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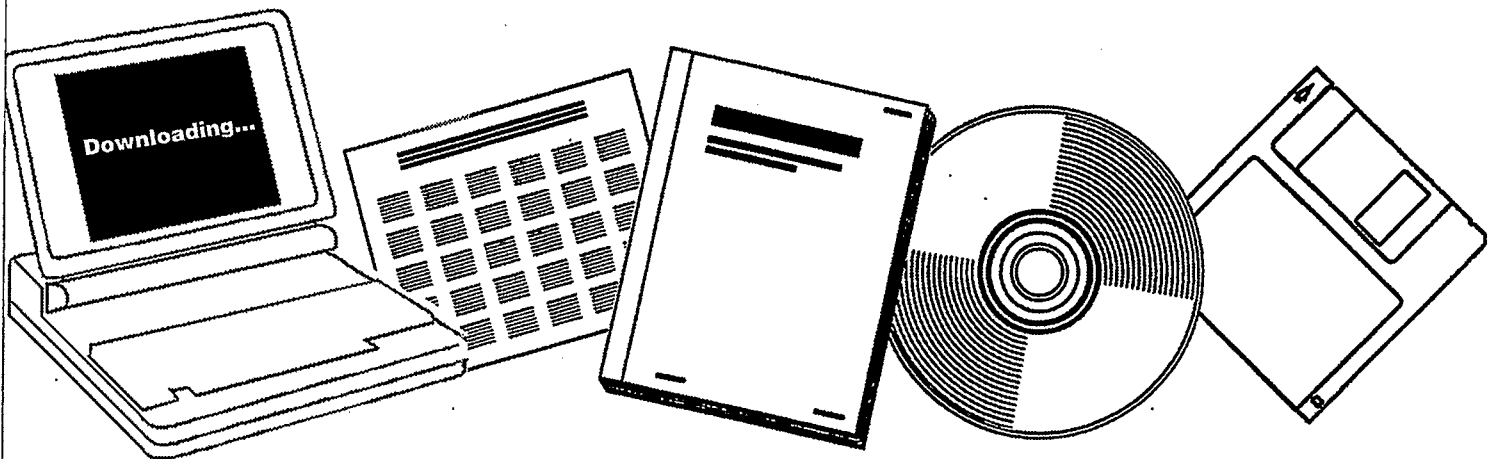
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**TWO-STAGE PROCESS FOR CONVERSION OF  
SYNTHESIS GAS TO HIGH QUALITY  
TRANSPORTATION FUELS. QUARTERLY REPORT, 1  
APRIL-30 JUNE 1985**

**MOBIL RESEARCH AND DEVELOPMENT CORP.  
PAULSBORO, NJ**

**AUG 1985**



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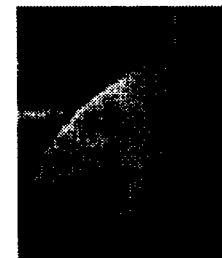
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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS  
TO HIGH QUALITY TRANSPORTATION FUELS

QUARTERLY REPORT FOR THE PERIOD  
1 APRIL - 30 JUNE, 1985

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## I. Abstract

In this Quarter three separate runs of the two-stage Fischer-Tropsch/ZSM-5 pilot plant were completed. A fourth, Run CT-256-12, was started at the end of the Quarter. Catalyst settling in the first-stage bubble-column reactor caused the ending of Runs 9 and 11, so the unit was modified before the latest run to help prevent this. Initial results from all three of these runs showed that Catalyst I-B gave low methane + ethane yields and high  $H_2+CO$  conversions at moderate temperatures and pressures. Also, catalyst aging during Run CT-256-8 (Catalyst I-C) was analyzed using a mathematical model; a reactor-wax sample from Run CT-256-7 was analyzed using Field Ionization Mass Spectrometry; and hydrodynamic studies using the tall hot-flow bubble-columns were concluded. Investigated were real reactor waxes and the effect of solids and column diameter on gas holdup and bubble sizes. Lastly, design base data were developed for the conceptual process design of a high liquid fuels Fischer-Tropsch commercial plant.

### III. Objective and Scope of Work

The general objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H<sub>2</sub>/CO ratio synthesis gas, of the type produced in a coal gasification system, into maximum yield of transportation fuels. To accomplish this objective, the following tasks will be undertaken.

#### Task 1 - Process Studies in Two-Stage Bench-Scale Unit

Operation of the bench-scale unit will be directed toward production of hydrocarbons containing less than 8 wt % of methane plus ethane with high throughput, high conversion, and good catalyst stability. Together with Task 2, high quality liquid fuels, particularly the distillate, will be maximized. At least two tests shall be conducted using at least two different catalysts. One of these catalysts may be provided by DOE's alternate catalyst development projects.

#### Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

The methods for upgrading the reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated. These methods should include conventional refinery processes, such as Fluidized Catalytic Cracking, Hydrocracking, Catalytic Selective Cracking, Thermal Cracking, and Hydrodewaxing. Proprietary mathematical models and open literature information will be used to the extent possible for these process evaluations.

Means for separating the reactor-wax from the catalyst fines, if such a separation is needed prior to reactor-wax upgrading, shall be investigated.

#### Task 3 - Product Evaluation

The quality of the hydrocarbon liquid products from the two-stage unit and the reactor-wax upgrading processes shall be evaluated. Gasoline octane and distillate cetane quality, as well as pour points should also be determined.

#### Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

The effect of different feed-gas distributor designs on the slurry Fischer-Tropsch reactor performance will be investigated. Tests will be conducted in the BSU slurry reactor, or other bubble-column reactors, to provide guidance for subsequent runs in Task 1 as well as for design and operation of



the non-reacting models. For hydrodynamic studies, the design, construction, and operation of hot, non-reacting bubble-column models will be required.

Task 5 - Development of Conceptual Process Schemes

A conceptual process scheme to maximize gasoline and distillate yield using a combined system of slurry Fischer-Tropsch/ZSM-5 reactor plus reactor-wax upgrading will be developed. Scoping costs of the plant will be estimated.

### III. Summary of Progress to Date

Run CT-256-9 of the two-stage pilot plant was ended early in this Quarter, with no success in resuspending the settled catalyst. Possible reasons for the settling are presented here, including microscope photos of slurry samples showing seemingly enlarged catalyst particles. Run CT-256-10, which lasted 10 days, demonstrated that the reactor hardware was not responsible for the settling. Also, the run showed that Catalyst I-D could not be fully activated at synthesis conditions, nor could it be further activated by various means after the initial activity level was reached. The eleventh run of the BSU, which used Catalyst I-B, gave results similar to Run 9: high conversion, low methane + ethane selectivity for 13 days then catalyst settling taking place.

A simple catalyst distribution mathematical model was used to evaluate the feasibility of using an upflowing slurry to improve the catalyst suspension in the bubble-column reactor. We found that a small slurry upflowing velocity of 0.05 cm/s can substantially improve the catalyst suspension. Such a small slurry flow is expected to affect very little the bubble residence time in the reactor. The circulation of slurry from the bottom to the top of the column can further improve the catalyst suspension. We therefore decided to modify the unit to set up a liquid circulation throughout the entire column (the circulation had been only in the top half). Also, a sintered-metal plate feed-gas distributor replaced the single orifice which had been used to that point, though it was found later that it made no significant change on the catalyst concentration profile. Run CT-256-12 was then started toward the end of the Quarter.

Also in this Quarter, the catalyst aging which was observed in Run CT-256-8 (Catalyst I-C) was analyzed using a mathematical model. The aging rate was found to be unacceptably high.

Reactor-wax from Run CT-256-7 was analyzed using Field Ionization Mass Spectrometry and found to be similar to wax from Run CT-256-4. Both runs had similar methane + ethane selectivities.

Hydrodynamic studies in the tall hot-flow bubble-columns were concluded during the Quarter. For the first time, real reactor-waxes from the two-stage pilot plant were used. These waxes did not foam and produced substantially lower holdups than did FT-200, a F-T derived paraffin wax used in previous studies. Gas holdups in the 10.2 cm ID column were found to be higher than those in the 5.1 cm ID column. In another study, catalyst particles were found to decrease gas holdup.

Finally, a data base for a conceptual process design is discussed. The reactor-wax upgrading schemes are presented in the Appendix-Restrictive Distribution.

IV: Detailed Description of Technical Progress

A. Task 1 - Process Studies in Two-Stage Bench-Scale Unit

1. Run CT-256-8 - Analysis of Aging of Catalyst I-C

During Run CT-256-8, Catalyst I-C (Fe/Cu/K<sub>2</sub>CO<sub>3</sub>) was found to age significantly under moderate operating conditions. In the following we analyze the aging rate of this catalyst. The major highlights were:

- Assuming first-order kinetics for H<sub>2</sub>+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.

The aging rate of the catalyst has been obtained at two different conditions from the conversion versus DOS data. The conversion data for Run 8 has been reported in last Quarterly Report. 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 first-order kinetics to translate the H<sub>2</sub>+CO conversions to catalyst activities and a negligible gas-liquid interphase mass-transfer resistance. The resulting equation is:

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

T<sub>c</sub> is the contact time of H<sub>2</sub>+CO with the catalyst. The precise definitions of the k and T<sub>c</sub> are not needed here, since we are interested only in the relative changes in the activity, k.

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

$$k = k^{\circ} \exp (-At) \quad (2)$$

where  $k^{\circ}$  is the initial  $k$  and  $A$  is the first-order aging rate constant. Combining Equations (1) and (2), the  $H_2+CO$  conversion can be related to catalyst age,  $t$ , as follows:

$$\ln (-\ln(1-X_{H_2+CO})) = \ln (k^{\circ}T_c) - At \quad (3)$$

Figure 1 is a plot of the left-hand side of Equation (3) 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 can be attributed to higher temperature, pressure and space velocity (2.0 vs 1.4 NL/gFe-hr).

The aging rate constants,  $A$ , in Equation (2) 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 1.48 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 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.

## 2. Run CT-256-9 - Conclusion

Run CT-256-9 of the two-stage pilot plant was ended on April 12, after eighteen days on-stream. The main objective of the run was to demonstrate long-term low methane + ethane operation with high  $H_2+CO$  conversion using Catalyst I-B (Fe/Cu/ $K_2CO_3$ ) at elevated pressures.

The January-March 1985 Quarterly Report summarized the first 13 days on-stream of this run. The following are the major highlights of the run:

- Low methane + ethane selectivity ( $\approx 5.4$  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 has lower surface area than that of the older batch.
- Successful high  $H_2+CO$  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 ( $\sim 40$  mol %). Photographs of the catalyst sample taken through a microscope revealed somewhat larger particle sizes.
- High velocity  $H_2+CO$  (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 the bottom of the reactor and cleaning the single-orifice feed-gas distributor also showed no improvement.

The run was ended on April 12. What follows is a description of the final period of Run CT-256-9.

a. First-Stage Fischer-Tropsch  
Reactor Operation

As described in the last Quarterly Report, Run CT-256-9 produced high and stable  $H_2+CO$  conversion, low methane + ethane selectivity and smooth operation for ten days using Catalyst I-B. The operating conditions and performance for that period were:

|                                     |           |
|-------------------------------------|-----------|
| Temperature, °C                     | 257       |
| Pressure, MPa                       | 1.48-1.82 |
| Feed $H_2/CO$ Ratio, Molar          | 0.67      |
| Space Velocity, NL/gFe-hr           | 2.0-2.5   |
| Superficial Feed Gas Velocity, cm/s | 4.3-4.8   |
| $H_2+CO$ 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       |

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 that 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 BET surface area of this new batch of catalyst is 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 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).

Following the electrical power outage (see previous Quarterly Report), the H<sub>2</sub>+CO conversion dropped to 40 mol % while the catalyst settled in the first-stage bubble-column reactor. Over the remainder of the run, we attempted to resuspend the catalyst and recover high conversion, but all efforts were unsuccessful. A plot of the run is shown in Figure 2 and a summary of the material balances taken during the run is in Appendix A.

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 3 shows the gas holdup profiles for three different velocities, taken using the newly installed steam-jacketed 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 50/50 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 4 is a sampling of catalyst concentration profiles taken before and after the settling took place. The profile at 9.9 DGS (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  $H_2+CO$  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 power shutdown. 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 5. 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 samples from before the upset was taken from a mixture of the samples from each of the four sampling ports, while the sample from after the upset is only from the 30 cm port. These photos are not, therefore, definitive proof that the catalyst particles increased in size.

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 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.<sup>(1)</sup> 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

<sup>(1)</sup> A proprietary high molecular-weight paraffinic base stock.

be detected. Upon cleaning and reassembling the reactor and starting up, the catalyst remained settled.

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

#### b. 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 gas-hourly space velocity 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 A.

#### 3. Run CT-256-10

The tenth run of the two-stage pilot plant was started on April 16. The main objective of the run was to determine whether Catalyst I-D (Fe/Cu/K<sub>2</sub>CO<sub>3</sub>) 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 original 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 were observed.

A summary of the run follows:



a. Fischer-Tropsch Slurry  
Catalyst Loading and Operation

Run CT-256-10 was initially 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 Ratio, Molar | 0.67 |
| Space Velocity, NL/gFe-hr            | 2.0  |
| Superficial Feed-Gas Velocity, 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 6, 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 7 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 I-D catalyst 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.

Starting at 22 DOS, 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.
- In-situ 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 at 260°C, 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. No material balances were performed during the run, and the second-stage ZSM-5 reactor was not operational.

#### 4. Run CT-256-11

Following the unfortunate 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. The objectives were identical to those of Run 9: demonstrate long-term low methane + ethane operation with high H<sub>2</sub>+CO conversion using Catalyst I-B (see Subsection IV.A-2).

Run 11 lasted twenty days. The highlights were:

- High H<sub>2</sub>+CO conversion (80-90 mol %), low methane + ethane selectivity (3.5-4.3 wt %) was achieved for thirteen days. These results were virtually identical to Run 9.
- Catalyst settling occurred at thirteen 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, after we were unable to restore high conversion or completely reestablish slurry circulation.

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

Run CT-256-11 was charged with 2,200 g of Catalyst I-B (Fe/Cu/K<sub>2</sub>CO<sub>3</sub>). 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 Gas Velocity, cm/s | 5.9  |
| Initial Loading, wt. %         | 20   |

The catalyst activated in an identical fashion to Run 9 (see last Quarterly Report), 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.

b. First-Stage Fischer-Tropsch Reactor Operation

As mentioned earlier, the first thirteen days produced the kind of operation which had been the goal of the run. The range 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 Velocity, cm/s  | 5.3-6.0 |
| 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 8. Material balances were performed daily and the results are summarized in Appendix B.

During the early part of the run, reactor operations went very smoothly, with the reactor-wax being removed with very low (<0.05 wt %) solids content. Slurry samples showed no indications of any catalyst settling, as illustrated in Figure 9, which also shows a catalyst concentration profile from Run CT-256-10 for comparison.

At 13 DOS, however, the catalyst in the slurry-reactor began settling, as evidenced by increasing temperatures at the reactor bottom, and a decrease in H<sub>2</sub>+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 particles in that upper section, preventing its settling (see Subsection IV.A.6).

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 highest ever used in the pilot plant. The catalyst concentration at 30 cm dropped to 15.8 wt %, indicating that the settling had been averted for the moment. The H<sub>2</sub>+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<sub>2</sub>+CO conversion remained at roughly 30 mol %, while slurry samples indicated a steep catalyst profile in the reactor. This can be seen in Figure 10, which should also be compared with Figure 9. 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.

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.

##### 5. Modifications of BSU and Startup 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 prevent 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.

- Using a lower initial catalyst loading. Recent runs had been started with 2,100 to 2,300 g of catalyst. Future runs would start with ~1,600 g.
- Replacing the single-orifice feed-gas distributor with a 20 micron sintered-metal-plate, 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 sintered-metal-plate distributor. The unit was brought back to synthesis conditions, with H<sub>2</sub>/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. However, we decided to use the sintered-metal plate in the future runs since neither type was clearly superior.

Run CT-256-12 was then started on June 26, 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 is expected that lower catalyst loading should minimize the catalyst settling problem. So far, four days-on-stream have been accumulated.

a. Fischer-Tropsch Slurry -  
Catalyst Loading and Pretreatment

Run CT-256-12 was initially 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 <sub>2</sub> /CO, molar      | 0.7  |
| Space Velocity, NL/gFe-hr           | 2.0  |
| Superficial Feed-Gas Velocity, cm/s | 4.8  |

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

b. Brief Description of Pilot Plant Operations

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<sub>2</sub>+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 %. The second-stage ZSM-5 reactor was put on-stream, with an initial inlet temperature of 316°C. As of the end of this Quarter, four days of excellent operation and results had been accumulated.

#### 6. Bubble-Column with Upflowing 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 (see details in Subsections IV.A.2. and 4). Subsequent analysis of the particle size showed larger particles (7-10 versus 5 micron, Figure 5). Hence, a settling mathematical model was used to investigate the use of upward slurry circulation to improve the catalyst suspension.

##### a. 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:

$$(u_{cs}-u_{sl})dC_c/dx + E_c d^2C_c/dx^2 = 0 \quad (4)$$

with the boundary conditions:

$$(u_{cs}-u_{sl})C_c + E_c dC_c/dx = -u_{sl}C_c^e; \quad \text{at } x = 0 \quad (5a)$$

$$u_{cs}C_c + E_c dC_c/dx = 0; \quad \text{at } x = L \quad (5b)$$

The first term of Equation (4) 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 (4) and (5) 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 catalyst 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 shall not be 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 is 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 relations are needed:

$$u_{s1} = 0; \quad \text{at } 0 < x < L_0 \quad (6)$$

$$u_{s1}C_c^e + E_c dC_c/dx \Big|_{L_0^-} = (-u_{s1}C_c + E_c dC_c/dx) \Big|_{L_0^+}; \quad \text{at } x = L_0 \quad (7)$$

Equations (4) to (7) can be solved analytically to give the catalyst concentration profiles in the bubble-column.

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

It is essential to find out if a small slurry circulation will significantly affect the catalyst suspension in the bubble-column of the BSU. The existing slurry pump has a maximum capacity equivalent to 0.05 cm/s superficial slurry velocity. It will take too much time 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 (4) and (5) were solved analytically to estimate the effect of varying the slurry circulation velocities from 0 to .05 cm/s, and the results are given in Figure 12. The steep catalyst concentration profile for the non-circulation case is significantly improved by raising the slurry velocity to 0.05 cm/s.

Equation (4) to (7) were used to judge whether it is necessary to relocate the slurry return line from 305 cm above the feed-gas distributor to a location just above the distributor. Figure 13 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 improves the profile to a large degree. However, a significantly more uniform profile can be obtained by relocating the slurry return line to the bottom of the column.

c. Effect of Catalyst Particle Size on the Catalyst Suspension

Equations (4) and (5) were used to evaluate this effect for the particle size range of 5 to 10 microns. The results are summarized in Figure 14. Within this particle size range, the catalyst concentration profile deteriorates drastically with increasing particle size.

d. Possible Scenario for the Catalyst Settling Phenomena From Runs CT-256-9 and 11

Equations (4) to (7) were used to analyze the catalyst settling phenomena observed during 10-13 DOS of Runs CT-256-9 and -11. The results for the Run 11 are given in Figure 15. 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.

7. Future Work

Continue Run CT-256-12 at high  $H_2+CO$  conversion, low methane + ethane selectivity.



## B. Task 3 - Product Evaluation

### 1. Field Ionization Mass Spectrometry (FIMS) for Fischer-Tropsch Reactor-Wax Analyses

We have analyzed CT-256-7 reactor-wax using FIMS. The sample was obtained from a homogenized blend of the reactor-waxes produced throughout the run. This is the same blend from which the DOE was supplied with a 22 kg sample. The raw FIMS spectrum of the wax is shown in Figure 16. As explained in previous Quarterly Report (July-September, 1984), the C<sub>55</sub><sup>+</sup> content can be estimated from the FIMS spectrum. Table 1 compares the results to those for Run CT-256-4 reactor-wax which was produced under similar operating conditions and using the same catalyst. The similarity between the two waxes are clearly evident from the table.

As discussed previously, one of the limitations of the FIMS is that the extent of fragmentation of these heavy reactor-waxes during the analyses is unknown. To define the extent of the fragmentation we have resubmitted the samples from Runs CT-256-4 and -5 reactor-waxes to SRI International, Inc. (Menlo Park, CA).

