6. Rate of Carbon Formation

As originally conceived, this task involved a series of five runs with each feed gas/catalyst pair operating at fixed reaction conditions for variable times, from 100 to 1200 hours duration. However, additional tests were conducted in order to repeat runs which experienced operating problems and to provide further data on the initial rates of carbon formation, with run durations less than 100 hours. Nominal operating conditions for all the runs were 35 atm, 480°C, 3.85 percent steam with a Lurgi gas at a 10,000 hr^{-1} VHSV.

Run 8; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 100 hours)
Run 9; Lurgi Gas/G-87P (35 atm, 380°C, 3.85% steam, 310 hours)
Run 10; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 580 hours)
Run 11; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 900 hours)
Run 12; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 1200 hours)

Five runs were initiated early in May, 1978 to study cumulative carbon formation as a function of time on-stream. The operating conditions were identical to those of Run 2 except for slightly lower steam injection level.

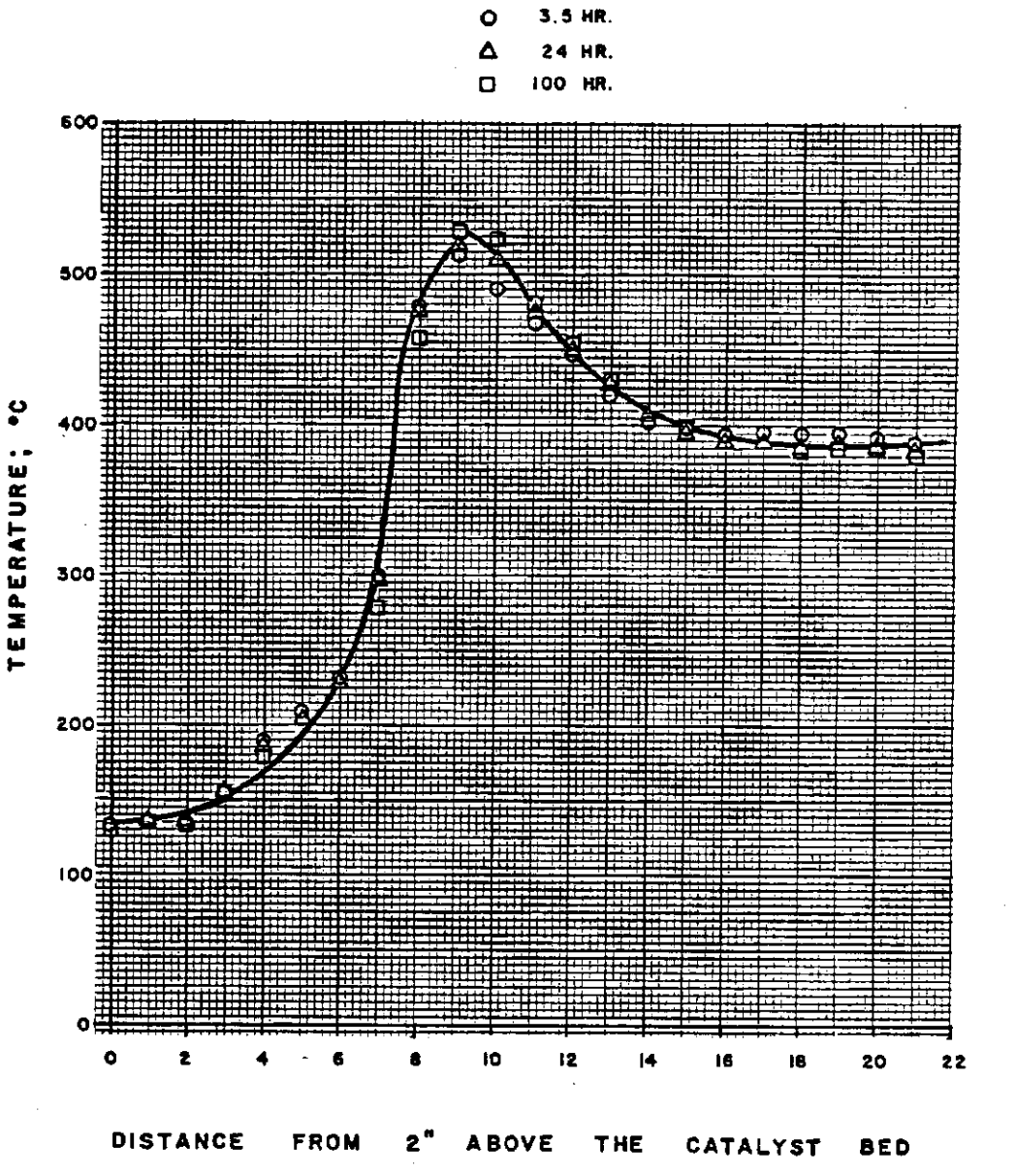
Run 8 was completed after operating for 100 hours. The temperature profile is given in Figure IV-D-30. The profile remained stable throughout the test period with the hot spot located one inch from the top of the catalyst bed. The conversion obtained at 24 hours and 100 hours was consistent and close to the equilibrium value. The spent catalyst appeared uniformly black with no difference between the bed sections. Some carbon coating was noted on the external surface of the top section catalyst basket.

Run 9 was completed after operating for 310 hours. The temperature profile, plotted in 100-hour intervals (see Figure IV-D-31), appears

FIGURE IV-D-30

CARBON FORMATION STUDY- TEMPERATURE PROFILE OF RUN # 8

LURGI / G - 87P (35 ATM., 480 °C, 3.85% STEAM, 100 HRS.)

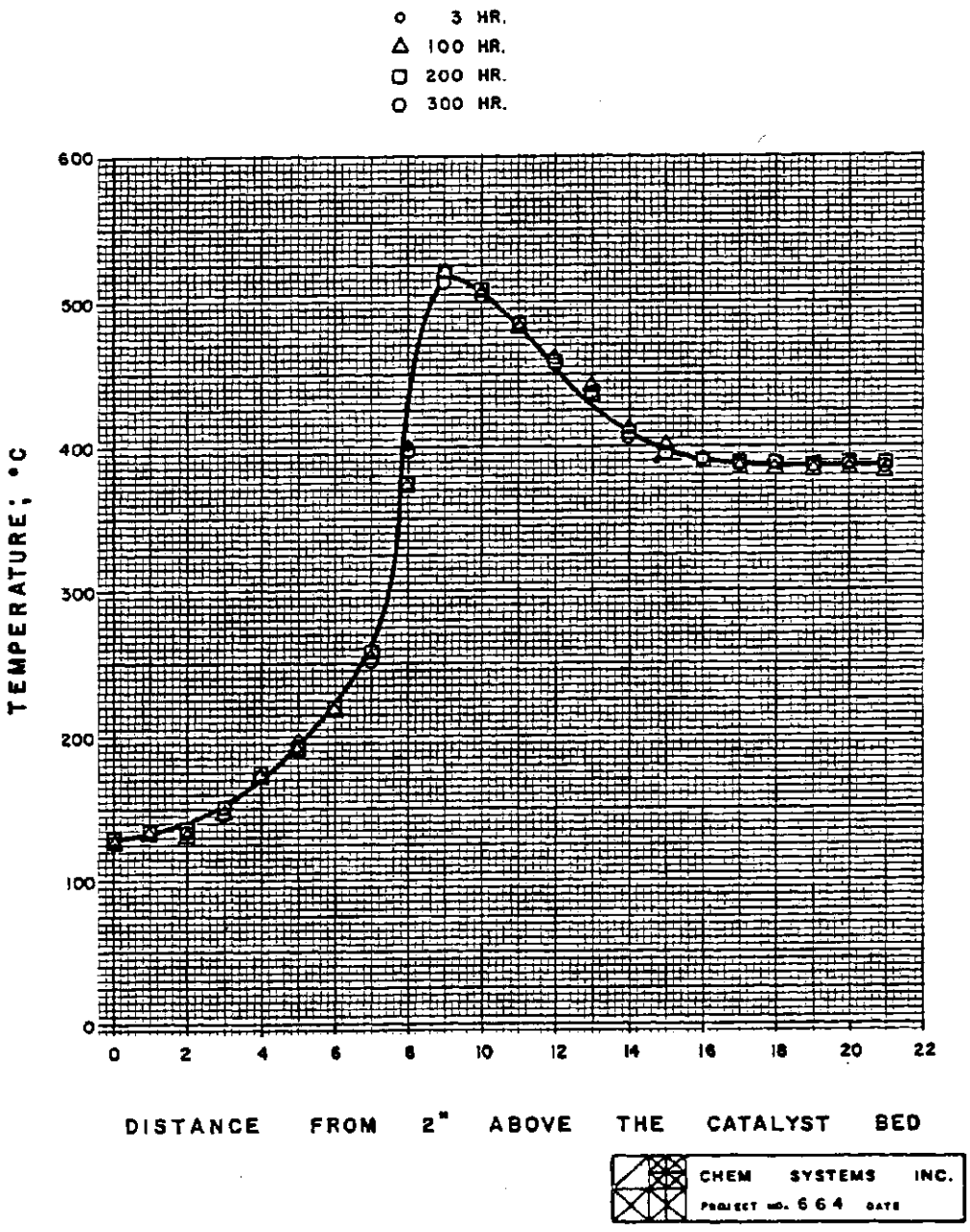


CHEM SYSTEMS INC.
PROJECT NO. 564 DATE

FIGURE IV-D-31

CARBON FORMATION STUDY- TEMPERATURE PROFILE OF RUN #9

LURGI / G-87P (35 ATM., 480°C, 3.85% STEAM, 310 HRS.)



identical to that of Run 8. The results of product gas analyses indicate that equilibrium conversion was achieved at all times.

