3. Standard Runs

Based on preliminary runs, the optimum carbon oxide content in the feed gas seemed to be 4 percent. Since the Lurgi gas (scrubbed, but nonshifted) was chosen to be used first, a set of simultaneous equations was solved that resulted in the atomic C-H-O fraction = 0.18:0.69:0.13. It was impossible to formulate such a composition from CO, H_2, CO_2 and CH_4 and, at the same time, limit the total reactable carbon oxide content to 4 percent.

In an effort to solve this problem, a decision was made to eliminate CO_2 and to dilute the feed gas with an inert (nitrogen) in order to hold the CO content to 4 percent and still maintain the same atomic C-H-O fraction of the Lurgi gas. This resulted in a unique mixture consisting of 30.6 percent CO, 57.7 percent H_2 and 11.8 percent CH_4. The final diluted feed composition is 6.1 percent CO, 11.5 percent H_2, 2.4 percent CH_4 and 80 percent N_2. Dilution with N_2 does not have any adverse effect on this study, since the carbon formation isotherms are relatively insensitive to pressure.

Three reactors were loaded with 93.2 gms of United Catalyst's G-87P (1/8" extrudates). The catalyst charge was separated into four equal sections with spacer rings. The rest of the catalyst basket was filled with alumina beads that would serve as a preheat zone. Catalyst was reduced in the standard manner and then switched to nitrogen. The target nominal reactor conditions for these three runs were 480°C at 500 psig for 500 hours.

Runs 1, 2 and 3 utilized the G-87P catalyst at the 0 percent, 5 percent, and 30 percent steam levels, respectively. Runs 15, 16 and 14 were the corresponding runs using the Ni-104T catalyst.

Run #1: Lurgi Gas/G-87P (35 atm, 480°C, 0% steam, 500 hours)

Run #2: Lurgi Gas/G-87P (35 atm, 480°C, 5% steam, 500 hours)

Run #3: Lurgi Gas/G-87P (35 atm, 480°C, 30% steam, 500 hours)

Run #1 was initiated by gradually increasing the feed gas rate. The hot spot temperature immediately began to rise. When the feed rate was further increased to 10 L/min, the hot spot temperature rose to well over 500°C. The insulation covering the top half of the catalyst

bed was removed to slow the hot spot temperature rise. At 16.7 L/min (10,000 v/v/hr), the hot spot seemed to stabilize at about 520°C and was located 2" from the top of the catalyst bed. The temperature profile, which was measured at 1" intervals starting from 2" above the inert bed and going to 2" below the bottom of the catalyst bed, was found to be very stable over the 500 hour run. Temperature profiles for Run #1 are plotted in Figure IV-D-14.

Run #2 was started in the same manner as Run #1 and water was pumped in at a rate equivalent to 5 mol percent. The temperature profiles are plotted in Figure IV-D-15.

Run #3 was started in the same manner as Run #1 and, after the hot spot temperature reached equilibrium, water was pumped in at a rate equivalent to 30 mol percent. The temperature profiles are plotted in Figure IV-D-16.

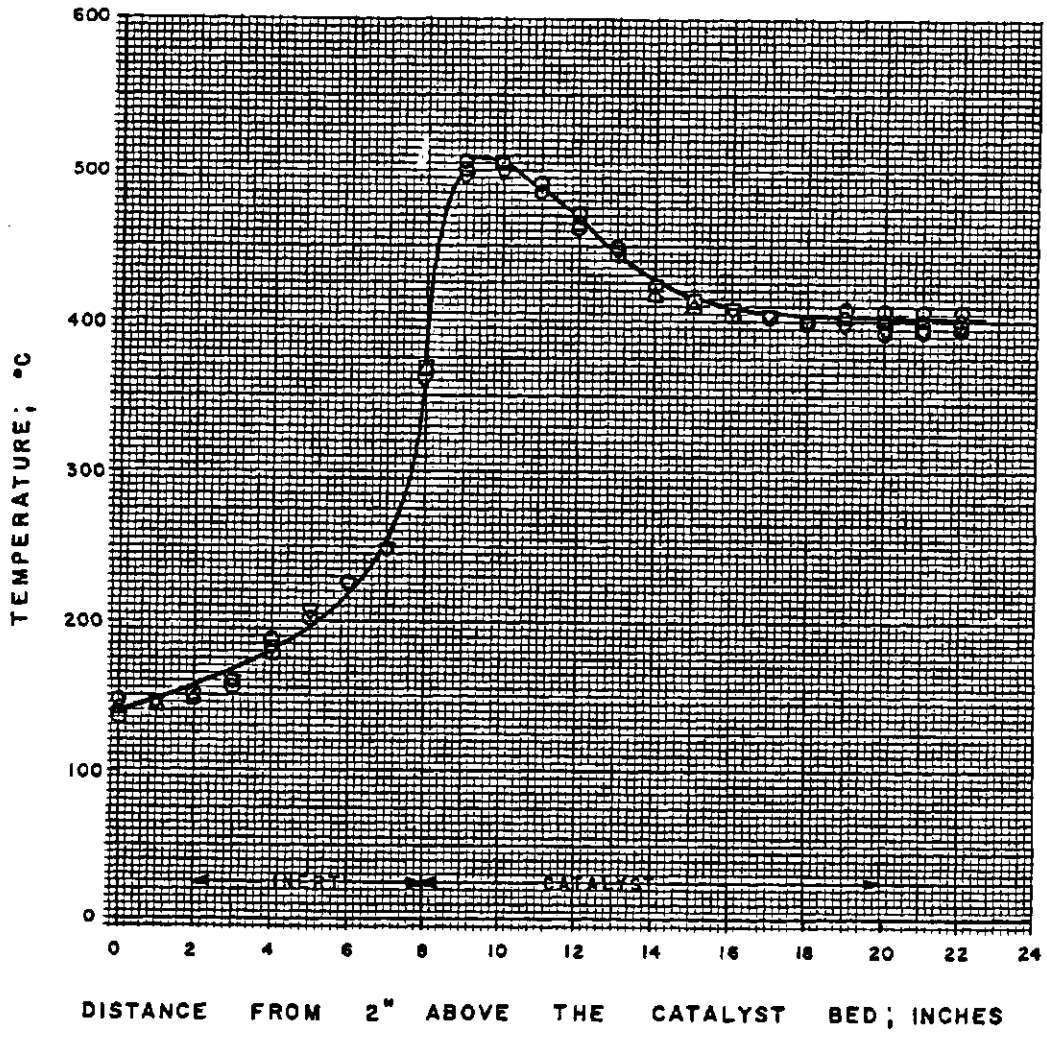
A similarity exists between the profiles of Run #1 (with no steam injection) and Run #2 (with 5 percent steam injection). Both had hot spot temperatures in the range of 505-520°C and their hot spots were 2" from the top of the catalyst bed. The profile of Run #3 (with 30 percent steam injection) is somewhat different from the other two. Here, the hot spot was further down in the catalyst bed. The shallow dip in the preheat region of Run #3 is due to the cooling effect of the relatively large quantity of added water.

