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CHAPTER 1

THE FISCHER TROPSCH SYNTHESIS

1.1 Historical Overview

Synthetic fuels have become a major research interest in the current world wide attempt to develop alternate energy sources. Since many countries (including the U.S.) contain an abundance of coal relative to crude petroleum, the technology required to convert this solid energy source to liquid fuels economically is very desirable. By gasifying coal into a mixture of carbon monoxide and hydrogen one can use the Fischer Tropsch (FT) synthesis process to manufacture a myriad of hydrocarbon and alcohol products. A recent investigation (85) reports 120 identifiable product compounds obtained at typical reaction conditions (10 atm., 220°C). In fact the main problem with this process is producing only a select range of products.

In the mid 1920's, researchers Franz Fischer and Hans Tropsch (44) discovered the process conditions by which a mixture of carbon monoxide and hydrogen can be catalytically converted to hydrocarbons. Thermodynamically, it is possible to produce hydrocarbon products including olefins, paraffins, alcohols, aromatics and oxygenated derivatives at the Fischer-Tropsch synthesis conditions (1-30 atm at 180-300°C). Indeed over 120 seperate products have been identified under the typical FT conditions (85). The transition metals used in the synthesis (Fe, Co, Ni, Rh) generally have different activities, selectivities, and overall catalytic behavior when alloyed or combined with oxide promoters.

Historically, the research and development effort in this area often paralleled a growing shortage of liquid fuel. In the late twenties, Germany was faced with a gasoline and diesel fuel shortage and needed a synthetic process for the production of liquid fuels from coal. At the end of World War II, the United States initiated an extensive research effort (6,91) following up on the German work. However, the development of the Mid-East oil fields in the late 1950's postponed all major investigations until the 1973 "oil embargo" created a renaissance in research activities.

1.21 Primary FT Reactions and Secondary Complication Reactions

The synthesis process is actually a set of sequential and/or parallel reactions. Only the production of methanol and methane can be controlled selectively but only over non-FT catalysts (i.e., Pt, ZnO). If a process were developed which would selectively produce one or two products under FT conditions, it would deserve its own distinctive title. The synthesis reactions are given in Table 1.1 (123).

Table 1.2.1: Possible Synthesis Reactions

(1)	Methanation:	$3H_2 + CO \rightarrow CH_4 + H_2O$
(2)	Parafins:	$(2n + 1)H_2 + n\ CO \rightarrow C_n H_{2n+2} + n\ H_2O$
(3)	Olefins:	$2nH_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$
(4)	Methanol:	$2H_2 + CO \rightarrow CH_3OH$
(5)	Alcohols:	$2nH_2 + n\ CO \rightarrow C_nH_{2n+1}\ OH + (n-1)\ H_2O$

A number of other reactions, commonly called complicating reactions, (132) can occur at reaction conditions. These are listed in Table 1.2. Isomerization and hydrogenation are commonly termed secondary reactions since they involve the primary FT products as reactants.

Table 1.2.2: Complicating Reactions in the Synthesis Process

(1)	Water gas shift: $CO + H_2O \rightleftarrows CO_2 + H_2$
(2)	Boudouard rxn: $2CO \rightarrow C + CO_2$
(3)	Coke Deposition: $H_2 + CO \rightarrow C + H_2O$
(4)	Carbide formation: $xM + yC \rightarrow MxCy$ (where M is metal atom)
(5)	Olefin Isomerization: $C = C - C - R \rightarrow R - C = C - R$
(6)	Olefin Hydrogenation: $R = CH_2 + H_2 \rightarrow H - R - CH_3$
(7)	Hydroformulation: $RCH = CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO$