ethane compared to the pure component catalyst. Higher pressures enhance the hydrogenation activity over the ethylene production rate for the FeCo catalyst while the relative values of these activities for the Fe and Co catalyst remain relatively unchanged.

At higher pressures there is a decrease in the $N_{C_3^=}/N_{C_3}$ ratio compared to the values obtained at one atmopshere (Compare $N_{C_3^=}/N_{C_3}$ ratios in Figures 4.3.21 and 4.3.28). The Co catalyst again yields the highest values of this ratio while the values for FeCo appear to be slightly lower than those of the Fe catalyst. At 14 atmospheres the alloy catalyst again produces much lower $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ values compared to pure iron, again indicating that the hydrogenation activity of the FeCo catalyst has a greater pressure dependence than that of the pure Fe catalyst (Figure 4.3.29)

4.3.7 Methane Yields for 1/1 CO/H_2 Mixture

Figures 4.3.30, 4.3.31 and 4.3.32 present the methane yields for the Fe, Co, and FeCo catalyst respectively at various pressures with the 1/1 CO/H_2 feed. Both pure component catalysts show a larger decrease in Y_{CH_4} with increasing pressure compared to the decrease observed for the alloy catalyst. The methane yields obtained with this feed are significantly lower than those obtained with the 1/3 feed for a given conversion level (Compare Figures 4.3.15 through 4.3.17 with Figures 4.3.29 - 4.3.32) This result is expected since the methane production is generally near first order in hydrogen partial pressure.

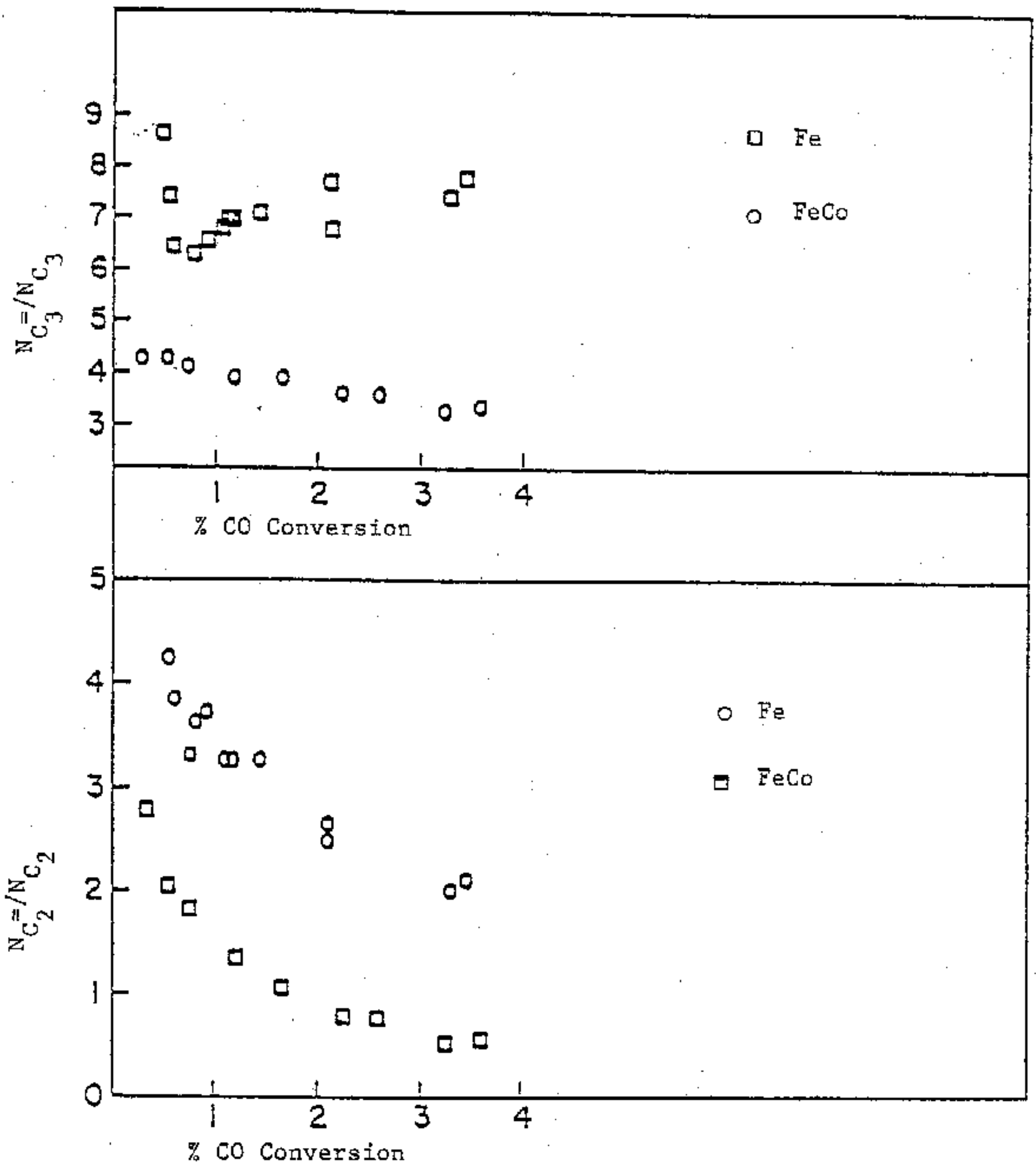

Figure 4.3.29 $N_{C_3^=}/N_{C_3}$ (top) and $N_{C_2^=}/N_{C_2}$ (bottom) versus % CO conversion for the Fe and FeCo catalyst in the 1/1 CO/H_2 feed at 14 atmospheres.

