4. Low Temperature Runs

Run 4: Lurgi Gas/G-87P (35 atm, 315°C, 0% steam, 500 hours)

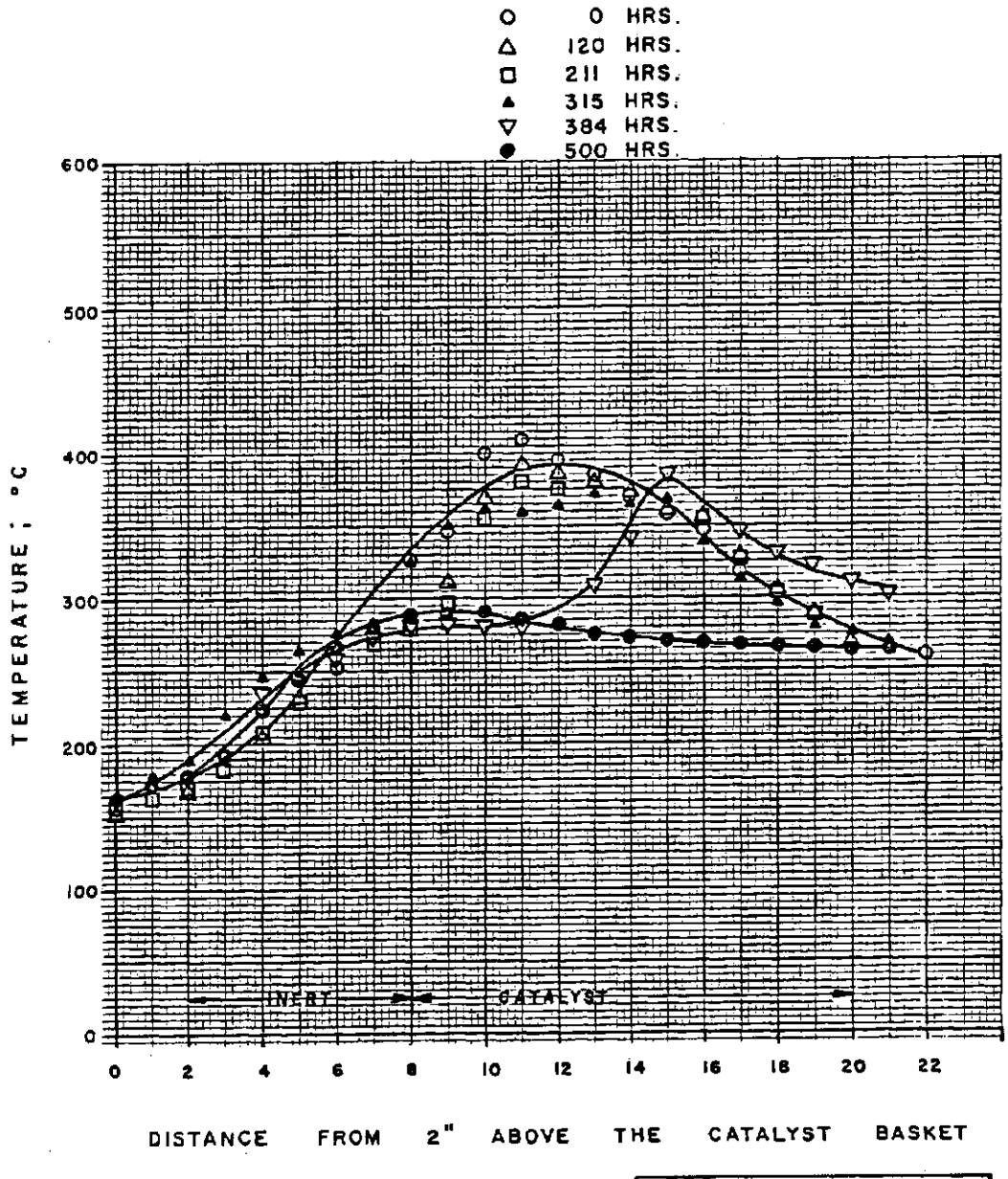
A 500-hour run with Lurgi gas at 500 psig and a nominal temperature of 315°C using catalyst G-87P was started. However, it was not possible to operate the reactor in the proposed temperature range of 315 + 55°C at 10,000 v/v/hr, even without reactor insulation. The temperature rise resulting from methanation was simply too great to be controlled within this limit. To solve this problem, the catalyst was first diluted with 80 percent inert. With a feed rate of 16.6 L/min, the reactor was operating at 50,000 v/v/hr, but the hot spot temperature of 430°C was still too high. The catalyst bed was further diluted to 90 percent inert and 10 percent catalyst by loading each section (25 ml) of the catalyst bed with a mixture of 2.5 ml catalyst and 22.5 ml inerts. Operating at 100,000 v/v/hr (16.7 L/min), the hot spot was 8" into the bed and its temperature was 385°C. Thus, the initial profile was within the desired temperature range.

