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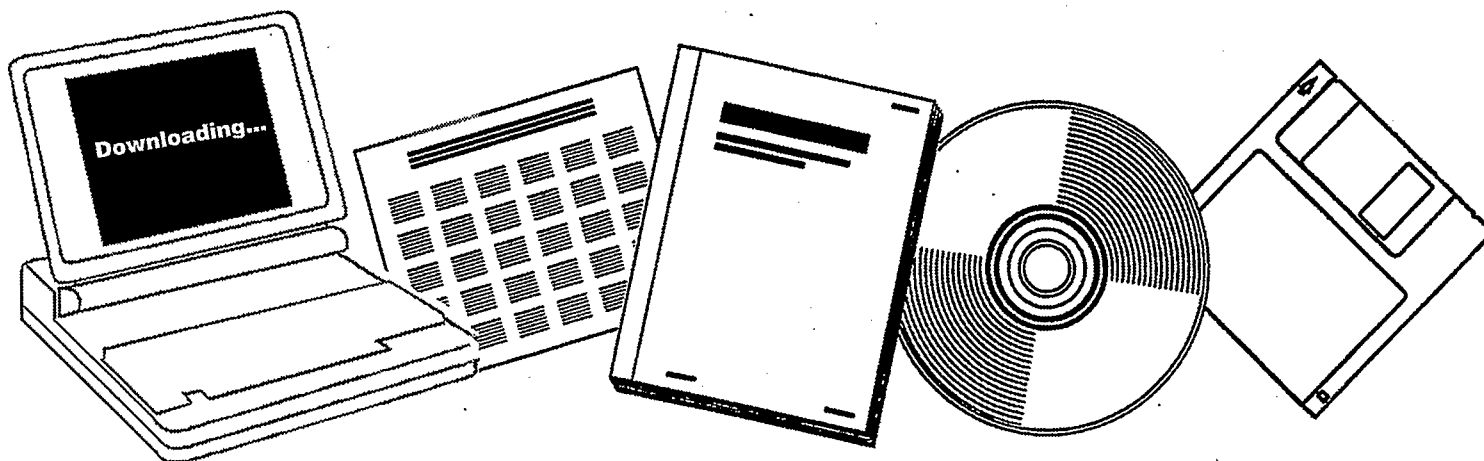
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**SLURRY FISCHER-TROPSCH/MOBIL TWO-STAGE
PROCESS OF CONVERTING SYNGAS TO HIGH
OCTANE GASOLINE. QUARTERLY REPORT, 1
JANUARY-31 MARCH 1982**

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

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SLURRY FISCHER-TROPSCH/MOBIL TWO-STAGE PROCESS
OF CONVERTING SYNGAS TO HIGH OCTANE GASOLINE

QUARTERLY REPORT FOR THE PERIOD
1 JANUARY - 31 MARCH, 1982

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I. Abstract

The shakedown of the portion of the BSU that was essential to the operation of the two-stage reactors was initiated in late December 1981 and has now been successfully complete as planned. The break-in operations of the portions of the BSU that are not essential to the current operation of the two-stage reactors will be carried out during future operations.

A limited hydrodynamic study using the slurry bubble-column of the BSU has been conducted. The data included the system pressure-drop and the gas holdup at various gas velocities using Mobil base stock F-509. Limited data on gas holdup during normal synthesis operation was also obtained. This hydrodynamic data is part of the effort to improve our understanding of the hydrodynamics of a bubble-column reactor.

The evaluation of the first slurry Fischer-Tropsch catalyst, a Fe/Cu/K₂CO₃ catalyst designated I-A, was initiated, and its first 350 hours of operation is reported. The run is being continued. The break-in operation of a second-stage ZSM-5 reactor, containing a ZSM-5 catalyst designated II-A, has also commenced without any problem. The operation was very smooth and highly successful considering the complexity of the pilot plant.

During this operation, high gas holdup in the bubble-column reactor has been observed. This may limit the catalyst loading and the gas throughput of the reactor. Large amounts of heavy hydrocarbons retained in the slurry reactor have been observed also. This reactor-wax yield increased greatly with decreasing methane yield.

II. Objective and Scope of the Project

The overall objective of the contract is to develop a two-stage slurry Fischer-Tropsch/ZSM-5 process for direct conversion of syngas, of the type produced in a coal gasification system, to high octane gasoline. The specific objective is to design, construct, and operate a bench-scale pilot plant so that the economic potential of this process concept can be evaluated. To accomplish these objectives, the following specific tasks will be undertaken:

Task 1 - Design of Bench-Scale Pilot Plant

A two-stage slurry F-T/ZSM-5 bench-scale pilot plant will be designed for conversion of syngas to high octane gasoline. The slurry F-T reactor will be 2" ID and 25' high. The fixed-bed ZSM-5 reactor will be 2" ID and 4-18" high. A distillation column will be designed to obtain stabilized gasoline products.

Task 2 - Construction and Shakedown of Pilot Plant

The pilot plant will be constructed in MRDC Paulsboro Laboratory. The unit will be shaken down when completed.

Task 3 - Operation of Pilot Plant

At least three slurry F-T catalysts will be tested in the bench-scale pilot plant. One of these catalysts may be provided by DOE's alternate catalyst development projects. The best first-stage catalyst together with a ZSM-5 class zeolite catalyst will be used for process variable studies and catalyst aging tests in the bench-scale unit. Products obtained from the unit will be evaluated to define their qualities.

Task 4 - Conceptual Design Study

A preliminary conceptual design of the process will be developed for a commercial size plant for the conversion of syngas to high octane gasoline. Scoping costs of the plant will be estimated.

III. Summary of Progress to Date

The shakedown of all essential portions of the BSU was initiated in late December 1981, and was completed smoothly as planned in this quarter. The break-in operation of the portions of the BSU that are not essential for the current operation of the two-stage reactors will be carried out in the future during normal operation. These portions include the liquid hydrocarbon distillation section and the regeneration circuit of the ZSM-5 reactors.

Limited data on the system pressure-drop and the gas holdup in the BSU bubble-column were collected. The system pressure-drops were very small at various gas flow rates up to the design gas flow rate when the unit was dry. Small pressure drops through the feed-gas distributor were observed when the bubble-column was loaded with first the Mobil base stock F-509 (a heavy hydrocarbon oil) and then a catalyst slurry. At 2 cm/s superficial feed-gas velocity, the pressure drop was 120-130 KPa. These pressure drops were satisfactory for the current operation.

The bubble-column gas holdup data was estimated using the Mobil base stock F-509 in the BSU bubble-column. A liquid-level-measurement system consisting of DP-cells was successfully used for this purpose. Unfortunately, the system did not work properly with FT-200 Vestowax, a Fischer-Tropsch paraffin wax. However, gas holdup data were estimated by the use of the viewports on the bubble-column to observe the slurry level, and by the withdrawal of the slurry between the viewports. The value of the gas holdup obtained was substantially higher than the corresponding value from a published correlation reported by Deckwer, et al. Further study of this phenomenon is needed. Such a high gas holdup may limit the catalyst loading and the gas throughput of the pilot plant.

The break-in operation of both the first-stage F-T slurry bubble-column and the second-stage fixed-bed ZSM-5 reactors was initiated smoothly. A Fe/Cu/K₂CO₃ catalyst, designated I-A, was used in the first reactor, and a ZSM-5 catalyst, designated II-A, was used in the second reactor. The second-stage reactor was brought on-stream after the first-stage reactor was in operation for 300 hours. The run, designated CT-256-1, was still being continued at the end of this reporting period.

