2. Run #2

A meeting between IGT and CSI personnel was held on May 2, 1977 to discuss feedgas requirements and scheduling necessary to continue with the LPM experimental program. Two of the more important items in this regard were:

1. Attempting to lower the steam-methane reformer gas from a 10 $H_2/CO$ ratio to a 4-5/1 mole ratio, and

2. Scheduling a 30-day uninterrupted run on steam-methane reformer gas.

It was decided to attempt to lower the reformer product $H_2/CO$ ratio during the start-up of Run #2 and, indeed, a 6.5 $H_2/CO$ ratio was achieved on May 16, 1977 as discussed later. Scheduling for the short-term continuous run was not resolved. In another matter, a more efficient procedure for replacement of spare parts was initiated by CSI and IGT personnel.

All work around the circulating oil cooler was completed and the new flanges were tested. Conduits were run from the new surface thermocouples to the junction boxes, but the thermocouples were not yet connected to the temperature indicator in the control room. The hydrogen exchanger was repaired and returned. It was re-installed upon completion of Run #2.

The entire system was filled with water on May 2, 1977 to clean out all piping and vessels. After starting circulation, the water was heated to 150°F and a set of main oil filters plugged immediately. The circulating oil pump was also plugged and had to be cleaned out. After a day and a half of flushing the systems, the water cleared up by putting a second set of filters on stream. Also, a seal flush filter plugged and was changed. The unit was drained completely.

On Wednesday, May 4, 1977, the reactor was dried with nitrogen at 300°F and the remainder of the system was filled with fresh Freezene-100 oil. The next day, the reactor was loaded to height of 2.3 feet with 900 pounds of 13/16" inert pellets and 500 pounds of 1/2" pellets. A catalyst charge of 625.5 pounds of Calsicat Ni-230S was added on May 5. This gave a bed 4-feet high, bringing the top of the catalyst bed to 6.3 feet above the bottom reactor flange. The charged catalyst was then placed under a nitrogen blanket.

Meanwhile, oil was circulated and heated to remove the residual water from the system exclusive of the reactor. Another set of filter plugged during this operation and some difficulties were encountered with the main circulating pumps. However, these problems cleared up as the oil heated. Oil circulation was then terminated until the start-up of Run #2.

Heating the reactor with nitrogen began on Wednesday, May 11, 1977. Thursday, the feed was switched to hydrogen containing 1.5 percent CO and catalyst reduction began. The reactor was raised to 800°F and held for four hours. Upon completion of reduction, the feed was switched back to nitrogen and the reactor was cooled to 550°F. Meanwhile, the circulating oil system was started and heated to 550°F.

On May 13, the heated oil was carefully introduced into the reactor and the system stabilized at 500°F and 100 psi. The gas heater was turned off and the system was switched to HP nitrogen which by-passed the reactor. System pressure was raised to 500 psi and a series of liquid-only fluidization tests were conducted.

Steam-methane reformer gas feed to the LPM Pilot Plant began on May 14 at a rate of 24,000 SCFH. IGT gradually reduced the steam to methane ratio to 4.2 in the reformer by May 16 which lowered the reformer product from its initial 10 $H_2/CO$ ratio to approximately 6.5.

On May 15 the first set of filters plugged. While switching to the spare, an oil leak developed at a pipe flange which caught fire. The fire was quickly put out and the filter by-passed so that the flange could be tightened. A few hours later, the filter was successfully put back into operation.

The LPM Pilot Plant was running continuously for 44 hours of accumulated reaction time when feed gas was interrupted for two hours due to a problem with the IGT steam-methane reformer. Methanation was resumed, but continued for only two hours when a problem with the IGT hydrogen compressor caused a feed gas interruption after 46 hours of accumulated reaction time. The LPM unit remained on standby for five days.

The IGT hydrogen plant was restarted and the LPM Pilot Plant began taking gas at 1 A.M., May 22, 1977. By 10 A.M., standard conditions (650$^{o}$F, 400 psig, 4,000 VHSV and 187 GPM oil) had been reached and preparations were being made to start the process variable scans. The feed gas had a 6.5 $H_2/CO$ ratio. At 2:30 P.M., a fire occurred while placing a clean process oil filter on-line. The fire started when hot oil escaped from an open vent valve on top of the filter and contacted the surrounding hot pipes. The fire was brought under control in fifteen minutes with the use of fire extinguishers and, finally, by shutting the vent valve. Damage to the unit was slight with the major losses being several pressure measuring devices, instrument air lines and process insulation. The process piping metallurgy was to be checked, but there appeared to be no visible damnage. Run #2 was terminated during the fire and the unit was rapidly depressurized to minimize the extent of the fire.

