Figure 24 shows the effect of second-stage operating severity index on the hydrocarbon yield. As mentioned earlier, the alkylate yield is estimated by alkylating first butenes and then propylene with i-butanes. If there is an excess of light olefins, they are converted to "Cat-Poly gasoline" using conventional catalytic polymerization process. In making this plot the product yields are normalized excluding the reactor-wax and C_4^- paraffins carried over from the first-stage reactor. Peak C_5^+ gasoline yields of 85-90 wt % could be achieved at severity index of 0.5-1. High pressure operation (2.51 MPa versus 1.48 MPa) had no significant effect on the second-stage operation and yield.

Figure 25 shows the Research Octane Number and the aromatic and olefin content of the raw liquid hydrocarbon product collected in the cold and chilled condensers as a function of the second-stage operating severity index. Peak octane number of 90-94 is obtained for severity indexes of 0.3-2.0. The corresponding aromatics content is 30-50 wt % and olefins content is 5-25 wt %. Too high aromatics content is equivalent to high severity or reduced gasoline yield. Too low aromatics content, however, also results in a low gasoline yield. Hence, optimal gasoline yield is restricted to a severity index of 0.5-1.0. Motor octane number for the raw liquid hydrocarbon products are summarized in Table D-8.

Another indication of the second-stage catalyst performance is the acid number of the raw liquid hydrocarbon products, also reported in Table D-8. Acid numbers of 0.04-0.4 show the ability of the ZSM-5 catalyst to convert organic acids. For comparison, first-stage F-T liquid hydrocarbon products have acid number of 1.1-3.0. Finally, the ASTM distillation properties of the raw hydrocarbon products did not vary much with catalyst aging or changing operating severity (Table D-8).

E. Run CT-256-4

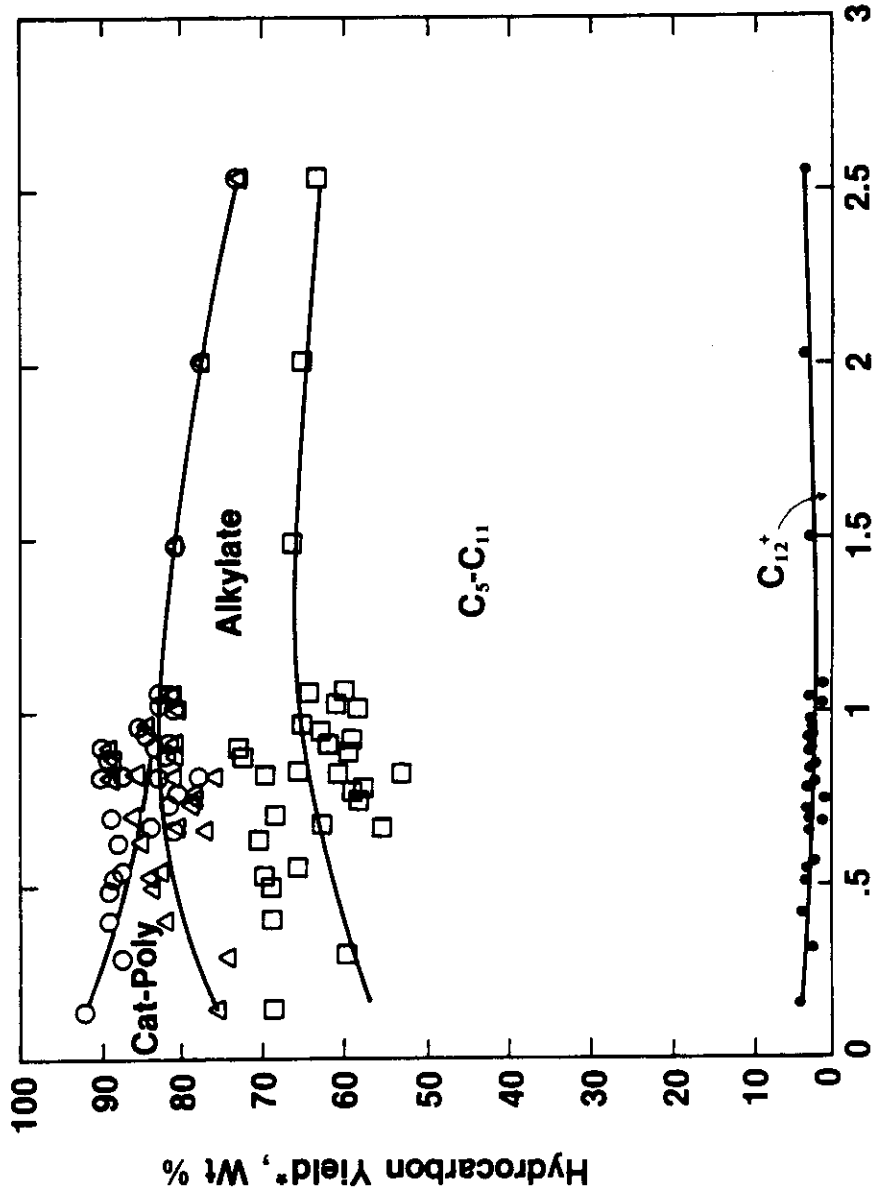
1. Highlights

The fourth BSU run, designated as Run CT-256-4, using the same gasoline-mode F-T catalyst I-B used in Run CT-256-3, was smoothly started up on January 10, 1983 and was concluded after thirty-seven DOS. The major objective was to operate the same gasoline-mode catalyst under higher pressure and slightly lower temperature to reduce methane + ethane yield. Another objective of this run was to test different reactor-wax withdrawal systems. The major events and ranges of process variables and operating results of this run are summarized in Tables 20 and 21, respectively.

FIGURE 24

PRODUCT YIELDS VERSUS
SECOND-STAGE OPERATING SEVERITY

(Run CT-256-3)



*Excluding C_4^- paraffins in feed and reactor-wax

FIGURE 25

SECOND-STAGE
RAW LIQUID HYDROCARBON PROPERTIES

(Run CT-256-3)

