

Sections 5.4 and 6.3 with respect to the relative hydrogenation (termination) and propagation rates for all three catalysts.

### 5.2.2.3 Co Catalyst

The  $C_6$  product yields are higher with the 1-pentene/ $CO/H_2$  feed however the total fraction of 1-pentene consumed in chain growth reactions is less than 0.5%. The  $C_2$  through  $C_4$  product yields are comparable for both feeds at one atmosphere. Figure 5.2.9 presents the 1-butene, 1-hexene and n-hexane yields for the pure and 1-pentene  $CO/H_2$  mixture at one atmosphere. It appears that at this pressure no appreciable 1-pentene hydrocracking is occurring over the Co catalyst since there is no measurable increase in any of the low molecular weight ( $C_{n<4}$ ) product yields.

At 7.8 atmospheres there is a significant increase in the lower molecular weight product yields with the 1-pentene containing feed as opposed to the pure feed. The ethylene, propylene and 1-butene yields for both feeds are shown in Figure 5.2.10. The total molar fraction of 1-pentene which need be consumed to account for the  $C_2$  through  $C_5$  product yield increases is approximately 7% at a nominal 3% CO conversion. The methane activity is found to substantially higher for this feed (Section 5.1), corresponding to the equivalent fraction of 3.6% of the total 1-pentene in the feed. The  $C_6$  product yields are shown in Figure 5.2.11. The increase in the 1-hexene and n-hexane yields accounts for approximately 3% of the total 1-pentene at a nominal 3% CO conversion (GHSV approximately  $450hr^{-1}$ ).

If these yield increases are due to 1-pentene hydrocracking they

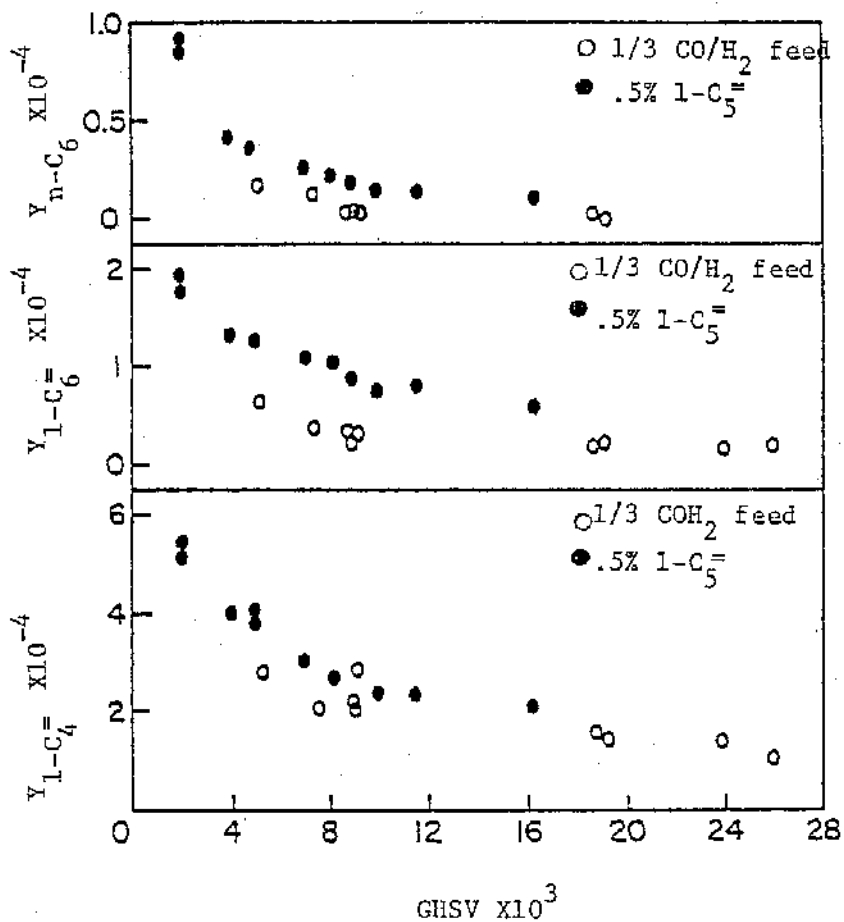


Figure 5.2.9 1-butene (bottom), 1-hexene (middle) and n-hexane (top) yields versus GHSV for the Co catalyst at 1 atm. in both the 1-pentene and pure  $1/3 \text{CO}/\text{H}_2$  feed.

