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DE93 006474

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

Report for

July 1, 1990 to September 30, 1990

Report No.: DOE/PC79816-10

Contract No.: DE-AC22-87PC79816

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Summary

A $Co/MgO/SiO_2$ Fischer-Tropsch catalyst was operated simultaneously with a $Cu/ZnO/Al_2O_3$ water-gas-shift catalyst in a slurry reactor for over 400 hours. The process conditions were held constant at a temperature of 240°C, a pressure of 0.79 MPa, and a 1.1 H_2/CO feed of 0.065 Nl/min-g.cat. The Fischer-Tropsch activity remained constant at the level predicted by the operation of the $Co/MgO/SiO_2$ catalyst alone. The water-gas-shift reaction was near equilibrium. The hydrocarbon product distribution of the combined catalyst system was stable and matched that of the $Co/MgO/SiO_2$ operating alone under similar conditions. The combined catalyst system exhibited a high selectivity to n-alkanes. Neither catalysts's operation appeared to have a detrimental effect on that of the other, showing promise for future optimization.

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Introduction

Cobalt Fischer-Tropsch catalysts exhibit many operating characteristics superior to iron. First, carbon formation on cobalt is minimal, which may increase catalyst life and facilitate separation of the product. Additionally, oxygenates such as aldehydes, ketones and alcohols are formed in very low quantities, making product workup easier. Cobalt may also provide a product selectivity to $C_{10}+$ hydrocarbons that is higher than iron catalysts (Schulz et al. 1982). High molecular weight product selectivity maximizes the production of fuel range products, as higher molecular weight hydrocarbons can be hydrocracked to the appropriate range. Finally, the hydrocarbon product distributions on cobalt-based catalysts appear to be affected far more by process variables than those on iron-based catalysts, allowing the opportunity for product optimization to the high molecular weight hydrocarbons of interest. Unfortunately, cobalt catalysts lack the water-gas-shift activity necessary for efficient operation with the hydrogen-lean synthesis gas produced by modern coal gasifiers. Thus, a mechanical mixture of a cobalt catalyst and a water-gas shift catalyst may make possible a combination of the product advantages of cobalt and the operating advantages of a slurry reactor which could be fed with low H_2/CO synthesis gas.

Shell patents (Post et al., 1985a,b) indicate that a mechanical mixture of a cobalt catalyst and a $Cu/ZnO/Al_2O_3$ catalyst can be successfully used to carry out Fischer-Tropsch synthesis. Post et al. describe a $Co/ZrO_2/SiO_2$ Fischer-Tropsch catalyst in a mechanical mixture with a $Cu/Zn/Al_2O_3$ shift catalyst in a fixed-bed reactor. The Shell process produces "distillate fuels" at 125 to 325°C, 0.5 to 10 MPa, and H_2/CO feed ratios between 0.25 and 1.0. No indication of "best conditions" of operation are provided. The ratio of cobalt to shift catalyst is adjusted depending on the H_2/CO feed ratio, with a higher portion of shift catalyst recommended for lower H_2/CO. For hydrogen lean feeds with H_2/CO ratios as low as 0.55, Post and co-workers report that 86 wt% of the product is C_5+. These patents indicate the feasibility of this type of a catalyst mixture in a fixed-bed.

Tominaga et al. (1987) report results of work performed with a 10 wt% Co on SiO_2 combined with a Cu/Cr_2O_3 shift catalyst. They operated in a fixed-bed at 0.3 MPa and between 220 and 280°C. The primary focus of Tominaga et al.'s research was to study the Köelbel-Engelhardt synthesis. In the Köelbel-Engelhardt synthesis, CO and H_2O, rather than synthesis gas, are fed to the reactor; however, they report some data on feeds containing only H_2 and CO with a H_2/CO ratio of 0.5. Two trends are observed from these runs. First, when the shift catalyst is added the mol.% of CO_2 in the products increases from 0.1 to 6.0, indicating a large enhancement in shift activity. Second, the weight fraction of C_5+ products remains unaffected by addition of the shift catalyst to the system. Tominaga et al.'s work provides further indications that a combination of cobalt and shift catalysts may be viable, at least in a fixed-bed.

In conjunction with the development of a cobalt-based Fischer-Tropsch catalyst, researchers at Union Carbide investigated a number of low-temperature shift catalysts (Union Carbide, 2/84; 5/84; and 9/84). Of the 13 runs performed, four used only shift catalysts and nine were based on Fischer-Tropsch formulations to which Cu and Zn were added. In all four runs in which the shift catalysts were tested independently, rapid deactivation was observed and stable activity was not achieved. When added to Fischer-Tropsch catalysts, either in a mechanical mixture or by co-precipitation with cobalt and its promoters, no water-gas shift activity was observed. In fact, the researchers report decreased activity of the the Fischer-Tropsch catalysts relative to the activity in the absence of a shift catalyst.

No plausible explanation is presented for these effects except for the possible poisoning of the Cu-Zn based catalysts by alkenes. This hypothesis was tested by a separate run in which a novel Cu-Zn catalyst loaded on a small pore zeolite was examined; however, this catalyst also deactivated rapidly.

Examination of Union Carbide's experimental procedure indicates that at least two other explanations for the deactivation of the shift catalysts may exist. First, the conditions to which the catalysts were subjected may have caused sintering. The catalysts were reduced at temperatures comparable to those required to reduce the cobalt catalysts. The shift catalysts were calcined in air at 400°C and reduced in H_2 at 350°C. Various investigators indicate (See Table 1) that this activation and reduction procedure would almost certainly cause sintering of the copper. Carbide's experiments were all performed at either 260 or 270°C, above the recommended operating temperature of 250°C for copper-based catalysts (Young and Clark, 1973). Second, the catalysts may not have been prepared in a manner that would produce a stable and active dispersion of copper. Preparation of Cu-ZnO and $Cu\text{-}ZnO/Al_2O_3$ shift catalysts is difficult (Table 1). Union Carbide prepared its own shift catalysts via co-precipitation of Cu and Zn or Cu, Zn, and Co on proprietary supports and promoters. The pH of precipitation may not have been optimal for maximum distribution of copper on the catalyst surface. Incorrectly formulated catalysts tend to sinter more readily (Young and Clark, 1973).

Both Post's and Tominaga's groups report that they were able to add a shift catalyst to a Fischer-Tropsch catalyst and maintain water-gas shift activity. Post and co-workers report that good activity is maintained for extended periods of time, but present no data on prolonged catalyst stability. Tominaga et al. report that the yield of CO_2, which is a measure of the shift activity, decreased to 50% of its initial value within the first 6 hours of operation. They attribute this drop in activity to competitive inhibition by hydrocarbons. They state that this 50% of initial activity is the steady-state value, but present no data after 12 hours-on-stream. In all of the 13 runs they performed, researchers at Union Carbide observed low activity and no shift catalyst stability.

Therefore, no data on the long-term stability of a water-gas shift and a Fischer-Tropsch catalyst system are available. Further, the activity of such a system may be easier to maintain in a fixed-bed, because of changing conditions along the bed. Poisons or reaction conditions may deactivate the shift or the Fischer-Tropsch catalyst in one region of the bed, while the catalyst's activity may be maintained in another region. In a slurry reactor, such as a bubble-column, any potential poisons may be distributed throughout the entire catalyst system.

The primary objective of this work was to find a combination of a shift catalyst and a cobalt Fischer-Tropsch catalyst which could operate simultaneously and efficiently in a slurry reactor. The combined system should exhibit long-term stability with regards to both activity and selectivity and neither catalyst's operation should adversely affect the other. Such a system could combine the product advantages of the Fischer-Tropsch cobalt catalyst, with the ability to operate with a hydrogen-lean syngas feed.

Experimental Procedures

The experiments were performed in a continuous, mechanically-stirred, one-liter autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere (Huff and Satterfield, 1982). The reactor and its contents are well-mixed and the reactor has been shown to operate free of heat and mass transfer limitations (Huff, 1982; Huff and Satterfield, 1982; Huff and Satterfield, 1984).

The reactor was initially charged with 360 g of n-octacosane. The octacosane had been previously recrystallized in tetrahydrofuran (HPLC grade) to remove a bromine impurity (Huff and Satterfield, 1982).

The water-gas-shift catalyst used for this study was a commercially available $Cu/ZnO/Al_2O_3$ catalyst, Katalco K 52-2. The nominal composition of the catalyst, as reported by the manufacturer, is 33 wt.% CuO, 33 wt.% ZnO, and 33 wt.% Al_2O_3. The catalyst was ground and sieved to 52 to 92 μm (170 to 270 ASTM Mesh). 33 grams were subsequently loaded into the one-liter autoclave reactor. The catalyst was then reduced according to a procedure developed by Yates (1990) and outlined in Table 2. This reduction procedure has been shown in previous quarterly reports to provide stable catalyst activity in our slurry-reactor system.