The temperature profile as shown in Figure IV-D-22 indicates that the catalyst was losing its activity over the 500-hour period. During the first 300 hours, the profile was stable. Catalyst deactivation became apparent when the hot spot moved down in the bed and temperature decreased. After 400 hours, the profile became virtually flat (below 300°C), indicating that the catalyst was dead.

FIGURE IV-D-22

TEMPERATURE PROFILE OF RUN #4

LURGI / G-87P (35 ATM., 315°C, 500 HRS., 0% STEAM)
10% CATALYST / 90% INERTS



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Analysis of product gas confirms the behavior of the temperature profile. It shows that 79 percent of equilibrium conversion was achieved at 24 hours, but that only 13 percent conversion was taking place by 500 hours. The spent catalyst was analyzed and the results appear in Table IV-D-4.

Run 5: Lurgi Gas/G-87P (35 atm, 315°C, 5% steam, 300 hours

Operating conditions for Run 5 were the same as those for Run 4 except for 5 percent steam injection. The temperature profile, as shown in Figure IV-D-23, is fairly stable up to 100 hours of operation with the hot spot located 6 inches from the top of the catalyst bed. At 200 hours, however, a sign of deterioration appeared as the hot spot moved down in the catalyst bed. At 300 hours, most of the catalyst bed seemed deactivated. The reactor was shut down at this point, instead of at 500 hours, as originally planned. Product gas analyses indicate that, at a space velocity of 100,000 v/v/hr, equilibrium conversion was not achieved. A gradual decrease in conversion was evident along with the decaying temperature profile: 72 percent at 150 hours, 67 percent at 200 hours, and 44 percent at 300 hours.

Run 5a: Lurgi Gas/G-87P (35 atm, 315°C, 5% steam, 215 hours)

Run 5a was a repeat of Run 5 conditions to see if it had been poisoined by air trapped in the system. The temperature profiles of Run 5a for each 50 hours interval are plotted in Figure IV-D-24. At start-up, the profile was ideal, with the hot spot at 400°C and 2 inches from the top of the catalyst bed. A sign of catalyst deterioration appeared at 50 hours, when the hot spot moved down 4 inches. At 115 hours the hot spot was 8 inches below the top of the catalyst bed. After about 215 hours on-stream, a mechanical problem with the feed gas booster compressor caused a 500-hour shutdown with the unit held at temperature under nitrogen. When the unit was restarted, the temperature profile and

FIGURE IV-D-23

TEMPERATURE PROFILE OF RUN #5

LURGI / G – 87 P (35 ATM., 315 °C, 300 HRS., 5 % STEAM)