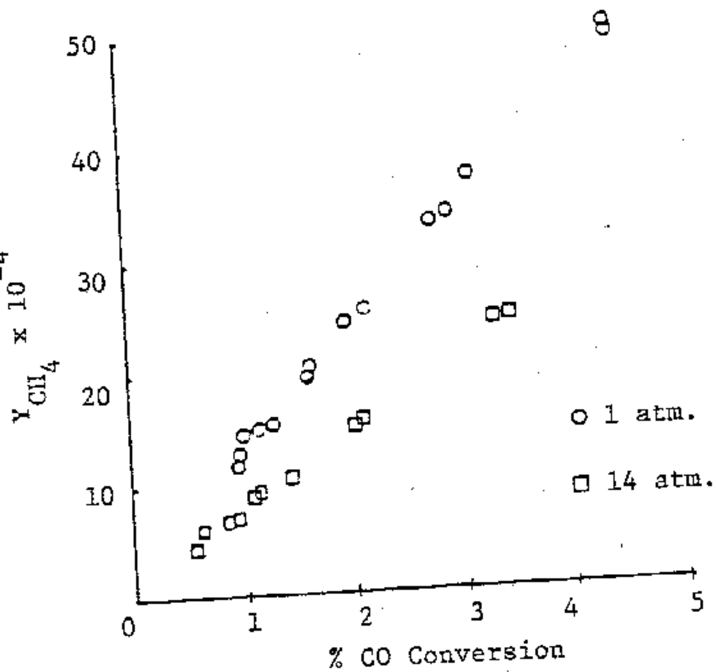

Figure 4.3.30 Methane yield versus percent CO conversion for the Fe catalyst using the 1/1 CO/H_2 feed at 1 and 14 atm. and 250°C.

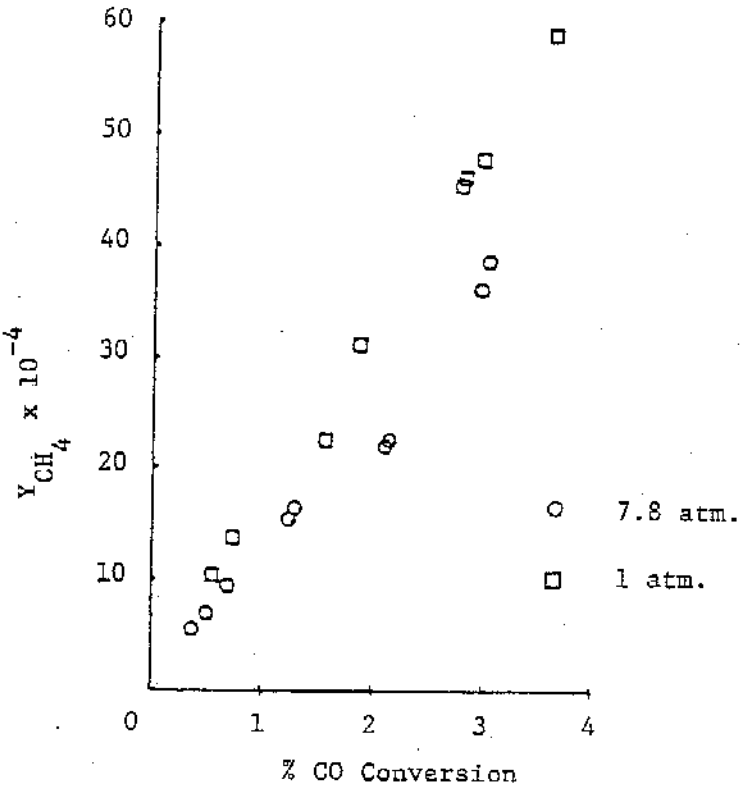

Figure 4.3.31 Methane yield as a function of percent CO conversion for the Co catalyst using the 1/1 CO/H_2 feed at 1 and 7.8 atm. and 250°C.

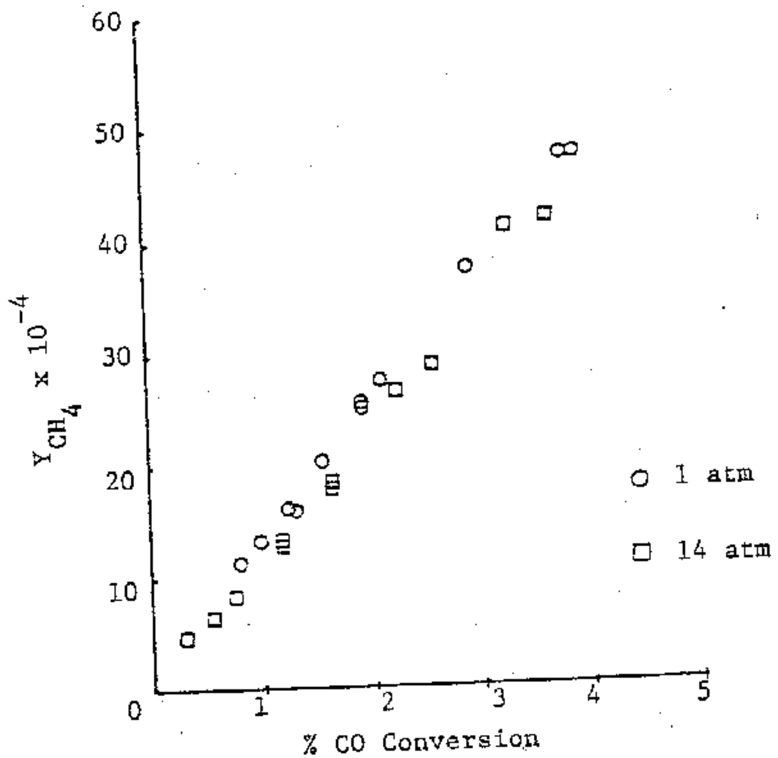

Figure 4.3.32 Methane yield as a function of percent CO conversion for the FeCo catalyst using the 1/1 CO/H_2 feed at 1 and 14 atm. and 250°C.

