5. Run #5

During the week of October 17, work continued on the design of new gas and process liquid spargers as well as a catalyst support plate for the pilot plant reactor. Several alternatives were considered. A meeting was held in the New York office on October 25 to discuss all design alternatives. It was decided to go ahead with a screen catalyst support and then modify the two spargers. No inerts were to be used in this configuration. A meeting was held on October 27 at the screen manufacturer facilities to finalize design considerations.

It was decided to redrill the gas sparger with 1/8" holes which represented a decrease of 50 percent in cross-sectional hole area to improve gas distribution. The oil sparger was to be removed and an oil disperser inserted through the oil inlet pipe which also attached to a plug for the catalyst withdrawal hole in the support screen. Catalyst removal is thus accomplished by withdrawing the oil disperser and plug. This work was to be done at IGT.

A meeting with IGT, DOE and CSI personnel was held on November 1, 1977 in Chicago. The strategy, timetable and costs of LPM reactor modifications were discussed as well as the need for additional operators during future runs.

During the week of November 1, work orders for the reactor modifications were submitted to IGT since some of this work could proceed while the catalyst support screen was being fabricated.

During the period November 7 - 20, some of the mechanical work was completed including alterations to the circulating oil inlet line to the reactor. However, most of the operations at IGT were halted until the delivery of the catalyst support screen. The support screen was ordered on November 18 and it was scheduled to take 3 - 4 weeks for delivery.

The screen was to have 0.004-inch slot widths for gas and oil distribution and a 2.5-inch hole in the center for catalyst removal.

A meeting was held with Hydrocarbon Research Inc. on November 5 to discuss the possibility of adapting a distribution system similar to that used in H-Oil and H-Coal reactors. HRI-type distributors showed promise for improving the distribution in the LPM reaction system and, therefore, this was pursued as an alternative to the screen support design. Subsequently, during December, an alternative distribution system to the catalyst support screen was designed by CSI and sent to fabricators for estimates. A prototype of this design was to be built for the PDU and, therefore, tested at the Fairfield Research Center prior to installation at the pilot plant.

At the pilot plant during the period November 21 - 30, the inlet gas sparger was redrilled with 1/8" holes. Physical properties of Freezene-100 circulating oil were compiled and documented. Pilot plant data reduction procedures were revised and inquiries were initiated about incorporating these procedures into the HYGAS data aquisition system. The LPM kinetic model was re-examined in light of recent pilot plant and PDU data.

During December most of the work at the pilot plant was halted pending delivery of the catalyst support screen. The screen was received on December 28. Work orderd were immediately issued for installation of the screen and reassembly of the bottom head of the reactor.

Earlier in the month, the case drains on the main circulating oil pumps were resealed with lead seals. The mechanical seals on the BFW pump were checked out because they were operating noisily during the last run. The steam-water mixer was removed and relocated to a more accessible position near the LPM skid.

A dual pen strip chart recorder was installed for combined use with the chromatograph and the CO monitor. While checking the chromatograph, it was found that the relay box was inoperable. Evidently, the relays had corroded as a result of the DGA upset last spring. A new relay box was designed and fabricated at the Fairfield Research Center.

A complete list of flanges to be insulated with removable flange shields was transmitted to IGT. These flange shields were to improve plant safety and allow hot bolt tightening during start-up. Operating instructions were updated to include a hot bolt tightening checklist for these flanges during start-up.

During the first two weeks of January, 1978, designs for the assembly of the catalyst support screen, catalyst removal plug and surrounding piping were reviewed and finalized. The reactor head and screen assembly were inspected. Holes were drilled in the screen, and the screen was mounted. The oil inlet flange within the reactor was cut out. All piping (except one weld) below the bottom head of the reactor was completed in the shop, and the catalyst removal plug was nearly finished.

