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FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

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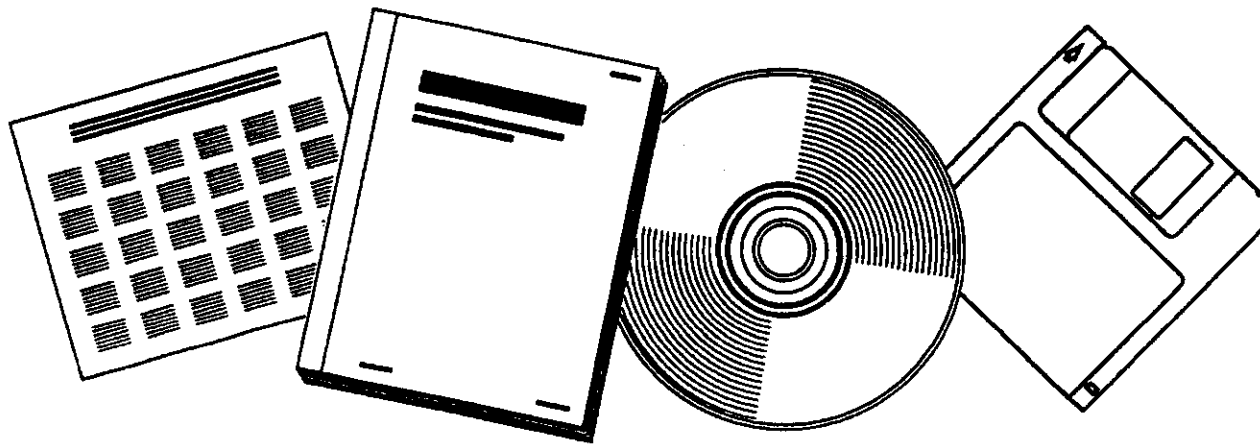

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FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

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BROOKHAVEN STATION
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
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DEDICATION

The Brookhaven Station of the MIT School of Chemical Engineering Practice was established in the summer of 1983. It represents a new direction for the Laboratory which could not have been implemented without the strong support and encouragement of our former Deputy Director, the late Dr. Warren E. Winsche. Establishment of the station at BNL embodies three of Dr. Winsche's interests during his long and notable career in chemical engineering and research management. These are the continued pursuit of the high standards of professional chemical engineering practice; the role of the National Laboratories in providing both facilities and staff to assist in the training of engineers and scientists; and thirdly, and perhaps most important, an appreciation for the stimulus and fresh ideas often provided by students and those still in a "learning" mode, as an essential to the well being of any research organization.

These reports amply demonstrate the above characteristics and represent only a portion of the success of the first year of operation of the station.

We expect this cooperative effort between BNL and MIT to continue well into the future and for this we gratefully dedicate these reports to the memory of Dr. Winsche.

ABSTRACT

The performance of an iron-copper Fischer-Tropsch catalyst was studied in a slurry CSTR at 227°C and 790 kPa (100 psig). Catalyst performance was similar to other iron-based catalysts studied previously with respect to conversion of CO, conversion of CO + H_2, and to the product distribution. CO conversion increased with decreasing space velocity, ranging from approximately 60% at 1570 hr^{-1} to over 90% at 488 hr^{-1}. The H_2 to CO usage ratio was approximately 0.7, indicating that the catalyst is a good water-gas shift catalyst as well as a Fischer-Tropsch catalyst. Reaction products could be described by a Flory distribution with a chain growth probability (α) of 0.67, which is in the gasoline range. In some runs, methanol was added continuously to the reactor feed, but instead of being incorporated into the reaction, the methanol oxidized and deactivated the catalyst.

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1 SUMMARY

The performance of an iron-copper Fischer-Tropsch catalyst was studied in a slurry continuous stirred tank reactor (CSTR) at 227°C and 790 kPa (100 psig). While extensive Fischer-Tropsch studies have been published with iron-based catalysts in fixed-bed, fluidized-bed, and slurry reactors [Anderson (1956), Schlesinger (1951), Huff (1982)], no published work was found for an iron-copper catalyst in a slurry CSTR. The objectives of this study were to evaluate the catalyst performance on the basis of carbon monoxide conversion and product distribution, and to determine if methanol could be incorporated into the Fischer-Tropsch reaction by adding it continuously to the feed.

