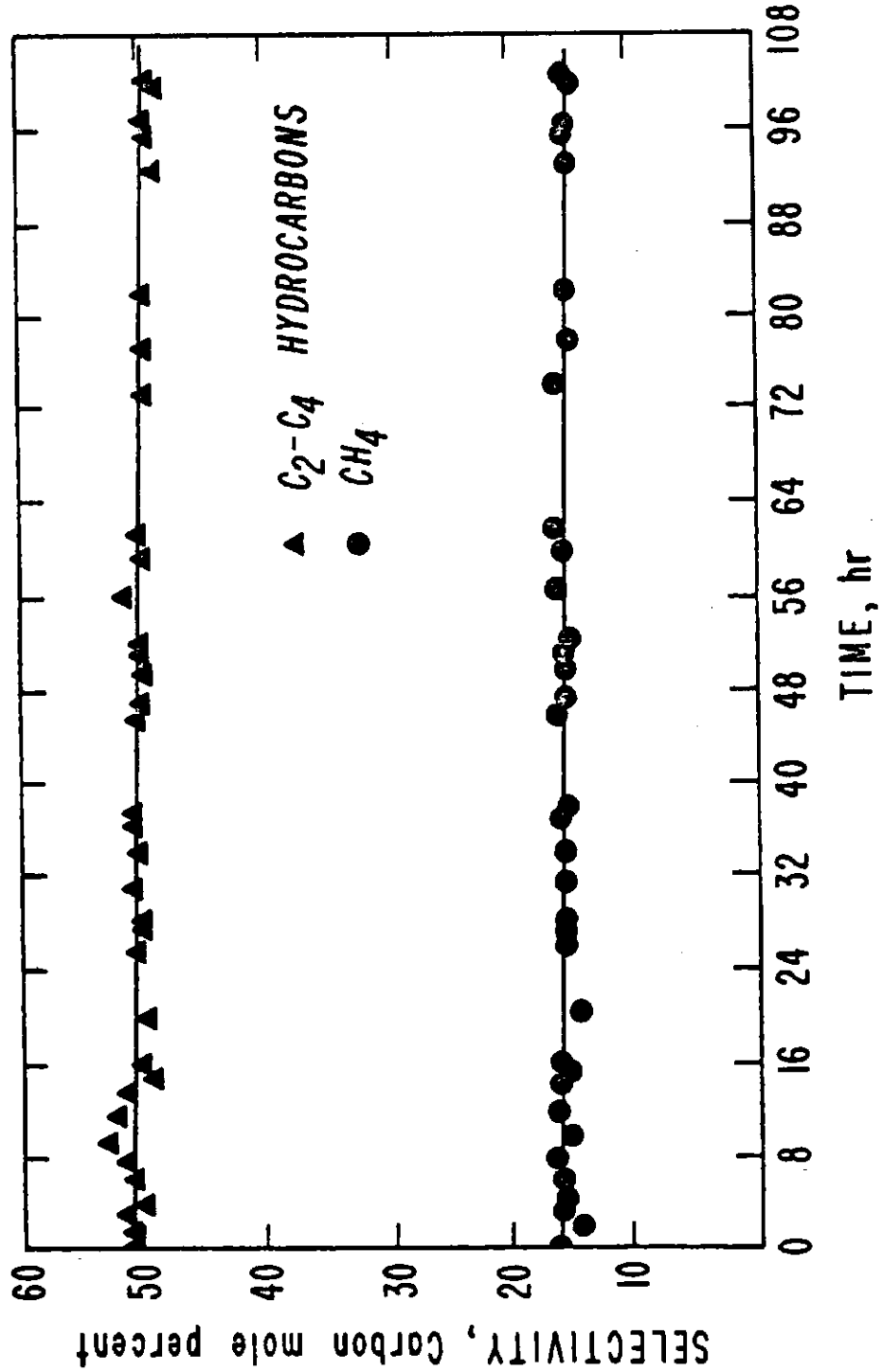

SELECTIVITY, Carbon mole percent
60
50
40
30
20
10
0
8
16
24
32
40
48
56
64
72
80
88
96
104
TIME, hr
▲ C_2-C_4 HYDROCARBONS
● CH_4

