

TABLE I-1

REDUCTION PROCEDURE FOR WATER-GAS SHIFT CATALYSTS

Hours- on-stream	Temperature (°C)	Flow, (Nl/min/g.cat.)
Initial Procedure		
0 to 2	70 to 120	0.015 of gas C
2 to 2.5	120	0 to 0.015 gas A, 0.015 to 0 of gas C
2.5 to 6	120 to 200	0.015 of gas A
6 to 7	200	0 to 0.015 of gas B, 0.015 to 0 of gas A
7 to 20	200	0.015 of gas B
Modified Procedure		
0 to 16	70	0.015 of gas C
16 to 18	70 to 120	0.015 of gas C
18 to 19	120	0 to 0.015 of gas A, 0.015 to 0 of gas C
19 to 21.5	120 to 200	0.015 of gas A
21.5 to 24	200	0 to 0.015 of gas D, 0.015 to 0 of gas A
24 to 25	200	0.015 of gas D

TABLE I-1 (Continued)

Notes: Time and temperature periods shown indicate a smooth ramping of conditions. Typically, process changes were made every 15 minutes. The modified procedure was used for the data reported here.

Gas A was 1000 ppm prepurified H₂ in prepurified N₂ (Matheson Gases, Inc.).

Gas B was prepurified H₂ (MedTech Gases, Inc.).

Gas C was prepurified He (Colony, Inc.).

Gas D was 3 vol.% prepurified H₂ in prepurified N₂ (Matheson Gases, Inc.).

TABLE I-2

PROCESS CHANGES FOR Cu/ZnO/Al ₂ O ₃ ALONE	
Time-on-stream [hours]	Process Change
0	On-stream with base case conditions ^a .
303	Base case except pressure = 1.48 MPa.
358	Returned to base case conditions.
425	Base case except H ₂ /CO feed ratio increased to 1.0.
473	Returned to base case conditions.
637	Base case except temperature increased to 220°C.
693	Returned to base case conditions.
783	Base case except H ₂ /CO feed ratio increased to 0.7.
830	Returned to base case conditions.
924	Base case except 2 mol.% 1-butene added to H ₂ feed.
1030	Returned to base case conditions.

^a "Base case" conditions are 200°C, 0.79 MPa, and a feed of 42.9 mol.% CO, 21.4 mol.% H₂, and 35.7 mol.% H₂O. Feed rate (includes water vapor) = 0.019 Nl/min/g.cat. (unreduced basis). 25 g. of catalyst (unreduced basis) were charged to the reactor containing 400 g. of recrystallized octacosane.

TABLE I-3

**STANDARD OPERATING CONDITIONS AND PRODUCT DISTRIBUTIONS
FOR COMBINED SYSTEMS AND COBALT CATALYST ALONE**

	Run L	Run H	Cobalt-Catalyst
	[Co/MgO/SiO ₂]/ [Cu-ZnO/Al ₂ O ₃]=0.27	[Co/MgO/SiO ₂]/ [Cu-ZnO/Al ₂ O ₃]=0.51	Only ^a
Temperature (°C)	240	240	240
Pressure (MPa)	0.79	0.79	0.79
(H ₂ /CO) <i>In Situ</i>	1.02	0.98	1.52
Feed Flow Rate (NI/min-g.Co-cat.)	0.065	0.035	0.026
Weight Fraction C ₁	0.26	0.08	0.09
Weight Fraction C _{2,4}	0.24	0.14	0.15
Weight Fraction C _{3,9}	0.27	0.29	0.31
Weight Fraction C ₁₀₊ ^b	0.23	0.48	0.45

^a Data of Yates.⁷

^b Calculated for the C₁₀-C₁₀₀ fraction by extrapolation, using overhead composition data for the C₃-C₁₆ fraction.⁷

