

the liquid product receivers. no liquid product analysis is available.

E. Run CT-256-7

Before this run, we installed a pump to continuously withdraw the clean reactor-wax at a controllable rate from the catalyst settling vessel. This new system allowed high flexibility and reduced manpower in unit operation.

The seventh run of the two-stage BSU, designated as Run CT-256-7, was started successfully on May 31, 1984. The main objectives of the run were:

- Demonstrate long-term low methane + ethane operation using Catalyst I-B (Fe/Cu/K₂CO₃) at high pressure, as was done in Run CT-256-4.
- Evaluate for the first time in the BSU bubble-column a 1 mm single-orifice feed-gas distributor.

The run was voluntarily ended on October 11, 1984 after 98 days-on-stream. A summary of major events during the run is given in Table IV-4.

The material balance data for this run are given in Appendix B. Tables B-1 and B-3 summarize the operating conditions and results for the first-stage operation. Tables B-2 and B-4 give the corresponding hydrocarbon product compositions. Similarly, Tables B-5 and B-6 report the operating conditions and results and hydrocarbon product compositions for second-stage operation. Only those balances which had recoveries between 90-110 wt % are reported, as long as the recovery of hydrocarbons produced was within 20% of the expected hydrocarbons production (i.e., 204 gHC/Nm³ H₂+CO converted). Since not all the F-T hydrocarbon liquid streams (light and heavy hydrocarbons and reactor-wax) were analyzed for detailed composition, a CH₂ composition was assumed for all these streams for estimation of the hydrocarbon production per Nm³ H₂+CO. The second-stage gasoline, on the other hand, was assumed to be CH_{1.7}, whenever the detailed composition was not available.

The major highlights of the run were:

- Methane + ethane selectivity was maintained at less than 6.0 wt % over most of the run. Reactor-wax yields were 35-65 wt %.

Table IV-4

Major Events in Run CT-256-7
(Excluding Reactor-Wax and Slurry Inventory)

<u>DOS</u>	<u>Major Events</u>
-0.2-0	Pretreatment
0	2.52 MPa; 257°C; 0.67 H ₂ /CO; 4.0 cm/s
1.0	Wax withdrawal started
6.9	Second-stage on at 253°C
14.1	Lost 150 g catalyst (leak on wax removal system)
19.9	2.52 ----> 2.00 MPa
20.8	2.00 ----> 1.48 MPa
21.7	1.48 ----> 2.52 MPa
25	Second-stage temp. ----> 327°C
36.9	600 g Catalyst I-D added
40.7	Second-stage out
49.9	700 g Catalyst I-D added
56.1	Potassium added
57.8-58.8	Potassium added
60.7-61.4	Potassium added
62.5-63.0	277°C operation
64.8-65.1	280°C H ₂ -treatment
67.7	257 -----> 277°C
76	Unit shutdown (slurry solidifying in-situ)
76+	Unit restarted; 277°C; 2.52 MPa; 4.0 cm/s
81.1-81.7	1.14 MPa operation
84	277 ----> 280°C

Table IV-4 (Cont'd)

85	Flow interruption; N ₂ in for 17 hours
85.7	Re-established flow at 2.52 MPa, 260°C
88.4	2.52 ----> 2.17 MPa
88.9	2.17 ----> 1.48 MPa
90.4	260 ----> 277°C
92.3	1.48 ----> 2.52 MPa
98	End of run

- No definitive conclusions on the effects of the single-orifice distributor could be drawn, due to leakage around its perimeter, which was discovered during a shutdown at 76 DOS. The distributor was repaired before the run was restarted.
- H₂+CO conversion ranged from 40 to 86 mol %, with the higher conversions occurring early in the run (0-20 DOS). The leaking distributor may have caused gas-flow maldistribution as well as catalyst losses, which combined to lower the conversion.
- Additions of a new batch of Catalyst I-D, as well as potassium, had little effect on the H₂+CO conversion.
- F-T operation at high (277°C) temperature, with little effect on methane + ethane selectivity, was shown toward the end of the run. However, the H₂+CO conversion declined rapidly at this condition.
- The new reactor-wax removal system was successfully demonstrated.
- The second-stage ZSM-5 fixed-bed reactor was run for 25 days with a new batch of catalyst. However, an erratic GC analysis did not allow proper adjustment of the reactor inlet temperature for maintaining a constant severity, and consequently, no second-stage data are reported here.

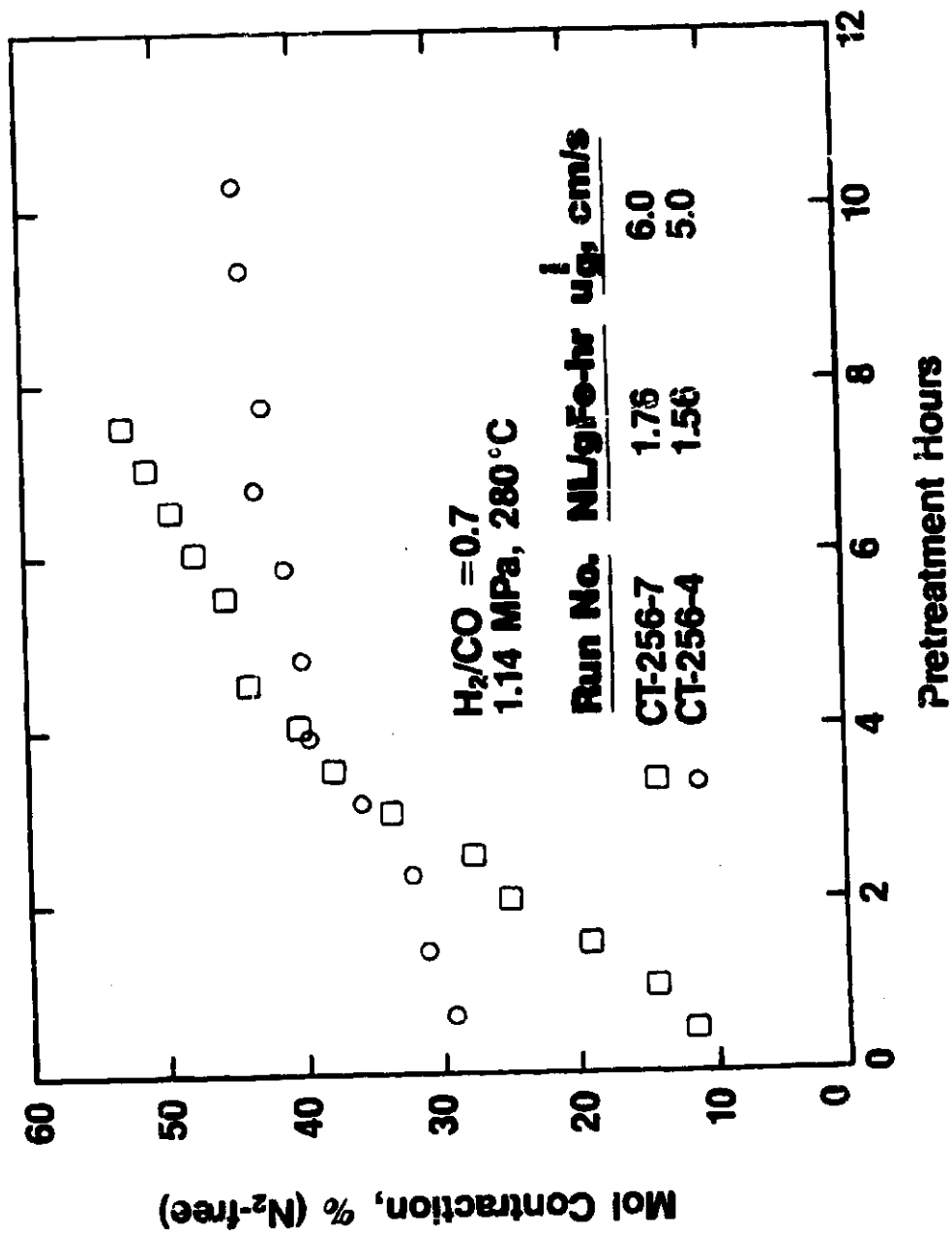
E.1. Fischer-Tropsch Slurry-Catalyst Loading and Pretreatment

