

CHAPTER 2

CATALYST DEVELOPMENT AND EVALUATION

2.1 OVERVIEW

This chapter gives firstly an overview of literature relevant to Fischer-Tropsch catalysts, followed by an experimental section describing the equipment used for this investigation, the development and characterisation of the ChemFT catalyst and the evaluation of the catalyst developed for this investigation.

The aim of the chapter is to give an overview of some of the relevant literature and/or patents available on the traditional Fischer-Tropsch synthesis process, with specific attention to the catalysts and the product spectra associated with it. The role of different promoters as found in literature will be discussed in an effort to show that by understanding their role it should be possible to formulate a catalyst with desired activity and selectivity. The developed ChemFT catalyst is evaluated on laboratory scale to determine its selectivity towards alcohols and olefins.

There are very few references to the simultaneous optimisation of the alcohol and olefin selectivity in the open literature. The overview will thus be divided into catalysts with the aim of optimising the alcohol content and those aimed at optimising the olefin content of the synthesis product. Product selectivity is not only determined by the catalyst, but also the operating conditions. The influence of parameters such as temperature, pressure and space velocity will be shown and discussed. It is believed that the literature review will give an adequate background to be able to understand the specific characteristics of the catalyst under investigation.

The experimental section will follow the literature review. This section of the chapter will discuss the preparation procedure followed as well as pre-treatment and synthesis evaluation of the catalyst. Pre-treatment studies (that consist of the calcination and some aspects concerning the reduction of the catalyst) are included to ensure that optimum conditions are used for the eventual kinetic study. Results will be compared to available literature results to illustrate the uniqueness of the product spectrum obtained with this specific catalyst.

2.2 LITERATURE SURVEY OF FISCHER-TROPSCH SYNTHESIS

2.2.1 Fischer-Tropsch synthesis catalysts and reactors in general

2.2.1.1 Catalysts for FT synthesis

Most commonly used FT catalysts are group VIII metals – Co, Fe and Ru. Comparing the relative prices (Dry, 1990) of the different metals (Table 2.1), iron catalysts would be the economically preferred catalyst, followed by Co and Ni, with Ru very expensive due to its limited supply. Nickel is however not a suitable FT catalyst due to the fact that it is an active hydrogenation catalyst, therefore produces a large amount of methane under FT conditions (Dry, 1996). Adesina (1996) comments that Mo, although not a group VIII metal, also exhibits moderate FT activity, while its nitrate and carbonate show an excellent olefin synthesis rate. The sulphur resistance of Mo is an added benefit. Adesina also mentions that metals such as Rh, Re, Os, Pd, Pt and Ir mostly yield oxygenated compounds partly because CO does not chemisorb dissociatively on these metals.

Table 2.1: Relative prices of metals used for FT catalysts

Metal	Relative price (1990)
Fe	1.0
Co	230
Ni	250
Ru	31 000
Rh	570 000

The earlier catalysts were prepared via precipitation techniques, while later other methods like sintering and fusion of metal oxides with desired promoters became more common (Van der Laan and Beenackers, 1999). Precipitated Co catalyst on kieselguhr was the standard FT catalyst used during World War 2, while alkali (normally K_2O) promoted Fe catalysts (supported catalyst via impregnation, precipitated and fused) are still used industrially (South Africa's Sasol plants). Iron catalysts possess properties such as high WGS activity (resulting in high CO_2 rather than H_2O production (Bartholomew, 1990)), high olefin product selectivity and stable operation when synthesis gas with a high H_2/CO ratio is converted (Van der Laan and Beenackers, 1999). Fe catalysts can be operated at lower H_2/CO ratios such as 0.6 – 1.0 compared to a ratio of 2.0 for Co and Ru (Bartholomew, 1990). Co catalysts on the other hand give higher yields and increased

lifetime, while predominantly producing linear paraffins. Co catalysts are not inhibited by water and as a result can operate at high synthesis gas conversion levels for higher productivity. Pressure has a pronounced effect on Co catalysts, while little effect on product selectivity is

