

## VI. REJUVENATION

As this program evolved and process data became available to provide preliminary operating costs, it became apparent that the ultimate catalyst life would become a factor in the process economics. With this in mind, a modest effort was spent examining the possibilities of rejuvenating spent catalysts, with the hope of extending their ultimate life.

The first attempt was to employ an oxidative regeneration to remove the carbonaceous build-up on the catalyst. The catalyst from Run No. 4 was oxidatively regenerated, reactivated with hydrogen, and tested for F-T performance (Run No. 7). The results were briefly reported in the First Quarterly Report and in detail in the Second Quarterly Report. The catalyst in question was a Co/UCC-103, which was the starting point for this contract. This rejuvenation failed to improve the performance of the catalyst, in fact; the performance deteriorated further.

The next attempt was to test the feasibility of a hydrogen rejuvenation. This was performed on the spent catalyst from Run No. 13. The hydrogen treatment was carried out at 350 C and 300 psig. The results were reported initially in the Second Quarterly Report and in detail in the Third Quarterly Report. The catalyst in Run No. 13 exhibited an initial conversion of 56% which declined to 45% after over 236 hours on stream. Following the hydrogen treatment, the conversion returned to 46% following a brief period at 48%.

The attempt at regeneration with hydrogen was unsuccessful.

The catalyst development program subsequently made some major breakthroughs in performance and in life, as cited in the previous section. Consequently, the next effort took place following this work when the TC-123 catalyst base had been identified. The spent catalyst from Run No. 45 (Co/X11/TC-123) was oxidatively regenerated and tested for F-T performance. The results are reported in Run No. 76, first reported in the Tenth Quarterly Report, and the details are presented in the Eleventh Quarterly Report. The carbon content was reduced from 47% to 0.2%. The oxidation was carefully controlled, with limited oxygen content present to insure that thermal damage would not cloud the results of the rejuvenation. The F-T performance of the rejuvenated catalyst was inferior to the fresh catalyst. Conversion was down about 20%, methane production up at least 50% and the C5+ yield was down. It was felt that the conditions of the rejuvenation may have been too severe.

The next run related to rejuvenation studies was Run No. 78. This run was designed to provide a deactivated catalyst for rejuvenation. The catalyst for the run was prepared in the same manner as that used to prepare the catalyst for Run No. 55. It was subsequently installed and operated at F-T conditions aimed at coking up and rapidly deactivating the catalyst, i.e., running at a 0.5 to 1.0 H<sub>2</sub> to CO ratio vs. the stoichiometric 1/1. It was noteworthy that this catalyst

(details reported in the Tenth and Eleventh Quarterly Reports) exhibited a surprising stability at the low syn gas ratios. Conversion was cut in half vs. the stoichiometric ratio but the stability was quite good. Furthermore, upon returning to the 1/1 syngas ratio, the conversion returned to the previous value. The methane make was slightly increased, indicating some change in the catalyst, but the resilience of the catalyst to low H<sub>2</sub>/CO feed ratios was most encouraging.

Run No. 83 was made with the rejuvenated catalyst recovered from Run No. 81. The rejuvenation conditions were milder than previously employed but effective carbon reduction was still achieved (35.7% to 0.13% carbon). The performance was poorer than the fresh catalyst, activity was down, methane make was up, and the C<sub>5</sub>+ yield was down. In general, the rejuvenated catalyst exhibited poor performance. The results were reported in the Eleventh and Twelfth Quarterly Reports.

Run No. 85 tested the rejuvenated catalyst from Run No. 82. The carbon was effectively reduced from 48% to 0.08% at even milder conditions than employed previously. However, as before, the performance of the catalyst did not approach that of the fresh catalyst; methane yield was up, C<sub>5</sub>+ yield was down, and the performance was inferior. In fact, the performance following the regeneration was no better than that achieved by the deactivated catalyst at the end of the previous run (1368 hours). This fact

suggested that catalyst coking may not be the cause of deactivation, but rather, some other mechanism, such as sintering of the active metal species, may be the real source of deactivation of the catalysts. One further test was needed.

Run No. 88 was made with the rejuvenated catalyst from Run No. 86. The rejuvenation procedure was milder than used previously but still successful in reducing carbonaceous deposits on the catalyst (54% before and 0.8% after the treatment). The performance of the rejuvenated catalyst showed no improvement over that of the spent catalyst. The rejuvenation did not damage the catalyst further. The results were reported in the Twelfth and Thirteenth Quarterly Reports. Based upon this test, it was concluded that further attempts at rejuvenation would have to identify some other cause for the deactivation than coke build-up, such as sintering, and address that problem, if necessary, in a separate study.

## VII. XPS/MICROREACTOR SURFACE STUDIES

### A. 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.

### B. 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 of

the Fifteenth Quarterly report 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)
- II. Co/TC-123 (12524-76)
- III. Co/X11/TC-123 (13168-22)
- IV. Co/X11/X9/TC-123(12524-43)
- V. Co/X11/X9/TC-123(13168-19)

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 Co 1s and Si 2p) for the silicon support and the surface cobalt, and d) the percent reduction of surface cobalt.

