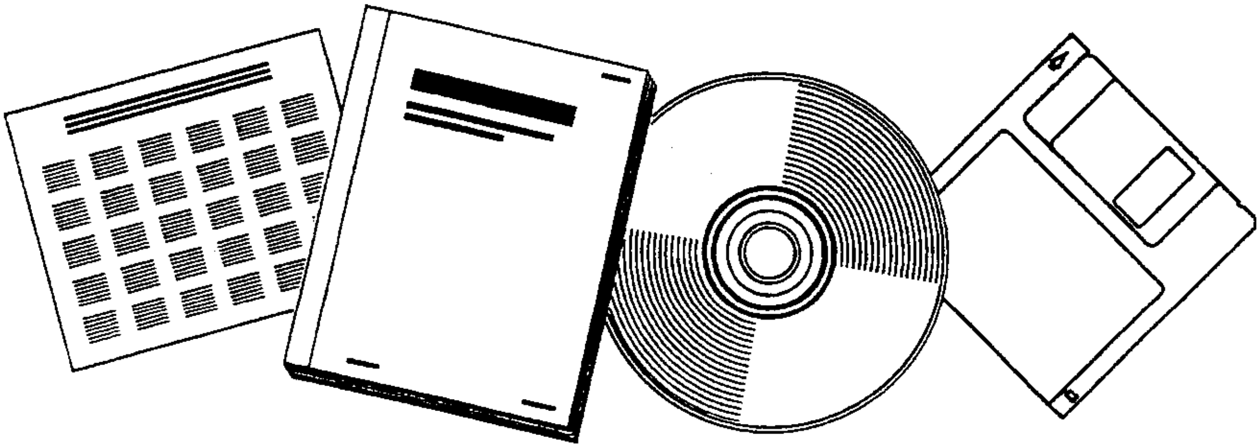
DE81027010 40771-1

FISCHER-TROPSCH SYNTHESIS IN SLURRY REACTOR SYSTEMS. TECHNICAL PROGRESS REPORT FOR PERIOD ENDING JULY 31, 1981

MASSACHUSETTS INST. OF TECH., CAMBRIDGE

1981



DOE/PC/40771-1

Fischer-Tropsch Synthesis in Slurry Reactor Systems

MASTER

Technical Progress Report for Period Ending
July 31, 1981

Department of Chemical Engineering
and
Energy Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

Report No.: DOE/PC40771-1
Grant No.: DE-FG22-81PC40771

Submitted by
C.N. Satterfield
G.A. Huff, Jr.

I. SUMMARY

This is the first technical progress report on this grant, which had an effective date of initiation of March 9, 1981. During this period we have obtained preliminary experimental results on the effects of reactant transport across the gas-liquid interface on synthesis gas conversion and product selectivity, utilizing an iron catalyst in a laboratory-scale, well-mixed slurry reactor. These are described in more detail below.

During the period before March 9, 1981, studies proceeded with limited financial support from other sources. Several papers have been prepared for publication on this earlier work and to provide background they are listed below. A copy of each is appended.

1. C.N. Satterfield and G.A. Huff, Jr. "Usefulness of a Slurry-Type Fischer-Tropsch Reactor for Processing Synthesis Gas of Low Hydrogen-Carbon Monoxide Ratios", *Can. J. Chem. Eng.*, in press.
2. C.N. Satterfield, G.A. Huff, Jr., and H.G. Stenger, "Effect of Carbon Formation on Liquid Viscosity and Performance of Fischer-Tropsch Bubble-Column Reactors", *Ind. Eng. Chem., Process Design Develop.*, in press.
3. 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. Cat.*, submitted.
4. C.N. Satterfield, G.A. Huff, Jr., and J.P. Longwell, "Product Distribution from Iron Catalysts in Fischer-Tropsch Slurry Reactors", *Ind. Eng. Chem., Process Design Develop.*, submitted.

Preprints removed.

