3. Run #3

During July, 1977, work continued on relocating the main process filters. Final drawings were prepared and issued by IGT for these revisions. The first item completed was the 4" piping leading to the relocated filters. All of the more than thirty butt welds on this piping were radiographed and found acceptable. Upon completion of radiography, these butt welds were stress relieved and the sections of pipe were installed in their proper pilot plant locations.

All the fill and drain piping was installed on the process oil filters with the exception of a pressure gauge on each of the filters. Work on filter head removal devices and a few other minor items was begun, but not completed by the end of July.

The filter piping was subjected to a successful hydrostatic test. Upon completion, part of the 4" piping was disassembled and removed to the shop area for further heat treating. Installation of the pressure differential indicators and pressure relief valve piping was completed.

Routine maintenance and inspection scheduled for the annual IGT turnaround continued throughout July. A screening hopper was fabricated to separate spent catalyst from inerts when emptying the reactor. Instruments were recalibrated. Surface thermocouple hookups were worked on, but not completed.

The demister was opened, found to be clean and closed again. A heater bundle in the process oil heater was also removed and found to contain no scale. The bottom flange and vortex assembly in the reactor separator was rebuilt and installed.

After completion of radiographic inspection and hardness testing, the bottom flange and vortex breaker assembly of the reactor separator was dismantled and removed for heat treating. Level-trols were installed and calibrated on the product gas separator completing the instrument items required for start-up.

During the week of August 8, 1977, the entire system was filled with water and flushed. All filters were filled with new elements. The unit was drained and flushed again. Dry nitrogen was used to blow out the water and the hydrogen reduction heater was turned on to aid in drying out the reactor. The pilot plant was pressure tested to 500 psi with nitrogen.

Inerts from the reactor were found in the main circulating oil pump suction lines. It was decided to install larger cross-sectional area strainers in these lines. Meanwhile, the pumps were opened for thorough inspection, but no additional inerts were found in the pumps. Mechanical seals for one of the BFW pumps were received and installed.

A meeting was held at IGT on August 17, 1977 to review project status and schedules for the start-up planned for the following week. A new shipment of 1500 gallons of Freezene-100 oil was received.

The entire pilot plant was filled with fresh Freezene-100 oil and heated to 500°F at 700 psi to check for leaks and to check out process instrumentation. The system was found to be in good shape once corrective action was taken on some faulty instruments. Once all water had been dried out of the unit, the system was cooled down and depressurized in preparation for loading catalyst.

On August 22, 340 pounds of 13/16" inerts were charged to the reactor followed by 100 pounds of 1/2" inerts to cover the inlet gas and oil spargers. The inerts level was at the bottom reactor flange which is equivalent to the top of the oil sparger. The inerts charged were reused from Run #2 after cleaning. The charging operation took place into a reactor half filled with cold Freezene-100 oil.

After completing inerts loading, 2320 pounds (10.8 ft^3) of INCO catalyst batch #087 H were charged. The catalyst as charged contained considerable fines and a wide distribution of particle sizes. The catalyst bed height after charging was 4.7 ft.

Once the reactor charging port was closed, the circulating oil system was started, by-passing the reactor. Attempts to initiate cold oil flow into the reactor failed. However, with a nitrogen flow of 2000 SCFH at 100 psig and oil heated to 250°F, a breakthrough occurred and oil flow commenced. The circulating oil was then gradually heated to 500°F.

Run #3 which began on August 22, contained 70 hours of successful operation on HYGAS product. Reactor conditions ranged up to 675°F and 750 psig. CO conversions ranging from 46 to 96 percent were obtained depending upon flow rates and reactor conditions. A limited process

variable scan was conducted to determine catalyst activation energy, fluidization parameters and the effects of other process variables on catalyst activity. The major events of Run #3 are summarized in Table IV-B-5.