In other work, the two electrical heaters were rewired. The BFW pump was rewired and tested. Steam tracing and cooling water systems were checked. Work continued on reinsulating pipes and vessels that had become stripped because of steam tracing freeze-up early in December. An extraneous line in the cooling water system was removed to prevent problems in cold weather. Overhead lighting was installed near the relocated main oil filters. The pressure relief valve on top of the reactor and the main oil flow element were checked and reinstalled.

The bottom head of the reactor containing the catalyst support screen was reinstalled during the week of January 16-22. Also, a seal flush line was found to be interfering with the final connection of a flange on the oil inlet line.

Meanwhile, a pre-startup checkout of the pilot plant began. Low-pressure nitrogen lines leading to the LPM skid were found to be frozen as were lines on the skid leading to the oil make-up drum and to the reactor from the hydrogen exchanger. These low pressure nitrogen lines to the skid and through the reduction system were steamed out and the blockages broken. Both the oil and gas heaters were static tested and found to be working. The gas heater was then subjected to a heatup test with nitrogen flow and was judged to be performing satisfactorily.

Because of inclement weather, modifications to the bottom head of the reactor proceeded slowly during the week of January 23-29. The one remaining weld was completed and radiographed, but the pipe was not reinstalled until January 31. The interfering seal flush line was moved. Installation of a differential pressure gauge across the reactor was completed on January 31.

In the meantime, the reactor level detector lift mechanism and thermocouple connections around the reactor were reassembled. Feed and product gas flowmeters were calibrated, and PDI-108 across the demister was repaired. All instrument air lines were checked for ice blockages and found to be functioning properly. An "off" switch was installed in the feed gas lockout system for emergency shutdowns, and a problem in the seal flush flowmeter was checked and resolved.

Pre-startup checkout of the pilot plant continued. The entire system, except for the reactor separator, was filled with oil. A number of problems were discovered and corrected. The system was successfully pressure-tested on January 31.

Run #5 on Calsicat Ni-230S was successfully completed in February. Twenty-five hours of reaction time were achieved on HYGAS synthesis gas before the plant was shut down. While the newly installed catalyst support screen functioned satisfactorily, no improvement in catalyst

activity was noted over Runs #1 and #2 on the same catalyst. The one problem encountered in the LPM Pilot Plant was a high rate of catalyst attrition that continued throughout the 329 hours of operation.

On February 7, Calsicat Ni-230S catalyst was charged to the reactor for Run #5. A total of 686 pounds, equivalent to a settled bed height of 5 feet, were charged. During nitrogen heatup of the reactor, it was noticed that large quantities of water were coming through the nitrogen system. In fact, portions of the nitrogen system were frozen and required steaming out.

When the height of the bed was checked on February 9, it was found to be only 3.3 feet. Inaccurate scales or catalyst agglomeration due to water in the nitrogen lines were suspected to have caused this drop. Another 270 pounds of catalyst were added to the reactor to bring the bed height to 5 feet and nitrogen heatup was resumed.

Hydrogen was introduced into the reactor on February 11, and twenty hours at reduction temperature (above 800°F average in the catalyst bed) were completed on February 12. The reactor temperature was then decreased to 500°F and the system switched back to nitrogen.

The oil system was started up on February 13 and heated to 500°F. Hot bolt tightening of the flanges was begun. On February 14, the oil was diverted into the reactor for the first time. For the next nine days, the system continued to idle at 500°F and 100 psig, awaiting feed gas. The major events of Run #5 are listed in Table IV-B-10.

The first filter plugged five hours after integration of oil into the reactor. At that time, the settled bed height was 5.65 feet or 875 pounds of catalyst. By hour 270 (immediately before gas was introduced into the reactor), seven more filters had plugged. Filters were changed at approximately 16 hour intervals throughout this period except when oil