### 2. Product Analyses

Product analyses to support other tasks were carried out.

### 3. Future Work

- Continue evaluation of FIMS technique.
- Continue providing product analyses to support other tasks.

## C. Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

### 1. Hydrodynamic Studies Using Tall Hot-Flow Bubble-Columns

Previously most of the hydrodynamic studies have been carried out using FT-200, a F-T derived paraffinic wax. In this quarter we have studied reactor-waxes produced in our slurry bubble-column reactor. These studies were planned to be carried out at the end, fearing that these reactor-waxes may darken the glass column permanently. We have studied two reactor-waxes

produced in Runs CT-256-7 and 8 using both (5.1 and 10.2 cm ID) hot-flow bubble columns. The results were compared with those obtained with FT-200 wax. Also, gas holdup profiles along the column have been obtained.

a. Effect of Liquid Mediums  
Using 5.1 cm ID Column

Figure 17 shows gas holdups given by Run CT-256-7 and -8 reactor-waxes using 5.1 cm ID hot-flow bubble-column at 260°C. The gas distributor used was a 1 mm single orifice. Also, the gas holdups obtained previously with FT-200 wax are depicted here as a correlation ( $\epsilon_g = 6.5 u_g^{1.1}$ ) (see Quarterly Report January-March, 1984).

Major conclusions from these studies are:

- Both reactor-waxes behave very similarly, even though their viscosities and compositions are substantially different.
- Both reactor-waxes gave substantially lower gas holdup than that given by FT-200 wax.
- Unlike FT-200 wax, the reactor-waxes did not foam.
- In contrast to FT-200 wax, the gas holdup of Run CT-256-7 reactor-wax decreased along the hot-flow column above superficial gas velocity of 2.5 cm/s.

Table 2 compares the physical properties of different reactor-waxes and FT-200 wax. Clearly the Run CT-256-8 reactor-wax has significantly higher viscosity and average molecular weight than Run CT-256-7 reactor-wax. The two reactor-waxes were produced under different operating conditions and using different catalysts. The difference in their compositions is hence expected. The surface tensions of all waxes are, however, very similar. In spite of the differences in their physical properties, the Runs CT-256-7 and -8 reactor-waxes behaved very similarly and also appeared to have similar bubble sizes.

Similar behavior was also observed previously using short hot-flow bubble-column (5.2 cm ID x 2 m height) with Runs CT-256-4 and -5 reactor-waxes, which were produced under operating conditions similar to those of Runs 7 and 8 respectively. These results have also been shown in Figure 17 for comparison. Based on our previous knowledge of effect of static height on gas holdup, the holdups of Runs 4 and 5 reactor-waxes in the short column are expected to be higher than those of Runs 7 and 8 reactor-waxes in the tall column. However, the short column studies were carried out at 200°C instead of

260°C. The slightly lower gas holdups in the short column may, therefore, be due to lower temperature.

Unlike FT-200 wax, the reactor-waxes did not produce very fine bubbles (e.g., <1 mm) which are conducive to foaming. The bubbles produced by the reactor-waxes appeared to be larger than those produced by FT-200 wax. Consequently, the gas holdups were substantially lower with the reactor-waxes. Slugging was observed with all waxes, and the slug frequency was found to increase with increasing superficial velocity.

Figure 18 gives the gas holdup profiles along the column obtained at various superficial velocities using Run CT-256-7 reactor-wax. Previously we have reported the gas holdup profiles for FT-200 wax using the same 1 mm orifice distributor in the same column (see April-June, 1984 Quarterly Report). In the case of FT-200 wax the relatively larger bubbles produced at the column bottom tend to break up along the column. Hence, the gas holdup was found to increase along the height. In the case of reactor-wax, however, the gas holdup was found to decrease along the column at superficial velocities greater than 2.5 cm/s. This may be due to the presence of slugs in the top zone (which cause lower holdup). With FT-200 wax, the large number of very fine bubbles accompanying the foam seem to compensate for the lower holdup of slugs. Therefore, even in the presence of slugs the gas holdup increases along the column height. At superficial velocities lower than 2.5 cm/s slugging was very infrequent, and consequently the holdup increased along the column height for both the reactor-wax and FT-200 wax.

#### b. Effect of Column Diameter

The effect of column diameter was studied using FT-200 wax in the 10.2 cm ID hot-flow bubble-column. The gas distributor used was a 2 mm single orifice. Previously we had studied the same FT-200 wax in the 5.1 cm ID column using a 1 mm single orifice. Thus, the gas jet velocities at the orifices in both columns were identical for a given superficial velocity.

Figure 19 compares the gas holdups for these two cases. As seen from the figure, the gas holdups in the larger column are lower. Also, the bubbles in the larger column appeared larger. Similar to the smaller column slugging was observed in the 10.2 cm ID column. However, unlike the slugs in the 5.1 cm ID column, the slugs in the larger column did not occupy the whole cross-section of the column. These were really large bubbles with widths about 80-90% of the column diameter. Also, they were only 5-10 cm long compared to the 5-25 cm long slugs in the 5.2 cm ID column. For simplicity, we always refer to them as slugs. The larger bubbles produced in the larger column may have been due to a larger size orifice, even though the jet velocities were the same in both columns. Hence, the gas distributor was changed

to a 1 mm 4-hole distributor.

With the new distributor the orifice size as well as the jet velocities are identical in both columns. Using this distributor, we have studied the same three liquid mediums (FT-200 wax, CT-256-7 and -8 reactor-waxes), which were studied previously (see last subsection) in the 5.1 cm ID column. Figure 20 compares the gas holdups obtained in the two columns for these waxes.

The two reactor-waxes gave about 30-40% higher gas holdups in the larger column over the superficial gas velocity range of 1.5 to 6.5 cm/s. The bubble sizes appeared similar in both columns. However, there was less slugging in the larger column and the slugs were also shorter than those in the smaller column. Again the slugs were large bubbles about 5-10 cm long and occupied 80-90% of the column diameter. The higher gas holdup in the larger column may have been due to fewer and smaller slugs.

In contrast to the reactor-waxes, FT-200 gave the same gas holdup in both columns. Even though large slug-like bubbles were observed in the larger column with the 1 mm 4-hole distributor, a large number of smaller bubbles accompanied by foam gave higher holdups. In this case, the contribution of slugs to the gas holdup is relatively less. Hence, unlike in the case of reactor-waxes, the fewer and smaller slugs in the larger column probably did not increase the gas holdup.

#### c. Effect of Solids in a Reactor-Wax

The last experiment in the hot-flow column hydrodynamic studies was to use an actual slurry containing F-T catalyst. We reserved this experiment as the last one to avoid the possibility that use of a slurry will prevent further visual observation through the glass section of the column. Also, to save time, the 10.2 cm ID column (with the 1 mm 4-hole distributor) which was in operation at that time was used. Since there was not enough catalyst to load this large column, we used a relatively low (2 wt %) catalyst loading. The liquid medium was Run CT-256-8 reactor-wax. The gas holdup was about 9% lower than that given by the same reactor-wax without any catalyst. The trend of lower gas holdup due to the presence of solids is consistent with literature findings.

#### d. Dynamic Gas Disengagement Studies

To obtain information about the bubble-size distribution, dynamic gas-disengagement experiments were carried out in the 5.1 cm ID hot-flow bubble-column using FT-200 wax and a 2 mm single-orifice distributor. The gas holdups were reported in the last Quarterly Report.

Figure 21 shows a plot of expanded liquid height as a function of elapsed time for three superficial gas velocities. As seen from the figure the data cannot be fitted by a single straight line. As explained previously in the theory of dynamic gas disengagement (July-September, 1984 Quarterly Report), this data can be explained by a bi-modal bubble-size distribution. The initial straight lines represent time periods where both large and small bubbles are disengaging and leaving the column. The straight lines after the break in the slopes represent the disengagement of small bubbles only.

The slopes and intercepts of the two straight lines yield the bubble rise velocities and volume fraction of the bubbles in the two size ranges (see Equations (7a) and (7b), July-September, 1984 Quarterly Report). The results are summarized in Table 3. The fraction of small bubbles having bubble rise velocities of 5.1 to 7.6 cm/s was found to decrease with increasing superficial gas velocity. The bubble rise velocities of larger bubbles range from 32 to 36 cm/s. Since a good correlation of bubble rise velocity and bubble size is not available in the literature for a F-T liquid medium, it is not practical to estimate average bubble sizes from the bubble rise velocities estimated above.

## 2. Future Work

Continue model applications to compare slurry CSTRs with bubble-columns.

### D. Task 5 - Development of Conceptual Process Schemes

#### 1. Introduction

The objective of this contract is to minimize methane + ethane yield and maximize liquid fuel (gasoline and distillate) yields. This can only be achieved at increased reactor-wax yields from the first-stage F-T reactor. For instance, in the previous contract work (Kuo, 1983) we showed that when the methane + ethane yield dropped from 10 wt % of the total hydrocarbons produced to 4 wt %, the reactor-wax yield increased from 8 to 50 wt %. A further drop of the methane + ethane yield to 2 wt % increased the wax yield to 80 wt %. Hence, in the high wax (low methane + ethane) operation mode, it is essential to convert efficiently the reactor-wax into high quality fuels. In the Appendix-Restrictive Distribution of previous Quarterly Reports, we described scoping studies to upgrade reactor-wax into gasoline and distillate products. The results of these studies are incorporated in the conceptual design.

To maintain a reasonable G/D product ratio and sufficiently low methane + ethane yield, we set a target reactor-wax of 50 wt % with a corresponding methane + ethane yield of 4 wt %. The material balance #10 of Run CT-256-7 was chosen as a basis for F-T process data. The balance gave a reactor-wax yield of 57 wt % and a methane + ethane yield of 3.8 wt %, at 81 mol % H<sub>2</sub>+CO conversion. These data were adjusted slightly to give the target methane + ethane reactor-wax yields. The target H<sub>2</sub>+CO conversion was 84 mol % (corresponding to 90% CO conversion). Unfortunately, detailed analysis of the overhead C<sub>5</sub><sup>+</sup> F-T product of Run 7 was not available. To fill this gap, the hydrocarbon distribution of the same stream used to develop the design base case data of our previous contract (Kuo, 1983) was used. Based on our experience, the C<sub>5</sub><sup>+</sup> hydrocarbon distributions in the overhead of the slurry F-T reactor changed only slightly with the process conditions. The ZSM-5 reactor data is based on material balance #14 of Run CT-256-7, which had a severity index (molar isobutane/(butenes + propene) ratio) of .73. This data was adjusted to give the same severity as that in the previous contract (.78). All material balance data were slightly adjusted to give exact C-H-O balances.

The reactor-wax upgrading to gasoline and distillate is based on our scoping studies using Run CT-256-4 reactor-wax. Runs CT-256-4 and -7 both used the same F-T Catalyst I-B at the same reaction conditions, and produced similar hydrocarbon selectivities. Thus, the reactor-waxes produced in these runs are also expected to have similar compositions. A detailed carbon number distribution of Run CT-256-4 reactor-wax is available up to C<sub>55</sub> by GC, and the C<sub>55</sub><sup>+</sup> content is known from FIMS analysis.

Two reactor-wax upgrading schemes are included in the conceptual design and are described in the Appendix-Restrictive Distribution.

## 2. Design Base Data For Slurry Fischer-Tropsch/ZSM-5 Unit

The operating conditions of the slurry F-T and ZSM-5 reactors are summarized in Table 4. The heats of reaction and adiabatic temperature rise were estimated. The space velocity for the ZSM-5 reactor was estimated from that of the previous contract, assuming the same contact time. The space velocity of the F-T reactor was estimated from that of the previous contract, but we allowed a 15% drop due to a slight pressure effect, i.e., higher pressure at the same superficial gas velocity will somewhat reduce the H<sub>2</sub>+CO conversion.

Tables 5 and 6 show product yields for F-T and ZSM-5 reactors, as mol/100 mol feed H<sub>2</sub>+CO. Table 6 also includes the feed H<sub>2</sub>+CO+H<sub>2</sub>O to the F-T reactor. We assume that the water-gas

shift reaction will convert rapidly the excess CO and water into H<sub>2</sub> and CO<sub>2</sub>, to give an effective H<sub>2</sub>/CO ratio of 0.67.

3. Future Work

Complete the conceptual design and scoping cost estimates for a low methane + ethane mode F-T/ZSM-5 plant.

V. Nomenclature

|              |  |
|--------------|--|
| A            | First-order aging kinetic constant, (1/day)                            |
| $C_c$        | Catalyst concentration, (g/cm <sup>3</sup> )                           |
| $C_c^e$      | Catalyst concentration in the bubble-column exit, (g/cm <sup>3</sup> ) |
| $D_c$        | Catalyst particle size, (micron)                                       |
| $E_c$        | Catalyst axial dispersion coefficient, (cm <sup>2</sup> /s)            |
| k            | First-order kinetic rate constant, (1/s)                               |
| $k^o$        | Initial k, (1/s)   |
| L            | Reactor height, (cm)   |
| $L_o$        | Slurry return location, (cm)   |
| t            | Catalyst age, (day)  |
| $T_c$        | Synthesis gas-catalyst contact time, (s)                               |
| $u_g$        | Superficial gas velocity, (cm/s)                                       |
| $u_{sl}$     | Slurry circulation velocity, (cm/s)                                    |
| $u_{cs}$     | Catalyst settling velocity, (cm/s)                                     |
| $u_{BL}$     | Average bubble rise velocity of large bubbles, (cm/s)                  |
| $u_{BS}$     | Average bubble rise velocity of small bubbles, (cm/s)                  |
| $w_c$        | Weight fraction of catalyst in slurry, (gCat/g slurry)                 |
| x            | Axial distance, (cm)   |
| $X_{H_2+CO}$ | H <sub>2</sub> +CO conversion, (mol %)                                 |

Greek Letters

|              |  |
|--------------|--|
| $\epsilon_g$ | Gas holdup, (cm <sup>3</sup> gas/cm <sup>3</sup> expanded slurry). |
|--------------|--|



Acronyms

|      |   |
|------|---|
| BSU  | Bench-Scale Unit                                    |
| CSTR | Continuous Stirred-Tank Reactor                     |
| DOE  | Department of Energy                                |
| DOS  | Days on Stream                                      |
| DP   | Differential Pressure                               |
| FIMS | Field-Ionization-Mass-Spectrometry                  |
| F-T  | Fischer-Tropsch                                     |
| GC   | Gas Chromatography                                  |
| GHSV | Gas Hourly Space Velocity, (NL per hour/L-Cat)      |
| HC   | Hydrocarbons  |
| ID   | Inside Diameter                                     |
| MW   | Molecular Weight                                    |
| WHSV | Weight Hourly Space Velocity, (gFeed per hour/gCat) |

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Table 1  
Results of FIMS  
Analysis of Reactor-Waxes

|                    | <u>Reactor-Waxes*</u> |                 |
|--------------------|-----------------------|-----------------|
|                    | <u>CT-256-7</u>       | <u>CT-256-4</u> |
| C55+ Content, wt % | 60.3                  | 65.0            |
| Number Avg. MW     | 857                   | 814             |
| Wt. Avg. MW        | 1,189                 | 1,135           |

\*Both Runs CT-256-4 and -7 used the same Catalyst I-B and were run in low methane + ethane mode under similar operating conditions.

Table 2

Physical Properties of Liquid Mediums

|                   | Viscosity            | Surface<br>Tension |
|-------------------|----------------------|--------------------|
|                   | 149/204/260 °C<br>cP |                    |
| FT-200 Wax        | 4.4/2.2/1.7          | 24                 |
| Run 3 Reactor-Wax | 2.8/1.7/ -           | 26-27              |
| Run 4 Reactor-Wax | 6.1/4.3/3.4          | "                  |
| Run 5 Reactor-Wax | 17.6/8.5/5.5         | "                  |
| Run 7 Reactor-Wax | 8.2/4.1/2.3          | "                  |
| Run 8 Reactor-Wax | 13.1/6.8/ -          | "                  |

Table 3

Dynamic Gas-Disengagement Results

| $u_g$ ,<br>cm/s | $\epsilon_g$ ,<br>Vol % | Fraction<br>of Small<br>Bubbles<br>Vol % | $\bar{u}_{BL}$ ,<br>cm/s | $\bar{u}_{BS}$ ,<br>cm/s |
|-----------------|-------------------------|--|--------------------------|--------------------------|
| 1.5             | 6.6                     | 57                                       | 32                       | 7.4                      |
| 2.2             | 9.4                     | 52                                       | 35                       | 5.1                      |
| 4.4             | 11.5                    | 25                                       | 36                       | 7.6                      |

Table 4

## Slurry Fischer-Tropsch/ZSM-5

## Process Conditions

|   | First-Stage<br>(F-T)                            | Second-Stage<br>(ZSM-5) |
|---|---|-------------------------|
| Catalyst  | I-B(Pptd Fe/Cu/K <sub>2</sub> CO <sub>3</sub> ) | ZSM-5                   |
| Feed H <sub>2</sub> /CO, molar                        | 0.5   |                         |
| Inlet P, MPa  | 2.87  | Cascaded                |
| Inlet T, °C   | 227   | 371                     |
| Outlet T, °C  | 258   | 393                     |
| Space Velocity  | 3.50 NL/gFe-hr                                  | 1.57 (*)WHSV            |
| Heat of Reaction,<br>kJ/g-mol Feed H <sub>2</sub> +CO | 56.3  | 0.6                     |

(\*)Based on hydrocarbons.