During the 12 hours after starting oil flow through the reactor, both of the main oil filters plugged and the system had to be run on filter by-pass. When these filters were cleaned out, 280 pounds of catalyst containing some oil were removed from the first unit and 175 pounds from the second excluding what was impregnated on the filter elements themselves. Checking the expanded bed height on August 23 with 2360 SCFH of N_2 and 207 GPM (0.17 ft/sec) oil flow at 500°F revealed that the bed was 3.4 ft. At 192 GPM (0.16 ft/sec) the bed was 3.2 ft and at 157 GPM (0.13 ft/sec), it was 3.0 ft. Based upon this information, the reactor was estimated to contain approximately 1600 lbs. of catalyst.

HYGAS product was sent through the zinc oxide bed to the LPM skid at 1700 hours on August 24. One and a half hours later, after determining the sulfur content to be 0.12 PPM, HYGAS was fed to the reactor. Approximately 20,000 SCFH of gas were available to LPM because of reduced capacity in the HYGAS acid absorber. Initially, the LPM reactor was reducing the CO concentration from 15% in the feed to 4% in the product. On August 25, gas flow rates were reduced to decrease the exit CO concentration to 0.8 percent. However, at the low flow rates encountered during periods of high conversion, it was not possible to make accurate material balance calculations due to instrumentation inaccuracies.

A few hours on August 25 were devoted to trying to run the second main circulating oil pump to raise the oil flow rate above 220 GPM to increase bed fluidization. The flow rate could only be raised to 270 GPM with both pumps in operation.

TABLE IV.B.5

LPM PILOT PLANT

Run #3 Summary

Hour	Accumulated Reaction Time	Description
0	0	Started heating integrated system and holding pressure with nitrogen. 8/22/77
4	0	First filter plugged with 280 lbs. of catalyst.
18	0	Second filter plugged with 175 lbs of catalyst.
43	0	Started feeding Hygas into unit.
49	6	Reactor at 500 psig, 650°F and 200 GPM oil flow.
64	21	Increased conditions to 750 psig, 657°F and 15,000 SCFH gas flow.
77	34	Temperature upset in system, but continued feeding gas.
82	39	Repeated conditions of hour 64.
87	44	Switched to 650°F.
94	51	Switched to 600°F. Third filter plugged with 100 lbs. of catalyst.
101	58	Returned to 675°F.
106	63	Reactor seperator relief valve leaking into vent heater. Conditions lowered to 500 psig and 650°F where valve reseated.
113	70	Hygas feed interrupted to IGT. Switched to HP nitrogen.
129	70	Hygas coming down. Lowered to 500°F and 300 psig. Bed fluidization checked.
155	70	Lowered conditions to 100 psig and 506°F to study bed fluidization with nitrogen.
181	70	Run terminated.

Since simultaneous operation of both pumps had a deleterious effect upon system stability, it was decided to return to single pump operation and raise conditions to 675°F and 750 psig.

A temperature upset occurred at hour 76 when the circulating oil temperature dropped to 530°F before conditions were stabilized and restored. At hour 106, an oil loss was traced to an open relief valve on top of the reactor separator. System pressure was lowered to 500 psig where the valve reseated.

At 1630 hours on August 27, IGT interrupted HYGAS feed due to a blockage in their unit. The LPM Pilot Plant was switched over to HP nitrogen.

On August 28, bed fluidization was checked at 300 psig, 500°F, 208 GPM oil and 11,800 SCFH N_2 (0.056 ft/sec). At this condition, which is similar to the condition checked before HYGAS feed, the bed height was 2.9 ft; a loss of 15 percent.

On August 29, with 8,200 SCFH of N_2 at 100 psig (0.31 ft/sec) the bed height was found to be 3.2 ft which represents a gas-only expansion of 10 percent from the previous reading. The reactor was blocked in and nitrogen flow was by-passed around the reactor. After allowing 15 minutes for the bed to settle, oil flow through the reactor was resumed. Since no problems were encountered, it is felt that the system could be restarted at a later date provided it is started hot. The unit was then cooled down to 200°F and the reactor was blocked in. On August 30, oil flow was terminated.

Oil was drained out of all process equipment requiring maintenance. Approximately 470 pounds of catalyst were removed from the bottom of the reactor separator and another 150 pounds from the bottom of the circulating oil cooler. Some catalyst remained in the main circulating oil filter which was last in use.