The following highlights were observed during this operation:

- A large gas holdup, as high as 63 vol% at 2.2 cm/s superficial gas velocity, in the BSU bubble-column reactor was observed at the beginning of the run. This high gas holdup was probably due to foaming of the startup wax.
- The F-T catalyst was pretreated at 280°C, 1.14 MPa, and 7.9 NL/gFe-hr space velocity with 0.7 H₂/CO synthesis gas for seven hours.
- Various operating conditions were used to explore the limits and the responses of this new pilot plant. The ranges of the operating conditions were:

Temperature, °C	260-266
Pressure, MPa	1.14-1.34
Superficial gas velocity, cm/s	1.3-2.2
Space velocity, NL/gFe-hr	4.4-11.9

The H₂+CO conversion was 38-80 mol% and the methane and ethane yield ranged from 7 to 11 wt% of the total hydrocarbons produced. A very uniform temperature profile was observed in the bubble-column reactor.

- High reactor-wax yields (the heavy hydrocarbons remained in the slurry reactor), from 7 to 33 wt% of the total hydrocarbons produced, were observed. The yield went up drastically with a low methane yield, a trend consistent with the Schulz-Flory distribution for F-T products.

IV. Detailed Description of Technical Progress

A. Task 2 - Construction and Shakedown of Pilot Plant

1. Status of Task

The construction of the bench-scale unit was completed on schedule and the shakedown operation was initiated in late December, 1981. The shakedown of all essential portions of the BSU is now complete. The break-in operations of the portions of the BSU that are not essential to the current operation, such as the liquid hydrocarbon distillation section, and the regeneration circuit of the ZSM-5 reactor will be carried out in the future during normal operation. Basically, the shakedown operation includes:

- Checking of all pipings and valves.
- Calibration of equipment.
- Training of operators.
- Testing of equipment.

All shakedown tasks were carried out smoothly as planned. In the following sections, the description of tasks conducted for the Gas Feed Section, the First- and Second-Stage Reactors and Product Recovery Sections, and a final BSU pressure testing, are given separately in detail.

2. Gas Feed Section

An in-house H₂ supply was used for the BSU operation. Using a conventional gas chromatographic analysis, its purity was estimated to be 99.89 mol% with N₂ as the only impurity. The CO supply was delivered in a cylinder-trailer holding approximately 35,000 SCF at 2,000 psig pressure. It was purchased from Airco Company and contained less than 2 mol% impurities. Its composition was analyzed using a conventional GC to be:

CO	98.12 mol%
H ₂	0.34
N ₂	1.17
CH ₄	0.37
	100.00

The in-house N₂ was also used for the BSU operation. Its purity was higher than 99.99 mol% based on a GC analysis. The

compositions of these gas supplies will be checked occasionally to insure their purity. Analysis of the gas composition of each new CO shipment will be mandatory also.

In addition to the checking of the feed gas supplies, the following tasks were also performed during the shakedown operation of this section.

- Purged and cleaned all lines with N₂.
- Tested and calibrated flow indicators and controllers.
- Pressure tested the entire section with 2.86 MPa (400 psig) N₂ followed by 2.86 MPa H₂.
- Calibrated Glycol-Flow-Measurement systems for H₂, CO, and total feed.
- Checked the operation of the emergency feed-gas shut-off valves.

3. First- and Second-Stage Reactors and Product Recovery Sections

This portion of the BSU is the most essential part with the exception of the regeneration circuit of the second-stage ZSM-5 reactor. The latter is not essential for the immediate operation and its break-in operation will be initiated after one of the second-stage reactors has some coke deposition. The specific tasks that were conducted for the shakedown operation of the first- and second-stage reactors and the product recovery sections are listed below.

- Cleaned and flushed the slurry reactor, slurry-loading tanks, wax-withdrawal lines and receivers, slurry-sample receivers, and all associated lines with n-hexane.
- Cleaned and pressure-tested the inter-stage sampling loop with N₂.
- Flushed the fixed-bed reactors, the condensers and the separators with n-hexane.
- Pressure-tested section by section the slurry reactor and associated vessels, two second-stage fixed-bed reactors, and the product recovery section with 2.86 MPa H₂ at ambient temperature; repaired all leaks.

- Checked all steam tracings for proper operation.
- Tested the slurry-loading tanks by loading n-hexane into the cold reactor.
- Tested all temperature indicators, recorders, and controllers.
- Successfully tested the "Chromalox" oil circulation system (using Mobiltherm-600) to heat the slurry reactor up to 316°C. Also checked the "Cascade" temperature controllers (TIC-2 and -4) for maintaining a constant reactor temperature.
- Pressure-tested the slurry reactor with 2.86 MPa H₂ at 260°C to achieve less than 6.9 KPa/hr (1 psi/hr) pressure loss.
- Pressure-tested two fixed-bed reactors with 2.86 MPa H₂ at 371°C.
- Pressure-tested condensers and separators at operating temperatures.
- Pressure-tested and run the recycle compressor and regeneration-recycle compressor of the second-stage reactor with N₂.
- Calibrated all level indicators and controllers.

The heating and cooling medium, Mobiltherm-600, is a high-temperature petroleum oil which is thermally stable up to 316°C. However, slight deterioration is expected at a temperature higher than 232°C due to oxidation and thermal cracking. Periodic testing of the fluid is planned to insure its proper heat-transfer characteristics. The following physical properties of this oil were obtained from Mobil's Technical Bulletin:

Sp. Gr., 15.5/15.5 °C	0.97
Flash Point, °C	177
Pour Point, °C	-18
ASTM Distillation, °C	
10%	338
50%	371
90%	404

4. Liquid Hydrocarbon Distillation Section

The operation of this section is not essential to the operation of either the slurry F-T reactor or the combined two-stage reactors. The break-in operation of this section will be carried out in the future when there is a high rate of liquid hydrocarbon production. Nevertheless, the following minor tasks were performed during the shakedown of this section:

- Cleaning the whole section with hexane.
- Pressure-testing with H₂ at 0.38 MPa (40 psig) and 204°C.
- Checking and calibration of temperature, pressure, and level indicators and controllers.

5. Final BSU Pressure Testing

After the shakedown operation of each section of the BSU, the whole unit was pressure tested. The unit back-pressure controller PIC-2 was successfully checked to handle up to 2.86 MPa unit pressure with H₂ flowing through the unit at up to 4.25 Nm³/hr. During this testing, the temperatures of the first- and second-stage reactors were maintained at 260°C and 316°C, respectively. This portion of the shakedown operation was also completed with no major problems.

6. Conclusions

The shakedown operation of the BSU was initiated in late December, 1981. The shakedown of all essential portions of the BSU has now been complete. All operations were smoothly carried out as planned. The break-in operation of the portions of the BSU that are not essential to the immediate operation of the first-stage slurry F-T reactor and the second-stage ZSM-5 reactor will be carried out in the future during normal operation. These include the operation of the liquid hydrocarbon distillation section and the regeneration of the second-stage reactor.