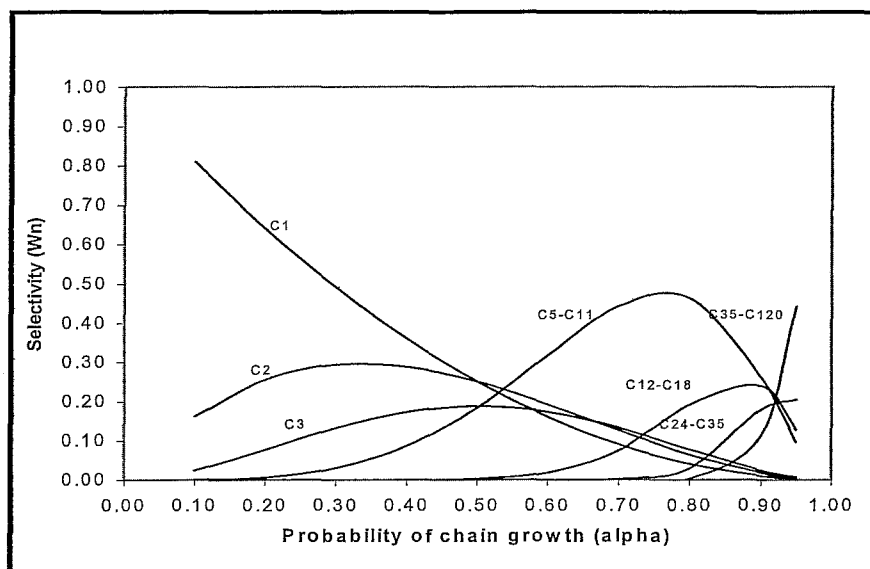


Figure 2.1: Calculated hydrocarbon selectivity vs. probability of chain growth

observed for Fe catalysts (Jager and Espinoza, 1995). Disadvantageous of Co as a catalyst is its relatively high cost compared to Fe and the low WGS activity. Co catalysts are more hydrogenating than alkalised iron and will consequently produce more methane and fewer olefins (Dry, 1996). Co is preferred for natural gas based FT processes for production of middle distillate and high molecular weight products. This is mainly because of the fact that sulphur levels in natural gas are negligible, therefore Co which is normally very sensitive to such poisons can be used to operate at high conversion levels.

Rh is a very active FT catalyst, but also very expensive (Van der Laan and Beenackers, 1999). At operating pressures less than 100 bar(g) it produces a lot of methane, but at lower temperatures and very high pressures it will produce high molecular weight waxes. It was shown that when the group VIII metals are supported on Al_2O_3 , the activity decreases in the order Ru, Fe, Co, Rh, Pd, Pt and Ir (Vannice, 1977).

FT products are predominantly linear with high 1-olefin content, and unlike conventional olefin synthesis processes, the FT olefins also include the odd carbon number olefins. Olefins are primary products and are therefore influenced by the residence times within the catalyst particle

and how hydrogenating the systems are. Olefins would typically undergo secondary reactions in the form of hydrogenation to paraffins (Dry, 1981).

There are however theoretical limits to the yields of specific cuts within the FT product range, which are controlled by the so-called Anderson-Schulz-Flory (ASF) distribution (Dry, 1996 and Caldwell, 1981). Figure 2.1 (Dry, 1996) illustrates that the maximum yield of gasoline ($C_5 - C_{11}$) is about 45 mass % and of diesel fuel ($C_{12} - C_{18}$) about 25 %. Further increases of the yield would require the application of additional downstream operations.

Conventional FT catalysts/processes have limitations (Bartholomew, 1990) such as limited selectivity for premium products (olefins, gasoline, diesel), catalyst deactivation, high capital cost, heat removal due to the exothermic nature of the FT reaction and a less than optimal thermal efficiency. FT research is mainly focussed on the improvement of catalyst selectivity via (Bartholomew, 1990):

- Chemical modifications (includes additives, promoters, supports, pre-treatment, preparation methods),
- Interception of intermediates (dual functionalism and secondary reactions),
- Limitation of chain growth by shape selectivity of the supports, and
- Unsteady state operation of the system.

It can be said that the objectives of catalyst development are two fold: to obtain the highest activity and life together with obtaining the highest possible selectivity in terms of certain synthesis reactions and suppression of side reactions (Srivastava, 1990).

Bartholomew (1990) states that the above-mentioned research areas are based on some fundamental design principles for FT, namely:

- The degree to which the FT process is affected by the above-mentioned limitations depends on catalyst, reactor and process design.
- It is possible to achieve the maximum yield of a given hydrocarbon product within the constraints of the ASF kinetics by design of catalyst through promoters, support, gaseous additives, interstitial addition and bimetallics. Additives change the chemistry of the reaction by changing the localised chemical/electronic structure of the active metals. Together with the above-mentioned goes the controlling of reaction conditions such as temperature, pressure, residence time and H_2/CO synthesis gas ratio.

- The variations in pre-treatment, preparation and reaction conditions enable almost infinite variations in the composition/structure of group VIII metal catalysts, especially for Fe based catalysts. The unique combination of these variables will determine in turn the catalyst's unique activity and selectivity properties.

Referring to the research on the FT catalysts, Bartholomew (1990) mentions the following as key areas for improvement:

- Improvements in Fe/Mn catalysts prepared from mixed oxides, spinels and carbonyls, which are promoted with Ce for high selective production of olefins and low methane production (Fiato and Soled, US patent 4 618 597, 1986),
- Co and Ru catalysts promoted with Zr, Ti or Cr for wax production (Sie, 1988),
- Co/TiO₂ catalyst promoted with lanthanides, having improved thermal stability, high activity and selectivity for premium transport fuels (Iglesia *et al.*, US patent 4 738 948, 1988 and Mauldin *et al.*, US patent 4 755 536, 1988),
- High activity and olefin selective Fe₂O₃C_x catalysts (Snel, 1988),
- Preparation techniques involving non-aqueous impregnation (Bartholomew and Boudart, 1972), controlled pH precipitation, decomposition of metal carbonyl on dehydrated supports to produce highly dispersed, highly reduced, contaminant free supported metals,
- Bi-functional or mixed metal/zeolite catalysts for interception reactions.

