4. Run #4

The pilot plant was prepared for Run #4. All pockets in the oil system were drained of catalyst. All instrument taps were cleaned out. The instruments were recalibrated. Replacement seal rings were installed in the leaking Walworth valves. Most of the flanges in the system were tightened while the circulating oil was running hot.

On September 19, all remaining catalyst was charged to the reactor which was isolated from the oil system. The reactor was full of oil at 350°F. As catalyst was charged, excess oil overflowed through a specially constructed line to drums located below the reactor. This oil was later recycled to the oil makeup drum. Approximately 2450 pounds of catalyst were added. Upon completion of catalyst addition, the oil overflow line was disconnected and the reactor was buttoned up. LP nitrogen was used to heat the reactor to 350°F over the next three days. Meanwhile, the circulating oil system was maintained at 375°F and 80 psig.

On September 23, oil was slowly bled into the reactor by first partially closing the reactor oil by-pass and then cracking open the oil inlet to the reactor. The oil dropped to 275°F and took about six hours to reach 530°F. At this time, oil flow to the reactor was stopped in order to measure the settled bed height which was 4.7 ft or 2780 pounds of catalyst. This is the number used throughout this run to calculate catalyst kinetics. Oil flow to the reactor was restarted and, over the next two hours, the oil flow rate was brought up to 0.11 ft/sec very carefully.

Feed gas from the steam-methane reformer containing 13 percent CO was begun at 1600 hours on September 23 at approximately 2000 SCFH. System pressure was raised from 80 to 500 psig over the next half hour. This pressure increase was evidently too rapid because it was immediately discovered that the main circulating oil pump seals were leaking excessive seal flush oil into the system and the system was cooling down rapidly. An attempt to switch to the spare circulating oil pump was aborted when a loose fitting was discovered on its seal flush line and repair was impossible. At 1700 hours, gas flow was stopped, the reactor isolated and the oil system cooled down while depressurizing to 80 psig.

After the spare pump was repaired on September 24, the system was reheated and pressurized to 500 psig. Reactor integration was carried out similarly to the previous attempt except that the pressure was already 500 psig. The pump seals held. The settled bed height was still 4.7 ft. Liquid-only fluidization was checked at 520°F and steam-methane reformer gas was introduced into the reactor at 1600 hours on September 25.

Reactor temperature was increased to 650°F over a six-hour period and the feed gas flow rate was gradually increased to 39,000 SCFH over a 24-hour period. During the next 20 hours, four points from the process variable scan were completed plus a duplicate of the standard condition.

The target conditions for these data points are listed in Table IV-B-7. Any attempt to increase the oil flow rate above 0.13 ft/sec was abandoned because the filters were plugging at a rapid rate. However, one point at a gas rate of 48,000 SCFH was tried.

The second filter plugged after 34 hours of reaction time and contained 575 pounds of catalyst or 20 percent of the original bed. Ten hours later, the third filter plugged with 355 pounds of catalyst or 13 percent of the original bed. Since there was not time to clean out the second filter before the third filter plugged, the system was placed on filter by-pass while this work proceeded. In addition, oil and gas flow rates were temporarily reduced and the system pressure gradually raised to 750 psig in order to minimize the catalyst carryover while the by-pass was open.

Before the filter cleanout could be completed, a fire developed at a leaking head flange on the circulating oil cooler. The flange bolts became red hot. Using extinguishers, the fire was put out. Once the fire was out, a steam hose was directed to envelope the leak site and prevent reoccurance. Meanwhile, after 46 hours of reaction time, feed gas was terminated and shutdown of the unit began. Inspection revealed no visible damage caused by the fire.

A summary of the major events of Run #4 is shown in Table IV-B-8. Upon completion of the shutdown, all lines were flushed to remove catalyst deposits. A total of 1825 pounds of catalyst were removed from filters, reactor separator and other low points in the system. The reactor was dumped and 1240 pounds of catalyst were removed. Allowing for catalyst holdup below the oil sparger and oil holdup within the dumped catalyst reveals that only 40 percent of the original catalyst bed remained at the end of the run.