Conversion and product distribution data were obtained from gas chromatography and nuclear magnetic resonance (NMR) analysis, flow contraction measurements, and mass balances. The conversions and product distributions obtained with the iron-copper catalyst were within the range reported by other investigators using iron-based catalysts [Huff (1982), Satterfield (1982)]. Overall mass balance closures were between 88% and 94% for carbon and 91% and 99% for oxygen.

Carbon monoxide conversion decreased from 92% to 58% when the flowrate was increased from 0.3 to 0.9 liters/minute, corresponding to an increase in space velocity from 488 to 1570 hr^{-1}. The decrease in CO conversion was caused by a decrease in the average residence time of the gas in the reactor. Product distributions were identical for both 1:1 and 2:1 hydrogen to carbon monoxide ratios in the feed gas, and could be described by a Flory model with an average chain-growth probability (α) of 0.67 ± 0.02, indicating that most of the products (on a weight basis) were in the gasoline range.

While changing the hydrogen to carbon monoxide feed ratio from 2:1 to 1:1 did not affect the product distribution, this change did decrease the CO conversion from 77% to 50% at a space velocity of approximately 950 hr^{-1}. We postulated that the decrease in CO conversion was caused by the lower hydrogen partial pressure in the reactor, but this could not be confirmed due to a partial catalyst deactivation, possibly during the change over from 1:1 back to 2:1 H_2/CO feed gas.

To determine if Fischer-Tropsch reaction products could be incorporated into the production of higher molecular weight products, methanol was added continuously to the reactor feed at a rate of 0.072 ml/min. No noticeable incorporation was observed, and the methanol slowly oxidized and deactivated the catalyst over a period of approximately 12 hours.

Future Fischer-Tropsch studies using this iron-copper catalyst should be carried out over a range of different temperatures and pressures to fully characterize catalyst performance in the slurry reactor. In addition, the reactor should be operated for longer periods of time (over 50 hours) to allow the larger molecular weight products to come to vapor-liquid equilibrium in the slurry phase, thus preventing product accumulation in the reactor and creating fewer errors in product analysis.

2 INTRODUCTION

2.1 Background

Hydrocarbon fuels such as gasoline and diesel fuel can be synthesized by reacting carbon monoxide and hydrogen gas over a metal catalyst. This reaction, known as the Fischer-Tropsch (F-T) synthesis, is an attractive future source of hydrocarbon fuel since the carbon monoxide and hydrogen feed (synthesis gas) can be made directly by coal gasification. Currently, Fischer-Tropsch synthesis is carried out commercially at two plants in South Africa, operated by South African Synthetic Oil Limited (SASOL).

The nominal stoichiometry of the F-T reaction is

$$2H_2 + CO \xrightarrow{\text{metal}} -CH_2- + H_2O \qquad (2\text{-}1)$$

Water produced by this reaction can then participate in the water-gas shift reaction,

$$CO + H_2O \overset{\text{metal}}{\rightleftharpoons} CO_2 + H_2, \qquad (2\text{-}2)$$

which is advantageous because water is consumed. Water is known to inhibit hydrocarbon formation [Huff (1982)]. Also, the water-gas shift consumes carbon monoxide and produces hydrogen, thereby reducing the overall ratio of H_2 used to CO used (usage ratio).

The Boudouard reaction, in which carbon monoxide disproportionates to produce carbon dioxide and carbon, may lead to catalyst deactivation due to coke formation on the metal surface:

$$2CO_{(g)} \longrightarrow CO_{2(g)} + C_{(s)} \qquad (2\text{-}3)$$

To reduce carbon deposition, the fixed and entrained-bed reactors run by SASOL are operated at H_2/CO ratios of 1.8 and 6.0, respectively [Satterfield (1980)]. Lurgi coal gasifiers, which produce synthesis gas with H_2/CO ratios greater than 2.0, are used to achieve the high feed ratios required [Probstein and Hicks (1982)]. Based on thermal efficiency calculations, the most economical production of synthesis gas yields a H_2/CO ratio well below 1.0 [Shinnar (1978)]. Thus, additional costs are incurred by operating at the H_2/CO ratios used in the SASOL F-T synthesis.

