7. Run #7

A meeting was held at the Fairfield Research Center on May 3, 1978 to review the results of Run #6 and to plan the next run. It was decided to proceed with designing reactor internals which minimize axial mixing and to install them prior to the next run. Also, a decision about which catalyst would be used next in the pilot plant run was made and a batch of INCO-J was ordered. The preliminary design for the reactor internals consisting of baffles and a catalyst retention screen for the top of the reactor cavity was discussed with IGT personnel on May 9 - 10.

The design was subsequently finalized to consist of thirty-six 1-1/4 inch stainless steel tubes, each 13-feet long and closed at the upper end. The tubes are assembled into a bundle with supports at the upper and lower ends and in the middle. Since the tube was to be inserted through the bottom reactor head, limited clearance required that the assembly be fabricated in two sections and welded together as it is pushed up into the reactor. A space was left in the 3-inch triangular pitch tube bundle arrangement for the reactor thermowell. The entire assembly was to be anchored to supports welded to the bottom of the inside wall of the reactor. The former catalyst support screen was to be inverted and attached to the top of the tube bundle to act as a catalyst retention screen. Since three 3-inch diameter holes had to be cut out of the screen to allow for the thermowell and catalyst addition, not all catalyst particles were prevented from carrying over into the reactor separator, but the majority of particles should have been stopped in the case of poor reactor hydrodynamics.

The use of verticle baffles had been proposed as a method of reducing the degree of backmixing within fluidized reactors. Unconnected vertical surface area can reduce the reactor equivalent diameter without compartmentalizing which could result in by-passing through some of the compartments. For the LPM Pilot Plant reactor, tubes were expedient from a structural viewpoint. In the present design, the space within the tubes is not utilized. The resulting free cross-sectional area of the reactor was reduced by 11.2 percent to 2.44 sq. ft. and the reactor equivalent diameter was reduced from 21.0 inches (including thermowell) to 6.5 inches.

The bottom reactor head was opened and the former catalyst support screen was remachined for use as a retention screen. By the end of the month, the upper half of the tube bundle had been fabricated in the shop.

A new catalyst support plate containing 36 two-inch bubble caps with non-return valves was fabricated. It was inspected at the Fairfield Research Center and shipped to the pilot plant. A single bubble cap prototype of this design had been tested successfully in the PDU. The design has the advantage that catalyst particles can re-enter the bottom of the reactor if necessary. With the catalyst support screen, recirculating catalyst could be trapped underneath the screen causing plugging. Also, the bubble cap support should be a better gas and liquid distributor than the screen.

During the period of June 1 - 11, 1978, work proceeded on the assembly and installation of verticle baffles in the reactor. The two sections of the baffle assembly were pre-fabricated and on-site assembly was completed. The bubble-cap tray catalyst support plate arrived at the pilot plant. The tray was inspected and found to be satisfactory. It was installed in the bottom head of the reactor as part of the modified reactor internals and the bottom head was reinstalled.

The pump seals on two of the four process oil pumps were removed and replaced by new seals. Replacement of the remaining two pump seals was awaiting arrival of new seals, expected by the end of June. In the meantime, the pilot plant was to operate without spare pumps.

In other work, the four process oil filters were cleaned out, repacked and reassembled, and made ready for the operation. Seal flush system instruments and instrument lines were cleaned and overhauled.

The assembly of reactor internals was completed by June 12 and the reactor was buttoned up. On June 15, the system was filled with water and circulated to remove as much residual catalyst fines as possible from Run #6. Some sludge remained in the unit after water cleanout. The reactor level detector was recalibrated to compensate for the new reactor internals. Hot nitrogen was then passed through the unit to dry it out.

A shipment of 1500 gallons of Freezene-100 oil was received on June 16 and the system was immediately filled. Oil circulation was initiated and heated to 300^{o}F. During the night, the operator on duty had problems with oil level control in the system. The unit had to be shut down until the engineer arrived on site on the morning of June 17 to restart the unit. It was discovered that some oil had overflowed the product gas separator and entered the flare header.

After restarting oil circulation, flow was directed through the reactor and heating to 400^{o}F was begun under nitrogen blanketing. Inspection during the afternoon of June 17 revealed that the IGT cooling water supply to the LPM skid had been shut off which could have affected circulating oil pump operation. Cooling water was restarted and heating of circulating oil continued. On June 18, seal flush flow was found to be by-passing the main oil pump seals internally and the unit had to be shut down. A set of reconditioned seals were installed on June 19, but an attempted startup had to be aborted when the seal was found to be leaking.

