

Figure 3. Component Schulz-Flory diagram for overhead products. Purhchemie Catalyst. 263°C, 2.4 MPa, 0.034 Nl/min/g<sub>cat</sub>, (H<sub>2</sub>/CO)<sub>feed</sub> = 0.7, 600 hours-on-stream.

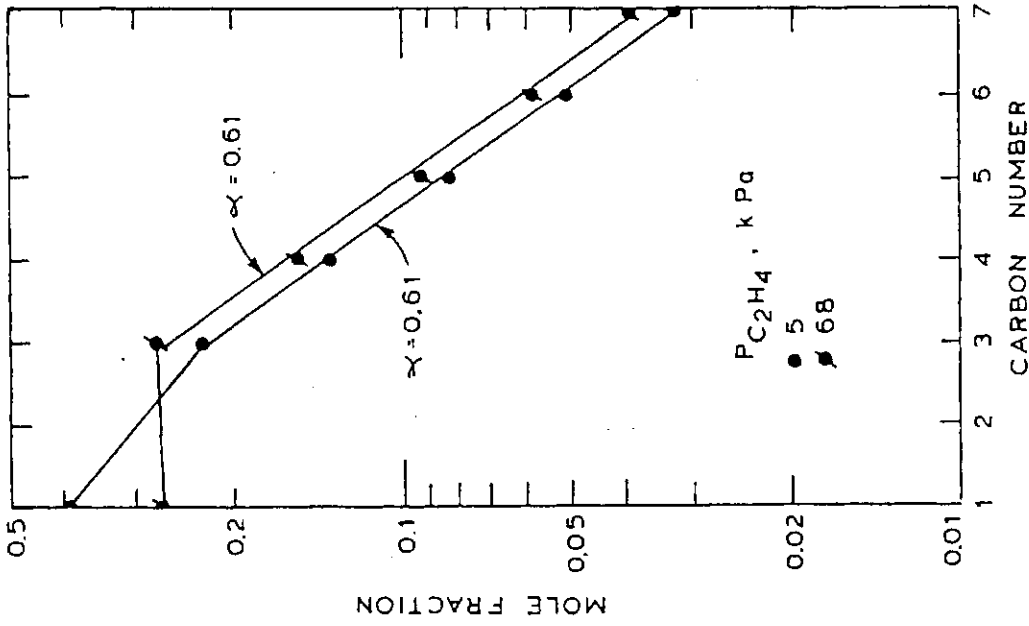


Figure 5. Effect of ethylene addition on Flory distribution. No significant effect is observed, except for methane. Data normalized by excluding  $C_2$  fraction. Total pressure = 0.92-0.98 MPa; temperature = 248°C; high CO conversions.

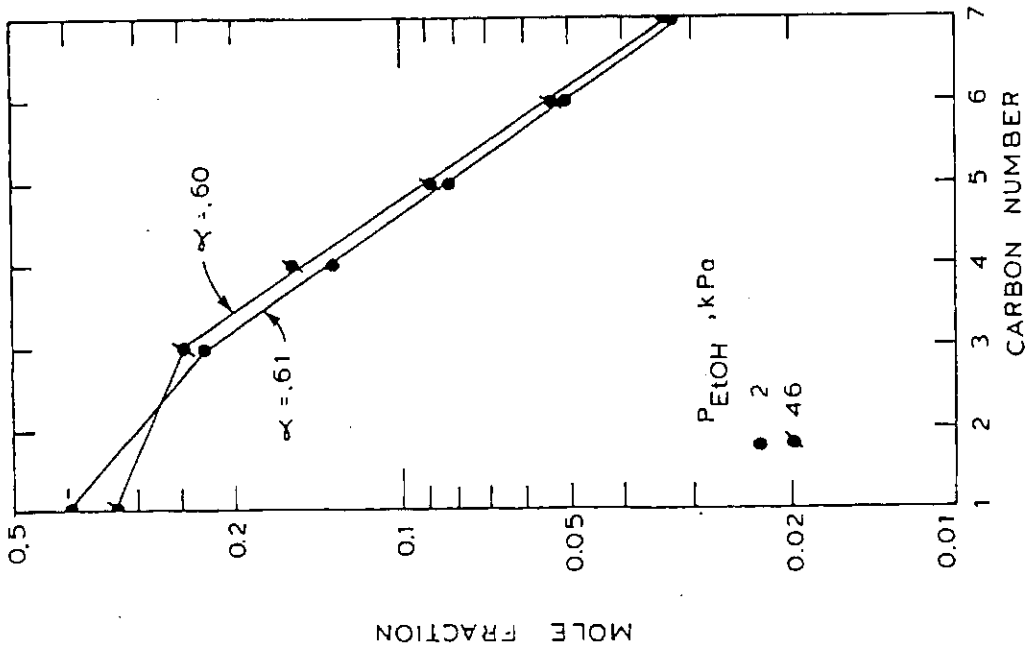


Figure 4. Effect of ethanol addition on Flory distribution. No effect is observed, except for methane. Data normalized by excluding  $C_2$  fraction. Total pressure = 0.92 MPa; temperature = 248°C.

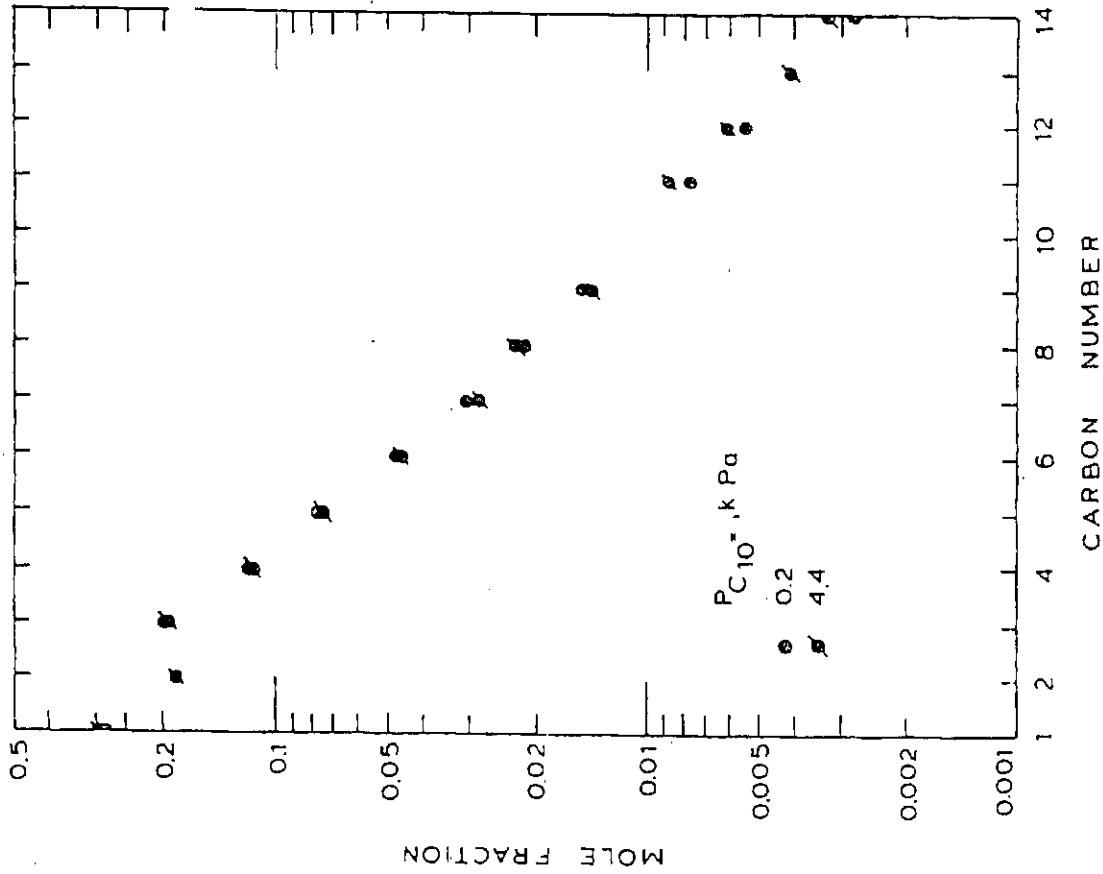


Figure 6. Effect of 1-butene addition. A slight increase in the  $C_5^+$  fraction is observed. Overlapping points at  $C_2$  and  $C_3$ . Data normalized excluding  $C_4$  fraction. Total pressure = 0.92-0.95 MPa.

