

mixed in a volume ratio of 1:4 in a way so as to insure a uniform distribution of the catalyst throughout the Denstone. The different reactor configurations used in this investigation are presented in Figure 12.

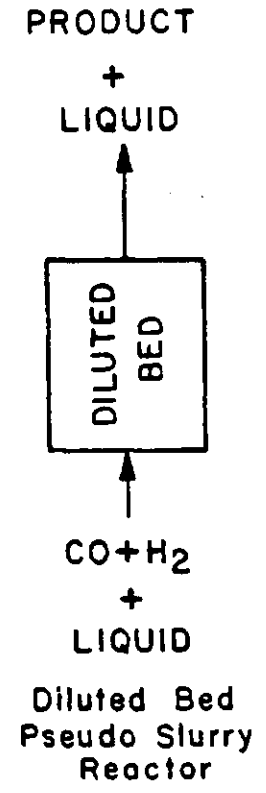
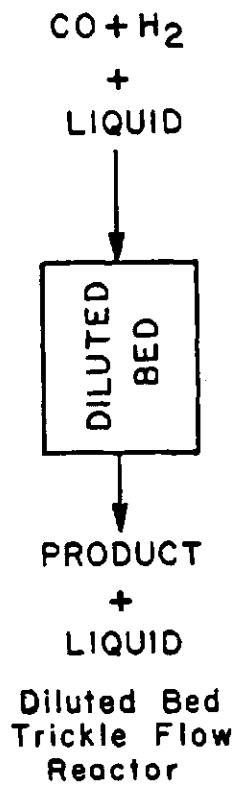
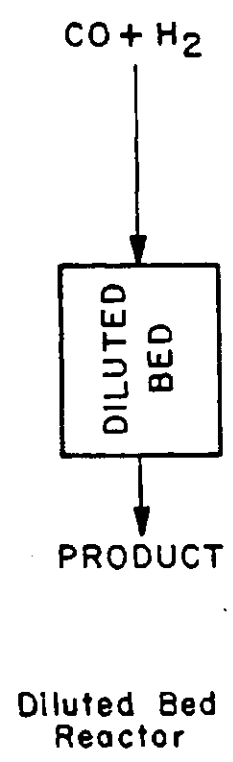
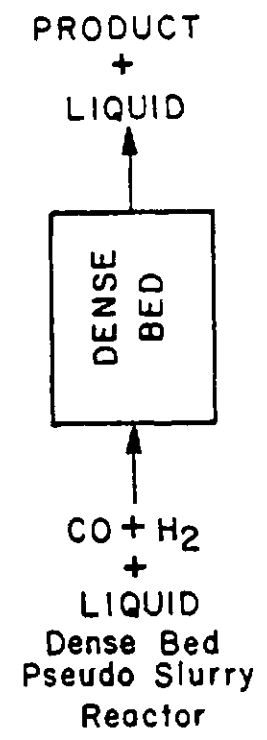
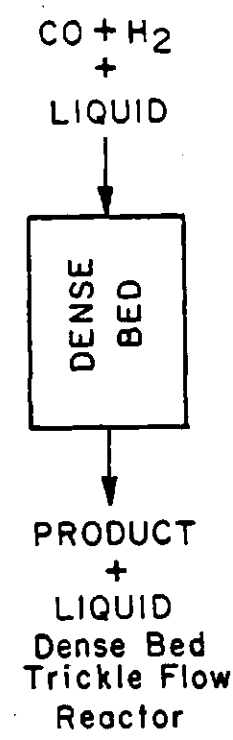
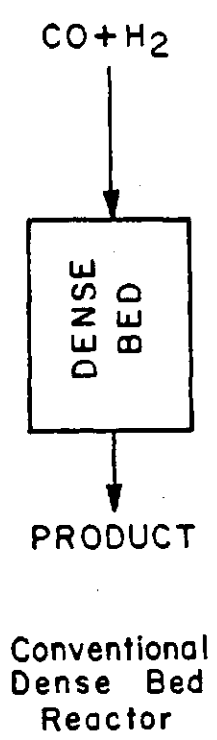
3.2 Materials