#### C. DISCUSSION OF RESULTS

##### 1) Fresh (as synthesized) Catalyst Studies

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).

## 2) 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.

The first important observation 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	
	<u>XPS (surface)</u>	<u>Titration (bulk)</u>
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.

### 3) 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 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	% Cobalt Metal	Para./Ole.	Relative	
Type	Reduction	Reaction (in C4's)	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 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.

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.

<u>Temperature</u> <u>of Reaction</u>	<u>% Co Metal</u> <u>(from syngas)</u>	<u>Para./Ole.</u> <u>(in C4's)</u>	<u>Relative</u> <u>Activity</u>
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.

The effect of exposure time is shown in the following table (for Co/X11/TC-123, 240 C, 1:1 syngas, 320 psi).

<u>Time</u>	<u>% Co Metal</u>	<u>P/O (C4's)</u>	<u>Rel. Act.</u>
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).

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.

H <sub>2</sub> /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.

#### D. SUMMARY

1) 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.

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

3) 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.

4) It is believed that the promoters diminish 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.

## VIII. TECHNO-ECONOMIC STUDIES

### ON THE

### Co/X11/X9/TC-123 CATALYST

(Catalyst No. 55)

#### 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 H<sub>2</sub>: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 VIII-1 shows that fresh syngas feed is combined with the recycled feed before entering the F-T reactors. The effluent passes sequentially through a CO<sub>2</sub> removal system, hydrocarbon recovery columns, a compressor, and an autothermal reformer (which converts methane and ethane into syngas). The C<sub>3</sub>+ product is separated into standard grades of C<sub>3</sub>-C<sub>4</sub>, gasoline, and diesel fuel.

The F-T reactors incorporated into Figure VIII-1 are parallel trains of ARGE-type, fixed bed, tubular reactors. Figure VIII-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 VIII-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 H<sub>2</sub> and CO conversion levels, the methane make, and the C<sub>2</sub>+ product distribution for the reactor when the pressure, temperature, local recycle ratio, H<sub>2</sub>:CO fresh feed ratio, GHSV, catalyst density, and the rate correlations for the catalyst in question are inputted 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, H<sub>2</sub>: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 three levels of H<sub>2</sub>:CO feed ratio. All of the

catalyst runs were started at the standard conditions of 300 psig, 240 C, 300 GHSV, and 1:1 H<sub>2</sub>: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:

Design- nation	Press. psig	Temp. C	Sp.Vel. vg/v/hr	Feed H <sub>2</sub> :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:

$$RCO = K \cdot (p_{H_2})^a \cdot (p_{CO})^b \cdot \exp\left(\frac{A \cdot (t_c - 240)}{R \cdot T_1 \cdot T_2}\right) \cdot \exp(m \cdot Hr) \quad \text{Ln}$$

$$RCO = \text{Ln}K + a \text{ Ln } p_{H_2} + b \text{ Ln } p_{CO} + \frac{A \cdot dt}{R \cdot T_1 \cdot T_2} + m \cdot Hr$$

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

pH<sub>2</sub> partial pressure of H<sub>2</sub> in psia

pCO partial pressure of CO in psia

a, b power coefficients on H<sub>2</sub> and Co partial pressures

A2 Arrhenius activation energy in 10,000 calorie/gmole

dt (t<sub>c</sub>-240), with 240 C as reference, T<sub>1</sub> and T<sub>2</sub> 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 H<sub>2</sub> consumption to that of CO

LRHC Ln ratio of H<sub>2</sub>/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:

$$\ln RCH_4 = \ln K + a \ln p_{H_2} + b \ln p_{CO} + A_2 \cdot dt / (R \cdot T_1 \cdot T_2)$$

The coefficients are:

<u>LnK</u>	<u>a</u>	<u>b</u>	<u>A2</u>
-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:

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

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:

<u>LnK</u>	<u>a</u>	<u>A</u>	<u>b</u>	<u>c</u>
-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 VIII-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 VIII-1. The non-condensables from the knock-out pot contain C1-C4 hydrocarbons, CO<sub>2</sub>, and unreacted syngas which becomes part of the overall recycle stream.

#### b) The Computer Program

Figure VIII-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 inputted 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 H<sub>2</sub>/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 H<sub>2</sub> and CO concentrations so that additional looping results in convergence of the effluent H<sub>2</sub>/CO ratio from the opposite direction (i.e., if the H<sub>2</sub>/CO ratio was asymptotically decreasing during the initial looping period, then the direction of the step changes in the H<sub>2</sub> and CO concentrations will cause the effluent H<sub>2</sub>/CO ratio to asymptotically increase during the second looping period). Once such two directional convergences (to the same H<sub>2</sub>/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	Simulation
	<u>Berty Reactor</u>	<u>FIXBD Program</u>
Feed H <sub>2</sub> /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. %	Wt. %
Methane	10.0	12.7
C <sub>2</sub> -C <sub>4</sub>	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 independent testing. These companies tested the catalyst samples in fixed bed reactors, with and without recycle streams, and free of condensables.