Another set of new seals was picked up on June 20 and installed. Meanwhile, the analytical system was made operational and the chromatograph was calibrated. Oil flow was started in the afternoon and, after checking that the seals were functioning properly, the system was heated to 400°F overnight.

On June 21, the reactor was isolated from the circulating oil system and 2200 pounds of INCO-J catalyst were loaded into the hot reactor following the procedure developed in Run #4 for this type of catalyst which does not require reduction. At 1200 hours, oil flow was slowly integrated into the reactor, thus initiating Run #7. The settled catalyst bed height was 4.6 feet. Heating the system to 600°F was started and the unit was pressurized to 500 psig using hydrogen bypassing the reactor since HP nitrogen was unavailable from IGT. A summary of the events of Run #7 is listed in Table IV-B-15.

Steam-methane reformer feed was initiated to the LPM reactor at 1600 hours on June 21. Most of the 32 hours of methanation consisted of operation at 30,000 SCFH feed gas, 150 GPM oil flow, 500 psig and 600°F. The results of Run #7 are listed in Table IV-B-16, where feed and product gas compositions are based upon CSI analyses and catalyst rate constants are based upon the initial catalyst charged to the reactor. CO conversion ranged from 48 to 65 percent. The catalyst rate constant started out initially at 0.13 X 10^{-6} lb-mol/(atm-lb catalyst-sec) and dropped to 0.06 X 10^{-6} by the end of the run. The drop in catalyst activity was accompanied by a loss in expanded catalyst bed height as shown in Table IV-B-16. Evidently, the INCO-J catalyst was being carried out of the reactor in a manner similar to previous experiences with other INCO catalysts (Runs #3 and #4), despite the inclusion of baffles and a catalyst retention screen within the reactor. Because of the smaller diameter of INCO-J particles (250 - 500 microns), these solids cause bubble coalescence in a three-phase fluidized system.

Table IV-B-15
Major Events of LPM Pilot Plant Run #7

Hours on Stream	Accumulated Reaction Time	Date	Event
0	0	6/21/78	Run #7 started. Integrated oil into reactor.
1	0	6/21/78	Oil flow at 150 GPM through reactor, 100 psig.
2	0	6/21/78	Switched to steam-methane reformer gas by-passing reactor to pressurize unit.
4	0	6/21/78	Unit at 510°F and 500 psig. Started reformer feed gas to reactor.
8	4	6/21/78	Reached operating conditions of 30,000 SCFH at 600°F.
11	7	6/21/78	Leak on water drain from D-101 caused temporary shutdown. Conditions restored in 10 minutes.
20.5	16.5	6/22/78	Completed scans at standard conditions and began increasing temperature.
22.5	18.5	6/22/78	Reached 650°F, 500 psig 150 GPM and 30,000 SCFH.
24.5	20.5	6/22/78	Closed filter by-pass and inboard filter plugged.
25	21	6/22/78	Switched to outboard filter and isolated inboard filter.
26	22	6/22/78	Returned to 600°F, 500 psig, 150 GPM and 30,000 SCFH.
35.7	31.7	6/22/78	Fire at inboard filter.
37	—	6/23/78	Fire out and unit secured.

Table IV-B-16 LPM Pilot Plant Run # 7 Results

Hour	5.5	8	14	16	17	18
Accumulated Reaction Time (Hrs)	1.5	4	11	13	14	15
Feed Gas:						
H_2/CO Ratio	9.37	9.33	8.85	9.08	9.08	9.20
% H_2	88.12	87.72	87.84	87.98	87.98	87.88
% N_2	0.51	0.50	0.49	0.48	0.48	0.40
% CH_4	1.96	2.38	1.74	1.85	1.85	2.08
% CO	9.40	9.40	9.93	9.69	9.69	9.55
% CO_2	—	—	—	—	—	—
% C_2+	—	—	—	—	—	—
VHSV (Hr^{-1})	4,210	3,370	2,960	2,980	2,980	2,980
Oil Flow Rate: GPM/Ft^2	61.2	61.2	61.2	61.2	61.2	61.2
Temperature (°F)	550	600	600	600	600	600
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	86.25	85.06	85.43	85.96	86.05	86.04
% N_2	0.63	0.60	0.62	0.57	0.56	0.57
% CH_4	7.95	10.26	9.21	8.48	8.27	8.28
% CO	5.17	4.08	4.70	5.00	5.11	5.11
% CO_2	—	—	0.05	—	—	—
% C_2+	—	—	—	—	—	—
MW	4.64	4.67	4.71	4.65	4.65	4.65
SCFH	37,290	28,310	25,310	26,090	26,259	26,440
CO Conversion (%)	52.40	64.38	60.44	55.85	54.54	53.53
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	100.00	100.00	99.26	100.00	100.00	100.00
Catalyst Rate Constant:						
K_{TR} (x 10^6)	0.079	0.089	0.073	0.064	0.061	0.059
$K_{650°F}$ (x 10^6)	0.128	0.112	0.092	0.080	0.077	0.074
Run Number	—	7-A	7-A	7-A	7-A	7-A
Bed Height (FT)	5.5	—	4.3	4.0	—	3.8