Throughout the 500 hour period, the temperature profiles of Runs 1, 2 and 3 indicated that the reaction was taking place mainly in the upper quarter of the catalyst bed. Catalyst deactivation, which is usually noticeable by the hot spot moving down in the bed or by a gradual decrease in conversion, was not observed. The sampling line from the reactor operating with 30 percent steam injection (Run 3) became flooded with product water several times over one weekend. This problem was corrected by substituting automatic drains for manual drains in the sampling line.

FIGURE IV-D-14

CARBON FORMATION STUDY – LURGI GAS
TEMPERATURE PROFILE OF RUN # 1

500 PSIG, NO STEAM, NOMINAL 480 °C



CHEM SYSTEMS INC.
PROJECT NO. 6 6 4 DATE

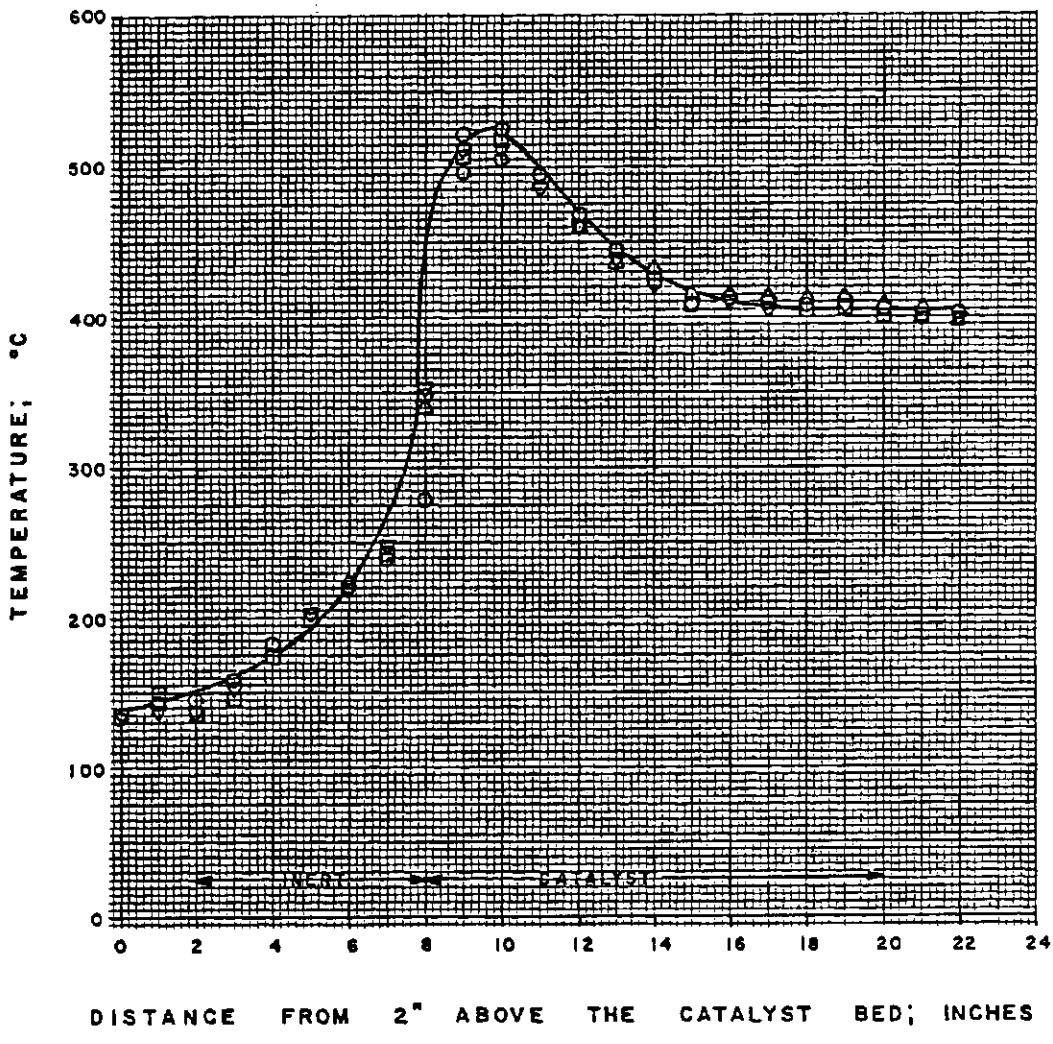
FIGURE IV-D-15

CARBON FORMATION STUDY - LURGI GAS
TEMPERATURE PROFILE OF RUN #2

500 PSIG, 5% STEAM, NOMINAL 480 °C

HOURS OF REACTION

○	72 HRS.
△	192 HRS.
□	305 HRS.
○	401 HRS.
▽	501 HRS.



