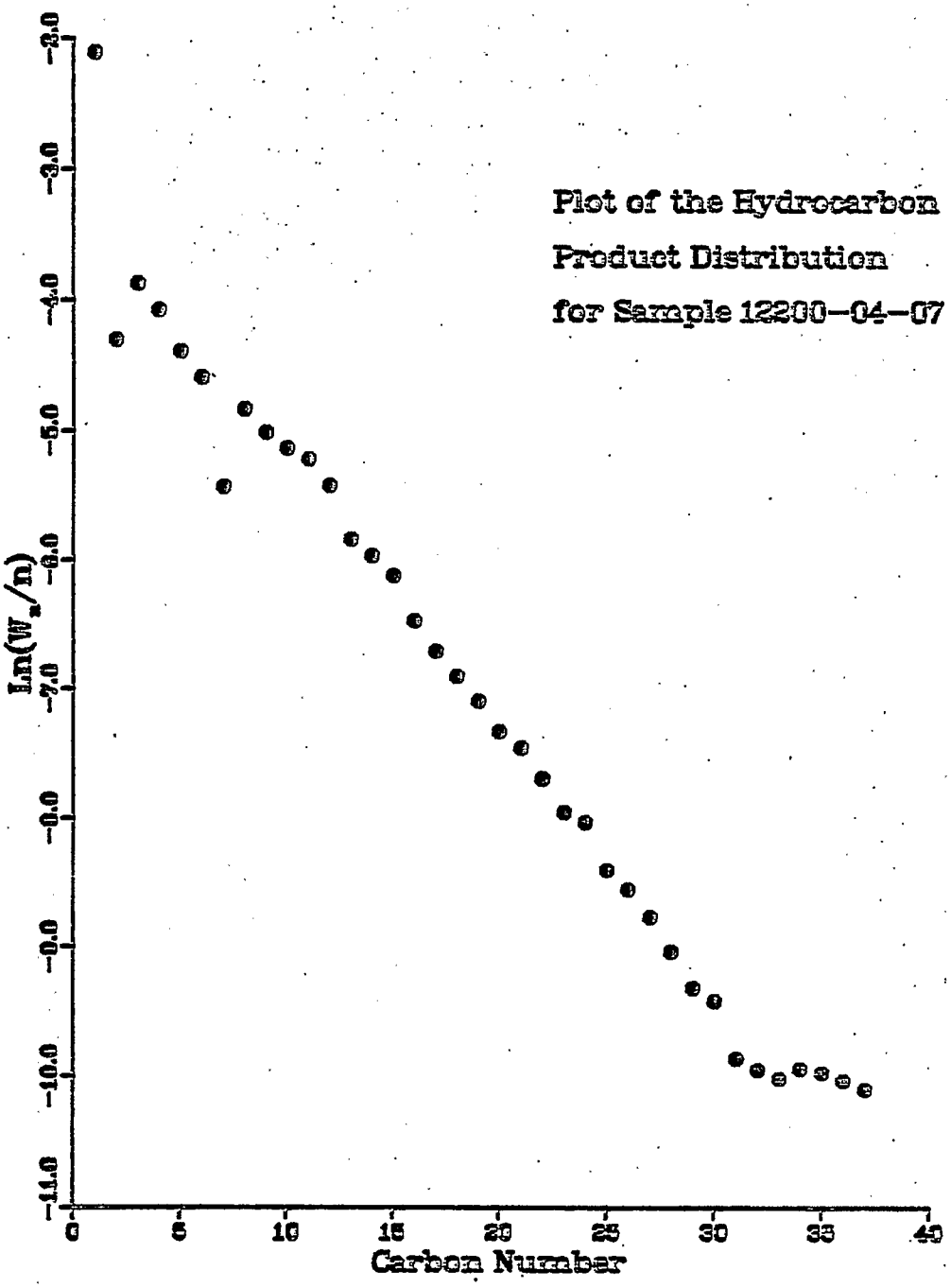

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-07
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B96

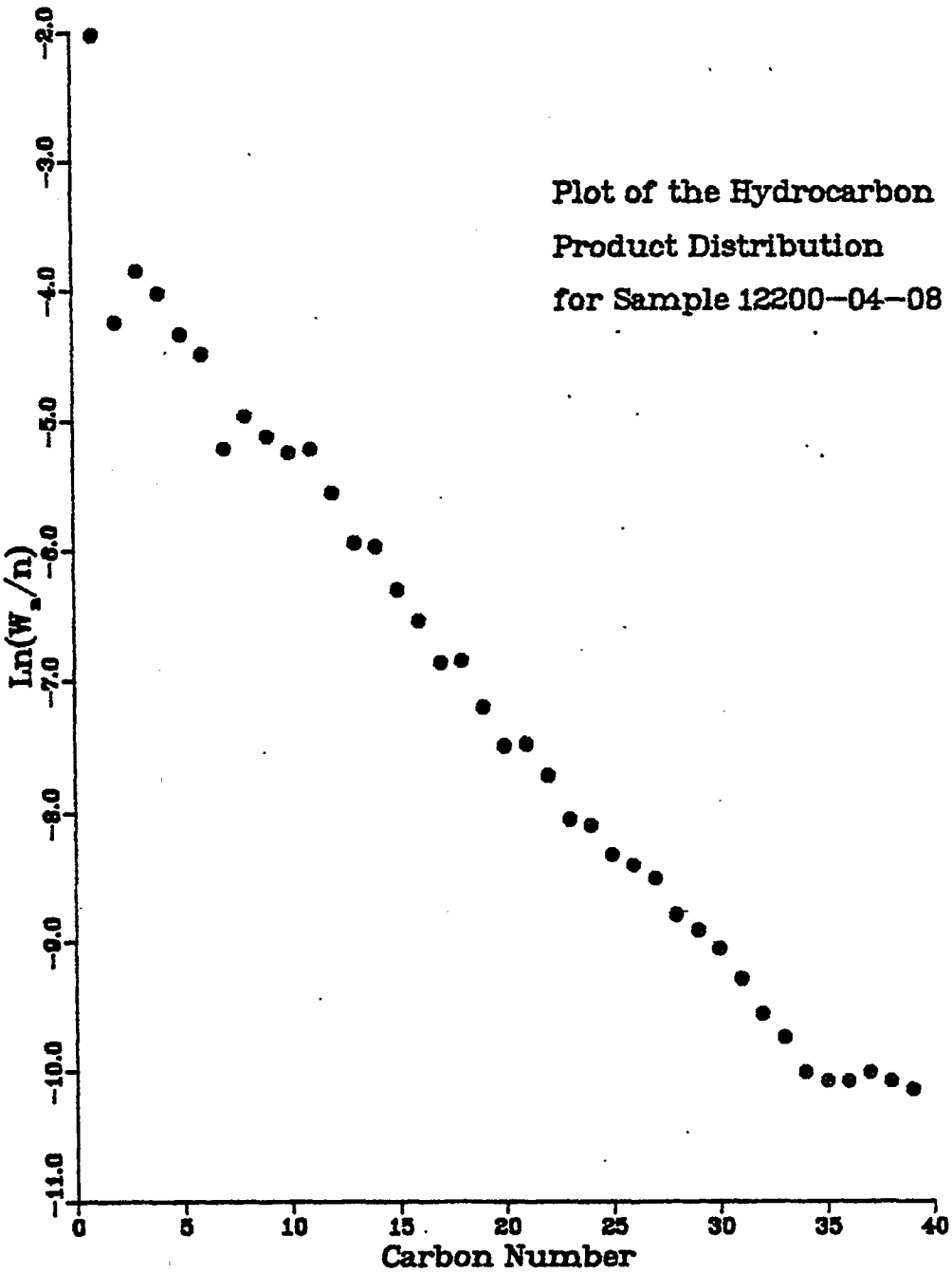

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-08
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B97

