

4.5.1 Schulz Flory Parameterization for the Fe catalyst

Based on the data presented in Table 4.5.1 it appears that α is dependent on pressure and to a lesser extent on feed composition. In Figure 4.5.1 the product distributions are presented for both feeds at one atmosphere pressure for the Fe catalyst. The general behavior of the product distribution is similar in both cases with the α value yielding an average value of .489 for the 1/1 CO/H₂ feed compared to a value of .425 for the 1/3 feed. At lower conversion (>1%) there appears to be a decrease in α . This may be due to either of two entirely different reasons.

The first reason deals with product kinetics. At high space velocities (low conversions) the net product desorption is most likely enhanced since the concentration of products in the gas phase is low. This would result in an increase in the termination rate relative to the propagation rate, hence a decrease in α . Dwyer and Somorjai (40) report an α value of 0.3 for an Fe(111) single crystal with a 1/3 CO/H₂ feed at 6 atmospheres. Their data were obtained at less than 1% conversion at 300°C. This α value (.3) is considerably less than the values obtained for the Fe catalyst at 7.8 atmospheres ($\alpha=.527$), obtained at 2 and 3.1% conversion. The propagation rate is most likely positive order in the concentration of adsorbed intermediates and the termination rate is proportional to the desorption rate, lower conversions should yield smaller α values. The product distributions obtained by Dwyer and Somorjai (40) are under transient reaction conditions since there was approximately a 75% loss in activity during the first two hours of reaction. Hence the product distribution observed may not be

representative of that obtained at steady state.

Although there is a kinetic rationale for diminished growth probabilities at low conversions experimental inaccuracies in quantitative product analysis are most likely the principal factor for this observation. At 1% conversion the amount of C_5 products typically varies from 1 to 10 PPM. This concentration range represents the limit of reproducibility in measurements within 10% accuracy. Lower concentrations can lead to greater inaccuracies in product mole analysis. Henrici-Olivé and Olivé (56) have reviewed published data on product distributions (59) and concluded that experimental uncertainties exist in the values of Y_i for the high molecular weight components due to inaccuracies in the product analysis. There is an underestimation of the longer chain product yields since the corresponding peak areas can be comparable to the fraction of product moles undetected due to chromatographic sensitivity.

At one atmosphere the linear portion of the SF distribution extends from C_3 to the higher carbon chains (Figure 4.5.1). However at higher pressures (Figure 4.5.2) the linear relationship between chain length and $\ln(Y_{Ci})$ begins at the C_4 products. This difference may be due to the shift in the hydrocarbon product distribution towards higher molecular weight products with increasing pressure. The α value obtained with the Fe catalyst with the 1/1 feed at 7.8 and 14 atmospheres is 0.57. This agrees with a previously reported value of 0.6185 obtained over a fluidized iron catalyst at similar reactor conditions but at much higher conversions (6).

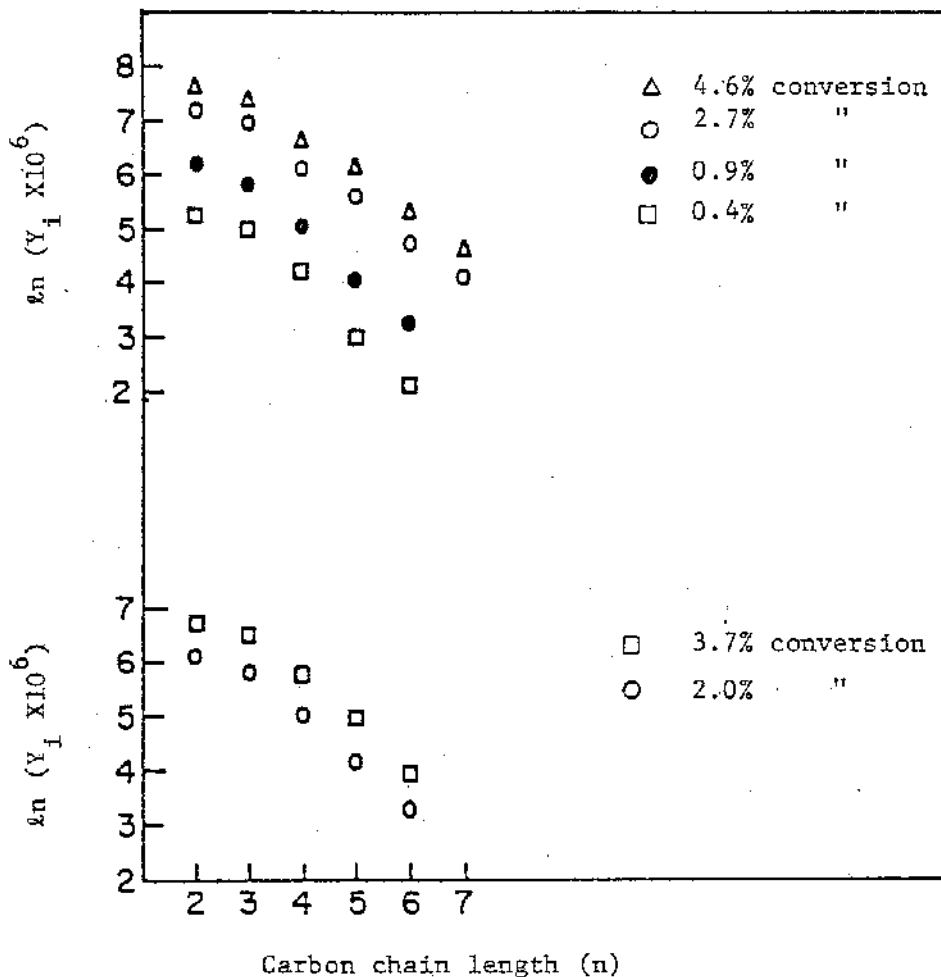


Figure 4.5.1 Schulz Flory plot for the Fe catalyst at 1 atm. and 250°C using the 1/1 CO/H₂ feed (top) and 1/3 CO/H₂ feed (bottom) at various CO conversion levels.