4.4 Steady State Product Distributions

Product yields and specific activities do not clearly present the selectivity shifts in the overall product distribution with changes in pressure, CO conversion and CO/H_2 feed ratios. In order to show these shifts the complete product distributions are presented for the various reaction conditions employed in this study in terms of the product mole fraction P_i defined below as

$$P_i = \frac{\text{moles of product } i}{\text{total product moles}} \qquad 4.4.1$$

It should be noted that product yields cannot be quantitively computed from such data since each catalyst generally produces a different amount of total product moles for a given set of reactor conditions. The principal intention of this discussion is to show the qualitative shifts in the overall product distributions obtained by each catalyst with increasing pressure. In Section 4.4.1 these shifts are compared among the catalyst at the same CO conversion level. The shifts in the product distribution associted with changes in CO conversion and pressure are presented in Section 4.4.2. The hydrocarbon product distribution is treated seperately in the Section 4.5.

4.4.1 Overall Product Distributions

Figures 4.4.1 and 4.4.2 present the steady state product distributions for all three catalyst at one atmosphere for the 1/3 and 1/1 CO/H_2 respectively. The results obtained with the lower CO/H_2 feed ratio are in agreement with Amelse et al. (1,3). The Co catalyst produces the largest fraction of methane while the iron containing catalysts produce smaller amounts. The FeCo and Fe catalyst yield similar product mole fractions of C_2 and C_3 components while the Co

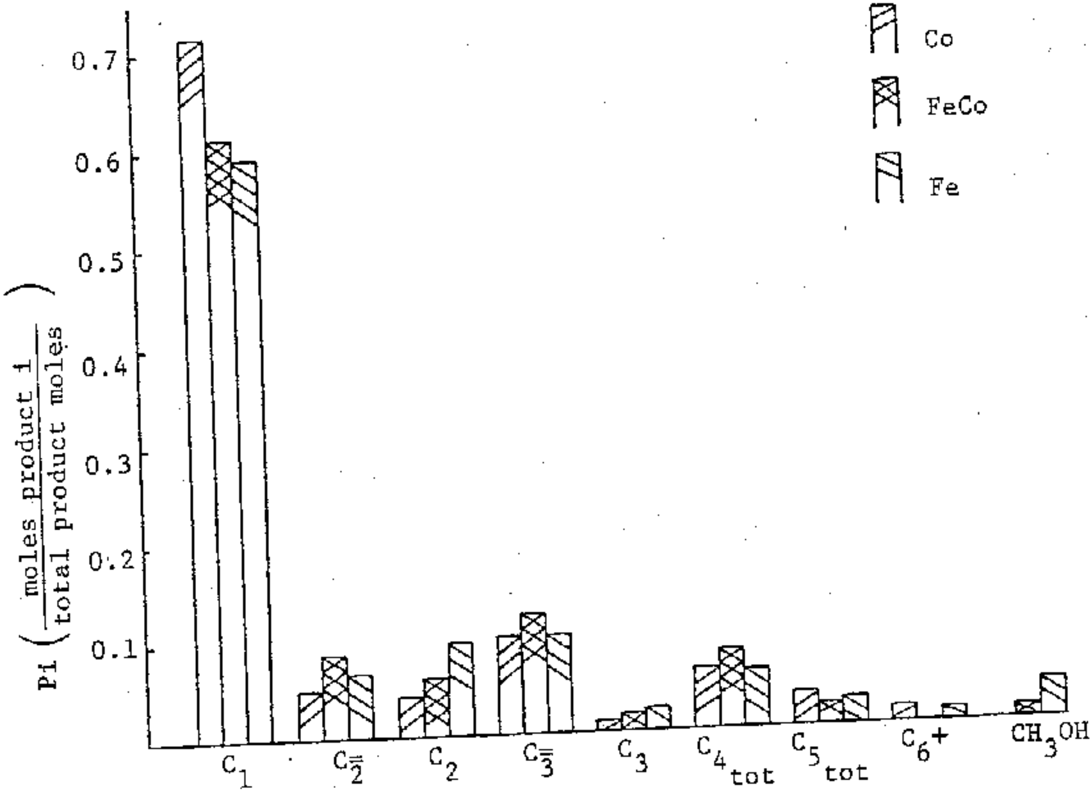

Figure 4.4.1 Product mole fractions for all three catalysts at 1 atm. and 250°C using the 1/3 CO/H_2 feed. Nominal CO conversion is 2.5%.