The cobalt catalyst used was a Co/MgO on SiO_2. This catalyst was prepared by an outside laboratory and is of the approximate composition of the cobalt catalysts used at Ruhrchemie (Storch et al., 1951). The nominal compostion of the catalyst, as reported to us by its manufacturer, is 21.4 wt.% Co (as Co), 3.9 wt.% Mg (as Mg), and the remainder diatomaceous earth.

Supplied as an extrudate, the catalyst was ground and sieved to 50 to 90 μm. Following seiving, 17 grams of the catalyst were placed in an external reduction vessel. The catalyst was held in this reduction unit with a 7 μm frit while hydrogen (prepurified, MedTech Gases, Inc.) was brought on stream at a flow of 1.36 Nl/min (approximately 10,000 V/V/hr). At this flow rate the pressure in the vessel was approximately 0.72 MPa. The temperature of the reduction tube was increased steadily from 25°C to 330°C over 4.75 hours while the inlet flow rate was held constant. The reduction unit was held at 330°C for 0.75 hours and subsequently the unit was pressurized with helium and rapidly cooled. During this procedure, some of the catalyst was lost.

The unit with the reduced catalyst was weighed and comparison with the weight of the empty unit, shows that 7.4 grams of reduced catalyst were retained. This corresponds to a weight of 9.0 grams on an unreduced basis, assuming a reduction of 18 wt% as obtained previously with this procedure (Yates, 1990).

The reduction of the water-gas shift catalyst and the cobalt catalyst were timed to end simultaneously. The reduced cobalt catalyst was transferred under helium to the one-liter autoclave reactor which contained the reduced water-gas shift catalyst, also under helium. The reactor was brought on-stream at 0.79 MPa, 187°C, and $H_2/CO = 1.5$ at a flow rate of 1 Nl/min. The CO used in these experiments was CP grade (North East Airgas, Inc.) and the H_2 was prepurified grade (MedTech Gases, Inc.).

The reactor conditions were held constant for the first 66 hours and then the H_2/CO feed was adjusted to 1.1 with an inlet flow of 0.585 Nl/min and the temperature was increased to 240°C over a period of 8 hours. The reactor was then held at 0.79 MPa, 240°C, and inlet $H_2/CO = 1.1$ at a flow rate of 0.585 Nl/min for the remainder of the run.

Material balances were performed over periods of 24 to 48 hours, with at least 24 hours allowed between material balances to ensure steady state operation. Products such as liquid hydrocarbons and water were condensed in two traps, one kept at 85°C and reactor pressure, the other at 1°C and 0.34 MPa. Non-condensable products were sampled by an on-line gas chromatograph and passed through bubble-flow meters before being vented. Gaseous, aqueous, and liquid products were analyzed with three gas chromatographs as described by Huff et al. (1983). Tie components, CO_2, CH_4, and C_2 and C_3 compounds, were used to match the analyses from three gas chromatograms and provide complete product distributions for each material balance. Material balances were required to close between 97 and 103% on oxygen, which was chosen as the closure criteria because carbon and hydrogen accumulate in the reactor (Huff, 1982; Donnelly et al., 1988). The appendix contains complete material balance results for the data obtained in this study.

Results and Discussion

Activity

Figure 1 shows that the combined catalyst system retained steady-state Fischer-Tropsch activity for over 400 hours-on-stream. The average rate of H_2+CO consumption was 4.73($\pm$.34) mmol/min. On an unreduced basis, this corresponds to *ca.* 0.53 mmol/min-g.cat.

Yates and Satterfield (in press) developed the following rate expression for this cobalt catalyst operating alone.

$$-R_{H_2+CO}=\frac{aP_{CO}P_{H_2}}{(1+bP_{CO})^2} \tag{1}$$

They non-linearly regressed values of $a=75.76$ mmol/min-g.cat.-MPa^2 and $b=11.61$ 1/MPa at 240°C.

Figure 2 shows the average rate of H_2+CO consumption and the 67% confidence interval as predicted from equation (1). The activity of the combined system appears to be somewhat higher than that predicted. We do not attribute this effect to any catalyst synergies; instead, this trend may possibly be attributed to slight variations in the reduction of the cobalt catalyst. The constant a in equation (1) represents the surface rate constant, which is approximately proportional to the number of active sites on the catalyst surface; thus, more active sites per gram catalyst would lead to a higher value of a. Within our ability to reproduce catalyst reduction procedures, the cobalt catalyst acting alone and the cobalt catalyst operating in conjunction with the water-gas shift catalyst display remarkably similar activity.

Figure 3 shows the excellent stability of the Cu-based water-gas-shift catalyst in our system. On the left vertical axis, the rate of CO_2 production divided by the rate of CO consumption is plotted. Because CO can react in the system to form hydrocarbons via the Fischer-Tropsch synthesis or CO_2 via the shift reaction, this ratio is an indication of the selectivity of the catalyst system for the water-gas shift reaction. For this system, the fraction of reacted CO consumed by the water-gas shift was constant at appoximately 0.44.

On the right vertical axis of Figure 3 $X_{WGS}\%$ is plotted, which we have defined as:

$$X_{WGS}\% = \frac{P_{CO_2}}{P_{CO_2} + P_{H_2O}} \times 100\% \qquad (2)$$

Water, a primary product of the synthesis, can react through the water-gas-shift reaction to become CO_2. This variable, $X_{WGS}\%$, is a measure of the percentage of water formed which went on to react and become carbon dioxide. For over 400 hours-on-stream, an average 94% of the H_2O formed was converted to CO_2, as compared to an equilibrium $X_{WGS}\%$ at this temperature of 99%. Therefore, the catalyst system was near equilibrium conversion for the water-gas-shift reaction.

Figures 1, 2, and 3 show that the two catalysts exhibited stable, independent behavior for over 400 hours-on-stream. The products of the Fischer-Tropsch synthesis did not appear to poison the Cu-Zn water-gas-shift catalyst. Similarly, the Cu of the water-gas-shift system had no detrimental effects on the cobalt Fischer-Tropsch catalyst.

The stable activity in this system is attributed to the reduction procedures developed for both the cobalt Fischer-Tropsch and $Cu/ZnO/Al_2O_3$ shift catalyst (Yates, 1990). Extensive scouting work was done on each catalyst operating alone. In early work, the reduction conditions were more severe, possibly leading to over-reduction and subsequent sintering. The current reduction procedures, which have been optimized for stability not activity, allow long-term continuous operation in a mixed catalyst system.

Selectivity

Figure 4 shows the long-term product stability of the combined catalyst system, as exemplified by the nearly identical Schulz-Flory plots obtained over a 354-hour time period. Table 3 gives the average selectivity to various product cuts. The selectivity to fuel range products (C_5+) is 50 wt.%. However, the operating conditions and catalyst preparation procedures have not been optimized to maximize this selectivity.

Figure 5 shows a component Schulz-Flory diagram from which we can observe that the predominant products of the combined catalyst system are n-alkanes. The selectivity to 2-alkenes, 1-alkenes, and n-alcohols drops off sharply. On a mole-basis, the only significant product aside from n-alkanes, is methanol. On average methanol represented 16 mol% of the yield; however, on a weight basis, the selectivity to methanol was low, typically in the range of 9%.

Methanol is probably being formed on the $CuO-ZnO/Al_2O_3$ water-gas-shift catalyst, not on the Fischer-Tropsch catalyst. Herman et al. (1978) report on a low-pressure methanol synthesis process using a similar copper-based catalyst with typical operating conditions in the range of 240 to 260°C and 5 to 10 MPa. Based on evidence that the yield to methanol is enhanced by the presence of CO_2, H_2O, or O_2, they postulate that the active phase for synthesis is a solution of Cu^+ in ZnO. The reduction of the copper to metal is accompanied by a loss in methanol synthesis activity.

In contrast, the active phase for the low-temperature shift reaction is copper metal (Satterfield, 1980). Thus, the methanol appears to be formed on sites of unreduced copper on the water-gas-shift catalyst, indicating incomplete reduction. A longer reduction period, with similarly mild conditions (i.e. very low concentrations of H_2), may decrease the selectivity to methanol.

Figure 6 shows that the rate of H_2 + CO consumption was not significantly affected by the production of methanol. Here, the rate of syngas consumption minus that required to produce methanol is plotted for each material balance. The rate of syngas consumption still compares well to that predicted by equation (1).

Figure 7 shows that for similar operating conditions (See Table 4), the overall Fischer-Tropsch product distribution of the catalyst system matches that of the cobalt catalyst operating alone. The mole fraction of methanol was subtracted from the products of the combined system, and the mole fractions of other products normalized to produce the "Co + WGS" Schulz-Flory plot.