Table 5  
FIRST-STAGE PRODUCT YIELDS  
 (BASIS: 100 MOL FEED H<sub>2</sub>+CO)

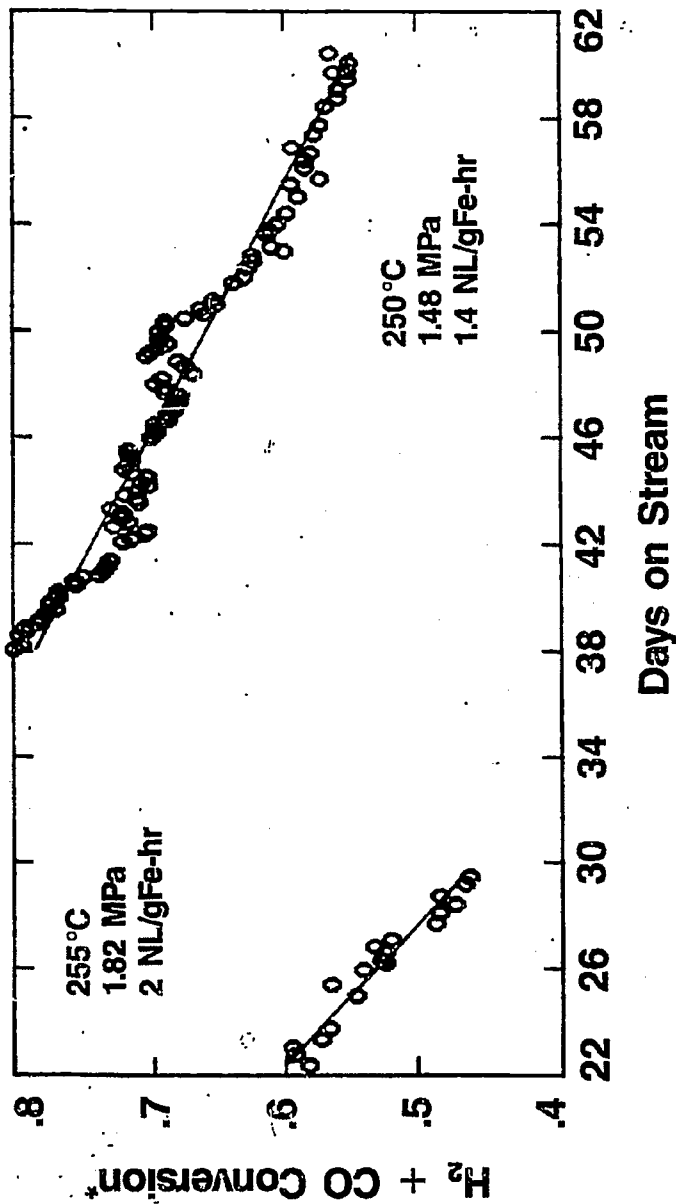
|   | <u>FEED MOLES</u> | <u>MW</u> | <u>SP. GR</u> | <u>MOLES</u> |
|---|-------------------|-----------|---------------|--------------|
| WATER   | 6.7864            | 18.02     |               | 0.7902       |
| HYDROGEN                                      | 33.3333           | 2.02      |               | 9.9537       |
| CO  | 66.6667           | 28.01     |               | 5.9880       |
| CO <sub>2</sub>                               |                   | 44.01     |               | 33.1333      |
| METHANE                                       |                   | 16.04     |               | 0.8249       |
| ETHENE  |                   | 28.05     |               | 0.2611       |
| ETHANE  |                   | 30.07     |               | 0.0875       |
| PROPENE                                       |                   | 42.08     | 0.5218        | 0.2615       |
| PROPANE                                       |                   | 44.10     | 0.5077        | 0.0688       |
| N-BUTANE                                      |                   | 58.12     | 0.5832        | 0.0648       |
| C <sub>4</sub> OLEFINS                        |                   | 56.11     | 0.6011        | 0.1731       |
| N-PENTANE                                     |                   | 72.15     | 0.6306        | 0.0694       |
| C <sub>5</sub> OLEFINS                        |                   | 70.14     | 0.6471        | 0.2291       |
| N-HEXANE                                      |                   | 86.18     | 0.6641        | 0.0586       |
| C <sub>6</sub> OLEFINS                        |                   | 84.16     | 0.6781        | 0.1517       |
| N-HEPTANE                                     |                   | 100.11    | 0.6886        | 0.0314       |
| C <sub>7</sub> -OLEFINS                       |                   | 98.19     | 0.7026        | 0.0766       |
| N-OCTANE                                      |                   | 114.23    | 0.7067        | 0.0343       |
| C <sub>8</sub> -OLEFINS                       |                   | 112.21    | 0.7201        | 0.0721       |
| N-NONANE                                      |                   | 128.26    | 0.7179        | 0.0318       |
| C <sub>9</sub> -OLEFINS                       |                   | 126.24    | 0.7339        | 0.0565       |
| C <sub>10</sub> -C <sub>15</sub> (P+O)        |                   | 167.82    | 0.7572        | 0.2273       |
| C <sub>16</sub> -C <sub>20</sub> (P+O)        |                   | 245.95    | 0.7861        | 0.0538       |
| C <sub>21</sub> -C <sub>25</sub> (P+O)        |                   | 311.75    | 0.7994        | 0.0092       |
| C <sub>26</sub> + (P+O, EXCL. WAX)            |                   | 384.55    | 0.8101        | 0.0007       |
| METHANOL                                      |                   | 32.04     | 0.7960        | 0.0413       |
| FORMIC ACID                                   |                   | 46.03     | 1.2210        | 0.0022       |
| ETHANOL                                       |                   | 46.07     | 0.7900        | 0.0855       |
| ACETIC ACID                                   |                   | 60.05     | 1.0500        | 0.0055       |
| ACETONE                                       |                   | 58.08     | 0.7920        | 0.0144       |
| N-PROPANOL                                    |                   | 60.10     | 0.8050        | 0.0425       |
| I-PROPANOL                                    |                   | 60.10     | 0.7900        | 0.0098       |
| PROPANOIC ACIDS                               |                   | 74.08     | 0.9930        | 0.0021       |
| C <sub>4</sub> -C <sub>9</sub> (OXYGENATES)   |                   | 94.24     | 0.8248        | 0.0721       |
| C <sub>10</sub> -C <sub>15</sub> (OXYGENATES) |                   | 181.43    | 0.8471        | 0.0164       |
| C <sub>16</sub> -C <sub>20</sub> (OXYGENATES) |                   | 261.93    | 0.8472        | 0.0017       |
| C <sub>21</sub> -C <sub>25</sub> (OXYGENATES) |                   | 330.75    | 0.8460        | 0.0000       |
| C <sub>26</sub> + (OXYGENATES)                |                   | 417.58    | 0.8450        | 0.0000       |
| SLURRY REACTOR WAX                            |                   | 821.41    | 0.8700        | 0.2414       |
| <hr/>   |                   |           |               |              |
| TOTAL MOLES                                   | 106.7864          |           |               | 53.2448      |
| TOTAL WT                                      | 2056.80           |           |               | 2056.80      |
| HYDROCARBON WT                                |                   |           |               | 396.5330     |

Table 6  
SECOND-STAGE PRODUCT YIELDS  
 (BASIS: 100 MOL FEED H<sub>2</sub>+CO)

|                       | <u>MW</u> | <u>SP. GR.</u> | <u>MOLES</u> |
|-----------------------|-----------|----------------|--------------|
| WATER                 | 18.02     | -              | 1.0977       |
| HYDROGEN              | 2.02      | -              | 9.9537       |
| CO                    | 28.01     | -              | 5.9880       |
| CO <sub>2</sub>       | 44.01     | -              | 33.1334      |
| METHANE               | 16.04     | -              | 0.8434       |
| ETHANE                | 30.07     | -              | 0.0923       |
| ETHENE                | 28.05     | -              | 0.1561       |
| PROPANE               | 44.10     | 0.5077         | 0.2836       |
| PROPENE               | 42.08     | 0.5218         | 0.1617       |
| N-BUTANE              | 58.12     | 0.5844         | 0.1860       |
| I-BUTANE              | 58.12     | 0.5631         | 0.2355       |
| N-BUTENE              | 56.11     | 0.6011         | 0.0866       |
| I-BUTENE              | 56.11     | 0.6100         | 0.0577       |
| N-PENTANE             | 72.15     | 0.6312         | 0.1134       |
| I-PENTANE             | 72.15     | 0.6248         | 0.1980       |
| N-PENTENE             | 70.14     | 0.6461         | 0.0045       |
| I-PENTENE             | 70.14     | 0.6325         | 0.1236       |
| CYCLOPENTANE          | 70.14     | 0.7505         | 0.0343       |
| N-HEXANE              | 86.18     | 0.6840         | 0.0624       |
| I-HEXANE              | 86.18     | 0.6579         | 0.1144       |
| N-HEXENE              | 84.16     | 0.6780         | 0.0010       |
| I-HEXENE              | 84.16     | 0.6722         | 0.0273       |
| METHYLCYCLOPENTANE    | 84.16     | 0.7505         | 0.0254       |
| CYCLOHEXANE           | 84.16     | 0.7834         | 0.0010       |
| BENZENE               | 78.11     | 0.8845         | 0.0114       |
| N-HEPTANE             | 100.21    | 0.6882         | 0.0305       |
| I-HEPTANE             | 100.21    | 0.6630         | 0.0538       |
| N-HEPTENE             | 98.19     | 0.7068         | 0.0273       |
| I-HEPTENE             | 98.19     | 0.6992         | 0.0051       |
| DIMETHYL-CYCLOPENTANE | 98.19     | 0.7496         | 0.0221       |
| METHYLCYCLOHEXANE     | 98.19     | 0.7740         | 0.0123       |
| TOLUENE               | 92.14     | 0.8719         | 0.0447       |
| N-OCTANE              | 114.23    | 0.7068         | 0.0149       |
| I-OCTANE              | 114.23    | 0.7090         | 0.0249       |
| N-OCTENE              | 112.21    | 0.7272         | 0.0289       |
| I-OCTENE              | 112.21    | 0.7180         | 0.0065       |
| C8-N5                 | 112.21    | 0.7729         | 0.0225       |
| C8-N6                 | 112.21    | 0.7841         | 0.0126       |
| P-XYLENE              | 106.17    | 0.8657         | 0.0148       |
| M-XYLENE              | 106.17    | 0.8687         | 0.0471       |
| O-XYLENE              | 106.17    | 0.8848         | 0.0153       |
| ETHYLBENZENE          | 106.17    | 0.8717         | 0.0175       |
| N-NONANE              | 128.26    | 0.7176         | 0.0057       |
| I-NONANE              | 128.26    | 0.7250         | 0.0129       |
| N-NONENE              | 126.24    | 0.7369         | 0.0162       |
| I-NONENE              | 126.24    | 0.7385         | 0.0036       |
| C9-N5                 | 126.24    | 0.7848         | 0.0084       |
| C9-N6                 | 126.24    | 0.7845         | 0.0047       |
| N-PROPYLBENZENE       | 120.20    | 0.8666         | 0.0036       |
| I-PROPYLBENZENE       | 120.20    | 0.8690         | 0.0007       |
| METHYL-ETHYL-BENZENE  | 120.20    | 0.8696         | 0.0530       |
| TRIMETHYL-BENZENE     | 120.20    | 0.7340         | 0.0250       |
| N-DECANE              | 142.28    | 0.7451         | 0.0015       |
| N-C4-BENZENE          | 134.22    | 0.7493         | 0.0107       |
| METHYL-I-C3-BENZENE   | 134.22    | 0.7954         | 0.0029       |
| TETRA-METHYL-BENZENE  | 134.22    | 0.8079         | 0.0031       |
| DIETHYLBENZENE        | 134.22    | 0.8700         | 0.0171       |
| C11-ALKYLBENZENE      | 148.25    | 0.8000         | 0.0050       |
| C12-PARAFFIN          | 170.34    | 0.7526         | 0.0034       |
| C12-ALKYLBENZENE      | 161.27    | 0.8617         | 0.0061       |
| C13-PARAFFIN          | 184.37    | 0.7601         | 0.0027       |
| C13-ALKYLBENZENE      | 176.30    | 0.8609         | 0.0050       |
| C14-PARAFFIN          | 198.39    | 0.7667         | 0.0015       |
| C14-ALKYLBENZENE      | 190.33    | 0.8603         | 0.0036       |
| TOTAL MOLES           |           |                | 53.6507      |
| TOTAL WT              |           |                | 1858.54      |
| HYDROCARBON WT        |           |                | 198.273      |

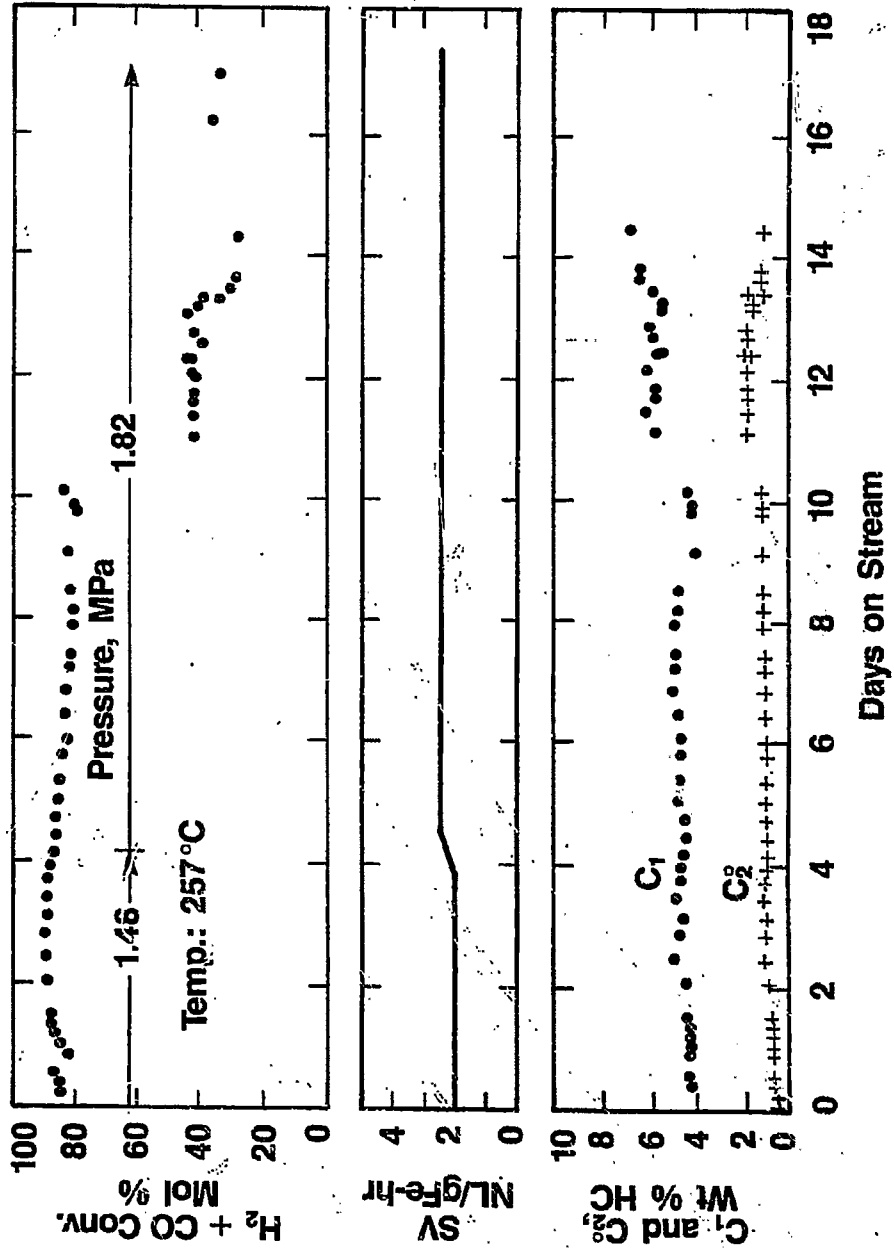


**Figure 1**  
**AGING OF CATALYST I-C**  
**(RUN CT-256-8)**

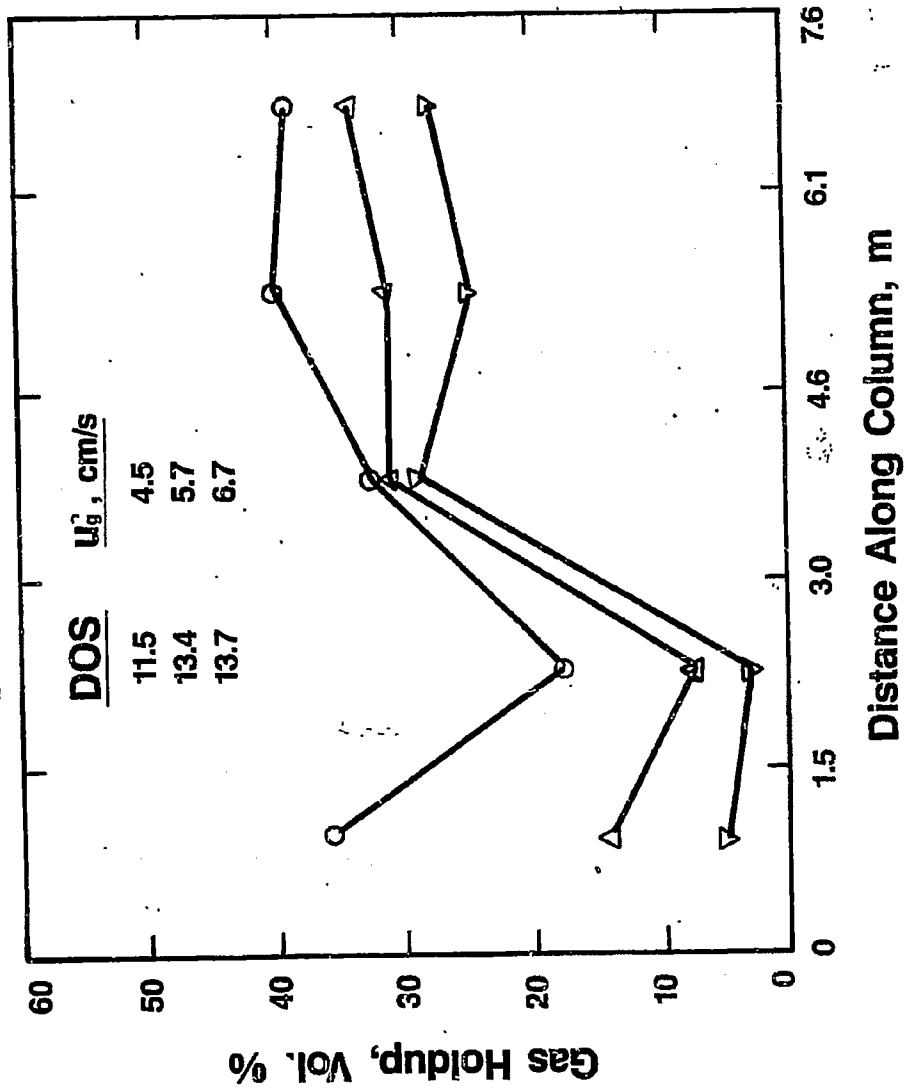


\*Plotted as  $\ln(1 - X_{H_2 + CO})$  representing first-order conversion kinetics and first-order aging kinetics

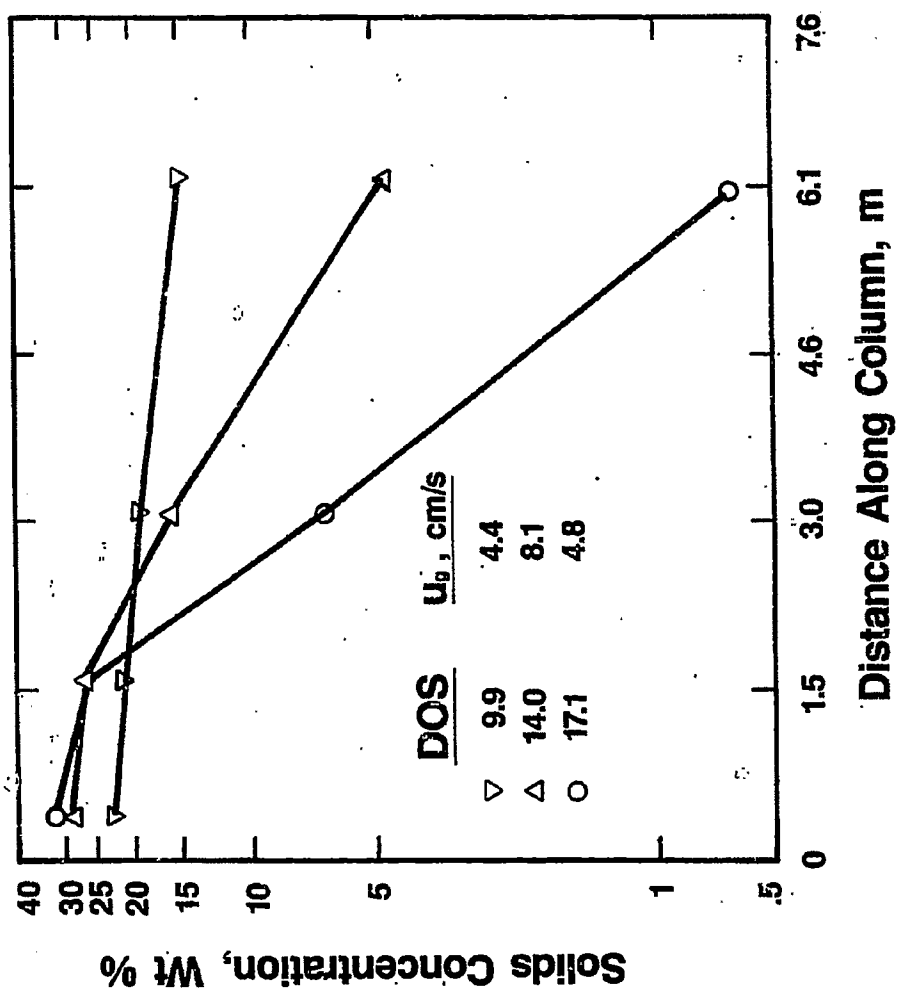
**Figure 2**  
**SYNTHESIS GAS CONVERSION**  
**AND METHANE & ETHANE YIELD**  
**(RUN CT-256-9;**  
**1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K<sub>2</sub>CO<sub>3</sub>)**