Comparison of the experimental test results from the independent 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 6 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 VIII-1 and is based 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 VIII-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 stream (i.e., the CO<sub>2</sub> removal unit, the hydrocarbon recovery columns, the gas compressor, and the hydrothermal reformer that encircle the refinery and upgrading block in Figure VIII-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. And, 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 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 VIII-3 shows that the only operating

conditions that can be varied in the FIXBD program are the GHSV and the H<sub>2</sub>/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 H<sub>2</sub>/CO ratio constant and trying different GHSV's until the desired conversion is obtained. This procedure is repeated for a series of different H<sub>2</sub>/CO ratios, all for the same conversion level. Once the selected conversion level has been adequately defined by these different sets of H<sub>2</sub>/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 VIII-1 shows the results of these H<sub>2</sub>/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 H<sub>2</sub>/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 C<sub>3</sub>+ production due to the oxidation loss in the steam reformer. Figure VIII-4 shows 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 VIII-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 VIII-2 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 VIII-4 as the inlet reactor stream and the recycle stream, respectively. These streams were used to size the CO<sub>2</sub> removal unit (RR), the light hydrocarbon recovery unit (RR), and the autothermal reformer (RR-1).

Additional streams used for sizing were the total CH<sub>x</sub> production, the methane and ethane make, and the C<sub>3</sub>+ production. The total CH<sub>x</sub> 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 volume 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 CH<sub>4</sub> make, and the liquid product distribution. They also include the overall usage ratio, U, and the X in CH<sub>x</sub>, values that were required for determining the total amount of CH<sub>x</sub> produced ( $\Delta$  CH<sub>x</sub>) and the shift requirements (SHIFT).

Table VIII-3 is the output of this program for the 70% conversion level and three of the H<sub>2</sub>/CO-GHSV pairs listed in Table VIII-1. The top part of Table VIII-3 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 3 of Table VIII-3) divided by the life expectancy of the catalyst

(one year in Table VIII-3). The full cost of the initial charge of catalyst was determined from the number of reactors required ( $N_{rx} + R$  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  $\Delta CH_x$ ) 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) Optimization Study

The optimization study consisted of running the cost estimate program for some of the H<sub>2</sub>/CO-GHSV-conversion level sets presented in Table VIII-1 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.

Table VIII-4 shows that the unit costs for the one year life case were generally higher at both the lower H<sub>2</sub>/CO feed ratios (where more reactors are required) and the higher H<sub>2</sub>/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

H<sub>2</sub>/CO feed ratio was 1.5 and the GHSV was 380 (Table VIII-1).

This same information is shown more dramatically in Figures VIII-6 and VIII-7, where the unit costs are plotted, respectively, against the H<sub>2</sub>/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 VIII-4 and Figures VIII-6 and VIII-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 VIII-3 (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/upgrading 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. The 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/X11/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 No. 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 H<sub>2</sub>/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 H<sub>2</sub>/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 difference 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.

