

The aging rate constants, A, in Equation (IV-4) can also be translated into the half-life of the catalyst activity at the given operating conditions. For the two sets of operating conditions given above, the half-life of the catalyst activity are 13 and 24 days, respectively.

The operating conditions of 250°C, 1.48 MPa and 1.4 NL/gFe-hr are rather moderate. However, the corresponding catalyst aging rate is high. One can estimate, based on the observed aging rate, that a daily catalyst makeup rate of more than 5% is needed to compensate the aging. This catalyst makeup rate is equivalent to a hydrocarbon production rate of less than 200 gHC/gFe. This low production rate is not acceptable.

### F.3. Second-Stage ZSM-5 Fixed-Bed Operation

Operation of the second-stage ZSM-5 reactor did not begin until 54 DOS. This was because the focus of attention was on the declining first-stage catalyst activity and ways of improving it. The second-stage catalyst was the same which was run for 25 days in Run CT-256-7 before being regenerated, so this was the start of the catalyst's second cycle. Second-stage material balances are shown in Appendix C. Over the final 14 days of the run, the feed temperature to the bed was increased from 260 to 299°C in an effort to maintain the severity index (molar i-butane/(propene + butenes) ratio) at approximately 1.0. The actual severity index ranged from .76 to 1.5.

### G. Run CT-256-9

Run CT-256-9 of the two-stage BSU was started on March 18, 1985 and ended on April 12, 1985. The main objective of the run was to demonstrate low methane + ethane operation with high H<sub>2</sub>+CO conversion using Catalyst I-B. The material balance data of this run are summarized in Appendix D.

The following are the major highlights of the run:

- Low methane + ethane selectivity (~5.4 wt %) was achieved at 1.48 MPa, which is the same pressure used in gasoline-mode operation with this composition F-T catalyst. It was found later that this batch of catalyst had only about 40% of the surface area of the older batch.
- Successful high H<sub>2</sub>+CO conversion and high reactor-wax mode operation was demonstrated for 10 days.

- The F-T catalyst settled in the bubble-column reactor following an electrical power interruption, causing a hot spot and low conversion (~40 mol %). Photographs of the catalyst taken through a microscope revealed larger particle sizes.
- High velocity H<sub>2</sub>+CO (up to 9.1 cm/s) did not completely resuspend the catalyst; however, high velocity nitrogen did. This remains unexplained.
- Ball-milling most of the catalyst and then returning it to the unit showed no improvement on the catalyst suspension. Removing and cleaning the single-orifice feed-gas distributor also showed no improvement. There was no visible blockage on the orifice.

#### G.1. Fischer-Tropsch Slurry-Catalyst Loading and Pretreatment

The first-stage bubble-column was initially loaded with 2,300 g of Catalyst I-B containing 1,534 g of a newly prepared batch. The wax medium at the start consisted of reactor-wax from Run CT-256-7. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
Feed H <sub>2</sub> /CO, molar	0.67
Space Velocity, NL/gFe-hr	
Superficial Feed Gas Vel., cm/s	
Initial Catalyst Loading, wt %	25

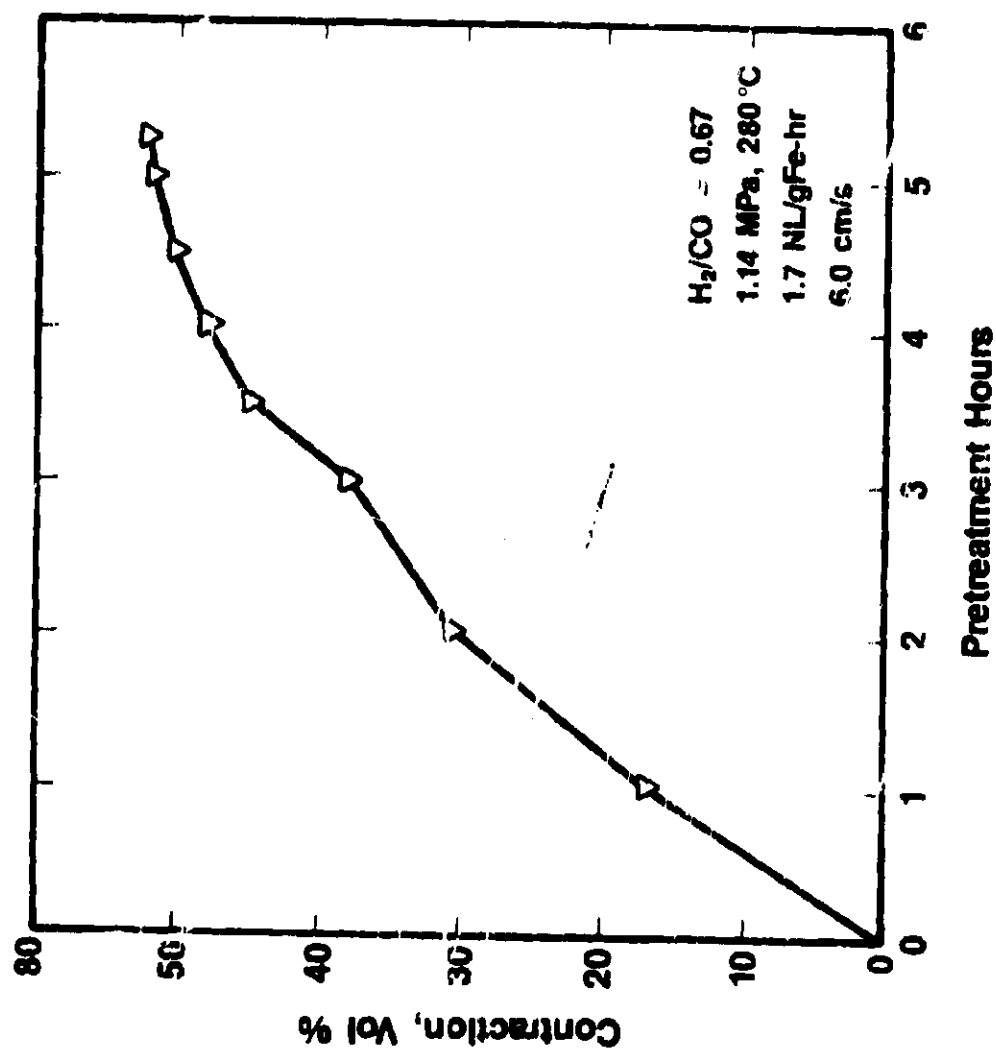
After 5.5 hours, the volume contraction reached 50%, our usual target for the end of pretreatment. A plot of the contraction during pretreatment is shown in Figure IV-30.

