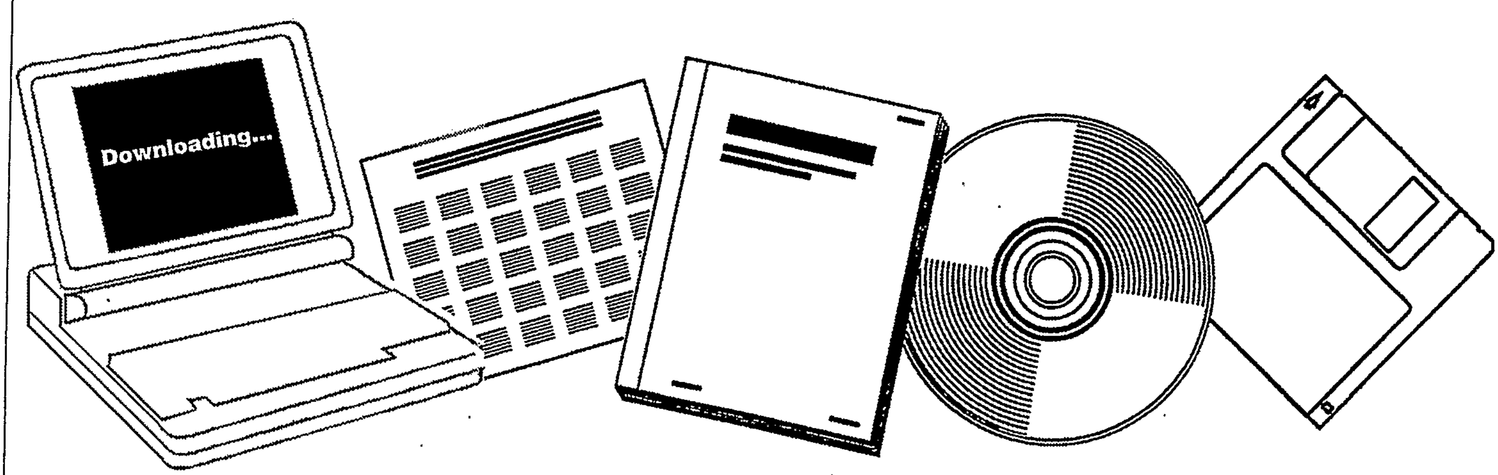
IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. SEVENTH QUARTERLY TECHNICAL PROGRESS REPORT, APRIL-JUNE 1986

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

1986



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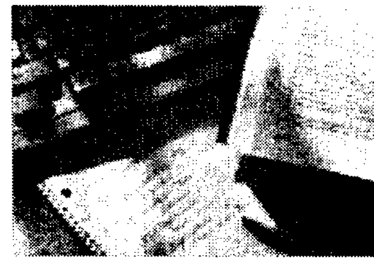

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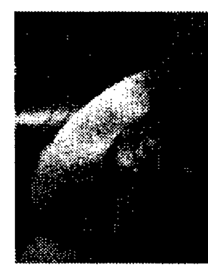

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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

Seventh Quarterly Report
April - June 1986

IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Services Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

MASTER

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DE87 000519

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Appendixes

I. CONTRACT OBJECTIVE

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

II. SCHEDULE

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

Work on the program is divided into six tasks.

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

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

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

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

Task 5 consists of the optimization of a UCC process/catalyst system based upon a tubular reactor with a recycle loop (i.e., the Arge reactor) containing the most promising catalysts developed under the Tasks 3 and 4 studies. This optimal performance will be estimated from a mathematical model of the tubular reactor which incorporates reaction rate constants determined from appropriate Berty reactor runs. This effort will run through the first 24 months of the contract.

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

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

III. ORGANIZATION

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

The principal investigator is Dr. Jule A. Rabo.

The program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

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

B. Task 2

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

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

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

C. Tasks 3 and 4

The catalytic testing during this quarter was focused on further developing and understanding X_{11} promoted cobalt oxide catalysts intimately contacted with the Molecular Sieve TC-123.

Included in the testing were attempts at determining the beneficial effects of incorporating the promoter X_9 into the catalyst formulation (first used in Run 55), at incorporating higher cobalt concentrations into the catalyst, and at screening the effects of using a new Molecular Sieve support, TC-124.

Two catalysts were tested to determine the potential beneficial effect of the promoter X_9 under high temperature and pressure conditions (260C, 500 psig, 1.5:1 H_2:CO). Catalyst 60, containing no X_9, showed inferior stability to Catalyst 55, which contained 1.1 percent X_9 (described in Run 55, Appendix B of this report). Increasing the concentration to 1.6 percent also showed decreased catalyst stability, indicating that an optimum quantity of X_9 lies between zero and 1.6 percent.

A new method of increasing the cobalt concentration was tried to further improve the catalyst's activity (Run 59). The catalyst demonstrated an initially high activity, but it quickly dropped to the level normally observed for a typical 8.2 percent loading.

A new support, TC-124, was tested for its effect on catalyst performance. Both attempts (Runs 58 and 61) produced catalysts with poor performance, but these catalysts did show improved isomerization activity as evidenced by the C_5^+ fraction.

D. Task 5

Berty reactor data for the promising Catalyst 45 were correlated into rate and selectivity expressions. These correlations were then incorporated into the FIXBD computer simulation of the Arge reactor to yield preliminary design curves for a "kick-off" presentation to MITRE, who will be carrying out an updated economic evaluation of our new catalyst system (see Task 6, below).

E. Task 6

As mentioned above, MITRE is expected to begin their economic evaluation of our Catalyst 45 shortly. This evaluation will be for a base case which will run at 400 psig, 250C, and with an 85 percent overall syngas conversion.

The feed space velocity chosen for that conversion will require a certain H_2:CO feed ratio, which, in turn, will determine how much CH_4 is produced (high H_2:CO feed ratios will allow high space velocities, but they will also create high CH_4 makes).

The relationship between feed space velocity and methane make was presented to MITRE in the form of a single curve. This plot was accompanied by additional plots which showed what the feed H_2:CO ratio, the C_2 make, and the alpha for the $C3^+$ product would be for any chosen combination of feed space velocity and CH_4 make. See Appendix C.

MITRE is expected to use these operating curves in conjunction with their techno-economic background to pick a single space velocity-CH_4 make combination as the basis for a complete economic evaluation.

This evaluation will be accompanied by a thorough sensitivity analysis which could be in the form of ten plots, one for each of the ten operating variables of pressure, temperature, overall conversion, methane make, feed space velocity, feed H_2:CO ratio, C_2 make, alpha for C_3^+ product, catalyst cost, and catalyst life.

Each of these operating variables would be plotted against the corresponding cost differential (cents per gallon, plus or minus) which would arise if the value of that variable (and only that variable) were changed to a different value from that used in the base case. Three or four such determinations by MITRE would thus define a sensitivity curve for that operating variable.

The sensitivity curves would be used in conjunction with sets of new operating curves for new cases. Values for ten new operating variables for a new case would be taken from these new operating curves and costed with the sensitivity curves. The sum of all the plus and minus differentials thus determined from the sensitivity curves would define the total cost (relative to the cost of the base case) for that new case.

In other words, these MITRE supplied sensitivity curves will allow UCC to determine the worth of any set of operating conditions for Catalyst 45, or for any set of operating conditions for any new, improved catalyst that we may develop in the future.

V. CHANGES

There were no contract changes during the Seventh Quarter.

VI. FUTURE WORK

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

Task 5 will continue to be devoted to examining various operating conditions for Catalyst 45, as well as to supplying MITRE with any requested supporting material.

Albert C. Frost

APPENDIX A. <u>CATALYST TESTING: SUMMARY OF RUNS REPORTED DURING THIS QUARTER</u>

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

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

This report describes the five catalyst tests conducted from April through June 1986, the seventh quarter of this contract.

A list of the catalysts tested, a description of their preparation, and a brief statement of each test's objective, are shown in Table A1. All of the catalysts tested involved cobalt oxide and additive X_{11} intimately contacted with one of two Molecular Sieve supports: TC-123 in Runs 57, 59, 60, and TC-124 in Runs 58 and 61. Runs 57 and 60 were designed to assess the effects of the promoter X_9, which was first used in combination with the X_{11} promoter in Run 55 (described in Appendix B of this report). Run 59 tested a new method of increasing the cobalt concentration in the catalyst. Runs 58 and 61 examined the use of the newly developed catalyst support, TC-124.

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

Table A1. Description of catalysts tested during the seventh quarter.

Run	Catalyst	Catalyst preparation	Objective of test
57	$Co/X_{11}/TC$-123 (11617-10)	The X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 55, except that the additive X_9 was not included. Theoretical pct Co=8.2, pct X_{11}=1.6.	To determine the effects of X_9 in Catalyst 55.
58	$Co/X_9/X_{11}/TC$-124 (12561-07)	The X_9, X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 55, except that TC-123 was replaced with the new Molecular Sieve TC-124. Theoretical pct Co=8.2, pct X_{11}=1.6, pct X_9=1.1.	To test the use of TC-124 as the catalyst support.
59	$Co/X_{11}/TC$-123 (12561-08)	The X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 57, except that a new formulation step was added. Theoretical pct Co=11.6, pct X_{11}=2.3.	To test a new method of increasing the cobalt concentration in the catalyst.
60	$Co/X_9/X_{11}/TC$-123 (12570-05)	The X_9, X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 55, except that the X_9 concentration was increased 1.5 times. Theoretical pct Co=7.9, pct X_{11}=1,6, pct X_9=1.6.	To test the effect of varying the X_9 concentration.
61	$Co/X_9/X_{11}/TC$-124 (11617-11)	The X_9, X_{11} promoted cobalt oxide catalyst was formulated similarly to Catalyst 58, except that an additional calcining step was incorporated in the formulation procedure. Theoretical pct Co=8.2, pct X_9=1.1, pct X_{11}=1.6.	To test the use of TC-124 as the catalyst support.

Table A2. Preliminary catalyst test results for runs made during the seventh quarter.

Run	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Stability
57	Co/X_{11}/TC-123 (11617-10)	52.5	46.8	3.7	87.6	3.40	—[1]
		97.5	47.8	3.3	88.9	3.17	
		145.5	79.6	12.8	77.6	1.67	Fair[2]
		599.5	75.0	9.9	81.6	1.23	
58	Co/X_9/X_{11}/TC-124 (12561-07)	20.0	39.7	10.6	74.9	2.05	Poor[1]
		114.0	35.1	11.1	75.1	1.34	
		138.5	38.5	9.1	78.6	1.02	—[3]
		163.0	39.0	8.7	79.8	1.02	
59	Co/X_{11}/TC-123 (12561-08)	43.0	55.2	4.6	86.6	3.40	Good after initial deactivation[1]
		182.0	49.5	4.5	86.0	2.69	
60	Co/X_9/X_{11}/TC-123 (12570-05)	39.5	47.4	3.9	88.6	3.57	Excellent[1]
		89.5	47.5	3.5	88.9	3.35	
		169.0	76.8	9.8	80.7	1.40	Fair[2]
		737.0	71.0	11.9	76.3	0.97	
61	Co/X_9/X_{11}/TC-124 (11617-11)	21.5	30.1	10.3	73.3	1.72	Poor[1]
		209.5	21.9	12.5	69.9	0.63	

Reactor conditions:
1. 240C, 300 psig, 1:1 H_2:CO.
2. 260C, 500 psig, 1.5:1 H_2:CO.
3. 240C 500 psig, 1:1 H_2:CO.

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

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

Contents

I. INTRODUCTION

Presented in this report are detailed analyses of the first six catalyst test runs (Runs 59-54) of the eight runs summarized in Appendix A of the Sixth Quarterly Report, which constituted the major thrust of the work during that quarter. Runs 55 and 56 will be discussed in the Eighth Quarterly Report.

One run (Run 52) was a blank in which quartz chips alone were used.

In the five remaining runs the catalysts contained cobalt oxide promoted with X_{11}. All were formulated by the method first used with Catalyst 11 (Run 12185-07) of the Third Quarterly Report.

One of these also contained a new Molecular Sieve, TC-121; one contained γ-alumina; and three contained TC-123, the most effective Molecular Sieve developed to date. The three latter tests were run to assess the effects of the promoters X_9, X_{13} and K/Ni/Mo-γ-alumina when used in combination with the Co/X_{11}/TC-123 type of catalyst. The X_9 and X_{13} were intimately mixed with the catalyst, while the K/Ni/Mo-γ-alumina, a water gas shift component, was physically mixed.

II. Run 49 (12561-04) with Catalyst 49 ($Co/X_{11}/\gamma-Al_2O_3$)

The purposes of this run were (1) to establish a reference benchmark by which to isolate the effects of the promising catalyst support TC-123 (Catalyst 45, Sixth Quarterly Report), and at the same time (2) to compare these with the effects of the supports TC-103 and TC-133 (Catalyst 32, Fourth Quarterly Report, and Catalyst 46, Sixth Quarterly Report, respectively).

The catalyst consisted of cobalt oxide promoted with X_{11} and intimately contacted with $\gamma-Al_2O_3$. Preparation was by the same method used for Catalyst 45. The theoretical content of cobalt and X_{11} was 8.2 and 1.6 percent respectively, the same as in Catalysts 32, 45 and 46.

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. B5-11. Carbon number product distributions are plotted in Figs. B12-18. Chromatograms from simulated distillations are reproduced in Figs. B19-25. Detailed material balances appear in Tables B1-3.

The following table compares the activity and selectivity of this catalyst with those of Catalysts 32, 45 and 46, all consisting of X_{11} promoted cobalt oxide but intimately contacted with different supports.

Performances of Co/X11 catalysts with four different supports. Conditions: 240C, 1:1 H_2:CO, 300 psig, 300 GHSV.

	Catalyst number and support			
	Cat. 49 γ-Al_2O_3	Cat. 32 TC-103	Cat. 45 TC-123	Cat. 46 TC-133
Conversion, CO+H_2, pct	45.0	42.8	46.7	50.3
C_1, pct	7.1	5.3	3.8	5.3
C_2-C_4, pct	10.4	9.7	6.0	9.0
C_5-420F, pct	36.5	31.2	28.1	33.2
420-700F, pct	28.7	27.8	31.2	29.5
700F+, pct	17.3	26.0	30.9	23.0
C_5^+, pct	82.5	85.0	90.2	85.6
C_4 olefin:paraffin	1.8	2.1	2.7	2.0

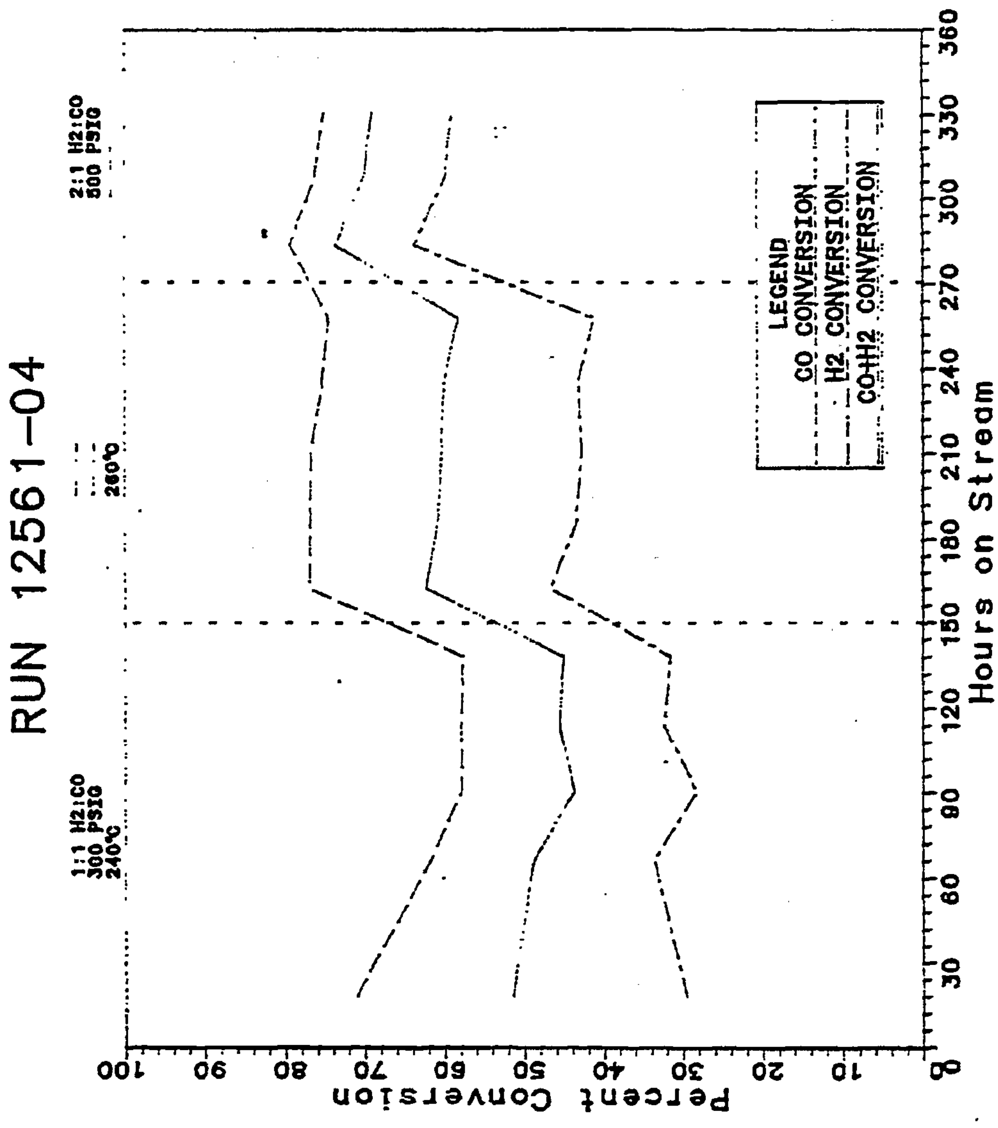
The syngas conversion of this γ-Al_2O_3 catalyst was well within the range of the conversion values demonstrated by the three catalysts with Molecular Sieves--somewhat higher than that of Catalyst 32 with TC-103, but a little lower than that of Catalyst 45 with TC-123 and substantially lower than that of Catalyst 46 with TC-133.

Comparison of the selectivity showed this catalyst to be the poorest of the four, its yield both highest in methane and lowest in C_5^+ and olefins. The catalysts with TC-103 and TC-133 were nearly identical in selectivity. By far the best selectivity of the four belonged to the one with TC-123, demonstrating a low methane level of 3.8 percent and a high C_5^+ yield of 90.2 percent. Its olefin content, as indicated by the iso-normal ratio of the C_4 fraction, was also substantially superior to that of the other three catalysts.

The stability of all four catalysts, at least for the relatively short duration of their runs, was excellent. But when its operating temperature was raised from 240C to 260C, the stability of this γ-Al_2O_3 catalyst dropped to an estimated loss in conversion of one percentage point every 30 hours on stream, well below that of Catalyst 32 with TC-103.

When the H_2:CO feed ratio was raised from 1:1 to 1.5:1, and the pressure from 300 to 500 psig, the conversion of this catalyst rose to about 70 percent and the methane production to about 15 percent. During the short time under these conditions, however, the stability appeared only fair.

The testing of this non-Molecular Sieve catalyst provided important reference data to illustrate the role that the Molecular Sieve has on the performance of these X_{11} promoted cobalt Fischer-Tropsch catalysts. The Molecular Sieve catalysts demonstrated selectivity benefits over the γ-Al_2O_3 catalyst, with TC-123 being the superior of the three tested.



RUN 12561-04
1:1 H2:CO
300 PSIG
240°C
260°C
2:1 H2:CO
300 PSIG
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Hours on Stream
Percent Conversion
0
30
60
90
120
150
180
210
240
270
300
330
360
10
20
30
40
50
60
70
80
90
100

Fig. B1

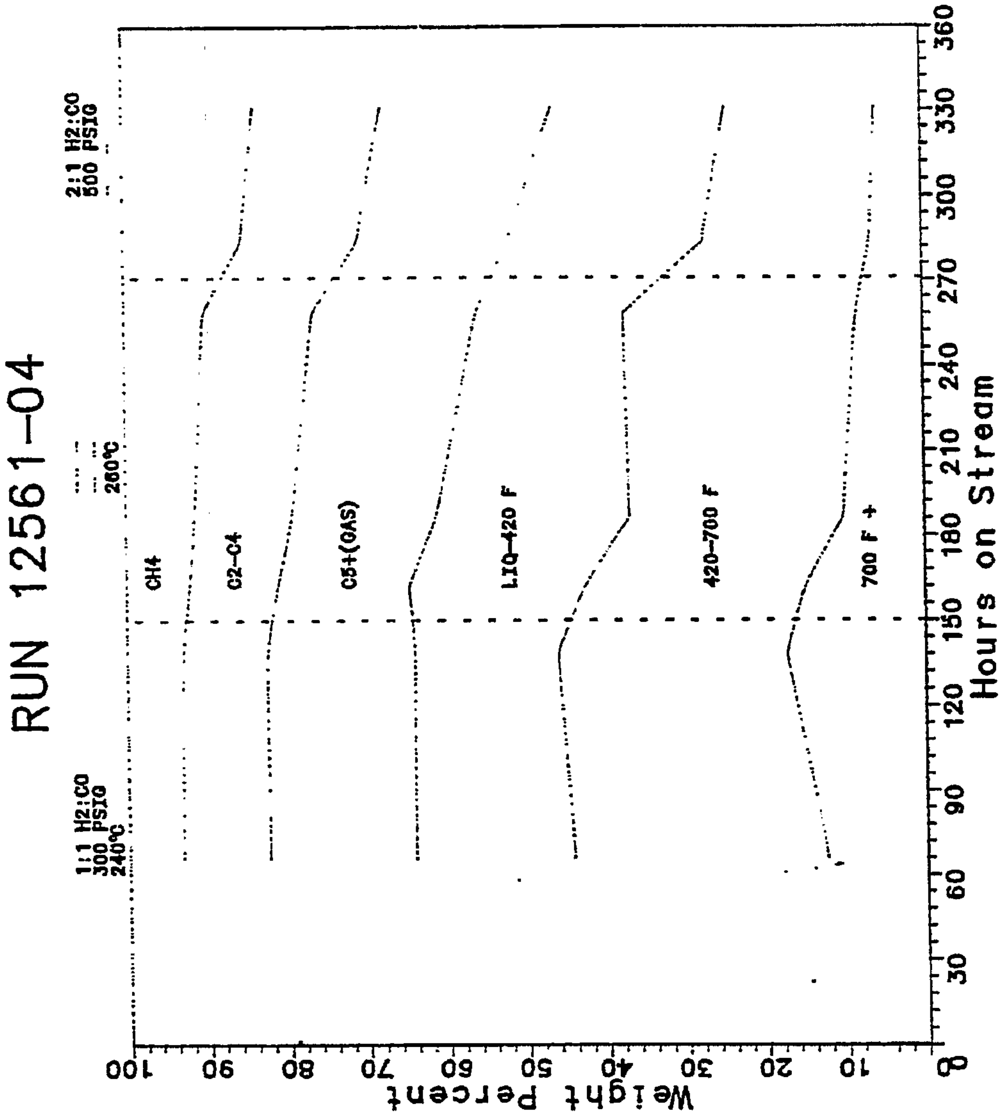

RUN 12561-04
Weight Percent
Hours on Stream
1:1 H2:CO
300 PSIG
240°C
260°C
2:1 H2:CO
500 PSIG
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
300
330
360

Fig. B2

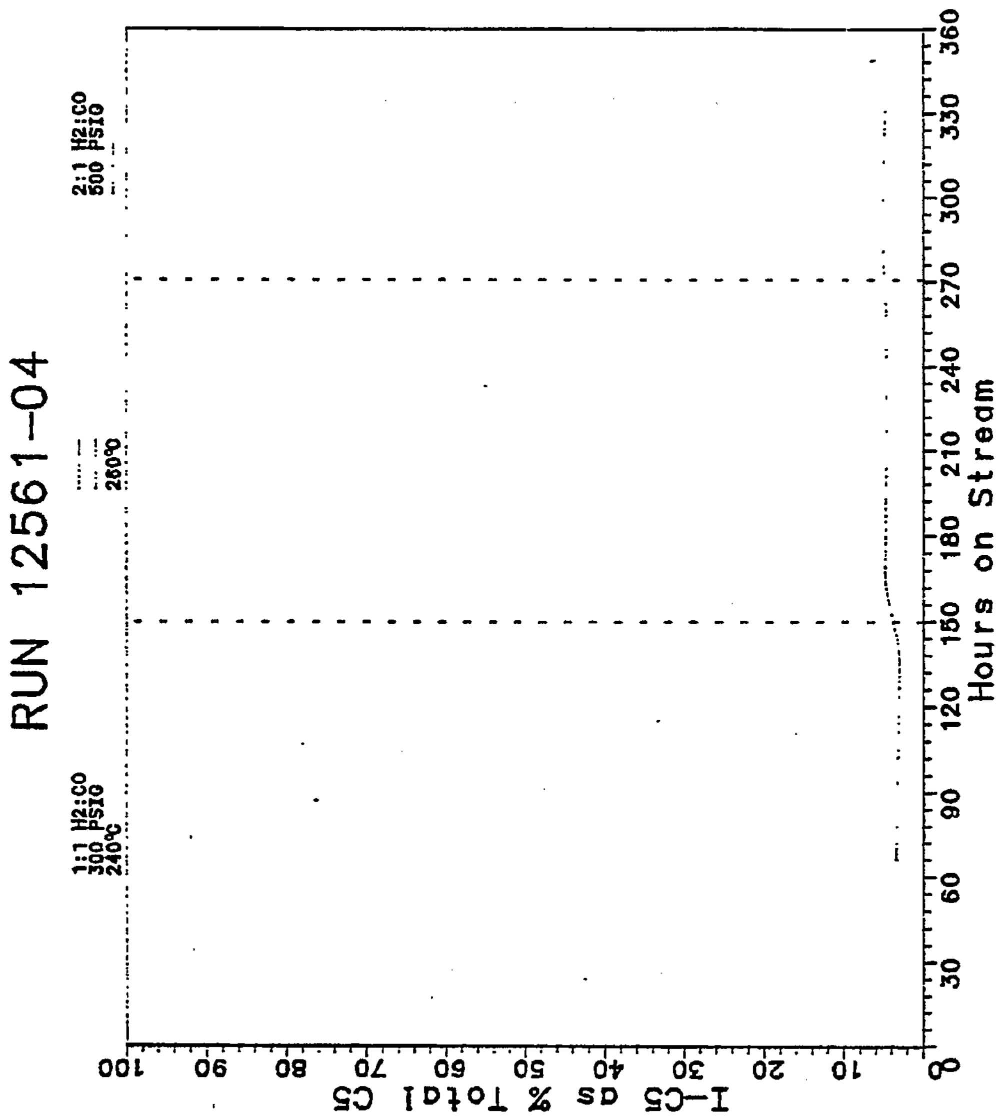

RUN 12561-04
1:1 H2:CO
300 PSIG
240°C
260°C
2:1 H2:CO
500 PSIG
Hours on Stream
I-C5 as % Total C5

Fig. B3

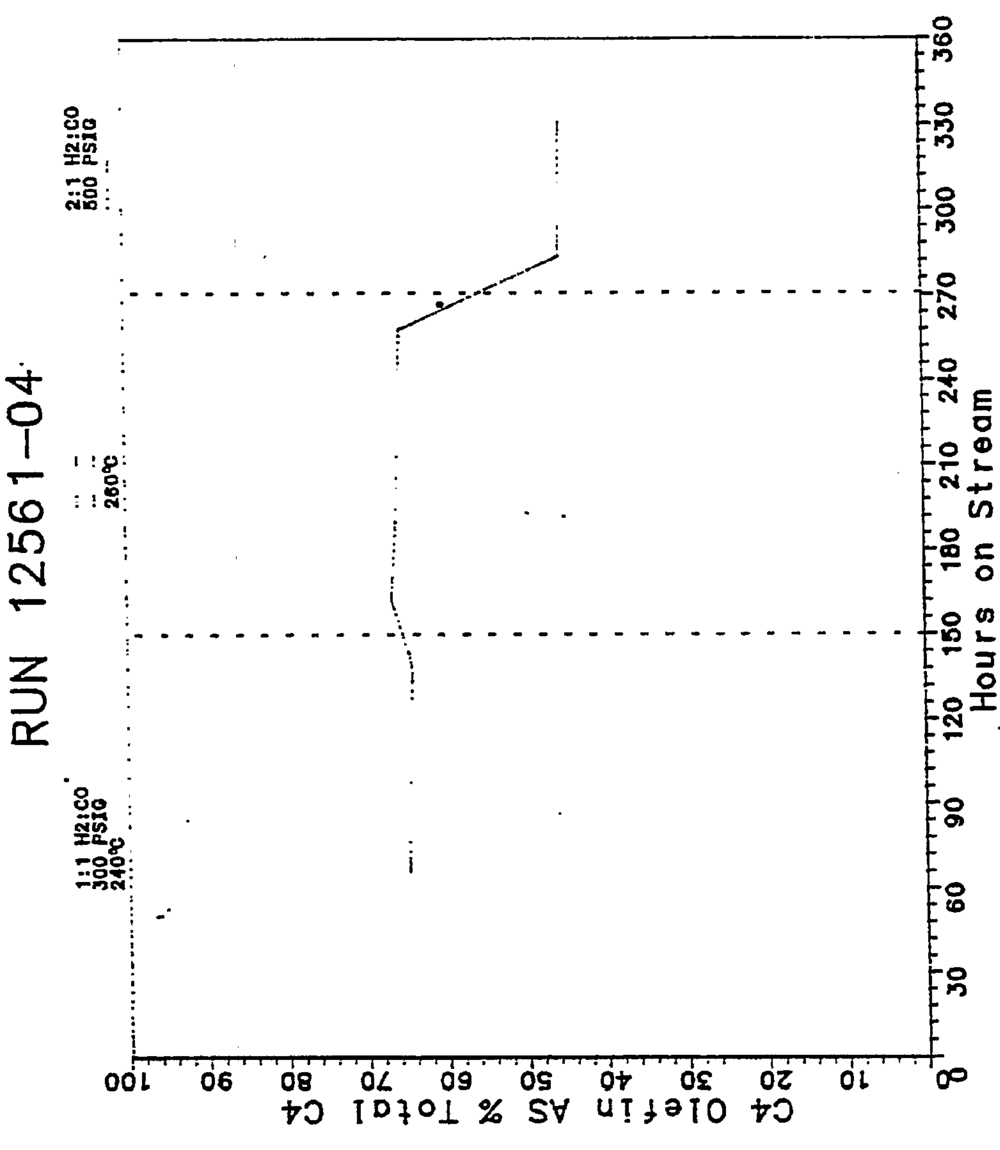

RUN 12561-04
1:1 H2:CO
300 PSIG
240°C
260°C
2:1 H2:CO
500 PSIG
Hours on Stream
C4 Olefin AS % Total C4

Fig. B4

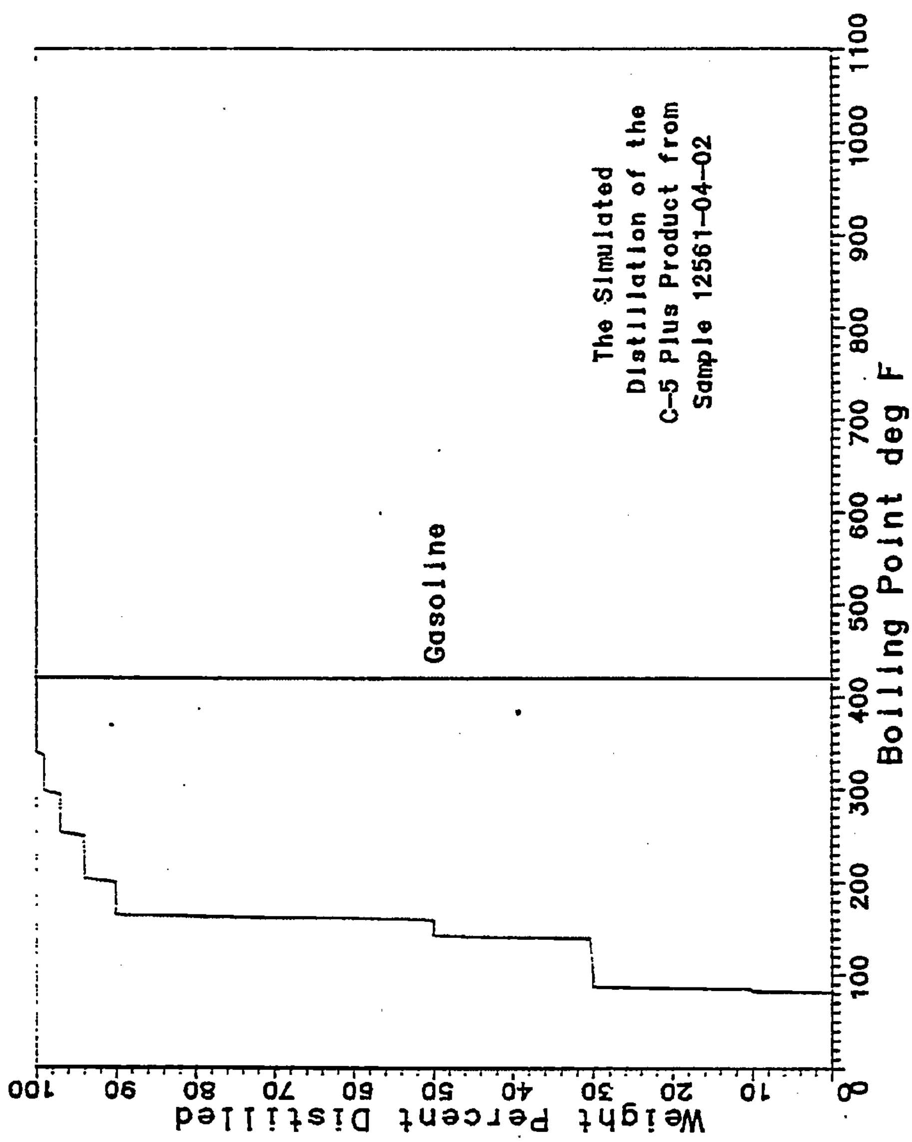

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-02
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B5

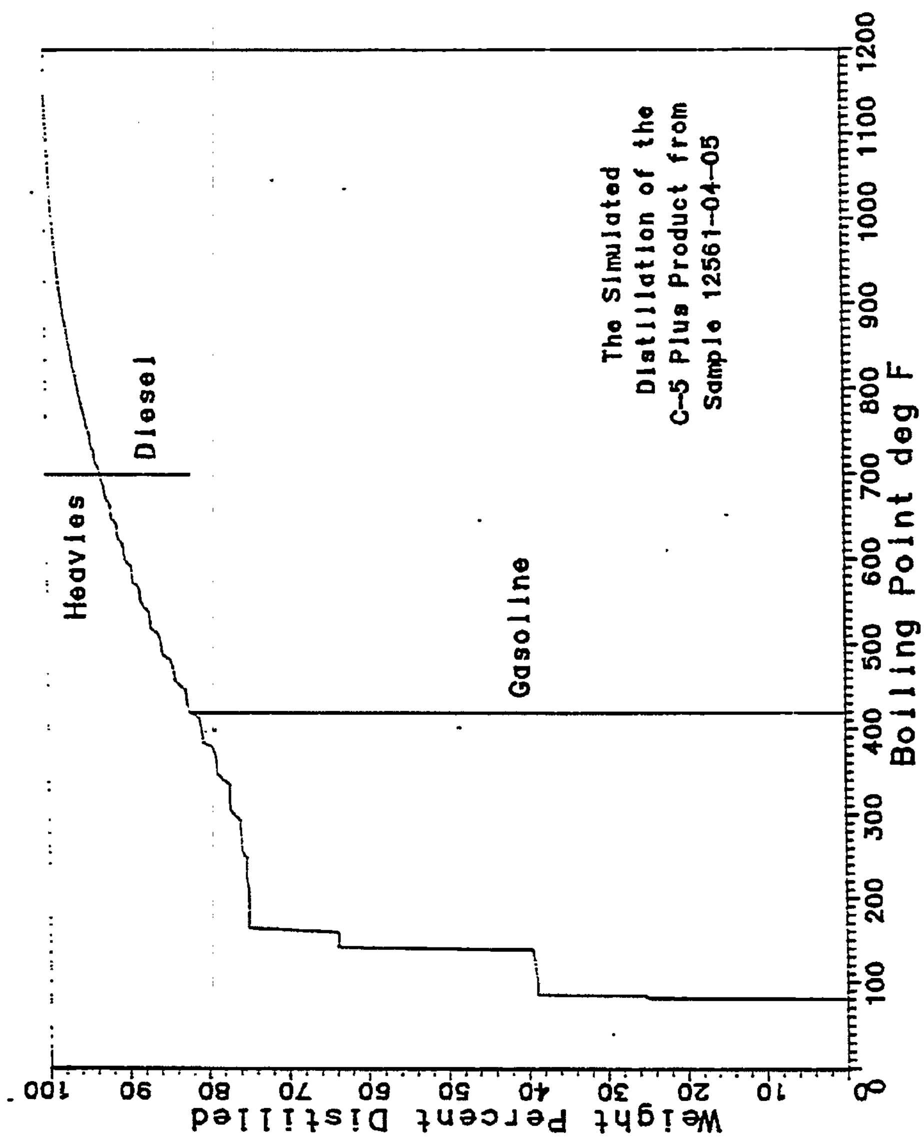

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-05
Boiling Point deg F
Weight Percent Distilled

Fig. B6

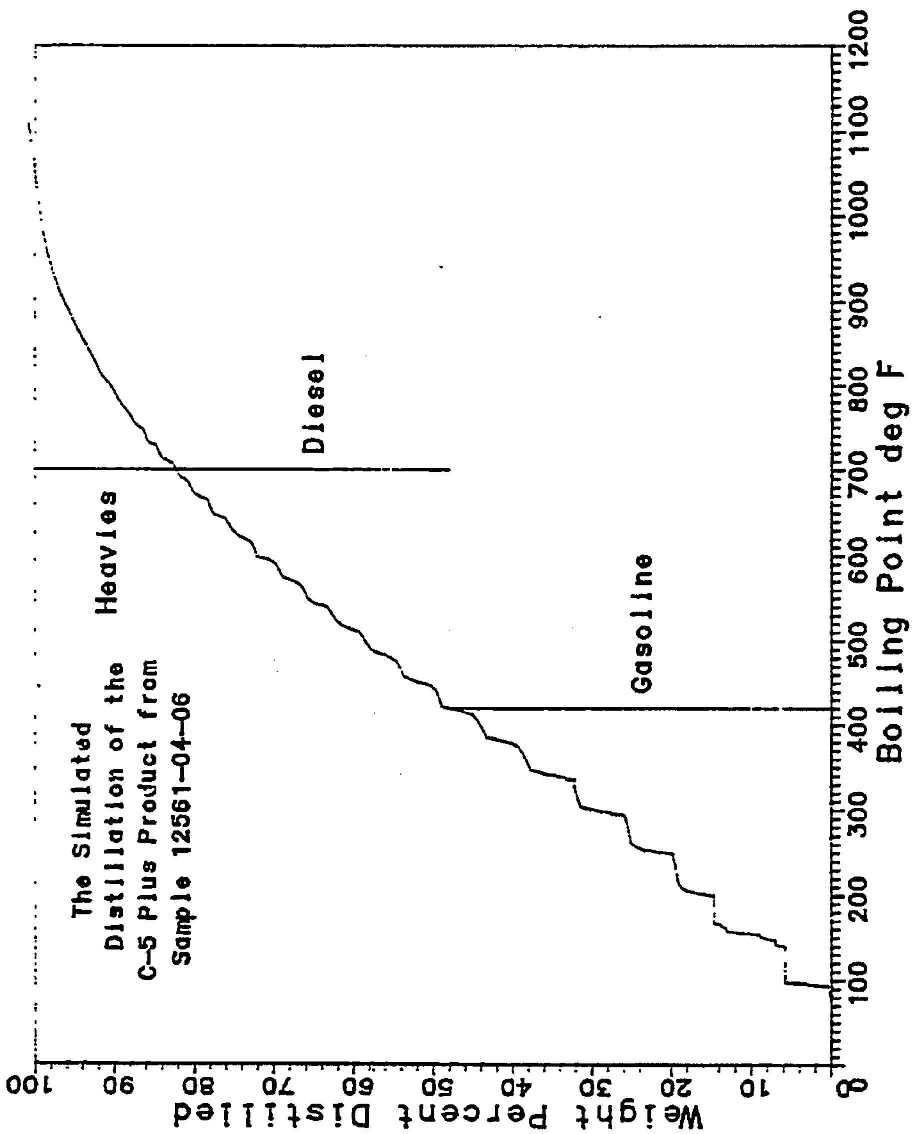

The Simulated Distillation of the C-5 Plus Product from Sample 12561-04-06
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
0 10 20 30 40 50 60 70 80 90 100

Fig. B7

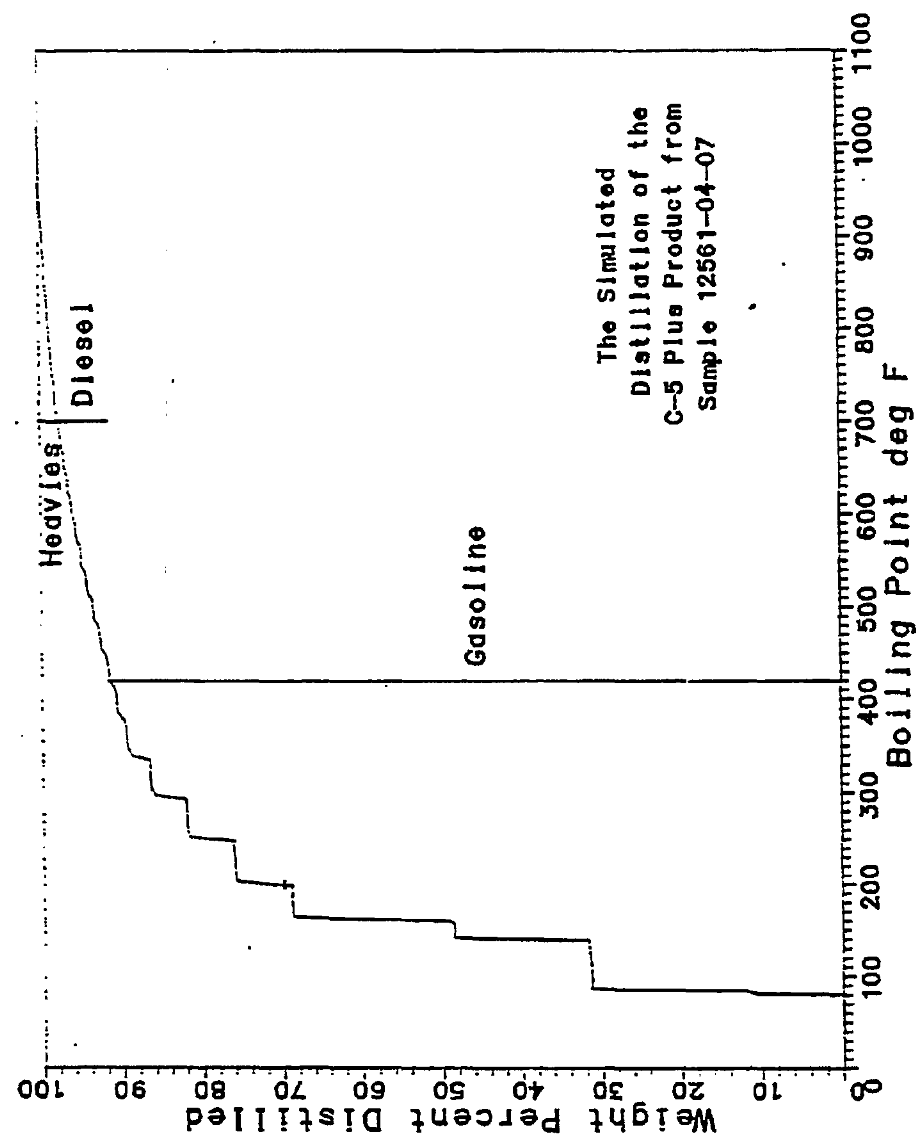

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-07
Boiling Point deg F
Weight Percent Distilled

Fig. B8

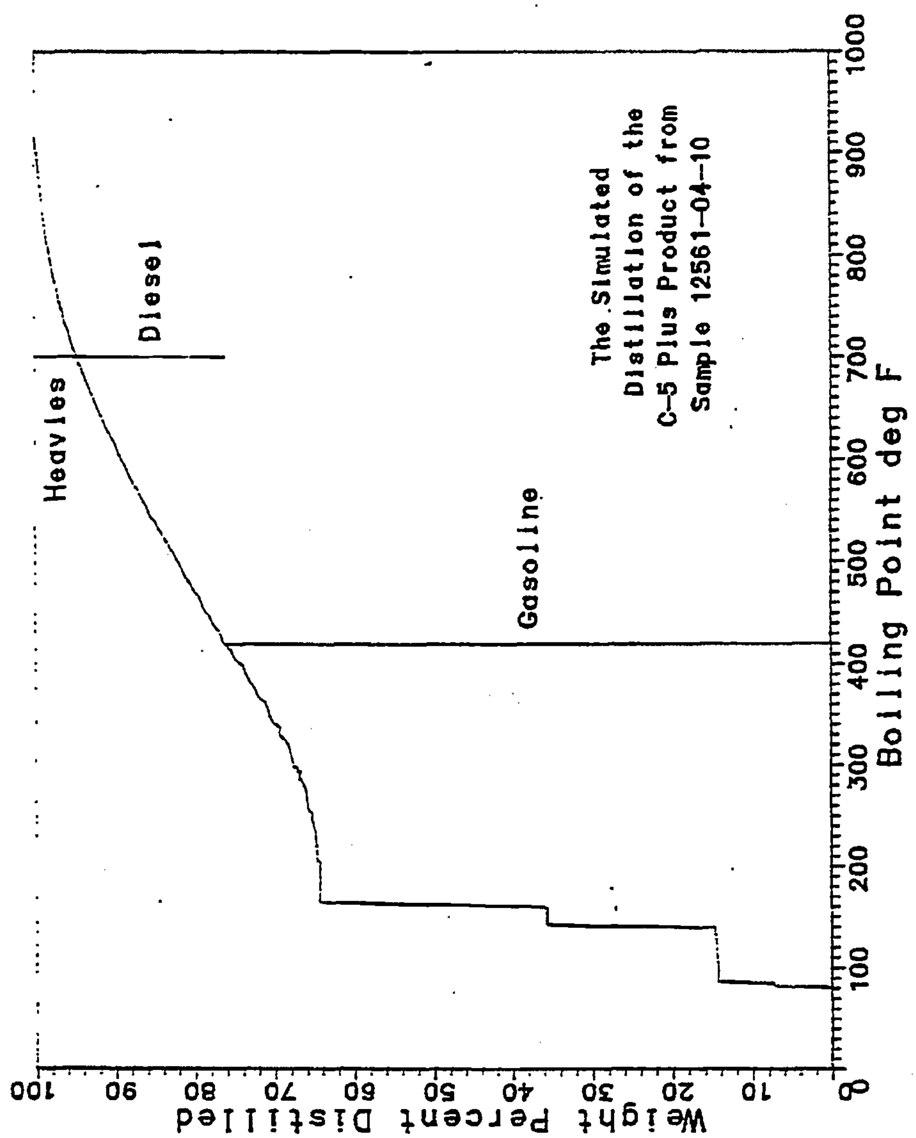

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-10
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B9

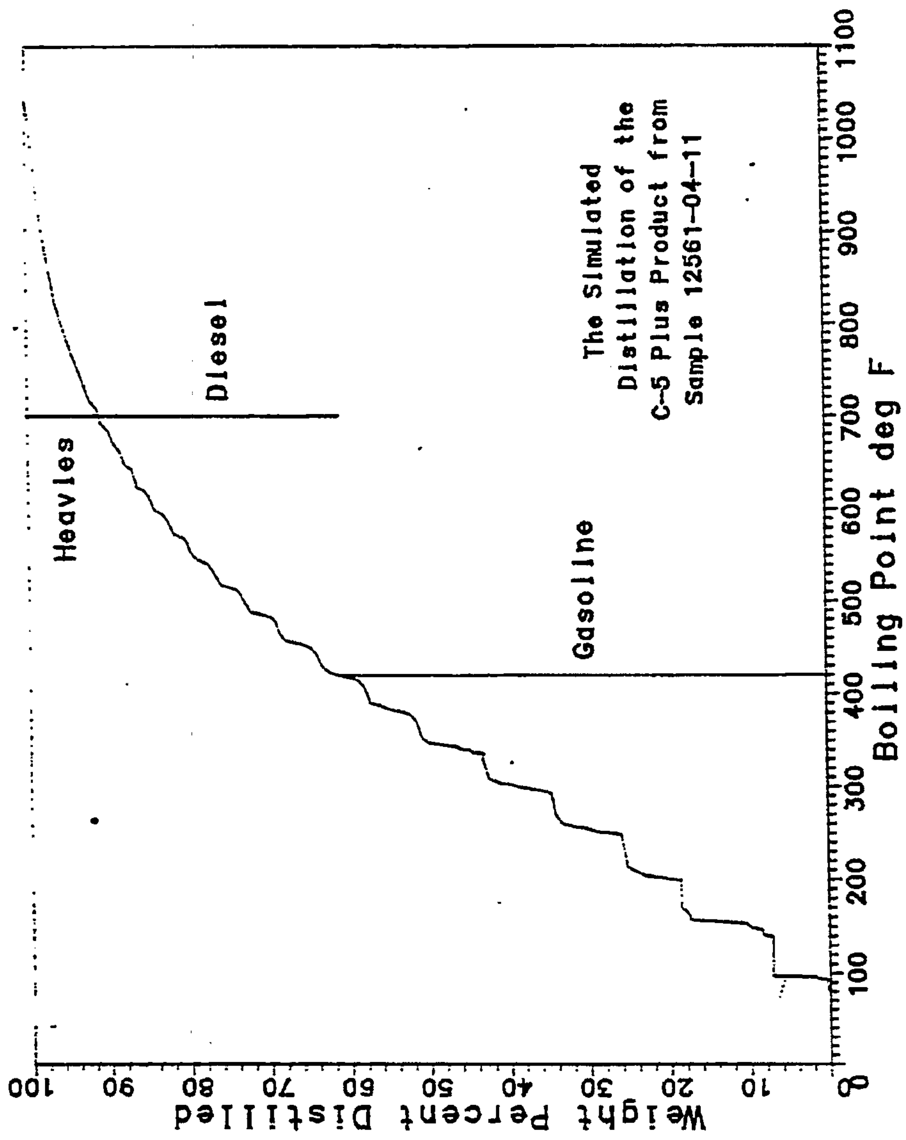
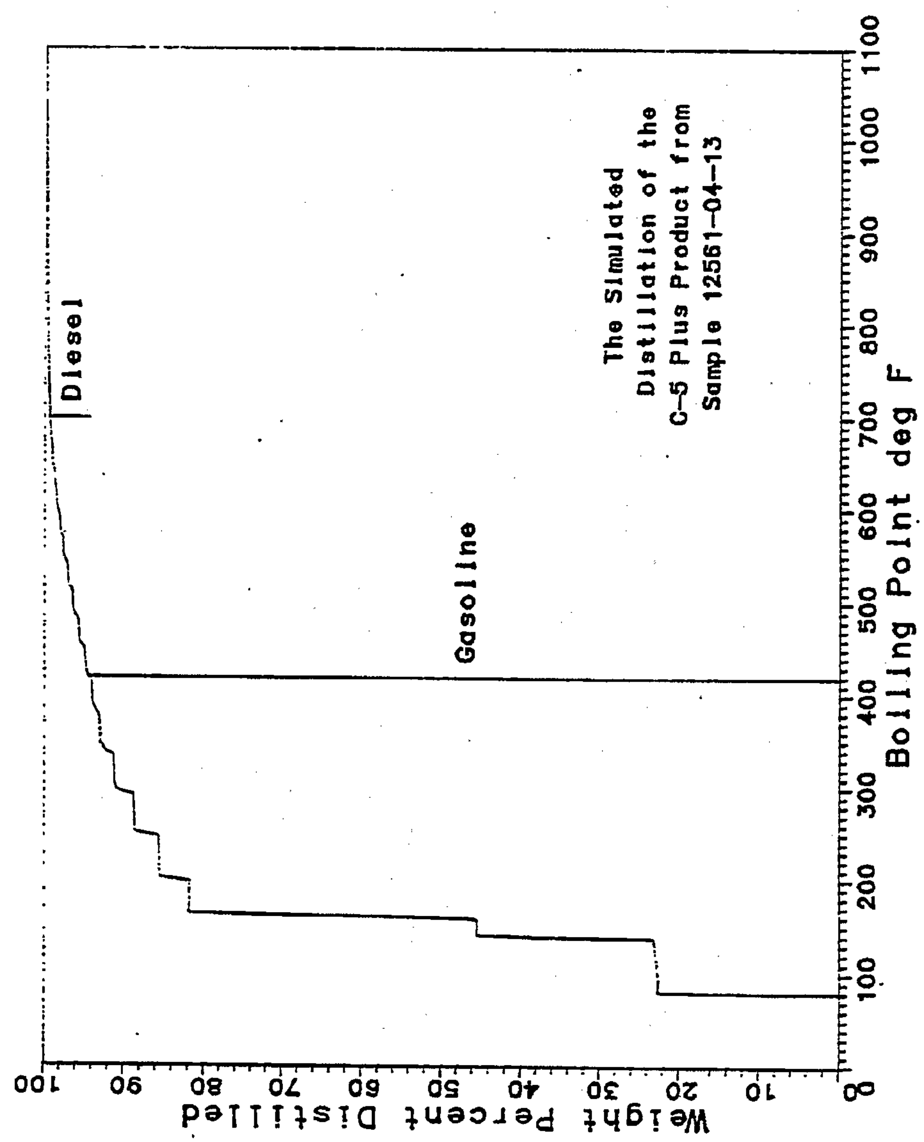

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-11
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100

Fig. B10



The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-04-13
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100

Fig. B11

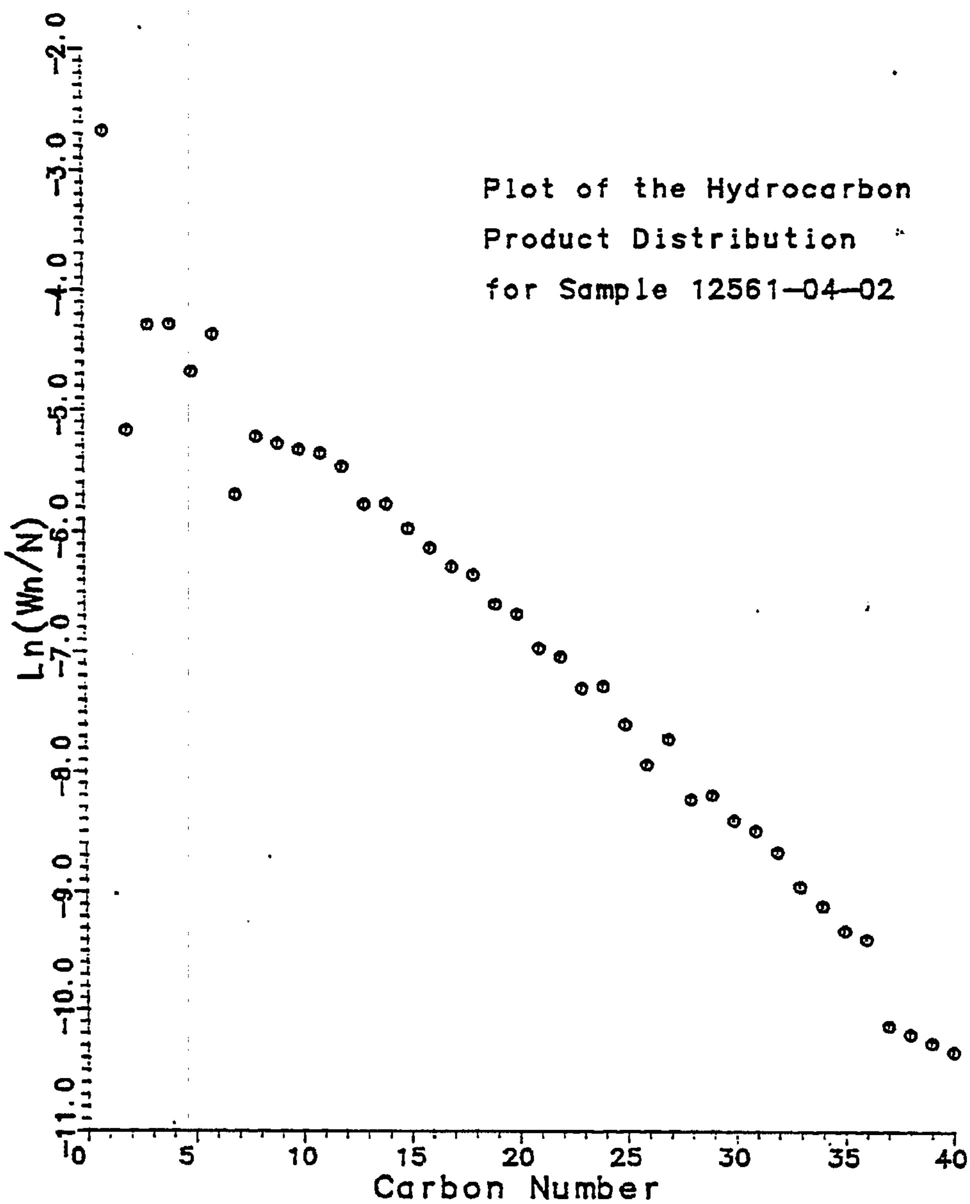
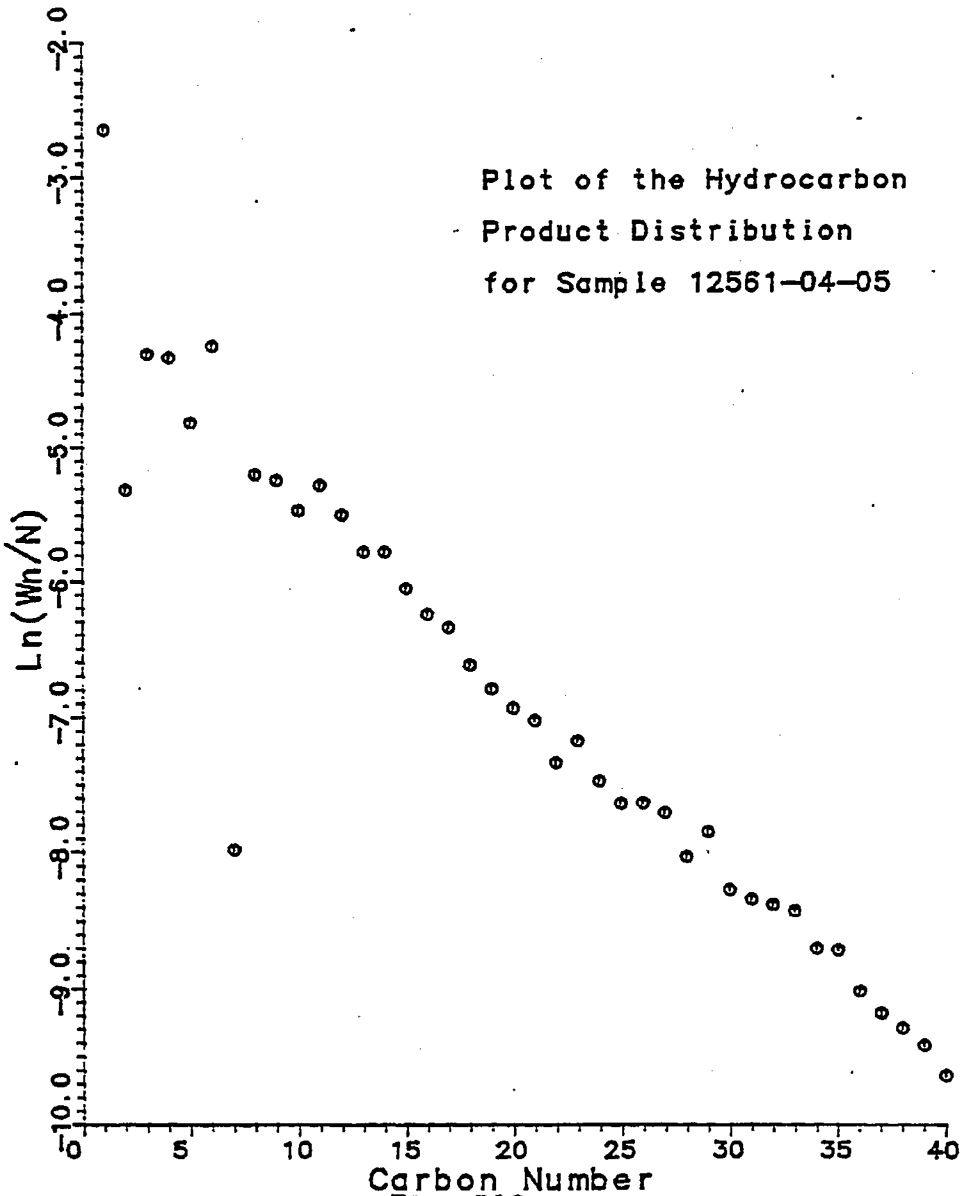

Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B12


Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-05
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B13

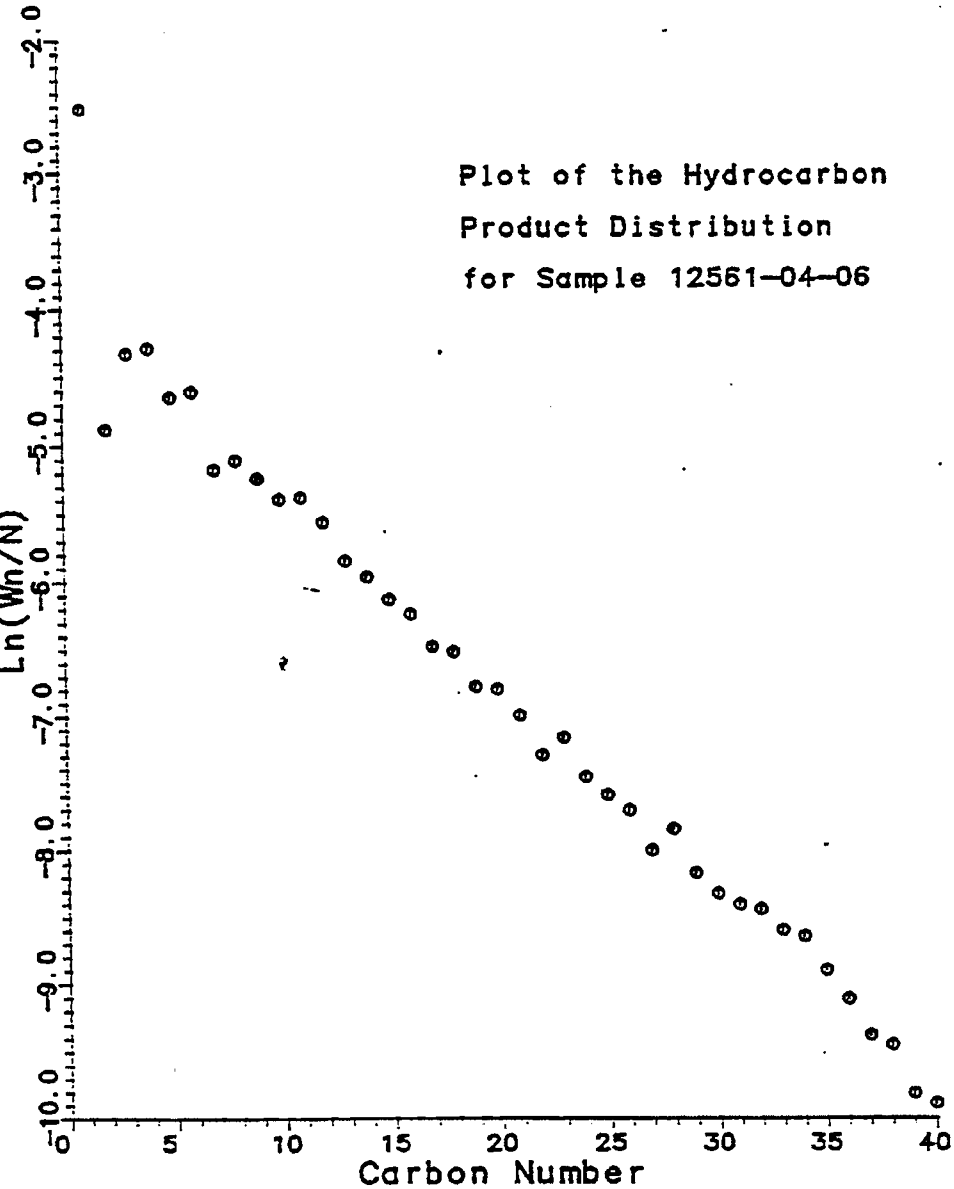

Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B14

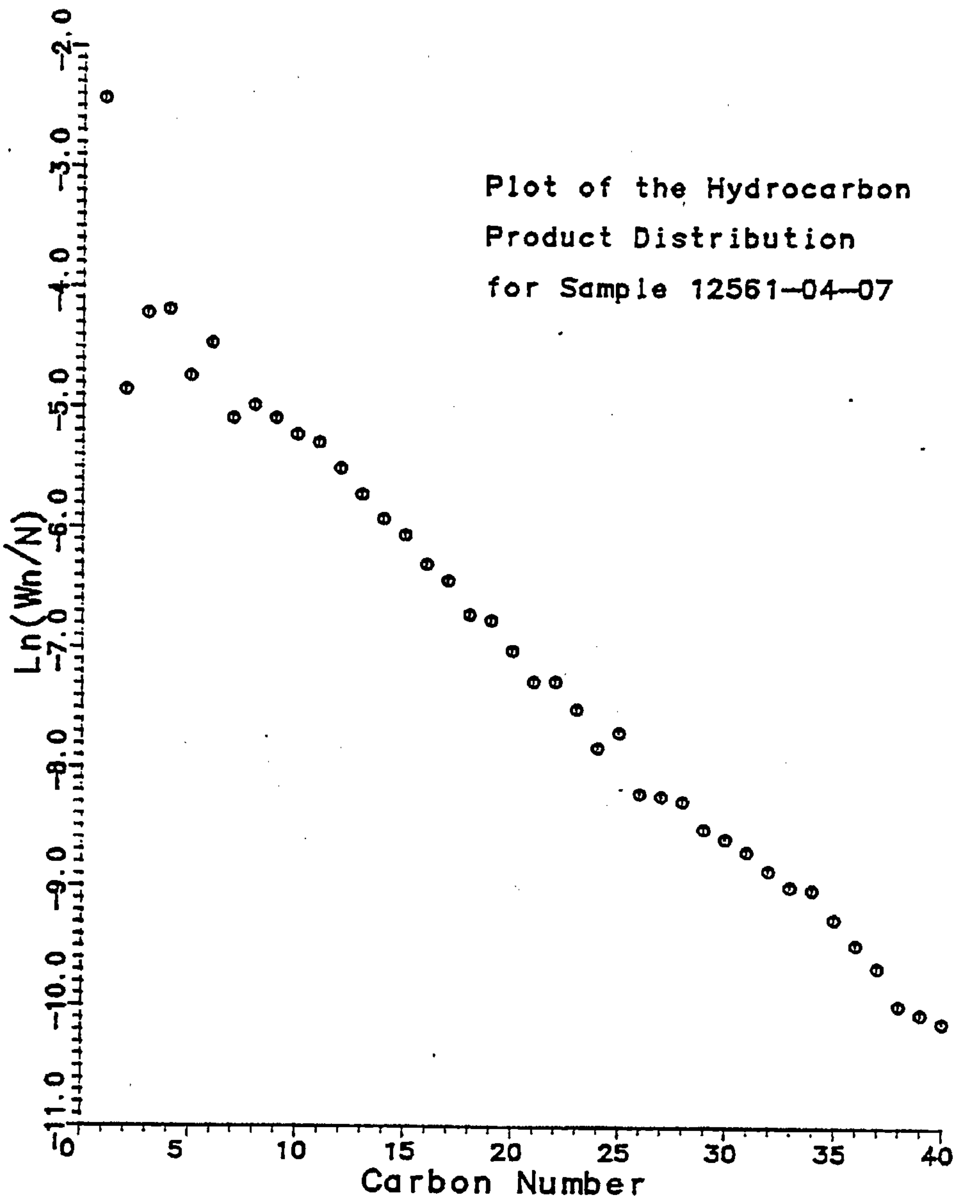
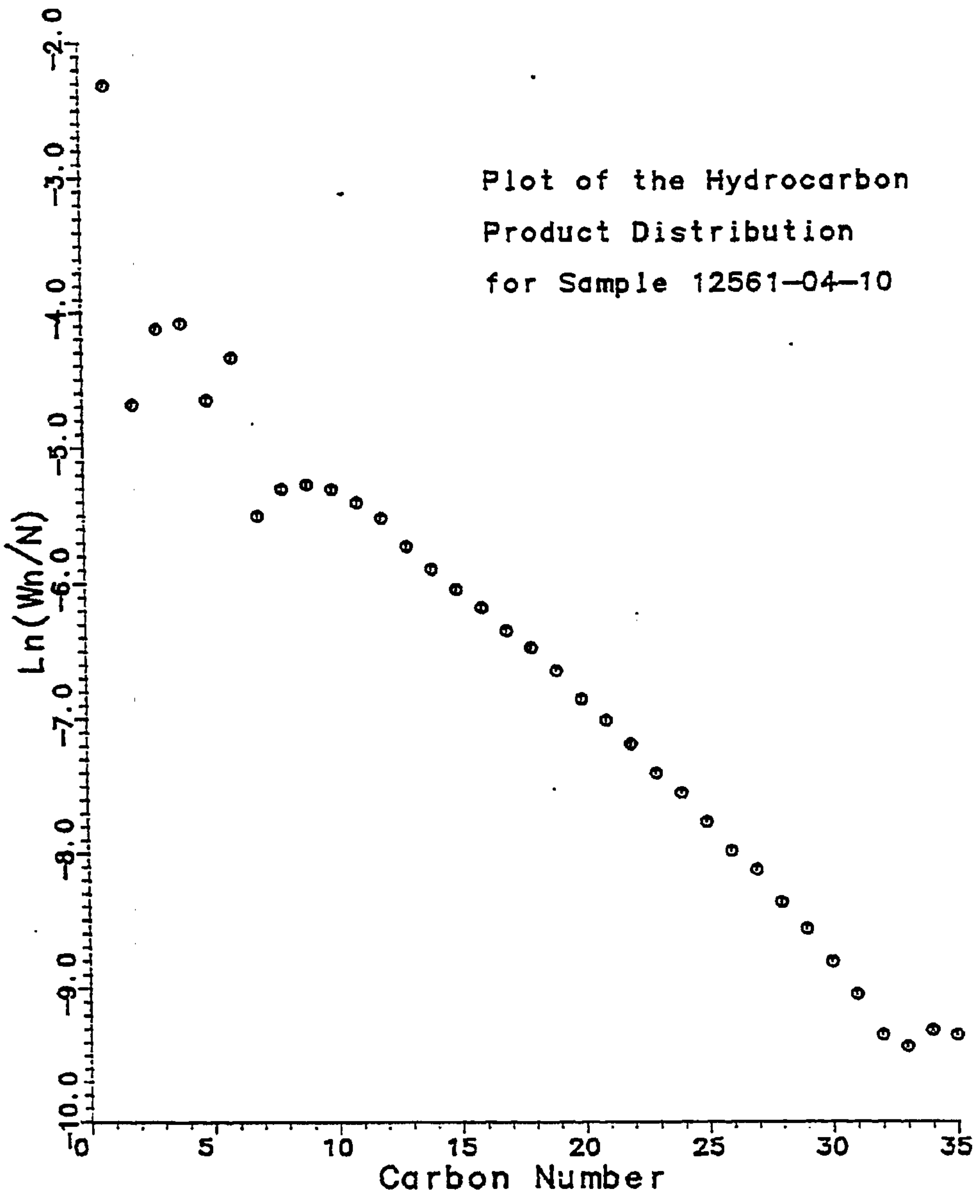
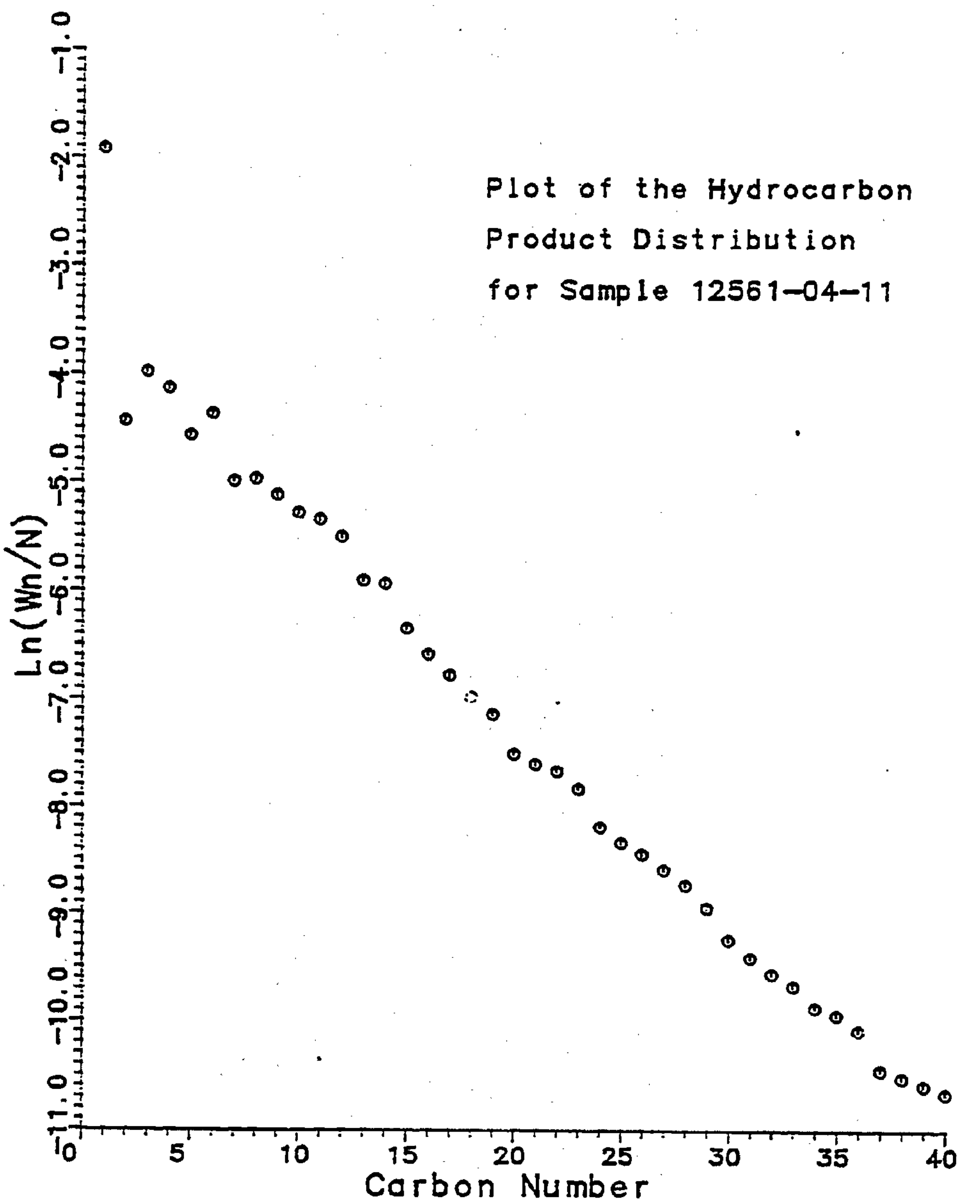

Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-07
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B15



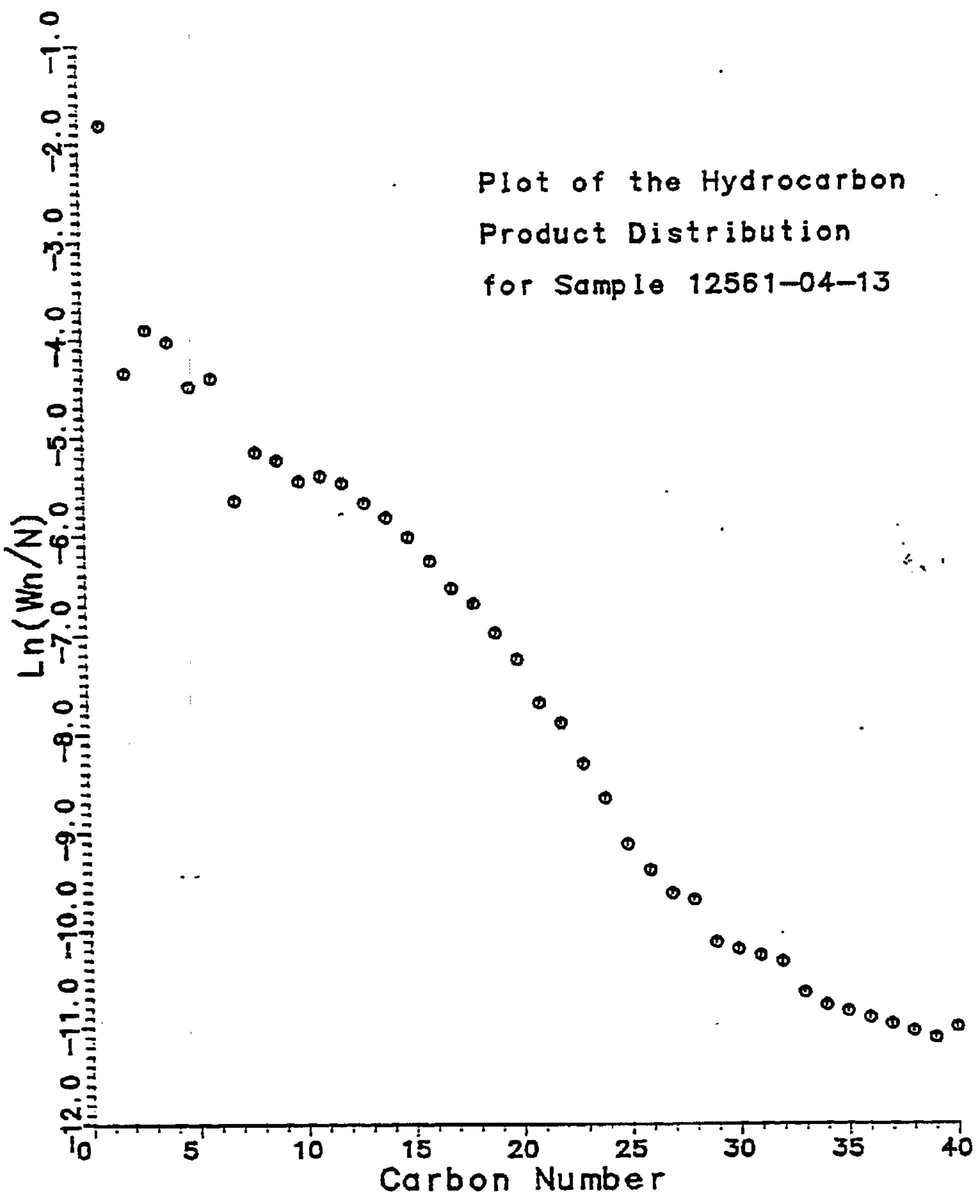
Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-10
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

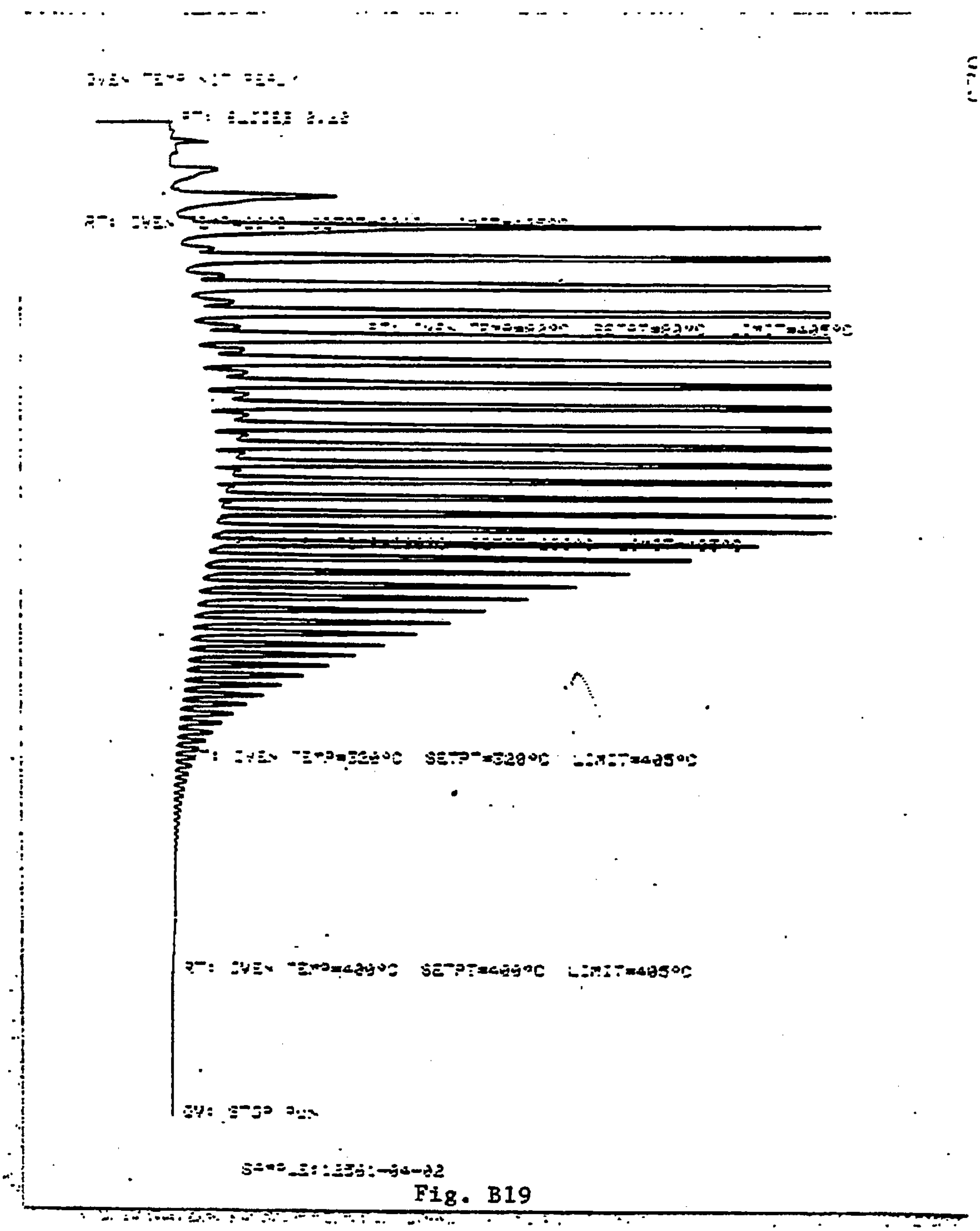
Fig. B16



Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-11
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B17


Plot of the Hydrocarbon
Product Distribution
for Sample 12561-04-13
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B18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OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B19

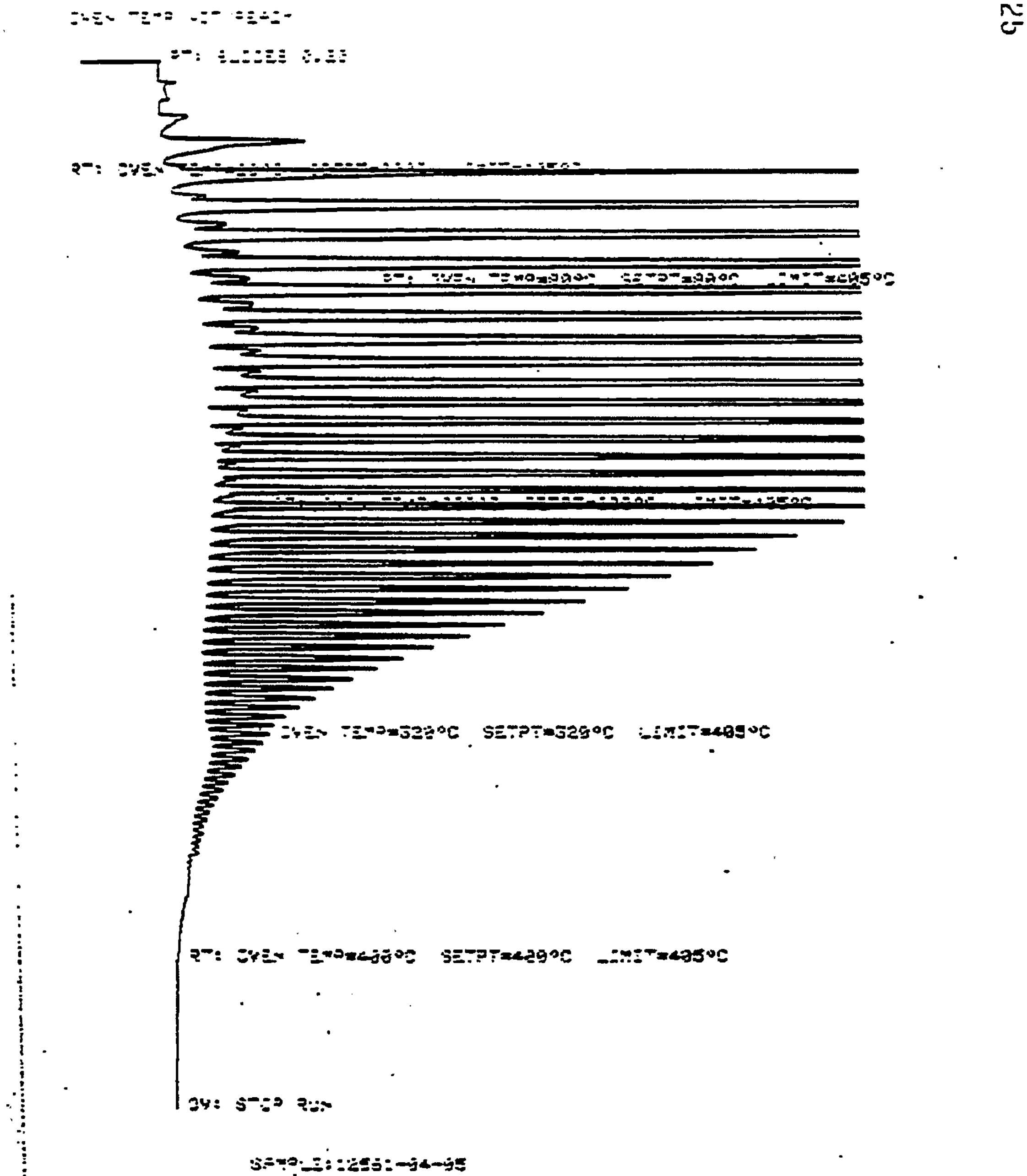


Fig. B20

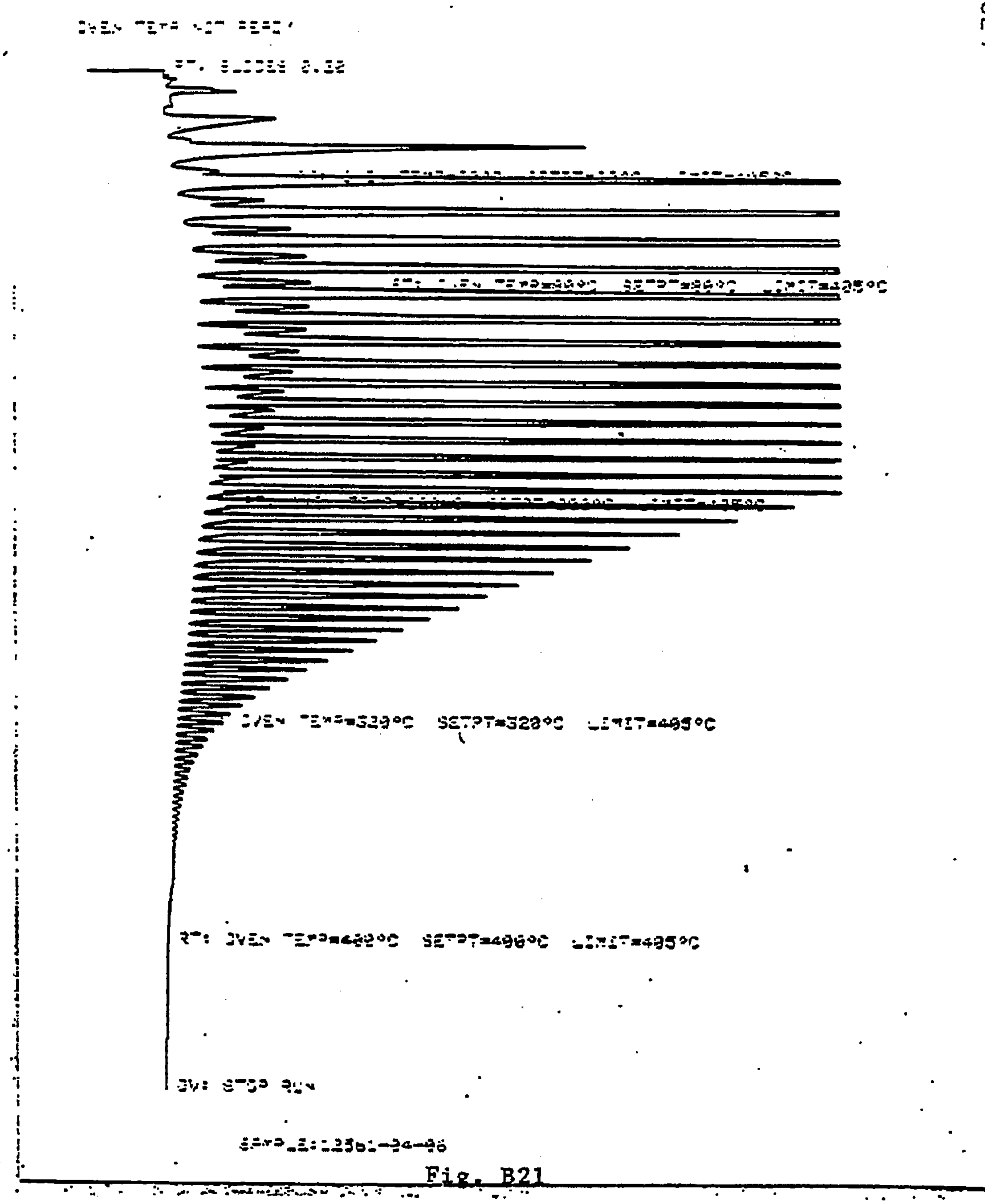


Fig. B21

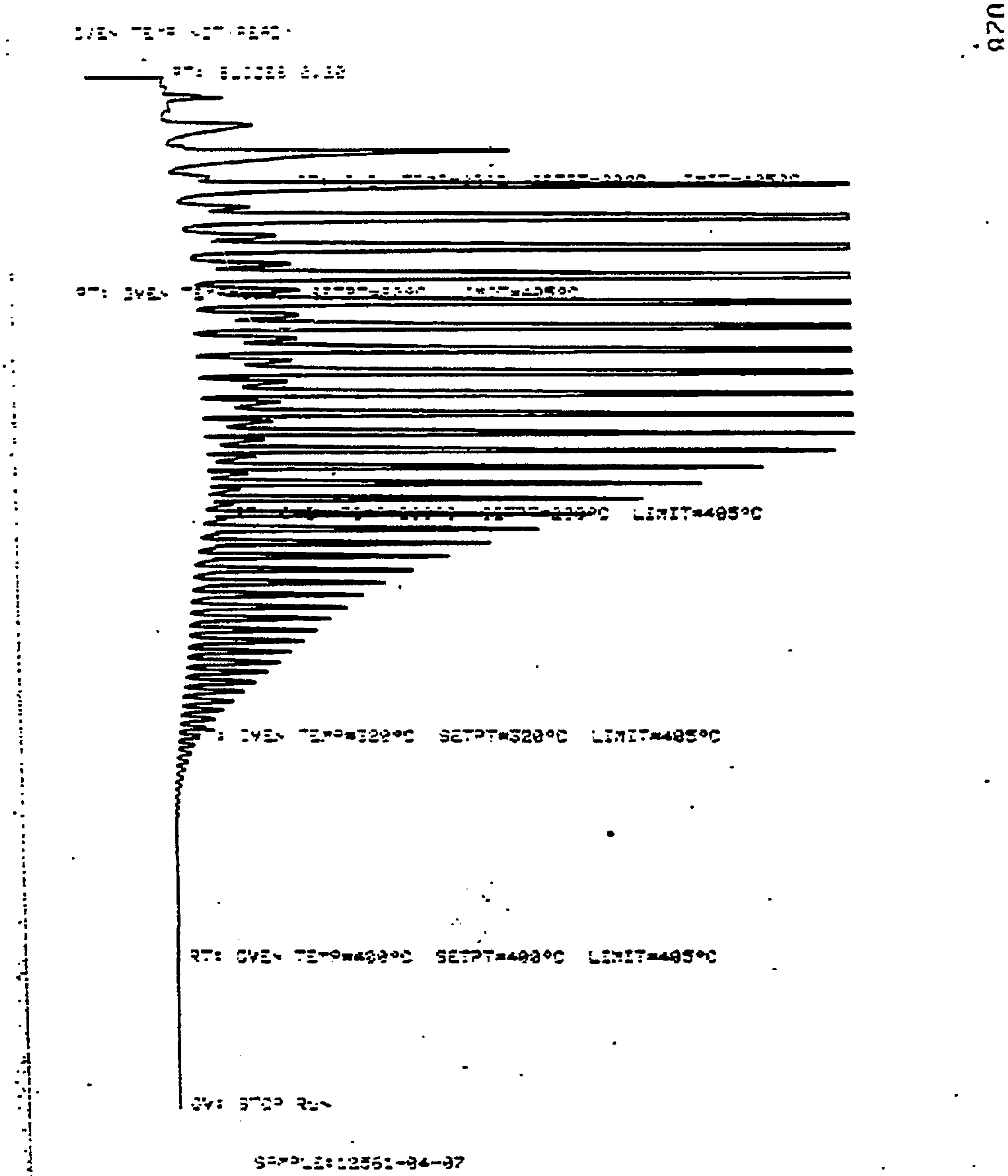


Fig. B22

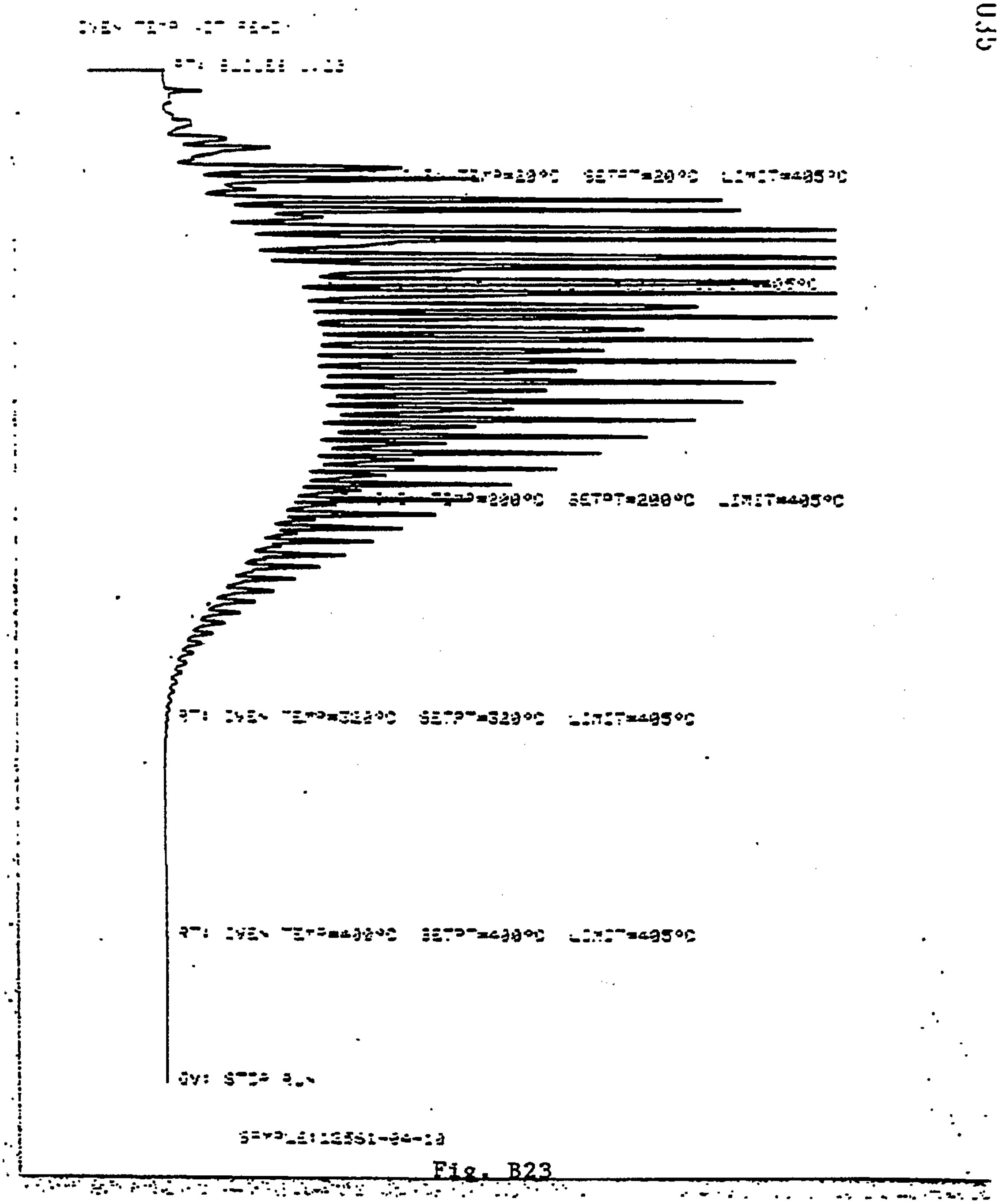


Fig. B23

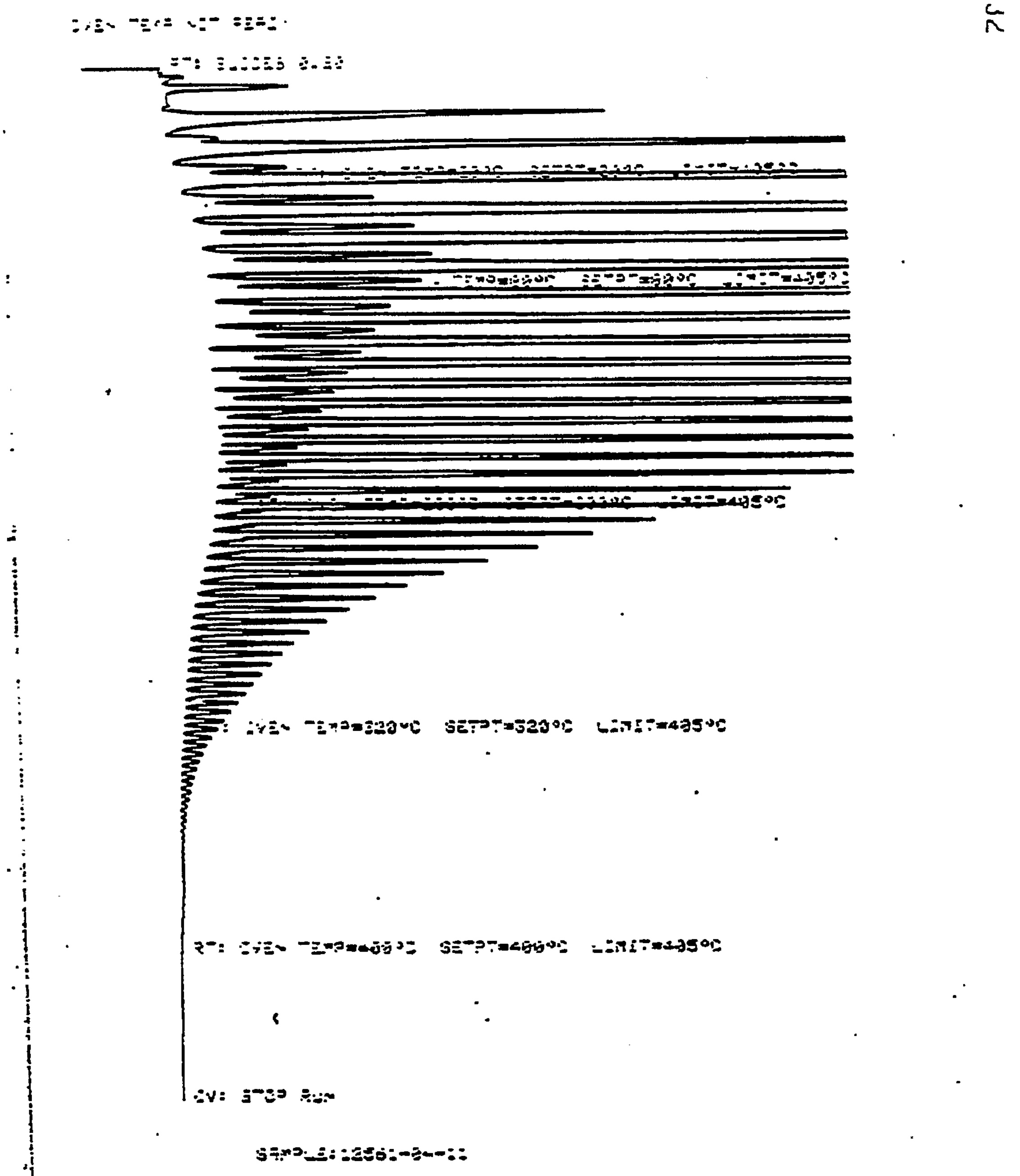


Fig. B24

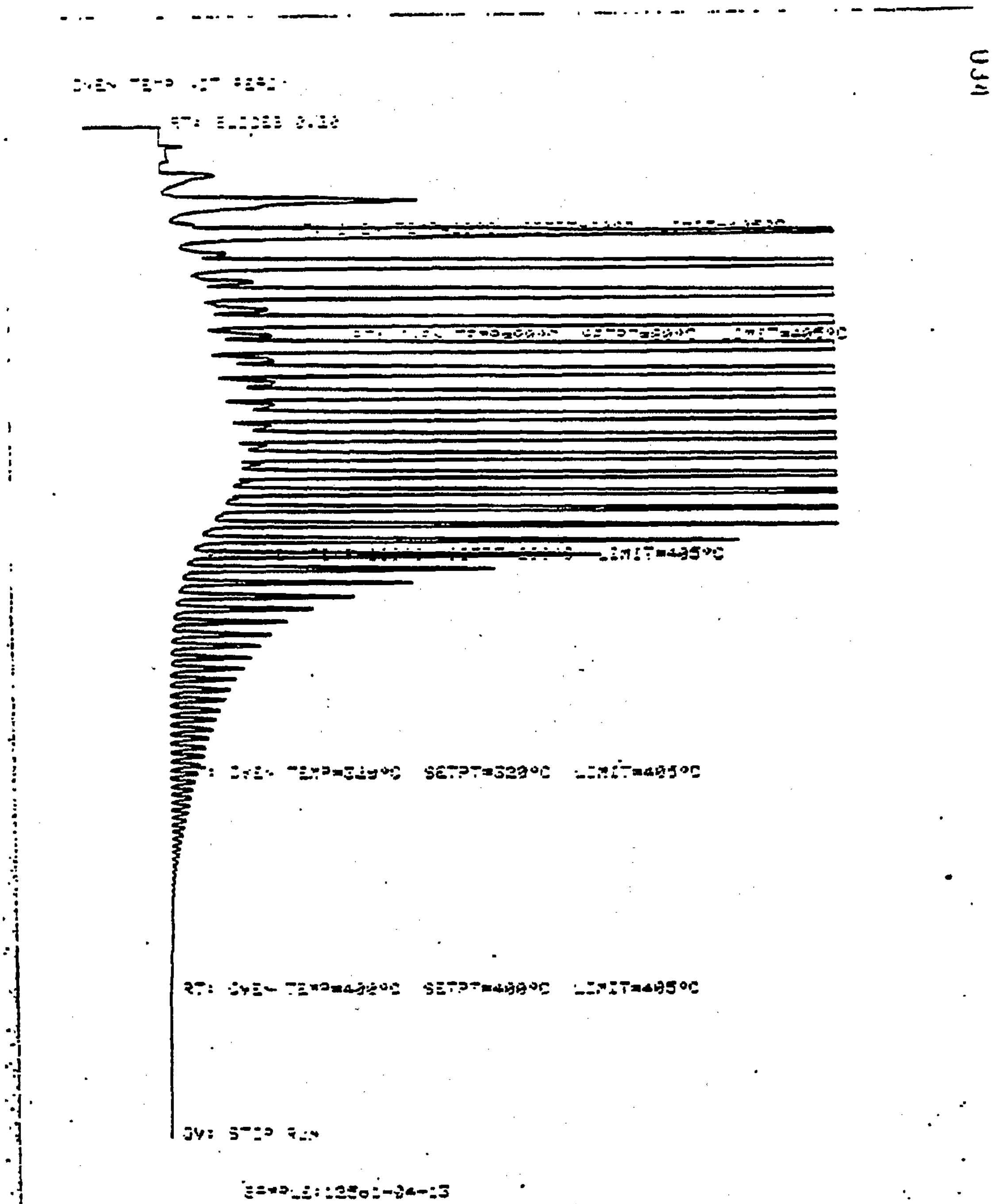


Fig. B25

Table B1

FILE: 1256104A T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12561-04
CATALYST CO/X11- AL2O3 80 CC 24.7 G AFTER USE:46.9 G (+22.2 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-31)

RUN & SAMPLE NO.	12561-04-01	561-04-02	561-04-03	561-04-04	561-04-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.00	66.00	90.00	114.00	138.00
PRESSURE,PSIG	297.00	304.00	304.00	302.00	301.00
TEMP. C	243.00	243.00	242.00	240.00	241.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	18.00	48.00	24.00	24.00	24.00
EFFLNT GAS LITER	178.80	603.40	329.15	334.55	338.50
GM AQUEOUS LAYER	53.42	122.23	58.19	50.64	51.72
GM OIL	15.54	62.25	24.19	33.49	31.95
MATERIAL BALANCE					
GM ATOM CARBON %	74.85	88.29	90.34	96.36	96.52
GM ATOM HYDROGEN %	82.71	102.33	99.67	103.93	103.98
GM ATOM OXYGEN %	89.87	91.16	96.21	92.70	94.16
RATIO CHX/(H2O+CO2)	0.5832	0.9092	0.8066	1.1375	1.0868
RATIO X IN CHX	2.2687	2.2663	2.3004	2.2533	2.2597
USAGE H2/CO PRODT	2.6584	2.1272	2.2638	1.9328	1.9757
FEED H2/CO FRM EFFLNT	1.1050	1.1589	1.1033	1.0785	1.0773
RESIDUAL H2/CO RATIO	0.4539	0.6684	0.6482	0.6713	0.6664
RATIO CO2/(H2O+CO2)	0.0304	0.0307	0.0312	0.0283	0.0271
K SHIFT IN EFFLNT	0.0142	0.0212	0.0209	0.0196	0.0186
SPECIFIC ACTIVITY SA	4.9684	3.2784	2.9323	3.6769	3.4753
CONVERSION					
ON CO %	29.53	33.63	28.17	32.28	31.38
ON H2 %	71.05	61.72	57.80	57.85	57.56
ON CO+H2 %	51.33	48.71	43.71	45.55	44.96
PRDT SELECTIVITY,WT %					
CH4	7.80	6.90	8.80	6.73	7.12
C2 HC'S	1.02	1.14	1.52	1.02	0.99
C3H8	1.74	1.82	2.29	1.72	1.80
C3H6=	3.45	2.31	2.89	2.26	2.31
C4H10	2.18	1.99	2.48	1.91	1.95
C4H8=	4.92	3.55	4.29	3.29	3.37
C5H12	2.81	2.57	3.19	2.39	2.49
C5H10=	3.42	2.09	1.99	1.55	1.58
C6H14	4.42	6.19	4.96	3.69	3.78
C6H12= & CYCLO'S	2.64	1.46	2.33	4.74	4.91
C7+ IN GAS	7.41	6.00	7.12	5.50	5.87
LIQ HC'S	58.20	63.97	58.14	65.19	63.84
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	21.11	17.72	22.28	16.93	17.53
C5 -420 F		38.14			36.50
420-700 F		31.79			28.66
700-END PT		12.35			17.30

Table B1 (continued)

FILE: 1256104A T6Q1 A1

C5+-END PT	78.89	82.28	77.72	83.07	82.47
ISO/NORMAL MOLE RATIO					
C4	0.0206	0.0148	0.0160	0.0171	0.0000
C5	0.0375	0.0350	0.0320	0.0285	0.0301
C6	0.1974	0.8804	0.2270	0.1953	0.1919
C4=	0.0427	0.0513	0.0468	0.0459	0.0466
PARAFFIN/OLEFIN RATIO					
C3	0.4819	0.7511	0.7572	0.7241	0.7417
C4	0.4270	0.5422	0.5581	0.5603	0.5581
C5	0.7973	1.1936	1.5597	1.5042	1.5333
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8564			0.8565
RATIO CH4/(1-A)**2		3.3480			3.4576
ALPHA FRM CORRELATION		0.8314			0.8317
ALPHA (EXPTL/CORR)		1.0301			1.0299
W%CH4 FRM CORRELATION		16.4259			15.8938
W%CH4 (EXPTL/CORR)		0.4204			0.4477
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F		303.00			337.00
16		343.00			367.00
50		517.00			541.00
84		728.00			801.00
90		784.00			875.00
RANGE(16-84 %)		385.00			434.00
WT % @ 420 F		31.00			28.00
WT % @ 700 F		80.70			72.90

Table B2

FILE: 1256104B T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12561-04
CATALYST CO/X11- AL203 80 CC 24.7 G AFTER USE:46.9 G (+22.2 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-31)

RUN & SAMPLE NO.	12561-04-06	561-04-07	561-04-08	561-04-09	561-04-10
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	162.00	186.00	210.00	234.00	258.00
PRESSURE,PSIG	299.00	303.00	299.00	299.00	300.00
TEMP. C	261.00	261.00	261.00	261.00	261.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	24.00	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	236.50	256.00	260.37	267.23	277.90
GM AQUEOUS LAYER	61.81	70.61	70.74	70.35	67.08
GM OIL	43.28	40.16	38.91	37.06	36.29
MATERIAL BALANCE					
GM ATOM CARBON %	91.63	95.94	96.75	97.21	99.32
GM ATOM HYDROGEN %	98.39	103.20	103.44	106.33	104.25
GM ATOM OXYGEN %	85.75	94.81	95.82	95.42	97.09
RATIO CHX/(H2O+CO2)	1.1748	1.0301	1.0249	1.0477	1.0620
RATIO X IN CHX	2.2823	2.2988	2.3078	2.3082	2.3232
USAGE H2/CO PRODT	1.7723	1.9060	1.9206	1.9043	1.9008
FEED H2/CO FRM EFFLNT	1.0738	1.0757	1.0691	1.0938	1.0496
RESIDUAL H2/CO RATIO	0.4651	0.4399	0.4348	0.4766	0.4561
RATIO CO2/(H2O+CO2)	0.0933	0.0759	0.0733	0.0737	0.0741
K SHIFT IN EFFLNT	0.0478	0.0361	0.0344	0.0379	0.0365
SPECIFIC ACTIVITY SA	3.3701	3.2338	3.2454	2.7868	2.8822
CONVERSION					
ON CO %	46.57	43.36	42.69	43.23	41.08
ON H2 %	76.86	76.84	76.69	75.26	74.40
ON CO+H2 %	62.25	60.71	60.26	59.97	58.15
PRDT SELECTIVITY,WT %					
CH4	8.06	8.80	9.26	9.45	9.97
C2 HC'S	1.53	1.56	1.72	1.74	1.87
C3H8	1.93	2.12	2.24	2.29	2.43
C3H6=	2.03	2.32	2.42	2.25	2.47
C4H10	1.87	2.11	2.23	2.26	2.41
C4H8=	3.63	3.99	4.25	4.07	4.40
C5H12	2.44	2.82	2.95	2.91	3.15
C5H10=	2.37	1.57	1.63	1.51	1.65
C6H14	3.76	4.48	4.42	4.83	5.14
C6H12= & CYCLO'S	2.17	2.47	2.64	6.04	2.72
C7+ IN GAS	5.66	6.74	6.83	7.10	7.86
LIQ HC'S	64.55	61.04	59.41	55.55	55.94
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	19.05	20.89	22.12	22.07	23.54
C5 -420 F	38.35	42.18			38.99
420-700 F	27.69	26.80			29.14
700-END PT	14.91	10.13			8.33

Table B2 (continued)

FILE: 1256104B T6Q1 A1

C5+-END PT	80.95	79.11	77.88	77.93	76.46
ISO/NORMAL MOLE RATIO					
C4	0.0178	0.0182	0.0197	0.0188	0.0192
C5	0.0508	0.0507	0.0503	0.0514	0.0494
C6	0.3494	0.3846	0.3122	0.3982	0.4065
C4=	0.0626	0.0595	0.0604	0.0623	0.0604
PARAFFIN/OLEFIN RATIO					
C3	0.9062	0.8706	0.8843	0.9722	0.9369
C4	0.4967	0.5118	0.5062	0.5355	0.5282
C5	0.9975	1.7482	1.7567	1.8676	1.8548
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8599	0.8415			0.8458
RATIO CH4/(1-A)**2	4.1049	3.5016			4.1918
ALPHA FRM CORRELATION	0.8480	0.8507			0.8490
ALPHA (EXPTL/CORR)	1.0139	0.9892			0.9962
W%CH4 FRM CORRELATION	15.1660	14.3262			14.8707
W%CH4 (EXPTL/CORR)	0.5316	0.6139			C.6706
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	295.00	289.00			308.00
16	336.00	304.00			341.00
50	515.00	480.00			501.00
84	764.00	707.00			690.00
90	833.00	780.00			743.00
RANGE(16-84 %)	428.00	403.00			349.00
WT % @ 420 F	34.00	39.50			33.00
WT % @ 700 F	76.90	83.40			85.10

Table B3

FILE: 1256104C T5Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12561-04
CATALYST CO/X11- AL2O3 80 CC 24.7 G AFTER USE:46.9 G (+22.2 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-31)

RUN & SAMPLE NO.	12561-04-11	561-04-12	561-04-13
FEED H2:CO:AR	60:40: 0	60:40: 0	60:40: 0
HRS ON STREAM	283.50	307.00	331.00
PRESSURE,PSIG	500.00	500.00	500.00
TEMP. C	260.00	260.00	260.00
FEED CC/MIN	400.00	400.00	400.00
HOURS FEEDING	25.50	23.50	24.00
EFFLNT GAS LITER	170.30	195.70	214.80
GM AQUEOUS LAYER	85.64	81.10	85.22
GM OIL	34.33	32.80	32.30
MATERIAL BALANCE			
GM ATOM CARBON %	76.68	88.72	91.75
GM ATOM HYDROGEN %	87.29	97.27	101.73
GM ATOM OXYGEN %	83.10	92.23	95.74
RATIO CHX/(H2O+CO2)	0.8762	0.9342	0.9272
RATIO X IN CHX	2.4360	2.4527	2.4712
USAGE H2/CO PRODT	2.1267	2.0954	2.1181
FEED H2/CO FRM EFFLNT	1.7076	1.6446	1.6632
RESIDUAL H2/CO RATIO	0.9717	0.9720	1.0105
RATIO CO2/(H2O+CO2)	0.0652	0.0608	0.0583
K SHIFT IN EFFLNT	0.0677	0.0629	0.0625
SPECIFIC ACTIVITY SA	1.1869	1.0335	0.9568
CONVERSION			
ON CO %	63.71	59.87	58.93
ON H2 %	79.35	76.28	75.05
ON CO+H2 %	73.58	70.08	69.00
PRDT SELECTIVITY,WT %			
CH4	14.77	15.60	16.48
C2 HC'S	2.39	2.58	2.61
C3H8	4.24	4.33	4.63
C3H6=	1.41	1.58	1.51
C4H10	3.59	3.71	4.00
C4H8=	2.88	3.08	3.18
C5H12	4.29	4.35	4.73
C5H10=	0.92	1.30	0.93
C6H14	5.51	5.95	5.96
C6H12= & CYCLO'S	1.59	1.58	1.42
C7+ IN GAS	6.61	7.02	8.36
LIQ HC'S	51.81	48.92	46.18
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	29.27	30.89	32.41
C5 -420 F	43.27		43.11
420-700 F	21.03		18.80
700-END PT	6.42		5.68

Table B3 (continued)

FILE: 1256104C T6Q1 A1

C5+-END PT	70.73	69.11	67.59
ISO/NORMAL MOLE RATIO			
C4	0.0246	0.0288	0.0268
C5	0.0555	0.0529	0.0510
C6	0.1928	0.2431	0.1772
C4=	0.0891	0.0875	0.0918
PARAFFIN/OLEFIN RATIO			
C3	2.8614	2.6134	2.9143
C4	1.2043	1.1625	1.2146
C5	4.5293	3.2573	4.9513
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))	0.8195		0.7931
RATIO CH4/(1-A)**2	4.5360		3.8478
ALPHA FRM CORRELATION	0.8122		0.8103
ALPHA (EXPTL/CCRR)	1.0091		0.9787
W%CH4 FRM CORRELATION	26.0773		26.6678
W%CH4 (EXPTL/CORR)	0.5665		0.6179
LIQ HC COLLECTION			
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F	256.00		301.00
16	297.00		340.00
50	428.00		457.00
84	660.00		618.00
90	729.00		665.00
RANGE(16-84 %)	363.00		278.00
WT % @ 420 F	47.00		38.50
WT % @ 700 F	87.60		93.30

III. Run 50 (11617-08) with Catalyst 50 ($Co/X_{11}/TC-121$

The purpose of this run was to test the new Molecular Sieve TC-121 as the catalyst support. The catalyst was formulated in the same way as the X_{11} promoted, TC-123 supported Catalyst 45 of the Sixth Quarterly Report, with which it is to be compared. The theoretical content of cobalt and X_{11} was 8.2 and 1.6 percent respectively.

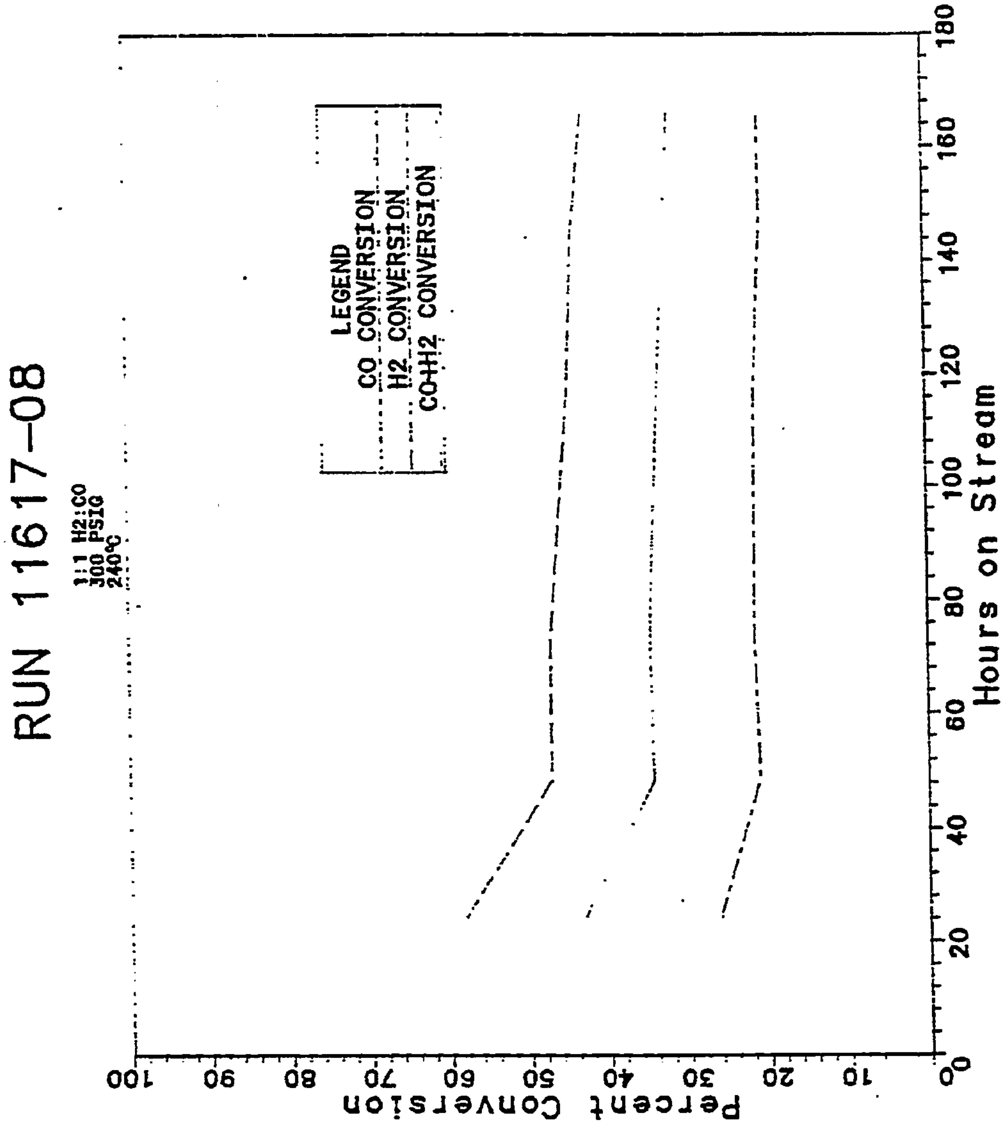
Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B26-29. Simulated distillations of the C_5^+ product are plotted in Figs. B30-33. Carbon number product distributions are plotted in Figs. B34-37. Chromatograms from simulated distillations are reproduced in Figs. B38-41. Detailed material balances appear in Tables B4-5.

The performance of this catalyst was significantly poorer than that of Catalyst 45. Its syngas conversion, after good material balances were obtained, was about 34 percent as against about 47 percent with Catalyst 45 under similar conditions. Product selectivity was also poorer with about 10 percent methane and 77 percent C_5^+ as against about 4 and 90 percent respectively with Catalyst 45. The poorer selectivity may be due in part to the elevated H_2:CO ratio in the Berty reactor resulting from the lower activity.

The stability of this catalyst was difficult to determine due to the shortness of the test, but there was a significant decrease in syngas conversion over the test period.

Only in its isomerization activity did this catalyst outperform Catalyst 45. After about 115 hours on stream the iso:normal ratios of its C_5's and C_6's were 0.11:1 and 0.57:1 respectively, as against 0.04:1 and 0.24:1 respectively for Catalyst 45. The Schulz-Flory plots were linear except for the usual excess of methane.

The Molecular Sieve TC-121 proved inferior to TC-123 as a catalyst support with one exception, its higher isomerization activity.



RUN 11617-08
1:1 H2:CO
300 PSIG
240°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
120
140
160
180

Fig. B26

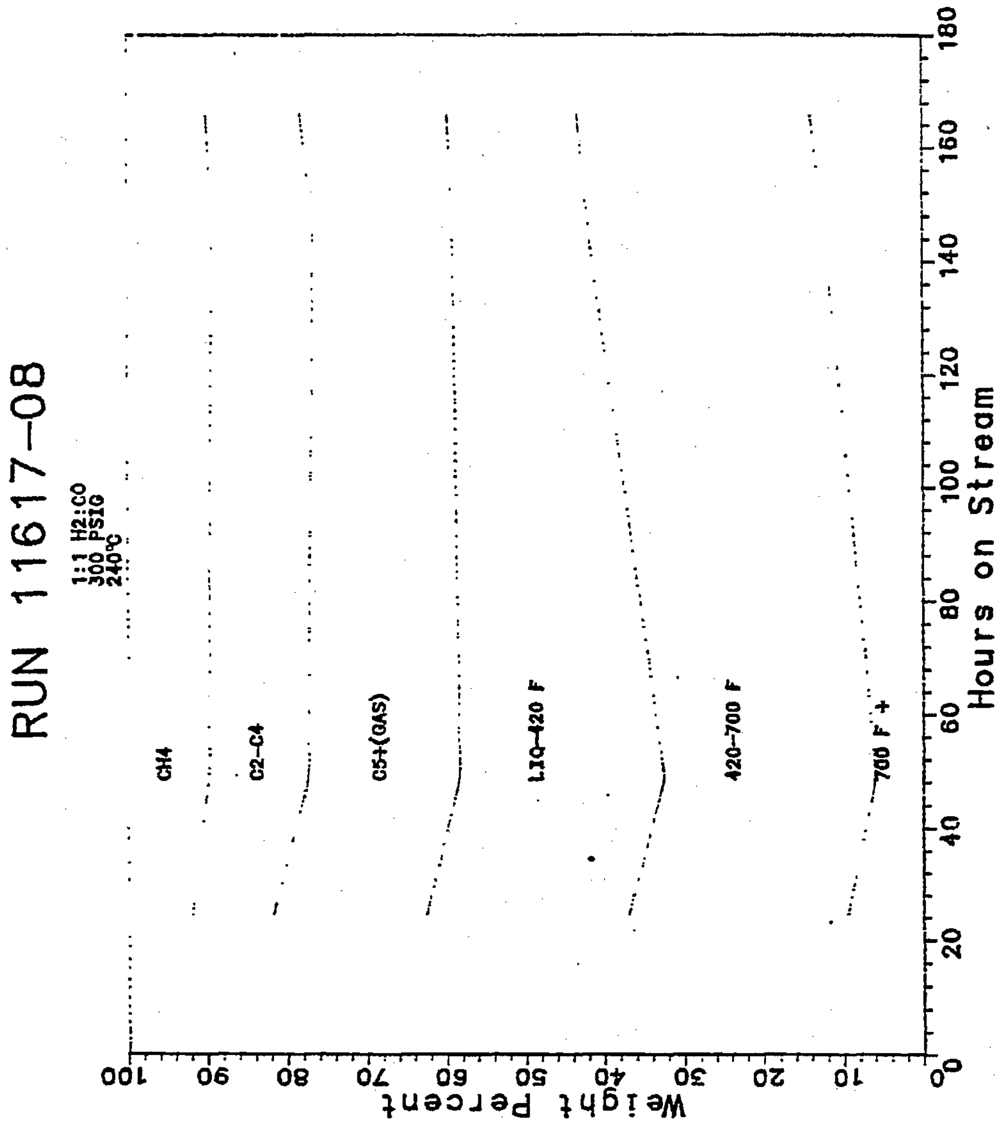

RUN 11617-08
1:1 H2:CO
300 PSIG
240°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. B27

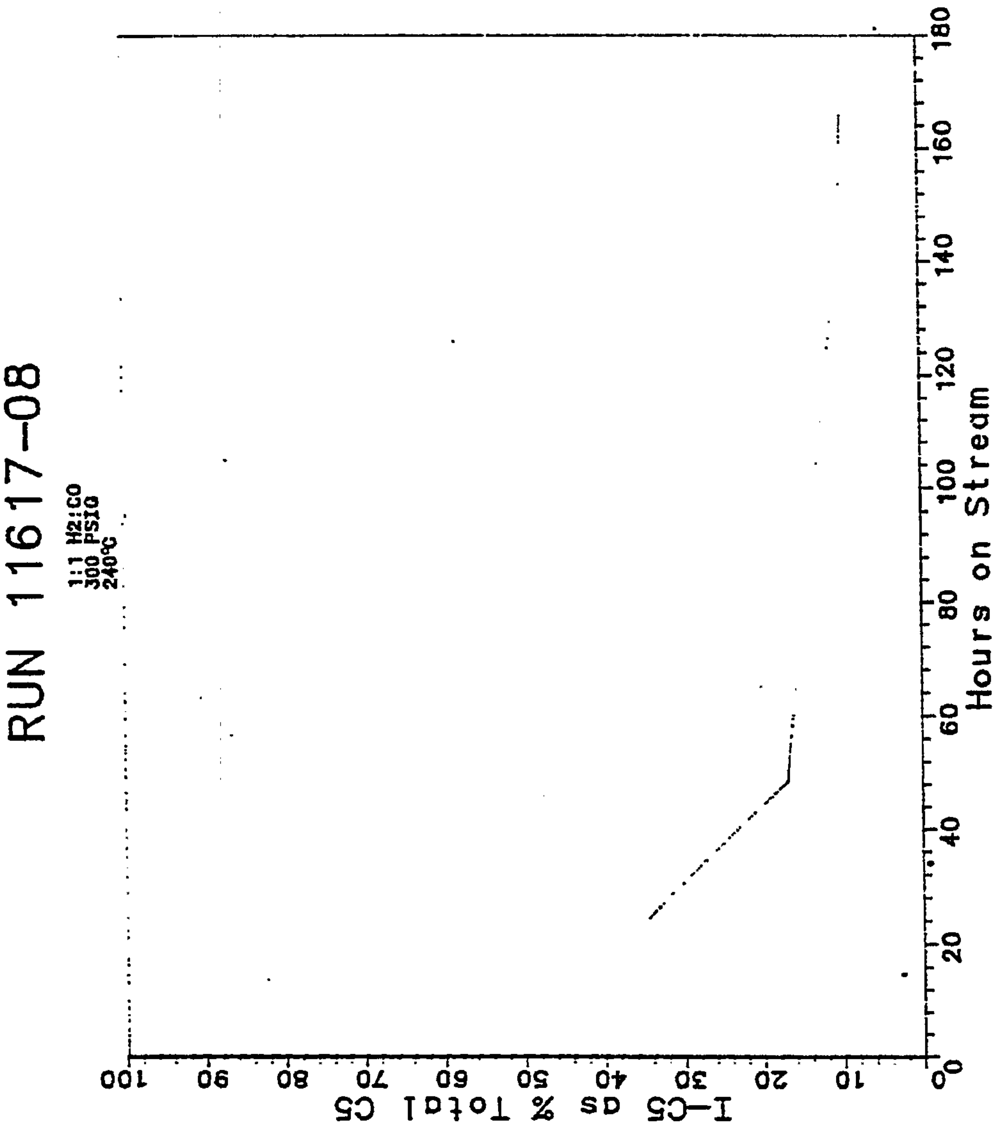

RUN 11617-08
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
I-C5 as % Total C5

Fig. B28

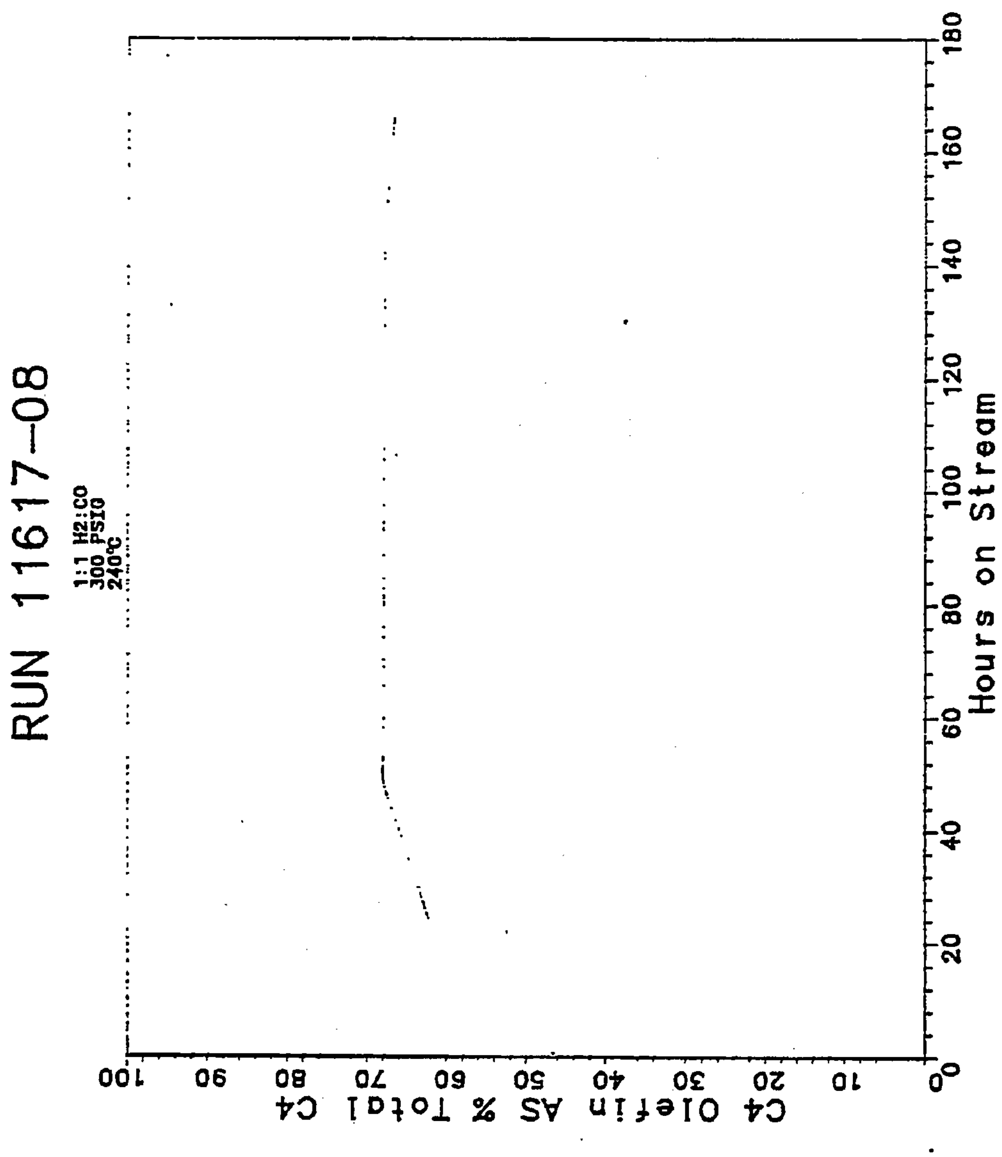

RUN 11617-08
1:1 H2:CO
300 PSIG
240°C
Hours on Stream
C4 Olefin AS % Total C4

Fig. B29

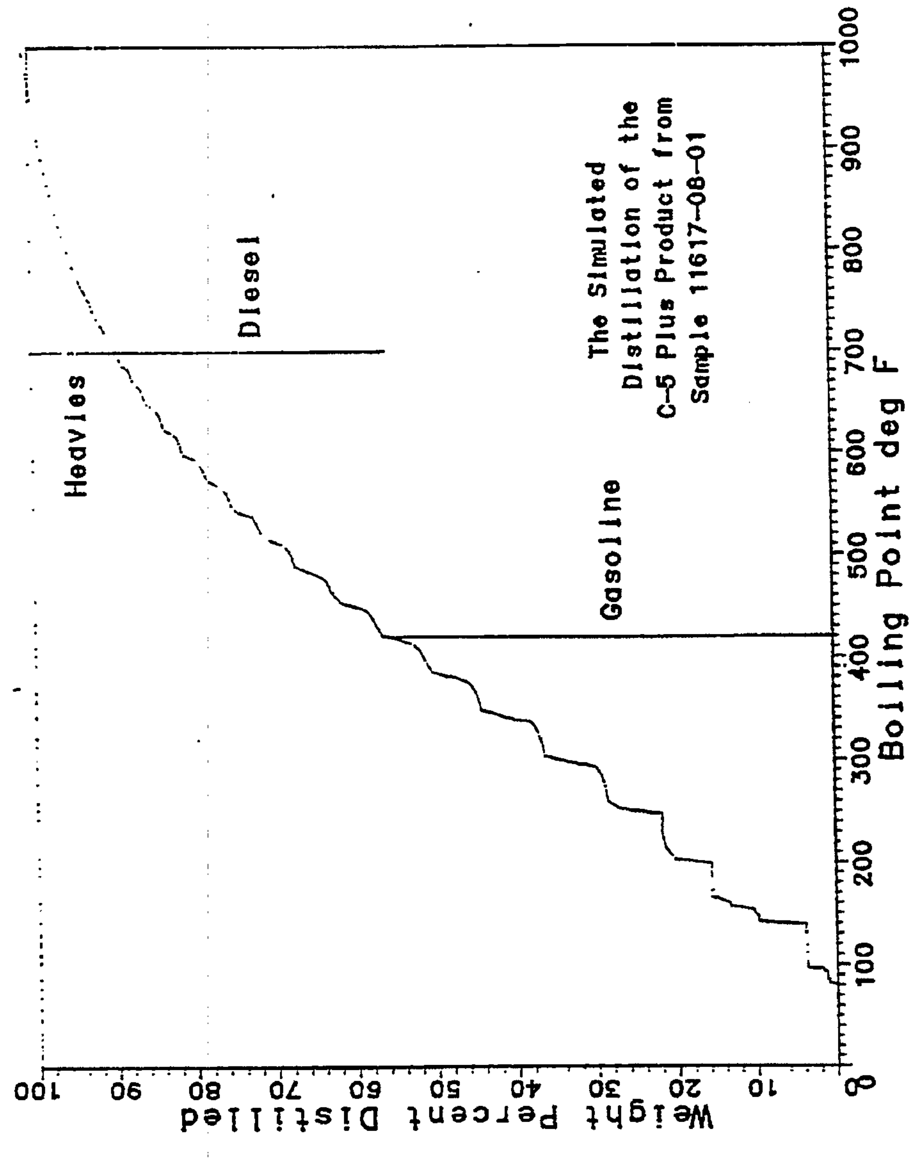

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-08-01
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B30

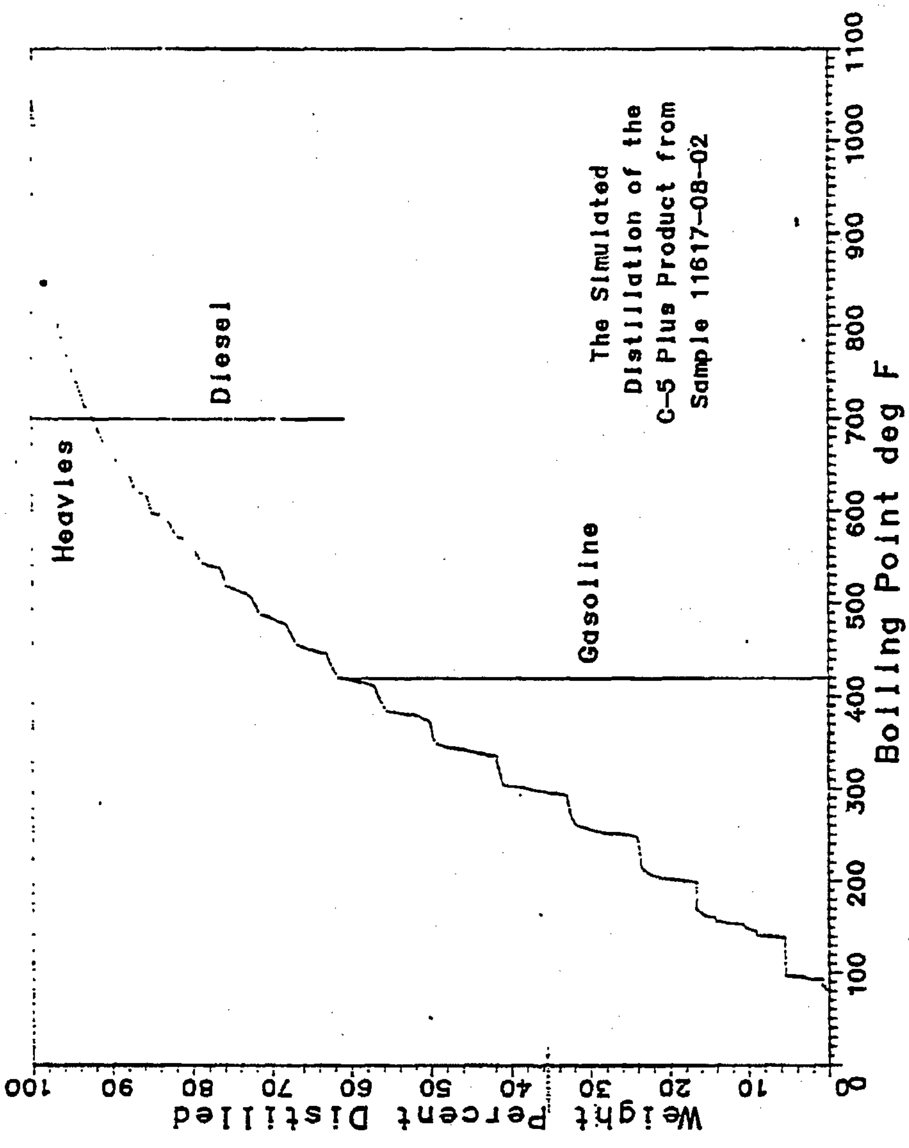

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-08-02
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
1100
10
20
30
40
50
60
70
80
90
100

Fig. B31

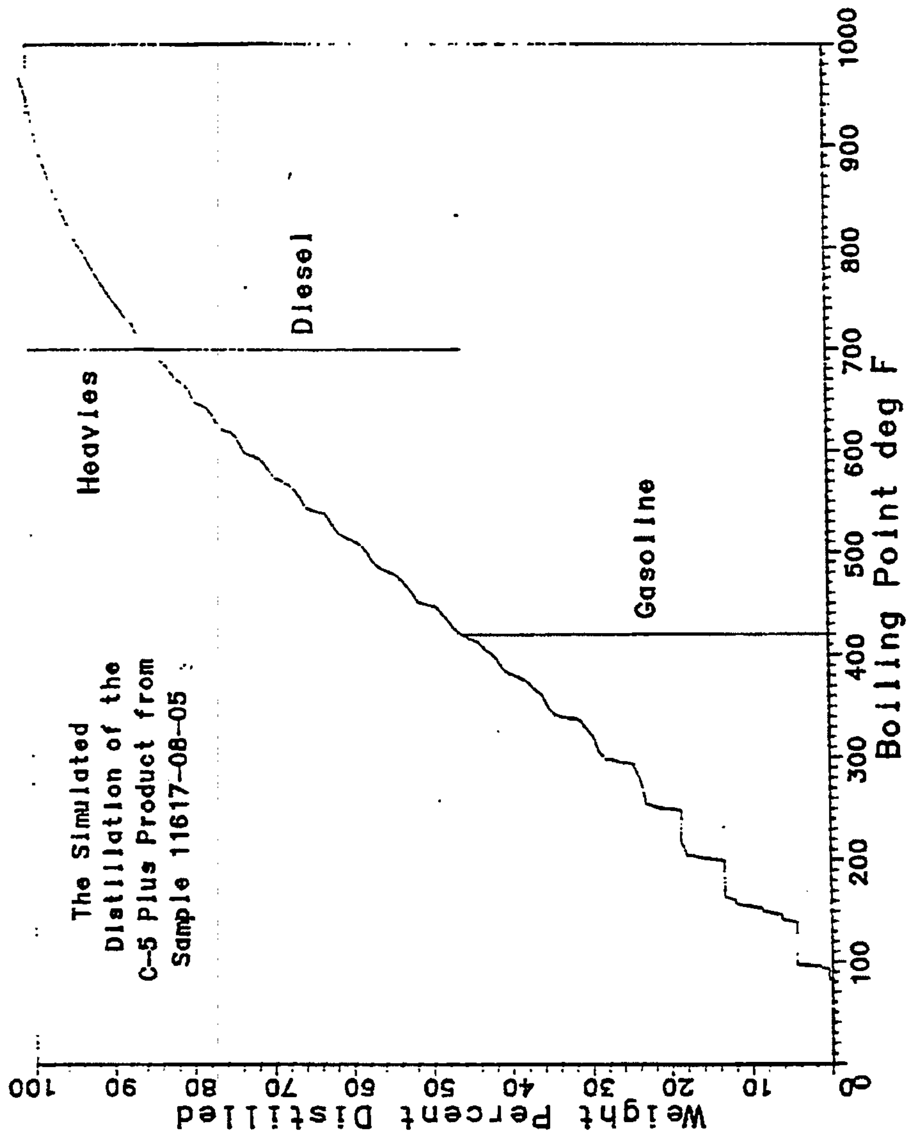
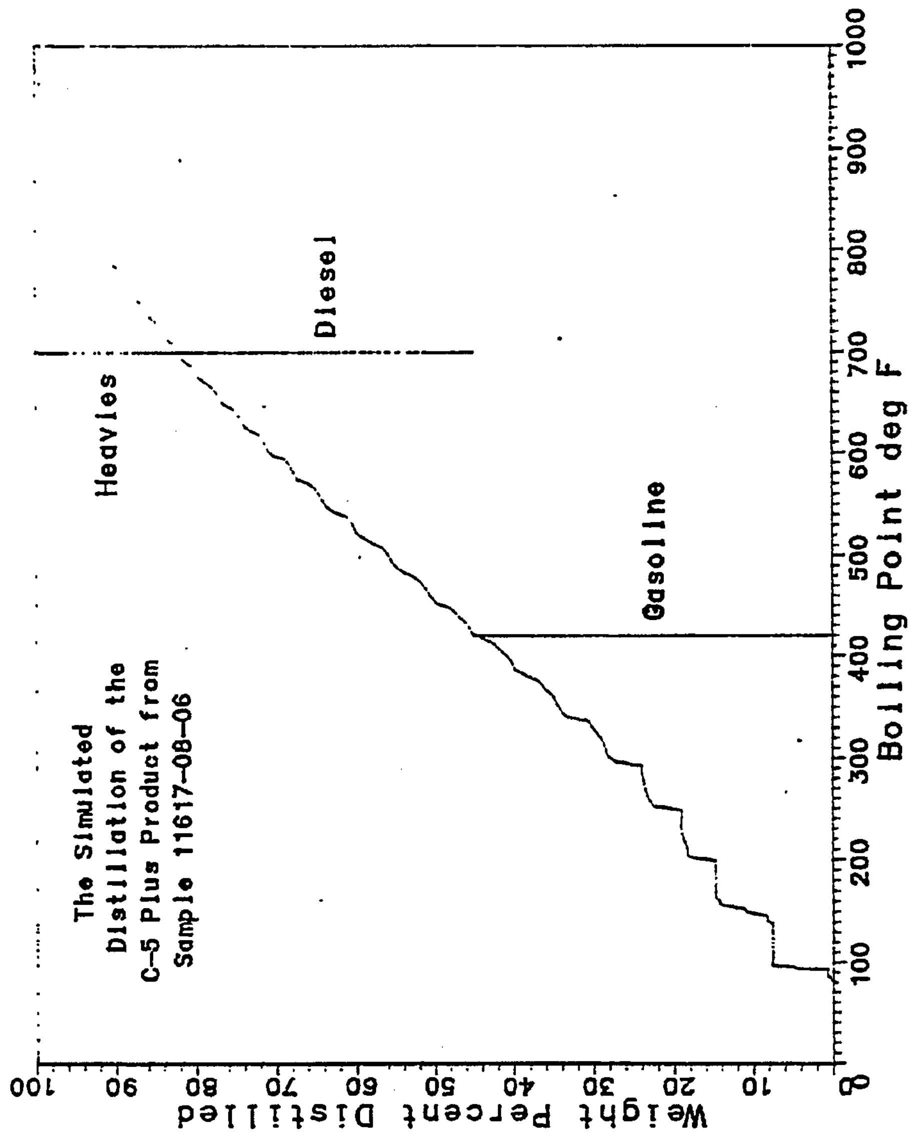

