

5.2 Product Yields and Selectivities for Olefin Containing Feeds

5.2.0 The product yields, Y_j ($\frac{\text{moles product } j \text{ produced}}{\text{moles feed gas initially present}}$) are presented in terms of the GHSV for both the ethylene CO/H₂ feed (Section 5.2.1) and the 1-pentene CO/H₂ feed (Section 5.2.2). These data are used for determining the extent of ethylene consumption due to chain growth into higher molecular weight products. Olefin/Paraffin selectivity ratios are presented in section 5.2.3. These data provide insight into the nature of secondary hydrogenation of α olefin products and its effect on the hydrocarbon product distribution. The secondary reactions of olefin isomerization of 1-pentene are contained in section 5.2.4. In section 5.2.5 the methanol yields for the iron containing catalyst are presented for all three feeds.

5.2.1 Product Yields for the Ethylene CO/H₂ Feed

The presence of 5.4 mole % ethylene in a 1/3 CO/H₂ mixture produces significant increases in the propylene and 1-butene product yields. Figure 5.2.1 presents the yields of these products as a function of the GHSV for both the pure and ethylene enhanced feed at one atmosphere. Similar increases but to a lesser extent are observed for the corresponding paraffin yields (Figure 5.2.2). The propylene yields for both iron containing catalysts at 7.8 atmospheres obtained with the pure and ethylene CO/H₂ feeds are given in Figure 5.2.3. Both iron based catalyst exhibit comparable increases (approximately 400%) over the GHSV range studied. The Co catalyst undergoes a smaller net increase (approximately 280%) as is shown in Figure 5.2.4. Typical product yield plots for the C₃ and C₄ products at 1 and 7.8 atmospheres are

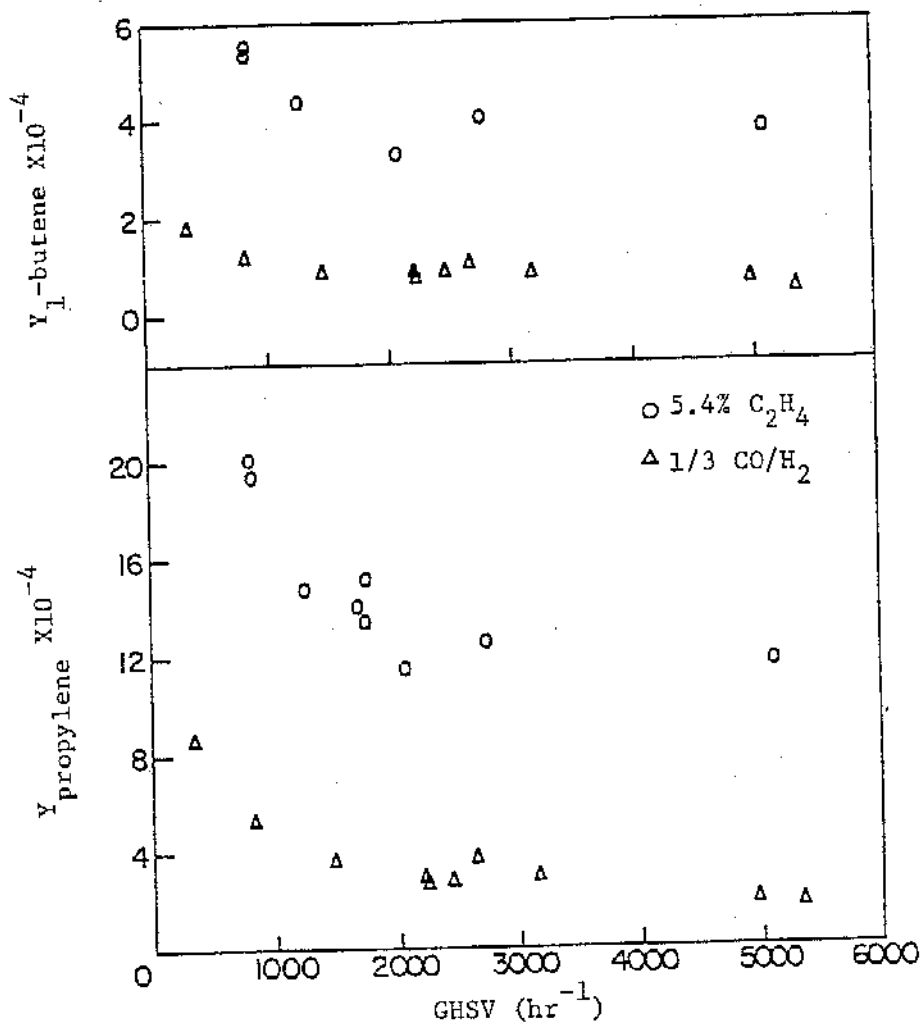


Figure 5.2.1 Propylene (Bottom) and 1-butene (top) product yields versus GHSV for the Fe catalyst using the ethylene containing and 1/3 CO/H₂ feeds at 1 atm. and 250 °C.

