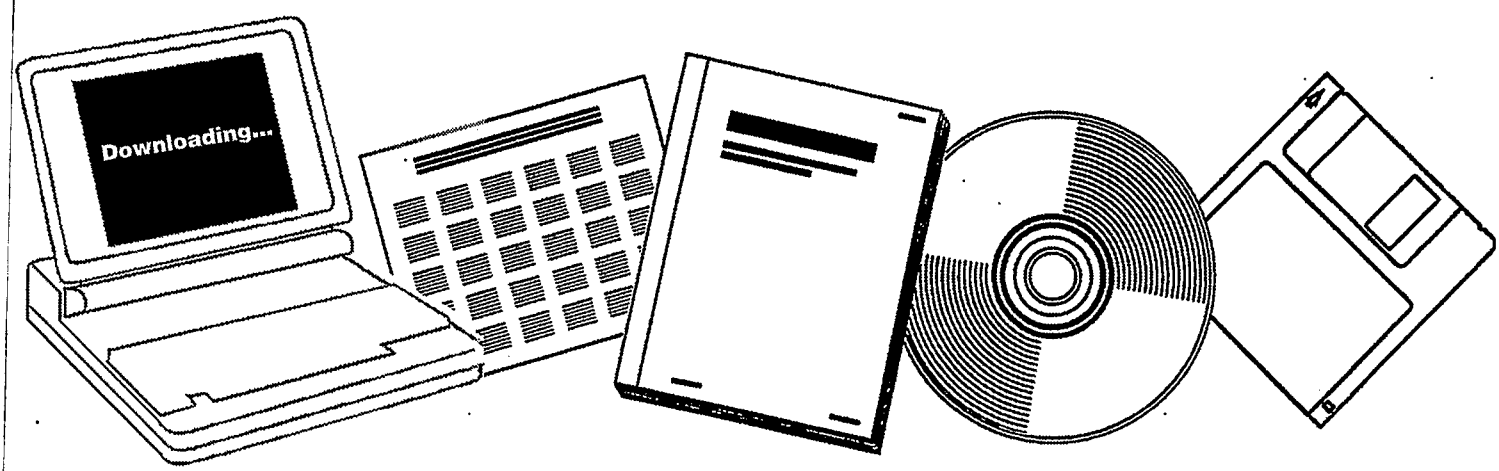
IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. TECHNICAL PROGRESS REPORT, APRIL-JUNE 1988

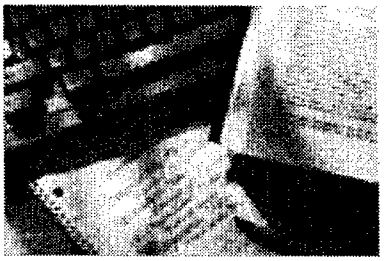
UNION CARBIDE CORP., TARRYTOWN, NY.
TARRYTOWN TECHNICAL CENTER

1988



One Source. One Search. One Solution.

NTIS



Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

TECHNICAL PROGRESS REPORT

DE-AC22-84PC70028

Fifteenth Quarterly Report
April-June 1988

IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Services Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

DOE/PC/70028--T11
DE89 015524

DISCLAIMER

Table of Contents

Appendixes

I. CONTRACT OBJECTIVE

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

II. SCHEDULE

The contract work was initially planned for the twenty-eight month period beginning September 18, 1984. The completion date has been extended to January 17, 1989.

Work on the program is divided into six tasks.

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

Task 2 consists of a preliminary techno-economic assessment of the UCC catalyst/ process system. This assessment, based on a sensitivity analysis which MITRE conducted on an updated version of their previously completed economic evaluation of the Union Carbide Corporation (UCC) system, was completed in 1986.

Task 3 consists of the optimization of the most promising catalysts developed under prior contract DE-AC22-81PC40077 toward goals defined by the MITRE and Task 2 studies. This work was completed last quarter.

Task 4 consists of the optimization of the UCC catalyst system in a manner which will give it the longest possible service life. This work was completed last quarter.

Task 5 consists of the optimization of a UCC process/catalyst system based upon a tubular reactor with a recycle loop (i.e., the ARGE reactor) containing the most promising catalyst developed under the Tasks 3 and 4

studies. This optimal performance was estimated from a mathematical model of the tubular reactor which incorporated reaction rate constants determined from completed Berty reactor runs. This effort is completed this quarter.

Task 6 consists of an economic evaluation of the optimal performance found under Task 5 for the UCC process/catalyst system. This effort was based upon the MITRE sensitivity analysis referred to in the description of Task 2, and was completed this quarter.

III. ORGANIZATION

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

The principal investigator was Dr. J. G. Miller.

The program manager was Dr. A. C. Frost

The program director is Dr. Jule A. Rabo

IV. SUMMARY OF PROGRESS

A. Task 1

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

B. Task 2

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

This sensitivity study graphically showed the differential cost (around the base case cost), expressed as differential cents per gallon of motor fuels, for changes in each of the operating parameters of space velocity, catalyst life, methane make, product alpha values, overall conversion, feed H2:CO ratio, reactor temperature, and reactor pressure.

These differential cost-operating parameter curves showed that catalyst activity, methane make, and catalyst life all contributed significantly to the cost of the process.

C. Tasks 3 and 4

Since the experimental program ended last quarter, there are no new runs to report for this quarter. However, Appendix B does list the details of the runs reported during the previous quarter. Appendix A was used to present the details of past XPS/micro-reactor data.

D. Tasks 5 and 6

Appendix C details (a) the correlation of the process runs into rate and selectivity expressions for the Co/X11/X9/TC-123 catalyst (No. 55), (b) the incorporation of these equations into the FIXBD computer simulation of a commercial ARGE-type reactor, (c) the checking of this program against experimental results, and (d) the final use of the program in the techno-economic evaluation.

This evaluation showed that the economically optimum set of process conditions was 250 C, 500 psig, 450 GHSV, and a 1.75 H_2/CO feed ratio.

While the resulting conversion per pass through the reactors at these conditions was only 70 %, this was an optimum balance between more (or larger) reactors for a higher conversion per pass (with less downstream equipment for a smaller recycle stream) and fewer (or smaller) reactors for a lower conversion per pass (with more downstream equipment for a larger recycle stream).

At these conditions, the cost was $1.88 per gallon of all liquid fuels with a one year life for the catalyst in 1983 dollars or $2.12 per gallon in 1988 dollars.

V. CHANGES

There were no contract changes during the Fifteenth Quarter.

VI. FUTURE WORK

Since all experimental and study work has been completed, future work will be directed towards the writing of the final technical report.

Jule A. Rabo

APPENDIX A. XPS/MICROREACTOR STUDIES OF FISCHER-TROPSCH CATALYSTS

TABLE OF CONTENTS

APPENDIX A. XPS/MICROREACTOR STUDIES OF FISCHER-TROPSCH CATALYSTS

XPS/MICROREACTOR SURFACE STUDIES

I. OBJECTIVE AND METHODOLOGY

The objective of these studies was to further the understanding of the role of the catalyst components (F-T metal, promoters, and supports) and the processing conditions upon F-T catalyst activity and life. The technique employed was X-ray photoelectron spectroscopy (XPS/ESCA) analyses of fresh and used catalysts samples to monitor the chemical state of the cobalt. A special XPS/microreactor system, which allows for the in situ treatment and examination of the catalyst, provided the means to expose the catalyst samples to selected reduction and reaction conditions and to obtain the cobalt chemical state information.

II. EXPERIMENTAL STUDIES

The catalysts studied included Co on both alumina and TC-123 supports with and without the X11 and X9 promoters. The chemical state of the cobalt was studied: a) as synthesized, b) following reduction, and c) following use as a F-T catalyst. The effect of the promoters and time upon the cobalt under the reduction conditions was studied. In addition, the effect of the promoters, time, temperature, and syngas composition upon the state of the cobalt was examined following use of the catalyst in F-T service. Ninety three (93) XPS/ESCA analyses were made on fresh and used samples. These are listed in Table A1 along with the test conditions employed

for reduction or reaction, as appropriate.

The XPS experimental summaries reported here cover sixty three (63) samples (selected from the ninety three) from a group of five catalyst types. These are:

I.	Co/X11-alumina	(12524-31)	Tables A2-A5
II.	Co-TC 123	(12524-76)	Tables A6-A12
III.	Co/X11-TC 123	(13168-22)	Tables A13-A31
IV.	Co/X11/X9-TC 123	(12524-43)	Tables A32-A53
V.	Co/X11/X9-TC 123	(13168-19)	Tables A54-A64

The results of the XPS studies include: a) the relative atomic percent of the surface species, b) selected elemental ratios, c)corrected binding energies (referenced to both C 1s and Si 2p) for the silicon support and the surface cobalt, and d) the percent reduction of surface cobalt.

III. DISCUSSION OF RESULTS

a) Fresh (as synthesized) Catalyst Studies

The results of these tests will be found in Tables A2, A6 and A7, A13 to A18, A32 to A38, and A54 to A57 for the five catalyst types delineated above. The surface atom ratios (Co/Si, X9/Si, and X11/Si) were found to be similar to the bulk ratios of the catalysts based upon chemical analysis. The chemical state of the cobalt was different depending upon the presence of promoters. This was determined by inspection of the peak shapes of the spectra. The cobalt in the Co-TC 123 catalyst was found

as Co (+2) and Co(+3), whereas the cobalt in the promoted catalysts was mainly Co(+2).

b) Hydrogen Activated Catalyst Studies

The purpose of these studies was to determine the chemical state of the cobalt in the catalyst following hydrogen activation (reduction). The variables employed were time and promoters. The conditions employed were hydrogen at 320 psi at 350 C and at a flow rate of 50 ml./minute over the sample. Three hours of exposure was typical and, although shorter times did show an effect, longer exposures were tested with little or no effect. These results will be found in Tables A3, A8 to A9, A19 to A24, A39 to A48, and A58 to A61, respectively for the five catalyst types delineated above.

The first observation of importance is that the surface analyses by XPS showed essentially the same analysis as the bulk analyses (by oxygen titration). The following table presents a comparison:

Catalyst Type	% Cobalt Metal of Total Cobalt	
	XPS (surface)	Titration (bulk)
Co TC-123	< 3	3
Co/X11 TC-123	15	17
Co/X9/X11 TC-123	22	21 and 23

These numbers represent the averages of the results obtained from the tables listed in the previous paragraph. It is also apparent that the presence of the promoters has a striking effect upon the reduction of the metal. The

presence of both promoters yields an even higher level of cobalt as the metal.

In the case of the cobalt on alumina, even in the presence of the X11 promoter, no reduction of the cobalt to metal was observed, Table A3.

c) Syngas Reaction Studies

The objective of these studies was to monitor the changes in the chemical state of the cobalt under simulated reaction conditions. The parameters studied included time, temperature, syngas composition, and the effect of promoters. The reactions were carried out at 300 psi and at a GHSV of 600. A gas chromatograph attached to the reactor was used to monitor the product. Schulz-Flory plots, olefin to paraffin ratios of the C4 fraction, and relative activity measurements were determined for each catalyst run.

The results of these studies will be found in Tables A4 and A5, A10 to A12, A25 to A31, A49 to A53, and A62 to A64 for the five catalyst as delineated previously.

The primary effect observed relates to the impact of the promoter upon the reduction in the presence of the syngas. The following table provides the comparison.

Catalyst Type	% Cobalt Metal Reduction	Reaction	Para./Ole. (in C4's)	Relative Activity
Co	< 3	83	1.00	3.2
Co/X11	15	21	0.34	1.8
Co/X11/X9	22	25	0.36	1.0

Although the promoters assist in the reduction of the catalyst in the case of a hydrogen only atmosphere, they act as a stabilizer in the case where syngas is employed. Note the high degree of reduction achieved in the presence of syngas in the unpromoted cobalt catalyst. The promoters improve the olefin ratios at the expense of some overall activity.

The product distribution was not effected by the presence of the promoters. Even though less conversion was achieved, the ratio of the carbon numbers in the product were equivalent. This is shown for a typical C4 to C10 fraction in Figure A1.

The temperature of the reaction affects the degree of metal reduction and the activity. The following table presents typical results for a Co/X9/X11 TC-123 catalyst exposed to a 50:50 mixture of syngas.

Temperature of Reaction	% Co Metal (from syngas)	Para./Ole. (in C4's)	Relative Activity
240 C	2.7	0.36	1.0
260 C	4.1	0.47	3.1
280 C	12.6	0.59	5.6

As the temperature increases, the conversion of cobalt to metal increases. The relative activity is proportional to the metal content. Here, as before, the product distribution is not affected, even though the conversion changes greatly. These results are shown in Figure A2.

The effect of exposure time is shown in the following

table (for Co/X11 TC-123, 240 C, 1:1 syngas, 320 psi).

Time	% Co Metal	P/O (C4's)	Rel. Act.
6 hrs.	21	0.34	1.0
12 hrs.	45	0.60	2.3

The amount of cobalt metal increases with time. Here again, the activity is proportional to the amount of metallic cobalt present. Again, as % cobalt metal increases, the paraffin to olefin ratio in the product increases. The product distribution is not affected by the time (cobalt metal content). These results are shown in Figure A3.

Finally, a study of the effect of the syngas composition was made. This was performed on a Co/X11 TC-123 catalyst at 260 C. The results are given below.

H2/CO (vol:vol)	% Cobalt Metal (from syngas)	Relative Activity
66:33	5.9	2.1
50:50	13.6	1.5
33:66	30.6	1.0

As the CO content increases, the percentage of cobalt metal increases dramatically. However, the activity is decreased since the reaction is in effect being starved of hydrogen. In the hydrogen rich case, the paraffin content is overwhelming, as might be expected.

IV. SUMMARY

a) The presence of the X11 and X9 promoters dramatically effect the extent of cobalt reduction in

hydrogen. This may be due to differences in the original cobalt chemical state (Co 2+ vs. Co 2+ and 3+) after calcination.

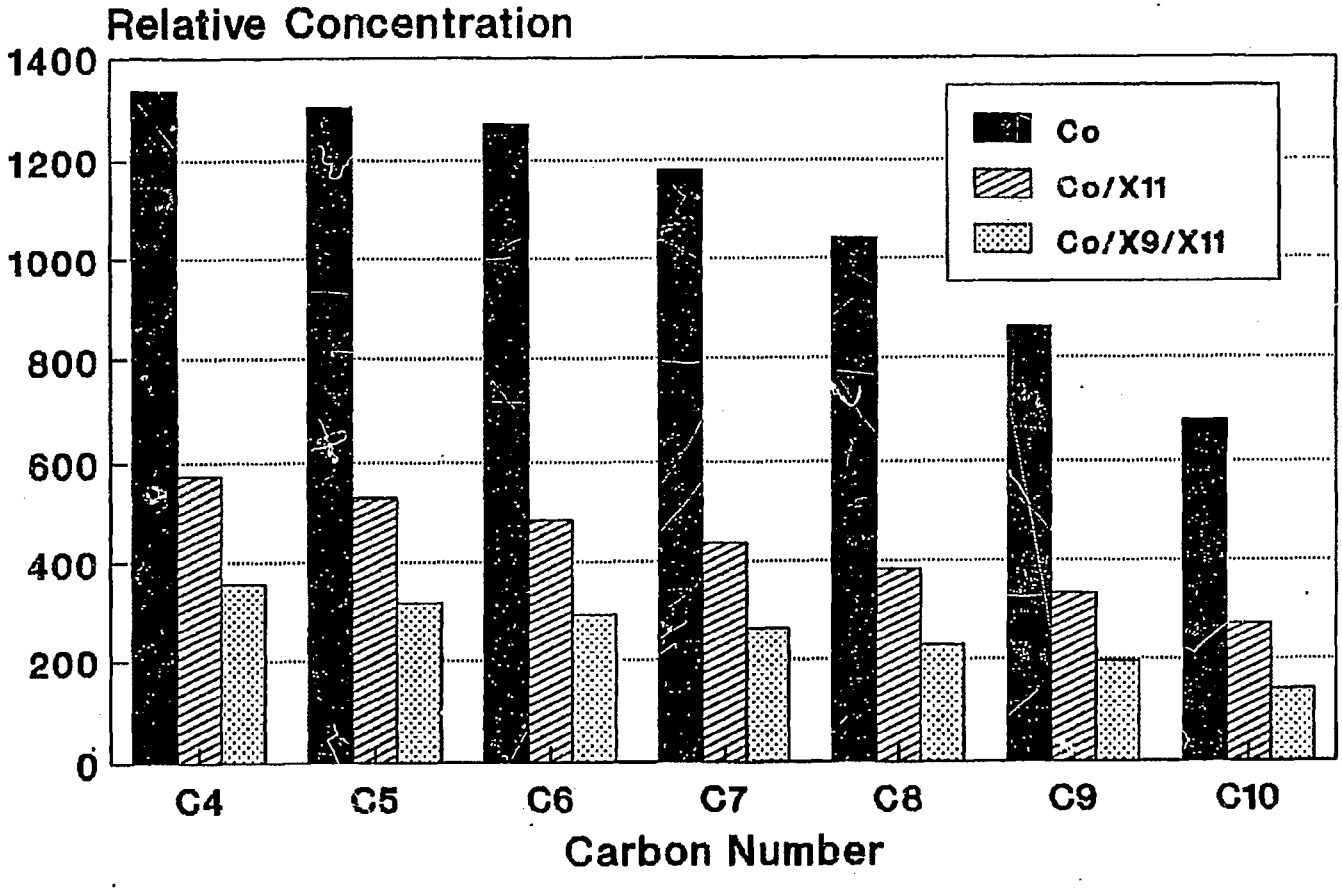
b) Additional metallic cobalt is produced upon exposure to syngas. The extent of reduction is influenced by time, temperature, and syngas composition.

c) The presence of the promoters had the greatest influence on the extent of cobalt reduction upon exposure to syngas. This indicates a fairly strong interaction between the cobalt and the promoters.

d) It is believed that the promoters reduce the cobalt reduction in the early stages of syngas reaction such that cobalt metal sintering is reduced relative to unpromoted catalysts. This in turn, results in better catalyst life.

Figure A1

Product Distribution
Effect of Promoter



240C; 50:50; 320 psi; 600 GHSV

Figure A2

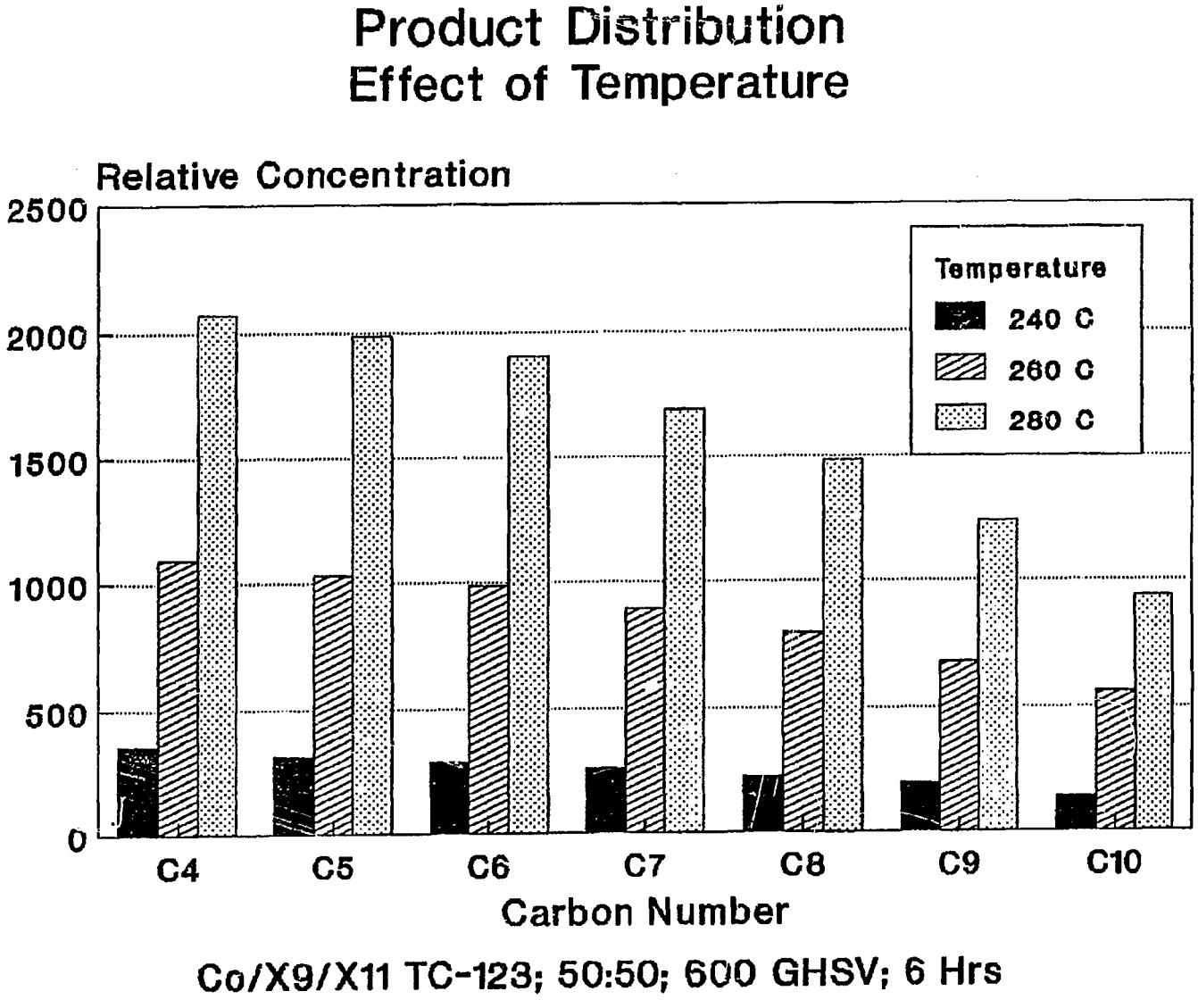
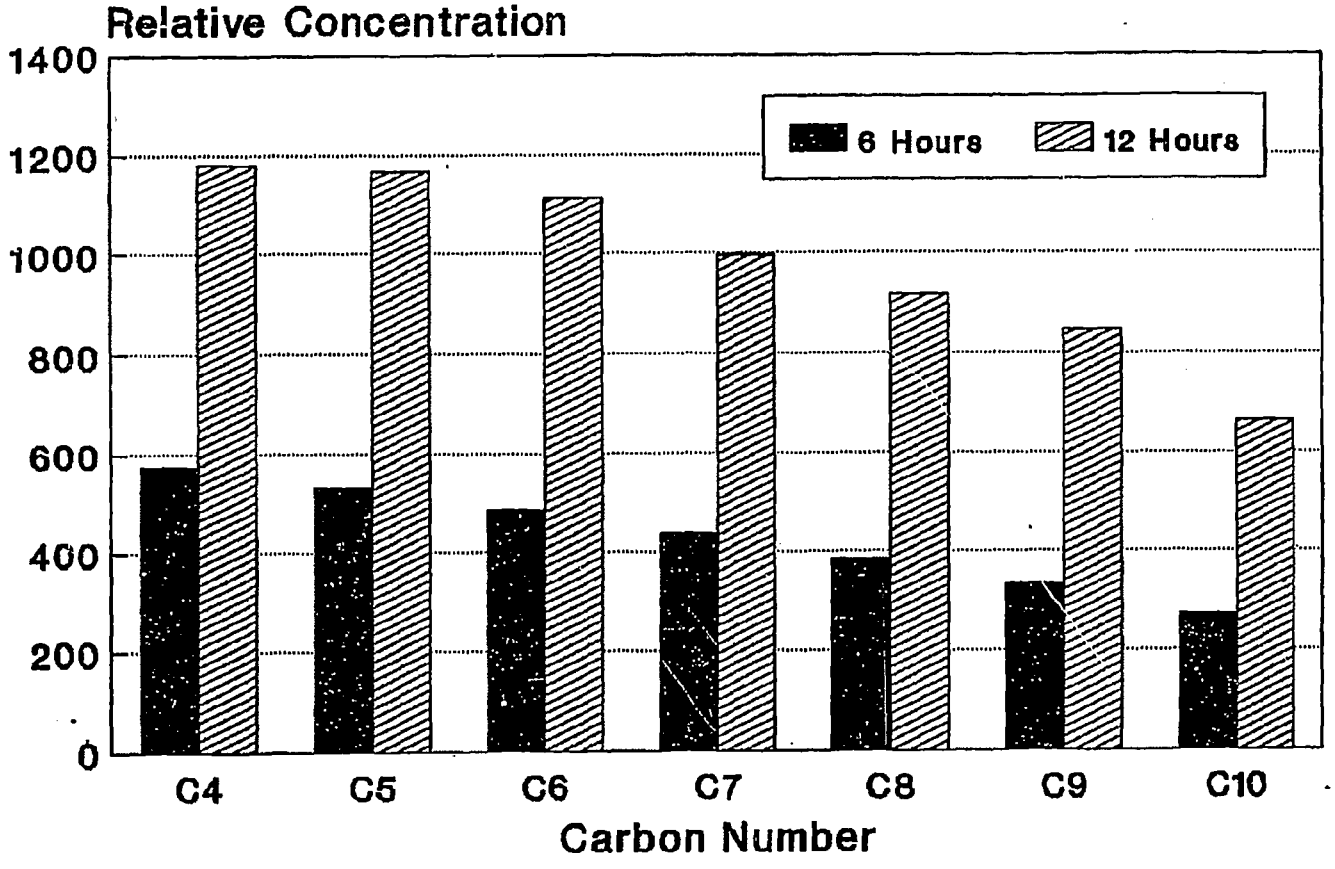

Product Distribution
Effect of Temperature
Relative Concentration
2500
2000
1500
1000
500
0
Temperature
240 C
260 C
280 C
C4
C5
C6
C7
C8
C9
C10
Carbon Number
Co/X9/X11 TC-123; 50:50; 600 GHSV; 6 Hrs

Figure A3

Product Distribution
Effect of Time



Co/X11 TC-123; 240C; 50:50; 320 psi

Table A1

LIST OF EXPERIMENTAL RUNS

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mill 1	12524-43 Co/X9/X11 TC123 As is (XPS survey spectrum)
Mill 2	12524-43 Co/X9/X11 TC123 As is
Mill 3	12524-43 Co/X9/X11 TC123 Redn 1hr 350C 320 PSI
Mill 20	12524-43 Co/X9/X11 TC123 As is
Mill 21	12524-43 Co/X9/X11 TC123 As is (XPS survey spectrum)
Mill 22	12524-43 Co/X9/X11 TC123 Redn 1hr 350C 320 PSI
Mill 23	12524-43 Co/X9/X11 TC123 As is
Mill 24	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320 PSI
Mill 25	12524-43 Co/X9/X11 TC123 Redn 3+5 hr 350C 320 PSI
Mill 26	12524-43 Co/X9/X11 TC123 Redn 23hr 350C 320 PSI
Mill 27	12524-43 Co/X9/X11 TC123 Redn 23hr 350C 320 PSI
Mill 28	12524-43 Co/X9/X11 TC123 Redn 23hr 350C 320 PSI 50/50 syn 5hr 230C 320 PSI
Mill 29	12524-43 Co/X9/X11 TC123 Redn 1hr 350C 320 PSI
Mill 30	12524-43 Co/X9/X11 TC123 50/50 syn 1hr 230C 320 PSI
Mill 31	12524-43 Co/X9/X11 TC123 Redn 23hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI

Table A1 (cont.)

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mill 38	12524-31 Co/X11 Alumina As is (XPS survey spectrum)
Mill 39	12524-31 Co/X11 Alumina As is
Mill 40	12524-31 Co/X11 Alumina Redn 3hr 350C 320 PSI
Mill 41	12524-31 Co/X11 Alumina Redn 3hr 350C 320 PSI 50/50 syn 2hr 230C 320 PSI
Mill 42	12524-31 Co/X11 Alumina Redn 3hr 350C 320 PSI 50/50 syn 2+3hr 230C 320 PSI
Mill 48	12524-76 Co TC123 As is (XPS survey spectrum)
Mill 49	12524-76 Co TC123 As is
Mill 50	12524-76 Co TC123 Redn 3hr 350C 320 PSI
Mill 51	12524-76 Co TC123 Redn 3hr 350C 320 PSI 50/50 syn 24hr 230C 320 PSI
Mill 52	12524-76 Co TC123 Redn 3hr 350C 320 PSI 50/50 syn 24hr 230C 320 PSI 50/50 syn 2hr 260C 320 PSI
Mill 53	12524-31 Co/X11 TC123 As is
Mill 54	13168-22 Co/X11 TC123 As is
Mill 55	13168-22 Co/X11 TC123 Redn 3hr 350C 320 PSI
Mill 56	13168-22 Co/X11 TC123 Redn 3hr 350C 320 PSI 50/50 syn 7hr 230C 320 PSI 50 eV pass energy

Table A1 (cont.)

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mill 57	13168-22 Co/X11 TC123 Redn 3hr 350C 320 PSI 50/50 syn 7hr 230C 320 PSI 100 eV pass energy
Mill 58	13168-22 Co/X11 TC123 As is
Mill 59	13168-22 Co/X11 TC123 Redn 3hr 350C 320 PSI
Mill 60	13168-22 Co/X11 TC123 Redn 3hr 350C 320 PSI 50/50 syn 8hr 230C 320 PSI 50 eV pass energy
Mill 61	13168-22 Co/X11 TC123 Redn 3hr 350 C 320 PSI 50/50 syn 8hr 230C 320 PSI 100 eV pass energy
Mill 62-63	Reference Co_2O_3
Mill 64-65	Reference CoO_2
Mill 66	12524-43 Co/X9/X11 TC123 As is
Mill 67	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320 PSI
Mill 68	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI
Mill 69	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI expose to air/scraped
Mill 70	12524-76 Co TC123 As is
Mill 71	12524-76 Co TC123 Redn 3hr 350C 320 PSI
Mill 72	12524-76 Co TC123 Redn 3hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI
Mill 73-74	Reference Co_3O_4

Table A1 (cont.)

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mill 75	12524-76 Co TC123 Redn 3hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI 50 eV pass air/scraped
Mill 76	12524-76 Co TC123 Redn 3hr 350C 320 PSI 50/50 syn 6hr 230C 320 PSI 100 eV pass air/scraped
Mill 79	12524-43 Co/X9/X11 TC123 As is
Mill 80	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320PSI
Mill 81	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI exposed to air
Mill 82	13168-19 Co/X9/X11 TC123 As is
Mill 83	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI
Mill 84	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI
Mill 85	13168-22 Co/X11 TC123 As is
Mill 86	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI
Mill 87	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI
Mill 88	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI 50/50 syn 6hr 260C 320PSI 50 eV pass energy

Table A1 (cont.)

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mill 89	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI 50/50 syn 6hr 260C 320PSI 100 eV pass energy
Mill 90	13168-19 Co/X9/X11 TC123 As is
Mill 91	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI
Mill 92	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 280C 320PSI
Mill 93	13168-19 Co/X9/X11 TC123 As is
Mill 94	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI
Mill 95	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 260C 320PSI
Mill 96	12524-43 Co/X9/X11 TC123 As is
Mill 97	12524-43 Co/X9/X11 TC123 As is
Mill 98	12524-43 Co/X9/X11 TC123 Redn 4hr 350C 320PSI
Mill 99	12524-43 Co/X9/X11 TC123 Redn 4hr 350C 320PSI 50/50 syn 6hr 250C 320PSI
Mil 100	13168-19 Co/X9/X11 TC123 As is
Mil 101	Reference Co_3O_4
Mil 102	Reference CoO_2
Mil 103	12524-43 Co/X9/X11 TC123 As is
Mil 104	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320PSI

Table A1 (cont.)

XPS DATA (File Name)	SAMPLE AND CONDITIONS
Mil 105	12524-43 Co/X9/X11 TC123 Redn 3hr 350C 320PSI 50/50 syn 6hr 240C 320PSI
Mil 106	13168-19 Co/X9/X11 TC123 As is
Mil 107	13168-19 Co/X9/X11 TC123 Redn 3hr 350C 320PSI
Mil 108	Reference cobalt metal
Mil 109	13168-22 Co/X11 TC123 As is
Mil 110	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI
Mil 111	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI $66CO/33H_2$ 6hr 240C 320PSI
Mil 112-113	13168-22 Co/X11 TC123 As is
Mil 114	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI
Mil 115	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI $66CO/33H_2$ 6hr 240C 320PSI
Mil 116-117	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI $66CO/33H_2$ 6hr 240C 320PSI argon sputtered
Mil 118	13168-22 Co/X11 TC123 As is
Mil 119	13168-22 Co/X11 TC123 As is argon sputtered
Mil 120	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI
Mil 121-122	13168-22 Co/X11 TC123 Redn 3hr 350C 320PSI $33CO/66H_2$ 6hr 240C 320PSI

XPS EXPERIMENTAL SUMMARIES

I. Co/X11-Alumina; Sample# 12524-31

II. Co-TC123; Sample# 12524-76

III. Co/X11-TC123; Sample# 13168-22

IV. Co/X11/X9-TC123; Sample# 12524-43

V. Co/X11/X9-TC123 (second batch); Sample# 13168-19

I. Co/X11-Alumina
(12524-31)

Table A2

XPS Analysis of As-Synthesized Co/X11 Alumina

Sample #	XPS File ID
12524-31	Mill 39

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Al	Co(metal)	Co(oxide)	X11
6.4	58.4	30.2	---	4.2	0.8
	(62.4)	(32.2)	(---)	(4.5)	(0.8)

Elemental Ratios

Co(oxide)/Al	Co(metal)/Al	X11/Al
0.14	---	0.025

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Al 2p
780.6	---	74.1

3. **COMMENTS**

a. Initial run for subsequent Mill 40 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A3

XPS Analysis of As-Synthesized Co/X11 Alumina After Hydrogen Reduction

Sample #	XPS File ID
12524-31	Mill 40

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Al	Co(metal)	Co(oxide)	X11
7.8	56.4	31.2	---	3.6	0.9
	(61.2)	(33.8)	(---)	(3.9)	(1.0)

Elemental Ratios (peak area calculation)

Co(oxide)/Al	Co(metal)/Al	X11/Al
0.12	----	0.030

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Al 2p
780.9	---	74.2

4. **COMMENTS:**

a. Activation of catalyst for Mill 41 syngas experiment.
b. < 3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. --- Specie absent or below XPS detection limit.

Table A4

XPS Analysis of Activated Co/X11 Alumina After Syngas Reaction

Sample #	XPS File ID
12524-31	Mill 41

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	2 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Al	Co(metal)	Co(oxide)	X11
8.3	57.5	30.0	---	3.3	0.8
	(62.7)	(32.7)	(---)	(3.6)	(0.9)

Elemental Ratios (peak area calculation)

Co(oxide)/Al	Co(metal)/Al	X11/Al
0.11	---	0.028

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Al 2p
780.8	---	74.1

4. **COMMENTS:**

a. < 3% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A5

XPS Analysis of Activated Co/X11 Alumina After Syngas Reaction

Sample #	XPS File ID
12524-31	Mill 42

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	2 hrs
50/50 H_2/CO	240°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Al	Co(metal)	Co(oxide)	X11
30.3	42.7	24.6	---	1.7	0.6
	(61.3)	(35.3)	(---)	(2.5)	(0.8)

Elemental Ratios (peak area calculation)

Co(oxide)/Al	Co(metal)/Al	X11/Al
0.070	---	0.024

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Al 2p
780.5	---	74.1

4. **COMMENTS:**

a. < 3% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A6

XPS Analysis of As-Synthesized Co TC-123

Sample #	XPS File ID
12524-76	Mill 49

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical state(s) of the cobalt.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
5.9	58.7	26.4	---	9.1
	(62.3)	(28.0)	(---)	(9.6)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si
0.34	---

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 50 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A7

XPS Analysis of As-Synthesized Co TC-123

Sample #	XPS File ID
12524-76	Mill 70

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical state(s) of the cobalt.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
4.5	60.2	26.7	---	8.6
	(63.0)	(28.0)	(---)	(9.0)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si
0.32	---

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	---	103.3

3. **COMMENTS**

a. Initial run for subsequent Mill 71 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A8

XPS Analysis of As-Synthesized Co TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-76	Mill 50

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical state(s) of the cobalt. Determine the amount of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
8.1	56.1	25.9	0.7	9.2
	(61.1)	(28.2)	(0.7)	(10.0)

Elemental Ratios (peak area calculations)

Co(oxide)/Si	Co(metal)/Si
0.36	0.023

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.0	777.9	103.7
[781.7]	[777.6]	[103.4]

4. **COMMENTS**

a. Activation run for subsequent Mill 51 experiment.
b. 6.1% cobalt reduction.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A9

XPS Analysis of As-Synthesized Co TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-76	Mill 71

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical state(s) of the cobalt. Determine the amount of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
12.5	55.0	25.1	0.3	7.1
	(62.9)	(28.6)	(0.4)	(8.1)

Elemental Ratios (peak area calculations)

Co(oxide)/Si	Co(metal)/Si
0.28	0.014

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.0	777.7	103.9
[781.5]	[777.2]	[103.4]

4. **COMMENTS**

a. Activation run for subsequent Mill 72 experiment.
b. < 3% cobalt reduction.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A10

XPS Analysis of Activated Co TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-76	Mill 51

1. OBJECTIVE: Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical state(s) of the cobalt. Determine the amount of cobalt reduction.

2. EXPERIMENTAL CONDITIONS:

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	24 hrs

3. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
83.5	9.7	5.8	0.1	0.9
	(58.8)	(35.2)	(0.5)	(5.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si
0.16	0.014

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.9	777.9	103.6
[781.7]	[777.7]	[103.4]

4. COMMENTS

a. 8.3% cobalt reduction.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A11

XPS Analysis of Activated Co TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-76	Mill 52

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical state(s) of the cobalt. Determine the amount of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	24 hrs
50/50 H_2/CO	260°C	320 PSI	2 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
75.3	14.9	8.6	0.1	1.1
	(60.2)	(34.8)	(0.6)	(4.4)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si
0.12	0.018

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.8	777.7	103.6
[781.6]	[777.5]	[103.4]

4. **COMMENTS**

a. 12.8% cobalt reduction.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A12

XPS Analysis of Activated Co TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-76	Mill 72

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical state(s) of the cobalt. Determine the amount of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)
71.3	18.9	9.1	0.4	0.3
	(65.7)	(31.8)	(1.4)	(1.1)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si
0.035	0.044

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.0	103.7
[781.3]	[777.7]	[103.4]

4. **COMMENTS**

a. 75.3% cobalt reduction.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A13

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 54

1. **OBJECTIVE:** Determine the surface elemental composition of t catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
9.6	56.5	25.3	---	6.9	1.7
	(62.5)	(28.0)	(---)	(7.6)	(1.9)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.27	---	0.068

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 55 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A14

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 58

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
8.4	57.2	25.6	---	6.9	1.8
	(62.5)	(28.0)	(---)	(7.6)	(2.0)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.27	---	0.070

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 59 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A15

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 85

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
11.5	56.0	24.7	---	6.2	1.7
	(63.3)	(27.9)	(---)	(7.0)	(1.9)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.25	---	0.067

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.9	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 86 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A16

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 109

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
13.8	53.9	24.3	---	6.7	1.4
	(62.5)	(28.1)	(---)	(7.8)	(1.6)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.28	---	0.056

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.7	---	103.9

3. **COMMENTS**

a. Initial run for subsequent Mill 110 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A17

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 113

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
12.6	54.1	24.8	---	6.9	1.7
	(61.9)	(28.3)	(---)	(7.9)	(1.9)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.28	---	0.067

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.4	---	103.9

3. **COMMENTS**

a. Initial run for subsequent Mill 114 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A18

XPS Analysis of As-Synthesized Co/X11 TC-123

Sample #	XPS File ID
13168-22	Mill 118

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
9.4	62.4	22.1	---	4.5	1.5
	(68.9)	(24.4)	(---)	(5.0)	(1.7)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.20	---	0.069

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.0	---	103.5

3. **COMMENTS**

a. Initial run for subsequent Mill 120 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A19

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 55

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
12.3	54.8	24.3	---	6.6	2.0
	(62.4)	(27.7)	---	(7.6)	(2.3)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.27	----	0.081

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.1	---	103.6
[781.9]		[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 57 syngas experiment.
b. < 3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. --- Specie absent or below XPS detection limit.
g. [ ] Referenced to Si 2p.

Table A20

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 59

1. OBJECTIVE Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. EXPERIMENTAL CONDITIONS:

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
13.0	51.2 (58.8)	26.5 (30.5)	0.8 (0.9)	6.3 (7.3)	2.2 (2.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.24	0.029	0.083

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7 [781.4]	777.7 [777.4]	103.7 [103.4]

4. COMMENTS:

a. Activation of catalyst for Mill 61 syngas experiment.
b. 10.8% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p at 103.4 eV.

Table A21

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 86

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
14.2	50.8 (59.2)	26.6 (31.0)	1.2 (1.4)	5.1 (6.0)	2.1 (2.4)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.19	0.046	0.078

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7 [781.4]	777.7 [777.4]	103.7 [103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 87 syngas experiment.
b. 19.2% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p at 103.4 eV.

Table A22

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 110

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
15.0	61.3	16.7	0.8	4.8	1.4
	(72.0)	(19.7)	(1.0)	(5.7)	(1.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.29	0.051	0.082

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	777.7	104.0
[781.0]	[777.1]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 111 syngas experiment.
b. 14.9% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p at 103.4 eV.

Table A23

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 114

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
11.6	53.3	25.6	0.9	6.4	2.2
	(60.3)	(29.0)	(1.0)	(7.3)	(2.4)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.25	0.036	0.084

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.9	778.4	104.0
[781.3]	[777.8]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 115 syngas experiment.
b. 12.7% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p at 103.4 eV.

Table A24

XPS Analysis of As-Synthesized Co/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-22	Mill 120

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
9.2	55.1	26.3	1.2	6.2	2.0
	(60.7)	(29.0)	(1.4)	(6.8)	(2.1)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.23	0.047	0.074

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.9	778.3	103.9
[781.4]	[777.8]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 122 syngas experiment.
b. 16.7% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p at 103.4 eV.