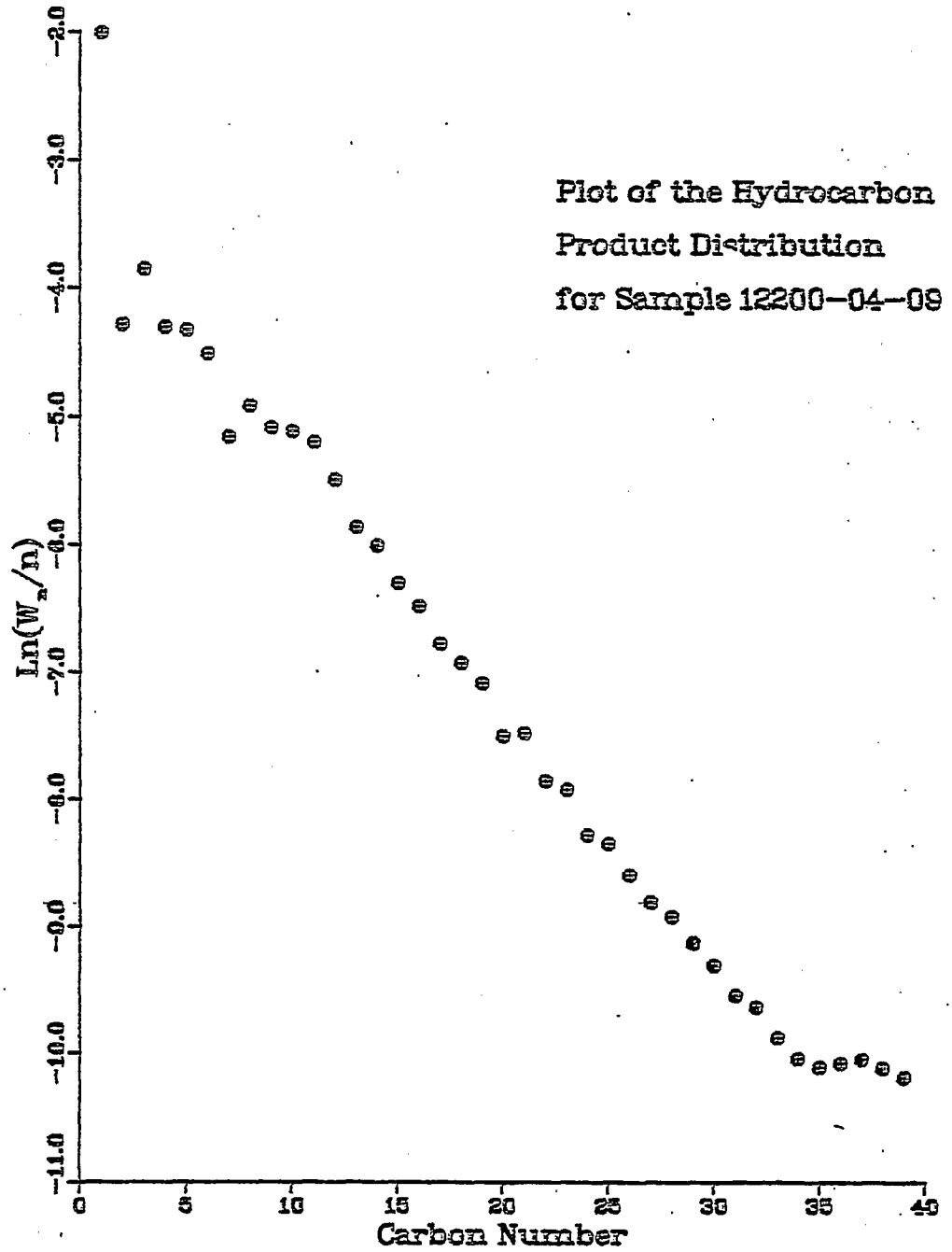
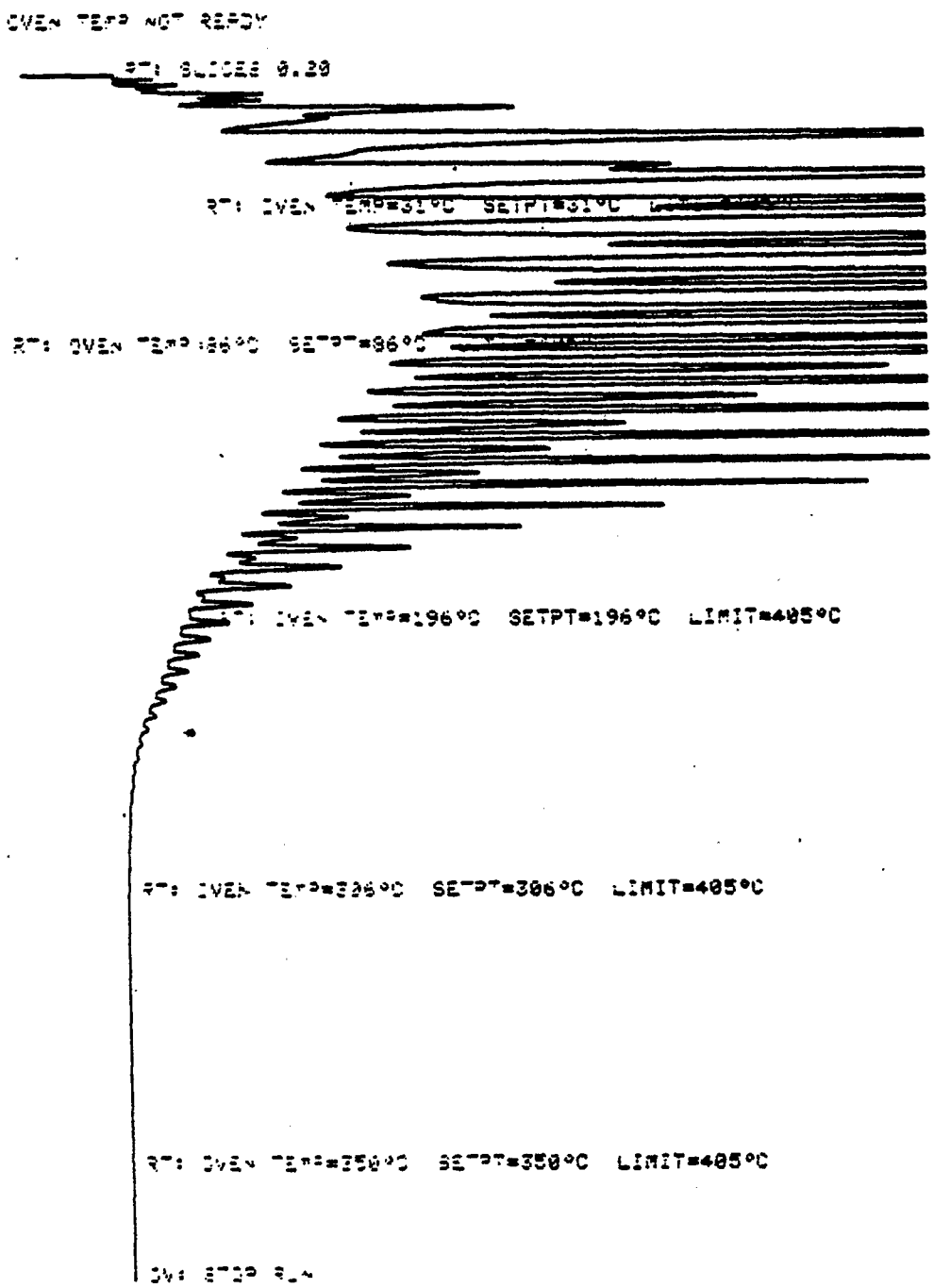

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-04-09
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B98


OVEN TEMP NOT READY
RT: SLICES 0.20
RT: OVEN TEMP=31°C SETPT=31°C
RT: OVEN TEMP=86°C SETPT=86°C
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
OVEN SETPT REACHED