2,200 g of Catalyst I-B were loaded at the start of Run CT-256-7, which corresponds to an initial loading of 23.5 wt % catalyst. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
Feed H ₂ /CO, molar	0.67
Superficial Feed-Gas Vel., cm/s	6
Space Velocity, NL/gFe-hr	1.76

These conditions are identical to those used in Run CT-256-4 except that the space velocity there was 1.56 NL/gFe-hr. A plot of the volume contraction during pretreatment is shown in Figure IV-20. It can be seen that the pretreatment resulted in a high volume contraction at the end. This was our first

Figure IV-20
PRETREATMENT OF FISCHER-TROPSCH CATALYST I-B
 (RUNS CT-256-7 and -4)



indication that the 1 mm orifice feed gas distributor would not inhibit the slurry reactor performance.

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

The ranges of operating conditions and performance for the run were:

Temperature, °C	255-277
Pressure, MPa	2.51
Feed H ₂ /CO molar	0.67
Superficial Feed-Gas Vel., cm/s	2.7-4.0
Space Velocity, NL/gFe-hr	2-7
Catalyst Loading, wt % (Average)	14
H ₂ +CO Conversion, mol %	35-86
Methane + Ethane Yield, wt % of HC	2.4-8.0
Reactor-Wax Yield, wt % of HC	35-65

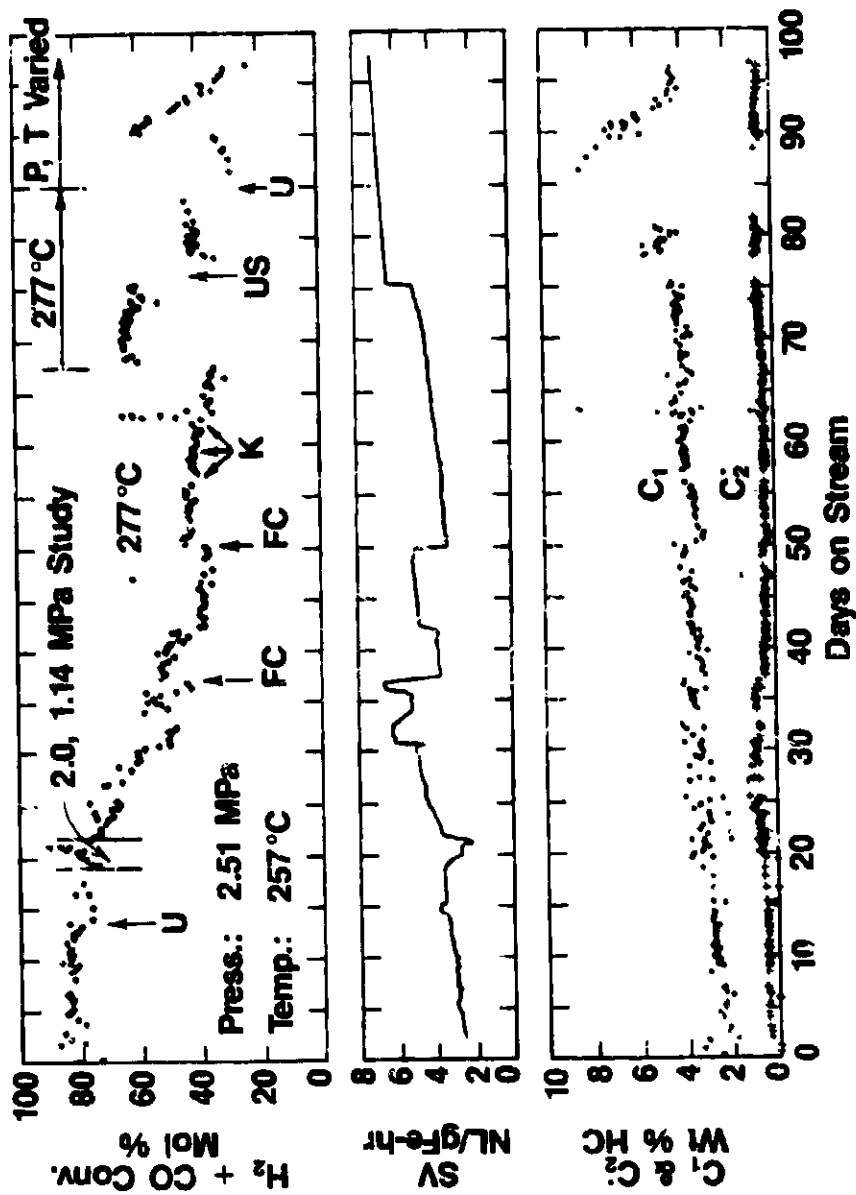
Figure IV-21 shows the conversion and methane and ethane selectivities, as well as the temperature, pressure, space velocity and superficial gas velocity for the run. It is seen on the run plot that the methane and ethane selectivity remained low (<6.0 wt %) throughout most of the run. This is the longest period for which we maintained such low methane + ethane yields. This of course also corresponded to the production of heavier hydrocarbons, and consequently the reactor-wax yield ranged from 35 to 65 wt %. This high wax production was successfully handled by the new wax removal system, which continuously withdrew up to 7 kg of clean (<0.1 wt % solids) reactor-wax per day.

Figure IV-22 is a plot of the accumulated reactor-wax which was removed from the first-stage slurry reactor. It can be seen that the slope of this curve generally lessens with time on stream, which corresponds, among other things, to increasing methane and ethane yields. By measuring the slope at a given point and knowing the H₂+CO conversion, the reactor-wax yield as a function of methane selectivity can be estimated. This has been done for other runs, and our data for Run CT-255-7 are compared with them, as well as literature results, in Figure IV-23. These data cover a wide range of methane selectivities, which were achieved using a variety of catalysts and operating conditions. Our data at 3-4 wt % methane yield have wide spread because of variation in operating temperature and space velocity.

Early in the run, the catalyst activity was comparable to previously studied F-T catalysts. This appeared to indicate that the orifice distributor had no ill effects on activity. However, measurements of the pressure drop across it turned out to be less than that predicted by pressure-drop correlations (see

Figure IV-21
SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD

(RUN CT-256-7; 1ST-STAGE CATALYST I-B: PPTD Fe/Cu K₂CO₃)



FC: Fresh Catalyst Addition (I-D) U: Upset
 K: Potassium Addition US: Unit Shutdown

Figure IV-22
CUMULATIVE REACTOR-WAX PRODUCTION
(RUN CT-256-7)

