At eighteen DOS, an in-situ hydrogen regeneration of the F-T catalyst was tried. Run CT-256-2 was terminated after twenty days on stream with the total hydrocarbons produced estimated to be about 135 g/gFe.

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

A second-stage reactor, containing 215 g of II-B ZSM-5 catalyst, was brought into operation two hours after the beginning of the synthesis operation. The material balances for the run are summarized in Table C-3 of Appendix C. Table C-4 gives the detailed product hydrocarbon compositions.

Also, catalyic severity of the second-stage operation was guided by the $i-C_4/(C_3^= +C_4^=)$ molar ratio in the combined gas stream after the second-stage reactor. To achieve a ratio of 0.8-1.0, an initial temperature of 288°C to the inlet of the second-stage reactor was used. The reactor inlet temperature was then adjusted upward by about 5.3°C per day to compensate for the second-stage catalyst aging. This temperature policy was found to be adequate for the run.

Figure 14 shows the effect of second-stage operating severity, expressed as the $i-C_4/(C_4^= +C_3^=)$ molar ratio in the product, on the gasoline yield. On this plot, the alkylate yield is estimated by alkylating first the $C_4^=$ and then $C_3^=$ with $i-C_4$. If there is an excess of light olefins, they are then converted to "cat-poly gasoline" using conventional catalytic polymerization process. In making this plot, the product yields are normalized after excluding the components that are either nonreactive to or bypassing the ZSM-5 catalyst, such as C_4^- paraffins and the reactor-wax. Peak C_5^+ gasoline yields of 90-95 wt % could be achieved when the second-stage reactor operating severity was maintained at an $i-C_4/(C_3^= +C_4^=)$ molar ratio of 0.6 to 1.2. The corresponding raw liquid hydrocarbon R+O octanes were 89 to 92.
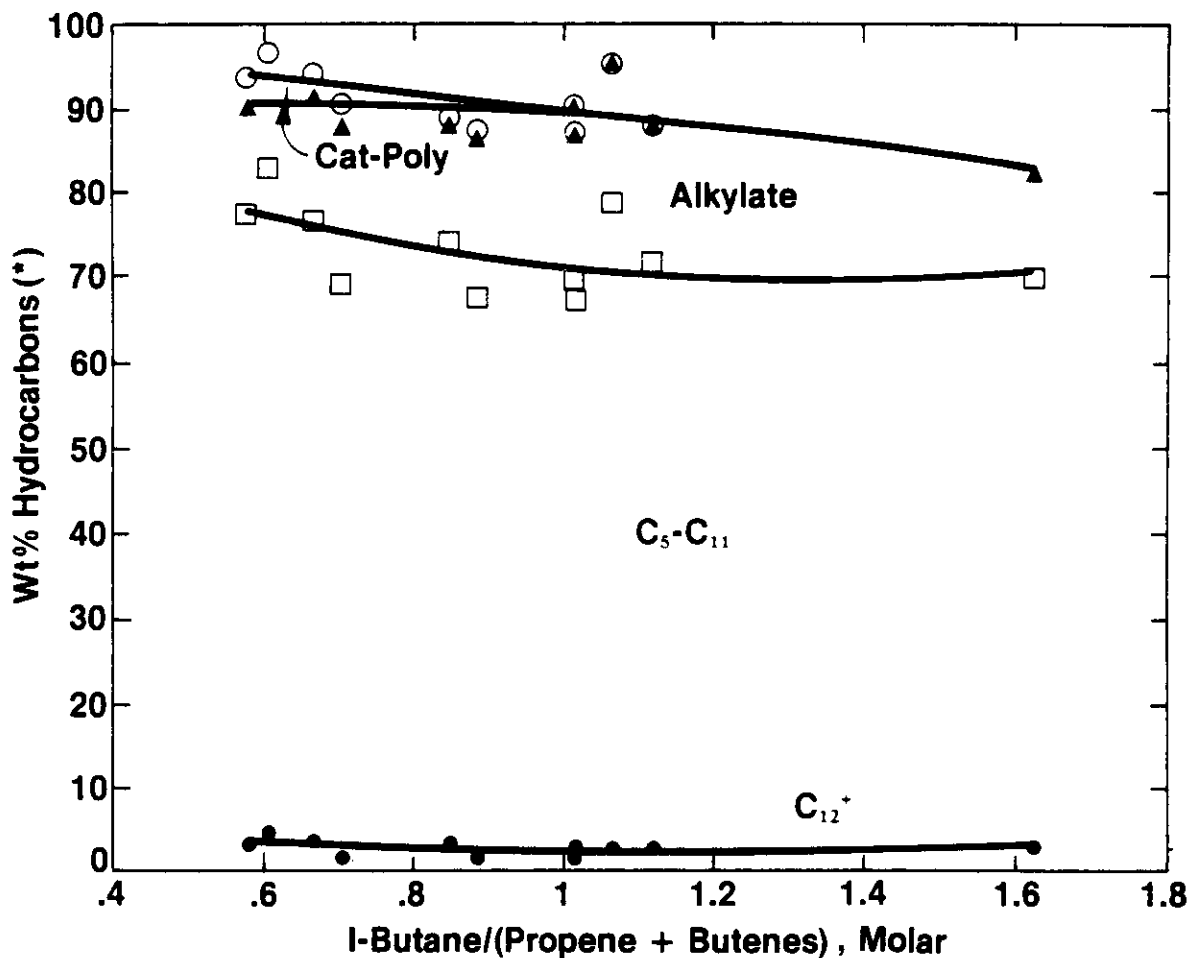
D. Run CT-256-3

1. Highlights

The third BSU run, designated as Run CT-256-3, using Catalyst I-B (containing $Fe/Cu/K_2CO_3$) in the first-stage bubble-column F-T reactor and Catalyst II-B (a ZSM-5 class catalyst) in the second-stage fixed-bed reactor, was smoothly started up on July 27, 1982. The major objectives were to evaluate the performance of the F-T catalyst I-B over an extended period of time and then to perform process variable studies. The major events and operational results of this run are summarized in Tables 15 and 16, respectively.

FIGURE 14

PRODUCT YIELDS VERSUS
SECOND-STAGE OPERATING SEVERITY
(RUN CT-256-2)

*Excluding C_4^- Paraffins in Feed and Reactor-wax

Table 15

Major Events in Run CT-256-3

(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
-0.4-0.0	Pretreatment: 1st-Stage: 282°C; 1.14 MPa; 4.2 cm/s.
0.0-8.0	Syntheses started: 1st-Stage: 282-260°C, 1.48 MPa; 4.2-3.7 cm/s.
8.0-16.0	2nd-Stage on: 329-385°C.
16.3-17.9	2nd-Stage regeneration Upset: Unit under nitrogen nine hrs.
18.0-29.4	1st-Stage: 260-261°C; 3.7-3.5 cm/s. 2nd-Stage: 343-304-346°C.
29.7	Upset: Leak at 305 cm level flange; unit under nitrogen purge 36.5 hrs.
29.7-45.9	1st-Stage: 3.45-3.0 cm/s. 2nd-Stage: 346-466°C.
46.5-47.8	2nd-Stage regeneration
50.0-59.7	1st-Stage: 261-266°C. 2nd-Stage: 304-318°C.
59.8-60.8	1.48-2.17 MPa Upset: Leak at 0 cm level flange. Slurry unloaded, then reloaded after fifty hrs.
60.9-67.9	1st-Stage: 267°C; 1.48 MPa; 3.1-2.5 cm/s. H_2/CO in feed: 0.7-0.6 2nd-Stage: 323-349°C.
67.9-80.0	1st-Stage: 1.48-2.5 MPa: 2.5-3.7-1.0-2.8-2.5 cm/s. 2nd-Stage: 349-408°C.
80.8	Addition of a potassium-salt.
81.3-85.9	Hydrodynamic upset 1st-Stage: 2.51-1.48-2.51 MPa. 2nd-Stage: 408⟶426°C.
86.0	End of Run CT-256-3

