Following the pretreatment, synthesis operation was started at the same conditions which were used in Run CT-225-112. Figures IV 7 shows the conversion and methane + ethane selectivity for the run At these conditions, the initial H_2+CO conversion of 53 mol % was comparable to other F-T catalysts we have studied.

The catalyst continued to activate over the first fourteen hours on stream, while the methane + ethane selectivity dropped to 2.0 wt % of hydrocarbons. The reactor wax produced during the run was allowed to build up in the reactor, since wax removal might have resulted in some catalyst loss, as happened in Run CT-225-112.

These results, combined with the previous study, indicated that Catalyst I-D can produce low methane + ethane yields, and it was slated for further testing in the BSU.

This run also marked the first time in our studies that an orifice-type feed-gas distributor was used in a reacting bubble-column reactor. No adverse effects could be detected. An orifice distributor was chosen for the later BSU operation.

C. Other Supporting Studies

C.1. Evaluation of a Method for Measuring F-T Catalyst Size Distribution

The catalyst particle size distribution in a F-T slurry is essential for determining the catalyst settling characteristics. We identified a particle size analyzer (Sedigraph 5000E made by Micromeritics, Inc.) which can be applied to fresh slurry F-T catalysts. This analyzer uses a low intensity X-ray beam to measure the size of solid particles settling in a liquid, and it has the following important features:

- The instrument limit on the minimum particle size is 0.1 micron, which allows detection of the small particles in F-T slurries.

- The catalyst sample can be suspended in any hydrocarbon liquid, provided the density and viscosity of the liquid at room temperature are known.

The second feature may be especially useful, since catalyst can be separated from the reactor-wax by diluting the slurry with solvent and centrifuging several times.

Figure IV-7

SYNTHESIS GAS CONVERSION AND METHANE AND ETHANE YIELD
(RUN CT-225-113; CATALYST I-D: PPTD Fe/Cu/K$_2$CO$_3$)
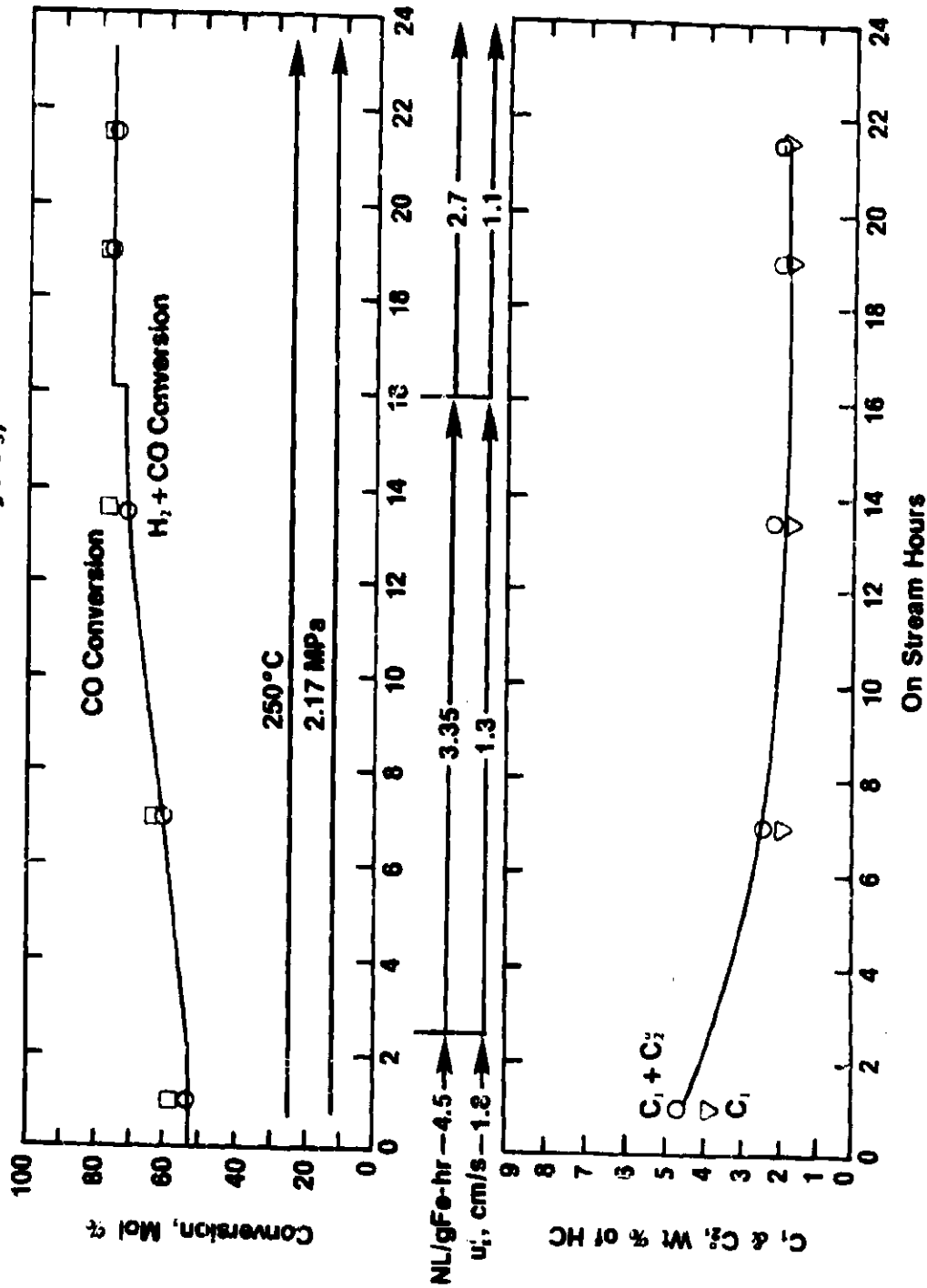
The Sedigraph 5000E analyzer was used to analyze a sample of fresh F T Catalyst I B (Fe/Cu/K$_2$CO$_3$), as shown in Figure IV 8. The mean particle size was 4.2 micron, the range being .15-40 micron. The sample size was 1-2 g.

To test the accuracy of the Sedigraph 5000E analyzer, two standard samples from the Community Bureau of Reference, Brussels, Belgium (obtained through Gilson Co., Inc.), were analyzed by a standard method. These samples had quartz particles in the range .35 3.5 micron and 1 20 micron, respectively. Table IV-1 shows the small discrepancies between the results of the Sedigraph 5000E analyzer and the data reported on the Certificate of Measurement of the standards. Part of these discrepancies may be due to the inhomogeneity of a small sample obtained from the original standard sample.

A sample of spent catalyst from Run CT-256-3 (after 86 DOS) and separated from reactor-wax by centrifuging in toluene, was sent to Micromeritics for analysis. Preliminary results indicated that the particles were smaller than 3 micron and a significant portion was in the submicron range. Based on this, it appeared that there was substantial disintegration during that run. However, this catalyst could not be analyzed for detailed particle size distribution. Micromeritics claimed that they could not settle the particles.

The major difficulty in analyzing spent F-T catalyst is to separate the catalyst from the reactor-wax without changing the particle size distribution. Since the Micromeritics' technique was only applied at room temperature, it appears that it is unsuitable for spent catalyst particle size analysis. We are not aware of any high temperature technique suitable to analyze such small particles.

C.2. Effect of Water-Gas Shift Activity on Conversion: Mathematical Model Calculations

Since the Fe-based F-T catalyst is also a water-gas shift catalyst, it can be used with a low H$_2$/CO ratio synthesis gas to obtain high H$_2$+CO conversion. Thus, the water gas shift activity plays an important part in the performance of the two-stage slurry reactor. We used our multi-component mathematical model to establish the relative importance of the shift activity and F-T activity of the catalyst:

The model is based on the following kinetic rate expressions (Kuo, 1983):

$$\text{F-T:} \quad r_1 = k_1 \, [H_2] \, [CO] / ([CO] + k_3 [H_2O]) \tag{IV-1}$$

