ABSTRACT

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TITLE: Slurry Phase Fischer-Tropsch Synthesis: Cobalt plus a Water-Gas-Shift Catalyst

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OBJECTIVE: To determine the feasibility of using a mechanical mixture of cobalt Fischer-Tropsch catalyst and a water-gas-shift catalyst in a slurry reactor. To evaluate the performance of a representative cobalt catalyst.

TECHNICAL APPROACH: Study of the kinetics of a cobalt catalyst by itself, of the primary and secondary products of the synthesis and of the performance of a mechanical mixture of the cobalt catalyst and a water-gas-shift catalyst.

SIGNIFICANT ACCOMPLISHMENTS: In earlier work we demonstrated that synergism occurs between a mechanical mixture of a $Cu/ZnO/Al_2O_3$ water-gas shift catalyst and a reduced $Co/MgO/SiO_2$ Fischer-Tropsch catalyst in a slurry reactor. Yield of $C_{10}+$ hydrocarbons was comparable to that from K-promoted iron catalysts, but the cobalt catalyst slowly deactivated with time-on-stream, possibly because of a less than optimum activation procedure.

With a modified activation method, the cobalt catalyst by itself showed essentially constant activity over 2000 hours-on-stream. Over a substantial range of conditions, the rate of synthesis followed the expression: $-R_{H_2+CO} = a P_{CO}P_{H_2}/(1+bP_{CO})^2$ with an apparent activation energy of 93-95 kJ/mol. This is much different than the rate expression for iron catalysts, which has significant implications for estimating the performance of a slurry reactor containing a cobalt catalyst. Decreasing space velocity (higher conversion) also increased the yield of heavy products.

The weight fraction of $C_{10}+$ increased and that of methane decreased with decreasing H_2/CO ratio in the reactor. Olefins such as ethylene, propylene and 1-butene added to the synthesis gas incorporate into products to some extent, but hydrogenation and isomerization (e.g., to 1-butene) seem to predominate. The ratio of the rates of the various 1-alkene reactions are affected predominantly by the H_2/CO ratio, but not by total pressure or by temperature within the range of 220-240°C.

SUMMARY DESCRIPTION OF FIGURES

Slurry Phase Fischer-Tropsch Synthesis:

Cobalt plus a Water-Gas-Shift Catalyst

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Figure 1 The kinetic expression for Fischer-Tropsch synthesis on cobalt is compared to those on iron. In the Anderson expression the "constants" A and B showed an (undisclosed) trend with feed gas composition at constant temperature.

The improved kinetic expression by Huff was developed on C-73 fused magnetite catalyst.

The kinetic expression for cobalt is significantly different than that for iron. There was no effect of H_2O at partial pressures up to 0.29 MPa, the highest measured.

Figure 2 Precautions on interpreting kinetics on iron.

Figure 3 Kinetics as derived at MIT on cobalt. This is probably the most reliable expression available. It is based on a greater range of reaction conditons than any other study. (Details are available in Report DOE/PC79816-7.) A paper based on this report will be published in Energy & Fuels.

Figure 4	The form of the cobalt kinetics expression means that the rate of reaction varies with total pressure, temperature, (H_2/CO) ratio, conversion, etc., in a complex manner. Depending on conditions, in principle a doubling of total pressure can increase rate by a factor of four at one extreme or have no effect at all at the other extreme.
Figure 5	This illustrates some of the effects outlined in Fig. 4. Notably rate increases less than proportionally with total presusre, unlike that predicted for an iron catalyst.
Figure 6	Summary of water gas shift activity on cobalt. It is essentially negligible except at very high temperatures.

Figure 7 Analysis of a recent published paper from Air Products (Withers et al., Ind. Eng. Chem. Res., 1990, 29, 1807) on performance of a Co carbonyl derived catalyst (4.4 wt% Co, at 260°C and 207 MPa). Comparison with MIT catalyst (21.4 wt% Co, at 220°C, 0.79 MPa) and an iron catalyst from Mobil (about 60 wt% Fe, at 260°C and 1.5-1.8 MPa).

Data on activity are adjusted to 260°C or 240°C using an activation energy of 94 kJ/mole.

On the basis of total catalyst weight, the MIT catalyst is about 2.5 times more active than the Co carbonyl catalyst. On the basis of metal weight the Co carbonyl catalyst is twice as active.

Per gram of metal, the Co carbonyl catalyst is ten times the activity of the iron catalyst. Per gram of catalyst, the iron catalyst is about 34% more active.

Figure 8 Comparison of product selectivities of above catalysts.

The largest amount of data for the Co carbonyl catalyst were obtained at 260°C. Data shown are from their Fig. 2, for their best catalyst. Comparison is with MIT cobalt catalyst at 220°C. Note that the C-number product distributions are remarkably similar for the two catalysts. With both Co catalysts, methane yields are much higher than on iron.