A summary of the major events of Run #2 is presented in Table IV-B-3.

Liquid-only fluidization data were repeated at two temperatures during hours 169-175 when it was noticed that the settled bed height had decreased from 4.0 to 3.7 feet. Bed porosity as a function of liquid velocity is shown in Figure IV-B-4. A bed profile was taken at hour 234 with an oil superficial velocity of 0.15 ft/sec and a gas superficial velocity of 0.21 ft/sec. The gas had a molecular weight of 5.5. The total bed expansion was 24.3 percent of which 10.3 percent can be attributed to liquid-only fluidization and the remaining 14.0 percent to gas flow.

A summary of analytical results from Run #2 is presented in Table IV-B-4. During the first twenty hours of reaction, the IGT steam-methane reformer was producing a gas with an 8.5 $H_2/CO$ ratio. Thereafter, reformer feed was adjusted until, near the end of the run, a 6.5 $H_2/CO$ feed gas was produced. The results indicate an initial CO conversion of 95 percent with a gas hourly space velocity of 2,100 $Hr^{-1}$. The conversion decreased to 72 percent when the space velocity was increased to 4,000 $Hr^{-1}$. The kinetic rate constant leveled off at 0.65 X $10^{-6}$ lb-mol/(atm-lb. catalyst-sec.) after the first 15 hours of reaction as shown in Figure IV-B-5. Because the run was suddenly terminated at 60 hours of accumulated reaction time, no data for the process variable scan were accumulated with the exception of the standard condition of 650$^{o}$F, 500 psig, 4,000 $Hr^{-1}$ VHSV and 187 GPM oil flow. However, analysis of the initial pilot plant data at 650$^{o}$F indicates that the kinetic model, as developed for the bench scale unit and the PDU, yields consistent rate constants as a function of gas flow rate and feed composition.

The rate constants achieved during this run were approximately one-third of the value of those obtained from PDU runs. This phenomenon was also noted at the end of Run #1. There are several possible explanations for the low catalyst activity, including:

TABLE IV.B.3

SUMMARY OF EVENTS FOR PILOT PLANT RUN #2

| Hour | Date | Accumulated Hours of Reaction | |
|---|---|---|---|
| 0 | 5/12/77 | 0 | Start of hydrogen reduction |
| 18 | 5/13/77 | 0 | Reduction completed. Switched to LP nitrogen. |
| 32 | 5/13/77 | 0 | Integrated heated oil into reactor and stabilized at 500°F, 100 psi and 150 GPM oil flow. |
| 38 | 5/14/77 | 0 | Raised pressure to 500 psi and began liquid only fluidization tests. |
| 43 | 5/14/77 | 0 | Completed fluidization studies. |
| 48 | 5/14/77 | 0 | Started feeding steam-methane reformer gas to system. Began adjusting reformer to produce lower $H_2/CO$ feed gas. |
| 62 | 5/15/77 | 14 | First filter plugged. Switched to second filter. |
| 91 | 5/16/77 | 43 | Feed contains 12% CO, but interrupted temporarily by IGT. |
| 93 | 5/16/77 | 43 | Feed gas resumed. |
| 96 | 5/16/77 | 46 | Feed gas interrupted at IGT $H_2$ compressor. |
| 169 | 5/19/77 | 46 | Repeated liquid-only fluidization studies. |
| 180 | 5/20/77 | 46 | Lowered unit to 300 psig and 550°F. |
| 195 | 5/20/77 | 46 | Lowered unit to 100 psig to repair leak. |
| 226 | 5/21/77 | 46 | Increased pressure to 500 psig in anticipation of reformer gas. |
| 227 | 5/22/77 | 46 | Started reformer gas feed. |
| 234 | 5/22/77 | 53 | Second filter plugged. Switched to third filter. |
| 241 | 5/22/77 | 60 | Fire at F-101B filter. Unit shut down and Run #2 terminated. |

FIGURE IV-B-4

# BED POROSITY VS. LIQUID VELOCITY

RUN #2
HOURS 169—175
SETTLED BED HEIGHT: 3.7 FT.

