APPENDIXES

Appendix A. CATALYST TESTING

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Contents

I. INTRODUCTION

This report is organized around ten catalyst tests conducted from November 1983 through January 1984, the twelfth quarter of this contract. These ten catalysts represent the major thrusts of catalyst development during the third year of this contract. The analysis of the catalysts from this twelfth quarter depends heavily upon comparison with earlier results. Data from the Tenth and Eleventh Quarterly Reports, in particular, are cited and analyzed throughout this report, making this an Annual Report.

All the Fischer-Tropsch catalysts discussed in this report have metal components containing cobalt. All the catalysts from the twelfth quarter have the metal component in close contact with a Molecular Sieve, either UCC-103 or UCC-101. Much of the analysis in this report involves the comparison between these catalysts and like catalysts with the metal component and shape selective component in less intimate contact. This change in formulation has a strong effect upon the stability of the catalysts.

The ten catalysts from this last quarter contain one catalyst with X_4 and one with X_6, the two important metal component additives which were discovered during the past year. The effects of the additives are discussed in detail, for both the present cata-

lyst formulation and the prior physical mixture catalysts, as well as for the differences caused by these two methods of constructing the catalysts. Three of the catalysts from the twelfth quarter contain two different Molecular Sieves. In all three the metal component is in close contact with one Sieve, UCC-103, and just physically mixed with the other Sieve: UCC-101 for Catalyst 2, and UCC-108 for Catalysts 3 and 4. While these last two catalysts have the same formulation, three times as much catalyst was loaded into the reactor in Run 4 as was done in Run 3.

Catalyst 7 is strictly a water gas shift catalyst without any Fischer-Tropsch activity. Catalysts 8 through 10 contain a component capable of water gas shift activity along with a component capable of Fischer-Tropsch activity.

II. Run 1 (11677-10) with Catalyst 1 (Co/Th + UCC-101)

This catalyst is similar to Tenth Quarter Catalyst 3 (Run 10112-15) except that the thorium-promoted cobalt oxide was formed in the presence of UCC-101, resulting in a more intimate physical contact between the metal component and the Molecular Sieve. After bonding with 15 weight percent silica and forming as an extrudate, the final catalyst contained about 8.5 percent cobalt. It is to be compared with the Eleventh Quarter Catalyst 7 (Run 10225-16), in which the Molecular Sieve was UCC-103 instead of UCC-101, as well as with the Tenth Quarter 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. 1-4 for this run, in Figs. 5-8 for Run 10112-15, and in Figs. 9-12 for Run 10225-16. Simulated distillations of the C_5^+ product are plotted in Figs. 13-14. Carbon number product distributions are plotted in Figs. 15-23. Chromatograms from simulated distillations are reproduced in Figs. 24-32. Detailed material balances appear in Tables 1-3 for this run, and in Tables 4-5 and Tables 6-9 for Runs 10112-15 and 10225-16 respectively.

The most notable property of this catalyst is its exceptional stability, free even of the initial deactivation which is characteristic of Fischer-Tropsch catalysts generally. The data were

fitted to a straight line by the method of least squares: from the calculated initial value of 57.4 percent, the conversion dropped by one percentage point every 33 hours on stream. The deactivation was due primarily to loss of H_2 conversion which, although initially twice as high as the CO conversion, also deactivated twice as fast.

Tenth Quarter Catalyst 3 (Run 10112-15), with the same composition but with less intimate contact between metal component and Molecular Sieve, deactivated significantly during the first 140 hours on stream. As calculated by the method of least squares, its overall deactivation rate was one percent every 6.5 hours. (During the last 48 hours of its run it deactivated by only one percentage point, but this is too short a period for meaningful conclusions.)

Eleventh Quarter Catalyst 7 (Run 10225-16), prepared by the same method as the present catalyst but with UCC-103 in place of UCC-101, contained 17.5 percent more cobalt. Its initial conversion was 37 percent higher, but it deactivated rapidly at first so that its overall deactivation rate, by least squares, was one percentage point every 27 hours. After the first 100 hours on stream, however, the least squares deactivation rate was one percentage point every 125 hours. After the first 120 hours (a duration of only four days), the calculated deactivation rate was one percentage point every 21 days--well within the error of the measurement and effectively zero. Much if not all of the difference in activity can probably be ascribed to the 7C higher reac-

ter Catalyst 11 (Co/Th Al_2O_3, Run 11677-07), raising the reaction temperature from 250C to 260C increased methane production from 15 to 32 percent. With Tenth Quarter Catalyst 3 (Run 10112-15), methane production was 14 percent initially and increased by one percentage point every 17 hours. In selectivity to methane both the present catalyst and Eleventh Quarter Catalyst 7 are superior to Tenth Quarter Catalyst 3 and Eleventh Quarter Catalyst 11.

Typical of cobalt Fischer-Tropsch catalysts, including the three others herein cited, the production of C_2-C_4 was low and fairly steady.

Production of C_5^+ was 75 percent initially, and dropped by one percentage point for every 37 hours on stream. Heavies accounted for a constant 5 percent of total production. Most of the C_5^+ was motor fuels, about two-thirds of which boiled between room temperature and 420F, and 53 percent boiled in the midbarrel (diesel) range of 300-700F. Selectivity to motor fuels is higher than with Eleventh Quarter Catalyst 7, but so also is the deactivation rate. By extrapolation, and assuming that the rates of selectivity change remain constant, it can be predicted that after 25 days on stream both catalysts should be producing 53 percent motor fuels. Motor fuel production of Tenth Quarter Catalyst 3 (Run 10112-15), in contrast, was lower initially and deaactivated more rapidly, although it leveled off in the five samples taken during the last two days.

Isomerization of the pentane was initially moderate (30 percent isopentane in Sample 3) but deactivated rapidly over the

tion temperature in Run 10225-16.

These findings suggest that the physical preparation of the catalyst may have far-reaching effects on its performance, and in particular on its stability.

Fig. 1 points up another distinguishing characteristic of this catalyst--its low water-gas shift activity, lower than that of most cobalt catalysts. Only 5 percent of the oxygen was rejected as CO_2, the remainder as H_2O, resulting in a very high H_2:CO usage ratio of 2.0:1, which is an inefficient use of a low-hydrogen syngas. Tenth Quarter Catalyst 3, in contrast, rejected 21 percent of the oxygen as CO_2 for a usage ratio of 1.7:1, and Eleventh Quarter Catalyst 7 rejected 25-30 percent of the oxygen as CO_2 for a usage ratio of 1.5:1.

Both Tenth Quarter Catalyst 3 and Eleventh Quarter Catalyst 7 are more representative than the present catalyst of the water-gas shift activities of the majority of cobalt catalysts tested in this program.

The selectivity of this catalyst was relatively constant as well. Production of methane, calculated by least squares, was 13 percent initially and increased by one percentage point every 65 hours on stream, well below the rates of other cobalt catalysts at 265C. With Eleventh Quarter Catalyst 7 (Run 10225-16) the methane production was 20 percent initially but increased less than one percentage point during the 10-day test. Again, the difference in methane production may be due to the 7C difference in reaction temperature; as a case in point, with Eleventh Quar-

course of the run. With Eleventh Quarter Catalyst 7 (Run 10225-16), which contained UCC-103 in place of UCC-101, the isomerization was still lower; UCC-103 adds little or nothing, apparently, to the isomerization of cobalt alone. At the end of the run the isomerization with the present catalyst was 12 percent, only slightly more than the 10 percent obtained with cobalt alone.

The C_4 hydrocarbon product was much more olefinic than that from Eleventh Quarter Catalyst 7 (Run 10225-16) and more like that from Tenth Quarter Catalyst 3 (Run 10112-15), although somewhat more steady.

Except for the excess methane, the Schulz-Flory plots, like those for Eleventh Quarter Catalyst 7 (Run 10225-16), show a straight line distribution. The chromatograms from the simulated distillations show only an initially small extent of isomerization. The low isomerization makes it hard to understand why the product of this catalyst was a clear oil whereas that of Tenth Quarter Catalyst 3 (Run 10112-15) contained solid wax. This lack of wax is even harder to explain for the Eleventh Quarter Catalyst 7 (Run 10225-16) which had little isomerization ability and produced an even more paraffinic product.