2.2.1.2 Reactors for FT synthesis

Various reactor types and processes are to be found in the literature for FT applications, but they can easily be divided into low temperature FT (LTFT) and high temperature FT (HTFT) applications. LTFT fixed bed reactors employed by Germany during World War 2, operated with a 100 Co: 5 ThO₂: 8 MgO: 200 SiO₂ catalyst at pressures as low as 1 bar(g) and at higher pressures of 10 – 15 bar(g) (Dry, 1996). Ruhrchemie and Lurgi developed the ARGE reactors employed by Sasol since 1955 for LTFT. These reactors make use of a Fe based catalyst (original catalyst was 100 Fe: 5 Cu: 5 K₂O: 25 SiO₂) and operate at 225°C and 26 bar(g), with liquid wax accounting for about 50 % of the reactor product. Shell's tubular fixed bed reactors (TFBR) make use of a Co based catalyst (Bartholomew, 1990).

Sasol also makes use of the Sasol slurry bed reactors (SSBR) (Jager and Espinoza, 1995) for the LTFT process, which operates on a promoted Fe based precipitated and spraydried catalyst at temperatures in the order of 240°C and pressures of around 20 bar(g). The Fe based catalyst is

prepared via precipitation from an Fe nitrate solution by an alkaline solution (this step determines the surface area and pore structure through changing variables such as temperature, order of addition, rate of precipitation, concentration of the solutions, the nature of the precipitation agent, etc.). Thereafter, the precipitate is washed, reslurried and chemical and structural promoters added. The fixed bed precipitated catalyst is filtered, extruded and dried while the slurry bed catalyst is spraydried.

Exxon makes use of a Co based catalyst for slurry LTFT operation (Dry, 1996). Earlier Co catalysts used unsupported oxides such as pure Co oxide, Co chromium oxide or Cobalt-zinc oxide. The development of the support of the metal on a silica carrier was an important breakthrough for Co catalysis (Jager and Espinoza, 1995). Modern Co catalysts are promoted cobalt on a metal oxide support. LTFT is normally aimed at wax production and is operated at temperatures below 250°C (depending on Fe or Co) to minimise methane production and to avoid high temperature wax hydrocracking (Dry, 1999).

HTFT is geared mainly at producing olefins and gasoline (Dry, 1999). It is operated at temperatures of around 350°C, as lower temperatures will cause the two-phase system (gas and catalyst) to be defluidised due to the formation of liquid waxes. This higher operating temperature results in higher conversions and therefore high gas throughput. Sasol made use of the Kellogg designed circulating fluidised bed (CFB) reactors for its initial HTFT plant. This developed into the Synthol reactors operating at temperatures of 330–360°C. In 1989, the fixed fluidised bed (FFB) reactors came on-line at Sasol's Secunda plant.

Advances in design have ensured that heat exchange for the fluidised mode of operation (both LTFT and HTFT) to the cooling coils is very high, thereby resulting in near isothermal conditions prevailing within the reactor (Dry, 1999).

The typical product spectra associated with a Fe catalyst operating in the LTFT and HTFT modes are summarised in Table 2.2 (Dry, 1999). The hydrocarbons produced by the LTFT synthesis are predominantly linear, with the olefins mostly 1-olefins (advantageous for the production of chemicals, while linearity of the hydrocarbon chains influences the quality of the diesel and gasoline). The higher temperature of the HTFT process will result in more branched products.

The conventional FT processes produce less but still significant amounts of oxygenates comprising alcohols, aldehydes, ketones and acids. Ketones and aromatics are very low for

LTFT and are known to be secondary products. The configuration of typical FT plants ensures the removal of sulphur compounds upstream from the reactors, thereby producing FT products that are sulphur free. The products are also free from nitrogen compounds and thus cannot contribute to NO_x gases being formed in combustion engines (Dry, 1999). LTFT is thus best suited for production of large quantities of high quality diesel fuel through the hydrocracking of the predominantly waxy product.

Table 2.2: Typical FT product distributions associated with Fe-based catalysts

	235°C (LTFT) 20 bar(g)	340°C (HTFT) 25 bar(g)
Selectivity (C atom %)		
CH ₄	3	8
C ₂ H ₄	0.5	4
C ₂ H ₆	1	3
C ₃ H ₆	1.5	11
C ₃ H ₈	1.5	2
C ₄ H ₈	2	9
C ₄ H ₁₀	2	1
C ₅ – C ₆	7	16
C ₇ – 160°C	9	20
160 – 350°C	17.5	16
+350°C (waxes)	51	5
Oxygenates (acid and alcohols)	4	5
% Breakdown (C ₅ – C ₁₂ cut)		
% Total paraffins	29	13
% Total olefins	64	70
% Aromatics	0	5
% Oxygenates (acids and alcohols)	7	12

Table 2.3 was obtained from an article by Bartholomew (1990) in which he describes the most recent FT improvements at that time (updated for Sasol advances). The table summarises some of the technology options available for specific FT premium products.