Table 16

Ranges of Operation Results (Run CT-256-3)

First Stage	Range of Results
H_2+CO Conv., Mol %	54-93
Methane + Ethane Yield, Wt % HC	6-18
Reactor-Wax Yield, Wt % HC	3-13

Second-Stage Hydrocarbon Yield, Wt %

	Before Alkylation	After Alkylation
C_1+C_2	9-20	9-20
C_3-C_4	14-38	12-28
C_5-C_{11}	32-55	46-68
C_{12}+ (excel. reactor-wax)	1-9	1-9

Properties of Raw Liquid Hydrocarbons [1]

Aromatics, Wt %	12-41
Acid No., mgKOH/gHC (unwashed)	0.04-0.4
Octane No., R+0	82-94
M+0	74-84

[1] Collected in ambient and chilled condensers.

Major highlights of this run were:

- Smooth operation of the slurry F-T reactor with high catalyst loading (20.7 wt % initially), high synthesis gas throughput, and high conversion was demonstrated over a period of eighty-six days.

  The ranges of the first-stage slurry F-T reactor operating conditions and performance were:

H_2+CO Flow Rate, Nm^3/hr	1.0-2.6
Temperature, °C	259-267
Pressure, MPa	1.13-2.51
H_2/CO Feed Molar Ratio	0.6-1.0
Superficial Feed-Gas Velocity, cm/s	1.2-4.4
SV, NL/gFe-hr	1.3-3.4
Catalyst Loading, wt % (nominal)	11-21
H_2+CO Conversion, mol %	54-93
Methane + Ethane Yield, wt % HC	6-18
Hydrocarbon Production, gHC/gFe	815

- The ranges of the second-stage fixed-bed reactor operating conditions were:

Temperature, Inlet, °C	288-466
GHSV (STP), l/hr	1,350-4,580

  This catalyst performed satisfactorily in converting the first-stage F-T products into high octane gasoline.

- There were two small and one large interruptions in the Fischer-Tropsch synthesis operation. A slight loss in Fischer-Tropsch catalyst activity and a slight increase in methane yield were observed during the small interruptions. The major interruption took place at sixty-one DOS due to a leak at the bottom flange of the slurry reactor. The slurry was unloaded and reloaded into the reactor after a new gasket was installed. Substantial deterioration of the catalyst activity and substantial increase in the methane + ethane yield were observed. The F-T catalyst seems to be very sensitive to exposure to the air.

- The reactor-wax yield increased significantly with decreasing methane + ethane yield.

- A H_2/CO feed ratio of 0.6 (instead of 0.7) was used for twenty-six days with no significant effect on the F-T catalyst stability. Lower methane + ethane yield was observed during this time. The H_2/CO usage ratio is very close to 0.6 as indicated by the fact the exit

H_2/CO ratio remained at nearly 0.6 over a wide range of conversion. The usage of the synthesis gas is better at 0.6 feed-gas H_2/CO ratio.

- Higher operating pressure with constant superficial feed-gas velocity in the slurry F-T reactor resulted in a slightly lower H_2+CO conversion, but a significantly lower methane + ethane yield (from 11 wt % to 9% when pressure increased from 1.48 MPa to 2.51 MPa). The oxygenate yield also increased significantly over the same pressure range.

- Addition of a potassium-salt to the slurry reactor drastically decreased the methane + ethane yield from 13 wt % to 8%. Unfortunately, no conclusions on synthesis gas conversion and catalyst stability could be drawn.

- The gas holdup data in the slurry bubble-column were estimated using a system of DP-cell legs. There was no significant change of gas holdup profiles in the first seventy-five DOS. Catalyst concentration profiles along the bubble-column were also measured and found to follow profiles predicted by a published mathematical model on slurry settling.

- A "hydrodynamic upset" of the slurry reactor occurred at eighty-two DOS, probably due to catalyst settling, resulting in a low H_2+CO conversion and a 5°C lower temperature at the upper portion of the reactor. The upset disappeared after eight hours of high gas velocity operation, but reappeared after the velocity was lowered.

- A second-stage ZSM-5 reactor operating severity index, expressed as the $i-C_4/(C_3^= + C_4^=)$ molar ratio in the product, of 0.5-1.0 gave maximum gasoline yield. Higher pressure operation had no significant effect on the second-stage operation and yield. Peak research octane numbers of 90-94 were obtained for the raw gasoline at severity indexes of 0.3-2.0.

2. First-Stage Fischer-Tropsch Reactor Operation

Catalyst loading and pretreatment similar to those in Run CT-256-2 were used in this run. 1,407 g of F-T catalyst I-B along with 4,572 g of spent reactor-wax were loaded. The initial catalyst loading was 20.7 wt %.

The F-T catalyst pretreatment conditions were:

H_2+CO Flow Rate, Nm^3/hr	1.89
H_2/CO Feed Ratio, Molar	0.70

Superficial Feed-Gas Vel., cm/s	4.0
SV, NL/gFe-hr	2.0
Temperature, °C	282
Pressure, MPa	1.14

The pretreatment operation was ended after ten hours when the CO conversion reached 82 mole %. Figure 15 shows the product gas volume contraction, CO and H_2+CO conversions, and CO_2 and methane concentration in the product gas during the pretreatment.

Immediately after the catalyst pretreatment, the slurry reactor temperature was lowered to 260°C in steps of 3°C over a thirty-seven hour period. With each drop in temperature, the conversion first declined, then gradually increased back to the original conversion level. This policy of temperature reduction kept the conversion high during this transition period. The pressure was increased to 1.48 MPa at this time, establishing the conditions which were used for the majority of the run. This brought the carbon monoxide conversion to about 90%, the target.

