V. Construction, Shakedown, and Modification of Two-Stage Bench-Scale Pilot Plant

A. Unit Construction

The fabrication of the BSU components was started in March 1981. The on-site construction began in July 1981 with the erection of the steel structure to house the slurry F-T reactor. A total of 106 vessels, 607 valves, 19 pneumatic control valves, 25 pressure gauges, and 123 thermocouples were used in the BSU. The BSU construction was completd in December 1981 and was ready for shakedown. A preliminary pressure test was also carried out as part of the construction.

Two elevation-views of the 13 m high slurry reactor steel-structure can be seen in Figure A-8. The elevation "A-A" gives the view from the north; while the elevation "B-B" gives the view from the west. The slurry F-T reactor is the tall center piece in two elevation views shown in this figure. The gas-feed pre-heater (E-32) can be seen on the floor next to the slurry-reactor. The slurry-tank (E-48) and slurry transfer vessel (E-49) are placed on the first floor. The inter reactor sampling-loop components, hot (E-93), and cold (E-94) condensers, sample pots (E-87,88) and gas-meter (E-76) are mounted on the first-floor (see elevation "B-B"). Two fixed bed reactors (E-36, 37) are mounted on the outside of the first floor. The three Unistrut-frames for the sections 1,3,4 are located on the north side of the slurry-reactor structure below the fixed bed reactors (see elevation "A-A").

A photograph of the completed unit is shown in Figure 3. Figure 4 shows the completed fixed-bed reactors. The top-view of the three sections can also be seen. A ground level view of the same three sections is shown in Figure 5. Some major vessels, piping, and valving are clearly shown in the figure.

All instruments have been mounted on the control panel seen in the left-bottom corner of Figure 3. On the left section of the control panel, nine Liquid-Indicator Controllers (LICs), five Flow-Indicator-Controllers (FICs), and three Pressure-Indicator-Controllers (PICs) are located. The twenty-three Temperature-Indicator-Controllers (TICs) with eight Adiabatic-Temperature-Controllers (ATCs) are mounted on the middle and right sections of the panel. The two digital temperature indicators can display temperatures at eighty four different locations around the unit. The important temperatures, such as those of the reactors and condensers, are recorded by the computer for permanent storage.

Any alarm condition at the unit, such as high temperature, high pressure, or gas leaks, sets off an alarm siren at the control panel and necessary actions are automatically taken. For example, in the case of excessive temperature rise in the slurry reactor, the heater for the circulating oil would be