Table IV-B-10
Major Events of Pilot Plant Run #5

Hours on Stream	Accumulated Reaction Time	Date	Event
0	0	2/11/78	Started hydrogen flow into reactor.
12	0	2/12/78	Reached reduction temperature of 800°F in reactor.
32	0	2/12/78	Reduction completed and started lowering reactor to 500°F.
42	0	2/13/78	Started up oil system.
51	0	2/13/78	Oil system at 500°F, 100 psi and 162 gpm.
64	0	2/14/78	Integrated oil into reactor.
69	0	2/14/78	First filter plugged.
135	0	2/17/78	Second filter plugged.
187	0	2/19/78	Third filter plugged
204	0	2/20/78	Fourth filter plugged.
220	0	2/20/78	Fifth filter plugged
235	0	2/21/78	Sixth filter plugged.
248	0	2/22/78	Seventh filter plugged.
268	0	2/22/78	Eighth filter plugged.
272	0	2/23/78	Started HYGAS feed into reactor at 250 psig and 10,000 SCFH.
282	10	2/23/78	Ninth filter plugged. Reactor at 250 psig, 650°F, 135 GPM oil and 10,000 SCFH gas.
290	16	2/23/78	Shut off gas feed because filter is nearly plugged. Reactor at 500 psig.
293	16	2/23/78	Tenth filter plugged.
294	16	2/23/78	Restarted feed gas at 250 psig.
299	21	2/24/78	Feed gas system upset caused reactor temperature to drop 100°F in 15 minutes.

Table IV-B-10 (continued)

Hours on Stream	Accumulated Reaction Time	Date	Event
301	23	2/24/78	IGT interrupted HYGAS product flow to LPM and substituted hydrogen.
303	23	2/24/78	Switched to nitrogen by-passing reactor.
305	23	2/24/78	Measured settled bed height of 4.5 ft (698 lbs).
309	23	2/24/78	Eleventh filter plugged.
311	23	2/24/78	Restarted feed gas at 500 psig and 540°F.
313	25	2/24/78	Shut off gas feed because filter is nearly plugged.
320	25	2/25/78	Twelfth filter plugged.
327	25	2/25/78	Thirteenth filter plugged with system at 100 psig and no gas flow.
329	25	2/25/78	Run terminated and began cooling system.

was bypassed around the reactor to slow plugging and allow more time for filter changes. Prior experience with Calsicat catalyst suggested that a maximum of five filters should have been required during this time and that the interval between changes should have lengthened as the run proceeded. Possible explanations for this high catalyst attrition rate include:

1. Water in the nitrogen lines during initial reactor heatup.

2. Weakening of the catalyst's physical structure because of the long-term outdoor storage at IGT.

During the final 60 hours of operation, an additional five filters plugged, bringing the total to 13 for the run. The plugging rate increased dramatically when gas was introduced into the reactor (one filter plugged in only four hours). Since filter cleanout takes 12-15 hours, gas and oil flow through the reactor had to be interrupted frequently to allow changing the filters without by-passing oil around them. The history of filter changes, catalyst bed loading and oil and gas flow through the reactor are plotted as a function of hours on-stream in Figure IV-B-11.

Oil-only fluidization was measured periodically during the run; the averaged results for one temperature are presented in Figure IV-B-12. Bed expansion differed considerably from that observed in previous runs with Calsicat catalyst. The minimum fluidization velocity was lower, and the bed expansion was less sensitive to increasing oil velocity. This can be attributed either to a large amount of catalyst fines in the reactor or to altered reactor hydrodynamics caused by replacing inerts in the bottom of the reactor with a catalyst support screen.

HYGAS synthesis gas was introduced into the reactor at hour 272. The unit was heated to 650°F and the pressure gradually raised to 500 psig.