In contrast, Figure 8 shows that the component selectivities were quite different. For each product cut, the mole-fraction of products which are n-alkanes is graphed. The selectivity of the combined catalyst system to n-alkanes is much higher than that of cobalt operating alone. This greater hydrogenation activity may be related to the water-gas-shift catalyst, which contains copper, a known hydrogenation catalyst (Satterfield, 1980).

Figure 9 shows an analysis from the end-of-run slurry. The normalized Schulz-Flory, with the carrier, $C_{28}H_{58}$, subtracted from the distribution, shows a terminal α of 0.83. This value was regressed from C_{29} to C_{40}. The end-of-run slurry from the cobalt catalyst alone, operated over a wide range of conditions, exhibited a terminal α of 0.87. These values for α are comparable and the difference may be attributed to variations in reduction procedure or operating conditions.

In summary, the selectivity of the catalyst system remained constant for over 400 hours-on-stream. The overall product distribution of the system matches that of the Fischer-Tropsch catalyst operating alone under similar conditions. The combined system shows a much higher selectivity to n-alkanes, forming few other products to a significant extent.

Conclusions

A $Co/MgO/SiO_2$ Fischer-Tropsch catalyst was operated in conjunction with a Cu-ZnO/Al_2O_3 water-gas-shift catalyst for over 400 hours. The Fischer-Tropsch and water-gas-shift activity of the system remained constant throughout this time period. Neither catalysts's operation appeared to have detrimental effects on the other.

The selectivity of the catalyst system remained constant for over 400 hours, with approximately 50 wt.% of the products formed being in the fuel range (C_5+). The carbon-number production distribution of the catalyst system matched that of the Fischer-Tropsch catalyst alone under similar operating conditions; however, the selectivity to n-alkanes was much higher in the combined system.

Future Work

This combined catalyst system shows great promise. Optimization must still be performed to maximize the selectivity to desired products and minimize the ratio of water-gas-shift catalyst to Fischer-Tropsch catalyst. This work can be performed in part by determining the effect of process conditions through fundamental and applied analyses. The present study proves the feasibility of a mechanical mixture of a cobalt Fischer-Tropsch catalyst and a water-gas-shift catalyst in a slurry reactor.

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Tables

TABLE 1

CRITICAL FACTORS AFFECTING THE ACTIVITY OF LOW-TEMPERATURE SHIFT CATALYSTS

Desired Factor	References
Oxidation state of Cu^+ for shift activity	Kul'kova et al. (1949), Shchibrya et al. (1965a,b), McDonald (1969), Chinchen and Waugh (1986), Chinchen et al. (1987), and on similar methanol synthesis catalysts by Herman et al. (1979).
High dispersion of copper for high activity	Uchida et al. (1967) and Uchida et al. (1968).
Optimal precipitation pH for copper and zinc (near 7)	Campbell (1970).
Low calcination temperature (below ~300°C)	Petrini and Gabrassi (1984), Shchibrya et al. (1971).
Reduction in low H_2/N_2 mixture at low temperature	Newsome (1980), Allen (1974).
Operating temperature below 250°C to avoid sintering	Young and Clark (1973).
<u>Poisons</u>:	
Sulfur	Allen (1974), Newsome (1980).
Chlorine	Allen (1974), Young and Clark (1973).

TABLE 2

REDUCTION PROCEDURE FOR LOW-TEMPERATURE SHIFT CATALYST

Catalyst	Hours-on-stream[†]	Temperature (°C)	Gas Composition/Flow (Nl/min/gcat)
$Cu/ZnO/Al_2O_3$ (Run 2)	0 to 16	70	0.015 of B[b]
	16 to 18	70 to 120	0.015 of B
	18 to 19	120	0 to 0.015 A[a], 0.015 to 0 B
	19 to 21.5	120 to 200	0.015 of A
	21.5 to 24	200	0 to 0.015 C[c], 0.015 to 0 A
	24 to 25	200	0.015 C

Note: Pressure was held at 0.79 MPa and the impeller was stirring faster than 800 RPM. Oulet line temperature was held at 250°C to minimize potential reflux of water vapor.

[†] When a time period is shown it indicates a smooth ramping of conditions. Typically, process changes were made every 15 minutes.

[a] Gas A is 1000 ppm prepurified H_2 in prepurified N_2 (Matheson Gases, Inc.).

[b] Gas B is prepurified He (Colony, Inc.).

[c] Gas C is 3 vol.% prepurified H_2 in prepurified N_2 (Matheson Gases, Inc.).

Table 3

Average Weight Distribution
of the Combined Cobalt and Water-Gas-Shift Catalyst System

Product Cut	Wt%
C_1	25.9
C_2-C_4	24.2
C_5-C_9	26.8
$C_{10}+$	23.1

Table 4

Operating Conditions of Material Balances Used for Comparison

	Co Only	Co + WGS
Temperature (°C)	240	240
Pressure (MPa)	0.79	0.79
Reactor H_2/CO	1.36	1.02
Feed Flow Rate (Nl/min-g.cat.)	0.0093	0.065

Figures

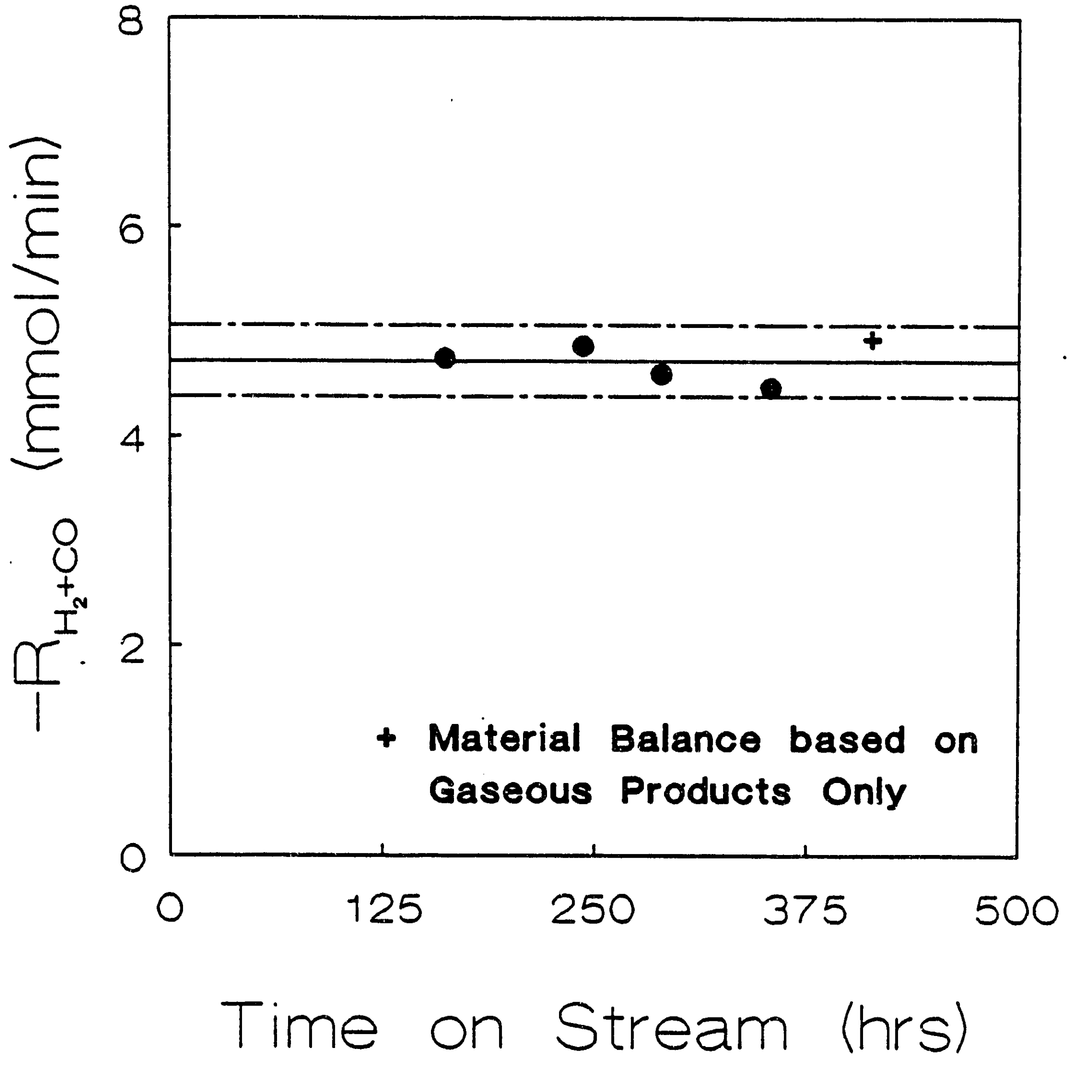

Figure 1:

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

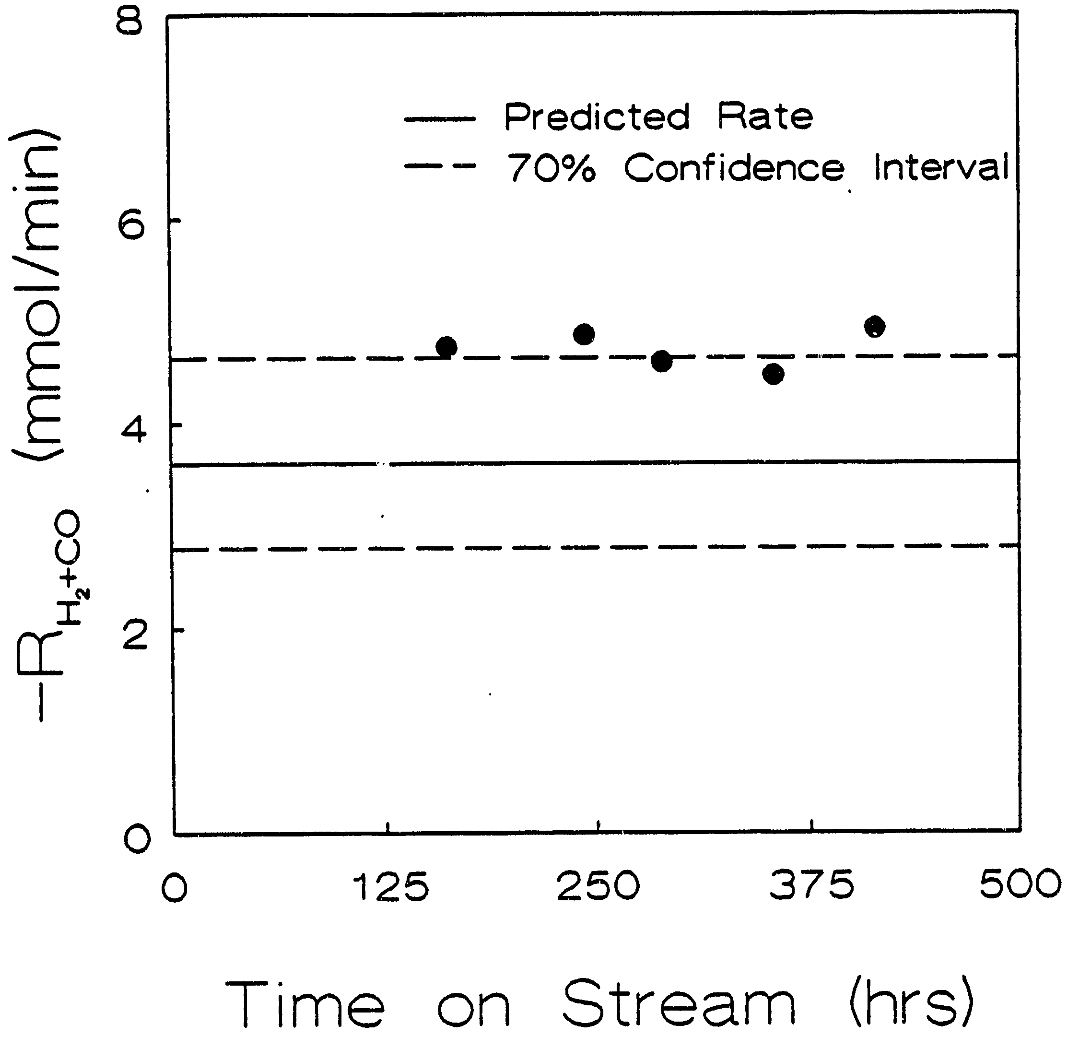

Figure 2:

Activity of Combined Catalyst System Matches that Predicted by Yates and Satterfield (in press).

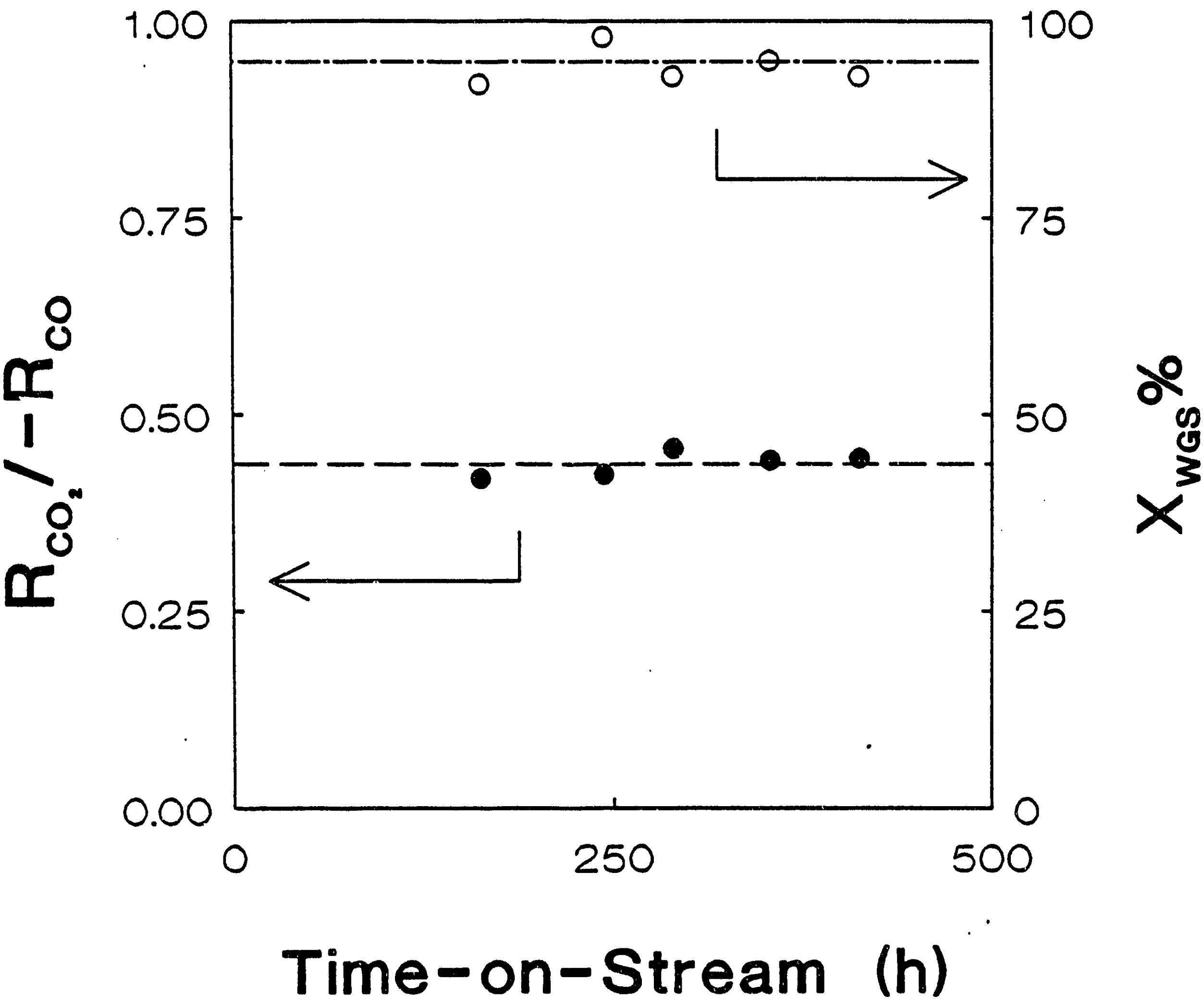

Figure 3:

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

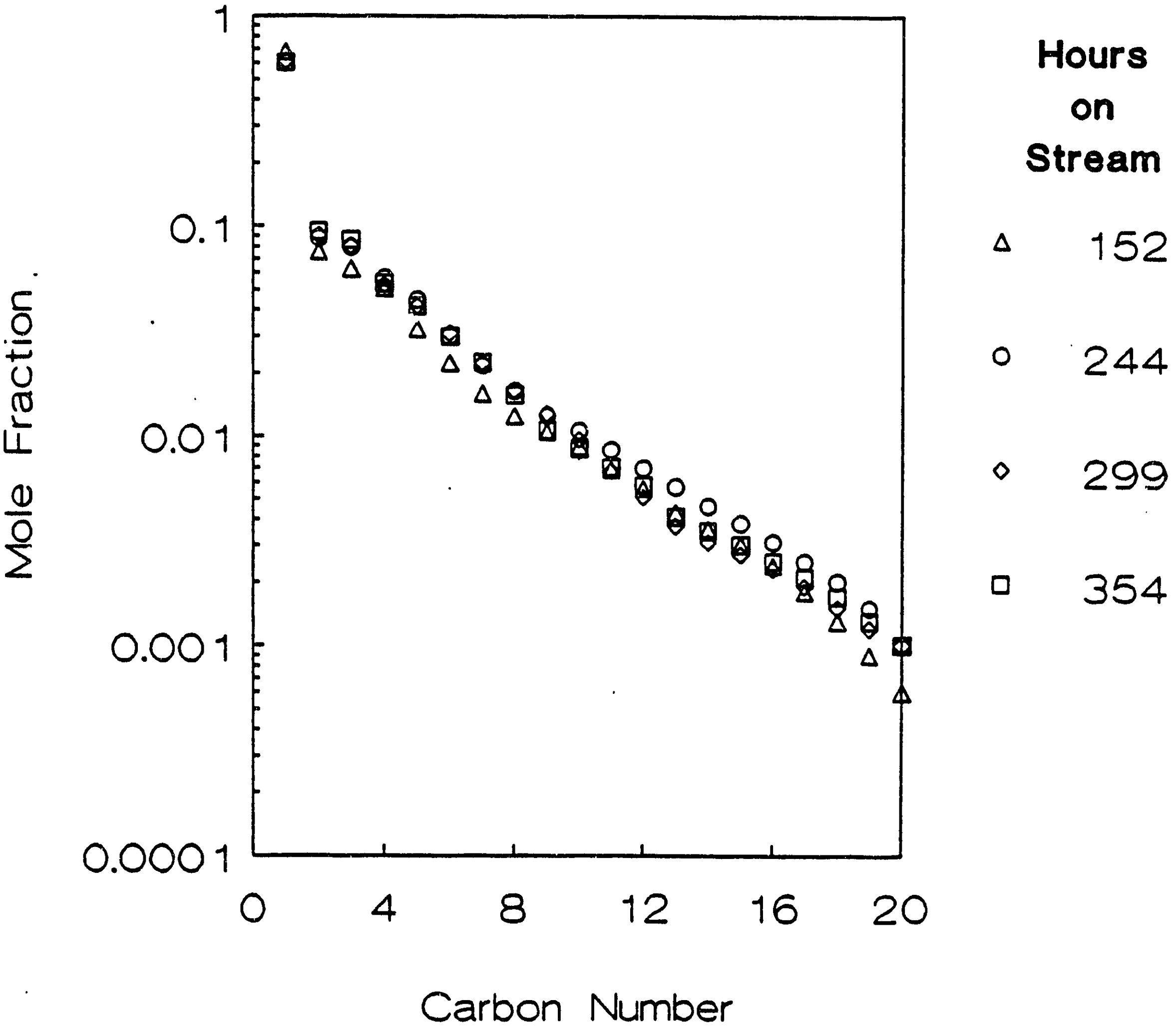

Figure 4:

The Hydrocarbon Product Distribution of the Combined System Remained Stable

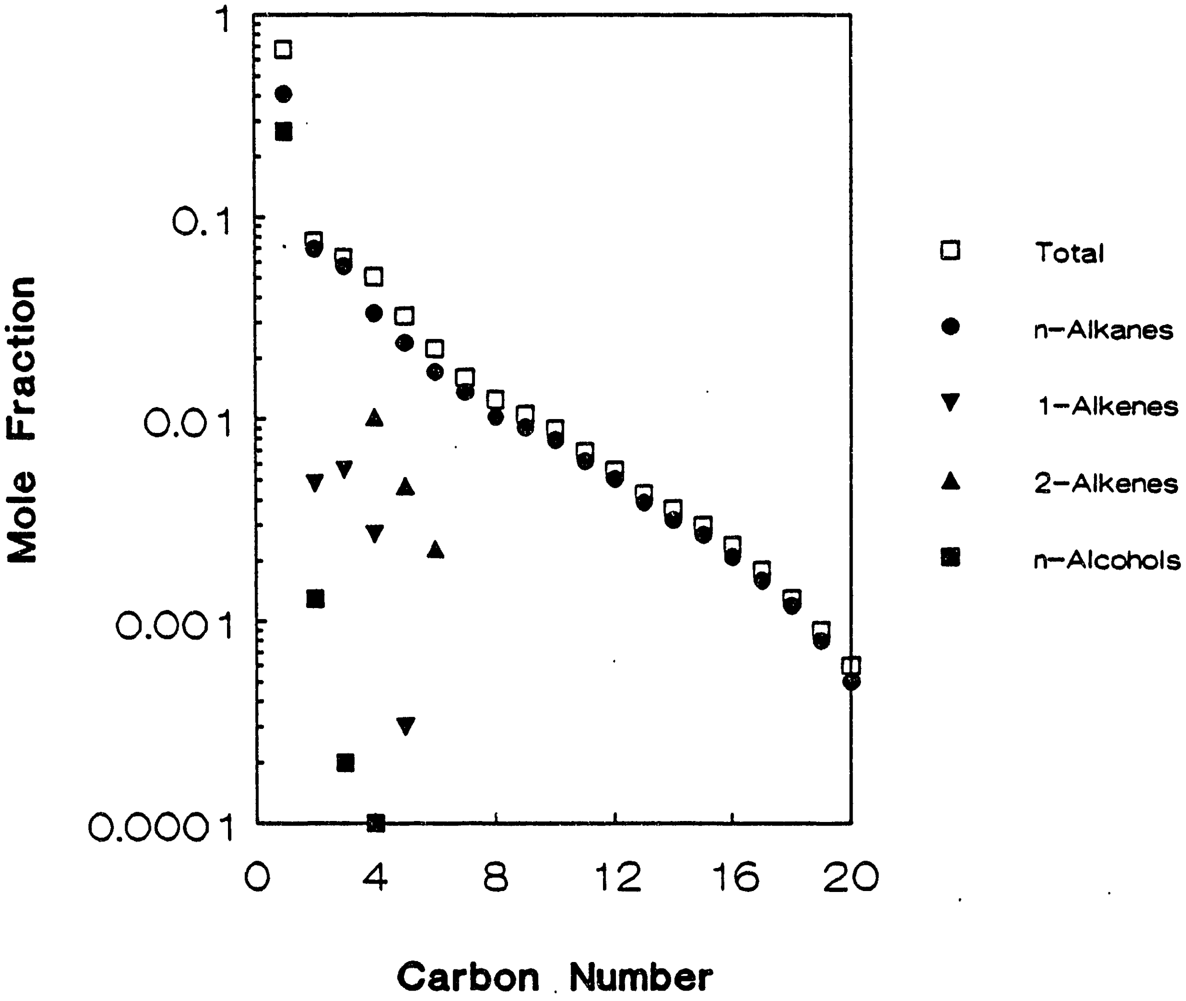

Figure 5:

Component Schulz-Flory Diagram for the Combined Catalyst System

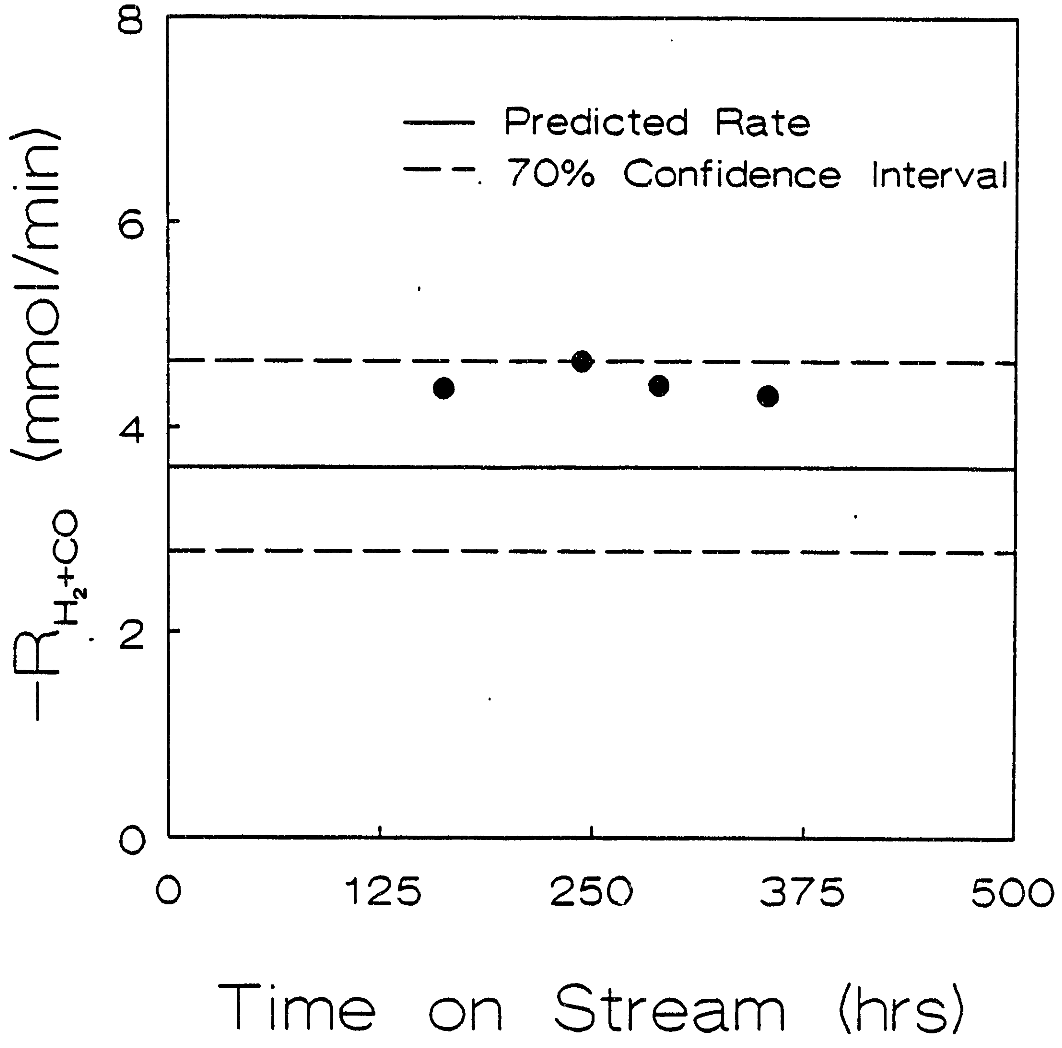

Figure 6:

Rate of Syngas Consumption Minus That Required for MeOH Production

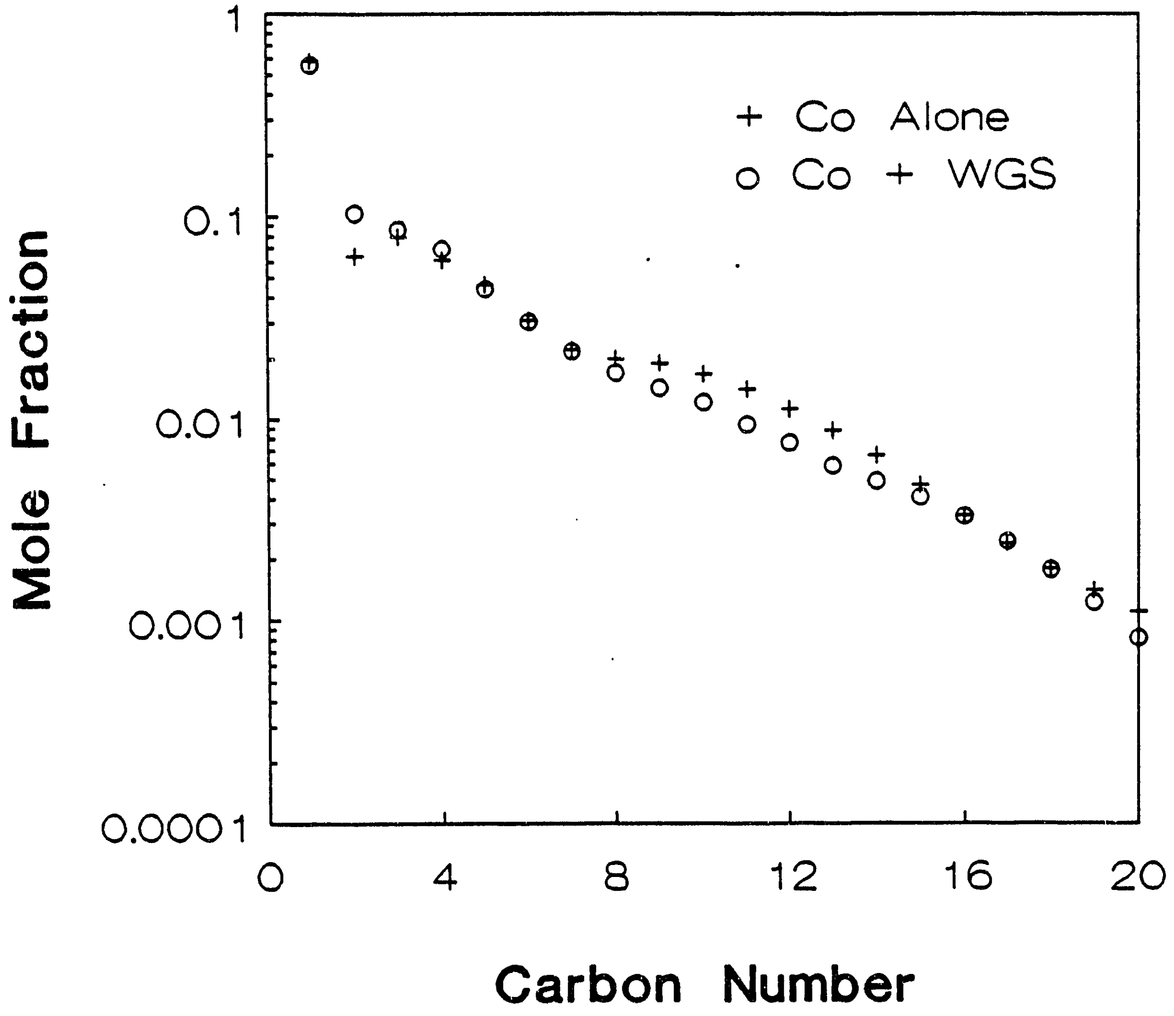

Figure 7:

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

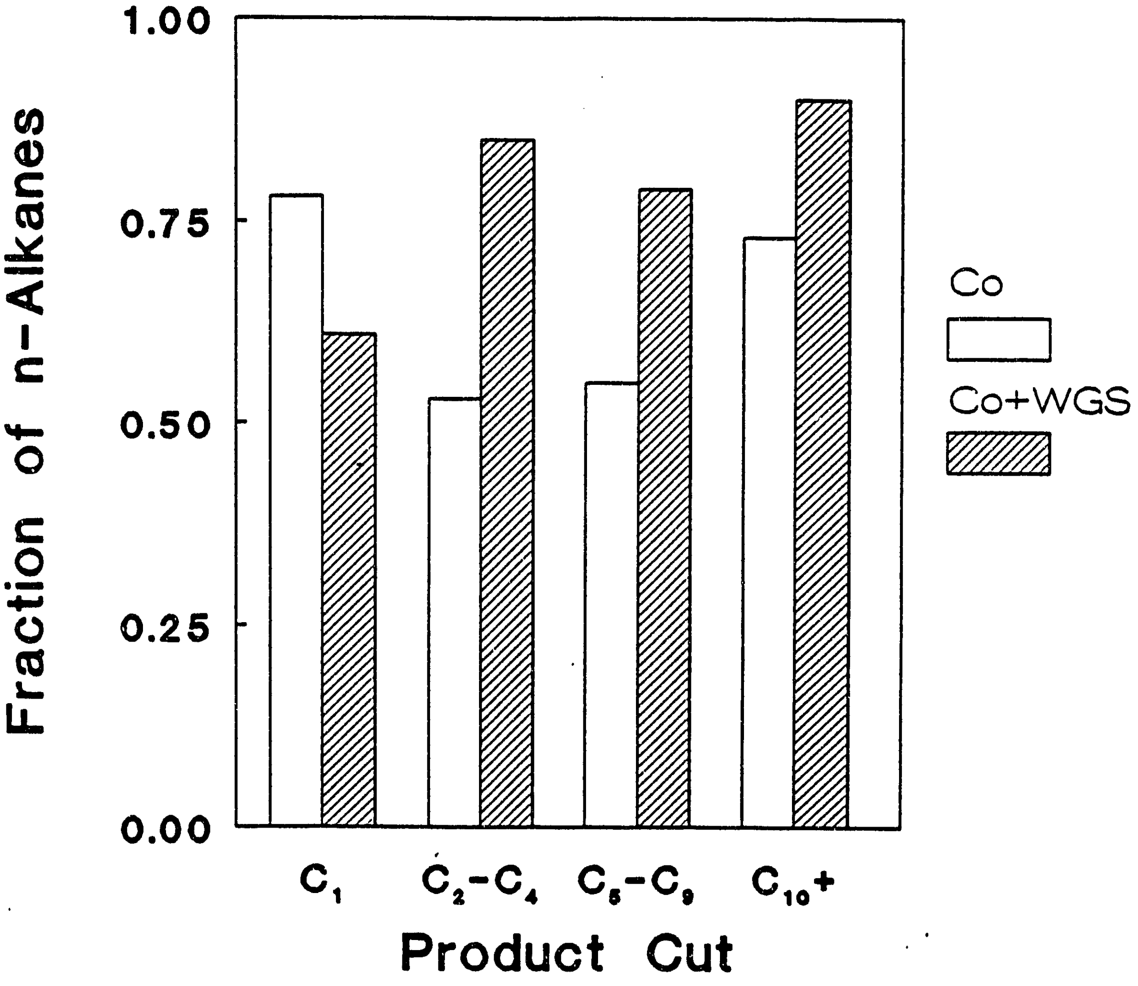

Figure 8:

Combined Catalyst System Exhibits Greater Selectivity to n-Alkanes

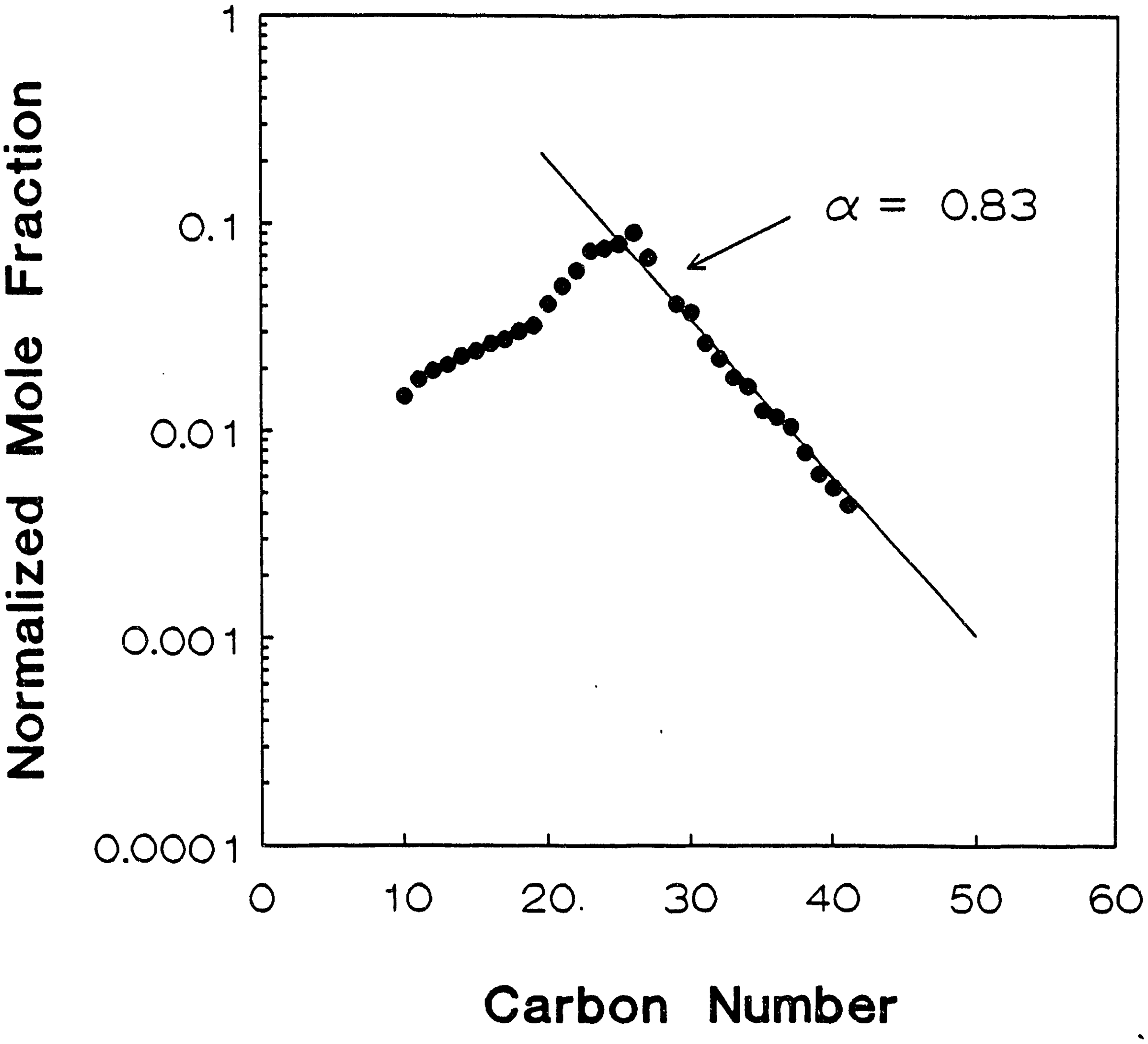

Figure 9:

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

Appendix

RUN: Cobalt-Water-Gas-Shift SAMPLE#: Material Balance 1
TIME (MIN): 2550.0
TEMP(C)= 240.0 PRESS(ATM ABS)=: 7.81722 L/M IN= 0.585
FEED RATIO= 0.990
FT MOLES OUT/MIN= 0.4657E-03 OCTACOSANE MOLES OUT/MIN= 0.3549E-05
AVE.MOLWT= 39.12 RATE CO+H2 (MILLIMOLES/MIN) = 4.752

XH2= 17.24 XCO= 19.17 XCO+H2= 18.21

PERCENT OXYGENATES= 22.027 PERCENT METHANE= 16.749
PERCENT OLEFINS= 4.179

BALANCES
C= 97.22 H= 96.18 O= 98.58 TOTWT= 97.88
PRESSURES(ATM ABS)
H2= 3.65795 CO= 3.60876 H2O= 0.03171 CO2= 0.35908

MOLE BASIS PERCENT OF FT PRODUCTS

C#	PARA	AOLE	BOLE	ISOM	ACID	NALC	CRBO	AROM	TOT
1	40.96	0.00	0.00	0.00	0.00	26.65	0.00	0.000	67.61
2	6.98	0.48	0.00	0.00	0.00	0.13	0.01	0.000	7.60
3	5.74	0.56	0.00	0.00	0.00	0.02	0.00	0.000	6.32
4	3.35	0.27	1.02	0.42	0.00	0.01	0.00	0.000	5.07
5	2.38	0.03	0.47	0.36	0.00	0.00	0.00	0.000	3.24
6	1.71	0.00	0.23	0.29	0.00	0.00	0.00	0.000	2.23
7	1.36	0.00	0.00	0.23	0.00	0.00	0.00	0.000	1.60
8	1.03	0.00	0.00	0.22	0.00	0.00	0.00	0.000	1.25
9	0.91	0.00	0.00	0.14	0.00	0.00	0.00	0.000	1.05
10	0.79	0.00	0.00	0.10	0.00	0.00	0.00	0.000	0.89
11	0.62	0.00	0.00	0.07	0.00	0.00	0.00	0.000	0.69
12	0.51	0.00	0.00	0.05	0.00	0.00	0.00	0.000	0.56
13	0.39	0.00	0.00	0.04	0.00	0.00	0.00	0.000	0.43
14	0.32	0.00	0.00	0.03	0.00	0.00	0.00	0.000	0.36
15	0.27	0.00	0.00	0.03	0.00	0.00	0.00	0.000	0.30
16	0.21	0.00	0.00	0.02	0.00	0.00	0.00	0.000	0.24
17	0.16	0.00	0.00	0.02	0.00	0.00	0.00	0.000	0.18
18	0.12	0.00	0.00	0.01	0.00	0.00	0.00	0.000	0.13
19	0.08	0.00	0.00	0.01	0.00	0.00	0.00	0.000	0.09
20	0.05	0.00	0.00	0.01	0.00	0.00	0.00	0.000	0.06
21	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.04
22	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.03
23	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.02
24	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.01
25	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.01
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00
28	0.76	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00

```
RUN: Cobalt-Water-Gas-Shift          SAMPLE#: Material Balance 2
TIME (MIN):   3020.0
TEMP(C)= 240.0       PRESS(ATM ABS)=:  7.81327     L/M IN= 0.585
FEED RATIO= 0.990
FT  MOLES  OUT/MIN=  0.4729E-03        OCTACOSANE  MOLES  OUT/MIN=
0.3801E-05
AVE.MOLWT= 42.78     RATE CO+H2 (MILLIMOLES/MIN)   =   4.871

XH2=  17.41    XCO=  19.90    XCO+H2=  18.66

PERCENT  OXYGENATES=   12.132           PERCENT METHANE=  16.432
PERCENT OLEFINS=   5.318

BALANCES
C=   98.40   H=   97.05   O=   97.72   TOTWT=   97.95
PRESSURES(ATM ABS)
H2=  3.66945   CO=  3.59475   H2O=  0.00725   CO2=  0.37869

                 MOLE BASIS PERCENT OF FT PRODUCTS

C#  PARA   AOLE   BOLE   ISOM   ACID   NALC   CRBO   AROM   TOT

 1 43.93   0.00   0.00   0.00   0.00  15.89   0.00  0.000  59.82
 2  8.09   0.55   0.00   0.00   0.00   0.12   0.01  0.000   8.77
 3  6.85   1.09   0.00   0.00   0.00   0.04   0.00  0.000   7.98
 4  3.95   0.40   1.01   0.29   0.00   0.01   0.00  0.000   5.67
 5  3.14   0.00   0.77   0.56   0.00   0.01   0.00  0.000   4.47
 6  2.15   0.00   0.40   0.46   0.00   0.00   0.00  0.000   3.00
 7  1.81   0.00   0.00   0.36   0.00   0.00   0.00  0.000   2.17
 8  1.29   0.00   0.00   0.35   0.00   0.00   0.00  0.000   1.64
 9  1.06   0.00   0.00   0.18   0.00   0.00   0.00  0.000   1.25
10  0.91   0.00   0.00   0.15   0.00   0.00   0.00  0.000   1.06
11  0.75   0.00   0.00   0.11   0.00   0.00   0.00  0.000   0.86
12  0.62   0.00   0.00   0.08   0.00   0.00   0.00  0.000   0.70
13  0.51   0.00   0.00   0.06   0.00   0.00   0.00  0.000   0.57
14  0.42   0.00   0.00   0.05   0.00   0.00   0.00  0.000   0.46
15  0.34   0.00   0.00   0.04   0.00   0.00   0.00  0.000   0.38
16  0.28   0.00   0.00   0.03   0.00   0.00   0.00  0.000   0.31
17  0.22   0.00   0.00   0.03   0.00   0.00   0.00  0.000   0.25
18  0.18   0.00   0.00   0.02   0.00   0.00   0.00  0.000   0.20
19  0.13   0.00   0.00   0.02   0.00   0.00   0.00  0.000   0.15
20  0.09   0.00   0.00   0.01   0.00   0.00   0.00  0.000   0.10
21  0.06   0.00   0.00   0.01   0.00   0.00   0.00  0.000   0.07
22  0.04   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.04
23  0.02   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.03
24  0.01   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.02
25  0.01   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.01
26  0.01   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.01
27  0.00   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.00
28  0.80   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.00
29  0.00   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.00
30  0.00   0.00   0.00   0.00   0.00   0.00   0.00  0.000   0.00
```