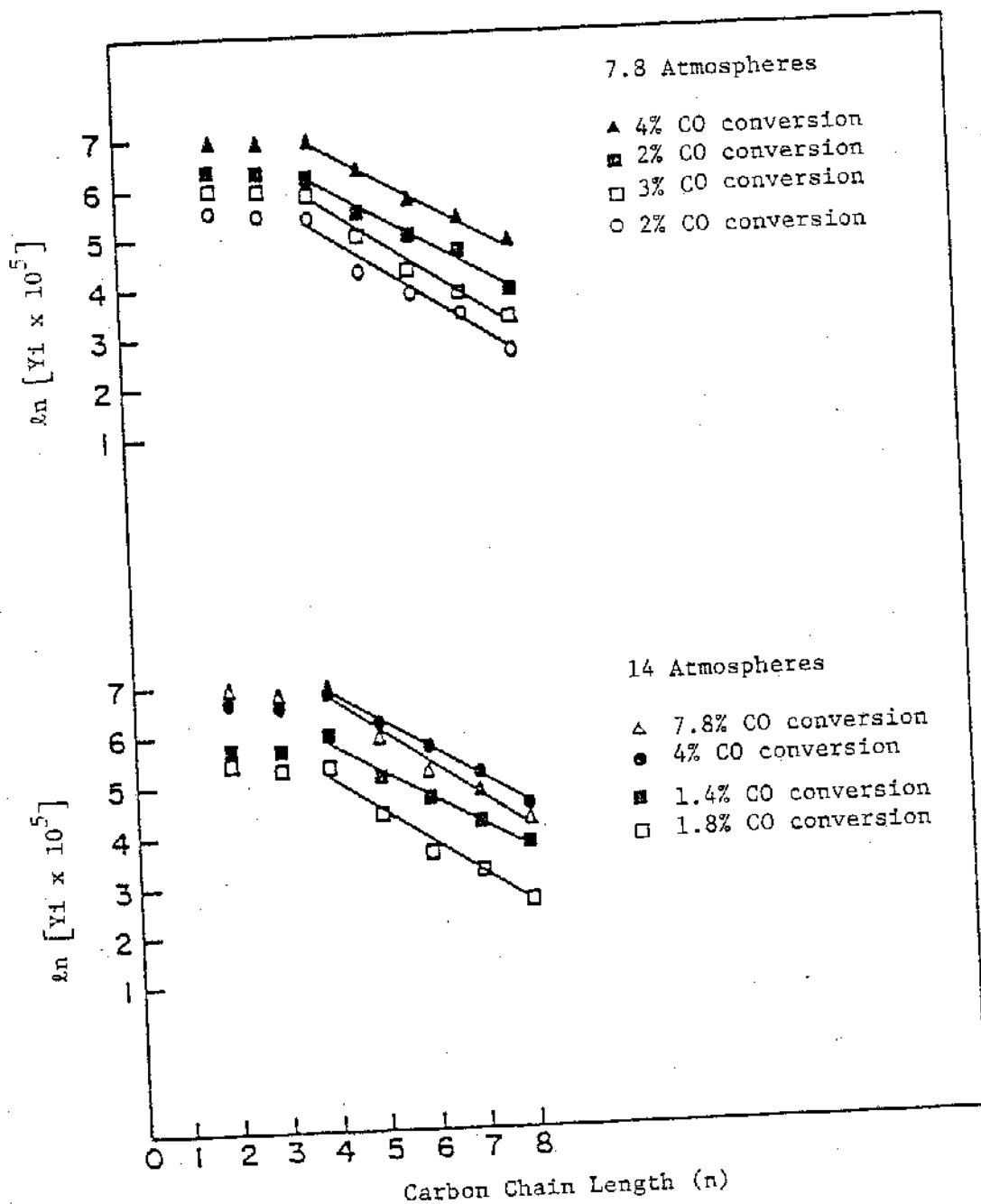


Figure 4.5.2 Schulz Flory plot for the Fe catalyst at 7.8 (top) and 14 (bottom) atmospheres at 250°C. Solid symbols denote data obtained with 1/1 CO/H₂ feed. Open symbols correspond to 1/3 CO/H₂ feed.

4.5.2 Schulz Flory Parameterization for the Co catalyst

Figures 4.5.3 and 4.5.4 present the SF product distribution plots for the Co catalyst using the 1/1 and 1/3 feeds respectively. In both cases there is a significant increase in α at higher pressures (Table 4.5.1). This suggests that the intrinsic kinetics of CO (or CH_x) incorporation into long chained hydrocarbons is pressure dependent. The lower $\ln(Y_{C_2})$ values compared to the $\ln(Y_{C_3})$ values for the Co catalyst suggest that ethylene is more reactive in chain initiation for this catalyst as compared to Fe, where $\ln(Y_{C_2}) > \ln(Y_{C_3})$. Further discussions on the secondary reactions of ethylene are given in Chapter 5. For the Co catalyst, ethylene is the only multicarbon product which shows significant deviation from the classical SF model at all the conditions studied.