#### G.2. First-Stage Fischer-Tropsch Reactor Operation

This run produced high and stable H<sub>2</sub>+CO conversion, low methane + ethane selectivity and smooth operation for ten days. The operating conditions and performance for that period were:

Temperature, °C	257
Pressure, MPa	1.48-1.82
Feed H <sub>2</sub> /CO, molar	0.67
Space Velocity, NL/gFe-hr	2.0-2.5
Superficial Feed Gas Vel., cm/s	4.3-4.8
Initial Catalyst Loading, wt %	25

**Figure IV-30**  
**PRETREATMENT OF FISCHER-TROPSCH CATALYST I-B**  
**(RUN CT-256-9)**



H <sub>2</sub> +CO Conversion, mol %	80-91
Methane + Ethane Yield, wt % of HC	4.7-5.7
Reactor-Wax Yield, wt % of HC	40-50
Hydrocarbon Production, gHC/gFe	100

Figure IV-31 shows the conversion and methane and ethane selectivities and other operating parameters over the whole run.

Following pretreatment, the temperature was dropped gradually down to 257°C, while the pressure was increased to 1.48 MPa. The space velocity was adjusted to 2.0 NL/gFe-hr, and the H<sub>2</sub>+CO conversion climbed to 91 mol % in 2.5 days. The methane + ethane selectivity stayed low through the first ten days, averaging 5.4 wt % of hydrocarbons produced.

The low methane + ethane (and high reactor-wax) yield at 1.48 MPa was a surprise, since Catalyst I-B (a different batch) was used as the gasoline-mode catalyst in Run CT-256-3 (Kuo, 1983) at the same pressure and nearly the same temperature. Analysis of the catalysts from both runs showed identical Fe/Cu/K<sub>2</sub>CO<sub>3</sub> compositions. However, the surface area of this new batch of catalyst was substantially less than that of the old batch. This may have led to higher concentrations of Cu and K<sub>2</sub>CO<sub>3</sub> on the catalyst surface, causing changes in pretreatment time (5.5 instead of 10.5 hours) and product selectivity. Regardless of the reason, it was decided not to increase pressure as long as the methane + ethane selectivity remained low (the pressure was increased later to 1.82 MPa to permit higher throughput).

At 10 DOS, all electrical power to the unit was accidentally interrupted for three hours. During that period, we depressured the reactor so that any water in the F-T reactor would be removed. The unit was kept under nitrogen overnight (17 hours) at 177°C. Still under N<sub>2</sub>, the reactor was pressured back to 1.82 MPa and heated to 256°C, and the H<sub>2</sub>/CO feed kicked in at 4.4 cm/s superficial gas velocity. Volume contraction and reactor temperature profile looked normal for 1.5 hours, but then the temperatures in the upper section (3-7.6 m) began to drop. After a short time, there was a temperature difference of 8.3°C between the top and bottom of the reactor. The H<sub>2</sub>+CO conversion dropped to 40 mol %, and slurry samples taken from the 30 cm level showed a 30% increase in solids (see Table IV-7).

DF-readings were being taken during the run. The average gas holdup calculated from readings before the catalyst settling was 26 vol % and readings taken before and after the settling show dramatic differences (see Figure IV-32). The increased solids loading at the reactor bottom apparently caused very low gas holdup in that zone, whereas the consequently low concentrations in the upper section resulted in a higher holdup.

**Figure IV-31**  
**SYNTHESIS GAS CONVERSION**  
**AND METHANE & ETHANE YIELD**  
**(RUN CT-256-9;**  
**1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K<sub>2</sub>CO<sub>3</sub>)**

