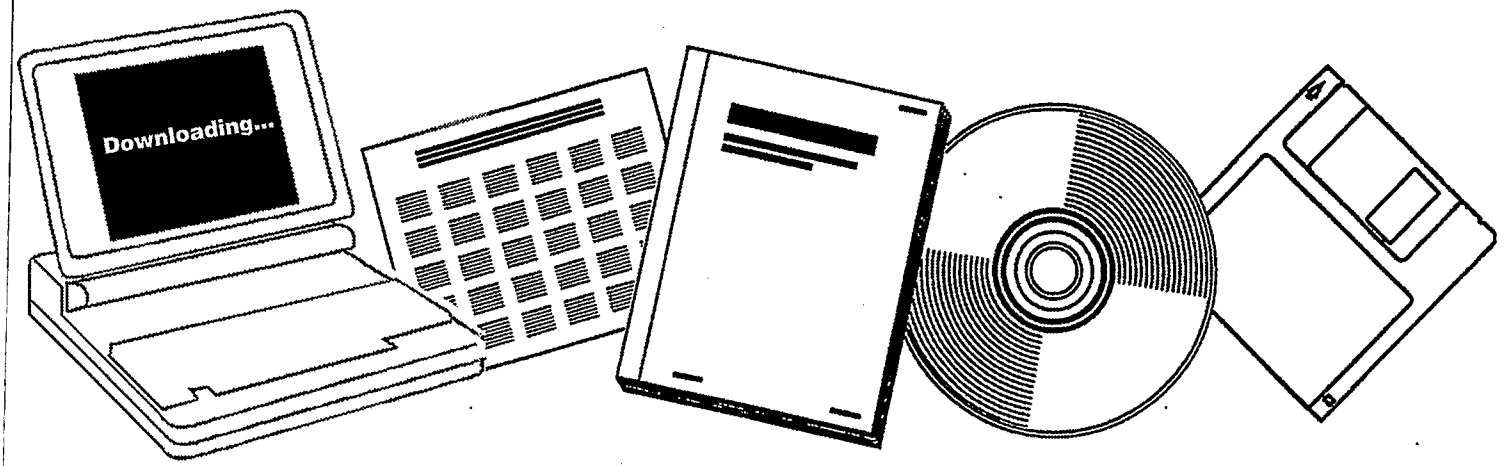
LIQUID HYDROCARBON FUELS FROM SYNGAS. FIFTEENTH QUARTERLY REPORT, AUGUST-SEPTEMBER 1984

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

1986



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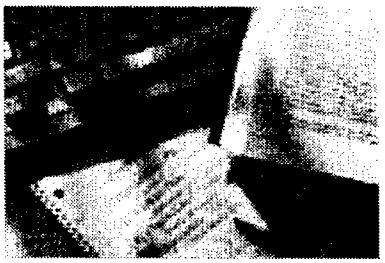

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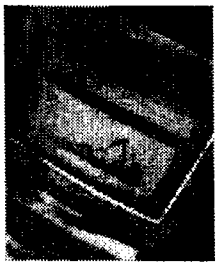

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TECHNICAL PROGRESS REPORT
DE-AC22-81PC40077

Fifteenth Quarterly Report
August - September 1984

LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Contents

Appendixes

I. CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals ("Molecular Sieves") in combination with transition metals.

II. SCHEDULE

The contract work was planned for the 36-month period beginning March 6, 1981.

Work on the program is divided into four tasks.

Task 1, completed, was the conversion of low molecular weight liquids, such as methanol and propylene, to gasoline and diesel fuel, with catalysts consisting of only a Molecular-Sieve component, commonly designated as the shape-selective component (SSC).

Task 2 is the conversion of syngas (carbon monoxide and hydrogen) to gasoline and diesel fuel, using catalysts consisting of both a SSC and a transition-metal component (MC). The work reported in this last progress report is the last work performed under this contract.

Task 3, a study of surface effects by Professor Gabor A. Somorjai of the University of California, has been completed and was reported in the Third Annual Report.

Task 4 comprises the management and technical reports for the contract. There remains only the writing of the final technical report.

III. ORGANIZATION

Synthesizing "Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysis conducted by the Molecular Sieve Department, Catalysts and Process Systems Division, Union Carbide Corporation.

The work is performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown NY 10591.

Principal investigator is Dr. Jule A. Rabo.

Program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

Task 1 has been essentially completed.

B. Task 2

Catalyst Development Effort

Five catalyst test runs were completed during the abbreviated work period between August 1 and the end of this contract on September 17, 1984.

Four runs were devoted to exploring potential further applications of three selected additives which were among the constituents of some of the most effective catalysts developed to date. In particular, the object was to test whether these additives might enhance the effectiveness of the thorium-promoted cobalt oxide class of catalyst.

Copper exchanged 13X is a proven water gas shift catalyst. X_4 was an additive in the Third Annual Report Catalyst 6 (Run 11677-11), the single most effective and stable catalyst yet developed. X_6 in earlier tests contributed significantly to catalytic stability and H_2:CO usage ratio. In the four runs of this period they were tested in catalysts containing cobalt oxide intimately contacted with UCC-103, two of which were promoted with thorium. A fifth catalyst containing Co/UCC-103 and UCC-101, but unpromoted and without additive, served as a reference.

The run with X_6 also tested a method of incorporating it into the catalyst, different from the method previously used. Two other runs also tested the presence and absence of an extruding agent.

Catalyst Test Results

For the most part the three additives tested, despite their proven usefulness in other formulations, contributed little or nothing to the performance of catalysts using cobalt oxide intimately contacted with UCC-103, with or without promoters.

In Catalyst 1 (Cu/Th/UCC-103+Cu-13X), the copper exchanged 13X failed to enhance either the water gas shift or the Fischer-Tropsch activity.

In Catalyst 3 (Co/X_4/UCC-103+UCC-101), the additive X_4 failed to improve the catalyst's conversion, selectivity or stability. In Catalyst 4, formulated in the same way as Catalyst 3, but without the extruding agent, no appreciable difference was found.

In Catalyst 5 (Co/Th/X_6/UCC-103+UCC-101), the presence of X_6 appears to have substantially improved the efficiency with which the catalyst used its cobalt. The run was designed specifically to test both a different source of X_6 and a different method of incorporating it than was done in previous tests. The results this time confirm that its presence improves both the stability and the H_2:CO usage ratio of the intimately contacted Co/UCC-103 catalyst, and suggest that the method of incorporating it into the catalyst may influence its effectiveness.

Catalyst 2 (Co/UCC-103+UCC-101) was the reference catalyst.

Process Design Data

A design package was submitted to the MITRE Corporation for their economic evaluation of our cobalt Fischer-Tropsch catalysts used in conjunction with an isothermal tubular reactor operating at 270C and 300 psig, using a 2.3:1 recycle:feed gas recycle ratio, and giving an 85 percent overall syngas conversion for discretely different levels of methane production.

A computer program, loaded with reaction rate data obtained from the Berty reactor, was used to generate this design data for MITRE. It was in the form of a series of graphs, each one of which depicted the space velocities and the H_2:CO usage ratios required to obtain a fixed methane yield with catalysts having various activities and H_2/CO usage ratios. These graphs were supplemented with detailed material balances for all of the product streams.

The details of how the catalyst test data were correlated, of how the computer program used these correlations to generate the design curves, and of what the design curves showed, are presented in Appendix B.

V. CHANGES

There were no changes in the contract during the Fifteenth Quarter.

VI. FUTURE WORK

All development work under this contract ended on September 17th. However, a continuation of such work is being carried out under Contract No. DE-AC22-84PC70028.

The only other work remaining under the old contract is the filing of an outstanding patent and the writing of the final Technical Report.

A. C. Frost

Appendix A. CATALYST TESTING: DETAILS OF RUNS REPORTED DURING FIFTEENTH QUARTER

Appendix A. CATALYST TESTING: DETAILS OF RUNS REPORTED DURING FIFTEENTH QUARTER

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

Contents

I. Introduction

This report presents the results of five tests conducted during the Fifteenth Quarter of the current contract. The runs were made in August and September, 1984.

The Fischer-Tropsch active metal in all of the tests was cobalt in intimate contact with UCC-103. The primary objective was to assess the effects of certain additives on the properties of this class of catalyst.

In one test, in which the cobalt/UCC-103 was promoted with thorium, the additive was the water gas shift component, copper exchange 13X. In two tests the additive was X_4, and in one of these an extruding agent used in synthesizing the catalyst was tested as well. In a fourth test the additive was X_6, the cobalt/UCC-103 again promoted with thorium. The catalyst in the fifth test, unpromoted and with no additive, served as a reference.

II. Run 1 (12064-01) with Catalyst 1 (Co/Th/UCC-103+Cu-13X)

The purpose of this run was to ascertain whether the water gas shift activity of a Co/Th/UCC-103 catalyst can be improved by the addition of copper exchange 13X, a known water gas shift catalyst.

The catalyst was prepared by promoting cobalt oxide with thorium, and intimately contacting it with UCC-103. The resulting powder was bonded with 15 weight percent silica and extruded to 1/8-inch pellets. The extrudate was then combined in a 1.125:1 ratio with 1/16-inch 13X extrudate which had been ion exchanged with copper. The theoretical content of the final catalyst was 4.3 percent cobalt and 0.5 percent thorium.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. A1-4. Detailed material balances appear in Table A1.

The catalyst was inactive for both the Fischer-Tropsch and the water gas shift reactions. The conversion of syngas was approximately 2 percent.

As in previous trials, this attempt to improve water gas shift activity has been unsuccessful.

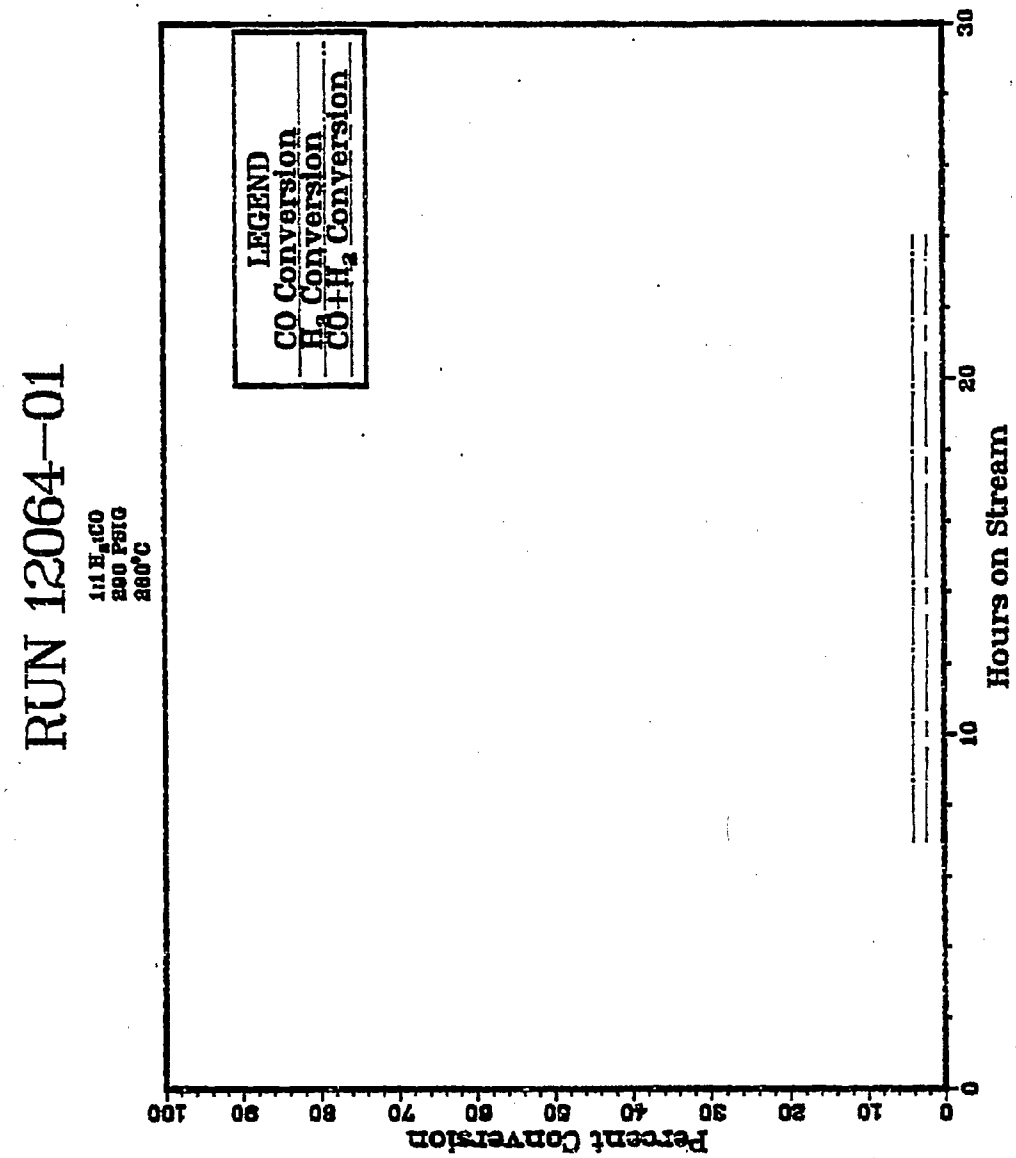
RUN 12064-01
1:1 H_2:CO
250 PSIG
260°C
LEGEND
CO Conversion
H_2 Conversion
$CO+H_2$ Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. A1

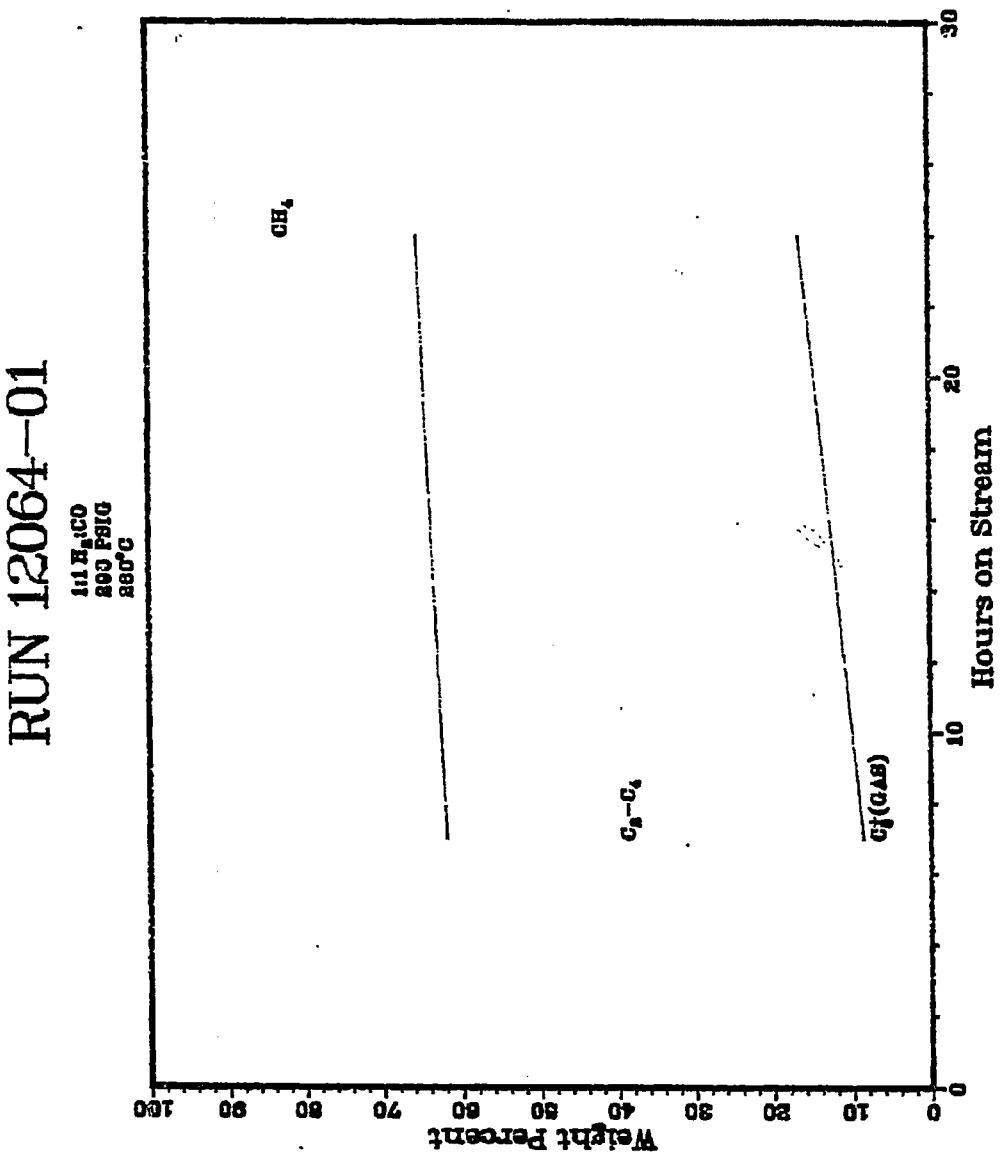
RUN 12064-01
1:1 H2:CO
200 PSIG
280°C
CH4
C2-C4
C5+(GAS)
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. A2

RUN 12064–01

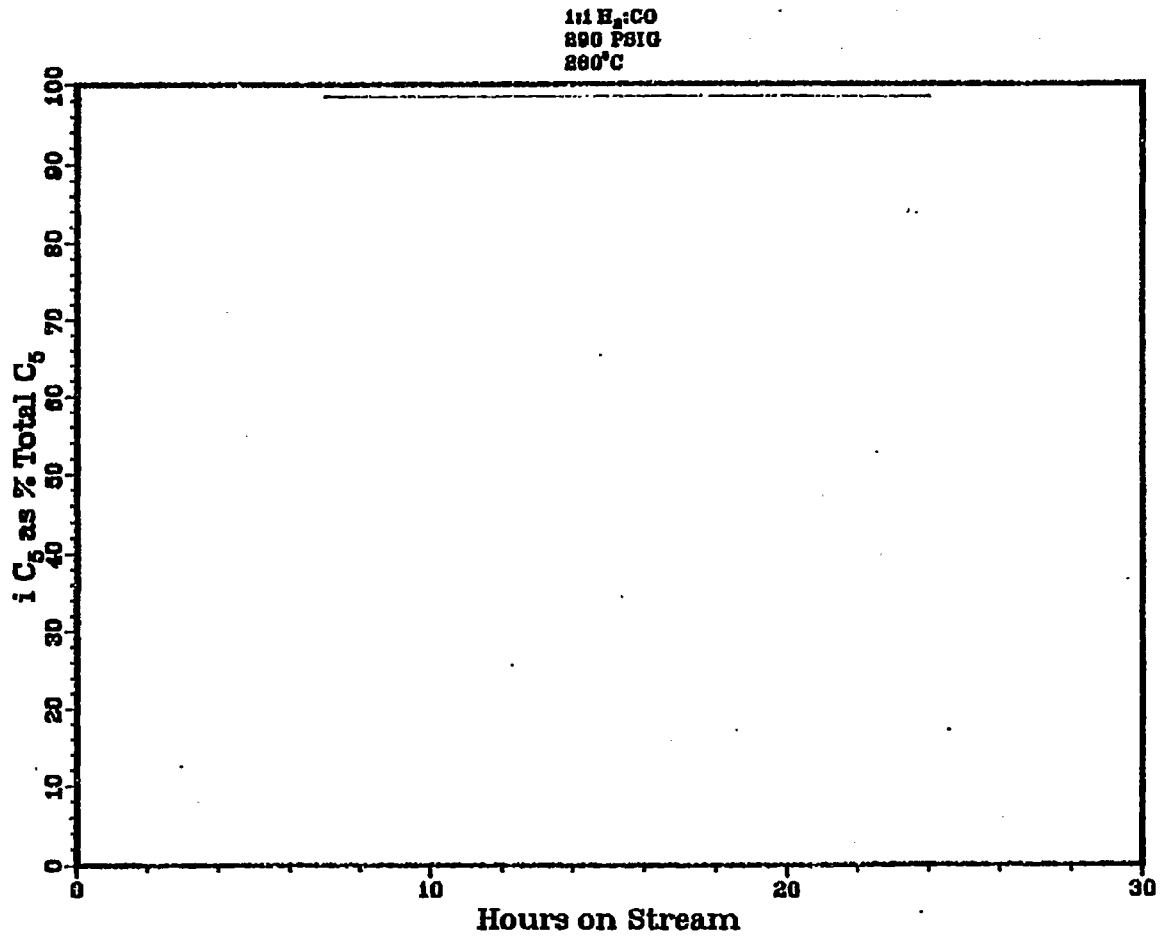

Fig. A3

RUN 12064–01

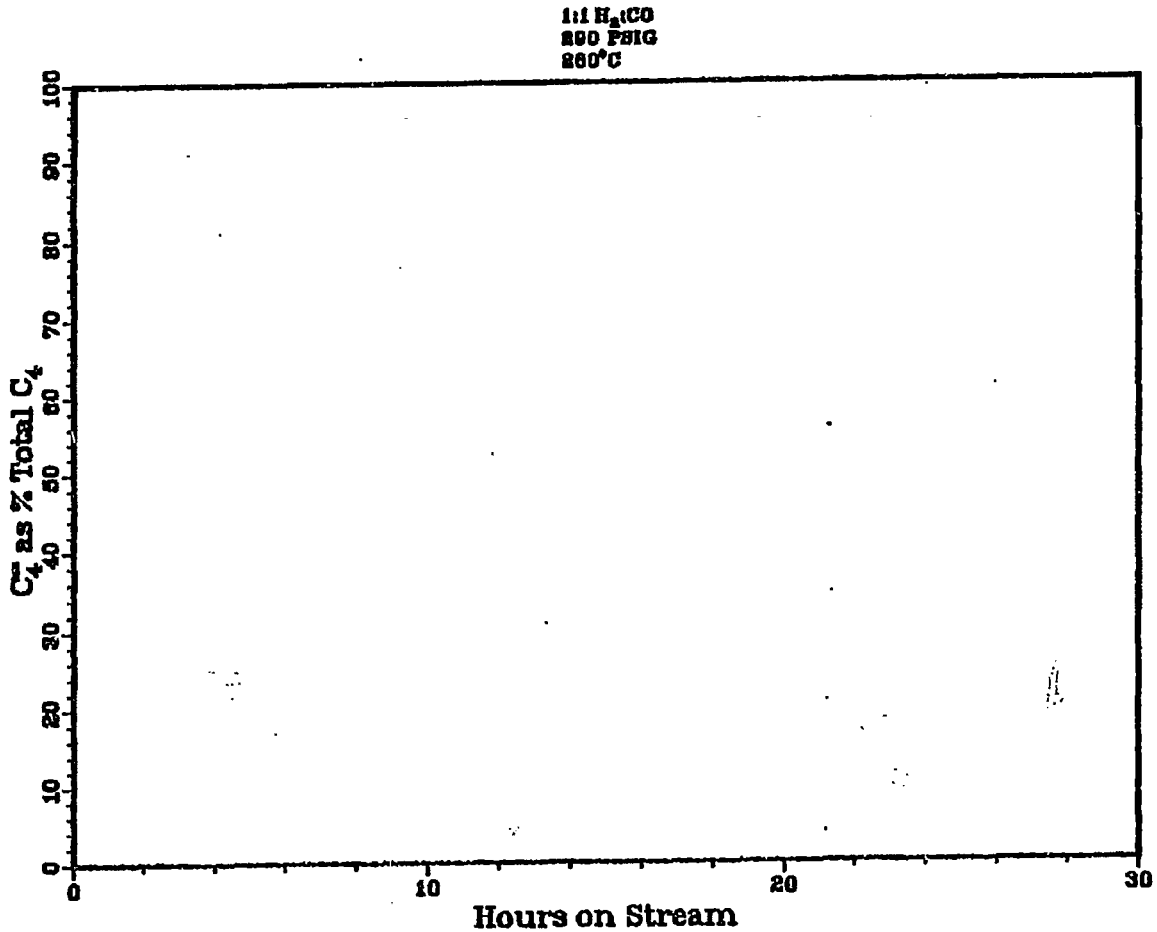

Fig. A4

Table A1

RESULT OF SYNGAS OPERATION

RUN NO. 12064-01
CATALYST CO/TH-U103+CU-13X 11684-44-C +9546-33 200 CC 120.2 G(TO: N/A)
FEED H2:CO of 50:50 @ 630 CC/MN OR 189 GHSV

RUN & SAMPLE NO.	12064-01-01	064-01-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	7.0	24.0
PRESSURE,PSIG	291	296
TEMP. C	263	261
FEED CC/MIN	630	630
HOURS FEEDING	7.00	17.00
EFFLNT GAS LITER	193.50	635.20
GM AQUEOUS LAYER	0.00	0.00
GM OIL	0.00	0.00
MATERIAL BALANCE		
GM ATOM CARBON %	70.68	94.42
GM ATOM HYDROGEN %	75.66	103.11
GM ATOM OXYGEN %	73.25	98.03
RATIO CHX/(H2O+CO2)	0.0765	0.0405
RATIO X IN CHX	3.0563	2.9635
USAGE H2/CO PRODT	14.6084	26.1564
FEED H2/CO FRM EFFLNT	1.0705	1.0920
RESIDUAL H2/CO RATIO	1.0296	1.0515
RATIO CO2/(H2O+CO2)	0.0000	0.0000
K SHIFT IN EFFLNT	0.0000	0.0000
SPECIFIC ACTIVITY SA	0.0015	0.0009
CONVERSION		
ON CO %	0.30	0.16
ON H2 %	4.10	3.86
ON CO+H2 %	2.27	2.09
PRDT SELECTIVITY,WT %		
CH4	38.12	34.69
C2 HC'S	0.00	0.00
C3H8	16.30	13.14
C3H6=	0.00	0.00
C4H10	36.95	35.63
C4H8=	0.00	0.00
C5H12	8.49	9.89
C5H10=	0.03	0.06
C6H14	0.08	0.15
C6H12= & CYCLO'S	0.04	6.45
C7+ IN GAS	0.00	0.00
LIQ HC'S	0.00	0.00
TOTAL	100.00	100.00

Table A1 (continued)

SUB-GROUPING		
C1 -C4	91.36	83.46
C5 -420 F	8.64	16.54
420-700 F	0.00	0.00
700-END PT	0.00	0.00
C5+-END PT	8.64	16.54
ISO/NORMAL MOLE RATIO		
C4	4.8750	4.1429
C5	260.0000	160.0000
C6	1.0000	1.0000
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	0.0000	0.0000
C4	0.0000	0.0000
C5	261.0000	161.0000
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.1554	0.5686
RATIO CH4/(1-A)**2	0.5344	1.8639
ALPHA FRM CORRELATION		
ALPHA (EXPTL/CORR)		
W%CH4 FRM CORRELATION		
W%CH4 (EXPTL/CORR)		
LIQ HC COLLECTION		
PHYS. APPEARANCE		
DENSITY		
N, REFRACTIVE INDEX		
SIMULT'D DISTILATN		
10 WT % @ DEG F		
16		
50		
84		
90		
RANGE(16-84 %)		
WT % @ 420 F		
WT % @ 700 F		
NEW FORMAT JAN 25,85		

III. Run 2 (12064-02) with Catalyst 2 (Co/UCC-103+UCC-101)

This catalyst was formulated to serve as a reference against which to measure the effects on water gas shift activity of such additives as X_4 and thorium. It is to be compared with Catalyst 2 of the Third Quarterly Report (Co/Th/UCC-103+UCC-101, Run 11677-09) and with Catalyst 3 of this Report.

The catalyst was prepared in the same way as Catalyst 1 except for the omission of thorium and of copper exchanged 13X, and the addition of UCC-101. The theoretical cobalt content was 6.5 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. A5-8. Simulated distillations of the C_5^+ product are plotted in Figs. A9-15. Carbon number product distributions are plotted in Figs. A16-34. Chromatograms from simulated distillations are reproduced in Figs. A35-41. Detailed material balances appear in Tables A2-5.

Due to the high initial H_2:CO feed ratio of 5.4:1, the initial syngas conversion at 260C was 62.6 percent and the initial methane production more than 97 percent. After the first sample, at 18.5 hours on stream, the feed ratio was adjusted to 1:1; both functions then fell to more typical levels. By 66.5 hours on stream the conversion was about 50 percent (specific activity

1.65), and the methane production 11.7 percent.

The stability was good, but not exceptionally so. Between 66.5 and 234.5 hours on stream the loss of conversion, as estimated by least squares analysis, was one percentage point every 90 hours--considerably poorer than with Catalyst 6 of the Third Annual Report (Co/Th/X_4/UCC-103+UCC-101, Run 11677-11).

At 270C the conversion rose to about 58 percent. But the stability fell sharply, the conversion decreasing at a rate of about one percentage point every 26 hours. Lowering the feed ratio to 0.74:1 restored the stability almost exactly to its earlier level, about one percentage point loss of conversion every 89 hours. This is unusual for a Fischer-Tropsch catalyst with hydrogen deficient feed, and may significantly improve the stability of a catalyst at the end of a fixed-bed reactor where it is exposed to a low ratio of H_2 to CO.

The stability at 270C was similar to that of Third Quarterly Report Catalyst 2, which was promoted with thorium and which contained only about two-thirds as much cobalt/UCC-103. The estimated deactivation rate in both, during the first 120 hours on stream, was about one percentage point every 24 hours. The product of this catalyst was, however, slightly heavier--about 66 percent C_5^+ as against about 64 percent, alpha value of 0.80 as against 0.79, methane 15-17 percent as against 17-19 percent, and significantly higher wax content. The olefin content of the C_4's was about 60 percent as against about 50 percent.

Except for the excess of methane the Schulz-Flory distribu-

tion plots are linear, with no apparent carbon number cut-off even under high wax (low H_2:CO feed) conditions.

This catalyst should prove useful as a reference against which to measure the effects of various promoters in this type of formulation. As an example, the thorium promoted Catalyst 4 of the Eleventh Quarterly Report (Run 11677-03) yielded a product significantly lighter and lower in olefins. However, the available data disclose no useful measure of comparative stability.

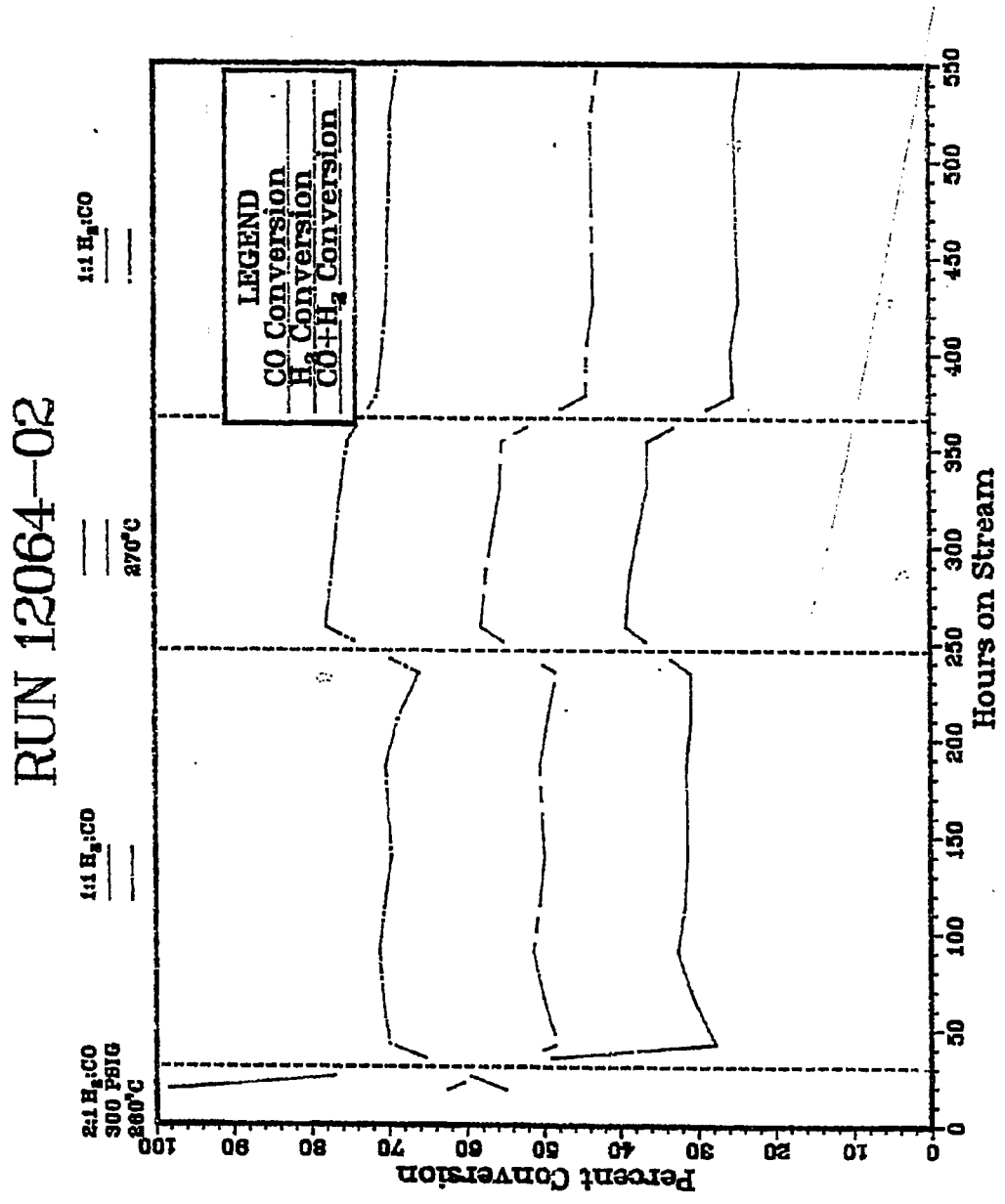
RUN 12064-02
2:1 H2:CO
300 PSIG
260°C
1:1 H2:CO
270°C
1:1 H2:CO
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450
500
550

Fig. A5

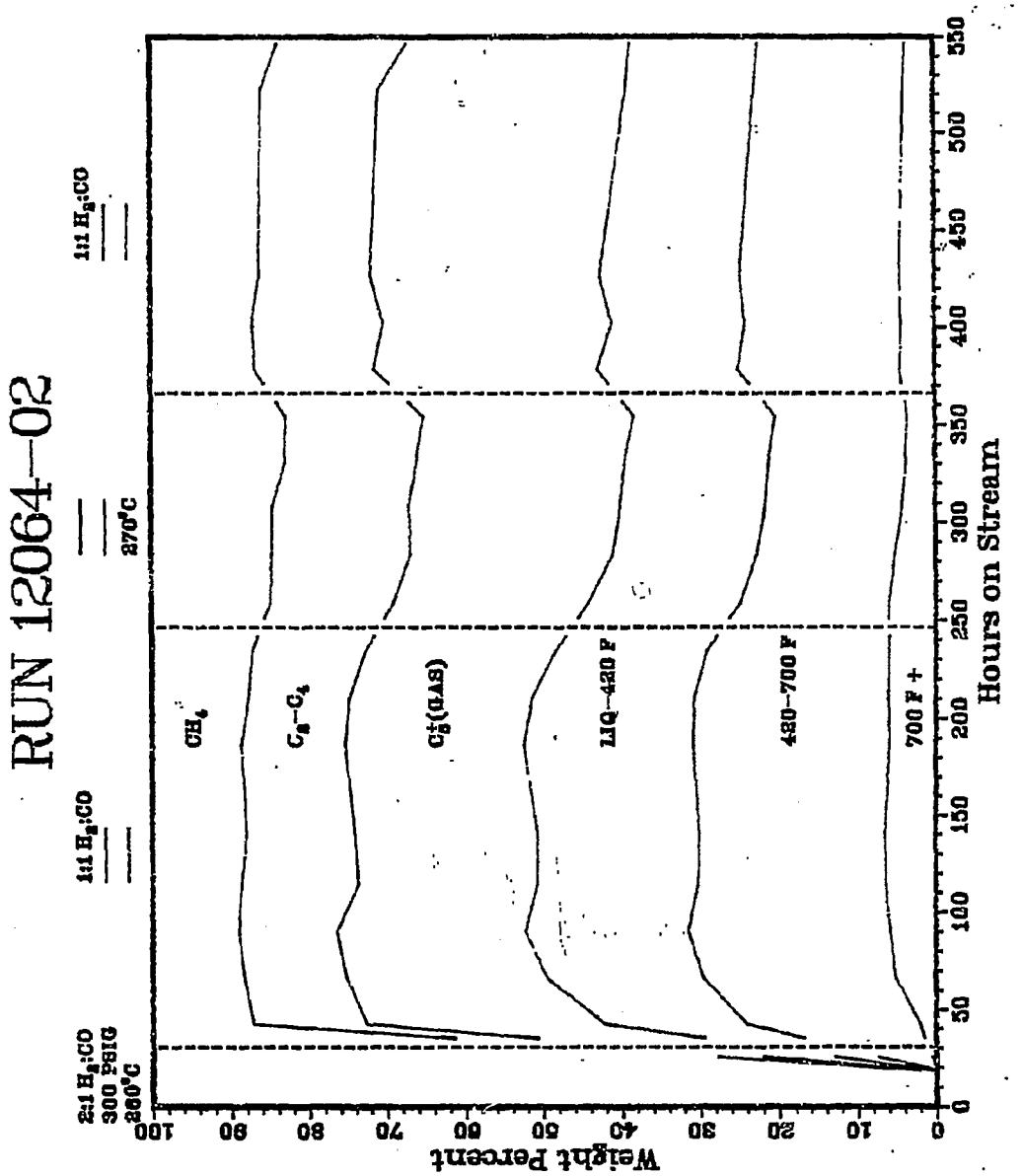
RUN 12064-02
2:1 H2:CO
300 PSIG
260°C
1:1 H2:CO
270°C
1:1 H2:CO
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450
500
550

Fig. A6

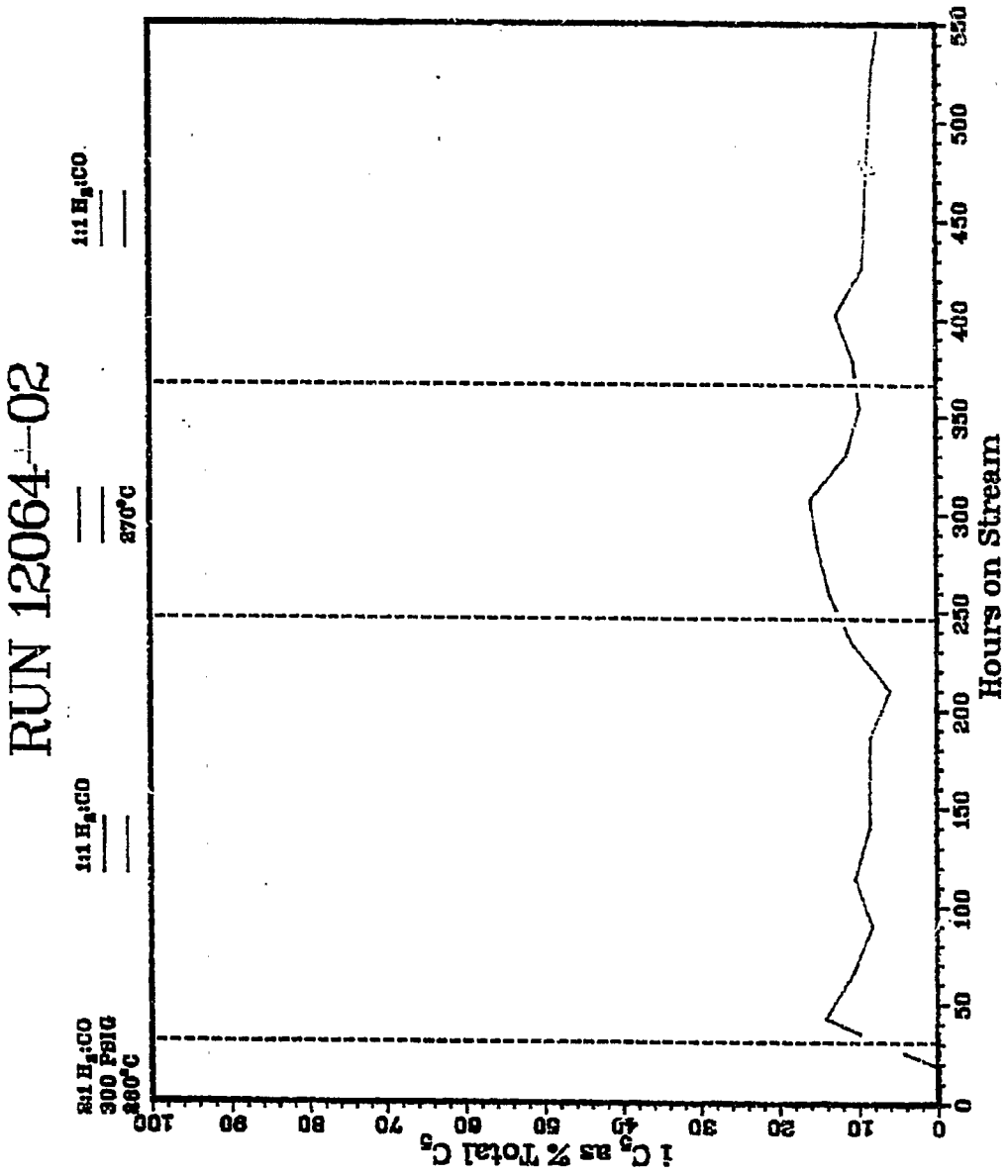
RUN 12064-02
2:1 H2:CO
300 PSIG
260°C
1:1 H2:CO
1:1 H2:CO
270°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450
500
550

Fig. A7

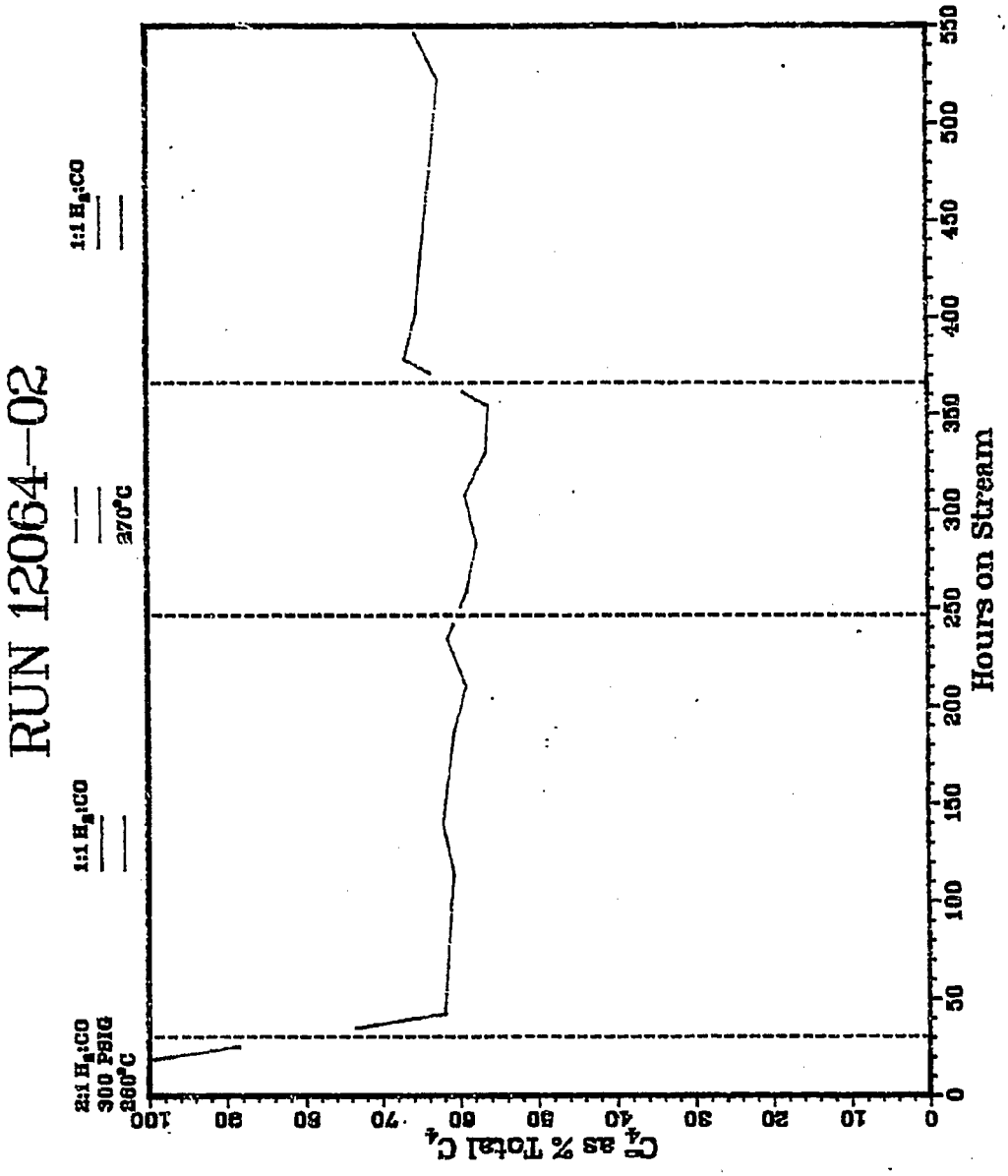
RUN 12064-02
2:1 H2:CO
300 PSIG
260°C
1:1 H2:CO
270°C
1:1 H2:CO
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450
500
550

Fig. A8

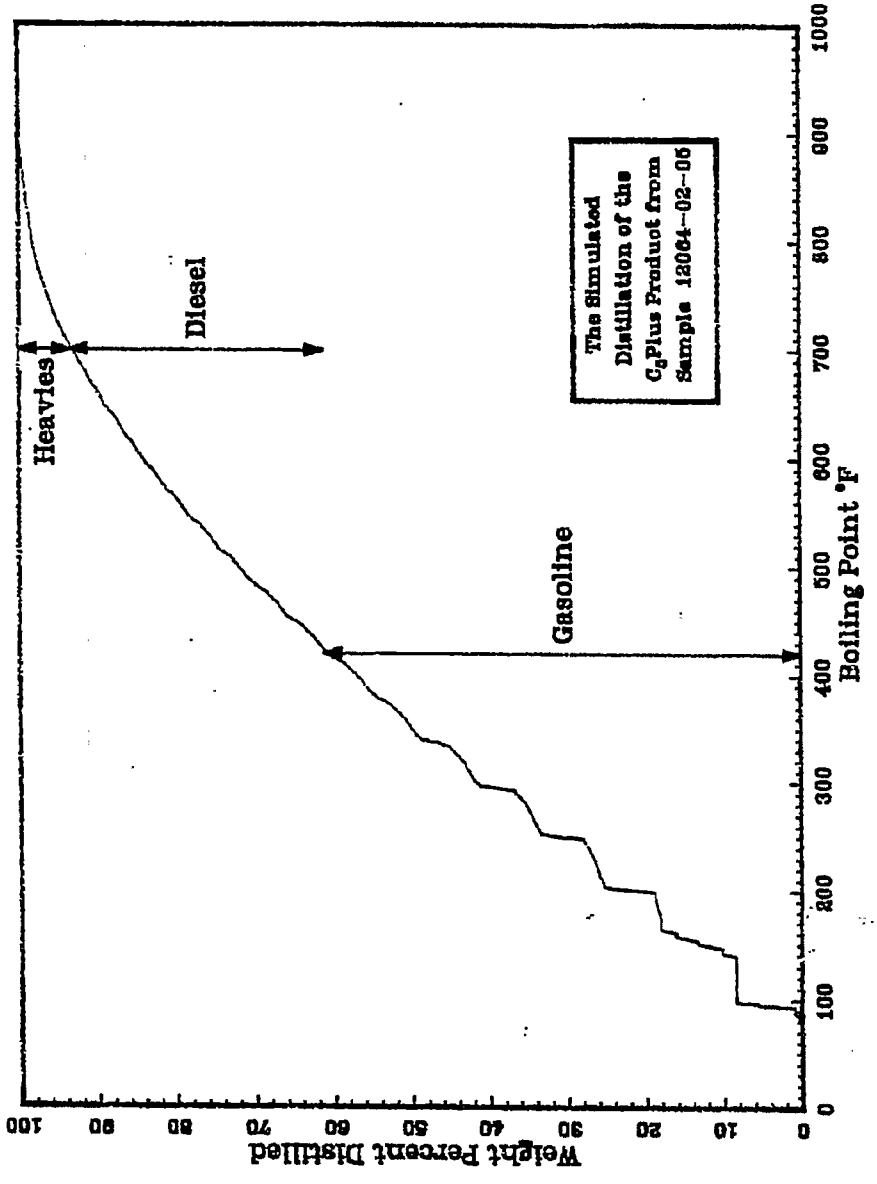
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5Plus Product from Sample 12064-02-05

Fig. A9

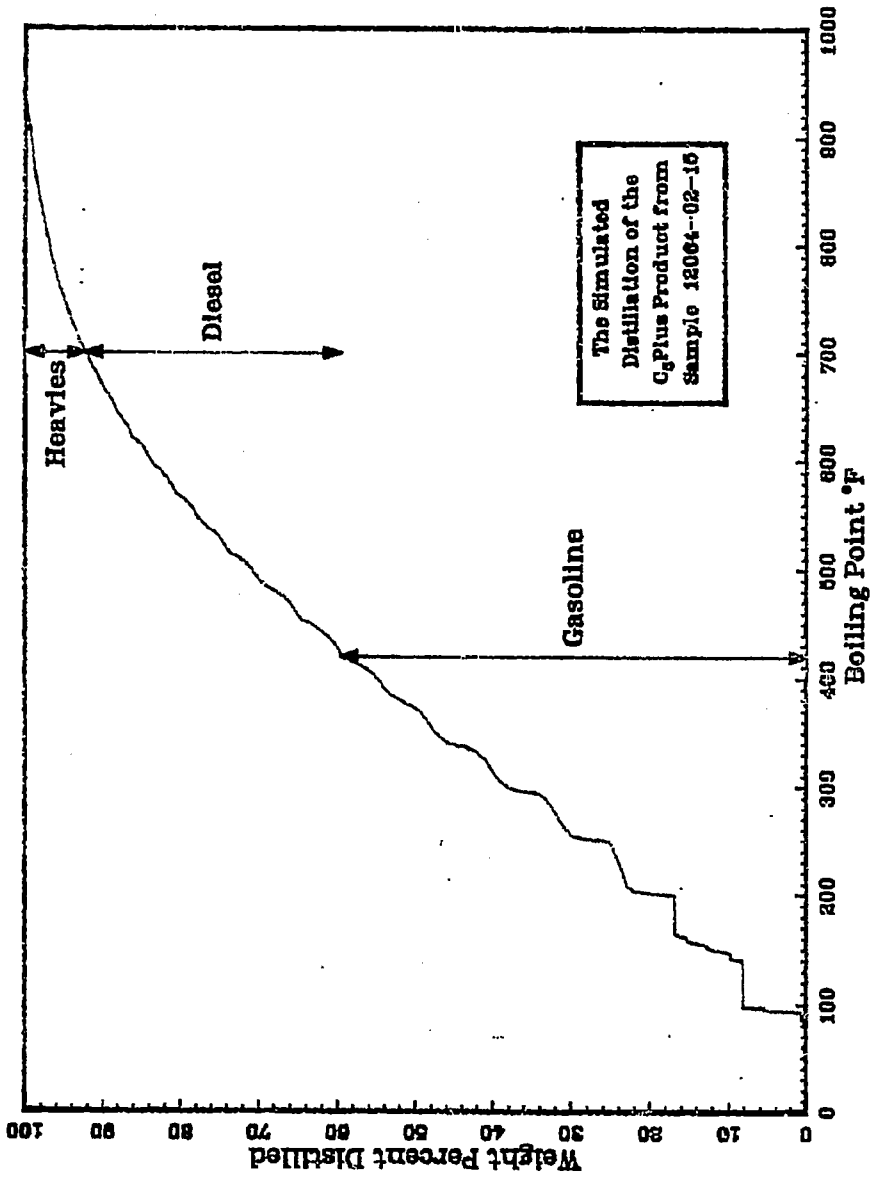
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C9Plus Product from Sample 12064--02-15

Fig. A10

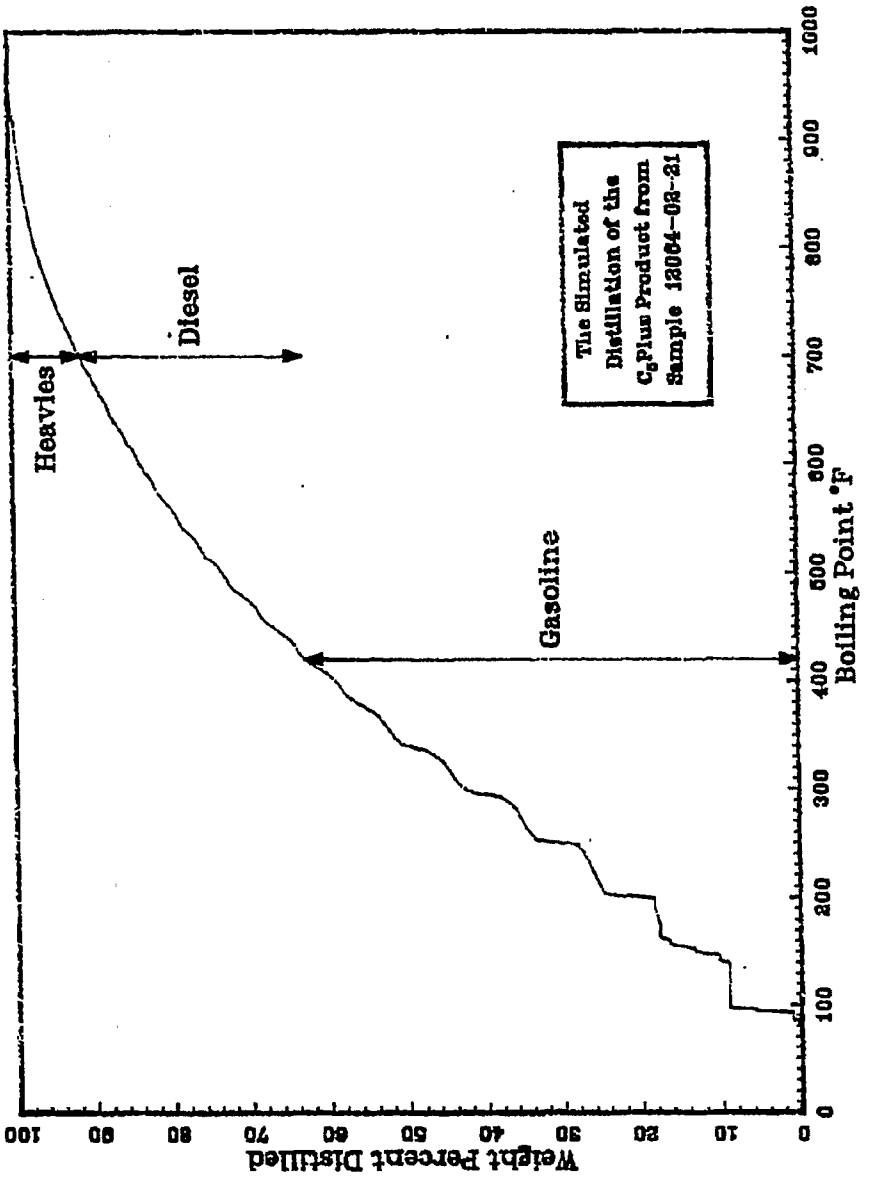
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12064-03-21

Fig. A11

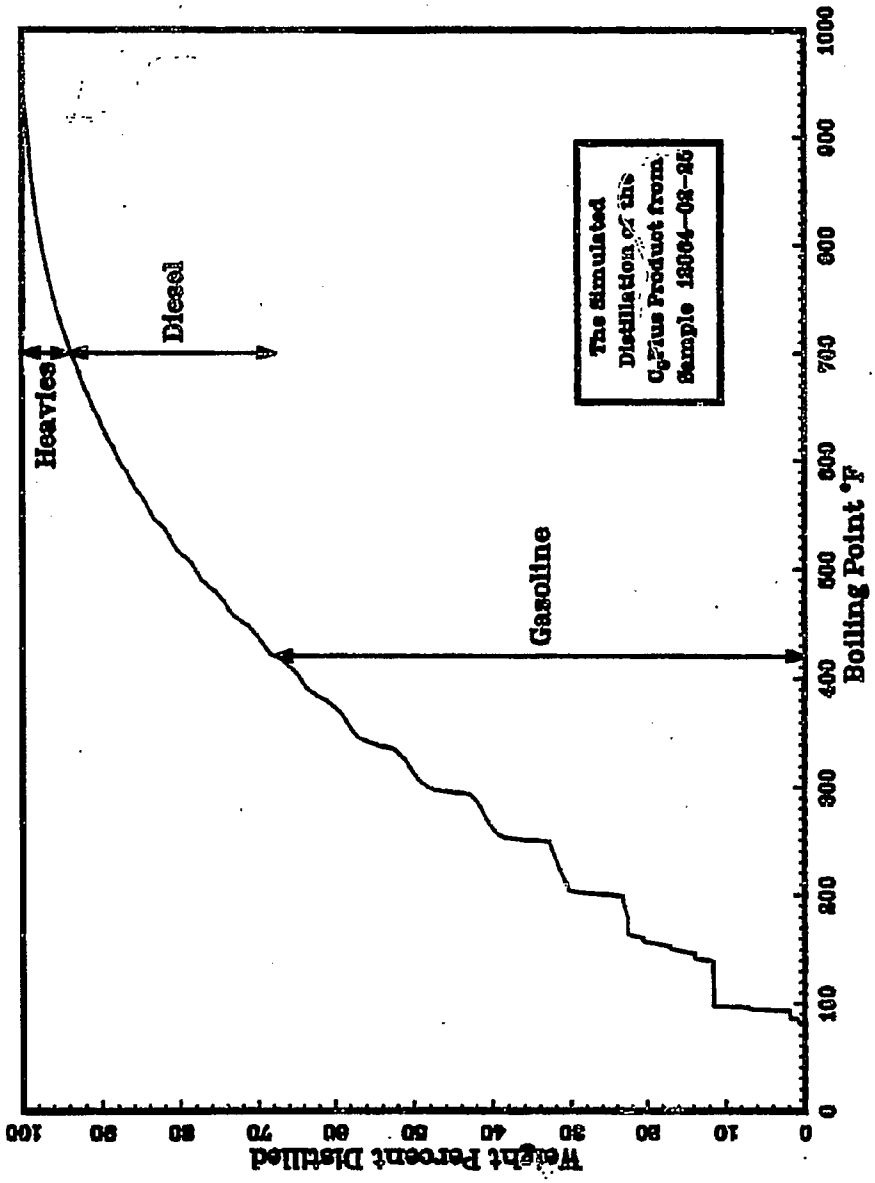
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 12064-08-25
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. A12

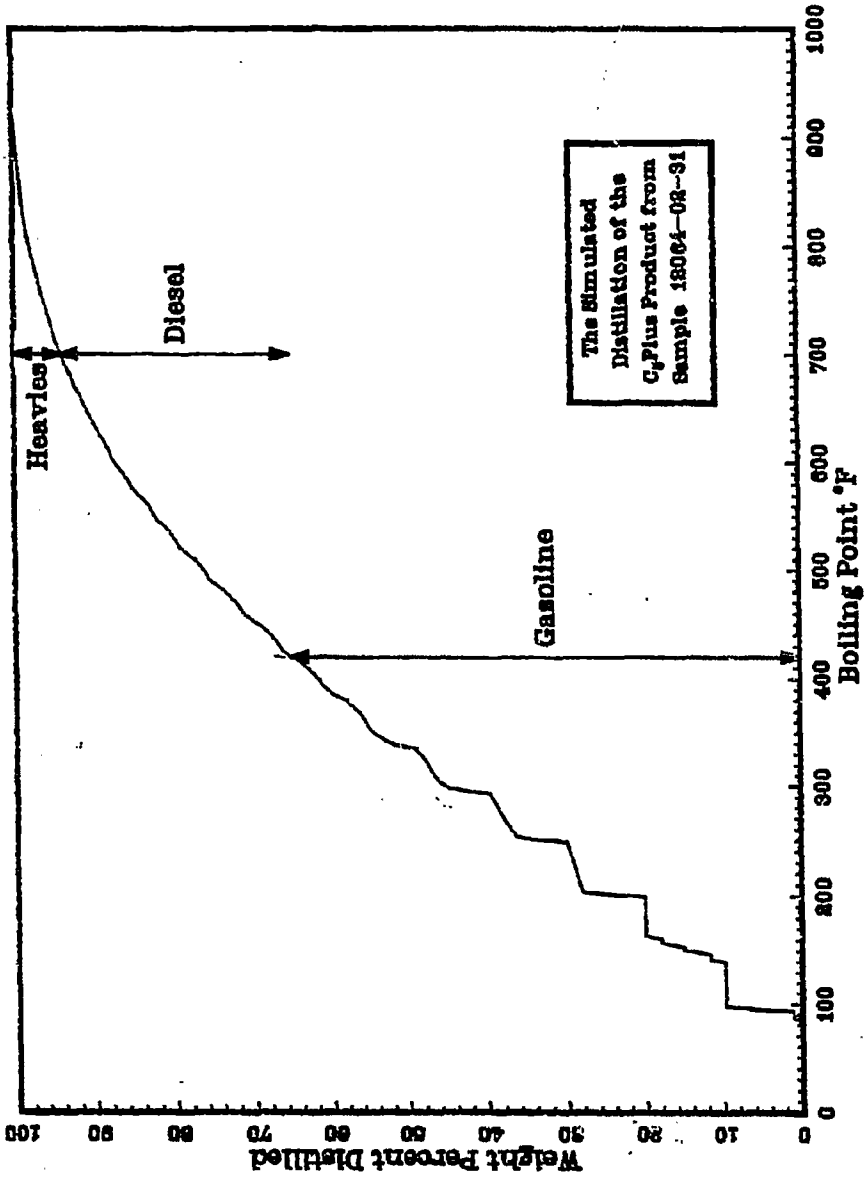
The Simulated Distillation of the C5 Plus Product from Sample 18064-08-91
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Fig. A13

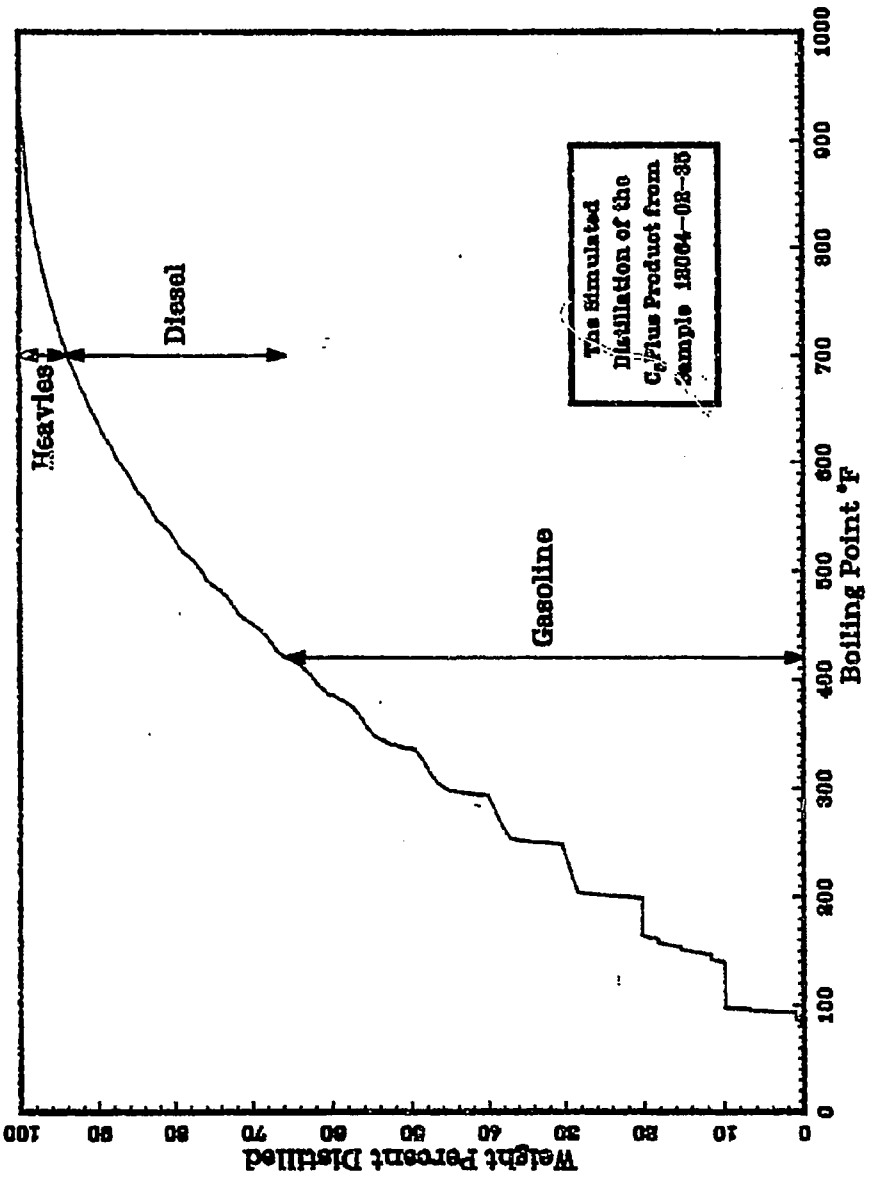
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 13064-03-35

Fig. A14

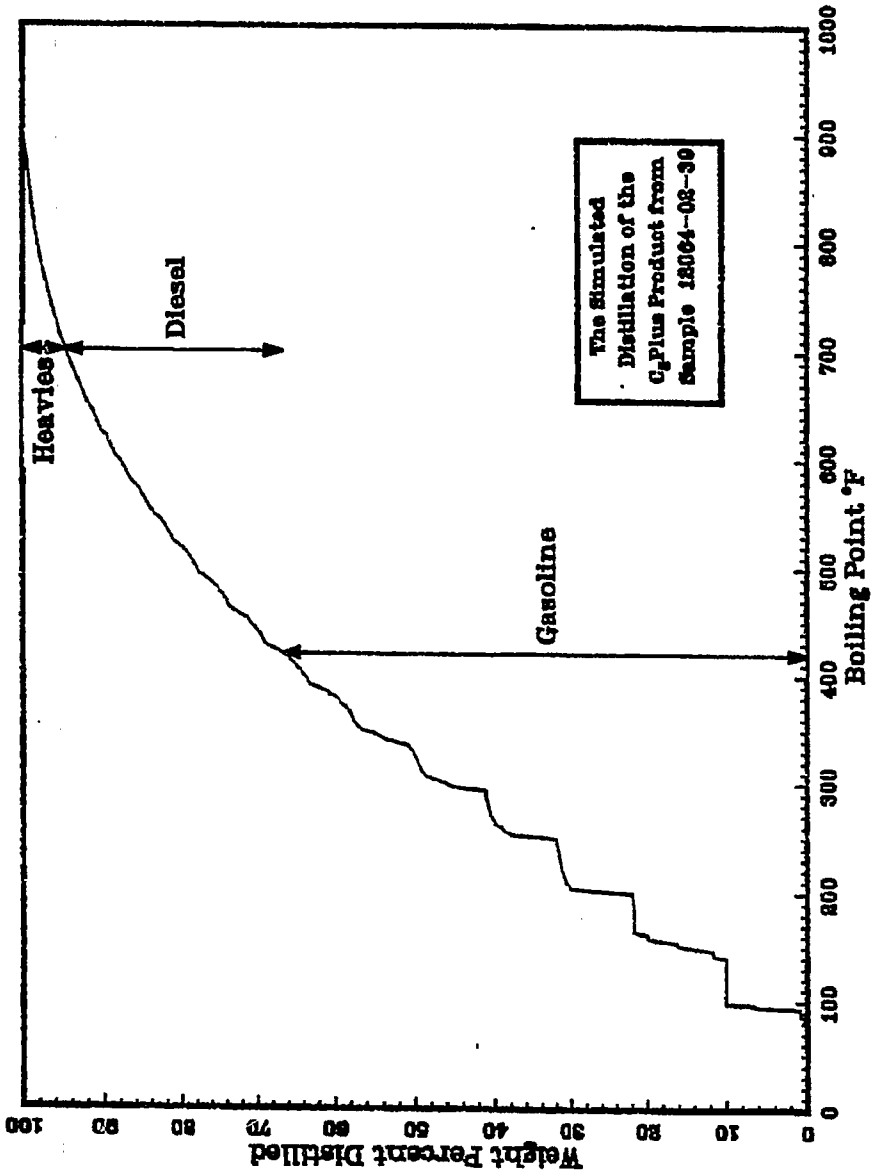
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 12064-08-30

Fig. A15

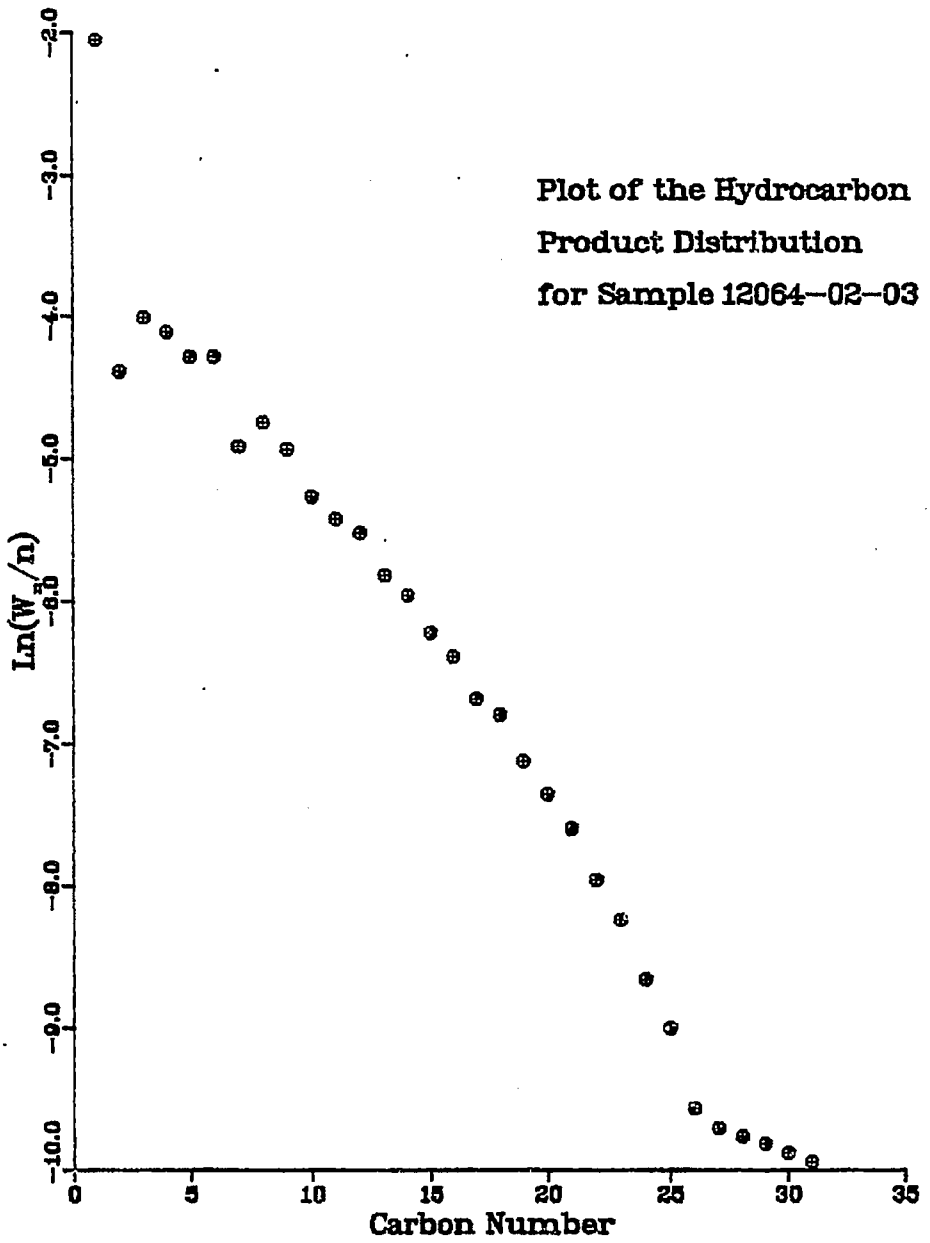
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-03
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A16

