

- Successfully demonstrated a F-T catalyst/reactor-wax separation method using batch external catalyst settling vessels.
- Demonstrated that exposure of F-T catalyst slurry to air reduced its catalytic activity and increased the methane + ethane yield. Also, on two occasions of minor operational upsets, when the synthesis gas flow to the first-stage reactor was replaced by nitrogen for twenty-five to forty-five hours, the subsequent F-T catalyst activity reduced slightly, while the methane + ethane increased slightly.
- Demonstrated that addition of a potassium-salt in the first-stage F-T reactor resulted in rapid reduction of methane + ethane yield. However, its effect on the long-term operation of the reactor is unknown.
- Demonstrated that a methane + ethane yield of less than 5 wt % of the total hydrocarbons produced could be achieved using F-T catalyst I-B at 2.52 MPa (350 psig) and 257°C. However, reactor-wax yields were increased to 46-51 wt %.
- Discovered that a F-T catalyst (designated as I-C) could be activated without using a specific pretreatment step. Methane + ethane yield of less than 3.5 wt % was also demonstrated at reactor conditions of 240-250°C and 1.48 MPa (200 psig). Reactor-wax yields ranged from 57 to 85 wt %.

## B. Run CT-256-1

### 1. Highlights

The first run of the BSU, CT-256-1, using Catalyst I-A (containing Fe/Cu/K<sub>2</sub>CO<sub>3</sub>) in the first-stage bubble-column reactor and Catalyst II-A (a ZSM-5 class catalyst) in the second-stage fixed-bed reactor was successfully concluded on May 17, 1982. The main objectives of this run were to break in the BSU, and to evaluate the F-T catalyst I-A. The total on-stream time was sixty-one days for Catalyst I-A and forty-nine days for Catalyst II-A. The unit was then shut down for modifications and maintenance in preparation for the second F-T catalyst evaluation. The major events of this run are summarized in Tables 3 and 4. Tables 5 and 6 summarize, respectively, the ranges of the process variables studies and the results from this run.

Major highlights from this run are:

Table 3

## Major Events in Run CT-256-1

(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
0	Pretreatment
0.5	Upset: High slurry-level alarm
5-8.1	1st stage: 1.3--2.2 cm/s 260--266°C
12.6	2nd stage: Start-up
13.7-19.0	1st stage: 1.14--1.48 MPa 1.6--1.8 cm/s 266--268°C
	2nd stage: 371--329°C
21.3	Upset: Steam and cooling water failure
21.7	Upset: Power failure
26.7	1st stage: 268--271°C
29.8-36.1	2nd stage: 329--302°C
36.2	Upset: Power failure
41.9-47.6	1st stage: 268--274°C 1.8--3.2 cm/s
	2nd stage: 292--316°C
48.0-52.8	1st stage: 0.7--1.2--0.7 H <sub>2</sub> /CO
54.8-58.0	1st stage: 268--282°C 1.3--2.2 cm/s 1.14--1.83 MPa
58.0	Charge H <sub>2</sub> off. 1.8--1.0 cm/s
58.1	Charge H <sub>2</sub> back on. 1.0--1.8 cm/s
58.3	Syn-gas off; N <sub>2</sub> on
58.4	Syn-gas on
60.5-60.8	Hydrodynamic study
61.1	End of Run CT-256-1

Table 4

Major Events in Run CT-256-1

(Reactor-Wax and Slurry Inventory)

DOS	Major events
-1.3	Slurry loading
-0.6	Slurry unloading: 2,041 g, 6.7% solid
0.1	Slurry sampling : 35 g, from 152 cm, 4.66% solid
1.9/3.0	Wax withdrawal : 291/440 g, 2.54% solid
4.0	Slurry sampling : 42 g, from 152 cm, 2.64% solid
6.8	Wax withdrawal : 1,624 g, 2.6% solid
6.8/18.9	Slurry sampling : 60/64 g, from 152 cm, 2.6/1.78% solid
33.9/34.7	Wax withdrawal : 1,351/626 g, 1.6% solid
34.8	Slurry sampling : 30 g, from 152 cm, 1.69% solid
	Slurry loading : 200 g cat I-A, 11.8 g Mobil base stock F-509, 1,048 g FT-200 wax
40.8	Slurry sampling : 19.2 g, from 152 cm, 1.5% solid
	Wax withdrawal : 1,026 g, 1.59% solid
	Slurry loading : 190 g cat I-A, 119 g Mobil base stock F-509, 1,000 g FT-200 wax, 1,000 g n-decane
41.8/42.7	Slurry sampling : 50/54 g, from 152 cm, 1.9% solid
43.5	Solvent loading : 1,500 g n-decane
43.8	Slurry sampling : 34 g, from 152 cm, 2.64% solid
46.9	Solvent loading : 1,500 g n-decane
47.8/55.7	Slurry sampling : 118/245 g, from 30/152 cm, 3.85/2.62% solid
	Wax withdrawal : 1,473 g, 2.54% solid
60.8	Slurry sampling : 265.2/38.7/53.8/135.1 g from 30/152/305/610 cm, 3.04/2.53/2.69/1.91% solid
	Wax withdrawal : 5,093 g, 2.22% solid
61.1	Slurry unloading: 2,660 g, 2.6% solid
	End of Run CT-256-1

Table 5

Ranges of Process Variables Studied  
in Run CT-256-1

First-Stage	Range of Process Variables
Temperature, °C	260-282
Pressure, MPa	1.14-1.83
Superficial Feed-Gas Vel., cm/s	1.0-3.2
SV, NL/gFe-hr	5-18
Feed H <sub>2</sub> /CO Molar Ratio	0.6-1.2
Second-Stage	
Inlet Temperature, °C	288-371
GHSV (STP), 1/hr	716-2600

Table 6  
 Ranges of Operation Results  
 -----  
 (Run CT-256-1)

First-Stage	Range of Results	
H <sub>2</sub> +CO Conv., Mol %	26-91	
Methane + Ethane Yield, Wt % HC	6-20	
Reactor-Wax Yield, Wt % HC	5-33	
Second-Stage Hydrocarbon Yield, Wt %		
	Before Alkylation	After Alkylation
C <sub>1</sub> +C <sub>2</sub>	10-14	10-14
C <sub>3</sub> -C <sub>4</sub>	29-44	19-40
C <sub>5</sub> -C <sub>11</sub>	36-51	39-62
C <sub>12</sub> <sup>+</sup> (excl. reactor-wax)	1-4	1-4
Properties of Raw Liquid Hydrocarbons <sup>(1)</sup>		
Aromatics, Wt %	17-81	
Acid No., mgKOH/gHC	0.09-1.8	
Octane No., R+0	90-98	
R+3	96-101	
M+0	79-85	
M+3	85-93	

(1) Collected in ambient and chilled condensers.

- A smooth operation of the BSU was demonstrated. Process conditions were varied over a wide range to explore the operational limit of the unit.
- An evaluation of a Fe/Cu/K<sub>2</sub>CO<sub>3</sub> F-T catalyst (I-A) was completed. The results were used to compare this catalyst against other F-T catalysts which were evaluated later.
- The conversion of the F-T products into high octane gasoline over ZSM-5 catalyst was demonstrated.
- A significant reactor-wax accumulation in the F-T slurry reactor was observed. This accumulation is expected to increase greatly with decreasing methane and ethane yield.

Detailed operational data of this run are given in the next subsection.

In this first run, the catalyst loading in the slurry reactor was not sufficiently high to obtain both a high synthesis gas throughput (higher than 3 cm/s superficial feed gas velocity) and high H<sub>2</sub>+CO conversion (higher than 85 mol %). The low catalyst loading resulted from three causes:

1. High gas holdup at the beginning of the run limited the amount of catalyst loaded into the F-T reactor.
2. Large amounts of catalyst were lost during the reactor-wax withdrawal due to a pin-hole in the wax-withdrawal filter.
3. A substantial amount of the F-T catalyst remained in the slurry loading tank and the long line between the loading tank and the reactor.

All these problems were corrected during the subsequent turnaround.

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

Before loading the first-stage catalyst I-A, the slurry reactor was heated to 260°C, with N<sub>2</sub> preheated to 260°C at a flow rate of approximately .085 Nm<sup>3</sup>/hr (superficial gas velocity of 1 cm/s). However, the top of the reactor was maintained at 204°C to minimize wax carryover in the vapor. The second-stage fixed-bed reactor was bypassed and the effluent gas was sent directly to the hot condenser. The gas stream from the hot condenser was diverted to a wax-stripper containing a mineral

spirit to help avoid any plugging downstream from the hot condenser. The distillation section was also bypassed. The hot, cold, and chilled separators were initially filled with the mineral spirit, again to dissolve any heavy hydrocarbons coming over during the early part of the run. During this period, since little or no hydrocarbon products are formed, the vapor coming over from the slurry reactor contains mostly heavy hydrocarbons stripped from the slurry wax. These hydrocarbons may condense out as wax to plug the downstream lines. The preventive design and the cautious operation procedures adopted resulted in a smooth start-up operation of this unit.