Two methods can be used to estimate the amount of catalyst in the reactor at any given time. The first method is based on catalyst actually removed from the system and the second is based upon extrapolating the expanded bed heights to settled bed heights. Both of these estimates are shown in Figure IV-B-6 to be in fairly close agreement.

Table IV-B-6 contains a summary of the results obtained in Run #3. Feed gas to the LPM unit had a H_2/CO mole ratio of 2.7 - 3.1 and contained small amounts of CO_2 and ethane as well as approximately 12% N_2 and 28% methane. The 0.5% CO_2 came from some water-gas shift taking place in the HYGAS ZnO bed. Methanation product had a methane concentration ranging up to 64 percent. CO conversions ranged up to 96 percent and selectivity to methane ranged from 85 percent at 657°F to 96 percent at 600°F. The remainder was mostly CO_2 resulting from shift reaction. Conversion of ethane in the feed was negligible.

An activation energy of 12,000 cal/g-mole was used to calculate the kinetic rate constant corrected to 650°F. Rate constants in the range 0.12 - 0.16 x 10^{-6} lb-mol/atn-lb/catalyst-sec) were obtained which is equivalent to 0.5-0.6X10^{-6}.for an equal volume of Calsicat catalyst.

An Arrhenius plot for the dependence of the kinetic rate constant upon temperature is shown in Figure IV-B-7. The activation energy obtained by linear regression was 11,905 cal/g-mole with a correlation coefficient of 0.965. Catalyst activity as a function of reaction time is plotted in Figure IV-B-8. The results tend to indicate that the catalyst maintained its activity throughout the run. CO conversion as a function of contact time is shown in Figure IV-B-9. The data agreed with the LPM kinetic model and result in a kinetic rate constant of 0.135 X 10^{-6} lb mol/(atm-lb catalyst/sec) at 650°F.

Samples of INCO-H catalyst were sent to the Fairfield Research Center to obtain sieve analysis of the material charged in Run #3 and the material removed from the filters during the run, and to study fluidization in the PDU.