Figure VIII-1

# PROCESS FLOW DIAGRAM

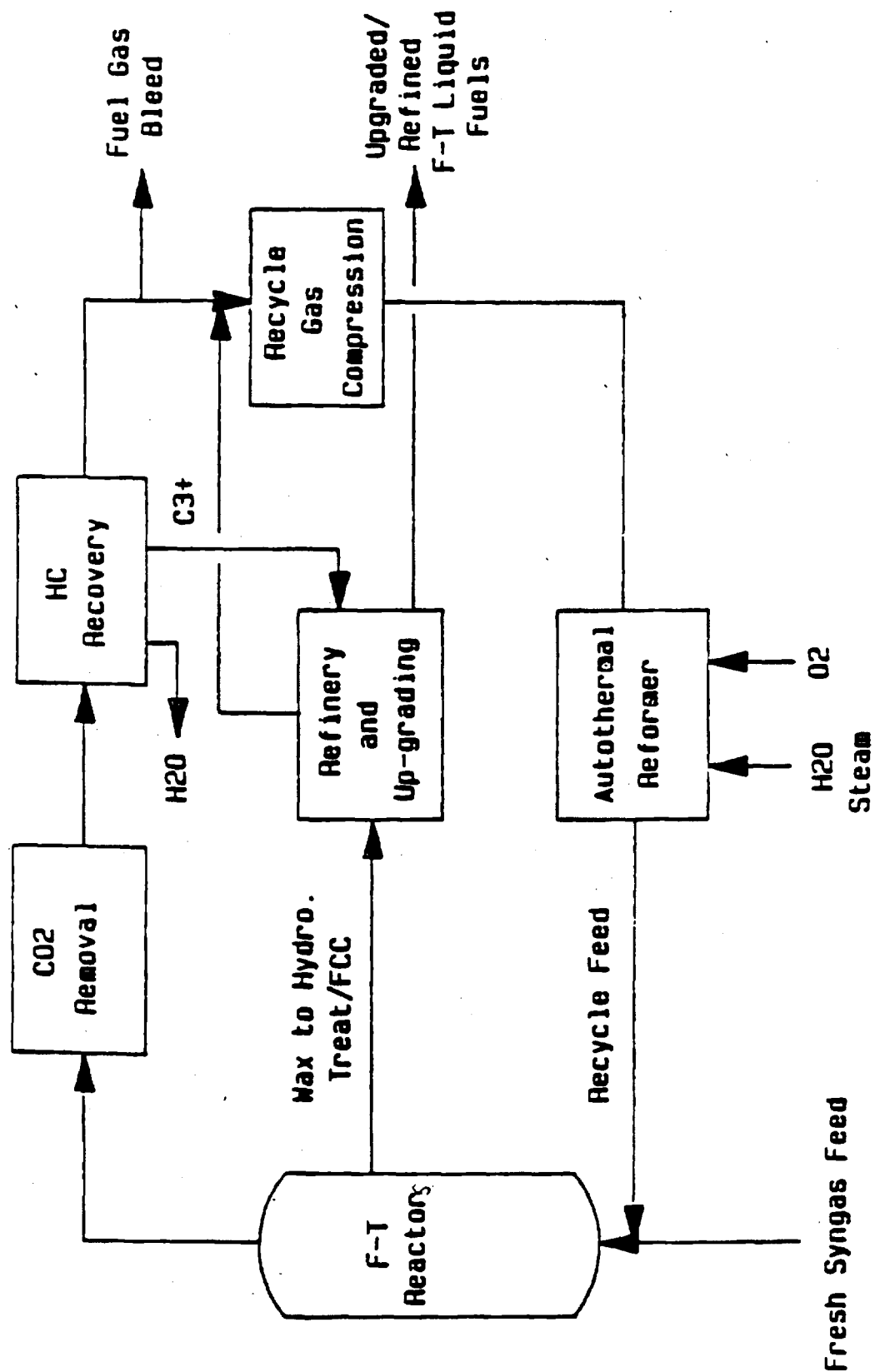


Figure VIII-2

Detail of Flow Around the  
F-T Reactor

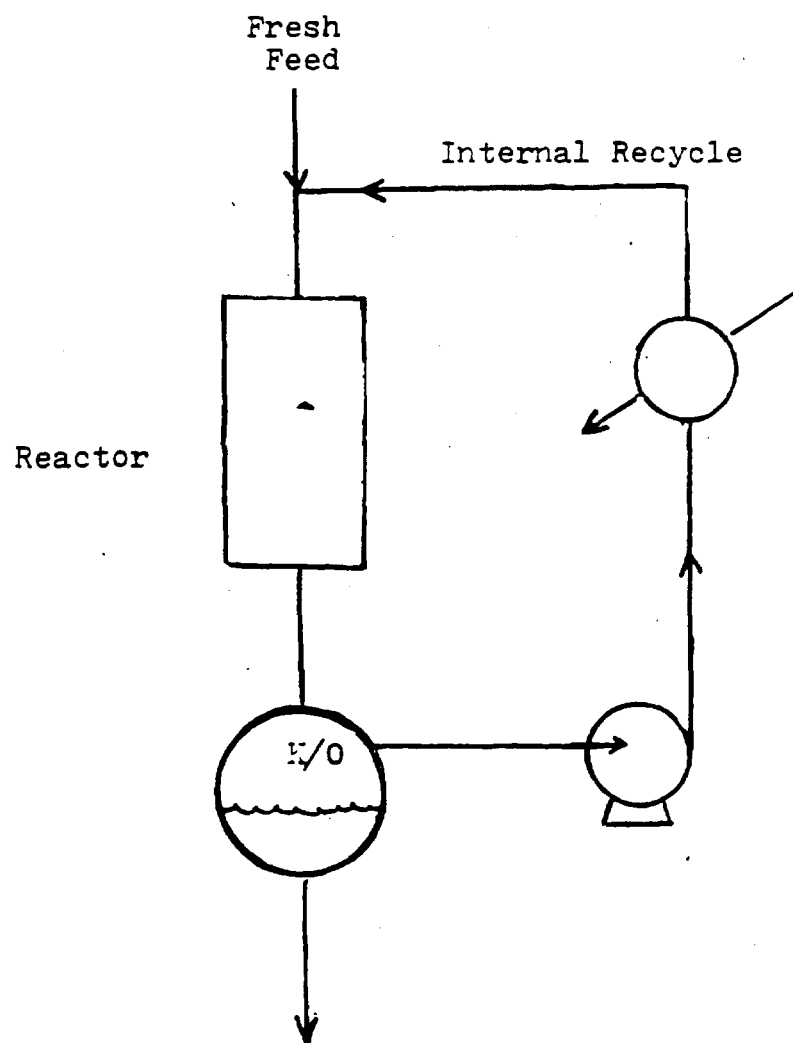


Figure VIII-3

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
  - . H<sub>2</sub>/CO ratio
3. Reactor conditions
  - . Pressure
  - . Temperature
  - . Recycle ratio