Figure 15

Long Term Activity and Selectivity Test

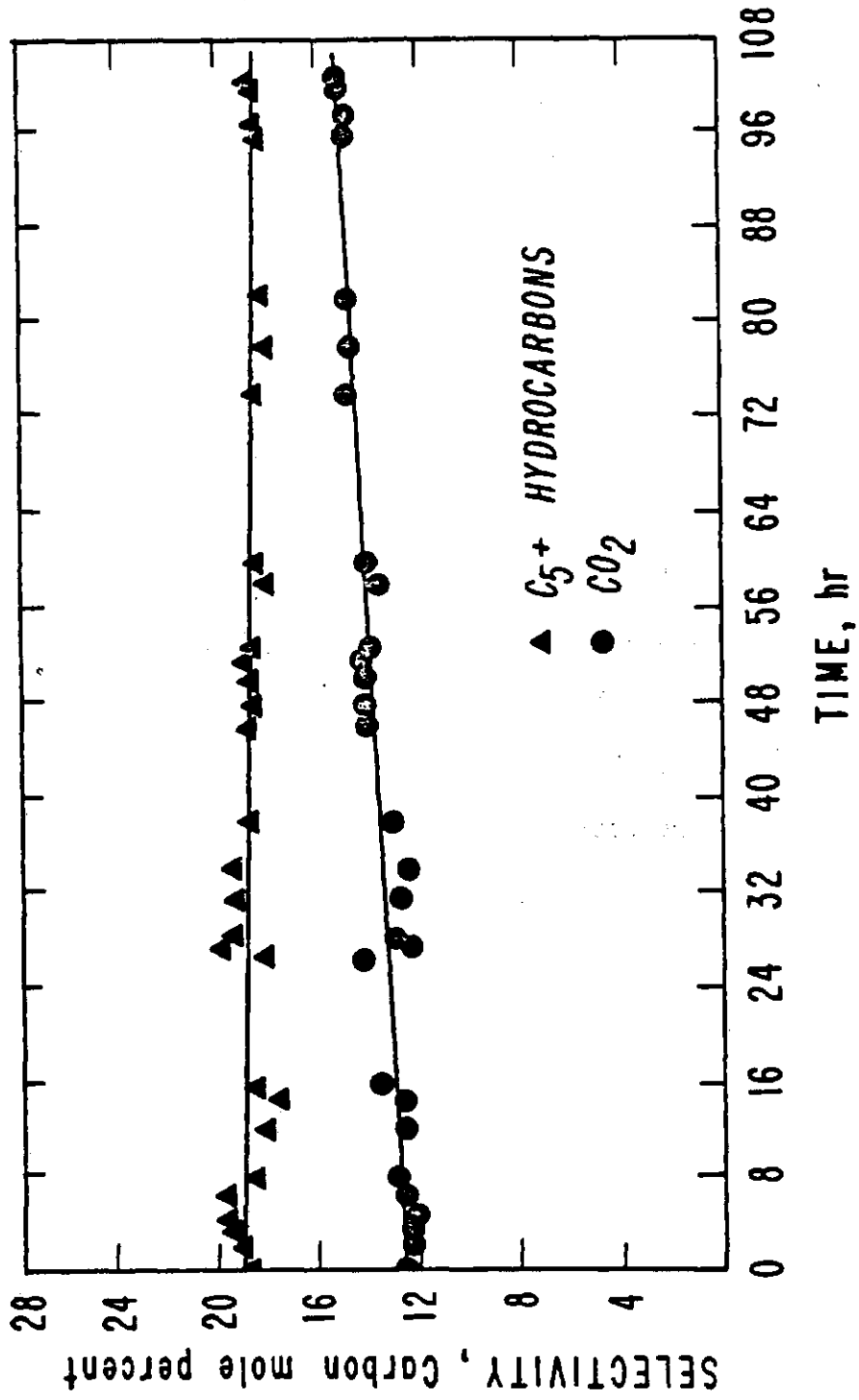
Diluted Bed Reactor; Iron-Manganese Catalyst

Mn/Fe Atomic Ratio = 2.4/100

Carbon Dioxide and C_5^+ Hydrocarbon Yields

Temperature = 523 K; Pressure = 3450 KPa

H_2/CO = 2/1; Space Velocity = 1.08 $cm^3 g^{-1} s^{-1}$.


SELECTIVITY, Carbon mole percent
28
24
20
16
12
8
4
0
8
16
24
32
40
48
56
64
72
80
88
96
108
TIME, hr
▲ C_5+ HYDROCARBONS
● CO_2

Twenty grams of the 20/32 mesh fraction of an iron-manganese catalyst (manganese to iron atomic ratio = 2.1:100) was used in this experiment. After the standard catalyst pretreatment, the catalyst was further stabilized as follows:

(1) Hydrogen and carbon monoxide were passed over the catalyst at 463 K and at ambient pressure for 16 hours at a space velocity of 0.4 $cm^3g^{-1}s^{-1}$. The hydrogen-to-carbon monoxide ratio was 2/1.

(2) Hydrogen and carbon monoxide were passed over the catalyst at 463 K and at the desired reaction pressure at a space velocity of 0.4 $cm^3g^{-1}s^{-1}$ for four hours. The hydrogen-to-carbon monoxide ratio was 2/1.

(3) The reaction conditions in step (2) were maintained and the heat transfer liquid, n-hexadecane, was introduced to the reactor in the upflow mode of operation at a flow rate of 0.103 cm^3s^{-1}.

The results of the selectivity and activity test for the hydrogenation of carbon monoxide in the diluted bed pseudo slurry reactor are presented in Table 3 and in Figures 16 and 17. The test was conducted continuously for a 24 hour period. The reactor operating conditions were as follows: a reaction temperature of 493 K, a total reactor pressure of 2760 KPa, a hydrogen to carbon monoxide ratio of 2 and a reactant gas space velocity of 1 $cm^3g^{-1}s^{-1}$ The heat transfer liquid was n-hexadecane and it passed upflow through the reactor at a flow rate of 0.103 cubic centimeters per second.

Table 3

Long-Term Carbon Monoxide Hydrogenation Test of #913 Catalyst in Heat Transfer Liquid, n-Hexadecane. Diluted Pseudo Slurry Reactor.

Temperature = 493 K; Pressure = 2760 KPa; H_2/CO = 2/1; Space Velocity = 1 $cm^3g^{-1}s^{-1}$; and n-Hexadecane Flow Rate = 0.103 cm^3s^{-1}.

