II. Run No.62 (12561-09) Co/X11/TC-201

The goal of this experiment was to evaluate the use of the new molecular sieve component TC-201 for its' utility as a cobalt Fischer-Tropsch metal support.

The X11 promoted cobalt oxide catalyst was formulated similarly to Catalyst 57, except that TC-123 was replaced with the new molecular sieve support TC-210. The theoretical percent Co = 8.2 and X11 = 1.6.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C4's are plotted against time on stream in Figures B1-4. Simulated distillations of the C5+ product are plotted in Figures B5 and B6. Carbon number product distributions are plotted in Figures B7 and B8. Chromatograms from simulated distillations are reproduced in Figures B9 and B10. A detailed material balance appears in Table B1.

This catalyst will be compared against the similar TC-123 catalyst described in Run No. 57 of the Eighth Quarterly Report.

Initially problems were encountered with the H2:CO ratio of the feed. The ratio was found to be 2.09:1 H2:CO instead of the targeted 1:1. As expected the conversion of syngas was very high (75 %) and the product selectivity was shifted towards light product. Upon adjusting the ratio closer to the target 1:1 (actually 1.15:1) the conversion fell in the range expected for the Co/X11/TC-123 catalyst. The table below compares the performance of this TC-201 catalyst to that of the TC-123 catalyst (run no. 57).

	Co/X11/TC-201	Co/X11/TC-123
H2:CO Ratio	1.15:1	1:1
Conversion	42.0	47.8
CH4, wt.%	7.5	3.3
C5+, wt.%	80.9	88.9
C6+,iso/norm.	0.62	0.09

The overall performance of the TC-201 catalyst was inferior to the TC-123 catalyst. Conversion activity was over 5 % lower and the product slate was significantly lighter. An interesting feature was an apparent boost in the iso/normal ratio of the C6 fraction over that of the TC-123 catalyst. This phenomenon was observed only for the C6's which is one of the four molecules (C4, C4=, C5, C6) monitored to observe the isomerization activity of the catalysts and warrants further investigation.

III. Run No. 63 (11617-12) Co/X11/X9/TC-123

This run was performed to test the performance of the Co/X11/X9/TC-123 catalyst tested in Run No. 55 (Eighth Quarterly Report) under the following conditions: 250 C, 400 psig, 1.5:1 H2:CO ratio, and 300 GHSV. The purpose was to determine the impact of these conditions on catalyst stability.

The X11/X9 promoted cobalt oxide catalyst was formulated similarly to Catalyst No. 55 with theoretical Co = 8.0 %, X11 = 1.6 %, and X9 = 1.1 %.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C4's are plotted against time on stream in Figures B11-14. Simulated distillations of the C5+ product are plotted in Figures B15-23. Carbon number product distributions are plotted in Figures B24-32. Chromatograms from simulated distillations are reproduced in Figures B33-B41. Detailed material balances appear in Tables B2-6.

The initial 233 hours of the experiment were run under the following conditions: 240 C, 300 psig, 1:1 H2:CO, 300 GHSV. This was to verify that the catalyst performed similar to that previously observed for Run No. 55. The conversion was slightly higher, 43.7 % syngas conversion vs. 40.7 % for Run No. 55. The catalyst exhibited excellent stability as predicted previously under these conditions, showing no deactivation after 233 hours. The product selectivity was very similar with this catalyst showing a slightly reduced methane production.

On changing process conditions to the 250 C, 400 psig, 1.5:1 H2:CO ratio, the syngas conversion increased greatly. The table below presents a comparison of the performance of this catalyst with a similar catalyst run at 260 C, 500 psig, and 1.5:1 H2:CO ratio in terms of conversion, product selectivity, and estimated catalyst stability.

	Run No. 63	Run No. 55
Temperature, C	250	260
Pressure, psig	400	500
H2:CO	1.5:1	1.5:1
Conversion(H2+CO)	70.0	77.0
CH4, wt.%	6.0	10.0
C5+, wt.%	87.8	79.0
Stability(% loss/hr.)	0.007	0.007

Running the catalyst under these less severe conditions (250 C, 400 psig) results in about seven percent (7 %) less conversion, however, the catalyst produced about four percent (4 %) less methane.

The primary goal of this experiment, improved catalyst stability, was found not to be improved over the catalyst run under the 260 C, 300 psig conditions. A linear least squares estimate found the syngas loss to be approximately one percent per 150 hours over the last 260 hours of the test. This is similar to that observed in Run No. 55. Further work is needed to establish whether this deactivation rate vs. that of the catalyst run at 240 C is temperature and/or pressure related. That the higher H2:CO ratio feed is a cause of a higher deactivation rate is unlikely in the light of previous tests which consistently have shown improved stability with increased H2:CO ratios.

IV. Run No. 64 (12561-10) Co/X11/TC-211

The purpose of this catalyst test was to evaluate the use of the molecular sieve TC-211 as a Fischer-Tropsch catalyst support. The support was prepared through a modification of TC-123.