This is one of the more important catalysts tested to date. Its products, and those of Eleventh Quarter Catalyst 7 (Run 10225-16), point up the contribution of intimate physical contact between the metal component and the Molecular Sieve toward improving the catalyst's stability.

Fig. 1

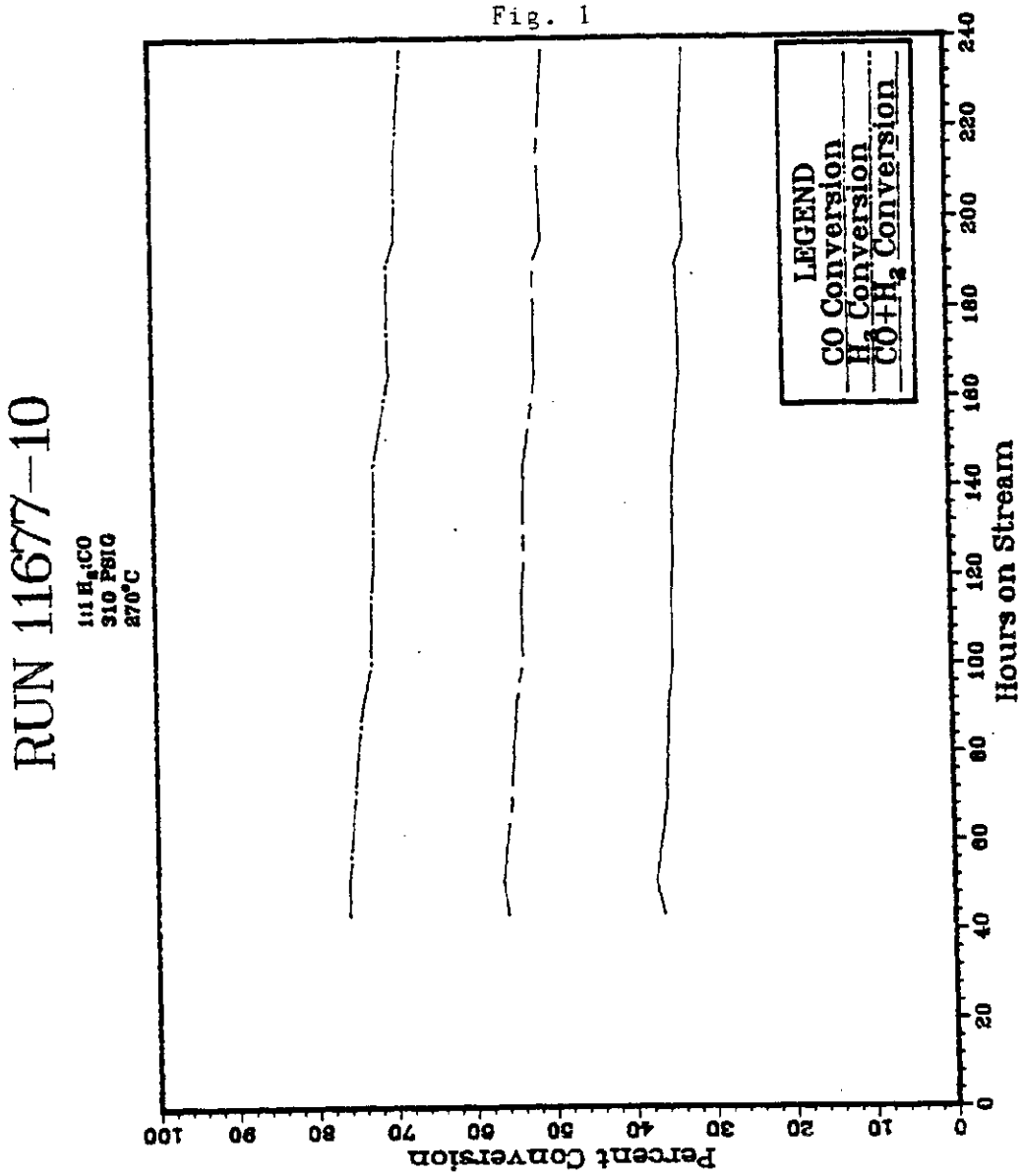

RUN 11677-10
111 H_2:CO
310 PSIG
270°C
LEGEND
CO Conversion
H_2 Conversion
$CO+H_2$ Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 2

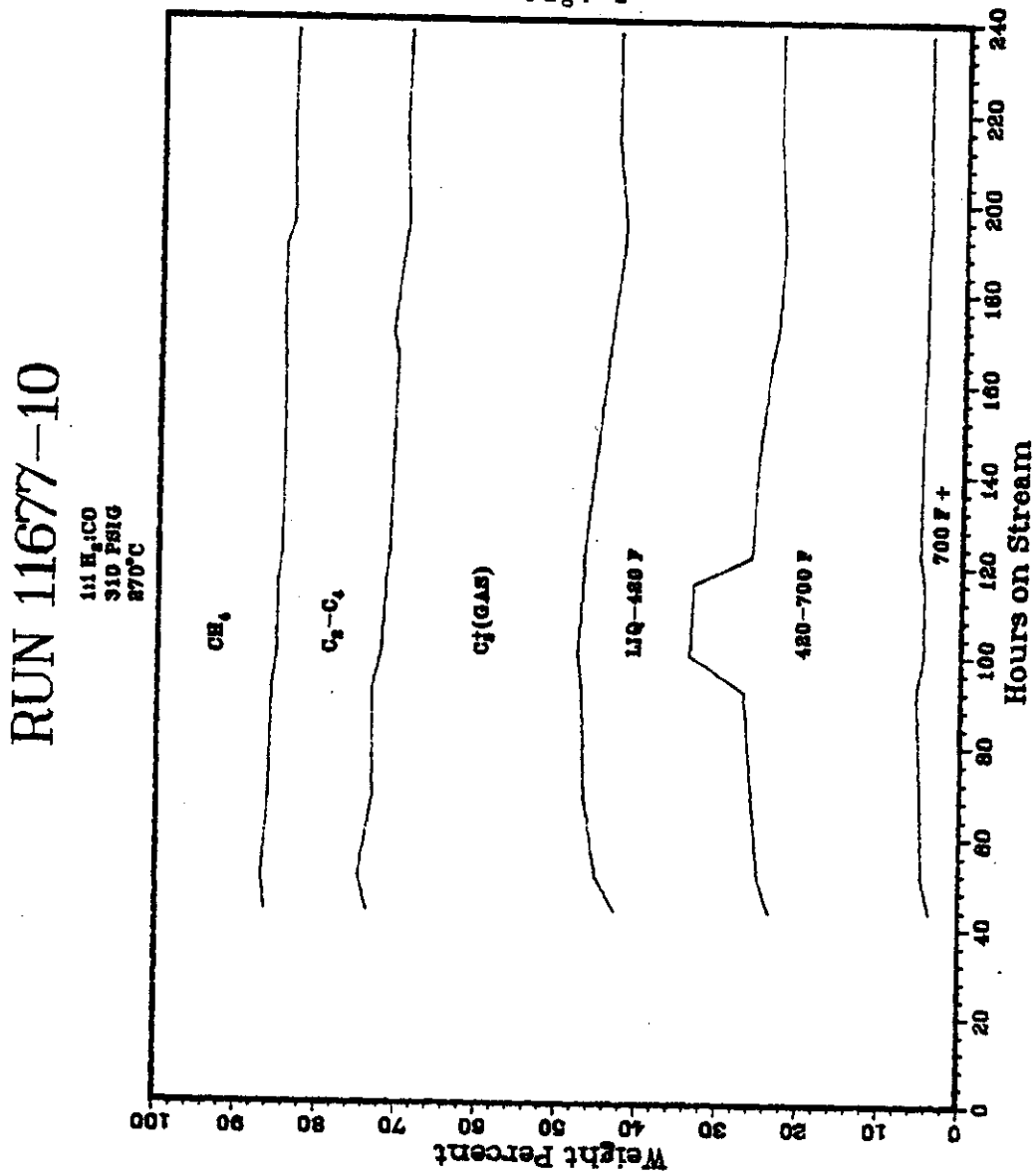

RUN 11677–10
111 H2:CO
310 PSIG
270°C
CH4
C2–C4
C5+(GAS)
LIQ–420 F
420–700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3