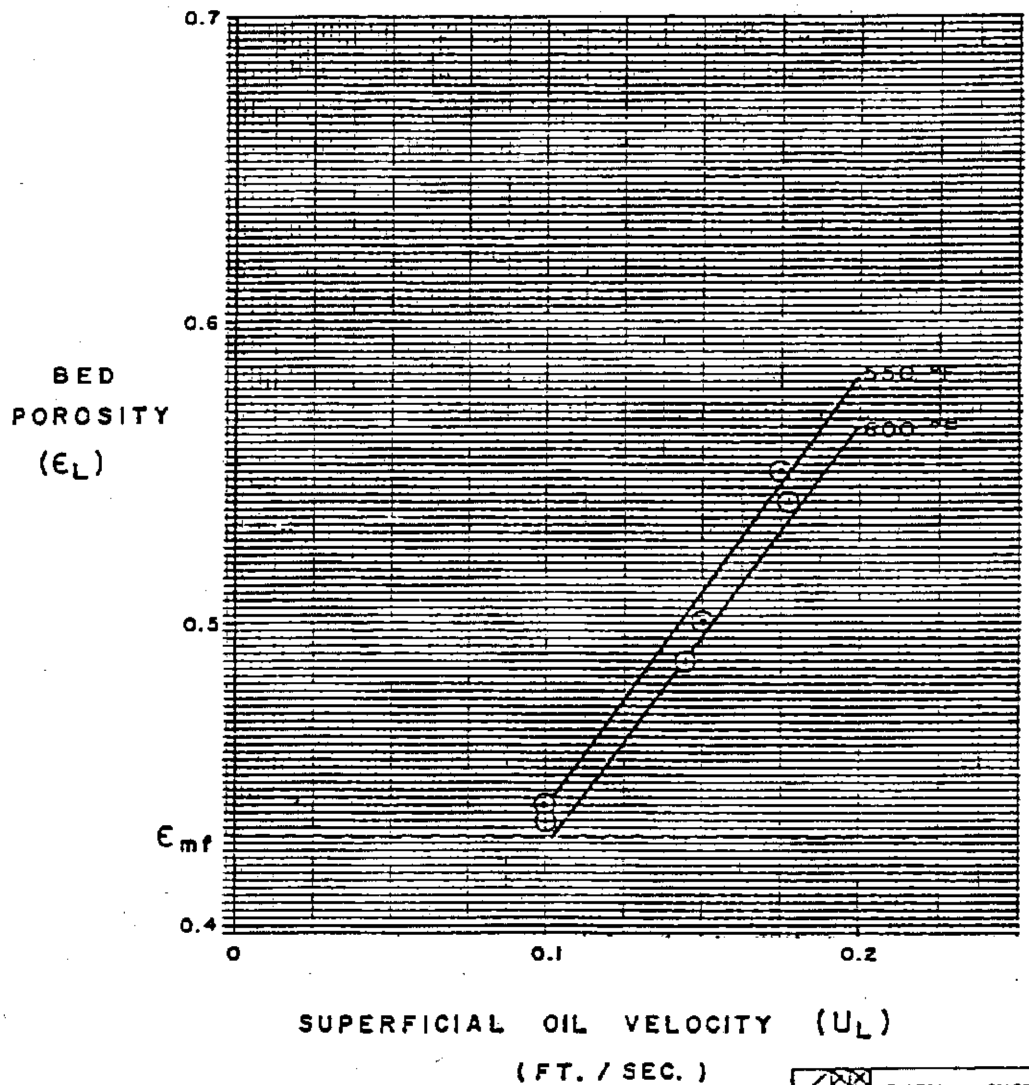


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TABLE IV-B-4

LPM Pilot Plant
Run #2 Results

| Hour | 49 | 53 | 56 | 58 | 60 | 62 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 1 | 5 | 8 | 10 | 12 | 14 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | 8.28 | 8.64 | 8.60 | 8.28 | 8.36 | 8.48 |
| % $H_2$ | 88.78 | 88.82 | 88.70 | 88.40 | 88.60 | 88.70 |
| % $N_2$ | 0.33 | 0.27 | 0.23 | 0.21 | 0.21 | 0.20 |
| % $CH_4$ | 0.41 | 0.62 | 0.76 | 0.71 | 0.59 | 0.64 |
| % CO | 10.48 | 10.28 | 10.31 | 10.68 | 10.59 | 10.96 |
| % $CO_2$ | - | - | - | - | - | - |
| % $C_2$+ | - | - | - | - | - | - |
| VHSV ($Hr^{-1}$) | 2,199 | 2,116 | 2,119 | 2,117 | 2,215 | 2,315 |
| Oil Flow Rate: $GPM/Ft^2$ | 65.9 | 66.0 | 67.0 | 67.7 | 67.8 | 68.0 |
| Temperature (°F) | 600 | 616 | 630 | 640 | 650 | 656 |
| Pressure (psig) | 510 | 510 | 510 | 510 | 510 | 510 |
| Product Gas: | | | | | | |
| % $H_2$ | 83.43 | 83.50 | 83.78 | 83.64 | 83.41 | 83.60 |
| % $N_2$ | 1.35 | 1.32 | 1.21 | 0.47 | 0.87 | 0.28 |
| % $CH_4$ | 14.78 | 14.52 | 14.15 | 15.04 | 14.93 | 15.34 |
| % CO | 0.44 | 0.66 | 0.86 | 0.85 | 0.80 | 0.78 |
| % $CO_2$ | - | - | - | - | - | - |
| % $C_2$+ | - | - | - | - | - | - |
| MW | 4.55 | 4.57 | 4.54 | 4.47 | 4.54 | 4.44 |
| SCFH | 16,500 | 17,100 | 17,300 | 17,500 | 17,400 | 17,600 |
| CO Conversion (%) | 97.00 | 95.41 | 93.85 | 94.32 | 94.65 | 94.90 |
| $CO_2$ Conversion (%) | - | - | - | - | - | - |
| $CH_4$ Selectivity (%) | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Catalyst Rate Constant: | | | | | | |
| $K_{TR}$ (x $10^6$) | 0.757 | 0.675 | 0.606 | 0.667 | 0.677 | 0.711 |
| $K_{650°F}$ (x $10^6$) | 1.111 | 0.872 | 0.703 | 0.718 | 0.677 | 0.681 |

TABLE IV-B-4 LPM Pilot Plant Run #2 Results (Continued)