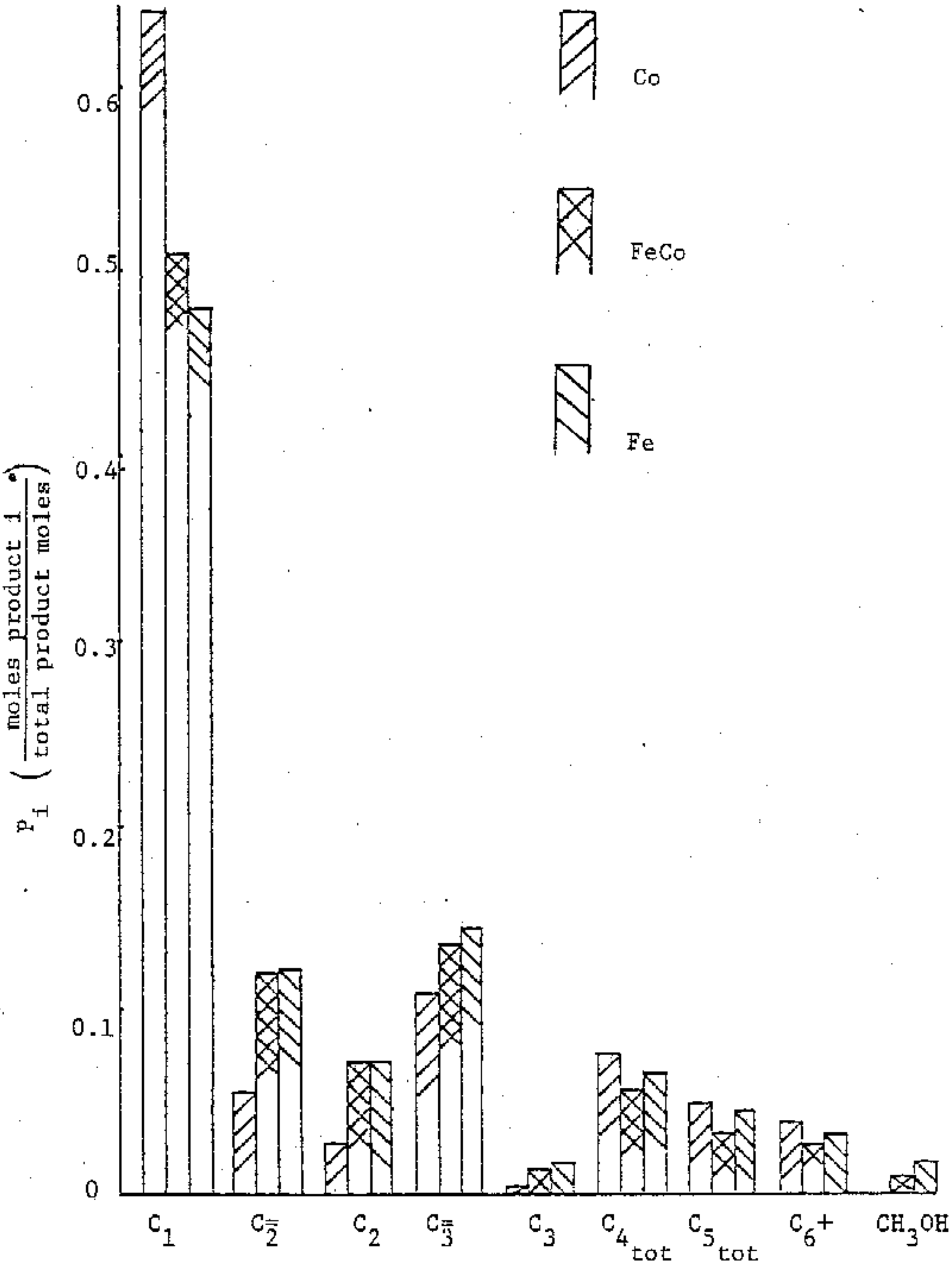

Figure 4.4.2 Product mole fractions for all three catalysts at 1 atm. and 250°C using the 1/1 CO/H_2 feed at a nominal 2.8% CO conversion.

catalyst consistently yields smaller amounts at these conditions. However for hydrocarbon products Cn ⩾ 5 the reverse is true. It is interesting to note that measurable amounts of methanol are produced at one atmosphere over both the Fe and FeCo catalyst. This product was not detected by Amelse et al. (1) at similar conditions. The improved analytical capabilities of this laboratory presently available allow for a more thorough analysis of product peaks compared to the capabilities at the time of their investigations (1).

The product fraction of methane is, as expected, lower in the 1/1 CO/H_2 feed compared to the 1/3 feed. This is the case for all of the catalysts under the pressure conditions studied. Figure 4.4.3 presents the product distributions obtained with the Fe catalyst under similar CO conversions for the two feed ratios at 1 atm. The decrease in the paraffin fractions of the C_2 through C_6 products indicate that secondary reactions involving the hydrogenation of olefin products are less pronounced with the 1/1 feed. The decrease in the methanol fraction at the higher CO/H_2 ratios suggest that its product yield is inhibited by higher CO concentrations.

Figures 4.4.4 and 4.4.5 are plots of the product mole fractions of the catalysts at 7.8 and 14 atmospheres respectively using the 1/3 feed. At higher pressures the mole fraction of methane is considerably less than obtained at one atmosphere. However, there is no appreciable increase in the product fractions of the $C_{n \geq 2}$ hydrocarbon products for the iron based catalyst. (Compare Figures 4.4.1 with 4.4.4 and 4.4.5). The principle shift in the mole fraction product distribution with increasing pressure appears to be enhanced methanol fractions while the total amount of product moles at a given conversion remain relatively