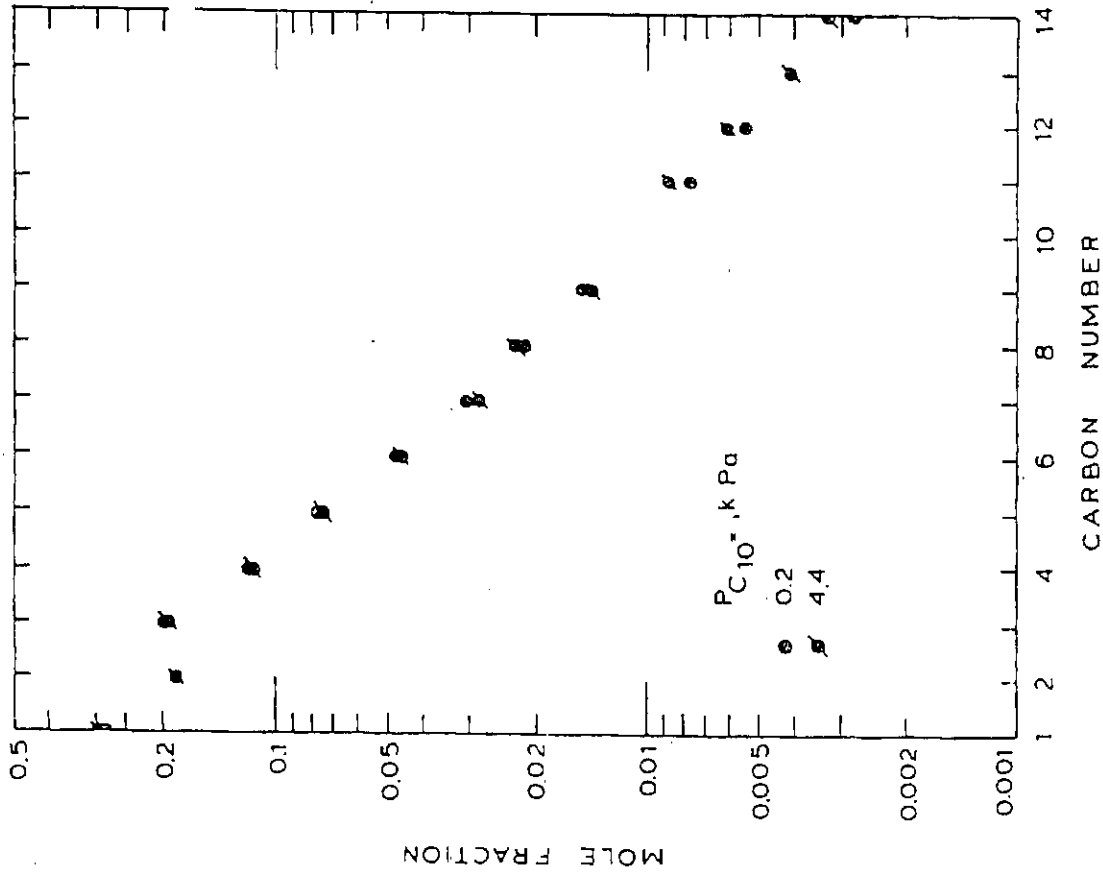


Figure 7. Effect of 1-decene addition. A slight increase in the  $C_{11}^+$  fraction is observed with overlapping points at  $C_2$  and  $C_{13}$ . Data normalized by excluding  $C_{10}$  fraction. Total pressure = 0.92 MPa.

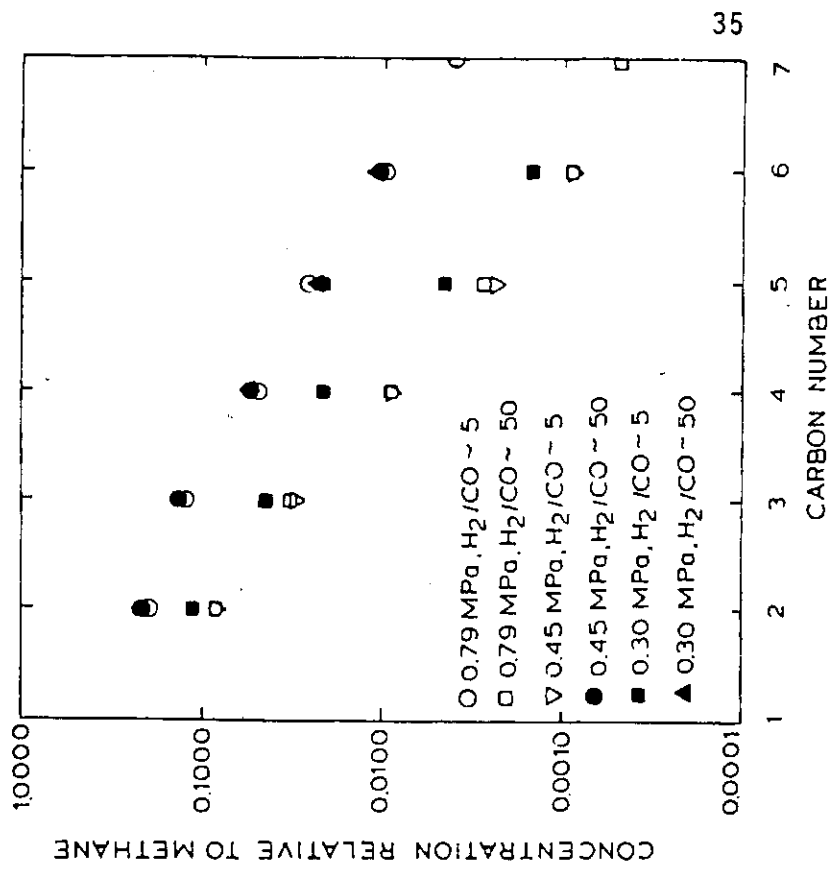


Figure 9. Effect of H<sub>2</sub>/CO feed ratio on carbon number distribution.

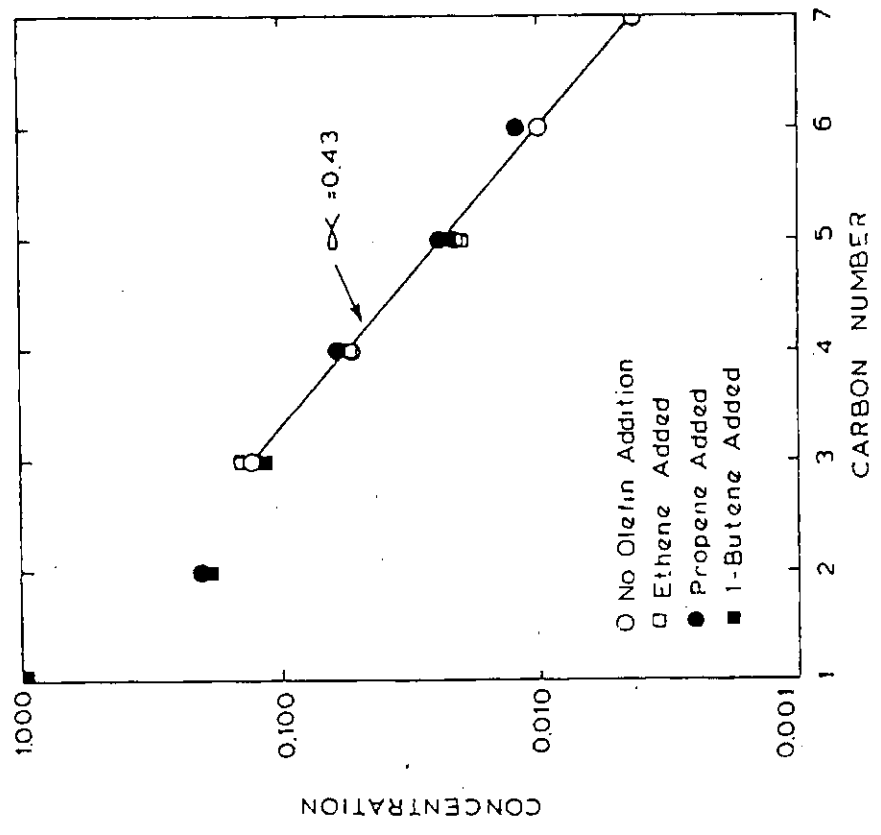


Figure 8. Effect of added olefin on Fischer-Tropsch carbon number distribution. H<sub>2</sub>/CO in feed = 5; total pressure = 0.79 MPa. No significant effect is observed.