135

Fig. B99

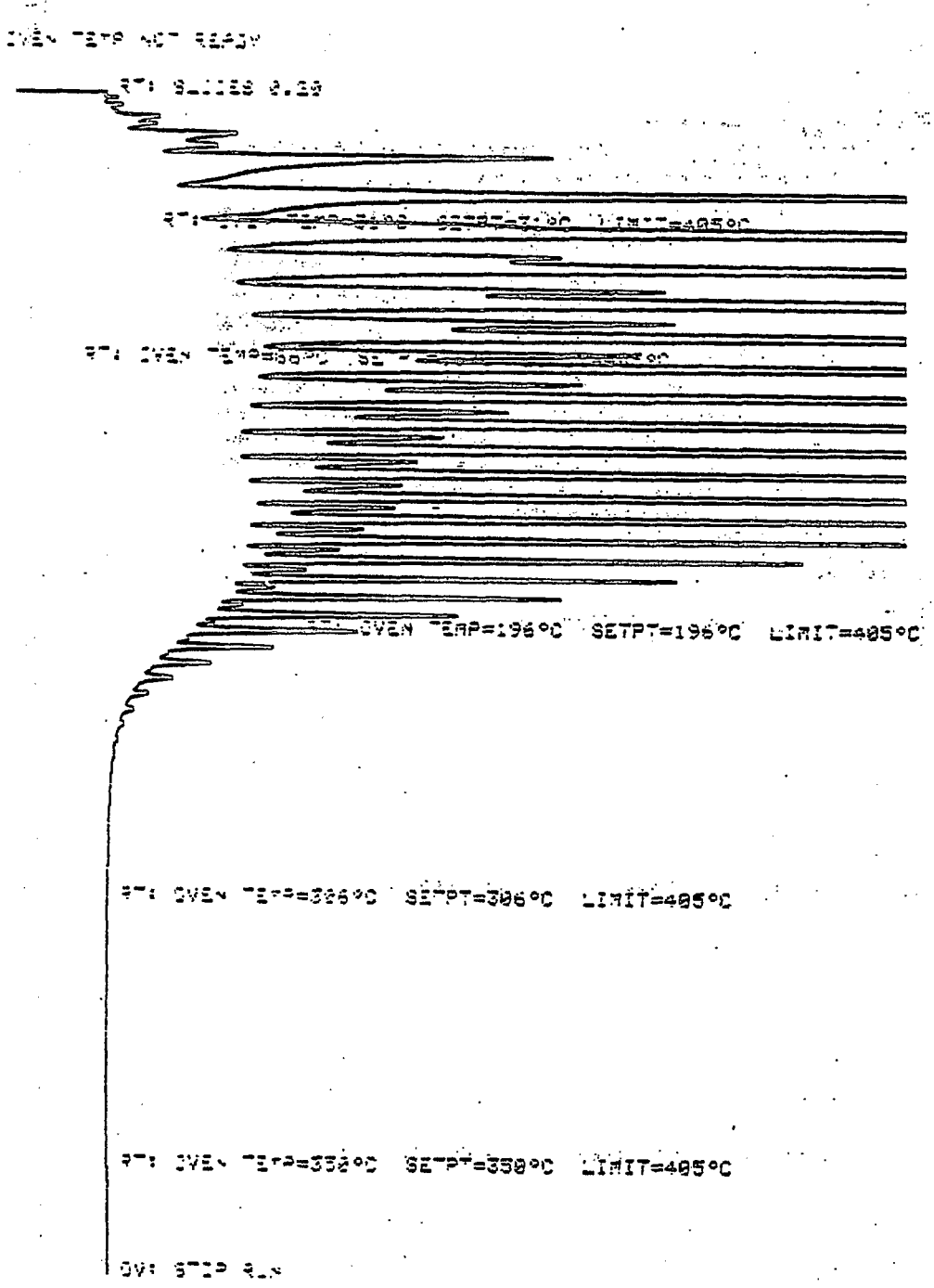
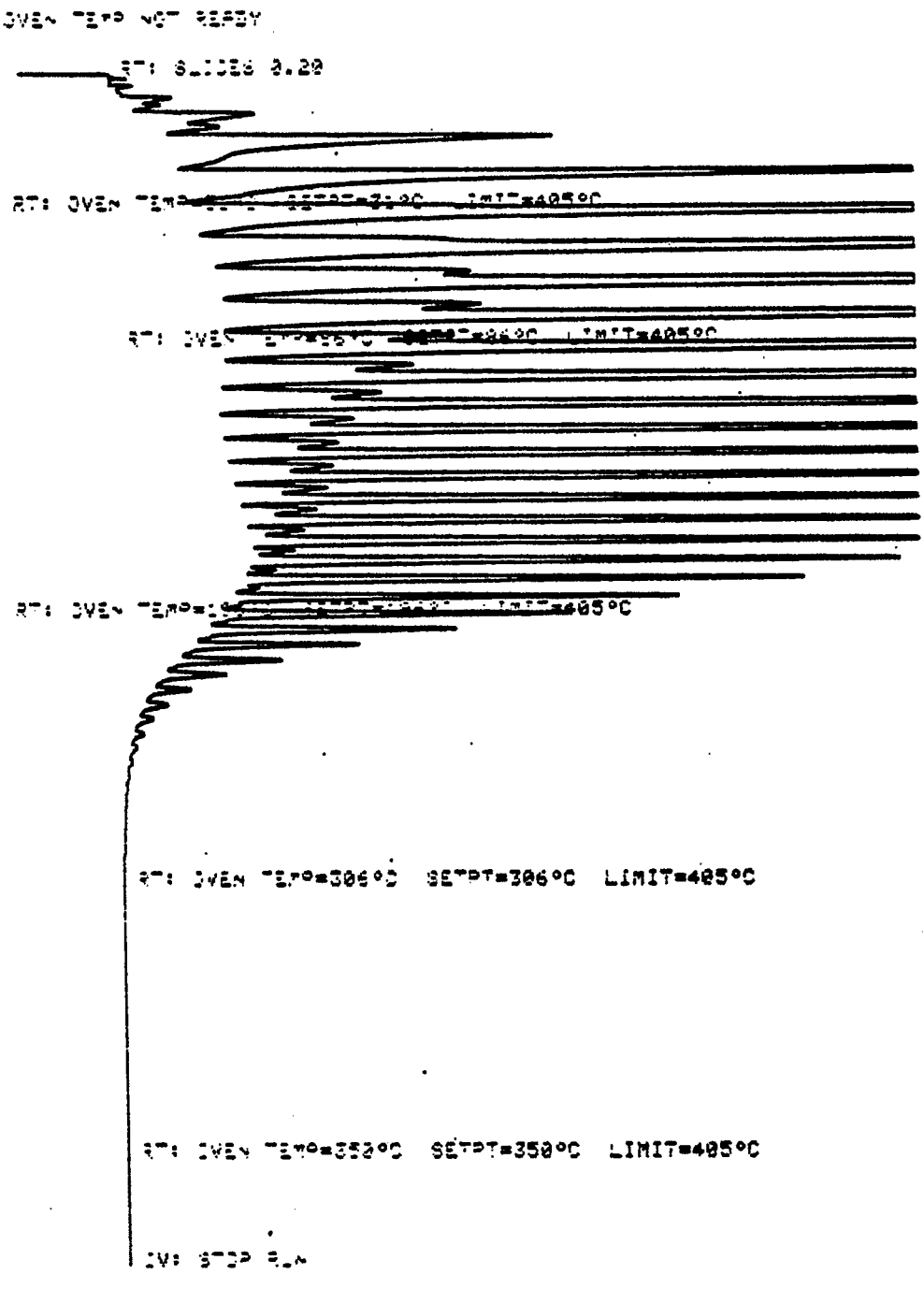

OVEN TEMP NOT READY
PT: SLIDES 0.00
PT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
PT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
PT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
OV: STOP RUN

Fig. B100


OVEN TEMP NOT READY
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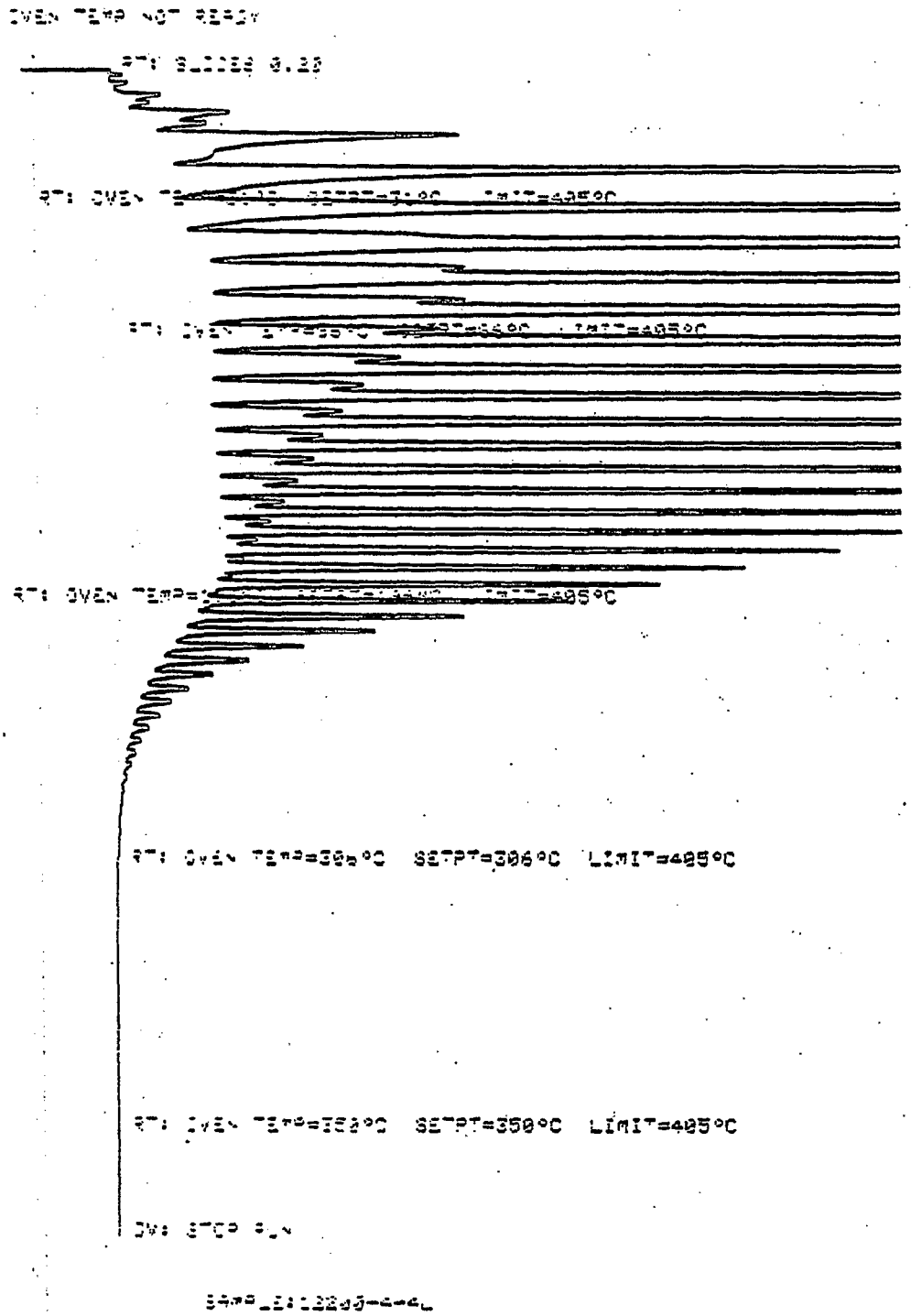
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
SAMPLE:2200-4-3L