B. Task 3 - Operation of Pilot Plant

1. Slurry Bubble-Column Hydrodynamic Studies

Some important information on bubble-column hydrodynamics was obtained using the bubble-column reactor of the BSU during the current quarter. System pressure-drops and gas holdups were measured. The system pressure-drop is important to the BSU operation because an excessive pressure-drop will limit

the gas throughput of the BSU. The gas holdup is also an important process variable. A too large or too small a gas holdup is undesirable. Too large a gas holdup results in a low apparent catalyst density, and therefore a very large reactor height and volume will be required to achieve a high synthesis gas throughput and conversion. At the other extreme, too small a gas holdup may indicate large bubble-size and low gas-liquid interphase surface area, resulting in large mass-transfer resistance. The approximate range of desirable gas holdup is 10-35 vol%. In the following, both system pressure-drop and gas holdup data are reported.

a. System Pressure-Drop Data

Pressure drops through the feed-gas distributor of the bubble-column reactor, the effluent filter at the top of the bubble-column reactor, and the total system (from the bubble-column reactor feed-gas distributor to the back-pressure regulator) were constantly monitored. Before the bubble-column reactor was loaded with any liquid, the whole BSU was pressurized to 2.86 MPa and the bubble-column reactor was heated up to 260°C. The system pressures were checked by varying the flow rate of a 50/50 (mole %) H₂+N₂ gas from 0 to 2 Nm³/hr, the design flow rate. The pressure-drop within the system was very small over the whole flow rate range. At the highest flow rate, the pressure drop between the bubble-column feed distributor and the back-pressure regulator was less than 14 KPa (2 psi). Since all the pressure gauges have 34 KPa (5 psi) graduation reading, no accurate readings with a small pressure drop are possible. A N₂+H₂ mixed gas was used in this test because the CO gas line was not yet operational at the time.

Next, the system pressure-drop was monitored with 5,614 gm Mobil F-509⁽¹⁾ base stock in the bubble-column reactor. The only significant pressure drop observed was the pressure drop across the bubble-column reactor feed-gas distributor. At 100 KPa (0 psig) pressure in the reactor effluent line, and 38°C and 149°C reactor temperature, the following pressure drops were estimated from the measured pressure difference between the top of the slurry reactor and the distributor:

u_g^i , cm/s	Pressure Drop Through Feed-Gas Distributor, KPa
1.3-4	76
4	76
5	97
13.5	140

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

At the superficial gas velocity of less than 1.3 cm/s, the pressure drop was too small to be meaningfully read from the pressure gauges; between 1.3 and 4 cm/s, the variation of the pressure drop was small and irregular. However, the pressure drops in all cases were substantially higher than the corresponding pressure drops of the dry distributor. The additional pressure drop probably resulted from the blocking of some free-flow area of the gas distributor by the liquid. The gas distributor is a sintered stainless-steel plate of 6.4 mm thickness. It has a mean pore size of 10 μm and a free flow area of larger than 90%.

The system pressure-drop was also monitored after the bubble-column reactor was loaded with catalyst slurry (182 gm of Catalyst I-A, 747 gm of Mobil base stock F-509, and 3,400 gm of FT-200 Vestowax⁽¹⁾). The following results were obtained with flowing N_2 and with the bubble-column reactor at a temperature of 260°C and an effluent pressure of 1.14 MPa (150 psig):

u_g^i , cm/s	Pressure Drop Through Gas Distributor, KPa	Total Pressure Drop, KPa
2	110	170
4	300	370

Contrary to previous pressure drop measurements, there were some pressure drops in the downstream of the unit, as shown above. This is probably due to resistance arising from the condensation of some liquid products in the downstream lines. The pressure drop resulting from the liquid height in the bubble-column is about 21 KPa.

During the run CT-256-1, the system pressure-drop did not vary significantly for the same gas-flow rate. The following pressure drop data was obtained:

Time on Stream, Hrs.	u_g^i , cm/s	Pressure Drop Through Gas Distributor, KPa	Total Pressure Drop, KPa
150	1.3	55	124
143	1.8	90	159
125	2.1	120	186
110	2.2	130	193

The pressure drops at 2.2 cm/s superficial gas velocity were nominally in agreement with those measured before the startup of

(1) A Fischer-Tropsch paraffin wax probably from SASOL. Average molecular weight = 600.

the run.

All these pressure drop data indicated that the design gas throughput of the pilot plant (4 cm/s superficial gas velocity) may be satisfactorily achieved. Further evaluation at higher gas velocity may be needed.

b. Bubble-Column Gas Holdup Data

A liquid-level-measurement system, described in the April-June, 1981 Quarterly Report, was designed to measure the liquid level in the bubble-column reactor of the BSU using DP-cells to measure pressure drops at six positions along the reactor. It is the first time that devices of this type were ever used in a slurry bubble-column. Consequently, there was a risk factor involved, the risk that the devices would work improperly. To prevent the slurry from entering the DP-cell legs, all six legs were purged with N_2 at a high rate so that the purge-gas velocity at the nozzle tip into the reactor was 50 cm/s. The break-in operation of this system was done with Mobil base stock F-509, because this stock can be used at room temperature and also at higher temperatures. The system was run smoothly with this base stock at 38°C and 149°C. The gas holdups calculated from the liquid level measurements at various superficial gas velocities are summarized in Table 1. The same table also contains the values of the gas holdup calculated based on a correlation reported by Deckwer, et al. (1980), $\epsilon_g = 0.053 (u_g^i)^{1.1}$, for F-T Vestowax. The Mobil base stock F-509 has a viscosity at 149°C similar to that of the F-T Vestowax at 260°C; however, its gas holdup values are consistently lower than the equivalent values calculated from the above correlation at the same superficial gas velocity. Obviously, some other physical parameters may be also important in determining a liquid's hydrodynamic behavior in a bubble-column.

After the successful break-in operation of the bubble-column with the Mobil base stock F-509, the reactor was unloaded, and then loaded with FT-200 Vestowax at 149°C with N_2 flowing at 2 Nm³/hr. The liquid-level-measurement system did not function properly because the melting wax easily seeped through the nozzles, where the DP-cell legs and the reactor were connected, and solidified in the unheated section of the legs. The pressure-drop readings became meaningless when this happened. This occurred even when the N_2 gas velocity at the nozzle was as high as 200 cm/s. Nevertheless, the DP-cell legs at the top of the disengagement zone and below the feed-gas distributor were not contaminated by the melting wax. Unfortunately, the range of the DP-meter is not large enough to cover such a large pressure drop. Several ideas have been developed in order to measure the liquid-level in the F-T bubble-column reactor since then. Some modifications of the BSU may be implemented after the completion

of the first run to try out some of these ideas.

The slurry bubble-column of the BSU is equipped with four viewports along the column, at 305, 457, 610, and 762 cm above the feed-gas distributor. Through the use of these viewports for the observation of liquid levels together with the proper withdrawal of reactor liquid, one can estimate the gas holdup in the bubble-column. This was first tried at 162 hours time-on-stream in the first BSU run, CT-256-1, which is described later in this report. At that time, the slurry level reached 762 cm viewport after the feed-gas superficial velocity was raised to 3.0 cm/s. The reactor liquid was then withdrawn until the level reached 609 cm viewport. The total amount of the reactor liquid withdrawn was 1,200 gm including 30 gm of catalyst. The volume of the liquid withdrawn was estimated to be 1,740 mL, which gave a gas holdup value of about 47 vol%. The superficial gas velocity between the 610 and 762 cm viewports was estimated to be 2.6 cm/s, slightly lower than the feed gas velocity because of the molar contraction due to F-T reactions. The estimated gas holdup was substantially larger than the value (15 vol%) at the equivalent gas velocity reported by Deckwer, et al. (1980) using the FT-300 Vestowax in a non-reacting column at 260°C. This gas holdup is substantially larger than that of the design basis. Such a high gas holdup will probably limit catalyst loading in the reactor, and therefore result in a lower gas throughput than what the reactor was originally designed for. However, further experimentation will be needed before a final conclusion may be drawn. Similar experiments will be carried out in the later part of this run and in the future runs.