FIGURE IV-B-11

CATALYST BED HISTORY

LPM PILOT PLANT RUN # 5
CALSICAT Ni-230 S / FREEZENE-100

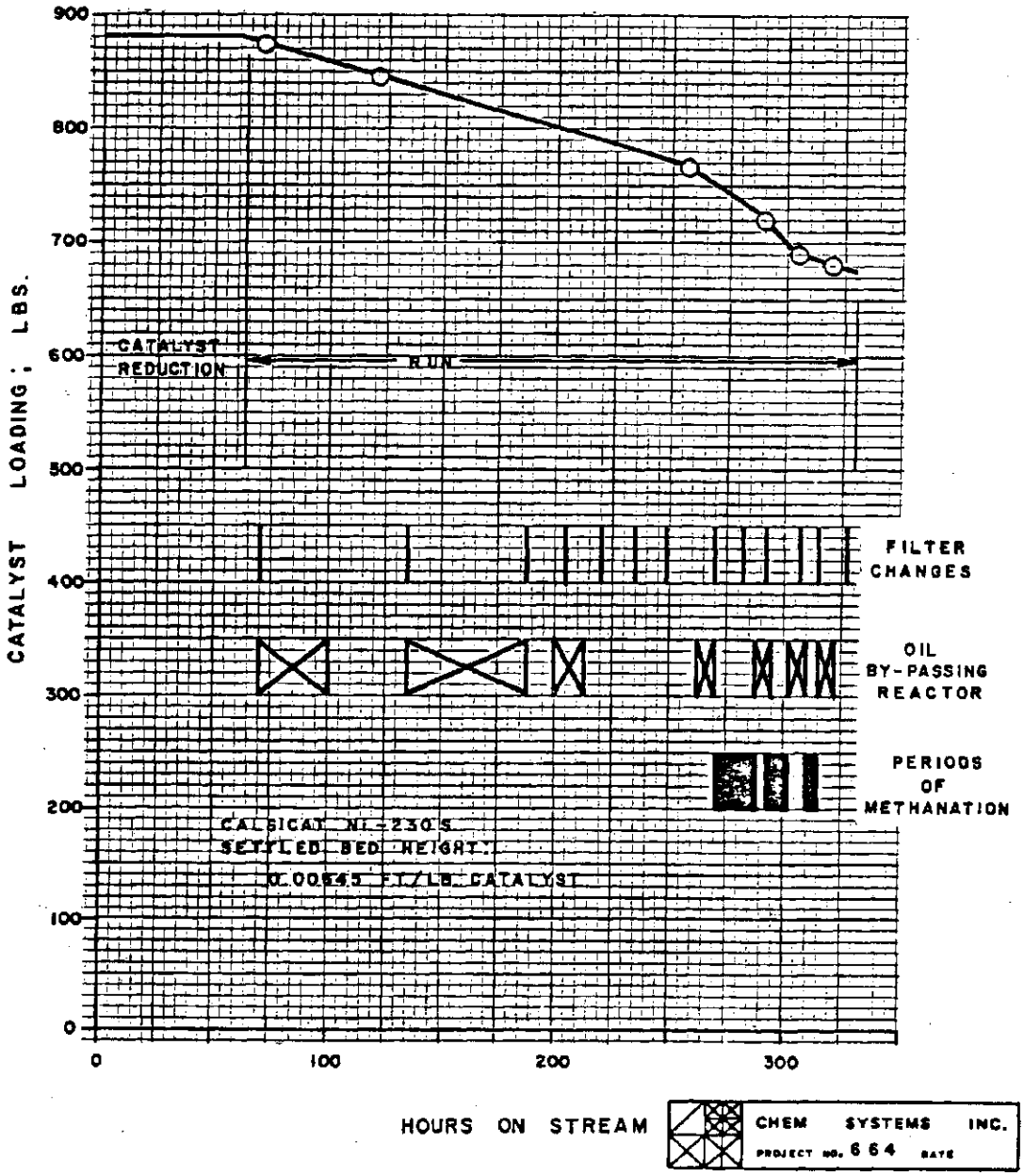
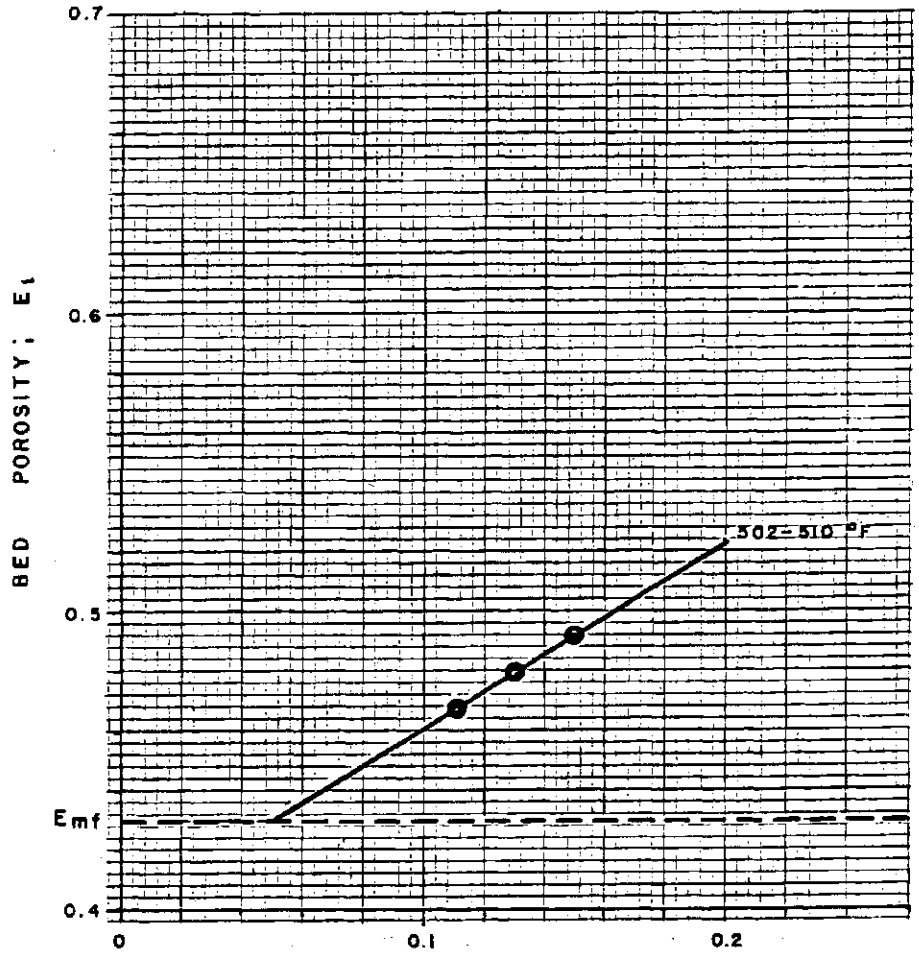