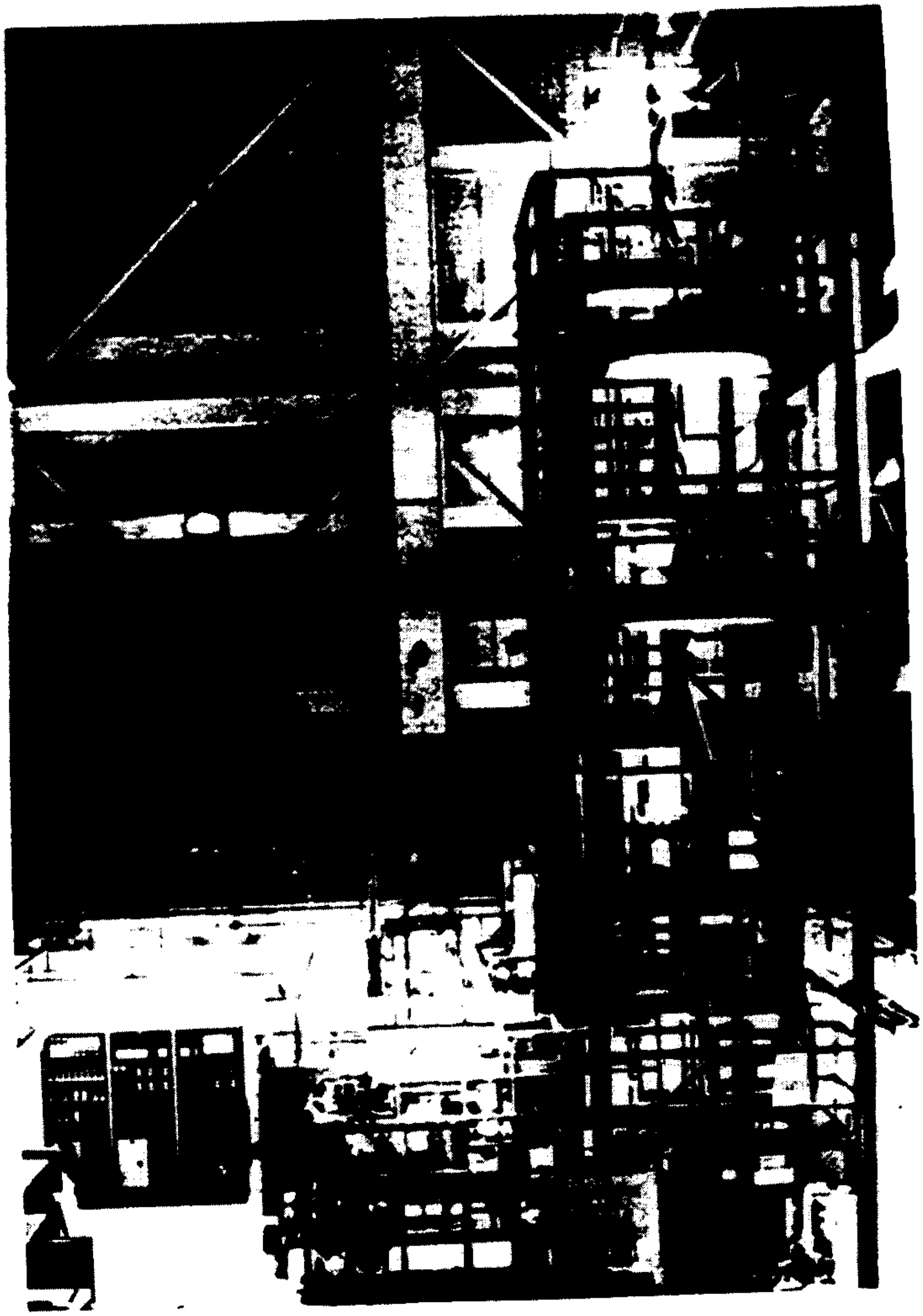


FIGURE 3

A North-west View of the Pilot Plant
— Control Panel (Left Bottom)
— Slurry Reactor "With White Insulation" (Right)
— Other Three Sections (Middle Bottom)