The reactor was maintained at 0.17-0.20 MPa (10-15 psig) with flowing  $N_2$  at  $0.085 \text{ Nm}^3/\text{hr}$ . 600 g of FT-200 Vestowax<sup>(1)</sup> was first loaded into the reactor through a slurry-loading tank followed by 2,775 g of slurry containing 625 g of catalyst, 750 g of Mobil F-509<sup>(2)</sup> and 1,400 g of FT-200 wax. The loading tank and the lines were then rinsed twice with 700 g of FT-200 wax each time. The unit was then pressured to 1.14 MPa (150 psig) with  $N_2$  bubbling at  $0.935 \text{ Nm}^3/\text{hr}$  (2.2 cm/s superficial gas velocity) in the reactor.

The unexpanded slurry level for 4,772 g of slurry (density of uniform slurry =  $0.71 \text{ g/cm}^3$ ) was estimated to be 311 cm. The direct observation through the 762 cm viewport indicated that the slurry level reached the lower part of the disengagement zone at 2.2 cm/s superficial gas velocity. The gas holdup at that time was more than 63 vol %, which was five times higher than that reported in the literature at the same superficial gas velocity (Deckwer, et al., 1980). This high gas holdup was probably due to a significant foaming of the FT-200 Vestowax used as the startup reactor wax. It was feared that, at the planned catalyst pretreatment gas velocity of 3.5 cm/s, the slurry level could have overflowed the top of the disengagement zone. Consequently, 2,041 g of slurry were drained from the reactor. Two samples of this slurry were taken and shown to contain 6.6 and 6.8 wt % solid based on solid content analyses. These solid contents were smaller than that of the slurry originally prepared (12.3 wt %). It was suspected that a substantial amount of the catalyst remained in the catalyst loading tanks. This suspicion was confirmed to some degree later. Based on these analyses, the amount of catalyst loaded into the reactor was 319 g instead of 625 g; the amount of the catalyst in the reactor after partial unloading was 182 g.

(1) A F-T paraffin wax probably from SASOL, with an average molecular weight of 600.

(2) A proprietary high molecular-weight parafinic base stock.

The pretreatment of the F-T catalyst I-A is reported in Figure 7. During the pretreatment, the  $H_2+CO$  conversion and the concentration of  $CO_2$  and methane in the product combined gas are monitored very closely to avoid excessive pretreatment. The use of on-line GC analytical equipment is limited to about one analysis per hour; therefore, the exact values of the conversion and the  $CO_2$  and methane concentrations may only be obtained once per hour. However, the total molar contraction of the product-gas stream was continuously monitored, which can be directly translated into the synthesis gas conversion as shown in Figure 7.

The pretreatment was terminated when the  $H_2+CO$  conversion reached 65 mol %. At that stage the reactor temperature was reduced to  $260^\circ C$ , the synthesis temperature, while keeping the same space velocity. There was no definitive criterion to judge the end of the pretreatment. Several factors such as the  $H_2+CO$  conversion, the rate of change of the conversion, the rate of change of the  $CO_2$  and  $CO$  concentrations in the effluent gas, and the total pretreatment time could all be important. In the present case, the decision was made to terminate the pretreatment because the total pretreatment time was long in comparison to prior experience.

After the pretreatment, the material balances for the first-stage operation were obtained on a daily basis. After the second-stage reactor was in operation, the material balance for the first-stage was obtained through the inter-reactor sampling of about 10% of the total first-stage reactor effluent. A prorating factor reflecting the total mass flow of the first-stage reactor effluent was used to convert that material flow into a total material balance.

The material balance data collected in the conventional way are summarized in Table B-1 of Appendix B while those collected using the inter-reactor sampling are summarized in Table B-2. Both tables also show the process conditions for the first-stage operation. The  $H_2+CO$  conversion and methane + ethane yield data vs the time-on-stream are depicted in Figure 8. Since the methane and ethane have lower product value than the  $C_3^+$  hydrocarbons and they are inert over the second-stage ZSM-5 reactor, a low yield on the methane and ethane is essential for obtaining a good process economics for this two-stage process.

The reactor-wax yields reported in Tables B-1, B-2, and B-3 (and also Tables B-7 and B-9) are those of hydrocarbons remaining in the slurry reactor under processing conditions. These values are not very accurate since the accumulated reactor-wax was withdrawn very infrequently and the reactor-wax inventory in the reactor was not monitored. The yields seemed to decrease quickly with time on-stream. The hydrocarbon yields in  $gHC/Nm^3$  ( $H_2+CO$ ) converted are also reported in these tables. A



FIGURE 7

RUN CT-256-1, PRETREATMENT OF F-T CATALYST I - A  
 (CATALYST I-A: Ppted. Fe/Cu/K<sub>2</sub>CO<sub>3</sub>)

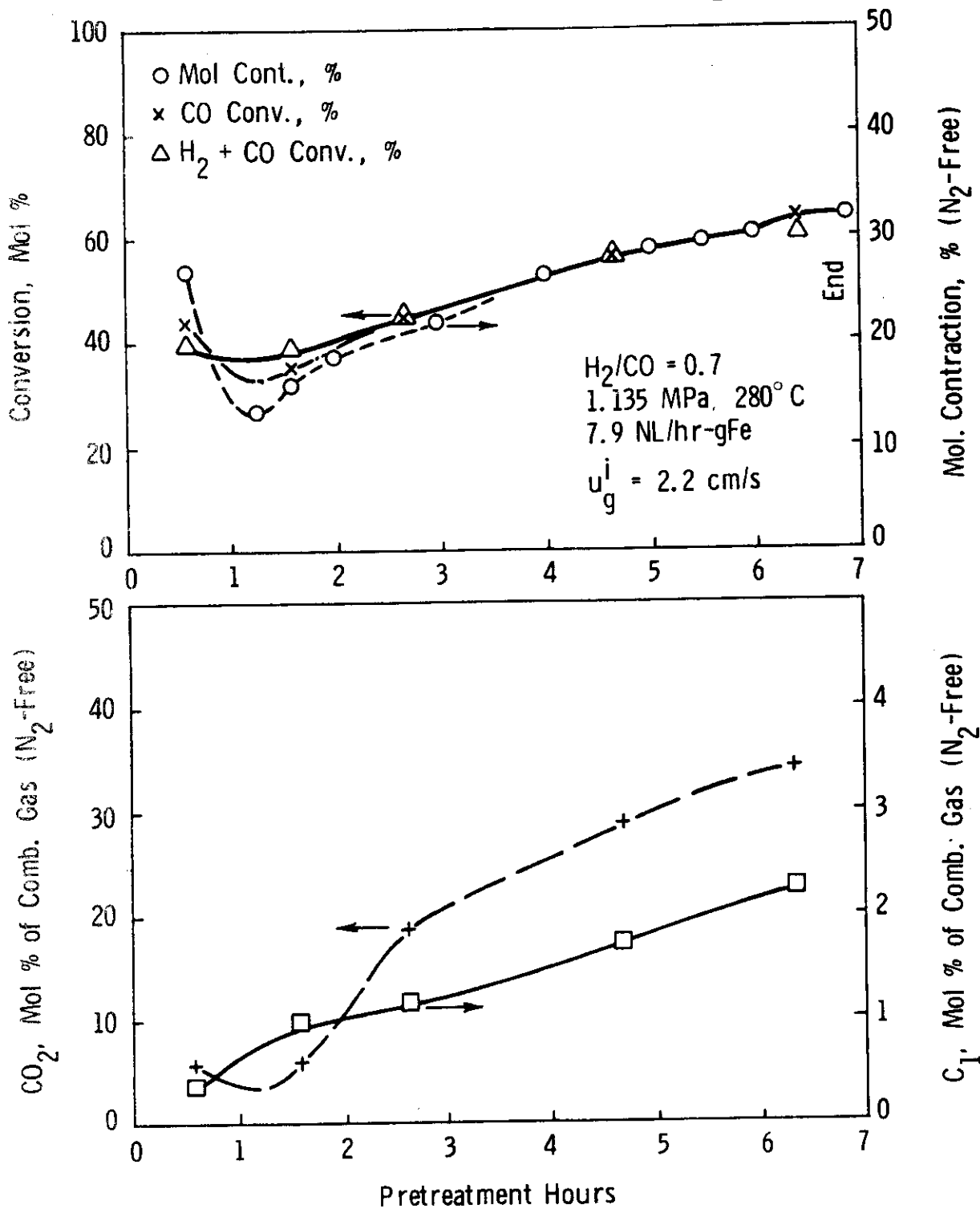
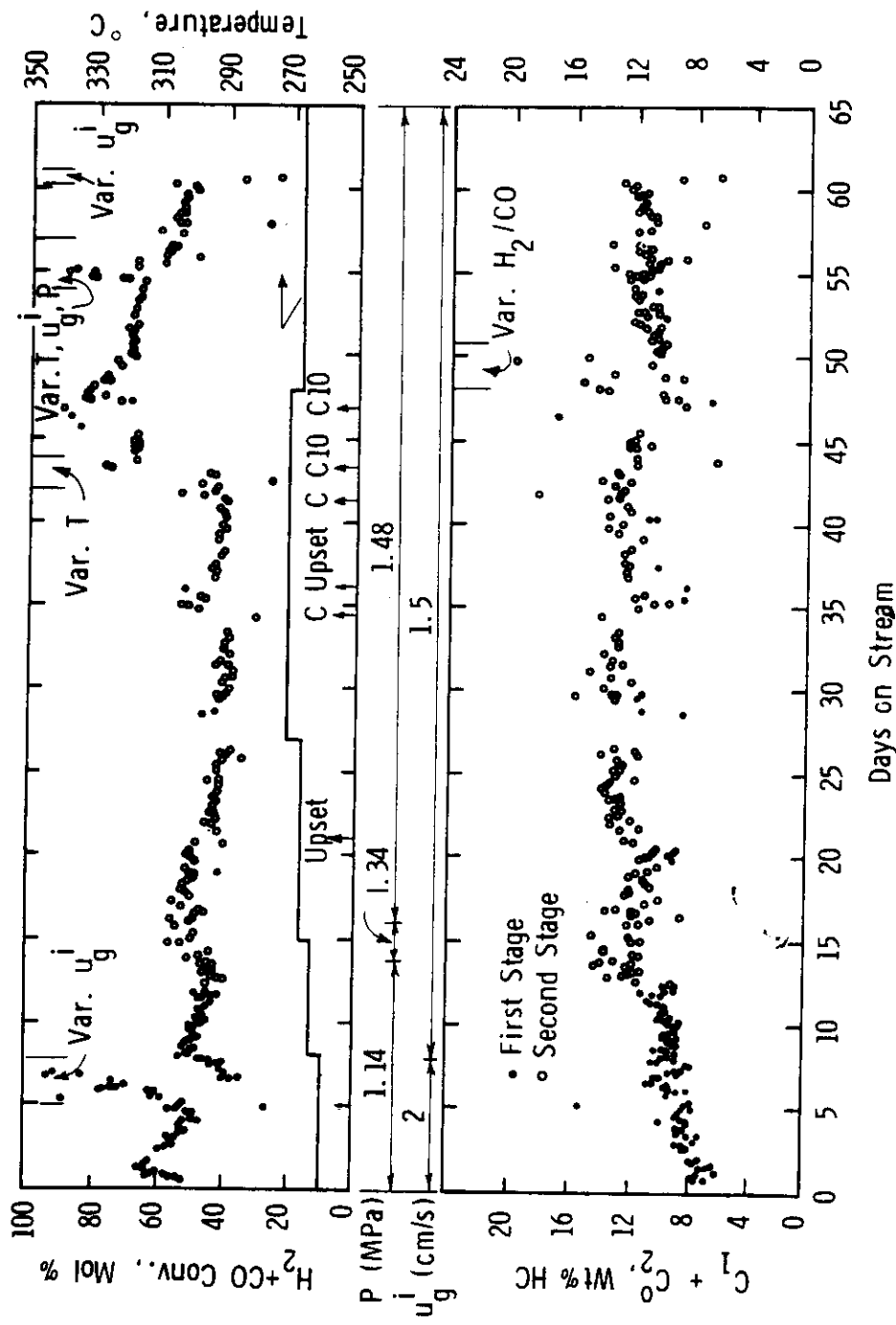