Figure IV-8

PARTICLE SIZE DISTRIBUTION OF FRESH
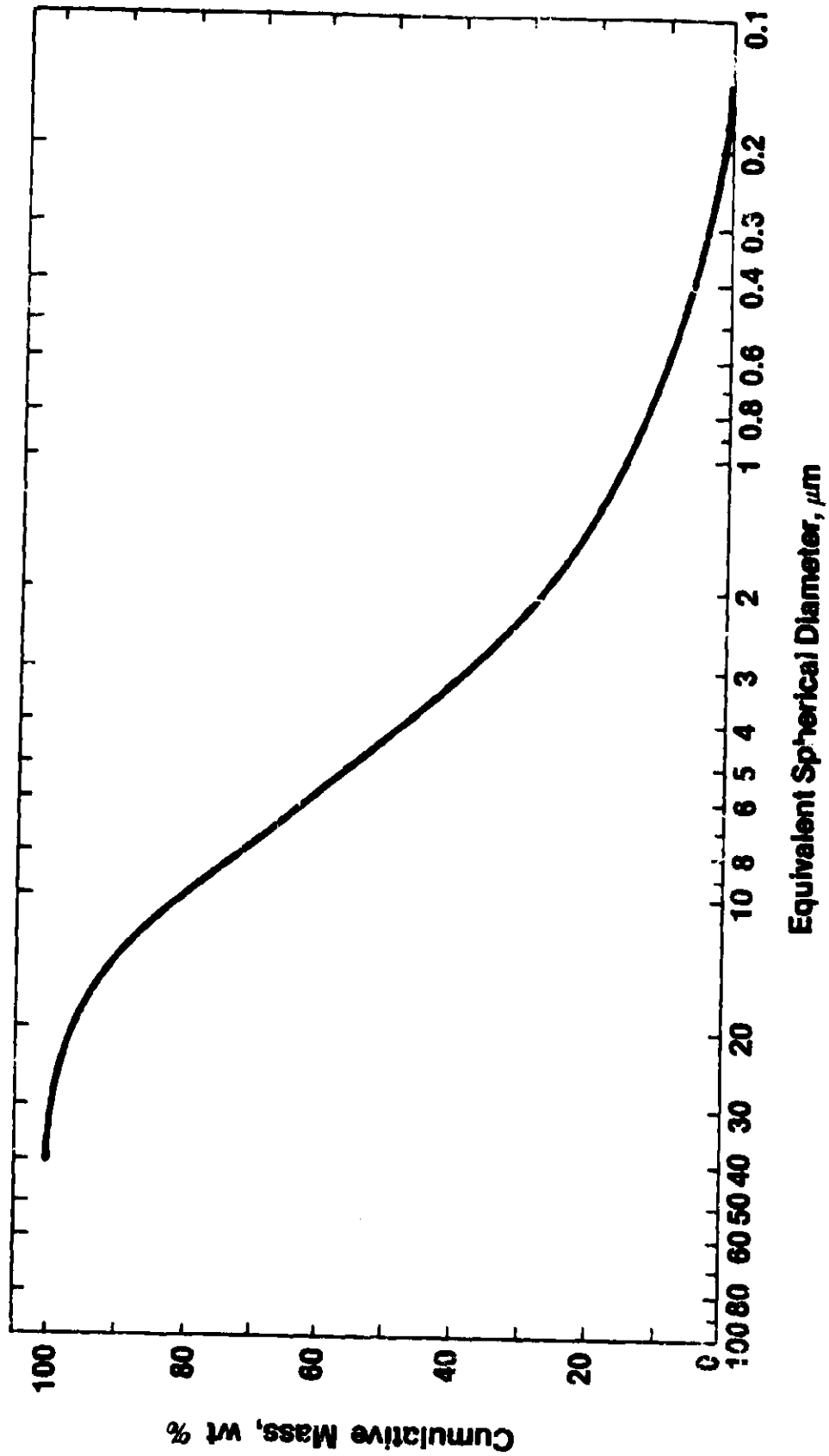## CATALYST I-B MEASURED BY SEDIGRAPH 5000E
PARTICLE SIZE ANALYZER

Table IV-1

Testing of Sedigraph 5000E Particle
Size Analyzer with Standard Samples[1]

Wt. % Less Than	Particle Size, µm		
Standard A (.35-3.5µm)	Sed. 5000E	Standard[2]	Error (%)
10	.84	.57 ± .12	46.9
50	1.45	1.13 ± .20	28.3
90	2.37	2.15 ± .30	10.1
Standard B (1-20µm)			
10	1.54	1.20 ± .25	28.3
50	3.10	2.92 ± .30	5.8
90	7.20	7.27 ± .60	1.0

(1)Samples were obtained indirectly from the Community Bureau
of Reference, Brussels, Belgium.

(2)Data reported in the Certificate of Measurement issued by the
Community Bureau of Reference (November 6, 1979).

Shift: $r_2 = k_2([CO][H_2O] - H_2 \cdot CO_2/k_4)/([CO] + k_3[H_2O])$ (IV-2)

The k_1 and k_2 are the F-T and shift kinetic rate constants, k_3 is the ratio of water and CO adsorption constants, and k_4 is the shift equilibrium constant. [ ] signifies volumetric concentrations in the liquid phase. We varied k_1 and k_2 over a wide range to study their relative effects on the H_2, CO, H_2+CO conversion and H_2/CO usage ratio. In the slurry reactor, the variation in k_1 and k_2 can be a result of either temperature variation or catalyst aging.
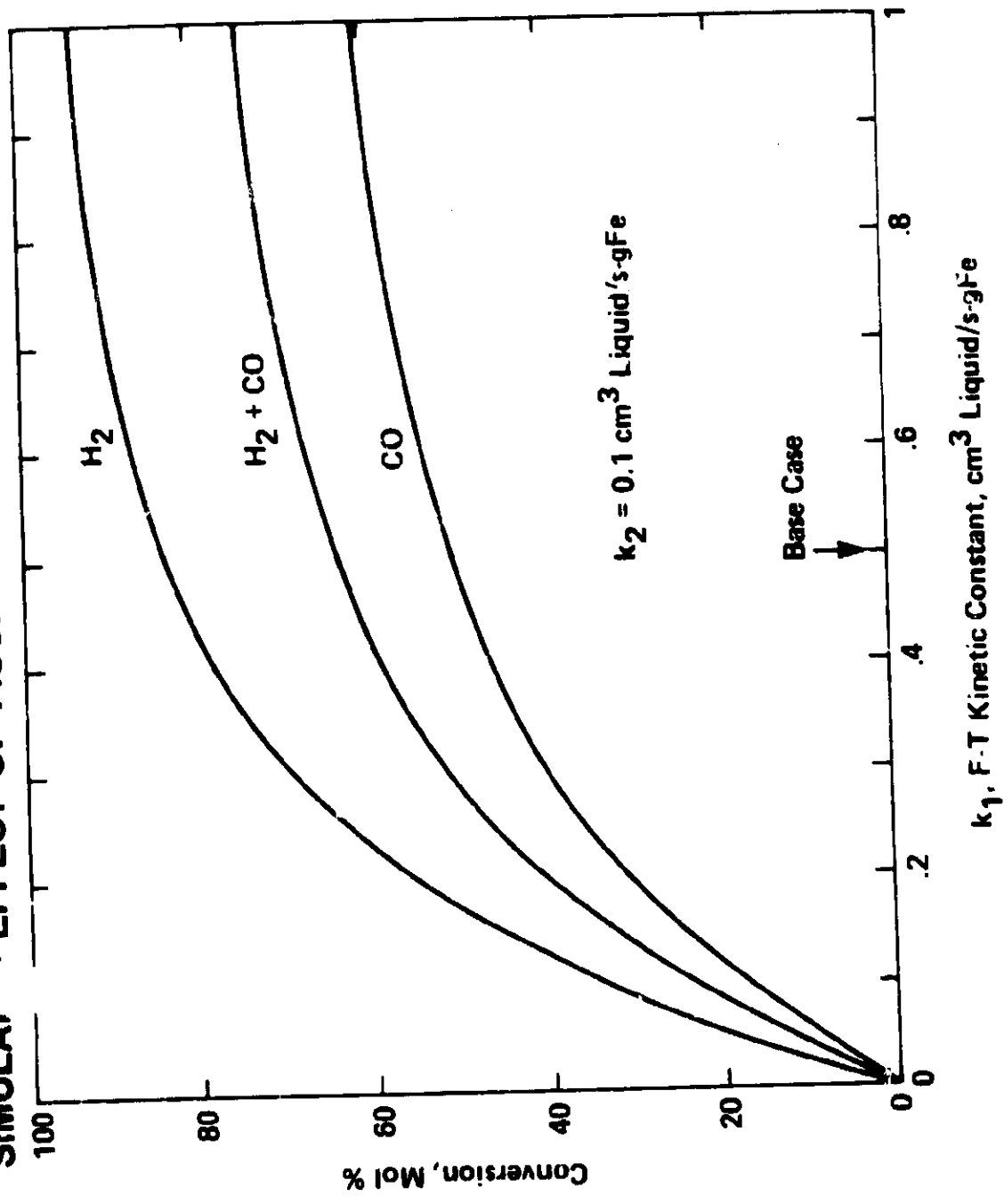
The major conclusions are:

- H_2/CO usage ratio increases with declining shift activity (i.e., decreasing k_2).