II. DETAILED RESULTS

In our one-liter, mechanically-agitated, slurry reactor, gas bubble size decreases as the shear rate at the impeller increases. We can thus alter the degree of gas-to-liquid mass transport by varying the degree of agitation while minimizing the effect on other reaction variables. During this past period, we have performed experiments that will enable us to understand the effects of mass transfer on catalytic activity and product selectivity.

We employed a fused-iron catalyst (from United Catalysts, Inc. and designated C-73) normally employed for ammonia synthesis. It was crushed to a particle size smaller than 45 microns (325 A.S.T.M. sieve) and pre-reduced in a separate vessel with hydrogen at 400-425°C for 72 hours at atmospheric pressure and space velocity of 5000 cm^3 gas/cm^3 catalyst-hr. It was then slurried with the liquid carrier (normal octacosane) to product a 15 weight-percent suspension, based on unreduced weight. Synthesis gas with a H_2/CO ratio of 0.68 was passed into the reactor which was held at 100 psig. Temperature was varied from 232 to 263°C. Synthesis gas flow was maintained at 160 cm^3 gas (S.T.P.)/cm^3 liquid carrier-hr. Steady-state operation was rapidly achieved with the iron catalyst and activity declined by only 4% after 1000 hours of continuous operation, as observed by repeating an initial run. With the low hydrogen to carbon monoxide feed ratio, we were attempting to match the feed and usage ratios, which varied from 0.55 to 0.71 over the course of the experiments. If this is not done, separating mass transfer from intrinsi effects is complicated as the hydrogen to carbon monoxide ratio in the reactor will vary considerably with conversion. Finally, cold studies in a transparent mock-up indicated that the dense iron catalyst did not settle on the reactor bottom at stirring speeds above 200 RPM. Experiments with several types of agitators showed that the most effective design for suspension of catalyst consisted of a propellor arranged above a six-bladed turbine.

Figure 1 depicts the results of changing the stirring speed on hydrogen plus carbon monoxide conversion over the three temperatures. In all cases, intrinsic kinetics are observed at stirring speeds above 500 RPM. The data are replotted in Figure 2 on a reduced basis relative to that for conversion free of mass transport limitations. The curve for the lowest temperature, 232°C, is the highest of the three. This would be expected on the basis of theory. Mass transfer effects become more pronounced at higher temperatures since the intrinsic activation energy of the Fischer-Tropsch synthesis (about 27 kcal/mol) is much greater than the activation energy for mass transfer which is typically only 3 to 5 kcal/mol.

Preliminary data on product selectivity indicate that the paraffin to olefin ratio increases with stirring speed in the mass-transfer-limited domain. In the absence of mass transfer, we find that this ratio increases with higher hydrogen concentrations in the liquid carrier. In other words, as the reaction becomes starved for hydrogen under mass transfer influenced conditions, the reaction rate decreases as evidenced by lower reactant conversions and the paraffin to olefin ratio declines.

III. FUTURE WORK

During the next few months, we will be expanding our base of intrinsic kinetic data over the iron catalyst in order to better understand the effects of reaction variables on product selectivity.

This information will allow us to develop preliminary models for analyzing the mass transfer data. Although there exists an abundance of published Fischer-Tropsch studies, few investigations have been conducted under a carefully controlled environment so as to understand the effect of individual reaction variables on catalyst selectivity and activity.

We have had a number of inquiries about the detailed design of our reactor, trapping procedures and analytical system. Hence we are preparing detailed reports on these which we expect to be completed during the next quarter. Our g.c. analytical equipment provides highly detailed analyses. Most peak assignments have been clearly established by spiking experiments with known compounds but a few uncertainties remain, largely with respect to a few oxygenated compounds. We are subjecting some representative product samples to gas chromatographic/mass spectrometry analysis to resolve the matter.