Figure 16 shows the conversion and methane and ethane selectivities, as well as the temperature pressure, and superficial gas velocity for the entire run. The range of synthesis conditions and performance of the first stage F-T reactor were:

H_2+CO Flow Rate, Nm^3/hr	1.0-2.6
H_2/CO Feed Ratio, Molar	0.6-1.0
Superficial Feed-Gas Vel., cm/s	1.2-4.4
SV, NL/gFe-hr	1.3-3.4
Temperature, °C	259-267
Pressure, MPa	1.13-2.51
H_2+CO Conversion, mol %	54-93
Methane + Ethane Yield, wt %	6-18

The run can be roughly divided into two parts. In the first part, a long-term aging study on the Catalyst I-B was carried out. After the long-term stability of the synthesis operation was well established, a period of process variable studies was commenced at sixty-one DOS. The process variables examined include:

● Superficial feed-gas velocity

● Reactor pressure

● Feed H_2/CO ratio

FIGURE 15

RUN CT-256-3
FISCHER-TROPSCH CATALYST PRETREATMENT
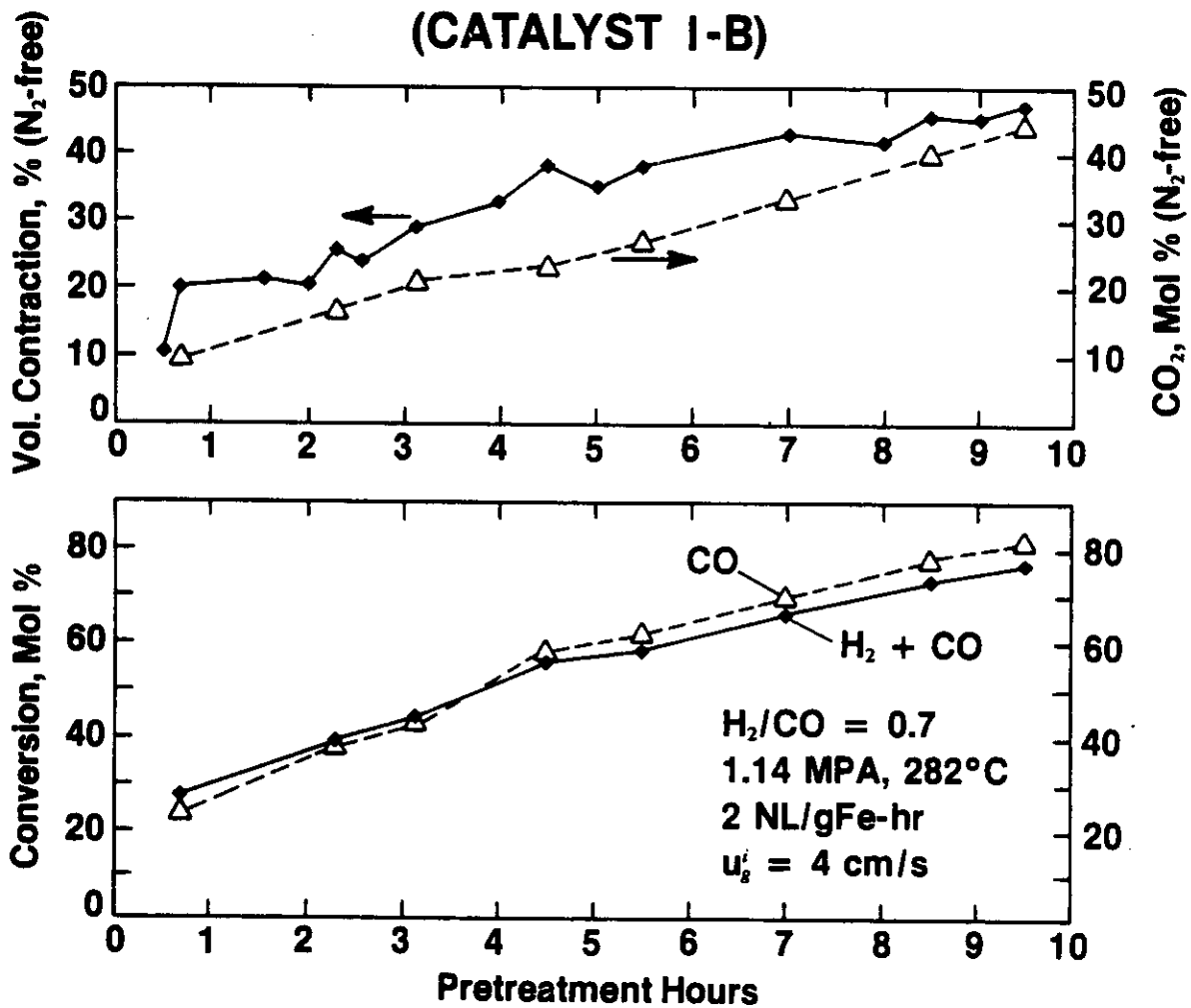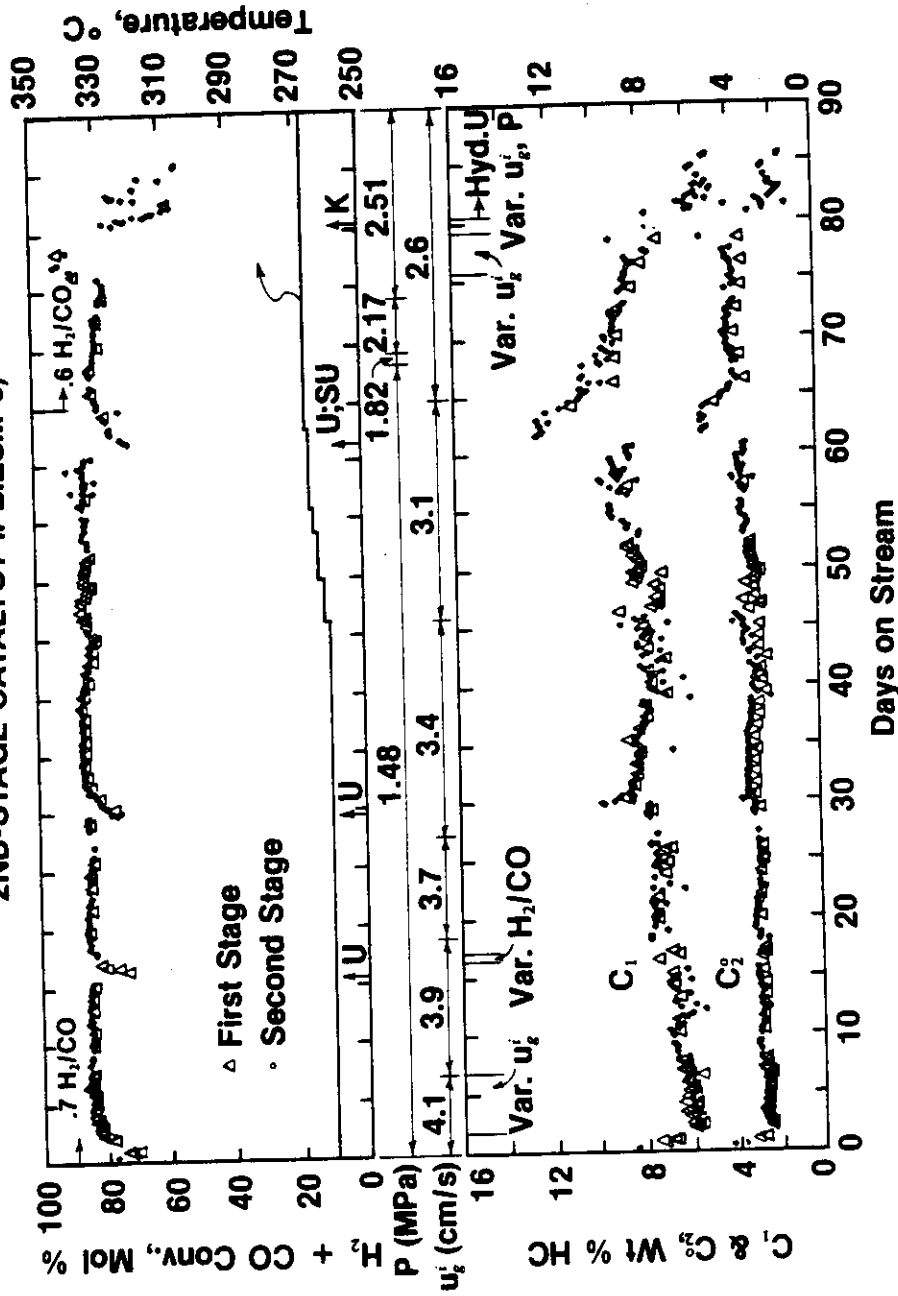## (CATALYST I-B)