Three time variation runs (Runs 10, 11 and 12) experienced a loss of feed over a weekend starting on June 3, 1978 due to booster breakdown caused by excessive condensate in the compressed air line. Water was continuously pumped into the reactor at 0.1 ml/min for 50 hours while no feed gas was flowing. The reactors were put under nitrogen flow until normal operation could be resumed. Both booster compressors had to be overhauled. At the same time, a three-way valve was installed to automatically cut off the feed gas and to switch to nitrogen when the feed pressure drops below the operating pressure. A modification on the electrical system was also made to shut off all metering pumps in such an event.

Run 10 operated for 383 hours before it was interrupted by the booster compressor breakdown for 240 hours. It was restarted on June 13 and completed on June 21 after 580 hours of operation. The temperature profile of Run 10, as shown in Figure IV-D-32, exhibits two distinct patterns as in Run 7, which also experienced a similar incident. The first pattern is the initial profile prior to the feed loss, with the hot spot located one inch from the top of the catalyst bed. When the feed flow was restored, a new profile was established with the hot spot temperature down about 5 inches from its original position. No significant increase in the hot spot temperature was observed, contrary to findings in Run 7. The profile remains unchanged for the rest of the run period. The conversion results indicated that equilibrium conversion was approached at all times. The results seem insensitive to the history of the catalyst bed, since as long as the hot spot exists most of the conversion is achieved in the vicinity of the hot spot. Some white spots were detected in the spent catalyst from the top three sections. The catalyst from the bottom section appeared uniformly black.

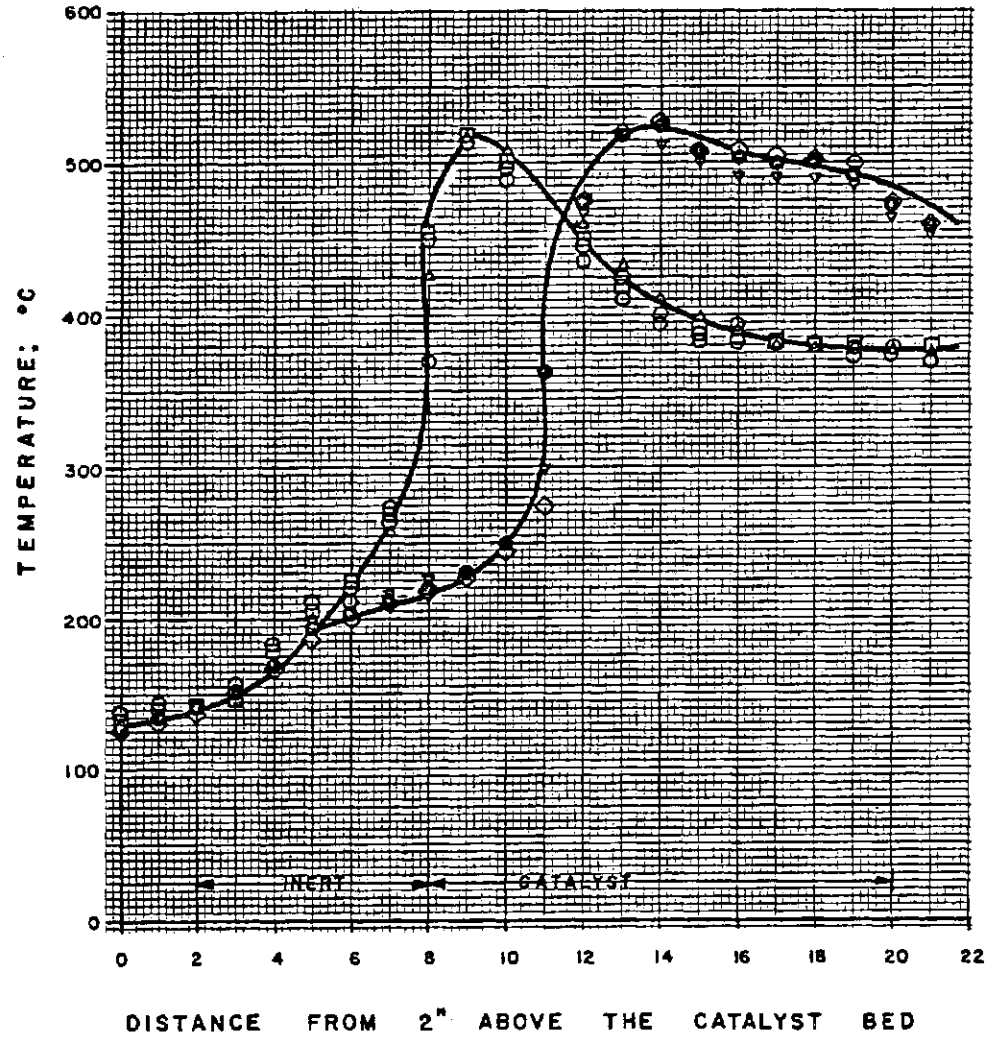
FIGURE IV-D-32

CARBON FORMATION STUDY – TEMPERATURE PROFILE OF RUN #10

LURGI/G-87P (35 ATM., 480 °C, 3.85% STEAM, 580 HRS.)

○	3 HR.
△	94 HR.
□	190 HR.
○	312 HR.
▽	388 HR. *
◇	526 HR.
○	575 HR.

* FEED LOSS OCCURRED @ HOUR 383



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

Run 11 operated for 237 hours before it was interrupted by the booster breakdown. It was restarted on June 13 and completed 900 hours of operation.

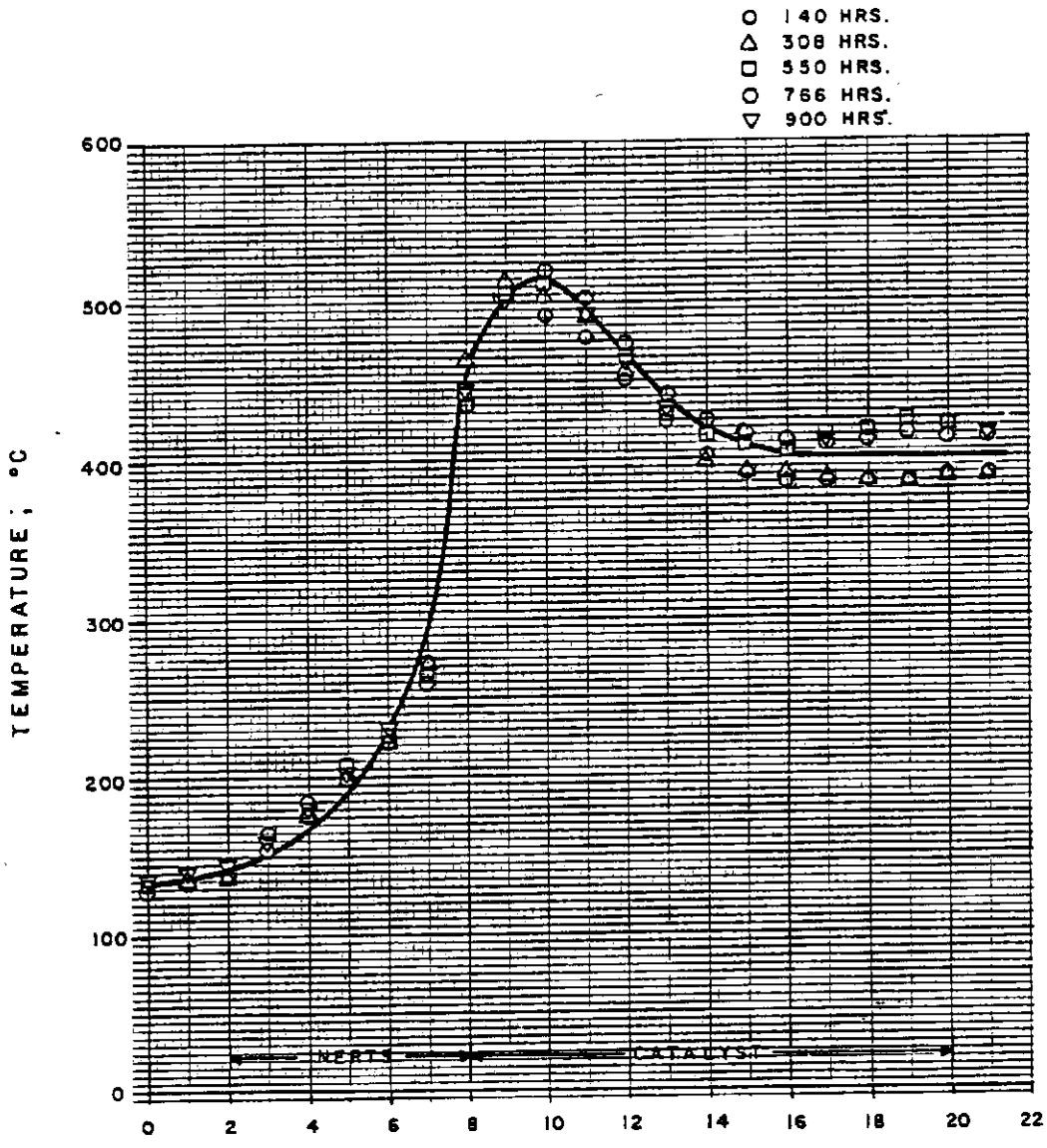
Run 12 operated for 213 hours before it was interrupted by the booster breakdown. It was restarted on June 13, and completed 1200 hours of operation.

