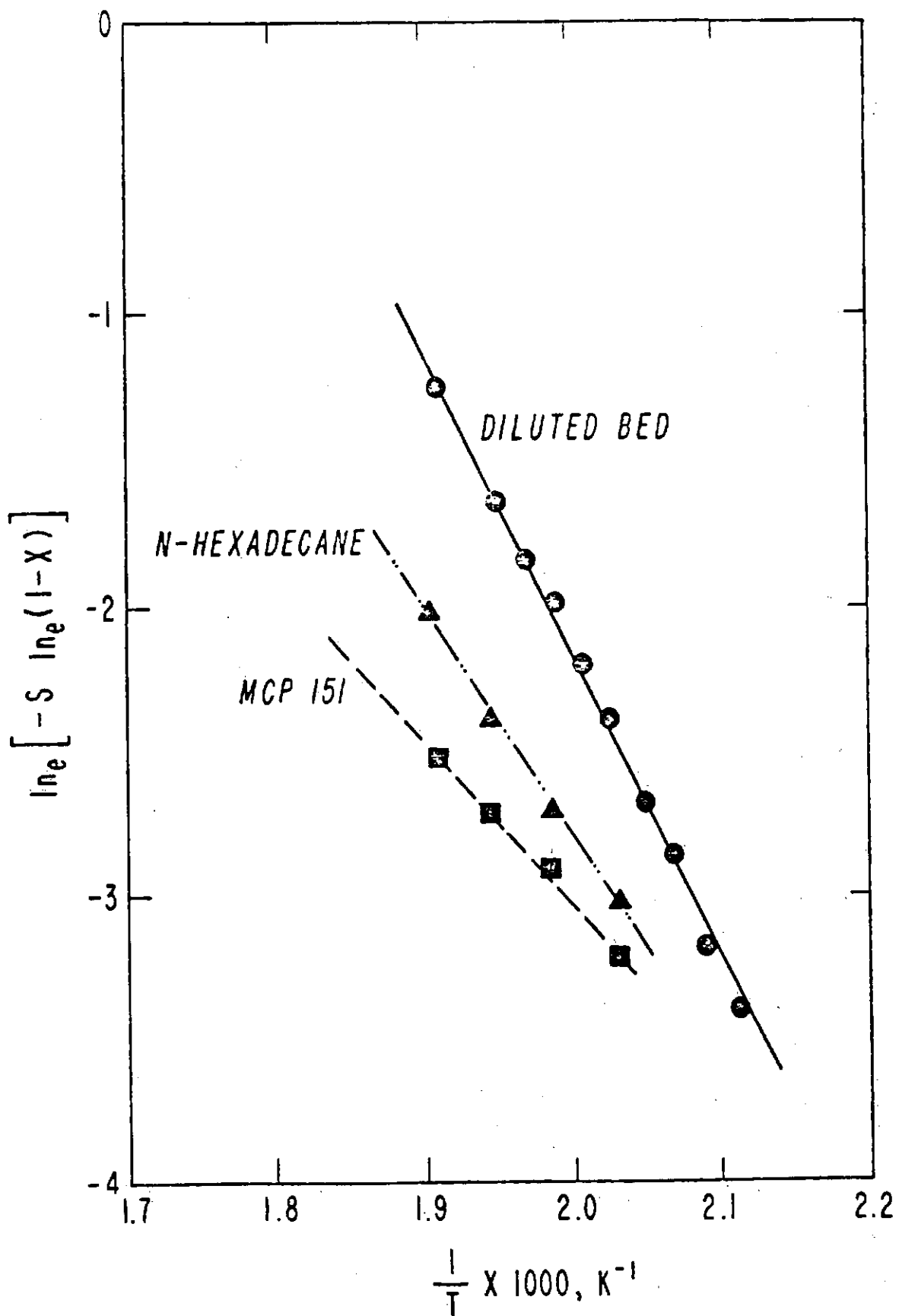Figure 77

Arrhenius Plot for the Hydrogenation of Carbon Monoxide
Diluted Bed Reactor and Diluted Bed, Pseudo Slurry Reactors
[ln (- S ln(1 - X)] Versus 1/T;
Pressure = 2760 KPa; H_2/CO = 2/1;
Space Velocity = 1 $cm^3 g^{-1} s^{-1}$