Fig. B101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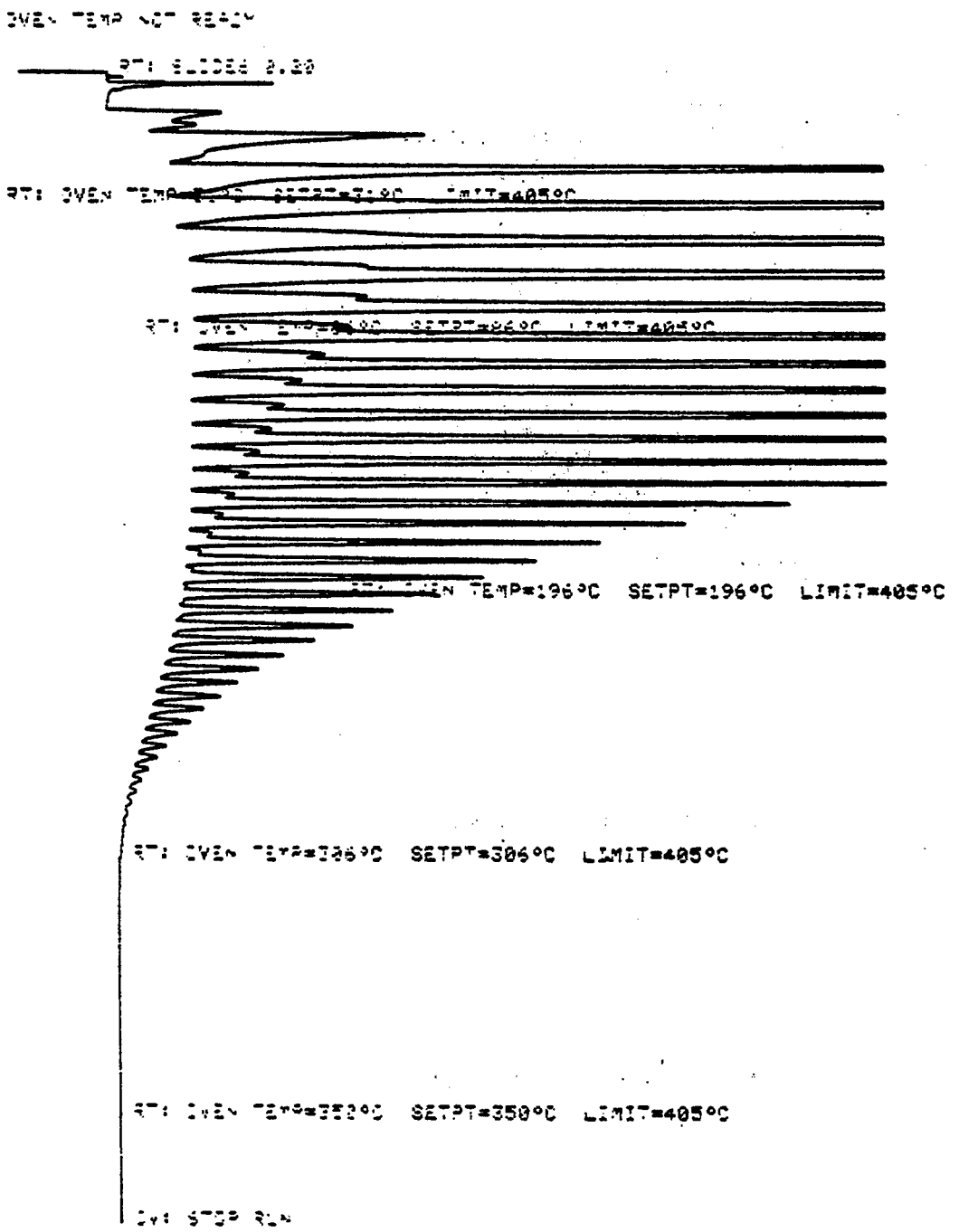
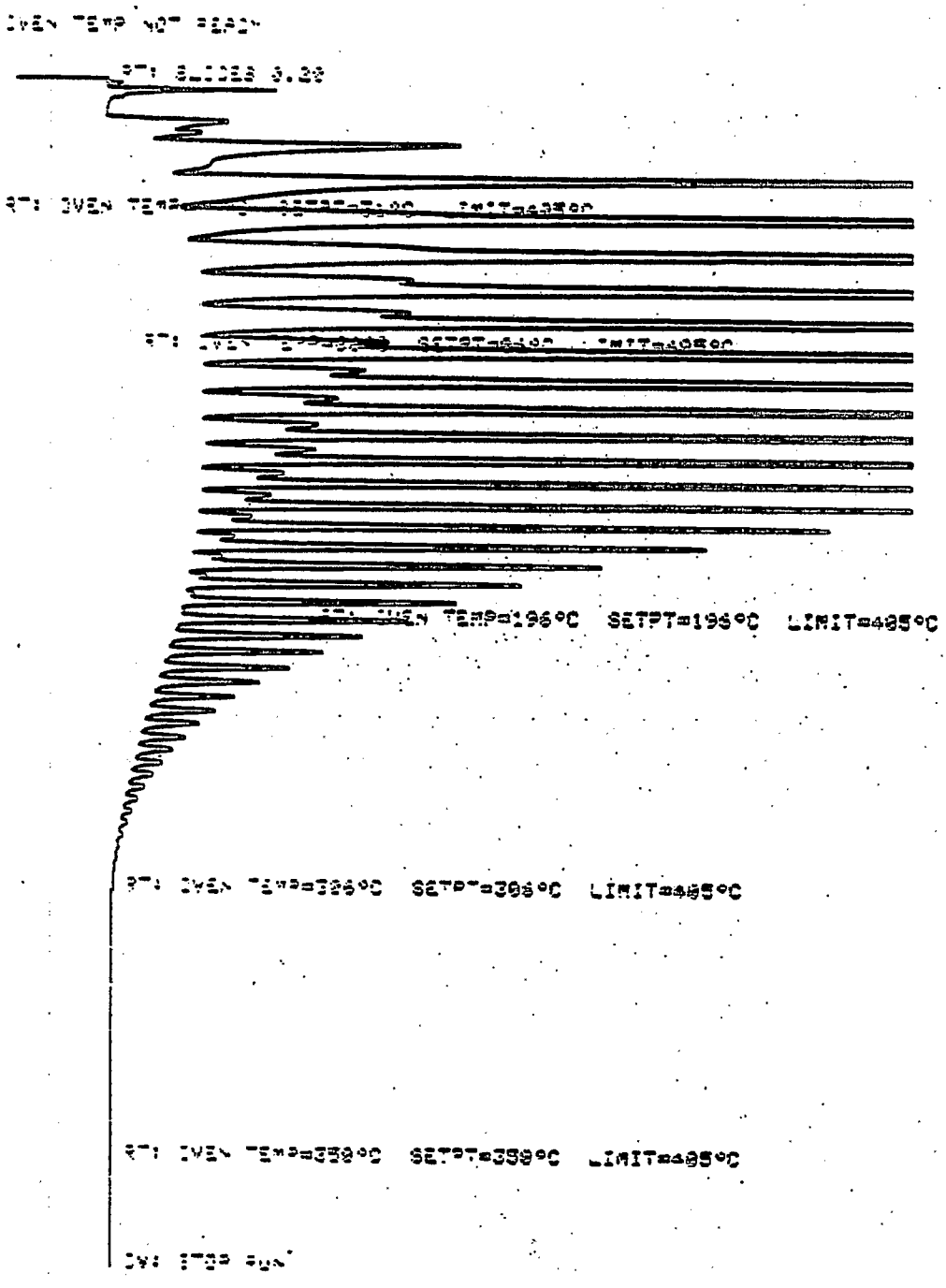
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. B102


RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

140

Fig. B103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SET PT=306°C LIMIT=405°C
SET PT=350°C LIMIT=405°C