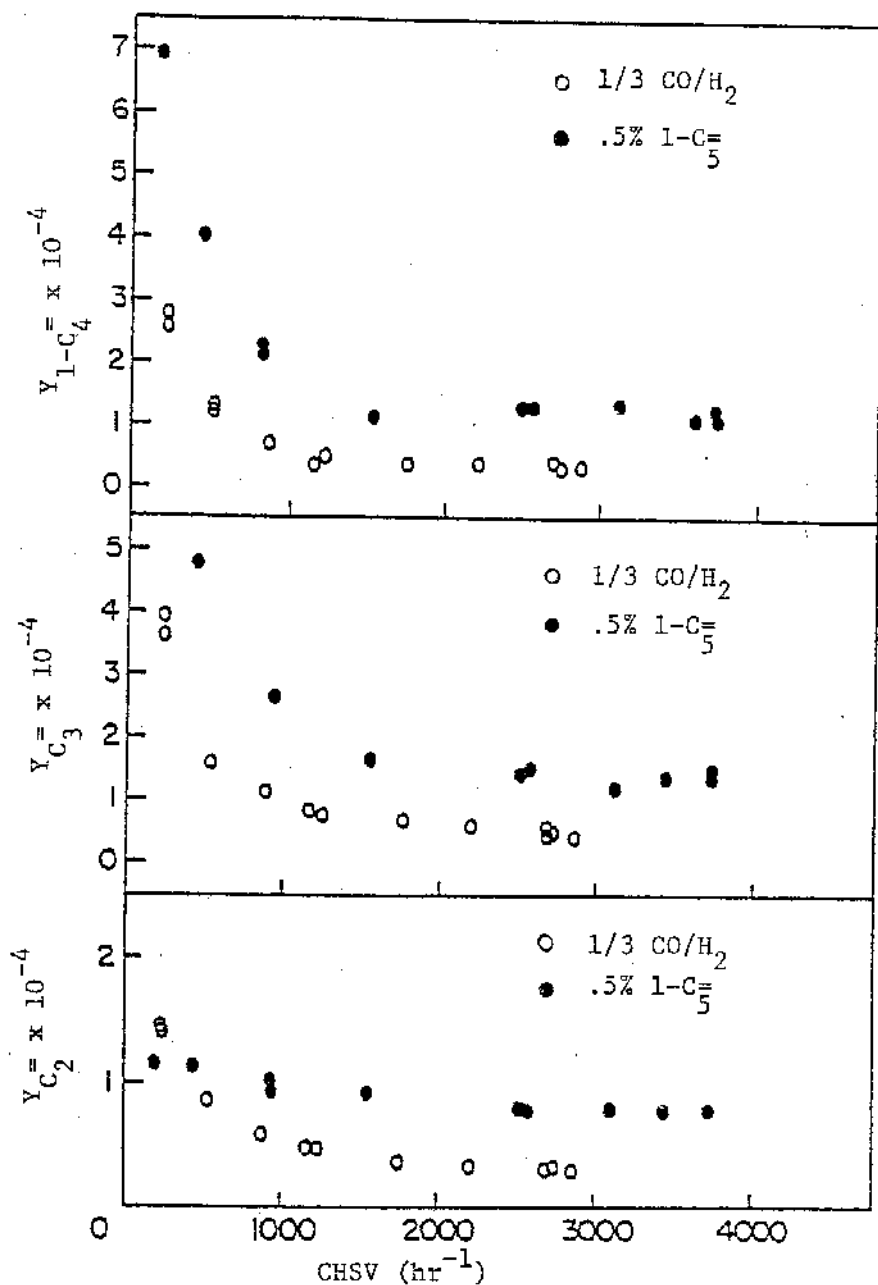


Figure 5.2.10 Ethylene (bottom), propylene (middle), and 1-butene (top) yields versus GHSV for the Co catalyst using the .5 mole % 1-penten and pure CO/H<sub>2</sub> feeds at 7.8 atm and 250°C.

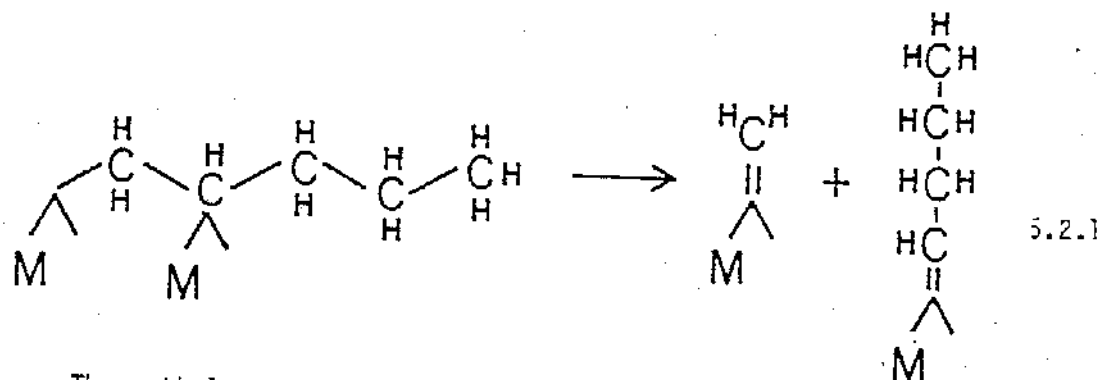
would reflect a combined decrease of approximately 13% in the total  $C_5$  product moles relative to the amount of 1-pentene in the feed mixture. Unfortunately this decrease is not observed since the accuracy in determining the total  $C_5$  product areas in these experiments is generally 20%. The poor analytical measurements associated with the 1-pentene feed studies is due to the nonisothermal conditions maintained in the NaCl ice water bath used with the 1-pentene/ $CO/H_2$  feed. The conductive heat loss of this copper trap is very rapid relative to the small ice reservoir contained in the dewar. The ice bath was typically replaced every two to six hours. Consequently the temperature of the silica in the trap varied during the course of an experiment. The constantly changing trap temperature resulted in an unsteady 1-pentene feed mole fraction due to absorption-desorption transients on the silica. This problem is not present when a dry ice/acetone bath is used since one is able to continually add dry ice thereby maintaining a constant trap temperature.

#### 5.2.2.4 Hydrocracking over the Co catalyst

The product yields obtained with Co catalyst using the 1-pentene/ $CO/H_2$  feed suggest that a significant amount of hydrocracking is occurring at 7.8 atmospheres. The methane yield increase is the highest on a fraction 1-pentene consumed basis being 3.6% compared to a total of 7% for all the  $C_2$  through  $C_4$  products. This product distribution is not expected for catalytic hydrocracking where methane is generally a minor product (29). For example the catalytic cracking of octene produces mostly  $C_3$ ,  $C_4$ , and  $C_5$  products and only trace amounts of methane (10). Methane is a dominant product when thermal hydrocracking is the principal reaction mechanism. This process

generally occurs at temperatures greater than 500°C. At the FT reaction temperature of 250°C it is unlikely that any thermal hydrocracking is occurring.

The observed product yield increases may be due to the transfer of the  $\alpha$  carbon in the 1-pentene as a methylene species to other surface intermediates. This can be illustrated by equation 5.2.1.