to 128 KJ mole^{-1}. This activation energy (87.1 KJ mole^{-1}) was also in the range of activation energies (71 - 113 KJ mole^{-1}) reported earlier for the iron catalyst.[54] For carbon monoxide hydrogenation in the diluted bed, pseudo slurry reactor with n-hexadecane as the heat transfer liquid, the activation energy was 73.9 KJ mole^{-1}. This somewhat lower activation energy than that in the diluted bed reactor (87.1 KJ mole^{-1}) indicated little mass transfer resistance in the n-hexadecane circulated pseudo slurry reactor. However, in the diluted-bed, pseudo slurry reactor with MCP 151 as the heat transfer liquid, the calculated activation energy was only 48.1 KJ mole^{-1}, indicating a more significant mass transfer effect. This can be explained from the low solubility and diffusivity of the reactant gas in MCP 151. Deckwer and coworkers[86] investigated the hydrogenation of carbon monoxide over a precipitated iron-manganese catalyst (manganese to iron weight ratio = 6/1) in a bubble column reactor and calculated an activation energy of 109 KJ mole^{-1}. This value of the activation energy for the hydrogenation of carbon monoxide indicated that mass transfer effects were negligible in the bubble column reactor with very fine catalyst particles and small reactant gas bubbles. Zaidi[47] measured the activation energy for the hydrogenation of carbon monoxide over different amounts of iron-manganese catalysts loaded in a bubble column slurry reactor and reported that the activation energy decreased as the catalyst loading increased. When the catalyst loading was increased to 10 weight percent in the slurry reactor, the calculated activation energy for the hydrogenation of carbon monoxide was determined to be less than 20 KJ mole^{-1}, indicating that mass transfer has become the rate-determining step.

Lower values of the pre-exponential factors calculated from the results of the hydrogenation of carbon monoxide in the diluted-bed, psudo slurry reactor indicated that the number of collisions between the catalyst and the reactant gas per gram of catalyst per unit time in the slurry reactors are fewer than those in the diluted-bed reactor.

5.4 Effects of Process Variables on Carbon Monoxide Hydrogenation

Effects of process variables such as reaction temperature, reactor pressure, hydrogen to carbon monoxide ratio, and space velocity have been investigated in a diluted-bed reactor and a diluted-bed, pseudo slurry reactor with n-hexadecane as the heat transfer liquid. The data from the diluted-bed operations are presented in Figure 30 through Figure 42 and the data for the diluted-bed, pseudo slurry operations are presented in Figure 43 through Figure 76. Since there are so many similarities of these process variables on the catalyst activity and selectivity in the diluted-bed reactor and in the diluted-bed, pseudo slurry reactor, the process variable effects will be discussed together in this section.

5.4.1 Effect of Reaction Temperature

The reaction temperature in the reaction temperature range of this investigation (460 K to 530 K) showed an increasing effect on carbon monoxide conversion as shown in Figures 42 and 43. As the temperature was increased at different reaction conditions, methane and C_2-C_4 hydrocarbons selectivities decreased, carbon dioxide selectivity and olefin to paraffin ratio of the C_2-C_4 hydrocarbons