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-08-05
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. B32



The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-08-06
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B33

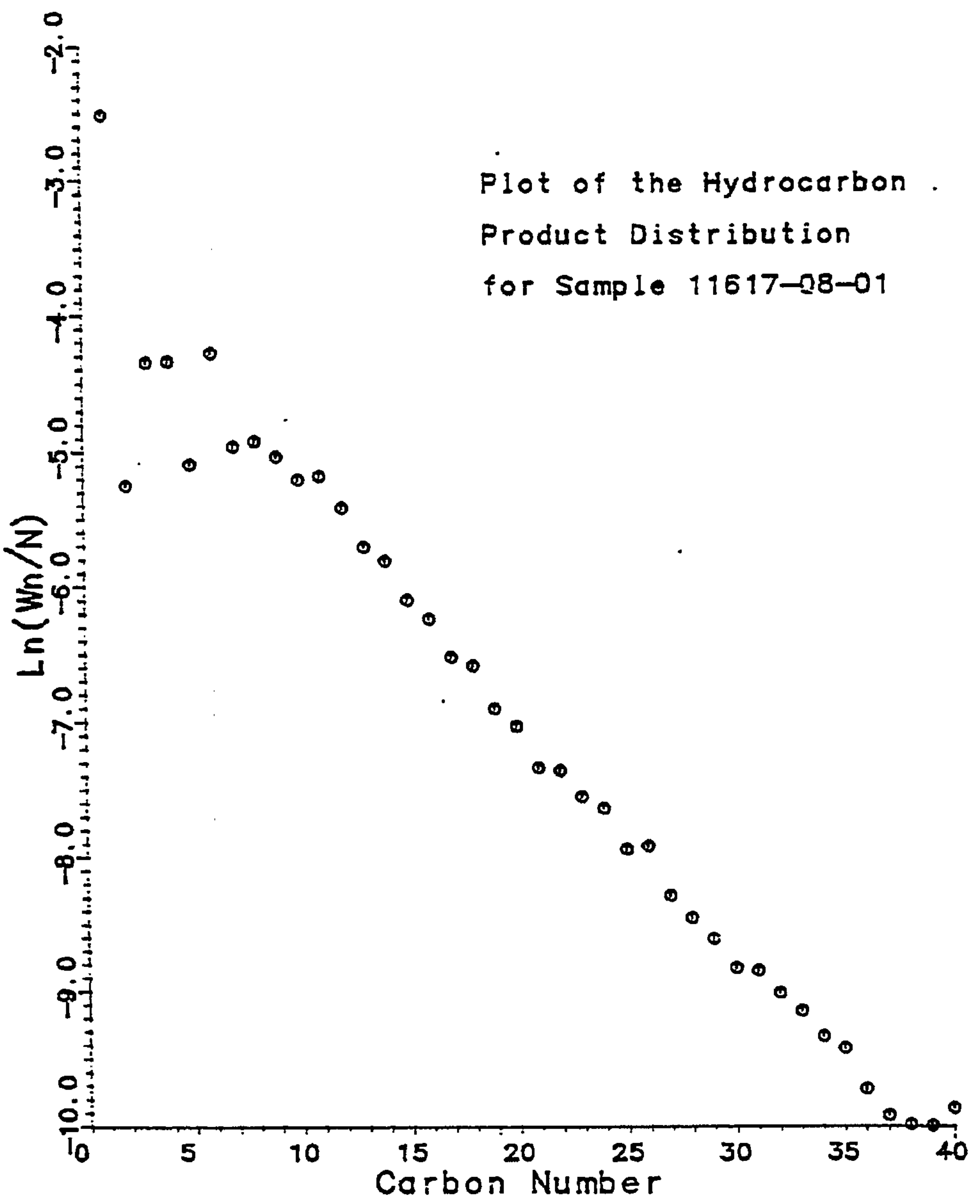
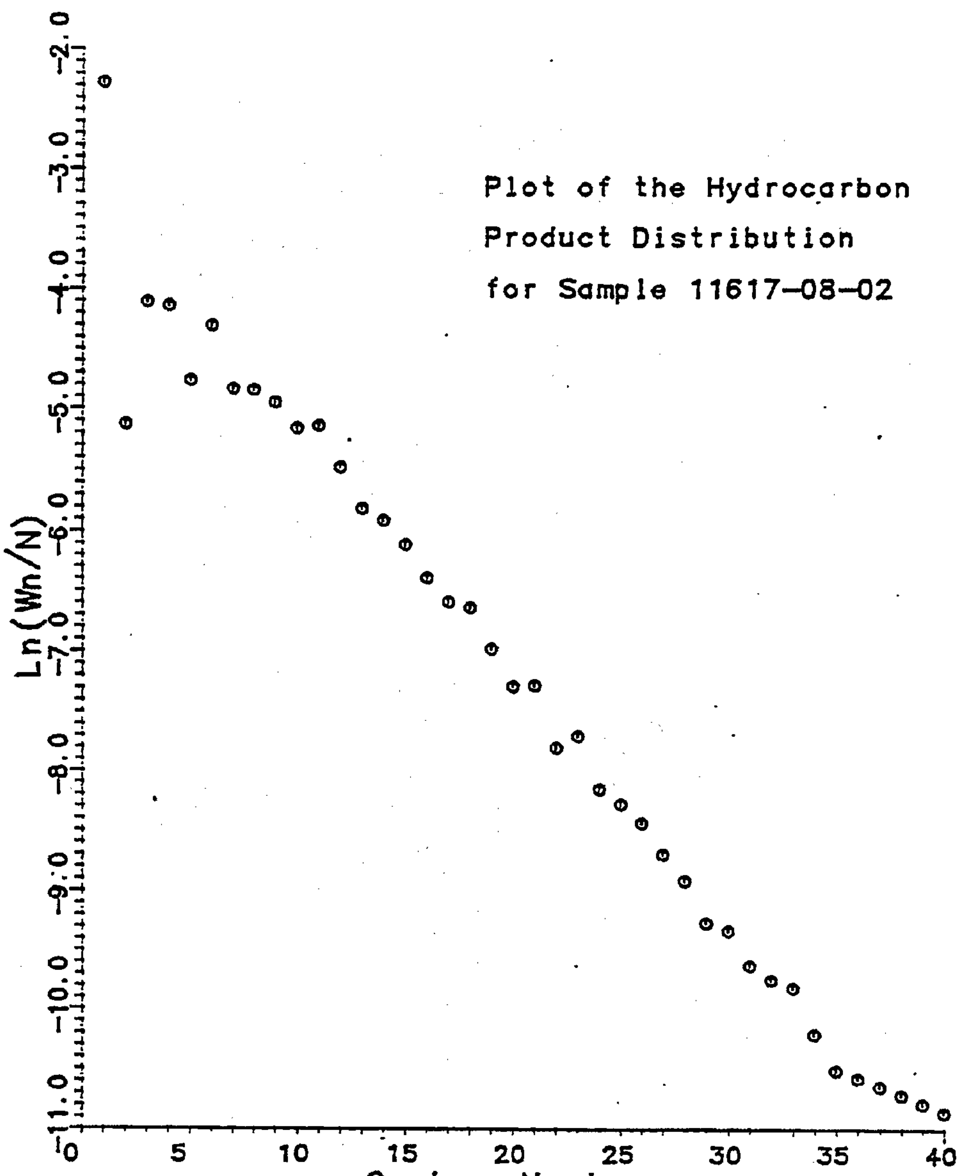
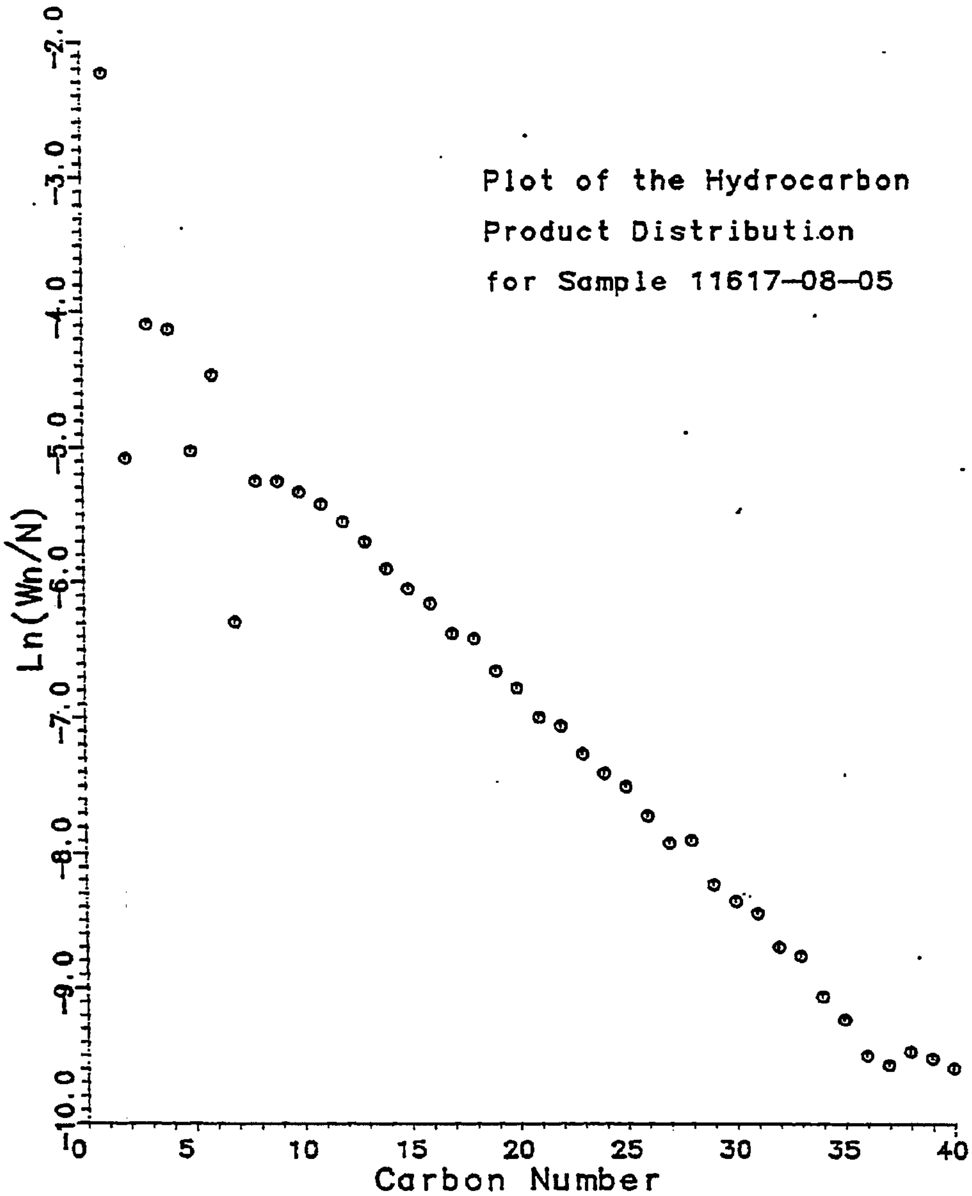

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-08-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B34



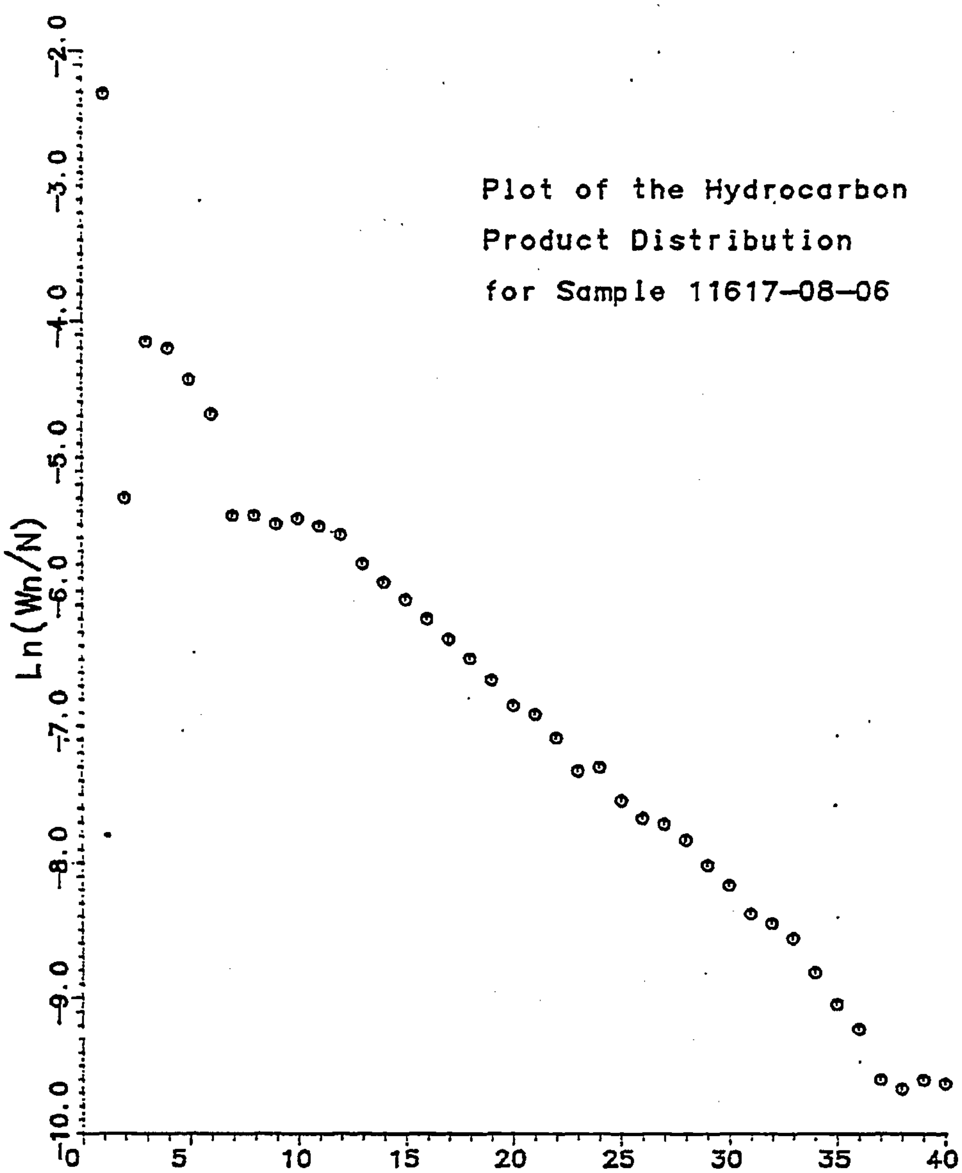
Plot of the Hydrocarbon
Product Distribution
for Sample 11617-08-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B35



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-08-05
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B36



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-08-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B37

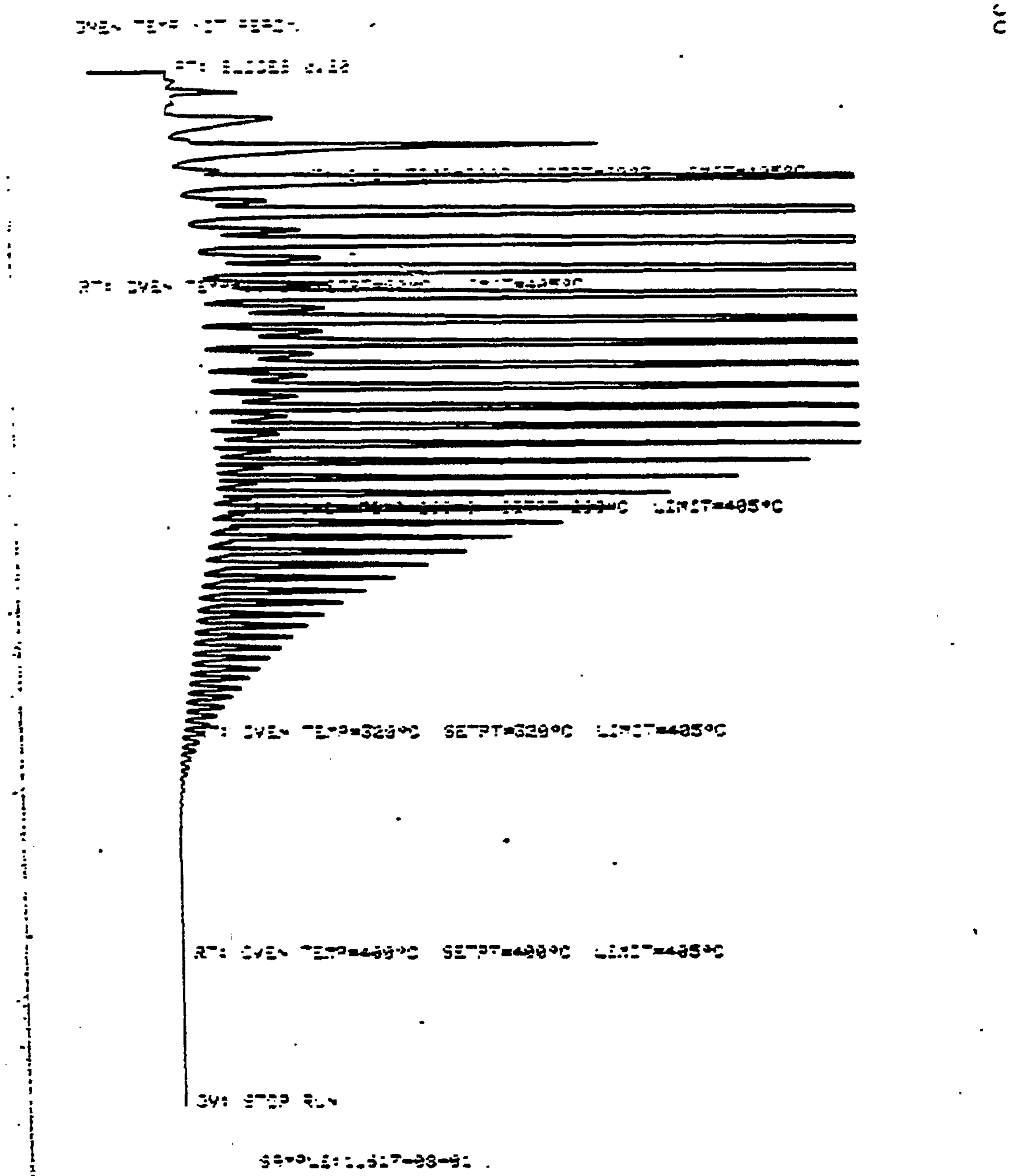


Fig. B38

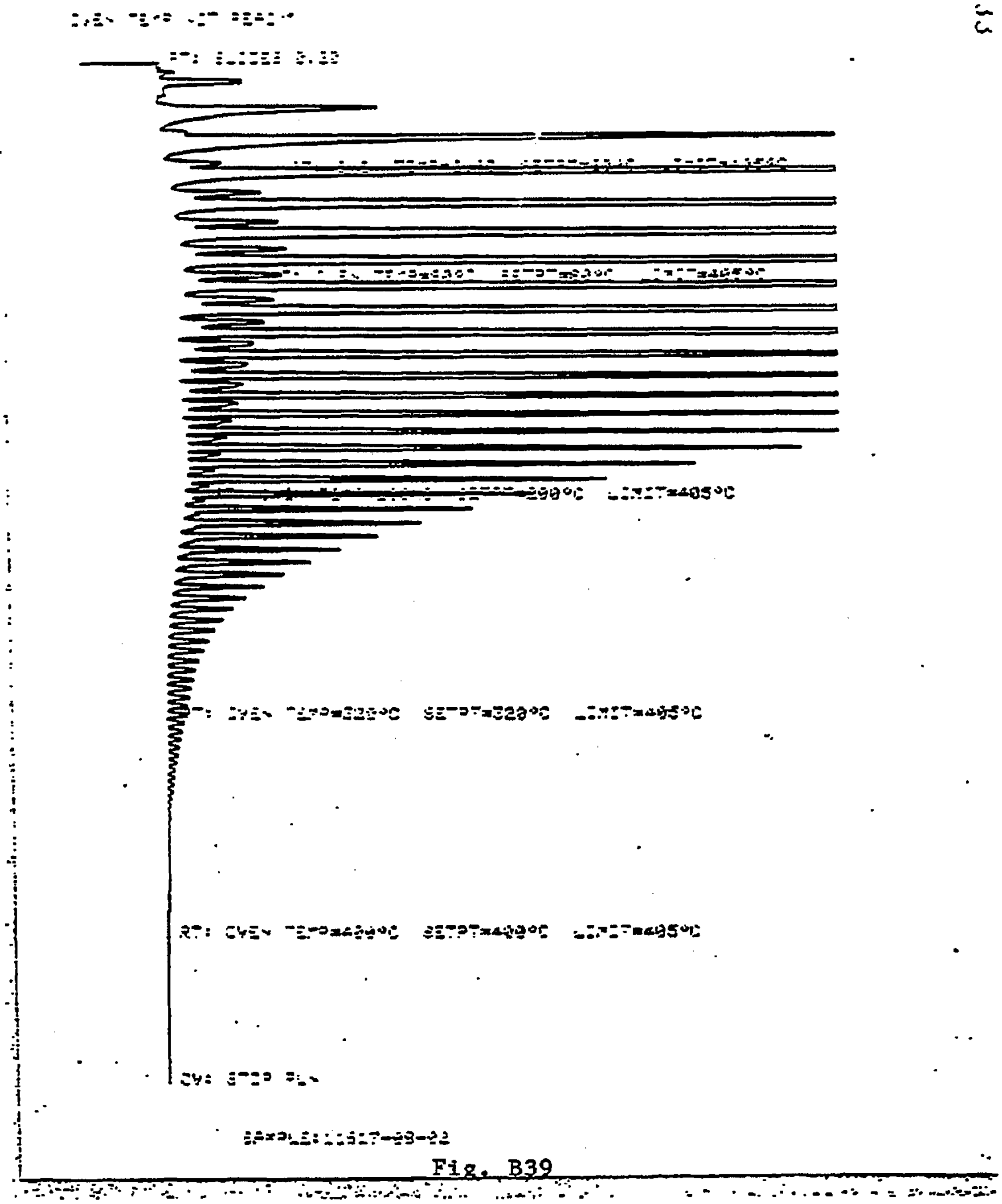


Fig. B39

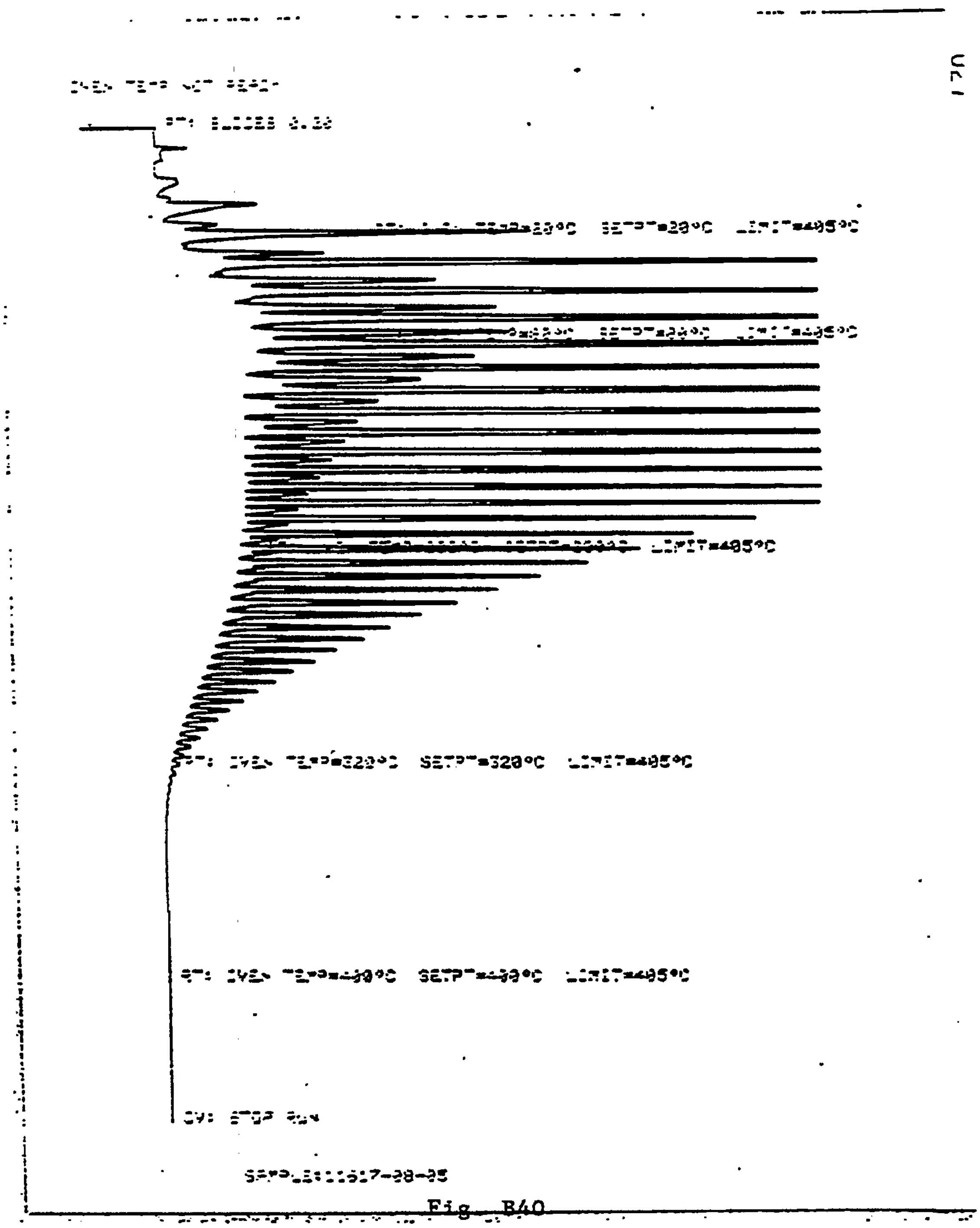

LIMIT=485°C
LIMIT=485°C
SETPT=320°C LIMIT=485°C
SETPT=430°C LIMIT=485°C

Fig. B40

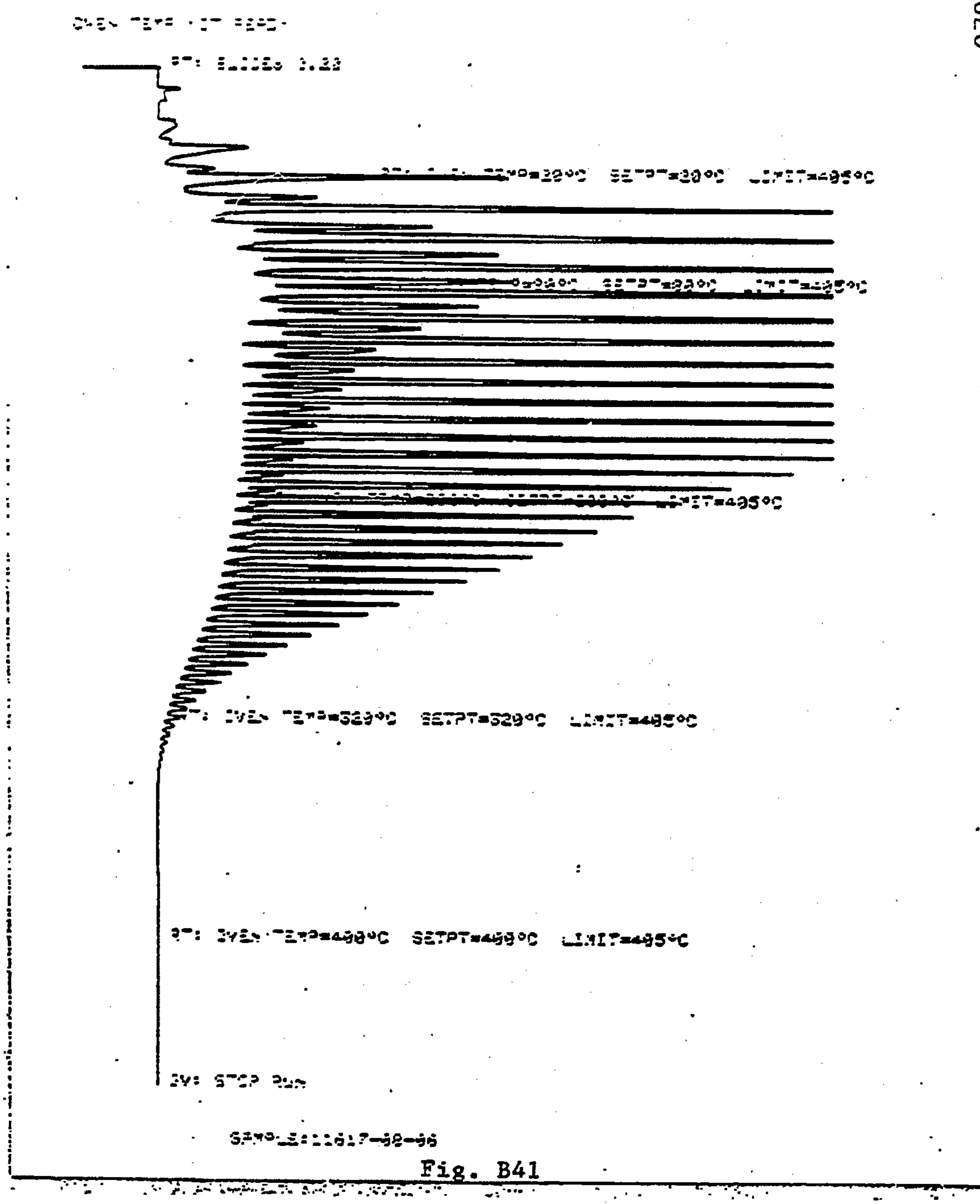


Fig. B41

Table B4

FILE: 1161708A T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-08
CATALYST CO/X11-TC121 215 CC 114.9 G AFTER USE:158.1 (+43.2 G)
FEED H2:CO OF 50:50 @ 1080 CC/MN OR 300 GHSV (CAT#12524-33)

RUN & SAMPLE NO.	11617-08-01	617-08-02	617-08-03	617-08-04	617-08-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	24.50	48.50	72.50	117.00	145.00
PRESSURE,PSIG	310.00	300.00	300.00	300.00	300.00
TEMP. C	240.00	240.00	240.00	240.00	240.00
FEED CC/MIN	1080.00	1080.00	1080.00	1080.00	1080.00
HOURS FEEDING	24.50	24.00	24.00	44.50	28.00
EFFLNT GAS LITER	835.40	1084.20	1028.20	2015.80	1311.10
GM AQUEOUS LAYER	164.42	124.98	120.15	208.59	132.47
GM OIL	61.81	55.24	54.73	100.80	63.65
MATERIAL BALANCE					
GM ATOM CARBON %	81.99	99.44	93.73	96.83	99.72
GM ATOM HYDROGEN %	93.28	102.36	98.90	102.70	104.11
GM ATOM OXYGEN %	90.99	103.39	97.33	98.89	102.36
RATIO CHX/(H2O+CO2)	0.7020	0.8396	0.8473	0.9083	0.8839
RATIO X IN CHX	2.2866	2.3181	2.3234	2.3324	2.3262
USAGE H2/CO PRODT	2.5291	2.3081	2.2966	2.2249	2.2504
FEED H2/CO FRM EFFLNT	1.1376	1.0294	1.0552	1.0606	1.0441
RESIDUAL H2/CO RATIO	0.6457	0.6889	0.7120	0.7451	0.7348
RATIO CO2/(H2O+CO2)	0.0077	0.0106	0.0116	0.0119	0.0120
K SHIFT IN EFFLNT	0.0050	0.0074	0.0084	0.0090	0.0089
SPECIFIC ACTIVITY SA	1.7037	1.2903	1.2701	1.1705	1.1339
CONVERSION					
ON CO %	26.12	21.03	21.66	21.32	20.41
ON H2 %	58.06	47.15	47.14	44.73	43.99
ON CO+H2 %	43.12	34.28	34.74	33.37	32.45
PRDT SELECTIVITY,WT %					
CH4	8.15	10.24	10.51	10.98	10.74
C2 HC'S	1.05	1.18	1.42	1.46	1.25
C3H8	1.79	2.15	2.20	2.31	2.31
C3H6=	2.12	2.77	2.76	2.77	2.70
C4H10	2.02	2.08	2.09	2.14	2.12
C4H8=	3.22	4.28	4.27	4.31	4.32
C5H12	2.51	2.40	2.38	2.42	2.48
C5H10=	0.59	1.85	0.78	0.88	0.80
C6H14	6.67	5.02	3.99	4.10	4.03
C6H12= & CYCLO'S	1.71	2.44	2.65	2.93	2.86
C7+ IN GAS	7.75	7.32	7.43	7.66	7.26
LIQ HC'S	62.41	58.27	59.52	58.04	59.16
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	18.35	22.70	23.25	23.97	23.42
C5 -420 F	44.83	44.85	46.99	47.01	34.58
420-700 F	27.46	26.57	23.81	23.22	29.64
700-END PT	9.36	5.89	5.95	5.80	12.36

Table B4 (continued)

FILE: 1161708A T6Q1 A1

C5+-END PT	81.65	77.30	76.75	76.03	76.58
ISO/NORMAL MOLE RATIO					
C4	0.3079	0.1418	0.1063	0.0857	0.0795
C5	0.5249	0.2030	0.1399	0.1122	0.1109
C6	2.6349	1.2308	0.6787	0.5723	0.5452
C4=	0.0233	0.0388	0.0391	0.0380	0.0418
PARAFFIN/OLEFIN RATIO					
C3	0.8064	0.7390	0.7632	0.7954	0.8168
C4	0.6058	0.4687	0.4722	0.4792	0.4741
C5	4.1098	1.2584	2.9592	2.6667	3.0307
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8417	0.8199	0.8086	0.8191	0.8593
RATIO CH4/(1-A)**2	3.2498	3.1572	2.8674	3.3544	5.4226
ALPHA FRM CORRELATION	0.8332	0.8301			0.8270
ALPHA (EXPTL/CORR)	1.0101	0.9877			1.0391
W%CH4 FRM CORRELATION	15.1731	16.1514			17.1252
W%CH4 (EXPTL/CORR)	0.5369	0.6339			0.6269
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	283.00	254.00			326.00
16	303.00	296.00			360.00
50	462.00	431.00			529.00
84	687.00	640.00			738.00
90	757.00	702.00			795.00
RANGE(16-84 %)	384.00	344.00			378.00
WT % @ 420 F	41.00	48.00			29.00
WT % @ 700 F	85.00	89.90			79.10

Table B5

FILE: 1161708B T6Q1   A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-08
CATALYST CO/X11-TC121 215 CC 114.9 G AFTER USE:158.1 (+43.2 G)
FEED H2:CO OF 50:50 @ 1080 CC/MN OR 300 GHSV (CAT#12524-33)

RUN & SAMPLE NO.	11617-08-06
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	166.00
PRESSURE,PSIG	300.00
TEMP. C	240.00
FEED CC/MIN	1080.00
HOURS FEEDING	21.00
EFFLNT GAS LITER	979.00
GM AQUEOUS LAYER	90.87
GM OIL	47.89
MATERIAL BALANCE	
GM ATOM CARBON %	98.38
GM ATOM HYDROGEN %	102.81
GM ATOM OXYGEN %	99.48
RATIO CHX/(H2O+CO2)	0.9479
RATIO X IN CHX	2.3065
USAGE H2/CO PRODT	2.1636
FEED H2/CO FRM EFFLNT	1.0450
RESIDUAL H2/CO RATIO	0.7557
RATIO CO2/(H2O+CO2)	0.0134
K SHIFT IN EFFLNT	0.0103
SPECIFIC ACTIVITY SA	1.0990
CONVERSION	
ON CO %	20.55
ON H2 %	42.54
ON CO+H2 %	31.79
PRDT SELECTIVITY,WT %	
CH4	9.93
C2 HC'S	1.00
C3H8	2.27
C3H6=	2.48
C4H10	2.05
C4H8=	3.96
C5H12	2.36
C5H10=	3.60
C6H14	3.05
C6H12= & CYCLO'S	2.50
C7+ IN GAS	6.95
LIQ HC'S	59.85
TOTAL	100.00
SUB-GROUPING	
C1 -C4	21.69
C5 -420 F	34.92
420-700 F	29.33
700-END PT	14.07

Table B5 (continued)

FILE: 1161708B T6Q1 A1

C5+-END PT	78.31
ISO/NORMAL MOLE RATIO	
C4	0.0846
C5	0.1066
C6	0.2024
C4=	0.0337
PARAFFIN/OLEFIN RATIO	
C3	0.8726
C4	0.4993
C5	0.6374
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8641
RATIO CH4/(1-A)**2	5.3754
ALPHA FRM CORRELATION	0.8256
ALPHA (EXPTL/CORR)	1.0466
W%CH4 FRM CORRELATION	17.5503
W%CH4 (EXPTL/CORR)	0.5658
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL WAX
DENSITY	
N, REFRACTIVE INDEX	
SIMULT'D DISTILATN	
10 WT % @ DEG F	334.00
16	366.00
50	540.00
84	761.00
90	816.00
RANGE(16-84 %)	395.00
WT % @ 420 F	27.50
WT % @ 700 F	76.50

IV. <u>Run 51 (12570-03) with Catalyst 51 ($Co/X_9/X_{11}$/TC-123)</u>

The purposes of this run were to test the effect of adding the promoter X_9 to the promising formulation (Co/X_{11}/TC-123) of Catalyst 45 of the Sixth Quarterly Report, and also to test its stability under high temperature and pressure conditions. This catalyst will be compared both with Catalyst 45 and with Catalyst 49 of this report.

The catalyst was formulated in the same way as Catalyst 45 except for the addition of X_9. The theoretical content of cobalt, X_9 and X_{11} was 8.2, 1.1 and 1.6 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B42-45. Simulated distillations of the C_5^+ product are plotted in Figs. B46-54. Carbon number product distributions are plotted in Figs. B55-63. Chromatograms from simulated distillations are reproduced in Figs. B64-72. Detailed material balances appear in Tables B6-9.

Once a good material balance had been obtained, the syngas conversion of this catalyst remained highly stable at about 46 percent, nearly the same as with Catalyst 45 (with TC-123) and Catalyst 49 (with γ-Al_2O_3), neither of which contained X_9. The product selectivity was similar to that of Catalyst 45, yielding about 3-4 percent methane and about 90 percent C_5^+.

When the temperature was raised from 240C to 260C the syngas conversion rose sharply to about 55 percent, with no significant deterioration during 144 hours at this temperature. The conversion of Catalyst 49 at 260C, although some five percentage points higher initially, degraded rapidly at an estimated rate of one percentage point every 30 hours. Catalyst 45 has not yet been tested at 260C.

During the last 120 hours of the run the catalyst was subjected to still more severe conditions designed to improve conversion while hopefully maintaining acceptable selectivity: H_2:CO ratio raised from 1:1 to 1.5:1, pressure raised from 300 to 500 psig, temperature 260C. Under these conditions the conversion rose sharply to about 78 percent, substantially higher than Catalyst 49's conversion of about 70 percent under similar conditions. The selectivity to methane was less than or equal to 10 percent, and C_5^+ production was about 81 percent--both far superior to the selectivity of Catalyst 49, which demonstrated levels of about 15 and 70 percent respectively. However, due to mechanical problems near the end of the run, and the short duration of this stage of the run, the catalyst's stability under these conditions could not be reliably determined.

This run has demonstrated the potential benefits of using X_9 as a promoter in the Co/X_{11}/TC-123 type of catalyst at elevated temperatures, pressures, and H_2:CO feed ratios. More extended testing of this catalyst is needed, as well as testing of Catalyst 45 under the same conditions of high temperature, pressure and feed ratio.

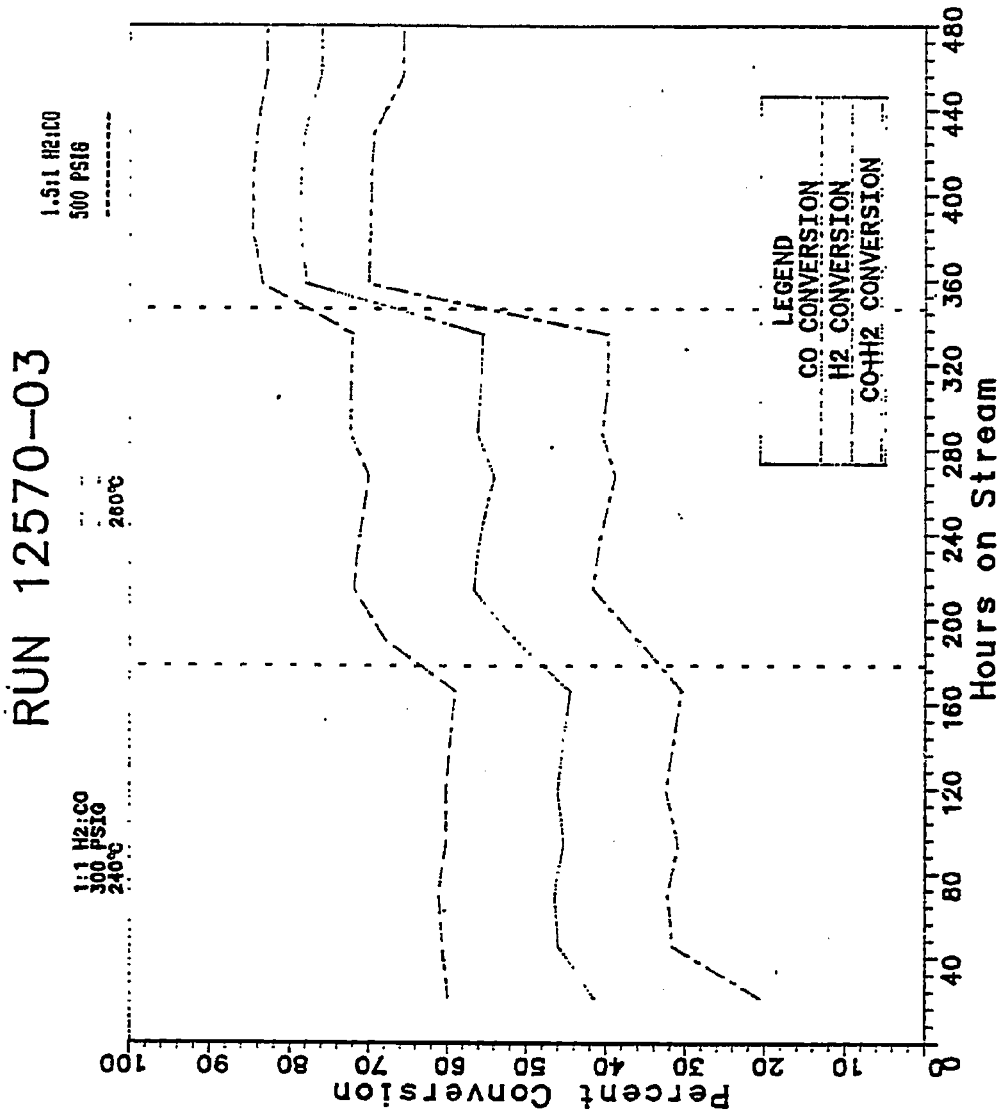

RUN 12570-03
1:1 H2:CO
300 PSIG
240°C
260°C
1.5:1 H2:CO
500 PSIG
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream

Fig. B42

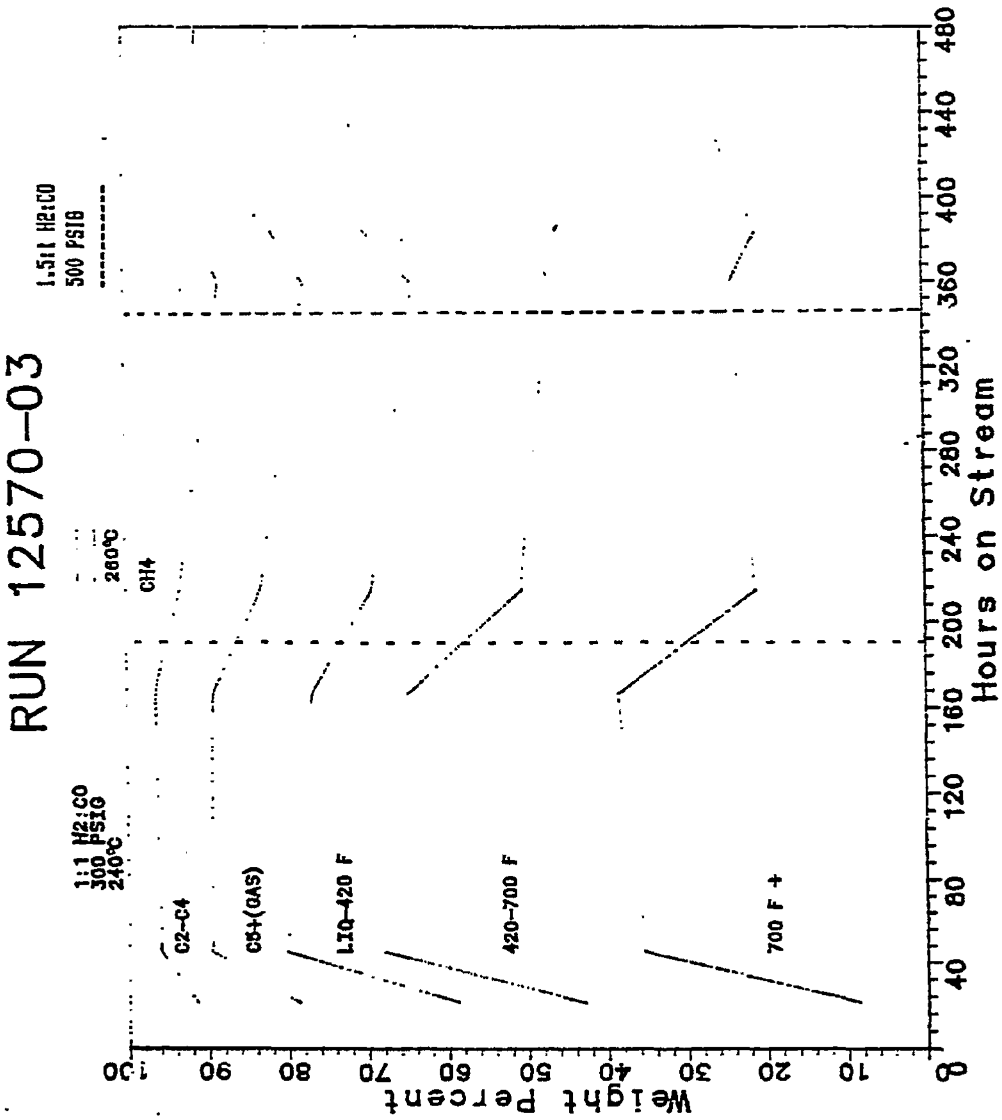

RUN 12570-03
Weight Percent
Hours on Stream
1:1 H2:CO
300 PSIG
240°C
260°C
CH4
1.5:1 H2:CO
500 PSIG
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
100
90
80
70
60
50
40
30
20
10
0
40
80
120
160
200
240
280
320
360
400
440
480

Fig. B43

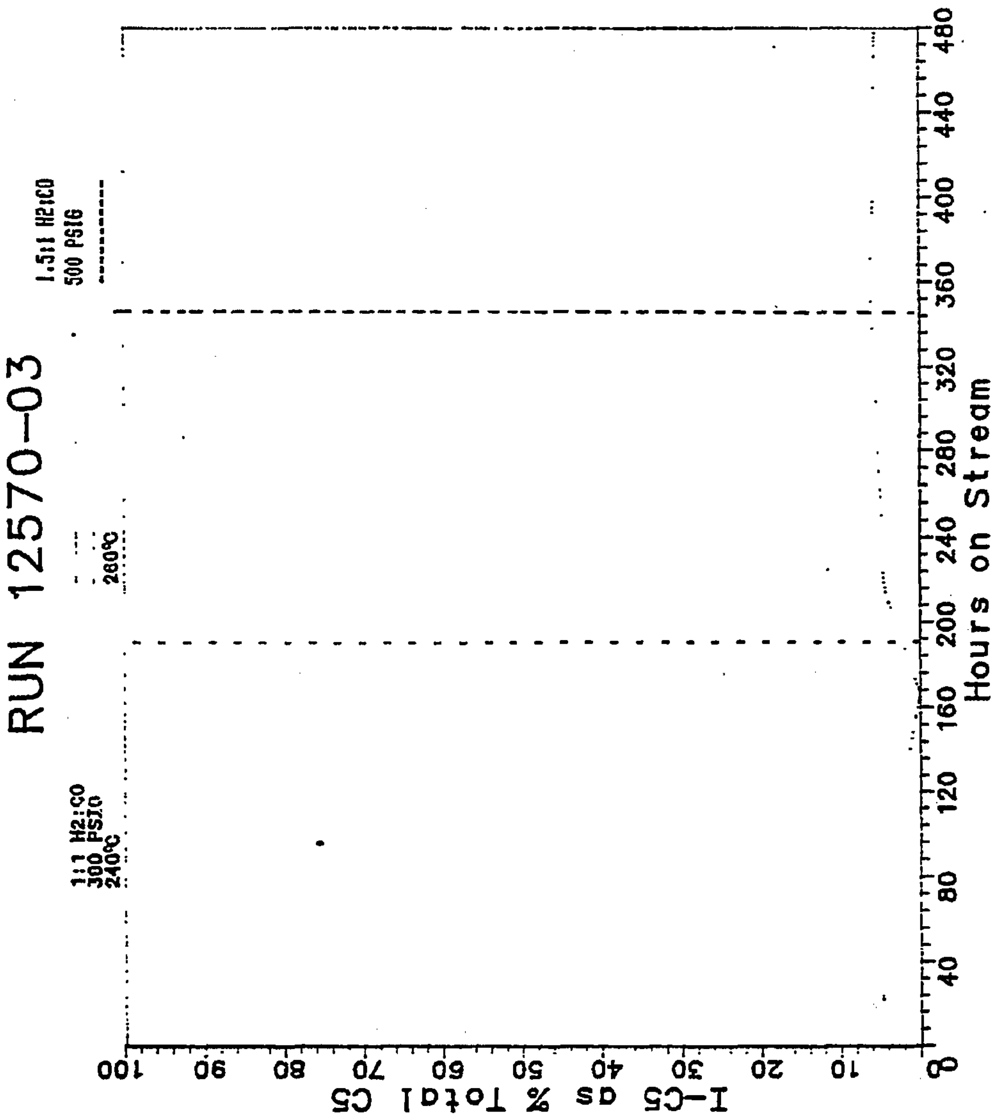

RUN 12570-03
Hours on Stream
I-C5 as % Total C5
0
40
80
120
160
200
240
280
320
360
400
440
480
10
20
30
40
50
60
70
80
90
100
1:1 H2:CO
300 PSIG
240°C
260°C
1.5:1 H2:CO
500 PSIG

Fig. B44

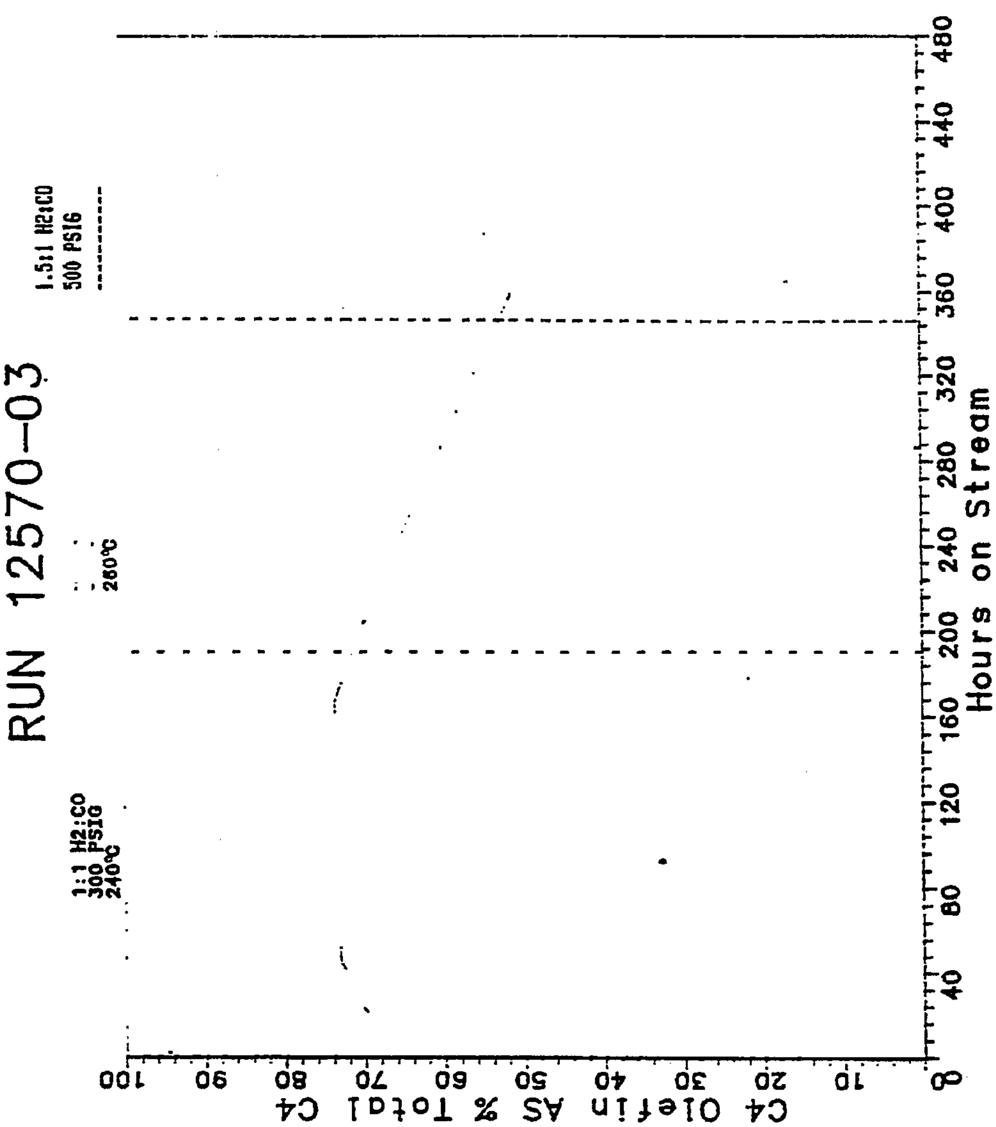

RUN 12570-03
1:1 H2:CO
300 PSIG
240°C
260°C
1.5:1 H2:CO
500 PSIG
Hours on Stream
C4 Olefin AS % Total C4
0 40 80 120 160 200 240 280 320 360 400 440 480
0 10 20 30 40 50 60 70 80 90 100

Fig. B45

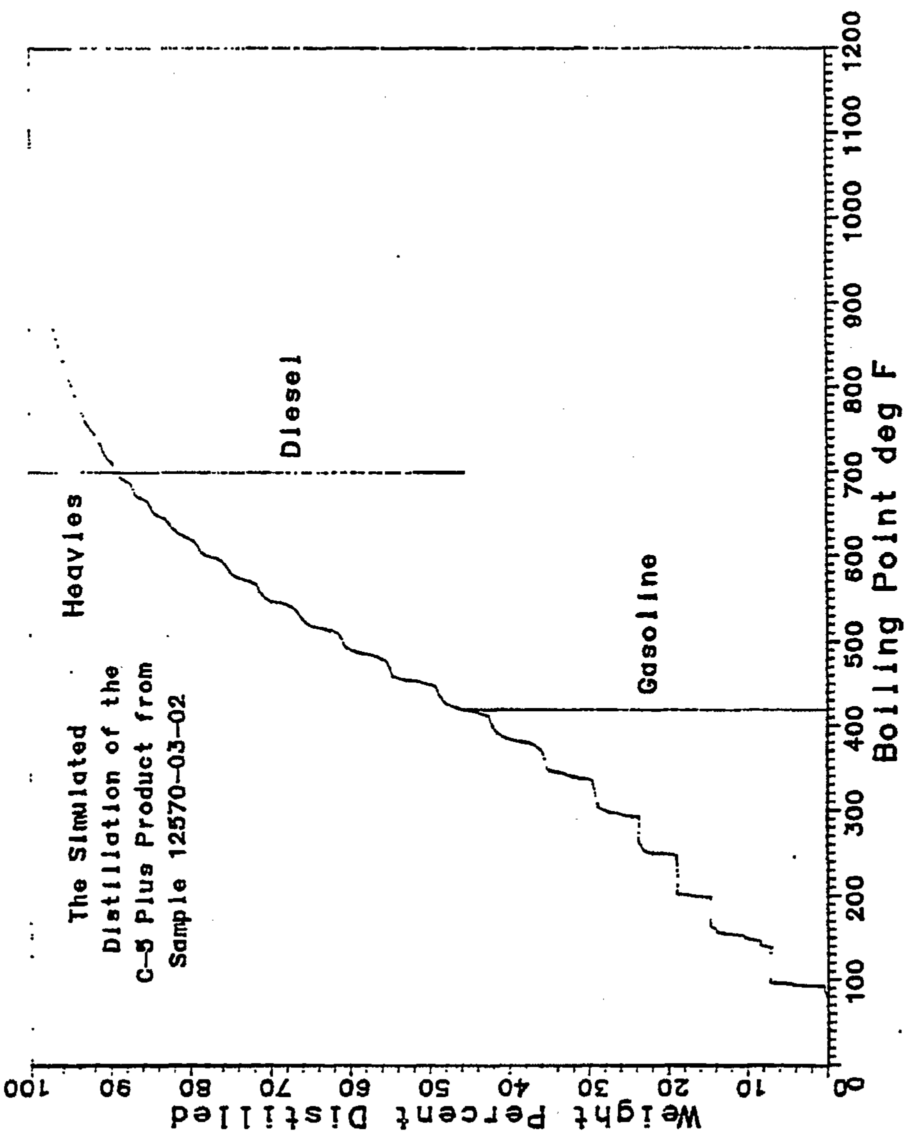

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12570-03-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point deg F
100
200
300
400
500
600
700
800
900
1000
1100
1200

Fig. B46

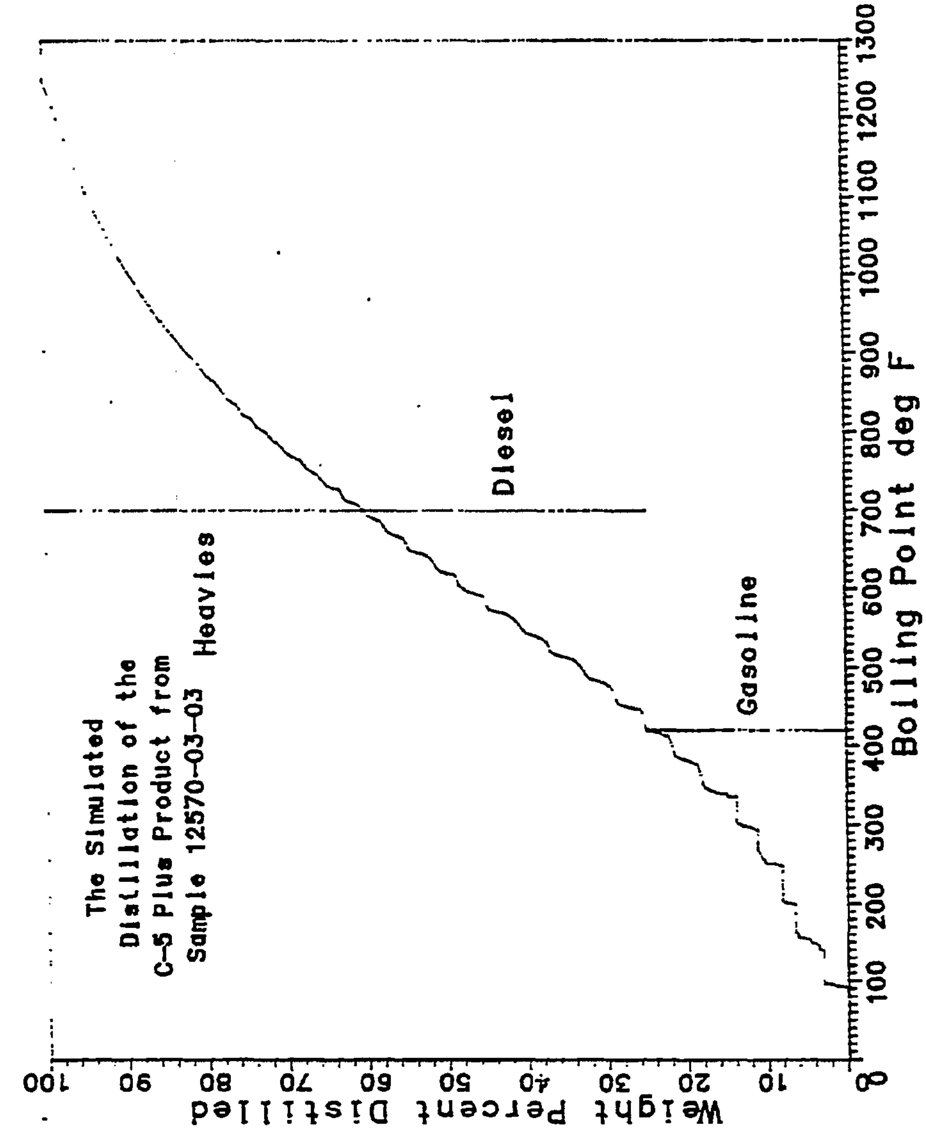

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12570-03-03
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300

Fig. B47

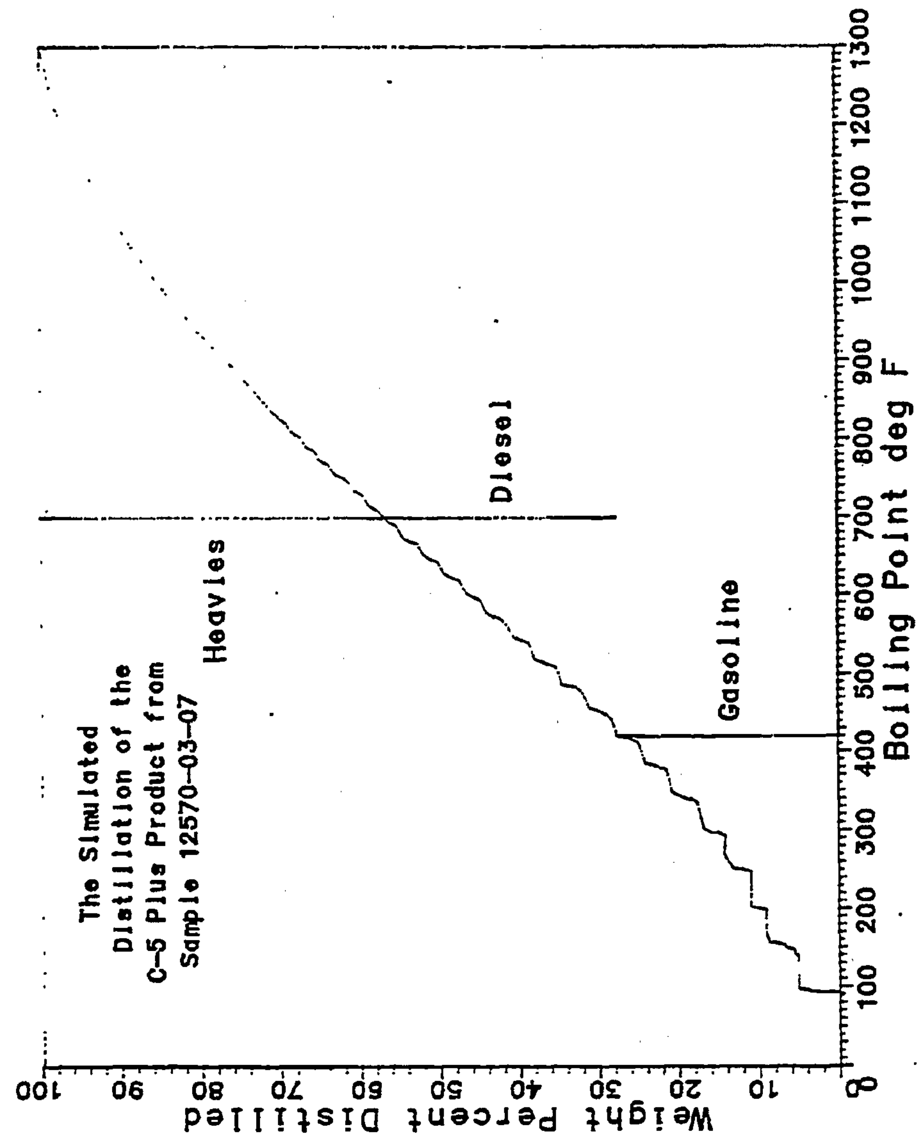

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12570-03-07
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B48

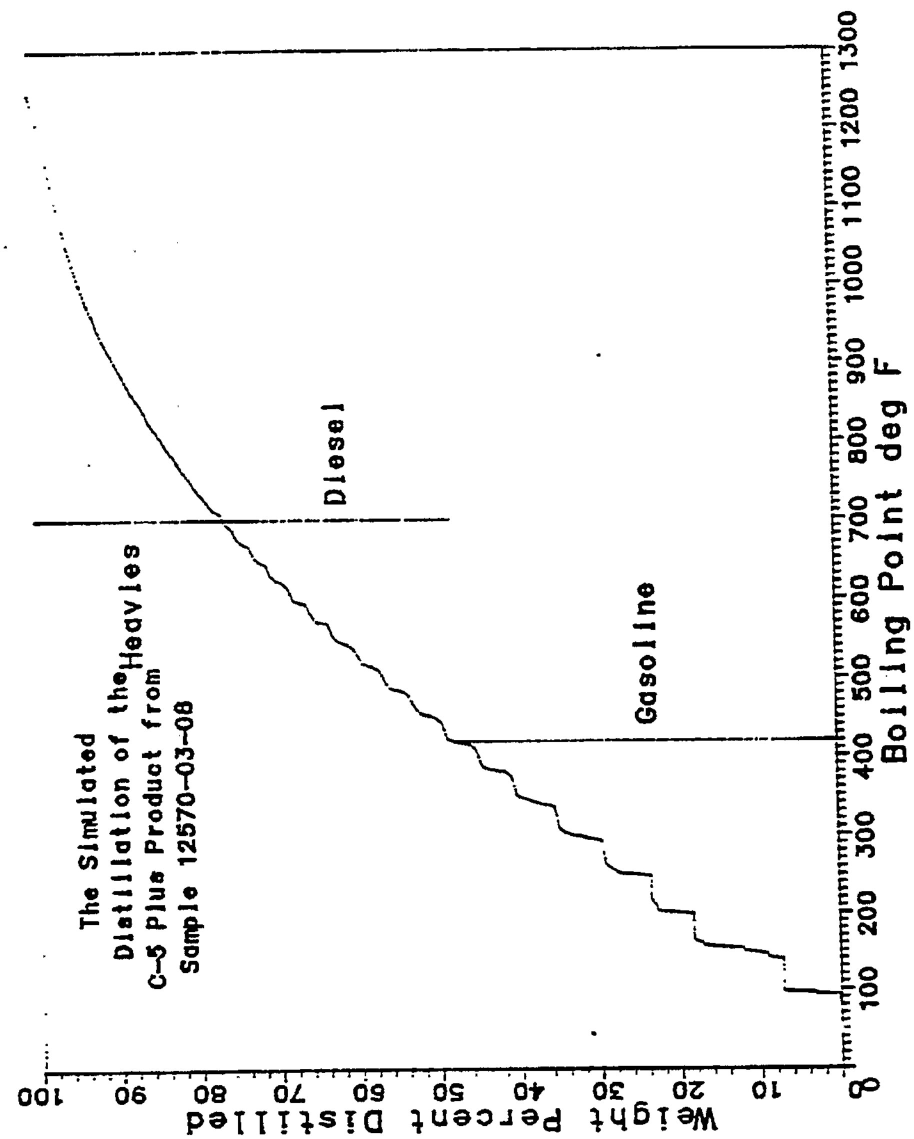

The Simulated
Distillation of the Heavies
C-5 Plus Product from
Sample 12570-03-08
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300

Fig. B49

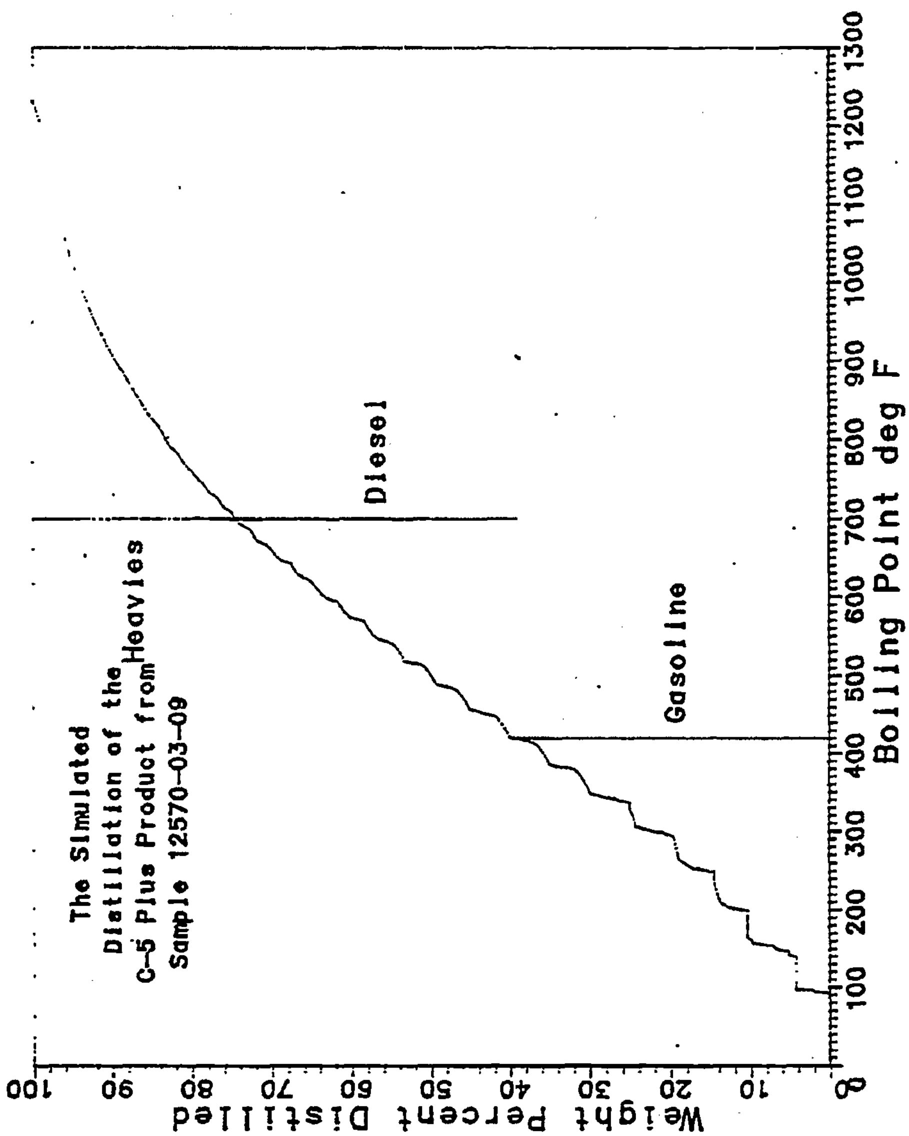

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 12570-03-09
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B50

