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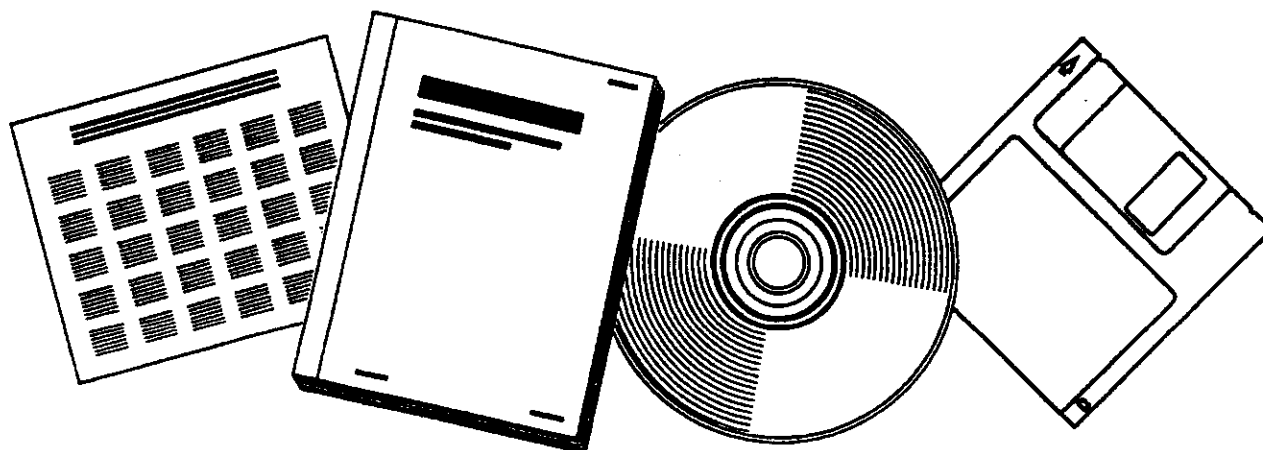
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# FISCHER-TROPSCH SYNTHESIS IN SLURRY REACTOR SYSTEMS. FINAL REPORT

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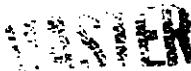
Fischer-Tropsch Synthesis in  
Slurry Reactor Systems

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FINAL REPORT

Department of Chemical Engineering  
and  
Energy Laboratory  
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Cambridge, Massachusetts



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Submitted by:  
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### Summary

The purpose of this grant was to support a variety of studies of Fischer-Tropsch synthesis in a slurry reactor. Experimental reaction studies were performed in a semi-continuous mechanically-stirred autoclave using iron catalysts, primarily a reduced fused magnetite catalyst promoted with potassium, as manufactured for ammonia synthesis. Our findings have been published in 14 papers with 3 more accepted and in press. These are listed below together with the abstracts, which highlight our accomplishments.

### Papers Published

1. C.N. Satterfield and G.A. Huff, Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor," J. Catalysis, 73, 187-197 (1982).

Studies at 234 to 269°C and at 790 kPa showed a precise linear relationship between the log of mole fraction  $m_n$  of products of carbon number  $n$ , and  $n$ , as predicted by the Flory molecular-weight distribution provided that all products, including oxygenated species, are considered. The chain growth probability,  $\alpha$ , increased slightly from 0.67 at 269°C to 0.71 at 234°C.

2. G.A. Huff, Jr., and C.N. Satterfield, "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry Bed. I. Reactor and Trapping Procedures." Ind. Eng. Chem., Fundam., 21, 479-483 (1982).

A mechanically stirred autoclave provides advantages over other types of reactors for fundamental studies of liquid-phase Fischer-Tropsch synthesis, but no information has been published on such use. Particular attention must be paid to obtaining complete suspension of the catalyst, use of noncatalytic materials of construction, and procedures to avoid loss of portions of the wide range of products formed. Many of the aspects of design and operation are applicable to stirred autoclave reactors in general.

3. G.A. Huff, Jr., C.N. Satterfield, and M.H. Wolf, "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry Bed. II. Analysis of Products." Ind. Eng. Chem., Fundam., 22, 258-263 (1983).