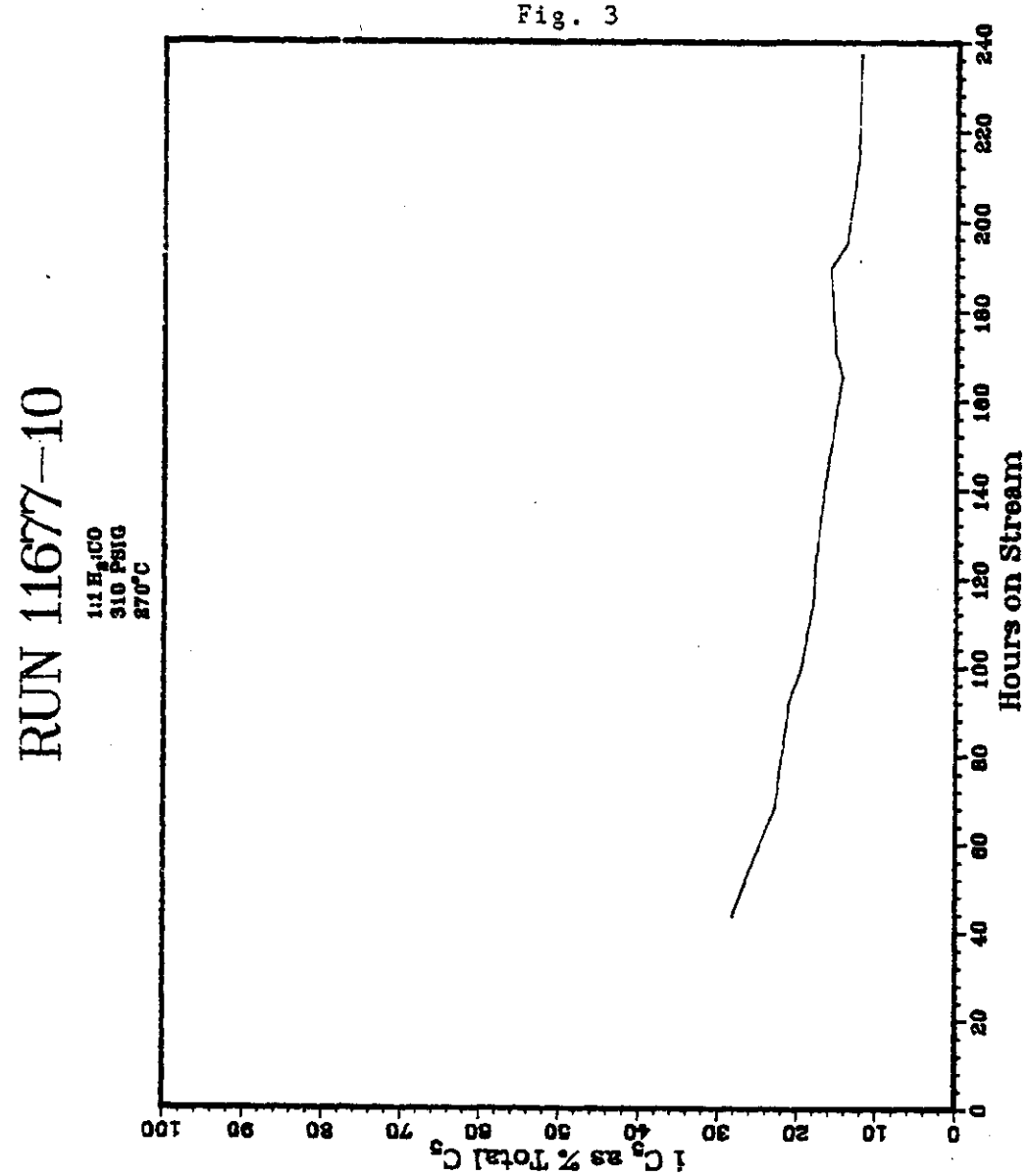

RUN 11677-10
1:1 H2:CO
310 PSIG
270°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 4

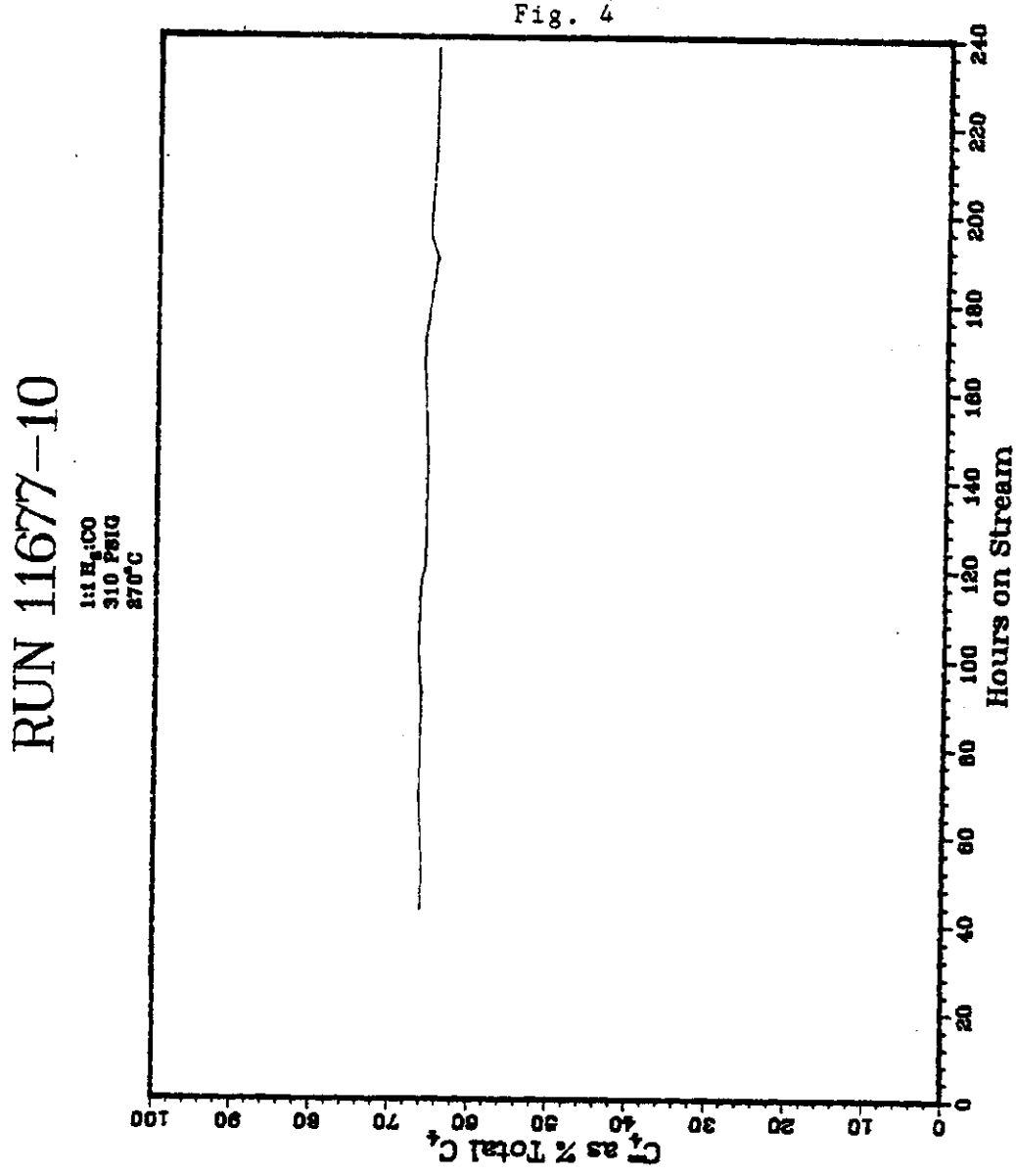

RUN 11677-10
1:1 H2:CO
310 PSIG
270°C
C4= as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 5