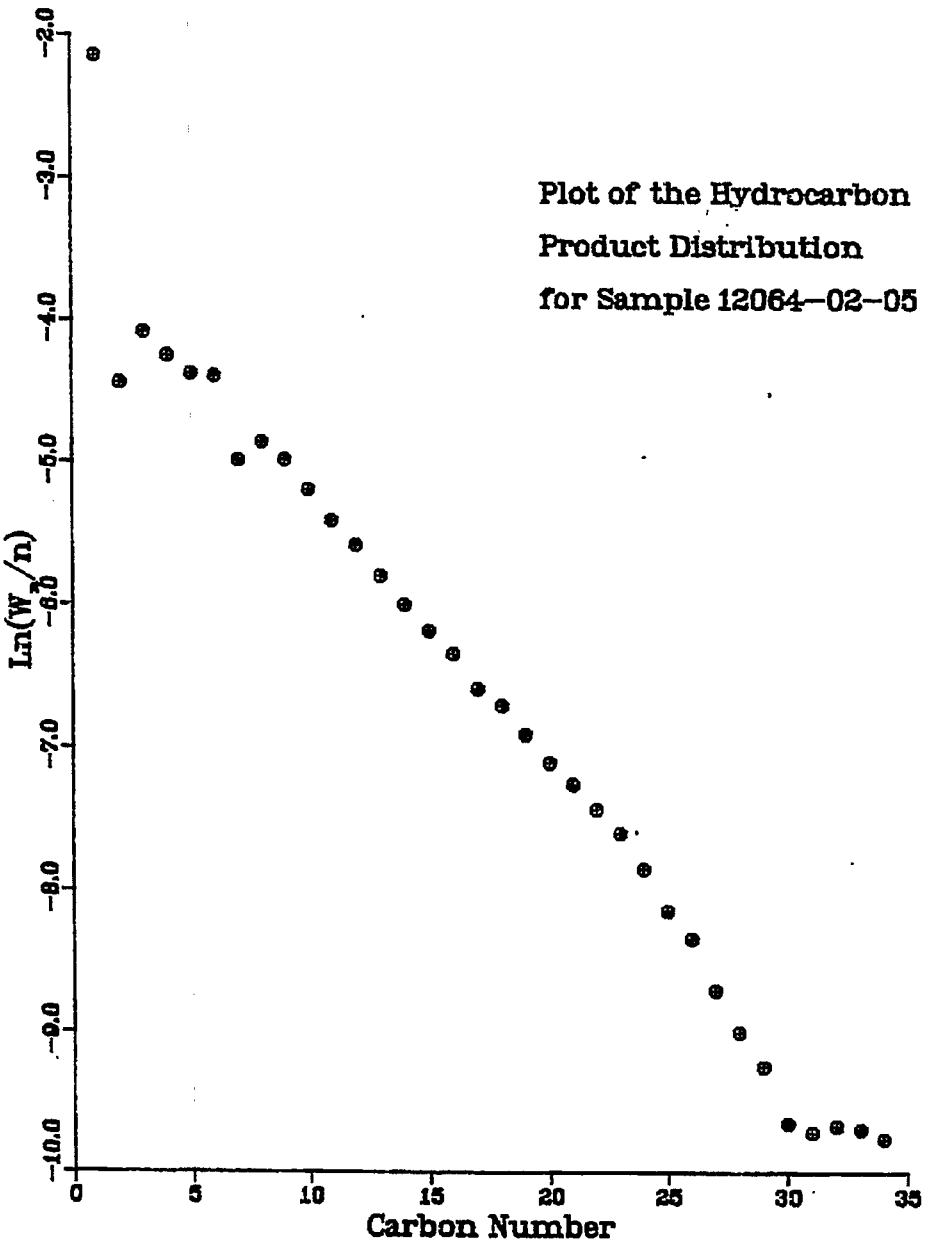
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-05
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A17

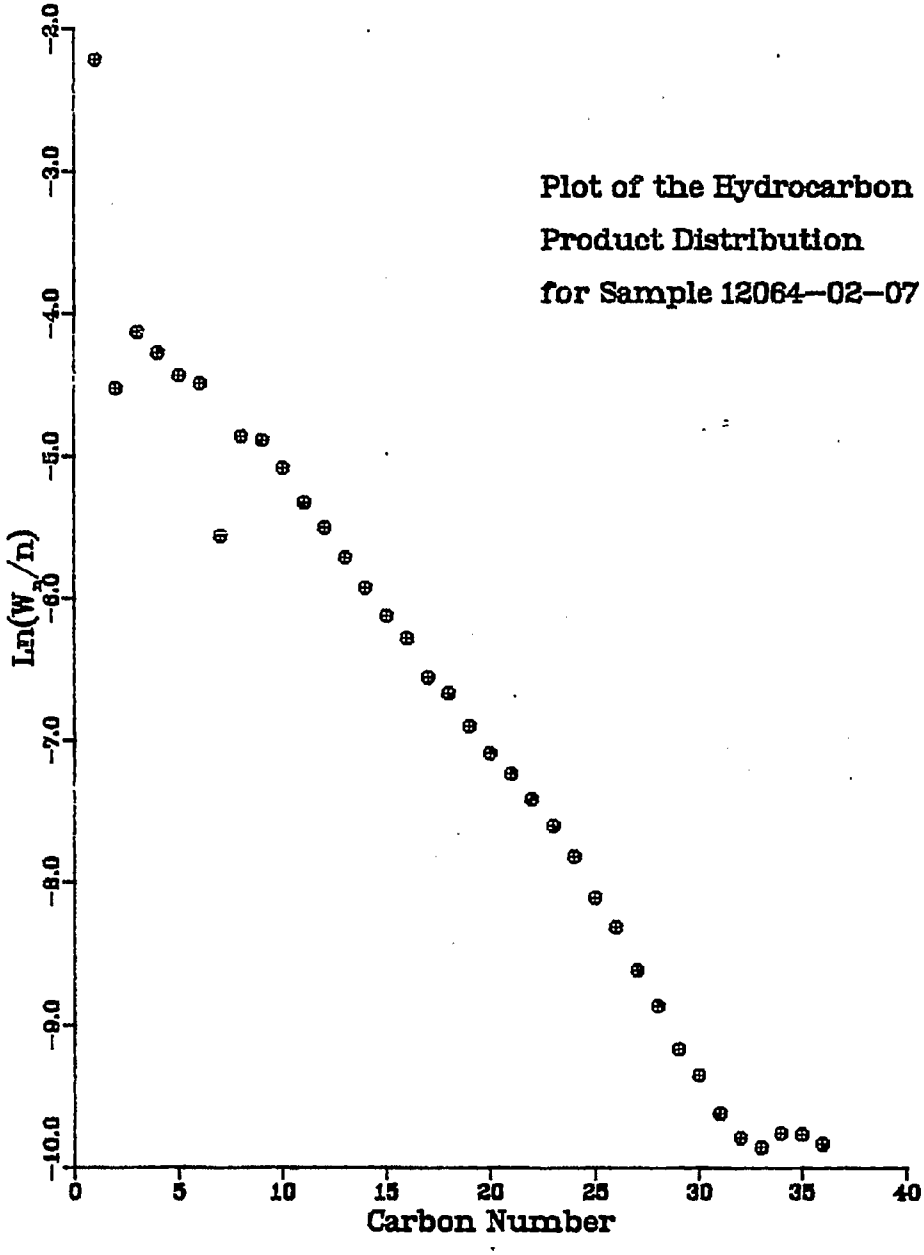
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-07
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A18

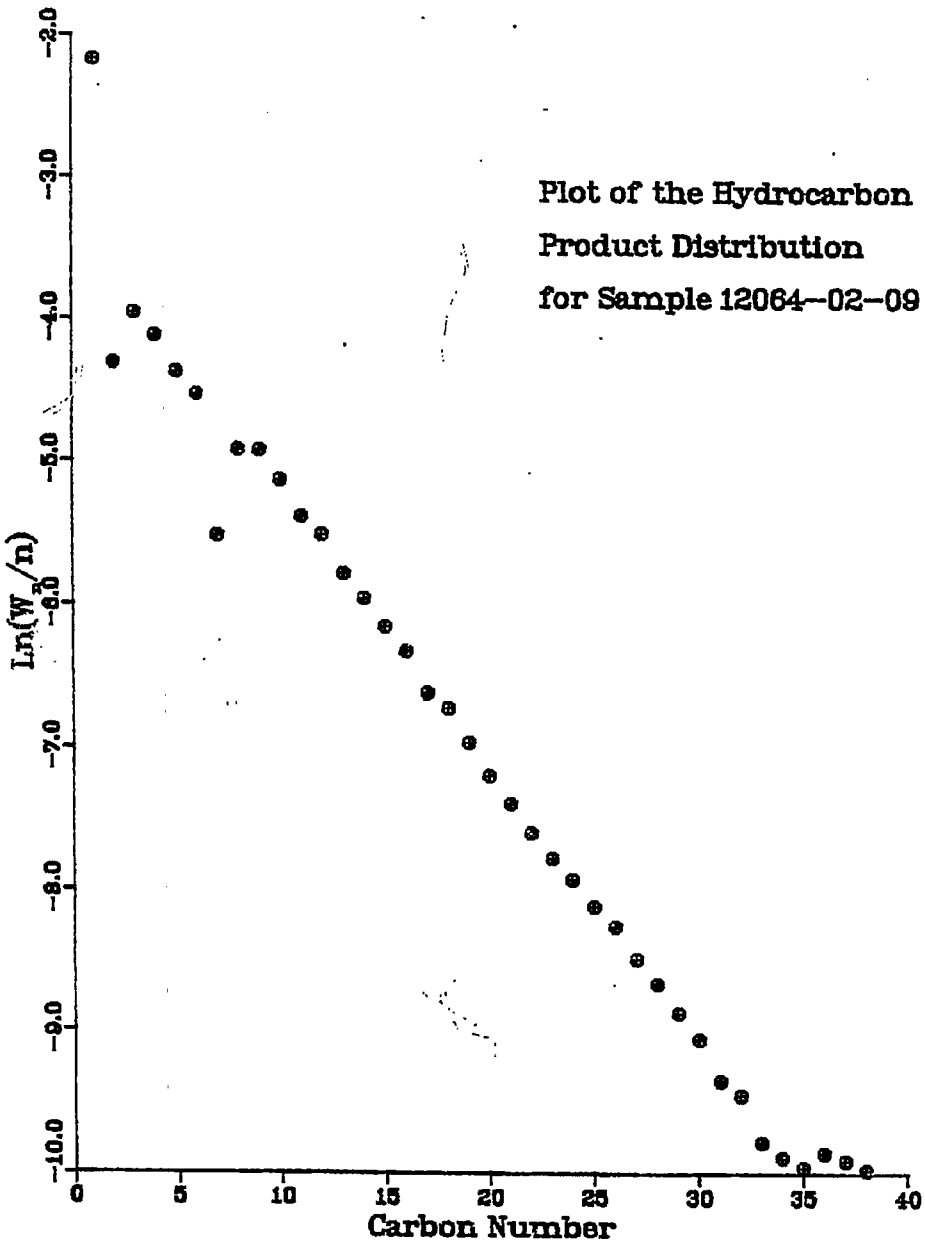
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-09
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A19

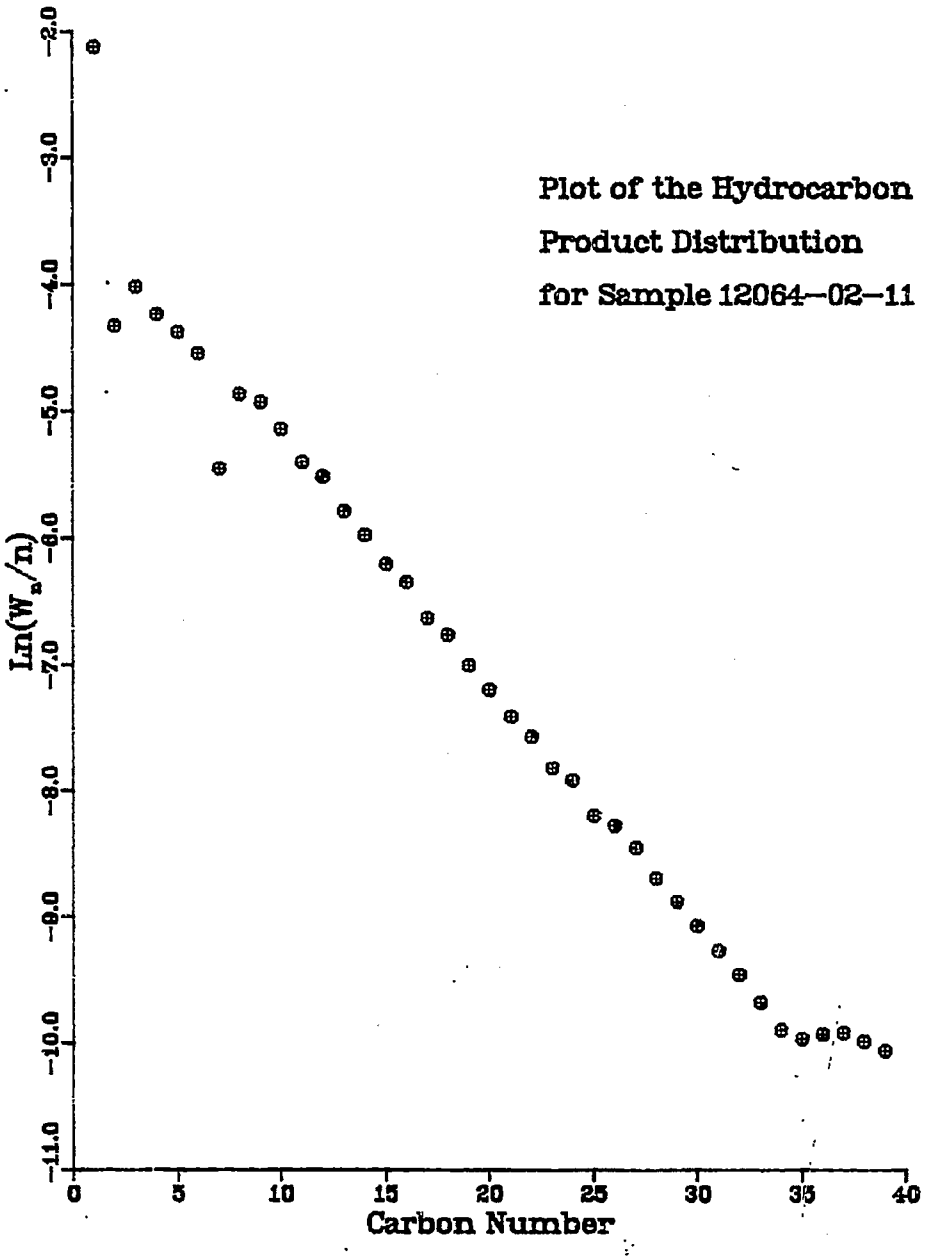
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-11
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A20

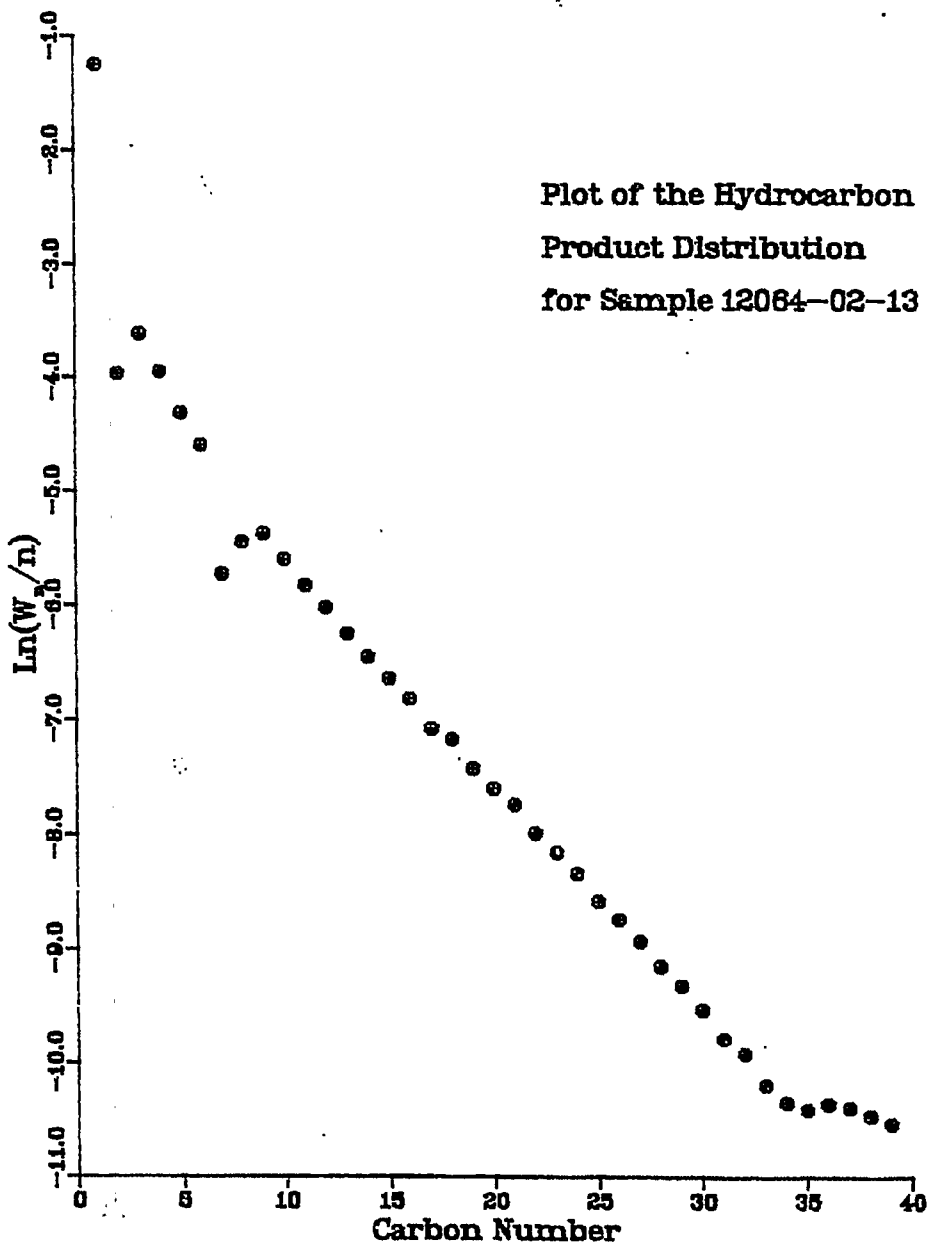
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A21

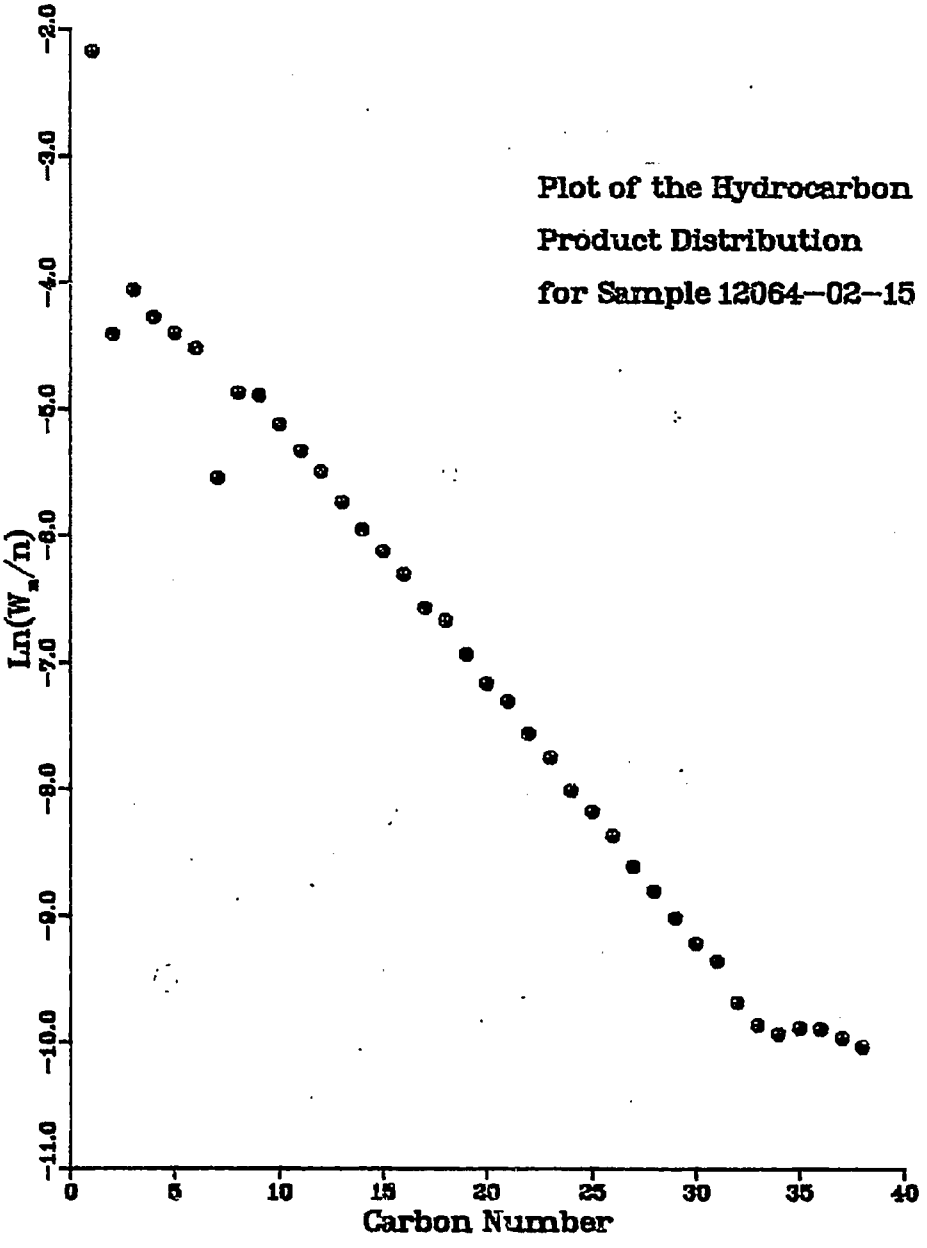
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-15
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A22

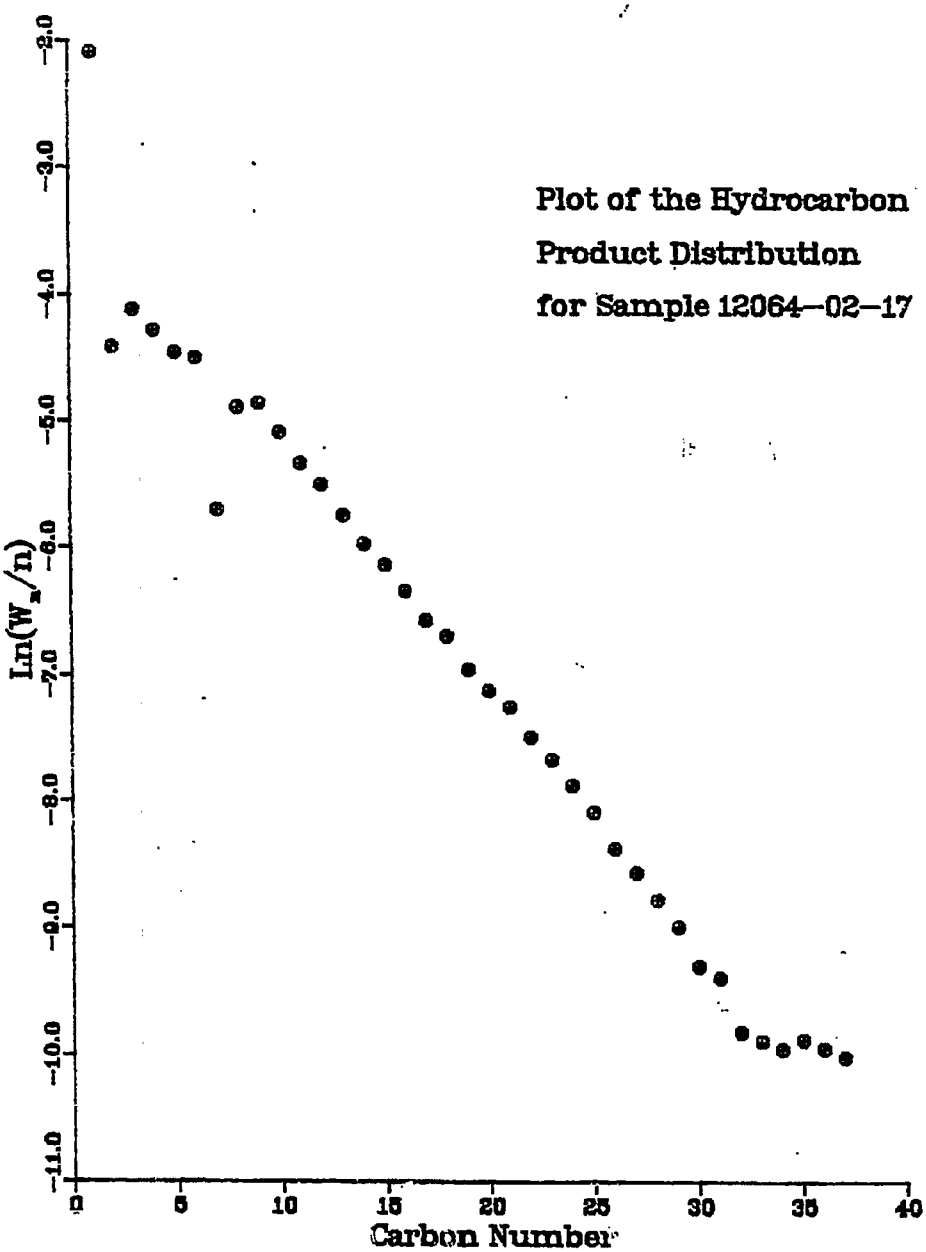
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-17
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A23

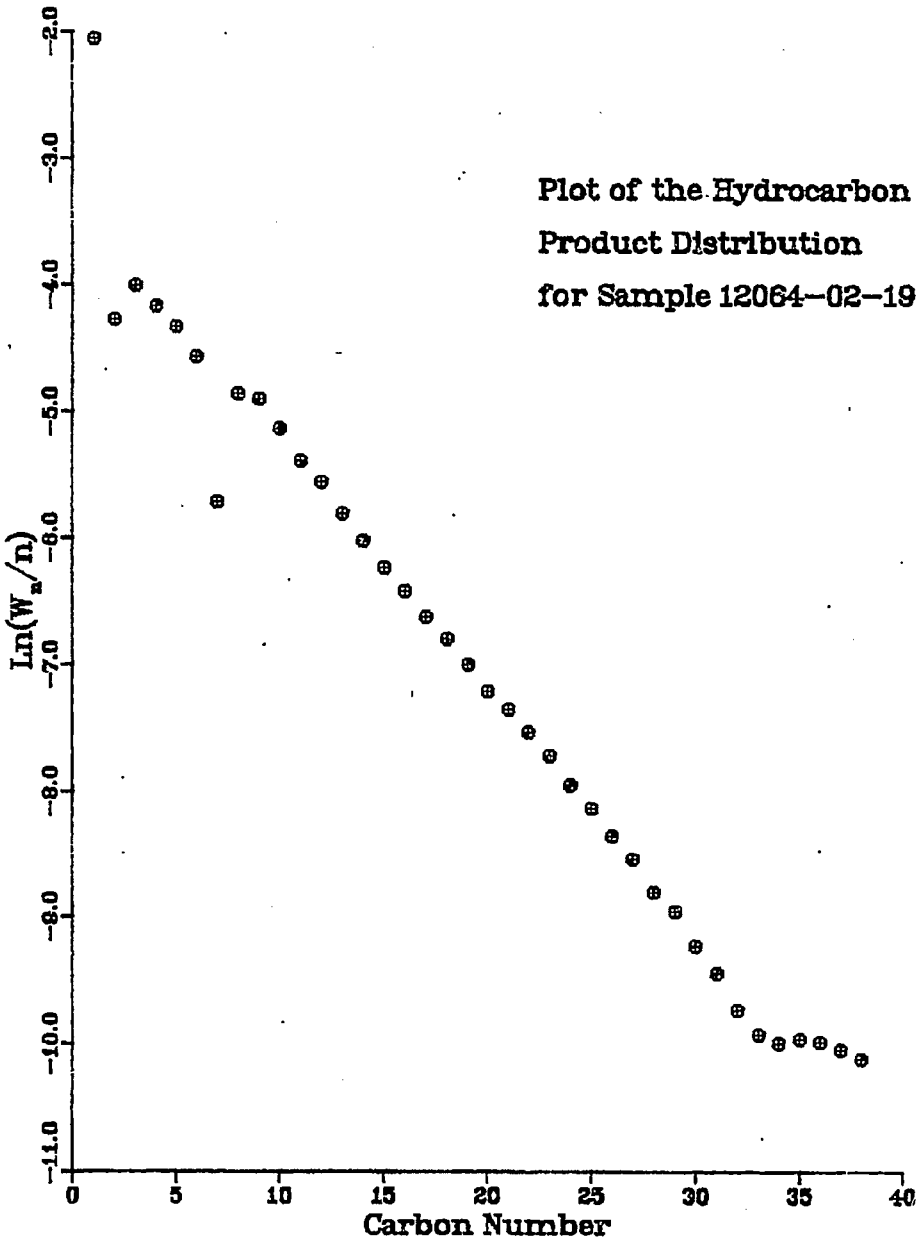
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-19
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A24

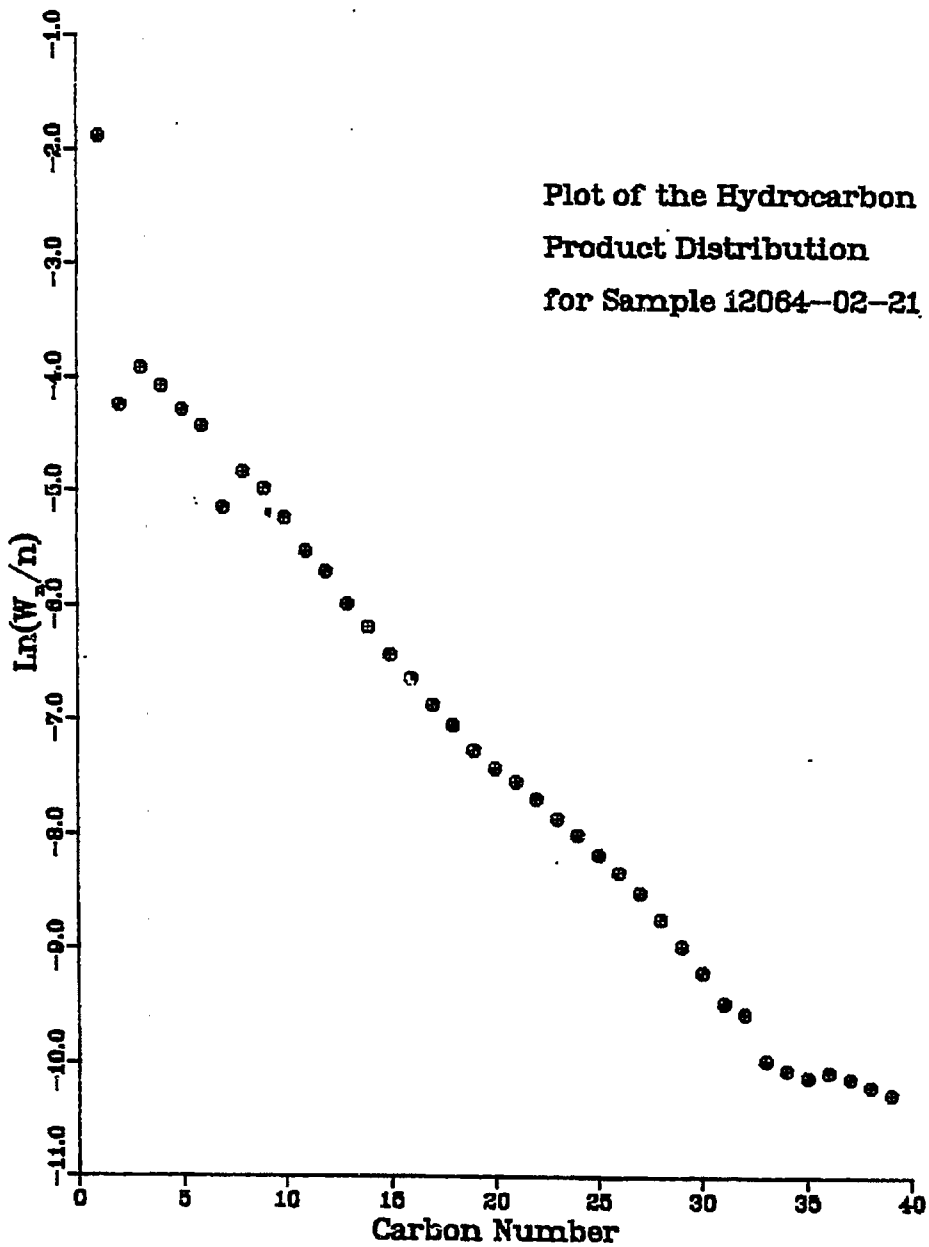
Plot of the Hydrocarbon
Product Distribution
for Sample 12064--02--21
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A25

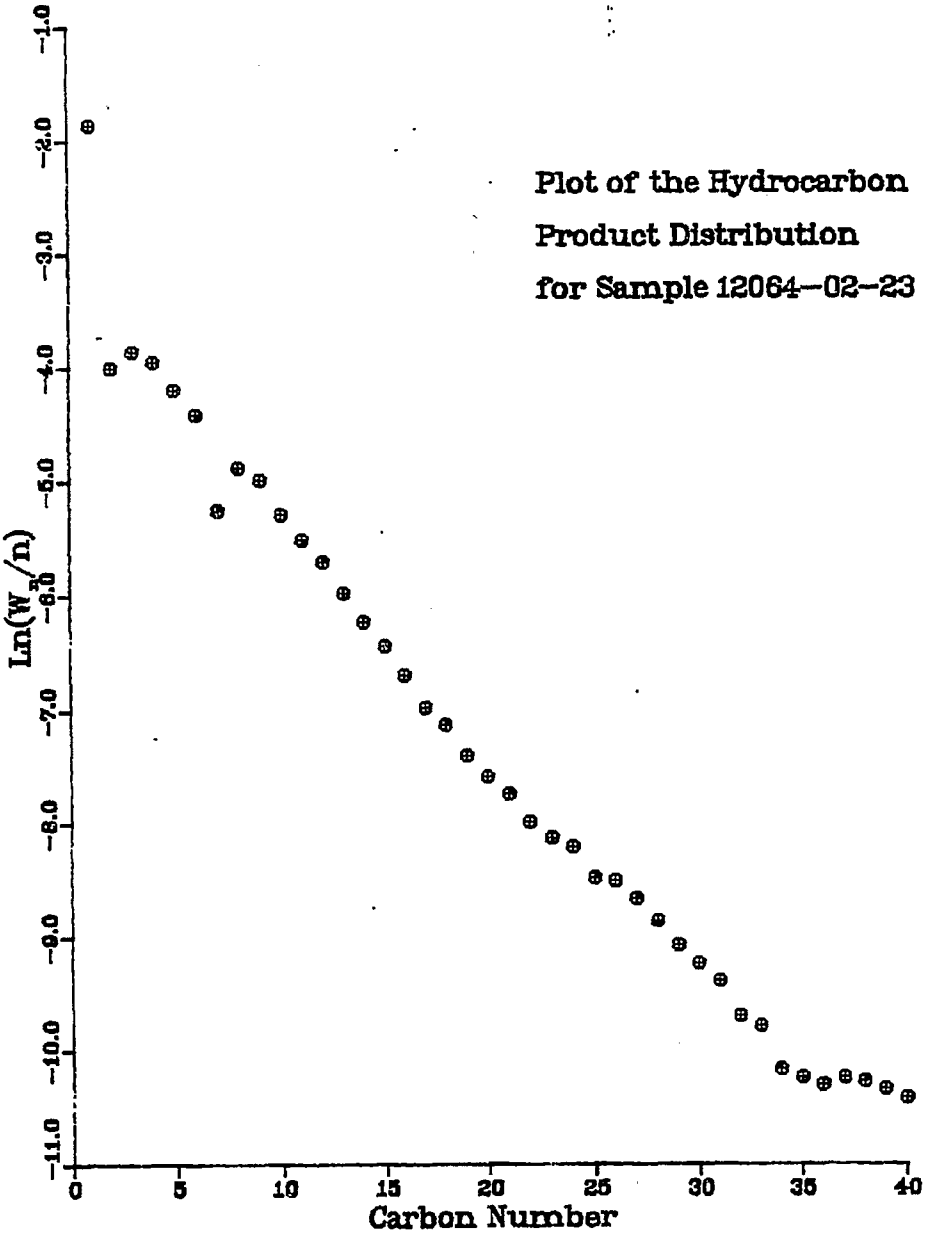
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-23
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A26

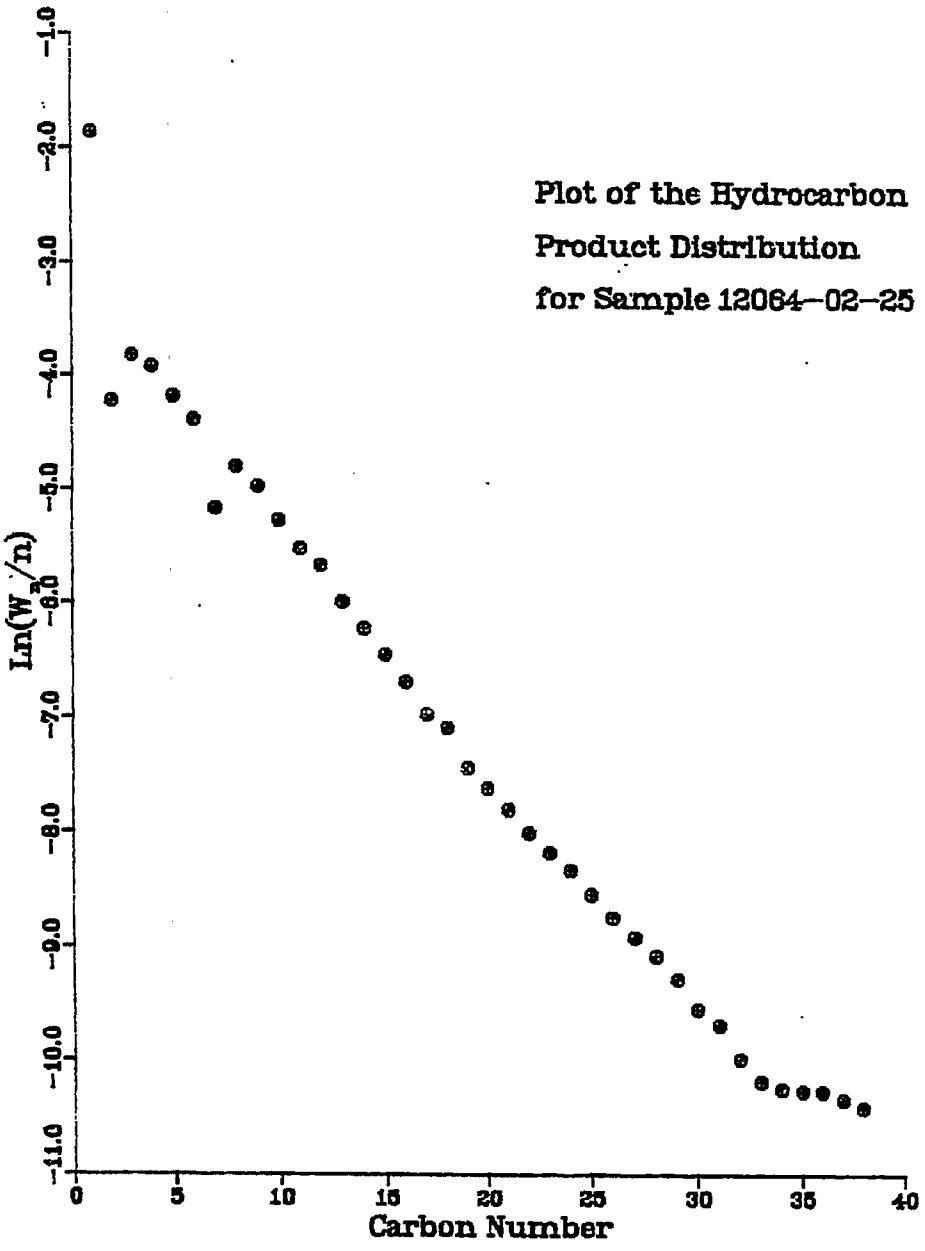
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-25
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A27

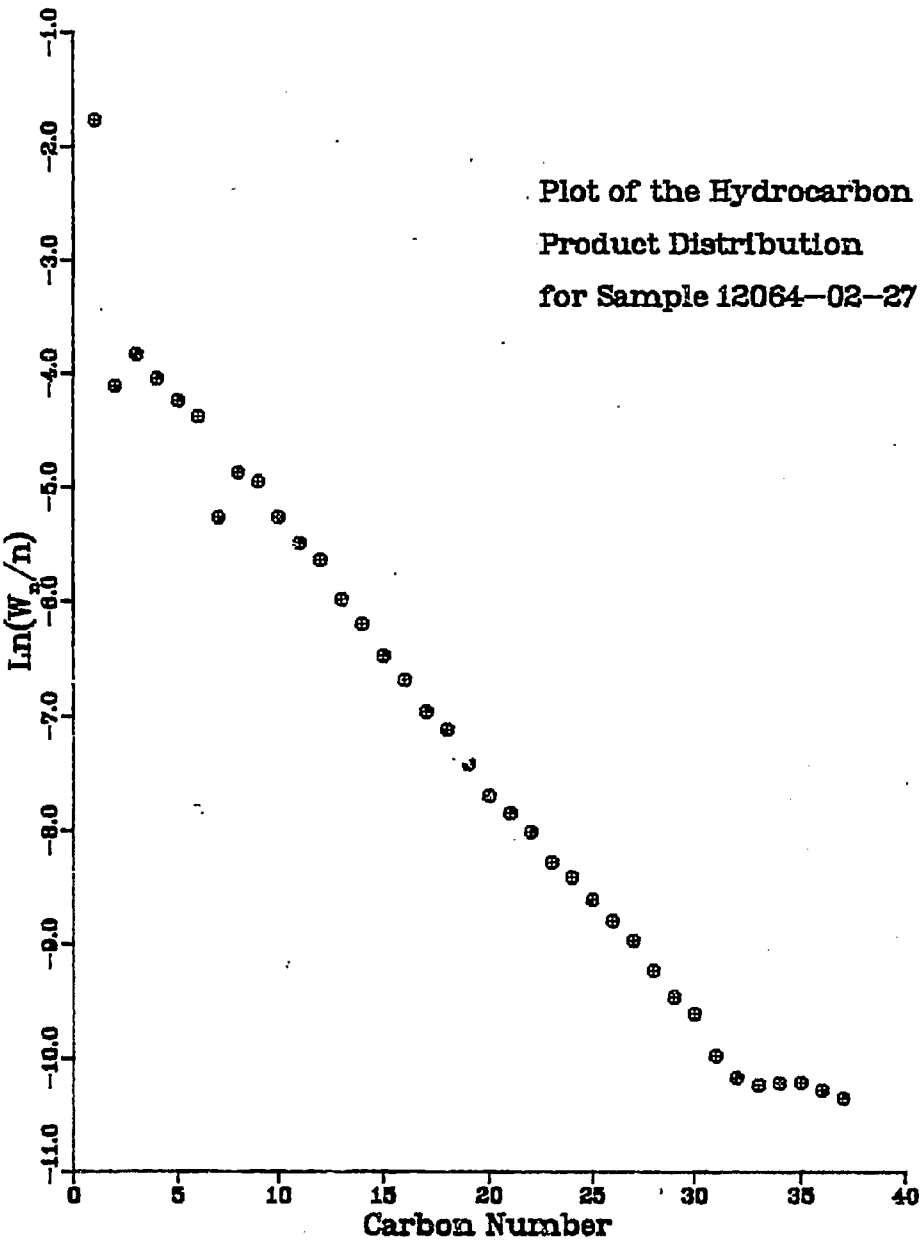
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-27
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A28

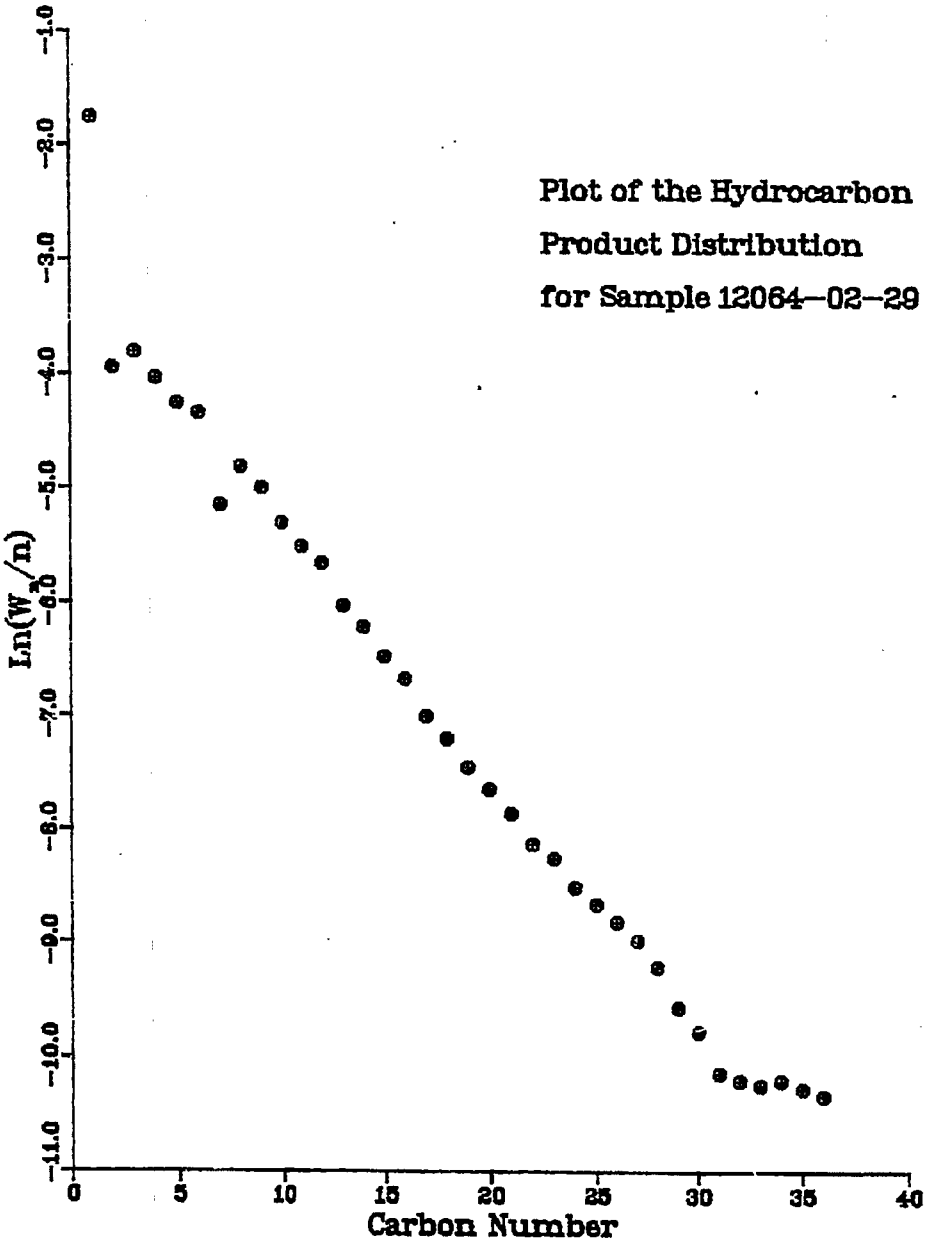
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-29
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A29

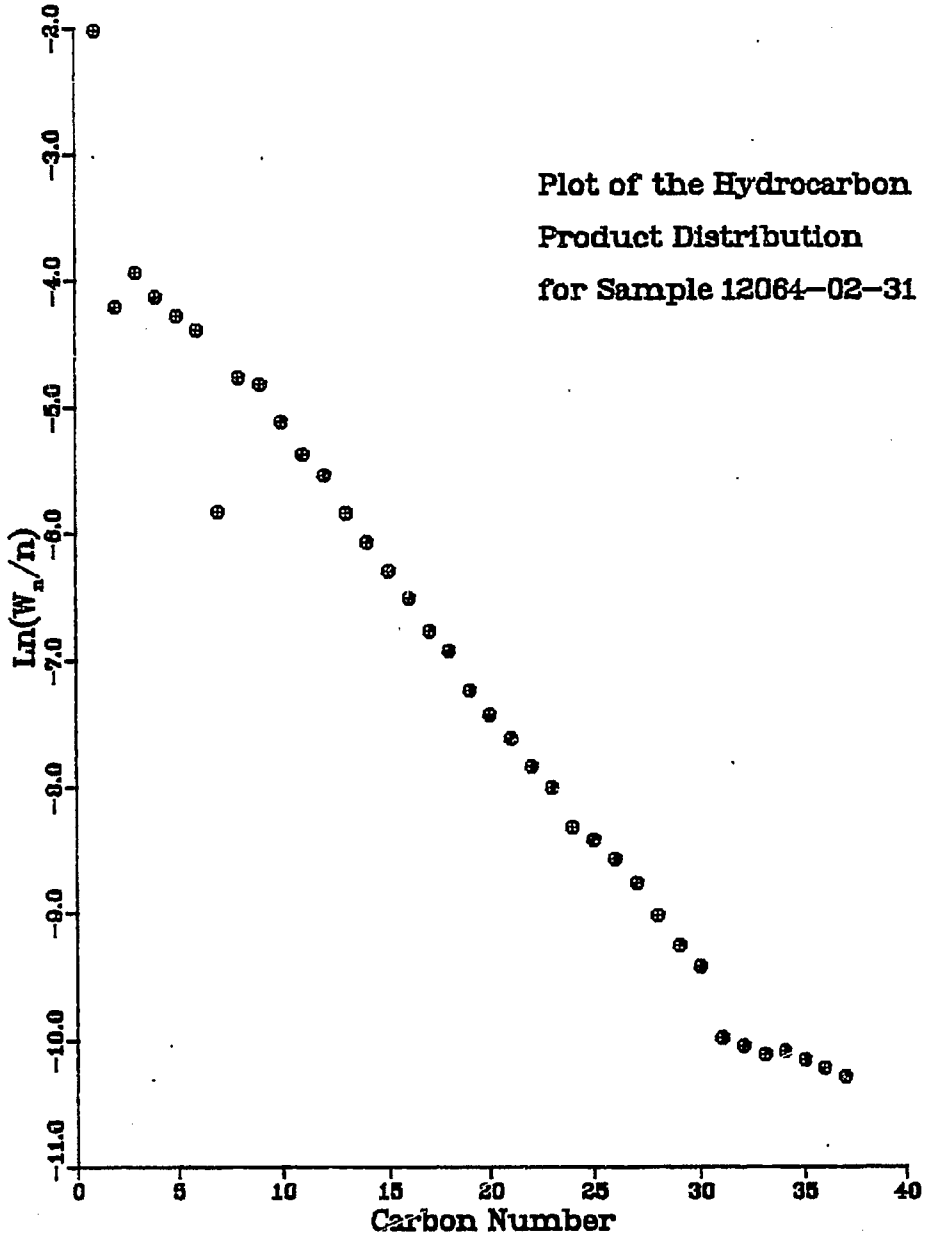
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-31
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A30

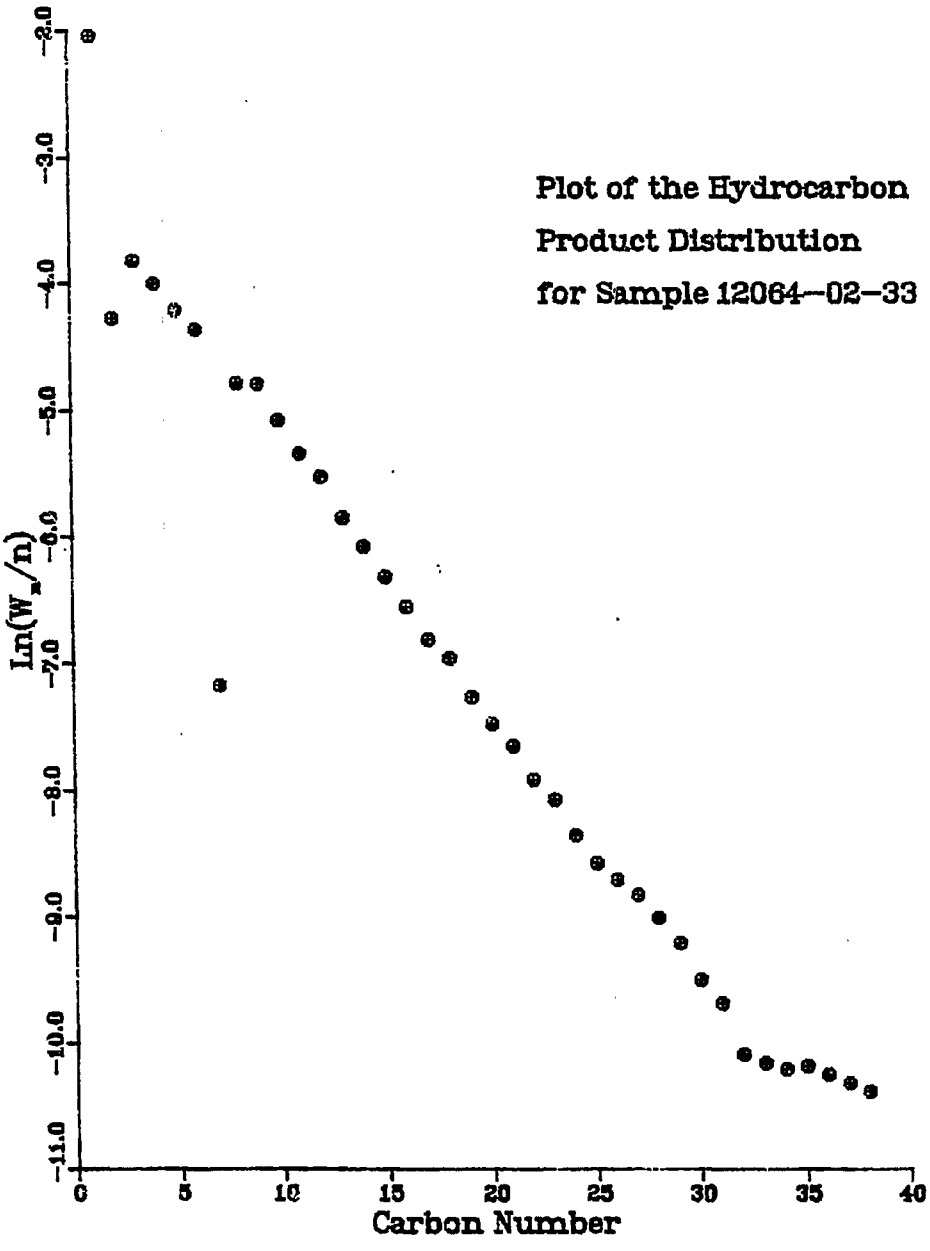
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-33
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A31

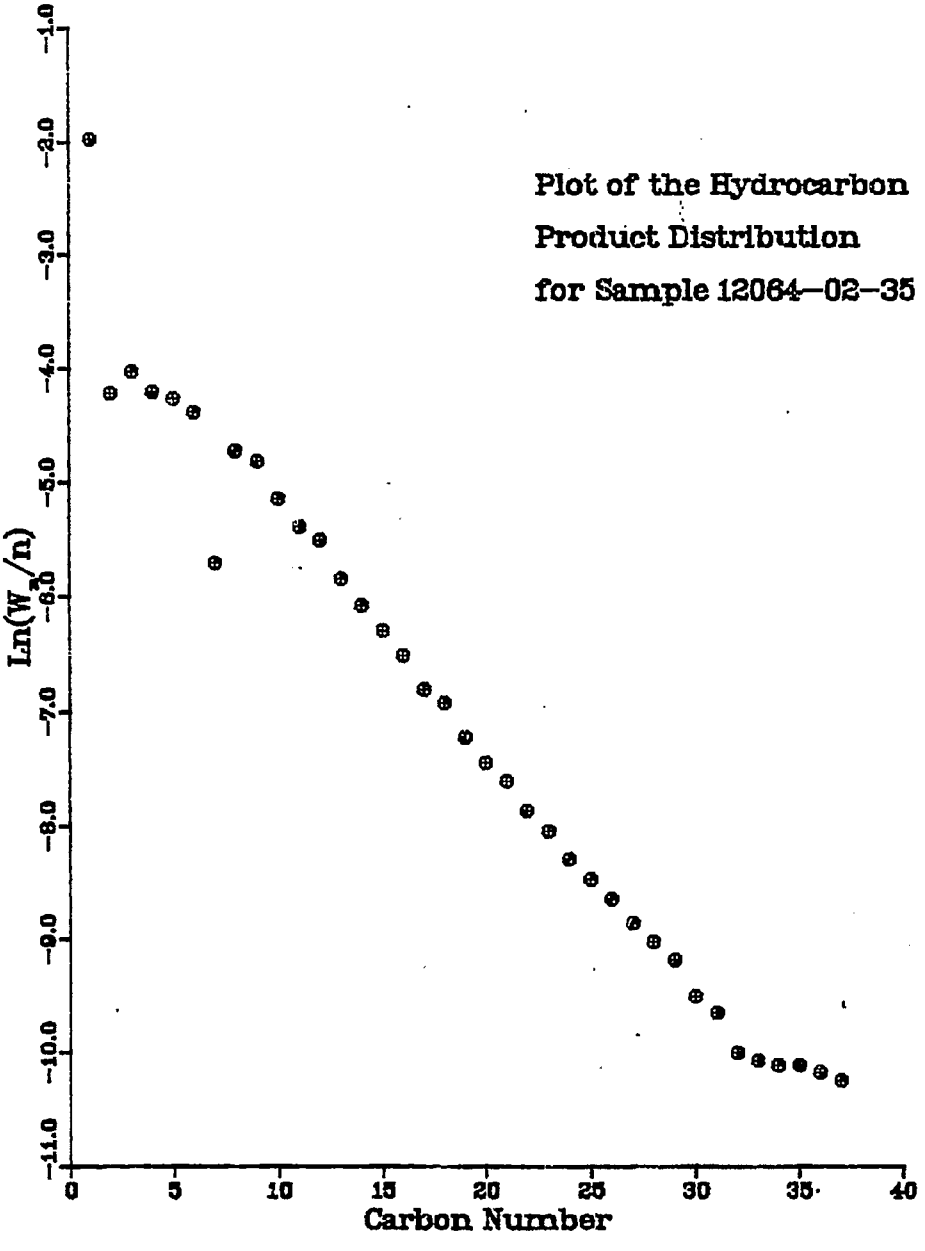
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-35
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A32

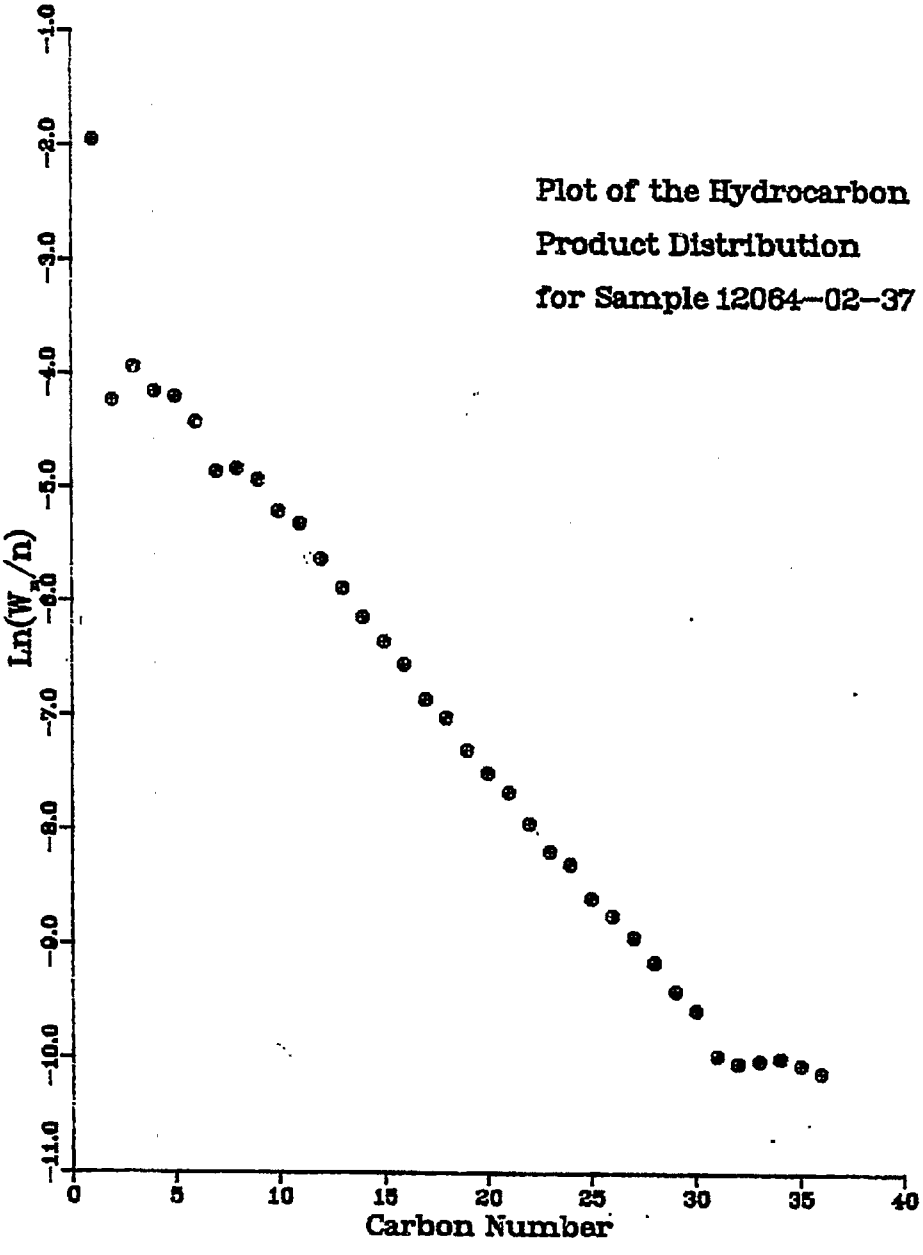
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-37
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. A33

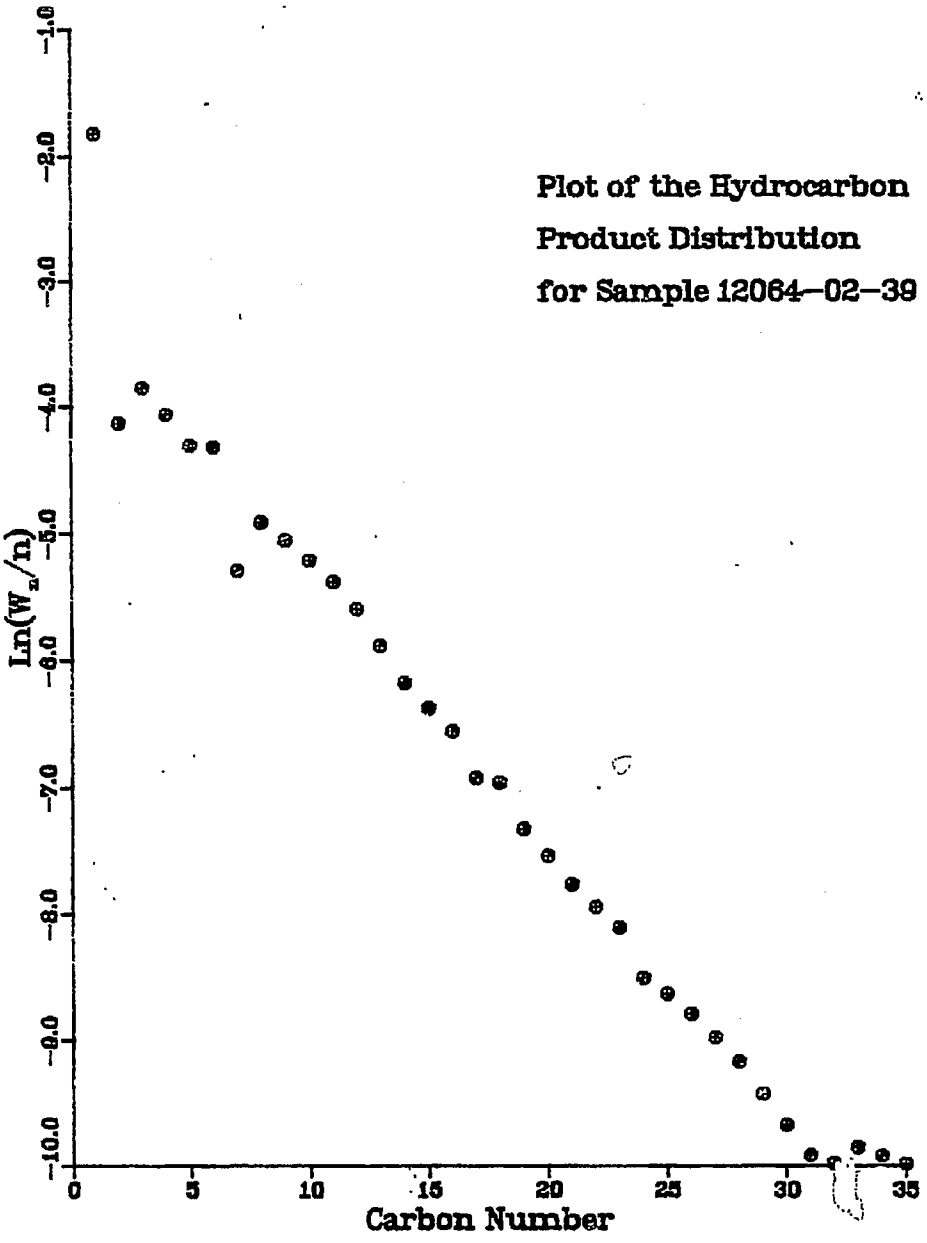
Plot of the Hydrocarbon
Product Distribution
for Sample 12064-02-39
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A34

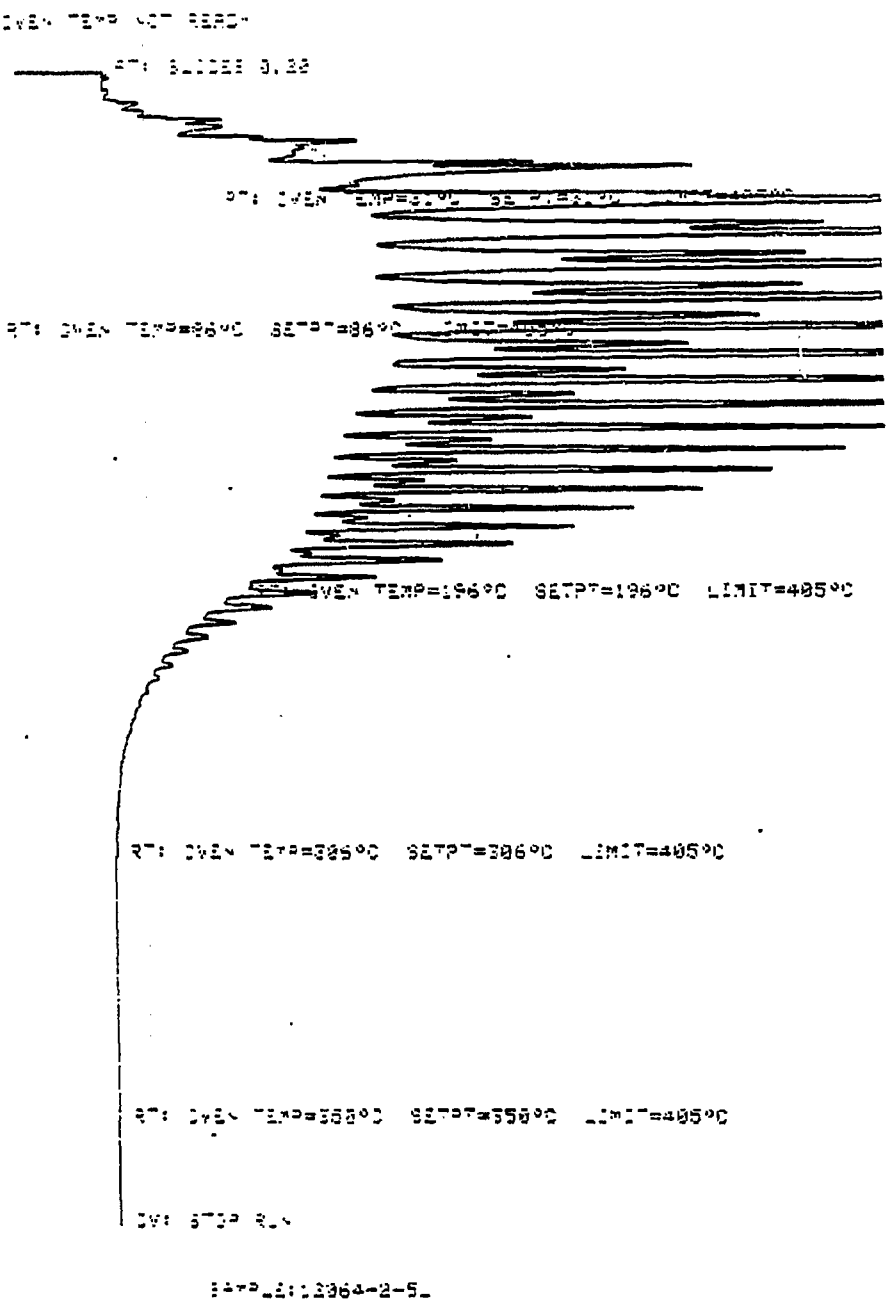
OVEN TEMP SET POINT
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=386°C SETPT=386°C LIMIT=405°C
RT: OVEN TEMP=356°C SETPT=356°C LIMIT=405°C
OVEN TEMP=196°C SETPT=196°C LIMIT=405°C

