Figure 74

Effect of $H_2$/CO Ratio on Olefin Selectivity

Diluted Bed, Pseudo Slurry Reactor

Temperature = 503 K; Pressure = 2600 KPa;

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

Heat Transfer Liquid Flow Rate (n-C16) = 0.103 $cm^3s^{-1}$.

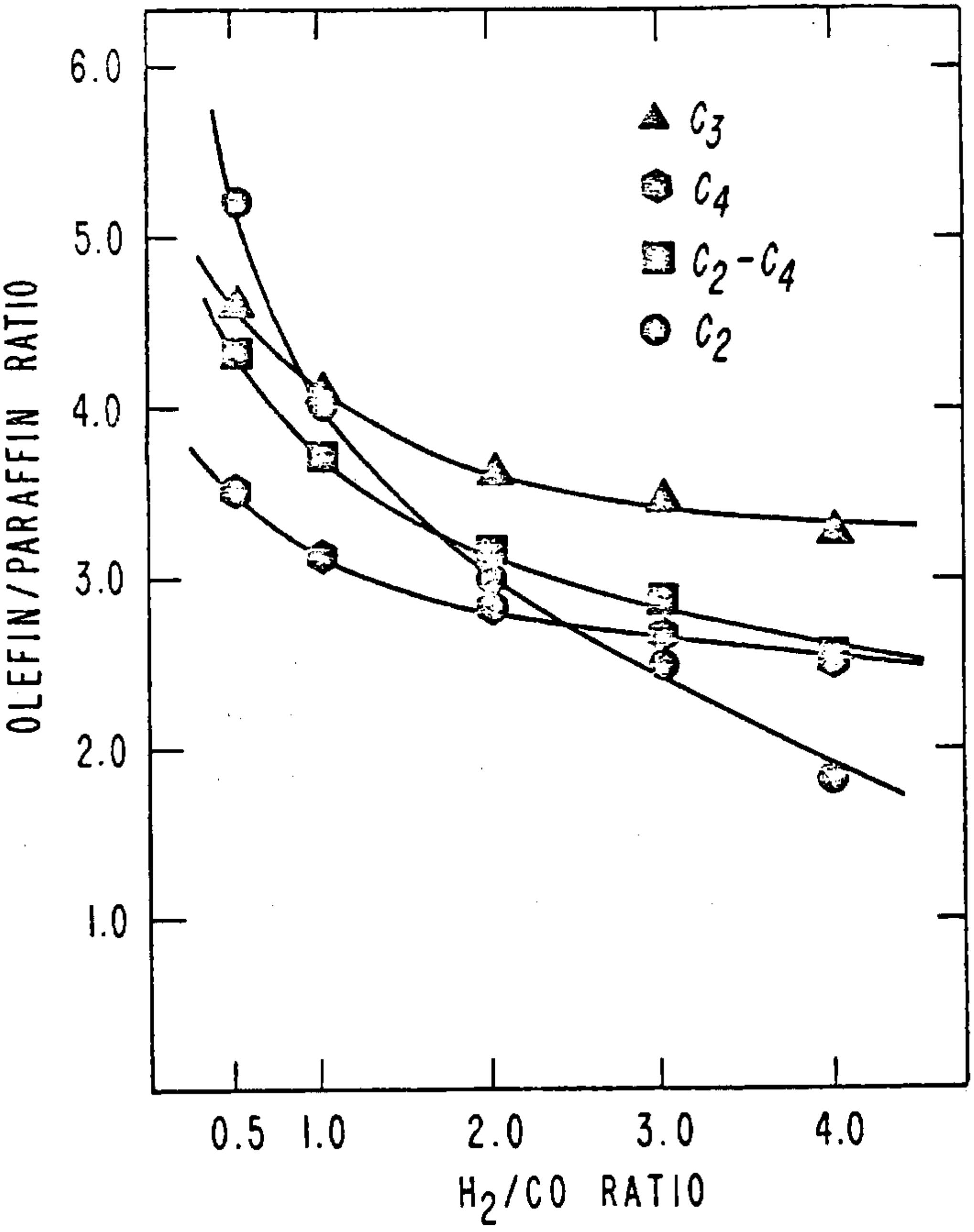

6.0
5.0
4.0
3.0
2.0
1.0
OLEFIN/PARAFFIN RATIO
0.5
1.0
2.0
3.0
4.0
$H_2$/CO RATIO
▲ $C_3$
⬢ $C_4$
■ $C_2$-$C_4$
● $C_2$

Figure 75

Effect of $H_2$/CO Ratio on Olefin Selectivity
Diluted Bed, Pseudo Slurry Reactor
Temperature = 503 K; Pressure = 3200 KPa;
Space Velocity = 1 $cm^3g^{-1}s^{-1}$;
Heat Transfer Liquid Flow Rate (n-C16) = 0.103 $cm^3s^{-1}$.