Table A25

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 57

1. OBJECTIVE Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. EXPERIMENTAL CONDITIONS:

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	7 hrs

3. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
96.4	2.2	1.2	0.1	---	0.1
	(59.6)	(34.4)	(2.3)	(0.7)	(3.0)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.020	0.066	0.087

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.0	103.4

4. COMMENTS:

a. 75.0% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A26

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 61

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	8 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
69.6	18.0	10.8	0.4	0.5	0.7
	(59.5)	(35.6)	(1.2)	(1.5)	(2.2)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.043	0.034	0.062

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.2	103.5
[781.5]	[778.1]	[103.4]

4. **COMMENTS:**

a. 42.9% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A27

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 87

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
56.8	28.0	12.3	0.5	1.6	0.8
	(64.7)	(28.4)	(1.2)	(3.8)	(1.9)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.13	0.043	0.065

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	777.9	103.5
[781.4]	[777.8]	[103.4]

4. **COMMENTS:**

a. 25.0% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A28

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 89

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	6 hrs
50/50 H_2/CO	260°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
84.6	8.7	6.2	0.1	0.1	0.3
	(56.5)	(40.0)	(1.1)	(0.6)	(1.8)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.014	0.030	0.044

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.2	778.2	103.5
[782.1]	[778.1]	[103.4]

4. **COMMENTS:**

a. 67.5% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A29

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 111

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
33/66 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
29.4	42.6	22.0	0.9	3.6	1.5
	(60.2)	(31.1)	(1.4)	(5.1)	(2.2)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.17	0.044	0.069

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	778.0	103.7
[781.2]	[777.7]	[103.4]

4. **COMMENTS:**

a. 21.2% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p

Table A30

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 115

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify t chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
33/66 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
46.6	35.8	14.3	0.5	1.9	0.9
	(67.0)	(26.8)	(0.9)	(3.6)	(1.7)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.14	0.034	0.062

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.4	777.9	103.5
[781.3]	[777.8]	[103.4]

4. **COMMENTS:**

a. 20.3% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A31

XPS Analysis of Activated Co/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-22	Mill 122

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
66/33 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X11
65.4	23.7	9.3	0.3	0.6	0.6
	(68.6)	(27.0)	(0.6)	(2.0)	(1.8)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X11/Si
0.073	0.023	0.067

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.4	777.9	103.5
[781.3]	[777.8]	[103.4]

4. **COMMENTS:**

a. 24.4% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

IV. Co/X11/X9-TC123 (12524-43)

Table A32

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 2

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
16.6	57.6	17.8	---	5.3	0.8	1.8
	(69.1)	(21.3)	(---)	(6.4)	(1.0)	(2.2)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.030	---	0.048	0.103

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.7
[780.7]	[---]	[103.4]

3. **COMMENTS**

a. Initial run for subsequent Mill 3 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.
f. [ ] Referenced to Si 2p.

Table A33

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 20

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
10.4	62.2	21.9	---	3.2	1.0	1.5
	(69.4)	(24.4)	(---)	(3.5)	(1.0)	(1.6)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.14	---	0.042	0.067

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.8	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 22 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A34

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 23

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
12.8	56.1	22.2	---	6.1	1.0	1.8
	(64.3)	(25.4)	(---)	(7.0)	(1.1)	(2.1)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.28	---	0.044	0.082

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.9	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 24 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A35

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 66

1. OBJECTIVE: Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
11.9	55.2	25.0	---	4.6	1.1	2.1
	(62.6)	(28.4)	(---)	(5.2)	(1.3)	(2.5)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.18	---	0.044	0.087

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.6	---	103.3

3. COMMENTS

a. Initial run for subsequent Mill 67 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A 36

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 79

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
13.4	53.8	23.8	---	5.8	1.1	2.0
	(62.2)	(27.5)	(---)	(6.7)	(1.3)	(2.3)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.25	---	0.046	0.083

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.7	---	103.4

3. **COMMENTS**

a. Initial run for subsequent Mill 80 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A37

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 97

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
22.6	48.5	20.8	---	5.3	1.0	1.7
	(62.7)	(26.9)	(---)	(6.8)	(1.3)	(2.2)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.25	---	0.050	0.082

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.6	---	103.3

3. **COMMENTS**

a. Initial run for subsequent Mill 98 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A38

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
12524-43	Mill 103

1. **OBJECTIVE:** Determine the surface elemental compositon of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
20.5	49.6	20.0	---	7.7	0.7	1.5
	(62.4)	(25.1)	(---)	(9.7)	(0.9)	(1.9)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.38	---	0.036	0.075

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.4	---	103.5

3. **COMMENTS**

a. Initial run for subsequent Mill 3 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.
f. Co(oxide) binding energy is high.

Table A39

XPS Analysis of As-Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 3

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
22.5	50.2	18.3	---	6.1	0.9	2.0
	(64.7)	(23.6)	(---)	(7.9)	(1.2)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.34	---	0.049	0.112

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.9	---	103.4

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. < 3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. --- Specie absent or below XPS detection limit.

Table A40

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 22

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	1 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
14.4	51.8	23.9	0.5	6.2	1.0	2.2
	(60.5)	(28.0)	(0.5)	(7.3)	(1.2)	(2.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.26	0.020	0.043	0.090

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
780.9	777.3	103.3
[781.0]	[777.4]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for time dependence study.
b. < 3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table 41

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 24

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
7.5	56.9	25.3	1.8	5.1	1.1	2.3
	(61.6)	(27.3)	(2.1)	(5.4)	(1.2)	(2.4)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.20	0.074	0.044	0.089

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.0	103.4

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 27.0% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.

Table A42

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 25

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	8 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
1.7	59.7	27.5	2.3	5.3	1.2	2.3
	(60.8)	(27.8)	(2.5)	(5.3)	(1.2)	(2.4)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.19	0.087	0.044	0.085

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7	778.1	103.6
[781.5]	[777.9]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 31.3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A43

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 27

1. OBJECTIVE: Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. EXPERIMENTAL CONDITIONS:

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	23 hrs

3. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
11.5	53.8	24.8	1.4	5.0	1.2	2.3
	(60.7)	(28.0)	(1.7)	(5.6)	(1.4)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.20	0.060	0.049	0.092

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7	777.8	103.6
[781.5]	[777.6]	[103.4]

4. COMMENTS:

a. Activation of catalyst for Mill 34 syngas experiment.
b. 23.1% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A44

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 29

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	1 hr

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
9.7	55.3	24.8	1.0	5.7	1.2	2.3
	(61.3)	(27.5)	(1.2)	(6.2)	(1.3)	(2.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.23	0.043	0.048	0.092

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	777.8	103.6
[781.3]	[777.6]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 16.1% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A45

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 67

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
12.1	53.2	25.1	1.0	5.2	1.1	2.3
	(60.5)	(28.6)	(1.2)	(5.8)	(1.3)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.21	0.039	0.045	0.090

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	777.7	103.7
[781.3]	[777.4]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 16.2% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Table A46

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 80

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.2	52.2	23.4	1.7	4.3	1.1	2.1
	(61.5)	(27.6)	(2.1)	(5.0)	(1.3)	(2.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.19	0.073	0.048	0.090

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	777.6	103.5
[781.0]	[777.5]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 28.6% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A47

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 98

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	4 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.7	55.2	20.8	0.8	4.1	1.2	2.2
	(65.5)	(24.7)	(0.9)	(4.9)	(1.4)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.19	0.036	0.058	0.100

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	777.8	103.3
[781.6]	[777.9]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 15.3% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A48

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
12524-43	Mill 104

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.4	50.5	24.6	1.6	4.8	0.9	2.2
	(59.6)	(29.0)	(2.0)	(5.7)	(1.1)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.20	0.065	0.039	0.089

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.2	778.0	103.8
[781.8]	[777.6]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 34 syngas experiment.
b. 26.0% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A49

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-43	Mill 28

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	230°C	320 PSI	5 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
34.6	38.9	20.7	2.7	---	1.0	2.1
	(59.5)	(31.6)	(4.2)	(---)	(1.5)	(3.2)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
---	0.13	0.047	0.10

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.1	103.5
[781.5]	[778.0]	[103.4]

4. **COMMENTS:**

a. ca. 100% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.
f. [ ] Referenced to Si 2p.

Table 50

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-43	Mill 30

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	230°C	320 PSI	1 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
46.2	36.4	13.6	0.7	1.7	0.6	0.8
	(67.7)	(25.3)	(1.0)	(3.3)	(1.2)	(1.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.13	0.043	0.046	0.060

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.2	777.9	103.4

4. **COMMENTS:**

a. 25.4% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.

Table A51

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-43	Mill 68

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	230°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
87.8	7.8	3.8.	0.1	0.2	0.1	0.2
	(63.9)	(31.5)	(0.9)	(1.1)	(1.1)	(1.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.034	0.029	0.035	0.046

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.3	777.6	103.4

4. **COMMENTS:**

a. 45.2% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.

Table A52

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-43	Mill 99

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	250°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
85.0	8.5	5.9	0.2	---	0.2	0.2
	(56.3)	(38.9)	(1.8)	(---)	(1.5)	(1.5)

Elemental Ratios (peak area calcu ion)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
---	0.046	0.039	0.037

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.3	103.4

4. **COMMENTS:**

a. ca. 100% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A53

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
12524-43	Mill 105

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
68.4	20.8	8.9	(1.1)	---	0.3	0.5
	(65.5)	(28.1)	(3.5)	(---)	(1.1)	(1.8)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
---	0.12	0.038	0.062

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	778.1	103.4

4. **COMMENTS:**

a. ca. 100% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

V. Co/X11/X9-TC123
(13168-19)

Table 54

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
13168-19	Mill 82

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
16.2	52.3	21.4	---	7.2	0.8	1.9
	(62.5)	(25.6)	(---)	(8.7)	(1.0)	(2.3)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.34	---	0.039	0.088

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.3

3. **COMMENTS**

a. Initial run for subsequent Mill 83 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table 55

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
13168-19	Mill 90

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
27.4	45.2	18.3	---	6.8	0.8	1.5
	(62.3)	(25.2)	(---)	(9.3)	(1.1)	(2.1)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.37	---	0.042	0.084

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.2

3. **COMMENTS**

a. Initial run for subsequent Mill 91 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table 56

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
13168-19	Mill 93

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.8	51.2	22.7	---	7.7	0.9	1.8
	(60.8)	(26.9)	(---)	(9.2)	(1.0)	(2.2)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.34	---	0.038	0.081

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.1	---	103.2

3. **COMMENTS**

a. Initial run for subsequent Mill 94 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A57

XPS Analysis of As-Synthesized Co/X9/X11 TC-123

Sample #	XPS File ID
13168-19	Mill 106

1. OBJECTIVE: Determine the surface elemental composition of the catalyst prior to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species.

2. XPS RESULTS:

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
16.1	51.6	21.9	---	7.7	0.8	1.8
	(61.5)	(26.1)	(---)	(9.2)	(1.0)	(2.2)

Elemental Ratios

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.35	---	0.039	0.084

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	---	103.6

3. COMMENTS

a. Initial run for subsequent Mill 107 experiment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. --- Specie absent or below XPS detection limit.

Table A58

XPS Analysis of As-Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-19	Mill 83

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.9	49.0	23.1	1.7	7.0	1.0	2.3
	(58.3)	(27.5)	(2.0)	(8.3)	(1.2)	(2.7)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.30	0.072	0.043	0.100

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7	777.8	103.5
[781.6]	[777.7]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 84 syngas experiment.
b. 19.5% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
f. [ ] Referenced to Si 2p.

Table A59

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-19	Mill 91

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
21.2	47.1	21.7	0.9	6.1	0.9	2.1
	(59.8)	(27.6)	(1.2)	(7.7)	(1.1)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.28	0.043	0.042	0.095

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	777.7	103.4

4. **COMMENTS:**

a. Activation of catalyst for Mill92 syngas experiment.
b. 13.5% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.

Table A60

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-19	Mill 94

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
15.5	49.1	23.8	0.8	7,8	0.9	2.1
	(58.0)	(28.2)	(0.9)	(9.3)	(1.1)	(2.5)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.33	0.032	0.039	0.088

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.7	777.7	103.5
[781.6]	[777.6]	[103.4]

4. **COMMENTS:**

a. Activation of catalyst for Mill 95 syngas experiment.
b. 8.8% cobalt reduction after hydrogen treatment.
c. 50 eV pass energy, Al anode.
d. Binding energies referenced to C 1s at 284.6 eV.
e. ( ) Normalized without carbon contribution.
fg. [ ] Referenced to Si 2p.

Table A61

XPS Analysis of As Synthesized Co/X9/X11 TC-123 After Hydrogen Reduction

Sample #	XPS File ID
13168-19	Mill 107

1. **OBJECTIVE:** Determine the surface elemental composition of the catalyst subsequent to hydrogen treatment. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
Hydrogen	350°C	320 PSI	3 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
19.0	44.2	24.7	1.4	7.2	0.9	2.6
	(54.6)	(30.5)	(1.8)	(8.9)	(1.1)	(3.2)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.29	0.059	0.035	0.100

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
782.2	778.1	104.0
[781.6]	[777.5]	[103.4]

4. **COMMENTS:**

a. 16.8% cobalt reduction after hydrogen treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A62

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-19	Mill 84

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	240°C	320 PSI	5 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
30.2	40.8	19.6	1.6	5.1	0.8	1.9
	(58.5)	(28.1)	(2.2)	(7.3)	(1.2)	(2.7)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.26	0.078	0.042	0.096

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.5	777.8	103.4

4. **COMMENTS:**

a. 23.2% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.

Table A63

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-19	Mill 92

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	280°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
31.3	41.2	20.5	1.3	3.2	0.7	1.8
	(59.9)	(29.8)	(2.0)	(4.6)	(1.1)	(2.6)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.15	0.067	0.036	0.088

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	777.9	103.5
[781.5]	[777.8]	[103.4]

4. **COMMENTS:**

a. 30.3% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

Table A64

XPS Analysis of Activated Co/X9/X11 TC-123 After Syngas Reaction

Sample #	XPS File ID
13168-19	Mill 95

1. **OBJECTIVE** Determine the surface elemental composition of the catalyst subsequent to reaction with syngas. Identify the chemical states of the cobalt, X9 and X11 species. Determine the percent of cobalt reduction.

2. **EXPERIMENTAL CONDITIONS:**

Gas	Temperature	Pressure	Time on Stream
50/50 H_2/CO	260°C	320 PSI	6 hrs

3. **XPS RESULTS:**

Relative Atomic Percents

C	O	Si	Co(metal)	Co(oxide)	X9	X11
28.4	43.9	19.4.	0.9	5.1	0.7	1.6
	(61.2)	(27.1)	(1.3)	(7.0)	(1.1)	(2.3)

Elemental Ratios (peak area calculation)

Co(oxide)/Si	Co(metal)/Si	X9/Si	X11/Si
0.26	0.048	0.039	0.084

Corrected Binding Energies (eV)

Co(oxide) 2p3/2	Co(metal) 2p3/2	Si 2p
781.6	777.8	103.5
[781.5]	[777.7]	[103.4]

4. **COMMENTS:**

a. 15.7% cobalt reduction after syngas treatment.
b. 50 eV pass energy, Al anode.
c. Binding energies referenced to C 1s at 284.6 eV.
d. ( ) Normalized without carbon contribution.
e. [ ] Referenced to Si 2p.

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

TABLE OF CONTENTS

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

J. G. Miller, C-L Yang, K. N. Beals

Contents

I. INTRODUCTION

Presented in this report are detailed analyses of the six catalyst runs summarized in Appendix A of the Fourteenth Quarterly Report (Runs No. 98-103).

Four of the catalysts studied were X11, X9 promoted cobalt oxide catalysts intimately contacted with the molecular sieve TC-123 (Run Nos. 98, 99, 100, and 101). Run No. 102 employed gamma-alumina as the support but employed an X11, X9 promoted cobalt oxide catalyst. Run No. 103 was a X11, X9 promoted TC-123 catalyst which used iron oxide as the Fischer-Tropsch active metal catalyst.

Two of the catalysts (used in Run Nos. 98 and 100) were studied to provide additional performance data under various process conditions for the kinetic modeling of the most promising Co/X11/X9/TC-123 catalyst system (Run No. 55, Eighth Quarterly report). Two catalysts (Run Nos. 99 and 101) were studied to provide better long term stability data for this same catalyst system. Run No. 102 was performed to provide additional evidence of the benefits of the TC-123 support over a typical support media such as gamma-alumina. The iron oxide catalyst was tested to evaluate the effect of replacing the cobalt oxide on the TC-123 support.

II. Run No. 99 (13521-04) and Run No. 101 (13521-05)

The purpose of these runs was to extend the understanding of the stability of the Co/X11/X9/TC-123 catalyst used in Run No. 55 reported in the Eighth Quarterly report. These runs were a repeat of Run Nos. 91, 93, and 96, reported on in the Fourteenth Quarterly report, which failed to provide long term stability data (greater than 1000 hours on-stream) due to unexpected shutdowns of the Berty reactor system. Pre-mature shutdowns occurred during the course of these two runs as well. Performance and stability data were obtained for approximately 300 hours of on-stream time at the target conditions of 260 C, 1.5:1 H2:CO, 500 psig, and 300 GHSV.

Both catalysts were prepared using the same method as used for the preparation of the catalyst tested in Run No. 55. The theoretical percentages of Co, X11, and X9 in the catalysts were 8.0, 1.6, and 1.1, respectively.

In general, these catalysts performed very similar to the catalyst tested in Run No. 96 of the Fourteenth Quarterly report. All exhibited a slightly higher syngas conversion and yielded a lighter product than the catalyst tested in Run No. 55. The stability of the catalyst tested in Run No. 55 was measured as a decrease of one percent of conversion activity every 160 to 175 hours over an 800 hour period. Run No. 96 was less stable and exhibited a one percent conversion loss every 88 hours during a 700 hour

run. The data for Run No. 99, which is the best of the two runs, showed a one percent loss in conversion activity every 78 hours over the nearly 200 hours of testing.

As was observed and reported in the last quarterly report, the catalysts prepared to repeat the performance of the catalysts tested in Run No. 55, have all been inferior. However, the catalyst tested in Run No. 96, the longest repeat test completed, did demonstrate an improved stability with time on stream. As stated previously, and repeated here, although the Berty reactor is an excellent medium for studying complex, highly exothermic reactions, the difficulty of performing long term stability tests has proved to be a difficult, at best, and, consequently, long term stability testing should be performed in a larger scale, fixed bed pilot plant reactor.

III. Run No. 102 (13625-01) Co/X11/X9/gamma-alumina

The purpose of this run was to establish a reference benchmark by which the beneficial effects of the molecular sieve support, TC-123, possessed over a classical support, such as gamma-alumina. The primary goal was to establish stability, although conversion and selectivity were also of concern.

The catalyst was prepared in the same fashion as that prepared for Run No. 55, which is the best catalyst developed during this contract, except that gamma-alumina was used as the support in place of the zeolite. The

theoretical percentages of Co, X11, and X9 on the catalyst were 8.0, 1.6, and 1.1, respectively.

It should be noted that a previous preparation of a cobalt catalyst supported on gamma-alumina was reported in the Seventh Quarterly report. However, this catalyst was promoted with X11 and not the X11/X9 combination which has proved so successful. This particular catalyst was also activated in a slightly different manner. Thus, the need to prepare and test this catalyst.

The performance of this catalyst will be compared to that of the catalysts tested in Run No. 55 and Run No. 69 (a repeat of Run No. 55). The performance of these catalysts at 260 C, 500 psig, 1.5:1 H2:CO, and 300 GHSV are tabulated below.

Catalyst	Co/X11/X9	Co/X11/X9	Co/X11/X9
Support	TC-123	TC-123	gamma-alumina
Run Number	55	96	102
Hours on stream (260 C)	960	504	304
Conversion (CO+H2) %	77.0	75.1	65.1
CH4, %	10.0	14.4	15.6
C5-420 F, %	36.1	38.9	38.3
420-700 F, %	24.3	22.8	23.6
700 F +, %	18.6	12.8	10.7
C5 +, %	79.0	74.5	72.6
C4, olefin/paraffin	1.03	0.87	1.23
Stability, hours/% loss	168	102 *	56

* After an initial deactivation period (169 hours) at 260 C, 500 psig, 1.5:1 H2:CO, and 300 GHSV

A comparison of the activities shows the gamma-alumina supported catalyst to have about 10 % less than that of the zeolite supported catalysts in terms of % conversion. Product selectivity for the gamma-alumina catalyst was towards the lighter products although similar to that observed for Run No. 96. A significant factor effecting the selectivity of the performance of the catalyst tested in Run No. 102 was the lower initial activity which would favor a lighter product when tested under these conditions in the Berty reactor system.

The most significant difference between the performance of the gamma-alumina and TC-123 supported catalysts was their relative stability. The gamma-alumina catalyst deactivated much faster than the TC-123 supported material. The stability numbers were based upon a linear least squares estimate of the conversion loss with time on stream. The number presented represents the number of hours required to lose one percent (1 %) of conversion activity. The discrepancy between the numbers obtained on the zeolite supported catalysts is not clear. The stability of the catalyst tested in Run No. 96 was significantly less than that of the catalyst tested in Run No. 55, although the former was demonstrating continued improvement with time on stream. The gamma-alumina

supported catalyst was found to be significantly less stable than either zeolite supported catalyst.

This test succeeded in demonstrating the impact upon stability of the TC-123 support upon a promoted cobalt catalyst versus a conventional support such as gamma-alumina. A small difference is observed for product selectivity as well, however, the main impact is upon activity and stability, at least at this level of cobalt metal loading.

IV. Run No. 103 (13521-06) Fe/TC-123

The purpose of this run was to determine the effect of the Union Carbide zeolite support (TC-123) upon the performance of an iron oxide Fischer-Tropsch catalyst.

This iron oxide catalyst was prepared by the same method used to prepare the catalyst for Run No. 68 (Tenth Quarterly report), which was a Co/X11/X9/TC-123 catalyst, wherein the Fischer-Tropsch metal was formed in close contact with the TC-123. The percentage of iron on the catalyst was 7.9 %.

The activation procedure employed was that developed in the previous contract (DE-ACT22-81PC40077), shown below.

Step	Gas rate cc/min.	Pressure psig	Temperature C	Time hrs.
1	1000 N2	65	ramp 20 - 270	17
2	1200/450CO	65	270	24
3	2000 H2	15	270	24
4	400 H2	300	270-250	4

The catalyst was run under the conditions of 250 C, 300 psig, 1:1 H2:CO, and 300 GHSV. A comparison of the iron catalyst with that of the Co/X11/X9/TC-123 catalyst in Run No. 68 under similar conditions is shown below. The nominal (planned) percent of Co, X11, X9 present in the catalyst was 8.2, 1.6, and 1.1 % respectively. An equivalent molar quantity of Co for Fe atoms was present for this test.

Catalyst	Co/X11/X9/TC-123	Fe/TC-123
Temperature, C	240	250
Conversion, (CO+H2)	46.3	23.2
CH4, %	2.4	15.7
C5 +, %	89.8	33.6
C4, olefin/paraffin	3.75	3.9

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

As expected, the activity of the Fe catalyst was significantly lower than that of the cobalt catalyst. Even at a 10 C higher temperature, the iron catalyst showed only half of the activity of the cobalt catalyst.

The selectivity of the iron catalyst yielded a much lighter product, including a large amount of methane. Some of this could be attributed to the higher reaction temperature, however, similar cobalt catalysts would be expected to yield 75 to 80 % of C5 + product in the 260 C range of operating temperature.

The olefin content of the product demonstrated the high olefin content typical of iron catalyzed Fischer-

Tropsch reactions. The cobalt catalyst exhibits a similarly attractive ratio, however, this is also enhanced by the lower operating temperature.

The iron catalyst appeared to be fairly stable over the modest time period tested. This may be due to a contribution of the TC-123 component on stability as was observed for the cobalt systems. Overall, this catalyst performed inferior to the identified cobalt system. Further improvements in additives may prove to be helpful, however, the activity of the iron based catalysts compared to the cobalt based materials may significantly affect the selection of the Fischer-Tropsch metal component.

V. Summary

The work reported during this quarter was aimed at broadening the understanding and improving the performance of the catalyst formulation utilized in Run No. 55 (Co/X11/X9/TC-123) which was reported in the Eighth Quarterly report.

The studies were to:

1. Obtain performance data under a variety of process conditions to provide for the kinetic modeling of the process.
2. Improve the estimates of the long term stability of the Co/X11/X9/TC-123 system
3. Provide data for a catalyst utilizing a conventional support such as gamma-alumina for comparison with the TC-123 based material.

4. Evaluate the substitution of iron for cobalt as the Fischer-Tropsch component in the TC-123 supported system.

The two runs made to extend and confirm the stability data of the Co/X11/X9/TC-123 catalysts were unsuccessful due to premature termination of the test runs. From the data obtained over a modest period of time, the catalysts tested and reported here exhibited inferior stability when compared to the catalyst prepared and tested in Run No.55. It has been concluded that further long term stability tests may ultimately be necessary, if warranted, to determine catalyst life.

The results of tests comparing gamma-alumina with TC-123 as a catalyst support demonstrated the beneficial effects of the zeolite support. Both an increased activity and stability were observed for the zeolite based material.

The use of iron oxide in place of the cobalt oxide component of the TC-123 promoted catalyst, showed the iron oxide to be inferior in terms of activity and to also yield a larger amount of lighter products, including methane. The stability of the iron oxide catalyst appeared similar to that of the cobalt based material, although it was run for only a short period of time.

Figure B1

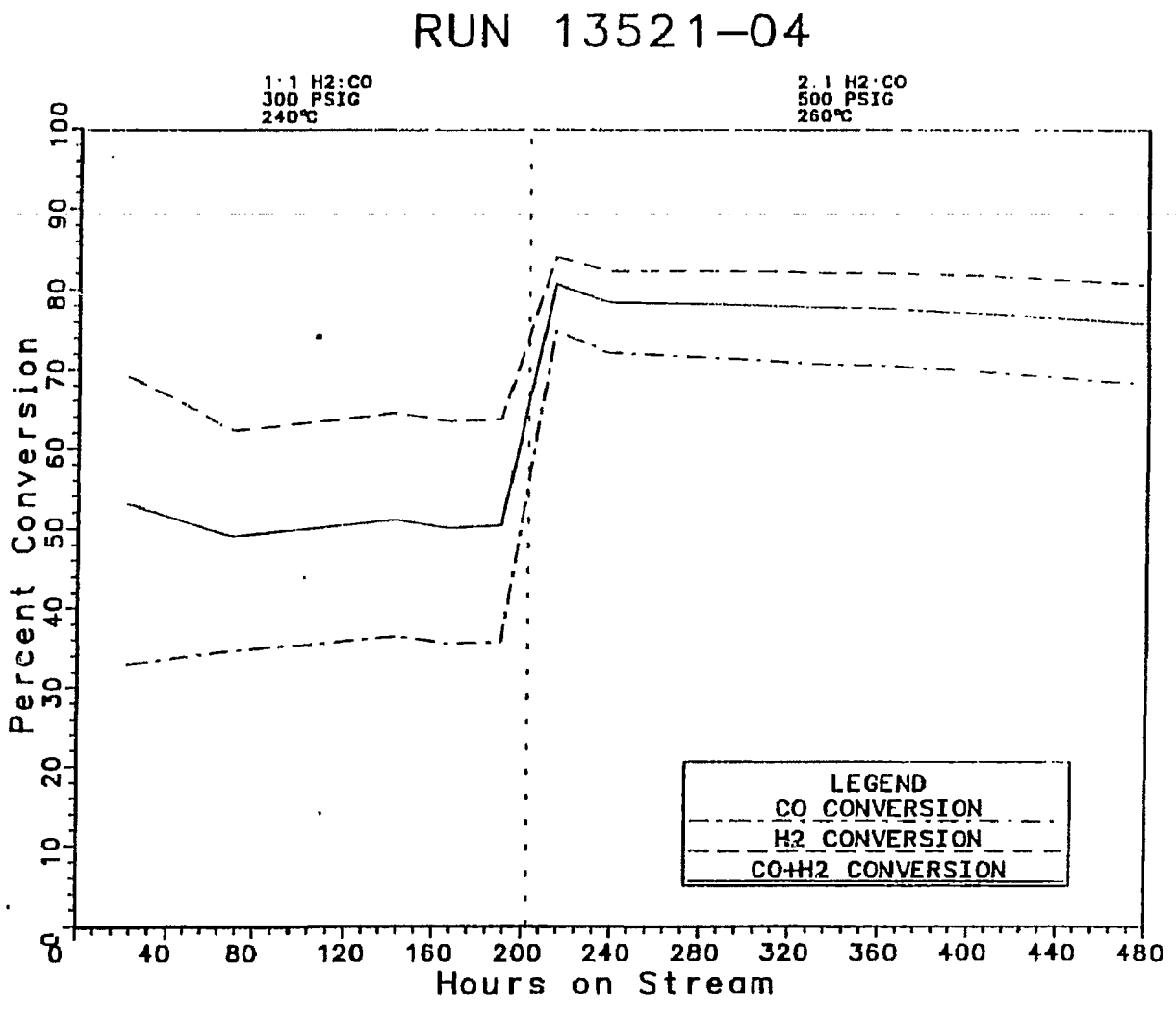

RUN 13521-04
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440
480
Hours on Stream
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION

Figure B2

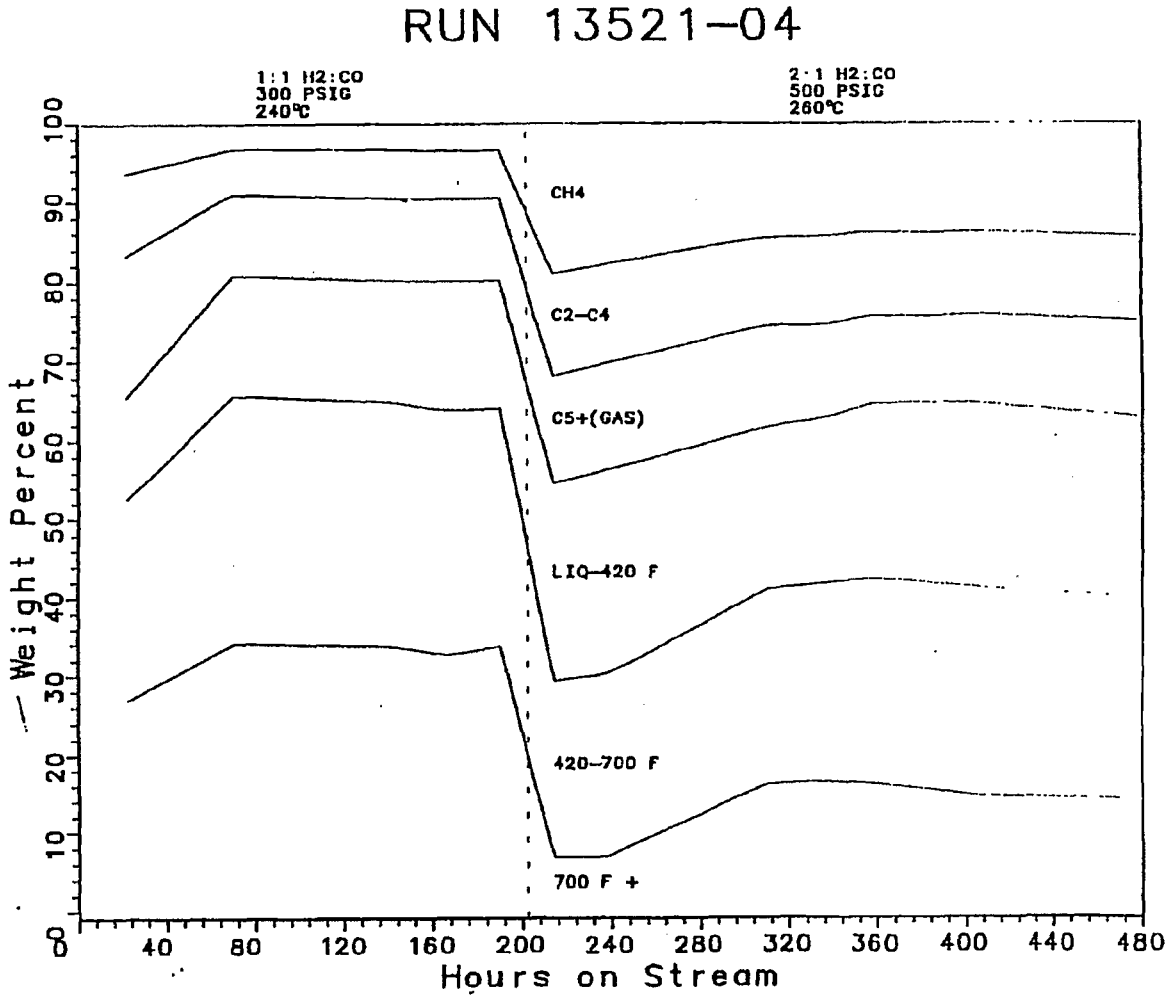

RUN 13521-04
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
40
80
120
160
200
240
280
320
360
400
440
480

Figure B3

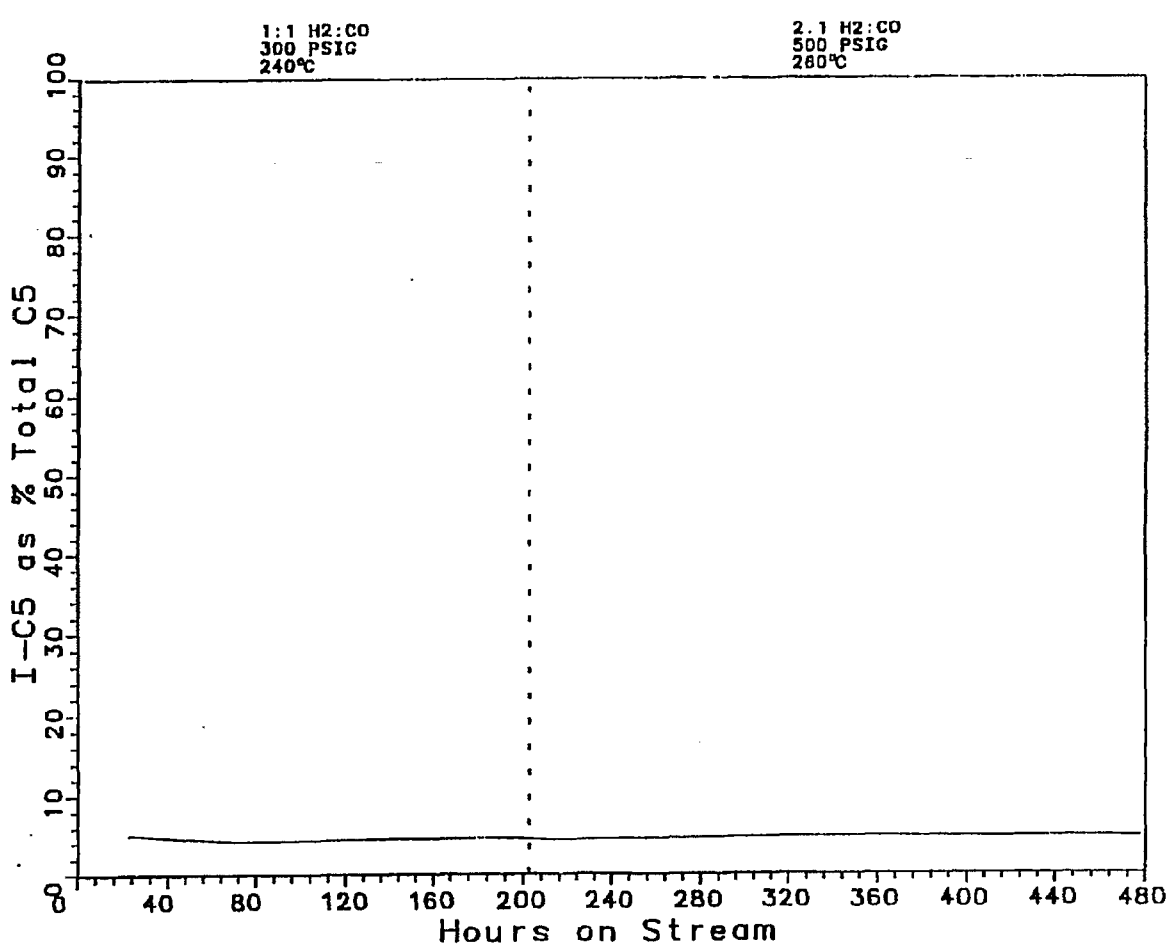

RUN 13521-04
1:1 H2:CO
300 PSIG
240°C
2.1 H2:CO
500 PSIG
280°C
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440
480
Hours on Stream

Figure E4

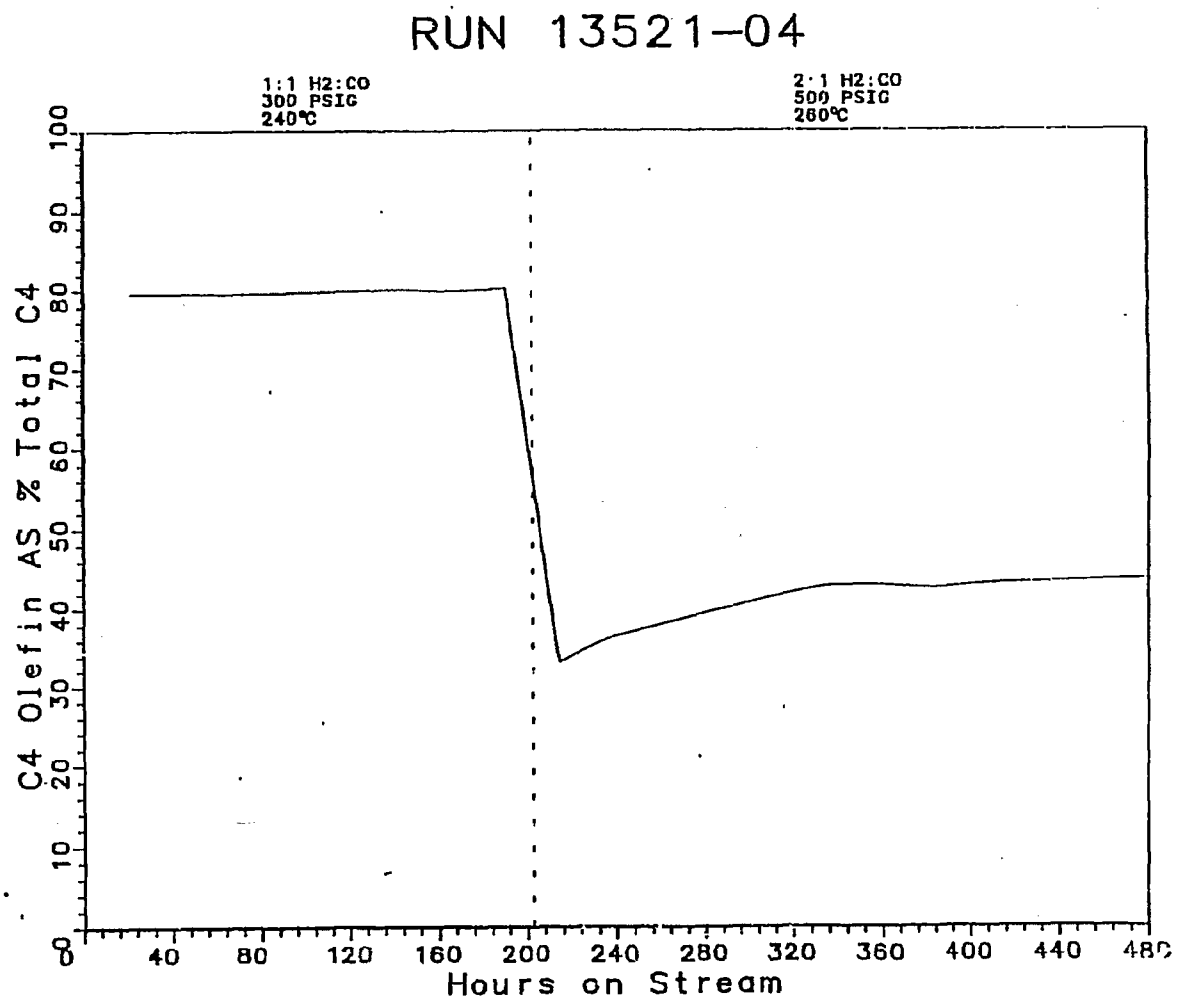

RUN 13521-04
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
280°C
C4 Olefin AS % Total C4
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440
480
Hours on Stream

Figure 35

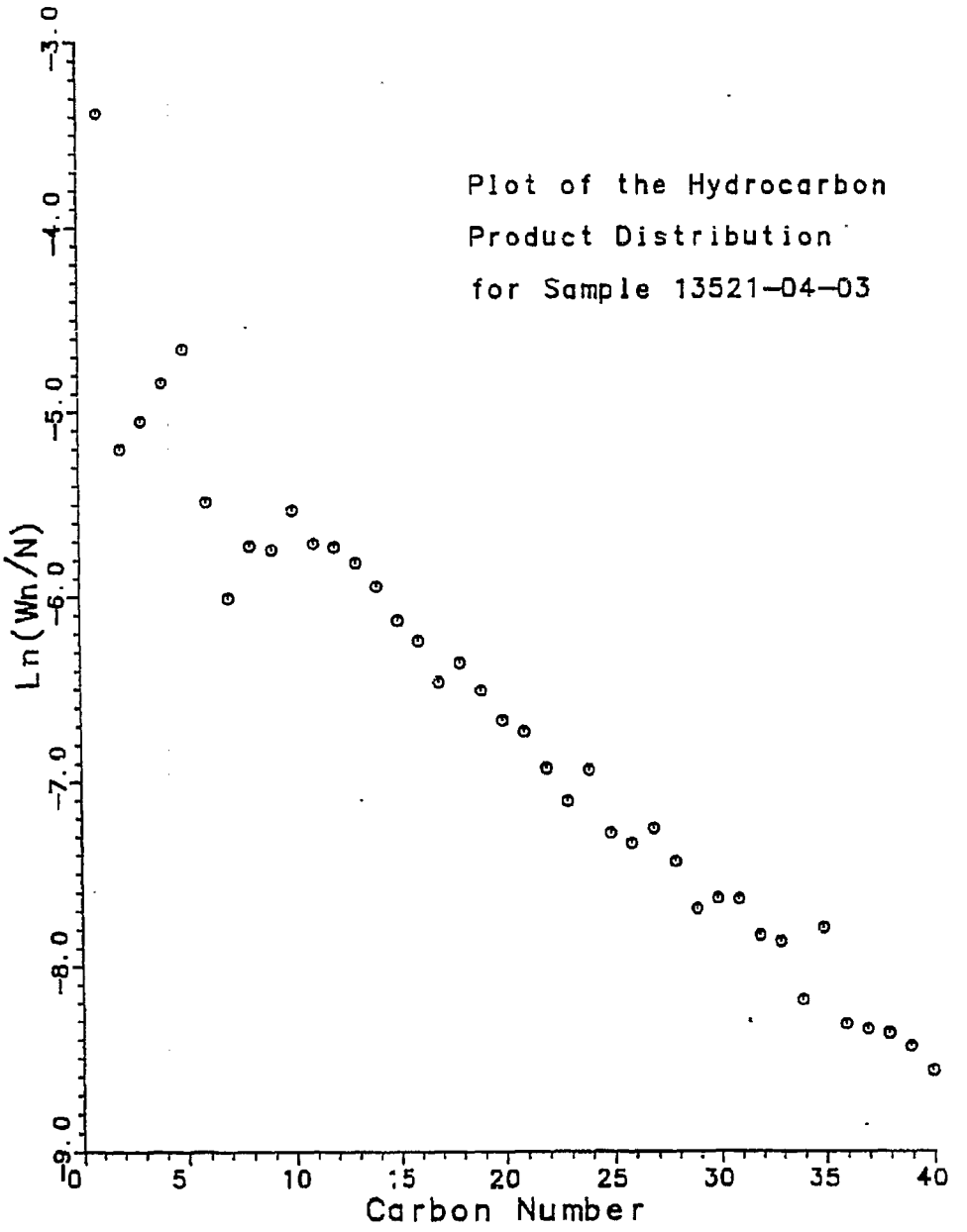

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-04-03
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure 36