increased (see Figures 30, 32, 34, 44, and 45). As the reaction temperature increased, lower hydrocarbon selectivities reflected the more rapid increase of carbon dioxide yield. Two possible reasons for the higher carbon dioxide selectivity at higher reaction temperature have been mentioned before: (1) the Boudouard reaction becomes more important at higher reaction temperature, and (2) the water gas shift reaction converts water into carbon dioxide as a byproduct of carbon monoxide hydrogenation. It was confirmed again in this investigation that more carbon dioxide was produced in the diluted bed, pseudo slurry reactor which caused a drastic decrease of hydrocarbon selectivities, especially at high reaction temperatures. Reaction temperature also showed an important effect on the olefin to paraffin ratio of hydrocarbons produced from the Fischer-Tropsch synthesis. The olefin to paraffin ratios of hydrocarbons at different reaction temperatures are shown in Figure 30 through Figure 34, and Figure 46 through Figure 50. Generally speaking, the olefin to paraffin ratio of hydrocarbons in the C_2-C_4 range always increased as the reaction temperature increased. This is also true for C_3 and C_4 hydrocarbons in the temperature range of this investigation. However, for C_2 hydrocarbons, the temperature effect on the olefin to paraffin ratio is not clear. Since olefins are the primary products of the Fischer-Tropsch synthesis reaction and the following hydrogenation reaction produces olefins to paraffins,[73] thus the olefin to paraffin ratio of the hydrocarbon products is determined by the possibility of olefin hydrogenation on the catalyst surface. As the reaction temperature increased, more propylene and butene were produced as a result of the strong inclination of the chain propogation reaction of

ethylene and propylene. However, the hydrogenation of propylene and butene was not enhanced to the same degree by the higher reaction temperature and this resulted in the higher olefin to paraffin ratios of C_3 and C_4 hydrocarbons. The temperature effect is quite different for C_2 hydrocarbons. The strong inclination of ethylene splitting and chain propagation[73,77] compensated for the effect of reaction temperature increase on ethylene production. The increasing trend of the olefin to paraffin ratio for hydrocarbons in the C_2-C_4 range agreed with Tasi's report.[7]

5.4.2 Effect of Total Reactor Pressure

Effects of reactor pressure on the hydrogenation of carbon monoxide in a diluted-bed reactor are shown in Figure 35 and Figure 36. According to Le Chatelier's principle, higher reactor pressure favors the production of heavier hydrocarbons. The observed decreasing trends of methane and carbon dioxide selectivities agrees with this principle. The secondary hydrogenation of olefins that consumes one mole of hydrogen for each mole of paraffin produced is favored under higher reactor pressure. This was confirmed by the decreasing trend of olefin to paraffin ratio of C_2-C_4 hydrocarbons as total pressure increased. Similar total pressure effect on product distribution was found in the diluted-bed, pseudo slurry reactor (see Figures 44, 45, 52 and 66). However, the effect of reactor pressure on product selectivity in carbon monoxide hydrogenation is not as significant as that of the other process variables, namely reaction temperature and hydrogen to carbon monoxide ratio. Tsai[7]

found that at a fixed reaction temperature, space velocity, and reactant gas hydrogen to carbon monoxide ratio, the reactor pressure had no significant effect on the C_2-C_4 hydrocarbon yield. The result of this investigation showed little advantage in the production of C_2-C_4 hydrocarbons at higher total pressure. Similar results were reported earlier by Pannell,[60] Nack,[88] and Murchison.[89] Dry[21,61,62] studied the reactor pressure effect on carbon deposition on iron catalyst and concluded that the carobn deposition rate was proportional to the reciprocal to reactor total pressure. Although it is still not clear whether most of the carbon dioxide oroduced in this investigation was from the Boudouard reaction, a relationship between carbon dioxide selectivity and reactor total pressure was observed, that is, the higher the total pressure, the lower the carbon dioxide yield. The effect of total reactor pressure on carbon monoxide conversion is clear as indicated in Figures 42, 43, 51 and 65. A close to linear conversion versus total pressure relationship was observed in Figure 42 for carbon monoxide hydrogenation in the diluted-bed reactor. Dry[61] developed a simplified kinetic equation for the hydrogenation of carbon monoxide over iron catalysts in a differential reactor with very little water produced based on the Langmuir adsorption theory:

$$R = k\,P_{H_2} = k\,P_T\,y_{H_2}$$

where R is the rate of carbon monoxide hydrogenation, k is the specific rate constant, y_{H_2} is the hydrogen mole fraction, and P_T is the total pressure in the reactor. The reaction rate is proportional to

the total pressure at a fixed hydrogen to carbon monoxide ratio.
Vannice[22] analyzed data for the hydrogenation of carbon monoxide over
different iron catalysts and found most of the results were quite close
to this kinetic model. The result of this investigation agrees with
this kinetic model. A similar linear relationship can be observed
from Figures 43, 51 and 65 for the reaction in the diluted-bed,
pseudo slurry operations.