The SASOL fixed-bed reactors suffer from poor temperature control and low conversion per pass. The catalyst must be pelletized to minimize crushing. Also, despite the H_2/CO feed ratio of 1.8, carbon deposition and subsequent catalyst deactivation is still a problem. In the entrained-bed reactors, high gas velocities cause attrition of the catalyst. The H_2/CO ratio of 6.0 makes it necessary to have recycle streams 2-3 times the volume of the feed stream, resulting in large capital and energy costs.

An alternative type of reactor which may be used for F-T synthesis is the slurry reactor, in which the reacting gases are bubbled through a paraffin wax containing a suspension of fine catalyst particles. Agitation may be achieved with mechanical stirring in a continuous stirred tank reactor (CSTR) or by the motion of the gas bubbles moving up through a slurry-filled tube in a bubble column reactor (BCR).

The paraffin solvent in the slurry reactor has a thermal mass over 500 times greater than that of the gas in the fixed or entrained-bed reactors, resulting in excellent temperature control (± 1°C) and more efficient heat recovery. Compared to fixed or fluidized-bed reactors, slurry reactors achieve high conversions per pass and high rates of reaction per unit weight of catalyst [Deckwer et al. (1980)]. In addition, slurry reactors can process synthesis gas of low H_2 to CO ratios (0.6 - 0.8) which are typical of coal gasification products [Huff (1982)].

2.2 Previous Work

2.2.1 Fischer-Tropsch Synthesis in Slurry Reactors. The study of the F-T reaction in a slurry phase reactor began in the late 1940's. Kölbel et al. (1955) used an Fe-Cu catalyst in a bubble column reactor and obtained CO conversions in excess of 90% (for certain reaction conditions). A summary of F-T synthesis in bubble columns is shown in Table (2-1).

Huff (1982) performed an extensive F-T study with an iron ammonia-synthesis catalyst in a slurry CSTR. The range of experimental conditions and conversions achieved in his study is presented in Table (2-2). Huff reported CO conversions ranging from 16% to 98% with no evidence of catalyst deactivation. He also reported that analysis of the liquid carrier, octacosane, showed that the heavier, less volatile reaction products accumulated in the reactor until vapor-liquid equilibrium was reached, this effect still being noticeable after 100 hours of operation. In addition, Huff found that the water-gas-shift reaction proceeded to equilibrium at temperatures above 260°C.

Kern et al. (1960) and Raymond et al. (1980) added water to the synthesis gas feed and found that the rate of the water-gas-shift reaction increased while the rate of F-T synthesis nearly stopped, suggesting that the water-gas-shift reaction is much faster than the F-T reaction and that water inhibits F-T synthesis. Feiner et al. (1981) determined that the rate of CO_2 production by water-gas-shift is first order with respect to CO concentration.

2.2.2 Fischer-Tropsch Reaction Kinetics. Although extensive work has been done on Fischer-Tropsch synthesis, the reaction is complicated and involves many unknown intermediates and the exact intrinsic rate expression has yet to be discovered. A detailed discussion of previous work will not be presented here; for a summary of the many proposed intrinsic rate expressions the reader is referred to Huff (1982). In general, however, the rate of F-T synthesis is approximately first order with respect to hydrogen, zero order with respect to carbon monoxide, and inhibited by water. A commonly

Table (2-1)
Summary of Fischer-Tropsch Bubble Column Research
[Modified from Huff (1982)]