Time hr.	CO Conv. %	PRODUCT SELECTIVITY (%)								OLEFIN/PARAFFIN RATIO			
		C_1	C_2	C_3	C_4	C_2-C_4	C_5^+	R-OH	CO_2	C_2	C_3	C_4	C_2-C_4
0	5.66	16.0	13.7	17.9	11.5	43.1	18.9	4.7	18.3	2.7	3.5	3.0	3.1
3	5.57	15.4	14.0	18.0	12.9	45.0	14.5	5.9	18.2	2.7	3.4	2.9	3.0
6	6.05	15.4	13.8	17.1	12.8	43.7	17.4	5.3	18.3	2.9	3.5	2.8	3.1
9	5.38	15.8	14.6	18.0	13.0	45.6	16.5	4.5	18.5	2.9	3.6	2.9	3.2
12	6.43	14.6	14.0	17.8	13.9	45.7	15.9	5.3	18.5	2.9	3.6	2.8	3.1
15	5.32	15.8	14.6	17.9	13.1	45.6	15.9	4.1	18.6	2.9	3.6	2.9	3.2
18	6.19	15.4	14.2	17.6	13.7	45.4	16.2	4.2	18.7	2.8	3.6	2.8	3.1
21	4.99	15.8	14.9	18.3	13.5	46.8	15.2	3.7	18.5	2.9	3.6	2.8	3.1
24	5.55	15.8	15.1	18.6	13.8	47.5	14.8	3.8	18.1	3.0	3.6	2.8	3.2

Figure 16

Long-Term Activity and Selectivity Test in
Heat Transfer Liquid: n-Hexadecane.
Diluted Bed Pseudo Slurry Reactor
Iron-Manganese Catalyst
Carbon Monoxide Conversion and C_2-C_4 Olefin Selectivity
Temperature = 493 K; Pressure = 2760 KPa; H_2/CO = 2/1;
Space Velocity = 1 $cm^3 g^{-1} s^{-1}$; Flow Rate (n-C16) = 0.103 $cm^3 s^{-1}$.

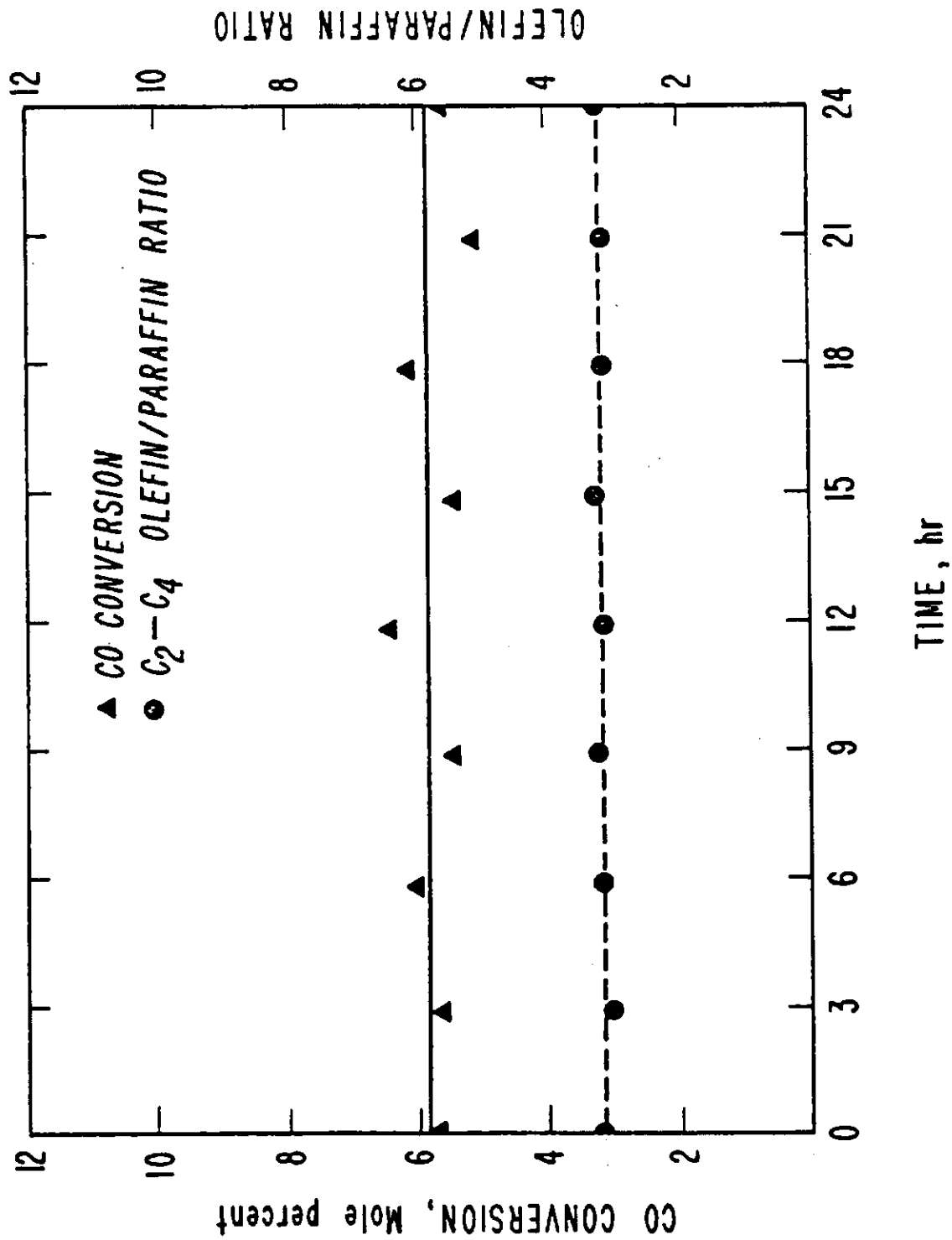

CO CONVERSION, Mole percent
OLEFIN/PARAFFIN RATIO
TIME, hr
▲ CO CONVERSION
● C_2-C_4 OLEFIN/PARAFFIN RATIO
0
3
6
9
12
15
18
21
24
2
4
6
8
10
12

Figure 17

Long-Term Activity and Selectivity Test in

Heat Transfer Liquid: n-Hexadecane.