Fig. A35

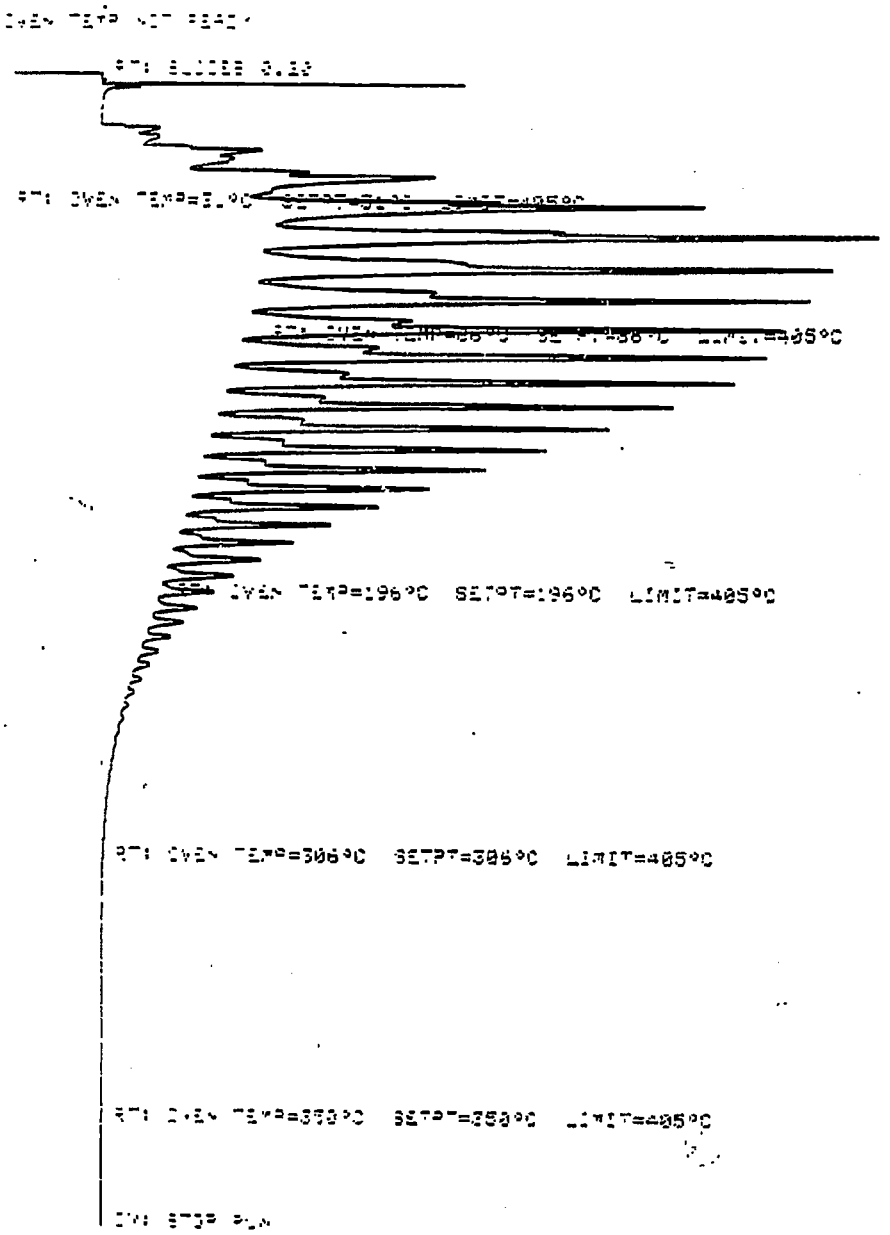

Fig. A36

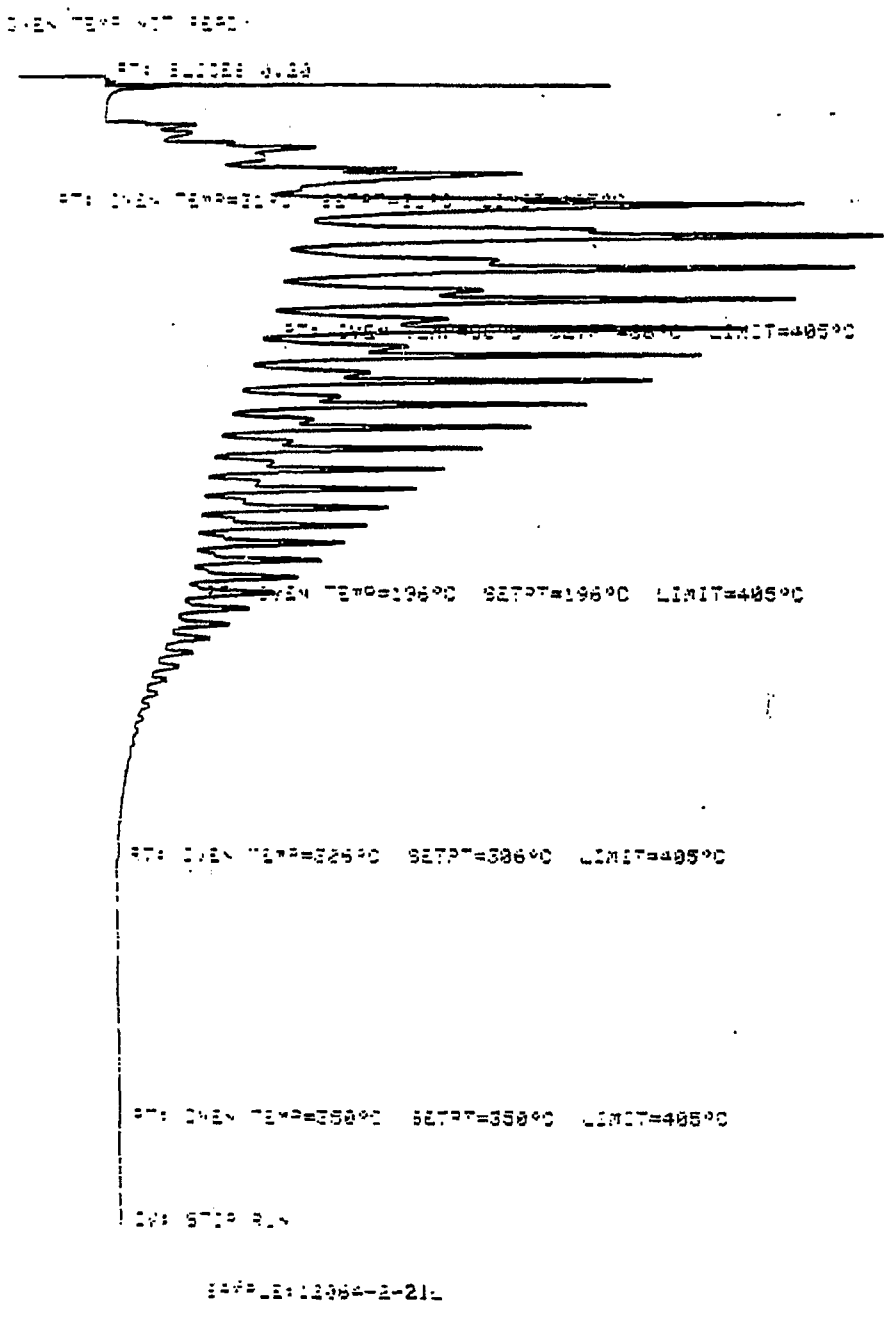

Fig. A37

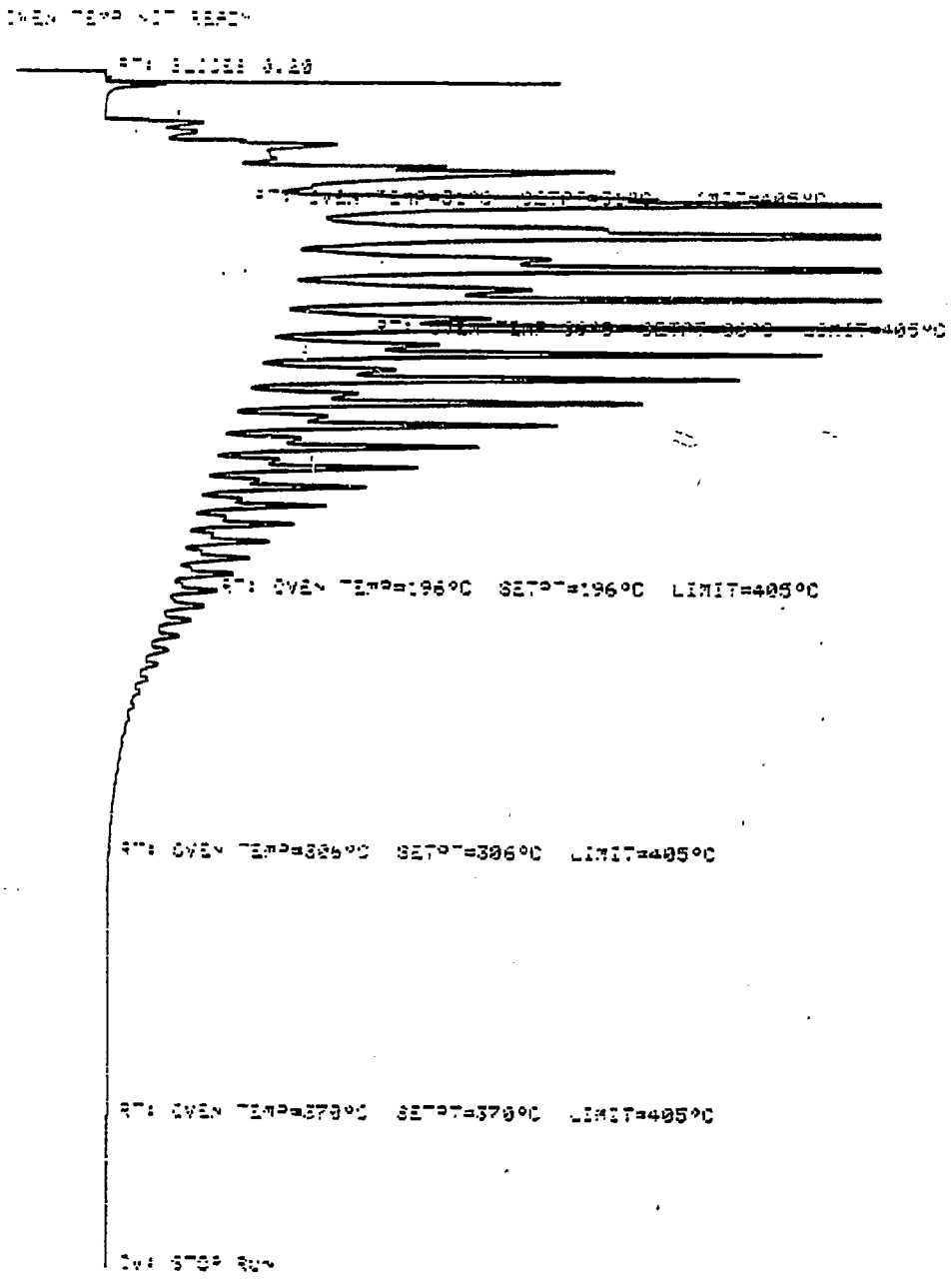
RT: OVEN TEMP=196°C SET PT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SET PT=306°C LIMIT=405°C
RT: OVEN TEMP=370°C SET PT=370°C LIMIT=405°C

Fig. A38

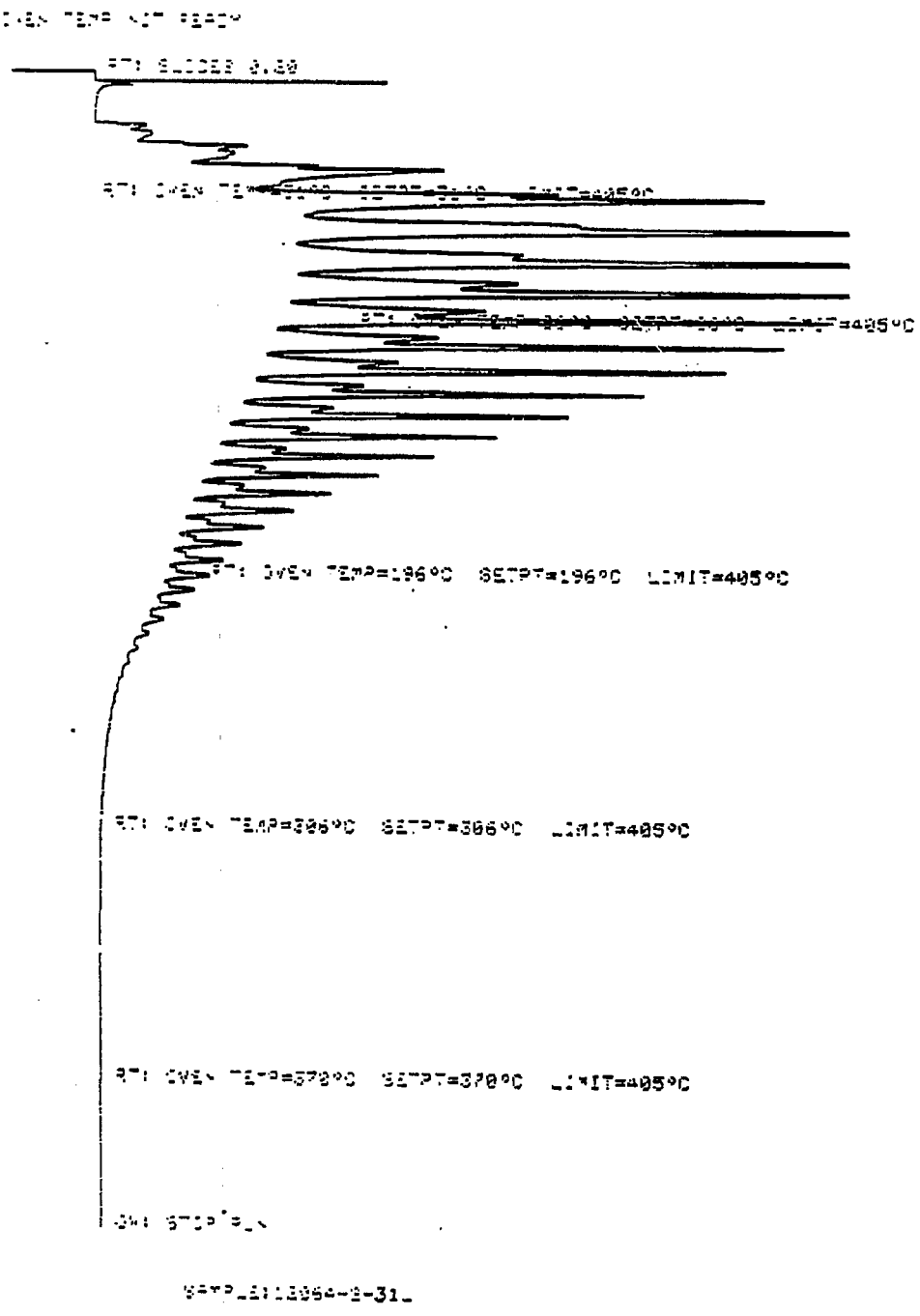

Fig. A39

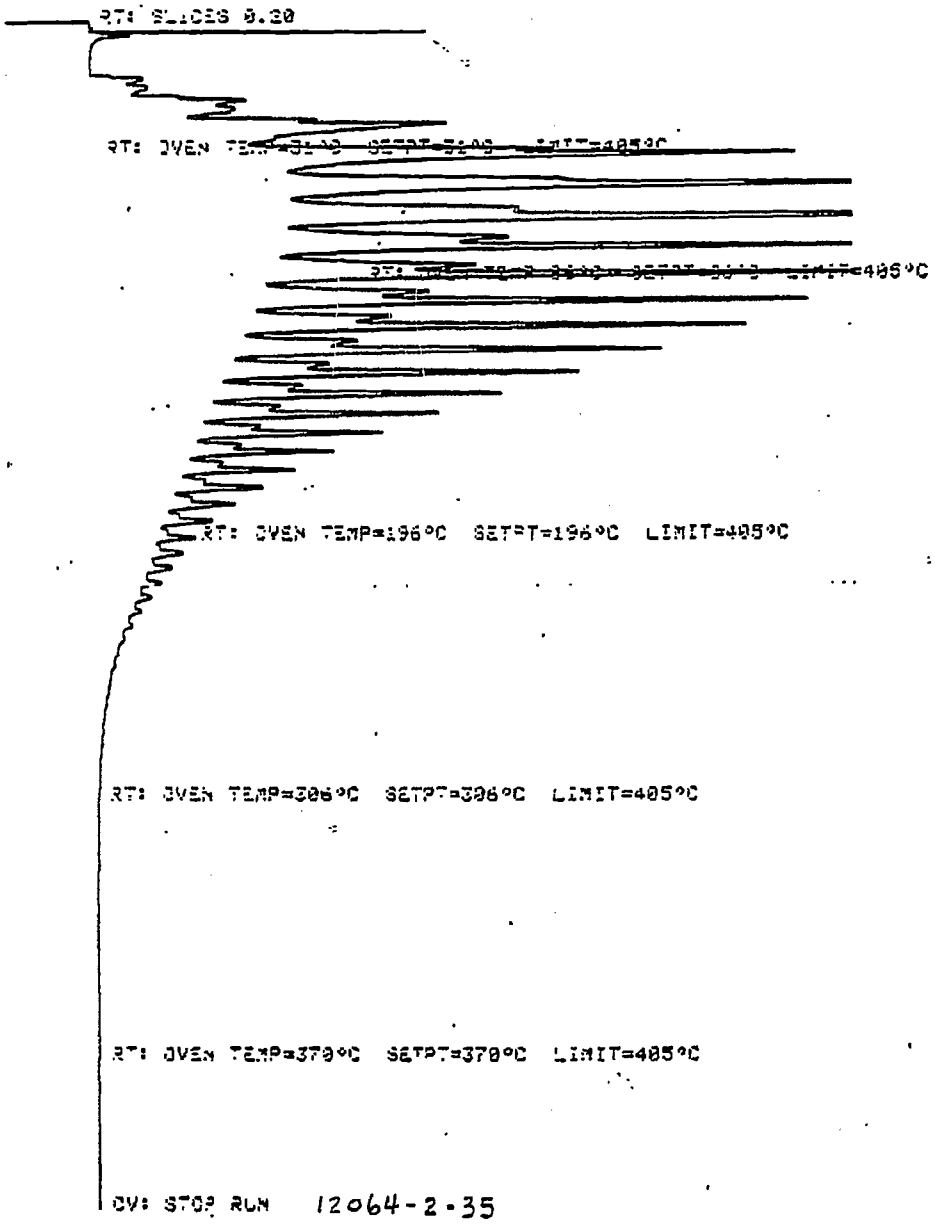
RT: SLICES 0.30
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=370°C SETPT=370°C LIMIT=405°C
OV: STOP RUN 12064-2-35

Fig. A40

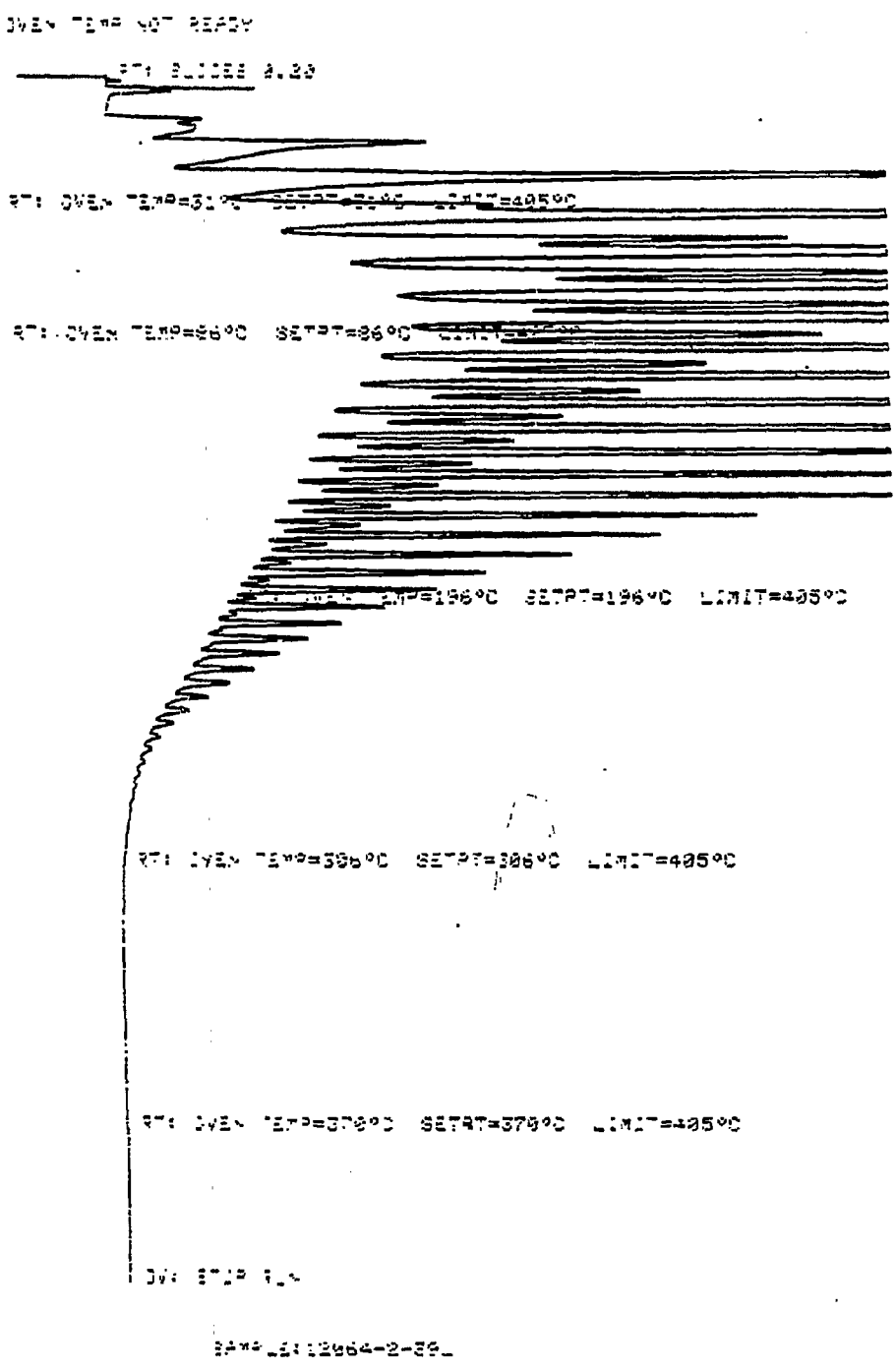
OVEN TEMP NOT READY
PT: 0.1188 0.00
PT: OVEN TEMP=31°C SETPT=[illegible] LIMIT=405°C
PT: OVEN TEMP=86°C SETPT=86°C
PT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
PT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
PT: OVEN TEMP=376°C SETPT=376°C LIMIT=405°C
OVEN STOP TIME
DATA FILE: 12664-2-39

Fig. A41

Table A2

RESULT OF SYNGAS OPERATION

RUN NO. 12064-02
CATALYST CO-U-103+U-101 12006-13 250 CC 114.0G(TO 125.7 +11.7)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	12064-02-01	064-02-03	064-02-05	064-02-07	064-02-09
FEED H2:CO:AR	83:16: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.5	42.5	66.5	90.5	114.5
PRESSURE,PSIG	296	300	296	296	296
TEMP. C	264	261	261	260	260
FEED CC/MIN	755	1260	1260	1260	1260
HOURS FEEDING	18.50	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	423.80	832.15	883.40	895.05	895.25
GM AQUEOUS LAYER	71.27	188.45	187.78	188.16	184.74
GM OIL	0.13	48.82	69.59	81.58	75.86
MATERIAL BALANCE					
GM ATOM CARBON %	97.00	82.92	91.34	94.46	93.00
GM ATOM HYDROGEN %	89.64	78.86	85.56	89.56	88.04
GM ATOM OXYGEN %	92.81	92.67	96.61	96.95	96.08
RATIO CHX/(H2O+CO2)	1.0504	0.6880	0.8326	0.9212	0.9004
RATIO X IN CHX	3.9738	2.3632	2.3439	2.3287	2.3406
USAGE H2/CO PRODT	2.6084	2.3975	2.1664	2.0698	2.1017
FEED H2/CO FRM EFFLNT	4.6596	0.9510	0.9367	0.9481	0.9467
RESIDUAL H2/CO RATIO	120.1363	0.3952	0.3953	0.4060	0.4106
RATIO CO2/(H2O+CO2)	0.0962	0.0481	0.0543	0.0540	0.0520
K SHIFT IN EFFLNT	12.7871	0.0200	0.0227	0.0232	0.0225
SPECIFIC ACTIVITY SA	0.0187	1.4455	1.6474	1.8124	1.7250
CONVERSION					
ON CO %	98.25	27.76	30.57	32.58	31.70
ON H2 %	55.00	69.98	70.70	71.13	70.38
ON CO+H2 %	62.64	48.34	49.98	51.34	50.51
PRDT SELECTIVITY,WT %					
CH4	97.96	12.86	11.71	10.91	11.37
C2 HC'S	1.38	2.49	2.35	2.18	2.68
C3H8	0.39	3.00	2.81	2.67	3.10
C3H6=	0.00	2.45	2.23	2.16	2.63
C4H10	0.10	2.55	2.23	2.21	2.59
C4H8=	0.00	4.00	3.46	3.37	3.89
C5H12	0.00	2.55	2.35	2.18	2.41
C5H10=	0.00	4.35	3.94	3.77	3.86
C6H14	0.00	3.96	3.44	3.25	3.06
C6H12= & CYCLO'S	0.00	4.30	3.94	3.51	3.36
C7+ IN GAS	0.00	15.26	12.06	11.44	10.31
LIQ HC'S	0.16	42.24	49.48	52.35	50.74
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A2 (continued)

SUB-GROUPING					
C1 -C4	99.84	27.35	24.79	23.50	26.26
C5 -420 F	0.07	48.58	45.65	44.93	43.50
420-700 F	0.08	22.02	24.39	25.76	23.90
700-END PT	0.01	2.05	5.17	5.81	6.34
C5+-END PT	0.16	72.65	75.21	76.50	73.74
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.1551	0.1096	0.0976	0.1245
C5	0.0000	0.1652	0.1186	0.0893	0.1165
C6	0.0000	0.6965	0.6004	0.5763	0.5465
C4=	0.0000	0.0624	0.0694	0.0787	0.0922
PARAFFIN/OLEFIN RATIO					
C3	0.0000	1.1704	1.1987	1.1831	1.1213
C4	0.0000	0.6151	0.6226	0.6332	0.6442
C5	0.0000	0.5711	0.5806	0.5623	0.6076
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.0418	0.7878	0.8250	0.8272	0.8254
RATIO CH4/(1-A)**2	1.0669	2.8574	3.8202	3.6530	3.7294
ALPHA FRM CORRELATION		0.8560	0.8560	0.8547	0.8542
ALPHA (EXPTL/CORR)		0.9204	0.9638	0.9678	0.9663
W%CH4 FRM CORRELATION		12.7077	12.7101	12.8863	13.0567
W%CH4 (EXPTL/CORR)		1.0120	0.9210	0.8464	0.8709
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLR OIL	BLUE OIL	CLDY OIL	WAXY OIL
DENSITY		0.760	0.765	0.764	0.763
N, REFRACTIVE INDEX		1.4273	1.4292	1.4292	1.4290
SIMULT'D DISTILATN					
10 WT % @ DEG F		286	287	292	291
16		315	319	325	322
50		447	467	468	466
84		603	656	659	664
90		647	704	709	728
RANGE(16-84 %)		288	337	334	342
WT % @ 420 F		43.00	40.25	39.70	40.40
WT % @ 700 F		95.14	89.55	88.90	87.50

NEW FORMAT JAN 25,85

A1

Table A3

RESULT OF SYNGAS OPERATION

RUN NO. 12064-02
CATALYST CO-U-103+U-101 12006-13 250 CC 114.0G(TO 125.7 +11.7)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	12064-02-11	064-02-15	064-02-17	064-02-19	064-02-21
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	140.0	186.5	210.5	234.5	258.5
PRESSURE,PSIG	295	295	296	295	296
TEMP. C	261	260	261	259	273
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	25.50	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	984.55	892.10	915.25	954.55	844.45
GM AQUEOUS LAYER	194.19	188.45	182.02	173.52	191.08
GM OIL	81.65	77.10	74.52	71.16	81.37
MATERIAL BALANCE					
GM ATOM CARBON %	95.35	92.25	92.68	93.49	96.88
GM ATOM HYDROGEN %	89.62	88.21	88.59	91.39	91.83
GM ATOM OXYGEN %	97.86	96.28	96.25	95.33	96.71
RATIO CHX/(H2O+CO2)	0.9182	0.8718	0.8832	0.9370	1.0051
RATIO X IN CHX	2.3503	2.3396	2.3588	2.3672	2.4199
USAGE H2/CO PRODT	2.0847	2.1390	2.1279	2.0904	1.8859
FEED H2/CO FRM EFFLNT	0.9400	0.9562	0.9559	0.9776	0.9478
RESIDUAL H2/CO RATIO	0.4173	0.4149	0.4332	0.4821	0.3451
RATIO CO2/(H2O+CO2)	0.0535	0.0494	0.0519	0.0486	0.1111
K SHIFT IN EFFLNT	0.0236	0.0215	0.0237	0.0246	0.0431
SPECIFIC ACTIVITY SA	1.5812	1.6766	1.4531	1.3850	1.4825
CONVERSION					
ON CO %	31.35	31.40	30.84	30.81	39.12
ON H2 %	69.53	70.24	68.66	65.88	77.83
ON CO+H2 %	49.85	50.38	49.32	48.14	57.96
PRDT SELECTIVITY,WT %					
CH4	12.01	11.39	12.35	12.83	15.19
C2 HC'S	2.64	2.44	2.42	2.78	2.88
C3H8	2.96	2.87	2.94	3.10	3.69
C3H6=	2.46	2.32	1.96	2.36	2.29
C4H10	2.24	2.25	2.31	2.44	2.86
C4H8=	3.54	3.35	3.22	3.76	3.97
C5H12	2.46	2.33	2.28	2.73	3.20
C5H10=	3.83	3.81	3.50	3.86	3.73
C6H14	3.12	3.21	3.21	3.10	3.73
C6H12= & CYCLO'S	3.26	3.32	3.43	3.15	3.43
C7+ IN GAS	10.80	10.29	11.00	11.53	10.82
LIQ HC'S	50.68	52.43	51.39	48.36	44.20
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A3 (continued)

SUB-GROUPING					
C1 -C4	25.85	24.61	25.20	27.28	30.88
C5 -420 F	44.10	44.59	44.10	43.71	44.37
420-700 F	23.67	24.95	24.76	23.08	18.90
700-END PT	6.39	5.86	5.94	5.93	5.86
C5+-END PT	74.15	75.39	74.80	72.72	69.12
ISO/NORMAL MOLE RATIO					
C4	0.0764	0.0683	0.0634	0.0596	0.0756
C5	0.0941	0.0927	0.0633	0.1217	0.1572
C6	0.4263	0.5535	0.4223	0.4097	0.6288
C4=	0.0757	0.0805	0.0807	0.0781	0.0976
PARAFFIN/OLEFIN RATIO					
C3	1.1448	1.1820	1.4327	1.2537	1.5422
C4	0.6101	0.6478	0.6946	0.6261	0.6955
C5	0.6252	0.5950	0.6328	0.6868	0.8345
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8262	0.8244	0.8269	0.8246	0.8204
RATIO CH4/(1-A)**2	3.9745	3.6942	4.1241	4.1711	4.7118
ALPHA FRM CORRELATION	0.8533	0.8537	0.8515	0.8464	0.8619
ALPHA (EXPTL/CORR)	0.9682	0.9658	0.9712	0.9743	0.9519
W%CH4 FRM CORRELATION	13.5266	13.2133	14.0937	15.2553	13.3170
W%CH4 (EXPTL/CORR)	0.8878	0.8618	0.8764	0.8410	1.1407
LIQ HC COLLECTION					
PHYS. APPEARANCE	WAXY OIL	GRN CLDY	WAXY &SLD	WAXY &SLD	WAXY &SLD
DENSITY	0.762	0.761	0.762	0.772	0.756
N, REFRACTIVE INDEX	1.4287	1.4277	1.4280	1.4284	1.4282
SIMULT'D DISTILATN					
10 WT % @ DEG F	290	289	292	293	274
16	319	316	322	326	300
50	465	459	467	470	450
84	666	656	661	665	673
90	729	712	716	723	734
RANGE(16-84 %)	347	340	339	339	373
WT % @ 420 F	40.70	41.25	40.25	40.00	44.00
WT % @ 700 F	87.40	88.83	88.44	87.73	86.75

NEW FORMAT JAN 25,85

Table A4

RESULT OF SYNGAS OPERATION

RUN NO. 12064-02
CATALYST CO-U-103+U-101 12006-13 250 CC 114.0G(TO 125.7 +11.7)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	12064-02-23	064-02-25	064-02-27	064-02-29	064-02-31
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	42:57: 0
HRS ON STREAM	283.1	307.5	330.2	354.2	378.2
PRESSURE,PSIG	295	299	296	298	298
TEMP. C	273	273	273	273	273
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	24.58	24.42	23.00	24.00	24.00
EFFLNT GAS LITER	875.45	878.45	836.50	881.85	1027.80
GM AQUEOUS LAYER	194.23	190.41	176.99	183.96	152.97
GM OIL	76.39	71.94	64.23	65.11	57.20
MATERIAL BALANCE					
GM ATOM CARBON %	96.52	96.37	95.65	95.43	94.46
GM ATOM HYDROGEN %	91.96	90.89	89.53	90.60	89.26
GM ATOM OXYGEN %	96.37	96.62	96.99	96.53	96.77
RATIO CHX/(H2O+CO2)	1.0044	0.9923	0.9589	0.9661	0.9039
RATIO X IN CHX	2.4270	2.4292	2.4585	2.4608	2.3726
USAGE H2/CO PRODT	1.9030	1.9211	1.9529	1.9556	1.9871
FEED H2/CO FRM EFFLNT	0.9528	0.9431	0.9361	0.9494	0.7087
RESIDUAL H2/CO RATIO	0.3559	0.3562	0.3566	0.3750	0.2753
RATIO CO2/(H2O+CO2)	0.1059	0.1023	0.1037	0.1013	0.0924
K SHIFT IN EFFLNT	0.0422	0.0406	0.0412	0.0423	0.0280
SPECIFIC ACTIVITY SA	1.3943	1.3224	1.2768	1.1762	1.2527
CONVERSION					
ON CO %	38.58	37.50	36.30	36.34	25.32
ON H2 %	77.06	76.39	75.74	74.86	70.99
ON CO+H2 %	57.35	56.38	55.37	55.10	44.26
PRDT SELECTIVITY,WT %					
CH4	15.43	15.57	17.09	17.22	13.31
C2 HC'S	3.66	2.93	3.29	3.89	2.97
C3H8	3.93	3.99	3.97	4.16	3.08
C3H6=	2.42	2.59	2.55	2.49	2.78
C4H10	3.34	3.31	3.12	3.16	2.18
C4H8=	4.39	4.61	3.89	3.90	4.25
C5H12	3.63	3.57	3.46	3.33	2.48
C5H10=	3.91	4.08	3.78	3.75	4.45
C6H14	3.86	4.03	3.98	4.25	3.47
C6H12= & CYCLO'S	3.36	3.43	3.56	3.54	3.99
C7+ IN GAS	11.06	11.92	11.76	11.98	14.14
LIQ HC'S	41.02	39.98	39.55	38.34	42.90
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A4 (continued)

SUB-GROUPING					
C1 -C4	33.16	33.00	33.91	34.81	28.57
C5 -420 F	44.14	45.41	44.93	44.87	46.55
420-700 F	17.52	17.41	17.43	16.87	20.49
700-END PT	5.18	4.18	3.73	3.45	4.39
C5+-END PT	66.84	67.00	66.09	65.19	71.43
ISO/NORMAL MOLE RATIO					
C4	0.1097	0.1254	0.0655	0.0661	0.0753
C5	0.1773	0.1903	0.1286	0.1080	0.1175
C6	0.6385	0.6475	0.5003	0.5207	0.6332
C4=	0.1178	0.1214	0.1000	0.1106	0.0978
PARAFFIN/OLEFIN RATIO					
C3	1.5533	1.4684	1.4824	1.5950	1.0567
C4	0.7346	0.6929	0.7743	0.7812	0.4956
C5	0.9006	0.8497	0.8896	0.8632	0.5417
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8098	0.8026	0.8004	0.7991	0.8092
RATIO CH4/(1-A)**2	4.2655	3.9946	4.2897	4.2668	3.6567
ALPHA FRM CORRELATION	0.8604	0.8604	0.8603	0.8579	0.8729
ALPHA (EXPTL/CORR)	0.9412	0.9328	0.9304	0.9315	0.9270
W%CH4 FRM CORRELATION	13.7827	13.7974	13.8115	14.5720	9.9005
W%CH4 (EXPTL/CORR)	1.1194	1.1282	1.2370	1.1817	1.3443
LIQ HC COLLECTION					
PHYS. APPEARANCE	WAXY &SLD	WAXY &SLD	WAXY &SLD	WAXY &SLD	WAXY &SLD
DENSITY	0.767	0.774	0.757	0.759	0.764
N, REFRACTIVE INDEX	1.4274	1.4261	1.4253	1.4250	1.4283
SIMULT'D DISTILATN					
10 WT % @ DEG F	275	273	276	273	294
16	302	300	302	300	323
50	446	439	436	434	453
84	663	640	627	623	643
90	732	706	692	687	703
RANGE(16-84 %)	361	340	325	323	320
WT % @ 420 F	44.67	46.00	46.50	47.00	42.00
WT % @ 700 F	87.38	89.54	90.57	91.00	89.77

NEW FORMAT JAN 25,85

Table A5

RESULT OF SYNGAS OPERATION

RUN NO. 12064-02
CATALYST CO-U-103+U-101 12006-13 250 CC 114.0G(TO 125.7 +11.7)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	12064-02-33	064-02-35	064-02-37	064-02-39
FEED H2:CO:AR	42:57: 0	42:57: 0	42:57: 0	42:57: 0
HRS ON STREAM	402.2	426.2	522.2	546.2
PRESSURE,PSIG	297	298	300	299
TEMP. C	272	273	272	273
FEED CC/MIN	1260	1260	1260	1260
HOURS FEEDING	24.00	24.00	96.00	24.00
EFFLNT GAS LITER	1043.15	1037.30	4200.50	1066.10
GM AQUEOUS LAYER	150.50	147.03	580.79	143.78
GM OIL	56.27	55.20	211.53	50.29
MATERIAL BALANCE				
GM ATOM CARBON %	95.59	94.31	95.13	95.10
GM ATOM HYDROGEN %	90.76	88.09	90.31	90.02
GM ATOM OXYGEN %	96.89	96.36	95.95	96.66
RATIO CHX/(H2O+CO2)	0.9450	0.9114	0.9639	0.9311
RATIO X IN CHX	2.3689	2.3817	2.3845	2.4274
USAGE H2/CO PRODT	1.9624	1.9888	1.9679	2.0053
FEED H2/CO FRM EFFLNT	0.7121	0.7005	0.7120	0.7099
RESIDUAL H2/CO RATIO	0.2832	0.2801	0.2915	0.2952
RATIO CO2/(H2O+CO2)	0.0894	0.0913	0.0850	0.0875
K SHIFT IN EFFLNT	0.0278	0.0281	0.0271	0.0283
SPECIFIC ACTIVITY SA	1.2828	1.1844	1.1884	1.0716
CONVERSION				
ON CO %	25.54	24.60	25.09	24.25
ON H2 %	70.39	69.85	69.33	68.50
ON CO+H2 %	44.19	43.24	43.49	42.62
PRDT SELECTIVITY,WT %				
CH4	12.99	13.90	14.14	16.19
C2 HC'S	2.79	2.95	2.88	3.20
C3H8	3.45	2.99	3.41	3.43
C3H6=	3.16	2.36	2.44	2.98
C4H10	2.60	2.14	2.40	2.43
C4H8=	4.73	3.82	3.86	4.45
C5H12	2.71	2.45	2.73	2.59
C5H10=	4.70	4.60	4.72	4.10
C6H14	3.53	3.33	2.77	3.69
C6H12= & CYCLO'S	4.13	4.16	4.36	4.26
C7+ IN GAS	14.14	14.72	17.08	14.01
LIQ HC'S	41.07	42.06	39.21	38.67
TOTAL	100.00	100.00	100.00	100.00

Table A5 (continued)

SUB-GROUPING				
C1 -C4	29.72	28.17	29.13	32.68
C5 -420 F	46.19	47.15	48.03	44.89
420-700 F	19.83	20.29	19.03	18.82
700-END PT	4.26	4.40	3.81	3.61
C5+-END PT	70.28	71.83	70.87	67.32
ISO/NORMAL MOLE RATIO				
C4	0.1375	0.0667	0.0489	0.0585
C5	0.1454	0.1026	0.0896	0.0807
C6	0.6566	0.5674	0.2000	0.4115
C4=	0.1144	0.0930	0.0989	0.0794
PARAFFIN/OLEFIN RATIO				
C3	1.0433	1.2075	1.3300	1.0990
C4	0.5302	0.5416	0.6007	0.5277
C5	0.5618	0.5178	0.5614	0.6152
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.8034	0.8084	0.8048	0.8025
RATIO CH4/(1-A)**2	3.3601	3.7864	3.7122	4.1501
ALPHA FRM CORRELATION	0.8716	0.8721	0.8702	0.8695
ALPHA (EXPTL/CORR)	0.9217	0.9270	0.9249	0.9229
W%CH4 FRM CORRELATION	10.1129	10.1641	10.5498	10.9544
W%CH4 (EXPTL/CORR)	1.2834	1.3676	1.3401	1.4775
LIQ HC COLLECTION				
PHYS. APPEARANCE	WAXY &SLD	WAXY &SLD	WAXY &SLD	WAXY &SLD
DENSITY	0.770	0.765	0.7563	0.7731
N, REFRACTIVE INDEX	1.4286	1.4283	1.4280	1.4278
SIMULT'D DISTILATN				
10 WT % @ DEG F	298	294	298	301
16	327	322	314	321
50	454	453	453	453
84	643	644	638	634
90	705	704	696	692
RANGE(16-84 %)	316	322	324	313
WT % @ 420 F	41.33	42.00	41.75	42.00
WT % @ 700 F	89.62	89.67	90.29	90.67

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IV. Run 3 (11885-06) with Catalyst 3 ($Co/X_4/UCC-103+UCC-101$)

The purpose of this run was to test the effect of the additive X_4 on the activity, selectivity and stability of the intimately contacted Co/UCC-103 type of catalyst. It is to be compared with Catalyst 2 of this report and with Third Annual Report Catalyst 6 (Run 11677-11, $Co/Th/X_4/UCC-103+UCC-101$).

Preparation was the same as for Catalyst 2 except for the addition of X_4. The theoretical content of cobalt and X_4 was 6.3 and 0.9 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. A42-45. Simulated distillations of the C_5^+ product are plotted in Figs. A46-52. Carbon number product distributions are plotted in Figs. A53-70. Chromatograms from simulated distillations are reproduced in Figs. A71-77. Detailed material balances appear in Tables A6-9.

The initial activity, 45.6 percent conversion of syngas, was substantially lower than the 50 percent conversion of reference Catalyst 2, an effect which has been found with most of the promotive additives which have been tested.

The stability at 260C was poor, with an estimated loss of conversion, based on linear least squares analysis, of one percentage point every 22 hours--far inferior to that of Catalyst 2,

with which the loss of conversion was one percentage point every 90 hours.

The nearly ideal stability of Third Annual Report Catalyst 6 (Co/Th/X_4/UCC-103+UCC-101, Run 11677-11), in contrast to the relatively poor stability of Catalysts 2 and 3 of this Report (Co/UCC-103+UCC101, Run 12064-02, and Co/X_4/UCC-103+UCC-102, Run 11885-06, respectively) and of Third Annual Report Catalyst 2 (Co/Th/UCC-103+UCC-101), strongly suggests that the stability of this type of catalyst depends on a cooperative interaction among the constituents cobalt, thorium and X_4.

When the reaction temperature was raised from 260C to 270C the stability was depressed still further to an estimated loss of conversion of one percentage point every 18 hours. Then when the H_2:CO feed ratio was reduced from 1:1 to 0.39:1, the conversion dropped to about 25 percent but the stability jumped to an estimated loss of conversion of one percentage point every 809 hours. Once again, as with Catalyst 2 and possibly characteristic of this type of catalyst, stability has been improved in a hydrogen-poor environment.

The product quality was considerably lighter than that of reference Catalyst 2, 65 percent C_5^+ as against 73 percent, 15-16 percent methane as against 11-13 percent, and calculated Schulz-Flory alpha value of 0.796 as against 0.825.

The high proportion of methane in the product is probably due to the elevated H_2:CO ratio in the reactor resulting from the low catalytic activity. This is borne out by the similar experiment-

al vs. correlation values of weight percent methane produced at 260C by this catalyst and by the unpromoted reference Catalyst 2: 0.82 and 0.86 respectively. Based on this parameter, the X_4 promoted catalyst produces approximately the same proportion of methane as the unpromoted catalyst, or a little less, when run at an equal residual H_2:CO ratio in the reactor.

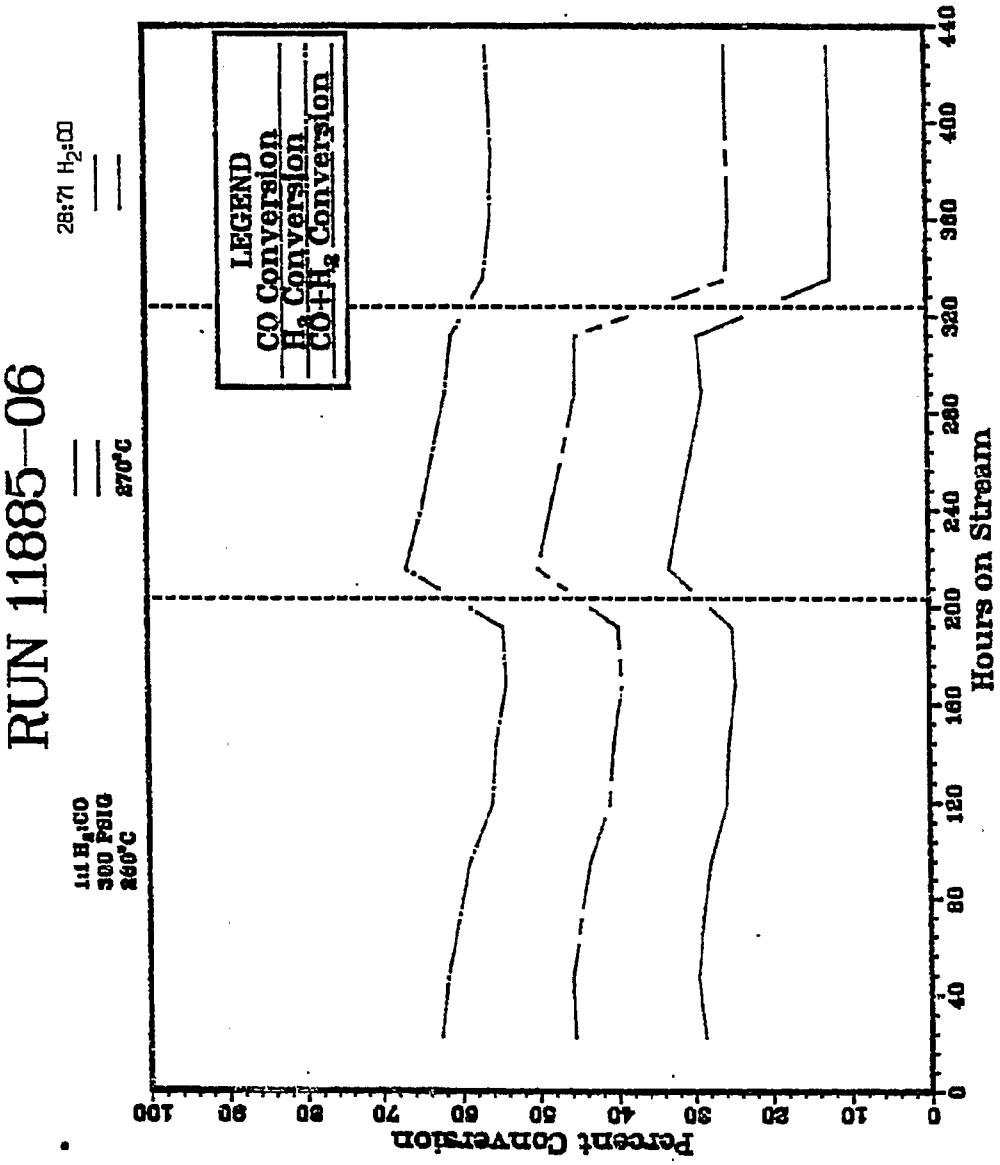

RUN 11885–06
111 H2:CO
300 PSIG
260°C
270°C
28:71 H2:CO
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440

Fig. A42

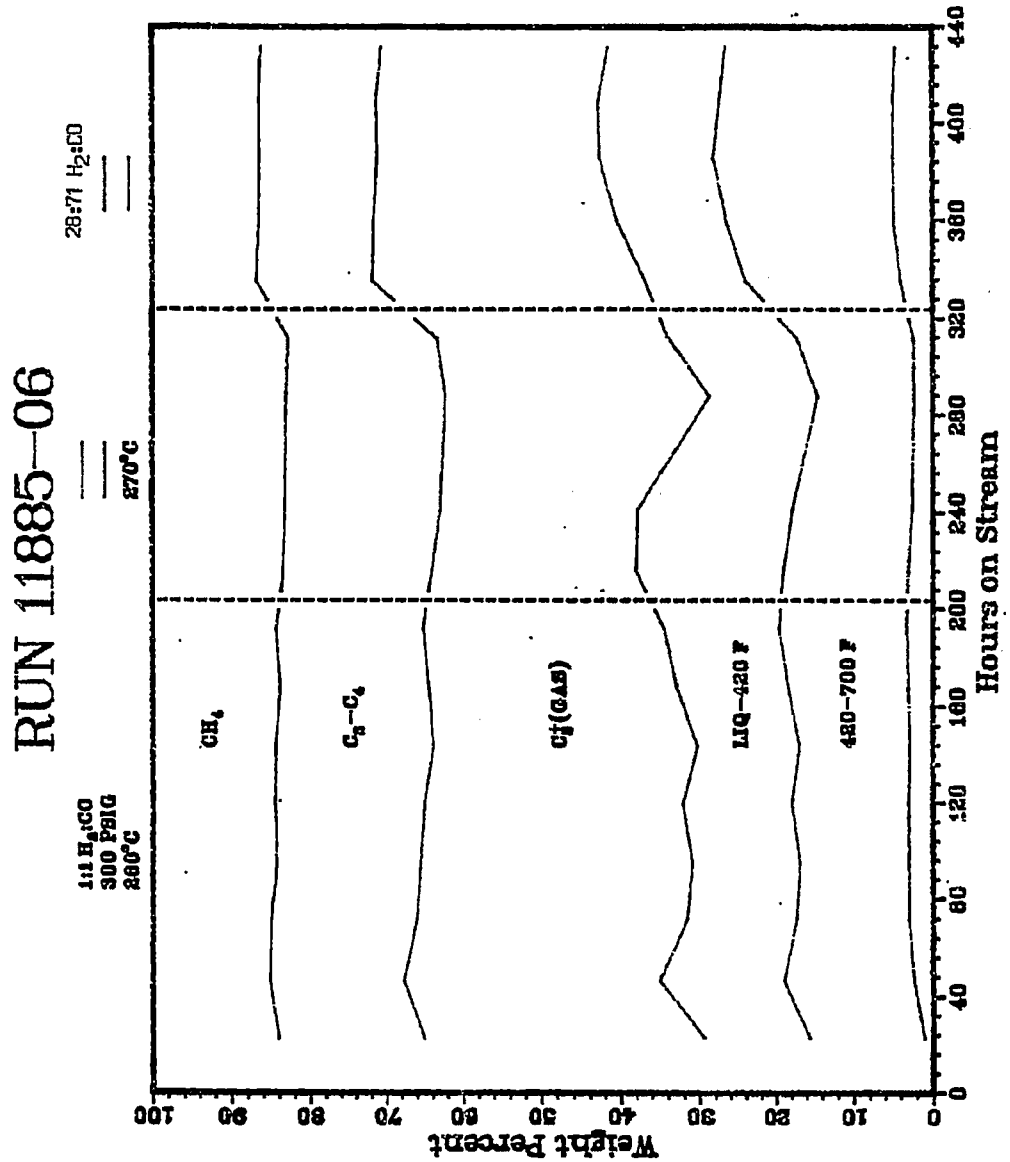

RUN 11885-06
1:1 H2:CO
300 PSIG
280°C
270°C
28:71 H2:CO
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440

Fig. A43

RUN 11885-06

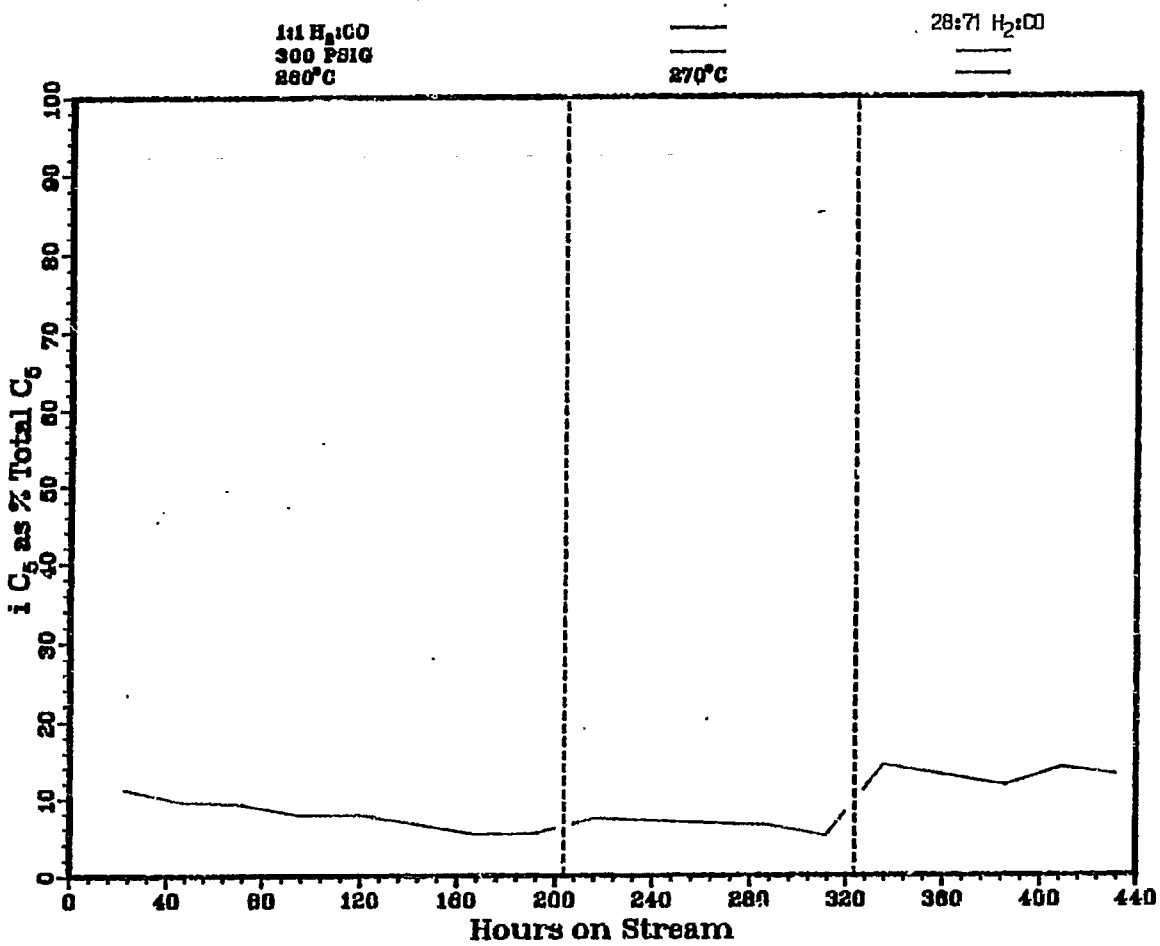


Fig. A44

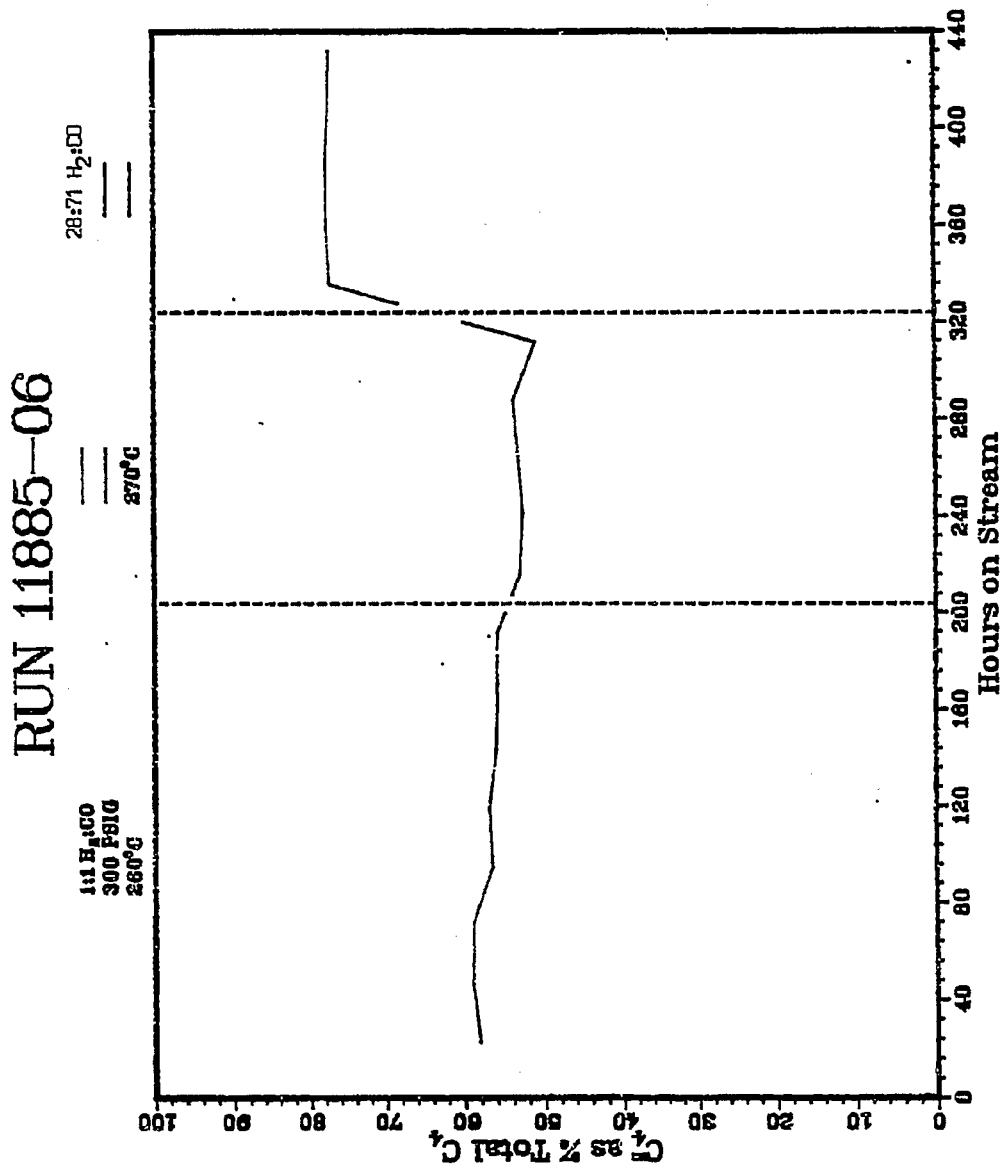

RUN 11885-06
28:71 H2:CO
1:1 H2:CO
300 PSIG
260°C
270°C
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440

Fig. A45

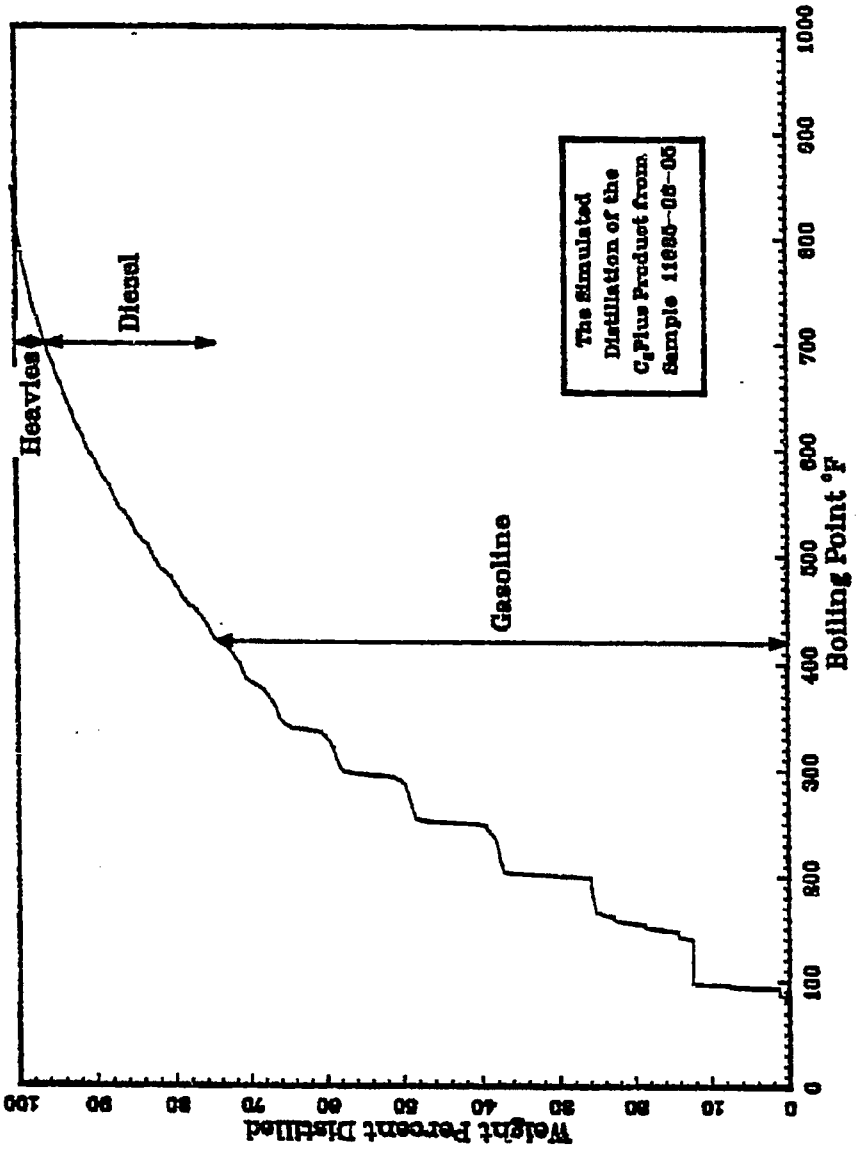

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11690-08-06

Fig. A46

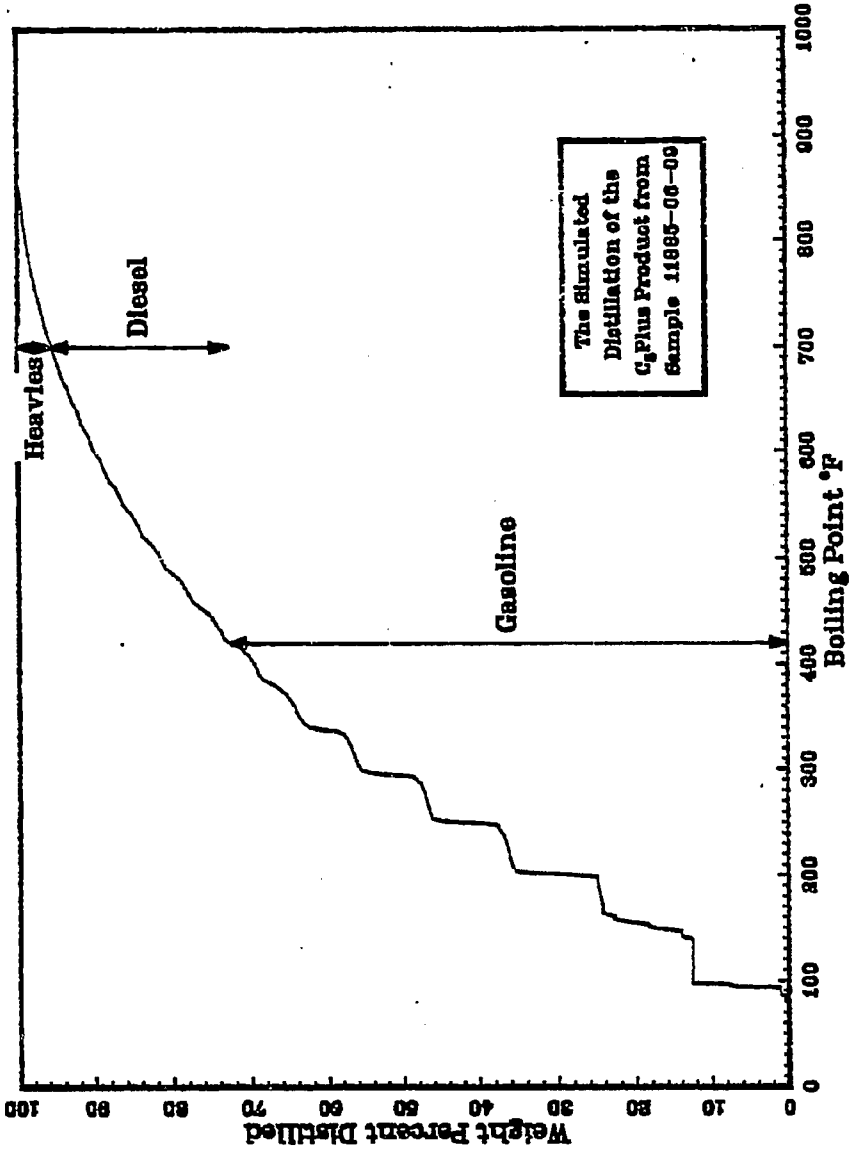

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11885-06-09

Fig. A47

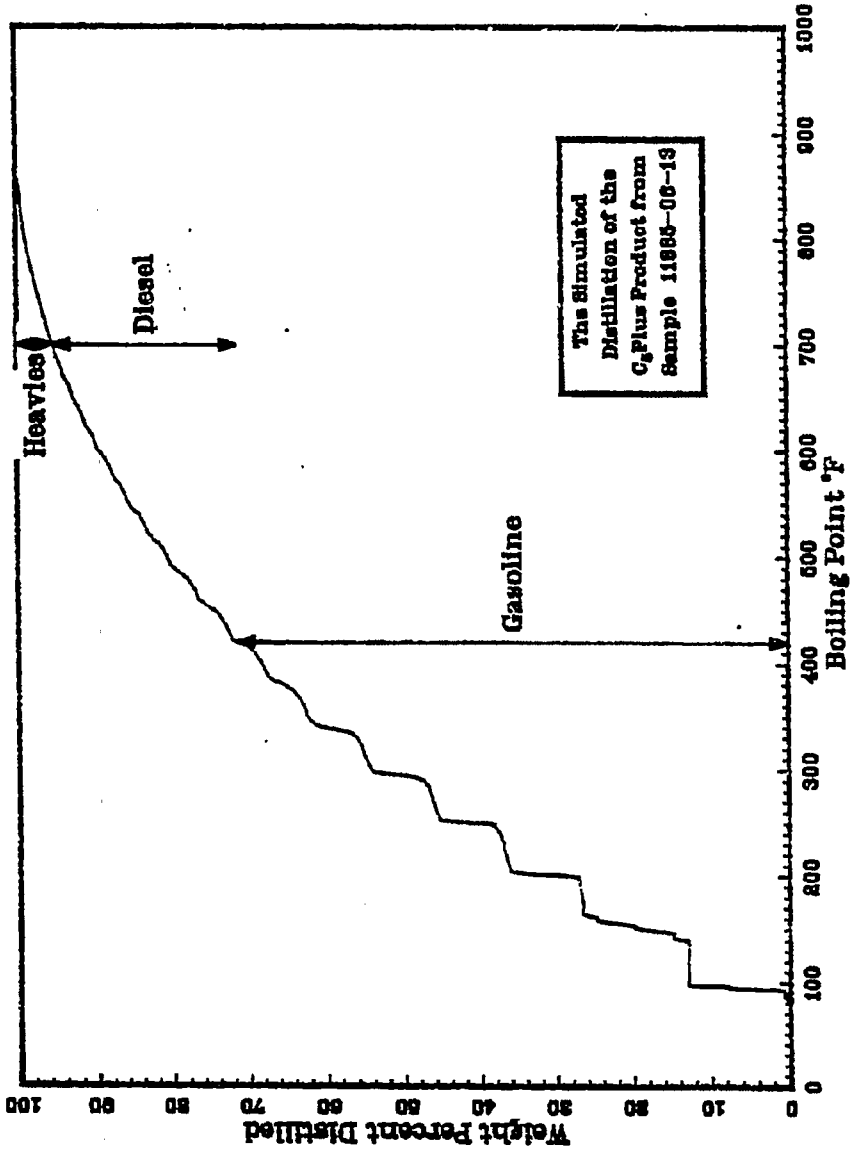

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11885-06-13

Fig. A48

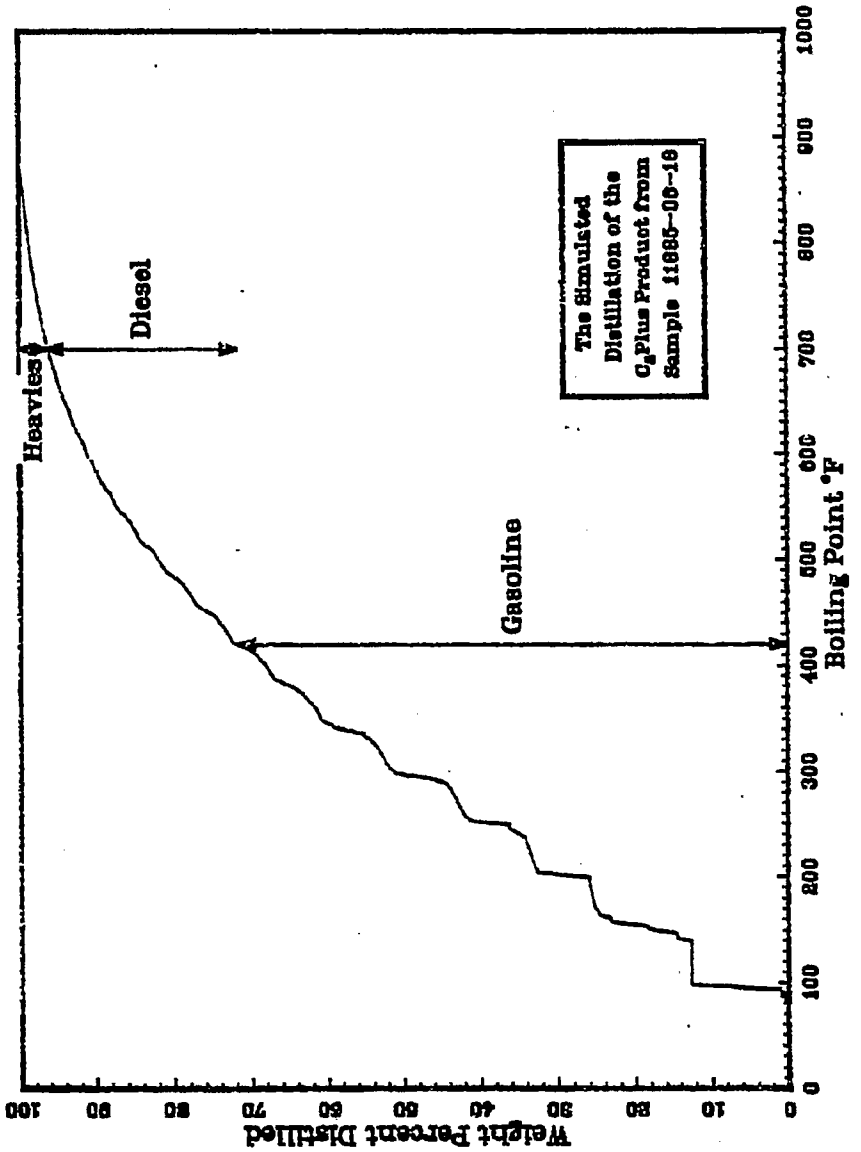

The Simulated Distillation of the C5 Plus Product from Sample 11685-06-18
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. A49

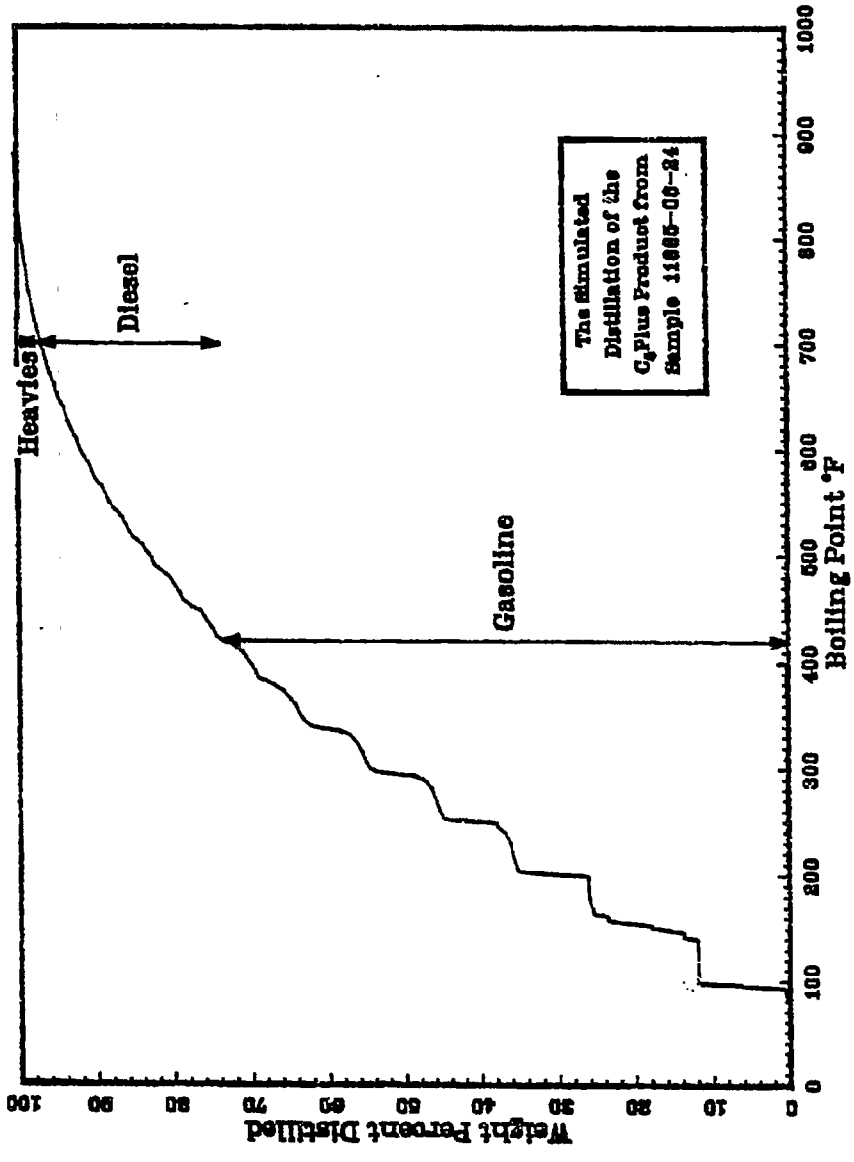

Heaviest
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11885-05-24
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. A50