The X11 promoted cobalt oxide catalyst was formulated like Catalyst No. 57 except that the TC-123 was replaced by TC-211 with theoretical Co = 8.2 % and X11 = 1.6 %.

The catalyst was activated under H2 following the procedure used for a typical TC-123 catalyst. When exposed to syngas feed at the conditions: 240 C, 300 psig, and 1:1 H2:CO the catalyst was completely inactive, yielding no hydrocarbon product.

A probable cause of this lack of activity was that the procedure used to synthesize the TC-211 may have generated a poison which adversely affected the Fischer-Tropsch metal component in the catalyst.

V. Run No. 65 (12561-11) Co/TC-123

This catalyst was prepared as a reference to be used to help isolate the promoter effects upon two previously tested TC-123 catalysts, Run No. 57 (Co/X11/TC123) and Run No. 55 (Co/X11/X9/TC-123) reported in the Eighth Quarterly Report.

The cobalt oxide catalyst was formulated similarly to Catalyst No. 55 except that the promoters X11 and X9 were excluded. The theoretical percent Co in the catalyst equalled 8.3 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C4's are plotted against time on stream in Figures B42-45. Simulated distillations of the C5+ product are plotted in Figures B46-53. Carbon number product distributions are plotted in Figures B54-61. Chromatograms from simulated distillations are reproduced in Figures B62-69. Detailed material balances appear in Tables B7-9.

Shown below is a comparison of the performance of this non-promoted catalyst to that of Runs No. 57 and 55 promoted with X11 and X11/X9 respectively. The three catalysts contain equal amounts of cobalt and were all tested under two sets of conditions; at 240 C, 300psig, 1:1 H2:CO and at 260 C, 500 psig, 1.5:1 H2:CO.

PROMOTER EFFECTS ON Co/TC-123

FISCHER-TROPSCH CATALYST

Conditions: 240 C, 300 psig, 1:1 H2:CO, 300 GHSV

Catalyst	Co/TC-123	Co/X11/TC-123	Co/X11/X9/TC-123
Conversion	42	48	41
C1	6.7	3.3	3.5
C2-C4	9.2	7.8	7.7
C5-420 F	31.4	28.0	27.6
420-700 F	34.7	26.6	28.9
700+ F	18.7	34.4	32.4
C5+	84.8	88.9	88.8
C4 olefin/par.	1.8	3.7	2.6
Stability	Fair	Excel.	Excel.

Conditions: 260 C, 500 psig, 1.5:1 H2:CO, 300 GHSV

Conversion	73	81	77
C1	26.0	12.2	10.0
C2-C4	14.3	10.4	11.0
C5-420 F	35.7	37.5	36.1
420-700 F	20.1	25.9	24.3
700+ F	4.0	14.0	18.6
C5+	59.7	77.4	79.0
Stability (% loss/Hr.)	0.2	0.02	0.007

Under both sets of conditions, the X11 promoted catalyst was more active than the non-promoted catalyst indicating that X11 played a significant role in boosting activity. The addition of the second promoter, X9, to the X11 promoted catalyst was found to reduce catalyst activity in the 240 C case down to the level of the non-promoted catalyst.

The dramatic effect the X11 promoter had on product selectivity was clearly brought out in this comparison. The methane production, again under both sets of conditions, was reduced to about half of the non-promoted catalyst levels. The whole product slate was shifted toward heavier products as indicated by the increased C5+ and high wax (700+ F) production. The addition of the X9 promoter showed little or no effect on product selectivity.

The major effect of the X11 promoter on product quality was observed in the olefin content of the Fischer-Tropsch product. Under the 240 C conditions, the X11 promoter boosted the olefin yield in the C4's from about 64 % to about 79 %. This phenomenon in combination with the observed reduction in methane and the shift in the product slate to heavier product indicates that X11 greatly reduces the hydogenation ability of the cobalt metal. The X9 promoter serves to diminish some of the X11 effects, showing a reduction of the olefin content down to 72 %, however, with almost no change in the product slate from that of the catalyst promoted by X11 only.

One of the most beneficial effects of these promoters was on catalyst stability. Under the 240 C conditions, the unpromoted catalyst showed substantial loss in syngas conversion with time. The X11 and the X11/X9 promoted catalysts showed excellent stability with no apparent deactivation over the time tested. The benefit of these promoters on stability was more clearly illustrated during the tests made at the 260 C conditions. The addition of the X11 resulted in a nearly ten fold decrease in the deactivation rate and the addition of the X9 improved stability by an additional factor of three. The 0.02 and 0.007 loss/hour translate into a 1 % loss in conversion every 50 and 150 hours respectively.