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RUN: Cobalt-Water-Gas-Shift        SAMPLE#: Material Balance 3
TIME (MIN):   1440.0
TEMP(C)= 241.0      PRESS(ATM ABS)=:  7.74980    L/M IN= 0.583
FEED RATIO= 1.100
FT  MOLES  OUT/MIN=  0.4416E-03        OCTACOSANE  MOLES  OUT/MIN=
0.3555E-05
AVE.MOLWT= 40.46       RATE CO+H2 (MILLIMOLES/MIN)   =    4.603

XH2=  14.99    XCO=  20.68    XCO+H2=  17.70

PERCENT  OXYGENATES=   11.597          PERCENT METHANE=  18.431
PERCENT OLEFINS=   5.038

BALANCES
C=   97.99   H=   97.87   O=   99.41   TOTWT=   98.74
PRESSURES(ATM ABS)
H2=  3.88498   CO=  3.29516   H2O=  0.02755   CO2=  0.39281


                         MOLE BASIS PERCENT OF FT PRODUCTS

C#  PARA    AOLE    BOLE    ISOM    ACID    NALC    CRBO   AROM     TOT

 1 46.61    0.00    0.00    0.00    0.00   14.48    0.00   0.000   61.09
 2  8.40    0.54    0.00    0.00    0.00    0.10    0.01   0.000    9.05
 3  6.90    1.19    0.00    0.00    0.00    0.01    0.00   0.000    8.10
 4  3.93    0.47    0.62    0.24    0.00    0.00    0.00   0.000    5.26
 5  2.91    0.00    0.85    0.42    0.00    0.00    0.00   0.000    4.17
 6  2.16    0.00    0.01    0.92    0.00    0.00    0.00   0.000    3.10
 7  1.84    0.00    0.02    0.37    0.00    0.00    0.00   0.000    2.23
 8  1.27    0.00    0.03    0.35    0.00    0.00    0.00   0.000    1.65
 9  1.02    0.00    0.03    0.22    0.00    0.00    0.00   0.000    1.28
10  0.78    0.05    0.00    0.13    0.00    0.00    0.00   0.000    0.96
11  0.60    0.00    0.00    0.08    0.00    0.00    0.00   0.000    0.68
12  0.45    0.00    0.00    0.06    0.00    0.00    0.00   0.000    0.51
13  0.32    0.00    0.00    0.04    0.00    0.00    0.00   0.000    0.37
14  0.28    0.00    0.00    0.03    0.00    0.00    0.00   0.000    0.31
15  0.24    0.00    0.00    0.03    0.00    0.00    0.00   0.000    0.27
16  0.20    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.23
17  0.17    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.19
18  0.14    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.15
19  0.11    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.12
20  0.09    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.10
21  0.06    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.07
22  0.04    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.05
23  0.03    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.03
24  0.02    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.02
25  0.01    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.01
26  0.01    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.01
27  0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
28  0.81    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
29  0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
30  0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
```

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RUN: Cobalt-Water-Gas-Shift          SAMPLE#: Material Balance 4
TIME (MIN):    2465.0
TEMP(C)= 240.0       PRESS(ATM ABS)=:   7.82314     L/M IN= 0.583
FEED RATIO= 1.080
FT  MOLES  OUT/MIN=  0.4191E-03        OCTACOSANE  MOLES  OUT/MIN=
0.3462E-05
AVE.MOLWT= 40.47          RATE CO+H2 (MILLIMOLES/MIN)  =   4.473

XH2=  13.57     XCO=  21.11     XCO+H2=  17.20

PERCENT  OXYGENATES=   10.084            PERCENT METHANE=  18.839
PERCENT OLEFINS=   6.743

BALANCES
C=    96.97    H=    98.65    O=    98.44    TOTWT=    97.87
PRESSURES(ATM ABS)
H2=  3.93875    CO=  3.32868    H2O=  0.01925    CO2=  0.39387


                      MOLE BASIS PERCENT OF FT PRODUCTS

C#   PARA    AOLE    BOLE    ISOM    ACID    NALC    CRBO    AROM    TOT

 1  47.65    0.00    0.00    0.00    0.00   12.58    0.00   0.000   60.23
 2   8.86    0.53    0.00    0.00    0.00    0.07    0.00   0.000    9.46
 3   7.22    1.40    0.00    0.00    0.00    0.02    0.00   0.000    8.64
 4   3.85    0.52    0.77    0.20    0.00    0.01    0.00   0.000    5.35
 5   2.82    0.00    0.93    0.42    0.00    0.00    0.00   0.000    4.17
 6   2.07    0.00    0.46    0.45    0.00    0.00    0.00   0.000    2.98
 7   1.83    0.00    0.21    0.20    0.00    0.00    0.00   0.000    2.24
 8   1.23    0.00    0.02    0.33    0.00    0.00    0.00   0.000    1.57
 9   0.87    0.00    0.00    0.19    0.00    0.00    0.00   0.000    1.07
10   0.76    0.00    0.00    0.12    0.00    0.00    0.00   0.000    0.87
11   0.63    0.00    0.00    0.08    0.00    0.00    0.00   0.000    0.71
12   0.51    0.00    0.00    0.06    0.00    0.00    0.00   0.000    0.58
13   0.36    0.00    0.00    0.05    0.00    0.00    0.00   0.000    0.41
14   0.31    0.00    0.00    0.04    0.00    0.00    0.00   0.000    0.35
15   0.27    0.00    0.00    0.03    0.00    0.00    0.00   0.000    0.30
16   0.23    0.00    0.00    0.03    0.00    0.00    0.00   0.000    0.25
17   0.19    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.21
18   0.15    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.17
19   0.12    0.00    0.00    0.02    0.00    0.00    0.00   0.000    0.13
20   0.09    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.10
21   0.07    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.07
22   0.05    0.00    0.00    0.01    0.00    0.00    0.00   0.000    0.05
23   0.03    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.03
24   0.02    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.02
25   0.01    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.01
26   0.01    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.01
27   0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
28   0.83    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
29   0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
30   0.00    0.00    0.00    0.00    0.00    0.00    0.00   0.000    0.00
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END

DATE
FILMED

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