



DE90004174

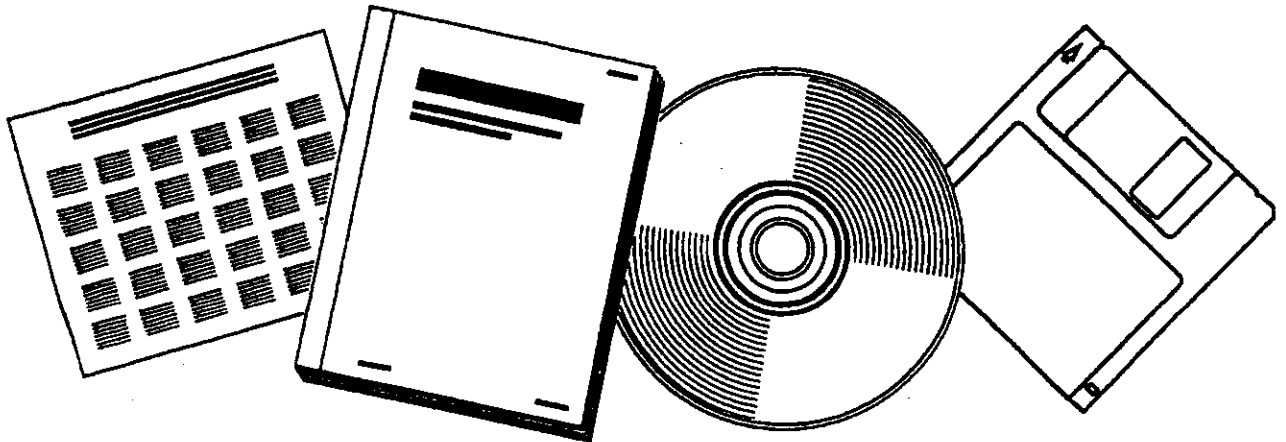
80015 T-5

NTIS[®]
Information is our business.

FISCHER-TROPSCH SLURRY PHASE PROCESS VARIATIONS TO UNDERSTAND WAX FORMATION. FINAL TECHNICAL REPORT

MASSACHUSETTS INST. OF TECH., CAMBRIDGE.
DEPT. OF CHEMICAL ENGINEERING

OCT 1989



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

FISCHER-TROPSCH

DE90004174



**FISCHER-TROPSCH SLURRY PHASE PROCESS VARIATIONS TO UNDERSTAND
WAX FORMATION**

Final Technical Report

By
Charles N. Satterfield
Robert T. Hanlon
David K. Matsumoto
Timothy J. Donnelly
Ian C. Yates

October 1989

Work Performed Under Contract No. AC22-85PC80015

For
U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Massachusetts Institute of Technology
Cambridge, Massachusetts

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

Price: Printed Copy A04
Microfiche A01

**FISCHER-TROPSCH SLURRY PHASE
PROCESS VARIATIONS TO UNDERSTAND
WAX FORMATION**

Final Technical Report

Charles N. Satterfield

Robert T. Hanlon

David K. Matsumoto

Timothy J. Donnelly

Ian C. Yates

Department of Chemical Engineering
Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

October 1989

Prepared for the

U.S. Department of Energy

under

Contract No. DE-AC22-85PC80015

Table of Contents

	<u>page</u>
Introduction	1
1A. Effect of Potassium Secondary Reactions	1 4
1B. Comparison of Performance of Selected Iron Catalysts Activity for Synthesis Water-Gas-Shift Activity	5 7 9
1C. Possible Incorporation of Olefins into Growing Chains High Conversion Region	9 11
1D. Synthesis Gas Composition Light Products	12 12
1E. Poisoning by Sulfur Compounds	14
2A. Wax Analyses Discussion of α_2 for Heavier Products	16 18
2B. Theoretical Analysis of Data to Determine C-number Product Distributions	19
2C. Observed Product Distribution during Start-Up (Fused Magnetite)	21
2D. Effect of Water	21
3A. Performance Testing	22
3B. Effect of CO ₂ on Fischer-Tropsch Kinetics	23
References	
Figures	
Tables	
Appendix A Papers Published	
Appendix B Performance Testing in a Mechanically- Stirred Reactor	