This catalyst run (Run No. 65) was important in helping to isolate the effects of the promoters X11 and X11/X9 on a Co/TC-123 type catalyst. The X11 was found to greatly improve activity, selectivity, and stability. The additional promotion with X9 resulted in a slight loss in activity but a greatly improved stability.

VI. <u>Run No. 66 (12570-06) Co/X11/TC-123</u>

This experiment tests the potential utility of the molecular sieve TC-12365 for use as a cobalt Fischer-Tropsch metal support. The results obtained, like those for TC-201 (Run No. 62) will be compared to a similar catalyst containing the most promising support developed to date, namely TC-123 (Run No. 57, Eighth Quarterly Report of this contract).

The X11 promoted cobalt oxide catalyst was formulated similarly to Catalyst 57, except that TC-123 was replaced by TC-12365. The theoretical percent Co = 8.2 and X11 = 1.6.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C4's are plotted against run time in Figures B70-73. Simulated distillations of the C5+ product are plotted in Figures B74-77. Carbon number product distributions are plotted in figures B78-81. Chromatograms from simulated distillations are reproduced in Figures B82-85. Detailed material balances appear in Tables B10 and B11.

The activity of this catalyst proved to be substantially lower than the corresponding TC-123 catalyst under similar conditions. After about 50 hours on stream the syngas conversion was 29 % compared to 48 % for the TC-123 catalyst (Run No. 57). The activity peaked at about 34 % after 139 hours and remained constant throughout the remaining 200 hours of the run.

Analysis of the product selectivity showed that this TC-12365 catalyst produced a slightly lighter product as indicated below.

Catalyst	Co/X11/TC-123	Co/X11/TC-12365	Co/X11/TC-12365
Onstrm Hrs.	98	139	332
Resid.H2:CO	0.60	0.67	0.69
Conversion	48 %	29 %	31 %
CH4	3.3 %	5.9 %	4.5 %
C5+	88.9 %	83.5 %	84.6 %

The lighter product was not unexpected due to the higher residual H2:CO ratio found in the Berty reactor tests, resulting from the lower conversion of this catalyst. The selectivity did, however, appear to be improving with time, with the methane dropping from 5.9 to 4.5 % and the C5+ increasing from 83.5 to 84.6 %.

Overall, the performance of the TC-12365 catalyst was similar to the TC-123 catalyst except for the reduced activity.

VII. Run No.67 (11617-13) Co/X11/X9/TC-123

The purpose of this run was to test a variation in the calcining procedure used in the formulation of the catalyst used in Run No. 55 (Eighth Quarterly Report).

The X11,X9 promoted cobalt oxide catalyst was formulated similarly to Catalyst 55 except that the calcination procedure was varied. The theoretical percent Co = 8.0, X11 = 1.6, and X9 = 1.1.

Conversion, product selectivity, isomerization of the pentane, and percentage olefins in the C4's are plotted against time on stream in Figures B86-89. Simulated distillations of the C5+ product are plotted in Figures B90-96. Carbon number distributions are plotted in Figures B97-103. Chromatograms from simulated distillations are reproduced in Figures B104-109. Detailed material balances are given in Tables B12-15.

The catalyst was first tested under the following conditions: 240 C, 300 psig, 1:1 H2:CO. The performance of the catalyst was very similar to that of Run No. 55. Under more severe conditions (260 C, 500 psig, 1.5:1 H2:CO) differences became more apparent. The activity was found to be significantly lower, i.e., syngas conversion was about 5 % lower than that observed for Run No. 55. The product selectivity was also affected. This catalyst produced an overall lighter product. Methane levels were 2 to 4 % higher and C5+ yields were 2 to 3 % lower than for Run No. 55.

The most pronounced effect was on catalyst stability. Under these conditions it was previously reported that for Run No. 55, the catalyst showed a 1 % drop in syngas conversion every 150 hours on stream. Linear least squares estimates of the deactivation rate for this catalyst showed a 1 % drop in syngas conversion every 77 hours for the 400 hours tested under these conditions. Very little improvement in the deactivation rate was observed as the run progressed. The catalyst showed an estimated 1 % drop every 88 hours during the last 170 hours on stream.

This catalyst test probed the effects of varying the calcination procedure first introduced in the formulation of the catalyst used in Run No. 55. The variation of the procedure proved detrimental to the overall catalyst performance, especially catalyst stability.

VIII. Summary

The work reported in this quarter consisted of six runs directed toward improving on the promising Catalyst No. 55 (Co/X11/X9/TC-123) reported in the Eighth Quarterly Report. Four lines of investigation were pursued: i.e. 1) new molecular sieve supports were tested as replacements for TC-123, 2) a non-promoted catalyst was tested to determine the effects of X11 and X9 promoters, 3) new reaction conditions were tested, and 4) a variation in the catalyst calcination procedure was evaluated for its effect on performance.