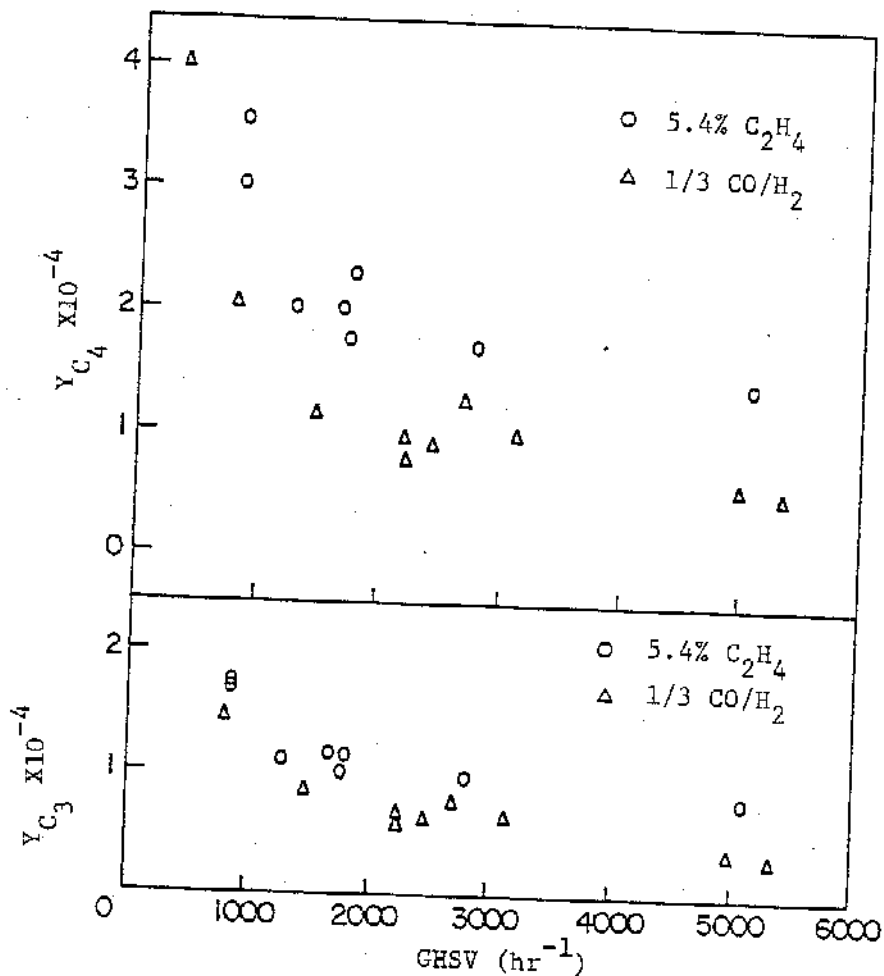


Figure 5.2.2 Propane (Bottom) and n-butane product yields as a function of the GHSV for the Fe catalyst using the ethylene containing and pure $1/3 CO/H_2$ feed at 1 atm. and $250^\circ C$.

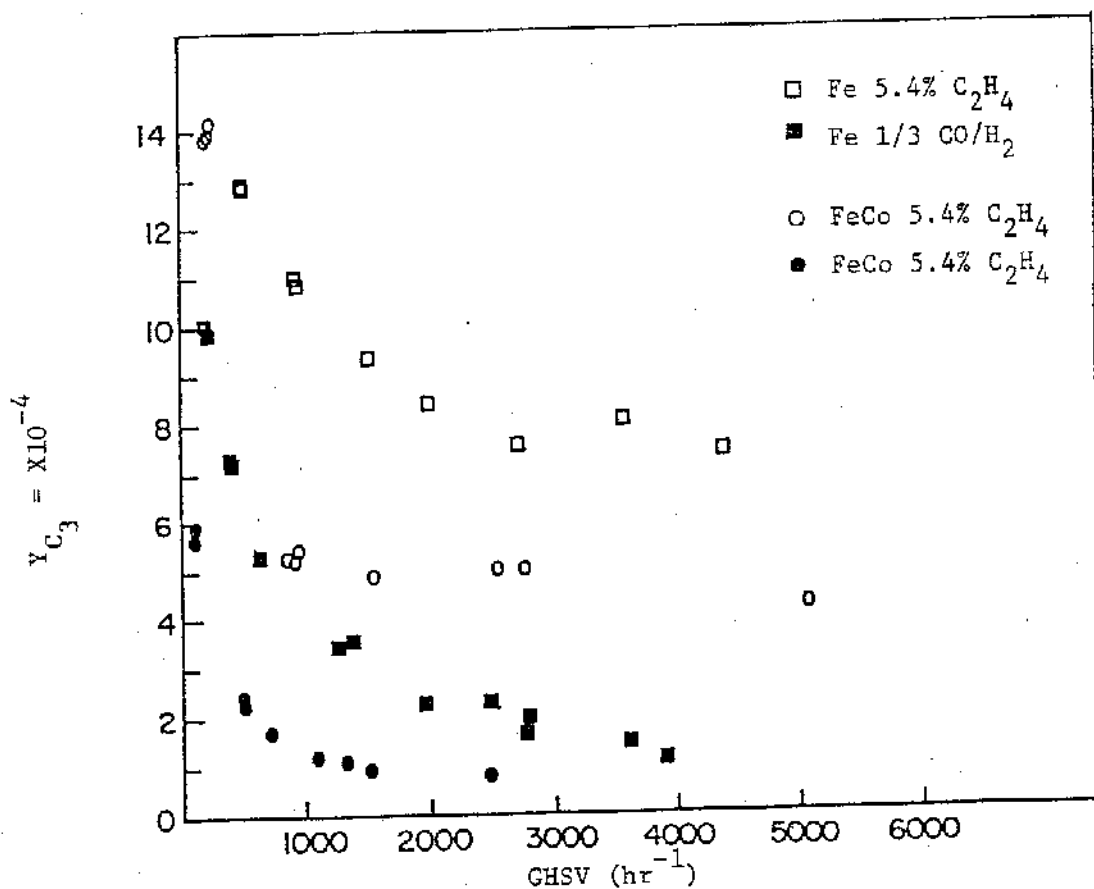


Figure 5.2.3 Propylene product yield as a function of the gas hourly space velocity for the Fe and FeCo catalyst using the 5.4 mole % ethylene and pure 1/3 CO/H₂ feeds at 7.8 atm. and 250°C.