- Low H_2 conversion is the result of low F-T activity irrespective of shift activity.

- Low shift activity with good F-T activity gives high H_2 conversion but low (H_2+CO) conversion.

- When the effect of temperature on both k_1 and k_2 is considered for Run CT-256-3 start-of-cycle catalyst, the water-gas shift activity is sufficient to maintain a low H_2/CO usage ratio at temperatures > 245°C. The activation energies for k_1 and k_2 were 100 and 140 kJ/mol, respectively.

In the following the detailed results are discussed.

Figures IV-9 and -10 show the effect of F-T activity, k_1, on the H_2+CO conversion for a very low and a very high shift activity ($k_2 = 0.1$ and 2.4 cm^3 liquid/s-gFe) respectively. From these two plots, it can be seen that the H_2+CO conversion drops rapidly as the F-T activity (i.e., k_1) declines at both low and high levels of shift activity. The main difference between the low and high shift activity is in the H_2/CO usage ratio. This fact is more clearly borne out by Figures IV-11 and -12, where the conversion is plotted as a function of shift kinetic constant, k_2, (i.e., shift activity) at two levels of F-T activity.

These two figures show that shift activity has a significant effect on H_2+CO conversion only when it is very low (<0.5 cm^3 liquid/s-gFe). In this case, the H_2/CO usage ratio increases substantially and hence even though the H_2 conversion increases with decrease in k_2, the overall conversion decreases. As seen here, the lower shift activity does not reduce the H_2

Figure IV-9

SIMULAT? EFFECT OF FISCHER-TROPSCH KINETIC CONSTANT

$k_2 = 0.1$ cm^3 Liquid/s-gFe

Base Case

k_1, F-T Kinetic Constant, cm^3 Liquid/s-gFe

Conversion, Mol %

H$_2$

H$_2$ + CO

CO

Figure IV-10

SIMULATED EFFECT OF FISCHER-TROPSCH KINETIC CONSTANT

$k_2 = 2.47$ cm^3 Liquid/s-gFe

Base Case

k_1, F-T Kinetic Constant, cm^3 Liquid/s-gFe

Conversion, Mol %

H$_2$ + CO

H$_2$

CO
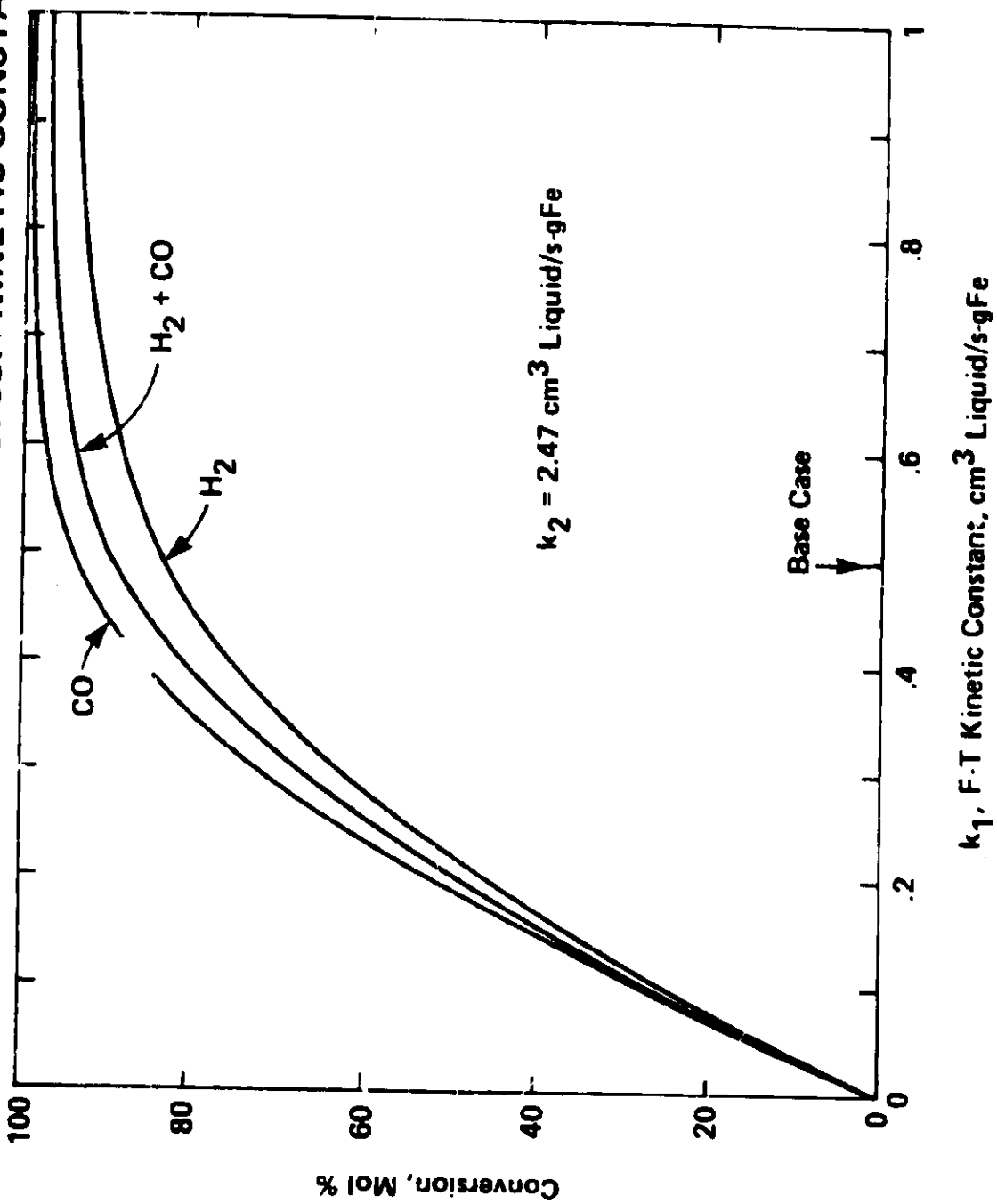
Figure IV-11

SIMULATED EFFECT OF WATER-GAS SHIFT KINETIC CONSTANT

$k_1 = 0.2 \text{ cm}^3$ Liquid/s·gFe

CO

$H_2 + CO$

H_2

Base Case

k_2, Shift Kinetic Constant, cm^3 Liquid/s·gFe
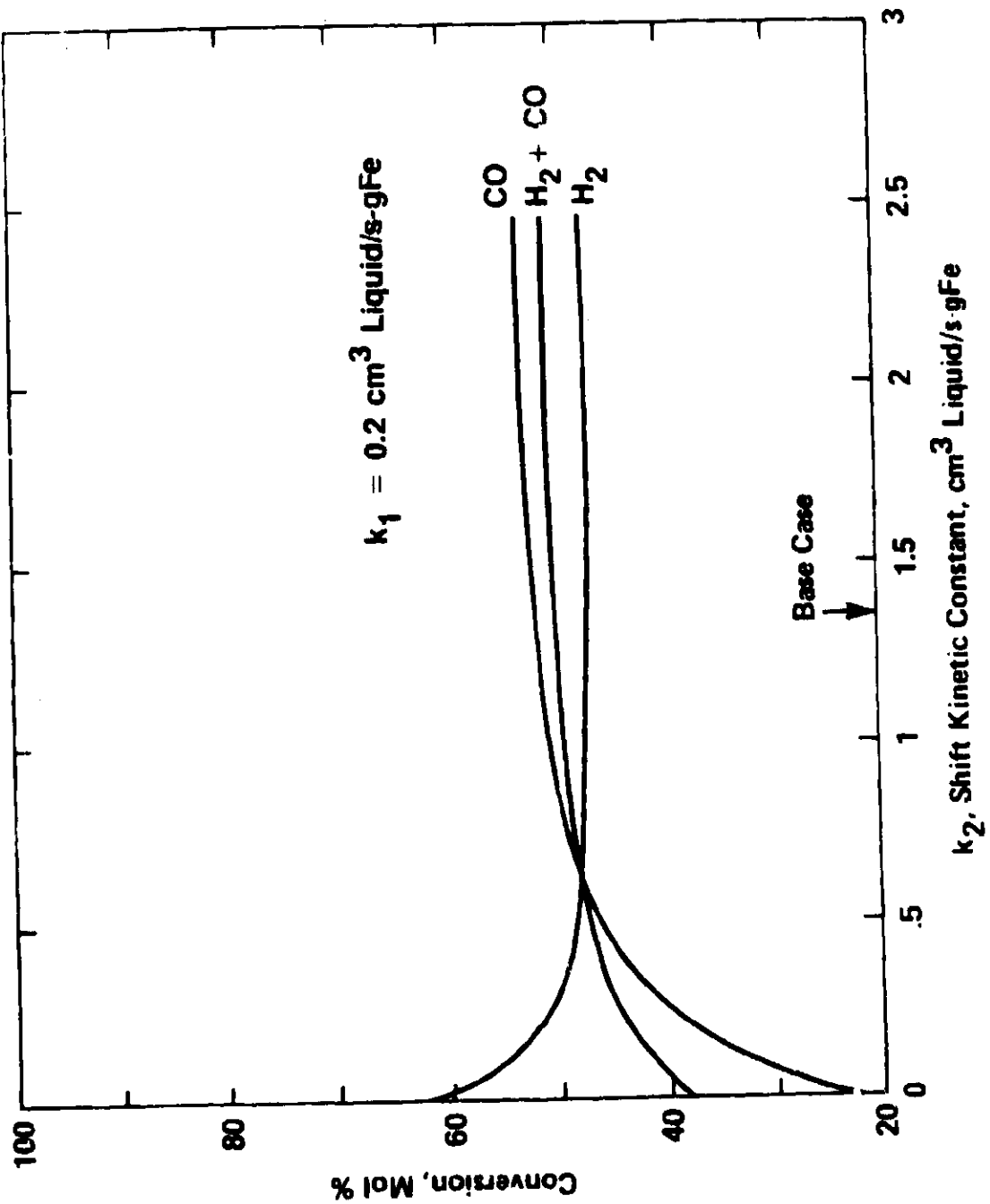
Conversion, Mol %