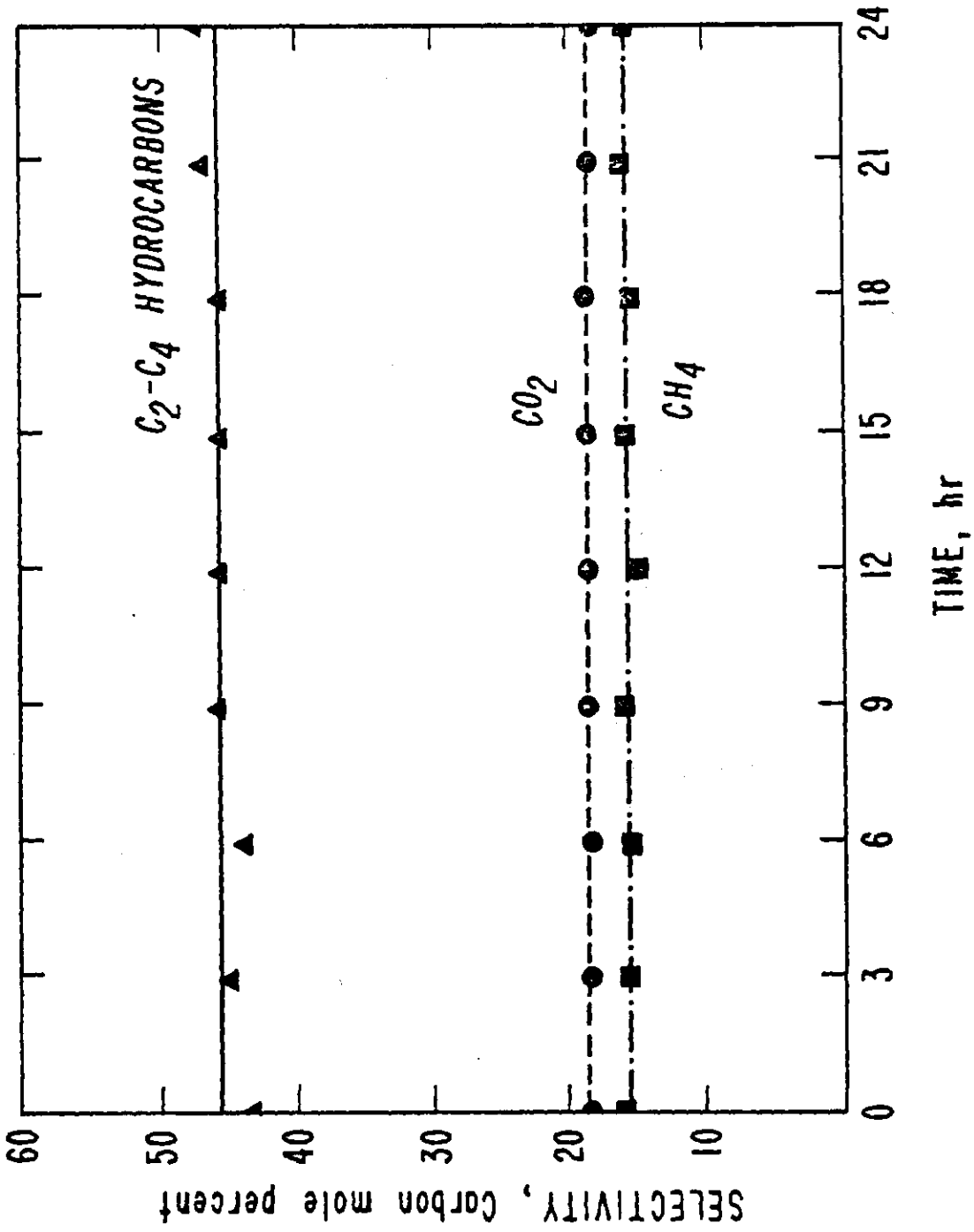
Diluted Bed Pseudo Slurry Reactor

Iron-Manganese Catalyst

Carbon Dioxide, Methane and C_2-C_4 Hydrocarbon Selectivity

Temperature = 493 K; Pressure = 2760 KPa; H_2/CO = 2/1;

Space Velocity = 1 $cm^3g^{-1}s^{-1}$; Flow Rate (n-C16) = 0.103 cm^3s^{-1}.


SELECTIVITY, Carbon mole percent
60
50
40
30
20
10
0
3
6
9
12
15
18
21
24
TIME, hr
C_2-C_4 HYDROCARBONS
CO_2
CH_4

The activity as measured by carbon monoxide conversion was reasonably stable throughout the course of this experiment (Table 3 and Figure 16). The individual and total C_2-C_4 olefin selectivities were invariant in this test (Table 3 and Figure 16). The methane, the C_2-C_4 hydrocarbons and the carbon dioxide yields were invariant at the standard operating conditions up to 24 hours on stream (Table 3 and Figure 17). The catalyst appeared to be stabilized after 6 - 8 hours on stream and consequently all process variable data reported in the investigation were obtained after 8 hours on stream at the specified reaction conditions.

4.2 The Effect of Reactor Mode on Carbon Monoxide Hydrogenation

The highly exothermic nature of the carbon monoxide hydrogenation reaction requires that the conversion level in the conventional dense bed reactor be kept quite low to ensure the acquisition of reliable kinetic data. A temperature excursion or "hot spot" in the conventional dense, fixed bed reactor due to high conversions accelerates undesireable side reactions like the 'Boudouard reaction' (disproportionation reaction of carbon monoxide to carbon dioxide and carbon) which fouls the catalyst and leads to a loss in activity. The objective of these experiments was to compare the performance of different types of reactor operating modes for the hydrogenation of carbon monoxide.