Table 2.3 Technology options available for FT synthesis

Premium product	Catalyst	Reactors	Process
C ₂ -C ₄ olefins	Fe/K, Fe/Mn, Fe/Mn/Ce Fe/K/S, Ru/TiO ₂ , Fe ₂ O ₃ C _x Fe/C, Mo/C	Slurry, fluid-bed: Circulating bed (CFB), Sasol advanced Synthol (SAS)	Synthol, Koelbel, Rheinpreussen-Koppers DowLPG, Synthol
Gasoline	Fused Fe/K Co/ThO ₂ /Al ₂ O ₃ /Silicalite Fe/K/ZSM-5, Co/ZSM-5, Ru/ZSM-5 Fe/Cu/K and ZSM-5	Fluid-bed: CFB, SAS Fixed-bed Slurry / Fixed-bed	Synthol Gulf-Badger Mobil One-stage Mobil Two-stage
Diesel fuel	Fe/K, Ru/V/TiO ₂ Co/Zr, Ti or Cr/Al ₂ O ₃ Co/Zr/TiO ₂ Co-Ru/Al ₂ O ₃	Fixed-bed (low T) Slurry-bed (low T)	Sasol-Arge, Gulf-Badger Sasol FT GTL Shell-Middle Distillate Eisenlohr / Gaensslen
Waxes	Fe/K, Fe/Cu/K Co/Zr, Ti or Cr/Al ₂ O ₃ Co/R/Al ₂ O ₃ prom. Fe/Ru	Slurry-bed (low T) Fixed-bed (low T)	Mobil (First stage) Shell-Middle Distillate (First stage) Sasol-Arge

2.2.2 Promoter effects on Fischer-Tropsch catalysts

Fischer-Tropsch catalysts (Fe, Co, etc.) are multi component systems made up of a combination of promoters. It is thus important to understand the role of each promoter to be able to formulate a catalyst with a desired activity and selectivity.

Basu *et al.* (1985) investigated the effect of some promoters on the activity and selectivity of a Fe based catalyst. They started their work by preparing a basic Fe catalyst by means of co-precipitation from the metal nitrate using sodium carbonate, filtering followed by a washing step and thereafter adding K₂O.

The catalyst was used in an extrudate form. Their base catalyst was a combination of Fe₂O₃ – CuO – K₂O (from literature they believed Cu and K to be essential as basic promoters for activity). They followed the same procedure to prepare two more catalysts, one with Mn₂O₃ followed by one with Dolomite added (Dolomite added CaO, MgO and SiO₂ to the system). They observed that the physical properties did not change significantly, although the activities

changed and the performance of the catalysts progressively improved. This they believe showed that Cu and K₂O act primarily as chemical promoters.

The role of Cu is explained by Basu *et al.* (1985) as enhancing the adsorption of H₂ thereby increasing the Fe catalyst activity through its redox properties during preparation and thus making reduction possible at lower temperatures. This in turn helps the catalyst to retain a higher surface area after pre-treatment thus resulting in a lower synthesis temperature and lower methane formation.

Basu *et al.* (1985) assigns K the role of increasing the activity and selectivity of the Fe catalyst through its ability during synthesis to influence the electronic state of the surface iron atoms. Being a strong base it donates electrons. K promotion also enhances selectivity to higher hydrocarbon formation (Pennline *et al.* (1987)).

Adesina (1996) reports the same observation namely that the presence of alkali metals on transition metal surfaces alter the binding energy as well as the sticking probability of the reactive molecules. The claim is made that the improvement in olefin-to-paraffin ratio and the increase in WGS for promoted Fe catalysts is due to a lower surface H:C ratio (Dry, 1981). It was reported by Somorjai (1981) that K addition has an inhibitory effect of Fe oxide poisoning during CO/H₂ reaction. Adesina summarises the general effects of alkali addition from a report of Van der Lee and Ponc (1987) as follows:

- Enhancement of mobility of supports such as SiO₂ or TiO₂ – effecting the spreading of the support over the metal and thus the promoting effect of the support.
- It decreases the rate of the Mⁿ⁺ (active metal oxide) reduction and result in more Mⁿ⁺ ions surviving a standard reduction.
- It decreases the accessible active metal surface area and this might have a negative or positive effect on the catalyst activity and selectivity.
- Leads to improvement in the rate of CO dissociation but at the same time provides stability for oxygen-containing intermediates like formates or acetates.
- Enhance the activation of CO molecules by influencing the C-O bond strength and by increasing the migratory properties of CO.

The above-mentioned conclusions are also used by Dry (1990) when he explains that K promotion increases both the selectivity to the longer chained products and oxygenates. Dry explains that the K promotion increases the strength of CO chemisorption as it does the rate of

carbon formation, and thus either way it would result in a higher surface coverage of CO and/or $\text{-CH}_2\text{-}$. The latter being the result of the hydrogenation of the surface C atoms formed by CO dissociation. These would result in a higher rate of chain growth due to the higher surface concentration of inserting entities -CO or $\text{-CH}_2\text{-}$. Dry thus concluded that the higher production of oxygenates as a result of K promotion is due to higher CO coverage.

The promoting effect of K is attributed to a geometric influence rather than to electronic promotion (Boskovic *et al.*, 1994). A potassium and Al promoted Fe-MgO catalyst was used for the referred-to investigation. The paper explains that Fe agglomeration and the decrease of active surface for CO adsorption with K promotion are caused by the “cement effect” of K. Electron promotion (if any) occurs most probably through an interaction with the electron-rich oxygen of CO, since K distribution was found to be independent of Fe agglomerates. The effect of Al is seen as that of a “skin effect”, covering the major part of the Fe oxide and protecting it from reduction.

Srivastava *et al.* (1990) sees the role of K as that of resisting oxidation of the catalyst, because:

- A greater reducing atmosphere (higher $\text{H}_2/\text{H}_2\text{O}$ ratio) is attained in the system, because of the promoted catalyst that is more active for WGS reaction (Pennline *et al.*, 1987). CO_2 is less oxidising than H_2O ; thus the possibility of oxidation is smaller.
- As K enhances the adsorption of CO, it results in the acceleration of carbidisation.

It is mentioned that careful control of the K level is important as it (and other alkalis) lowers the surface area of precipitated Fe catalysts, resulting in loss of catalyst activity. This was clearly showed by Miller and Moskovits (1988) who tested K levels on a Fe catalyst prepared by electrochemical techniques. They obtained a maximum activity at a particular level of K, after which there was a sharp decline in activity at K levels in excess of the optimum. This result showed that this is a typical K behaviour, as the results from the novel catalyst were similar to that of conventional Fe catalysts.

With increased alkali metal content the hydrogenation reactivity of the catalyst decreased (indicated by H_2 consumption decreasing and an increase in product olefinitiy). Lee *et al.* (1992) showed the same result on addition of K to a Fe-Mn catalyst, where the addition of K promoter caused the bulk phase to transform to carbides, while the selectivity towards olefins and large chain hydrocarbons was remarkably enhanced. Pennline *et al.* (1987) showed that a high level of

K promotion was needed on a Fe-Mn catalyst to increase and stabilise the olefin selectivity of the product.

During Basu *et al.*'s experimentation it was observed that the addition of Dolomite increased the catalyst activity from that of the base catalyst, while MnO caused a decrease in activity. It is reported that Mn causes a decrease in the consumption of CO during synthesis, while the oxide promoters enhanced the adsorption of hydrogen. Reference is made to work done by Lohrengel and Baerns (1983) who showed that coverage of the surface with CO is affected when MnO is added to Fe catalysts. It also indicates surface interaction between Fe and MnO. Adesina (1996) refers to explanations of the above mentioned observation which say that light transition metal oxides (Mn, V, Ti) facilitate CO dissociation at the metal/promoter interface due to electronic interaction with the metal surface, thereby lowering the surface H:C ratio. In particular, formation of spinels such as Fe_2MnV_4 , which resist carbide formation, help reduce the rate of carbon deposition and hence improve the catalyst lifetime. This higher resistance to bulk oxidation through Mn addition and improved catalyst lifetime was also confirmed by Lee *et al.* (1992).

Concerning the influence of Mn and Dolomite (Mg & Ca) on the selectivity of the catalysts, Basu *et al.* observed a higher yield of lighter hydrocarbons ($\text{C}_1 - \text{C}_4$) for both promoters. However a closer look shows that the Dolomite increased methane formation and caused a decrease in the $\text{C}_2 - \text{C}_4$ olefin fraction. Mn led to an increase in the methane formation (although less than Dolomite), but the absolute yield of $\text{C}_2 - \text{C}_4$ olefins were slightly higher. The authors concluded that the olefin yield of a Fe based FT catalyst can be improved by increasing the Mn/Fe ratio. This is echoed by a patent of Fiato and Soled (1986b), which claims that Fe-Mn catalysts promoted by Cu and group IA or IIA elements have shown exceptionally high activity and selectivity to 1-olefins. This is also echoed by Lee *et al.* (1992) who concluded that the promotional effect of Mn on the product selectivity is negligibly small and only with the co-existence of K (which promotes the bulk phase transformation to carbides) was the production of valuable olefins and long chain hydrocarbons significantly enhanced.

From a study on unsupported Fe-Mn-K, Das *et al.* (1994) concluded that the influence of Mn on the catalyst appeared to be three-fold:

- Using low Mn content catalysts, the promoter effect seems to be rather small. In moderate promotion (Mn 17 – 33 mol %) greater activity and olefin selectivity were observed.
- The role of Mn is influenced by the presence of K. K seems to override the influence of Mn in controlling the secondary hydrogenation reactions.
- High Mn content catalysts appeared to behave somewhat like supported iron catalysts with increased carbon dioxide formation and decreased secondary hydrogenation tendency.

High conversion along with high olefin selectivity for the C₂ – C₄ range was observed when using a catalyst with 17 – 20 mol % Mn and 0.5 mol % K.