Figure IV-12

SIMULATED EFFECT OF WATER-GAS SHIFT KINETIC CONSTANT

$k_1 = 1.0$ cm^3 Liquid/s-gFe

k_2, Shift Kinetic Constant, cm^3 Liquid/s-gFe

Conversion, Mol %

Base Case

CO

H$_2$ + CO

H$_2$
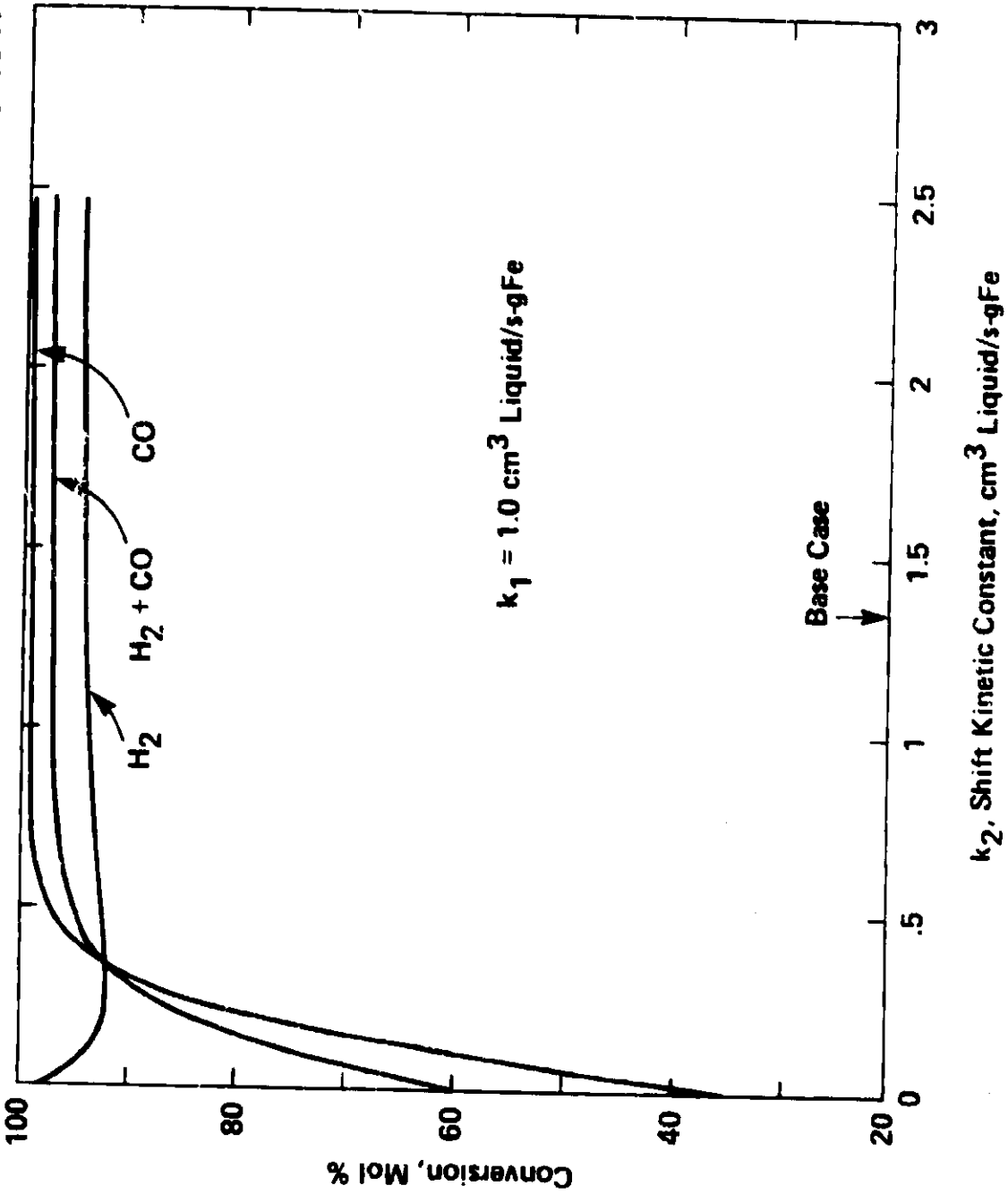
conversion. Hence, a low H_2 conversion is always due to lower F-T activity. On the other hand, a drop in CO conversion with the H_2 conversion staying the same is a result of decreasing shift activity.

From the above, it follows that lower shift activity increases the H_2/CO usage ratio. The higher H_2/CO usage ratio results in lower H_2/CO ratio in the reactor than was in the feed. This may affect the F-T activity, which in turn may further decrease the overall H_2+CO conversion. Hence, a higher shift activity is desired.

Since both F-T and shift kinetic constants decrease with temperature, it is important to study the effect of temperature on the overall conversion. Figure IV-13 shows the effect of temperature on conversion through decrease in both F-T and shift activities. Unlike previous parametric studies where only one kinetic constant was changed at a time, both k_1 and k_2 were varied with temperature assuming appropriate activation energies (Deckwer et al. (1982), and Newsome (1980)). As expected, the H_2+CO conversion decreases substantially with a decrease in temperature. But it is important to note that at temperatures > 245°C the h_2/CO usage ratio is still lower than the feed H_2/CO ratio. Thus, the H_2/CO ratio in the reactor is higher than the feed ratio. A higher H_2/CO ratio in the reactor is always preferable to minimize catalyst aging. At temperatures below 245°C the H_2/CO usage ratio is higher than the feed ratio. It may be advisable to avoid this to prevent any catalyst aging due to the lower H_2/CO ratio environment. Thus, for a 0.67 H_2/CO ratio feed-gas reaction temperatures should be maintained above 245°C. Of course, if a feed gas of higher H_2/CO ratio is used, then temperatures lower than 245°C may be tolerated.

D. Run CT-256-6

The sixth run of the two-stage BSU, designated as Run CT-256-6, using Catalyst I-D in the first stage F-T bubble-column reactor and Catalyst II-B (a ZSM-5 class catalyst) in a second-stage fixed-bed reactor, was smoothly started up on March 21, 1984. The major objectives of the run were to evaluate the performance of Catalyst I-D for low methane + ethane operation and to test many new features of the F-T slurry bubble-column, including an on-line slurry catalyst/reactor-wax separation system, and a purgeless DP system.