Figure 9	First of 6 Figures on MIT studies of a mixture of a water gas shift catalyst with a cobalt catalyst. For this run, 220° C, 0.79 MPa, $(H_2/CO)_{feed}$ = 2.6 at 0.012 Nl/(min)(g. cat). Careful reduction procedures are needed for both catalysts to achieve long-term stability (see DOE/PC 79816-10). Figure 9 shows constant rate for over 400 hours-on-stream. Fischer-Tropsch synthesis was slightly greater than that predicted from Yates' kinetic expression.
Figure 10	Constant water gas shift activity for entire time-on-stream. $x\%_{WGS}$ of 94 is close to the equilibrium value of 99%.
Figure 11	Hydrocarbon product distribution was constant with time.
Figure 12	Considerable MeOH (~9 wt%) was formed, presuambly from the water gas shift catalyst. Olefin in product was very low.
Figure 13	Hydrocarbon distribution from mixed system matches that from Co catalyst alone.
Figure 14	$\alpha_2 = 0.83$ on end-of-run slurry for the set of conditions. (Values up to ~0.87 are found on cobalt under other conditions.)

FIGURE 1

KINETIC EXPRESSIONS

IRON:

ANDERSON: $$-R = \frac{A\, P_{H_2}\, P_{CO}}{(P_{CO} + B\, P_{H_2O})}$$

HUFF: $$-R = \frac{AB'\, P_{H_2}^{\;2}\, P_{CO}}{(B'\, P_{CO}\, P_{H_2} + P_{H_2O})}$$

THE TWO EXPRESSIONS ARE EQUIVALENT IF $B \propto \frac{1}{P_{H_2}}$.

FOR CONVERSIONS BELOW ABOUT 60%, BOTH REDUCE TO:

$$-R = A'\, P_{H_2}$$

COBALT:

$$-R = \frac{A\, P_{CO}\, P_{H_2}}{(1 + B\, P_{CO})^2}.$$

FIGURE 2

IRON – PRECAUTIONS IN INTERPRETING KINETICS

- WITH HIGH WATER GAS SHIFT ACTIVITY, P_{H_2} IS NEARLY CONSTANT UP TO HIGH CONVERSIONS.
- "WATER INHIBITION" TERM MAY ACTUALLY REPRESENT FORMATION OF AN INERT SURFACE OXIDE. THIS MAY VARY SIGNIFICANTLY WITH IRON CATALYST COMPOSITION.
- CONTRARY TO SOME LITERATURE, CO_2 IS ACTUALLY INERT. IT MAY FORM H_2O BY REVERSE WATER-GAS-SHIFT.

FIGURE 3

COBALT

KINETICS AS DERIVED AT M.I.T. WELL-MIXED, CONTINUOUS-FLOW SLURRY REACTOR (CSTR).

- 21.4 WT% Co (AS Co), 3.9 WT% MG (AS MG), REMAINDER DIATOMACEOUS EARTH. PARTICLE SIZE = 52-92 µM.

- 220-240°C, 0.5-1.5 MPA, (H_2/CO) FEED = 1.5-3.5. H_2 CONVERSION 6-68%, CO CONVERSION 11-73%.

- $$-R_{H_2+CO} = \frac{A\, P_{CO} P_{H_2}}{(1 + B P_{CO})^2} \qquad \frac{(\text{M MOL})}{(\text{MIN})(\text{G. CAT})\ (\text{MPA})^2}$$

  AT 240°C B = 11.6 1/MPA

  AT 220°C B = 22.3 1/MPA

  $BP_{CO} >> 1$ AT LOW TEMPERATURES, LOW CONVERSION AND HIGH PRESSURE

  $BP_{CO} << 1$ AT HIGH TEMPERATURE, HIGH CONVERSION AND HIGH PRESSURE

- APPARENT ACTIVATION ENERGY = 93-95 KJ/MOL FOR DATA AT WHICH $BP_{CO} = 0.4 - 0.6$.

FIGURE 4

COBALT

$$-R = \frac{A\, P_{CO} P_{H_2}}{(1 + B P_{CO})^2}$$

SOME LIMITING CASES:

1. $T > 240°C$, LOW PRESSURE; SO $BP_{CO} << 1$

$$-R = A\, P_{CO} P_{H_2}$$

- DOUBLING TOTAL PRESSURE INCREASES RATE BY FACTOR OF 4.
- KINETICS REDUCE TO A "SECOND ORDER" EXPRESSION.

2. $T < 220\text{-}200°C$, HIGHER PRESSURE; SO $BP_{CO} >> 1$

$$-R = \frac{A}{B^2} \cdot \frac{P_{H_2}}{P_{CO}}$$

- RATE AT LOW CONVERSIONS IS INDEPENDENT OF TOTAL PRESSURE.
- IF H_2/CO USAGE RATIO = FEED RATIO, P_{H_2} AND P_{CO} DECREASE PROPORTIONALLY.

$$-R = \frac{2A}{B}$$

- RATE IS INDEPENDENT OF CONVERSION AND INDEPENDENT OF PRESSURE.
- KINETICS REDUCE TO A "ZERO ORDER" EXPRESSION.
- IF USAGE RATIO IS LESS THAN FEED RATIO, RATE INCREASES WITH PRESSURE. EFFECT OF CONVERSION IS COMPLEX.