Executive Summary

Use of a slurry-type reactor with an iron catalyst for Fischer-Tropsch synthesis from low H_2/CO syngas offers the potential advantages of excellent temperature control, flexibility in catalyst addition and removal and internal water gas shift. The most important likely process variations were studied here to determine how they affect product selectivity. A C-73 reduced fused magnetite was used as a base-line catalyst since it is mechanically rugged and resistant to process upsets, but several precipitated iron catalysts were also studied and the performances of the various catalysts are compared. The precipitated catalysts are more active on a weight basis, but they may break up more readily and may be more readily deactivated by process upsets. If heavy wax is to be hydrocracked in a subsequent processing step, as presently visualized, it will be necessary to reduce catalyst fines to an extremely low level to avoid plugging in a downstream hydrocracker. Carbon number distribution is directed more to heavy products by increased potassium content, as has been previously established, but is also affected by the way in which potassium is chemically combined.

We find no evidence that 1-olefins are incorporated into growing chains to any significant extent under representative process conditions. Instead they are isomerized to form the 2-olefins or are hydrogenated to a paraffin. The C-number product distribution on all iron catalysts studied presents a double- α on a Schulz-Flory plot, breaking at about C_{10} . The chain growth

probability is greater at C₁₀⁺ than at C₁₀⁻. Contrary to previous reports a single α distribution is not found in the absence of potassium.

We have also developed an improved method of analyzing product distribution data. For C₁₀⁻ products, there is no significant effect of H₂/CO ratio on α , over a very wide range. With proper analysis we show good agreement between our results and those of other investigators.

The increase in average carbon number with increased potassium content seems to be related to an increase in the fraction of total product formed by the mechanism leading to α_2 . α_2 decreases significantly with increased temperature. At temperatures above about 300°C a variety of new products appear, probably formed by secondary alkylation reactions.

Information is provided on changes in product distribution during start-up, effect of water content, and correlations of these with composition of the iron catalyst as determined by Mossbauer spectroscopy. CO₂ in the system is an inert gas as such but can cause reaction inhibition through formation of H₂O by the reverse water-gas shift. More details are provided in a series of published papers. Appendix A lists these together with an abstract of each.

Reliable performance testing in a slurry reactor requires meticulous attention to operating procedures and methods of product trapping and analysis. Useful methods based on our many years of experience are discussed in detail in Appendix B.

Introduction:

The only currently operating commercial Fischer-Tropsch plants in the world are at SASOL in South Africa. They utilize an iron catalyst in either fixed bed or entrained bed reactors, feeding synthesis gas derived from coal. Considerable recycling is involved to suitably adjust feed gas composition. In contrast a slurry-type reactor offers the operating advantages of excellent temperature control and flexibility in catalyst addition and removal. An iron catalyst is cheap and in many formulations is active for the water-gas-shift. Thus syngas of low H_2/CO ratio as can be produced by modern coal gasification plants can be fed directly to the slurry reactor and internal water gas shift makes an external shift reactor unnecessary.

Present D.O.E. focus of attention is to develop a process that will maximize production of diesel and jet fuel ($C_{10}-C_{20}$) by optimization of the Fischer-Tropsch synthesis combined with secondary hydrocracking of C_{20+} wax products. The objective of this work was to study several process variations that need to be understood to put a commercial plant into operation. We pioneered the use of a laboratory-scale mechanically stirred autoclave system for Fischer-Tropsch studies over 10 years ago and have published extensively on our results. A particular advantage of this system in contrast to, e.g., bubble column reactors, is that the contents are uniform, thus allowing kinetic and product information to be obtained unambiguously without the intrusions of hydrodynamic effects.

The results are organized as follows:

- (1A) effect of potassium;
- (1B) comparison of the performance of several iron catalysts of industrial interest;
- (1C) possible incorporation of olefins into growing chains;
- (1D) effect of synthesis gas composition;
- (1E) poisoning effects.

To interpret these results four additional topics were studied:

- (2A) wax analyses;
- (2B) theoretical studies of methods of analyzing data for prediction of product distributions;
- (2C) observed product distribution during start-up;
- (2D) effect of water on products.

In addition, we have prepared two supplemental studies:

- (3A) a critical analysis of performance testing in a slurry reactor; and
- (3B) the effect of CO₂ on the kinetics of Fischer-Tropsch synthesis.