TABLE IV.B.7
LPM PILOT PLANT
EXPERIMENTAL PROGRAM COMPLETED
Run #4

| Run Number | Pressure (psig) | Temperature (°F | Oil Flow (ft/sec) | Gas VHSV $Hr^{-1}$) |
|---|---|---|---|---|
| A-1 | 500 | 550 | 0.11 | 0 |
| A-B (std.) | 500 | 650 | 0.11 | 3000 |
| D-4 | 500 | 650 | 0.13 | 3000 |
| A-7 | 500 | 650 | 0.11 | 2000 |
| A-9 | 500 | 650 | 0.11 | 4000 |
| A-8 (std.) | 500 | 650 | 0.11 | 3000 |
| A-6 | 500 | 650 | 0.11 | 0 |

TABLE IV.B.8

SUMMARY OF EVENTS

For Run #4

| Time | Accumulated Reaction Time | Description |
|---|---|---|
| 0 | 0 | Integrated oil and gas flows through reactor at 0800 hours on 9/23/77. |
| 7 | 0 | Started steam-methane reformer gas flow into a reactor. |
| 8 | 1 | Shut down because of leaking circulating oil pump seals. First filter changed and 85 lbs of catalyst were removed. |
| 48 | 1 | Restarted oil heatup of reactor at 500 psig. |
| 56 | 1 | Started steam-methane reformer gas into reactor. |
| 62 | 7 | Reactor at 650°F, 500 psig and 135 gpm. |
| 77 | 22 | Reached standard conditions at 650°F, 500 psig and 39,000 SCFH of feed gas (Run A 8). |
| 81 | 26 | Run A 8 completed. |
| 83 | 28 | Run D 4 completed. |
| 87 | 32 | Run A 7 completed. Second filter plugged and removed 475 lbs. of catalyst. |
| 92 | 37 | Run A 9 completed. |
| 96 | 41 | Completed duplicate of standard conditions (A 8). Third filter plugged and removed 355 lbs. of catalyst. |
| 101 | 46 | Run terminated due to fire at E .- 103 head flange. |

A summary of the data obtained is presented in Table IV-B-9. Compositions are based upon the LPM chromatograph since the HYGAS analyses were inaccurate during this run. It can be seen that the expanded bed height steadily decreased throughout the run as long as there was gas flow through the reactor.

Catalyst activity as a function of accumulated reaction time is plotted in Figure IV-B-10. There are some slight changes in catalyst activity as a function of flow conditions. These may be due to experimental error. The catalyst activity dropped only 20 percent while 60 percent of the catalyst was carried out of the reactor. This evidence, coupled with the large catalyst carryover, indicates that the hydrodynamics within the reactor is far from ideal. Evidently, the gas is spouting through the bed and some of the catalyst never contacts the gas. This is further verified by the magnitude of the rate constants which, at 0.10-0.12 X $10^{-6}$ lb-mols/ (atm-lb/catalyst-sec), are similar to those obtained in Run #3, but only 25 - 30 percent of those obtained in the laboratory.

A meeting was held in October, 1977 at the Fairfield Research Center to review the results of Run #4 and to plan future work. Evidence points to the fact that there were some hydrodynamic problems in the pilot plant reactor, possibly caused by spouting of the gas through the catalyst bed. To remedy this problem, reactor modifications including internal baffles, sparger design and distribution plates were being considered before preparing the pilot plant for another run.

Catalyst from Run #4 was dumped from the reactor and cleaned from all low spots in the pilot plant. Out of the 2780 pounds originally charged to the reactor, 1240 pounds were removed at the end of the run. The entire pilot plant was cleaned up including some of the flow elements and transmitters.