Six different reactor modes were tested, that is, (1) a conventional dense bed reactor, (2) a dense bed trickle flow reactor, (3) a dense bed pseudo slurry reactor, (4) a diluted bed reactor, (5) a

diluted bed trickle flow reactor, and (6) a diluted bed pseudo slurry reactor. For each reactor study, twenty grams of fresh catalyst were loaded into the reactor for each experiment. The catalyst pretreatment and stabilization procedures were the same as those described in the previous section. A standard reaction condition was established to facilitate the comparisons between different reactor modes, that is, a reaction temperature of 493 K; a total reactor pressure of 2760 Kpa; a hydrogen-to-carbon monoxide reactant ratio of 2/1; and a space velocity of 1 $cm^3g^{-1}s^{-1}$. Mobil #1 base stock MCP 151 without additives and n-hexadecane were used as heat transfer liquids at a fixed circulation rate of 0.103 cm^3s^{-1}. The data for the hydrogenation of carbon monoxide at the standard reaction condition for the different reactor modes are listed in Table 4. The highest carbon monoxide conversion was attained in the dense bed reactor. However, lower carbon monoxide conversions were observed in the pseudo slurry reactor with both MCP 151 and n-hexadecane as heat transfer liquid. The temperature profiles for the various reactor modes at the standard reaction conditions are presented in Figure 18. The profiles in Figure 18 were plotted with reactor temperature versus relative position inside the reactor measured from the top of the reactor. The shaded area in each temperature profile indicates the location of the catalyst zone inside the reactor. A significant temperature rise was observed in the catalyst zone in the dense bed reactor at a carbon monoxide conversion of 7.34 percent. The introduction of the heat transfer liquid, MCP 151, reduced the temperature rise in the dense bed trickle flow reactor and in the pseudo slurry reactor as shown in Figure 18. In both cases the carbon monoxide

Table 4

Carbon Monoxide Hydrogenation, Activity and Selectivity, Different Reactor Modes

Reaction Temperature = 493 K; Total Pressure = 2760 KPa; H_2/CO = 2/1; Space Velocity = 1 $cm^3\ g^{-1}s^{-1}$; and Heat Transfer Liquid Circulating Rate = 0.103 cm^3 per Second When Used.

Reactor Type	Heat Transfer Liquid	CO Conv. %	PRODUCT SELECTIVITY								OLEFIN/PARAFFIN RATIO			
			C_1	C_2	C_3	C_4	C_2-C_4	C_5+	CO_2	ROH	C_2	C_3	C_4	C_2-C_4
Dense Bed	--	7.34	12.7	13.8	18.5	15.1	47.4	20.7	13.8	5.5	3.7	3.0	2.3	2.9
Dense Trickle	MCP 151	4.24	15.7	16.9	19.8	13.8	50.5	13.3	16.1	4.4	2.9	3.1	2.3	2.8
Dense Slurry	MCP 151	2.45	11.6	13.4	17.5	13.5	44.4	21.2	21.2	1.6	1.9	2.8	2.3	2.3
Diluted Bed	--	7.08	15.1	14.0	18.9	15.9	48.9	21.2	9.8	5.1	2.6	2.9	2.4	2.7
Diluted Trickle	MCP 151	6.69	12.3	13.7	17.2	14.8	45.8	27.5	10.6	3.7	2.3	2.2	1.7	2.1
Diluted Slurry	MCP 151	3.14	10.5	13.3	17.1	12.6	43.0	16.9	26.0	3.6	2.1	2.3	1.7	2.0
Diluted Bed	--	7.07	15.0	13.4	18.3	15.5	47.2	23.4	8.4	6.2	2.5	2.8	2.4	2.6
Diluted Trickle	normal-hexadecane	6.33	12.9	17.0	22.6	15.0	54.5	10.6	11.9	4.2	1.3	2.5	2.0	1.9
Diluted Slurry	normal-hexadecane	3.56	13.8	14.8	17.6	13.2	45.6	18.7	16.5	5.4	3.2	3.2	2.4	2.9

