



# THE FISCHER-TROPSCH SYNTHESIS

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*With a chapter on the Kölbel-Engelhardt Synthesis  
by H. Kölbel and M. Ralek*

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# **THE FISCHER-TROPSCH SYNTHESIS**



**PROFESSOR FRANZ FISCHER**  
*19 March 1877–1 December 1947*

*To the second generation of researchers on the Fischer–Tropsch  
Synthesis, including Professor Paul H. Emmett, Dr. C. Charles Hall,  
Professor Herbert Kölbel, Professor Helmut Pichler, and Dr. Henry H.  
Storch*

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## Preface

The author chose to write this book as a retirement project to keep him busy; it has. Papers based on the researches spawned by the OPEC oil embargo have been appearing in large numbers since about 1979. An attempt has been made to include pertinent papers through 1982 and a few from 1983. The current global overabundance of oil may again diminish research on coal-to-oil processes. The possibility of new plants producing fluid fuels from coal before 2000 seems unlikely. Material covered in the book begins in 1955 and continues from the major reviews of the Fischer-Tropsch synthesis published by authors from the United States Bureau of Mines at Bruceton, Pennsylvania.

I wish to acknowledge the assistance of many in preparing this book: D. S. Hodgson, McMaster University, for preparing all of the graphical material; Professors H. Kölbel and M. Ralek, Technical University, Berlin, for contributing Chapter 7 on the Kölbel-Engelhardt synthesis; Dr. R. C. McLane, Chemical Abstracts Services, Columbus, Ohio, for aiding in the translation of Chapter 7 and for preparing the "Quest for a Homogeneous Fischer-Tropsch Synthesis" in Chapter 5; Professor Günther Wilke, Max-Planck Institute for Coal Research, Mülheim an der Ruhr, West Germany, for furnishing biographical material and the excellent photograph of Franz Fischer; Dr. Jacques Monnier, McMaster, and Energy, Mines and Resources, Ottawa, for technical editing of the manuscript and checking the thermodynamic data; Dr. Masa Saito, National Research Institute for Pollution and Resources, Japan, for reviewing the manuscript; Ms. E. M. Tooke, McMaster, for a literature review; Amy Stott, Laura Honda, and Jan Reid, Engineering, Word Processing Center, McMaster, for making the task easier; graduate student Henry Meng and Dr. Kevin S. Smith, SASOL I, South Africa, for technical editing; and my wife Jane, for putting up with another major project, even in retirement.

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# THE FISCHER–TROPSCH SYNTHESIS



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# Contents

Preface	xi
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## 1 Introduction

1.1 Scope of the Book	1
1.2 A Short Historical Sketch	2
1.3 A Brief Appraisal of the Present Status of the Fischer–Tropsch Synthesis	6
References	7

## 2 Thermodynamics of the Fischer–Tropsch Synthesis

2.1 Thermodynamics of Producing Organic Molecules	9
2.2 Thermodynamics of Reactions of Catalytic Materials	18
2.3 Thermodynamics of Carbon, Carbides, Nitrides, and Carbonyls	21
2.4 Summary	23
References	24

## 3 Carbides, Nitrides, and Carbonitrides of Iron as Catalysts in the Fischer–Tropsch Synthesis

3.1 Introduction	26
3.2 Preparation and Composition of Catalysts	28
3.3 Preparation of Carbides, Nitrides, and Carbonitrides of Iron in Catalytic Form	29
3.4 Synthesis Tests with Carbides of Iron	31
3.5 Synthesis Tests with Nitrides and Carbonitrides of Iron	57
3.6 Structural and Chemical Changes in Catalysts during Pretreatment and Synthesis	80
References	97

## 4 Tests of Catalysts

4.1	Introduction	100
4.2	Platinum-Group Metal Catalysts	100
4.3	Cobalt and Nickel Catalysts	122
4.4	Iron Catalysts	140
4.5	Molybdenum and Tungsten Catalysts	159
	References	169

## 5 Mechanism of the Fischer–Tropsch Synthesis

5.1	Introduction	174
5.2	Detailed Characterizations of Synthesis Products	175
5.3	Prediction of Carbon-Number Distributions	186
5.4	Origin and Prediction of Branched Species	190
5.5	Incorporation of Molecules Other than Olefins	202
5.6	Mechanisms Based on Analogies to Organometallic Chemistry and the Quest for a Homogeneous Fischer–Tropsch Synthesis	205
5.7	Mechanisms with Intermediates Containing Oxygen	208
5.8	Surface Carbides and/or $\text{CH}_{1-3}$ Radicals as Intermediates	211
	References	225