FIGURE 8  
 SYNTHESIS GAS CONVERSION AND METHANE + ETHANE YIELD  
 (Run CT-256-1, 1st-Stage Catalyst, 1-A: Pptd. Fe/Cu/K<sub>2</sub>CO<sub>3</sub>;  
 2nd-Stage Catalyst, 11-A: ZSM-5)



C - Catalyst Loaded; C10 - n-Decane Loaded; W - Wax Withdrawal

theoretical yield may be estimated when the fixed H/C atomic ratio for the total hydrocarbons produced is known. For example, if the H/C ratio for the total hydrocarbons produced is 2.25, then the theoretical hydrocarbon yield is 204 gHC/Nm<sup>3</sup> (H<sub>2</sub>+CO) converted. This theoretical yield value is adopted here as a base line value. Any deviation from this yield indicates the accuracy of the material balances.

To test the operational limit of the pilot plant and to gain experience in unit operations, a wide range of process variables was studied (Table 3). For most of the time, the H<sub>2</sub>/CO feed ratio was 0.7. Reactor temperatures of 260-271°C, pressures of 1.14-1.48 MPa and superficial feed gas velocities of 1.5 to 2 cm/s were mostly used.

In the first thirty-five HOS, there was an increase of H<sub>2</sub>+CO conversion, probably due to the under-pretreatment of the catalyst. The first reactor-wax withdrawal was carried out at two days TOS. This wax was withdrawn through a 2 μm-size sintered-plate filter. However, what was observed was a dark-colored slurry, which was later found to contain 2.5 wt% of catalyst. Obviously, the filter was not working properly, and it was later found to have a large hole in its filtering element. After about two DOS, the H<sub>2</sub>+CO conversion started to decline gradually. This decline was partially due to catalyst aging, and partially to the loss of some catalyst resulting from two reactor-wax withdrawals and one slurry withdrawal between two and five DOS. Based on solid-content analyses of the three withdrawal samples, about 11% of the catalyst originally in the reactor was withdrawn. Consequently, the space velocity increased to 8.8 at five DOS from the 7.9 NL/gFe-hr used earlier.

After five DOS, variations in the feed gas velocity were studied. At a low space velocity of 4.4 NL/gFe-hr, equivalent to a superficial gas velocity of 1.3 cm/s, the conversion increased to 80%, but seemed to decline rapidly immediately afterwards. The gas velocity was brought back to 2.2 cm/s after twelve hours of operation at 1.3 cm/s gas velocity.

The methane + ethane yield demonstrated a smooth but continuous upward trend with time. It began with about 7 wt % of the total hydrocarbons produced and increased to about 11 wt % before the second-stage ZSM-5 reactor was switched on at 13 DOS.

From fifteen to thirty-five days, the H<sub>2</sub>+CO conversion ranged from 42 to 57 mol %. There was only a small decline in the H<sub>2</sub>+CO conversion over this period. The methane + ethane yield stayed fairly constant and averaged about 13 wt % of the total hydrocarbons produced during this period. The reactor-wax yield was estimated to be about 6 wt %.

To achieve high  $H_2+CO$  conversion at a high synthesis gas throughput, it is essential to obtain high catalyst loading in the slurry reactor. Based on solid-content analysis, the catalyst loading in the bubble-column during the period of fifteen to thirty-five DOS was very low (as low as 1.6 wt %). To increase the catalyst loading, a slurry containing 210 g of fresh catalyst was put into the slurry loading tank and injected into the reactor at thirty-five DOS. An immediate, but small increase in the  $H_2+CO$  conversion was observed. However, this increase was erased at thirty-six days when the unit was shut down for fifteen minutes due to a power failure. Another injection of a slurry containing 200 g of fresh catalyst at forty-one DOS showed practically no effect on the  $H_2+CO$  conversion. It was speculated that a substantial amount of the catalyst had remained in the slurry loading tank and the line connecting the tank and the slurry reactor. This hypothesis was consistent with the unusually low catalyst loadings measured by the solid-content analysis of the slurry samples withdrawn. Higher  $H_2+CO$  conversions (70-90 mol % from 45%) were observed after washing the slurry loading tank with 1,500 g n-decane on two occasions (at forty-three and forty-seven DOS). After the n-decane washing, the solid-content of the slurry sample increased to 3.85 wt %. This problem was corrected during the subsequent turnaround.

Table 7 summarizes the effect of the reactor temperature on the slurry reactor performance. As expected, the  $H_2+CO$  conversion went up strongly with the temperature (ranged from 268 to 282°C). However, the methane, ethane, and propane yields changed little over this range of temperature. This is contrary to what was reported by Koelbel and Ralek (1980). An activation energy for the  $H_2+CO$  conversion of 135 kJ/gMol was estimated assuming first-order kinetics without accounting for the effect of the mass-transfer resistance on the  $H_2+CO$  conversion. This value is substantially larger than values ranging from 81 to 94 kJ/gMol on Fe/Cu catalysts reported by various sources (Schlesinger, et al., 1954; Deckwer, et al., 1980). Note that if the mass-transfer resistance is taken into account, the estimated activation energy would become even larger.