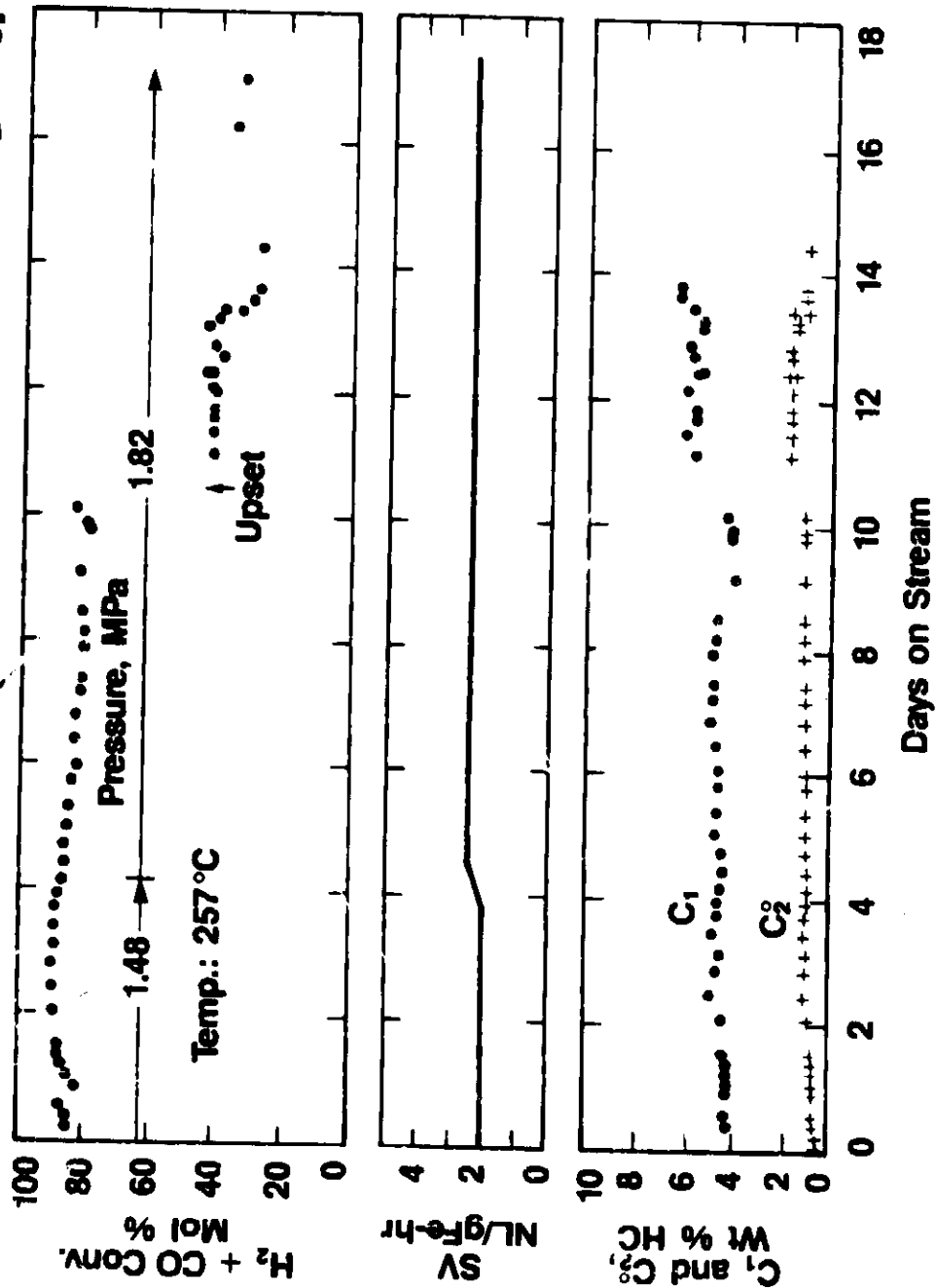
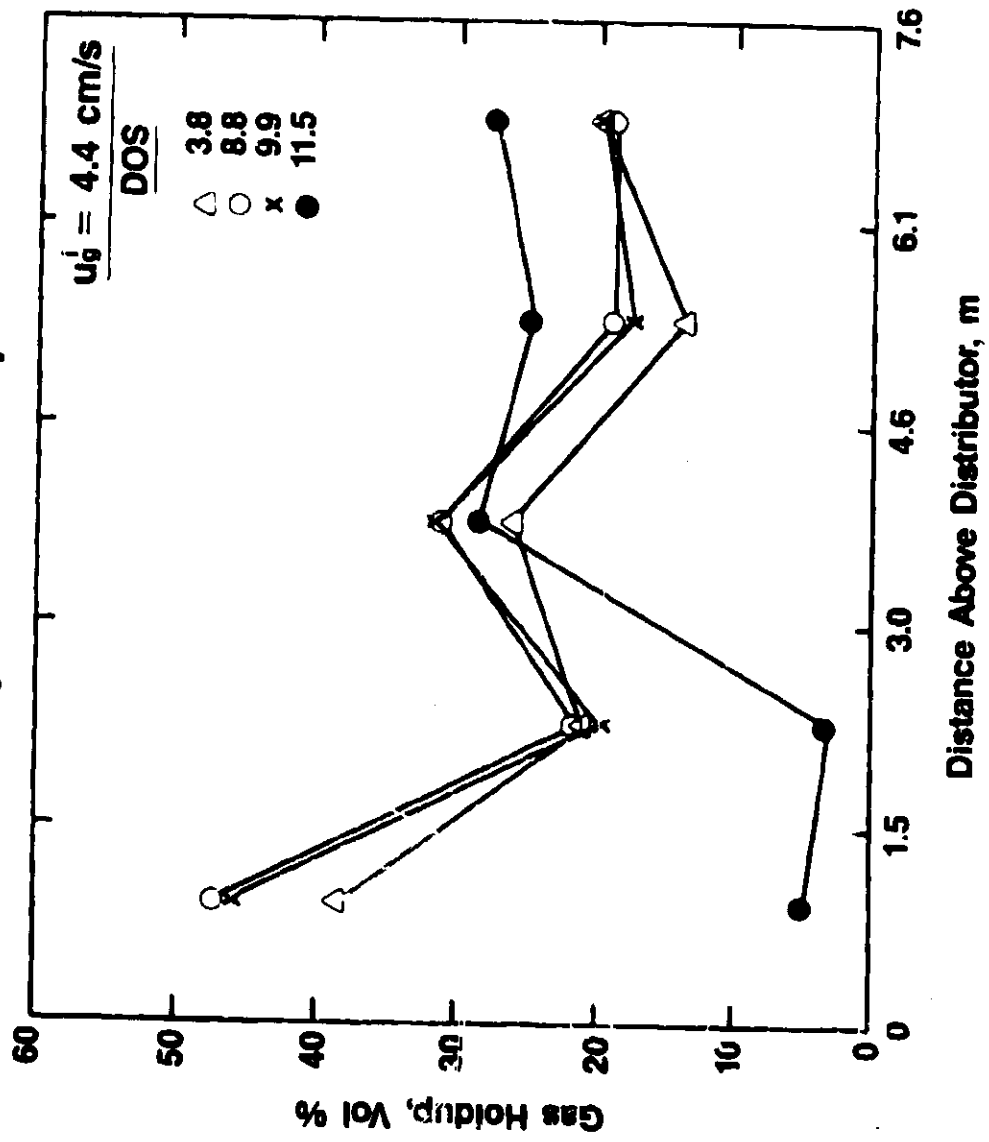


Table IV-7

Evidence for Catalyst Settling  
(Run CT-256-9)

<u>Bubble-Column Location, m</u>	<u>Slurry Reactor Temperature Profile, °C</u>		<u>Catalyst Conc., Wt %</u>	
	<u>Normal</u>	<u>Catalyst Settling</u>	<u>Normal</u>	<u>Catalyst Settling</u>
0.3	254.4	256.7	22.7	29-32
1.5	256.1	253.9	-	-
3.0	253.9	247.2	-	-
4.6	255.6	248.9	-	-
6.1	255.0	248.3	-	-

**Figure IV-32**  
**GAS HOLDUP PROFILES**  
 (RUN CT-256-9)



The first attempts at resuspending the catalyst were done by increasing the feed-gas velocity. Superficial gas velocities as high as 9.1 cm/s were attempted, using H<sub>2</sub>+CO. Slurry samples taken at the 30 cm level, however, showed virtually no change in catalyst concentration over the entire range of velocities (~30 wt %). Figure IV-33 shows the gas holdup profiles for three different velocities, taken using the DP-cells. It can be seen that the gas holdup at the bottom of the reactor was very low, consistent with the existence of a high solids concentration. The holdup at the top of the column is higher, consequently, due to the relative absence of solids. Overall, the holdup increased as the velocity was raised but the catalyst remained at the bottom.