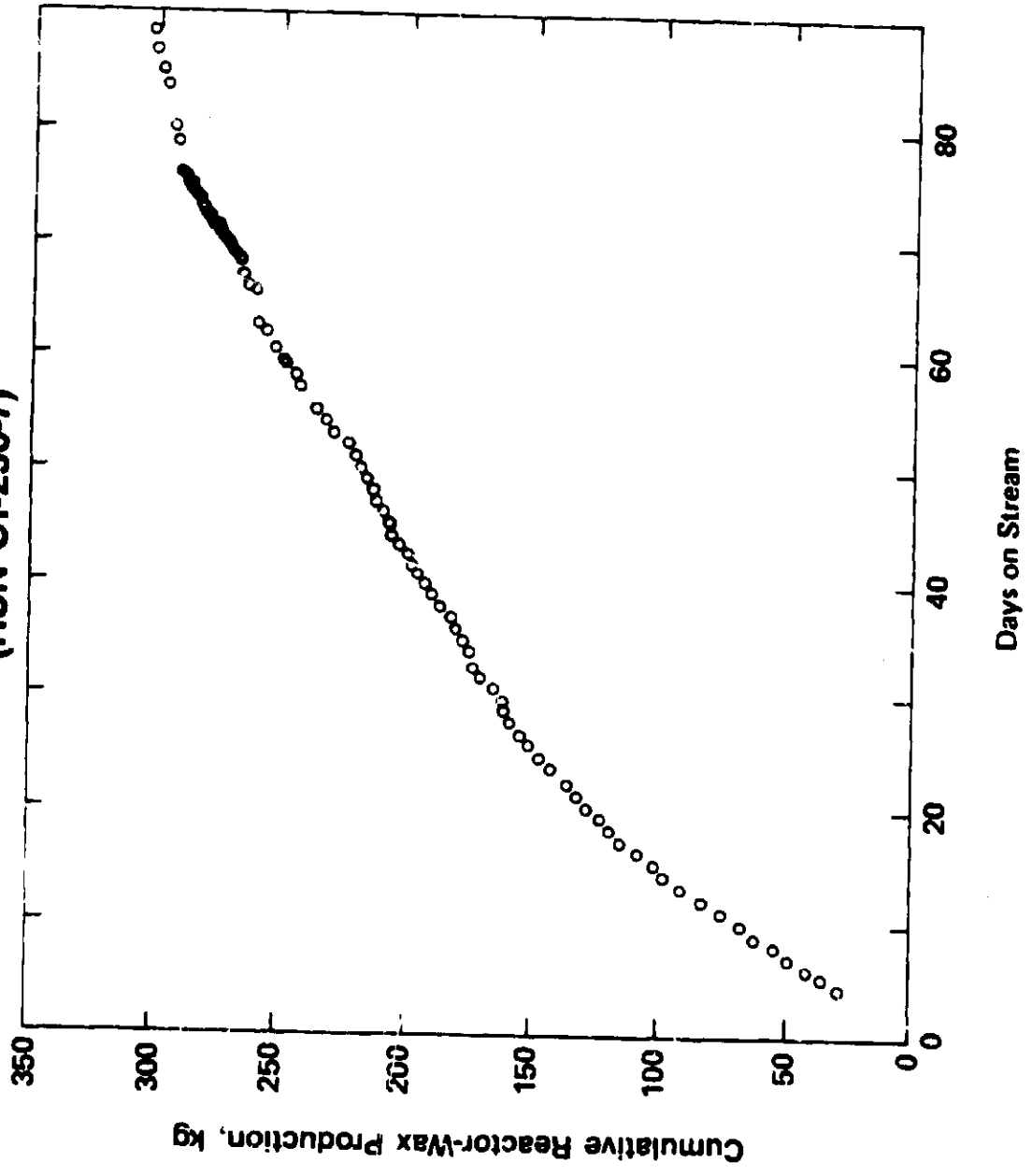
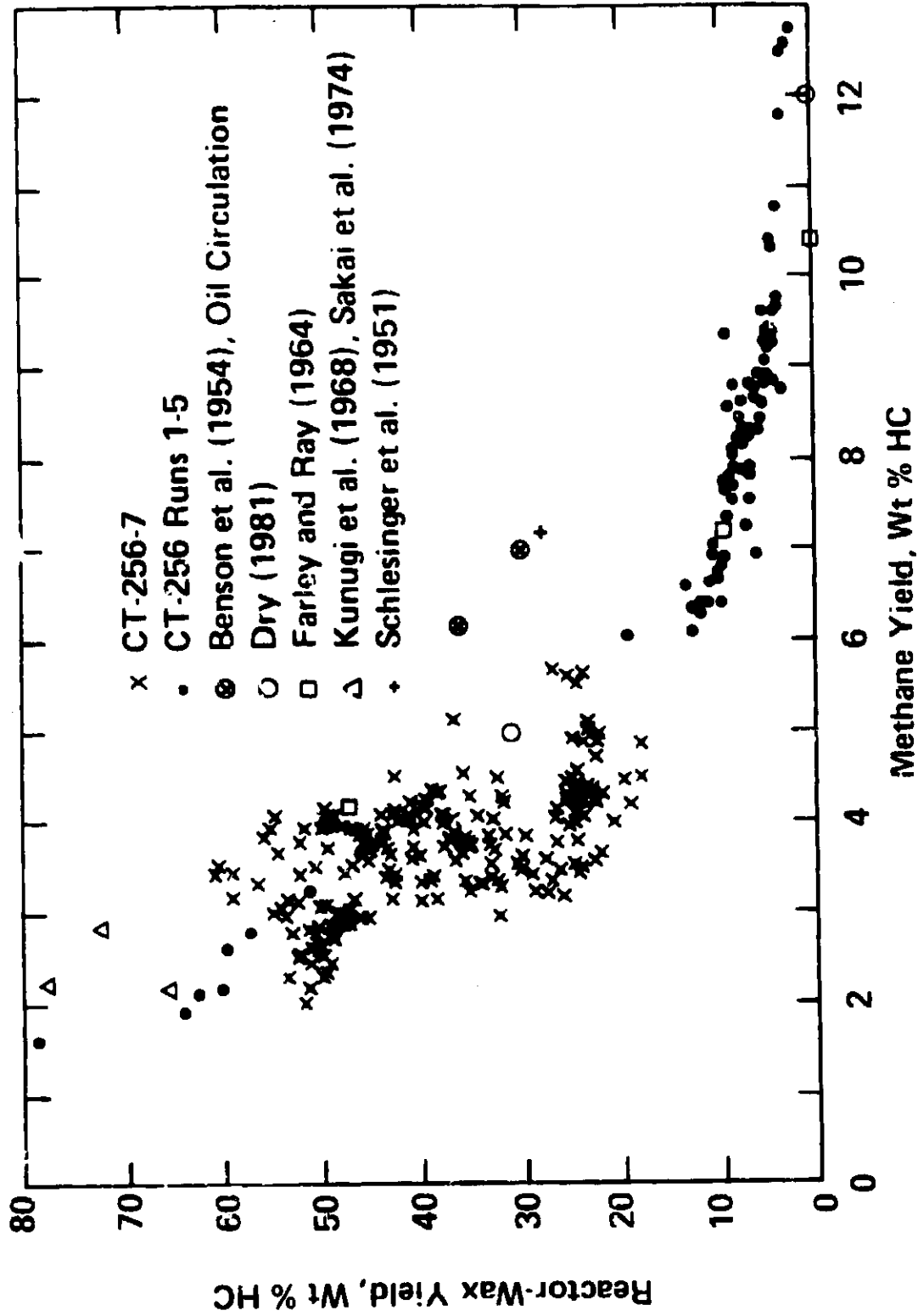


Figure IV-23
REACTOR-WAX YIELD VERSUS METHANE YIELD



Section VII-B), possibly indicating that the distributor had developed a leak around its edge.

Over the first twenty days on stream, the H_2+CO conversion was between 80 and 86 mol %. The next twenty days, however, saw the conversion drop steadily to about 40 mol % and remained there for almost 25 days. The cause of this decline is uncertain, but evidence seems to indicate that a loss of catalyst, combined with gas flow maldistribution caused by the leaking distributor, was responsible. This will now be discussed.

The run plot shows that the space velocity climbed from about 4.0 to over 6.0 NL/gFe-hr between 22 and 36 DOS. The amount of catalyst in the reactor was obtained by sampling the slurry at different points along the column, and then integrating the concentrations with respect to column height. Over this time period, the catalyst concentration dropped, indicating that catalyst was being lost from the reactor. Also, the catalyst concentration profiles were becoming steeper (higher concentration toward the bottom of the column) with time. This is shown in Figure IV-24, which is a sample of catalyst profiles taken throughout the run. It clearly shows the steep, non-uniform profiles during most of the run, and the more uniform profiles early in the run and after the distributor was repaired. This was an indication that gas flow was improperly distributed when the orifice plate was leaking.

When we suspected that the distributor was leaking (around 30 DOS), we began to check the space below the plate for any slurry which might have leaked around it. Using a small drain attached to the vessel, any accumulated slurry was removed once per day. A plot of the accumulated slurry removed is shown in Figure IV-25. From 30 to 45 DOS, nearly 250 g of catalyst was lost. At that point, the superficial gas velocity in the column was increased, with the rationale that the higher flow would cause less slurry "weeping" around the plate. This had limited success, as shown in the figure, and catalyst continued to be lost. After repair work at 76 DOS, the leakage was stopped completely.

We attribute the conversion drop during the run to catalyst loss and hydrodynamic factors. The fact that the methane + ethane selectivity remained steady during the decline indicates that the catalyst was not damaged.

In an effort to raise the H_2+CO conversion, both fresh catalyst and potassium additions were tried. A new batch of Catalyst I-D was tested for catalyst addition, but while significant increases in conversion were seen using an earlier batch of this catalyst in Run CT-256-6, addition of the catalyst

Figure IV-24
SLURRY BUBBLE-COLUMN CATALYST CONCENTRATION PROFILES
(RUN CT-256-7)

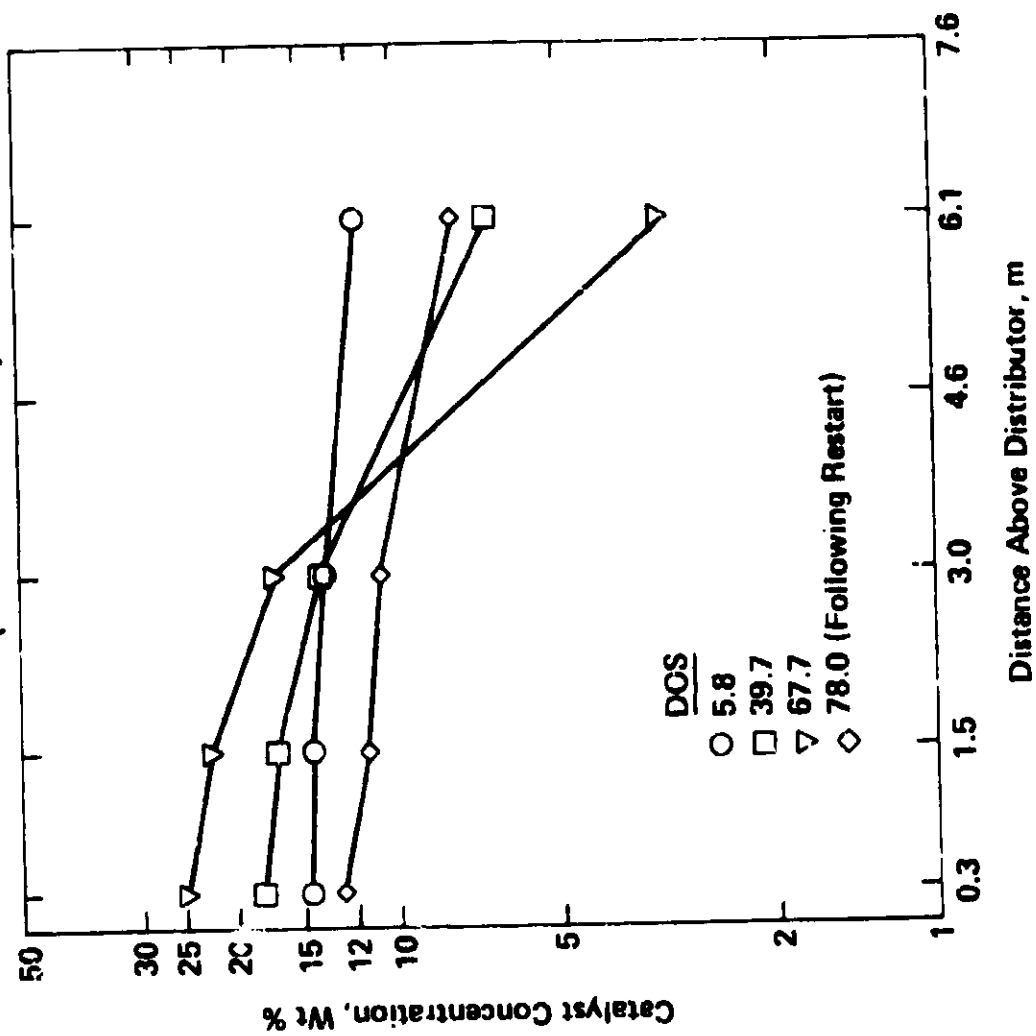
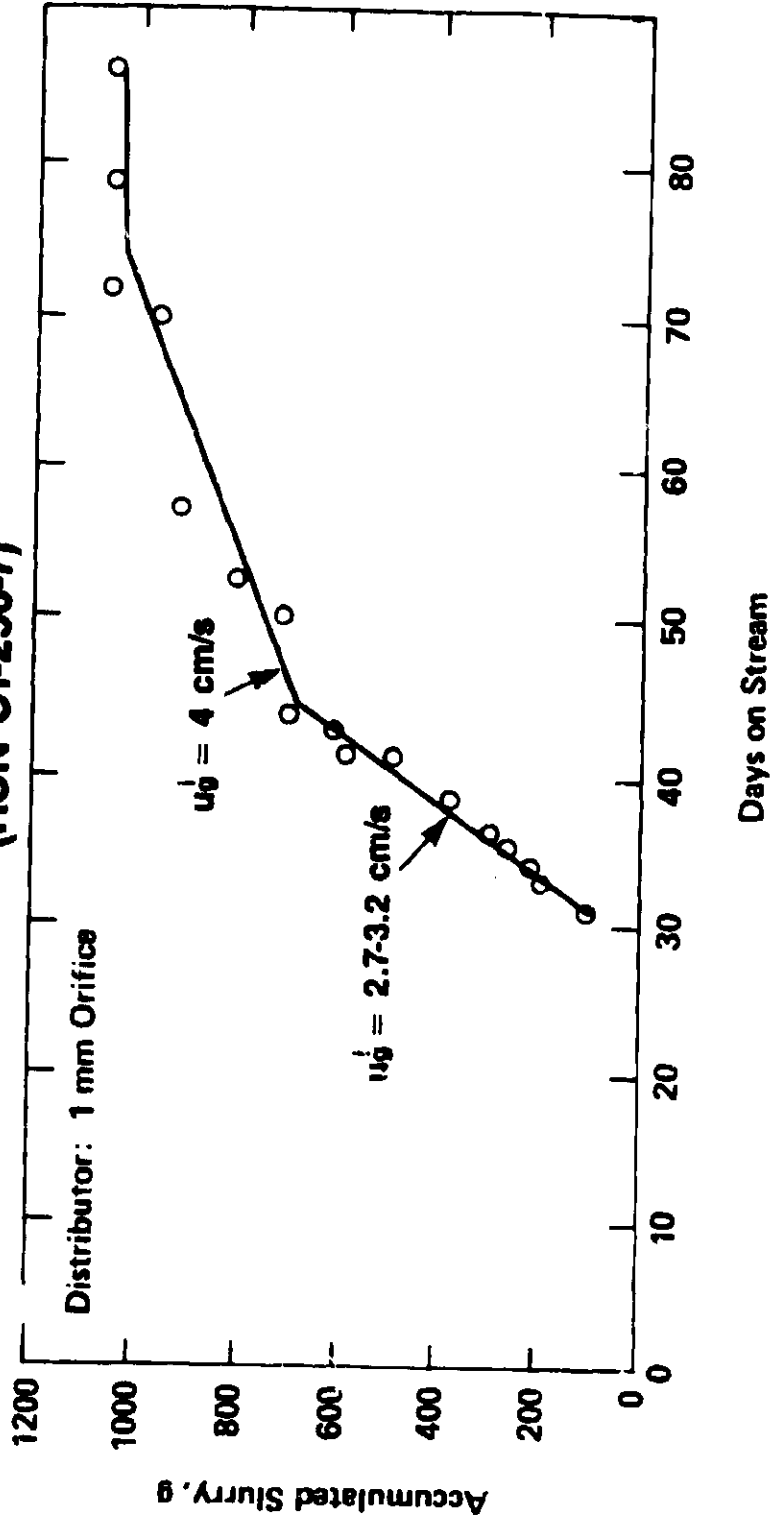