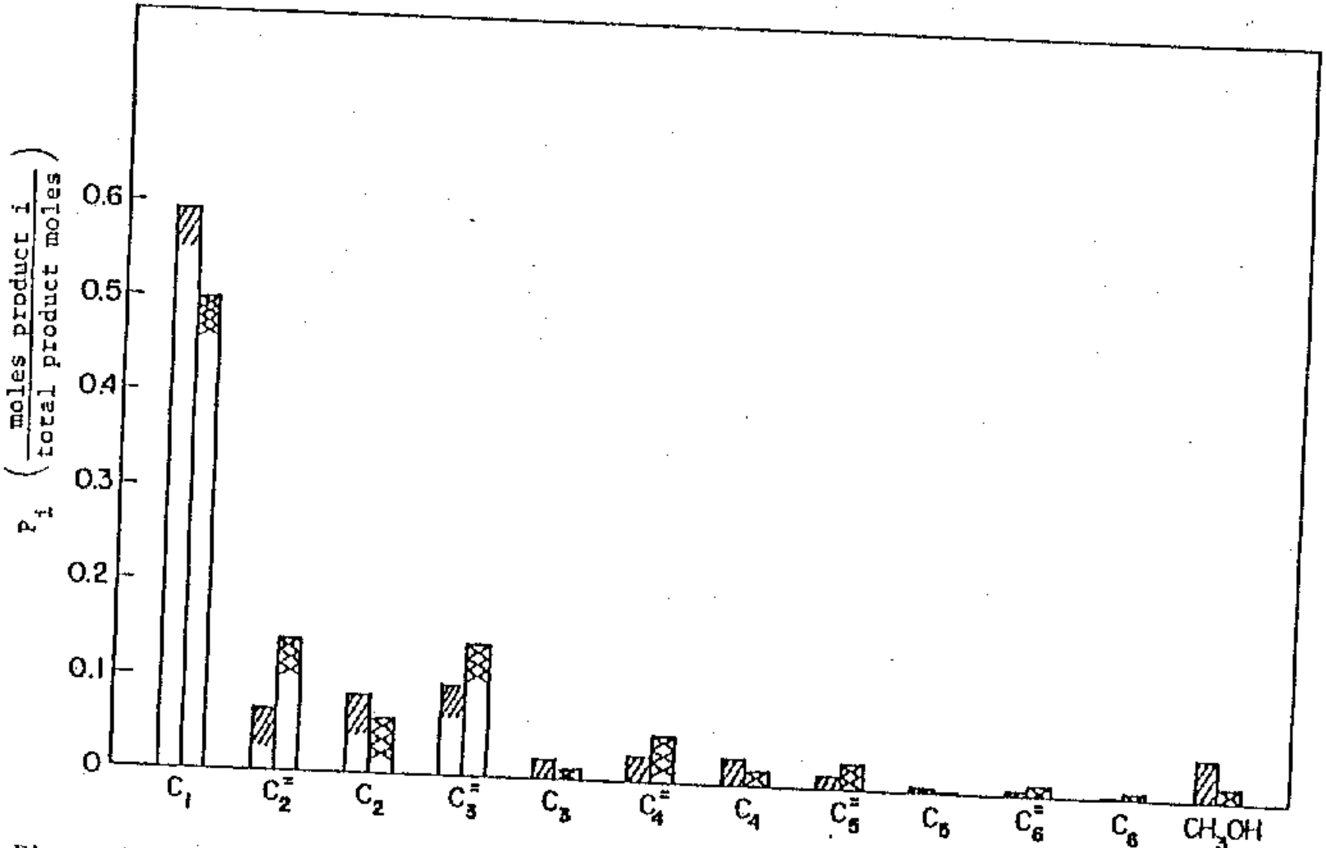

Figure 4.4.3 Product mole fractions for the Fe catalyst at 1 atm and 250°C with the 1/1 and 1/3 CO/H_2 feeds.

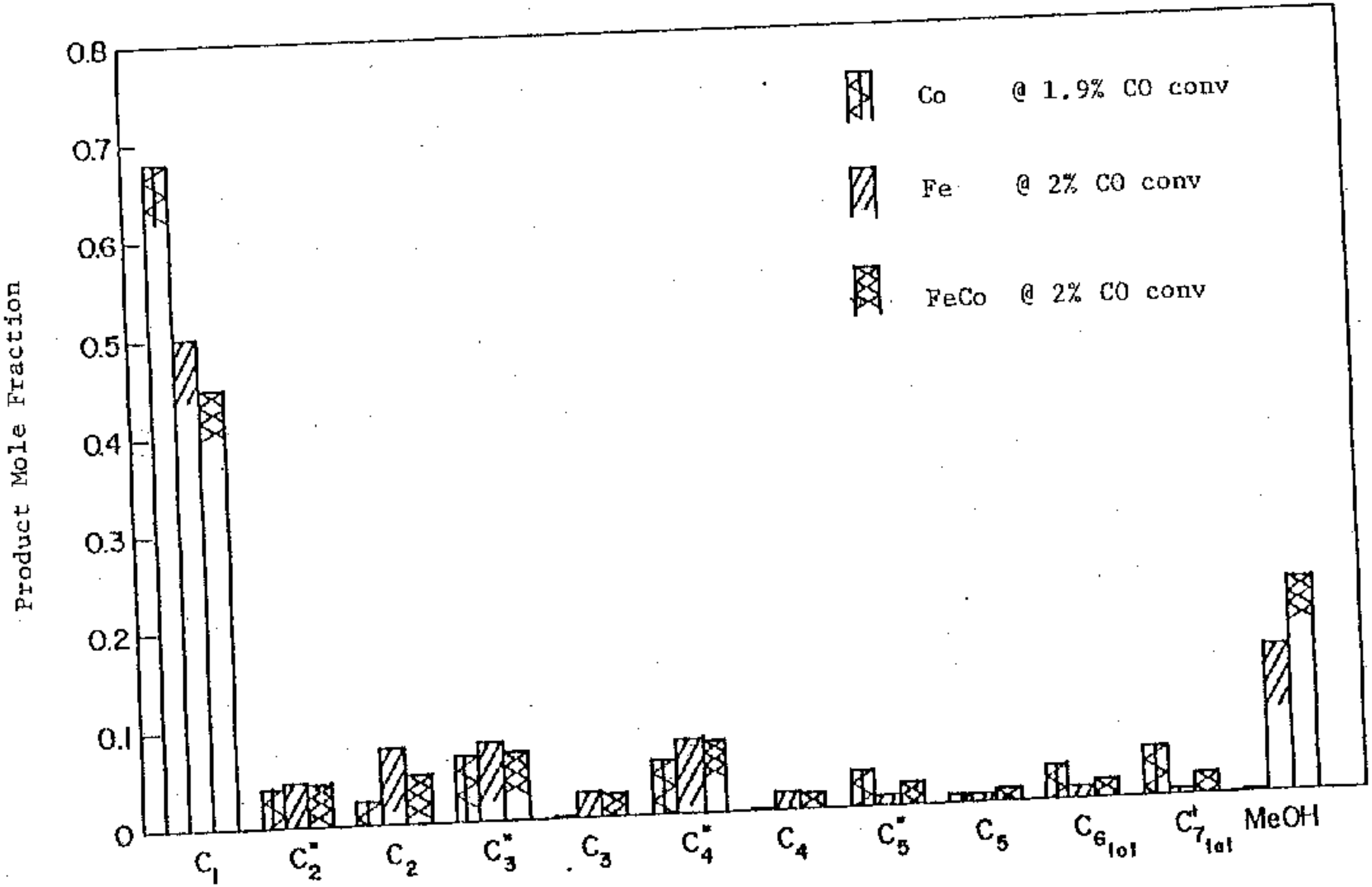

Figure 4.4.4 Product mole fractions for all three catalysts at 7.8 atm. and 250°C with the 1/3 CO/H_2 feed.