CHEM SYSTEMS INC.
PROJECT NO. 6 6 4 DATE

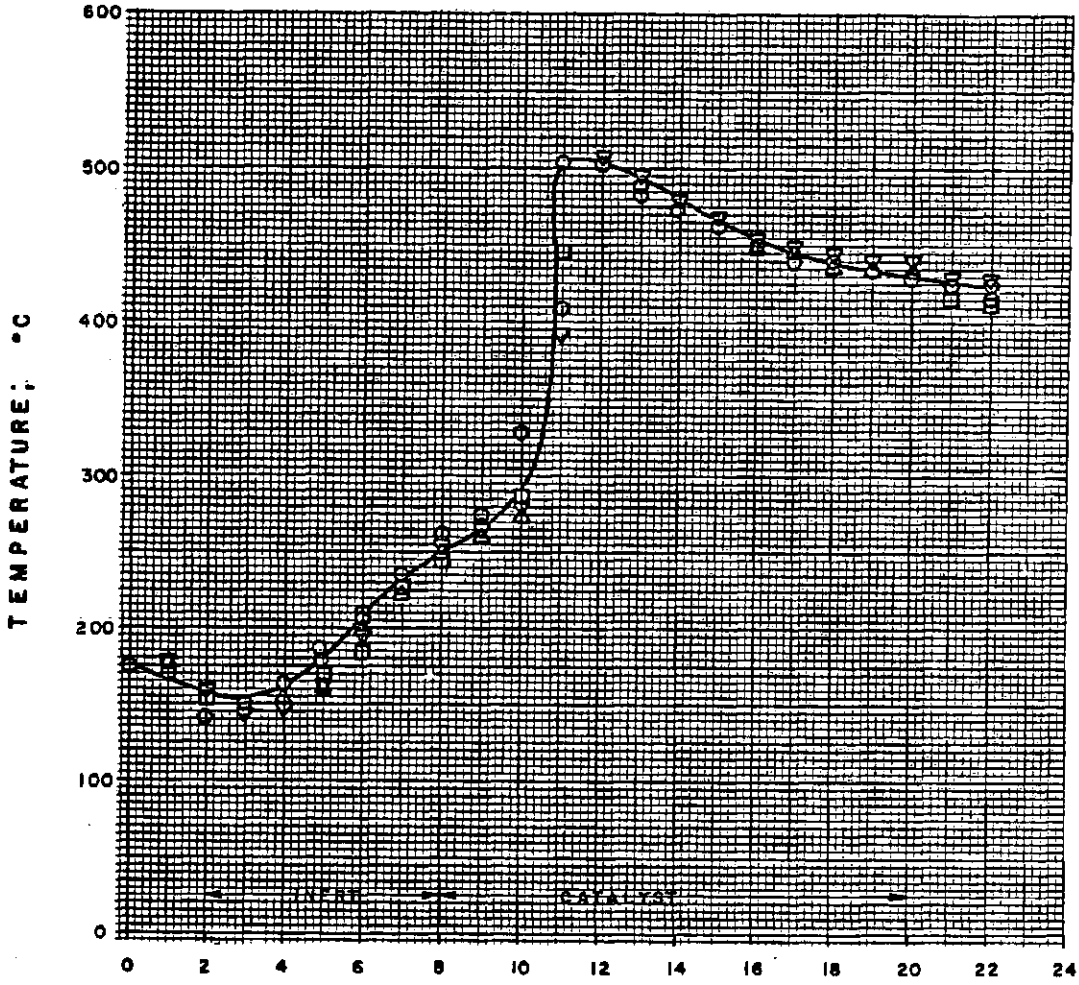
FIGURE IV-D-16

CARBON FORMATION STUDY – LURGI GAS
TEMPERATURE PROFILE OF RUN #3

500 PSIG, 30% STEAM, NOMINAL 480 °C

HOURS OF REACTION

- ○ 72 HRS.
- △ 208 HRS.
- □ 305 HRS.
- ○ 401 HRS.
- ▽ 497 HRS.



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

A theoretical equilibrium composition for the product gas was calculated so that the measured product gas composition could be compared with it and reactor performance thereby evaluated. Equilibrium compositions for 0, 5 and 30 percent steam injection were obtained by solving the equilibrium relationships of reactions (1) and (2) simultaneously.

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

A comparison between the actual and theoretical equilibrium composition of product gas (calculated on the basis of the same feed) showed that a higher product gas conversion is achieved at all steam injection levels than can theoretically be expected. This apparently high conversion, which is not possible in a strict theoretical sense, may be attributed to the fact that the actual methanation reaction occurs at a much higher catalyst surface temperature than the measured bulk temperature upon which all equilibrium calculations are based. Most of the reaction also took place in the top quarter of the catalyst bed, where the hot spot temperature was higher than the average operating temperature.

After accumulating 500 hours of methanation, the spent catalyst from each reactor was unloaded in a nitrogen tent. The catalyst from each basket section was sent to United Catalyst, Inc. for analysis. When the catalyst basket was taken out of the reactor, some carbon coating on the outside basket wall was observed, mostly at the top section. Inert alumina beads in contact with catalyst were also lightly coated with carbon. Some carbon was also found inside the reactor. The spent catalyst from Run 1 (0 percent steam) and Run 2 (5 percent steam) appeared black in all sections. The top section of catalyst from Run 3 (30 percent steam) looked gray because of excess steam while catalyst from the other sections appeared black as in Runs 1 and 2.