The exit  $H_2/CO$  ratio increased greatly with the higher  $H_2+CO$  conversion. This trend is expected because the feed  $H_2/CO$  ratio of 0.7 is higher than the  $H_2/CO$  usage ratio.

The effect of the reactor pressure is summarized in Table 8. The experiments were run with the same superficial feed-gas velocity, and no appreciable change on the  $H_2+CO$  conversion was observed. At low pressure operation (1.14 MPa or 150 psig), a moderate increase in the methane and ethane yield was observed. No definitive trend of the exit  $H_2/CO$  ratio can be observed.

Table 7

Effect of Temperature on Slurry F-T Reactor Performance<sup>(1)</sup>-----  
(Run CT-256-1)

Temperature, °C	268	271	277	282	268
DOS	54.2	54.8	55.1	55.5	55.7
H <sub>2</sub> +CO Conv., Mol %	68	72	84	91	69
Methane, Wt %	10	10	10	9	9
Methane + Ethane, Wt %	13	13	13	11	12
Exit H <sub>2</sub> /CO, Molar	.79	.76	1.0	1.5	.77

(1) 0.7 H<sub>2</sub>/CO, 1.48 MPa, 1.8 cm/s superficial feed-gas velocity  
(4.9 NL/gFe-hr space velocity).

Table 8

Effect of Pressure on Slurry F-T Reactor Performance<sup>(1)</sup>-----  
(Run CT-256-1)

DOS	56.6	56.8	56.9	57.6
Pressure, MPa	1.48	1.83	1.14	1.48
SV, NL/gFe-hr	5.8	7.2	4.5	5.8
H <sub>2</sub> +CO Conv., Mol %	59	58	59	56
Methane, Wt %	9	9	11	10
Methane + Ethane, Wt %	12	12	14	12
Exit H <sub>2</sub> /CO, Molar	.66	.63	.88	.73

(1) 0.7 H<sub>2</sub>/CO, 268°C, 1.8 cm/s superficial feed-gas velocity.

Table 9 summarizes the effect of the superficial feed-gas velocity on the slurry F-T reactor performance. The variation on the feed-gas velocity reflected directly on the space velocity. As expected, the H<sub>2</sub>+CO conversion went up with decreasing space velocity. No other significant variations on the reactor performance were observed.

The last process variable studied was the feed H<sub>2</sub>/CO ratio and the results are reported in Table 10. The effect on the H<sub>2</sub>+CO conversion showed no definitive trend. The fact that the H<sub>2</sub>+CO conversion at forty-eight DOS was significantly higher than that at fifty DOS further complicated the matter. The difference may be due mainly to the dynamic behavior of the system resulting from the changing H<sub>2</sub>/CO ratio. Nevertheless, the effect on the methane and ethane yield could be clearly observed. High H<sub>2</sub>/CO feed significantly increased the methane and ethane yield. Furthermore, when the feed H<sub>2</sub>/CO ratios are substantially higher than the H<sub>2</sub>/CO usage ratio (about 0.6), the exit H<sub>2</sub>/CO ratios become very large because there is a large excess of the hydrogen. In the middle and at the end of the feed H<sub>2</sub>/CO variable study, the ratio was restored to that at the beginning of the experiment (0.7) to check the state of the catalyst. The H<sub>2</sub>+CO conversion changed drastically from 84 mol % to 74% and then to 72%. It is questionable if this change can be attributed to the one-day operation at the 0.6 H<sub>2</sub>/CO feed gas.

Analyses of F-T products are very complicated and costly. There are altogether five product phases, i.e., gaseous, light hydrocarbon liquid, heavy hydrocarbon liquid, reactor-wax, and aqueous. The light and heavy hydrocarbon liquid phases were collected from the chilled and ambient condensers, and the hot condenser, respectively, and usually were combined into a single hydrocarbon liquid phase for analysis. The analyses of the gaseous phase posed no problem. The analyses of all other streams to give detailed breakdowns of the hydrocarbons and oxygenates, however, were very time-consuming and only made occasionally. The selectivities of hydrocarbon lumps given in Tables B-1 and B-2 were mainly based on the following analyses and assumptions:

- On-line GC analyses of the gaseous phases.
- "Carbon-number distribution" analyses of the liquid hydrocarbon phases using capillary-column GC technique.
- No analyses of the organic oxygenates in the aqueous and the liquid hydrocarbon phases.

The "Carbon-Number Distribution" analysis does not give PONA or oxygenate component breakdowns, but it does provide quick and consistent carbon-number breakdown for the F-T hydrocarbon

Table 9  
 Effect of Superficial Feed-Gas  
 Velocity on Slurry F-T Reactor Performance<sup>(1)</sup>  
 -----  
 (Run CT-256-1)

DOS	55.8	56.0	56.2	56.3
Superficial Feed-Gas Vel., cm/s	1.8	1.3	2.2	1.8
SV, NL/gFe-hr	5.8	3.9	7.8	5.8
H <sub>2</sub> +CO Conv., Mol %	61	70	51	61
Methane, Wt %	9	8	9	9
Methane + Ethane, Wt %	12	10	12	12
Exit H <sub>2</sub> /CO, Molar	.76	.76	.75	.70

(1) 0.7 H<sub>2</sub>/CO, 268°C, 1.48 MPa.



Table 10

Effect of Feed H<sub>2</sub>/CO Ratio on  
Slurry F-T Reactor Performance<sup>(1)</sup>

-----  
(Run CT-256-1)

DOS	47.7	48.1	48.8	49.6	49.9	50.4
Feed H <sub>2</sub> /CO, Molar	.7	1	.6	.7	1.2	.7
H <sub>2</sub> +CO Conv., Mol %	84	85	79	74	76	72
Methane, Wt %	8	10	7	9	14	9
Methane + Ethane, Wt %	11	14	9	11	20	11
Exit H <sub>2</sub> /CO, Molar	1.2	6.1	.88	.82	17	.90

(1) 268°C, 1.48 MPa, 1.8 cm/s superficial feed-gas velocity  
(4.9 NL/gFe-hr space velocity).

fraction. This analysis is very useful for monitoring the slurry F-T reactor operation.

In four balances covering DOS from two to five, detailed analyses of the  $C_{11}^-$  liquid hydrocarbon fraction and the aqueous phases were done. The  $C_{11}^-$  fractions were distilled from the liquid hydrocarbon phases. A Sep-Pak<sup>(1)</sup> Silica Gel Liquid Chromatography was used for the separation of the hydrocarbons and the oxygenates. Each fraction was then analyzed by gas chromatographs. The results are summarized in Tables B-3 and B-4. Table B-3 also includes those balances in which no liquid phase analyses were carried out. In those cases, only the compositions from the gaseous phase are reported. Since at the startup of this run the separators were filled with a mixture of non-F-T hydrocarbons, it took about five days for the oxygenates in the liquid hydrocarbon phases to reach a steady state, as indicated in Table B-4. The total oxygenates, mostly alcohols, reached about 5 g/100 g of the total hydrocarbon yield. For the same four balances, the aqueous phases were analyzed using a gas chromatograph and their compositions are reported in Table B-5. The yield of the oxygenates in the aqueous phases reached about 1.8 g/100 g of the total hydrocarbon yield in three days. The components were dominated by alcohols (94 wt %, mainly in  $C_1$ - $C_3$  alcohols) with small yields of ketones (5 wt %) and esters (<1 wt %). The method for detailed analysis of the  $C_{12}^+$  fraction of the hydrocarbon liquid phases has been developed, but was not used in this run.

Six reactor-wax samples were analyzed for  $C_{13}$ - $C_{74}$  hydrocarbons by a GC and results are given in Table B-6. Although the carbon-number distribution in the reactor-wax was complicated by the two intermittent injections of fresh catalyst slurries at thirty-five and forty-one DOS, some definitive trends of the shifting of the carbon-number distribution during the run can be observed:

- Large reduction of  $C_{26}$ - $C_{28}$  (from about 20 wt % to about 10 wt %).
- Large increase of  $C_{29}$ - $C_{32}$  (from about 9 wt % to about 19 wt %).
- Moderate reduction of  $C_{34}$ - $C_{36}$  (from about 27 wt % to 18-20 wt %).
- Large increase of  $C_{44}$ - $C_{63}$  (from about 10 wt % to 18-22 wt %).

(1)A registered trade mark.

It was not possible to determine if the distribution reached an equilibrium at fifty-six DOS. Further investigation will be needed.

