At this point, the conversion was in the 35-45 mol % range and so it was decided to end the run and make modifications to the unit to help prevent catalyst settling from occurring again.

J. Improvment of Catalyst Suspension in Bubble-Columns Using Upward Slurry Circulation --Mathematical Model Calculations

In Runs CT-256-9 and -11, very steep catalyst profiles developed at about 10-13 days on-stream. These caused low conversion, nonuniform temperature profiles, and eventually termination of the runs. Subsequent analysis of the particle size showed larger particles. Hence, a mathematical settling model was used to investigate the use of upward slurry circulation to improve the catalyst suspension.

J.1. A Catalyst Settling Mathematical Model

For catalyst distribution with or without slurry circulation in a whole column, a settling model developed by Cova (1966) was used (a similar model was used in catalyst profile calculations in the final report of our previous Contract; page 121, Kuo, 1983). The catalyst mass balance equations are given below:

$$(u_{cs}-u_{sl})dC_c/dx + E_c d^2C_c/dx^2 = 0 \qquad \text{(IV-6)}$$

with the boundary conditions:

$$(u_{cs}-u_{sl})C_c + E_c dC_c/dx = -u_{sl}C_c^e; \text{ at } x = 0 \qquad \text{(IV-7a)}$$

$$u_{cs}C_c + E_c dC_c/dx = 0; \text{ at } x = L \qquad \text{(IV-7b)}$$

The first term of Equation (IV-6) represents the transport of the catalyst due to convective force, while the second term represents the transport of the catalyst due to axial eddy dispersion. Under an additional constraint of a known total catalyst mass in the column, the linear Equations (IV-6) and (IV-7) can be easily integrated analytically to give the catalyst concentration profiles.

The correlations needed to estimate the catalyst settling velocity u_{cs}, and the axial dispersion coefficient, E_c, are summarized in Table 27 of our previous DOE final report (Kuo, 1983). However, one shall notice that this model contains some

major assumptions including uniform catalys size, u_{cs}, and E_c over the whole column. Furthermore, the correlations for the parameters were developed mainly for non F-T mediums. Consequently, this model was not used for exact comparison with the experimental data; rather it is useful as a tool to evaluate qualitatively the importance of several parameters, such as the catalyst particle size, the slurry circulation velocity, the slurry return location, on the catalyst concentration profiles.

An upward slurry circulation was already used in the slurry bubble-column of the BSU for the purpose of circulating the slurry to a catalyst settling vessel. The circulation was established between 305 and 610 cm above the feed-gas distributor and the circulation velocity is restricted to less than 0.05 cm/s by the pump capacity. The model is an ideal tool to investigate if it was necessary to relocate the slurry return location to other places, such as the bottom of the bubble-column, to improve the catalyst suspension. For this purpose, the following two additional conditions were needed:

$$u_{sl} = 0; \quad \text{at } 0 < x < L_o \tag{IV-8}$$

$$u_{sl}C_c^e + E_c dC_c/dx|_{L_o^-} = (-u_{sl}C_c + E_c dC_c/dx)|_{L_o^+}; \quad \text{at } x = L_o \tag{IV-9}$$

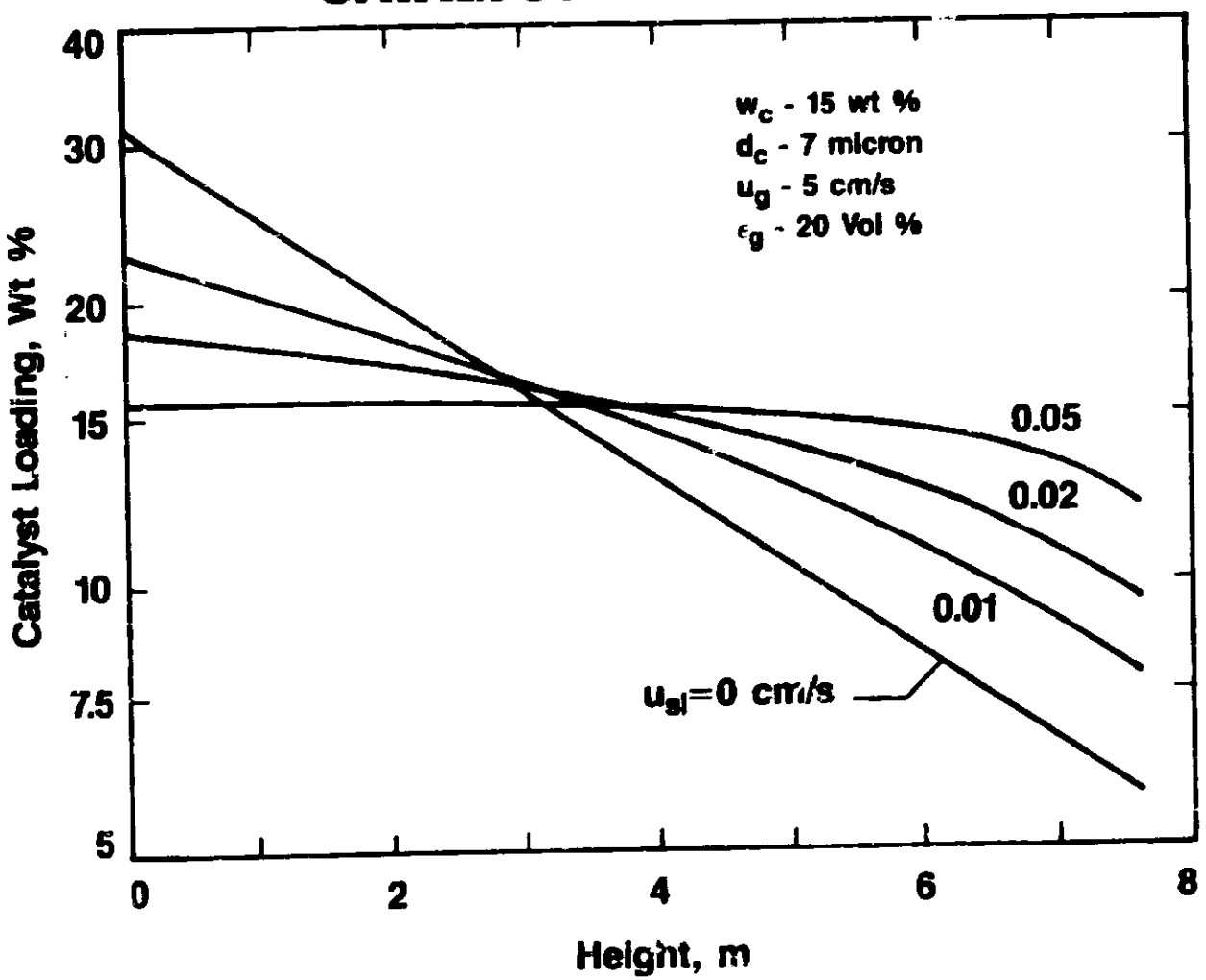
Equations (IV-6) to (IV-9) can be solved analytically to give the catalyst concentration profiles in a bubble-column.

J.2. Effect of Slurry Circulation on the Catalyst Suspension in Bubble-Columns

It was essential to find out if a small slurry circulation significantly affects the catalyst suspension in the bubble-column of the BSU. The slurry pump had a maximum capacity equivalent to 0.05 cm/s superficial slurry velocity. It was too time-consuming to order and then install a larger pump. Furthermore, too high a slurry circulation velocity may not be desirable since it may result in lower synthesis gas conversion due to shorter residence time of the bubbles in the reactor. Equations (IV-6) and (IV-7) were solved analytically to estimate the effect of varying the slurry circulation velocities from 0 to 0.05 cm/s, and the results are given in Figure IV-41. The steep catalyst concentration profile for the noncirculation case was significantly improved by raising the slurry velocity to 0.05 cm/s.