**Figure 3**  
**GAS HOLDUP PROFILES**  
**(RUN CT-256-9)**

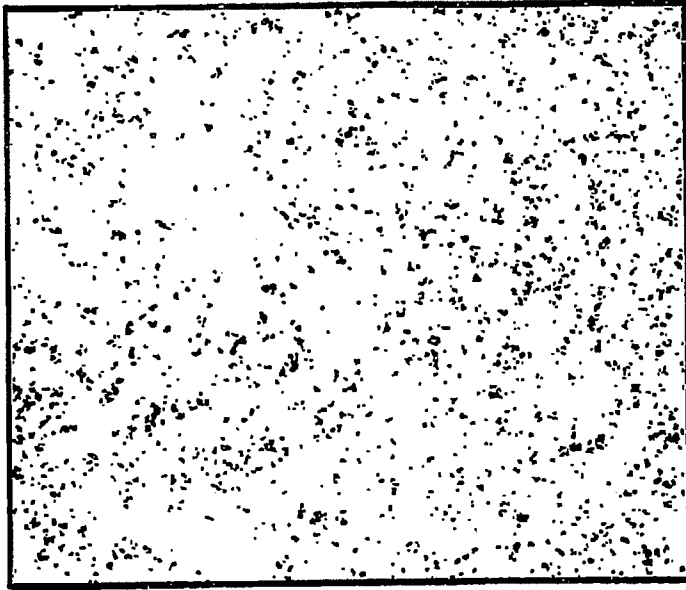


**Figure 4**  
**CATALYST CONCENTRATION PROFILES**  
**(RUN CT-256-9)**



**Figure 5**  
**PHOTOGRAPHS OF SLURRY SAMPLES**  
**(RUN CT-256-9)**

**Before Settling**

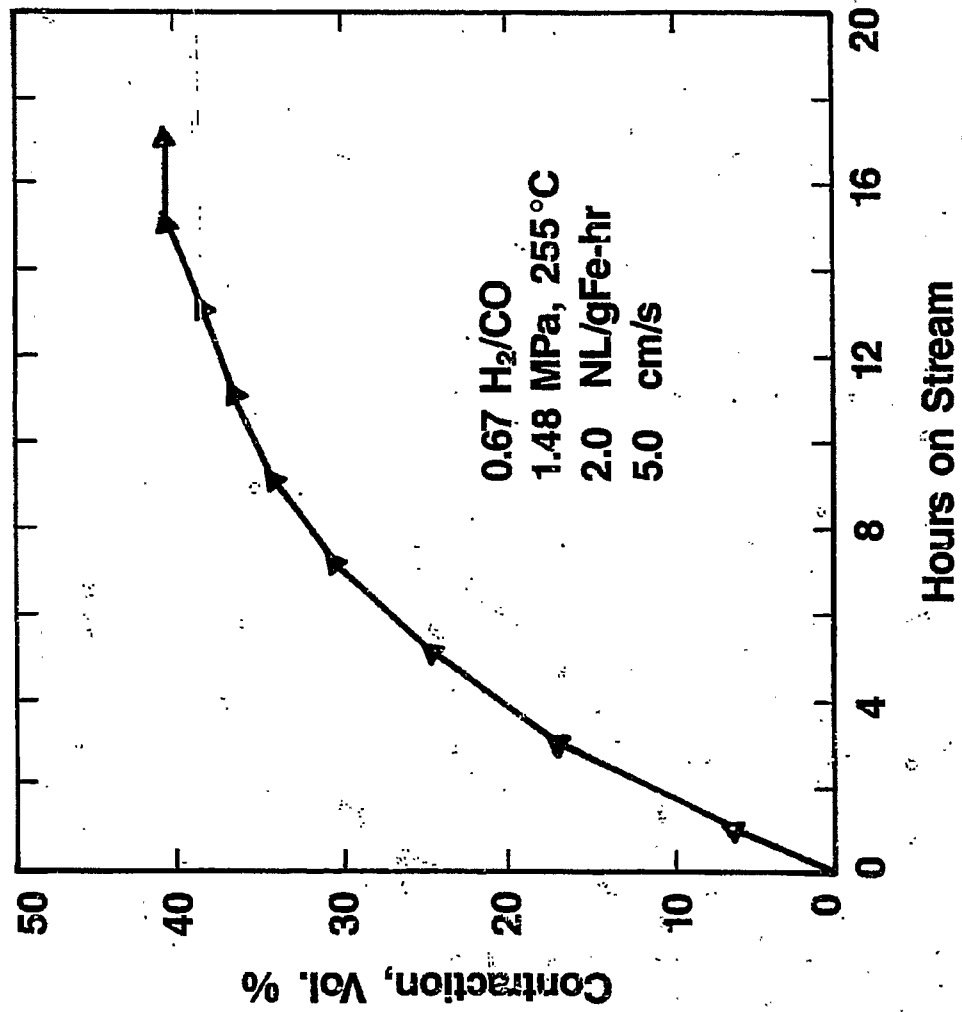


**After Settling**

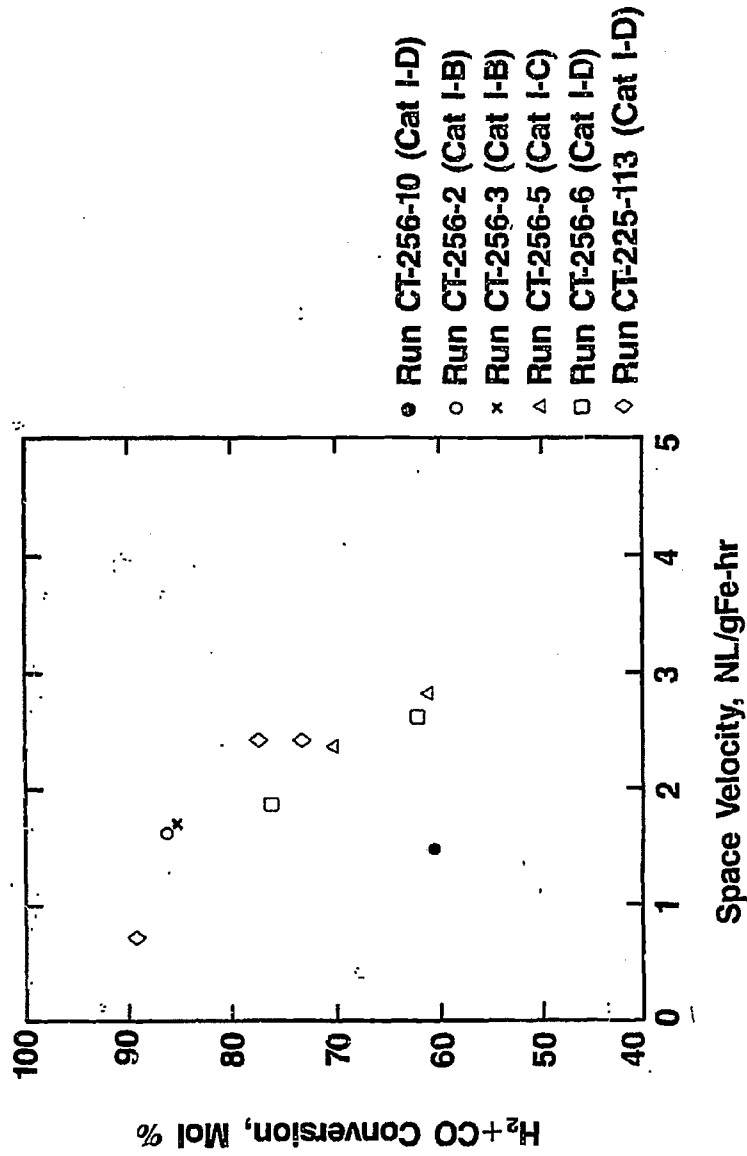


100 Micron

**Figure 6**  
**ACTIVATION OF FISCHER-TROPSCH CATALYST I-D**  
**(RUN CT-256-10)**



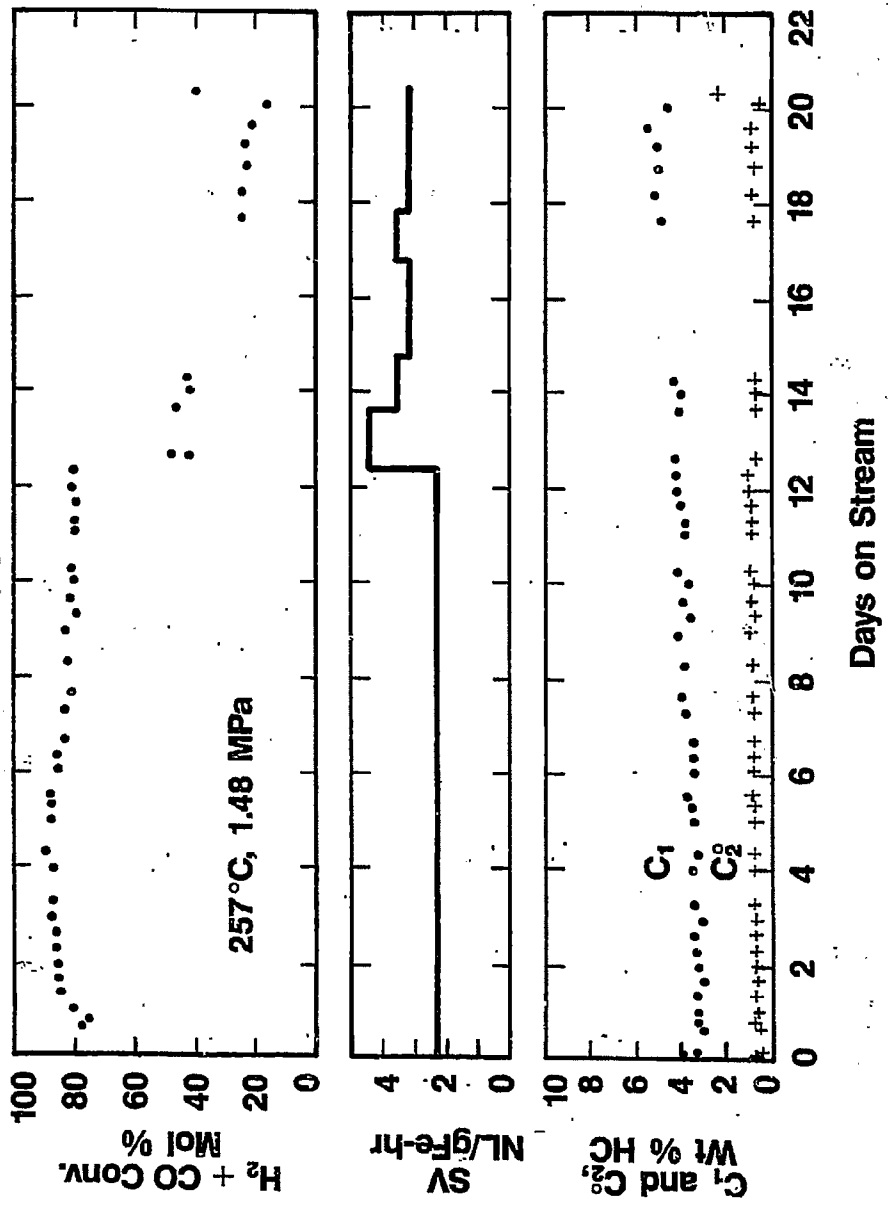
**Figure 7**  
**COMPARISON OF INITIAL FISCHER-TROPSCH CATALYST ACTIVITIES**



All data corrected to 1.48 MPa, 250 °C

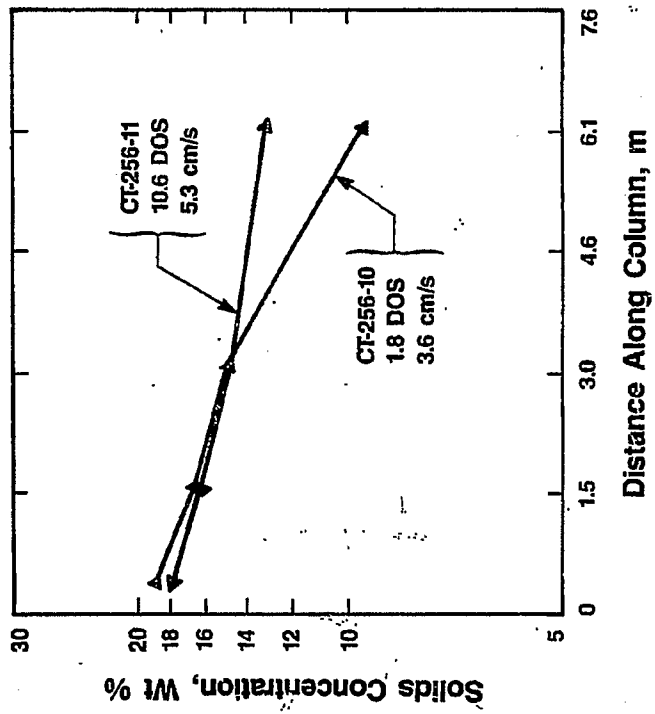
Figure 8

**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>)**

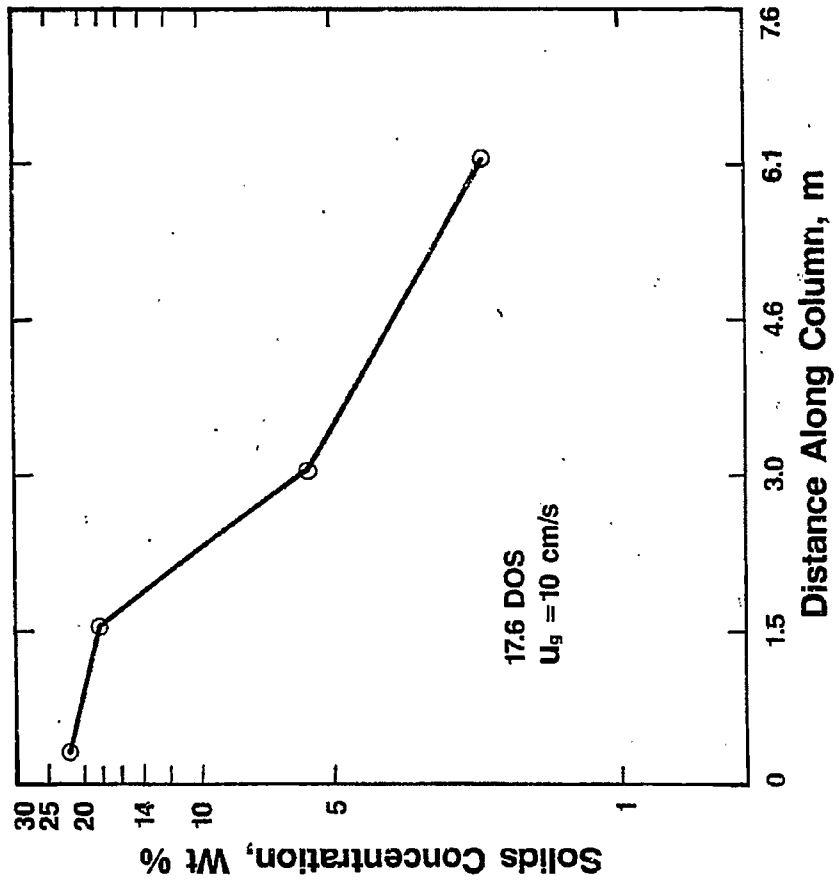




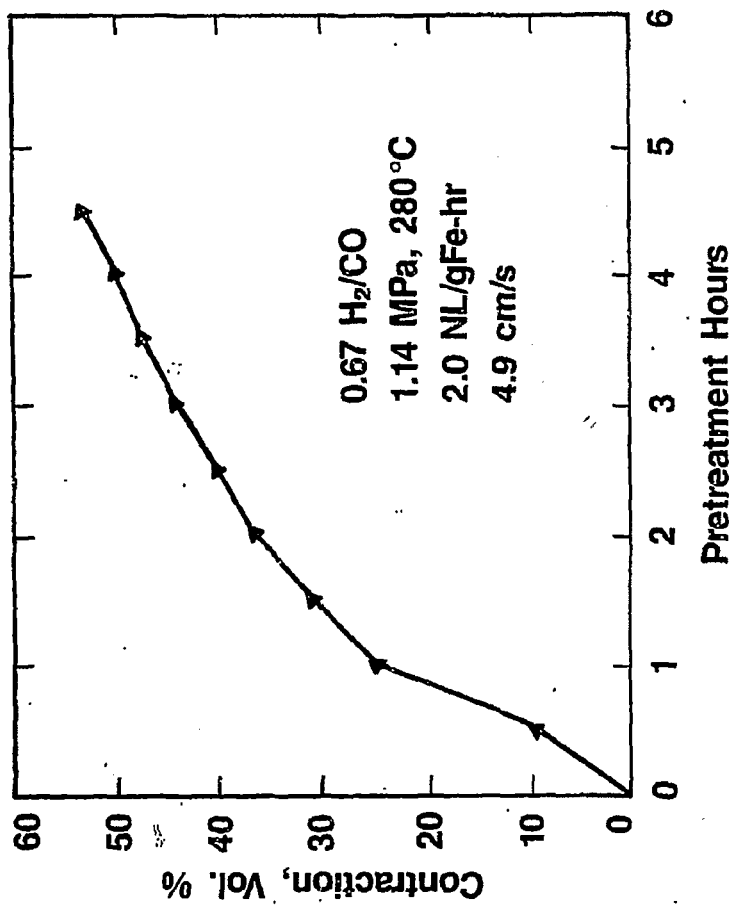
**Figure 9**  
**CATALYST CONCENTRATION PROFILES BEFORE SETTLING**  
**(RUN CT-256-10, 11)**



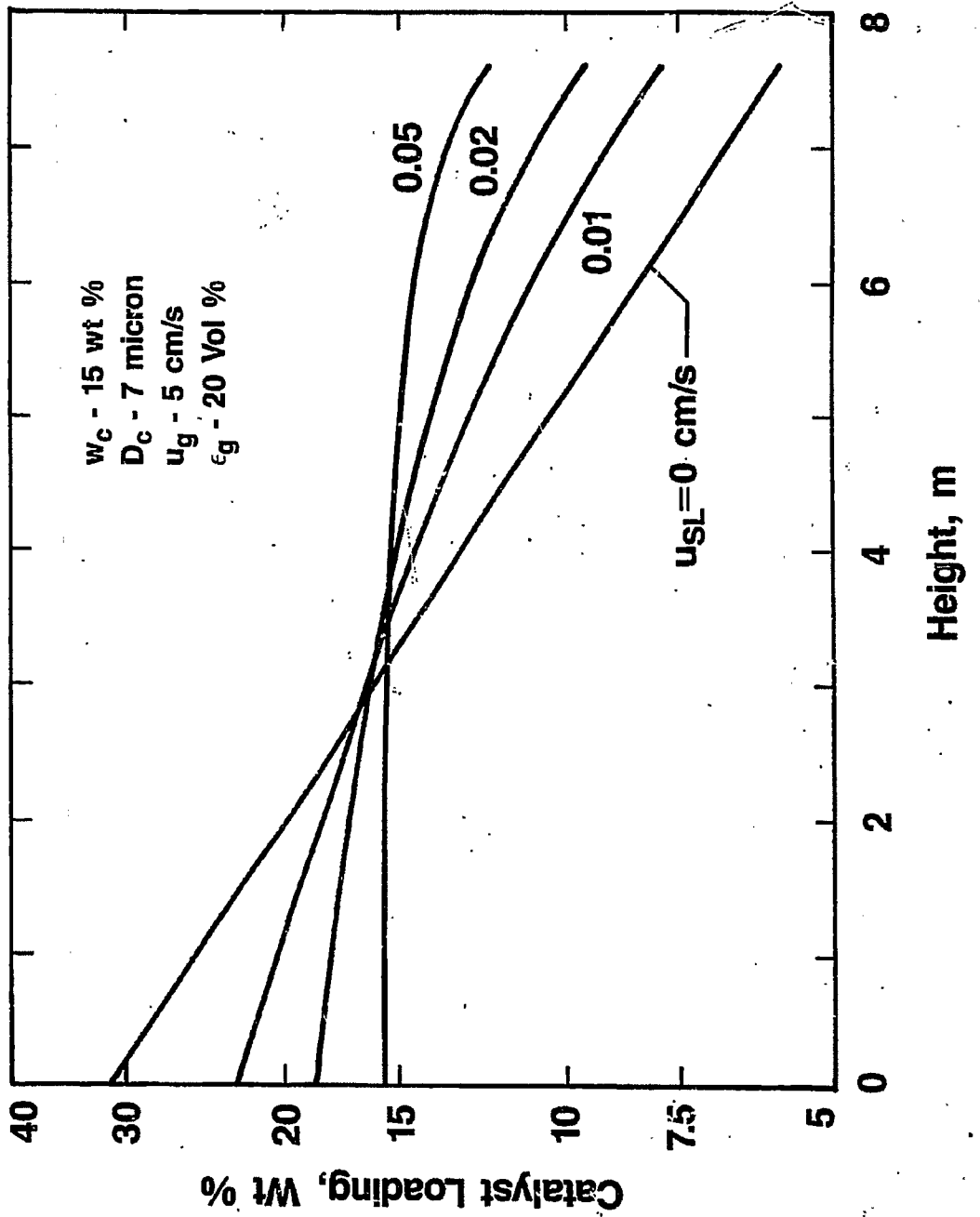
**Figure 10**  
**CATALYST CONCENTRATION PROFILE AFTER SETTLING**  
**(RUN CT-256-11)**



