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

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I. ABSTRACT

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

TECHNICAL APPROACH: The proposed mixture should make possible a combination of the product advantages of a cobalt catalyst (minimum oxygenate and carbon formation) with the operating advantages of a slurry reactor while feeding syngas of low H_2/CO ratio as can be produced by modern coal gasification plants. Previous scouting experiments in fixed beds at two U.S. laboratories showed no effect of the water-gas-shift catalyst, but recent patents to Shell claim successful operation in a fixed bed. In preliminary work with a slurry reactor we also found synergism.

SIGNIFICANT ACCOMPLISHMENTS: Several water-gas-shift catalysts we studied by themselves showed unacceptable loss in activity with time, even though the reduction procedures recommended by the manufacturer were carefully followed. These were United Catalysts C-18HC, $Cu/Zn/Al_2O_3$; Harshaw 1803-P, $Cu/Zn/Cr_2O_3$;

Harshaw Cu 1920 P, Cu/MnO/Cr_2O_3. However, we have now had good success with Katalco 52-2, which has a nominal composition of 33 wt% CuO, 33 wt% ZnO and 33 wt% Al_2O_3, using a modified reduction system that we have developed. In a 1000-hour-on-stream run, this catalyst showed excellent resistance to changes in pressure, temperature, (H_2/CO) ratio and presence of 1-butene. A first long run with a cobalt catalyst mixed with the Katalco 52-2 catalyst showed excellent product distribution selectivities.

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1. Introduction and Background

According to patents from Shell a mechanical mixture of a cobalt catalyst and a copper-based water-gas-shift catalyst has been used in a fixed-bed reactor to carry out the Fischer-Tropsch synthesis. However, in other fixed-bed studies performed by Union Carbide (February, 1984; May, 1984 and September, 1984) and Tominaga et al. (1987), water-gas shift catalysts have been oberved to deactivate rapidly when combined with a cobalt Fischer-Tropsch catalyst in a fixed-bed. In our slurry reactor, we also encountered substantial deactivation with an early Cu/ZnO/Al_2O_3 catalyst combined with a cobalt catalyst, although synergistic effects clearly occurred.

2. Scouting Experiments

A representative result was obtained as follows: A cobalt catalyst (United Catalysts G-61, 78.7 wt% CoO, 17.2 wt% SiO_2 and 4 wt% graphite) was ground to 50 to 90 μm (170 to 270 ASTM mesh) and reduced in a fluidized bed reduction bed using pure hydrogen. The reduction temperature was increased from 25 to 400°C over a period of 8 hours and then held at 400°C for 7 hours. 25 g of the catalyst (unreduced basis) was then loaded under helium into the slurry reactor which was charged with 410 g of purified n-octacosane (Humphrey Chemical). A simplified diagram of the system is shown on Fig. 1. Its operation has been described previously (Huff and Satterfield, 1982; Huff, Satterfield, and Wolf, 1983). Water was added, when desired, by a HPLC pump.

The reactor was brought on-stream at 240°C, 1.48 MPa, and inlet gas feed with a H_2 to CO ratio of 0.74 at a space velocity of 0.02 Nl/min/gcat (0.5 Nl/min). For 24 hours, only the cobalt catalyst was present in the reactor. The conversion of synthesis gas, H_2 + CO, was constant at about 55%. A small amount of water-gas shift activity was observed (defined as $100 \cdot P_{CO_2}/(P_{CO_2} + P_{H_2O})$). Under equilibrium conditions at 240°C, the extent of water-gas shift should be essentially 100%.

After 24 hours on-stream, a finely-divided pre-reduced water-gas shift catalyst was charged to the reactor (United Catalysts C18HC, 42 wt% CuO, 47 wt% ZnO, 10 wt% Al_2O_3 and 1 wt% graphite).

Figure 1a shows the effect of adding the shift catalyst to the cobalt catalyst, at time 0. The water-gas shift activity jumped to 74%. With the increased hydrogen produced from the shift reaction, the conversion of synthesis gas also rose substantially, from 54 to 68%.

During the subsequent 24 hours, the activity of the water-gas shift catalyst dropped dramatically, and the rate of synthesis gas consumption fell back to its previous mark of 55%, a decrease in the synthesis rate in response to a decrease in hydrogen partial pressure.

In an effort to understand the underlying causes of this deactivation, we have performed a number of runs in which a water-gas shift catalyst was the only catalyst present in the slurry reactor. To avoid problems of catalyst instability due to incorrect preparation, we limited these studies to commercially manufactured copper-based catalysts. Great care was taken to remove any potential poisons from our system.

Low-temperature, copper-based shift catalysts are typically operated in fixed-bed units. As a result, little information is available on the operation of these catalysts in any other type of reactor. Therefore, a challenge for us was to adapt established fixed-bed operating procedures, particularly the reduction procedure, to a slurry reactor system. We have studied three commercial catalysts with compositions shown on Fig. 2. Effect of time-on-stream on conversion is shown on Fig. 3. In all cases about 25 g. of ground and sieved catalyst (50-90 μm) were added to the reactor previously charged with 400 g of octacosane. Reaction procedures were those supplied by the manufacturer.

3. Cu/Cr_2O_3 (Harshaw Cu 1803-P)

Four runs with different feed compositions, all at 220°C and 0.79 MPa, all showed a steady deactivation of the catalyst with time-on-stream. Sintering and/or poisoning appeared to cause the deactivation.

4. $Cu/MnO/Cr_2O_3$ (Harshaw 1920-P):

According to Harshaw, the $Cu/MnO/Cr_2O_3$ catalyst possesses greater temperature stability than the Cu/Cr_2O_3 catalyst tested above. The catalyst was prereduced according to the manufacturer's instructions and tested at 200°C and 0.79 MPa. Despite its alleged stability, the $Cu/MnO/Cr_2O_3$ catalyst deactivated at approximately the same rate as the previously tested Cu/Cr_2O_3 catalyst, even though a slightly lower temperature was used.

5. $Cu/ZnO/Al_2O_3$ (Katalco 52-2):

The reduction procedure recommended by the manufacturer was carefully followed. Helium was first passed thorugh the reactor and then a temperature-composition profile shown on Fig. 4 was applied. Temperature and pressure were held constant at 200°C and 0.79 MPa as the reactor was brought on stream using a flow of 43 mol% CO, 21.4 mol% H_2, and 35.6 mol% H_2O at 0.019 Nl/min/gcat. These settings are defined as "base case" conditions and are those used to monitor the long-term activity of the catalyst. The rate at which water was fed is approximately three to five times that which would be typically synthesized in our reactor with a cobalt Fischer-Tropsch catalyst. To give an accurate measure of catalyst activity at these conditions, no process changes were made during the first 300 hours-on-stream.