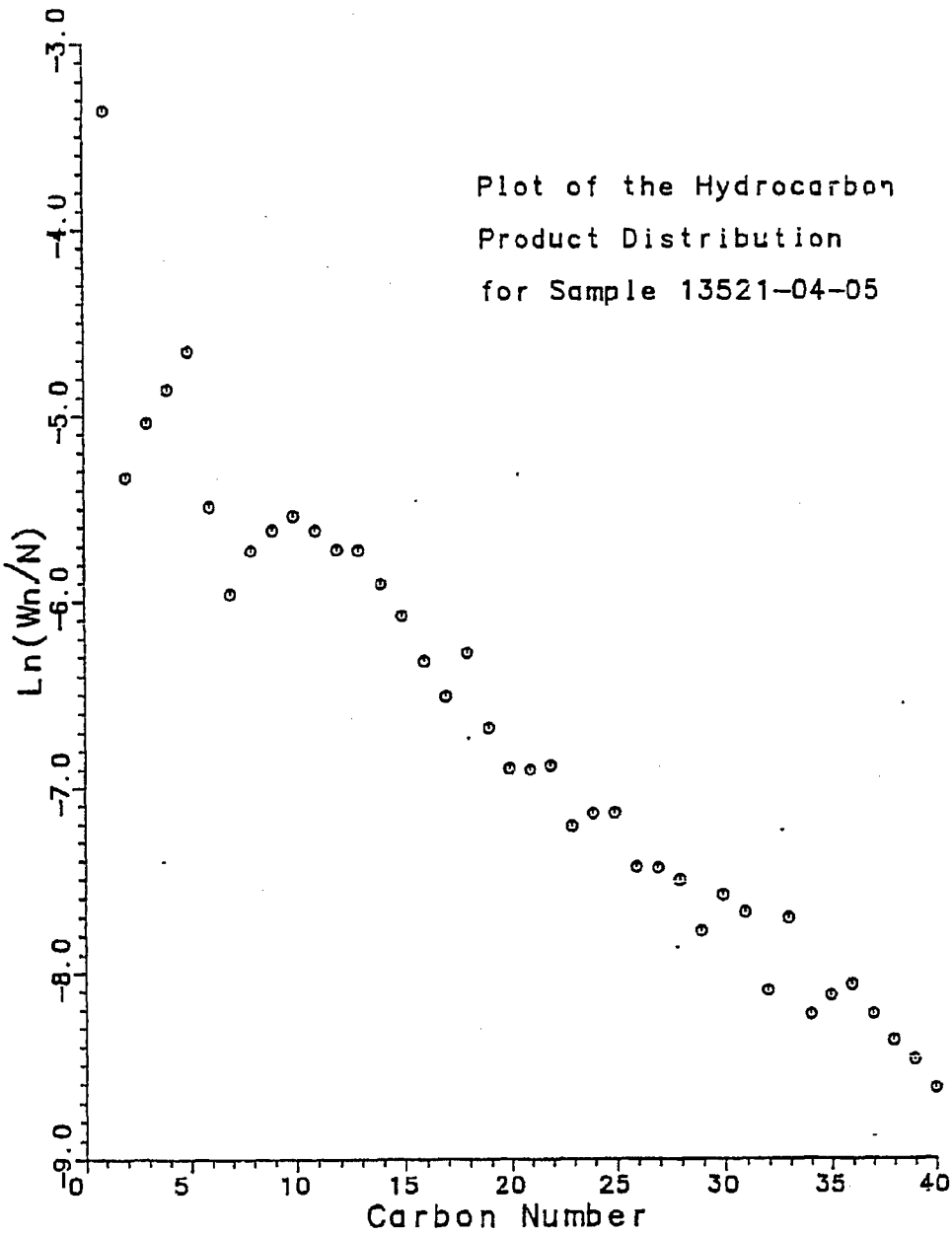

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-04-05
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure 37

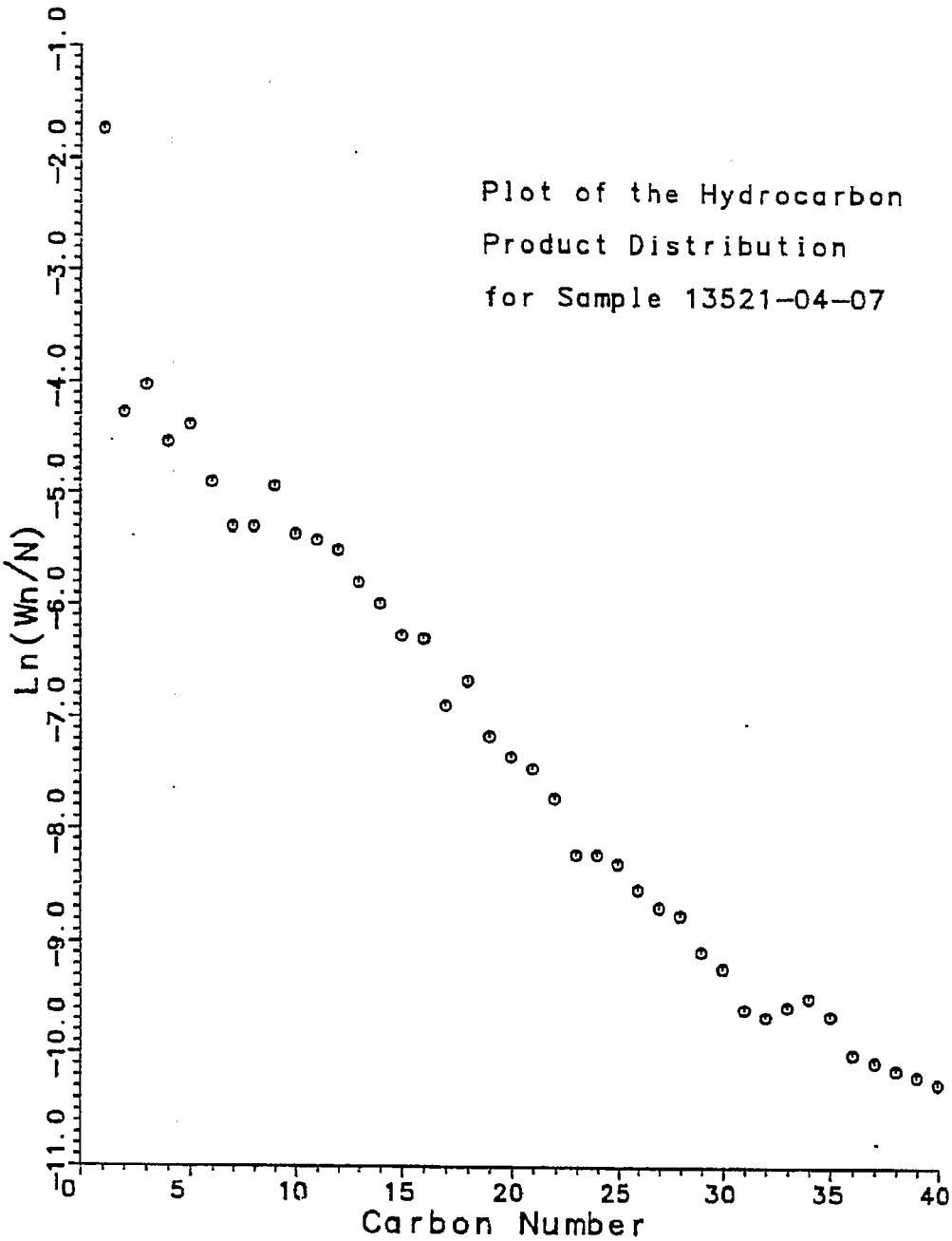

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-04-07
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B8

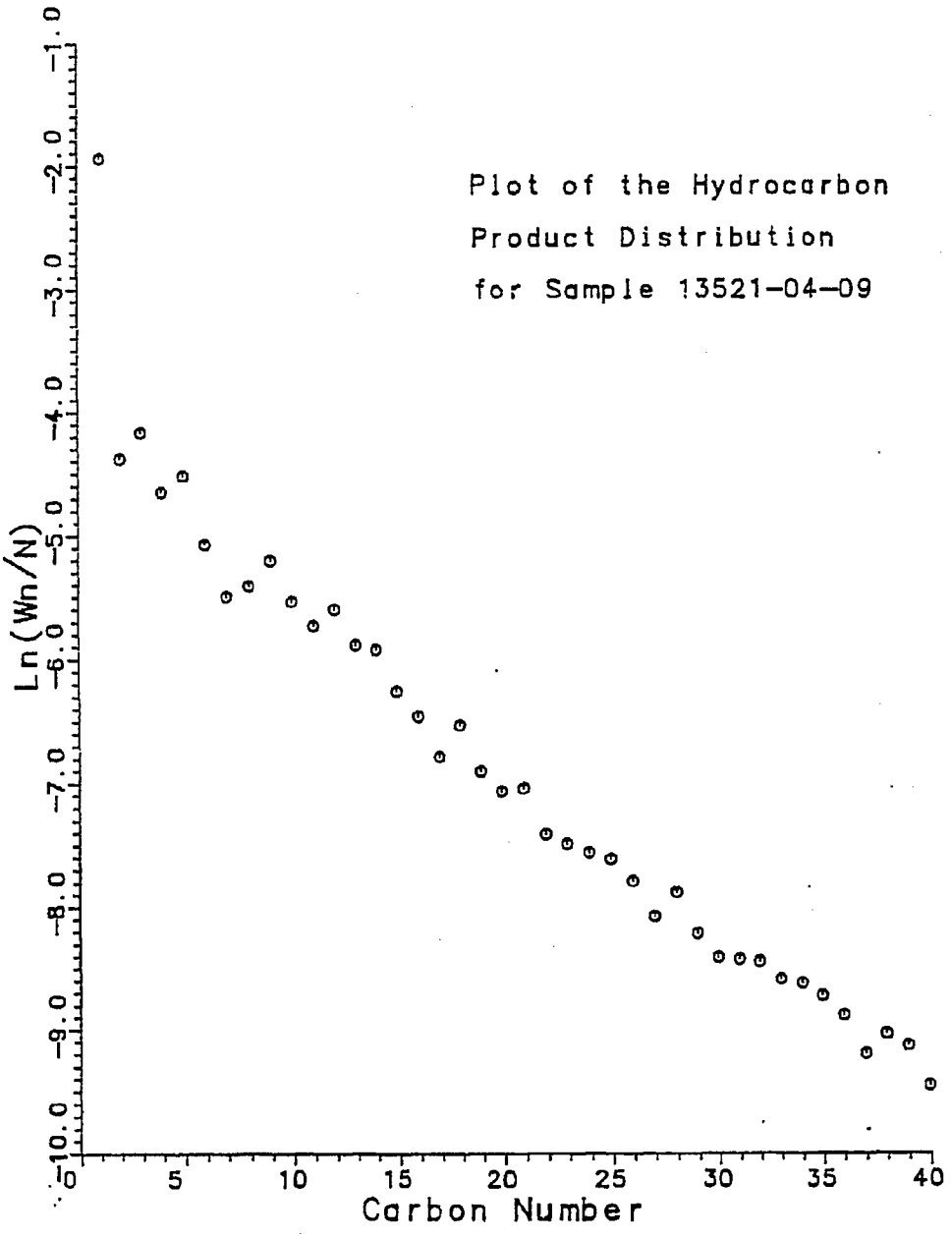

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-04-09
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B9

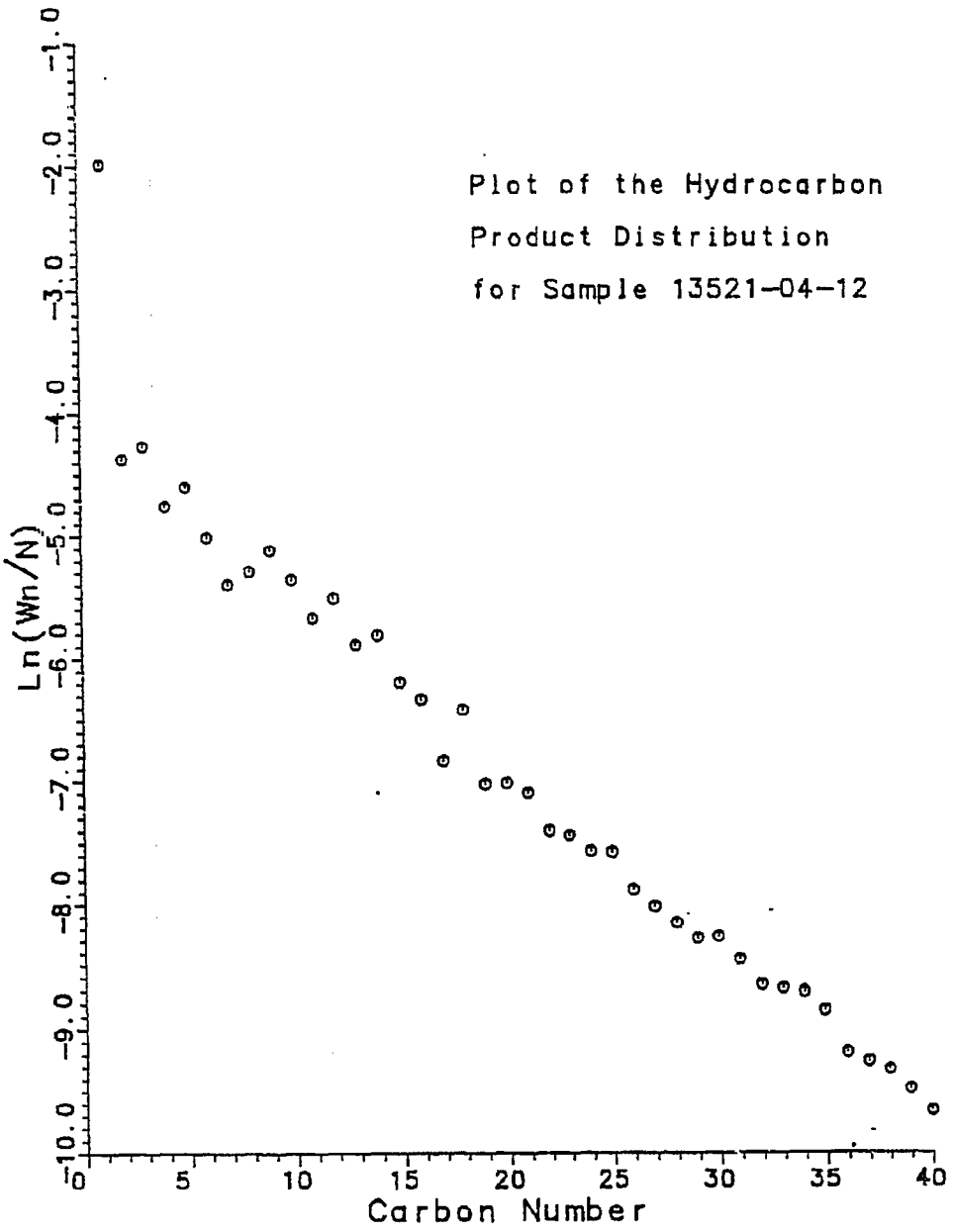

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-04-12
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B10

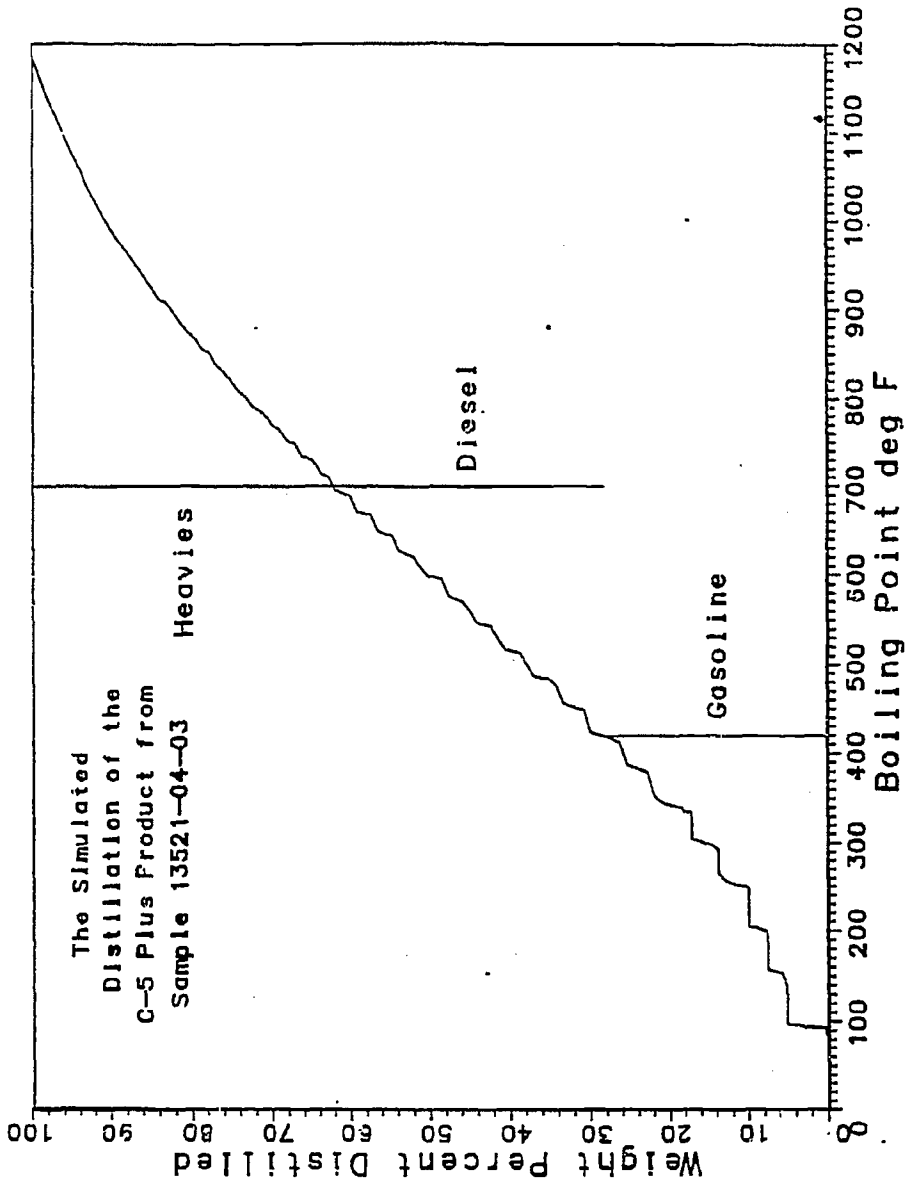

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-04-03
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B11

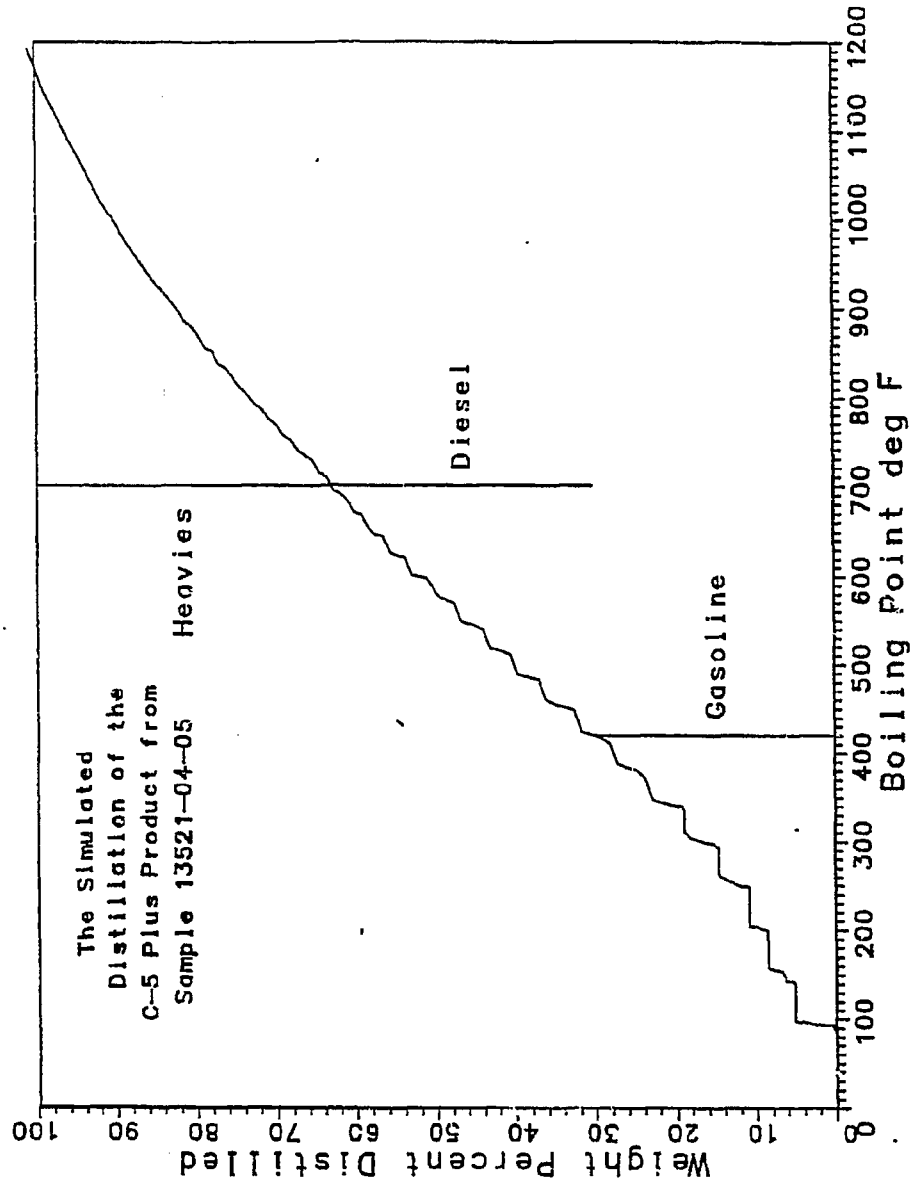

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-04-05
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B12

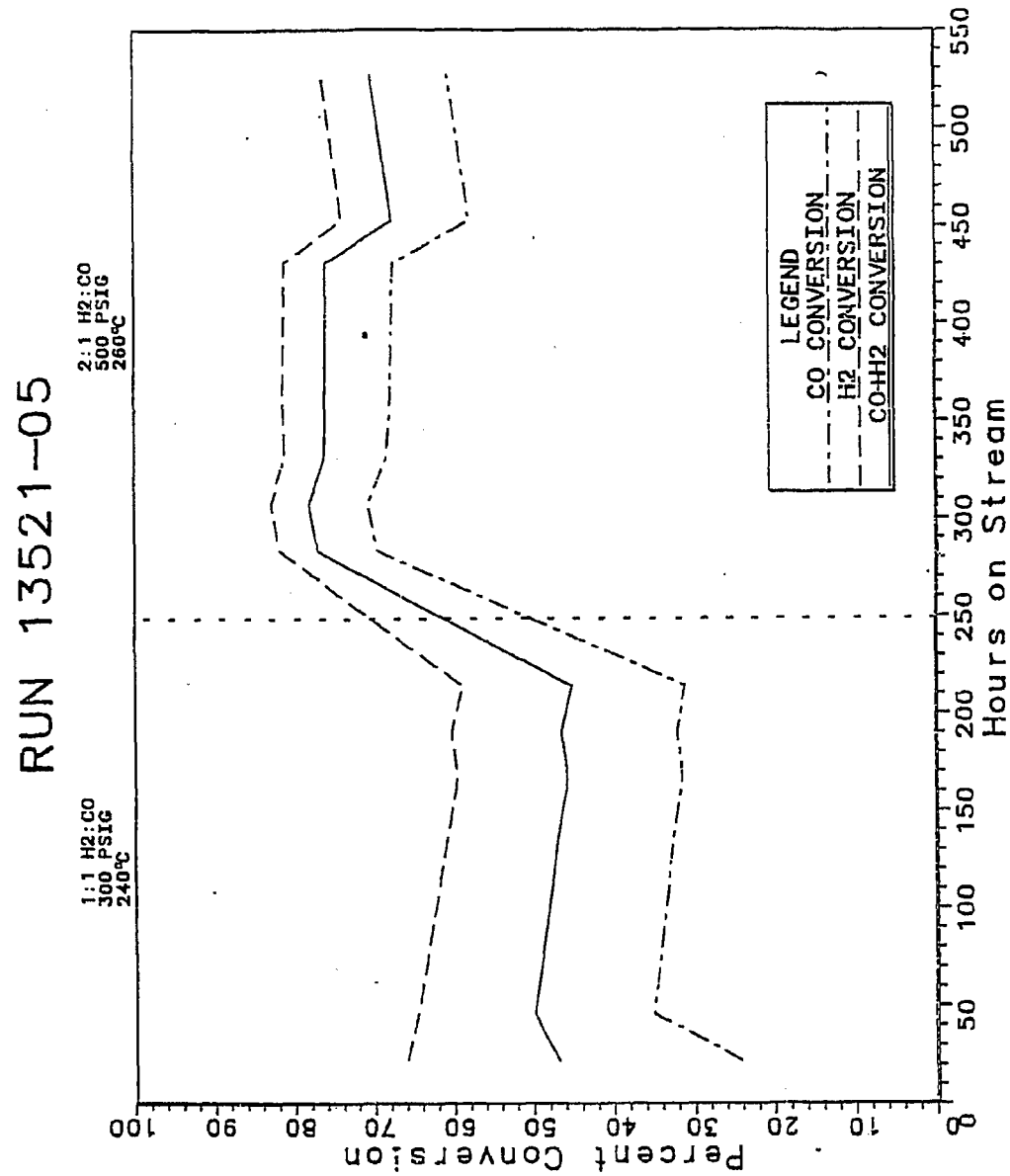

RUN 13521-05
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550

Figure 313

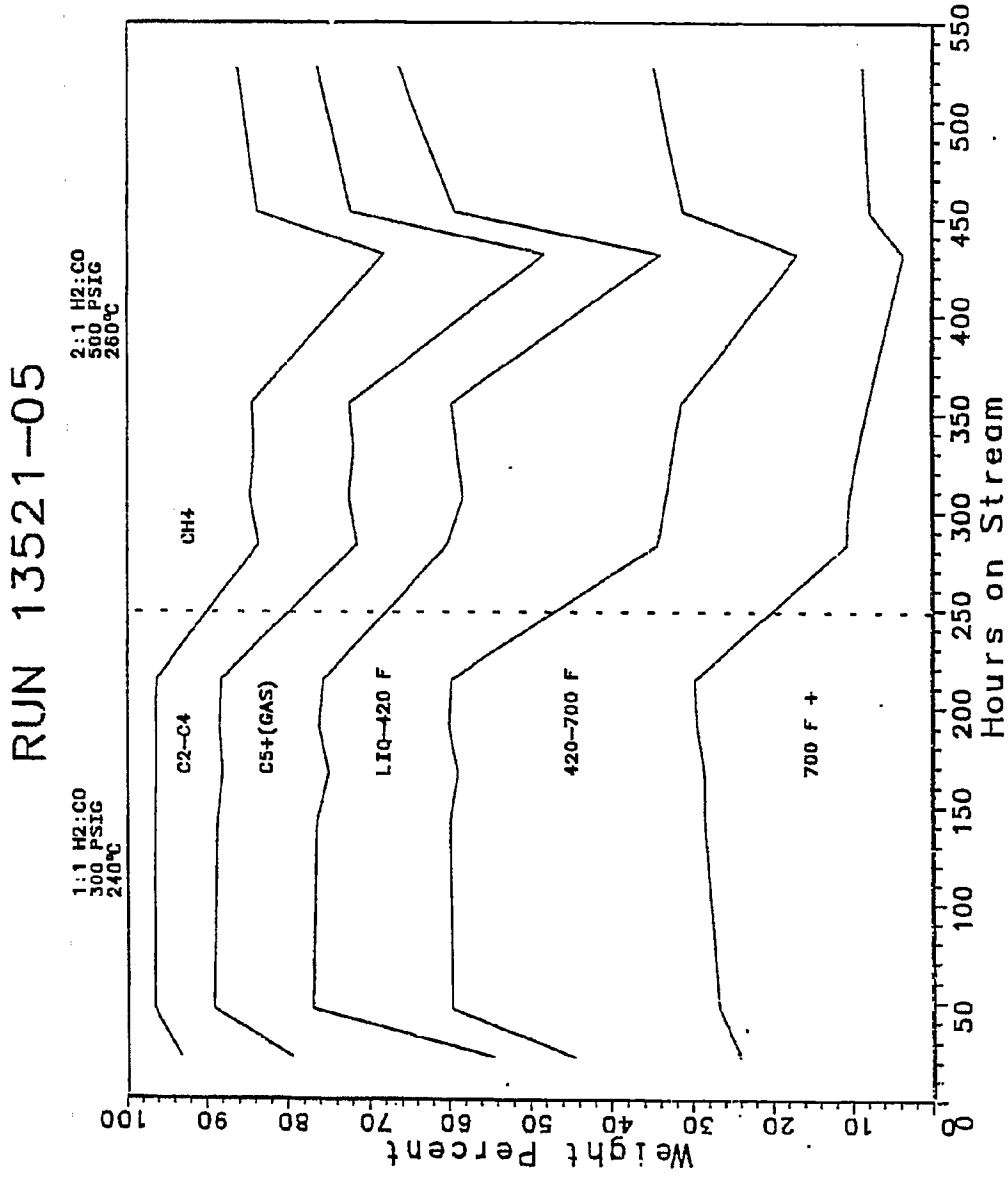

RUN 13521-05
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350
400
450
500
550

Figure B14

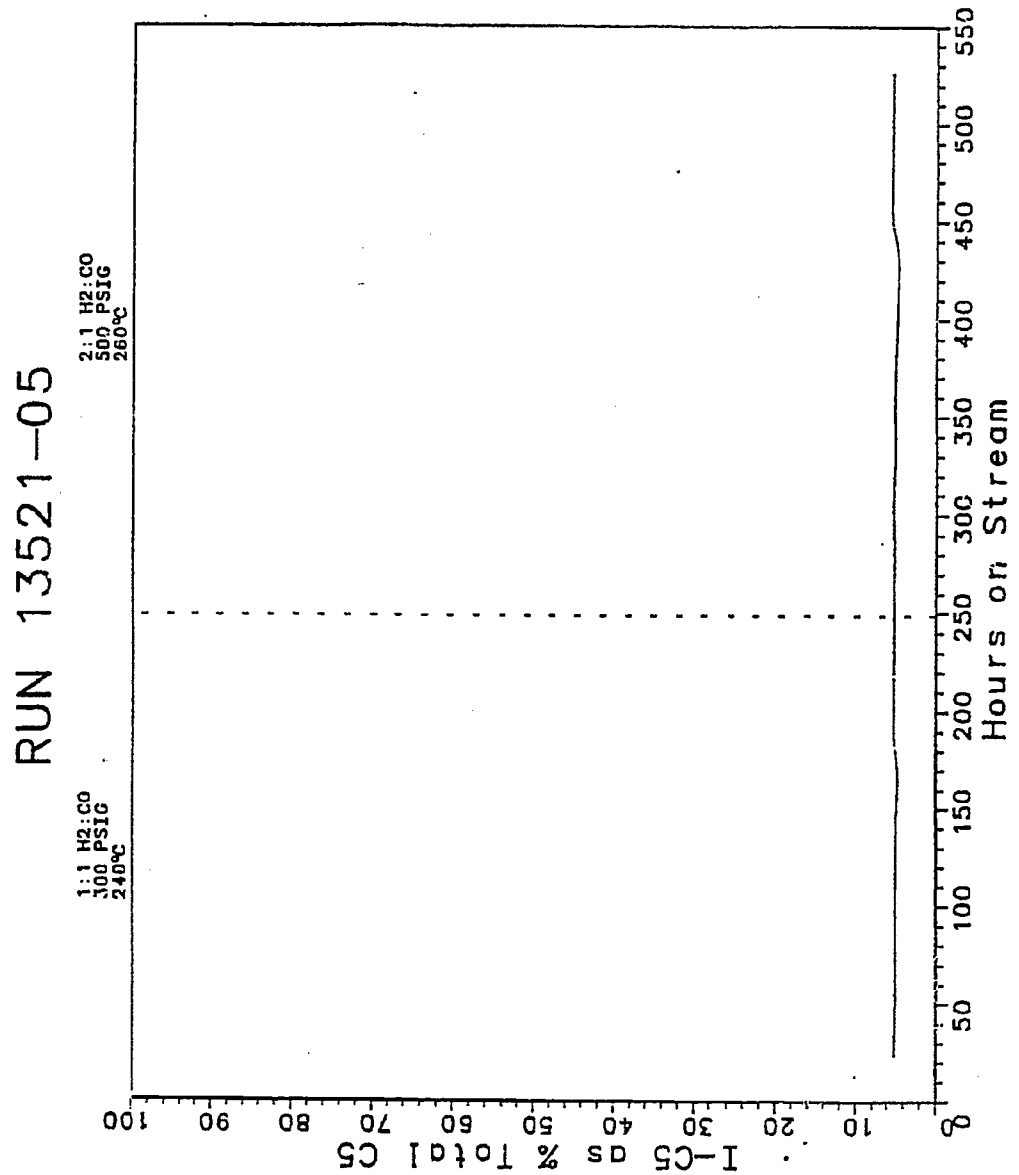

RUN 13521-05
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
I-C5 as % total C5
Hours on Stream
0
50
100
150
200
250
300
350
400
450
500
550
10
20
30
40
50
60
70
80
90
100

Figure B15

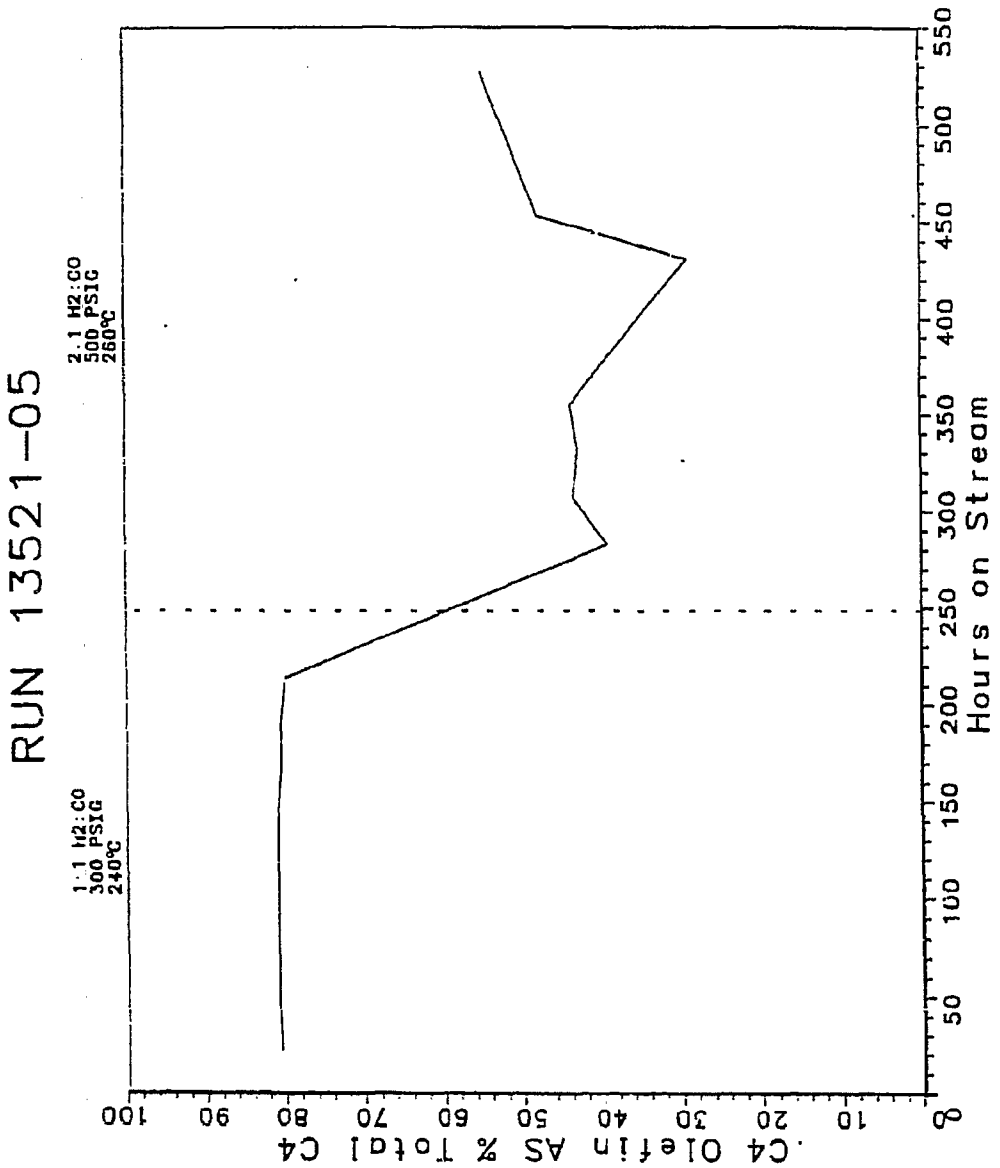

RUN 13521-05
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
C4 Olefin AS % Total C4
Hours on Stream
0
50
100
150
200
250
300
350
400
450
500
550
10
20
30
40
50
60
70
80
90
100

Figure B16

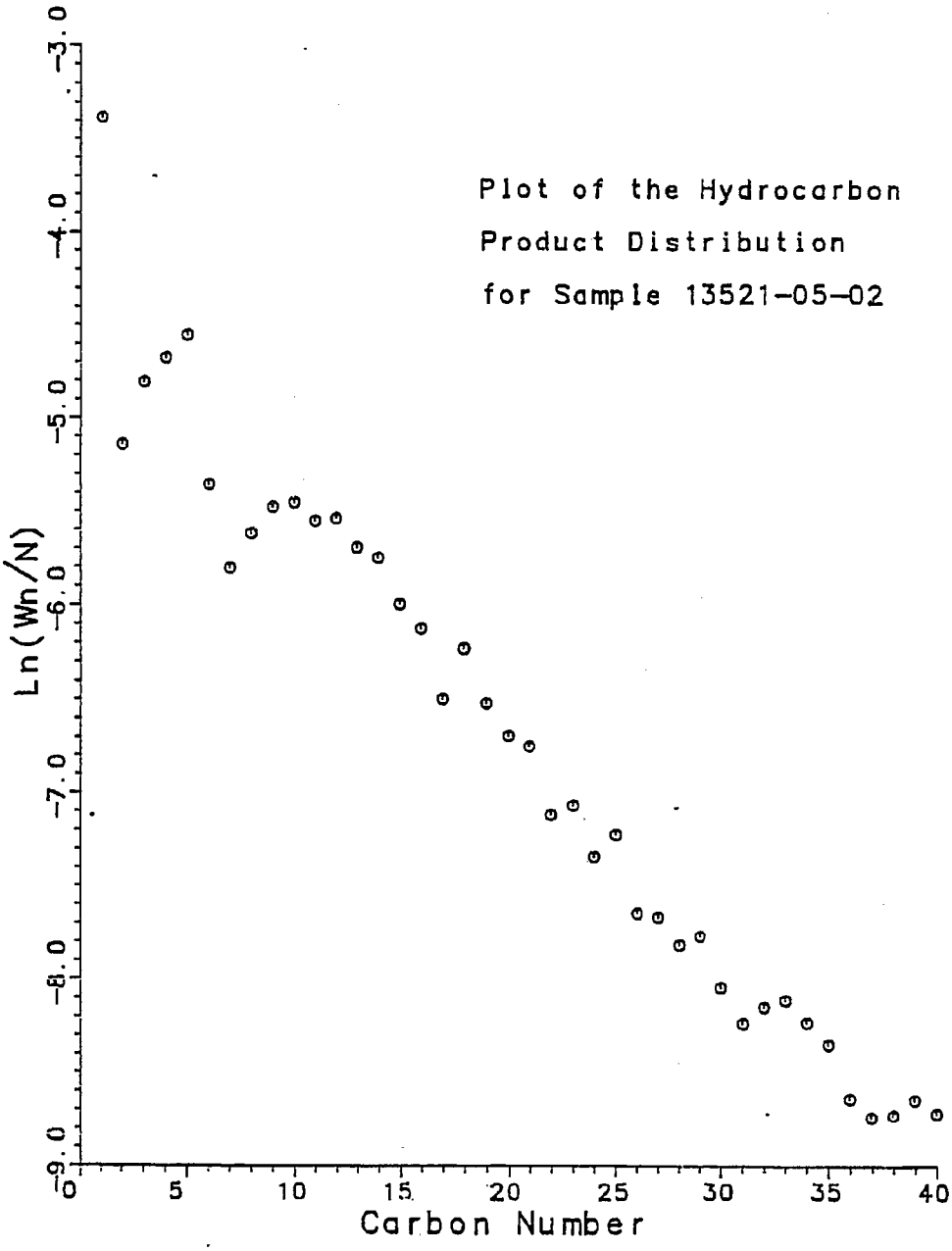

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-05-02
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B17