2. Run CT-256-1 - Evaluation of the First F-T Catalyst and a Break-in Operation of a Second-Stage ZSM-5 Reactor

The first run of the BSU, CT-256-1, was successfully initiated on March 17, 1982 using catalyst I-A, a Fe/Cu/K₂CO₃ catalyst. One of the second-stage ZSM-5 reactors was loaded with a ZSM-5 catalyst II-A. The reactor was initially bypassed for the first-stage bubble-column reactor operation; its break-in operation started on March 30, 1982. The major events of this run up to the end of this reporting period are summarized in Table 2. The run was continuing satisfactorily at the end of this period. In the following, a detailed description of the run within this reporting period is given.

a. Slurry Bubble-Column Catalyst Loading

The slurry reactor was heated to 260°C with N₂ preheated to 260°C at a flow rate of approximately .085 Nm³/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 of the BSU. The preventive design of this unit 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 N₂ at 0.085 Nm³/hr. 600 gms of FT-200 Vestowax was first loaded into the reactor through a slurry-loading tank followed by 2,775 gms of slurry containing 625 gms of catalyst, 750 gms of Mobil base stock F-509 and 1,400 gms of FT-200 wax. The loading tank and the lines were then rinsed twice with 700 gms of FT-200 wax each time. The whole unit was then pressured to 1.14 MPa (150 psig) with N₂ bubbling at 0.935 Nm³/hr (2.2 cm/s superficial gas velocity) in the reactor.

The unexpanded slurry level for 4,772 gm of slurry (density of uniform slurry = 0.71 gm/mL) was estimated to be 311 cm high. 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 more than 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 from the top of the disengagement zone. Consequently, 2,041 gm of slurry were drained from the reactor. Two samples of this slurry were taken and shown to contain 6.6 and 6.8 gm/s 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 substantial amount of the catalyst remained in the catalyst loading tanks. This suspicion was confirmed to some degree later. Based on these solid content analyses, the amount of catalyst loaded into the reactor was 319 gm instead of 625 gm; the amount of the catalyst in the reactor after partial unloading was 182 gm.

b. Fischer-Tropsch Catalyst Pretreatment

The F-T catalyst, I-A, was in an oxide form when it was loaded into the reactor and must be reduced to an active form using synthesis gas. The pretreatment conditions were:

H ₂ + CO flow rate	=	0.952 Nm ³ /hr
H ₂ /CO, molar ratio	=	0.7
SV, NL/gFe-hr	=	7.9
u _g ⁱ , cm/s	=	2.6
T, °C	=	280
P, MPa	=	1.14

The planned space velocity was 4 NL/gFe-hr. The higher space velocity given here was based on the solid-content measurement of the slurry unloaded from the reactor. The feed gas also contained a small amount of N₂. This N₂-flow resulted from a leak in the valve for the emergency N₂-supply to the BSU. The N₂-leakage was at a constant rate of 0.11-0.12 Nm³/hr. The resulting N₂-concentration in the feed gas varied with the synthesis gas flow-rate. Typically, for a feed gas superficial velocity of 2 cm/s in the BSU slurry bubble-column at 1.14 MPa (150 psig) and 260°C, the N₂-concentration in the feed gas amounted to 10-11 mol%. This minor difficulty did not significantly affect the current run and will be corrected after the current run is complete.

During the pre-treatment, the H₂+CO conversion and the concentration of CO₂ 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 CO₂, methane concentrations may only be obtained once per hour. However, the total molar contraction of the product-gas stream after reaction can be continuously monitored. This product gas molar contraction can be directly translated into the synthesis conversion as shown in Figure 1. Other results of the pretreatment are also given in this figure.

The pretreatment was terminated when the H₂+CO conversion reached 65 mol%. At that stage the reactor temperature was reduced to 260°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 H₂+CO conversion, the rate of change of the conversion, the rate of change of the CO₂ and CO 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.

c. Fischer-Tropsch Synthesis

The F-T synthesis was initiated immediately after catalyst pretreatment. The synthesis conditions and major changes of the reaction conditions during this reporting period are summarized in Table 2. The zero Time-On-Stream (TOS) corresponds to the beginning of the F-T synthesis. The TOS for pretreatment are, hence, shown in negative hours. Figure 2 gives preliminary results of H_2+CO conversion, wt% of the C_1+C_2 ° (i.e., methane + ethane) in total hydrocarbons produced for the 350 hours of TOS in this reporting period. It also summarizes the reaction conditions during this time.

Many changes of the operational conditions were made during this short period in order to explore the limits and responses of this new unit with respect to these changing conditions. In the first thirty-five hours TOS, there was an increase of H_2+CO conversion probably due to the under-pretreatment of the catalyst. The first reactor-wax withdrawn was carried out at forty-five hours 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 was later found to have a large hole in its filtering element. After about forty hours TOS, the H_2+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 taking place between 40 and 120 hours TOS. 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 120 hours TOS from the 7.9 NL/gFe-hr used earlier.

After 120 hours TOS, a series of variations on the feed gas velocity was done. 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 and 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 300 hours TOS. After the second-stage reactor was switched on, the methane and ethane increased somewhat to 12-15%, probably due to the additional methane and ethane formed in the second-stage reactor.

Two total-material balances from the first-stage reactor operation are reported in Table 3. These are the total balances obtained by combining the gaseous product and the three liquid product streams after the condensation and the separation of the total reactor effluent from the first reactor, but excluding the heavy hydrocarbons that were accumulated in the reactor. The quantification of the yield of this reactor-wax is not an easy task. Two approximate methods were used in the current evaluation.

The results of the first method are reported in Table 3. With this method, one first calculates the total amount of hydrocarbons produced assuming that the total hydrocarbon product had an atomic formula of $\text{CH}_{2.25}$. The reactor-wax yield was then estimated by subtracting from this estimated total hydrocarbons the amount of the hydrocarbons collected from all the downstream product streams. Obviously, this was an inexact way to estimate the reactor-wax yield unless the material balance had good C/H/O atomic balances. Unfortunately, a checking on the atomic balances requires detailed analyses of all product streams, which are seldomly available. Even when good atomic balances are available, the estimated reactor-wax yield may still be only a rough estimate because it contains all the analytical inaccuracies. However, this estimation can still give a rough idea of the trend on the reactor-wax yield.

The other method of estimating the reactor-wax yield is to take an inventory of all the reactor-wax withdrawals from and accumulations in the reactor. However, an inventory of the reactor-wax accumulation in the reactor is also inexact. It requires information on the liquid level and the gas holdup in the reactor, which are not accurately known. An attempt to estimate the reactor-wax yield in the current period of the run gave the following:

TOS, Hours	Methane Yield Wt%	Estimated Reactor- Wax, gm	Estimated Reactor-Wax Yield, Wt%
0-162	6- 9	4,960	23.0
162-350	9-12	850	7.3
0-350	6-12	5,810	17.2

In making this estimation, it was assumed that the bubble-column gas holdup at 162 hours TOS was 47 vol%, an estimation based on the reactor-wax withdrawal between 762 and 610 cm levels at 3.0 cm/s superficial gas velocity. Furthermore, it was assumed that, at 350 hours TOS, the expanded bubble-column liquid-level was

about 549 cm and the average gas holdup was 30 vol%.

Both methods of estimation showed that the reactor-wax yield decreased substantially with increasing methane yield. This was probably due to a shift of the hydrocarbon products to the light end following the Schulz-Flory carbon number distribution (Flory, 1967).

Although the accumulation of the reactor-wax in the bubble-column reactor was not completely unexpected, its large quantity was a surprise. From the point of the view of the process economy, it is most desirable to have a F-T catalyst and the process conditions that minimize the formation of methane and ethane, since those are lower-valued products. However, if the Schulz-Flory distribution holds for the formation of the methane and ethane, a low methane and ethane yield would imply a very high reactor-wax yield. Then the upgrading of the reactor-wax into high-valued marketable products becomes an important technical problem. To resolve this problem will require substantial exploratory research and development work, which is outside the scope of the current contract. Our immediate task is to search for a combination of a F-T catalyst and process conditions such that the yield of the light hydrocarbon gases and the reactor-wax is minimized.