Figure IV-25
ACCUMULATED SLURRY FROM BELOW DISTRIBUTOR
(RUN CT-256-7)



in the current run appeared to have only a small effect on conversion. This was done twice, at 37 and 50 DOS, and both times the amount added was more than half of the prevailing catalyst inventory. This indicates that the new batch of Catalyst I-D may have been somehow different from the old batch.

A potassium salt was then added in an attempt to promote activation of the added catalyst. Three such additions, done from 56 to 82 DOS, appeared to have little influence on the H_2+CO conversion, though the methane + ethane selectivity seemed to stabilize.

At 63 DOS, the reactor temperature was increased to $277^\circ C$ for eight hours in an attempt to activate the catalyst on-stream. As seen in Figure IV-21, this was not successful. The conversion dropped to the same low level when the temperature was reduced.

After this, we attempted to increase conversion by raising the reactor temperature. This usually results in a higher catalyst aging rate and higher methane + ethane yields. As seen in the run plot, however, raising the temperature to $277^\circ C$ at 67 DOS nearly doubled the H_2+CO conversion, while the methane + ethane yield remained at its low level of about 4.7 wt %.

The unit was shut down at 76 DOS (the slurry was allowed to cool in-situ), and the distributor was removed and examined.

It was found that several screws which hold down the distributor plate were loose, which in turn caused leakage around the perimeter of the plate. To correct this, the plate was cleaned off and then welded in place before being placed back in the reactor. The unit was then restarted. The improvement was immediately evident, Table IV-5 shows the smoother reactor temperature profile which was achieved and higher distributor pressure drop, which corresponded to our calculations. Subsequent catalyst profiles were also considerably less steep (Figure IV-24) than before the restart. Figure IV-25 shows that the leakage was halted after the repair.

After the restart, the H_2+CO conversion was 40 mol %, and the methane + ethane selectivity had climbed only slightly, to 6.0 wt %. We feel that this was not a consequence of the new distributor. While this was the first time that a cold shutdown and restart was performed in the two-stage BSU, there had been other occasions where the H_2 and CO flows were cut and the unit was "idling" under nitrogen. In those cases the conversion dropped and the methane + ethane yield increased somewhat when

Table IV-5
Improved Performance
of Repaired Distributor Plate

Reactor Temperature Profile:

<u>Level, cm</u>	<u>Temperature, °C</u>	
	<u>Before</u>	<u>After</u>
30.5	276.1	276.7
152	277.2	276.7
305	277.1	278.1
457	273.3	277.2
610	271.7	276.1

Pressure Drop Across Distributor:

	<u>Before</u>	<u>After</u>	Δ P by <u>Calculation</u>
	P, kPa	.05	.16-.17

the synthesis gas was reintroduced. It appears that the catalyst is affected when removed from the H₂-CO environment. This could also have contributed to the lower conversion observed after the restart.

At 84 DOS, the temperature was reduced to 260°C. Several hours after this, a valve in the feed-gas system malfunctioned, causing the reactor to be under nitrogen for 15 hours. When the synthesis conditions were resumed, the H₂-CO conversion had fallen to 30 mol %, and the methane + ethane yield was up to over 9.0 wt %.

Feeling the high pressure operation may have been inhibiting the catalyst activity, as was observed in Run CT-256-6 with Catalyst I-D, the pressure was lowered to 2.17, then 1.48 MPa. This had only a small effect, however, raising the H₂-CO conversion to 35 mol % with little change in the methane + ethane selectivity.

Next, the temperature was raised back to 277°C, and the conversion reached 60 mol %. Increasing the temperature should also have increased the methane + ethane yield, but the opposite occurred; the methane + ethane yield dropped rapidly down to 6.7 wt %. While this was happening, the H₂-CO conversion was also falling, reached 53 mol % in only 36 hours.

The pressure was then increased for the last time, to 2.51 MPa at 92 DOS. The methane + ethane selectivity decreased as expected, to 4.9 wt %, but the conversion continued to decline at a high rate, falling to 30 mol % by the end of the run. This type of behavior had not been observed previously under identical conditions (87-84 DOS), so it was logical to assume that the catalyst had somehow been damaged when the flow was interrupted at 85 DOS. This makes any conclusions on the end-of-run performance risky.

E.3. Second-Stage ZSM-5 Fixed-Bed Operation

The second-stage ZSM-5 reactor was run for 25 days early in the run, using a fresh load of catalyst. Unfortunately the GC system did not work properly, so adjustments to the reactor inlet feed temperature for maintaining constant catalytic severity could not be made accurately. Therefore, none of the data from the second-stage operation are presented here.

F. Run CT-256-8

The eighth run of the two-stage pilot plant was started on November 20, 1984 and voluntarily ended on February 15, 1985. The main objective of the run was to evaluate Catalyst I-C (Fe/Cu/K₂CO₃) for low methane + ethane mode operation. An

important incentive for evaluating Catalyst I-C is that it can be activated without a separate pretreatment step, as was demonstrated in Run CT-256-5 (Kuo, 1983). Also, this run marked the first conclusive test of the 1 mm single-orifice feed-gas distributor in the bubble-column reactor. The same distributor was used in Run CT-256-7, but leakage around its edges prevented definitive conclusions on its performance.

The material balance data for this run are summarized in Appendix C and a summary of the major events appears in Table IV-6.

The major highlights of the run were:

- The catalyst activated in an identical fashion to Run CT-256-5 (a preliminary evaluation of Catalyst I-C), indicating no adverse influence of the orifice distributor.
- Unacceptable aging rates were observed, on the order of 1-2 mol % drop in H₂+CO conversion per day, at 250-255°C and 1.8-2.2 MPa.
- Additions of fresh Catalyst I-C were unsuccessful in raising the H₂+CO conversion.
- Both Catalyst I-C and a new batch of Catalyst I-B raised the conversion when added to the first stage, after being activated in a small bubble-column reactor.
- Catalyst which was reloaded into the reactor after being accidentally removed regained a significant portion of its activity.
- Despite the high aging rate, the methane + ethane selectivity stayed very low throughout the run (2.3-4.3 wt %).
- Stopping the circulation of the slurry through the catalyst settling vessel did not lessen the catalyst aging rate.