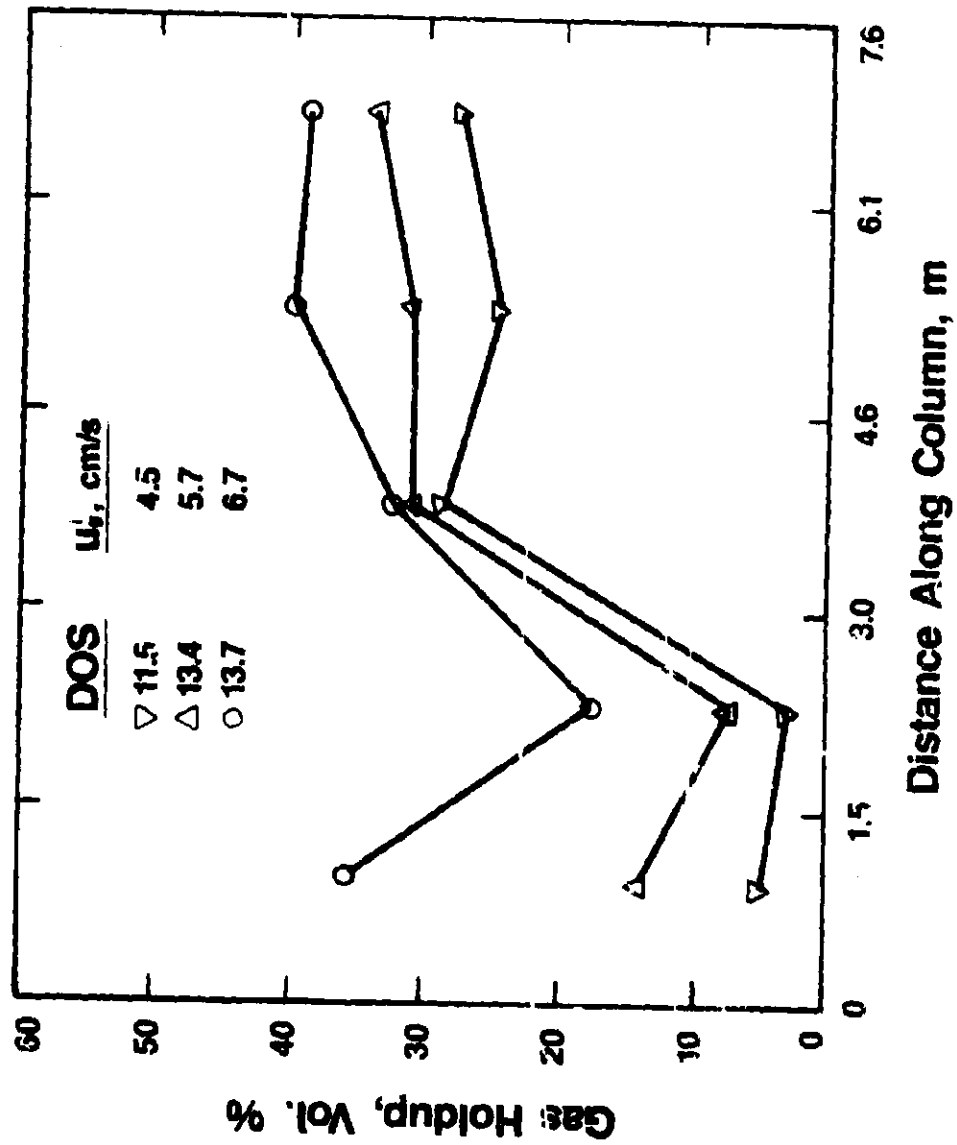
One interesting note during this time was the fact that at the same high velocities, nitrogen seemed to resuspend the catalyst while H<sub>2</sub>+CO did not. Slurry samples taken from the 30 cm level at a nitrogen superficial gas velocity of 8.1 cm/s showed only 19.3 wt %. Even when a 50x50 mixture of nitrogen and H<sub>2</sub>+CO was used at this velocity, the slurry sample showed 20.0 wt %. Every time the nitrogen was shut off, however, the steep catalyst profiles would return. At the present time, there is no explanation for this phenomenon.

Figure IV-34 is a sampling of catalyst concentration profiles taken before and after the settling took place. The profile at 9.9 DOS (before settling) shows a relatively uniform concentration throughout the column. The other two profiles clearly illustrate the settling phenomenon. All three profiles were taken using H<sub>2</sub>+CO and the steeper profile at 17.1 DOS is due more to the later time-on-stream than it is to the lower superficial gas velocity. This is because the settling seemed to get more pronounced as time progressed, perhaps indicating a particle agglomeration phenomenon.

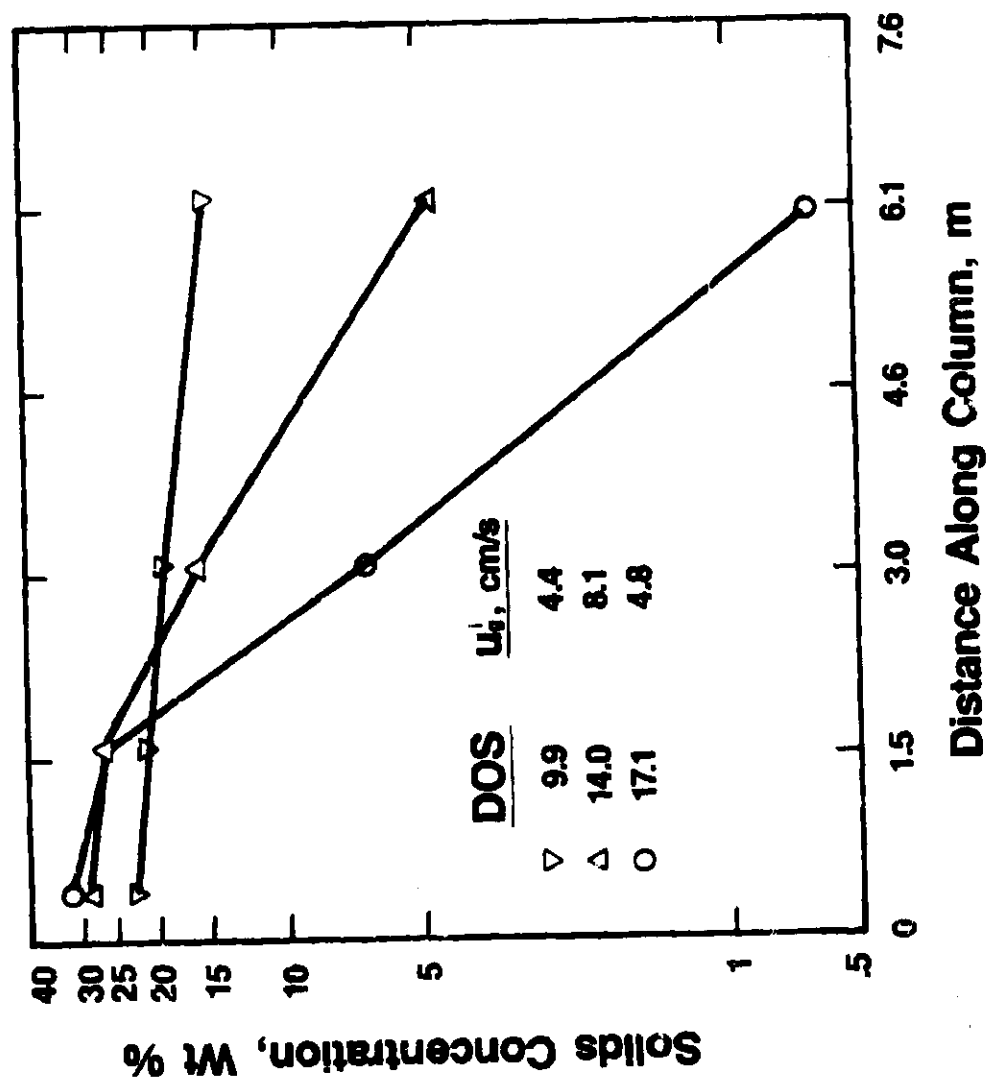
To investigate the possibility that the particle size had changed, we examined slurry samples from immediately before and after the catalyst settling. Using an optical microscope equipped with a camera, we photographed samples which had been diluted (roughly 1000:1) with mineral oil while hot, then allowed to cool. The results are shown in Figure IV-35. At 200x magnification, catalyst particles are apparently clearly defined. That being established, it appears that the particles are roughly twice as large after the upset (~10 vs ~5 microns). This would, of course, lead to higher catalyst concentrations at the reactor bottom. An important note must be made here, however: the slurry sample from before the settling was taken from a mixture of the samples from each of the four sampling ports, while the sample from after the settling was only from the 30 cm port. These photos are not, therefore, definitive proof that the catalyst particles increased in size.