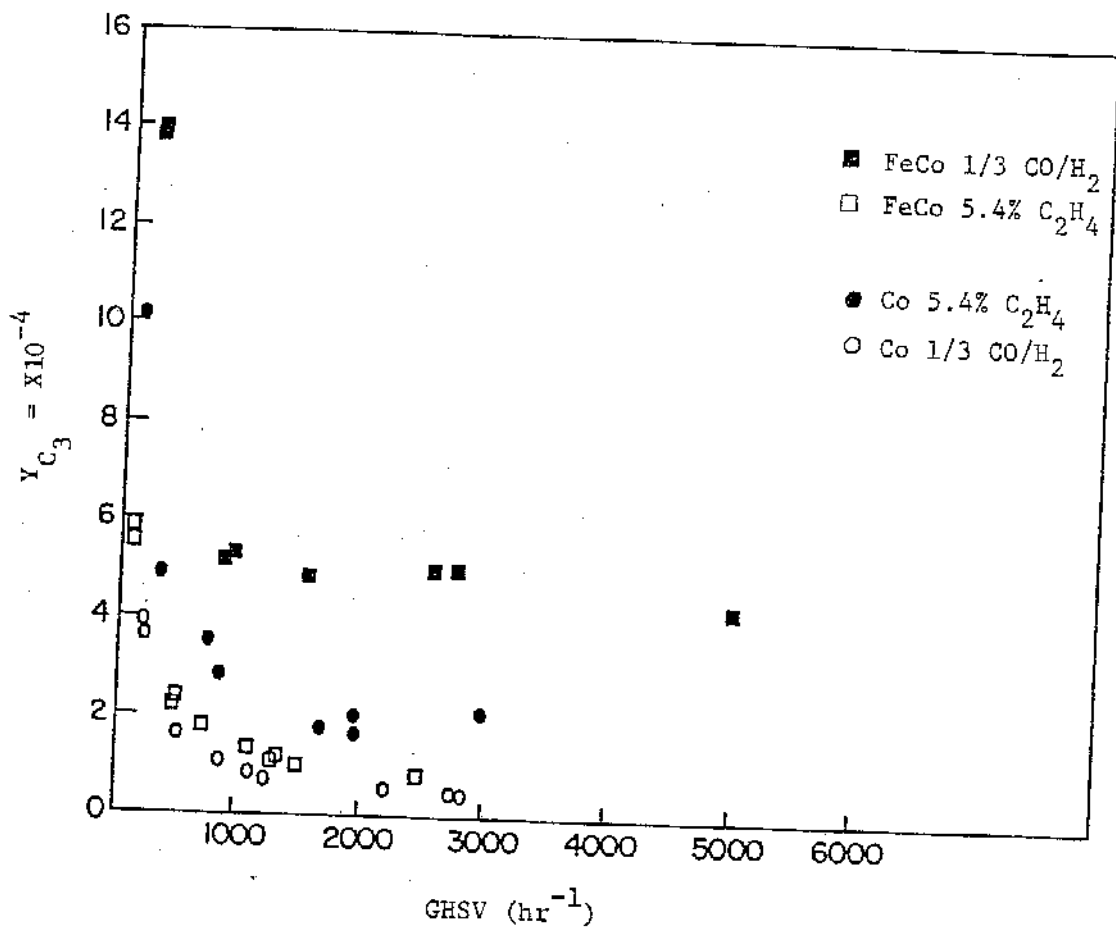


Figure 5.2.4 Propylene product yield as a function of the gas hourly space velocity for the Co and FeCo catalyst using the 5.4 mole % ethylene and pure 1/3 CO/H₂ feeds at 7.8 atm. and 250°C.

contained in Appendix VI for both the pure and ethylene enhanced feed mixtures.

The increased product yields for all the C_3 and C_4 products obtained with the ethylene enhanced feed are given in Tables 5.2.1 and 5.2.2 for 1 and 7.8 atmospheres respectively. These values are obtained by subtracting the product yields obtained with the pure feed from the corresponding yield obtained with the olefin containing feed at the same GHSV. The amount of ethylene consumed is calculated assuming that the carbon monoxide activity is equal at the same GHSV for both feeds. The increased product yields result from ethylene acting as a chain initiator for subsequent addition of a carbon containing intermediate to form longer chain products. Consequently, the amount of ethylene consumed corresponds to the total molar increase in products (or product yields since all molar amounts are based on a mole fraction basis). Corresponding to each product yield increase is a percent increase value based on the yield obtained in a pure CO/H_2 feed for a given product at the conditions specified by the table.