10 % CATALYST / 90 % INERTS

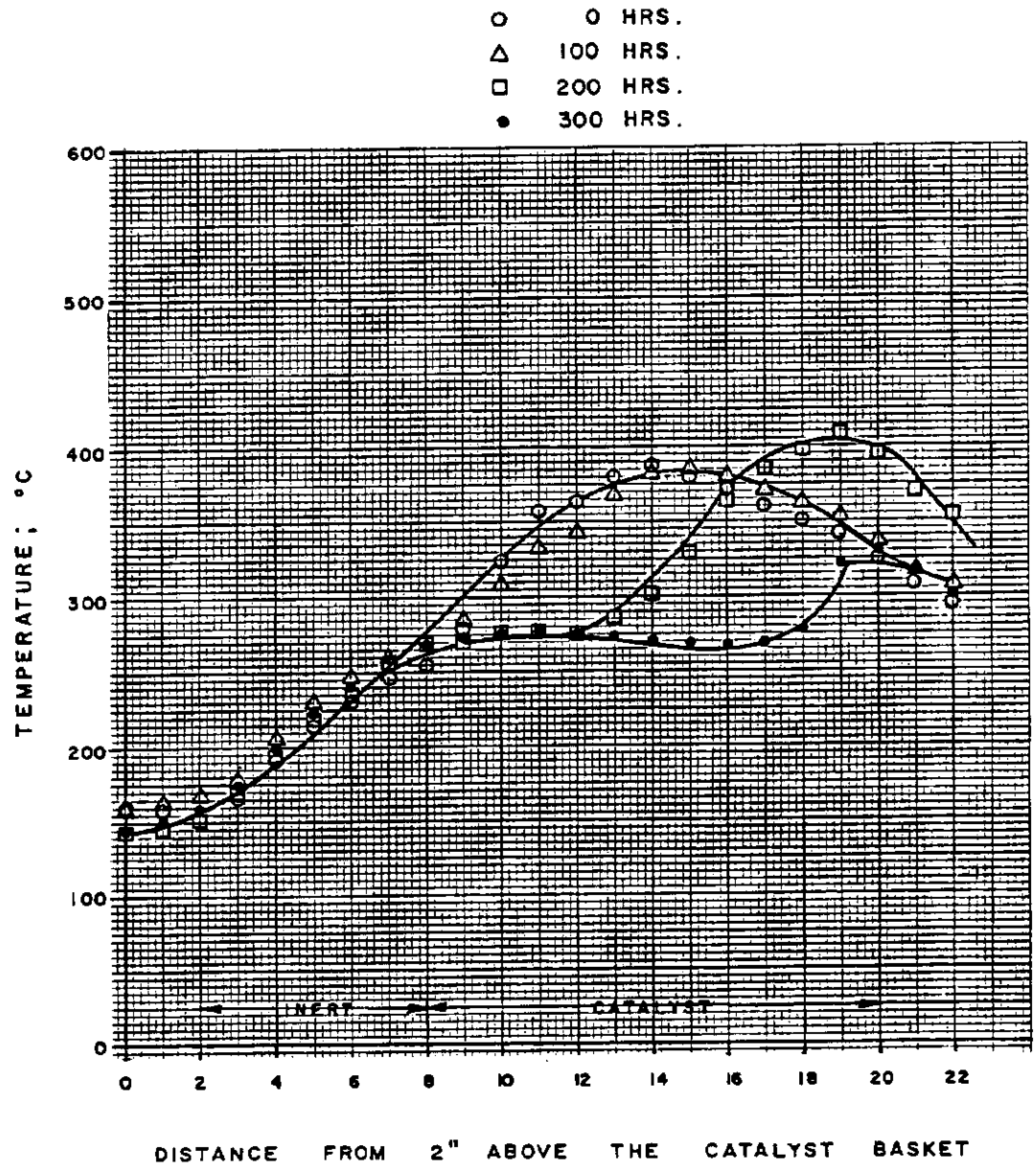

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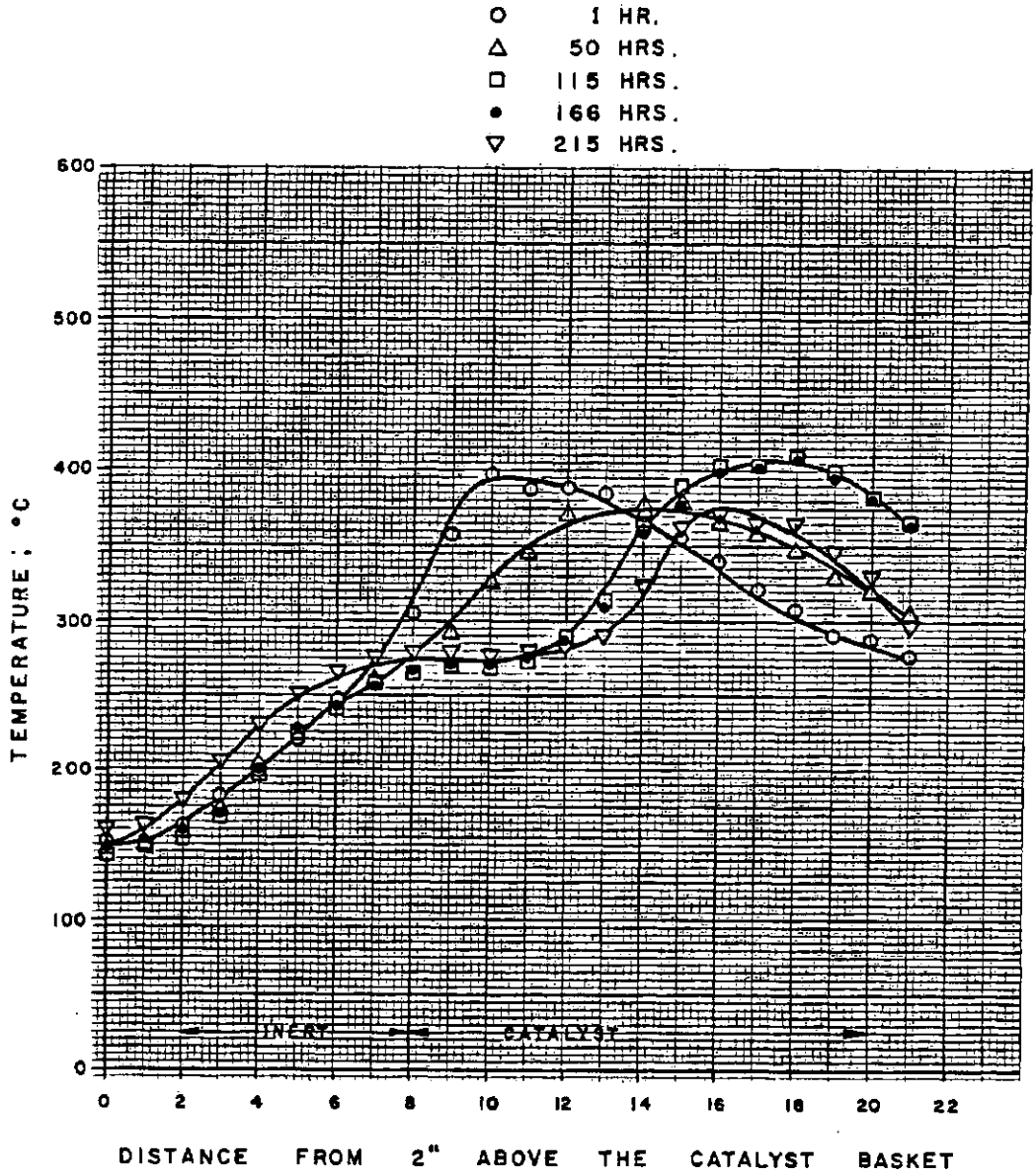
FIGURE IV-D-24

TEMPERATURE PROFILE OF RUN #5a

LURGI / G - 87P, (35 ATM., 315 °C, 500 HRS., 5 % STEAM)
10 % CATALYST / 90 % INERTS



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conversion levels were consistent with the results prior to the shutdown. Due to the obvious loss in activity over the relatively short time on-stream, the run was terminated. The spent catalyst appeared gray in the top section and uniformly black in all other sections. Product gas analyses indicated that, initially, conversion to methane was 80 percent of the equilibrium value. It then gradually decreased to 70 percent after 200 hours of operation.

Crystallographic examination of the spent catalysts of Runs 4, 5 and 5a offered no clues as to the possible cause of the deactivation. All values were within acceptable limits, with the nickel crystallite size somewhat larger than usual, 350-400^{0}A, instead of 200^{0}A. Carbon deposition was evident as shown in Table IV-D-4; although it was more evenly distributed among the four catalyst sections, probably a result of the progressive nature of the hot-spot temperature. The levels of carbon deposited were lower than those observed at the high operating temperature.

Several explanations for the deactivation process were advanced. Poisoning or natural aging, seemingly accelerated by the high effective space velocity, was at first suspected. However, trace component analysis of the spent catalyst for sulfur, chlorine and iron were negative (See Tables IV-D-1 and IV-D-2). In addition, tests with undiluted beds had logged equivalent feed gas loadings over the course of the run and had not shown the same deactivation behavior. One possibility, supported by experimental evidence in Run 5b, is that the catalyst reaction initiation temperature increased above its initial 250^{0}C level. More specifically, operation at the lower temperatures of 315^{0}C requires that the preheat zone remain below 260-270^{0}C in order to prevent too rapid a rise in temperature. If the reaction initiation temperature increases to a value greater than this, the reaction would cease, appearing as if the catalyst deactivated. This increase in initiation temperature may very well be a normal catalyst aging characteristic.