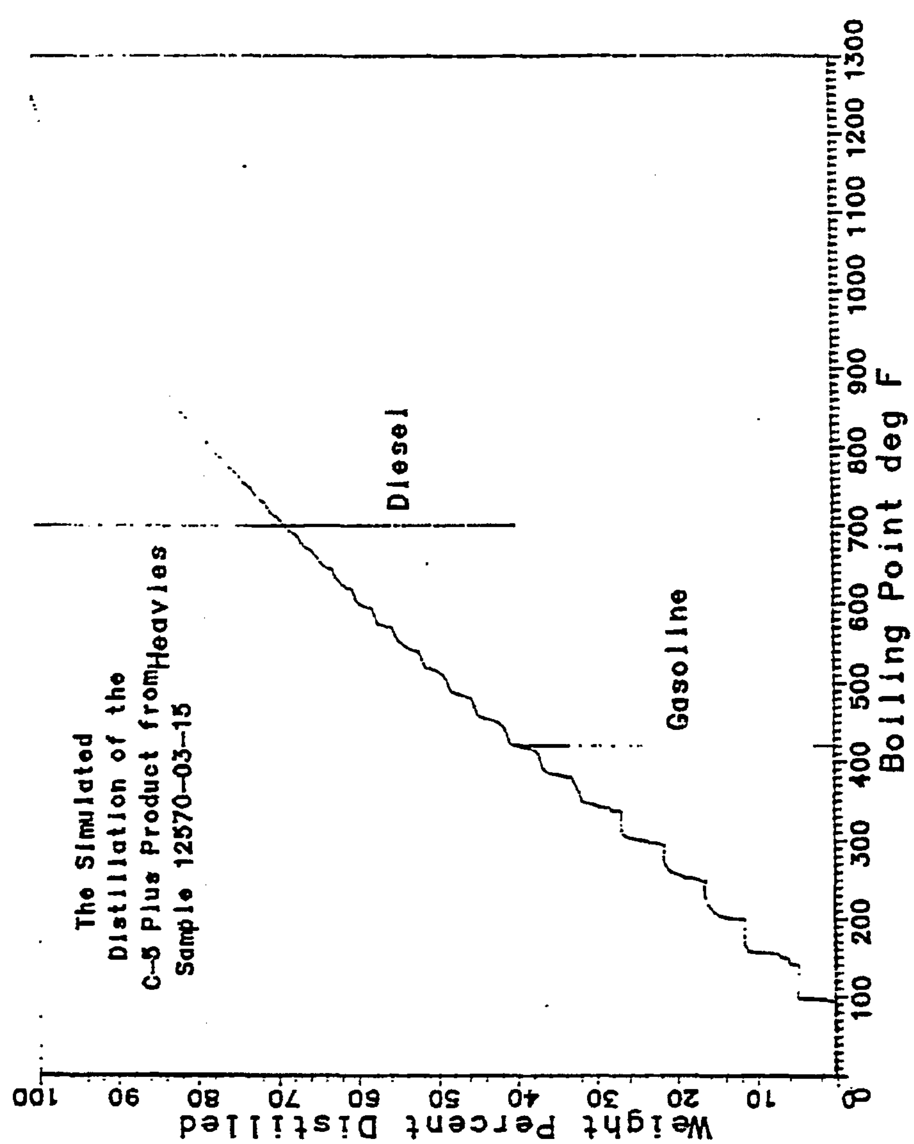

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 12570-03-15
Diesel
Gasoline
Boiling Point deg F
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B51

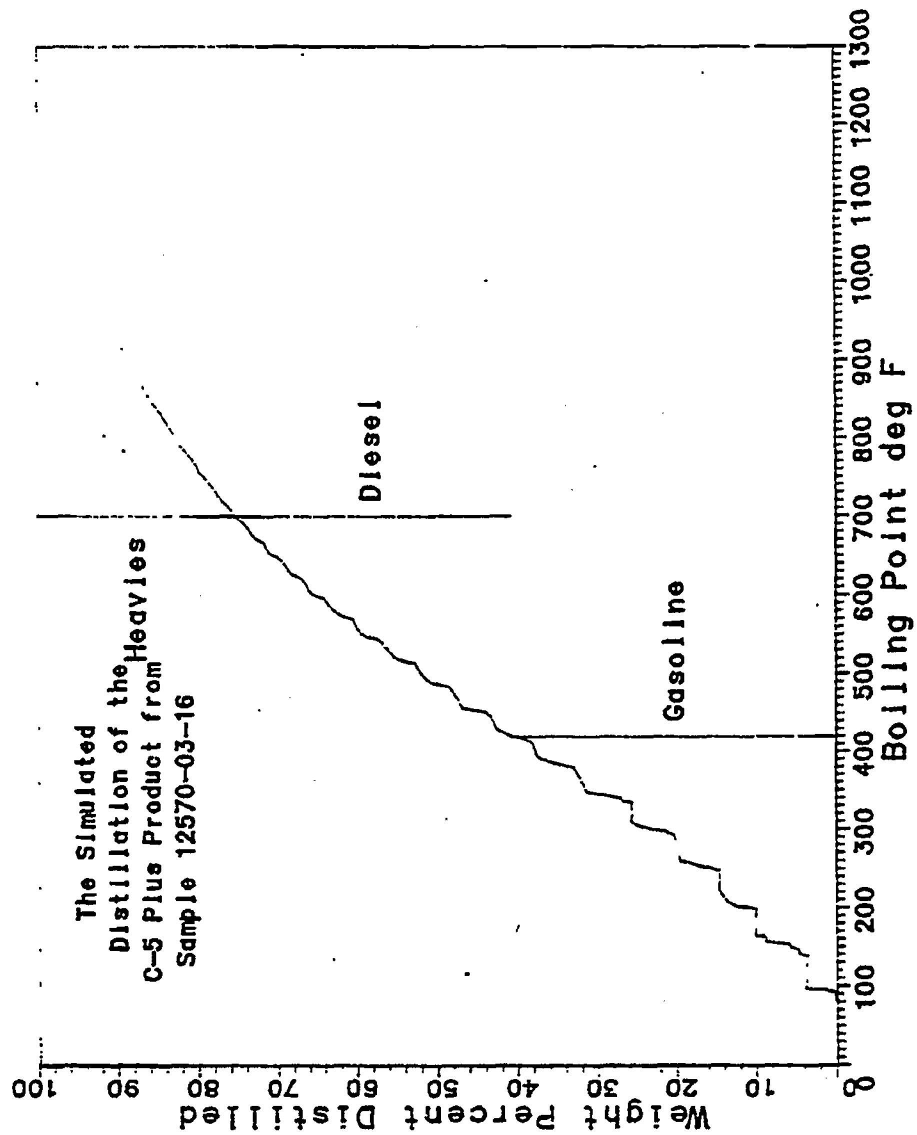

The Simulated
Distillation of the Heavies
C-5 Plus Product from
Sample 12570-03-16
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B52

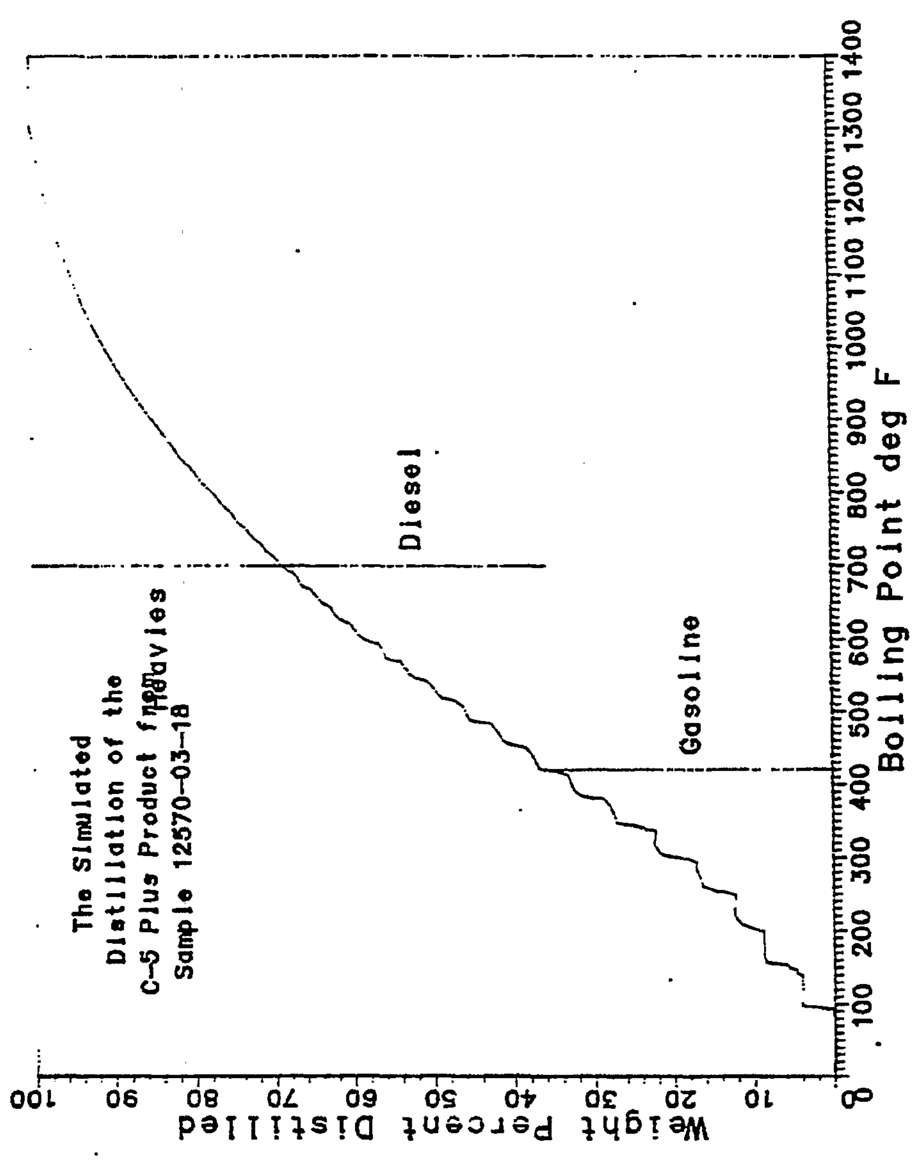

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 12570-03-18
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400

Fig. B53

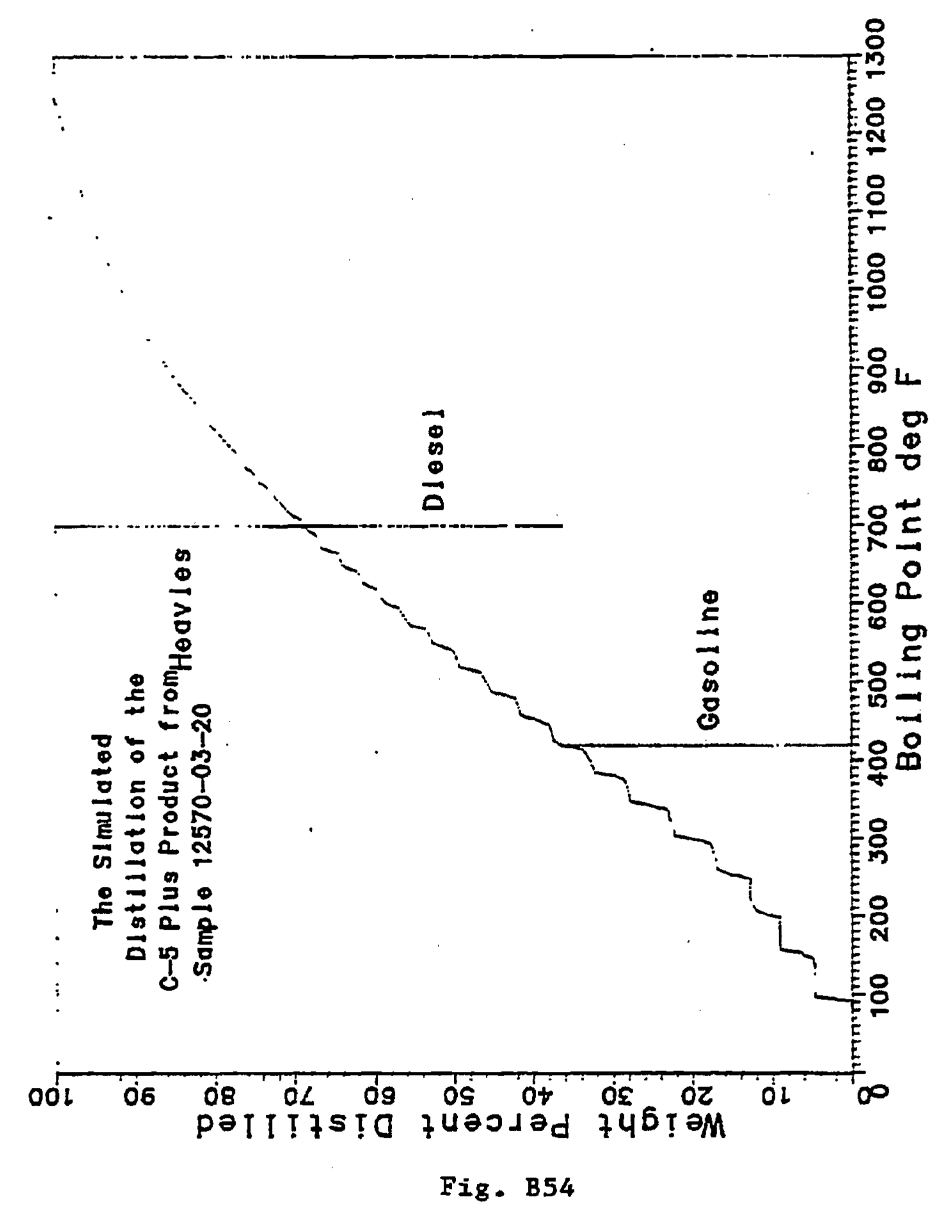

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 12570-03-20
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B54

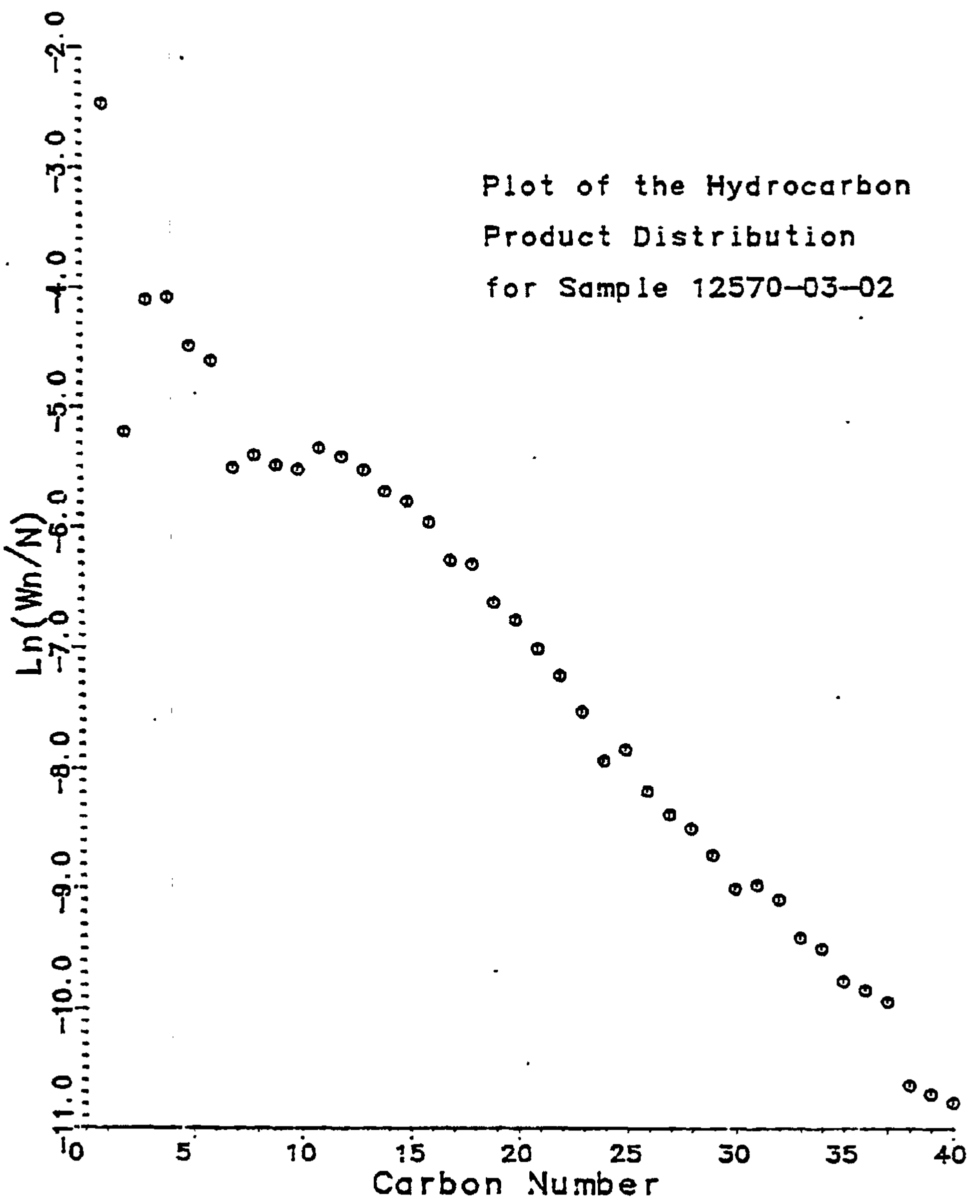
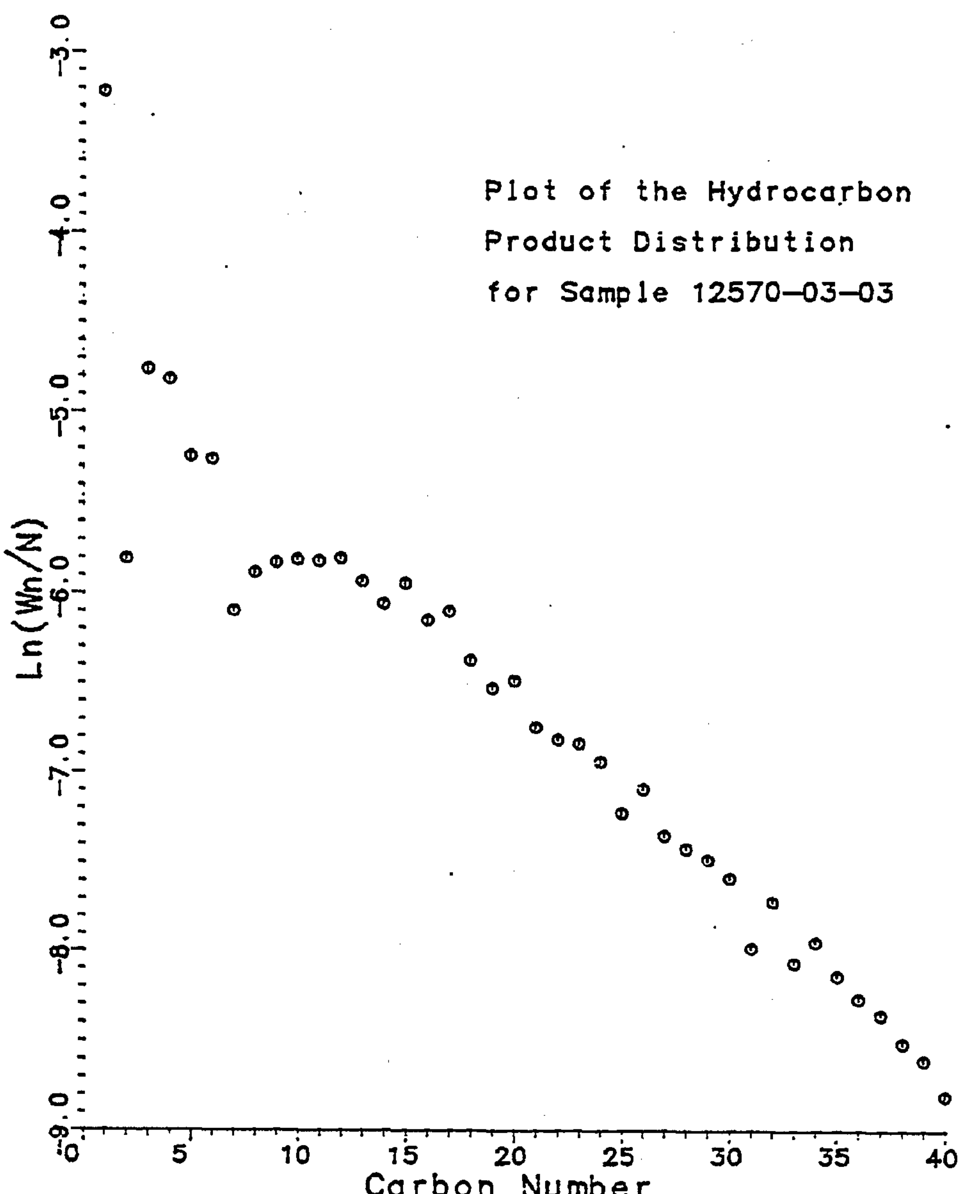
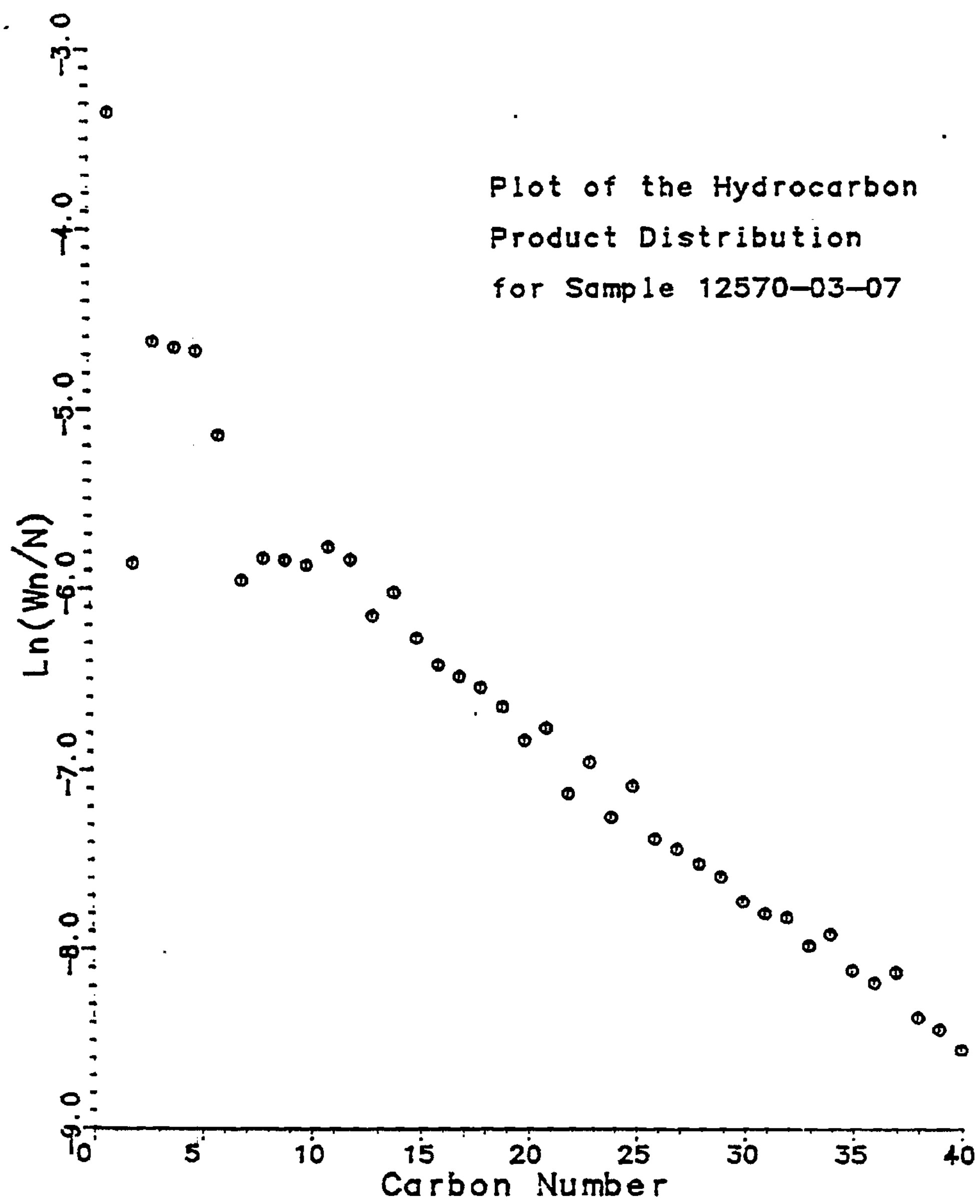

Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B55



Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-03
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B56



Plot of the Hydrocarbon
Product Distribution
for Sample 12570—03—07
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B57

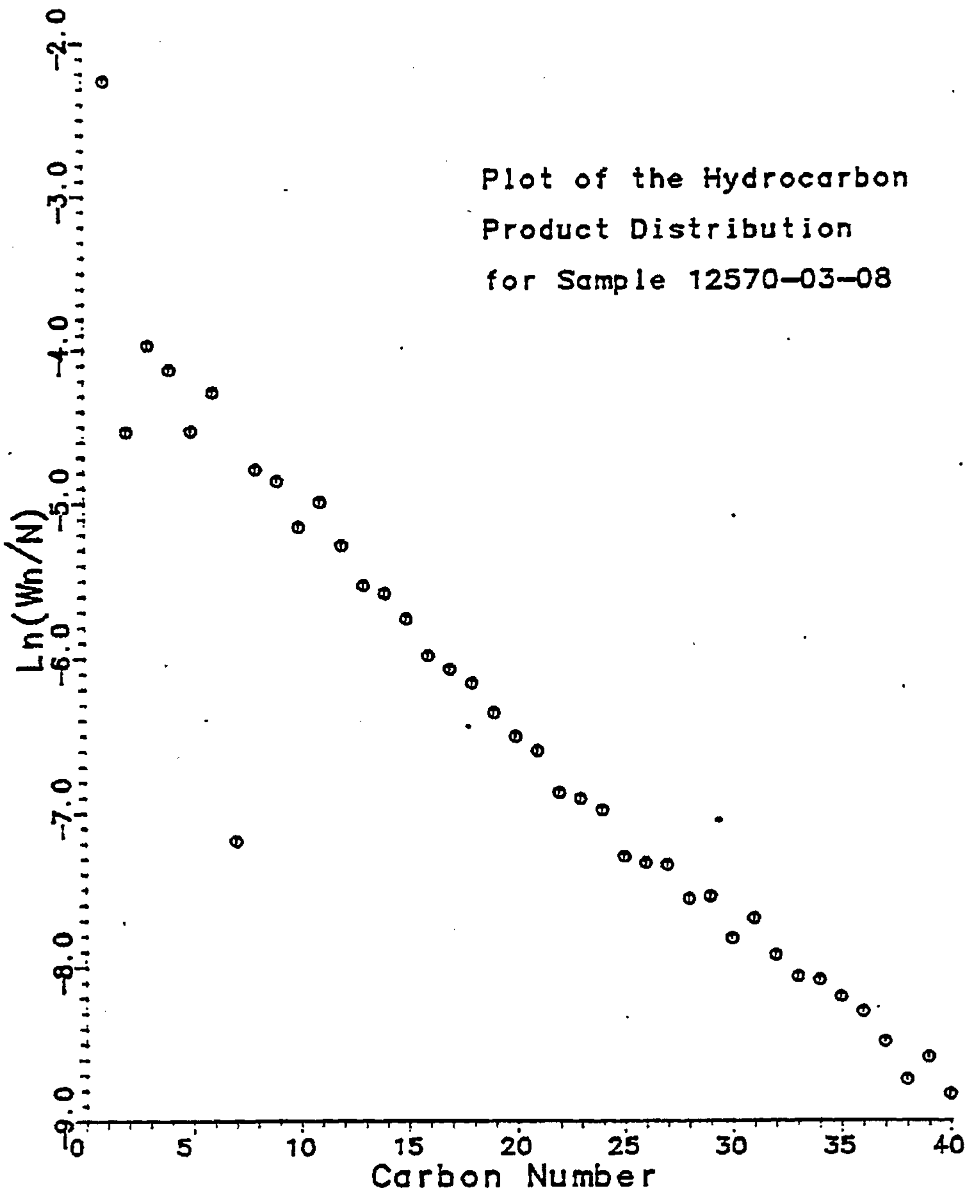

Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-08
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B58

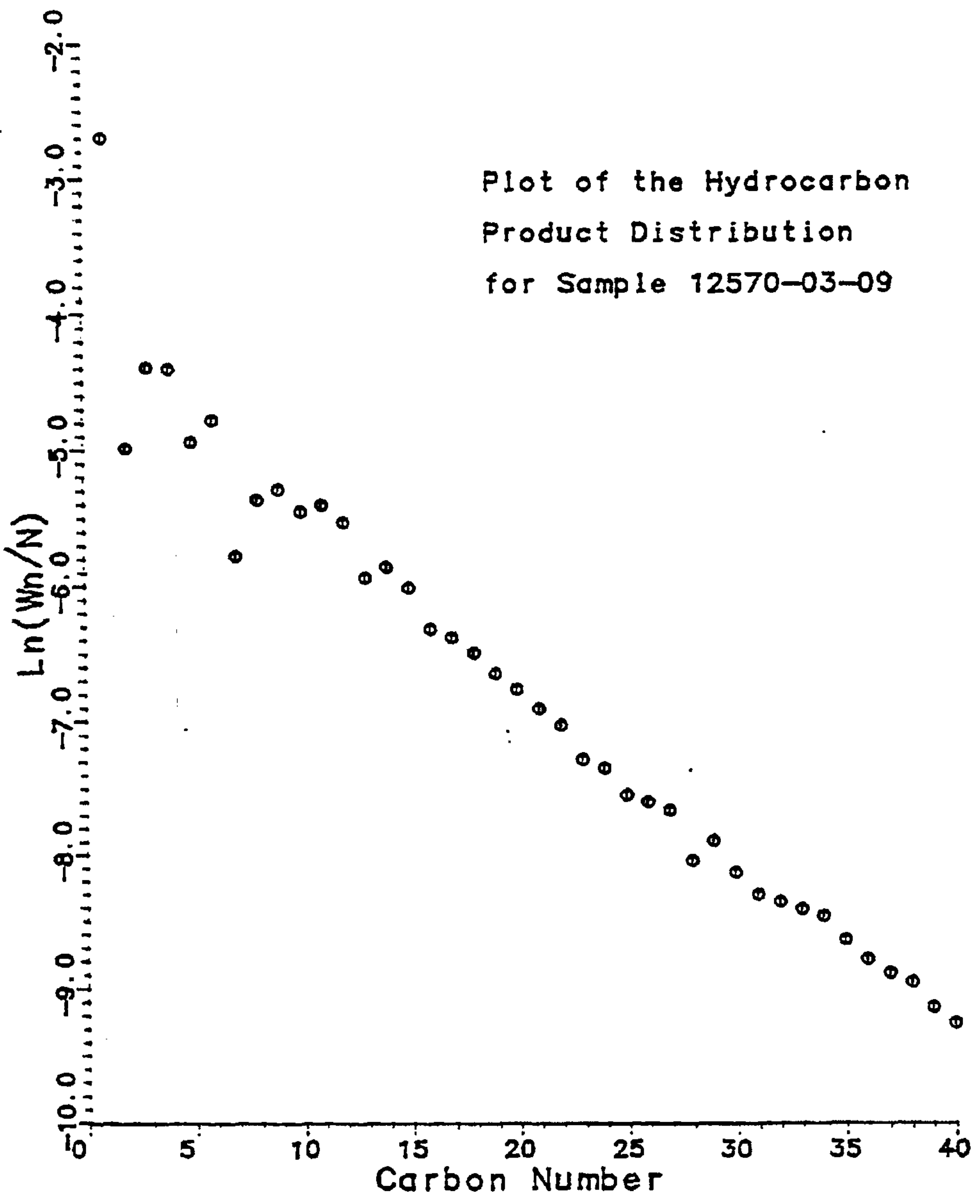
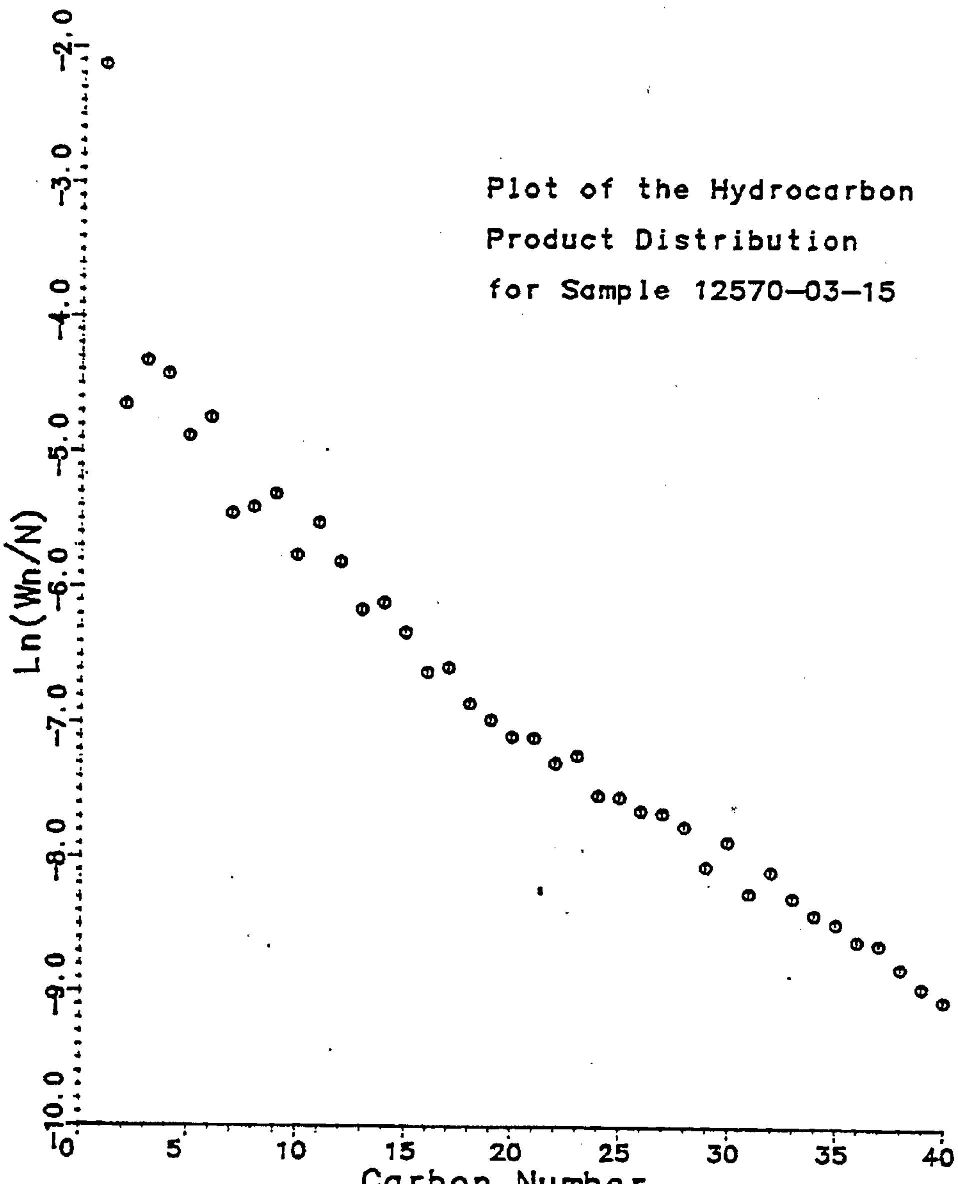
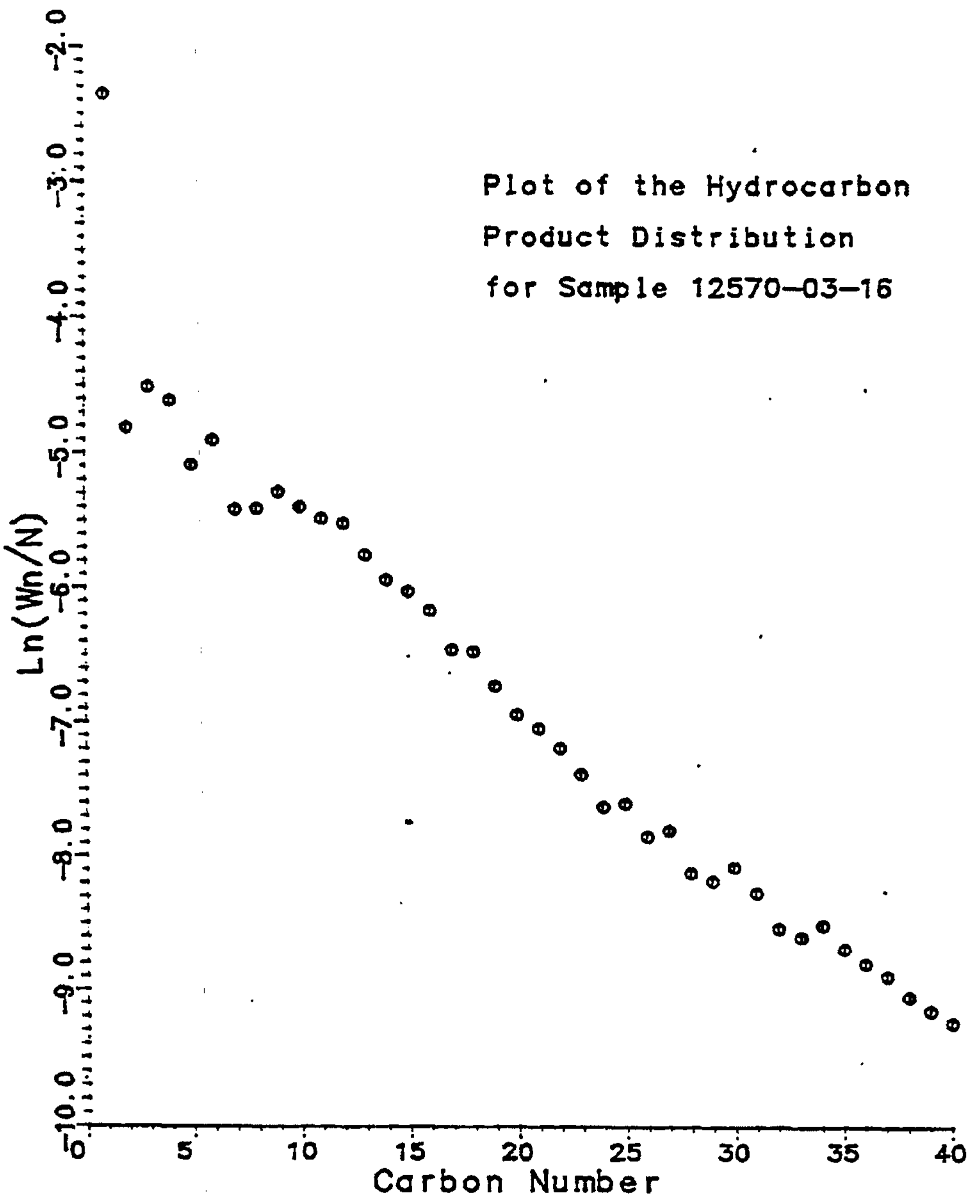

Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-09
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B59


Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-15
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. B60


Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-16
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B61

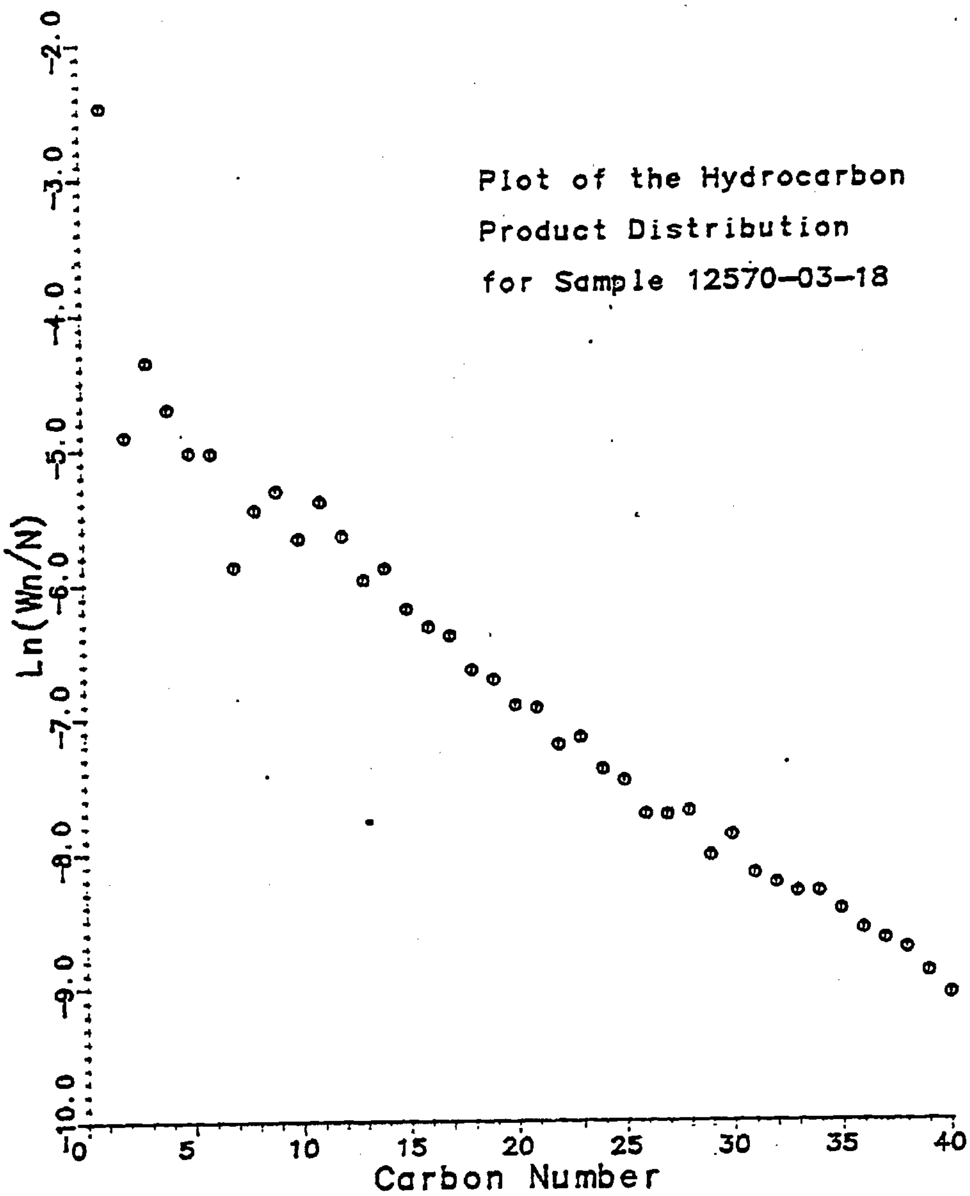
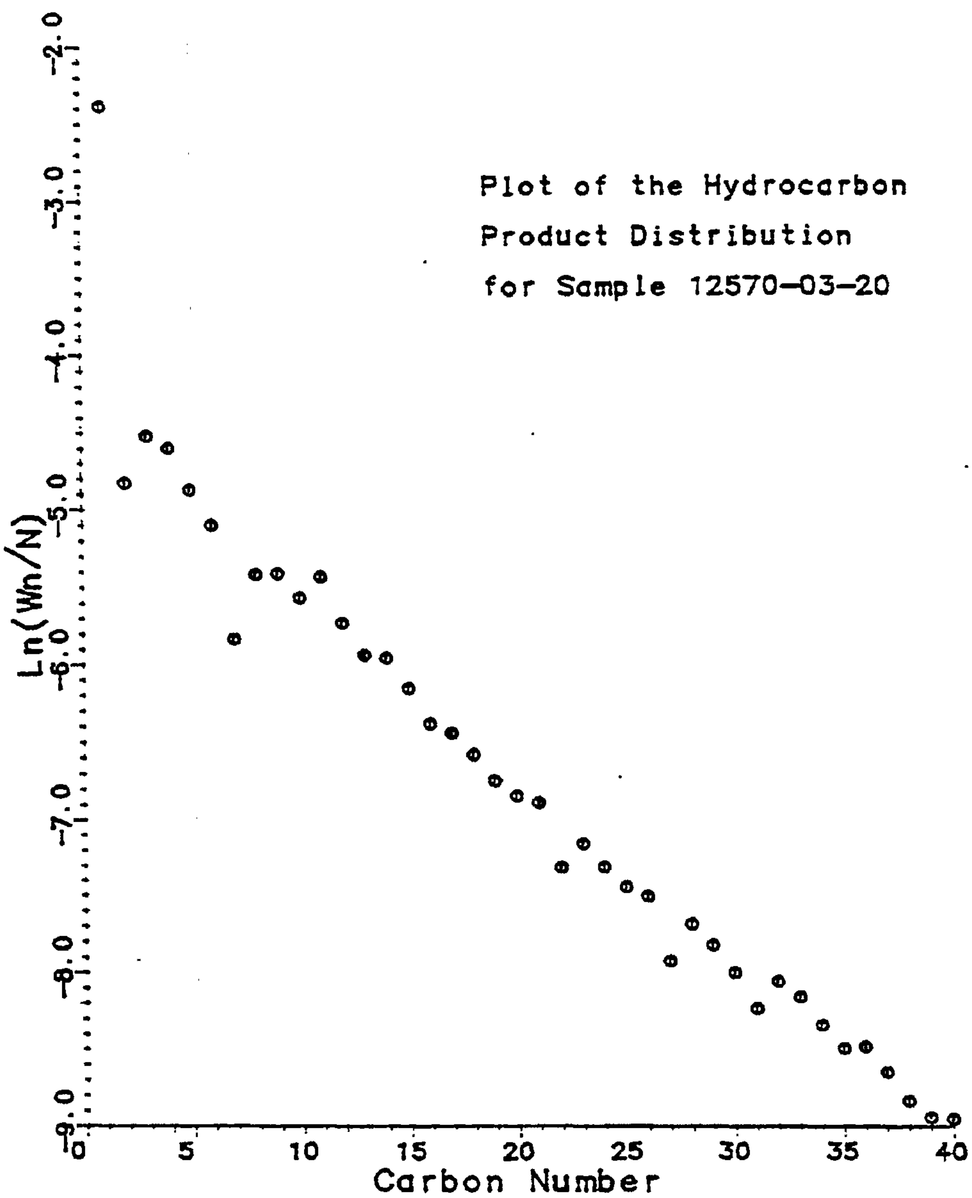

Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-18
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B62



Plot of the Hydrocarbon
Product Distribution
for Sample 12570-03-20
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B63

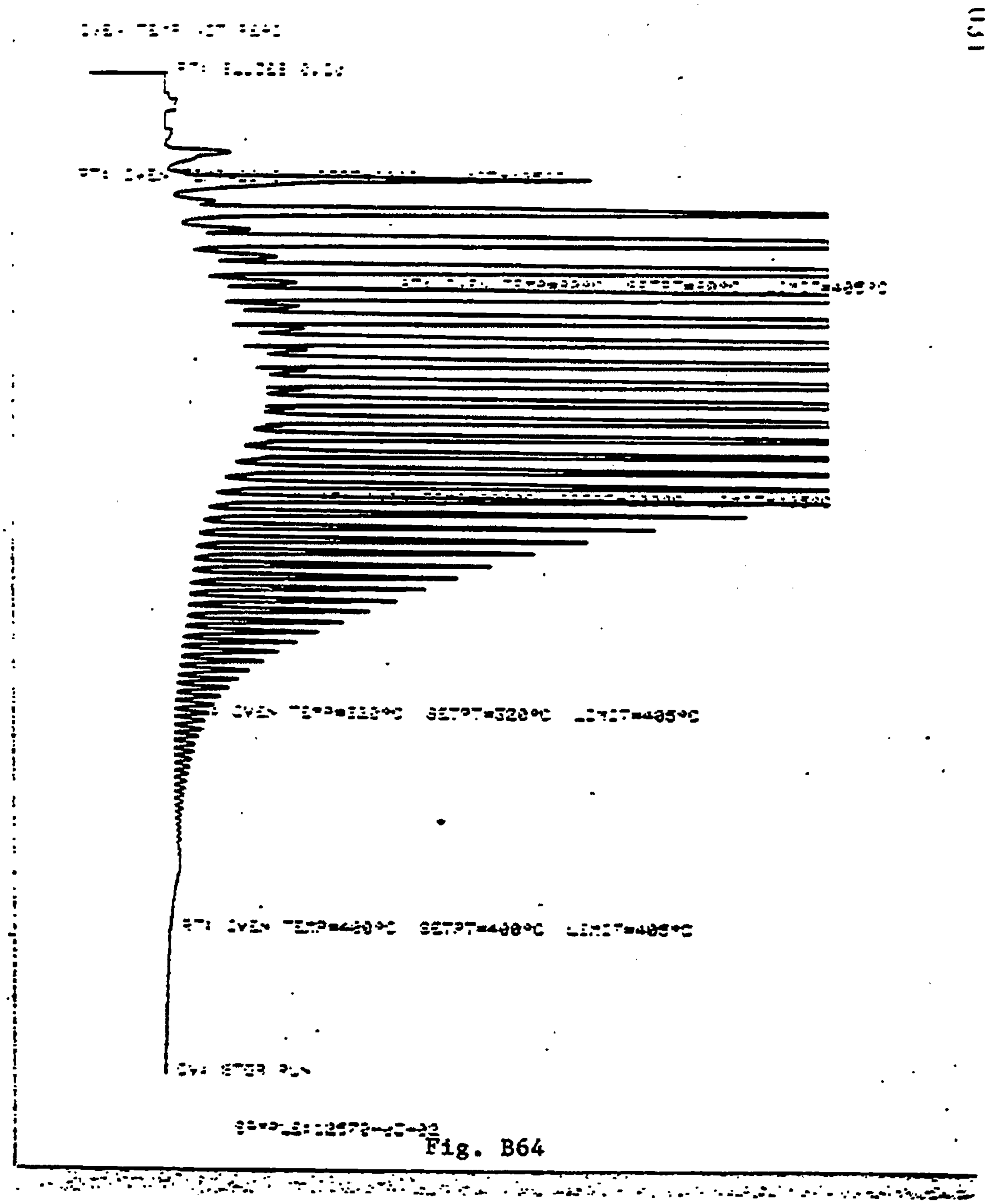


Fig. B64

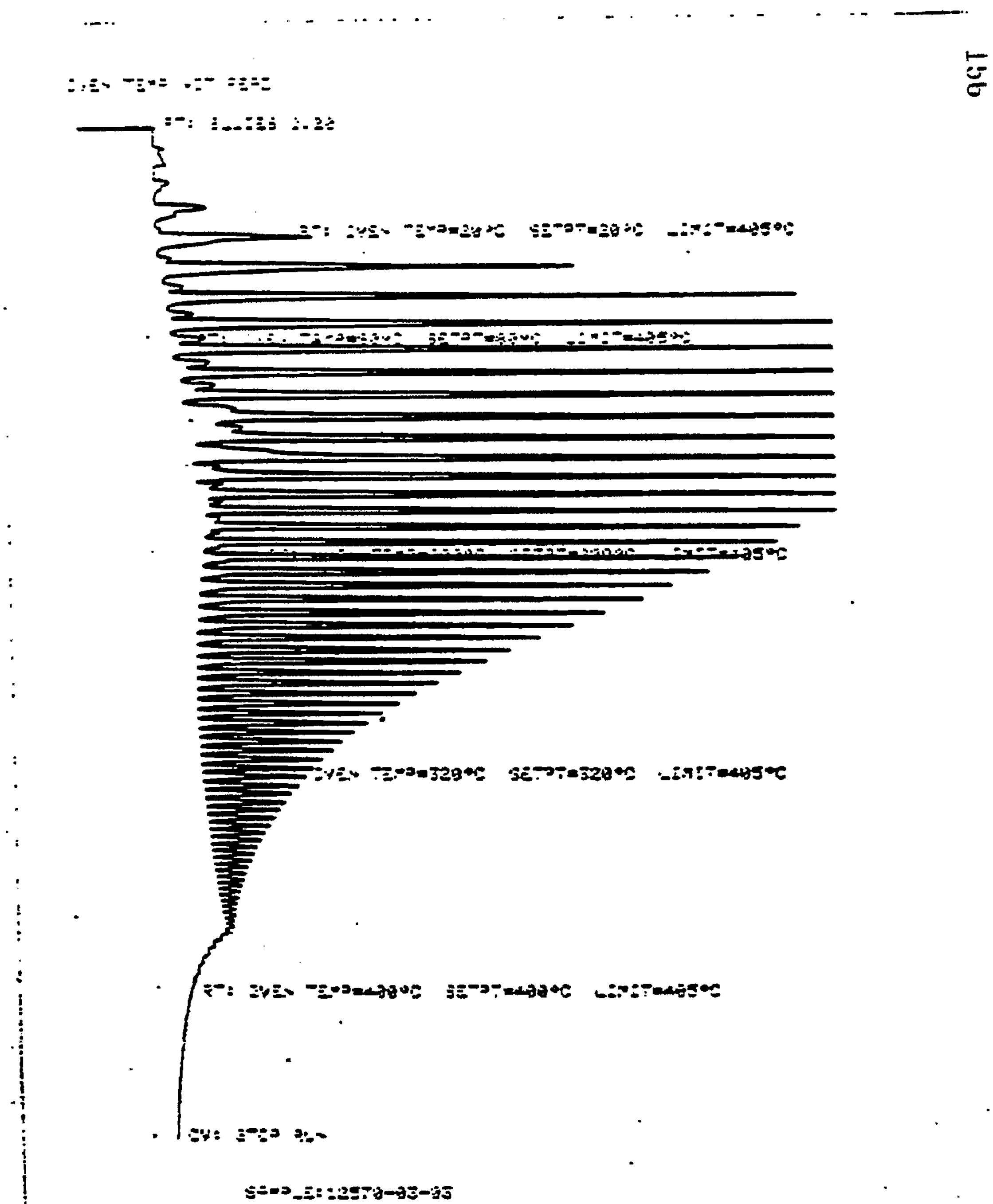


Fig. B65

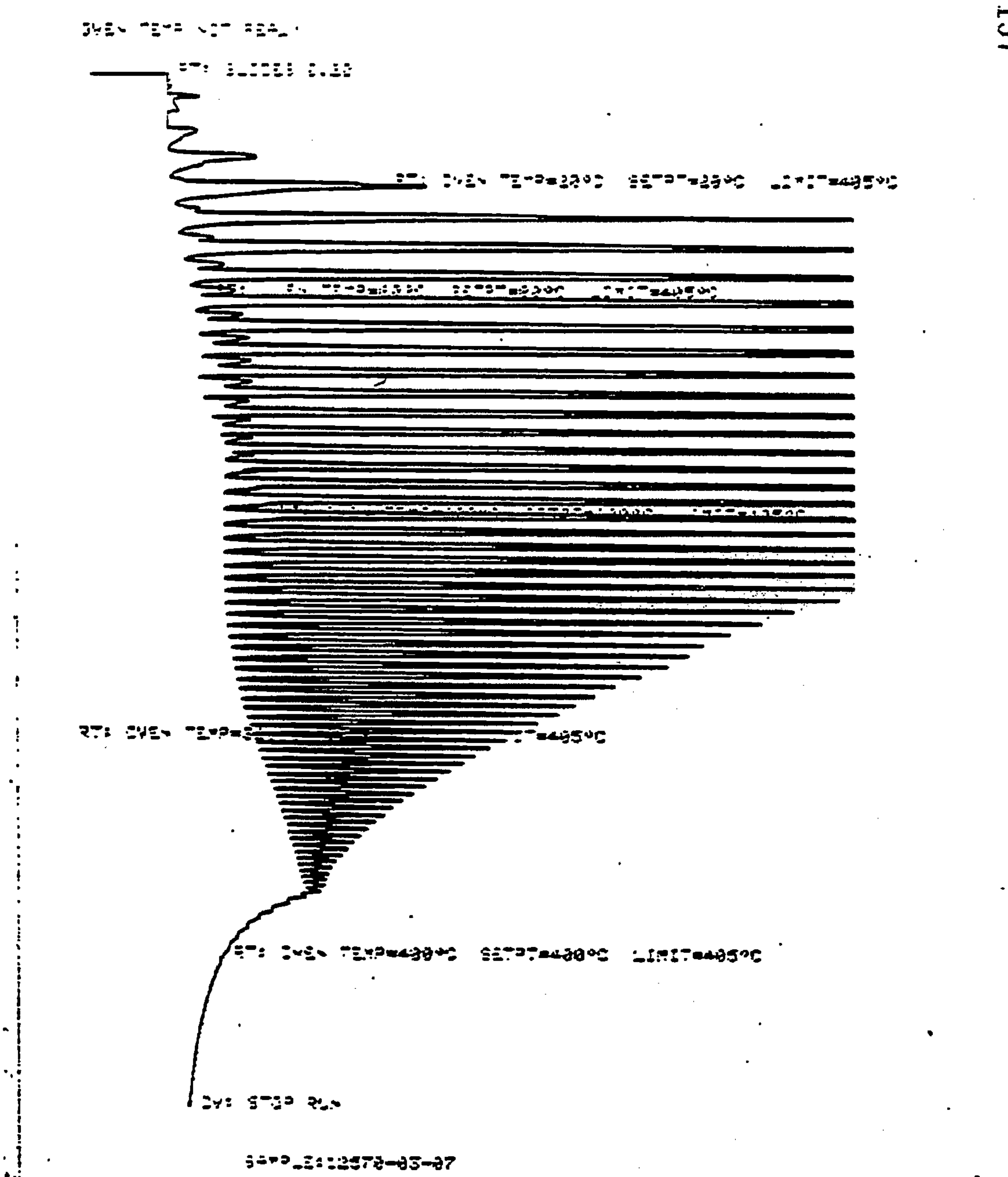


Fig. B66

158

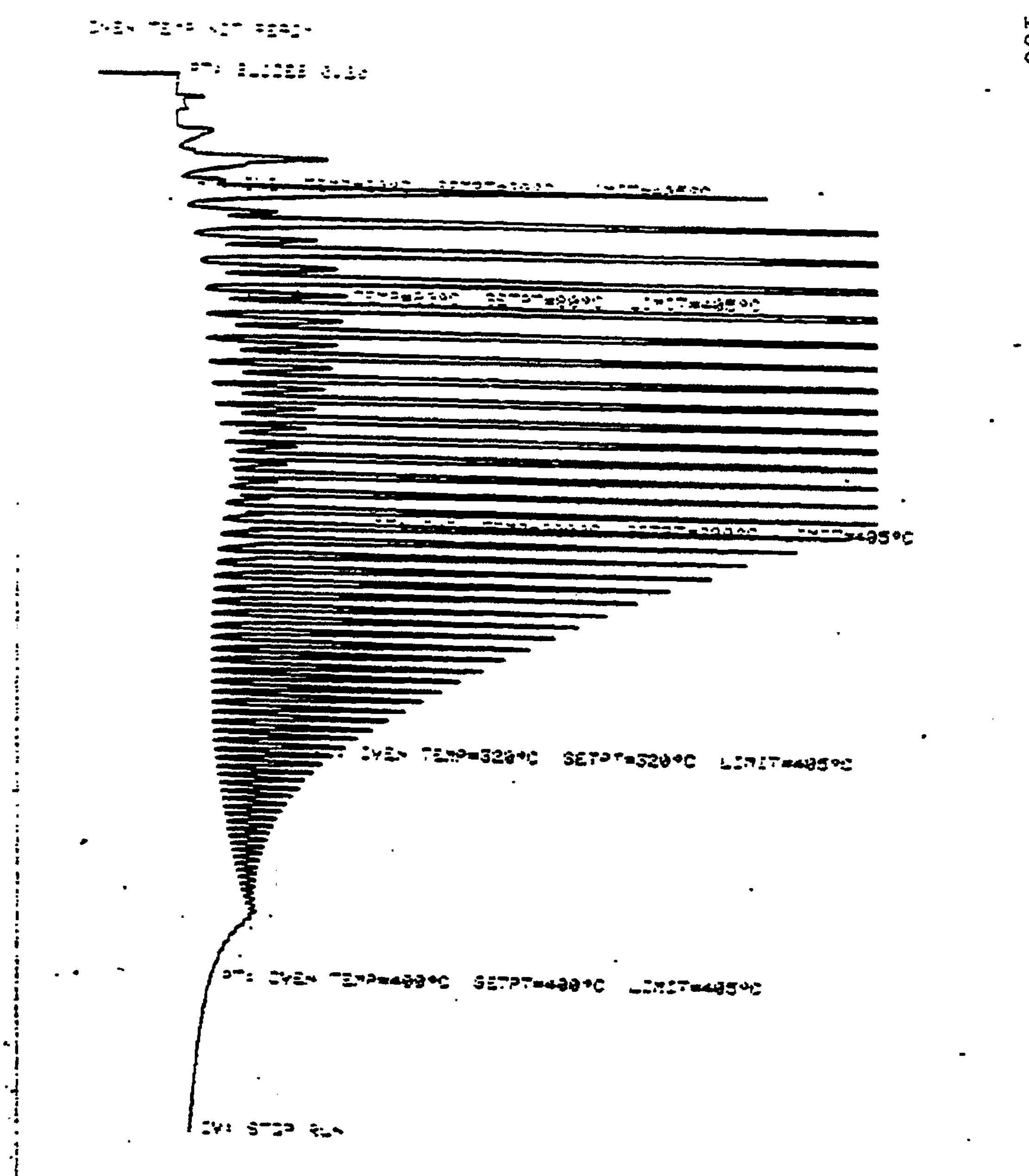


Fig. B67

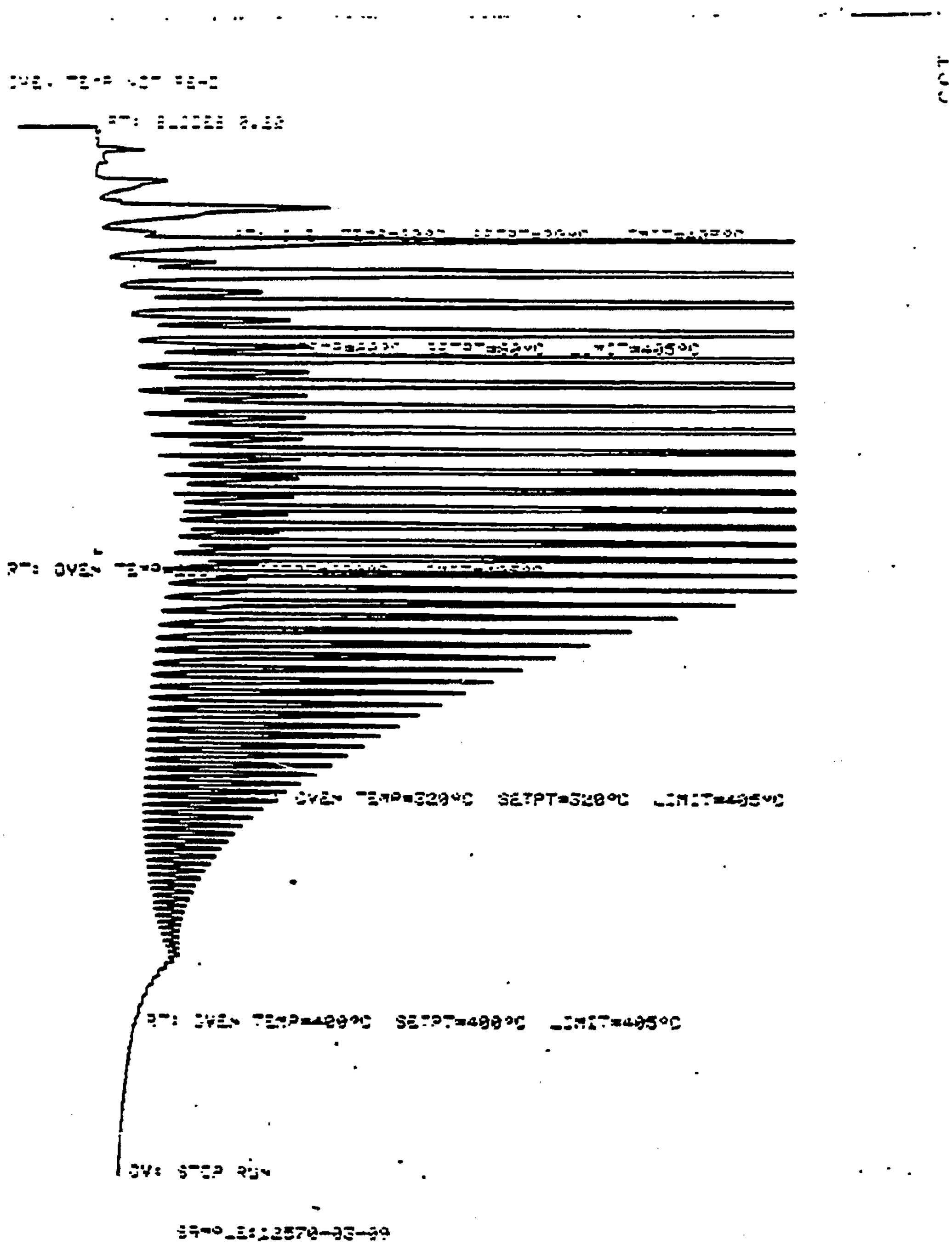


Fig. B68

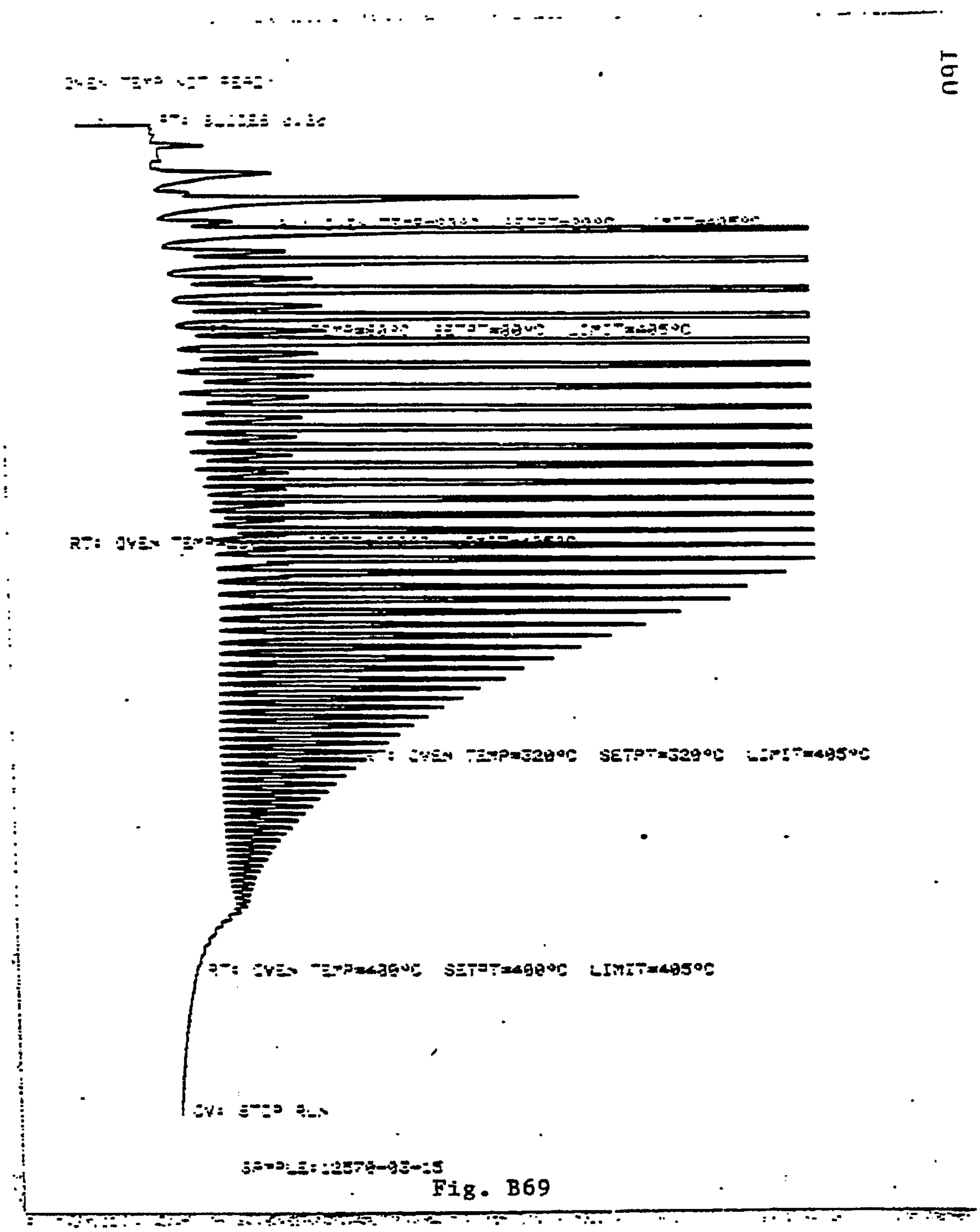


Fig. B69

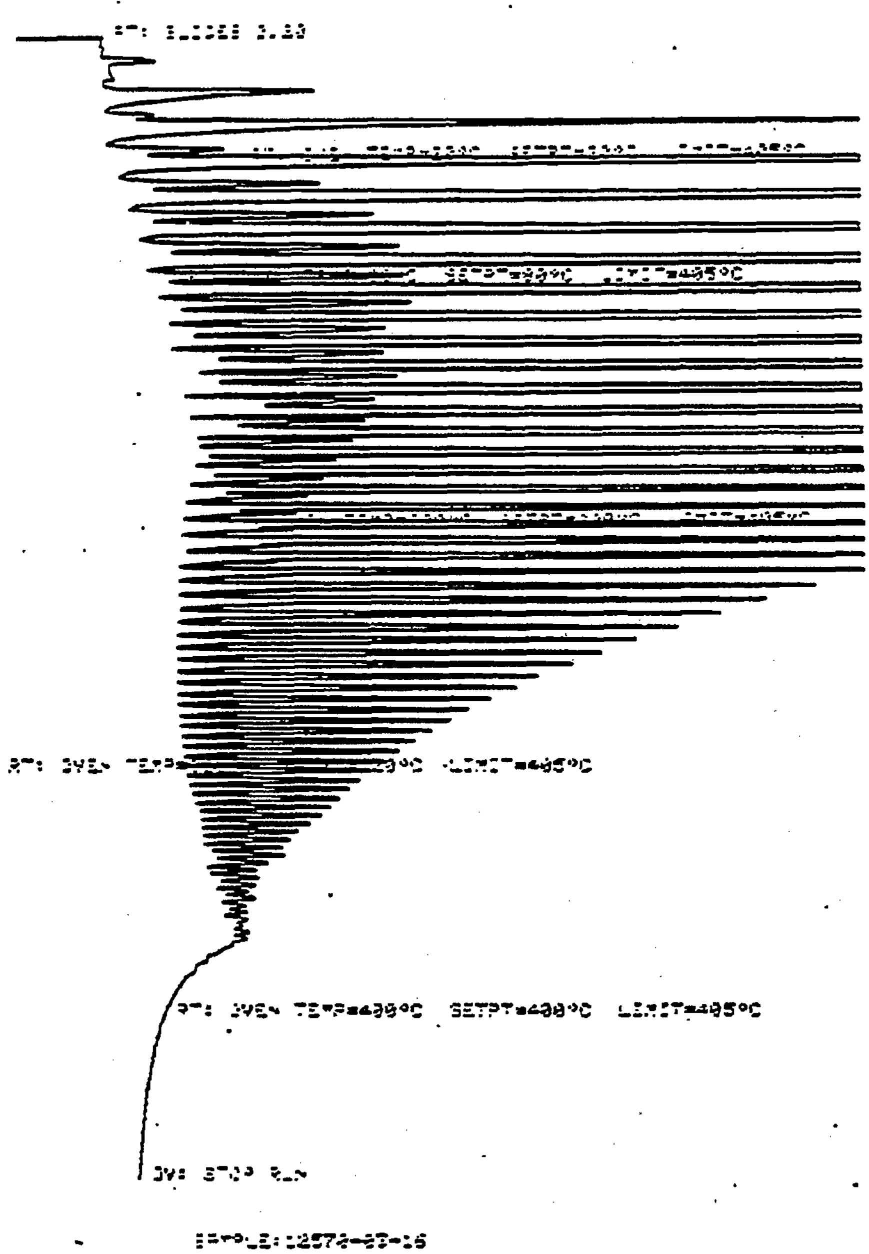


Fig. B70

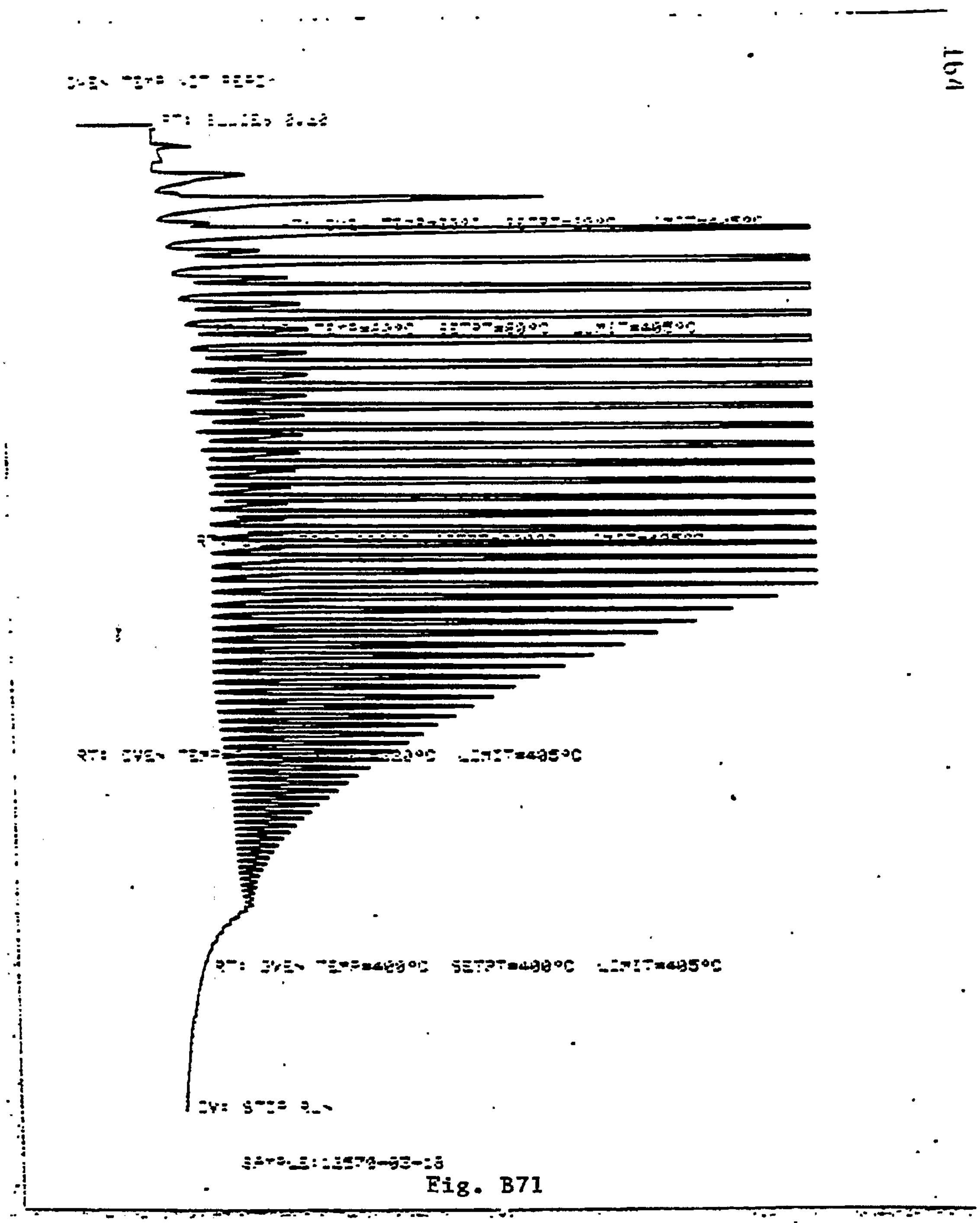


Fig. B71

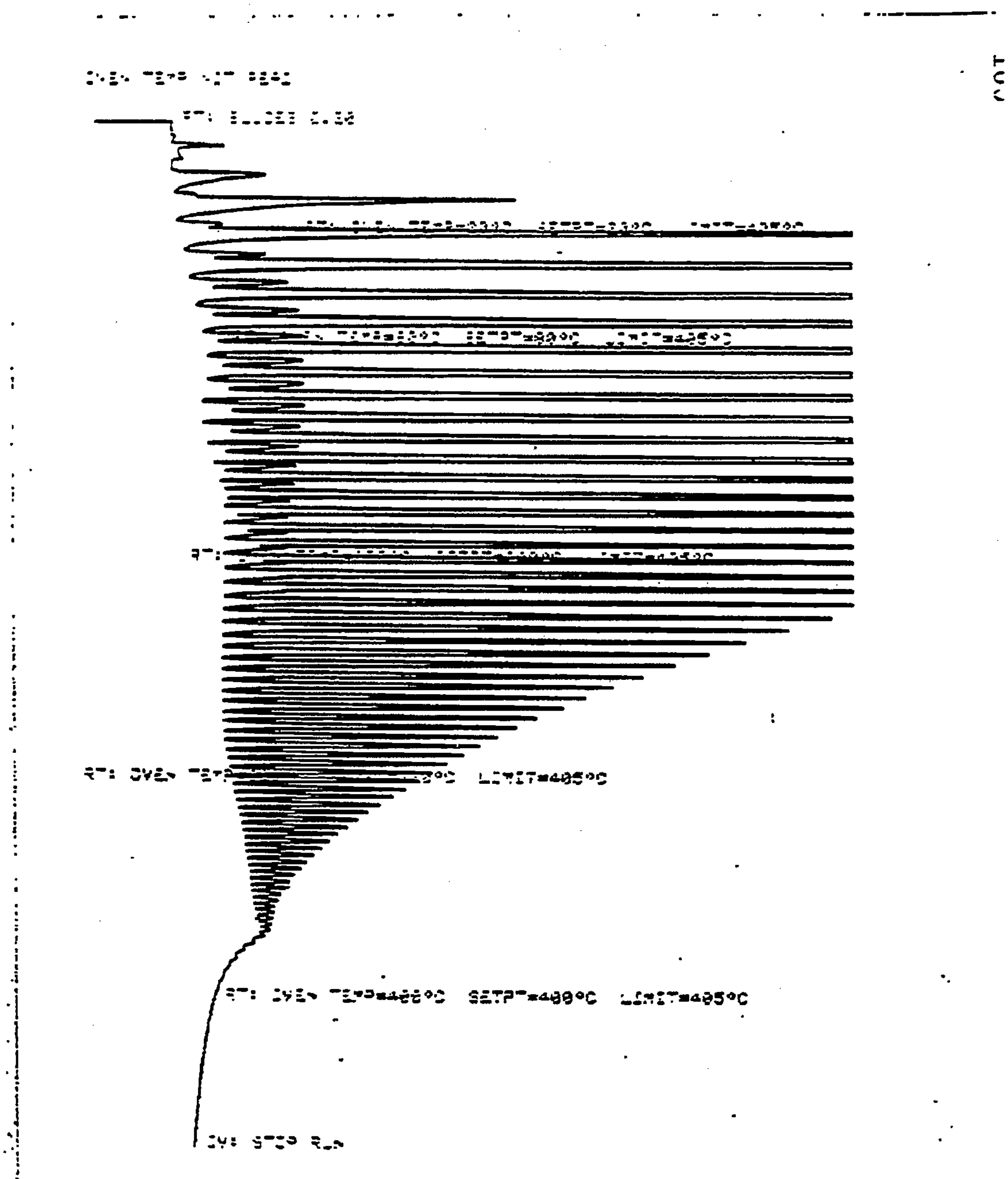


Fig. B72

Table B6

FILE: 1257003A T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12570-03
CATALYST CO/X9/X11-TC123 80 CC 41.3 G AFTER USE:60.2 G (+18.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-27)