Reduction heater H-102 was opened for inspection and thoroughly cleaned during October. Some carbon deposits were found from the back up of oil

Table IV-B-9 LPM Pilot Plant Run #4 Results

| Hour | 56 | 63 | 64 | 65 | 66 | 68 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 1 | 8 | 9 | 10 | 11 | 13 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | — | 8.20 | 8.16 | 7.85 | 8.33 | 7.50 |
| % $H_2$ | — | 86.03 | 85.99 | 85.79 | 86.42 | 85.78 |
| % $N_2$ | — | 0.18 | 0.18 | 0.14 | 0.17 | 0.13 |
| % $CH_4$ | — | 3.30 | 3.30 | 3.14 | 3.05 | 2.65 |
| % CO | — | 10.49 | 10.53 | 10.93 | 10.37 | 11.44 |
| % $CO_2$ | — | — | — | — | — | — |
| % $C_2^+$ | — | — | — | — | — | — |
| VHSV ($Hr^{-1}$) | 0 | 1780 | 1760 | 1950 | 2040 | 2000 |
| Oil Flow Rate: $GPM/Ft^2$ | 130 | 135 | 135 | 135 | 135 | 135 |
| Temperature (°F) | 520 | 648 | 649 | 652 | 653 | 653 |
| Pressure (psig) | 500 | 500 | 500 | 510 | 510 | 500 |
| Product Gas: | | | | | | |
| % $H_2$ | — | 76.09 | 75.75 | 76.16 | 76.30 | 78.02 |
| % $N_2$ | — | 0.28 | 0.24 | 0.22 | 0.20 | 0.19 |
| % $CH_4$ | — | 21.96 | 21.45 | 21.77 | 21.22 | 19.29 |
| % CO | — | 1.48 | 1.61 | 1.72 | 2.08 | 2.30 |
| % $CO_2$ | — | 0.20 | 0.94 | 0.13 | 0.20 | 0.20 |
| % $C_2^+$ | — | — | — | — | — | — |
| MW | — | 5.64 | 5.90 | 5.63 | 5.67 | 5.45 |
| SCFH | — | 13,430 | 13,090 | 15,050 | 15,020 | 16,730 |
| CO Conversion (%) | — | 91.77 | 91.18 | 90.66 | 88.56 | 87.02 |
| $CO_2$ Conversion (%) | — | — | — | — | — | — |
| $CH_4$ Selectivity (%) | — | 98.81 | 94.39 | 99.22 | 98.75 | 98.69 |
| Catalyst Rate Constant: | | | | | | |
| $K_{T_R}$ (x $10^6$) | — | 0.126 | 0.124 | 0.135 | 0.122 | 0.126 |
| $K_{650°F}$ (x $10^6$) | — | 0.129 | 0.125 | 0.133 | 0.120 | 0.123 |
| Run Number | A-1 | — | — | — | — | — |
| Bed Height (FT) | 7.3 | 6.1 | N.D. | 6.05 | N.D. | 6.0 |