At one atmosphere the cobalt catalyst consumes the most ethylene since its product yield increases for the C_3 and C_4 products are much larger than the iron containing catalyst (Table 5.2.1). There appears to be an increase in the percent of ethylene consumed at higher CO conversions especially for the cobalt containing catalyst. However quantitative analysis is not possible since the data in Table 5.2.1 are based on yield values obtained on rapidly rising curves and are subject to about 20% uncertainty in measuring differences. The Fe catalyst exhibits the smallest (if any) increase in ethylene consumption with

Table 5.2.1

Increase in Product Yields with C₂H₄/CO/H₂ Feed
At One Atmosphere Total Pressure

Catalyst	Nominal * CO Conversion	Nominal GHSV	Product Yields Increase ** x10 ⁻⁴										Percent of Feed C ₂ H ₄ consumed ²
			C ₃ H ₆	% ¹	C ₃ H ₈	% ¹	C ₄ H ₈	%	C ₄ H ₁₀	%	C ₄ H ₁₀	%	
CO	1	10000	16	350	1.2	350	7 ^o	400	1	200	4.6	%	
	3	5000	20	350	1.6	350	11	400	2	300	6.4		
FeCo	1	1250	5.2	350	.4	350	1.5	300	.1	50	1.3	%	
	3	300	3	150	.2	350	1.0	100	.7	50	2.6		
Fe	1	5300	10	600	.42	100	3	700	.1	100	2.7	%	
	3	1500	11	350	.44	30	3.3	400	1.2	30	3		

* CO conversions based on pure 1/3 CO/H₂ feed

** Assuming any increases in product yields over that obtained in pure CO/H₂ feed are due to ethylene initiation of hydrocarbon chains

¹ Increase in yield calculated by $\frac{Y_i(C_2H_4/CO/H_2)}{Y_j(CO/H_2)} \times 100$

² Based on 5.4 mole % Ethylene in Feed

Table 5.2.2

Increase in Product Yields with C₂H₄/CO/H₂ Feed

At 7.8 Atmospheres Total Pressure

Catalyst	Nominal * CO Conversion	Nominal GHSV	Product Yields Increase ** x10 ⁻⁴							Percent of Feed C ₂ H ₄ consumed ²			
			C ₃ H ₆	C ₃ H ₈	% ¹	C ₄ H ₈	%	C ₄ H ₁₀	%	%	%		
Co	%	hr-1											
	1	1000	2.0	0.5	---	1.2	250	0.3	300	.33			
	4	400	5.0	1.0	300	1.3	250	0.75	300	1.5			
FeCo	1	1200	3.6	0.5	400	.7	400	1	200	1.1			
	4	300	5.5	2.0	300	1.8	200	3	50	2.3			
Fe	1.2	4000	6	1.2	700	3	400	.5	200	2			
	4	500	6	1.2	200	2.6	50	.6	50	2			

* CO conversions based on pure 1/3 CO/H₂ feed** Assuming any increases in product yields over that obtained in pure CO/H₂ feed are due to ethylene initiation of hydrocarbon chains1 Increase in yield calculated by $\frac{Y_i(C_2H_4/CO/H_2)}{Y_j(CO/H_2)} \times 100$

2 Based on 5.4 mole % Ethylene in Feed

decreasing GHSV and the percent increase in product yields due to ethylene incorporation undergoes the greatest decrease with increasing conversion. These trends suggest that the mechanism responsible for chain growth becomes less dependent on the gas phase ethylene concentration at lower space velocities.

The amount of ethylene consumed by initiating longer chained hydrocarbon products decreases with increasing pressure. In fact the Co catalyst which produces the greatest amount of higher molecular weight products at 7.8 atmospheres, (Section 4.4), incorporates the smallest amount of ethylene at this pressure (Table 5.2.2). It appears that the presence of ethylene does not readily enhance the high molecular weight product yields at increased pressures for this catalyst. This conclusion is supported in subsequent sections in which the SF distribution data (Section 5.3) and product mole fraction results (Section 5.4) are presented.

AT 7.8 atmospheres the Fe catalyst consumes smaller amounts of ethylene (Table 5.2.2) compared to the corresponding values at 1 atmosphere (Table 5.2.1). The percent product yield increase diminishes as the GHSV is decreased at the higher pressure indicating that the product yields of the longer chained products are less influenced by gas phase composition at higher CO conversions. In a recent review article Biloen and Sachtler (20) suggest that the reason why ethylene lies below the SF linear parameterization, defined by $\ln Y_i$ (for $i > 2$), is due to a significant amount of C_2 insertion into growing hydrocarbon chains. The data presented in Tables 5.2.1 and 5.2.2 indicates that gas phase readsorption and subsequent insertion into longer chained products does not appear to be a principal reaction pathway for ethylene. In order to

illustrate this point the following comparative calculations are made.

Assume that the low $\ln(Y_{C_2})$ values obtained in the SF parameterization are entirely due to the readsorption and subsequent reaction of gas phase ethylene into longer hydrocarbon chains. As a typical example, the $\ln(Y_{C_2})$ values of Figure 4.5.2 for the Fe catalyst at 7.8 atmospheres with the 1/3 CH/H₂ are employed. Extending the linear portion of the hydrocarbon product distribution from the C₄ to C₈ region to the smaller carbon product one obtains a $\ln(Y_{C_2})$ value of approximately 7.5. This corresponds to the $\ln(Y_{C_2})_{SF}$ value for the 2 carbon chained products if the C₂ product yield followed the classical SF polymerization scheme. The value of $\ln(Y_{C_2})_{exp}$ obtained experimentally at these conditions is 6.0. Each of these values can be converted to molar yields via the relation

$$Y_{C_2} = [\exp(\ln Y_{C_2})]/10^6 \quad 5.2.1$$

If one assumes that the $(Y_{C_2})_{SF}$ value corresponds to the total amount of two carbon chains produced then the ratio of $(Y_{C_2})_{exp}/(Y_{C_2})_{SF}$ represents the fraction of material which did not undergo secondary insertion reactions (fraction of ethylene consumed). The numerical values in this example are $\frac{4.0 \times 10^{-4}}{18 \times 10^{-4}}$, indicating that the observed C₂ product yields are approximately 20% of those corresponding to ideal SF behavior. Since typically only 2% of the gas phase ethylene undergoes chain growth reactions it appears that gas phase ethylene is not very reactive. Similar arguments can be made for the remaining catalyst at all conditions studied.