Investigator	Reactor	Range of Conditions					Catalyst
		Temperature °C	Pressure MPa	$(H_2/CO)_{feed}$	Space Velocity Gas (S.T.P.)/ Slurry - HR	Catalyst Loading G. Cat./ Slurry	
Kölbel et al. (1955)	6 and 10,000 Bubble Columns	266-268	1.1-1.2	0.67	2500-3125	70-90	Unsupported, precipitated iron promoted with an unspecified amount of K_2O and CuO
Schlesinger et al. (1951)	13.5 Bubble Column	240-275	0.8-1.8	1.0	1009-2330	300	Unsupported, precipitated iron promoted with 62 CuO and 0.5% K_2O
Schlesinger et al. (1954)	13.5 Bubble Column	220-260	2.2	1.0	3470	150	Nitrided, precipitated iron promoted with 64 CuO and 0.4% K_2O; Nitrided, fused-iron promoted with 5% MgO, 0.8% Cr_2O_2, 0.6% SIO_2 and 0.6% K_2O
Hall et al. (1952)	2.4 Bubble Column	265-320	2.2-4.2	2.0	480-2480	150-940	Fused-iron (NH_3 synthesis) promoted with 3% MgO and 0.7% K_2O
Calderbank et al. (1963)	9 Bubble Column	265	1.1-2.2	0.67	2600-14560	10-40	Unsupported, precipitated iron
Mitra and Roy (1963)	6 Bubble Column	240-260	0.8-1.1	1.3	1440-2170	180	Precipitated iron on 30% Kieselguhr promoted with 6% CuO, 2% MgO, 24 CuO, and unspecified amount of K_2O
Farley and Ray (1964)	270 Bubble Column	260-280	1.1	0.7	13000	40	Unsupported, precipitated iron promoted with 1% CuO and 1% K_2O
Sakai and Kunugi (1974)	1 Bubble Column	200-290	1.1-1.4	0.63	?	?	Unsupported, precipitated iron promoted with 0.3% CuO and 0.6% K_2O
Zaidi et al. (1979)	2.8 Bubble Column	250-290	0.9	$(H_2O/CO)_{feed}$=3.5	6070-3200	15-150	Girdler 660 catalyst (33% Cuo, 65% ZnO and 2% Al_2O_3

Table (2-2)
Summary of Huff Slurry CSTR Experimental Run Conditions
(After Huff 1982)

Run	Total Time on Stream, hr	Catalyst Loading,** g/ Slurry	Total Pressure, kPa	Space Velocity, hr^{-1}	H_2/CO Feed Ratio	Temperature, °C	% Conversion		Partial Pressure Out, kPa		Remarks
							Hydrogen	Carbon Monoxide	Hydrogen	Carbon Monoxide	
4	280	0.143	790	1100,1800,2700,5100,8500	1.32	234,249,269	30-53	64-96	360-440	23-170	
8*	860	0.142	790	3300	0.69	232,248,263	16-49	17-59	250-300	290-440	Stirring Speed Investigated
9	680	0.139	445,790, 1480	1500,2300,4000	0.55,0.90,1.81	232,248,263	17-68	16-98	140-920	19-780	
10	144	0.152	790	2300	0.55,0.90,1.81	263	39-61	92	280-470	35-70	
11*	——	0.153	275,445,620,790,960,1130	2300	0.34	248	——	——	60-170	190-720	Stirring Speed Investigated

*Runs 8 and 11 were designed specifically to study mass transfer effects. Only the intrinsic results for these runs are reported here.
**430 g C_{28} carrier for Runs 4, 8, and 9; 400 g C_{28} carrier for Runs 10 and 11.

used rate expression exhibiting these characteristics was proposed by Dry (1976) who used a Langmuir-Hinshelwood kinetic model and assumed that hydrogen reacts with adsorbed reaction intermediates and that CO and H_2O are the major surface intermediates. The following expression resulted:

$$-\frac{d[CO + H_2]}{dt} = \frac{d[-CH_2-]}{dt} = \frac{k\, K_{CO}\, P_{CO}\, P_{H_2}}{[1 + K_{CO}\, P_{CO} + K_{H_2O}\, P_{H_2O}]} \qquad (2\text{-}4)$$

where

k = intrinsic rate constant
K = adsorption equilibrium constant
p = partial pressure

For large values of the $K_{CO}\, P_{CO}$ term, Eq. (2-4) reduces to the simple expression proposed by Andersen (1956):

$$-\frac{d[CO + H_2]}{dt} = \frac{d[-CH_2-]}{dt} = k' P_{H_2} \qquad (2\text{-}5)$$

While Eqs. (2-4) and (2-5) were derived for gas-solid reactions, they may also be applied to slurry reactors in which no mass transfer limitations exist.

2.2.3 Product Selectivity. Although the exact mechanism of the F-T reaction is unknown, a statistical polymerization model derived by Flory (1936) often represents the product distributions obtained. The Flory model, given in Eq. (2-6) assumes that the products are formed by the addition of one carbon unit at a time to the end of a growing chain and that the probability of the addition of a carbon atom to a chain, represented by α, is independent of chain length:

$$M_N = (1-\alpha)\, \alpha^{(N-1)} \qquad (2\text{-}6)$$

where

N = number of carbon units
M_N = mole fraction of molecules with carbon number N
α = chain growth probability given by

$$\alpha = \frac{R_p}{R_p + R_t} \qquad (2\text{-}7)$$

where R_p and R_t are the rates of propagation and termination respectively.