Table IV-B-9: LPM Pilot Plant Run #4 Results

| Hour | 70 | 72 | 74 | 76 | 77 | 80 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 15 | 17 | 19 | 21 | 22 | 25 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | 8.27 | 8.08 | 8.79 | 8.14 | 7.68 | 7.59 |
| % $H_2$ | 86.78 | 86.79 | 87.67 | 87.22 | 87.02 | 86.88 |
| % $N_2$ | 0.12 | 0.10 | 0.10 | 0.11 | 0.14 | 0.19 |
| % $CH_4$ | 2.62 | 2.36 | 2.26 | 1.95 | 1.52 | 1.48 |
| % CO | 10.49 | 10.75 | 9.98 | 10.71 | 11.33 | 11.45 |
| % $CO_2$ | — | — | — | — | — | — |
| % $C_2^+$ | — | — | — | — | — | — |
| VHSV ($Hr^{-1}$) | 2220 | 2380 | 2870 | 2670 | 2740 | 2910 |
| Oil Flow Rate: $GPM/Ft^2$ | 135 | 135 | 135 | 135 | 135 | 135 |
| Temperature (°F) | 650 | 651 | 650 | 652 | 643 | 650 |
| Pressure (psig) | 500 | 500 | 500 | 505 | 500 | 505 |
| Product Gas: | | | | | | |
| % $H_2$ | 79.76 | 79.98 | 80.99 | 81.69 | 82.52 | 81.78 |
| % $N_2$ | 0.22 | 0.13 | 0.14 | 0.16 | 0.19 | 0.20 |
| % $CH_4$ | 17.60 | 17.05 | 15.98 | 14.90 | 13.55 | 13.77 |
| % CO | 2.38 | 2.64 | 2.90 | 3.04 | 3.51 | 4.01 |
| % $CO_2$ | 0.04 | 0.21 | — | 0.22 | 0.24 | 0.25 |
| % $C_2^+$ | — | — | — | — | — | — |
| MW | 5.18 | 5.21 | 5.05 | 5.03 | 4.98 | 5.14 |
| SCFH | 18,800 | 20,330 | 24,090 | 24,060 | 26,320 | 26,980 |
| CO Conversion (%) | 85.16 | 83.83 | 81.15 | 80.22 | 76.99 | 74.91 |
| $CO_2$ Conversion (%) | — | — | — | — | — | — |
| $CH_4$ Selectivity (%) | 99.73 | 98.50 | 100.00 | 98.24 | 97.97 | 97.91 |
| Catalyst Rate Constant: | | | | | | |
| $K_{T_R}$ ($\times 10^6$) | 0.122 | 0.127 | 0.131 | 0.124 | 0.128 | 0.122 |
| $K_{650°F}$ ($\times 10^6$) | 0.122 | 0.126 | 0.131 | 0.122 | 0.130 | 0.122 |
| Run Number | — | — | — | — | — | A-8 |
| Bed Height (FT) | 5.95 | 5.85 | 5.7 | 5.55 | 5.35 | 4.95 |

Table IV-B-9: LPM Pilot Plant Run #4 Results

| Hour | 81 | 83 | 84 | 85 | 87 | 90 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 26 | 28 | 29 | 30 | 32 | 35 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | 7.81 | 7.42 | 7.87 | 7.84 | 7.44 | 6.89 |
| % $H_2$ | 87.03 | 86.51 | 87.06 | 86.68 | 86.56 | 85.42 |
| % $N_2$ | 0.29 | 0.25 | 0.25 | 0.25 | 0.24 | 0.31 |
| % $CH_4$ | 1.54 | 1.57 | 1.63 | 2.01 | 1.56 | 1.88 |
| % CO | 11.15 | 11.66 | 11.06 | 11.06 | 11.64 | 12.39 |
| % $CO_2$ | — | — | — | — | — | — |
| % $C_2^+$ | — | — | — | — | — | — |
| VHSV ($Hr^{-1}$) | 2910 | 2860 | 2930 | 1850 | 1860 | 3460 |
| Oil Flow Rate: $GPM/Ft^2$ | 135 | 162 | 162 | 135 | 135 | 135 |
| Temperature (°F) | 650 | 648 | 648 | 649 | 650 | 652 |
| Pressure (psig) | 500 | 510 | 510 | 510 | 510 | 510 |
| Product Gas: | | | | | | |
| % $H_2$ | 81.54 | 81.63 | 81.96 | 80.56 | 79.73 | 80.51 |
| % $N_2$ | 0.34 | 0.35 | 0.37 | 0.33 | 0.35 | 0.38 |
| % $CH_4$ | 13.69 | 14.08 | 13.90 | 16.71 | 17.34 | 13.81 |
| % CO | 4.00 | 3.74 | 3.68 | 2.35 | 2.53 | 5.18 |
| % $CO_2$ | 0.44 | 0.20 | 0.09 | 0.05 | 0.06 | 0.13 |
| % $C_2^+$ | — | — | — | — | — | — |
| MW | 5.25 | 5.14 | 5.05 | 5.08 | 5.22 | 5.45 |
| SCFH | 26,340 | 27,130 | 27,170 | 16,340 | 15,970 | 33,340 |
| CO Conversion (%) | 74.89 | 76.48 | 76.08 | 85.48 | 85.60 | 68.84 |
| $CO_2$ Conversion (%) | — | — | — | — | — | — |
| $CH_4$ Selectivity (%) | 96.33 | 98.32 | 99.26 | 99.61 | 99.63 | 98.85 |
| Catalyst Rate Constant: | | | | | | |
| $K_{T_R}$ (x $10^6$) | 0.120 | 0.126 | 0.122 | 0.104 | 0.110 | 0.130 |
| $K_{650°F}$ (x $10^6$) | 0.120 | 0.128 | 0.124 | 0.105 | 0.110 | 0.127 |
| Run Number | A-8 | D-4 | D-4 | A-7 | A-7 | A-9 |
| Bed Height (FT) | N.D. | 4.75 | N.D. | 4.45 | 4.35 | 4.3 |