5.4.3 Effect of Reactant Gas
Space Velocity

The effects of reactant gas space velocity on activity and
selectivity in the diluted-bed reactor are presented in Figure 37
through Figure 39. The space velocity data for the diluted-bed,
pseudo slurry reactor are presented in Figure 51 through Figure 64.

Higher space velocity results in a shorter contact time of the
reactant gas and better mixing in the reactor. The carbon monoxide
conversion decreased as the space velocity increased from 0.5 to 1.5
$cm^3 g^{-1} s^{-1}$ (Figure 42). However, for most of the cases, a linear
correlation between carbon monoxide conversion and space velocity was
not observed (see Figure 42 and Figure 51). Especially for space
velocities less than 1 $cm^3 g^{-1} s^{-1}$ in the diluted-bed, pseudo slurry
reactor, further decrease of space velocity causes a drastic increase
of carbon monoxide conversion. This was probably because of the
localized higher reaction temperature on the catalyst surface. Higher
carbon dioxide selectivity and lower hydrocarbon selectivities at
lower space velocity agreed with this explanation. There are two
major reactions responsible for the carbon dioxide production:

(1) the water gas shift reaction between hydrogen and water produced as the byproduct of carbon monoxide hydrogenation, and (2) the Boudouard reaction that converts carbon monoxide into carbon and carbon dioxide. It is believed that the reactant gas space velocity has a greater effect on the first reaction. At lower space velocity, water produced from the first step carbon monoxide hydrogenation reaction has a longer period of time to react with hydrogen and forms carbon dioxide through the water gas shift reaction. The Boudouard reaction, however, is mostly affected by the reactant gas hydrogen to carbon monoxide ratio and reaction temperature on the catalyst surface. As space velocity increased, the lower carbon dioxide selectivity resulted in relatively higher hydrocarbon product selectivity. For the Fischer-Tropsch synthesis in the slurry phase, the C_2-C_4 hydrocarbon selectivity increased as the space velocity increased from 0.5 to 1.0 $cm^3 g^{-1} s^{-1}$. Methane selectivity, however, did not show such a great increase in the same range of space velocity (see Figures 53 through 57 and Figure 58). Changing the space velocity did not have a measurable effect on the combined C_2-C_4 hydrocarbon olefin-to-paraffin ratio over the iron-manganese catalyst in either the diluted-bed reactor or the diluted-bed, pseudo slurry reactor with the tested space velocity range. This result agrees with Deckwer's investigation for carbon monoxide hydrogenation in a bubble column reactor.[86] Detailed effects of space velocity on the olefin-to-paraffin ratio of C_2, C_3, and C_4 hydrocarbons are shown in Figure 59 through Figure 64. In the space velocity range of this investigation, higher space velocity favored the production of methane and ethylene; however, it suppressed the propylene

selectivity. The olefin to paraffin ratio of hydrocarbons produced from the hydrogenation of carbon monoxide is greatly affected by the residence time of olefins remaining on the catalyst active sites before desorption or hydrogenation. Higher methane and ethylene selectivities at higher space velocity showed shorter molecular catalyst contact time of these two species. For heavier hydrocarbons with a carbon number greater than 3, this 'blowing effect' becomes less important.