There is a significant increase in the growth probability, α , with increasing pressure for the pure Co catalyst. For the 1/3 CO/H₂ mixture, α increases from a value of .464 at one atmosphere to a value of .777 at 14 atmospheres (Table 4.5.1). The growth probability obtained at 7.8 and 14 atmospheres agrees with the value obtained with bulk Co ($\alpha = 0.76 - 0.85$) at comparable pressures but much higher conversions (6). This increase corresponds to the shift in the product distribution towards high molecular weight products. The Co catalyst α values also exhibit the greatest dependence on feed composition among the catalysts studied:

4.5.3 Schulz Flory Parameterization for the FeCo catalyst

At one atmosphere the alloy catalyst SF product distributions (Figure 4.5.5) are similar to those of iron (Figure 4.5.1); the calculated α values are slightly higher (Table 4.5.1). The linear

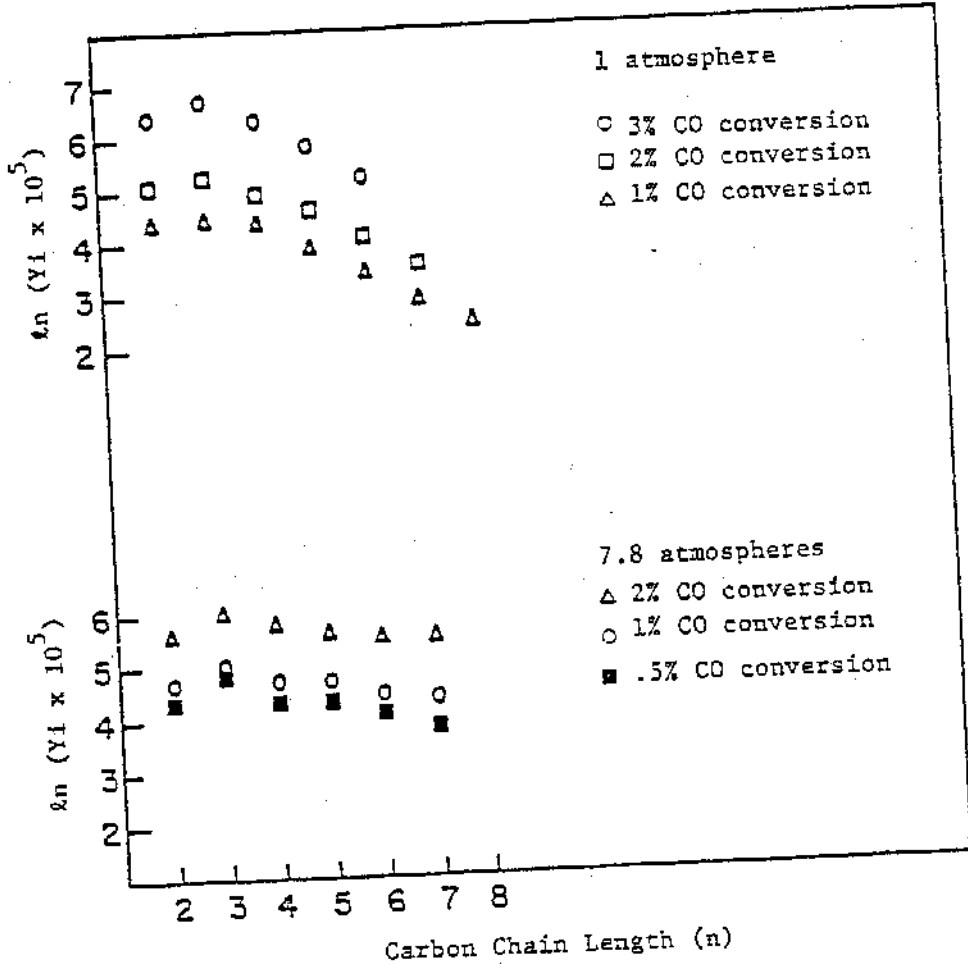


Figure 4.53 Schulz Flory plot for the CO catalyst at 1 atmosphere (top) and 7.8 atmospheres (bottom). 1/1 CO/H₂ feed and 250°C.