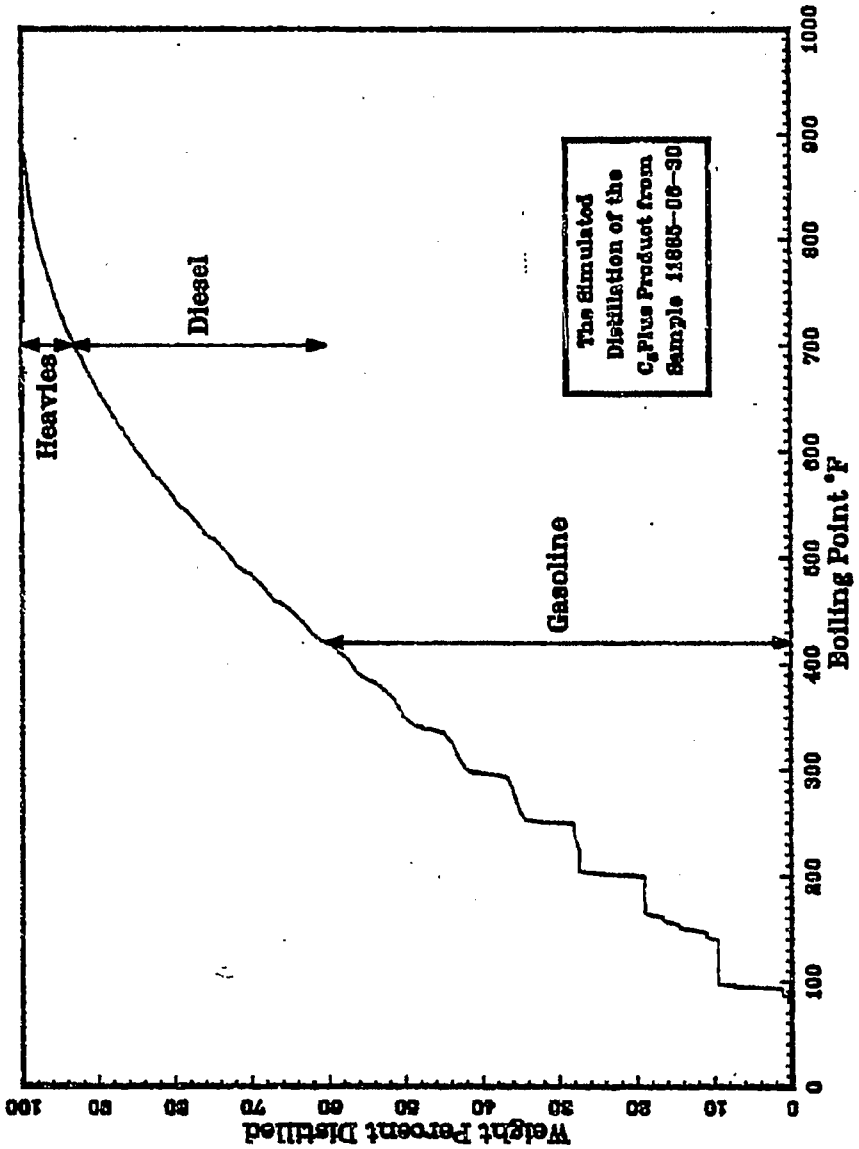

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11885-06-30

Fig. A51

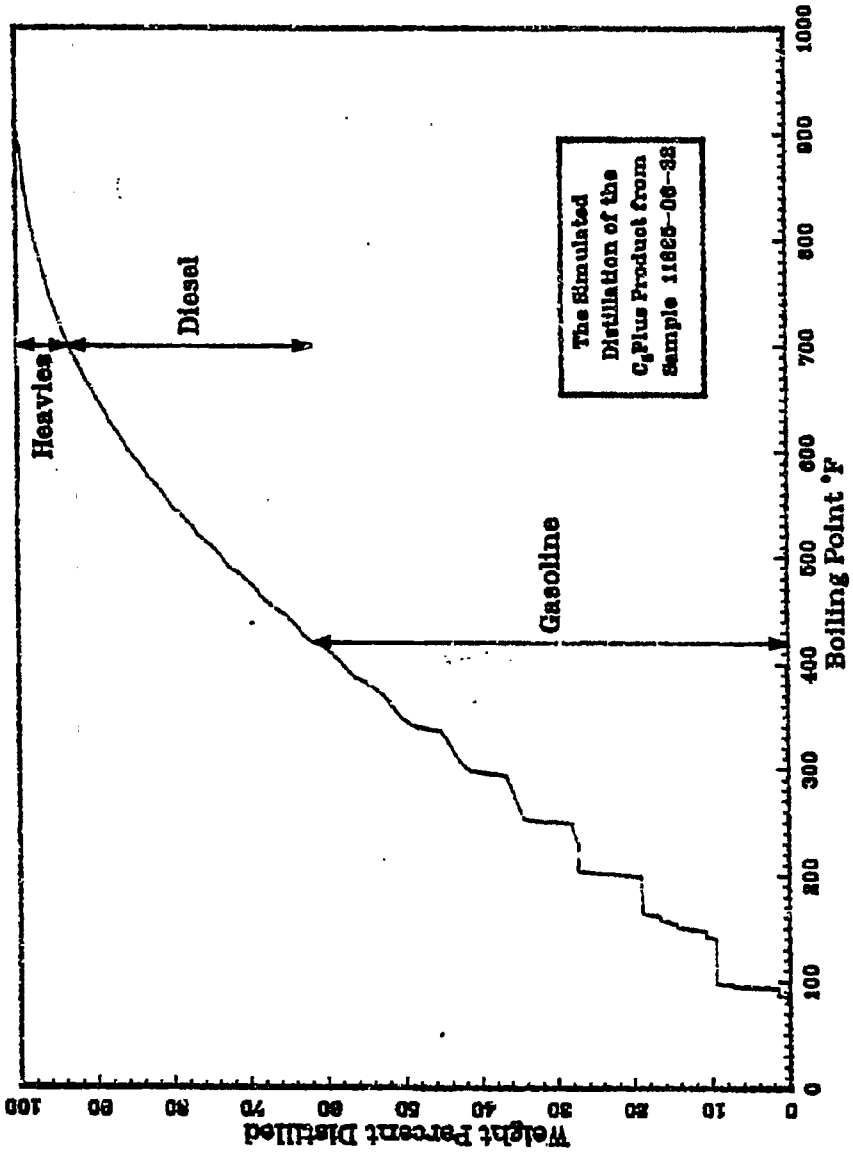

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5Plus Product from Sample 11825-06-3B

Fig. A52

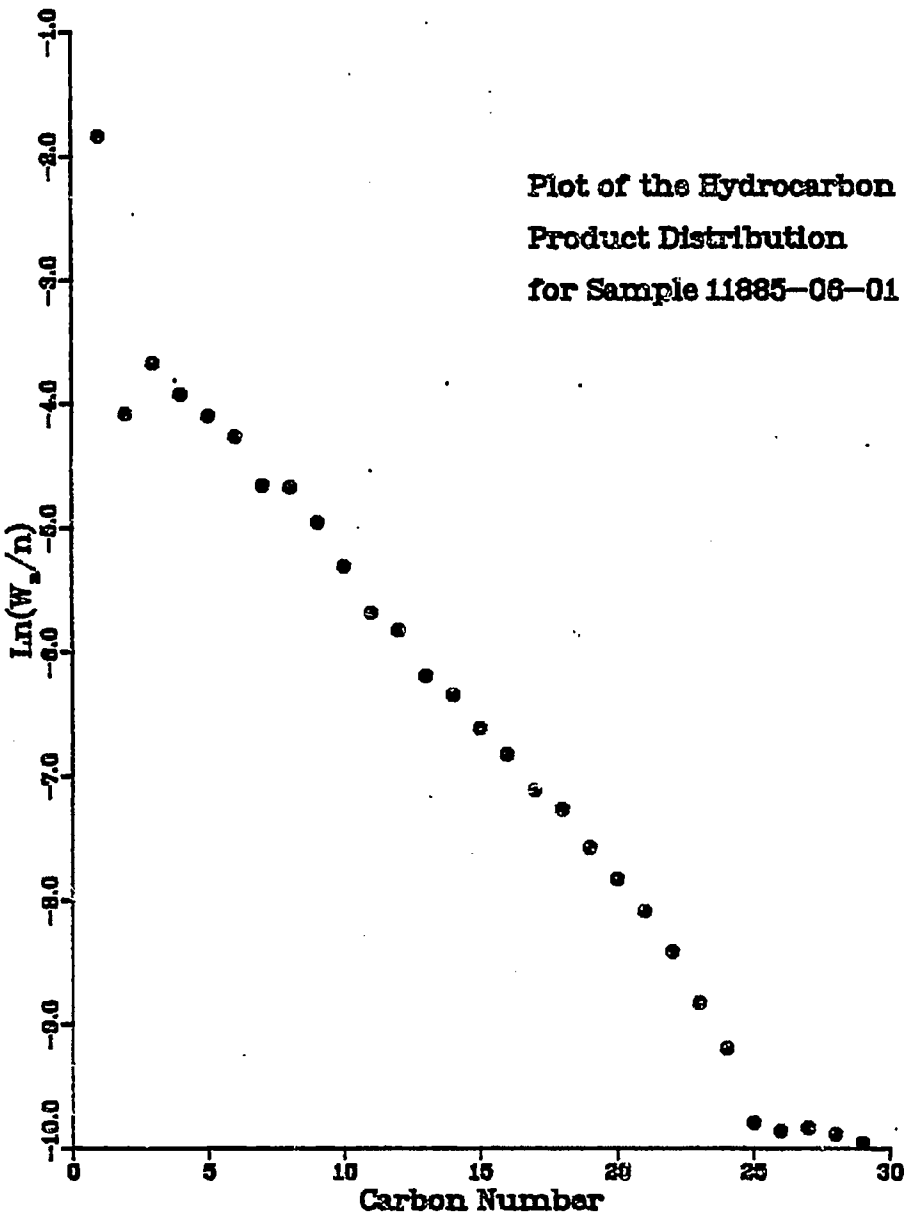

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-01
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A53

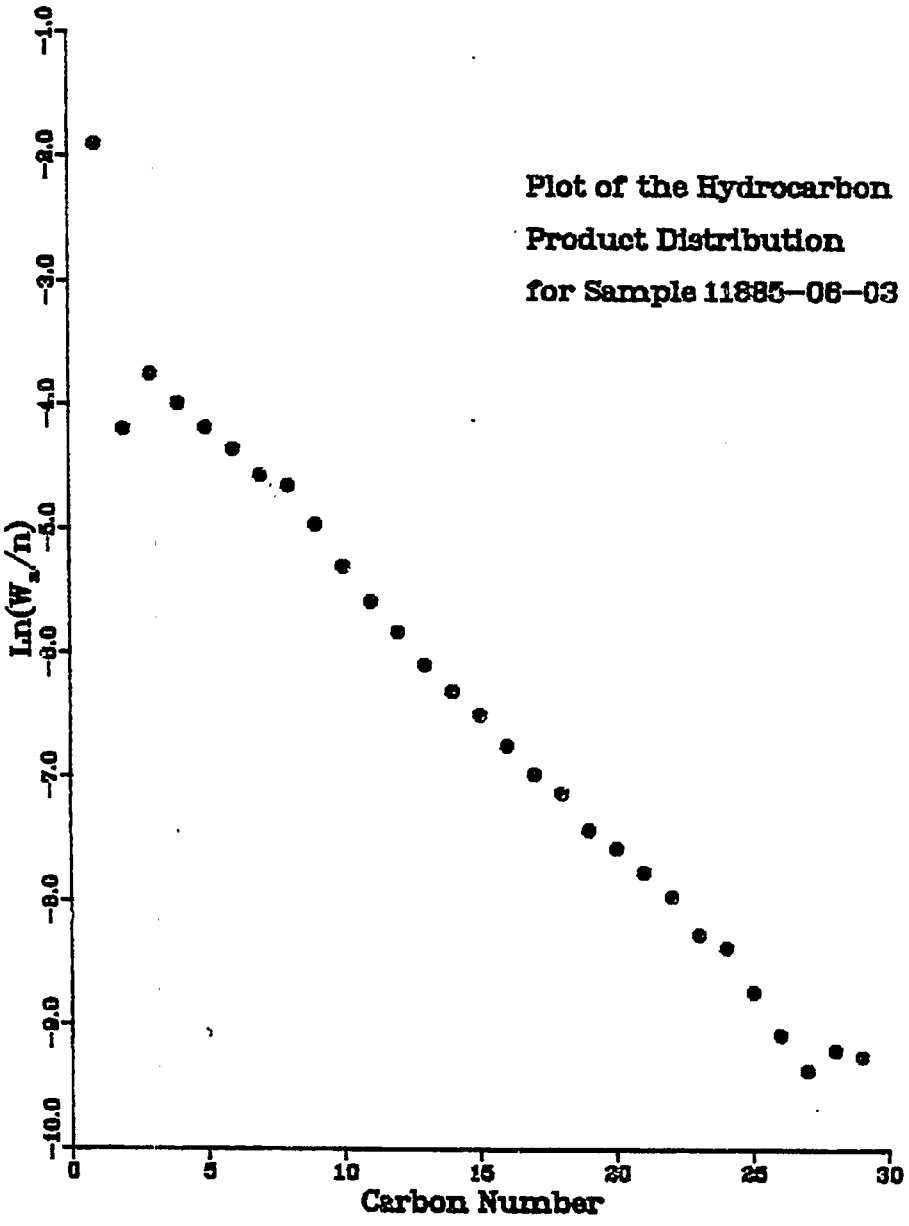

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A54

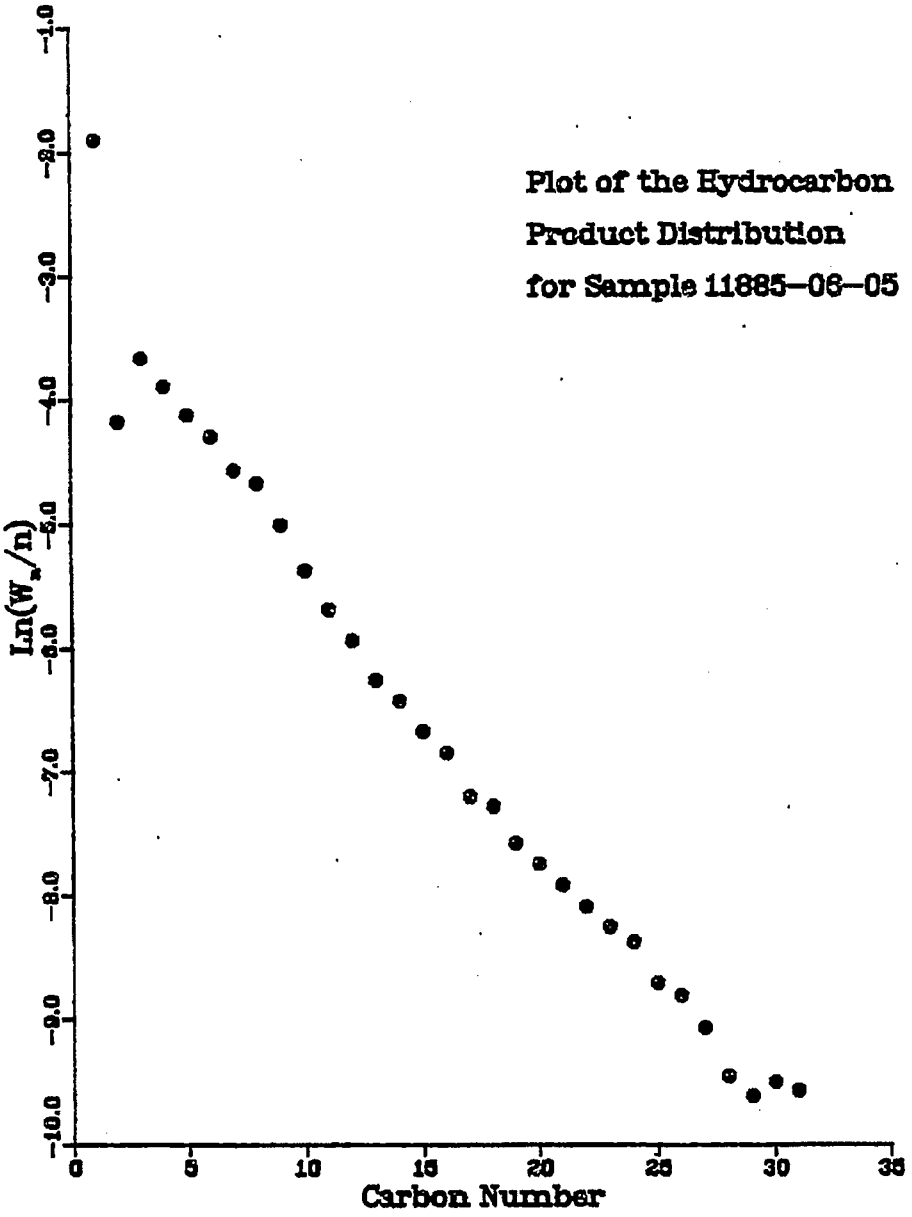

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A55

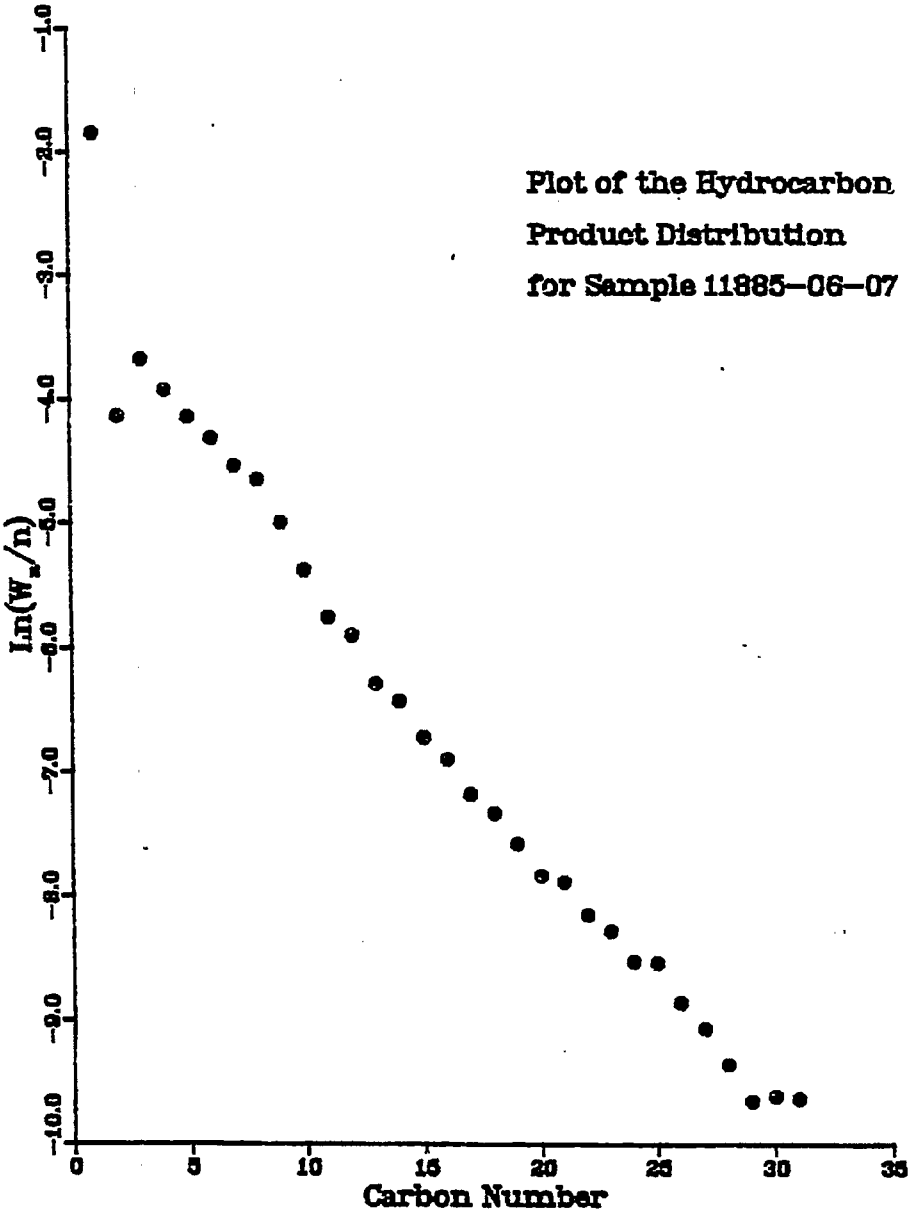

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-07
ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A56

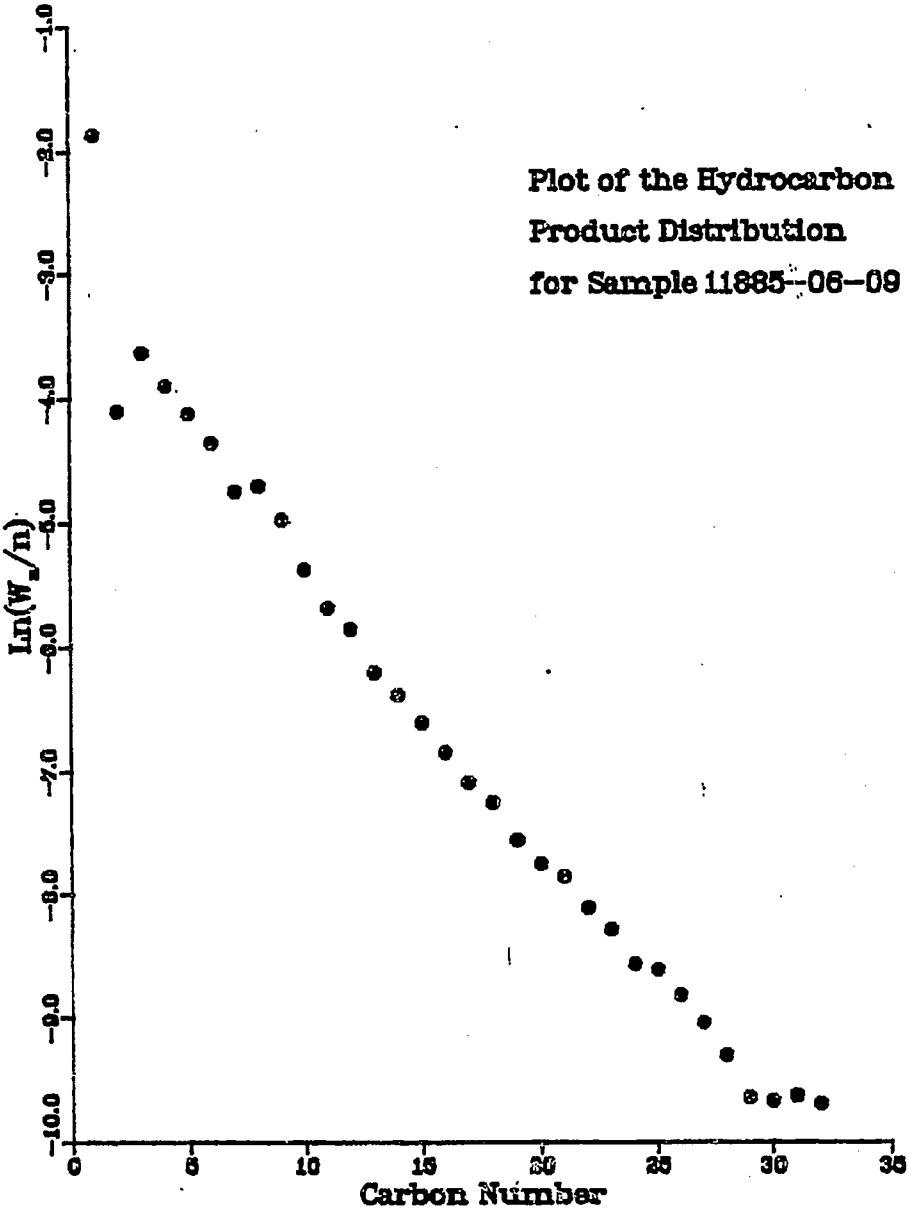

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A57

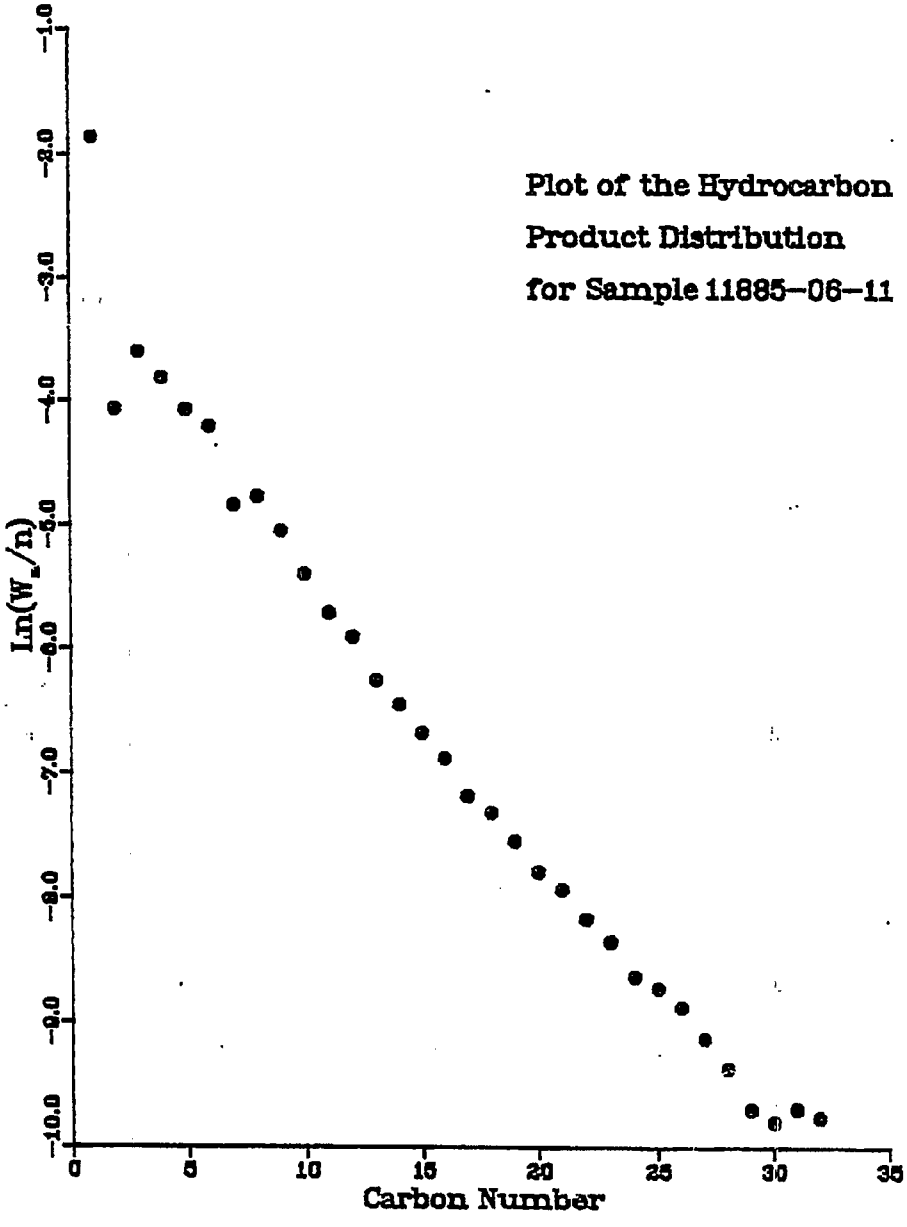

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A58

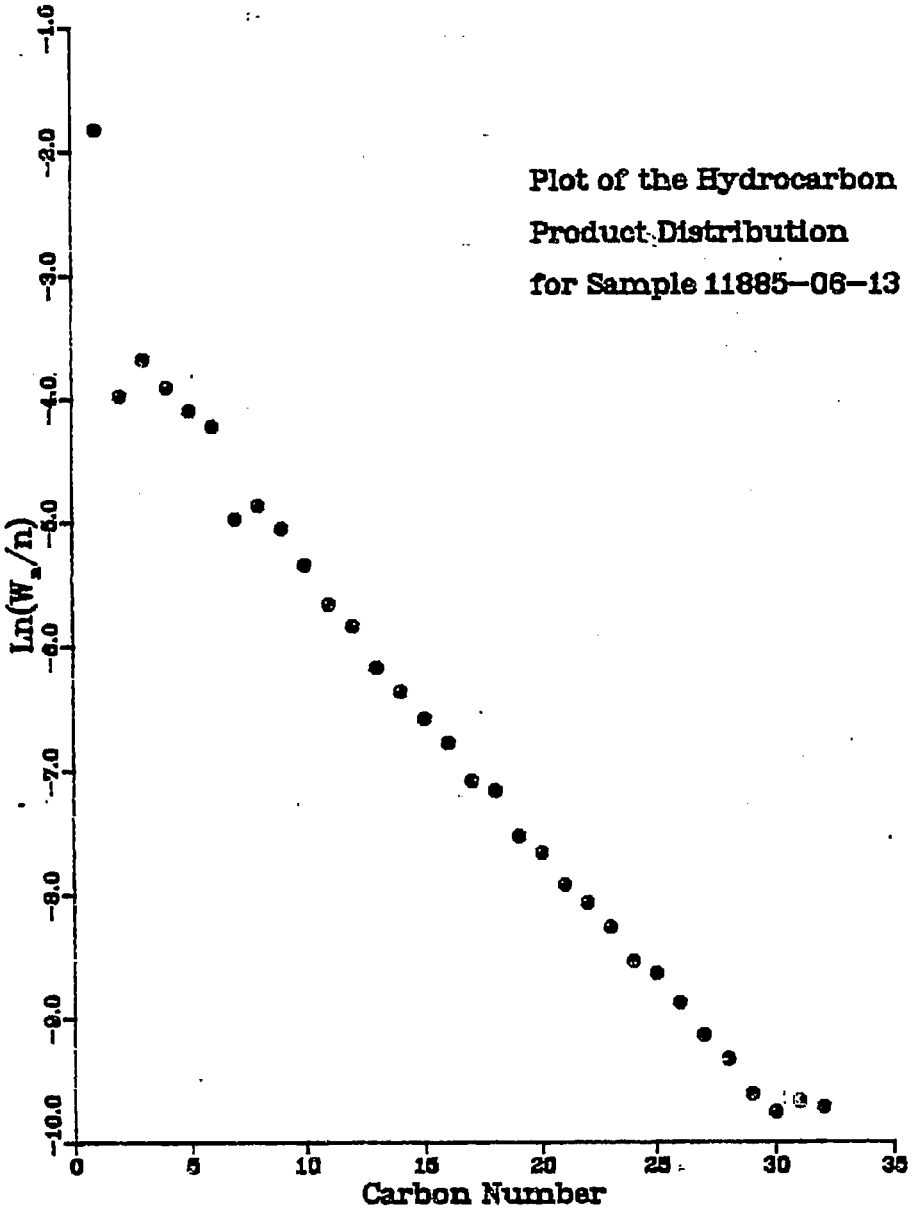

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A59

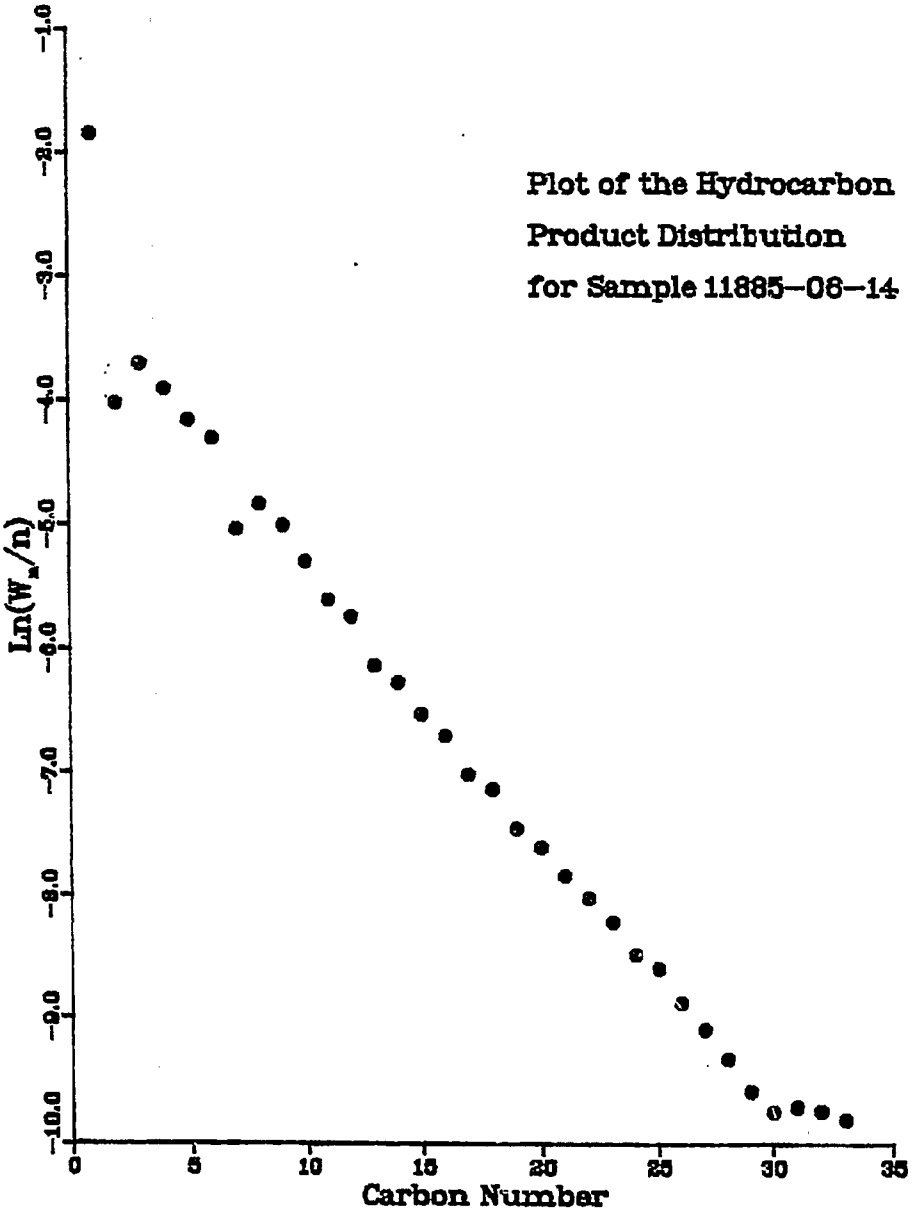

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-14
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A60

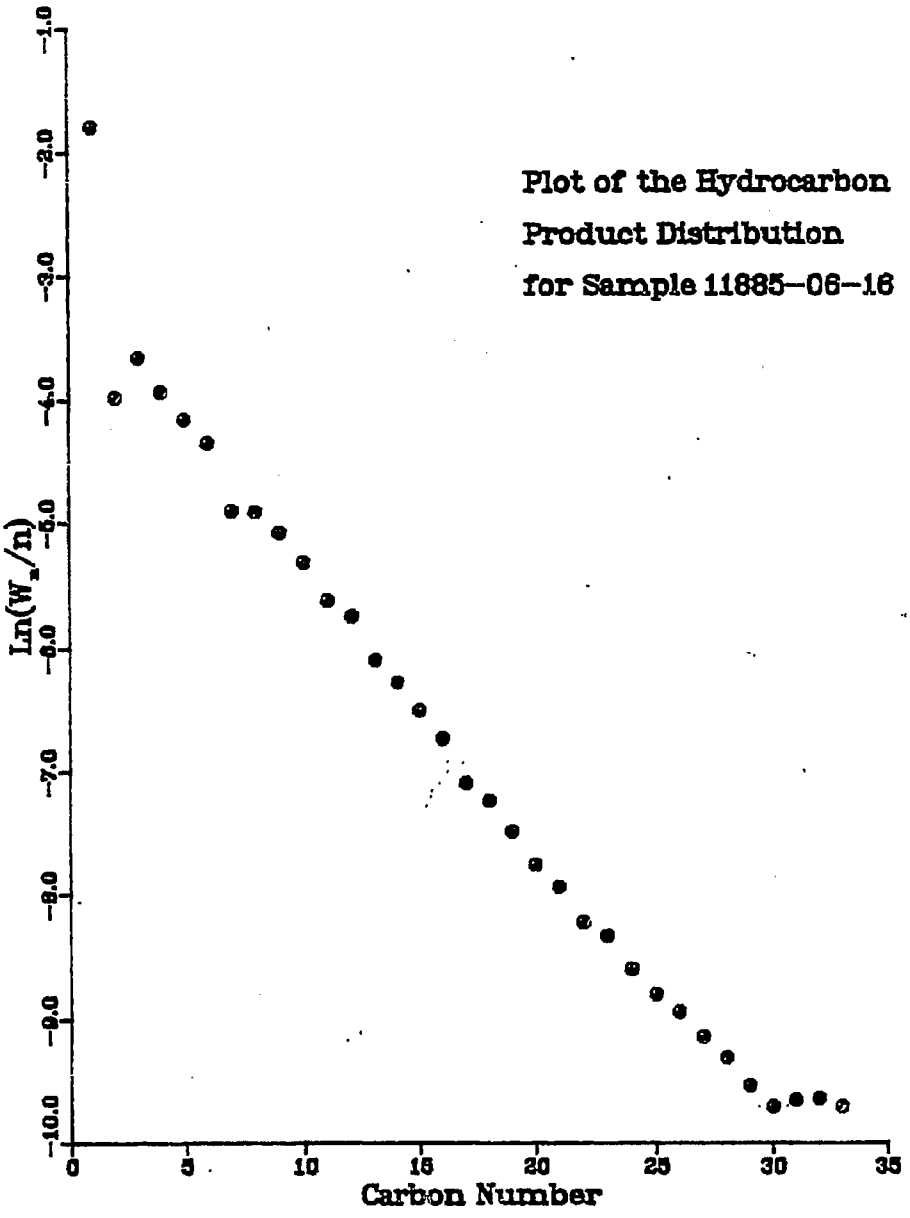

Plot of the Hydrocarbon
Product Distribution
for Sample 11685-06-16
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A61

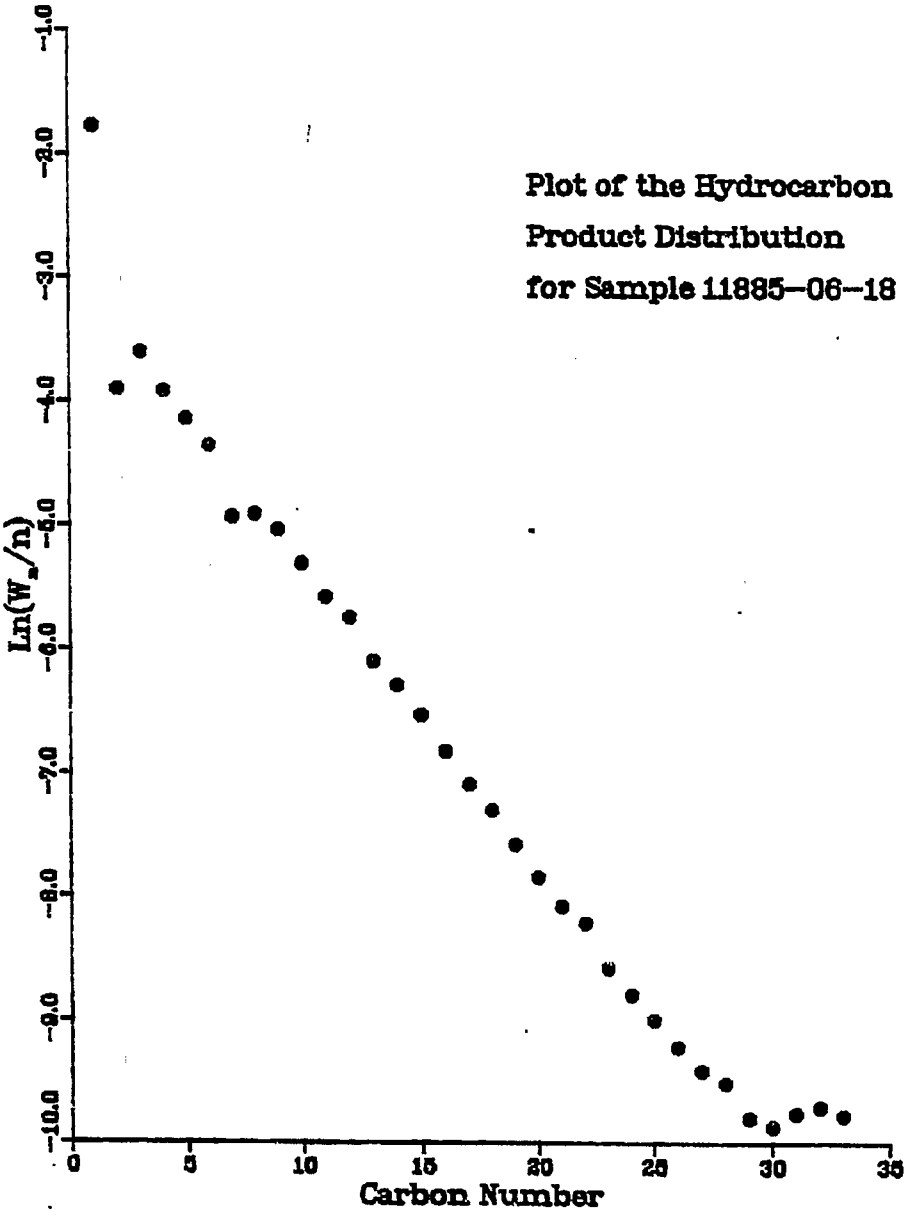

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-18
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A62

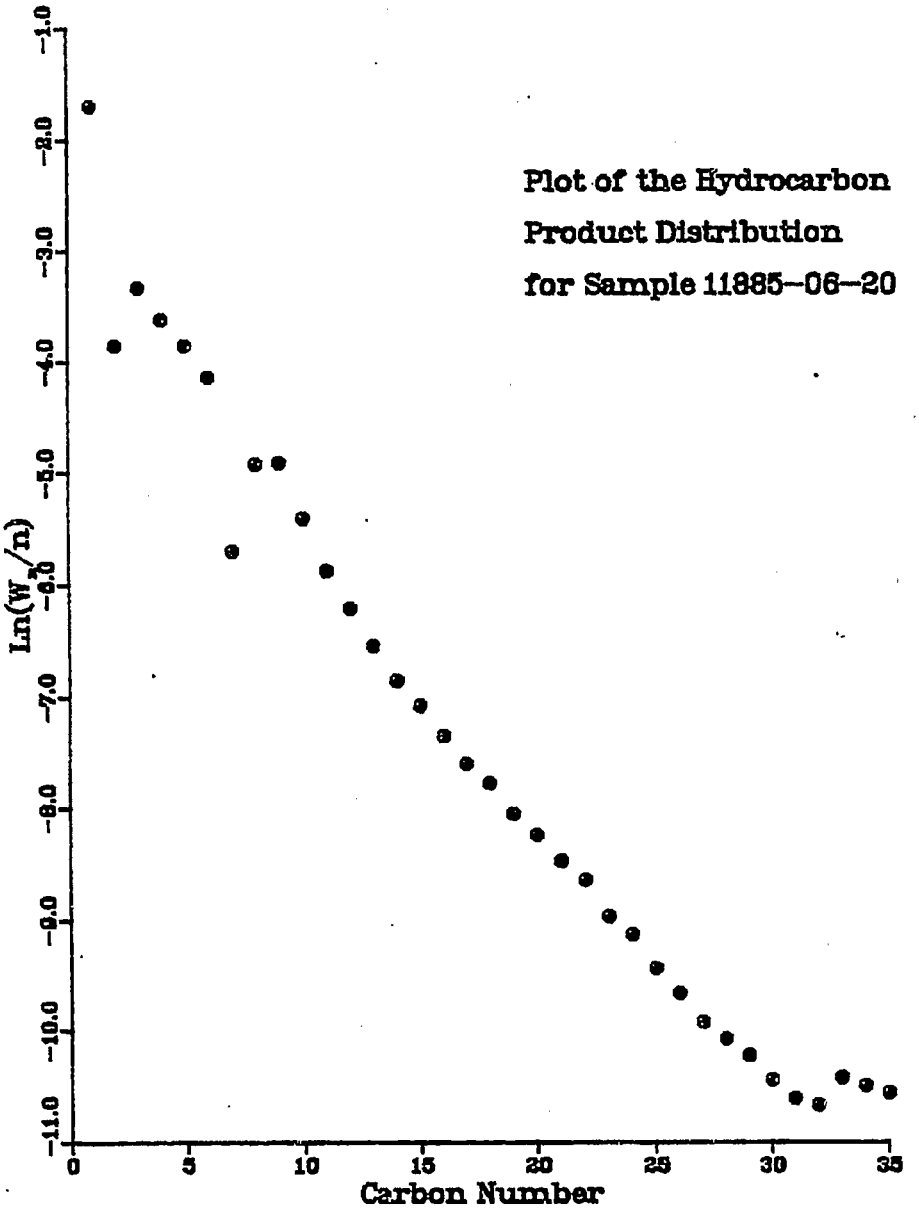

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-20
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A63

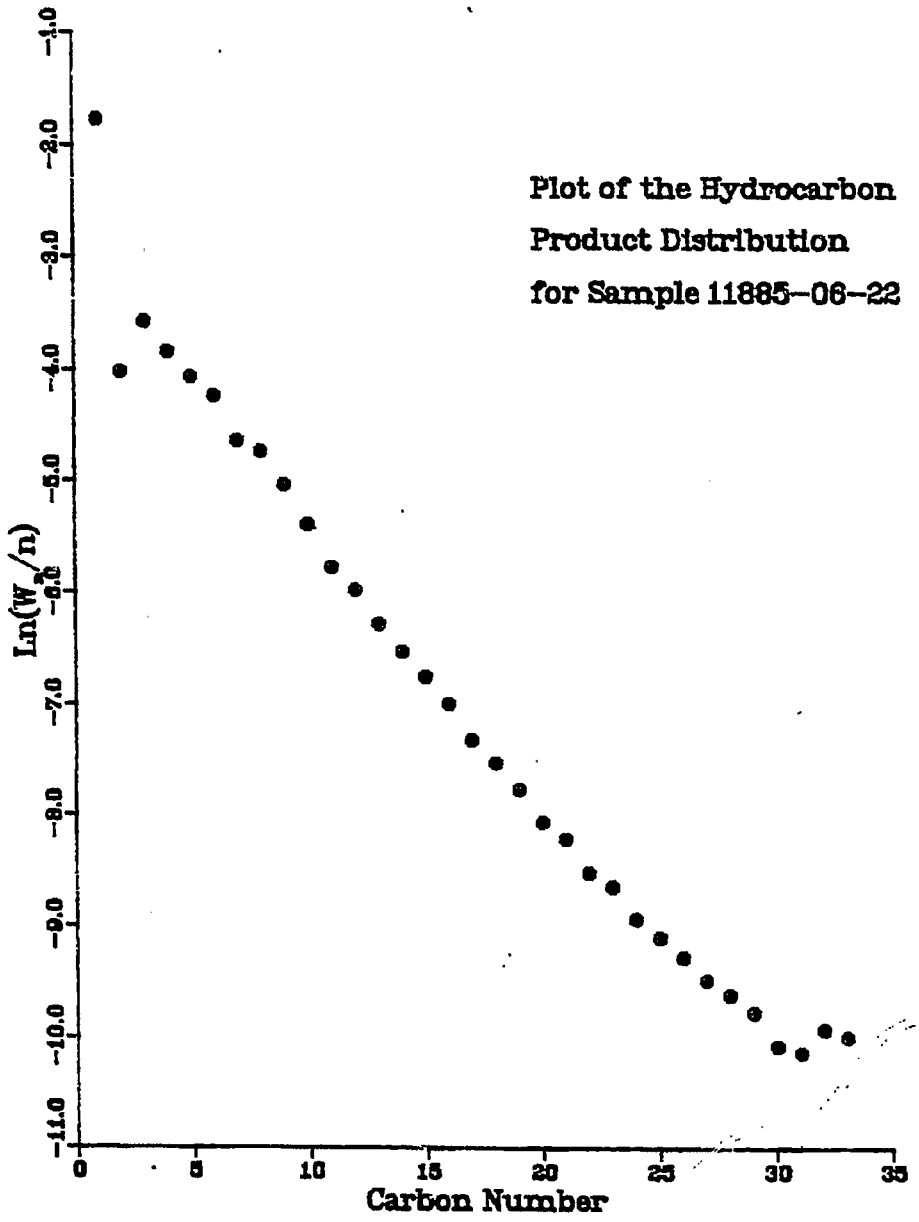

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-22
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A64

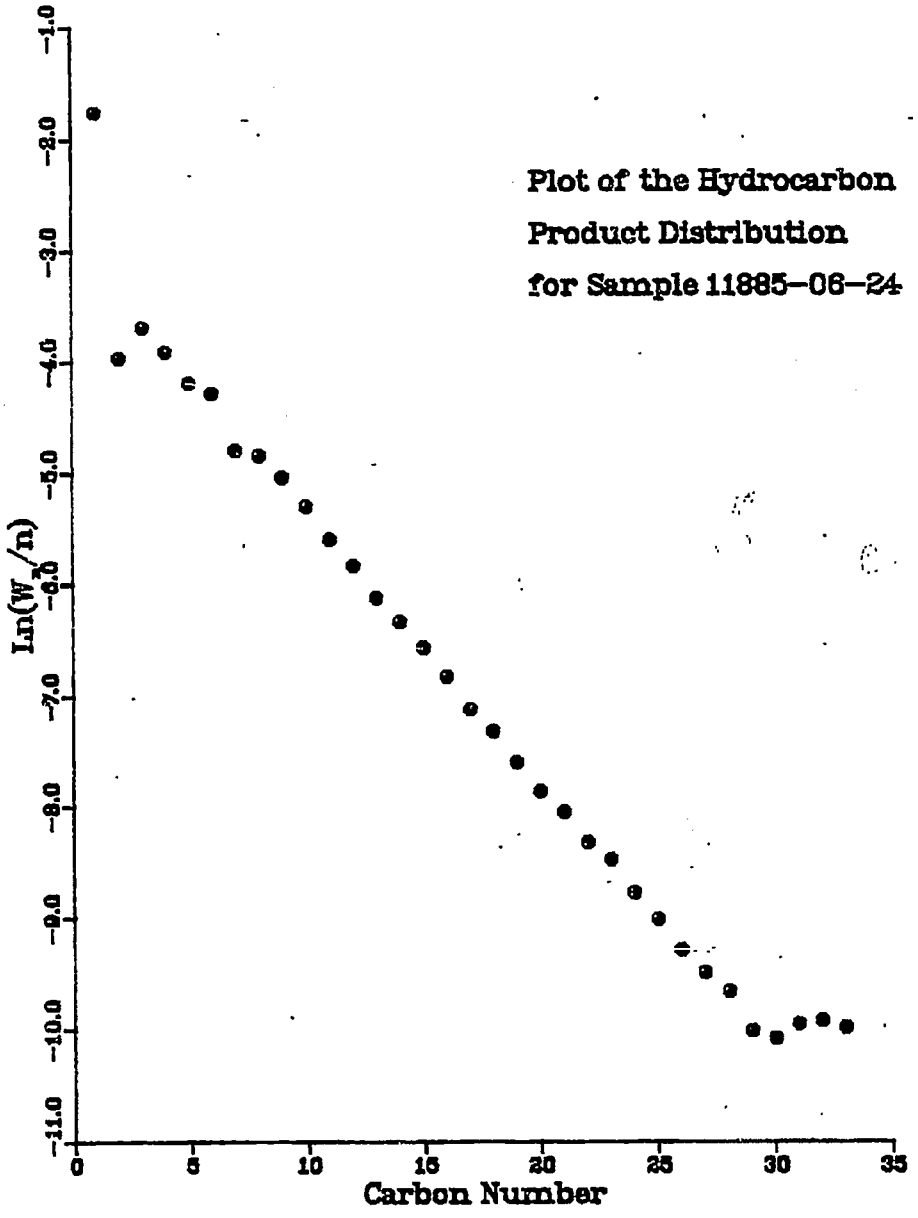

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-24
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A65

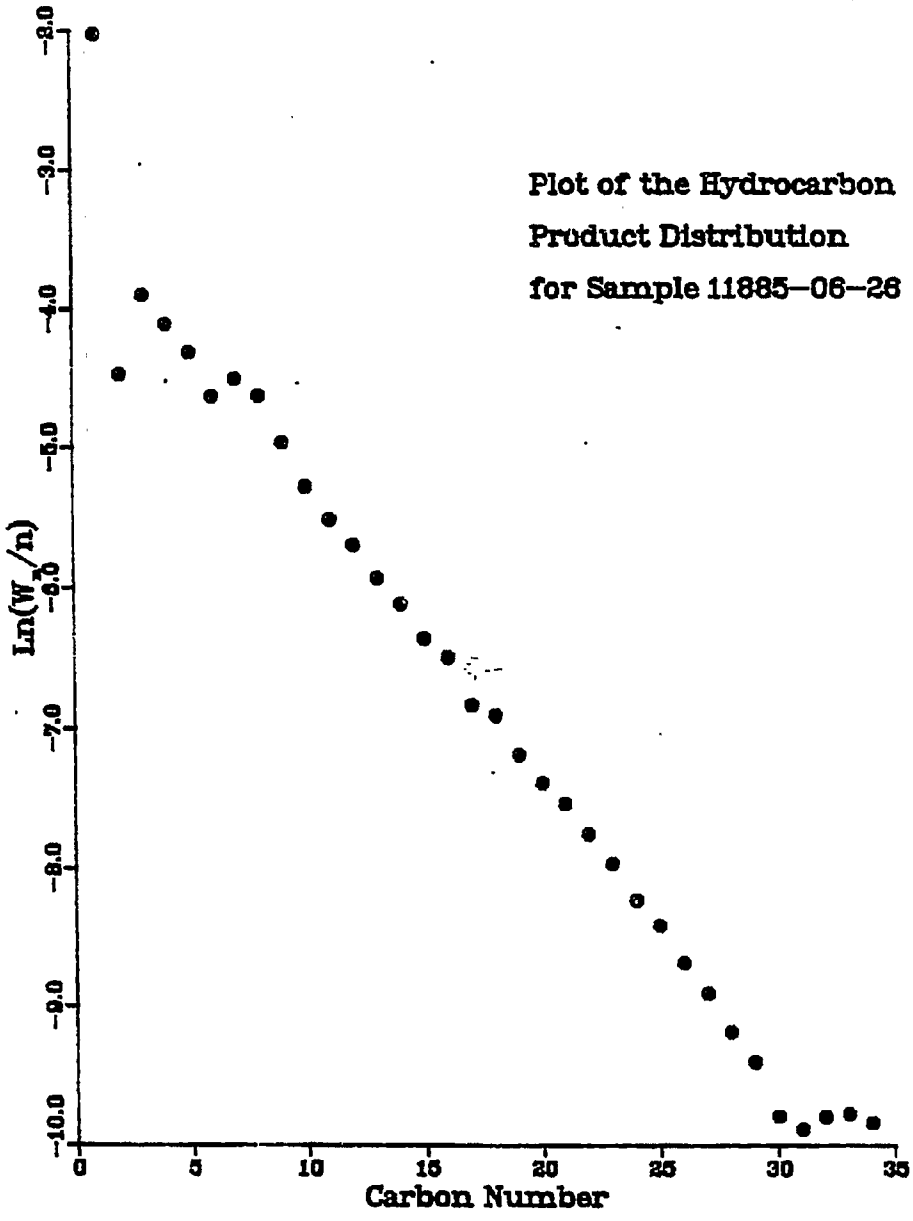

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-26
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A66

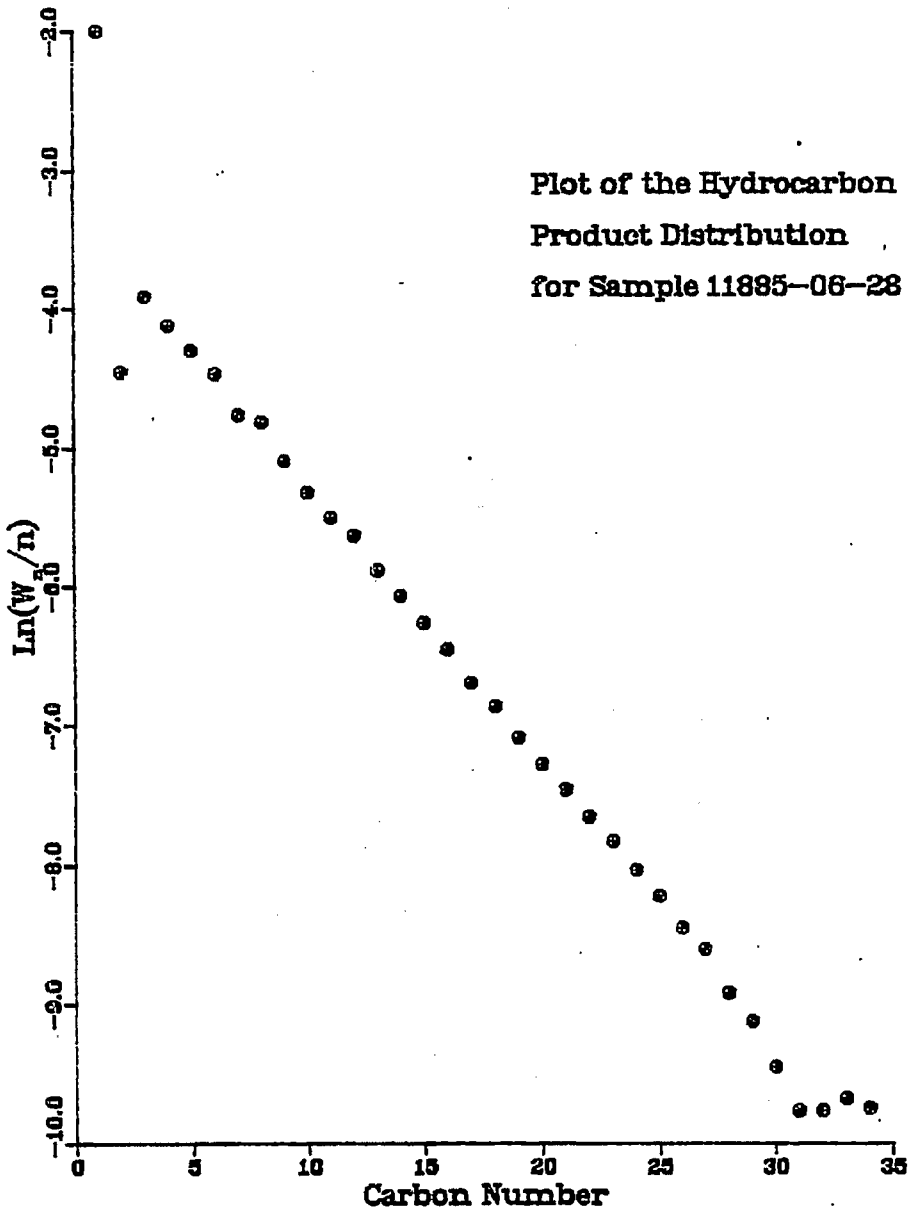

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-28
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A67

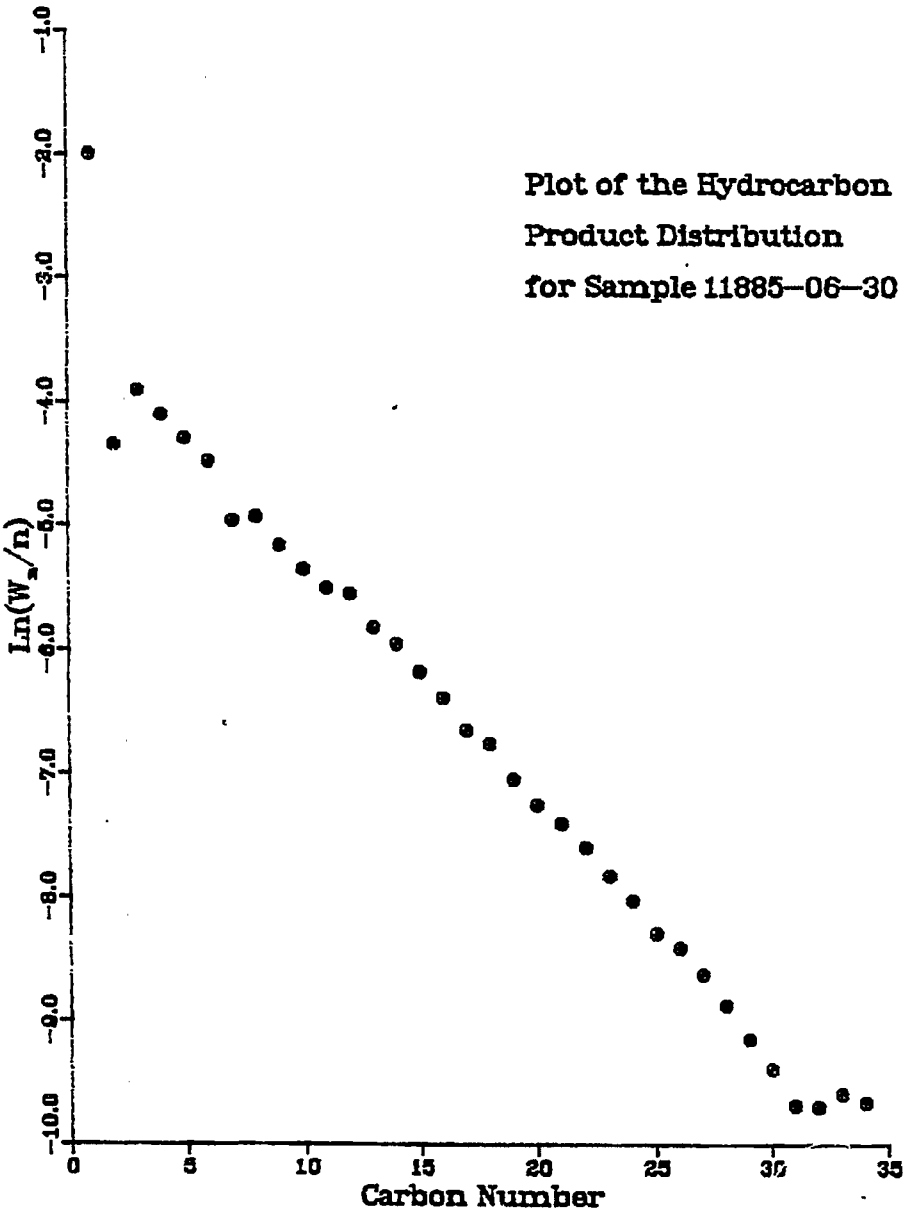

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-30
Ln(Ws/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A68

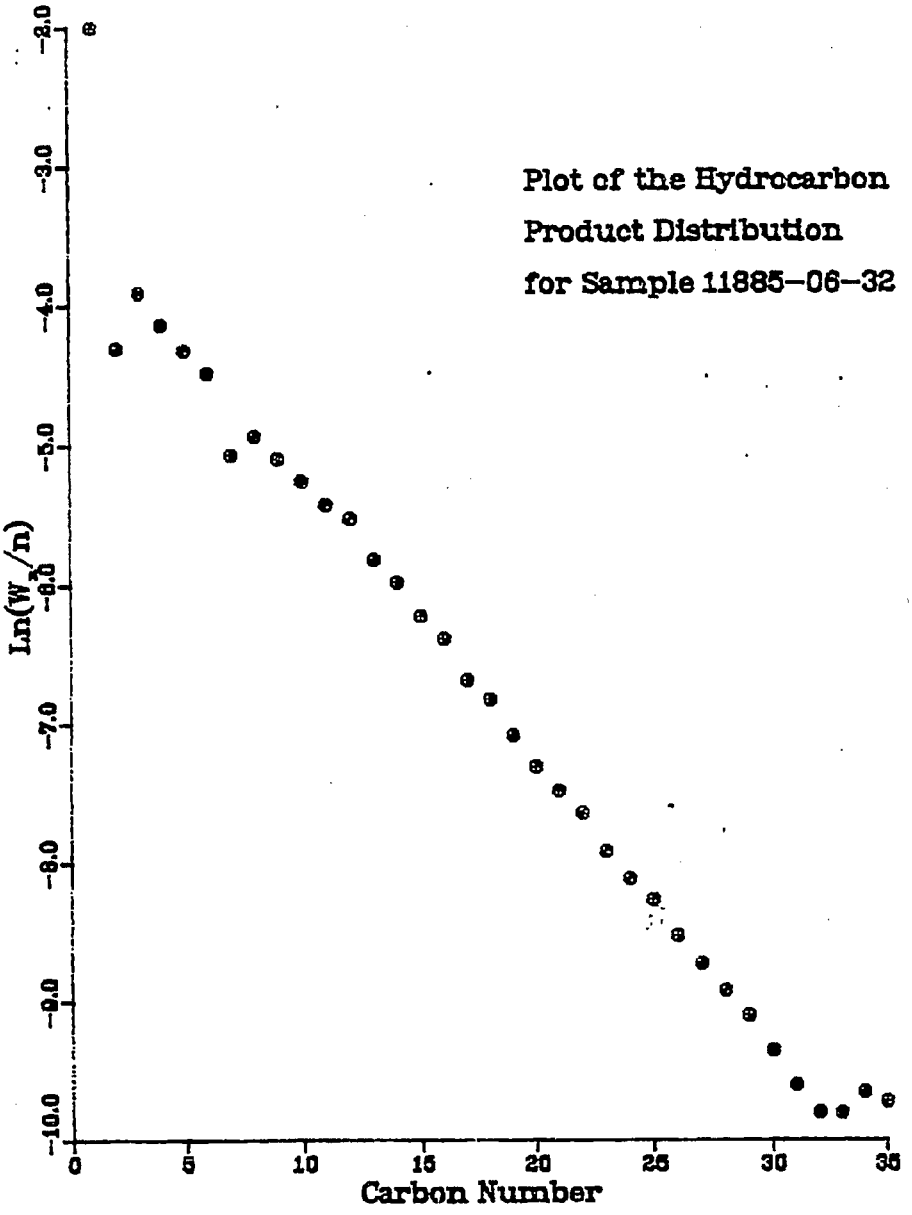

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-32
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A69

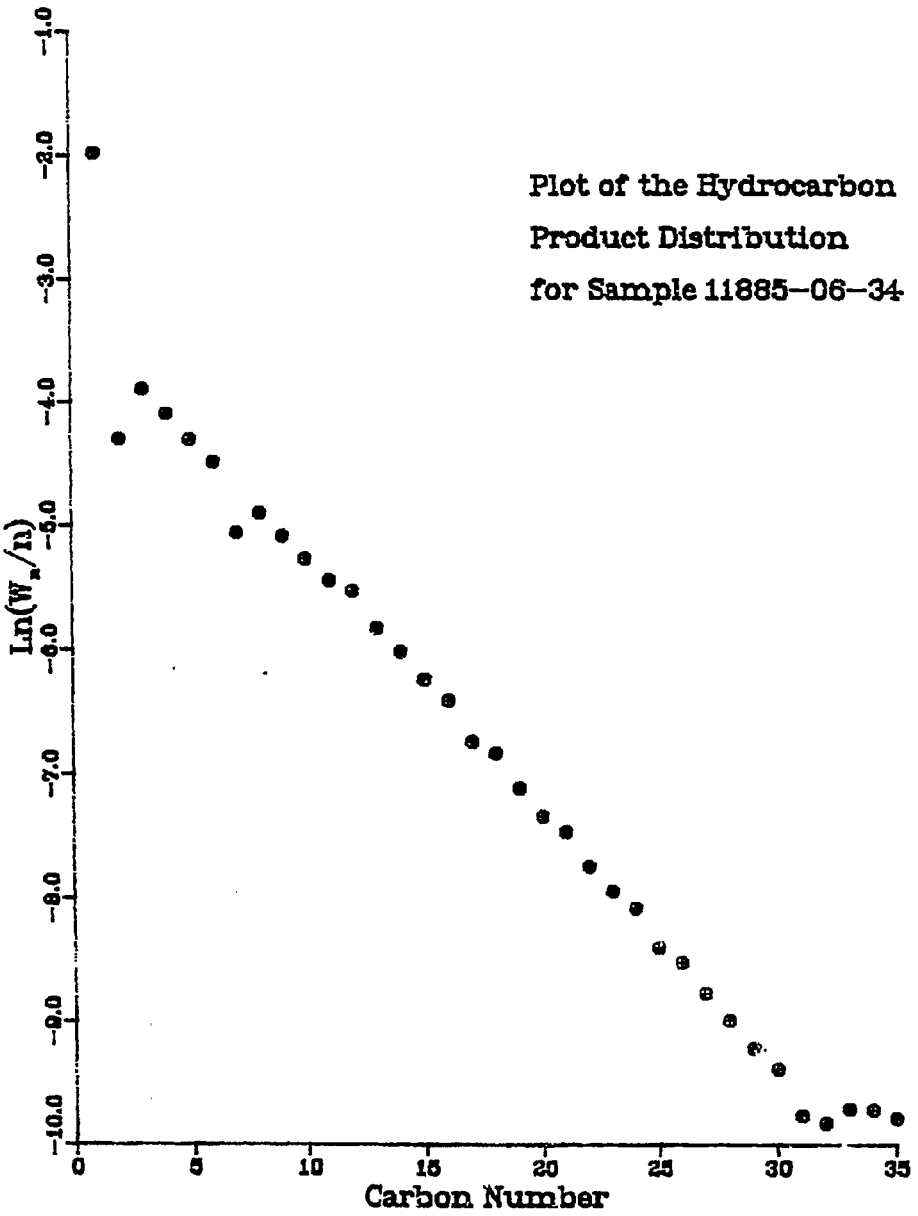

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-06-34
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A70