Outputs

1. H<sub>2</sub> and CO conversion
2. H<sub>2</sub>O and CO<sub>2</sub> production
3. Methane make
4. C<sub>2</sub>+ hydrocarbon make  
by individual cuts

Figure VIII-4

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

WT%CH<sub>4</sub> VS. SV AT VARIOUS SYNGAS CONVERSIONS  
WHILE EMPLOYING H<sub>2</sub>/CO FEED OF 1.2 TO 2.0

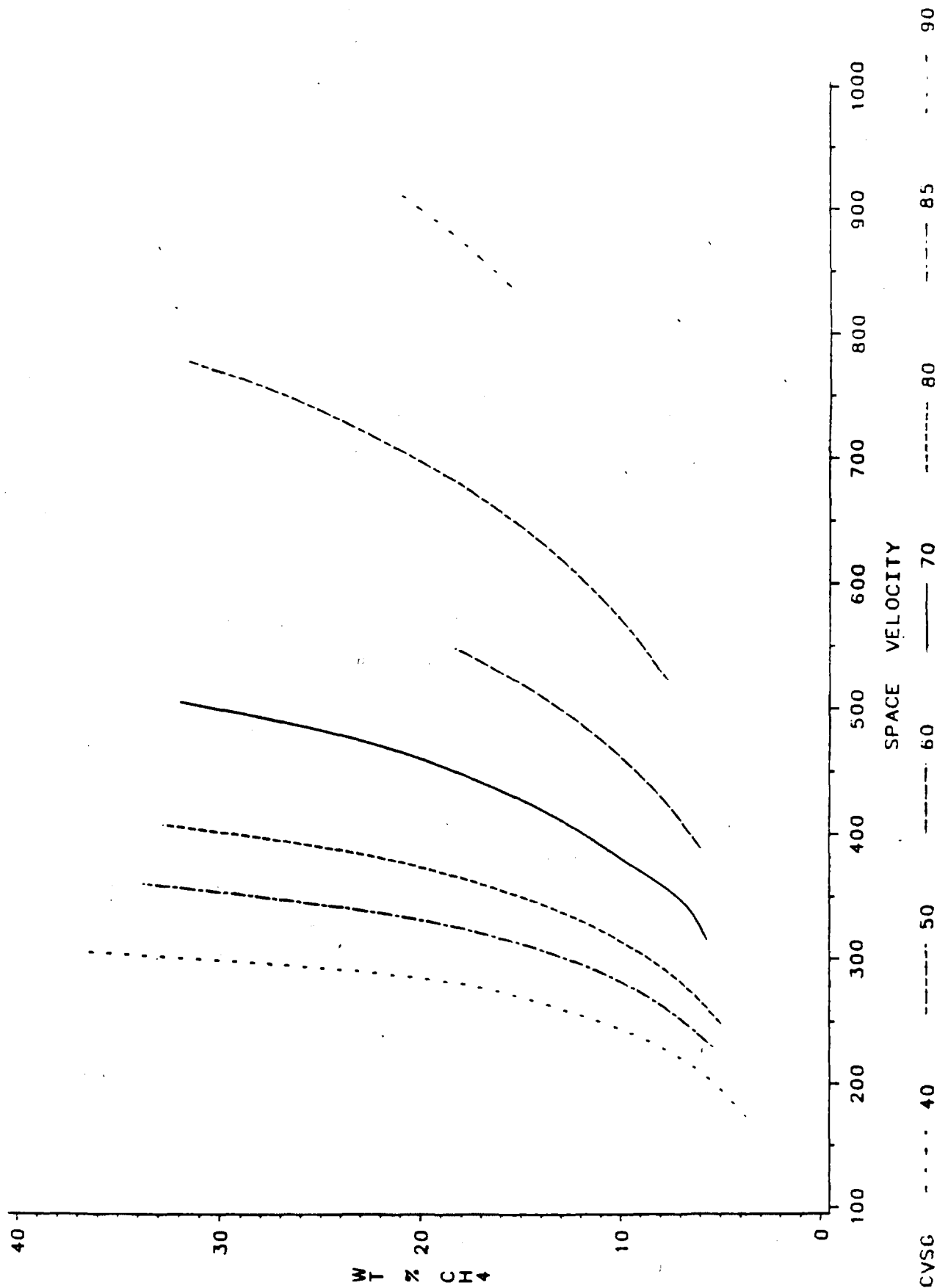
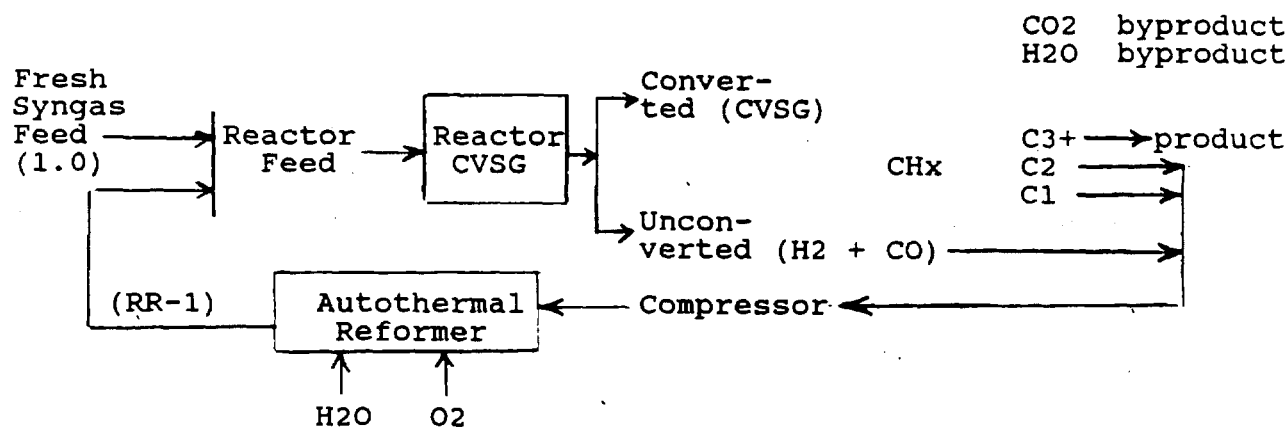
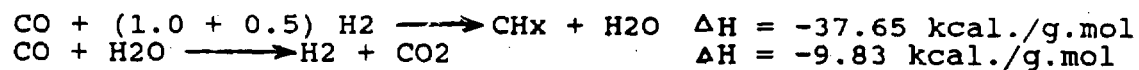