F.1. Fischer-Tropsch Slurry Catalyst
Loading and Activation, and Testing
of a Single-Orifice Feed-Gas Distributor

Run CT-256-8 was initially loaded with 2,300 g of Catalyst I-C. The starting wax medium consisted of Run CT-256-5 reactor-wax. The following catalyst activation conditions were then established:

Table IV-6

Major Events in Run CT-256-8
(Excluding Reactor-Wax and Slurry Inventory)

<u>DOS</u>	<u>Major Events</u>
0	Started F-T catalyst activation: 250°C, 1.48 MPa, 5.0 cm/s
1-4	Approximately 1/3 catalyst inventory lost due to malfunction in wax withdrawal system. Additional catalyst lost through reactor feed line; cold shutdown made for repairs.
6-9	Reloaded wax drains with high solids content into first-stage reactor.
11.8	Added 300 g fresh Catalyst I-C
14.8- 15.3	Attempted to activate fresh catalyst on-stream: - High throughput - 8.0 cm/s superficial gas velocity - 3/1 H ₂ /CO @ 7.0 cm/s
16.8	First-stage temperature ---> 255°C
17.6	1.48 ---> 1.82 MPa
18.8	1.82 ---> 2.17 MPa
21.5	2.17 ---> 1.82 MPa
30	Added 200 g activated Catalyst I-C
35.4	First-stage temperature ---> 250°C 1.82 -----> 1.48 MPa 3.7 -----> 2.3 cm/s
37.6	Added 200 g activated catalyst (a new batch of Catalyst I-B)
53.9	Second-stage on; inlet temperature 312°C
62.6	1.48 ---> 1.82 MPa
70	End of run

Temperature, °C	250
Pressure, MPa	1.48
Feed H ₂ /CO, molar	0.67
Superficial Feed-Gas Vel., cm/s	5.0
Space Velocity, NL/gFe-hr	2.0

These conditions are identical to those used in Run CT-256-5, except that the space velocity there was 2.7 NL/gFe-hr. A plot of the volume contraction versus time during activation is shown in Figure IV-26.

Also shown in Figure IV-26 is the corresponding curve from Run CT-256-5. The similarity of these two catalyst activations shows that the orifice distributor was not a hindrance to the reactor performance. Furthermore, virtually no liquid was needed to be removed from the space below the distributor plate during the entire run, which showed that no "weeping" through the orifice was present. The pressure drop across the orifice throughout the run was in agreement with our correlation. Slurry samples taken throughout the run also indicated that the catalyst was being suspended nearly uniformly over the column length, another sign that the orifice distributor is applicable to this system (see Figure IV-27).

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

The ranges of operating conditions and performance for the entire run were:

Temperature, °C	250-255
Pressure, MPa	1.48-2.17
Feed H ₂ /CO, molar	0.67
Superficial Feed-Gas Vel., cm/s	2.3-8.0
Space Velocity, NL/gFe-hr	1.1-3.5
Initial Catalyst Loading, Wt %	25.0

H ₂ -CO Conversion, mol %	35-80
Methane + Ethane Yield, wt % of HC	2.3-4.2
Reactor-Wax Yield, wt % of HC	40-70

Figure IV-28 shows the conversion and methane and ethane selectivities for the run.

After 22 hours, the H₂+CO conversion leveled off at ~70 mol %. This level of activity is equivalent to other F-T catalysts we have used. At the same time, the methane + ethane selectivity was falling to 2.1 wt % of hydrocarbons.

Figure IV-26
ACTIVATION OF FISCHER-TROPSCH CATALYST I-C
(RUNS CT-256-8 and -5)

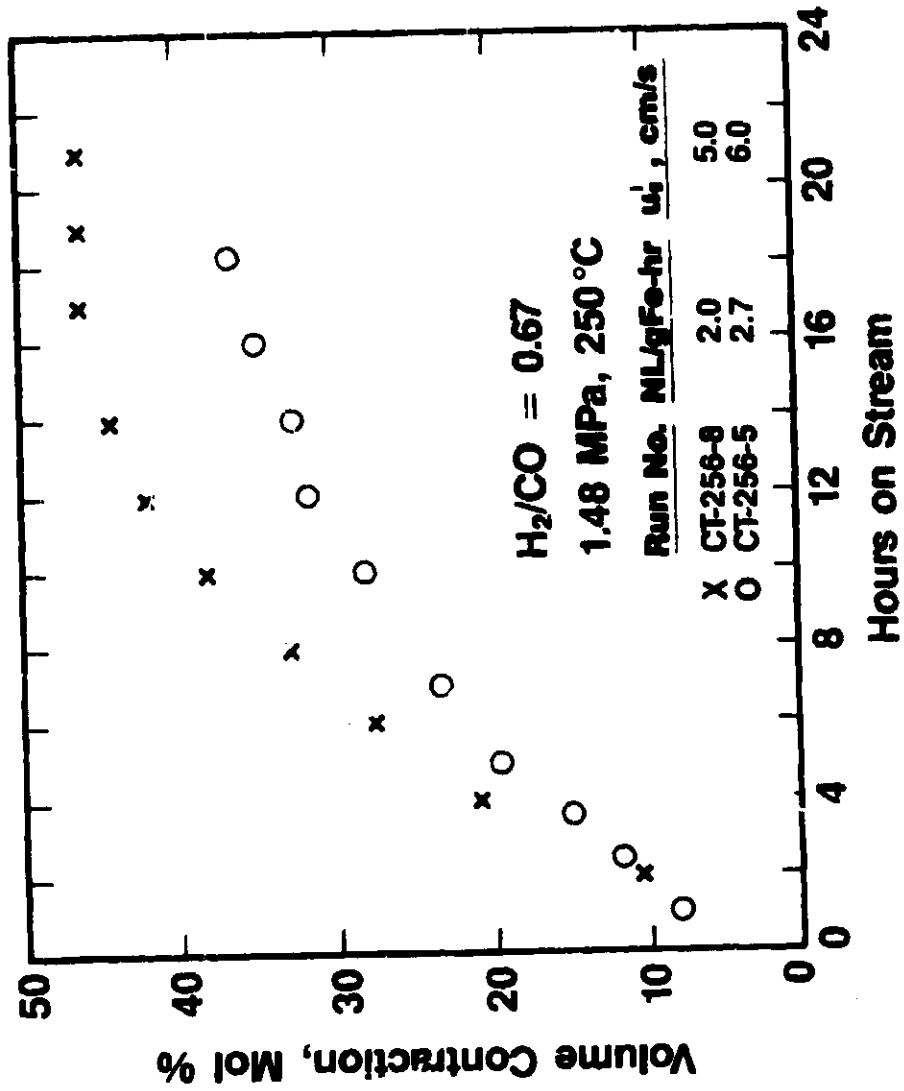


Figure IV-27
SLURRY BUBBLE-COLUMN CATALYST CONCENTRATION PROFILES
 (RUN CT-256-8)