The temperature profile for Run 11 is plotted in Figure IV-D-33 and the profile for Run 12 is shown in Figure IV-D-34. Even after 1200 hours of reaction, no decline in catalyst activity was observed. Extensive carbon laydown was noted in the longer duration runs and these spent catalysts also appeared structurally weak.

The analytical results of the catalyst samples from this series are presented in Table IV-D-4 and the carbon content of the top bed sections is plotted in Figure IV-D-39. Surface area and pore volume values for all of the runs in this series are within normal bounds. In fact, based upon these analyses, there is no explanation for the apparent deactivation noted for Run 10. Unlike the catalyst for Run 7, which clearly lost its micropore structure due to 100 percent steam operation with a concurrent drop in surface area to the 10 m^2/gm range, the values obtained are virtually the same as for the other runs in this series. It must, therefore, be concluded that there is a set of temperature and time conditions at the 100 percent steam level which alter the catalyst structure sufficiently so that the formation of carbon is kinetically unfavorable (Runs 10 and 12). Too little treatment neither affects activity nor the catalyst's inherent carbon forming characteristics (Runs 9 and 11), while too much of the treatment results in catalyst deactivation (Runs 7 and 10). Further, since the approximate time of 100 percent steam flow was the same for Runs 10, 11 and 12, temperature must play a critical role.

FIGURE IV-D-33

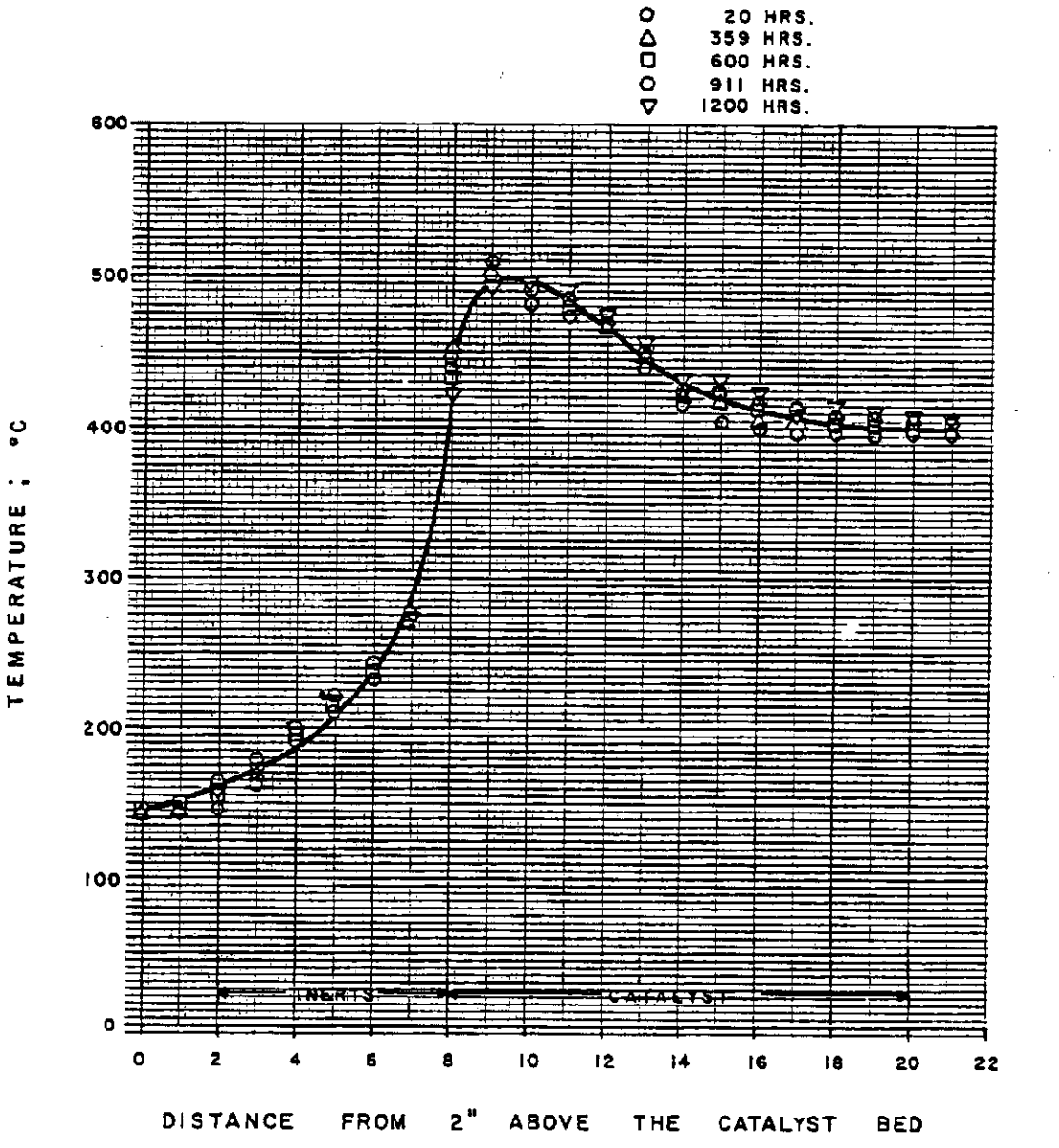
CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN # 11
LURGI/G-87P (35 ATM, 480°C, 3.85% STEAM, 900 HRS.)



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

FIGURE IV-D-34

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #12
LURGI/G-87P (35 ATM, 480 °C, 3.85% STEAM, 1200 HRS.)



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

Run 8a; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 0 hours)
Run 8b; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 25 hours)
Run 8c; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 50 hours)
Run 8d; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 100 hours)
Run 12a; Lurgi Gas/G-87P (35 atm, 480°C, 3.85% steam, 1105 hours)

An additional five runs were initiated in order to clarify the data obtained from Runs 8 - 12. Data from Run 2 was used in place of Run 10 while Run 12 was repeated as Run 12a. Additional runs were also performed (Runs 8a, 8b, 8c and 8d) in order to obtain data for operating times of less than 100 hours.

Temperature profiles of Runs 8b, 8c and 8d are shown in Figures IV-D-35, IV-D-36 and IV-D-37, respectively. Run 8a included no methanation time, but the catalyst bed was reduced in the standard manner prior to sending the catalyst out for analysis.

Near equilibrium conversion was obtained at all times. In all runs, the spent catalyst appeared black. No extensive carbon buildup was observed on the catalyst itself, but a carbon coating was noticed on the catalyst basket.

The repeat of Run 12 (Run 12a) with G-87P catalyst was completed after 1105 hours of reaction. The temperature profile (Figure IV-D-38) appears normal except the hot spot, usually located one inch from the top of the catalyst bed, is spread over 1 - 3 inches from the top. This abnormality is also reflected in the conversion results. During the entire operating period, the average CO conversion was 94 percent which is less than full equilibrium conversion. However, examination of both the temperature profile and conversion data indicate no sign of gradual decay in catalyst activity. The spent catalyst appeared loaded with carbon in all sections and a carbon coating was also observed on the top catalyst basket.

FIGURE IV-D-35

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #8b
LURGI GAS/G-87P (35 ATM, 480°C, 3.85% STEAM, 25 HRS.)