**Figure IV-33**  
**GAS HOLDUP PROFILES**  
**(RUN CT-256-9)**



**Figure IV-34**  
**CATALYST CONCENTRATION PROFILES**  
**(RUN CT-256-9)**



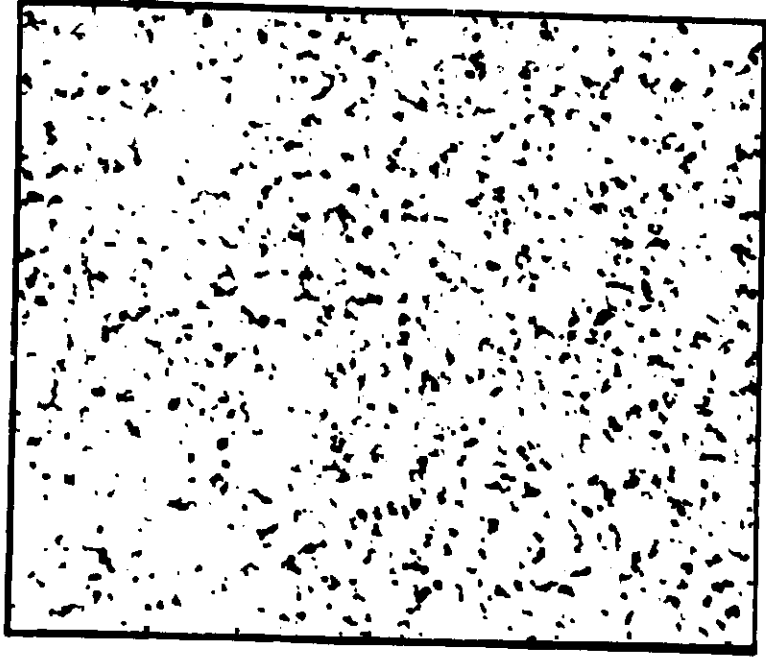
**Figure IV-35**  
**PHOTOGRAPHS OF SLURRY SAMPLES**  
**(RUN CT-256-9)**

**Before Settling**



100 Micron

**After Settling**



The cause of the catalyst settling, therefore, remains a mystery. It is known, however, that catalysts used in polymerization reactions grow in size due to the incorporation of long-chain polymers on the surface (Nagel et al., 1980). Since the F-T reaction is essentially a polymerization reaction, particle growth may also be due to this phenomenon. Of course, the degree of polymerization in the F-T reaction is much less than that in commercial polymer production, with consequently shorter chain lengths, but the phenomenon is still something to be considered.

Another attempt to resuspend the catalyst was the reball-milling of a portion of the slurry. This was done to possibly reduce the catalyst size, if that was indeed the problem. About one-half the slurry, containing nearly all the catalyst, was drained from the bottom of the reactor. The catalyst was then concentrated and removed, then diluted with Mobil F-509 oil. The catalyst/wax/oil mixture was ball-milled at room temperature for 2.5 hours, after which the catalyst was recombined with the reactor-wax and loaded into the reactor. This was done at ~14 DOS, and apparently had no effect on the catalyst concentration profile.

Lastly, it was decided to examine the single-orifice feed-gas distributor to see if any changes in the gas distribution may have led to the settling. A cold shutdown was performed, with the slurry solidifying in-situ. The distributor was then removed and the lower 10 cm of solid slurry was chipped out of the reactor. No irregularities on the distributor could be detected. Upon cleaning and reassembling the reactor and restarting, the catalyst remained settled.

Following this last attempt, the run was voluntarily ended on April 11, 1985. Further photographic studies of slurry samples did not clearly reveal any more changes in particle size.

### G.3. Second-Stage ZSM-5 Reactor Operation

The second-stage ZSM-5 reactor was in operation for the entire run. The inlet temperature to the bed ranged from 310 to 380°C and the outlet temperature ranged from 350 to 400°C. The severity index (i-butane/(propenes + butenes), molar) averaged about 0.75 throughout the run, and the GHSV averaged about 3,500 NL per hour/L-Cat. No octane or stability tests were performed on the gasoline produced, but a breakdown of the second- (and first-) stage hydrocarbons appears in Appendix D.

### H. Run CT-256-10

The tenth run of the two-stage BSU was started on April 16, 1985. The main objective of the run was to determine whether Catalyst I-D could be fully activated without a high

temperature pretreatment step. Another important goal of the run was to verify that catalyst could be suspended normally in the reactor, following the catalyst settling problem of Run CT-256-9. If all went well, the run would be continued, in a low methane + ethane, high reactor-wax mode operation.

Run CT-256-10 was terminated after nine days when the major objectives were accomplished. The major highlights were:

- The catalyst could not be fully activated at synthesis conditions. The H<sub>2</sub>-CO conversion leveled off at only 62 mol %.
- Subsequent attempts to activate the catalyst were unsuccessful, including H<sub>2</sub> and CO treatments.
- No indications of catalyst settling was observed.