To some degree, the reactor-wax yield can be decreased by increasing the F-T reactor temperature and decreasing the F-T reactor pressure. However, there are side effects associated with those changes. An increase of the reactor temperature will cause an increase on the catalyst aging and the methane and ethane yield. A decrease of the reactor pressure will cause a decrease on the catalyst utilization rate and an increase on the downstream processing cost. These side effects are expected to limit any substantial change on the F-T reactor temperature and pressure. Those effects will be evaluated in future runs.

The slurry reactor temperature was controlled using cascade temperature controllers which controlled the temperature of circulating Mobiltherm-600. Figure 3 shows a typical temperature profile of this reactor. The slurry level at that time was between 457 cm and 610 cm based on observations through the viewports. As seen in the figure, the reactor temperatures recorded at the locations below the slurry level showed a uniform temperature profile except at the 30 cm location. The thermocouple at that location always recorded 40-45°C lower than the expected slurry temperature. Upon inspection, it was found that the thermocouple was not properly inserted into the reactor and was about 1.25 cm away from the reactor wall. This small mishap will be corrected after the end of the current run.

The temperatures recorded in the vapor space at 610 cm and 762 cm locations were also significantly lower (35-45°C) than the expected vapor temperatures. These locations are unheated and contain bulky flanges. It is expected that the wall temperature there may be substantially lower than the neighboring vapor temperature. This results in a low thermocouple reading because of a large heat loss from the thermocouple tip to the cooler wall. Similar phenomenon happened at the thermocouple located at 305 cm position. However, the thermocouple there was immersed in slurry, which gave an excellent heat transfer between the slurry and the thermocouple and thus resulted in a much closer temperature reading (within 2°C) between the reading there and those measured by the thermocouples at the heated locations (152 and 457 cm above the feed-gas distributor). In Figure 3, the locations of these unheated flanges are designated by upward arrows.

Because of this large difference in the temperature reading when the slurry reached the thermocouples located at the unheated flanges, the readings there became an excellent indicator for the slurry level. The significantly lower (40°-45°C) temperature readings in the unheated vapor space above the slurry, however, indicated the possibility of the condensation of some heavy hydrocarbon product on the cold surfaces there. The reflux of this condensate into the slurry may affect the rate of the reactor-wax accumulation in the reactor. To minimize this complication, it is desirable to maintain the flanges at a temperature close to the reactor slurry temperature. A plan of using electric heating tapes to heat those flanges will be implemented after the completion of the current run.

Figure 3 also shows two Mobiltherm temperatures, one before its entrance to the reactor jacket and the other after its leaving from the disengagement zone jacket. At steady state operation, the Mobiltherm always leaves the disengagement zone jacket at a temperature a few degrees higher than that when it enters the reactor jacket. This increase on temperature represents a removal of reaction heat generated by the F-T synthesis. It was essential to minimize the Mobiltherm temperature change within the cooling jacket in order to maintain a uniform slurry temperature in the reactor. This was achieved by maintaining a high Mobiltherm flow-rate through the cooling jacket. Figure 3 shows that the temperature difference between the Mobiltherm and the neighboring slurry was only a few degrees.

d. Break-in Operation of a ZSM-5 Reactor

After a smooth operation of the first-stage reactor for 300 hours, break-in operation of a second-stage reactor, loaded with a ZSM-5-class catalyst, designated II-A, was initiated. The

reactor was smoothly brought on-stream under the following conditions:

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

The second-stage reactors were designed for an adiabatic operation. In the design stage of this contract, it was found that the conversion of the F-T products using a ZSM-5 catalyst is moderately exothermic. Consequently, a moderate adiabatic temperature increase in this reactor was expected. This adiabatic temperature increase was confirmed by the two catalyst temperature profiles given in Figure 4 for two different inlet temperatures. At 374°C inlet temperature, the maximum temperature of about 398°C occurred at about 10 cm from the entrance into the catalyst bed. The slight decline of the temperature between the 10 cm position and the end of the catalyst bed probably indicated an imperfect adjustment of the zoned heaters in simulating an adiabatic operation. The temperature profile for an inlet temperature of 357°C behaved similarly. The adiabatic temperature increases for both cases were close to what were originally expected.

Other than the adiabatic temperature increases, the performance of the ZSM-5 catalyst can also be demonstrated based on the combined gas analyses, on the liquid hydrocarbon product properties, and on the total material balances before and after the second-stage reactor. Table 4 shows the C₃⁻ hydrocarbon selectivity based on the combined gas analysis before and after the second-stage reactor was in operation. The ZSM-5 catalyst converted a large portion of light olefins to gasoline-range hydrocarbons. Furthermore, as soon as the ZSM-5 reactor was in operation, the heavy hydrocarbon liquid that condensed in the hot condenser became nil. This indicated that the ZSM-5 catalyst also converted the heavy hydrocarbon product from the F-T reactor into gasoline-range hydrocarbons. During this conversion, large quantities of aromatics were formed together with large quantity of propane as shown in Table 4. Based on our prior experience on two-stage operation, a high propane level after the ZSM-5 reactor, as shown in Table 4, showed very high severity operation for the second-stage ZSM-5 catalyst. Very high severity operation is less desirable since the gasoline yield will be low. To lower the severity of the second-stage operation, its reactor inlet temperature was lowered to 354°C from 371°C at 330 hours TOS.

3. Conclusions

Both the first-stage slurry Fischer-Tropsch bubble-column and a second-stage fixed-bed ZSM-5 reactor were brought on-stream smoothly in this quarter. The evaluation of the first F-T catalyst, designated I-A (containing Fe/Cu/K₂CO₃), has been initiated.

Some information on the system pressure-drops and the gas holdups in the BSU slurry bubble-column were collected. The pressure drop for a dry system was very small. A small pressure drop of 76-97 KPa through a feed-gas distributor of the bubble-column reactor was observed at superficial gas velocities of 4-5 cm/s after the column was loaded with Mobil base stock F-509 (a heavy hydrocarbon oil). This pressure drop increased to 110-330 KPa at 2-4 cm/s superficial gas velocities after the column was loaded with a catalyst slurry. The same pressure drops were maintained in the remaining period of the F-T synthesis. These pressure drops were satisfactory for the current operation.

The liquid-level-measurement system using DP-cells to measure pressure drops at six positions along the bubble-column reactor was first successfully broken-in using Mobil base stock F-509. Unfortunately, the same system did not work at 149°C with an F-T wax, FT-200 Vestowax, because the wax migrated through the DP-cell legs to the unheated section of the legs and plugged the lines. This happened even when the DP-cell legs were purged with N₂ at 200 cm/s through the nozzles where the DP-cell legs were connected with the bubble-column. Several new ideas for measuring the bubble-column liquid height are being considered and may be tried in the next BSU modification. In the current run, however, one method of estimating the gas holdup using the viewports along the column together with reactor-liquid withdrawals was tried. At 162 hours TOS, by withdrawing the column liquid-level from 762 to 610 cm (above the feed-gas distributor), a gas holdup value of 48 vol% at 2.6 cm/s superficial gas velocity was estimated. This gas holdup value was substantially higher than the corresponding value of 15% reported by Deckwer, et al. (1980). Such a high gas holdup may strongly limit the catalyst loading and the gas throughput of the BSU bubble-column reactor.