FIGURE 5

COBALT CATALYST

$$-R_{H_2+CO} = \frac{a P_{CO} P_{H_2}}{(1 + b P_{CO})^2} \qquad 220°C$$

$\frac{H_2}{CO}$ USAGE RATIO = FEED RATIO = 2

—— = CONTRACTION FACTOR = −0.5

– – – = " " = 0

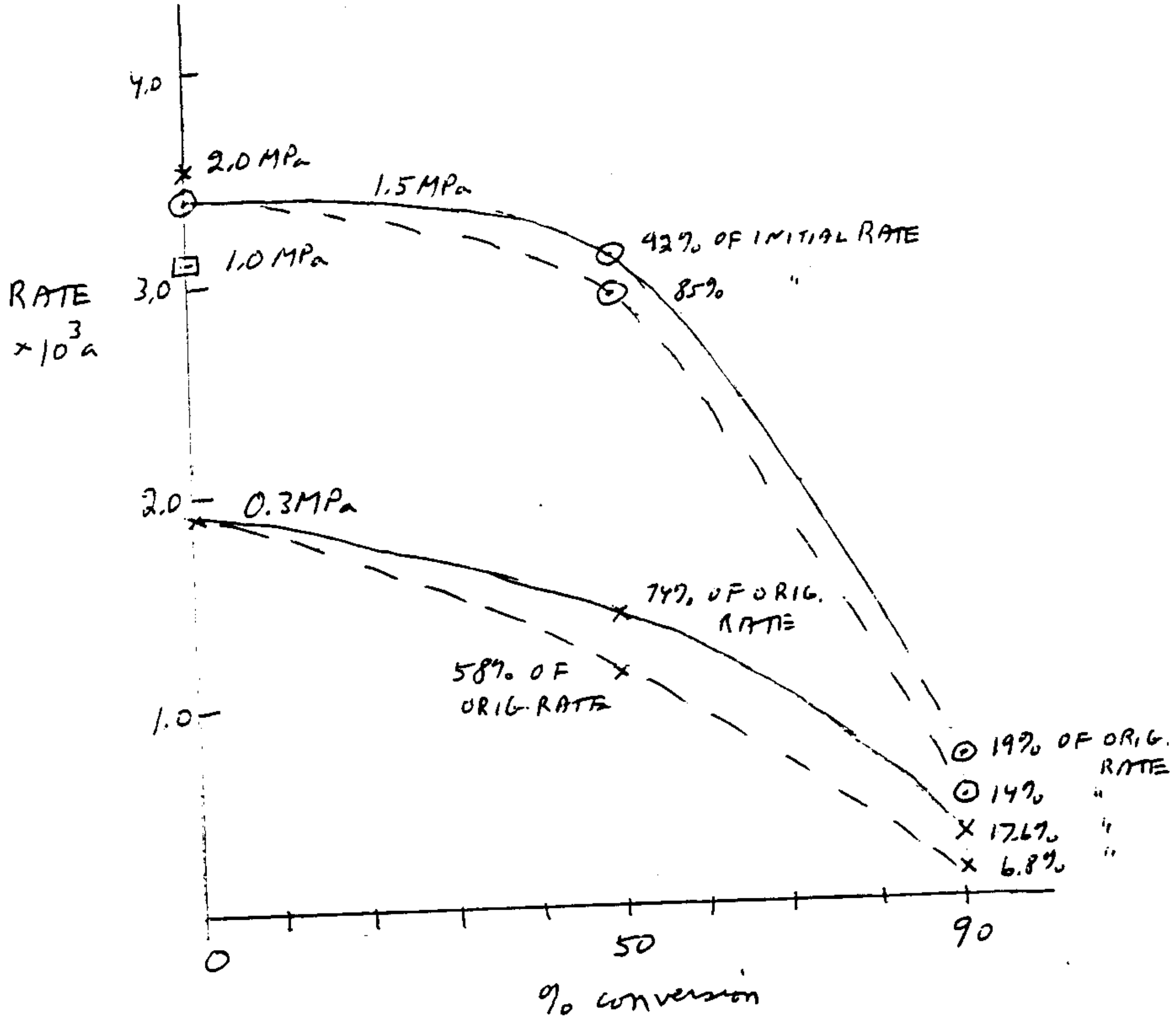

FIGURE 6

WATER GAS SHIFT ACTIVITY ON COBALT

	Conditions	$\frac{P_{CO_2}}{P_{CO_2} + P_{H_2O}}$	Reference
$Co/ZrO_2/SiO_2$	220°C, 2.1 MPa	Negligible	Post et al. (1989)
"Co Catalyst"	190°C	Negligible	Wojciechowski (1989)
21.4% Co, 3.9 wt% Mg, Remainder SiO_2	220°C 240°C	0.01-0.02 0.01 to 0.08 (conversions of 20% to 71%)	M.I.T.
~9% Co on ZSM-5	280°C, 2.1 MPa 63% conversion	0.06	Rao et al. (1985)
Same, plus 0.4-1.5% ThO_2	Same ~80% conversion	0.22	