Based on a hypothesis of a single parameter of chain-growth probability, the carbon-number distribution of the F-T products may be described by the well-known Schulz-Flory distribution (Flory, 1967) represented by the following equation:

$$\log (M_1/I) = \log (\ln^2 \alpha') + I \log \alpha' \quad (4)$$

A Schulz-Flory type carbon-number distribution plot based on the material balance at fifty-two DOS is given in Figure 9. An  $\alpha$  value, representing the chain-growth probability, of 0.70 is estimated from the plot for the hydrocarbons excluding the reactor-wax. The distribution, however, shows large deviation from the Schulz-Flory distribution when the reactor-wax is included. This phenomena may be due to the fact that in a slurry system large molecules can re-absorb onto active catalyst sites, allowing for further chain growth. The approximate reactor-wax yield at fifty-two DOS was estimated to be about 6 wt % of the total hydrocarbon produced.

The operation of this run was voluntarily terminated after sixty-one DOS. After the shutdown, the catalyst slurry was drained from the reactor. Slurry samples were taken for solid-content analysis and an attempt was made to account for the catalyst inventory. The 605 g of the catalyst initially loaded into the slurry loading tank plus the 390 g added during the run gave a total of 995 g added into loading tank. However, the solid analysis of the slurry sample unloaded after the end of the run gave only sixty-nine g of the catalyst. Later rinsing of the slurry loading tank and the slurry reactor gave another 125 g. Analysis of the solid-content of all the slurries withdrawn during the run gave 429 g. Altogether, 372 g of the catalyst could not be accounted for because of the difficulties discussed above.

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

The second-stage reactor, containing a ZSM-5 class catalyst, designatd II-A, was smoothly brought on-stream under the following conditions:

Inlet Temperature, °C	371
Reactor Pressure,	Cascaded
GHSV (STP), l/hr	880

The second-stage reactors were designed for an adiabatic operation. The conversion of the F-T products over ZSM-5 is moderately exothermic as shown by the temperature profiles given in Figure 10 for different inlet temperatures. The slight

FIGURE 9

SCHULZ-FLORY DISTRIBUTIONS FOR  
FIRST-STAGE F-T PRODUCTS  
(Run CT-256-1, 52 DOS)

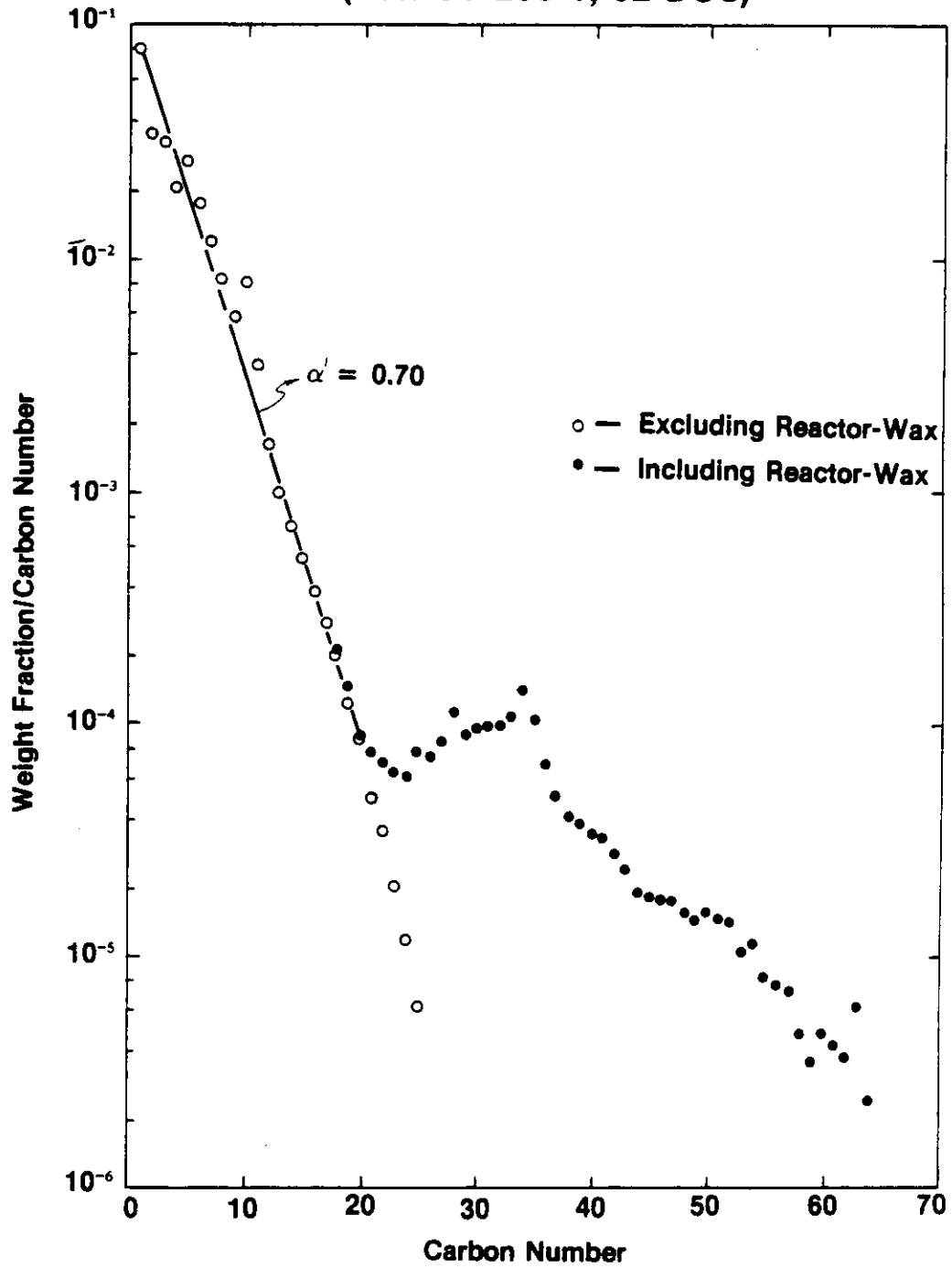
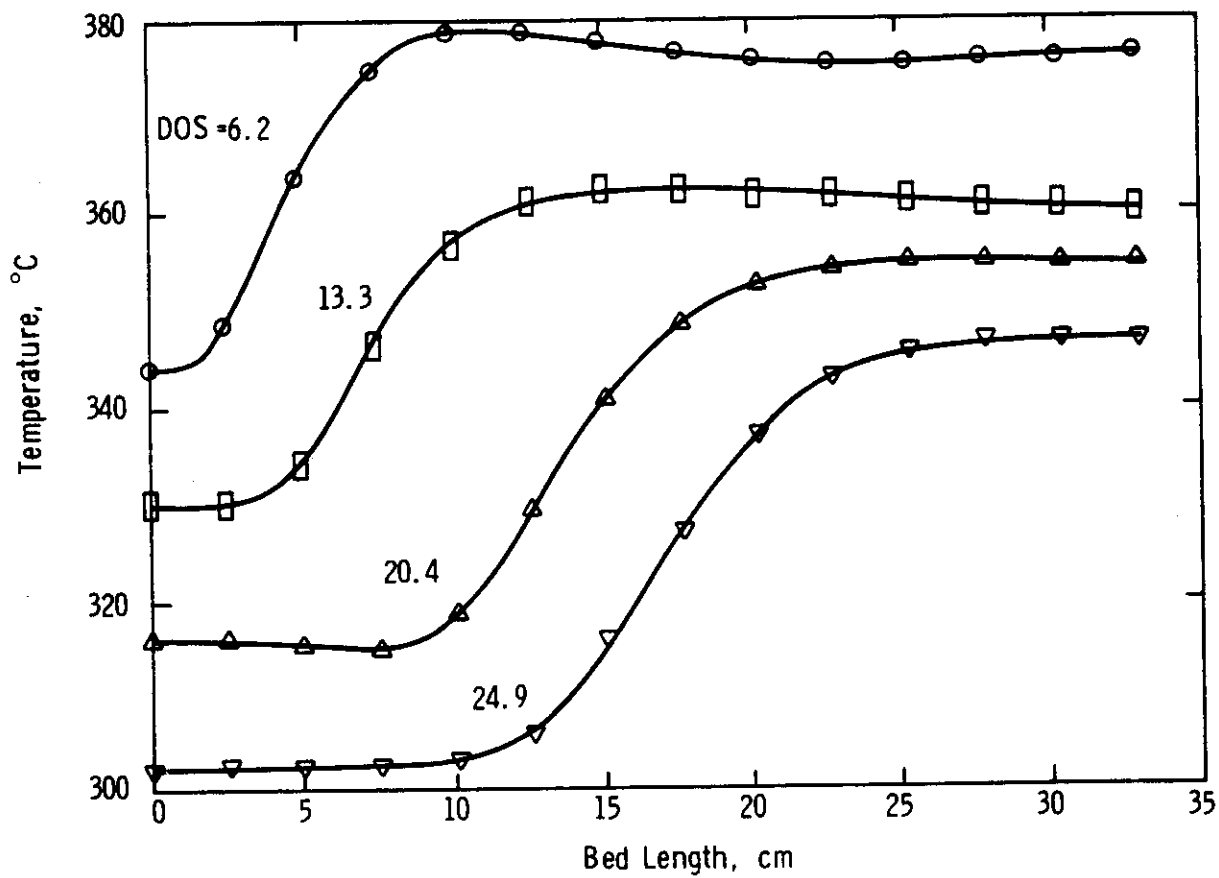


FIGURE 10  
SECOND-STAGE FIXED-BED ZSM-5 REACTOR TEMPERATURE PROFILES  
(Run CT-256-1)



decline of the temperature near the end of the catalyst bed probably indicated an imperfect adjustment of the zoned heaters in simulating an adiabatic operation.