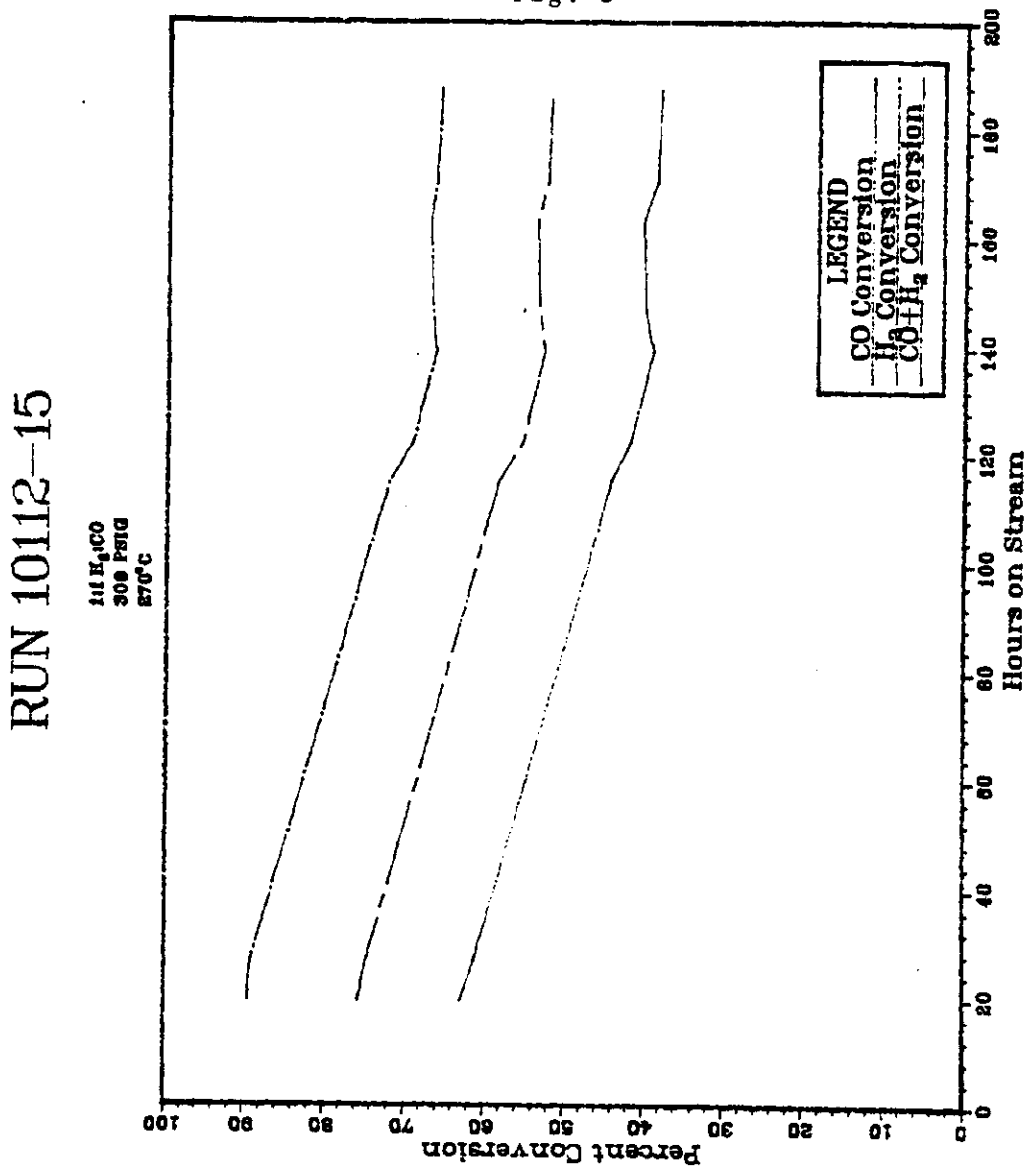

RUN 10112-15
111 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 6

RUN 10112-15

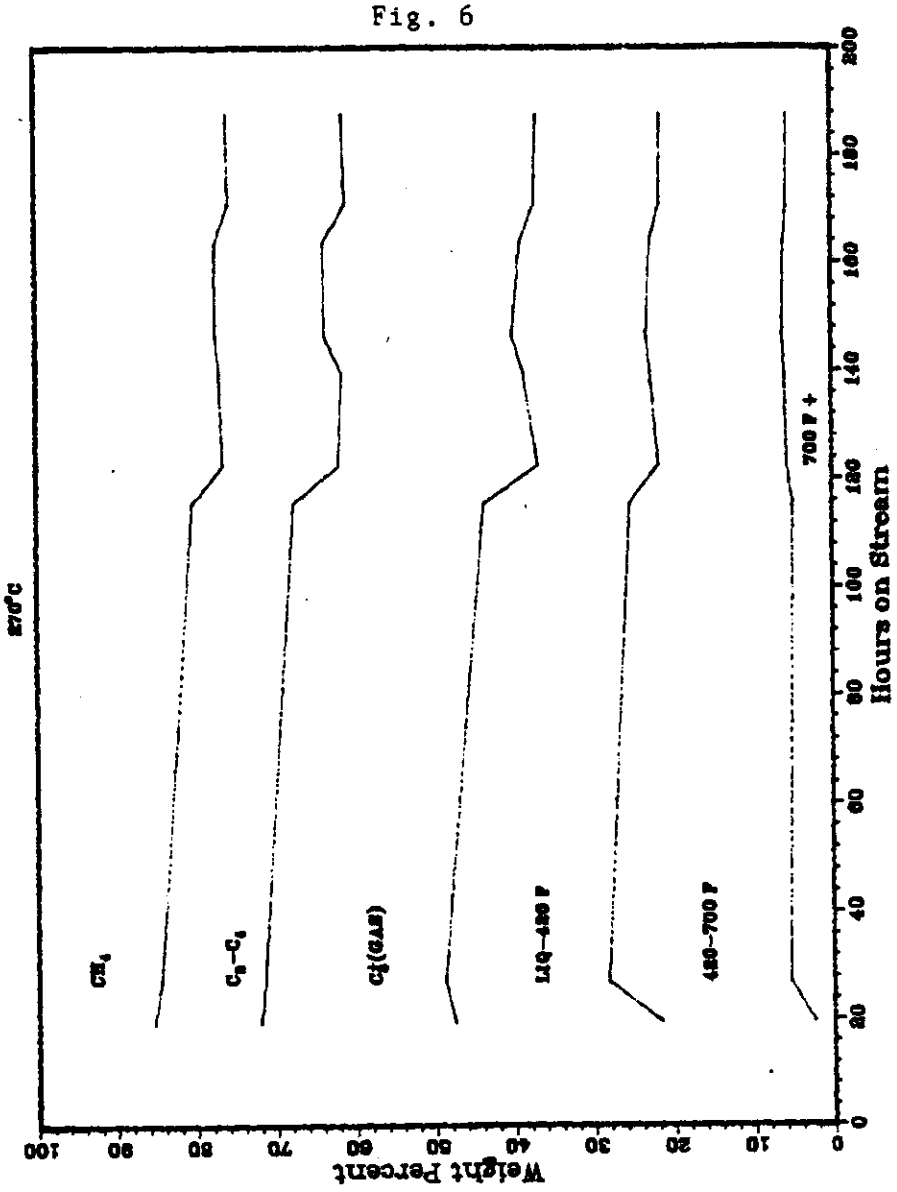


Fig. 7

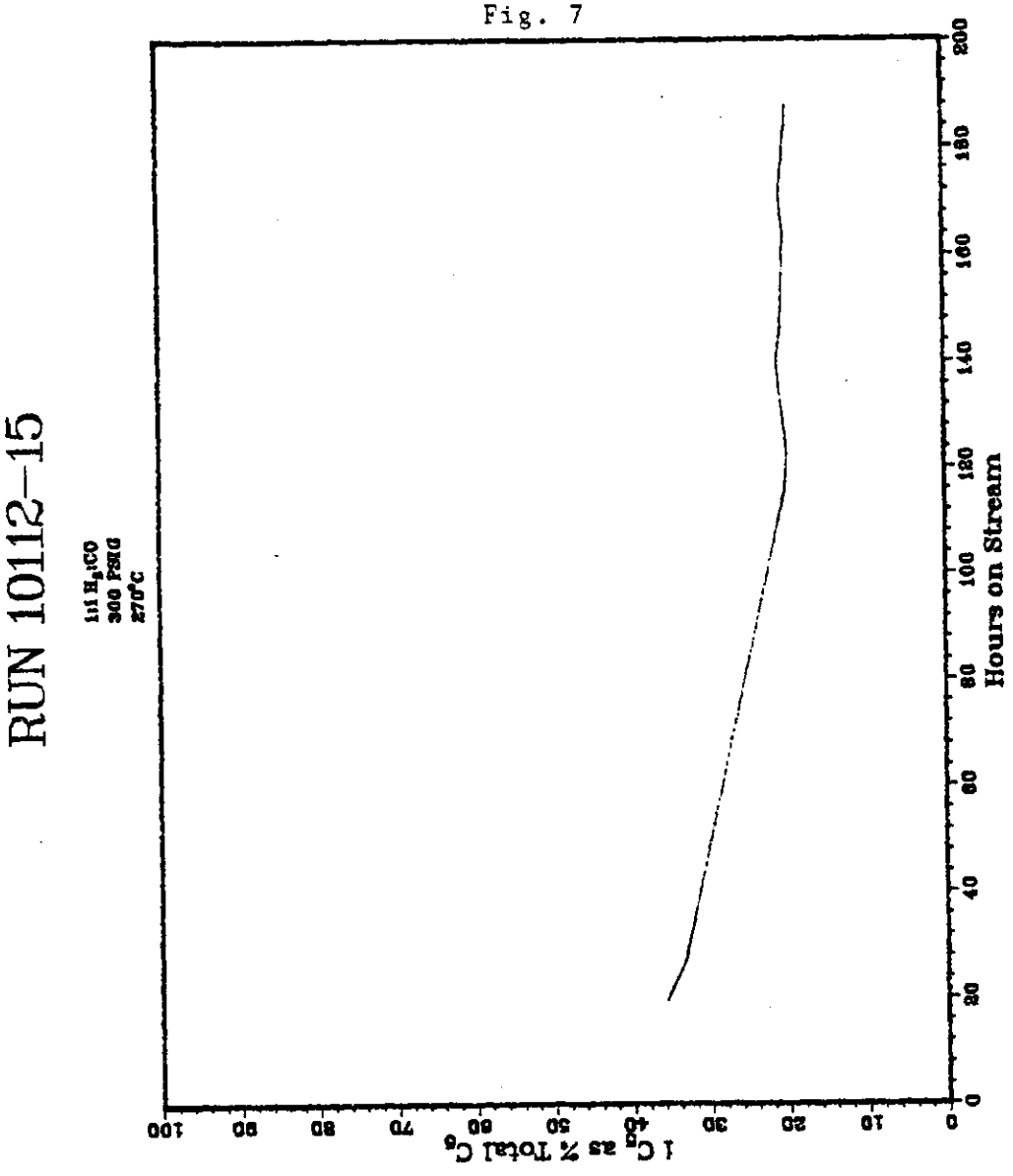

RUN 10112-15
1:1 H2:CO
300 PSIG
270°C