The first F-T synthesis run, CT-256-1, was successfully started-up on March 17, 1982. After two weeks of smooth operation of the first-stage reactor, a second-stage ZSM-5 fixed-bed containing II-A ZSM-5 catalyst was broken-in on March 30, 1982. The run was being continued at the end of this period. The highlights of this run are summarized in the following:

- A batch of F-T catalyst slurry, 4,775 gm containing 625 gm I-A Fe/Cu/K₂CO₃ catalyst, was loaded into the BSU slurry reactor. At 2.2 cm/s superficial gas velocity, the column gas holdup was found to be about 63 vol%, probably due to foaming of the startup wax. Part of the slurry, 2,041 gm, was immediately unloaded because it was feared that such a high gas holdup might make high gas velocity operation impossible. Later analysis of the solid-content of the unloaded slurry indicated that only about 182 gm catalyst was in the reactor. A substantial amount of the catalyst might remain in the loading pots and slurry lines. A plan to resolve this difficulty has been developed.
- The slurry F-T catalyst was then pretreated at 280°C, 1.14 MPa, and 7.9 NL/gFe-hr space velocity with 0.7 H₂/CO synthesis gas for seven hours.
- During the F-T synthesis, changing operating conditions were made to explore the limits and the responses of this new pilot plant. The ranges of the operating variables were:

T, °C	260-266
P, MPa	1.14-1.34
u _g ⁱ , cm/s	1.3-2.2
NL/gFe-hr	4.4-11.9

The H₂+CO conversion ranged 38-80 mol%. The C₁+C₂^o yield trended upwards with respect to increasing time-on-stream from 7 to 11 wt% of the total hydrocarbons produced before the second-stage reactor was switched on.

- The yield of the reactor-wax, the heavy hydrocarbons remaining in the slurry reactor, ranging approximately from 7 to 33 wt% of the total hydrocarbons produced, was surprisingly high. A low methane yield gave a high reactor-wax yield, a trend consistent with the well-known Schulz-Flory distribution for F-T products (Flory, 1967). The upgrading of the reactor-wax would become a critical problem when a low C₁+C₂^o yield is desired.
- The temperature profile in the slurry reactor was extremely uniform. The vapor phase temperature readings of the thermocouples in the unheated flange regions, however, were 35-45°C lower than the slurry temperature. The large heat loss from the thermocouple to the unheated wall was the major cause for such low temperature readings.

- A second-stage fixed-bed reactor loaded with a ZSM-5 catalyst, designated II-A, was brought on-stream smoothly. The operating conditions were 354-371°C inlet temperature and 880 l/hr GHSV. Catalyst temperature increases of 24-30°C were observed in the reactor. The analyses of the combined gas also showed a drastic reduction of light olefins and a high production of propane, indications of a very high aromatic yield.

4. Future Work

- The run CT-256-1 consisting of the evaluation and process-variable study of the F-T catalyst I-A will be complete.
- The mechanical modification of the BSU will be carried out.
- The evaluation of the second F-T catalyst, I-B, will commence as soon as the BSU modification is complete.
- A hydrodynamic study using a hot, non-reacting bubble-column will be initiated.

V. NOMENCLATURE

GHSV	Gas phase space velocity, (mL gas (STP)/hr-mL reactor)
P	Pressure, (mPa)
SV	Space velocity, (NL/gFe-hr)
T	Temperature, (°C)
u	Superficial velocity, (cm/s)

Greek Letters

ϵ_g	Gas holdup, (mL gas/mL expanded slurry)
μ	Viscosity, (g/s-m)

Superscripts

i	At reactor inlet
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Subscripts

g	Gas
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VI. Literature

Deckwer, W. D., Louisi, Y., Zaidi, A., and Ralek, M., I&EC, Proc. Res. & Dev., 19, 699-708 (1980).

Flory, P J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY (1967).

Table 1

Gas Holdup Data Obtained Using Mobil Base
Stock F-509 in BSU Bubble-Column (N₂ Gas)

	Mobil Base Stock F-509		F-T Vestowax(1)

T, °C	38	149	260
μ , gm/cm-s	0.25	0.02	0.022
u_g , cm/s	-----		
	ϵ_g , Vol%		

1.33	-	5.7	7.2
1.60	4.4	-	8.9
2.30	-	10.5	13.2
3.00	8.4	-	17.7
4.00	7.2	12.7	24.4
5.00	-	17.4	31.1
13.5	-	32.0	-

(1) The gas holdup values given here are based on an experimental correlation, $\epsilon_g = .053(u_g^i)^{1.1}$, reported by Deckwer, et al. (1980).

Table 2

Major Events of Run CT-256-1
(Up to March 31, 1982)

<u>TOS, Hrs.</u>	<u>Events</u>
-30	Loaded the first-stage reactor with 625 gm Catalyst I-A, 747 gm Mobil Base Stock F-509, and 3400 gm FT-200 Vestowax
-15	Unloaded 2041 gm slurry (6.7 wt% catalyst)
- 7	Began catalyst pretreatment (280°C, 1.14 MPa, .7 H ₂ /CO, 7.9 NL/gFe-hr)
0	Began F-T synthesis at 6 pm, March 17, 1982 (260°C, 1.14 MPa, 2.2 cm/s, 0.7 H ₂ /CO)
3	Slurry sample withdrawal (35 gm, 4.66 wt% catalyst)
11	Upset - High slurry level alarm, unit down for 10 minutes
45	Wax withdrawal (291 gm, 2.54 wt% catalyst)
71	Wax withdrawal (440 gm, 2.54 wt% catalyst)
95	Slurry sample withdrawal (42 gm, 2.64 wt% catalyst)
120	2.2 cm/s ----> 2.1 cm/s (superficial gas velocity)
138	2.1 cm/s ----> 1.8 cm/s (superficial gas velocity)
148	1.8 cm/s ----> 1.3 cm/s (superficial gas velocity)
160	1.3 cm/s ----> 2.2 cm/s (superficial gas velocity)
162	Wax withdrawal (1624 gm, 2.5 wt% catalyst) Slurry sample withdrawal (60 gm, 2.6 wt% catalyst)
184	2.2 cm/s ----> 1.8 cm/s (superficial gas velocity)
190	260°C ----> 262.8°C (1st reactor temperature)
195	262.8°C ----> 265.5°C (1st reactor temperature)
303	Began second-stage reactor operation with Catalyst II-A (371°C - inlet temperature)
328	1.14 MPa ----> 1.34 MPa (1st reactor pressure) 1.8 cm/s ----> 1.5 cm/s (superficially gas velocity)
330	371°C ----> 354°C (2nd reactor inlet temperature)

Table 3

Slurry Fischer-Tropsch Material Balances
(Run CT-256-1 up to March 31, 1982)

Operation Conditions:

	48-64	125-135
TOS, hrs	48-64	125-135
Temperature, °C	260	260
Pressure, MPa	1.14	1.14
H ₂ /CO	0.7	0.7
SV _i , NL/gFe-hr	8.5	7.9
u _G ⁱ , cm/s	2.2	2.1
(H ₂ + CO) conv., mol%	62	54

Selectivity: wt%

	48-64	125-135
C ₁ ^o	6.1	7.2
C ₂ ^o	1.4	1.4
C ₂ ⁼	3.4	4.1
C ₃ ⁼ /C ₃	6.1/0.9	7.0/1.0
C ₄ ⁼	6.0	6.4
nC ₄ ⁼ /iC ₄	0.9/0	1.0/0.1
C ₅ ⁻ -C ₁₁		
P	4.5	7.0
O	20.0	33.8
N	0	0
A	0	0
C ₁₂ ⁻ -C ₁₉	15.6	16.4
C ₂₀ ⁺	2.3	5.1
Reactor Wax ⁽¹⁾	32.8	9.5
	100.0	100.0

(1) Estimated by a difference between the estimated total hydrocarbons made (assuming CH₂.25) and the hydrocarbons collected in the downstream gaseous and liquid streams. The actual amount of the reactor wax may be more or less than these values.