Three new molecular sieves were tested as Fischer-Tropsch catalyst supports: TC-201 (Run No. 62), TC-211 (Run No. 64), and TC-12365 (Run No. 66). The TC-201 catalyst showed inferior activity and produced a lighter product. It did, however, exhibit potentially improved isomerization activity. The TC-211 catalyst was completely inactive. The TC-12365 catalyst demonstrated performance similar to that of the TC-123 (Catalyst No. 55), but at a reduced activity.

In Run No. 65, a non-promoted TC-123 catalyst was tested as a reference to help isolate X11 and X9 promoter effects.

The X11 promoter was found to greatly reduce the hydrogenation ability of the cobalt metal, but was also found to improve the activity, selectivity, and stability of the Co/TC-123 catalyst. The X9 promoter proved most beneficial in improving catalyst stability. This additive had little effect on selectivity although activity was reduced slightly.

Run No. 63 tested the Co/X11/X9/TC-123 catalyst at a new set of operating conditions that were less severe than those used for Run No. 55. The activity and selectivity were as expected, but the anticipated improvement in catalyst stability was not observed.

The last run reported in this series, Run No. 67, examined the variation in calcination procedures on catalyst performance. The modified procedures showed no benefit in catalyst performance over those previously used for the Run No. 55 catalyst.

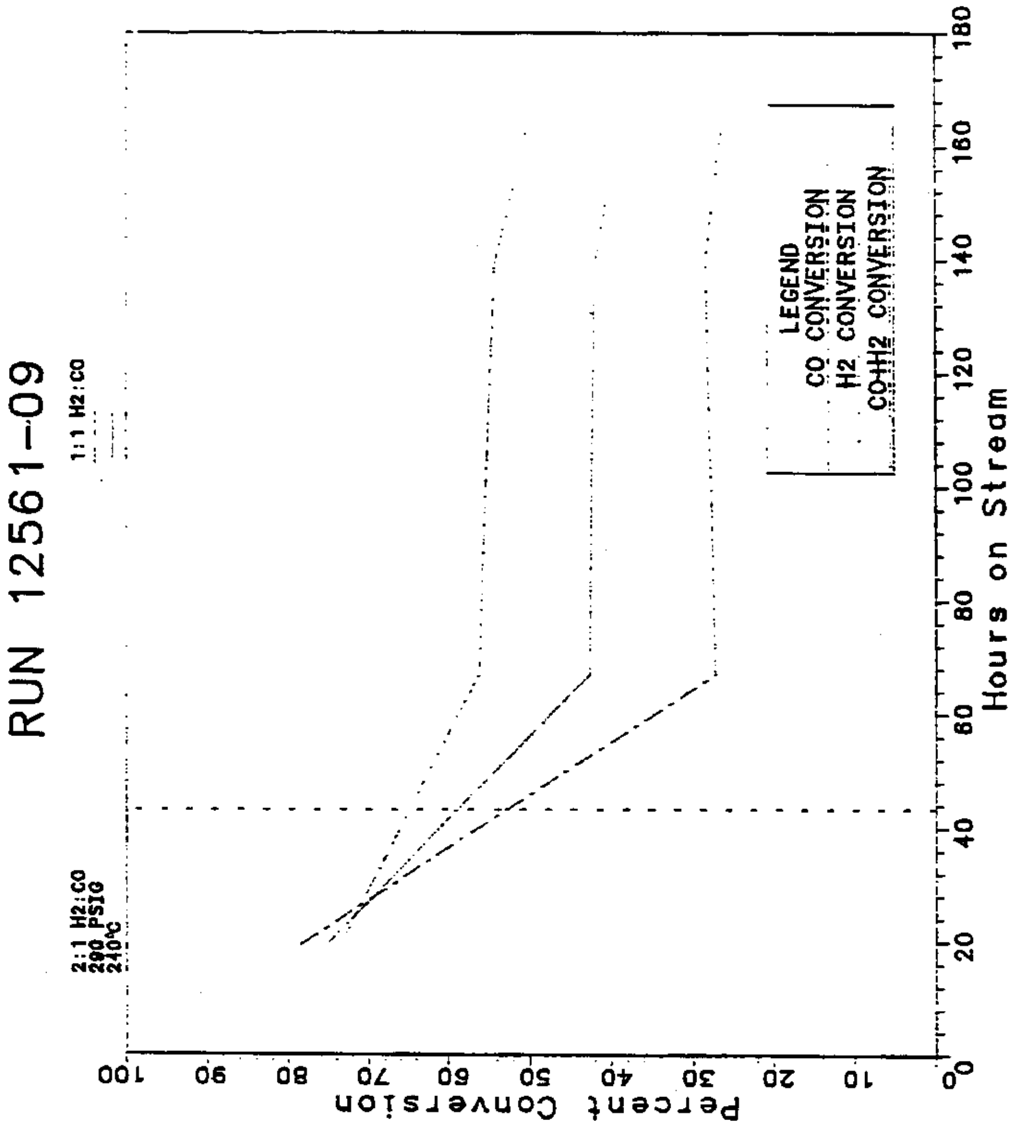
RUN 12561-09
2:1 H2:CO
290 PSIG
240°C
1:1 H2:CO
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160
180