FIGURE IV-B-12

BED POROSITY VS. LIQUID VELOCITY

LPM PILOT PLANT – RUN # 5
CALSICAT Ni-230 S / FREEZENE-100



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Since gas flow was interrupted peridically to change filters, the space velocity never reached standard conditions. Some data were obtained, however, and these results are presented in Table IV-B-11. Reactor conditions ranged up to 650°F, 500 psig, 135 GPM oil flow and 15,000 SCFH feed gas flow. Conversions up to 92 percent were achieved with methane selectivities up to 94 percent. Feed and product gas compositions are based upon IGT analyses.

Catalyst activity was comparable to that observed in previous pilot plant runs with Calsicat catalyst, namely 0.5 X 10^{-6} lb-mol/(atm-lb catalyst-sec). This activity is plotted as a function of reaction time in Figure IV-B-13. While activity seems to decrease with time, data for the last hours of methanation are based on very low gas flow rates, which tend to make these activity calculations imprecise.

During methanation, no water buildup in the product gas separator was noticed. Finally, at approximately hour 300, it was discovered that the water-oil interface level gauge has been turned off and that water had been recirculating through the condensed oil return pump to the circulating oil system. This was corrected, but the catalyst bed may have been damaged. In any case, the filters seemed to plug more quickly in the last few hours on the run after this water recirculation problem had been noticed.

At hour 313, HYGAS shut down because of mechanical problems. LPM caught all the HYGAS production time that was available during this tun. The LPM pilot plant was shut down 16 hours later because hydrogen reformer gas was not available for the next ten days and also because of the filter plugging problems.