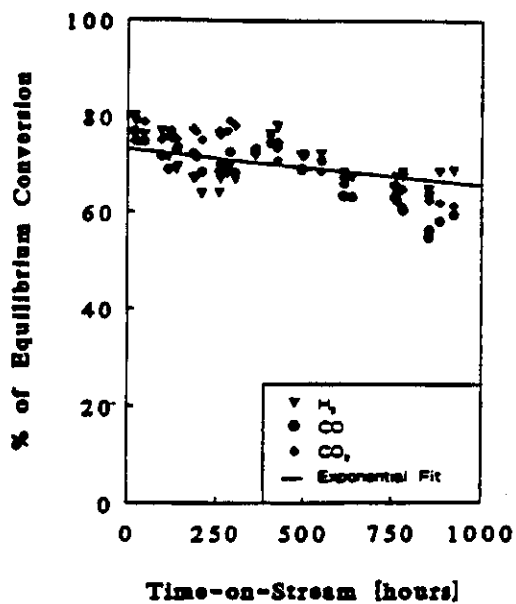


Fig.I-1 Stable activity of Cu-ZnO/Al₂O₃ at "base case" conditions (see note to Table 2).

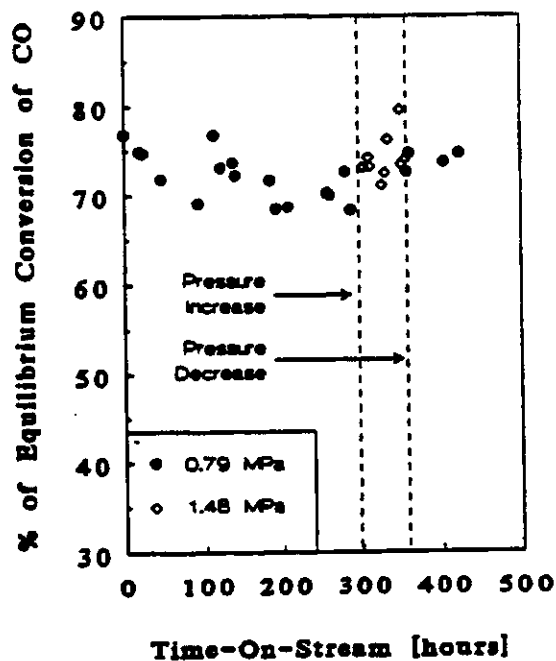


Fig.I-2 Pressure has no deleterious effect on the activity of the Cu-ZnO/Al₂O₃ shift catalyst.

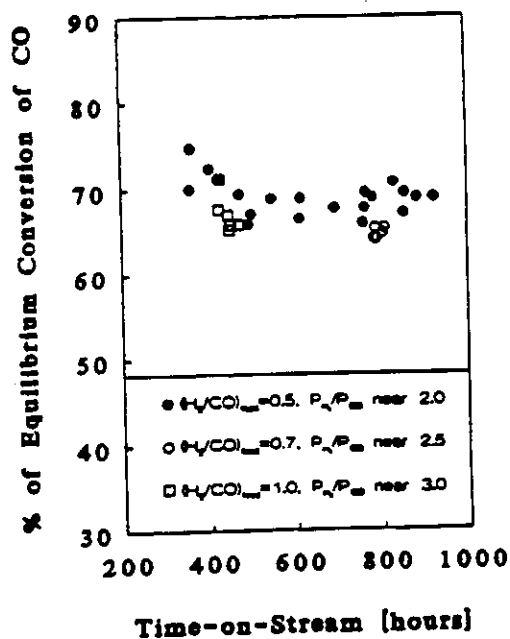


Fig.I-3 Increasing hydrogen-to-carbon monoxide ratio reduces rate, but intrinsic activity remains stable for the Cu-ZnO/Al₂O₃ shift catalyst (200°C, 0.79 MPa, H₂+CO=0.0122 NI/min/g.cat., and H₂O at 0.0068 NI/min/g.cat. (unreduced basis)).