RUN & SAMPLE NO.	12570-03-02	570-03-03	570-03-04	570-03-05	570-03-06
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	21.50	45.50	69.50	93.50	118.5
PRESSURE,PSIG	300.00	300.00	298.60	300.00	293.00
TEMP. C	239.00	239.00	239.00	239.00	239.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	17.00	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	180.65	306.95	304.45	310.00	324.74
GM AQUEOUS LAYER	44.58	48.61	48.29	48.09	48.12
GM OIL	8.68	38.04	39.09	37.68	42.58
MATERIAL BALANCE					
GM ATOM CARBON %	66.83	94.20	94.46	94.61	100.47
GM ATOM HYDROGEN %	75.30	91.82	92.26	91.49	97.71
GM ATOM OXYGEN %	87.28	92.54	91.52	92.84	95.24
RATIO CHX/(H2O+CO2)	0.3754	1.0627	1.1129	1.0678	1.2010
RATIO X IN CHX	2.2781	2.1959	2.1885	2.1921	2.1831
USAGE H2/CO PRODT	3.2557	1.8648	1.8497	1.8808	1.8052
FEED H2/CO FRM EFFLNT	1.1268	0.9747	0.9767	0.9671	0.9725
RESIDUAL H2/CO RATIO	0.5691	0.5612	0.5607	0.5579	0.5733
RATIO CO2/(H2O+CO2)	0.0483	0.0646	0.0559	0.0563	0.0510
K SHIFT IN EFFLNT	0.0289	0.0387	0.0332	0.0333	0.0308
SPECIFIC ACTIVITY SA	1.7570	3.0447	3.1785	3.0559	3.1750
CONVERSION					
ON CO %	20.76	31.72	32.27	30.93	32.41
ON H2 %	59.98	60.69	61.12	60.16	60.15
ON CO+H2 %	41.53	46.02	46.53	45.30	46.09
PRDT SELECTIVITY,WT %					
CH4	8.48	4.00	3.54	3.72	3.25
C2 HC'S	1.09	0.60	0.64	0.62	0.64
C3H8	1.65	0.77	0.79	0.86	0.79
C3H6=	3.30	1.79	1.79	1.95	1.81
C4H10	2.09	0.89	0.90	0.97	0.88
C4H8=	4.67	2.34	2.51	2.65	2.39
C5H12	2.33	1.13	1.15	1.21	1.13
C5H10=	3.27	1.51	1.70	0.18	1.42
C6H14	3.80	1.82	1.86	1.81	1.74
C6H12= & CYCLO'S	2.14	1.31	1.24	1.43	1.25
C7+ IN GAS	8.39	3.73	3.95	4.17	3.75
LIQ HC'S	58.80	80.11	79.92	80.43	80.95
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	21.27	10.40	10.18	10.78	9.76
C5 -420 F	35.80	21.75			
420-700 F	34.28	32.37			
700-END PT	8.64	35.49			

Table B6 (continued)

FILE: 1257003A T6Q1   A1

C5+-END PT	78.73	89.60	89.82	89.22	90.24
ISO/NORMAL MOLE RATIO					
C4	0.1332	0.0000	0.0000	0.0000	0.0000
C5	0.0483	0.0562	0.0259	0.0000	0.0347
C6	0.3475	0.3428	0.1900	0.1523	0.2072
C4=	0.0534	0.0445	0.0266	0.0261	0.0155
PARAFFIN/OLEFIN RATIO					
C3	0.4766	0.4112	0.4178	0.4201	0.4157
C4	0.4314	0.3678	0.3474	0.3533	0.3537
C5	0.6933	0.7311	0.6584	6.4536	0.7770
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8429	0.9084			
RATIO CH4/(1-A)**2	3.4366	4.7664			
ALPHA FRM CORRELATION	0.8395	0.8401			
ALPHA (EXPTL/CORR)	1.0041	1.0812			
W%CH4 FRM CORRELATION	13.0182	12.8053			
W%CH4 (EXPTL/CORR)	0.6512	0.3124			
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N. REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	343.00	381.00			
16	380.00	422.00			
50	515.00	664.00			
84	690.00	945.00			
90	753.00	1034.00			
RANGE(16-84 %)	310.00	523.00			
WT % @ 420 F	27.00	15.30			
WT % @ 700 F	85.30	55.70			

Table B7

FILE: 1257003B T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12570-03
CATALYST CO/X9/X11-TC123 80 CC 41.3 G AFTER USE:60.2 G (+18.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-27)

RUN & SAMPLE NO.	12570-03-07	570-03-08	570-03-09	570-03-10	570-03-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	166.50	190.50	214.50	238.50	267.50
PRESSURE,PSIG	300.00	297.00	299.00	300.00	300.00
TEMP. C	238.00	260.00	259.00	259.00	259.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	48.00	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	628.56	266.85	262.95	265.10	286.99
GM AQUEOUS LAYER	93.91	51.70	54.72	55.95	54.87
GM OIL	71.19	40.54	40.25	38.88	38.44
MATERIAL BALANCE					
GM ATOM CARBON %	94.37	85.17	93.53	92.64	98.69
GM ATOM HYDROGEN %	91.90	80.14	92.09	92.53	94.36
GM ATOM OXYGEN %	92.09	91.95	91.20	91.37	96.73
RATIO CHX/(H2O+CO2)	1.0902	0.7859	1.0731	1.0397	1.0614
RATIO X IN CHX	2.1861	2.2788	2.2565	2.2574	2.2595
USAGE H2/CO PRODT	1.8854	1.7754	1.6970	1.7437	1.7209
FEED H2/CO FRM EFFLNT	0.9738	0.9410	0.9846	0.9987	0.9561
RESIDUAL H2/CO RATIO	0.5749	0.4727	0.4764	0.4877	0.4708
RATIO CO2/(H2O+CO2)	0.0472	0.1802	0.1445	0.1314	0.1369
K SHIFT IN EFFLNT	0.0285	0.1039	0.0804	0.0738	0.0747
SPECIFIC ACTIVITY SA	2.9688	1.4817	1.8516	1.7266	1.7046
CONVERSION					
ON CO %	30.44	35.94	41.64	40.69	38.82
ON H2 %	58.94	67.82	71.76	71.03	69.87
ON CO+H2 %	44.50	51.40	56.58	55.85	54.00
PRDT SELECTIVITY,WT %					
CH4	3.51	10.59	6.77	6.85	7.01
C2 HC'S	0.57	2.15	1.38	1.42	1.49
C3H8	0.90	2.52	1.58	1.57	1.62
C3H6=	2.03	3.16	2.18	2.21	2.29
C4H10	1.02	2.43	1.58	1.55	1.58
C4H8=	2.77	4.02	3.36	3.35	3.50
C5H12	1.28	3.15	2.02	2.03	2.04
C5H10=	3.37	2.26	1.58	1.53	2.27
C6H14	2.17	5.27	3.19	3.27	3.55
C6H12= & CYCLO'S	1.34	3.08	1.90	2.00	2.20
C7+ IN GAS	4.30	8.56	5.20	5.59	5.55
LIQ HC'S	76.74	52.80	69.27	68.63	66.90
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	10.80	24.88	16.84	16.95	17.49
C5 -420 F	24.35	4.08	32.59		
420-700 F	26.24	38.88	29.37		
700-END PT	38.60	32.16	21.20		

Table B7 (continued)

FILE: 1257003B T6Q1 A1

C5+-END PT	89.20	75.12	83.16	83.05	82.51
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0195	0.0192	0.0158	0.0000
C5	0.0000	0.0471	0.0464	0.0468	0.0000
C6	0.2075	0.3706	0.3237	0.2901	0.2358
C4=	0.0280	0.0719	0.0504	0.0499	0.0483
PARAFFIN/OLEFIN RATIO					
C3	0.4225	0.7590	0.6920	0.6786	0.6726
C4	0.3569	0.5841	0.4542	0.4460	0.4368
C5	0.3704	1.3526	1.2441	1.2920	0.8749
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8940	0.8650	0.8686		
RATIO CH4/(1-A)**2	3.1202	5.8137	3.9212		
ALPHA FRM CORRELATION	0.8390	0.8473	0.8470		
ALPHA (EXPTL/CORR)	1.0655	1.0209	1.0256		
W%CH4 FRM CORRELATION	12.9241	15.1865	15.0740		
W%CH4 (EXPTL/CORR)	0.2714	0.6975	0.4490		
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	381.00	333.00	306.00		
16	421.00	373.00	348.00		
50	703.00	573.00	568.00		
84	1015.00	882.00	852.00		
90	1093.00	970.00	940.00		
RANGE(16-84 %)	594.00	509.00	504.00		
WT % @ 420 F	15.50	26.00	27.00		
WT % @ 700 F	49.70	66.50	69.40		

Table B8

FILE: 1257003C TSQ1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12570-03
CATALYST CO/X9/X11-TC123 80 CC 41.3 G AFTER USE;60.2 G (+18.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-27)

RUN & SAMPLE NO.	12570-03-12	570-03-13	570-03-14	570-03-15	570-03-16
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	60:40: 0	60:40: 0
HRS ON STREAM	287.50	310.50	334.50	358.50	383.50
PRESSURE,PSIG	298.00	298.00	299.50	500.00	500.00
TEMP. C	259.00	259.00	259.00	259.00	260.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	25.00	47.00	24.00	23.00	25.00
EFFLNT GAS LITER	278.76	535.54	271.90	163.63	155.70
GM AQUEOUS LAYER	58.80	111.28	54.72	67.98	83.99
GM OIL	42.59	78.40	39.89	50.23	57.13
MATERIAL BALANCE					
GM ATOM CARBON %	95.70	97.54	96.84	100.15	92.67
GM ATOM HYDROGEN %	93.46	93.97	92.57	90.94	90.48
GM ATOM OXYGEN %	92.91	94.69	93.32	92.91	90.46
RATIO CHX/(H2O+CO2)	1.0869	1.0886	1.1127	1.1369	1.0399
RATIO X IN CHX	2.2493	2.2475	2.2545	2.3668	2.3164
USAGE H2/CO PRODT	1.7388	1.7471	1.7289	1.6292	1.7829
FEED H2/CO FRM EFFLNT	0.9766	0.9634	0.9559	1.3622	1.4646
RESIDUAL H2/CO RATIO	0.4571	0.4457	0.4458	0.7420	0.7318
RATIO CO2/(H2O+CO2)	0.1214	0.1170	0.1211	0.1875	0.1259
K SHIFT IN EFFLNT	0.0632	0.0591	0.0614	0.1713	0.1054
SPECIFIC ACTIVITY SA	1.8967	1.9090	1.9100	1.4234	1.3426
CONVERSION					
ON CO %	40.53	39.78	39.76	69.90	69.71
ON H2 %	72.17	72.14	71.91	83.60	84.87
ON CO+H2 %	56.16	55.66	55.47	77.80	78.72
PRDT SELECTIVITY,WT %					
CH4	6.48	6.41	6.76	11.89	9.50
C2 HC'S	1.29	1.33	1.30	1.91	1.63
C3H8	1.48	1.50	1.53	2.74	2.15
C3H6=	2.18	2.26	2.27	1.22	1.15
C4H10	1.50	1.54	1.56	2.36	1.86
C4H8=	3.26	3.46	3.41	2.41	2.14
C5H12	2.09	2.14	2.11	2.94	2.31
C5H10=	1.66	2.42	2.33	0.86	0.78
C6H14	3.28	3.58	3.43	3.98	3.29
C6H12= & CYCLO'S	2.16	2.22	2.04	1.25	1.15
C7+ IN GAS	5.38	5.61	5.39	4.54	4.07
LIQ HC'S	69.25	67.54	67.87	63.91	69.97
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	16.19	16.49	16.83	22.52	18.43
C5 -420 F				30.83	32.24
420-700 F				22.43	28.41
700-END PT				24.22	20.92

Table B8 (continued)

FILE: 1257003C T6Q1 A1

C5+-END PT	83.81	83.51	83.17	77.48	81.57
ISO/NORMAL MOLE RATIO					
C4	0.0166	0.0140	0.0152	0.0262	0.0234
C5	0.0464	0.0454	0.0464	0.0666	0.0617
C6	0.2936	0.3661	0.3746	0.2971	0.3106
C4=	0.0482	0.0470	0.0483	0.0848	0.0765
PARAFFIN/OLEFIN RATIO					
C3	0.6457	0.6344	0.6432	2.1473	1.7838
C4	0.4427	0.4293	0.4411	0.9478	0.8397
C5	1.2204	0.8620	0.8780	3.3076	2.8613
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))				0.8678	0.8661
RATIO CH4/(1-A)**2				6.8032	5.2997
ALPHA FRM CORRELATION				0.8254	0.8260
ALPHA (EXPTL/CORR)				1.0514	1.0486
W%CH4 FRM CORRELATION				21.7723	21.7921
W%CH4 (EXPTL/CORR)				0.5460	0.4360
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F				302.00	301.00
16				346.00	344.00
50				596.00	546.00
84				919.00	874.00
90				1004.00	978.00
RANGE(16-84 %)				573.00	530.00
WT % @ 420 F				27.00	29.50
WT % @ 700 F				62.10	70.10

Table B9

FILE: 1257003D T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12570-03
CATALYST CO/X9/X11-TC123 80 CC 41.3 G AFTER USE:60.2 G (+18.9 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV (CAT#12524-27)

RUN & SAMPLE NO.	12570-03-17	570-03-18	570-03-19	570-03-20
FEED H2:CO:AR	60:40: 0	60:40: 0	60:40: 0	60:40: 0
HRS ON STREAM	407.50	429.00	456.00	478.50
PRESSURE,PSIG	500.00	500.00	500.00	500.00
TEMP. C	260.00	260.00	260.00	260.00
FEED CC/MIN	400.00	400.00	400.00	400.00
HOURS FEEDING	24.00	21.50	26.00	22.50
EFFLNT GAS LITER	151.50	139.50	172.20	151.90
GM AQUEOUS LAYER	81.48	70.57	87.81	76.75
GM OIL	54.56	54.47	57.46	51.06
MATERIAL BALANCE				
GM ATOM CARBON %	92.82	98.49	92.28	94.38
GM ATOM HYDROGEN %	91.42	94.18	90.66	92.36
GM ATOM OXYGEN %	90.99	89.14	90.86	91.80
RATIO CHX/(H2O+CO2)	1.0326	1.1758	1.0264	1.0475
RATIO X IN CHX	2.3289	2.2925	2.3136	2.3068
USAGE H2/CO PRODT	1.7970	1.7449	1.8613	1.8559
FEED H2/CO FRM EFFLNT	1.4774	1.4343	1.4736	1.4680
RESIDUAL H2/CO RATIO	0.7444	0.7346	0.7306	0.7292
RATIO CO2/(H2O+CO2)	0.1240	0.1079	0.0968	0.0925
K SHIFT IN EFFLNT	0.1054	0.0888	0.0783	0.0743
SPECIFIC ACTIVITY SA	1.3289	1.3074	1.1577	1.1398
CONVERSION				
ON CO %	69.63	69.26	65.71	65.58
ON H2 %	84.70	84.26	83.00	82.90
ON CO+H2 %	78.62	78.10	76.01	75.88
PRDT SELECTIVITY,WT %				
CH4	10.12	8.47	9.46	9.20
C2 HC'S	1.73	1.48	1.56	1.60
C3H8	2.31	1.89	2.05	2.01
C3H6=	1.17	1.98	1.28	1.25
C4H10	1.94	1.65	1.82	1.77
C4H8=	2.20	2.00	2.16	2.25
C5H12	2.30	2.05	2.24	2.18
C5H10=	0.75	1.26	1.38	1.66
C6H14	3.14	2.85	2.99	2.56
C6H12= & CYCLO'S	1.10	1.09	1.15	1.10
C7+ IN GAS	3.79	3.61	3.52	3.94
LIQ HC'S	69.46	71.67	70.39	70.46
TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	19.46	17.47	18.33	18.09
C5 -420 F		29.49		29.41
420-700 F		27.23		26.78
700-END PT		25.80		25.72

Table B9 (continued)

FILE: 12S7003D T6Q1 A1

C5+-END PT	80.54	82.53	81.67	81.91
ISO/NORMAL MOLE RATIO				
C4	0.0251	0.0246	0.0257	0.0243
C5	0.0628	0.0604	0.0568	0.0589
C6	0.2367	0.2254	0.2311	0.0809
C4=	0.0787	0.0746	0.0208	0.0750
PARAFFIN/OLEFIN RATIO				
C3	1.8763	0.9070	1.5299	1.5369
C4	0.8507	0.7959	0.8137	0.7611
C5	2.9852	1.5852	1.5786	1.2796
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))		0.8757		0.8772
RATIO CH4/(1-A)**2		5.4785		6.1008
ALPHA FRM CORRELATION		0.8258		0.8262
ALPHA (EXPTL/CORR)		1.0604		1.0618
W%CH4 FRM CORRELATION		21.8482		21.7368
W%CH4 (EXPTL/CORR)		0.3875		0.4233
LIQ HC COLLECTION				
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY				
N, REFRACTIVE INDEX				
SIMULT'D DISTILATN				
10 WT % @ DEG F		304.00		304.00
16		348.00		349.00
50		592.00		595.00
84		917.00		909.00
90		1010.00		997.00
RANGE(16-84 %)		569.00		560.00
WT % @ 420 F		26.00		25.50
WT % @ 700 F		64.00		63.50

V. Run 52 (12561-03) with Quartz Chips

The purpose of this run was to test the reactor system for any residual Fischer-Tropsch activity. The reactor, containing quartz chips, was subjected to a typical activation procedure and exposed to syngas feed.

No residual activity was observed.

VI. Run 53 (12561-05) with Catalyst 53 ($Co/X_{11}/TC-123+K/Ni/Mo-\gamma$-alumina)

This run continued the search for ways to improve the water gas shift (WGS) activity of Co/TC-123 type catalysts. Previous attempts, which have consisted in adding to the Fischer-Tropsch formulation either new promoters or separate WGS catalysts, have been unsuccessful. The promoters tested showed little or no improvement, and the separate WGS catalysts have actually degraded the combined catalyst's overall performance, due apparently to mutual poisoning of the WGS and Fischer-Tropsch components (example, Catalyst 1, Fifteenth Quarterly Report, of the previous contract, DE-AC22-81PC40077).

The additive in this test was the WGS catalyst K/Ni/Mo-γ-alumina, reported by M. Kantschewa [J.Catal., (1984), 87, 482], which appears potentially compatible with the cobalt Fischer-Tropsch catalyst.

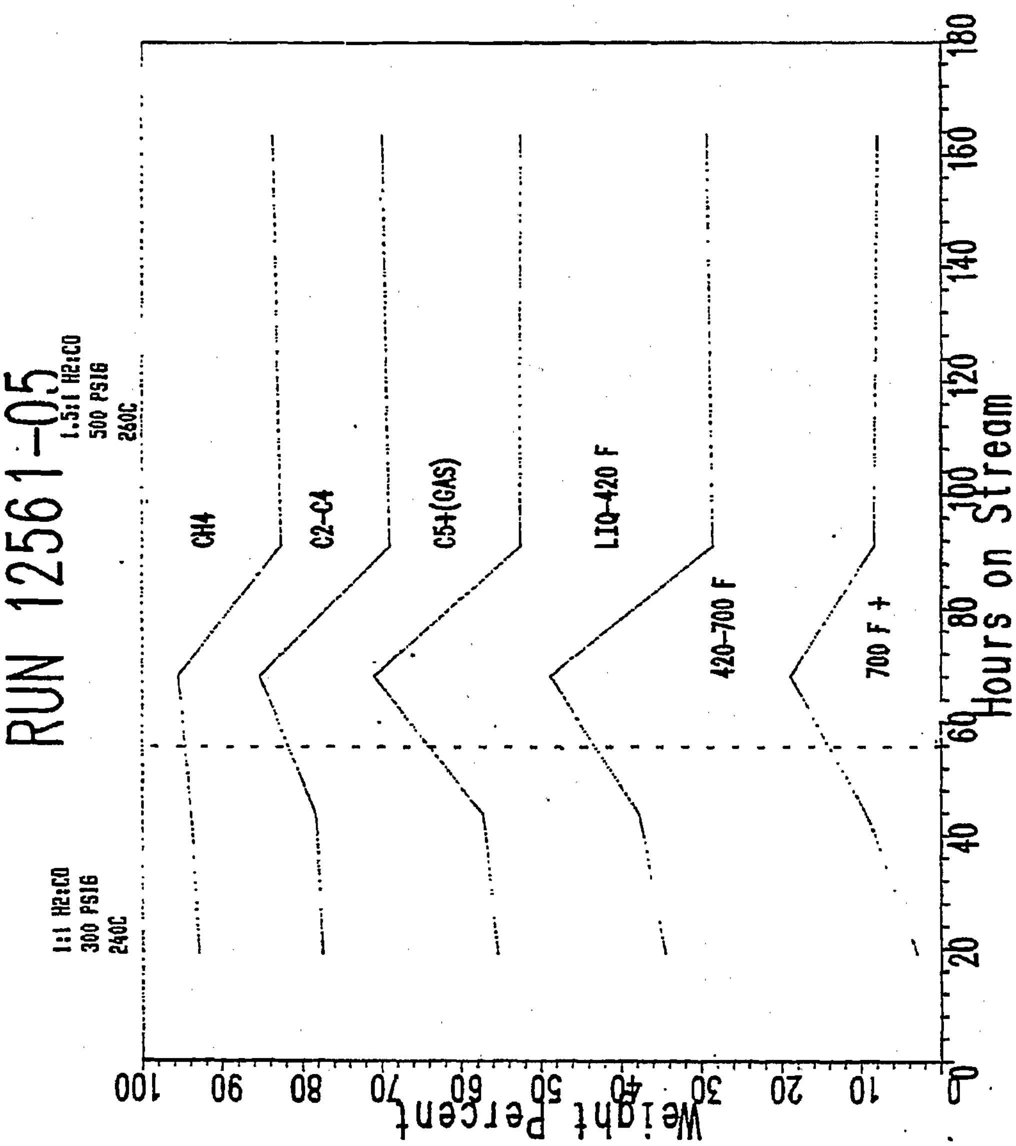
The X_{11} promoted cobalt oxide catalyst was prepared similarly to Catalyst 45 and formed into 1/8-inch extrudates. This was combined with 1/8-inch extrudates of K/Ni/Mo-γ-alumina, which made up 30 percent of the total catalyst volume. The theoretical content of cobalt and X_{11} was 5.7 and 1.1 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B73-76. Simulated distillations of the C_5^+ product are plotted in Figs. B77-81. Carbon number product distributions are plotted in Figs. B82-86. Chromatograms from simulated distillations are reproduced in Figs. B87-91. Detailed material balances appear in Table B10.

During the first stage of the test (at 1:1 H_2:CO ratio, 240C, 200 psig, 300 GHSV), 4.5 percent of the oxygen was converted to CO_2--poor even in comparison with the 6.5 percent conversion of Catalyst 45, a similar catalyst with no WGS component. The equilibrium constant K shift, which should be insensitive to variations in catalyst conversion, were similar, each fluctuating between 3 and 4, indicating again that the WGS component was not improving the WGS activity of the Fischer-Tropsch catalyst.

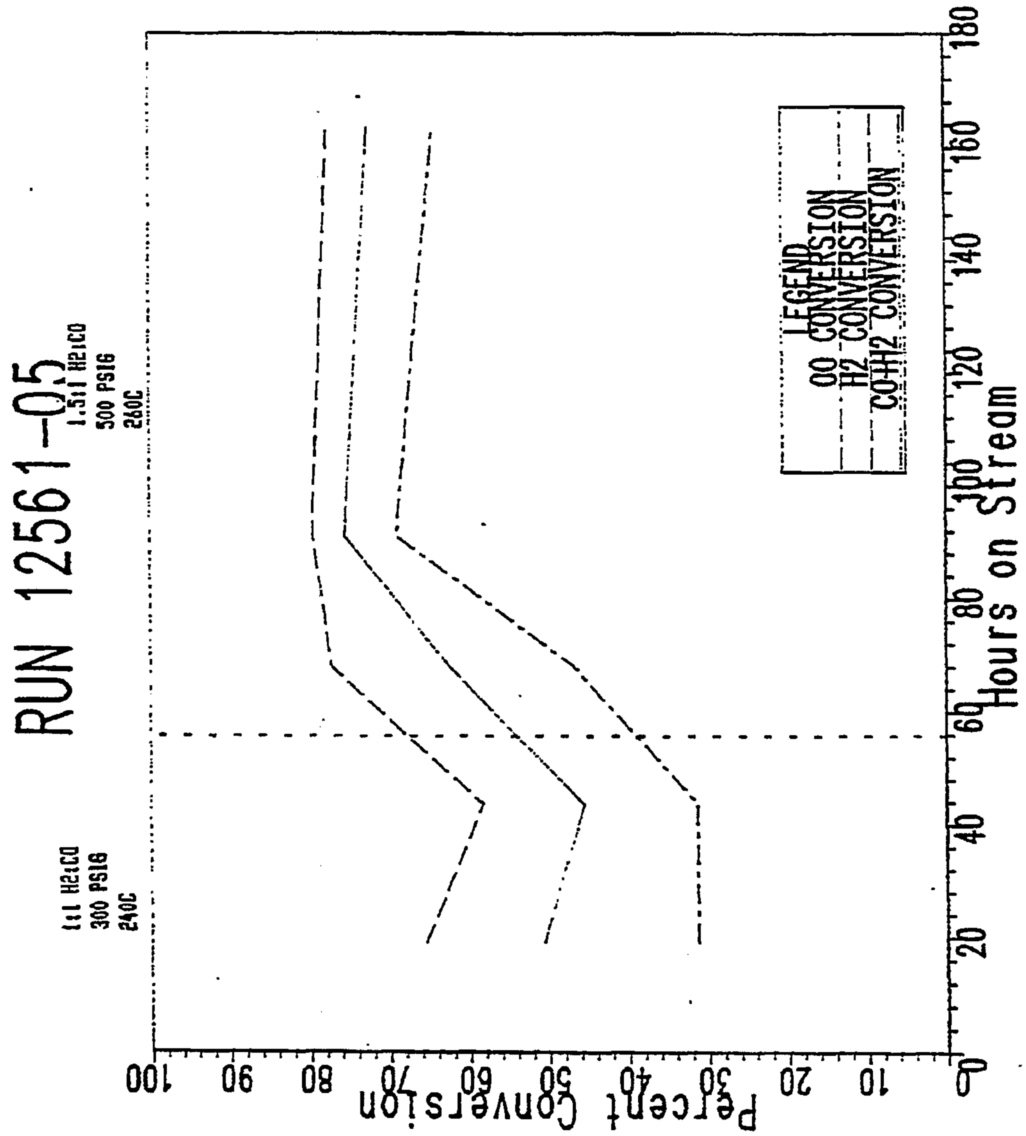
In succeeding stages (1) the temperature and pressure were raised to 260C and 500 psig respectively, and (2) the H_2:CO feed ratio was increased to 1.5:1. In neither case was there any significant improvement in the WGS activity.

Once again the addition of a WGS component has failed to improve the cobalt/TC-123 catalyst's WGS activity. Unlike the WGS components previously tested, this component did not impair the catalyst's overall Fischer-Tropsch activity.



RUN 12561-05
1:1 H2:CO
300 PSIG
240C
1.5:1 H2:CO
500 PSIG
260C
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

Fig. B74



RUN 12561-05
1:1 H2:CO
300 PSIG
240C
1.5:1 H2:CO
500 PSIG
260C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Hours on Stream
Percent Conversion
0
20
40
60
80
100
120
140
160
180
10
30
50
70
90

Fig. B73

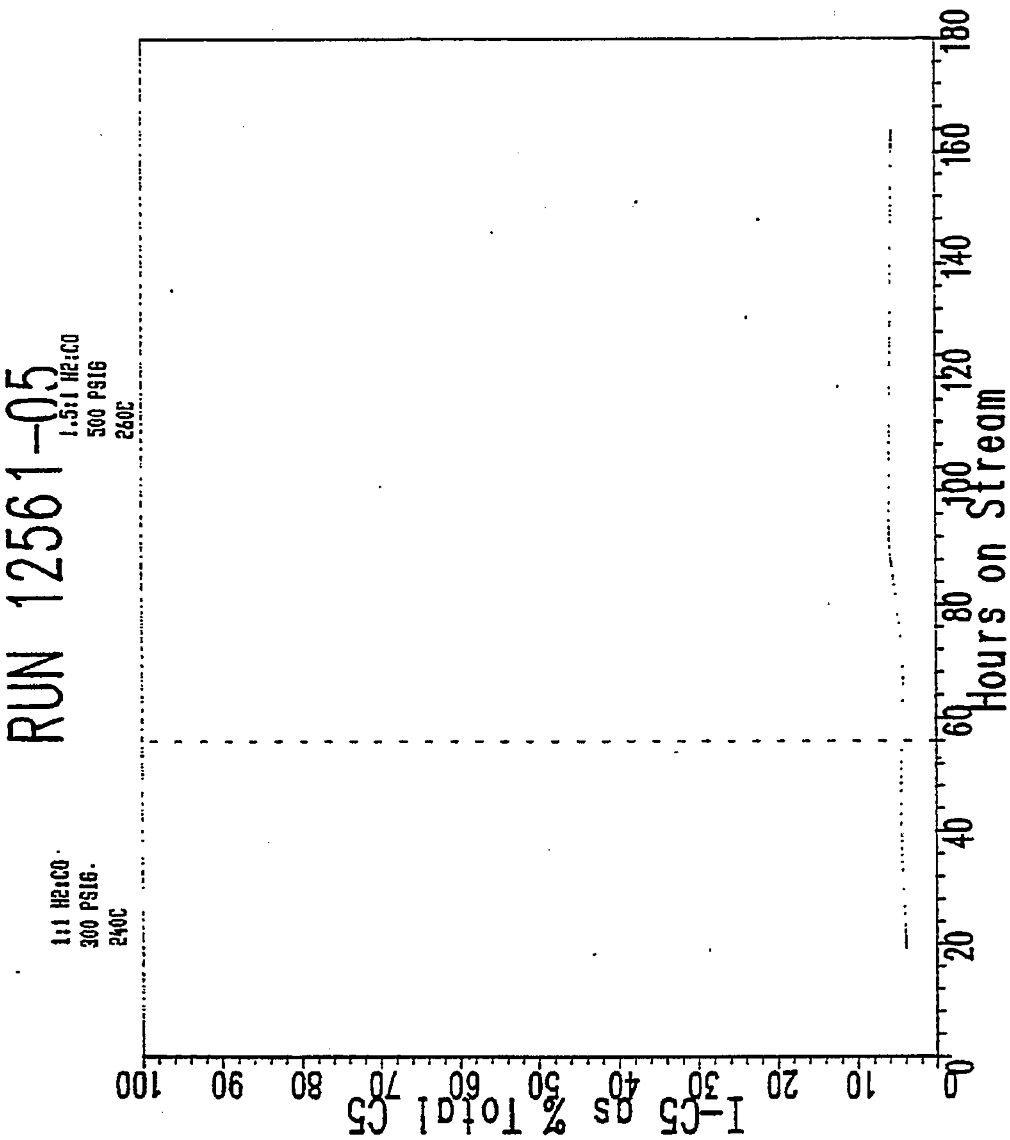
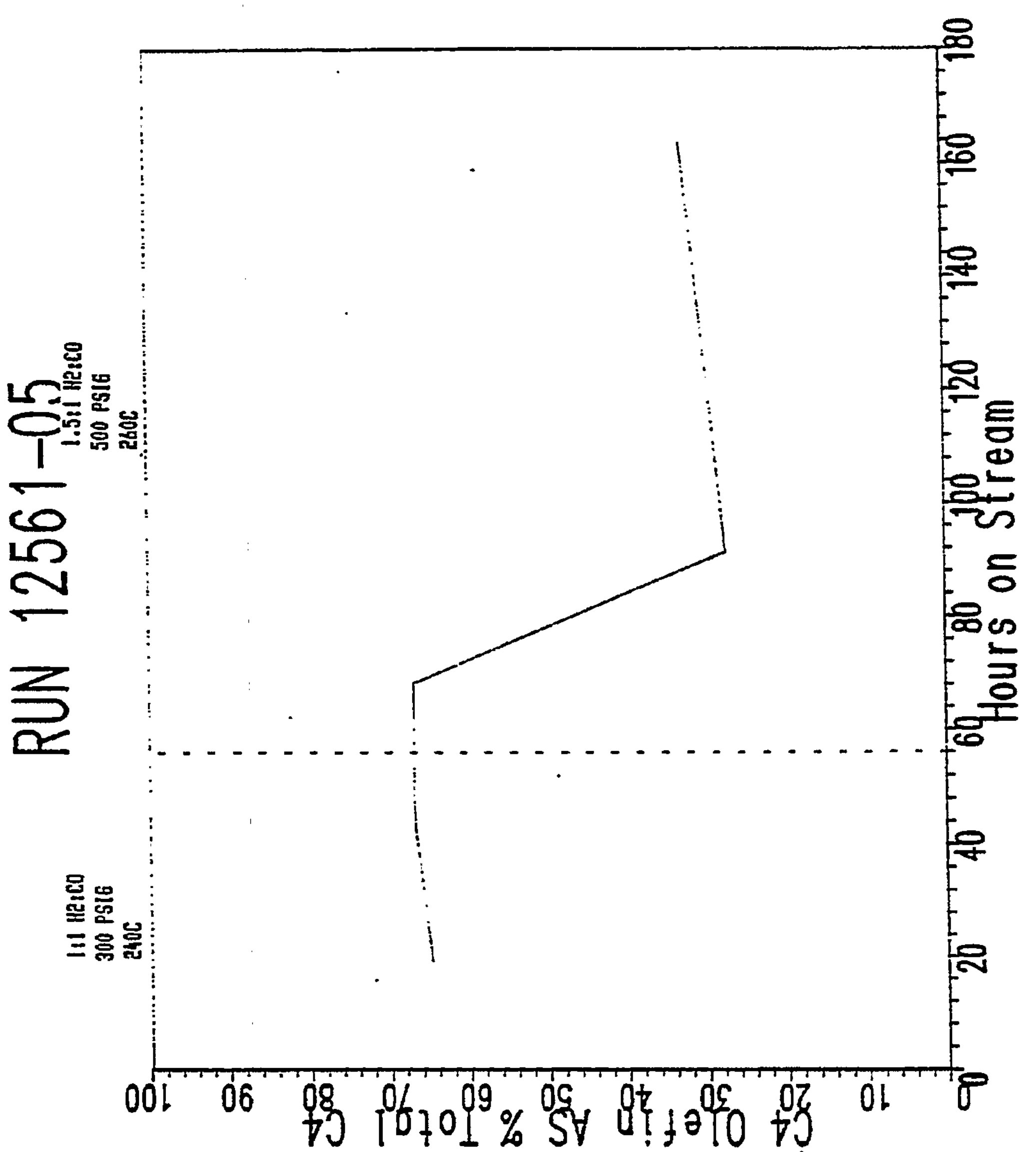
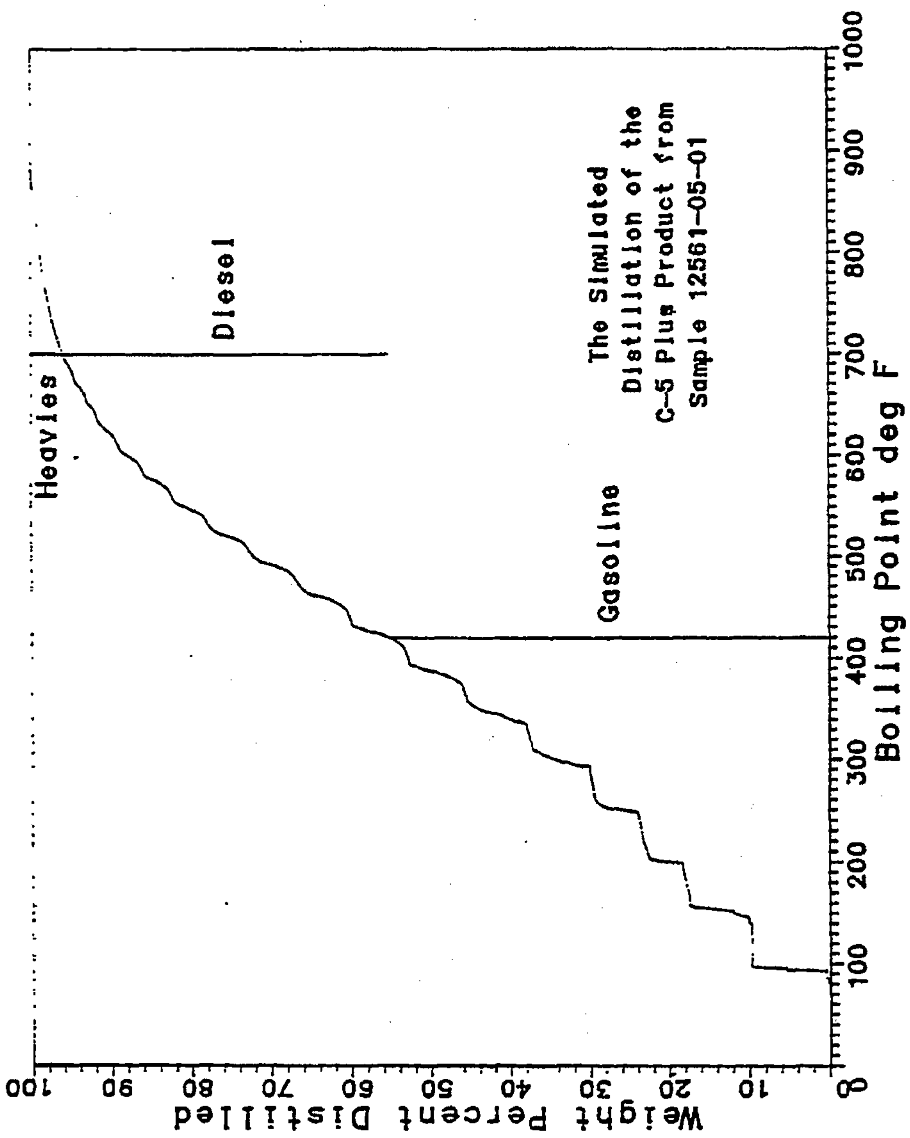

RUN 12561-05
1:1 H2:CO
300 PSIG
240C
1.5:1 H2:CO
500 PSIG
260C
Hours on Stream
I-C5 as % Total C5

Fig. B75



RUN 12561-05
1:1 H2:CO
300 PSIG
240C
1.5:1 H2:CO
500 PSIG
260C
Hours on Stream
C4 Olefin AS % Total C4
0
20
40
60
80
100
120
140
160
180
10
20
30
40
50
60
70
80
90
100

Fig. B76



The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-05-01
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B77

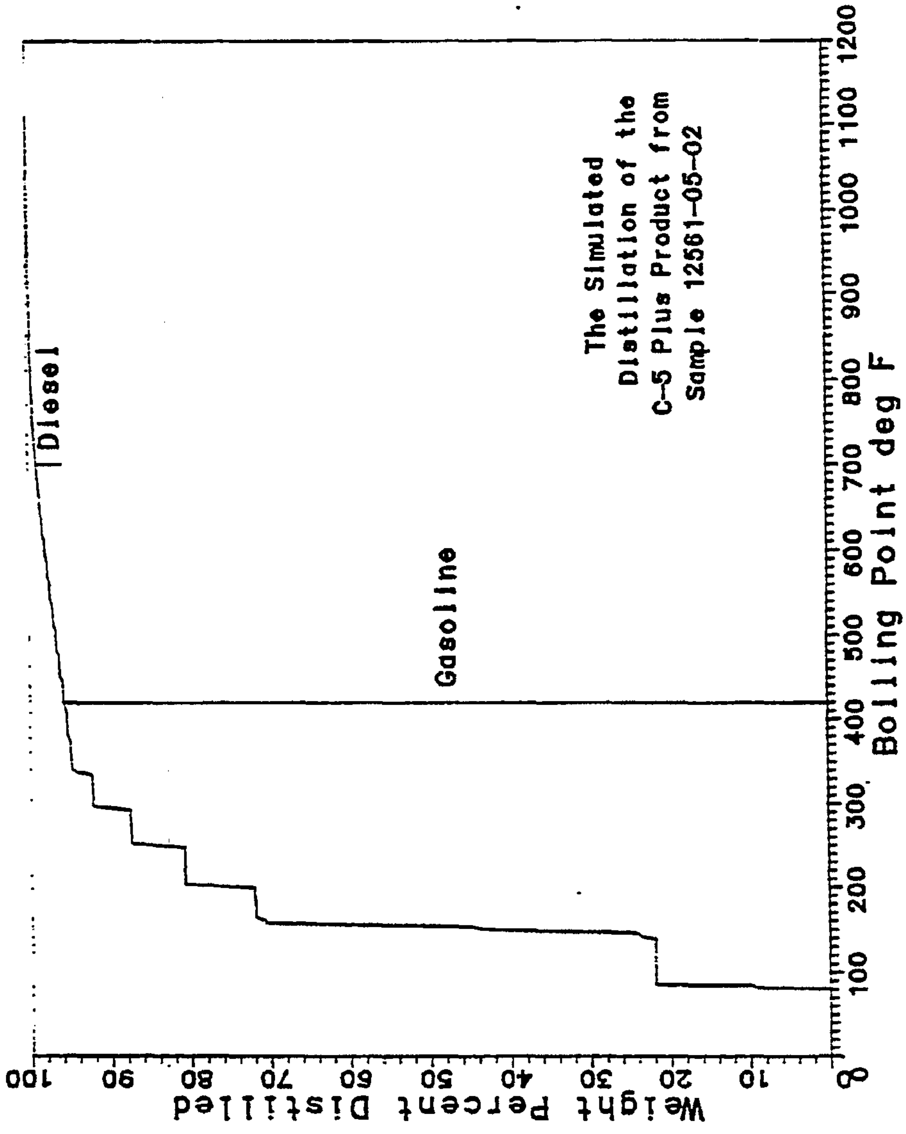

Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-05-02
Boiling Point deg F
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B78

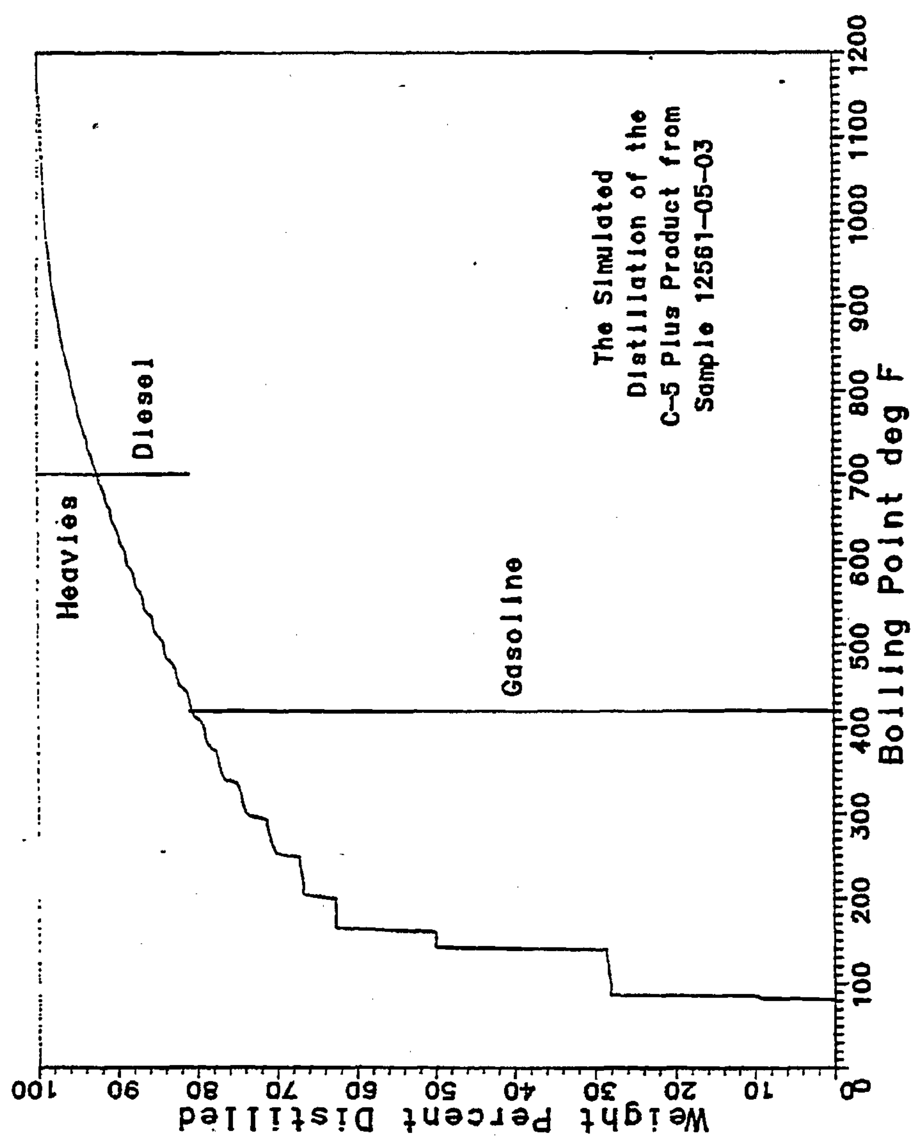

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-05-03
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
10
20
30
40
50
60
70
80
90
100

Fig. B79

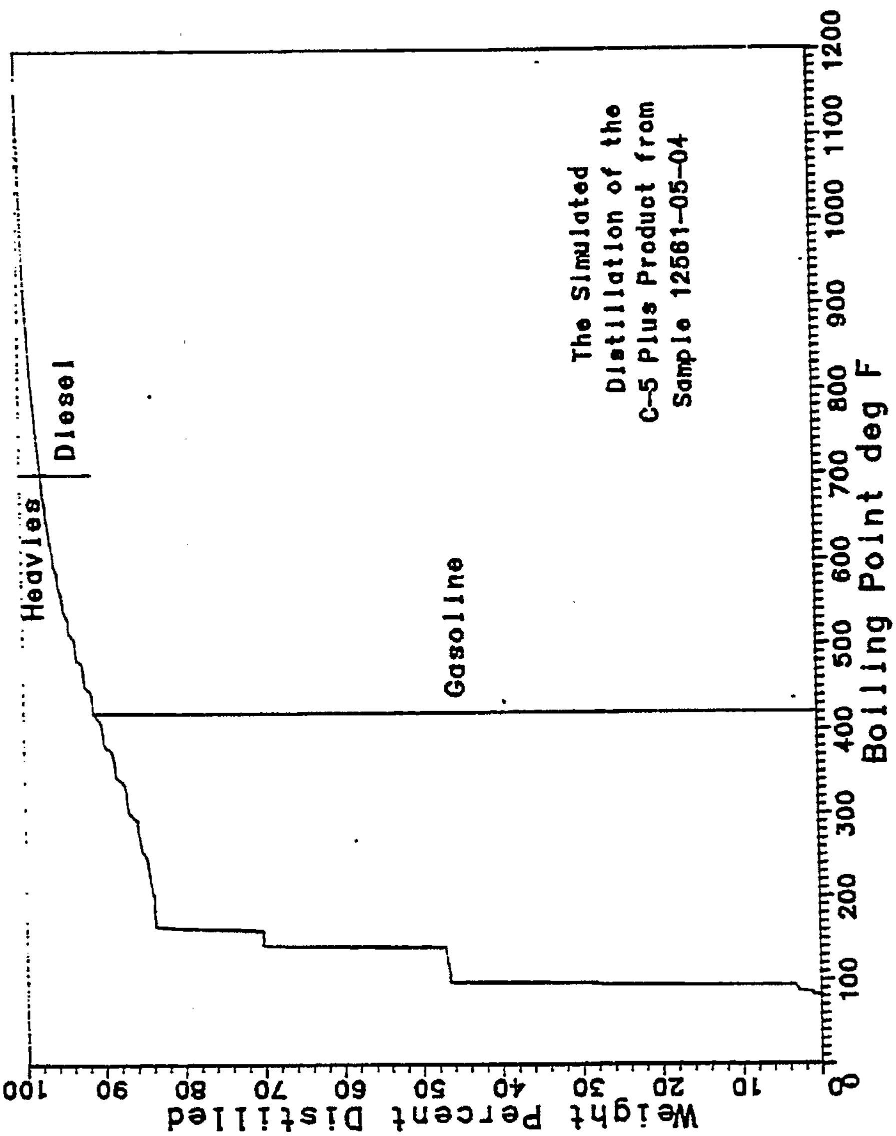
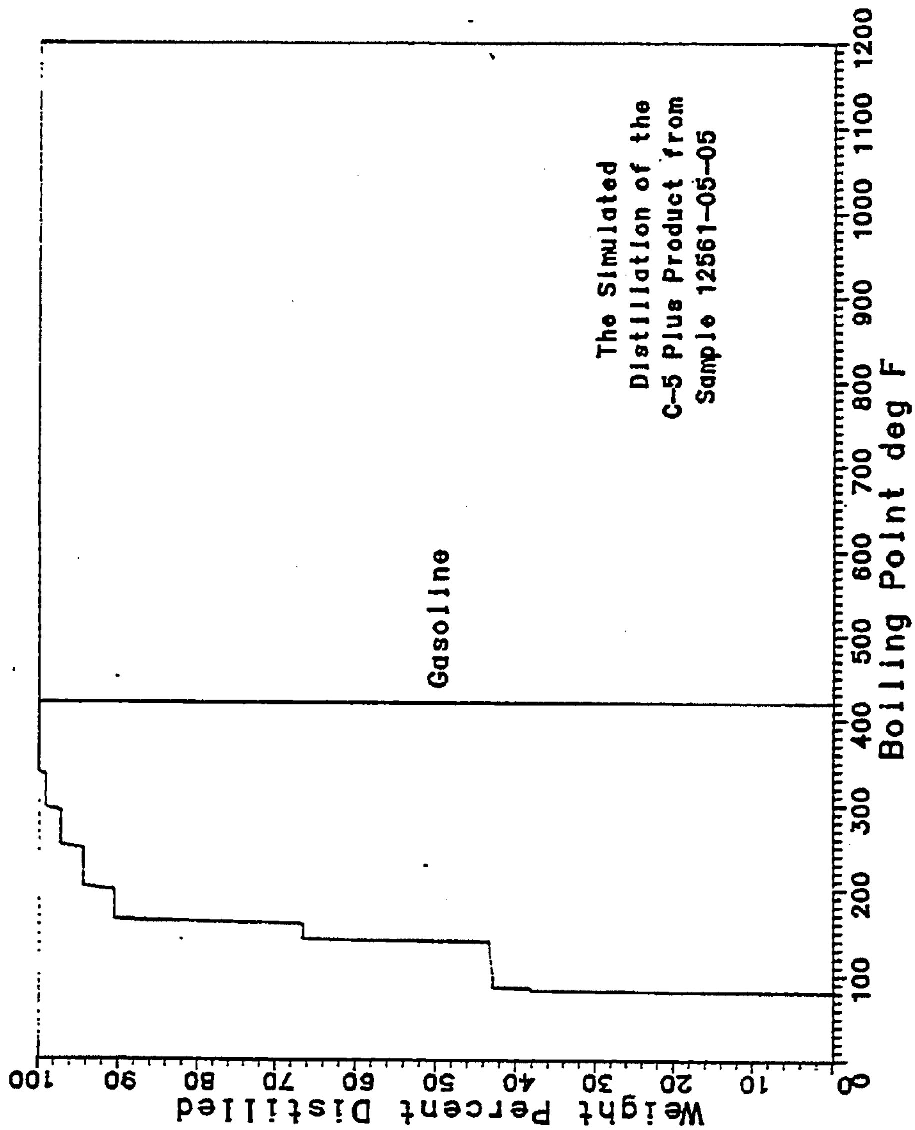
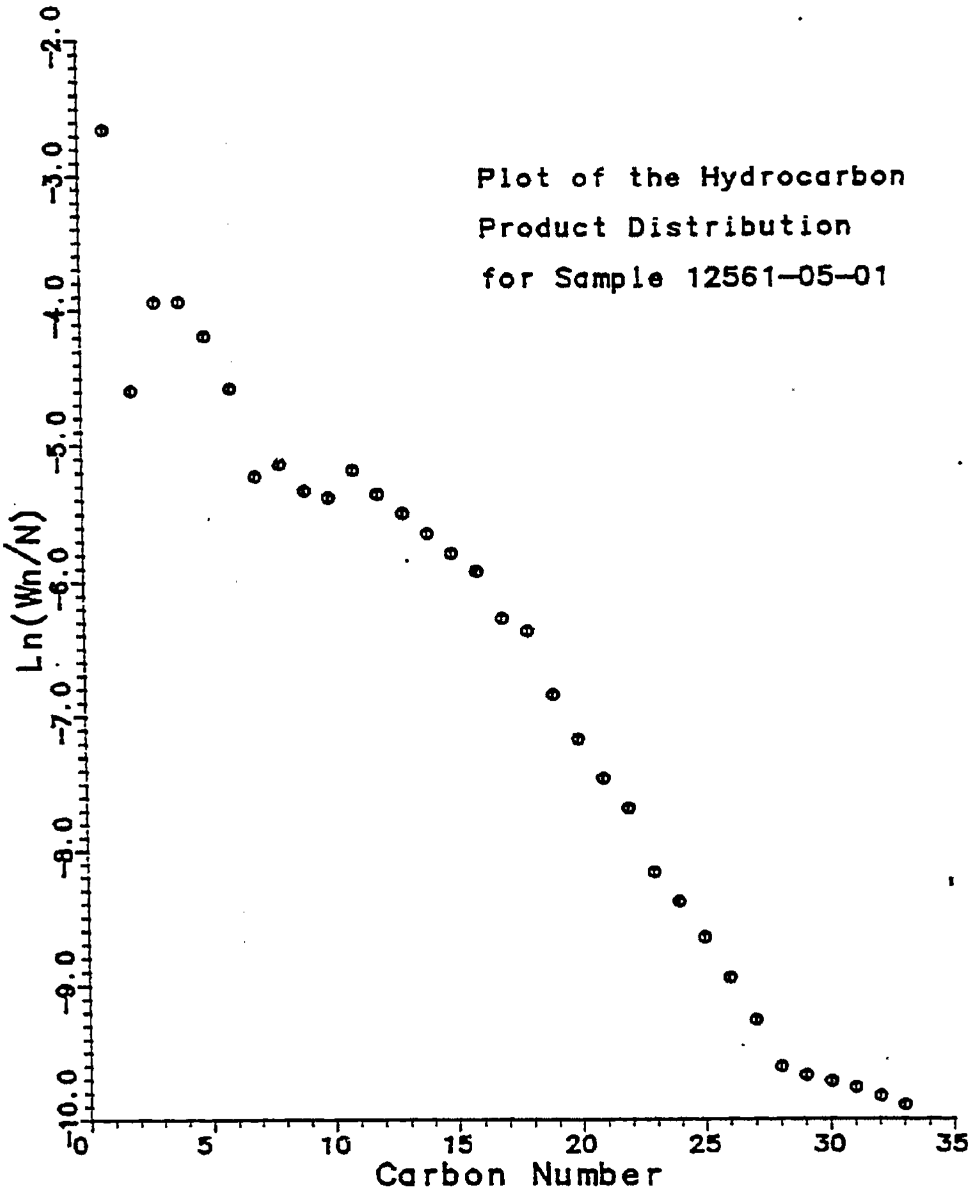

The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-05-04
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Fig. B80



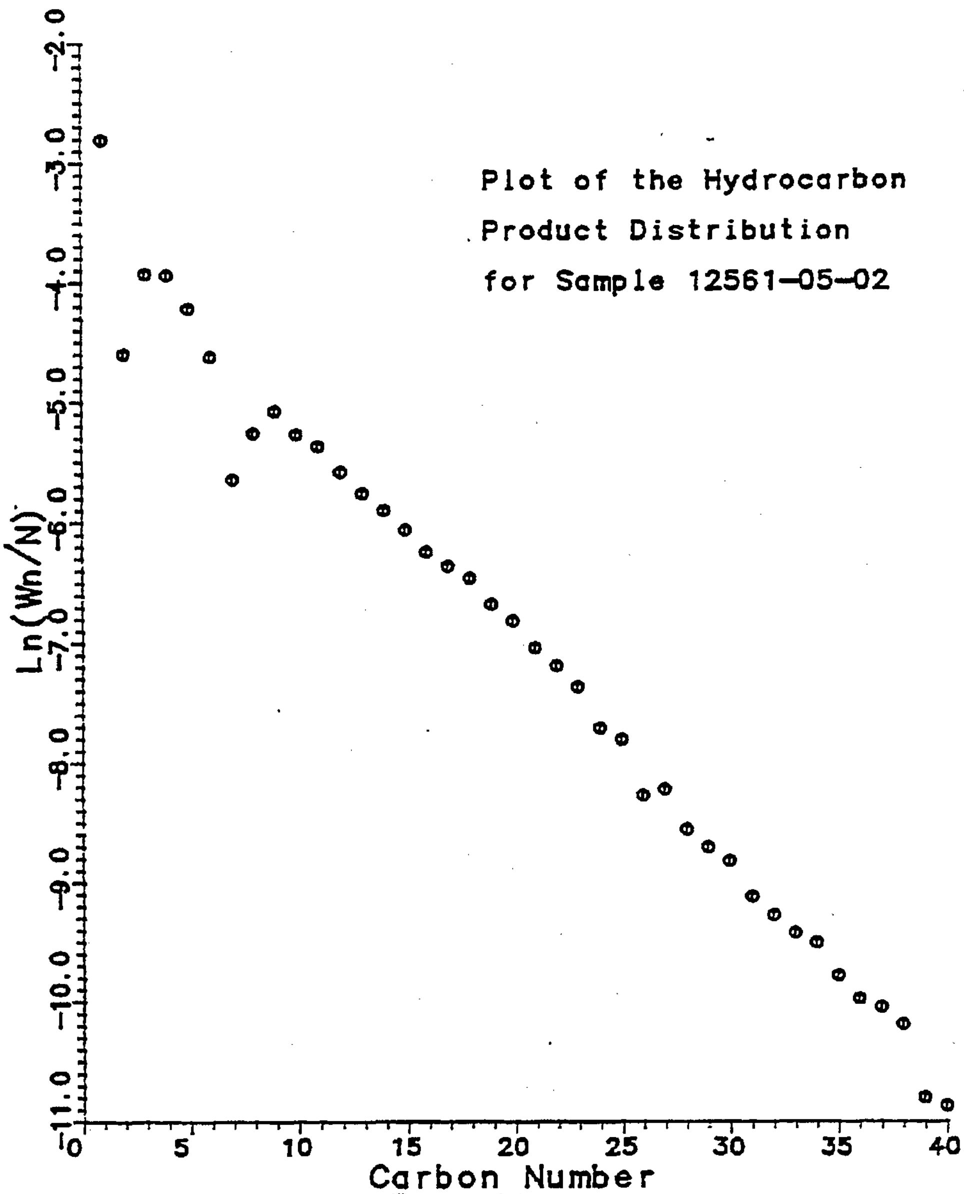
The Simulated Distillation of the C-5 Plus Product from Sample 12561-05-05
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B81



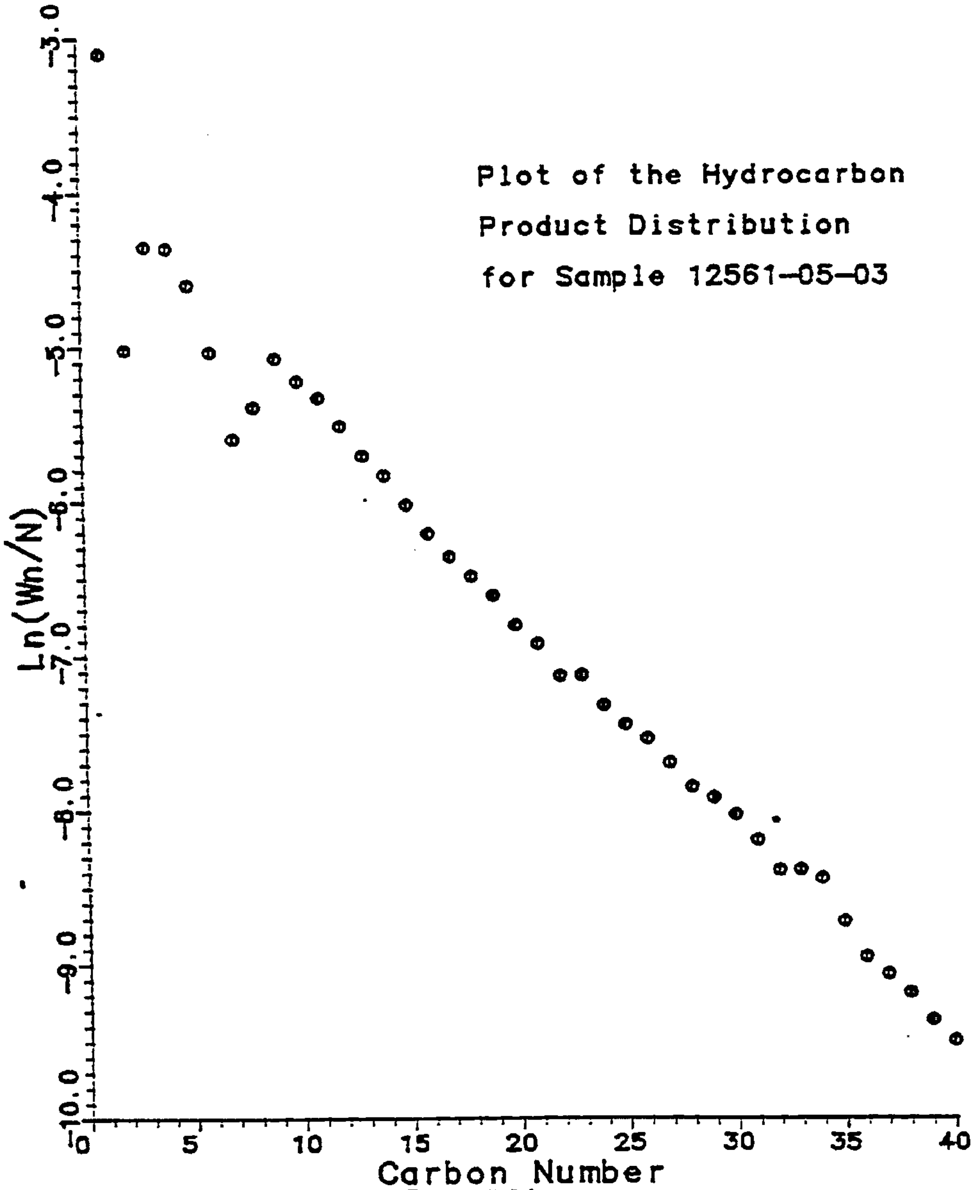
Plot of the Hydrocarbon
Product Distribution
for Sample 12561-05-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