Figure 18

Catalyst Bed Temperature Profiles

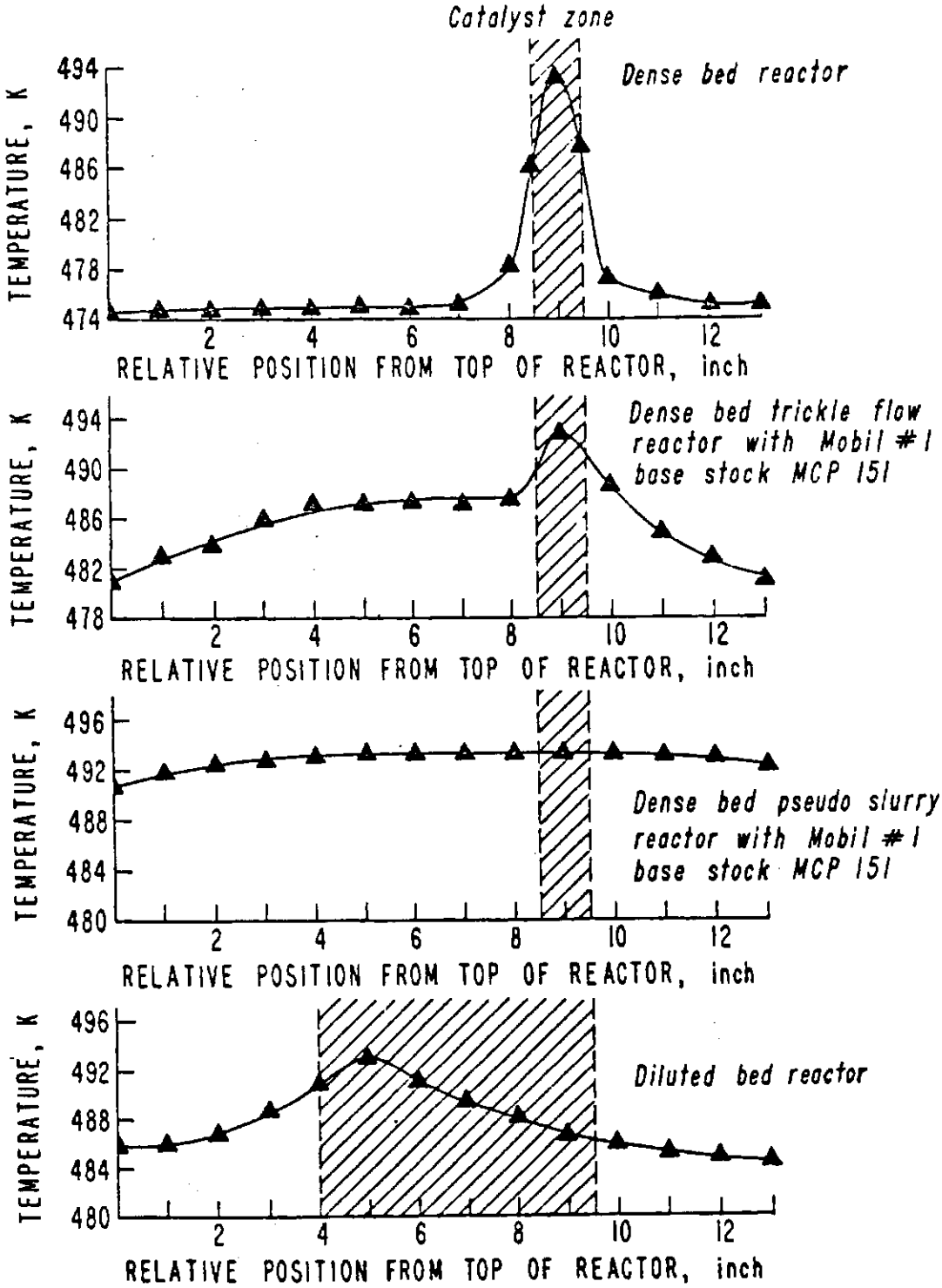
Carbon Monoxide Hydrogenation

Different Reactor Modes

Temperature = 593 K; Pressure = 2760 KPa;

H_2/CO = 2/1; Space Velocity = 1 $cm^3g^{-1}s^{-1}$; and

Flow Rate (MCP 151 or n-C16) = 0.103 cm^3s^{-1} when used.


Catalyst zone
Dense bed reactor
TEMPERATURE, K
494
490
486
482
478
474
2
4
6
8
10
12
RELATIVE POSITION FROM TOP OF REACTOR, inch
Dense bed trickle flow reactor with Mobil #1 base stock MCP 151
TEMPERATURE, K
494
490
486
482
478
2
4
6
8
10
12
RELATIVE POSITION FROM TOP OF REACTOR, inch
Dense bed pseudo slurry reactor with Mobil #1 base stock MCP 151
TEMPERATURE, K
496
492
488
484
480
2
4
6
8
10
12
RELATIVE POSITION FROM TOP OF REACTOR, inch
Diluted bed reactor
TEMPERATURE, K
496
492
488
484
480
2
4
6
8
10
12
RELATIVE POSITION FROM TOP OF REACTOR, inch