## 6 Sulfur Poisoning of Fischer–Tropsch Catalysts

6.1	Introduction	229
6.2	Sulfur Poisoning of Iron Catalysts	230
6.3	Sulfur Poisoning of Cobalt, Nickel, Ruthenium, and Rhenium Catalysts	249
6.4	Sulfur Poisoning of Molybdenum and Tungsten Catalysts	257
6.5	Concluding Statement	261
6.6	Addendum	262
	References	262

## 7 The Kölbel–Engelhardt Synthesis

*H. Kölbel and M. Ralek*

7.1	Introduction	265
7.2	Reaction Mechanism	266
7.3	Stoichiometry	267
7.4	Thermodynamics	268
7.5	Catalyst	268
7.6	Kinetics	269
7.7	Fixed-Bed Reactor Synthesis	275
7.8	Comparison of Fischer–Tropsch and Kölbel–Engelhardt Reactions	278

7.9	Conclusion for Large-Scale Operation	280
7.10	Liquid-Phase Kölbel–Engelhardt Synthesis of High Molecular Weight Paraffinic Hydrocarbons	285
7.11	Direct Synthesis of Amines	287
7.12	Technical and Economic Prospects	288
	References	290
	Addendum	293
	Index	295

# Introduction

## 1.1 Scope of the Book

A definition of the Fischer–Tropsch synthesis (FTS) that delineates the material covered here is as follows: a hydrogenation of oxides of carbon producing higher hydrocarbons and/or alcohols, the carbon chains of the molecules being predominantly straight in the range  $C_4$  to  $C_{10}$ . The FTS is a practical way of converting coal to gasoline, diesel oil, wax, and alcohols. Coal is gasified to furnish the hydrogen plus carbon monoxide. The FTS is currently used commercially in three large plants in South Africa, and during World War II about one-fifth of the gasoline used in Germany was obtained in this way. When coal-to-oil processes are required in North America, the FTS will be a prime contender. In addition to liquid fuels, the FTS can provide largely straight-chain higher alcohols and olefins for the chemical industry.

The early German and other research on FTS to about 1950 was summarized by the author and his colleagues at the United States Bureau of Mines (*1, 6, 12, 13, 23*). The present volume brings this account up to date, through 1982. Usually, engineering aspects of FTS are not covered in this book, and the reader is referred to references *5, 8, 20, and 22* and older work (*9, 18, 23*).

Chapter 1 begins with a short history of the FTS and related reactions, followed by a brief appraisal of the current situation. Chapter 2 covers the thermodynamics of the hydrogenations of oxides of carbon, as well as reactions that catalytic materials may undergo. Chapter 3 describes the preparation of iron carbides, nitrides, and carbonitrides and their properties as catalysts for the FTS; Bureau of Mines work from 1950 to 1960 is summarized. Then, Chapter 4 reports on tests of all types of catalysts, including a number of metals not usually regarded as catalysts for the FTS. The mechanism of the FTS is the subject of Chapter 5. Despite the use of modern research tools, many aspects of the reaction are still the subject of polemics. Chapter 6 describes the poisoning of catalysts in the

FTS by sulfur compounds. Apparently, it is still best to remove virtually all of these molecules from the feed. In the final chapter, Professors H. Kölbel and M. Ralek report on the Kölbel–Engelhardt synthesis. Professor Herbert Kölbel was a codiscoverer of this process in 1949, and earlier, a co-worker of Franz Fischer at the Kaiser-Wilhelm Institute at Mülheim.

## 1.2 A Short Historical Sketch

- 1902 P. Sabatier and J. D. Senderens hydrogenated CO over Ni to produce CH<sub>4</sub> (21).
- 1910 A. M. Mittasch, C. Bosch, and F. Haber developed promoted Fe catalysts for the synthesis of NH<sub>3</sub> (15).
- 1912–1913 The Kaiser-Wilhelm Association for the Advancement of Knowledge established its third institute in Mülheim, dedicated to coal research, the Kaiser-Wilhelm-Institut für Kohleforschung (KWIK). Franz Fischer, Professor of Electrochemistry at the Technical University, Berlin, was appointed Director of the new institute.<sup>1</sup>
- 1913 Badische Anilin und Soda Fabrik (BASF) received patents on the preparation of hydrocarbons and oxygenates by the hydrogenation of CO at high pressure, usually on oxide catalysts.
- 1920 Brennstoff-Chemie was started by Fischer. KWIK also had been publishing *Abhandlung zur Kenntnis der Kohle* since 1917.
- 1922–1923 Fischer and Hans Tropsch obtained Synthol, mostly oxygenates, from H<sub>2</sub> + CO on alkalized Fe and other catalysts.
- 1923 BASF and I. G. Farben (IG) obtained patents on Zn-based, Fe-free catalysts for the methanol synthesis.
- 1925 Fischer and Tropsch announced the synthesis of higher hydrocarbons at atmospheric pressure; Co and Ni seemed to be promising catalysts. A reason for working at 1 atm was that BASF had patents covering higher pressures. The idea developed that hydrocarbons are produced at 1 atm and oxygenated molecules at higher pressure; this notion may have delayed the development of useful Fe catalysts for a decade.
- 1926–1930 Studies were made on the new process in England, Japan, and the United States. Workers at the U.S. Bureau of Mines incorporated ethylene in the synthesis on Co catalysts.