Fig. 31

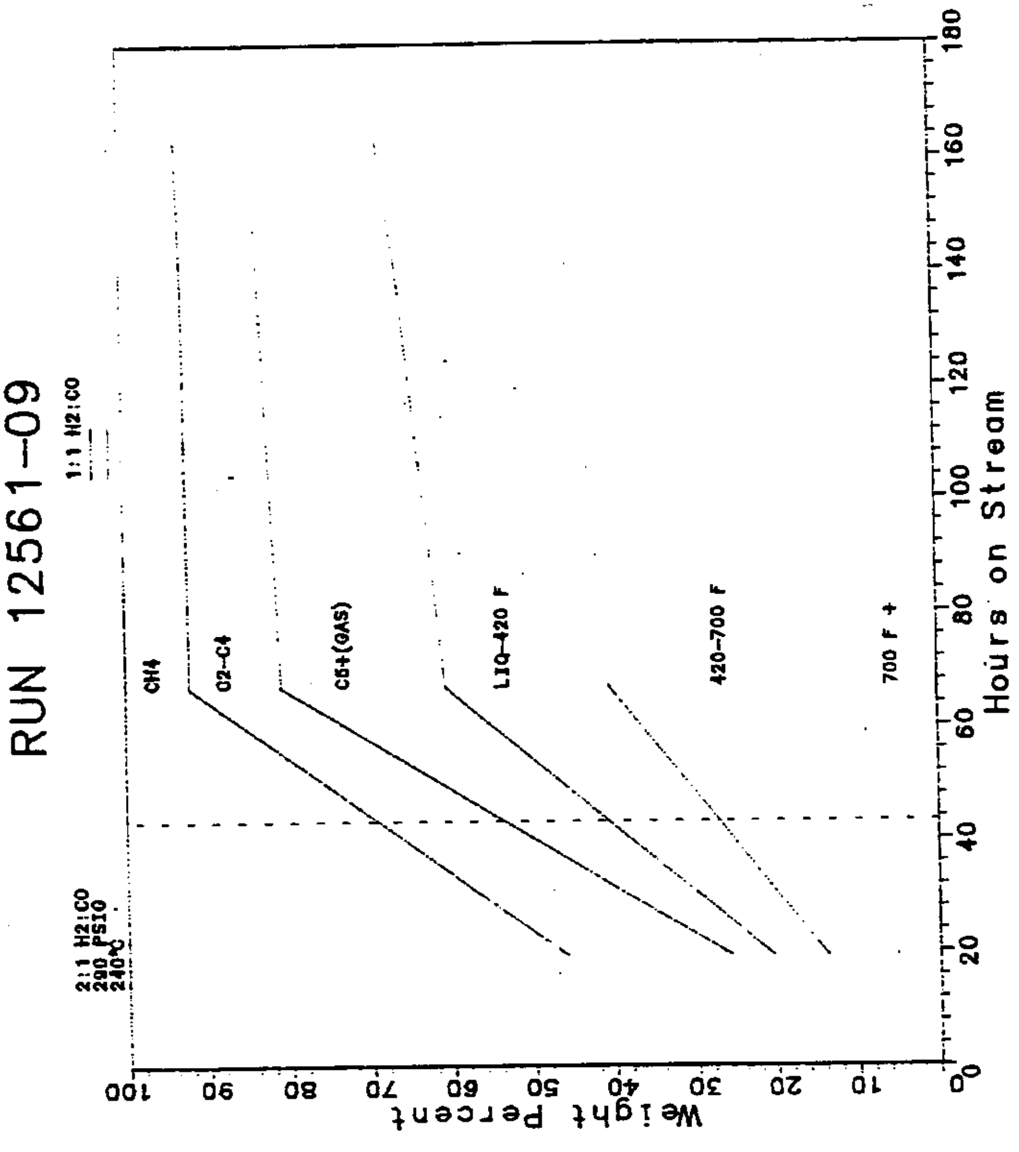
RUN 12561-09
2:1 H2:CO
290 PSIG
240°C
1:1 H2:CO
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160
180