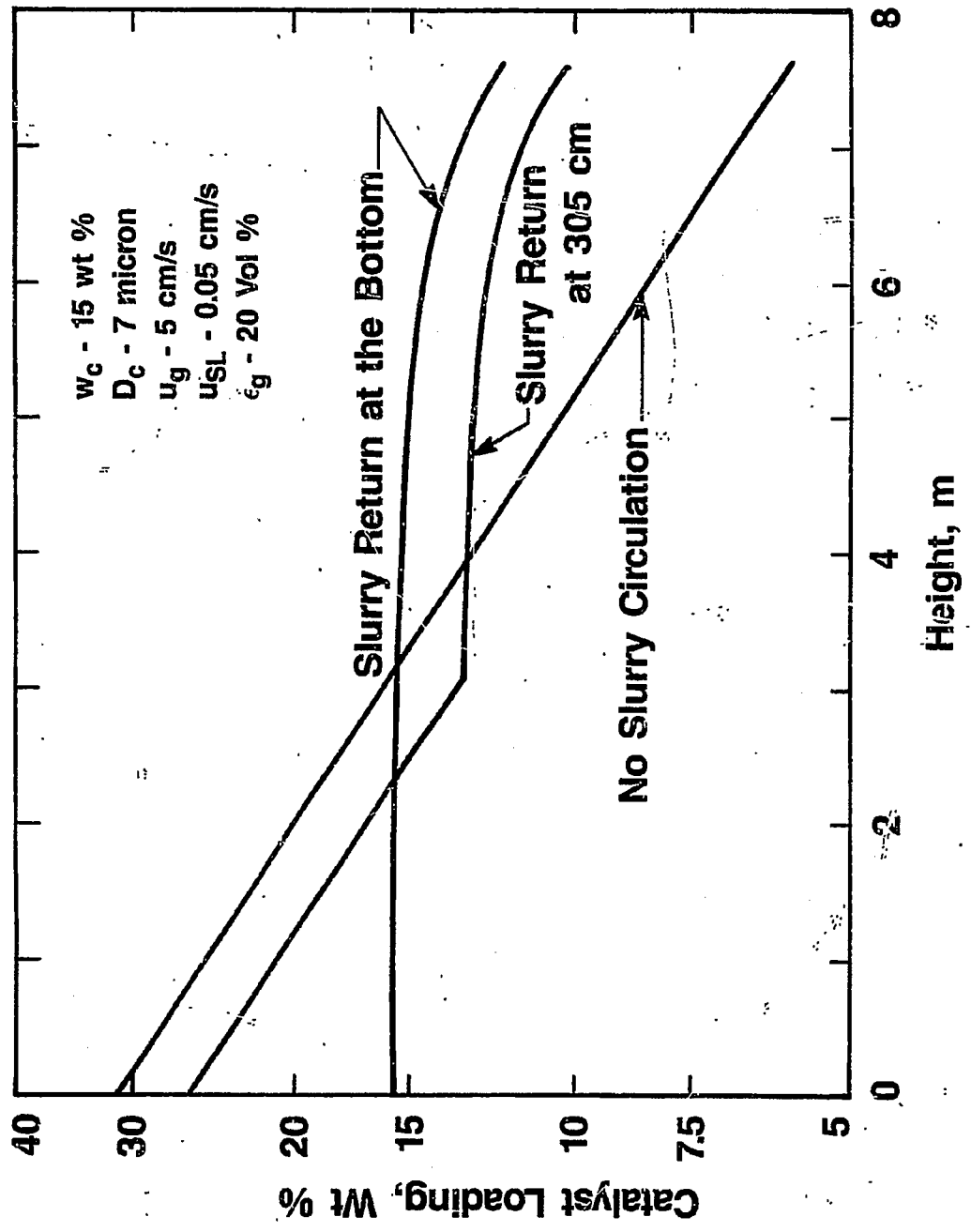
**Figure 11**  
**PRETREATMENT OF FISCHER-TROPSCH CATALYST I-B**  
**(RUN CT-256-12)**



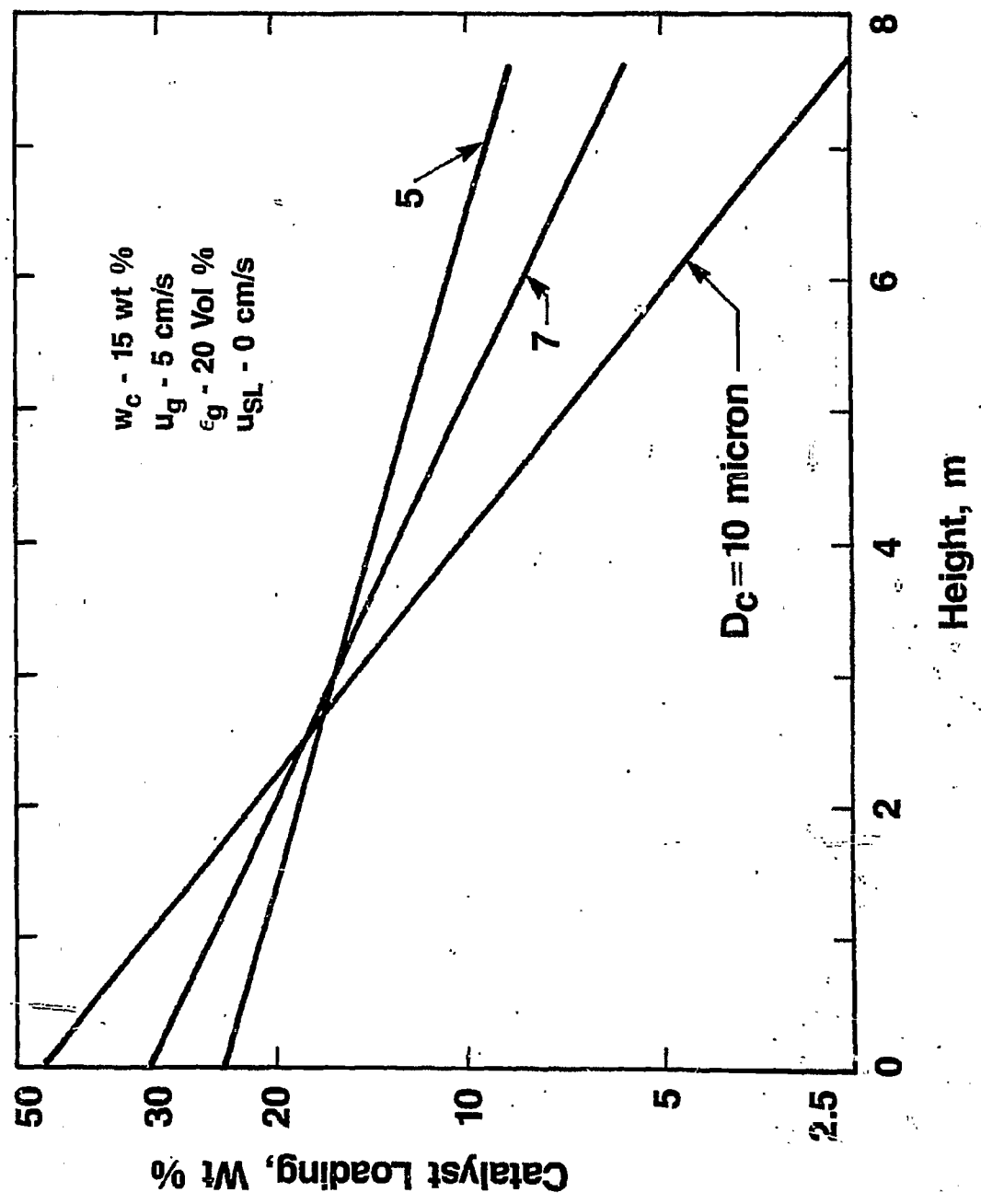
**Figure 12**  
**ESTIMATED EFFECT OF LIQUID CIRCULATION ON**  
**CATALYST SUSPENSION**