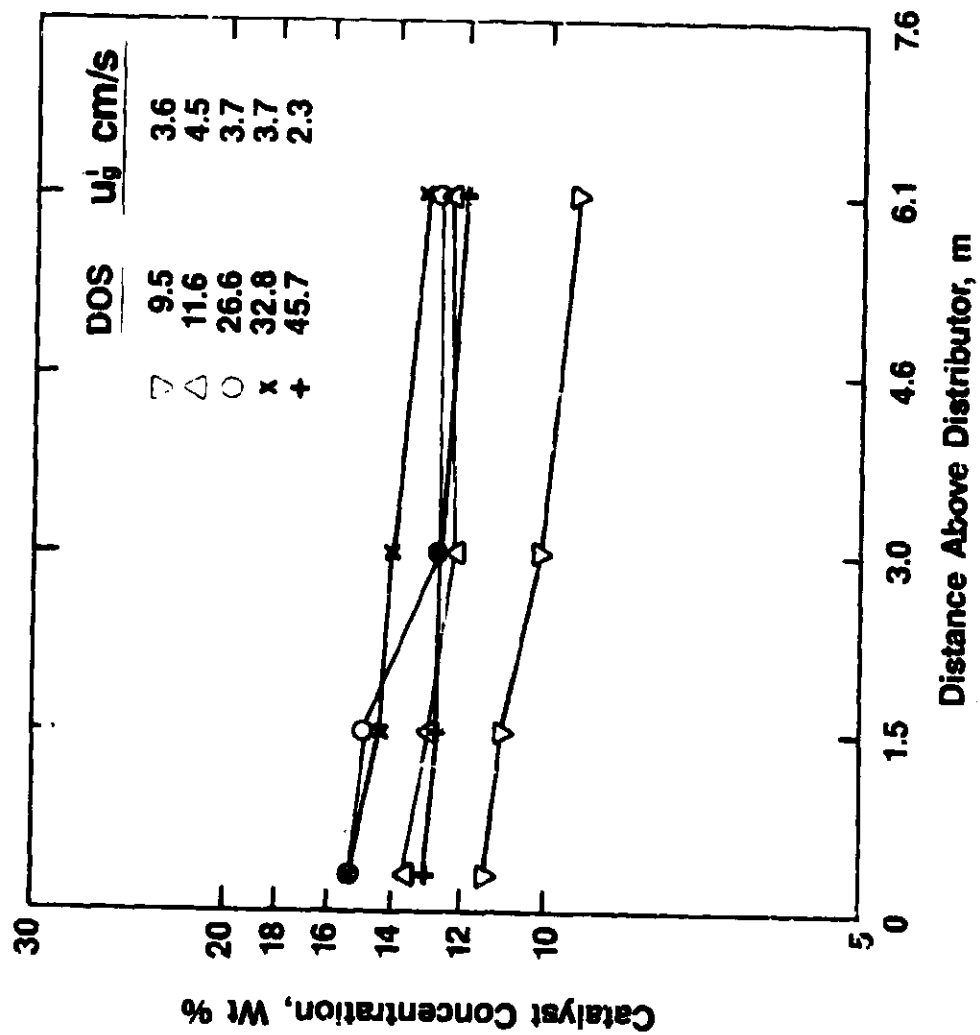
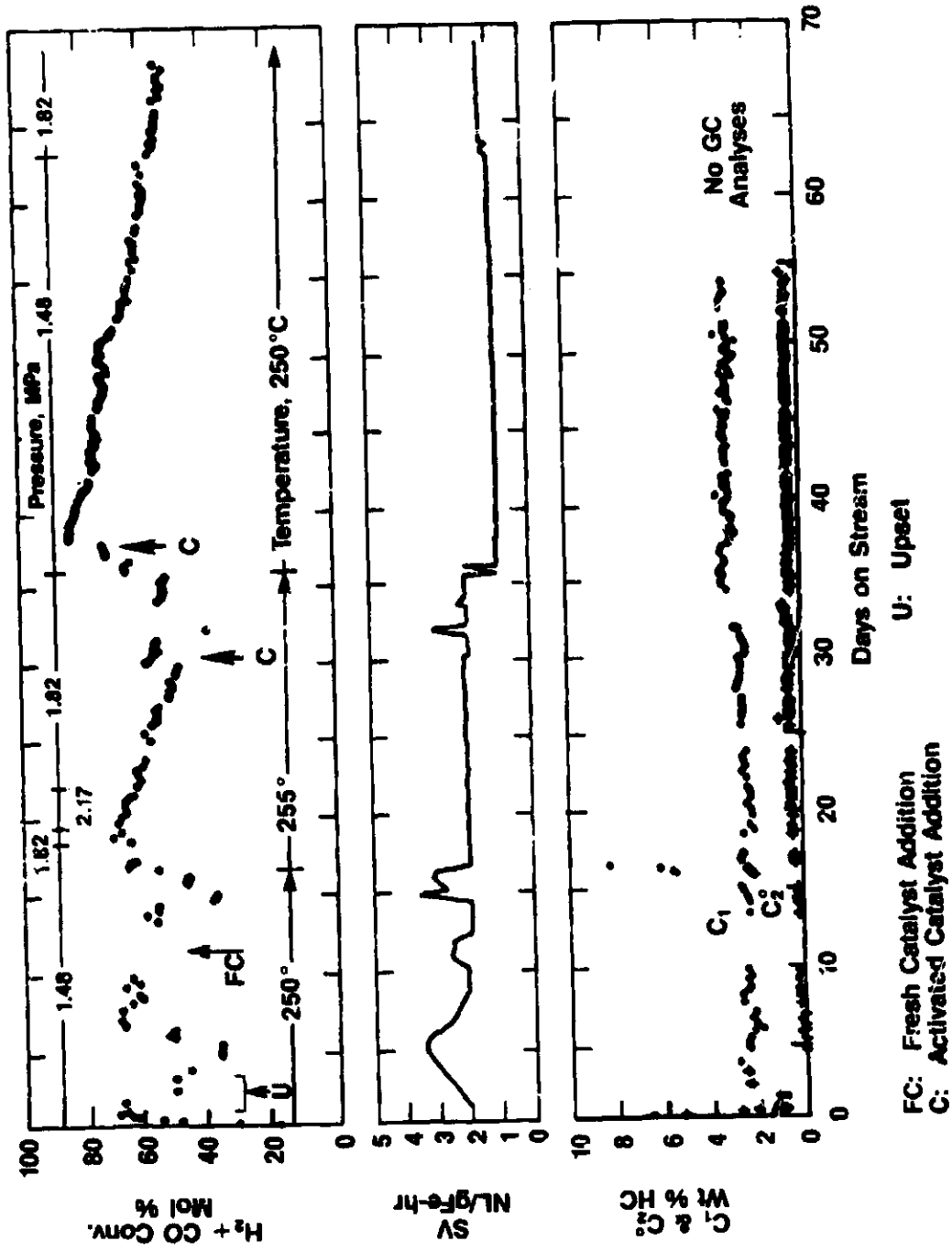


Figure IV-28
 SYNTHESIS GAS CONVERSION
 AND METHANE & ETHANE YIELD
 (RUN CT-256-8; 1ST-STAGE CATALYST I-C:PPTD Fe/Cu/K₂CO₃)



Reactor-wax withdrawal operations were started after two days on-stream, using our continuous catalyst/wax withdrawal device which had worked very well during Run CT-256-7. This time, however, it malfunctioned, causing roughly one-third of the catalyst inventory to be removed in the wax drains. While trying to correct this, the feed-gas line to the unit plugged at 4.3 DOS, causing further catalyst loss and forcing a cold shutdown of the reactor, with the remaining slurry still inside.

With the unit down, modifications were made to the wax withdrawal and feed-gas systems. On November 30, the run was restarted. Upon re-establishing conditions, the conversion had dropped to 37 mol % due to catalyst losses and possible damage to the catalyst from the shutdown. Then, between six and eight DOS, most of the catalyst which had been removed in the wax drains was reloaded into the reactor. This, combined with a 20% lower feed-gas rate, raised the conversion to about 65 mol %. The methane + ethane yield was unaffected.

In an attempt to increase conversion, 300 g of fresh Catalyst I-C was added to the reactor at 12 DOS. This amount represented close to 20% of the catalyst inventory in the reactor at the time. No change was observed in either the conversion or the methane + ethane selectivity. Since the catalyst had activated under similar conditions at the start of the run, it was felt that high partial pressures of H₂ or CO may be needed for activation. Consequently, the superficial gas velocity was increased from 4.4 to 8.0 cm/s, dropping the conversion from 53 to 36 mol % for 18 hours. After this, a 3:1 H₂/CO feed gas at 7.0 cm/s was used for 17 hours. When operating conditions were re-established, however, the conversion and selectivity showed no improvement.

At 17 DOS, the temperature was raised to 255°C, and the pressure was increased to 1.82 MPa, then to 2.17 MPa. This increased the conversion to 67 mol %. At these conditions, though, the conversion dropped steadily over the next five days to 60 mol %. The pressure was then dropped back to 1.82 MPa, but the decline continued, with the conversion reaching 45 mol % by 30 DOS. The space velocity throughout this period was maintained constant (~2.2 NL/gFe-hr).