The reactant hydrogen used in this investigation was high purity grade supplied by the Stores and Receiving Department of the University of Utah. The carbon monoxide reactant used in this investigation was purchased from the Linde Specialty Gas Corporation. The helium used to test the high pressure reaction system and the nitrogen that supplied the reference gas pressure for the Grove loader back pressure regulators were also purchased from the Stores and Receiving Department of the University of Utah. Two heat transfer liquids were used in the trickle flow and pseudo slurry operations to remove the heat of reaction, that is, Mobil #1 base stock MCP 151 without any additives supplied by the Mobil Chemical Company and n-hexadecane purchased from the Sigma Chemical Company. The hydrated ferric nitrate, manganous nitrate solution and concentrated ammonium hydroxide used to prepare the coprecipitated iron-manganese catalysts were purchased from the J. T. Baker Chemical Company.

3.3 Catalyst Preparation

A standard method of preparation for the coprecipitated iron-manganese catalysts was established at the outset of this investigation. Hydrated ferric nitrate crystals (724 grams) were dissolved in 2500 cubic centimeters of deionized water with a specified amount of

Figure 12
Reactor Configurations for Different
Modes of Operation.



manganous nitrate solution depending upon the proposed manganese-to-iron weight ratio; for example, 12.696 grams of manganous nitrate solution was needed to prepare a catalyst with a manganese to iron weight ratio of 2:100. The iron-manganese solution was then heated to 373 K under continuous stirring. The coprecipitated catalyst was formed by adding concentrated ammonium hydroxide drop by drop into the homogeneous iron-manganese solution until the solution reached a pH value of 9.5. The pH of the solution was controlled accurately to guarantee complete coprecipitation. After precipitation, the catalyst was collected by filtration. The wet cake was then washed with deionized water at 373 K and filtered again. The washing procedure was repeated several times until no trace of nitrate ions was found in the filtrate. The procedure for the nitrate ion test is described in detail in Appendix A.

The wet filter cake obtained from the final filtration was dried in air in an oven at 393 K for 16 hours. The dried catalyst was crushed into small pellets by using a mortar and pestle. Catalyst pellets in the range 20/32 mesh were collected for the activity and selectivity studies. The catalyst particles smaller than 48 mesh were used to determine the composition by atomic absorption spectroscopy.

The catalyst compositions as determined by atomic absorption are listed in Table 1. The application of the atomic absorption technique to the determination of the catalyst compositions is discussed in Appendix B.

Table 1
Catalyst Compositions
Atomic Absorption Analysis

<u>Catalyst No.</u>	<u>Manganese-Iron Weight Ratio</u>
1	2.4 : 100
2	17.8 : 100
3	4.1 : 100
4	9.4 : 100
5	1.3 : 100
6	0.6 : 100
7	1.8 : 100
8	1.7 : 100
9	0.9 : 100
10	0.8 : 100
913	2.1 : 100

3.4 Operating Procedures

3.4.1 Dense Bed Catalyst Loading

The reactor was thoroughly cleaned with soap and then rinsed with deionized water and acetone. The cleaned reactor was blown dry with compressed air. The reactor outlet assembly was tightened with the thermocouple well in position. The partially assembled reactor was then mounted in a vertical position with the open end upward. The spacer tubing and the catalyst support screen were then placed in the reactor. A long tube with 1.91 cm outside diameter was used to locate the support screen at the proper position. Different sizes of the inert Denstone packing particles and catalyst were then loaded in the following order: (1) small amount of 0.32 cm x 0.32 cm Denstone 57 ceramic particles; (2) 4/14 mesh Denstone 57 ceramic particles; (3) 14/20 mesh Denstone 57 ceramic particles; (4) 20/32 mesh Denstone 57 ceramic particles; (5) 20/32 mesh catalyst pellets; (6) 20/32 mesh Denstone 57 ceramic particles; (7) 14/20 mesh Denstone 57 ceramic particles; (8) 4/14 mesh Denstone 57 ceramic particles; (9) 0.32 cm x 0.32 cm Denstone 57 ceramic particles; (10) 0.635 cm O.D. Denstone 57 ceramic balls if required. The amount of each layer depended upon the amount of catalyst to be loaded in the reactor. In each instance the catalyst bed was located in the center part of the reactor. The inlet and outlet of the catalyst bed inside the reactor were accurately located in order that the temperature profile in the catalyst bed could be accurately determined. The reactor head was then secured and the reactor was leak tested with helium at high pressures.