Fig. B104

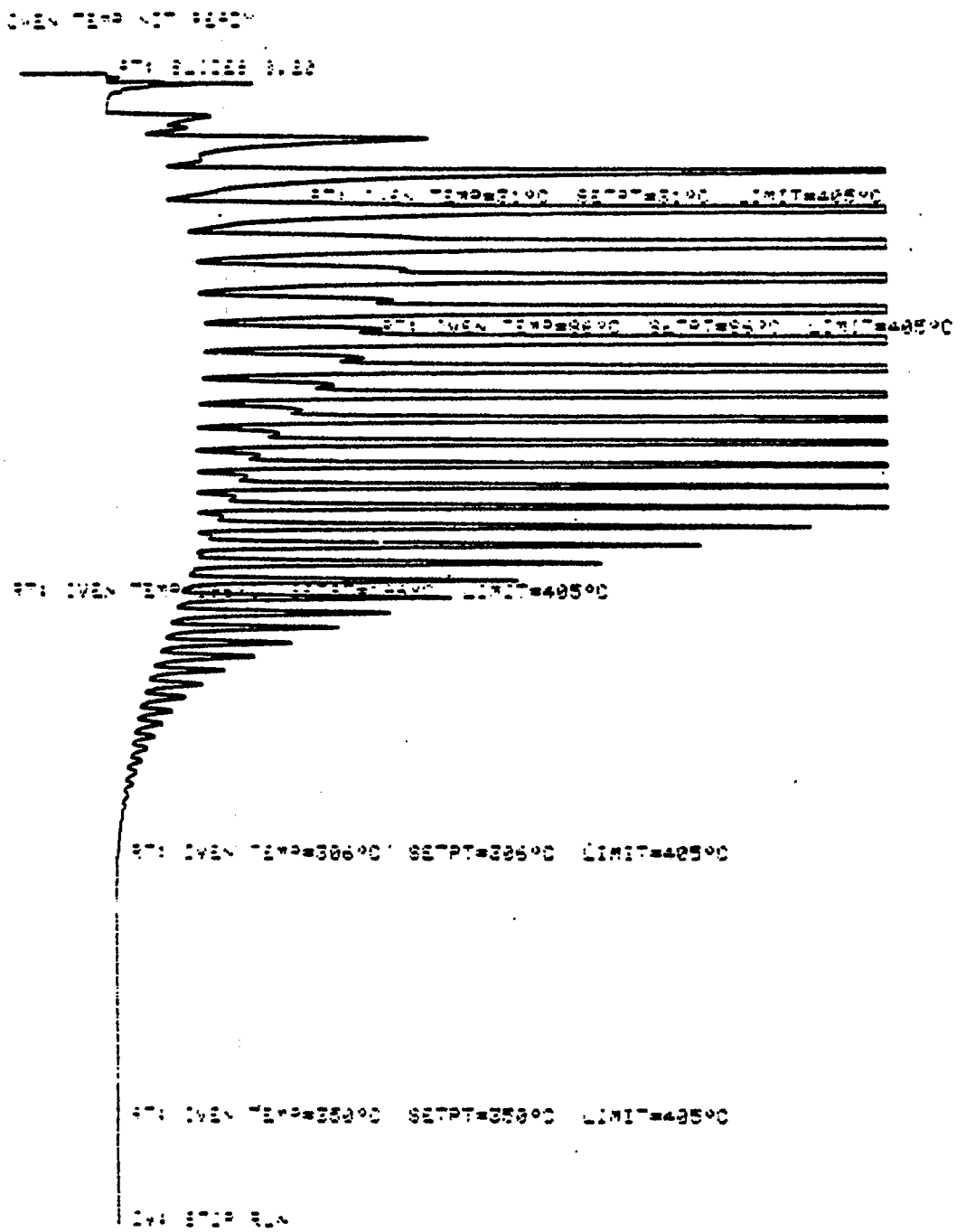

Fig. B105

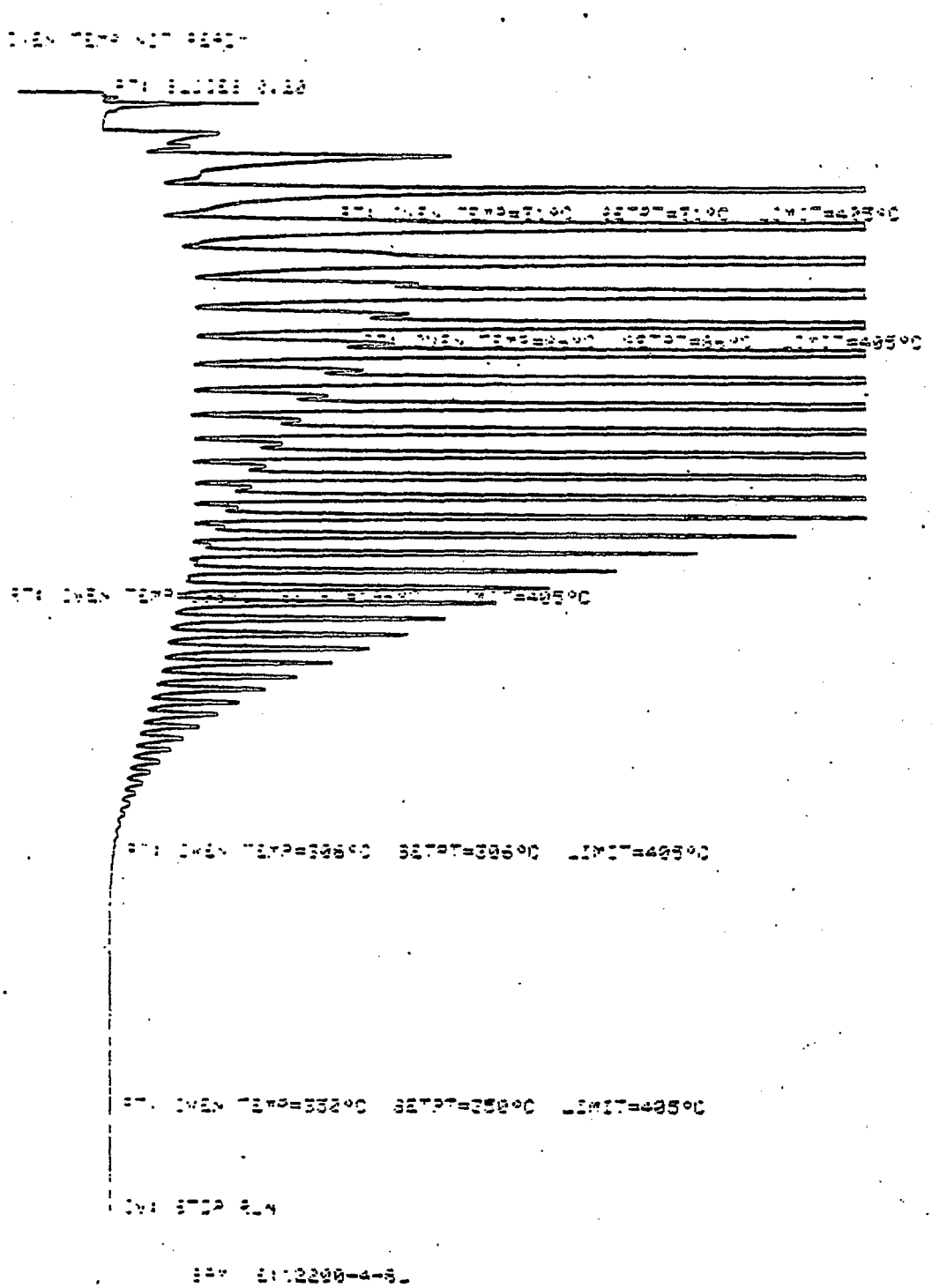

Fig. B106

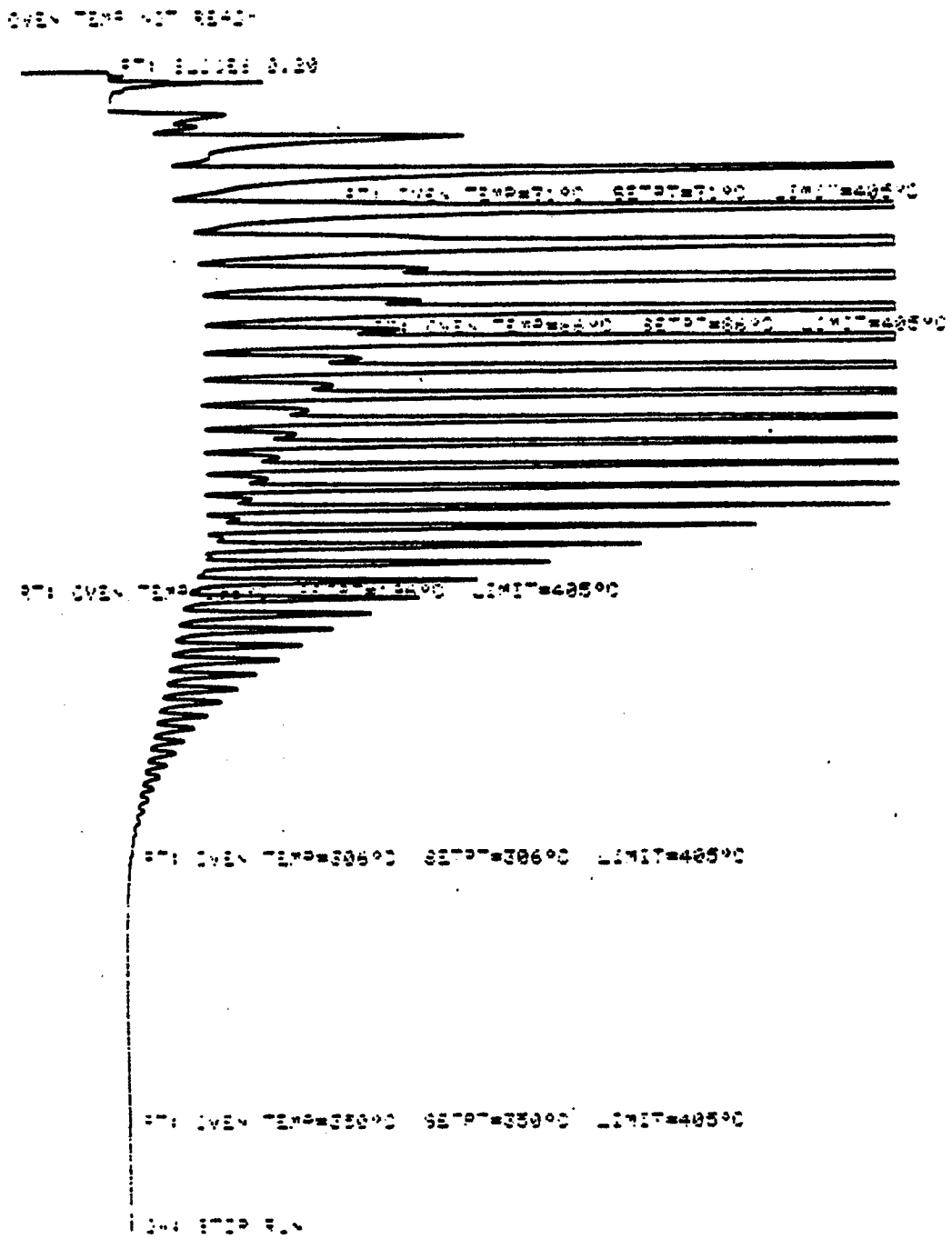

Table B6

RESULT OF SYNGAS OPERATION

RUN NO. 12200-04
CATALYST CO/TH/X4-U103+S115-HE 250 CC 132.77 GM (147.9 G AFTER RUN)
FEED H2:CO OF 52.7:47.3 @ 1195 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-04-01	200-04-02	200-04-03	200-04-04	200-04-05
FEED H2:CO:AR	52:47: 0	52:47: 0	52:47: 0	52:47: 0	52:47: 0
HRS ON STREAM	18.50	42.50	68.00	90.50	114.50
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	259	256	259	260	262
FEED CC/MIN	1195	1195	1195	1195	1195
HOURS FEEDING	18.50	24.00	25.50	22.50	24.00
EFFLNT GAS LITER	408.20	795.05	884.55	840.25	890.00
GM AQUEOUS LAYER	173.72	209.90	215.85	182.02	202.81
GM OIL	62.31	67.65	68.94	71.66	79.34
MATERIAL BALANCE					
GM ATOM CARBON %	67.70	85.17	89.33	98.90	100.20
GM ATOM HYDROGEN %	88.86	93.78	96.11	97.52	98.47
GM ATOM OXYGEN %	76.53	94.37	96.56	102.21	104.60
RATIO CHX/(H2O+CO2)	0.7858	0.7598	0.8099	0.9092	0.8854
RATIO X IN CHX	2.3553	2.3169	2.3901	2.3562	2.3695
USAGE H2/CO PRODT	2.1894	2.2886	2.1844	2.0743	2.0757
FEED H2/CO FRM EFFLNT	1.4624	1.2267	1.1987	1.0986	1.0949
RESIDUAL H2/CO RATIO	0.6818	0.6272	0.6176	0.5558	0.5315
RATIO CO2/(H2O+CO2)	0.0643	0.0430	0.0624	0.0602	0.0687
K SHIFT IN EFFLNT	0.0468	0.0282	0.0411	0.0356	0.0392
SPECIFIC ACTIVITY SA	1.3371	1.0566	0.9526	1.0178	1.0016
CONVERSION					
ON CO %	51.78	36.09	37.09	35.75	36.49
ON H2 %	77.52	67.32	67.59	67.49	69.17
ON CO+H2 %	67.07	53.30	53.71	52.36	53.57
PRDT SELECTIVITY,WT %					
CH4	11.43	10.06	13.20	11.59	12.10
C2 HC'S	2.23	2.29	2.85	2.96	2.71
C3H8	3.59	2.99	3.87	3.44	3.49
C3H6=	1.92	2.48	2.64	2.70	2.58
C4H10	2.88	2.51	3.29	3.06	3.09
C4H8=	3.51	3.76	3.91	3.77	3.80
C5H12	3.51	3.05	3.96	3.69	3.77
C5H10=	3.33	3.13	3.06	3.72	3.68
C6H14	3.63	3.30	4.17	3.78	4.12
C6H12= & CYCLO'S	1.70	1.94	1.85	2.28	2.64
C7+ IN GAS	10.49	16.10	13.53	11.18	9.54
LIQ HC'S	51.78	48.40	43.67	47.85	48.49
TOTAL	100.00	100.00	100.00	100.00	100.00

Table B6 (continued)

SUB-GROUPING					
C1 -C4	25.56	24.09	29.76	27.51	27.76
C5 -420 F	53.21	50.02	45.57	45.22	45.09
420-700 F	19.36	23.23	20.61	22.73	21.24
700-END PT	1.86	2.66	4.06	4.55	5.92
C5+-END PT	74.44	75.91	70.24	72.49	72.24
ISO/NORMAL MOLE RATIO					
C4	0.0338	0.0310	0.0257	0.0266	0.0254
C5	0.1013	0.0941	0.0878	0.0892	0.0863
C6	0.1252	0.0915	0.0906	0.0980	0.0997