At this time, 200 g of fresh Catalyst I-C was activated in the small bubble-column reactor (Unit CT-225). Activation conditions were identical to those used at the start of the run. The entire slurry from the small reactor was then drained and transferred to the BSU, where it was loaded into the first-stage bubble-column reactor one hour later. As seen on the run plot, the catalyst addition increased the H₂+CO conversion to 55 mol %. The activity decline, however, continued at the same rate, as the conversion fell to 48 mol % over the next five days.

This was the first time that catalyst had been successfully activated in one reactor and then transferred to another.

To increase the conversion, conditions were made milder -- 250°C, 1.48 MPa and the space velocity was reduced to 1.1 NL/gFe-hr. This increased the conversion to 59 mol %. At this point (38 DOS), another load of catalyst was activated in Unit CT-225. This time, the catalyst was a new batch of Catalyst I-B. The addition increased the conversion to 80 mol %, again dropping the methane + ethane selectivity slightly. The conditions were then kept constant over the next twenty-five days. The activity decline continued, however, though at a slightly reduced rate. The conversion dropped to 55 mol % over this time.

During this period, the slurry circulation to the catalyst settling pot was shut off for long stretches of time in an effort to determine whether this was contributing to the aging. Four times, the circulation was stopped and the system flushed, with the reactor-wax product allowed to build up in the reactor for a three-day period. No change on the conversion decline could be detected, however, and this practice was discontinued. Reactor-wax yield ranged between 35 and 50 wt % for the run.

At 62 DOS, the pressure was increased for the last time, to 1.82 MPa, while the feed-gas throughput was increased proportionately, maintaining the same superficial gas velocity in the column (2.3 cm/s). The H₂+CO conversion remained constant (54-55 mol %), indicating no adverse effect of pressure in this range. The run was then ended after 70 DOS, the evaluation of Catalyst I-C being completed.

In the following we analyze the aging rate of Catalyst I-C. The major conclusions are:

- Assuming a first-order kinetics for H₂+CO conversion, first-order aging kinetics fits the experimental data quite well. At 250°C, 1.48 MPa and 1.4 NL/gFe-hr, the half-life of the catalyst activity is estimated to be about 24 days.
- At 255°C, 1.82 MPa and 2 NL/gFe-hr, the catalyst activity half-life decreased to about 13 days.
- This catalyst is not acceptable because its aging rate is high at moderate operating conditions.

There are two time periods (22-30 and 38-60 DOS) when constant operating conditions were maintained. We have estimated the aging rates during these two time periods.

To simplify the analysis, we assumed a first-order kinetics to translate the H₂+CO conversions to catalyst activities and a negligible gas-liquid interphase mass-transfer resistance. The resulting equation is:

$$\ln (1-X_{H_2+CO}) = -kT_c \quad (IV-3)$$

T_c is the contact time of H₂+CO with the catalyst. The precise definitions of the k and T_c are not needed here, since we are interested only in the relative changes in the activity, k.

If a first-order kinetics is assumed for the catalyst aging rate, then

$$k = k^* \exp (-At_c) \quad (IV-4)$$

where k* is in initial k and A is the first-order aging rate constant and t_c is the catalyst age. Combining Equations (IV-3) and (IV-4), the H₂+CO conversion can be related to catalyst age as follows:

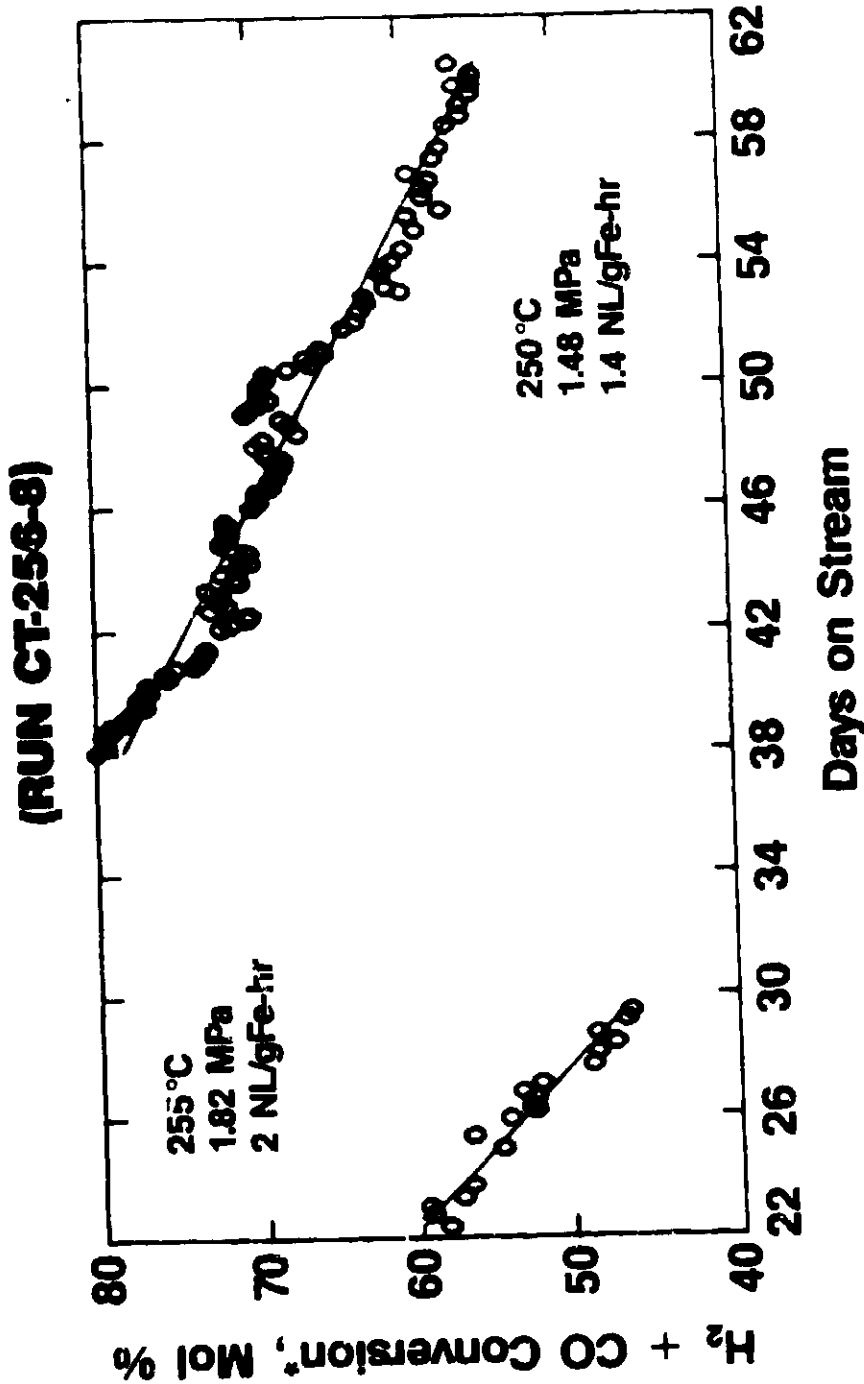
$$\ln (-\ln(1-X_{H_2+CO})) = \ln (k^*T_c) - At_c \quad (IV-5)$$

Figure IV-29 is a plot of the left-hand side of Equation (IV-5) versus DOS. The slope of the straight line fitted to the data gives the first-order aging constant, A. The data are summarized below:

<u>DOS</u>	<u>Temp., °C</u>	<u>Pres., MPa</u>	<u>A, 1/Day</u>
22-30	255	1.82	0.053
38-60	250	1.48	0.029

The higher aging rate over 22-30 DOS may be attributed to higher temperature, pressure and space velocity (2.0 vs 1.4 NL/gFe-hr).

Figure IV-29 AGING OF CATALYST I-C (RUN CT-256-8)



• Plotted as $\ln(1 - X_{H_2 + CO})$ representing first-order conversion kinetics and first-order aging kinetics