An important question in Fischer-Tropsch synthesis is the extent to which α-olefins, the primary products, may be reincorporated into new growing hydrocarbon chains, since this can have a major effect on the overall product distribution. Recently Dwyer and Samorjai (<u>J. Catalysis</u>, <u>56</u>, 269 (1979)) presented data that indicated that incorporation of ethylene or propylene into growing chains was a significant secondary reaction on an iron catalyst that markedly affected the value of α in the Flory-Schulz distribution. Our studies under intrinsic kinetic conditions show no effect of degree of conversion on α, which indicates that under our conditions the phenomenon does not occur. To help resolve the question we are embarking on a short study with synthesis gas spiked with ethylene, to see if the product distribution is altered from that observed in the absence of ethylene.

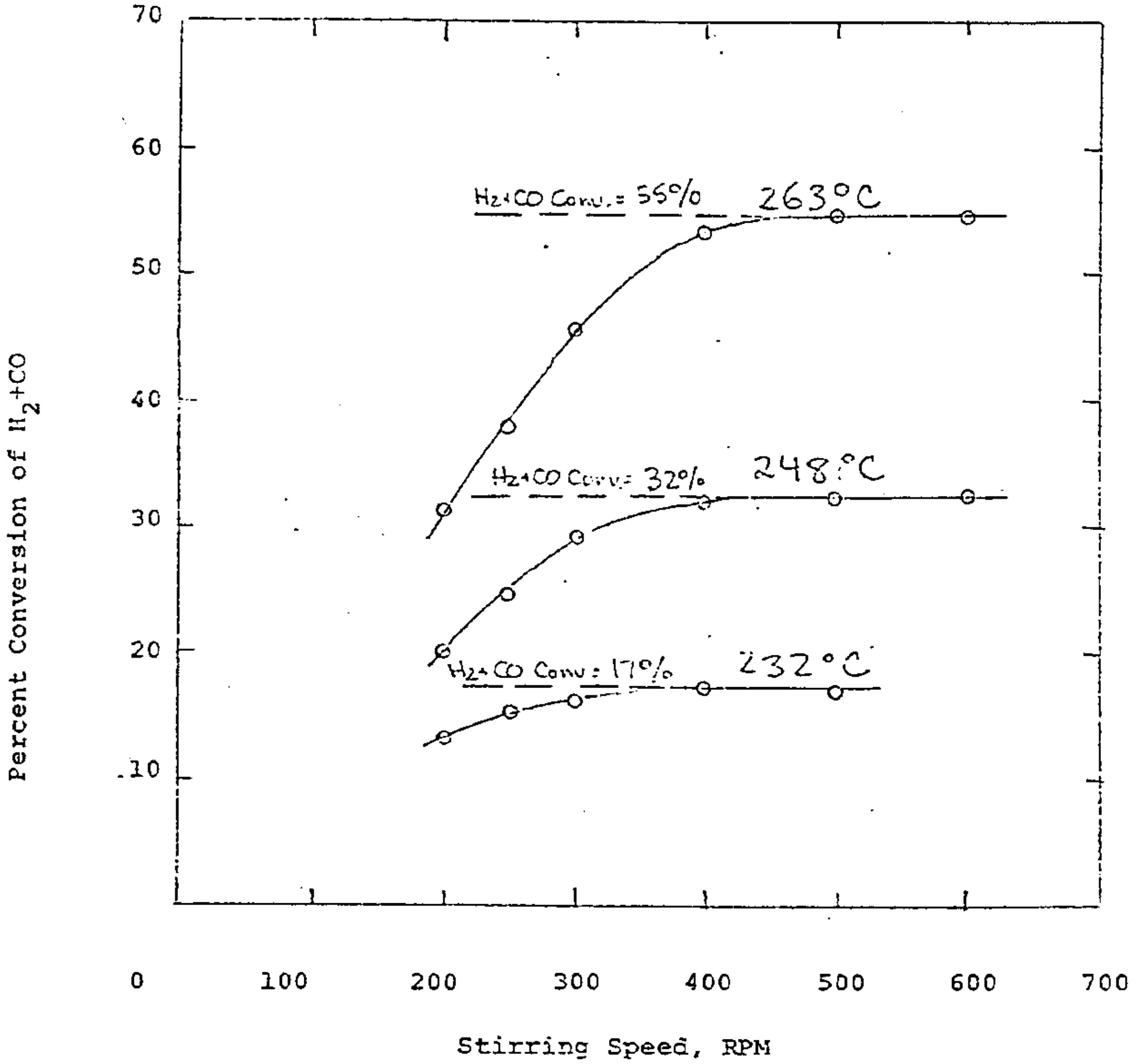


Figure 1 Effect of Gas-Liquid Mass Transfer on Synthesis Gas Conversion over an Iron Catalyst in a Slurry Reactor

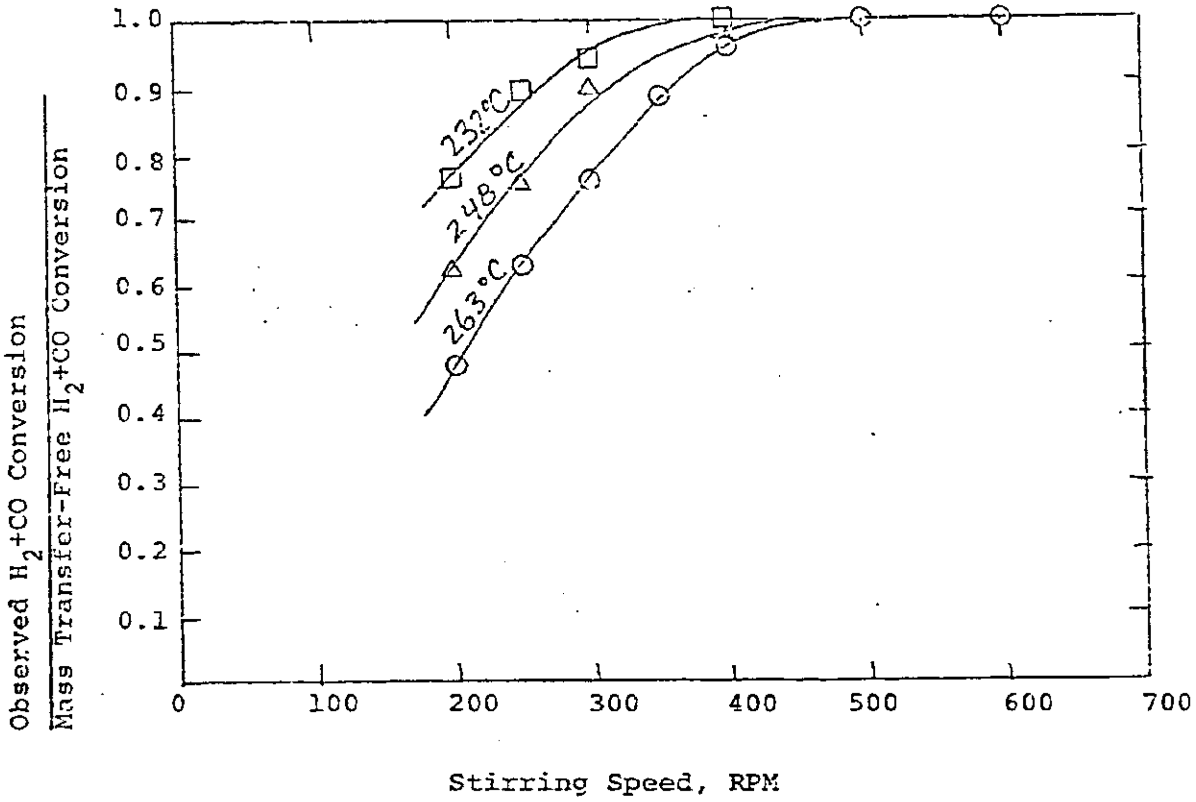


Figure 2 Effect of Gas-Liquid Mass Transfer on a Reduced Basis over an Iron Catalyst in a Slurry Reactor