Figure IV-13

SIMULATED EFFECT OF TEMPERATURE
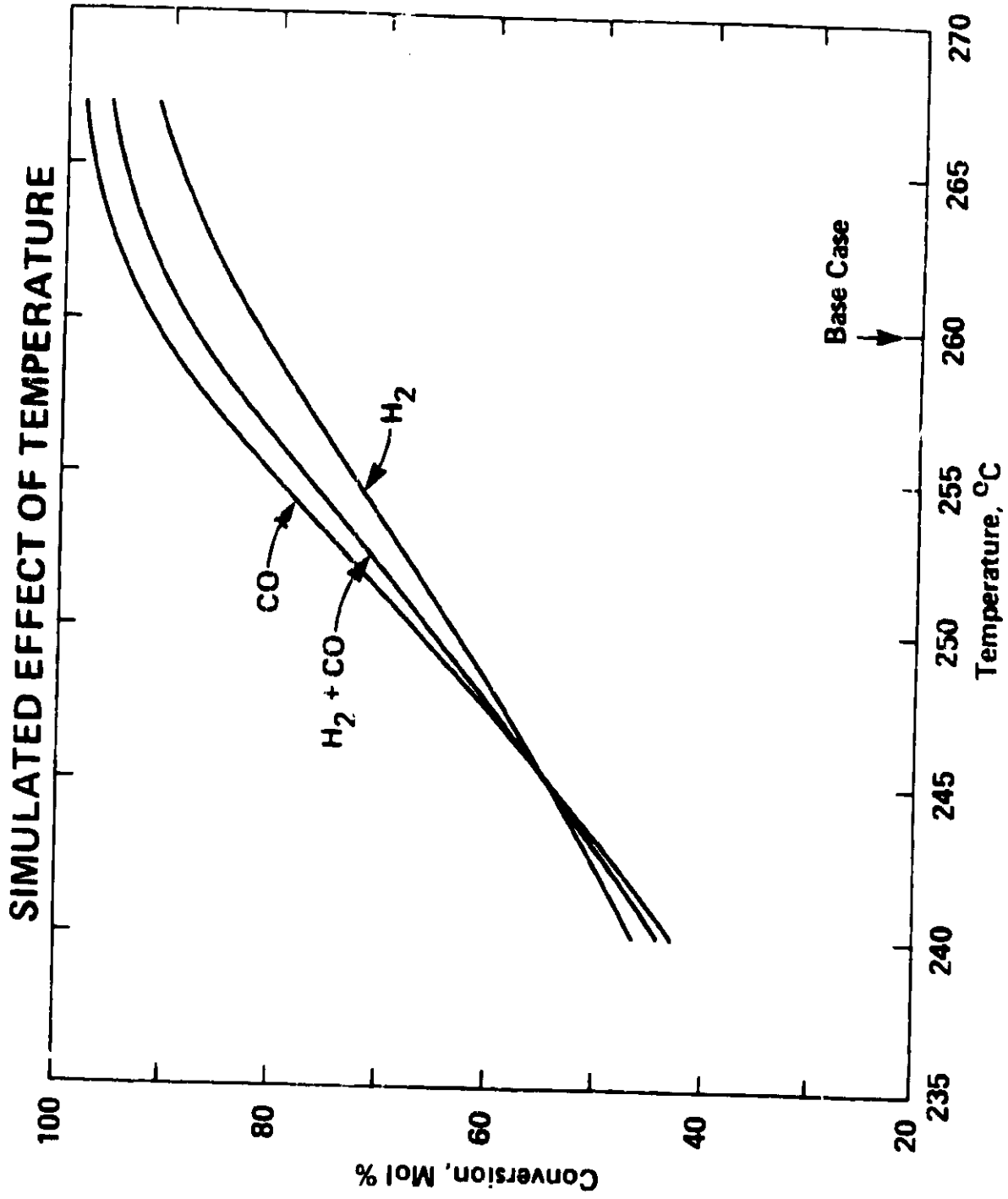
Major highlights from this run are:

- The catalyst was activated in two hours in a standard high temperature (280°C) pretreatment step.

- Initial catalyst activity was equivalent to that of the most active F-T catalysts evaluated so far.

- The low methane + ethane yield over 33 days of operation demonstrated the stability of catalyst I-D for maximum liquid fuels production.

- The second-stage fixed-bed reactor was operated for only two days (due to end zone heater burnout) at:

Inlet Temperature, °C	288
GHSV, NL per hr/L-Cat.	2,419-5,067

- Increased pressure (from 1.14 to 2.18 MPa) significantly decreased the H_2+CO conversion (e.g. at 9 DOS conversion dropped from 63 to 42 mol %). This contradicts previous experience with other catalysts (e.g. Catalyst I-B, Run CT-256-3) and requires further investigation.

- Two minor and one major interruption occurred in the F-T operation. Significant loss in activity and increased methane + ethane yield resulted only after a major upset at 26 DOS. This upset was caused by a faulty surge check valve on the CO feed line. N_2 was fed to the slurry reactor for 76 hours. After this upset, the activity was very low and the run was terminated, even though the methane + ethane yield was a low 3.8 wt %.

- Demonstrated addition of fresh Catalyst I-D and in-situ activation without separate (high temperature) pretreatment.

- Demonstrated reliable operation of an on-line slurry catalyst/reactor-wax separation system and of a purgeless DP-system.

Material balances were performed daily and summarized in Appendix A. Table A-1 summarizes the operating conditions and results for this run. Detailed analytical breakdowns of the first-stage product are given in Table A-2. Breakdown of the reactor-waxes and oxygenates were not available. The major events are listed in Table IV-2.

Table IV-2

Major Events in Run CT-256-6
(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
-0.1- 0	Pretreatment.
0 - 0.8	1.14 MPa; 250°C; 4 cm/s; 0.7 H_2/CO
0.8- 2.0	1.14 ---> 2.18 MPa
1.1	Upset: Slurry leak at on-line catalyst/wax separation system
2.0- 9.1	2.18 ---> 1.14 MPa, 4 ---> 3 cm/s
9.1-11.8	1.14 ---> 2.18 MPa
11.8-14.6	2.18 ---> 1.14 MPa
14.2	Second-stage on at 288°C
14.6-22.6	1.14 ---> 2.19 MPa
15.8	Second-stage off: end zone heater burnout
16.1	350 g of fresh F-T catalyst (I-D) added
19.3.	Upset: CO leak caused synthesis gas cut off for 10 hours
21.6	400 g of fresh F-T catalyst (I-D) added
22.6-25.9	2.18 ---> 1.14 MPa; 3 ---> 1.1 cm/s
25.9	Upset: No CO flow due to safety surge check valve shut off -- no synthesis gas to unit for 3 days
25.9-33.1	1.14 MPa; 250°C, 3 cm/s; 0.7 H_2/CO
32.1	0.7 ---> 0.4 H_2/CO and stoichiometric steam cofeed to the slurry reactor for 4 hours
33.1	End of Run

D.1. Fischer-Tropsch Slurry Catalyst Loading and Pretreatment

Catalyst loading and pretreatment similar to those of Run CT-256-4 (see Kuo, 1983) were used in this run. 1,863 g of F-T Catalyst I D, along with 1,327 g of Mobil F-509 and 6,046 g of spent reactor wax (from Runs CT-256-4 and 5) were loaded. The initial catalyst loading was 20.2 wt %.

The F-T catalyst pretreatment conditions were:

$H_2 \cdot CO$ Flow Rate, Nm^3/hr	2.57
Feed H_2/CO, molar	0.7
Superficial Feed-Gas Vel., cm/s	6
Space Velocity, NL/gFe-hr	2.0
Temperature, °C	280
Pressure, MPa	1.4

The pretreatment operation was ended after two hours, when the gas volume contraction reached 49.4% and the CO conversion reached 74%. Figure IV-14 shows the product gas volume contraction and CO conversion during pretreatment.

D.2. First-Stage Fischer-Tropsch Reactor Operation

Immediately after catalyst pretreatment, at which point the CO conversion reached 75%, the slurry reactor temperature was lowered to 250°C. Twelve hours later, when the H_2+CO conversion gradually increased back to about 68 mol %, the pressure was increased to 2.18 MPa for increased throughput, and the on-line catalyst/reactor-wax separation system was started up to remove the reactor-wax accumulated in the reactor.

Figure IV-15 shows the conversion and methane and ethane selectivities, as well as the temperature, pressure, superficial gas velocity, and space velocity for the entire run. The ranges of synthesis conditions and performance of the first-stage F-T reactor were:

H_2+CO Flow Rate, Nm^3/hr	0.5-3.4
Temperature, °C	250
Pressure, MPa	1.14-2.18
Feed H_2/CO, molar	0.7
Superficial Feed-Gas Vel., cm/s	1.1-4.0
Space Velocity, NL/gFe-hr	C 4-4.1
H_2+CO Conversion, mol %	35-75
Methane + Ethane Yield, wt %	1.7-3.8
Reactor-Wax Yield, wt %	30-80
Hydrocarbon Production. gHC/gFe	250

The weight of the hydrocarbon production per weight of Fe was calculated by accumulating the daily total hydrocarbon production based on estimated daily Fe inventory in the reactor.