Analytical results for the spent catalyst are presented in Table IV-D-4. The top section of each reactor was analyzed for carbon, surface area, pore volume and x-ray diffraction. All remaining sections were analyzed for carbon only.

As expected, most carbon was formed in the top catalyst bed section in Runs 1 and 2. These runs operated in the carbon forming region. In Run 1, the top section had twice as much carbon as the other sections, confirming that most of the methanation had occurred in this section, which was the site of the hot spot throughout the run. Carbon seemed equally distributed among the three bottom sections. In Run 2, which operated with 5 percent steam injection, more carbon was also formed in the top section (but not as much as in Run 1), suggesting that the steam had a moderating effect. In Run 3, which operated with 30 percent steam injection outside the carbon forming region, carbon was discovered to have formed in all sections of the catalyst bed. This unexpected result was investigated further. A separate set of samples from Run 3 was sent out to an independent laboratory for re-examination of the carbon content. Despite the 30 percent steam injection level, the results confirm that carbon was indeed formed although the gas composition was outside the theoretical carbon forming region. While steam addition did not wholly prevent the formation of carbon, it did have an ameliorating effect, reducing the upper section carbon level from 9.2 percent for the 0 percent steam level, down to 7.4 percent and 6.5 percent carbon for the 5 percent and 30 percent steam levels respectively.

Throughout the duration of the runs, changes in physical properties were monitored. For this particular series of runs it should be noted that while the surface area remained fairly stable at about 45 m^2/gm there were marked, irregular increases in the pore volume, associated with the macropore structure. The manufacturer has noted similar behavior in their own tests but could not offer any further explanation. Nickel surface area, which is an inverse function of the nickel crystallite size

is somewhat lower for the spent catalyst. For Runs 1 and 2, 203°C crystallite size appears to be a normal value as a result of some slight sintering (compared to 120°A for the freshly reduced catalyst). The 357°A crystallite size for Run 3 can be attributed to the high steam level, although this increase is still insufficient to affect catalytic activity.

The base carrier for the G-87P catalyst is a Co promoted mixture of $-Al_2O_3$ and $CaCO_3$, with graphite used as an extrusion lubricant. Based upon the x-ray diffraction data, it appears that this material is extremely stable.

In general, the overall assessment of the G-87P is quite favorable. In spite of significant levels of carbon deposition, the catalyst activity is very stable, achieving near equilibrium conversion throughout the test duration. Physical property changes were consistent with normal industrial experience. What is disturbing though, is its propensity for carbon formation, even under conditions thermodynamically unfavorable to carbon formation. Such carbon buildup could eventually lead to the plugging of a fixed bed reactor, even though the catalyst is still catalyticly active.

Run 14: Lurgi Gas/Ni-104T(35 atm, 480°C, 30% steam, 510 hours)
Run 15: Lurgi Gas/Ni-104T(35 atm, 480°C, 0% steam, 500 hours)
Run 16: Lurgi Gas/Ni-104T(35 atm, 480°C, 5% steam, 500 hours)

The first run of the Harshaw NI-104T catalyst series was intended to repeat Run 3 by operating at identical conditions since carbon was found in the spent catalyst of Run 3. Theoretically, the Lurgi feed gas with 30 percent steam should operate without forming carbon (graphite). The atomic fraction of Lurgi gas (dry basis, C:H:O = 0.18:0.69:0.13) is within the carbon forming region. With 30 percent steam, however, the overall atomic fraction (C:H:O = 0.13:0.68:0.19) is definitely located outside the carbon forming region.

The Ni-104T catalyst from Harshaw Chemical Co. has about 58 percent Ni on Kieselguhr support and is in 1/8" X 1/8" tablet form. This catalyst is manufactured in reduced form and then stabilized by absorbing CO_2 on the reduced Ni sites.

Run 14 was started similarly to previous runs with G-87P catalyst. The feed gas was preheated to 275°C, which was found to be high enough to initiate the methanation reaction. The insulation covering the top half of the catalyst bed was taken off when the exothermic temperature rise reached 400°C at the hot spot. It was observed that the hot spot stabilized at 470°C instead of 510°C which had been the case with G-87P. The insulation was put back on and the effect was hardly noticeable. The preheat zone temperature was raised to 300°C. A slight increase in hot spot temperature was observed, but not proportionate to the 25°C increase in the preheat zone temperature. It appears that this catalyst is less sensitive to changes in the feed inlet temperature than G-87P.

Runs 15 and 16 were designed to operate within the region thermodynamically favorable for graphite formation. These runs were carried out similarly to Run 14.

Near-equilibrium conversion was obtained for all the reactors throughout the test period. The temperature profile and hot spot location for these runs are quite similar to those for Runs 3, 1, and 2 with the G-87P catalyst and are plotted in Figures IV-D-17 through IV-D-19. The results of spent catalyst analysis are presented in Table IV-D-4 in Section IV-D-8.

Virtually no carbon was formed in any of these three standard runs (Runs 16, 14 and 15). This is in sharp contrast to the results for the runs with the G-87P catalyst operating at similar conditions. The base, three percent carbon level is a result of the organic lubricant used in the

FIGURE IV-D-17

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #14
LURGI / Ni-104T (35 ATM, 480°C, 30% STEAM, 510 HRS.)