Fig. 32

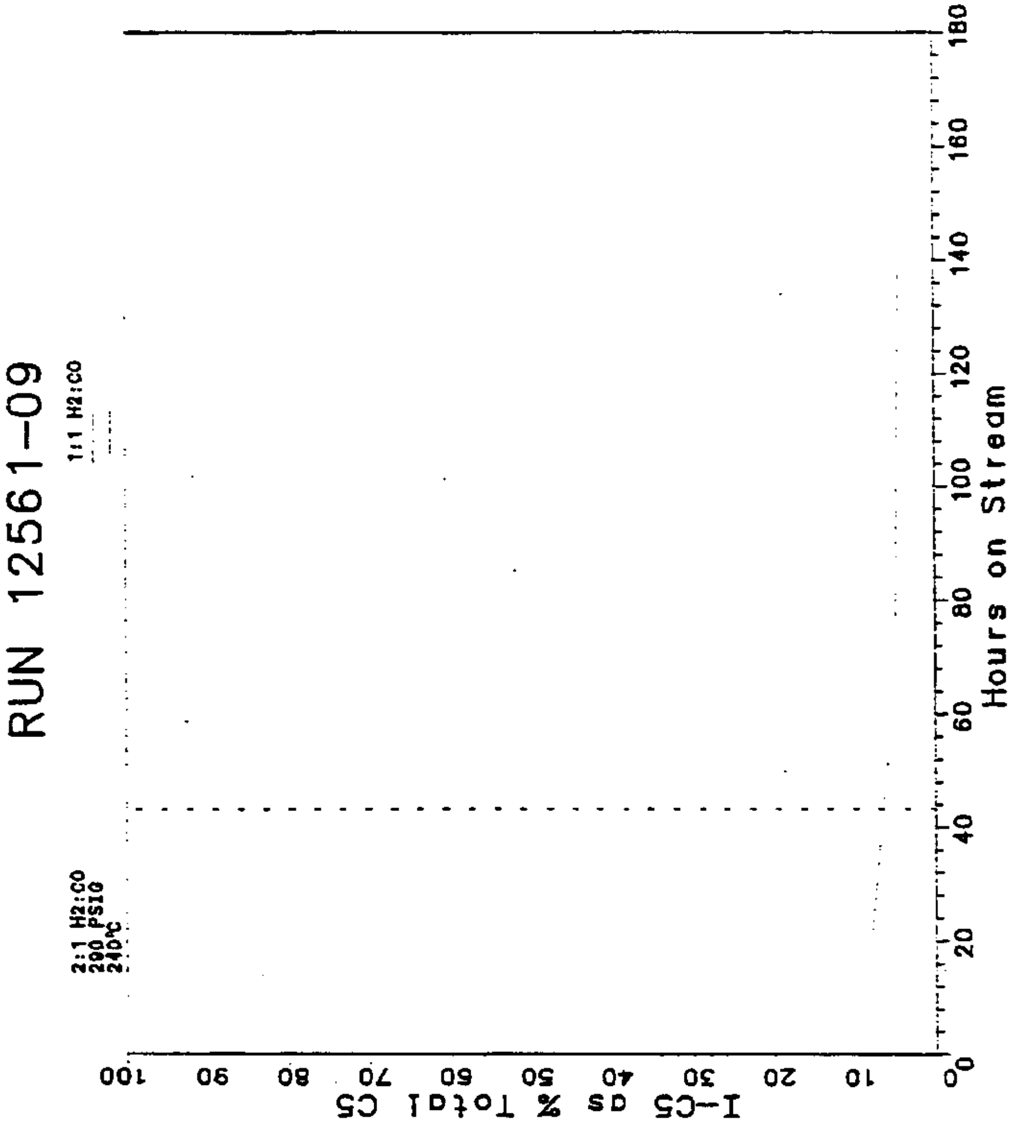
RUN 12561-09
2:1 H2:CO
200 PSIG
240°C
1:1 H2:CO
Hours on Stream
0
20
40
60
80
100
120
140
160
180
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100