Figure IV-41

ESTIMATED EFFECT OF LIQUID CIRCULATION ON CATALYST SUSPENSION



Equations (IV-6) to (IV-9) were used to judge whether it was necessary to relocate the slurry return line from 305 cm above the feed-gas distributor to a location just above the distributor. Figure IV-42 shows concentration profiles for three cases: no slurry circulation, slurry return to the 305 cm level, and slurry return to the bottom of the column. The slurry circulation in the upper section of the column improved the profile to a large degree. However, a significantly more uniform profile was obtained by relocating the slurry return line to the bottom of the column.

J.3. Effect of Catalyst Particle Size on the Catalyst Suspension

Equations (IV-6) and (IV-7) were used to evaluate this effect for the particle size range of 5 to 10 microns. The results are summarized in Figure IV-43. Within this particle size range, the catalyst concentration profile deteriorates drastically with increasing particle size

J.4. Possible Scenario for the Catalyst Settling Phenomena from Runs CT-256-9 and 11

Equations (IV-6) to (IV-9) were used to analyze the catalyst settling phenomena observed during 10-13 DOS of Runs CT-256-9 and -11. The results for Run 11 are given in Figure IV-44. Before catalyst settling (10.6 DOS), a 5 micron particle size is sufficient to match the catalyst concentration profile at that time. After catalyst settling (17.7 and 21 DOS), a 13 micron particle size is needed to match the steep profile. This suggests a strong possibility that the catalyst may have increased in size either by agglomeration or by the growth of heavy polymers on the outside of the catalyst particles.

K. Bench-Scale Unit Modifications and Run CT-256-12

K.1. Bench-Scale Unit Modifications and Start-up of Run CT-256-12

Following Run CT-256-11 and the recurrence of catalyst settling, several modifications to the pilot plant were made, along with changes in the operating procedures. These changes were designed to help minimizing settling in future runs. They were:

- setting up the slurry circulation (used for the catalyst/reactor-wax separation) throughout the entire column. The superficial liquid velocity between the 8 cm and 7.9 m levels would be 0.05 cm/s.