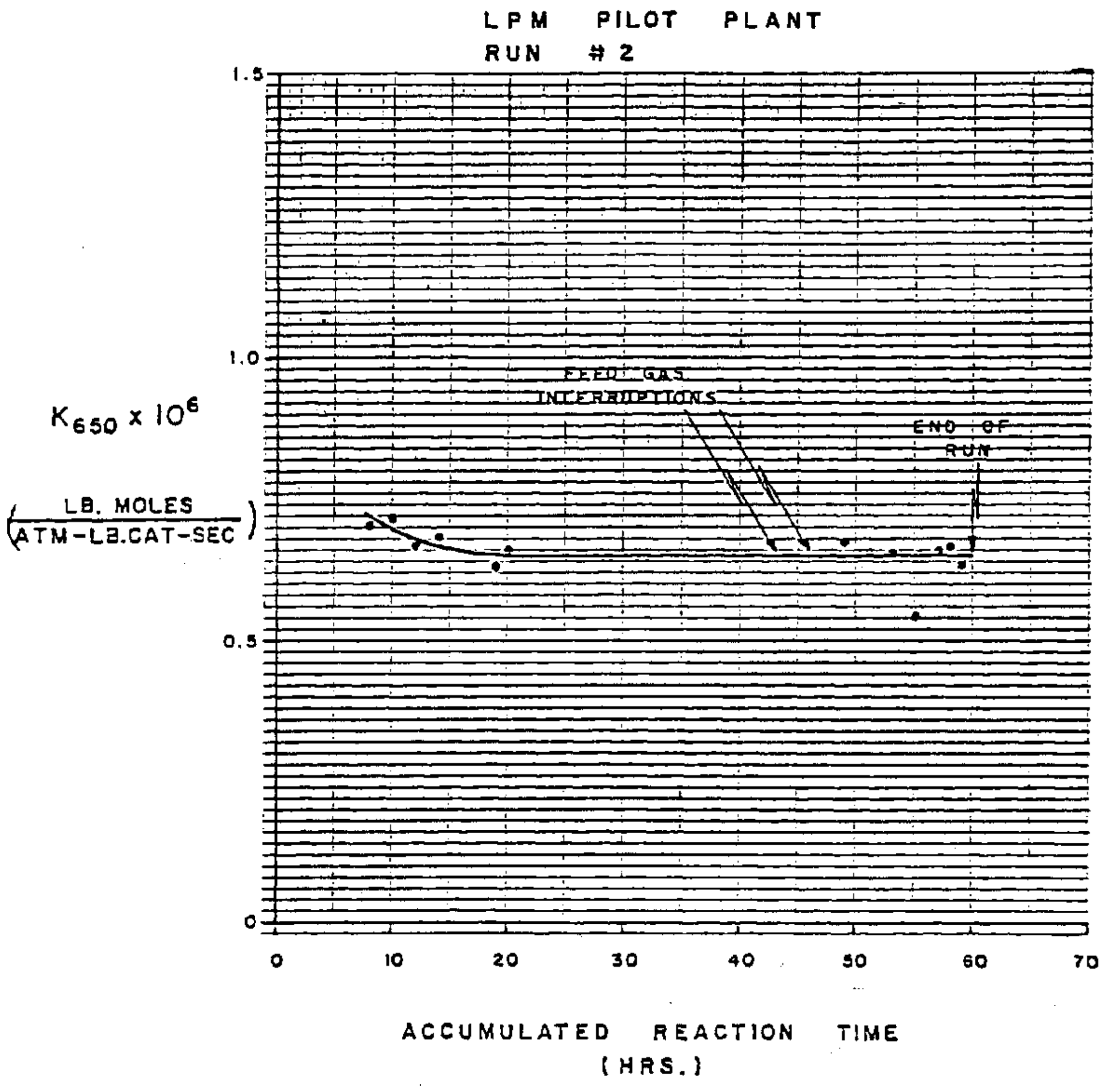
| Hour | 67 | 68 | 86 | 230 | 234 | 236 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 19 | 20 | 38 | 49 | 53 | 55 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | 8.70 | 8.44 | 6.85 | 7.59 | 7.36 | 7.36 |
| % $H_2$ | 88.31 | 87.99 | 84.61 | 86.11 | 85.96 | 85.48 |
| % $N_2$ | 0.20 | 0.20 | 0.38 | 0.23 | 0.24 | 0.27 |
| % $CH_4$ | 1.35 | 1.38 | 2.66 | 2.29 | 2.65 | 2.53 |
| % CO | 10.15 | 10.43 | 12.36 | 11.35 | 11.68 | 11.61 |
| % $CO_2$ | - | - | - | - | - | 0.11 |
| % $C_2$+ | - | - | - | - | - | - |
| VHSV ($Hr^{-1}$) | 2,258 | 2,207 | 2,245 | 2,860 | 2,855 | 2,861 |
| Oil Flow Rate: $GPM/Ft^2$ | 68.0 | 68.0 | 65.9 | 67.7 | 66.0 | 67.7 |
| Temperature (°F) | 655 | 658 | 600 | 656 | 635 | 650 |
| Pressure (psig) | 510 | 510 | 510 | 500 | 500 | 500 |