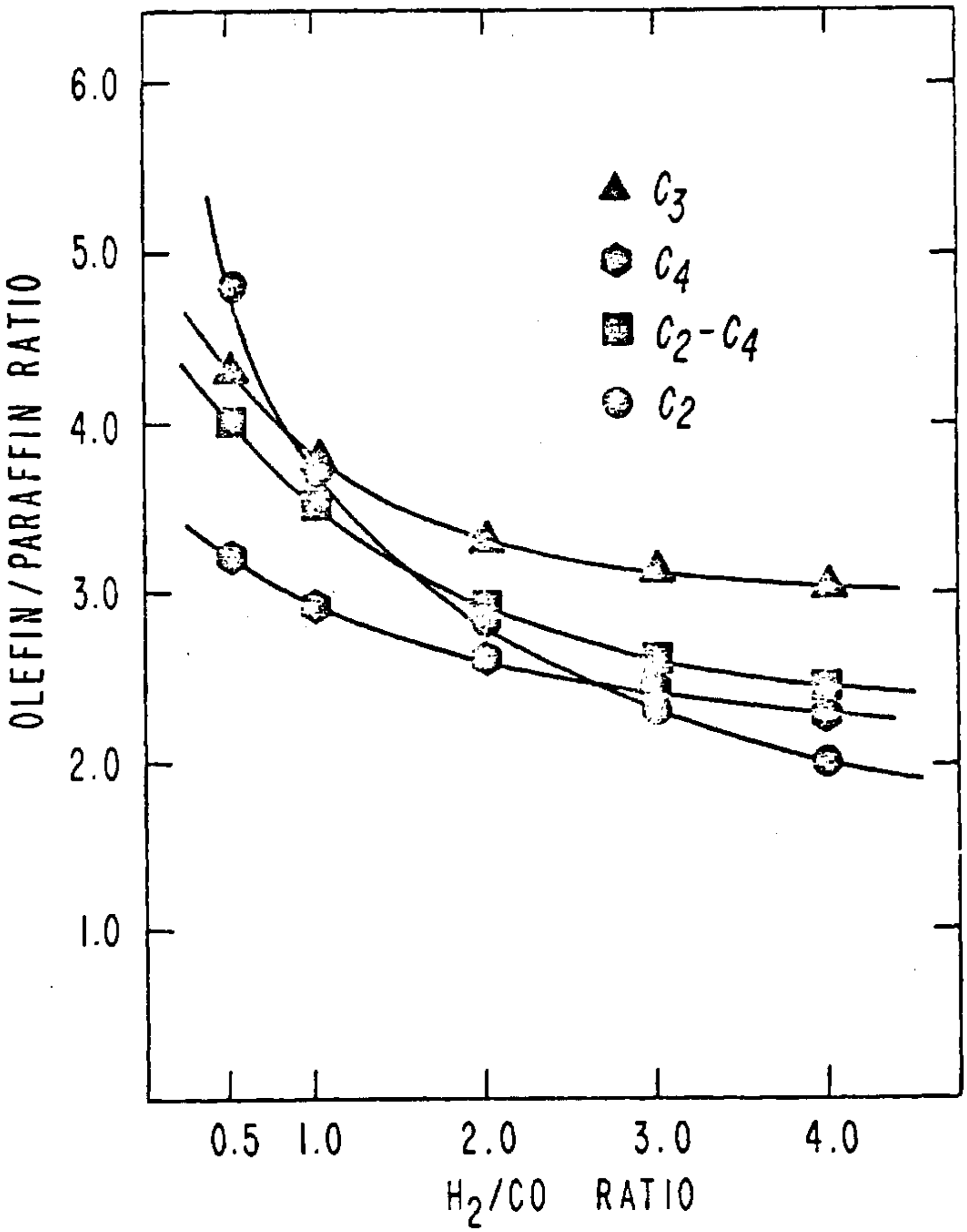

▲ $C_3$
⬢ $C_4$
■ $C_2$-$C_4$
● $C_2$
OLEFIN/PARAFFIN RATIO
6.0
5.0
4.0
3.0
2.0
1.0
0.5
1.0
2.0
3.0
4.0
$H_2$/CO RATIO

Figure 76

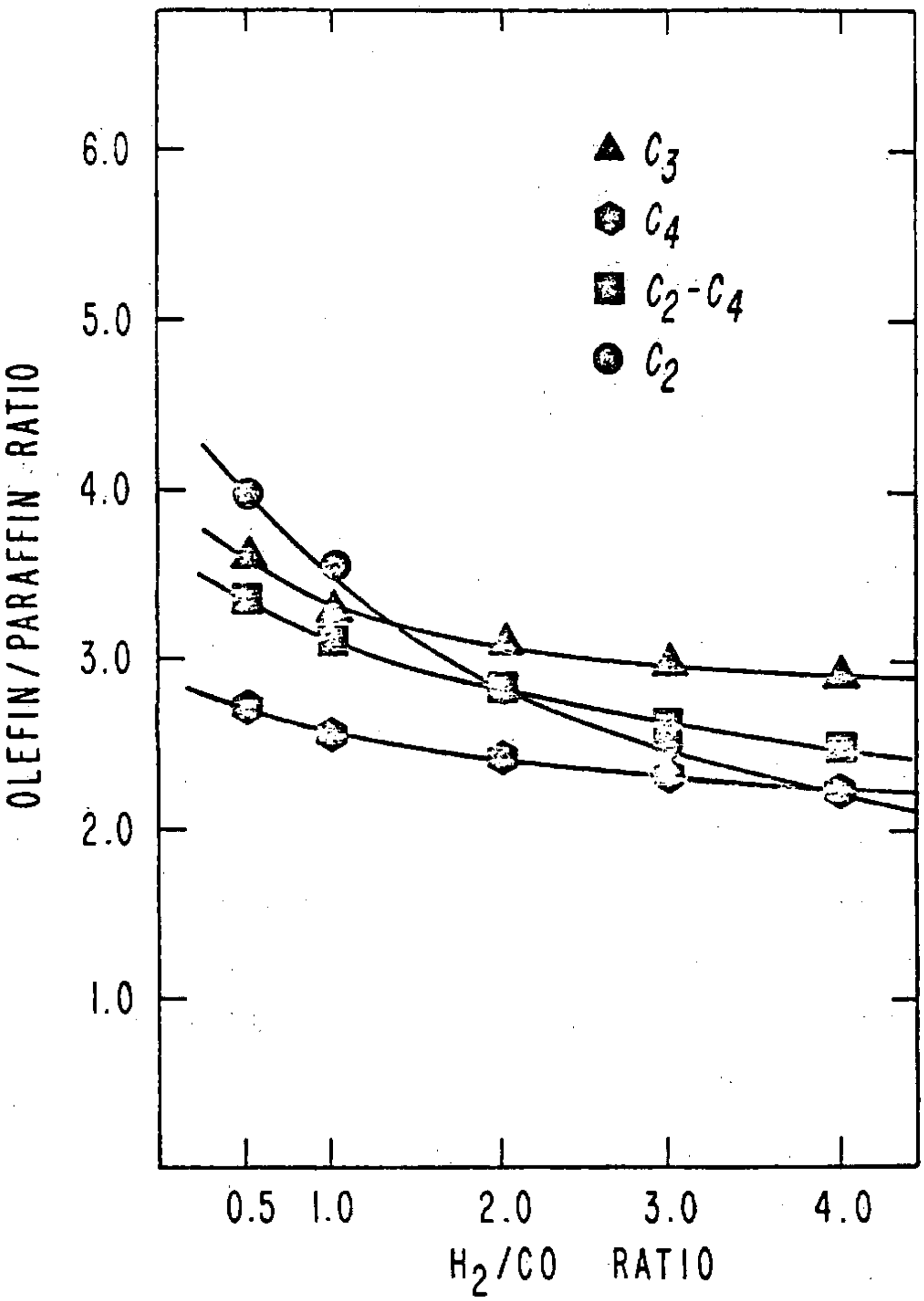
Effect of $H_2$/CO Ratio on Olefin Selectivity

Diluted Bed, Pseudo Slurry Reactor

Temperature = 503 K; Pressure = 4400 KPa;

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

Heat Transfer Liquid Flow Rate (n-C16) = 0.103 $cm^3s^{-1}$.