A procedure is presented that provides a detailed quantitative analysis of Fischer-Tropsch products from an iron or a cobalt catalyst including oxygenates and hydrocarbons. Notably hydrogen and

water are also determined, so that complete material balances can be obtained on all elements.

4. C.N. Satterfield and G.A. Huff, Jr., "Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor," Seventh International Symposium on Chemical Reaction Engineering, A.C.S. Symposium Series, No. 196, 225-236, 1982.

With a reduced fused magnetite catalyst a substantial gas-to-liquid mass transfer resistance can be encountered, which causes the paraffin-to-olefin ratio of the hydrocarbon products to decrease. Under intrinsic kinetic conditions this ratio increases with hydrogen concentration in the liquid but is independent of carbon monoxide concentration. Hence with significant mass-transfer, this ratio is governed by the resistance to  $H_2$  transfer rather than by the effective  $H_2/CO$  ratio in the liquid.

5. C.N. Satterfield, G.A. Huff, Jr., and R. Summerhayes, "Olefin Addition in Fischer-Tropsch Synthesis on an Iron Catalyst," J. Catalysis, 80, 486-491 (1983).

Contrary to a report by Dwyer and Somorjai, we found no effect on the Flory distribution upon adding ethylene or 1-butene to syngas reacted over a reduced fused magnetite catalyst at 790-1480 kPa and 248°C. The difference is probably because the Dwyer and Somorjai catalyst contained no alkali and it had not reached steady-state activity.

6. G.A. Huff, Jr., and C.N. Satterfield, "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Reduced Fused-Magnetite Catalyst," Ind. Eng. Chem., Process Des. Dev., 23, 696-705 (1984).

The rate of synthesis was measured in a well-mixed continuous flow slurry reactor at 232 to 263°C, 445 to 1480 kPa,  $H_2/CO$  feed ratios of 0.55 to 1.81, and conversions of 17 to 68% of  $H_2$  and 16 to 98% of CO. The inhibiting effects of CO and  $H_2O$  were determined quantitatively and led to the following rate expression:  $-R_{H_2+CO} = ab'P_{CO}^2 / (P_{H_2O} + b'P_{CO}P_{H_2})$ . In most previous kinetic studies the partial pressure

of hydrogen did not vary significantly with conversion so the hydrogen functionality was not clearly established. In our model,  $b'$  is a function of temperature only, but the above expression reduces to the form proposed by Anderson if  $b$  in his expression is inversely proportional to  $P_{H_2}$ .

7. C.N. Satterfield and H.G. Stenger, "Fischer-Tropsch Synthesis on a Precipitated Mn/Fe Catalyst in a Well-Mixed Slurry Reactor," Ind. Eng. Chem. Process Des. Dev., 23, 26-29 (1984).

The olefin/paraffin ratio of the products at all carbon numbers was less than that with a reduced fused magnetite catalyst containing 0.4 to 0.8 wt%  $K_2O$  and the  $\beta$ -olefin/ $\alpha$ -olefin ratio was much greater. Secondary hydrogenation and olefin isomerization reactions appear to be much more significant with the Mn/Fe catalyst. With both catalysts the Flory distribution was followed but in each case two values of the

chain growth probability,  $\alpha$ , were found, with a sharp increase above about  $C_{11}$ . Values of  $\alpha$  based on the  $C_1$ - $C_{10}$  products were less for the Mn/Fe catalyst than for the fused magnetite catalyst, attributed to the absence of potassium in the Mn/Fe catalyst. The activity of the present Mn/Fe catalyst was moderately less than that reported for a similar catalyst studied elsewhere in a bubble column.

8. G.A. Huff, Jr., and C.N. Satterfield, "Evidence for Two Chain Growth Probabilities on Iron Catalysts in the Fischer-Tropsch Synthesis," J. Catal., 85, 370-379 (1984).