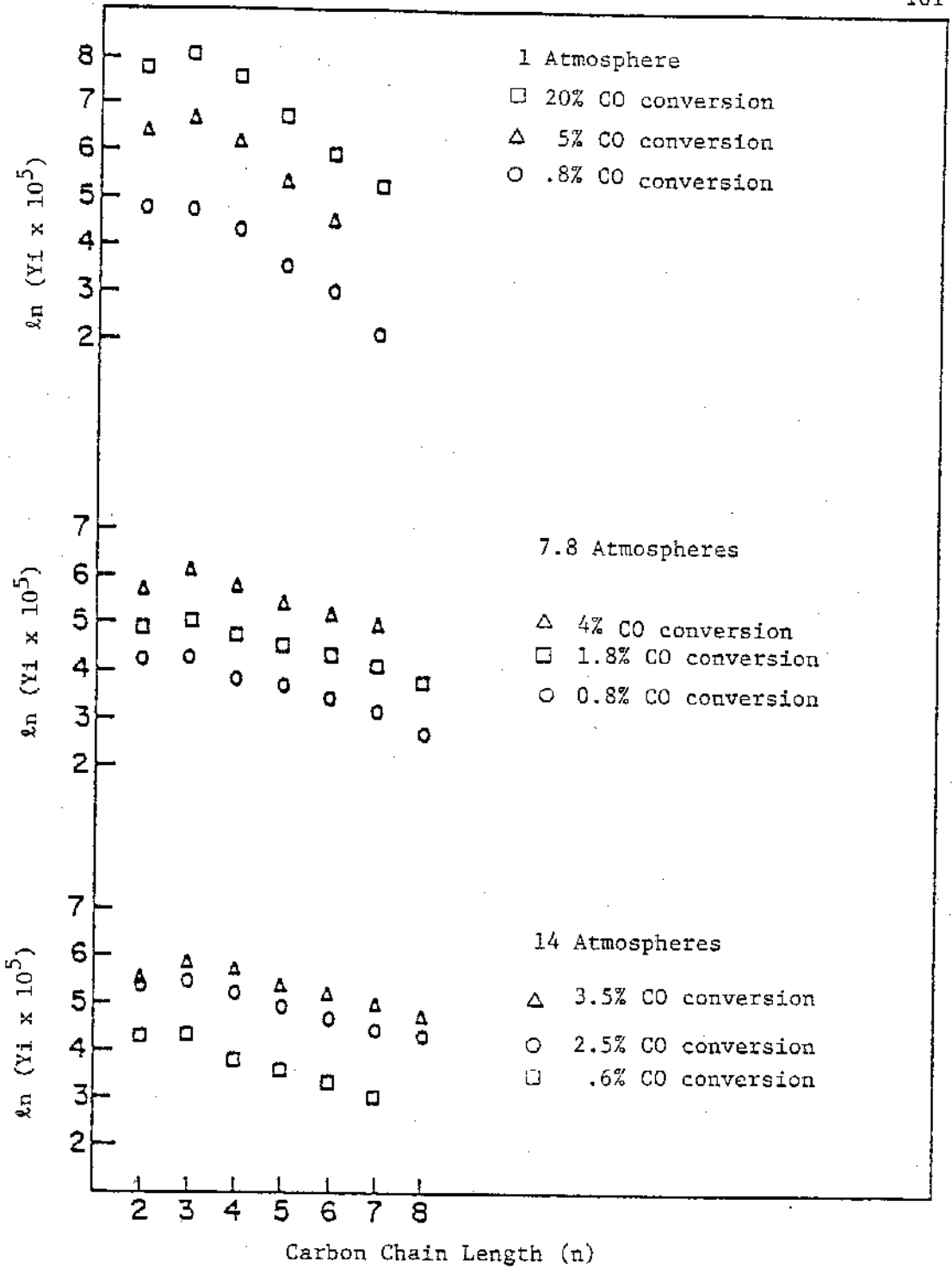


Figure 4.5.4 Schulz Flory plot for the Co catalyst at 1 (top) 7.8 (middle), and 14 (bottom) atmospheres. 1/3 CO/H₂ feed at 250°C.

portion extends from the C_3 products at this pressure and the α values appear to be independent of conversion. At elevated pressures the linear portion of the product distribution is conversion-dependent for both feed mixtures. At the lower CO conversions (<5%) there is a larger value in the slope ($\ln \alpha_n$) in going from $\ln(Y_{C_4})$ to $\ln(Y_{C_5})$ as compared to the slope value obtained between the points $\ln(Y_{C_5})$ and $\ln(Y_{C_6})$. At higher conversions the slope becomes approximately equal between these three points. The α values calculated for this catalyst are obtained through the linear portion containing the $C_{n>5}$ hydrocarbons for a given conversion level. (Table 4.5.1) Both linear chainlength regions (C_4-C_8 or C_5-C_7) yielded similar values of α for the 1/3 feed where data are available (Table 4.5.1).

Figure 4.5.8 presents the SF distributions for the Fe and FeCo catalyst at 14 atm. using the 1/3 CO/H₂ feed. The major difference between the two product distributions lie in the value of the growth parameter α . The FeCo catalyst has a much lower value for the $C_{n>4}$ product range indicating that the alloy has a reduced ability to produce longer chain products although not illustrated in Figure 4.5.8. The Co catalyst has an α value much larger than either iron containing catalyst. Nakamura et. al. (82) observed a similar decrease in long chain ($C_{n>4}$) product yields over FeCo alloy catalyst at 1 atm.

4.5.4. Influence of Pressure and Feed Ratio on the Growth Probability

Comparison of the growth probability parameters at various pressures reveals a very interesting trend for the FeCo catalyst. There is a significant decrease in α with increasing pressure. This trend is completely opposite of that observed with the pure component catalysts where the growth parameter increased with increasing pressure. Figure