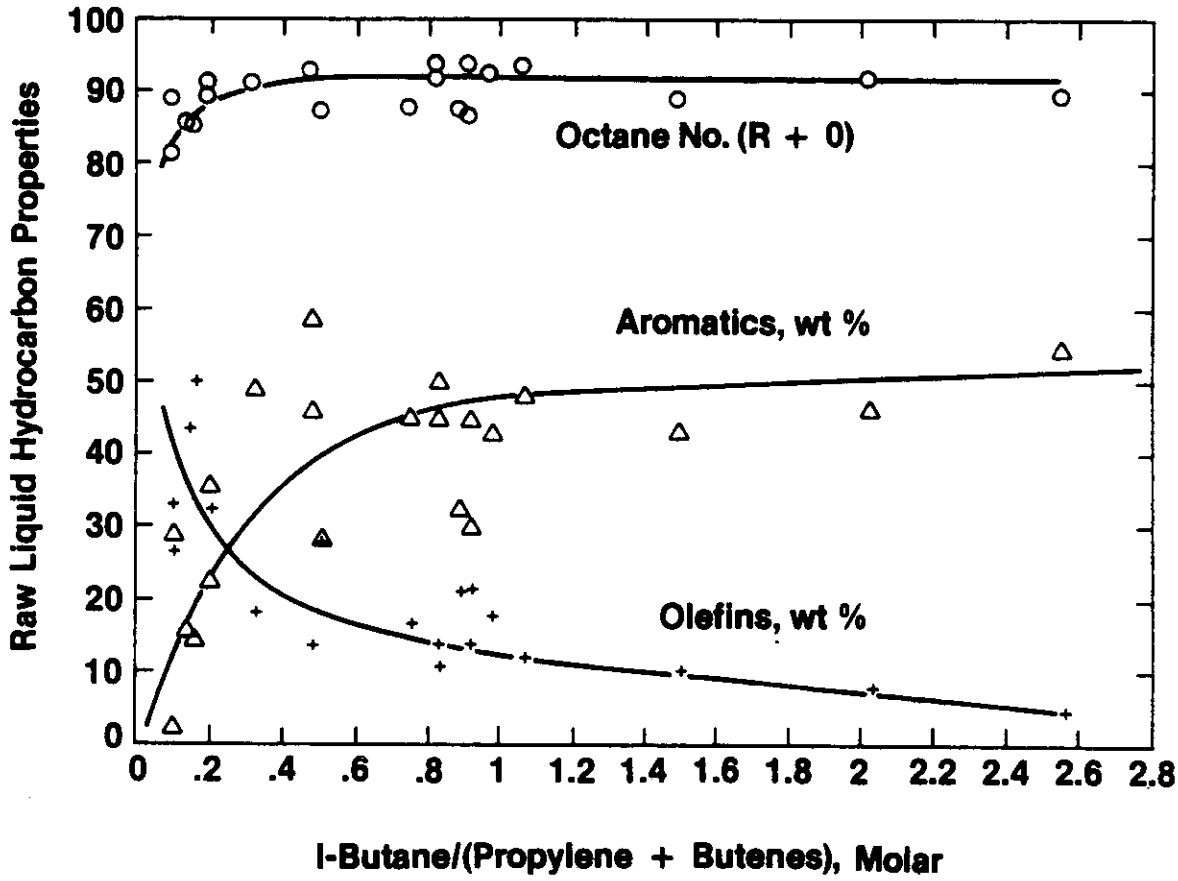


Table 20

Major Events in Run CT-256-4

DOS	Major Events
-0.4 - 0	Pretreatment
0 - 0.5	280----->260°C; 5 cm/s; 1.56 NL/gFe-hr
0.5 - 2.7	1.14----->2.52 MPa; 257°C; 4 cm/s
2.7 - 6.6	2.52 MPa; 257°C; 3 cm/s; 3 - 6.5 NL/gFe-hr
6.6 - 34.8	2.52 MPa; 257°C; 2 cm/s
29.8	493 g fresh catalyst added
34.8 - 36.7	2.52----->1.48 MPa; 257-260°C; 2 cm/s
36.7	End of Run CT-256-4

Table 21

Ranges of Process Variables & Operating Results

(Run CT-256-4)

First-Stage Process Variable	Range
Temperature, °C	257 - 280
Pressure, MPa	1.14 - 2.52
Superficial Feed-Gas Velocity; cm/s	2 - 5
SV, NL/gFe-hr	1.2 - 6.5
Catalyst Loading (Nominal), Wt %	4.4 - 22.2
Operation Results	
H_2 + CO Conversion, Mol %	17 - 75
Methane + Ethane Yield, Wt % HC	3.5 - 5
Reactor-Wax Yield, Wt % HC	46 - 51

Major highlights of this run were.

- Methane + ethane yield of less than 5 wt % of hydrocarbons produced was obtained throughout the run.

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

H_2+CO Flow Rate, Nm^3/hr	1.18-3.43
Temperature, °C	257- 280
Pressure, MPa	1.14-2.52
H_2/CO Feed Molar Ratio	0.7
Superficial Feed-Gas Velocity, cm/s	2-5
SV, NL/gFe-hr	1.2- 6.5
Catalyst Loading, wt % (nominal)	4.4-22.2
H_2+CO Conversion, mol %	17- 75
Methane + Ethane Yield, wt % HC	3.5-5
Reactor-wax Yield, wt % HC	46-51

- A high reactor-wax yield (46-51 wt % of the total hydrocarbons produced) was observed, which was consistent with the low methane + ethane yield. With this mode of operation, reactor-wax upgrading to liquid fuels becomes essential.

- During the first sixteen days of operation, about 55% of initial catalyst load was lost via reactor-wax withdrawals through filters. An external catalyst settling method was successful in recovering withdrawn catalyst from the slurry, but significant deactivation of the catalyst occurred, probably due to exposure to air.

- An on-line catalyst settling method was successfully tested. The external filter assembly at the 762 cm location was converted to a slurry settling vessel and was used to remove 300-400 g/hr of reactor-wax containing less than 0.2 wt % catalyst.

- A batch of fresh catalyst was added to the slurry reactor to make up for the lost catalyst. The fresh catalyst, however, did not seem to activate at the synthesis conditions.

- The reactor-wax obtained after seventeen DOS was heavier and more viscous than that produced in Run CT-256-3. This was probably due to operation at higher pressure and slightly lower temperature.

- The acid numbers of the F-T hydrocarbon liquid and aqueous phase were substantially higher (10-32, and 35-109 mgKOH/g, respectively) than those from Run CT-256-3 (1-3, and 2-7 mgKOH/g, respectively). The oxygenate contents are also expected to be higher.

The second-stage ZSM-5 reactor was not operated during this run since the first-stage operation was not steady. This was due to continuous catalyst loss at the early part of the run. Also, high H_2+CO conversion and high synthesis gas throughput could not be achieved during the latter part of the run.

2. First-Stage Fischer-Tropsch Reactor Operation

Due to higher catalyst loading the pretreatment conditions were slightly different from those used in Run CT-256-3. 2,000 g of F-T catalyst I-B in 1,100 g Mobil F-509 was loaded along with 5,900 g of spent reactor-wax from previous run. The initial catalyst loading was 22.2 wt %. To avoid pretreating this catalyst at too low a space velocity, a high feed-gas superficial velocity of 5 cm/s was used.

The F-T catalyst pretreatment conditions were:

H_2+CO Flow Rate, Nm^3/hr	2.16
H_2/CO Feed Ratio, Molar	0.70
Superficial Feed-Gas Velocity, cm/s	5.00
Temperature, °C	280
Pressure, MPa	1.14

The pretreatment was ended after ten hours, the same number of hours as in Run CT-256-3. The CO conversion at this time was 77 mol %. This conversion was somewhat lower than what was expected from the high catalyst loading. It may be due to the high superficial gas velocity employed. Figure 26 shows the product gas volume contraction, CO and H_2+CO conversion, and CO_2 concentration in the product gas during the pretreatment.