**Figure 13**  
**ESTIMATED EFFECT OF SLURRY RETURN LOCATION**  
**ON CATALYST SUSPENSION**

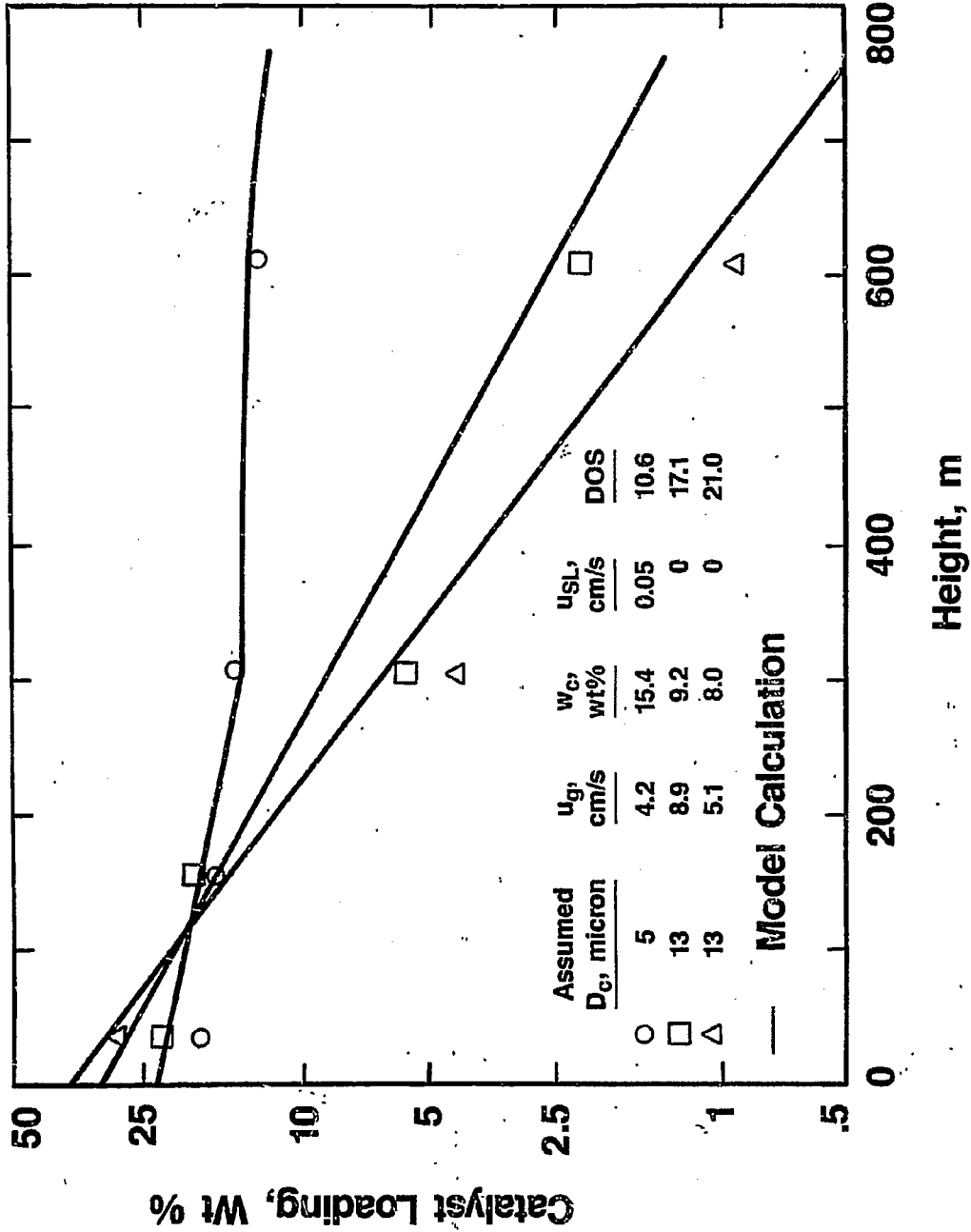


**Figure 14**  
**ESTIMATED EFFECT OF PARTICLE SIZE ON**  
**CATALYST SUSPENSION**

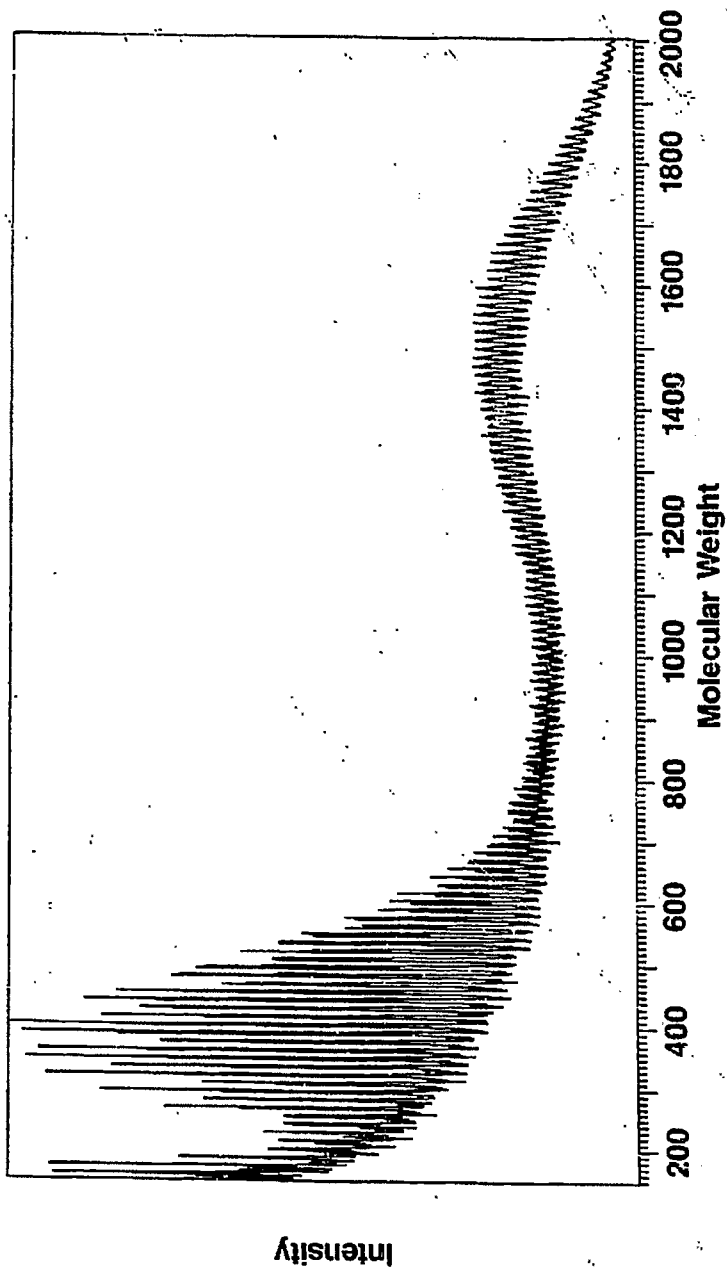


**Figure 15**

**CATALYST SETTLING DURING RUN CT-256-11**

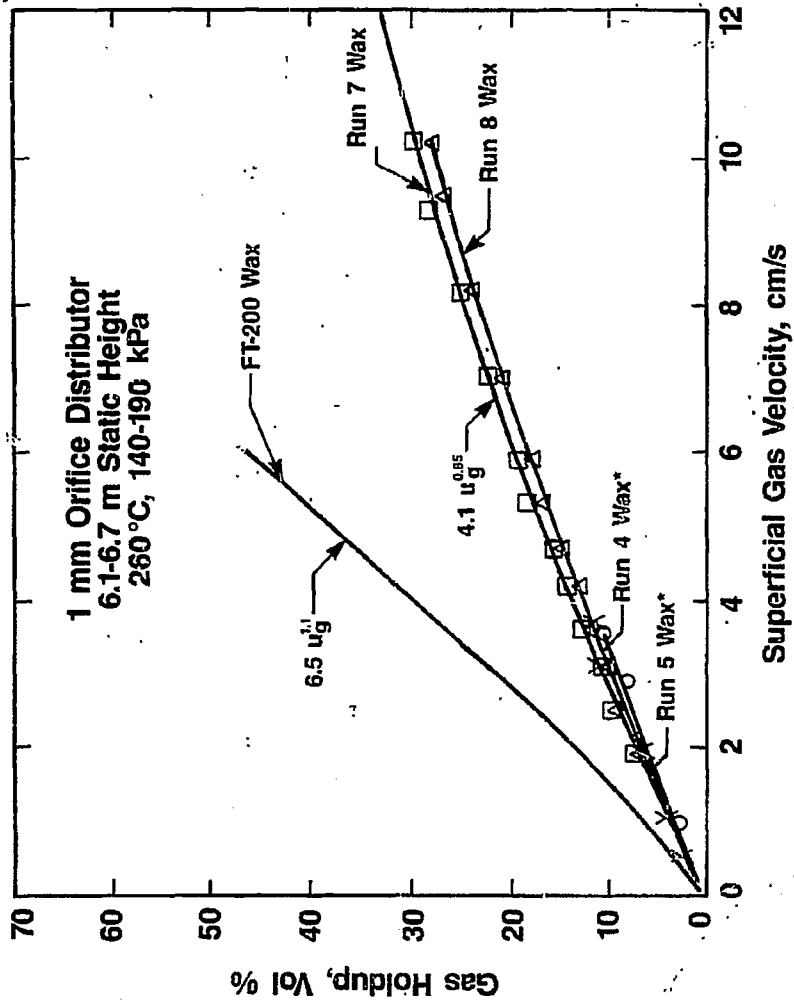


**Figure 16**  
**FIMS SPECTRUM OF RUN CT-256-7 WAX**  
**(WIDE RANGE)**

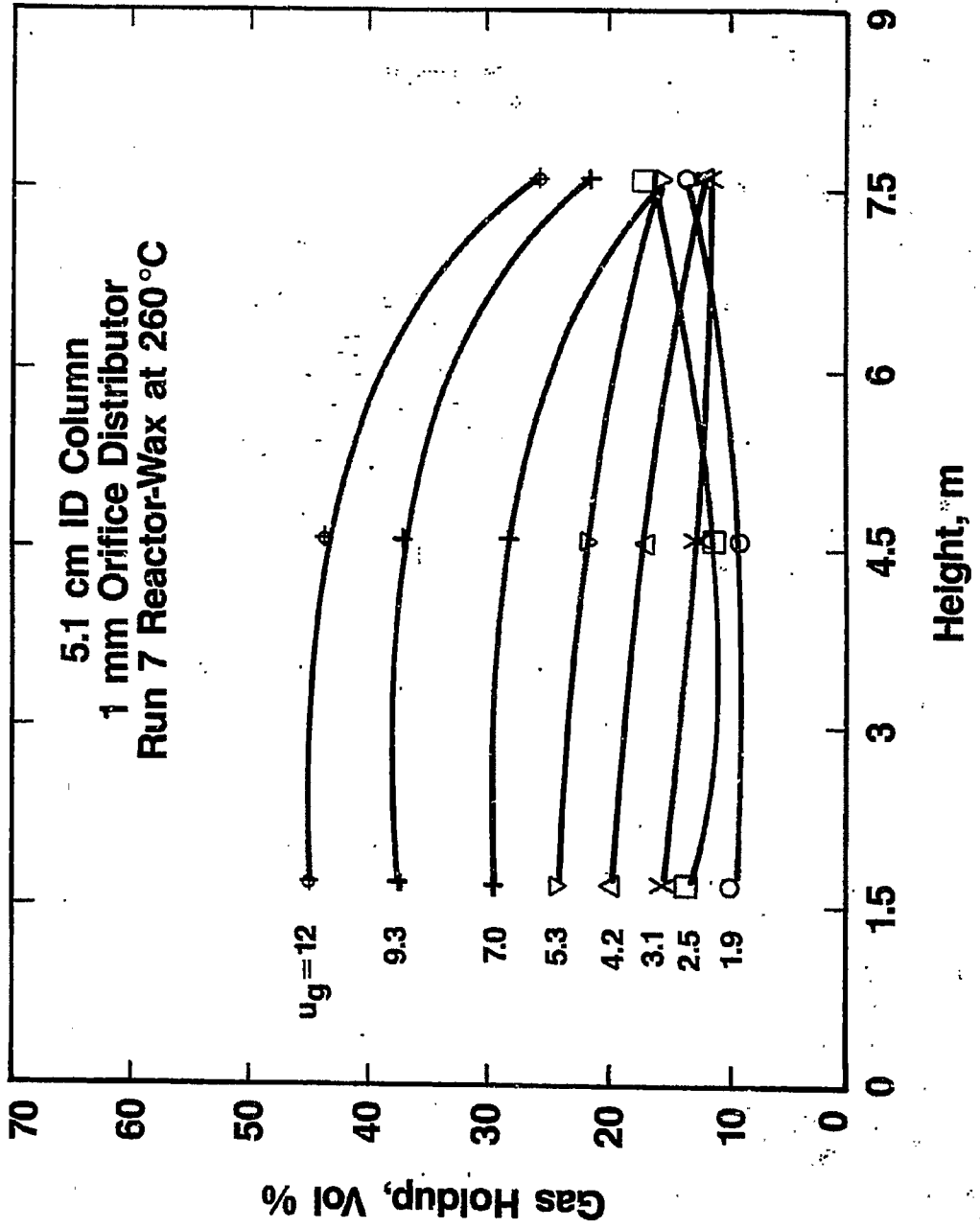




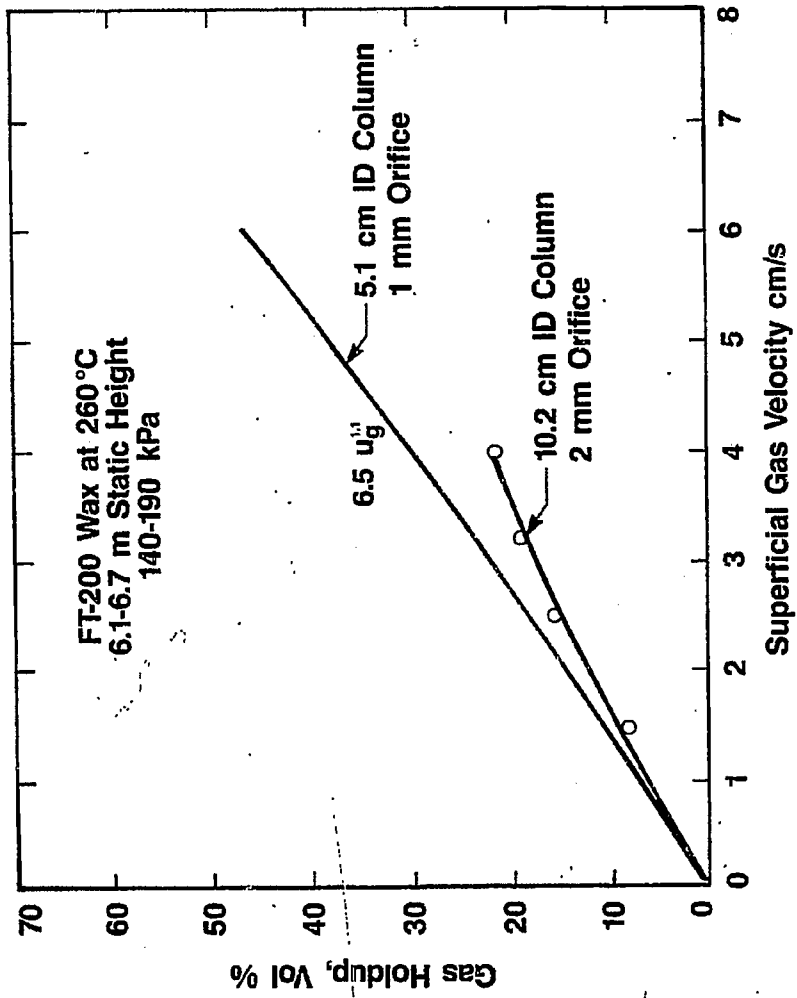
**Figure 17**  
**EFFECT OF LIQUID MEDIUM IN 5.1 cm ID COLUMN**



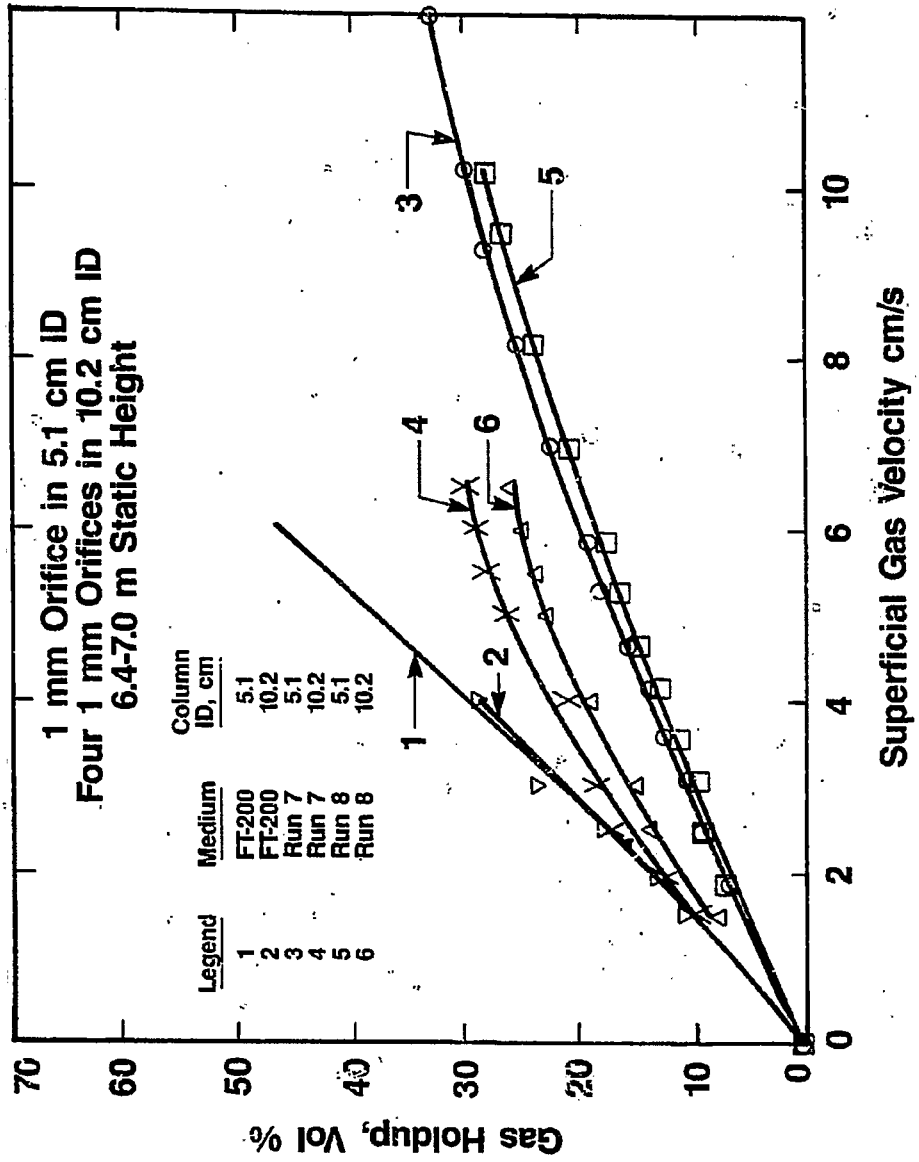
**Figure 18**  
**GAS HOLDUP PROFILES**



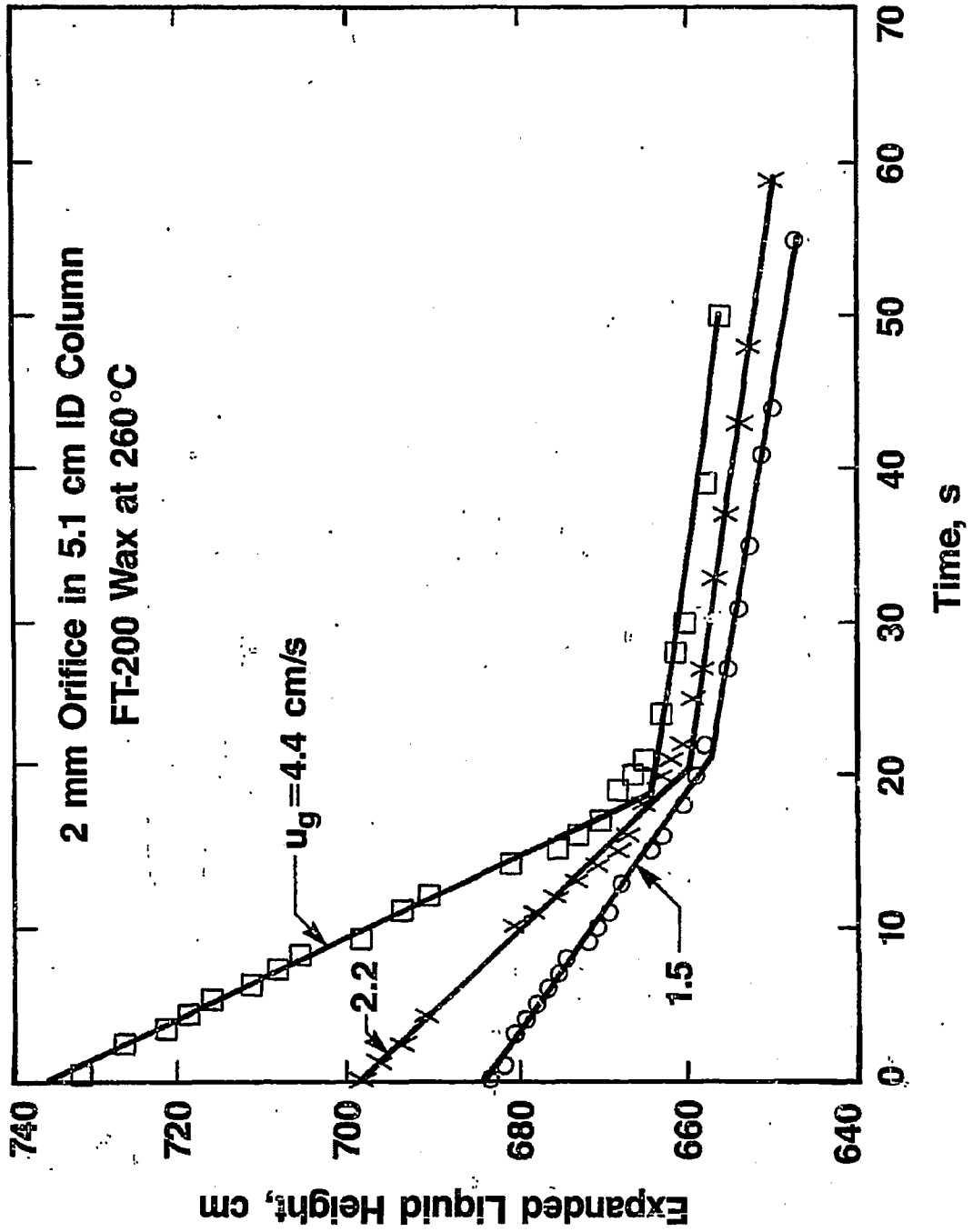
**Figure 19**  
**EFFECT OF COLUMN DIAMETER**



**Figure 20**  
**EFFECT OF COLUMN DIAMETER**



**Figure 21**  
**DYNAMIC GAS-DISENGAGEMENT**



**APPENDIX A**

**SUMMARY OF DATA FROM RUN CT-256-9**

Table A-1  
**First Stage Fischer-Tropsch Slurry Reactor**  
**Operating Conditions and Material Balances**  
 (Based on Inter-reactor Sample)  
 (Run CT-256-9)

| (Nitrogen-Free Basis)   | 9- 1*  | 9- 3  | 9- 4   | 9- 5   | 9- 7   | 9- 9  | 9- 11 |
|---|--------|-------|--------|--------|--------|-------|-------|
| M.B. No.  |        |       |        |        |        |       |       |
| Days On-stream  | 1.5    | 3.5   | 4.5    | 5.5    | 7.5    | 9.5   | 12.7  |
| First-Stage Conditions:                                       |        |       |        |        |        |       |       |
| Charge H <sub>2</sub> /CO (Molar)                             | 0.668  | 0.681 | 0.673  | 0.669  | 0.663  | 0.675 | 0.670 |
| Temperature, °C   | 257    | 256   | 255    | 256    | 255    | 255   | 252   |
| Pressure, MPa   | 1.487  | 1.487 | 1.832  | 1.832  | 1.825  | 1.825 | 1.825 |
| Feed Sup. Vel., cm/s  | 4.645  | 4.823 | 4.792  | 4.803  | 4.780  | 4.831 | 4.748 |
| Space Vel., NL/gFe-hr   | 1.857  | 1.957 | 2.403  | 2.408  | 2.394  | 2.420 | 2.396 |
| N <sub>2</sub> in Feed, Mol %                                 | 0.7    | 0.6   | 0.6    | 0.6    | 0.6    | 0.7   | 0.6   |
| Conversions, Mol % :  |        |       |        |        |        |       |       |
| H <sub>2</sub>  | 81.01  | 79.73 | 73.95  | 77.06  | 69.49  | 72.11 | 33.23 |
| CO  | 93.81  | 95.99 | 92.12  | 90.87  | 87.39  | 86.58 | 42.88 |
| H <sub>2</sub> +CO  | 88.68  | 89.41 | 84.02  | 85.34  | 80.25  | 80.75 | 39.01 |
| Yields, Wt % of Products :                                    |        |       |        |        |        |       |       |
| Hydrocarbons (1)  | 23.68  | 23.81 | 24.07  | 24.19  | 22.50  | 20.96 | 11.30 |
| CO <sub>2</sub>   | 67.81  | 69.57 | 65.76  | 65.07  | 63.60  | 63.72 | 28.91 |
| H <sub>2</sub> O (1)  | 2.07   | 1.79  | 1.56   | 1.19   | 1.41   | 1.10  | 0.79  |
| H <sub>2</sub>  | 0.83   | 0.96  | 1.19   | 1.03   | 1.30   | 1.31  | 3.15  |
| CO  | 5.61   | 3.87  | 7.42   | 8.51   | 11.19  | 12.90 | 55.84 |
| Total   | 100    | 100   | 100    | 100    | 100    | 100   | 100   |
| Bal Recovery, Wt % of Charge:                                 | 105.06 | 98.50 | 101.01 | 102.11 | 107.32 | 99.01 | 97.43 |
| (CO <sub>2</sub> ) (H <sub>2</sub> )/(CO) (H <sub>2</sub> ) : | 27.63  | 55.08 | 38.58  | 37.77  | 29.82  | 33.32 | 11.76 |
| gHC/Nm <sup>3</sup> (H <sub>2</sub> +CO) conv.:               | 219    | 204   | 223    | 226    | 236    | 200   | 219   |
| (H/C) Atomic Ratio in HC :                                    | 2.15   | 2.16  | 2.16   | 2.15   | 2.16   | 2.15  | 2.17  |
| Selectivities, Wt % of HC :                                   |        |       |        |        |        |       |       |
| Methane   | 3.87   | 4.17  | 4.23   | 3.82   | 4.36   | 3.72  | 4.03  |
| Ethene  | 2.17   | 2.00  | 2.12   | 1.94   | 1.99   | 2.24  | 2.43  |
| Ethane  | 0.84   | 1.02  | 0.95   | 0.94   | 1.12   | 1.10  | 1.43  |
| Propene   | 3.52   | 3.55  | 3.44   | 3.19   | 3.49   | 3.59  | 4.11  |
| Propane   | 0.63   | 0.77  | 0.84   | 0.82   | 0.90   | 1.01  | 1.08  |
| Butenes :   | 2.75   | 2.88  | 2.77   | 2.59   | 2.81   | 2.89  | 3.17  |
| i-Butane  | 0.04   | 0.05  | 0.06   | 0.06   | 0.06   | 0.08  | 0.09  |
| n-Butane  | 0.63   | 0.82  | 0.92   | 0.86   | 0.94   | 1.05  | 1.06  |
| C <sub>5</sub> - C <sub>11</sub> (2)                          | 4.85   | 7.55  | 7.45   | 6.72   | 7.34   | 8.33  | 12.08 |
| Light Hydrocarbons (3)  | 10.96  | 10.60 | 10.71  | 12.58  | 13.21  | 11.92 | 12.34 |
| Heavy Hydrocarbons (4)  | 13.22  | 16.00 | 15.78  | 15.83  | 18.10  | 18.28 | 16.90 |
| Slurry Rx.-Wax  | 56.20  | 50.00 | 50.00  | 50.00  | 45.00  | 45.00 | 40.00 |
| Total   | 100    | 100   | 100    | 100    | 100    | 100   | 100   |

\* Not based on Inter-reactor sample; Second-Stage not in operation

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condensers

(4) Collected in Hot Condenser

Table A-2  
Composition of Hydrocarbon Products from  
First-Stage Slurry F-T Reactor  
(Based on Inter-Reactor Sample)  
(Run CT-256-9)

| M.B. No.<br>Days On-stream      | 9- 1*<br>1.5 | 9- 3<br>3.5 | 9- 4<br>4.5 | 9- 5<br>5.5 | 9- 7<br>7.5 | 9- 9<br>9.5 | 9- 11<br>12.7 |
|---------------------------------|--------------|-------------|-------------|-------------|-------------|-------------|---------------|
| METHANE                         | 3.87         | 4.17        | 4.23        | 3.82        | 4.36        | 3.72        | 4.03          |
| ETHENE                          | 2.17         | 2.00        | 2.12        | 1.94        | 1.99        | 2.24        | 2.43          |
| ETHANE                          | 0.84         | 1.02        | 0.95        | 0.94        | 1.12        | 1.10        | 1.43          |
| PROPENE                         | 3.52         | 3.55        | 3.44        | 3.19        | 3.49        | 3.59        | 4.11          |
| PROPANE                         | 0.63         | 0.77        | 0.84        | 0.82        | 0.90        | 1.01        | 1.08          |
| I-BUTANE                        | 0.04         | 0.05        | 0.06        | 0.06        | 0.06        | 0.09        | 0.09          |
| 1-BUTENE+2-METHYLPROPENE        | 2.66         | 2.79        | 2.71        | 2.52        | 2.73        | 2.82        | 3.09          |
| N-BUTANE                        | 0.63         | 0.82        | 0.92        | 0.86        | 0.94        | 1.06        | 1.06          |
| TRANS-2-BUTENE                  | 0.03         | 0.04        | 0.02        | 0.03        | 0.03        | 0.03        | 0.03          |
| CIS-2-BUTENE                    | 0.06         | 0.06        | 0.04        | 0.04        | 0.05        | 0.04        | 0.06          |
| 3-METHYL-1-BUTENE               | 0.15         | 0.15        | 0.14        | 0.14        | 0.15        | 0.16        | 0.20          |
| I-PENTANE                       | 0.05         | 0.06        | 0.00        | 0.00        | 0.00        | 0.10        | 0.11          |
| 1-PENTENE                       | 1.84         | 2.14        | 2.06        | 1.89        | 2.05        | 2.16        | 2.33          |
| 2-METHYL-1-BUTENE               | 0.08         | 0.08        | 0.07        | 0.07        | 0.07        | 0.07        | 0.10          |
| N-PENTANE                       | 0.44         | 0.61        | 0.68        | 0.62        | 0.69        | 0.78        | 0.82          |
| TRANS-2-PENTENE                 | 0.03         | 0.03        | 0.02        | 0.02        | 0.02        | 0.02        | 0.02          |
| CIS-2-PENTENE                   | 0.03         | 0.03        | 0.02        | 0.02        | 0.00        | 0.02        | 0.03          |
| UNKNOWN C5-MONOLEFINS           | 0.00         | 0.00        | 0.00        | 0.00        | 0.03        | 0.00        | 0.00          |
| CYCLOPENTANE                    | 0.00         | 0.01        | 0.01        | 0.00        | 0.01        | 0.01        | 0.03          |
| HEXENES + ISO-HEXANES           | 0.14         | 0.24        | 0.23        | 0.22        | 0.23        | 0.27        | 0.52          |
| 2,3-DIMETHYLBUTANE              | 0.02         | 0.02        | 0.02        | 0.02        | 0.02        | 0.03        | 0.05          |
| 2-METHYLPENTANE                 | 0.03         | 0.06        | 0.07        | 0.06        | 0.07        | 0.09        | 0.12          |
| 3-METHYLPENTANE                 | 0.02         | 0.02        | 0.03        | 0.02        | 0.02        | 0.03        | 0.04          |
| 1-HEXENE                        | 1.03         | 1.54        | 1.47        | 1.32        | 1.45        | 1.57        | 1.85          |
| N-HEXANE                        | 0.26         | 0.46        | 0.50        | 0.46        | 0.50        | 0.58        | 0.66          |
| HEPTENES + ISO-HEPTANES         | 0.13         | 0.26        | 0.23        | 0.21        | 0.22        | 0.26        | 0.47          |
| 1-HEPTENE                       | 0.36         | 0.81        | 0.80        | 0.70        | 0.77        | 0.89        | 1.32          |
| N-HEPTANE                       | 0.10         | 0.26        | 0.28        | 0.25        | 0.27        | 0.34        | 0.50          |
| C8-OLEFINS + ISO-P              | 0.03         | 0.09        | 0.06        | 0.06        | 0.06        | 0.06        | 0.20          |
| 1-OCTENE                        | 0.07         | 0.32        | 0.34        | 0.29        | 0.31        | 0.39        | 0.81          |
| N-OCTANE                        | 0.02         | 0.11        | 0.13        | 0.10        | 0.12        | 0.15        | 0.32          |
| C9-OLEFINS + ISO-P              | 0.01         | 0.26        | 0.28        | 0.25        | 0.27        | 0.33        | 1.56          |
| METHANOL                        | 0.06         | 0.06        | 0.07        | 0.07        | 0.07        | 0.09        | 0.23          |
| ACETONE                         | 0.12         | 0.36        | 0.39        | 0.34        | 0.36        | 0.48        | 0.77          |
| I-PROPANOL                      | 0.13         | 0.17        | 0.26        | 0.24        | 0.26        | 0.22        | 0.28          |
| UNKNOWN LITE HYDRO-CARB LIQ (1) | 10.96        | 10.60       | 10.71       | 12.58       | 13.21       | 11.92       | 12.34         |
| UNKNOWN HVY HYDRO-CARB LIQ (2)  | 13.22        | 16.00       | 15.78       | 15.83       | 18.10       | 18.20       | 16.90         |
| SLURRY REACTOR-WAX              | 56.20        | 50.00       | 50.00       | 50.00       | 45.00       | 45.00       | 40.00         |