Table IV-B-16: LPM Pilot Plant Run # 7 Results

Hour	20	23	25	26	27	29
Accumulated Reaction Time (Hrs)	16	19	21	22	23	25
Feed Gas:						
H_2/CO Ratio	9.47	8.97	9.03	9.03	8.82	8.86
% H_2	87.84	88.25	88.29	88.25	88.32	88.38
% N_2	0.52	0.30	0.20	0.24	0.15	0.14
% CH_4	2.38	1.62	1.73	1.73	1.51	1.50
% CO	9.28	9.83	9.78	9.78	10.02	9.97
% CO_2	—	—	—	—	—	—
% C_2+	—	—	—	—	—	—
VHSV (Hr^{-1})	3,010	2,740	2,650	2,650	2,650	2,920
Oil Flow Rate: GPM/Ft^2	61.2	61.2	61.2	61.2	61.2	61.2
Temperature (°F)	600	650	580	594	597	596
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	86.15	85.27	86.48	86.47	86.55	86.66
% N_2	0.62	0.36	0.28	0.27	0.18	0.17
% CH_4	8.22	9.78	7.93	8.02	7.96	7.68
% CO	5.01	4.59	5.31	5.24	5.32	5.49
% CO_2	—	—	—	—	—	—
% C_2+	—	—	—	—	—	—
MW	4.63	4.67	4.58	4.57	4.56	4.57
SCFH	27,090	22,310	23,560	23,500	23,570	26,060
CO Conversion (%)	52.42	62.82	52.82	53.51	53.90	52.03
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	100.00	100.00	100.00	100.00	100.00	100.00
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	0.057	0.073	0.052	0.053	0.055	0.057
$K_{650°F}$ (x 10^6)	0.071	0.073	0.072	0.069	0.070	0.073
Run Number	7-A	7-B	—	7-A	7-A	7-A
Bed Height (FT)	3.4	3.2	—	—	—	—

Table IV-B-16: LPM Pilot Plant Run # 7 Results

Hour	30	31	33	34	35	36
Accumulated Reaction Time (Hrs)	26	27	29	30	31	32
Feed Gas:						
H_2/CO Ratio	8.92	9.07	8.64	8.64	8.64	R
% H_2	88.31	88.25	88.22	88.22	88.22	U
% N_2	0.14	0.15	0.15	0.15	0.15	N
% CH_4	1.64	1.87	1.42	1.42	1.42	
% CO	9.90	9.73	10.21	10.21	10.21	T
% CO_2	—	0.00	—	—	—	E
% C_2+	—	—	—	—	—	R
VHSV (Hr^{-1})	2,930	2,920	2,650	2,650	2,650	M
Oil Flow Rate: GPM/Ft^2	61.2	61.2	61.2	61.2	61.2	I N
Temperature (°F)	601	600	601	601	600	A
Pressure (psig)	500	500	490	490	490	T
Product Gas:						E
% H_2	86.72	86.72	86.38	86.87	86.61	D
% N_2	0.16	0.16	0.17	0.16	0.18	
% CH_4	7.55	7.79	7.52	7.13	7.19	
% CO	5.57	5.32	5.93	5.84	6.01	
% CO_2	0.01	0.00	—	—	0.01	
% C_2+	—	—	—	—	—	
MW	4.57	4.54	4.66	4.58	4.64	
SCFH	26,380	26,450	23,440	24,290	23,020	
CO Conversion (%)	50.53	51.58	49.79	48.66	48.14	
CO_2 Conversion (%)	—	11.46	—	—	—	
CH_4 Selectivity (%)	99.91	100.00	100.00	100.00	99.86	
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	0.055	0.055	0.051	0.049	0.046	
$K_{650°F}$ (x 10^6)	0.068	0.070	0.063	0.061	0.058	
Run Number	7-A	7-A	7-A	7-A	7-A	
Bed Height (FT)	—	—	—	—	—	