FIGURE 16

SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD

(RUN CT-256-3, 1ST-STAGE CATALYST I-B:PPTD Fe/Cu/K$_2$CO$_3$;
2ND-STAGE CATALYST II-B:ZSM-5)

U - Upset   SU - Slurry Unloaded   K - Addition of a Potassium-Salt

● Addition of a potassium-salt

The synthesis operation was interrupted three times during the run. The first interruption was due to a false alarm and lasted nine hours, during which time the unit was purged with nitrogen. The second interruption was caused by a small slurry leak at the 305 cm flange. Tightening the flange stopped the leak, and synthesis gas flow was restored after thirty-six hours. Both of these interruptions caused a slight decrease in conversion and a corresponding increase in methane + ethane selectivity. This type of behavior has been observed before. The third interruption was another slurry leak, this time at the bottom flange. The leak could not be stopped by merely tightening the flange, so the slurry had to be removed while the gasket was replaced. The slurry was then reloaded after fifty hours and synthesis continued. The result was a substantial increase in the methane + ethane selectivity (from 13 to 19 wt %) and a substantial decrease in H_2+CO conversion (from 87 to 70%). Conversion increased for the next five-day period to 80%, aided by a 2°C temperature increase. It demonstrated that exposure to air is detrimental to catalyst performance.

At eighty-one DOS, an amount of potassium-salt was added to the slurry reactor through the catalyst slurry loading pot in an effort to lower the methane + ethane yield. It is clear from Figure 16 that the methane + ethane selectivity dropped from 13 to 8 wt % with little change on synthesis gas conversion. Unfortunately, however, an unexpected upset which occurred about twelve hours after the potassium-salt addition negated any improvement that addition of the potassium-salt might have imparted to the H_2+CO conversion. Addition of a potassium salt to a slurry F-T reactor has been previously reported by Koelbel and Ackermann (1951) and Koelbel and Ralek (1980).

This "Hydrodynamic Upset" took place following a sensitivity study of the superficial gas velocity. The velocity had been brought down as low as 1.1 cm/s for the study, after which it was reestablished at 2.6 cm/s. The potassium-salt was then added, and the conversion then dropped rapidly from over 80% to 55%, while the reactor temperature above the 305 cm level was 5°C lower than that below 305 cm. It was suspected that the catalyst had settled during the low-velocity operation. Therefore, at eighty-two DOS, the reactor pressure was dropped in stages to 1.48 MPa (200 psig) in order to increase the linear superficial gas velocity in the slurry reactor. This higher gas velocity reestablished uniform reactor temperature after three days. At that time, the synthesis gas conversion also rose to 78%. The superficial feed-gas velocity at this point was 4.2 cm/s. However, when the pressure was increased back to 2.51 MPa (350 psig) the next day, the temperature discrepancies returned with conversion slowly dropping back to the 55% level.

At this time, it was decided to terminate the run. The total accumulative hydrocarbon production for the run was 815 gHC/gFe, a new record.

Material balances were performed daily. Tables D-1 and D-2 summarize the operating conditions and results for this run. Detailed analytical breakdowns of the first-stage products were also performed. Table D-3 shows the composition of the hydrocarbon products produced by the Fischer-Tropsch catalyst for several balances. The oxygenated products were broken down separately and are displayed in Table D-4. In addition, the oxygenates contained in the aqueous phase were analyzed, as shown in Table D-5. The reactor-wax, which was removed by filtration, was broken down on the basis of carbon number. Table D-6 tabulates the results of these studies, while Figures 17 and 18 are graphical representations of some of these distributions. It is interestsing to note that between six and twenty-one DOS the distribution had reached a steady-state at 1.48 MPa reactor pressure with peak carbon numbers of 27-28 and similar average carbon numbers. The initial wax medium obviously contained some heavier components as indicated by a peak carbon number of 35 at six DOS. At higher reactor pressures (2.17 MPa and higher), however, slightly heavier hydrocarbons are retained in the slurry reactor as shown in Figure 18. The shift is small with a peak carbon number about 30-31 and an average carbon-numbers of about 28-29.

Reactor-wax was removed regularly to keep the level in the slurry reactor at 610-670 cm. DP-cell readings were used to determine the slurry inventory in the reactor at any given time. A cumulative reactor-wax production curve (Figure 19) is very smooth up to sixty-one DOS as indicated by the least-squares-fitted curve. The reactor-wax production rate at any given time was estimated using the corresponding slope of the curve. In this way, the reactor-wax yields as a percentage of the total hydrocarbon yield were calculated and included in Tables D-1 and D-2. The reactor-wax production data between sixty-one and seventy-four DOS were out-of-line because the major operational upset occurred at sixty-one DOS. During that time, the slurry was unloaded from and reloaded into the reactor. The reactor-wax yields up to sixty-one DOS are plotted against the methane + ethane selectivities in Figure 20. It confirms that at lower methane + ethane yields, the reactor-wax yield increases significantly.