i C5 as % Total C6
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200

Fig. 8

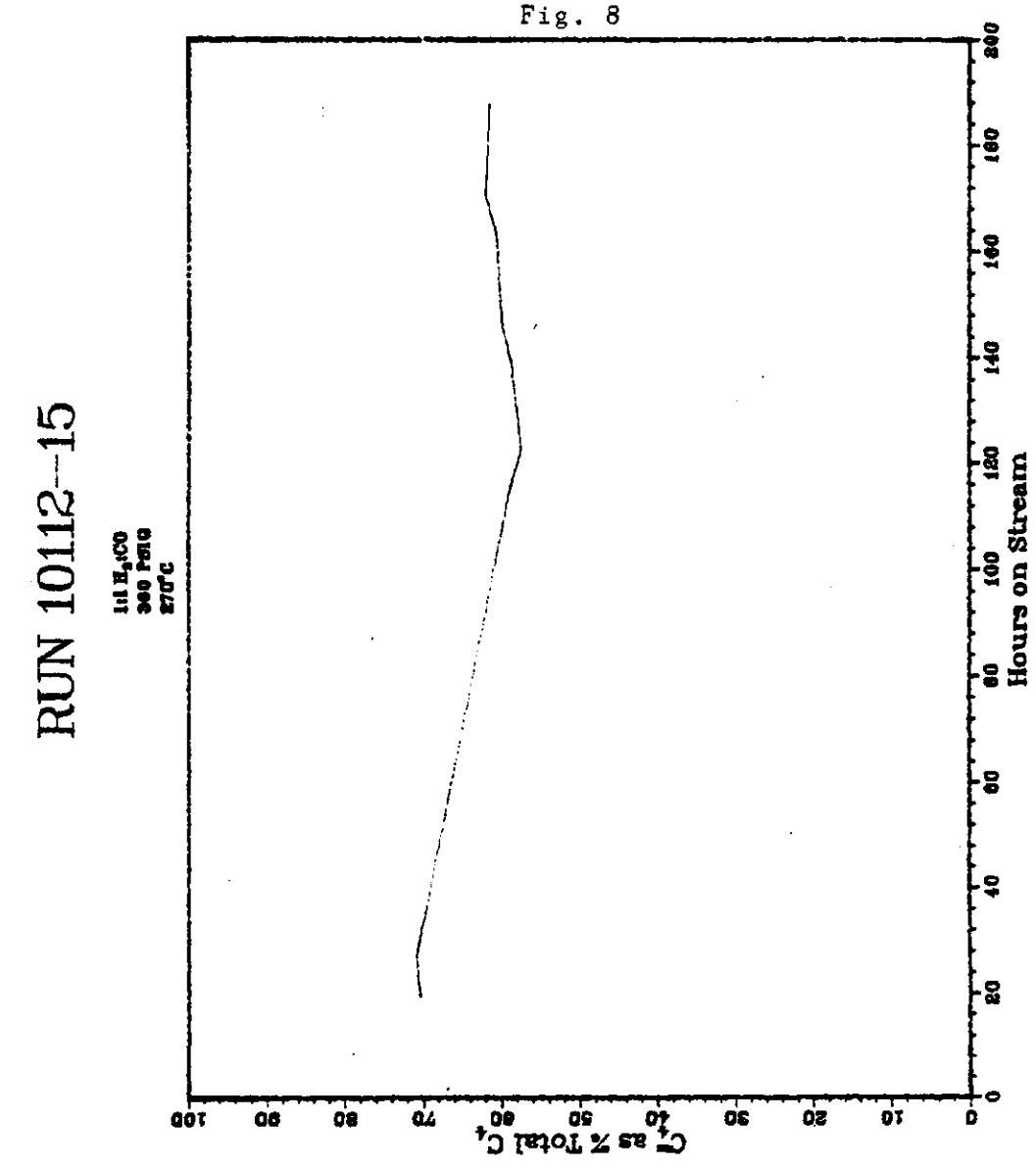

RUN 10112-15
111 H2tCO
300 Psig
270°C
C4 as % Total C4
Hours on Stream
0
20
40
60
80
100
120
140
160
180
200
10
20
30
40
50
60
70
80
90
100