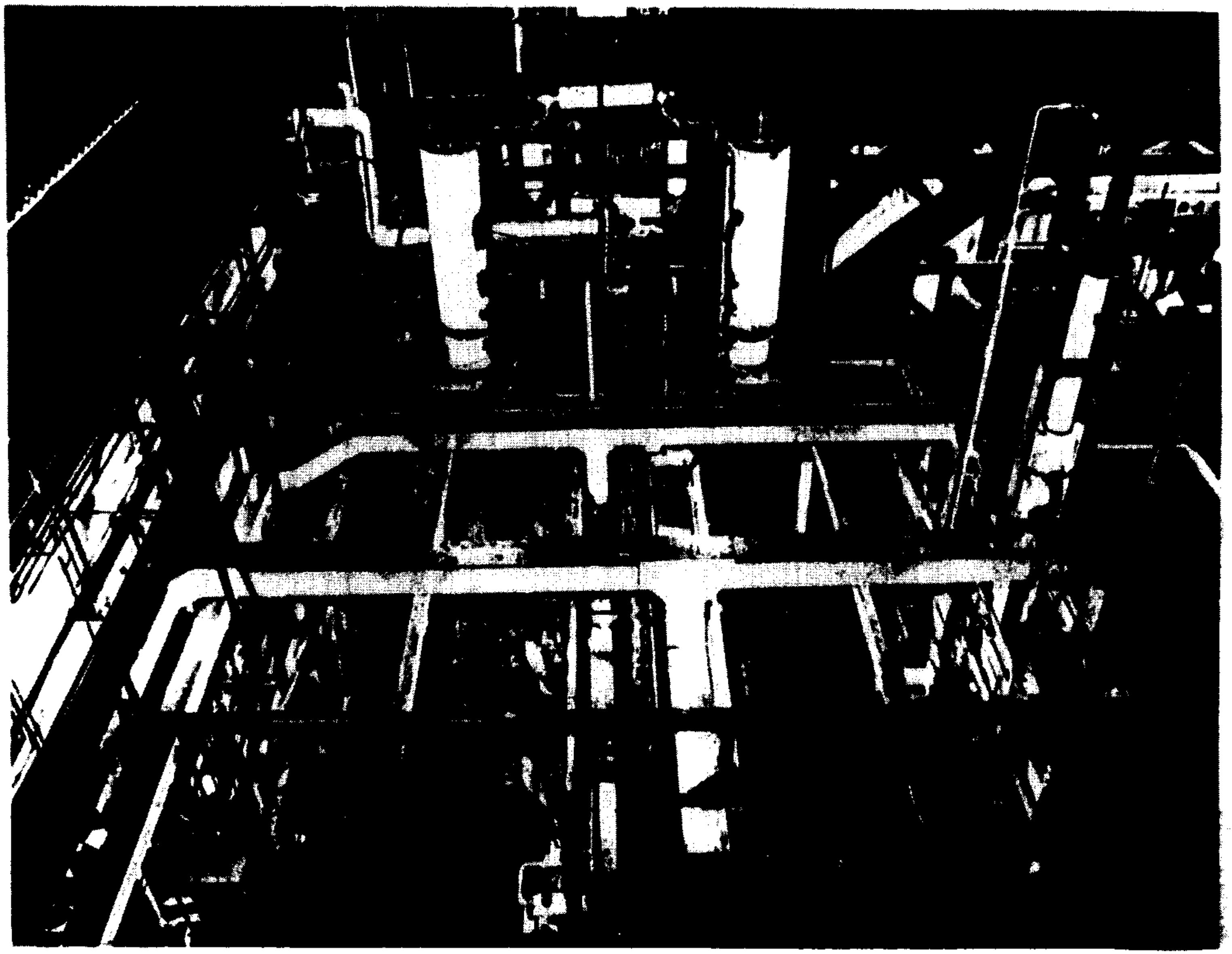


FIGURE 4

A View of Two Fixed-Bed Reactors (Top) and Three Sections — 1, 3, and 4 (Bottom Half)