Ethylene does not appear to insert as a two carbon species since the C_4 product yields are not preferentially increased over those of the C_3 products under the conditions studied. Indeed it is shown in section 5.3 that the feed ethylene has no measurable effect on the growth probability (α) of longer chained products. The low ethylene consumption fractions indicate that the readsorption of ethylene with subsequent chain initiation/insertion reactions is not a major reaction pathway leading to the production of long chain hydrocarbon products. In Section 5.4 it is shown that the predominant reaction involving the feed ethylene is hydrogenation to ethane, since typically 30 to 50% of the feed ethylene undergoes this reaction.

Previous findings by Hall, Kokes and Emmett(54) indicate that although ethylene can initiate hydrocarbon chains it is not likely the dominant growth mechanism in the FT synthesis at higher pressures. Using a bulk iron catalyst, approximately 12% of the hydrocarbon products ($C_n > 3$) were formed from the 12.5 mole % radioactive ethylene 1/1 CO/H₂ feed at one atmosphere (54). The corresponding value at 7.8 atmospheres decreased to 6%. The authors (54) do not specify the conversions employed in the reaction studies but it is evident from the reported product distribution that the CO conversion levels greatly exceed 5%. Indeed in one case there was no ethylene present in the product stream (54). This product was predominantly hydrogenated in addition to entering longer chained products. Nijs and Jacobs (87) found that less than 4% of the 1-butene added to 2/3 CO/H₂ feed was consumed via chain growth reactions while over 50% underwent isomerization at 14 atmospheres using a Ru on aerosil catalyst.

Combining these results with the results obtained in the present study (Tables 5.2.1 and 5.2.2) one can compare the relative importance of the studies reaction of ethylene initiated chain growth over an Fe catalyst. At low CO conversion the fraction of ethylene consumed is quite small ($\approx 2\%$) yet the fraction of total hydrocarbon products formed by this consumption can be quite high. For example, with the Fe catalyst at one atmosphere over 70% of the total $C_{n>3}$ product fraction is due to ethylene. This by itself seems to indicate a high ethylene activity towards chain growth reaction but it must be compared to the fraction hydrogenated which is typically 30 to 50%. At higher pressure this value drops down to about 30%. At higher CO conversions the total fraction of hydrocarbon products due to ethylene insertion decreases. The result suggests that the influence of readsorption and chain growth on the product distribution diminishes with increasing CO conversion. Further experimental work is required to confirm the above mentioned conclusions since they are based on two different feed stream compositions and the relative rates of ethylene consumption through chain initiation and hydrogenation are most likely influenced by the gas phase compositions. Further discussions involving the secondary reactions of ethylene are given in sections 5.3 and 6.32.

5.2.2 Product Yields for the 1-Pentene CO/H₂ Feed

Typical product yields obtained with the 0.5% 1-pentene (1/3)CO/H₂ feed are presented in Figures 5.2.5 through 5.2.9. At each pressure the yields obtained with the pure CO/H₂ feed are also presented for comparative purposes.

5.2.2.1 Fe Catalyst

Since the methane activity for the Fe catalyst is lower for the 1-pentene CO/H₂ mixture as compared to the pure feed at a given GHSV (Section 5.1) it appears that no 1-pentene hydrocracking is occurring during the FT synthesis. Indeed the product yields for the C₂ through C₄ hydrocarbon products are smaller for the 1-pentene feed. Figure 5.2.5 presents the ethylene, propylene, and 1-hexene yields as a function of the GHSV for both the 1-pentene enhanced and pure feeds at one atmosphere. There is a small increase in the 1-hexene yield with the olefin containing feed at the higher GHSV values. This, most likely is due to 1-pentene insertion into longer product chains. However the fraction of this olefin consumed in chain growth reactions is less than .3% of the total contained in the feed.

At 7.8 atmospheres there is no appreciable difference in the product yields for the C₂ through C₆ hydrocarbons. Figure 5.2.6 presents the yield data for 1-butene and 1-hexene at these conditions. The decrease in 1-pentene consumption to longer chain products with increasing pressure agrees with the observed behavior for ethylene. The principal reaction products of the 1-pentene secondary reactions are n-pentane and 2-pentene. The isomerization and hydrogenation of this olefin is discussed in Section 5.4.3.