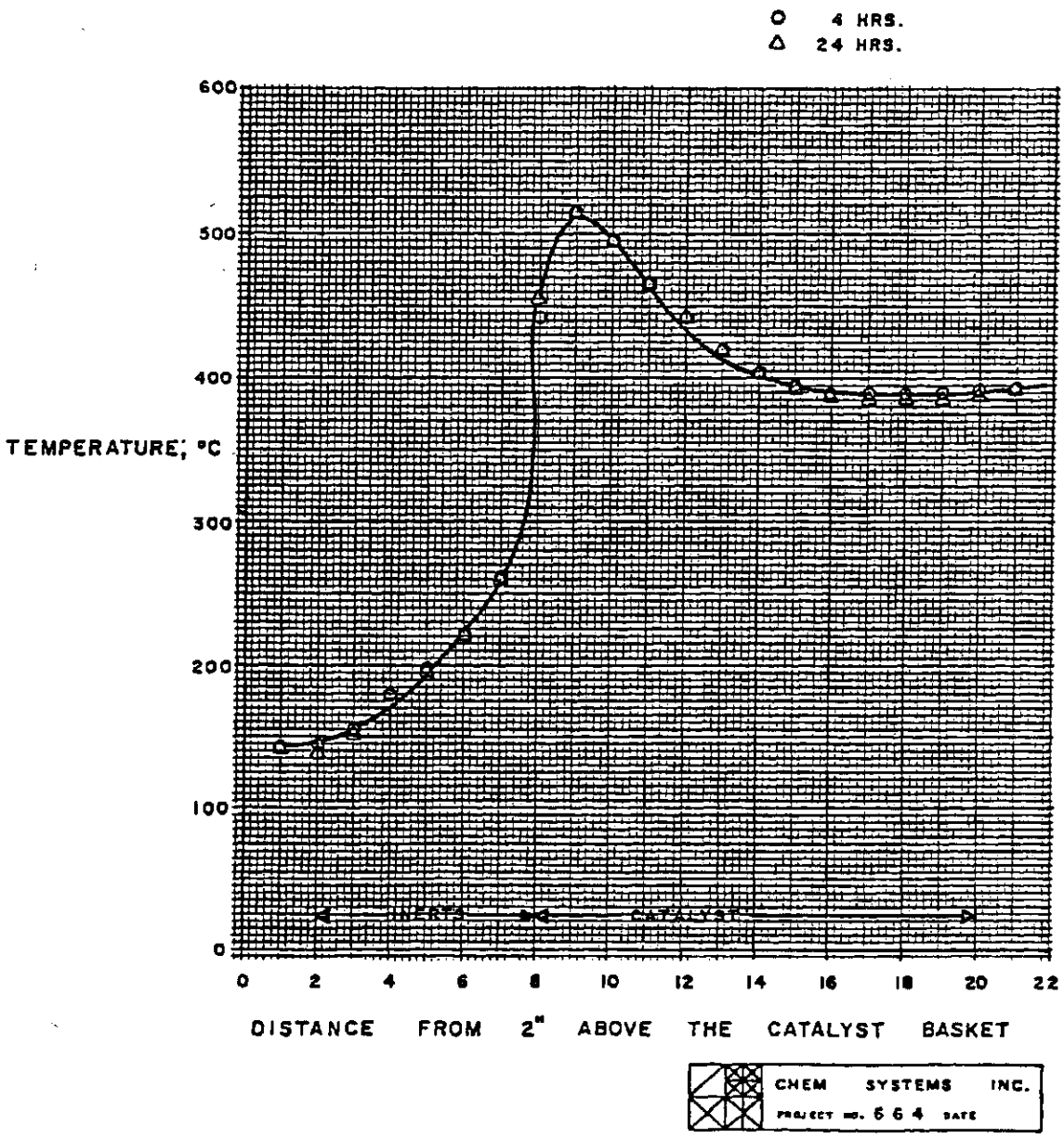


FIGURE IV-D-36

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN # 8C

LURGI GAS/G-87P(35 ATM, 480°C, 3.85% STEAM, 50 HRS.)

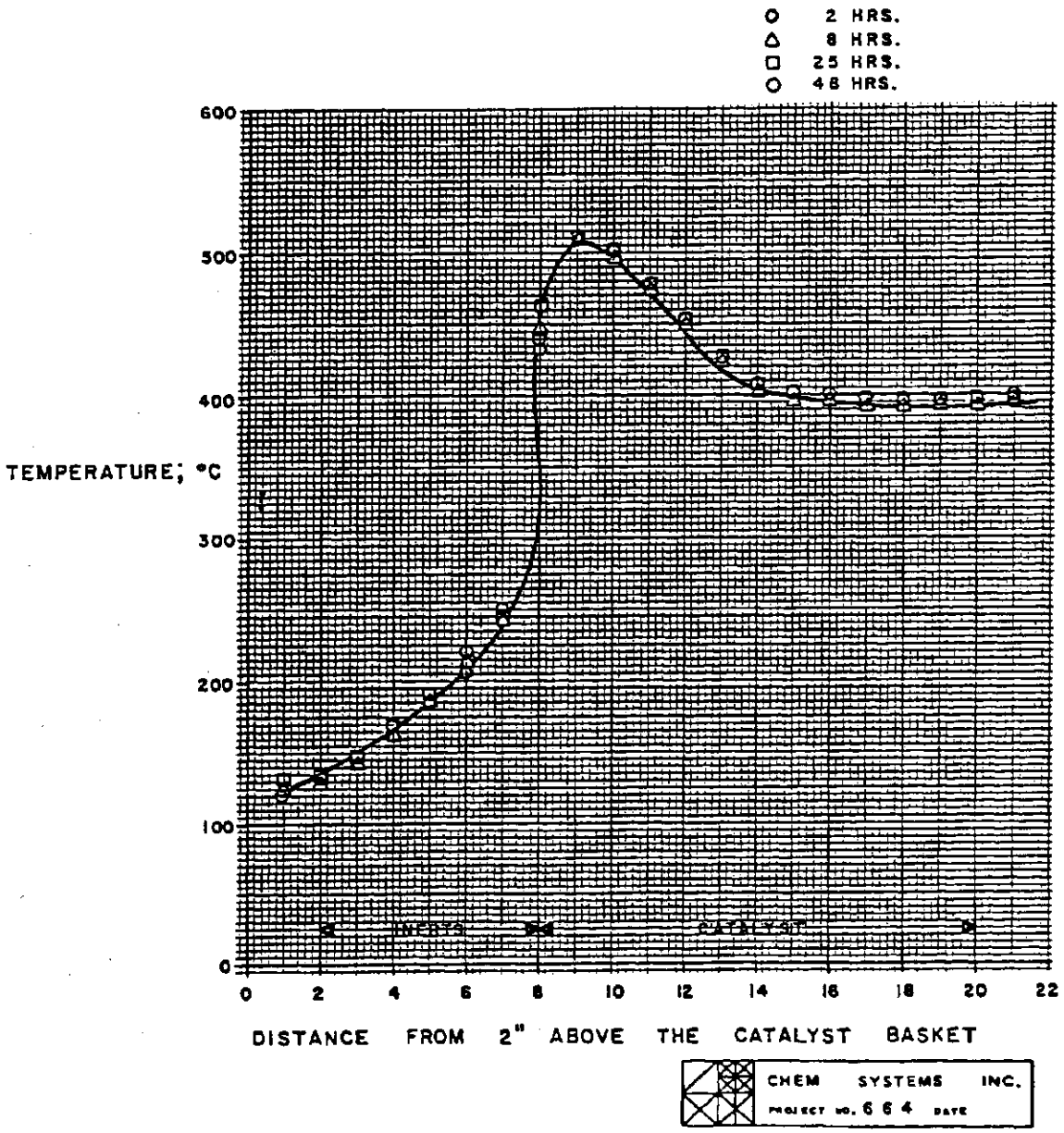


FIGURE IV-D-37

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN # 8d

LURGI GAS / G 87 P (35 ATM, 480°C, 3.85% STEAM, 100 HRS.)

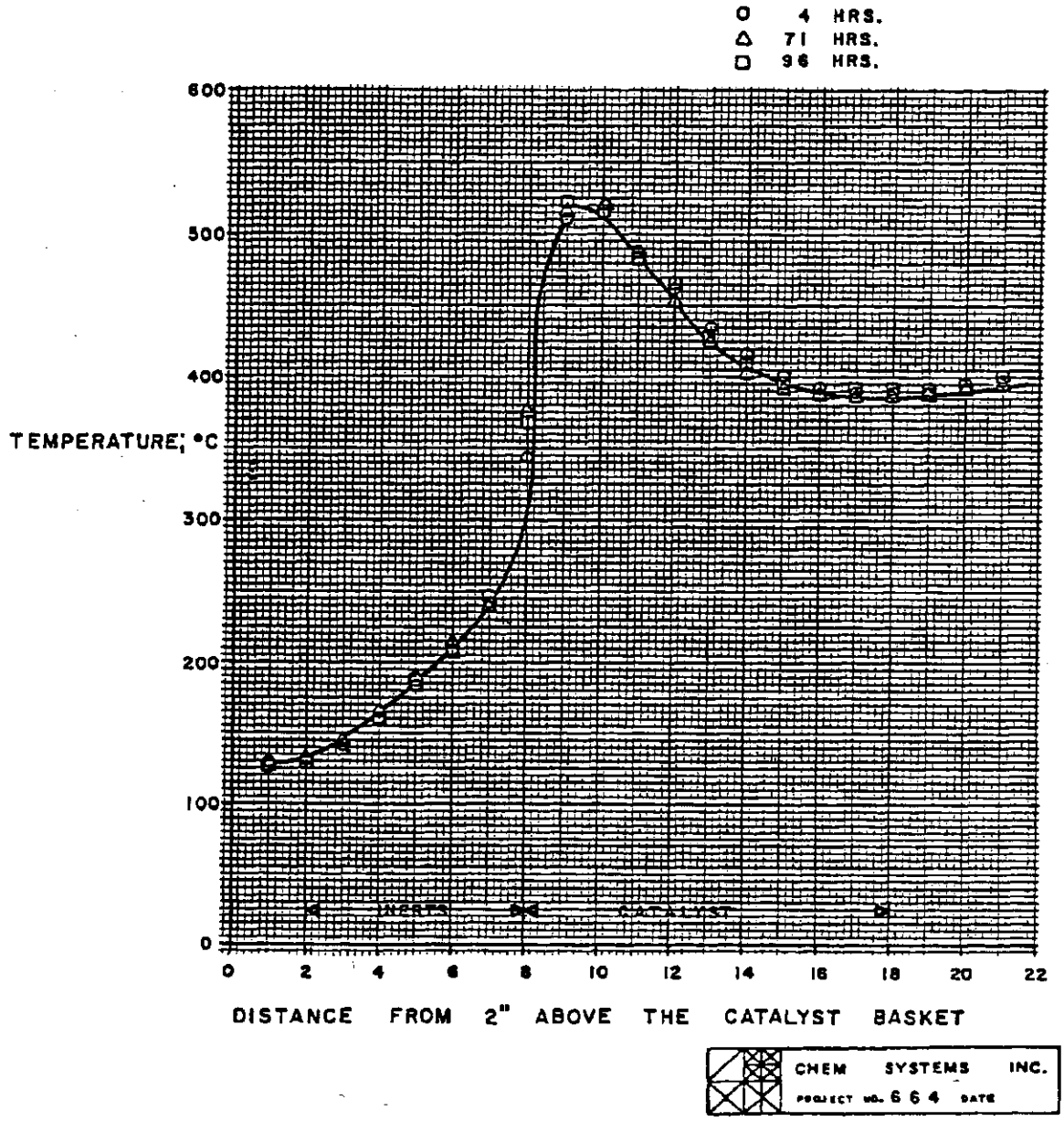
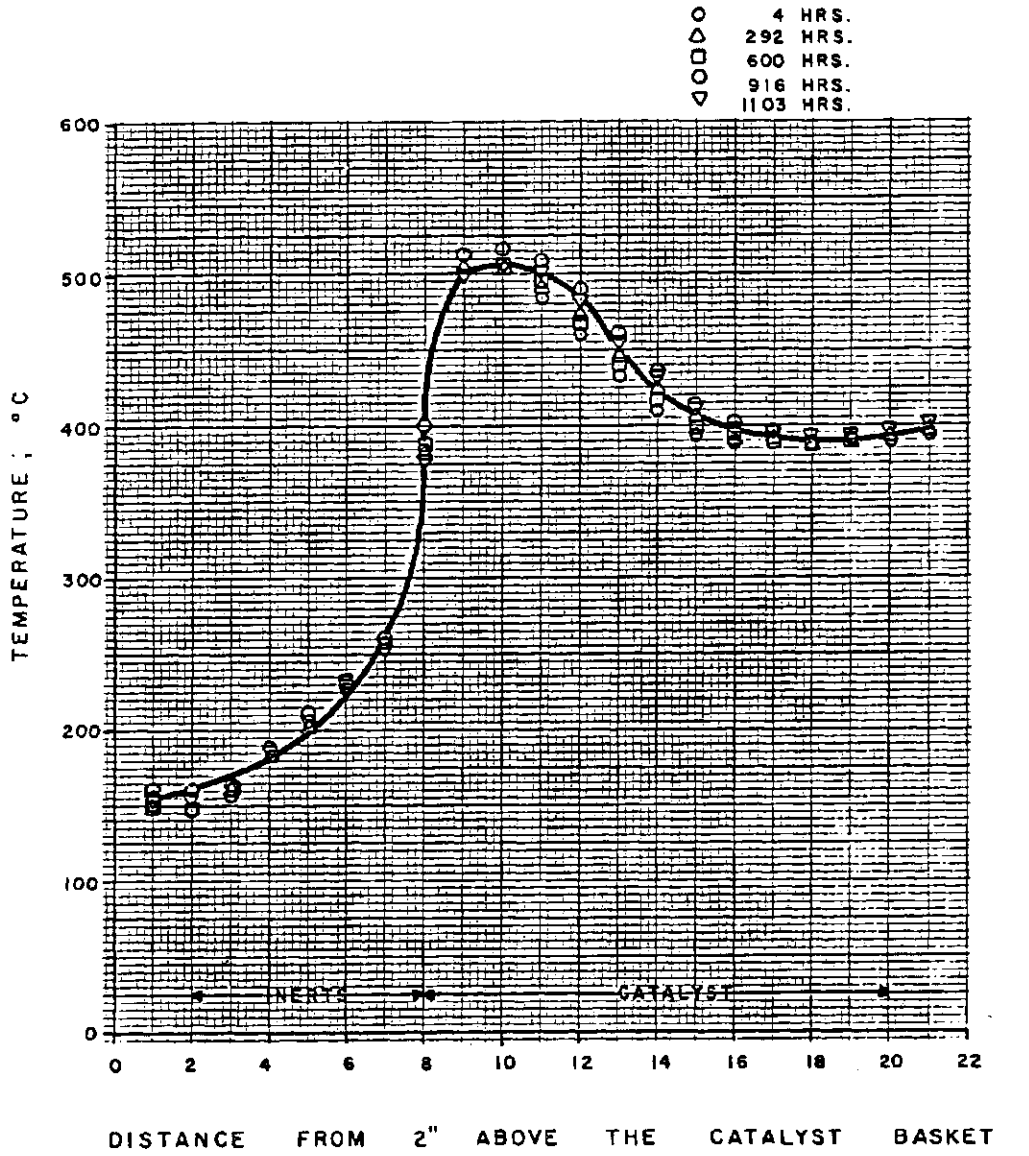