<sup>1</sup> The early history of the Kaiser-Wilhelm-Institut für Kohleforschung and biographical material on Franz Fischer are largely taken from references 10, 11, 18, 19, and 23.

- 1928 Tropsch left KWIK to become director of a coal research institute in Prague. In 1931, he went to Chicago to work at Universal Oil Products and to be Adjunct Professor at the Armour Institute and later at the University of Chicago.
- 1928–1930 P. K. Frohlich and W. K. Lewis studied the synthesis of higher alcohols on alkalized  $\text{ZnO-Cr}_2\text{O}_3$  and other catalysts.
- 1931–1932 Fischer and K. Meyers developed Ni– $\text{ThO}_2$ –kieselguhr and Co– $\text{ThO}_2$ –kieselguhr, which were relatively sophisticated catalysts designed for the primitive reactors of that time. Initial studies were on Ni because of the short supply of Co; however, the Ni catalysts did not operate properly in large reactors. The yields of  $\text{CH}_4$  were too large. Pilot plant work was started at KWIK in 1930.
- 1933–1939 Pilot-plant tests and further development of Co catalysts were made by Ruhrchemie AG.
- 1935 Tropsch returned to Germany critically ill; he died on 8 October.
- 1935–1945 The FTS was operated commercially in Germany using Co catalysts.
- 1936 Fischer and Helmut Pichler found that Co catalysts also operated satisfactorily in the middle pressure range, 5–20 atm.
- 1936 The first commercial catalytic cracking unit, developed by Eugene Houdry, was installed (14).
- 1937 Fischer and Pichler discovered that synthesis on Fe was greatly improved by operating at 5–20 atm. At about the same time, Herbert Kölbel at Rheinpreussen also performed medium-pressure tests of Fe catalysts. Alkalized Fe in this pressure range became a possible replacement for Co in the German commercial plants.
- 1938 Fischer and Pichler produced high-melting-point waxes in high-pressure synthesis on Ru.
- 1939–1944 German industry joined in the development of an Fe catalyst to replace Co in the existing plants. Improved reactors were also studied, including fixed-bed reactors with recycle, hot-gas recycle, oil recycle, and slurry reactors.
- 1939–1944 Fischer and Pichler developed the Isosynthesis, and Otto Roelen the OXO process.
- 1942–1950 Fears of an impending shortage of petroleum in the United States caused wide interest in coal-to-oil processes. A large research and development program was authorized for the U.S. Bureau of Mines, and the American petroleum and related industries initiated studies of the FTS, often on Fe in fluidized or entrained reactors.

- 1943 Fischer retired from KWIK and moved to Munich. Karl Ziegler became the second Director of KWIK at Mülheim.
- 1943–1944 Kölbel initiated and directed the comparative tests I and II held at Schwarzheide to select an Fe catalyst to replace Co in existing reactors; KWIK and five companies participated (18). Although the results were remarkably good, no replacement catalyst was selected, probably because of the overall disarray of activity that attended the approach of the end of the war.
- 1945 World War II ended, and the operation of FTS plants in Germany stopped. Some plants in what is now East Germany (GDR) were confiscated by the Soviet Union.
- 1947 Fischer died in Munich on 1 December.
- 1948 P. H. Emmett used molecules tagged with  $^{14}\text{C}$  to study the mechanism of the FTS.
- 1948 The Kaiser-Wilhelm Gesellschaft becomes the Max-Planck Gesellschaft, and the institute at Mülheim became a Max-Planck Institute.
- 1949 Kölbel and F. Engelhardt discovered that  $\text{H}_2\text{O}$  and  $\text{CO}$  react on FTS catalysts to yield typical FTS products.
- 1950 A fluidized–fixed bed process developed by Hydrocarbon Research, Trenton, New Jersey was installed in Brownsville, Texas. This plant, called Carthage Hydrocol, Inc., used reformed natural gas. Severe operating difficulties required designing a new reactor, which was installed in 1953. The new reactor operated properly, but the plant was promptly shut down, sold, and dismantled. By the time the plant was operating correctly, the price of natural gas had more than doubled. Merely selling the gas was more profitable than converting it to gasoline and chemicals. At the same time, in South Africa, the SASOL FTS plant using coal was constructed and opened in 1955. Lurgi gas generators and Rectisol gas-cleaning units were employed. Two types of FTS reactors, both with Fe catalysts, were used: a fixed-bed with recycle unit designed by Ruhrchemie in West Germany, having long tubes with an internal diameter of  $\sim 2$  in., and an entrained-solids reactor by M. W. Kellogg in New Jersey. After a year or more of start-up problems, these units have operated successfully up to the present (7).
- 1953 R. B. Anderson and J. F. Shultz found that Fe nitrides are unique, durable catalysts for the FTS that produce large yields of alcohols (3). Anderson developed equations that predict