TABLE IV-D-1

SULFUR ANALYSIS OF SPENT CATALYST from Runs 4 and 5

Run	Catalyst Position	Sulfur Content (wt %)
4	Top	0.01
	Mid Top	< 0.01
	Mid Bottom	< 0.01
	Bottom	< 0.01
5	Top	< 0.01
	Mid Top	< 0.01
	Mid Bottom	< 0.01
	Bottom	< 0.01
Fresh Catalyst		0.01 - 0.02

TABLE IV-D-2

ANALYTICAL RESULTS OF SPENT CATALYST from Run 5a

Run	Catalyst Position	Carbon (wt %)	Sulfur (wt %)	Chlorine (ppmw)	Iron (wt %)
5a	Top	6.01	0.080	49	0.05
	Mid Top	6.93	--	--	0.08
	Mid Bottom	5.08	--	--	0.07
	Bottom	5.82	0.086	<30	0.07
Fresh Catalyst		2.00	0.01-0.02	--	~0.04

Run 5b: Lurgi Gas/G-87P (35 atm, 315°C, 5% steam, 510 hours)

Run 5b operated at nominally the same conditions of Runs 5 and 5a, with the exception that the preheat zone prior to the catalyst bed was maintained about 20 - 30°C higher, at about 285°C.

After 7 hours, the temperature profile appeared as shown in Figure IV-D-25. The hot spot, located 4 inches down from the top of the catalyst bed, was 393°C. The conversion level was 87 percent based upon CO. After 22 hours, the hot spot temperature had fallen to 381°C. The hot spot region broadened, showing signs of moving down the bed, and the conversion level continued to fall. At 142 hours of operation, the whole catalyst bed appeared deactivated. The conversion was only 4 percent. The catalyst bed inlet temperature was still at 284°C.