Figure IV-42

ESTIMATED EFFECT OF SLURRY RETURN LOCATION ON CATALYST SUSPENSION

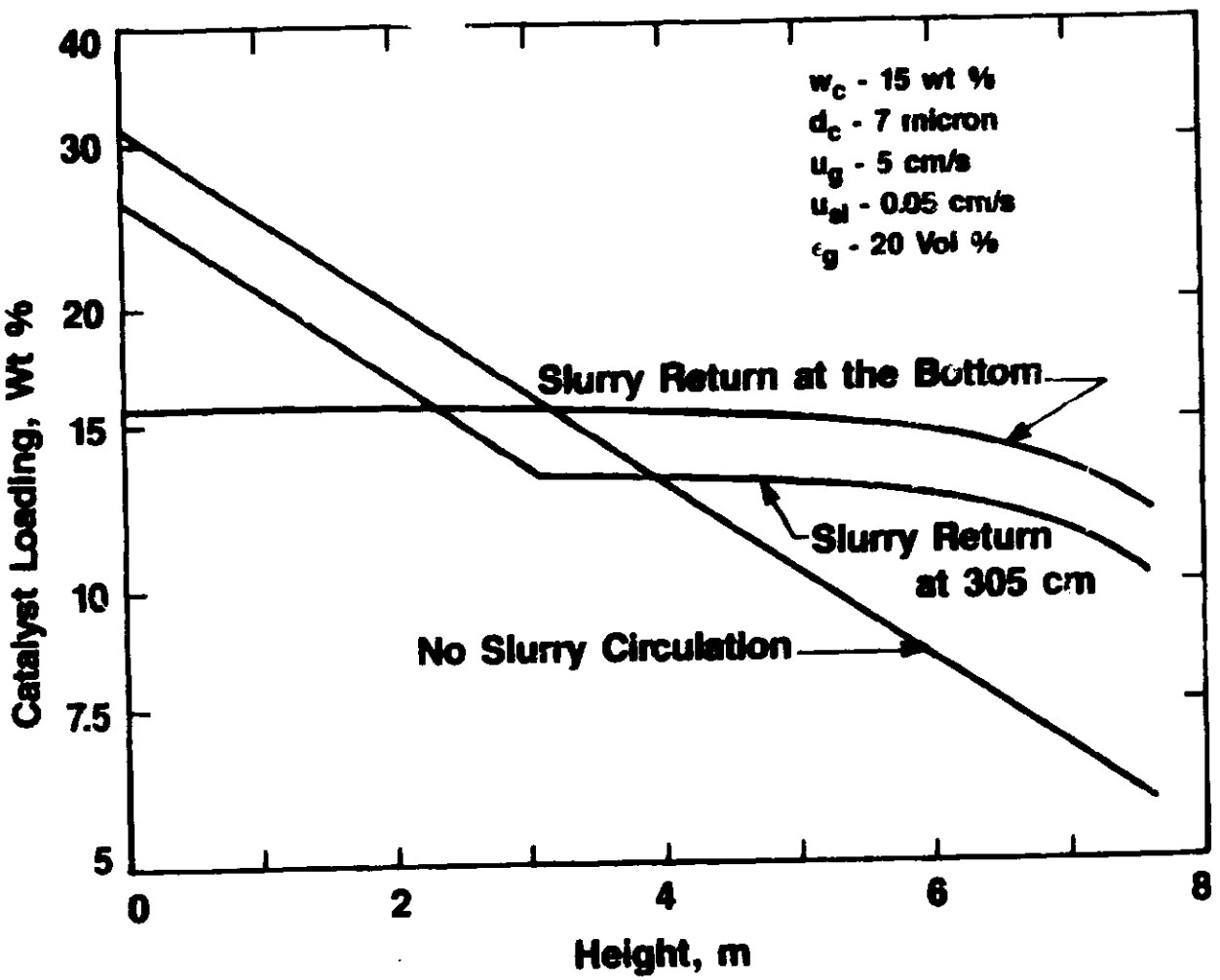


Figure IV-43

ESTIMATED EFFECT OF PARTICLE SIZE ON CATALYST SUSPENSION

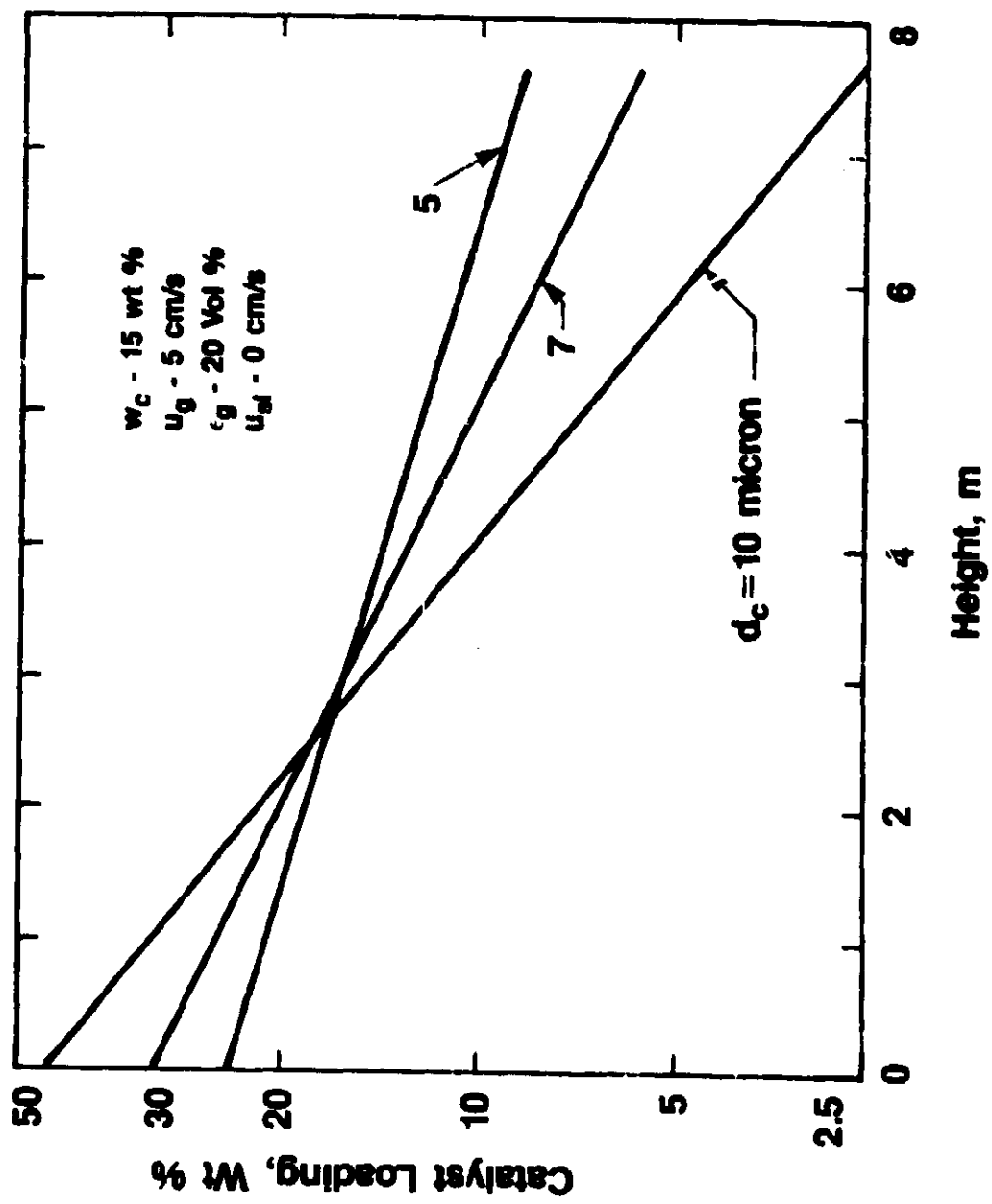
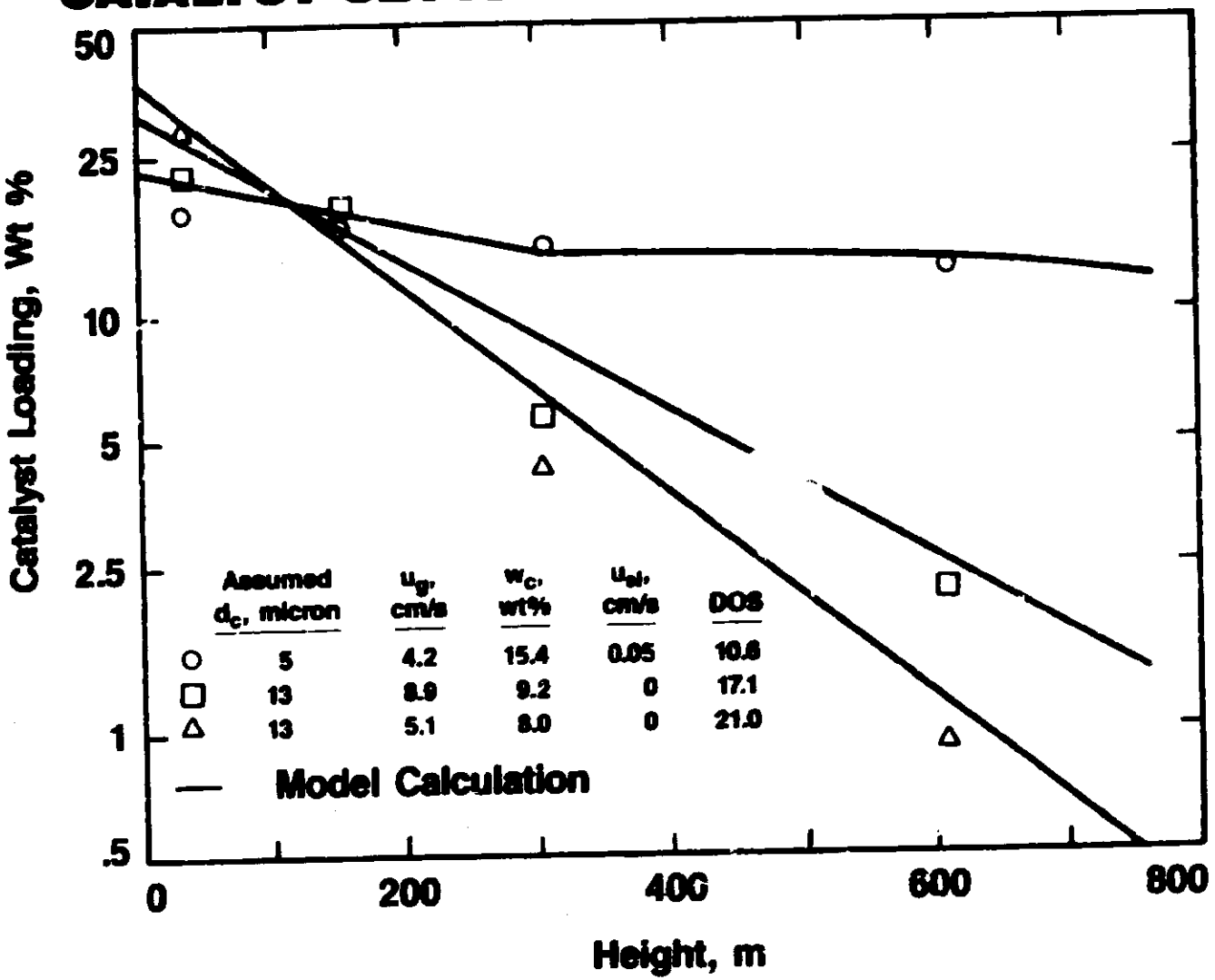


Figure IV-44

CATALYST SETTLING DURING RUN CT-256-11



- replacing the single-orifice feed-gas distributor with a 20 micron sintered-metal-plate (SMP), the same type which was used in Runs CT-256-1 through -6.

Before the start of the next run, the end-of-run slurry from Run 11 was used to test the new SMP distributor. The unit was brought back to synthesis conditions, with H_2/CO as the feed gas at 5.7 cm/s superficial gas velocity. Slurry samples were then taken to assess the extent of settling. A 7.8°C differential persisted between the bottom and top of the reactor, and the 30 and 600 cm level catalyst concentrations were 29 and 1.0 wt %, respectively. This was clear indication that the new distributor had no effect on the catalyst settling.

Run CT-256-12 was then started on June 26, 1985 with the same objectives as Runs 9 and 11. A new batch of Catalyst I-B was prepared for this run. A lower catalyst loading than those used in Runs 9 and 11 (1,600 g versus 2,100-2,300 g) was used. It was expected that lower catalyst loading would minimize the catalyst settling problem.