FIGURE 7

COMPARISON OF ACTIVITIES

WITHERS ET AL. Co/ZrO$_2$/SiO$_2$	M.I.T. Co/MgO/SiO$_2$	KUO (MOBIL) FE/CU/K$_2$O/SiO$_2$	
	260°C		
45.00	110.00	60.00	$\frac{\text{MOLES}}{\text{(H)(KG. CAT)}}$
1.01	2.46	1.34	$\frac{\text{N}\ell}{\text{(H)(G. CAT.)}}$
1015.80	514.15	100.00	$\frac{\text{MOLES}}{\text{(H)(KG. OF Co OR FE}}$
23.12	11.55	2.24	$\frac{\text{N}\ell}{\text{(H)(G. OF Co OR F}}$
	240°C		
19.13	27.13	25.51	$\frac{\text{MOLES}}{\text{(H)(KG.CAT.)}}$
0.43	0.61	0.57	$\frac{\text{N}\ell}{\text{(H)(G. CAT.)}}$
438.76	127.13	42.51	$\frac{\text{MOLES}}{\text{(H)(KG. OF Co OR FE)}}$
9.83	2.85	0.95	$\frac{\text{N}\ell}{\text{(H)(G. OF Co OR FE)}}$

FIGURE 8

COMPARISON OF FISCHER-TROPSCH SELECTIVITY

	Cobalt, MIT[A]	Precipitated[B] Iron, MIT	Fused Iron,[C] MIT	Withers, et al. (Fig. 2)
Wt.% Yields:				
C_1	16.07	5.77	6.09	14
C_2-C_4	17.14	22.20	27.63	16
C_5-C_9	21.38	26.11	24.53	25
C_{10}+	45.52	45.42	41.75	45

[A] 220°C, 0.79 MPa, $(H_2/CO)_{\text{FEED}}$ = 2.6 at 0.012 Nℓ/(Min)(g. Cat).

[B] Ruhrchemie cat.- 263°C, 2.6 MPa $(H_2/CO)_{\text{FEED}}$ = 0.73 at
0.034 Nℓ/(Min)(g. Cat)

[C] 263°C, 0.55 MPa, $(H_2/CO)_{\text{FEED}}$ = 0.55 at 0.040 Nℓ/(Min)(g. Cat)