In switching from the pretreatment to the synthesis operation, the slurry reactor temperature was lowered to 260°C in steps of 3°C at a time over a twelve hour period. The conversion continuously dropped during this period due to lower temperature. The synthesis gas flow rate was also adjusted to reach 4 cm/s superficial velocity at 260°C. The catalyst was continuously activated during this period and consequently the conversion increased from 41% at twelve HOS to 75% at thirty-six HOS. Figure 27 gives the H_2+CO conversion, methane and ethane yields, and space velocity during the synthesis operation. Figure 28 gives the cumulative reactor-wax production during this run.

FIGURE 26

RUN CT-256-4
FISCHER-TROPSCH CATALYST PRETREATMENT
(CATALYST I-B)

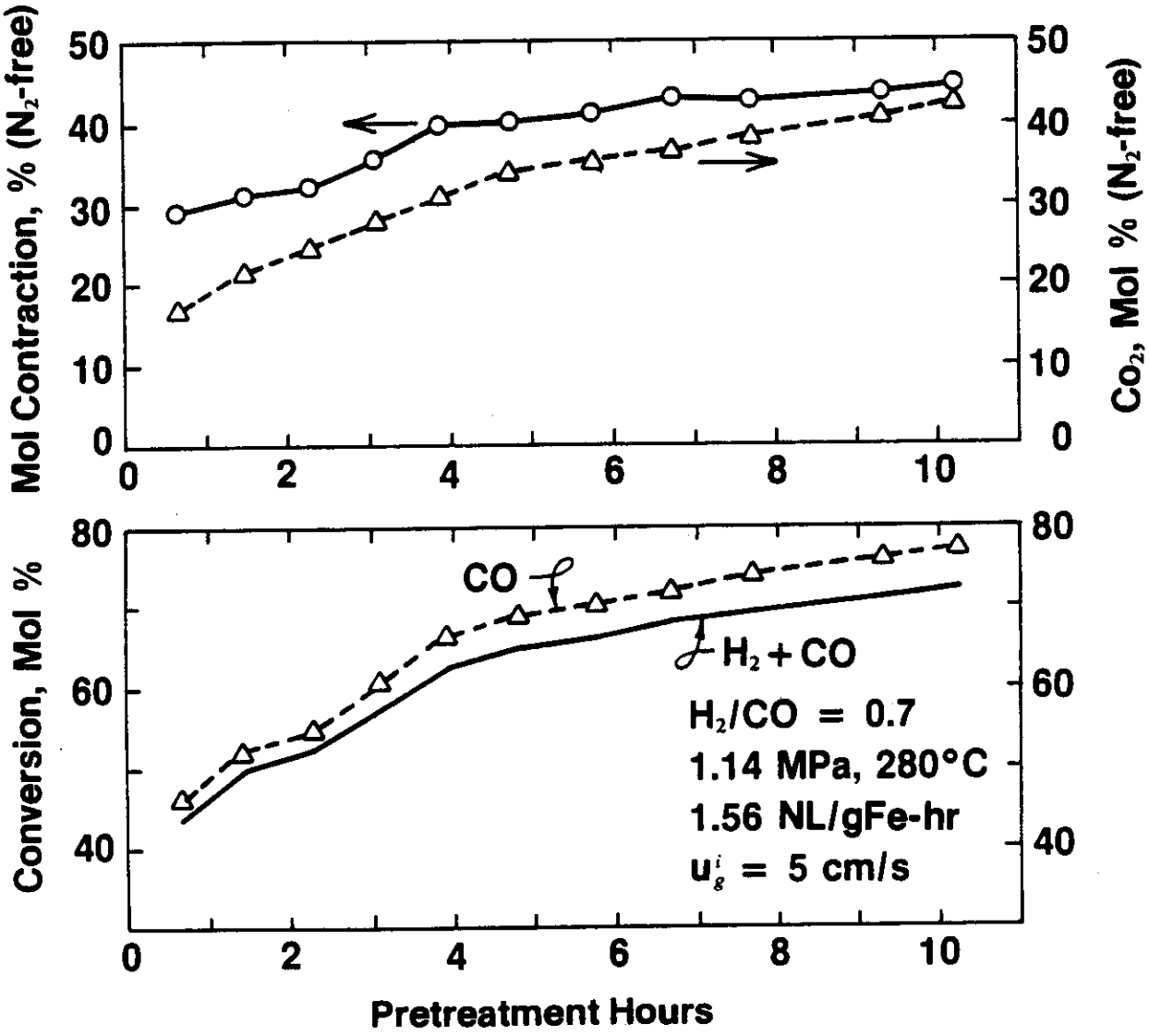
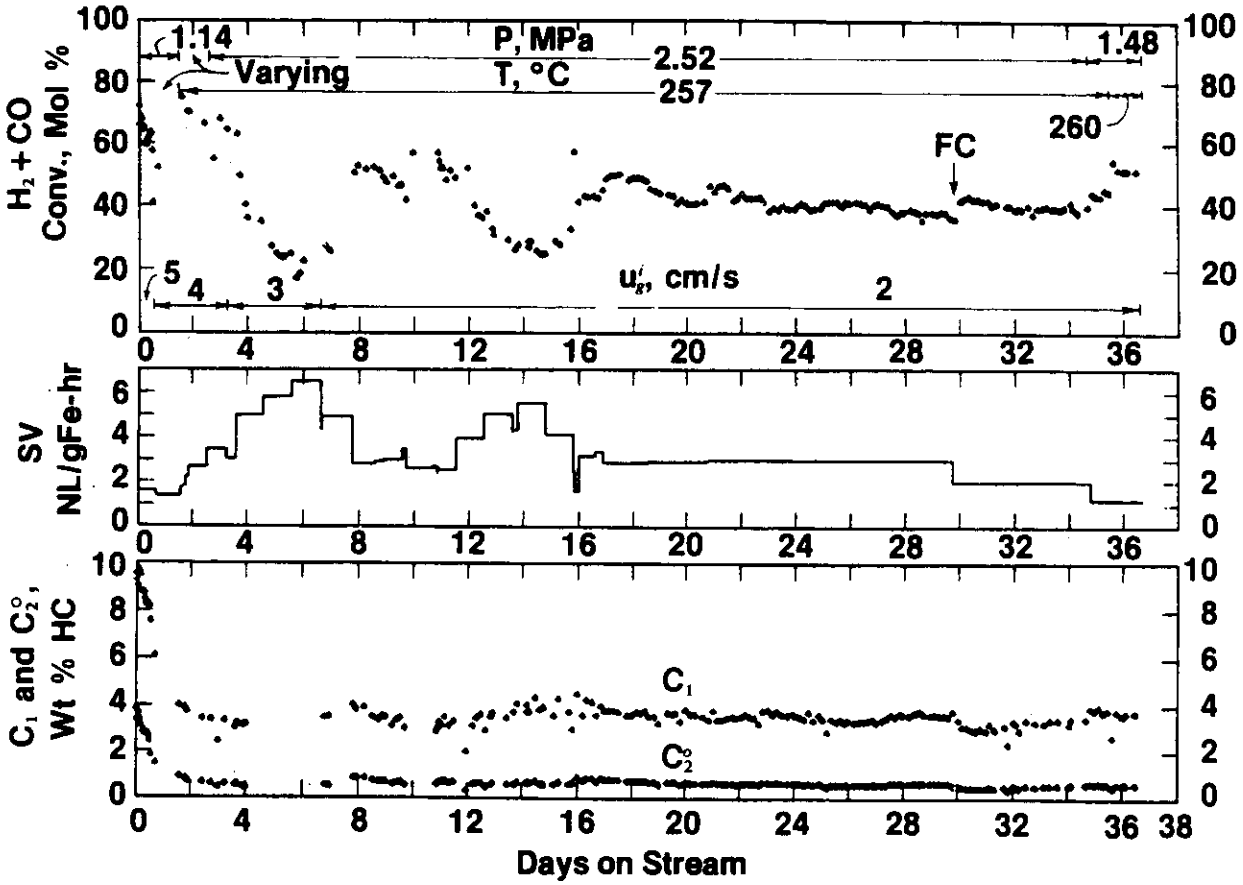