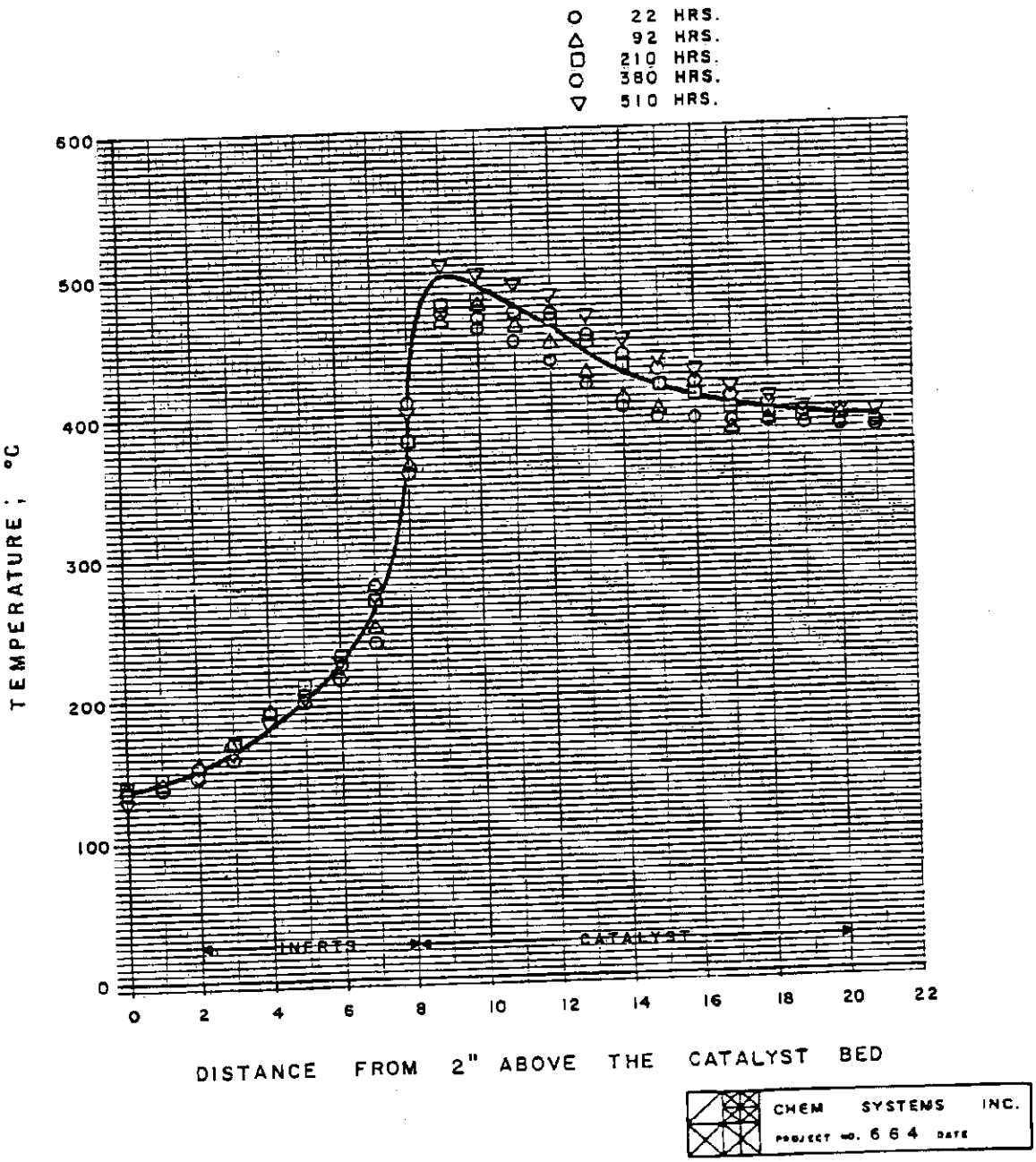


FIGURE IV-D-18

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN # 15
LURGI GAS / Ni-104 T (35 ATM, 480°C, 0% STEAM, 500 HRS)