Inclusion of all hydrocarbons and oxygenates from a total material balance allows the construction of a Schultz-Flory type plot (Flory, 1967), as shown in Figure 21. There is a distinct change in the slope (α) of the distribution (probability of chain growth) from 0.79 to 0.88 at carbon number twenty-two, coinciding approximately with the inclusion of the reactor-wax. This trend resembles that of a similar plot given for Run
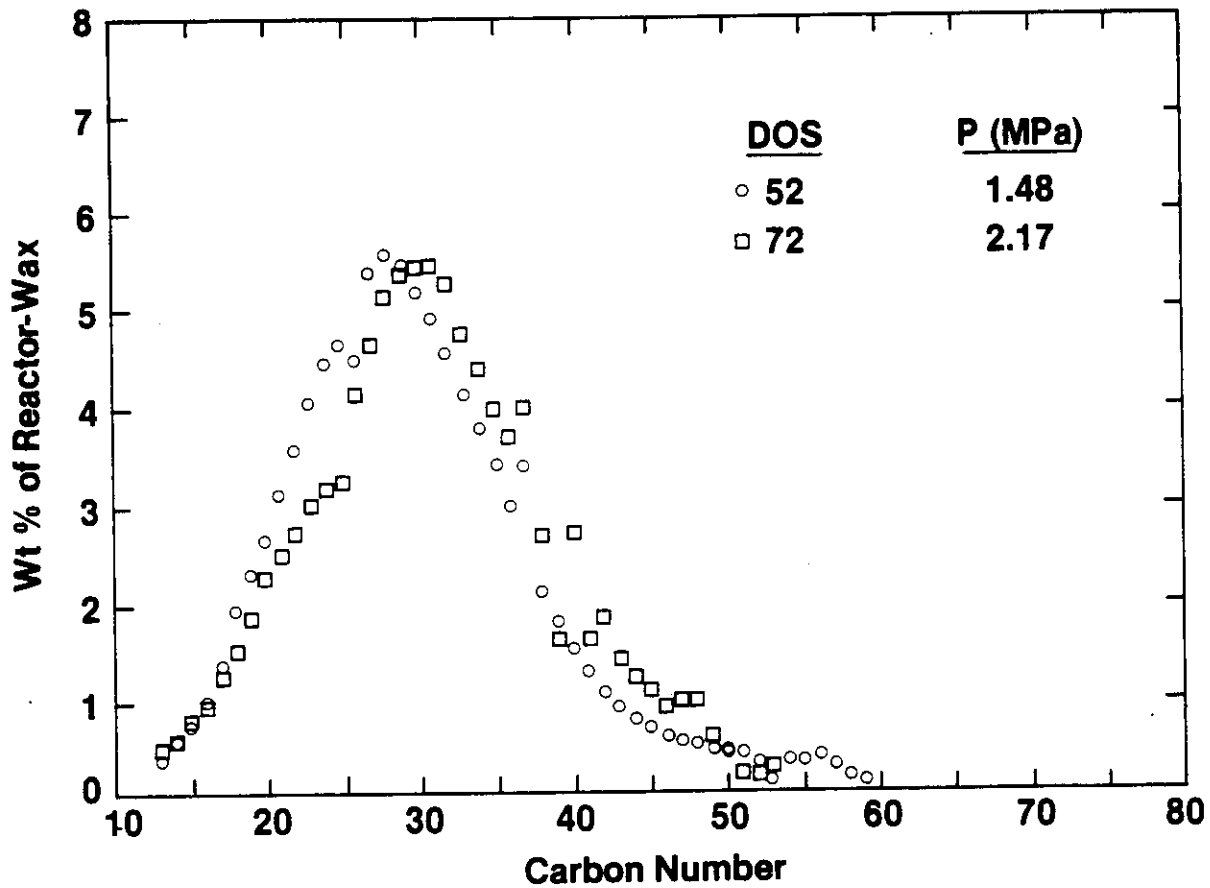
FIGURE 17

REACTOR-WAX CARBON-NUMBER DISTRIBUTION
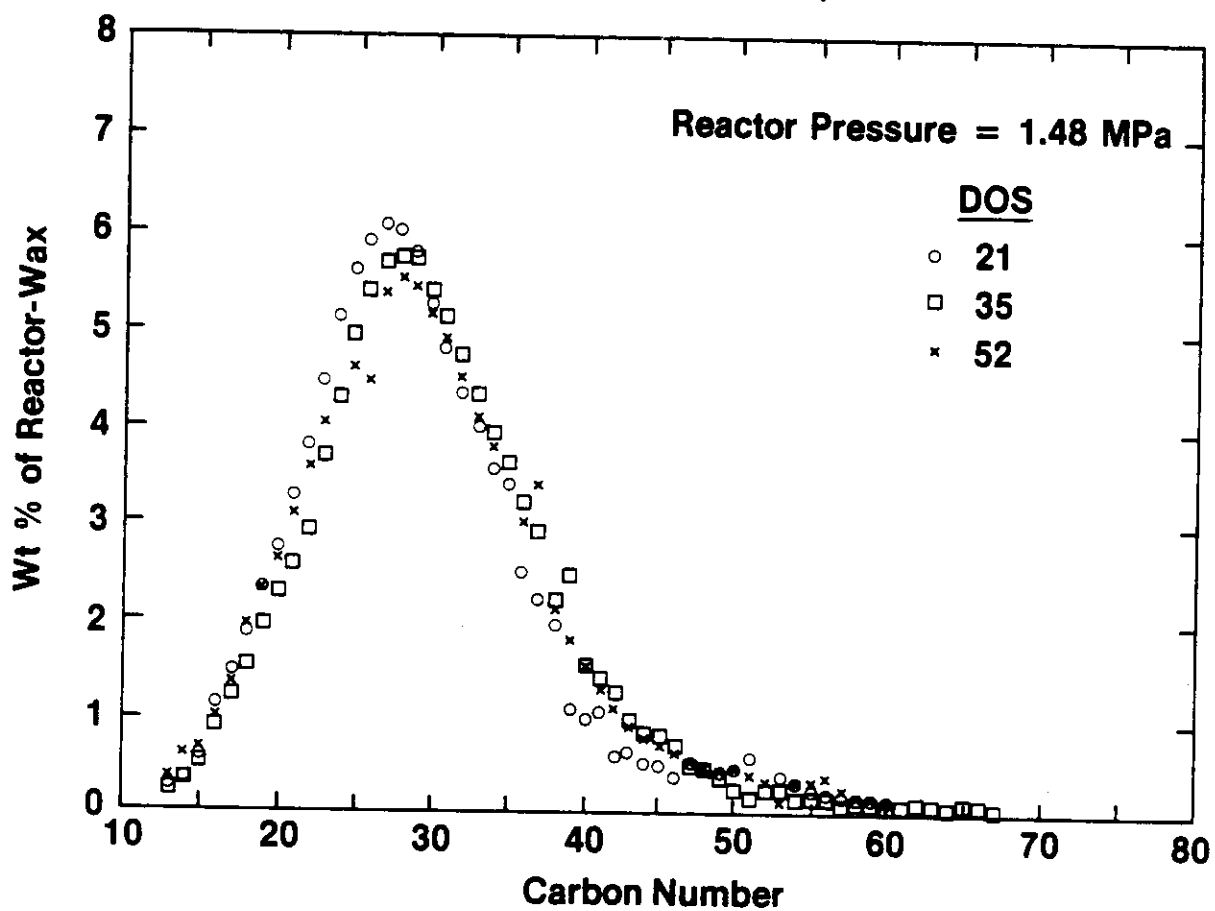
(Run CT-256-3)