Figure IV-14

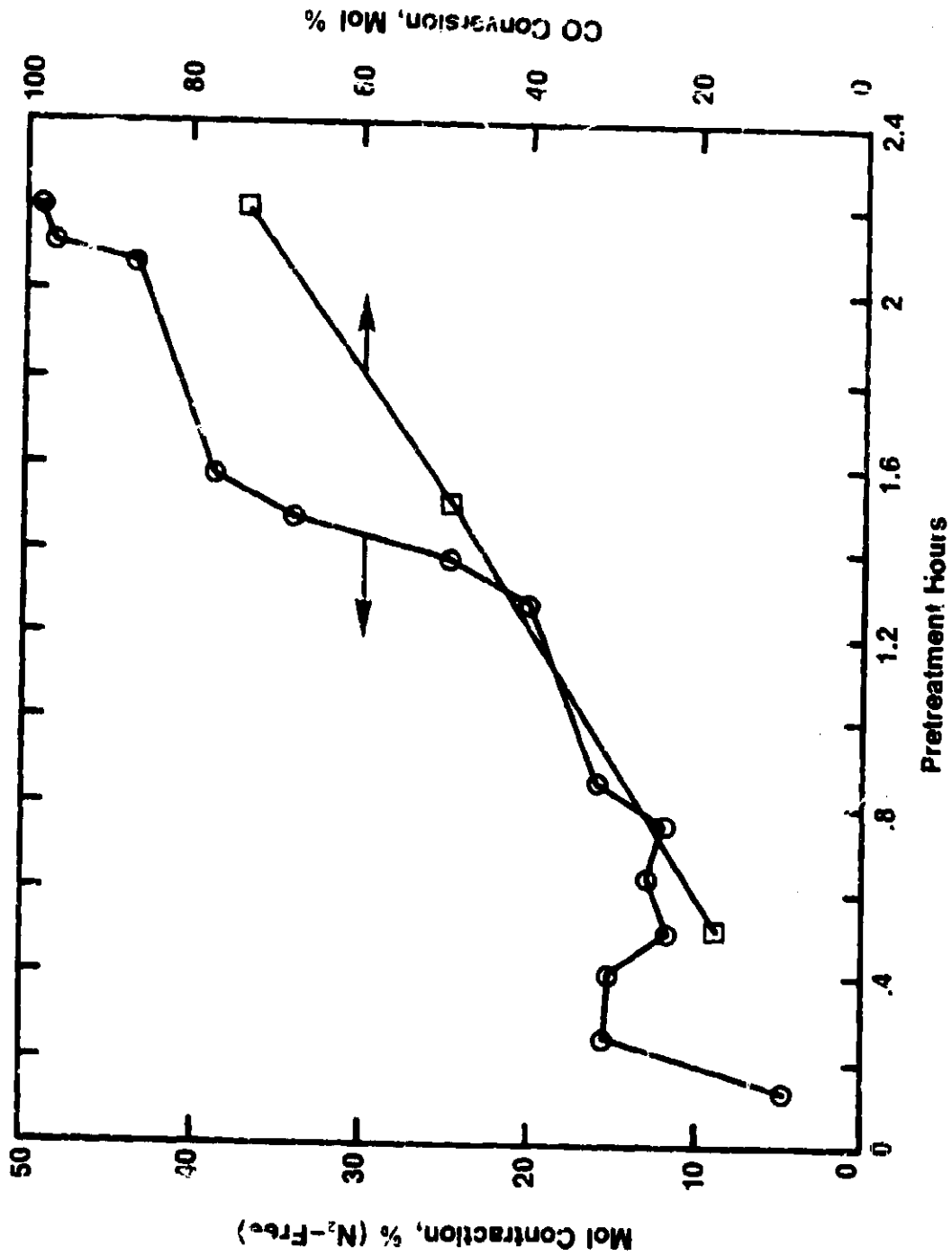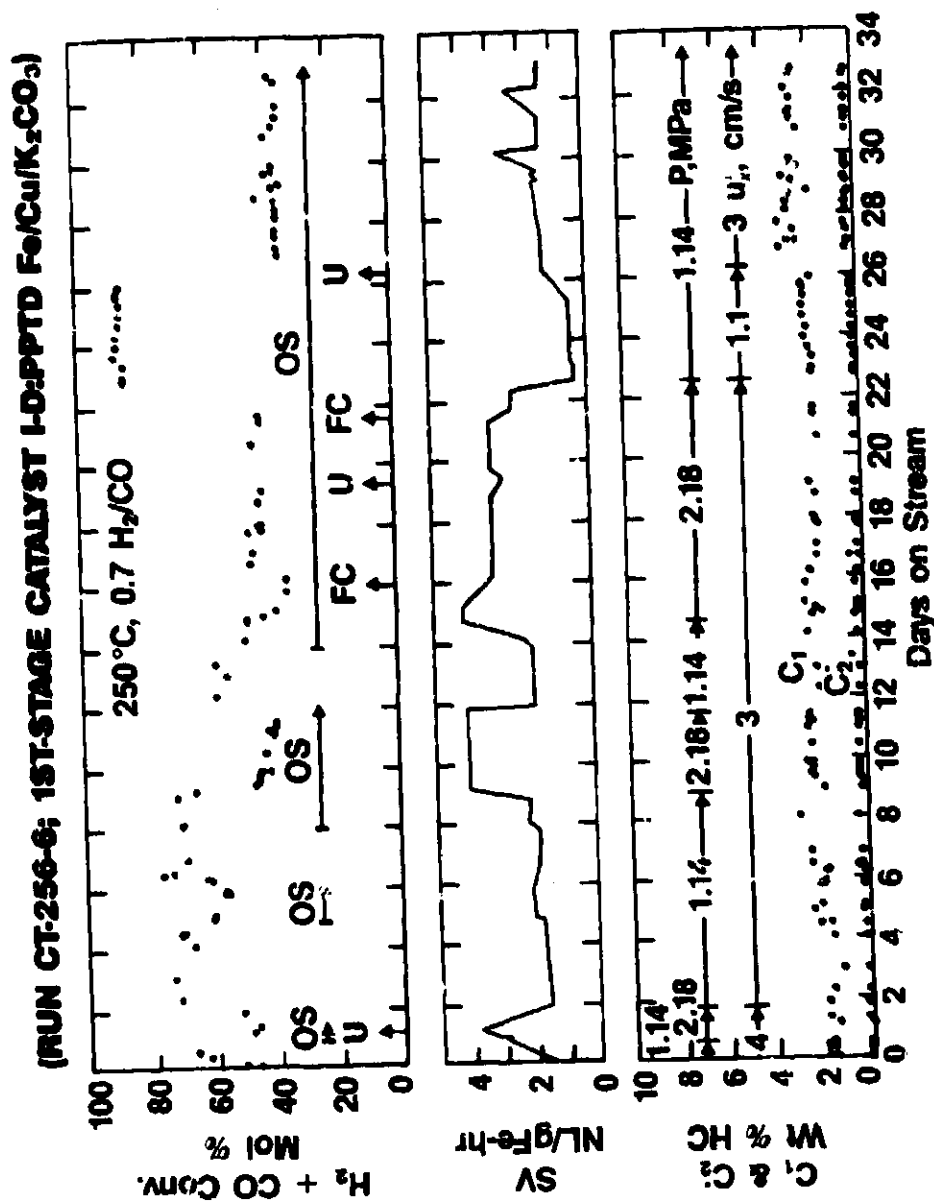## PRETREATMENT OF FISCHER-TROPSCH CATALYST I-D
(RUN CT-256-6)

Figure IV-15

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD

(RUN CT-256-6; 1ST-STAGE CATALYST I-D2PPTD Fe/Cu/K₂CO₃)

U - Upset   FC - Fresh Catalyst Added   OS - On-line Catalyst/Wax Separation

The synthesis operation was interrupted three times. The first interruption was due to a slurry leak in the on-line slurry catalyst/reactor-wax separation system, which resulted in the loss of about 480 g of catalyst. The second interruption was caused by a faulty surge check valve on the CO feed line. N_2 was fed to the slurry reactor for 9 hours, while the surge check valve was replaced. This upset had no detrimental effect on reactor performance.