FIGURE IV-B-6

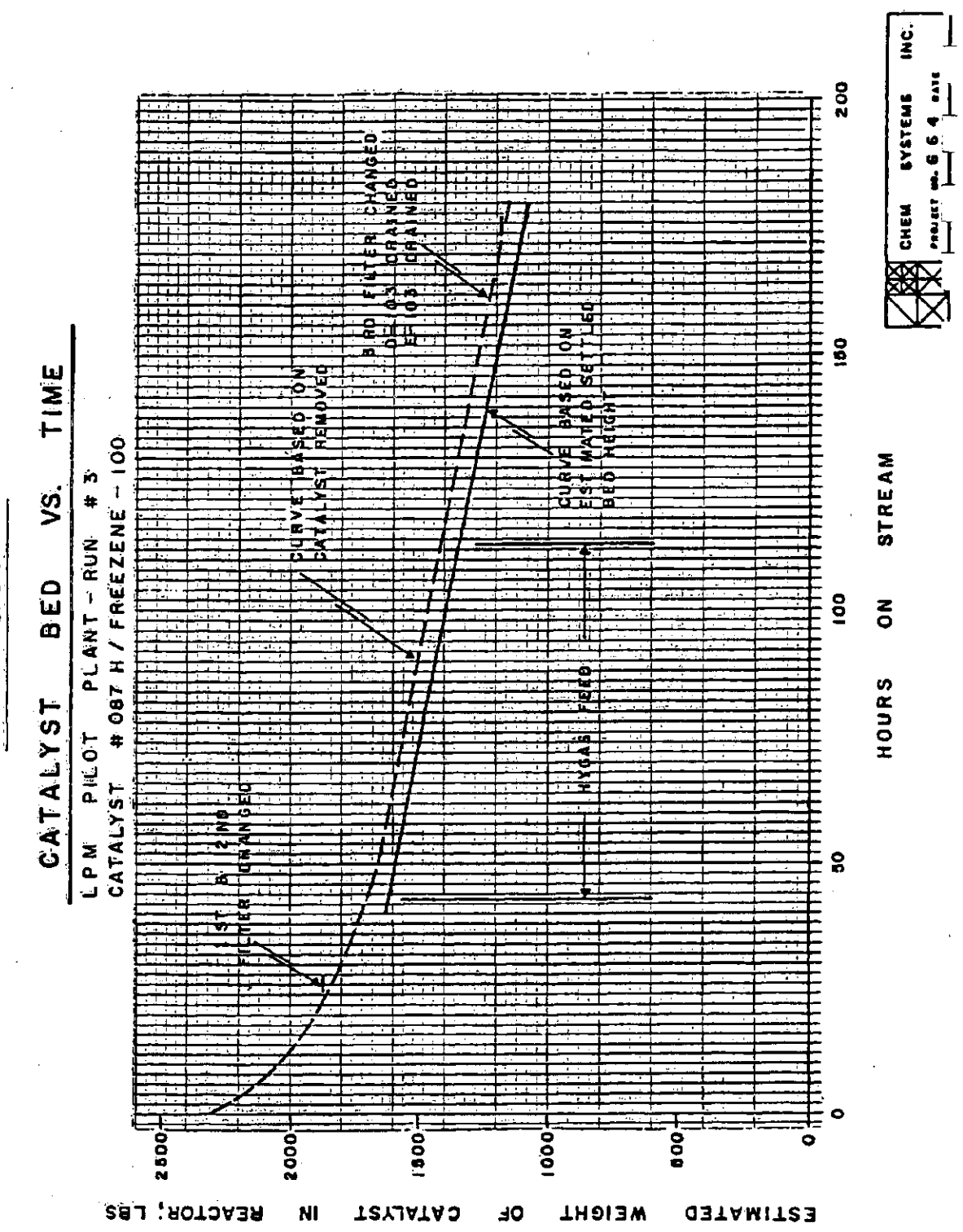
CATALYST BED VS. TIME
LPM PILOT PLANT - RUN # 3
CATALYST # 087 H / FREEZENE - 100
1ST & 2ND FILTER CHANGED
CURVE BASED ON CATALYST REMOVED
3RD FILTER CHANGED
DE-OIL DRAINED
EF-03 DRAINED
CURVE BASED ON ESTIMATED SETTLED BED HEIGHT
HYGAS FEED
ESTIMATED WEIGHT OF CATALYST IN REACTOR; LBS
2500
2000
1500
1000
500
0
0
50
100
150
200
HOURS ON STREAM
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Table IV-B-6
LPM Pilot Plant
Run #3 Results

Hour	48	49	55	66	67	71
Accumulated Reaction Time (Hrs)	5	6	12	23	24	28
Feed Gas:						
H_2/CO Ratio	2.98	2.91	3.01	2.98	3.05	3.10
% H_2	44.09	43.83	43.88	43.57	43.80	44.15
% N_2	11.53	11.57	11.66	11.80	12.56	13.23
% CH_4	28.42	28.34	28.78	28.70	27.98	27.07
% CO	14.81	15.05	14.57	14.63	14.38	14.26
% CO_2	0.37	0.43	0.26	0.44	0.46	0.47
% C_2^+	0.78	0.78	0.85	0.86	0.83	0.83
VHSV (Hr^{-1})	N.D.	N.D.	N.D.	2150	2200	2190
Oil Flow Rate: GPM/Ft^2	68	77	85	82	82	82
Temperature (^oF)	650	651	646	677	667	677
Pressure (psig)	500	500	500	750	750	750
Product Gas:						
% H_2	21.11	22.02	12.37	19.00	18.53	21.63
% N_2	15.64	15.87	17.72	16.80	17.10	18.49
% CH_4	54.75	53.52	64.31	56.64	56.34	52.20
% CO	4.49	4.55	0.84	3.14	3.76	3.75
% CO_2	2.98	3.02	3.62	3.32	3.08	2.87
% C_2^+	1.03	1.02	1.14	1.10	1.10	1.06
MW	16.47	16.39	17.70	16.85	16.94	16.62
SCFH	N.D.	N.D.	N.D.	10,600	10,590	10,860
CO Conversion (%)	78.70	78.27	96.32	85.05	82.23	81.24
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	86.16	86.02	87.13	86.46	87.53	87.62
Catalyst Rate Constant:						
K_{TR} ($\times 10^6$)	N.D.	N.D.	N.D.	0.196	0.179	0.171
K_{650^oF} ($\times 10^6$)	N.D.	N.D.	N.D.	0.156	0.155	0.135