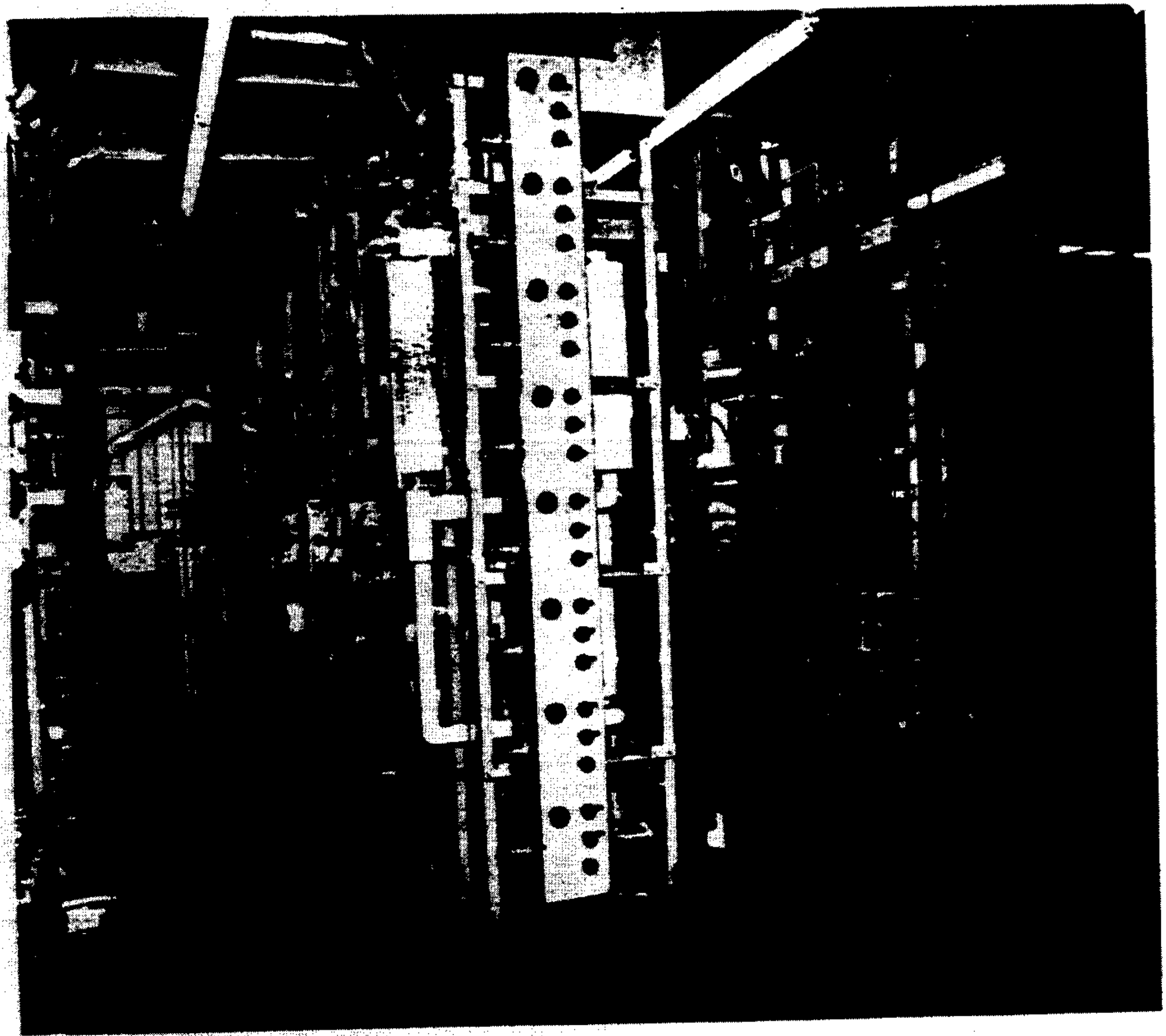


FIGURE 5

A View of Gas-Feed Section at Left, Product Recovery Section in the Middle, and Distillation Section at Right

turned off and the cooling water turned on. Similarly, when a H_2 or CO gas leak is detected, the alarm circuit would shut off the gas feed as well as the power to the unit.

B. Shakedown Operation

The construction of the BSU was completed on schedule and the shakedown operation was initiated in late December, 1981. The shakedown of all essential portions was completed in two months. The break-in operation of the portions of the unit that were not essential to the start-up of the reactors, such as the liquid hydrocarbon distillation section and the regeneration loop of the ZSM-5 reactors, was carried out during normal operation.

Basically, the shakedown operation included:

- 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.

An in-house H_2 supply was used for the BSU operation. Using a conventional gas chromatographic analysis, its purity was estimated to be 99.89 mol % with N_2 as the only impurity. The CO supply was delivered in a cylinder-trailer holding approximately 940 Nm_3 (35,000 SCF) at 13.9 MPa (2,000 psig). 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 N_2 was also used for the BSU operation. Its purity was higher than 99.99 mol %. The compositions of these gas supplies were checked occasionally to insure their purity. Analysis of the gas composition of each new CO shipment was also mandatory.

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 N_2.