Equation (2-8) is obtained by taking the natural logarithm of both sides of Eq. (2-6):

$$\ln (M_N) = N \ln \alpha + \ln \frac{1 - \alpha}{\alpha} \qquad (2\text{-}8)$$

A plot of $\ln (M_N)$ vs. N gives a slope of $\ln\alpha$ and an intercept of $\ln[(1-\alpha)/\alpha]$.

Under the assumptions of this model, the entire product distribution is determined by one parameter, α. If α is known the distribution can be calculated or, given a product distribution, α can be determined empirically from the slope of the line given by Eq. (2-8). The relationship between α and the product selectivity is shown in Fig. (2-1). As shown in this figure, as α increases, the amount of higher molecular weight products increases, and there are optimum α's for each desired product range (e.g., 0.75 for gasoline and 0.85 for diesel). Figure (2-2) shows the carbon number distributions obtained using Eq. (2-8) for α's at the optimum gasoline and diesel ranges.

An excellent review of previous studies of product distribution behavior is found in Satterfield et al. (1982), who found that Fischer-Tropsch products fit a Flory distribution if all the organic products produced at each carbon number are considered. Chain growth probabilities calculated by Satterfield from other published data ranged from 0.55 to 0.94 and are summarized in Table 2.3. Many of these α's were calculated based on the C_1 and C_2 fractions, since, in most cases, total product distributions were not reported. In these studies, α was insensitive to changes in space velocity (ratio of the volumetric gas feed at STP to the volume of catalyst), but decreased with increasing temperature and decreasing pressure.

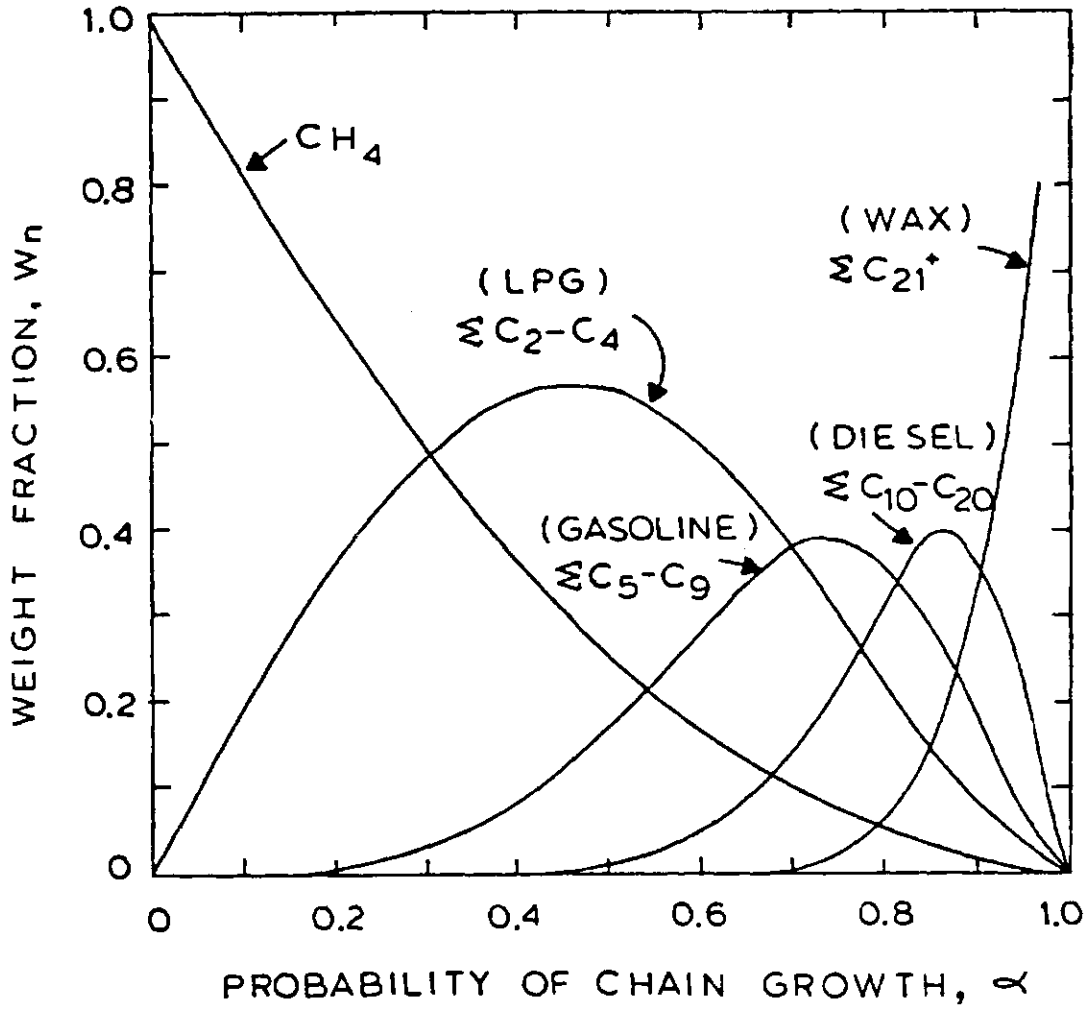
There are several reports in the literature describing Flory distributions with different α's for different carbon number ranges. Huff (1982) reported α's of 0.68 and 0.77 for the C_1 to C_9 and the C_9^+ products, respectively. Huff also found that α values of 0.69 and 0.81 fit the C_1 to C_9 and the C_9^+ fractions reported by Atwood and Bennett (1979). This behavior has been observed by other researchers under a wide variety of reaction conditions [Weingaertner (1956)].