Fig. 33

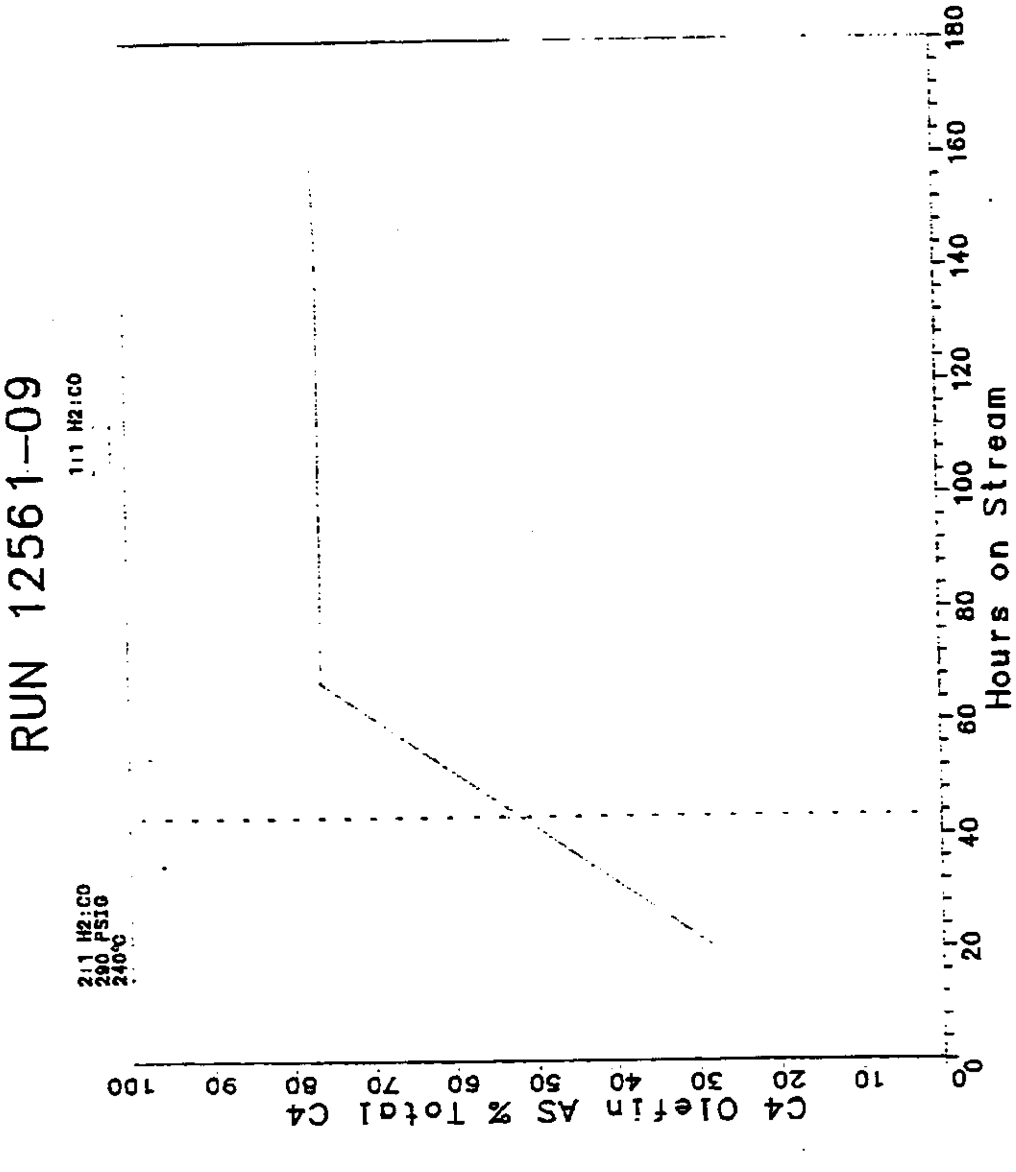
RUN 12561–09
2:1 H2:CO
290 PSIG
240°C
1:1 H2:CO
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
20
40
60
80
100
120
140
160
180

Fig. 34

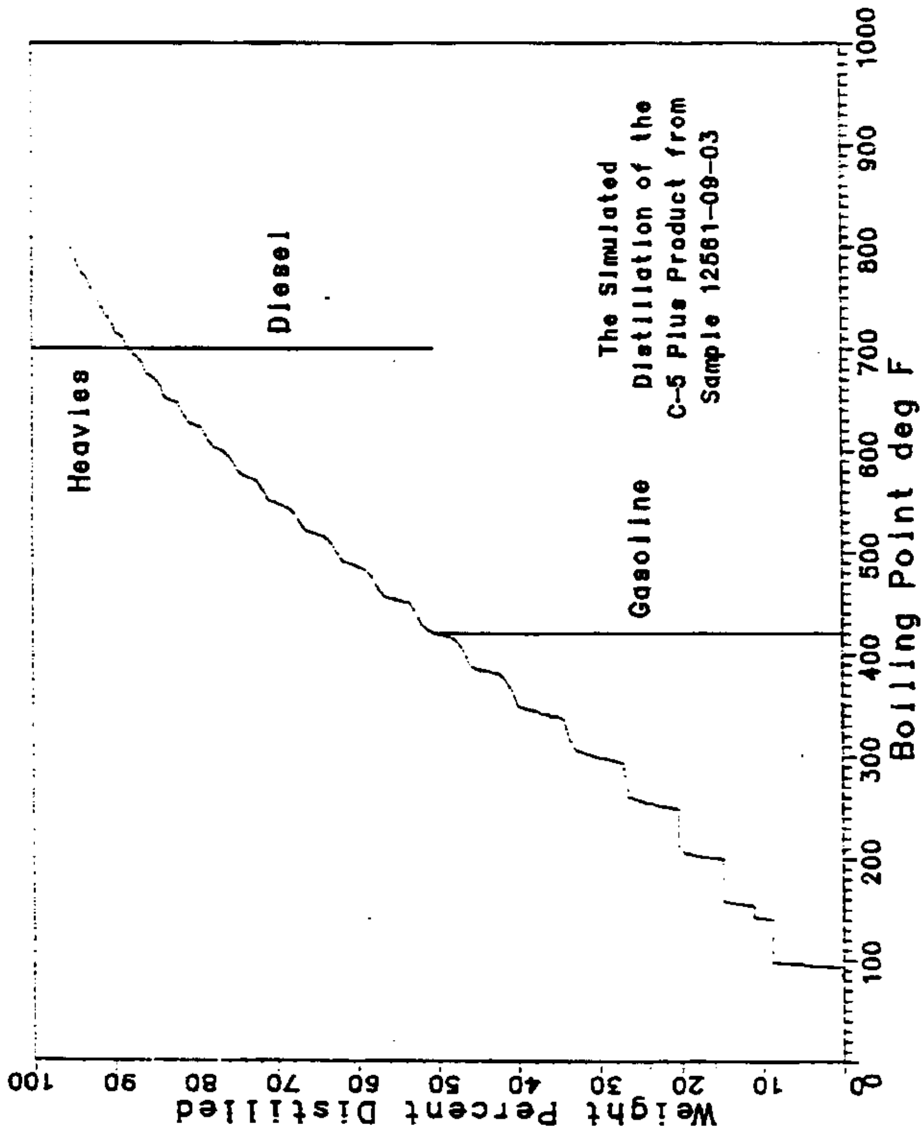
The Simulated Distillation of the C-5 Plus Product from Sample 12581-09-03
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B5