Where Run #5 terminated, the pilot plant was cleaned out in preparation for the next run. Insulated flange covers were fabricated and installed on all major vessel and pipe flanges.

Table IV-B-11 LPM Pilot Plant Run #5 Results

Hour	274	276	278	280	283	285
Accumulated Reaction Time (Hrs)	2	4	6	8	11	13
Feed Gas:						
H_2/CO Ratio	2.98	3.03	3.05	3.07	3.10	3.15
% H_2	48.84	49.46	49.22	48.82	50.24	49.14
% N_2	9.29	10.09	10.36	10.36	9.75	11.14
% CH_4	24.42	23.10	23.37	23.76	23.26	22.68
% CO	16.37	16.31	16.15	15.93	16.19	15.59
% CO_2	0.54	0.55	0.40	0.72	0.10	0.95
% C_2^+	0.54	0.49	0.50	0.41	0.45	0.50
VHSV (Hr^{-1})	650	620	680	720	830	1,110
Oil Flow Rate: GPM/Ft^2	135	135	135	135	135	135
Temperature (°F)	630	650	654	654	622	655
Pressure (psig)	250	250	250	260	360	480
Product Gas:						
% H_2	25.11	24.55	25.98	21.12	24.78	20.68
% N_2	13.52	14.02	14.25	15.14	14.78	17.63
% CH_4	51.94	52.18	50.33	55.26	53.08	54.39
% CO	5.87	5.54	5.90	4.12	4.11	3.84
% CO_2	2.58	2.77	2.59	3.51	2.37	2.49
% C_2^+	0.98	0.94	0.96	0.84	0.88	0.97
MW	15.70	15.85	15.67	16.49	15.62	16.54
SCFH	6,010	5,460	6,040	5,990	7,161	9,280
CO Conversion (%)	75.60	77.70	75.39	83.49	83.24	84.19
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	88.14	87.99	86.54	86.66	87.33	93.20
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	0.469	0.475	0.486	0.634	0.505	0.538
$K_{650°F}$ ($\times 10^6$)	0.513	0.475	0.478	0.626	0.573	0.526
Run Number	—	—	—	—	—	—
Bed Height (FT)	—	—	—	—	—	—

Table IV-B-11 LPM Pilot Plant Run #5 Results (continued)