FIGURE 27

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD

(RUN CT-256-4; 1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K_2CO_3)

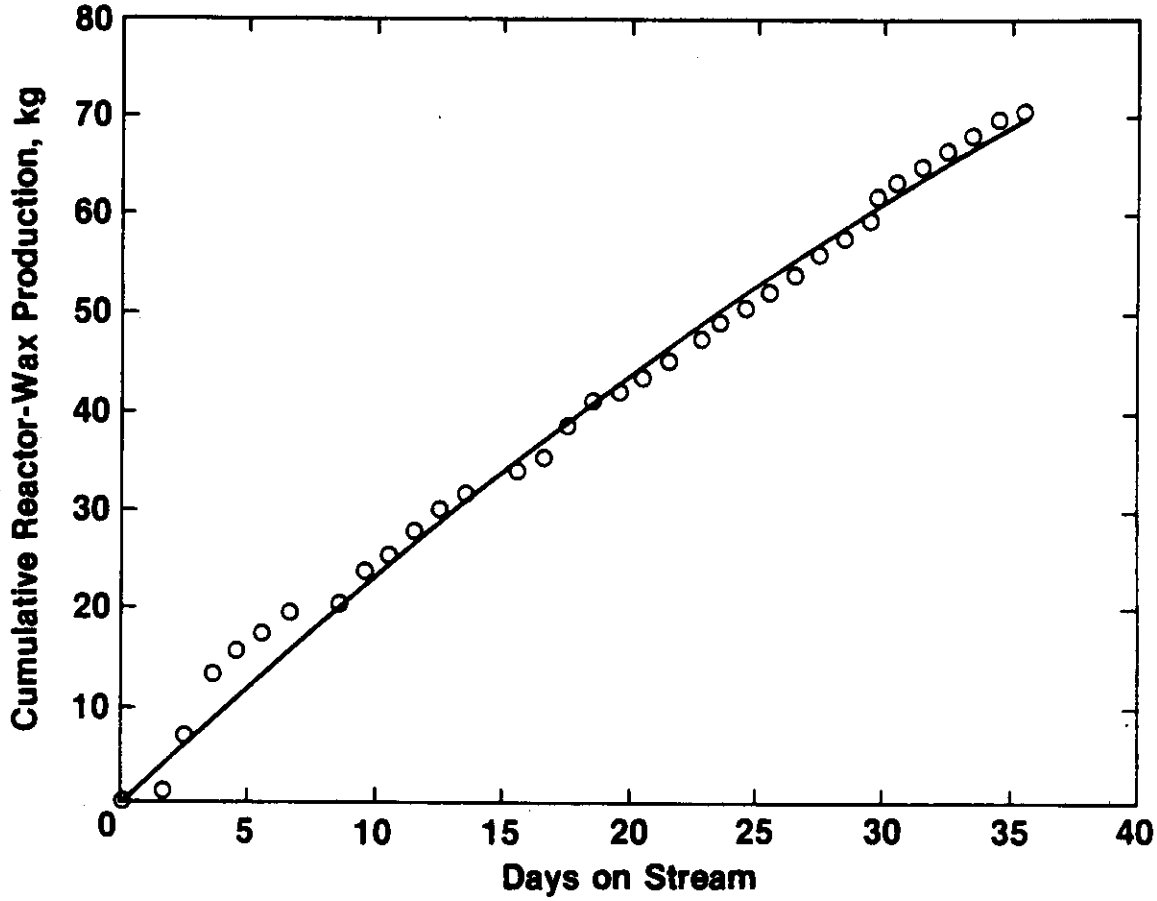


FC: Fresh catalyst added

FIGURE 28

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

(RUN CT-256-4)



Over the next twenty hours, the reactor pressure was raised to 2.52 MPa (350 psig). The H_2+CO conversion dropped from 75 to 55 mol % during this period, mainly due to catalyst loss which occurred during the reactor-wax withdrawal using the filters. The reactor-wax yield at this time was about 51 wt % of the total hydrocarbons produced. Later analysis showed that the reactor-wax contained as high as 5 wt % of catalyst. The space velocity hence increased as indicated in Figure 27.

The superficial velocity was then lowered to 3 cm/s at three DOS to increase the H_2+CO conversion to 62 mol %. The conversion, however, as seen in Figure 27, kept decreasing due to continuous catalyst loss via reactor-wax withdrawals. The lower catalyst inventory in the reactor was confirmed later by slurry samples taken. Using the catalyst content analyses of slurry samples and the total liquid height obtained from DP-cell readings, the catalyst in the reactor was estimated to be 891 g; a total catalyst loss of 55% from the initial loading. The space velocity shown in Figure 27 was based on estimated catalyst inventories in the slurry reactor. The catalyst inventories were periodically checked by taking slurry samples from the taps.

At seven DOS the feed-gas superficial velocity was further lowered to 2 cm/s to compensate for further catalyst loss. An attempt was then made to reload some of the lost catalyst into the reactor after a concentrated slurry was obtained by settling the withdrawn reactor-wax in an oven (149-178°C) over magnets for six to eight hours. By doing so the space velocity was maintained nearly constant during seven to eleven DOS. The H_2+CO conversion of 42-50 mol %, however, was substantially lower than the high conversion achieved at an earlier period of the run at an equivalent space velocity. This indicated that the catalyst was substantially damaged during the settling operation when it was exposed to air. This was consistent with what was observed during the major operational upset in Run CT-256-3. Catalyst loss due to reactor-wax withdrawal continued up to seventeen DOS. Further addition of the lost catalyst during fifteen to seventeen DOS increased the H_2+CO conversion.

At that time, a new test of the slurry loading tank as an on-line batch catalyst settling vessel was carried out. This was done by replacing the loading funnel with a dip-tube positioned about two-thirds the way into the loading tank. A batch of slurry was brought into the loading tank, maintained at 232°C (450°F), and allowed to settle for one hour with magnets beneath the tank. The reactor-wax withdrawn through the dip-tube contained only 0.2-0.3 wt % of catalyst. The concentrated slurry at the bottom of the tank was pushed back into the reactor using high pressure nitrogen. However, some slurry always stayed in the tank and some was lost through the vent-line of the tank. The latter catalyst loss was not accounted for.