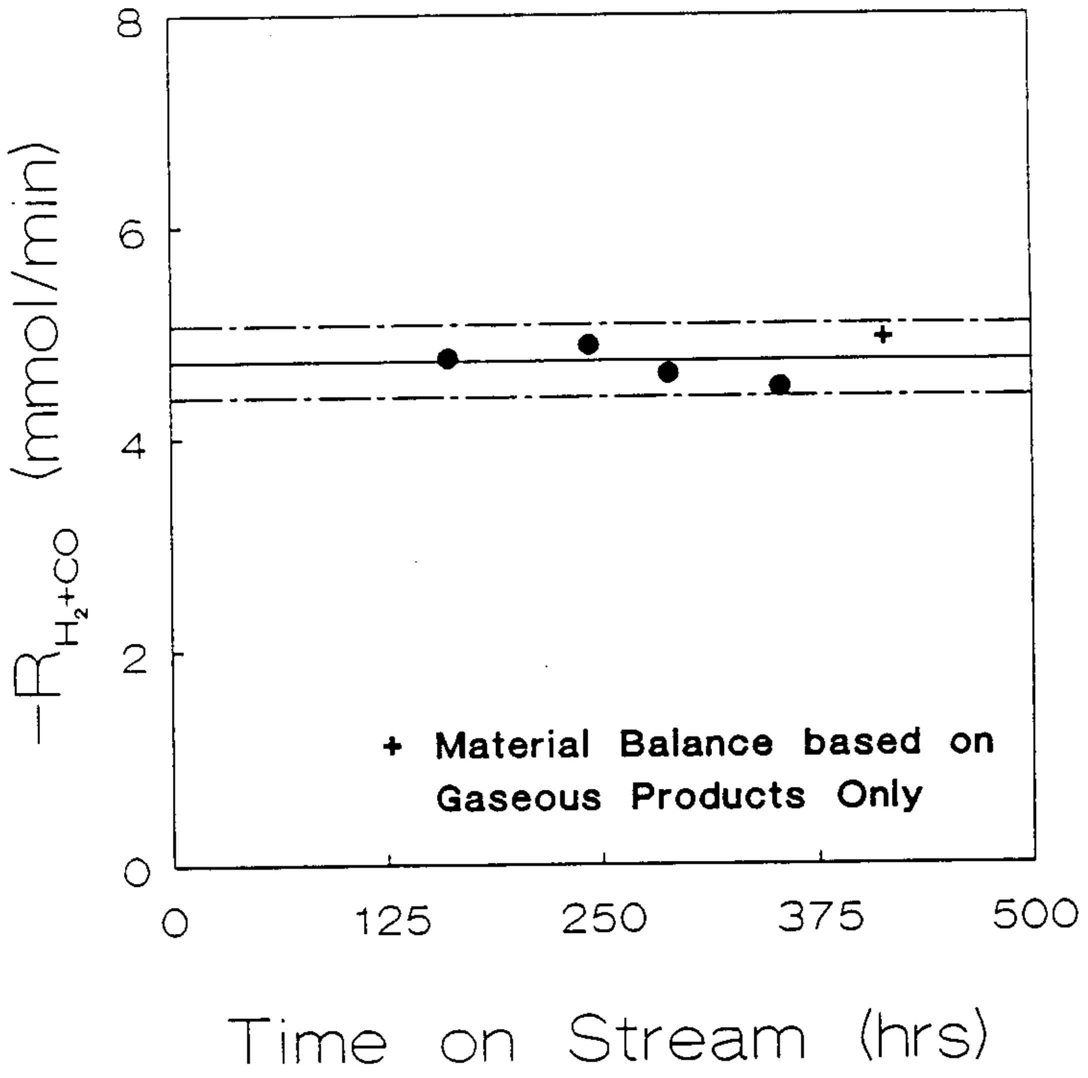

Figure 9

Constant Rate of Syngas Consumption for Over 400 Hours-on-Stream

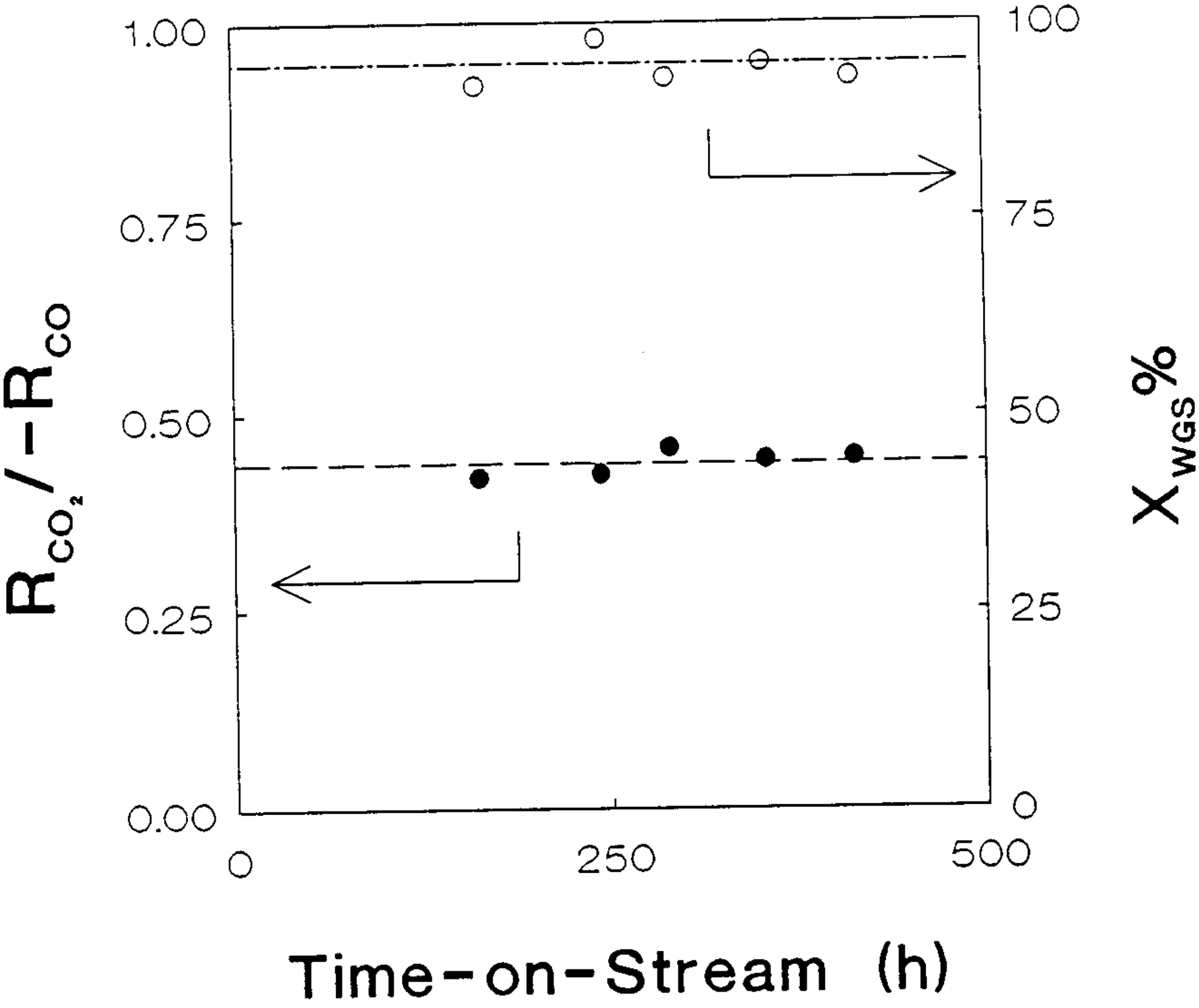

Figure 10