The methylene species can either hydrogenate to methane or combine with other surface species to produce multi-carbon components. This possible reaction sequence is supported by the investigations of Pichler and Schulz (92) who found that there was significant radioactivity in the small chained products when labeled  $^{14}\text{CH}_2 = \text{CH} - \text{C}_{14}\text{H}_{24}$  was present in the  $\text{CO}/\text{H}_2$  feed gas over a cobalt catalyst. However, the product distribution radioactivity was the least for methane and increased roughly linearly with carbon number up to  $\text{C}_{15}$ . This result does not rule out the possibility of methylene species transfer since the resultant product distribution would most likely depend on the hydrocarbon selectivity of the catalyst and FT reaction conditions. However the increase in the methane yield is significantly higher than the yield obtained for the  $\text{C}_2$  through  $\text{C}_4$  products. Pichler and Schulz (92) operated at much higher conversion where the overall product distribution contained a higher fraction of high molecular weight hydrocarbons

compared to the conditions employed in the present investigations.

### 5.2.5 Methanol Yields for All 1/3 CO/H<sub>2</sub> Feed Mixtures

In section 4.6.4 reaction mechanisms for the synthesis of carbon dioxide and methanol are introduced and discussed in conjunction with their transient and yield-pressure responses. It is suggested that CO<sub>2</sub> and CH<sub>3</sub>OH can be produced competitively over the same catalytic site, which is possibly independent of the FT hydrocarbon production sites. However, it appears that for the iron based catalyst that the presence of high concentrations of olefins in the feed stream depresses the methanol activity.

Figures 5.2.13 and 5.2.13 presents the methanol yields for the pure CO/H<sub>2</sub> and both olefin containing feeds and 1 and 7.8 atmospheres respectively. At both pressures there is a significant reduction in the yield of this product. The depression is more severe for the ethylene containing feed. In fact at one atmosphere there is no measureable amount of methanol produced. The FeCo catalyst did show a significant yield decrease and in this case it appears that the methanol yield is independent of feed stream olefin concentration. The Co catalyst which produces only small quantities (less than 4% of total products) did not exhibit any yield change due to feed compositions.

The CO<sub>2</sub> yields are found to be independent of olefin feed composition for all three catalyst at both 1 and 7.8 atmospheres and in the case of the iron catalyst the 1-pentene and pure CO/H<sub>2</sub> feed yield similar amounts of CO<sub>2</sub> at 14 atmospheres. Typical results for this catalyst are presented in Appendix VI.

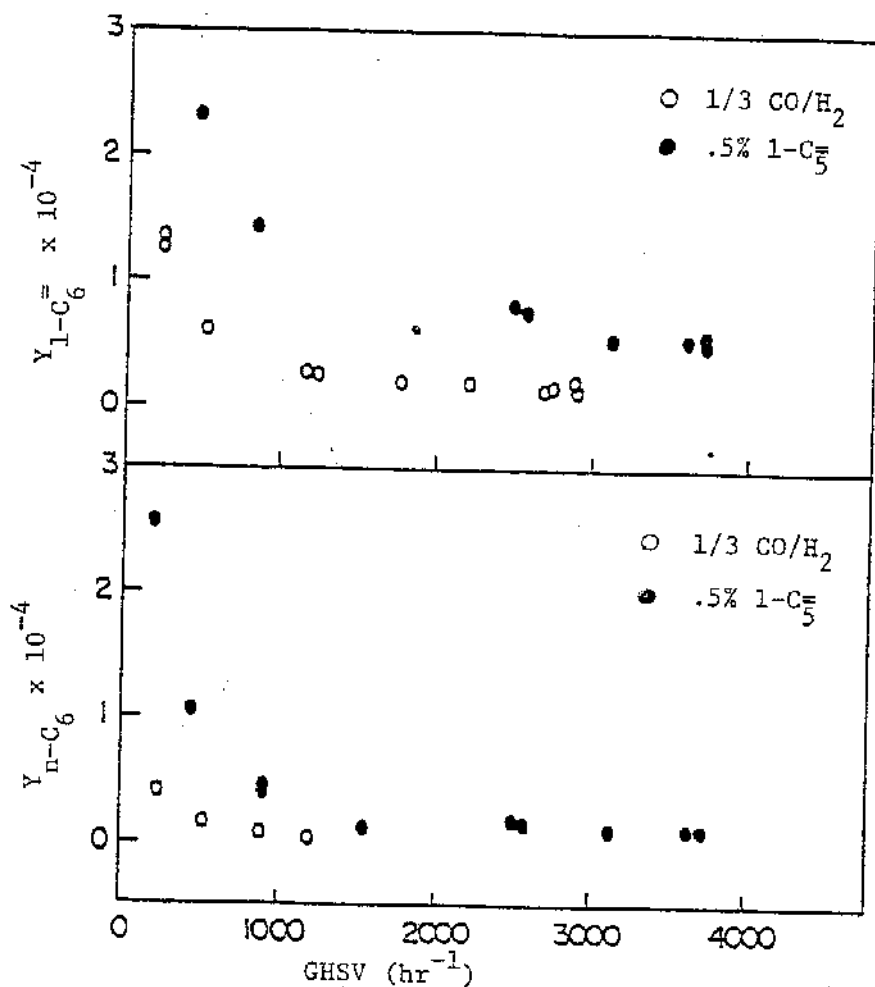


Figure 5.2.11 1-Hexene (top) and n-hexene (bottom) yields versus GHSV for both the .5 mole % 1-pentene and pure 1/3 CO/H<sub>2</sub> feed at 7.8 atm and 250°C.