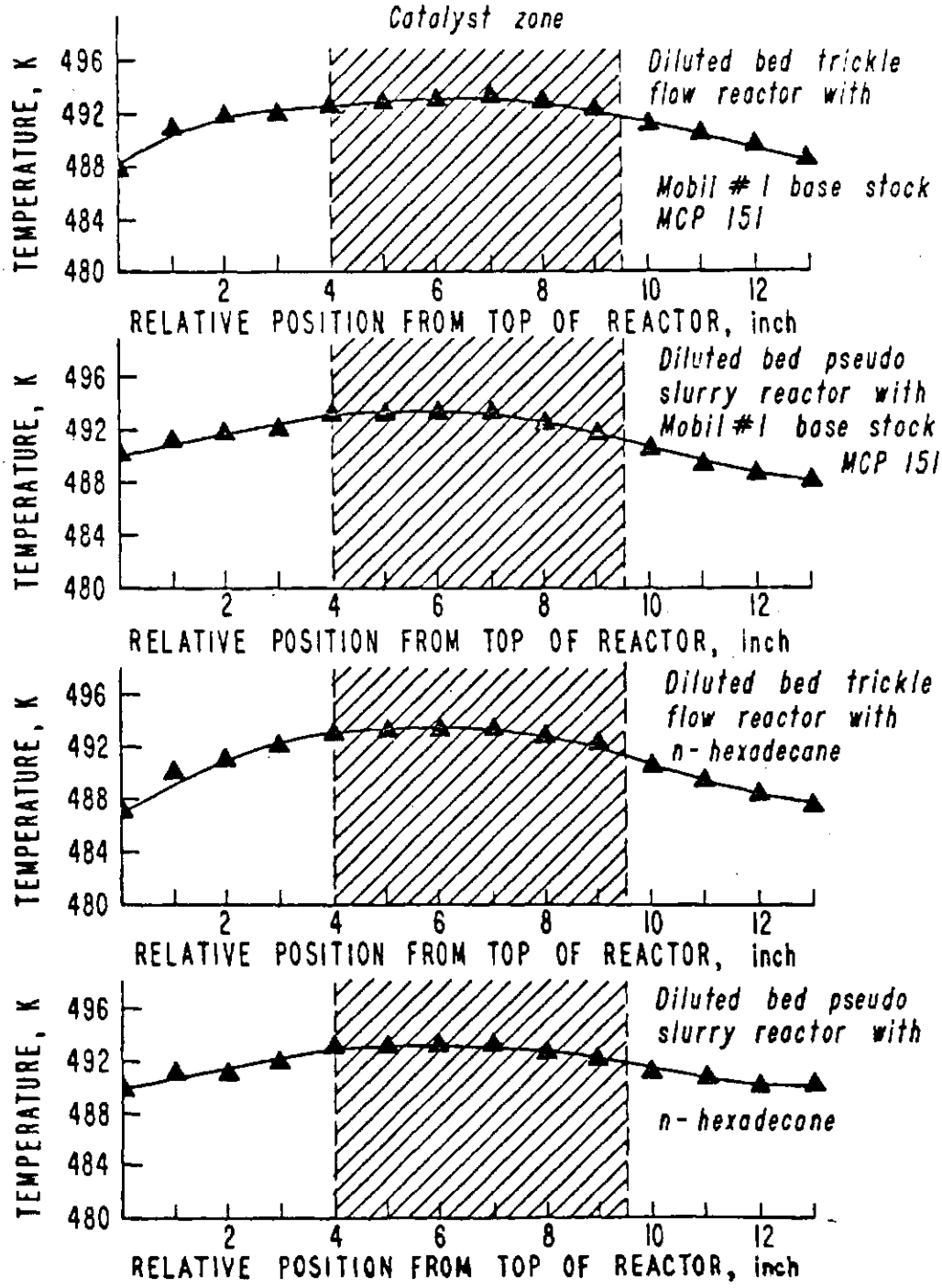


Figure 18 - Continued

conversions decreased and the yields and olefin selectivity were affected. The temperature rise in the catalyst zone was suppressed in the diluted bed relative to the dense bed at the same conversion level, that is, the temperature rise in the diluted bed was 4 K whereas in the dense bed it was 18 K. MCP 151 and n-hexadecane were both effective in controlling the temperature rise in the diluted bed reactor. The temperature rise in the dense bed reactor at different carbon monoxide conversions was determined with a catalyst charge of 9.233 grams of 20/32 mesh iron-manganese catalyst (Mn/Fe atomic ratio = 2.4:100). The conversion of carbon monoxide is plotted as a function of the catalyst bed temperature rise, in Figure 19. At a carbon monoxide conversion of ten percent a 15 K temperature rise was detected in the catalyst bed. Obviously, the catalyst surface temperature rise was even greater. The temperature profiles in the diluted bed, pseudo slurry reactor was also determined at high carbon monoxide conversions. n-Hexadecane was used as the heat transfer liquid in these experiments. The temperature profile in the diluted pseudo slurry reactor at a carbon monoxide conversion of 10.14 percent is presented in Figure 20. It confirmed again that the diluted bed, pseudo slurry reactor provided a uniform temperature distribution profile in the catalyst bed at our reaction conditions.

4.3 Effect of Heat Transfer Liquid on Activity and Selectivity

The hydrogenation of carbon monoxide has been investigated in a diluted bed reactor and in a diluted bed, pseudo slurry reactor. The heat transfer liquids evaluated in this phase of the project were

Figure 19

Temperature Rise in Dense Bed Reactor

Carbon Monoxide Hydrogenation

Carbon Monoxide Conversion versus Temperature Rise

Pressure = 3450 KPa; H_2/CO = 2/1;

Space Velocity = 1.08 $cm^3g^{-1}s^{-1}$.