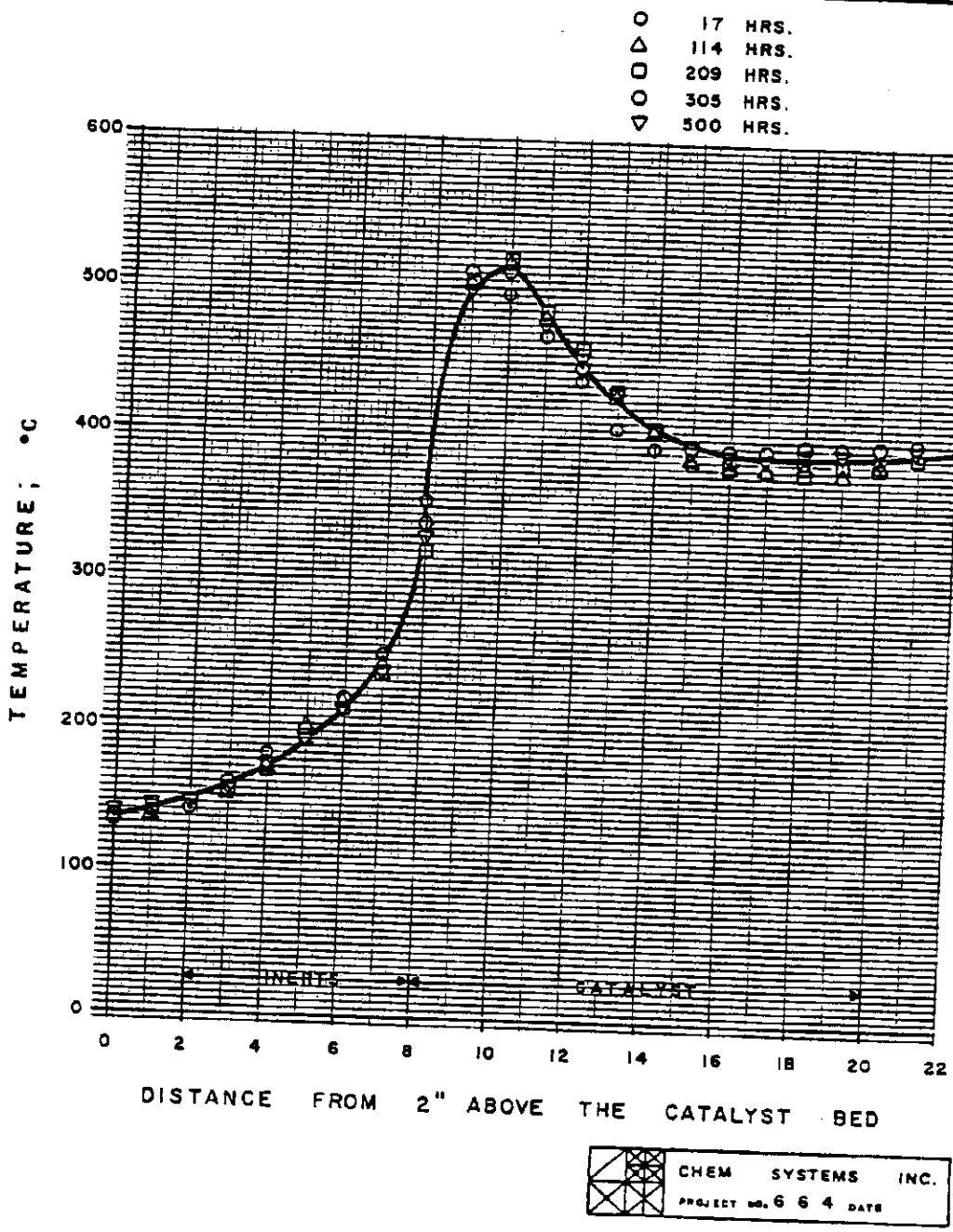
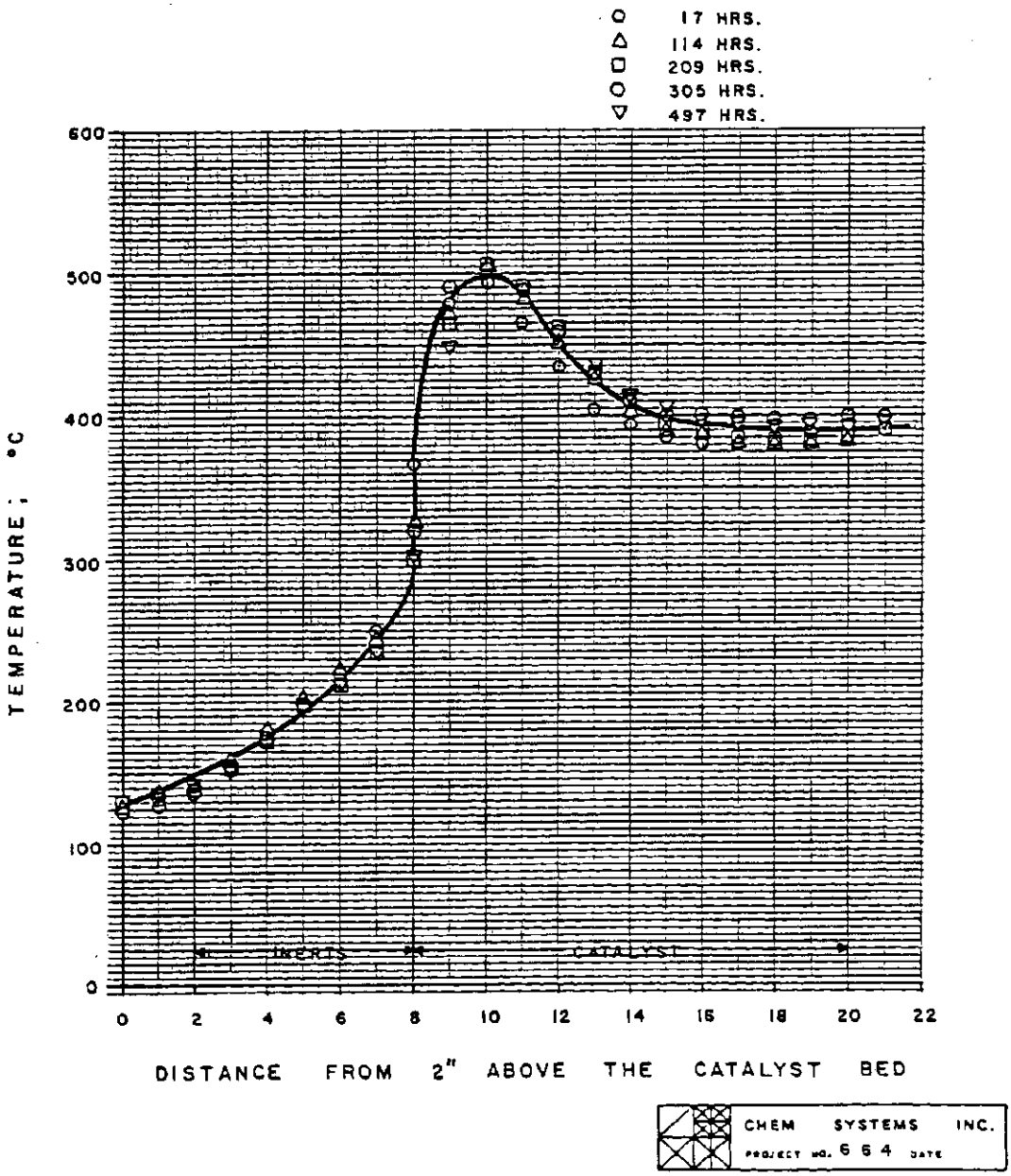


FIGURE IV-D-19

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #16
LURGI GAS/Ni-104T (35 ATM, 480°C, 5% STEAM, 500 HRS.)



tableting procedure. All twelve catalyst samples contained essentially the same level of carbon as the freshly reduced catalyst. This was true of virtually every subsequent sample of this catalyst, from all the remaining runs.