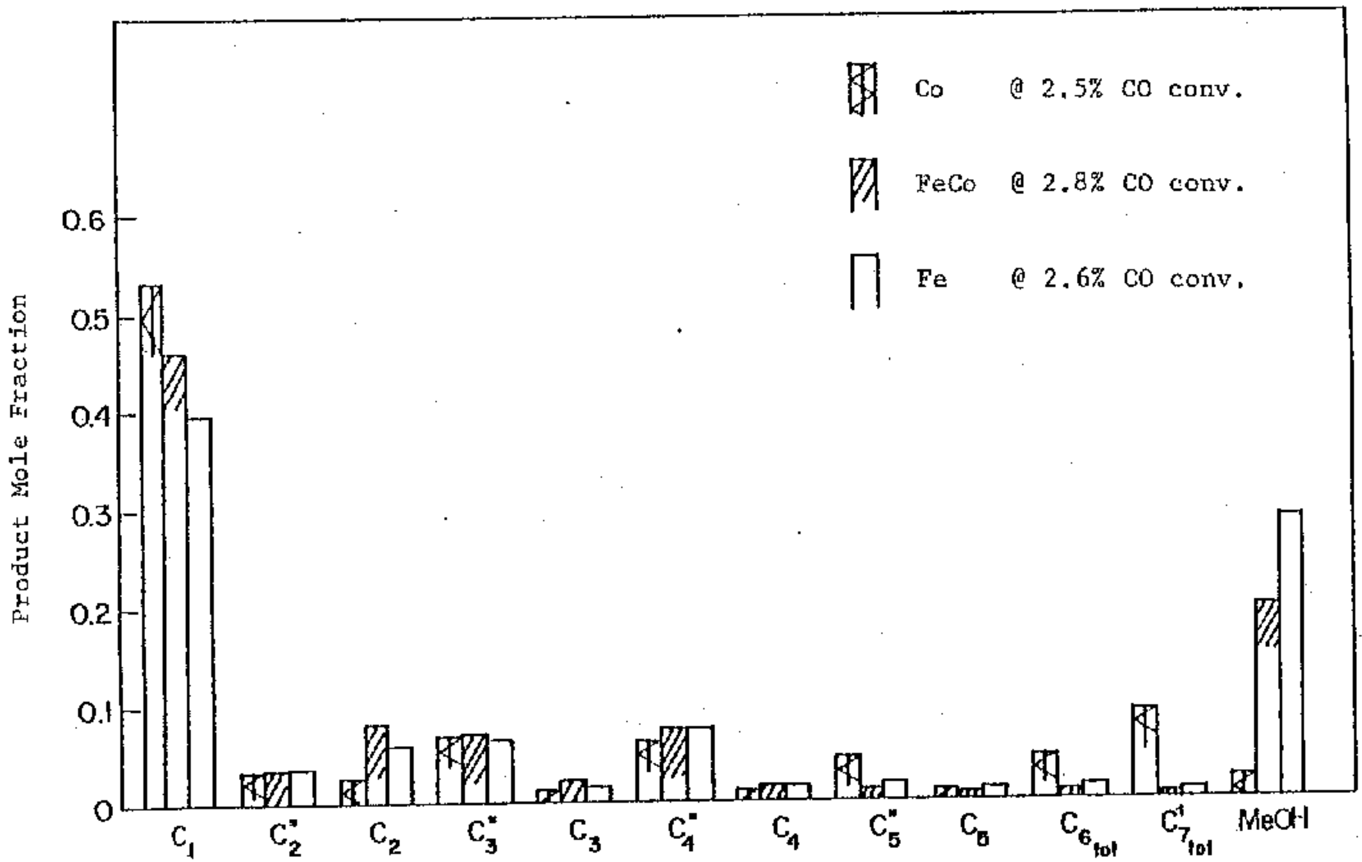

Figure 4.4.5 Product mole fractions of all three catalysts at 14 atm. and 250°C with the 1/3 CO/H_2 feed.

constant. For the Fe catalyst the sum of the methane and methanol fractions at 1 atmosphere (Figure 4.4.1) is .63 compared to a sum of .68 at 14 atmospheres (Figure 4.4.5). A similar calculation for the FeCo catalyst yields values of .625 and .655 respectively. At the 1/3 feed ratio it appears that increasing pressure shifts the CO consumption from methane production to methanol production for the iron-based catalyst. These observations are further discussed in Section 4.4.2.

With increasing pressure the Co catalyst produces less total product moles at a fixed CO conversion and there is a significant shift in the product distribution towards higher molecular weight. The behavior of the Co catalyst is typical to that encountered when operating at higher CO conversion levels (6). The atypical product distribution shifts mentioned above for the iron based catalyst could be due to the relatively high space velocities (low CO conversion levels) employed in this study. Since methanol can initiate hydrocarbon chains (71) over iron catalysts and can be converted almost completely to hydrocarbons over zeolite catalysts (58), it is possible that the high methanol product fractions observed at high space velocity conditions may be due to the absence of secondary reactions which convert methanol to hydrocarbon products. Support for this hypothesis is provided by the fact that the methanol product fraction decreases with increasing conversion at a fixed total pressure (Figure 4.1.9).