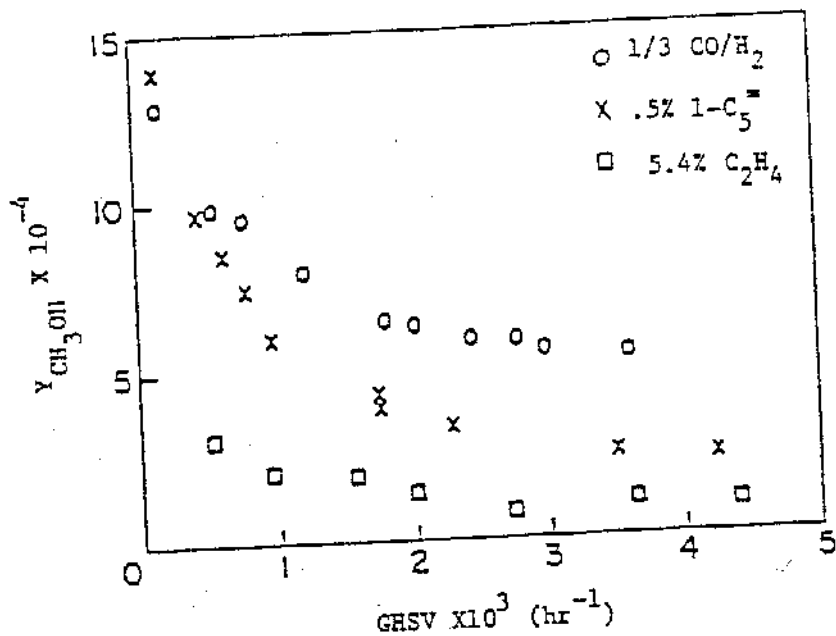


Figure 5.2.13  $Y_{\text{CH}_3\text{OH}}$  versus GHSV for the Fe catalyst using both the pure 1/3 CO/H<sub>2</sub> and olefin enhanced feeds at 7.8 atm.

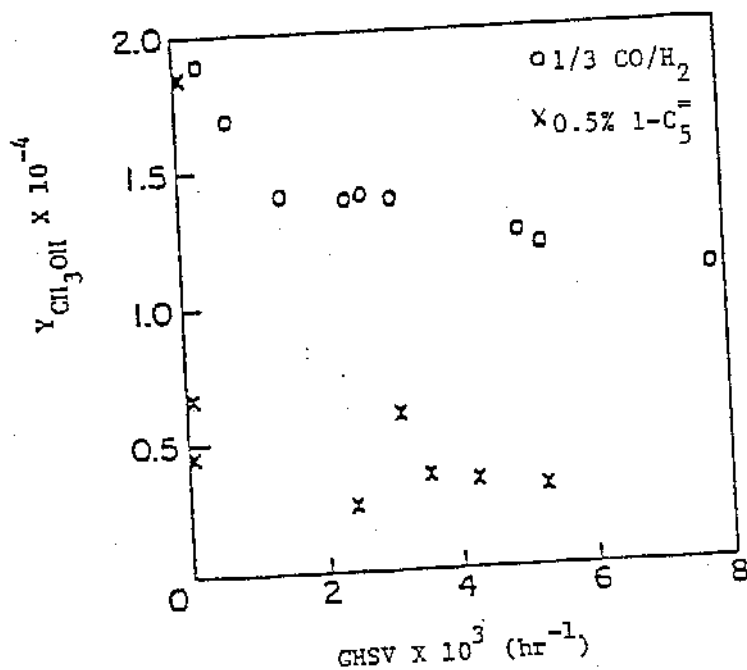


Figure 5.2.12  $Y_{\text{CH}_3\text{OH}}$  versus GHSV for the Fe catalyst using the pure 1/3 CO/H<sub>2</sub> and olefin enhanced feed at 7.8 atm. and 250°C.



The fact that the presence of relatively high olefin concentrations in the feed stream suppresses the methanol activity raises some interesting questions. Can the methanol and carbon dioxide products be linked by a common reaction intermediate as suggested in Section 4.2.4? If so, why is only the methanol yield depressed with increased gas phase hydrocarbon concentrations? In section 4.1 it is shown that the methanol activity decreases more rapidly than the hydrocarbon activity with increasing CO conversion. Another way to state this is that the methanol yield increases more slowly than the hydrocarbon yield with decreasing GHSV. Hall, Kokes, and Emmett (54) have shown that methanol can readily initiate hydrocarbon chains and indeed this secondary reaction is at least partially responsible for the observed yield trends in Section 4.1. However, the observed methanol yield decrease due to hydrocarbons in the feed stream indicates that the methanol activity can also be subject to a conversion dependent inhibition effect in a manner similar to methane.

### 5.3 Schulz Flory Parameterization of Hydrocarbon Product Distribution Using Olefin Containing 1/3 CO/H<sub>2</sub> Feeds

5.3.0 The product yield data presented in section 5.2 indicates that the hydrocarbon product distributions are not significantly altered by the presence of high olefin concentrations in the gas phase. This result is further illustrated by the Schulz Flory (SF) plots of the product distributions at the various pressures studied. The distributions obtained with the olefin containing feeds are presented in conjunction with the distributions obtained with the pure 1/3 CO/H<sub>2</sub> feed so comparisons between feed conditions can be made conveniently.

### 5.3.1 Schulz Flory Parameterization for the Fe Catalyst.

Figures 5.3.1 and 5.3.2 present typical SF plots for the iron catalyst at one atmosphere for the ethylene and 1-pentene feeds respectively. The presence of ethylene (Figure 5.3.1) has essentially no effect on the growth probability,  $\alpha$ , associated with the  $C_{n>4}$  products since the value obtained over this product range ( $\alpha = 0.45$ ) agrees with the value obtained with the pure feed ( $\alpha = 0.42$ ). This may seem surprising since there is significant yield increases in the  $C_3$  and  $C_4$  products due to ethylene insertion. These yield increases are occurring approximately in proportion to the carbon number in such a way as to increase the  $\ln(Y_i)$  values while maintaining the same slope of the line defining the growth parameter  $\alpha$ . One may argue that the ethylene containing feed should possess a higher  $\alpha$  value however the uncertainty in  $\alpha$  is approximately 5% based on the accuracy in determining the peak areas of the high molecular weight products. It should also be noted that  $\ln(Y_{C_6})$  is not included in the determination of  $\alpha$  since this product yield is too small to measure accurately.

The linear portion associated with the SF parameterization of the 1-pentene feed hydrocarbon product distribution is poorly defined at one atmosphere compared to the other feed mixtures. This is due to a combination of reasons. At this pressure there is a limited product chain length range (up to  $C_6$ ). More importantly, there is a depression in the  $C_3$  and  $C_4$  product yields with the feed while the  $C_6$  product yields are enhanced due to 1-pentene insertion. These shifts in product yields tend to increase the value of  $\alpha$ . The value of the growth probability with the  $CO/H_2$  feed is 0.42 (based on  $C_3$  to  $C_6$ ) compared to a value of 0.45 with the 1-pentene feed over the same product range.