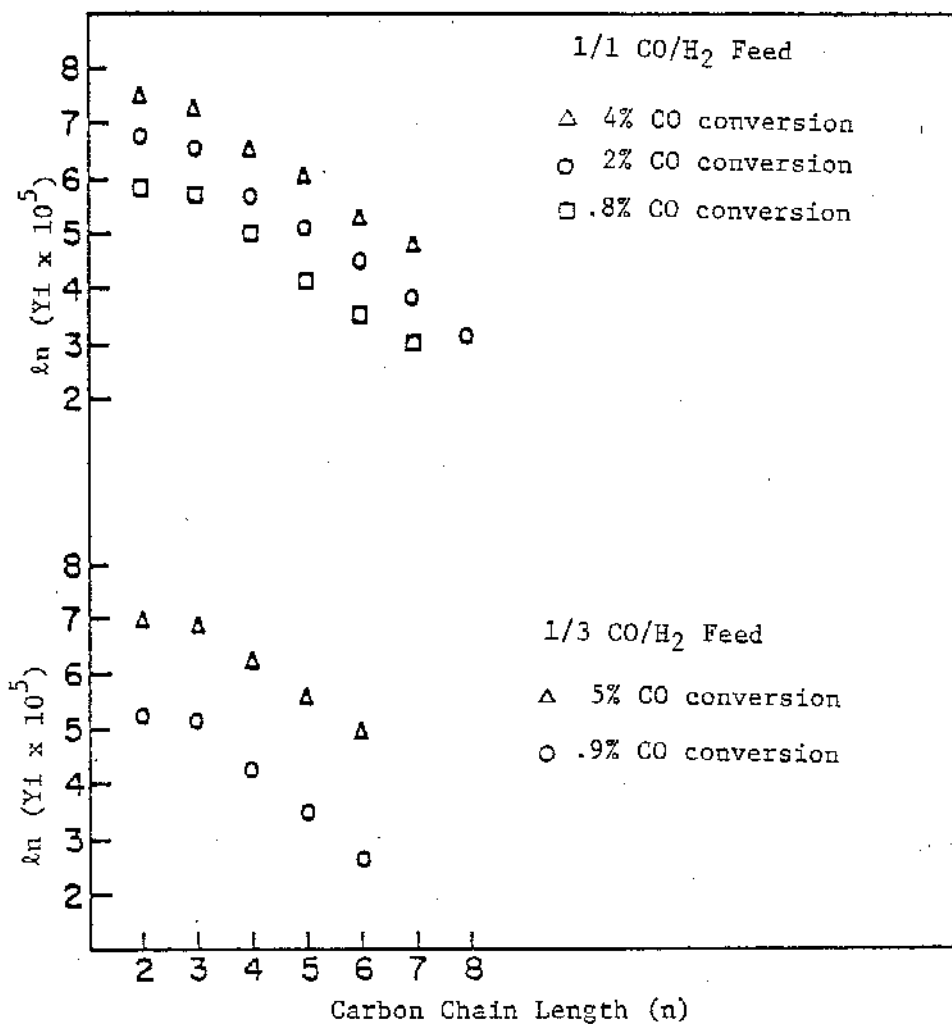


Figure 4.5.5 Schulz Flory plot for the FeCo catalyst at 1 atmosphere and 250°C with the 1/1 CO/H₂ feed (top) and 1/3 CO/H₂ feed (bottom).

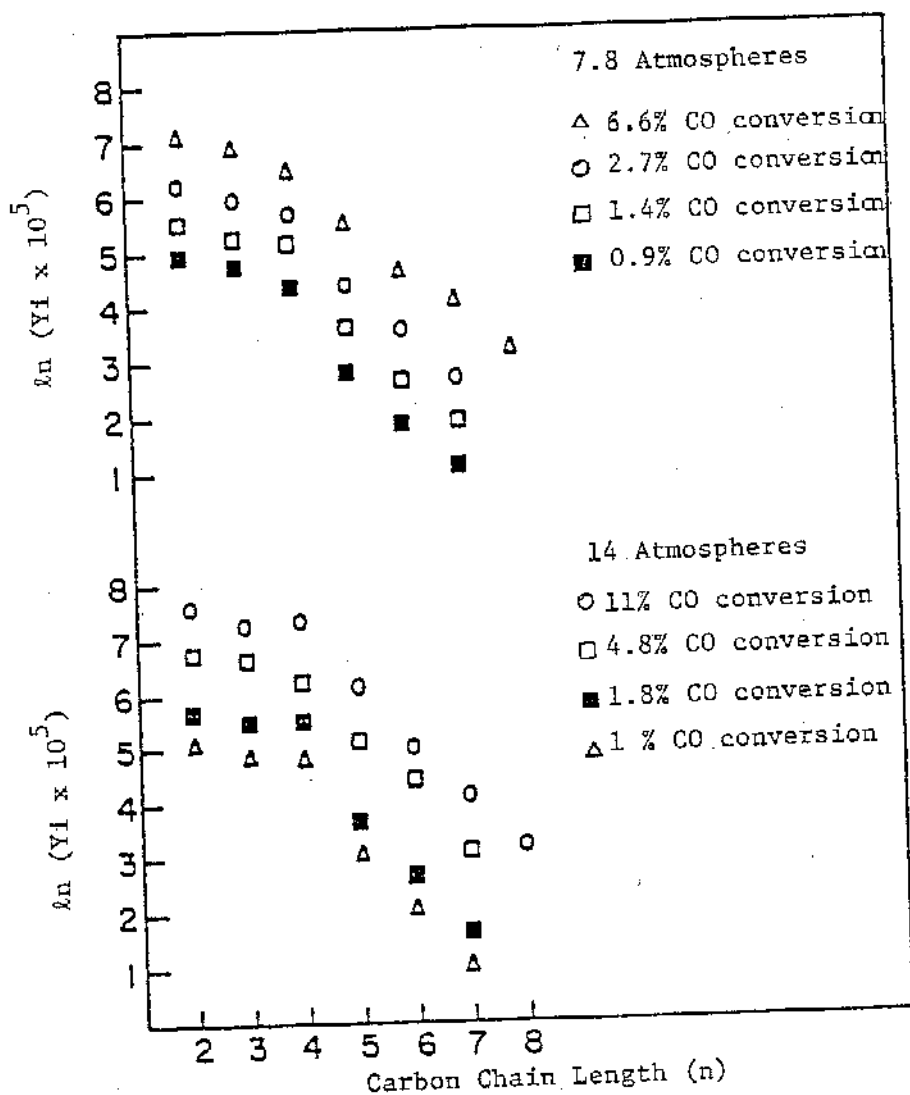


Figure 4.5.6 Schulz Flory plot for the FeCo catalyst at 7.8 atmospheres (top) and 14 atmospheres (bottom). 1/3 CO/H₂ Feed, 250°C.