5.2.2.2 FeCo Catalyst

There is no change in the low molecular weight product yields for the alloy catalyst at one atmosphere. Figure 5.2.7 presents the

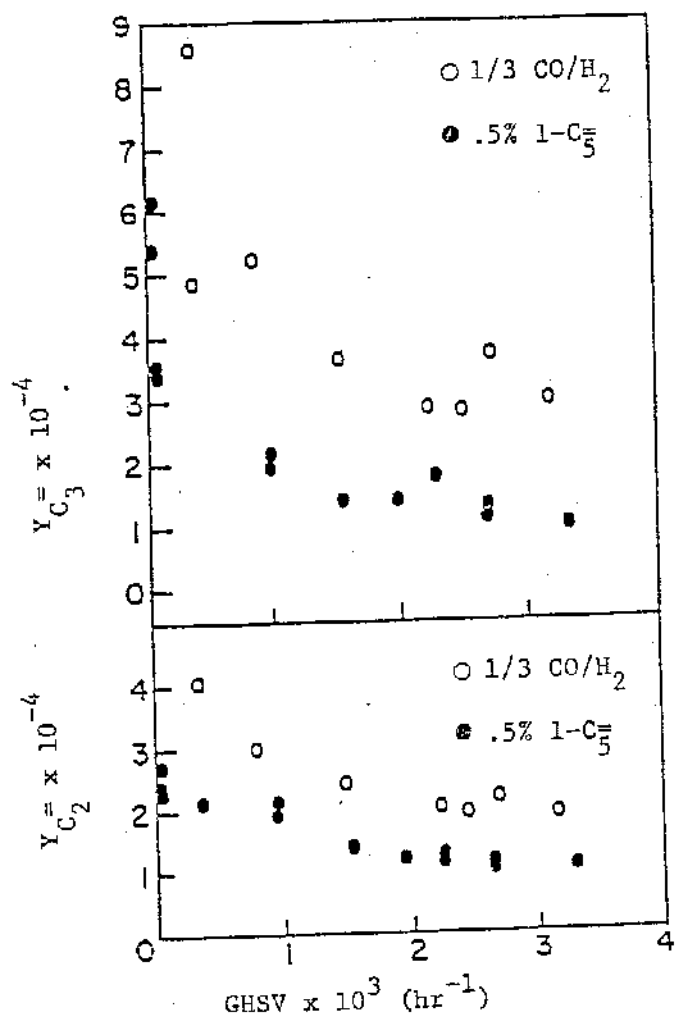
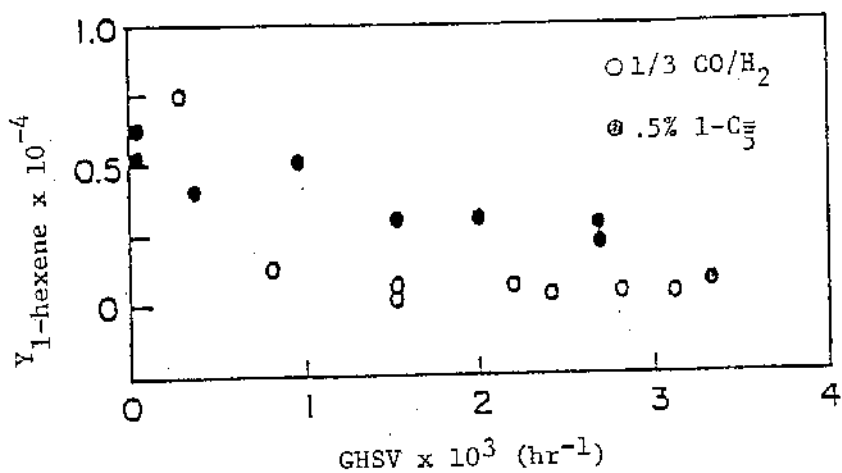


Figure 5.2.5 Various olefin yields versus the GHSV for the Fe catalyst using the 1-pentene containing and pure 1/3 CO/H₂ feed at 1 atm and 250°C.