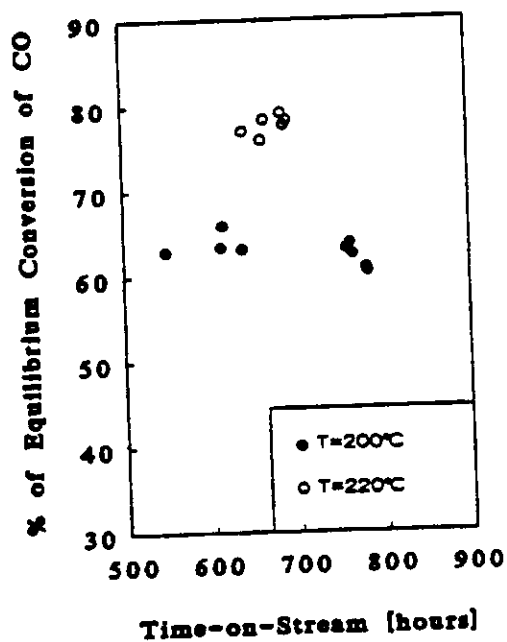


Fig.I-4 Temperature increases % of equilibrium conversion. Standard conditions.

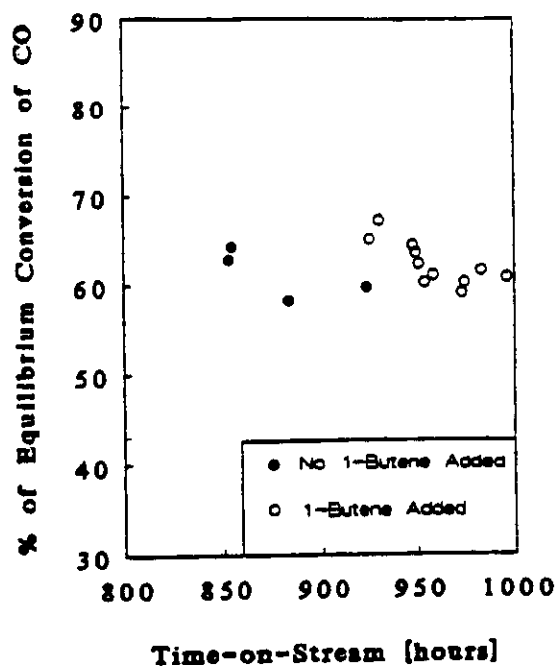


Fig. I-5 1-Butene has no significant inhibiting effect on the shift activity of the Cu-ZnO/Al₂O₃ shift catalyst. 1-butene added as 2 mol.% of H₂.

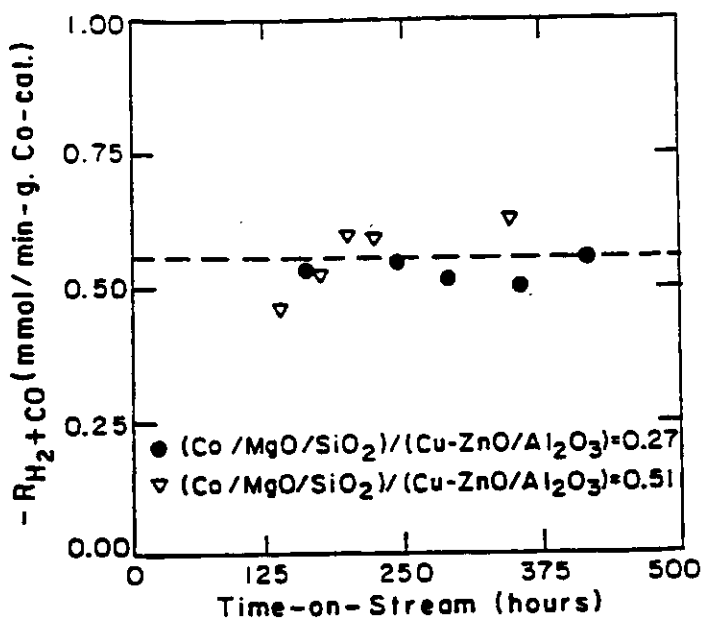


Fig. I-6 The Fischer-Tropsch activity of the catalysts in both run H and run L remained stable for the entire runs of about 400 hours-on-stream each. Feed rate about 0.60 NI/min.