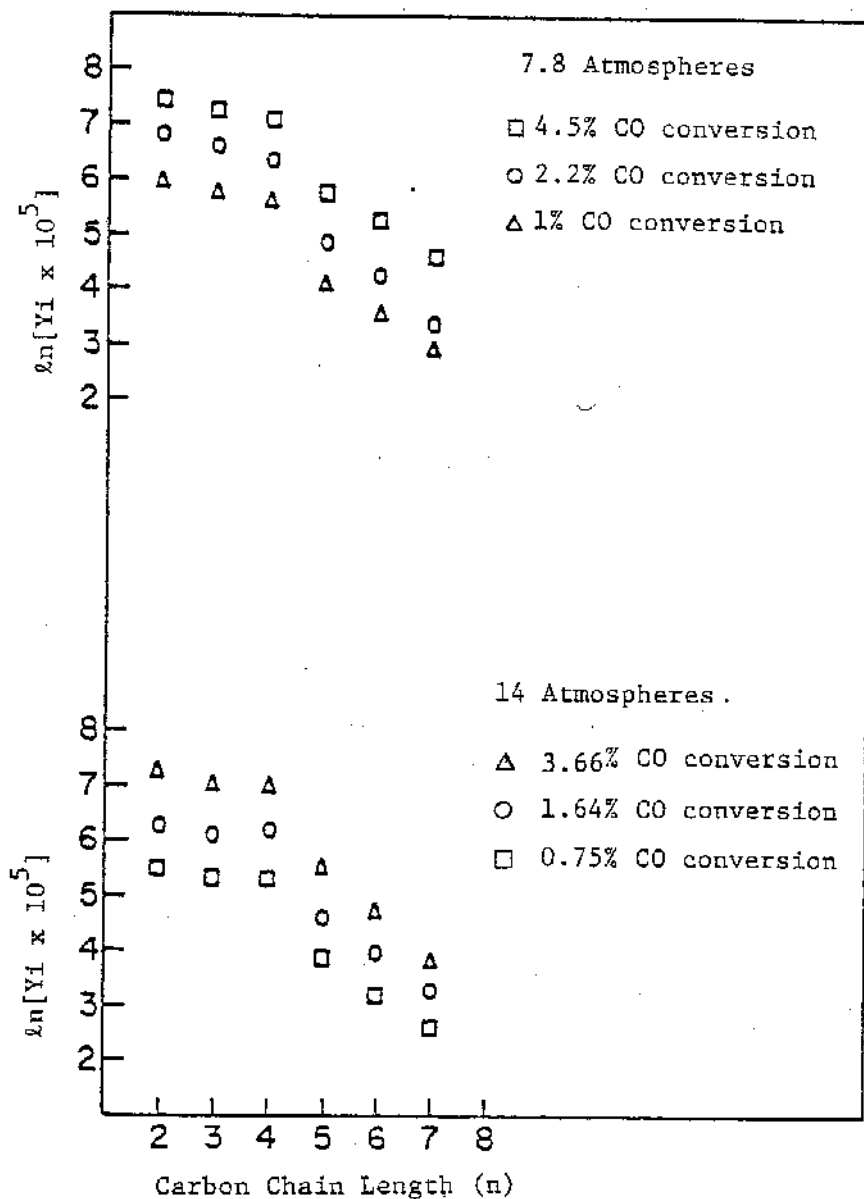


Figure 4.5.7 Schulz Flory plot for FeCo catalyst at 7.8 atmospheres (top) and 14 atmospheres (bottom). 1/1 CO/H₂ feed, 250°C.

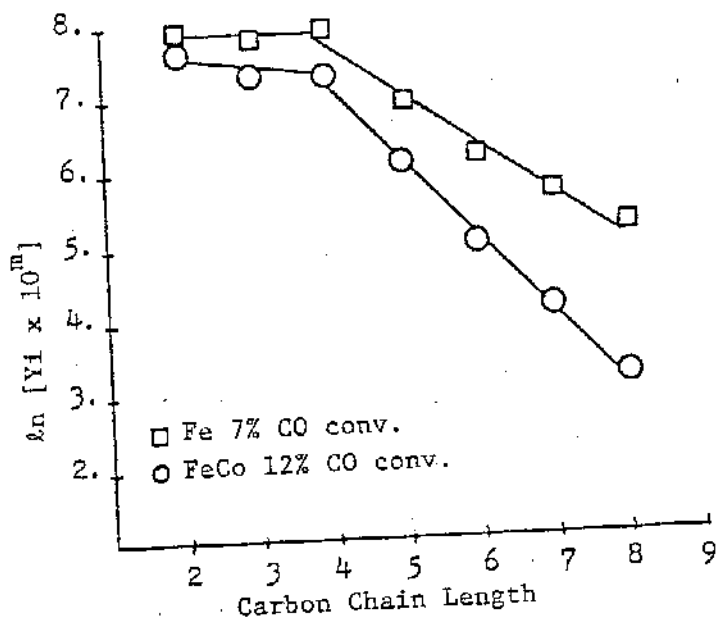


Figure 4.5.8 Schulz Flory plot for the Fe and FeCo catalyst at 14 atm. and 250°C.
For Fe $m=6$; FeCo $m=5$

4.5.9 illustrates the functional dependence of α on the total pressure for the two feed mixtures. The decrease in α at higher pressures indicates that the alloy catalyst has a lesser tendency to produce long hydrocarbon chains ($C_{n>5}$) with increasing pressure. In section 4.4 it is shown that the overall product distribution for the FeCo catalyst predominantly shifts towards methanol and low molecular weight paraffins (C_2 and C_3). The ability to produce long chain hydrocarbons is greater for the 1/1 CO/H₂ feed as compared to the 1/3 feed for all three catalysts at a given total pressure. This is most likely due to the lower relative hydrogenation rate due to the higher CO/H₂ rates.