Fig. 9

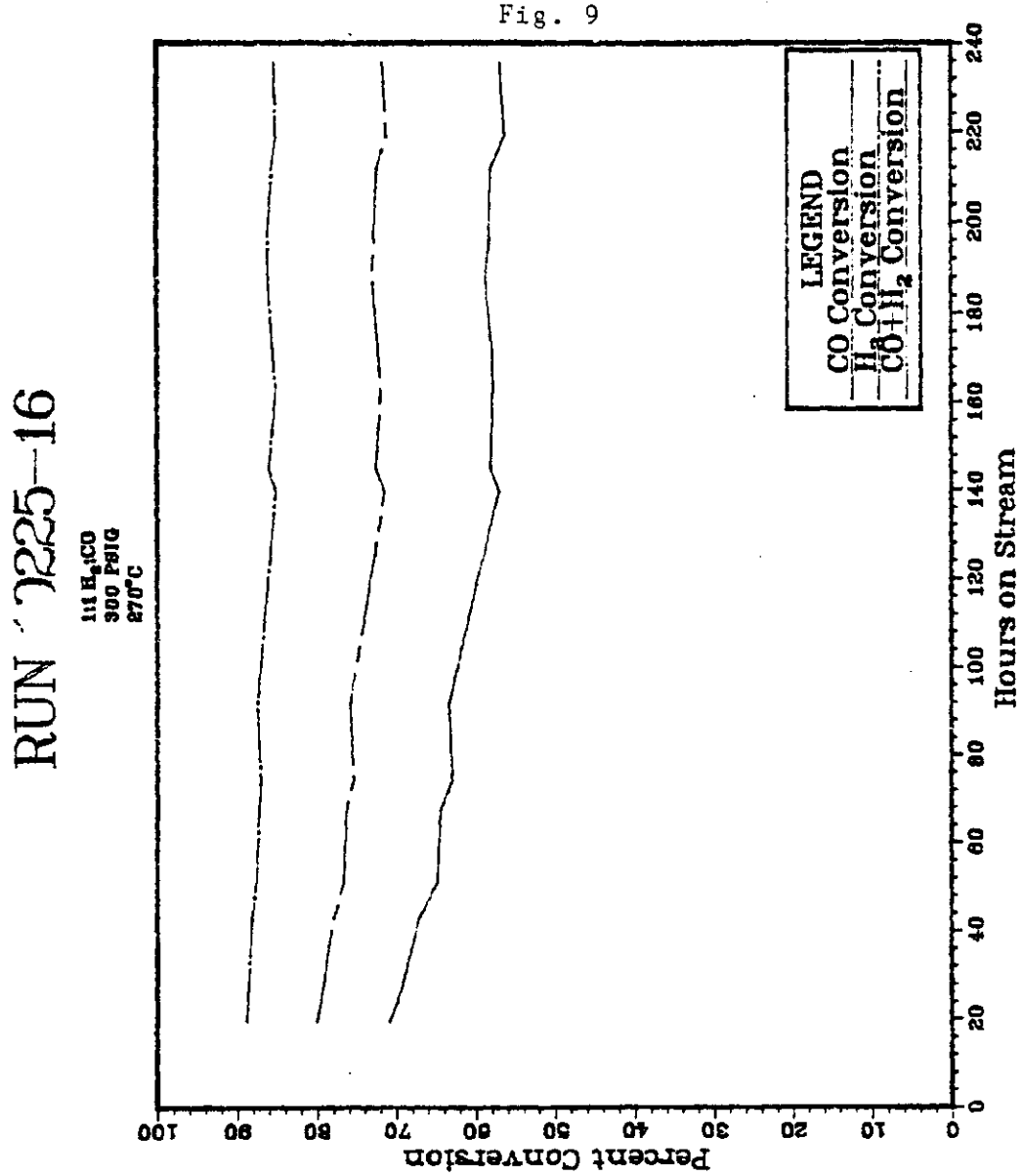

RUN 7225-16
1:1 H2:CO
300 PSIG
270°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 10

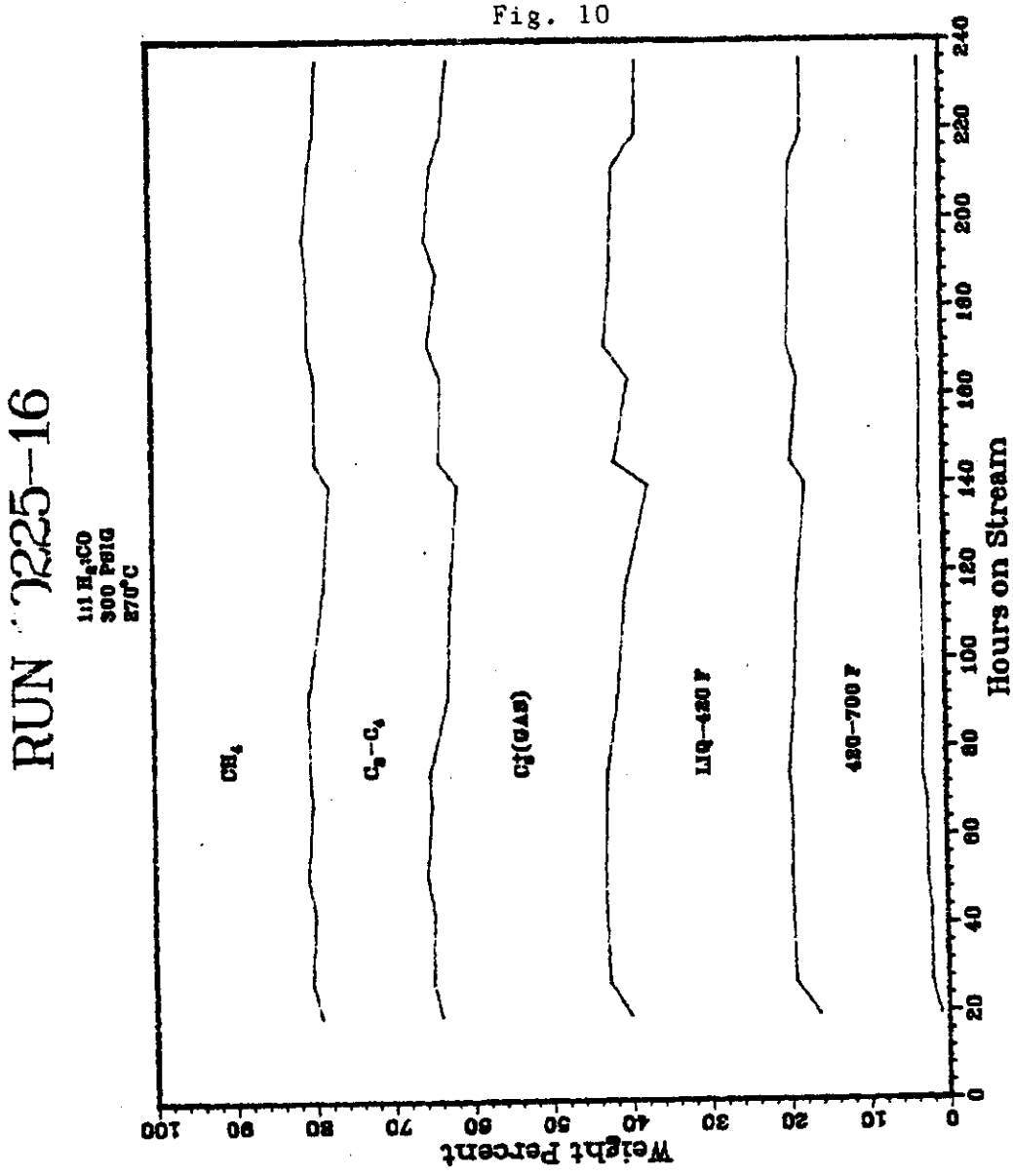

RUN 225-16
111 H2:CO
300 PSIG
270°C
CH4
C2-C4
C5(gas)
LTO-430 F
430-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 11