C4=	0.0930	0.0763	0.0889	0.0869	0.0914
PARAFFIN/OLEFIN RATIO					
C3	1.7880	1.1528	1.3994	1.2156	1.2916
C4	0.7907	0.6450	0.8134	0.7843	0.7852
C5	1.0245	0.9471	1.2546	0.9647	0.9966
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7892	0.8144	0.8191	0.8238	0.8259
RATIO CH4/(1-A)**2	2.5721	2.9232	4.0326	3.7332	3.9933
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	CLR OIL	CLR OIL	OIL WAX	OIL WAX
DENSITY (* @ 40 C)	0.7459	0.7535	0.7564	0.7431*	0.7572
N, REFRACTIVE INDEX	1.4195	1.4232	1.4243	1.4187*	1.419*
SIMULT'D DISTILATN					
10 WT % @ DEG F	247	273	284	295	287
16	259	299	301	306	301
50	384	440	451	451	450
84	553	614	644	643	662
90	602	658	690	695	725
RANGE(16-84 %)	294	315	343	337	361
WT % @ 420 F	59.00	46.50	43.50	43.00	44.00
WT % @ 700 F	96.40	94.50	90.70	90.50	87.80

Table B7

RESULT OF SYNGAS OPERATION

RUN NO. 12200-04
CATALYST CO/TH/X4-U103+S115-HE 250 CC 132.77 GM (147.9 G AFTER RUN)
FEED H2:CO OF 52.7:47.3 @ 1195 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12222-04-06	200-04-07	200-04-08	200-04-09
FEED H2:CO:AR	52:47: 0	52:47: 0	52:47: 0	52:47: 0
HRS ON STREAM	114.5	258.5	282.5	306.5
PRESSURE,PSIG	300	300	300	300
TEMP. C	259	257	263	262
FEED CC/MIN	1195	1195	1195	1195
HOURS FEEDING	30.00	114.00	24.00	24.00
EFFLNT GAS LITER	1097.00	4690.05	940.20	951.35
GM AQUEOUS LAYER	251.14	845.50	191.80	188.97
GM OIL	100.12	329.29	71.44	69.07
MATERIAL BALANCE				
GM ATOM CARBON %	93.08	99.68	99.75	97.83
GM ATOM HYDROGEN %	97.54	98.78	99.37	99.22
GM ATOM OXYGEN %	99.52	103.17	103.92	102.92
RATIO CHX/(H2O+CO2)	0.8260	0.8956	0.8849	0.8567
RATIO X IN CHX	2.3508	2.3745	2.3975	2.4022
USAGE H2/CO PRODT	2.2114	2.1394	2.1137	2.1595
FEED H2/CO FRM EFFLNT	1.1676	1.1041	1.1099	1.1301
RESIDUAL H2/CO RATIO	0.6147	0.6268	0.5853	0.6186
RATIO CO2/(H2O+CO2)	0.0449	0.0469	0.0611	0.0566
K SHIFT IN EFFLNT	0.0289	0.0308	0.0381	0.0371
SPECIFIC ACTIVITY SA	0.8808	0.8574	0.7614	0.7084
CONVERSION				
ON CO %	34.63	31.55	34.33	33.19
ON H2 %	65.58	61.14	65.37	63.43
ON CO+H2 %	51.30	47.08	50.66	49.23
PRDT SELECTIVITY,WT %				
CH4	11.08	12.20	13.25	13.42
C2 HC'S	2.31	2.71	2.87	2.77
C3H8	3.13	3.55	3.80	3.89
C3H6=	2.35	2.72	2.62	2.48
C4H10	2.91	3.27	3.50	3.55
C4H8=	3.32	3.56	3.67	1.88
C5H12	3.55	4.03	4.17	4.19
C5H10=	2.19	2.16	2.35	2.47
C6H14	3.89	4.32	4.51	4.47
C6H12= & CYCLO'S	1.59	1.78	2.22	2.17
C7+ IN GAS	9.28	11.65	10.90	11.80
LIQ HC'S	54.40	48.08	46.16	46.91
TOTAL	100.00	100.00	100.00	100.00