Figure VIII-5  
Schematic Flow Diagram



For Fischer-Tropsch synthesis:



For Autothermal reformer:

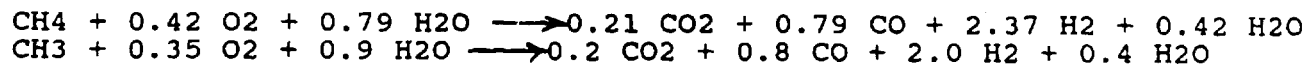
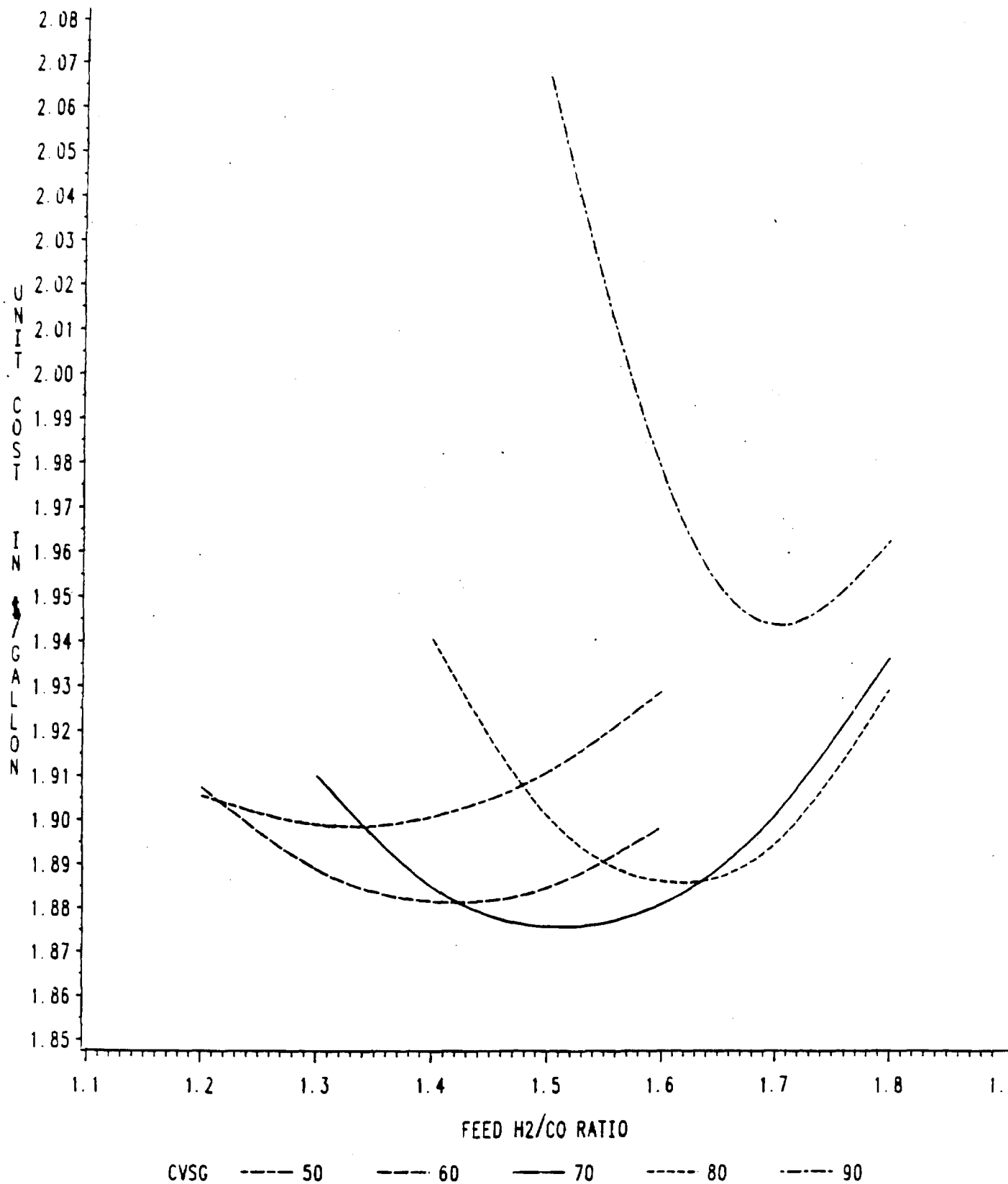