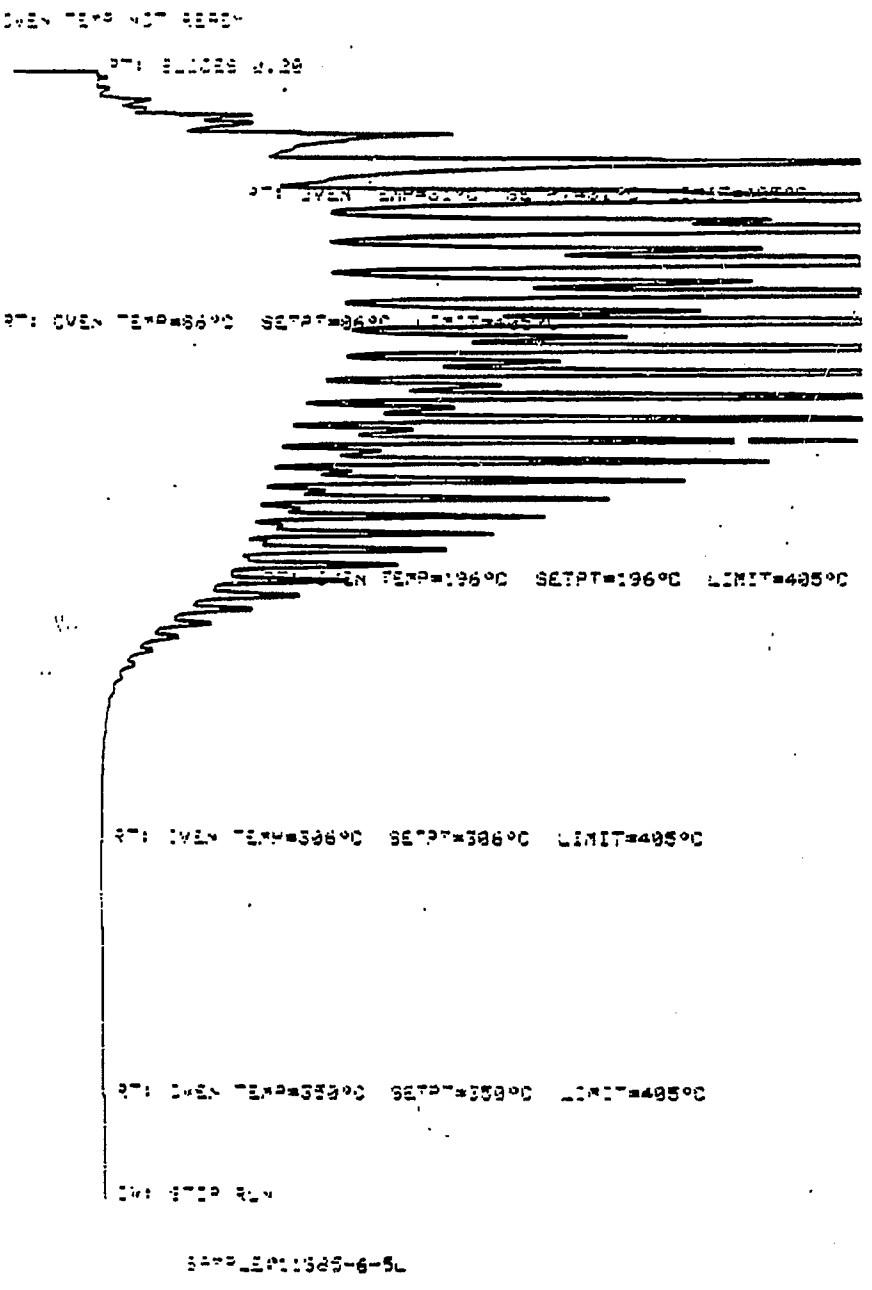

RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=359°C SETPT=359°C LIMIT=405°C

Fig. A71

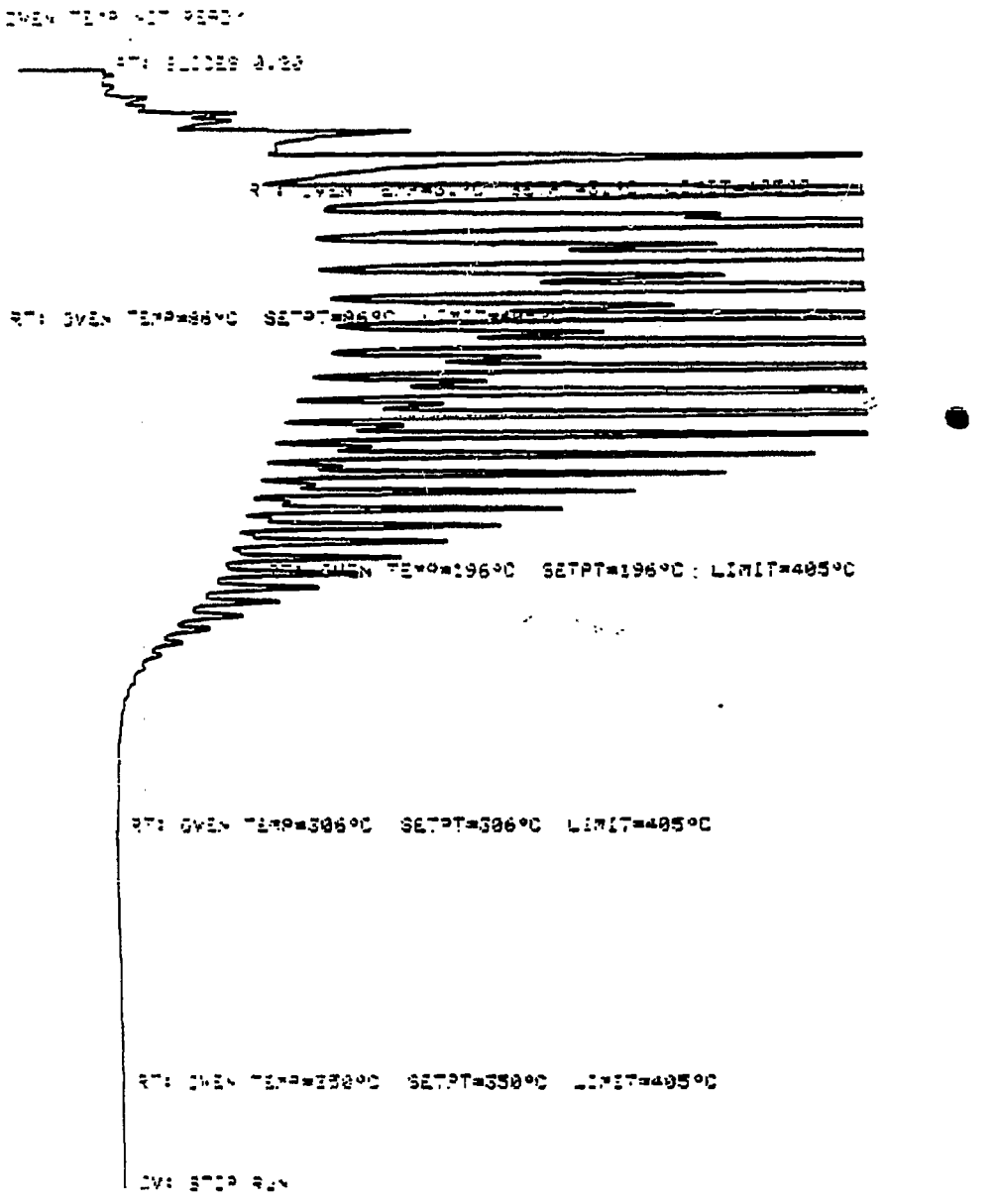

RT: OVEN TEMP=196°C SETPT=196°C : LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C

Fig. A72

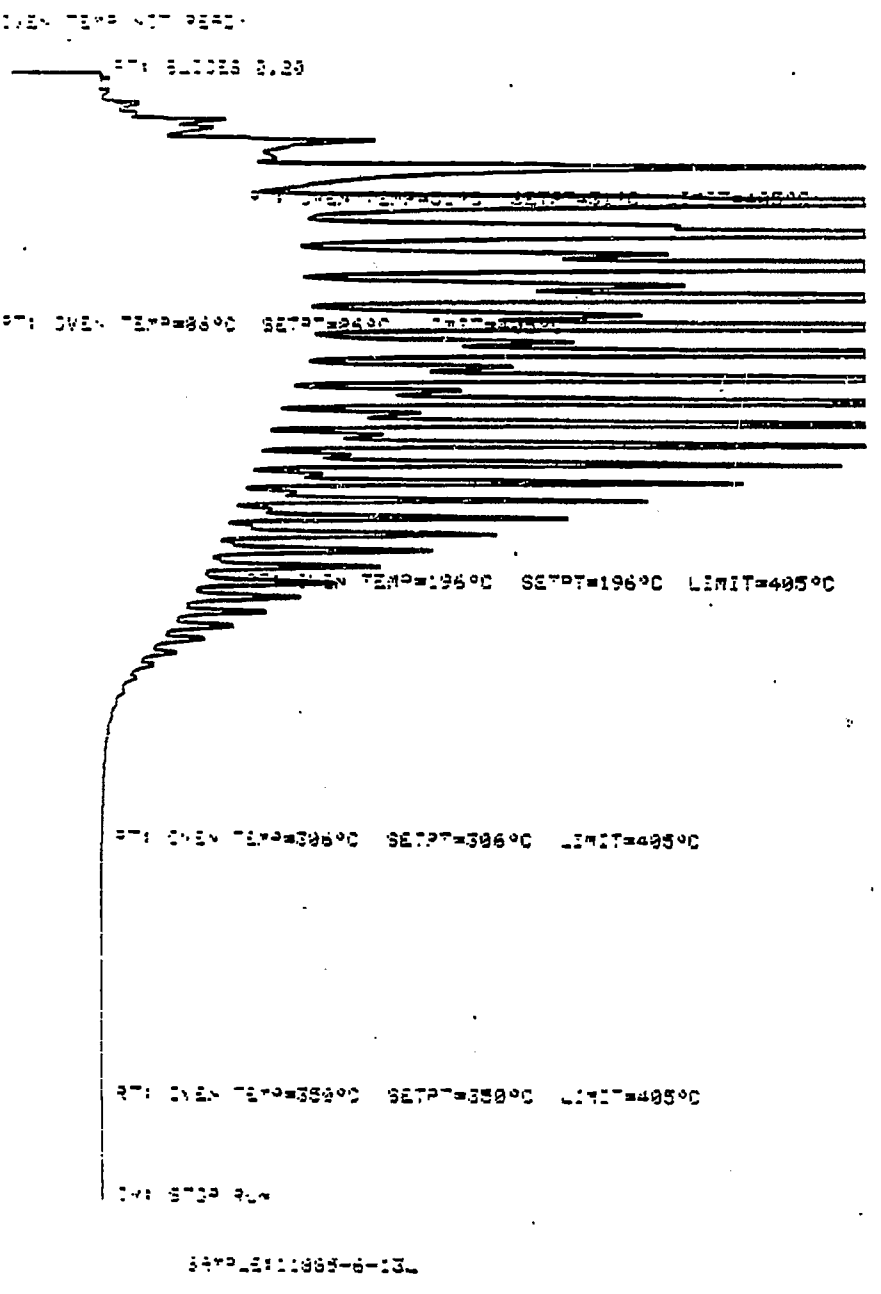

TEMP=196°C SETPT=196°C LIMIT=405°C
SETPT=306°C LIMIT=405°C
SETPT=350°C LIMIT=405°C

Fig. A73

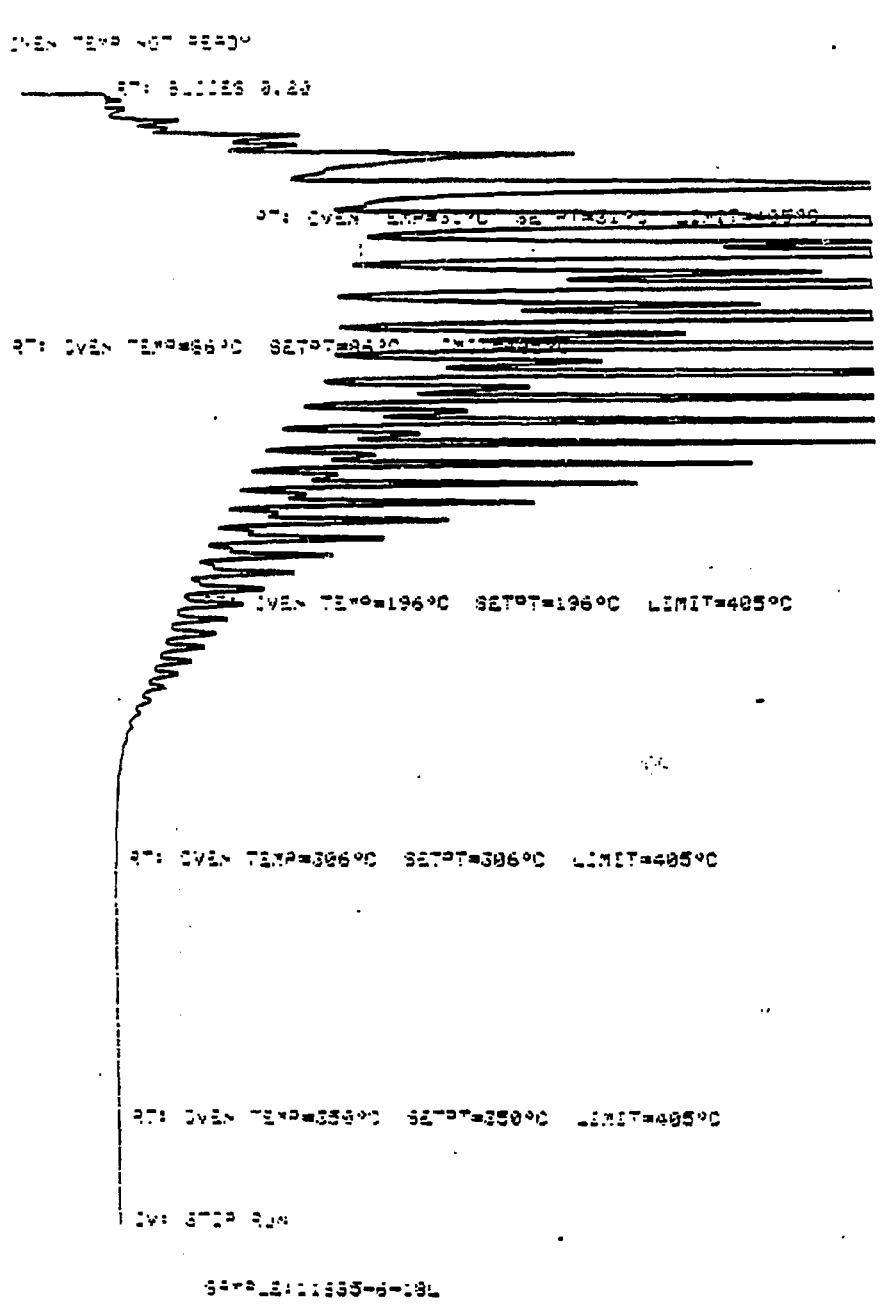

OVEN TEMP SET 385°
RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=356°C SETPT=350°C LIMIT=405°C

Fig. A74

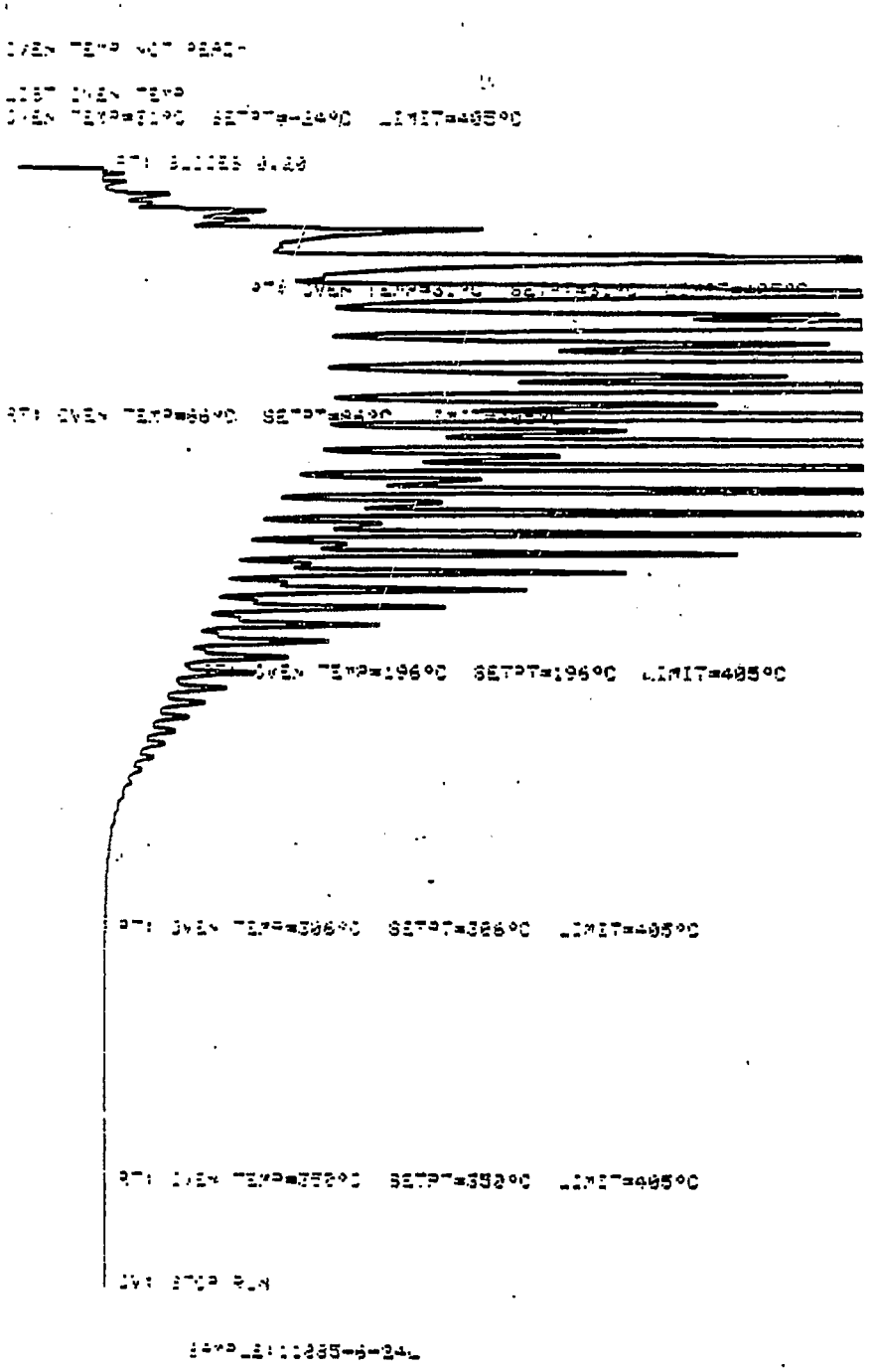


Fig. A75

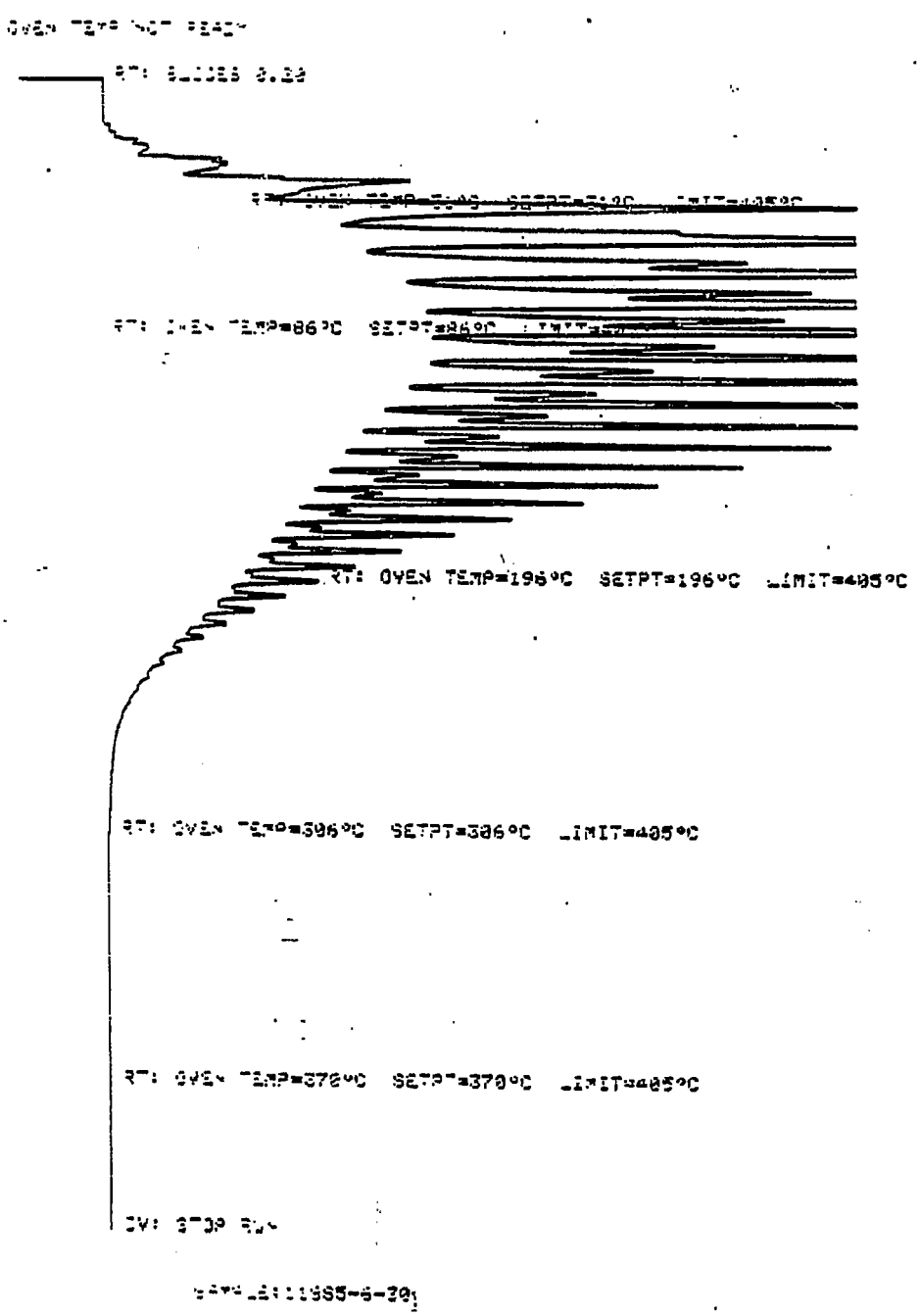

RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
RT: OVEN TEMP=370°C SETPT=370°C LIMIT=405°C

Fig. A76

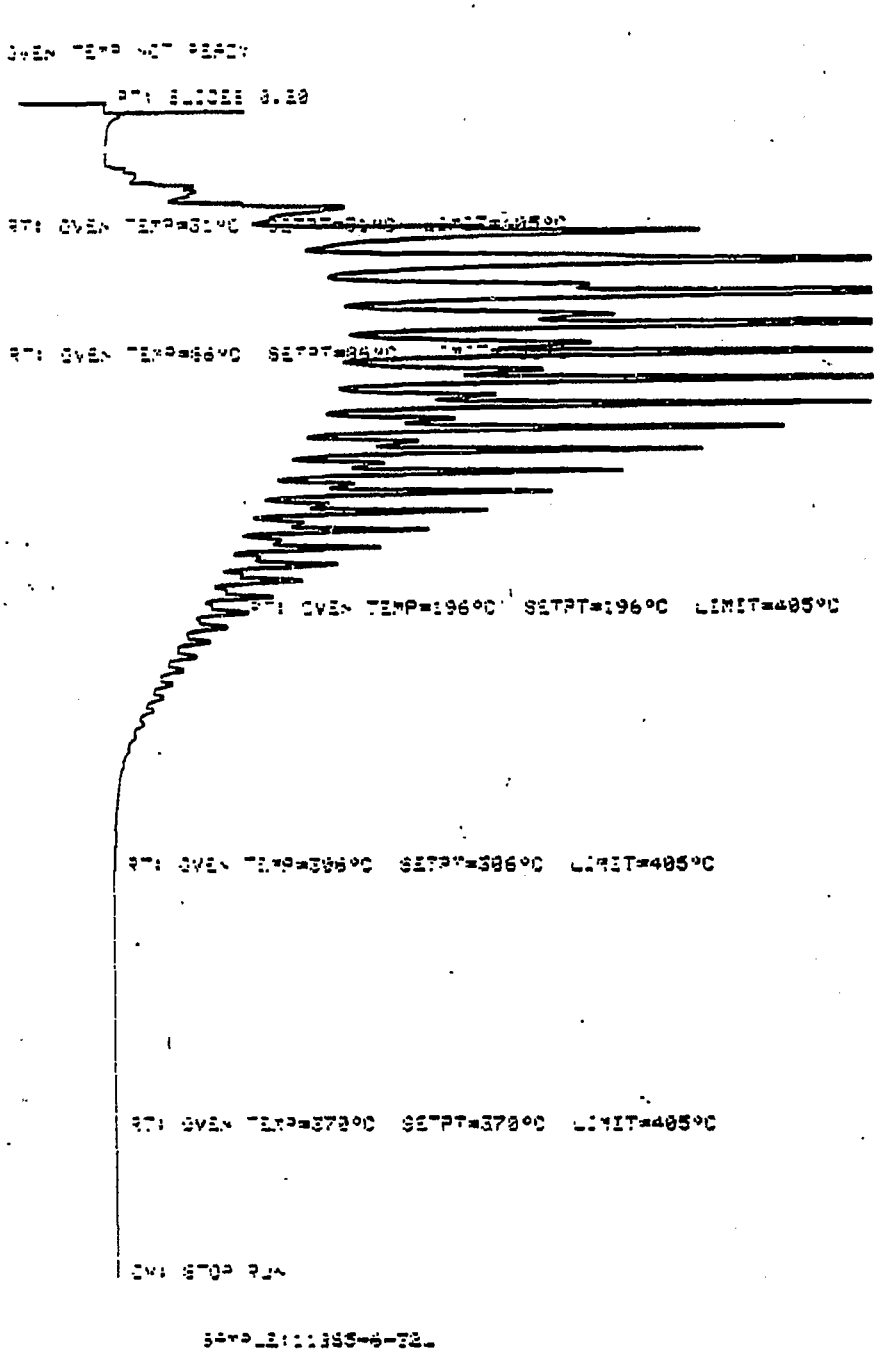

RT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
RT: OVEN TEMP=386°C SETPT=386°C LIMIT=405°C
RT: OVEN TEMP=378°C SETPT=378°C LIMIT=405°C

Fig. A77

Table A6

RESULT OF SYNGAS OPERATION

RUN NO. 11885-06
CATALYST CO/X4-U-103+U-101 12006-15 250 CC 111.3G(TO 122.6 +11.3)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-06-01	885-06-03	885-06-05	885-06-07	885-06-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	22.5	46.5	71.8	94.5	119.5
PRESSURE,PSIG	297	296	296	296	297
TEMP. C	262	263	263	263	261
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	22.50	24.00	25.25	22.75	25.00
EFFLNT GAS LITER	970.15	1055.22	1146.12	1045.06	1182.25
GM AQUEOUS LAYER	168.01	182.93	186.89	164.00	174.37
GM OIL	36.74	48.91	46.21	39.18	41.34
MATERIAL BALANCE					
GM ATOM CARBON %	94.51	95.82	97.23	96.62	95.82
GM ATOM HYDROGEN %	93.86	98.08	99.26	98.58	98.43
GM ATOM OXYGEN %	101.11	101.61	102.29	102.07	102.07
RATIO CHX/(H2O+CO2)	0.7889	0.8174	0.8360	0.8197	0.7852
RATIO X IN CHX	2.4295	2.4068	2.4127	2.4275	2.4262
USAGE H2/CO PRODT	2.1685	2.1463	2.1369	2.1566	2.2280
FEED H2/CO FRM EFFLNT	0.9931	1.0236	1.0209	1.0203	1.0272
RESIDUAL H2/CO RATIO	0.5206	0.5544	0.5694	0.5810	0.6106
RATIO CO2/(H2O+CO2)	0.0781	0.0729	0.0708	0.0720	0.0629
K SHIFT IN EFFLNT	0.0441	0.0436	0.0434	0.0451	0.0410
SPECIFIC ACTIVITY SA	0.9879	0.8836	0.8259	0.7709	0.7229
CONVERSION					
ON CO %	28.67	29.47	28.80	27.88	25.76
ON H2 %	62.61	61.80	60.29	58.93	55.86
ON CO+H2 %	45.58	45.83	44.71	43.56	41.01
PRDT SELECTIVITY,WT %					
CH4	15.99	14.85	15.02	15.75	15.51
C2 HC'S	3.37	3.00	3.08	3.19	3.31
C3H8	4.40	4.13	4.52	4.56	4.71
C3H6=	3.25	2.86	3.19	3.04	3.25
C4H10	3.36	3.09	3.43	3.50	3.58
C4H8=	4.51	4.29	4.76	4.41	4.57
C5H12	3.41	3.14	3.54	3.43	3.57
C5H10=	4.89	4.43	4.59	4.53	4.57
C6H14	4.22	3.69	3.92	4.05	3.80
C6H12= & CYCLO'S	4.20	3.97	4.26	3.98	3.85
C7+ IN GAS	18.96	17.56	18.13	18.64	17.10
LIQ HC'S	29.44	35.00	31.55	30.93	32.18
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	34.87	32.22	34.00	34.46	34.93
C5 -420 F	49.52	48.88	48.81	48.69	47.20
420-700 F	14.51	16.60	14.33	13.94	14.87
700-END PT	1.09	2.30	2.87	2.91	3.00
C5+-END PT	65.13	67.78	66.00	65.54	65.07
ISO/NORMAL MOLE RATIO					
C4	0.0931	0.0790	0.0839	0.0573	0.0547
C5	0.1262	0.1060	0.1017	0.0846	0.0849
C6	0.4884	0.4018	0.4472	0.3504	0.3487
C4=	0.0688	0.0761	0.0872	0.0820	0.0846
PARAFFIN/OLEFIN RATIO					
C3	1.2944	1.3810	1.3515	1.4342	1.3846
C4	0.7191	0.6947	0.6960	0.7666	0.7559
C5	0.6779	0.6882	0.7506	0.7360	0.7589
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7676	0.7967	0.7955	0.7963	0.7963
RATIO CH4/(1-A)**2	2.9612	3.5921	3.5917	3.7948	3.7376
ALPHA FRM CORRELATION	0.8425	0.8394	0.8381	0.8371	0.8348
ALPHA (EXPTL/CORR)	0.9111	0.9492	0.9492	0.9512	0.9539
W%CH4 FRM CORRELATION	17.0967	18.2741	18.6775	18.9824	19.2817
W%CH4 (EXPTL/CORR)	0.9352	0.8125	0.8043	0.8299	0.8046
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL	CLR OIL	CLR BLU	CLR OIL
DENSITY	0.760	0.759	0.759	0.759	0.759
N, REFRACTIVE INDEX	1.4270	1.4266	1.4267	1.4262	1.4266
SIMULT'D DISTILATN					
10 WT % @ DEG F	283	274	278	277	287
16	302	297	298	298	303
50	434	439	444	445	448
84	590	617	635	639	638
90	632	667	688	693	691
RANGE(16-84 %)	288	320	337	341	335
WT % @ 420 F	47.00	46.00	45.50	45.50	44.50
WT % @ 700 F	96.29	93.42	90.92	90.58	90.69

NEW FORMAT JAN 25,85

Table A7

RESULT OF SYNGAS OPERATION

RUN NO. 11885-06
CATALYST CO/X4-U-103+U-101 12006-15 250 CC 111.3G(TO 122.6 +11.3)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-06-11	885-06-13	885-06-14	885-06-16	885-06-18
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	143.5	167.5	191.5	215.5	241.0
PRESSURE,PSIG	296	296	297	297	296
TEMP. C	261	261	261	272	272
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	24.00	24.00	24.00	24.00	25.50
EFFLNT GAS LITER	1167.05	1170.85	1153.25	1030.35	1124.95
GM AQUEOUS LAYER	162.44	157.52	157.43	186.08	192.77
GM OIL	37.92	39.40	41.37	60.52	61.68
MATERIAL BALANCE					
GM ATOM CARBON %	98.61	97.40	96.39	99.72	99.74
GM ATOM HYDROGEN %	99.11	98.07	97.37	99.23	99.41
GM ATOM OXYGEN %	103.80	102.92	101.68	103.62	103.84
RATIO CHX/(H2O+CO2)	0.8177	0.8008	0.8080	0.8830	0.8737
RATIO X IN CHX	2.4314	2.4449	2.4340	2.4644	2.4694
USAGE H2/CO PRODT	2.1866	2.2114	2.2036	2.0061	2.0342
FEED H2/CO FRM EFFLNT	1.0050	1.0069	1.0102	0.9951	0.9966
RESIDUAL H2/CO RATIO	0.6017	0.6142	0.6140	0.4962	0.5168
RATIO CO2/(H2O+CO2)	0.0647	0.0648	0.0633	0.1054	0.0994
K SHIFT IN EFFLNT	0.0416	0.0426	0.0415	0.0584	0.0570
SPECIFIC ACTIVITY SA	0.7339	0.6850	0.6920	0.7471	0.6701
CONVERSION					
ON CO %	25.45	24.59	24.92	33.04	31.62
ON H2 %	55.36	54.00	54.37	66.61	64.55
ON CO+H2 %	40.44	39.34	39.72	49.79	48.06
PRDT SELECTIVITY,WT %					
CH4	15.60	16.20	15.73	16.64	16.87
C2 HC'S	3.42	3.76	3.58	3.74	4.04
C3H8	4.77	4.69	4.64	5.06	5.27
C3H6=	3.47	2.87	2.78	2.67	2.94
C4H10	3.97	3.61	3.62	3.77	3.84
C4H8=	4.89	4.42	4.42	4.08	4.11
C5H12	3.62	3.55	3.40	3.73	3.83
C5H10=	4.89	4.78	4.43	4.14	4.08
C6H14	4.49	4.43	4.07	4.23	4.27
C6H12= & CYCLO'S	4.42	4.39	4.04	3.54	3.36
C7+ IN GAS	16.26	14.38	14.91	10.39	9.52
LIQ HC'S	30.21	32.91	34.39	37.99	37.87
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A7 (continued)

SUB-GROUPING					
C1 -C4	36.12	35.56	34.76	35.97	37.09
C5 -420 F	46.97	46.01	45.63	45.03	45.12
420-700 F	14.10	15.42	16.48	16.01	15.35
700-END PT	2.81	3.01	3.12	2.99	2.45
C5+-END PT	63.88	64.44	65.24	64.03	62.91
ISO/NORMAL MOLE RATIO					
C4	0.0929	0.0530	0.0535	0.0589	0.0586
C5	0.0699	0.0552	0.0560	0.0785	0.0747
C6	0.3830	0.3663	0.3127	0.3985	0.3710
C4=	0.1021	0.0863	0.0868	0.0933	0.0963
PARAFFIN/OLEFIN RATIO					
C3	1.3105	1.5616	1.5904	1.8081	1.7089
C4	0.7840	0.7892	0.7916	0.8901	0.9018
C5	0.7195	0.7231	0.7463	0.8764	0.9128
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7917	0.7949	0.7968	0.7937	0.7843
RATIO CH4/(1-A)**2	3.5951	3.8515	3.8071	3.9092	3.6263
ALPHA FRM CORRELATION	0.8355	0.8345	0.8345	0.8443	0.8423
ALPHA (EXPTL/CORR)	0.9476	0.9526	0.9548	0.9401	0.9312
W%CH4 FRM CORRELATION	19.0602	19.3700	19.3659	18.5889	19.2025
W%CH4 (EXPTL/CORR)	0.8185	0.8361	0.8120	0.8953	0.8785
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL	CLR OIL	CLR OIL	CLR OIL
DENSITY	0.759	0.759	0.759	0.754	0.752
N, REFRACTIVE INDEX	1.4265	1.4265	1.4266	1.4245	1.4230
SIMULT'D DISTILATN					
10 WT % @ DEG F	289	290	291	256	250
16	308	311	320	292	290
50	449	450	451	420	413
84	639	636	636	611	592
90	691	689	688	670	651
RANGE(16-84 %)	331	325	316	319	302
WT % @ 420 F	44.00	44.00	43.00	50.00	53.00
WT % @ 700 F	90.69	90.85	90.92	92.14	93.53

NEW FORMAT JAN 25,85

Table A8

RESULT OF SYNGAS OPERATION

RUN NO. 11885-06
CATALYST CO/X4-U-103+U-101 12006.15 250 CC 111.3G(TO 122.6 +11.3)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-06-22	885-06-24	885-06-26	885-06-28	885-06-30
FEED H2:CO:AR	50:50: 0	50:50: 0	28:71: 0	28:71: 0	28:71: 0
HRS ON STREAM	287.5	311.5	335.5	359.5	385.7
PRESSURE,PSIG	297	296	296	297	293
TEMP. C	271	272	269	270	270
FEED CC/MIN	1260	1260	1190	1190	1190
HOURS FEEDING	24.00	24.00	24.00	24.00	26.17
EFFLNT GAS LITER	1066.40	1100.80	1339.75	1346.95	1465.15
GM AQUEOUS LAYER	178.08	170.60	84.81	81.55	87.90
GM OIL	38.37	48.07	27.40	29.89	34.63
MATERIAL BALANCE					
GM ATOM CARBON %	95.70	98.85	97.24	97.49	97.15
GM ATOM HYDROGEN %	96.17	98.91	102.94	102.87	103.26
GM ATOM OXYGEN %	102.41	103.13	99.80	99.77	99.31
RATIO CHX/(H2O+CO2)	0.7862	0.8593	0.8009	0.8182	0.8268
RATIO X IN CHX	2.4665	2.4754	2.3362	2.3482	2.3562
USAGE H2/CO PRODT	2.1628	2.0772	2.0070	1.9847	1.9678
FEED H2/CO FRM EFFLNT	1.0049	1.0007	0.4286	0.4272	0.4304
RESIDUAL H2/CO RATIO	0.5417	0.5558	0.2125	0.2155	0.2185
RATIO CO2/(H2O+CO2)	0.0851	0.0905	0.1091	0.1128	0.1170
K SHIFT IN EFFLNT	0.0504	0.0553	0.0260	0.0274	0.0289
SPECIFIC ACTIVITY SA	0.5783	0.5478	1.0672	0.9820	0.9869
CONVERSION					
ON CO %	28.57	29.24	12.05	11.97	12.11
ON H2 %	61.50	60.70	56.40	55.59	55.38
ON CO+H2 %	45.08	44.97	25.35	25.03	25.13
PRDT SELECTIVITY,WT %					
CH4	17.06	17.29	13.19	13.53	13.60
C2 HC'S	3.59	3.79	2.28	2.32	2.57
C3H8	5.40	5.23	1.98	2.00	2.08
C3H6=	3.03	2.27	4.11	3.98	3.96
C4H10	4.05	4.00	1.54	1.49	1.51
C4H8=	4.55	4.03	5.03	5.00	5.10
C5H12	4.16	3.74	1.71	1.73	1.78
C5H10=	4.44	3.82	4.96	5.04	4.98
C6H14	4.79	4.75	2.21	2.48	2.44
C6H12= & CYCLO'S	3.85	3.50	3.63	4.39	4.28
C7+ IN GAS	16.35	13.64	22.49	17.62	15.01
LIQ HC'S	28.74	33.95	36.87	40.40	42.67

Table A8 (continued)

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	37.68	36.61	28.13	28.33	28.83
C5 -420 F	47.81	46.25	47.91	45.21	43.01
420-700 F	12.27	14.84	20.05	21.61	23.23
700-END PT	2.24	2.31	3.91	4.85	4.93
C5+-END PT	62.32	63.39	71.87	71.67	71.17
ISO/NORMAL MOLE RATIO					
C4	0.0551	0.0561	0.0948	0.0852	0.0760
C5	0.0688	0.0524	0.1673	0.1500	0.1318
C6	0.3607	0.3315	0.7178	0.6524	0.6667
C4=	0.0945	0.1017	0.0840	0.0796	0.0842
PARAFFIN/OLEFIN RATIO					
C3	1.7031	2.1982	0.4595	0.4799	0.5000
C4	0.8603	0.9601	0.2951	0.2881	0.2864
C5	0.9089	0.9515	0.3354	0.3347	0.3468
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7777	0.7828	0.8124	0.8205	0.8219
RATIO CH4/(1-A)**2	3.4539	3.6643	3.7467	4.2014	4.2872
ALPHA FRM CORRELATION	0.8401	0.8388	0.8858	0.8850	0.8844
ALPHA (EXPTL/CORR)	0.9258	0.9333	0.9171	0.9271	0.9293
W%CH4 FRM CORRELATION	19.6960	20.3040	5.1142	5.5457	5.7533
W%CH4 (EXPTL/CORR)	0.8663	0.8513	2.5790	2.4399	2.3645
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL	CLR OIL	CLR OIL	CLR OIL
DENSITY	0.754	0.754	0.770	0.771	0.762
N, REFRACTIVE INDEX	1.4236	1.4235	1.4324	1.4329	1.4322
SIMULT'D DISTILATN					
10 WT % @ DEG F	265	271	324	325	326
16	293	294	345	346	347
50	421	421	480	483	484
84	608	599	656	667	663
90	668	660	706	718	714
RANGE(16-84 %)	315	305	311	321	316
WT % @ 420 F	49.50	49.50	35.00	34.50	34.00
WT % @ 700 F	92.21	93.21	89.40	88.00	88.45

NEW FORMAT JAN 25,85

Table A9

RESULT OF SYNGAS OPERATION

RUN NO. 11885-06
CATALYST CO/X4-U-103+U-101 12006-15 250 CC 111.3G(TO 122.6 +11.3)
FEED H2:CO:ARGON= 28:71:0 @ 1190 CC/MN OR 286 GHSV

RUN & SAMPLE NO.	11885-06-32	885-06-34
FEED H2:CO:AR	28:71: 0	28:71: 0
HRS ON STREAM	409.1	431.5
PRESSURE,PSIG	294	296
TEMP. C	271	271
FEED CC/MIN	1190	1190
HOURS FEEDING	23.42	22.42
EFFLNT GAS LITER	1322.35	1251.73
GM AQUEOUS LAYER	81.14	75.31
GM OIL	31.53	29.30
MATERIAL BALANCE		
GM ATOM CARBON %	98.05	97.25
GM ATOM HYDROGEN %	104.77	102.79
GM ATOM OXYGEN %	100.33	99.27
RATIO CHX/(H2O+CO2)	0.8208	0.8377
RATIO X IN CHX	2.3553	2.3594
USAGE H2/CO PRODT	1.9874	1.9620
FEED H2/CO FRM EFFLNT	0.4326	0.4280
RESIDUAL H2/CO RATIO	0.2182	0.2144
RATIO CO2/(H2O+CO2)	0.1122	0.1164
K SHIFT IN EFFLNT	0.0276	0.0282
SPECIFIC ACTIVITY SA	0.9369	0.9630
CONVERSION		
ON CO %	12.12	12.22
ON H2 %	55.69	56.01
ON CO+H2 %	25.28	25.34
PRDT SELECTIVITY,WT %		
CH4	13.52	13.78
C2 HC'S	2.71	2.71
C3H8	2.08	2.11
C3H6=	3.96	4.00
C4H10	1.49	1.56
C4H8=	4.91	5.10
C5H12	1.77	1.80
C5H10=	4.90	4.92
C6H14	2.43	2.33
C6H12= & CYCLO'S	4.37	4.39
C7+ IN GAS	15.06	15.65
LIQ HC'S	42.81	41.63
TOTAL	100.00	100.00

Table A9 (continued)

SUB-GROUPING		
C1 -C4	28.65	29.27
C5 -420 F	43.95	44.08
420-700 F	22.53	22.07
700-END PT	4.86	4.58
C5+-END PT	71.35	70.73
ISO/NORMAL MOLE RATIO		
C4	0.0903	0.0914
C5	0.1626	0.1505
C6	0.6083	0.6432
C4=	0.0774	0.0802
PARAFFIN/OLEFIN RATIO		
C3	0.5023	0.5027
C4	0.2924	0.2953
C5	0.3515	0.3557
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8178	0.8159
RATIO CH4/(1-A)**2	4.0727	4.0681
ALPHA FRM CORRELATION	0.8844	0.8852
ALPHA (EXPTL/CORR)	0.9248	0.9217
W%CH4 FRM CORRELATION	5.9508	5.6910
W%CH4 (EXPTL/CORR)	2.2712	2.4219
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLDY &SLD	OIL &SLD
DENSITY	0.757	0.741
N, REFRACTIVE INDEX	1.4322	1.4318
SIMULT'D DISTILATN		
10 WT % @ DEG F	321	322
16	345	345
50	477	476
84	660	656
90	714	710
RANGE(16-84 %)	315	311
WT % @ 420 F	36.00	36.00
WT % @ 700 F	88.64	89.00

NEW FORMAT JAN 25,85

V. Run 4 (11885-07) with Catalyst 4 ($Co/X_4/UCC-103+UCC-101$)

The purpose of this run was to test the effects of the extruding agent used during the catalyst's preparation. The catalyst was formulated in the same way as Catalyst 3, with the same constituents, but without the extruding agent used in Catalyst 3.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. A78-81. Simulated distillations of the C_5^+ product are plotted in Figs. A82-85. Carbon number product distributions are plotted in Figs. A86-91. Chromatograms from simulated distillations are reproduced in Figs. A92-94. Detailed material balances appear in Tables A10-11.

The syngas conversion after about 40 hours on stream was 47.7 percent, for a specific activity of 0.98. This was only slightly better than the performance of Catalyst 3, with which the conversion was 45.8 percent and the specific activity 0.88.

By linear least squares analysis the loss of conversion was one percentage point every 34 hours as against one percentage point every 20 hours with Catalyst 3, but the difference is within the experimental error. The product selectivity, also, was similar to that of Catalyst 3.

Evidently the extruding agent has little or no effect on this catalyst's activity.

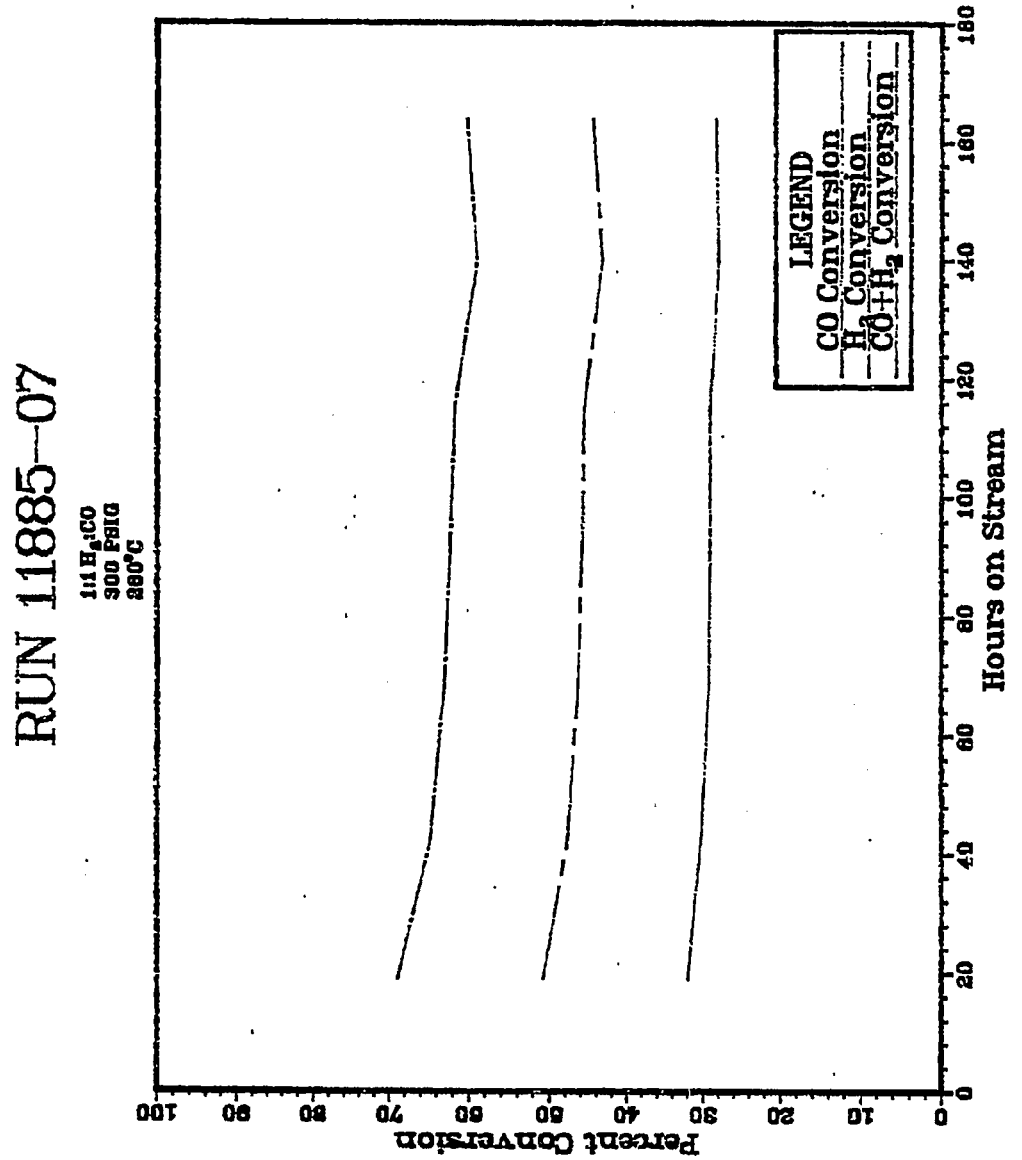

RUN 11885-07
1:1 H2:CO
300 Psig
260°C
Percent Conversion
Hours on Stream
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion

Fig. A78

RUN 11885-07

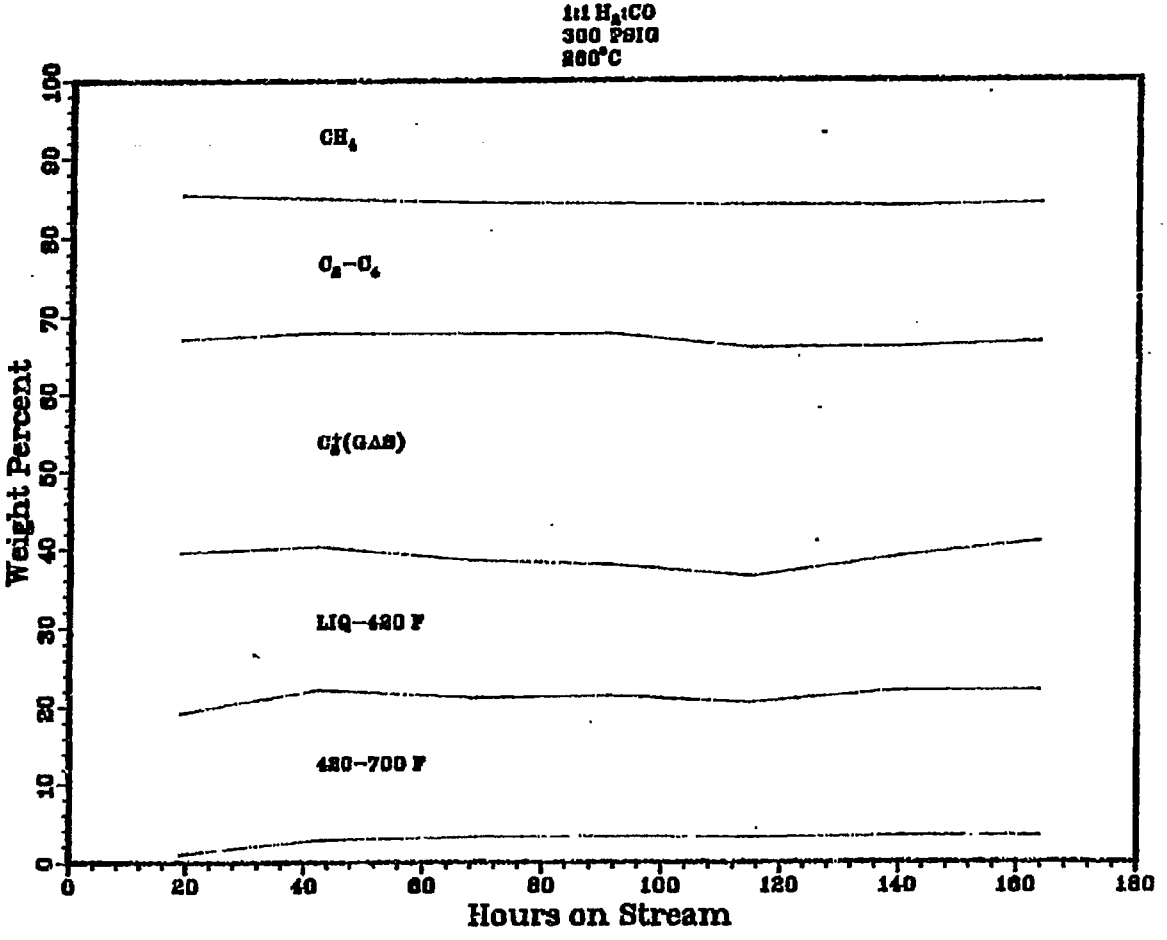


Fig. A79

RUN 11885-07

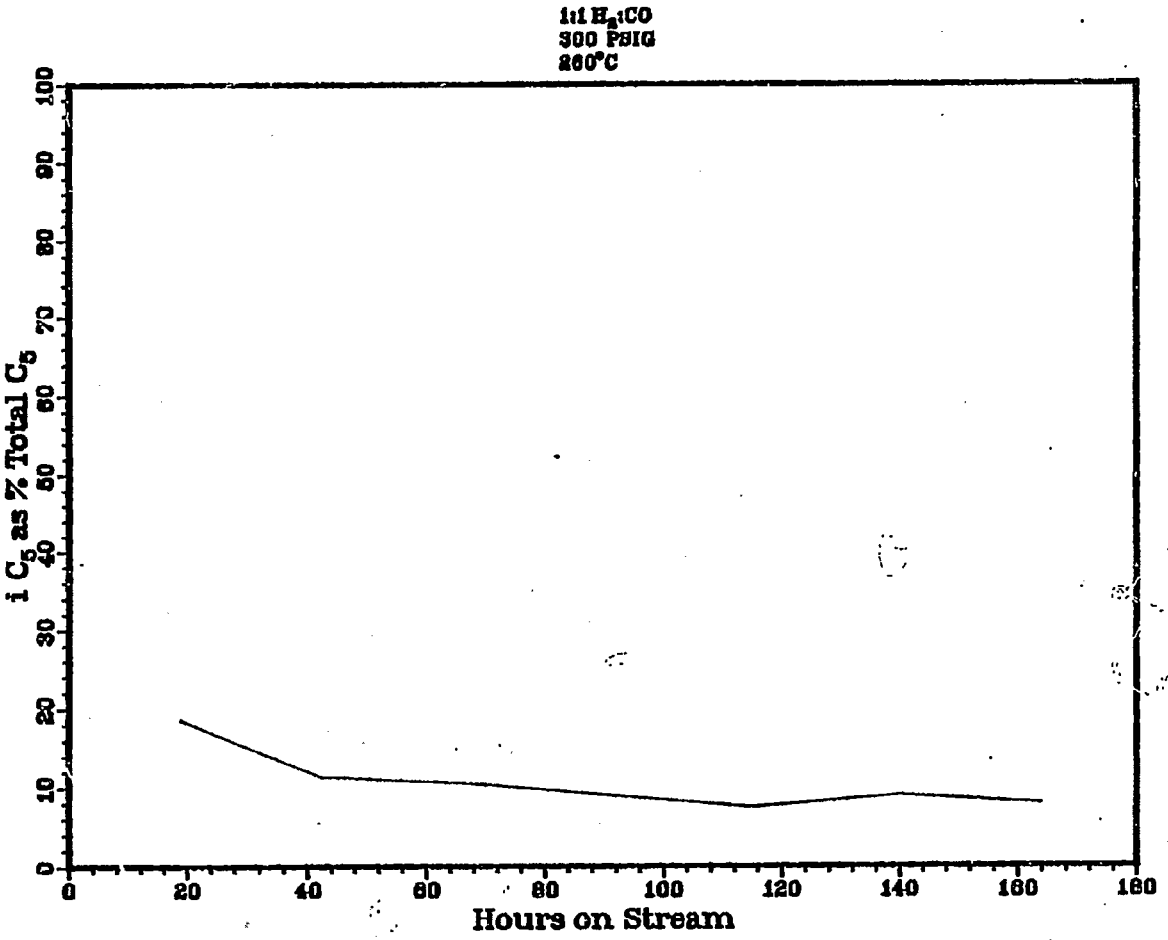


Fig. A80

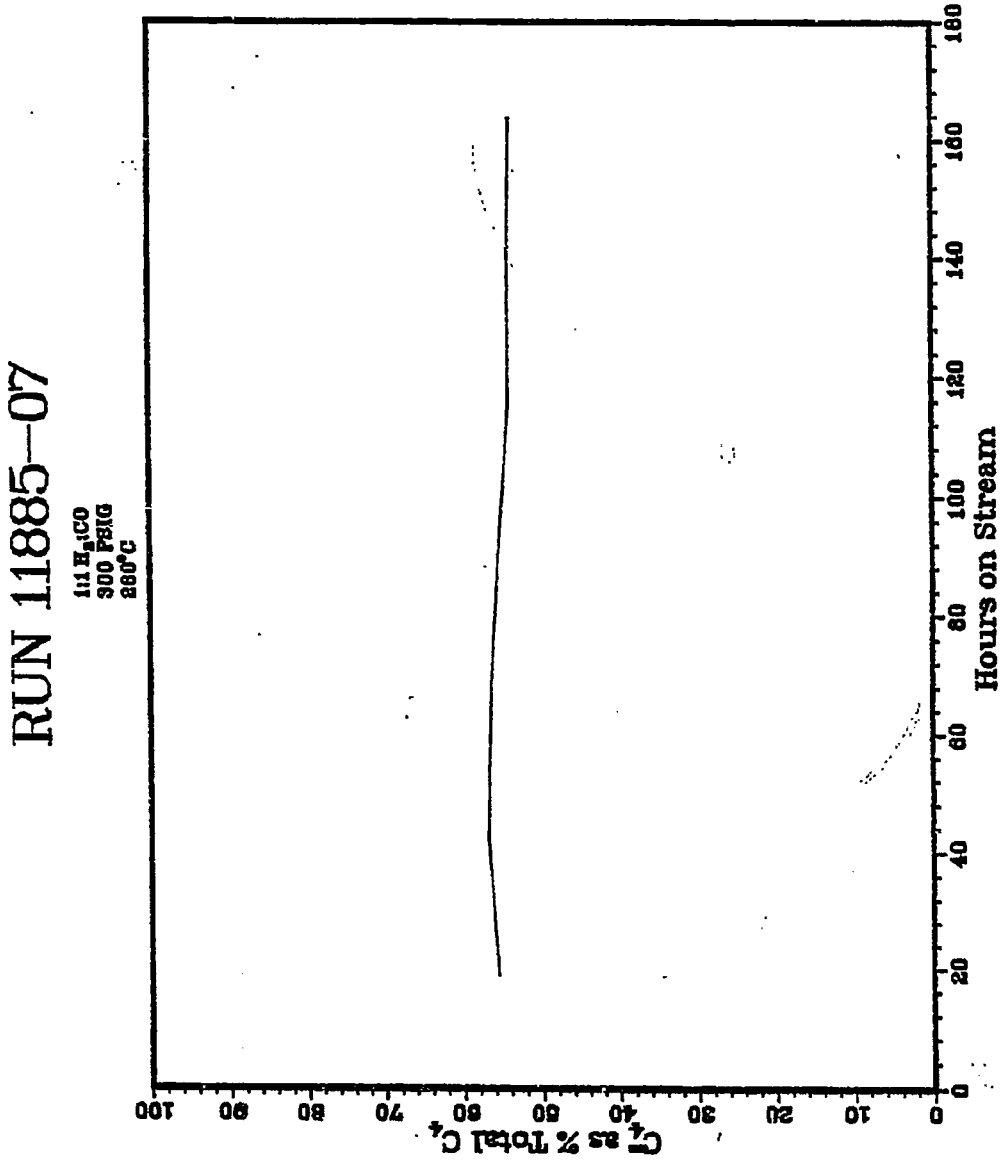

RUN 11885-07
1:1 H2:CO
300 PSIG
280°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. A81

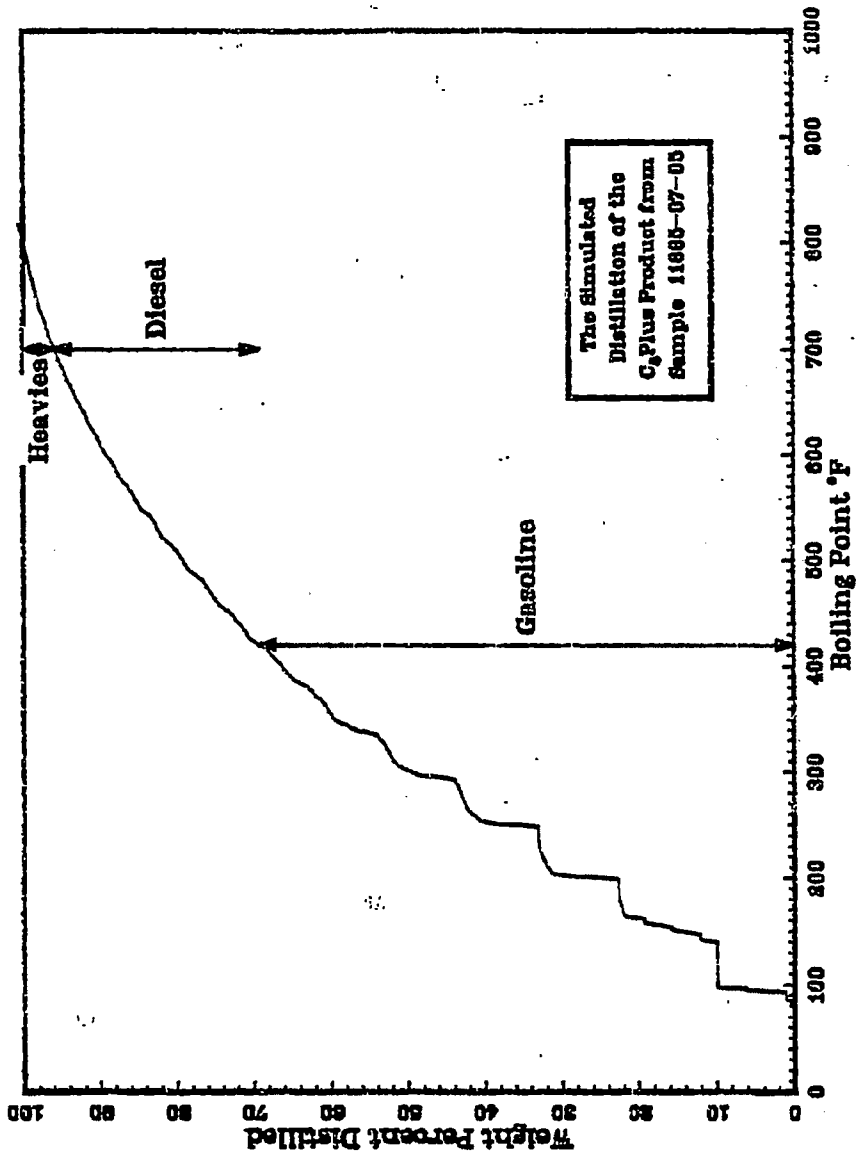

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5Plus Product from Sample 11605-07-05

Fig. A82

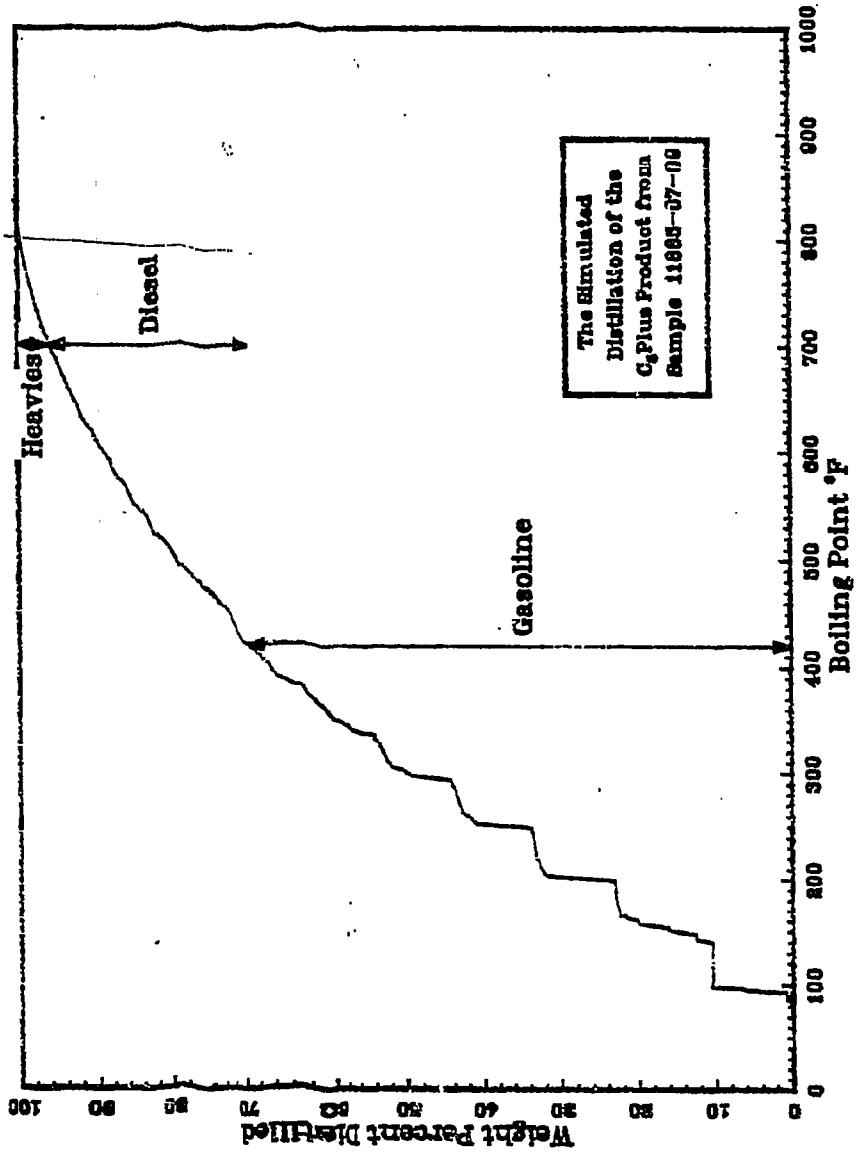

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample 11865-57-08

Fig. A83

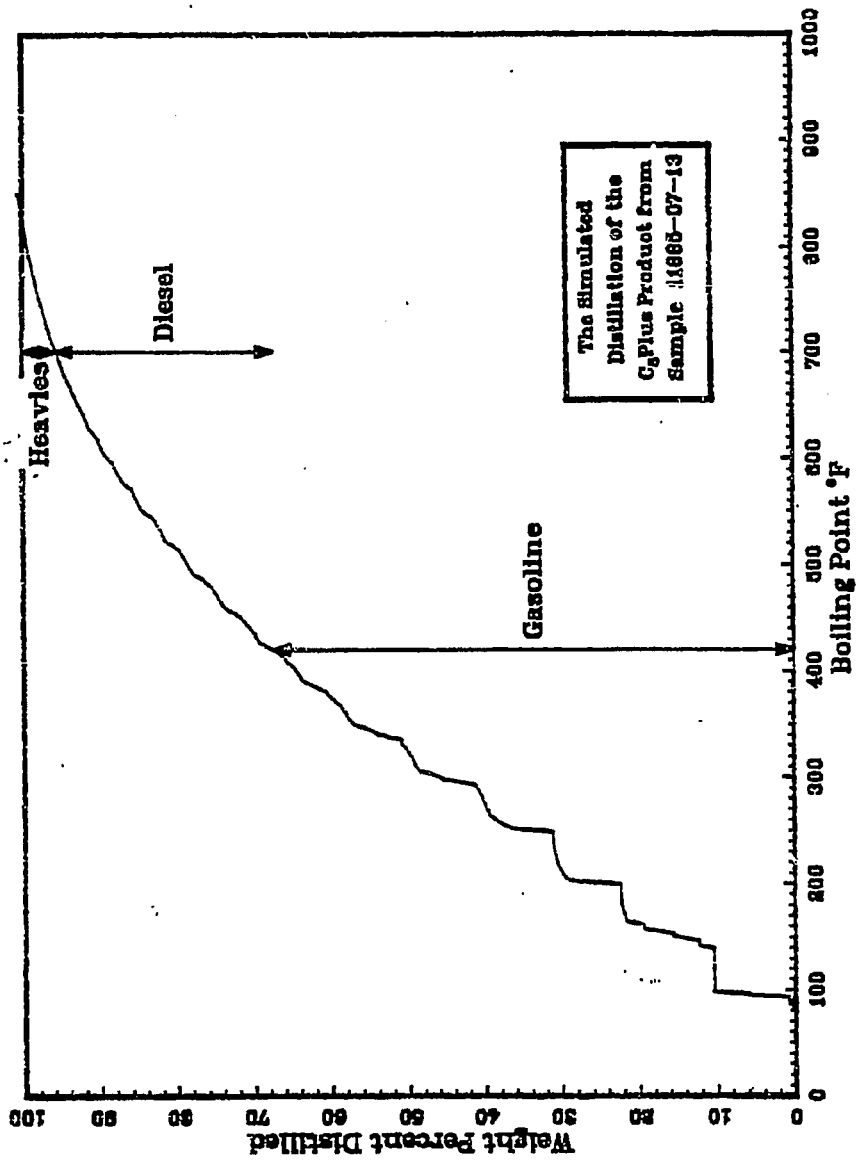

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Gasoline
Diesel
Heavies
The Simulated Distillation of the C5 Plus Product from Sample #1666-07-13

Fig. A84

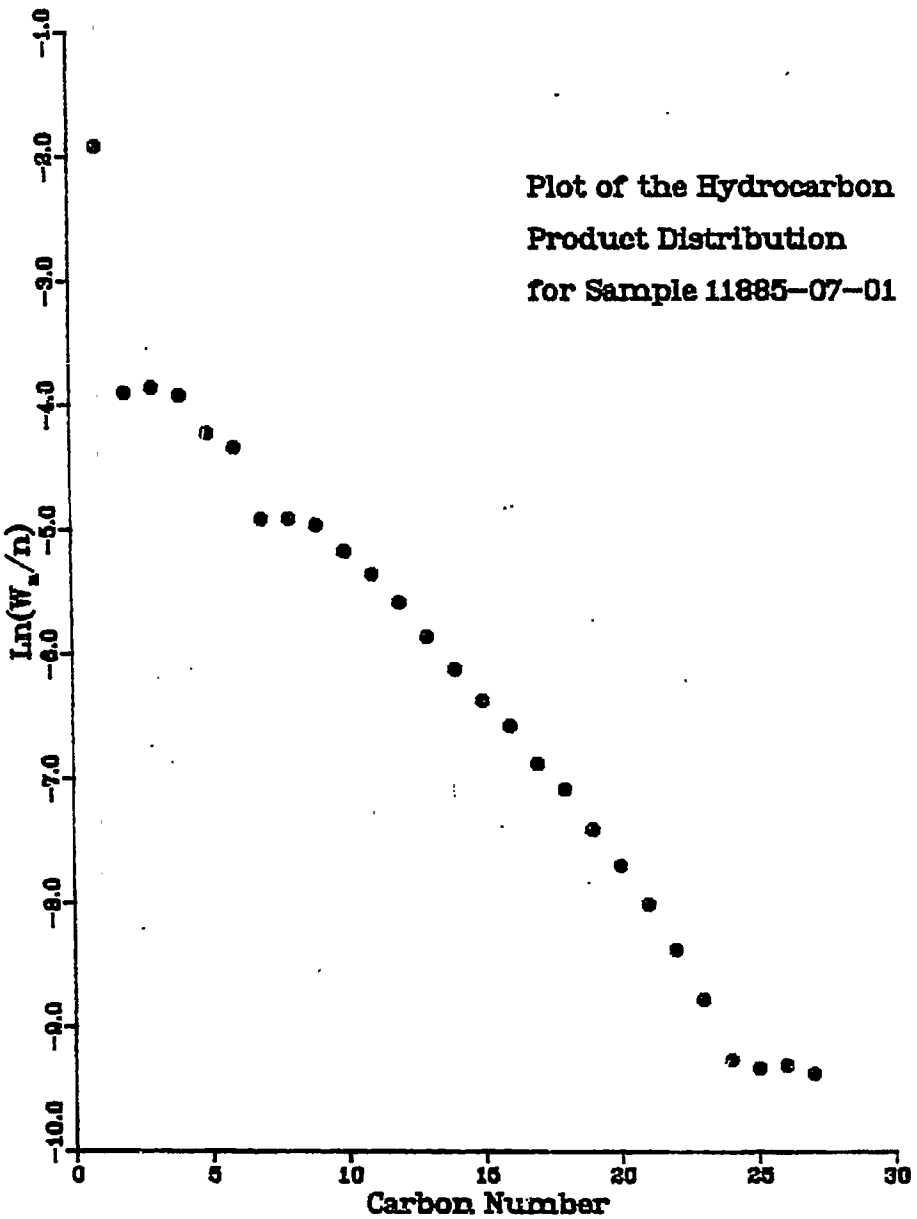

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-01
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A85