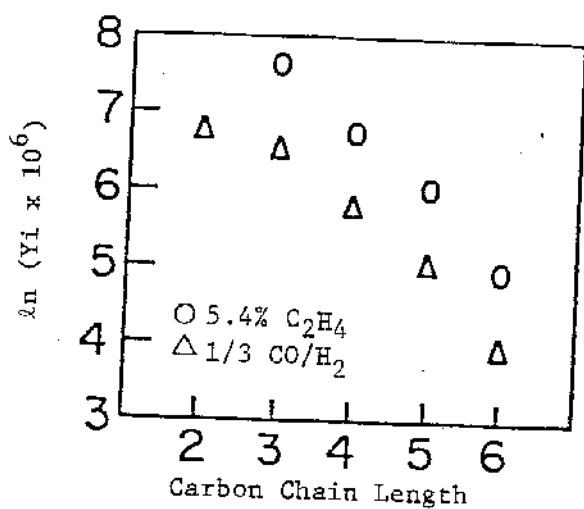


Figure 5.3.1 Schulz Flory plot for the Fe catalyst using the ethylene containing and pure 1/3 CO/H<sub>2</sub> feed at 1 atm. and 250°C. Nominal GHSV = 700.  $\alpha = 0.45$

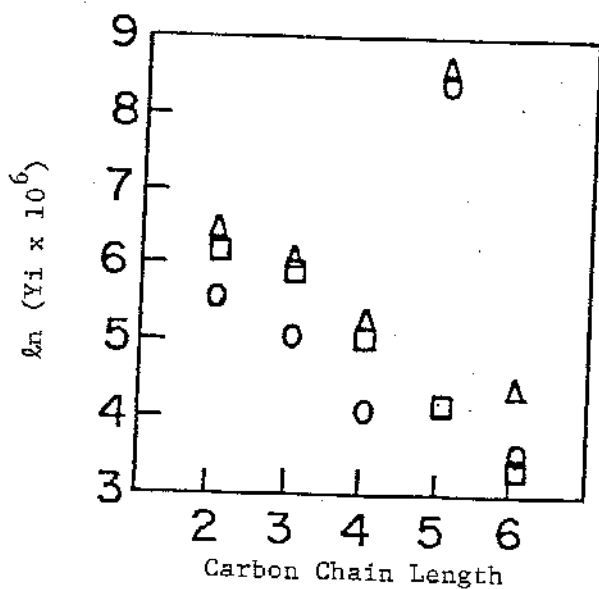


Figure 5.3.2 Schulz Flory plot for the Fe catalyst using the 1-pentene containing and pure 1/3 CO/H<sub>2</sub> feed at 1 atm and 250°C.

- 0.5% 1-Pentene GHSV = 1300 hr<sup>-1</sup>  $\alpha = 0.42$
- △ 0.5% 1-Pentene GHSV = 1000 hr<sup>-1</sup>  $\alpha = 0.45$
- 1/3 CO/H<sub>2</sub> GHSV = 1000 hr<sup>-1</sup>  $\alpha = 0.42$

At 7.8 atmospheres the presence of the feed ethylene does not appreciably change the value of  $\alpha$  determined by the  $C_4$  to  $C_7$  product yields (Figure 5.3.3). It is interesting to note that the increase in the total  $C_3$  yield is enough to bring the  $\ln(Y_{C_3})$  value up to the straight line established by the longer chain products. The polymerization kinetics obeyed by the  $C_{n>4}$  hydrocarbon fraction is now obeyed by the  $C_3$  products due to the presence of a large ethylene concentration in the feed gas. This shift in the  $\ln(Y_{C_3})$  value to a value consistent with the  $\alpha$  value may be entirely fortuitous due to the reaction conditions and the concentration of ethylene in the feed. However on the other hand it may reflect a maximum steady state yield condition brought about by the nature of the reaction mechanism which dictates the propagation and termination rates under a given set of reactor and feed conditions. Further discussion on this observation are given in Sections 5.4 and 6.2.

There is no effect on the growth parameter  $\alpha$  due to the presence of .5 mole % 1-pentene in the  $CO/H_2$  feed at either 7.8 atmospheres (Figure 5.3.4) or 14 atmospheres (Figure 5.3.5). In all cases the value of  $\alpha$  is approximately 0.54. In Figure 5.3.5 the SF plots for the two feeds are deliberately imposed on each other by using identical scaling factors for the  $\ln(Y_i)$  values.

### 5.3.2 Schulz Flory Parameterization for the Co Catalyst

Figures 5.3.6 and 5.3.7 present the SF plots for the Co catalyst using both the 1-pentene and pure  $CO/H_2$  feed at 1 and 7.8 atmospheres. At both pressures there is no observed change in  $\alpha$  for product chains greater than four carbon products. This again reflects the small amount of 1-pentene entering into chain growth reactions (<1%). On the other