Figure VIII-6

# 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

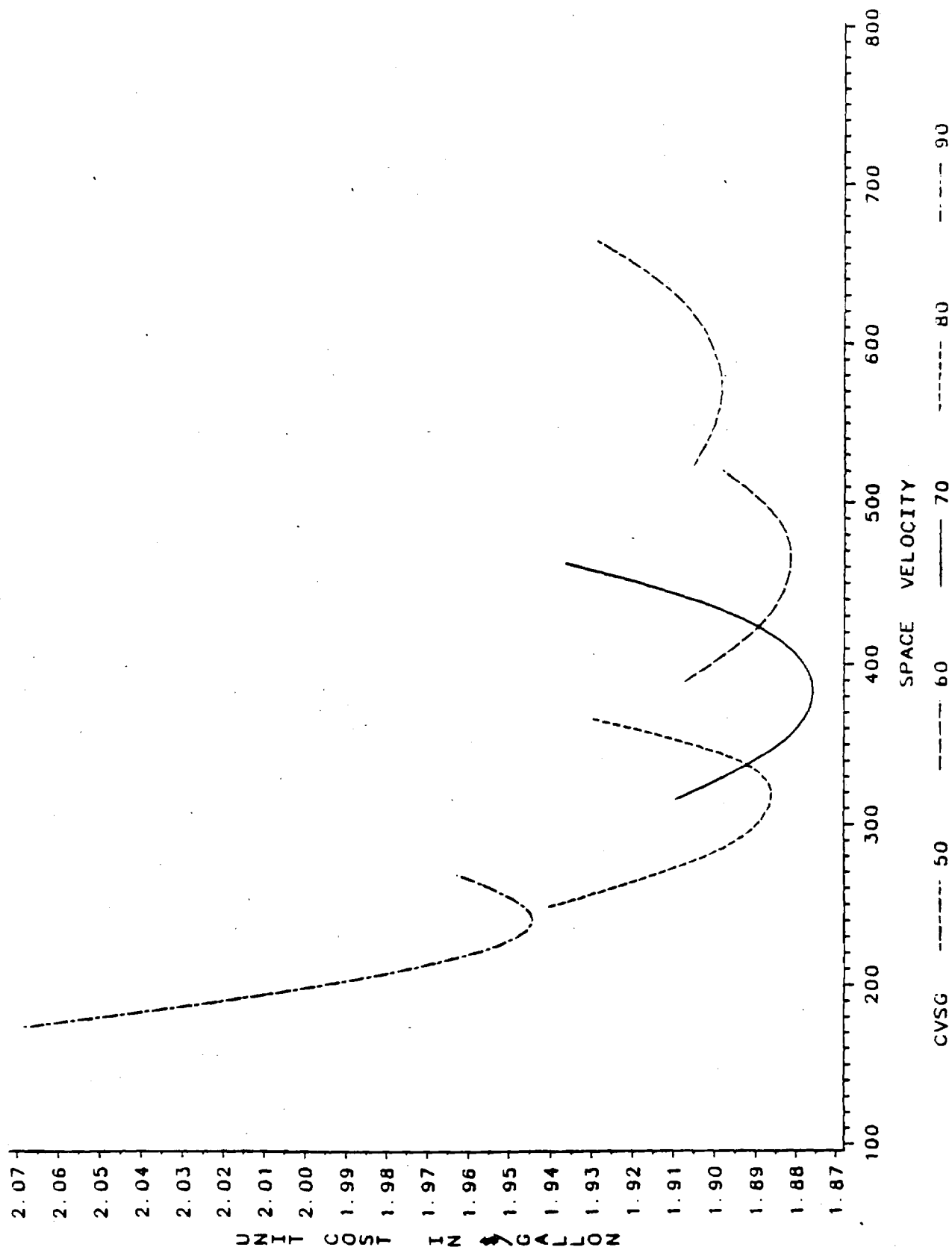


Figure VIII-7

Table VIII-1

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)

Conver- sion,	Reactor Feed H <sub>2</sub> /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			
% CH <sub>4</sub>				16.7	19.2	22.0			
% C <sub>2</sub> -C <sub>4</sub>				12.8	12.9	13.0			
% C <sub>5</sub> -C <sub>10</sub>				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			
% CH <sub>4</sub>				15.6	18.2	21.1			
% C <sub>2</sub> -C <sub>4</sub>				12.1	12.3	12.4			
% C <sub>5</sub> -C <sub>10</sub>				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
% CH <sub>4</sub>	7.64	9.52	11.6	14.1	16.8	19.9	23.4	27.3	31.7
% C <sub>2</sub> -C <sub>4</sub>	9.55	10.3	10.9	11.4	11.8	12.0	12.0	11.9	11.7
% C <sub>5</sub> -C <sub>10</sub>	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			
% CH <sub>4</sub>	5.95	7.73	9.81	12.2	15.1	18.4			
% C <sub>2</sub> -C <sub>4</sub>	8.22	9.19	9.99	10.6	11.1	11.5			
% C <sub>5</sub> -C <sub>10</sub>	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
% CH <sub>4</sub>		5.64	7.57	9.94	12.8	16.3	20.5	25.7	32.1
% C <sub>2</sub> -C <sub>4</sub>		7.63	8.73	9.65	10.4	10.9	11.2	11.2	10.9
% C <sub>5</sub> -C <sub>10</sub>		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 VIII-1 (continued)

Conver- sion	Reactor Feed H <sub>2</sub> /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
% CH <sub>4</sub>		3.32	4.92	7.03	9.80	13.4	18.2	24.5	32.9
% C <sub>2</sub> -C <sub>4</sub>		5.19	6.71	8.05	9.18	10.1	10.6	10.8	10.5
% C <sub>5</sub> -C <sub>10</sub>		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
% CH <sub>4</sub>			3.51	5.34	7.94	11.6	16.6	23.8	33.8
% C <sub>2</sub> -C <sub>4</sub>			5.16	6.77	8.22	9.39	10.2	10.5	10.1
% C <sub>5</sub> -C <sub>10</sub>			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
% CH <sub>4</sub>				3.67	5.92	9.38	14.8	23.2	36.9