Table IV-B-9: LPM Pilot Plant Run #4 Results

| Hour | 91 | 93 | 95 | 97 | 99 | 100 |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 36 | 38 | 40 | 42 | 44 | 45 |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | 6.98 | 6.88 | 6.95 | 7.08 | 7.25 | 7.25 |
| % $H_2$ | 85.63 | 85.34 | 85.35 | 85.16 | 85.50 | 85.50 |
| % $N_2$ | 0.26 | 0.28 | 0.25 | 0.30 | 0.24 | 0.24 |
| % $CH_4$ | 1.84 | 1.98 | 2.12 | 2.51 | 2.48 | 2.48 |
| % CO | 12.27 | 12.40 | 12.28 | 12.02 | 11.79 | 11.79 |
| % $CO_2$ | — | — | — | — | — | — |
| % $C_2^+$ | — | — | — | — | — | — |
| VHSV ($Hr^{-1}$) | 3550 | 3720 | 2820 | 2730 | 2000 | 2020 |
| Oil Flow Rate: $GPM/Ft^2$ | 135 | 135 | 49.1 | 49.1 | 47.8 | 45.2 |
| Temperature (°F) | 650 | 650 | 650 | 649 | 645 | 645 |
| Pressure (psig) | 510 | 510 | 510 | 510 | 570 | 650 |
| Product Gas: | | | | | | |
| % $H_2$ | 80.97 | 81.02 | 80.15 | 80.66 | 79.33 | 79.28 |
| % $N_2$ | 0.37 | 0.35 | 0.36 | 0.44 | 0.36 | 0.42 |
| % $CH_4$ | 13.19 | 12.84 | 14.36 | 13.61 | 17.43 | 17.47 |
| % CO | 5.37 | 5.68 | 5.07 | 5.21 | 2.80 | 2.75 |
| % $CO_2$ | 0.11 | 0.11 | 0.06 | 0.09 | 0.09 | 0.08 |
| % $C_2^+$ | — | — | — | — | — | — |
| MW | 5.40 | 5.43 | 5.47 | 5.43 | 5.32 | 5.32 |
| SCFH | 34,650 | 37,150 | 26,930 | 27,150 | 18,150 | 15,830 |
| CO Conversion (%) | 66.91 | 64.64 | 69.49 | 66.70 | 83.31 | 83.59 |
| $CO_2$ Conversion (%) | — | — | — | — | — | — |
| $CH_4$ Selectivity (%) | 99.00 | 98.93 | 99.47 | 99.18 | 99.40 | 99.46 |
| Catalyst Rate Constant: | | | | | | |
| $K_{T_R}$ ($\times 10^6$) | 0.125 | 0.125 | 0.107 | 0.095 | 0.099 | 0.089 |
| $K_{650°F}$ ($\times 10^6$) | 0.125 | 0.125 | 0.107 | 0.096 | 0.104 | 0.093 |
| Run Number | A-9 | A-9 | A-8 | A-8 | — | — |
| Bed Height (FT) | 4.2 | N.D. | 3.85 | 3.75 | N.D. | N.D. |