FIGURE IV-D-38

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #12a
LURGI GAS/G-87P (35 ATM., 480°C, 3.85% STM., 1105 HRS.)



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

Spent catalyst analytical results for this series are presented in Table IV-D-4. Cumulative carbon formation versus time on-stream is plotted in Figure IV-D-39 for the top catalyst bed sections. It appears that there is a short induction period of about 100 hours during which the carbon level slowly increases from 0.5 percent to 0.87. At that time, the rate rapidly accelerates, and, by 300 hours, the carbon level has increased to over 5 percent. The carbon level continued to regularly increase, reaching almost 10 percent after 900 hours. Then, for an as yet unexplained reason, since the repeat Run 12a ran without mishap, the carbon level at the 1200 hour mark was only 2 percent. Unfortunately since this result was unexpected, crystallographic or physical property analyses were not requested which might have provided corroborating evidence.

Run 17; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 96 hours)
Run 18; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 280 hours)
Run 19; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 570 hours)
Run 20; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 1200 hours)
Run 21; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 620 hours)
Run 18a; Lurgi Gas/Ni-104T (35 atm, 480°C, 3.85% steam, 305 hours)

This series of six runs was initiated in July, 1978 to study cumulative carbon formation versus time on-stream with Ni-104T catalyst. Temperature profiles of Runs 17 - 21 are shown in Figures IV-D-40 through IV-D-44.

Upon completion of Run 18, it was found that the spent catalyst in the top half of the catalyst bed was sintered. The catalyst tablets and the basket were coated with what appeared to be a nickel melt. All available records for Run 18 indicate no upsets in temperature profile or other abnormalities during the operating period. A brief feed loss was encountered due to a power failure, but the reactor presumably switched to nitrogen flow with the water feed shut off until the unit was restarted.

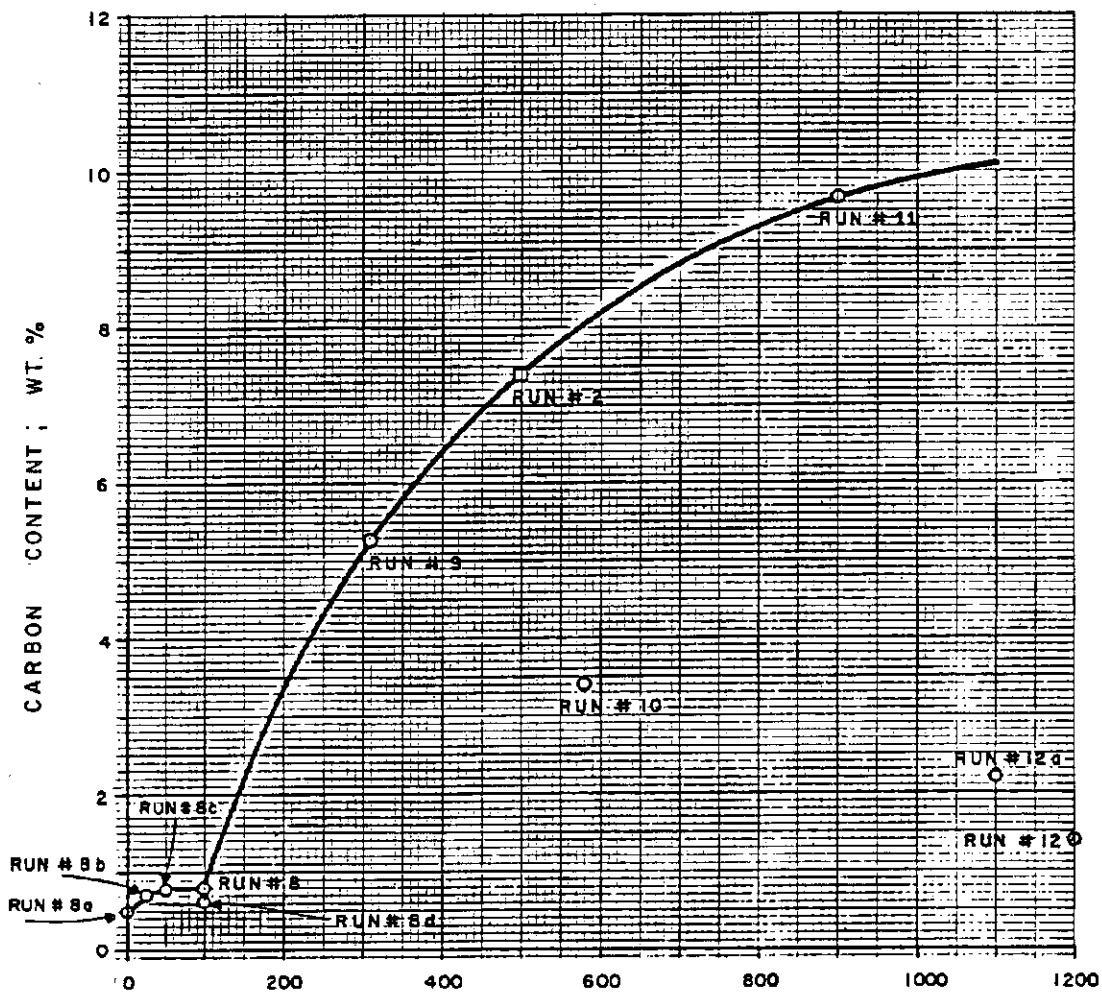
FIGURE IV-D-39

CARBON FORMATION STUDY

CARBON FORMATION VS. TIME ON-STREAM

LURGI GAS / G-87P

BASIS: CARBON CONTENT IN TOP BED SECTION



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PROJECT NO. 664 DATE

FIGURE IV-D-40

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN # 17
LURGI GAS / Ni-104 T (35 ATM, 480 °C, 3.85% STEAM, 96 HRS.)