FIGURE 18

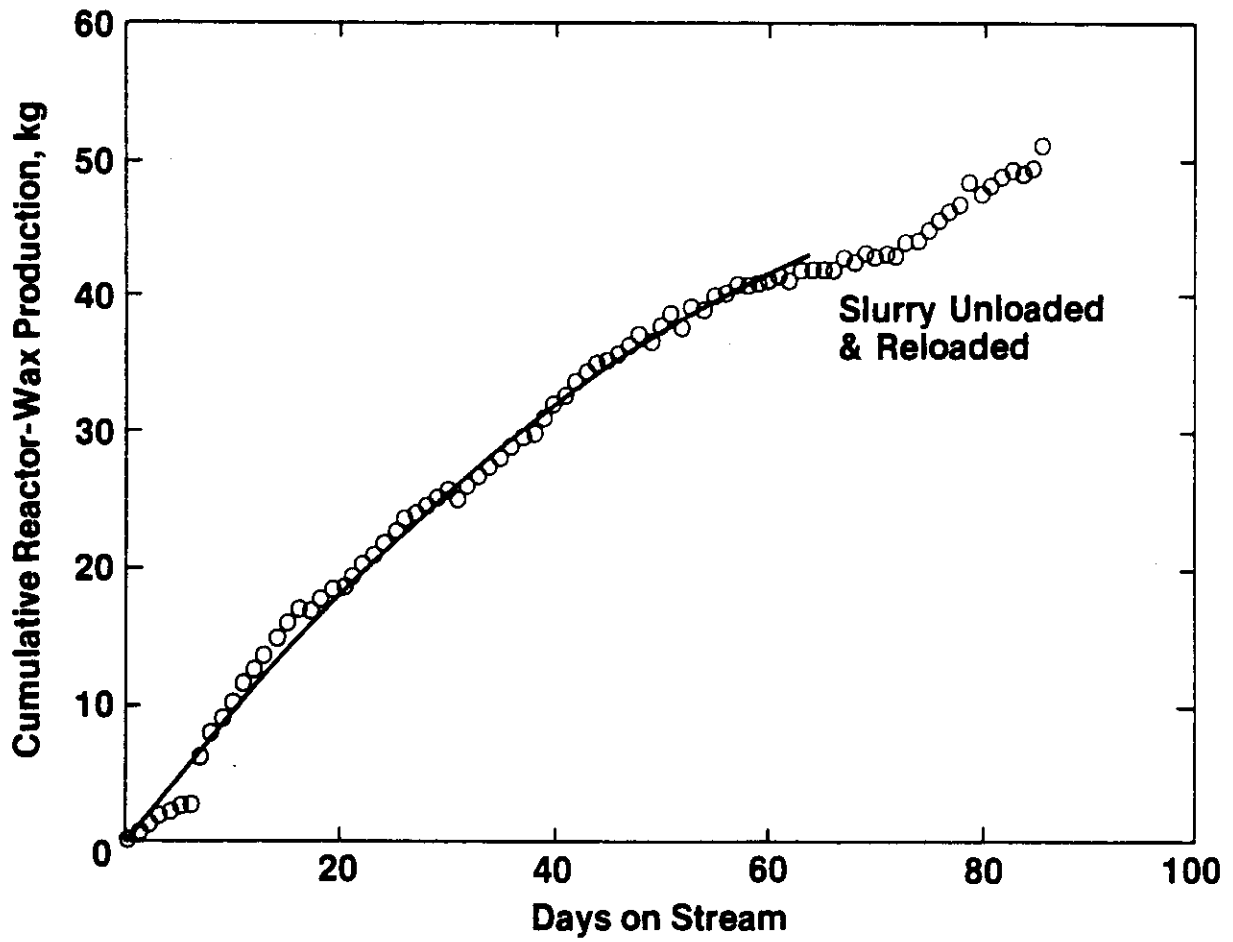**EFFECT OF REACTOR PRESSURE ON REACTOR-WAX CARBON-NUMBER DISTRIBUTION**

(Run CT-256-3)

DOS	P (MPa)
○ 52	1.48
□ 72	2.17

FIGURE 19

CUMULATIVE REACTOR-WAX PRODUCTION FROM FIRST-STAGE FISCHER-TROPSCH REACTOR

(Run CT-256-3)

Slurry Unloaded & Reloaded

X-axis: Days on Stream

Y-axis: Cumulative Reactor-Wax Production, kg

FIGURE 20

REACTOR-WAX YIELD

(Run CT-256-3)