- Flushed the fixed-bed reactors, the condensers and the separators with n-hexane.

- Pressure-tested section by section the slurry reactor and associated vessels, the two second stage fixed-bed reactors, and the product recovery section with 2.86 MPa H_2 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 ability of 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 H_2 at 260°C to achieve less than 6.9 kPa/hr (1 psi/hr) pressure loss.

- Pressure-tested the two fixed-bed reactors with 2.86 MPa H_2 at 371°C.

- Pressure-tested condensers and separators at operating temperatures.

- Pressure-tested and ran the regeneration recycle compressor of the second-stage reactor with N_2.

- 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 was 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 vol %	338
50 vol %	371
90 vol %	404

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 H_2 flowing through the unit at up to 4.25 Nm^3/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.

C. Unit Modifications

During the BSU operation, many modifications to the unit were done to correct problems which arose during the operation, or to improve the operation. Most of the modifications were carried out during unit turnaround after each run and are described below.

During the turnaround after the first run (Run CT-256-1), the following major modifications were carried out:

1. A new, smaller (1 L) catalyst slurry loading tank was constructed to replace the 19 L loading tank in the original design. The new tank was connected to the slurry reactor at 610 cm above the feed-gas distributor with a 90 cm line. The length of the connecting line was kept short to minimize catalyst loss in the line.

2. The wax withdrawal filter was replaced with a new filter of 10 μm openings. The old filter was found to have a pinhole.

3. A small, 2 μm filter was installed horizontally at 457 cm above the feed-gas distributor for testing.

4. The slurry sampling vessels E-1, 2, 3, and 4 were relocated from the ground level to the sampling points to minimize the catalyst loss and settling in the lines connecting the vessels and the reactor.

5. A new design was adopted for the N_2-purge orifices used for the DP-cell legs of the slurry reactor liquid-level measurement system. This new design had the orifice tip pointed downward instead of horizontally. A downward design may be better in keeping the slurry out of the DP-cell legs.

6. Heating tapes were installed at the originally unheated flanges located at 305, 610, and 762 cm above the feed-gas distributor. Temperature controllers TIC 24, 25, and 26 were assigned for their temperature control.

7. A new thermocouple was installed at 8 cm above the feed-gas distributor to monitor the slurry temperature close to the distributor. Also, the thermocouple at 30 cm location was found not completely inserted into the slurry reactor and was later reinserted properly.

8. The flow rate measurement of feed H_2, CO, total charge and the combined off-gas were automated.

The first two modifications were most essential to permit high catalyst loading that is required to achieve simultaneously high synthesis gas conversion and throughput. Their success was later demonstrated in the high catalyst loading operation of the second BSU run. The third modification was minor. The 2 μm filter was shown in the later run to be impractical since the wax withdrawal rate was very low.

The fourth modification contributed to less catalyst loss and improvement in obtaining slurry samples. The fifth modification was essential for measuring the slurry level in the slurry reactor. Its operation was not successful during the second run mainly due to operators' inexperience, but it has since proven successful.