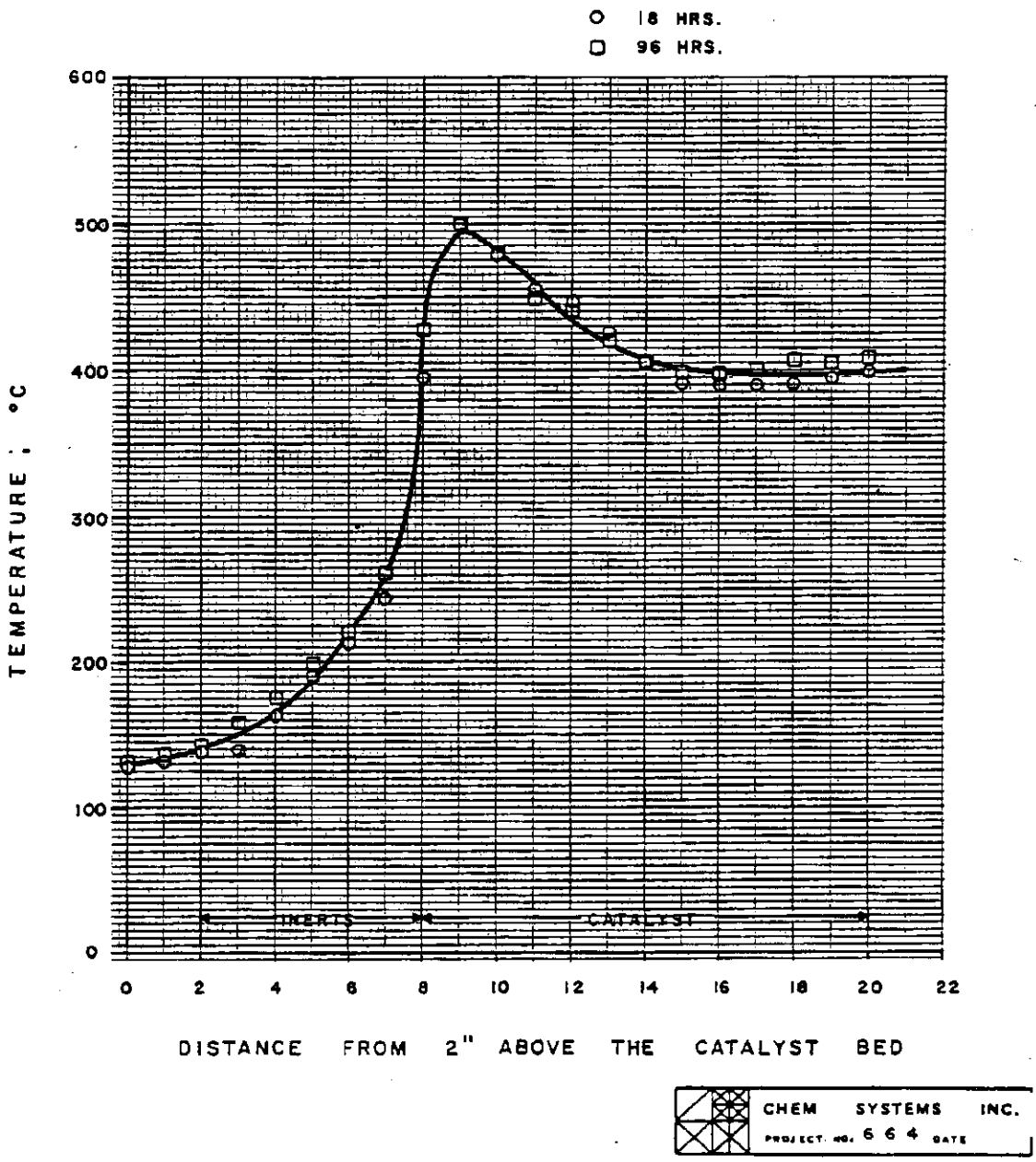
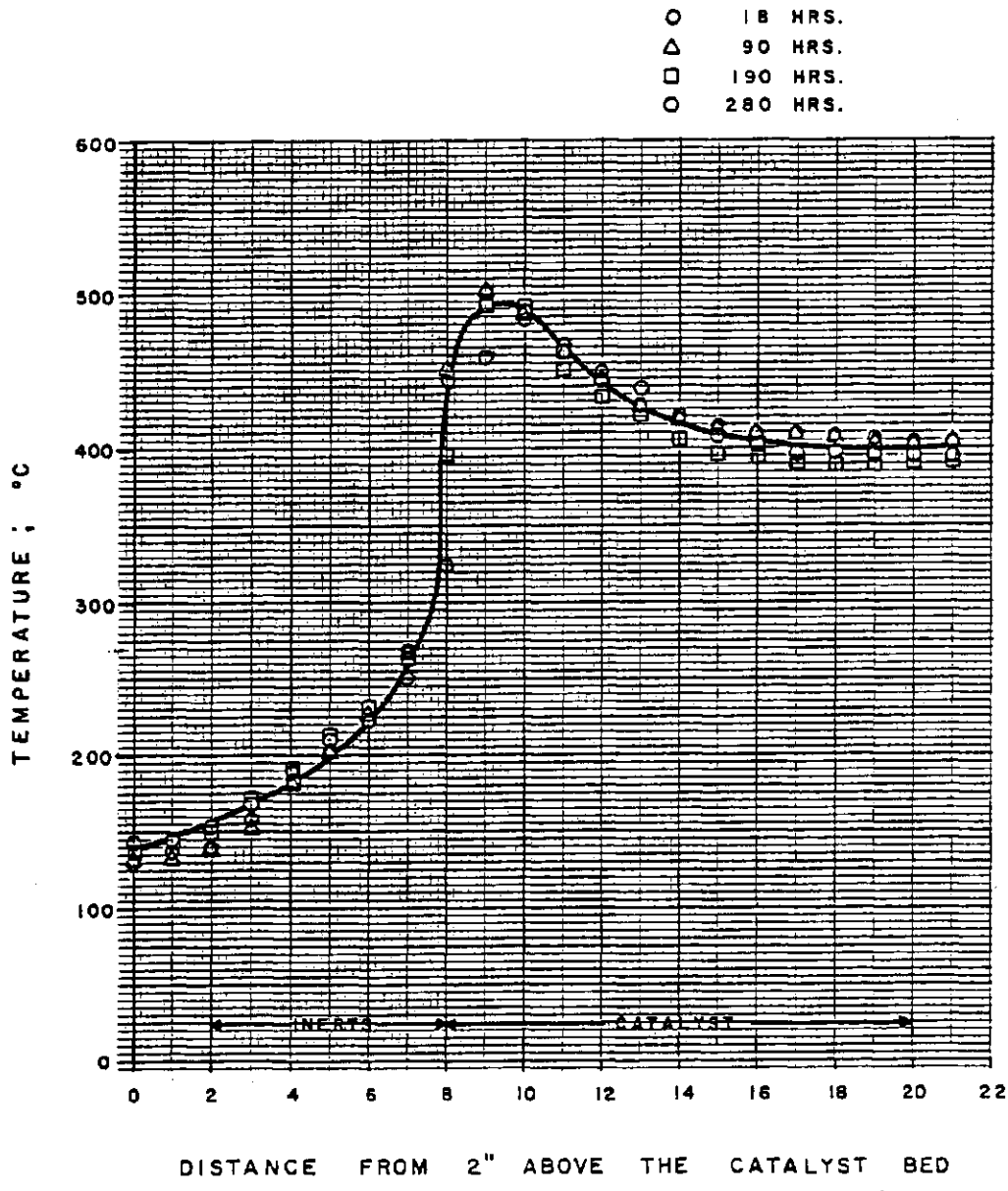


FIGURE IV-D-41

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #18
LURGI GAS / Ni-104 T (35 ATM, 480 °C, 3.85 STEAM, 280 HRS.)