Combined Catalyst System Exhibited Long-Term Water-Gas-Shift Stability

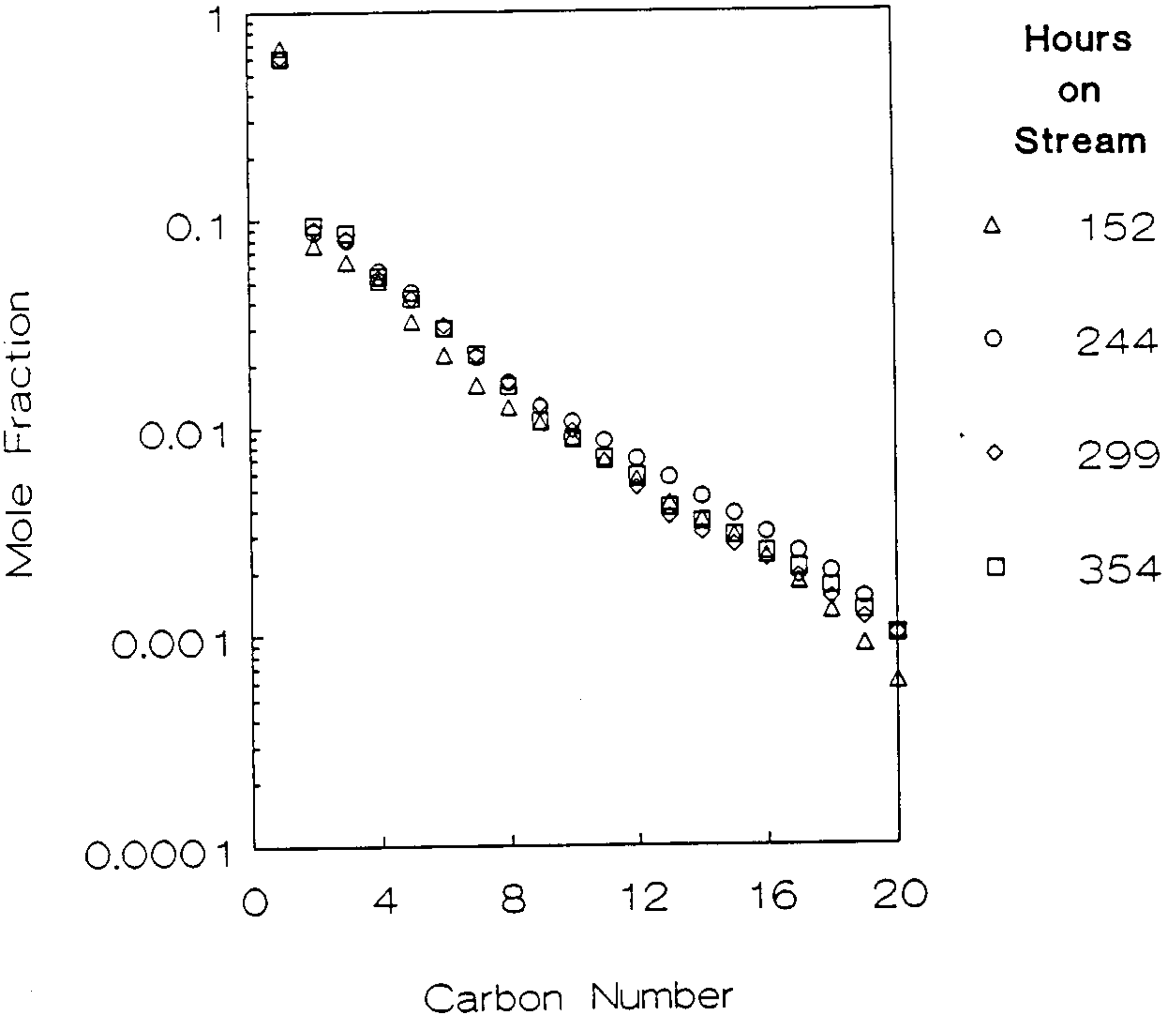

Figure 11

The Hydrocarbon Product Distribution of the Combined System Remained Stable