Due to the success of the catalyst settling test using the slurry loading tank, an external filter assembly was immediately converted into a catalyst settling vessel by installing a dip-tube from the top. During this test, the temperature of the vessel was maintained at 177-232°C (350-450°F). The reactor-wax withdrawn from the dip-tube after one hour's settling contained less than 0.05 wt % of catalyst. A daily reactor-wax removal rate of about 1,700 g was achieved. During twenty-two to twenty-nine DOS, the H_2+CO conversion varied only slightly (from 41 to 36 mol %) and methane + ethane yield was steady at 4.4 wt %. The slight decrease in H_2+CO conversion may be due to catalyst aging or some damage during the settling operation when the catalyst was removed from the synthesis gas atmosphere. The long-term effct on the F-T catalyst due to the on-line catalyst settling is unknown.

Figure 29 shows the schematic arrangement of the catalyst-settling vessel. The slurry from the reactor is brought into the catalyst settling vessel via valve V-1 which is then closed to isolate the slurry in the vessel from the reactor. The slurry can then be purged with H_2 or N_2 to remove any dissolved gases. It is then allowed to settle in the vessel for the desired length of time. The virtually catalyst-free reactor-wax can be withdrawn from the top by the dip-tube, leaving the concentrated catalyst slurry in the vessel. The concentrated slurry can then be pressurized back into the reactor.

A series of experiments were carried out to evaluate the following important factors for F-T catalyst settling:

- Settling Time
- Temperature
- Dip-Tube Position
- Magnets Beneath the Vessel
- Dilution with Light Hydrocarbons

The results are summarized in Table 22. The results show that a reactor-wax containing less than 0.2 wt % of catalyst can be obtained after settling for one hour at 177-204°C. They also show that magnets were beneficial in accelerating the settling process. Further, they show that a continuous H_2 purge at 1 cm^3/s was detrimental to the reactor-wax/catalyst separation (Experiment #5). The dilution of slurry with an equal amount of dodecane significantly improved the settling as shown in Experiment #7. A higher dip-tube position also improved the separation (Experiments #2 and 3). Higher settling temperature somewhat improved the separation efficiency (Experiments #4 and

FIGURE 29

SCHEMATIC OF A CATALYST SETTLING VESSEL FOR FISCHER-TROPSCH REACTOR-WAX REMOVAL

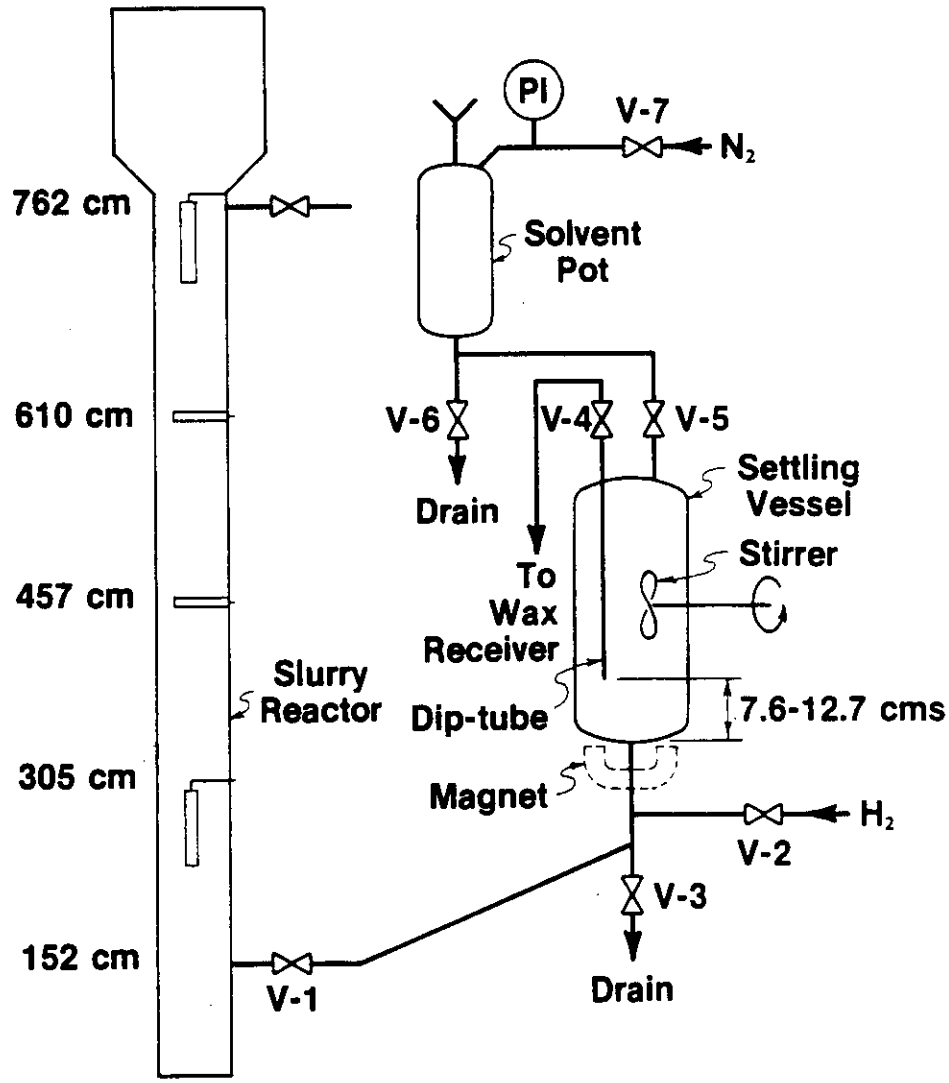


Table 22

Results of Fischer-Tropsch Catalyst Slurry Settling Study

Exp. No.	Temp. °C	Dip-Tube Position from Bottom	Magnet	Settling Time, Mins. 0	10	20	30	45	60	120	180
				Catalyst Concentration in Reactor-Wax After Settling, Wt %							
1	204	7.6	No	7.4	-	-	-	-	6.85	2.44	1.25
2	204	7.6	Yes	8.69	-	-	-	-	0.08	.005	.005
3	204	10.2	Yes	9.5	-	-	-	-	.05-0.2	-	-
4	204	10.2	Yes	5.5	-	0.03	0	0	-	-	-
5[1]	204	10.2	Yes	5.6	-	-	2.08	1.4	0.88	-	-
6	177	10.2	No	2.6	-	-	0.44	-	0	-	-
7[2]	177	10.2	No	3.5	0	0	-	-	-	-	-

[1] Continuous 1 cm^3/s hydrogen purge.

[2] The slurry was diluted with equal volume of n-dodecane.

6).