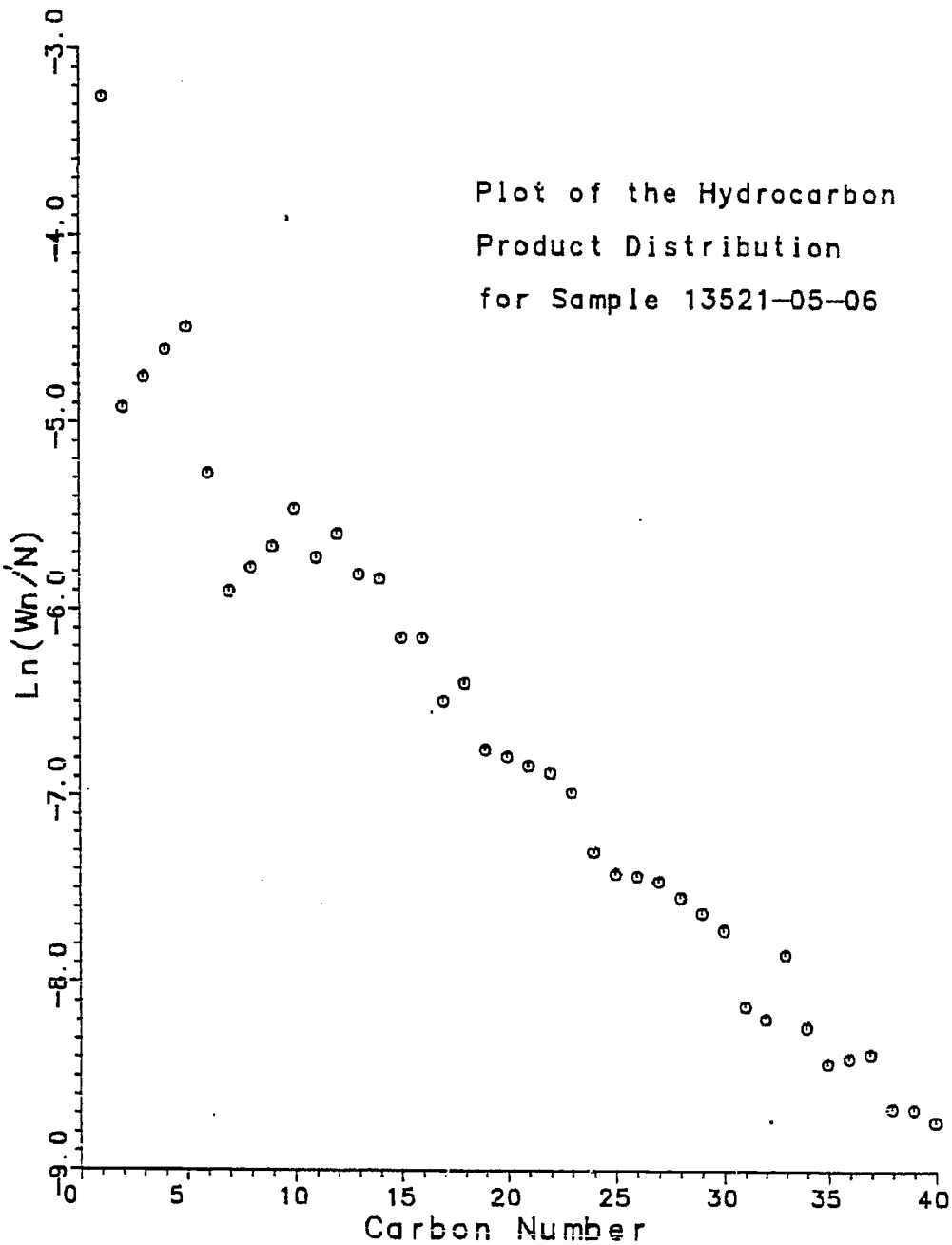

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-05-06
Ln(Wn/N)
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B13

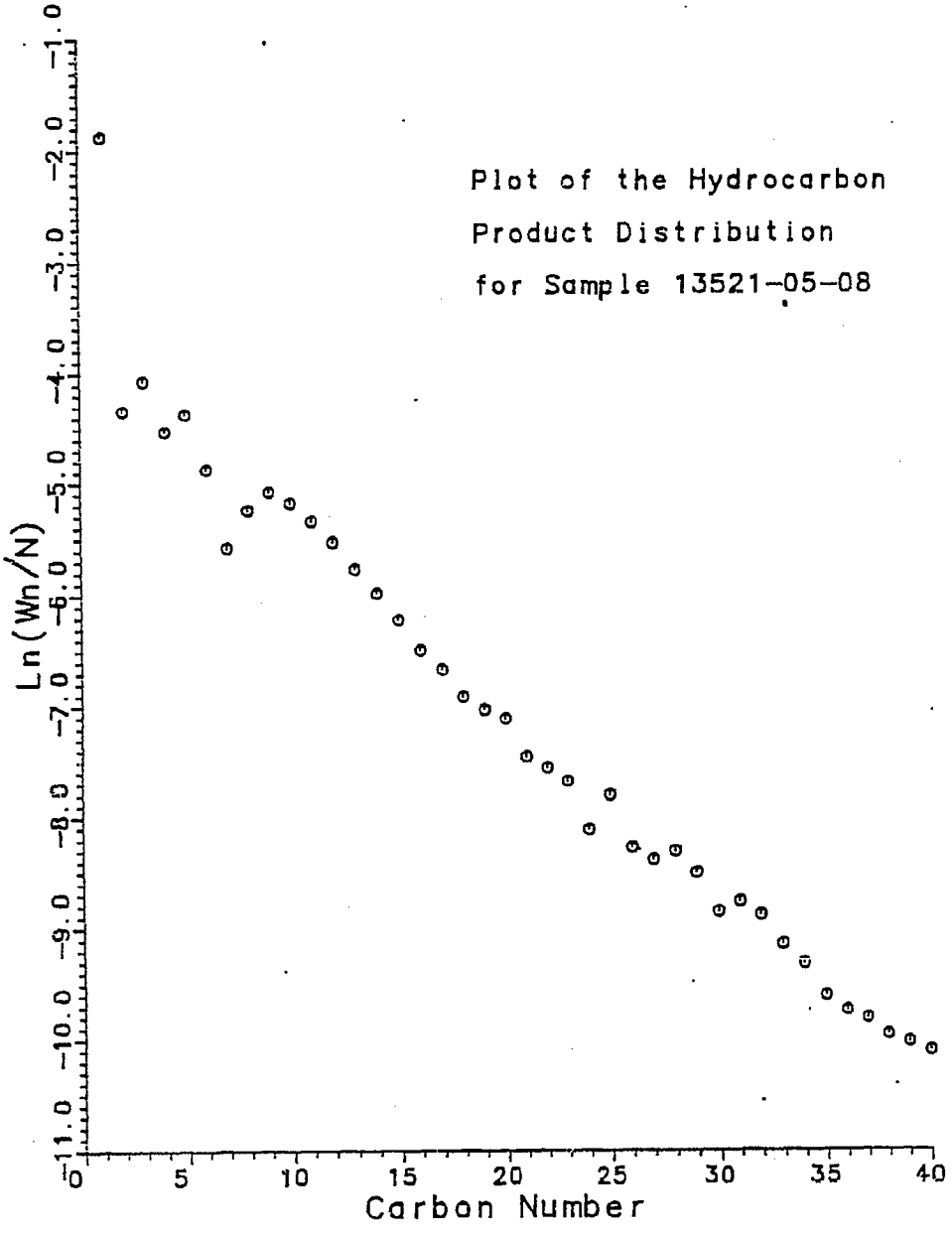

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-05-08
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B19

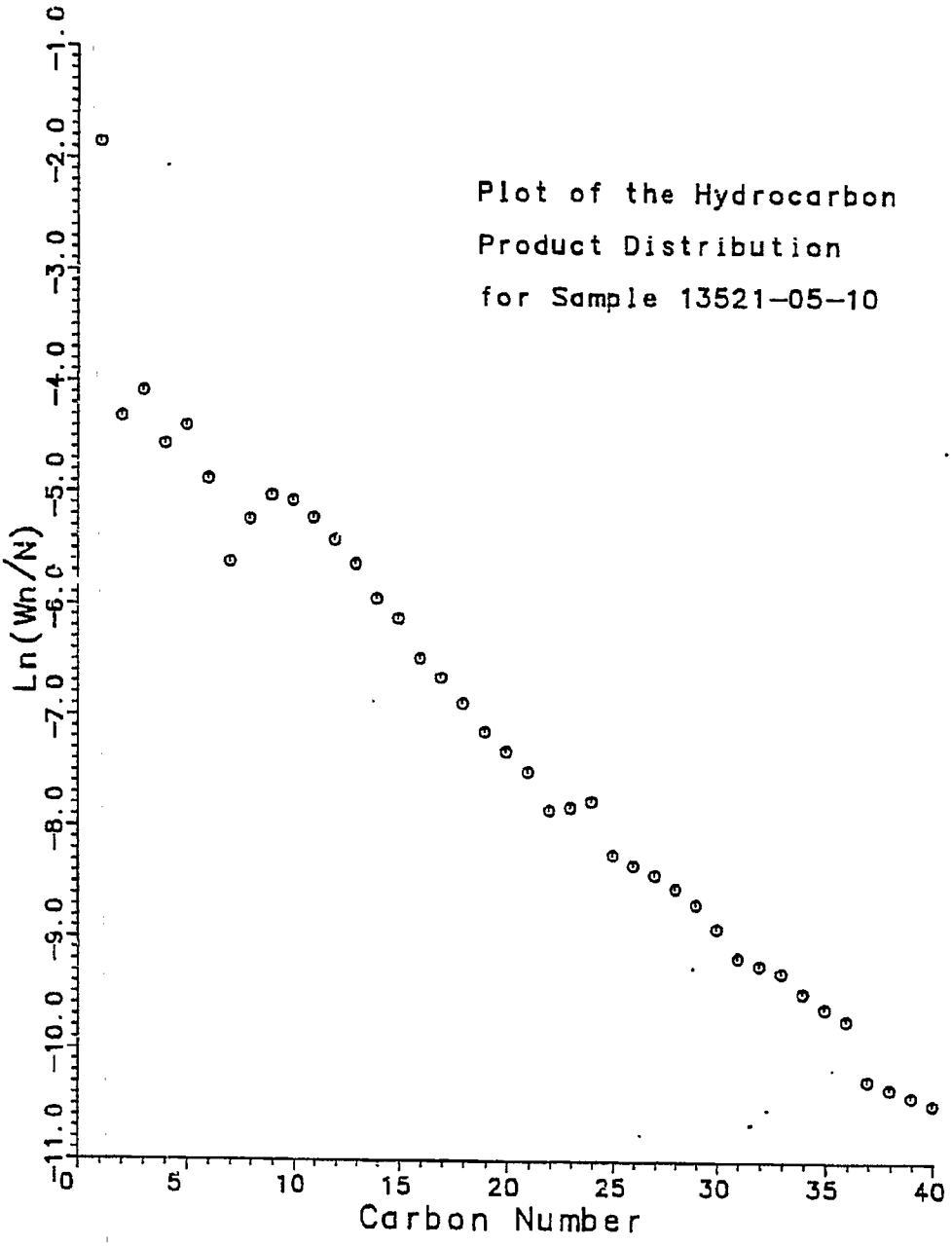

Plot of the Hydrocarbon
Product Distribution
for Sample 13521-05-10
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B20

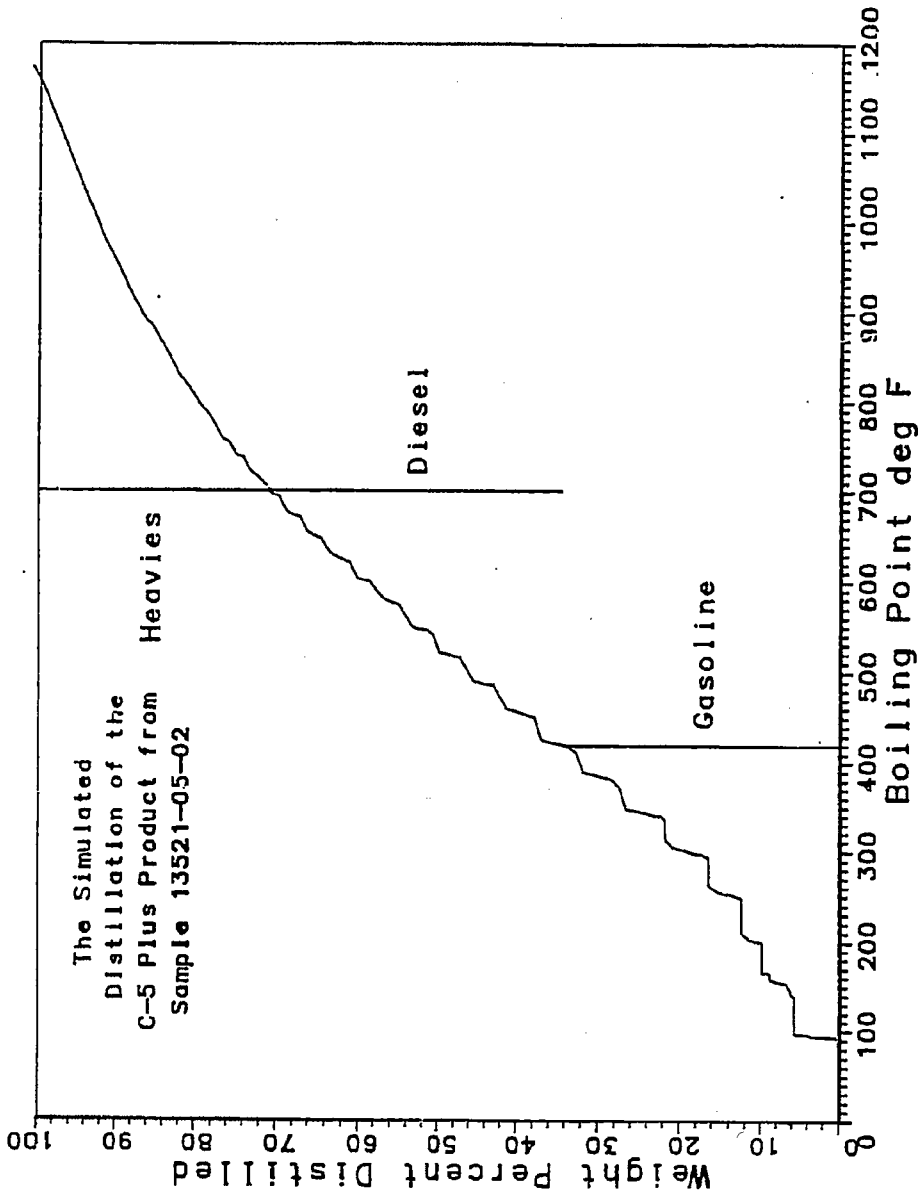

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-05-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B21

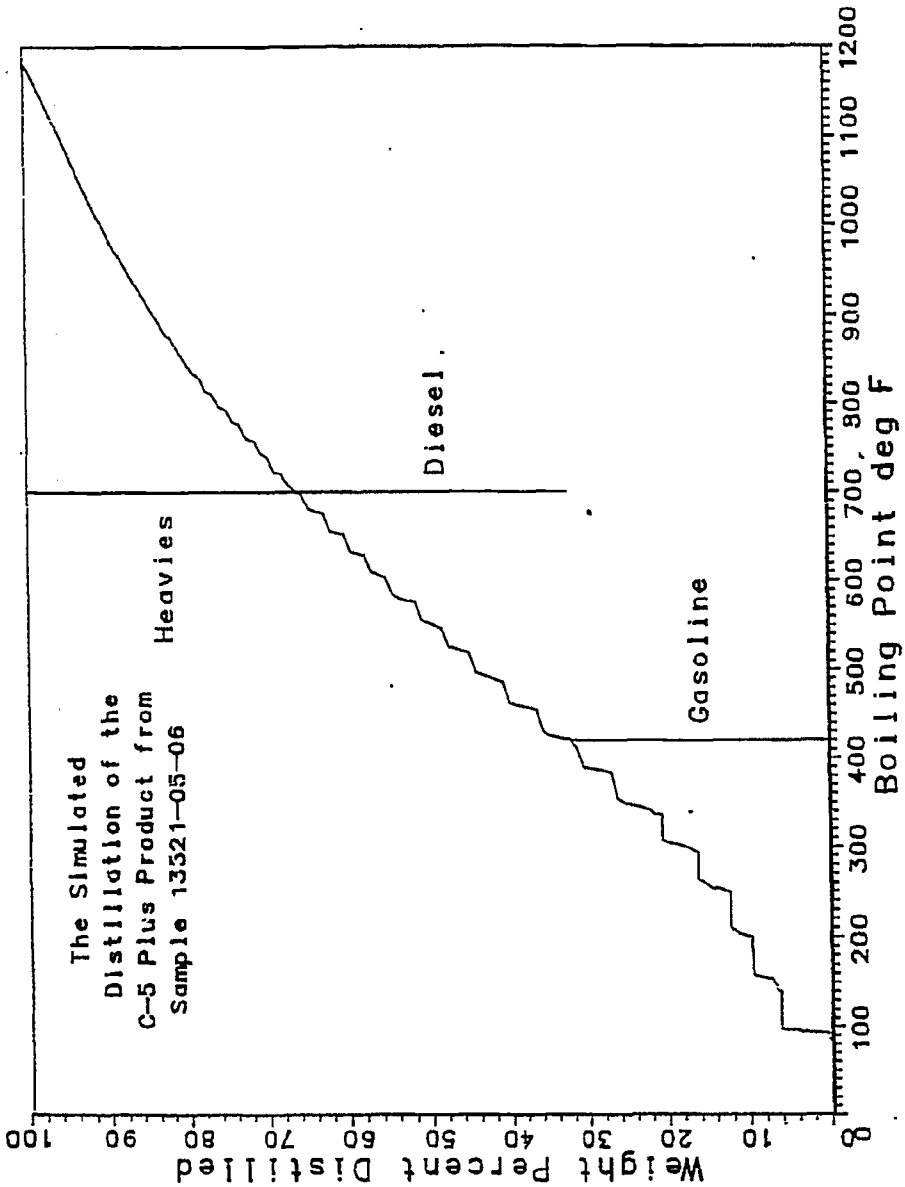

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-05-06
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B22

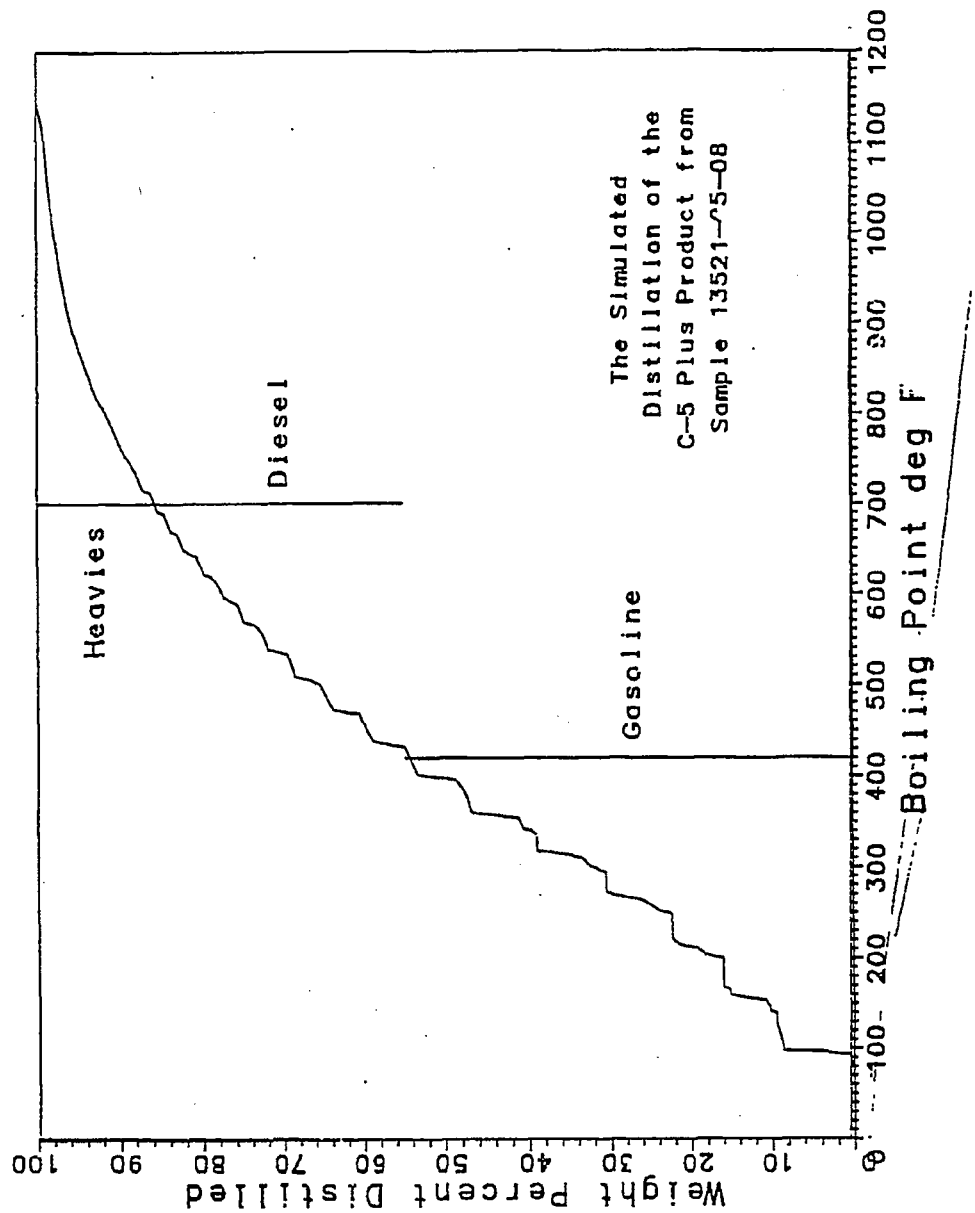

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-05-08
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
10
20
30
40
50
60
70
80
90
100

Figure B23

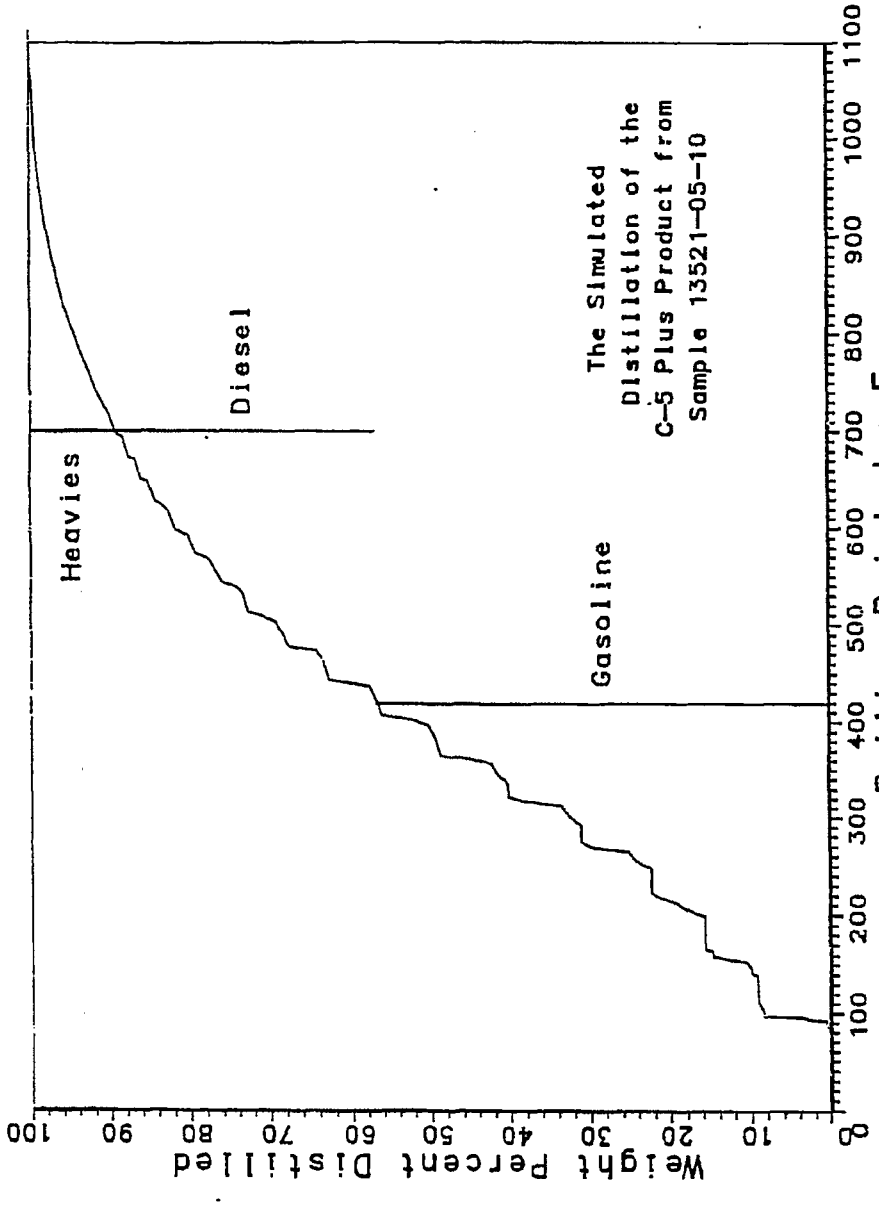
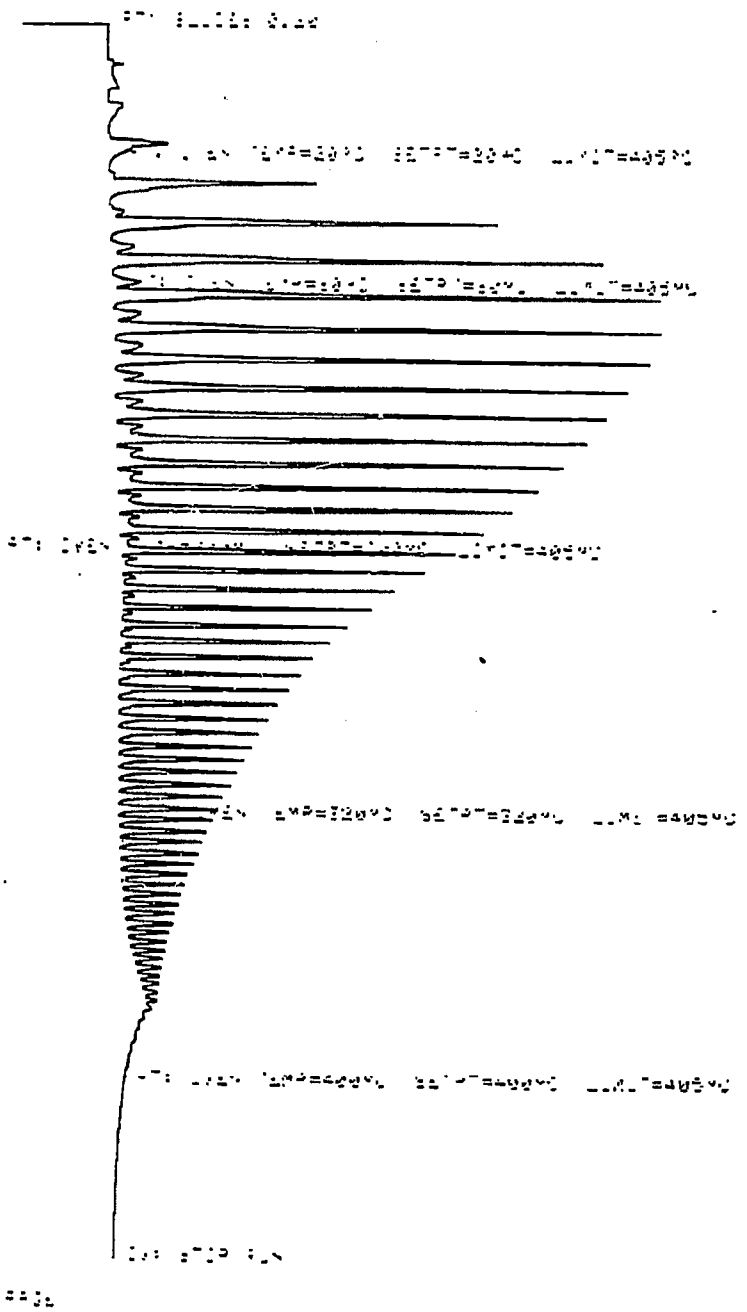

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13521-05-10
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100

Figure 324



12521-05-02

Figure B25

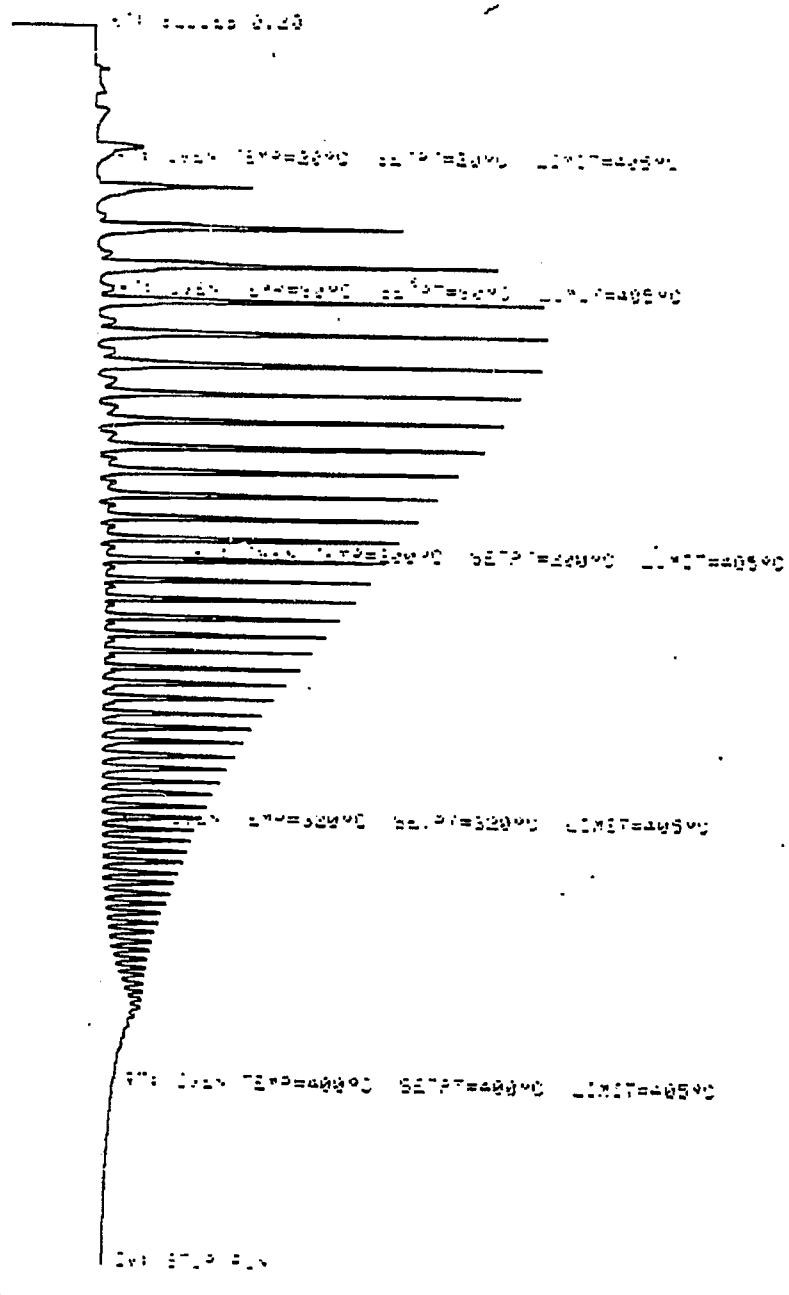


Figure 326

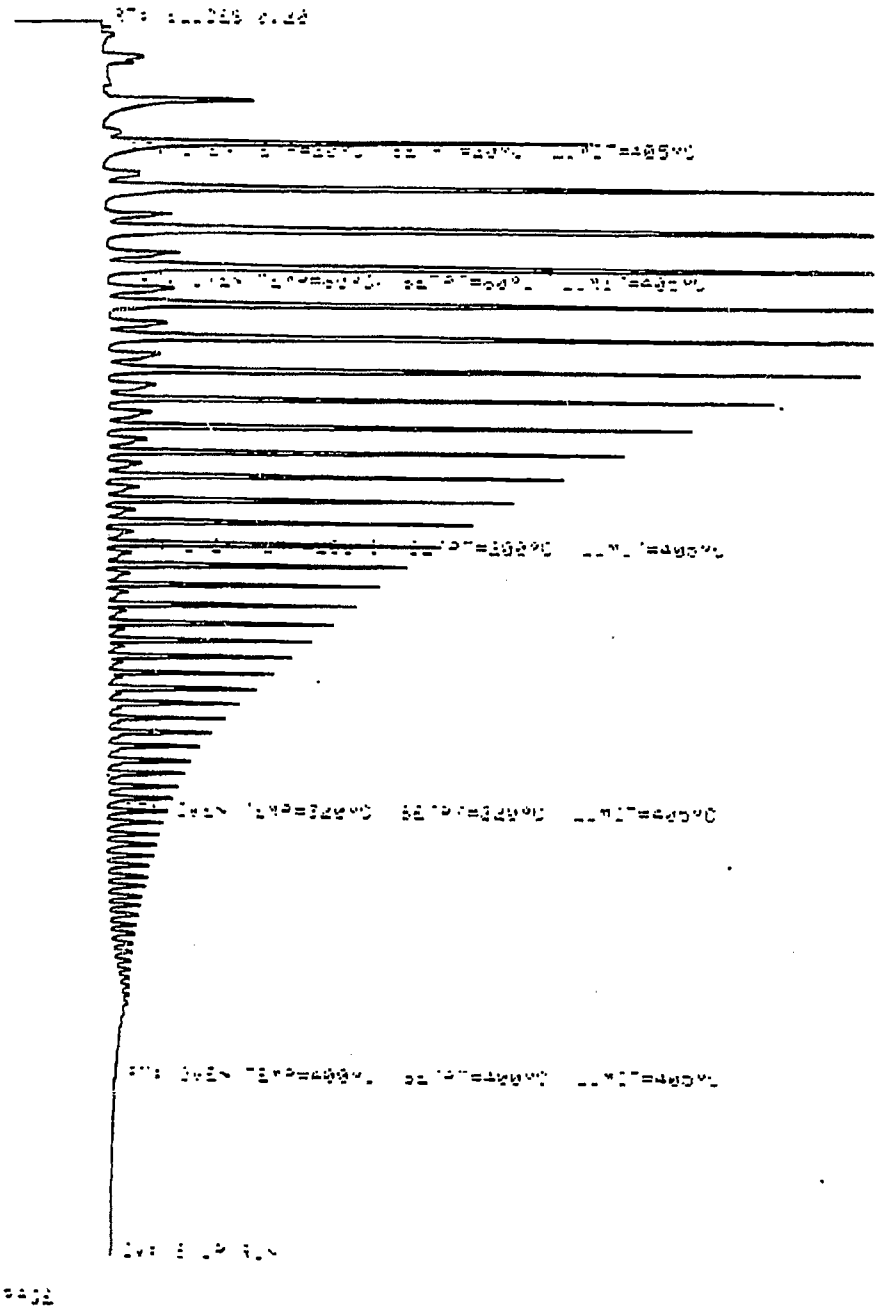


Figure B27

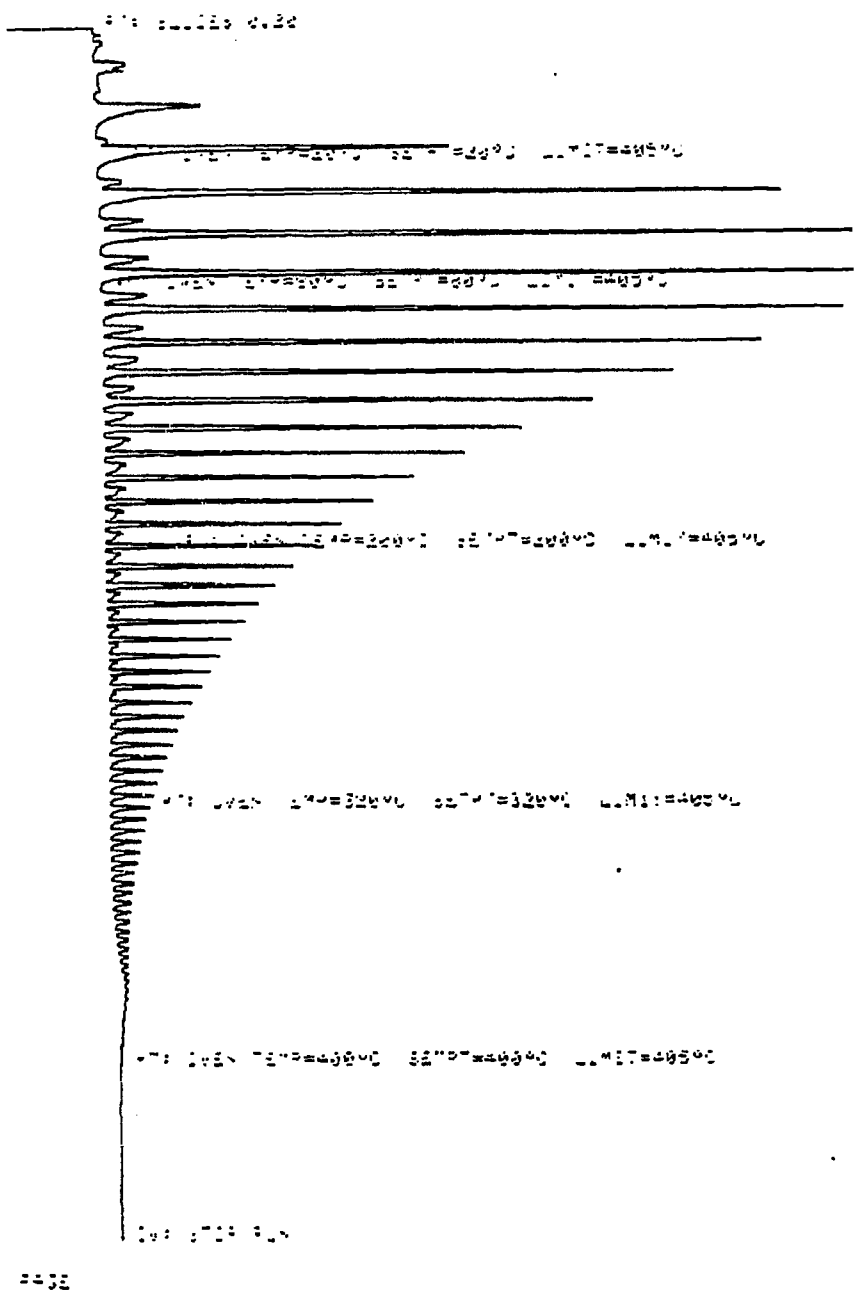


Figure 328

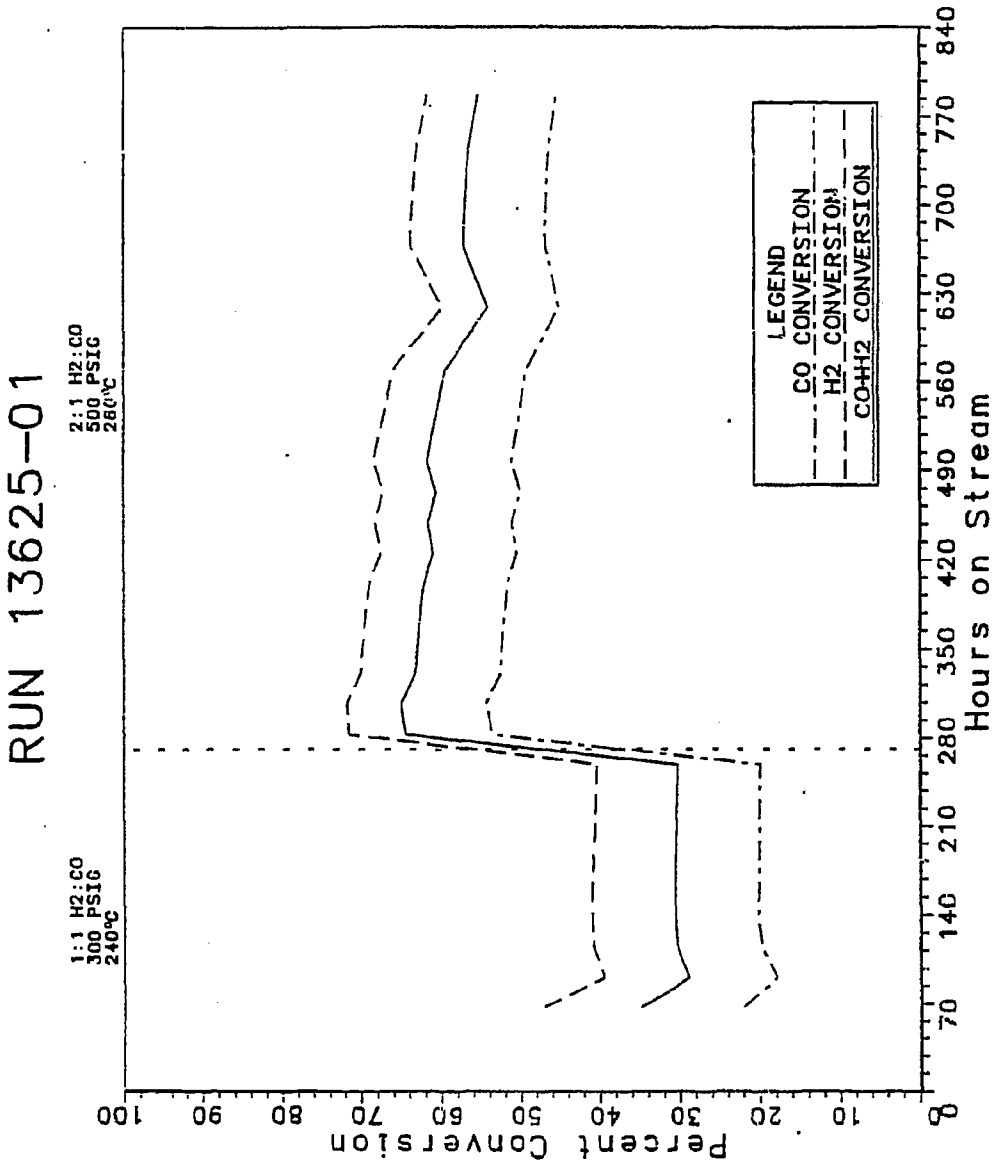

RUN 13625-01
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
280°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
70
140
210
280
350
420
490
560
630
700
770
840