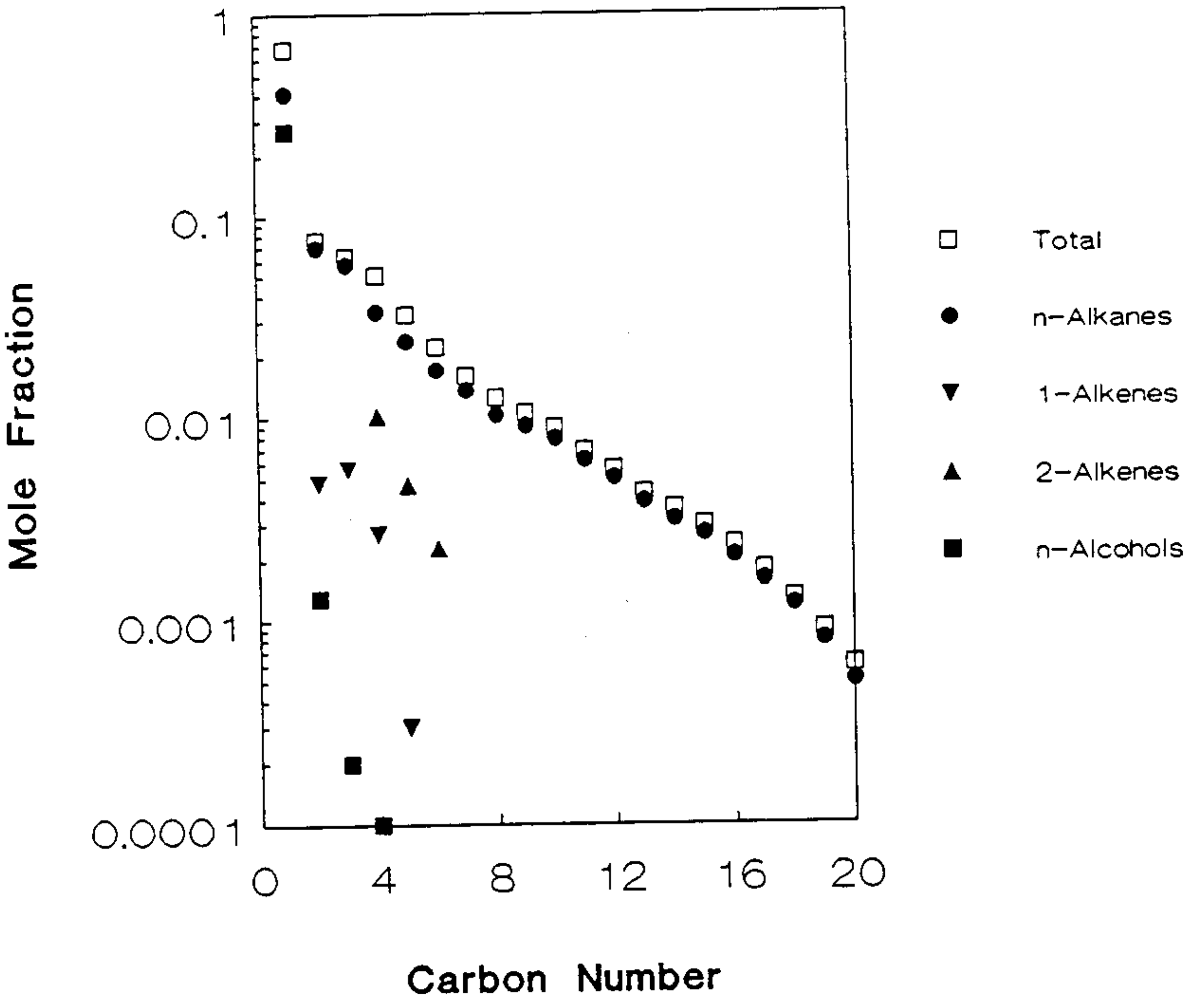

Figure 12

Component Schulz-Flory Diagram for the Combined Catalyst System

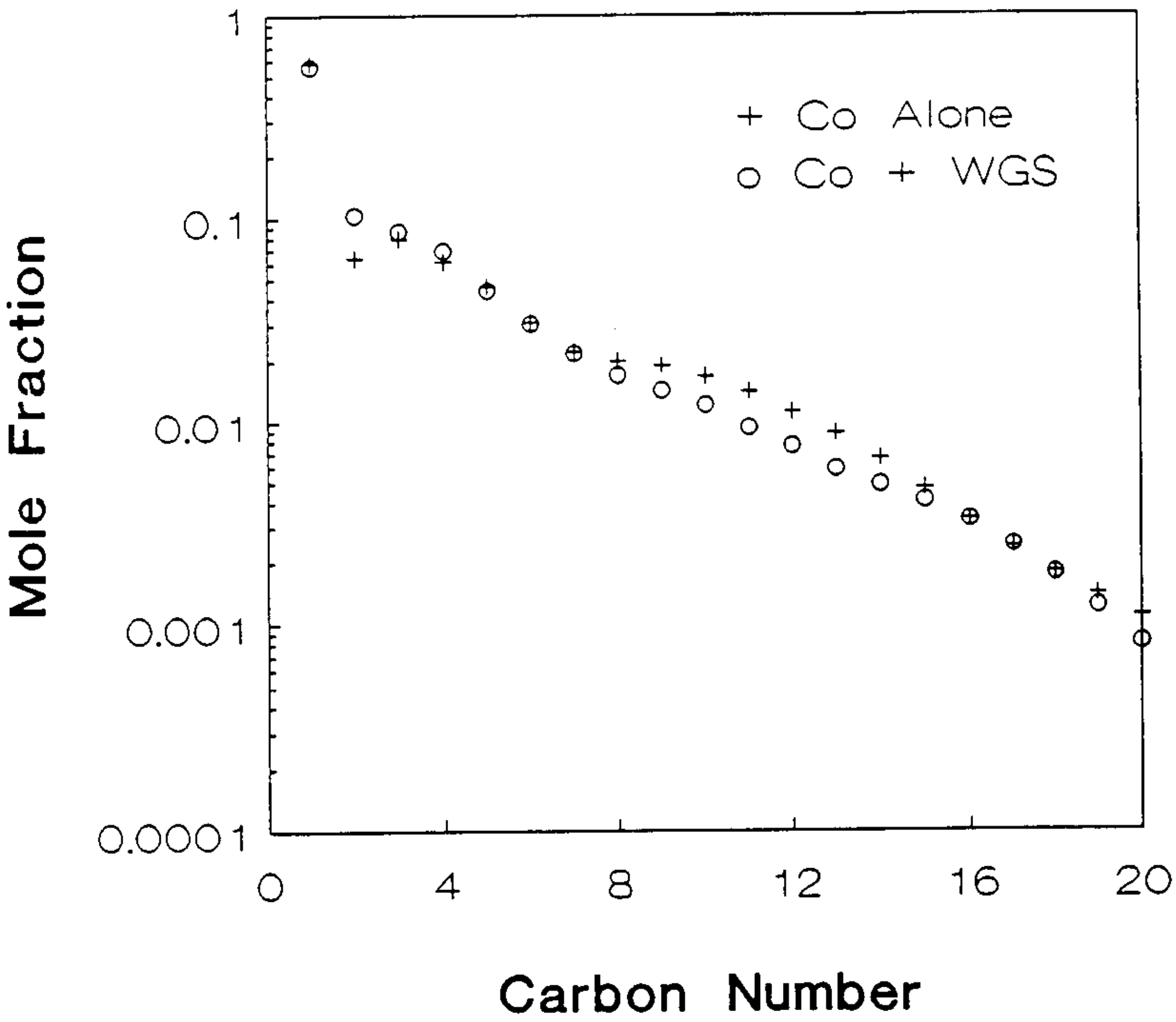

Figure 13