5.4.4 Effect of Hydrogen-to-Carbon Monoxide Ratio

The reactant hydrogen-to-carbon monoxide ratio is an important process variable for the hydrogenation of carbon monoxide. Results of the carbon monoxide hydrogenation in a diluted-bed reactor with changing hydrogen to carbon monoxide ratios are presented in Figure 40 and Figure 41. As reactant gas hydrogen to carbon monoxide ratio increases from 1.5 to 2.5 $cm^3 g^{-1} s^{-1}$ in the dilute-bed reactor, carbon dioxide yield decreased, C_2-C_4 hydrocarbon product yield increased, and the olefin to paraffin ratio of the C_2-C_4 hydrocarbons decreased. Similar results are found for the hydrogenation of carbon monoxide in a diluted-bed, pseudo slurry reactor as shown in Figure 67 through Figure 76. In the diluted-bed, pseudo slurry reactor, as the reactant gas hydrogen to carbon monoxide ratio increases from 0.5 to 4 $cm^3 g^{-1} s^{-1}$, a maximum C_2-C_4 hydrocarbon yield is obtained at a hydrogen to carbon monoxide ratio of 3. At a hydrogen to carbon monoxide ratio higher than 3, methane selectivity increases at about the same rate but the decreasing trend of carbon dioxide yield becomes smooth and a

smaller C_2-C_4 hydrocarbon yield is observed. This trend for the hydrogen to carbon monoxide ratio was also reported earlier by Tsai.[7] It is widely accepted that olefins are the primary products of the hydrogenation of carbon monoxide. Consecutive hydrogenation of these olefins on the catalyst surface is dependent on the surface hydrogen concentration. Higher reactant gas hydrogen concentration caused more secondary hydrogenation and thus decreased the olefin to paraffin ratio of the product hydrocarbons (see Figure 72 through Figure 76). It was observed in the diluted-bed, pseudo slurry operations, that as the reactant gas hydrogen-to-carbon monoxide ratio increased from 0.5 to 4, all the olefin-to-paraffin ratios of C_2, C_3, and C_4 hydrocarbons decreased and most of these declines occurred between the hydrogen-to-carbon monoxide ratio of 0.5 to 2. Possible reasons for the lower carbon dioxide selectivity have been discussed earlier. A high hydrogen-to-carbon monoxide ratio retards both the water gas shift reaction and the Boudouard reaction and results in a low carbon dioxide selectivity (see Figure 66). The effect of the hydrogen-to-carbon monoxide ratio on carbon monoxide conversion is presented in Figure 42 and Figure 65. As expected, higher carbon monoxide conversion was achieved at a higher hydrogen-to-carbon monoxide ratio in the reactant gas.

5.5 Reaction Order of Hydrogen and Carbon Monoxide

Vannice[27] studied the hydrogenation of carbon monoxide over different metal catalysts in a microreactor and proposed the following rate equation to describe the data:

$$R = A \exp(-E_a/RT) \, P_{H_2}{}^x \, P_{CO}{}^y$$

where A is the pre-exponential factor, E_a is the activation energy for the hydrogenation of carbon monoxide, R is the gas constant, T is the absolute reaction temperature, and x and y are the exponents for the hydrogen partial pressure (P_{H_2}) and the carbon monoxide partial pressure (P_{CO}), respectively. The value of the exponent x can be determined by fixing the carbon monoxide partial pressure and varying the hydrogen partial pressure of the reactant gas. Plotting $\ln_e R$ versus $\ln_e (P_{H_2})$ yields a straight line with slope x. The value of y can also be calculated by fixing the hydrogen partial pressure and varying the carbon monoxide partial pressure. In this investigation, for the hydrogenation of carbon monoxide in the diluted-bed, pseudo slurry reactors, the same amount of catalyst was used each time. At the conversion levels in this investigation, the above rate equation can be represented by the following form:

$$X = K \, P_{H_2}{}^x \, P_{CO}{}^y$$

where X is the carbon monoxide conversion and K is a constant. A careful interpolation of the data in Figure 65 indicated the values of x and y were 1.196 and -0.091. The calculation procedure is presented in Appendix I. The results indicated that the hydrogenation of carbon monoxide over an iron-manganese catalyst has an overall carbon monoxide and hydrogen order of 1.1. This result is quite close to Dry's observation (the reaction rate is first order to the

hydrogen partial pressure) and is also within the range of x and y values reported by Vannice.[27]