3.4.2. Diluted Bed Catalyst Loading

The loading procedure for the diluted bed was basically the same as that for the dense bed packing. The only difference was that the catalyst pellets were premixed with the same size Denstone 57 ceramic particles (catalyst/inert particle volume ratio = 1:4) in a bottle by rotating the bottle slowly for two minutes. This mixing procedure was found to give complete mixing, that is, all the catalyst pellets were dispersed uniformly in the white Denstone 57 ceramic particles. The Denstone 57 ceramic particles mixed with the catalyst decreased the amount of Denstone 57 particles packed below and above the catalyst bed. The position of the catalyst zone inside the reactor was carefully determined as previously described.

3.5 Catalyst Pretreatment

The loaded and assembled reactor was placed in the furnace. The catalyst was reduced in situ in flowing hydrogen (space velocity = $0.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) at 673 K and ambient pressure for 20 hours. A higher reducing temperature, 773 K, was used in the initial experiments; however, it was found by Kim⁹⁴ that 673 K was adequate to reduce the catalyst. The water produced during the reduction was trapped in an ice trap.

3.6 Gas Phase Reaction Operating Procedure

In the description of the operating procedures for the hydrogenation of carbon monoxide in the dense-bed and diluted-bed modes of operation, the identifying numbers and letters refer to Figure 9:

1. The loaded reactor is placed in position and the reactor furnace is closed.
2. The reactant gas (hydrogen and carbon monoxide) is introduced into the reactor from the top when operating in the dense bed and diluted bed operating modes, thus, valves K1, M1, K3, K7, and K8 are opened and valves K2, K4, and K6 are closed.
3. The electrical connections to the reactor furnace, heating tapes, and instruments are checked for safe operation. The temperature controllers are set at a position 30 K above the desired reaction temperature. The gas-liquid separators (I and J) are heated to 383 K.
4. The mass flow controllers (B1 & B2) are set at zero and the flow controllers are activated.
5. The hydrogen and carbon monoxide cylinder valves are opened and the delivery pressures are set at 1000 KPa above the desired reactor outlet pressure.
6. The desired flowrates of hydrogen and carbon monoxide are set on the mass flow controller (B1 and B2) using the calibration curves (see Appendix C). The actual flow rates are recorded from the flow controller readout and the position of the ball in the flowmeter (D) is recorded.
7. The reference gas pressure (nitrogen) to the Grove Loader back pressure regulator (G1) is increased in increments until the system pressure reaches the desired reaction pressure.

8. The reactor temperature profile is checked and the reactor furnace temperature is adjusted as required.
9. The reactor system is stabilized for 30 minutes after the desired reaction temperature and pressure have attained. After 30 minutes the system is in a state of thermal and hydrodynamic stability.
10. The reactor/catalyst bed temperature profile is recorded.
11. The effluent gas is passed through a wet test meter to monitor its flowrate.

3.7 Trickle Flow Reactor Operating Procedure

When the system is operated in the trickle flow mode, a heat transfer liquid (n-hexadecane or MCP 151) is pumped downflow through the reactor along with the reactant gas.

1. The loaded reactor is placed in position, and the reactor furnace is closed.
2. Valves K1, M1, K3, K4, K6, and M3 are opened and valves K2, K5, K7, K8, and M2 are closed.
3. The electrical connections to the reactor furnace, heating tapes, heat transfer liquid circulation pump (L), and instruments are checked for safe operation. The temperature controllers are set at a position 30 K above the desired reaction temperature.
4. The transfer line, the heat transfer liquid reservoir, and the circulation lines are checked to ensure adequate flow of liquid.