K.2. Fischer-Tropsch Slurry Catalyst Loading and Pretreatment

The first-stage bubble-column was loaded with 1,600 g of Catalyst I-B. The initial wax medium was Run CT-256-7 reactor-wax. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
Feed H_2/CO, molar	0.7
Space Velocity, NL/gFe-hr	2.0
Superficial Feed-Gas Vel., cm/s	4.4
Initial Catalyst Loading, Wt %	19.3

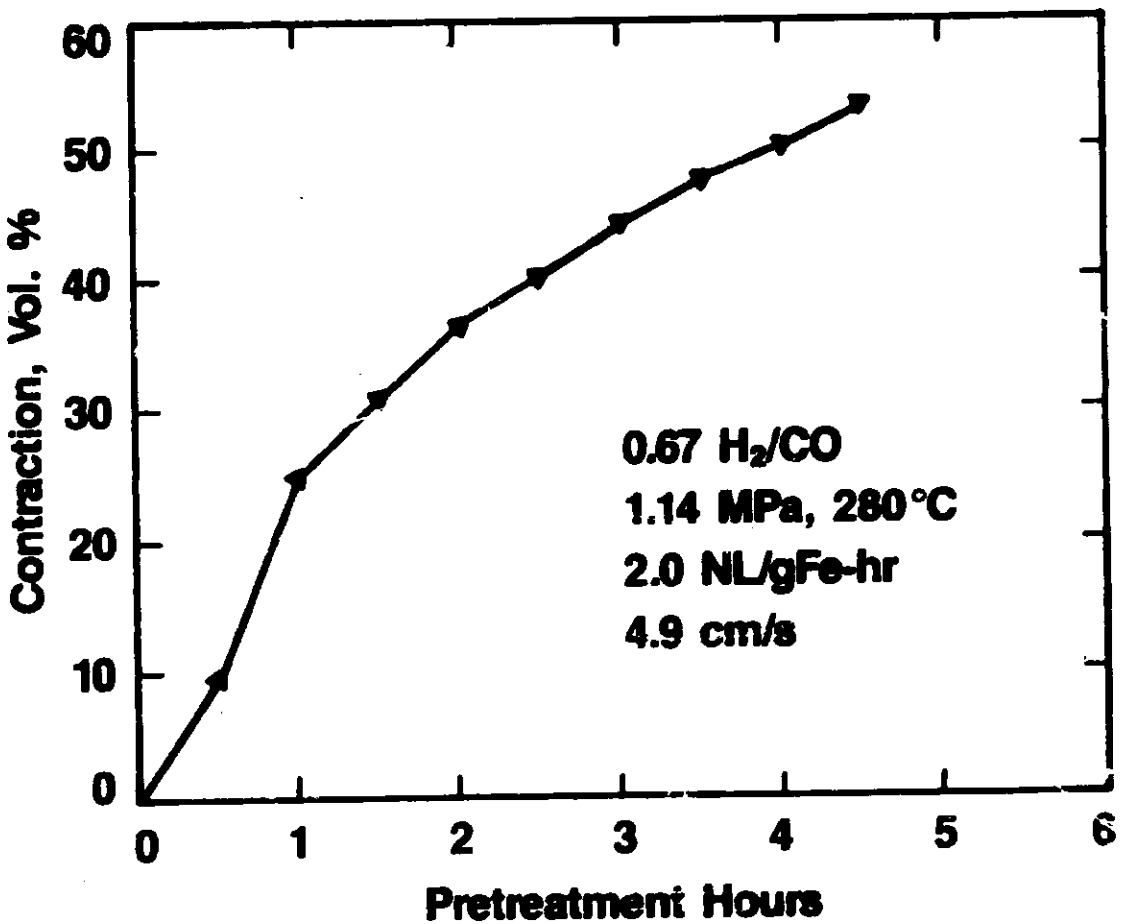
A plot of the gas volume contraction during pretreatment is shown in Figure IV-45. The 4.5 hour duration of the pretreatment was comparable to both Runs 9 and 11.

K.3. First-Stage Fischer-Tropsch Reactor Operation

Following pretreatment, the first-stage slurry reactor temperature was dropped 3.3°C/hour until an average of 257°C was reached. The pressure was then increased to 1.48 MPa and the space velocity changed to 2.4 NL/gFe-hr. After about 24 hours, the H_2+CO conversion had lined out at ~87 mol % (exactly what was expected), and the methane + ethane selectivity was 4.1 wt % of hydrocarbons produced. The slurry circulation and reactor-wax withdrawal system was started, and the wax yield was ~60 wt %.

Figure IV-45

PRETREATMENT OF FISCHER-TROPSCH CATALYST I-B (RUN CT-256-12)



A plot of the run is shown in Figure IV-46. As is shown, this excellent level of performance was maintained for 17 days while the operating conditions were held constant. This period represented the finest example of low methane + ethane mode operation we have ever produced in the pilot plant. Figure IV-47 shows the accumulation of reactor-wax during this period and the nearly constant slope verifies the steady operation. The slope is slightly higher at 2-4 DOS because no wax was removed the first two days.

Material balances were performed daily and the results are summarized in Appendix F.

At 17 DOS, however, the unit's CO monitor system malfunctioned, causing all power to be shut off, along with hydrogen and CO. Power was restored an hour later and the CO was back after six hours. Four hours later the system malfunctioned a second time and full operation was restored after one hour. Unfortunately, though, the slurry circulation pump on the catalyst/reactor-wax separation system had stopped during the shutdowns and repeated attempts to reestablish the liquid circulation failed.

Throughout this period, the catalyst in the bubble-column reactor was settling, as happened in Runs 9 and 11. This was evident from dropping H_2+CO conversion and an increasingly non-uniform reactor temperature profile. Despite immediate attempts to resuspend the catalyst with high-velocity nitrogen, the H_2+CO conversion dropped to ~30 mol %, while the methane + ethane selectivity rose to ~8.0 wt %. Slurry samples from the 30 cm level showed solids in excess of 25 wt %. The pump was taken out and repaired, but the catalyst settling persisted.

The run was ended on July 28, after 32 total days on-stream. Modifications were immediately made to prevent a malfunction of the CO monitor system from shutting down the unit, while maintaining a high level of operational safety.

K.4. Second-Stage ZSM-5 Reactor Operation

This run utilized a fresh loading of ZSM-5 catalyst. The loading was 300 g, making the gas-hourly space velocity an average of 1,880 NL per hr/L-cat for this run. Second-stage material balances also appear in Appendix F. The inlet temperature was raised from 312 to 330°C over the course of the run, which kept the severity index ($i\text{-}C_4/(C_3^{=}+C_4^{=})$, molar) between 2.4 and 3.3, somewhat higher than anticipated. The severity was being reduced at the time of the catalyst settling in the first-stage.