At twenty-nine DOS, a test of adding fresh I-B catalyst without pretreatment to the slurry reactor was carried out. Fresh catalyst (493 g) was mixed with 283 g of Mobil F-509 and 2,000 g of used reactor-wax, and added to the slurry reactor. This raised the catalyst loading in the reactor to about 12 wt %. As seen from Figure 27, the H_2+CO conversion increased slightly from 38 to 42%, but dropped slowly back to 40% at thirty-four DOS. The fresh catalyst did not seem to be activated at the synthesis conditions. The variation on methane + ethane yield was also small. This run was voluntarily terminated at thirty-seven DOS.

Table E-1 of Appendix E gives the operating conditions and material balances carried out during the run, while Table E-2 reports the corresponding hydrocarbon product compositions. Since there was substantial and continuous catalyst loss during the first seventeen days of operation, the synthesis operation was not steady. Hence, the material balances carried out during this period were not reported . All reported material balances were adjusted by deducting the estimated dodecane content from the total hydrocarbon liquids. The dodecane was used for washing the slurry settling tank at the end of each settling operation.

It seems that for all balances the weights of hydrocarbons produced per Nm^3 of H_2+CO converted were somewhat higher than 207 gHC/Nm^3 H_2+CO converted, estimated based on a formula of $CH_{2.1}$ for all hydrocarbons. This may be due to the following causes:

- The presence of oxygenates changes the stoichiometric balance of the synthesis reaction. For example, it was roughly estimated that the hydrocarbons produced in this run may contain about 3.5 wt % of oxygen due to the high oxygenates content as described later. Then, the stoichiometric weight of the hydrocarbons (including oxygenates) produced per Nm^3 H_2+CO converted shall have been increased to 217 instead of 207 g.

- Part of the dodecane used for washing the slurry settling tank could have been present in the reactor and some of it could have converted to other hydrocarbons. This unaccounted amount of dodecane could have increased the total hydrocarbon yield per Nm^3 of H_2+CO converted.

- Another speculation is that there may be a slight underestimation of the H_2+CO conversion due to some inaccuracies in analysis. At lower levels of H_2+CO conversion accompanied in this run, these inaccuracies may accentuate the error in H_2+CO conversion calculation.

Table E-3 shows a set of typical F-T hydrocarbon selectivities from this run (26.3 DOS).

Occasionally, the reactor-wax was analyzed for carbon-number distribution and viscosity; the results are summarized in Table E-4. The reactor-wax before seven DOS may still contain some amount of the start-up medium as indicated by a peak carbon number of 35. The compositions of reactor-wax at seventeen and thirty DOS are similar and, hence, these represent the steady-state reactor-wax composition under these conditions. The peak carbon number of the equilibrium reactor-wax is 27, with an average carbon number of about 29.4, which is higher than the average carbon number (28) of the reactor-wax obtained during Run CT-256-3. This is expected because of the higher operating pressure used in the current run. The higher average carbon number is also reflected in the higher viscosities measured (two to three times higher). Based on the literature correlations (Shah, et al., 1982) the bubble-column gas holdup is inversely proportional to a 0 to 0.17 power of the viscosity. The maximum reduction of the gas holdup resulting from the higher viscosity is about 17%, not a large reduction.

The acid numbers of the F-T liquid hydrocarbons were substantially higher (ranging from 10 to 32 mgKOH/g) than those of Run CT-256-3 (1-3 mgKOH/g). The acid numbers of the aqueous phase were also higher (35-109 mgKOH/g) compared to 2-7 mgKOH/g for Run CT-256-3. The effect of these high acid numbers on the second-stage catalyst performance was not studied.

F. Run CT-256-5

1. Highlights

The fifth BSU run, designated Run CT-256-5, was started on February 17, 1983, and shut down voluntarily after thirteen days. The objective of the run was to evaluate a new first-stage F-T catalyst ($Fe/Cu/K_2CO_3$, designated I-C). The second-stage ZSM-5 reactor was not run. The major events of this run and ranges of process variables and operating results are summarized in Tables 23 and 24, respectively.

Major highlights of the run were:

- The catalyst was activated at the same conditions as those for synthesis (250°C, 1.48 MPa).

Table 23

Major Events in Run CT-256-5

DOS	Event
0-1.2	Started synthesis (1st-stage only); 250°C; 1.48 MPa; 6.0 cm/s
1.2	250--->240°C; 3.5 cm/s
2.0-3.0	Lost appox. 25% of catalyst
3.4	240°C; 3.5--->3.1 cm/s
4.4	240--->245°C
6.2	245--->250°C; 3.2 cm/s
8.3	3.2--->3.0 cm/s
13.0	Cold shutdown

Table 24

Ranges of Process Variables and Operating Results

(Run CT-256-5)

First-Stage Process Variables	Range
Temperature, °C	240-250
Pressure, MPa	1.48
Superficial Feed-Gas Velocity, cm/s	3.0-6.0
SV, NL/gFe-hr	2.1-2.7
Catalyst Loading, Wt %	10-20
Operation Results	
H_2+CO Conversion, Mol %	50-70
Methane + Ethane Yield, Wt % HC	1.6-3.5
Reactor-Wax Yield, Wt % HC	57-85

- The ranges of operating conditions for the first-stage reactor were:

Temperature, °C	240-250
Pressure, MPa	1.48
H_2/CO Feed Ratio, Molar	0.7
Superficial Feed-Gas Velocity, cm/s	3.0-6.0
SV, NL/gFe-hr	1.7 2.7

  The H_2+CO conversion ranged from 50 to 72%, and the methane + ethane yield from 1.6 to 3.5 wt % of the total hydrocarbons produced.

- The reactor-wax yield was extremely high, ranging from 57 to 85 wt % of total hydrocarbons produced.

At the conclusion of the run the slurry was allowed to cool in-situ, without exposing it to air. In this way the catalyst may be used again at a future date. Catalyst loading at the start of this run was 20%, the same as in the previous run.

2. First-Stage Fischer-Tropsch Reactor Operation

To achieve an initial space velocity of 2.7 NL/gFe-hr, the superficial gas velocity was set at 6.0 cm/s, the highest ever attempted in the first-stage slurry reactor. No adverse effects of this were detected, and the activation of the catalyst proceeded smoothly. Figure 30 shows the conversion, as well as the methane and ethane yields, for the entire run. Material balances were performed daily after three DOS, and are tabulated in Table F-1 of Appendix F. From Figure 30 it is seen that the H_2+CO conversion rose steadily over the first twenty-four hours to 62%, while at the same time, the methane and ethane selectivity dropped to about 1.7 wt % of the total hydrocarbons produced. Under these conditions, the reactor-wax yield was over 85 wt % of hydrocarbons, which was more than what could be handled by the catalyst settling system. It was, therefore, decided to lower the synthesis gas throughput (3.5 cm/s) and the temperature (240°C), so that the conversion would remain nearly constant, while the reactor-wax make would be reduced. Initially, the conversion dropped to 54%, but it reached 60% after six hours. Reactor-wax withdrawals were begun at this time, lasting twelve hours each day, which was more than enough to keep up with the reactor-wax production for the rest of the run. Figure 31 is a plot of the cumulative reactor-wax production during the run. Table F-2 and F-3 tabulate the compositions of the non-wax and reactor-wax hydrocarbon products for different times on stream. Table F-4 summarizes two sets of F-T hydorcarbon selectivities. One represents those at 240°C (3.8 DOS) and the other those at 249°C (8.8 DOS).