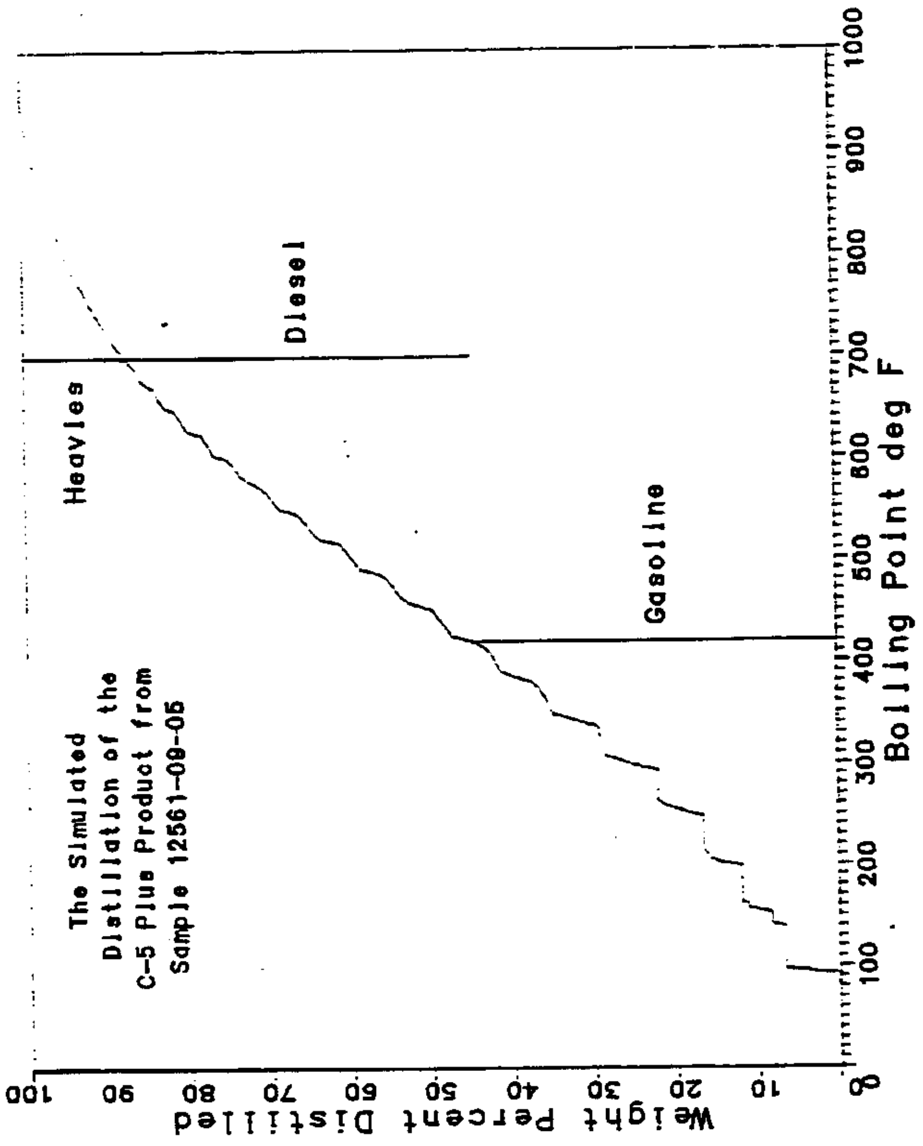
The Simulated
Distillation of the
C-5 Plus Product from
Sample 12561-09-05
Heavies
Diesel
Gasoline
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
Weight Percent Distilled
0
10
20
30
40
50
60
70
80
90
100

Fig. B6