Figure IV-46

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD (RUN CT-256-12; 1ST-STAGE CATALYST Lot: Fe/Cu/K_2CO_3)

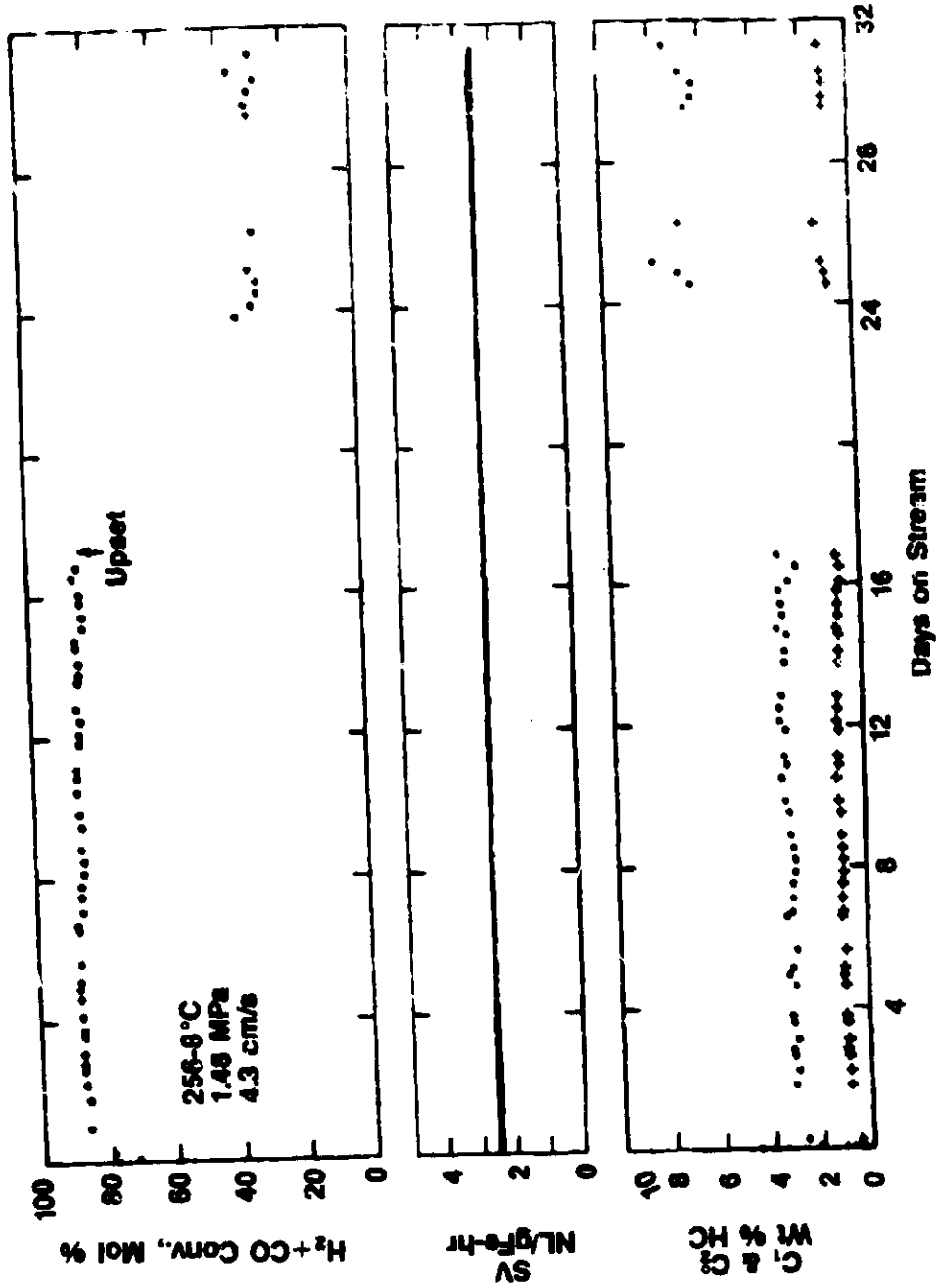
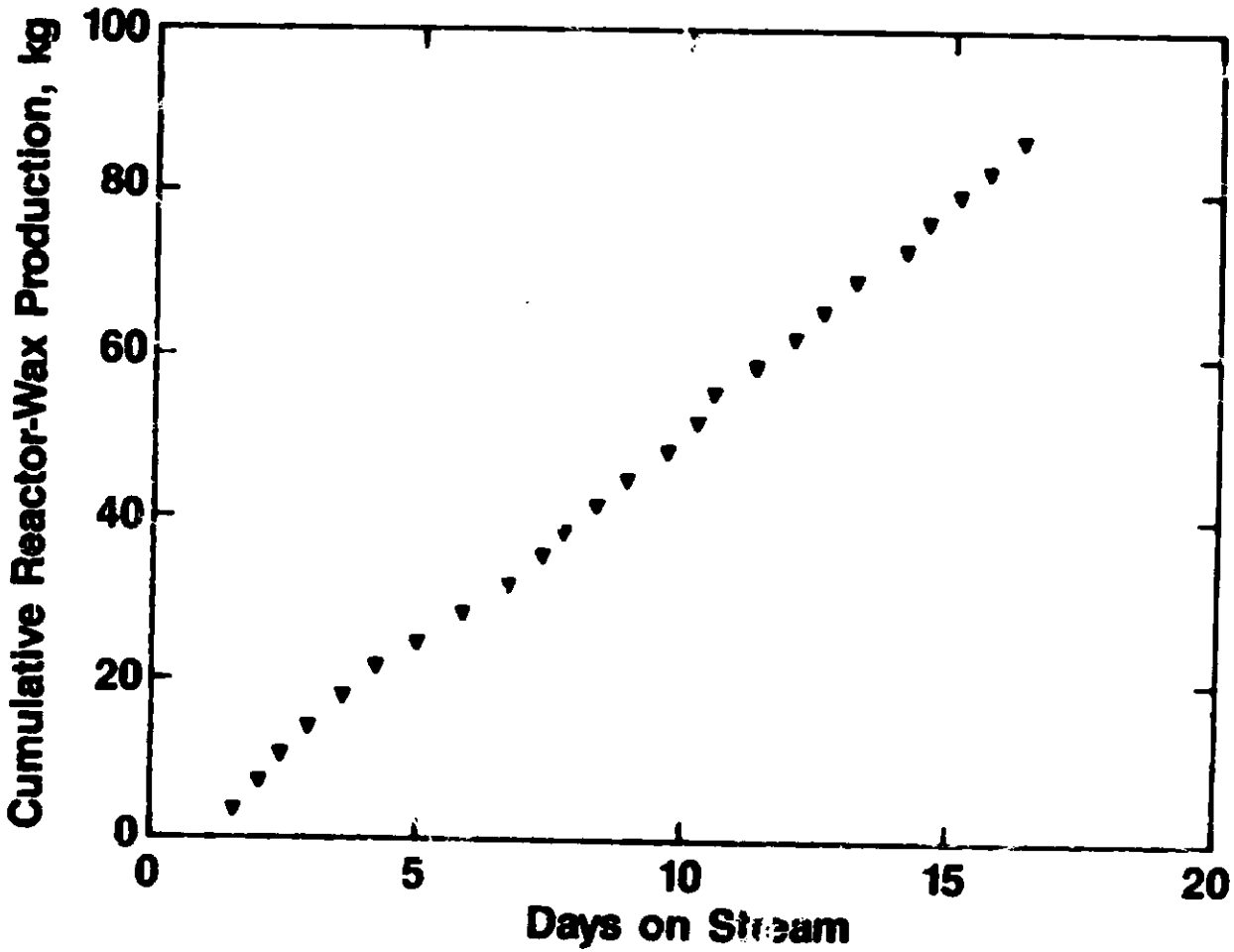


Figure IV-47

CUMULATIVE REACTOR-WAX PRODUCTION (RUN CT-256-12)



L. Run CT-256-13

Following a short, three-day turnaround, the thirteenth run of the two-stage pilot plant was started on August 2, 1985. The objective was to repeat the excellent performance of the first seventeen days of Run 12 and then demonstrate long-term stability. Operating conditions were therefore identical to Run 12. Highlights of the run were:

- High conversion, low methane + ethane operation was maintained for 35 days.
- Catalyst settling in the bubble-column reactor at 35 DOS caused low conversion, eventually forcing the end of the run. This occurred despite continuous slurry circulation (see Subsection IV.K.1).

The run was ended on September 11, after 39 days on-stream. The major events of this run are summarized in Table IV-8. Material balances were performed daily and are summarized in Appendix G.

For convenience, a summary of various F-T catalysts used in this and the earlier Contracts are given in Appendix H.