The vertical baffles were probably not sufficient to restrict bubble growth and spouting occurred which carried catalyst out of the reactor. Also, the catalyst retention screen did not cover the entire reactor cross-sectional area, so a portion of the rising solids were able to escape from the reactor through the openings in the screen created for catalyst addition, thermowell, etc. For a large diameter catalyst particle, such as Calsicat Ni-230 S, which would operate in the range where bubbles are broken up rather than coalesced, the vertical baffles in the reactor might have reduced backmixing as intended even though they did not reduce backmixing with INCO-J.

Using the information available on expanded bed heights, the amount of catalyst in the reactor as a function of time was estimated (see Figure IV-B-17). Catalyst activity as a function of time is plotted in Figure IV-B-18, based upon the initial catalyst charge as well as on the estimation of catalyst within the reactor as a function of time. An Arrhenius plot for the dependence of the kinetic rate constant upon temperature is shown in Figure IV-B-19. The activation energy obtained by linear regression was 5,460 cal/g-mol with a correlation coefficient of only 0.773. The rather poor correlation is due to very limited data at temperatures other than $600^{\circ}F$. During a previous run with an INCO catalyst (Run #3), the activation energy was more than double the present value. CO conversion as a function of contact time is shown in Figure IV-B-20. The results seem to agree with the LPM kinetic model and yield a kinetic rate constant of 0.128×10^{-6} lb-mol/(atm-lb catalyst-sec) at $650^{\circ}F$.

At 2300 hours on June 21, a leak through a double block system on the water drain from the product gas separator developed. Apparently, these valves had been left open and a plug within the valves let go. Approximately 50 to 100 gallons of fluids from the product gas separator vented to the atmosphere before the valves could be closed. The flow of oil and feed gas to LPM shut down automatically due to this leak.