After 300 hours-on-stream, various process changes in either the pressure, temperature or feed composition were made, including 200-220°C, 0.79 MPa to 1.48 MPa and H_2/CO ratios of 0.7 and higher. Following a process change conversions were monitored for between 48 and 100 hours. The reactor was then returned to "base case" conditions which would in turn be monitored for between 48 and 100 hours. Thus, we were able to monitor both the effect of the process change on activity (via conversions during the process change) and stability (via conversions after the return to the "base case" following the process change).

Figure 3 presents these "base case" data graphically. It can be seen that the catalyst deactivted only very slowly for the over 1000 hours during which it was on-stream. We regard this as a very satisfactory outcome.

6. Effect of 1-Butene:

In discussing the potential causes of the deactivation of water-gas shift catalysts in combination with a cobalt-based Fischer-Tropsch catalyst, it has been speculated that alkenes may adsorb on the surface of a shift catalyst, inhibiting its reactivity. Since it is well known that alkenes adsorb strongly on reduced metal surfaces, it is reasonable to postulate that alkenes could inhibit the rate of water-gas shift reaction.

To examine the effects of alkenes, 1-butene was added to the feed at 924 hours-on-stream. The 1-butene was in an analyzed mixture of 2 mol% 1-butene in 98 mol% prepurified hydrogen supplied by Matheson Gases, Inc.

The water-gas shift conversion remained essentially unchanged by the addition of the 1-butene to the feed. Over 95% of the 1-butene was reacted, either being hydrogenated to butane or isomerized to cis-2-butene and trans-2-butene. Essentially all of the consumed 1-butene formed C_4 hydrocarbons. No significant amount was cracked to smaller hydrocarbons.

7. Reduction of Cobalt-Based Fischer-Tropsch Catalyst.

In order to develop a reduction procedure that will provide repeatable activity and selectivity, a review of the available literature on cobalt catalysts has been performed. This includes reduction procedures used in large plants as well as in research facilities. Generally, the catalysts are reduced in hydrogen and temperature is increased from ambient to between 350°C and 400° over 4 to 6 hours. The catalyst is then held at this maximum temperature for between 2 and 16 hours.

On the basis of their own work at the Bureau of Mines and review of work done in Germany, Storch, et al. (1951, 1959) make four important conclusions about the reduction of Co/ThO_2/kieselguhr and $Co/ThO_2/MgO$/kieselguhr catalysts.

1. Sintering must be avoided during reduction. Hence, reduction should be performed in a short bed, with a high space velocity of hydrogen, at the lowest temperature possible, and in the shortest time possible.

2. The most active catalysts were obtained by ending the reduction before all the cobalt was reduced to metal. The most active catalysts had between 55 and 70 percent of available Co reduced. It was speculated that unreduced CoO prevented sintering of the catalyst.

3. When cobalt-based catalysts were reduced and then subsequently carbided with carbon monoxide, the activity of the catalyst was markedly less. A completely carbided sample,

presumed to have 100 percent of the cobalt as Co_2C, was shown to be inactive for the Fischer-Tropsch synthesis.

4. It was found that when MgO was present the catalyst was harder to reduce, and thus a maximum reduction temperature of 400°C is recommended for $Co/ThO_2/MgO$/keiselguhr as compared to 360°C for Co/ThO_2/kieselguhr.

On the basis of the literature cited above, we have used the following temperature profile for our first run.

A. 100°C for 1/2 to 1 hour.

B. 200°C for 1/2 to 1 hour.

C. 300°C for 1/2 to 1 hour.

D. Heating in 10°C increments from 300°C to 365°C. The temperature should be allowed to level off at each increment for at least 1/4 hour.

E. Holding at 365°C for 16 hours.

This is performed in an external reduction unit.

The results of a long preliminary run in which the water-gas shift catalyst and a reduced cobalt catalyst were studied together are shown on Figures 5-9. The cobalt catalyst was of a typical German commercial composition, consisting of cobalt oxide and magnesia on silica.

Fig. 5 shows that the Co catalyst had little effect on the activity of the water-gas-shift catalyst when the latter was properly reduced.

Fig. 6 shows a Schulz-Flory diagram for the combination. Of great significance is the fact that α_1 is about 0.8-0.83, much higher than is observed on iron catalysts. α_2 is about 0.96, as is further confirmed by analysis of pot wax (Fig. 7).

With time on stream, α_2 increases slightly (Fig. 8).

Fig. 9 shows a breakdown of products into components. The ratio of alkanes to alkenes is much higher than with iron catalysts, reflecting the greater hydrogenation functionality of cobalt over iron. Considerable isomerization of 1-alkane to 2-alkenes occurs. The only oxygenates that could be detected were alcohols, and of these, only ethanol and propanol.

The only negative observation is that the cobalt catalyst substantially deactivated over 200 hours-on-stream (Fig. 10). However, this is only our first run and we have as yet not had the opportunity to optimize cobalt reduction procedures.

Product selectivity is compared to that of two base-line iron catalysts in Figure 11. Relative to Ruhrchemie, the cobalt catalyst yielded slightly more CH_4, much less C_2-C_4 and more C_5+. Again, we note that this is only the first run we have made with the cobalt catalyst. We have as yet not studied it in isolation, but these studies will be needed for further evaluation.

References

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Huff, G.A., Jr., Satterfield, C.N., and Wolf, M.H., Ind. Eng. Chem. Fund., 22, 259 (1983).

Storch, H.H., Golumbic, N., and Anderson, R.B., The Fischer-Tropsch and Related Syntheses, Wiley, New York, 1951.

Tominaga, H., Miyachiharu, M. and Fujimoto, K., Bull. Chem. Soc. Jpn., 60, 2310 (1987).

Union Carbide Corporation (Tarrytown Technical Center, Tarrytown, New York), Liquid Hydrocarbon Fuels from Syngas, Technical Progress Report DE-AC22-81PC40077, Third Annual Report, March, 1983-February, 1984.

Union Carbide Corporation (Tarrytown Technical Center, Tarrytown, New York), Liquid Hydrocarbon Fuels from Syngas, Technical Progress Report DE-AC22-81PC40077, Fifteenth Quarterly Report, August, 1984-September, 1984.