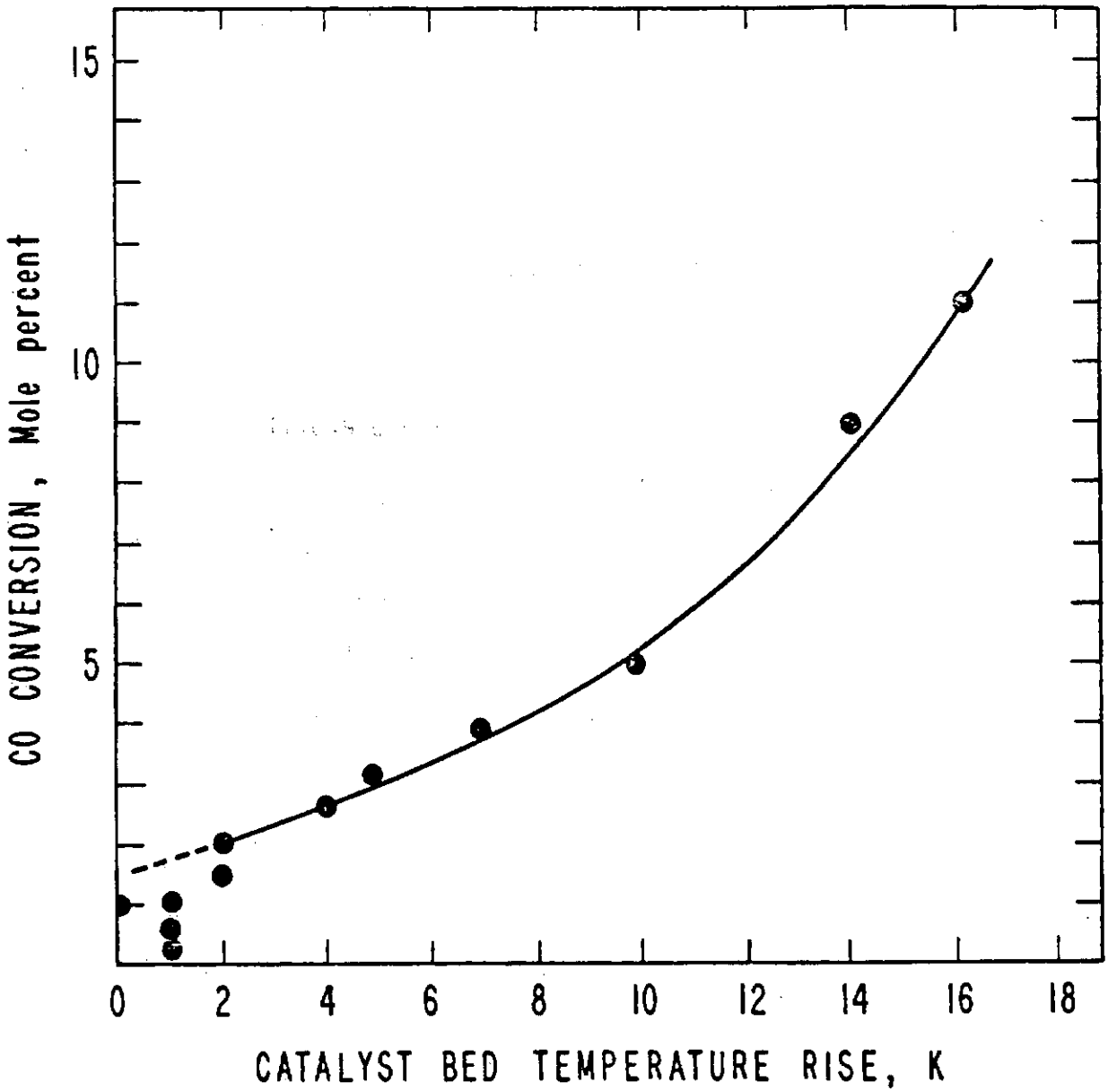

CO CONVERSION, Mole percent
15
10
5
0
2
4
6
8
10
12
14
16
18
CATALYST BED TEMPERATURE RISE, K

Figure 20

Catalyst Bed Temperature Profile

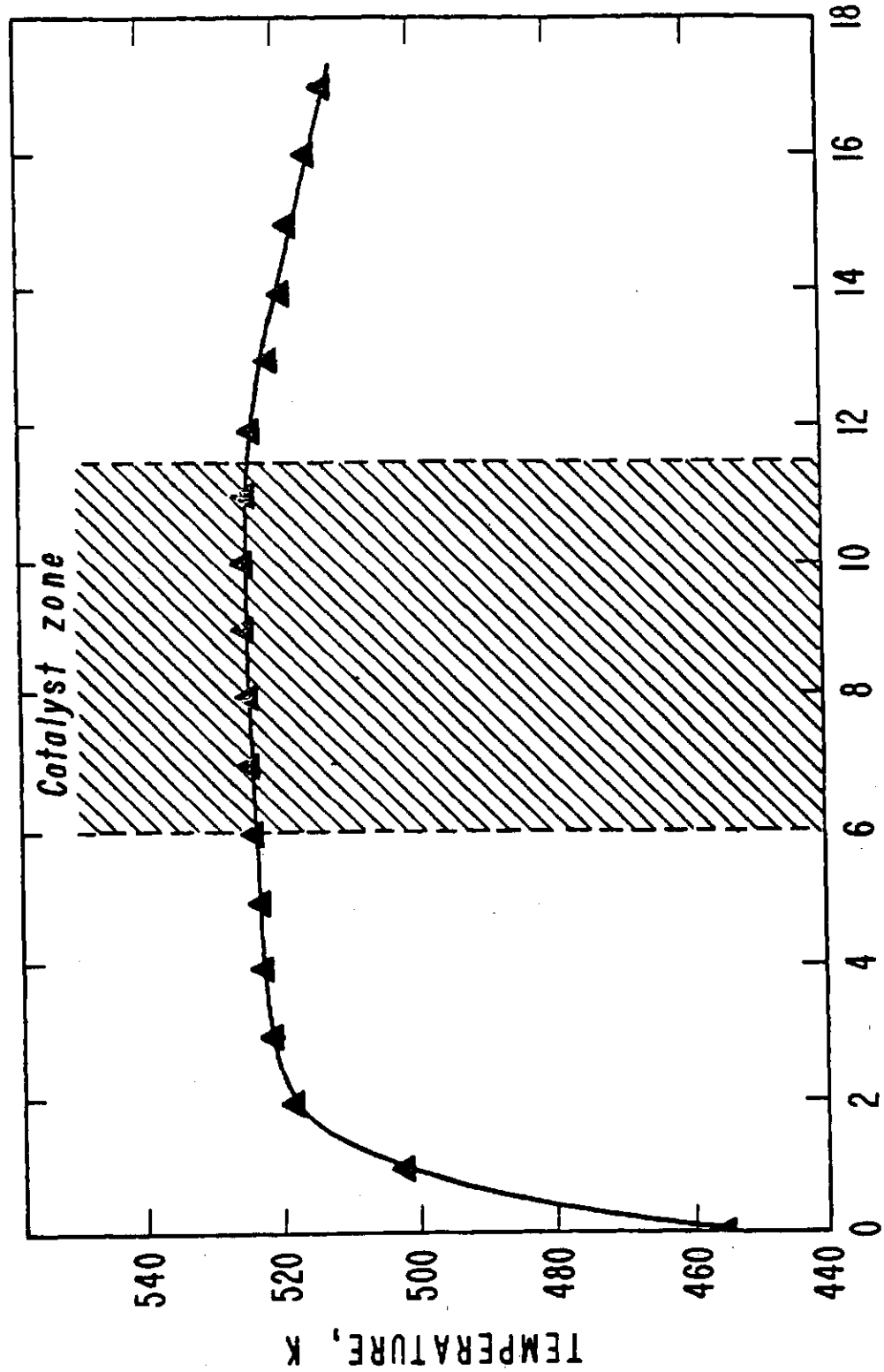
Diluted Bed Pseudo Slurry Reactor

Temperature Versus Relative Axial Distance

Pressure = 1400 KPa; H_2/CO = 2/1;

Space Velocity = 1 $cm^3 g^{-1} s^{-1}$;

n-Hexadecane Rate = 0.103 $cm^3 s^{-1}$.


Catalyst zone
TEMPERATURE, K
540
520
500
480
460
440
0
2
4
6
8
10
12
14
16
18
RELATIVE POSITION FROM TOP OF REACTOR, Inch