Figure B29

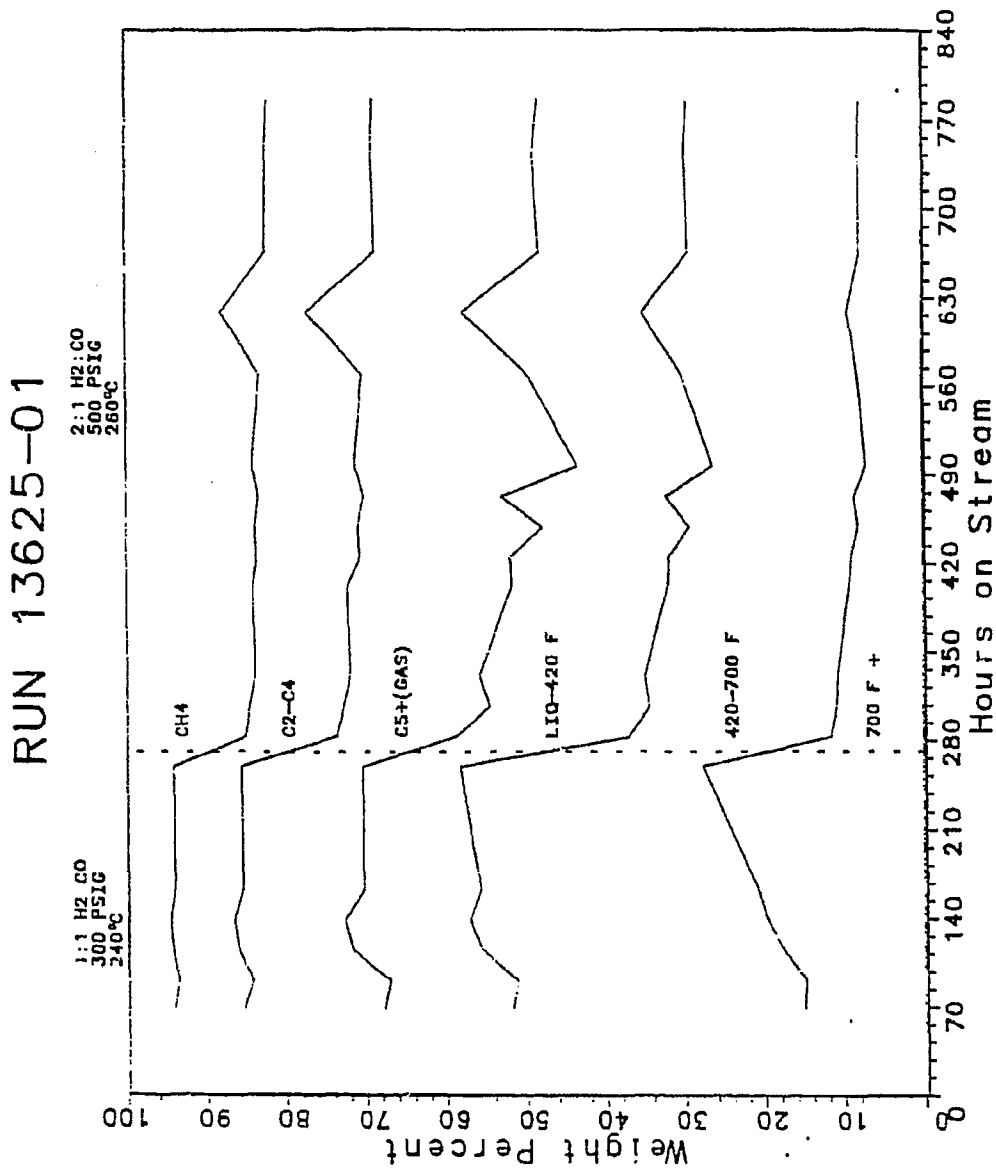

RUN 13625-01
1:1 H2 CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F +
Weight Percent
Hours on Stream
0
70
140
210
280
350
420
490
560
630
700
770
840
10
20
30
40
50
60
70
80
90
100

Figure 330

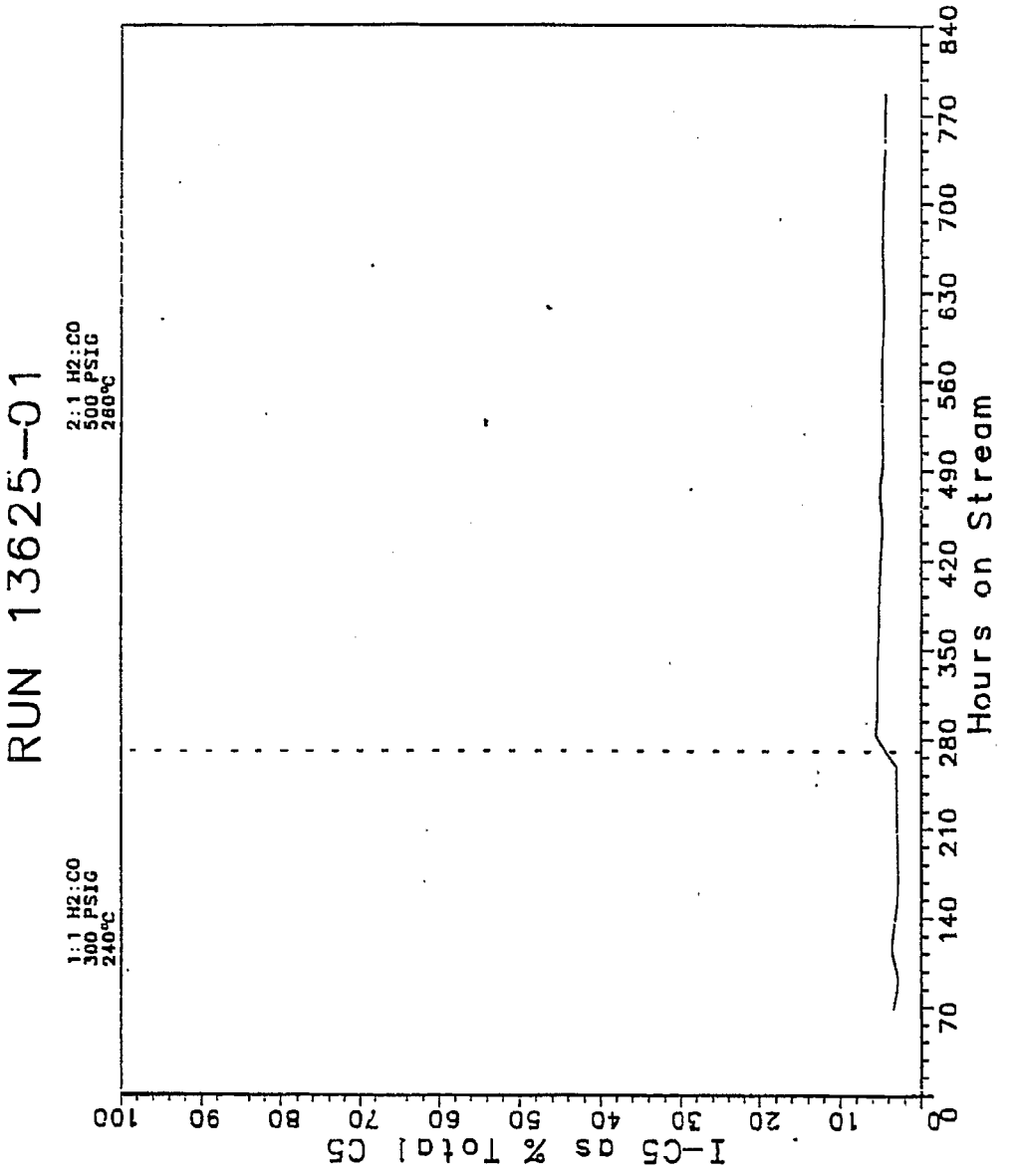

RUN 13625-01
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
280°C
I-C5 as % Total C5
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
70
140
210
280
350
420
490
560
630
700
770
840

Figure B31

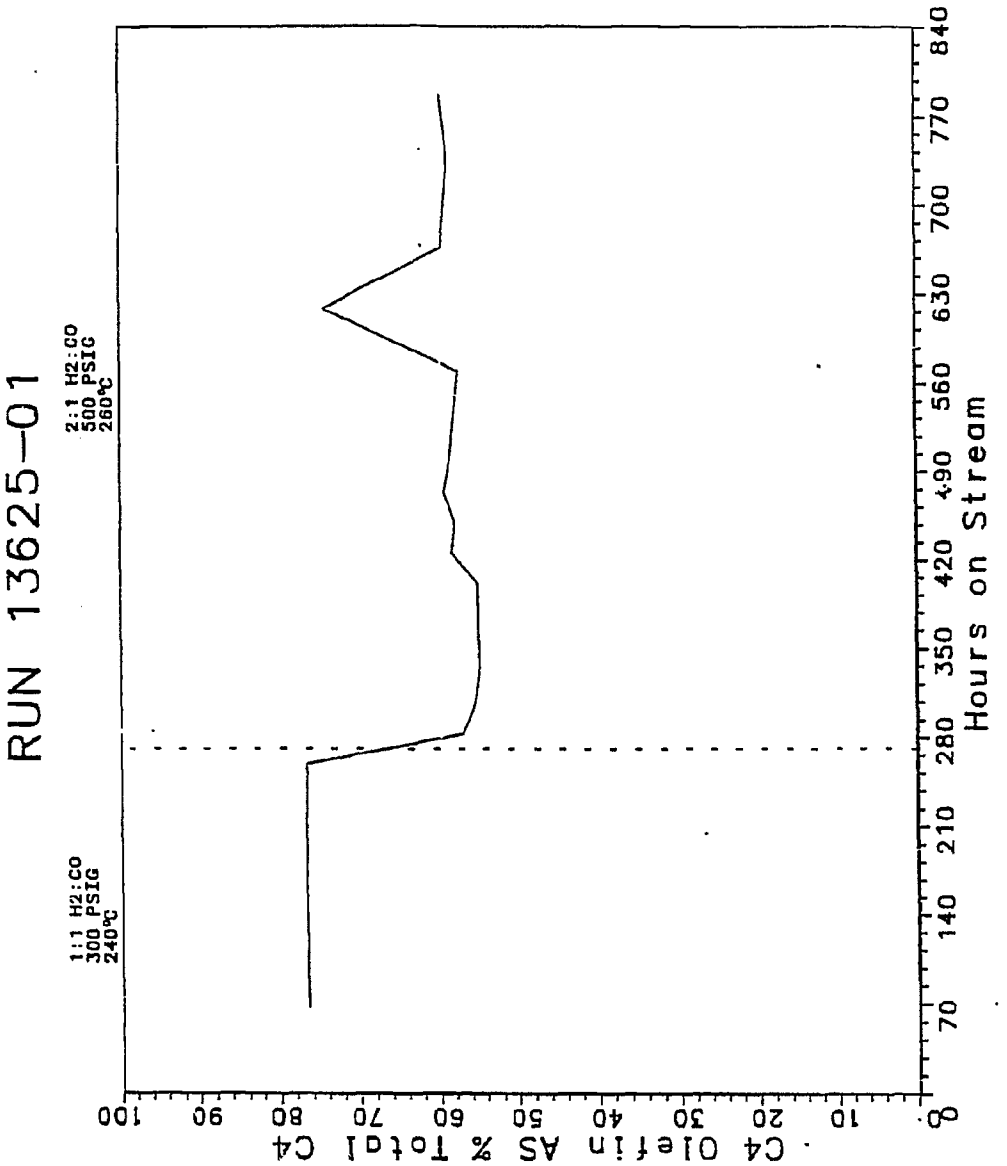

RUN 13625-01
1:1 H2:CO
300 PSIG
240°C
2:1 H2:CO
500 PSIG
260°C
C4 Olefin AS % Total C4
Hours on Stream
0
70
140
210
280
350
420
490
560
630
700
770
840
10
20
30
40
50
60
70
80
90
100

Figure 332

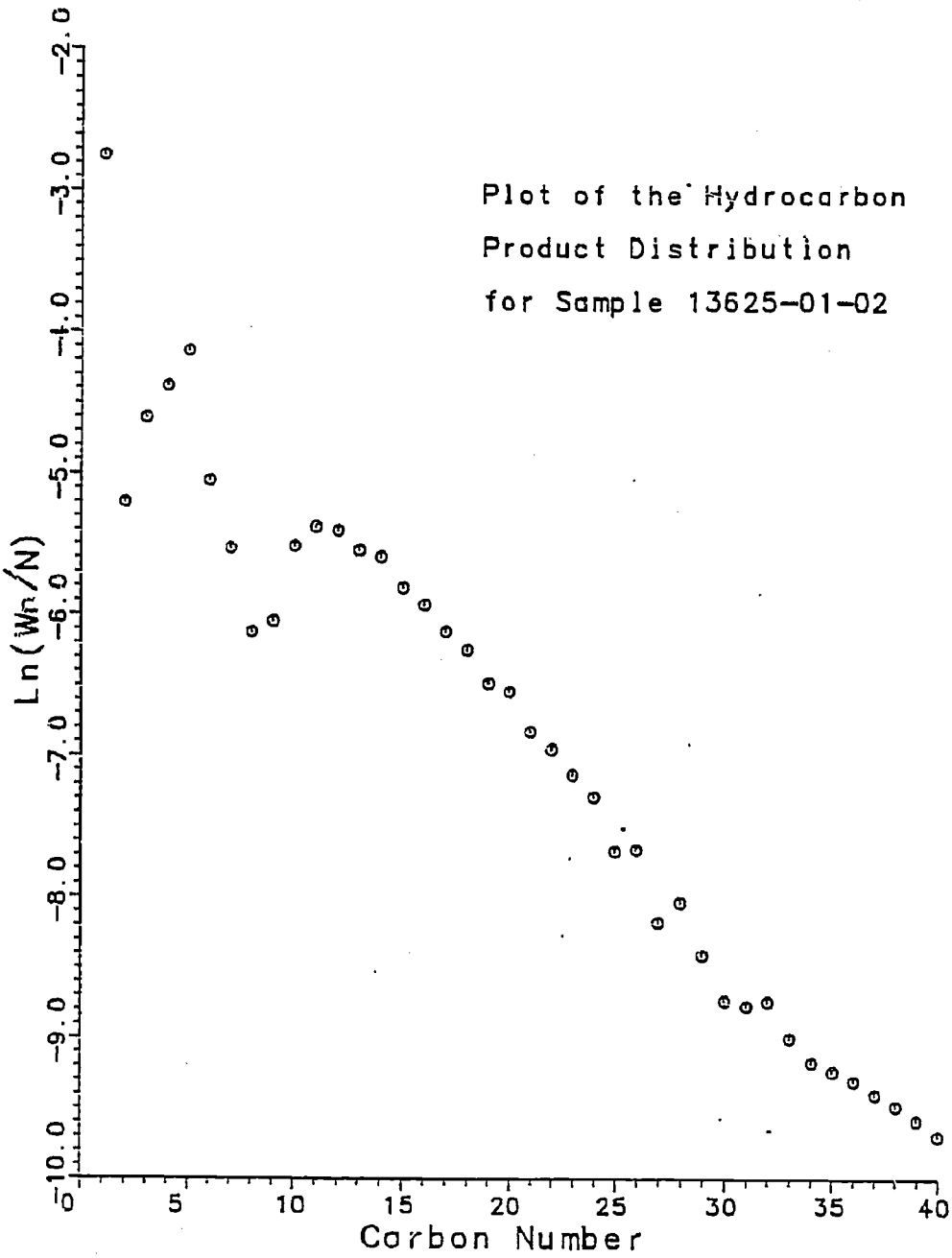

Plot of the Hydrocarbon
Product Distribution
for Sample 13625-01-02
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B33

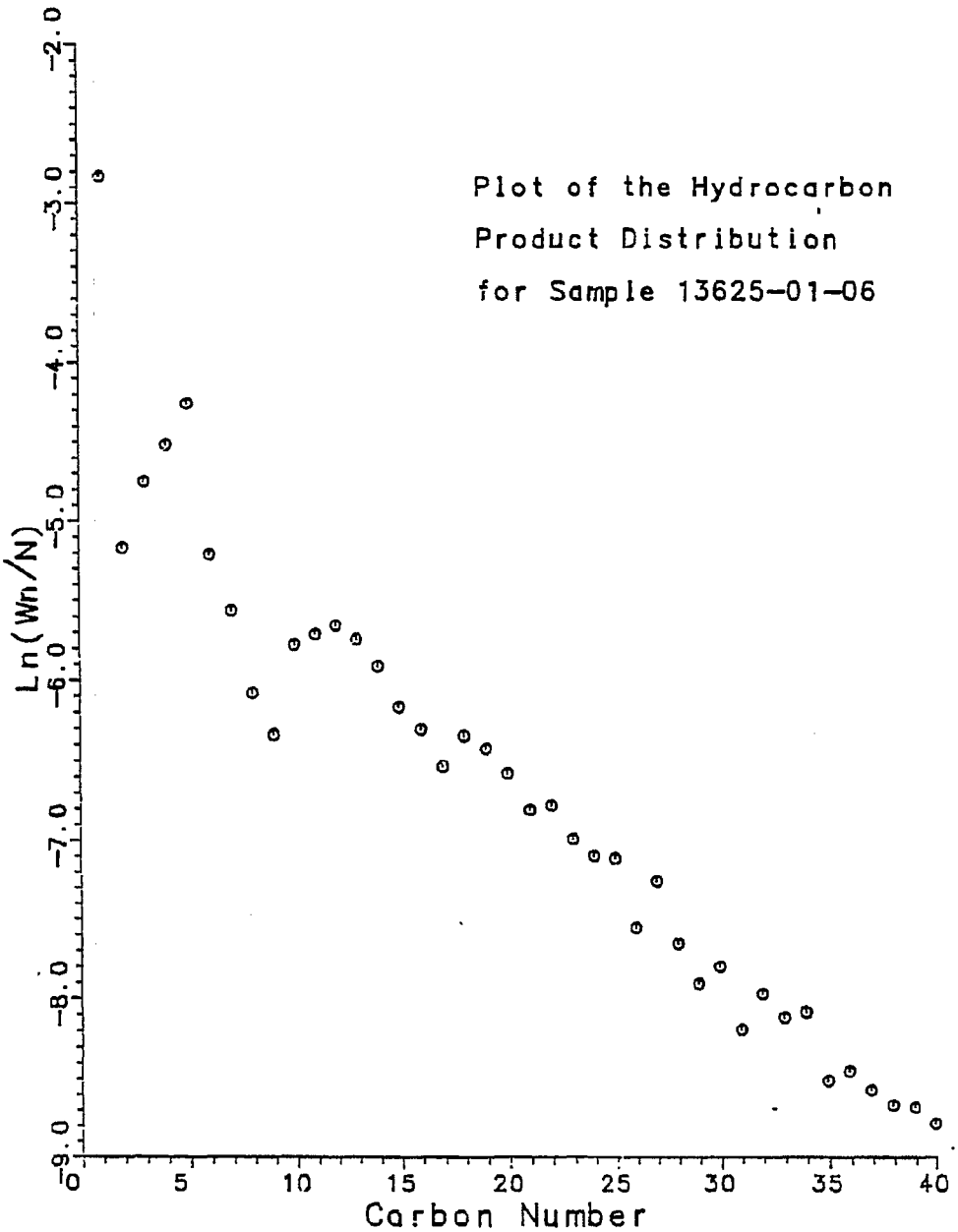

Plot of the Hydrocarbon
Product Distribution
for Sample 13625-01-06
Ln(Wn/N)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure 334

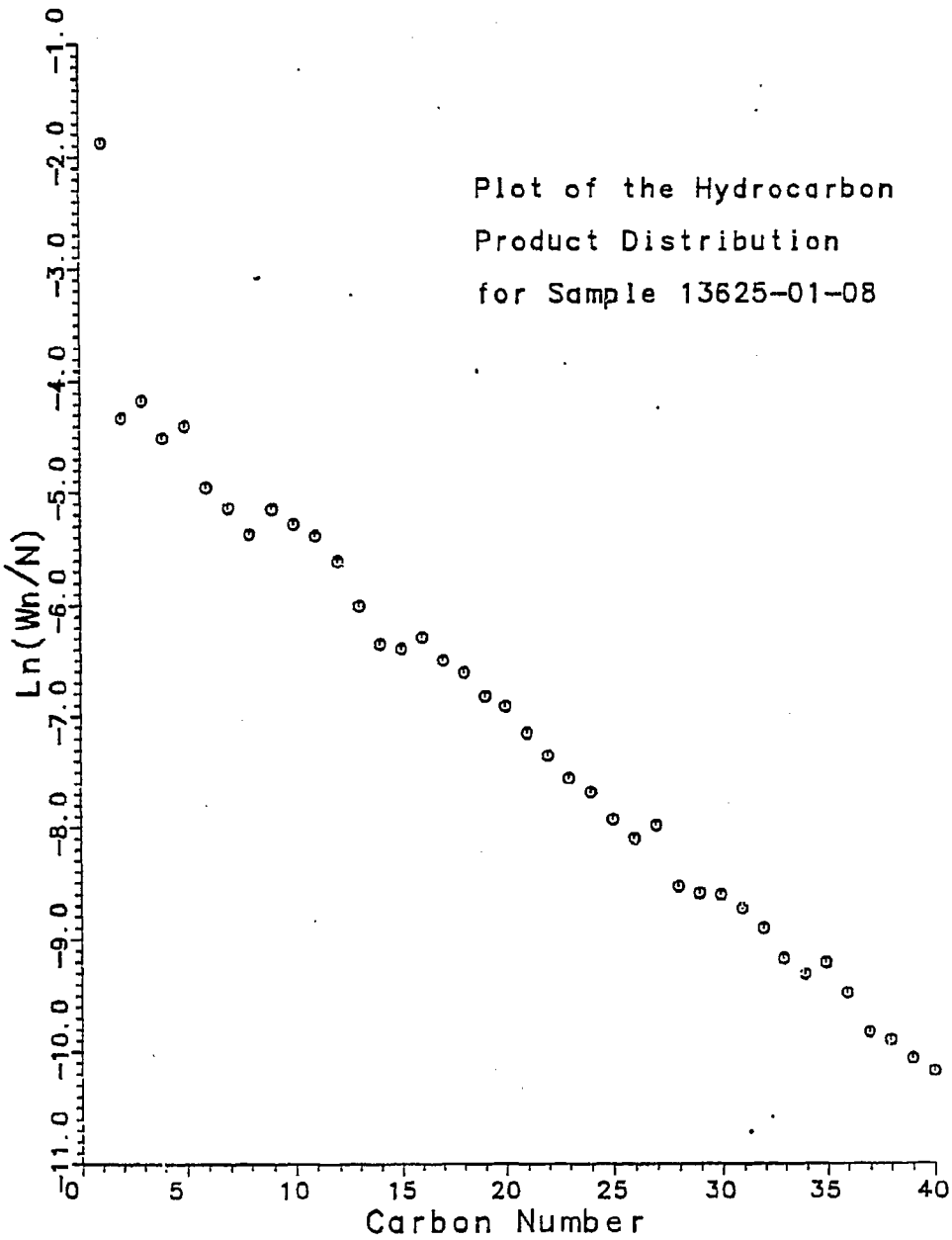

Plot of the Hydrocarbon
Product Distribution
for Sample 13625-01-08
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B35

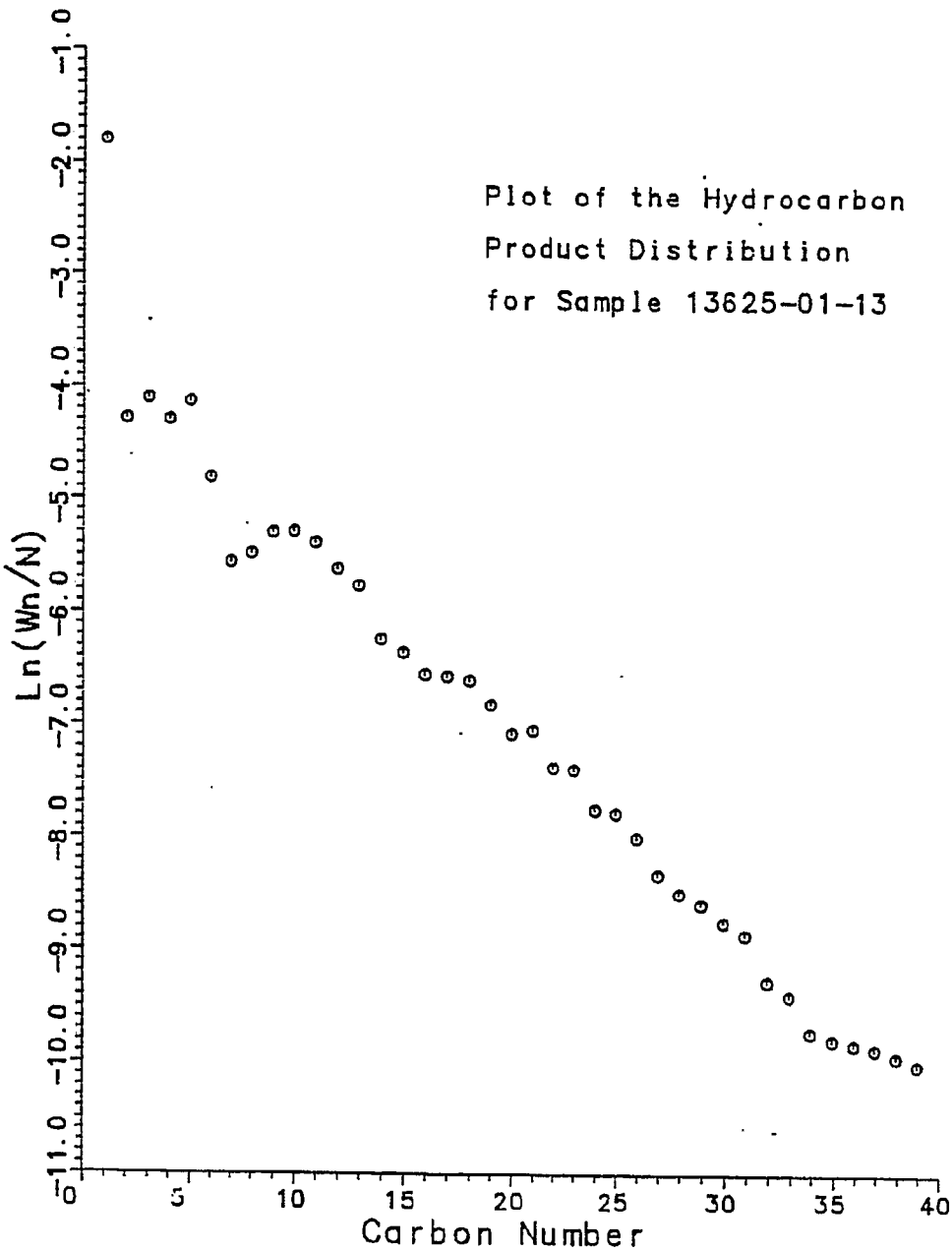

Plot of the Hydrocarbon
Product Distribution
for Sample 13625-01-13
Ln(Wn/N)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Figure B36

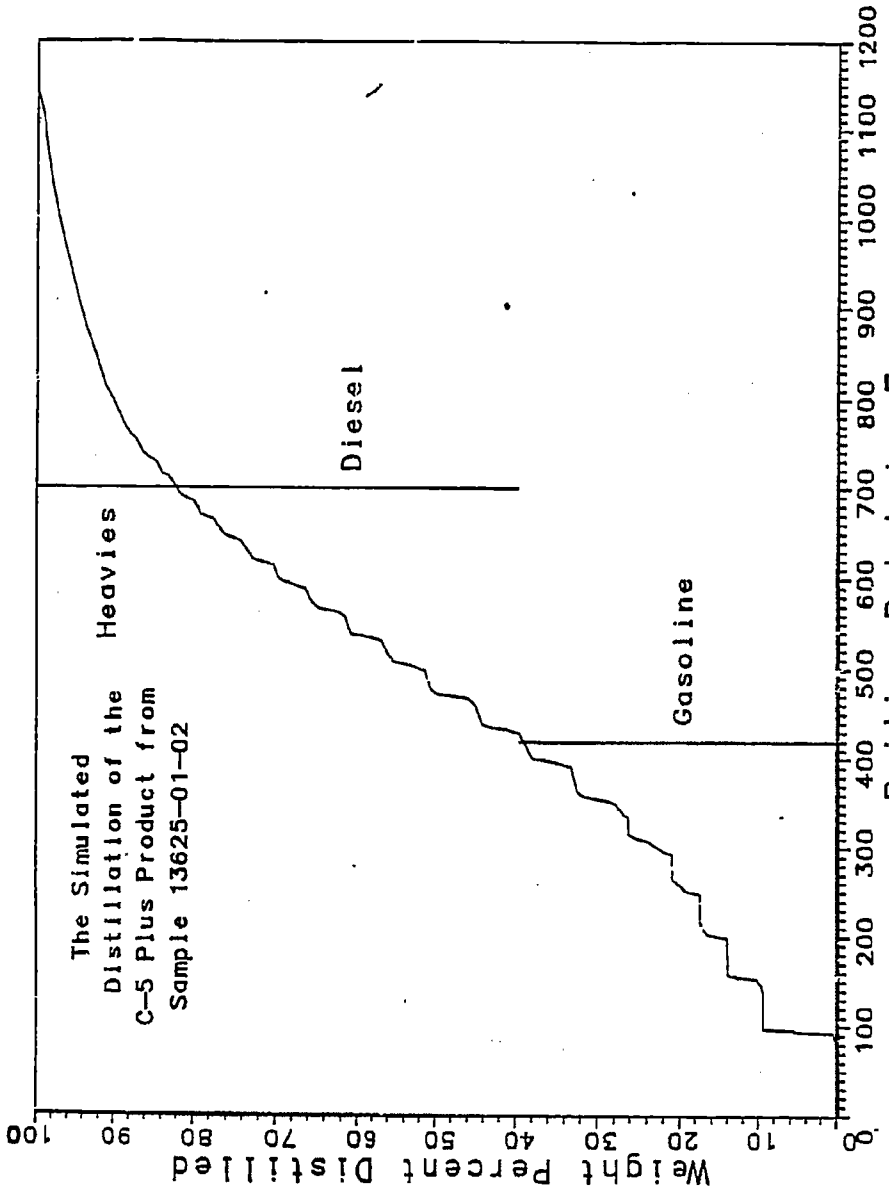

The Simulated Distillation of the C-5 Plus Product from Sample 13625-01-02
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure 337

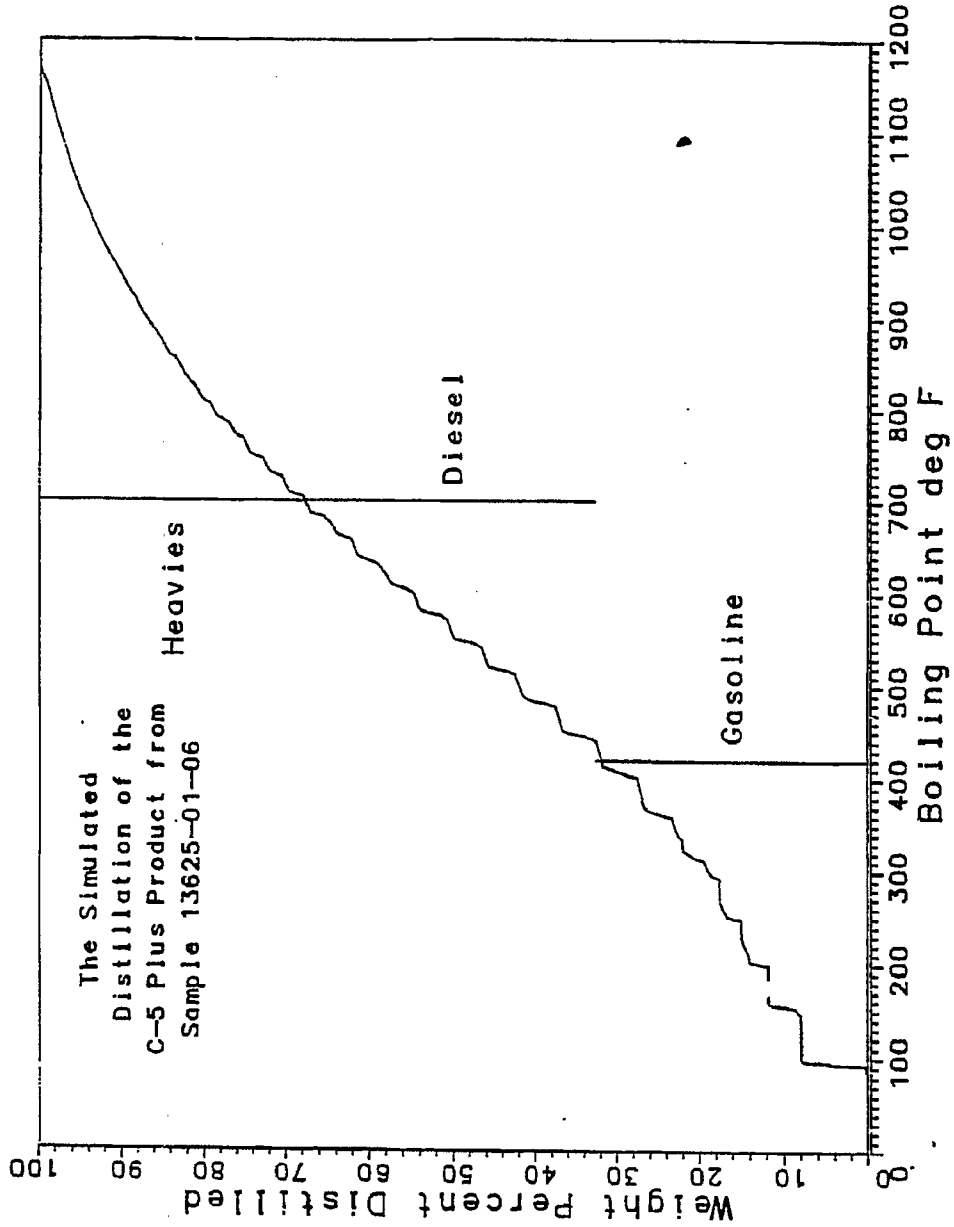

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13625-01-06
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B38

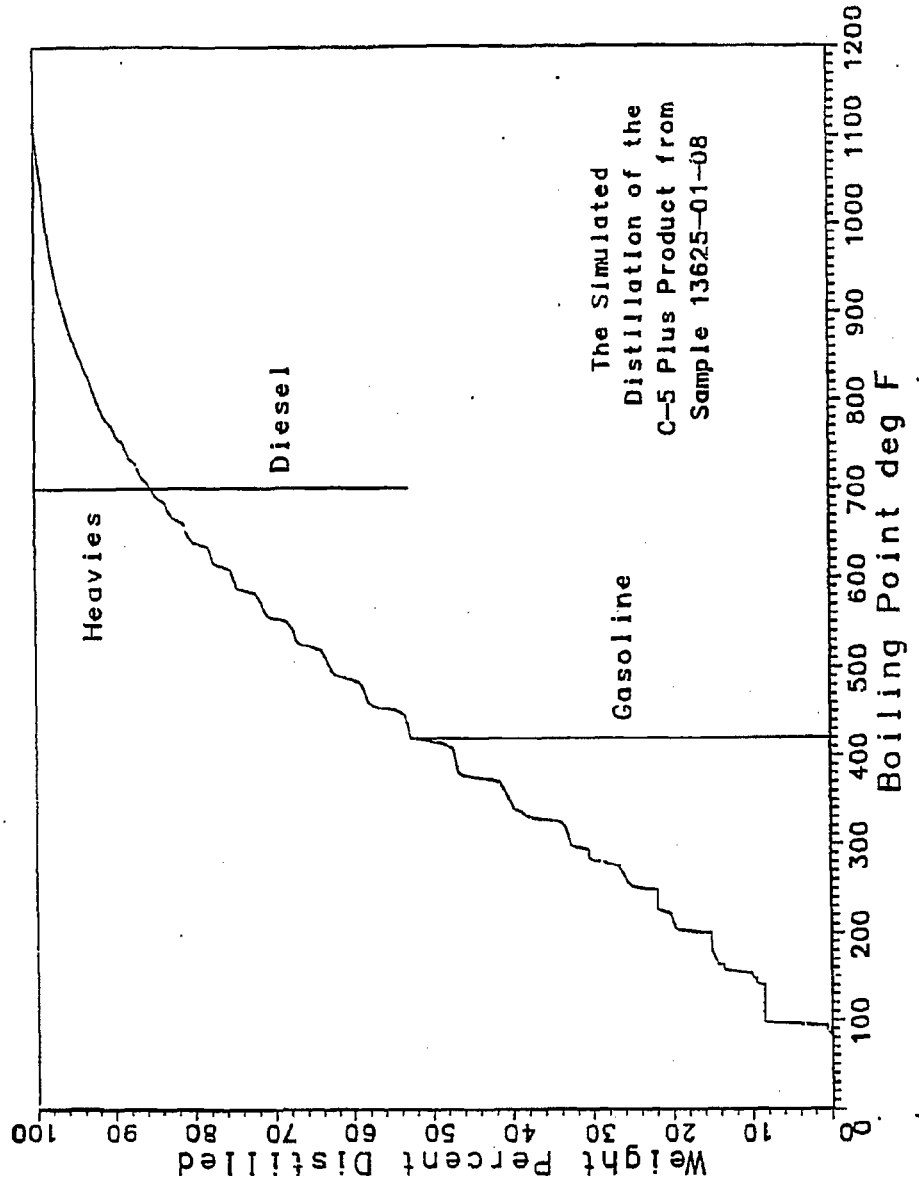

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13625-01-08
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000
1100
1200

Figure B39

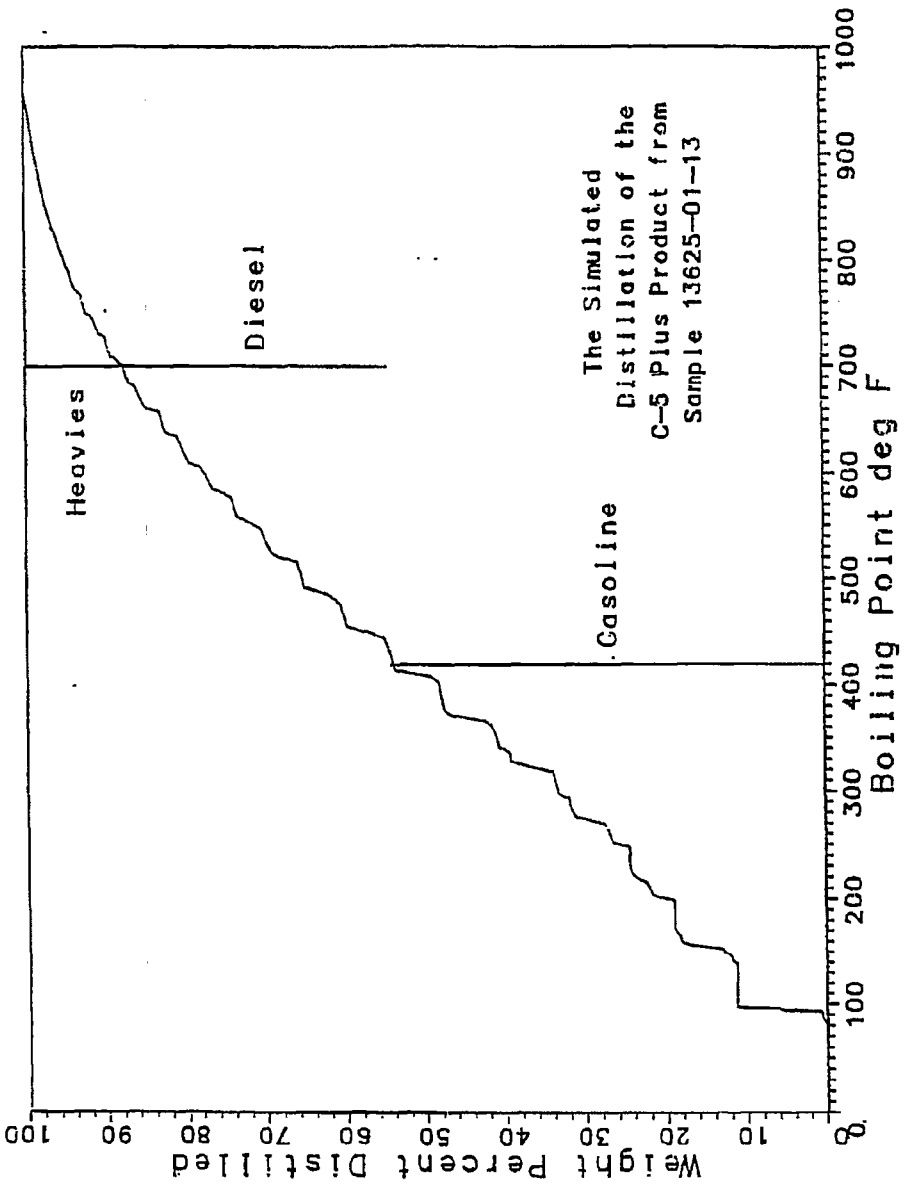
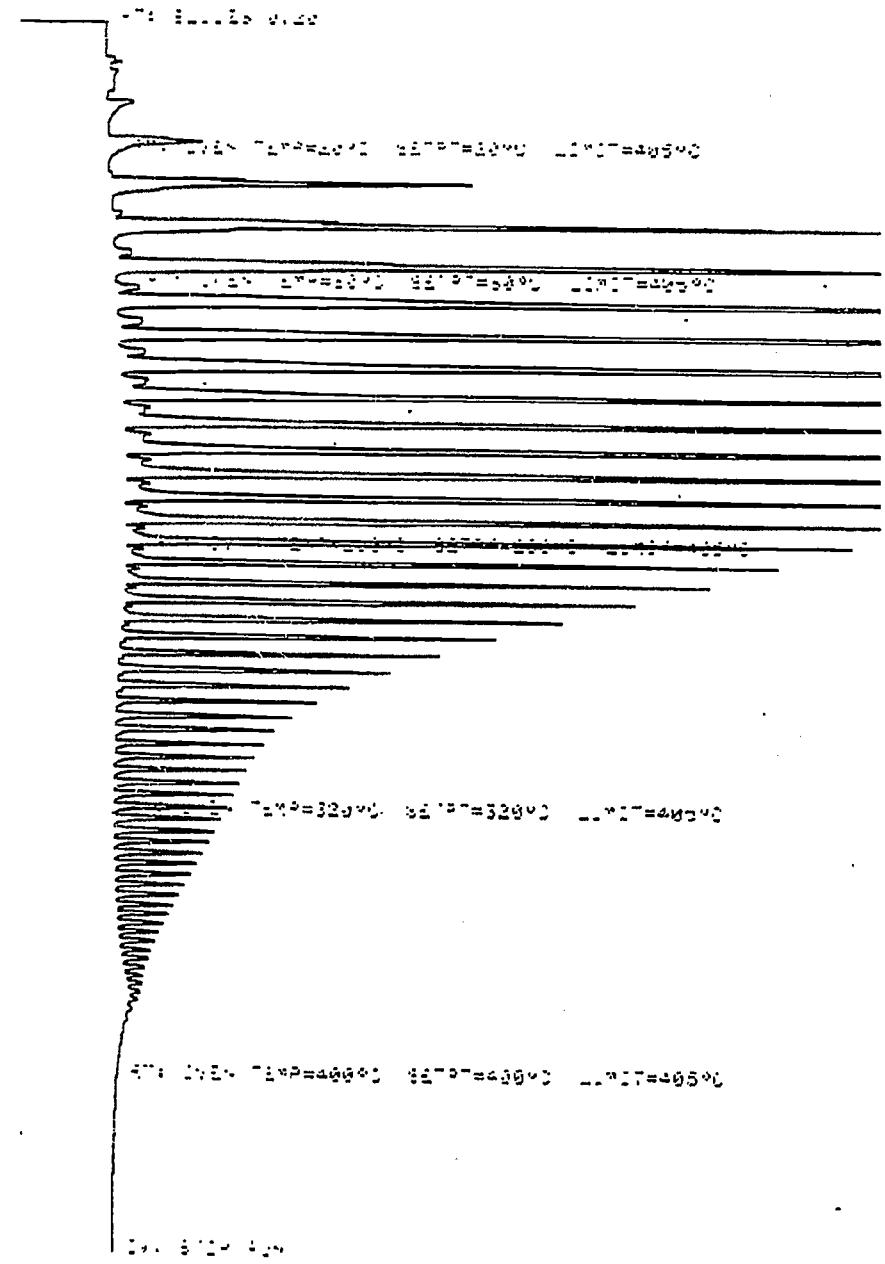
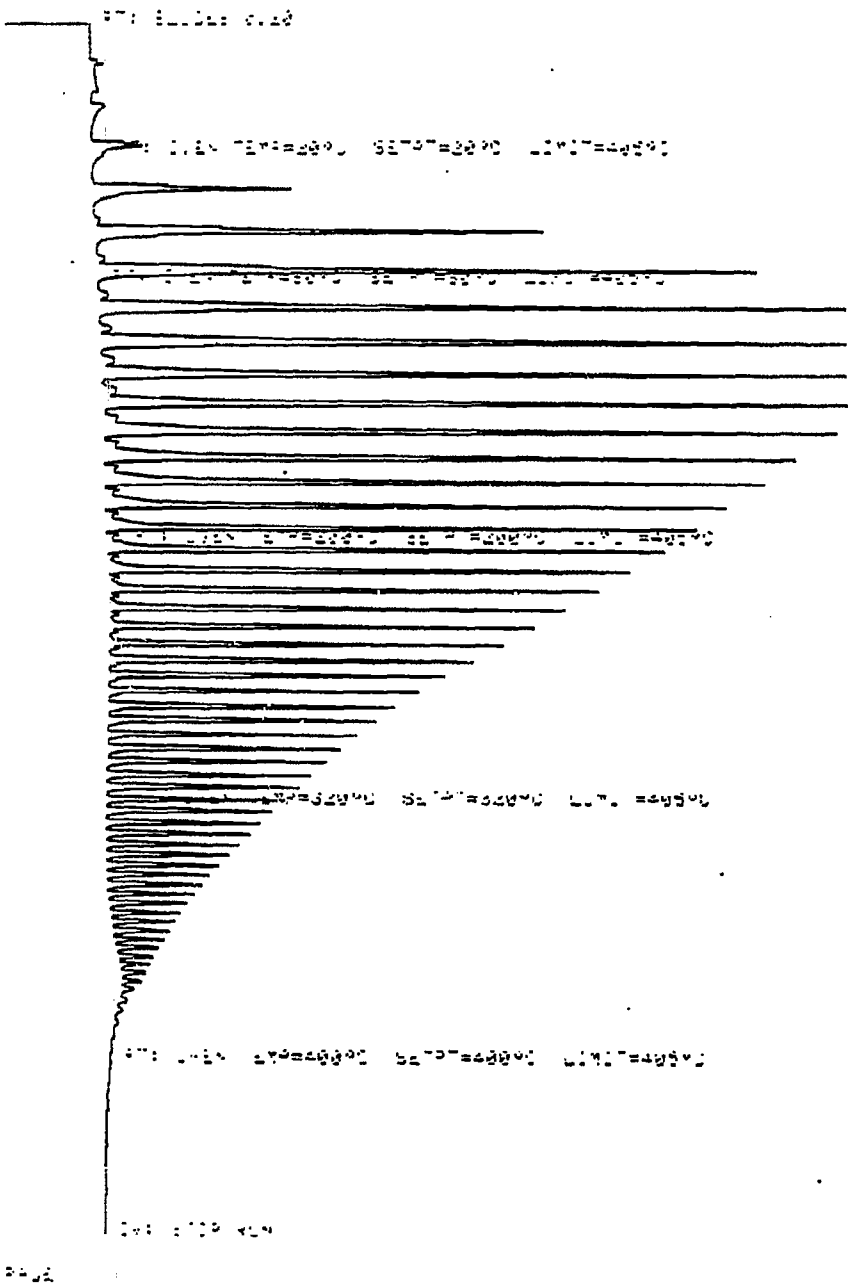