Table IV-B-6 (con't.)
LPM Pilot Plant
Run #3 Results

Hour	72	94	95	97	102	103
Accumulated Reaction Time (Hrs)	29	51	52	54	59	60
Feed Gas: H_2/CO Ratio	2.99	3.12	3.09	3.03	2.71	2.80
% H_2	43.27	43.08	42.98	42.36	42.00	43.21
% N_2	13.64	14.22	14.04	14.18	12.99	12.62
% CH_4	27.35	27.63	27.75	28.23	28.19	27.41
% CO	14.45	13.80	13.93	13.96	15.52	15.41
% CO_2	0.46	0.39	0.41	0.41	0.44	0.50
% C_2^+	0.83	0.88	0.89	0.87	0.87	0.85
VHSV (Hr^{-1})	1830	2340	2350	2380	2540	2540
Oil Flow Rate: GPM/Ft^2	82	80	80	80	82	82
Temperature (^oF)	676	600	596	601	676	675
Pressure (psig)	750	750	750	750	750	750
Product Gas: % H_2	21.74	28.48	26.91	26.68	19.73	22.13
% N_2	18.85	17.63	17.99	17.94	17.85	17.47
% CH_4	51.86	43.46	44.75	45.08	52.51	50.45
% CO	3.76	8.42	8.29	8.13	5.65	5.89
% CO_2	2.73	0.95	1.04	1.09	3.15	2.95
% C_2^+	1.06	1.06	1.03	1.08	1.11	1.11
MW	16.61	15.58	15.85	15.88	17.12	16.72
SCFH	9,240	12,220	12,140	12,150	11,720	11,870
CO Conversion (%)	81.10	51.60	53.51	54.27	73.72	72.04
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	88.04	96.00	96.97	94.63	85.00	85.72
Catalyst Rate Constant: K_{TR} (x 10^6)	0.146	0.078	0.083	0.087	0.180	0.165
K_{650^oF} (x 10^6)	0.117	0.123	0.137	0.137	0.144	0.133

Table IV-B-6 (con't.)
LPM Pilot Plant
Run #3 Results

Hour	105	110	111	113	181
Accumulated Reaction Time (Hrs)	62	67	68	69.5	70
Feed Gas: H_2/CO Ratio	2.79	2.68	3.03	2.86	RUN
% H_2	43.54	42.46	43.72	42.76	
% N_2	11.79	12.26	13.50	13.25	
% CH_4	27.74	28.13	27.08	27.51	TERMINATED
% CO	15.62	15.85	14.44	14.97	
% CO_2	0.47	0.44	0.42	0.64	
% C_2^+	0.85	0.86	0.85	0.87	
VHSV (Hr^{-1})	2580	2440	2520	2390	
Oil Flow Rate: GPM/Ft^2	82	81	81	81	
Temperature (^oF)	676	648	647	647	
Pressure (psig)	750	500	500	500	
Product Gas:					
% H_2	22.75	28.91	29.85	29.57	
% N_2	15.96	14.89	15.54	17.00	
% CH_4	51.01	43.46	42.28	41.87	
% CO	6.26	10.38	10.07	9.42	
% CO_2	2.94	1.35	1.26	1.16	
% C_2^+	1.09	1.01	1.00	0.99	
MW	16.49	15.53	15.42	15.52	
SCFH	12,010	12,360	12,400	12,360	
CO Conversion (%)	70.76	47.18	45.28	48.16	
CO_2 Conversion (%)	—	—	—	—	
CH_4 Selectivity (%)	85.82	92.63	93.18	97.12	
Catalyst Rate Constant:					
K_{TR} ($\times 10^6$)	0.162	0.124	0.107	0.117	
K_{650^oF} ($\times 10^6$)	0.129	0.126	0.110	0.121	