The third interruption was again due to the surge check valve on the CO line. The system was then modified to include two surge check valves in parallel. This allows replacement of one valve without interrupting CO supply to the unit. During this last interruption, leaks were found on the pancake valves which activate the H_2 and CO glycol systems used for feed flow rate measurement. While these were being fixed, N_2 was fed to the slurry reactor over a total of 76 hours. This last upset seemed to have a detrimental effect on both H_2+CO conversion and methane + ethane yield. It is not clear whether the interruption itself or the four-day operation at very low gas superficial velocity (about 1 cm/s) preceding the interruption caused the drop in H_2+CO conversion and the increased methane + ethane yield. Such low velocity operation had caused problems before (e.g. Run CT-256-3, Kuo 1983).
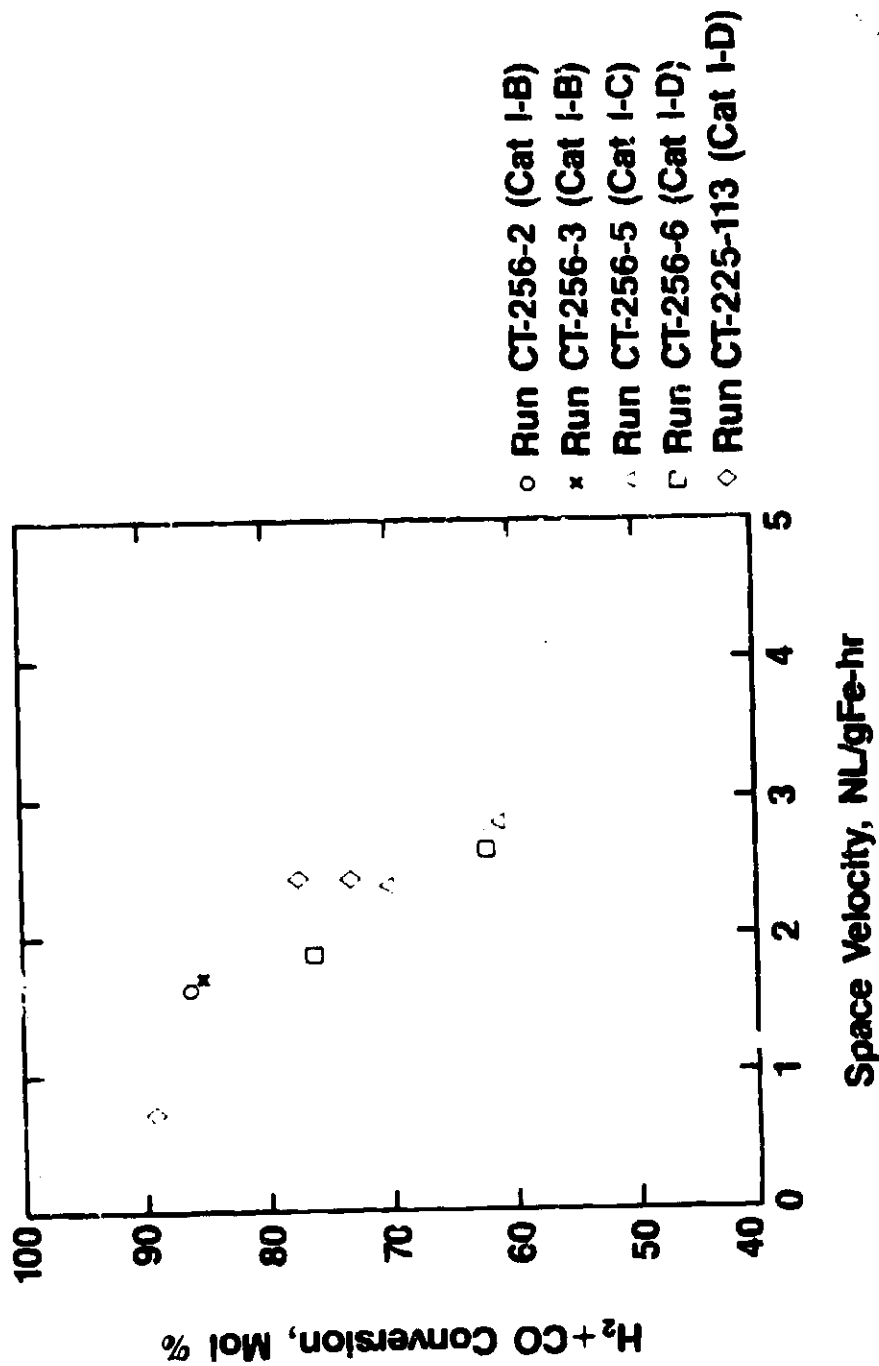
The initial catalyst activity was found to be comparable to that of the most active F-T catalysts used. This is shown in Figure IV-16, as H_2+CO conversion versus space velocity. Except for the low velocity data, all data fall within the same range for a given space velocity.

During the run, fresh I-D catalyst was added twice, to bring the catalyst content to the initial level, and to test on-stream activation without separate pretreatment. The results are shown in Figure IV-17. Volume contraction, which is proprotional to H_2+CO conversion, was used to determine the extent of catalyst activation. It is seen that, in two cases, the catalyst reached 95 and 75% of the full expected activity, respectively, within ~10-20 hours, indicating the capability of on-stream catalyst makeup without separate high temperature pretreatment.

Increased pressure had a detrimental effect on the H_2+CO conversion, without affecting the methane + ethane yield. For instance, increasing the pressure from 1.14 to 2.18 MPa reduced the H_2+CO conversion at 9 DOS from 63 to 42 mol %.
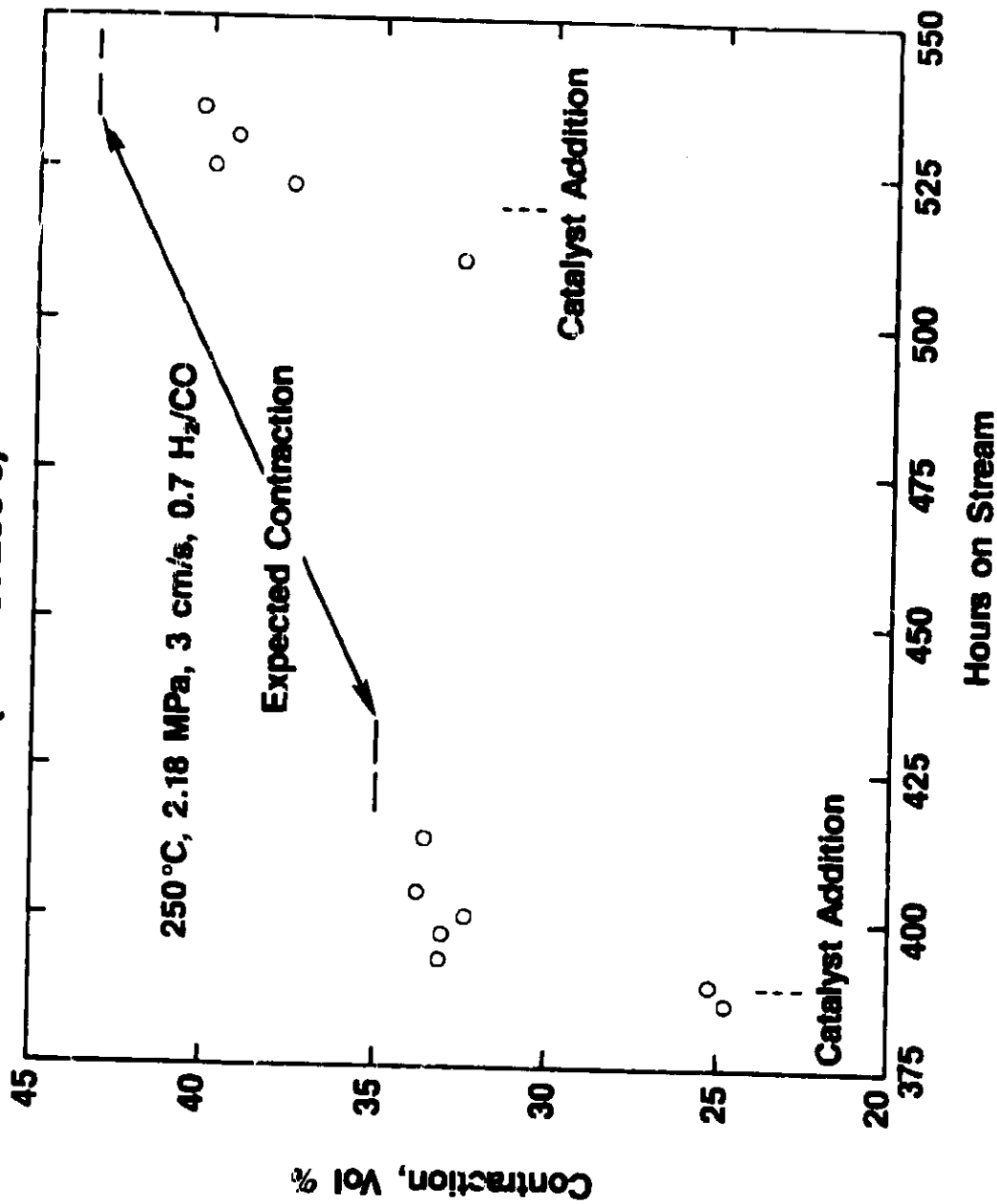
Although the H_2+CO conversion varied significantly throughout the run, mostly the result of upsets and pressure variation (between 1.14 and 2.18 MPa), the methane + ethane yield was a low 1.7-3.8 wt % over the whole run (33 days). This