FIGURE 30

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD

(RUN CT-256-5; 1ST-STAGE CATALYST I-C: PPTD Fe/Cu/K_2CO_3)

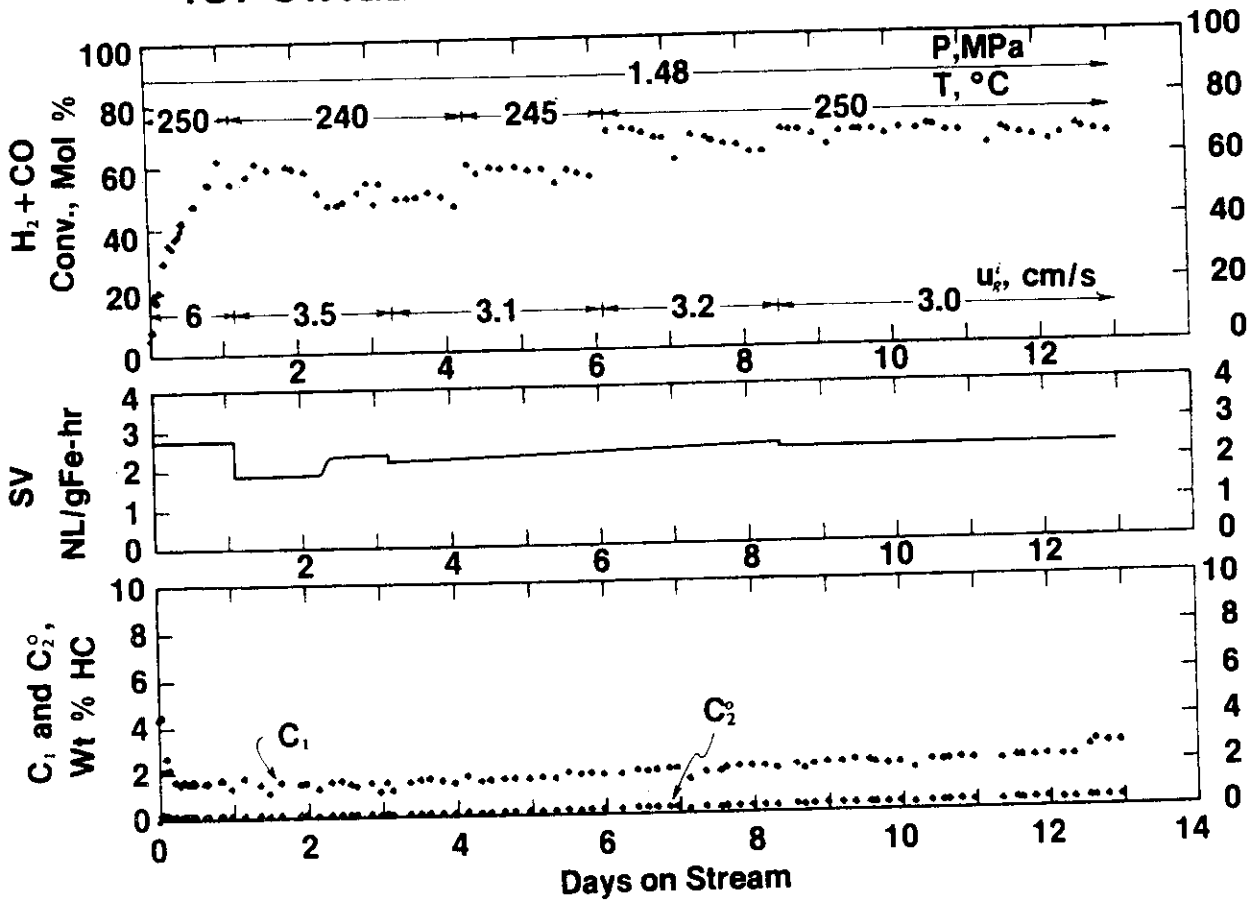
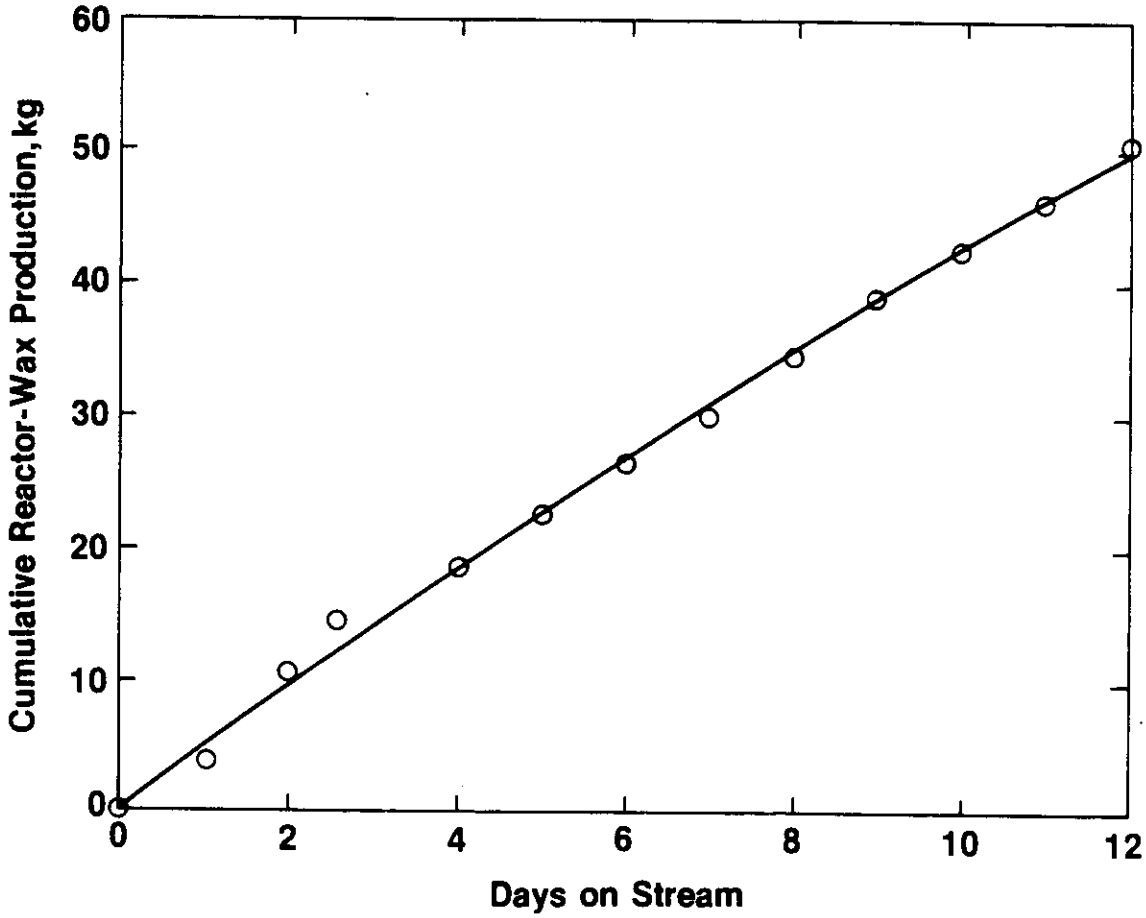


FIGURE 31

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

(RUN CT-256-5)



The reactor-wax withdrawal was carried out smoothly up to three DOS. Unfortunately, however, an operational error had occurred while draining wax at that time, and approximately 25% of the catalyst in the slurry reactor was accidently removed. This caused the H_2+CO conversion to drop to 50%. The superficial gas velocity was then reduced to 3.1 cm/s to increase the H_2+CO conversion. After this point, catalyst losses were relatively constant, averaging less than 1% of the total inventory per day.