New data and reexamination of several previous studies in either fixed bed or slurry liquid reactors with iron catalysts show that the products frequently may be characterized as the sum of two Flory carbon number distributions. In many cases the dominating distribution shifts at about  $C_{10}$ . At higher carbon numbers hydrocarbons are produced with a much higher probability of chain growth than for lower carbon numbers. Results are interpreted in terms of a two-site catalyst structure.

9. C.N. Satterfield and H.G. Stenger, Jr., "Fischer-Tropsch Synthesis in a Slurry Reactor: Precipitated Iron-Copper Catalyst," Ind. Eng. Chem., Process Des. Dev., 23, 849-851 (1984).

The performance of this catalyst in a slurry reactor is compared to that of the same catalyst as reported from fixed-bed reactor studies. Comparison is also made with a reduced fused magnetite catalyst in the same slurry reactor system.

10. G.A. Huff, Jr., and C.N. Satterfield, "Some Kinetic Design Considerations in the Fischer-Tropsch Synthesis on a Reduced Fused-Magnetite Catalyst," Ind. Eng. Chem., Process Des. Dev., 23, 851-854 (1984).

The results of calculations, based on a newly developed kinetic model, show here the extent to which the simple first-order kinetic expression commonly used will be in error, as a function of degree of conversion and other variables. The effect of conversion on  $H_2/CO$  usage ratio is also presented.

11. H.G. Stenger, H.E. Johnson and C.N. Satterfield, "Molecular Weight Distribution of the Heavy Wax Fraction from Fischer-Tropsch Synthesis," J. Catal., 86, 447-480 (1984).

The molecular weight distribution for wax from a reduced fused magnetite catalyst corresponded to  $\alpha = 0.89$ - $0.90$  in the Flory distribution. That from a precipitated Fe-K-Cu catalyst corresponded to  $\alpha = 0.92$ . Gel chromatography and high-temperature gas chromatography gave essentially the same results. Molecular weights corresponding to carbon numbers as high as  $C_{105}$  were identified. There was no evidence for any limit on the maximum molecular weight product produced.

12. C.N. Satterfield, H.G. Stenger, Jr., "Effect of Liquid Composition on the Slurry Fischer-Tropsch Synthesis, I. Rate of Reaction.", Ind. Eng. Chem., Process Des. Dev., 24, 407-411 (1985).

With a reduced fused magnetite catalyst, the rate of reaction in the presence of phenanthrene is nearly twice that observed in the presence of n-octacosane even though the solubility of H<sub>2</sub> and CO is moderately less in phenanthrene. The rate in the presence of triphenylmethane was about the same as in n-octacosane. In the presence of a perfluoropolyether, the rate of reaction was markedly reduced, even though H<sub>2</sub> and CO solubilities are much higher than in hydrocarbons. This was attributed to substantial mass transfer resistances through an encapsulating hydrocarbon layer around the catalyst particles. The effect of the nature of a liquid on several other reactions is also discussed.

13. H.G. Stenger, C.N. Satterfield, "Effect of Liquid Composition on the Slurry Fischer-Tropsch Synthesis, II. Product Selectivity.", Ind. Eng. Chem., Process Des. Dev., 24, 411-415 (1985).

With a reduced, fused magnetite catalyst, secondary reactions, consisting of olefin hydrogenation, olefin isomerization, and incorporation of ethylene and/or ethyl alcohol into product, were slightly greater in octacosane than in phenanthrene at 232°C but essentially the same at 263°C. This is attributed to competitive adsorption effects with phenanthrene which adsorbs significantly onto the catalyst at 232°C, but not at 263°C. All secondary reactions are enhanced by conditions minimizing CO adsorption. Oxygenates were greatly diminished at high conversions. C<sub>2</sub> incorporation into product stops chain growth by a scavenging effect. In the presence of a perfluoropolyether (Fomblin), in which hydrocarbons are immiscible, catalyst is preferentially wetted by hydrocarbons and secondary reactions are greatly enhanced by mass transfer resistances.

14. H.G. Stenger, Jr., C.N. Satterfield, "Effects of Sulfur Poisoning of a Reduced Fused Magnetite Catalyst in the Fischer-Tropsch Synthesis.", Ind. Eng. Chem., Process Des. Dev., 24, 415-420 (1985).