5. The mass flow controllers (B1 and B2) are set at zero and the flow controllers are activated.
6. The hydrogen and carbon monoxide cylinder valves are opened and the delivery pressures are set at 1000 KPa above the desired reactor outlet pressure.
7. The desired hydrogen and carbon monoxide flow rates are set on the mass flow controller (B1 and B2) using the calibration curves (see Appendix C). The actual flow rates are recorded from the flow controller readout and the position of the ball in the flowmeter (D) is recorded.
8. The heat transfer liquid circulation pump is started and the pumping rate is set at 0.103 cm^3 per second by adjusting the micrometer.
9. The reference gas pressure (nitrogen) to the Grove Loader back pressure regulator (G2) is increased in increments until the system pressure reaches the desired reaction pressure.
10. The liquid levels in the gas-liquid separators are monitored by the Jerguson liquid level indicators (J1 and J2). When liquid level in the high pressure gas-liquid separator (I) reaches about two-thirds of the full height, valve M2 is opened until the liquid level in the site glass (J1) drops at a very slow rate. Valve M3 is closed incrementally until the liquid level in the site glass (J1) stabilizes.
11. The heat transfer liquid collected in the low pressure gas-liquid separator is filtered and then recycled back to the system.

12. The reaction system is stabilized and the temperature profile in the catalyst bed is recorded.

3.8 Pseudo Slurry Reactor Operating Procedure

The operating procedures for the pseudo slurry reactor operating mode are exactly the same as those described for the trickle flow mode except that in the beginning, valves K1, M1, K4, K8, K5, and M3 are opened and valves K2, K3, K6, K7, and M2 are closed. This arrangement allows the reactant gas and the heat transfer liquid pass upflow through the reactor.

3.9 Shut-Down Procedure

The shut-down procedures are the same regardless of the operating mode, that is, dense-bed reactor, diluted-bed reactor, diluted bed trickle flow reactor, and diluted-bed pseudo slurry reactor.

1. After the final gas sample has been injected into the gas chromatograph, the temperature controllers are deactivated and all heaters on the systems are shut off.
2. The heat transfer liquid circulation pump (L) is shut down and valves M2 and M3 are closed.
3. The hydrogen, carbon monoxide, and nitrogen cylinder valves are closed and the regulators are depressured.
4. The metering valve connected to the Grove Loader (G1) nitrogen outlet is opened slowly to release the nitrogen pressure which depressures the system.

5. The system is purged with helium after it has returned to room temperature and atmospheric pressure.
6. The reactor is removed from the system, the catalyst is withdrawn from the reactor, and the reactor is cleaned.

3.10 Sample Analysis

The gas samples taken during the course of the reaction were analyzed in a series 5830A Hewlett-Packard gas chromatograph using helium as carrier gas (45 cm³ per minute at 273 K). Two 6.1 m x 0.3175 cm stainless steel columns with Chromosorb 102 80/100 mesh powder as packing material were used to analyze the gas product. The thermal conductivity detector (TCD) and the flame ionization detector (FID) were used alternatively to analyze hydrogen, nitrogen, carbon monoxide, carbon dioxide, and water (TCD) and the hydrocarbons (FID). Table 2 lists the operating conditions and oven temperature program for the gas chromatograph.

The liquid hydrocarbon product collected from the condenser for the long-term gas-phase reaction was analyzed in a series 5730A Hewlett Packard gas chromatograph with dual flame ionization detectors (FID) using a 3 percent Dexil 300 on Anachrome Q column (6.35 mm O.D. x 0.46 m long) with helium as carrier gas. The procedure was similar to the ASTM D2887-70T method.