| Product Gas: | | | | | | |
| % $H_2$ | 83.44 | 82.27 | 77.78 | 79.75 | 80.25 | 81.91 |
| % $N_2$ | 0.29 | 0.28 | 0.56 | 0.36 | 0.51 | 0.38 |
| % $CH_4$ | 15.43 | 16.71 | 20.95 | 17.76 | 16.38 | 14.82 |
| % CO | 0.84 | 0.74 | 1.71 | 1.96 | 2.75 | 2.90 |
| % $CO_2$ | - | - | - | 0.14 | 0.11 | - |
| % $C_2$+ | - | - | - | - | - | - |
| MW | 4.47 | 4.62 | 5.56 | 5.17 | 5.21 | 4.95 |
| SCFH | 17,600 | 17,600 | 16,400 | 21,700 | 23,500 | 25,400 |
| CO Conversion (%) | 94.18 | 95.22 | 90.85 | 88.14 | 82.43 | 79.91 |
| $CO_2$ Conversion (%) | - | - | - | - | - | - |
| $CH_4$ Selectivity (%) | 100.00 | 100.00 | 100.00 | 99.01 | 99.13 | 100.00 |
| Catalyst Rate Constant: | | | | | | |
| $K_{TR}$ (x $10^6$) | 0.651 | 0.697 | 0.659 | 0.702 | 0.584 | 0.541 |
| $K_{650°F}$ (x $10^6$) | 0.628 | 0.658 | 0.967 | 0.672 | 0.652 | 0.541 |