0-61 DOS

Methane + Ethane, Wt % of Total Hydrocarbons

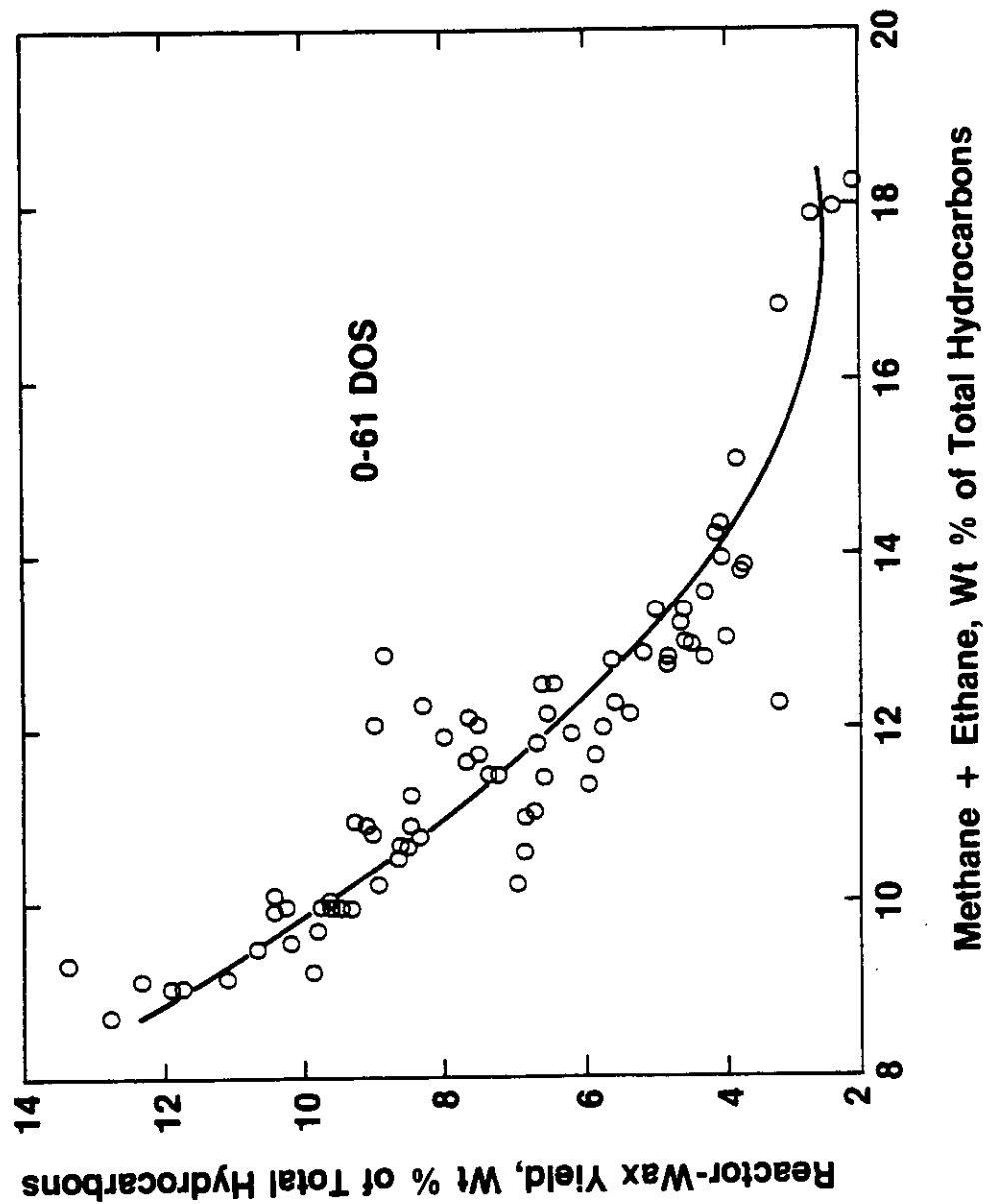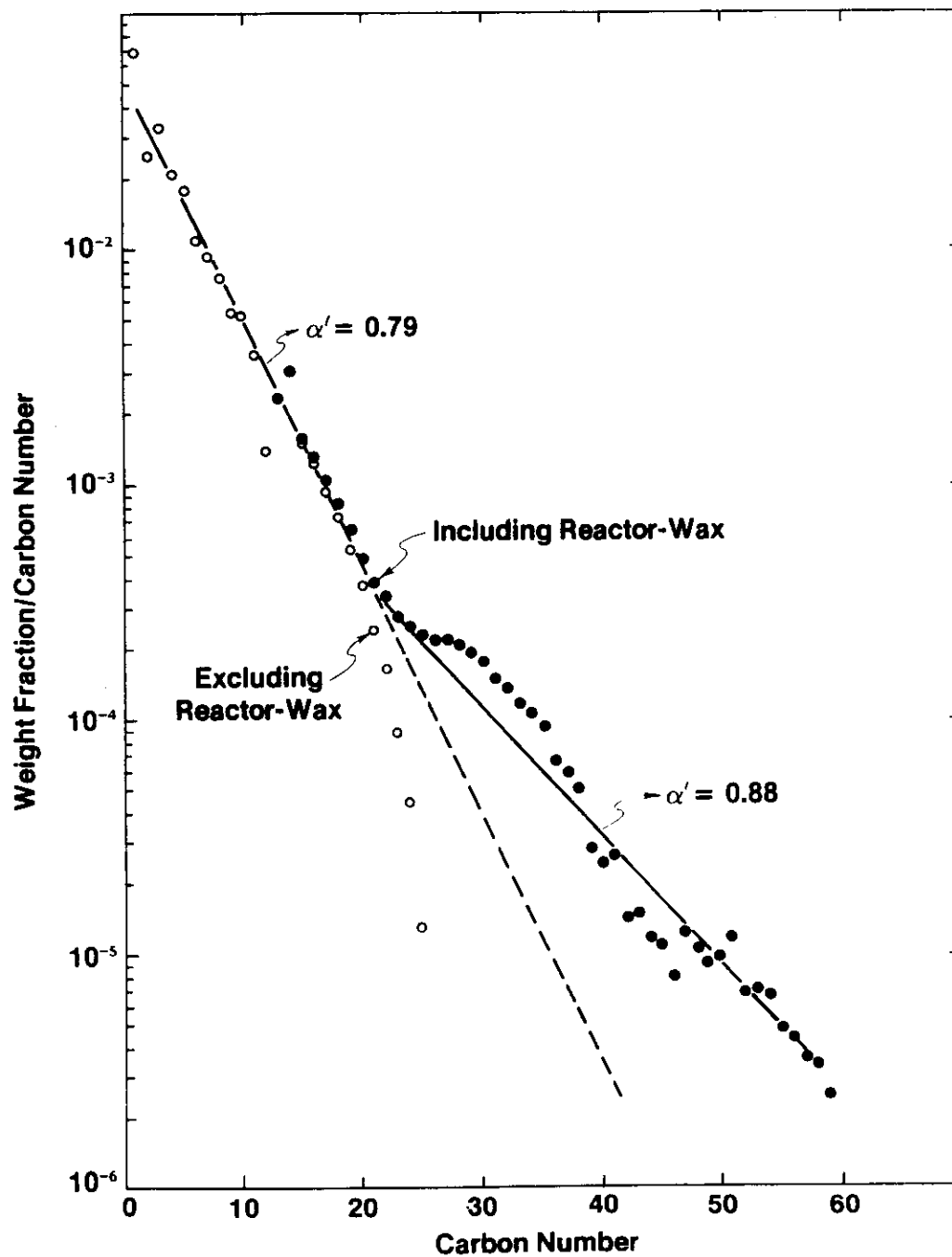Reactor-Wax Yield, Wt % of Total Hydrocarbons

FIGURE 21

SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE FISCHER-TROPSCH PRODUCTS

(Run CT-256-3, 11.5 DOS Reactor-Wax Yield — 9.5 wt %)

CT-256-1 shown in Figure 9. As explained earlier, this phenomena may be due to the fact that in a slurry system large molecules can re-absorb themselves onto active catalyst sites, allowing for further chain growth.

As the superficial gas velocity is lowered, the residence time of the synthesis gas is increased, which should increase synthesis gas conversion (Table 17). In addition the methane yield goes down slightly.

In another study, the H_2/CO ratio in the feed gas was changed from 0.7 to 0.6 to observe its effect on slurry reactor performance. This was done at sixty-five DOS and continued until the end of the run. At the time of the switch, however, the catalyst was in the process of recovering from the third upset, which had occurred at sixty-one DOS. Following an upset such as this, the conversion is initially low, then climbs steadily to a point slightly lower than that before the upset. Similarly, the methane + ethane selectivity is initially high, but then declines gradually to a level somewhat above the previous one. This seems to correspond to a "reactivation" of the catalyst. Looking at Figure 16, this same trend is evident following the upset, but it appears that the methane + ethane selectivity declines to the same level as before the upset. It is logical to conclude that the lower H_2/CO ratio in the feed enabled this to occur. By decreasing the amount of available hydrogen, the yields of hydrogen-rich components, such as methane and ethane, were decreased.

Also interesting is the effect of the feed H_2/CO ratio on the H_2/CO ratio in the exit gas shown in Figure 22. Data from the whole run are used to construct this plot. Consequently, they include wide ranges of operational variables and result in a large spread of the data. The lines shown on the figure are least-squares-fitted. Here it is seen that a feed ratio of 0.6 causes the exit ratio to remain nearly same ratio over a wide range of conversions. At 0.7 H_2/CO feed ratio, however, an excess of hydrogen appears at all times, particularly at the higher conversions. This figure indicates that the H_2/CO usage ratio is very close to 0.6. When a feed H_2/CO ratio higher than the usage ratio is used, the excess hydrogen is reflected as higher H_2/CO in the exit gas. The exit H_2/CO ratio increases with increasing synthesis gas conversion because the water-gas shift reaction favors the formation of hydrogen according to thermodynamic equilibrium. It appears, then, that there are distinct advantages to operate the synthesis at a feed H_2/CO ratio close to the usage ratio, i.e., lower methane + ethane yield and better usage of the synthesis gas. However, the long-term effects on catalyst aging have yet to be determined. Also, note that most of the 0.6 H_2/CO data were taken at higher pressure.