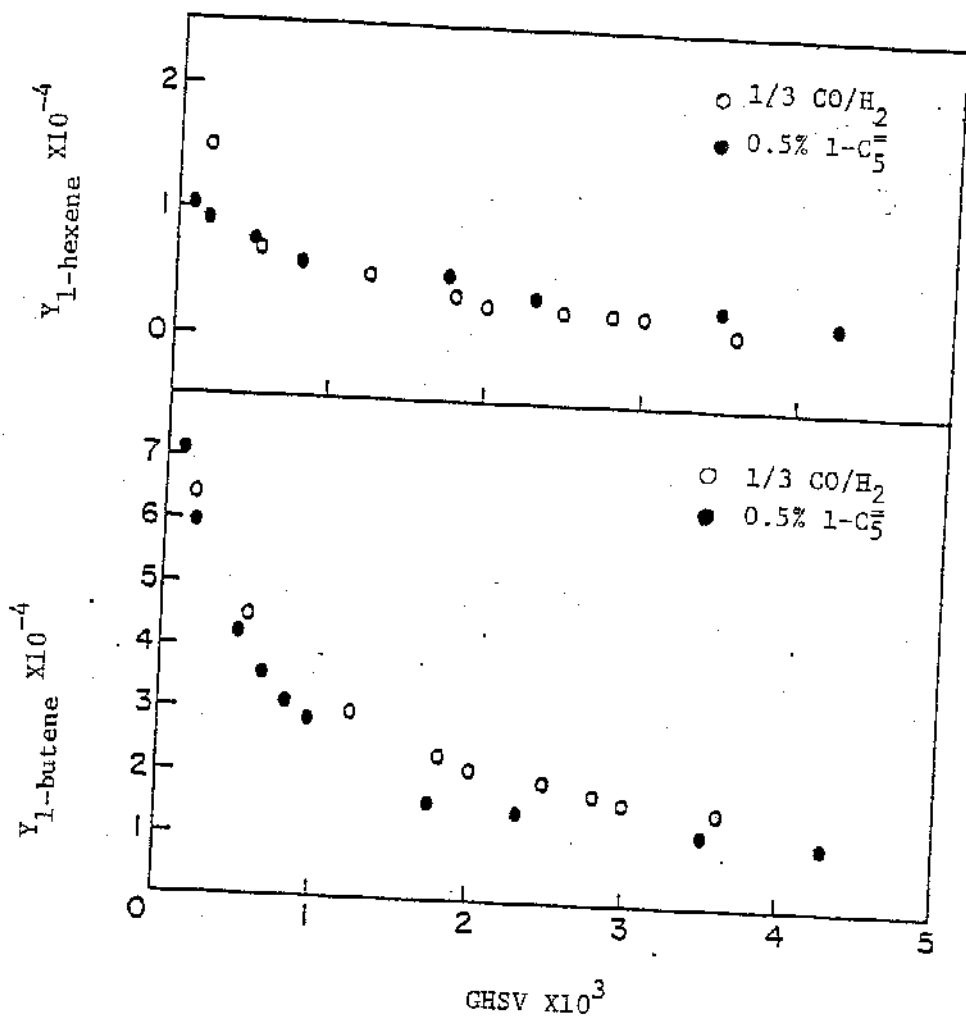


Figure 5.2.6 1-butene and 1-hexene yields in the 1-pentene and pure $1/3 \text{ CO}/\text{H}_2$ feed for the Fe catalyst at 7.8 atm. and 250°C .

ethylene, propylene, and 1-butene yields for both feed mixtures at this pressure. The 1-hexene product yields could not be measured for the FeCo catalyst at one atmosphere with the pure 1/3 feed. The fraction consumed into C_6 products for the alloy catalyst corresponds to approximately 1.5% of the feed 1-pentene at a nominal 3% CO conversion.

Similar behavior is observed at 7.8 atmospheres. Figure 5.2.8 presents the 1-butene and 1-hexene yields for both feeds as a function of the GHSV. The C_6 paraffin yields are also enhanced in the 1-pentene/CO/ H_2 feed. The fraction of 1-pentene consumed, based on the increase in the total C_6 product yields is found to be approximately 1% and a nominal 4% CO conversion. The amount of 1-pentene inserted into longer hydrocarbon chains is greater for the alloy catalyst as compared to the Fe Catalyst since at 7.8 atmospheres the Fe catalyst exhibits no measurable increase in the C_6 yields. The greater C_6 yield enhancement of the FeCo catalyst may be related to the relatively low steady state surface concentration of C_5 intermediates due to and the greater hydrogenation activity of this catalyst.

The FeCo catalyst exhibits greater relative hydrogenation activity on a CO consumption basis at higher pressures compared to the iron catalyst. Consequently one would expect a lower steady state surface concentration of long chained ($C_{n>5}$) carbon intermediates compared to the pure component catalyst since the $C_{n<5}$ intermediates are more readily hydrogenated to nonreactive paraffins. If the hydrogenation rate of the surface precursors C_i^* is much higher than the rate of carbon monomer addition to yield C_{i+1} than one would expect catalyst with greater relative hydrogenation rates to exhibit smaller product yields due to the presence of olefins in the feed mixture. This behavior is discussed in detail in