▲ $C_3$
⬢ $C_4$
■ $C_2$-$C_4$
● $C_2$
OLEFIN/PARAFFIN RATIO
6.0
5.0
4.0
3.0
2.0
1.0
0.5
1.0
2.0
3.0
4.0
$H_2$/CO RATIO

# CHAPTER 5

# DISCUSSION

## 5.1 Long-Term Catalyst Activity Test

The development of catalysts that exhibit high activity, desired selectivity, and reasonably long life has been the focus of the majority of the carbon monoxide hydrogenation investigations since the initial studies of Sabatier.[12] Although hundreds of catalysts have been evaluated for the Fischer-Tropsch synthesis,[1,2] little data have been reported on the long-term activity and selectivity of catalysts for the hydrogenation of carbon monoxide. In order to obtain reliable process data, the stability of the catalyst with respect to activity (conversion of carbon monoxide) and selectivity (olefin-to-paraffin ratio) must be determined and the run time to achieve steady state determined. It was observed in this investigation that after the standard catalyst pretreating procedure used by Tsai[7] and Yang,[3] more than eight hours was needed to stabilize the coprecipitated iron-manganese catalysts. This catalyst induction period was later confirmed by Tsai.[95,96]

The long-term activity and selectivity tests with the coprecipitated iron-manganese catalysts were conducted in both the diluted-bed reactor and the diluted-bed, pseudo slurry reactor. The data from the 100-hour continuous evaluation test in the diluted-bed reactor are presented in Figure 13 to Figure 15. After 100 hours on-stream, the catalyst exhibited the same activity level as was observed at the outset of the experiment, that is 9.4% and 9.5% conversion of carbon monoxide at 523 K, respectively. The carbon dioxide yield increased from 12 mole percent to 14 mole percent during the course of the experiment, resulting in relatively small declines in the yields of the hydrocarbon products. This would seem to indicate that the long-term catalyst coking/deactivation rate is relatively low at the standard operating conditions used in this investigation and that the catalyst is stabilized with respect to deactivation after 8 - 12 hours on-stream. The long term activity and selectivity test with the iron-manganese catalyst in the diluted-bed, pseudo slurry reactor (n-hexadecane as heat transfer liquid) exhibited similar trends with time on-stream as indicated in Figure 16 and Figure 17. The catalyst activity and selectivity did not change during the course of the experiment (24 hours on-stream). This consistent catalyst performance makes later investigations meaningful.

## 5.2 Test of Schulz-Flory Distribution Law

Henrici-Olive and Olive[73] proposed that the hydrogenation of carbon monxide could be treated as a typical polymerization reaction and therefore could be fit by the Schulz-Flory distribution law,

$$\log_{10}(m_p/p) = \log_{10}(\ln_e^2\alpha) + p \log_{10}\alpha$$

where $m_p$ is the weight fraction of hydrocarbons with a carbon number of $p$ and $\alpha$ is the chain growth probability. The Schulz-Flory distribution law was tested with the data obtained during the long term deactivation experiment with the diluted-bed mode of operation (Figures 28 and 29). The $\log_{10}(m_p/p)$ was plotted versus P and a straight line was drawn for P = 3 to P = 15. The low values of $\log_{10}(m_p/p)$ for those hydrocarbons with a carbon number between 6 to 10 can be explained due to inefficient sampling techniques and the need to combine the gas analysis and the liquid analysis in order to achieve a total material balance on the system. The evaporation of dissolved light ends ($C_6$-$C_7$) from the liquid sample and the condensation of heavier ends ($C_8$-$C_{10}$) in the gas sampling system could account for the hydrocarbon material lost in the overlap region ($C_6$-$C_{10}$). The slightly higher values of methane and lower values of $C_2$ hydrocarbons can be explained as a result of the ethylene hydrogenolysis reaction over the iron-manganese catalyst at the reaction conditions:

$$C_2H_4 + 2H_2 \longrightarrow 2CH_4$$

The occurrence of this reaction was confirmed by Schulz and coworkers[77] by adding $^{14}C$-tagged ethylene to the synthesis gas and by monitoring the product hydrocarbons by radio gas chromatography. Ninety percent of the ethylene added to the reaction mixture was converted to other hydrocarbons over cobalt catalysts. It was also reported[77] that propene underwent hydrogenolysis reactions when added to the reaction mixture as indicated by the following reaction sequence:

$$CH_3CH{=}CH_2 + 2H_2 \longrightarrow H_3C\text{-}CH_3 + CH_4$$

$$CH_3CH{=}CH_2 + 3H_2 \longrightarrow 3CH_4 \, .$$

These olefin hydrogenolysis reactions also occurred over iron catalysts, however, not to the same extent as over the cobalt catalysts. The data presented in Figure 28 and Figure 29 seem to agree with the explanation proposed by Schulz. The reason for the change of slope in the region of carbon numbers greater than 15 is still not clear. The relatively low mobility of the heavier hydrocarbons on the catalyst surface could favor the chain propogation reaction and resulted in greater $\alpha$ value and slope. Schulz, Rosch and Gökcebay[23] investigated the carbon monoxide hydrogenation reaction over a series of iron and cobalt catalysts and reported that a larger (less negative) slope was obtained in the region of carbon numbers greater than $C_{10}/C_{13}$. Hydrocarbon products with a carbon number greater than 18 were not reported. Data on the hydrogenation of carbon monoxide reported earlier by Storch[1] were also analyzed to fit the Schulz-Flory distribution law by Henrici-Olivé and Olivé,[73] but hydrocarbons with a carbon number greater than 15 were not included.

If the graphical representation of $\log_{10}(m_p/p)$ versus p gives a straight line for a given polymerization reaction, and $\alpha$, the probability of chain growth, as determined from the slope (= $\log_{10} \alpha$) and from the intercept with the ordinate [= $\log_{10}(\ln_e^2 \alpha)$], are in good agreement, the molecular weight distribution of this polymer obeys the Schulz-Flory distribution law. At a reaction temperature of 518 K and a total pressure of 3450 KPa, hydrocarbon products with a carbon number p = 3 to p = 15 fell on a straight line (Figure 28). The slope and intercept of this line were calculated by a linear regression method. The values of chain growth probability, α, calculated from slope and intercept were 0.598 and 0.594, respectively (see Table 7). The similarity of the values calculated from the slope and the intercept of the linear equation indicated that the carbon monoxide hydrogenation in a diluted bed reactor over an iron-manganese (Mn/Fe ratio = 2.4:100) catalyst obeyed the Schulz-Flory distribution law up to a carbon number of 15. For hydrocarbon products with a carbon number greater than 15, the data points were also correlated by a straight line; however, the values of α calculated from the slope (α = 0.722) and the intercept (α = 0.860) of this linear equation indicated that carbon monoxide hydrogenation no longer obeyed the Schulz-Flory distribution law. Similar results were obtained for the hydrogenation of carbon monxide in a diluted-bed reactor at other reaction conditions (Figure 29 and Table 8). Satterfield and Huff[79] determined that the chain growth probability factor, α, was in the range of 0.67 and 0.71, when carbon monoxide was reacted with hydrogen over a fused iron catalyst. Satterfield also calculated the values of α from the literature for the hydrogenation of carbon monoxide over iron catalysts. The range of values was 0.55 to 0.94. Deckwer and coworkers[86] used an iron-manganese catalyst for carbon monoxide hydrogenation in a slurry reactor and observed a chain growth probability value of 0.675. The values of α calculated in this investigation (0.60 and 0.66) are somewhat lower than Deckwer's value; however, they still are in the range of

Satterfield's review. It shows that for the hydrogenation of carbon monoxide over the coprecipitated iron-manganese catalyst in a diluted-bed reactor, the product distribution obeys the Schulz-Flory distribution law up to a carbon number of 15. For hydrocarbons with a carbon number greater than 15, the experimental data do not fit the Schulz-Flory distribution law.