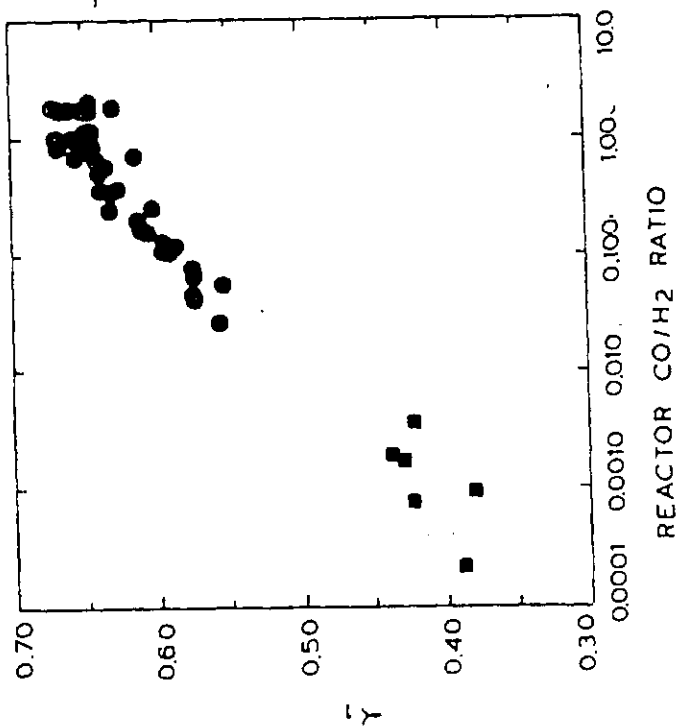


Figure 11. Log plot of abscissa of Figure 10 to separate data at low CO/H<sub>2</sub> ratios.

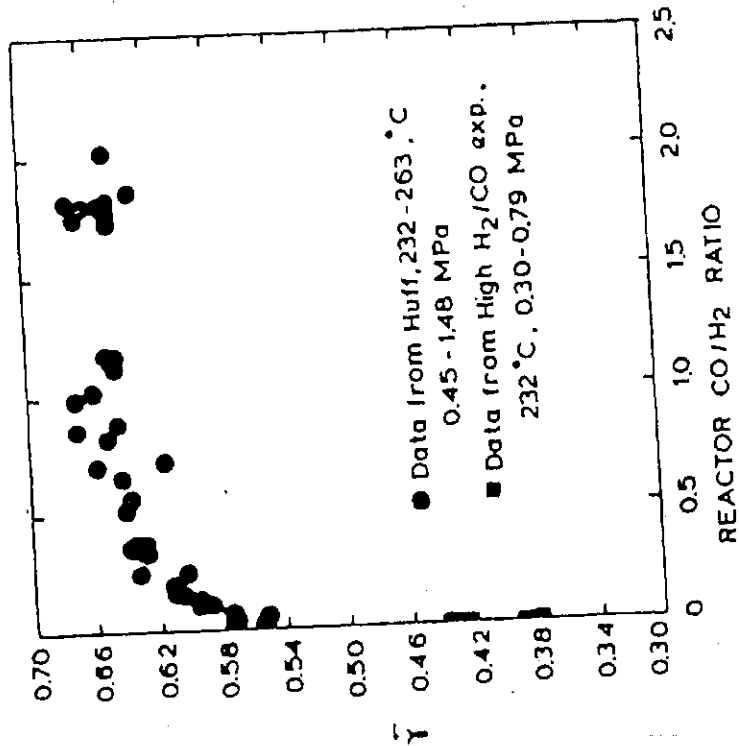


Figure 10. Effect of reactor CO/H<sub>2</sub> ratio on  $\alpha_1$ .

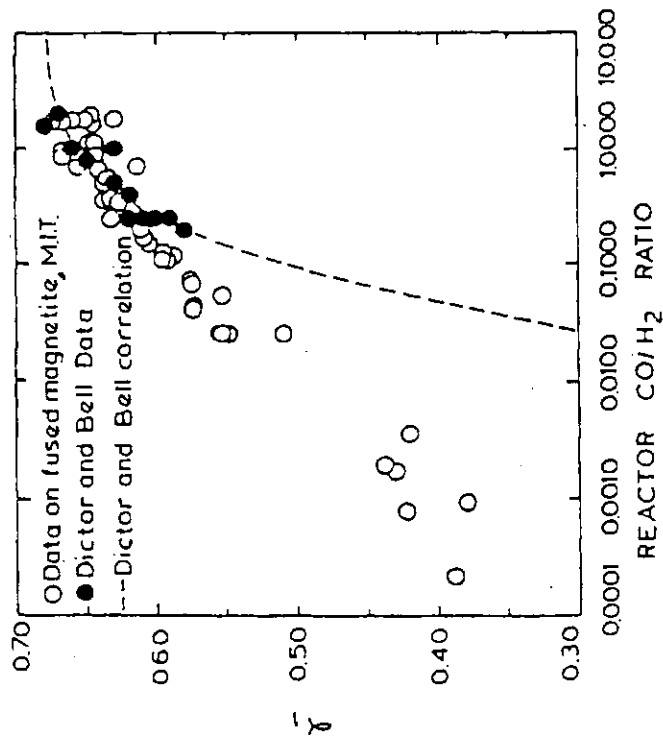


Figure 12. Comparison of present data and that of Huff with data of Dictor and Bell, all obtained on fused-magnetite catalyst C73.

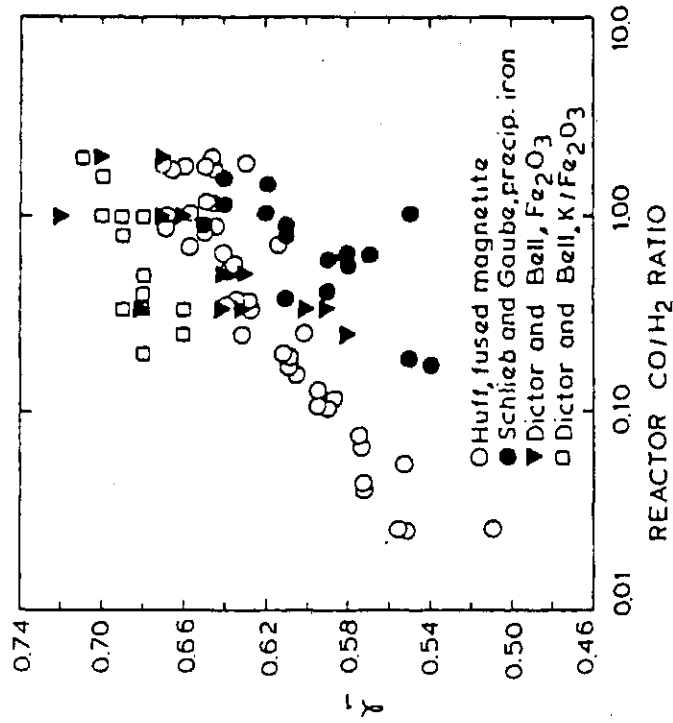


Figure 13. Comparison of  $\alpha_1$  versus CO/H<sub>2</sub> ratio from several iron catalysts.

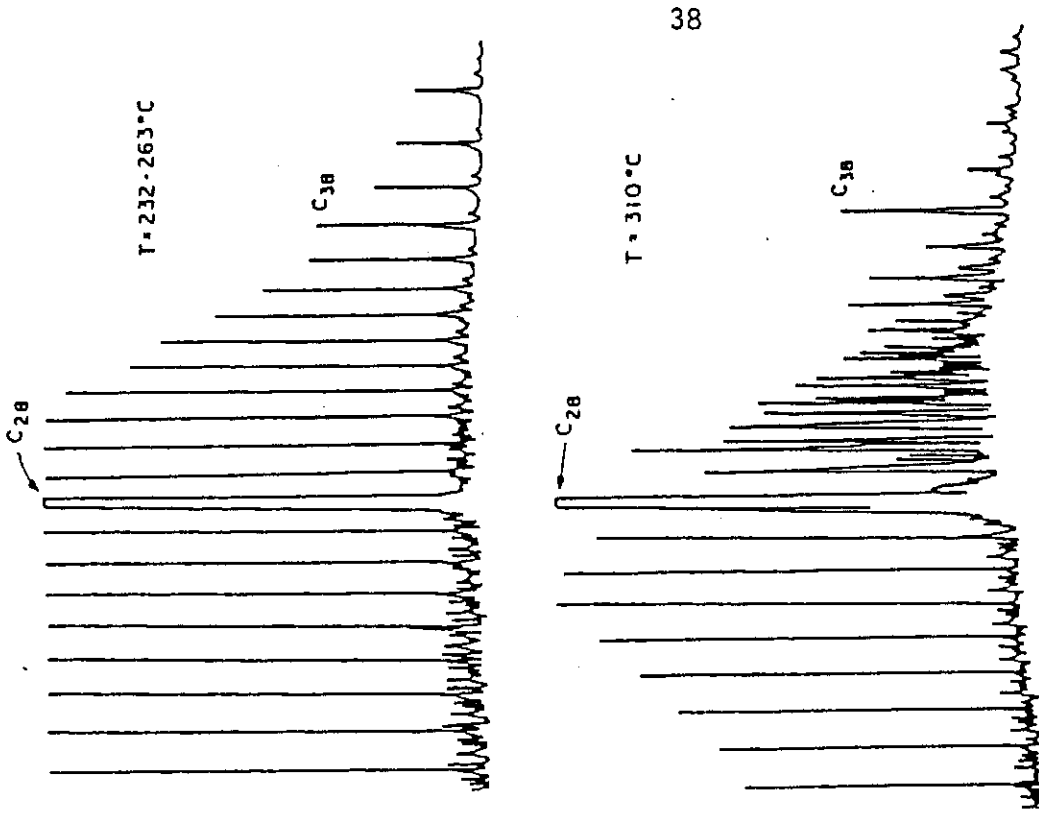


Figure 15. Gas chromatograms from high- and low-temperature runs.