These topics are summarized in the following:

1A. Effect of Potassium

The carbon number distribution from alkalized iron catalysts

has been found to follow a modified Schulz-Flory distribution with two chain growth probabilities. Such a distribution is sometimes referred to as a "double- α ," and suggests that two independent chain growth mechanisms contribute to the overall distribution. Schliebs and Gaube (1985) have hypothesized that these stem from potassium-promoted and potassium-free sites, and they present some data in support of their position. Our data, in contrast, indicate that a double- α distribution is clearly observed even on an unalkalized iron catalyst, as will be shown.

Our study was made with a PETC catalyst without potassium, the same catalyst with 1% K addition (at M.I.T.) and the Ruhrchemie catalyst, which contains K. Compositions are given in Table 1.

Reactor temperature was varied between 230 and 265°C. Pressures were varied from 0.77 to 2.98 MPa and H₂/CO feed ratios from 0.5 to 2.0. Conversions were varied from 10 to 65% by changing space velocity between 0.010 and 0.040 Nl/min/g_{cat}. The experiments with the Ruhrchemie catalyst were performed at H₂/CO feed ratios near 0.7, with temperature, pressure, and space velocity varied to study their effects. The PETC catalyst was studied under a range of H₂/CO ratios as well. Some of the conditions were chosen to allow comparison with data reported in the literature for other iron catalysts.

Representative results for the unalkalized catalyst are shown on Figures 1 and 2. For the conditions studied, α_1 is 0.64 and α_2 is 0.88. Fig. 2 is a Schulz-Flory diagram of a wax

sample taken after the first 170 hours-on-stream with the reactor held at the same conditions. The value of α_2 calculated by the non-linear regression of the volatile sample agrees with that calculated by linear regression of the wax sample (C₂₅-C₃₅ range), and is equal to 0.88.

Schliebs and Gaube (1985) and Konig and Gaube (1983) have reported that, in the absence of alkali promoters, the hydrocarbon products of the Fischer-Tropsch synthesis on precipitated iron catalysts can be described by a single- α . We do not find this to be the case. Atomic absorption spectroscopy by Galbraith Laboratories on two samples of the PETC catalyst detected no potassium or sodium at the measurable limits of 9 and 12 ppm. Dictor and Bell (1986b) and Itoh et al. (1988) have also reported that products from unalkalized Fe₂O₅ powders could not be described well by a single- α . Re-analysis of data from Schlieb's thesis (1983) by Donnelly et al. (1988) shows that the data reported by Schliebs and Gaube (1985) are not representative of typical experiments. In fact, all of the data collected by Schliebs on potassium-promoted and potassium-free precipitated iron require two values of α to be fit properly.

The carbon number distributions from the Ruhrchemie catalyst are described by two chain growth probabilities, with α_1 increasing from 0.66 at 260°C to 0.76 at 232°C. α_2 is nearly constant at 0.90. We found relatively little variation of α_1 in this temperature range for the C-73 fused magnetite catalyst. α_2 remained constant in this range, but decreased from 0.90 to

0.79 if the temperature was further increased to 310°C. (See 2.A.)

Addition of K to the PETC catalyst increased the average molecular weight of products, as would be expected (Table 2).

Secondary Reactions:

The extent to which observed products represent the primary synthesis versus secondary reactions depends on several variables. The consensus from many investigators is that, under the usual conditions of synthesis, the primary hydrocarbon products from iron catalysts are mostly 1-alkenes and some n-alkanes. For at least some iron-based catalysts, including an iron/manganese oxide catalyst, fused magnetite and a precipitated iron catalyst containing potassium but no Cu or SiO₂, the hydrocarbon formed by chain growth was predominantly the 1-alkene.

The 1-alkene may subsequently be hydrogenated to a n-alkane or isomerized to the 2-alkene. For a range of conditions, it appears that alkanes are produced predominantly by secondary hydrogenation of 1-alkenes. Increasing potassium content reduces the activity for the secondary reactions, especially isomerization, as does increased temperature. Fig. 3 shows a set of our results under conditions when secondary reaction was relatively minor.

In one of our studies with fused magnetite catalyst (0.31 wt.-% potassium and 64 wt.-% iron), unbranched 1-butene, 1-hexene, and 1-decene were added to the reactor during Fischer-

Tropsch synthesis (248°C and 0.78 to 1.48 MPa). The degree of alkene reaction increased markedly at high synthesis gas conversions, attributed to a decrease in competitive adsorption with carbon monoxide. At synthesis gas conversions (CO+H₂) on the order of 70 to 80%, 40 to 80% of the added 1-alkene reacted, forming the corresponding n-alkane or 2-alkene. There was little if any incorporation into chains. (Sect. 1C.)