#### H.1. Fischer-Tropsch Slurry Catalyst Loading and Operation

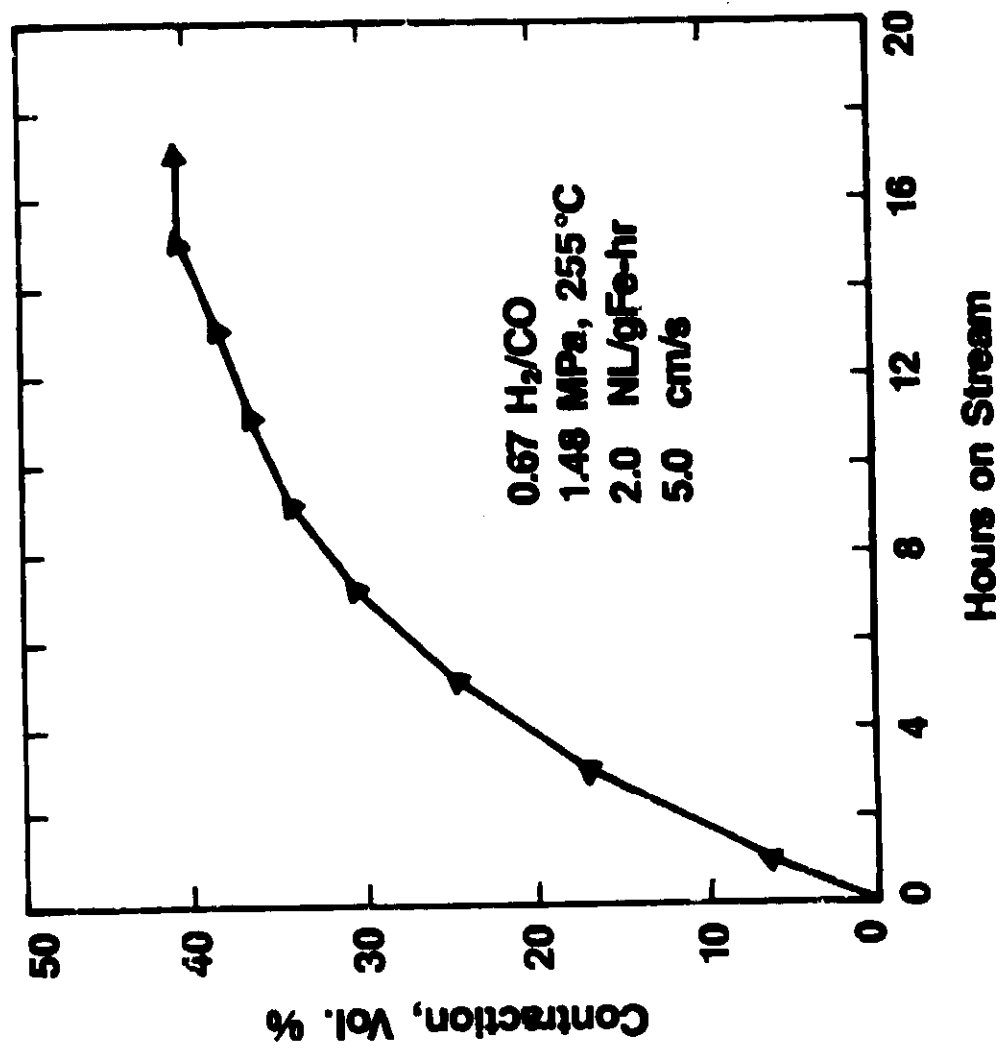
The first-stage bubble-column was loaded with 2,200 g of Catalyst I-D. The starting wax medium consisted of Run CT-256-9 reactor-wax. The synthesis conditions were then established.

Temperature, °C	255
Pressure, MPa	1.48
H <sub>2</sub> /CO Feed, molar	0.67
Space Velocity, NL/gFe-hr	2.0
Superficial Feed Gas Vel., cm/s	5.0
Initial Catalyst Loading, wt %	22

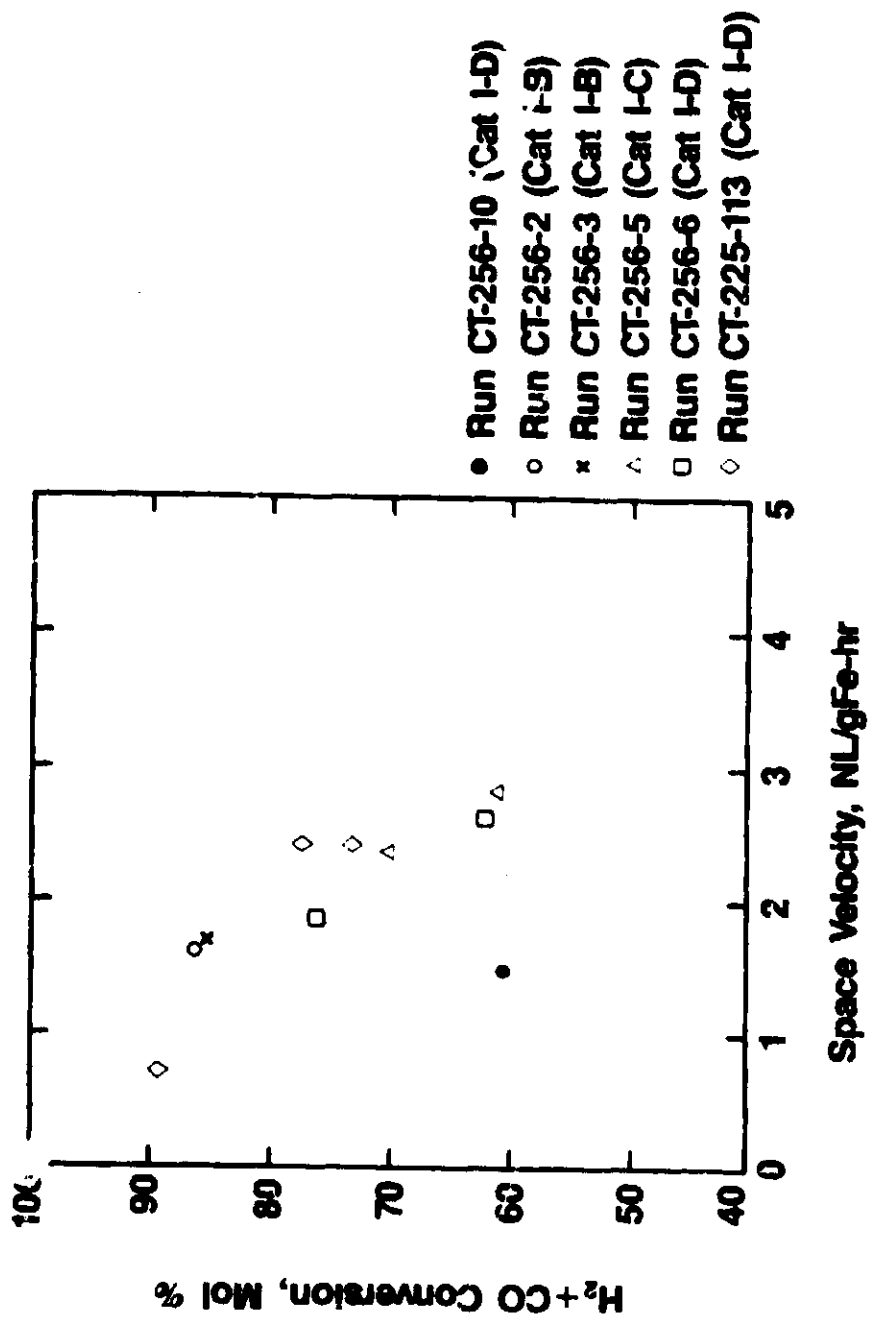
Fully activated catalysts, which we have used previously, gave H<sub>2</sub>+CO conversions of 85-90 mol % when operated at these conditions. It was expected here that the conversion would rise to this level over a period of 1-2 days.

As seen in Figure IV-36, however, the conversion never reached the expected levels. After ~15 hours, the volume contraction reached a steady value of 40%, corresponding to a conversion of only 62 mol %. Figure IV-37 is a comparison of initial F-T catalyst activities taken from some of our previous studies, corrected to the same base conditions. The initial activity of the Catalyst I-D used in this run is obviously well below any of the others. It is interesting to note that, on the same plot, Catalyst I-D shows "normal" activity for two other runs. In both those cases, however, the catalyst was pretreated at 280°C before normal synthesis was started. The methane + ethane selectivity, incidentally, was in the range of 3.5-4.0 wt % of hydrocarbons produced, which is good for high reactor-wax operation.