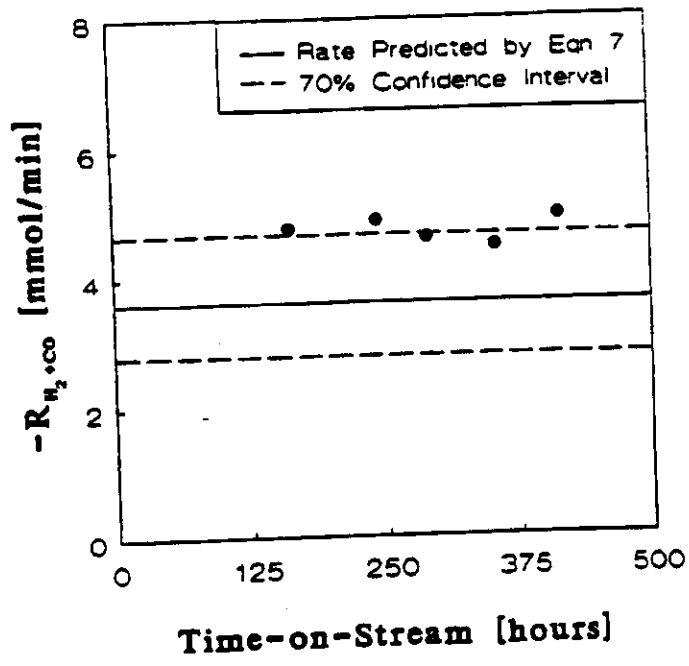


Fig. 1-7 Activity of combined catalyst system run L ($[Co/MgO/SiO_2]/[Cu-ZnO/Al_2O_3]=0.27$) matches that predicted by equation 7. (240°C, 0.79 MPa, *in situ* $H_2/CO=1.02$, and fed 0.065 NI/min-g.Co-cat).

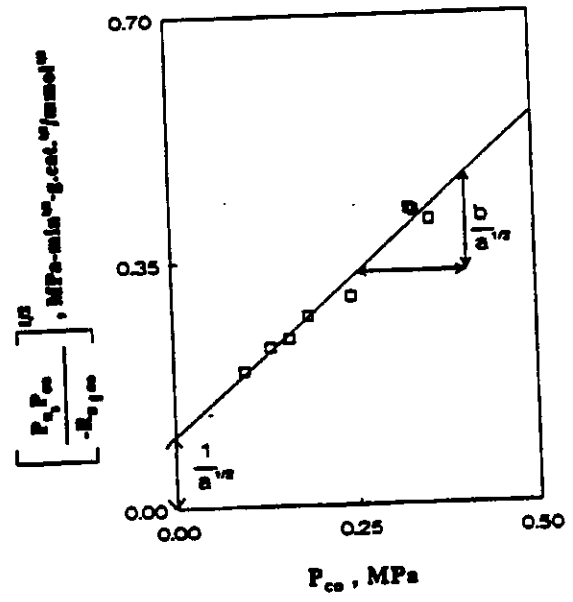


Fig. 1-8 Data from combined catalyst system, run H, are well fit by linearized form of recommended rate equation (equation 8). Intercept = $1/a^{1/2}$, Slope = $b/a^{1/2}$.