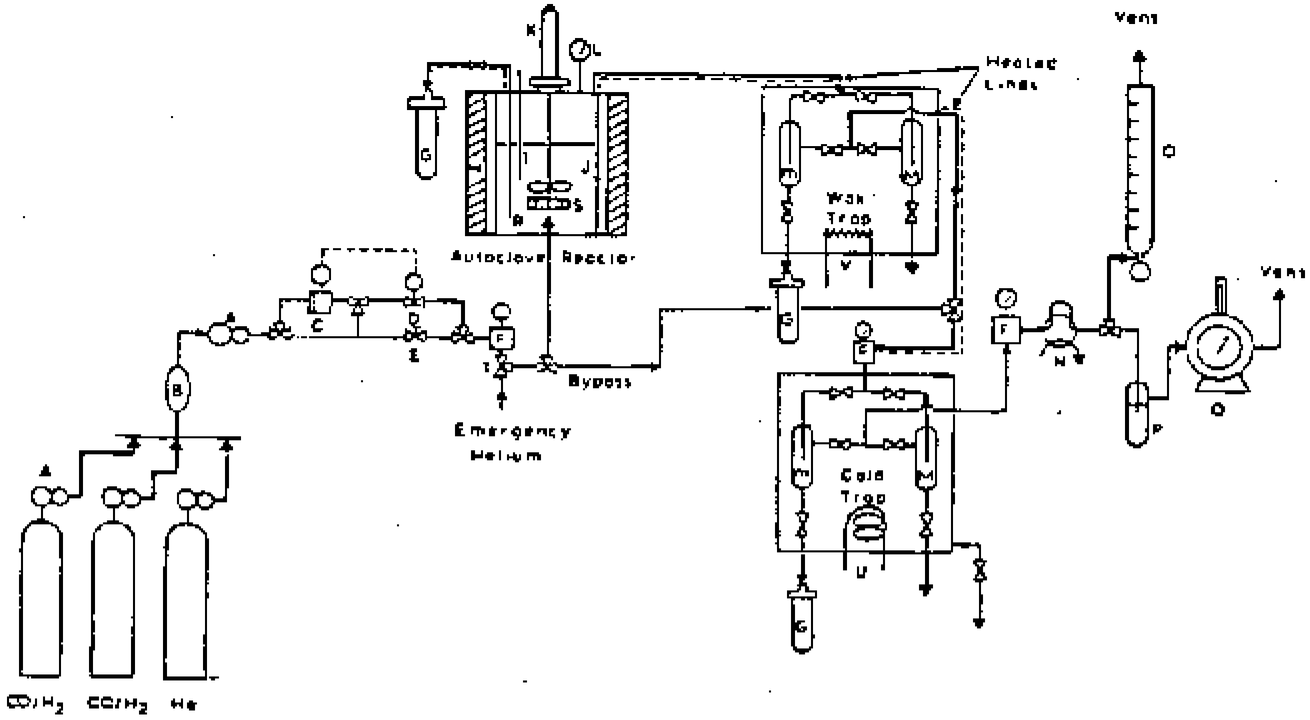


Figure 1: The M.I.T. Apparatus, Simplified Diagram

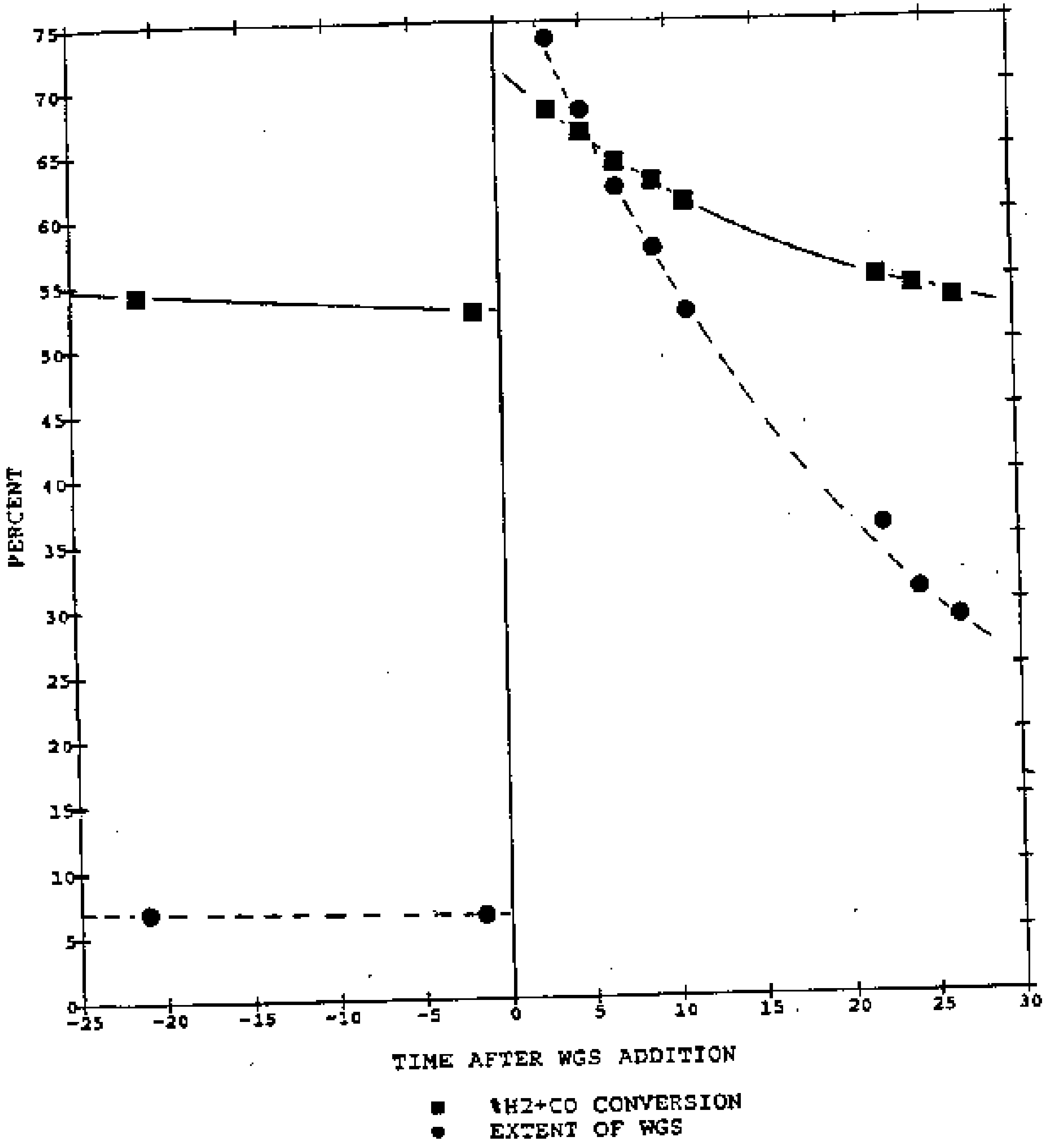


Figure 1a: Effect of addition of Cu-ZnO/Al_2O_3 shift catalyst on the water-gas shift and Fischer-Tropsch activity.