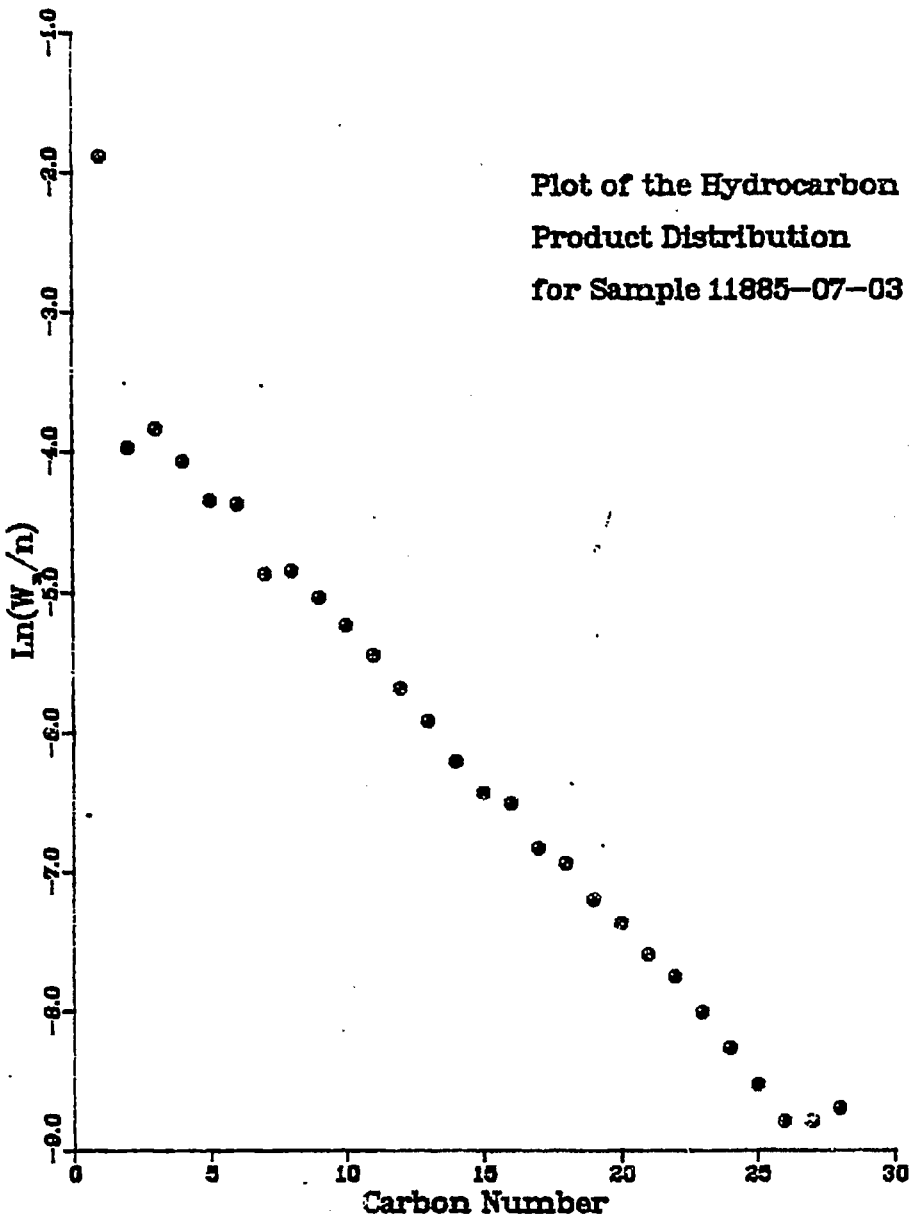

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-03
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. A86

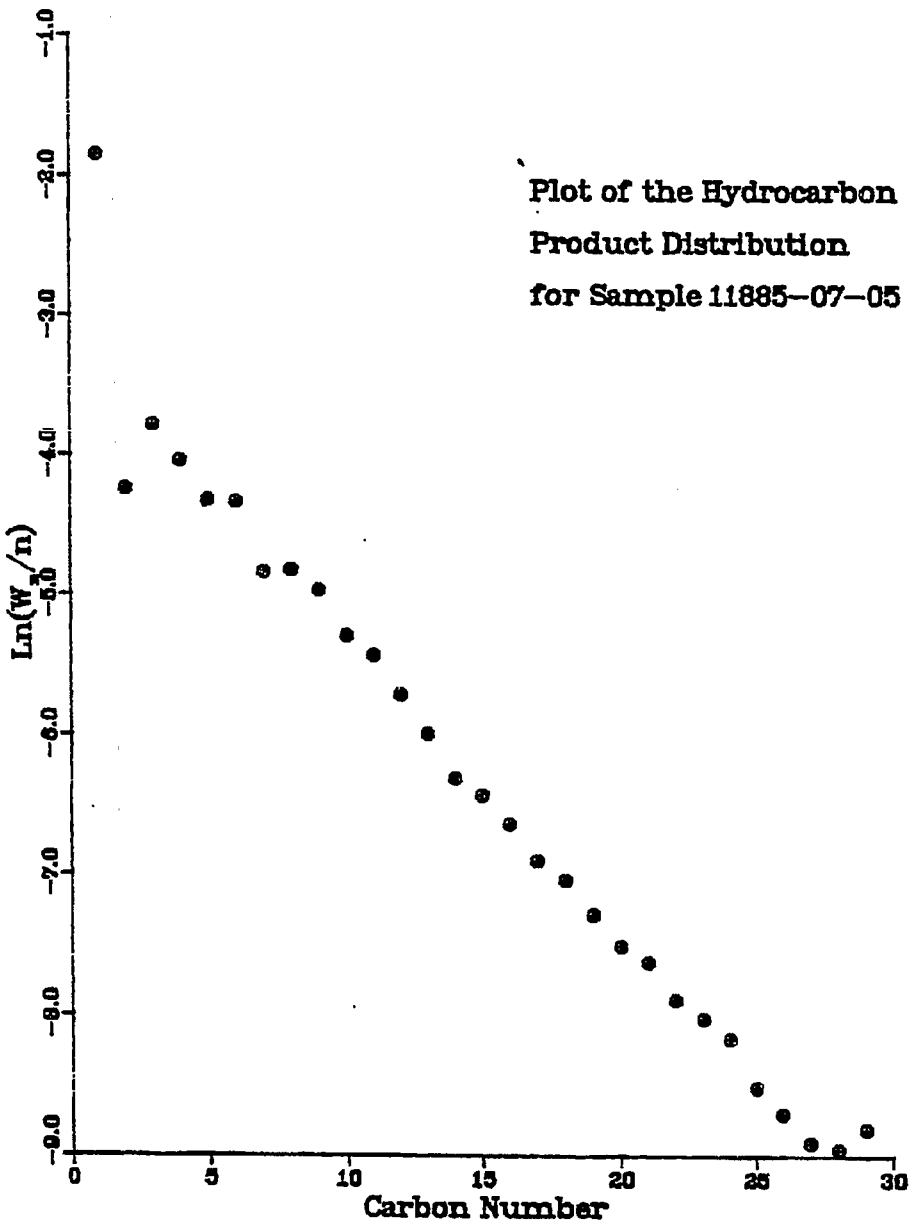

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
Carbon Number

Fig. A87

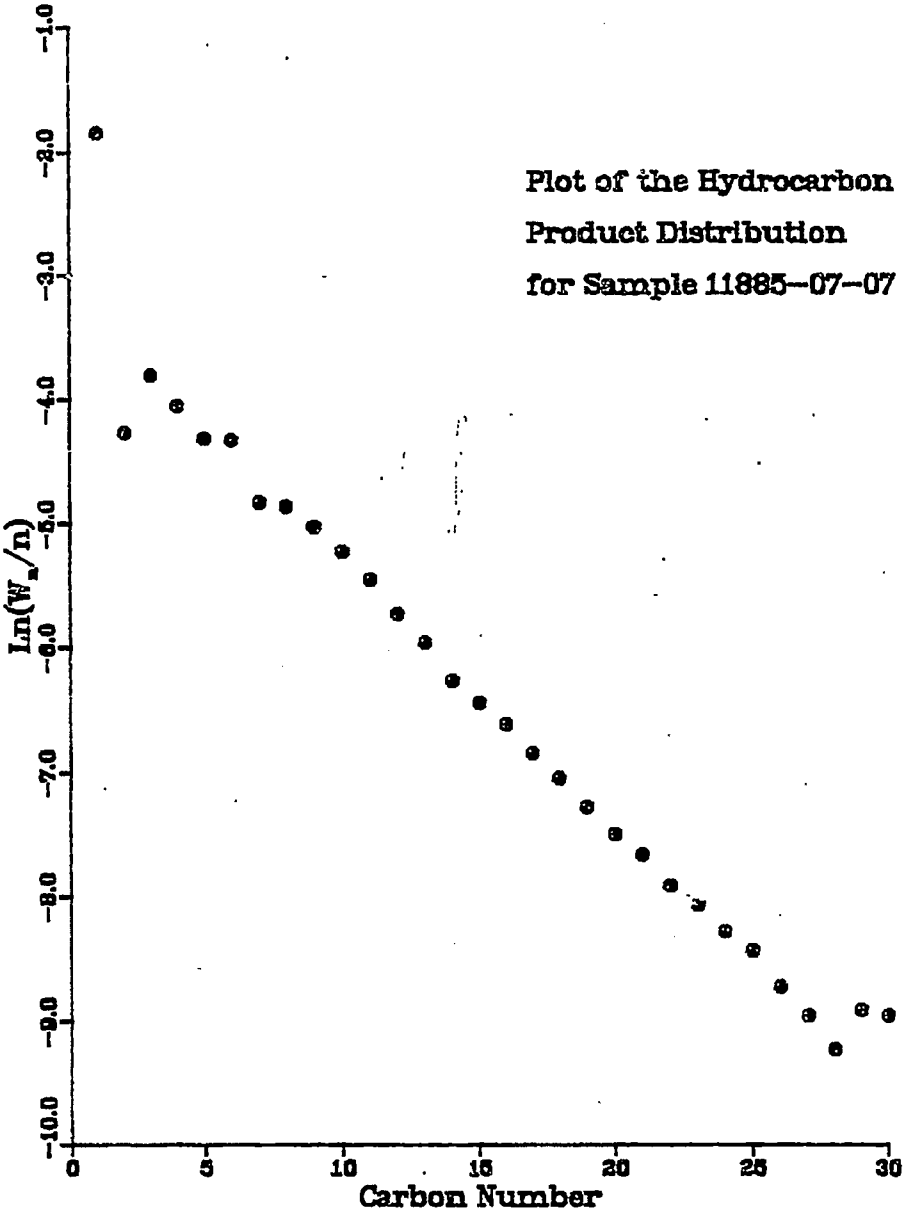

Plot of the Hydrocarbon
Product Distribution
for Sample 11885--07--07
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A88

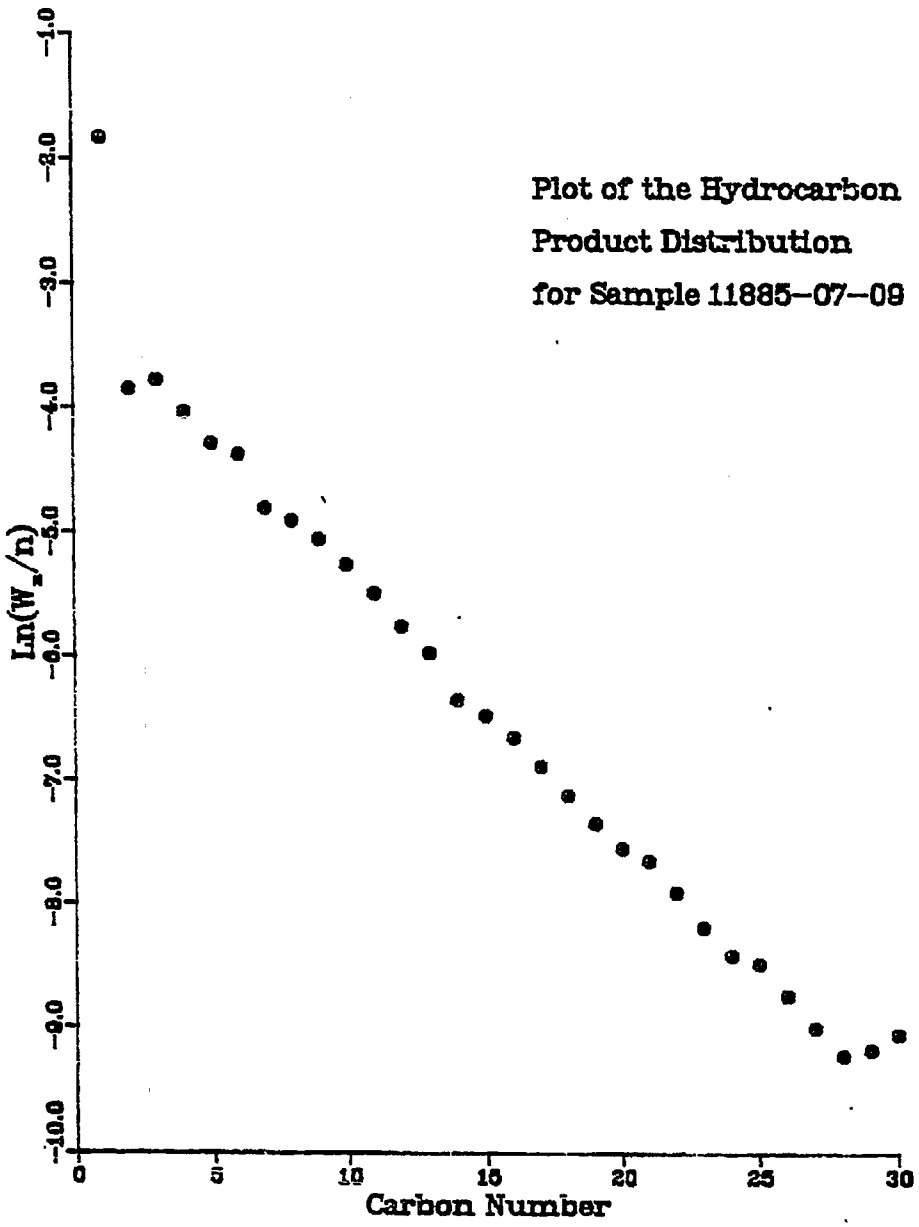

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-09
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A89

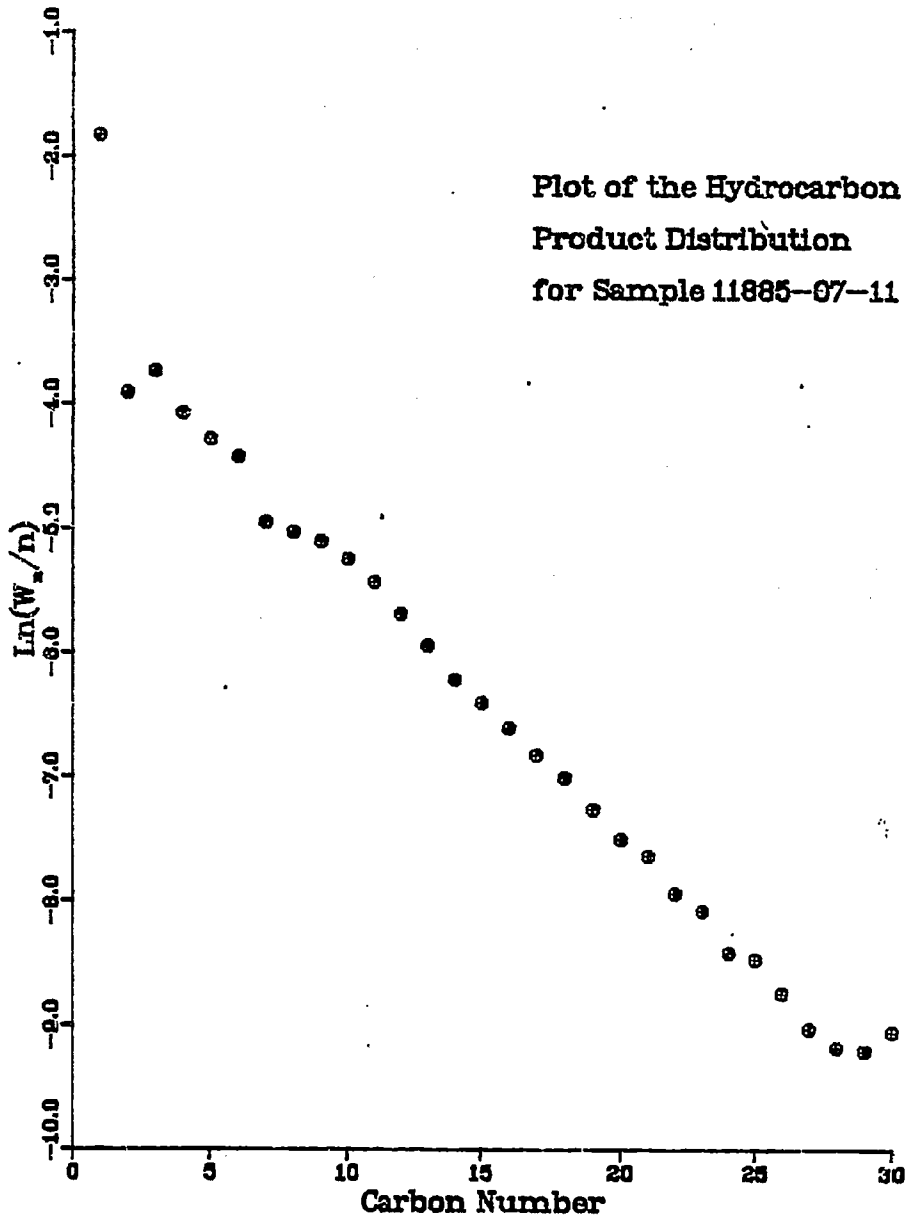

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-11
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A90

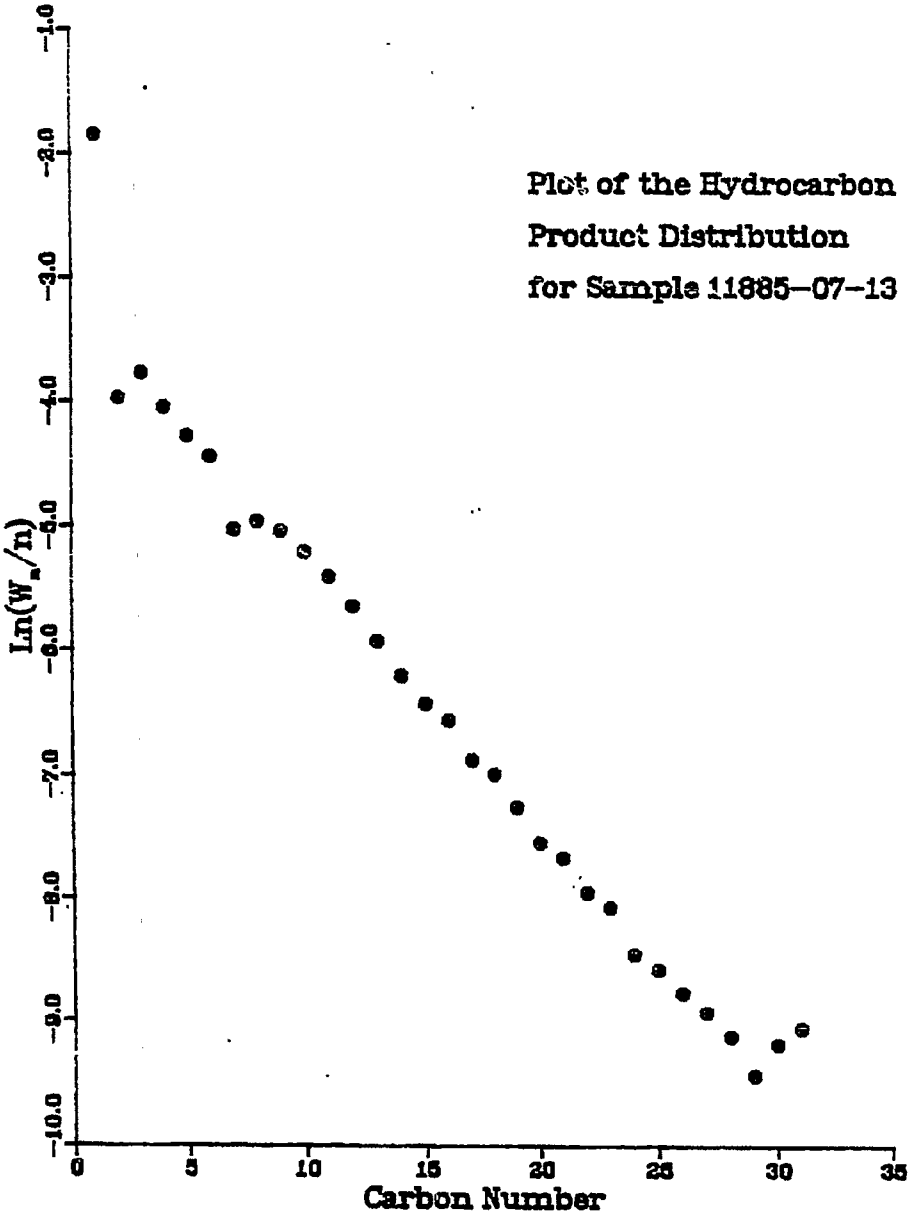
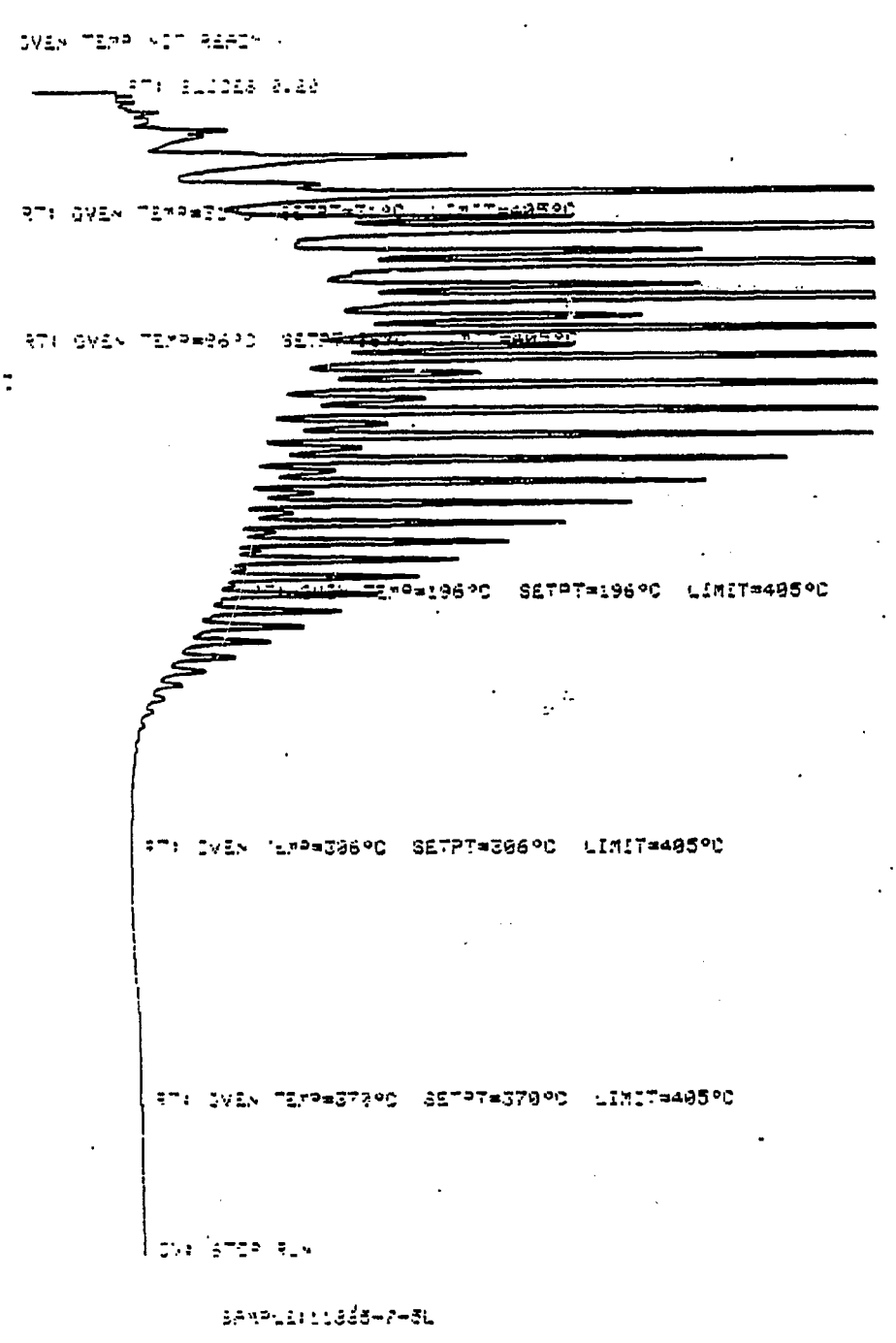

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-07-13
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A91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SETPT=396°C LIMIT=405°C
SETPT=370°C LIMIT=405°C

Fig. A92

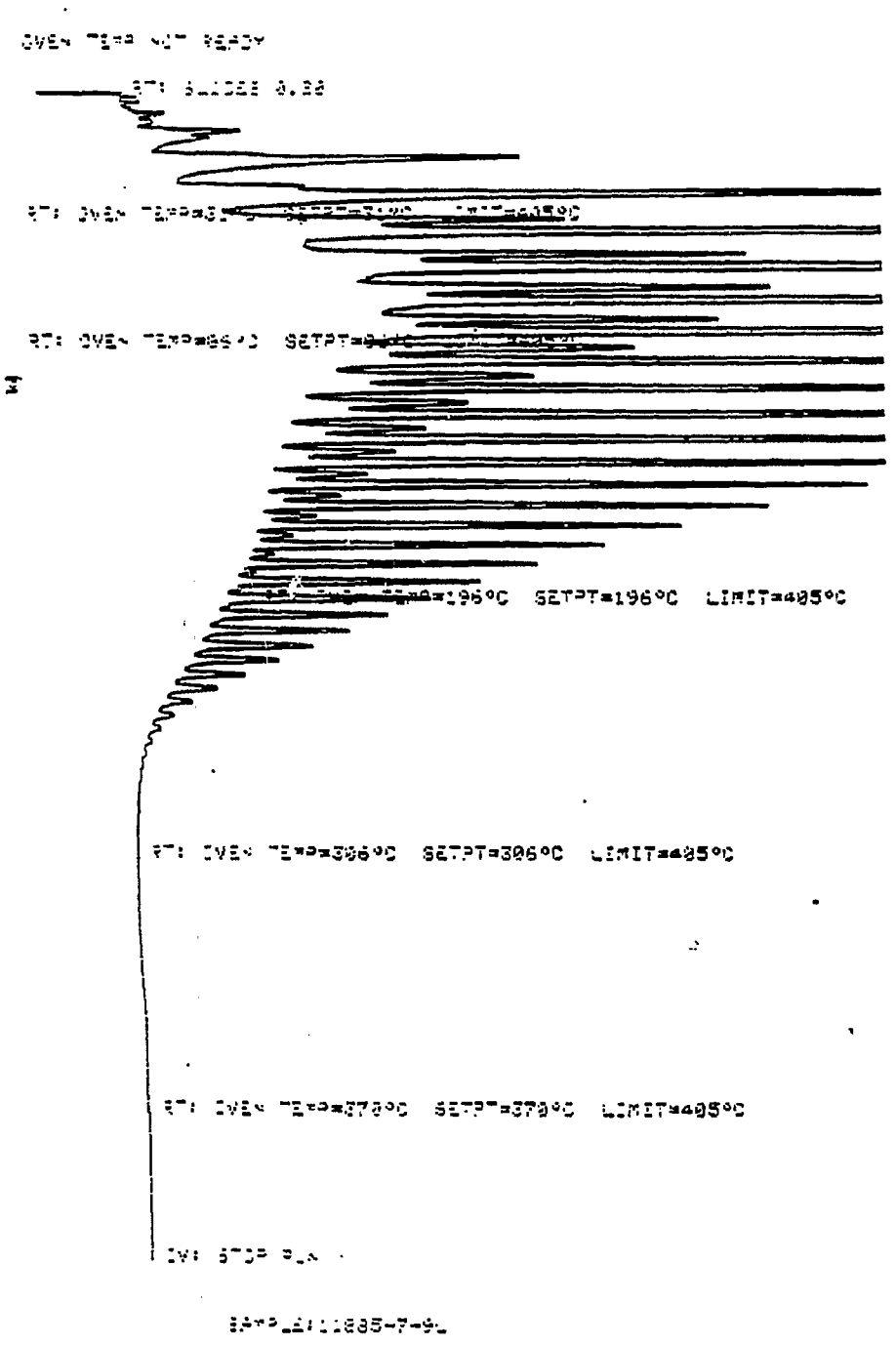

SETPT=196°C LIMIT=405°C
SETPT=306°C LIMIT=405°C
SETPT=370°C LIMIT=405°C

Fig. A93

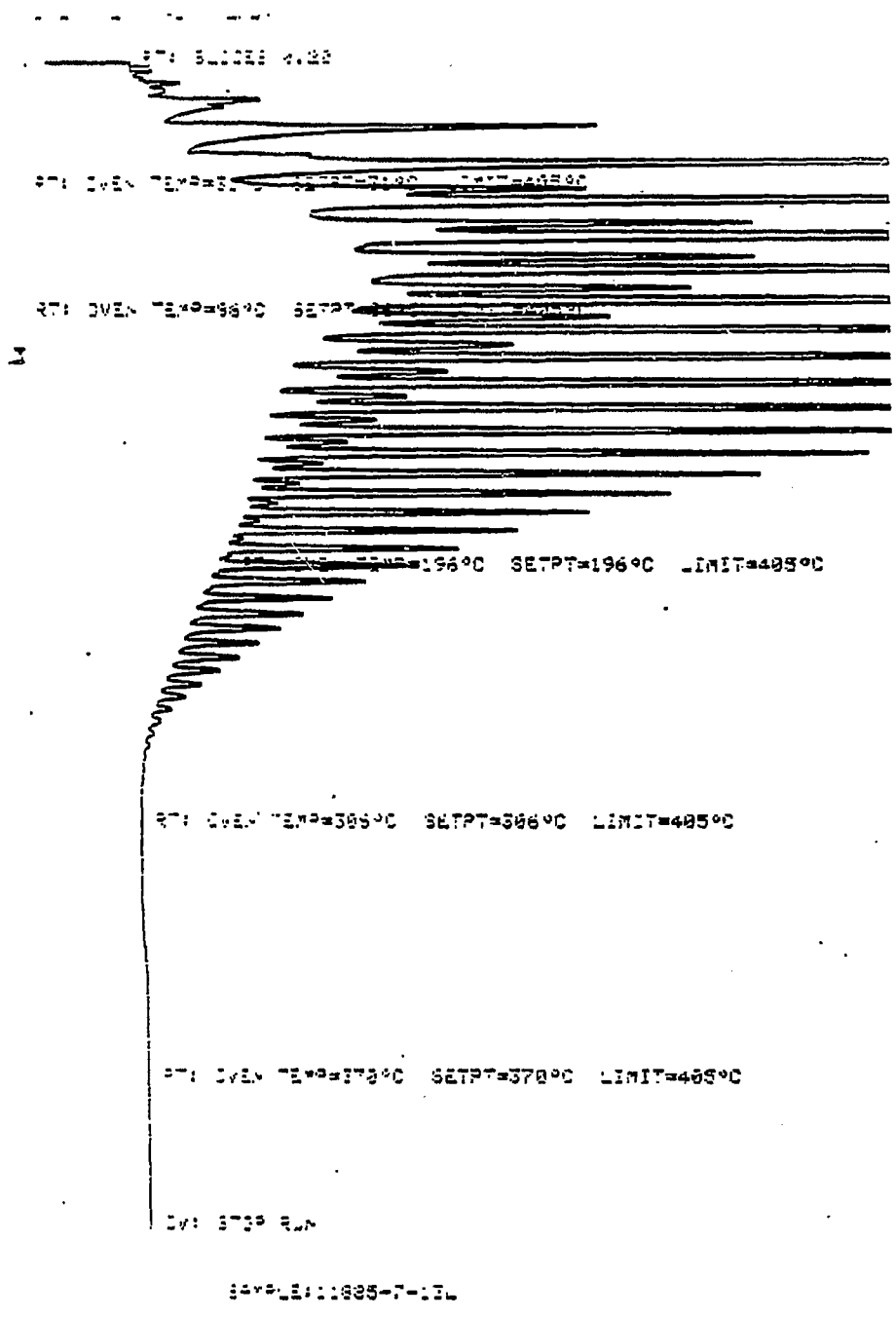

SETPT=196°C LIMIT=405°C
SETPT=366°C LIMIT=405°C
SETPT=370°C LIMIT=405°C

Fig. A94

Table A10

RESULT OF SYNGAS OPERATION

RUN NO. 11885-07
CATALYST CO/X4-U-103+U-101 12006-26 250 CC 121.1G(TO 122.9G +1.8)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-07-01	885-07-03	885-07-05	885-07-07	885-07-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.0	42.3	68.0	90.8	114.8
PRESSURE,PSIG	300	296	297	297	295
TEMP. C	264	262	262	262	262
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	19.00	23.25	26.00	22.75	24.00
EFFLNT GAS LITER	743.48	993.84	1124.56	1007.90	1080.40
GM AQUEOUS LAYER	168.07	186.41	203.07	174.15	181.32
GM OIL	45.93	57.66	58.91	51.74	53.14
MATERIAL BALANCE					
GM ATOM CARBON %	91.88	96.66	95.45	97.24	98.18
GM ATOM HYDROGEN %	96.41	98.54	98.02	99.20	100.34
GM ATOM OXYGEN %	100.20	101.86	100.99	101.89	102.15
RATIO CHX/(H2O+CO2)	0.7661	0.8404	0.8254	0.8512	0.8716
RATIO X IN CHX	2.4107	2.4153	2.4250	2.4284	2.4342
USAGE H2/CO PRODT	2.2663	2.1853	2.2166	2.1873	2.1652
FEED H2/CO FRM EFFLNT	1.0493	1.0195	1.0269	1.0202	1.0219
RESIDUAL H2/CO RATIO	0.4797	0.5146	0.5359	0.5420	0.5509
RATIO CO2/(H2O+CO2)	0.0573	0.0560	0.0532	0.0539	0.0549
K SHIFT IN EFFLNT	0.0292	0.0305	0.0301	0.0309	0.0320
SPECIFIC ACTIVITY SA	1.0201	0.9755	0.8788	0.8609	0.8514
CONVERSION					
ON CO %	31.88	30.22	29.21	29.06	29.18
ON H2 %	68.86	64.78	63.06	62.32	61.82
ON CO+H2 %	50.81	47.67	46.36	45.86	45.67
PRDT SELECTIVITY,WT %					
CH4	14.68	15.16	15.66	15.84	16.04
C2 HC'S	4.05	3.76	2.87	2.80	4.25
C3H8	3.85	4.00	4.21	4.25	4.44
C3H6=	2.49	2.46	2.58	2.47	2.43
C4H10	3.58	3.02	3.12	3.16	3.31
C4H8=	4.33	3.82	3.89	3.79	3.76
C5H12	3.28	2.74	2.80	2.78	3.04
C5H10=	4.01	3.72	3.84	3.86	3.79
C6H14	4.66	3.97	3.93	4.12	4.04
C6H12= & CYCLO'S	3.17	3.61	3.93	3.79	3.48
C7+ IN GAS	12.41	13.43	14.70	15.11	14.91
LIQ HC'S	39.49	40.30	38.47	38.04	36.52
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A10 (continued)

SUB-GROUPING					
C1 -C4	32.98	32.23	32.34	32.30	34.22
C5 -420 F	47.80	45.60	46.51	46.27	45.21
420-700 F	18.15	19.48	17.98	18.24	17.47
700-END PT	1.07	2.69	3.17	3.19	3.10
C5+-END PT	67.02	67.77	67.66	67.70	65.78
ISO/NORMAL MOLE RATIO					
C4	0.2095	0.1141	0.0963	0.0889	0.0779
C5	0.2271	0.1277	0.1168	0.0991	0.0807
C6	0.8975	0.6981	0.5969	0.6100	0.4913
C4=	0.0687	0.0769	0.0813	0.0824	0.0836
PARAFFIN/OLEFIN RATIO					
C3	1.4756	1.5509	1.5559	1.6436	1.7455
C4	0.7981	0.7615	0.7732	0.8061	0.8493
C5	0.7952	0.7156	0.7089	0.7007	0.7790
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7780	0.8120	0.8080	0.8057	0.8041
RATIO CH4/(1-A)**2	2.9779	4.2895	4.2487	4.1963	4.1788
ALPHA FRM CORRELATION	0.8464	0.8430	0.8411	0.8405	0.8397
ALPHA (EXPTL/CORR)	0.9192	0.9631	0.9607	0.9586	0.9576
W%CH4 FRM CORRELATION	16.3113	16.9223	17.5365	17.7052	17.9537
W%CH4 (EXPTL/CORR)	0.8999	0.8961	0.8932	0.8945	0.8934
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	CLR OIL	CLR OIL	CLR OIL	CLR OIL
DENSITY	0.7522	0.7600	0.7599	0.7597	0.7593
N, REFRACTIVE INDEX	1.4250	1.4272	1.4272	1.4273	1.4271
SIMULT'D DISTILATN					
10 WT % @ DEG F	265	273	275	287	286
16	296	304	304	306	306
50	416	442	443	449	448
84	571	622	629	629	631
90	612	669	683	684	687
RANGE(16-84 %)	275	318	325	323	325
WT % @ 420 F	51.33	45.00	45.00	43.67	43.67
WT % @ 700 F	97.30	93.33	91.75	91.62	91.50

NEW FORMAT JAN 25,85

Table A11

RESULT OF SYNGAS OPERATION

RUN NO. 11885-07
CATALYST CO/X4-U-103+U-101 12006-26 250 CC 121.1G(TO 122.9G +1.8)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-07-11	885-07-13
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	139.8	163.8
PRESSURE,PSIG	295	295
TEMP. C	262	262
FEED CC/MIN	1260	1260
HOURS FEEDING	25.00	24.00
EFFLNT GAS LITER	1142.90	1095.90
GM AQUEOUS LAYER	158.30	175.19
GM OIL	57.01	58.19
MATERIAL BALANCE		
GM ATOM CARBON %	98.40	98.19
GM ATOM HYDROGEN %	95.83	100.15
GM ATOM OXYGEN %	98.96	101.80
RATIO CHX/(H2O+CO2)	0.9789	0.8796
RATIO X IN CHX	2.4379	2.4341
USAGE H2/CO PRODT	2.0475	2.1635
FEED H2/CO FRM EFFLNT	0.9739	1.0200
RESIDUAL H2/CO RATIO	0.5548	0.5658
RATIO CO2/(H2O+CO2)	0.0620	0.0530
K SHIFT IN EFFLNT	0.0367	0.0316
SPECIFIC ACTIVITY SA	0.8144	0.7957
CONVERSION		
ON CO %	28.08	28.42
ON H2 %	59.03	60.29
ON CO+H2 %	43.35	44.52
PRDT SELECTIVITY,WT %		
CH4	16.10	15.75
C2 HC'S	4.02	3.77
C3H8	4.54	4.47
C3H6=	2.60	2.43
C4H10	3.19	3.28
C4H8=	3.63	3.70
C5H12	3.09	3.21
C5H10=	3.82	3.74
C6H14	3.79	3.82
C6H12= & CYCLO'S	3.43	3.22
C7+ IN GAS	12.79	11.68
LIQ HC'S	39.00	40.94
TOTAL	100.00	100.00

Table A11 (continued)

SUB-GROUPING		
C1 -C4	34.08	33.40
C5 -420 F	43.88	44.50
420-700 F	18.75	18.76
700-END PT	3.29	3.34
C5+-END PT	65.92	66.60
ISO/NORMAL MOLE RATIO		
C4	0.0817	0.0676
C5	0.0991	0.0865
C6	0.4829	0.4581
C4=	0.0826	0.0871
PARAFFIN/OLEFIN RATIO		
C3	1.6653	1.7586
C4	0.8479	0.8562
C5	0.7862	0.8340
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8056	0.8047
RATIO CH4/(1-A)**2	4.2598	4.1293
ALPHA FRM CORRELATION	0.8394	0.8384
ALPHA (EXPTL/CORR)	0.9598	0.9598
W%CH4 FRM CORRELATION	18.0594	18.3572
W%CH4 (EXPTL/CORR)	0.8913	0.8579
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLR OIL	OIL &SLD
DENSITY	0.7590	0.7474
N, REFRACTIVE INDEX	1.4266	1.4255
SIMULT'D DISTILATN		
10 WT % @ DEG F	290	275
16	307	304
50	448	435
84	628	624
90	683	678
RANGE(16-84 %)	321	320
WT % @ 420 F	43.50	46.00
WT % @ 700 F	91.57	91.83

NEW FORMAT JAN 25,85

VI. Run 5 (11885-08) with Catalyst 5 (Co/Th/X_6/UCC-103+UCC-101)

The purpose of this run was to test the effect of additive X_6 (a) from a different source than previously used, and (b) incorporated by a different method. The X_6 had shown interesting properties in two earlier tests--Run 11677-03 of the Eleventh Quarterly Report (Co/Th/X_6/UCC-101) and Run 11723-04 of the Third Annual Report (Co/Th/X_6/UCC-103).

The catalyst was prepared by first combining X_6 with UCC-103, then forming in close contact with thorium-promoted cobalt oxide. The theoretical content of cobalt, thorium and X_6 was 6.16, 0.95 and 0.12 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. A95-98. Simulated distillations of the C_5^+ product are plotted in Figs. A99-102. Carbon number product distributions are plotted in Figs. A103-108. Chromatograms from simulated distillations are reproduced in Figs. A109-113. Detailed material balances appear in Tables A12-13.

After an initial deactivation the conversion of $CO+H_2$ stabilized at about 56 percent. This was slightly higher than with Third Annual Report Catalyst 5 (Run 11723-04, Co/Th/X_6/UCC-103), another intimately contacted catalyst with X_6; and since this catalyst contained less than three-quarters as much cobalt (6.16

vs 8.5 percent), its use of the cobalt was much more efficient.

The conversion was extremely stable during the 143 hours of the run following the first data point--which was, however, not long enough for any firm conclusions. This stabilizing effect of X_6 is familiar from previous trials.

The H_2:CO usage ratio, about 2.0, compared with about 1.8 for catalysts lacking X_6--another characteristic effect of X_6.

The most dramatic difference between this catalyst and that of Run 11723-04 is in selectivity. With methane production of about 15 percent and an alpha value of about 0.80, as against 20 percent and 0.77 respectively, the product of this catalyst was substantially heavier.

The ratio of weight percent methane produced, to weight percent predicted by the mathematical model, was 1.1:1. For the exceptionally stable Third Quarterly Report Catalyst 6 (Run 11677-11, Co/Th/X_4/UCC-103+UCC-101) the corresponding ratio was 0.9:1. At comparable H_2:CO ratios in the reactor, therefore, the product of the X_6 catalyst would be higher in methane.

The olefin content of the C_4's ranged from 50 to 54 percent. Isomerization of the C_5^+'s was less than 10 percent, characteristically low for this type of catalyst. The Schulz-Flory plots are linear except for the usual high methane.

The additive X_6 has been shown both to improve stability and to raise the H_2:CO usage ratio. But its effectiveness appears to depend on the method by which it is incorporated into the catalyst.

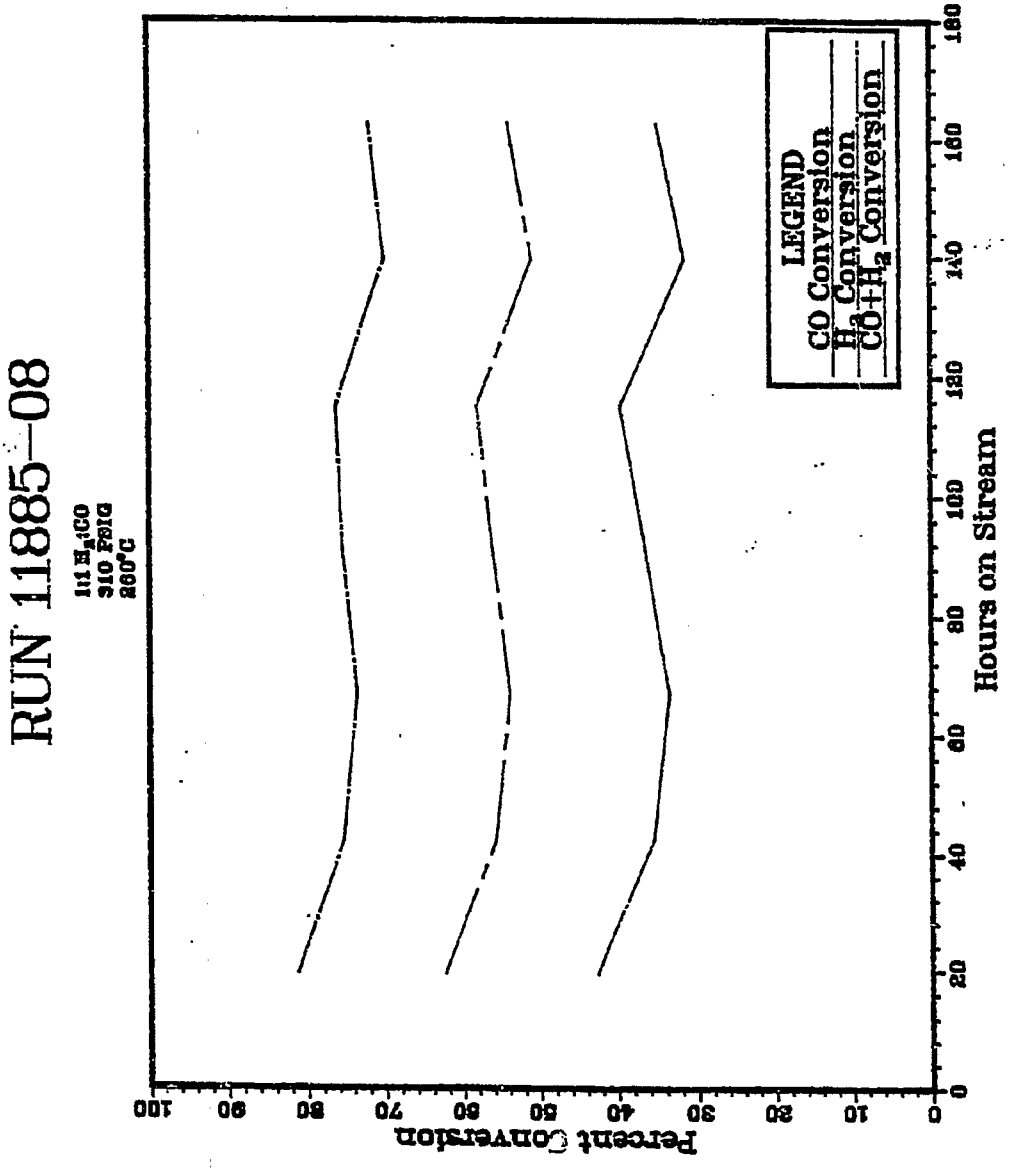

RUN 11885-08
1:1 H2:CO
310 Psig
260°C
Percent Conversion
Hours on Stream
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. A95

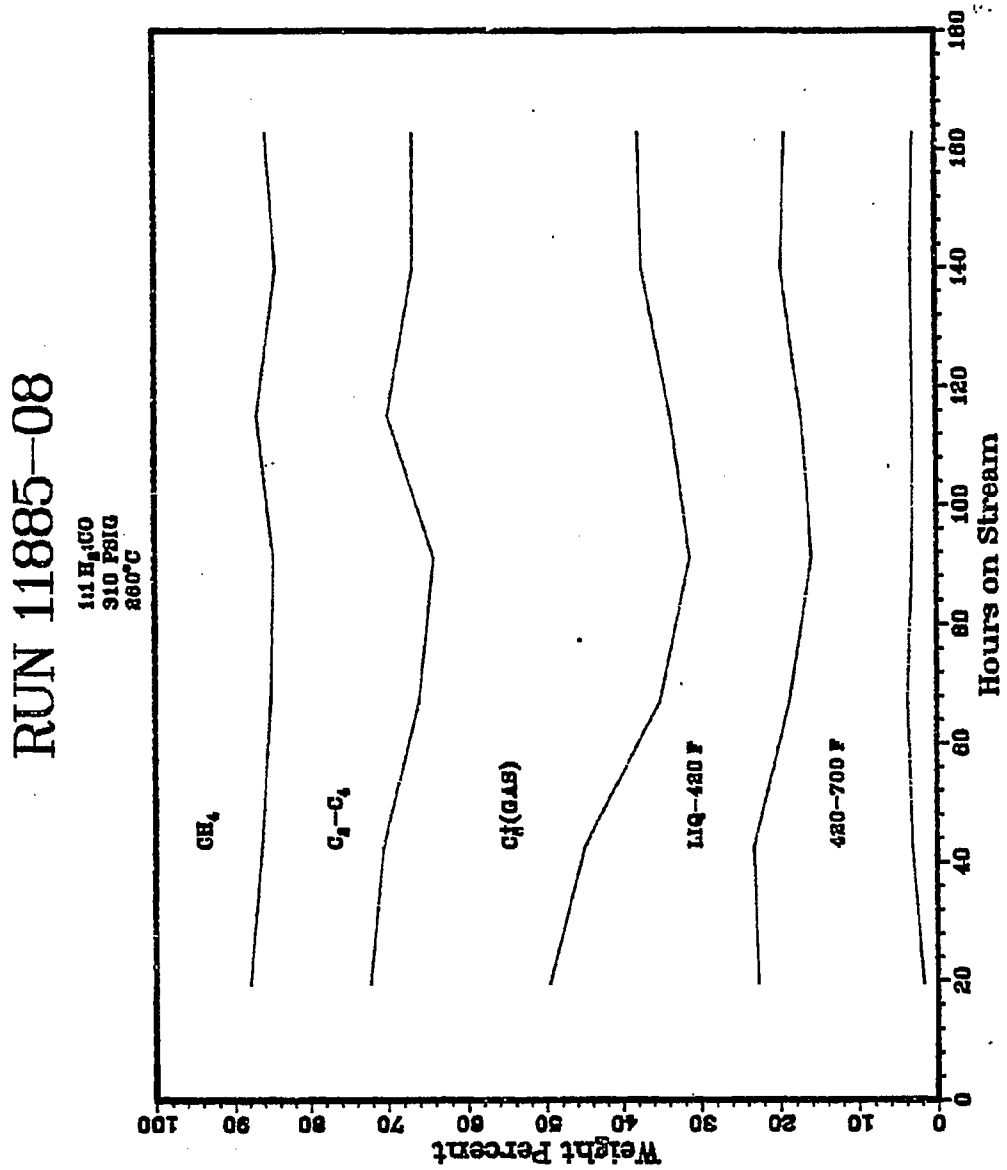

RUN 11885-08
1:1 H2:CO
310 PSIG
280°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. A96

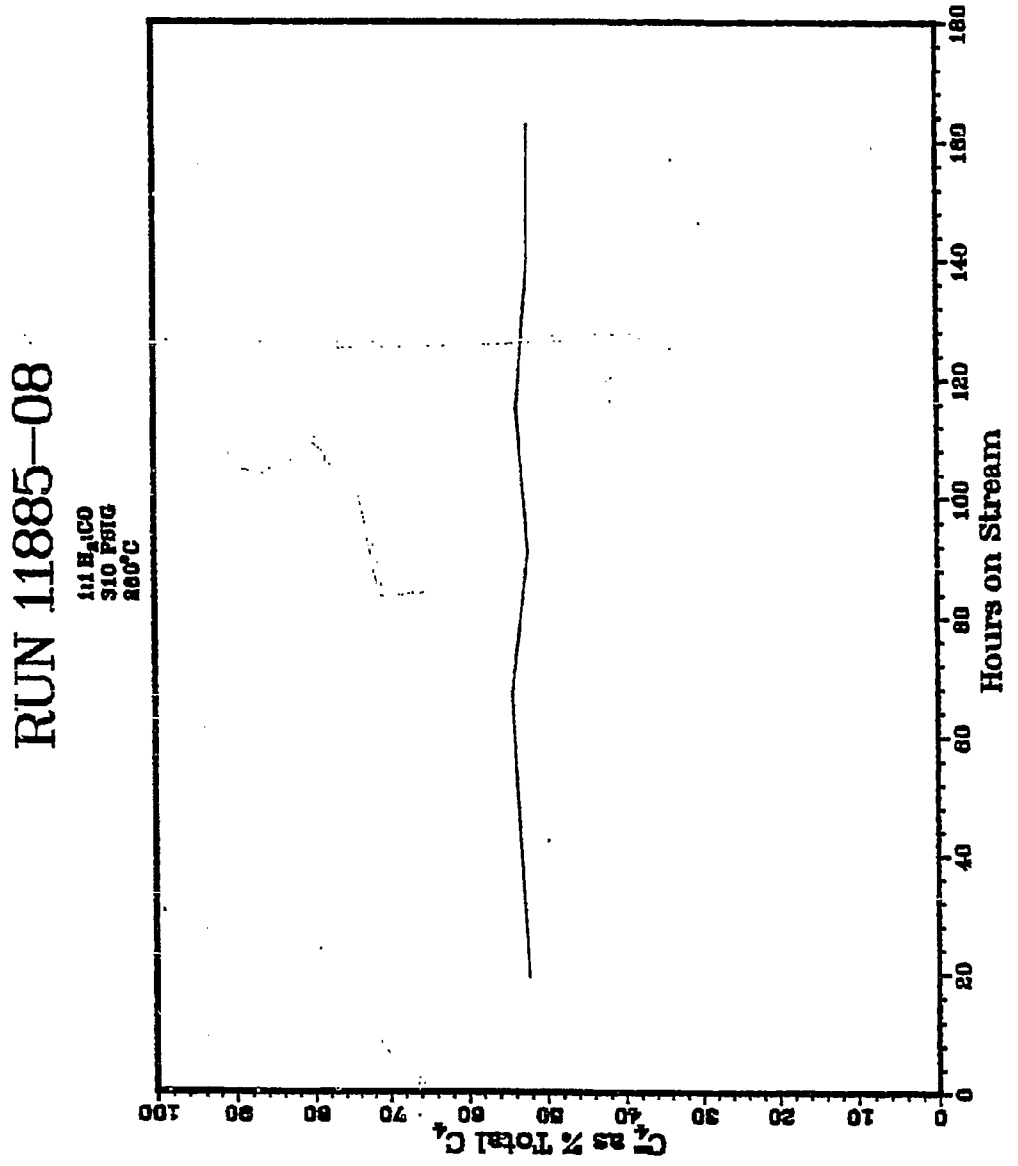

RUN 11885-08
111 H2:CO
310 PSIG
260°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. A97

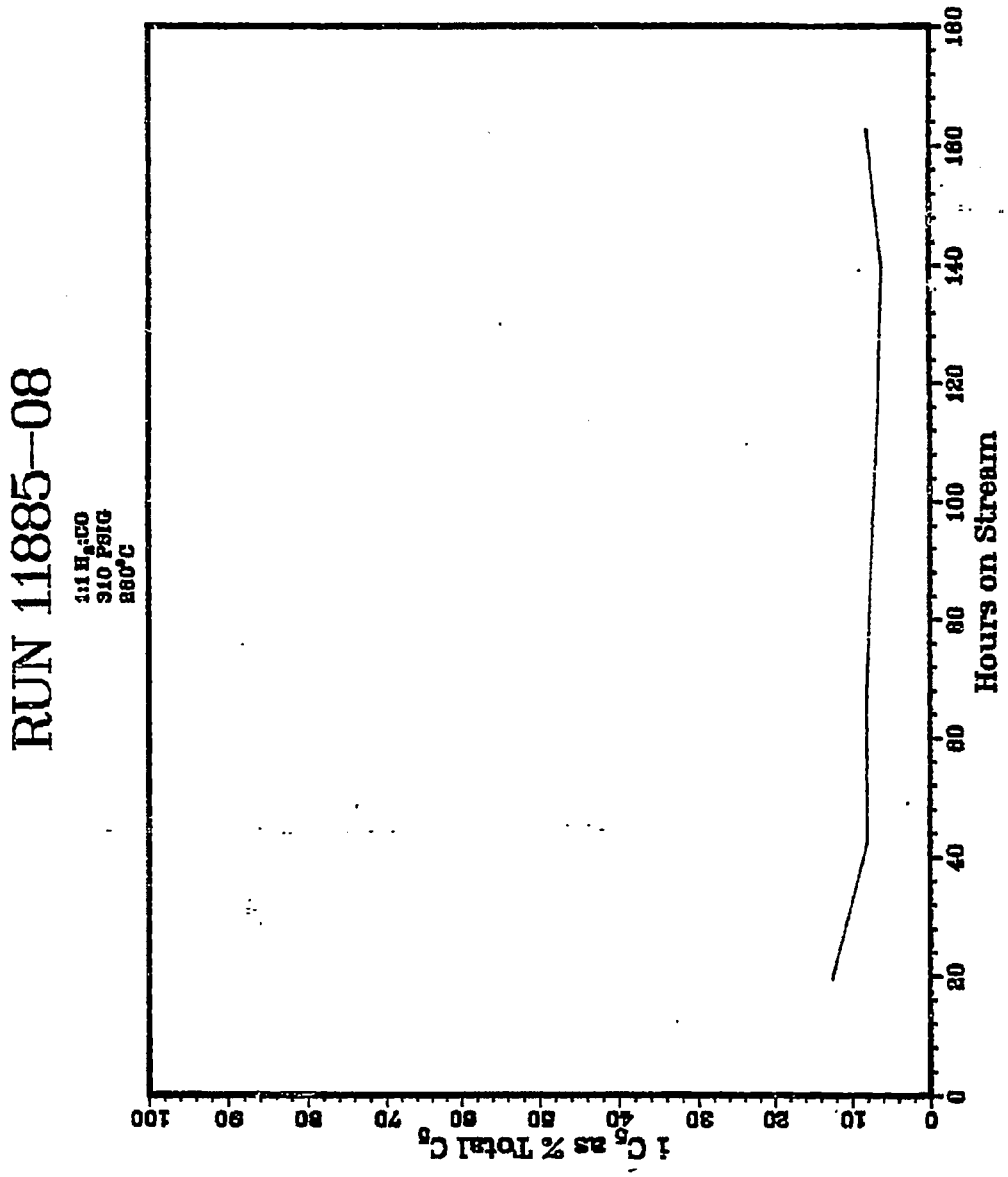

RUN 11885-08
1:1 H2:CO
310 PSIG
260°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. A98

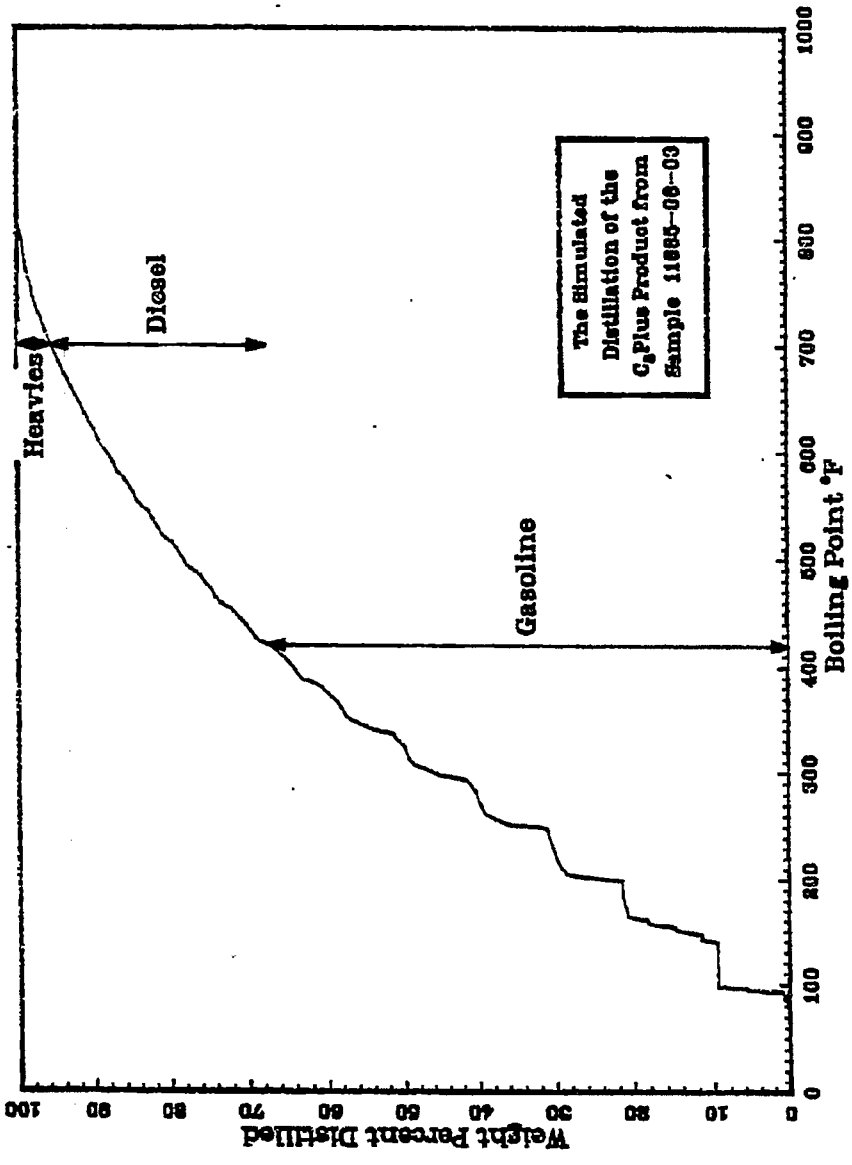

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11685-08-03

Fig. A99

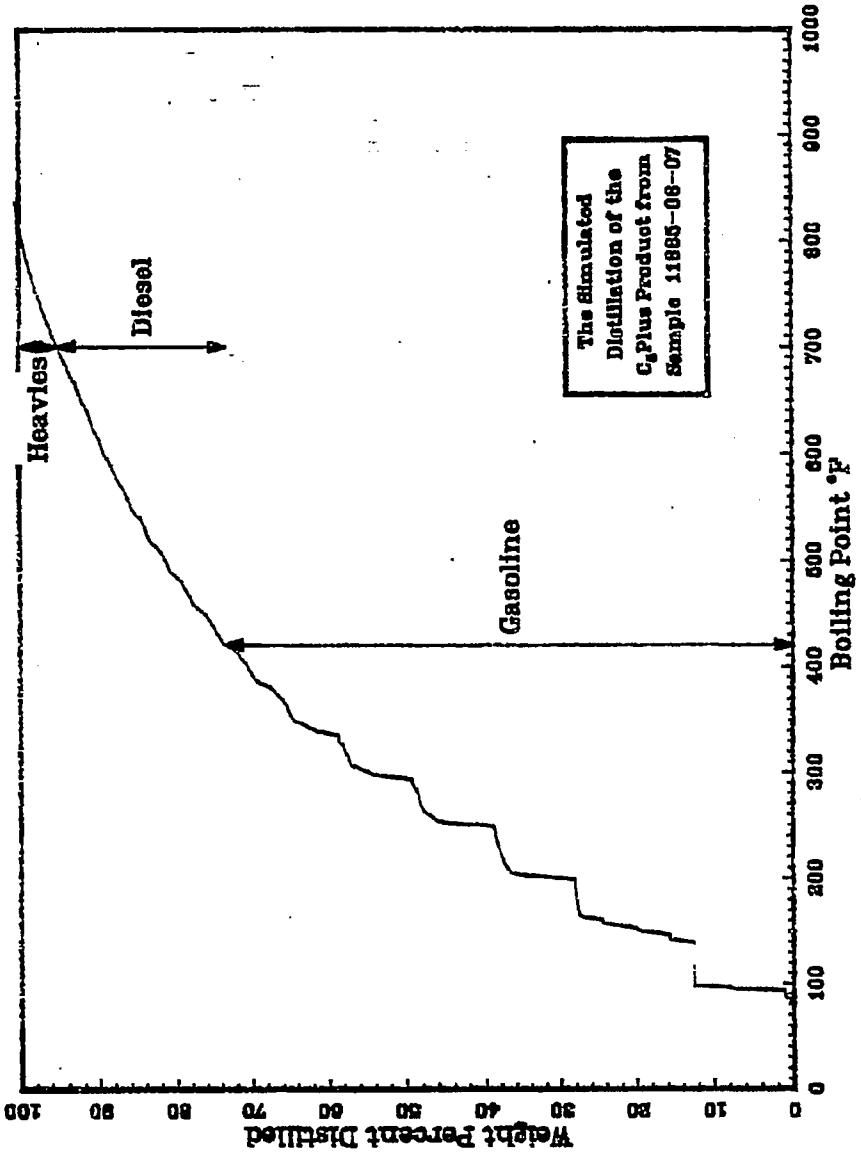

Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000
Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11885-08-07

Fig. A100

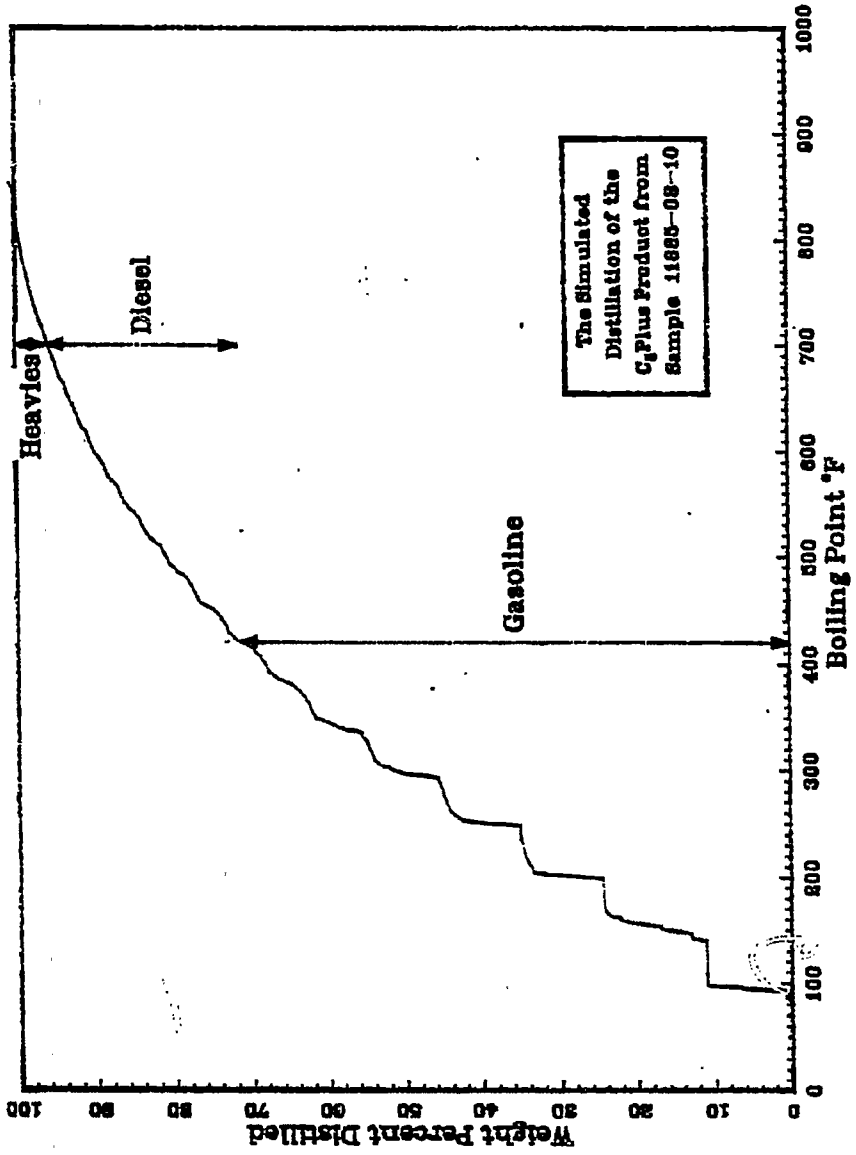

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11885-08-10
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. A101

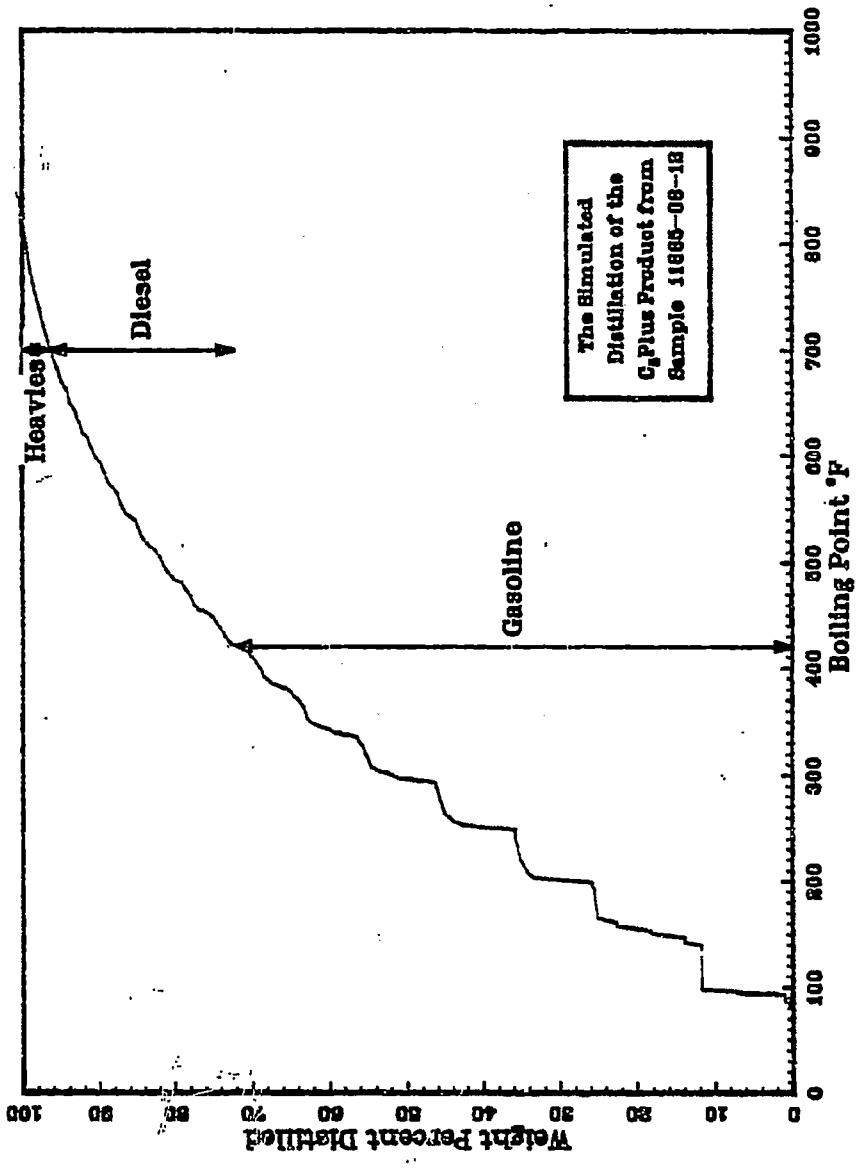

The Simulated Distillation of the C5 Plus Product from Sample 11885-08-18
Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Fig. A102