As with the G-87P catalyst, the Ni-104T exhibited stable catalytic behavior for the duration of the 500-hour tests. In spite of the expected higher activity, due to its smaller nickel crystallite size and higher nickel content, no discernible differences in behavior were evident in this series of tests. However, differences in activity were evident in subsequent tests, involving a diluted catalyst bed.

All the samples exhibited a marked reduction in surface area, from 150 m^2/gm for the fresh catalyst, down to about 80-90 m^2/gm. Irregular changes in pore volume were also observed. The nickel crystallite increased in all cases, from its initial value of $64^{o}A$ to the $90\text{-}100A^{o}$ range, which is still quite small. These changes appear to be normal for this catalyst. The base carrier for this catalyst is Kieselguhr, which is chiefly silica. Although silica possesses somewhat less high temperature stability than $-Al_2O_3$, not unfavorable changes in the crystallographic structure were detected by the x-ray diffraction analysis. The fairly large graphite crystallite size, $1000^{o}A$, is due to the high molecular weight organic lubricant used as a tableting aid.

Overall, this catalyst is quite active and appears to be stable at the temperatures of nearly $500^{o}C$. More importantly, the catalyst does not promote the formation of carbon, even in regions which are thermodynamically favorable to carbon formation.

Run 24: Lurgi Gas/Ni-104P(T) (35 atm, 480°C, 0% steam, 505 hours)
Run 25: Lurgi Gas/Ni-104P(T) (35 atm, 480°C, 5% steam, 505 hours)

Two runs were initiated with a tableted version of United Catalyst G-87P (3/16" dia. X 1/8"). The tableted catalyst has a bulk density of 1.14 gm/cc as compared to 0.93 gm/cc for the extrudate and 1.26 gm/cc for Ni-104T catalyst. The main objective of these runs was to determine whether catalyst physical properties are as important as chemical properties in carbon formation.

Run 24, without steam addition, is similar to the conditions of Run 1 while Run 25, with 5 percent steam addition, duplicated the conditions of Run 2. These runs were completed after operating for 505 hours.

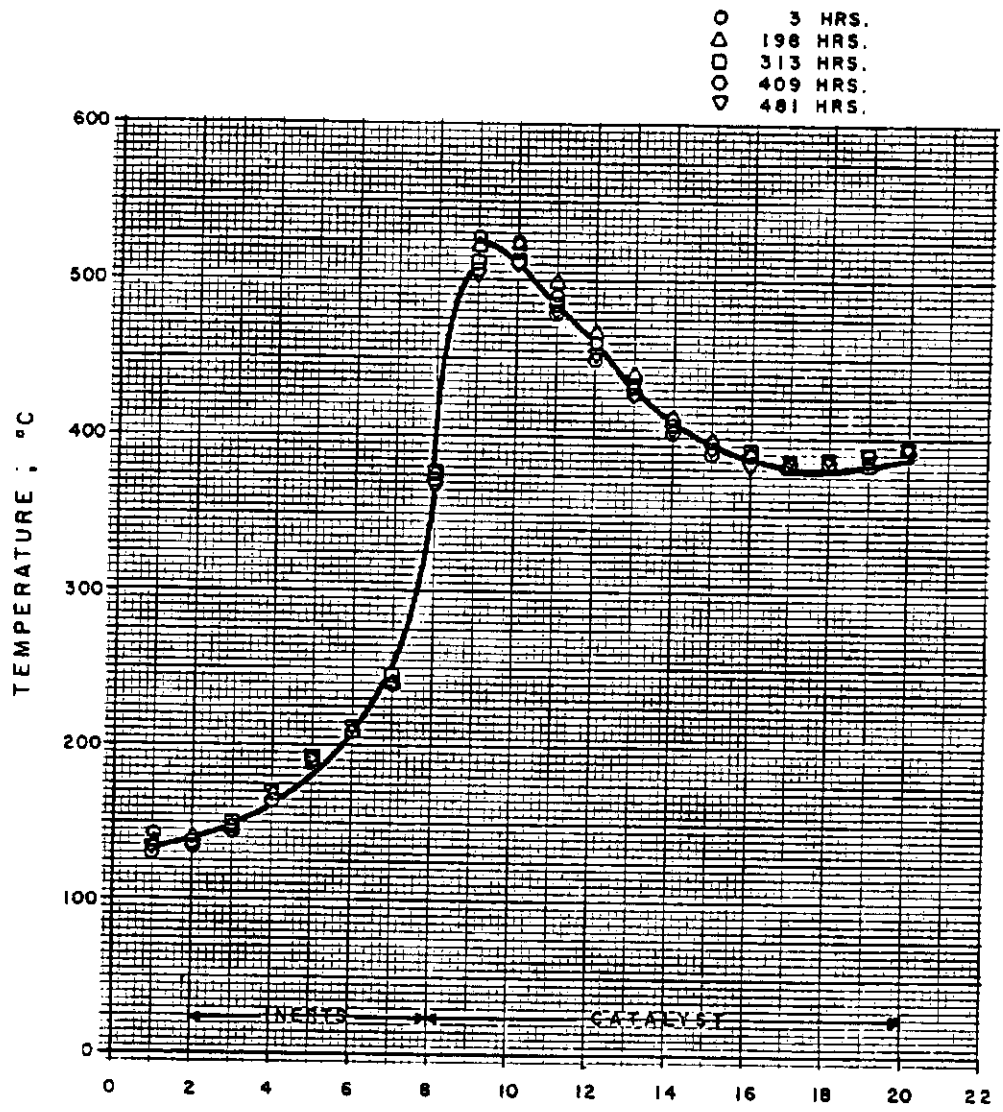
The temperature profiles (Figures IV-D-20 and IV-D-21) appear normal with the hot spot located one inch from the top of the catalyst bed. The conversion was nearly at equilibrium throughout the run.