Typical product distributions obtained at elevated pressures with the 1/1 CO/H_2 feed are presented in Figures 4.4.6 through 4.4.8. For the Fe catalyst, the methanol product mole fraction increases at higher pressures with this feed, but to a lesser extent as compared to the 1/3 feed. The alloy catalyst now produces the highest methanol fraction. It

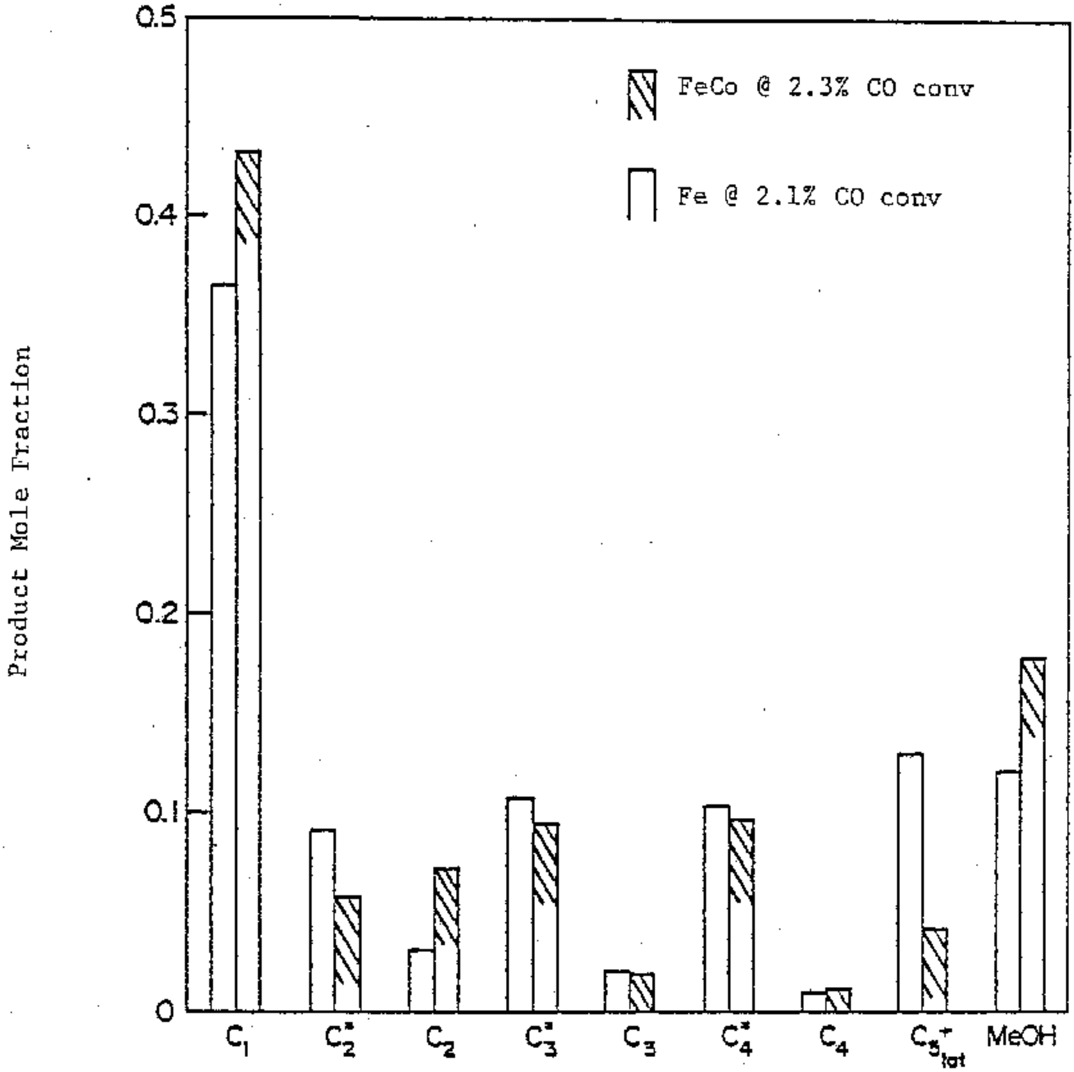

Figure 4.4.6 Product mole fractions of the Fe and FeCo catalyst at 7.8 atm. and 250°C with the 1/1 CO/H_2 feed.