Table 17

Effect of Superficial Feed-Gas Velocity on Slurry Fischer-Tropsch Reactor Performance (1)
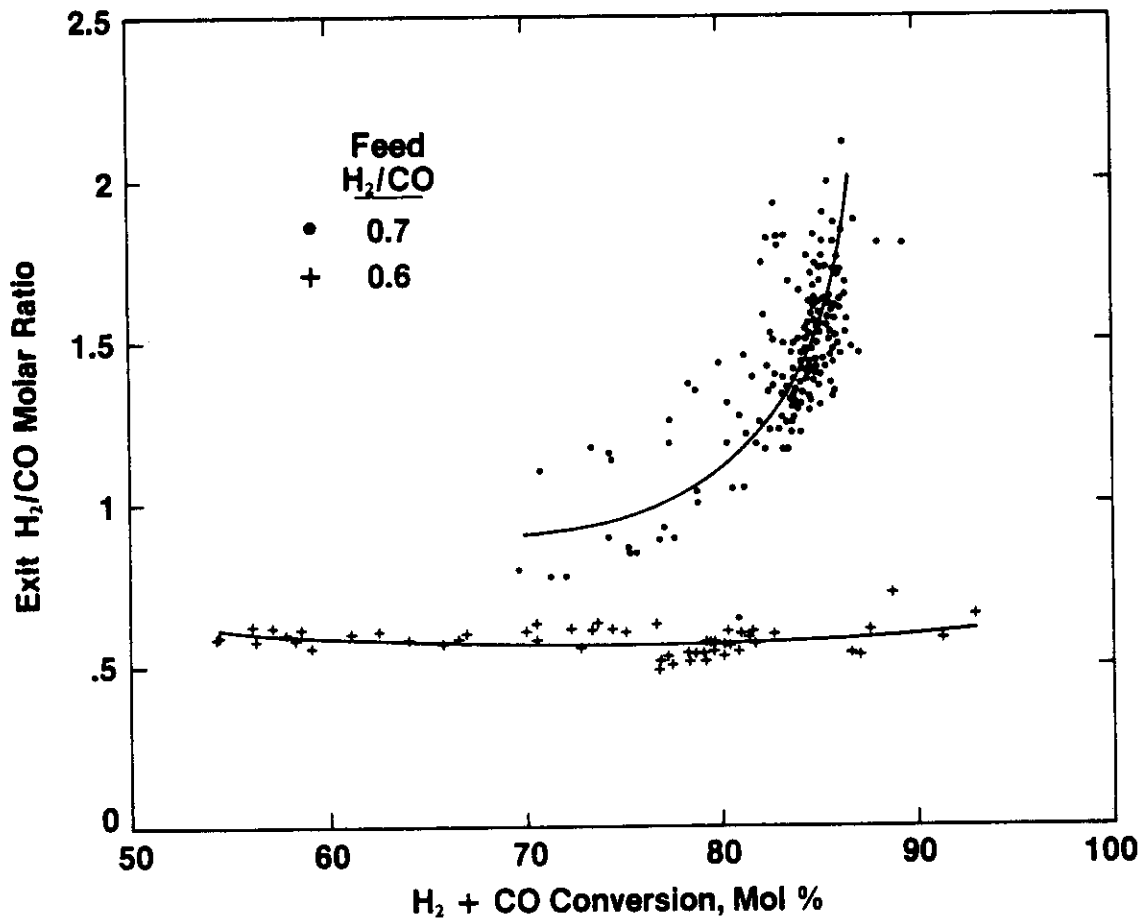
(Run CT-256-3)

DOS	75.4	76.5	77.4
Gas Superficial Velocity, cm/s	2.5	2.1	1.6
SV, NL/gFe-hr	3.12	2.53	1.95
H_2+CO Conv., Mol %	77.1	87.2	93.1
Methane, Wt % HC	8.8	8.5	7.8
Methane + Ethane, Wt % HC	12.7	12.6	12.2

(1)0.6 H_2/CO, 267°C, 2.51 MPa

FIGURE 22

EXIT H₂/CO RATIO OF FIRST-STAGE
SLURRY FISCHER-TROPSCH REACTOR

(Run CT-256-3)

Pressure effects were studied at a feed H_2/CO ratio of 0.6 and a temperature of 267°C. As the pressure was changed, the synthesis gas flow rate was altered so that the same superficial feed-gas velocity was maintained at 2.6 cm/s. Table 18 shows the results of this process variable study. The pressure was varied from 1.48 to 2.51 MPa (200 to 350 psig) over an eight-day period. It is seen that the methane and ethane yields decrease as the pressure is raised. This is due to the higher probability of the chain-growth under higher pressure. The effect on synthesis gas conversion, though, is less clear. The conversion drops slightly with increasing pressure although the superficial feed-gas velocity is maintained constant. The 2% drop in conversion between 2.17 and 2.51 MPa may be mainly due to experimental data scattering. However, the space velocities were greatly increased due to higher pressure operation. This increase in the space velocity is more than sufficient to compensate for the slightly lower conversion at the same feed-gas velocity. Of course, the other major advantage is the significant drop in the methane yield.

The effect of pressure on the yield of oxygenated products was also noted, as shown in Table 19. This shows that as the pressure is increased, so is the oxygenate yield. The magnitude of the increase is not clear from this table, however, because the other process variables were also changed (H_2/CO ratio, superficial velocity, and temperature).

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

The second-stage reactor, containing 215 g of II-B ZSM-5 catalyst, was brought on-stream one hour after the end of the F-T catalyst pretreatment. The material balances performed over the sixty-seven days of second-stage operation are summarized in Table D-7 of Appendix D. The properties of the raw liquid hydrocarbons collected from the ambient and chilled condensers are reported in Table D-8, while Table D-9 gives the detailed product hydrocarbon compositions.

Also, as mentioned in previous runs, the severity of the second-stage operation was guided by the $i\text{-}C_4/(C_3^=+C_4^=)$ molar ratio (the severity index) in the combined gas stream after the second-stage reactor. To achieve a severity index of 0.8-1.0, the initial inlet temperature of the second-stage reactor was set to 343°C. This cycle was started in Run CT-256-2 (see Subsection VI.C.2.) In this run, the catalyst was regenerated twice with no apparent loss of activity. During the twenty-eight day second cycle and the unfinished thirty day third cycle operation, the second-stage inlet temperature had to be increased at about 5.3 °C/day to maintain the target severity. The fixed-bed inlet temperature and the temperature rise across the catalyst bed are reported in Figure 23.

Table 18

Effect of Pressure on Slurry Fischer-Tropsch
Reactor Performance [1]

(Run CT-256-3)

DOS	66.8	68.8	72.4	74.8
Pressure, MPa	1.48	1.82	2.17	2.51
SV, NL/gFe-hr	1.95	2.32	2.77	3.12
H_2+CO Conv., Mol %	81.2	81.7	79.5	77.5
Methane, Wt % HC	10.8	10.1	9.4	8.7
Methane + Ethane, Wt % HC	14.8	14.4	13.6	12.6

[1] 0.6 H_2/CO, 267°C, 2.6 cm/s superficial feed-gas velocity.

Table 19

Effect of Pressure on Oxygenates Yield from
First-Stage Fischer-Tropsch Reactor
(Run CT-256-3)

DOS	50.6	74.5
Pressure, MPa	1.48	2.51
Temperature, $^{\circ}C$	263	267
Feed H_2/CO, Molar	0.7	0.6
Superficial Feed-Gas Velocity, cm/s	3.1	2.6
SV, NL/gFe-hr	2.18	3.15
H_2+CO Conversion, Mol %	85.2	77.5
Oxygenates, Wt % of HC	8.6	12.0

FIGURE 23

SECOND-STAGE FIXED-BED ZSM-5 REACTOR
INLET AND OUTLET TEMPERATURES

(Run CT-256-3)