Material balances were performed almost daily as summarized in Table B-7 of Appendix B. The properties of the raw liquid products collected from the ambient and chilled condensers are summarized in Table B-8, while detailed hydrocarbon compositions are given in Table B-9. Two types of material balance information are included in Table B-7; one obtained without inter-reactor sampling and the other with inter-reactor sampling.

In this trial run, the initial reactor inlet temperature was set arbitrarily at 371°C, which resulted in a very high severity. This high severity reflected in a high conversion of the light olefins, and large formation of propane, butanes and aromatics. This yield trend means a low C<sub>5</sub>+ and alkylate yields. Therefore, to increase the gasoline yield (including the alkylate), it was imperative to lower the second-stage ZSM-5 catalyst severity. This was achieved by lowering the reactor inlet temperature to 329°C over a six-day period. The inlet temperature was further reduced to 302°C after another seventeen days. However, for a majority of the time, the severity of the second-stage operation was very high. This was mainly caused by the unexpected low gas throughput in the first-stage reactor resulting from the low catalyst loading problem.

One useful criterion to measure the severity of the second-stage operation is the molar  $i\text{-C}_4 / (\text{C}_3 + \text{C}_4)$  ratio. A high severity operation indicates high conversion of propene and butenes and large formation of *i*-butanes which gives a high ratio of  $i\text{-C}_4 / (\text{C}_3 + \text{C}_4)$ . In addition, a value of unity of this ratio indicates theoretically the best alkylate yield by the alkylation of the propene and butenes with the *i*-butanes produced. A ratio of unity, therefore, usually coincides with a high total gasoline yield. From Table B-7, this ratio was above 1.39 at all times and above 3.0 most of the time.

The operability of the second-stage reactor was very satisfactory. However, its severity must be optimized in order to maximize gasoline yield.

The raw gasoline collected in the chilled and ambient condensers contained small amounts of acids based on acid number analyses. Those acids, however, can be removed by simple water washing. In one instance, twenty g of a raw gasoline sample with an acid number of 0.19 mgKOH/g was washed twice with fifty g of distilled water. The acid number was reduced to zero after the washings.

#### 4. Second-Stage ZSM-5 Catalyst Regeneration

The second-stage ZSM-5 catalyst, though only moderately deactivated after forty-nine DOS, was oxidatively regenerated to check out the regeneration facilities of the BSU. These facilities include a regeneration recycle compressor, make-up air compressor and regeneration product GC system.

For safety reasons, the reactor to be regenerated was first physically isolated from the rest of the BSU by disconnecting the piping between them. The reactor was then connected with the regeneration circuit and the whole circuit was purged and pressured by nitrogen to 1.14 MPa. A nitrogen flow rate of 6.1 Nm<sup>3</sup>/kg catalyst-hr was maintained by the recycle compressor. The reactor was then heated up to 343°C and 0.079 Nm<sup>3</sup>/hr make-up air was then introduced. The maximum catalyst bed temperature was maintained at or below 485°C by adjusting the reactor inlet temperature and the make-up air flow rate.

The O<sub>2</sub>-concentration at the reactor exit was continuously monitored during the course of regeneration using an electrochemical oxygen analyzer. The exit O<sub>2</sub>-concentration was maintained at less than 1 mol % by adjusting the make-up air flow rate when the reactor inlet temperature was less than 466°C. At the end of regeneration, the reactor exit O<sub>2</sub>-concentration was allowed to increase to 7 mol %. At that time, the axial catalyst bed temperature was practically uniform at about 483°C. The total regeneration took about fourteen hours and the total product water collected during that period was 6.3 g. After regeneration, the activity of ZSM-5 was restored.

#### C. Run CT-256-2

##### 1. Highlights

The second BSU run, designated as Run CT-256-2, using Catalyst I-B (containing Fe/Cu/K<sub>2</sub>CO<sub>3</sub>) in the first-stage bubble-column F-T reactor and Catalyst II-B (a ZSM-5 class catalyst) in a second-stage fixed-bed reactor, was smoothly started up on June 24, 1982. The major events of this run are summarized in Tables 11 and 12, while the operational results are summarized in Table 13. In spite of the excellent performances of the catalysts, the run was terminated prematurely after twenty days on stream due to an operational upset which is described later.

Other major highlights of this run were:

- Smooth operation of the slurry F-T reactor with a high catalyst loading (19.5 wt % initially); high synthesis gas throughput, and high conversion was demonstrated over a period of seventeen days.

Table 11

Major Events in Run CT-256-2  
(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
0-5.3	Pretreatment 1st-Stage: 0.7 H <sub>2</sub> /CO, 1.14 MPa, 3.2-4.1 cm/s, 260-257°C 2nd-Stage: 288-324°C
5.4- 7.3	1st-Stage: 1.14-1.48 MPa, 260-263°C 2nd-Stage: 324-330°C
7.4-12.1	1st-Stage: 1.48-1.14 MPa, 4.1-3.5 cm/s, 260-263°C 2nd-Stage: 330-348°C
12.3-14.1	1st-Stage: 1.14-1.48 MPa 2nd-Stage: 348-352-346°C
15.2-16.1	1st-Stage: 1.48-1.83 MPa 2nd-Stage: 346-350°C
16.2	Upset: Slurry reactor bottom flange temperature went up
17.1	10-day shutdown: - Unloaded slurry - Replaced plugged-up distributor plate - Reloaded the same slurry
17.1-17.7	1st-Stage: 1.48 MPa, 3.4-2.8 cm/s, 263-279°C 2nd-Stage: 343°C
19.6	End of Run CT-256-2



Table 12

Major Events in Run CT-256-2

(Reactor-Wax and Slurry Inventory)

<u>DOS</u>	<u>Major Events</u>
-0.7	Slurry loading
0.1	Slurry sampling: 2 g, from 30 cm, 23.6% solid
1.4	Wax withdrawal: 50 g, 0.9% solid
4.1	Slurry sampling: 41/29.9/23.1/42 g, from 30/152/305/610 cm, 17.6/16.1/14.3/9.9% solid
6.1	Wax withdrawal: 161/549/227/542/422 g , 4/1.2/0.1/0.2/0.4% solid
6.2	Tried wax withdrawal from the side filter at 457 cm: Negligible filtration rate
7.1	Wax withdrawal: 642/633 g, 4.7/0.2% solid
16.2	Wax withdrawal: 520/301/476/264 g, 8.5/3.4/1.1/1.2% solid
17.1	Wax withdrawal: 324/548 g, 0.2/0.3% solid  Slurry unloading: 2,663/2,736/756 g, 9.9/8.6/8.2% solid  Slurry reloading: 6,100 g of the same slurry plus 600 g of high- solid-content waxes from earlier time; slurry solid content was 7.9%
17.5	Slurry sampling: 5/5/6.1 g from 30/152/305 cm, 10.1/10.7/9% solid
19.6	Wax withdrawal: 563/998 g, 10.5% solid Slurry unloading: 4,214 g End of Run CT-256-2

Table 13

Ranges of Operation Results

(Run CT-256-2)

<u>First-Stage</u>	<u>Range of Results</u>
H <sub>2</sub> +CO Conv., Mol %	45-86
Methane + Ethane Yield, Wt % HC	9-15
Reactor-Wax Yield, Wt % HC	1-14

Second-Stage Hydrocarbon Yield, Wt %

	<u>Before Alkylation</u>	<u>After Alkylation</u>
C <sub>1</sub> +C <sub>2</sub>	9-14	9-14
C <sub>3</sub> -C <sub>4</sub>	18-33	9-15
C <sub>5</sub> -C <sub>11</sub>	49-62	59-70
C <sub>12</sub> +(excl. reactor-wax)	1-4	1-4

Properties of Raw Liquid Hydrocarbons<sup>(1)</sup>

Aromatics, Wt %	27-47
Acid No., mgKOH/gHC (unwashed)	0.02-0.5
Octane No., R+0	86-94
M+0	76-82

(1) Collected in ambient and chilled condensers.