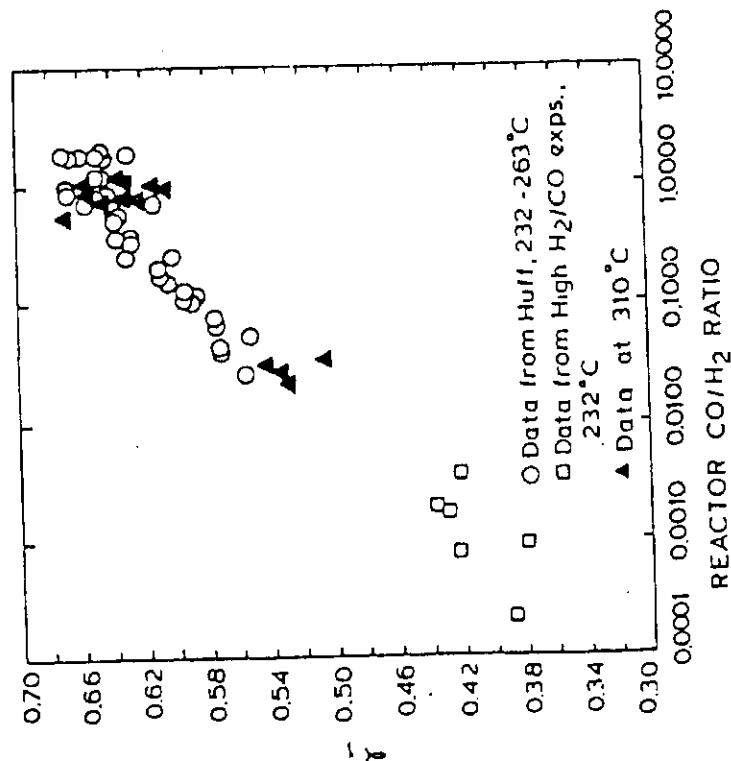
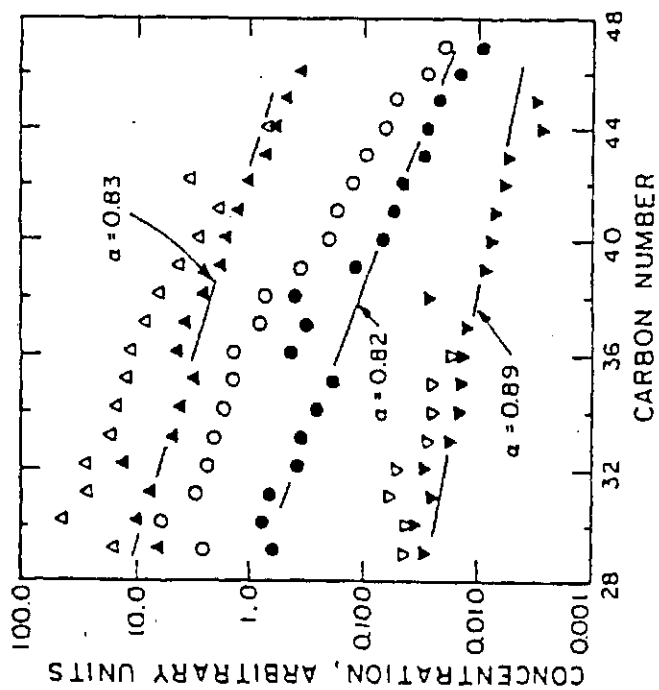


Figure 14. Comparison of  $\alpha_1$  for high- and low-temperature runs.



Total n-paraffins

△	310°C, $(H_2/CO)_{in} = 3.8$
○	310°C, $(H_2/CO)_{in} = 0.7$
▽	234-269°C, $(H_2/CO)_{in} = 1.32$

Figure 16. Heavy product analyses from high- and low-temperature runs.

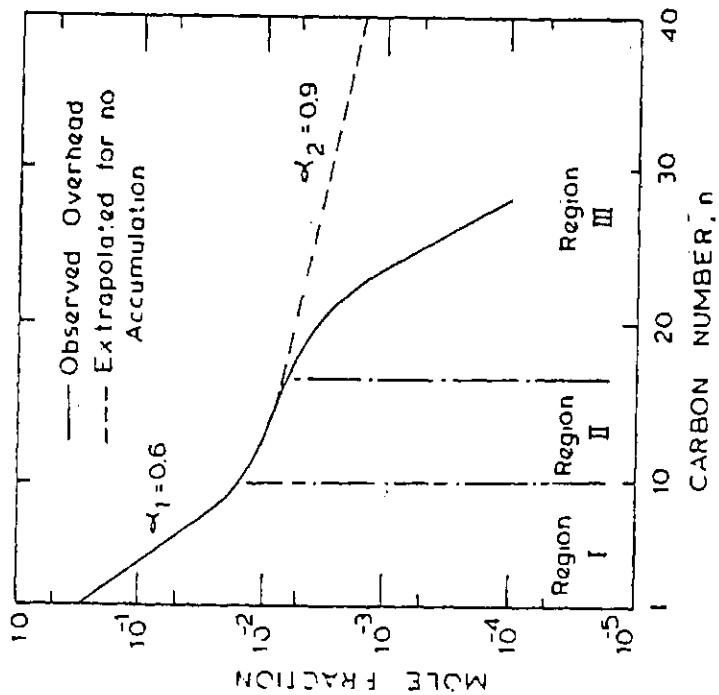


Figure 17. General form of the Schulz-Flory plot for reactor effluent from an iron catalyst.



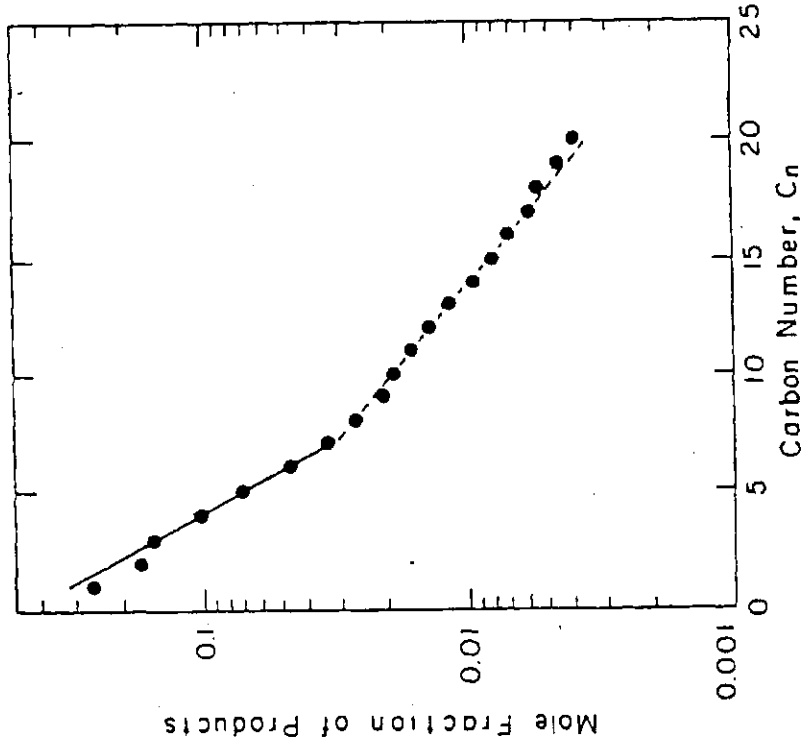


Figure 18. Schulz-Flory diagram of data from a potassium-promoted precipitated iron catalyst with asymptotic regression lines.