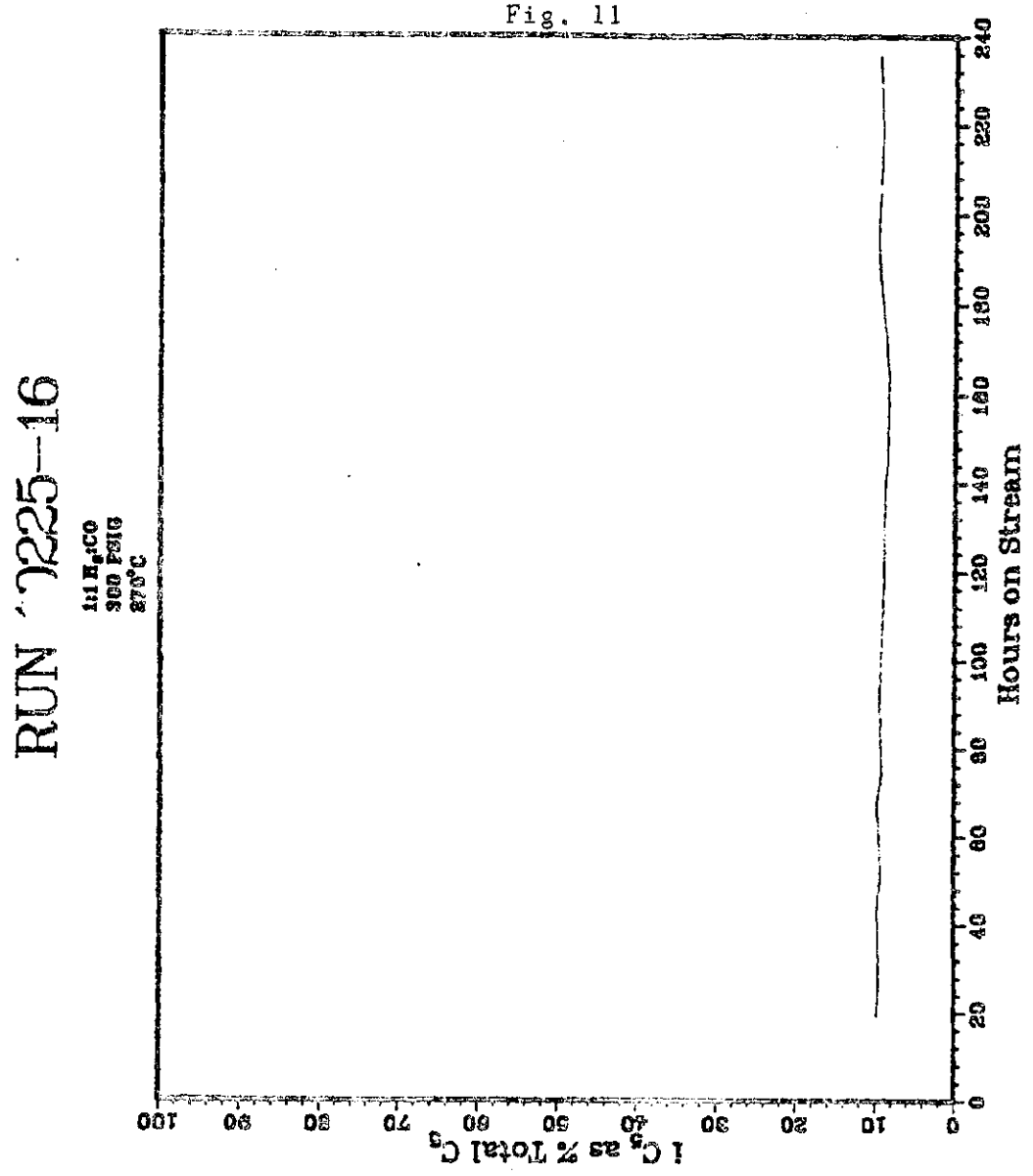

RUN 7225-16
1:1 H2:CO
300 PSIG
270°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 12

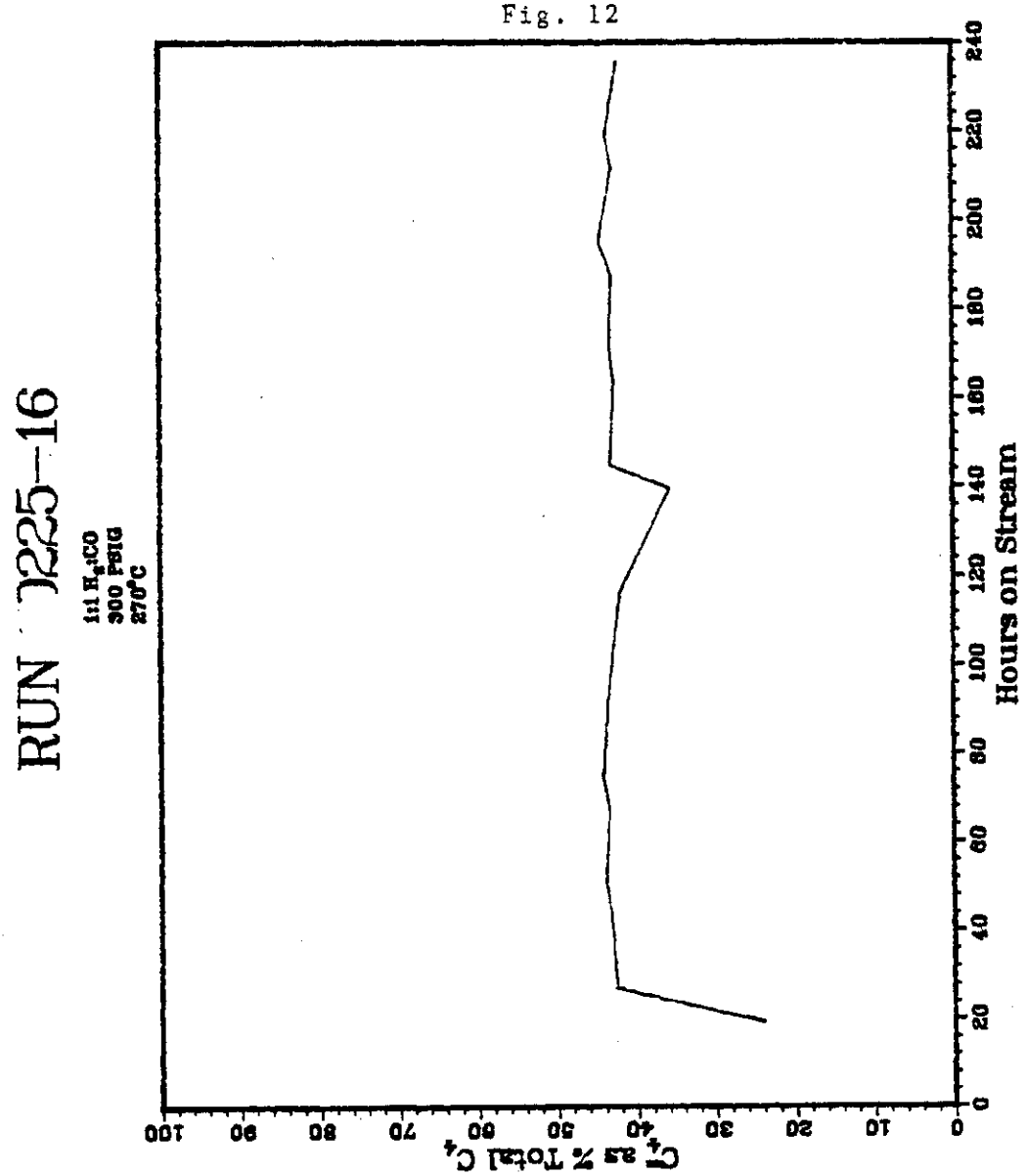

RUN 7225-16
1:1 H2:CO
300 PSIG
270°C
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 13

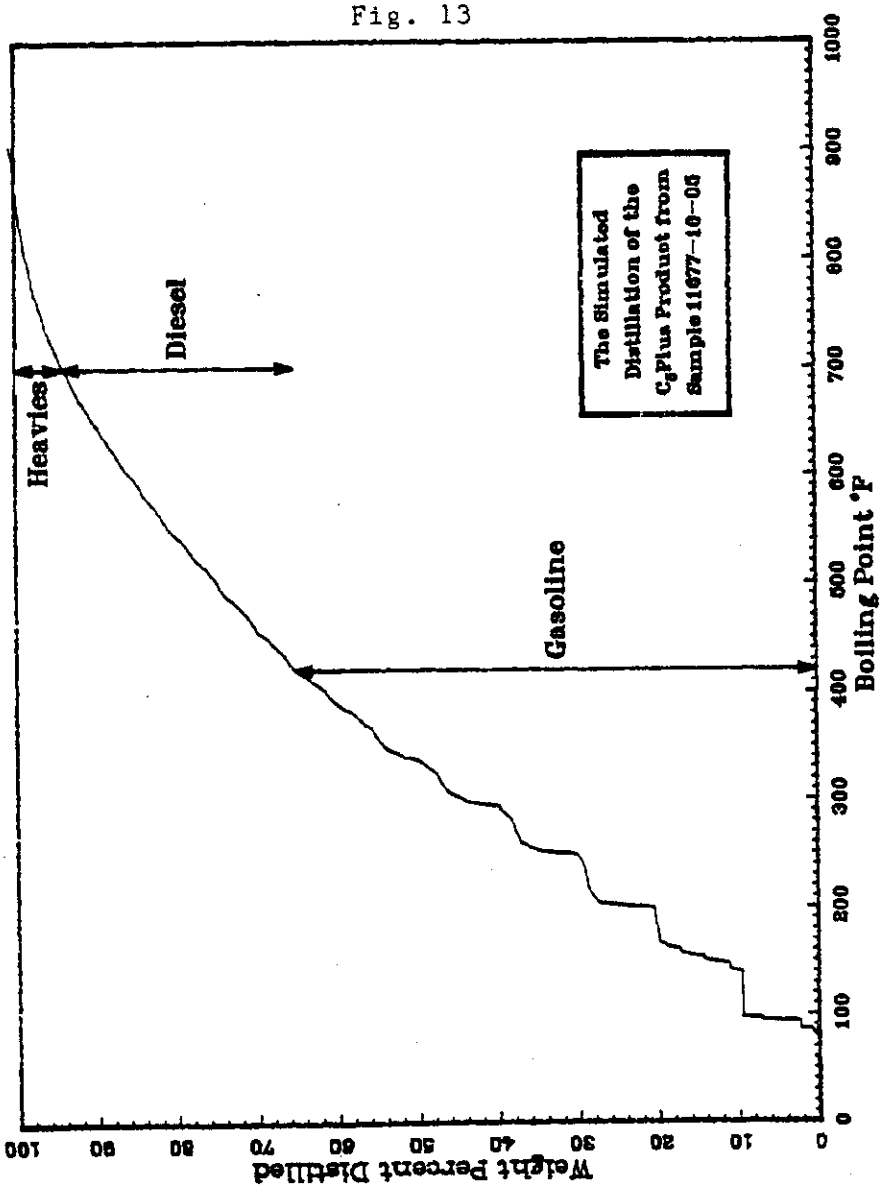

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-10-05
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 14