FIGURE 2

Copper-Based Catalysts

Active for Low Temperature Water-Gas Shift

Manufacturer/	Nominal Composition (Wt. %)				
Catalyst	CuO	ZnO	Al_2O_3	Cr_2O_3	MnO
Katalco 52-2	33	33	33	--	--
Harshaw Cu 1803-P	52	--	--	48	--
Harshaw Cu 1920-P	48	--	--	48	4

FIGURE 3

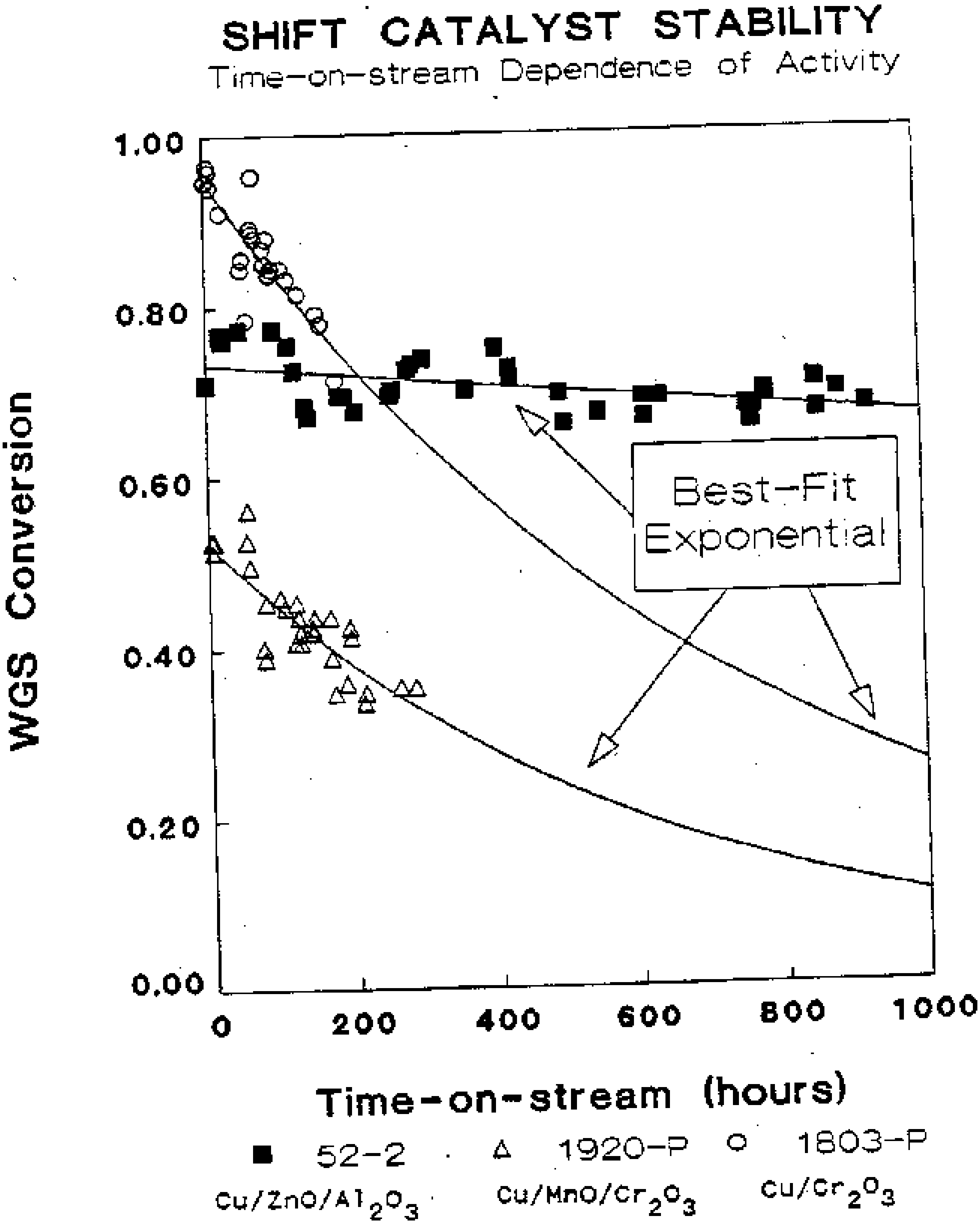
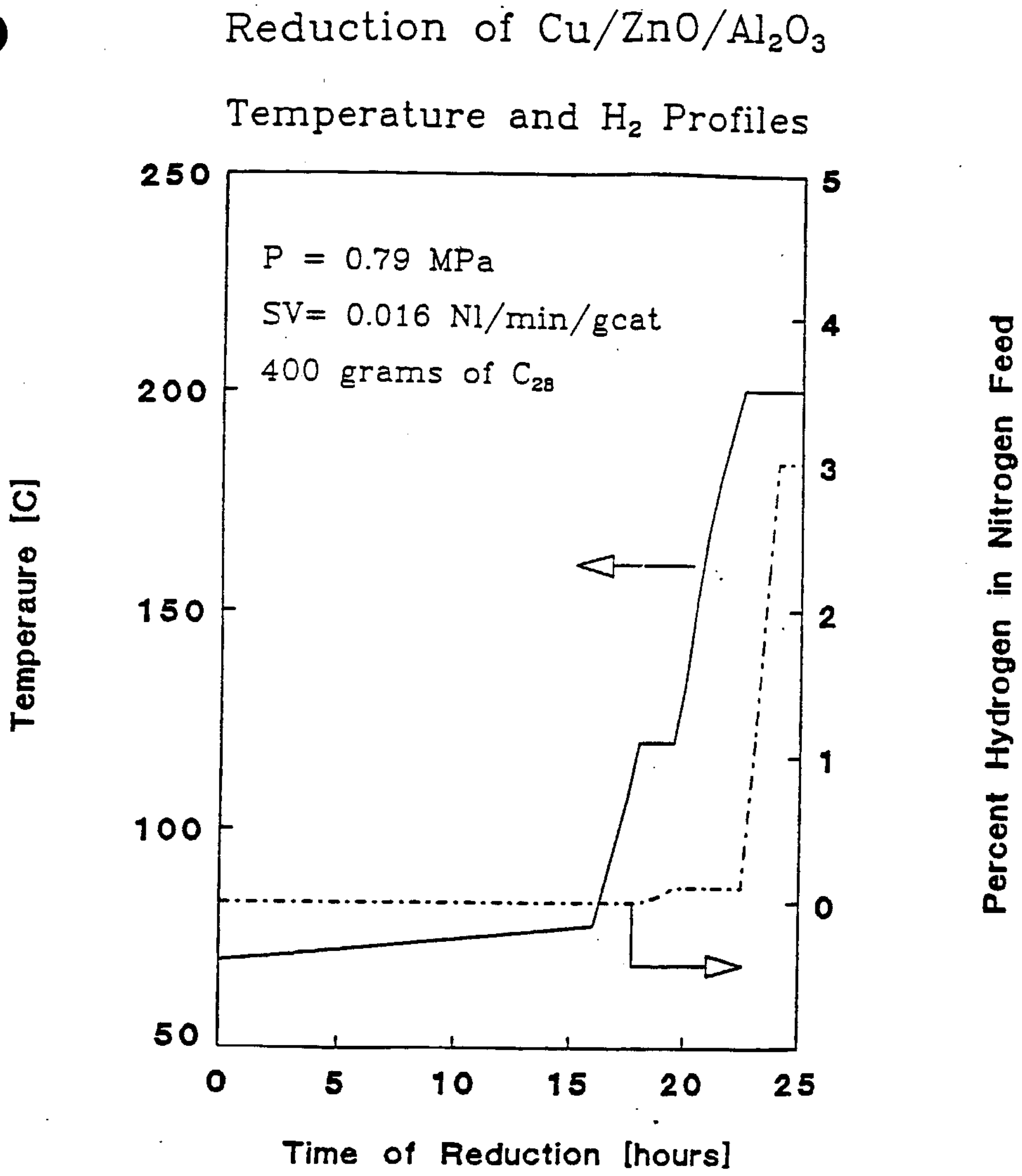