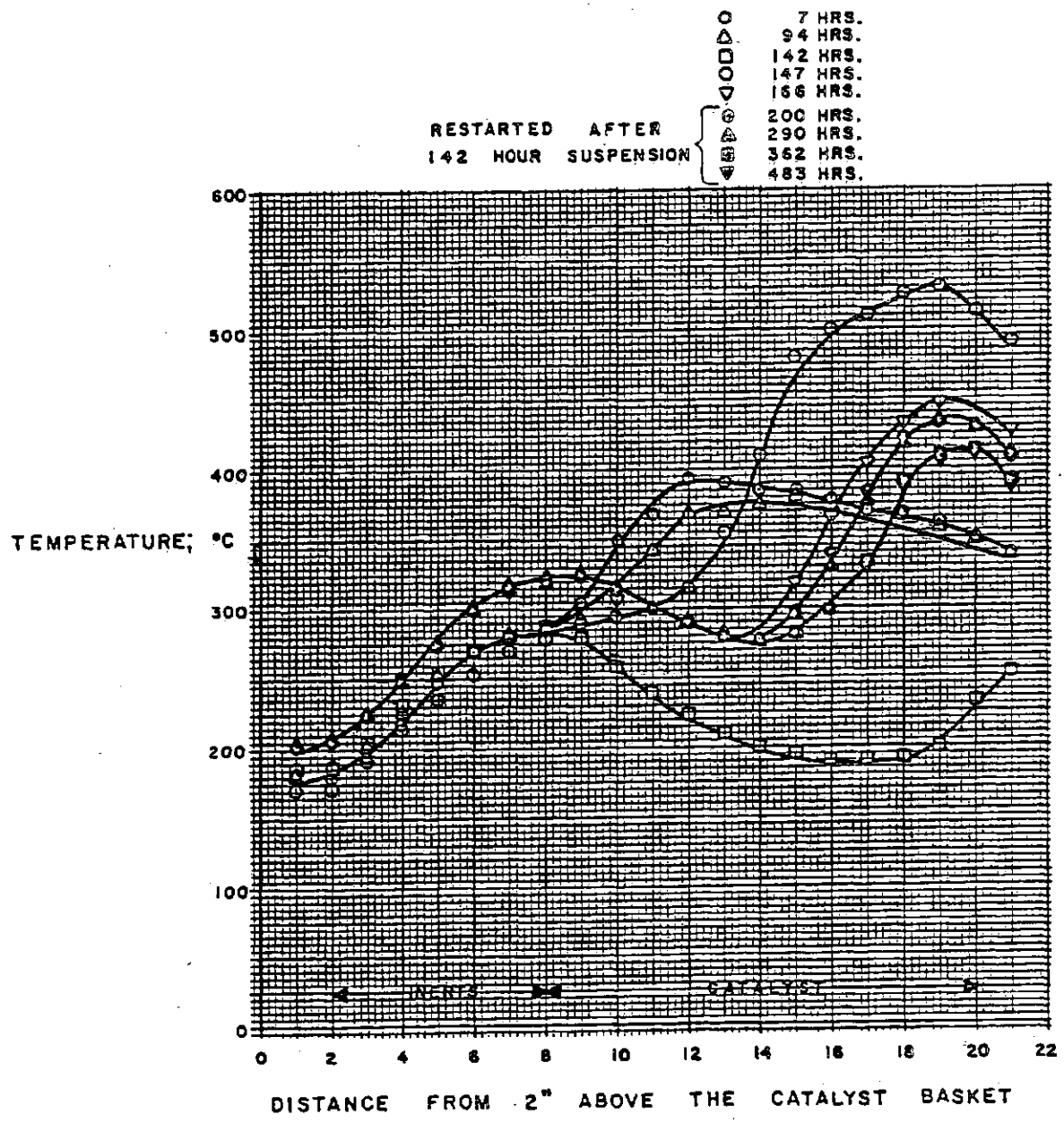
In an attempt to "reactivate" the catalyst, the heater on the catalyst bed was raised to about 300°C. With this moderate increase in temperature, the reaction again took off with a marked exotherm across the bed, to over 500°C, resulting in a CO conversion of 67 percent. In an attempt to control this exotherm, the catalyst bed heater temperature set point was lowered 50°C while the inlet was raised 50°C. Subsequent data up to the 190-hour mark showed a gradual decrease in CO conversion, down to 33 percent. At that time, the reactor was put on standby conditions for 140 hours. The run was subsequently restarted and operated for an additional 320 hours, up to a cumulative run time of 510 hours. Throughout the last reaction period it was evident that the conversion level was very sensitive to the inlet and initial catalyst bed temperature, lending support to the original hypothesis that the apparent deactivation is strongly related to an increase in the catalyst initiation temperature.

FIGURE IV-D-25

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN # 5b

LURGI GAS/G-87 P (35 ATM, 315°C, 5% STEAM, 510 HRS.)



Run 22: Lurgi Gas/Ni-104T (35 atm, 315°C, 0% steam, 500 hours)
Run 23: Lurgi Gas/Ni-104T (35 atm, 315°C, 5% steam, 500 hours)

Runs 22 and 23 were designed to study carbon formation at low temperature on Ni-104T catalyst. Run 22 had no steam injection and Run 23 contained five percent steam. Both runs were started in August and completed on September 21, 1978. The temperature profile histories of these runs are shown in Figures IV-D-26 and IV-D-27, respectively. Without steam injection in Run 22, apparently more than half of the bed was not utilized. A sharp rise in hot spot temperature occurred at 188 hours and remained for the duration of the run. The hot spot temperature was well over 400°C for the entire test period despite efforts to bring it down to 315°C as originally intended. Such a high hot spot temperature may be related to the higher activity of Ni-104T catalyst as compared to G-87P.

With a 5 percent steam injection in Run 23, the profile was quite different. Initially, most of the bed appeared fully utilized as indicated by a broad hot spot covering the middle of the bed. Then, the hot spot moved progressively down and finally ended at the bottom of the bed. The hot spot temperature was again well over 400°C throughout the entire 500 hour period.

The conversion results indicate an average of 51 percent in Run 22 and 67 percent in Run 23 of equilibrium conversion were obtained. Conversion decreased somewhat as a function of time, but much slower than in comparable runs with G-87P catalyst (Runs 4, 5 and 5a). With both catalysts, the runs without steam injection achieved higher conversion levels than the runs with 5 percent steam injection.