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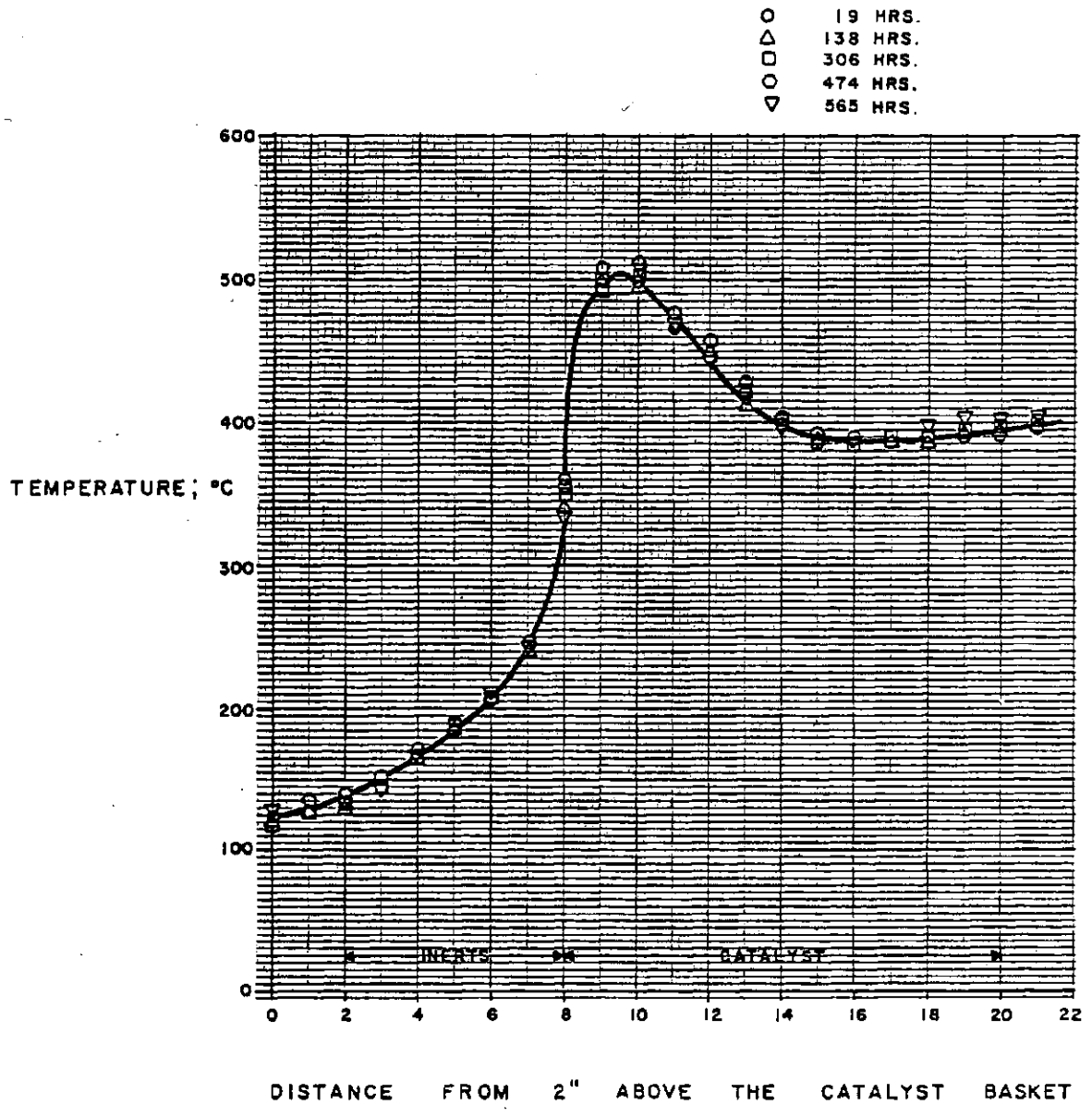
PROJECT NO. 664 DATE

FIGURE IV-D-42

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN #19

LURGI GAS / Ni-104 T (35 ATM, 480°C, 3.85% STEAM, 570HRS.)



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PROJECT NO. 664 DATE

FIGURE IV-D-43

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN #20

LURGI GAS/NI-104T (35 ATM, 480°C, 3.85% STEAM, 1200 HRS.)

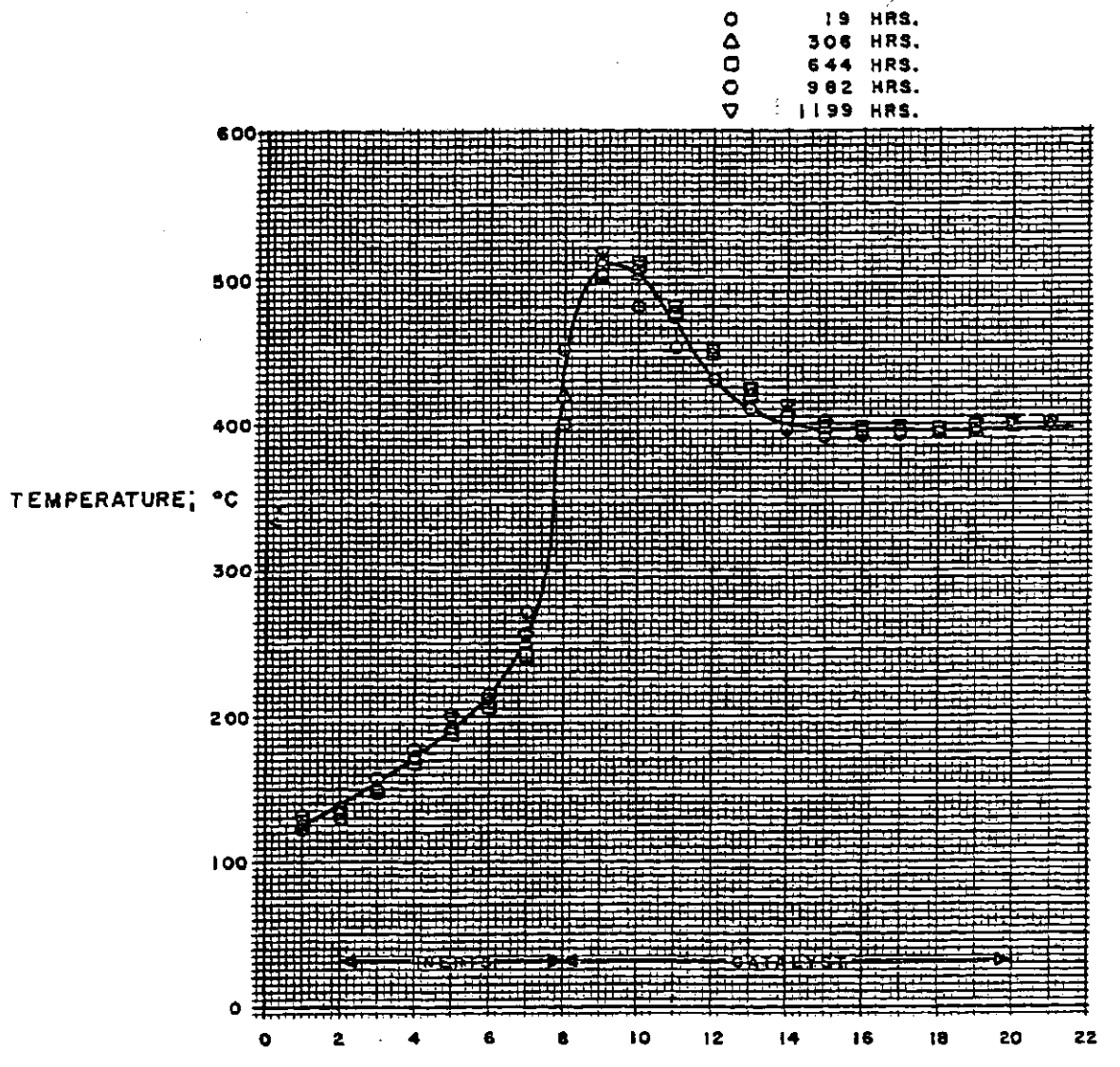
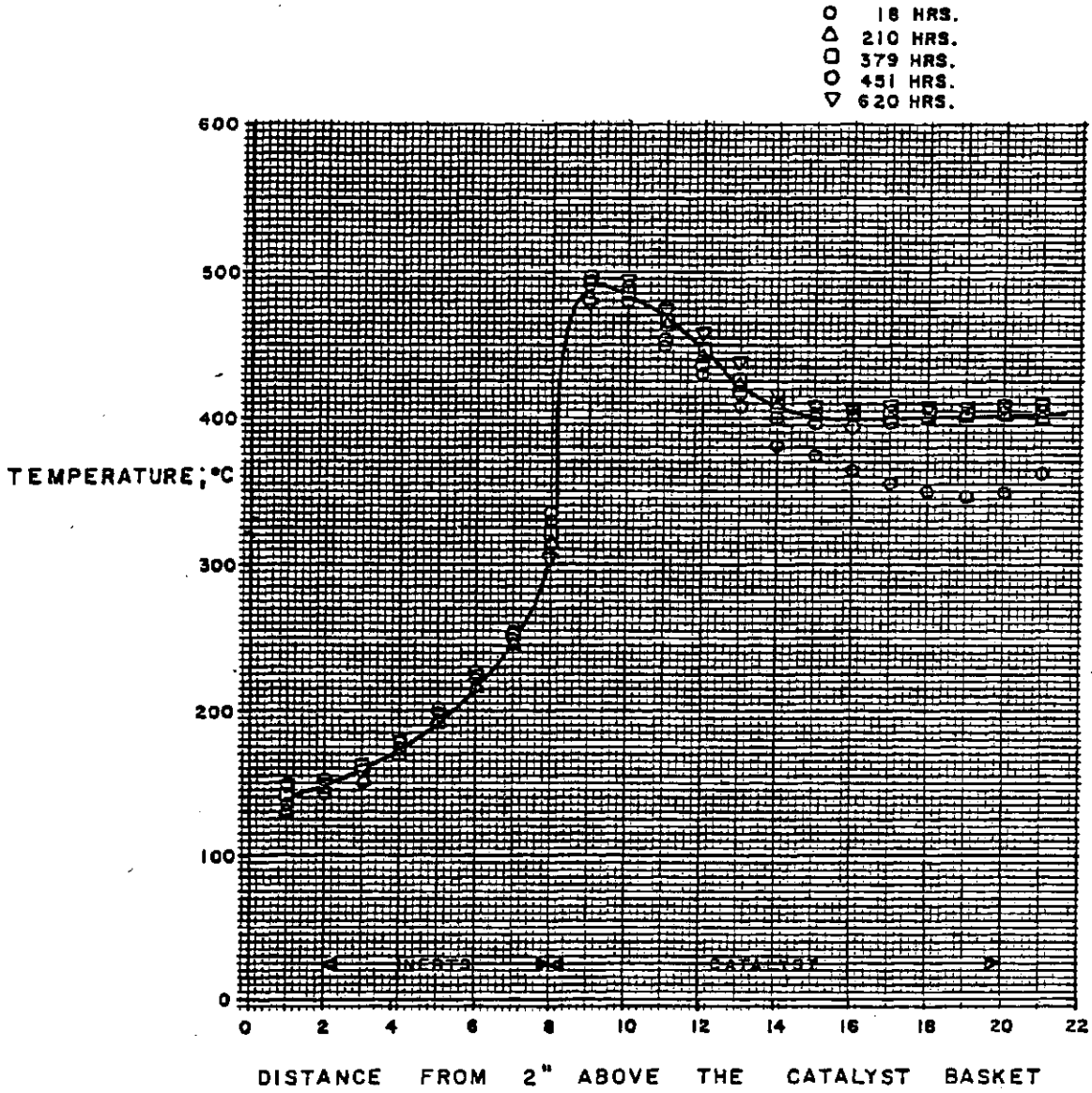


FIGURE IV-D-44

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #21
LURGI GAS/Ni-104T (35 ATM, 480°C, 3.85% STM, 620 HRS)



Since the sintering was not noticed in Run 19 which also experienced the power failure, a repeat of Run 18 was initiated. This run is designated Run 18a. The temperature profile for Run 18a (Figure IV-D-45) appeared normal and the conversion data indicated that equilibrium was attained at all times. The spent catalyst appeared black and free of sintering.