FIGURE IV-B-17

CATALYST IN REACTOR AS A FUNCTION OF TIME — L P M PILOT PLANT RUN #7

— INCO J / FREEZENE - 100
— REACTOR CONTAINS INTERNALS
— ESTIMATED ON BASIS OF EXPANDED BED HEIGHT RATIOS

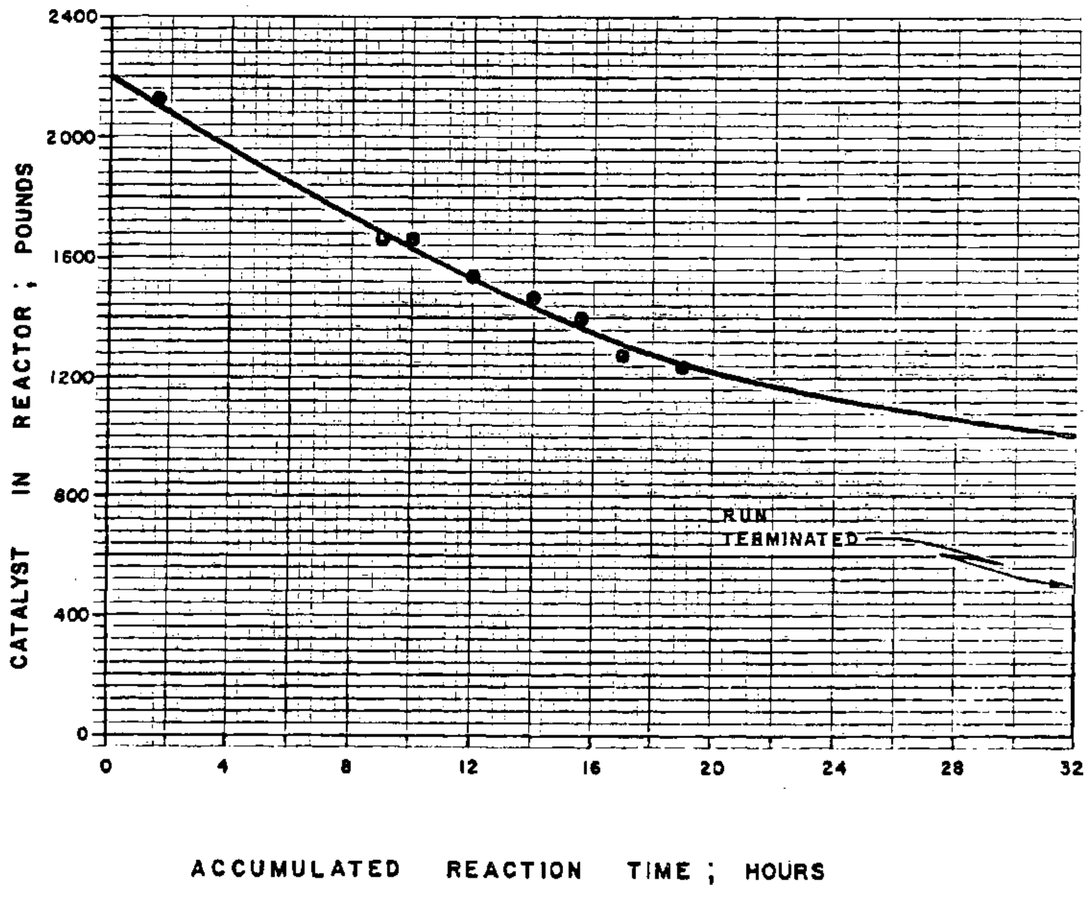

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FIGURE IV-B-18

CATALYST ACTIVITY AS A FUNCTION OF TIME - LPM PILOT PLANT RUN #7