The Simulated
Distillation of the
C-5 Plus Product from
Sample 13625-01-13
Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point deg F
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
700
800
900
1000

Figure B40



13625-01-02

Figure 341



136 25 -01-06

Figure B42

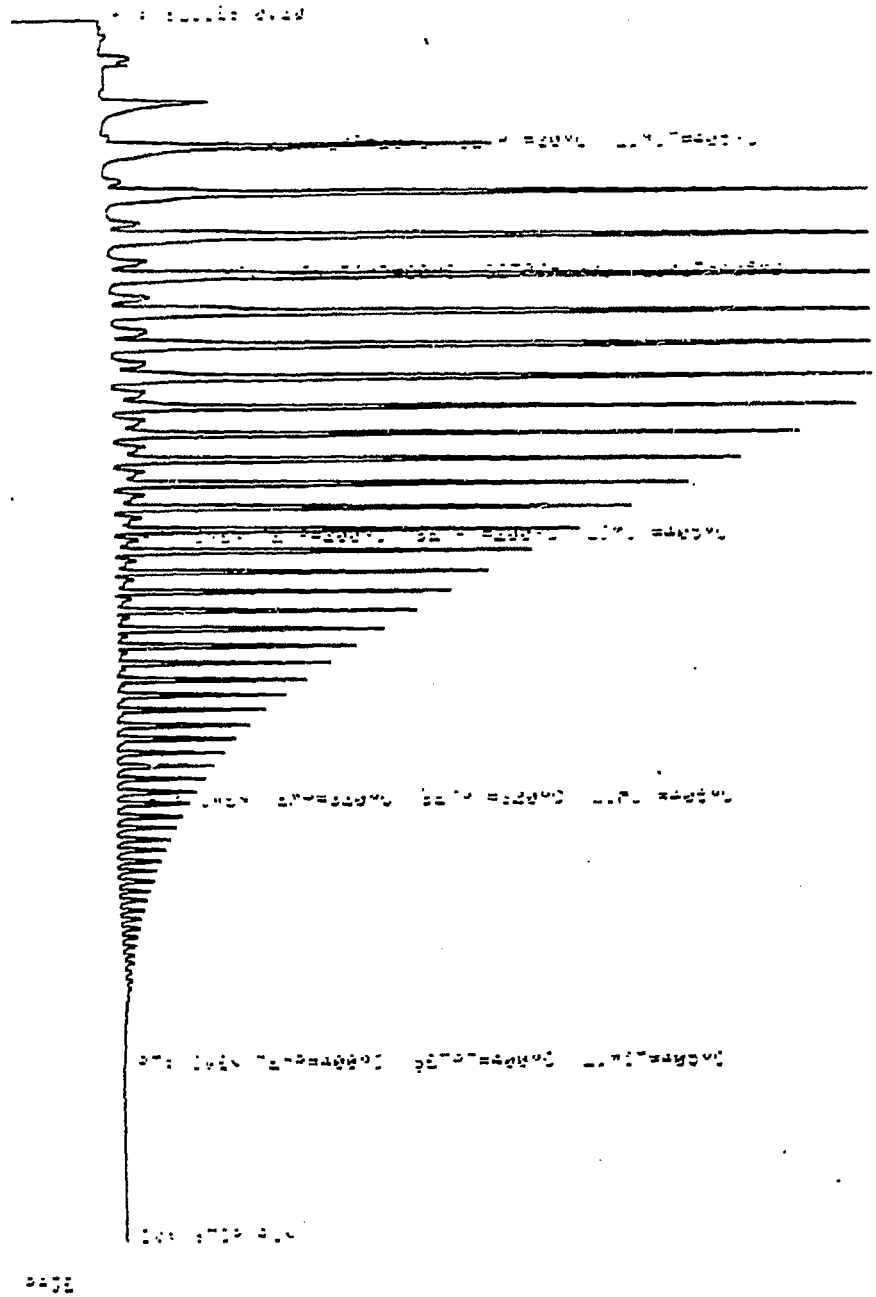


Figure 343

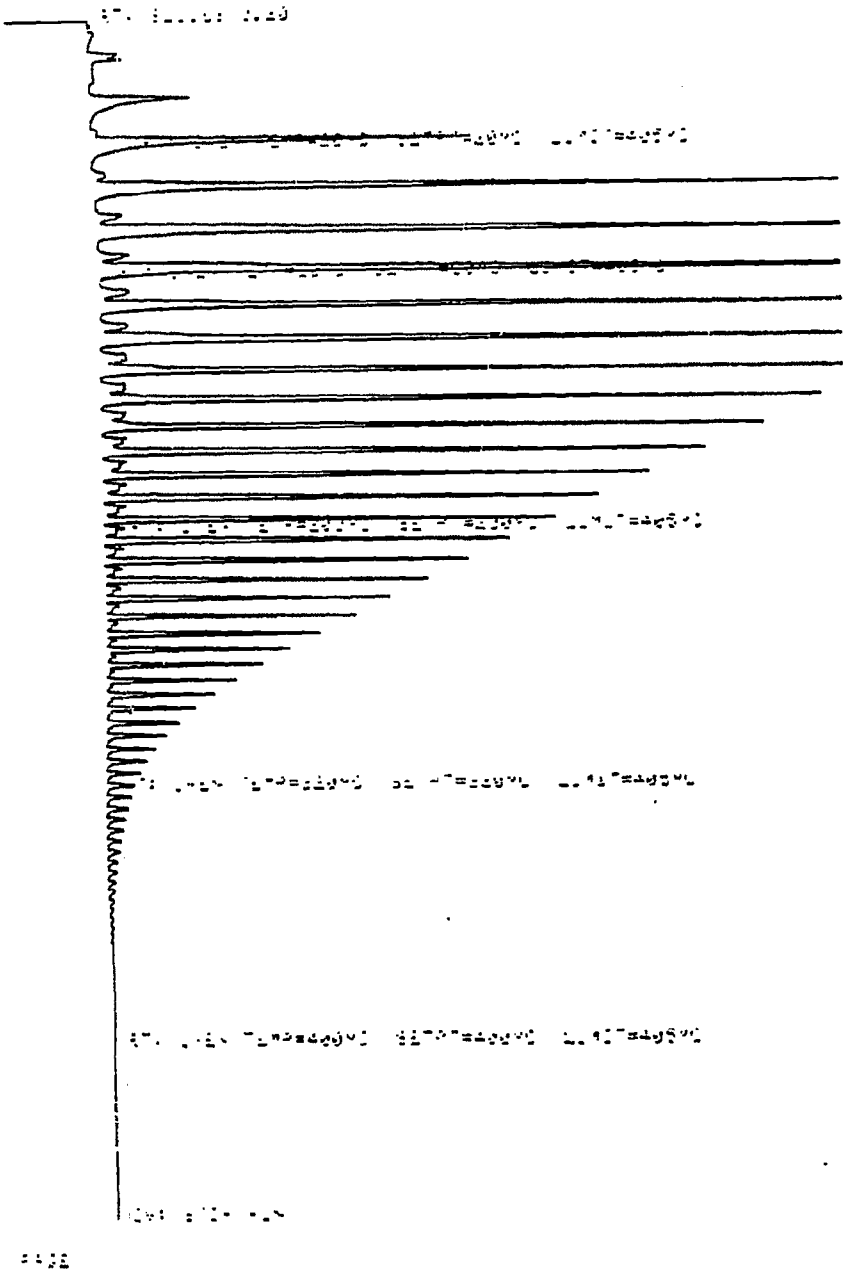


Figure B44

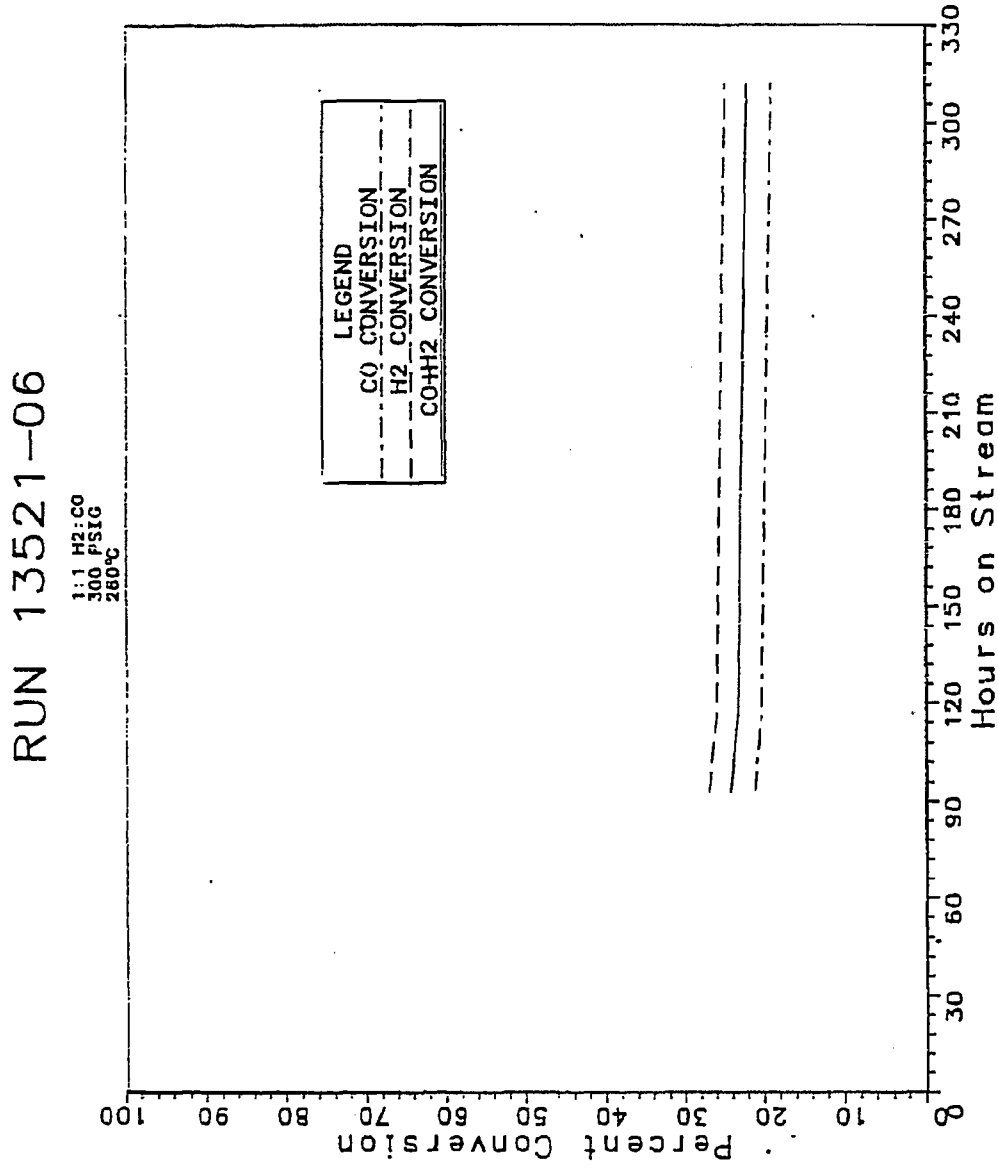

RUN 13521-06
1:1 H2:CO
300 PSIG
280°C
LEGEND
CO CONVERSION
H2 CONVERSION
CO+H2 CONVERSION
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
Hours on Stream
0
30
60
90
120
150
180
210
240
270
300
330

Figure B45

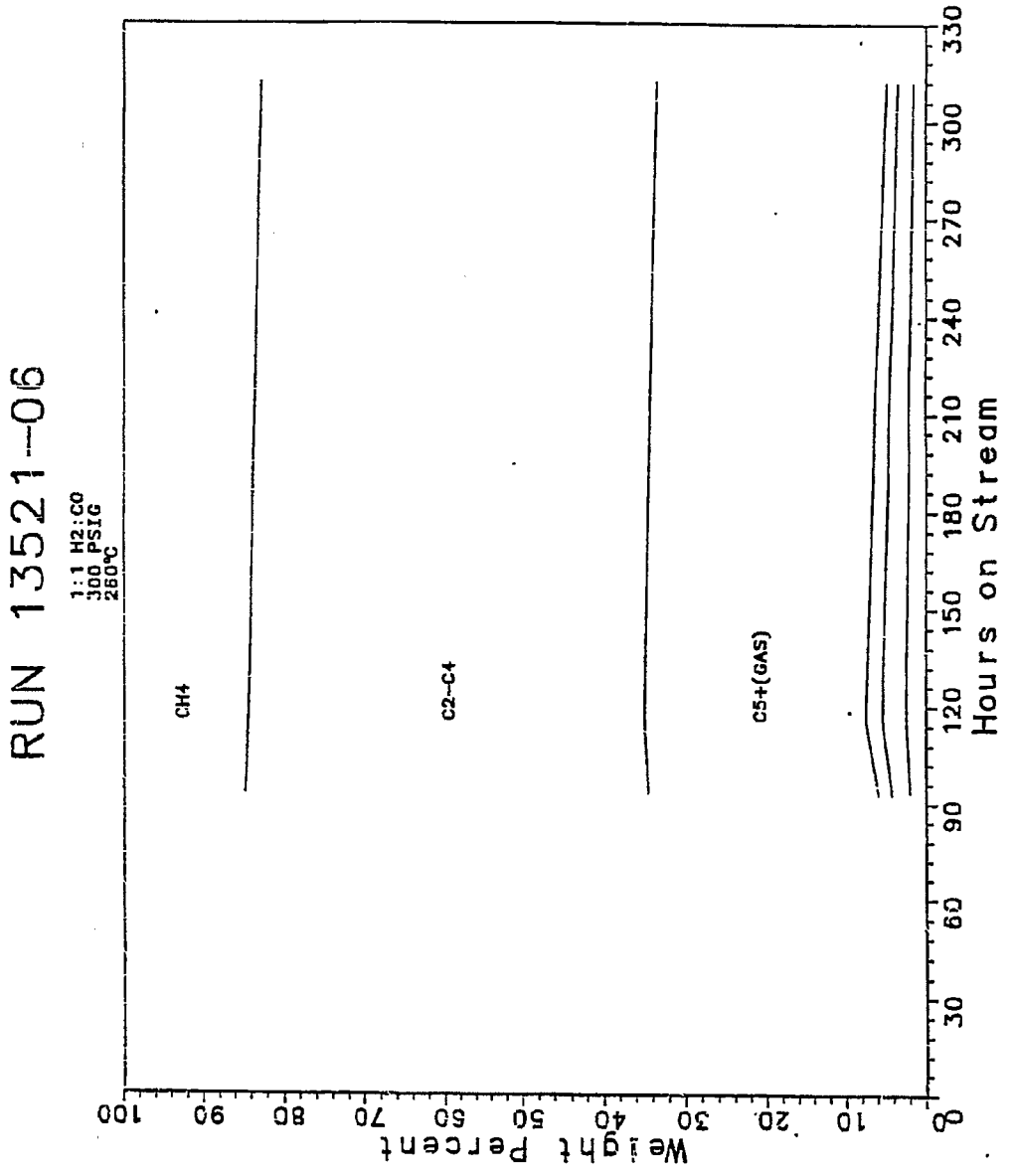

RUN 13521-06
1:1 H2:CO
300 PSIG
260°C
CH4
C2-C4
C5+(GAS)
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
30
60
90
120
150
180
210
240
270
300
330

Figure B46

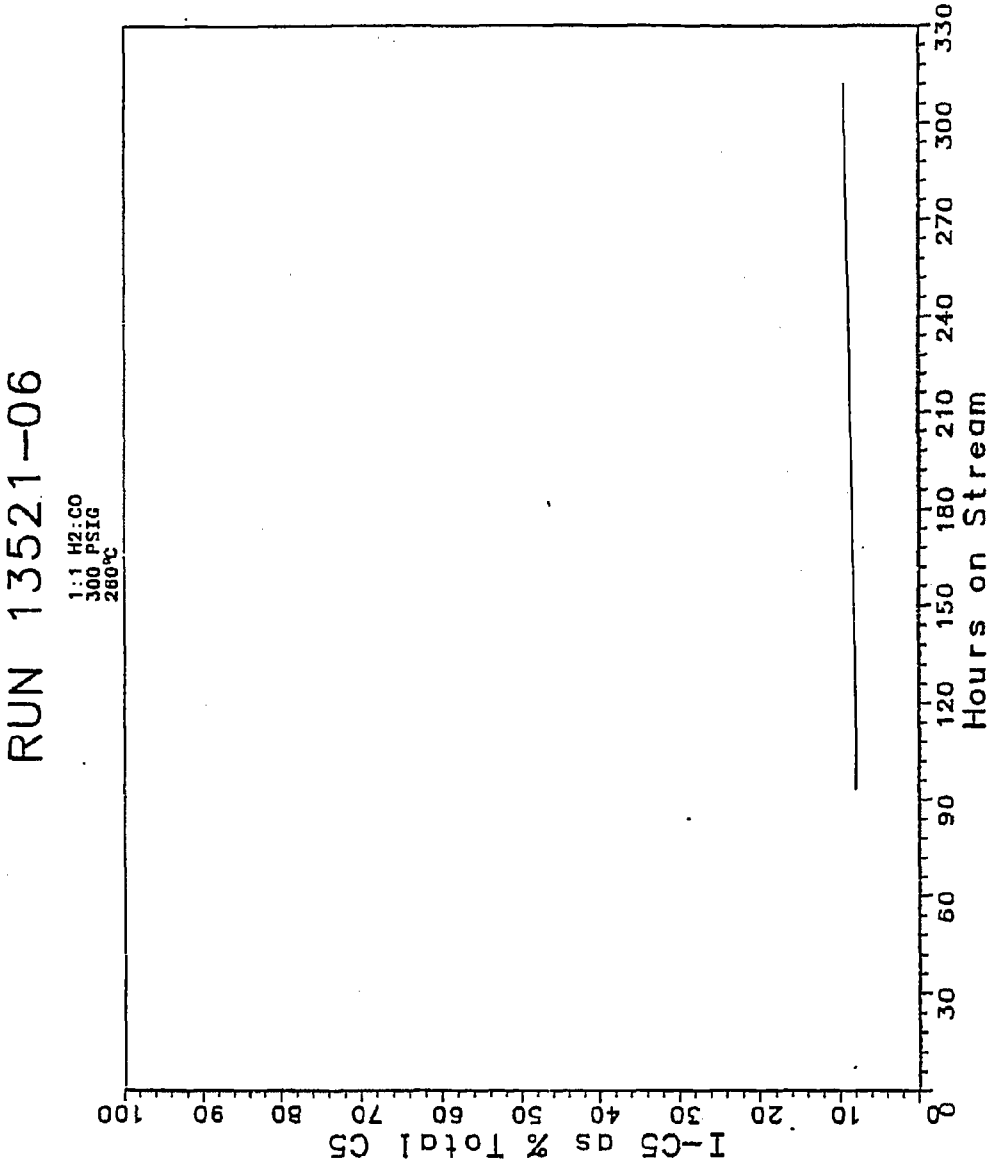

RUN 13521-06
1:1 H2:CO
300 PSIG
280°C
I-C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
30
60
90
120
150
180
210
240
270
300
330

Figure B47

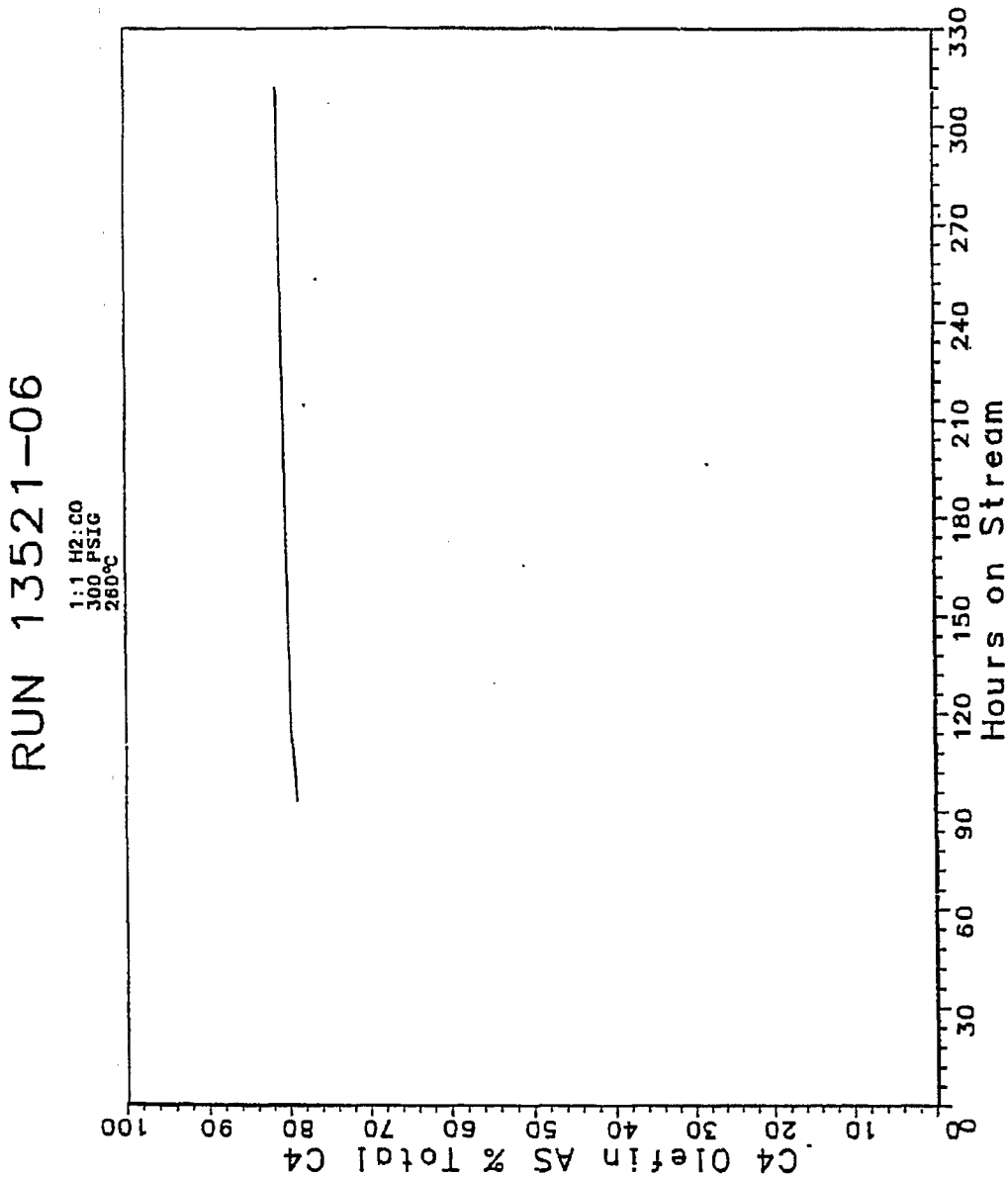

RUN 13521-06
1:1 H2:CO
300 PSIG
280°C
C4 Olefin AS % Total C4
Hours on Stream
0
30
60
90
120
150
180
210
240
270
300
330
10
20
30
40
50
60
70
80
90
100

Table B1

FILE: 1352104A T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-04
CATALYST CO/X11/X9-TC-123 CAT.# 13168-39 80 CC 40.01G(TO 49.8 +9.75G)
FEED H2:CO:ARGON= 50:50:0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	13521-04-01	521-04-02	521-04-03	521-04-04	521-04-05
FEED H2:CO:AR	50:50: 0	52:48: 0	52:48: 0	52:48: 0	52:48: 0
HRS ON STREAM	22.00	70.00	142.00	166.00	190.00
PRESSURE,PSIG	298.20	299.00	299.90	300.20	299.30
TEMP. C	243.00	238.00	242.00	242.00	242.00
FEED CC/MIN	400.00	373.23	382.67	384.48	385.74
HOURS FEEDING	21.42	24.00	72.00	24.00	24.00
EFFLNT GAS LITER	194.25	290.92	861.23	294.41	293.27
GM AQUEOUS LAYER	63.69	55.57	178.75	58.42	59.21
GM OIL	18.45	40.13	127.79	41.86	42.33
MATERIAL BALANCE					
GM ATOM CARBON %	65.37	99.99	99.98	99.98	100.00
GM ATOM HYDROGEN %	80.88	100.00	100.00	100.00	100.00
GM ATOM OXYGEN %	84.34	100.01	100.02	100.02	100.00
RATIO CHX/(H2O+CO2)	0.4965	0.9994	0.9990	0.9990	1.0000
RATIO X IN CHX	2.2498	2.1866	2.1909	2.1920	2.1910
USAGE H2/CO PRODT	2.5977	1.9384	1.9297	1.9304	1.9365
FEED H2/CO FRM EFFLNT	1.2374	1.0795	1.0932	1.0821	1.0889
RESIDUAL H2/CO RATIO	0.5696	0.6250	0.6123	0.6146	0.6161
RATIO CO2/(H2O+CO2)	0.0747	0.0529	0.0569	0.0568	0.0542
K SHIFT IN EFFLNT	0.0460	0.0349	0.0369	0.0370	0.0353
SPEC ACTVTY SA,CO/X11	0.7545	0.9571	0.8605	0.8410	0.8490
CONVERSION					
ON CO %	32.93	34.61	36.50	35.53	35.81
ON H2 %	69.12	62.14	64.43	63.38	63.68
ON CO+H2 %	52.95	48.90	51.09	50.00	50.34
PRDT SELECTIVITY,WT %					
CH4	6.63	3.25	3.42	3.53	3.51
C2 HC'S	1.58	0.82	1.11	1.00	0.97
C3H8	1.21	0.61	0.61	0.62	0.61
C3H6=	2.16	1.24	1.31	1.34	1.35
C4H10	1.13	0.65	0.65	0.66	0.64
C4H8=	4.21	2.43	2.52	2.53	2.48
C5H12	2.89	1.81	1.79	1.78	1.76
C5H10=	4.84	2.99	2.95	3.10	3.00
C6H14	3.24	1.96	1.92	1.96	1.95
C6H12= & CYCLO'S	0.68	0.33	0.34	0.34	0.35
C7+ IN GAS	6.12	3.16	3.29	3.09	3.30
LIQ HC'S	65.31	80.76	80.08	80.03	80.08
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	16.92	9.00	9.62	9.69	9.55
C5 -420 F	30.74	25.34	25.51	26.42	26.38
420-700 F	24.97	31.02	30.66	30.71	29.92
700-END PT	27.37	34.64	34.20	33.18	34.15

Table B1 (cont.)

FILE: 1352104A T8Q1	A1				
C5+-END PT	83.08	91.00	90.38	90.31	90.45
ISO/NORMAL MOLE RATIO					
C4	0.0360	0.0259	0.0644	0.0266	0.0231
C5	0.0526	0.0431	0.0473	0.0473	0.0483
C6	0.1497	0.1102	0.1128	0.1268	0.1150
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.5371	0.4658	0.4448	0.4434	0.4285
C4	0.2588	0.2583	0.2499	0.2532	0.2473
C5	0.5804	0.5881	0.5877	0.5584	0.5704
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))			0.9034		0.8972
RATIO CH4/(1-A)**2			3.6639		3.3198
ALPHA FRM CORRELATION	0.9040	0.9024	0.9018	0.9017	0.9016
ALPHA (EXPTL/CORR)			1.0017		0.9952
W%CH4 FRM CORRELATION	3.4120	3.6699	3.9602	3.9925	4.0263
W%CH4 (EXPTL/CORR)	1.9435	0.8868	0.8637	0.8853	0.8708
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F			344.00		343.00
16			388.00		385.00
50			647.00		645.00
84			936.00		950.00
90			1007.00		1025.00
RANGE(16-84 %)			548.00		565.00
WT % @ 420 F	19.85	18.70	19.00	20.17	20.00
WT % @ 700 F	58.09	57.11	57.29	58.54	57.36

Table B1 (cont.)

FILE: 1352104B T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-04
CATALYST CO/X11/X9-TC-123 CAT. #13168-39 80 CC 40.01G(TO 49.8 +9.75G)
FEED H2:CO:ARGON= 62:38:0 @ 378 CC/MN OR 284 GHSV

RUN & SAMPLE NO.	13521-04-06	521-04-07	521-04-08	521-04-09	521-04-10
FEED H2:CO:AR	62:38: 0	62:38: 0	62:38: 0	62:38: 0	62:38: 0
HRS ON STREAM	214.00	238.00	310.00	334.00	358.00
PRESSURE,PSIG	498.70	497.20	498.80	498.90	499.10
TEMP. C	260.00	260.00	259.00	259.00	260.00
FEED CC/MIN	364.29	375.82	383.41	385.46	381.82
HOURS FEEDING	24.00	24.00	72.00	24.00	24.00
EFFLNT GAS LITER	155.34	168.99	500.32	168.45	166.22
GM AQUEOUS LAYER	79.81	80.91	255.75	85.70	84.84
GM OIL	42.28	43.86	147.53	50.03	51.13
MATERIAL BALANCE					
GM ATOM CARBON %	99.98	100.00	99.99	99.98	99.99
GM ATOM HYDROGEN %	100.00	99.99	100.00	100.00	99.98
GM ATOM OXYGEN %	100.02	100.00	100.01	100.02	99.99
RATIO CHX/(H2O+CO2)	0.9995	1.0000	0.9997	0.9992	1.0000
RATIO X IN CHX	2.5208	2.4943	2.4259	2.4237	2.4124
USAGE H2/CO PRODT	1.8396	1.8501	1.8733	1.8800	1.8718
FEED H2/CO FRM EFFLNT	1.6369	1.6197	1.6186	1.6178	1.6088
RESIDUAL H2/CO RATIO	1.0310	1.0273	0.9930	0.9880	0.9797
RATIO CO2/(H2O+CO2)	0.1483	0.1393	0.1183	0.1154	0.1164
K SHIFT IN EFFLNT	0.1795	0.1663	0.1332	0.1289	0.1291
SPEC ACTVTY SA,CO/X11	0.4802	0.4689	0.4935	0.4941	0.4683
CONVERSION					
ON CO %	74.94	72.00	71.06	70.61	70.52
ON H2 %	84.22	82.24	82.25	82.05	82.05
ON CO+H2 %	80.70	78.33	77.98	77.68	77.63
PRDT SELECTIVITY,WT %					
CH4	19.11	17.86	14.58	14.48	13.94
C2 HC'S	2.93	2.80	2.51	2.51	2.58
C3H8	5.01	4.73	3.92	3.88	3.61
C3H6=	0.59	0.68	0.76	0.79	0.74
C4H10	2.92	2.75	2.25	2.24	2.04
C4H8=	1.39	1.52	1.54	1.62	1.48
C5H12	4.59	4.34	3.71	3.57	3.30
C5H10=	1.81	1.91	1.92	1.92	1.78
C6H14	3.15	3.05	2.74	2.62	2.46
C6H12= & CYCLO'S	0.30	0.32	0.80	0.32	0.31
C7+ IN GAS	3.81	3.84	3.57	3.36	3.13
LIQ HC'S	54.39	56.20	61.71	62.68	64.64
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	31.95	30.34	25.56	25.53	24.38
C5 -420 F	38.41	39.03	33.10	32.48	32.96
420-700 F	22.20	23.03	24.37	24.76	25.76
700-END PT	7.44	7.60	16.97	17.24	16.90

Table 31 (cont.)

FILE: 1352104B T8Q1	A1				
C5+-END PT	68.05	69.66	74.44	74.47	75.62
ISO/NORMAL MOLE RATIO					
C4	0.0262	0.0268	0.0286	0.0272	0.0300
C5	0.0445	0.0465	0.0488	0.0500	0.0505
C6	0.2385	0.2294	0.2143	0.2232	0.2135
C4=	0.1135	0.1094	0.0977	0.0995	0.0978
PARAFFIN/OLEFIN RATIO					
C3	8.0592	6.6788	4.9147	4.6893	4.6675
C4	2.0237	1.7415	1.4135	1.3336	1.3290
C5	2.4642	2.2056	1.8819	1.8128	1.8013
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8239		0.8609	
RATIO CH4/(1-A)**2		5.7568		7.4855	
ALPHA FRM CORRELATION	0.8904	0.8905	0.8921	0.8923	0.8923
ALPHA (EXPTL/CORR)		0.9252		0.9648	
W%CH4 FRM CORRELATION	8.6414	8.6253	8.1654	8.1160	8.1484
W%CH4 (EXPTL/CORR)	2.2110	2.0705	1.7855	1.7841	1.7108
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F		255.00		262.00	
16		264.00		305.00	
50		429.00		519.00	
84		670.00		822.00	
90		766.00		910.00	
RANGE(16-84 %)		406.00		517.00	
WT % @ 420 F	45.50	45.50	33.00	33.00	34.00
WT % @ 700 F	86.32	86.47	72.50	72.50	73.85

Table B1 (cont.)

FILE: 1352104C T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-04
CATALYST CO/X11/X9-TC-123 CAT.# 13168-39 80 CC 40.01G(TO 49.8 +9.75G)
FEED H2:CO:ARGON= 62:38:0 @ 382 CC/MN OR 212 GHSV

RUN & SAMPLE NO.	13521-04-11	521-04-12	521-04-13
FEED H2:CO:AR	62:38: 0	62:38: 0	62:38: 0
HRS ON STREAM	382.00	406.00	478.00
PRESSURE,PSIG	499.90	498.70	500.20
TEMP. C	261.00	261.00	261.00
FEED CC/MIN	382.70	382.60	382.02
HOURS FEEDING	24.00	24.00	72.00
EFFLNT GAS LITER	167.89	168.59	525.91
GM AQUEOUS LAYER	85.02	85.06	250.45
GM OIL	51.12	50.91	145.80
MATERIAL BALANCE			
GM ATOM CARBON %	99.98	99.99	100.00
GM ATOM HYDROGEN %	100.00	100.00	100.00
GM ATOM OXYGEN %	100.01	100.01	100.00
RATIO CHX/(H2O+CO2)	0.9995	0.9997	1.0000
RATIO X IN CHX	2.4157	2.4105	2.4222
USAGE H2/CO PRODT	1.8834	1.8896	1.9000
FEED H2/CO FRM EFFLNT	1.6140	1.6115	1.6075
RESIDUAL H2/CO RATIO	0.9829	0.9744	0.9812
RATIO CO2/(H2O+CO2)	0.1127	0.1093	0.1073
K SHIFT IN EFFLNT	0.1248	0.1196	0.1179
SPEC ACTVTY SA,CO/X11	0.4427	0.4421	0.4245
CONVERSION			
ON CO %	70.08	69.61	68.16
ON H2 %	81.78	81.62	80.57
ON CO+H2 %	77.30	77.02	75.81
PRDT SELECTIVITY,WT %			
CH4	14.12	13.86	14.48
C2 HC'S	2.61	2.55	2.63
C3H8	3.63	3.55	3.65
C3H6=	0.68	0.70	0.72
C4H10	2.02	2.00	2.05
C4H8=	1.44	1.46	1.53
C5H12	3.27	3.29	3.41
C5H10=	1.72	1.78	1.86
C6H14	2.39	2.49	2.60
C6H12= & CYCLO'S	0.30	0.29	0.33
C7+ IN GAS	3.05	3.29	3.83
LIQ HC'S	64.77	64.73	62.92
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	24.50	24.14	25.05
C5 -420 F	33.40	34.44	34.68
420-700 F	26.03	26.24	25.51
700-END PT	16.07	15.18	14.76

Table B1 (cont.)

FILE: 1352104C T8Q1	A1		
C5+-END PT	75.50	75.86	74.95
ISO/NORMAL MOLE RATIO			
C4	0.0291	0.0289	0.0291
C5	0.0493	0.0489	0.0497
C6	0.2117	0.2052	0.2017
C4=	0.0968	0.0959	0.0970
PARAFFIN/OLEFIN RATIO			
C3	5.0908	4.8470	4.8369
C4	1.3575	1.3236	1.2918
C5	1.8475	1.7956	1.7859
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))		0.8585	
RATIO CH4/(1-A)**2		6.9276	
ALPHA FRM CORRELATION	0.8919	0.8922	0.8920
ALPHA (EXPTL/CORR)		0.9623	
W%CH4 FRM CORRELATION	8.2840	8.2159	8.2636
W%CH4 (EXPTL/CORR)	1.7045	1.6875	1.7518
LIQ HC COLLECTION			
PHYS. APPEARANCE			
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F		259.00	
16		302.00	
50		489.00	
84		776.00	
90		863.00	
RANGE(16-84 %)		474.00	
WT % @ 420 F	35.00	36.00	36.00
WT % @ 700 F	75.19	76.54	76.54

Table 32

FILE: 1352105A T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-05
CATALYST CO/X11/X9-TC-123 CAT. #13168-47 80 CC 40.21G(TO 59.4 +19.2G)
FEED H2:CO:ARGON= 50:50:0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	13521-05-01	521-05-02	521-05-03	521-05-04	521-05-05
FEED H2:CO:AR	50:50: 0	50:50: 0	51:49: 0	51:49: 0	51:49: 0
HRS ON STREAM	22.00	46.00	142.00	166.00	190.00
PRESSURE,PSIG	301.60	303.10	302.90	300.80	300.30
TEMP. C	241.00	240.00	240.00	240.00	240.00
FEED CC/MIN	400.00	400.99	376.96	375.43	382.37
HOURS FEEDING	22.00	22.00	96.00	24.00	24.00
EFFLNT GAS LITER	202.83	284.81	1229.04	312.28	312.93
GM AQUEOUS LAYER	62.84	53.89	211.33	51.46	53.53
GM OIL	10.17	38.50	146.48	35.02	36.76
MATERIAL BALANCE					
GM ATOM CARBON %	60.96	100.05	100.03	100.14	100.01
GM ATOM HYDROGEN %	71.67	100.00	100.00	100.30	100.02
GM ATOM OXYGEN %	85.12	99.94	99.97	100.09	100.01
RATIO CHX/(H2O+CO2)	0.3331	1.0035	1.0021	1.0015	1.0001
RATIO X IN CHX	2.2606	2.1905	2.1959	2.1982	2.1970
USAGE H2/CO PRODT	3.2069	1.8540	1.9326	1.9373	1.9467
FEED H2/CO FRM EFFLNT	1.1757	1.0140	1.0349	1.0239	1.0375
RESIDUAL H2/CO RATIO	0.5290	0.5568	0.6051	0.6049	0.6085
RATIO CO2/(H2O+CO2)	0.0733	0.0836	0.0558	0.0547	0.0515
K SHIFT IN EFFLNT	0.0418	0.0508	0.0357	0.0350	0.0330
SPEC ACTVTY SA,CO/X11	0.6281	1.0298	0.8365	0.8129	0.8386
CONVERSION					
ON CO %	24.15	35.24	32.38	31.44	32.06
ON H2 %	65.87	64.44	60.46	59.50	60.15
ON CO+H2 %	46.69	49.94	46.66	45.64	46.36
PRDT SELECTIVITY,WT %					
CH4	7.00	3.41	3.58	3.69	3.61
C2 HC'S	2.39	1.17	1.36	1.52	1.41
C3H8	1.51	0.77	0.81	0.85	0.83
C3H6=	2.83	1.68	1.69	1.85	1.81
C4H10	1.40	0.73	0.77	0.83	0.80
C4H8=	5.57	3.00	3.12	3.28	3.16
C5H12	3.71	1.91	2.04	2.18	2.11
C5H10=	6.28	3.35	3.40	3.76	3.58
C6H14	4.66	2.36	2.37	2.56	2.39
C6H12= & CYCLO'S	0.99	0.48	0.47	0.48	0.45
C7+ IN GAS	9.37	4.19	3.93	4.05	3.63
LIQ HC'S	54.30	76.94	76.45	74.95	76.21
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	20.69	10.77	11.32	12.02	11.62
C5 -420 F	34.90	29.47	28.67	28.99	28.25
420-700 F	20.63	33.04	31.48	30.53	30.71
700-END PT	23.79	26.72	28.52	28.45	29.42

Table B2 (cont.)