- the isomer and carbon-number distributions of FTS products (4). Kölbel and P. Ackermann successfully operated a large slurry reactor in a 10-ton-per-day demonstration plant.
- 1954 The abundance of petroleum in the world and its availability at very low prices caused the decrease or termination of most of the programs of research and development on coal-to-oil processes.
- 1957 G. Natta and co-workers (16, 17) studied the methanol and higher alcohol syntheses.
- 1959 Pichler resumed work on FTS on Ru, which led to the polymethylene synthesis.
- 1961 H. H. Storch died; he was the architect of the useful scientific and engineering research programs on coal-to-oil processes at the U.S. Bureau of Mines in Pittsburgh and Bruceton, Pennsylvania (2, 4).
- 1966 Imperial Chemical Industries (ICI) developed a moderate-pressure methanol synthesis employing copper–zinc oxide catalysts in a gas-recycle reactor.
- 1967 U.S. Bureau of Mines workers developed methods for flame spraying catalysts onto metals for the platelet assemblies of hot-gas-recycle reactors. These techniques led to the development of a new FTS unit, the tube-wall reactor (5).
- 1969 Domestic production of petroleum in the United States fell below demand; the United States became an importer of oil.
- 1973 The oil embargo by the Organization of Petroleum Exporting Countries (OPEC), followed by a fourfold increase in the price of petroleum, accelerated research on coal-to-oil processes in the United States and many other countries. With the demise of the U.S. Bureau of Mines, federally sponsored coal-to-oil research became part of the Energy Research and Development Administration (ERDA) and subsequently the Department of Energy.
- 1974 H. Pichler died in Karlsruhe on 13 October.
- 1975 In South Africa, the decision was made to build SASOL II, scheduled for operation in 1980, and in 1979, plans were made for SASOL III, to begin operation in 1982 (7). The new plants are similar to the initial plant, except that fixed-bed FTS reactors were not included in the new installations.
- 1976 Mobil announced a process for converting methanol to an aromatic gasoline and  $C_2$  to  $C_4$  olefins on the shape-selective catalyst ZSM5. This process may be a serious competitor for FTS.



- 1981 In New Zealand a methanol plant operating on natural gas plus the Mobil process was planned, scheduled for completion in 1985.
- 1982 The worldwide recession sharply decreased demand for petroleum. OPEC was unable to control the production and price of oil among its members. The relatively low cost and abundance of petroleum has discouraged new coal-to-oil ventures.

### 1.3 A Brief Appraisal of the Present Status of the Fischer–Tropsch Synthesis

In the decade following the end of World War II, research and development on the FTS was pursued vigorously in the United States, England, and West Germany, but this activity decreased abruptly in the 1950s. SASOL maintained a modest continuing research and development program devoted largely to practical problems, and the U.S. Bureau of Mines continued a small research activity.

The renewed interest in and funding for FTS research, starting in 1970, has involved academic workers to a very much larger extent than in the previous period. In most instances, the research teams of the 1950s had been dispersed, and the new researchers attacked the FTS with new ideas and excellent new research tools. However, neophytes in FTS research require 2–3 years to digest the voluminous literature. For this reason, most of the useful contributions have appeared since 1978.

Capillary gas chromatography, often coupled with mass spectrometry, has been an important research tool that has made the determination of carbon number and isomer distribution almost routine. Mössbauer spectroscopy has proved to be the ideal way of obtaining quantitative analyses of phases present in Fe catalysts. However, studies of Fe comprise only a small part of the current total research effort. Precipitated Fe containing as much as 10 Mn to 1 Fe has been shown to be highly selective, producing large yields of  $\alpha$ -olefins.

Many workers have chosen supported Ru as an ideal catalyst for investigation, because Ru is neither oxidized nor carburized during synthesis. Rhodium has been shown to have interesting properties in the FTS and probably should be included with Fe, Co, Ni, and Ru as FTS catalysts. Nickel has been studied widely, but often under conditions for which  $\text{CH}_4$  is the principal product. As catalysts, Mo and W also produce higher hydrocarbons, but their activity is low, possibly because these metals oxidize easily. Studies are in progress to test the idea that the pore struc-