# CHAPTER 1

# SCOPE OF WORK

## 1.1 INTRODUCTION

Two German scientists Franz Fischer and Hans Tropsch reported in 1923 the synthesis of mainly linear hydrocarbons via carbon monoxide hydrogenation (Dry, 1981). This followed earlier research in 1902 by Sabatier and Senderens who discovered this particular chemical reaction when they succeeded in converting carbon monoxide and hydrogen to methane over reduced nickel and cobalt catalysts (Anderson, 1984). The reactions involved in the Fischer-Tropsch (FT) synthesis are summarised in Table 1.1.

Table 1.1: Reactions involved in the Fischer-Tropsch synthesis

| | |
|---|---|
| Prominent reactions | |
| • Paraffins | $(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$ |
| • Olefins | $2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$ |
| • Water-gas-shift reaction | $CO + H_2O \leftrightarrow CO_2 + H_2$ |
| Less prominent reactions | |
| • Alcohols | $2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$ |
| • Boudouard reaction | $2CO \rightarrow C + CO_2$ |
| • Acids, ketones and aldehydes | Secondary reactions |
| Catalyst modifications | |
| • Catalyst oxidation/reduction | (a) $M_xO_y + yH_2 \leftrightarrow yH_2O + xM$ |
| | (b) $M_xO_y + yCO \leftrightarrow yCO_2 + xM$ |
| • Bulk carbide formation | $yC + xM \leftrightarrow M_xC_y$ |

FT technology utilising coal-based syngas was used during World War 2 by Germany to provide fuel for their war efforts. This equated to nine FT plants operating in 1938 with production of about $6*10^5$ tons per annum (Dry, 1996). These plants were shut down after the war, as they were uneconomic. The worldwide perceptions during the 1940s that the crude oil reserves were running out suggested a rise in oil prices during the 1950s. This perception together with relatively cheap coal reserves served as basis for the construction of Sasol One in South Africa.

This plant had the primary objective of supplying the fuel needs of South Africa when crude oil became unaffordable. Further oil deposits were however discovered in the Middle East and the price of crude oil did not rise. Sasol One survived by producing high-priced FT waxes besides its liquid fuel product (Dry, 1996).

The oil embargo of 1973 together with the resulting sharp increase in oil prices focussed the attention again on the FT process as an alternative fuel production process. This era thus saw the construction of two more FT plants within South Africa (Sasol 2 and 3 – coming on stream in 1980 and 1982 respectively) with a combined production of about 4,2 million tons per annum. Volatile crude oil prices were curbed by producing not only fuels during the 1970 to 1990 period, but also selling some commodity chemicals.

Towards the end of 1990, FT technology has seen advances in the reactor technology used, relating to Slurry and Fixed bed reactors. The development of the Sasol Advanced Synthol and the Slurry bed reactors are examples of such advances. This together with volatility experienced in the crude oil markets could be a trigger for a shift towards coal and natural gas as the feedstock of the chemical industry. FT gas-to-liquid technology could therefore play an important role in the chemical plants of the future by utilising specially developed catalysts, which will give chemical versatility.

## 1.2 MOTIVATION

The FT product spectrum is a complex multi-component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and 1-olefins. A major limitation in the FT process is the low selectivity to "desired" high value chemical products (Park *et al.,* 1991). The hydrocarbon product distribution observed for a variety of catalyst systems and under a variety of reaction conditions conforms to the Schulz-Flory polymerisation equation, which is inherently non-selective. Typical products from the FT synthesis have the following important characteristics (Van der Laan, 1999):

- The carbon-number distribution for hydrocarbons gives the highest concentration for $C_1$ and decreases monotonically for higher carbon numbers.
- Olefins formed over iron catalysts exceed 50 mass % of the hydrocarbon products at low carbon numbers (about $C_2$ to $C_5$), and more than 60 mass % of these are 1-olefins, with

less ethene than propene. The olefin content decreases asymptotically to zero with increasing carbon number for Co, Ru and Fe catalysts.

- Alcohol yield peaks at $C_2$ and decreases with carbon number.

It is not surprising that a lot of innovative efforts are put into the development of FT catalysts to improve selectivity, the understanding and modelling of the kinetics involved, and improvement of the yields obtained (Das *et al.*, 1994). Markets for the traditional waxy products produced from low temperature iron FT processes are relatively small and new plant development often sees these products being cracked to Diesel and Naphtha for the ever-increasing fuel demand. FT gas to liquid technology basically consists of three process steps, namely the syngas generation step, syngas conversion and hydroprocessing steps (Vosloo, 2001). The complexity of a FT plant therefore necessitates a large capital investment with returns maximised through value addition to products. The development of a catalyst, which will be able to manipulate the products obtained from the FT process, in such a way that it will mainly produce high priced chemicals such as olefins and alcohols, will result in an enhancement of the product value.

Figure 1.1 shows comparable values typically obtainable for various product cuts of the FT synthesis process during 2000 (Desmet, 2001). One can therefore define valuable chemicals as typically the $C_9$-$C_{16}$ alcohol range and the $C_6$-$C_{11}$ olefin range. To obtain economical yields of these so-called valuable chemicals the role of the alcohols formation reaction (see Table 1.1) will have to be seen as important to that of the olefin reaction if one aims to produce alcohols in similar or greater quantities to that of the olefins. Currently used kinetic rate equations need to be evaluated to see if they would effectively describe a catalyst with the above-mentioned product spectrum at the chosen operating conditions.

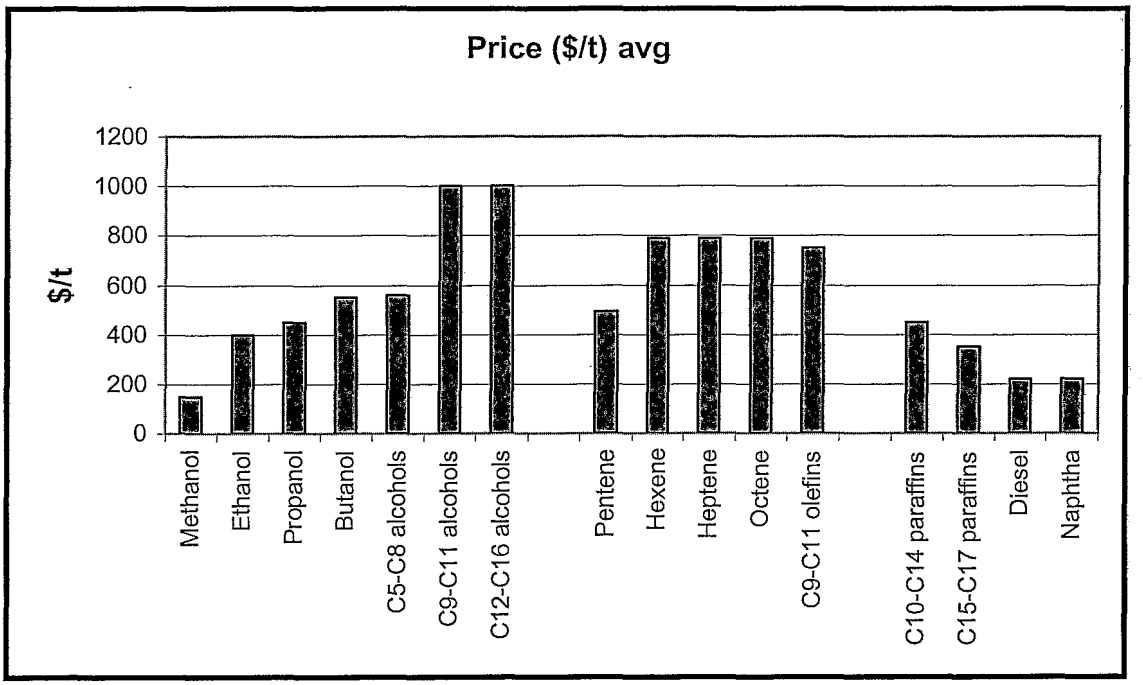


Figure 1.1: Typical product values for the year 2000

## 1.3 SCOPE

This investigation deals with an iron-based FT catalyst with the characteristics of being a valuable chemical selective catalyst thereby producing notable quantities of $C_9$+ alcohols and $C_6$+ olefins. This investigation will use the term "ChemFT" catalyst to differentiate it from traditional FT catalysts. Relevant literature regarding FT catalysts is overviewed, although the specific development of the catalyst does not form part of the scope of work. The investigation will however give some background to the development of the ChemFT catalsyt. This should give some understanding to the specific characteristics of this catalyst. The product spectrum achieved with this specific catalyst at selected operating conditions will be presented as a breakthrough in the sense that the process is commercially viable.

The characterisation of the ChemFT catalyst is given and its performance with respect to alcohol and olefin selectivity is evaluated on laboratory and pilot plant scale. Possible FT and WGS reaction rate equations for use with the ChemFT catalyst are evaluated and suitable equations are derived.

## 1.4 OBJECTIVE

The aim of this investigation is the review of the development of the new catalyst used in this investigation, the characterisation thereof and an experimental verification of its product spectrum at different operating conditions. Through the evaluation of current FT and WGS rate equations, suitable equations for this particular catalyst will be proposed.

## 1.5 REFERENCES


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