FILE: 1352105A T8Q1 A1

C5+-END PT	79.31	89.23	88.68	87.98	88.38
ISO/NORMAL MOLE RATIO					
C4	0.0328	0.0295	0.0294	0.0238	0.0344
C5	0.0514	0.0508	0.0498	0.0470	0.0531
C6	0.2464	0.2213	0.1946	0.2237	0.2056
C4=	0.6587	0.7343	0.7517	0.7457	0.7481
PARAFFIN/OLEFIN RATIO					
C3	0.5094	0.4369	0.4553	0.4395	0.4400
C4	0.2424	0.2368	0.2371	0.2441	0.2438
C5	0.5742	0.5533	0.5846	0.5630	0.5736
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8843			
RATIO CH4/(1-A)**2		2.5503			
ALPHA FRM CORRELATION	0.9075	0.9061	0.9031	0.9030	0.9027
ALPHA (EXPTL/CORR)		0.9760			
W%CH4 FRM CORRELATION	2.4164	2.7634	3.5620	3.5853	3.6479
W%CH4 (EXPTL/CORR)	2.8958	1.2346	1.0044	1.0288	0.9899
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F		341.00			
16		381.00			
50		588.00			
84		906.00			
90		995.00			
RANGE(16-84 %)		525.00			
WT % @ 420 F	18.21	22.33	21.51	21.30	21.10
WT % @ 700 F	56.19	65.27	62.69	62.04	61.40

Table B2 (cont.)

FILE: 1352105B T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-05
CATALYST CO/X11/X9-TC-123 CAT. #13168-47 80 CC 40.21G(TO 59.4 +19.2G)
FEED H2:CO:ARGON= 51:49:0 @ 385 CC/MN OR 289 GHSV

RUN & SAMPLE NO.	13521-05-06	521-05-07	521-05-08	521-05-09	521-05-10
FEED H2:CO:AR	51:49: 0	61:39: 0	62:38: 0	61:39: 0	61:39: 0
HRS ON STREAM	214.00	283.00	307.00	331.00	355.00
PRESSURE,PSIG	300.80	499.50	503.10	501.70	502.70
TEMP. C	240.00	260.00	261.00	261.00	261.00
FEED CC/MIN	374.49	384.66	398.06	382.59	385.98
HOURS FEEDING	24.00	69.00	24.00	24.00	24.00
EFFLNT GAS LITER	313.98	508.66	174.23	178.28	178.91
GM AQUEOUS LAYER	50.78	235.54	88.66	82.33	83.62
GM OIL	34.81	135.61	47.94	45.59	46.52
MATERIAL BALANCE					
GM ATOM CARBON %	100.15	99.85	99.78	100.02	100.03
GM ATOM HYDROGEN %	100.31	99.78	100.01	99.99	100.00
GM ATOM OXYGEN %	100.10	99.88	99.97	99.98	99.97
RATIO CHX/(H2O+CO2)	1.0017	0.9996	0.9970	1.0007	1.0010
RATIO X IN CHX	2.2024	2.4699	2.4469	2.4601	2.4530
USAGE H2/CO PRODT	1.9459	1.8529	1.8914	1.8905	1.9007
FEED H2/CO FRM EFFLNT	1.0295	1.5725	1.6137	1.5914	1.5848
RESIDUAL H2/CO RATIO	0.6160	0.9377	0.9484	0.9506	0.9217
RATIO CO2/(H2O+CO2)	0.0522	0.1340	0.1155	0.1173	0.1121
K SHIFT IN EFFLNT	0.0339	0.1451	0.1238	0.1263	0.1163
SPEC ACTVTY SA,CO/X11	0.7924	0.4740	0.4741	0.4324	0.4421
CONVERSION					
ON CO %	31.09	69.37	70.55	68.18	67.73
ON H2 %	58.77	81.73	82.69	81.00	81.23
ON CO+H2 %	45.13	76.92	78.04	76.05	76.01
PRDT SELECTIVITY,WT %					
CH4	3.87	16.66	15.46	16.08	15.76
C2 HC'S	1.47	2.81	2.64	2.74	2.70
C3H8	0.87	4.57	4.38	4.45	4.32
C3H6=	1.72	0.71	0.79	0.73	0.75
C4H10	0.83	2.41	2.50	2.45	2.38
C4H8=	3.17	1.51	1.88	1.79	1.81
C5H12	2.16	3.52	4.25	4.15	4.06
C5H10=	3.46	1.61	2.15	2.13	2.13
C6H14	2.51	2.69	3.17	3.16	3.08
C6H12= & CYCLO'S	0.46	0.32	0.37	0.38	0.37
C7+ IN GAS	3.94	3.06	4.32	3.03	3.05
LIQ HC'S	75.53	60.14	58.09	58.92	59.59
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	11.93	28.67	27.65	28.24	27.72
C5 -420 F	28.32	37.10	39.28	39.59	41.12
420-700 F	30.10	23.65	22.84	23.19	23.47
700-END PT	29.65	10.58	10.22	8.99	7.69

Table B2 (cont.)

FILE: 1352105B T8Q1 A1

C5+-END PT	88.07	71.33	72.35	71.76	72.28
ISO/NORMAL MOLE RATIO					
C4	0.0306	0.0272	0.0360	0.0290	0.0299
C5	0.0524	0.0523	0.0538	0.0511	0.0522
C6	0.2012	0.3453	0.2166	0.2057	0.2101
C4=	0.7789	0.1008	0.1054	0.0957	0.0995
PARAFFIN/OLEFIN RATIO					
C3	0.4828	6.1165	5.3037	5.8407	5.5118
C4	0.2521	1.5464	1.2834	1.3234	1.2666
C5	0.6073	2.1256	1.9229	1.8907	1.8498
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8886		0.8373		0.8314
RATIO CH4/(1-A)**2	3.1203		5.8448		5.5415
ALPHA FRM CORRELATION	0.9023	0.8939	0.8934	0.8932	0.8944
ALPHA (EXPTL/CORR)	0.9848		0.9372		0.9295
W%CH4 FRM CORRELATION	3.7589	7.7243	7.9027	7.9419	7.6351
W%CH4 (EXPTL/CORR)	1.0306	2.1567	1.9567	2.0144	2.0644
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	343.00		262.00		258.00
16	386.00		273.00		270.00
50	610.00		452.00		439.00
84	930.00		716.00		671.00
90	1012.00		804.00		741.00
RANGE(16-84 %)	544.00		443.00		401.00
WT % @ 420 F	20.90	43.08	43.08	45.40	47.71
WT % @ 700 F	60.75	82.40	82.40	84.75	87.10

Table B2 (cont.)

FILE: 1352105C T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-05
CATALYST CO/X11/X9-TC-123 CAT. #13168-47 80 CC 40.21G(TO 59.4 +19.2G)
FEED H2:CO:ARGON= 60:40:0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	13521-05-11	521-05-12	521-05-13
FEED H2:CO:AR	60:40: 0	61:39: 0	61:39: 0
HRS ON STREAM	431.00	453.00	527.00
PRESSURE,PSIG	501.40	502.00	500.20
TEMP. C	265.00	258.00	259.00
FEED CC/MIN	400.00	354.64	374.84
HOURS FEEDING	71.50	22.00	74.00
EFFLNT GAS LITER	540.00	184.79	595.19
GM AQUEOUS LAYER	232.02	63.81	244.32
GM OIL	63.51	34.65	144.02
MATERIAL BALANCE			
GM ATOM CARBON %	78.28	100.06	99.94
GM ATOM HYDROGEN %	90.34	100.00	99.90
GM ATOM OXYGEN %	88.63	99.94	99.95
RATIO CHX/(H2O+CO2)	0.8120	1.0022	0.9998
RATIO X IN CHX	2.8009	2.4559	2.4001
USAGE H2/CO PRODT	2.0637	1.9751	1.9990
FEED H2/CO FRM EFFLNT	1.7312	1.5447	1.5829
RESIDUAL H2/CO RATIO	1.0076	0.9555	0.9442
RATIO CO2/(H2O+CO2)	0.1444	0.0844	0.0671
K SHIFT IN EFFLNT	0.1700	0.0881	0.0679
SPEC ACTVTY SA,CO/X11	0.3488	0.3677	0.3930
CONVERSION			
ON CO %	67.24	57.79	60.56
ON H2 %	80.94	73.89	76.47
ON CO+H2 %	75.92	67.56	70.31
PRDT SELECTIVITY,WT %			
CH4	31.92	16.30	13.74
C2 HC'S	4.46	2.62	2.27
C3H8	8.19	3.67	2.92
C3H6=	0.72	1.08	0.99
C4H10	4.74	2.16	1.72
C4H8=	1.88	1.92	2.01
C5H12	7.17	3.97	3.17
C5H10=	2.36	2.68	2.17
C6H14	4.00	3.09	2.23
C6H12= & CYCLO'S	0.34	0.42	0.25
C7+ IN GAS	0.31	2.83	2.16
LIQ HC'S	33.92	59.27	66.39
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	51.90	27.75	23.63
C5 -420 F	31.38	41.26	41.65
420-700 F	13.36	23.35	26.15
700-END PT	3.36	7.65	8.56

Table B2 (cont.)

FILE: 1352105C T8Q1	A1		
C5+-END PT	48.10	72.25	76.37
ISO/NORMAL MOLE RATIO			
C4	0.0291	0.0396	0.0339
C5	0.0480	0.0578	0.0557
C6	0.3096	0.1804	0.1615
C4=	0.1124	0.0998	0.0000
PARAFFIN/OLEFIN RATIO			
C3	10.8313	3.2486	2.8206
C4	2.4369	1.0828	0.8219
C5	2.9472	1.4414	1.4175
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))			
RATIO CH4/(1-A)**2			
ALPHA FRM CORRELATION	0.8899	0.8940	0.8940
ALPHA (EXPTL/CORR)			
W%CH4 FRM CORRELATION	8.9584	7.6418	7.6659
W%CH4 (EXPTL/CORR)	3.5632	2.1327	1.7918
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	50.70	47.71	47.71
WT % @ 700 F	90.10	87.10	87.10

Table B3

FILE: 1362501A T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13625-01
CATALYST CO/X11/X9-AL2O3 CAT.# 13165-36 250 CC 82.9 G(TO 161.1 +78.G)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	13625-01-01	625-01-02	625-01-03	625-01-04	625-01-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	67.00	91.00	115.00	139.00	163.00
PRESSURE,PSIG	297.70	299.40	303.20	297.10	305.80
TEMP: C	243.00	240.00	241.00	241.00	241.00
FEED CC/MIN	1260.00	1260.00	1260.00	1260.00	1260.00
HOURS FEEDING	67.00	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	3202.31	1281.48	1298.15	1293.94	1297.04
GM AQUEOUS LAYER	397.82	114.24	108.90	107.15	109.53
GM OIL	195.79	58.41	73.04	76.41	72.87
MATERIAL BALANCE					
GM ATOM CARBON %	90.35	93.99	98.73	98.87	98.29
GM ATOM HYDROGEN %	95.92	96.71	98.68	99.02	99.68
GM ATOM OXYGEN %	94.99	97.64	98.90	98.15	98.19
RATIO CHX/(H2O+CO2)	0.8072	0.8174	0.9908	1.0377	1.0050
RATIO X IN CHX	2.2341	2.2458	2.2343	2.2283	2.2367
USAGE H2/CO PRODT	2.2788	2.2805	2.0697	2.0289	2.0635
FEED H2/CO FRM EFFLNT	1.0616	1.0290	0.9995	1.0015	1.0142
RESIDUAL H2/CO RATIO	0.7185	0.7591	0.7371	0.7411	0.7507
RATIO CO2/(H2O+CO2)	0.0190	0.0164	0.0183	0.0168	0.0164
K SHIFT IN EFFLNT	0.0139	0.0126	0.0137	0.0126	0.0125
SPEC ACTVTY SA,CO/X11	0.7085	0.6450	0.6999	0.7220	0.7011
CONVERSION					
ON CO %	21.99	17.74	19.69	20.22	20.08
ON H2 %	47.20	39.32	40.77	40.57	40.85
ON CO+H2 %	34.97	28.68	30.23	30.60	30.53
PRDT SELECTIVITY,WT %					
CH4	5.86	6.46	5.75	5.40	6.00
C2 HC'S	1.61	1.10	1.07	1.23	0.96
C3H8	0.91	1.06	0.91	0.86	0.96
C3H6=	1.69	1.94	1.68	1.60	1.77
C4H10	1.01	1.20	1.02	0.96	1.08
C4H8=	3.17	3.79	3.22	3.07	3.44
C5H12	2.77	3.38	2.90	2.71	2.95
C5H10=	4.02	4.63	4.17	3.87	4.12
C6H14	2.77	3.42	2.94	2.61	2.96
C6H12= & CYCLO'S	0.38	0.43	0.37	0.38	0.39
C7+ IN GAS	7.97	5.54	4.10	4.34	4.90
LIQ HC'S	67.85	67.05	71.87	72.97	70.48
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	14.24	15.54	13.66	13.12	14.21
C5 -420 F	33.75	33.07	30.64	29.69	29.94
420-700 F	36.94	36.50	38.00	37.43	35.05
700-END PT	15.06	14.89	17.71	19.76	20.80

Table B3 (cont.)

FILE: 1362501A T8Q1	A1				
C5+-END PT	85.76	84.46	86.34	86.88	85.79
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0000	0.0000	0.0000	0.0000
C5	0.0349	0.0280	0.0371	0.0323	0.0281
C6	0.0580	0.0498	0.0508	0.0000	0.0402
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.5145	0.5211	0.5174	0.5134	0.5183
C4	0.3074	0.3051	0.3070	0.3037	0.3033
C5	0.6710	0.7099	0.6765	0.6799	0.6947
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8723			
RATIO CH4/(1-A)**2		3.9606			
ALPHA FRM CORRELATION	0.8956	0.8947	0.8957	0.8951	0.8952
ALPHA (EXPTL/CORR)		0.9749			
W%CH4 FRM CORRELATION	5.6404	5.7747	5.5707	5.6975	5.7129
W%CH4 (EXPTL/CORR)	1.0392	1.1184	1.0324	0.9473	1.0495
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F		353.00			
16		391.00			
50		538.00			
84		753.00			
90		836.00			
RANGE(16-84 %)		362.00			
WT % @ 420 F	23.36	23.36	22.49	21.62	20.75
WT % @ 700 F	77.80	77.80	75.36	72.92	70.48

Table B3 (cont.)

FILE: 1362501B T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13625-01
CATALYST CO/X11/X9-AL2O3 CAT.# 13168-36 250 CC 82.9 G(TO 161. +78.2G)
FEED H2:CO:ARGON= 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	13625-01-06	625-01-07	625-01-08	625-01-09	625-01-10
FEED H2:CO:AR	50:50: 0	60:40: 0	61:39: 0	61:39: 0	61:39: 0
HRS ON STREAM	259.00	283.00	307.00	331.00	401.00
PRESSURE,PSIG	304.10	501.30	500.60	498.70	499.80
TEMP. C	240.00	261.00	261.00	261.00	261.00
FEED CC/MIN	1260.00	1189.42	1181.27	1161.32	1174.00
HOURS FEEDING	96.00	24.00	24.00	24.00	70.00
EFFLNT GAS LITER	5225.80	712.47	699.39	716.63	2160.68
GM AQUEOUS LAYER	427.30	231.40	232.67	221.68	647.84
GM OIL	290.30	120.32	111.62	109.03	293.19
MATERIAL BALANCE					
GM ATOM CARBON %	98.42	100.11	100.02	100.00	99.96
GM ATOM HYDROGEN %	100.04	100.17	100.00	100.00	100.06
GM ATOM OXYGEN %	97.98	100.09	99.99	100.00	99.92
RATIO CHX/(H2O+CO2)	1.0233	1.0005	1.0006	1.0000	1.0009
RATIO X IN CHX	2.2371	2.4196	2.4307	2.4451	2.4336
USAGE H2/CO PRODT	2.0510	2.0429	2.0625	2.0771	2.0947
FEED H2/CO FRM EFFLNT	1.0165	1.5310	1.5653	1.5580	1.5699
RESIDUAL H2/CO RATIO	0.7588	0.9385	0.9690	0.9826	1.0102
RATIO CO2/(H2O+CO2)	0.0150	0.0547	0.0497	0.0473	0.0392
K SHIFT IN EFFLNT	0.0116	0.0543	0.0507	0.0488	0.0412
SPEC ACTVTY SA,CO/X11	0.7276	0.4812	0.4769	0.4448	0.4313
CONVERSION					
ON CO %	19.94	53.65	54.53	52.57	51.61
ON H2 %	40.24	71.58	71.85	70.09	68.87
ON CO+H2 %	30.18	64.50	65.10	63.24	62.15
PRDT SELECTIVITY,WT %					
CH4	5.95	14.92	15.55	16.21	15.93
C2 HC'S	1.15	2.55	2.67	2.72	2.68
C3H8	0.94	2.84	3.10	3.20	3.18
C3H6=	1.67	1.67	1.58	1.52	1.42
C4H10	1.06	1.94	2.03	2.06	2.08
C4H8=	3.34	2.47	2.42	2.40	2.45
C5H12	2.93	3.45	3.60	3.50	3.57
C5H10=	4.18	2.65	2.60	2.66	3.04
C6H14	2.88	3.08	3.29	3.16	2.95
C6H12= & CYCLO'S	0.42	0.46	0.51	0.54	0.58
C7+ IN GAS	5.03	5.28	8.18	6.26	10.43
LIQ HC'S	70.45	58.70	54.45	55.78	51.68
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	14.11	26.39	27.37	28.11	27.75
C5 -420 F	27.61	36.63	38.33	36.94	40.38
420-700 F	30.62	25.44	23.59	24.27	22.79
700-END PT	27.67	11.55	10.71	10.68	9.08

Table B3 (cont.)

FILE: 1362501B T8Q1 A1

C5+-END PT	85.89	73.61	72.63	71.89	72.25
ISO/NORMAL MOLE RATIO					
C4	0.0000	0.0323	0.0311	0.0315	0.0335
C5	0.0310	0.0583	0.0559	0.0567	0.0533
C6	0.0194	0.3017	0.2850	0.2948	0.1522
C4=	0.0000	0.0681	0.0731	0.0754	0.0747
PARAFFIN/OLEFIN RATIO					
C3	0.5367	1.6263	1.8735	2.0046	2.1346
C4	0.3062	0.7573	0.8102	0.8270	0.8183
C5	0.6812	1.2671	1.3458	1.2814	1.1403
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8970		0.8485		
RATIO CH4/(1-A)**2	5.6074		6.7805		
ALPHA FRM CORRELATION	0.8951	0.8937	0.8925	0.8919	0.8909
ALPHA (EXPTL/CORR)	1.0022		0.9508		
W%CH4 FRM CORRELATION	5.7128	7.8248	8.1395	8.2964	8.5475
W%CH4 (EXPTL/CORR)	1.0412	1.9073	1.9108	1.9535	1.8640
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F	366.00		280.00		
16	411.00		327.00		
50	631.00		493.00		
84	895.00		733.00		
90	969.00		808.00		
RANGE(16-84 %)	484.00		406.00		
WT % @ 420 F	17.26	37.00	37.00	37.33	38.33
WT % @ 700 F	60.72	80.33	80.33	80.85	82.43

Table B3 (cont.)

FILE: 1362501C T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13625-01
CATALYST CO/X11, 19-AL2O3 CAT. #13168-36 250 CC 82.9 G(TO 161. +78.2G)
FEED H2:CO:ARGON= 61:39:0 @ 1165 CC/MN OR 280 GHSV

RUN & SAMPLE NO.	13625-01-11	625-01-12	625-01-13	625-01-14	625-01-15
FEED H2:CO:AR	61:39: 0	61:39: 0	61:39: 0	61:39: 0	61:39: 0
HRS ON STREAM	425.00	449.00	473.00	497.00	569.00
PRESSURE,PSIG	508.70	510.00	509.20	503.70	499.70
TEMP. C	260.00	261.00	261.00	261.00	261.00
FEED CC/MIN	1164.98	1180.00	1159.66	1194.20	1165.25
HOURS FEEDING	24.00	24.00	24.00	24.00	72.00
EFFLNT GAS LITER	757.14	756.35	760.19	765.17	2343.44
GM AQUEOUS LAYER	214.73	220.54	212.17	224.43	629.18
GM OIL	97.80	92.45	99.09	85.08	273.92
MATERIAL BALANCE					
GM ATOM CARBON %	100.00	99.91	100.08	100.00	100.00
GM ATOM HYDROGEN %	99.99	99.97	100.24	100.00	100.00
GM ATOM OXYGEN %	100.00	99.88	100.01	100.00	100.00
RATIO CHX/(H2O+CO2)	1.0000	1.0005	1.0015	1.0000	1.0000
RATIO X IN CHX	2.4509	2.4428	2.4577	2.4410	2.4585
USAGE H2/CO PRODT	2.1041	2.0997	2.1090	2.1057	2.1196
FEED H2/CO FRM EFFLNT	1.5752	1.5747	1.5697	1.5765	1.5815
RESIDUAL H2/CO RATIO	1.0362	1.0249	1.0314	1.0215	1.0615
RATIO CO2/(H2O+CO2)	0.0391	0.0391	0.0381	0.0370	0.0351
K SHIFT IN EFFLNT	0.0422	0.0417	0.0409	0.0392	0.0387
SPEC ACTVTY SA,CO/X11	0.4265	0.4219	0.4034	0.4296	0.3918
CONVERSION					
ON CO %	50.47	51.16	49.96	51.18	49.14
ON H2 %	67.42	68.21	67.12	68.37	65.87
ON CO+H2 %	60.84	61.59	60.44	61.70	59.39
PRDT SELECTIVITY,WT %					
CH4	16.44	16.23	16.68	15.92	16.85
C2 HC'S	2.60	2.71	2.77	2.72	2.70
C3H8	3.40	3.42	3.40	3.31	3.43
C3H6=	1.57	1.51	1.56	1.44	1.41
C4H10	2.31	2.26	2.26	2.26	2.31
C4H8=	3.11	3.00	3.19	3.09	3.01
C5H12	4.37	4.33	4.28	4.98	4.50
C5H10=	3.77	3.67	3.73	3.63	3.86
C6H14	3.54	3.75	3.65	6.00	3.84
C6H12= & CYCLO'S	0.71	0.73	0.73	0.96	0.75
C7+ IN GAS	6.30	10.58	4.66	12.32	7.71
LIQ HC'S	51.87	47.80	53.09	43.37	49.63
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	29.43	29.12	29.86	28.75	29.71
C5 -420 F	38.75	41.72	37.93	44.94	40.18
420-700 F	22.97	21.26	23.72	19.37	22.17
700-END PT	8.84	7.90	8.49	6.94	7.94

Table B3 (cont.)

FILE: 1362501C T8Q1 A1

C5+-END PT	70.57	70.88	70.14	71.25	70.29
ISO/NORMAL MOLE RATIO					
C4	0.0329	0.0327	0.0337	0.0321	0.0335
C5	0.0515	0.0499	0.0538	0.0491	0.0501
C6	0.1343	0.1372	0.1321	0.1024	0.1247
C4=	0.0693	0.0706	0.0691	0.0652	0.0000
PARAFFIN/OLEFIN RATIO					
C3	2.0590	2.1654	2.0819	2.1992	2.3172
C4	0.7170	0.7284	0.6853	0.7061	0.7400
C5	1.1246	1.1462	1.1170	1.3355	1.1343
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))			0.8441		
RATIO CH4/(1-A)**2			6.8582		
ALPHA FRM CORRELATION	0.8909	0.8911	0.8908	0.8908	0.8891
ALPHA (EXPTL/CORR)			0.9475		
W%CH4 FRM CORRELATION	8.5665	8.5601	8.6302	8.6060	9.0229
W%CH4 (EXPTL/CORR)	1.9195	1.8962	1.9322	1.8499	1.8679
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILATN					
10 WT % @ DEG F			274.00		
16			321.00		
50			485.00		
84			700.00		
90			750.00		
RANGE(16-84 %)			379.00		
WT % @ 420 F	38.66	39.00	39.33	39.33	39.33
WT % @ 700 F	82.95	83.48	84.00	84.00	84.00

Table B3 (cont.)

FILE: 1362501D T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13625-01
CATALYST CO/X11/X9-AL2O3 CAT.# 13168-36 250 CC 82.9 G(TO 161. +78.2G)
FEED H2:CO:ARGON= 62:38:0 @ 1129 CC/MN OR 271 GHSV

RUN & SAMPLE NO.	13625-01-16	625-01-17	625-01-18	625-01-19
FEED H2:CO:AR	61:39: 0	61:39: 0	61:39: 0	61:39: 0
HRS ON STREAM	618.50	666.50	738.00	787.00
PRESSURE,PSIG	508.00	502.60	509.90	496.00
TEMP. C	253.00	260.00	260.00	260.00
FEED CC/MIN	1128.65	1166.13	1153.45	1148.54
HOURS FEEDING	49.50	48.00	71.50	49.00
EFFLNT GAS LITER	1683.92	1636.20	2431.05	1701.95
GM AQUEOUS LAYER	393.94	402.32	587.81	391.18
GM OIL	195.23	170.17	253.00	165.97
MATERIAL BALANCE				
GM ATOM CARBON %	99.99	100.00	99.99	99.99
GM ATOM HYDROGEN %	99.99	100.00	99.99	99.99
GM ATOM OXYGEN %	99.99	100.00	100.00	99.99
RATIO CHX/(H2O+CO2)	1.0000	1.0000	1.0000	1.0000
RATIO X IN CHX	2.3464	2.4749	2.4750	2.4807
USAGE H2/CO PRODT	2.1310	2.1336	2.1377	2.1485
FEED H2/CO FRM EFFLNT	1.6059	1.5658	1.5722	1.5769
RESIDUAL H2/CO RATIO	1.1763	1.0654	1.0810	1.1034
RATIO CO2/(H2O+CO2)	0.0135	0.0331	0.0318	0.0292
K SHIFT IN EFFLNT	0.0161	0.0365	0.0355	0.0332
SPEC ACTVTY SA,CO/X11	0.4597	0.3878	0.3746	0.3613
CONVERSION				
ON CO %	45.00	46.84	46.49	45.31
ON H2 %	59.71	63.83	63.21	61.73
ON CO+H2 %	54.07	57.21	56.71	55.36
PRDT SELECTIVITY,WT %				
CH4	11.86	17.66	17.63	17.92
C2 HC'S	1.71	2.83	2.78	2.83
C3H8	1.88	3.51	3.49	3.41
C3H6=	1.36	1.55	1.39	1.40
C4H10	1.53	2.42	2.43	2.34
C4H8=	4.27	3.43	3.32	3.33
C5H12	3.50	4.76	4.78	4.95
C5H10=	3.91	4.13	4.11	4.30
C6H14	3.29	3.90	3.85	4.16
C6H12= & CYCLO'S	0.78	0.82	0.80	0.90
C7+ IN GAS	8.11	6.94	6.52	6.28
LIQ HC'S	57.79	48.04	48.91	48.18
TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	22.61	31.41	31.03	31.22
C5 -420 F	42.33	39.44	39.29	39.55
420-700 F	25.81	21.46	21.85	21.52
700-END PT	9.25	7.69	7.82	7.71

Table B3 (cont.)

FILE: 1362501D T8Q1	A1			
C5+-END PT	77.39	68.59	68.97	68.78
ISO/NORMAL MOLE RATIO				
C4	0.0376	0.0376	0.0322	0.0334
C5	0.0469	0.0503	0.0477	0.0462
C6	0.0922	0.1173	0.1172	0.1052
C4=	0.3059	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	1.3210	2.1560	2.3982	2.3296
C4	0.3454	0.6819	0.7071	0.6787
C5	0.8705	1.1202	1.1302	1.1212
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))				
RATIO CH4/(1-A)**2				
ALPHA FRM CORRELATION	0.8885	0.8895	0.8895	0.8878
ALPHA (EXPTL/CORR)				
W%CH4 FRM CORRELATION	8.9714	8.9071	8.9561	9.3235
W%CH4 (EXPTL/CORR)	1.3215	1.9826	1.9686	1.9217
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	39.33	39.33	39.33	39.33
WT % @ 700 F	84.00	84.00	84.00	84.00

Table B4

FILE: 1352106A T8Q1 A1

RESULT OF SYNGAS OPERATION

RUN NO. 13521-06
CATALYST FE-TC-123 CAT. #13168-48 80 CC 39.59G(TO
FEED H2:CO:ARGON= 50:50:0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	13521-06-01	521-06-02	521-06-03
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	92.75	115.75	312.25
PRESSURE,PSIG	296.90	296.60	296.20
TEMP. C	250.00	250.00	250.00
FEED CC/MIN	400.00	400.00	400.00
HOURS FEEDING	92.75	23.00	196.50
EFFLNT GAS LITER	1684.66	434.93	3755.27
GM AQUEOUS LAYER	54.00	12.85	111.07
GM OIL	4.79	1.52	7.88
MATERIAL BALANCE			
GM ATOM CARBON %	88.04	91.16	90.16
GM ATOM HYDROGEN %	93.01	95.58	96.37
GM ATOM OXYGEN %	91.04	94.24	93.93
RATIO CHX/(H2O+CO2)	0.8059	0.8000	0.7499
RATIO X IN CHX	2.5049	2.5197	2.5484
USAGE H2/CO PRODT	1.3496	1.3433	1.3987
FEED H2/CO FRM EFFLNT	1.0565	1.0485	1.0689
RESIDUAL H2/CO RATIO	0.9782	0.9736	0.9922
RATIO CO2/(H2O+CO2)	0.3923	0.3983	0.3780
K SHIFT IN EFFLNT	0.6313	0.6444	0.6029
SPEC ACTVTY SA,CO/X11	0.2785	0.2686	0.2451
CONVERSION			
ON CO %	21.10	20.26	18.86
ON H2 %	26.95	25.96	24.68
ON CO+H2 %	24.10	23.17	21.87
PRDT SELECTIVITY,WT %			
CH4	15.32	15.74	17.23
C2 HC'S	14.27	15.20	15.60
C3H8	5.04	4.88	4.79
C3H6=	12.30	11.37	11.41
C4H10	4.00	3.70	3.32
C4H8=	14.52	14.08	14.09
C5H12	7.99	7.43	8.24
C5H10=	6.10	5.84	7.32
C6H14	6.22	6.10	6.58
C6H12= & CYCLO'S	0.00	0.00	0.00
C7+ IN GAS	8.48	8.20	6.49
LIQ HC'S	5.76	7.46	4.93
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	65.45	64.97	66.44
C5 -420 F	30.41	29.67	30.03
420-700 F	2.28	2.95	1.95
700-END PT	1.86	2.41	1.58

Table B4 (cont.)

FILE: 1352106A T8Q1	A1		
C5+-END PT	34.55	35.03	33.56
ISO/NORMAL MOLE RATIO			
C4	0.0935	0.1046	0.1126
C5	0.0848	0.0850	0.1050
C6	0.2205	0.2488	0.2871
C4=	0.1288	0.1306	0.1215
PARAFFIN/OLEFIN RATIO			
C3	0.3914	0.4096	0.4004
C4	0.2662	0.2536	0.2271
C5	1.2725	1.2362	1.0947
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))			
RATIO CH4/(1-A)**2			
ALPHA FRM CORRELATION			
ALPHA (EXPTL/CORR)			
W%CH4 FRM CORRELATION	9.4506	9.4093	9.5956
W%CH4 (EXPTL/CORR)	1.6215	1.6728	1.7969
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	28.20	28.16	28.36
WT % @ 700 F	67.76	67.71	67.96

APPENDIX C. TECHNO-ECONOMIC STUDIES OF THE Co/X11/X9/TC-123 CATALYST

APPENDIX C
Techno-Economic Studies
on the
Co/X11/X9/TC-123 Catalyst

TABLE OF CONTENTS

Techno-economic Studies
on the
Co/X11/X9/TC-123 Catalyst
(Catalyst No. 55)

C-L Yang and A.C.Frost

I. Summary

Rate expressions determined from Berty (CSTR) reactor data for the Co/X11/X9/TC-123 catalyst were incorporated into a computer program that generated process design curves for a fixed bed tubular reactor.

These process design curves were used to predict the performance of the F-T reactors that were part of a plant that used syngas (95,061 pound moles per hour) to produce C3+ liquid fuels. Unreacted syngas leaving the F-T reactors was recycled back to the reactors after the methane and ethane present were steam reformed back to syngas.

The economic optimum reactor conditions for the Co/X11/X9/TC-123 catalyst were: 250 C, 500 psig, 380 GHSV, and a 1.5:1 H2:CO feed ratio.

While the resulting conversion per pass through the reactors at these conditions was only 70%, this proved to be the optimum balance between adding more reactors for a higher conversion per pass (with less downstream equipment for a smaller recycle stream) and fewer or smaller reactors for a lower conversion per pass (with more downstream equipment for a larger recycle stream).

At the optimum conditions, with a one year catalyst

life, the cost of liquid fuel was $2.12 per gallon in 1988 dollars. A two year catalyst life would lower the cost of the liquid fuel to $2.00 per gallon.

II. Introduction

The techno-economic evaluation required to complete the Task 5 and Task 6 studies was an extension of two previous studies carried out by an independent evaluator under contracts with the D.O.E. The first study examined the cost of producing liquid fuels with the Co-TC-101 catalyst developed under the first D.O.E. contract performed by Union Carbide (DE-AC22-81PC40077). The second study examined the cost of employing the Co/X11/TC-123 catalyst (Catalyst No. 45), developed under the present contract.

This final study uses the same process flow scheme used in the previous two studies. Figure 1 shows that fresh syngas feed is combined with the recycled feed before entering the F-T reactors. The effluent passes sequentially through a CO2 removal system, hydrocarbon recovery columns, a compressor, and an autothermal reformer (which converts methane and ethane into syngas). The C3+ product is separated into standard grades of C3-C4, gasoline, and diesel fuel.

The The F-T reactors incorporated into Figure 1 are parallel trains of ARGE-type, fixed bed, tubular reactors. Figure 2 shows that each reactor has its own, local 2.3:1 recycle stream for improved temperature control. The condensables removed from this local recycle stream are sent to the hydrocarbon recovery columns which handle the main flow

stream, as shown in Figure 1.

The performance of each of the F-T reactors was predicted from the FIXBD computer program developed under the previous contract (DE-AC22-81PC40077). This program calculates the H2 and CO conversion levels, the methane make, and the C2+ product distribution for the reactor when the pressure, temperature, local recycle ratio, H2:CO fresh feed ratio, GHSV, catalyst density, and the rate correlations for the catalyst in question are inputed to the program.

The rate correlations for the Co/X11/X9/TC-123 catalyst (Catalyst No. 55) developed under this contract were determined from numerous experimental runs in the Berty (CSTR) reactors at different temperatures, pressures, flow rates, H2:CO ratios, and GHSV's.

The details of how these catalyst rate correlations were obtained, of how they were used in the FIXBD computer simulation programs of an ARGE-type commercial F-T reactor, and of the techno-economic study that incorporated the simulations are given in the following sections, in the same order.

III. Catalyst Rate Correlations

a) Data Bank

A number of runs were conducted for the purpose of obtaining rate and product selectivity correlations for the Co/X11/X9/TC-123 catalyst. The runs at 500 psig covered thirteen different conditions: three levels of temperature, five levels of space velocity, and four levels of H2:CO feed ratio. All of the catalyst runs were started at the standard

conditions of 300 psig, 240 C, 300 GHSV, and 1:1 H2:CO feed ratio to establish an adequate catalyst activity. The last run was concluded with a test at 300 psig to complete the study. The following table presents the parametric study by run number:

Desig-nation	Press. psig	Temp. C	Sp.Vel. vg/v/hr.	Feed H2:CO	570--16	570--17	600--01	600--02	600--03
(A)	300	240	300	1.0	*	*	*	*	
(1)	500	240	300	1.0		*			
(2)	500	240	1000	1.0		*			
(3)	500	260	300	1.0		*			
(4)	500	260	1000	1.0		*	*	*	
(5)	500	240	300	1.5		*			
(6)	500	240	1000	1.5		*			
(7)	500	260	300	1.5	*		*		*
(8)	500	260	1000	1.5	*	*			
(9)	500	250	550	1.5				*	
(10)	500	250	1500	1.5				*	
(11)	500	250	550	1.9				*	
(12)	500	250	1500	1.9				*	
(13)	500	250	900	1.5					*
(14)	300	250	900	1.5					*

As can be seen , these conditions were all studied during the course of five different runs. Three different catalyst batches were used which were activated on five separate occasions. All of the catalyst preparations were of the same formulation and it was apparent that they all had a similar performance in

service.

b) CO Rate Correlation

The correlation model for the CO conversion rate is:

RCO = K*(pH2)**a*(pCO)**b*exp(A*(tc-240)/(R*T1*T2))*exp(m*Hr)

Ln RCO = LnK + a Ln pH2 + b Ln pCO + A2 dt/(R*T1*T2) + m*Hr

where a, b, A2, m, and intercept k are determined by regression. The terms used are listed below:

Ln	for natural logarithm
RCO	conversion rate in millimole CO/hr/gm of catalyst
pH2	partial pressure of H2 in psia
pCO	partial pressure of CO in psia
a,b	power coefficients on H2 and CO partial pressures
A2	Arrhenius activation energy in 10,000 calorie/gmole
dt	(tc-240), with 240 C as reference, T1 and T2 in K
m	deactivation rate, unit/hour, should be negative
LnK	intercept from the correlation

The values obtained from the regressions of the data are:

LnK	a	b	A2	m
-0.7113	0.7020	-0.2025	1.2115	-0.0003136

It is notable that "m" was obtained from a single long run (12570-04). This deactivation constant was then imposed upon the data of the five process study runs in consideration. Water vapor partial pressure was not found to be a significant factor for this cobalt catalyst.

c) Usage Ratio Expression

The usage expression is the ratio of the consumption of hydrogen to the consumption of carbon monoxide, and is used to compute the moles of hydrogen that are consumed from the carbon monoxide consumption rate defined in part b, above.

In the past, the usage ratio was assumed to be constant. However, with support from the data bank, the usage ratio is now defined more accurately as:

Ln US = -0.9371 + 0.06813 RHC + 1.2742 FT + 0.06652 LSV

where:

Ln for natural logarithm

US usage ratio, ratio of H2 consumption to that of CO

LRHC Ln ratio of H2/CO partial pressures in the reactor

FT 1000/(R*T), gas constant R and T in K

SV fresh feed gas space velocity, vol.gas/hr./vol.cat with gas volume measured at 70 F or 24,147 cc/gmole

LSV Ln of space velocity

The mean usage ratio (52 data points) = 2.03 +/- 0.14; the lowest was = 1.77 and the highest was = 2.27.

d) Methane Rate Expression

It was found that the best way to handle the methane make was to express the equation in terms of the following logarithmic rate function:

Ln RCH4 = LnK + a Ln pH2 + b Ln pCO + A2 dt/(R*T1*T2)

The coefficients are:

LnK	a	b	A2
-2.042	2.232	-2.017	3.196

Where:

RCH4 generation rate in millimole CH4/hr./gram catalyst

pH2 partial pressure of H2 in psia

pCO partial pressure of CO in psia

a,b power coefficients of H2 and CO partial pressures

A2 Arrhenius activation energy in 10,000 cal./gmole

dt (tc-240), with 240 C as reference, T1 and T2 in K

Ln K intercept from the correlation

e) Alpha, the Product Selectivity Correlation

Alpha, the chain growth factor, was also best correlated in a logarithmic form. The equation:

$$\text{Ln alpha} = \text{LnK} + a \text{ Ln RHC} + A\ 1000/(RT) + b \text{ Ln psi} + c \text{ Ln SV}$$

Where:

Ln for natural logarithm

RHC ratio of H2 to CO partial pressures in the reactor

RT gas constant (1.98726) times T in K

psi total system pressure in psig

SV fresh feed space velocity, vol. gas/hour/volume catalyst with gas measured at 70 F or 24,147 cc/gmole

The values for the coefficients are:

LnK	a	A	b	c
-1.293	-0.05238	0.9623	0.0500	-0.01370

IV. FIXBD Computer Simulation

a) What it Simulates

The FIXBD program computes the product composition of

the reactor effluent for the process flow as presented in Figure 2. It simulates an isothermal packed bed tubular reactor having its own, local recycle stream, a condenser, a knock-out pot, and an effluent stream. The knock-out pot removes the water and C5+ product, which is sent to the hydrocarbon recovery columns shown in Figure 1. The non-condensables from the knock-out pot contain C1-C4 hydrocarbons, CO2, and unreacted syngas which becomes part of the overall recycle stream.

b) The Computer Program

Figure 3 shows that the Berty reactor supplied rate and selectivity correlations discussed previously are incorporated into the FIXBD program. The fixed catalyst bed in the tubular reactor is assumed to operate at some average inputed temperature and is incremented into 50 segments. Starting with the first, top segment, the computer program sequentially calculates (from the Berty reactor derived equations and the partial pressures remaining in the prior segment) the CO conversion, the methane make, and the remaining C2+ product slate for each of the segments down the reactor. The effluent leaving the reactor is then split into condensed C5+ hydrocarbons, condensed water, off gas (free of C5+ hydrocarbons and water), and the desired quantity of recycle. That recycle stream is mixed with the fresh feed stream and the segment-by-segment calculations down the bed are repeated as before. This looping continues until the effluent H2/CO ratio (a sensitive indicator of reactor steady state) levels out to a nearly constant value, at which time appropriate step changes are made

in the H2 and CO concentrations so that additional looping results in convergence of the effluent H2/CO ratio from the opposite direction (i.e., if the H2/CO ratio was asymtotically decreasing during the initial looping period, then the direction of the step changes in the H2 and CO concentrations will cause the effluent H2/CO ratio to asymtotically increase during the second looping period). Once such two directional convergences (to the same H2/CO value) have taken place, steady state is assumed, and the program is ended.

c) Program Check Against Berty Reactor Data

A comparison was made of the predicted performance of the Co/X11/X9/TC-123 catalyst, based on the FIXBD computer simulation program, with an actual Berty run obtained at 500 psig, 260 C, an assumed catalyst age of 500 hours (equivalent to 85.5% of fresh catalyst activity), a catalyst bed density of 0.49 grams per cubic centimeter, a recycle ratio of 25.0 to 1, and nothing condensed from the recycle stream. The results:

Variable	Laboratory Berty Reactor	Simulation FIXBD Program
Feed H2/CO	1.50	1.50
Temperature,C	260.	260.
Pressure, psia	514.7	514.7
Syngas Conversion, %	77.0	76.6
Product Distribution,	Wt.%	Wt.%
Methane	10.0	12.7
C2-C4	11.0	9.9

C5-350 F (C10)	29.0	26.5
350 F-650 F (C20)	27.9	31.0
650 F+ and C21+	22.0	19.9
C5+	79.0	77.4

d) Program Check Against Third Party Data

Samples of Catalyst No. 55 were sent to several different companies during 1986 for independant testing. These companies tested the catalyst samples in fixed bed reactors, with and without recyucle streams, and free of condensables.