A possible explanation of a double α on a Flory plot is that two different types of catalyst sites are present [Huff (1982)]. On one kind of site, molecules are strongly adsorbed, and consequently longer chained molecules are produced. On the second type, the molecules are not as strongly adsorbed, thus shorter molecules are produced. Anderson (1956) found that higher alkali iron catalysts produce heavier products, suggesting that the double α results from the heterogenous distribution of alkali on the catalyst surface.

2.2.4 **Product Incorporation.** Product incorporation studies are performed by adding hydrocarbons or oxygenates to the F-T feed and observing changes in the products. A shift in product distribution may provide mechanistic information about the F-T reaction and may also result in important

PROBABILITY OF CHAIN GROWTH VS WEIGHT FACTOR

(AFTER SATTERFIELD, ET AL, 1982)



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WEIGHT FRACTION VS CARBON NUMBER

FOR VARIOUS VALUES OF α

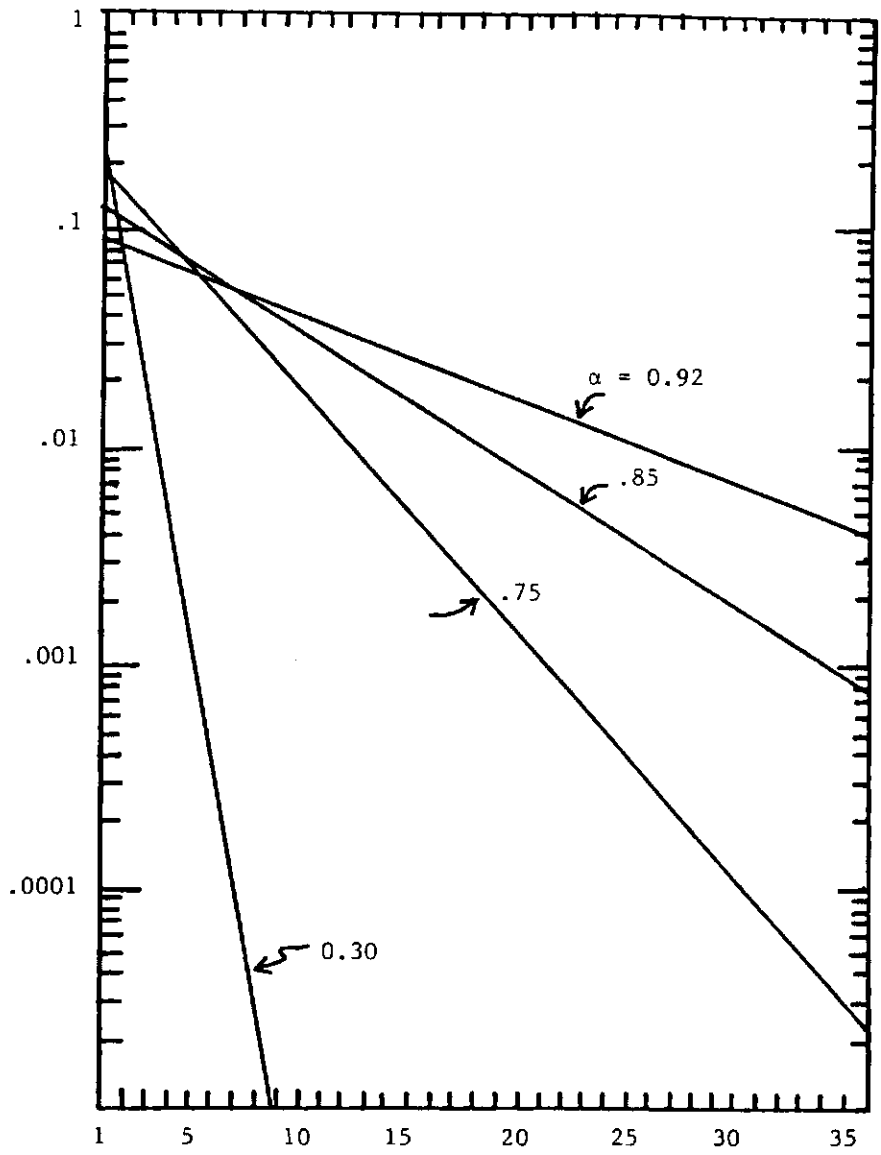

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Table (2-3)
Summary of Published Slurry Reactor Research [After Satterfield (1982)]

Investigation	Probability of chain growth[1]	Basis for estimation	Reaction conditions[2]	Catalyst
Kölbel et al. (1955)	0.84 - 0.85	$C_1 + C_2$	266-268°C, 1.1-1.2 MPa and 2500-3130 hr^{-1}	unsupported, precipitated iron promoted with an unspecified amount of K_2O and Cu
Hall et al. (1952)	0.64 - 0.71	C_1	265-320°C, 2.2-4.2 MPa and 480-2500 hr^{-1}	fused iron (normally used for NH_3 synthesis) promoted with 3% MgO and 0.7% K_2O