3.11 Calculation of Product Selectivities

Calculations based on hydrogen and oxygen balances were not attempted due to the lack of precision in the hydrogen and water analysis. Carbon was chosen as the basis for the calculation of the

Table 2

Operating Conditions and Oven Temperature Program
for Gas Chromatographic Analysis

TEMP 1	0	
TIME 1	5.0	
RATE	10.00	
TEMP2	200	
TIME2	75.0	
INJ TEMP	200	200
FID TEMP	250	250
TCD TEMP	250	250
OVEN MAX	250	
CHT SPD	0.20	
ATTN 2+	4	
TCD SGNL	-A+B	
SLP SENS	0.10	
AREA REJ	1	
FLOW A	45	
FLOW B	45	
OPTN	0	
4.0 FID SGNL	-A+B	
4.0 ATTN 2+	10	
4.0 SLP SENS	1.00	
4.1 ZERO		
4.2 ZERO		
8.0 TCD SGNL	-A+B	
8.0 ATTN 2+	4	
8.0 SLP SENS	0.10	
8.1 ZERO		
8.2 ZERO		
10.5 ZERO		
14.0 FID SGNL	-A+B	
14.0 ATTN 2+	10	
14.0 SLP SENS	1.00	
14.1 ZERO		
14.2 ZERO		
18.5 TCD SGNL	-A+B	
18.5 ATTN 2+	4	
18.5 SLP SENS	0.10	
18.6 ZERO		
18.7 ZERO		
21.0 FID SGNL	-A+B	
21.0 ATTN 2+	10	
21.0 SLP SENS	1.00	
21.1 ZERO		
21.2 ZERO		
35.0 ATTN 2+	10	
35.0 SLP SENS	0.30	
48.0 ATTN 2+	10	
48.0 SLP SENS	0.10	

conversion and product selectivities. A BASIC computer program was developed to compute conversions and selectivities in this investigation (see Appendix D). The program is currently stored on a tape disk at the University of Utah Computer Center.

The response areas of one cubic centimeter of nitrogen, carbon monoxide, carbon dioxide, and the hydrocarbon products of carbon monoxide hydrogenation reaction were calibrated and the relative response factors were stored in the computer program. Carbon monoxide and methane were chosen as the standards for the TCD and FID detectors, respectively. Prior to each analysis, one cubic centimeter of carbon monoxide and methane was injected into the chromatograph and the response areas were used to calculate the response areas of all the components. The carbon monoxide conversion and the selectivities for the different products were calculated as follows; that is,

$$\bar{X} = \text{CO} + \text{CO}_2 + \sum_{i=1}^{25} i \text{C}_i\text{H}_{2i+2} + \sum_{i=1}^{25} i \text{C}_i\text{H}_{2i} + \sum_{i=1}^3 i \text{C}_i\text{H}_{2i+1}\text{OH}$$

(all in the product)

$$Y = \text{CO}_2 + \sum_{i=1}^{25} i \text{C}_i\text{H}_{2i+2} + \sum_{i=1}^{25} i \text{C}_i\text{H}_{2i} + \sum_{i=1}^3 i \text{C}_i\text{H}_{2i+1}\text{OH}$$

(all in the product)

$$\text{Input - output CO conversion} = \frac{X_0 - (\bar{X} - Y)}{X_0} \cdot 100$$

$$\text{Output base CO conversion} = (Y/\bar{X}) \cdot 100$$

$$\text{Material balance} = \frac{X_0 - \bar{X}}{X_0} \cdot 100$$

$$\text{Carbon dioxide selectivity} = \frac{\text{CO}_2 \text{ in the product}}{Y} \cdot 100$$

$$\text{CH}_4 \text{ selectivity} = \frac{\text{methane in the product}}{Y} \cdot 100$$

$$\text{C}_2\text{-C}_4 \text{ selectivity} = \frac{\text{C}_2\text{-C}_4 \text{ in the product}}{Y} \cdot 100$$

$$\text{C}_5^+ \text{ selectivity} = \frac{\text{C}_5^+ \text{ in the product}}{Y} \cdot 100$$

$$\text{ROH selectivity} = \frac{\text{alcohols in the product}}{Y} \cdot 100$$

In the above equations, X_0 is the total amount of carbon monoxide that flowed into the system per unit time, Y is the total carbon product yield in the exit stream per unit time and \bar{X} is the summation of the total carbon in the products and the unreacted carbon monoxide in the exit stream per unit time. The C_5^+ fraction is the yield of hydrocarbon products containing five carbon atoms or more in the reactor effluent.