SHIFT CATALYST STABILITY
Time-on-stream Dependence of Activity
WGS Conversion
1.00
0.80
0.60
0.40
0.20
0.00
0
200
400
600
800
1000
Time-on-stream (hours)
Best-Fit Exponential
■ 52-2
Cu/ZnO/Al$_2$O$_3$
△ 1920-P
Cu/MnO/Cr$_2$O$_3$
○ 1803-P
Cu/Cr$_2$O$_3$

FIGURE 4



Reduction of $Cu/ZnO/Al_2O_3$

Temperature and H_2 Profiles

FIGURE 5

Effect of Reduction on Water-Gas-Shift Activity Cobalt and $Cu/Zn/Al_2O_3$ Catalysts Combined

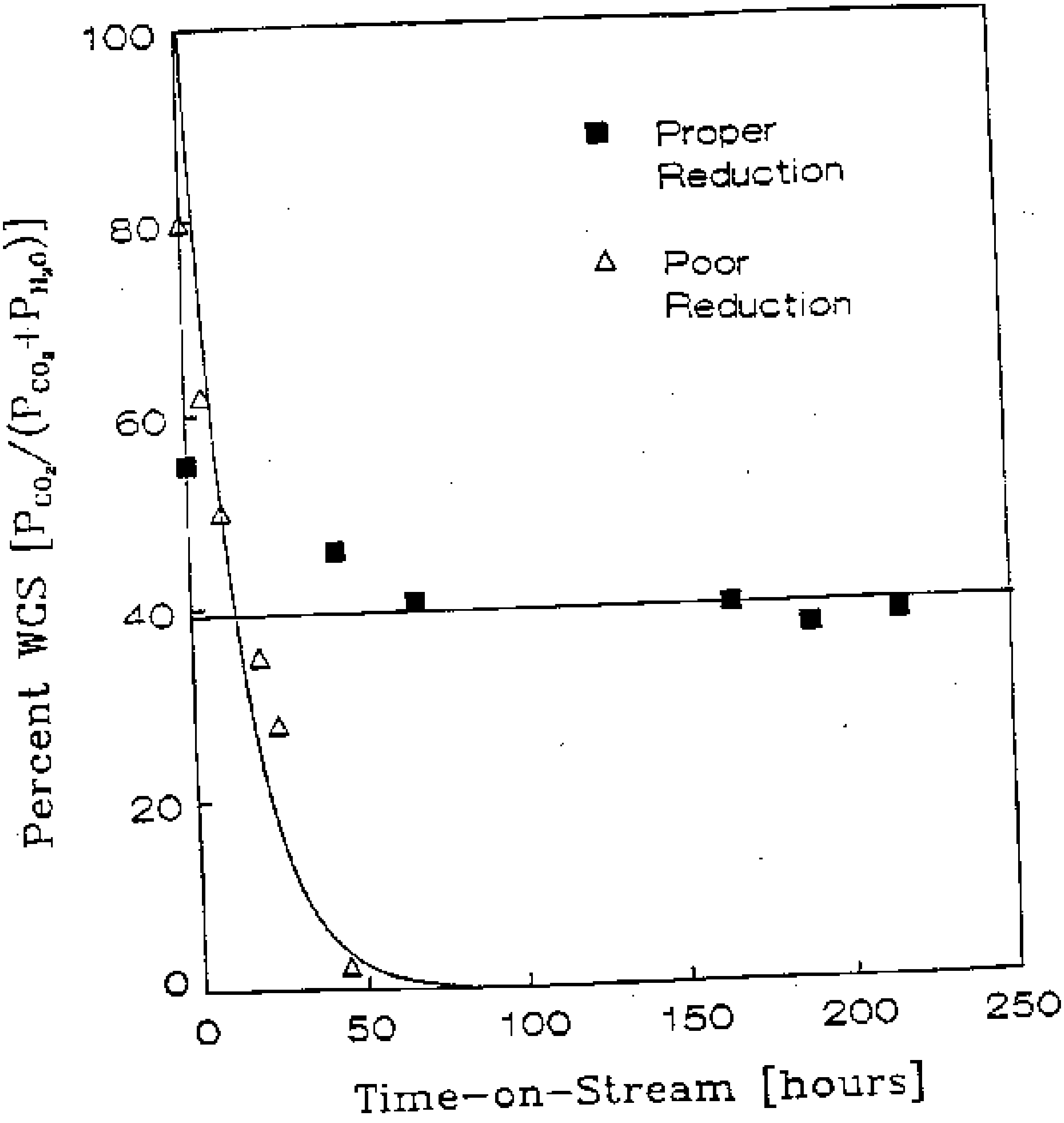


FIGURE 6

Schulz–Flory Diagram for
Cobalt and Cu/ZnO/Al_2O_3 Combined

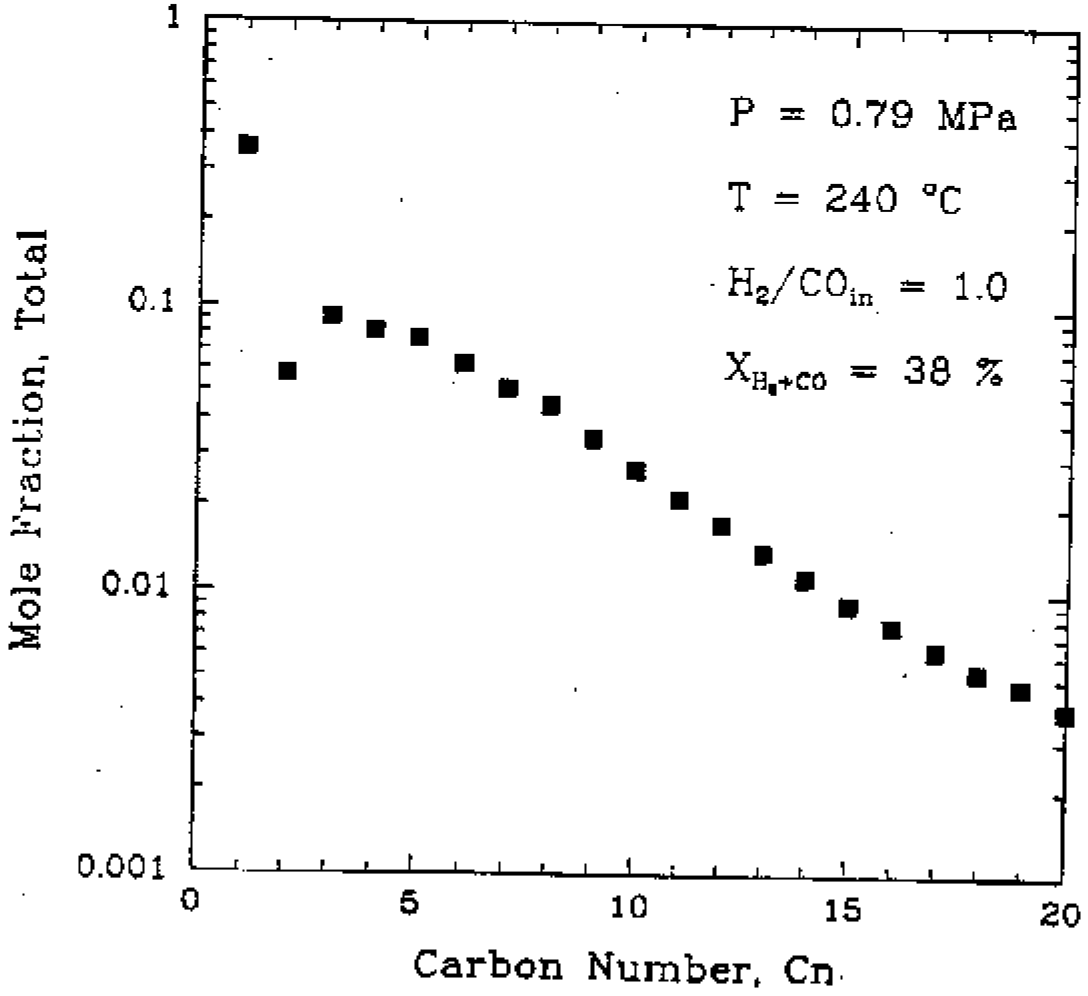


FIGURE 7

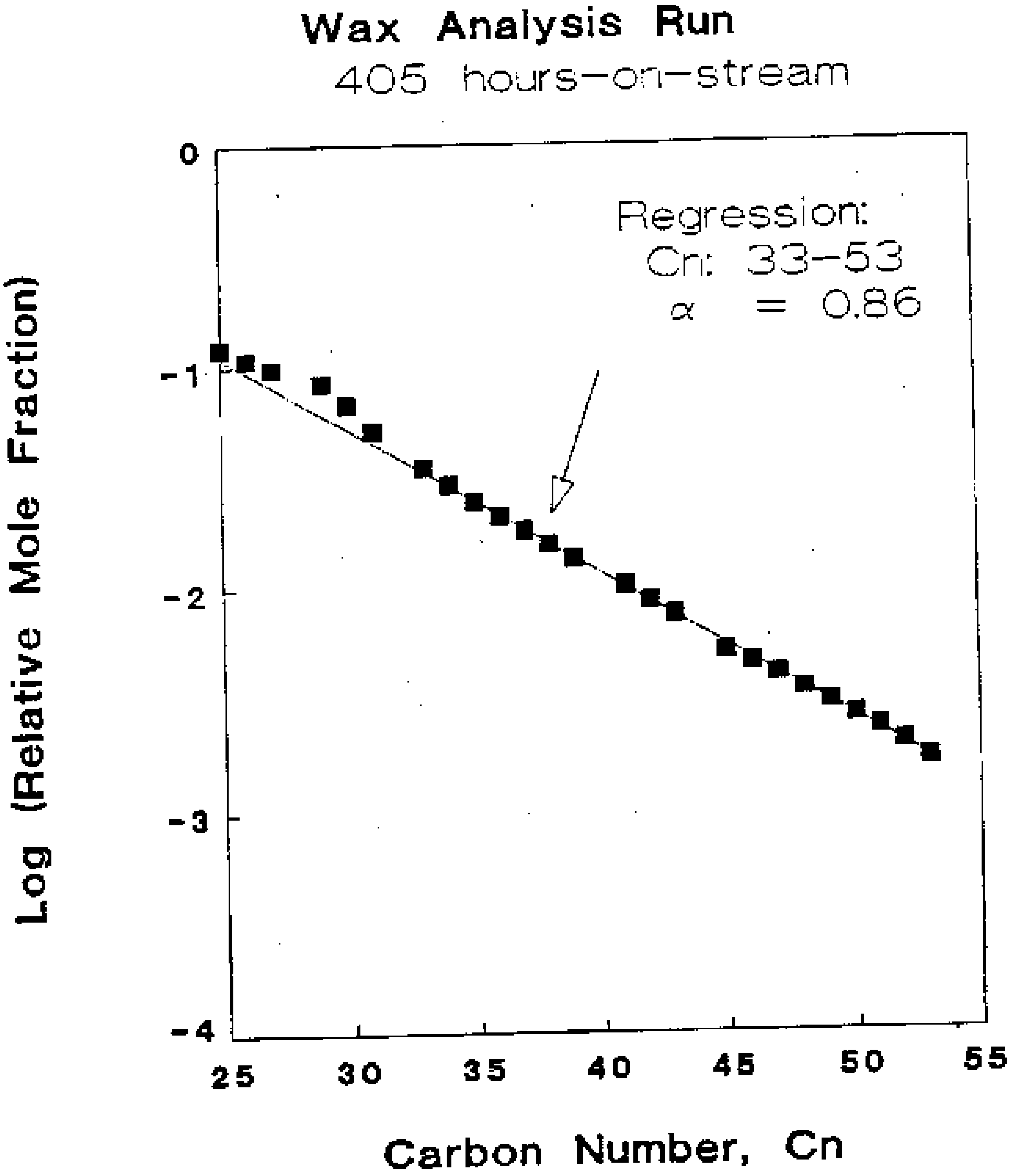

Wax Analysis Run
405 hours-on-stream
Regression:
Cn: 33-53
α = 0.86
0
-1
-2
-3
-4
Log (Relative Mole Fraction)
25
30
35
40
45
50
55
Carbon Number, Cn