## 5.3 Effects of Reactor Modes on Carbon Monoxide Hydrogenation

Carbon monoxide hydrogenation is a highly exothermic reaction and the heat released can cause temperature excursions in the catalyst bed. The effects of the heat of reaction on the catalyst temperature were investigated in different types of reactors: (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. The reactors were operated at a set standard reaction condition and the observed catalyst bed temperature profiles for the different reactors were recorded. The catalyst temperature profiles are presented in Figure 18. The dense-bed reactor exhibited the highest temperature rise at the standard reaction condition. The presence of heat transfer liquid (MCP 151) in the reactor suppressed a temperature rise in the catalyst bed. However, at a carbon monoxide conversion of 4.24%, the dense-bed trickle flow reactor (MCP 151 heat transfer liquid) still exhibited a temperature rise of 5 K. It is believed that at a higher carbon monoxide conversion level, the temperature rise in the dense-bed trickle flow reactor would be even larger. The observed temperature rise in the dense-bed trickle flow reactor prevented this reactor mode from being considered as a suitable reactor for carbon monoxide hydrogenation. In a dense bed, pseudo slurry reactor, almost no temperature rise was observed as shown in Figure 18. This was because of the lower carbon monoxide conversion (3.14% compared to 7.34% in the dense-bed reactor) and the improved heat transfer in a slurry reactor. The diluted-bed reactor should have a more uniform temperature profile than the dense-bed reactor because the reaction heat released per unit volume of the former is less than that of the later. This can be confirmed by comparing the catalyst bed temperature profile for the diluted-bed reactor to that for the dense-bed reactor. In the diluted-bed reactor, the highest temperature was observed at about one inch from the top of the catalyst zone. This temperature rise was eliminated by the heat transfer liquid. The heat transfer liquid was circulated through the system at a fixed rate of 0.103 $cm^3s^{-1}$. When n-hexadecane was used as the heat transfer liquid the elimination of the temperature rise was also achieved (see Figure 18). The temperature rise in the dense-bed reactor loaded with 9.233 grams of an iron-manganese catalyst is presented in Figure 19 as a function of conversion level. It confirmed once again that an isothermal profile could not be achieved in a dense-bed reactor even at carbon monoxide conversions as low as five percent. The temperature profile for the diluted-bed, pseudo slurry reactor at an average reaction temperature of 524 K is presented in Figure 20. This flat temperature profile in the catalyst bed indicated that even at a higher carbon monoxide conversion (10%), carbon monoxide hydrogenation occurred at the same reaction temperature throughout the reactor.

The conversions and product yields for the hydrogenation of carbon monoxide in the different reactors at the standard reaction conditions are listed in Table 4. The carbon monoxide conversion in the pseudo slurry reactor operation was lower than that in the dense-bed or diluted-bed reactors. These differences were attributed to the retardation of the gas diffusion rate by the liquid phase and the higher temperature rise in the catalyst bed in the absence of the heat transfer liquid as found by Hall and co-workers.[41] However, in Hall's[41] investigation, different amounts of catalyst were loaded into the fixed-bed reactor and into the slurry reactor making the comparison more difficult. Deckwer and co-workers[86] compared the catalyst activity and product distribution for carbon monoxide hydrogenation at approximately the same reaction temperature and pressure in a fixed-bed reactor and in a slurry reactor. The conversion was 76.6 mole percent in the fixed bed reactor and 44.3 mole percent in the slurry reactor. In this investigation, the carbon monoxide conversion in the diluted-bed, pseudo slurry reactor was 3.6 mole percent with n-hexadecane and 3.1 mole percent with MCP 151 (Table 4), whereas in the absence of heat transfer liquid the conversions were 7.1 mole percent and 7.1 mole percent. The degree of the reduction in conversion in the pseudo slurry reactor relative to the diluted-bed reactor in this study was close to that reported by Deckwer.[86] Regardless of the heat transfer liquid (MCP 151 or n-hexadecane) used in the diluted-bed trickle flow reactor, the carbon monoxide conversions (6.7 mole percent and 6.3 mole percent) were quite close to those in the diluted bed operation in the absence of heat transfer medium (7.1 mole percent and 7.1 more percent). On the other hand, a significant decrease in carbon monoxide conversion was observed in the dense-bed trickle flow reactor (4.2 mole percent) compared to that in the dense-bed reactor (7.3 mole percent). This difference is related to the hydrodynamics of the system, that is, in the diluted-bed trickle flow reactor not all the catalyst pellets were completely surrounded by the heat transfer liquid at the standard pumping rate (0.103 $cm^3s^{-1}$); thus gas phase reaction existed in the dense-bed trickle flow operations. The conversion level for the trickle flow reactor was always between that of the dense-bed reactor (or diluted-bed reactor) and the pseudo slurry reactor.