L.1. First-Stage Fischer-Tropsch Slurry-Catalyst Loading and Pretreatment

The bubble-column was initially loaded with 1,600 g of Catalyst I-B, 600 g of which was a new batch. The wax medium was from Run CT-256-7. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
Feed H_2/CO, molar	0.7
Space Velocity, NL/gFe-hr	2.0
Superficial Feed-Gas Vel., cm/s	4.8
Initial Loading, wt %	20.0

Pretreatment lasted 12 hours, nearly three times longer than the pretreatment in Run 12, though the conditions were identical. This was apparently due to the new catalyst batch.

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

Following pretreatment, the temperature was dropped by 5°C/hour until 257-258°C was reached. The pressure was then increased to 1.48 MPa and the space velocity adjusted to 2.4 NL/gFe-hr. At these conditions the initial H_2+CO conversion was ~60 mol %, but climbed to 82 mol % over 6-8 days. This gradual increase was again unlike Run 12, which showed full catalyst activation in only one day. The methane + ethane selectivity, meanwhile, dropped to ~2.7 wt %. A plot of the run appears in Figure IV-48.

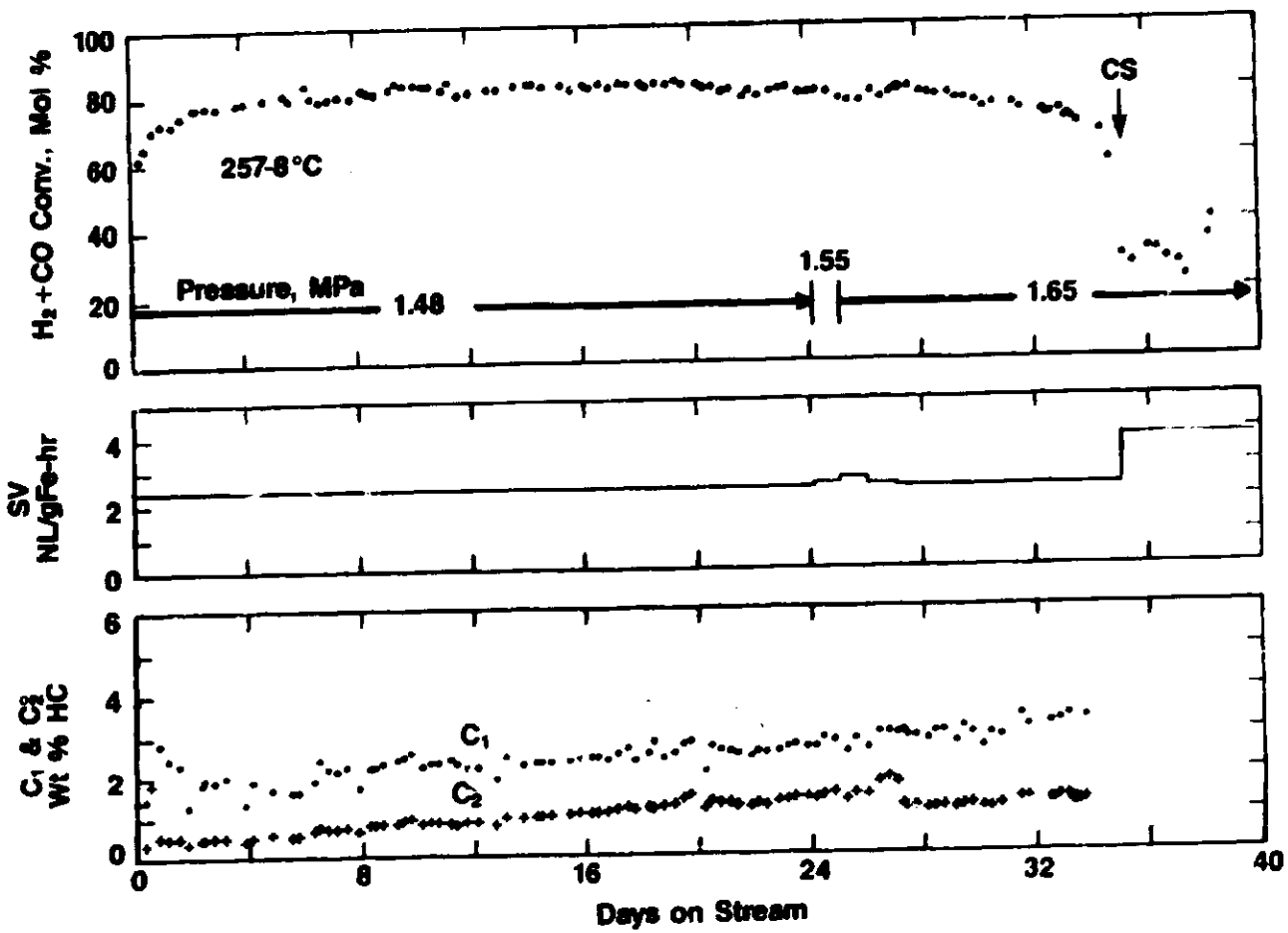
Table IV-8

Major Events in Run CT-256-13
(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
-0.5	Started F-T catalyst pretreatment
0	Started synthesis operation: 1.48 MPa, 257°C, 2.4 NL/gFe-hr
	Second-stage inlet temperature ---> 320°C
23	Second-stage inlet temperature ---> 400°C
24.2	1.48 ---> 1.55 MPa; 2.4 ---> 2.5 NL/gFe-hr
25.1	1.55 ---> 1.65 MPa; 2.5 ---> 2.7 NL/gFe-hr
26.1	2.7 ---> 2.5 NL/gFe-hr
27.1	2.5 ---> 2.4 NL/gFe-hr; New second-stage reactor on-stream -- inlet temperature 270°C
34.8	Catalyst settling occurred in first-stage reactor
37.5	Installed a new, higher capacity slurry circulation pump and raised the superficial slurry upward velocity from 0.05 to 0.2 cm/s.
38.0	H_2 treatment; 271°C, 12 hours
39.0	End of run

Figure IV-48

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD (RUN CT-256-13; 1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K_2CO_3)



CS: Catalyst Settling

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

Temperature, °C	257-258
Pressure, MPa	1.48-1.65
Feed H_2/CO, molar	0.7
Superficial Feed-Gas Vel., cm/s	3.5-6.0
Space Velocity, NL/gFe-hr	2.4-3.8
H_2+CO Conversion, mol %	23-82
Methane + Ethane Yield, wt % of HC	2.4-4 2
Reactor-Wax Yield, wt % of HC	50-65

Between 7 and 24 DOS, the H_2+CO conversion remained around 81 mol %, while the methane + ethane selectivity gradually increased to 4.2 wt %. This H_2+CO conversion was somewhat lower than expected; Run CT-256-12 produced 87 mol % conversion at the same conditions. Again, the new catalyst batch may have been the cause. The average reactor-wax yield over this period was ~60 wt %, and the continuous reactor-wax removal system was functioning well with the wax containing less than 0.03 wt % solids on average. Figure IV-49 is a plot of the accumulated reactor-wax for the run. The slope of the curve can be seen to gradually lessen with days-on-stream, indicative of the increasing methane + ethane selectivities.

By 24 DOS, the reactor-wax yield had dipped below 55 wt %. We then increased the pressure over a two-day period to 1.65 MPa to help "nudge" the wax selectivity back over 55 wt %. The feed-gas rate was also increased at the same time, so that the superficial velocity was held constant. This, however, dropped the conversion to 77 mol %, indicating an adverse pressure effect. To bring the conversion back up, the feed-gas rate was reduced until, at 27 DOS, the space velocity was nearly the same as it was before the pressure increase. In terms of conversion, this nullified any advantage of increased pressure, but there was only a slight decrease in methane + ethane selectivity and no appreciable change in wax make. We decided to hold the conditions where they were.