\* Not based on Inter-reactor sample; Second-Stage not in operation

(1) Collected in Ambient and Chilled Condensers

(2) Collected in Hot Condenser



Table A-3  
 Second-Stage Fixed-Bed ZSM-5 Reactor  
 Operating Conditions and Material Balances  
 (Run CT-256-9)

| (Nitrogen-Free Basis)   | 9- 3  | 9- 4   | 9- 5   | 9- 7   | 9- 8  | 9- 9  | 9- 11 |
|---|-------|--------|--------|--------|-------|-------|-------|
| M.B. No.  |       |        |        |        |       |       |       |
| Days On-stream  | 3.5   | 4.5    | 5.5    | 7.5    | 8.5   | 9.5   | 12.7  |
| <b>First-Stage Conditions:</b>                                |       |        |        |        |       |       |       |
| Charge H <sub>2</sub> /CO (Molar)                             | 0.681 | 0.673  | 0.669  | 0.663  | 0.669 | 0.675 | 0.670 |
| Temperature, °C   | 256   | 255    | 256    | 255    | 255   | 255   | 252   |
| Pressure, MPa   | 1.487 | 1.832  | 1.832  | 1.825  | 1.825 | 1.825 | 1.825 |
| Feed Sup. Vel., cm/s  | 4.823 | 4.792  | 4.803  | 4.779  | 4.809 | 4.830 | 4.747 |
| Space Vel., NL/gFe-hr   | 1.957 | 2.403  | 2.408  | 2.394  | 2.412 | 2.420 | 2.396 |
| N <sub>2</sub> in Feed, Mol %                                 | 0.6   | 0.6    | 0.6    | 0.6    | 0.5   | 0.7   | 0.6   |
| <b>Second-Stage Conditions:</b>                               |       |        |        |        |       |       |       |
| Temp., Inlet, °C  | 319   | 323    | 326    | 333    | 351   | 358   | 373   |
| Outlet, °C  | 354   | 358    | 358    | 371    | 393   | 402   | 394   |
| Pressure, MPa   | 1.487 | 1.825  | 1.825  | 1.825  | 1.825 | 1.818 | 1.825 |
| GHSV, °/hr  | 2511  | 3278   | 3352   | 3760   | 3350  | 3645  | 5650  |
| Days On-stream  | 17.5  | 18.5   | 19.5   | 21.5   | 22.5  | 23.5  | 28.8  |
| <b>Conversions, Mol % :</b>                                   |       |        |        |        |       |       |       |
| H <sub>2</sub>  | 81.27 | 78.75  | 77.78  | 71.92  | 75.12 | 72.12 | 90.63 |
| CO  | 95.99 | 92.28  | 91.15  | 86.44  | 87.77 | 86.67 | 43.89 |
| H <sub>2</sub> +CO  | 90.03 | 86.84  | 85.79  | 80.65  | 82.70 | 80.81 | 38.57 |
| <b>Yields, Wt % of Products :</b>                             |       |        |        |        |       |       |       |
| Hydrocarbons  | 24.72 | 23.27  | 24.13  | 22.82  | 22.36 | 20.57 | 12.16 |
| CO <sub>2</sub>   | 68.93 | 68.89  | 65.02  | 62.48  | 62.48 | 63.83 | 28.60 |
| H <sub>2</sub> O  | 1.61  | 1.55   | 1.59   | 1.51   | 1.56  | 1.45  | 1.32  |
| H <sub>2</sub>  | 0.88  | 0.98   | 1.00   | 1.19   | 1.22  | 1.31  | 3.27  |
| CO  | 3.85  | 7.31   | 8.28   | 12.02  | 12.38 | 12.84 | 54.65 |
| Total   | 100   | 100    | 100    | 100    | 100   | 100   | 100   |
| <b>Bal Recovery, Wt % of Charge:</b>                          | 99.01 | 100.58 | 102.07 | 107.49 | 94.07 | 98.82 | 97.78 |
| (CO <sub>2</sub> )(H <sub>2</sub> )/(CO)(H <sub>2</sub> O) :  | 55.67 | 32.83  | 28.27  | 23.35  | 22.38 | 25.52 | 7.36  |
| gHC/Nm <sup>3</sup> (H <sub>2</sub> +CO) conv.:               | 211   | 210    | 224    | 238    | 198   | 196   | 239   |
| (H/C) Atomic Ratio in HC :                                    | 2.16  | 2.16   | 2.10   | 2.15   | 2.16  | 2.18  | 2.15  |
| <b>Selectivities, Wt % of HC :</b>                            |       |        |        |        |       |       |       |
| Methane   | 4.03  | 3.85   | 3.88   | 4.10   | 4.10  | 3.64  | 3.90  |
| Ethene  | 0.44  | 0.48   | 0.54   | 0.62   | 0.69  | 0.79  | 1.38  |
| Ethane  | 1.07  | 0.97   | 1.04   | 1.14   | 1.20  | 1.34  | 1.64  |
| Propene   | 1.56  | 1.66   | 1.78   | 2.15   | 2.32  | 2.58  | 3.95  |
| Propane   | 2.58  | 2.42   | 2.30   | 2.76   | 3.95  | 4.97  | 3.99  |
| Butenes   | 2.92  | 3.28   | 3.14   | 3.91   | 3.34  | 3.34  | 4.64  |
| i-Butane  | 4.06  | 3.64   | 3.21   | 4.05   | 5.38  | 6.29  | 4.80  |
| n-Butane  | 2.80  | 2.88   | 2.29   | 2.90   | 3.54  | 4.06  | 3.12  |
| C <sub>5</sub> - C <sub>11</sub>                              | 30.09 | 30.49  | 31.45  | 33.18  | 29.78 | 27.49 | 32.33 |
| C <sub>12</sub> + (Excl. Rx.-Wax)                             | 0.44  | 0.54   | 0.37   | 0.20   | 0.70  | 0.49  | 0.25  |
| Slurry Rx.-Wax  | 50.00 | 50.00  | 50.00  | 45.00  | 45.00 | 45.00 | 40.00 |
| Total   | 100   | 100    | 100    | 100    | 100   | 100   | 100   |
| <b>i-C<sub>4</sub>/(C<sub>3</sub>+ C<sub>4</sub>) Molar :</b> | 0.78  | 0.64   | 0.56   | 0.58   | 0.81  | 0.89  | 0.47  |
| (C <sub>3</sub> /C <sub>3</sub> ) Molar Ratio :               | 1.58  | 1.39   | 1.24   | 1.22   | 1.63  | 1.84  | 0.96  |
| Alkylate, Wt % of HC :  | 7.73  | 7.10   | 6.31   | 7.96   | 10.11 | 11.68 | 9.42  |
| Cat-Poly, Wt % of HC :  | 0.82  | 1.48   | 1.81   | 2.15   | 0.92  | 0.54  | 3.96  |
| <b>C<sub>5</sub> - C<sub>11</sub> PDNA, Wt % :</b>            |       |        |        |        |       |       |       |
| Paraffins   | 46.68 | 46.68  | --     | 41.78  | 43.84 | 48.80 | --    |
| Diolefins   | 22.35 | 25.79  | --     | 27.60  | 17.52 | 13.97 | --    |
| Naphthenes  | 6.04  | 6.10   | --     | 5.91   | 8.09  | 8.62  | --    |
| Aromatics   | 24.92 | 22.43  | --     | 24.71  | 30.54 | 28.60 | --    |

Table A-4  
Composition of Hydrocarbon Products from  
Two-Stage Slurry F-T/ZSM-5 Syngas Conversion  
(Run 41-268-9)

| U.B. No.                        | 9- 3  | 9- 4  | 9- 5  | 9- 7  | 9- 8  | 9- 9  | 9- 11 |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Days On-stream                  | 3.5   | 4.5   | 5.5   | 7.5   | 8.5   | 9.5   | 12.7  |
| METHANE                         | 4.03  | 3.85  | 3.88  | 4.10  | 4.10  | 3.84  | 3.90  |
| ETHENE                          | 0.44  | 0.48  | 0.54  | 0.62  | 0.69  | 0.79  | 1.28  |
| ETHANE                          | 1.07  | 0.97  | 1.04  | 1.14  | 1.20  | 1.34  | 1.64  |
| PROPENE                         | 1.55  | 1.66  | 1.76  | 2.15  | 2.32  | 2.53  | 3.95  |
| PROPANE                         | 2.59  | 2.42  | 2.30  | 2.78  | 3.25  | 4.97  | 3.99  |
| I-BUTANE                        | 4.06  | 3.64  | 3.21  | 4.05  | 5.38  | 6.29  | 4.86  |
| 1-BUTENE-2-METHYLPROPENE        | 1.76  | 1.97  | 1.02  | 2.34  | 1.99  | 2.01  | 2.79  |
| N-BUTANE                        | 2.80  | 2.68  | 2.29  | 2.90  | 3.54  | 4.05  | 3.12  |
| TRANS-2-BUTENE                  | 0.70  | 0.78  | 0.73  | 0.94  | 0.90  | 0.79  | 1.09  |
| CIS-2-BUTENE                    | 0.46  | 0.52  | 0.49  | 0.53  | 0.55  | 0.54  | 0.75  |
| 3-METHYL-1-BUTENE               | 0.05  | 0.07  | 0.06  | 0.08  | 0.05  | 0.05  | 0.07  |
| 1-PENTANE                       | 3.28  | 2.97  | 2.02  | 3.27  | 3.05  | 3.85  | 2.92  |
| 1-PENTENE                       | 0.07  | 0.08  | 0.06  | 0.10  | 0.08  | 0.07  | 0.09  |
| 2-METHYL-1-BUTENE               | 0.44  | 0.52  | 0.37  | 0.60  | 0.43  | 0.37  | 0.46  |
| N-PENTANE                       | 2.06  | 1.99  | 1.21  | 2.14  | 2.14  | 2.16  | 1.52  |
| TRANS-2-PENTENE                 | 0.30  | 0.35  | 0.23  | 0.42  | 0.30  | 0.26  | 0.31  |
| CIS-2-PENTENE                   | 0.14  | 0.17  | 0.11  | 0.20  | 0.15  | 0.13  | 0.15  |
| 2-METHYL-2-BUTENE               | 1.27  | 1.46  | 0.88  | 1.05  | 1.11  | 0.82  | 1.06  |
| 2,2-DIMETHYLBUTANE              | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.04  |
| CYCLOPENTANE                    | 0.03  | 0.04  | 0.01  | 0.04  | 0.09  | 0.10  | 0.11  |
| HEXENES + ISO-HEXANES           | 0.05  | 0.07  | 0.06  | 0.06  | 0.04  | 0.09  | 0.08  |
| 2,3-DIMETHYLBUTANE              | 0.08  | 0.05  | 0.05  | 0.10  | 0.11  | 0.07  | 0.10  |
| 2-METHYLPENTANE                 | 1.01  | 1.51  | 0.53  | 1.57  | 1.43  | 1.34  | 0.69  |
| 3-METHYLPENTANE                 | 0.59  | 0.56  | 0.17  | 0.61  | 0.54  | 0.63  | 0.38  |
| HEXENES                         | 0.58  | 0.73  | 0.00  | 0.85  | 0.61  | 0.43  | 0.06  |
| N-HEXANE                        | 1.24  | 1.29  | 0.34  | 1.39  | 1.18  | 1.57  | 0.55  |
| 2,2-DIMETHYLPENTANE             | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| 2,4-DIMETHYLPENTANE             | 0.00  | 0.00  | 0.00  | 0.01  | 0.01  | 0.00  | 0.00  |
| METHYLCYCLOPENTANE              | 0.27  | 0.24  | 0.05  | 0.34  | 0.55  | 0.51  | 0.39  |
| 3,3-DIMETHYLPENTANE             | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| CYCLOHEXANE                     | 0.01  | 0.01  | 0.00  | 0.01  | 0.02  | 0.02  | 0.00  |
| HEPTENES + ISO-HEPTANES         | 0.21  | 0.23  | 0.25  | 0.24  | 0.14  | 0.13  | 0.35  |
| 2-METHYLHEXANE                  | 0.68  | 0.70  | 0.00  | 0.64  | 0.50  | 0.42  | 0.13  |
| 2,3-DIMETHYLPENTANE             | 0.56  | 0.55  | 0.00  | 0.58  | 0.11  | 0.12  | 0.04  |
| 3-METHYLHEXANE                  | 0.58  | 0.57  | 0.05  | 0.55  | 0.48  | 0.42  | 0.12  |
| 1-CIS-3-DIMETHYL-NS             | 0.13  | 0.11  | 0.01  | 0.15  | 0.20  | 0.20  | 0.09  |
| 1-TRANS-3-DIMETHYL-NS           | 0.12  | 0.11  | 0.00  | 0.14  | 0.19  | 0.19  | 0.08  |
| 1-TRANS-2-DIMETHYL-NS           | 0.09  | 0.09  | 0.02  | 0.10  | 0.14  | 0.14  | 0.06  |
| N-HEPTANE                       | 0.74  | 0.85  | 0.08  | 0.85  | 0.65  | 0.53  | 0.23  |
| C7-OLEFINS                      | 0.95  | 1.15  | 0.00  | 1.27  | 0.88  | 0.58  | 0.00  |
| METHYLCYCLOHEXANE               | 0.10  | 0.10  | 0.00  | 0.00  | 0.13  | 0.12  | 0.10  |
| C8-OLEFINS + ISO-P              | 0.02  | 0.01  | 0.01  | 0.02  | 0.04  | 0.04  | 0.20  |
| ISO-C8-P + 0 + N5 + N6          | 0.01  | 0.01  | 0.01  | 0.01  | 0.00  | 0.00  | 0.22  |
| MONOMETHYL-ISO-C8-P             | 0.09  | 0.76  | 0.00  | 0.54  | 0.45  | 0.37  | 0.00  |
| OTHER ISO-C8-P                  | 0.07  | 0.07  | 0.00  | 0.02  | 0.09  | 0.08  | 0.00  |
| C8-OLEFINS                      | 1.48  | 1.41  | 0.00  | 2.24  | 0.96  | 0.52  | 0.00  |
| C8-NAPHTHENES (NS+NS)           | 0.63  | 0.60  | 0.00  | 0.89  | 0.82  | 0.76  | 0.00  |
| N-OCTANE                        | 0.42  | 0.51  | 0.00  | 0.60  | 0.33  | 0.25  | 0.00  |
| C9-OLEFINS + ISO-P              | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.28  |
| MONOMETHYL-ISO-C9-P             | 0.38  | 0.41  | 0.00  | 0.34  | 0.19  | 0.14  | 0.00  |
| OTHER ISO-C9-P                  | 0.10  | 0.10  | 0.00  | 0.10  | 0.09  | 0.08  | 0.00  |
| C9-OLEFINS                      | 1.29  | 1.87  | 0.00  | 1.48  | 0.76  | 0.44  | 0.00  |
| C9-NAPHTHENES (NS+NS)           | 0.45  | 0.27  | 0.00  | 0.28  | 0.20  | 0.22  | 0.00  |
| N-NONANE                        | 0.01  | 0.20  | 0.00  | 0.00  | 0.13  | 0.00  | 0.00  |
| ISO-C10-P + 0 + NS + N6         | 0.75  | 0.77  | 0.00  | 1.18  | 0.43  | 1.39  | 0.00  |
| N-DECANE                        | 0.05  | 0.07  | 0.00  | 0.00  | 0.03  | 0.13  | 0.00  |
| C11-P + 0 + NS + N6             | 0.56  | 0.65  | 0.00  | 0.25  | 0.31  | 0.25  | 0.00  |
| BENZENE                         | 0.25  | 0.27  | 0.05  | 0.34  | 0.31  | 0.28  | 0.21  |
| TOLUENE                         | 0.79  | 0.64  | 0.54  | 0.92  | 1.47  | 1.62  | 0.34  |
| ETHYLBENZENE                    | 0.41  | 0.35  | 0.00  | 0.45  | 0.58  | 0.58  | 0.45  |
| M-XYLENE                        | 1.45  | 1.29  | 0.00  | 1.61  | 1.07  | 2.00  | 0.00  |
| O-XYLENE                        | 0.29  | 0.23  | 0.00  | 0.33  | 0.51  | 0.54  | 0.00  |
| N-PROPYLBENZENE                 | 0.14  | 0.18  | 0.00  | 0.18  | 0.11  | 0.09  | 0.00  |
| 1-METHYL-3-ETHYL-BENZENE        | 1.05  | 0.93  | 0.00  | 1.09  | 1.14  | 0.49  | 0.00  |
| 1-METHYL-4-ETHYL-BENZENE        | 0.52  | 0.47  | 0.00  | 0.54  | 0.54  | 0.01  | 0.00  |
| 1,3,5-TRIMETHYL-BENZENE         | 0.03  | 0.00  | 0.00  | 0.04  | 0.03  | 0.01  | 0.00  |
| 1-METHYL-2-ETHYLBENZENE         | 0.34  | 0.30  | 0.00  | 0.05  | 0.05  | 0.05  | 0.00  |
| 1,2,4-TRIMETHYLBENZENE          | 0.76  | 0.69  | 0.00  | 0.63  | 0.97  | 0.97  | 0.00  |
| 1-METHYL-2-ISO-C3-BENZENE       | 0.02  | 0.02  | 0.00  | 0.01  | 0.01  | 0.01  | 0.00  |
| 1,3-DIETHYLBENZENE              | 0.42  | 0.40  | 0.00  | 0.39  | 0.30  | 0.24  | 0.00  |
| 1-METHYL-3-N-C3-BENZENE         | 0.00  | 0.00  | 0.00  | 0.00  | 0.02  | 0.02  | 0.00  |
| N-C4-BENZENE                    | 0.25  | 0.25  | 0.00  | 0.24  | 0.15  | 0.12  | 0.00  |
| 1,2,4,5-TETRAMETHYLBENZENE      | 0.05  | 0.05  | 0.00  | 0.05  | 0.05  | 0.05  | 0.00  |
| 1,2,3,5-TETRAMETHYLBENZENE      | 0.01  | 0.01  | 0.00  | 0.01  | 0.01  | 0.01  | 0.00  |
| 1,2,3,4-TETRAMETHYLBENZENE      | 0.05  | 0.05  | 0.00  | 0.05  | 0.02  | 0.02  | 0.00  |
| NAPHTHALENE                     | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| UNKNOWN (HC AROMATICS)          | 0.33  | 0.28  | 0.00  | 0.47  | 0.33  | 0.32  | 0.00  |
| UNKNOWN LITE HYDRO-CARB LIQ (1) | 0.00  | 0.00  | 24.07 | 0.00  | 0.00  | 0.00  | 20.57 |
| UNKNOWN Hvy HYDRO-CARB LIQ (2)  | 0.44  | 0.54  | 0.37  | 0.29  | 0.70  | 0.49  | 0.25  |
| SLURRY REACTOR-WAX              | 50.00 | 50.00 | 50.00 | 45.00 | 45.00 | 45.00 | 45.00 |