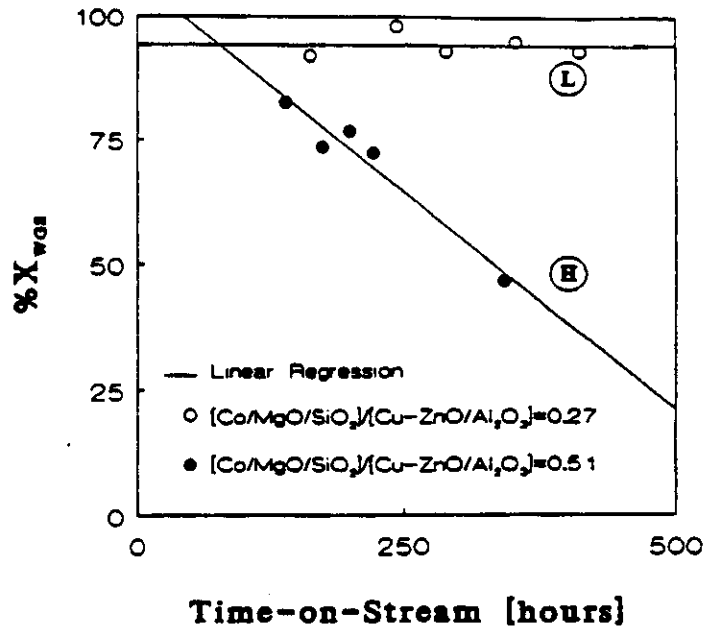


Fig. I-9 The water-gas-shift reaction approached equilibrium limitations for run L, while the activity declined for run H. Standard conditions.

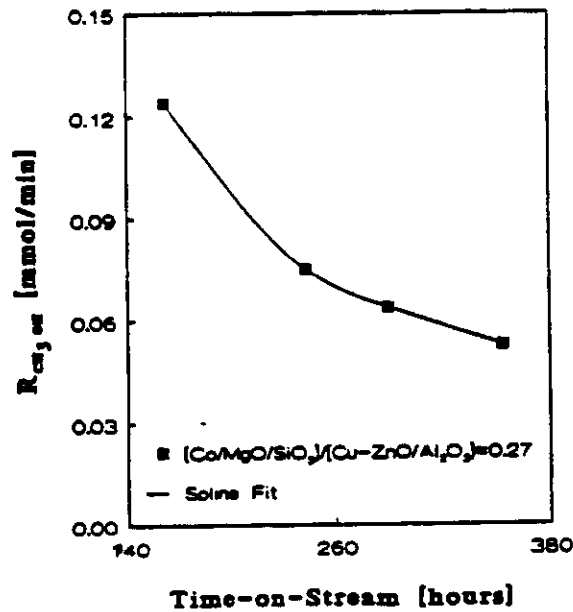


Fig. I-10 The rate of methanol synthesis decreased with time during run L. Standard conditions.

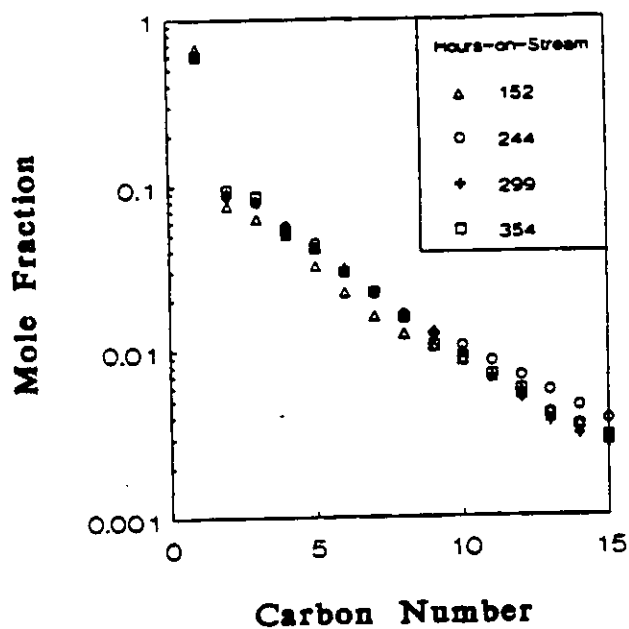


Fig. I-11a Schulz-Flory Diagrams obtained at various time periods show stable Fischer-Tropsch selectivity for run L. Standard conditions.