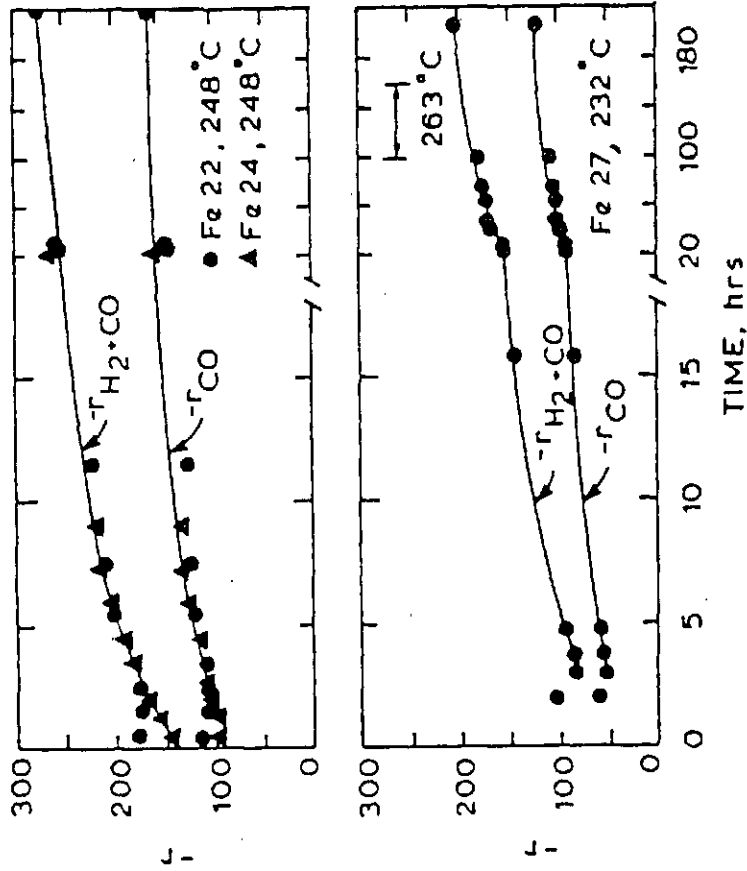


Figure 19. Catalyst activity increases with time on stream.

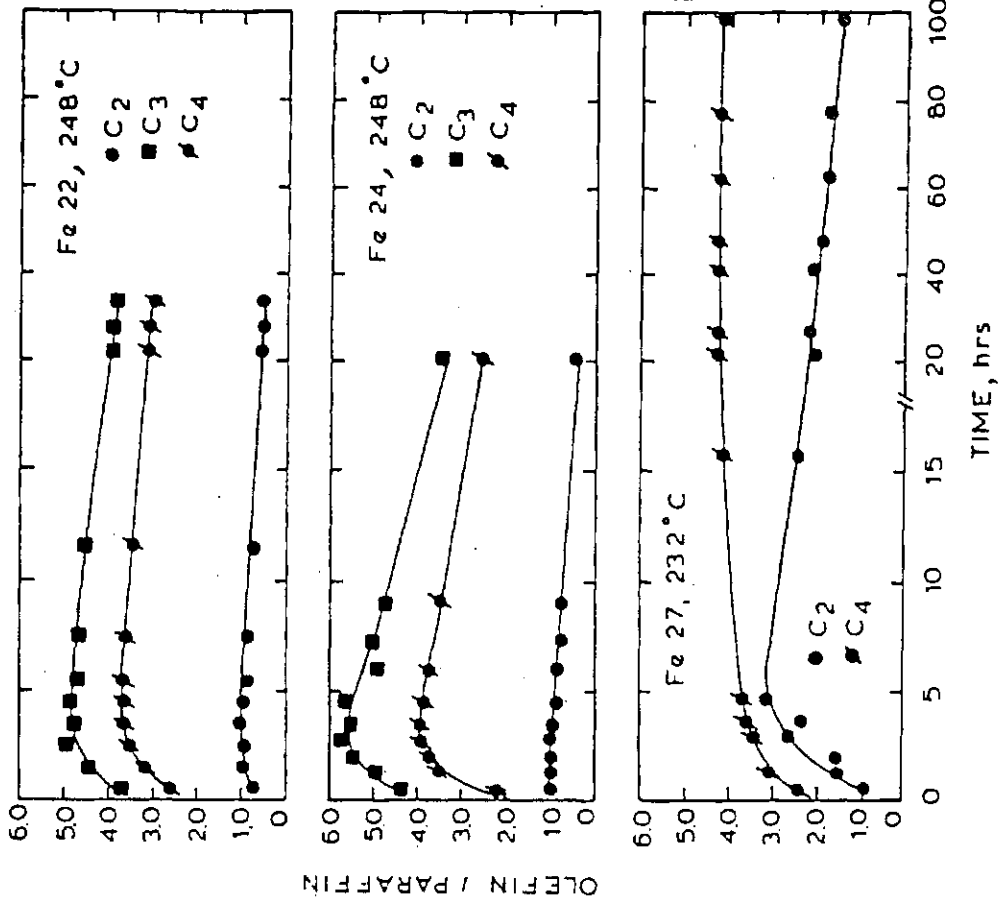


Figure 21. Olefin/paraffin ratio increases during first several hours of synthesis.

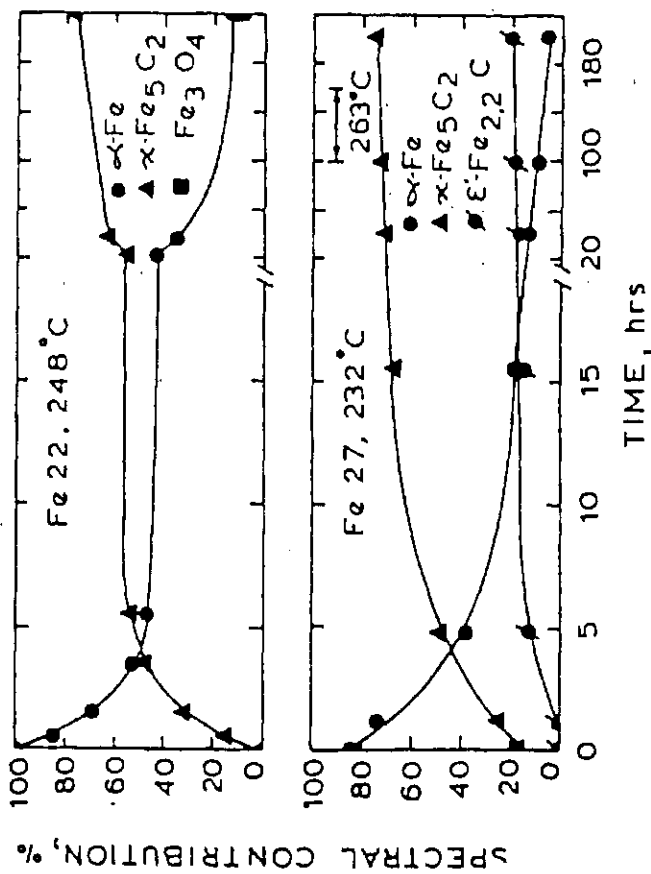


Figure 20. Iron carbide concentration in bulk catalyst increases at expense of metallic iron with time on stream.

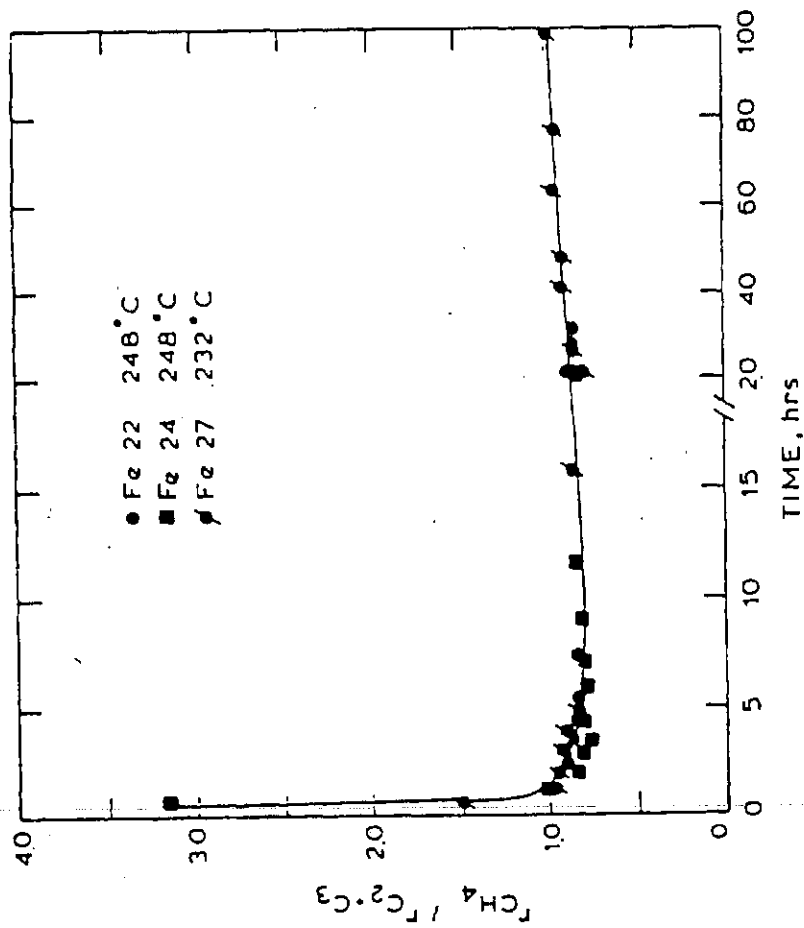


Figure 22. Methane selectivity decreases markedly during first hour of synthesis.