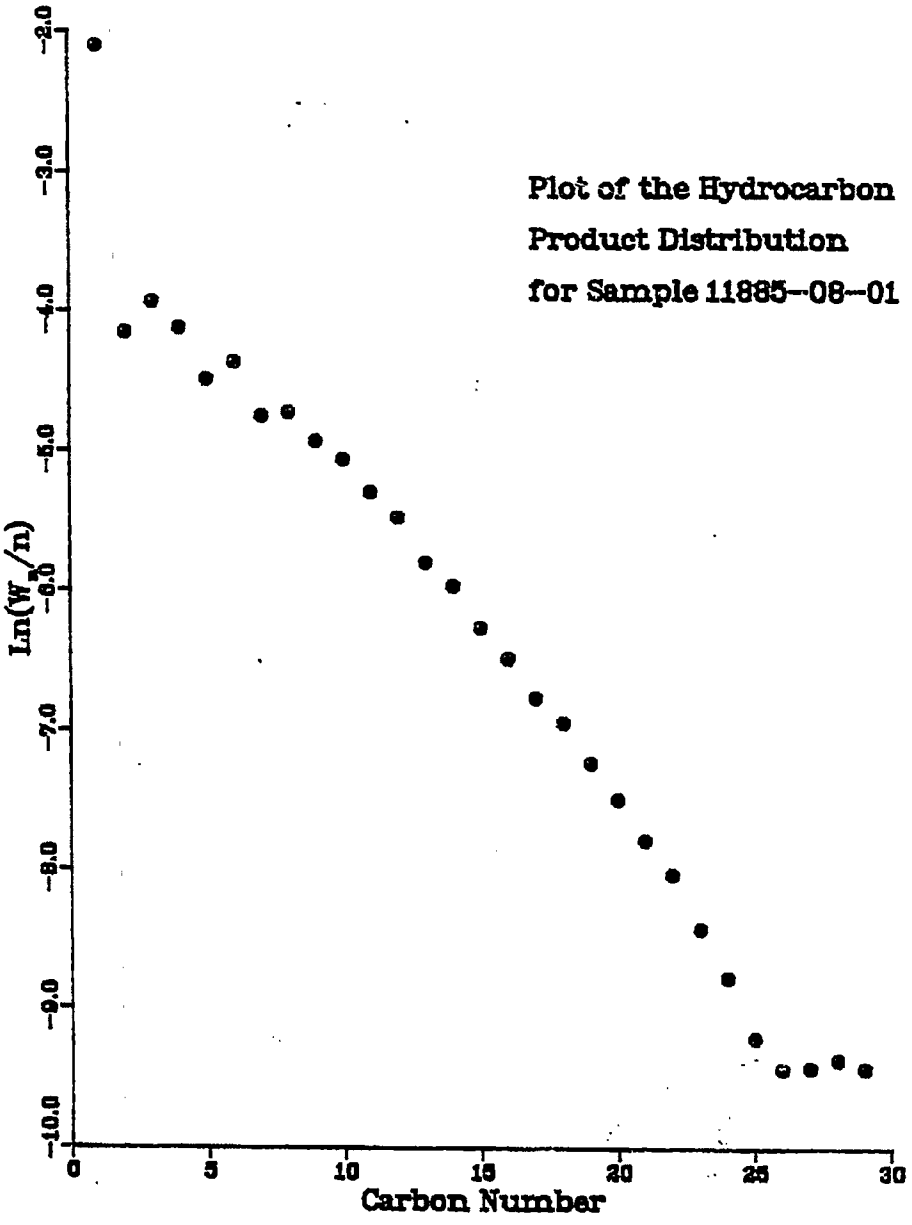

Plot of the Hydrocarbon
Product Distribution
for Sample 11885--08--01
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A103

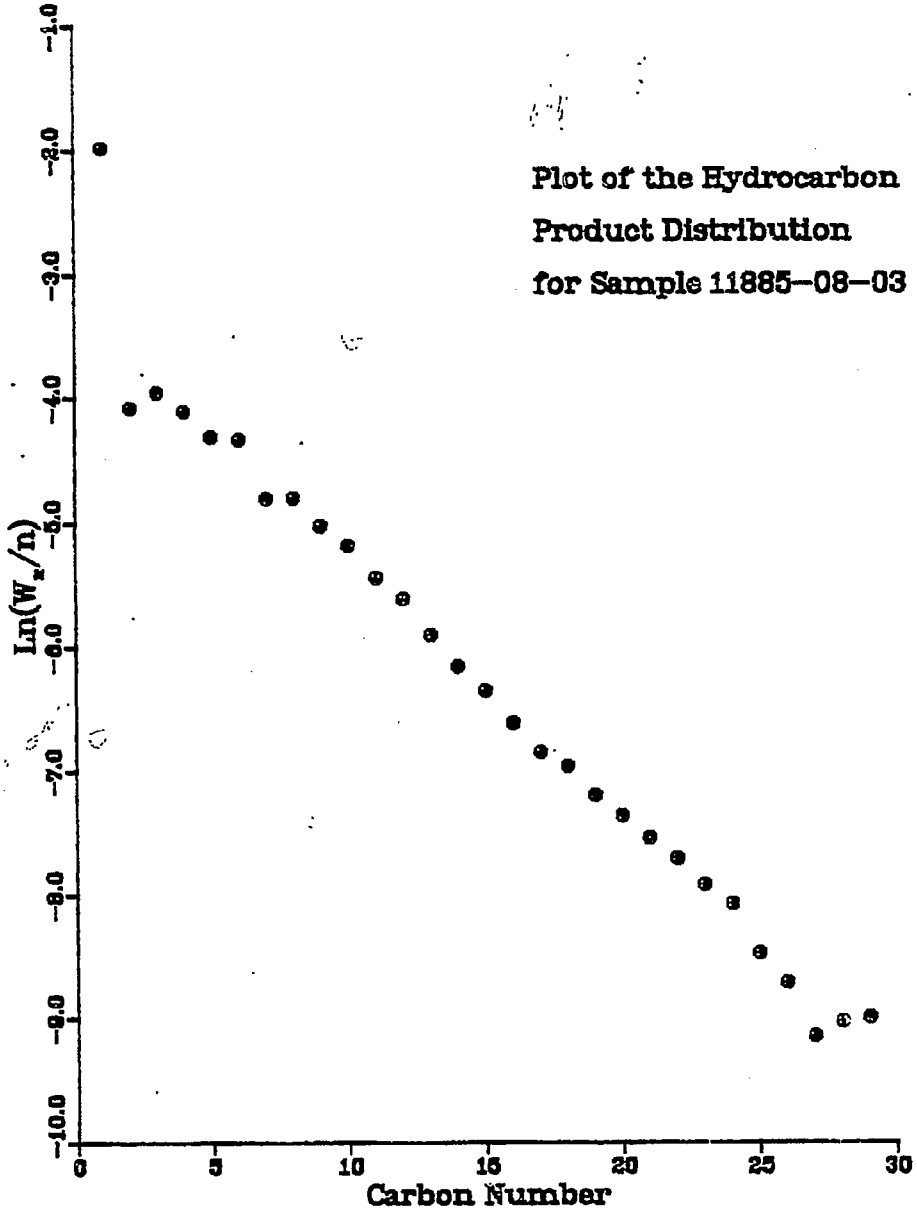

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-03
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A104

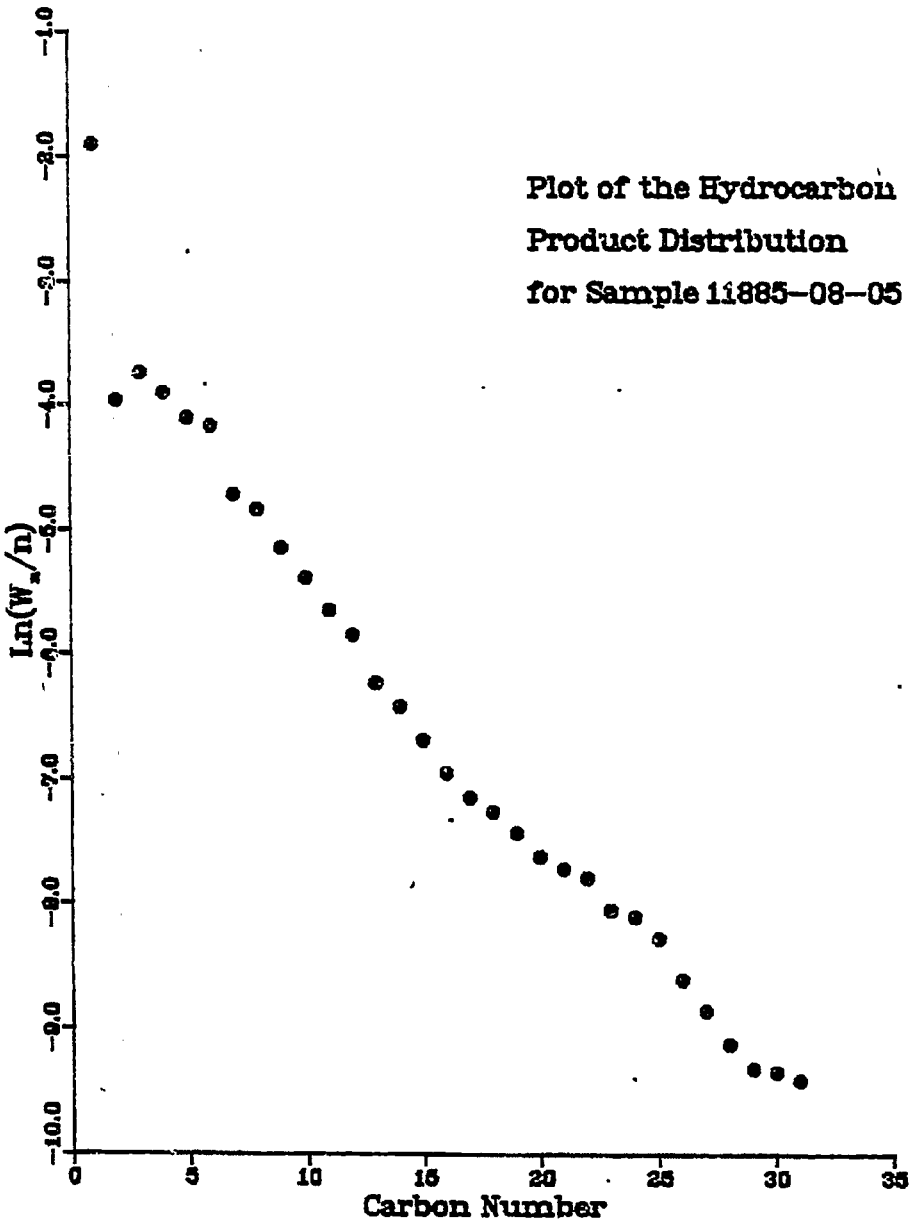

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-05
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A105

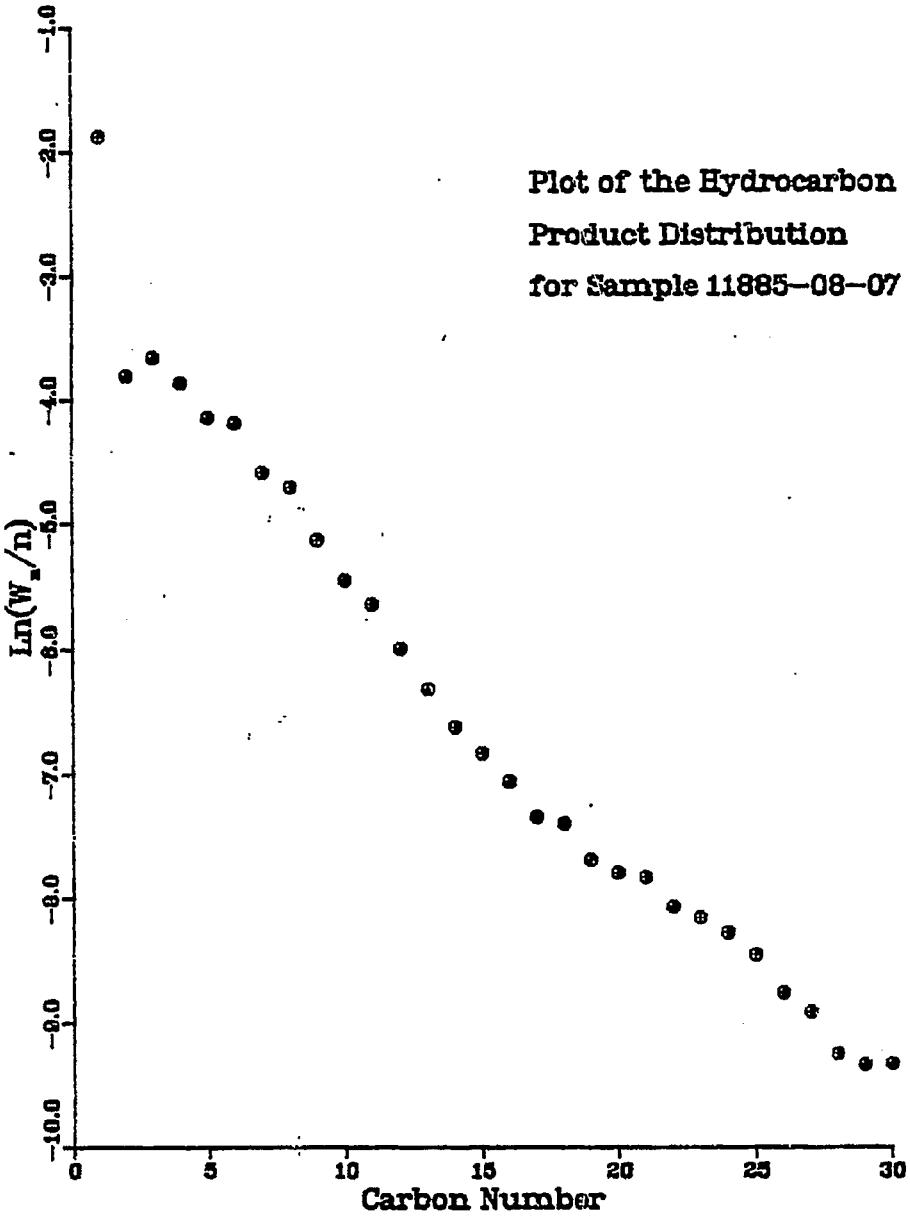

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-07
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. A106

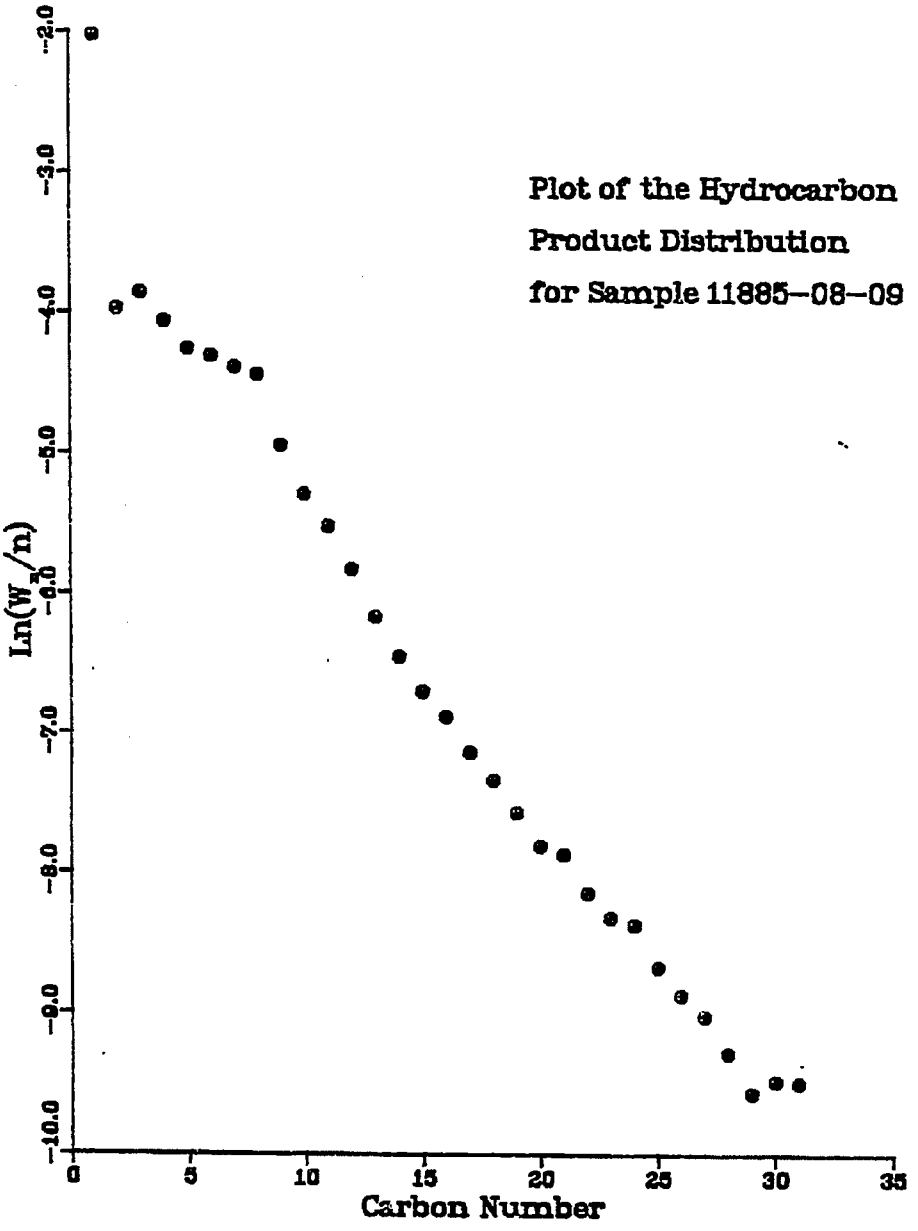

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-09
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A107

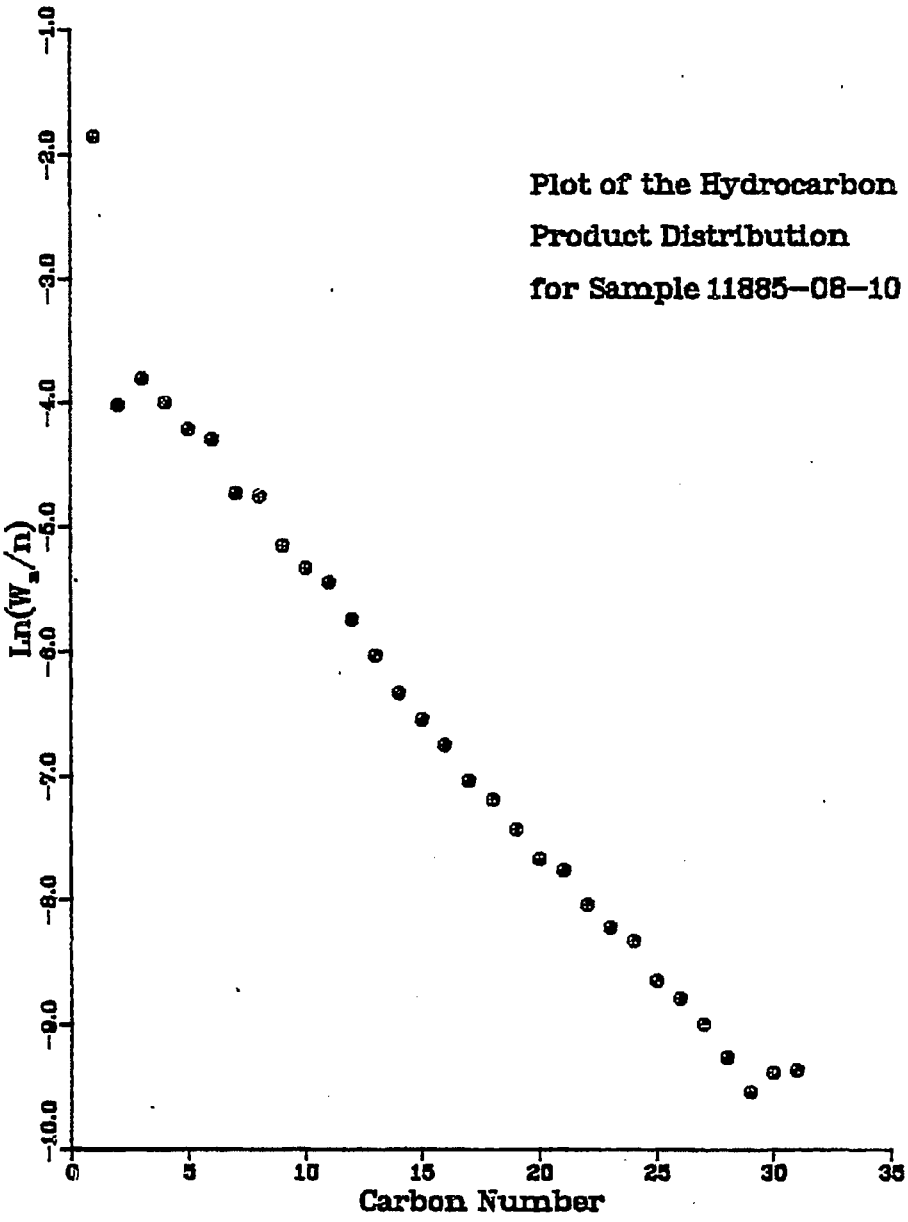

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-10
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A108

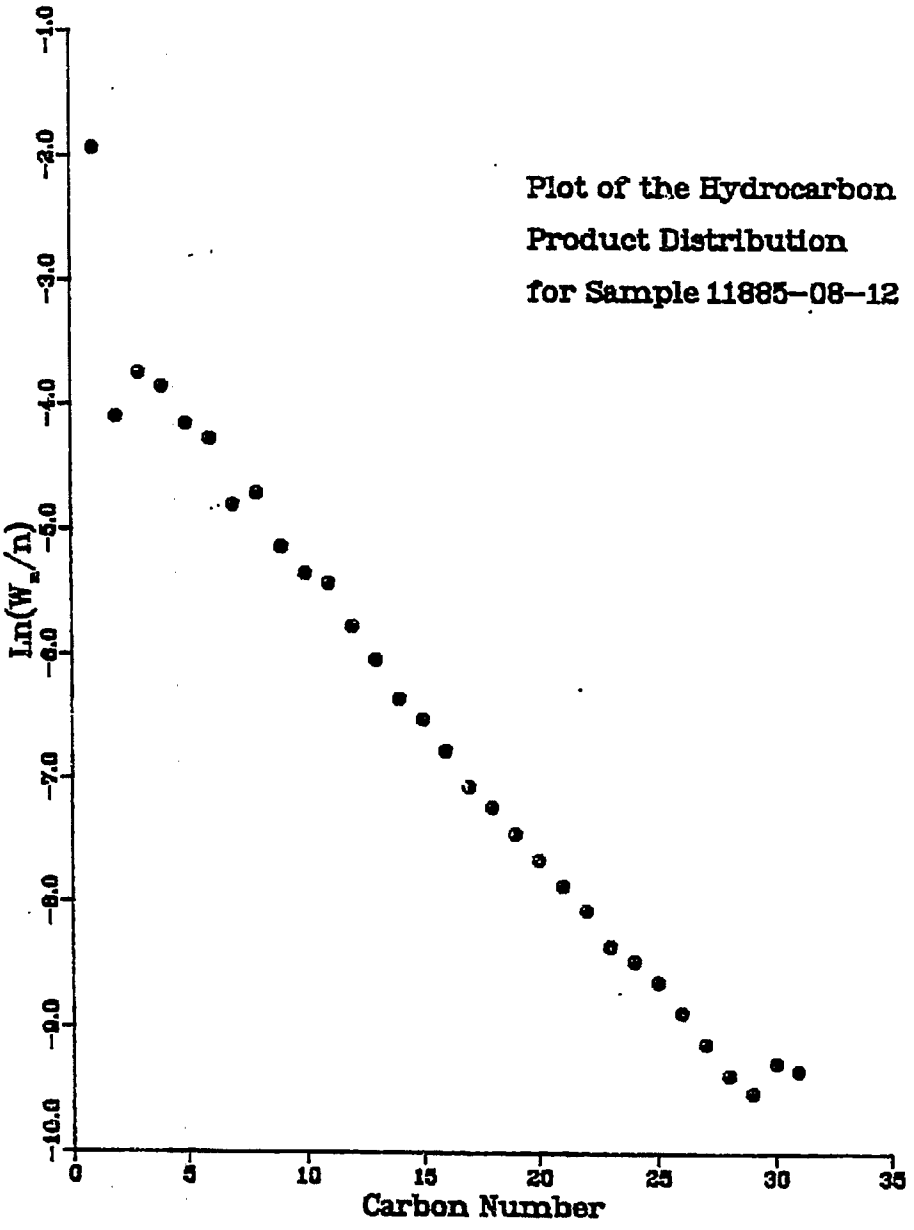

Plot of the Hydrocarbon
Product Distribution
for Sample 11885-08-12
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. A109

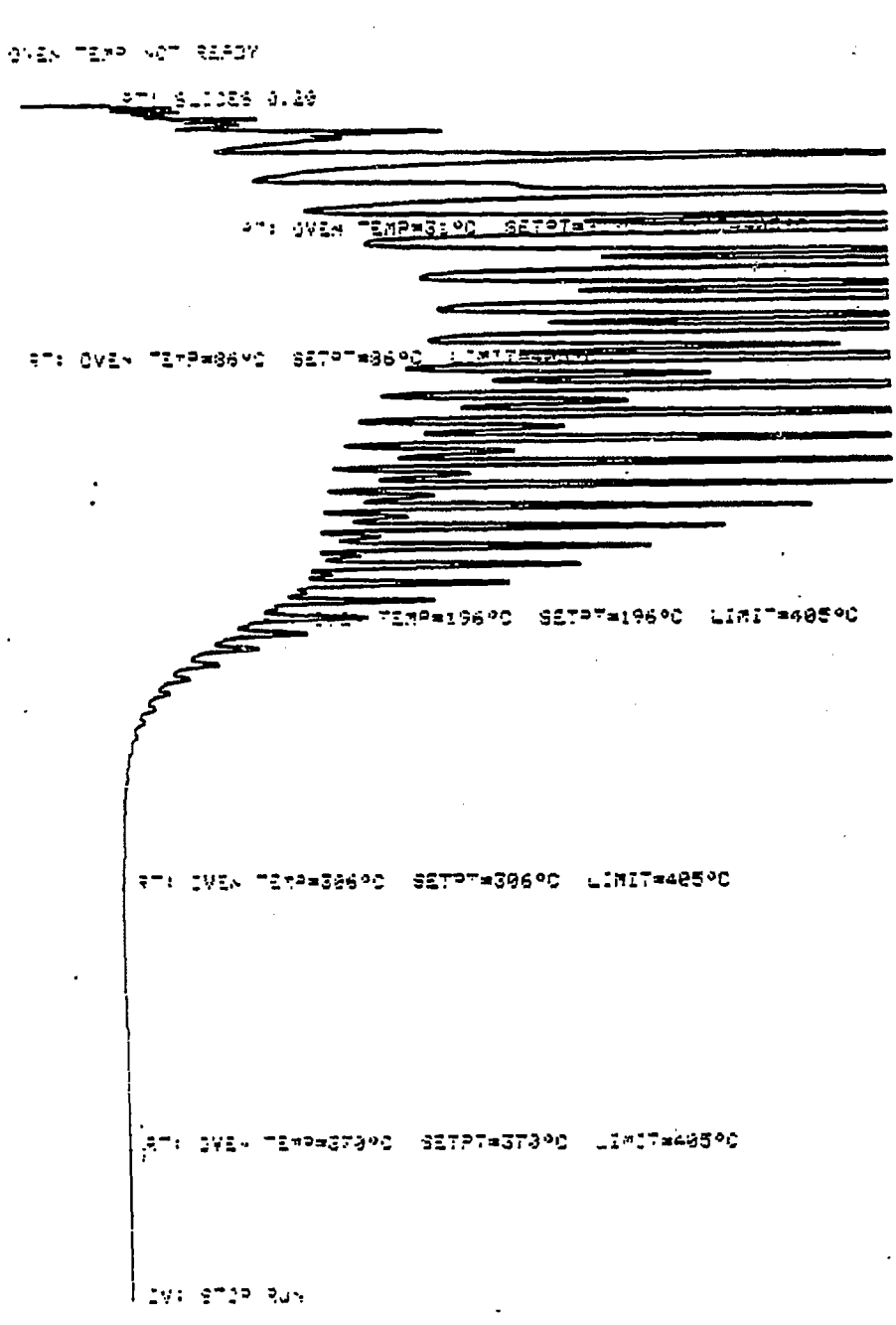

OVEN TEMP NOT READY
ST: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
ST: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
ST: OVEN TEMP=373°C SETPT=373°C LIMIT=405°C

Fig. A110

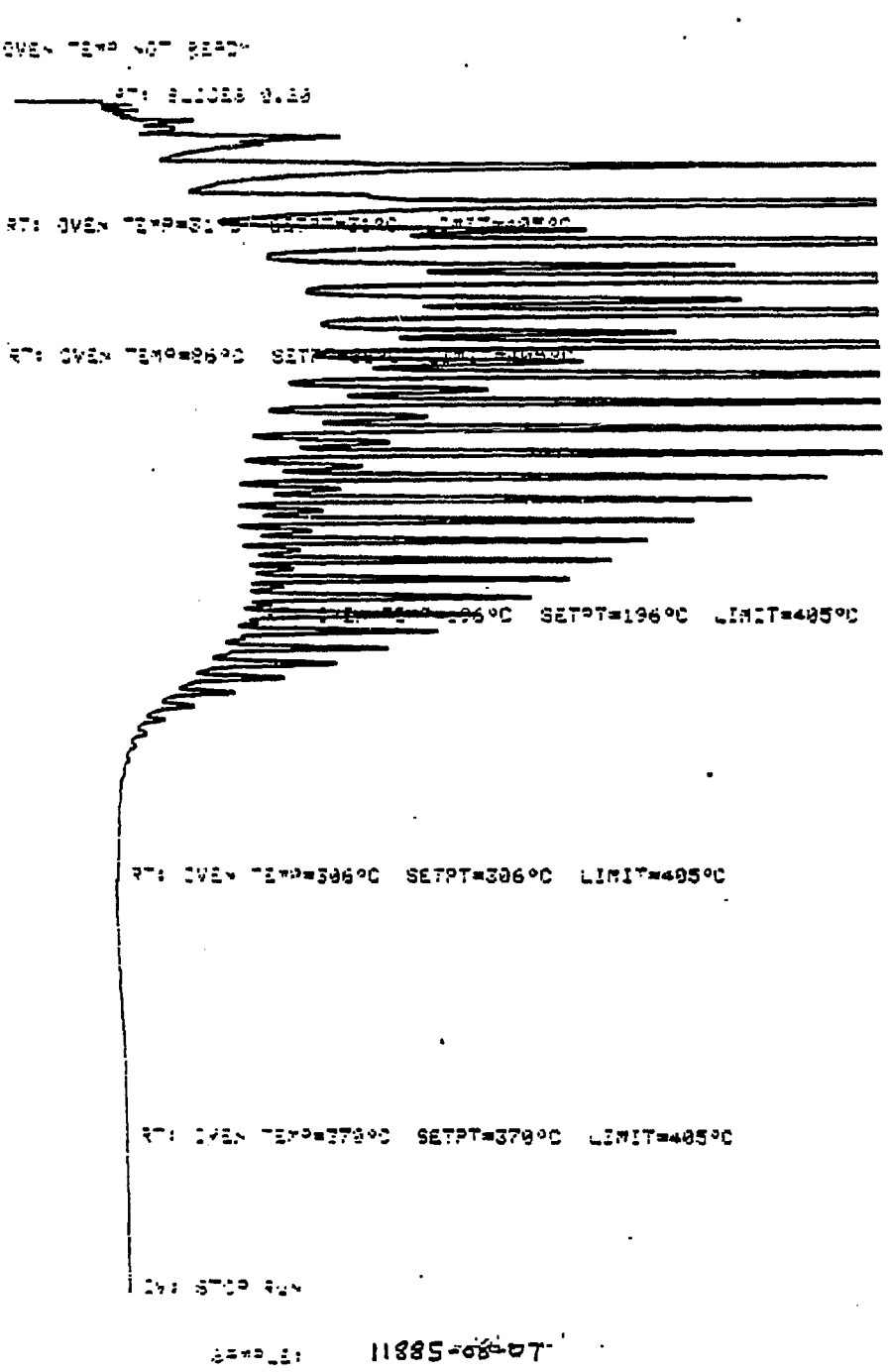
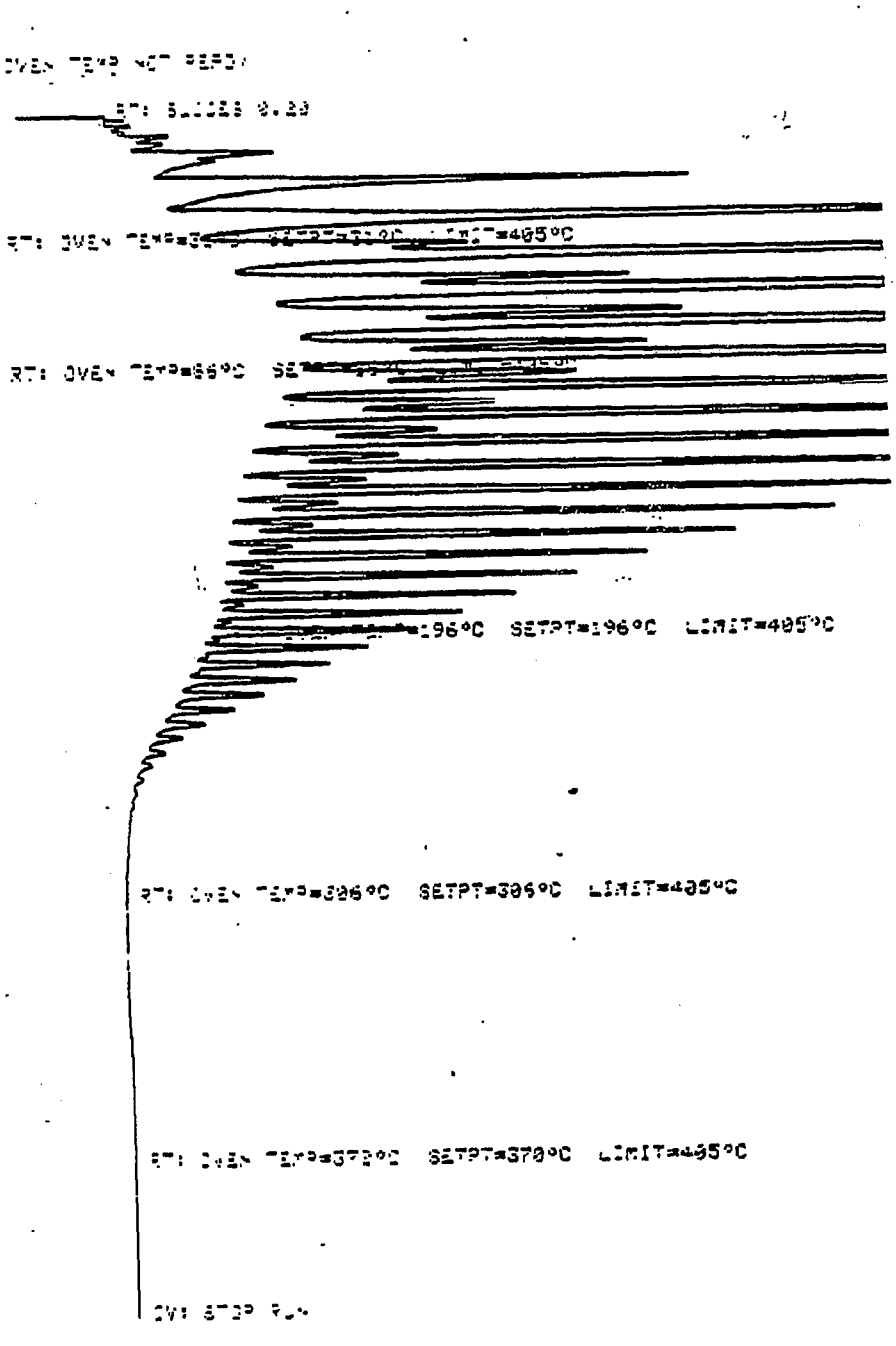

SET PT=196°C LIMIT=405°C
RT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C

Fig. A111



SAMPLE: 11885-08-10

Fig. A112

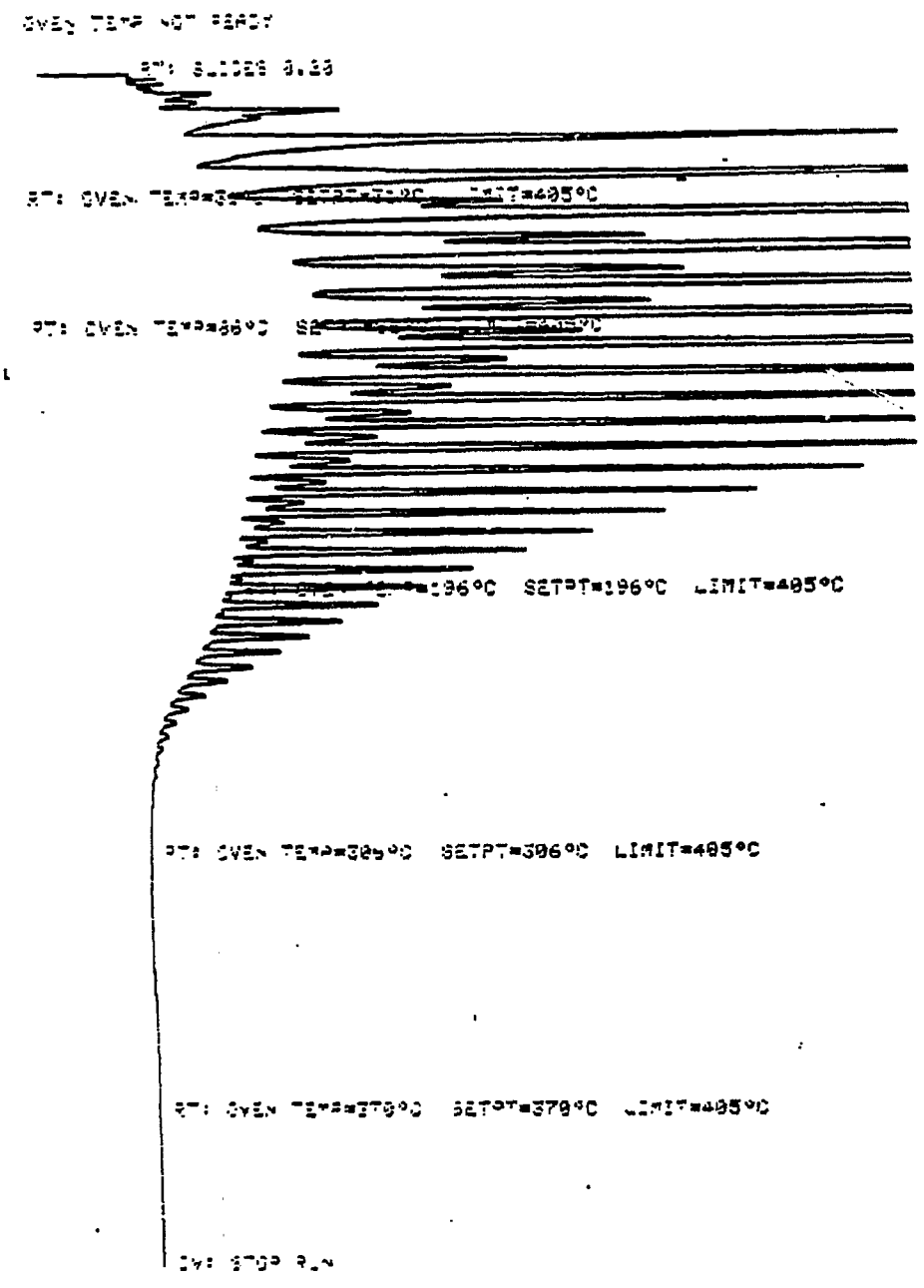

OVEN TEMP NOT READY
PT: OVEN TEMP=196°C SETPT=196°C LIMIT=405°C
PT: OVEN TEMP=306°C SETPT=306°C LIMIT=405°C
PT: OVEN TEMP=379°C SETPT=379°C LIMIT=405°C
DW: STOP RUN
11885-08-12

Fig. A113

Table A12

RESULT OF SYNGAS OPERATION

RUN NO. 11885-08
CATALYST CO/TH/X6-U103+U101 12006-30 250 CC 113.7G (TO 129.6G +15.9G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11885-08-01	885-08-03	885-08-05	885-08-07	885-08-09
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	19.5	42.5	67.0	91.0	115.0
PRESSURE,PSIG	314	302	306	305	306
TEMP. C	263	259	259	262	262
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	19.50	23.00	24.50	24.00	24.00
EFFLNT GAS LITER	594.30	818.05	905.40	881.70	901.40
GM AQUEOUS LAYER	193.65	220.63	228.95	223.97	221.24
GM OIL	69.73	67.64	53.21	50.94	65.33
MATERIAL BALANCE					
GM ATOM CARBON %	87.19	91.39	91.36	93.63	100.17
GM ATOM HYDROGEN %	92.62	94.32	93.42	95.54	102.16
GM ATOM OXYGEN %	96.96	101.67	102.26	102.44	102.52
RATIO CHX/(H2O+CO2)	0.7671	0.7389	0.7161	0.7740	0.9388
RATIO X IN CHX	2.3773	2.4033	2.4279	2.4351	2.3800
USAGE H2/CO PRODT	2.0237	2.1848	2.2338	2.1108	1.9579
FEED H2/CO FRM EFFLNT	1.0623	1.0321	1.0226	1.0205	1.0199
RESIDUAL H2/CO RATIO	0.3477	0.3959	0.4094	0.3966	0.4045
RATIO CO2/(H2O+CO2)	0.1189	0.0859	0.0834	0.0992	0.0943
K SHIFT IN EFFLNT	0.0469	0.0372	0.0372	0.0437	0.0421
SPECIFIC ACTIVITY SA	2.5755	2.1392	1.8630	1.8544	2.0358
CONVERSION					
ON CO %	42.64	35.56	33.61	36.39	39.62
ON H2 %	81.23	75.28	73.42	75.28	76.05
ON CO+H2 %	62.51	55.74	53.74	56.03	58.01
PRDT SELECTIVITY,WT %					
CH4	12.21	13.81	14.96	15.33	13.19
C2 HC'S	3.14	3.37	3.80	4.46	3.77
C3H8	3.96	3.98	4.87	5.20	4.38
C3H6=	1.91	1.76	2.28	2.51	1.92
C4H10	3.15	3.13	3.78	4.10	3.27
C4H8=	3.33	3.43	4.30	4.30	3.64
C5H12	2.80	2.86	3.37	3.55	3.16
C5H10=	2.85	3.83	4.88	4.43	3.93
C6H14	3.95	3.89	4.76	4.70	4.17
C6H12= & CYCLO'S	3.16	3.65	4.41	4.27	3.73
C7+ IN GAS	9.96	11.33	13.48	15.92	21.17
LIQ HC'S	49.58	44.99	35.11	31.23	33.68
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A12 (continued)

SUB-GROUPING					
C1 -C4	27.70	29.47	33.99	35.91	30.16
C5 -420 F	49.66	47.37	47.23	48.16	52.66
420-700 F	20.81	20.02	15.08	12.77	14.23
700-END PT	1.83	3.15	3.70	3.15	2.95
C5+-END PT	72.30	70.53	66.01	64.09	69.84
ISO/NORMAL MOLE RATIO					
C4	0.1426	0.0916	0.0833	0.1153	0.0704
C5	0.1432	0.0870	0.0877	0.0804	0.0708
C6	0.8229	0.5806	0.5695	0.5500	0.5429
C4=	0.0787	0.0874	0.0944	0.1097	0.1097
PARAFFIN/OLEFIN RATIO					
C3	1.9831	2.1614	2.0347	1.9748	2.1779
C4	0.9141	0.8810	0.8473	0.9194	0.8673
C5	0.9527	0.7257	0.6722	0.7782	0.7822
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7893	0.8099	0.8069	0.8004	0.7981
RATIO CH4/(1-A)**2	2.7517	3.8204	4.0140	3.8491	3.2353
ALPHA FRM CORRELATION	0.8621	0.8560	0.8544	0.8557	0.8548
ALPHA (EXPTL/CORR)	0.9156	0.9461	0.9445	0.9354	0.9337
W%CH4 FRM CORRELATION	11.2205	12.2784	12.7837	12.9864	13.2820
W%CH4 (EXPTL/CORR)	1.0884	1.1245	1.1702	1.1807	0.9931
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	CLR OIL	CLR OIL	CLR OIL	CLR OIL
DENSITY	0.7536	0.7560	0.7573	0.7580	0.757
N, REFRACTIVE INDEX	1.4245	1.4264	1.4264	1.4255	1.4249
SIMULT'D DISTILATN					
10 WT % @ DEG F	248	257	259	256	257
16	276	293	298	295	297
50	406	423	434	424	423
84	573	620	652	646	625
90	622	671	706	701	686
RANGE(16-84 %)	297	327	354	351	328
WT % @ 420 F	54.33	48.50	46.50	49.00	49.00
WT % @ 700 F	96.30	93.00	89.45	89.90	91.25

NEW FORMAT JAN 25,85

Table A13

RESULT OF SYNGAS OPERATION

RUN NO. 11885-08
CATALYST CO/TH/X6-U103+U101 12006-30 250 CC 113.7G (TO 129.6 G +15.9G)
FEED H2:CO OF 50:50 @ 1260 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	11885-08-10	885-08-12
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	139.7	162.7
PRESSURE,PSIG	307	303
TEMP. C	260	260
FEED CC/MIN	1260	1260
HOURS FEEDING	24.70	22.97
EFFLNT GAS LITER	977.45	883.47
GM AQUEOUS LAYER	205.58	210.42
GM OIL	60.75	59.38
MATERIAL BALANCE		
GM ATOM CARBON %	95.19	94.51
GM ATOM HYDROGEN %	96.65	99.77
GM ATOM OXYGEN %	98.24	101.03
RATIO CHX/(H2O+CO2)	0.9060	0.8243
RATIO X IN CHX	2.4414	2.4200
USAGE H2/CO PRODT	2.2467	2.1696
FEED H2/CO FRM EFFLNT	1.0152	1.0556
RESIDUAL H2/CO RATIO	0.4472	0.4578
RATIO CO2/(H2O+CO2)	0.0217	0.0659
K SHIFT IN EFFLNT	0.0099	0.0323
SPECIFIC ACTIVITY SA	1.4353	1.5918
CONVERSION		
ON CO %	31.57	34.92
ON H2 %	69.86	71.78
ON CO+H2 %	50.86	53.85
PRDT SELECTIVITY,WT %		
CH4	15.69	14.42
C2 HC'S	3.58	3.32
C3H8	4.74	4.83
C3H6=	1.97	2.29
C4H10	3.57	4.14
C4H8=	3.76	4.33
C5H12	3.25	3.46
C5H10=	4.09	4.37
C6H14	4.37	4.39
C6H12= & CYCLO'S	3.81	3.76
C7+ IN GAS	13.93	13.06
LIQ HC'S	37.23	37.64
TOTAL	100.00	100.00

Table A13 (continued)

SUB-GROUPING		
C1 -C4	33.32	33.33
C5 -420 F	47.13	47.67
420-700 F	16.38	16.16
700-END PT	3.16	2.85
C5+-END PT	66.68	66.67
ISO/NORMAL MOLE RATIO		
C4	0.0661	0.1092
C5	0.0649	0.0868
C6	0.4037	0.5007
C4=	0.0978	0.1275
PARAFFIN/OLEFIN RATIO		
C3	2.2947	2.0075
C4	0.9188	0.9233
C5	0.7720	0.7682
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8013	0.7955
RATIO CH4/(1-A)**2	3.9741	3.4492
ALPHA FRM CORRELATION	0.8500	0.8489
ALPHA (EXPTL/CORR)	0.9427	0.9372
W%CH4 FRM CORRELATION	14.3458	14.7019
W%CH4 (EXPTL/CORR)	1.0938	0.9807
LIQ HC COLLECTION		
PHYS. APPEARANCE		
DENSITY	0.757	0.752
N, REFRACTIVE INDEX	1.4256	1.4240
SIMULT'D DISTILATN		
10 WT % @ DEG F	262	256
16	301	297
50	428	421
84	623	617
90	684	670
RANGE(16-84 %)	322	320
WT % @ 420 F	47.50	49.50
WT % @ 700 F	91.50	92.43

NEW FORMAT JAN 25,85

VII. Summary

This quarter's tests have yielded valuable information, both positive and negative, on how three additives, X_4, X_6 and copper exchanged 13X, affect the activity and stability of catalysts formulated by intimately contacting cobalt oxide with UCC-103.

Copper exchanged 13X, a proven water gas shift catalyst in other formulations, in this series was inactive for both the water gas shift and the Fischer-Tropsch reactions.

The additive X_4, a constituent of the most stable catalyst developed to date, failed to enhance the stability of the catalysts in this series. Evidently its stabilizing effect depends on some cooperative interaction, as yet unidentified, with the cobalt and the thorium.

Comparative tests of an extruding agent showed it to have little or no effect on any aspect of a catalyst's performance.

Investigation of the additive X_6 was extended to test X_6 obtained from a different source than in previous tests, and different methods of incorporating it. The principal contributions of X_6 have been to increase the catalyst's H_2:CO usage ratio and to improve its stability. Both effects, it is now evident, depend to considerable degree on how it is incorporated in the catalyst.

Appendix B. PROCESS SIMULATION STUDIES OF UCC FISCHER-TROPSCH CATALYSTS IN AN ARGE-TYPE, FIXED BED, TUBULAR REACTOR SYSTEM

Appendix B. PROCESS SIMULATION STUDIES OF UCC FISCHER-TROPSCH CATALYSTS IN AN ARGE-TYPE, FIXED BED, TUBULAR REACTOR SYSTEM

Chang-Lee Yang and A. C. Frost

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Introduction

During the latter part of 1983 (see the Third Annual Report) Union Carbide developed several cobalt-based catalysts which showed high C_5^+ conversions and good stability. In order to evaluate these promising new catalysts, the Department of Energy requested Union Carbide to provide adequate process design data to the MITRE Corporation so that they could perform a techno-economic evaluation of the Union Carbide catalysts.

Methodology Used to Obtain Process Design Data

Toward this end, Union Carbide correlated the test data already available on these catalysts to obtain expressions for (1) syngas conversion rate, (2) the methane make, as weight percent of total hydrocarbons produced, and (3) the C_2^+ hydrocarbon distribution.

Figure B1 shows that these three expressions were then used in a computer program which simulated an Arge-type tubular reactor system operating at 270C and 300 psig, at an 85 percent overall syngas conversion, and with a 2.3:1 recycle ratio for the non-condensed $<C_5$ gases.

The output from this program was presented to MITRE in the form of a series of graphs, each depicting the space velocities and the H_2:CO feed ratios required to obtain a fixed methane yield with Union Carbide catalysts having varying specific activ-

ities and H_2:CO usage ratios.

Details of how the catalyst test data were correlated into the three expressions for the syngas conversion rate, the methane make, and the C_2^+ product selectivity, of how the computer simulation used these expressions with input data to generate design curves, and what these design curves were, are presented in the following sections.

Correlation of Catalyst Test Data

To derive an estimate of process economics from bench scale laboratory data, it is necessary to develop reaction rate and product distribution correlations as functions of the process variables. With this approach in mind we chose to operate the experimental program with the Berty test reactors. With its high internal recycle ratio, the reactor temperature can be closely controlled even with a highly exothermic reaction; and the reaction proceeds at, or very near, the discharge conditions. Such Continuous-flow Stirred Tank Reactor (CSTR) behavior makes data analysis simple.

For a first attempt at correlating reaction rates, we chose a power law expression because it is simple, straightforward and practical. Also at an early stage, we decided that the correlation should be done on the rate of the CO conversion, and that the hydrogen conversion could then be computed from the CO conversion and the H_2 usage ratio (relative consumption of H_2 to CO). The variation in usage ratio depends on the extent to which the water gas shift reaction accompanies the Fischer-Tropsch re-

action. In most of the runs since the first quarter of 1983, cobalt has been the primary metal component for the F-T reaction. Since the water gas shift activity of a cobalt catalyst is generally low, the usage ratio, as dictated by stoichiometry, will be about 2.0:1, with water as the primary by-product. A few promoted cobalt catalysts have, however, shown some water gas shift activity, with a usage ratio of 1.6:1. It has been observed that once a certain usage ratio has been established with a catalyst it remains fairly constant, and does not vary much under different process conditions. Consequently we regard the usage ratio (and the relative hydrogen consumption) as essentially a property of catalyst composition and preparation, and treat it as a constant. This greatly simplifies the syngas conversion rate correlation.

The data of Run 10011-14 were used for the conversion rate correlation. This run was operated at a variety of process conditions: two different feed compositions (H_2:CO ratios of 50:50 and 60:30), two different feed rates (400 and 800 cc per minute), and three different temperatures (219, 252 and 284C). The catalyst was a simple cobalt-loaded formulation (Eighth Quarterly Report), a reasonable choice for a baseline reference. The reactor was charged with 80cc of the catalyst, weighing 49.6 grams, of which about 11.3 weight percent was cobalt oxide. The various operating conditions of this run are summarized in Table B1.

The run lasted 264 hours, and 21 product samples were collected. For each sample an experimental CO conversion rate was com-

puted from the CO feed rate, the CO conversion, and the weight of catalyst. The same was done for the H_2 and syngas (H_2+CO) conversion rates. Partial pressures of H_2 and CO in the reactor were calculated from the conversion, the product distribution and the initial feed composition. The data on experimental conversion rates (H_2, CO and syngas), on partial pressures of H_2 and CO, on space velocities, and on temperatures were assembled and input as data for the conversion rate correlation. Results of these correlations are given in Figures B2-B4.

The coefficients of the non-linear multiple regression correlation are in the form:

$$\text{Ln(CO rate)} = B1 + B2 * \text{Ln}(pH_2) + B3 * \text{Ln}(pCO) + B4 * \frac{1000.0}{R * T}$$

with the results as follows:

Parameter	Estimate	Asymptotic std. error
B1	24.77733589	0.24579744
B2	1.65256709	0.06707165
B3	-0.46610804	0.02277398
B4	-30.11477997	0.38737307

Rearranging and transforming around a 250C base temperature, the CO rate expression is derived as follows:

$$R_{CO} = 0.01515617 * \frac{(pH_2)^{1.6515671}}{(pCO)^{0.466108}} * \frac{TCOEF}{1000.0} \quad \frac{\text{gm moles CO}}{\text{hr, gm catalyst}}$$

$$TCOEF = \exp \frac{30114.78 * (tc - 250)}{1.98726 * 523.15 * (tc + 273.15)}$$

where R_{CO} = rate of CO conversion, gm mole CO/hr, gm catalyst
pH_2 = partial pressure of hydrogen, psia
pCO = partial pressure of carbon monoxide, psia
TCOEF = Arrhenius temp. coefficient (250C as reference)
tc = temperature, deg C

The hydrocarbon product distribution has been reasonably well represented by the Schulz-Flory distribution for Fischer-Tropsch products. The theory assumes that the hydrocarbon chain grows one carbon atom by one carbon atom; that at each stage the chain can either terminate or add one more carbon atom; and that the rates of growth and termination will be the same regardless of carbon number. From these assumptions, the following relationship is derived:

$$W_n = n * (1 - \text{alpha})^2 * \text{alpha}^{(n-1)}$$

where W_n = wt. fraction of hydrocarbon fraction of carbon number n
alpha = chain growth probability, growth rate/(growth + termination)
alpha = exp(slope) of $Ln(W_n/n)$ vs. n plot (Schulz-Flory plot)

The validity of this equation is shown by a straight line relationship if the logarithm of (W_n/n) is plotted against carbon number n. The product distribution usually conforms to this general scheme for all carbon numbers except methane; with a cobalt catalyst the methane product usually exceeds the Schulz-Flory distribution, so that the methane must be separately calculated.

The methane make itself, as well as the value of alpha that must be used with the Schulz-Flory equation to describe the C_2^+ product distribution, were found to correlate with the H_2:CO ratio and temperature conditions used to test five cobalt and

thoria-promoted cobalt catalyst systems (Runs 10011-14, 10112-14, 10112-15, 10225-6 and 11677-07; Eighth, Tenth and Eleventh Quarterly Reports). The operating conditions and catalyst compositions for these runs are listed in Tables B2 and B3.

The statistical analysis program correlated alpha and weight percent methane in terms of H_2:CO ratio and a temperature function, as follows:

$$\begin{matrix}\text{alpha} \\ \text{or} \\ \text{wt.pct } CH_4\end{matrix} = B1 + B2 * Ln\frac{pH_2}{pCO} + B3 * \frac{1000.0}{1.98726 + (tc + 273.15)}$$

For alpha the parameters are:

Parameter	Estimate	Asymptotic std. error
B1	0.78124055	0.10287415
B2	-0.04872504	0.00436998
B3	0.03130488*	0.10777772

and for weight percent methane:

Parameter	Estimate	Asymptotic std. error
B1	147.79114170	8.11683887
B2	15.11426148	1.08845782
B3	-128.49758349	8.34160276

*Statistically insignificant.

Yielding:

$$\text{alpha} = 0.78124 - 0.048725 * Ln\frac{pH_2}{pCO} + 0.031305 * \frac{1000.0}{1.98726 * (tc + 273.15)}$$

$$\begin{matrix}\text{wt.pct.} \\ CH_4\end{matrix} = 147.791 + 15.1143 * Ln\frac{pH_2}{pCO} - 128.4976 * \frac{1000.0}{1.98726 * (tc + 273.15)}$$

The dependent variables, after rearrangement, are plotted

against the independent variables for both the alpha and the weight percent methane correlations in Figs. B4-B8. As the plots show, these variables are a strong function of the H_2:CO ratio but a weak function of temperature, especially for alpha.

Computer Simulation of the Fixed Bed Tubular Reactor

The three correlations of the catalyst test data were incorporated into a computer simulation of the process configuration, shown in Fig. B9. The fixed catalyst bed in the tubular reactor was assumed to operate at some average input temperature, and was incremented into 50 segments. Starting with the first (top) segment, the computer program sequentially calculated (from the Berty-reactor-derived equations and the partial pressures remaining in the prior segment) the CO conversion, the methane make, and the remaining C_2^+ product slate for each segment down the reactor. The effluent leaving the reactor was then split into condensed C_5^+ hydrocarbons, condensed water, off-gas (free of C_5^+ hydrocarbons and water), and the desired quantity of recycle. The recycle stream was mixed with the fresh feed stream and the segment-by-segment calculations down the bed were repeated as before. This looping continued until the effluent H_2:CO ratio, a sensitive indicator of reactor steady state, leveled off to a nearly constant value, at which time appropriate step changes were made in the H_2 and CO concentrations so that additional looping resulted in convergence of the effluent H_2:CO ratio from the opposite direction (i.e., if the effluent H_2:CO ratio were asymptotically decreasing during the initial looping period, then

the direction of the step changes in the H_2 and CO concentrations caused the effluent H_2:CO ratio to asymptotically increase during this second looping period). Once such two-directional convergences (to the same H_2:CO value) had taken place, steady state was assumed and the program was ended.

This computer simulation, designated FIXBD1, is listed in Table B4. A glossary of the terms used in FIXBD1 is given in Table B5, and a line by line guide for the different program steps in FIXBD1 is given in Table B6. Similarly, the subroutine BSF, used in FIXBD1 to quantify the product distribution obtained with the Schulz-Flory equation, is listed in Table B7, and a glossary of the terms used in BSF is given in Table B8.

These tables and Fig. 1 show that the inputs to the FIXBD1 program are the catalyst properties (specific activity, usage ratio, and bulk density), the feed gas conditions (space velocity and H_2:CO ratio), and the reactor conditions (pressure, temperature, and recycle ratio), while the outputs are the product quantities in both the off-gas (H_2, CO, CO_2, and C_1-C_4 hydrocarbons) and the liquid separator (C_5^+ hydrocarbons and water).

While this program is straightforward, it required a series of trials when it was run (as is the usual case) to determine what feed space velocity and feed H_2:CO ratio would yield a desired methane make at a desired overall syngas conversion. This time-consuming trial procedure was shortened by another computer program, designated MITRE, which used the desired syngas conversion and methane make, as well as the catalyst and reactor condi-

tions, as inputs to estimate (through approximate algebraic relationships) the feed gas space velocity and H_2:CO ratio. These estimated feed conditions were then used as starting input values to the FIXBD1 program to zero in on their exact values for the desired syngas conversion and methane make.

The soundness of the FIXBD1 program was checked during its development. At that time the recycle ratio was set at 25:1 with no condensation of the effluent leaving the bed prior to its recycle. Under these conditions the program simulated the experimental Berty reactor itself. When the feed and reactor conditions, as well as the properties of several tested catalysts, were used as the inputs to this early version of the FIXBD1 program, the calculated product stream did indeed match the experimentally obtained outputs, as would be expected for a properly operating program.

Design Curves for MITRE

Figs. 10 and 11 are the two primary design curves generated with FIXBD1 for the MITRE Corporation. They show the feed H_2:CO ratio--catalyst specific activity and usage ratio--feed space velocity relationships for an Arge type reactor operating at 270C and 300 psig, using a 2.3:1 recycle ratio, and having a packed catalyst density of 0.6 gm/cc to obtain an 85 percent overall syngas conversion while producing hydrocarbon product containing either 12.3 weight percent methane (Fig. 10) or 7.8 weight percent methane (Fig. 11).

Use of these two figures is straightforward. A single point

is located for a catalyst having a definite specific activity and a definite usage ratio by using the right-hand usage ratio ordinate with the specific activity curves. The feed space velocity and the feed H_2:CO ratio corresponding to that point (i.e., corresponding to that catalyst) are then read from the bottom ordinate and from the left-hand ordinate, respectively.

Comparison of the two figures shows that for a given catalyst (having a defined specific activity and usage ratio) both the H_2:CO feed ratio and the feed space velocity will be higher for the 12.3 weight percent methane case than for the 7.8 weight percent case. This is because the higher H_2:CO feed ratio used to obtain the higher methane make (as dictated by the equation for the methane make) will cause the syngas conversion rate to increase (as dictated by the equation for the syngas conversion rate), and thus permit a higher space velocity to be used for the same overall 85 percent syngas conversion.

It can thus be seen that running the reactor with a high H_2:CO feed ratio will ensure a desirably high space velocity, but at the same time will result in an undesirably high methane production rate.

MITRE decided to cost two cases. Case 1 would use a Union Carbide catalyst having a 1.6:1 usage ratio and a 2.68 specific activity, values which were considered readily achievable at that time; this catalyst would operate with a H_2:CO feed ratio that would allow a high space velocity at the expense of a high (12.3 weight percent) methane make. Case 2 would use a Union Carbide

catalyst having a 2.0:1 usage ratio (the increase in costs associated with the lower water gas shift activity was expected to be more than outweighed by the reduction of costs associated with the increased space velocity resulting from this higher usage ratio) and a 3.64 specific activity, values that were considered achievable over the course of an extended research effort. This higher activity catalyst would operate at a leaner H_2:CO feed ratio which would allow a low (7.8 weight percent) methane make at the expense of a lower space velocity (lower than would be required with a higher methane make). Case 2 would, in effect, use some of the anticipated increase in specific activity to reduce the methane make below that for Case 1.

When the Case 1 catalyst (having a usage ratio of 1.6:1 and specific activity of 2.68) is located on Fig. 10 (for a 12.3 weight percent methane make) the bottom and left-hand ordinates indicate that the feed space velocity must be 300 vol/vol/hr with a H_2:CO feed ratio of 1.20:1. Similarly, when the Case 2 catalyst (having a usage ratio of 2.0:1 and a specific activity of 3.64) is located on Fig. 11 (for a 7.8 weight percent methane make) the bottom and left-hand ordinates indicate that the feed space velocity must be 360 vol/vol/hr with a H_2:CO feed ratio of 1.39:1.

Table B9 lists the compositions of the off-gas and liquid streams calculated by the FIXBD1 program for the two cases. Table B10 lists the characterization of the various components in the two streams for both cases.

It should be mentioned that the 0.11:1 and 0.17:1 H_2:CO ratios in the off-gases of the cases shown in Table B9 are also the H_2:CO ratios seen by the last section of the catalyst bed. These H_2:CO ratios are far lower than the 0.68:1 and 0.39:1 ratios used in the correlations for the syngas conversion rate, methane make, and alpha. Consequently, the use of these correlations, particularly the one predicting the methane make, in such extrapolations is certain to lead to significant errors. Therefore future process development runs made under the anticipated follow-on contract for new, more promising catalysts will include runs made under low H_2:CO conditions, so that these future correlations will be used for interpolation rather than extrapolation. Furthermore, such increased data will permit the new syngas conversion rate equation to be expressed in the theoretically more exact Langmuir-Hinshelwood form rather than the presently used power law form.

Table B1. Catalyst and operating conditions for the CO conversion rate correlation.

Run No.	Catalyst	Catalyst wt, gm	Feed & rate H2:CO	Feed & rate cc/m	Temp., deg C 220	250	280
10011-14	Co/PF/UCC-101	49.6	50:50	400	*	*	
			50:50	800		*	
			60:30	400		*	*

Table B2. Catalysts and operating conditions (all at 300 psig) for the selectivity correlations.

GROUP	RUN No.	CAT. DESCRIPTION	CAT. WTgm	FEED &RATE H2/CO	CC/M	TEMPERATURES C 220	250	280
1	10011-14	Co-PF-UCC-101	49.6	50/50	400	*	*	
				50/50	800		*	
				60/30	400		*	*
2	10112-14	(Co,Th+U-101)SiO2	30.0	50/50	400		*	*
3	10112-15	(Co,Th+U-101)SiO2	37.2	"/"	"			*
4	10225-06	(Co,Th+U-101)SiO2	35.8	"/"	"		*	*
5	11677-07	(Co,Th+Al2O3)SiO2	46.3	"/"	"	*	*	*

Table B3. Catalyst compositions of the selected catalysts.

GROUP	RUN	CATALYST DESCRIPTION	WEIGHT PERCENT OF COMPONENTS CoO	ThO2	UCC-101/Al2O3	SiO2
1	10011-14	Co-PF-UCC-101	11.3	0.0	88.7	
2	10112-14	(Co,Th + U-101)*SiO2	12.5	2.55	70.0	15.
3	10112-15	(Co,Th + U-101)*SiO2	"	"	"	"
4	10225-06	(Co,Th + U-101)*SiO2	41.7	0.85	42.5	15.
5	11677-07	(Co,Th + Al2O3)*SiO2	12.5	2.51	70.0	15.