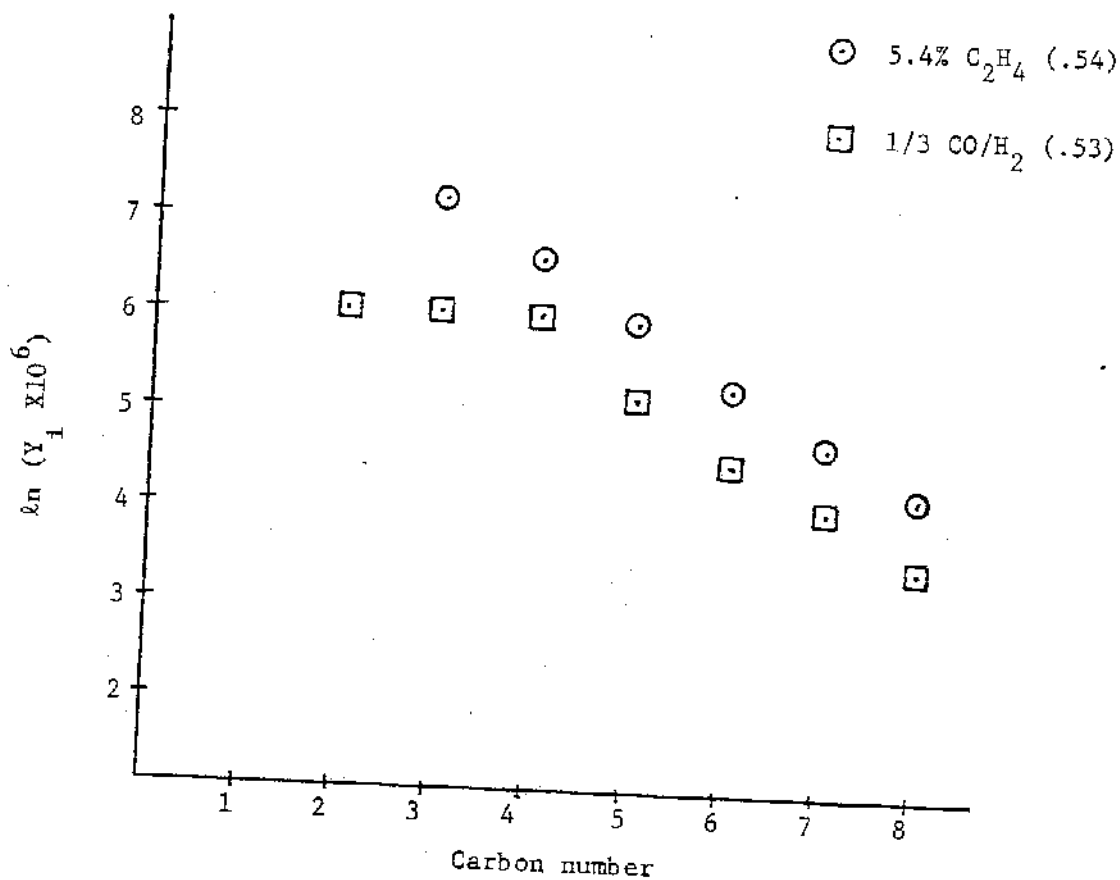


Figure 5.3.3 Schulz Flory plot for the Fe catalyst using the ethylene enhanced and 1/3 CO/H<sub>2</sub> feed at 7.8 atm. and 250°C. Nominal GHSV = 1000 hr<sup>-1</sup>. Numbers in parentheses refer to  $\alpha$  values.

hand there is a noticeable increase in the growth probability over the  $C_3$  to  $C_7$  carbon product range for this catalyst at one atmosphere with the ethylene/ $CO/H_2$  feed. Figure 5.3.8 presents some typical SF distribution data at these conditions. At comparable space velocities, the  $\alpha$  value in the ethylene  $CO/H_2$  feed is found to be approximately 0.61 compared to a value of 0.46 obtained with the pure  $CO/H_2$  feed.

The increase in  $\alpha$  due to feed gas ethylene for the Co catalyst at 1 atmosphere indicates that the ethylene insertion reaction can possibly affect the product distribution in a manner different from that observed for iron. The product yield increases observed with the Fe catalyst appeared to be exponentially decreasing with increasing carbon number. In other words the increases did not affect the slope of the log yield vs carbon chain length ( $n$ ) line used in determining the growth probability. However, it appears that this is not the case for the Co catalyst. The increase in  $\alpha$  observed for this catalyst indicates that the yield increase is greater for the longer chain products relative to the shorter chain products for  $3 < n < 7$ . A similar effect is reported by Dwyer and Somorjai (40) using an ethylene  $CO/H_2$  mixture over an Fe foil at 6 atmospheres. The  $\alpha$  value increased due to ethylene insertion into longer chain ( $C_{n>3}$ ) products. A discussion on the mechanistic implication of this effect is given in section 5.3.4. To complete the presentation on the Co catalyst, the SF plot for the catalyst at 7.8 atmospheres is shown in Figure 5.3.9. There is not change in the  $\alpha$  value with the ethylene present in the feed gas. The value of the growth probability ( $\alpha = 0.76$ )

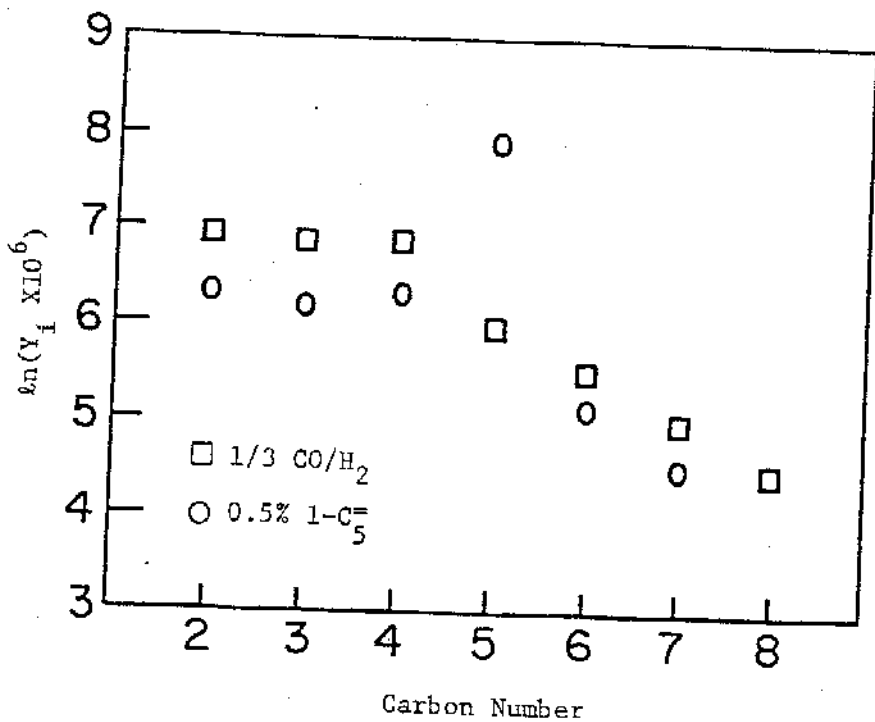


Figure 5.3.4 Schulz Flory plot for the Fe catalyst using the 1-pentene containing and pure 1/3 CO/H<sub>2</sub> feed at 7.8 atm. and 250°C. Nominal  $\alpha$  value is 0.53.