Table B7 (continued)

SUB-GROUPING				
C1 -C4	25.10	28.00	29.70	27.99
C5 -420 F	41.83	44.12	43.53	45.74
420-700 F	27.53	23.17	21.00	21.16
700-END PT	5.55	4.71	5.77	5.11
C5+-END PT	74.90	72.00	70.30	72.01
ISO/NORMAL MOLE RATIO				
C4	0.0277	0.0235	0.0238	0.0242
C5	0.0829	0.0757	0.0810	0.0650
C6	0.0835	0.0767	0.0906	0.0810
C4=	0.0880	0.0912	0.0960	0.1970
PARAFFIN/OLEFIN RATIO				
C3	1.2721	1.2479	1.3863	1.4982
C4	0.8474	0.8866	0.9202	1.8221
C5	1.5735	1.8152	1.7231	1.6488
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.8288	0.8221	0.8238	0.8201
RATIO CH4/(1-A)**2	3.7771	3.8555	4.2684	4.1480
LIQ HC COLLECTION				
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY (* @ 40 C)	0.7420*	0.7837	0.7816	0.7734
N, REFRACTIVE INDEX	1.4186*	1.4185*	1.4196*	1.4194*
SIMULT'D DISTILATN				
10 WT % @ DEG F	282	298	297	296
16	300	308	309	306
50	448	453	455	452
84	641	642	666	647
90	702	697	731	709
RANGE(16-84 %)	341	334	357	341
WT % @ 420 F	45.50	42.00	42.00	44.00
WT % @ 700 F	89.80	90.20	87.50	89.10

X. Run 9 (12200-05) with Catalyst 9 (X_3/K/UCC-103+UCC-101)

This catalyst is the same as Catalyst 2, being rerun to verify the suspiciously high initial C_5^+ activity obtained in Run 2.

The simulated distillation of the C_5^+ product from one sample is plotted in Fig. B107. The carbon number product distribution of one sample is plotted in Fig. B108. A chromatogram from the simulated distillation of one sample is reproduced in Fig. B109. Detailed material balances for one sample appear in Table B8.

After 22 hours on stream the conversion was 14.0 percent. The apparent 42.1 percent conversion at 19.5 hours on stream, obtained in the earlier run, is believed to have been due to a gas analysis error.

Fig. B107

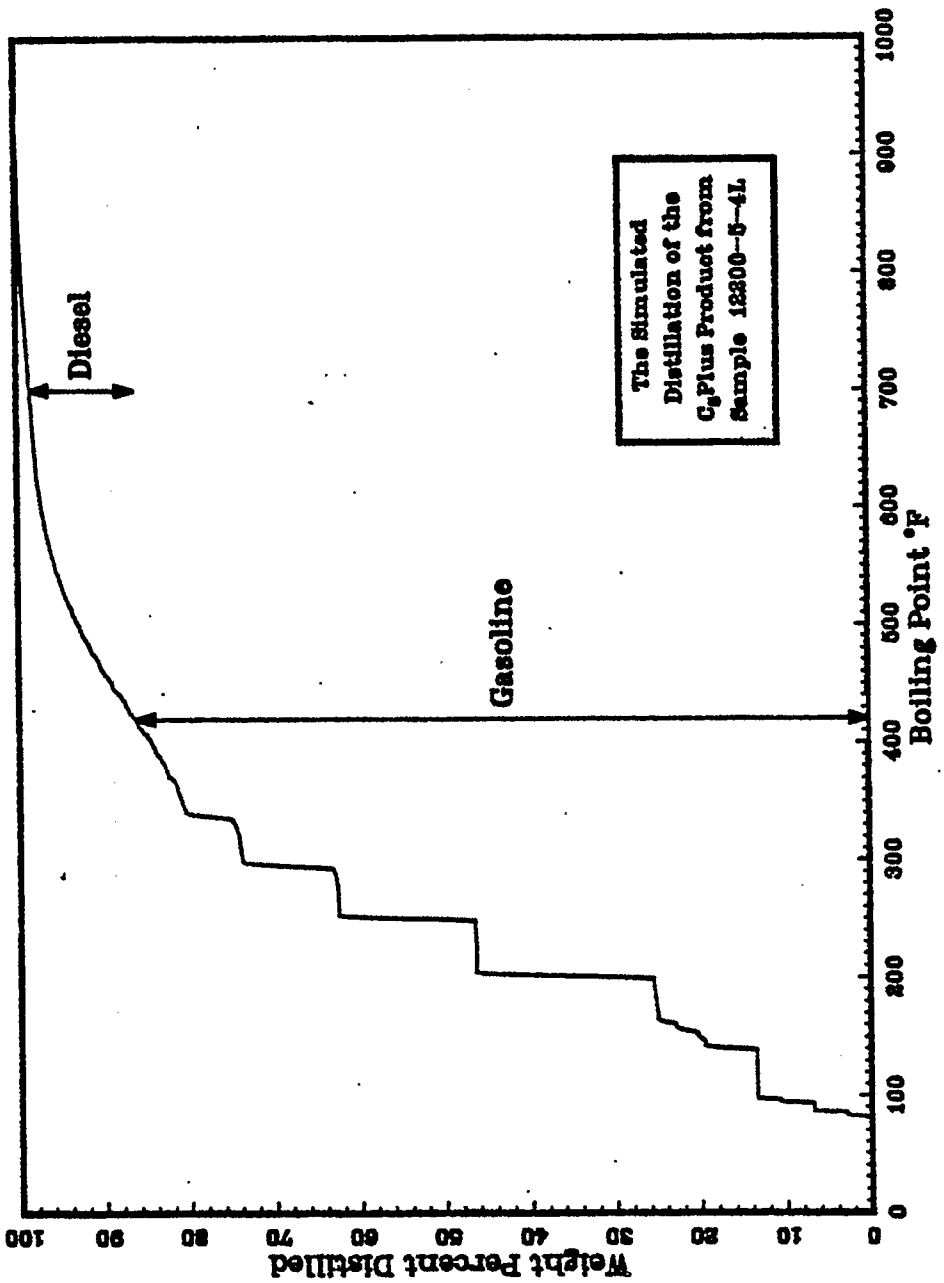
The Simulated Distillation of the C5 Plus Product from Sample 12300-6-4L
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B108

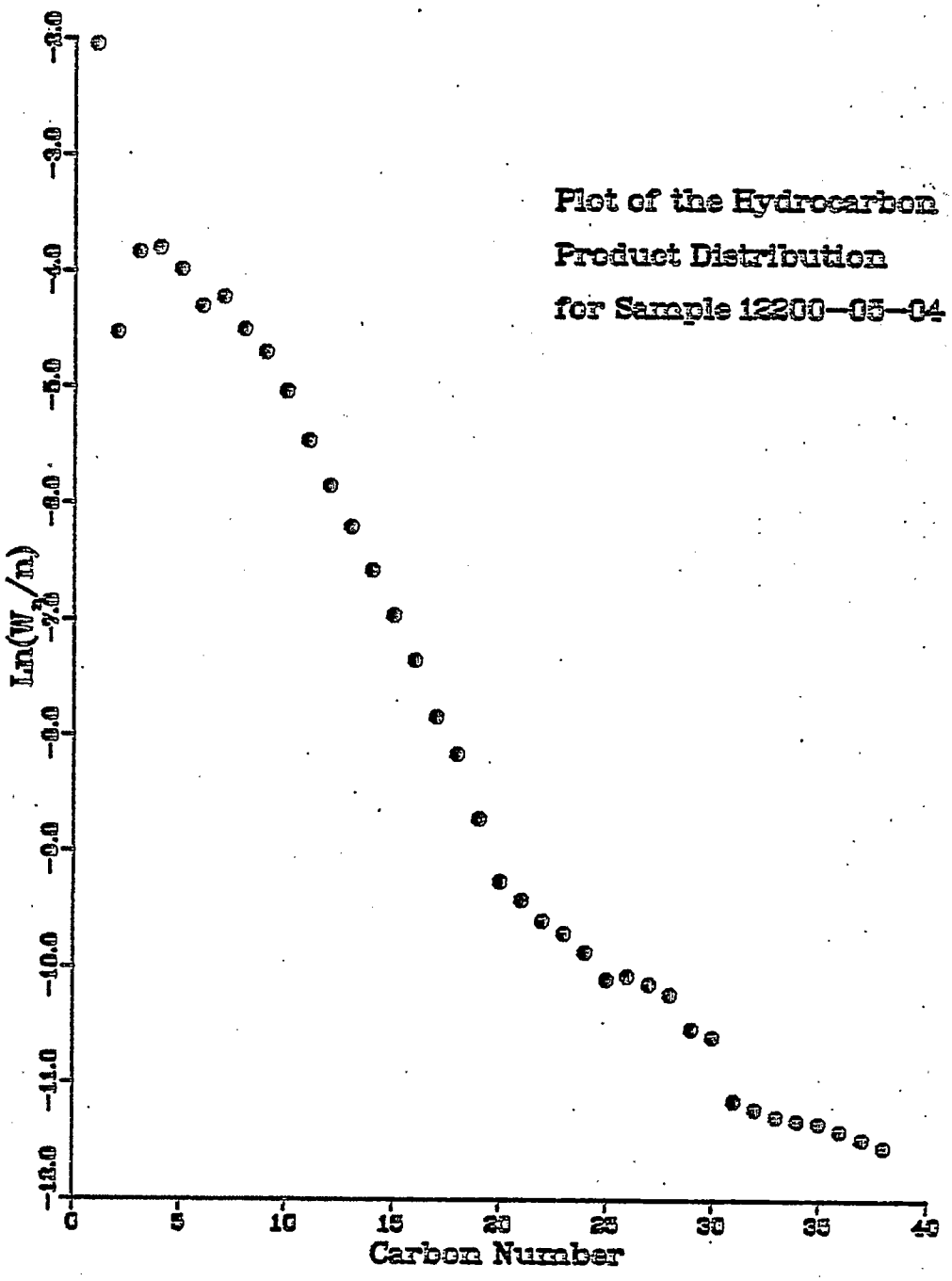
Plot of the Hydrocarbon
Product Distribution
for Sample 12200-05-04
Ln(W_n/n)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B109