Crystallographic analysis (see Table IV-D-4) indicated that all values were within normal levels. In addition, carbon levels were somewhat increased over the fresh catalyst levels, 3.5-4.5 percent as compared to

FIGURE IV-D-25

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN #22

LURGI GAS/Ni-104T (35 ATM, 315 °C, 0% STEAM, 500 HRS.)

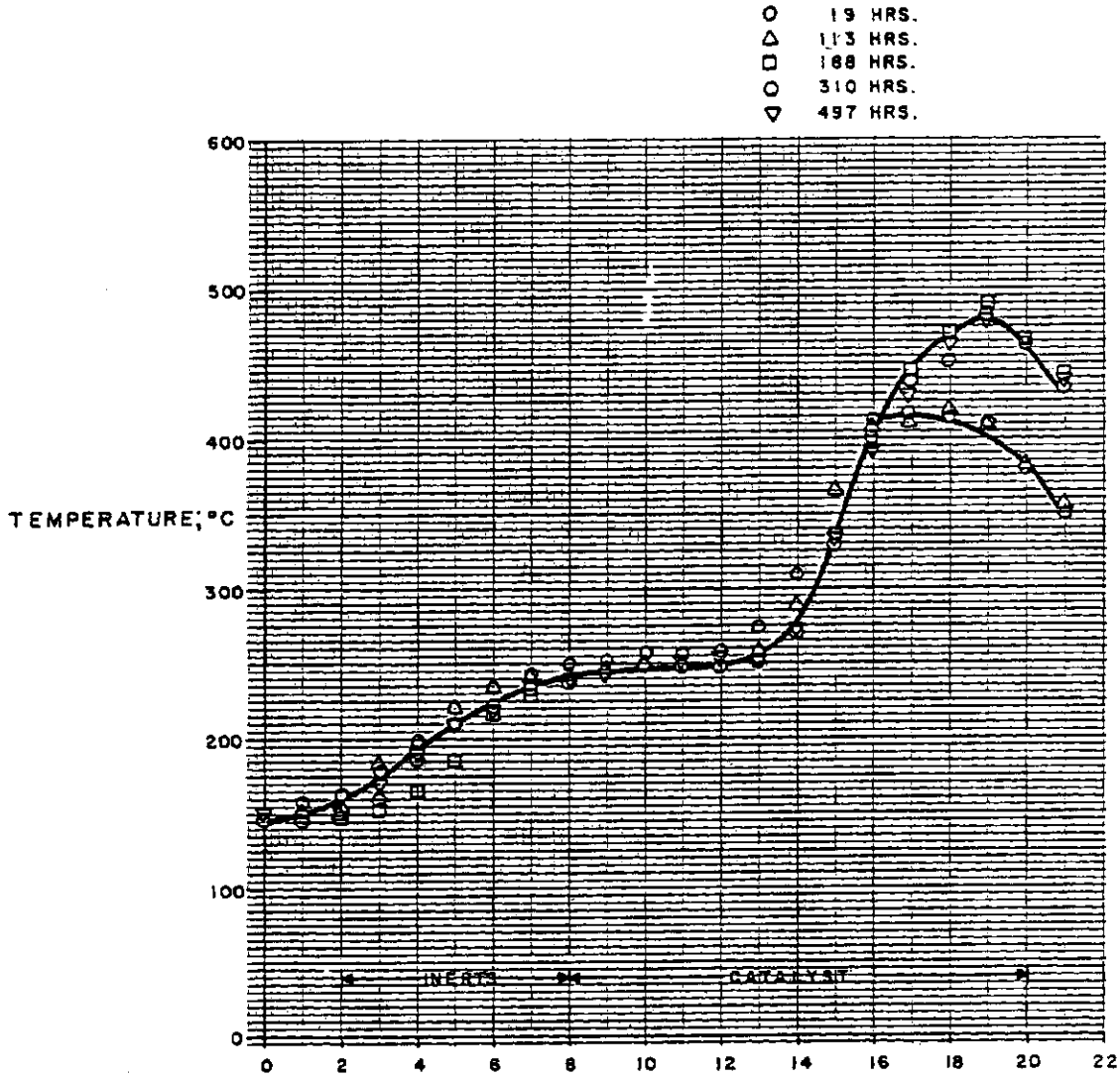