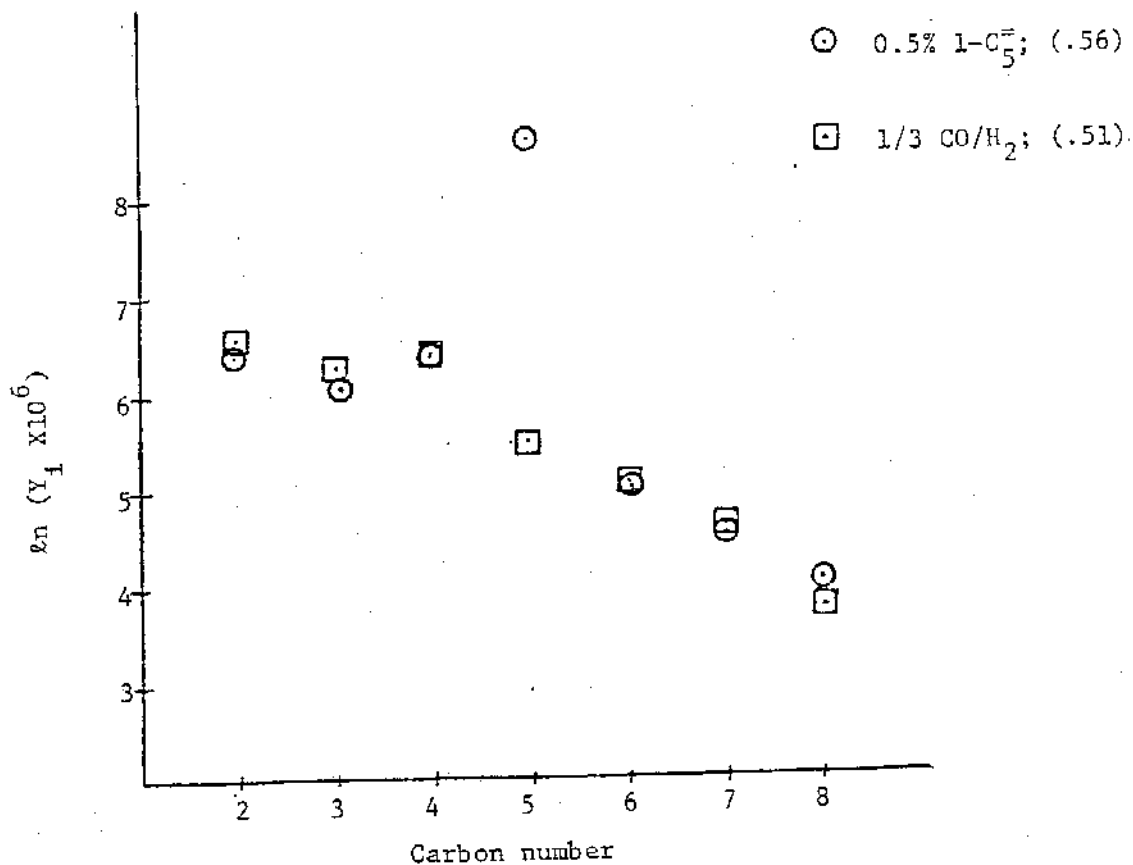


Figure 5.3.5 Schulz Flory plot for the Fe catalyst using the 1-pentene containing and 1/3 CO/H<sub>2</sub> feed at 14 atm. and 250°C. Nominal GHSV = 300 hr<sup>-1</sup>. Numbers in parentheses refer to  $\alpha$  values.



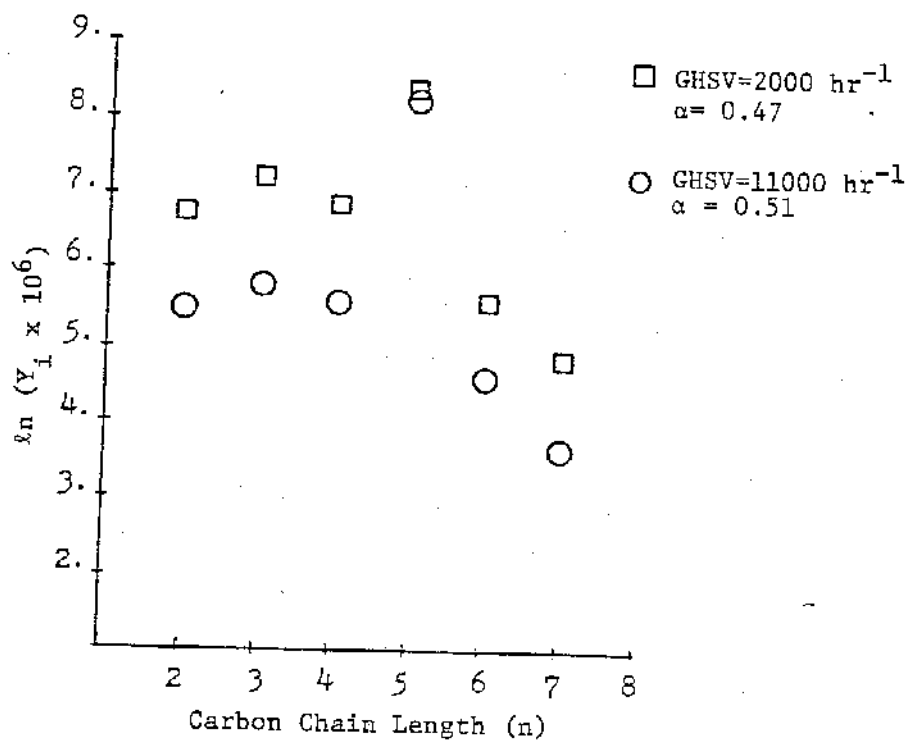


Figure 5.3.6 Schulz Flory plot for the Co catalyst using the 1-pentene 1/3 CO/H<sub>2</sub> feed at 1 atm and 250°C.