Table B4. Listing of FIXBD1 simulation of tubular reactor system.

```
      FIXBD1 FORTRAN A1
 1 *  PARTIAL RECYCLE TUBULAR REACTOR DESIGN FOR FISCHER-TROPSCH PROCESS
 2 *  REVISED  W,JUN 26,85: STATMNT 41 TO 32.  REV. JUL 25 ON PERTURBANCE
 3 *  COPIED FROM FIXBD8 ON MAY 13,85 TO CORRECT INCONSISTANCY IN CH4 MWT
 4 *  COPIED FROM FIXBD7 ON MAY 6,85 FOR REVISION ON H2O & C5+ IN REACTOR
 5       DIMENSION FCI(3), GMFI(8), GMIZ(11,51), SWFN(40), SBM(40), WRGK(6),
 6       DIMENSION TCK(3), SVM(3),  WPIZ(10,51),  SDJ(200), RHCJ(200)
 7       DIMENSION RHC2J(200),  JIR(3),  GMIJ(27,3)
 8       CHARACTER*8 ATIME
 9       CHARACTER*9 ADATE
10   120 FORMAT (2(1X,F7.2),F7.2,F7.2,F6.2,F7.3,F7.3,F6.3,F7.2,F6.2)
11   130 FORMAT (1X,A12,1X,I4,1X,I4)
12   140 FORMAT (1X,A12,F9.4,5F9.4)
13   150 FORMAT (1X,A12,2(1X,F8.2),1X,F8.6,3(1X,F8.4))
14   160 FORMAT (1X,A12,6(1X,A8))
15   170 FORMAT (7(1X,F9.4))
16   180 FORMAT (7(1X,F9.6))
17   190 FORMAT (1X,A12,6F9.5)
18   200 FORMAT (1X,A12,39X,A9,4X,A8)
19       DATA FCI/62.0250,37.9750,.0/
20       DATA TCK/250.0,260.0,270.0/
21       DATA SVM/250.00,255.3,260.00/
22       TUBD = 5.0
23       TUBL = 1200.0
24       VM   = 24147.0
25       RF   = FCI(1)/FCI(2)
26       SA   = 2.5000
27       U    = 1.800
28       X    = 2.33
29       PA   = 314.7
30 *     A2 = 0.86744346
31 *     FCH4 = 6.260231
32 ***** CUT UP TUBE LENGTH INTO 50 SEGMENTS (OR NL SEGMENTS)
33       NL = 50
34       L2 = NL +1
35 ------DO 48 K=3,3
36       TC = TCK(K)
37       FT = 1000.0/1.98726/(TC+273.15)
38 ------DO 46 M=2,2
39       SV = SVM(M)
40       FFLOW = 3.14159*TUBD*TUBD/4.0*TUBL/VM*SV
41       RR = 2.3
42       RMOLE = FFLOW*RR
43       WRITE (11,140) 'FEED H2 CO A',(FCI(I),I=1,3)
44       WRITE (11,140) 'TC SV FFLOW ',TC,SV,FFLOW
46
48                                                          continued
```

Table B4, continued

```
      ***** TEMP COEFF ON REACTN RATE FROM ACTIVATION ENERGY DE=30115 CALORIE
      ***** & RATE CO = 0.015156*(PH2**1.65157)/(PCO**.46611)/1000.0 MOL/H/G
      *****                        AT 250 DEGC, WITH P'S IN PSIA
            DE = 30114.78
            T1 = 250.0 +273.15
            T2 = TC +273.15
            DT = T2 -T1
            B2 = DE*DT/1.98726/T1/T2
            TCOEF = EXP(B2)
      *     SET ZERO TO WIPE THE SLATE CLEAN FOR EACH CASE
            DO 42 I=1,11
            GMIZ(I,1)  = 0.0
            GMIZ(I,L2) = 0.0
         42 CONTINUE
      **    SETTING UP GMOLES OF FEED COMPONENTS AT INLET
            DO 22 I=1,3
            GMFI(I) = FFLOW *FCI(I)/100.0
         22 CONTINUE
            FSG = GMFI(1) +GMFI(2)
      **    CUT UP TUBE LENGTH INTO 50 SEGMENTS
            DL = TUBL/NL
            RHOB = 0.60
            WCAT = 3.14159* TUBD*TUBD/4.0*DL*RHOB
            BNL = NL
            WRITE (11,140) 'D SEG W SA X',RHOB,BNL,WCAT,SA,X
      ***** ITERATE JR TIMES   *   *   *   *   *   *   *   *   *   *   *
            JR = 200
            DO 26 J=1,JR
            SDJ(J) = 0.0
            RHCJ(J) = 0.0
            RHC2J(J) = 0.0
         26 CONTINUE
            NPT = 1
            IR = 1
            J2 = 4
            CALL BSF(X,0.8800,7.0000,SWFN,SBM,SUMM,SM14,WRGK,0)
            DO 38 J=1,JR
      *     SETTING UP GMOLES OF COMPONENTS AT INLET WITH RECYCLE(RR)
            IL2 = 5
            SGM2 = 0.0
            DO 34 I=1,IL2
            SGM2 = SGM2 +GMIZ(I,L2)
         34 CONTINUE
            DO 37 I=1,IL2
            IF (J -1) 35,35,36
         35 GMIZ(I,1) = GMFI(I)
            GO TO 37
         37
         38
```

continued

Table B4, continued

```
 92        36 GMIZ(I,1) = GMFI(I) +GMIZ(I,L2)/SGM2*RMOLE
 93        37 CONTINUE
 94           RHCJ(J) = GMIZ(1,1)/GMIZ(2,1)
 95     * *** GOING INTO REACTOR TUBE SEGMENT BY SEGMENT   *   *   *   *
 96           IS2  = 7
 97           SDSG = 0.0
 98           DO 29 L=1,NL
 99           SGM = 0.0
100           DO 25 I=1,IS2
101           SGM = SGM +GMIZ(I,L)
102        25 CONTINUE
103     *     TO DAMPEN PURE FEED BY DILUTION FOR THE FIRST ROUND ITERATATION
104           IF (J-1) 43,43,44
105        43 SGM = SGM*SQRT(RR+1.0)
106        44 CONTINUE
107           PH2 = PA*GMIZ(1,L)/SGM
108           PCO = PA*GMIZ(2,L)/SGM
109           IF (U-RF) 57,58,58
110        57 CONTINUE
111           IF (J-3) 61,61,62
112        61 RHC = RHCJ(J)
113           GO TO 59
114        62 RHC = RHCJ(3)
115           GO TO 59
116        58 CONTINUE
117           RHC = PH2/PCO
118        59 CONTINUE
119           RCO = 0.01515617*(PH2**1.185459)*(RHC**0.466108)/1000.*TCOEF
120           DCO = RCO*WCAT*SA
121           DH2 = DCO *U
122           DSG = DCO +DH2
123           GMIZ(9,L+1) = DSG
124           SDSG = SDSG + DSG
125           GMIZ(10,L+1) = SDSG
126           DCHX = DSG/(2.0+0.5*X)
127           RCO2 = (1.0+0.5*X-U)/(1.0+U)
128           IF (RCO2) 21,24,24
129        21 RCO2 = 0.0
130        24 CONTINUE
131           DCO2 = DCHX*RCO2
132           DH20 = DCHX*(1.0-RCO2)
133           IF (NPT) 18,18,30
134        30 CONTINUE
135     *     GOING INTO SCHULZ-FLORY ROUTINE ONLY FOR THE LAST ITERATION
136     *     & COMPUTE PRODUCT DISTRIBUTION FOR EACH SEGMENT USING SFHC2
137           RHC2 = LOG(PH2/PCO)
138           A2   =  0.78124 -0.048725*RHC2 +0.031305*FT
```

continued

Table B4, continued

```
      PCTCH4 = 147.791 +15.1143*RHC2 -128.4976*FT
      FCH4 = PCTCH4/100.0/(1.-A2)/(1.-A2)
      IF (FCH4-1.) 13,13,14
   13 FCH4 = 1.0
   14 CONTINUE
      CALL BSF(X,A2,FCH4,SWFN,SBM,SUMM,SM14,WRGK,0)
      DO 17 I=1,6
      WPIZ(I,L) = DCHX*WRGK(I)
   17 CONTINUE
      WPIZ(7,L) = PH2/PCO
      WPIZ(8,L) = RHC2
      WPIZ(9,L) = A2
      WPIZ(10,L) = FCH4
      IF (L-1) 23,23,18
   23 CONTINUE
      WRITE (11,140) 'RECYCL & MOL',0.0,RR,SGM
      WRITE (11,150) 'PP RCO DH&CO',PH2,PCO,RCO,DH2,DCO
   18 CONTINUE
      SQM  = DCHX*SUMM
      SQ14 = DCHX*SM14
      GMIZ(1,L+1) = GMIZ(1,L) -DH2
      GMIZ(2,L+1) = GMIZ(2,L) -DCO
      GMIZ(3,L+1) = GMIZ(3,L)
      GMIZ(4,L+1) = GMIZ(4,L)
      GMIZ(5,L+1) = GMIZ(5,L) +DCO2
      GMIZ(6,L+1) = GMIZ(6,L) +DH2O
      GMIZ(7,L+1) = GMIZ(7,L) +SQM
      GMIZ(8,L+1) = GMIZ(8,L) +DCHX
      GMIZ(11,L+1) = GMIZ(11,L) +SQ14
   29 CONTINUE
*  *** EXIT REACTOR TUBE   *   *   *   *   *   *   *   *   *   *
      RHC2J(J) = GMIZ(1,L2)/GMIZ(2,L2)
      SDJ(J) = SDSG
      IF (NPT) 33,33,31
   31 CONTINUE
      WRITE (11,150) 'PP RCO DH&CO',PH2,PCO,RCO,DH2,DCO
      WRITE (11,130)
      WRITE (11,120) GMIZ(1,1),GMIZ(2,1),(GMIZ(I,1),I=4,11)
      WRITE (11,120) GMIZ(1,NL),GMIZ(2,NL),(GMIZ(I,NL),I=4,11)
      WRITE (11,120) GMIZ(1,L2),GMIZ(2,L2),(GMIZ(I,L2),I=4,11)
      WRITE (11,130)
      GO TO 19
*
   33 CONTINUE
      RHC2 = (RHCJ(J)+RHC2J(J))/2.0
      RHC2 = LOG(RHC2)
      A2   =  0.78124 -0.048725*RHC2 +0.031305*FT
```

continued

Table 4, continued

```
      PCTCH4 = 147.791 +15.1143*RHC2 -128.4976*FT
      FCH4 = PCTCH4/100.0/(1.-A2)/(1.-A2)
      IF (FCH4-1.) 15,15,16
   15 FCH4 = 1.0
   16 CONTINUE
      CALL BSF(X,A2,FCH4,SWFN,SBM,SUMM,SM14,WRGK,0)
   19 CONTINUE
      GMIZ(4,L2) = GMIZ(4,L2) + GMIZ(11,L2)
      IF (J- J2-10) 38,38,45
   45 CONTINUE
      RCOMP = RHC2J(J)/RHC2J(J-1)
      RCOMP = LOG(RCOMP)
      RCOMP = ABS(RCOMP)
      IF (RCOMP -0.00035) 41,41,38
   41 NPT = NPT +1
      IF (NPT-3) 38,38,32
   32 CONTINUE
      IF (RCOMP -0.00005) 39,39,38
***** OUT OF ITERATION  *  *  *  *  *  *  *  *  *  *  *
   39 CONTINUE
      J2 = J
      DO 52 I=1,10
   52 WPIZ(I,L2) = 0.0
      DO 56 I=1,6
      DO 54 L=1,NL
      WPIZ(I,L2) = WPIZ(I,L2) +WPIZ(I,L)/GMIZ(8,L2)*100.0
   54 CONTINUE
   56 CONTINUE
      DO 55 I=7,10
      DO 53 L=1,NL
      WPIZ(I,L2) = WPIZ(I,L2) + WPIZ(I,L)/NL
   53 CONTINUE
   55 CONTINUE
      WRITE (11,130) 'ITERATION J ',J
      JIR(IR) = J
      DO 66 I=1,10
      GMIJ(I,IR) = GMIZ(I,L2)
   66 CONTINUE
      DO 67 I=11,16
      GMIJ(I,IR) = WPIZ(I-10,L2)
   67 CONTINUE
      TDH2 = GMIZ(1,1) -GMIZ(1,L2)
      TDCO = GMIZ(2,1) -GMIZ(2,L2)
      CVH2 = TDH2/GMFI(1)*100.0
      CVCO = TDCO/GMFI(2)*100.0
      CVSG = SDSG/FSG*100.0
      U2 = TDH2/TDCO
```

continued

Table B4, continued

```
233       TDCO2 = GMIZ(5,L2) -GMIZ(5,1)
234       RCO2 = TDCO2/(TDCO2+GMIZ(6,L2))
235       GMIJ(17,IR) = TDH2
236       GMIJ(18,IR) = TDCO
237       GMIJ(19,IR) = SDSG
238       GMIJ(20,IR) = CVH2
239       GMIJ(21,IR) = CVCO
240       GMIJ(22,IR) = CVSG
241       GMIJ(23,IR) = U2
242       GMIJ(24,IR) = RCO2
243       GMIJ(25,IR) = A2
244       GMIJ(26,IR) = FCH4
245       GMIJ(27,IR) = PCTCH4
246       RHC2  = WPIZ(8,L2)
247       A2B   = WPIZ(9,L2)
248       FCH4B = WPIZ(10,L2)
249       FCH4C = WPIZ(1,L2)/100./(1.-A2B)/(1.-A2B)
250       CALL BSF(X,A2B,FCH4C,SWFN,SBM,SUMM,SM14,WRGK,0)
251       DO 64 I = 1,6
252       WRGK(I) = WRGK(I)*100.0
253    64 CONTINUE
254       WRITE (11,130)
255       WRITE (11,140) 'D H2 & CONV ',TDH2,CVH2
256       WRITE (11,140) 'D CO & CONV ',TDCO,CVCO
257       WRITE (11,140) 'D SG & CONV ',SDSG,CVSG
258       WRITE (11,140) 'H2/CO USAGE ',U2
259       WRITE (11,140) 'RCO2        ',RCO2
260       WRITE (11,190) 'RHC LR A F "',(WPIZ(I,L2),I=7,10),FCH4C
261       WRITE (11,160) 'S-F DISTRBTN','CH4 ','C2-C4','C5-C10',
262      &               '350-650','C00-C00','C21+WAX'
263       WRITE (11,140) 'CUM 50 SGMNT',(WPIZ(I,L2),I=1,6)
264       WRITE (11,140) 'FRM CUM ALFA',(WRGK(I),I=1,6)
265       WRITE (11,130)
266       WRITE (11,160) 'SUM D SYNGAS','   AND  ','H2/CO ON','ITERATN '
267       WRITE (11,170) (SDJ(JL),JL=1,J2)
268       WRITE (11,130)
269       WRITE (11,180) (RHCJ(JL),JL=1,J2)
270       WRITE (11,130)
271       WRITE (11,180) (RHC2J(JL),JL=1,J2)
272       WRITE (11,130)
273       IF (IR-1) 51,51,40
274    51 CONTINUE
275       IR = IR +1
276       IF (RHC2J(J)-RHC2J(J-2)) 71,71,72
277    71 CVH2 = CVH2 + (100.-CVH2)/3.00
278       GO TO 73
279    72 CVH2 = CVH2 - (100.-CVH2)/3.00
```

continued

Table B4, continued

```
 73 CONTINUE
    TDH2 = GMFI(1)*CVH2/100.
    GMIZ(1,L2) = GMIZ(1,1) -TDH2
    TDCO = TDH2/U
    GMIZ(2,L2) = GMIZ(2,1) - TDCO
38 CONTINUE
40 CONTINUE
   DO 68 I=1,27
   GMIJ(I,3) = (GMIJ(I,1) +GMIJ(I,2))/2.0
68 CONTINUE
   TW1    = GMIJ(11,3)/100.0
   TW4    = GMIJ(12,3)/100.0
   TWAX   = GMIJ(16,3)/100.0
   CALL BFITG(X,TW1,TW4,TWAX,A2,FCH4)
   CALL BSF(X,A2,FCH4,SWFN,SBM,SUMM,SM14,WRGK,0)
   DO 65 I=1,6
   WRGK(I) = WRGK(I)*100.0
65 CONTINUE
   CALL DATTIM(3,ATIME,ADATE,M,NDAY,MD,NY)
   WRITE (11,130)
   WRITE (11,200) 'PROGM FIXBD1',ADATE,ATIME
   WRITE (11,130)
   WRITE (11,140) 'FEED H2 CO A',(FCI(I),I=1,3)
   WRITE (11,140) 'TC SV FFLOW ',TC,SV,FFLOW
   WRITE (11,140) 'D SEG W SA X',RHOB,BNL,WCAT,SA,X
   WRITE (11,130)
   WRITE (11,130) 'ANSWER &ITRN',(JIR(J3),J3=1,2)
   WRITE (11,140) 'RECYCL      ',RR
   WRITE (11,130)
   WRITE (11,140) 'D H2 & CONV ',GMIJ(17,3),GMIJ(20,3)
   WRITE (11,140) 'D CO & CONV.',GMIJ(18,3),GMIJ(21,3)
   WRITE (11,140) 'D SG & CONV ',GMIJ(19,3),GMIJ(22,3)
   WRITE (11,140) 'H2/CO USAGE ',GMIJ(23,3)
   WRITE (11,140) 'RCO2        ',GMIJ(24,3)
   WRITE (11,190) 'FITD A F %C1',A2,FCH4,GMIJ(11,3)
   WRITE (11,160) 'S-F DISTRBTN','CH4 ','C2-C4','C5-C10',
  &               '350-650','C00-C00','C21+WAX'
   WRITE (11,140) 'CUM SO SGMNT',(GMIJ(I,3),I=11,16)
   WRITE (11,140) 'FRM FITTED A',(WRGK(I),I=1,6)
   WRITE (11,130)
46 CONTINUE
48 CONTINUE
   STOP
   END
```

Table B5. Glossary of terms used in FIXBD1 simulation.

FCI	Input data array for feed composition, %H2, %CO, %Inert
TCK	Input data array of 3 elements for temperature, deg C.
SVM	Input data array of 3 elements for space velocity, vol/vol/hr
TUBD	Reactor tube diameter, cm, 5 cm. for Arge reactor tube
TUBL	Reactor tube length, cm, 1200 cm for Arge reactor tube
VM	Molar volume at 70 d F, 24147 cc/g mole
RF	Feed ratio in H2/CO
SA	Specific Activity with the catalyst of Run 10011-14 as reference, or SA = 1.0 for the catalyst.
U	Usage ratio, relative consumption of H2 to CO, in mole ratio
X	Ratio x in the representative formula CHx for hydrocarbons. as in the following stoichiometry:

$$(1.0+X/2)\ H2 + CO \Longrightarrow CHx + H2O$$
$$H2O + CO \Longrightarrow H2 + CO2$$

Therefore

$$\text{delta CHx} = \frac{(\text{delta H2} + \text{delta CO})}{2.0 + 0.5*X}$$

and

$$\text{delta CHx} = \text{delta H2O} + \text{delta CO2}$$

PA	Pressure, psia
A2	alpha value in Schulz-Flory distribution
FCH4	Methane factor (= Wt%CH4/(1-A2)**2), a ratio of experimental Wt%CH4 found in the product to that expected from Schulz-Flory distribution, which is (1.0-alpha)**2.
NL	The reactor tube is cut into NL segments, 50 is used.
L2	Last array element for condition at tube exit, (= NL+1 = 51)
TC	Temperature in deg C.
FT	a function of temperature, =1000./(R*T)
FFLOW	Fresh feed flow for the space velocity, gmole/hr
RR	Recycle Ratio, ratio of recycle stream to fresh feed in moles
RMOLE	Recycle stream flow, gmole/hr
DE	Delta E, for Arrheius activation energy, 30114.78 cal/gmole.
T1	Temperature in deg K, for Arrhenius reference temp. of 250 d C
T2	Temperature in deg K
TCOEF	Arrhenius activation energy term with reference to 250 d C as base, it is a temperature coefficient, hence TCOEF.
GMIZ(I,L)	An array of 11*51, for various components in gm moles in each tube segments, arranged in 11 columns and 51 rows. To account for change from one tube segment to the next, in moles The first row is for tube inlet. The 51 st row is for tube exit. The columns: 1 2 3 4 5 6 7 8 9 10 11 The components: H2 CO AR C1-C4 CO2 H2O HC SmCHx D-SG SumDSG S(C1-C4)

continued

Table B5, continued

Arithmetic Oper. - - 0 0 + + + + 0 + +
for next segment
+ sign == being accumulated in the memory cell, or the tube segment
- sign == being deducted or consumed in the memory cell
0 sign == neither accumulated nor consumed in the cell, no change
"I"--an array index for component I
"L"--an array index for tube segment or length along reactor tube.
D -- for delta, as delta moles changed in the segment
Sm (or Sum) -- Sum moles, being accumulated in the cell

GMFI an array for fresh feed flow, gmole/hr of H2 CO ARGON
FSG feed syngas flow, gm moles (H2+CO) / hr
DL delta length, length of a tube segment, cm.
RHOB bulk density of catalyst bed, gm/cc., assumed to be 0.6
WCAT weight of catalyst in the tube segment
BNL number of tube segments, converted to floating point number
JR maximum number of iterations J, set at 200.
SDJ(J) an array for SDSG, sum delta syngas, on succesive iteration
RHCJ(J) an array for H2/CO ratio at tube inlet on each iteration J
RHC2J(J) an array for H2/CO ratio at tube exit on each iteration J
NPT an index for detail printout and other branching purpose
when NPT=0, it will save computing time by not going into Schulz-Flory routine for each tube segment right way, and instead it will use the average condition of tube inlet and exit as representative for the whole tube until the iteration gets fairly close to steady state condition.
when NPT=1, it will go into Schulz-Flory routine for each tube segment right way. The SF routine computes volume shrinkage, alpha, methane make & other product slade.
IR an iteration index stands for successful iteration closure. After the first successful iteration, a step change is made to change the reactor condition to the other side of steady state condition and start iteration again. IR to start at 1.
J2 an iteration index for the first successful closure of iteration, initially set at 4. Later used in a branching decision in line 194: IF (J -J2 -10) 38,38,45
BSF a Schulz-Flory subroutine for computing the volume shrinkage by converting a symbolic hydrocarbon formula CHx to moles of real hydrocarbons according to Schulz-Flory distribution, and other product slates such as C1-C4, & other fraction cuts in WRGK arranged in (C1 C2-C4 C5-C10 C11-C20 OO C21+WAX).
IL2 index (=5) for the purpose of summing component array at tube exit GMIZ(I,L2) for recycle gas, which is composed of the first 5 elements of the array, the arrangement of which is repeated below:

The columns:	1	2	3	4	5	6	7	8	9	10	11
The components:	H2	CO	AR	C1-C4	CO2	H2O	HC	SmCHx	D-SG	SumDSG	S(C1-C4)

continued

Table B5, continued

SGM2	sum gmoles of column elements 1-5, ie. (H2,CO,A,C1-C4,CO2) of 51 st row, at tube exit, for the recycle gas
IS2	index (=7) for the purpose of summing components inside the tube segment GMIZ(I,L), including H2O & hydrocarbons made in the tube segment.
SGM	sum gmoles of column elements 1-7, ie. (H2,CO,A,recyed C1-C4, CO2, H2O & hydrocarbons. The sum is used to compute mole fractions of H2 & CO in the tube for rate computation.
PH2	partial pressure of H2, psia
PCO	partial pressure of CO, psia
RHC	ratio H2/CO
RCO	rate of CO conversion, gmole/hr/gm catalyst from rate correlation
DCO	gmole/hr CO converted in the segment, from the rate, weight catalyst and the specific activity SA
DH2	gmole H2 converted in the segment, from DCO & usage ratio U
DSG	gmole syngas (=H2+CO) converted in the segment, "D"--generally stands for delta
SDSG	sum of gmole syngas converted so far. "S"--generally stands for sum
RCO2	ratio of moles CO2/(H2O+CO2) among the side products RCO2 = (1+.5*X-U)/(1+U) from stoichiometric relations
DCO2	gmole CO2 formed in the segment
DH2O	gmole H2O formed in the segment
RHC2	log(H2/CO)
A2	alpha value in Schulz-Flory distribution, from correlation
PCTCH4	Wt% CH4 from product selectivity correlation
WPIZ(I,L)	An array of 10*51 for product distribution achieved in each tube segment L, for the purpose of summing later. The first 6 elements come from array WRGK of subroutine BSF:
	The columns: 1 2 3 4 5 6 7 8 9 10
	The components: C1 C2-4 C5-10 C11-20 OO C21+WAX H2/CO LnR Alpha FCH4
SQM	real gmoles of hydrocarbon derived from gmole of symbolic formula CHx, computed from Schulz-Flory subroutine
SQ14	real gmoles of C1-C4 hydrocarbons derived from gmoles of symbolic formula CHx
RCOMP	ratio of composition change (H2/CO ratio @ tube exit) on successive iterations, used as an iteration closure criteria. A criteria of 0.00035 was used to increse the NPT value by 1, thereby initiate the use of Schulz-Flory routine in every segment of the tube. A criteria of 0.00005 was imposed for steady state requirement.
JIR	an array of 3 elements, for the storing of the iteration number of the 1st & 2nd successful closure on iteration.
IR	index for successful iterations, IR=1 for the first try, and then a step change is made in the tube effluent gas composition

continued

Table B5, continued

	so as to start iteration again on the other side of the conversion, meanwhile the iteration index IR is advanced by one unit.
GMIJ(I,IR)	An array of 27*3 to store results on successful iterations.
TDH2	total change in H2 moles over the tube length
TDCO	total change in CO moles over the tube length
CVH2	total conversion of H2 as % of H2 fed in fresh feed
CVCO	total conversion of CO as % of CO fed in fresh feed
CVSG	total conversion of syngas (H2+CO) as % of syngas fed
U2	calculated usage ratio of H2 to CO, from H2 & CO consumed
TW1	Wt fraction CH4
TW4	Wt fraction C2-C4
TWAX	Wt fraction C21+WAX
BFITG	subroutine to compute the best fitting alpha from light fraction (C2-C4 or TW4) and heavy fraction (C21+WAX or TWAX.

Table B6. Line by line guide for FIXBD1 computer simulation.

1- 18	Comments (by *), dimensions and format statements
19- 21	Input data for feed composition, temperatures and space velocities, FCI, TCK, & SVM each an array of 3.
22- 29	Define reactor configurations and other fixed input variables. Note that usage ratio U is considered as a fixed variable.
33- 34	Define number of segments for the reactor tube, 50 is used.
35- 37	Pick a temperature & compute temp. function.
38- 44	Pick a space velocity & compute feed flow, & recycle flow. Note recycle ratio RR is inputted in line 41.
48- 53	Compute Arrhenius temperature coefficient TCOEF.
55- 63	Set zero, compute gmoles of feed component flow & feed syngas.
65- 69	Cut the tube into segments, compute weight of catalyst
71- 79	Preparing for iteration by setting zero's & other constants, like NPT & IR. At the beginning we do not need too much printout, hence NPT=0. Likewise IR=1 for the first attempt.
80	Assume an alpha value & methane factor and enter Schulz-Flory routine for volume change due to reaction.
81- 94	Enter iteration loop and set up tube inlet composition profile. Access the array for reactor tube effluent gas GMIZ(I,51), and at the recycle ratio to combine with fresh feed to form an array of gmoles gas components for the tube inlet condition.
95-169	Going into reactor tube segment by segment, as follows:
96-120	Compute sum of the components, mole fractions, partial pressures, rate and CO conversion in the segment. The rate expression is changed to an equivalent expression of: RATE == const*(PH2**a)*((PH2/PCO)**b)*TCOEF/1000. where a = 1.6515671-0.466108 = 1.1854591 & b = 0.466108 and if (U less than RF), then the ratio (PH2/PCO) will be freezed after 3 iterations so to avoid a unreasonable situation where the rates will grow faster and faster as the gas moves down the tube.
120-168	Compute moles CO depleted, H2 depleted (from usage ratio U), syngas depleted, its cumulative sum, moles of symbolic hydrocarbon CHx formed and real moles of hydrocarbons SQM, C1-C4's SQ14, and moles of byproducts CO2 & H2O. These quantities are
159-167	deducted or added to the quantities in the current segment to form the quantities for the next segment. Thus the computation progressed from the inlet end to the exit end of the tube.
152-156	Printout of the partial pressures, rate, moles H2 & CO convert-
172-179	ed and gmoles of various components at tube inlet & exit conditions when NPT=1.
170-171	Retain the H2/CO ratio and the syngas converted at tube exit in RHC2J and SDJ array to be used as closure criteria.
182-193	if NPT=0 as when we wish to save computing time, the average value of H2/CO ratios of tube inlet and exit were taken for product selectivity, volume shrinkage and Schulz-Flory computa-
193	tion. Also the cumulative moles of C1-C4 light hydrocarbons

continued

Table B6, continued

	were transferred from array position GMIZ(11,L2) to GMIZ(4,L2) to be included for recycle. The components in the first 5 element (IL2=5) of the array are to be summed and recycled.
194	Set up minimum number of iteration required before testing for closure.
195-203	This is an iterative procedure. At the beginning, fresh feed is the tube inlet gas. From the second round and on, the recycle gas is mixed with the fresh feed to form the inlet gas. The gas composition changes with the iteration and hopefully it will reach a steady state and exit from the iteration. The criteria for exit is set by the ratio of composition change RCOMP being less than 0.00005(line 203). However before that happens, and at an easier criteria of 0.00035, the index NPT is advanced by 1, under which condition, the segment to segment computation will involve entering Schulz-Flory subroutine BSF each time, and compute product distribution on each segment for later summation.
205	Exit iteration.
206-218	After successful iteration, the product formed in each segment and other informations in array WPIZ(I,L) are summed, averaged and stored in WPIZ(I,51)
219-220	Save the iteration index J.
221-245	The component profile in GMIZ(I,51), the product selectivity informations in WPIZ(I,51), and conversions after the first successful iteration were saved in array GMIJ(I,1), an array of 27*3. Later it will be averaged with similar information in array GMIJ(I,2) and stored in array GMIJ(I,3).
227-234	Compute moles H2 and CO converted, conversions, usage ratio & RCO2 and save these in array GMIJ(I,IR)
246-253	Compute product slate expected from cumulated average value of alpha. This product slate shows some deviation from the cumulated product slate from 50 tube segments.
254-272	Print result of first iterative try, as well as the values in arrays SDJ, RHCJ & RHC2J for moles syngas converted, H2/CO ratios at tube inlet and exit on each iteration.
273-284	WE hope that the computation has reached a steady state answer. However we are not sure whether there is a steady state answer or keeps on drifting. To make sure that this is so, we will make a step change in the effluent gas composition in array GMIZ(I,51), continue the computation from the other side of the steady state answer and repeat the iterative process.
286	Out of the second iteration round from the other side of the answer.
287-289	Averaging the two sets of answer.
290-297	Take the average product slate, fit for an average alpha and calculate its product slate from the fitted alpha. This alpha value will be useful for material balance computation.

continued

Table 86, continued

298	Enter a system subroutine DATTIM for date and time.
299-319	Printout the averaged answer in conversions and product selectivity.
320-321	Repeat for other cases of different temperatures and space velocities.

Table B7. Listing of BSF subroutine for determining the hydrocarbon product distribution.

```
          BSF FORTRAN A1
 1        SUBROUTINE BSF(X,A2,FCH4,SWFN,SBM,SUMM,SM14,WRGK,NPT)
 2 *      EXTERNAL DIMENSION REQD: SWFN(40), SBM(40), WRGK(6)   W,MAY 15,85
 3 *      GIVEN: X, ALPHA,A2, FCH4(=W%CH4/(1-A2)/(1-A2))  COMPUTE PRDT SLATE
 4 *      DISTINCTION BEING MADE IN THE MOL.WT. OF CH4, CHX, CHZ(FOR C2 &+)
 5 *      X,AVG MOL FORMULA.   Z,MOL FORMULA FOR C2 &+, SO THAT CH4+CHZ=CHX
 6 *      WFN=WT.FR. SWFN=CUM SUM WT.FR.(SUM WT.FR.=1)
 7 *      CFN=CARBON FR.  BM=MOLS(FROM WT)  SBM=CUM SUM MOLS BM @N, SUMM(40)+
 8 *      WRGK=WTS OF VARIOUS CUTS: 1 2-4 5-10 11-20 0 21&+
 9        DIMENSION CFN(40), WFN(40), BM(40), SWFN(40), SBM(40), WRGK(6)
10        TC1 = (1.0-A2)*(1.0-A2)
11        WMCH4 = 12.0111 +4*1.008
12        WMCHX = 12.0111 +X*1.008
13        FCH5  = FCH4*WMCHX/WMCH4
14        F     = FCH5*(1.0-TC1)/(1.0-FCH5*TC1)
15        SUMC  = 1.0 +(F-1.0)*TC1
16        Z     = ((1.0+(F-1.0)*TC1)*X -F*TC1*4)/(1.0-TC1)
17        WMCHZ = 12.0111 + Z*1.008
18        RMW   = WMCHZ/WMCHX
19        WFN(1)  = TC1*FCH4
20        CFN(1)  = WFN(1)*WMCHX/WMCH4
21        BM(1)   = CFN(1)
22        SWFN(1) = WFN(1)
23        SBM(1)  = BM(1)
24        DO 32 N=2,40
25        CFN(N)  = N*TC1*A2**(N-1)/SUMC
26        WFN(N)  = CFN(N)*RMW
27        SWFN(N) = SWFN(N-1) +WFN(N)
28        BM(N)   = CFN(N)/N
29        SBM(N)  = SBM(N-1) + BM(N)
30     32 CONTINUE
31        SUMM = SBM(40) +(1.0-SWFN(40))/41.0
32        SM14 = SBM(4)
33        WRGK(1) = SWFN(1)
34        WRGK(2) = SWFN(4)  -SWFN(1)
35        WRGK(3) = SWFN(10) -SWFN(4)
36        WRGK(4) = SWFN(20) -SWFN(10)
37        WRGK(5) = 0.0
38        WRGK(6) = 1.0 -SWFN(20)
39        IF (NPT) 36,36,33
40     33 WRITE (11,120)
41        WRITE (11,130) ' X ALPHA FCH4   ',X,A2,FCH4
42        WRITE (11,120)
43        WRITE (11,130) 'N CF WF SW M CSM'
44        DO 34 N=1,40
45        WRITE (11,120)
```

continued

Table B7, continued

```
46          WRITE (11,120) N,CFN(N),WFN(N),SWFN(N),BM(N),SBM(N)
47       34 CONTINUE
48       36 CONTINUE
49      120 FORMAT (1X,I4,3(1X,F8.6),4X,2(1X,F8.6))
50      130 FORMAT (1X,A16,1X,F6.4,2(1X,F7.5))
51          RETURN
52          END



          BFITG FORTRAN A1
 1        SUBROUTINE BFITG(X,TW1,TW4,TWAX,A2,FCH4)
 2 *      This routine will find an alpha that best fit a Schulz-Flory
 3 *      product slate from Fischer-Tropsch synthesis.
 4 *      where TW1 = WtFrCH4, TW4 = C2-C4, TWAX = C21+WAX & A2=alpha
 5        DIMENSION SWFN(40), SBM(40), WRGK(6)
 6        RTWAX   = TWAX/TW4
 7        A2  = 0.800
 8        DO 14 I=1,20
 9        FCH4 = TW1/(1.-A2)/(1.-A2)
10        CALL BSF(X,A2,FCH4,SWFN,SBM,SUMM,SM14,WRGK,0)
11        RWAX  = WRGK(6)/WRGK(2)
12        DEV   = RWAX/RTWAX
13        DEV2  = LOG(DEV)
14        DEV2  = ABS(DEV2)
15        IF (DEV2-0.0002) 18,18,12
16     12 CONTINUE
17        DEV = DEV**0.04
18        A2  = A2/DEV
19     14 CONTINUE
20     18 CONTINUE
21        RETURN
22        END
```

Table B8. Glossary of terms used in BSF subroutine.

X	value of x in CHx, average number of hydrogen atoms associated with one carbon atom.
A2	Alpha value
FCH4	Methane factor
TC1	a function of alpha, fa = (1-A2)*(1-A2)
WMCH4	molecular weight of CH4
WMCHX	molecular weight of CHx
FCH5	a FCH4 factor in terms of the average molecular weight CHx.
F	a true methane factor
SUMC	a new sum, greater than 1.00, due to positive deviation of methane.
Z	average number of hydrogen atoms attached to the carbon atom for C2 and heavier fractions
WMCHZ	average molecular weight CHz for C2 and heavier.
WFN	An array of 40 for wt fractions of hydrocarbons from C1 to C40.
CFN	An array of 40 hydrocarbon fractions of C1 to C40 in terms of carbon atom fractions, which obey Schulz-Flory distribution.
BM	An array of 40, for mole fractions of C1 to C40.
SWFN	An array of 40, for cumulative running sum of WFN up to n.
SBM	Cumulative sum of the array BM from C1 to C40, total moles of hydrocarbons equivalent to one symbolic mole CHx. This value is always less than one due to shrinkage in moles from converting stoichiometric symbolic mole CHx to real hydrocarbon mole of various chain length n. For instance, for an alpha value of 0.81 and methane factor of 8, one gm mole of CHx shrinks to about 0.4 gm moles of real hydrocarbons.
SUMM	Estimated total sum of moles of real hydrocarbons, including those heavier than C40.
SM14	sum of moles of C1 to C4, derived from one symbolic mole CHx, used in partial recycle computation where only the light hydrocarbons of C1-C4 are recycled.
WRGK	An array of 6 elements, where weight fractions of CH4, C2-C4, C5-C10, C11-C20, 0, C21+Wax are stored.
NPT	An integer used for more detailed printout, when NPT > 0.

Table B9. Stream compositions for the two cases sent to the MITRE Corporation.

	Case 1	Case 2
Wt pct CH_4 selectivity	12.29	7.82
Conditions		
U H_2:CO usage ratio	1.60	2.00
RF H_2:CO feed ratio	1.20	1.39
Feed in		
H_2 feed moles	54.46	58.10
CO feed moles	45.54	41.90
H_2+CO feed moles	100.00	100.00
Wt feed lbs	1385.50	1290.67
Effluent out		
Off-gas		
H_2 moles	2.15	1.44
CO moles	12.85	13.56
CO_2 moles	5.84	1.48
C_1 moles	2.95	1.88
C_2 moles	0.37	0.32
C_3 moles	0.32	0.28
C_4 moles	0.28	0.25
Total moles	24.76	19.21
Total wt lbs	704.12	510.30
Liquid		
C_5 -C_6 wt lbs	35.46	32.18
C_7 -C_8	36.61	33.95
C_9 -C_{10}	34.78	33.46
C_{11}-C_{12}	31.70	31.41
C_{13}-C_{14}	28.02	28.59
C_{15}-C_{16}	24.21	25.45
C_{17}-C_{18}	20.58	22.27
C_{19}-C_{20}	17.25	19.24
C_{21}-C_{22}	14.32	16.44
C_{23+}	59.90	80.07
Total liq HC lbs	302.85	323.04
H_2) lbs	378.69	457.22
Grand total	1385.66	1290.56

Table B10. Characterization of hydrocarbon products for both cases, regardless of methane make.

Carbon No.	Percent		Iso:normal ratio	
	Olefins	Paraffins	Olefins	Paraffins
C_3	52	49	---	---
C_4	68	32	0.054	0.053
C_5	70	30	0.07	0.069
C_6	58	42	0.23	0.23
C_6+	50	50	0.23	0.23

185F-350F 42 (R+M)/2 octane
350F-600F 0°F pour point
76 cetane index

Fig. B1

SCHEMATIC DIAGRAM OF UNION CARBIDE
TUBULAR REACTOR SIMULATION PROGRAMS
INPUT/OUTPUT RELATIONS

THE BERTY REACTOR, a CSTR (CONTINOUS-FEED STIRRED TANK REACTOR) operates under steady state conditions with a high internal recycle rate, causing the catalyst to be exposed to a known and unvarying gas phase composition

YIELDS DATA

DATA CORRELATION by MULTIPLE REGRESSION FOR:

1. CO Conversion Rate as a function of partial pressures of H2, CO and Temp. in the Power Law form
2. Wt%CH4 as a function of H2/CO ratio and Temp.
3. Schulz-Flory alpha as a function of H2/CO ratio and Temp.

is put into

INPUTS ===>	The FIXBD program	===> OUTPUTS
1. CATALYST PROPERTIES . Specific Activity . Usage Ratio . Bulk Density 2. FEED GAS CONDITIONS . Space Velocity . H2/CO Ratio 3. REACTOR CONDITIONS . Pressure . Temperature . Recycle ratio	which is a simulation of an isothermal packed bed tubular reactor having a recycle stream, a condenser, a knock-out pot (to remove H2O & C5+ products) and off-gas stream	PRODUCT STREAM QUANTITIES: . H2 & CO Conversion . H2O & CO2 Production . CH4 make . C2+ hydrocarbon production

Fig. B2. Correlation of H_2 partial pressure in the rate expression.

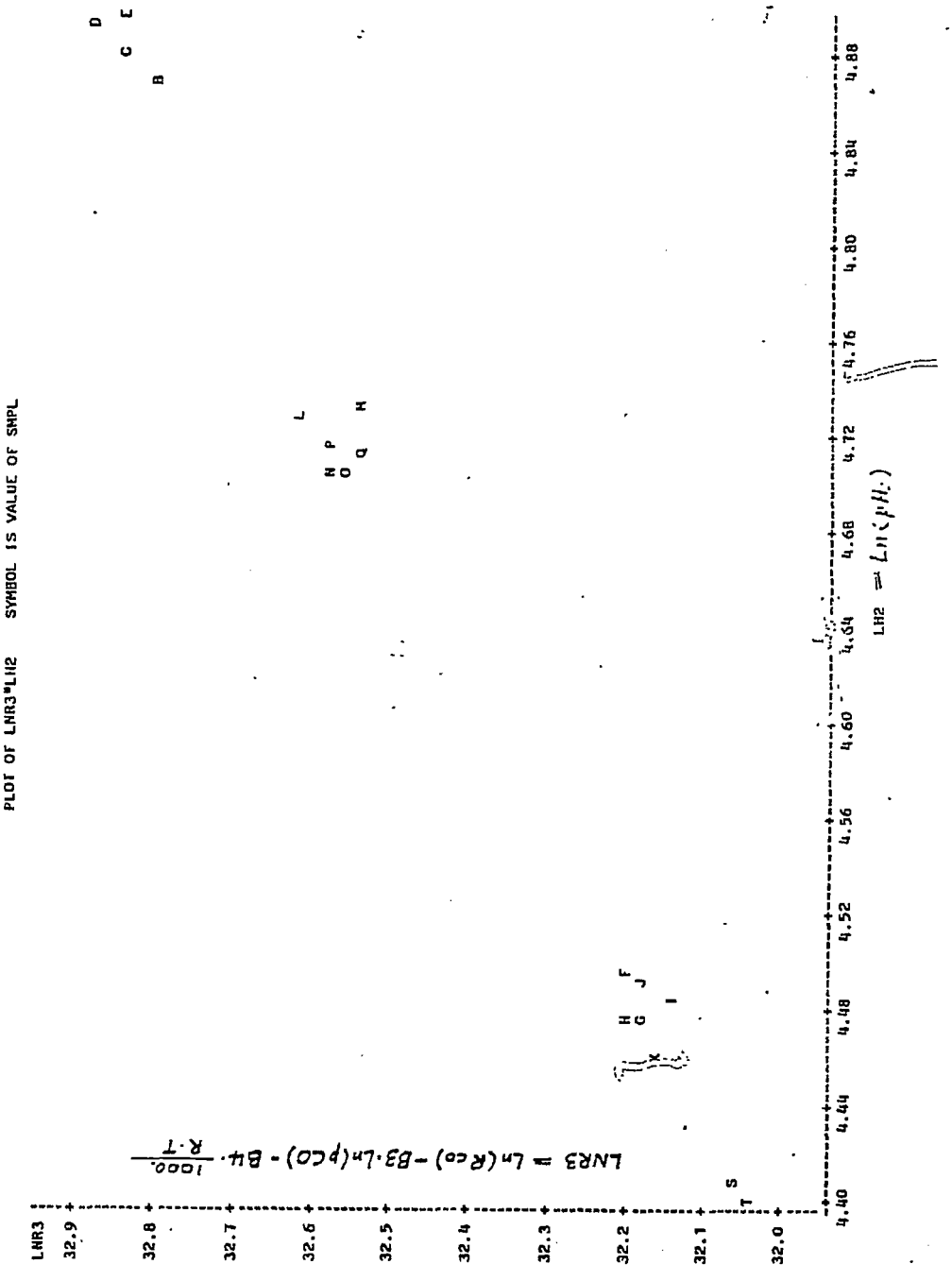


Fig. B3. Correlation of CO partial pressure in the rate expression.

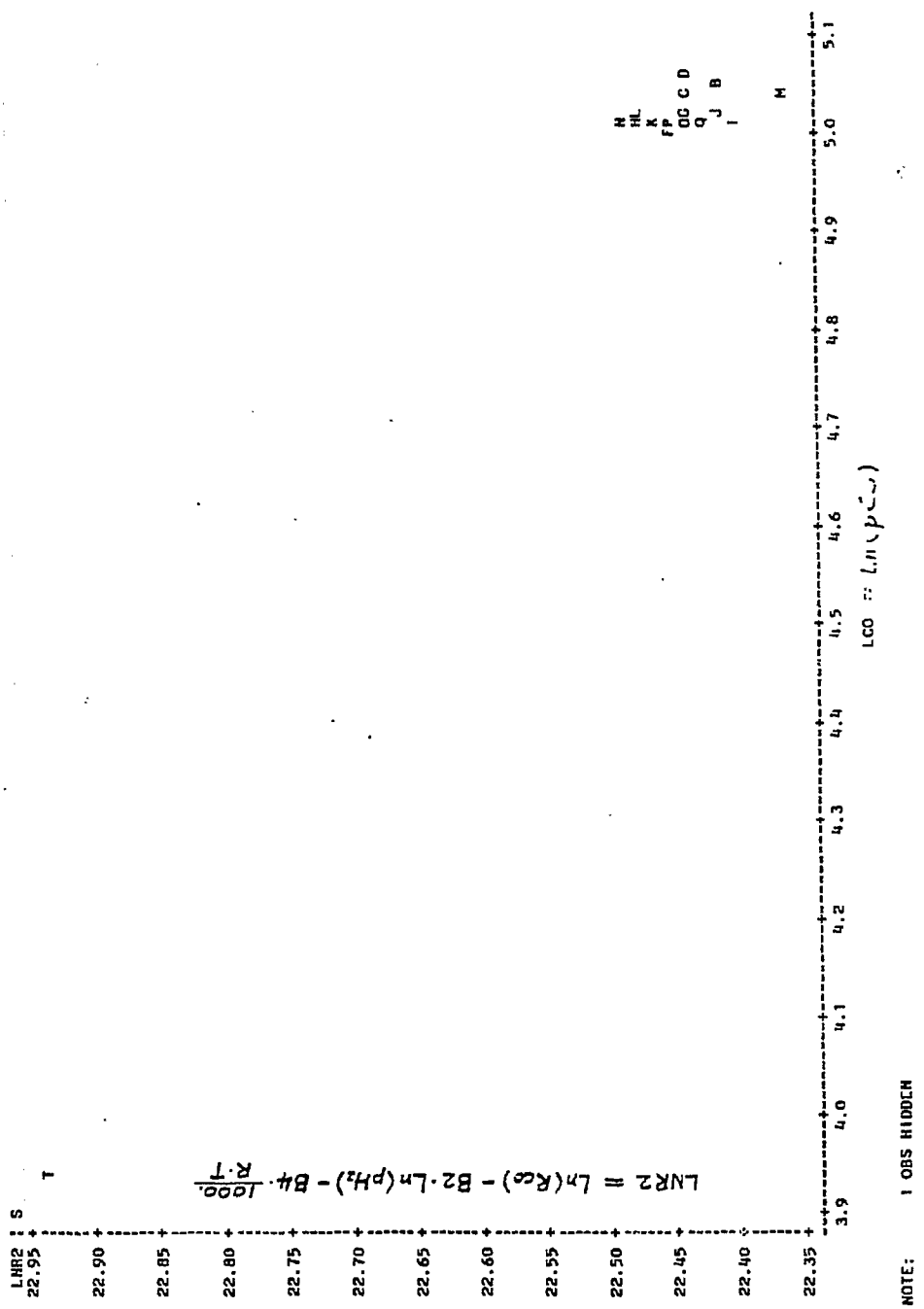


Fig. B4. Correlation of temperature in the rate expression.

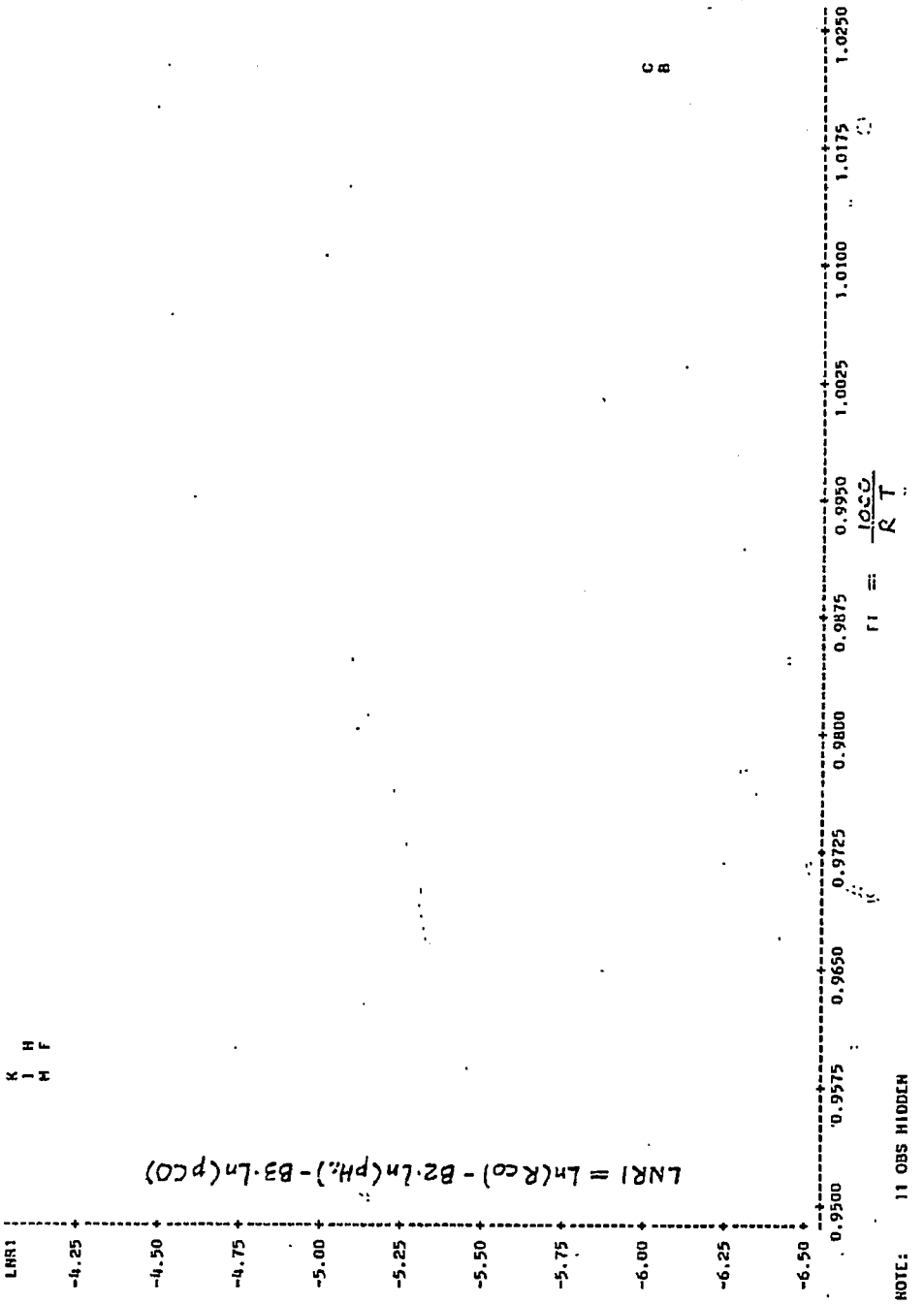


Fig. B5. Correlation of the temperature function in the expression for alpha.

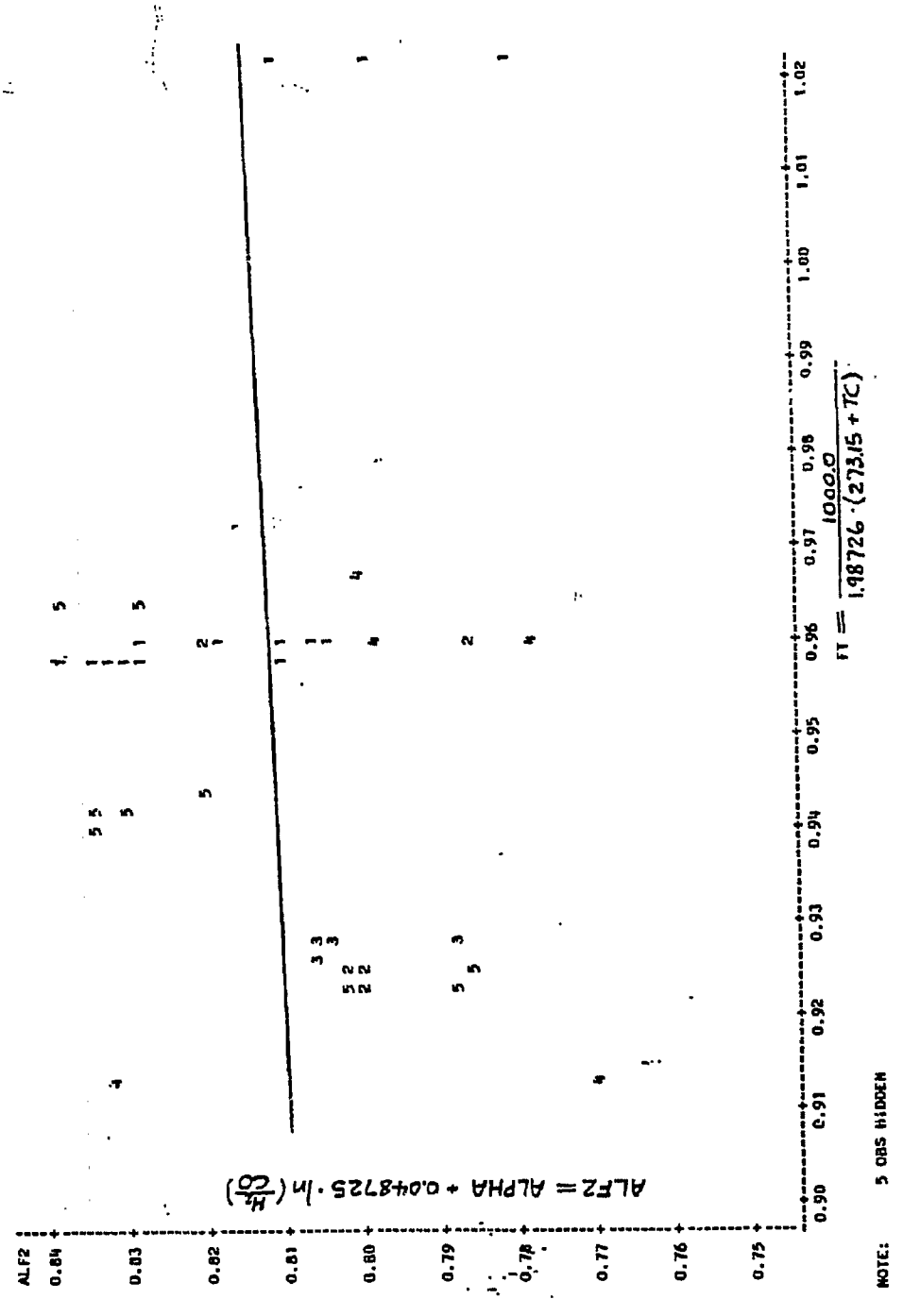


Fig. B6. Correlation of the H_2:CO ratio in the expression for alpha.

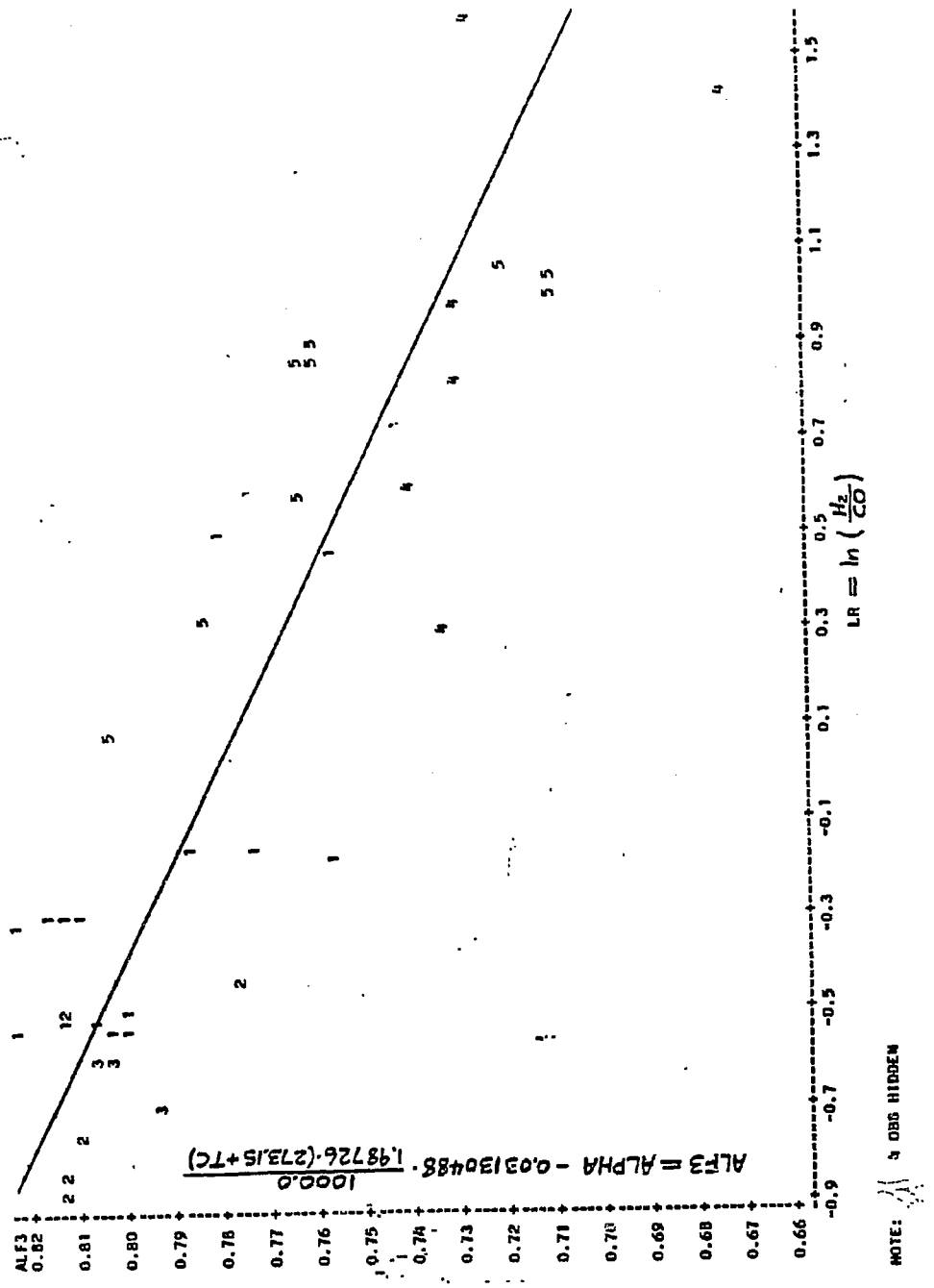
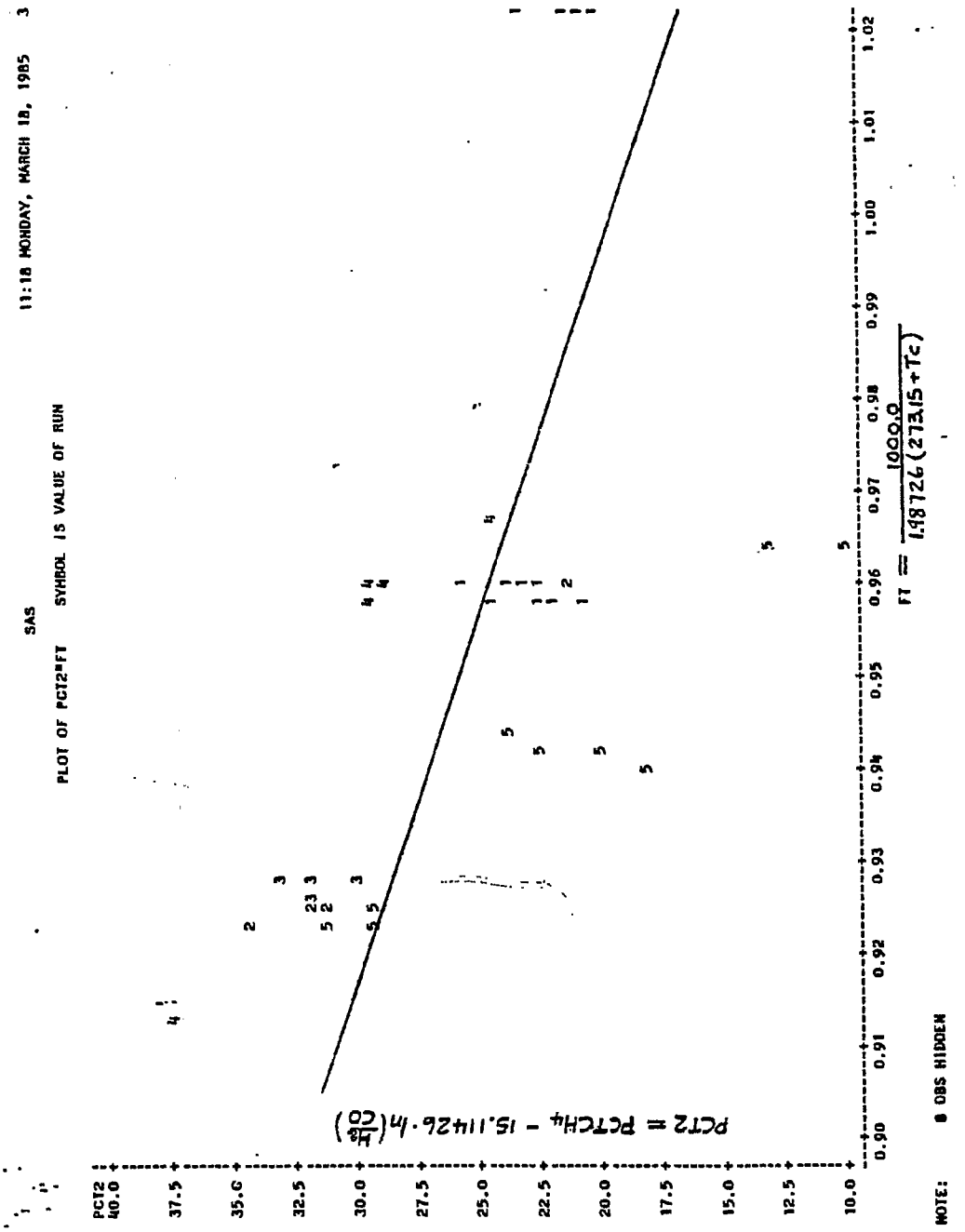


Fig. B7. Correlation of the temperature function in the expression for weight percent CH_4.



$$PCT2 = PCTCH_4 - 15.1426 \cdot ln\left(\frac{H_2}{CO}\right)$$

$$FT = \frac{1.98726\,(273.15+Tc)}{1000.0}$$

Fig. B8. Correlation of the H_2:CO ratio in the expression for weight percent CH_4.

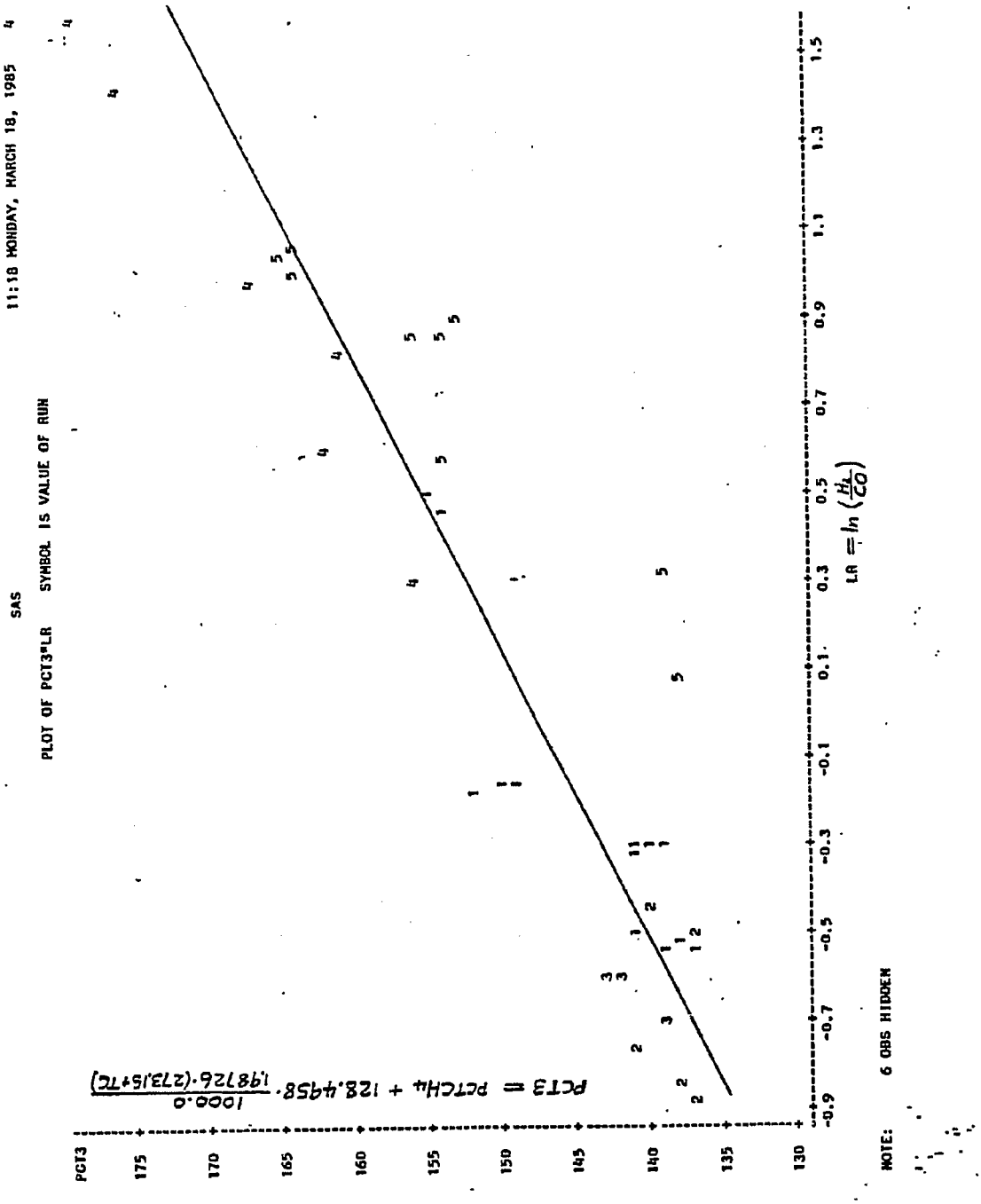
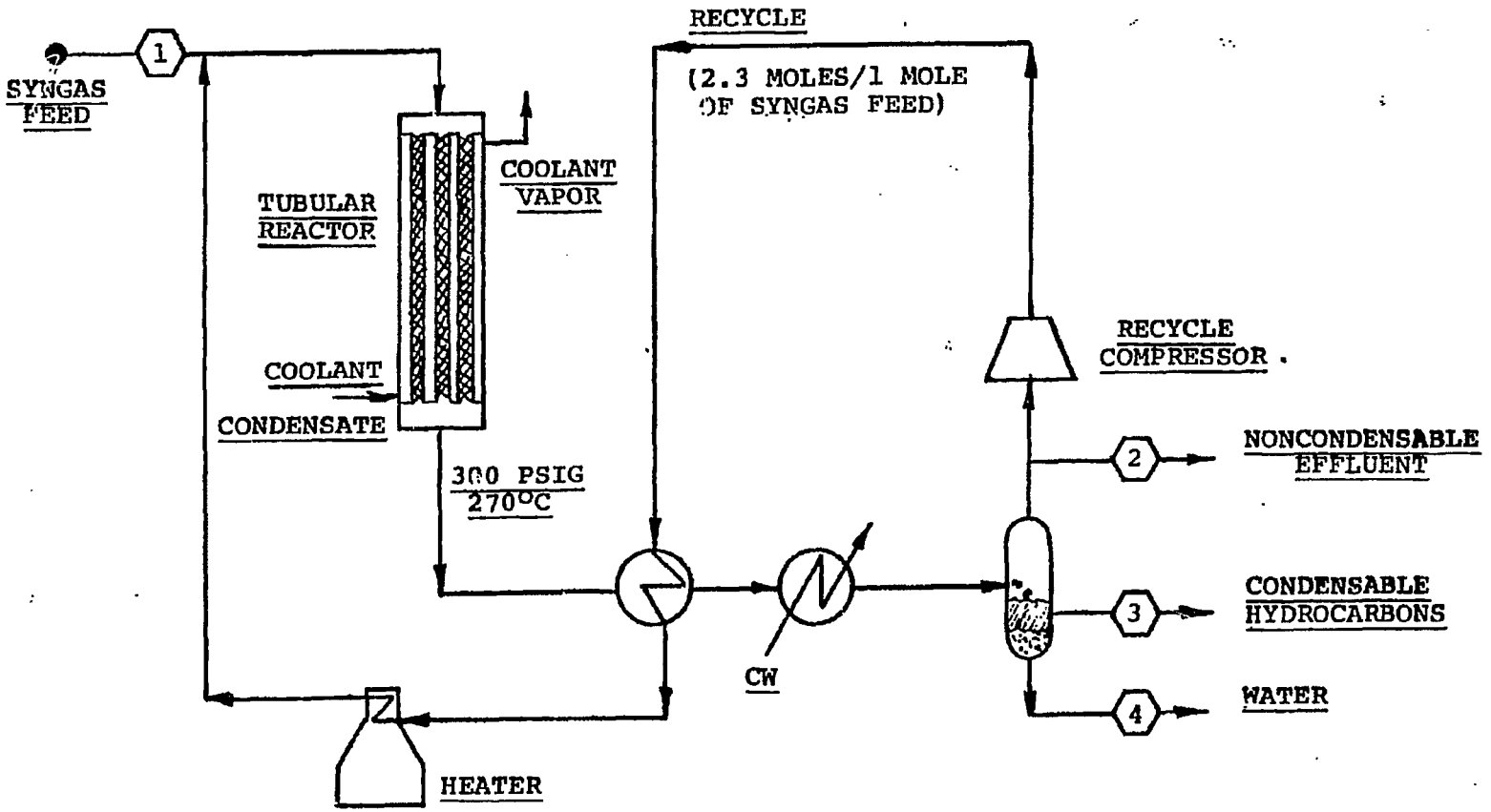


Fig. B9. Schematic diagram of the F-T reactor system.



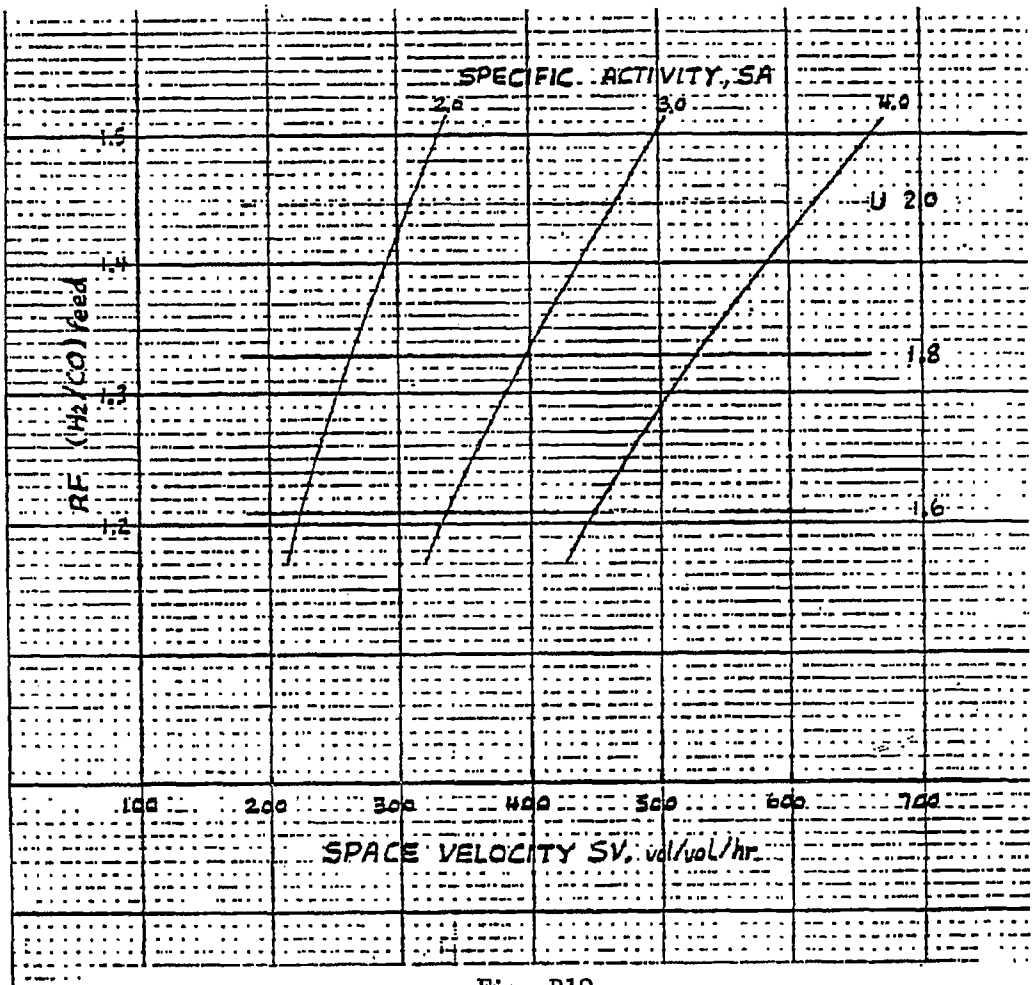


Fig. B10

SPACE VELOCITY AND FEED H2/CO RATIO REQUIREMENT
FOR TUBULAR REACTOR AT 270 C 300 PSIG 2.3 RECYCLE RATIO
WITH A CATALYST CAPABLE OF CERTAIN USAGE RATIO U
SPECIFIC ACTIVITY SA, AND BULK DENSITY 0.6 GM/CC
FOR 85 % SYNGAS CONVERSION AND 12.3 WT%CH4 PRODUCT SELECTIVITY

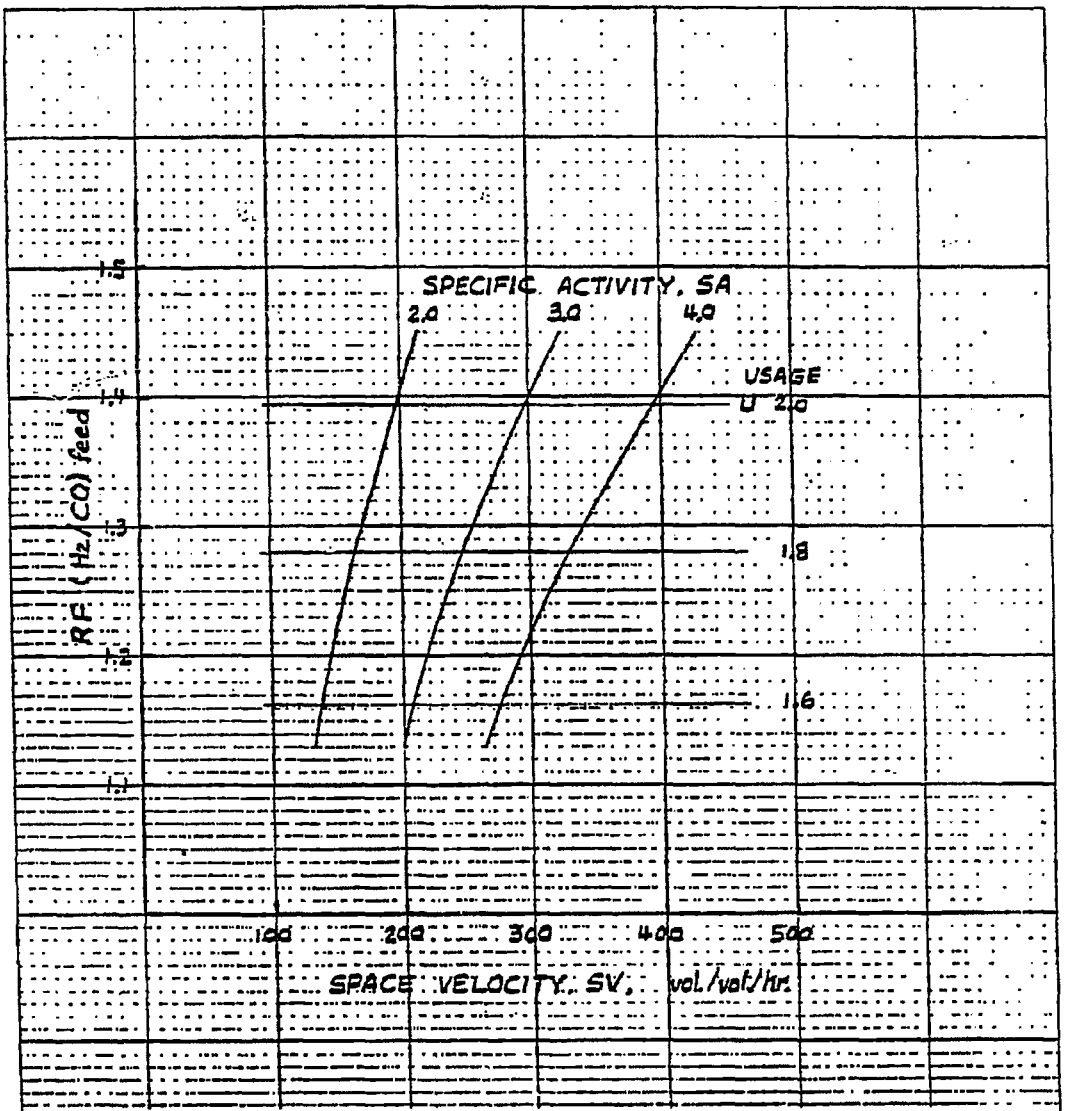


Fig. B11

SPACE VELOCITY AND FEED H2/CO RATIO REQUIREMENT
FOR TUBULAR REACTOR AT 270 C 300 PSIG 2.3 RECYCLE RATIO
WITH A CATALYST CAPABLE OF CERTAIN USAGE RATIO U
SPECIFIC ACTIVITY SA, AND BULK DENSITY 0.6 GM/CC
FOR 85 % SYNGAS CONVERSION AND 7.8 WT%CH4 PRODUCT SELECTIVITY

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