EXPERIMENTAL RESULTS

Prior to the initiation of the catalyst testing program it was necessary to determine whether the material from which the reactor had been fabricated or the Denstone 57 particles exhibited catalytic activity for the conversion of carbon monoxide and hydrogen. The hydrogenation of carbon monoxide was attempted in both a blank reactor and a reactor packed only with the Denstone 57 ceramic particles. The experiments were conducted at a reactor pressure of 3450 KPa, a hydrogen to carbon monoxide ratio of 2:1, and a flow rate of $10 \text{ cm}^3 \text{ s}^{-1}$. It was found that even at a reaction temperature of 628 K neither the stainless steel reactor nor the Denstone 57 ceramic particles contributed significantly to the conversion of carbon monoxide hydrogenation at the standard reaction conditions (see Appendix E). We were convinced that during the activity tests of the iron/manganese catalysts, the catalyst was the only entity that contributed to the conversion of the carbon monoxide and hydrogen.

4.1 Long Term Catalyst Deactivation Test

The long term activity and selectivity of a coprecipitated iron/manganese catalyst (iron to manganese atomic ratio = 2.4:100) was determined at standard operating conditions for the diluted bed

mode of operation. The experiment ran continuously for 100 hours. After completion of the standard catalyst reduction procedure, the catalyst was further stabilized in hydrogen and carbon monoxide (hydrogen-to-carbon monoxide ratio of 2 and space velocity of $0.4 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) at a pressure of 3450 KPa and a temperature of 463 K for 16 hours. The reactor operating variables for the deactivation tests were: total reactor pressure of 3450 KPa, reaction temperature of 523 K, hydrogen-to-carbon monoxide ratio of 2 and a space velocity of $1 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. The results of the deactivation test in the diluted bed reactor are presented in Figures 13 through 15. No significant change in catalyst activity as reflected by carbon monoxide conversion was observed during the course of the deactivation test (Figure 13). however, there was a slight (~ 20%) decline in olefin selectivity for the $\text{C}_2\text{-C}_4$ hydrocarbon fraction (Figure 13). The $\text{C}_2\text{-C}_4$ hydrocarbon and methane yields were independent of time on stream up to 100 hours (Figure 14). A slight decline in C_5^+ liquid yield with time on stream was observed (Figure 15). The carbon dioxide yield increased with time on stream and at 100 hours was ~ 15 percent greater than the initial yield obtained with the fresh catalyst. This increase in carbon dioxide yield is most likely related to an enhanced activity of the aged catalyst for the water gas shift reaction relative to the fresh catalyst.

The long term activity and selectivity trends for an iron/manganese catalyst (manganese to iron atomic ratio = 2.1:100) in the diluted bed, pseudo slurry reactor have been determined. n-Hexadecane was used as the heat transfer liquid in this experiment.

Figure 13

Long Term Activity and Selectivity Test
Diluted Bed Reactor; Iron-Manganese Catalyst

Mn/Fe Atomic Ratio = 2.4/100

Carbon Monoxide Conversion and

C₂-C₄ Olefin Selectivity

Temperature = 523 K; Pressure = 3450 KPa;

H₂/CO = 2/1; Space Velocity = 1.08 cm³g⁻¹s⁻¹.