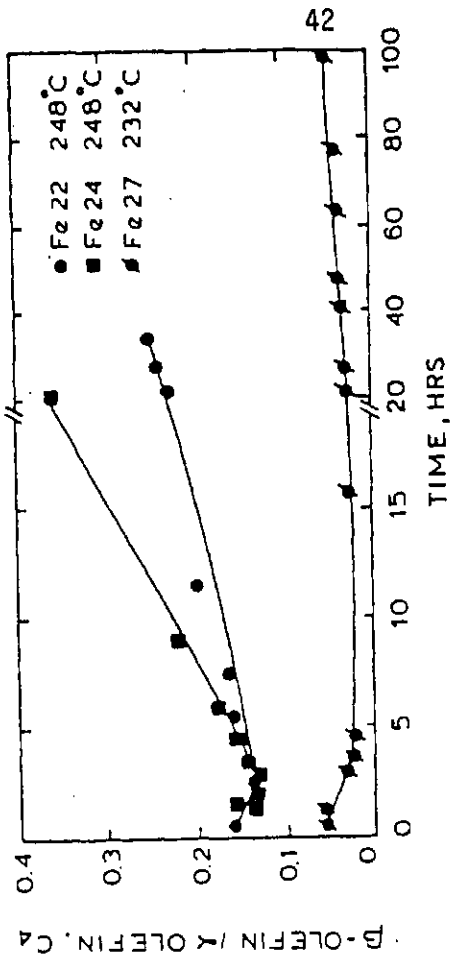


Figure 23.  $\beta$ -Olefin/ $\alpha$ -olefin ratio slowly increases with time on stream.

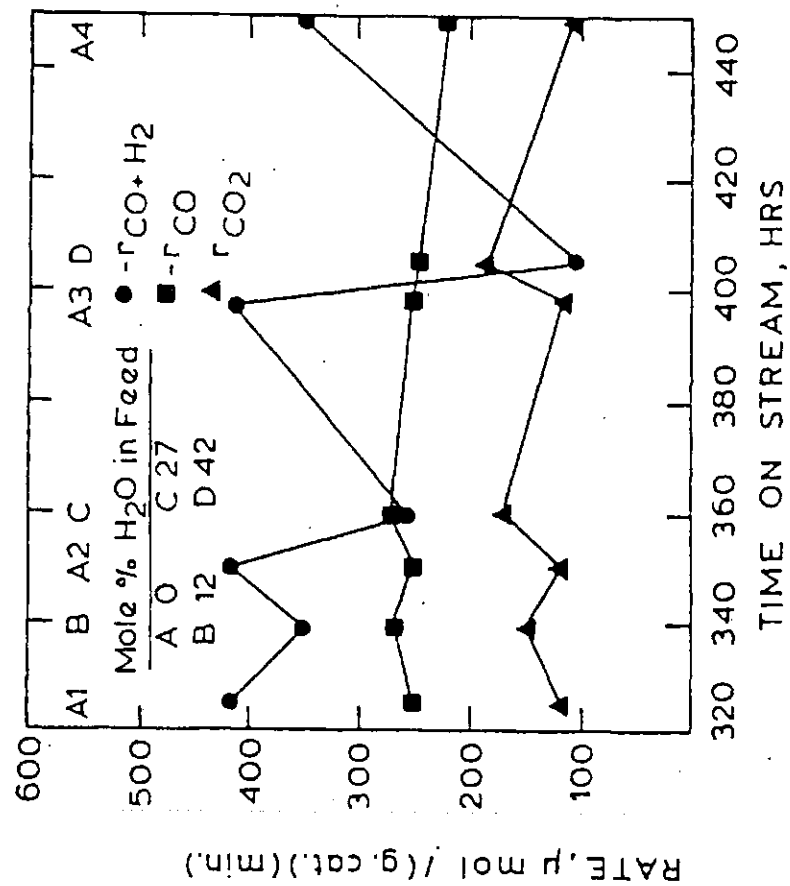


Figure 24. Effect of H<sub>2</sub>O on reaction rate.

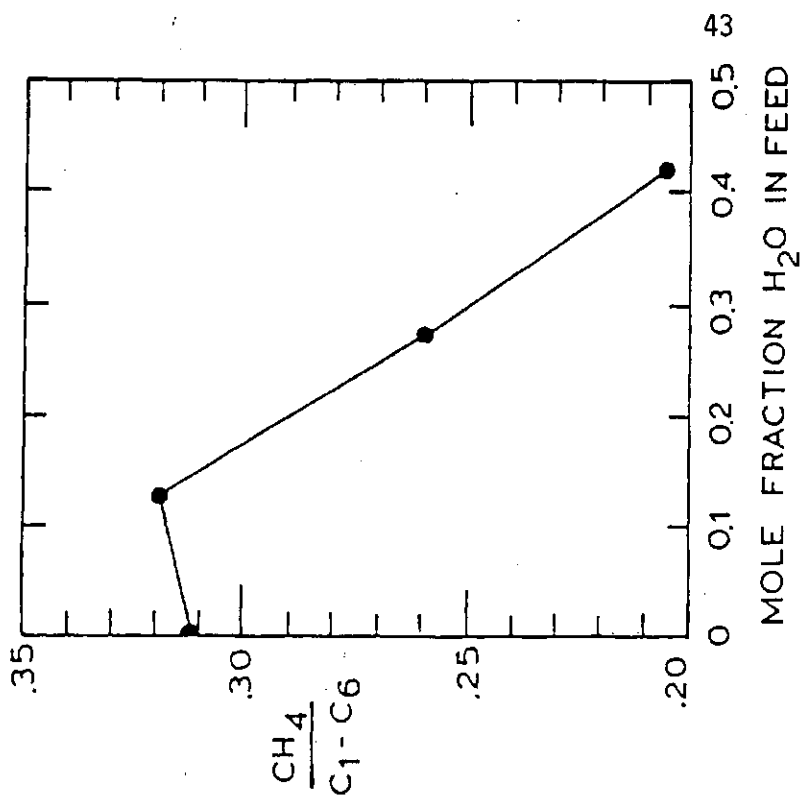


Figure 25. Methane selectivity drops with increased water concentration.

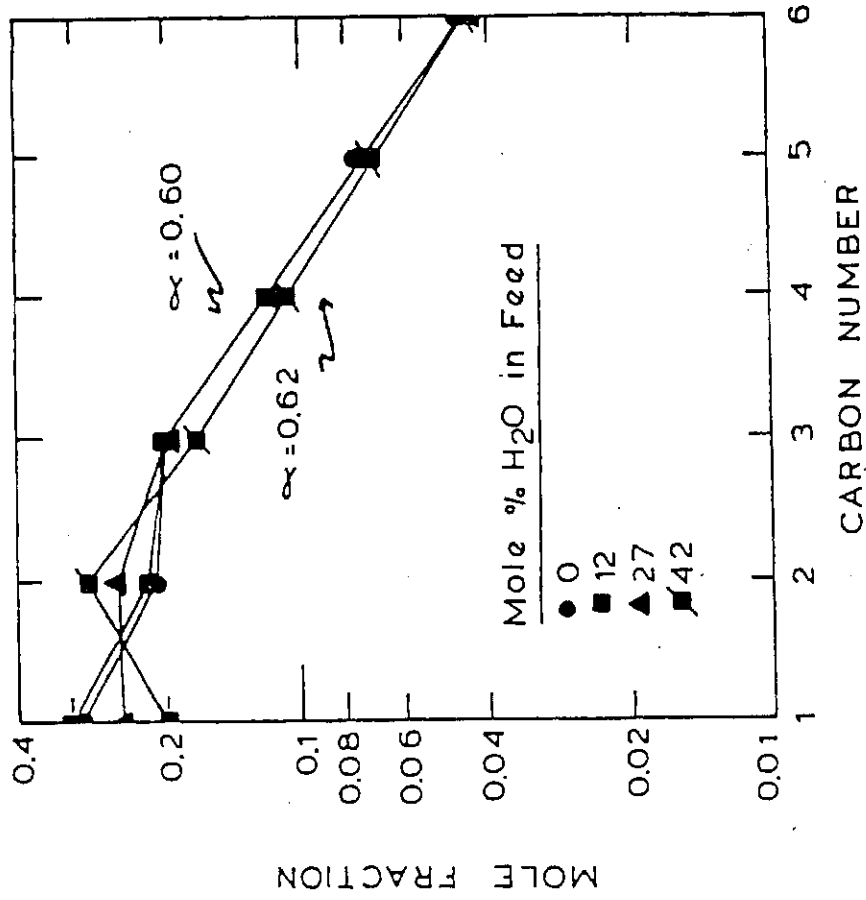


Figure 27. Effect of H<sub>2</sub>O on the carbon number product distribution.