FIGURE 8

Schulz–Flory Diagram

Cobalt and Cu/ZnO/Al_2O_3 Combined

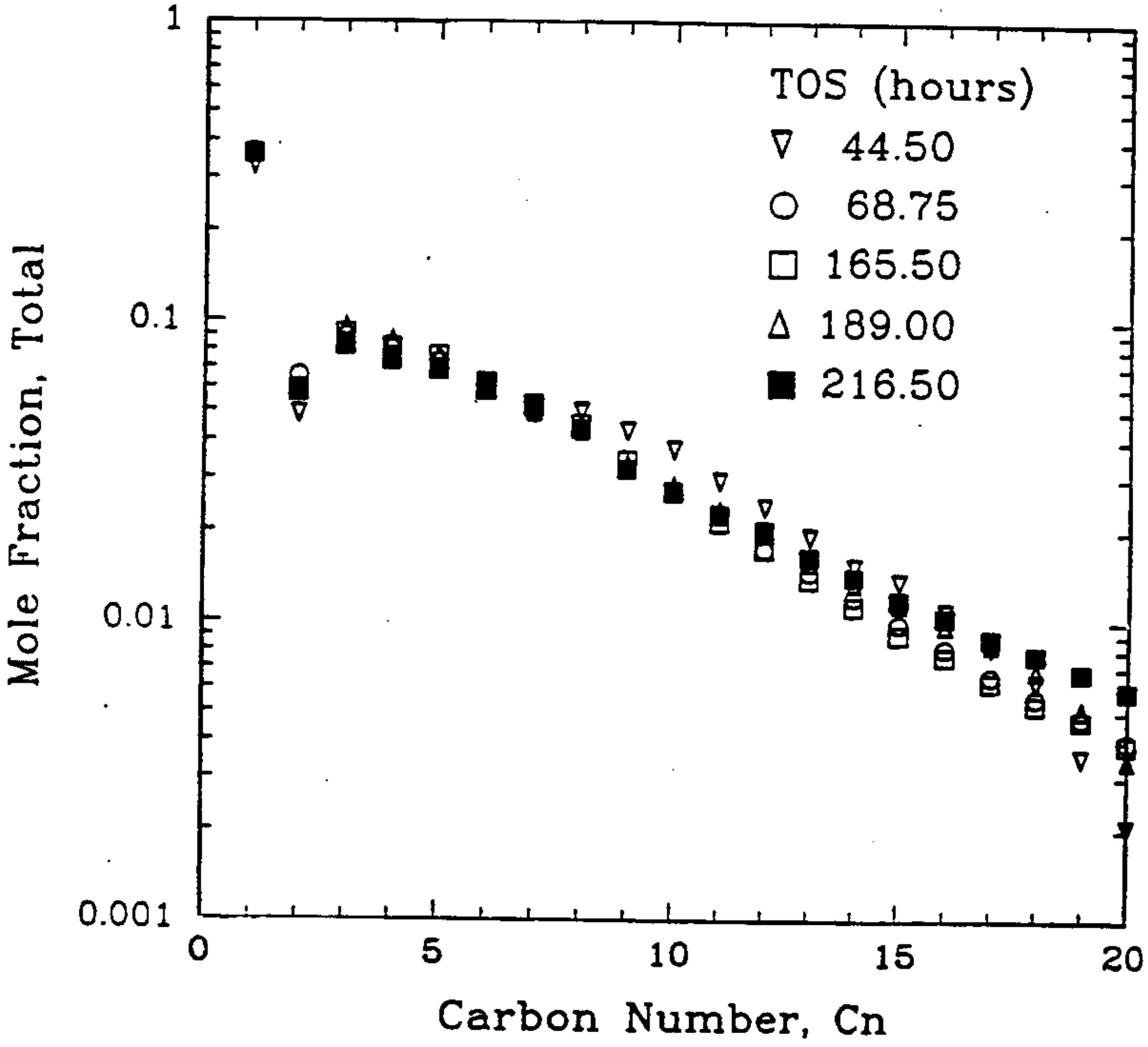


FIGURE 9

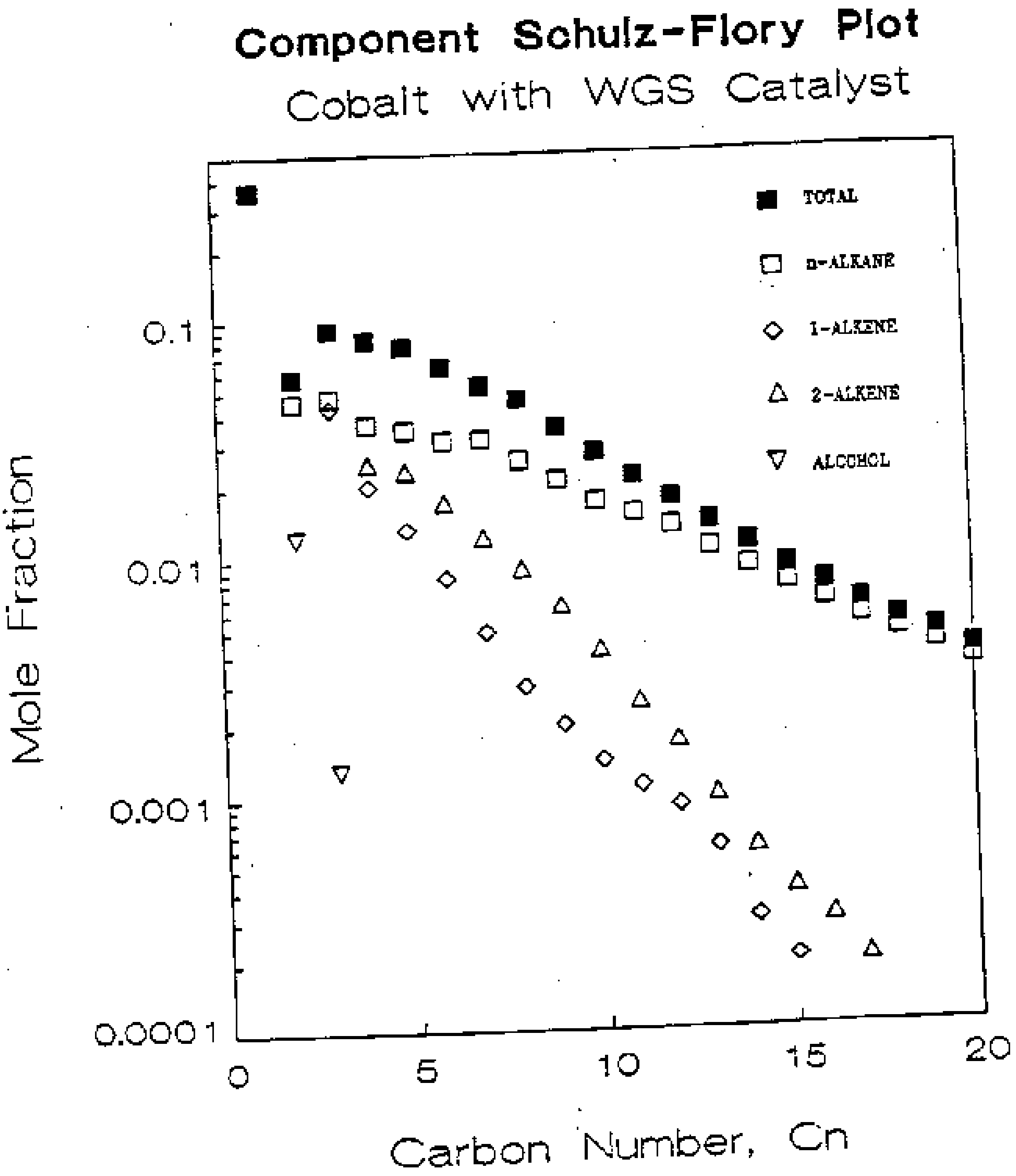
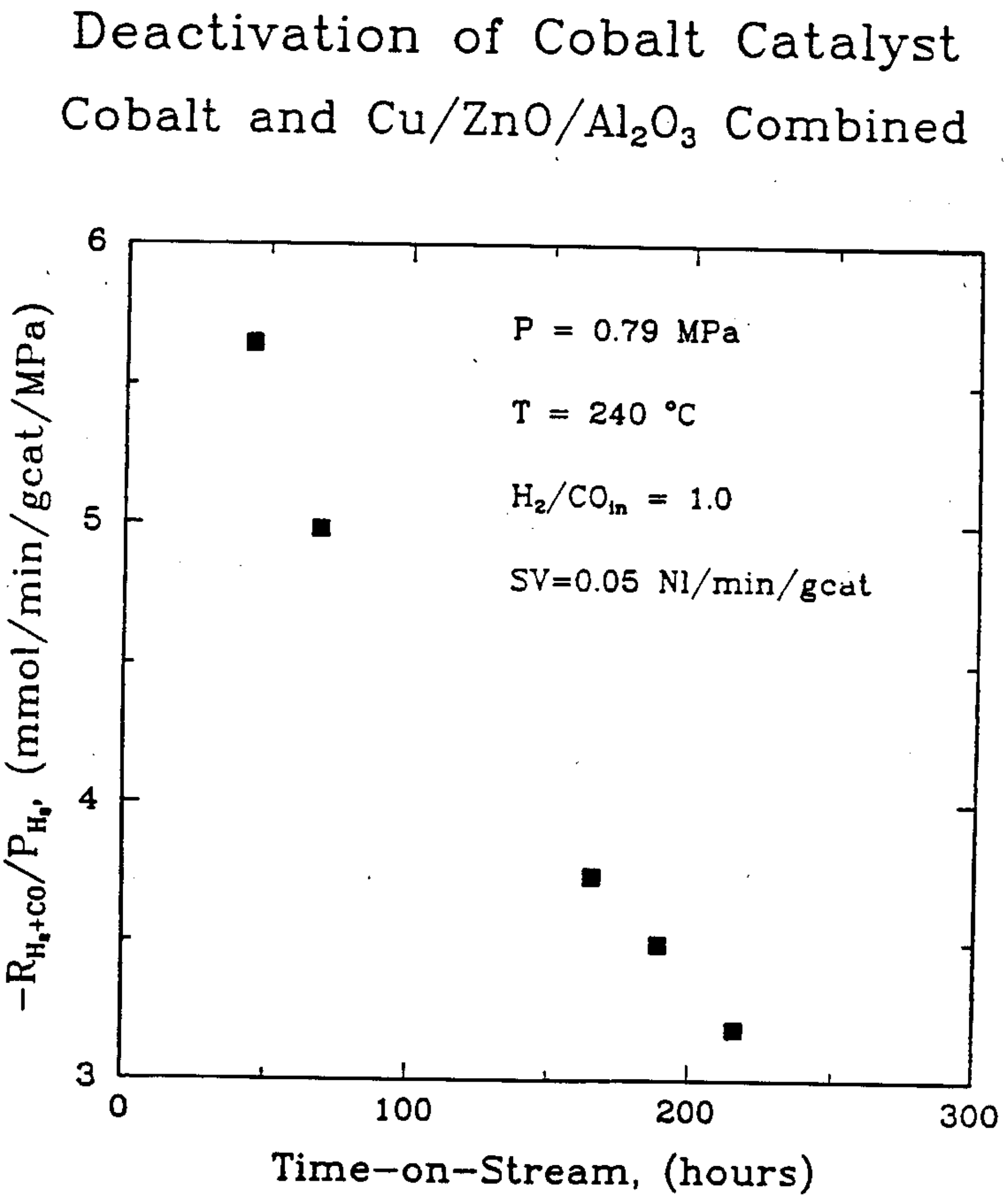

Component Schulz-Flory Plot
Cobalt with WGS Catalyst
TOTAL
n-ALKANE
1-ALKENE
2-ALKENE
ALCOHOL
Mole Fraction
0.1
0.01
0.001
0.0001
0
5
10
15
20
Carbon Number, Cn

FIGURE 10



Deactivation of Cobalt Catalyst

Cobalt and $Cu/ZnO/Al_2O_3$ Combined

Figure 11

SELECTIVITY COMPARISON

EXPERIMENTAL CONDITIONS	Cobalt with $Cu/ZnO/Al_2O_3$	Ruhrchemie (precip. Fe)	C-73 (fused Fe)
Catalyst			
Conversion	40.0	34.0	38.0
Feed H_2/CO	1.0	0.7	0.9
HYDROCARBON SELECTIVITY (WT. %)			
C_1	8.5	6.2	9.8
$\Sigma\ C_2-C_4$	14.6	24.6	38.5
$\Sigma\ C_5-C_{12}$	52.6	41.2	43.4
$\Sigma\ C_{13}-C_{19}$	18.5	18.9	7.7
$\Sigma\ C_{20}-C_{30}$	5.8	8.4	0.6
ADDITIONAL SELCTIVITY			
Oxygenates (Wt. %)	0.9	8.9	9.1
C_4 1-alkene/alkane (molar ratio)	0.37	3.54	4.08