5.6 C_5 Plus (C_5^+) Hydrocarbon
Selectivity

The C_5^+ hydrocarbon selectivity in the hydrogenation of carbon monoxide over iron-manganese catalysts strongly reflects the carbon dioxide selectivity. As the reaction temperature increased, while reactor pressure, space velocity, and hydrogen-to-carbon monoxide ratio were held constant, the C_5^+ hydrocarbon yield increased. However, the shift to carbon dioxide selectivity was more severe than that to C_5^+ hydrocarbon selectivity. This effect was very clear in the diluted bed, pseudo slurry reactor as indicated in Appendix G and Appendix H. At a fixed hydrogen-to-carbon monoxide ratio of 2/1, a fixed reaction temperature of 503 K, and a fixed reactant gas space velocity of 1 $cm^3g^{-1}s^{-1}$, an increase in reactor pressure resulted in a higher yield of C_5^+ hydrocarbons. This observation agreed with the trends reported in the literature. As expected, higher reactor pressure favored the production of heavy hydrocarbon products. However, the reactor pressure effect observed in this investigation was not very significant. In the diluted bed reactor, lower space velocity resulted in higher C_5^+ hydrocarbon selectivity. At low space velocities, the residence time of the reactants increases and the longer residence time favors the chain growth reaction, thus increasing the yield of higher molecular weight hydrocarbons. In the diluted bed, pseudo slurry reactor, this trend was less clear because of the high carbon dioxide selectivity at low space velocities and

low reactor pressures. Higher hydrogen-to-carbon monoxide ratios favor the hydrogenation of the primary olefins resulting in a termination of the chain growth reaction which results in a lower C_5^+ hydrocarbon yield. This trend was observed in the majority of the experiments reported in Appendix G and Appendix H.

CHAPTER 6

Conclusions

The Fischer-Tropsch reaction is a well-developed process to synthesize paraffins, olefins, and alcohols from carbon monoxide and hydrogen and in the forseeable future, the Fischer-Tropsch process could become more and more competitive because of the projected long-term shortage of crude oil and relatively abundant supply of coal in the United States. Recent reports show that the iron-manganese catalysts are very selective for the production of low molecular weight olefins from the hydrogenation of carbon monoxide. The slurry reactor indicated some advantage over the commercially used fixed-bed reactor and the fluidized-bed reactor in providing a uniform temperature distribution in the catalyst bed and the feasibility of using a lower hydrogen-to-carbon monoxide ratio reactant gas. In this investigation, six different reactor modes have been investigated for the hydrogenation of carbon monoxide over the iron-manganese catalysts. A complete process variable study was conducted in the diluted-bed, pseudo slurry reactor with n-hexadecane as the heat transfer liquid. The following conclusions were made based on the results obtained in this investigation:

1. The highly exothermic nature of the carbon monoxide hydrogenation reaction caused significant temperature excursions in the catalyst bed of a conventional dense-bed reactor. The "hot spot" which occurred in the dense bed reactor not only shifted the selectivity in favor of methane and carbon dioxide, but also deactivated the catalyst.

2. The dilution of the catalyst with an inert solid effectively alleviated the temperature rise in the catalyst bed for the hydrogenation of carbon monoxide in the range of variables studied in this investigation. A nearly isothermal temperature distribution was observed in the diluted-bed, pseudo slurry reactor with MCP 151 or n-hexadecane as the heat transfer liquid.

3. The values of the activation energies for the hydrogenation of carbon monoxide calculated in this investigation agreed with the data reported for similar catalysts in the literature. A moderate mass transfer effect was observed for the hydrogenation of carbon monoxide in the diluted-bed, pseudo slurry reactor with n-hexadecane as the heat transfer liquid. However, the lower observed activation energy (48.1 KJ mole^{-1}) for the hydrogenation of carbon monoxide in an MCP circulated diluted-bed, pseudo slurry reactor indicated some degree of mass transfer limitation.