TABLE IV-B-4 LPM Pilot Plant Run #2 Results (Continued)

| Hour | 238 | 239 | 240 | 241 | | |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 57 | 58 | 59 | 60 | | |
| Feed Gas: | | | | ** SHUTDOWN ** SHUTDOWN ** SHUTDOWN ** SHUTDOWN ** SHUTDOWN ** | | |
| $H_2/CO$ Ratio | 6.55 | 6.50 | 6.41 | | | |
| % $H_2$ | 84.64 | 84.19 | 83.80 | | | |
| % $N_2$ | 0.28 | 0.23 | 0.21 | | | |
| % $CH_4$ | 2.18 | 2.39 | 2.47 | | | |
| % CO | 12.93 | 12.96 | 13.07 | | | |
| % $CO_2$ | - | 0.19 | 0.46 | | | |
| % $C_2$+ | - | - | - | | | |
| VHSV ($Hr^{-1}$) | 4,033 | 4,015 | 3,912 | | | |
| Oil Flow Rate: $GPM/Ft^2$ | 67.7 | 67.7 | 67.7 | | | |
| Temperature (°F) | 653 | 649 | 651 | | | |
| Pressure (psig) | 500 | 500 | 500 | | | |
| Product Gas: | | | | | | |
| % $H_2$ | 78.83 | 78.10 | 77.49 | | | |
| % $N_2$ | 0.39 | 0.31 | 0.29 | | | |
| % $CH_4$ | 15.78 | 16.23 | 16.41 | | | |
| % CO | 4.84 | 5.02 | 5.13 | | | |
| % $CO_2$ | 0.21 | 0.35 | 0.64 | | | |
| % $C_2$+ | - | - | - | | | |
| MW | 5.68 | 5.83 | 6.00 | | | |
| SCFH | 32,300 | 31,900 | 31,200 | | | |
| CO Conversion (%) | 72.86 | 72.14 | 71.70 | | | |
| $CO_2$ Conversion (%) | - | - | - | | | |
| $CH_4$ Selectivity (%) | 98.39 | 99.34 | 99.99 | | | |
| Catalyst Rate Constant: | | | | | | |
| $K_{TR}$ (x $10^6$) | 0.673 | 0.661 | 0.642 | | | |
| $K_{650°F}$ (x $10^6$) | 0.658 | 0.666 | 0.638 | | | |

FIGURE IV-B-5

# CATALYST ACTIVITY VS. TIME

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1. Inadequate catalyst reduction procedure in the pilot plant.

2. A poor batch of catalyst.

3. Hydrodynamic considerations due to scale-up from the PDU to the pilot plant.

Several of these possibilities were to be tested at the Fairfield Laboratories. The close comparison of catalyst activities between Runs #1 and #2 also indicates that the catalyst in Run #1 was not deactivated by sulfur during the DGA upset. Evidently the sulfur was carried right through the system by the circulating oil.

The pilot plant was cooled down after the termination of Run #2. All downstream lines and vessels were drained and flushed with water. After cooling the reactor to 100°F, the catalyst was successfully dumped without water flooding. The form of the catalyst was found to be similar to that found in the PDU at the end of a run. Inerts were separated from the catalyst and size segregated for future use. After flushing the reactor, the entire unit was filled with water and circulated through the filters to remove all residual catalyst.

Two meetings were held with IGT, CSI and ERDA personnel to discuss the fire, future prevention of fires and general safety of the filter changing operation. It was decided that piping would be added to safely drain the filters, purge with nitrogen and refill the filters with cold oil. IGT was to prepare a piping layout for moving the filters off the LPM skid to a more accessible location, since the existing location of the main filters was extremely cramped.