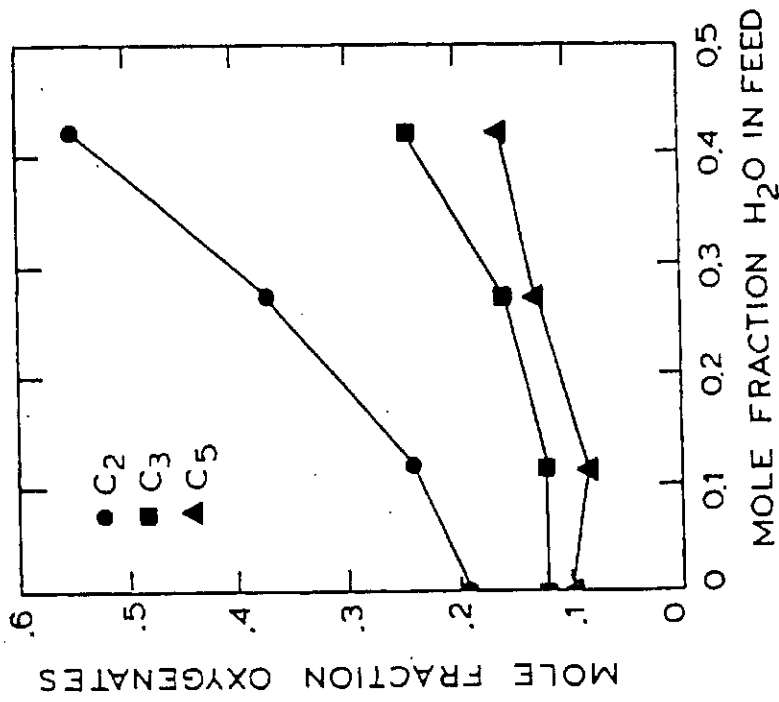


Figure 26. Oxygenate concentrations increase with increased water concentration.

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TABLE 1

## Composition of precipitated iron catalysts

All compositions determined by duplicate analysis using atomic absorption spectroscopy by Galbraith Laboratories, except oxygen by difference. Oxygen is assumed to be bound as metallic oxides. Traces of calcium, carbon and hydrogen are present on the Ruhrchemie catalyst, accounting for 1.33 wt.-% of the total.

	Unalkalized PETC	Ruhrchemie
Fe	60.46 wt.-%	47.30 wt.-%
Cu	0.58	2.36
SiO <sub>2</sub>	<0.002	12.69
K	<9 ppm	1.94
Na	<12 ppm	0.02
Al		34.36
O	38.96	

TABLE 2

## Effect of potassium on product cuts

	No Potassium	1 wt.-% Potassium
C <sub>1</sub>	10.2 wt.-%	5.3 wt.-%
C <sub>2</sub> -C <sub>4</sub>	32.4	23.1
C <sub>5</sub> -C <sub>12</sub>	39.8	34.1
C <sub>13</sub> -C <sub>19</sub>	11.7	20.6
C <sub>20+</sub>	5.9	16.9

TABLE 3

## Catalyst comparisons

	Ruhr- chemie	PETC <sup>a</sup>	Mobil <sup>b</sup> low wax	Mobil <sup>c</sup> high wax	UC C-73 <sup>d</sup>	SASOL <sup>e</sup> fixed bed	Precipi- tated Fe Catalyst, Unalka- lized <sup>f</sup>	Same, +1% K <sup>g</sup>
<i>Wt.-% Selectivity</i>								
C <sub>1</sub>	5.7	5.1	7.9	2.7	11.6	5.0	10.2	5.3
C <sub>2</sub> -C <sub>4</sub>	27.0	20.9	29.0	11.7	39.6	12.6	32.4	23.1
C <sub>5</sub> -C <sub>12</sub>	40.0	42.9	11.7	18.1	39.5	22.5	39.8	34.1
C <sub>13+</sub>	27.3	31.1	51.4	67.5	9.3	56.0	17.6	37.5
$\alpha_1$	0.66				0.63	0.64 (estimated)	0.64	0.68
$\alpha_2$	0.91				0.90	0.93 (estimated)	0.88	0.93
<i>Conditions</i>								
Temp., °C	263	260	262	258	263	220-250	260	260
Press., MPa	2.41	1.3	1.8	1.5	1.0	2.5	1.5	1.5
Flow, Nl/(h) (gcat)	2.0	2.4	2.7	2.4	1.0		2.2	2.2
$x_{CO+H_2}$ (H <sub>2</sub> /CO)	33.6	88.8	95.2	82.5	77.0		25.1	14.9
feed	0.70-0.78	1.0	0.67	0.74	0.70		1.0	1.0
Activity mmol/(min) (gcat)	0.49	1.3	1.2	1.0	0.37	-	-	-
Water-gas shift activity $\frac{[CO_2][H_2]}{[CO][H_2O]}$	1.0	20.0		23.5	40.0	-	-	-

<sup>a</sup>Zarochak et al. report 42.9 wt.-% "C<sub>5+</sub> liquids" and 31.1 wt.-% "wax" in their products. We have used these values<sup>5+</sup> as C<sub>5</sub>-C<sub>12</sub> and C<sub>13+</sub>, respectively.

<sup>b</sup>Kuo reports C<sub>5</sub>-C<sub>11</sub> fractions, which we have used as C<sub>5</sub>-C<sub>12</sub> products. The Mobil low wax run used high surface area I-B catalyst and is designated as CT-256-2. The data are those at a time-on-stream (T.O.S.) of 15.8 days.

<sup>c</sup>Kuo. The high wax run used low surface area I-B. catalyst and is designated as CT-256-13. Data were taken at a T.O.S. of 19.8 days.

<sup>d</sup>Huff.      <sup>e</sup>Caldwell.

<sup>f</sup>Unalkalized precipitated iron catalyst prepared by Pittsburgh Energy Technology Center (PETC) and studied in our laboratory.

<sup>g</sup>Same as f, but after addition of 0.7 g potassium tert-butoxide to 25.0 g catalyst as promoter.



Table 4. Effect of Temperature on  $\alpha_1$  and  $\alpha_2$ 

	temp, °C	$\alpha_1$	$\alpha_2$
this study	310 <sup>a</sup>	0.65–0.68	0.82 (C <sub>32</sub> –C <sub>40</sub> )
	310 <sup>b</sup>	0.50–0.55	0.83 (C <sub>32</sub> –C <sub>40</sub> )
Huff and Satterfield (1984)	248	0.62	0.93 (C <sub>25</sub> –C <sub>50</sub> )
Stenger et al. (1984)	232–263 <sup>d</sup>		0.89–0.90 (C <sub>25</sub> –C <sub>50</sub> )
	225–250 <sup>e</sup>		0.92 (C <sub>25</sub> –C <sub>50</sub> )
Schwarzheide tests	225 (max)	0.66–0.69	0.87–0.89
Mobil Kuo (1993)	255–280	0.66–0.70	0.88
Schliebs and Gaube (1985)	260	0.54–0.65	0.86–0.91
Hydrocol	315	0.66	0.79
Michael process	330		0.70

<sup>a</sup> (H<sub>2</sub>/CO)<sub>in</sub> = 0.7; 1.48 MPa; fused magnetite. (H<sub>2</sub>/CO)<sub>reactor</sub> ≈ 1–2. <sup>b</sup> (H<sub>2</sub>/CO)<sub>in</sub> = 3.8; 1.48 MPa; fused magnetite. (H<sub>2</sub>/CO)<sub>reactor</sub> ≈ 40. <sup>c</sup> (H<sub>2</sub>/CO)<sub>in</sub> = 1.81; 0.79 MPa; fused magnetite. <sup>d</sup> (H<sub>2</sub>/CO)<sub>in</sub> = 0.55–1.8; 0.4–1.48 MPa; fused magnetite. <sup>e</sup> (H<sub>2</sub>/CO)<sub>in</sub> = 1.38; 1.14–1.48 MPa; precipitated catalyst containing Cu and K. <sup>f</sup> Six catalysts were of the precipitated type and contained slightly different K contents. Cu content varied between 1 and 10 atoms of Cu per 100 atoms Fe. One catalyst was fused iron oxide without Cu. <sup>g</sup> Proprietary precipitated Fe/Cu/K<sub>2</sub>CO<sub>3</sub> catalyst. <sup>h</sup> Unpromoted and K-promoted precipitated iron catalysts; H<sub>2</sub>/CO = 0.6–5.8; 1.0–1.2 MPa.  $\alpha_1$  and  $\alpha_2$  calculated by fitting data to a two- $\alpha$  model. <sup>i</sup> Alkalized mill scale. <sup>j</sup> Iron powder treated with potassium borate.