The reaction temperature is a very important process variable for the hydrogenation of carbon monoxide; therefore, kinetic data are comparable only if the reaction occurs at the same kinetic temperature which may be different from the observed catalyst bed temperature. More methane and less carbon dioxide were produced in the diluted-bed reactor implying that there was actually a higher reaction temperature in the dense-bed reactor. This speculation is based on the reported effect of temperature on the product distribution for the hydrogenation of carbon monoxide. The yield of carbon dioxide increased and that of the $C_2$-$C_4$ hydrocarbon fraction decreased in the pseudo slurry operations relative to the dense- and diluted-reactors regardless of the heat transfer liquid used (MCP-151 or n-hexadecane). Using MCP 151 did not show any advantage for low molecular weight olefins production, although it did effectively suppress the temperature rise in the reactor.

It is clear that although the dense-bed reactor gives higher conversion, it is difficult to maintain the reaction temperature at a constant value. In the diluted-bed reactor, the same amount of heat is distributed throughout a larger reactor volume resulting in a nearly uniform temperature distribution. Due to the capacity limit of the heat transfer liquid circulation pump, channeling is not avoidable in the diluted-bed trickle flow reactor. The diluted-bed reactor and diluted-bed, pseudo slurry reactor were chosen for further investigation.

The hydrogenation of carbon monoxide was carried out in a diluted-bed reactor and a diluted-bed, pseudo slurry reactor with varying reaction temperatures at a fixed reactor total pressure of 2760 KPa, a hydrogen to carbon monxode ratio of 2, and a fixed space velocity of 1 $cm^3g^{-1}s^{-1}$. N-hexadecane and MCP 151 were both used as heat transfer liquids in the pseudo slurry operation. The results are presented in Table 5 and Table 6 and in Figure 21 thorugh Figure 26. At a given reaction temperature, the diluted-bed reactor exhibited the highest carbon monoxide conversions. A similar result was reported by Deckwer and co-workers[86] when comparing the product distribution and catalyst activity in the fixed-bed and slurry phase at the same reaction conditions. They also reported that although the conversions attainable in the two reactors differed greatly, the product distributions were only slightly different. Unfortunately, the yield of carbon dioxide was not reported in Deckwer's work.[86] In this investigation, the temperature distribution in the diluted-bed reactor was reasonably isothermal; however, the catalyst surface temperature may have been higher than that in the diluted-bed, pseudo slurry reactor and that would account for the higher carbon monoxide conversions in the diluted-bed reactor. Another possible explanation for the lower carbon monoxide conversion in the diluted-bed, pseudo slurry reactor is that it may be due to the higher mass transfer resistance of the reactant gas from the gas phase to the surface of the catalyst. The pseudo slurry reactor with MCP 151 circulated as the heat transfer liquid gave lower carbon monoxide conversion than when n-hexadecane was used as the heat transfer liquid. At the same reaction temperatures within the range of this investigation, $C_2$-$C_4$ hydrocarbons yield increased in the order of reactor mode: (1) MCP 151 pseudo slurry reactor, (2) n-hexadecane psuedo slurry reactor, and (3) diluted-bed reactor. However, the carbon dioxide yield increased in the reverse order as shown in Figure 22 and Figure 23 Another important characteristic of the hydrogenation of carbon monoxide is the olefin to paraffin ratio of $C_2$-$C_4$ hydrocarobns. The olefin-to-paraffin ratios of the products ($C_2$, $C_3$, $C_4$ and $C_2$-$C_4$) from three different reactors are presented in Figure 24 thorugh Figure 27. In the production of low molecular weight olefinic hydrocarbons, using n-hexadecane as the heat transfer liquid in a pseudo slurry reactor for the Fischer-Tropsch synthesis reaction shows some advantage over using MCP 151 as the heat transfer liquid. It is widely accepted that olefins are the primary products of the hydrogenation of carbon monoxide reaction and paraffins are produced through the secondary hydrogenation of olefins.[73] Higher olefin content in the product stream must result from lower hydrogen concentration on the catalyst surface or shorter residence time of olefins on the catalyst surface so that the degree of secondary hydrogenation is decreased. It is not clear which of the above mentioned reasons caused higher olefin to paraffin ratios in the pseudo slurry reactor with n-hexadecane as the heat transfer liquid. In this investigation, the heat transfer liquid circulation rate was fixed at 0.103 $cm^3s^{-1}$ for both MCP 151 and n-hexadecane. As reported by Stern, Bell, and Heinemann,[56] the liquid phase hydrogen to carbon monoxide ratio can differ substantially from that of the gas fed to the reactor. The liquid phase hydrogen to carbon monoxide ratio is a function of the hydrogen to carbon monoxide consumption ratio, the interfacial area, the Damkohler number, and the space velocity of the feed gas. The higher olefin to paraffin ratio for the $C_2$-$C_4$ hydrocarbon fraction in the diluted bed, pseudo slurry reactor (n-hexadecane as the heat transfer liquid) must be a result of the lower hydrogen to carbon monoxide ratio on the catalyst surface which results in higher carbon dioxide selectivity.