(1) Collected in Chilled and Ambient Condensers  
(2) Collected in Hot Condenser

**APPENDIX B**

**SUMMARY OF DATA FROM RUN CT-256-11**

Table B-1  
**First Stage Fischer-Tropsch Slurry Reactor**  
**Operating Conditions and Material Balances**  
 (Second-Stage Not Operative)  
 (Run CT-256-11)

| (Nitrogen-Free Basis)  |       |       |       |       |       |       |  |
|--|-------|-------|-------|-------|-------|-------|--|
| M.B. No.   | 11- 2 | 11- 3 | 11- 4 | 11- 5 | 11- 6 | 11- 7 |  |
| Days On-stream   | 2.3   | 3.3   | 4.3   | 5.3   | 6.3   | 7.3   |  |
| First-Stage Conditions:  |       |       |       |       |       |       |  |
| Charge H <sub>2</sub> /CO (Molar)                                | 0.692 | 0.682 | 0.661 | 0.678 | 0.679 | 0.688 |  |
| Temperature, °C  | 258   | 258   | 259   | 259   | 259   | 258   |  |
| Pressure, MPa  | 1.480 | 1.480 | 1.480 | 1.480 | 1.487 | 1.487 |  |
| Feed Sup. Vol., cm/s   | 5.270 | 5.331 | 5.254 | 5.486 | 5.995 | 6.013 |  |
| Space Vel., NL/gFe-hr  | 2.300 | 2.300 | 2.300 | 2.300 | 2.300 | 2.300 |  |
| N <sub>2</sub> in Feed, Mol %                                    | 0.6   | 0.5   | 0.6   | 0.5   | 0.5   | 0.5   |  |
| Conversions, Mol % :   |       |       |       |       |       |       |  |
| H <sub>2</sub>   | 76.80 | 76.11 | 81.25 | 78.77 | 78.73 | 73.70 |  |
| CO   | 92.64 | 94.07 | 95.22 | 93.98 | 91.75 | 89.67 |  |
| H <sub>2</sub> +CO   | 86.18 | 87.60 | 89.66 | 87.82 | 85.68 | 83.17 |  |
| Yields, Wt % of Products :                                       |       |       |       |       |       |       |  |
| Hydrocarbons (1)   | 21.44 | 22.26 | 20.98 | 24.32 | 21.95 | 21.42 |  |
| CO <sub>2</sub>  | 67.50 | 68.14 | 70.39 | 66.63 | 68.26 | 65.23 |  |
| H <sub>2</sub> O (1)   | 2.21  | 2.30  | 2.78  | 1.92  | 1.89  | 1.72  |  |
| H <sub>2</sub>   | 1.20  | 1.12  | 0.93  | 1.05  | 1.20  | 1.30  |  |
| CO   | 7.65  | 6.17  | 4.94  | 6.09  | 8.71  | 10.32 |  |
| Total  | 100   | 100   | 100   | 100   | 100   | 100   |  |
| Bal Recovery, Wt % of Charge:                                    |       |       |       |       |       |       |  |
| (CO <sub>2</sub> ) (H <sub>2</sub> ) / (CO) (H <sub>2</sub> O) : | 27.34 | 30.68 | 27.17 | 34.01 | 27.64 | 27.27 |  |
| gHC/Nm <sup>3</sup> (H <sub>2</sub> +CO) conv.:                  | 176   | 180   | 169   | 203   | 179   | 189   |  |
| (H/C) Atomic Ratio in HC :                                       | 2.14  | 2.14  | 2.14  | 2.13  | 2.14  | 2.14  |  |
| Selectivities, Wt % of HC :                                      |       |       |       |       |       |       |  |
| Methane  | 3.15  | 3.18  | 3.24  | 2.87  | 3.15  | 3.06  |  |
| Ethane   | 2.03  | 1.91  | 1.93  | 1.57  | 1.71  | 1.66  |  |
| Ethane   | 0.78  | 0.85  | 0.91  | 0.80  | 0.86  | 0.82  |  |
| Propene  | 3.27  | 3.24  | 3.63  | 2.88  | 3.15  | 3.02  |  |
| Propane  | 0.62  | 0.64  | 0.74  | 0.60  | 0.67  | 0.65  |  |
| Butenes  | 2.60  | 2.60  | 3.27  | 2.36  | 2.61  | 2.47  |  |
| i-Butane   | 0.04  | 0.04  | 0.05  | 0.04  | 0.04  | 0.03  |  |
| n-Butane   | 0.61  | 0.63  | 0.84  | 0.62  | 0.68  | 0.67  |  |
| C <sub>5</sub> - C <sub>11</sub> (2)                             | 5.24  | 5.11  | 6.98  | 4.62  | 5.21  | 5.21  |  |
| Light Hydrocarbons (3)   | 14.87 | 14.96 | 16.82 | 19.77 | 17.33 | 16.73 |  |
| Heavy Hydrocarbons (4)   | 16.47 | 16.55 | 11.04 | 13.00 | 14.23 | 15.33 |  |
| Slurry Rx.-Wax   | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |  |
| Total  | 100   | 100   | 100   | 100   | 100   | 100   |  |

- (1) Including Oxygenates
- (2) In Gas Phase Only
- (3) Collected in Chilled and Ambient Condensers
- (4) Collected in Hot Condenser

Table B-1 (Cont'd)  
 First Stage Fischer-Tropsch Slurry Reactor  
 Operating Conditions and Material Balances  
 (Second-Stage Not Operative)  
 (Run CT-255-11)

| (Nitrogen-Free Basis)  | 11- 8 | 11- 9 | 11- 10 | 11- 11 | 11- 12 |
|--|-------|-------|--------|--------|--------|
| M.B. No.   |       |       |        |        |        |
| Days On-stream   | 8.3   | 9.3   | 10.3   | 12.3   | 14.3   |
| First-Stage Conditions:                                      |       |       |        |        |        |
| Charge H <sub>2</sub> /CO (Molar)                            | 0.661 | 0.676 | 0.682  | 0.682  | 0.682  |
| Temperature, °C  | 259   | 258   | 258    | 258    | 257    |
| Pressure, MPa  | 1.480 | 1.480 | 1.480  | 1.480  | 1.480  |
| Feed Sup. Vel., cm/s   | 5.789 | 5.736 | 5.748  | 5.180  | 8.070  |
| Space Vel., NL/gFe-hr  | 2.300 | 2.300 | 2.300  | 2.300  | 2.300  |
| N <sub>2</sub> in Feed, Mol %                                | 0.6   | 0.5   | 0.6    | 0.6    | 0.6    |
| Conversions, Mol % :   |       |       |        |        |        |
| H <sub>2</sub>   | 73.11 | 69.12 | 70.72  | 71.19  | 36.75  |
| CO   | 89.23 | 85.97 | 87.92  | 86.22  | 48.79  |
| H <sub>2</sub> +CO   | 82.70 | 79.17 | 80.95  | 80.12  | 43.91  |
| Yields, Wt % of Products :                                   |       |       |        |        |        |
| Hydrocarbons (1)   | 21.88 | 21.61 | 22.82  | 22.91  | 12.11  |
| CO <sub>2</sub>  | 65.05 | 61.75 | 62.98  | 61.28  | 30.24  |
| H <sub>2</sub> O (1)   | 1.49  | 1.49  | 1.46   | 1.49   | 1.67   |
| H <sub>2</sub>   | 1.27  | 1.47  | 1.38   | 1.34   | 3.20   |
| CO   | 10.32 | 13.68 | 11.66  | 13.00  | 52.77  |
| Total  | 100   | 100   | 100    | 100    | 100    |
| Bal Recovery, Wt % of Charge:                                | 99.28 | 97.71 | 99.43  | 100.90 | 92.35  |
| (CO <sub>2</sub> )(H <sub>2</sub> )/(CO)(H <sub>2</sub> O) : | 30.61 | 25.31 | 29.24  | 24.03  | 8.28   |
| gHC/Nm <sup>3</sup> (H <sub>2</sub> +CO) conv.:              | 204   | 207   | 215    | 224    | 198    |
| (H/C) Atomic Ratio in HC :                                   | 2.14  | 2.13  | 2.14   | 2.14   | 2.14   |
| Selectivities, Wt % of HC :                                  |       |       |        |        |        |
| Methane  | 3.19  | 2.93  | 3.32   | 3.27   | 2.89   |
| Ethane   | 1.88  | 1.60  | 1.70   | 1.73   | 2.38   |
| Ethane   | 0.85  | 0.80  | 0.93   | 0.97   | 0.66   |
| Propene  | 3.26  | 2.99  | 3.17   | 3.23   | 3.27   |
| Propane  | 0.50  | 0.64  | 0.69   | 0.68   | 0.73   |
| Butenes  | 2.55  | 2.42  | 2.59   | 2.57   | 2.59   |
| i-Butane   | 0.04  | 0.04  | 0.04   | 0.05   | 0.05   |
| n-Butane   | 0.70  | 0.68  | 0.72   | 0.74   | 0.75   |
| C <sub>5</sub> - C <sub>11</sub> (2)                         | 5.23  | 5.11  | 5.19   | 5.10   | 7.21   |
| Light Hydrocarbons (3)                                       | 16.20 | 16.62 | 15.96  | 15.18  | 24.01  |
| Heavy Hydrocarbons (4)                                       | 15.48 | 15.97 | 15.34  | 16.22  | 4.78   |
| Slurry Rx.-Wax   | 50.00 | 50.00 | 50.00  | 50.00  | 50.00  |
| Total  | 100   | 100   | 100    | 100    | 100    |

- (1) Including Oxygenates
- (2) In Gas Phase Only
- (3) Collected in Chilled and Ambient Condensers
- (4) Collected in Hot Condenser

Table B-2  
Composition of Hydrocarbon Products from  
First-Stage Slurry F-T Reactor  
(Second-Stage Not Operative)  
(Run CT-258-11)

| M.B. No.                        | 11- 2 | 11- 3 | 11- 4 | 11- 5 | 11-6  | 11- 7 |
|---------------------------------|-------|-------|-------|-------|-------|-------|
| Days On-stream                  | 2.3   | 3.3   | 4.3   | 5.3   | 6.3   | 7.3   |
| METHANOL                        | 0.06  | 0.05  | 0.06  | 0.04  | 0.04  | 0.07  |
| METHANE                         | 3.15  | 3.18  | 3.24  | 2.87  | 3.15  | 3.06  |
| ETHENE                          | 2.03  | 1.91  | 1.93  | 1.57  | 1.71  | 1.66  |
| ETHANE                          | 0.78  | 0.85  | 0.91  | 0.80  | 0.88  | 0.82  |
| PROPENE                         | 3.27  | 3.24  | 3.63  | 2.88  | 3.15  | 3.02  |
| PROPANE                         | 0.62  | 0.64  | 0.74  | 0.60  | 0.67  | 0.65  |
| I-BUTANE                        | 0.04  | 0.04  | 0.05  | 0.04  | 0.04  | 0.03  |
| 1-BUTENE+2-METHYLPROPENE        | 2.51  | 2.51  | 3.15  | 2.27  | 2.52  | 2.43  |
| N-BUTANE                        | 0.61  | 0.63  | 0.64  | 0.62  | 0.68  | 0.67  |
| TRANS-2-BUTENE                  | 0.03  | 0.03  | 0.05  | 0.03  | 0.03  | 0.00  |
| CIS-2-BUTENE                    | 0.05  | 0.06  | 0.08  | 0.05  | 0.05  | 0.05  |
| 3-METHYL-1-BUTENE               | 0.14  | 0.13  | 0.17  | 0.11  | 0.12  | 0.11  |
| I-PENTANE                       | 0.05  | 0.05  | 0.07  | 0.04  | 0.00  | 0.04  |
| 1-PENTENE                       | 1.83  | 1.83  | 2.60  | 1.71  | 1.91  | 1.86  |
| 2-METHYL-1-BUTENE               | 0.08  | 0.07  | 0.09  | 0.06  | 0.06  | 0.06  |
| N-PENTANE                       | 0.45  | 0.46  | 0.68  | 0.45  | 0.51  | 0.50  |
| TRANS-2-PENTENE                 | 0.02  | 0.03  | 0.04  | 0.03  | 0.03  | 0.02  |
| CIS-2-PENTENE                   | 0.03  | 0.03  | 0.05  | 0.03  | 0.03  | 0.03  |
| CYCLOPENTANE                    | 0.00  | 0.00  | 0.02  | 0.00  | 0.00  | 0.00  |
| HEXENES + ISO-HEXANES           | 0.15  | 0.13  | 0.19  | 0.10  | 0.12  | 0.12  |
| 2,3-DIMETHYLBUTANE              | 0.02  | 0.02  | 0.00  | 0.01  | 0.02  | 0.01  |
| 2-METHYLPENTANE                 | 0.04  | 0.04  | 0.06  | 0.04  | 0.04  | 0.04  |
| 3-METHYLPENTANE                 | 0.02  | 0.02  | 0.02  | 0.01  | 0.02  | 0.02  |
| 1-HEXENE                        | 1.20  | 1.14  | 1.68  | 1.04  | 1.20  | 1.20  |
| N-HEXANE                        | 0.31  | 0.30  | 0.44  | 0.29  | 0.33  | 0.33  |
| HEPTENES + ISO-HEPTANES         | 0.14  | 0.12  | 0.15  | 0.10  | 0.10  | 0.11  |
| 1-HEPTENE                       | 0.48  | 0.46  | 0.46  | 0.38  | 0.48  | 0.48  |
| N-HEPTANE                       | 0.12  | 0.12  | 0.12  | 0.11  | 0.13  | 0.13  |
| C8-OLEFINS + ISO-P              | 0.01  | 0.02  | 0.02  | 0.02  | 0.00  | 0.02  |
| 1-OCTENE                        | 0.11  | 0.10  | 0.09  | 0.08  | 0.10  | 0.10  |
| N-OCTANE                        | 0.03  | 0.03  | 0.03  | 0.02  | 0.03  | 0.03  |
| C9-OLEFINS + ISO-P              | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  |
| ACETONE                         | 0.15  | 0.13  | 0.26  | 0.11  | 0.14  | 0.14  |
| I-PROPANOL                      | 0.13  | 0.12  | 0.19  | 0.12  | 0.18  | 0.14  |
| UNKNOWN LITE HYDRO-CARB LIQ (1) | 14.87 | 14.96 | 16.82 | 19.77 | 17.33 | 16.73 |
| UNKNOWN HVY HYDRO-CARB LIQ (2)  | 16.47 | 16.55 | 11.04 | 13.60 | 14.23 | 15.33 |
| SLURRY REACTOR-WAX              | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |

(1) Collected in Ambient and Chilled Condensers  
(2) Collected in Hot Condenser

Table B-2 (Cont'd)  
 Composition of Hydrocarbon Products from  
First-Stage Slurry F-T Reactor  
 (Second-Stage Not Operative)  
 (Run CT-256-11)

| M.B. No.                        | 11- 8 | 11- 9 | 11-10 | 11-11 | 11-12 |
|---------------------------------|-------|-------|-------|-------|-------|
| Days On-stream                  | 8.3   | 9.3   | 10.3  | 12.3  | 14.3  |
| METHANOL                        | 0.05  | 0.04  | 0.04  | 0.04  | 0.19  |
| METHANE                         | 3.19  | 2.93  | 3.32  | 3.27  | 2.89  |
| ETHENE                          | 1.68  | 1.60  | 1.70  | 1.73  | 2.38  |
| ETHANE                          | 0.85  | 0.80  | 0.93  | 0.97  | 0.86  |
| PROPENE                         | 3.25  | 2.90  | 3.17  | 3.23  | 3.27  |
| PROPANE                         | 0.50  | 0.64  | 0.69  | 0.66  | 0.73  |
| I-BUTANE                        | 0.04  | 0.04  | 0.04  | 0.05  | 0.05  |
| 1-BUTENE+2-METHYLPROPENE        | 2.46  | 2.34  | 2.50  | 2.47  | 2.55  |
| N-BUTANE                        | 0.70  | 0.68  | 0.72  | 0.74  | 0.75  |
| TRANS-2-BUTENE                  | 0.03  | 0.03  | 0.03  | 0.04  | 0.00  |
| CIS-2-BUTENE                    | 0.05  | 0.05  | 0.05  | 0.05  | 0.04  |
| 3-METHYL-1-BUTENE               | 0.11  | 0.11  | 0.12  | 0.13  | 0.15  |
| I-PENTANE                       | 0.08  | 0.06  | 0.00  | 0.06  | 0.07  |
| 1-PENTENE                       | 1.88  | 1.79  | 1.88  | 1.84  | 1.99  |
| 2-METHYL-1-BUTENE               | 0.08  | 0.05  | 0.05  | 0.06  | 0.07  |
| N-PENTANE                       | 0.51  | 0.50  | 0.53  | 0.53  | 0.58  |
| TRANS-2-PENTENE                 | 0.03  | 0.02  | 0.03  | 0.03  | 0.00  |
| CIS-2-PENTENE                   | 0.03  | 0.03  | 0.03  | 0.03  | 0.00  |
| HEXENES + ISO-HEXANES           | 0.11  | 0.11  | 0.11  | 0.12  | 0.20  |
| 2,3-DIMETHYLBUTANE              | 0.01  | 0.01  | 0.02  | 0.02  | 0.03  |
| 2-METHYLPENTANE                 | 0.04  | 0.38  | 0.04  | 0.04  | 0.08  |
| 3-METHYLPENTANE                 | 0.02  | 0.02  | 0.02  | 0.02  | 0.00  |
| 1-HEXENE                        | 1.18  | 1.14  | 1.18  | 1.11  | 1.64  |
| N-HEXANE                        | 0.34  | 0.00  | 0.34  | 0.33  | 0.45  |
| HEPTENES + ISO-HEPTANES         | 0.12  | 0.11  | 0.10  | 0.11  | 0.13  |
| 1-HEPTENE                       | 0.45  | 0.47  | 0.45  | 0.40  | 0.96  |
| N-HEPTANE                       | 0.13  | 0.14  | 0.13  | 0.13  | 0.28  |
| C8-OLEFINS + ISO-P              | 0.02  | 0.02  | 0.02  | 0.02  | 0.03  |
| 1-OCTENE                        | 0.10  | 0.10  | 0.10  | 0.08  | 0.41  |
| N-OCTANE                        | 0.03  | 0.03  | 0.03  | 0.03  | 0.11  |
| C9-OLEFINS + ISO-P              | 0.01  | 0.01  | 0.01  | 0.01  | 0.12  |
| ACETONE                         | 0.13  | 0.13  | 0.12  | 0.13  | 0.26  |
| I-PROPANOL                      | 0.13  | 0.12  | 0.19  | 0.14  | 0.21  |
| UNKNOWN LITE HYDRO-CARB LIQ (1) | 16.20 | 16.62 | 15.98 | 15.16 | 24.01 |
| UNKNOWN HVY HYDRO-CARB LIQ (2)  | 15.48 | 15.97 | 15.34 | 16.22 | 4.78  |
| SLURRY REACTOR-WAX              | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |

(1) Collected in Ambient and Chilled Condensers  
 (2) Collected in Hot Condenser

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