4. The product distribution from the hydrogenation of carbon monoxide in the diluted-bed, pseudo slurry reactor with n-hexadecane as the heat transfer medium gave higher carbon monoxide conversion, higher olefin-to-paraffin ratio of C_2-C_4

hydrocarbons, and less carbon dioxide selectivity than that obtained in the diluted-bed, pseudo slurry reactor with MCP-151 as the heat transfer medium. The higher olefin-to-paraffin ratio resulted in the choice of n-hexadecane as the heat trnasfer liquid for the diluted-bed, pseudo slurry process variable investigation.

5. The hydrogenation of carbon monoxide over an iron-manganese catalyst in a diluted-bed reactor obeyed the Schulz-Flory distribution law .or hydrocarbons having a carbon number of up to 15. The values of the chain growth probability (α = 0.67 and 0.60) were within the range of data reported in the literature. A higher chain growth probability was determined (α = 0.79 and 0.86) for hydrocarbons with carbon numbers greater than 15.

6. The effect of process variables on the hydrogenation of carbon monoxide over a coprecipitated iron-manganese catalyst in a diluted-bed reactor is quite similar to those in a diluted-bed, pseudo slurry reactor. A change in the circulation rate of n-hexadecane from 0.04 to 0.103 $cm^3 s^{-1}$ had lihtle effect on the product distribution. The conclusions from the process variable study in the diluted-bed, pseudo slurry reactor are presented below and are summarized in Figure 78.

7. Higher reaction temperature resulted in greater carbon dioxide selectivity at the expense of C_2-C_4 hydrocarbons. The olefin-to-paraffin ratio of C_2-C_4 product hydrocarbons increased as the reaction temperature increased. Higher

Figure 78

Summary of Conclusions from the Process

Variable Investigation in a

Diluted-Bed, Pseudo

Slurry Reactor

CONCLUSIONS

1.   T ↑ :   CO Conversion ↑

          CH_4 ↓

          C_2-C_4 ↓

          CO_2 ↑

          C_2-C_4 O/P ↑

2.   P ↑ :   CO Conversion ↑

          CH_4 ↓

          C_2-C_4 ↑

          CO_2 ↓

          C_2-C_4 O/P ↓

3.   S.V. ↑ :   CO Conversion ↓

          CH_4 ↑

          C_2-C_4 ↑

          CO_2 ↓

          C_2-C_4 O/P −

4. H_2/CO ↑ : CO Conversion ↑

          CH_4 ↑

          C_2-C_4 Max

          CO_2 ↓

          C_2-C_4 O/P ↓

carbon monoxide conversion was achieved at higher reaction temperatures.

8. Higher total reactor pressure favored the production of heavier hydrocarbons. Methane and carobn dioxide yields decreased as total reactor pressure increased. The hydrogenation of olefins was enhanced at a higher total reactor pressure, resulting in a lower olefin-to-paraffin ratio.

9. In the diluted-bed, pseudo slurry reactor, higher total reactor pressure resulted 'n closer olefin-to-paraffin ratios of C_2, C_3, and C_4 hydrocarbons. The carbon monoxide conversion was roughly proportional to the total rea..tor pressure.

10. Higher reactant gas space velocity resulted in lower carbon dioxide yield and in higher C_2-C_4 hydrocarbon yield. Increasing the reactant gas space velocity from 0.5 to 4.0 $cm^3 g^{-1} s^{-1}$ did not have a significant effect on the olefin-to-paraffin ratio of C_2-C_4 hydrocarbons.

11. Higher hydrogen-to-carbon monoxide ratio resulted in higher carbon monoxide conversion, and in lower olefin-to-paraffin ratio for the C_2-C_4 hydrocarbons. A reactant gas with a hydrogen-to-carbon monoxide ratio of unity or less produced a great amount of carbon dioxide. The maximum C_2-C_4 hydrocarbon yield was obtained with a reactant gas hydrogen to carbon monoxide ratio of 3.

12. In the diluted-bed, pseudo slurry reactor, over an iron-manganese catalyst, the hydrogenation of carbon monoxide had a reaction order of 1.2 for the hydrogen partial