4.5.5 C₁ Product Yields

In section 4.4 the product mole fractions obtained with the iron containing catalyst indicate that a principal shift in the product distribution is the increase of methanol with a corresponding decrease in methane at higher pressures. This shift is illustrated in Figure 4.5.10 where the fraction of the total amount of consumed CO converted into each of these products is plotted as a function of pressure for the iron containing catalyst. Figure 4.5.11 presents this data for the Co catalyst. The data is obtained at relatively constant CO conversion in order to account for the different N_{CH_4} and N_{CH_3OH} dependency on conversion associated with each catalyst. These results indicate that methanol is favored at higher pressures. For both iron containing catalysts the fraction of CO converted to $C_{n>2}$ hydrocarbon products is approximately 0.9 and it does not change appreciably with increasing pressure. The Co catalyst which produces very small quantities of methanol exhibits a relatively large decrease in the fraction of CO

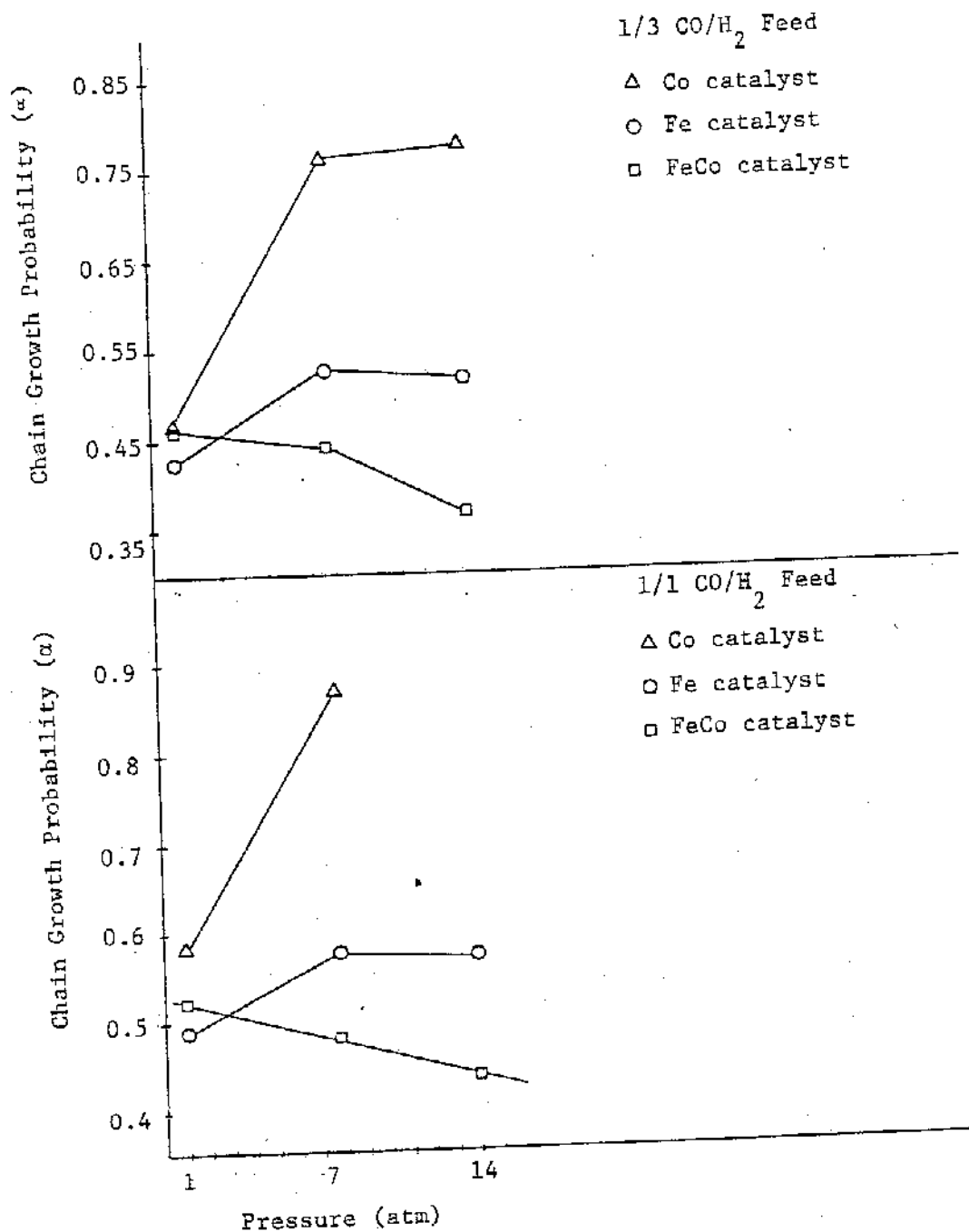


Figure 4.5.9 Growth probabilities as a function of pressure for the 1/3 and 1/1 CO/H₂ feed mixtures.