Run 20 was completed after operating 1200 hours. The temperature profile remained stable. Some carbon deposition was noticed on the spent catalyst and extensive carbon laydown was observed on the catalyst basket.

Run 21, scheduled for 900 hours, was accidentally terminated after operating for 620 hours. The conditions are, thus, similar to Run 19. At 18 hours the temperature profile dropped due to a faulty temperature controller. Subsequently, this problem was corrected.

Results of spent carbon analysis for these six runs are presented in Table IV-D-4. Cumulative carbon formation versus time on-stream is plotted in Figure IV-D-46. The results indicate a very slow rate of carbon formation with this catalyst. After 1200 operating hours, the spent catalyst carbon content was 3.6 weight percent as contrasted to 3.0 weight percent in the fresh catalyst. This is equivalent to an overall increase of 0.6 percent compared to more than 8 percent observed from 1200 hours of operation with G-87P catalyst. Although, with G-87P, most of the carbon appeared in the top catalyst bed sections, with Ni-104T, the carbon was uniformly distributed throughout the bed. Physical and crystallographic analyses corroborate existing evidence that this catalyst is particularly stable under these operating conditions.

FIGURE IV-D-45

CARBON FORMATION STUDY

TEMPERATURE PROFILE OF RUN #18a

LURGI GAS/NI-104T (35 ATM, 480°C, 3.85% STEAM, 307H

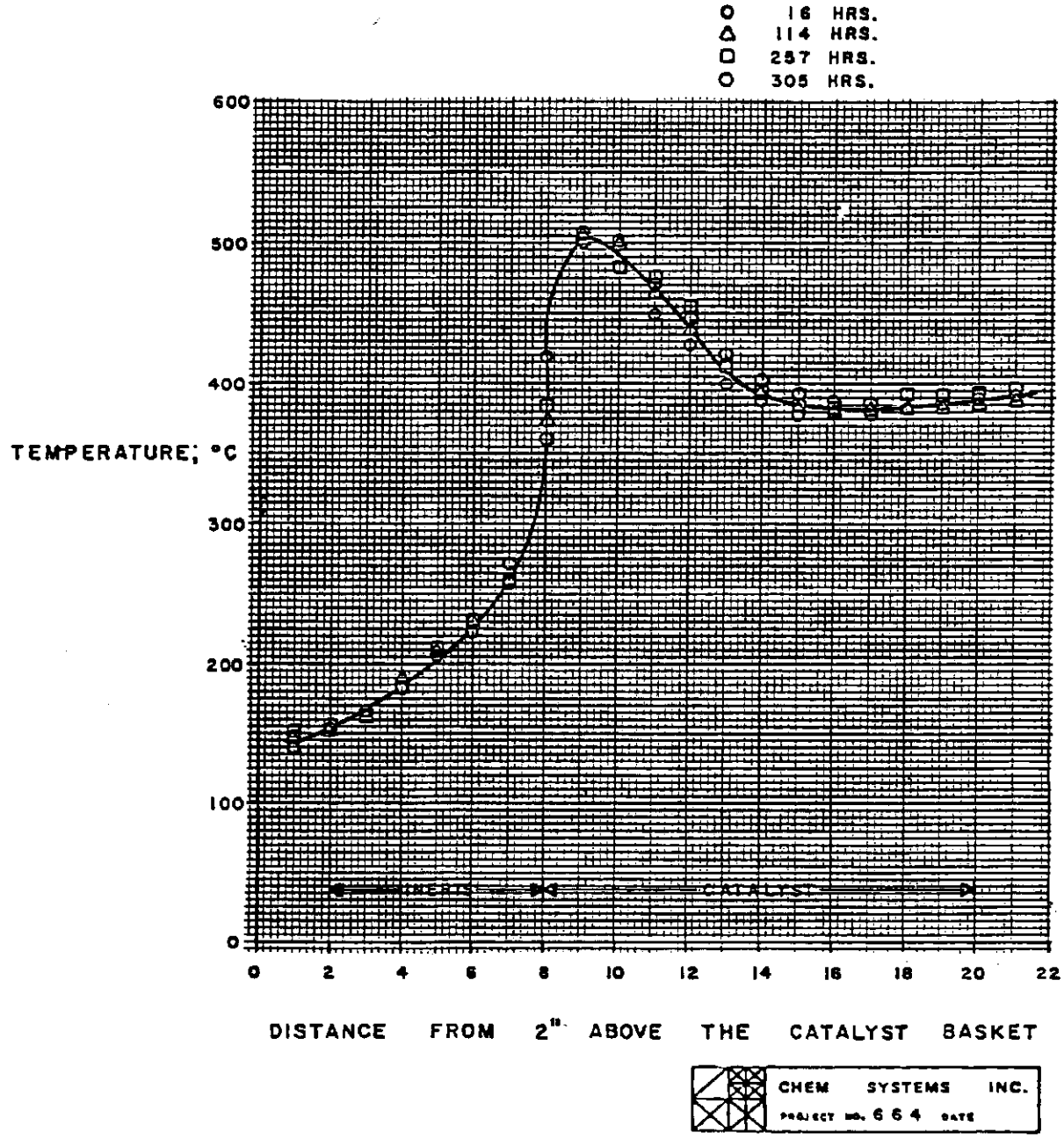


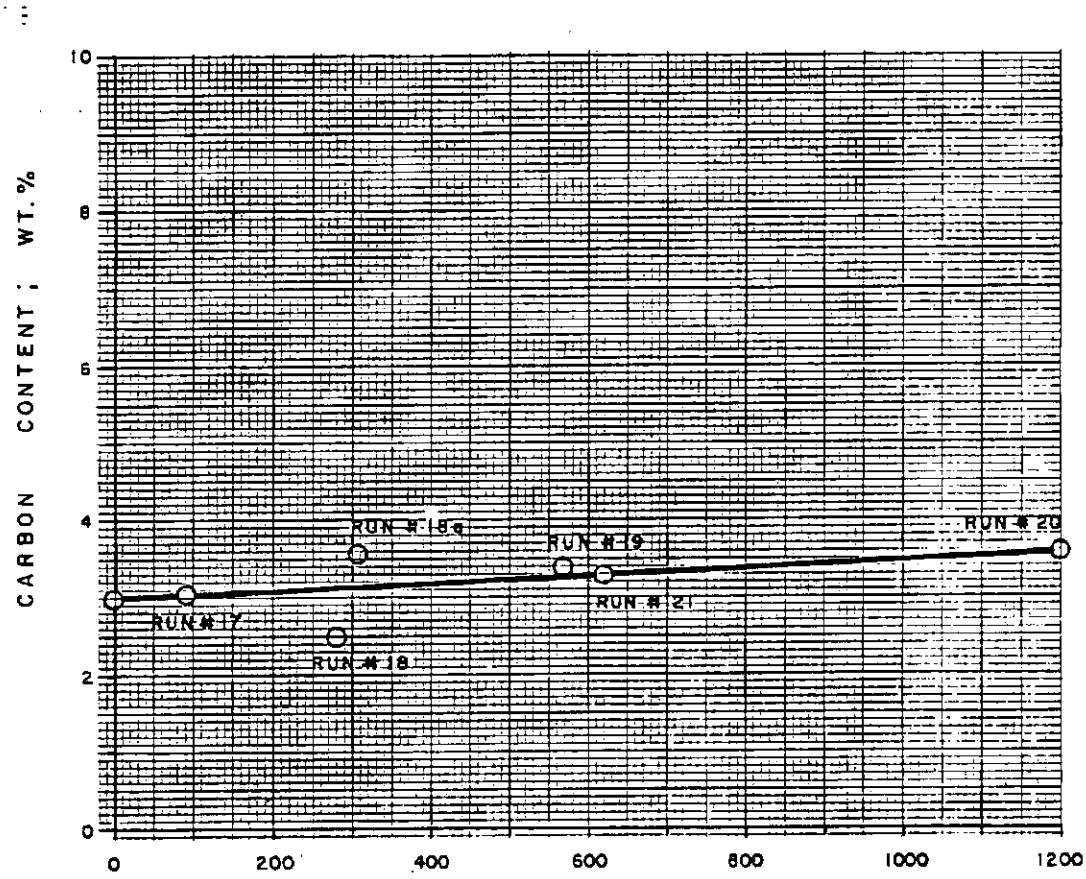
FIGURE IV - D - 46

CARBON FORMATION STUDY

CARBON FORMATION VS. TIME ON-STREAM

LURGI GAS / Ni—104 T

BASIS: CARBON CONTENT IN TOP BED SECTION



TIME ON - STREAM, HOURS

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