The ranges of the first-stage slurry F-T reactor operating conditions and performance over this seventeen-day period were:

H <sub>2</sub> +CO Flow Rate, Nm <sup>3</sup> /hr	1.4-2.7
Temperature, °C	257-263
Pressure, MPa	1.14-1.83
H <sub>2</sub> /CO Feed Molar Ratio	0.7
Superficial Feed-Gas Velocity, cm/s	3.2-4.1
SV, NL/gFe-hr	1.5-2.9
H <sub>2</sub> +CO Conversion, mol %	45-86
Methane + Ethane Yield, wt % HC	9-15

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

Temperature Inlet, °C	284-350
GHSV (STP), l/hr	1,435-3,255

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

- A large loss of the F-T catalyst activity (estimated to be about 40%) was observed after the operational upset. The methane + ethane yield also increased from about 10 wt % of the total hydrocarbon produced to 18-20 wt %. The catalyst was obviously damaged during the upset.

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

The procedure for loading the catalyst slurry into the first-stage reactor was basically the same as that used for Run CT-256-1 except for the following improvements:

- The startup slurry was prepared using 4,000 g of spent reactor-wax (containing about 0.5 wt % solid), 895 g of FT-200 Vestowax, and 1,375 g I-B catalyst in 791 g Mobil base stock F-509. The initial catalyst loading was 19.5 wt %.
- The slurry was loaded into the reactor through a new 1 L size loading tank, followed by washing with 500 cm<sup>3</sup> of n-decane. During washing, a portable stirrer was inserted into the tank to agitate the slurry to ensure a good washing.

The static slurry level, not including the washing n-decane, was estimated to be 427 cm. Reactor slurry samples withdrawn later showed that high catalyst loading was indeed achieved.

During run CT-256-1, the gas holdup in the F-T column in the latter part of the run was substantially lower than that at the beginning of the run. The reactor-wax produced by the F-T reactions might be the major contributor to this lower gas holdup. Since a moderate gas holdup is essential for achieving high catalyst loading in the reactor, spent wax from the first run was used in this run. Right after loading, with a nitrogen flow at 4 cm/s, the expanded slurry level was between the 610 and 762 cm viewports. The gas holdup was estimated to be approximately 35 vol % which is substantially less than the initial gas holdup (63 vol %) observed in the last run.

The pretreatment conditions for the F-T catalyst I-B were:

H <sub>2</sub> +CO Flow Rate, Nm <sup>3</sup> /hr	1.84
H <sub>2</sub> /CO Feed Ratio, molar	0.70
Superficial Feed-Gas Vel., cm/s	4.0
SV, NL/gFe-hr	2.0
Temperature, °C	280
Pressure, MPa	1.14

These conditions were similar to those used in the last run except for the low space velocity, which resulted directly from the high catalyst loading achieved in this run.

The course of pretreatment was carefully monitored by measuring the product gas volume contraction, H<sub>2</sub> and CO conversion, and CO<sub>2</sub> and methane concentration in the product gas. All these quantities increased with time-on-stream as shown in Figure 11. The pretreatment was terminated after eleven hours when CO conversion reached 82 mol %.

Figure 12 depicts the H<sub>2</sub>+CO conversion and methane and ethane yield versus time on-stream. The material balances were performed daily and results are summarized in Table C-1 of Appendix C. Table C-2 gives the detailed hydrocarbon product compositions.

The synthesis operation was commenced at 260°C, 1.14 MPa (150 psig) and 3.2 cm/s. The initial H<sub>2</sub>+CO conversion was 45 mol % and gradually increased to about 73 mol % after about one DOS. This increase in conversion was attributed to continual activation of the F-T catalyst. To take advantage of this continual increase of the catalyst activity, the feed-gas superficial velocity was increased from 3.2 to 4.1 cm/s. Responding to this higher superficial velocity, the H<sub>2</sub>+CO conversion first dropped to 61 mol % and then gradually increased, leveling off at 86 mol % after four DOS.

FIGURE 11

RUN CT-256-2 FISCHER-TROPSCH CATALYST PRETREATMENT  
(CATALYST I-B)

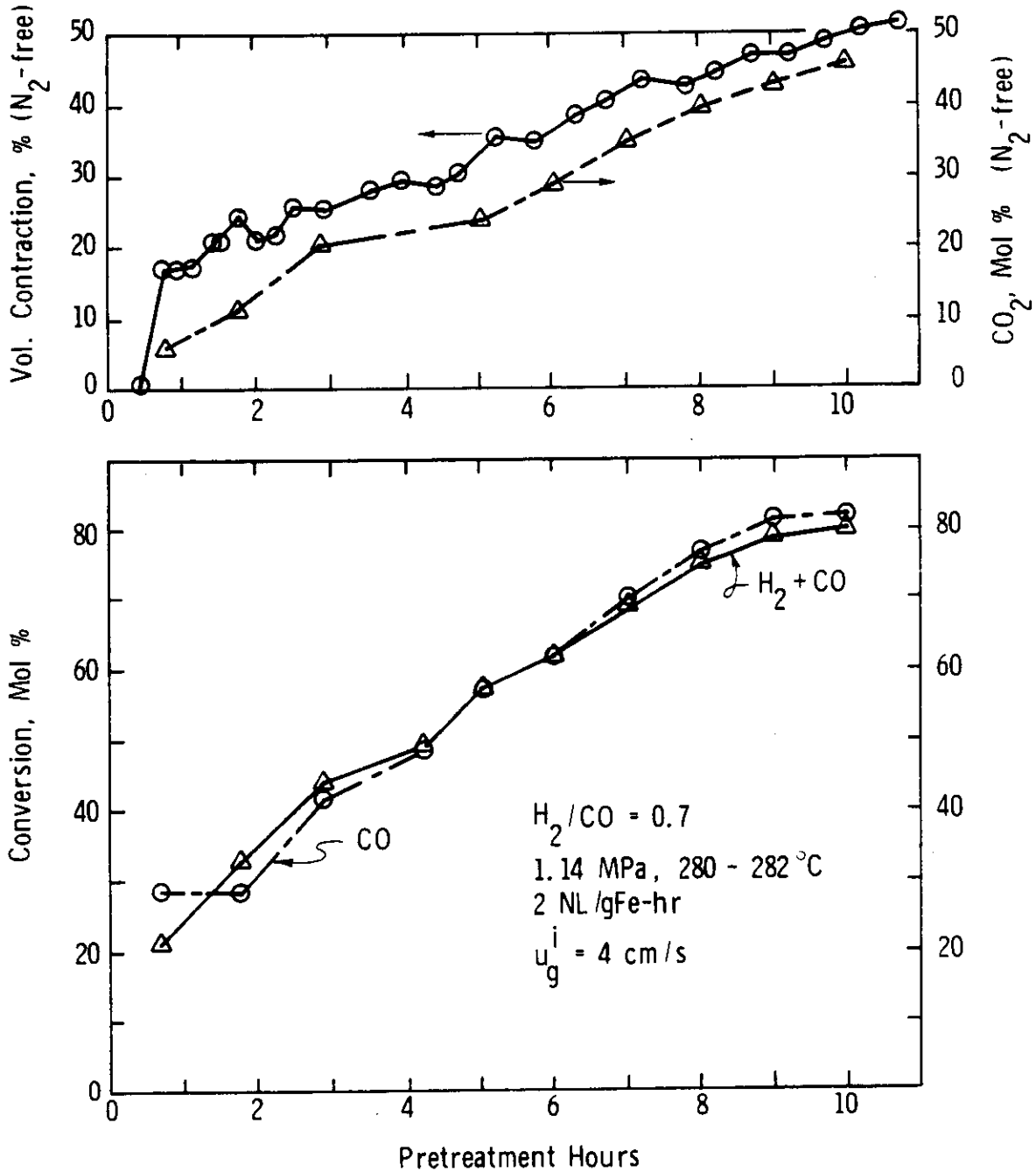
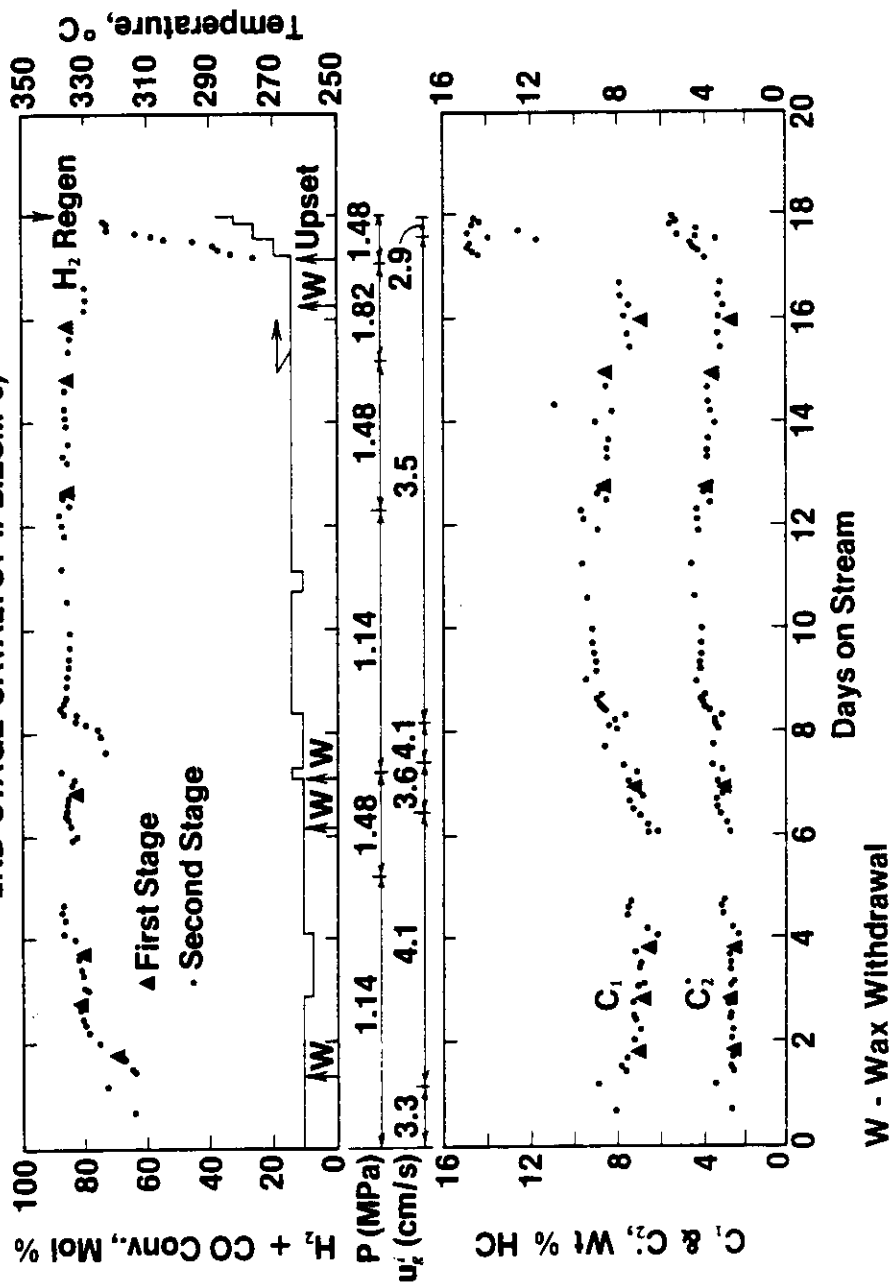