APPENDIX A

Our findings have been published in the form of 10 papers which are listed below together with an abstract of each.

Papers Published:

1. C.N. Satterfield, R.T. Hanlon, S.E. Tung, Z.-m. Zou, and G.C. Papaefthymiou, "Initial Behavior of a Reduced Fused-Magnetite Catalyst in the Fischer-Tropsch Synthesis," I&FC Product Research and Development, 25 (1986) 401.

In studies at 232 and 248°C and 0.92 MPa, during the first 20 hours on stream, both Fischer-Tropsch synthesis activity and CO consumption increased to quasi-steady-state values. The bulk catalyst, initially  $\alpha$ -Fe, was converted to a mixture of  $\alpha$ -Fe and iron carbides, as determined by Mössbauer spectroscopy. During the first few hours, methane selectivity decreased markedly while the olefin/paraffin ratio increased. No change was observed in the C<sub>2</sub>-C<sub>8</sub> product distribution with time on stream.

2. C.N. Satterfield, R.T. Hanlon, S.E. Tung, Z.-m. Zou, and Georgia C. Papaefthymiou, "Effect of Water on the Iron-Catalyzed Fischer-Tropsch Synthesis," I&EC Product Research and Development, 25 (1986) 407.

The addition of water vapor to dry synthesis gas to comprise as much as 27 mol% of the feed composition decreased catalyst activity, but the effect was completely reversible upon removal of the water vapor. Reversibility was not complete with water addition to comprise 42 mol% of feed. Water vapor decreased methane selectivity, increased oxygenate selectivity, and increased the rate of the water gas shift. However, these effects did not correlate with the relative Fe<sub>5</sub>C<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, and Fe content of the bulk catalyst as determined by Mössbauer spectroscopy, although the Fe<sub>5</sub>C<sub>2</sub> content did not change greatly. Molecular weight distribution of the C<sub>3</sub>-C<sub>7</sub> products was not affected by water.

3. D.K. Matsumoto and C.N. Satterfield, "Effects of Poisoning a Fused Magnetite Fischer-Tropsch Catalyst with Dibenzothiophene," Energy & Fuels, 1 (1987) 203.

Catalyst activity is decreased more if the catalyst is prereduced rather than precarbured before contact with poison. The inhibiting effect of water on the reaction decreases more markedly with increasing temperature on a poisoned catalyst than on an unpoisoned catalyst. Formation of methane is significantly less on poisoned catalysts than unpoisoned catalysts. On both poisoned and unpoisoned catalysts, the olefin/paraffin ratio decreases with increased CO conversion and isomerization of  $\alpha$ - to  $\beta$ -olefins increases. Isomerization activity is greater on a preduced/poisoned catalyst than on a precarbured/poisoned catalyst.

4. R.T. Hanlon and C.N. Satterfield, "Reactions of Selected 1-Olefins and Ethanol Added during the Fischer-Tropsch Synthesis," Energy & Fuels, 2 (1988) 196.

The effects of addition during synthesis of C<sub>2</sub>, C<sub>4</sub>, C<sub>6</sub>, C<sub>10</sub>, or C<sub>20</sub> normal 1-olefins was studied in a continuous-flow well-stirred liquid-phase reactor. Studies were performed at 248°C and 0.78-1.48 MPa, using a reduced fused magnetite catalyst containing potassium. Incorporation of these olefins into growing chains could be detected but was relatively minor. Instead the olefin was hydrogenated to the corresponding paraffin or isomerized to the 2-olefin. Disappearance of all added species was much less at low synthesis conversions than at high conversions, attributed to competitive adsorption with CO. The reactions of added ethanol were also studied. Ethanol or ethylene decreased the hydrogenation capabilities of the catalyst as reflected in decreased formation of CH<sub>4</sub> and increased olefin/paraffin ratio of the products. Neither addition affected the chain growth probability,  $\alpha$ .

5. I.C. Yates and C.N. Satterfield, "Effect of Carbon Dioxide on the Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts," I&EC Research, 28 (1989) 9.

A recently proposed kinetic expression applicable to feed ratios H<sub>2</sub>/CO of 0.8 or less correlates the synthesis rate by an equation containing an inhibition term for CO<sub>2</sub> and assumes that water vapor concentrations are too low to offer significant inhibition. Experimental studies here with synthesis gas of H<sub>2</sub>/CO ratios of 0.67-0.72 to which CO<sub>2</sub> was added show, in contrast, that CO<sub>2</sub> is relatively inert. The data are well correlated by an equation developed by Huff that contains an inhibition term for H<sub>2</sub>O but not for CO<sub>2</sub>. We suggest that the inhibition attributed to CO<sub>2</sub> was instead actually caused by H<sub>2</sub>O formed by the reverse water gas shift reaction.

6. T.J. Donnelly, I.C. Yates, and C.N. Satterfield, "Analysis and Prediction of Product Distributions of the Fischer-Tropsch Synthesis," Energy & Fuels, 2 (1988) 734.

A method is developed for calculating the three parameters needed to characterize the carbon number distribution of products of the Fischer-Tropsch synthesis. Experimental data are fit by a modified Schulz-Flory model that has two chain growth probabilities, using nonlinear regression. Excellent fit is shown for data from precipitated iron and fused magnetite catalysts. The model is used to calculate selectivity information of interest in catalyst comparison and reactor design. Advantages of this method over asymptotic regression methods are discussed in detail.

7. C.N. Satterfield, D.K. Matsumoto, and R.T. Hanlon, "Effects of Temperature on Product Selectivity in the Fischer-Tropsch Synthesis on Iron Catalysts," Proceedings: World Congress III of Chemical Engineering, Tokyo, 1986.

Studies over the range of 232°C to 310°C, and at 1.48 MPa, indicate the following trends with increasing temperature: marked decrease in the Schulz-Flory parameter  $\alpha$  for the C<sub>10</sub>+ fraction, increase in aromatic content and degree of branching of paraffin waxes, and shift in oxygenate composition from predominantly alcohols to predominantly aldehydes and ketones.

8. D.K. Matsumoto and C.N. Satterfield, "Effects of Temperature and Hydrogen/Carbon Monoxide Ratio on Carbon Number Product Distribution from Iron Fischer-Tropsch Catalysts," Energy & Fuels, 3 (1989) 249.

Present studies and analyses of the literature indicate that  $\alpha_1 = 0.60-0.70$  for the Schulz-Flory distribution up to about C<sub>10</sub> for a variety of iron catalysts.  $\alpha_1$  is relatively insensitive to the presence or absence of potassium and H<sub>2</sub>/CO ratios up to about 10. Values of  $\alpha_2$  for the C<sub>10</sub>+ fraction vary from about 0.89 to 0.93 at 225-263°C, decreasing to about 0.82 at 310°C.

9. D.K. Matsumoto and C.N. Satterfield, "Effect of Carbon Monoxide on Olefin Hydrogenation and Isomerization on a Reduced Fused Magnetite Catalyst," Energy & Fuels, 3 (1989) 287.

Some of the effects of high syngas conversion on the secondary reactions of olefins formed by Fischer-Tropsch synthesis on a reduced fused magnetite catalyst were simulated. Studies were of olefins in the presence of hydrogen and low concentrations of CO, or in hydrogen alone, at 232°C and total pressures of 0.30-0.79 MPa. No significant incorporation of olefins into growing chains was observed.

10. T.J. Donnelly and C.N. Satterfield, "Product Distributions of the Fischer-Tropsch Synthesis on Precipitated Iron Catalysts," Applied Catalysis, 52 (1989) 93.

The product distributions of the Fischer-Tropsch synthesis on alkalinized and unalkalinized precipitated iron catalysts were studied in a continuous-flow well-stirred slurry reactor at 230°C to 265°C and 0.77 to 2.98 MPa. A commercial Puhchemie catalyst with 1.9 wt.-% potassium and 12.7 wt.-% silica showed stable activity for 1300 hours-on-stream. The average molecular weight of products from this catalyst decreased with time-on-stream and, at the same time, oxygenate production increased substantially. In contrast, a precipitated iron catalyst with neither potassium nor silica showed stable selectivity but decreasing activity for 2000 hours-on-stream. Comparisons are presented among these two catalysts and other iron catalysts discussed in the literature. Particular attention is paid to the carbon number distributions of hydrocarbon products. These distributions from both alkalinized and unalkalinized catalysts are accurately described by a modified Schulz-Flory distribution with two chain growth probabilities.