- INCO J/FREEZENE - 100
- 500 PSIG
- REACTOR CONTAINS INTERNALS

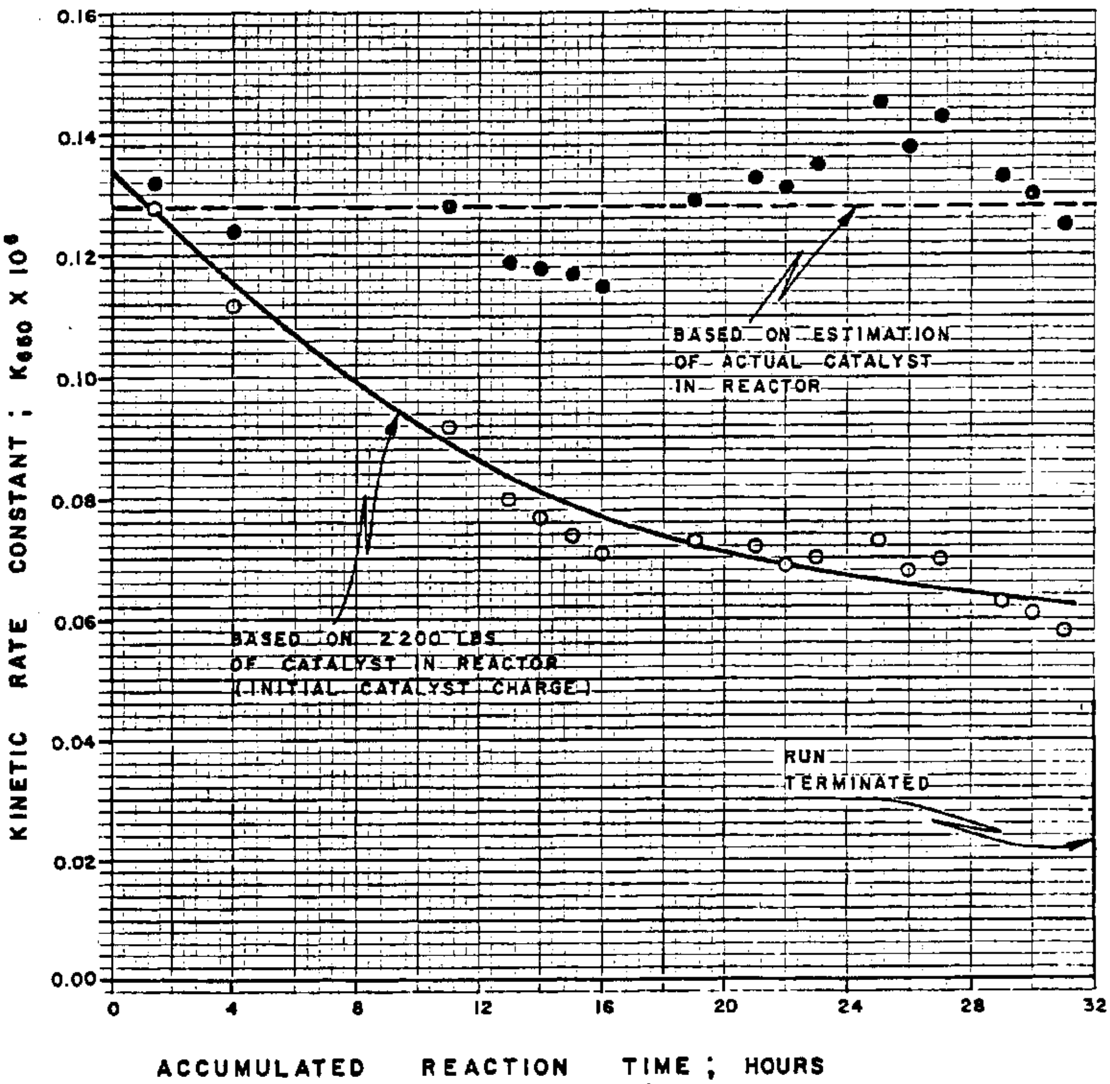

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FIGURE IV-B-19

TEMPERATURE EFFECT ON KINETIC RATE CONSTANT — LPM PILOT PLANT #7

— INCO J/FREEZENE — 100
— 500 PSIG
— REACTOR CONTAINS INTERNALS
— KINETIC RATE CONSTANTS BASED ON ESTIMATED CATALYST IN REACTOR