**Figure IV-36**  
**ACTIVATION OF FISCHER-TROPSCH CATALYST I-D**  
**(RUN CT-256-10)**



**Figure IV-37**  
**COMPARISON OF INITIAL FISCHER-TROPSCH CATALYST ACTIVITIES**



All data corrected to 1.48 MPa, 250°C

Starting at 22 HOS, we began a series of treatments which was hoped would activate the catalyst fully. In succession, the following were attempted:

- Operation at "standard" activation temperature (280°C) and high superficial gas velocity (9 cm/s) for two hours.
- High temperature (280°C) hydrogen treatment for five hours.
- 24-hour CO treatment at 260°C and 0.8 MPa, followed by a 20-hour H<sub>2</sub> treatment at the same conditions.
- High temperature (280°C) CO treatment, followed by a "standard" H<sub>2</sub>+CO activation.

All these efforts failed to activate the catalyst beyond the original level. It was therefore decided to end the run on April 26, 1985. No material balances were performed during the run, and the second-stage ZSM-5 reactor was not operational.

#### I. Run CT-256-11

Following the ending of Run CT-256-9 and the subsequent demonstration in Run 10 that the reactor hardware was not responsible for the catalyst settling, Run CT-256-11 was started on May 2, 1985. The objectives were identical to those of Run 9: demonstrate low methane + ethane operation with high H<sub>2</sub>+CO conversion using Catalyst I-B.

The highlights of the run were:

- High H<sub>2</sub>+CO conversion (80-90 mol %), low methane + ethane selectivity (3.5-4.3 wt %) was achieved for 13 days. These results were virtually identical to Run 9.
- Catalyst settling occurred at 13 DOS, dropping the conversion to ~40 mol % and creating steep temperature and catalyst profiles in the bubble-column reactor. This occurred simultaneously with the stoppage of the slurry circulating pump which is used in the reactor-wax removal system.
- Superficial feed-gas velocity higher than 10 cm/s was needed to satisfactorily suspend the catalyst. However, the H<sub>2</sub>+CO conversion became unacceptably low due to very high space velocity.



The run was ended on May 23, 1985 after we were unable to restore high conversion or completely re-establish slurry circulation. Material balances were performed daily and the results are summarized in Appendix E.

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

The first-stage bubble-column was charged with 2,200 g of Catalyst I-B. The initial wax medium was the reactor-wax from Run CT-256-7. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
Feed H <sub>2</sub> /CO, molar	0.67
Space Velocity, NL/gFe-hr	1.7
Superficial Feed-Gas Vel., cm/s	5.9
Initial Catalyst Loading, wt %	22.0

The catalyst activated in an identical fashion to Run 9, reaching 48% volume contraction (equivalent to 75 mol % H<sub>2</sub>+CO conversion) in 4-5 hours. The reactor temperature was then lowered 5.6°C/hr until it was at an average of 257°C.

### I.2. First-Stage Fischer-Tropsch Reactor Operations

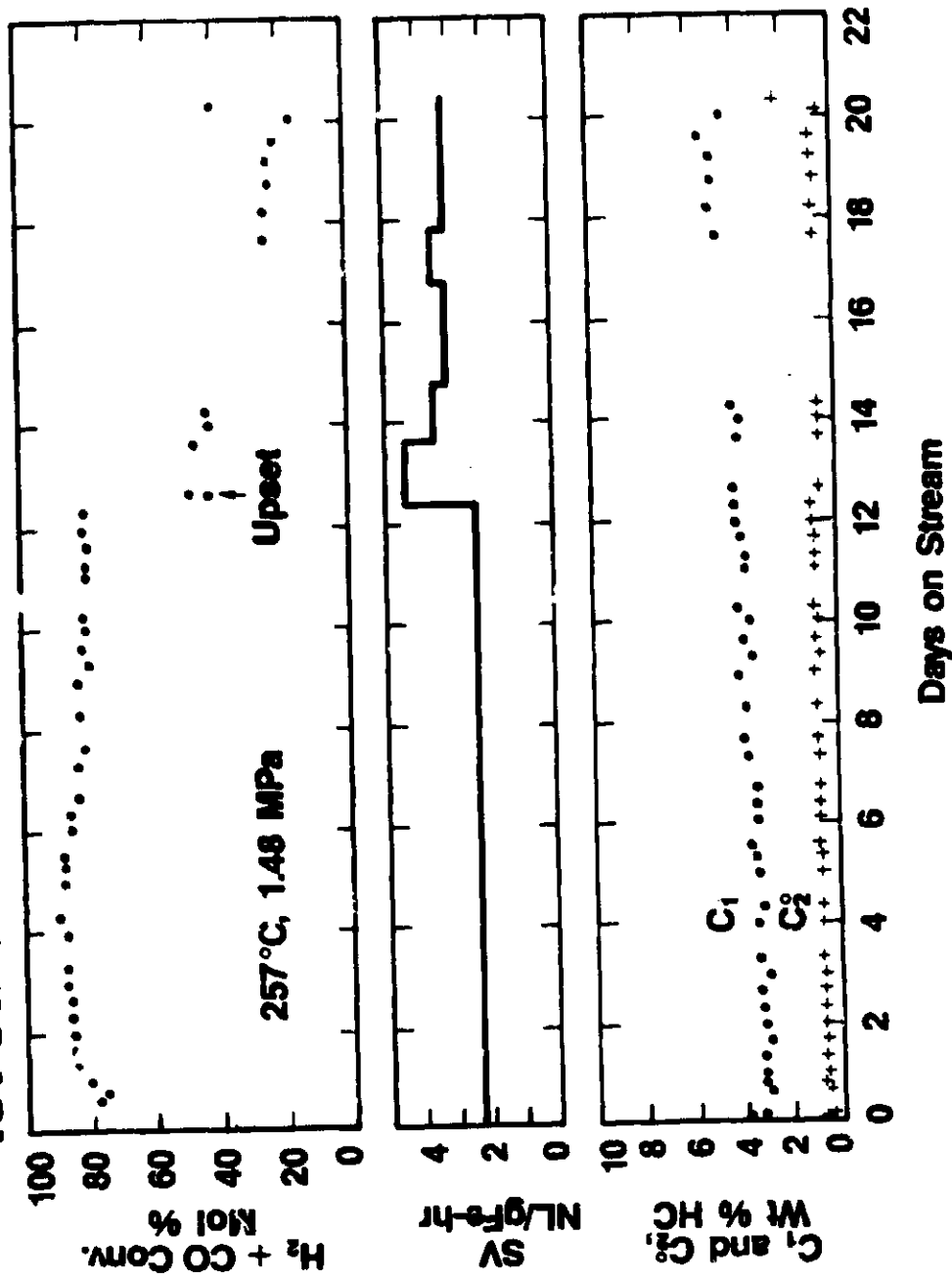
As mentioned earlier, the first thirteen days produced the kind of operation which had been the goal of the run. The ranges of operating conditions and performance during that period were:

Temperature, °C	257
Pressure, MPa	1.48
Feed H <sub>2</sub> /CO, molar	0.67
Superficial Feed-Gas Vel., cm/s	5.3-8.0
Space Velocity, NL/gFe-hr	2.3-2.6
H <sub>2</sub> +CO Conversion, mol %	80-90
Methane + Ethane Yield, wt % of HC	3.5-4.3
Reactor-Wax Yield, wt % HC	45-55
Hydrocarbon Production, gHC/gFe	135

Again in this run, as in Run CT-256-9, the low methane + ethane yield at these conditions was not expected. We decided, therefore, to leave the reactor pressure at this level until the methane + ethane selectivity increased. A plot of the run is shown in Figure IV-38.

During the early part of the run, reactor operations went very smoothly, with the reactor-wax production being removed with very low (<0.05 wt %) solids content. Slurry samples showed

**Figure IV-38**  
**SYNTHESIS GAS CONVERSION**  
**AND METHANE & ETHANE YIELD**  
**(RUN CT-256-11;**  
**1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K<sub>2</sub>CO<sub>3</sub>)**



no indications of any catalyst settling, as illustrated in Figure IV-39, which also shows a catalyst concentration profile from Run CT-256-10 for comparison.

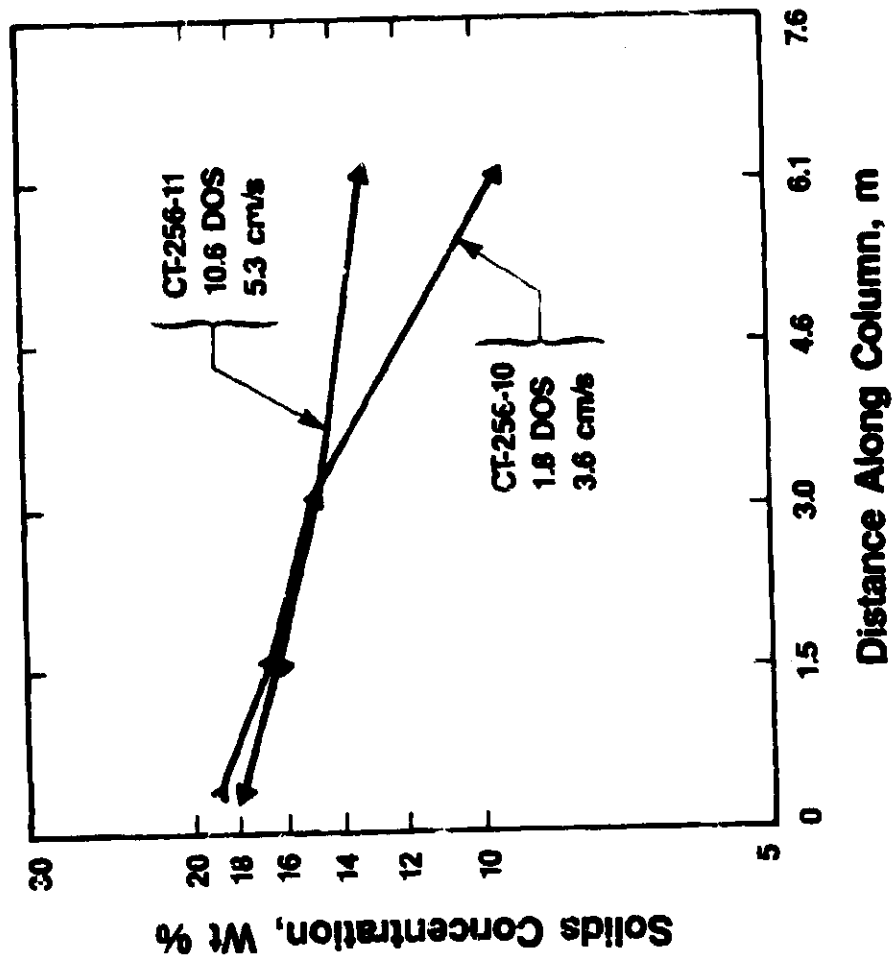
At 12 DOS, however, the catalyst in the slurry reactor began settling, as evidenced by increasing temperatures at the reactor bottom, and a decrease in  $H_2+CO$  conversion. The catalyst concentration at the 30 cm level showed an increase from 17.7 to 24.5 wt %, verifying the phenomenon. This settling coincided with a failure of the slurry circulating pump of the catalyst/wax separation system, which circulates slurry between the 3 and 6 m levels. This superficial liquid velocity (0.05 cm/s) may have been supporting catalyst suspension in that upper section, preventing settling. The viscosities of the reactor-waxes immediately before and after the catalyst settling showed little variation (see Table VII-10 later).

Immediate efforts to restart the circulation pump were unsuccessful, and it was clear that repair work was necessary. So to try to keep the catalyst suspended, the superficial feed-gas velocity was increased to 10 cm/s. The catalyst concentration at 30 cm dropped to 15.8 wt %, indicating that the settling had been averted for the moment. The  $H_2+CO$  conversion consequently dropped to the 40-50 mol % range, which was in fact the expected conversion at that high space velocity (~4.2 NL/gFe-hr). The methane + ethane selectivity was still low, so it appeared at this point as if the catalyst was still fully active.

With the catalyst apparently suspended, we decided to lower the feed-gas velocity in small steps, hoping to increase conversion and yet retain the suspension. The velocity was therefore dropped to 8.0 cm/s at 14 DOS and then to 7.0 cm/s at 15 DOS. Both changes failed to increase conversion, however, indicating that either settling had occurred or the catalyst was somehow damaged. The velocity was held at 7.0 cm/s for two days. During that time, the conversion dropped from 43 to 30 mol %, while the temperature profile in the reactor became more and more nonuniform. This appears to be an indication that the catalyst was settling during this time.

Further proof of the settling was attained when the velocity was raised back to 8.0 cm/s. The  $H_2+CO$  conversion remained at roughly 30 mol %, while slurry samples indicated a steep catalyst profile in the reactor. This can be seen in Figure IV-40, which should also be compared with Figure IV-39. An explanation for this behavior may be that once the catalyst had settled, the high bottom concentration changed the hydrodynamics there (perhaps causing the formation of large bubbles), preventing the resuspension of the catalyst.

**Figure IV-39**  
**CATALYST CONCENTRATION PROFILES BEFORE SETTLING**  
**(RUNS CT-256-10 and -11)**



**Figure IV-40**  
**CATALYST CONCENTRATION PROFILE AFTER SETTLING**  
**(RUN CT-256-11)**