At four DOS, the reactor temperature was raised to 245°C which resulted in higher H_2+CO conversion (60%), but no appreciable change in the methane or ethane yield. Over the next two days, however, gradual catalyst losses dropped the conversion to 56%, at which time the temperature was increased to 250°C where it remained for the balance of the run. Initially, the conversion was as high as 70%, but gradually declined to 63% in two days due to a slight catalyst loss. At this point the superficial gas velocity was lowered by 6% to compensate for the catalyst losses. This brought the conversion back to 69%, and it remained between 66 and 70% for the rest of the run.

The catalyst loss after eight DOS was substantially less than the loss at the earlier time due to an improved shorter dip-tube design of a new on-line slurry settling tank at the 152 cm level. This also resulted in less reactor-wax withdrawal per operation.

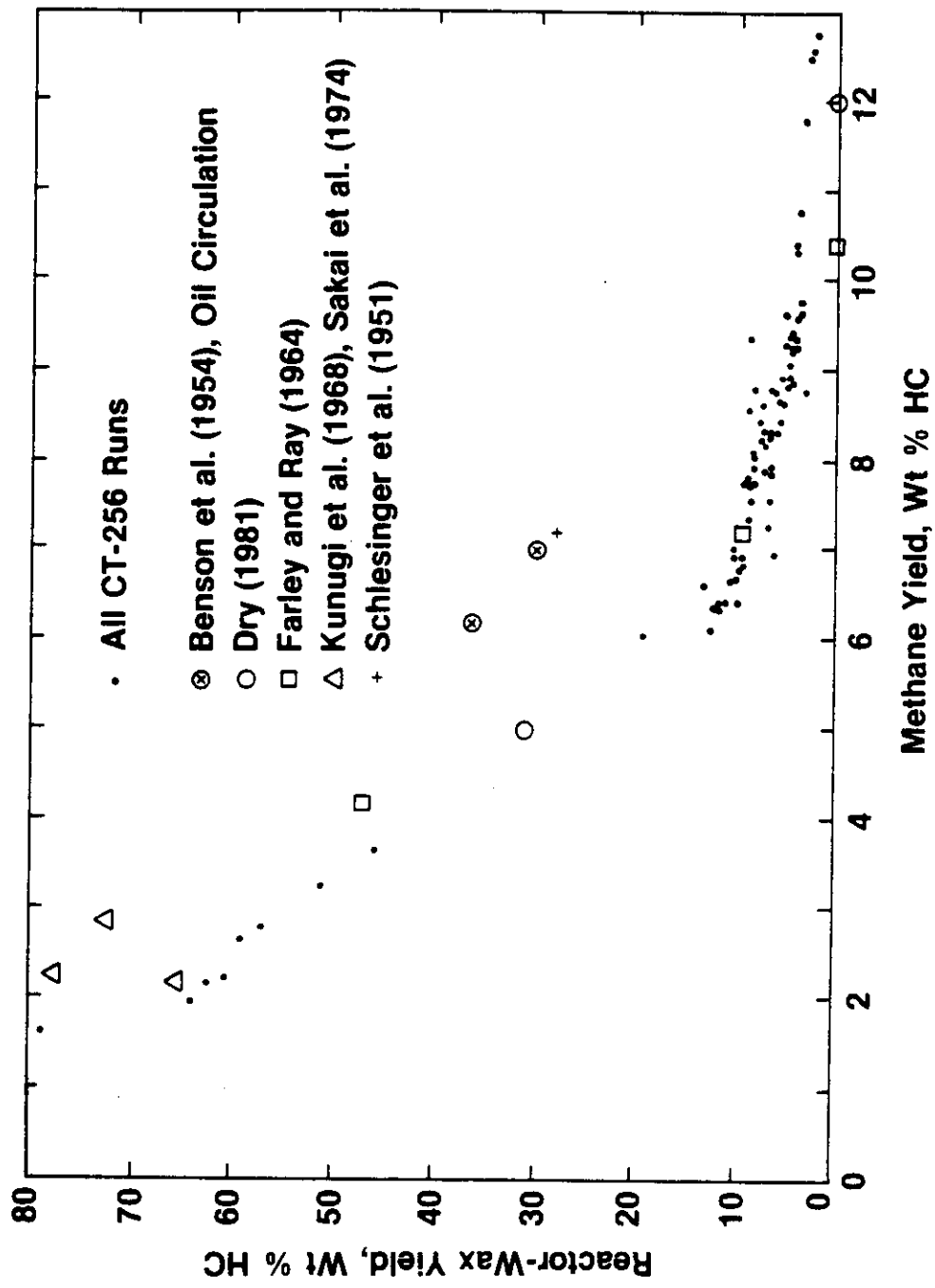
The methane + ethane yield increased slowly but constantly during this run. Changing temperature did not show any short-term effects. It appears that at low temperature (240°C) the methane + ethane yield changed more slowly than at higher temperature. This may indicate a long-term aging effect.

Figure 32 shows the reactor-wax yield as a function of the methane yield, covering all the BSU runs. The range of methane yield covered by Run CT-256-5 was 1.5 to 2.8 wt % of total hydrocarbons produced. Similar data from literature are also included in this figure showing good agreement.

Run CT-256-5 was ended after thirteen days when a seal on the Mobiltherm circulating pump ruptured. This caused the reactor temperature to drop, and it was decided to perform a cold in-situ shutdown. That is, the slurry was allowed to solidify in the reactor under nitrogen flow. In this way the slurry may be reused in the future.

Similar to what was observed in Run CT-256-4, the acid number of a F-T liquid hydrocarbon sample was substantially higher (27 mgKOH/g) than those of Run CT-256-3 (1-3 mgKOH/g). The acid number of an aqueous sample was also higher (92 mgKOH/g), compared to 2-7 mgKOH/g from Run CT-256-3. Since the second-stage reactor was not operating during this run, the

FIGURE 32


REACTOR-WAX YIELD VERSUS METHANE YIELD
All CT-256 Runs
Benson et al. (1954), Oil Circulation
Dry (1981)
Farley and Ray (1964)
Kunugi et al. (1968), Sakai et al. (1974)
Schlesinger et al. (1951)
Reactor-Wax Yield, Wt % HC
Methane Yield, Wt % HC
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10
12