Hydrocarbon Product Distribution of Catalyst System Matches that of Cobalt Catalyst Alone

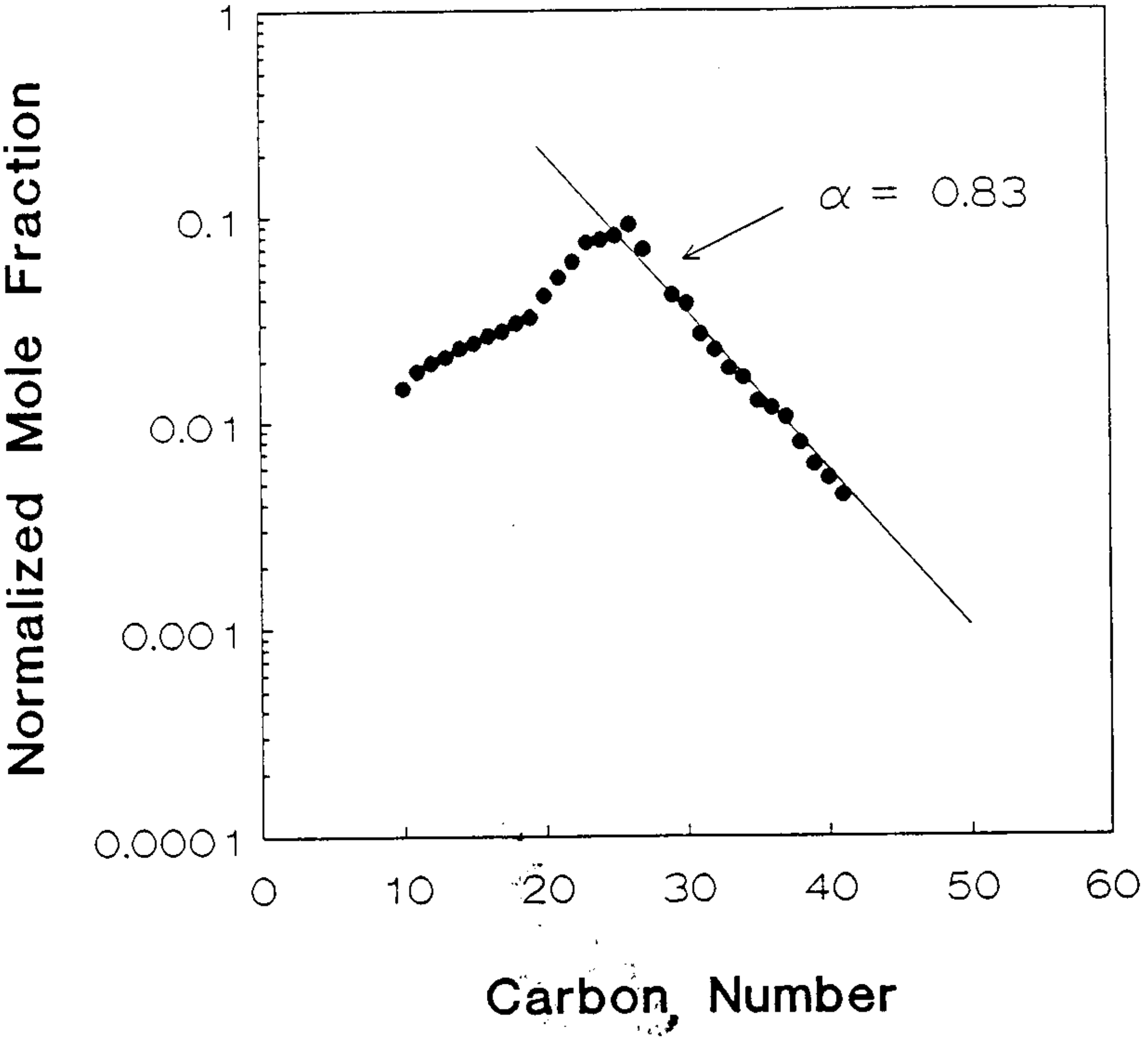

Figure 14

Schulz–Flory Analysis of End–of–Run Slurry Exhibits Terminal Alpha = 0.83