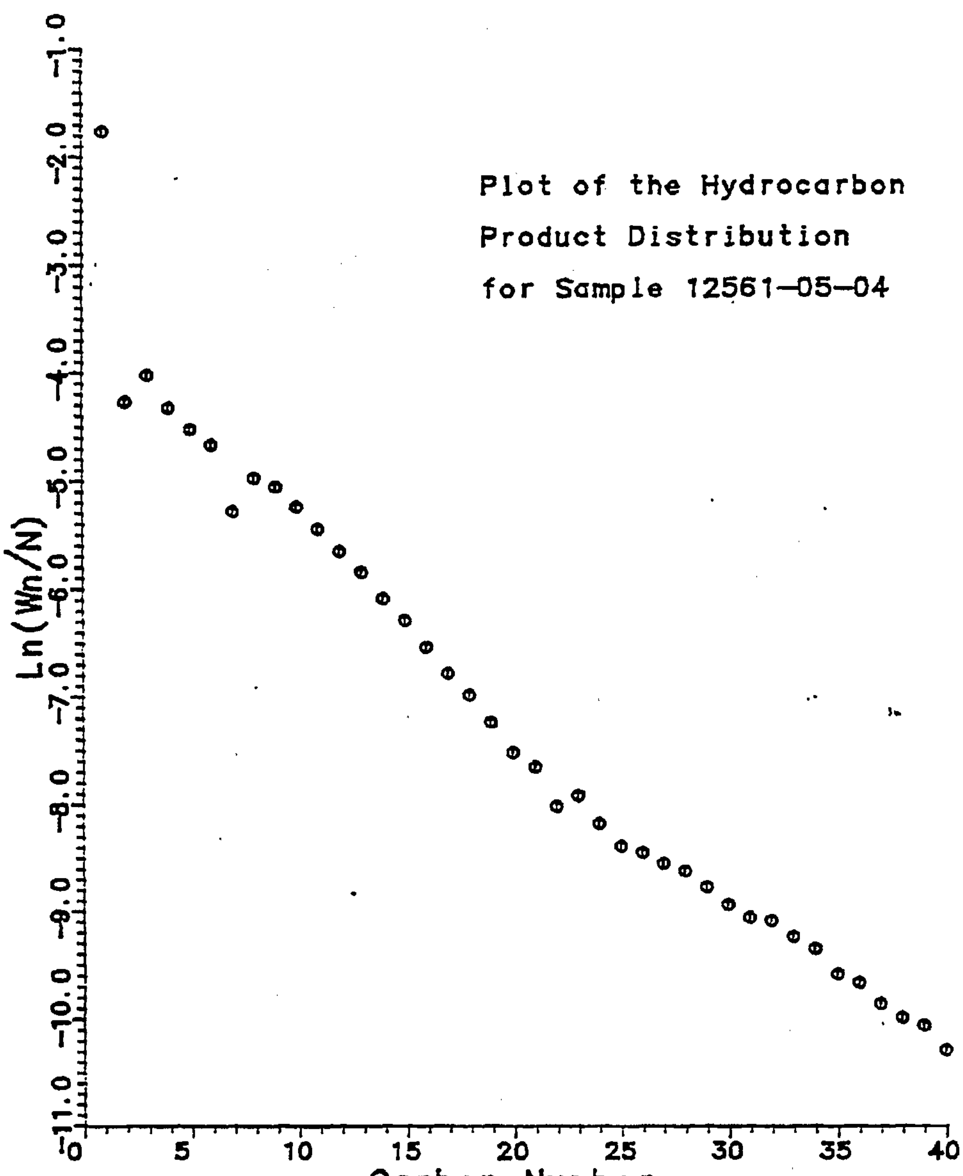
Fig. B82

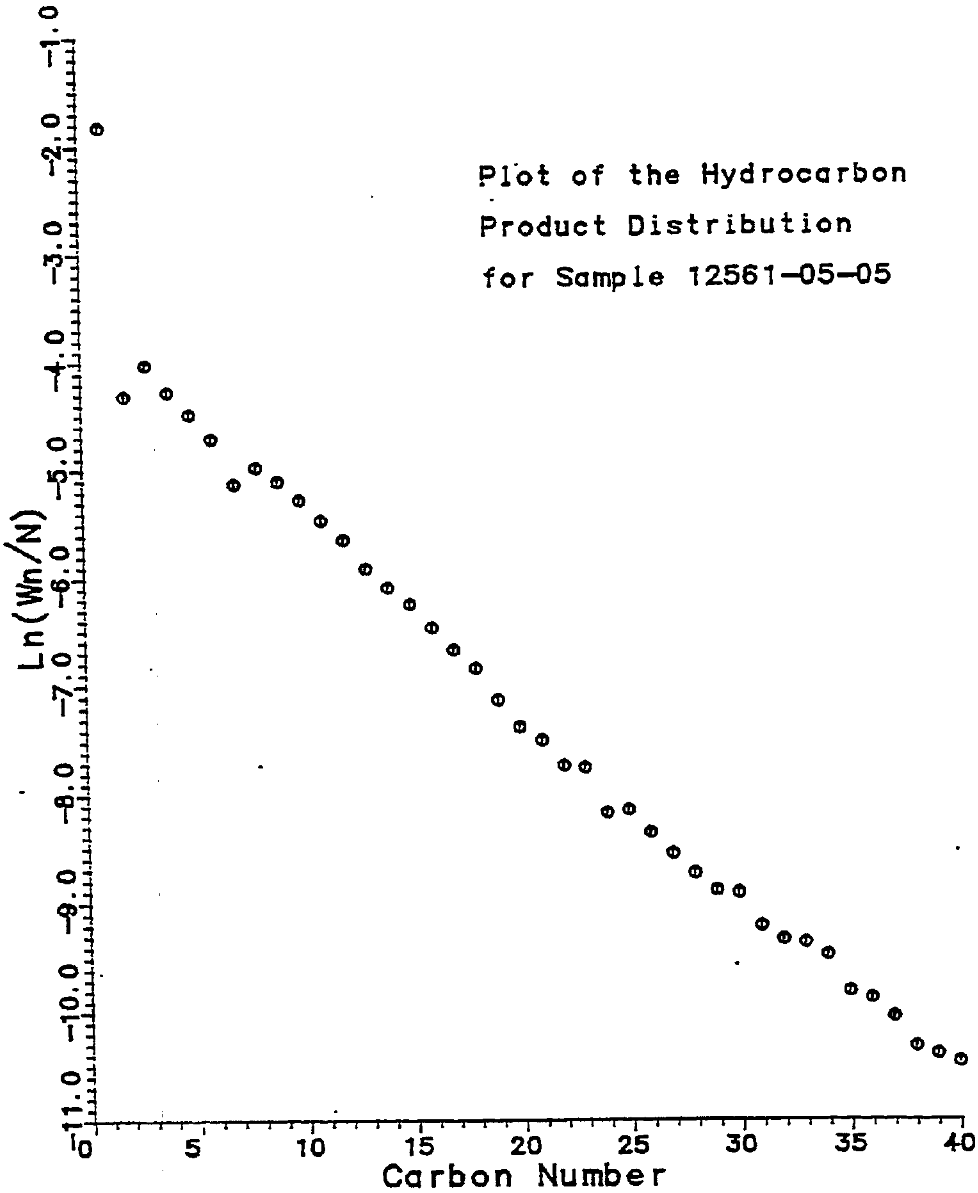


Plot of the Hydrocarbon
Product Distribution
for Sample 12561-05-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B83


Plot of the Hydrocarbon
Product Distribution
for Sample 12561-05-03
Ln(Wn/N)
-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. B84

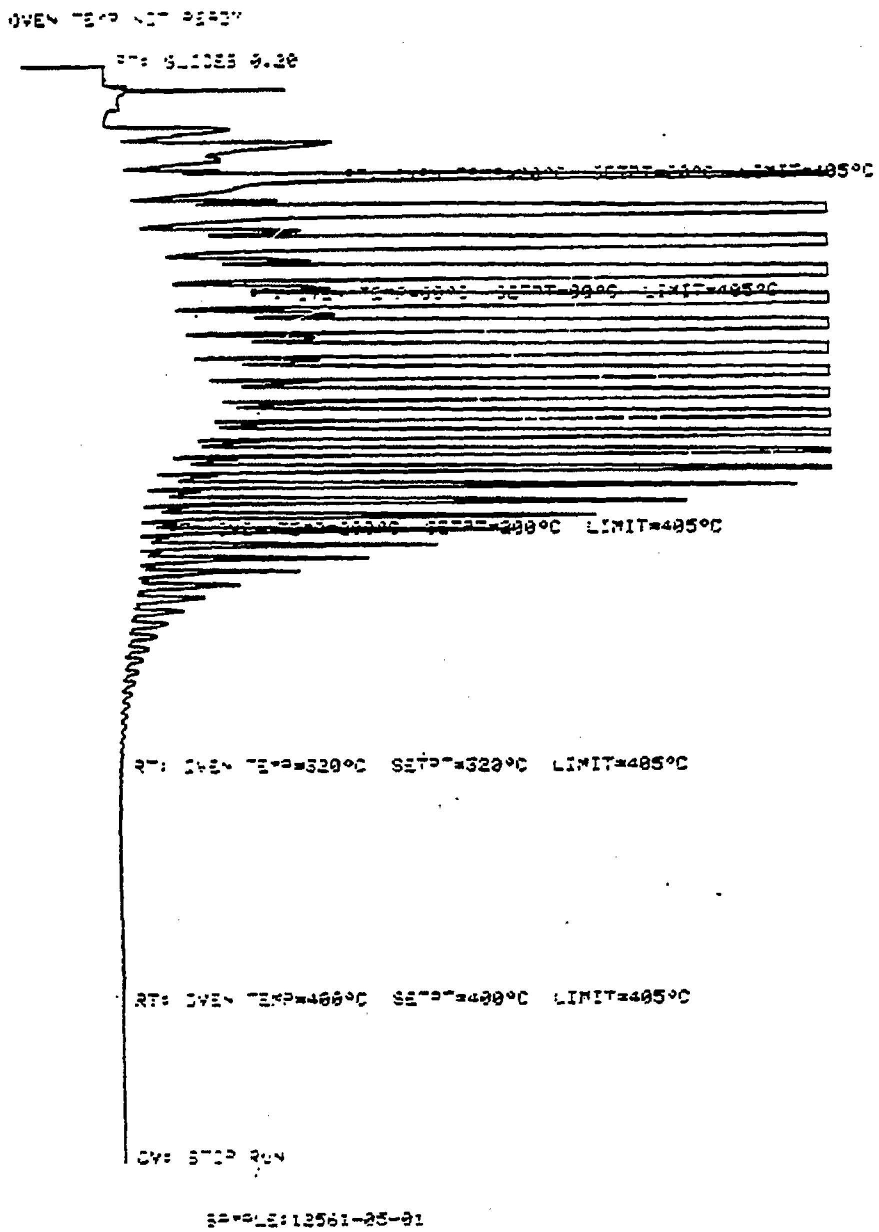

Plot of the Hydrocarbon
Product Distribution
for Sample 12561-05-04
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B85



Plot of the Hydrocarbon
Product Distribution
for Sample 12561-05-05
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B86

053



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SETPT=300°C LIMIT=405°C
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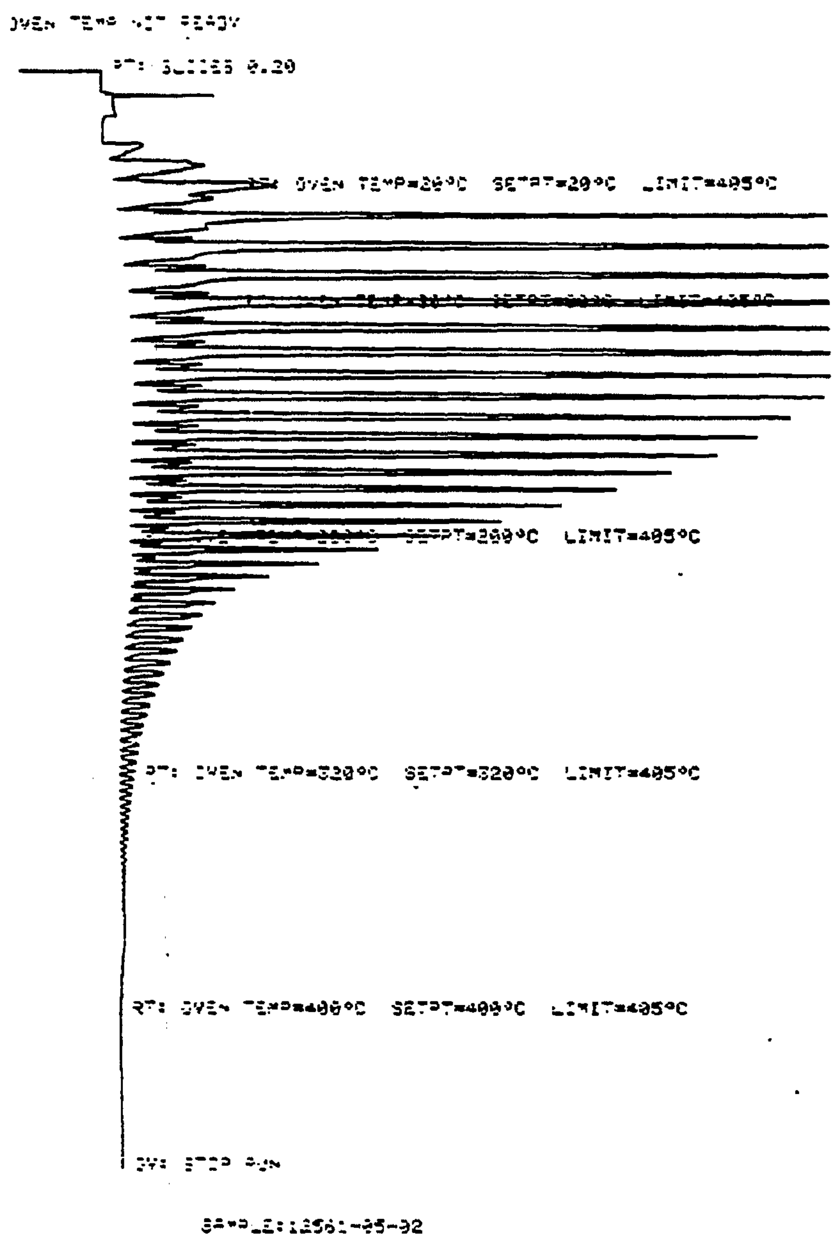
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
SAMPLE:12561-05-01

Fig. B87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SETPT=200°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B88

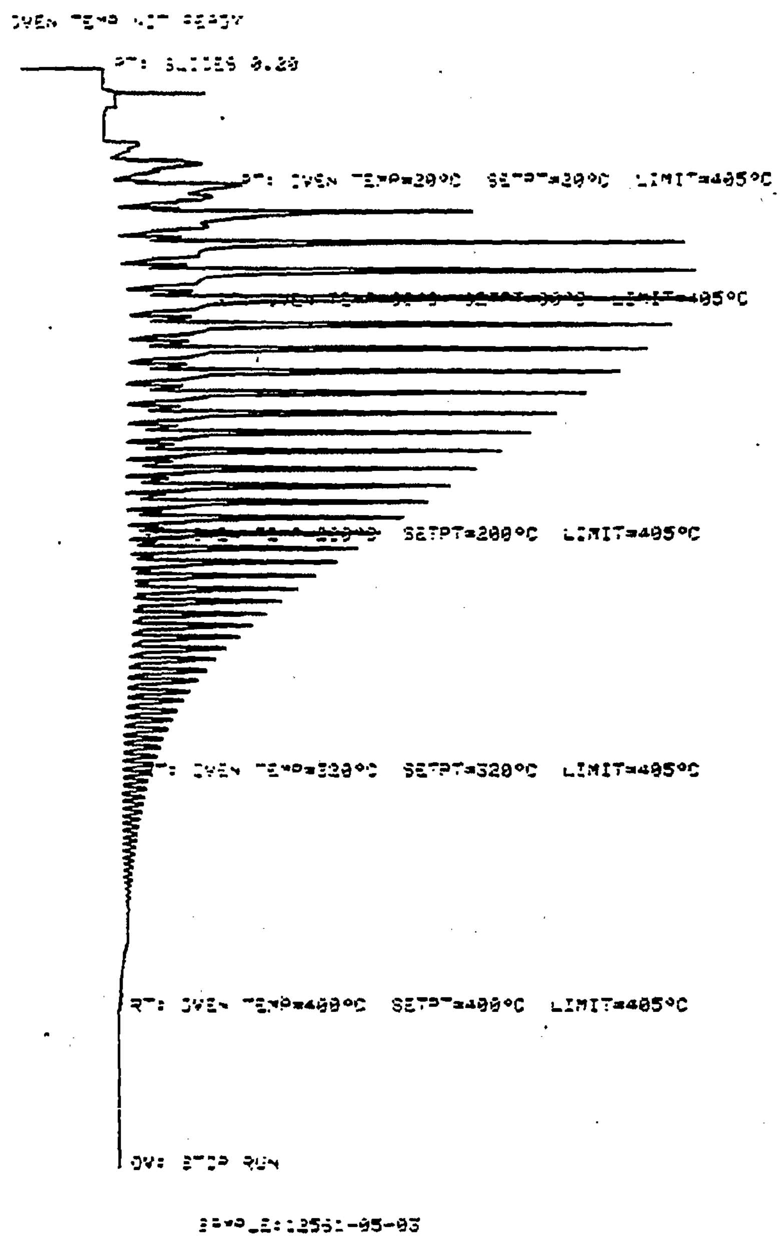

OVEN TEMP NOT READY
RT: OVEN TEMP=30°C SETPT=30°C LIMIT=405°C
LIMIT=405°C
SETPT=200°C LIMIT=405°C
RT: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B89

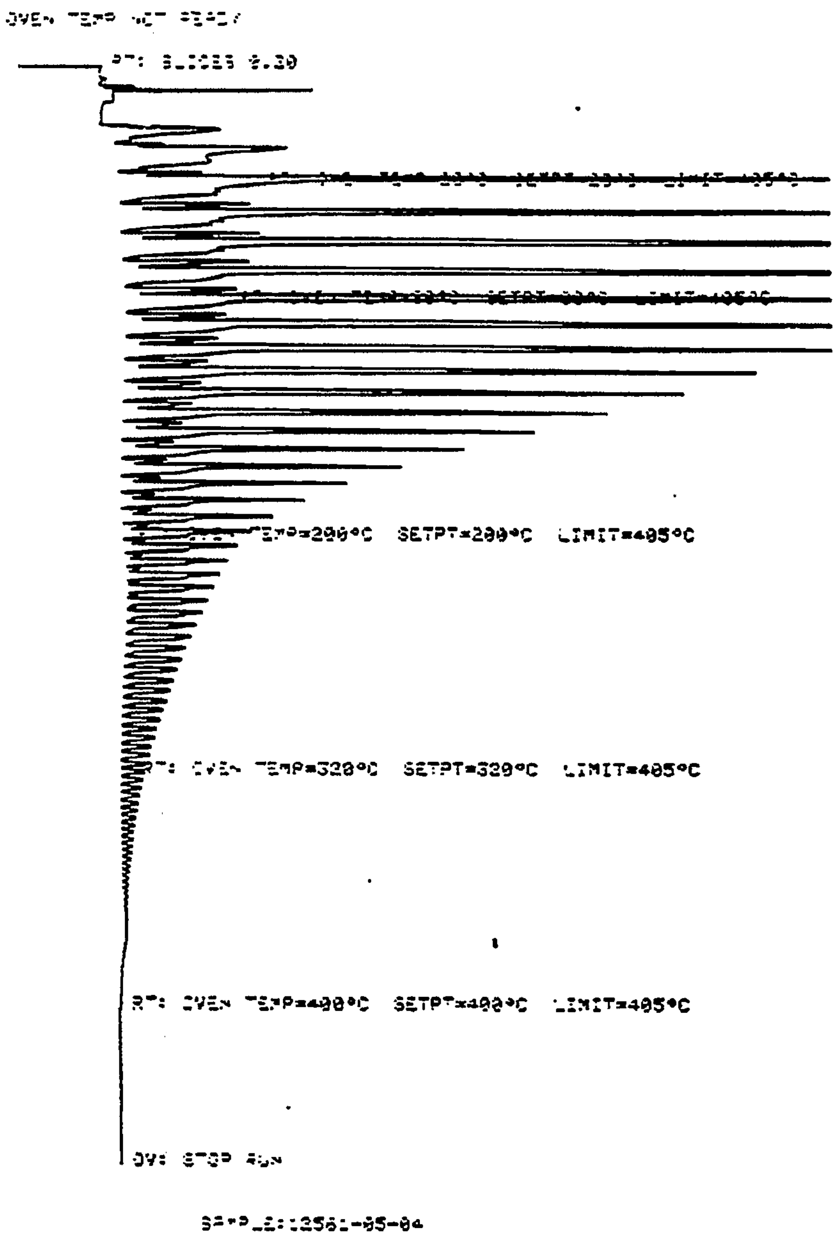

RT: SLICES 0.30
TEMP=200°C SETPT=200°C LIMIT=405°C
TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
SAMPLE:12561-05-04

Fig. B90

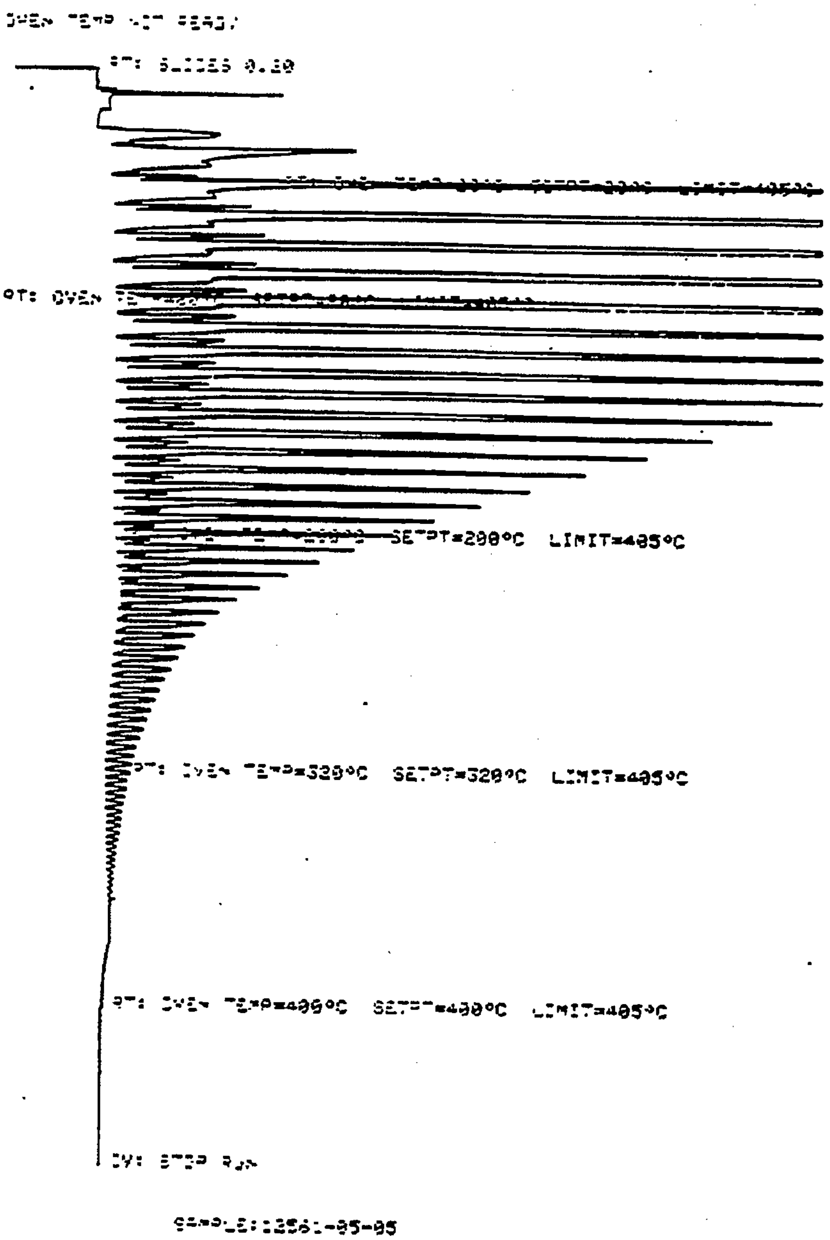


Fig. B91

Table B10

FILE: 1256105A T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 12561-05
CATALYST CO/X11-TC123 + K/NI/MO-AL2O3 80 CC 34.2 G AFTER USE: 48.8 G (+14.6 G) CAT# 12524-39
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12561-05-01	561-05-02	561-05-03	561-05-04	561-05-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	60:40: 0	60:40: 0
HRS ON STREAM	19.16	43.66	68.16	91.16	163.66
PRESSURE, PSIG	300.00	300.00	500.00	500.00	500.00
TEMP. C	240.00	240.00	260.00	261.00	260.00
FEED CC/MIN	400.00	400.00	400.00	400.00	400.00
HOURS FEEDING	19.16	24.50	24.50	23.00	72.50
EFFLNT GAS LITER	210.30	327.20	240.70	189.50	622.00
GM AQUEOUS LAYER	63.08	57.94	65.55	73.68	245.28
GM OIL	15.94	26.14	49.11	42.87	123.83
MATERIAL BALANCE					
GM ATOM CARBON %	74.15	89.36	93.67	99.35	96.67
GM ATOM HYDROGEN %	96.19	100.55	98.83	103.77	102.87
GM ATOM OXYGEN %	93.50	93.08	88.69	90.91	94.23
RATIO CHX/(H2O+CO2)	0.5234	0.8764	1.1413	1.1581	1.0448
RATIO X IN CHX	2.2729	2.2528	2.2190	2.4948	2.4722
USAGE H2/CO PRODT	2.7205	2.0993	1.7402	1.8072	1.9268
FEED H2/CO FRM EFFLNT	1.2973	1.1252	1.0550	1.5667	1.5962
RESIDUAL H2/CO RATIO	0.6524	0.6844	0.4529	1.0343	1.0042
RATIO CO2/(H2O+CO2)	0.0459	0.0475	0.1022	0.1253	0.0951
K SHIFT IN EFFLNT	0.0314	0.0342	0.0516	0.1481	0.1055
SPECIFIC ACTIVITY SA	2.6337	2.5298	1.4878	0.9294	0.8441
CONVERSION					
ON CO %	31.18	31.15	46.77	68.89	64.16
ON H2 %	65.39	58.12	77.15	79.46	77.45
ON CO+H2 %	50.50	45.43	62.37	75.34	72.33
PRDT SELECTIVITY, WT %					
CH4	7.04	6.07	4.50	17.42	16.36
C2 HC'S	2.02	2.02	1.32	2.82	2.71
C3H8	2.72	2.62	1.77	4.77	4.63
C3H6=	3.11	3.29	2.11	0.66	0.79
C4H10	2.81	2.65	1.74	3.89	3.82
C4H8=	4.98	5.14	3.37	1.42	1.80
C5H12	3.53	3.43	2.26	4.38	4.35
C5H10=	4.04	3.96	2.78	1.11	1.35
C6H14	4.59	4.37	2.97	4.95	4.97
C6H12= & CYCLO'S	1.57	1.54	0.94	0.25	0.31
C7+ IN GAS	8.17	7.63	5.40	5.72	6.47
LIQ HC'S	55.42	57.29	70.85	52.60	52.44
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	22.68	21.78	14.81	30.98	30.11
C5 -420 F	42.77	40.46	36.37	40.35	40.57
420-700 F	31.45	28.55	30.00	20.25	21.42

Table B10 (continued)

FILE: 125610SA T6Q1 A1

700-END PT	3.10	9.21	18.83	8.42	7.90
C5+-END PT	77.32	78.22	85.19	69.02	69.89
ISO/NORMAL MOLE RATIO					
C4	0.0171	0.0178	0.0246	0.0427	0.0390
C5	0.0402	0.0476	0.0420	0.0634	0.0577
C6	0.0660	0.0632	0.0671	0.1058	0.0871
C4=	0.0485	0.0501	0.0532	0.1268	0.1174
PARAFFIN/OLEFIN RATIO					
C3	0.8348	0.7586	0.8004	6.9151	5.5984
C4	0.5434	0.4969	0.4969	2.6539	2.0517
C5	0.8490	0.8419	0.7904	3.8317	3.1244
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8047	0.8375	0.8682	0.8229	0.8276
RATIO CH4/(1-A)**2	1.8462	2.2967	2.5929	5.5542	5.5004
ALPHA FRM CORRELATION	0.8327	0.8304	0.8494	0.8091	0.8106
ALPHA (EXPTL/CORR)	0.9664	1.0085	1.0222	1.0171	1.0209
W%CH4 FRM CORRELATION	15.3289	16.0531	14.5379	27.2468	26.5741
W%CH4 (EXPTL/CORR)	0.4593	0.3780	0.3098	0.6393	0.6155
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	300.00	298.00	300.00	254.00	258.00
16	339.00	340.00	338.00	295.00	299.00
50	460.00	507.00	534.00	447.00	452.00
84	603.00	701.00	797.00	700.00	685.00
90	649.00	758.00	872.00	795.00	766.00
RANGE(16-84 %)	264.00	361.00	459.00	405.00	386.00
WT % @ 420 F	37.67	34.09	31.09	45.50	44.09
WT % @ 700 F	94.41	83.93	73.43	84.00	84.94

VII. Run 54 (11617-09) with Catalyst 54 ($Co/X_{11}/X_{13}/TC-123$)

The purpose of this run was to test the effect of X_{13}, a newly developed promoter, on the $Co/X_{11}/TC-123$ catalyst (Catalyst 45, Sixth Quarterly Report). The results are to be compared with those of Catalyst 45, and also those of Catalyst 51 of this report ($Co/X_9/X_{11}/TC-123$).

The catalyst was prepared in the same way as Catalyst 45 except for the addition of X_{13}. The theoretical content of cobalt, X_{11} and X_{13} was 8.1, 1.6 and 0.7 percent respectively.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B92-95. Simulated distillations of the C_5^+ product are plotted in Figs. B96-108. Carbon number product distributions are plotted in Figs. B109-121. Chromatograms from simulated distillations are reproduced in Figs. B122-134. Detailed material balances appear in Tables B11-15.

The run was conducted in six stages of varying temperatures, pressures and syngas feed ratios for a total of 507 hours:

Stage A,	123 hrs:	240C,	300 psig,	1:2 H_2:CO
Stage B,	47 hrs:	"	"	1.5:1 H_2:CO
Stage C,	23 hrs:	260C,	500 psig,	"
Stage D,	73 hrs:	"	"	1:1 H_2:CO
Stage E,	220 hrs:	"	"	1:2 H_2:CO
Stage F,	21 hrs:	250C,	"	"

The initial activity (after a good material balance was obtained at about 28 hours on stream) of this catalyst was significantly higher than that observed for the X_{13}-free Catalyst 45, 55.2 percent syngas conversion as against about 46 percent respectively. The catalyst quickly deactivated to a level of about 51 percent, where it held constant for the next 72 hours, still five percentage points higher than the conversion of the X_{13}-free catalyst. The water gas shift activity, with about 8 percent of the oxygen converted to CO_2, was twice as high as that of Catalyst 45. This increased water gas shift resulted in raising the H_2:CO ratio in the reactor and could account for the improved syngas conversion.

Product selectivity, however, was inferior to that of Catalyst 45--about 4.5 percent methane and 83 percent C_5^+, as against about 3.7 and 90 percent respectively. The olefin content of the C_4 was lower as well, with a paraffin:olefin ratio of 0.44:1 as against 0.36:1 for Catalyst 45.

In Stage B, when the H_2:CO feed ratio was raised from 1:1 to 1.5:1, the syngas conversion rose sharply from about 51 to about 66 percent, again well above the 58 percent conversion of Catalyst 45 under similar conditions. Again, as compared with Catalyst 45 under similar conditions, the water gas shift activity was higher but with inferior selectivity:

	Catalyst 54 $Co/X_{11}/X_{13}/TC-123$	Catalyst 45 $Co/X_{11}/TC-123$
$CO+H_2$ conversion, pct	66	58
Ratio $CO_2:(H_2O+CO_2)$	0.143:1	0.058:1
Weight pct CH_4	16.5	7.3
C_5^+ product, pct	68.1	85.2

In Stage C the temperature was raised from 240C to 260C and the pressure from 300 to 500 psig, the same severe conditions as with Catalyst 51 ($Co/X_{11}/X_9/TC-123$). While the conversion rose to about 85 percent, the methane production also rose steeply to nearly 29 percent. Corresponding values for Catalyst 51 were about 70 and 15 percent.

In Stages D and E the catalyst was also tested for stability at successive $H_2:CO$ feed ratios of 1:1 and 1.2:1 (temperature and pressure constant at 260C and 500 psig). In both stages there was rapid deactivation with time, accompanied by a corresponding loss in water gas shift activity. Selectivity, however, improved with deactivation.

This run has demonstrated that the additive X_{13} has a significant effect on the performance of the $Co/X_{11}/TC-123$ catalyst. The additive's principal effect resulted in increasing the catalyst's water gas shift activity, which subsequently improved the catalyst's activity but adversely affected selectivity.

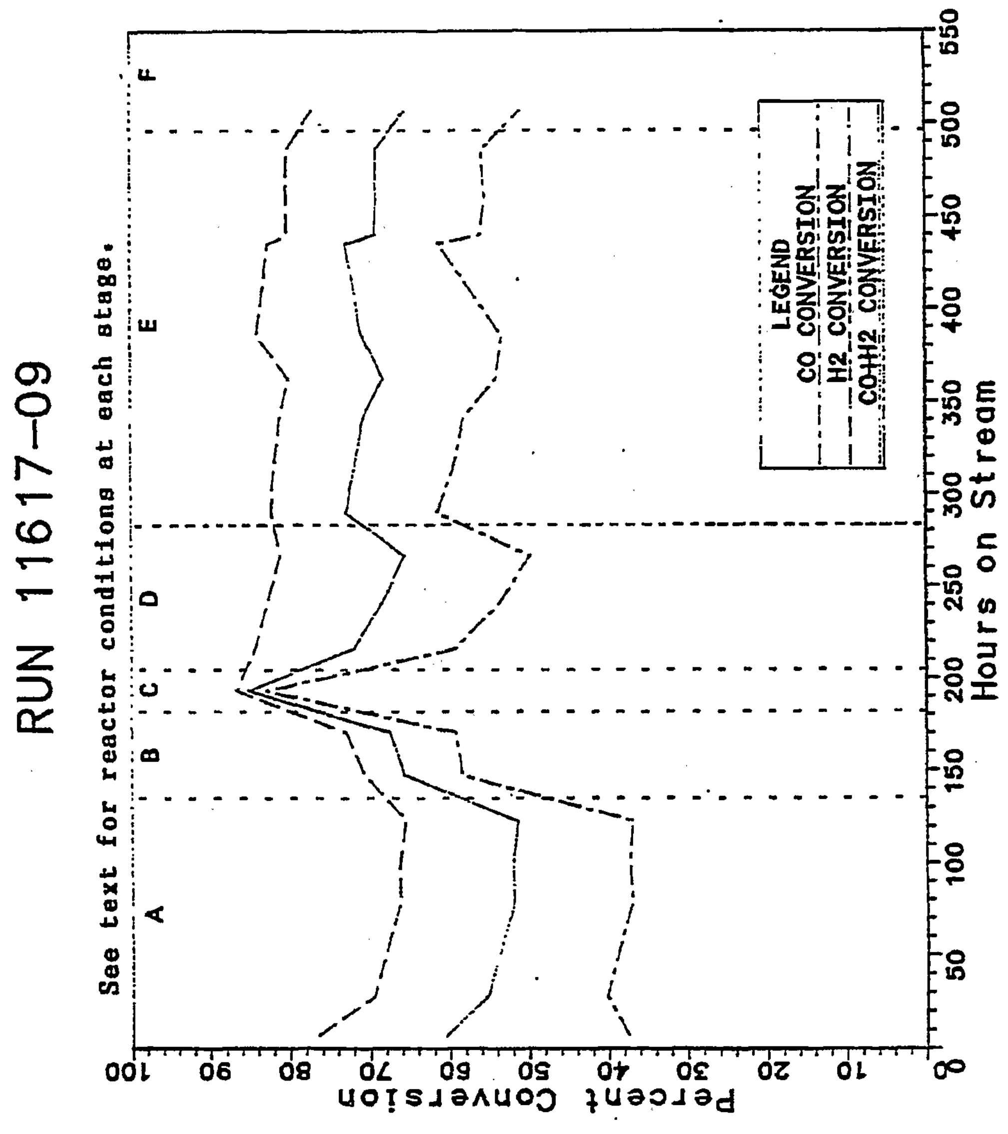

RUN 11617-09
See text for reactor conditions at each stage.
A
B
C
D
E
F
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550

Fig. B92

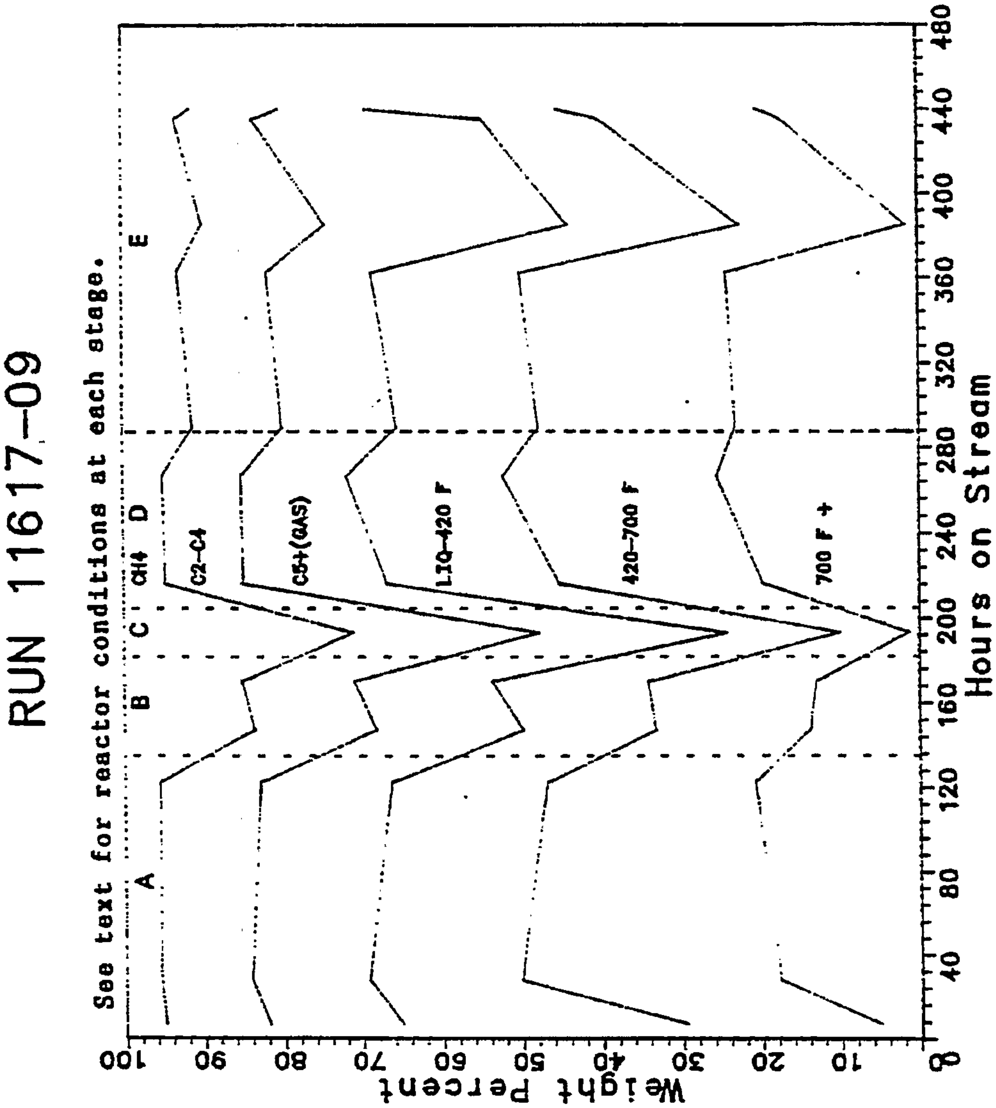

RUN 11617-09
See text for reactor conditions at each stage.
A
B
C
D
E
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440
480

Fig. B93

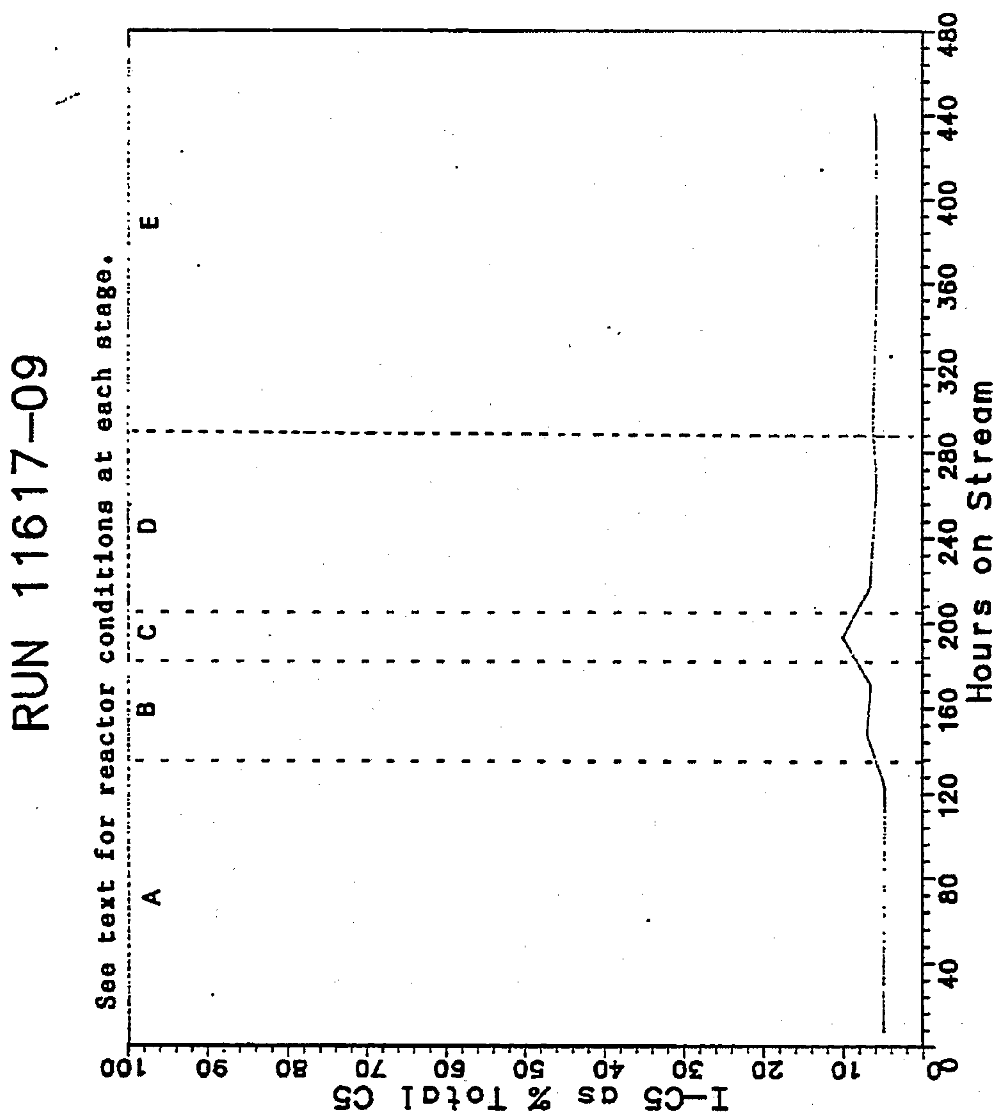
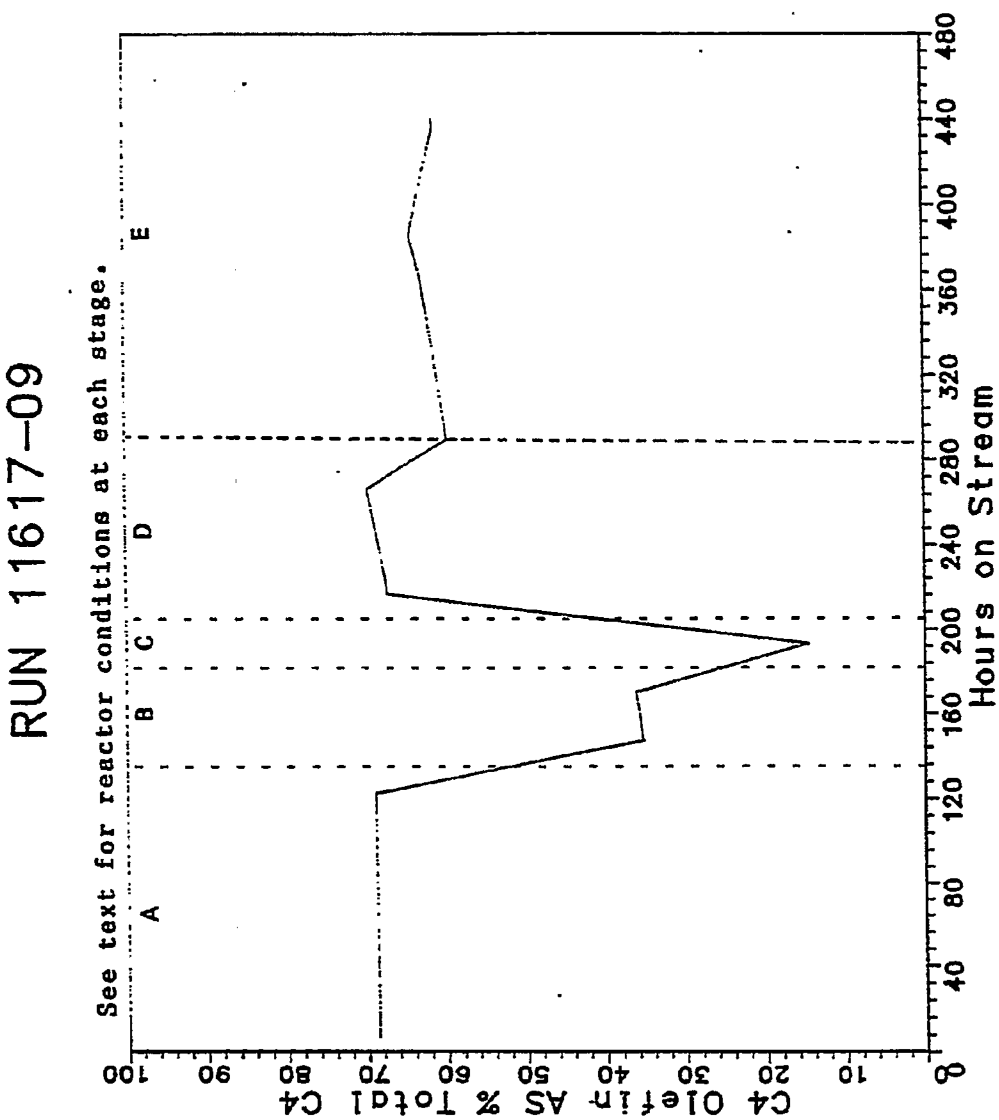
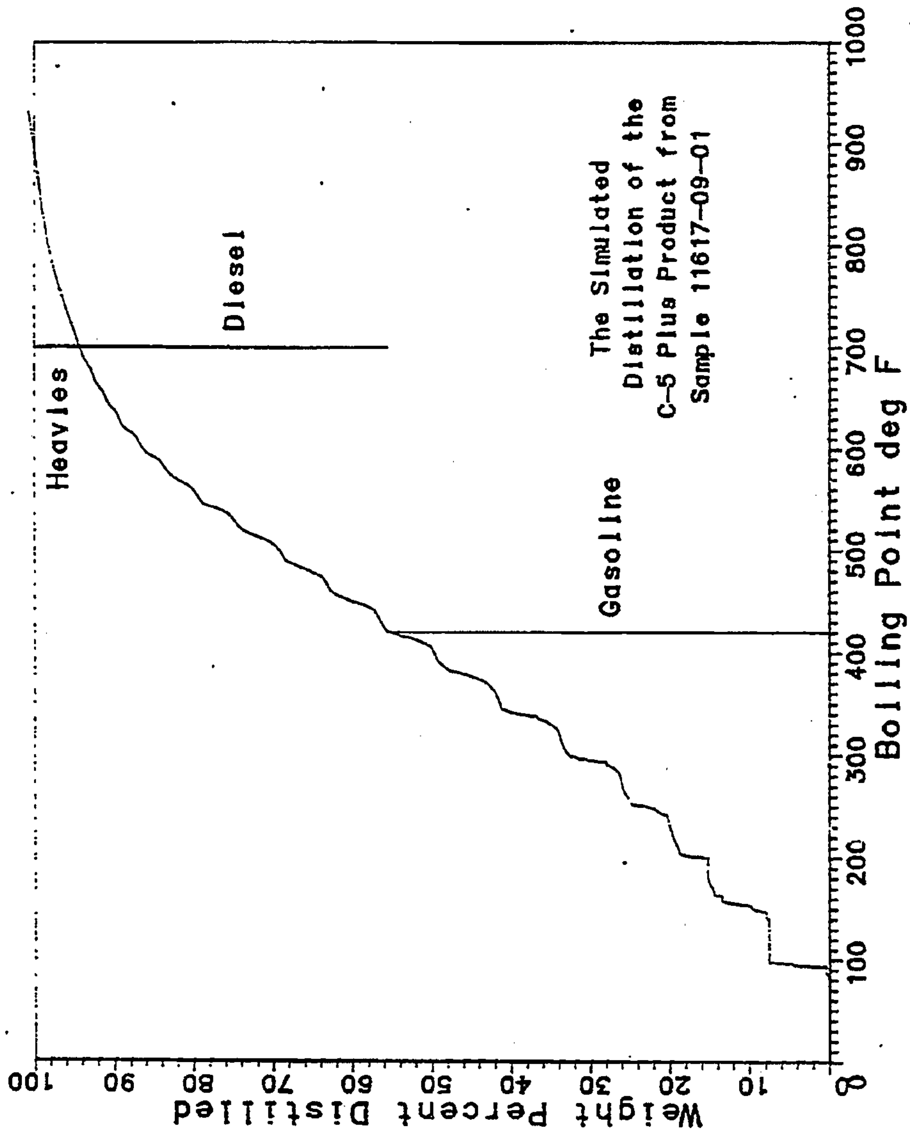

RUN 11617-09
See text for reactor conditions at each stage.
A
B
C
D
E
I-C5 as % Total C5
100
90
80
70
60
50
40
30
20
10
0
Hours on Stream
40
80
120
160
200
240
280
320
360
400
440
480

Fig. B94



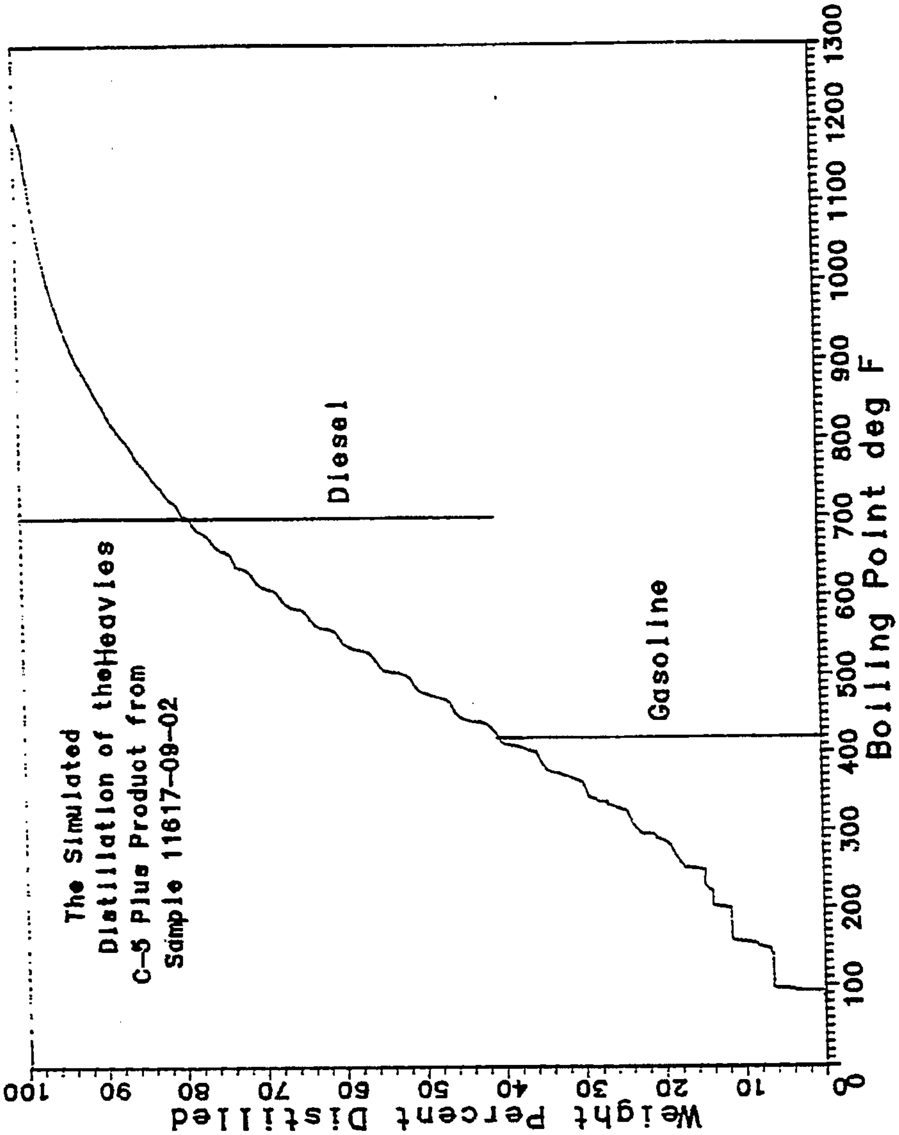
RUN 11617–09
See text for reactor conditions at each stage.
A
B
C
D
E
C4 Olefin AS % Total C4
100
90
80
70
60
50
40
30
20
10
0
Hours on Stream
40
80
120
160
200
240
280
320
360
400
440
480

Fig. B95



Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-09-01
Boiling Point deg F
100 200 300 400 500 600 700 800 900 1000
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B96



The Simulated
Distillation of the Heavies
C-5 Plus Product from
Sample 11617-09-02
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B97

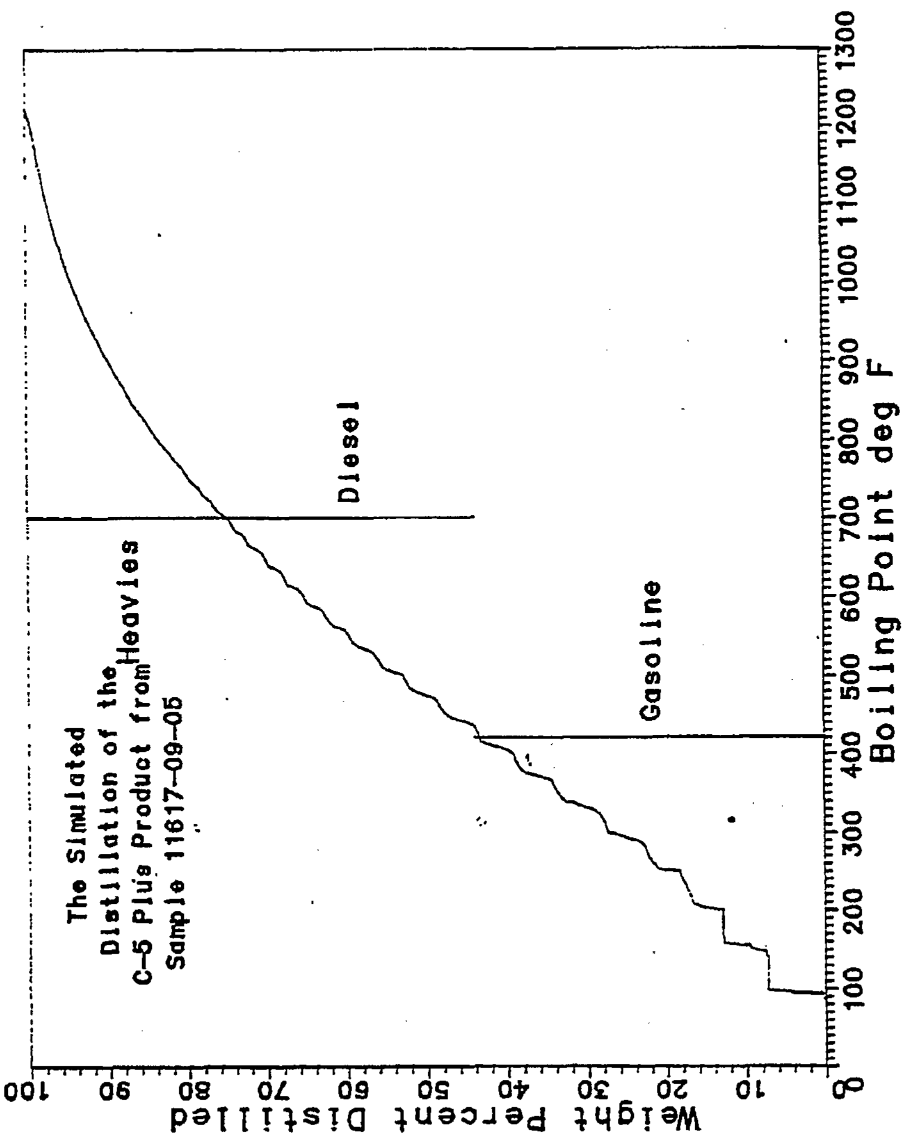
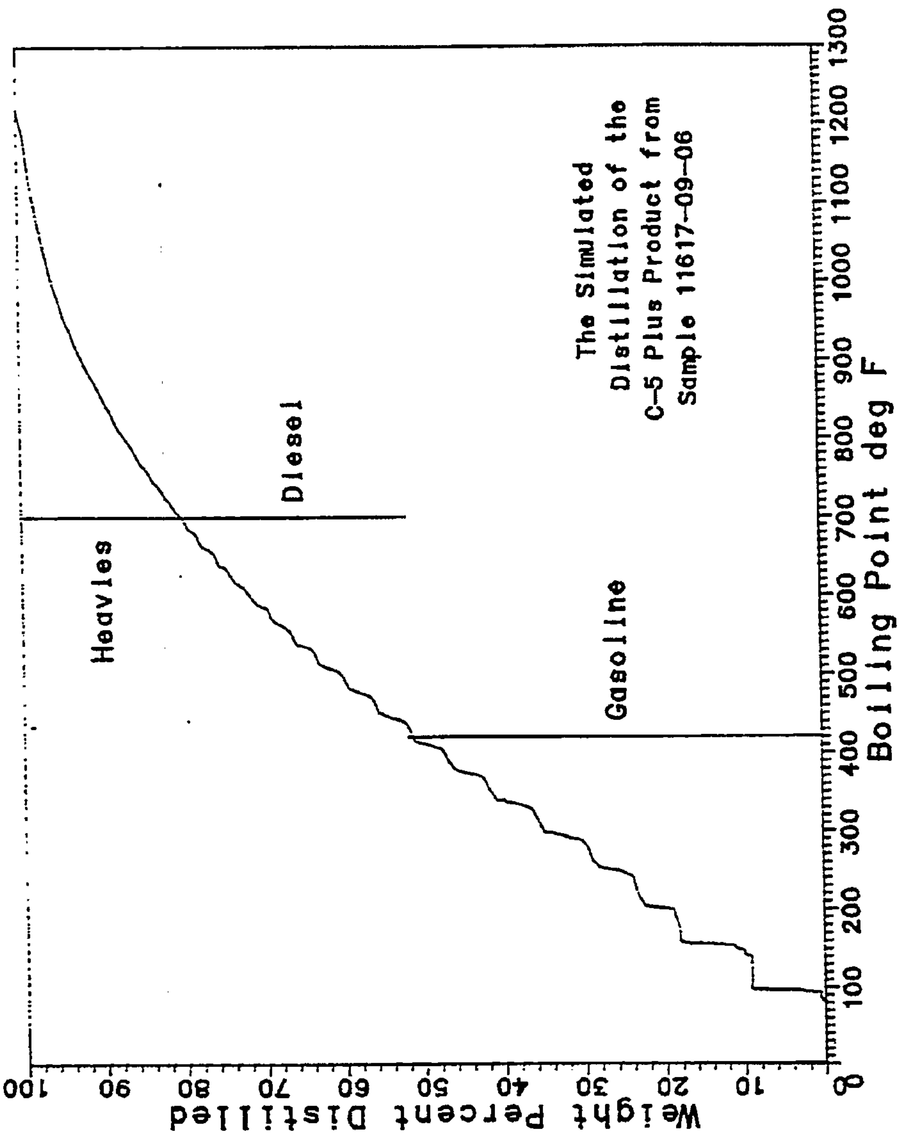

The Simulated Distillation of the C–5 Plus Product from Heavies Sample 11617–09–05
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B98



The Simulated Distillation of the C-5 Plus Product from Sample 11617-09-06
Heavies
Diesel
Gasoline
Boiling Point deg F
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
Weight Percent Distilled
0 10 20 30 40 50 60 70 80 90 100

Fig. B99

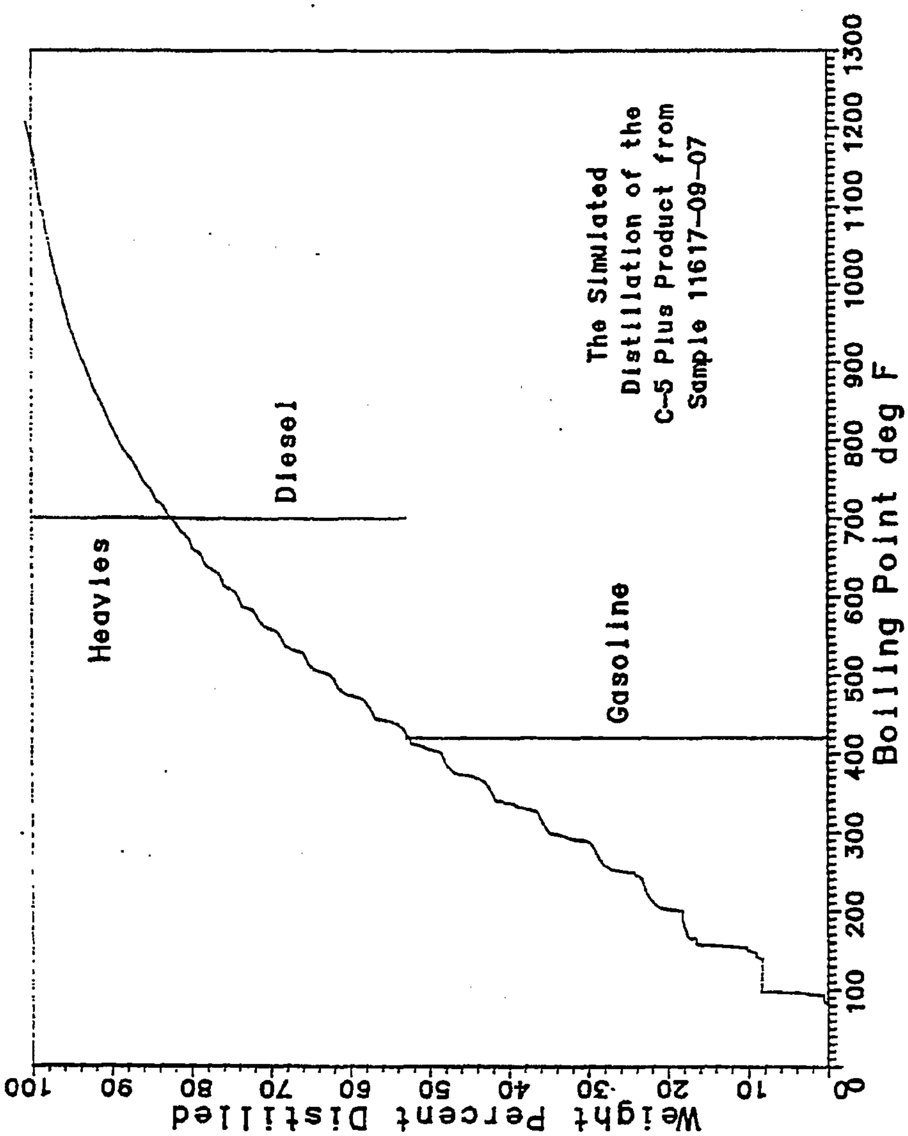
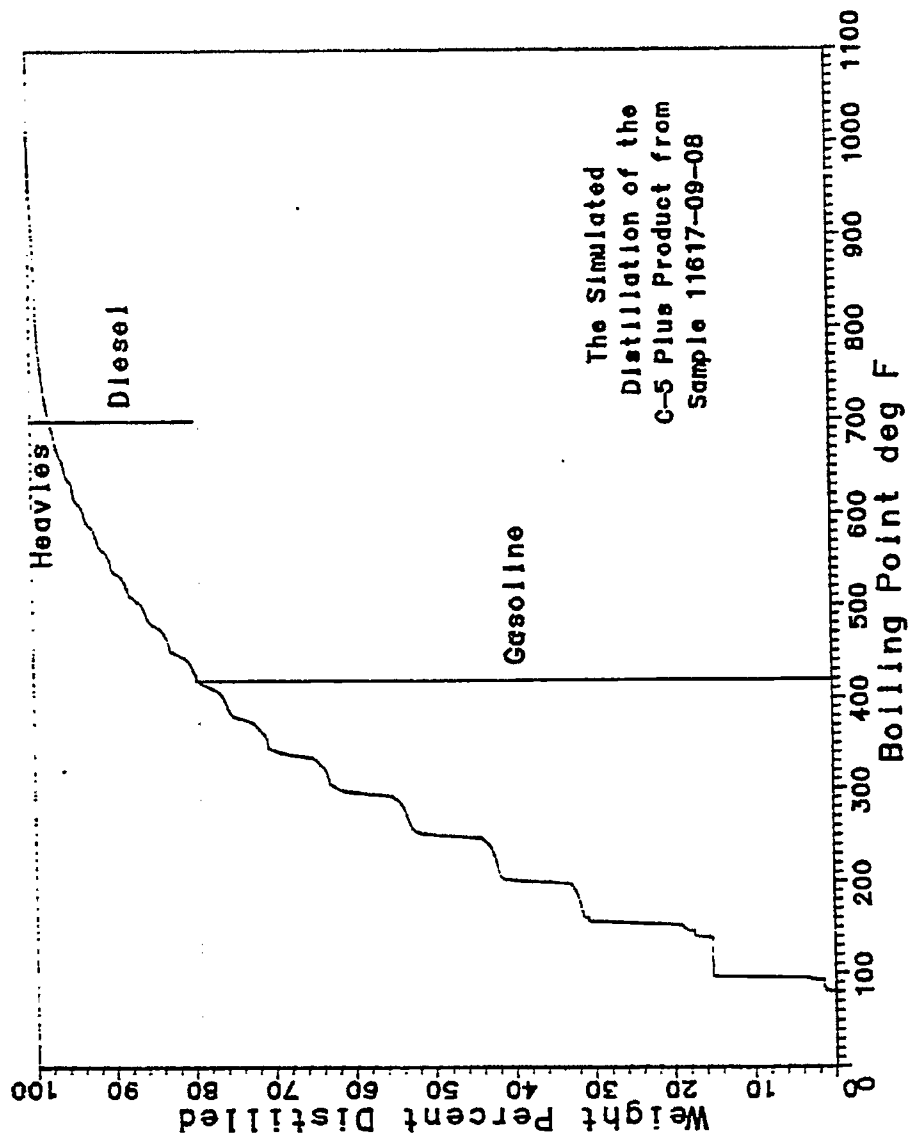

The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-09-07
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300

Fig. B100



The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-09-08
Heavies
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100

Fig. B101

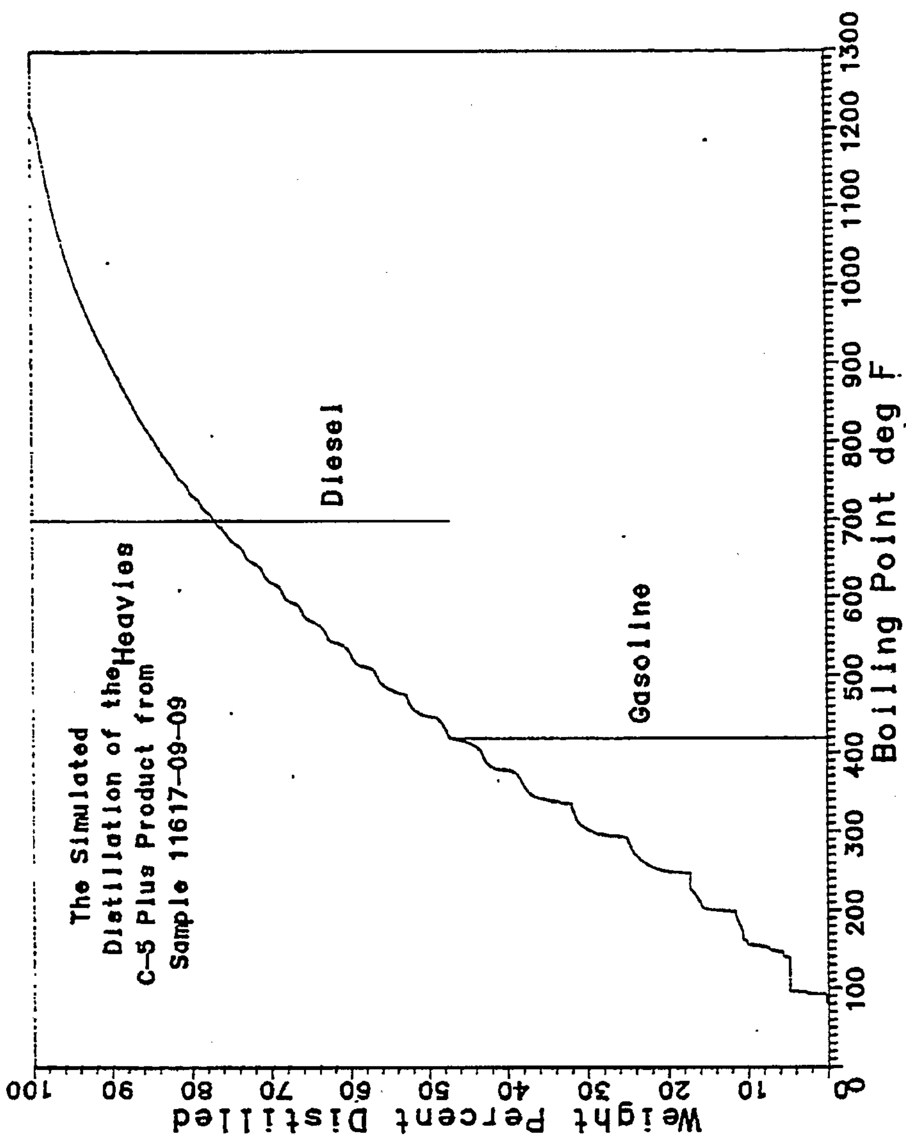
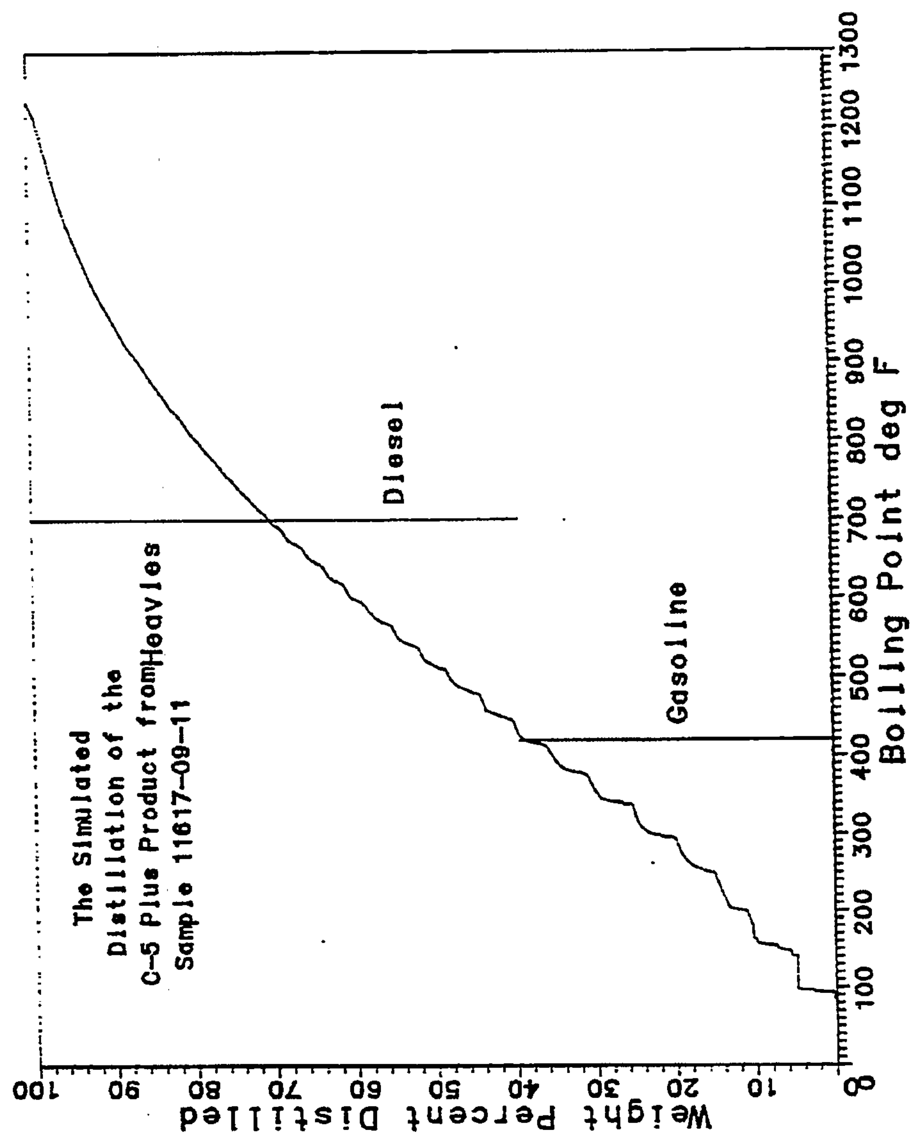

The Simulated
Distillation of the Heavies
C-5 Plus Product from
Sample 11617-09-09
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B102



The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 11617-09-11
Diesel
Gasoline
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
Weight Percent Distilled