The main emphasis of work at the LPM pilot plant during June, 1977, was to relocate the main process oil filters to make them more accessible and to revise the filter piping for safer operation. A preliminary drawing was prepared by IGT for relocating the inboard process oil filter to a new spot alongside the skid. It was decided to complete the piping revisions around the filters before starting up the pilot plant again, provided that the work could be completed by July.

A meeting was held at IGT on June 9 to review more detailed preliminary layouts for filter relocation and piping. A few changes were suggested and later incorporated into the finalized design. It was agreed that all new piping would conform to LPM Pilot Plant specifications and that all butt welds would be radiographed. In order to obtain fast delivery on required materials, specifications were upgraded to P-11 steel (1-1/4% Cr - 1/2% Mo-Si) which requires heat treatment after welding. IGT personnel immediately began expediting the purchase of pipe and fittings, and, by the end of the month, all the necessary materials had arrived.

Meanwhile, insulation was removed from all piping around the filters, the outboard filter was cut out and removed from the skid and the inboard filter was moved to the outboard position. A support structure and platform was built for the relocated filter alongside the existing skid. Both filters were raised 15 inches to allow access to the filter drain valves. All existing piping was brought to the shop for cutting and grinding in preparation for welding new lines. Welding of the four-inch lines had begun before the end of the month.

In other work, process piping was cleaned out and routine maintenance was begun after the completion of Run #2 in May. Both circulating oil pumps were pulled to inspect their oil inlet lines. Considerable debris, composed mainly of rust and catalyst, was found plugging the oil inlet basket strainers. The outboard pump, P-101B, was opened for inspection. No visible damage to the impeller or wear ring was noticed although this pump had been operating in excess of 1,000 hours with catalyst present in the reactor. The pumps were reinstalled after thorough cleaning.

The inlet lines to the condensed oil return pumps were also opened for inspection. Strainers were found and removed. The piping was cleaned out, but the suction lines required realignment before reassembly because they were sprung, causing unnecessary stress on the pump casings. The mechanical seals ordered for one of the BFW pumps were received, but were sent back to the manufacturer for redesign because they did not fit the pump mountings.

The hydrogen exchanger, E-104, was reinstalled. A pressure test revealed that the flanges, which were formerly misaligned, were perfect. However, a leak was found in the pressure relief valve, PSV-100, located upstream of the exchanger. The relief valve was sent out for repair. In addition, the relief valves on the main process oil filters and on the reactor separator were removed for inspection and testing.

A replacement for the pressure transmitter damaged in the fire, PT-116, was received and installed. Another transmitter, PT-104, was removed for inspection, recalibrated and reinstalled. The feed gas flow controller, FIC-101, was sent to Fischer & Porter for repair because the automatic mode did not work during Run #2. At the same time, the damaged PT-116 was sent out to be rebuilt and used as a spare. A damaged pressure gauge on top of the reactor separator was replaced. Local flow indicator, FI-100, was removed and recalibrated. The local reactor density gauge was repaired.

Two leaking Walworth valves were removed and inspected. The leaks occurred at the soft metal bonnet seal rings. Replacements were ordered for the three- and four-inch valves. Since delivery of these parts were to take two months, the valves were reassembled with the original parts after proper cleaning.

In order to repair a leaky flange under the reactor separator, piping spool pieces and the vortex breaker in the bottom of the reactor separator were removed. A ten-inch flange was found to be out of round. A new flange was ordered and IGT was to reinstall the vortex breaker assembly with the new flange once it arrived. Meanwhile, the reactor separator was inspected and cleaned out.

In other work, a leak in the BFW line was repaired, the damaged instrument air lines were replaced and the steam tracing line to the circulating oil pumps running through the area where the fire occurred was replaced. The gas sample take-off point from the water degasser was relocated to a position where it would be free of condensables. New conduits for the surface thermocouples were installed to replace those which were improperly located. Work began on the installation of the thermocouple lead wires. All major valves in the pilot plant were cleaned out and greased.

Detailed lists were prepared of all maintenance, repair and instrument calibration work on the LPM skid required as part of the annual IGT turnaround in July.