There have been various attempts in the literature to ascribe one or more values of α to each class of product, but this can be of fundamental significance only if secondary reactions can be shown to be unimportant under the conditions chosen.

On the unalkalized catalyst the only oxygenate observed was methanol. In contrast, oxygenates up to C₆ to C₇ were observed on catalysts with potassium. 2-Alkenes are observed in the absence of potassium, but are not significant in the presence of potassium. The isomerization of 1-alkene to 2-alkene suggests the existence of some acidic functionality on the unalkalized catalyst, which is eliminated by the addition of potassium. 2-Alkenes, once formed, are less readily hydrogenated than the 1-alkene.

Further details are given in papers by Hanlon and Satterfield (1988), Matsumoto and Satterfield (1989), and Donnelly and Satterfield (1989).

1B. Comparison of Performance of Selected Iron Catalysts.

A substantial amount of data have been presented in the

literature, but little effort has been made to compare detailed selectivity and activity information. In most previous work, catalysts have not been studied long enough to ensure that steady-state behavior was attained. We focused our comparisons on catalysts tested for long times-on-stream.

Table 3 shows a detailed comparison of product cuts from several iron catalysts. Prior to potassium addition, products collected over the unalkalized PETC catalyst followed a distribution similar to those obtained using the C-73 fused iron catalyst (Huff, 1982). After potassium addition, the products from the PETC catalyst followed a distribution similar to products from the alkalinized PETC catalyst used by Zarochak et al. (1985), a Mobil low-wax catalyst discussed by Kuo (1983,1985), and the Ruhrchemie catalyst studied in this laboratory.

The alkalinized PETC catalyst tested by Zarochak was prepared by the same technique as the unalkalinized catalyst we tested, except that 0.3 wt-% potassium was added by an incipient wetness technique.

The Mobil low-wax catalyst is an iron/copper/potassium catalyst with no alumina or silica, but further details have not been reported. The Mobil high-wax catalyst has the same nominal composition as the low-wax catalyst, but 40% less surface area. The Mobil low-wax data quoted here were taken from run CT-256-2, while the high-wax results were drawn from CT-256-13. The activities we report for the Mobil catalysts represent our assumption that space velocity was reported on a basis of grams

of iron, rather than grams of unreduced catalyst.

Some information on the performance of the fixed bed catalyst used by SASOL has been published by Caldwell (1980). He reports hydrocarbon selectivities normalized to exclude oxygenates. We cannot determine the activity of the SASOL catalyst from published data.

The United Catalysts C-73 is a reduced fused magnetite catalyst, which we have studied extensively in this laboratory. The C-73 catalyst is sold for use in ammonia synthesis and contains 64.4 wt.-% Fe, 0.76 wt.-% Al, and 0.31 wt.-% K (Galbraith). There is also a small amount of silica present, which may convert much of the potassium to an inactive form during fusion.

The Mobil catalysts and the SASOL fixed bed catalyst show the highest selectivities to heavy products (C_{10+}). The selectivity of the Ruhrchemie catalyst studied here is comparable to that of the precipitated alkalized catalyst tested by Zarochak et al. (1985). The C-73 catalyst shows the greatest selectivity to light products, which may reflect a very low effective potassium content, but since the precursor is fused magnetite it offers the advantage of high mechanical strength and high density, both of which would be important for a commercial slurry reactor.

Activity for Synthesis

The activities of catalysts are compared on the basis of mmol ($CO+H_2$) converted/min/g_{cat}, with grams of catalyst on an

unreduced basis. This alleviates the difficulties associated with determining the active stable phase of the catalyst under reaction conditions. We have picked sets of experimental conditions as similar as possible, for which conversions and other relevant data have been reported.

The comparison in Table 3 indicates that the iron/copper/potassium Mobil catalysts and the alkalinized precipitated iron catalyst tested by PETC have the highest activities. The C-73 catalyst studied by us and by Bukur and Brown (1987) shows a somewhat lower rate of conversion than the Ruhrchemie catalyst; however, if the rate is assumed to have a first-order dependence on hydrogen pressure, the activities of the two catalysts ($\text{mmol CO} + \text{H}_2 \text{ converted/min/g}_{\text{cat}}/\text{MPaH}_2$) are comparable. The unalkalinized PETC catalyst we tested deactivated continuously, and so was excluded from the comparison.