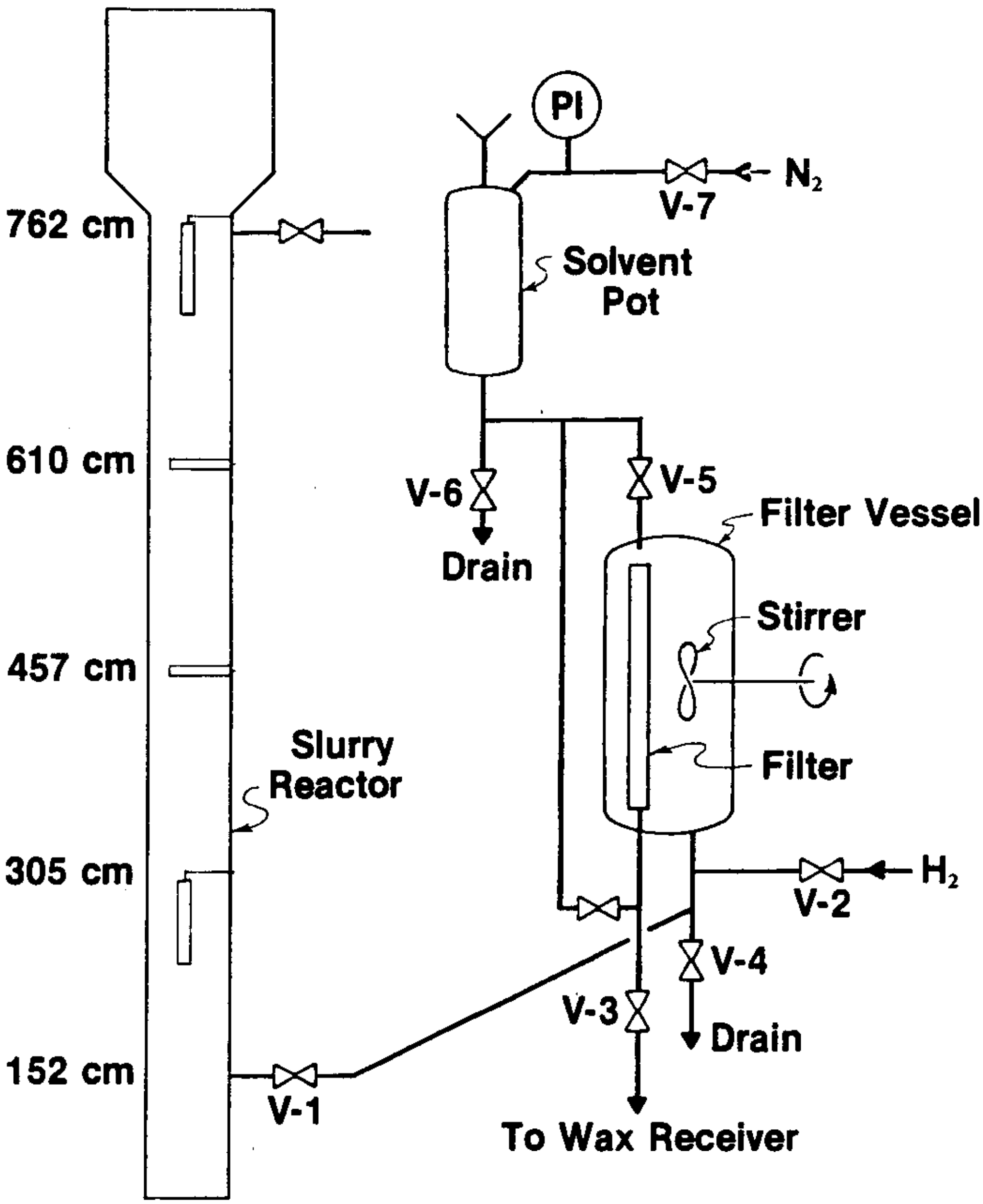
The sixth and seventh modifications were necessary for better temperature monitoring and control, and to achieve uniform reactor temperature without cold spots. The last modification was mainly for the ease of operation.

After the third run, the BSU was shut down for modifications. The major modification was addition of two external filter assemblies to withdraw reactor-wax from the first-stage reactor. The assemblies were installed to withdraw wax from 157 and 762 cm above the distributor.

A schematic of the external filter assembly is shown in Figure 6. The slurry from the reactor is brought into the filter vessel, maintained at 204-260°C, via valve V-1. The catalyst settling in the vessel is prevented by continuous agitation provided by the stirrer. The slurry can be purged with hydrogen to remove dissolved carbon monoxide, carbon dioxide, and water from the slurry. The filtered reactor-wax can be collected in the wax receiver maintained at a certain pressure depending upon the differential pressure desired across the filter. The concentrated slurry deposited in the filter vessel can be frequently flushed back into the reactor by pressuring the filter vessel through the wax receiver. If necessary, the filter vessel and filter surface can be flushed with hot solvent using the solvent pot, and the contents can then be pressurized back into

FIGURE 6

SCHEMATIC OF THE EXTERNAL WAX FILTER ASSEMBLY



the reactor. The size of the filter is 1.59 cm OD x 12 cm long with 10 μm pore size filter element.