CHEM S

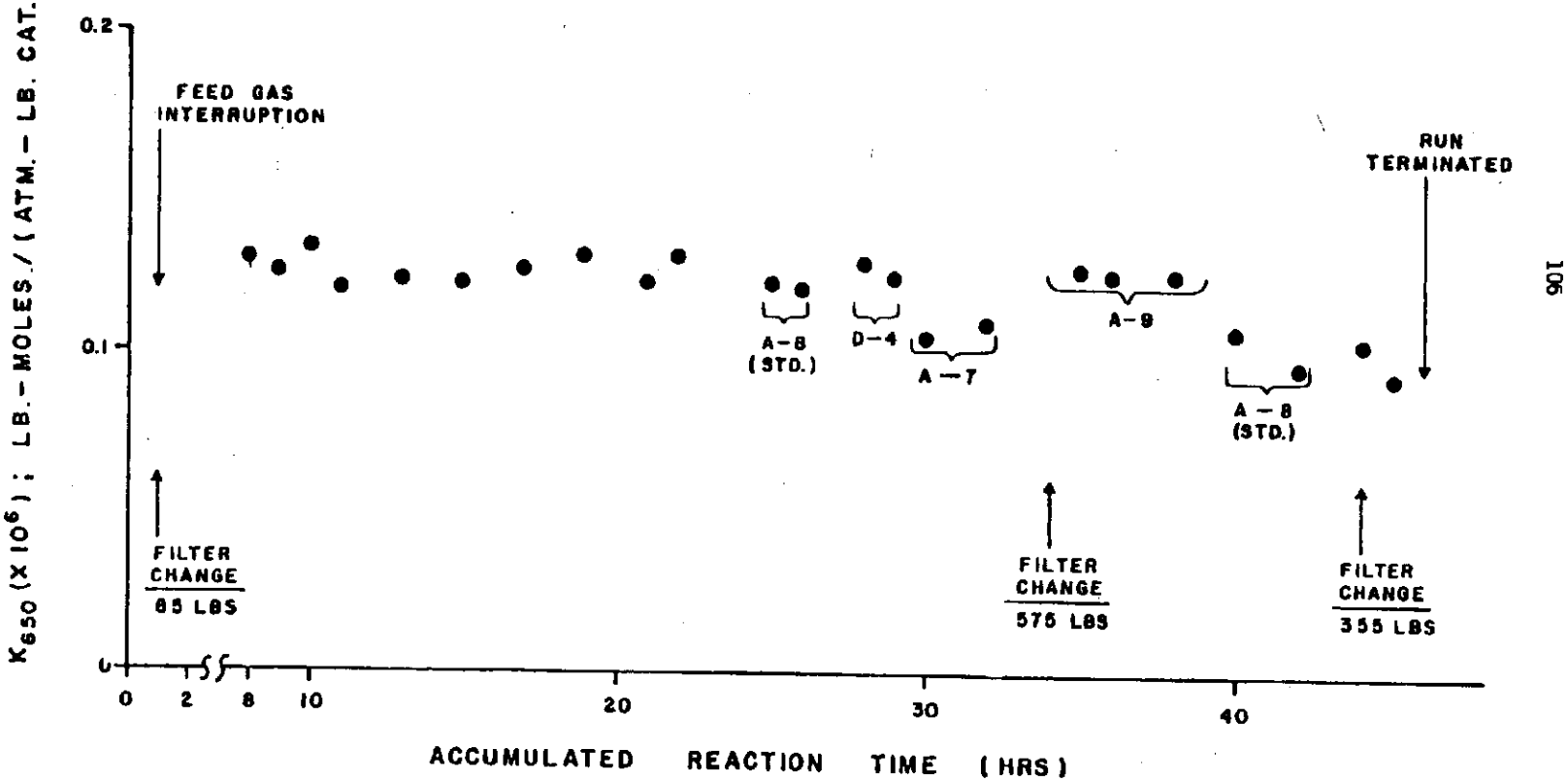
Table IV-B-9: LPM Pilot Plant Run # 4 Results