When MCP 151 was used as the heat transfer liquid in the diluted-bed, pseudo slurry reactor, no advantage for the $C_2$-$C_4$ olefinic hydrocarbon production was observed. On the contrary, the carbon dioxide yield increased. The hydrogen and carbon monoxide concentrations on the catalyst surface were not known. However, the secondary hydrogenation and water gas shift reaction played important rolls in the hydrogenation of carbon monoxide in a MCP 151 circulated diluted-bed, pseudo slurry reactor.

Anderson[2] reported an empirical equation for the hydrogenation of carbon monoxide over iron catalysts based on first order reaction kinetics. The equation was written as follows:

$$-\ln_e (1 - X) = \frac{k}{S} = \frac{A}{S} \exp (- E_a/RT)$$

where X is the carbon monoxide conversion, k is the specific rate constant, A is the Arrhenius pre-exponential factor, S is the gas hourly space velocity, $E_a$ is the activation energy, R is the gas constant, and T is the absolute temperature. The above empirical equation can be transformed to the following form:

$$- S \ln_e (1 - X) = A \exp (- E_a/RT)$$

or

$$\ln_e [- S \ln_e(1 - X)] = \ln_e A + (- E_a/R) (1/T) .$$

If the pre-exponential factor A is independent of the reaction temperature, a plot of $\ln_e[-S \ln_e(1 - X)]$ versus the reciprocal of temperature should give a straight line with slope of $(- E_a/R)$ and intercept of $\ln_e A$. The Arrhenius plots of data obtained in the diluted-bed and the diluted-bed, pseudo slurry reactors are presented in Figure 77. Three linear equations were established to correlate these data points by using the least mean square method. The values of the activation energies and the pre-exponential factors for the hydrogenation of carbon monoxide in the diluted-bed reactor and the diluted-bed, pseudo slurry reactor are listed in Table 9.

The activation energy calculated for the hydrogenation of carbon monoxide in the diluted-bed reactor (87.1 KJ mole$^{-1}$) was in the range of activation energies for different iron-manganese catalysts in a fixed-bed reactor reported by Tsai[7] which varied from 72.4 KJ mole$^{-1}$

### Table 9

### Activation Energies and Pre-Exponential Factors for Coprecipitated Iron-Manganese Catalysts Hydrogenation of Carbon Monoxide

| Reactor Type | Activation Energy $E_a$, KJ mole$^{-1}$ | Pre-exponential Factor, A |
|---|---|---|
| Diluted-Bed | 87.2 | $1.49 \times 10^8$ |
| Diluted-Bed, Pseudo Slurry Reactor with MCP 151 as Heat Transfer Liquid | 48.1 | $5.13 \times 10^4$ |
| Diluted-Bed, Pseudo Slurry Reactor witn n-Hexadecane as Heat Transfer Liquid | 73.9 | $3.07 \times 10^7$ |