Promotion with Dolomite makes the catalyst more hydrogenating, while Mn promotion reduces its hydrogenation activity. It is speculated that Fe-Mn systems increase the maximum C-O bond dissociation rate amongst the group VIII non-noble metals. The local promotion of CO dissociation caused by the presence of Mn oxides on the metal or carbide surface, together with its inhibiting effect on hydrogen adsorption and thus hydrogenation to paraffins, are also given by Bartholomew (1990) as the reason for high olefin production observed with Mn promotion. Together with this, the presence of Mn oxides at the same time lowers methane production by neutralising acidic sites on the support, which could crack hydrocarbon intermediates to methane. This observation was made for a supported catalyst and claims the opposite of that observed by Basu *et al.* mentioned earlier who did their work on an unsupported precipitated catalyst.

Lee *et al.* (1991) investigated the influence on catalyst behaviour and bulk phase changes of Cr, Mn and Mo as structural promoters on a Fe catalyst. The presence thereof decreased the reducibility of the iron oxides. Cr promoted iron showed a significant portion of Fe as a mixed spinel Fe_{3-y}Cr_yO₄ after reduction at 500°C. For the Mn a small amount of Fe²⁺ species was observed which was stabilised by the formation of a manganowustite intermediate, while super paramagnetic Fe³⁺ species as well as a spinel phase exist on the Mo iron catalyst along with fully reduced metallic alpha-iron and an Fe-Mo alloy. The paper concluded that the more stable behaviour and higher yield of hydrocarbons observed on the Mn-Fe and Mo-Fe catalysts with preference for carbidisation implies carbide phases to be active for production of hydrocarbons.

Soled *et al.* (1995) looked at Fe-Zn systems promoted with K and Cu. They reported an increase in both activity and selectivity, which was assigned to a synergistic enhancement by K and Cu and the in-situ conversion of iron oxides to carbides. A paper by Saglam (1989) also reports on the promotional effect of Zn. The investigation was done with the addition of Zn, V and the

combination thereof. The paper concludes that the addition of V separately or together with Zn greatly increased the olefin selectivity of Fe catalysts (especially the 1-olefin fraction). The separate addition of Zn had less effect on the olefin selectivity, although it was still an improvement over the unpromoted Fe catalyst. Falbe *et al.* (1984) observed that a Fe-V catalyst was best suited for the production of short-chained olefins, followed by Fe-Ti and Fe-Mn catalysts. Addition of K compounds and ZnO or MgO could increase the selectivity of the Fe-V system.

Adesina (1996) reports that like light transition metal oxides, rare earth oxides improve the performance of FT catalysts partly because their presence decrease support acidity. They also cover ("decorate") the metal crystallite surface thus promoting CO dissociation. Exxon (Fiato *et al.*, 1988) showed that catalyst stability and selectivity to olefins could be improved by the addition of Ceria to Fe-Mn-K catalysts. Reference is also made to observations that FT catalysts promoted by lanthanide and actinide elements often yield branched chain hydrocarbons (Madon *et al.*, 1977).

The addition of silica as a binder to a precipitated Fe-Cu catalyst, followed by spraydrying was investigated by Jothimurugesan *et al.* (1998). The addition of Si as a binder increased the attrition resistance of the catalyst significantly. An optimum of 12 wt % binder Si was determined and the addition of precipitated Si to it caused the attrition resistance to decrease and the methane selectivity to increase together with reduced wax formation. Work was also done by Bukur *et al.* (1990) in which the binder/support effects of silica and alumina binders (supports) on the activity and selectivity of Fe FT catalysts were investigated. The addition of silica or alumina to the precipitated unsupported Fe catalyst (Fe/Cu/K) influenced the activity, stability and selectivity of the catalyst during FT synthesis. The changes in the catalyst performance were only really pronounced at high binder (support) concentrations (FTS activity decreased with increased support content per gram of Fe). Interactions between the support and K and/or between the metal and support are seen as the cause of the performance changes (a dilution effect resulting in a reduction of the effective K content of the catalyst). Included in these is a lower degree of Fe reduction after pre-treatment and a decrease in the effective K content of the catalyst.

The improvement in catalyst stability with the addition of silica is attributed to the stabilisation of Fe crystallites during synthesis, or to a decrease in the carbon deposition rate caused by the

reduction in surface basicity. Increased silica content also caused a decrease in WGS activity and product selectivities (no significant changes with the alumina). Total olefin and branched hydrocarbon content decreased, but the fraction of internal olefins increased. These results were in agreement with those obtained by Dry (1981) and Egiebor and Cooper (1985).

The effect of promoters on Co based catalyst used for FT, is mentioned by Jager and Espinoza (1995). Noble metals from group VIII have a beneficial effect on the activity when used as promoters, probably because they facilitate the reduction of Co. Metals like Ru, Re, Hf, Ce, Th and U help to increase activity by re-reducing the catalyst.