| Hour | 101 | 101 | | | | |
|---|---|---|---|---|---|---|
| Accumulated Reaction Time (Hrs) | 46 | 46 | | | | |
| Feed Gas: | | | | | | |
| $H_2/CO$ Ratio | — | RUN | | | | |
| % $H_2$ | — | | | | | |
| % $N_2$ | — | | | | | |
| % $CH_4$ | — | TERMINATED | | | | |
| % CO | — | | | | | |
| % $CO_2$ | — | | | | | |
| % $C_2^+$ | — | | | | | |
| VHSV ($Hr^{-1}$) | 0 | | | | | |
| Oil Flow Rate: $GPM/Ft^2$ | 43.9 | | | | | |
| Temperature (°F) | 650 | | | | | |
| Pressure (psig) | 700 | | | | | |
| Product Gas: | | | | | | |
| % $H_2$ | — | | | | | |
| % $N_2$ | — | | | | | |
| % $CH_4$ | — | | | | | |
| % CO | — | | | | | |
| % $CO_2$ | — | | | | | |
| % $C_2^+$ | — | | | | | |
| MW | — | | | | | |
| SCFH | — | | | | | |
| CO Conversion (%) | — | | | | | |
| $CO_2$ Conversion (%) | — | | | | | |
| $CH_4$ Selectivity (%) | — | | | | | |
| Catalyst Rate Constant: | | | | | | |
| $K_{T_R}$ (x $10^6$) | — | | | | | |
| $K_{650°F}$ (x $10^6$) | — | | | | | |
| Run Number | A-6 | — | | | | |
| Bed Height (FT) | 3.1 | | | | | |

FIGURE IV-B-10

## CATALYST ACTIVITY VS. TIME (Run #4)

CATALYST # 087 H/FREEZENE – 100
BASIS: 2780 LBS OF CATALYST IN REACTOR



into the heater prior to Run #4. Two of the surface thermocouples were detached from the heater elements.

The oil and gas heater bundles were pulled out again during the period of November 21 - 30 and inspected. The two detached surface thermocouples were braised onto the heater surfaces and the bundles were reinstalled.

The circulating oil cooler, E-103, was opened for inspection. No damage was found at the site of the fire which occurred at the end of Run #4. The flange was hardness tested and then the unit was reassembled with a new gasket and bolts.

Disassembly of the bottom of the reactor was begun during the first week in October and completed during the following week. Inspection showed that both spargers were intact. The reactor bottom was full of catalyst and inerts. A steel rod and a steel claw scraping device were found in the reactor. When the two spargers were dismantled, they both were found to be filled with INCO catalyst #087H. Hammer-type indentations were found on one-half of the sparger surface and reactor bottom flange surface. These markings may have been caused by the steel objects found inside the reactor and they indicate an uneven flow distribution across the bottom of the reactor.

All steam tracing was turned on to prevent any possible freezing. The skid area was thoroughly cleaned with steam and detergent to remove spilled catalyst and oil from Run #4. The used catalyst from Runs #3 and #4 was prepared for shipment back to INCO.

On October 13, 1977, a meeting between DOE and CSI personnel was held at the Fairfield Research Center. Progress to date at the pilot plant was reviewed. Flow distribution problems in the LPM reactor were discussed including intended modifications and their effect upon the program schedule. The need for 2 man/shift operator coverage at the pilot plant was also discussed.