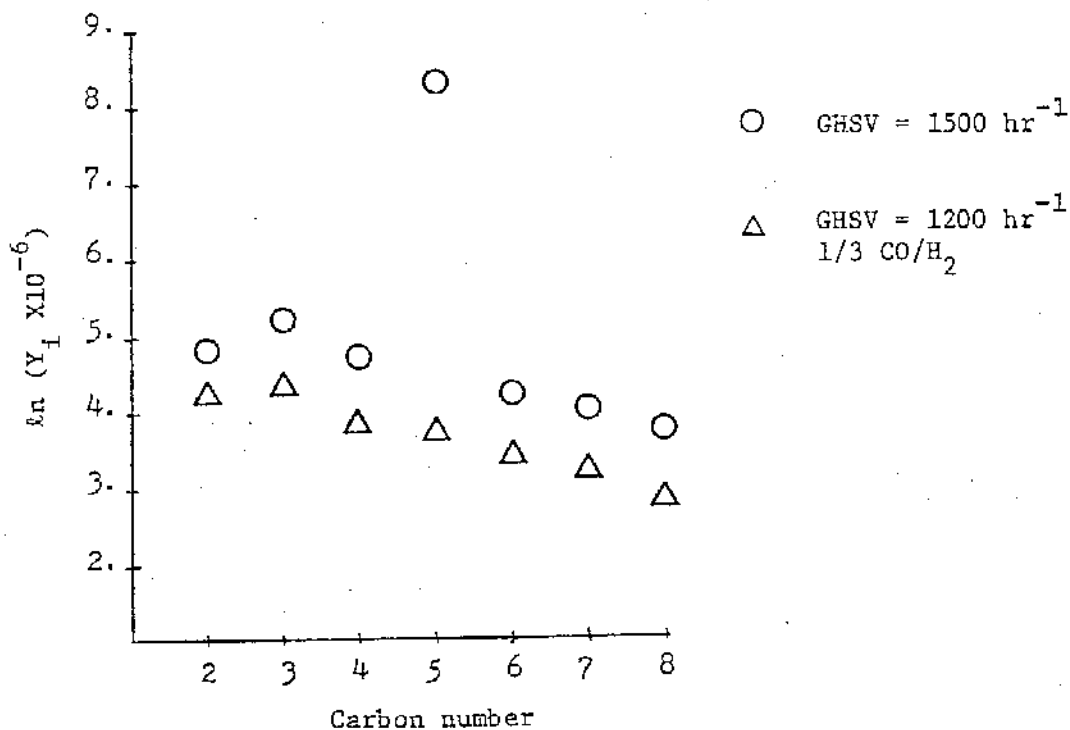


Figure 5.3.7 Schulz Flory plot for the Co catalyst using the 1-pentene and pure 1/3 CO/H<sub>2</sub> feed at 7.8 atm. and 250°C. Nominal  $\alpha$  value = 0.88.

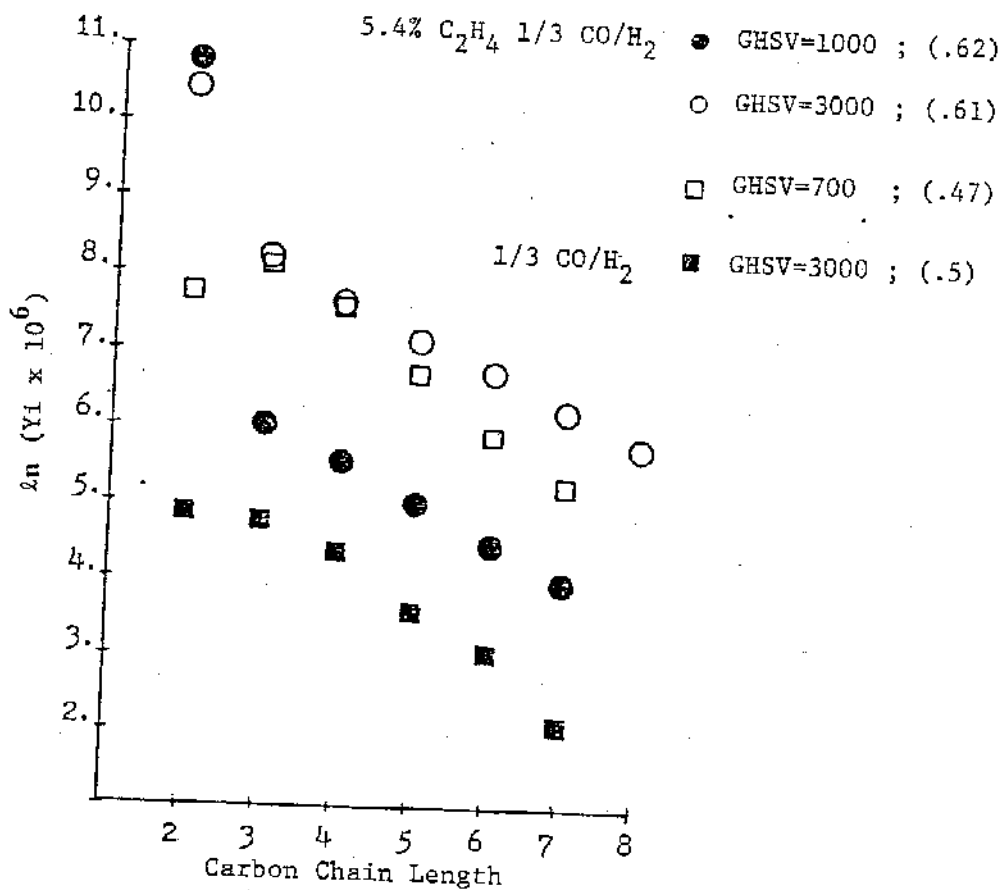


Figure 5.3.8 Schulz Flory plot for the Co catalyst using the ethylene/CO/H<sub>2</sub> feed at 1.0 atm. and 250°C. Numbers in parenthesis refer to  $\alpha$  values.