2.2.3 Alcohol production catalysts for Fischer-Tropsch application (H_2+CO conversion)

Available patent literature on the production of higher alcohols from syngas was fully reviewed by Xiaoding *et al.* in 1987. This particular paper will thus be used as basis in the discussion of available literature on alcohol synthesis from syngas via FT applications. Xiaoding *et al.* mentions that although many catalyst systems are reported to be active for the selective conversion of synthesis gas into higher alcohols, the results do not always prove the claims of the patents. Potential industrial systems are seen as those that produce alcohols at a rate comparable with the rate over industrial MeOH catalysts (that is 1.3 – 1.5 g MeOH/h/gcat). Xiaoding *et al.* sees four types of catalyst systems to be promising and thus representative of higher alcohol catalysts, if the industrial system criterion is used.

2.2.3.1 Modified MeOH synthesis catalysts

Addition of alkali or alkaline earth metals to some MeOH synthesis catalysts will result in a catalyst also capable of producing higher alcohols. The product will however normally contain mostly methanol and iso-butanol, while little ethanol and propanol are obtained. Süd Chemie has a patent (Hofstadt *et al.*, 1981) claiming the addition of other elements to a Cu/ZnO/Al₂O₃ catalyst in addition to alkali elements, for the production of higher alcohols. The catalyst is prepared by either co-precipitation of Cu-Zn-Al and an alkali compound, followed by calcination or by impregnation of mixed oxides of Cu, Zn, or Al with a solution containing the promoter(s) and alkali, followed by calcination. BET surface areas of between 38 and 61 m²/g are reported.

Operating at a typical temperature of 350°C, 100 bar(g) pressure and 2600 h⁻¹ gas hour space velocity (GHSV), the catalyst gave CO conversions between 21 and 28 mole %. The selectivity for alcohols is 66 – 78.5 %, while that for C₂+ alcohols is 29 – 44.7 % with selectivity for CO₂ 17.4 – 24.9 %. Maximum alcohol productivity calculated is 0.156 kg/h/lcat, with that for C₂+ calculated as 0.049 kg/h/lcat. The liquid product contain mainly methanol (62 – 73 wt %), while the higher alcohols (19 – 30 wt %) contain mainly ethanol (12 – 38 wt %). Few C₅+ alcohols were produced. Modified methanol catalysts require higher temperature and pressure, while the productivity and selectivity for total alcohols and C₂+ alcohols are not satisfactory (Xiaoding *et al.*, 1987).

2.2.3.2. Rh-based catalysts and related systems

Xiaoding *et al.* (1987) discusses a Rh-based catalyst system disclosed by Ichikawa (1985). The system contains Rh, Th and a metal selected from Co, In, Ir, Cd and Re, optionally promoted with Fe, on a suitable support (a silica carrier is preferred). An operating pressure range of atmospheric to more than 300 bar(g) and temperature of 150 – 450°C are disclosed. At fairly low CO conversions (~ 8 %) the selectivity for oxygenates is 37 % with the other products/oxygenates equal to 1.69.

Rh supported on silica and promoted by e.g. Fe, Mn, Mo, W, Th, U, etc. catalysts are disclosed by Union Carbide in two patents (Ellgen and Bhasin, 1977 and 1978). Best results were obtained with a 2.5 wt % Rh on SiO₂ catalyst promoted with 0.05 wt % Fe. Synthesis conversion levels were below 10 % and ethanol was the primary oxygenate produced. Xiaoding *et al.* mentions that Rh based catalysts are especially selective for C₂ oxygenates, but taking into account the price of the metal, it is not selective and active enough to be used on an industrial scale.

2.2.3.3 Catalysts patented by Dow Chemicals for alcohol synthesis

Dow Chemicals claim supported Mo based catalysts capable of making C₂ – C₅ straight chain alcohols (Quardere and Cochran, 1984). These catalysts contain alkalinised agglomerated Mo sulphides made by thermal decomposition of thiomolybdates on a suitable support, e.g. MoS₂/SiO₂-K. W or Re can be used instead of Mo. Interestingly, the catalyst should be free from Fe, Co, Cu, Zn, Rh, Ti, V, Ce, Th, U, Ir, Pd, Pt, Ag, Cd, and halogens, many of which are

the elements normally encountered in higher alcohol catalysts. High operating pressures are claimed (100 – 280 bar(g)). 15 – 30 wt % ethanol and less than 10 wt % C₅+ alcohols are produced. Xiaoding *et al.* reports that the selectivity and conversion for these catalyst systems are not well defined and that they produce too many hydrocarbons and CO₂ (with low total and C₂+ alcohol selectivity), although the fraction of ethanol produced is relatively high.

2.2.3.4 “Institut Francais du Petrole” (IFP) catalysts and related systems

Four patents were granted to the “Institut Francais du Petrole” (IFP) on Co-Cu based catalyst dealing with higher alcohol synthesis. (Sugier and Freund, 1978 and 1981, Courty *et al.*, 1983 and Chaumette *et al.*, 1985). The earliest patent starts with the following formula as a typical catalyst precursor: Cu₁Co₁Cr_{0.8}K_{0.09}O_x (atomic ratio), where Li or Na can replace K and Fe, V and Mn can replace Cr, with the incorporation of Zn sometimes. Preparation is either by co-precipitation from a common aqueous solution of the suitable salts or by preparation via an aqueous solution of Cu, Co and Cr salts of a multifunctional organic acid (preferably citric acid). Following this patent was the second in which other elements (M₁, M₂) were added to the initial catalyst, among which M₁ are rare earth elements and M₂ are noble metals.