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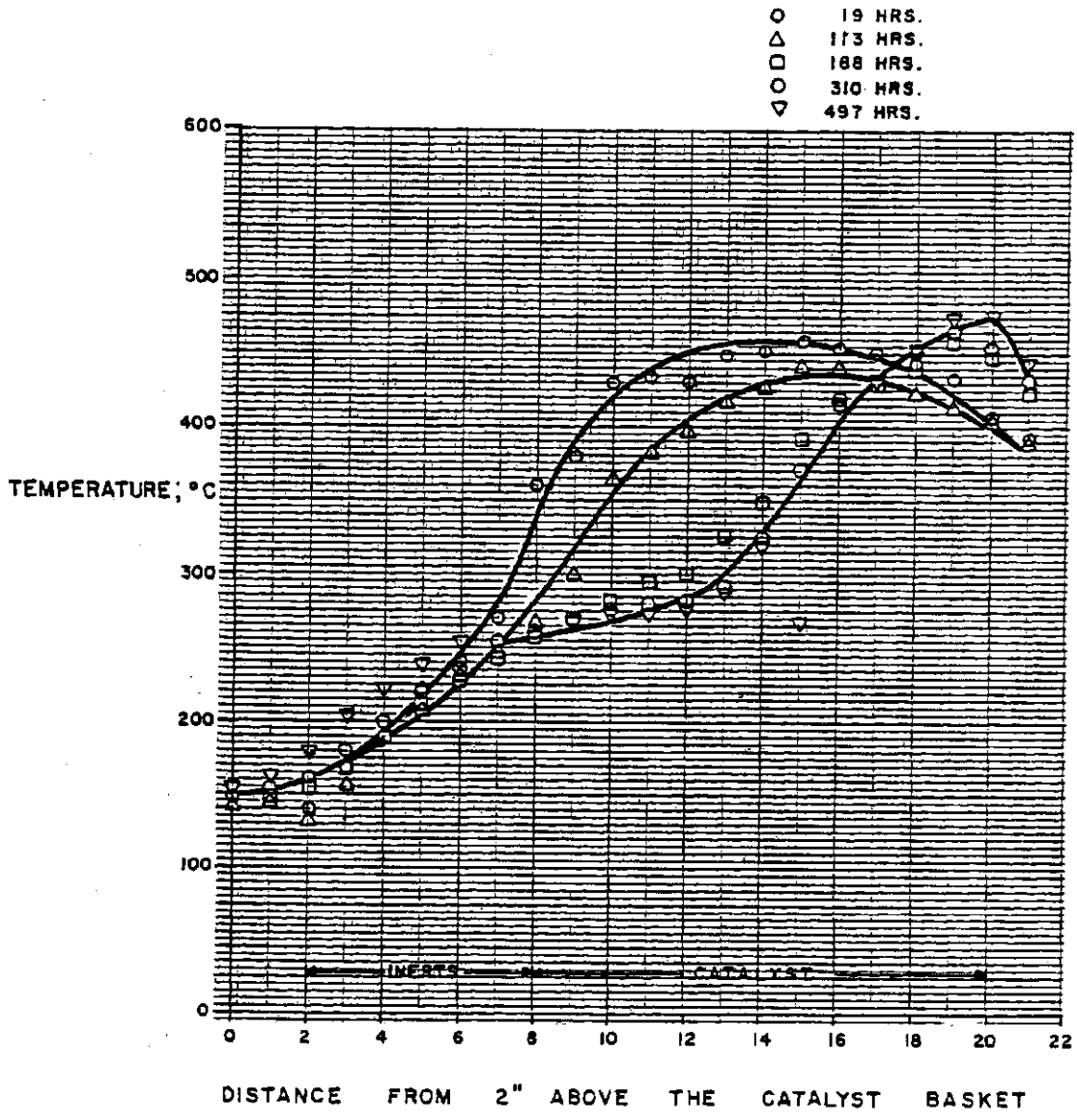
FIGURE IV-D-27

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN #23

LURGI GAS / Ni-104T (35 ATM, 315°C, 5% STEAM, 500 HRS.)



3.0 percent. This is primarily due to the high effective feed gas loading for the diluted catalyst bed experiments, as compared to the standard test Runs 14, 15 and 16, which had carbon levels of only 2.9-3.4 percent.