FIGURE 12

**SYNTHESIS GAS CONVERSION  
AND METHANE & ETHANE YIELD**

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



From five to seven DOS, the slurry reactor pressure was increased to 1.48 MPa (200 psig) while maintaining a constant feed-gas superficial velocity. The H<sub>2</sub>+CO conversion dropped slightly to 82 mol %. The methane + ethane yield stayed fairly constant at about 10.5 wt % of the total hydrocarbons produced. A small decrease in the feed-gas superficial velocity to 3.6 cm/s brought the H<sub>2</sub>+CO conversion back to 86 mol %.

During this seven-day period of synthesis operation, substantial reactor-wax accumulated in the slurry reactor. Three reactor-wax withdrawals through the filter located at the 305 cm level gave a total of 3,225 g reactor-wax to maintain a slurry level between 610 and 762 cm. Solid-content analyses indicated that about 68 g of catalysts were in the reactor-wax withdrawn. However, no noticeable drop in conversion was observed, probably due to continual activation of the F-T catalyst during this early period of synthesis operation.

To check F-T catalyst aging, the slurry reactor pressure was lowered back to 1.14 MPa and operated at 260°C and 3.9 cm/s from seven to twelve DOS. The H<sub>2</sub>+CO conversion first dropped to 72 mol % and then gradually climbed up to 78 mol %. The methane + ethane yield also increased from 10.5 to 12 wt % of the total hydrocarbons produced. At eight DOS, the feed-gas superficial velocity was lowered to 3.4 cm/s. The H<sub>2</sub>+CO conversion continued to increase and then leveled off at 86 mol % with a methane + ethane yield of about 15 wt %. Judging from the space velocity variation required to reach the same H<sub>2</sub>+CO conversion as the early part of this run, the catalyst had lost about 8% of its activity during the first eight days' operation. However, this estimated aging rate may not be meaningful in a longer time scale since, as mentioned later, a stable catalyst activity was observed during the next seven days.

From twelve to fifteen DOS, the charge synthesis gas throughput was again increased by raising the slurry reactor pressure to 1.48 MPa while maintaining the superficial velocity at 3.4 cm/s. The operation during this period was marked by a reduction in the methane + ethane yield from 15 to 12.5 wt % of the total hydrocarbons produced. The H<sub>2</sub>+CO conversion was very stable at 86 mol % for a seven-day period (eight to fifteen DOS) with slurry reactor conditions at 1.14-1.48 MPa, 262°C and 3.4 cm/s.

To further increase the synthesis gas throughput, the slurry reactor pressure was increased at fifteen DOS to 1.83 MPa (250 psig) while keeping the superficial velocity constant at 3.4 cm/s. The methane + ethane yield declined to 11 wt % while the H<sub>2</sub>+CO conversion decreased slightly to about 85 mol %. Table 14 summarizes the effect of reactor pressure on the slurry reactor performance. The major effect is the decreasing methane + ethane yield with increasing pressure.

Table 14

Effect of Pressure on Slurry F-T Reactor Performance<sup>(1)</sup>

(Run CT-256-2)

DOS	12.1	14.2	15.5
Pressure, MPa	1.14	1.48	1.82
SV, NL/gFe-hr	1.84	2.34	2.84
H <sub>2</sub> +CO Conv., Mol %	87.6	86.9	85.9
Methane, Wt %	9.6	8.3	7.5
Methane + Ethane Yield, Wt %	13.9	12.0	10.8
Exit H <sub>2</sub> /CO, Molar	1.07	1.30	1.31

(1) 0.7 H<sub>2</sub>/CO, 263°C, 3.5 cm/s superficial feed-gas velocity



At sixteen DOS, 1,560 g of reactor-wax was withdrawn from the slurry reactor to maintain the slurry level at 610-670 cm. The catalyst loss, according to solid-content analyses, was 63 g. Following the wax withdrawal, the H<sub>2</sub>+CO conversion declined to 80 mol %. This drop in conversion was attributed mainly to the catalyst loss and partially to the lowering of the slurry level (by about 152 cm) as a result of the reactor-wax withdrawal.

At sixteen DOS, while operating at a pressure of 1.83 MPa, the flange at the bottom of the slurry reactor, which was normally kept at 263°C with heating tapes, began to overheat and eventually reached 397°C. The cause of this was probably a leakage of slurry at the bottom flange. At this point, the feed-gas distributor was practically plugged. The unit was then temporarily shut down to unload the slurry and to replace the feed-gas distributor. The feed-gas distributor was found plugged with coke-like material. Figure 13 is a photograph of the feed-gas distributor and bottom-flange gasket removed from the slurry reactor after the upset.

It is speculated that the bottom flange gasket failed with increasing time on-stream. At the higher pressure operation (1.83 MPa), the slurry leaked through the gasket, came in contact with the heating tape and began to oxidize. The oxidation reaction then heated up the flange and the distributor. The overheated distributor then promoted the Boudouard reaction resulting in coke deposition which plugged the distributor.

After a downtime of ten days, the slurry was reloaded and the slurry reactor restarted at 263°C, 1.48 MPa and 3.4 cm/s. The H<sub>2</sub>+CO conversion was only 25 mol % and the methane + ethane yield was as high as 18 wt % of total hydrocarbons produced. The catalyst was obviously damaged during the operational upset. This damage could be attributed to several factors during the upset:

- Coking of the F-T catalyst due to high temperature operation near the bottom flange.
- Loss of catalyst due to leakage through the bottom flange and slurry unloading and reloading.
- Oxidation of the catalyst by CO<sub>2</sub> and H<sub>2</sub>O during synthesis gas flow stoppage and by oxygen during the slurry unloading and reloading.

In an attempt to reactivate the F-T catalyst, the slurry reactor temperature was gradually raised from 263 to 279°C to simulate a pretreatment operation. However, at 279°C, 1.48 MPa and 2.7 cm/s, the H<sub>2</sub>+CO conversion was only 75 mol % with a methane + ethane yield of about 21 wt %.

FIGURE 13

DISTRIBUTOR PLATE AND BOTTOM FLANGE GASKET OF THE  
SLURRY REACTOR AFTER THE UNIT UPSET

(Run CT-256-2)