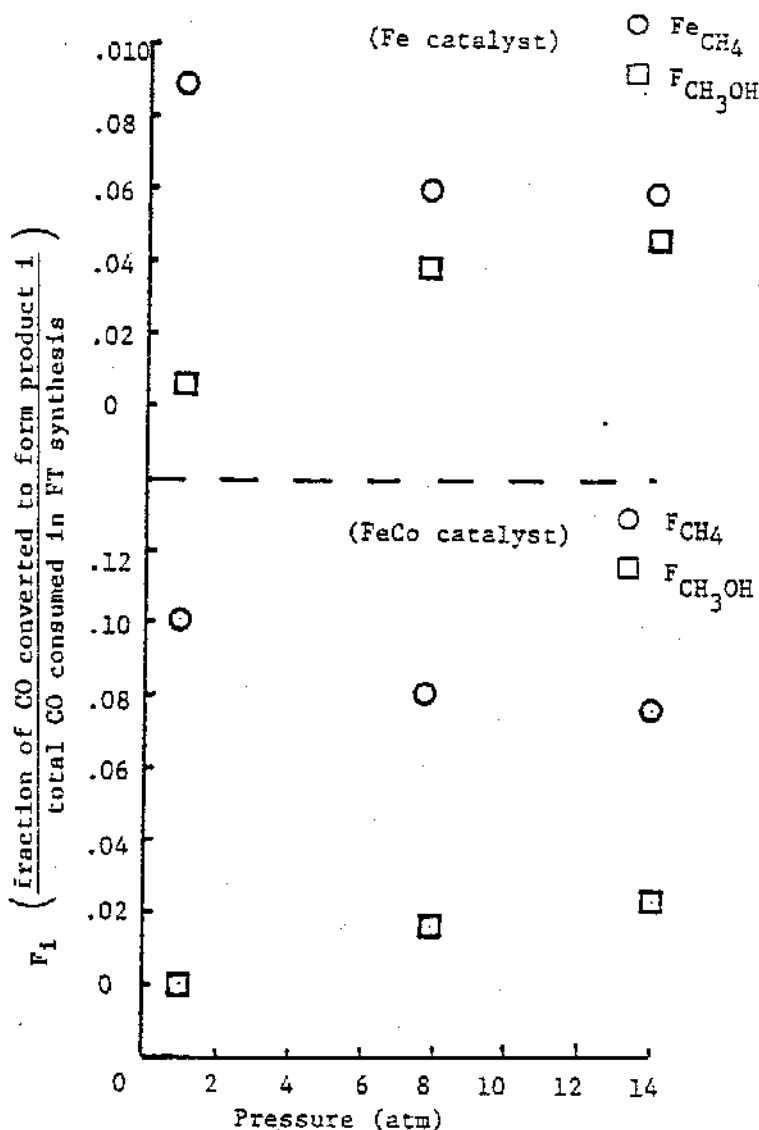


Figure 4.9.9 Fraction of converted CO reacted to form methanol and methane as a function of pressure for the Fe(top) and FeCo (bottom) catalysts using the 1/3 CO/H₂ feed at 250°C.

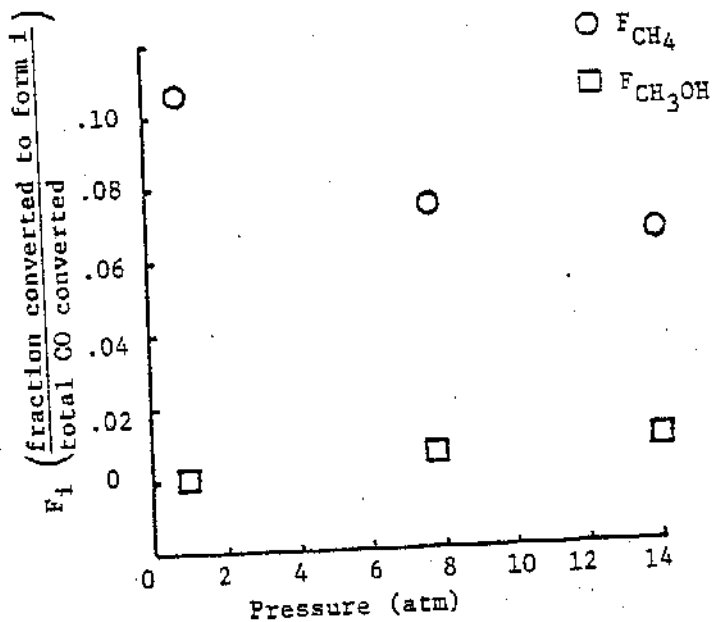


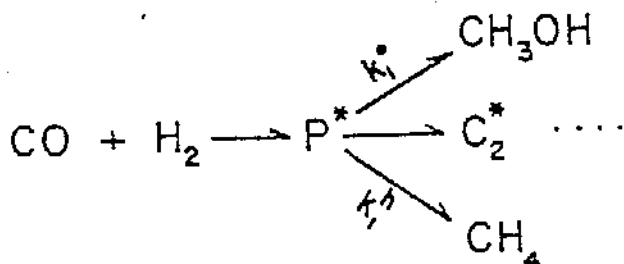
Figure 4.5.10 Fraction of converted CO reacted to form methanol and methane as a function of pressure for the Co catalyst using the 1/3 CO/H₂ feed at 250°C.

consumed into methane with increasing pressure. In this case the fraction of CO consumed into $C_{n>2}$ products increased from .88 to .94 in going from 1 to 14 atmospheres.

The noncompliance of the methane yield with SF kinetics have been reported in the literature (6,87,56) and in general the value of $\ln(Y_1)$ lies well above the linear portion established by longer chain products. Indeed this product can be produced by a different reaction sequence since it is not produced via a surface propagation reaction. The deviations observed in the C_1 and C_2 compounds imply that the propagation/termination kinetics of these products are different from those of longer chains. Consequently it is not unlikely that the kinetics of methane formation are different from that of longer chains.

Nijs and Jacobs (87) have proposed a FT mechanism in which the hydrogenation of a surface carbide leads to methane while the condensation of enol intermediates leads to longer chain products. This mechanism proposes the existence of both single carbon carbidic and enolic surface species and could explain the coproduction of hydrocarbons and alcohols under FT conditions.

One might envision that both methanol and methane are produced from a common surface precursor as shown below



4.5.2

where the surface precursor (p^*) could be of the form