Farley and Ray (1964)	0.71 - 0.74	C_1	275°C, 1.1 MPa and 13000	unsupported, precipitated iron promoted with 1% K_2O, 1% Cu and <0.5% each of MnO, TiO_2, CaO, and MgO; 0.1% SO, also present
Schlesinger et al. (1951)	0.76[1]	$C_1 + C_2$	260°C, 1.8 MPa and 300 v/v/h	unsupported, precipitated iron promoted with 6% Cu and 0.5% K_2O
Schlessinger et al. (1954)	0.55 - 0.66[3]	$C_1 + C_2$	220-258°C, 2.2 MPa and 2300 hr	nitrided, fused iron promoted with 5% MgO, 0.6% SiO_2, 0.8% CR_2O_3 and 0.6% K_2O
	0.63 - 0.68[3]	$C_1 + C_2$	259-259°C, 2.2 MPa and 200-300 v/v/h 3500-5200	nitrided, precipitated iron promoted with 6% Cu and 0.4% K_2O
Satterfield and Huff (1982b)	0.67 - 0.71	total mol % organic state, plotted as per eq 12	234-269°C, 0.79 MPa and 60-420 v/v/h 1000-3000	fused iron (normally used for NH_2 synthesis) promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O, 0.7-1.2% CaO, and <0.4% SiO_2
Kölbel and Ralek (1982)	0.64	$C_3 + C_4$	for low molecular weight products: 260-280°C and 1.1 MPa	iron catalyst promoted with alkali-high content for high molecular weight products and low content for low molecular weight products
	0.88	$C_3 + C_4$	for intermediate molecular weight products; about 260°C and 1.1 MPa	
	0.94	$C_3 + C_4$	for high molecular weight products; 240-260°C and 1.1 MPa	

[1]The aqueous phase was reported to contain 25 wt% oxygenates. We have taken ethanol to represent this.
[2]Volume of synthesis gas (STP)/h per volume catalyst.
[3]The aqueous phase was assumed to contain 40 wt % ethanol.