During the run, our on-line DP-cells provided information on gas holdup along the bubble-column. Up until 35 DOS, the DP-readings were almost unchanged, indicating stable operation. Some typical profiles are shown in Figure IV-50. The average gas holdup over the course of the run was ~20 vol %. The higher holdup between the 3 and 5 m levels has been observed before in Run CT-256-9 (see Figure IV-32), but the lower holdup at the bottom is in contrast to the higher holdups seen in Run 9. The difference may be due in part to the different gas distributors used in the two runs.

Figure iV-49

CUMULATIVE REACTOR-WAX PRODUCTION

(RUN CT-256-13)

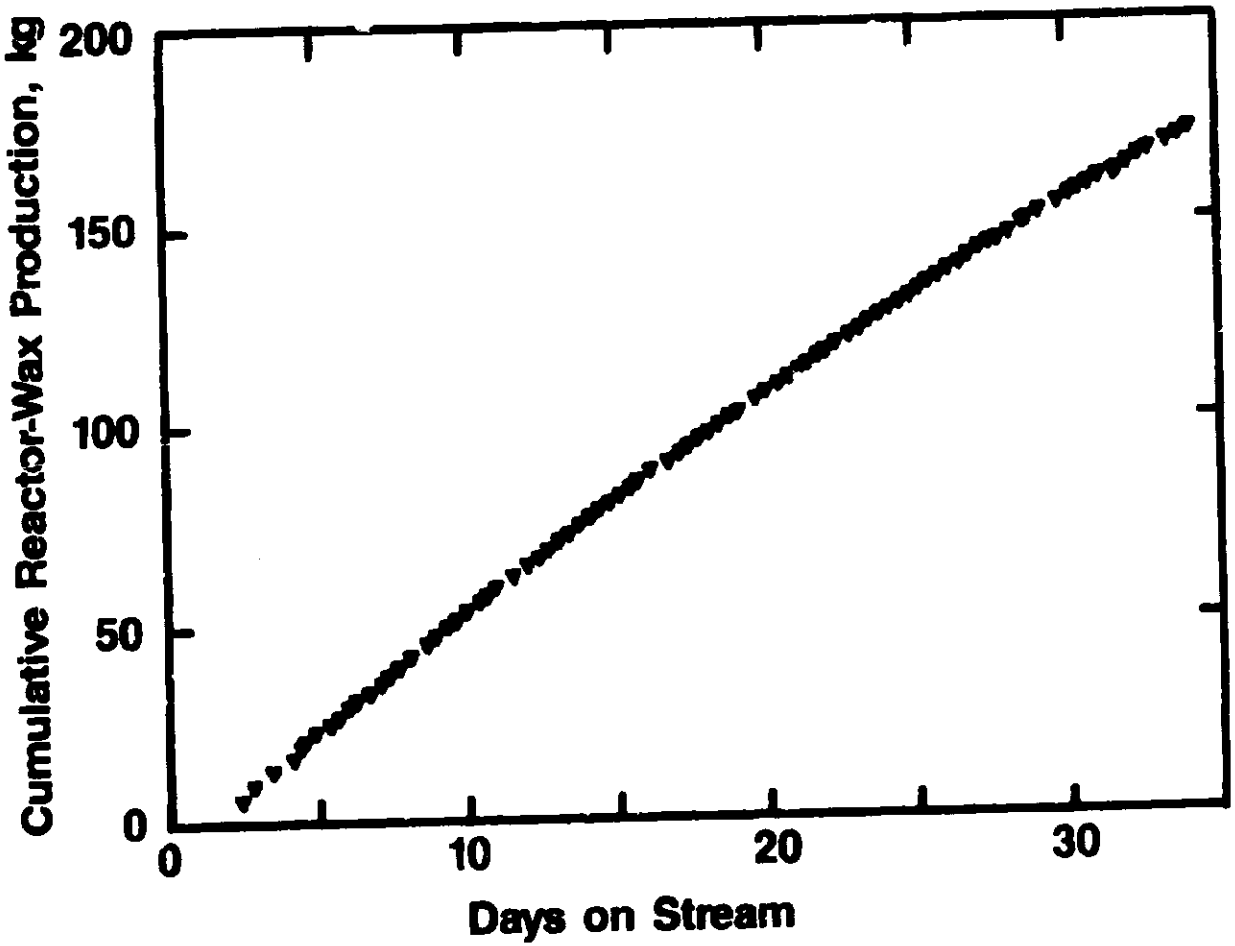
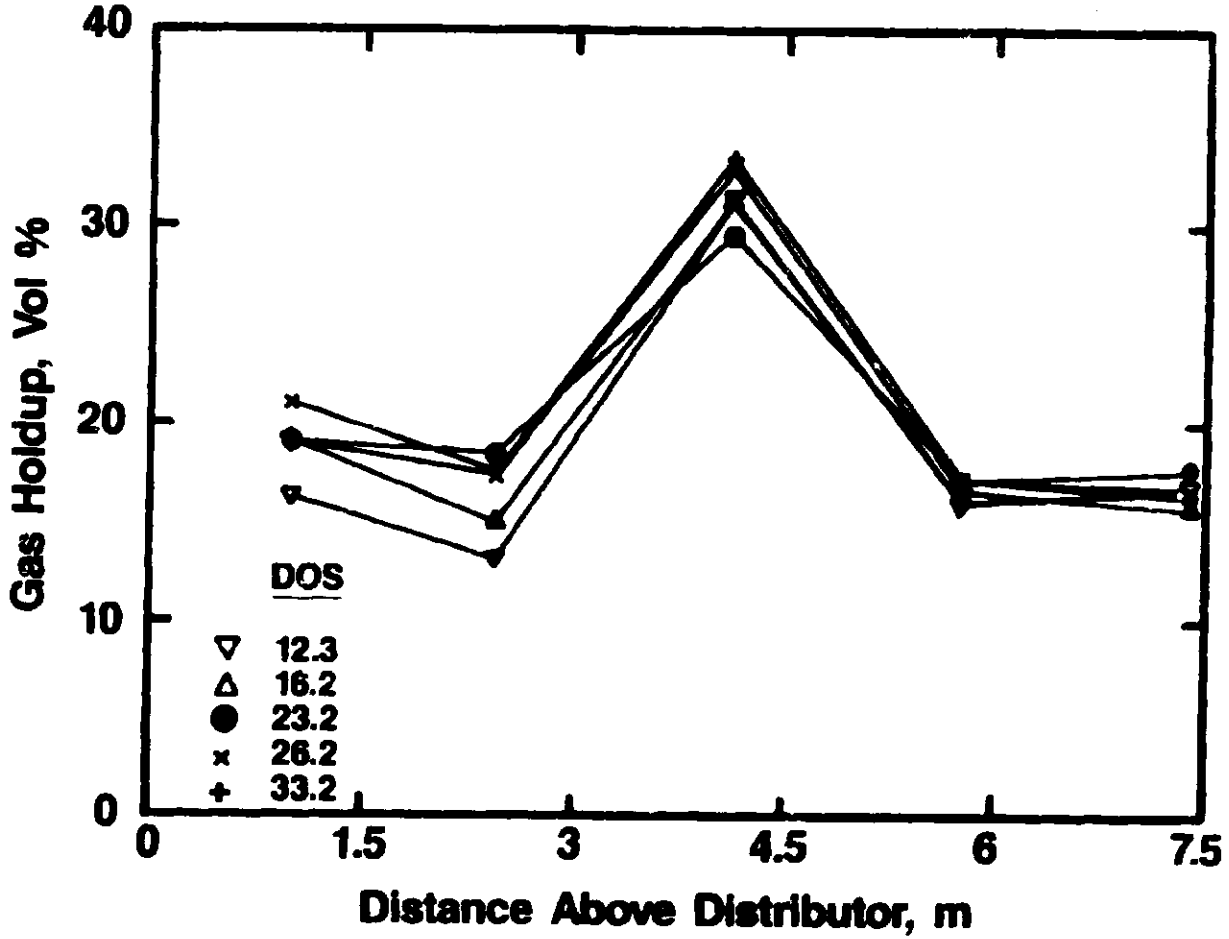