Figure IV-16

COMPARISON OF INITIAL FISCHER-TROPSCH CATALYST ACTIVITIES

o Run CT-256-2 (Cat I-B)
x Run CT-256-3 (Cat I-B)
△ Run CT-256-5 (Cat I-C)
□ Run CT-256-6 (Cat I-D);
◇ Run CT-225-113 (Cat I-D)

All data corrected to 1.48 MPa, 250°C

Figure IV-17

FRESH FISCHER-TROPSCH CATALYST ADDITION
(RUN CT-256-6)

250°C, 2.18 MPa, 3 cm/s, 0.7 H_2/CO

Expected Contraction

Catalyst Addition

Catalyst Addition

Contraction, Vol %

Hours on Stream

indicates that Catalyst I D has good stability for low methane + ethane operation. The run was terminated because of the very low activity after the last upset.

Note that the conversion dropped every time the on-line slurry catalyst/reactor-wax separation system was on. The reason for this is that the separation system has a slurry holdup of about 2,000 cm³, and the catalyst in this slurry does not participate in the reaction.

F T reactor wax was removed regularly (to keep the level in the slurry reactor at about 762 cm) by using the new on line slurry catalyst/reactor wax separation system. The slurry inventory in the slurry reactor was monitored by the new purgeless DP-system described earlier. Figure IV-18 shows the cumulative reactor-wax production versus time-on-stream. The reactor-wax production rate is estimated from the slope of the least squares fit of the data, shown as the continuous curves in the figure.

The purgeless DP-system was also used to estimate the gas holdup in the reactor. Table IV-3 shows the average gas holdup at two superficial gas velocities. The gas holdup at 3 cm/s velocity is substantially higher than that measured at the end of Run CT-256-5 (8.6 vol % at 4 cm/s velocity). The reason for this may be that Run CT-256-5 and -6 waxes are different.

Table IV-3 also shows the predicted gas holdup from Deckwer's correlation (Deckwer et al., 1980). At low velocity, the agreement is good; however, at high velocity, the actual gas holdup is substantially higher than that predicted by Deckwer.

Figure IV-19 shows catalyst concentration profiles obtained by sampling of the reactor slurries at 30, 152, 305, and 610 cm levels. The flatter profile at 29.4 DOS is due to the somewhat higher superficial gas velocity (3.8 vs. 3.0 cm/s). The increased catalyst loading between 15.1 and 19.7, and 19.7 and 29.4 DOS is the result of the two catalyst additions at 16.1 and 21.6 DOS. Good agreement exists between the measured catalyst loading (straight line fit of the data) and the catalyst loading estimated from the initial loading and from the estimated catalyst loss through leaks and reactor-wax removal.

D.3.   Second-Stage Fixed-Bed ZSM-5 Reactor Operation

The second-stage reactor, containing 215 g of fresh II-B ZSM-5 catalyst was brought on-stream at 14 DOS, using a start-of-cycle inlet temperature of 238°C. After 39 hours, the second-stage had to be shut down because of burnout of its end zone heater. Since 39 hours are not sufficient to equilibrate

Figure IV-18

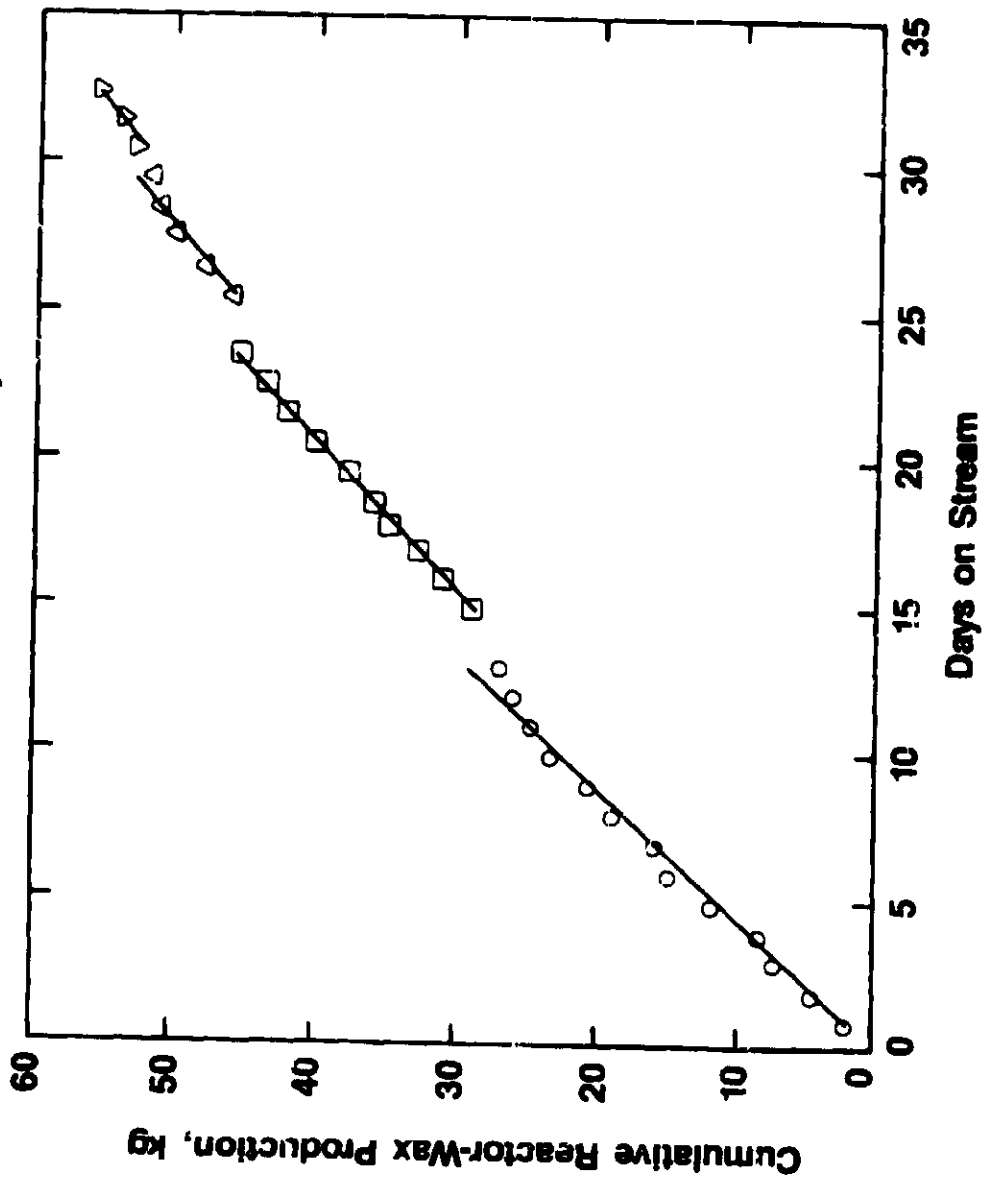## CUMULATIVE FISCHER-TROPSCH REACTOR-WAX PRODUCTION
(RUN CT-256-5)

Table IV-3

Average Gas Holdup
From Purgeless DP-System[1]
(Run CT-256-6)

DOS	17.0	20.4	23.6	24.3
Gas Sup. Vel., cm/s	3	3	1.2	1.2
Contraction, vol %	33.7	35.5	61.3	60.5
Avg. Gas Sup. Vel., cm/s	2.5	2.5	.8	.8
Avg. Gas Holdup, vol %	23.0	21.4	3.5	4.8
Est. Gas Holdup,[2] vol %	14.5	14.5	4.2	4.2

[1]250°C, 0.7 H_2/CO

[2]Deckwer et al., 1980

Figure IV-19

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN CATALYST CONCENTRATION PROFILES
(RUN CT-256-6)

DOS	u_g, cm/s	w_c, Wt %
○ 15.1	3.0	8.4
□ 19.7	3.0	10.9
△ 29.4	3.8	12.2

Reactor Height, cm

Catalyst Concentration, Wt %