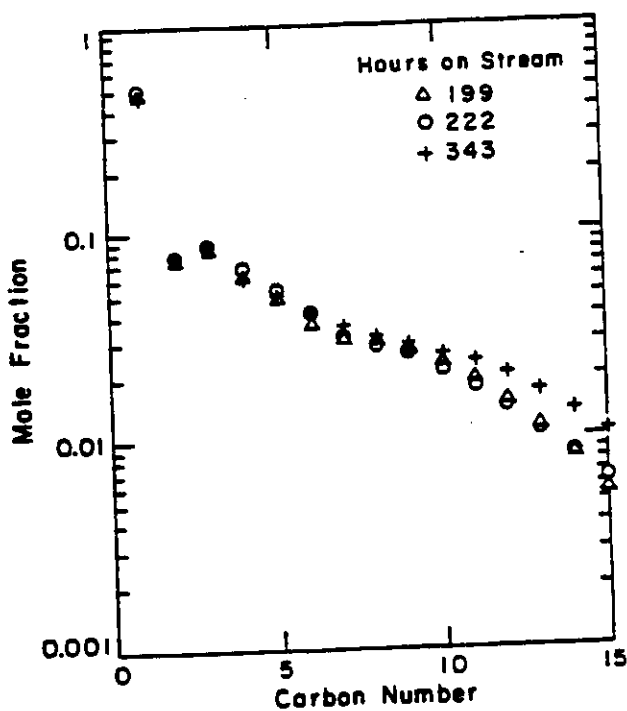


Fig. I-11b Schulz-Flory Diagrams obtained over a 400-hour time period show stable Fischer-Tropsch selectivity for run H. Standard feed conditions.

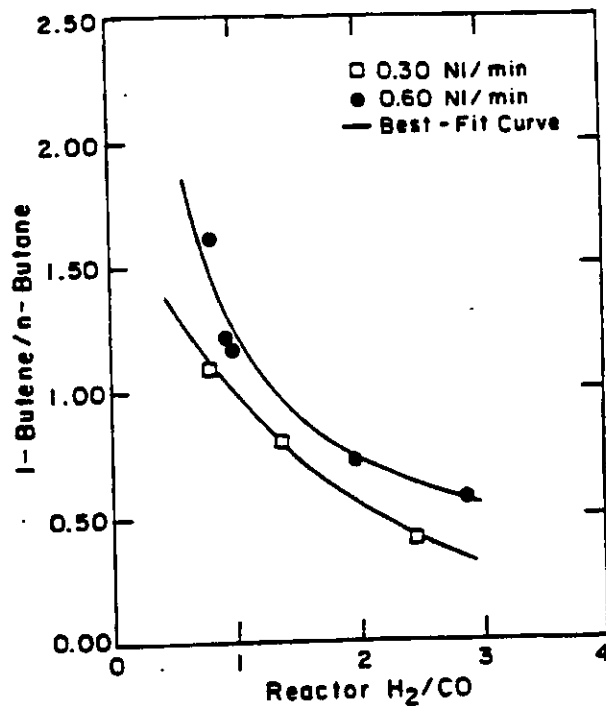


Fig. I-13 The hydrogenation activity was markedly affected by the *in situ* H₂/CO. Standard conditions but with 0.30 or 0.60 NI/min. feed rate (run H).

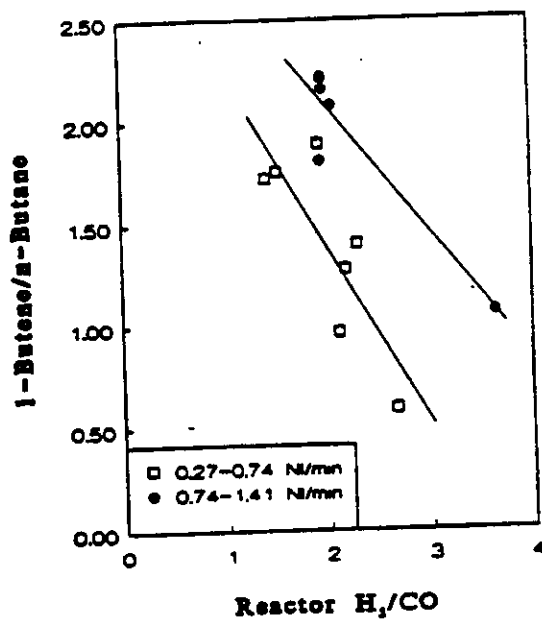


Fig. I-14 The hydrogenation activity of Co/MgO/SiO₂ alone increases with increasing *in situ* H₂/CO. (240°C, 0.79 MPa) Data of Yates.⁷