The relatively high potassium loading of the Ruhrchemie catalyst may decrease its activity, as suggested by Dry (1981) based on data from SASOL precipitated iron catalysts. Dry shows that silica supported Fe_2O_3 promoted by K_2O decreases in activity above some critical loading of potassium, but simultaneously increases its selectivity to heavy products. We speculate that the SASOL fixed bed reactors are operated with high-potassium catalysts to maximize wax selectivity and that high pressures are used to compensate for the activity loss incurred by the high alkali loading.

Water-Gas Shift Activity

Table 3 also compares water-gas shift activity of four catalysts by using reaction quotients:

$$RQ = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad (1)$$

The reaction quotient for water-gas shift on the Ruhrchemie catalyst is very low relative to that of other catalysts. The alkalized precipitated iron PETC catalyst and the Mobil low- and high-wax catalysts have relatively high reaction quotients. Continuous deactivation of the unalkalized PETC catalyst prevents its inclusion in this comparison.

At temperatures of interest in the Fischer-Tropsch synthesis, equilibrium is largely to CO_2 and H_2 , so a more intuitively obvious measure of the relative activity of these catalysts is given by the extent of reaction as represented by:

$$X_{WGS} = \frac{P_{CO_2}}{P_{CO_2} + P_{H_2O}} \quad (2)$$

For the Ruhrchemie catalyst, the extent of the water-gas shift reaction as defined by eq. (2) is about 35% at 263°C, as compared to about 90% for the C-73 catalyst.

Further details are presented by Donnelly and Satterfield (1989).

1C. Possible Incorporation of Olefins into Growing Chains.

As noted above, it is now well documented that the hydrocarbon products from a variety of iron catalysts generally exhibit two chain growth probabilities, the dominating probability in the Flory-Schulz distribution being significantly greater for the products above about C_{10} than for those of lower

carbon numbers. It has been suggested that the effect may be caused by secondary incorporation of olefins into growing chains. Such incorporation is hypothesized to be greater for higher molecular weight olefins because of their reduced volatility and longer reactor residence time. The fact that the change in the dominating distribution occurs at about C₁₀ lends some plausibility to the suggestion. We will show however that we could not adduce any substantial evidence for this hypothesis. (We did find, however, that at an unusually high temperature, 310°C, a high molecular weight material appeared that was not observed at lower temperatures. It may have been formed by secondary alkylation reactions. See Section 2A.)

As a test, ethanol, ethylene, 1-butene, 1-hexene, 1-decene, or 1-eicosene (C₂₀H₄₀) was added to the synthesis gas feedstream or directly to the reactor under representative Fischer-Tropsch synthesis conditions. In the primary synthesis ethanol is the dominant alcohol, and C₂ species appear to be unusually reactive. Studies with other olefins were made to see if significant differences might be encountered along the homologous series. Comparison of additive conversions at high and low syngas conversions showed that major competitive adsorption effects between CO and olefins occurred.

Runs were with the C-73 catalyst at 248°C, with pressures of 0.78-1.5 MPa, high and low CO conversions, and high and low concentrations of the additive in the feed. CO conversion was varied by changing the flow rate of synthesis gas to the reactor.

Representative results are shown in Fig. 4 (ethanol addition), Fig. 5 (ethylene addition), Fig. 6 (1-butene addition), and Fig. 7 (1-decene addition). In all cases chain incorporation was insignificant. Instead, the principal reactions of the added 1-olefin were hydrogenation to the corresponding paraffin and isomerization to the corresponding 2-olefin. The reactivity of the additive was markedly enhanced at high CO conversions (low CO partial pressure) attributed to a decrease in competitive adsorption by CO.

By extension from this and other studies in our laboratories, we conclude that the reaction network in the Fischer-Tropsch synthesis may be markedly affected by the extent of CO conversion, especially at very high degrees of conversion. This variable has received little attention in the past, probably because it is difficult to isolate its effect by studies in a plug-flow (fixed-bed) reactor. A continuous-flow stirred tank reactor (CSTR), as used here, is particularly well suited to study effects of this sort.

High Conversion Region

The high conversion region was studied further under conditions simulating nearly complete consumption of CO (Matsumoto and Satterfield, 1989). Representative results are shown in Fig. 8, for CO concentrations of 2% or less than those in Figures 4 through 7. This is a Flory plot of carbon number product distribution for four runs at approximately the same carbon monoxide partial pressure without and with added ethylene,