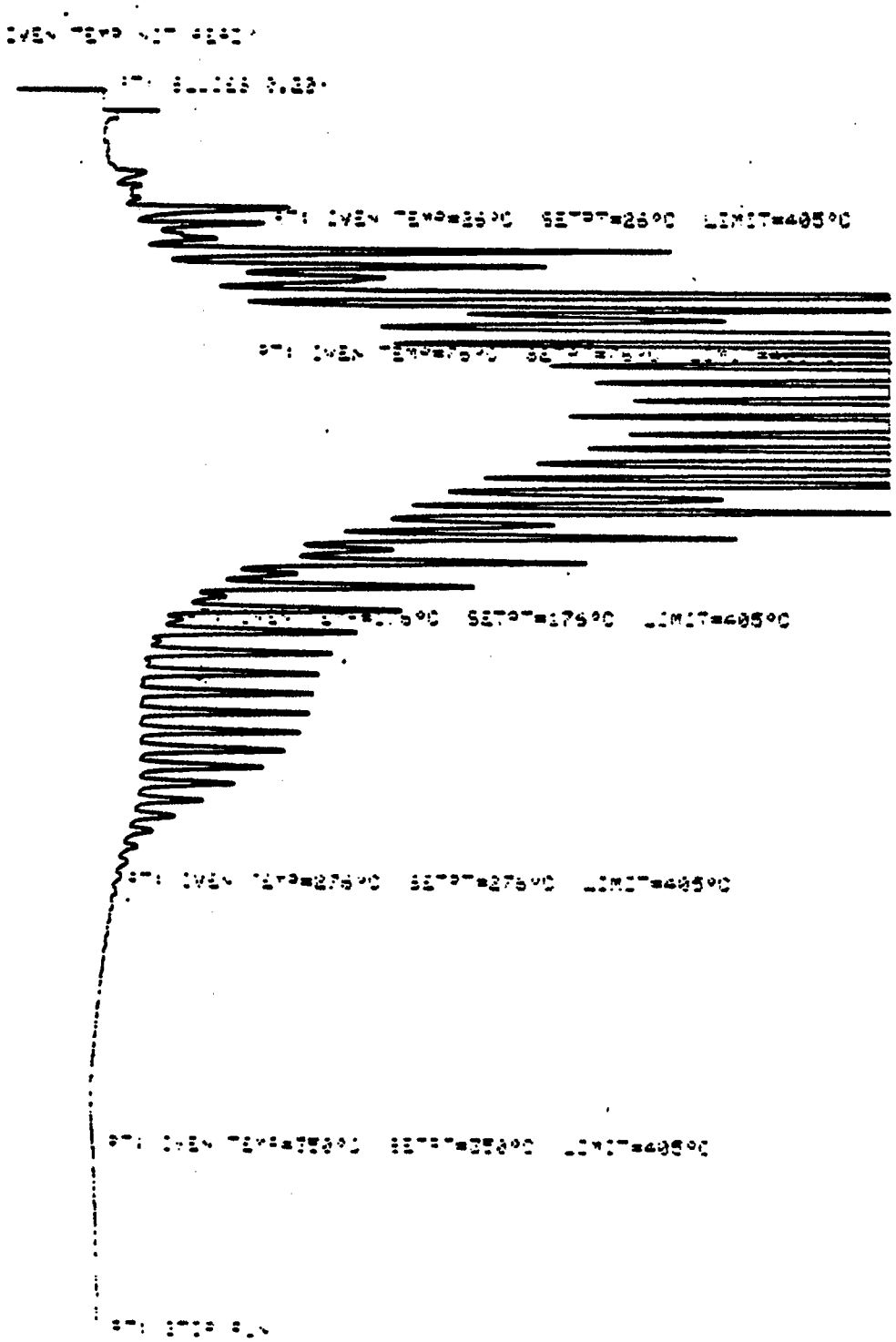

Table B8

RESULT OF SYNGAS OPERATION

RUN NO. 12200-05
CATALYST X3/K-U103+U101 12006-54 80 CC 36.83GM(37.0 AFTER RUN +.17G)
FEED H2:CO OF 50:50 @400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-05-04
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	22.00
PRESSURE,PSIG	100
TEMP. C	253
FEED CC/MIN	400
HOURS FEEDING	22.00
EFFLNT GAS LITER	416.10
GM AQUEOUS LAYER	15.52
GM OIL	1.51
MATERIAL BALANCE	
GM ATOM CARBON %	88.26
GM ATOM HYDROGEN %	89.00
GM ATOM OXYGEN %	92.82
RATIO CHX/(H2O+CO2)	0.5839
RATIO X IN CHX	2.3188
USAGE H2/CO PRODT	2.8457
FEED H2/CO FRM EFFLNT	1.0084
RESIDUAL H2/CO RATIO	0.8635
RATIO CO2/(H2O+CO2)	0.0040
K SHIFT IN EFFLNT	0.0035
SPECIFIC ACTIVITY SA	0.5621
CONVERSION	
ON CO %	7.31
ON H2 %	20.62
ON CO+H2 %	13.99
PRDT SELECTIVITY,WT %	
CH4	12.92
C2 HC'S	2.15
C3H8	1.44
C3H6=	5.06
C4H10	2.51
C4H8=	6.47
C5H12	3.86
C5H10=	5.45
C6H14	6.00
C6H12= & CYCLO'S	2.10
C7+ IN GAS	36.93
LIQ HC'S	15.12
TOTAL	100.00

Table B8 (CONTINUED)

SUB-GROUPING	
C1 -C4	30.54
C5 -420 F	59.93
420-700 F	8.39
700-END PT	1.13
C5+-END PT	69.46
ISO/NORMAL MOLE RATIO	
C4	0.4022
C5	1.0253
C6	2.4380
C4=	0.0471
PARAFFIN/OLEFIN RATIO	
C3	0.2712
C4	0.3745
C5	0.6897
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.7446
RATIO CH4/(1-A)**2	1.9806
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLD OIL
DENSITY (* 40 C)	N/A
N, REFRACTIVE INDEX	1.4279*
SIMULT'D DISTILATN	
10 WT % @ DEG F	341
16	368
50	452
84	577
90	644
RANGE(16-84 %)	209
WT % @ 420 F	37.00
WT % @ 700 F	92.50

XI. SUMMARY

Results of the nine tests conducted during the quarter have provided insights into the development of the intimately contacted, cobalt/UCC-103, class of catalyst which should prove useful in guiding future work.

Attempts at improving motor fuel quality by the incorporation of second shape-selective components into the cobalt/UCC-103 catalyst were unsuccessful. Problems with the testing of a UCC-107-containing catalyst were inconclusive, but a catalyst containing S115 showed no improved product quality. The metal additive X_7 was shown to have beneficial effects in reducing the production of methane, although it also greatly depressed the catalyst's conversion activity.

The advantages of replacing cobalt as the active Fischer-Tropsch metal with X_3 was investigated. The X_3 catalysts showed desirable properties in the highly olefinic product and the higher relative activity per weight percent metal; however, the catalyst produced excessive methane and showed poor stability.

A catalyst containing 17 percent cobalt produced an initial specific activity of 8; at the usual cobalt levels of 4 to 7 percent, the initial specific activity has rarely been as high as 2. This catalyst demonstrated the potential activity obtainable by increasing the cobalt concentration and removing any second

shape-selective component, and further demonstrated the need for metal additivies for stability. An attempt to regenerate this catalyst with oxygen--the first time this idea has been tested--proved unsuccessful.

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