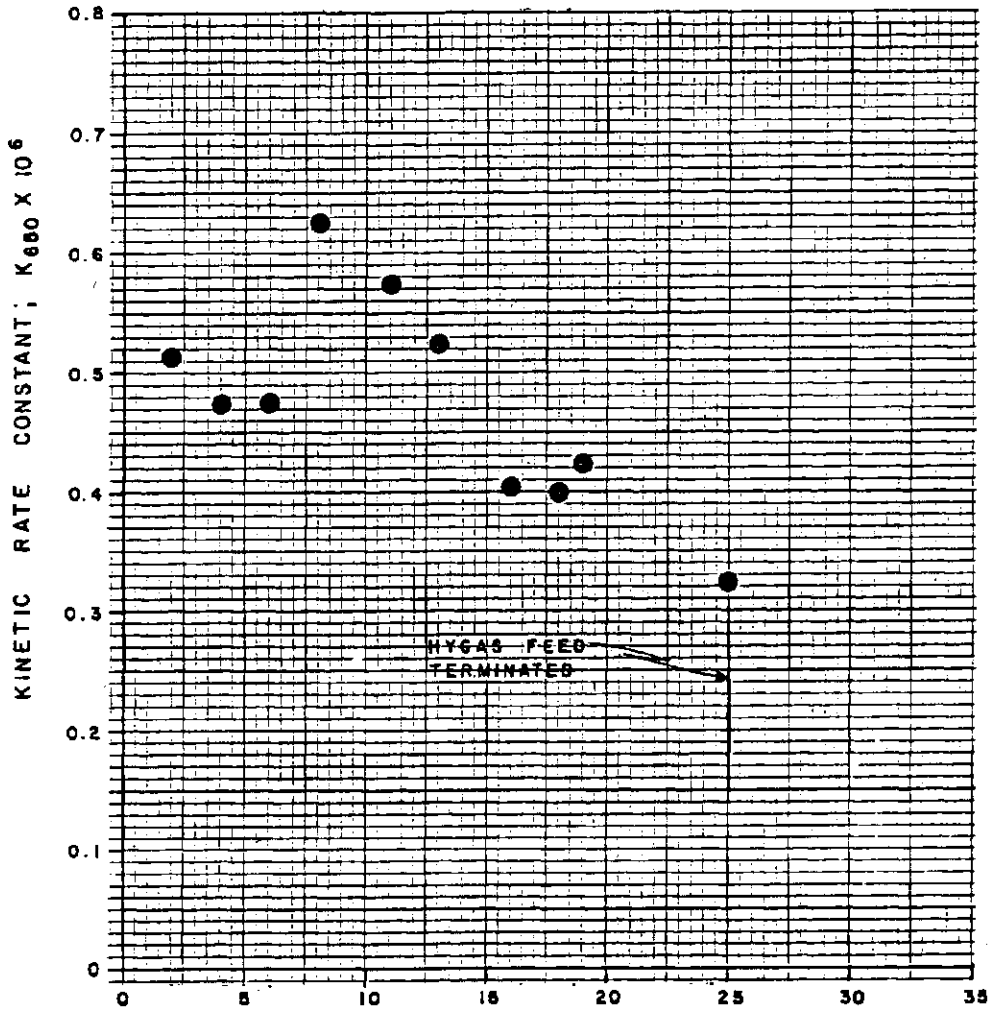
Hour	288	296	297	313	329	
Accumulated Reaction Time (Hrs)	16	18	19	25		
Feed Gas:						
H_2/CO Ratio	3.18	2.88	2.88	3.74	R	
% H_2	48.84	47.04	47.04	48.76	U	
% N_2	10.93	14.50	14.50	10.81	N	
% CH_4	23.06	21.46	21.46	26.76		
% CO	15.42	16.32	16.32	13.03	T	
% CO_2	1.25	0.18	0.18	0.14	E R M I N A T E D	
% C_2^+	0.50	0.50	0.50	0.49		
VHSV (Hr^{-1})	690	510	550	470		
Oil Flow Rate: GPM/Ft^2	135	135	135	135		
Temperature (°F)	644	607	616	548		
Pressure (psig)	500	500	500	500		
Product Gas:						
% H_2	24.50	22.00	23.18	24.99		
% N_2	16.37	19.65	19.81	17.85		
% CH_4	51.40	50.55	49.57	52.71		
% CO	2.31	2.28	2.08	2.79		
% CO_2	4.60	4.61	4.47	0.85		
% C_2^+	0.82	0.91	0.89	0.81		
MW	16.24	17.00	16.79	15.36		
SCFH	6,050	4,280	4,675	3,520		
CO Conversion (%)	89.82	90.80	91.41	84.88		
CO_2 Conversion (%)	—	—	—	—		
CH_4 Selectivity (%)	85.64	79.48	79.72	94.42		
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	0.393	0.328	0.362	0.197		
$K_{650°F}$ ($\times 10^6$)	0.404	0.400	0.422	0.323		
Run Number	—	—	—	—		
Bed Height (FT)	—	—	—	—		

FIGURE IV-B-13

CATALYST ACTIVITY VS. REACTION TIME

LPM PILOT PLANT RUN #5

CALSICAT Ni-230 S / FREEZENE 100



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A batch of Calsicat catalyst from pilot plant Run #5 was used in a run in the PDU at the Fairfield Research Center. The run proved that this batch of catalyst had, indeed, physically deteriorated because it had been stored outdoors for a long time. At a meeting in Fairfield on March 14, it was decided that this particular catalyst batch was too weak for further testing in the pilot plant. Instead, a 1/8" tableted catalyst was to be used for the next run. Two drums of catalyst batch #038-A were shipped to the pilot plant.