A trial operation of the filter assembly was, however, unsuccessful. The reactor-wax withdrawal rate was lower than expected and the filter element plugged after withdrawing about 200 g of reactor-wax. The solvent cleaning of the filter or the filter-blowback did not significantly improve the operation. The filter vessel was then modified to carry out separation of the catalyst from the slurry by catalyst settling and was very successful.

Other minor modifications included:

1. The 10 μm filter element at the 305 cm level of the first-stage reactor was replaced with a new element. The older element was in use for 106 days (Runs CT-256-2 and -3).

2. Another identical filter (10 μm 1.59 cm OD x 30.5 cm long) was installed inside the slurry reactor at the 762 cm level to provide additional wax withdrawal capability.

3. The 2 μm filter (1.25 cm OD x 12.7 cm long), inserted into the slurry reactor from the side tube at the 458 cm level, was replaced with a 5 μm filter to improve the filtration rate.

4. A new 10 μm (110 cm OD 2.7 cm long) was inserted into the slurry reactor from the side tube at the 610 cm level.

5. All gaskets between flanges of the first-stage reactor were replaced with new "Graphoil"[(1)] (0.3175 cm thick) gaskets. The old gaskets were made of "Bimetallic"[(1)] material and were found to split and leak during a run.

6. Ten pressure transducers were installed to record unit pressures on the datalogger computer.

7. Additional heating tape was added on the conical part of the disengager bottom and the flange at the 762 cm level of the slurry reactor. Previously only one tape was used for this section. Additional heating of this section should minimize heat loss.

[(1)] A registered trade mark.

VI. Operation of Two-Stage Bench-Scale Pilot Plant; Experimental Results and Discussions

A. Introduction

The major task of this contract is the development of the two-stage process in the bench-scale pilot plant. The operation began on March 17, 1982, immediately after construction and shakedown of the pilot plant. Five runs, with a total of two hundred twenty days of operation time, were carried out. The operation was smooth and uneventful except for a few occasions of mechanical upset due to leakage at the flanges of the first-stage slurry reactor, and some minor difficulty in separating the F-T reactor-wax from the catalyst slurry. Major accomplishments from the operations are summarized below.

- Evaluated three $Fe/Cu/K_2CO_3$ F-T catalysts. One of the catalysts (designated as I-B) accumulated an on-stream time of eighty-six days and produced 815 gHC/gFe, substantially higher than figures reported in the literature.

- Evaluated two ZSM-5 catalysts. The catalyst II-B accumulated a total on-stream time of eighty-seven days with two regenerations. No appreciable long-term aging of the catalyst was observed.

- Various process variables were studied with the slurry F-T reactor, including pressure, temperature, feed-gas superficial velocity, feed gas H_2/CO ratio, and addition of a potassium-salt.

- Operation of the second-stage fixed-bed ZSM-5 reactor at constant catalytic severity was demonstrated. A useful criterion for measuring this severity is the molar $i\text{-}C_4/(C_3^{=}+C_4^{=})$ ratio in the reactor effluent gas. Daily adjustment of the reactor inlet temperature was instituted to maintain a constant severity.

- Successfully demonstrated conversion of the F-T hydrocarbon and oxygenate products in the effluent of a slurry F-T reactor into high octane gasoline by a ZSM-5 catalyst. The maximum gasoline yield of 80-90 wt % (excluding light paraffins in the feed and reactor-wax) was obtained by maintaining the severity index ($i\text{-}C_4/(C_3^{=}+C_4^{=})$ ratio) between 0.8 and 1.0. The octane numbers of the raw gasoline ranged from 90 to 94 (Research clear).