ACTIVATION ENERGY = 5,460 CAL / g-MOL
CORRELATION COEFFICIENT = 0.773

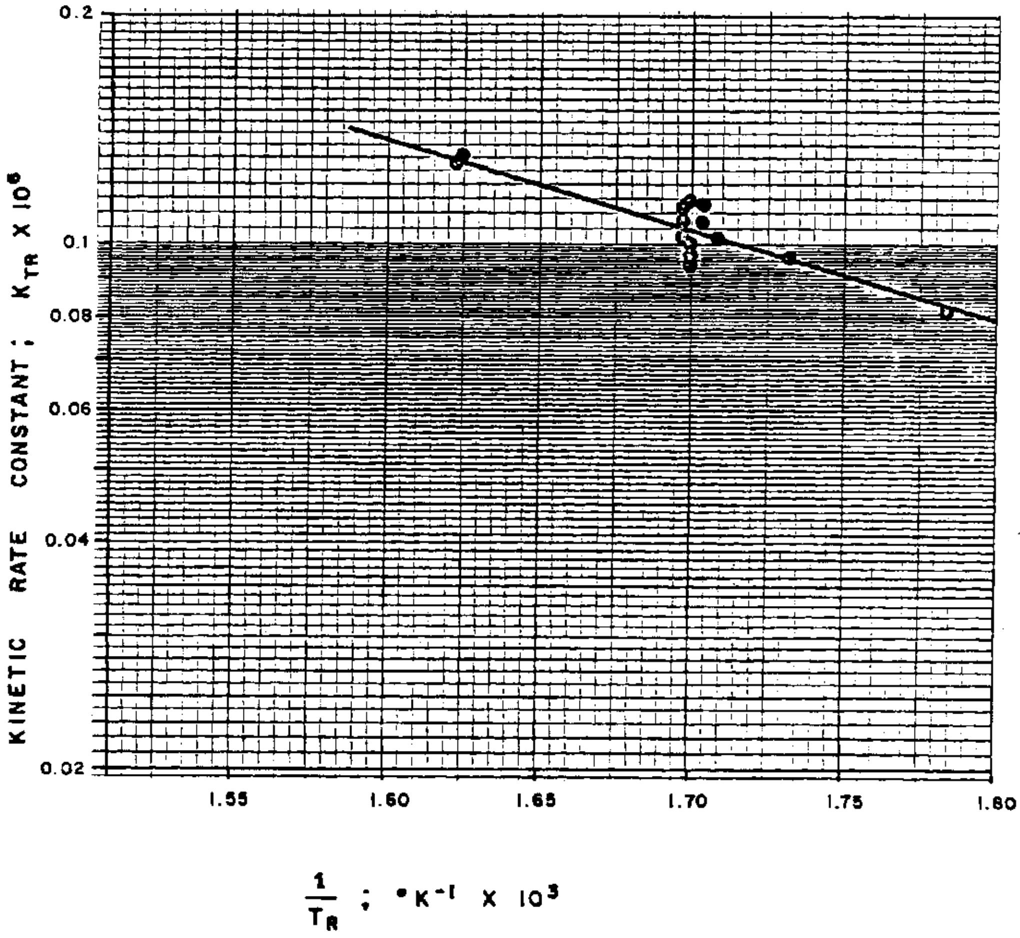

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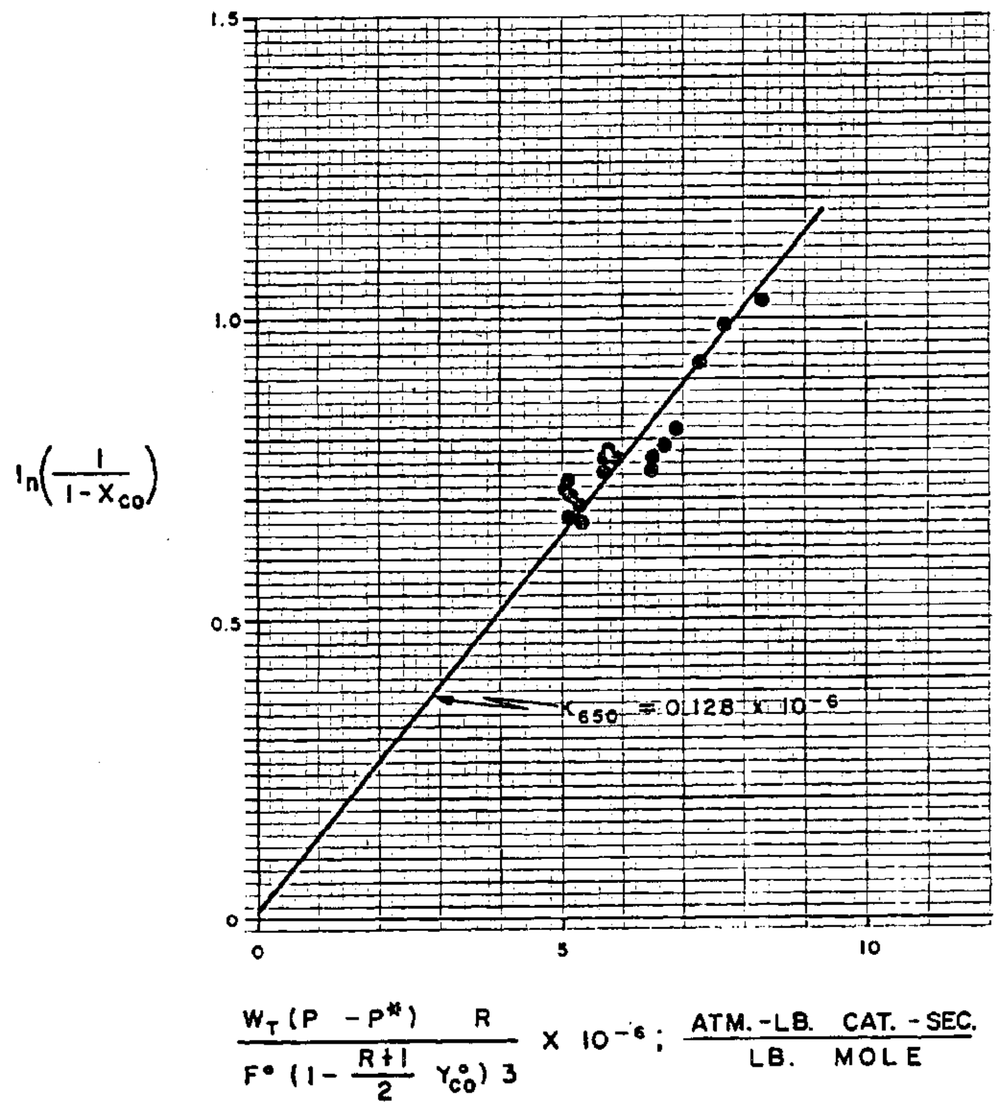
FIGURE IV-B-20

CONVERSION VS. CONTACT TIME
LPM PILOT PLANT RUN #7

- INCO J / FREEZENE - 100
- 500 PSIG @ 650 °F
- REACTOR CONTAINS INTERNALS
- BASED ON ESTIMATED CATALYST IN REACTOR



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The engineer on duty was able to restore the pilot plant to steady operating conditions approximately ten minutes after shutting the valves and the skid area was thoroughly washed down.