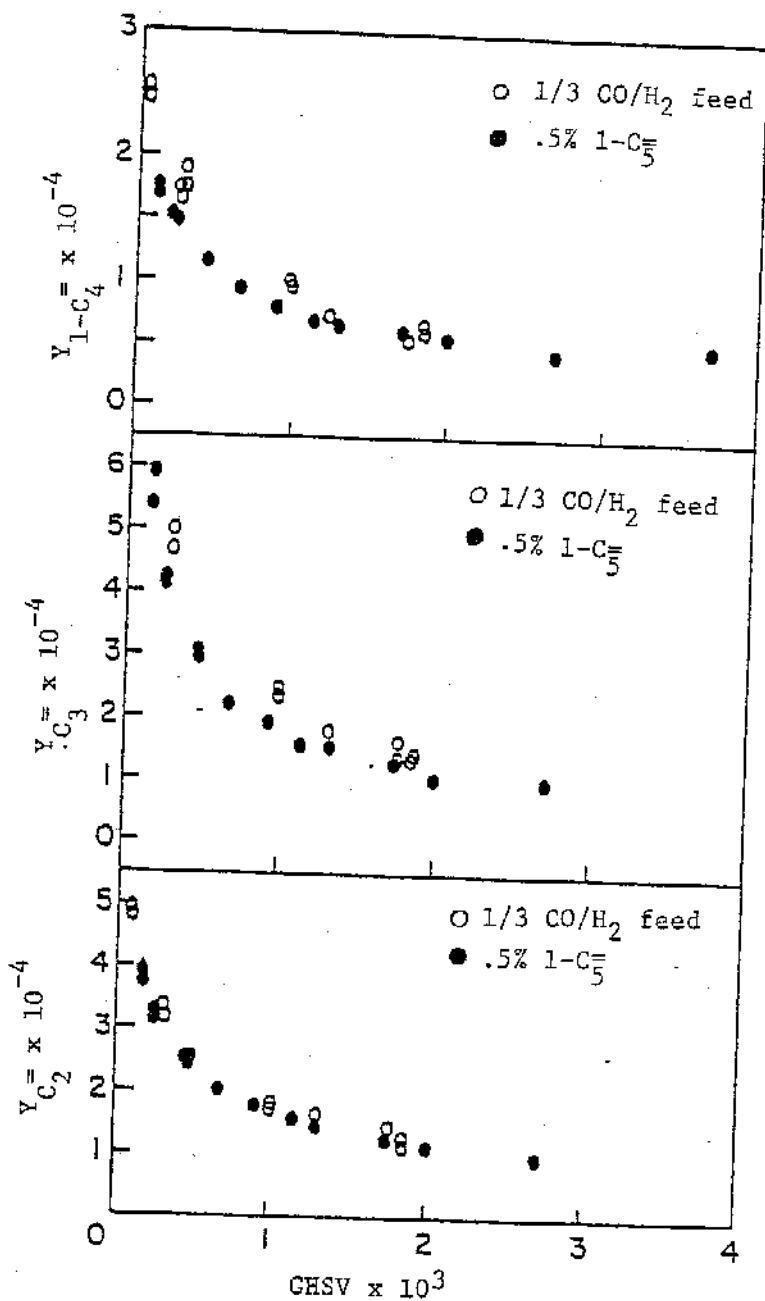


Figure 5.2.7 Ethylene (bottom), propylene (middle) and 1-butene (top) yields versus GHSV for FeCo catalyst using the .5 mole % 1-pentene and pure 1/3 CO/H₂ feed at 1 atm. and 250°C.

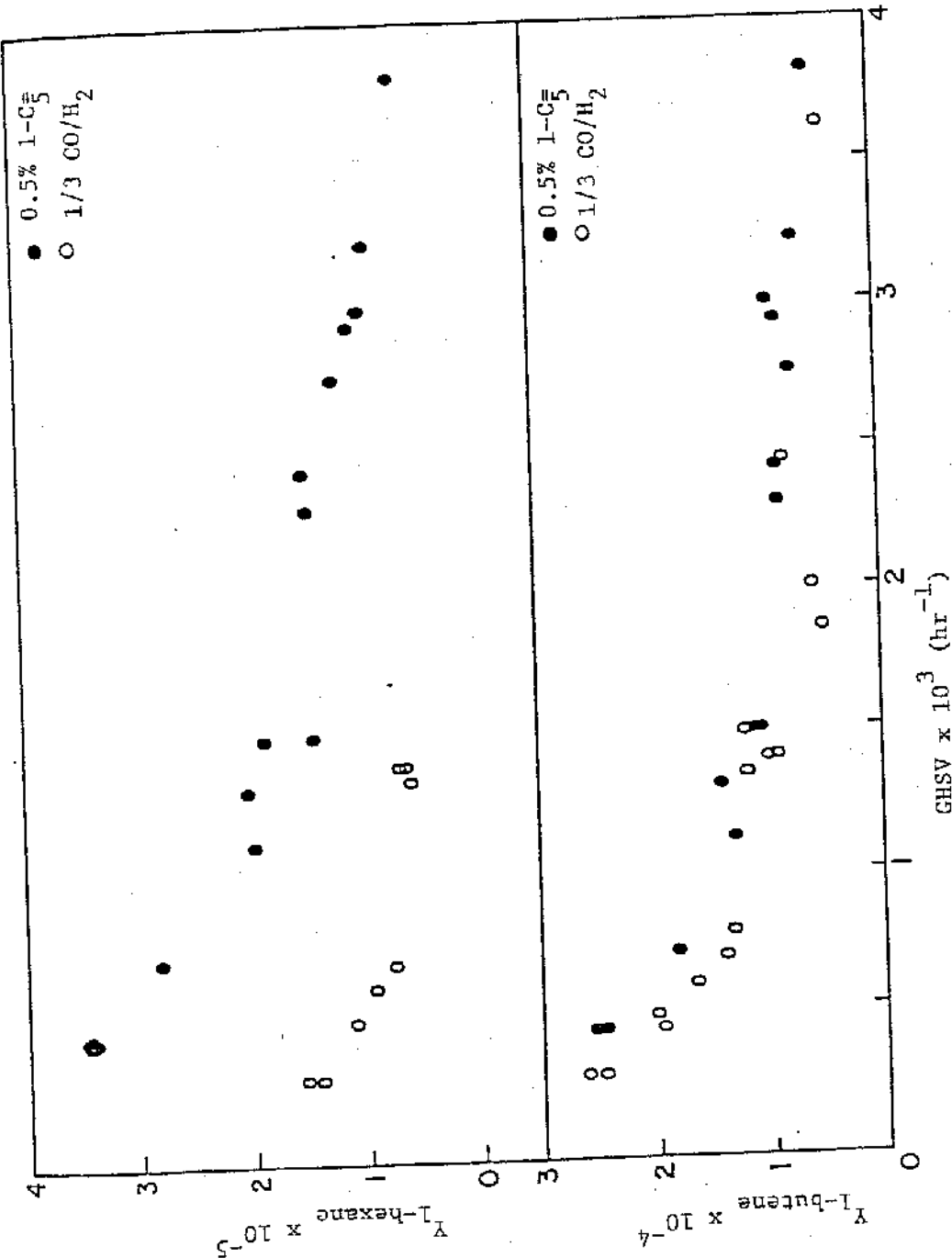


Figure 5.2.8 1-butene and 1-hexene product yields versus the GHSV for the FeCo catalyst using the 1-pentene containing and pure 1/3 CO/H₂ feed at 1 atm. and 250°C.