The spent catalyst from Run 25 appeared to have some carbon formation. When unloaded, however, the carbon fell off the catalyst easily, indicating that it was loosely bound to the catalyst surface. On the other hand, the spent catalyst from Run 25 appeared free of carbon. Both spent catalysts had a slight silvery appearance indicating a mild degree of sintering. The fresh G-87P tablets exhibit no glossy surface, as compared to Ni-104T, probably due to a lack of lubricating binder. Small crack marks were observed in several spent catalyst tablets. These were not regarded as a result of high temperature operation since some cracks are also found on fresh tablets.

As the catalyst analyses for Runs 24 and 25 indicate (see Table IV-D-4), this version of the catalyst forms only minor amounts of carbon, even an order of magnitude less than the extrudate form. Examination of the physical property data in Table IV-D-3 indicates that while there are

FIGURE IV-D-20

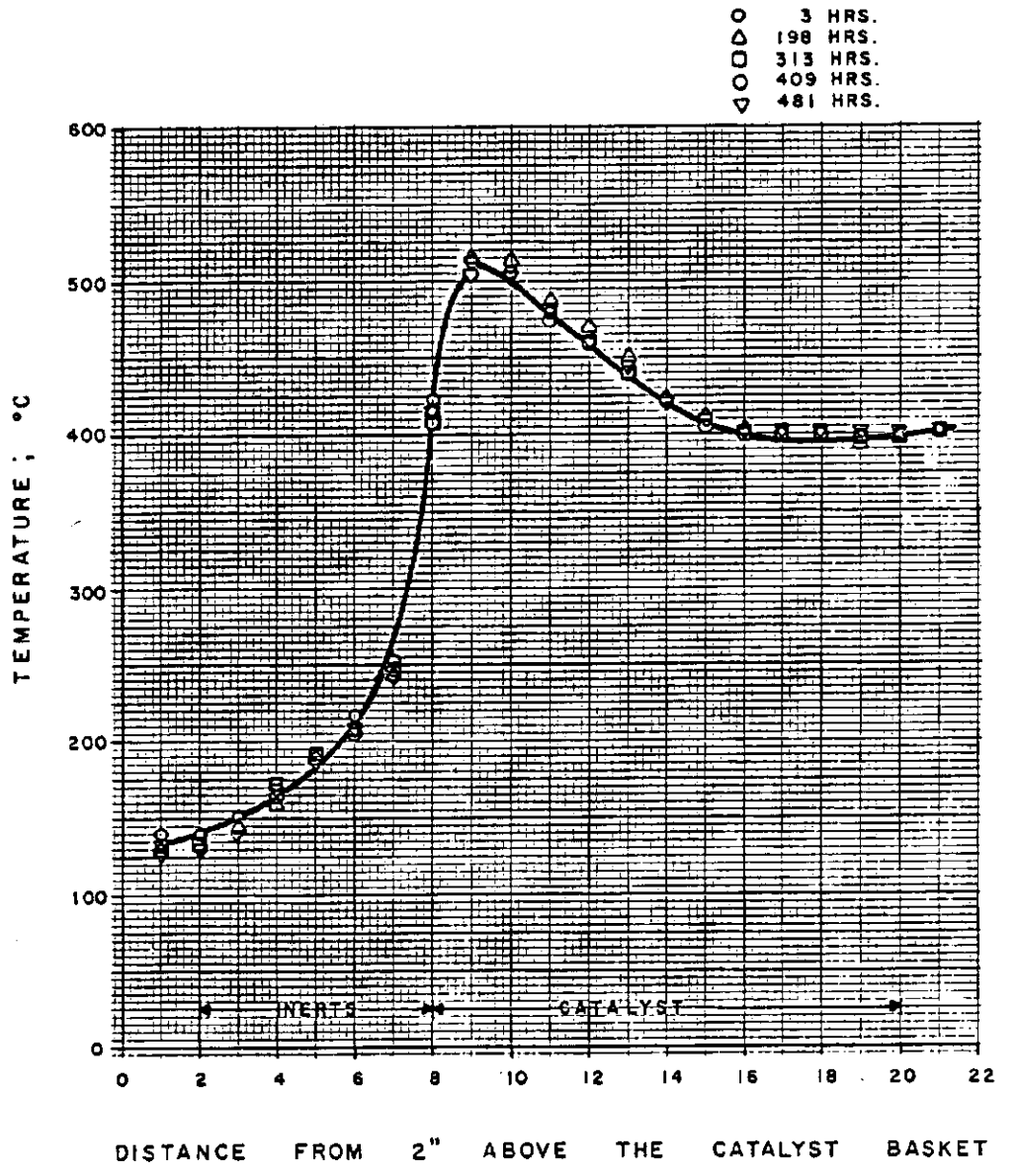
CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN #24
LURGI GAS/G-87P (T) (35 ATM., 480°C, 0% STM., 505 HRS.)



CHEM SYSTEMS INC.
PROJECT NO. 6 6 4 DATE

FIGURE IV - D - 21

CARBON FORMATION STUDY
TEMPERATURE PROFILE OF RUN # 25
LURGI GAS / G-87P(T)(35 ATM., 480°C, 5% STM., 505 HRS.)



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

measurable differences in pore volume and nickel crystallite sizes, no rationale exists which could account for this behavioral difference. One additional point to be noted, is that the carbon found has no regular crystallographic structure, which accounts for the absence of the graphite peak in the x-ray diffraction data.