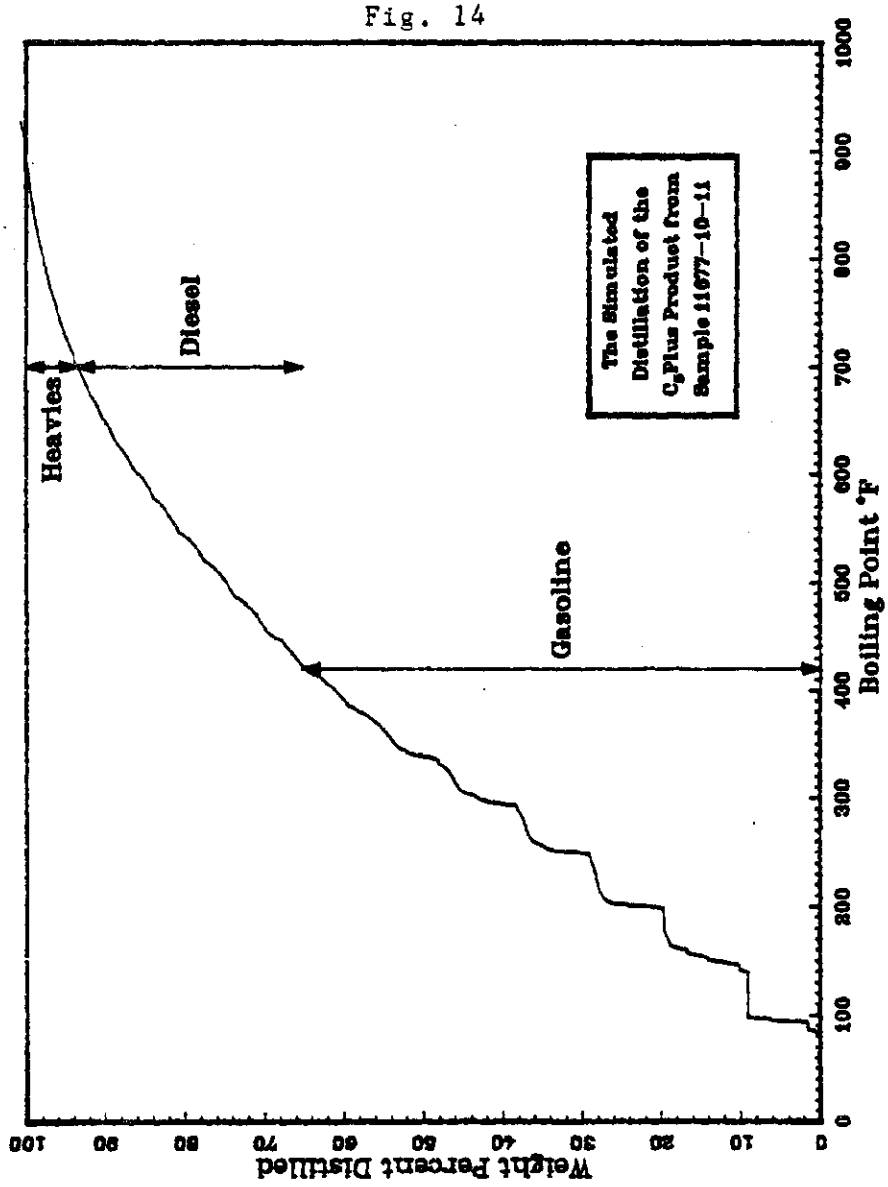
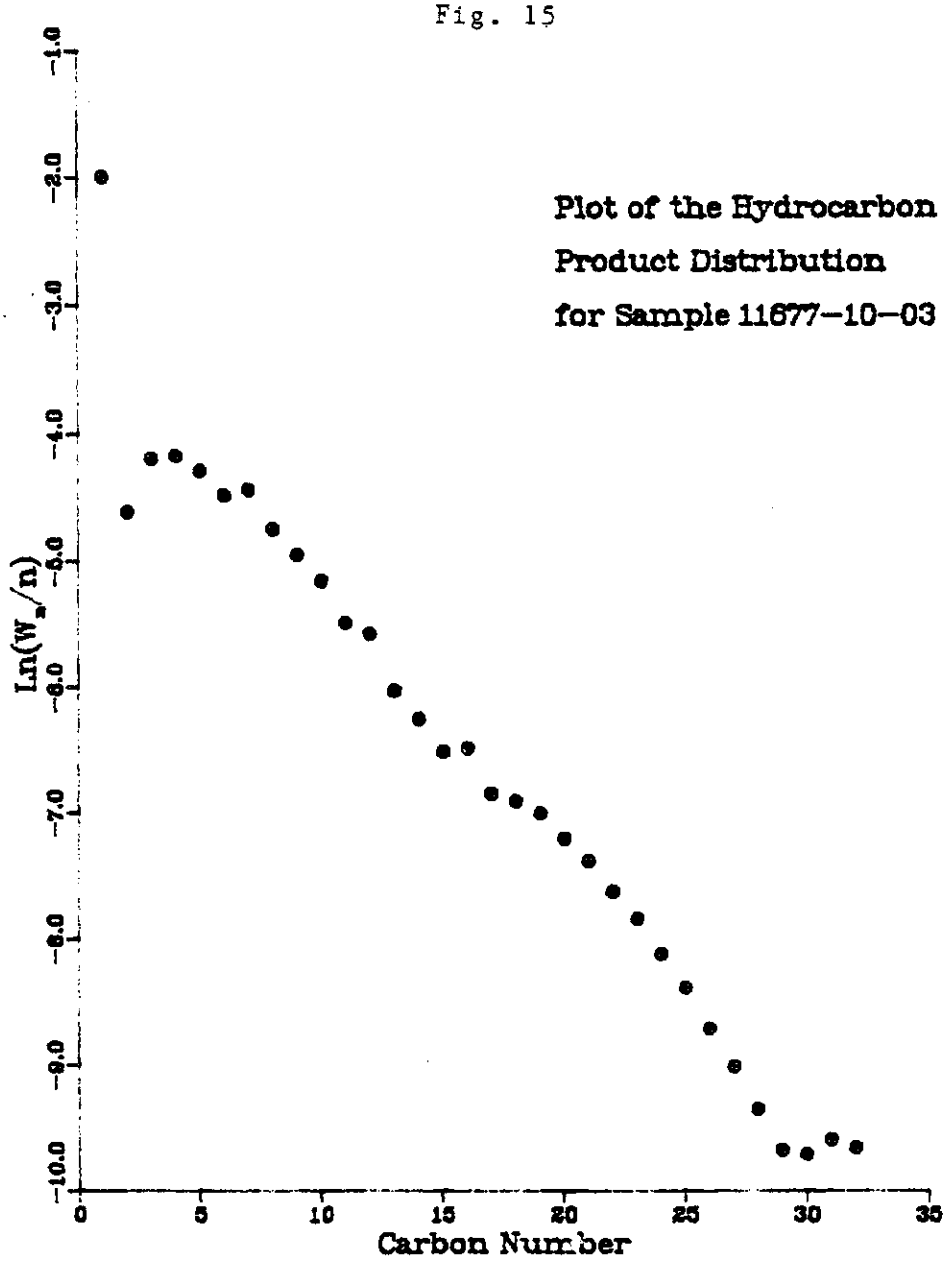

Heavies
Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 11677-10-11
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. 15


Plot of the Hydrocarbon
Product Distribution
for Sample 11677-10-03
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
35
Carbon Number