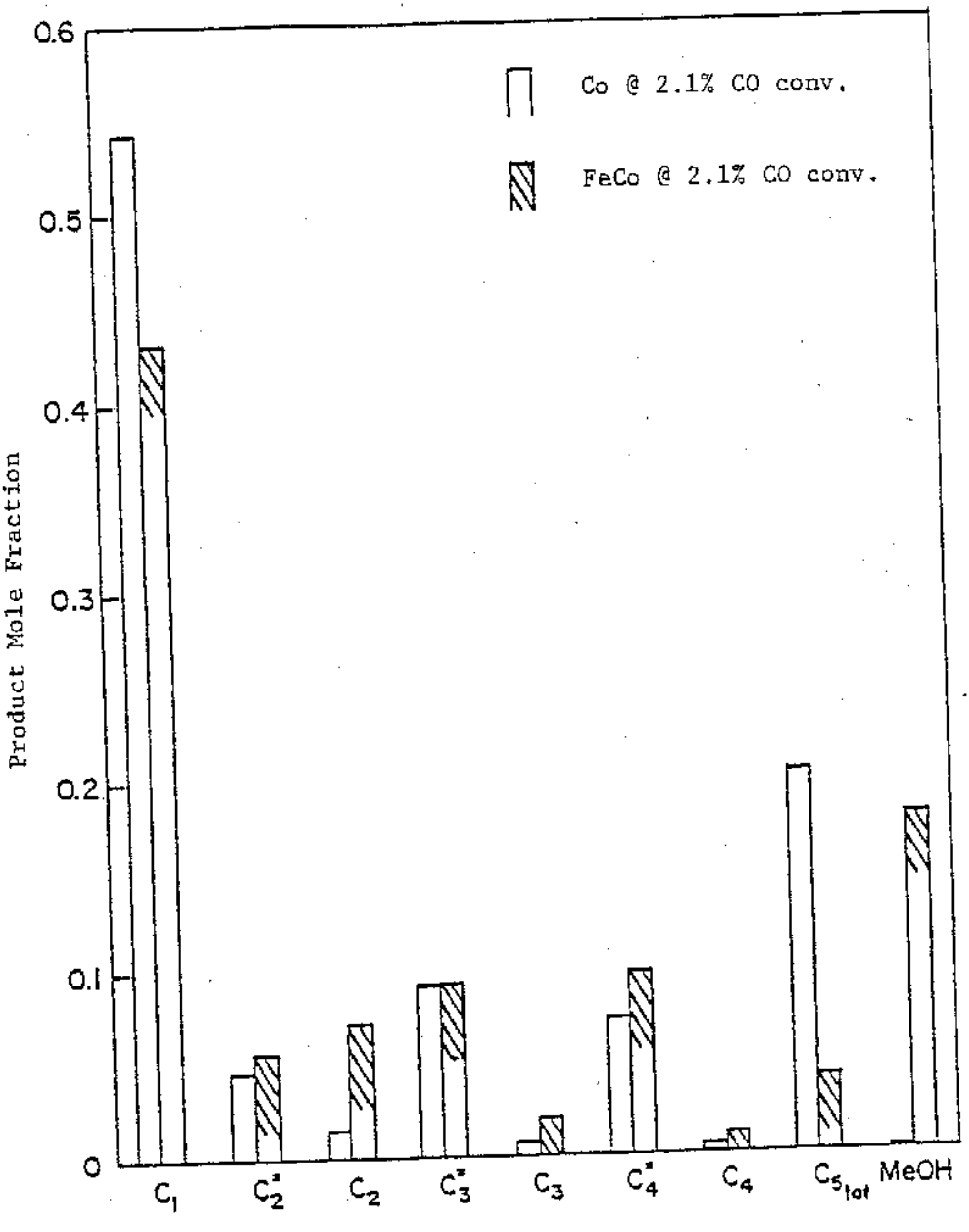

Figure 4.4.7 Product mole fractions for the FeCo and Co catalyst at 7.8 atm. and 250°C with the 1/1 CO/H_2 feed

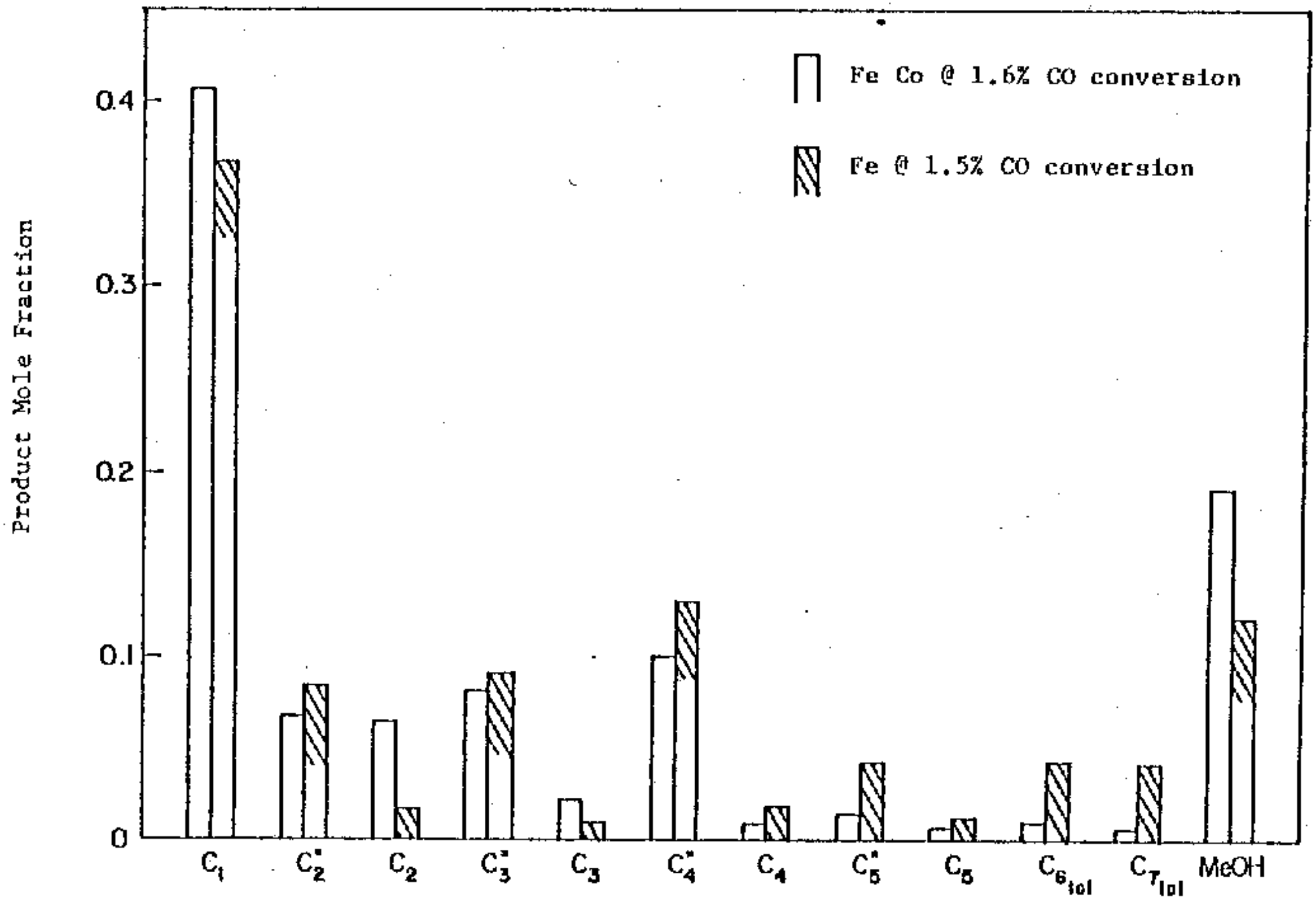

Figure 4.4.8 Product mole fractions of the Fe and FeCo catalyst at 14 atm. and 250°C with the 1/1 CO/H_2 feed.