Comparison of the experimental test results from the indepandent laboratory tests with the predicted results from the FIXBD simulation program were generally very good for the CO conversion level and the alpha value for the C2+ product. The comparison was not as good in the case of the methane make, with the experimental results being both higher and lower than the FIXBD program.

The good agreement shown in section c) and the generally good agreement with the third party results, proved the reliability of the FIXBD program for generating the process design curves required for the Task 6 techno-economic study.

V. Techno-Economic Study

a) Background and General Basis

The first techno-economic study made on one of UCC's catalysts was done by an independent contractor on behalf of the D.O.E. The study was based upon test results from a Co/UCC-101 catalyst. Design curves, generated in the same fashion as

described above, were provided to the contractor, who found the unit cost for producing an all liquid product with this catalyst under non-optimized conditions to be $2.70 per gallon of liquid fuel in 1988 dollars, assuming the $20 per pound catalyst had a one third year life (four months).

In 1985 and 1986 a second generation catalyst was developed which employed Co promoted by X11 and supported on TC-123. This catalyst was capable of higher activity and lower methane production. Performance curves were generated and the independent contractor again provided a techno-economic study that found the unit cost for producing an all liquid product under non-optimized conditions was $2.19 per gallon of liquid fuel in 1988 dollars when the $20 per pound catalyst was assumed to have a one half year life (six months) and a 0.47 grams per cubic centimeter bulk density.

Additionally, the contractor was asked to perform a sensitivity analysis for ten process parameters. The results of that sensitivity analysis was the basis of the Task 2 effort, and showed that the GHSV, methane make, and catalyst life were major contributors to the cost of the process.

The process scheme, equipment costs, operating costs, and overhead rates used by the independent contractors for these past studies became the basis for the UCC evaluation of the Co/X11/X9/TC-123 catalyst.

b) Process Scheme

The flow diagram used for the techno-economic evaluation is shown in Figure 1 and is basewd on an all liquid mode, with no

net production of methane or ethane. All methane and ethane produced is autothermally steam reformed back to syngas, and the only major stream that leaves the battery limits is the C3+ liquid product.

While such recycling to extinction of the internally produced methane and ethane requires that some of it be consumed through the oxidation to supply the heat required for the endothermic steam reforming reaction, most of the syngas entering the battery limits will be converted to C3= liquid product. Consequently the size, and hence the cost, of the refinery and upgrading section of the plant (shown in the center of the Figure 1 flow diagram) will remain fairly constant, regardless of the operating conditions chosen for the the F-T reactors.

The chosen F-T reactor conditions will, however, affect the size and cost of both the F-T reactors and the treating units in the overall recycle steam (i.e., the CO2 removal unit, the hydrocarbon recovery columns, the gas compressor, and the hydrothermal reformer that encircle the refinery and upgrading block in Figure 1). Furthermore, the size of the treating units in the overall recycle stream is inversely proportional to the size of the F-T reactors. For instance, very large F-T reactors (or very low GHSV's) yield a very high conversion per pass to C3+ liquid product and only a small amount of unreacted syngas to be recycled. Conversely, small F-T reactors (very high GHSV's) yield low conversions per pass and a large amount of unconverted syngas to be recycled.

Thus, for the case of a relatively constant C3+ refinery and upgrading cost, the optimal cost of the whole process will be the optimal balance between the size of the F-T reactors and the size of the supporting recycle stream units.

c) Sizing the F-T Reactors

One method to find the optimal balance between the size of the F-T reactors and the size of the recycle units is to use the FIXBD computer program. Incorporating the rate and selectivity correlations for the Co/X11/X9/TC-123 catalyst will allow the generation of performance for a wide range of operating conditions. All of these sets of operating conditions, along with the calculated reactor size (via the computer generated GHSV), and recycle stream size (through the defined conversion level), can then be costed to find the optimal (i.e.,lowest) cost for the combined reactor-recycle system.

Some of the operating conditions for the different sets of conditions have already been established from previous test runs. For instance, the highest pressure tested, 500 psig, showed the highest conversions without deleterious side effects. Likewise the testing at 250 C showed an acceptable level of conversion with minimal deactivation. Furthermore, it was found that the local recycle ratio would have to be near 2.3/1 for the given GHSV's used in the study to ensure an acceptably high film heat transfer coefficient at the inside surface of the tube wall.

With operating conditions assigned to these values and the bulk density of the catalyst assigned at its measured value of 0.49 grams/cc., Figure 3 shows that the only operating

conditions that can be varied in the FIXBD program are the GHSV and the H2/CO feed ratio. Since the GHSV is both the unknown variable and an input to the FIXBD program, its value must be determined by trial. This is done by holding the H2/CO ratio constant and trying different GHSV's until the desired conversion is obtained. This procedure is repeated for a series of different H2/CO ratios, all for the same conversion level. Once the selected conversion level has been adequately defined by these different sets of H2/CO-GHSV pairs, another conversion level is picked and defined using the same technique. This process is repeated until all of the desired conversion level sets have been defined.

Table I shows the results of these H2/CO-GHSV conversion level calculations as well as the breakdown of the hydrocarbons produced at each set of conditions. It will be seen that while the GHSV required to achieve any chosen conversion level can be increased by using a higher H2/CO ratio, the penalty for doing so is a rapid increase in the methane make, a subsequent increase in the size of the recycle stream, and a decrease in net C3+ production due to the oxidation loss in the steam reformer. Figure 4shows the exponential increase in methane make as the space velocity is increased for each conversion level.

Translation of the GHSV's into the required number of parallel ARGE-type reactors is done first by multiplying the GHSV by the catalyst volume in an ARGE-type reactor to determine the total amount of feed gas that each reactor will handle, and

then dividing this product into the total amount of feed gas that must be handled. Each ARGE-type reactor is assumed to be five meters in diameter, twelve meters long, and to contain a sufficient number of five centimeter ID tubes to hold 140 cubic meters of catalyst. The total amount of feed gas that must be handled will be the sum of the 95,061 pound moles per hour of fresh feed gas and the overall recycle stream, a sum that is represented by "RR" in Figure 5.

d) Sizing the Units

The costs obtained in this study were based upon the costs assigned to the units by the independent contractor in the previous studies mentioned. Table II shows that these costs were scaled further according to the stream sizes required for this study, either from a direct ratio of the size of the present stream to the size of the stream used by the independent contractor, or from this ratio raised to the 0.7 power.

The streams most commonly used for sizing were the streams "RR" and "RR-1", shown in Figure 5 as the inlet reactor stream and the recycle stream, respectively. These streams were used to size the CO2 removal unit (RR), the light hydrocarbon recovery unit (RR), and the autothermal reformer (RR-1).

Additional streams used for sizing were the total CHx production, the methane and ethane make, and the C3+ production. The total CHx production was used to size the power plant as well as to determine the amount of steam that was generated in the ARGE tubular reactors. The methane and ethane make were used to size the oxygen plant as well as to determine

the steam required for the oxygen plant. The C3+ production was used to size the refinery and upgrading units as well as to calculate the gallons of liquid C3+ fuel that was produced by the process.

e) Cost Estimate Program

A cost estimating program was written based upon; a) the costs assigned to the various units by the independent contractor, b) the scale-up factors described in Section d (above), and c) the FIXBD performance calculations described in Section c (above). The FIXBD performance calculations include the conversion level, the GHSV, the CH4 make, and the liquid product distribution. They also include the overall usage ratio, U, and the X in CHx, values that were required for determining the total amount of CHx produced (delta CHx) and the shift requirements (SHIFT).

Table III is the output of this program for the 70% conversion level and three of the eight different H2/CO - GHSV pairs listed in Table II. The top part of Table III describes the number of reactors and major stream quantities and compositions, while the bottom part of the table describes the capital costs and their associated charges (a 0.265 charge for capital recovery and a 0.092 charge for operating costs), the syngas feed cost, the catalyst replacement cost, the shift cost, and the credit for excess power.

The catalyst replacement cost was one full cost of the initial charge of the $20/lb catalyst (listed in line number 3 of Table III) divided by the life expectancy of the catalyst

(one year in Table III). The full cost of the initial charge of catalyst was determined from the number of reactors required (Nrx + R spare), the catalyst bed volume in each reactor (140 cubic meters), the density of the catalyst (0.49 g/cc), and the cost of the catalyst ($20/lb).

The credit for excess power was proportional to the difference between the amount of steam generated in the reactors (proportional to delta CHx) and the amount of steam required in the plant (slightly affected by the demand of the autothermal reformer).

The total cost of the process (line 18) divided by the total amount of C3+ fuels (proportional to delta C3+) yields the unit cost of the process (line 19) in 1983 dollars. It is this unit cost that was minimized in the optimization study.

f) Optimzation Study

The optimzation study consisted of running the cost estimate program for some of the H2/CO-GHSV-conversion level sets presented in Table I to determine their unit costs for the case where the catalyst was assumed to have a one-year life. Some of these sets were also run for the case where the catalyst was assumed to have a two-year life.

Tavle IV shows that the unit costs for the one-year life case were generally higher at both the lower H2/CO feed ratios (where more reactors are required) and the higher H2/CO feed ratios (where more methane and less fuels are made) at each conversion level. Furthermore, the conversion level that had the lowest minimal cost was the 70% conversion level when the

H2/CO feed ratio was 1.5 and the GHSV was 380 (from Table I).

This same information is shown more dramatically in Figures 6 and 7, where the unit costs are plotted, respectively, against the H2/CO feed ratio and the GHSV for the different conversion levels. In each case the optimum cost is the minimum of the locus of points defined by the minimum for each conversion curve.

Table IV and Figures 6 and 7 show that this minimum unit cost for a one-year catalyst life is approximately $1.88 gallon in 1983 dollars, or 2.12/gallon in 1988 dollars.

It is also worth noting from Table III (under the middle column for the 1.5 feed ratio) that approximately 46% of the unit cost stemmed from the cost of the feed syngas and that another 44% of the unit cost stemmed from the capital charges. The capital charges in turn were distributed as 43% for the F-T reactors and their initial catalyst charge, 18% for the refinery/uprgrading units, and 39% for all the other units.

A repeat of the same exercise for the case where the catalyst was assumed to have a two-year life showed the minimum unit cost to be $1.78/gallon in 1983 dollars and $2.00/gallon in 1988 dollars. Tthe feed and capital costs were distributed in approximately the same fashion as that described for the one-year catalyst life study.

g) Comparison of Co/S11/X9/TC-123 and Co/X11/TC-123 Unit Costs

The $2.12 optimized unit cost found in this study for the Co/X11/X9/TC-123 catalyst with a one-year life was lower than

the $2.19 non-optimized unit cost previously found for the Co/X11/TC-123 catalyst with a one-year life.

If the unit cost for the Co/X11/TC-123 catalyst had been optimized, it probably would have dropped down to near the $2.12 optimized cost for the Co/X11/X9/TC-123 catalyst. This means that the three-fold higher stability of the Co/X11/X9/TC-123 catalyst over that of the Co/X11/TC-123 catalyst offsets the slightly higher activity and lower methane production rate of the Co/X11/X9/TC-123 catalyst.

The deactivation rate of the Co/X11/X9/TC-123 catalyst was found (from Run #55) to be less than 0.007% loss of conversion/hour when the catalyst in the Berty Reactor was exposed to 260 C, 500 psig, and a 0.7 H2/CO ratio conditions. This deactivation rate could be expected to be cut by at least a third when the catalyst is exposed at 250 C to the 0.9 H2/CO ratio (average of the 1.0 inlet and the 0.83 outlet ratios) present in the reactors at the optimum operating conditions. This reduced deactivation rate amounts to a syngas conversion rate loss of approximately 20%/year.

Such a rate loss could probably be somewhat offset by continually adjusting the catalyst temperature to perhaps as high as 270 C to maintain the design activity. However, the actual estimated 250 C rate loss and the effectiveness of any steps that may be taken to offset it would have to be determined from additional long-term runs.

PROCESS FLOW DIAGRAM

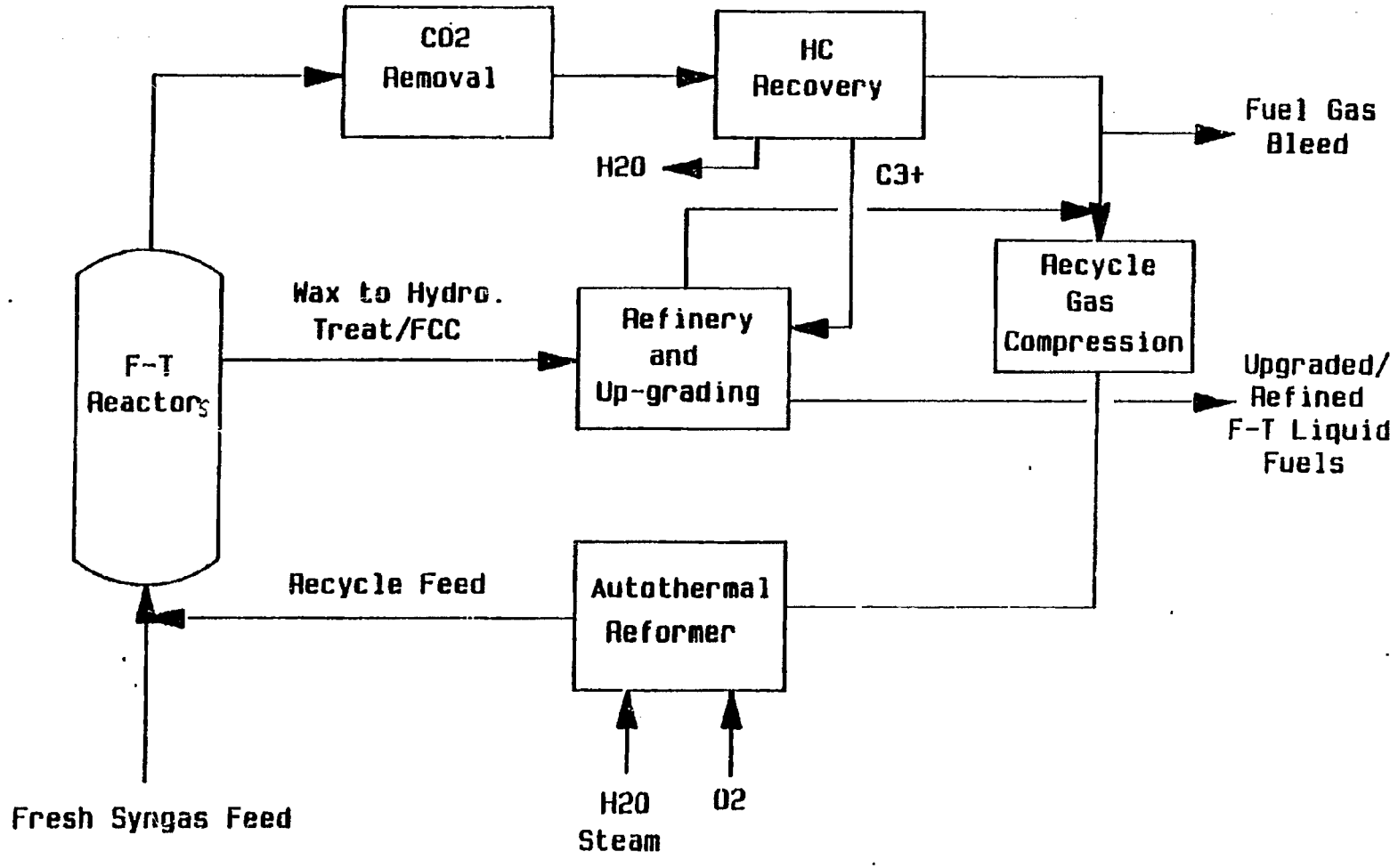


Figure C2
Detail of Flow Around the
F-T Reactor

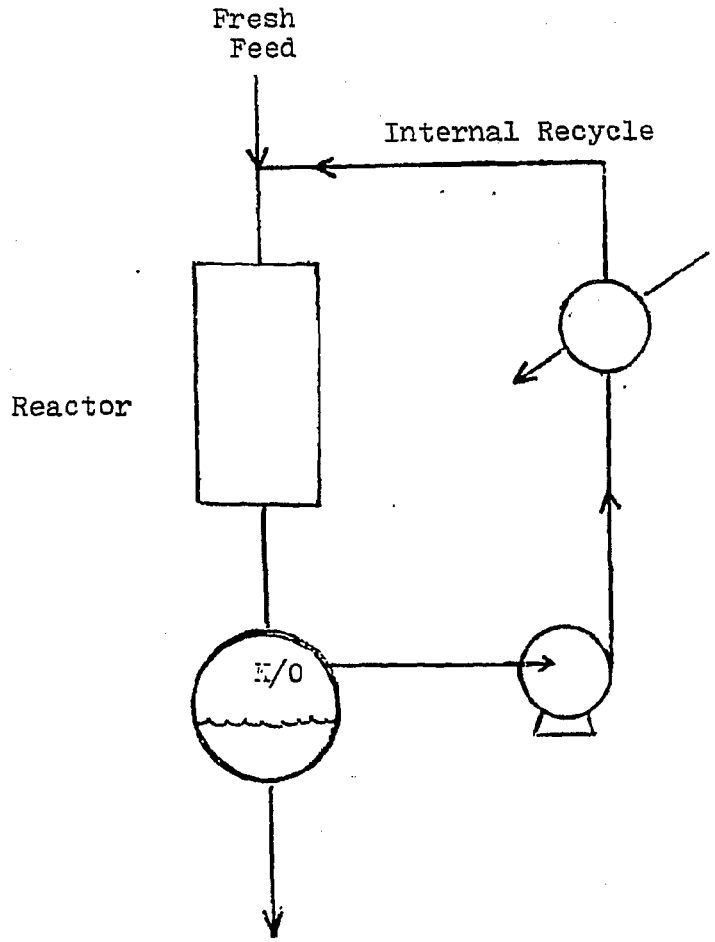


Figure C3

A Schematic Diagram
of the
Computational Sequence Employed
for the Development of the
Union Carbide Tubular Reactor Simulation Program

The Berty reactor, a CSTR (continuous-feed stirred tank reactor) is operated under steady state conditions with a high internal recycle rate, which results in the catalyst being exposed to a known and unvarying gas phase composition. Performing runs at different pressures, temperatures, space velocities, and feed gas compositions provides a data base.

↓

The data base contains conversion data for the feed components, product distribution by component and boiling range, and information on the composition of the product (olefins, isomers, etc.).

↓

Multiple Regression of the data base provides equations which express CO conversion rate, usage ratio, methane rate, and alpha, (Schulz-Flory coefficient), as a function of the operating parameters.

↓

These equations are put into the FIXBD program, which is a simulation of an isothermal packed bed tubular reactor having a recycle stream, a knock-out pot (to remove water and C5+ products) and an off-gas stream. The inputs and outputs are as follows:

Inputs
1. Catalytic properties
   . Bulk density
2. Feed gas conditions
   . Space velocity
   . H2/CO ratio
3. Reactor conditions
   . Pressure
   . Temperature
   . Recycle ratio

Outputs
1. H2 and CO conversion
2. H2O and CO2 production
3. Methane make
4. C2+ hydrocarbon make by individual cuts

Figure C4

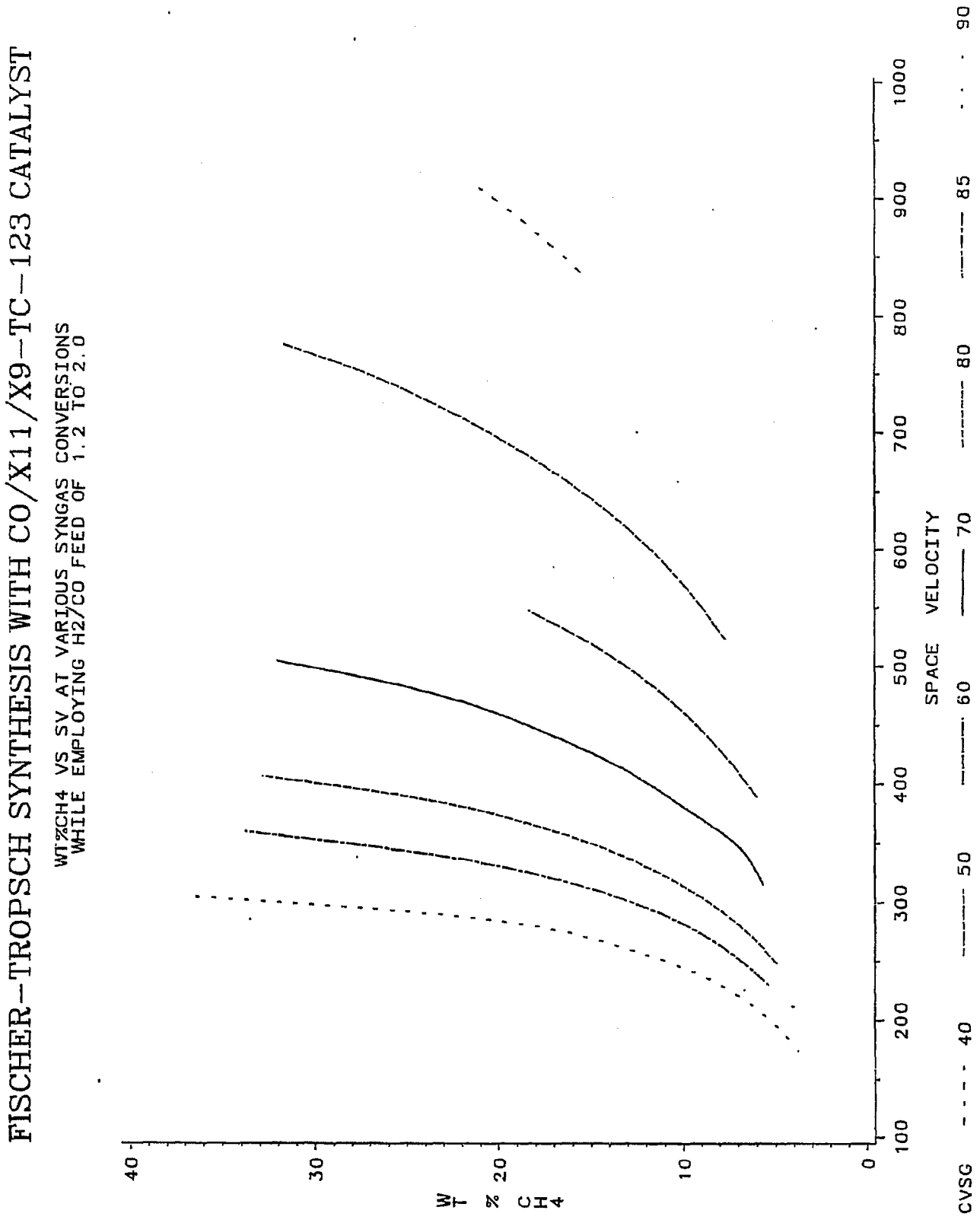
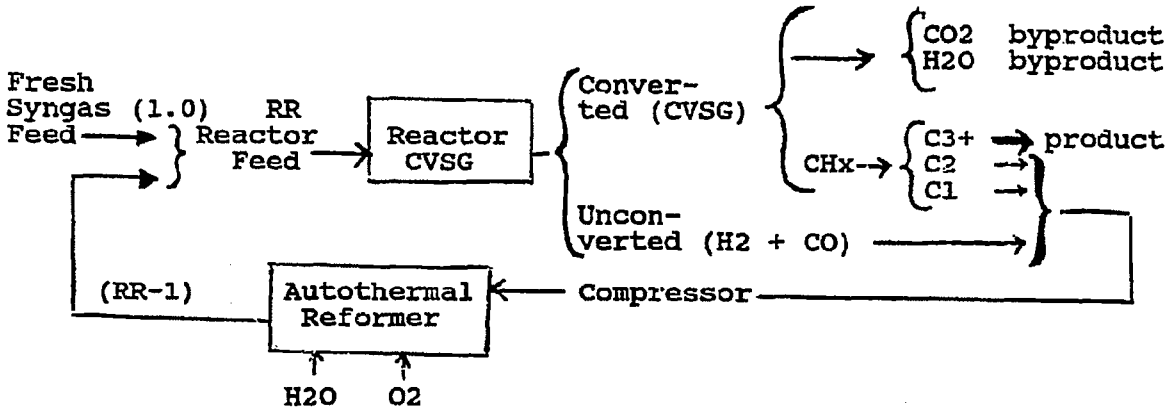

FISCHER-TROPSCH SYNTHESIS WITH CO/X11/X9-TC-123 CATALYST
WT%CH4 VS SV AT VARIOUS SYNGAS CONVERSIONS
WHILE EMPLOYING H2/CO FEED OF 1.2 TO 2.0
WT % CH4
0
10
20
30
40
SPACE VELOCITY
100
200
300
400
500
600
700
800
900
1000
CVSG
40
50
60
70
80
85
90

Figure C5

Schematic Flow Diagram



For Fischer-Tropsch synthesis:

CO + (1.0 + 0.5) H2 --- CHx + H2O H = -37.65 kcal./g.mol
CO + H2O --- H2 + CO2 H = -9.83 kcal./g.mol

For Autothermal reformer:

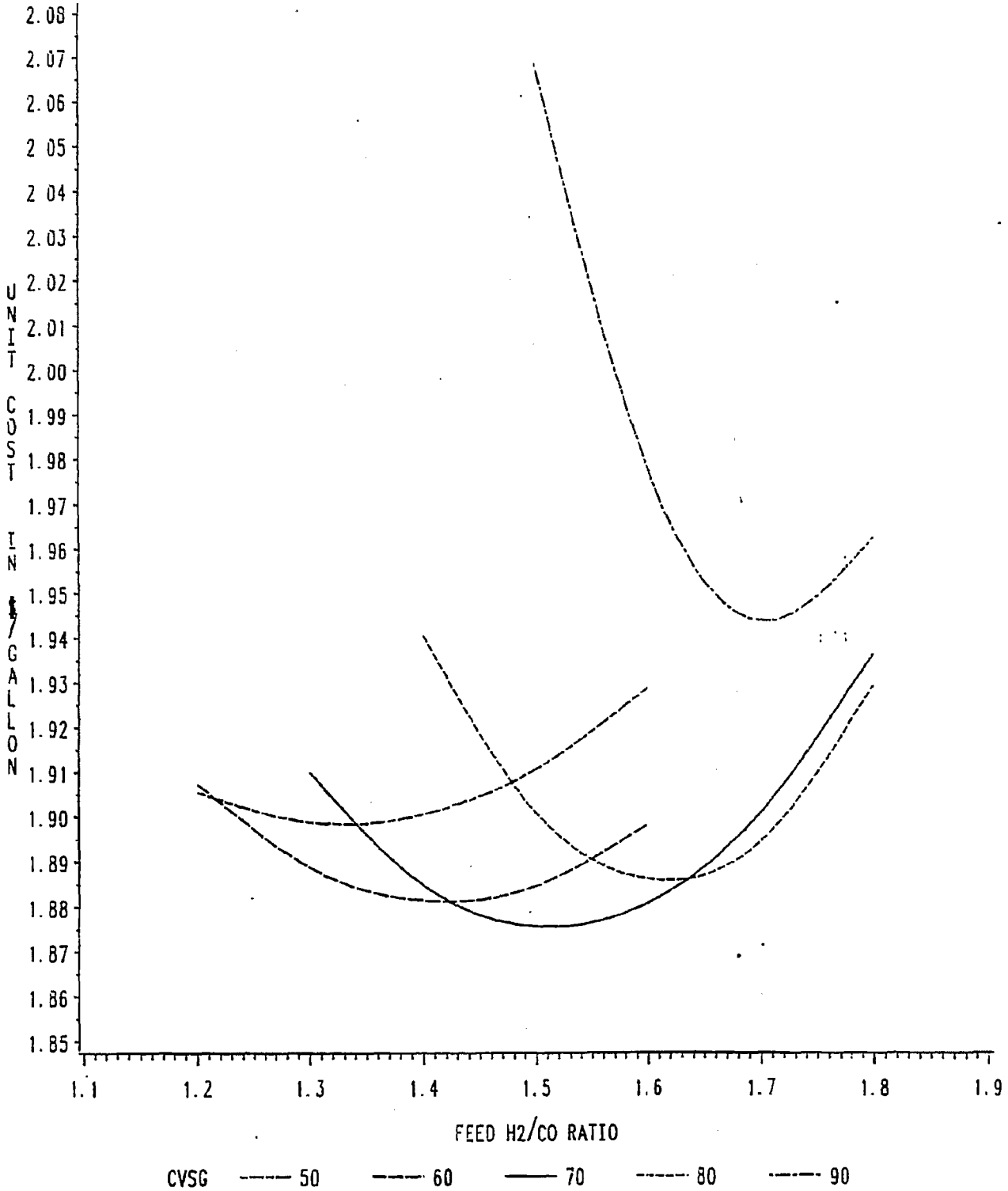
CH4 + 0.42 O2 + 0.79 H2O --- 0.21 CO2 + 0.79 CO + 2.37 H2 + 0.42 H2O
CH3 + 0.35 O2 + 0.9 H2O --- 0.2 CO2 + 0.8 CO + 2.0 H2 + 0.4 H2O

Figure C6

FISCHER–TROPSCH SYNTHESIS

WITH CO/X11/X9-TC-123 CATALYST

$/GAL VS RF AT VARIOUS SYNGAS CONVERSIONS



FISCHER-TROPSCH SYNTHESIS WITH CO/X11/X9-TC-123 CATALYST

$/GAL VS SV AT VARIOUS SYNGAS CONVERSIONS

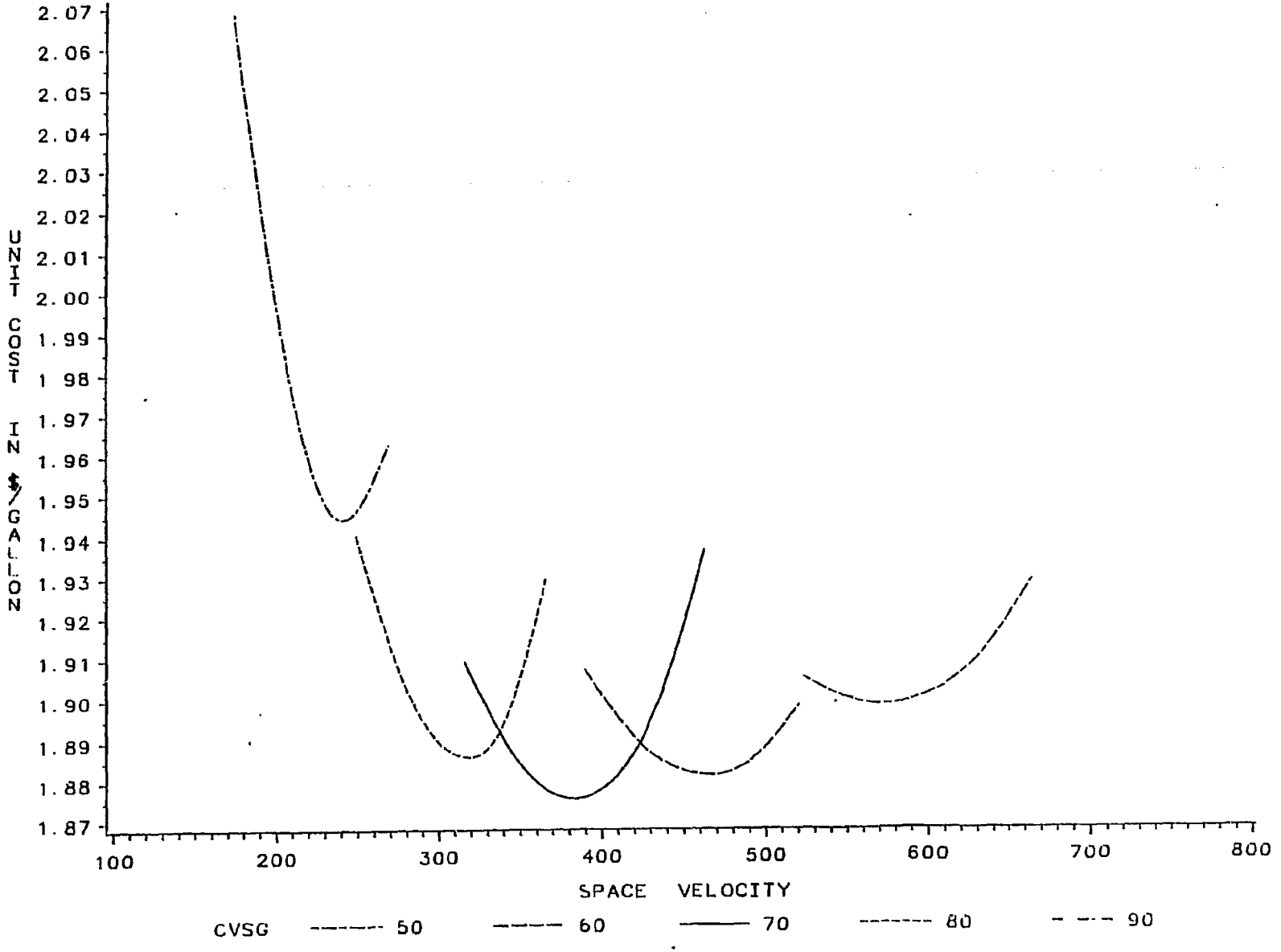


Figure C7

Table I

Product Distribution Produced by the Co/X11/X9/TC-123 Catalyst at Various Operating Parameters and Different Conversion Levels
(500 psig, 250 C, 2.3/1 local recycle ratio, 0.49 gm./cc. catalyst density, 86 % fresh catalyst activity)
(all in weight percent)

Conversion,	Reactor Feed H2/CO Ratios 1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
30 %									
GHSV				1173	1220	1264			
% CH4				16.7	19.2	22.0			
% C2-C4				12.8	12.9	13.0			
% C5-C10				30.1	29.8	29.4			
% 350-650 F				28.3	27.1	25.9			
% 650 F+				12.1	10.9	9.8			
40 %									
GHSV				837	874	909			
% CH4				15.6	18.2	21.1			
% C2-C4				12.1	12.3	12.4			
% C5-C10				29.4	29.2	28.9			
% 350-650 F				29.2	28.0	26.6			
% 650 F+				13.8	12.3	10.9			
50 %									
GHSV	523	562	598	632	664	695	723	751	776
% CH4	7.64	9.52	11.6	14.1	16.8	19.9	23.4	27.3	31.7
% C2-C4	9.55	10.3	10.9	11.4	11.8	12.0	12.0	11.9	11.7
% C5-C10	26.4	27.5	28.2	28.6	28.7	28.5	28.0	27.2	26.0
% 350-650F	32.8	32.1	31.2	30.1	28.9	27.5	25.9	24.2	22.4
% 650 F+	23.6	20.6	17.9	15.7	13.8	12.2	10.7	9.35	8.13
60 %									
GHSV	389	425	459	490	520	548			
% CH4	5.95	7.73	9.81	12.2	15.1	18.4			
% C2-C4	8.22	9.19	9.99	10.6	11.1	11.5			
% C5-C10	24.0	25.7	27.0	27.7	28.1	28.1			
% 350-650F	32.8	32.7	32.0	31.1	29.8	28.4			
% 650 F+	29.0	24.7	21.2	18.3	15.8	13.7			
70 %									
GHSV		315	349	380	409	436	462	485	505
% CH4		5.64	7.57	9.94	12.8	16.3	20.5	25.7	32.1
% C2-C4		7.63	8.73	9.65	10.4	10.9	11.2	11.2	10.9
% C5-C10		22.9	24.9	26.3	27.2	27.6	27.4	26.6	25.1
% 350-650F		32.5	32.6	32.0	30.9	29.4	27.6	25.4	22.8
% 650 F+		31.4	26.2	22.1	18.7	15.8	13.3	11.1	9.07

Table I (continued)

Conversion	Reactor Feed H2/CO Ratios 1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
80 %									
GHSV		213	249	282	312	341	366	388	407
% CH4		3.32	4.92	7.03	9.80	13.4	18.2	24.5	32.9
% C2-C4		5.19	6.71	8.05	9.18	10.1	10.6	10.8	10.5
% C5-C10		17.2	20.9	23.6	25.5	26.6	26.9	26.2	24.4
% 350-650 F		29.4	31.7	32.4	32.0	30.7	28.8	26.1	22.8
% 650 F+		44.9	35.8	29.0	23.6	19.2	15.5	12.3	9.50
85 %									
GHSV			196	230	263	293	319	341	360
% CH4			3.51	5.34	7.94	11.6	16.6	23.8	33.8
% C2-C4			5.16	6.77	8.22	9.39	10.2	10.5	10.1
% C5-C10			17.1	21.0	23.9	25.7	26.5	26.0	23.8
% 350-650 F			29.2	31.6	32.2	31.4	29.5	26.6	22.5
% 650 F+			45.0	35.3	27.8	21.9	17.2	13.2	9.65
90 %									
GHSV				174	209	241	269	290	306
% CH4				3.67	5.92	9.38	14.8	23.2	36.9
% C2-C4				4.99	6.80	8.39	9.59	10.1	9.50
% C5-C10				16.7	21.0	24.1	25.7	25.5	22.6
% 350-650 F				28.7	31.5	31.8	30.3	27.0	21.6
% 650 F+				46.0	34.8	26.3	19.7	14.2	9.45

Table II

Scale-up Factors for the Major Cost Items

Item	Scaling Factor	Stream or Quantity
Reactor	Linear	No. of reactors required plus 2 spare
CO2 Removal	0.7 power	Reactor effluent (1)
Light H/C Recovery	0.7 power	Reactor effluent (1)
F-T Prod. Fractionator	Constant	
Autothermal Reformer	0.7 power	Recycled stream (2)
Total Ferinery Equip.	0.7 power	C3+ produced
Catalyst costs	Linear	Catalyst density
Total H2 Equip.	Constant	
Power Generation	0.7 power	CHx Produced
O2 Plant Cost	0.7 power	O2 demand from CH4 and C2H6 make
Syngas Cost	Constant	
Shift Cost	0.7 power	Degree of shifting Required (3)
Catalyst Replacement	Years life	

(1) RR = ratio of total syngas (with CO2) fed to the reactors divided by the fresh syngas feed (see Figure 5).

(2) RR - 1 = the recycled gas exit from the autothermal reformer, including CO2, but not steam (see Figure 5).

(3) SHIFT = the relative amount of shift required from a raw syngas with a H2/CO ratio of 0.5 to the desired feed ratio.

Table III

Typical Output for the Cost Estimating Program

CVSG, Conv. Syngas	0.700006	0.699921	0.700000
RF, Feed ratio, H2/CO	1.400000	1.500000	1.600000
SV, Space velocity,v/v/hr.	348.830	380.179	409.146
Shift, rel.amount of shift	0.318136	0.319957	0.320970
Weight % CH4	7.570700	9.935600	12.810300
RR, recycle ratio (SG & CO2)	1.574006	1.617264	1.670312
Nrx = 2, Reactors + spares	33.150204	31.367120	30.183037
DCHx, lb. moles/hr. CHx	33428.580	34058.056	34837.038
DC3+, lb. moles/hr. C3+	30417.567	30168.278	29864.537
Steam genrtd, 5.195*CHx/1000	173.672	176.942	180.989
Steam Req'd.,M lb. moles/hr.	129.408	131.258	123.540
Excess steam for revenue	44.262	45.684	47.450
FT System:			
Reactor, 6.360036*Nrx	210.836	199.496	191.965
CO2 removal, RR**0.7	48.365	49.292	50.418
Lights recovery, RR**0.7	46.699	47.593	48.681
FT prod. fractnn, constant	27.350	27.350	27.350
Autothermal ref.,(RR-1)**0.7	25.619	26.955	28.557
1. Total FT Sys. Equip. Cost	358.869	350.686	346.971
2. Total ref. equip.(C3+**0.7)	123.040	122.334	121.470
3. Catalyst chg., Nrx @0.49 d	100.270	94.876	91.295
4. Toal H2 equip. cosnt.	27.140	27.140	27.140
5. Subtotal plant equip.cost	609.319	595.037	586.876
6 Power gen. cost, (CHx**0.7)	61.236	62.041	63.031
7. O2 plant cost (O2**0.7)	16.498	19.806	23.600
8. Subtotal 5, 6, 7	687.054	676.884	673.507
9. 10 % misc. cost	68.705	67.688	67.351
10.Total Equipment Cost	755.759	744.573	740.858
11.Capital cost, 1.59*Total	1201.658	1183.871	1177.964
12.Ann. chrg cost,0.265*captl	318.439	313.726	312.160
13.Syngas cost, const.	446.510	446.510	446.510
14.Shift cost,SHIFT**0.7	35.004	35.144	35.222
15.Operating cost,0.092*captl	110.553	108.916	108.373
16.Cat. replacemnt cost @ 1yr.	100.270	94.876	91.295
17.Excess power revenue	-34.454	-35.561	-36.935
18.Revenue req'd, MM 1983 $	976.321	963.612	956.625
19.Unit cost, $/gal.	1.8848	1.8756	1.8809

Table IV

Summary of the Unit Costs (1983 $/gallon of fuel) for the Conditions Specified in Table I for a One Year Catalyst Life

Conversion, %	Syngas Feed Ratio (H2/CO) 1.2	1.3	1.4	1.5	1.6	1.7	1.8
90 %	.	.	.	2.069	1.979	1.944*	1.963
80 %	.	.	1.941	1.901	1.886*	1.895	1.930
70 %	.	1.910	1.885	1.876*	1.881	1.901	1.937
60 %	1.907	1.889	1.881*	1.885	1.898	.	.
50 %	1.905	1.899*	1.901	1.911	1.929	.	.
40 %	.	.	.	1.953	.	.	.
30 %	.	.	.	2.019	.	.	.

* Approximate minimum unit cost at each conversion level.

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000