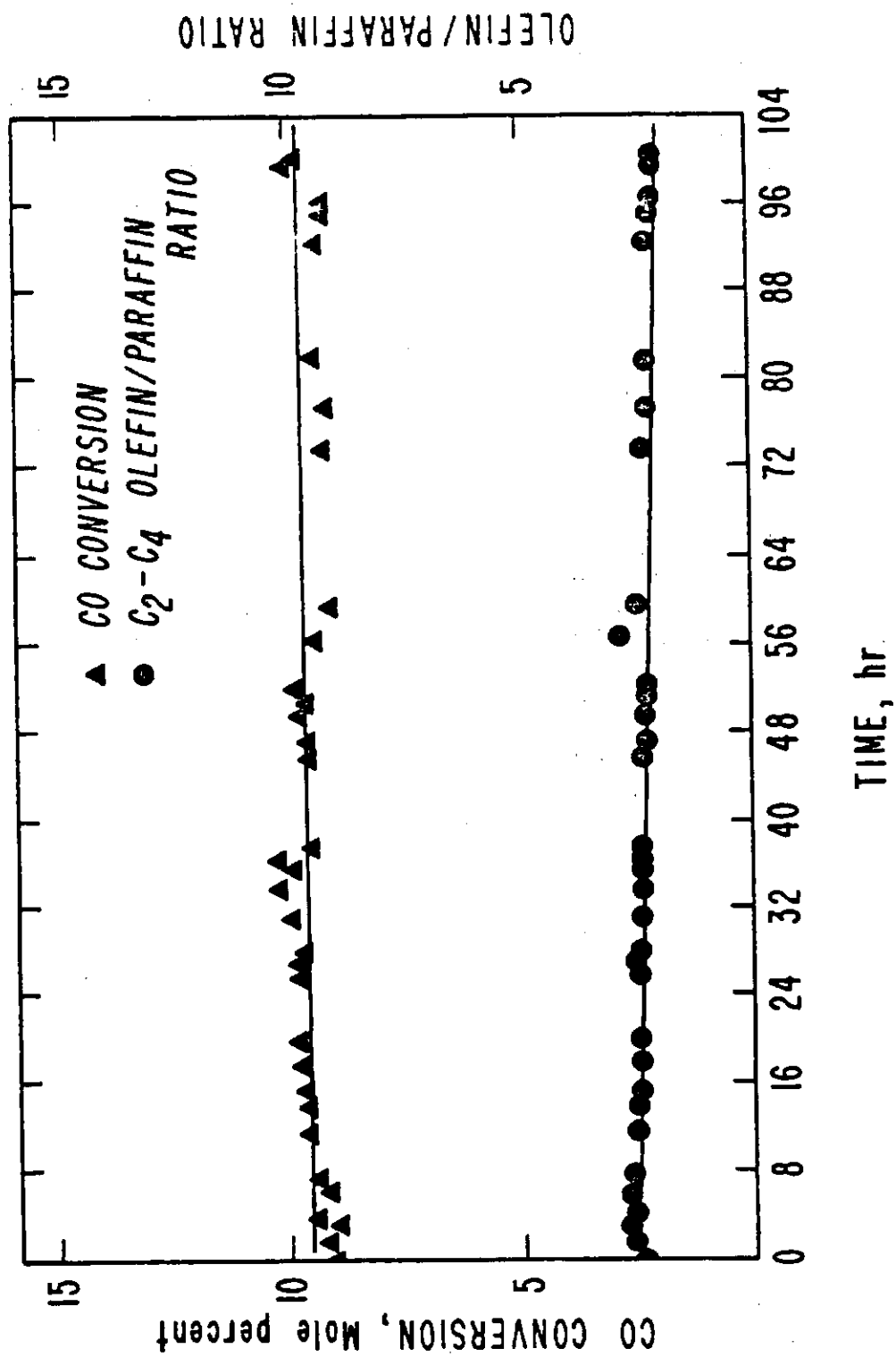


Figure 14

Long Term Activity and Selectivity Test
Diluted Bed Reactor; Iron-Manganese Catalyst
Mn/Fe Atomic Ratio = 2.4/100
Methane and C₂-C₄ Hydrocarbon Yield
Temperature = 523 K; Pressure = 3450 KPa;
H₂/CO = 2/1; Space Velocity = 1.08 cm³g⁻¹s⁻¹.