Figure IV-50
GAS HOLDUP PROFILES
(RUN CT-256-13)



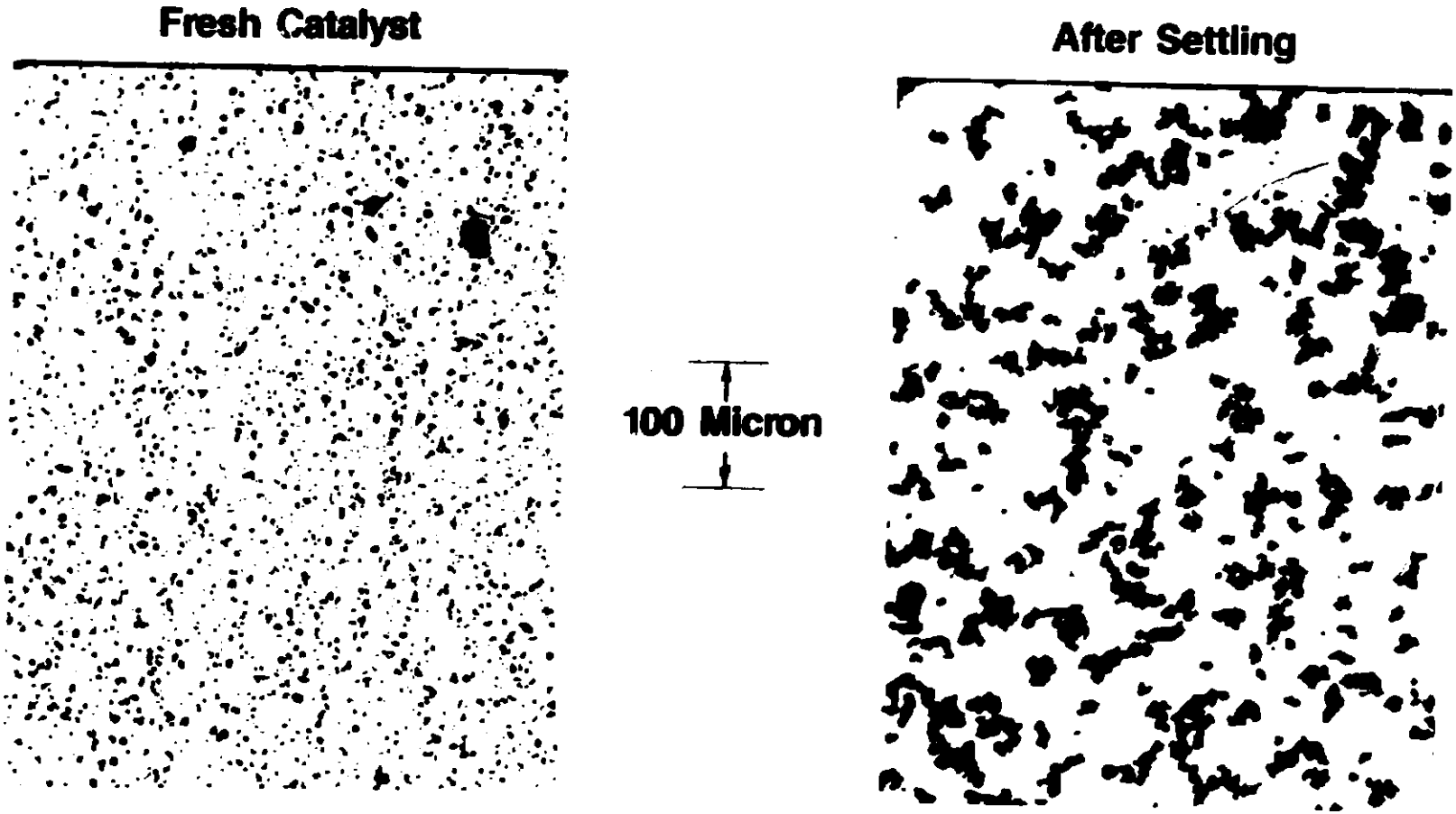
Starting at about 28 DOS, however, the H_2+CO conversion started dropping slowly. No explanation for this was apparent, save for the fact that a new CO supply had been put on-stream. It was immediately analyzed, but no sulfur, oxygen, or CO_2 could be detected. No significant loss of catalyst could be accounted for and slurry samples showed the catalyst concentration in the reactor to be the same as had been recorded earlier in the run. By 34 DOS, though, the conversion had dropped to 68 mol %. This decline in conversion may be the prelude for the catalyst settling described below.

Before any action could be taken to halt the decline, however, the catalyst suddenly settled in the bubble column at 34.8 DOS. The characteristics of the settling were similar to that which had been seen in Runs 9, 11, and 12: rapid (2-3 hours) degeneration of temperature and catalyst concentration profiles in the reactor, producing low H_2+CO conversion (see Subsection IV.G.2). All reactor systems, including the slurry circulation pump, were functioning properly at the time of the settling, so this phenomenon seemingly was not prompted by any upset or interruption. To try and resuspend the catalyst, the superficial feed-gas velocity was increased from 3.6 to 10.0 cm/s for 5 hours, then set at 6.0 cm/s. 30 cm slurry samples taken at all three velocities, however, showed solids contents of 25-27 wt % (over the first 34 days, this concentration was 15-16 wt %).

Feeling that increased upward liquid velocity might help, the slurry circulation pump was replaced by one that had ur times the capacity. This increased the superficial slurry ·city from 0.05 to 0.2 cm/s. This, however, did not reduce 30 cm catalyst concentration or change the H_2+CO conversion.

As a last resort, a hydrogen treatment was tried at 38 DOS. If atalyst particles were being held together by some heavy po ymers, a hydrogen treatment might remove some of it, allowing the particles to resuspend in the reactor. The conditions were: 1.65 MPa, 271°C, and 3.4 NL/gFe-hr for 12 hours. When synthesis conditions were re-established, however, no change in conversion was evident, and the catalyst remained settled. The run was ended soon afterward and slurry samples were taken for examination by microscope. Photographs comparing fresh (before pretreatment) catalyst with end-of-run catalyst are shown in Figure IV-51. The tremendous increase in apparent particle size is clearly evident. The large particles do appear to be aggregates, but a mechanism for their formation remains unknown.

Figure IV-51
PHOTOGRAPHS OF SLURRY SAMPLES
(RUN CT-256-13)



L.3. Second-Stage ZSM 5 Reactor Operation

Since the second-stage ZSM-5 catalyst used in Run CT-256-12 had been on-stream for only 17 days before the first-stage settling took place, the inlet temperature needed for proper operation was only 320°C. It was, therefore, decided to continue using this catalyst load as long as possible. Maintaining the severity index ($i\text{-}C_4/(C_3^{=}+C_4^{=})$, molar) as close to 1.0 as possible, the catalyst was used for the first 27 days-on-stream. By then, the inlet temperature was 430°C and the outlet was 466°C. The other ZSM-5 reactor was then put on-stream for the duration of the run.