Fig. B103

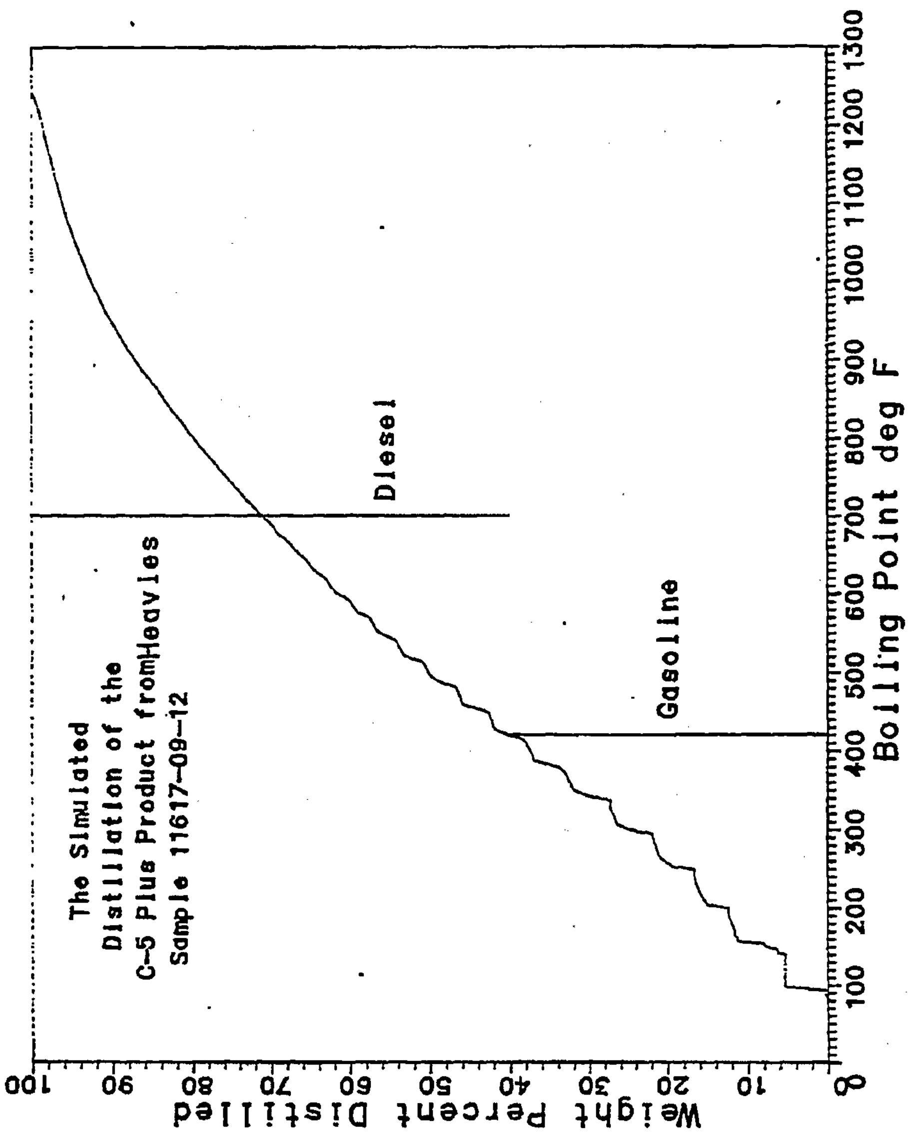

The Simulated
Distillation of the
C-5 Plus Product fromHeavies
Sample 11617-09-12
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B104

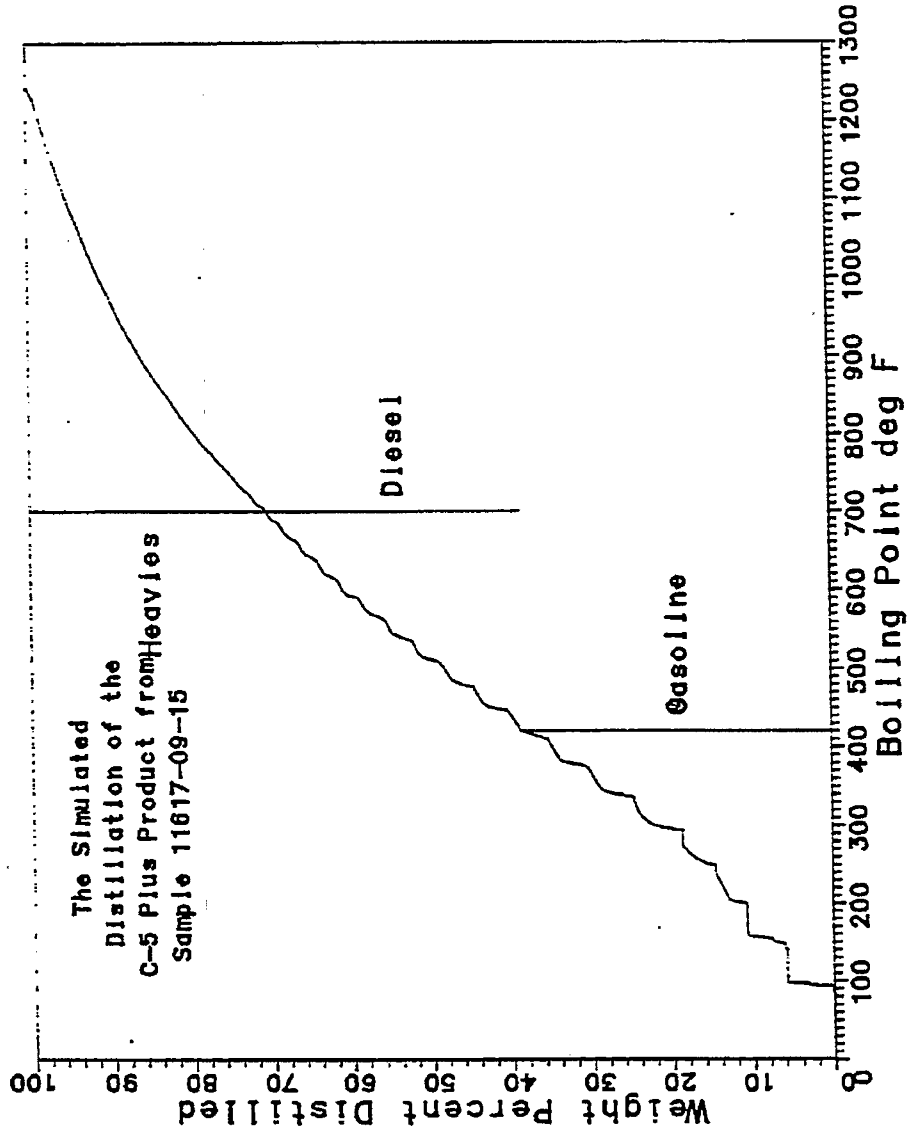

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 11617-09-15
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
0 10 20 30 40 50 60 70 80 90 100

Fig. B105

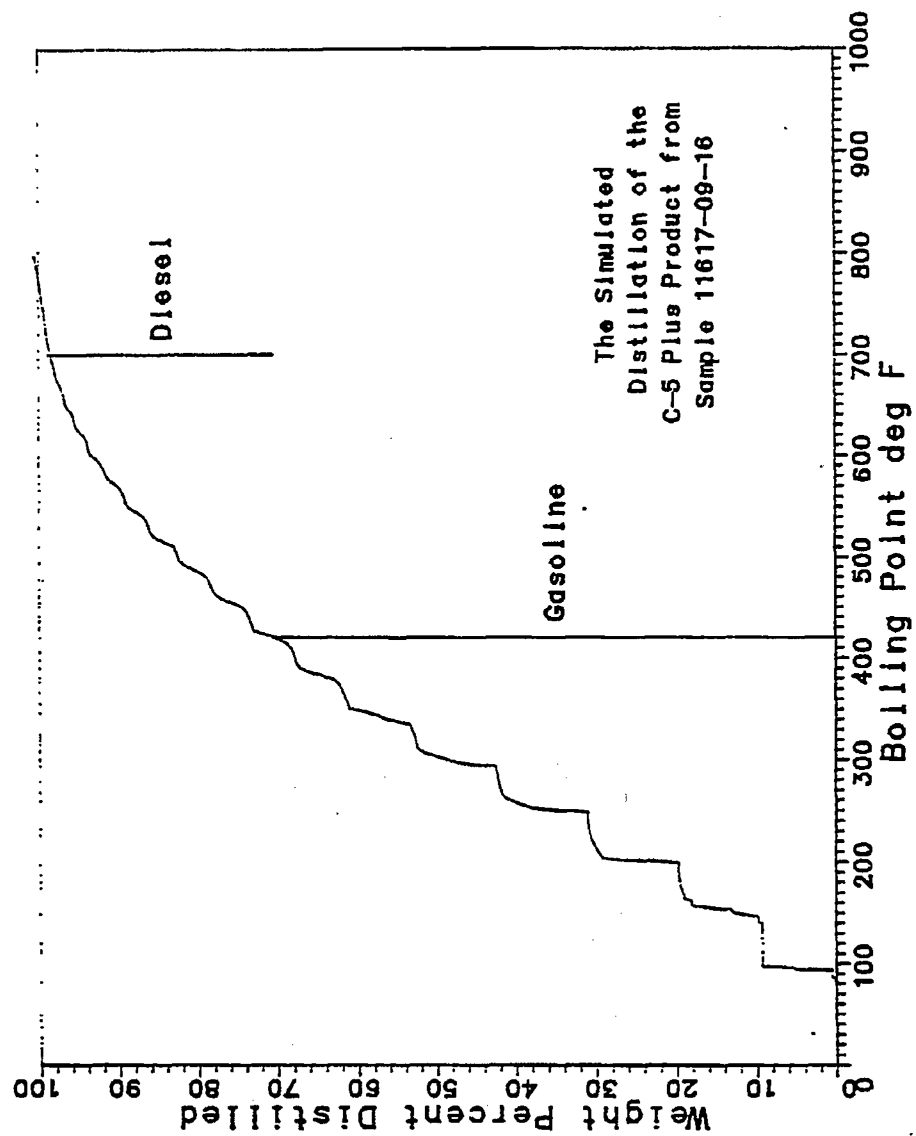

Diesel
Gasoline
The Simulated
Distillation of the
C-5 Plus Product from
Sample 11617-09-16
Boiling Point deg F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B106

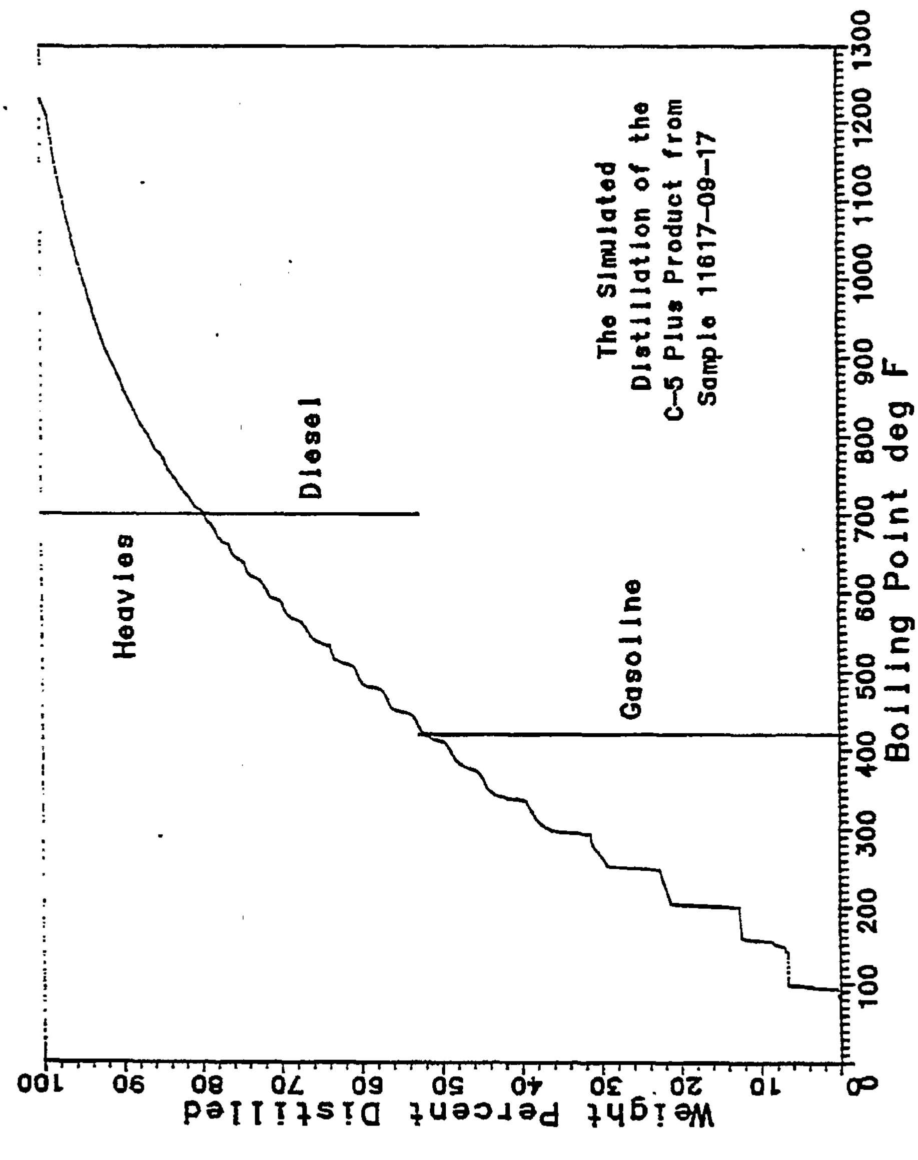

The Simulated Distillation of the C-5 Plus Product from Sample 11617-09-17
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0 10 20 30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300

Fig. B107

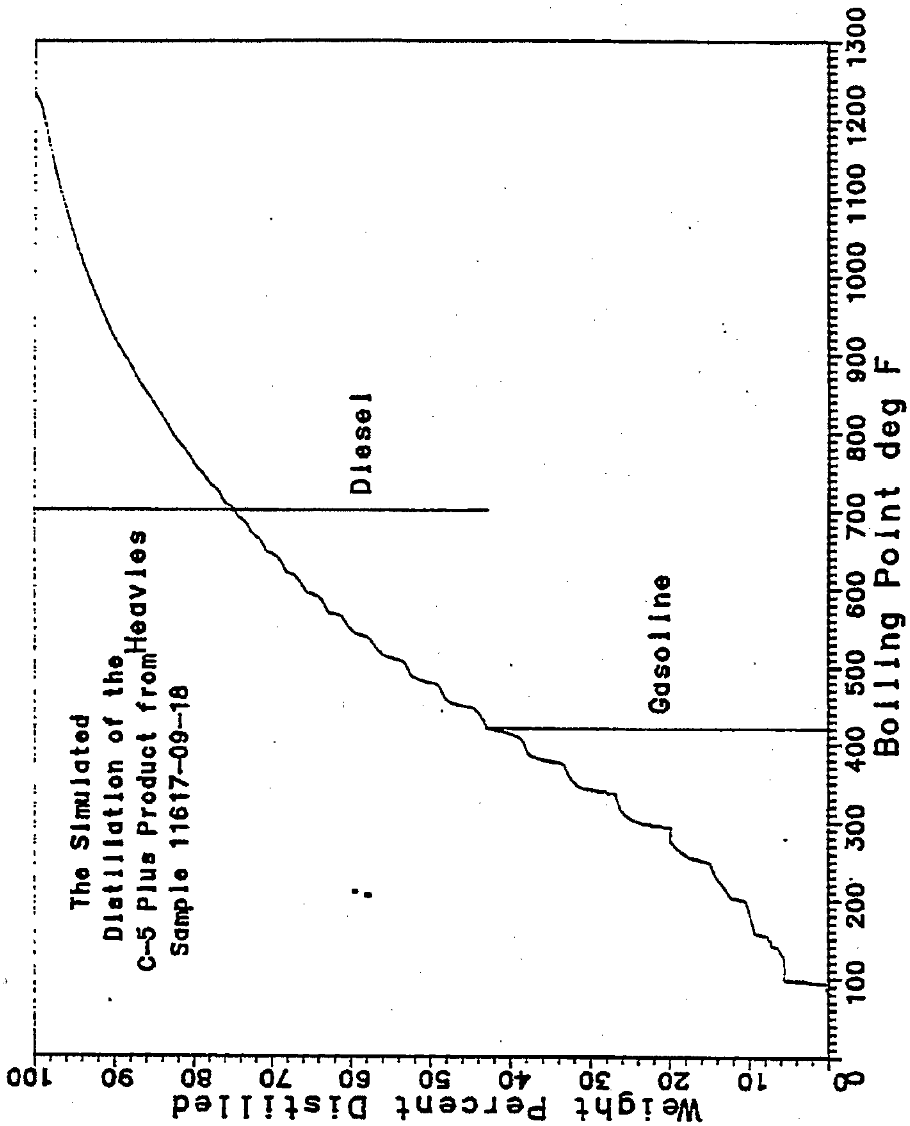

The Simulated
Distillation of the
C-5 Plus Product from Heavies
Sample 11617-09-18
Diesel
Gasoline
Boiling Point deg F
Weight Percent Distilled

Fig. B108

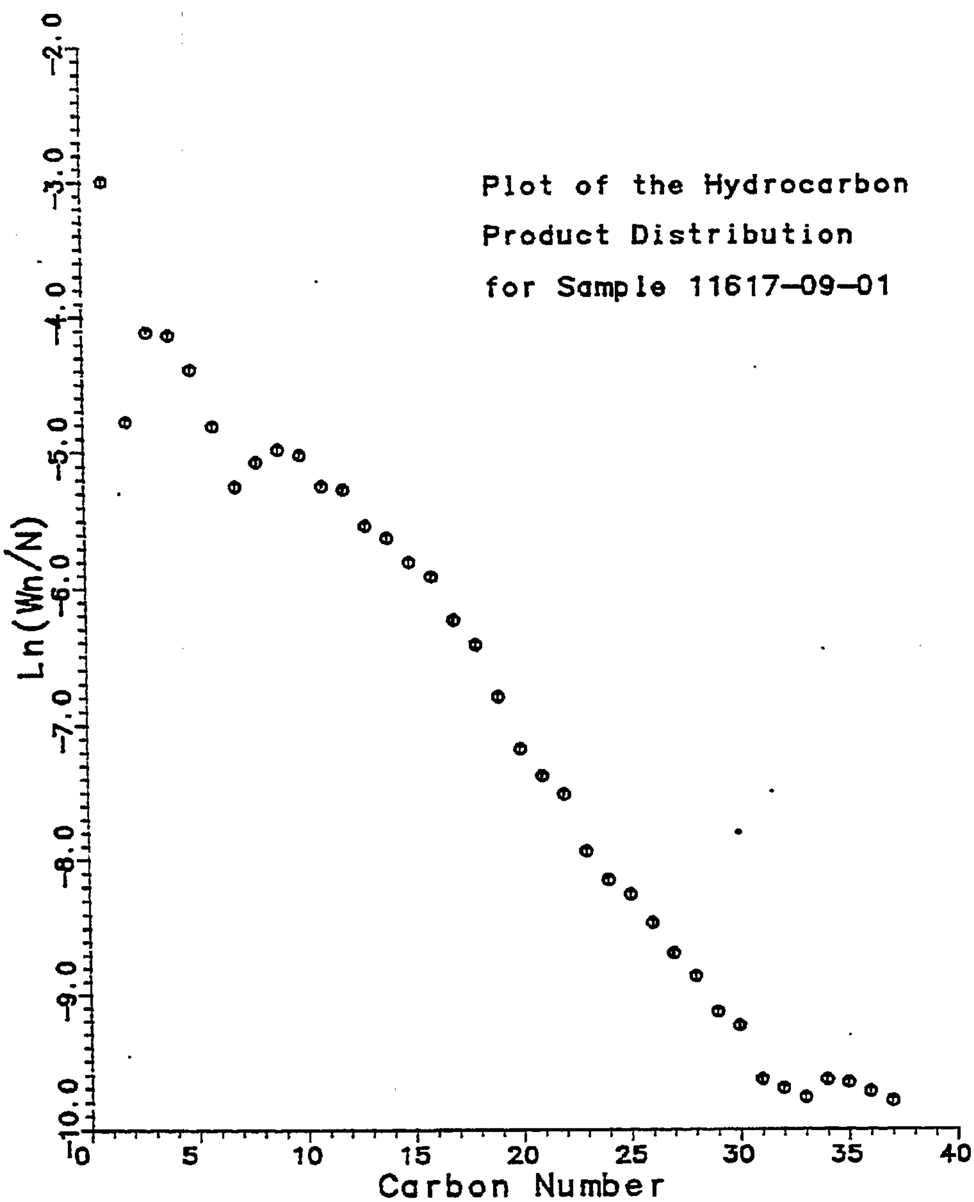

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-01
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B109

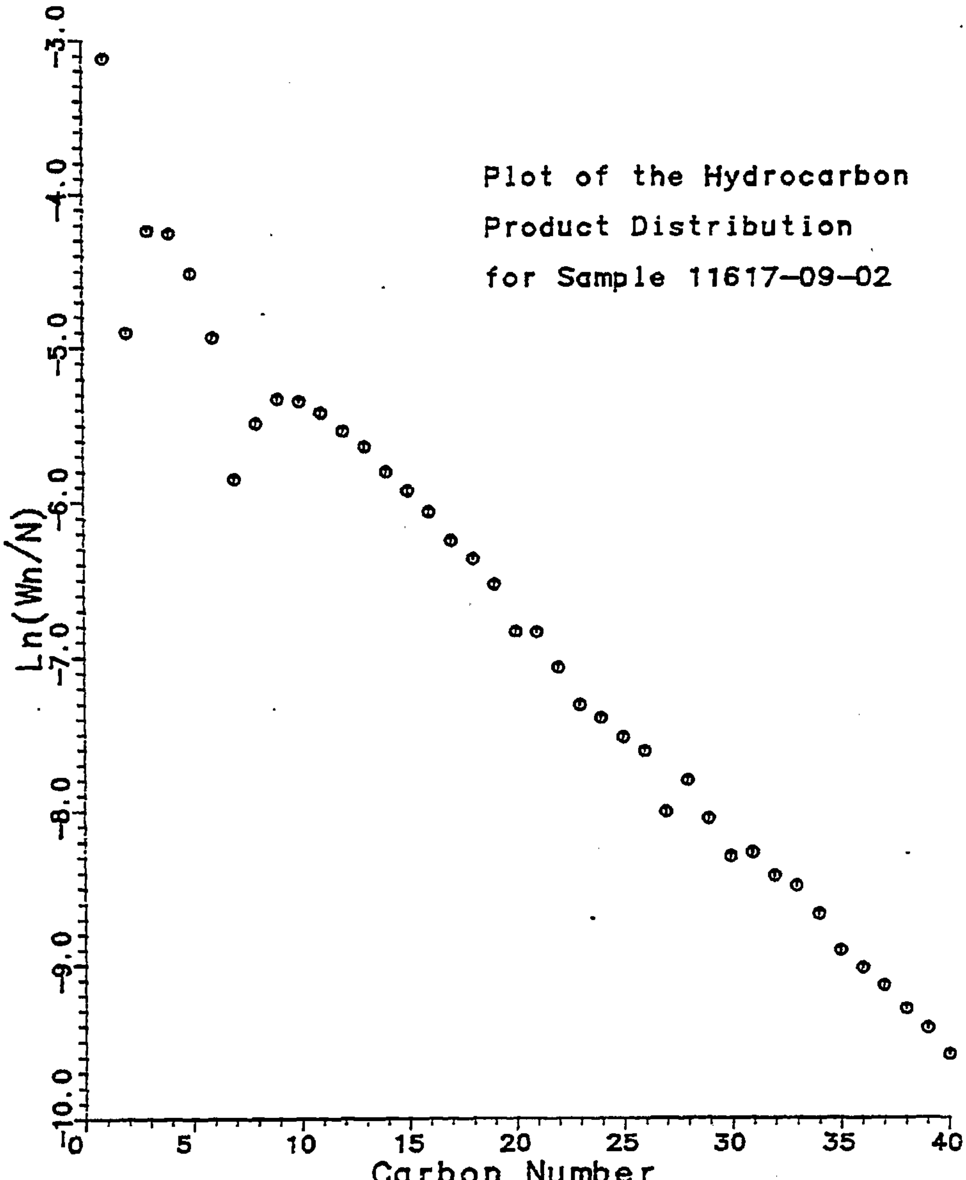
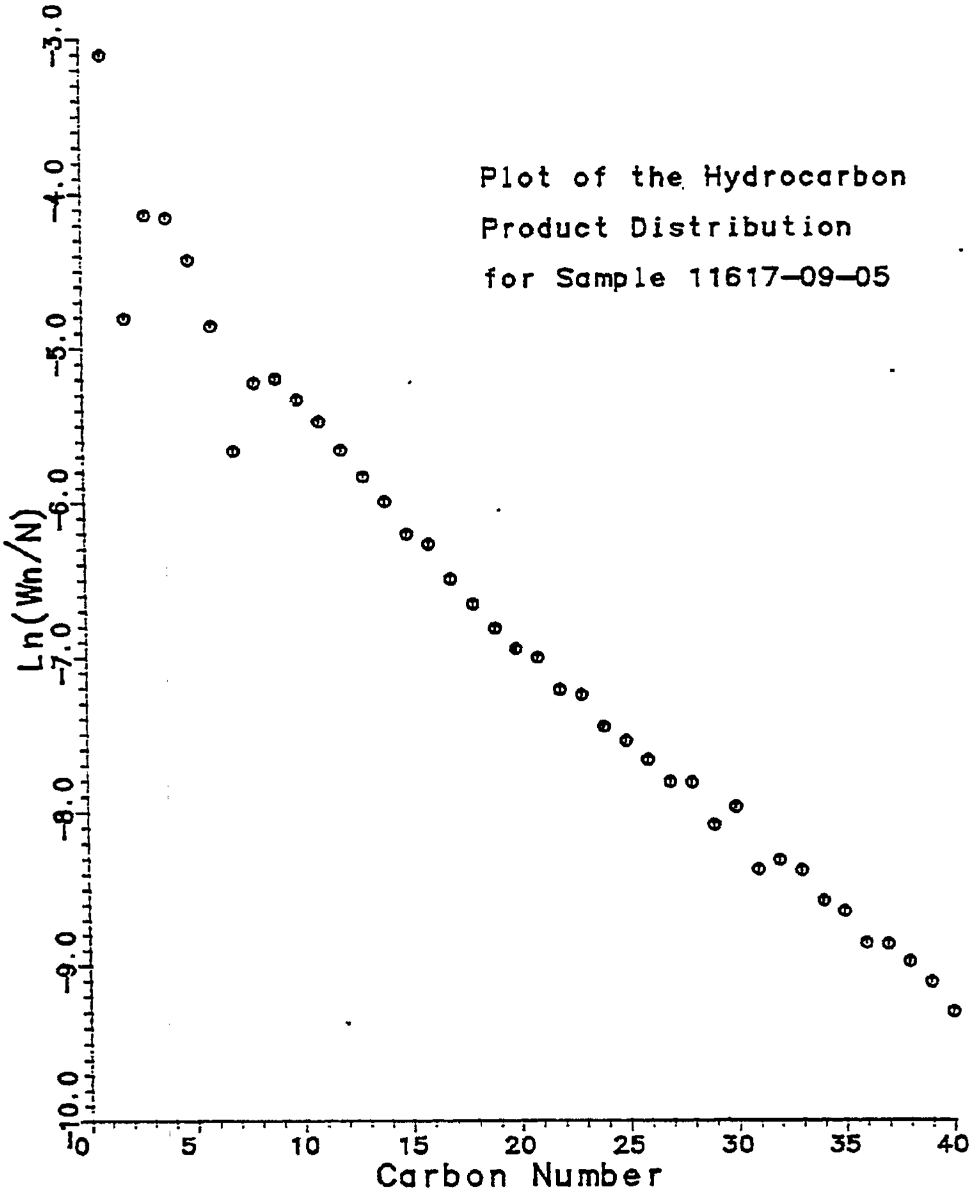

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-02
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B110



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-05
Ln(Wn/N)
-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. B111

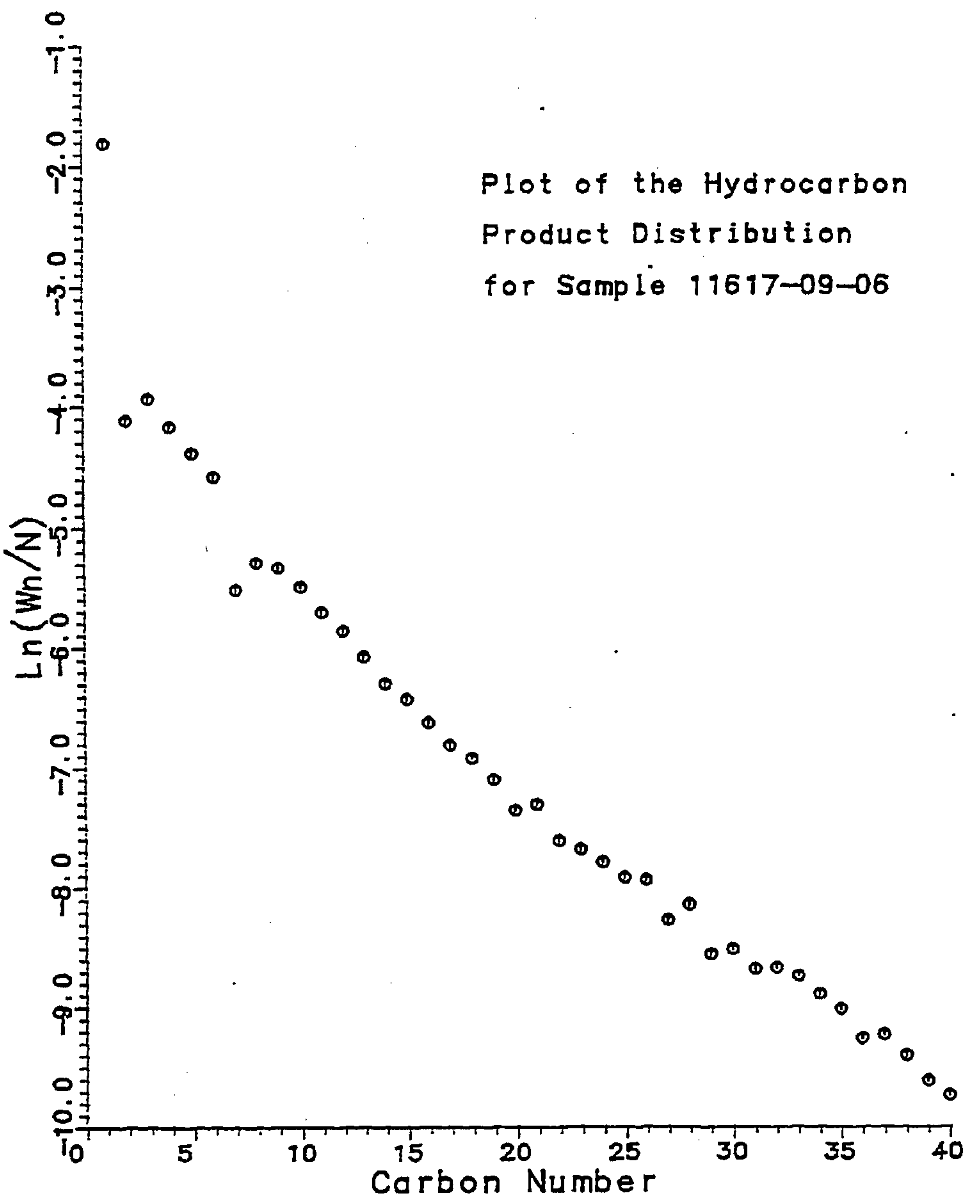
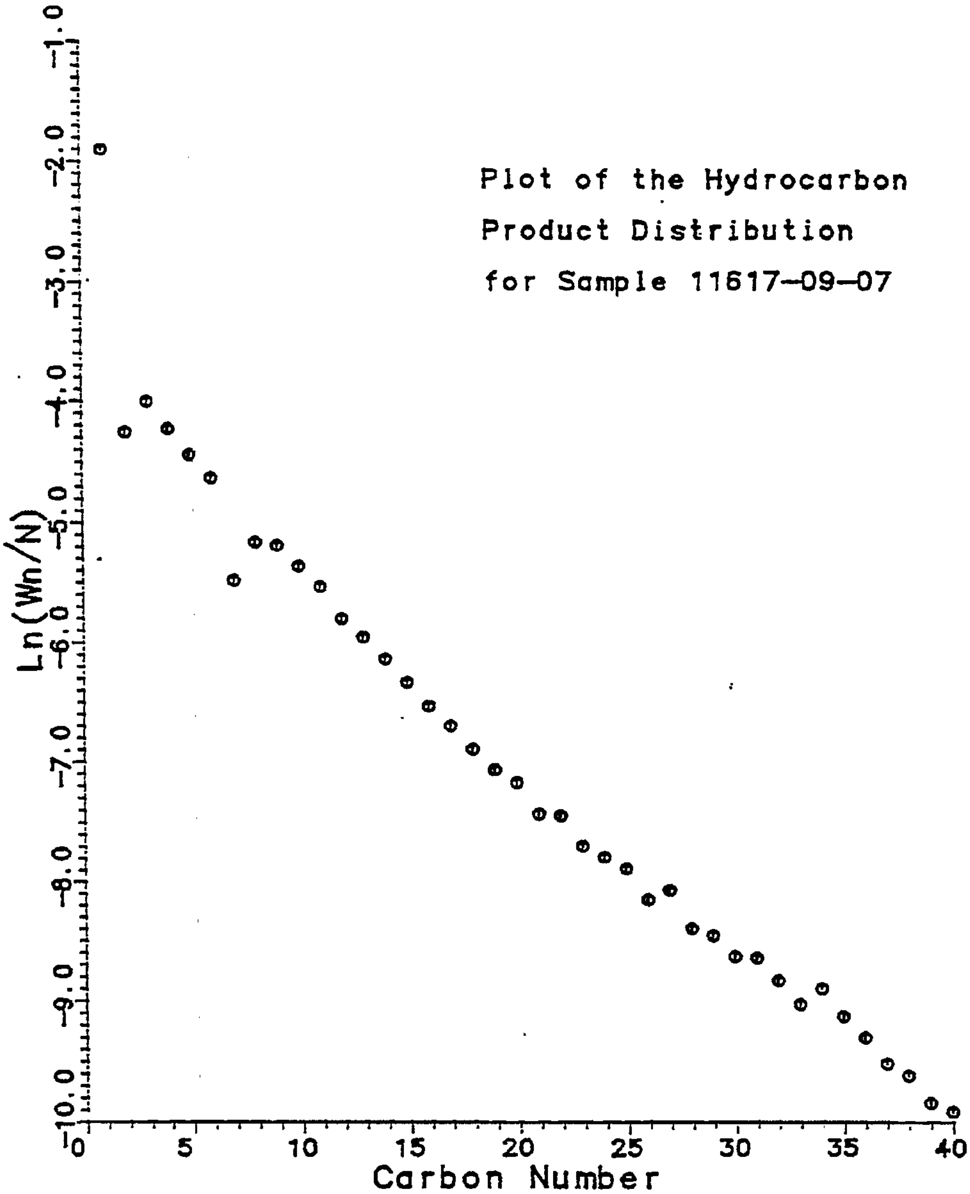
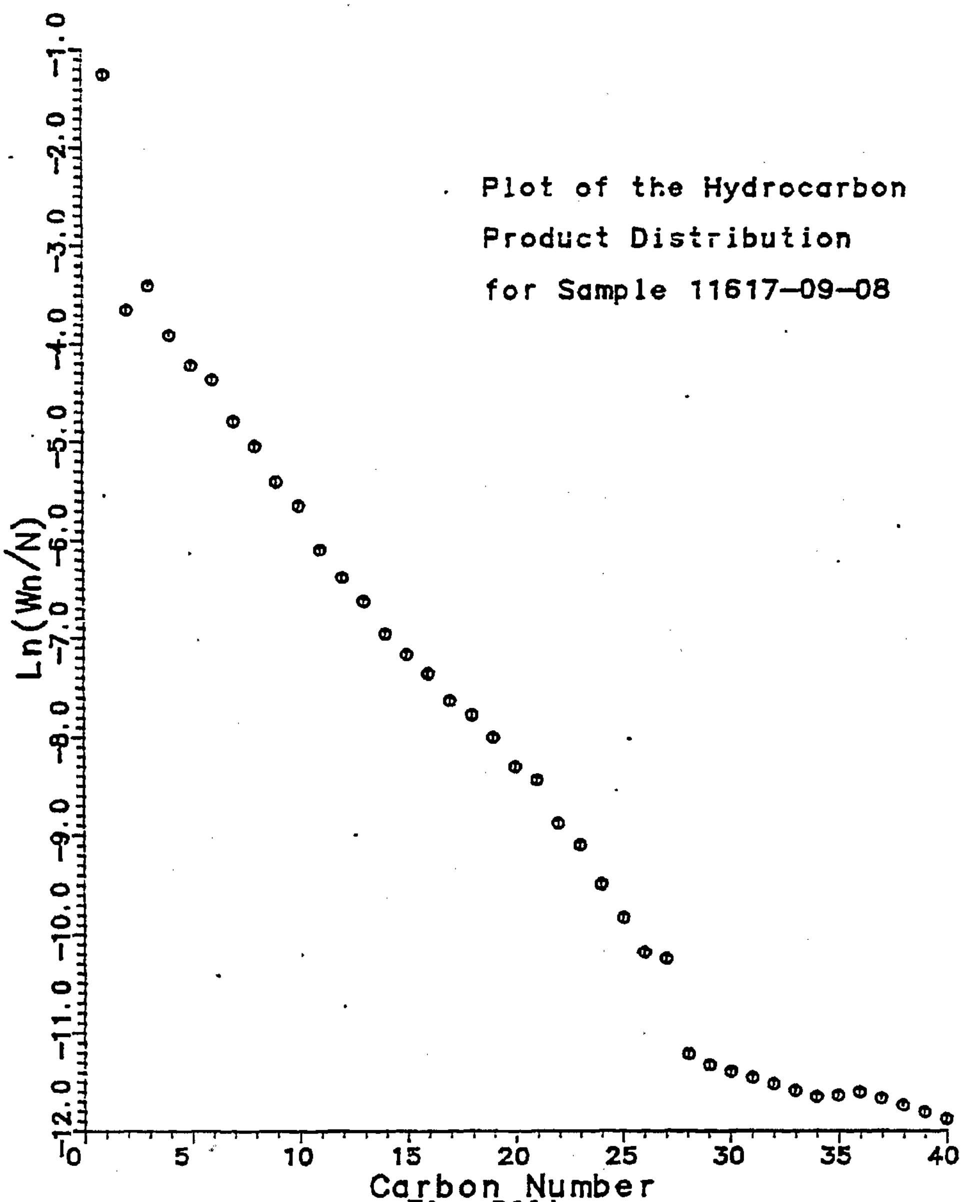
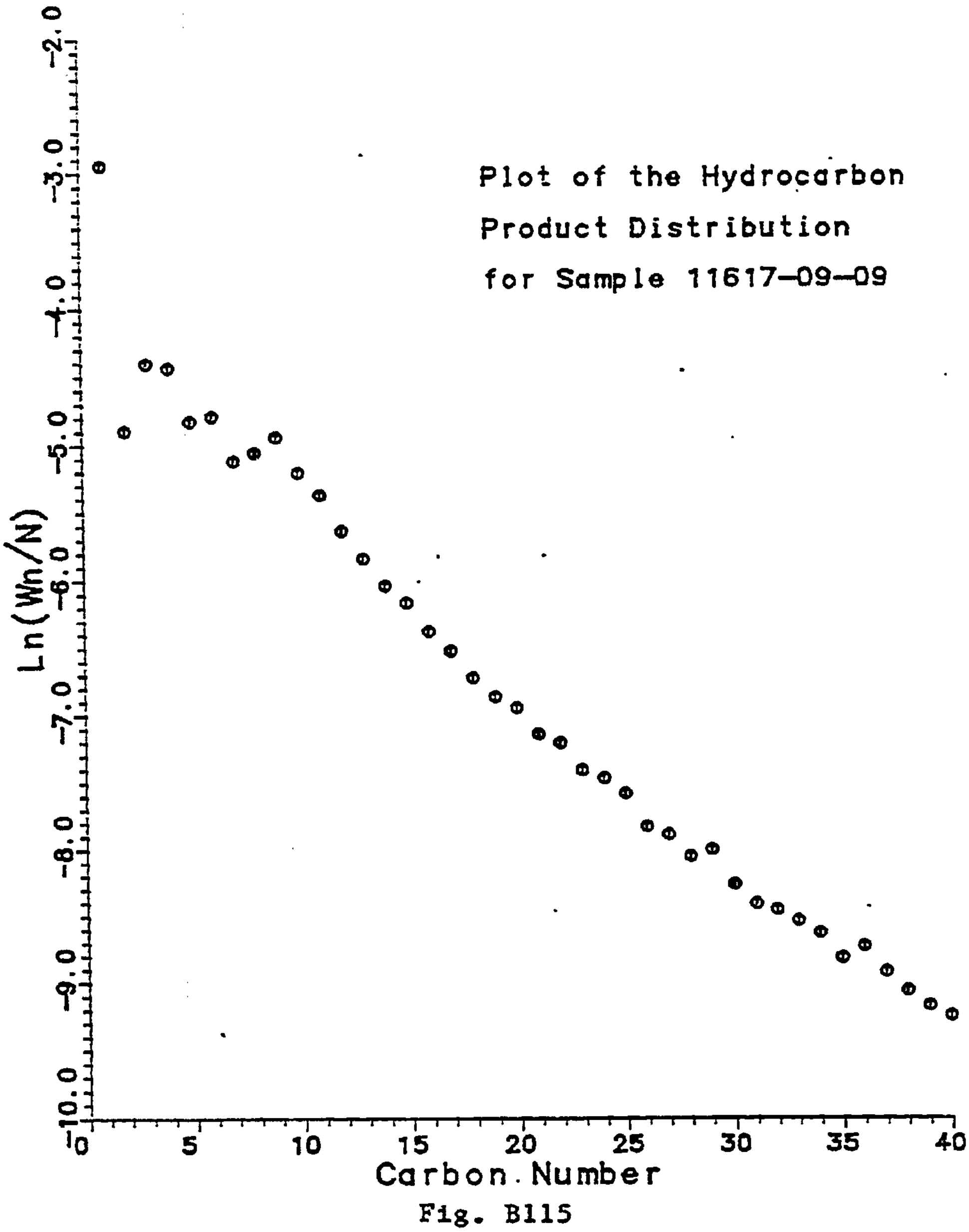

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-06
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B112


Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-07
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B113


Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-08
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0
5
10
15
20
25
30
35
40
Carbon Number
Fig. B114



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-09
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B115

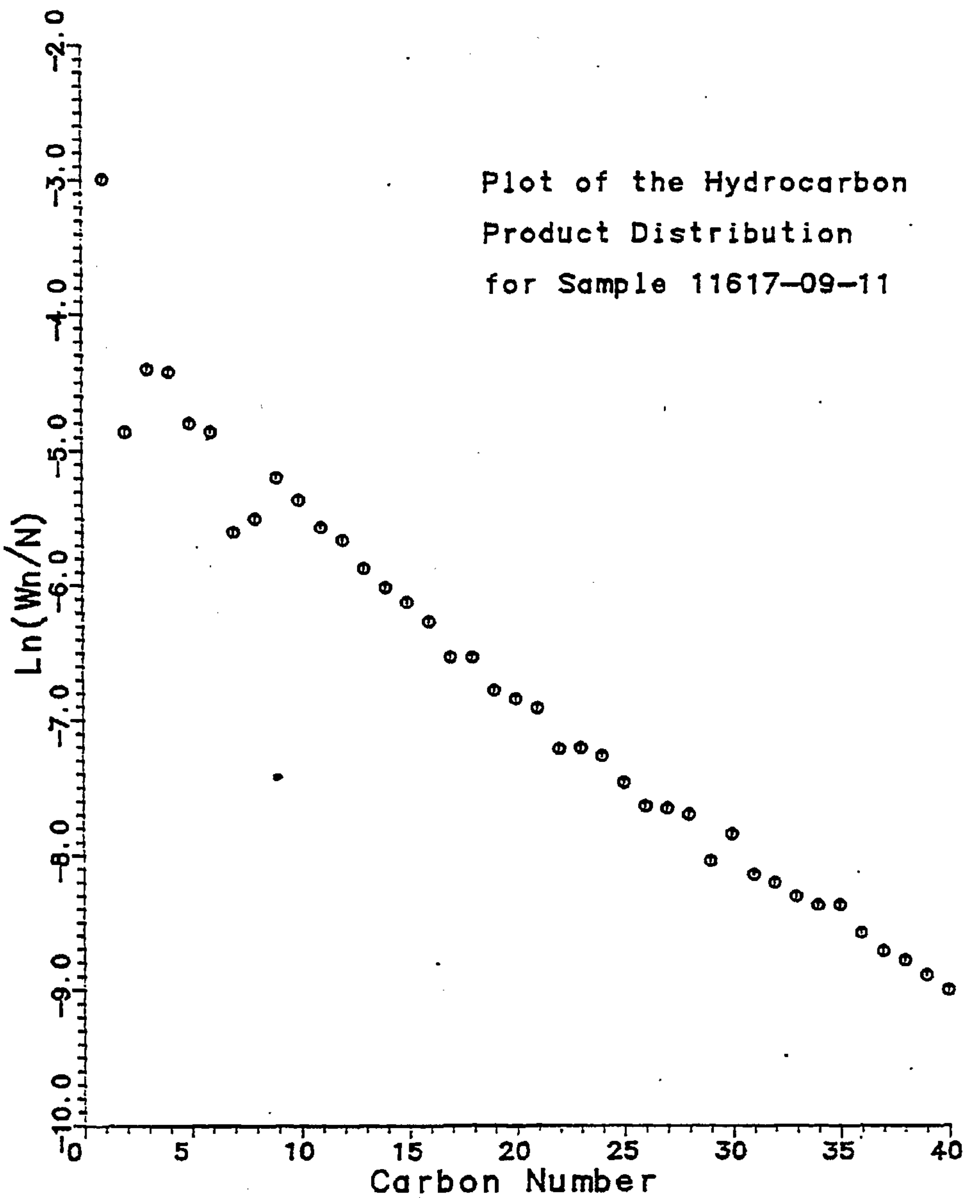
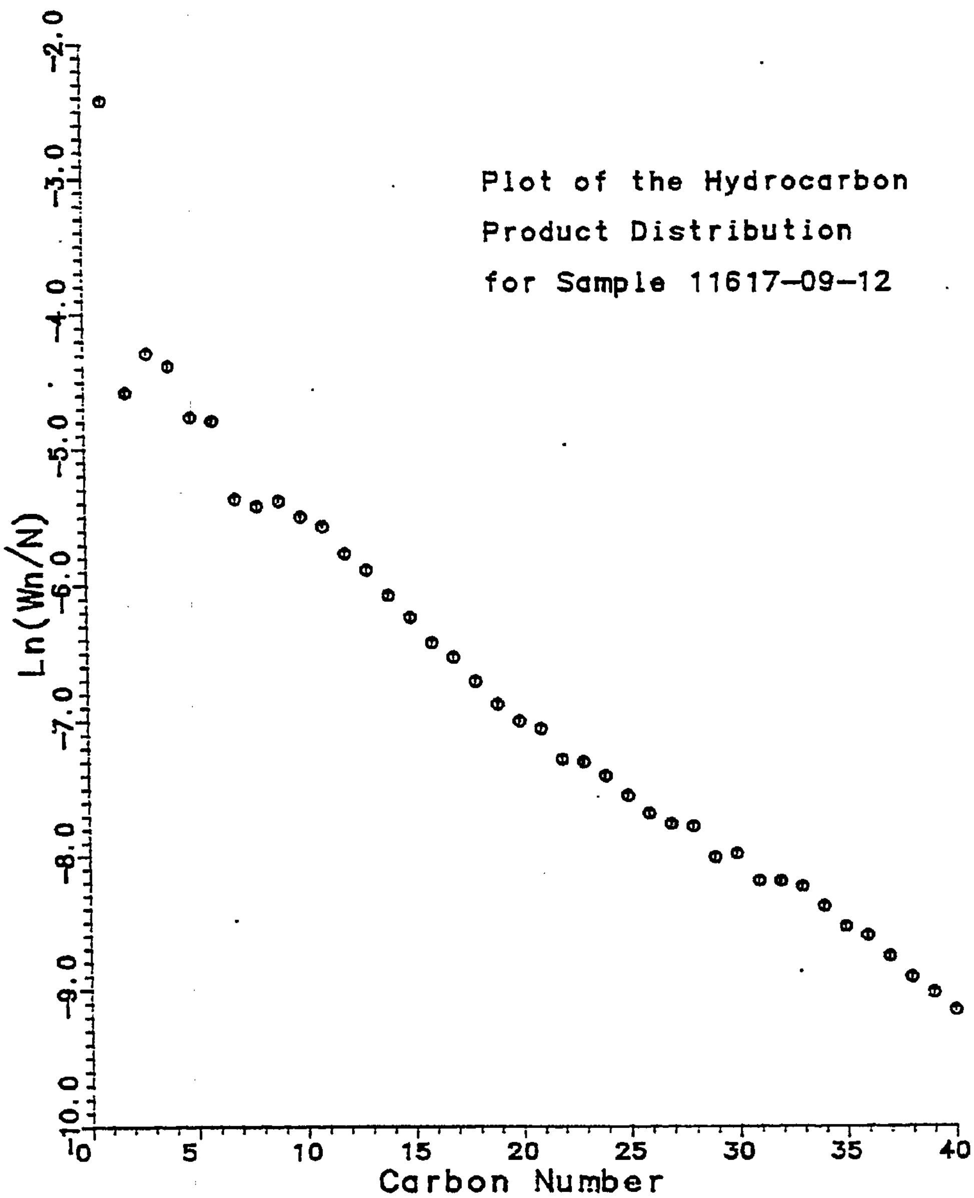
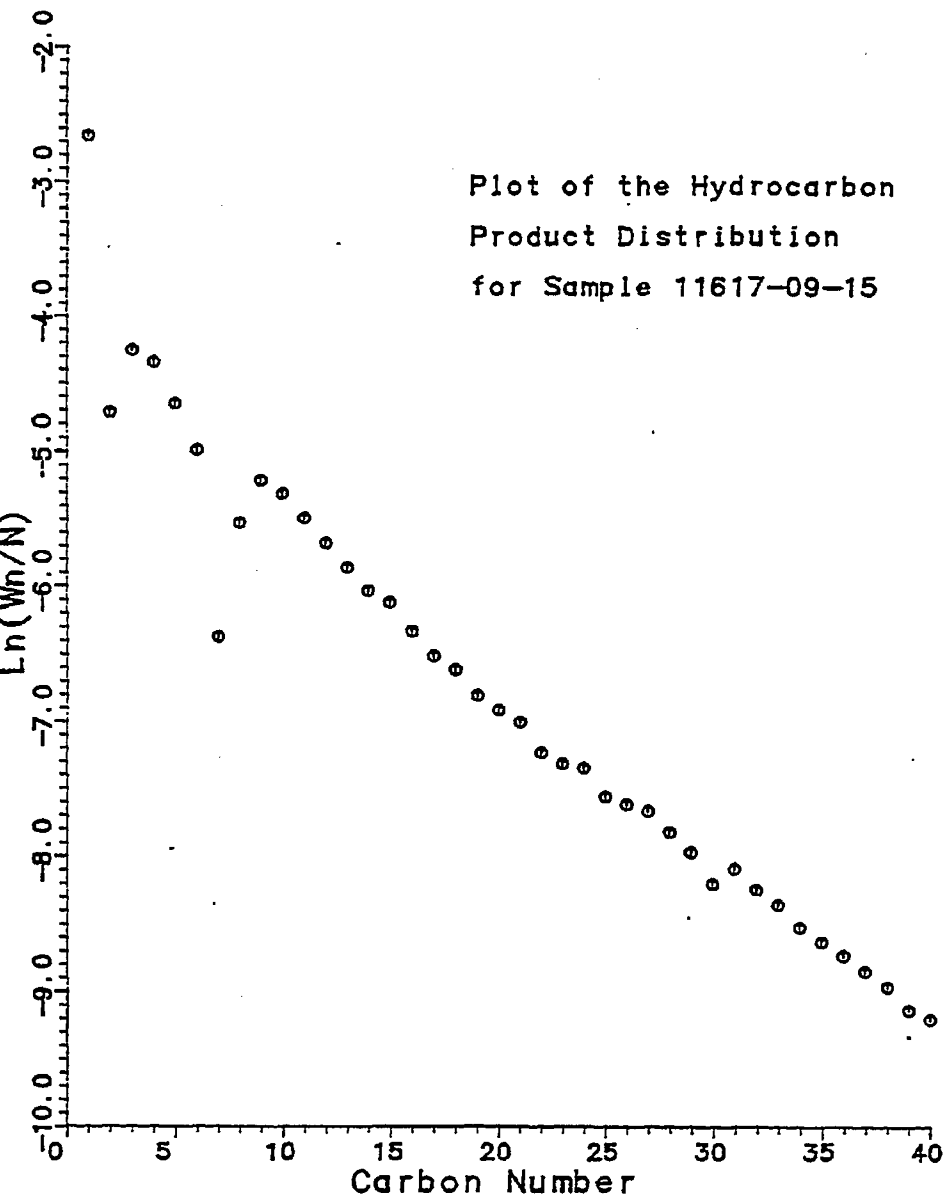

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-11
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B116



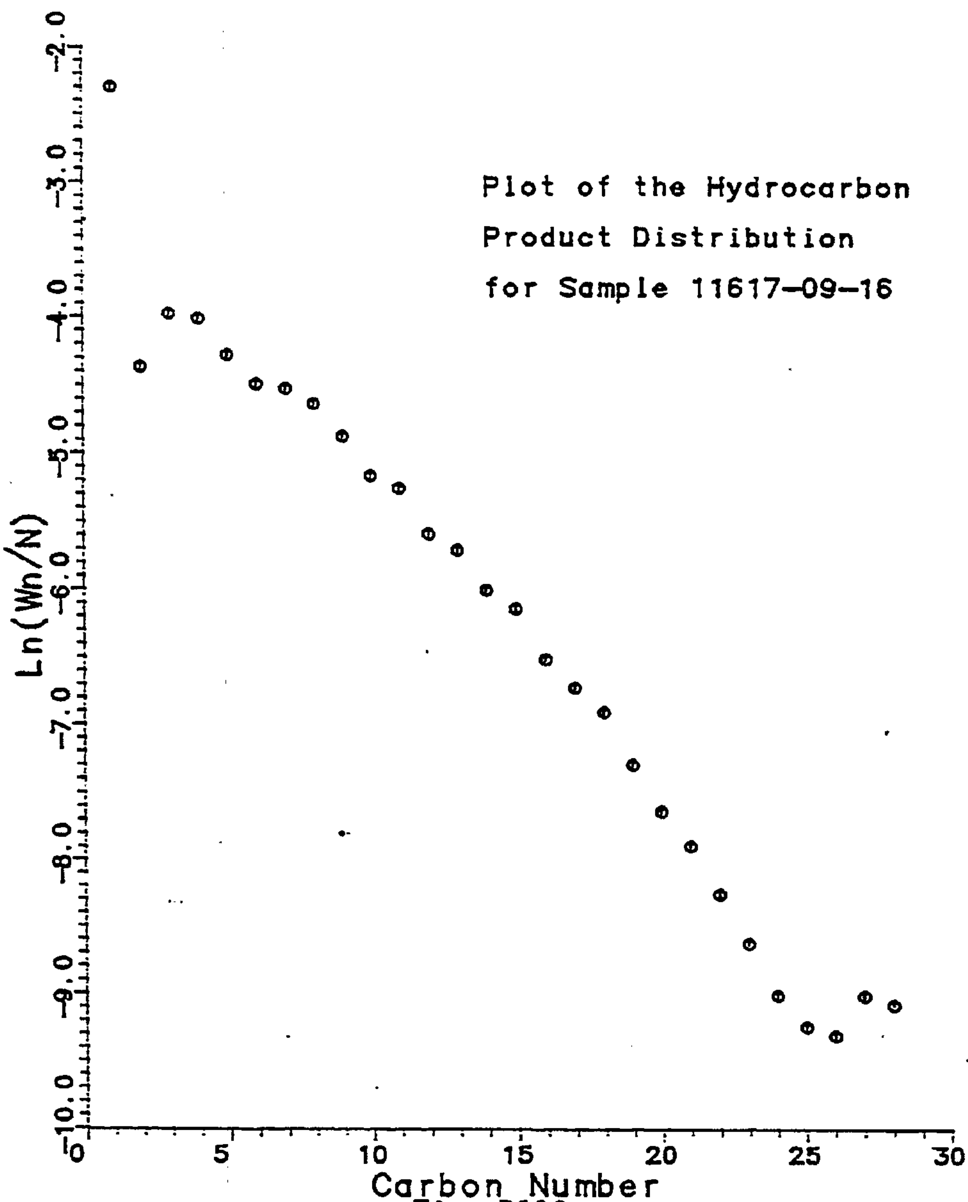
Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-12
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B117



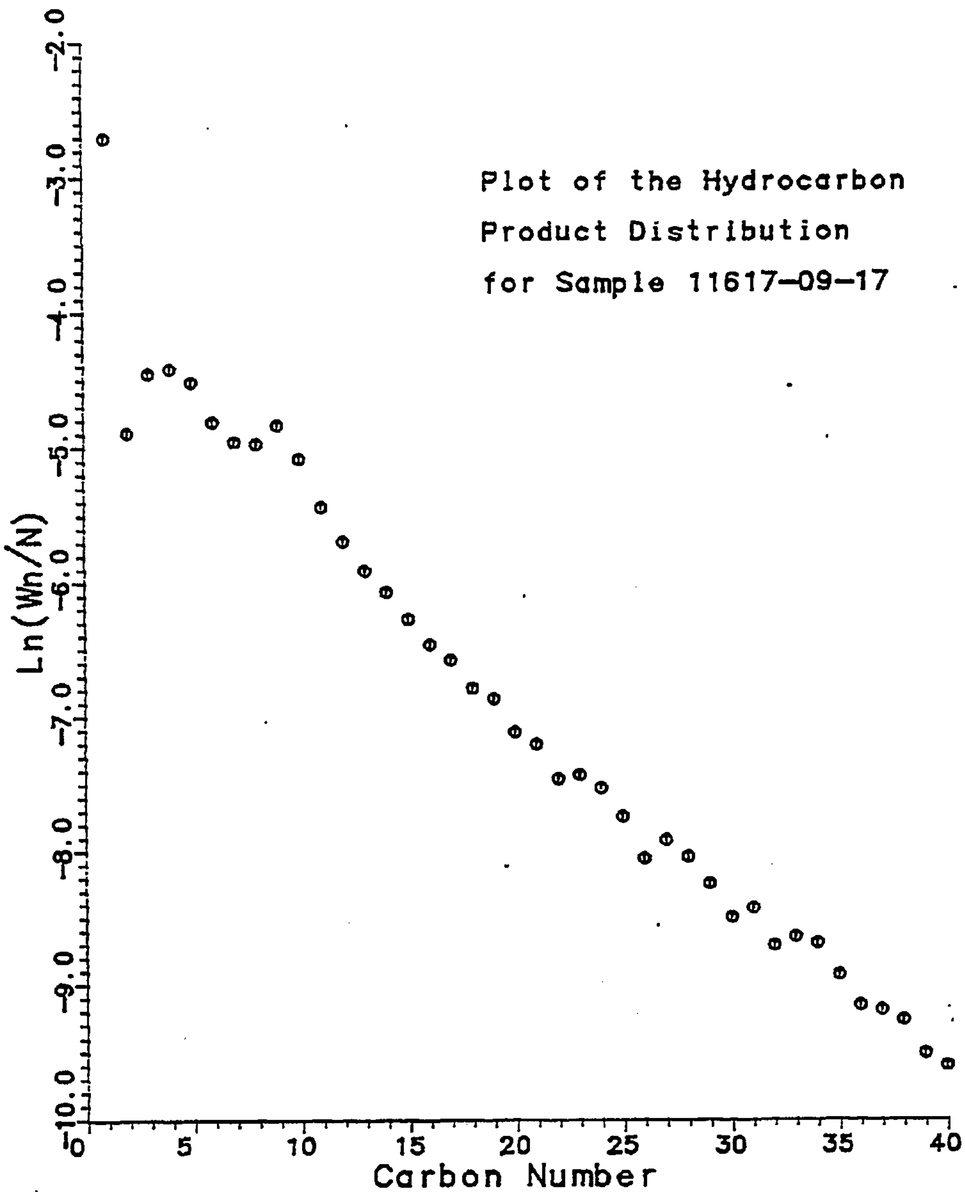
Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-15
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B118



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-16
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B119



Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-17
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
Ln(Wn/N)
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B120

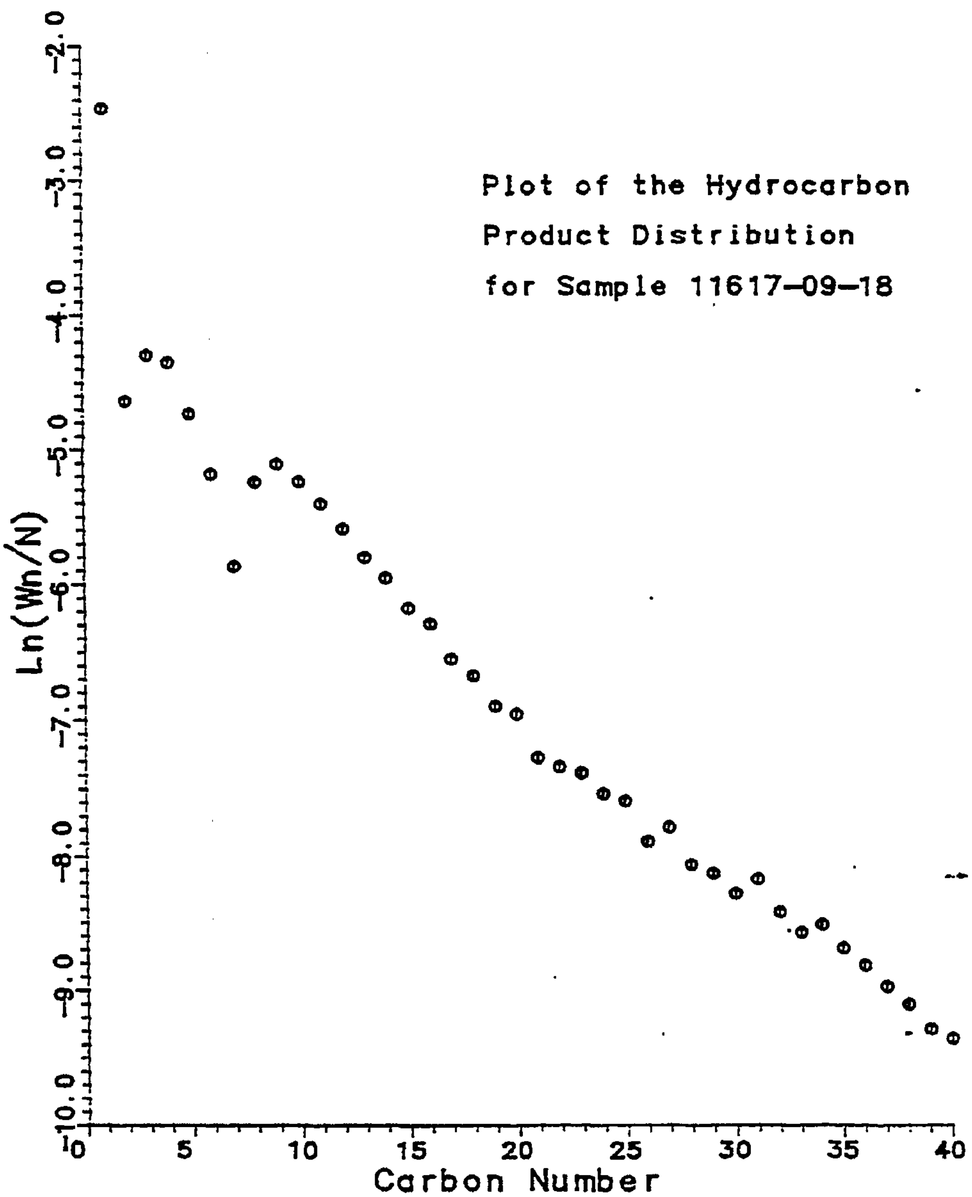

Plot of the Hydrocarbon
Product Distribution
for Sample 11617-09-18
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B121

077

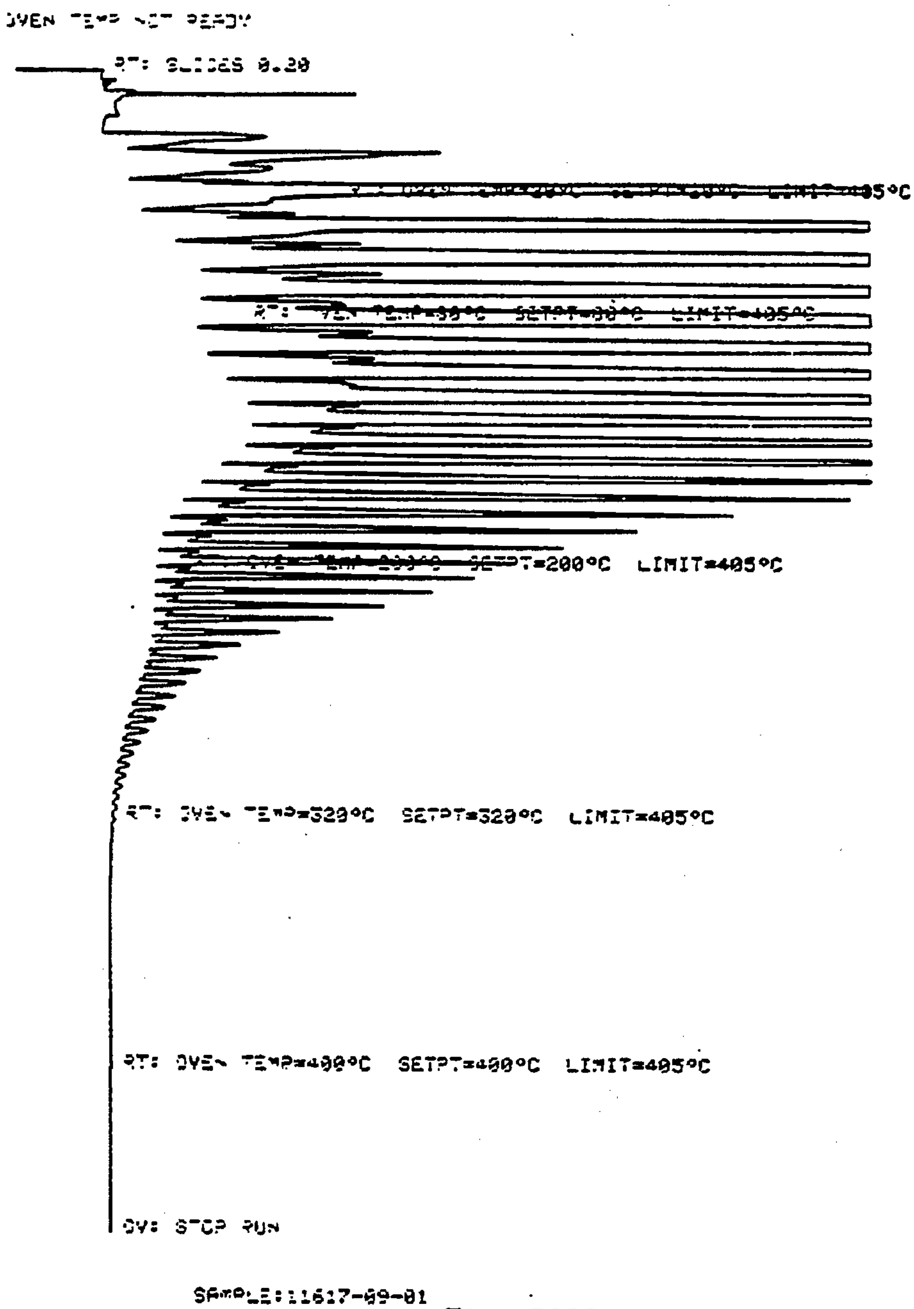

SETPT=200°C LIMIT=405°C
LIMIT=405°C
SETPT=400°C LIMIT=405°C
SAMPLE:11617-09-01

Fig. B122

078

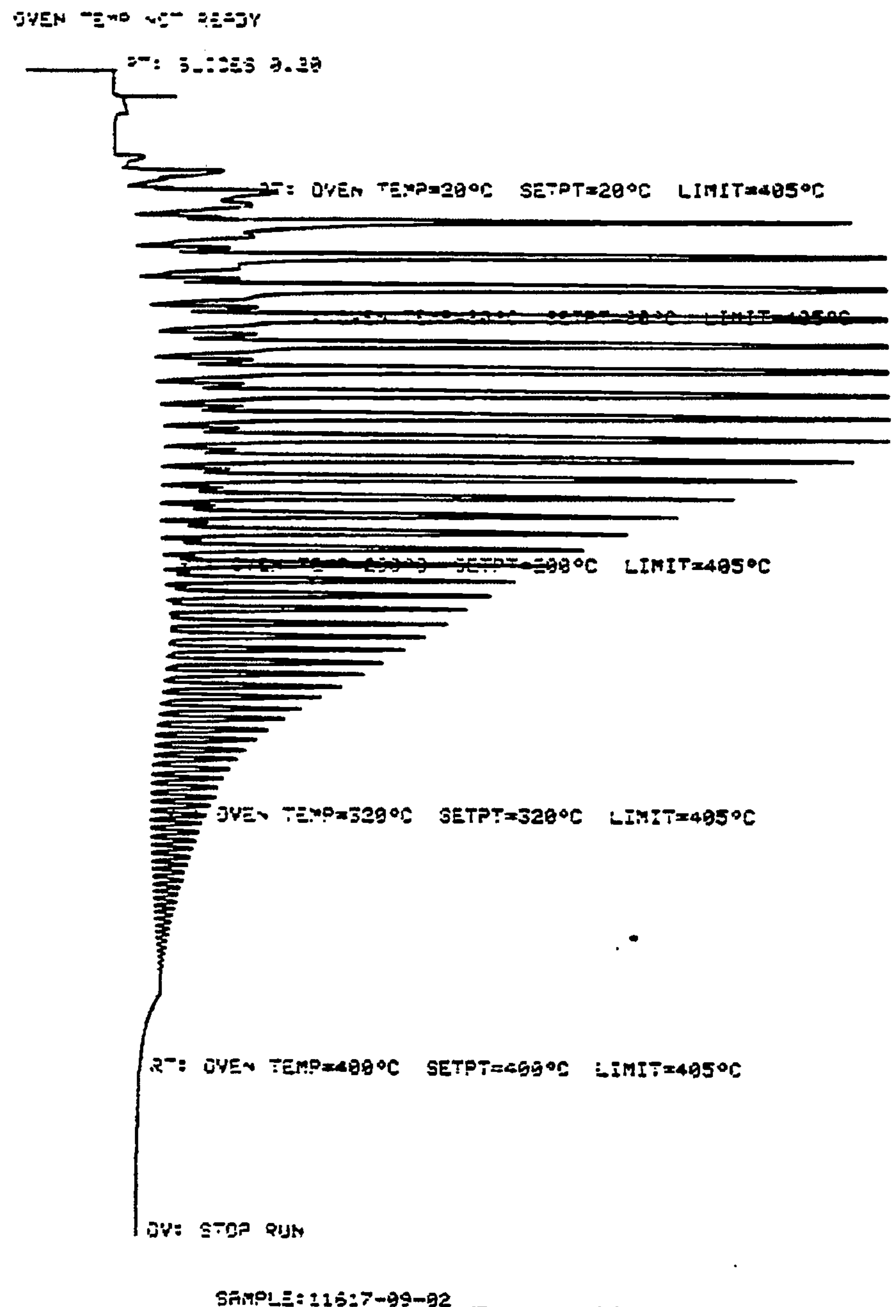

OVEN TEMP NOT READY
OVEN TEMP=20°C SETPT=20°C LIMIT=405°C
SETPT=200°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C
OV: STOP RUN
SAMPLE:11617-09-02

Fig. B123

079

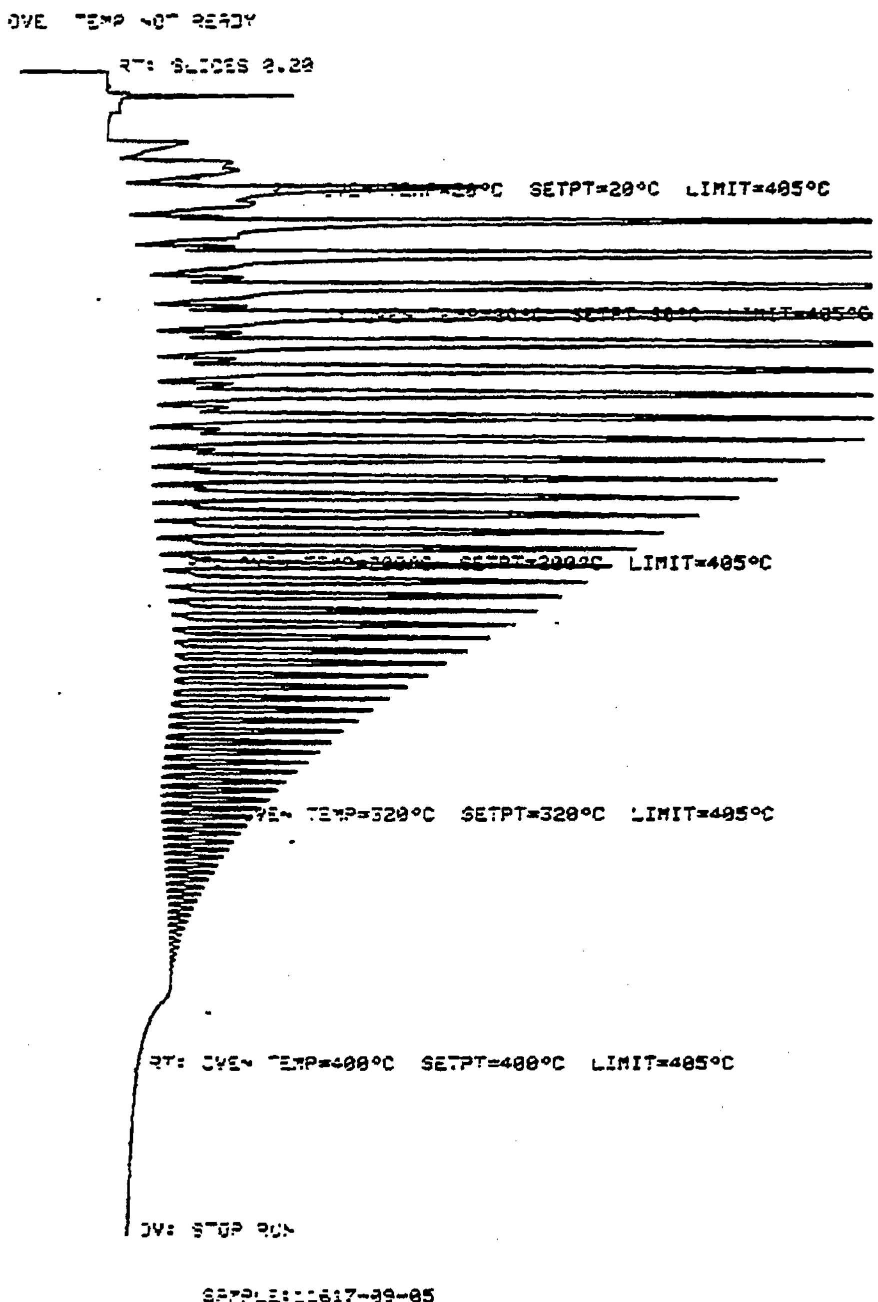

SETPT=20°C LIMIT=405°C
LIMIT=405°C
TEMP=320°C SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B124