Table 4

C₃ Hydrocarbon Selectivity

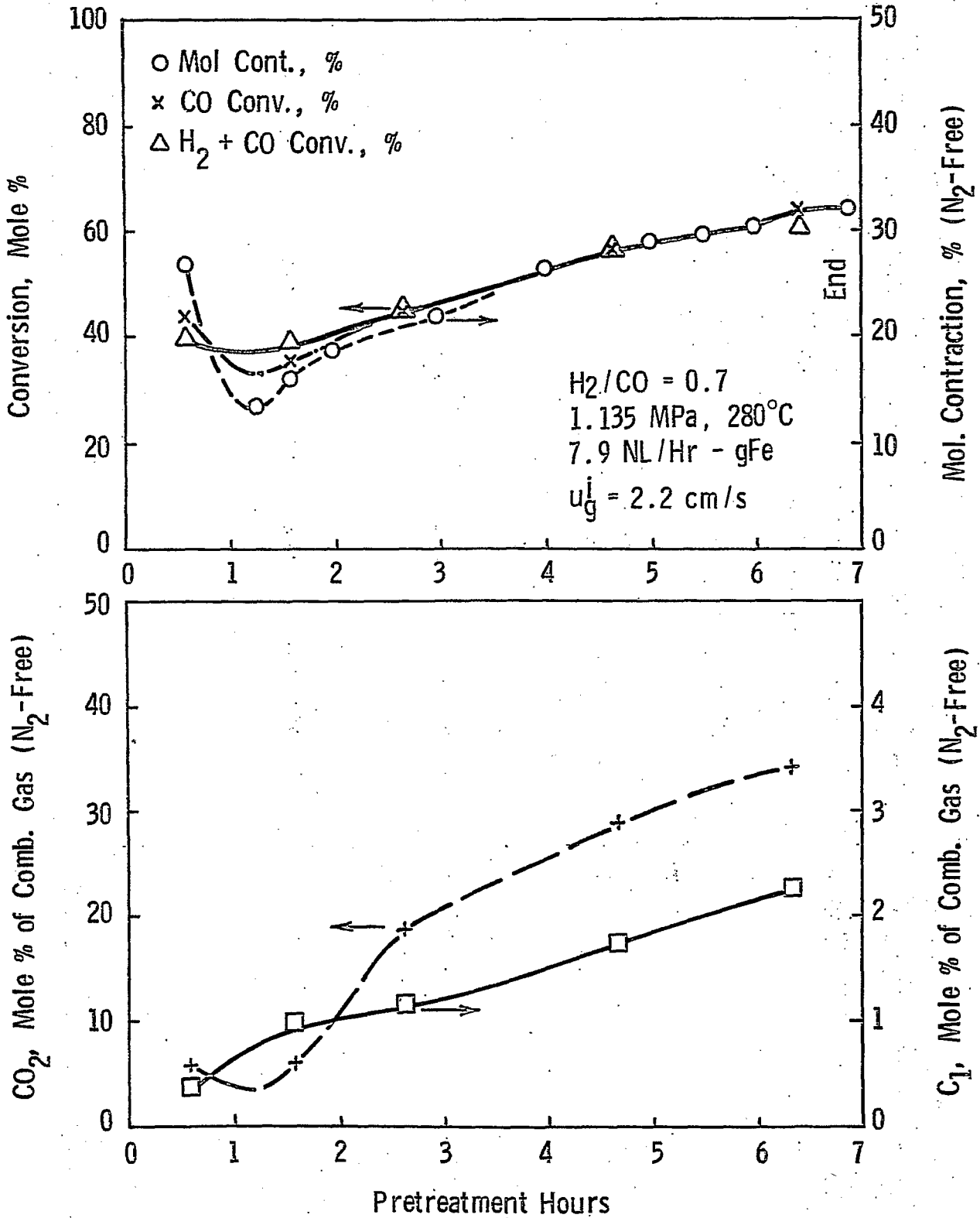
(First 350 hours TOS, Run CT-256-1)

TOS, Hours	Rx Temp., °C		C ₁	C ₂	C ₂ [≡]	C ₃	C ₃ [≡]
	1st Stage	2nd Stage					
0-195	260-263	-	6-9.1	1.5	3.5-4	1-1.2	6.5-7.5
195-303	266	-	8.3-9.1	1.5	4	1.2	7.5
303	266	Start-Up	-	-	-	-	-
303-350	266	371	10.5	2.6	0.7	18	1.1