At 1230 hours on June 22, the main circulating oil filter by-pass valve was found to be partially open. After closing it, the differential pressure across the inboard filter rose rapidly. The outboard filter was heated up and brought on stream at 1300 hours. Both the inboard filter and the filter by-pass were shut off.

Standard operating proceedures for cooling down the inboard filter were carried out, and the filter was opened for cleanout at 2000 hours. A leak developed through the filter discharge valves into the filter cavity. Attempts to stop the leak failed and, at 2340 hours, a fire started at this filter when the oil overflowed the filter cavity. Details of the events leading up to and including the fire have been covered in a separate "Report of Fire." The fire was out by 0100 hours on June 23 and CSI personnel began securing the unit. A visual inspection of damage was made on June 23 and DOE personnel were notified. A detailed damage list was drawn up and included with the "Report of Fire."

The pilot plant was completely drained of oil and entrained catalyst using low pressure nitrogen. The system was then filled with water and drained again to try to flush out as much of the trapped catalyst as possible. All process oil filters were opened, cleaned, and closed again, except for the filter in which the fire started. The reactor, reactor separator and product gas separator were opened, drained, and cleaned. An oil line leading from the oil cooler, E-103, was removed for a thorough cleaning. This line was found to be packed with INCO catalyst.

All utility lines leading to the LPM unit were blocked off, drained, and isolated. These include all instrument air lines, steam tracing, cooling water, electrical power, sampling lines, low pressure hydrogen, low and high pressure nitrogen, boiler feed water, and feed gas lines. The skid and skid area, as well as the control room itself were hosed down and cleaned. The LPM unit was then effectively inert, awaiting repair.

As a result of the fire, a preliminary estimate was made of the cost to repair the unit. The major uncertainty was whether any metallurgical damage occurred to the filters, heat exchangers and associated piping in the burn area.

At the pilot plant, a fire investigation committee, composed of CSI, IGT and DOE personnel, dismantled the suspect filter inlet and discharge block valves. A large solids deposit was found in one of the discharge valves and small nickel deposits were found adhering to the polished surfaces of all the valves. Subsequent hydrostatic testing proved that these deposits on the polished surfaces were sufficient to have caused the leak which resulted in the fire.

A meeting was held at the DOE offices in Washington on July 13 to discuss the LPM project planning for the next fiscal year. It was tentatively decided by DOE to temporarily discontinue operations at the LPM Pilot Plant although other phases of the LPM project were to continue.

Therefore, at the pilot plant, work continued on securing the pilot plant for short-term shutdown of four to six months. The reactor bottom head was opened and all remaining catalyst was removed. The reactor internals were found to be in place and 1.3 drums out of 4.0 drums of catalyst charged were cleaned out of the pilot plant. The bottom of the reactor-separator was opened on July 31 including the lines to the main circulating oil pumps and more catalyst was found.

During August, the reactor bottom head and the bottom of the reactor-separator were reassembled after removing all catalyst from these areas. The lines to the main circulating oil pumps were also reinstalled as were the lines around the main circulating oil filters. Catalyst was removed from the circulating oil cooler and the unit was reassembled. All vessels were dried with nitrogen.

The used INCO catalyst was shipped back to the manufacturer. Files in the LPM control room were shipped to the Fairfield Research Center for temporary storage.

On August 7, the fire investigation committee issued its report on the fire at the LPM Pilot Plant on June 22, 1978.

On September 27, a team from Argonne National Laboratories made a visual metallurgical inspection of the vessels damaged in the fire at the LPM Pilot Plant on June 22, 1978.

The report of the preliminary inspection of the vessels damaged in the fire at the LPM Pilot Plant was received in November from Argonne National Laboratories. This report covered observations and recommendations based upon a visual metallurgical inspection. Copies were forwarded to DOE.

The report states that metallurgical damage was confined to the vicinity of the main process oil filters. It was recommended that further destructive testing and hydrostatic testing of a number of pipes and welds in this area be conducted to confirm if metallurgical changes occurred as a result of the fire or quenching by water as the fire was extinguished. These recommendations would be carried out prior to resuming operations at the LPM Pilot Plant at a date to be designated by DOE.

In other work, IGT was to prepare all instruments on the skid for a short-term unattended shutdown of four to six months.

At this point, all activities at the pilot plant ceased until directed otherwise by DOE.