Addition of H<sub>2</sub>S to synthesis gas with catalyst suspended in octacosane increased catalyst activity by 60% at a sulfur loading of 1.3 mg of S/g of Fe, beyond which catalyst activity decreased. Dibenzothiophene (DBT) present in phenanthrene during catalyst activation did not exhibit this effect. The two poisons reduced activity comparably at loadings of about 10 mg of S/g of Fe. Unlike H<sub>2</sub>S, DBT caused a marked drop in selectivity to form methane and an increase in olefin/paraffin ratio of products, indicating that it decreased the hydrogenation capability of the catalyst. Effects of the two poisons on olefin isomerization and oxygenate concentrations are also presented.

15. G.A. Huff, Jr., and C.N. Satterfield, "Liquid Accumulation in Catalyst Pores in a Fischer-Tropsch Fixed Bed Reactor," Ind. Eng. Chem., Process Des. Dev., accepted and in press.

Some reports of catalyst preparations that purportedly minimize high molecular weight products may be misleading in that such products

may have accumulated in catalyst pores and insufficient time may have been allowed for the effluent to represent the true intrinsic kinetics.

Mathematical simulations here show the effect of pressure, temperature, rate constant, feed composition, space velocity and Flory parameter  $\alpha$ , on time required for pores to fill, upon liquid product distribution and vapor composition leaving the reactor. The pore filling rate and condensed product composition vary with position through the reactor but not with time. The maximum filling rate does not occur at the same position in the bed as the maximum synthesis rate. For reaction conditions of industrial interest, the greatest effect is caused by the assumed carbon number distribution of the products. A rigorous parameter to generalize the results is not immediately evident.

16. D.K. Matsumoto and C.N. Satterfield, "Solubility of Hydrogen and Carbon Monoxide in Selected Non-Aqueous Liquids," Ind. Eng. Chem., Process Des. Dev., accepted and in press.

New data at elevated temperatures and pressure are reported for n-octacosane, phenanthrene and Fomblin, a perfluorinated polyether, and compared to previous literature on a variety of liquids. When hydrogen solubilities are reported on a volumetric basis, substances of a similar chemical nature have very similar solubilities.

17. T.M. Bartos and C.N. Satterfield, "Effects of Finely Divided Solids on Mass Transfer Between a Gas and an Organic Liquid," A.I.Ch.E. J., submitted.

Interfacial area,  $a$ , was determined here by the so-called "chemical method" (unsteady-state absorption with simultaneous chemical reaction in the "fast-reaction regime") using the reaction of  $\text{CO}_2$  with cyclohexylamine (CHA) in a solution of 90% toluene and 10% isopropanol. The overall mass transfer coefficient,  $k_L a$  was determined by the unsteady state desorption of helium from the same liquid into a nitrogen purge stream. The solid properties investigated were particle concentration (0-45 volume%), size (35-200  $\mu\text{m}$ ), density (0.7-4.5 g/ml), and composition (glass, polytetrafluoroethylene, polypropylene). The effect of gas phase mixing upon the calculation of these parameters was also evaluated. Studies were made in a one-liter aerated and mechanically-agitated reactor.

The overall mass transfer coefficient and the interfacial area decreased linearly with inert solids loading. The decrease in  $k_L a$  can be attributed to the decrease in  $a$ :  $k_L$  was independent of solids loading for the conditions of this study. Gas holdup did not vary with inert solids loading, indicating that the decrease in  $a$  was due to bubble coalescence.

Both  $k_L a$  and  $a$  were independent of particle size for particle sizes below 200  $\mu\text{m}$ . Both were also independent of particle density. Stirring speed was shown to be an appropriate basis for comparison of mass transfer parameters. At high solids loadings  $k_L a$  and  $a$  were lower when the solids were relatively nonwetting. A mechanism for enhanced bubble coalescence was postulated.

The use of an apparent viscosity for prediction of mass transfer can be misleading because results differ depending upon whether a viscosity increase is caused by addition of solids, or, e.g., by addition of a high viscosity fluid.