Unit: Wt% of Total Hydrocarbon Produced

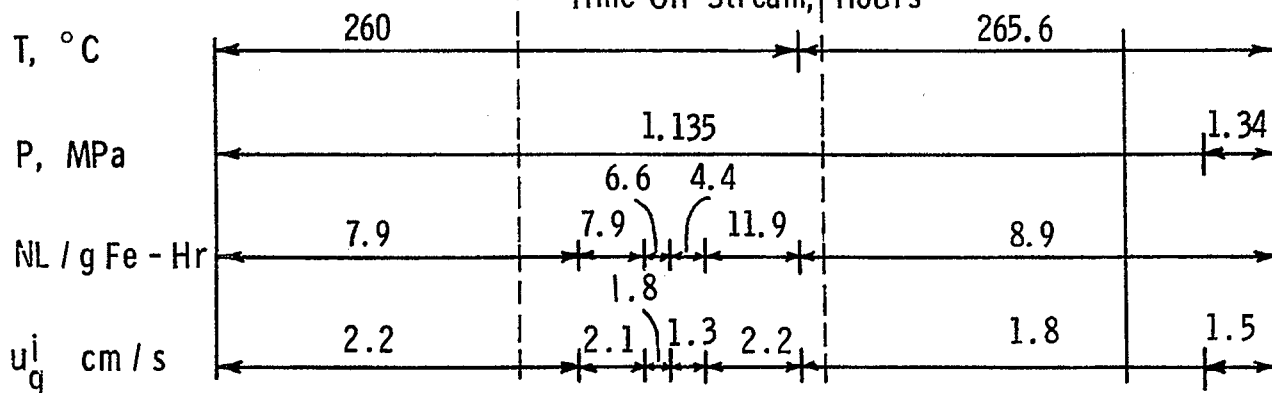
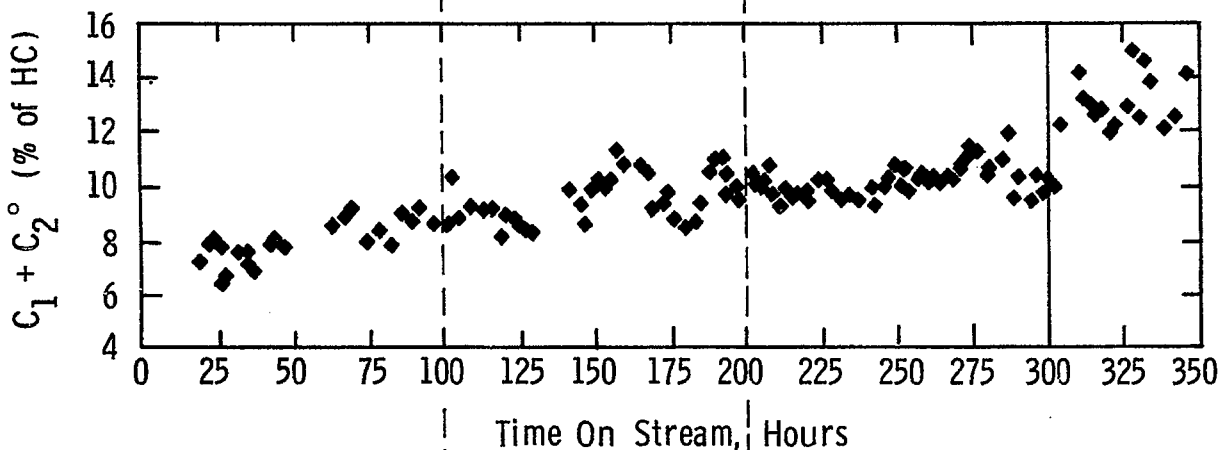
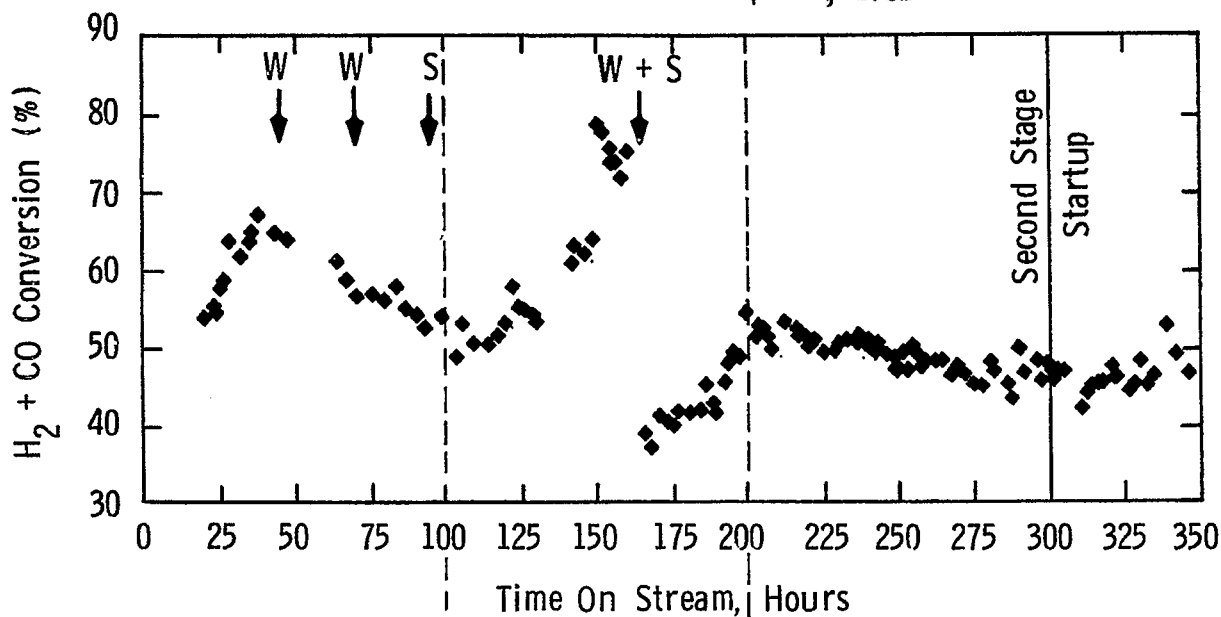
Figure 1

RUN CT-256-1, PRETREATMENT OF F-T CATALYST I - A
(CATALYST I - A: Ppted. Fe / Cu / K_2CO_3)



RUN CT-256-1, EVALUATION OF F-T CATALYST I-A
(Catalyst I-A: Ppted. Fe / Cu / K_2CO_3)

Data Collected Before April 1, 1982



W: Wax Withdrawal

S: Slurry Withdrawal

Figure 3

SLURRY BUBBLE COLUMN TEMPERATURE PROFILE
(RUN CT-256-1 TIME ON STREAM = 318 HRS)

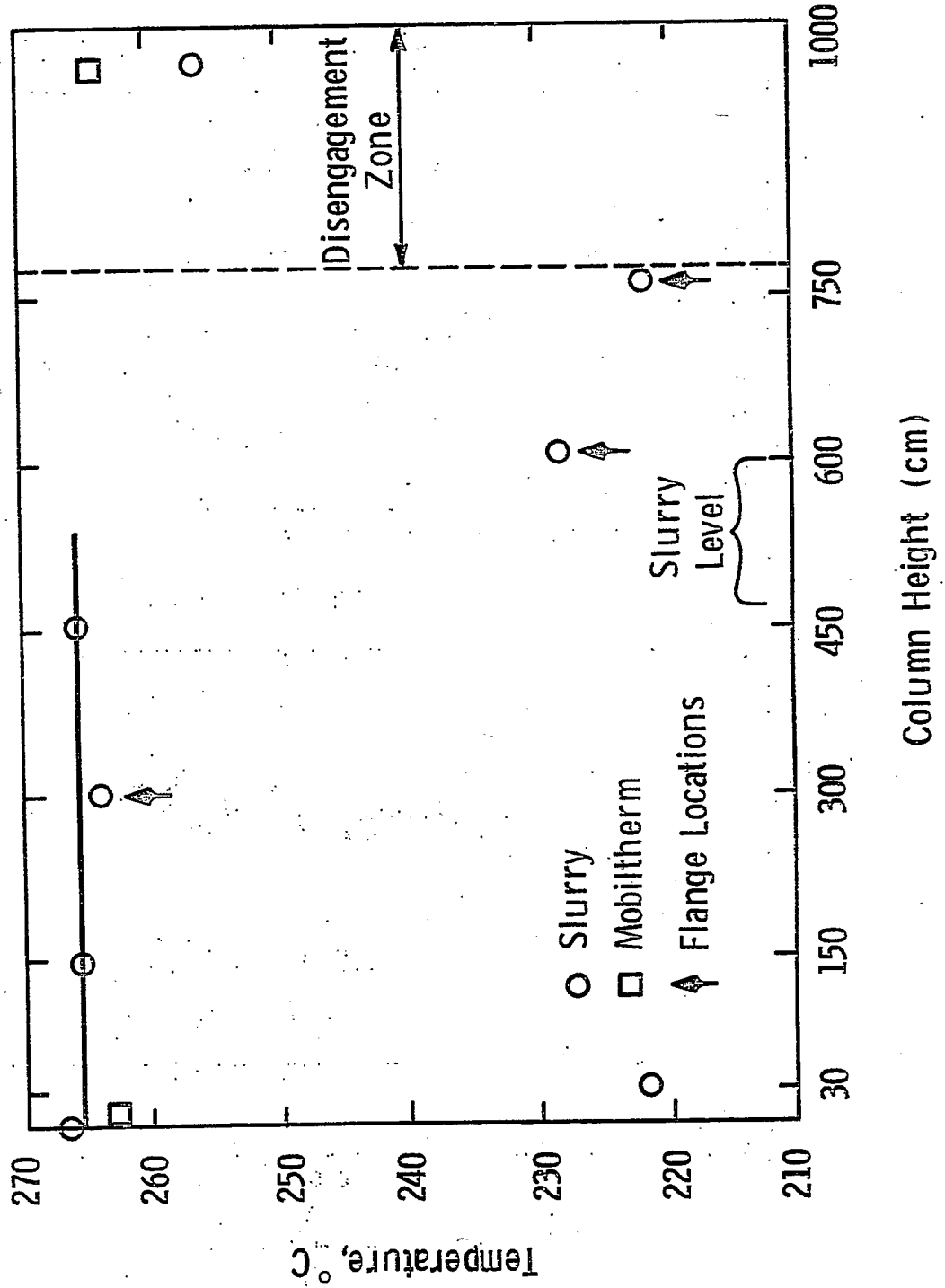


Figure 4