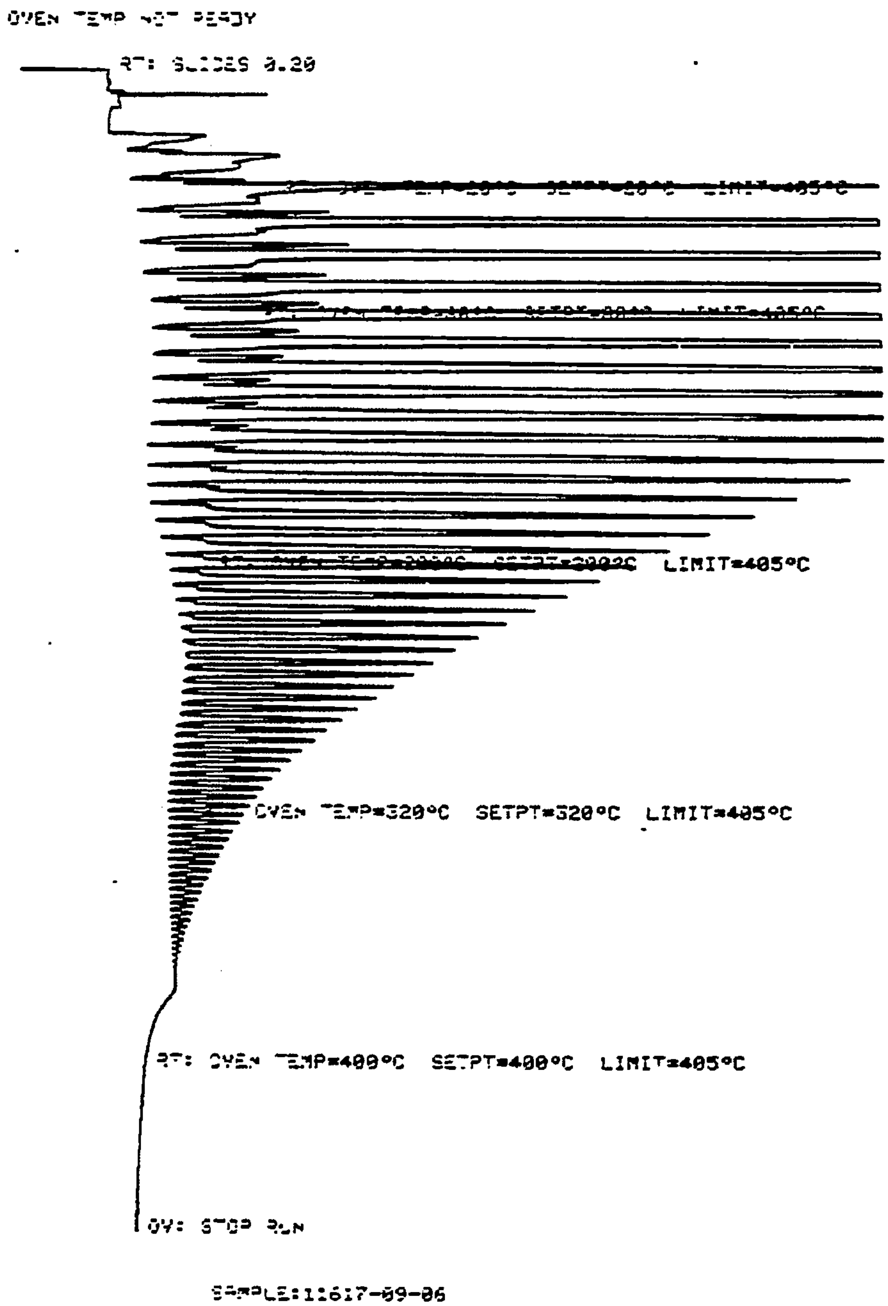
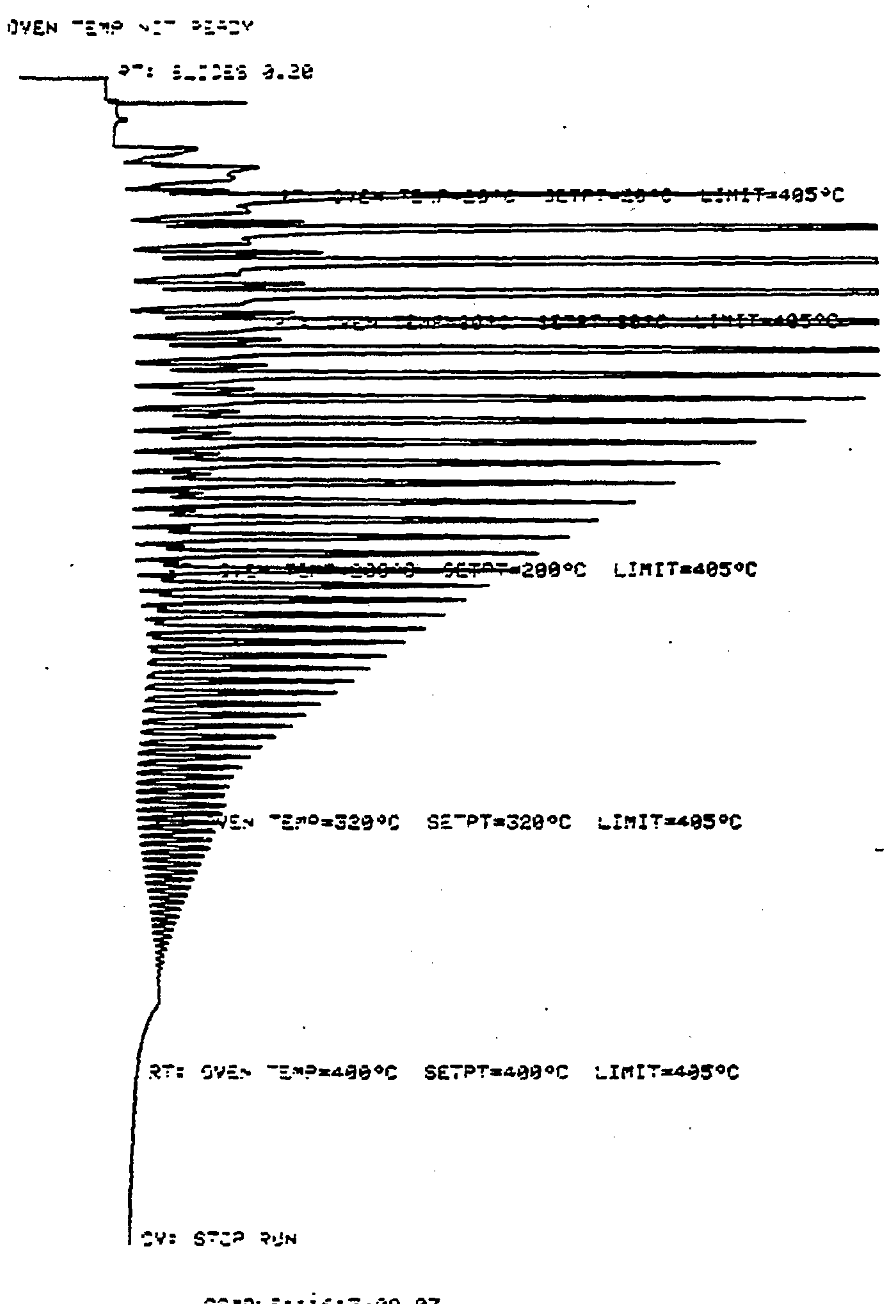


Fig. B125



LIMIT=405°C
SETPT=200°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
RT: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B126

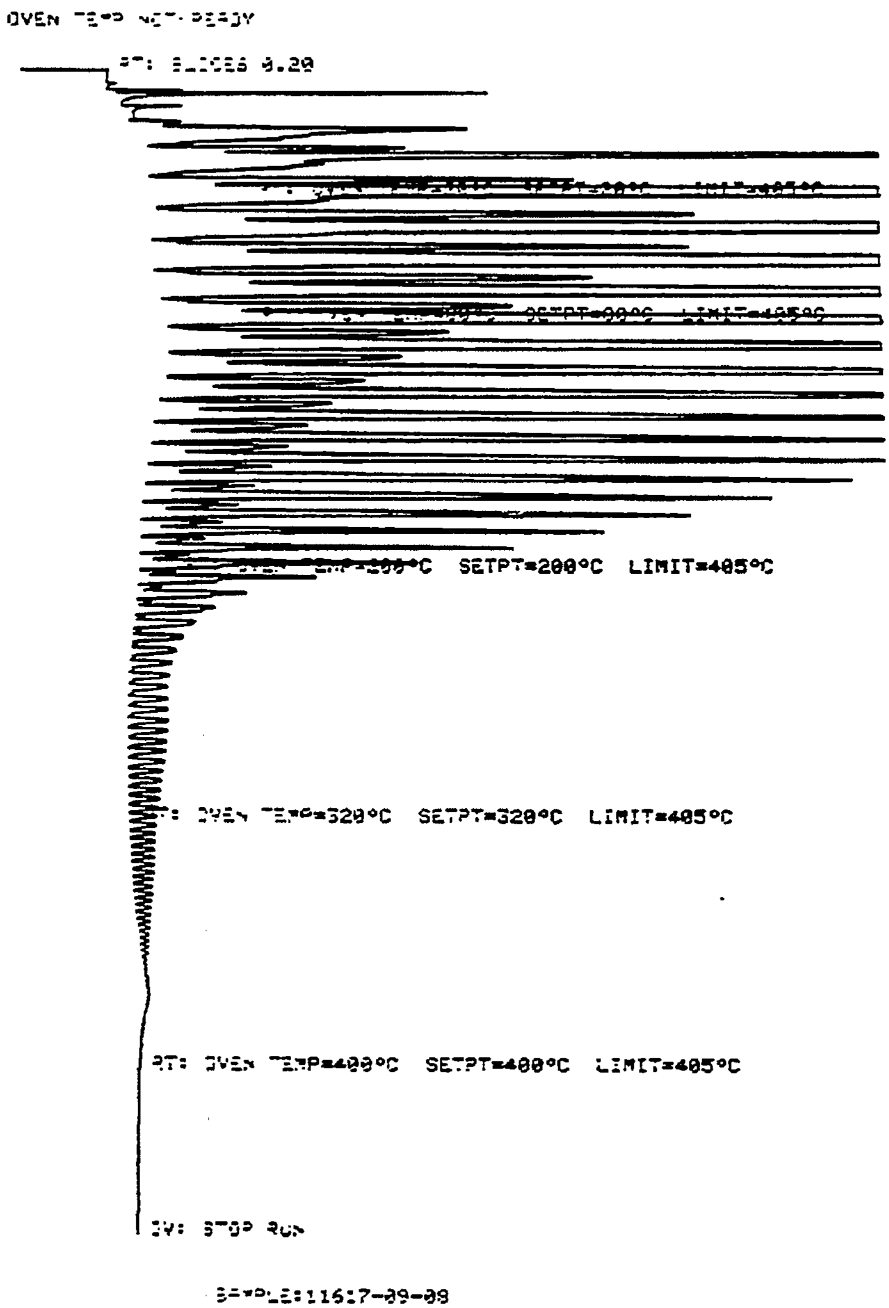

SETPT=200°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C

Fig. B127

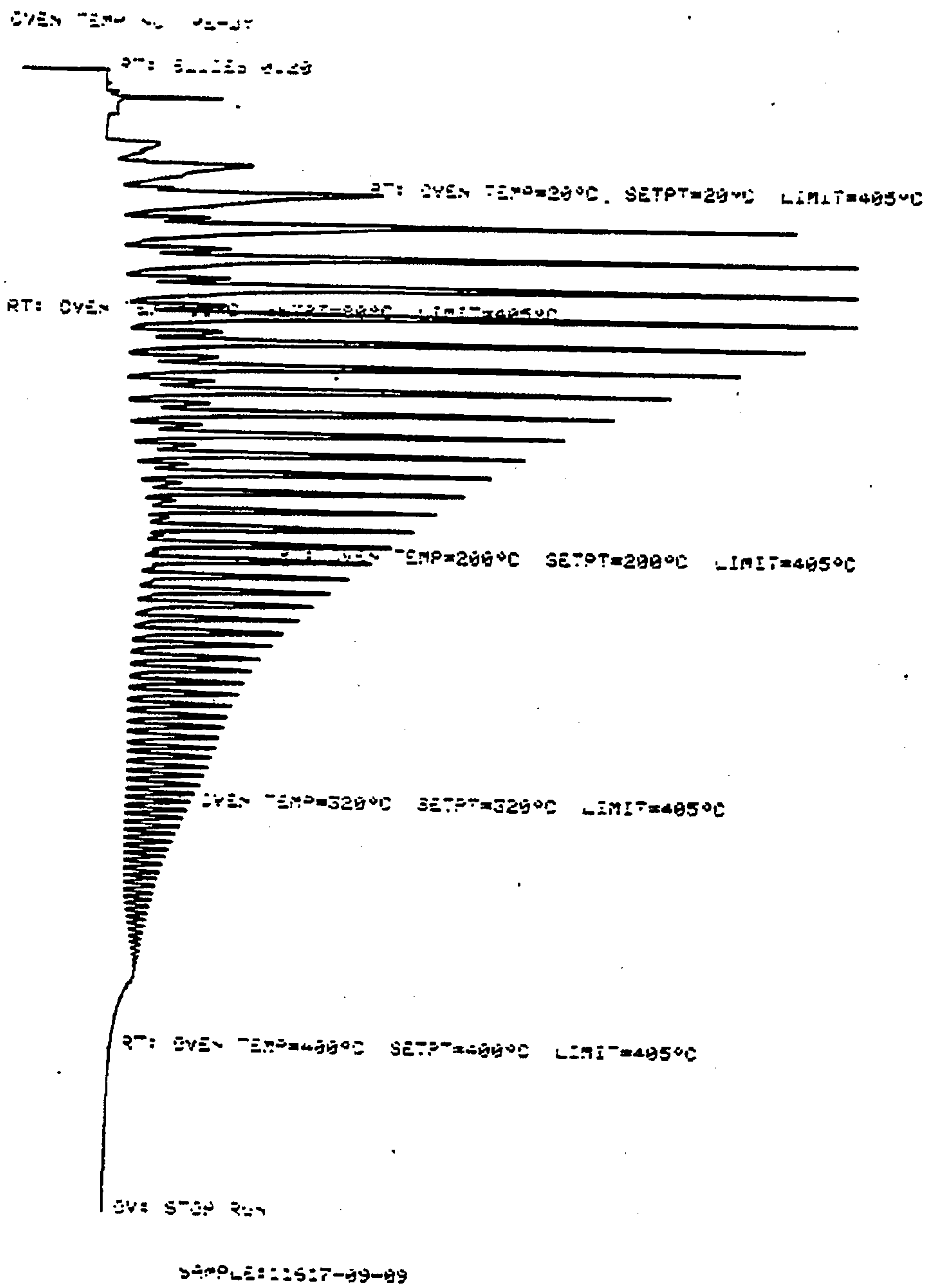


Fig. B128

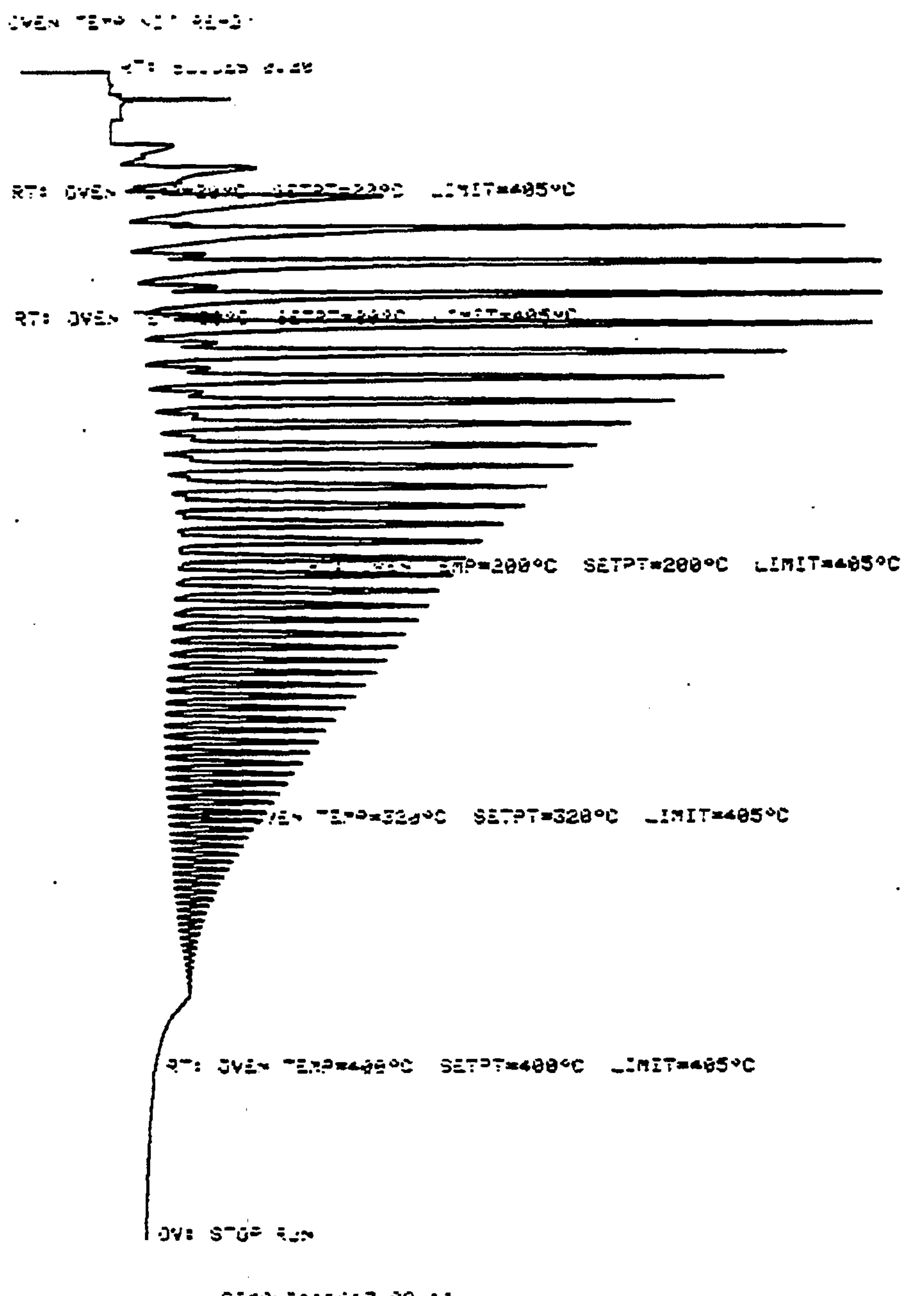
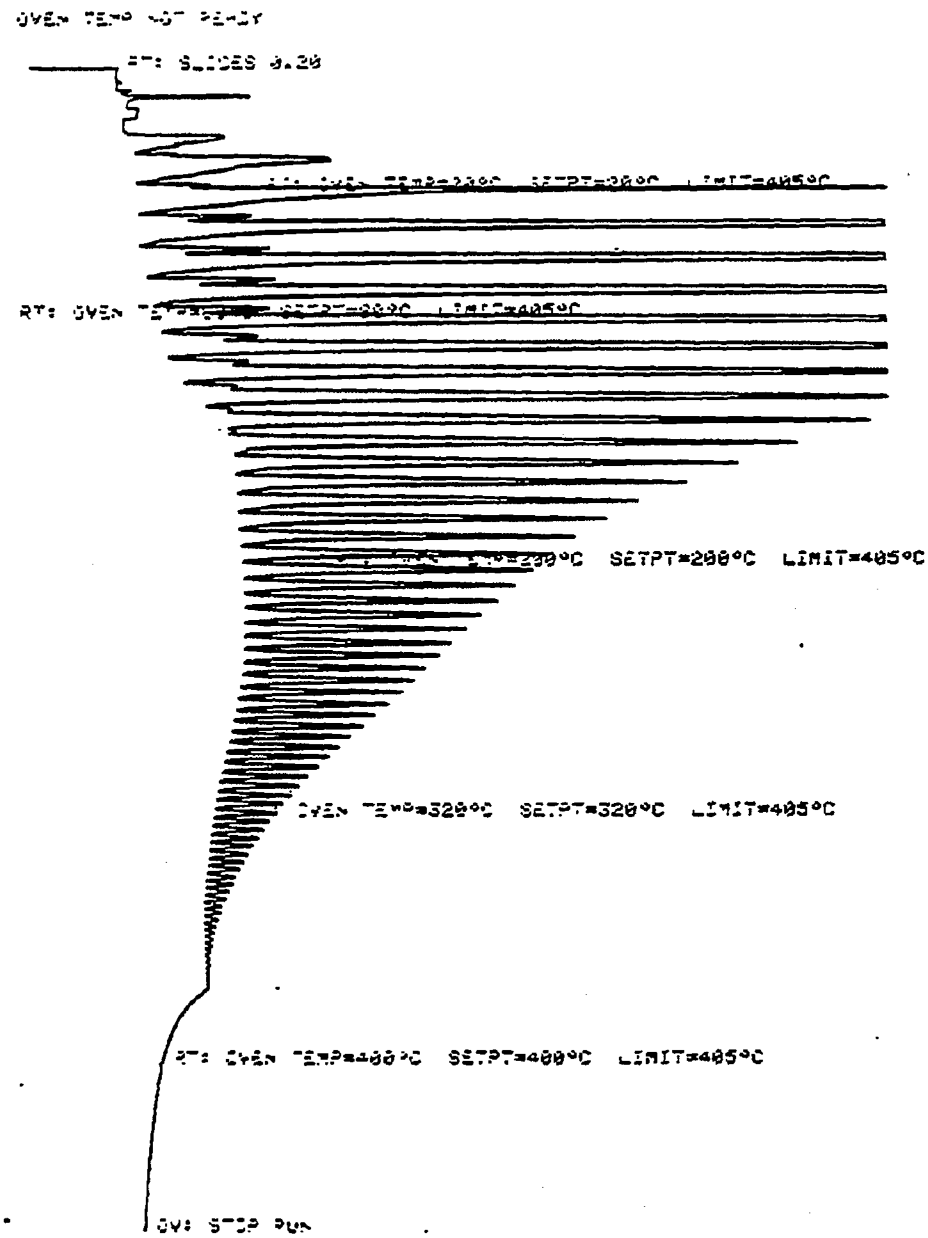

LIMIT=405°C
SETPT=200°C LIMIT=405°C
SETPT=320°C LIMIT=405°C
SETPT=400°C LIMIT=405°C
SAMPLE:11617-09-11

Fig. B129



SAMPLE:115:7-99-12 **Fig. B130**

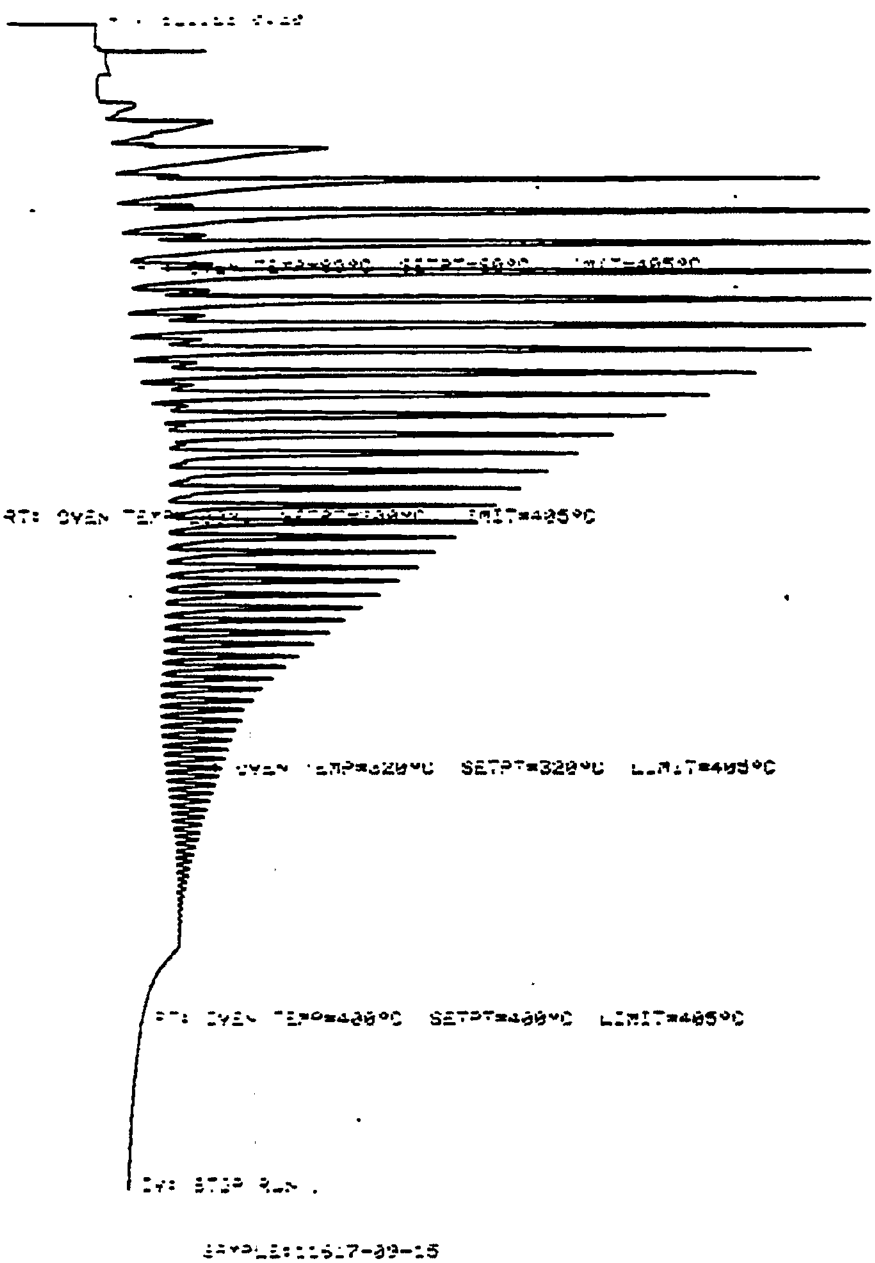
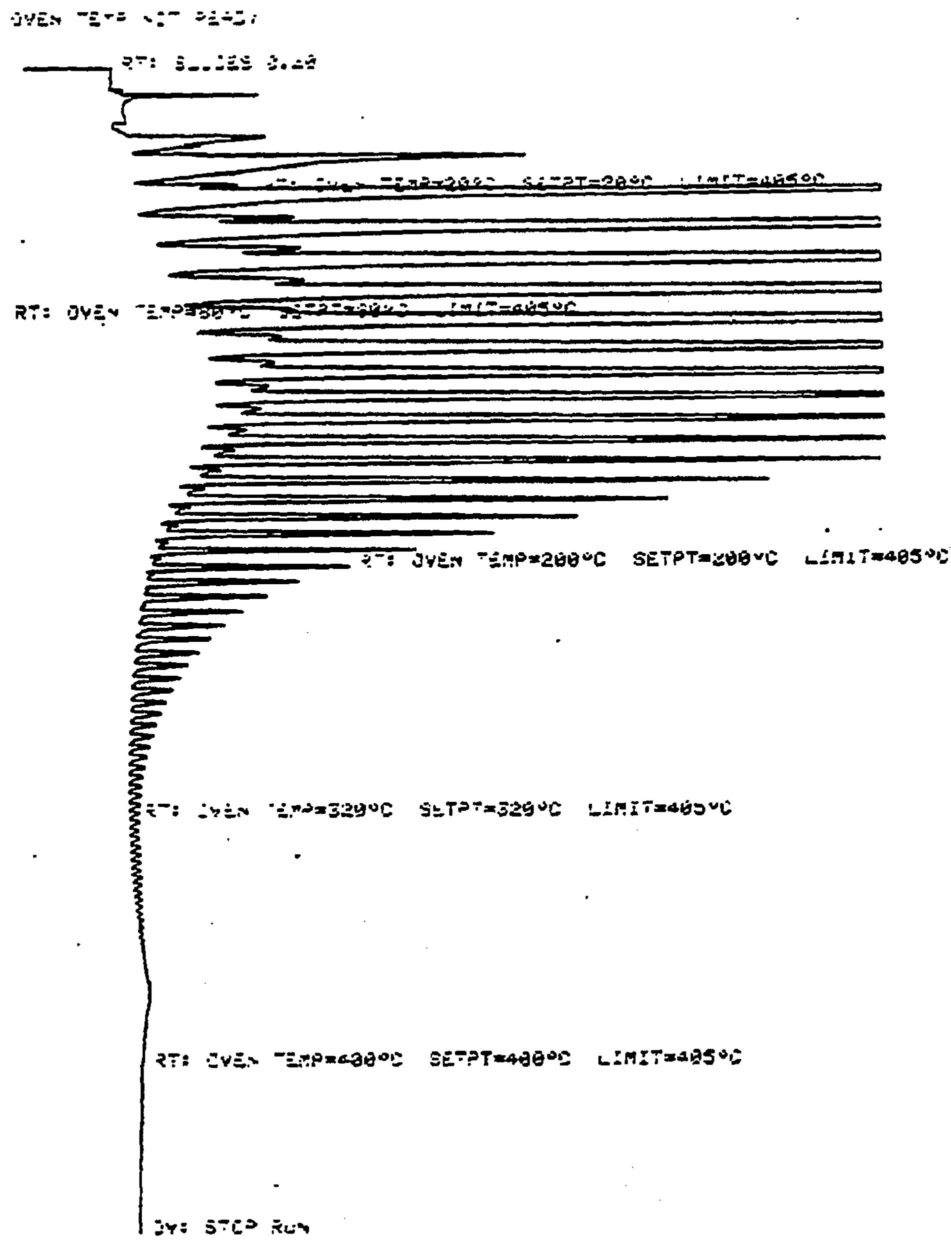


Fig. B131



SAMPLE:11617-19-16

Fig. B132

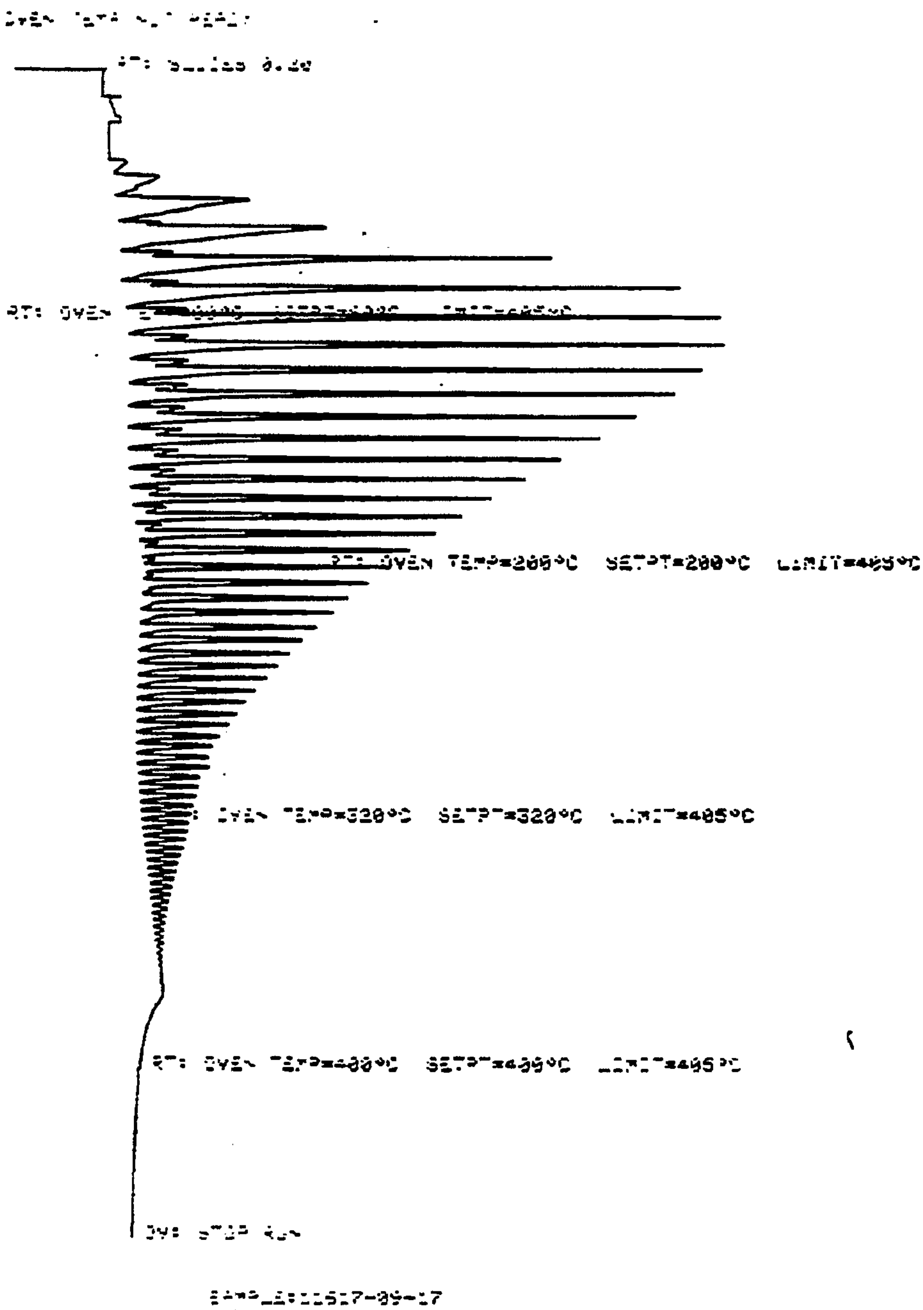

OVEN TEMP=200°C SETPT=200°C LIMIT=405°C
OVEN TEMP=320°C SETPT=320°C LIMIT=405°C
OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

Fig. B133

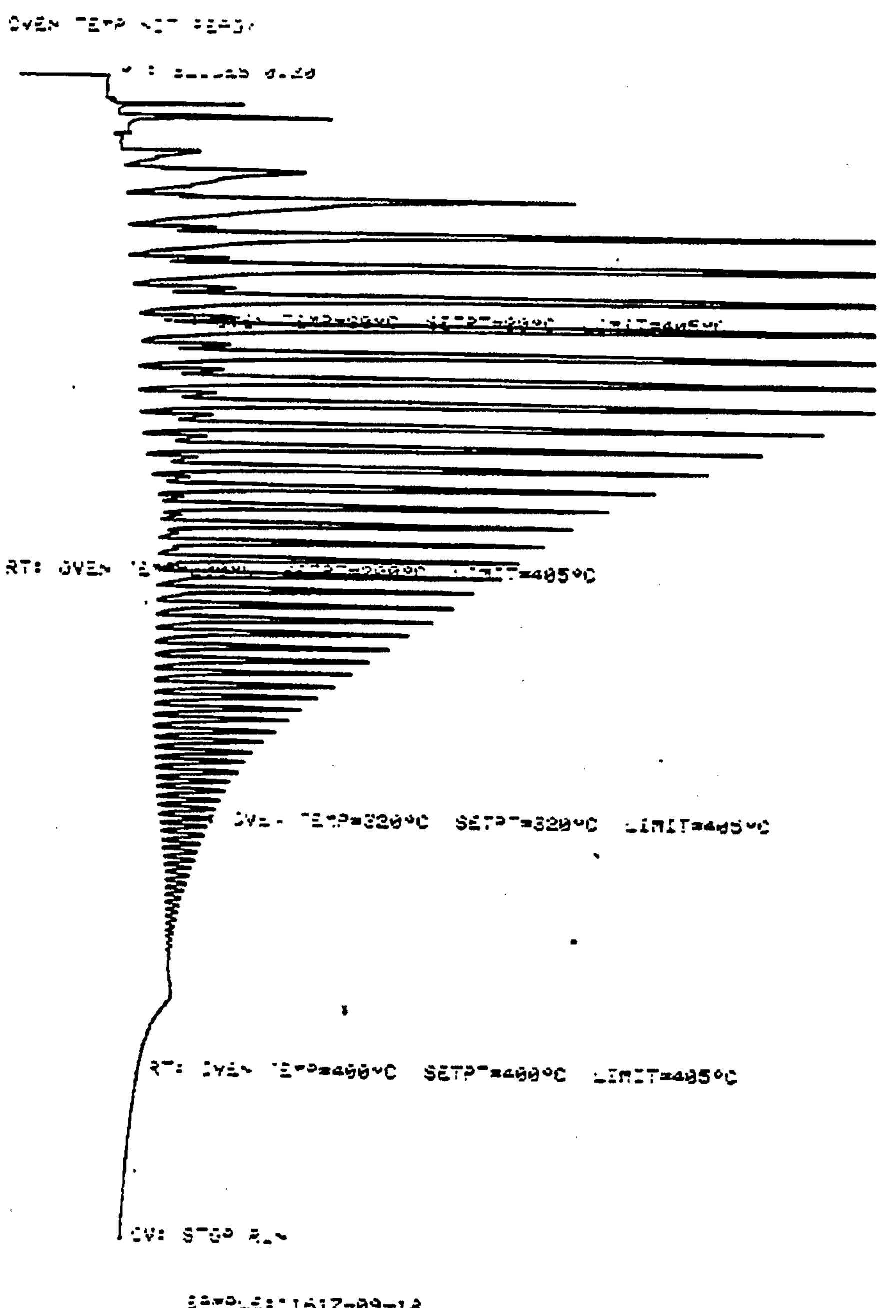


Fig. B134

Table B11

FILE: 11617C9A T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-09
CATALYST CO/X11/X13-TC123 250 CC 120.2 G AFTER USE:186.9 G (+66.7 G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12524-41)

RUN & SAMPLE NO.	11617-09-01	617-09-02	617-09-03	617-09-04	617-09-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	7.25	27.75	77.00	99.00	122.75
PRESSURE,PSIG	300.00	300.00	300.00	300.00	300.00
TEMP. C	240.00	238.00	239.00	239.00	239.00
FEED CC/MIN	1260.00	1260.00	1260.00	1260.00	1260.00
HOURS FEEDING	8.25	19.50	49.25	22.00	23.75
EFFLNT GAS LITER	179.70	692.60	1936.20	878.60	963.70
GM AQUEOUS LAYER	86.70	155.32	385.32	171.37	181.13
GM OIL	21.36	99.56	239.30	112.27	119.26
MATERIAL BALANCE					
GM ATOM CARBON %	54.15	92.31	97.01	99.07	99.94
GM ATOM HYDROGEN %	76.59	96.43	100.48	102.34	102.71
GM ATOM OXYGEN %	77.19	93.13	96.87	97.47	97.54
RATIO CHX/(H2O+CO2)	0.4376	0.9760	1.0045	1.0490	1.0754
RATIO X IN CHX	2.2304	2.2175	2.2225	2.2203	2.2176
USAGE H2/CO PRODT	2.8880	1.8080	1.8562	1.8387	1.8273
FEED H2/CO FRM EFFLNT	1.4144	1.0445	1.0357	1.0331	1.0277
RESIDUAL H2/CO RATIO	0.5316	0.5316	0.5554	0.5570	0.5623
RATIO CO2/(H2O+CO2)	0.0577	0.1131	0.0881	0.0831	0.0804
K SHIFT IN EFFLNT	0.0325	0.0678	0.0537	0.0504	0.0492
SPECIFIC ACTIVITY SA	3.9197	5.1487	4.1303	4.1553	3.9886
CONVERSION					
ON CO %	37.46	40.18	36.93	37.15	36.80
ON H2 %	76.50	69.56	66.18	66.11	65.42
ON CO+H2 %	60.33	55.19	51.81	51.86	51.30
PRDT SELECTIVITY,WT %					
CH4	5.04	4.43	4.76	4.66	4.49
C2 HC'S	1.69	1.49	1.69	1.59	1.63
C3H8	2.06	1.82	1.79	1.76	1.79
C3H6=	2.88	2.53	2.97	2.91	3.00
C4H10	2.07	1.82	1.90	1.86	2.00
C4H8=	4.38	3.86	4.35	4.24	4.27
C5H12	2.64	2.33	2.44	2.35	2.46
C5H10=	3.58	3.15	3.41	3.38	3.51
C6H14	3.27	2.88	3.00	2.86	3.01
C6H12= & CYCLO'S	1.64	1.44	1.72	1.62	1.64
C7+ IN GAS	5.62	4.95	5.42	5.25	5.96
LIQ HC'S	65.12	69.31	66.55	67.52	66.23
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	18.12	15.95	17.45	17.02	17.19
C5 -420 F	52.25	33.86	49.27	49.22	35.97
420-700 F	24.37	32.52	26.62	27.01	26.21
700-END PT	5.26	17.67	6.66	6.75	20.62

Table B11 (continued)

FILE: 1161709A T6Q1 A1

C5+-END PT	81.88	84.05	82.55	82.98	82.81
ISO/NORMAL MOLE RATIO					
C4	0.0185	0.0185	0.0204	0.0199	0.0329
C5	0.0506	0.0506	0.0466	0.0484	0.0480
C6	0.0920	0.0920	0.0690	0.0760	0.0859
C4=	0.0493	0.0493	0.0503	0.0527	0.0506
PARAFFIN/OLEFIN RATIO					
C3	0.6837	0.6837	0.5758	0.5766	0.5698
C4	0.4568	0.4568	0.4221	0.4231	0.4531
C5	0.7173	0.7173	0.6952	0.6765	0.6800
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8232	0.8648			0.8601
RATIO CH4/(1-A)**2	1.6113	2.4229			2.2959
ALPHA FRM CORRELATION	0.8427	0.8428			0.8400
ALPHA (EXPTL/CORR)	0.9768	1.0260			1.0239
W%CH4 FRM CORRELATION	12.2340	11.7410			12.8361
W%CH4 (EXPTL/CORR)	0.4117	0.3775			0.3500
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	288.00	328.00			299.00
16	306.00	366.00			338.00
50	454.00	537.00			556.00
84	617.00	799.00			858.00
90	677.00	881.00			945.00
RANGE(16-84 %)	311.00	433.00			520.00
WT % @ 420 F	54.50	27.58			29.29
WT % @ 700 F	91.93	74.50			68.86

Table B12

FILE: 1161709B T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-09
CATALYST CO/X11/X13-TC123 250 CC 120.2 G AFTER USE:186.9 G (+66.7 G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12524-41)

RUN & SAMPLE NO.	11617-09-06	617-09-07	617-09-08	617-09-09	617-09-10
FEED H2:CO:AR	60:40: 0	60:40: 0	60:40: 0	50:50: 0	50:50: 0
HRS ON STREAM	147.25	170.25	193.25	216.25	240.75
PRESSURE,PSIG	300.00	300.00	500.00	500.00	500.00
TEMP. C	240.50	241.00	258.00	259.00	259.00
FEED CC/MIN	1260.00	1260.00	1260.00	1260.00	1260.00
HOURS FEEDING	24.50	23.00	23.00	23.50	24.00
EFFLNT GAS LITER	839.00	705.00	555.20	645.80	706.50
GM AQUEOUS LAYER	220.47	225.63	219.45	202.93	215.23
GM OIL	122.21	118.39	62.50	164.42	178.80
MATERIAL BALANCE					
GM ATOM CARBON %	107.32	100.05	95.13	97.20	100.16
GM ATOM HYDROGEN %	104.77	101.03	98.13	100.73	102.82
GM ATOM OXYGEN %	101.15	98.90	97.45	92.46	94.63
RATIO CHX/(H2O+CO2)	1.1250	1.0221	0.9629	1.1116	1.1356
RATIO X IN CHX	2.4799	2.4459	2.7641	2.2273	2.2216
USAGE H2/CO PRODT	1.7754	1.8631	1.6153	1.4739	1.5828
FEED H2/CO FRM EFFLNT	1.4643	1.5147	1.5473	1.0363	1.0265
RESIDUAL H2/CO RATIO	1.0287	1.0059	1.2163	0.4014	0.3840
RATIO CO2/(H2O+CO2)	0.1432	0.1208	0.2965	0.2424	0.1796
K SHIFT IN EFFLNT	0.1720	0.1382	0.5125	0.1284	0.0841
SPECIFIC ACTIVITY SA	3.1564	3.2517	1.6376	2.5807	2.2766
CONVERSION					
ON CO %	58.34	59.35	82.94	59.20	53.59
ON H2 %	70.73	73.01	86.59	84.20	82.64
ON CO+H2 %	65.70	67.58	85.16	71.92	68.31
PRDT SELECTIVITY,WT %					
CH4	16.45	14.92	28.90	5.27	4.84
C2 HC'S	3.27	2.83	5.21	1.50	1.45
C3H8	4.74	4.36	9.47	1.65	1.44
C3H6=	1.15	1.11	0.57	2.02	2.08
C4H10	4.08	3.76	6.92	1.60	1.45
C4H8=	2.14	2.05	1.13	3.15	3.13
C5H12	4.60	4.33	6.40	1.98	1.83
C5H10=	1.62	1.55	0.90	2.05	2.16
C6H14	5.30	4.92	6.73	3.03	2.69
C6H12= & CYCLO'S	0.87	0.92	0.48	1.99	1.86
C7+ IN GAS	6.02	5.45	8.84	8.96	4.56
LIQ HC'S	49.74	53.80	24.46	66.79	72.52
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	31.84	29.03	52.20	15.20	14.39
C5 -420 F	34.96	36.82	37.80	39.60	49.35
420-700 F	19.49	21.27	8.80	25.52	29.01
700-END PT	13.71	12.88	1.20	19.68	7.25

Table B12 (continued)

FILE: 1161709B T6Q1 A1

C5+-END PT	68.16	70.97	47.80	84.80	85.61
ISO/NORMAL MOLE RATIO					
C4	0.0454	0.0408	0.0633	0.0207	0.0209
C5	0.0743	0.0680	0.1100	0.0702	0.0625
C6	0.1227	0.1126	0.1863	0.3116	0.3083
C4=	0.1219	0.1168	0.1935	0.0650	0.0589
PARAFFIN/OLEFIN RATIO					
C3	3.9423	3.7305	15.9363	0.7810	0.6616
C4	1.8410	1.7728	5.9001	0.4909	0.4476
C5	2.7592	2.7120	6.9488	0.9433	0.8234
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8412	0.8397	0.7537	0.8581	
RATIO CH4/(1-A)**2	6.5238	5.8034	4.7649	2.6165	
ALPHA FRM CORRELATION	0.8105	0.8116	0.8014	0.8553	
ALPHA (EXPTL/CORR)	1.0378	1.0346	0.9406	1.0032	
W%CH4 FRM CORRELATION	22.3345	22.1180	29.0130	12.4857	
W%CH4 (EXPTL/CORR)	0.7367	0.6745	0.9961	0.4222	
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N. REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	291.00	288.00	238.00	296.00	
16	333.00	324.00	253.00	337.00	
50	528.00	502.00	380.00	539.00	
84	827.00	792.00	575.00	852.00	
90	912.00	890.00	632.00	946.00	
RANGE(16-84 %)	494.00	468.00	322.00	515.00	
WT % @ 420 F	33.25	36.54	59.12	32.33	
WT % @ 700 F	72.43	76.07	95.10	70.54	

Table B13

FILE: 1161709C T6Q1   A1

RESULT OF SYNGAS OPERATION

RUN NO.   11617-09
CATALYST CO/X11/X13-TC123 250 CC 120.2 G AFTER USE:186.9 G (+66.7 G
FEED   H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV   (CAT#12524-41)

RUN & SAMPLE NO.	11617-09-11	617-09-12	617-09-13	617-09-14	617-09-15
FEED H2:CO:AR	50:50: 0	54:45: 0	54:45: 0	54:45: 0	54:45: 0
HRS ON STREAM	266.25	289.25	313.25	341.25	362.25
PRESSURE,PSIG	500.00	500.00	500.00	500.00	500.00
TEMP. C	259.00	259.00	259.00	260.00	257.00
FEED CC/MIN	1260.00	1260.00	1260.00	1260.00	1260.00
HOURS FEEDING	25.50	23.00	24.00	28.00	21.00
EFFLNT GAS LITER	789.00	631.60	651.50	780.30	590.50
GM AQUEOUS LAYER	236.30	222.95	239.76	278.47	210.29
GM OIL	178.17	166.43	164.40	187.67	140.24
MATERIAL BALANCE					
GM ATOM CARBON %	99.93	102.65	99.06	99.34	98.23
GM ATOM HYDROGEN %	103.04	103.97	101.81	101.86	99.62
GM ATOM OXYGEN %	96.48	96.41	96.01	96.46	95.82
RATIO CHX/(H2O+CO2)	1.0854	1.1295	1.0631	1.0603	1.0528
RATIO X IN CHX	2.2254	2.3077	2.3021	2.3046	2.2688
USAGE H2/CO PRODT	1.6798	1.6210	1.6948	1.7136	1.8004
FEED H2/CO FRM EFFLNT	1.0311	1.2132	1.2311	1.2282	1.2148
RESIDUAL H2/CO RATIO	0.3899	0.5610	0.5531	0.5573	0.5289
RATIO CO2/(H2O+CO2)	0.1435	0.1802	0.1566	0.1492	0.1067
K SHIFT IN EFFLNT	0.0653	0.1233	0.1027	0.0977	0.0632
SPECIFIC ACTIVITY SA	1.9366	1.6900	1.6081	1.4526	1.5632
CONVERSION					
ON CO %	49.71	61.53	59.38	58.02	53.94
ON H2 %	80.99	82.21	81.75	80.95	79.95
ON CO+H2 %	65.59	72.86	71.73	70.66	68.21
PRDT SELECTIVITY,WT %					
CH4	5.01	8.89	8.61	8.73	7.02
C2 HC'S	1.55	2.06	2.01	2.02	1.78
C3H8	1.47	2.42	2.32	2.45	2.08
C3H6=	2.22	1.71	1.82	1.98	2.17
C4H10	1.50	2.07	2.06	2.17	1.98
C4H8=	3.31	2.95	3.07	3.23	3.20
C5H12	1.88	2.48	2.50	2.64	2.37
C5H10=	2.24	1.80	1.89	2.51	2.40
C6H14	2.76	3.46	3.54	3.09	2.67
C6H12= & CYCLO'S	1.90	1.53	1.62	1.50	1.40
C7+ IN GAS	4.35	5.16	4.71	4.28	4.34
LIQ HC'S	71.82	65.47	65.86	65.39	68.58
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	15.06	20.10	19.89	20.59	18.24
C5 -420 F	32.63	32.11	47.18	46.72	31.69
420-700 F	26.98	24.73	26.34	26.15	25.97
700-END PT	25.33	23.06	6.59	6.54	24.10

Table B13 (continued)

FILE: 1161709C T6Q1 A1

C5+-END PT	84.94	79.90	80.11	79.41	81.76
ISO/NORMAL MOLE RATIO					
C4	0.0241	0.0237	0.0241	0.0236	0.0255
C5	0.0595	0.0666	0.0676	0.0634	0.0597
C6	0.2941	0.2609	0.2498	0.0860	0.0735
C4=	0.0588	0.0744	0.0713	0.0674	0.0649
PARAFFIN/OLEFIN RATIO					
C3	0.6296	1.3488	1.2186	1.1813	0.9177
C4	0.4365	0.6767	0.6473	0.6491	0.5973
C5	0.8163	1.3408	1.2864	1.0209	0.9576
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8709	0.8664			0.8666
RATIO CH4/(1-A)**2	3.0047	4.9784			3.9471
ALPHA FRM CORRELATION	0.8567	0.8390			0.8420
ALPHA (EXPTL/CORR)	1.0165	1.0326			1.0292
W%CH4 FRM CORRELATION	12.0457	17.5463			16.1962
W%CH4 (EXPTL/CORR)	0.4160	0.5066			0.4336
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	303.00	303.00			313.00
16	345.00	346.00			355.00
50	579.00	575.00			576.00
84	903.00	895.00			907.00
90	992.00	982.00			1011.00
RANGE(16-84 %)	558.00	549.00			552.00
WT % @ 420 F	27.17	27.00			27.00
WT % @ 700 F	64.73	64.78			64.86

Table B14

FILE: 1161709D T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-09
CATALYST CO/X11/X13-TC123 250 CC 120.2 G AFTER USE:186.9 G (+66.7 G
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12524-41)

RUN & SAMPLE NO.	11617-09-16	617-09-17	617-09-18	617-09-19	617-09-20
FEED H2:CO:AR	54:45: 0	54:45: 0	54:45: 0	54:45: 0	54:45: 0
HRS ON STREAM	385.25	435.25	440.25	458.75	485.75
PRESSURE,PSIG	500.00	500.00	500.00	500.00	500.00
TEMP. C	259.00	259.00	260.00	259.00	260.00
FEED CC/MIN	1260.00	1260.00	1260.00	1260.00	1260.00
HOURS FEEDING	17.00	50.00	5.00	18.50	27.00
EFFLNT GAS LITER	373.10	1416.40	142.00	534.50	771.00
GM AQUEOUS LAYER	191.33	490.27	48.73	185.86	254.83
GM OIL	48.71	340.81	34.98	124.54	159.07
MATERIAL BALANCE					
GM ATOM CARBON %	72.41	110.08	99.85	101.56	99.16
GM ATOM HYDROGEN %	82.10	110.63	101.02	102.85	99.15
GM ATOM OXYGEN %	92.08	94.41	95.95	97.54	94.86
RATIO CHX/(H2O+CO2)	0.6200	1.3415	1.0852	1.0863	1.0960
RATIO X IN CHX	2.3168	2.2472	2.2997	2.2822	2.3013
USAGE H2/CO PRODT	2.1434	1.6186	1.7384	1.7567	1.7191
FEED H2/CO FRM EFFLNT	1.3581	1.2038	1.2118	1.2131	1.1977
RESIDUAL H2/CO RATIO	0.4665	0.5469	0.5451	0.5392	0.5399
RATIO CO2/(H2O+CO2)	0.1238	0.1283	0.1319	0.1202	0.1387
K SHIFT IN EFFLNT	0.0659	0.0805	0.0828	0.0736	0.0869
SPECIFIC ACTIVITY SA	1.6480	1.7441	1.3699	1.4003	1.3286
CONVERSION					
ON CO %	53.17	61.29	55.87	55.35	55.78
ON H2 %	83.92	82.42	80.15	80.15	80.07
ON CO+H2 %	70.88	72.83	69.17	68.95	69.02
PRDT SELECTIVITY,WT %					
CH4	10.11	6.76	8.58	7.90	8.61
C2 HC'S	2.55	1.51	1.95	1.85	1.98
C3H8	2.88	1.94	2.26	2.11	2.39
C3H6=	2.77	1.58	1.86	1.86	1.93
C4H10	2.66	1.92	2.05	1.97	2.08
C4H8=	4.59	2.93	3.14	3.03	3.18
C5H12	3.22	2.74	2.49	2.34	2.61
C5H10=	3.73	2.74	1.94	1.90	4.45
C6H14	4.10	3.51	2.08	2.79	5.65
C6H12= & CYCLO'S	2.62	1.32	0.41	4.54	2.19
C7+ IN GAS	16.79	18.28	3.90	4.06	5.79
LIQ HC'S	43.97	54.77	69.35	65.66	59.15
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	25.56	16.64	19.84	18.71	20.16
C5 -420 F	51.87	43.44	34.81	48.46	50.26
420-700 F	21.08	22.87	25.14	26.26	23.66
700-END PT	1.49	17.06	20.21	6.57	5.92

Table B14 (continued)

FILE: 1161709D T6Q1 A1

C5+-END PT	74.44	83.36	80.16	81.29	79.84
ISO/NORMAL MOLE RATIO					
C4	0.0237	0.0219	0.0229	0.0263	0.0265
C5	0.0597	0.0609	0.0633	0.0597	0.0660
C6	0.0832	0.1020	0.4867	0.2849	6.0100
C4=	0.0633	0.0669	0.0693	0.0663	0.0711
PARAFFIN/OLEFIN RATIO					
C3	0.9926	1.1740	1.1582	1.0827	1.1827
C4	0.5595	0.6333	0.6312	0.6277	0.6313
C5	0.8384	0.9712	1.2526	1.1976	0.5703
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7904	0.8510	0.8605		
RATIO CH4/(1-A)**2	2.3014	3.0418	4.4067		
ALPHA FRM CORRELATION	0.8480	0.8403	0.8404		
ALPHA (EXPTL/CORR)	0.9321	1.0127	1.0239		
W%CH4 FRM CORRELATION	14.7570	17.1600	17.3392		
W%CH4 (EXPTL/CORR)	0.6849	0.3938	0.4948		
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	260.00	323.00	294.00		
16	301.00	364.00	332.00		
50	422.00	561.00	523.00		
84	575.00	856.00	854.00		
90	621.00	952.00	951.00		
RANGE(16-84 %)	274.00	492.00	522.00		
WT % @ 420 F	48.67	27.11	34.60		
WT % @ 700 F	96.61	68.86	70.86		

Table B15

FILE: 1161709E T6Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 11617-09
CATALYST CO/X11/X13-TC123 250 CC 120.2 G AFTER USE:186.9 G (+66.7 G
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV (CAT#12524-41)

RUN & SAMPLE NO.	11617-09-21
FEED H2:CO:AR	54:45: 0
HRS ON STREAM	506.75
PRESSURE, PSIG	500.00
TEMP. C	250.00
FEED CC/MIN	1260.00
HOURS FEEDING	21.00
EFFLNT GAS LITER	599.30
GM AQUEOUS LAYER	210.63
GM OIL	144.66
MATERIAL BALANCE	
GM ATOM CARBON %	95.59
GM ATOM HYDROGEN %	100.38
GM ATOM OXYGEN %	92.21
RATIO CHX/(H2O+CO2)	1.0784
RATIO X IN CHX	2.2203
USAGE H2/CO PRODT	1.9003
FEED H2/CO FRM EFFLNT	1.2579
RESIDUAL H2/CO RATIO	0.5911
RATIO CO2/(H2O+CO2)	0.0510
K SHIFT IN EFFLNT	0.0318
SPECIFIC ACTIVITY SA	1.7569
CONVERSION	
ON CO %	50.93
ON H2 %	76.95
ON CO+H2 %	65.43
PRDT SELECTIVITY, WT %	
CH4	4.75
C2 HC'S	1.15
C3H8	1.49
C3H6=	1.92
C4H10	1.50
C4H8=	2.67
C5H12	1.86
C5H10=	1.76
C6H14	2.85
C6H12= & CYCLO'S	1.51
C7+ IN GAS	5.06
LIQ HC'S	73.47
TOTAL	100.00
SUB-GROUPING	
C1 -C4	13.48
C5 -420 F	49.78
420-700 F	29.39
700-END PT	7.35

Table B15 (continued)

FILE: 1161709E T6Q1   A1

C5+-END PT	86.52
ISO/NORMAL MOLE RATIO	
C4	0.0247
C5	0.0598
C6	0.3656
C4=	0.0591
PARAFFIN/OLEFIN RATIO	
C3	0.7438
C4	0.5433
C5	1.0262
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	
RATIO CH4/(1-A)**2	
ALPHA FRM CORRELATION	
ALPHA (EXPTL/CORR)	
W%CH4 FRM CORRELATION	
W%CH4 (EXPTL/CORR)	
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL WAX
DENSITY	
N, REFRACTIVE INDEX	
SIMULT'D DISTILATN	
10 WT % @ DEG F	
16	
50	
84	
90	
RANGE(16-84 %)	
WT % @ 420 F	
WT % @ 700 F	

VII. Summary

In the work reported in this Quarter, consisting of six runs directed toward improving on the promising Catalyst 45 (Co/X_{11}/TC-123) of the Sixth Quarterly Report, two lines of investigation were explored. One was a search for a new Molecular Sieve to improve on TC-123, the other a search for additives to improve the performance of Catalyst 45.

Run 49, a X_{11} promoted cobalt γ-alumina catalyst, served as a reference with which to compare the performance of Molecular Sieve supported catalysts. The three Molecular Sieves compared—TC-103, TC-123 and TC-133—all demonstrated improved performance in product selectivity with TC-123 being best.

A newly developed Molecular Sieve, TC-121, improved on the isomerization activity typically observed for TC-123. In all other respects, however, its performance was inferior.

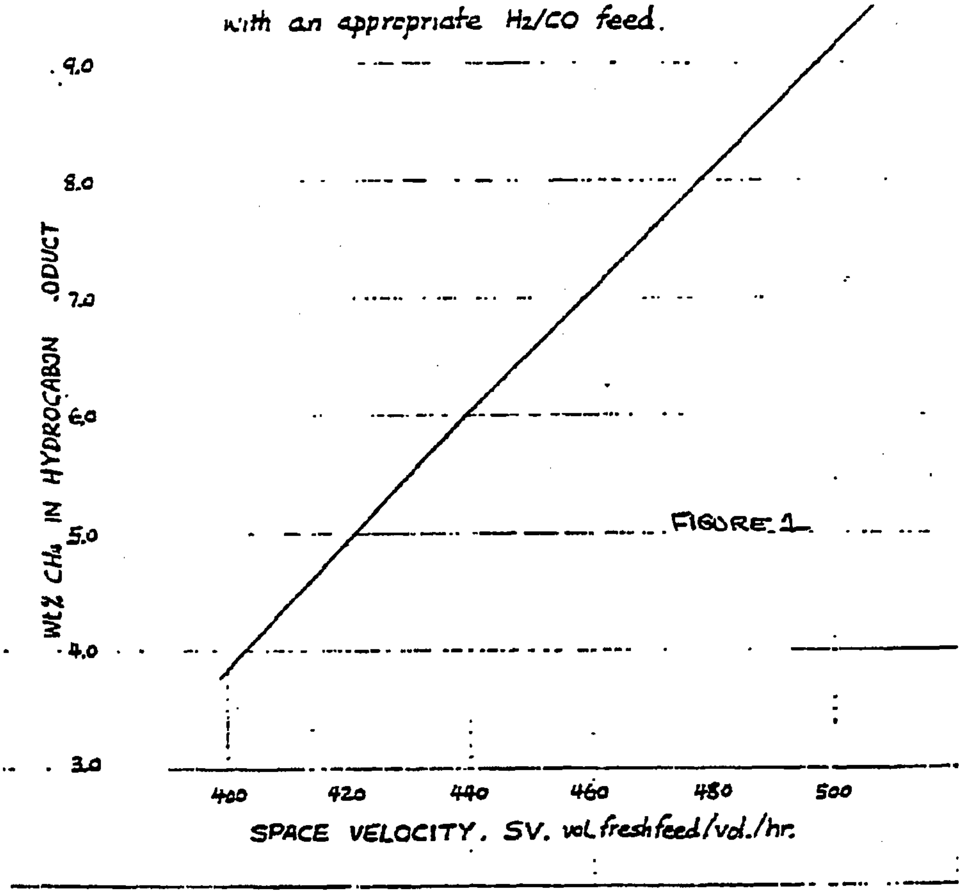
Three additives—X_9, X_{13} and K/Ni/Mo-γ-alumina—were tested in combination with the Catalyst 45 formulation. The addition of X_{13} improved the catalyst's water gas shift activity but impaired its overall performance. The additive K/Ni/Mo-γ-alumina, although itself an effective water gas shift catalyst, failed to improve the water gas shift activity of Catalyst 45. However, unlike other WGS components previously tested, it didn't act

adversely on the Fischer-Tropsch catalyst.

The most promising finding was the apparent beneficial effect of the additive X_9 on both the activity and selectivity of the Co/X_{11}/TC-123 catalyst in conditions of high temperature and pressure. Further investigation is required to verify these effects, and also to explore how X_9 may affect catalyst stability.

APPENDIX C. BASE CASE OPERATING CURVES FOR UPDATED MITRE STUDY

METHANE MAKE & SPACE VELOCITY RELATIONSHIP OF UCC's NEW Co, X-11-TC-123 CATALYST for FISCHER-TROPSCH SYNTHESIS, while operating at 400 PSIG, 250°C, 85% SYNGAS CONVERSION with an appropriate H_2/CO feed.



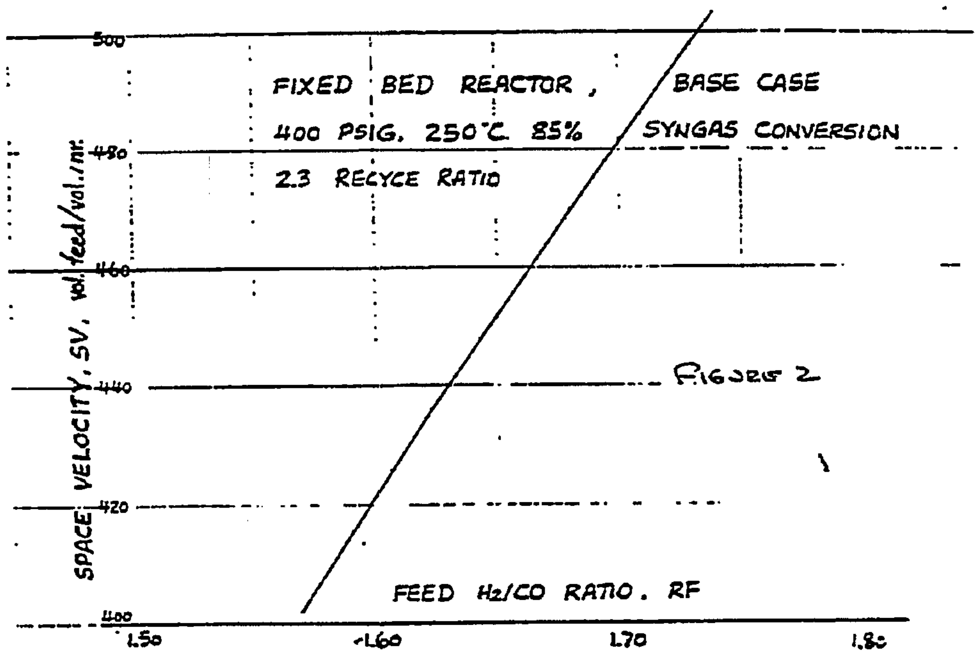


FIGURE 2

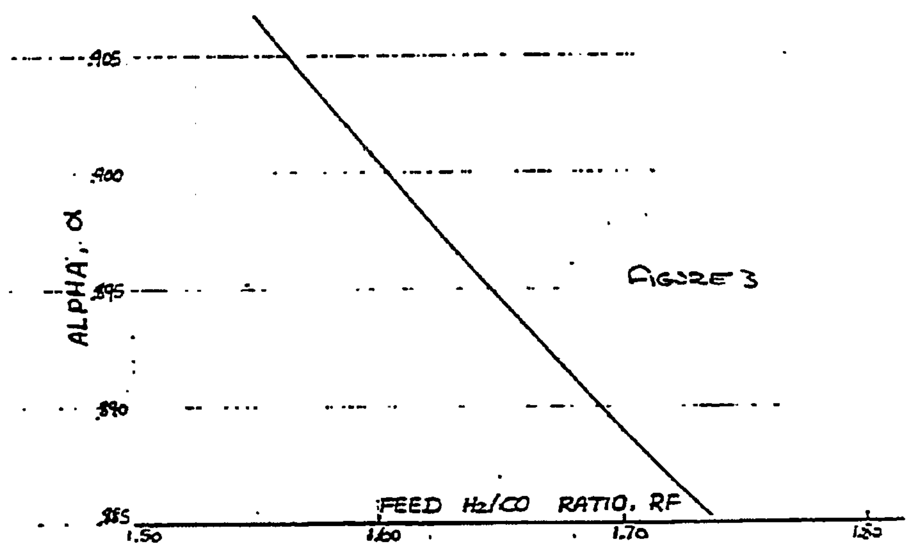
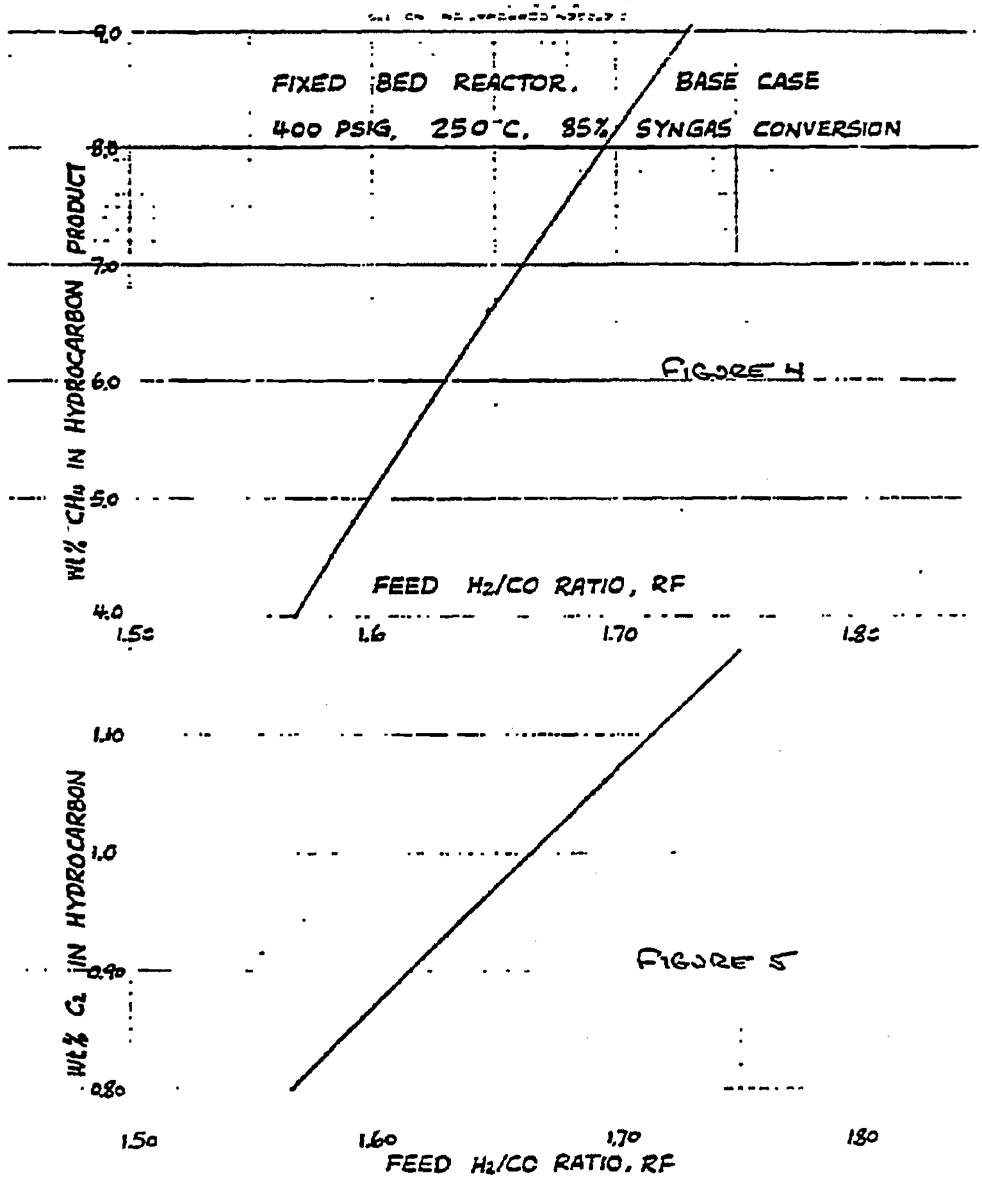


FIGURE 3



FIXED BED REACTOR. BASE CASE
400 PSIG, 250°C, 85% SYNGAS CONVERSION
Wt% CH4 IN HYDROCARBON PRODUCT
9.0
8.0
7.0
6.0
5.0
4.0
FEED H2/CO RATIO, RF
1.50
1.6
1.70
1.80
FIGURE 4
Wt% C2 IN HYDROCARBON
1.10
1.0
0.90
0.80
1.50
1.60
1.70
1.80
FEED H2/CO RATIO, RF
FIGURE 5

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