FIGURE IV-B-7

TEMPERATURE EFFECT ON KINETIC RATE CONSTANT

L P M PILOT PLANT – RUN #3
CATALYST #087 H/FREEZENE-100
P = 500 – 750 PSIG

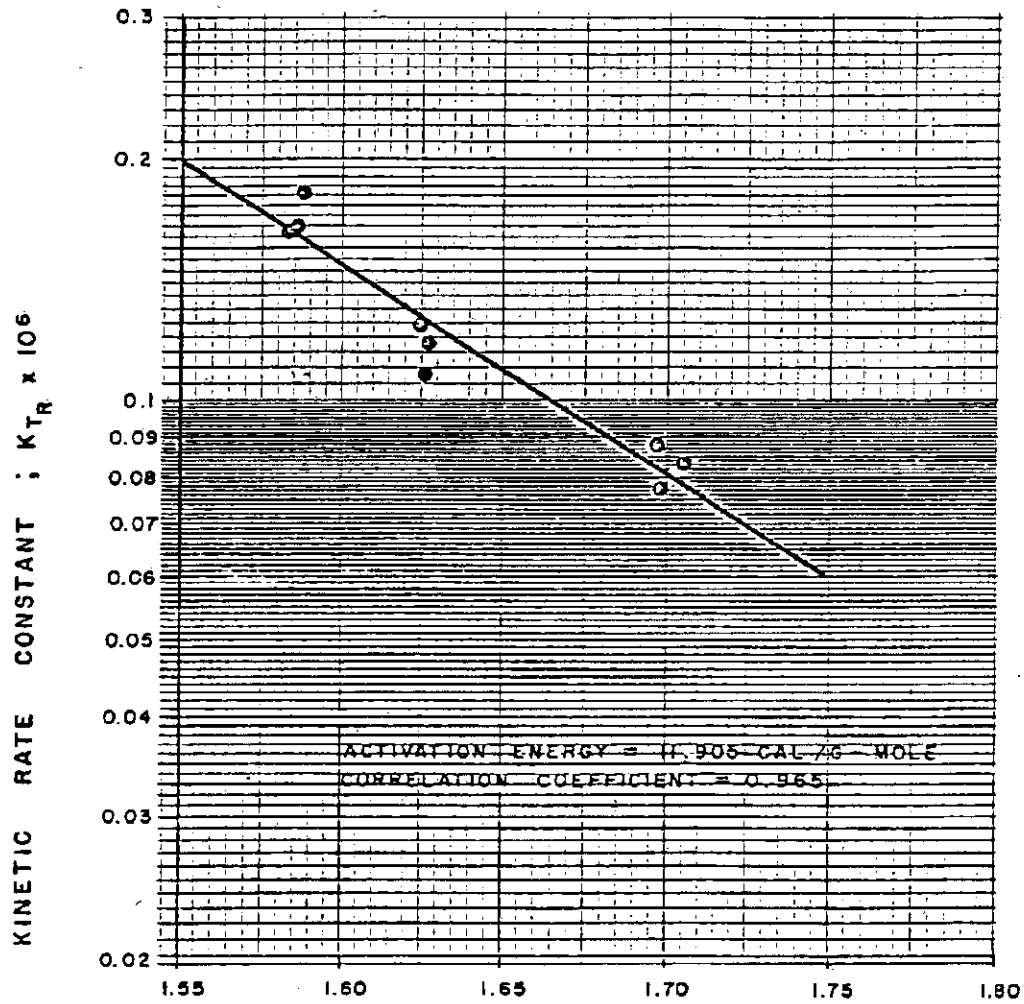

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FIGURE IV-B-8

CATALYST ACTIVITY VS. REACTION TIME

L P M PILOT PLANT – RUN #3
CATALYST #087 H/FREEZENE-100

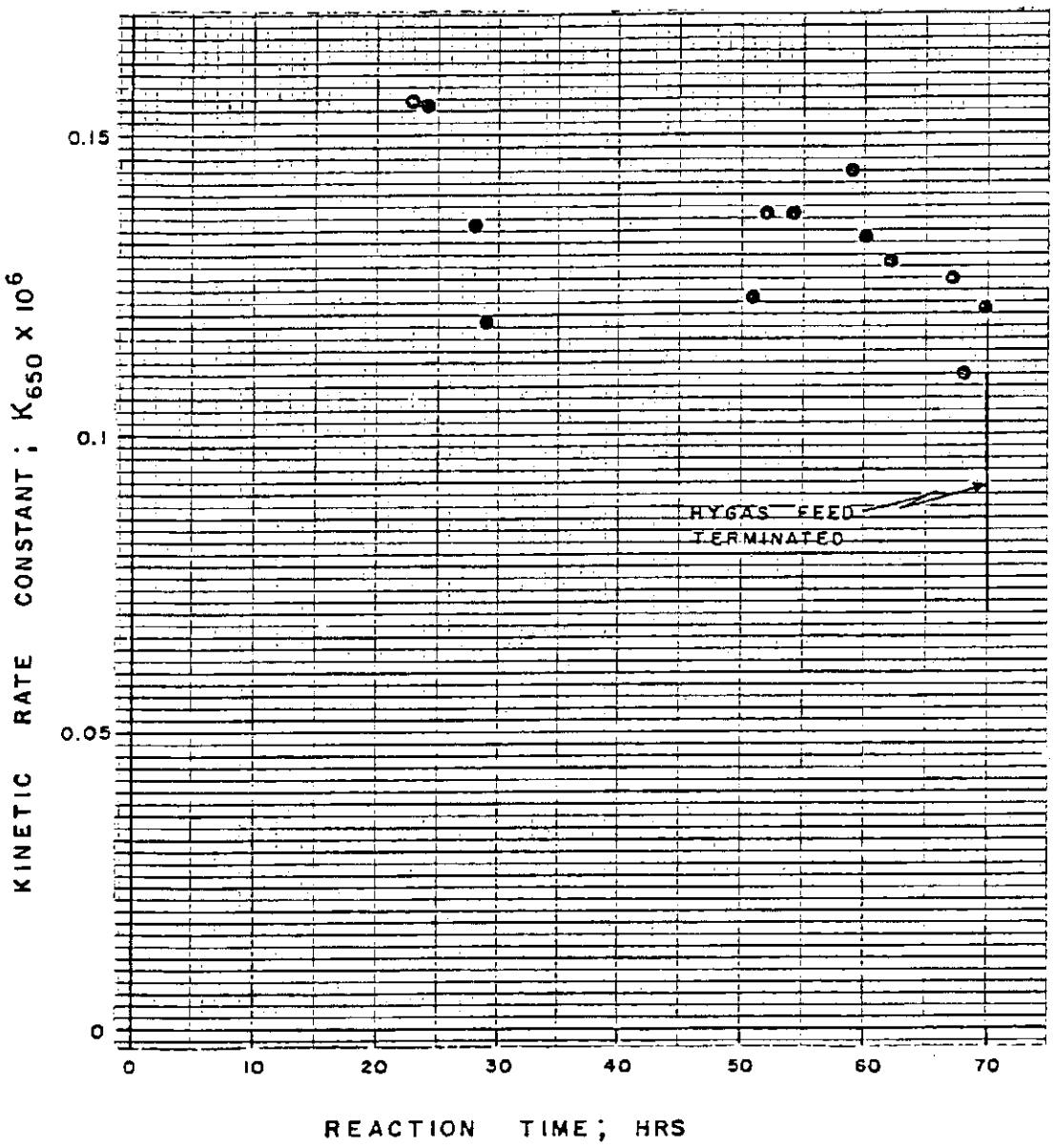

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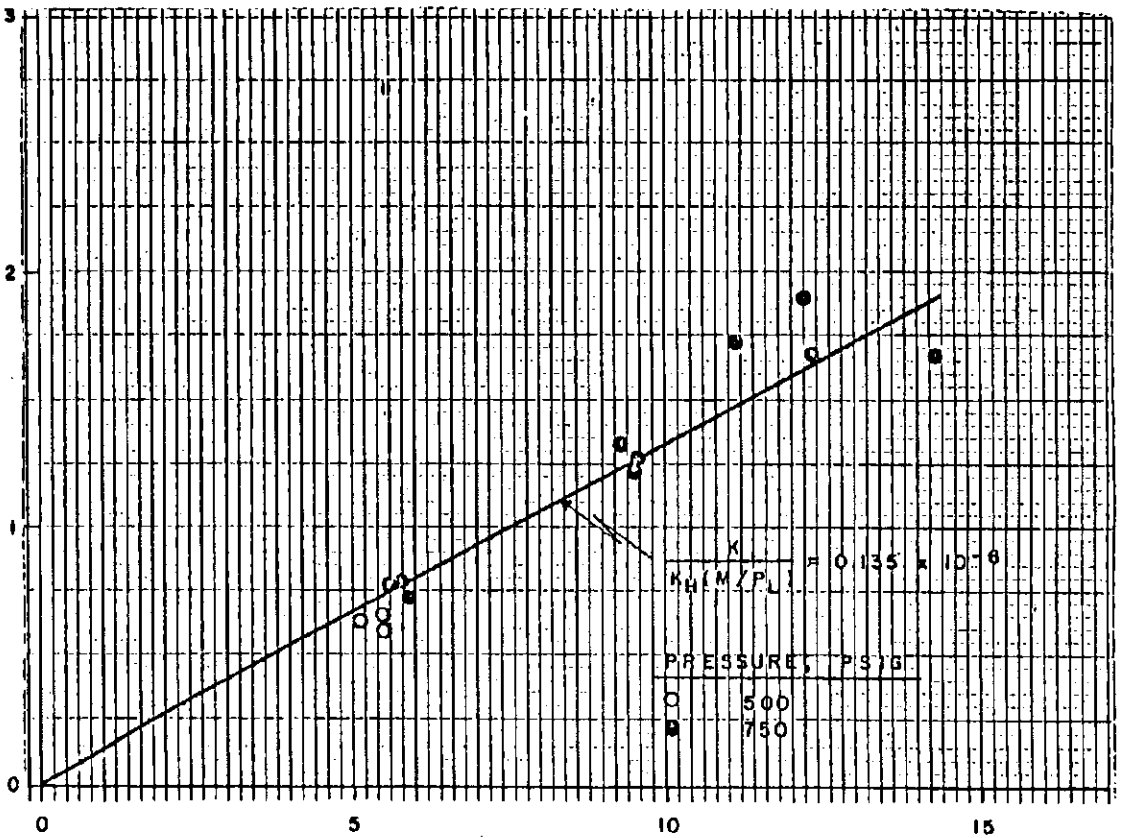
FIGURE IV-B-9

CONVERSION VS. CONTACT TIME

LPM PILOT PLANT - RUN #3
CATALYST #087 H/FREEZENE - 100
@ 650 °F



$\ln \left(\frac{1}{1-X_{CO}}\right)$

$$\frac{W_T (P - P^*)}{F^\circ \left(1 - \frac{R+1}{2} Y^\circ_{CO}\right) 3} \times 10^{-6}; \quad \frac{\text{ATM.-LB. CAT.-SEC.}}{\text{LB. MOLE}}$$

A meeting was held in New York on September 7, 1977, to review the results of Run #3. While considerable useful information was gained from this run, it was felt that the reactor actually contained less catalyst than originally estimated. In fact, measurements made at the end of the run revealed a settled bed height of 1.0 ft. or 590 pounds PDU fluidization studies with INCO catalyst #087 H have shown that oil velocities must be maintained lower than originally anticipated to prevent catalyst carryover. Below 500°F, this catalyst is easily carried out of the reactor with very low Freezene-100 flow rates. It was decided to continue with INCO catalyst #087 H in the next run.