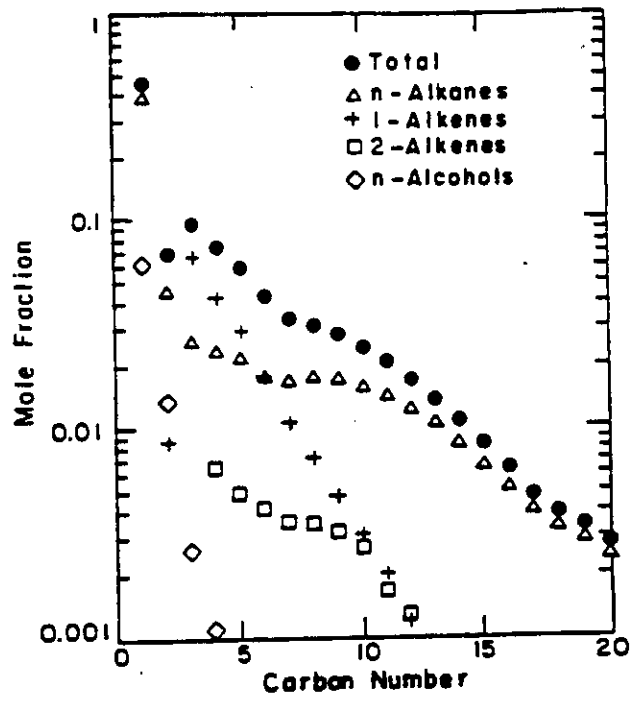


Fig. I-15a A typical component Schulz-Flory diagram from the Co/MgO/SiO₂ catalyst operating alone (Yates⁷).

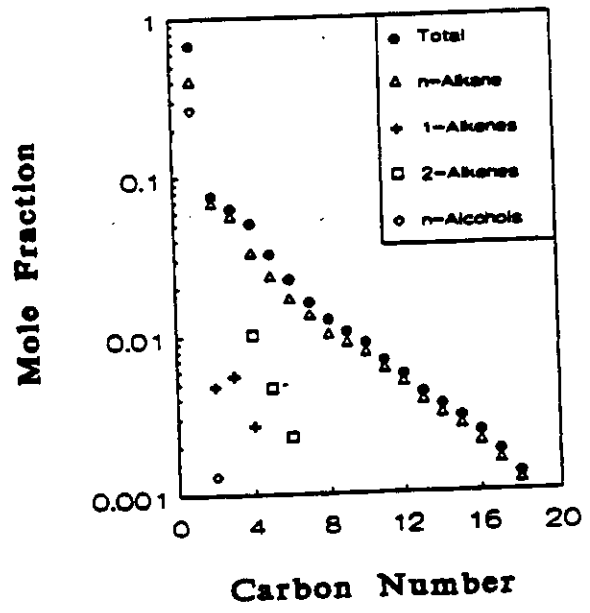


Fig. I-15b A typical component Schulz-Flory diagram from run L. Standard conditions.