% C <sub>2</sub> -C <sub>4</sub>				4.99	6.80	8.39	9.59	10.1	9.50
% C <sub>5</sub> -C <sub>10</sub>				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 VIII-2

Scale-up Factors for the Major Cost Items

<u>Item</u> Reactor	<u>Scaling Factor</u> Linear	<u>Stream or Quantity</u> No. of reactors required plus 2 spare Reactor effluent (1)
CO <sub>2</sub> 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	C <sub>3</sub> + produced
Catalyst costs	Linear	Catalyst density
Total H <sub>2</sub> Equip.	Constant	
Power Generation	0.7 power	CH <sub>x</sub> Produced
O <sub>2</sub> Plant Cost	0.7 power	O <sub>2</sub> demand from CH <sub>4</sub> and C <sub>2</sub> H <sub>6</sub> 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 CO<sub>2</sub>) 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 CO<sub>2</sub>, but not steam (see Figure 5).

(3) SHIFT = the relative amount of shift required from a raw syngas with a H<sub>2</sub>/CO ratio of 0.5 to the desired feed ratio.

Table VIII-3

Typical Output for the Cost Estimating Program

CVSG, Conv. Syngas	0.700006	0.699921	0.700000
RF, Feed ratio, H <sub>2</sub> /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 % CH <sub>4</sub>	7.570700	9.935600	12.810300
RR, recycle ratio (SG & CO <sub>2</sub> )	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
CO <sub>2</sub> removal, RR**0.7	48.365	49.292	50.418
Lights recovery, RR**0.7	46.699	47.593	48.681
FT prod. fractn, 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. Total H <sub>2</sub> equip. cost	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. O <sub>2</sub> plant cost (O <sub>2</sub> **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*capitl	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*capitl	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 VIII-4

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

Conver- sion, %	Syngas Feed Ratio (H <sub>2</sub> /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.