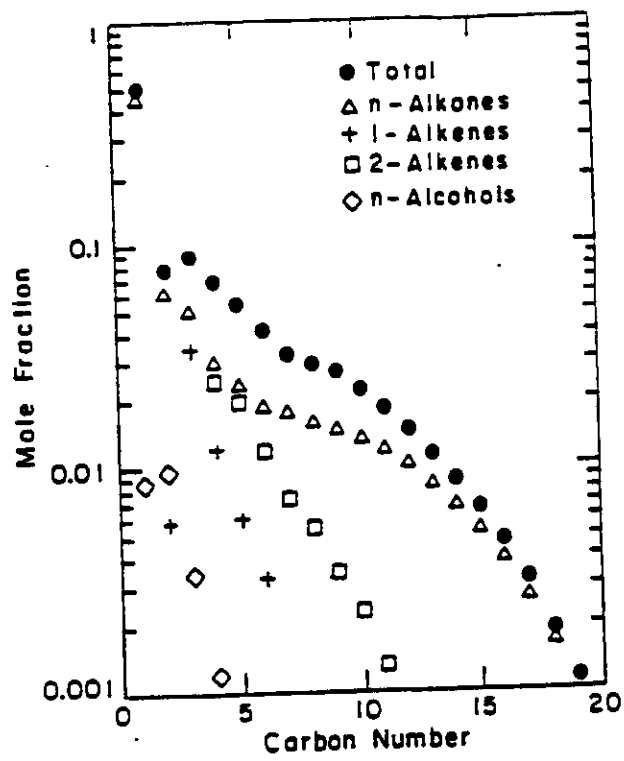


Fig. I-15c A typical component Schulz-Flory diagram from run H. Standard conditions.

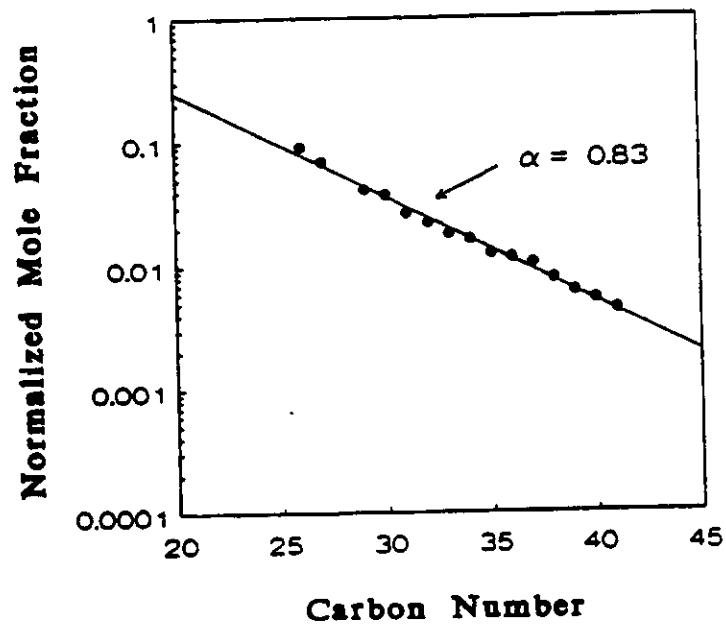


Fig. I-16a Normalized Schulz-Flory diagram from slurry wax sample of run L. Value of $\alpha = 0.83$ determined from linear regression of C_{29} - C_{40} . Standard conditions.

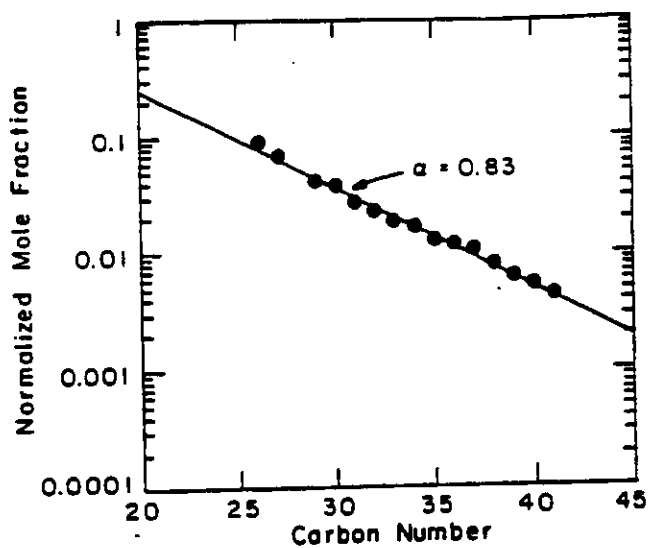


Fig. I-16b Normalized Schulz-Flory diagram from slurry wax sample of run H. Value of $\alpha = 0.83$ determined from linear regression of C_{29} - C_{40} . (240°C, 0.79 MPa, 0.80 \leq *in situ* $H_2/CO \leq$ 3.0).