Further modifications were made in the patent of County *et al.* (1983) , which include the possibility of replacing Cr by Re, the use of Al together with or instead of Cr and the addition of Sc, Yb, Zr, Th to the M₁ reported in the second patent. The incorporation of Zn is also claimed. This leads to the 1985 patent of Chaumette *et al.* where the main components are claimed to be Cu/Co/Zn/Al/A/(M), with A being alkali or alkaline-earth metals and M standing for group VIII noble metals of Ru, Rh, Pd, Os, Ir, and Pt. Zn can be replaced partially or wholly by Cd or Mn²⁺, and Al by Cr, Mn³⁺ or Ti. Detailed procedures are given which include precipitation temperature, pH value, ageing time and temperature, drying procedures, etc. For all the above-mentioned IFP catalysts the homogeneity of the catalysts precursors during each step of the preparation and pretreatments has been stressed to be a prerequisite for good performance. Operating pressures in the range 50 – 150 bar(g) and temperatures in the range 220 – 350°C are claimed. The performances of the four catalysts were summarised by Xiaoding *et al.* (1987) and this summary is given in Table 2.4.

Table 2.4: IFP alcohol catalysts - performance and composition summary

Catalyst composition	MeOH (wt %)	C ₂ + alcohols (wt %)	Selectivity towards all alcohols (wt %)	Yield (C ₁ -C ₄ OH) (g/gcat/h)
CuCoM _{0.8} A _{0.09} M=Cr,Fe,V or Mn A=alkali (US 4 122 110)	20 – 26	74 – 80	90 – 95	0.27 – 0.92
CuCo(M ₁ +M ₂) _{0.8} A _{0.09-0.01} M ₃ M ₁ =Cr,Mn,Fe or V M ₂ =rare earth M ₃ =noble metals A=alkali (US 4 291 126)	20 – 24	76 – 80	95	0.27 – 0.40
Cu/Co/Al/A/(M ₁)(M ₂)(M ₃)(Zn)(Cr) M ₁ =Mn,V,Fe,Re M ₂ =Sc,Yb,Th,Zr or rare earth M ₃ =noble metals A=alkali (GB 2 118 061)	28 – 61	39 – 72	62 – 70	0.11 – 0.15
Cu/Co/Zn(B)/Al(C)/A/(M) A=alkali or alkaline earth B=Cd or Mn ²⁺ C=Cr, Mn ³⁺ or Ti M=Group VIII metals (Rh,Ru,Pd,Os,Ir or Pt) (GB 2 158 730 A)	-	20 – 77	50 – 77	0.06 – 0.09

The initial IFP catalyst did not have good stability and therefore the activity deteriorated quickly. This was improved towards the later catalysts at the cost of lowered selectivity and activity (see Table 2.4 obtained from Xiaoding *et al.*(1987)). All of the catalyst appeared to be active for the WGS reaction. Xiaoding *et al.* (1987) concludes that these catalysts are the most promising catalysts for the synthesis of higher alcohols from syngas.

Literature reveals some catalysts, which might be seen as IFP-like catalysts. Meyé *et al.* (1985) discloses a Cu/Co/M/A/zeolites catalyst where M can be Cr, Mn or Fe and A is an alkali. The reported selectivities for the C₂ – C₅ alcohols were lower than that observed with the IFP catalysts, while operating at higher temperature and pressure. Xiaoding *et al.* (1987) made mention of other variants of the IFP catalysts, where substitutions or modifications were made,

e.g. replacing Co by Fe, replacing the alkali elements by other basic elements such as alkaline-earth elements. No substantial improvements, either in selectivity or in productivity have been noted.

2.2.4 Olefin production catalysts for Fischer-Tropsch application

This section discusses some of the literature available regarding catalysts developed for the specific purpose of increasing the selectivity towards olefins. Most literature relating to olefin production via FT synthesis deals with Fe catalysts with a lesser amount relating to Co catalysts. Fe based catalysts will thus also enjoy the bulk of the coverage in this section. Relevant patent disclosure as well as open literature regarding olefin production catalysts for FT will be reviewed.

Regarding patents for the production of olefins there is: a patent by Soled and Fiato (1986) which discloses an unsupported Fe-Mn FT catalyst promoted by a group I(a) or II(a) metal salt. This single-phase spinel has the formula $\text{Fe}_x\text{Mn}_y\text{O}_4$, where $x + y$ is 3 and the ratio x/y being 2:1 or above. The catalyst can be used in a fixed bed or slurry reactor type process to optimise $\text{C}_2 - \text{C}_6$ olefin production. The preferred operation temperature for the process is $250 - 300^\circ\text{C}$ and the pressure $6 - 20$ bar(g). The same authors have a similar patent (Soled and Fiato, 1985) with only small differences in the claims. Of the total product about 40 % $\text{C}_2 - \text{C}_5$ 1-olefins are formed with about 10 % methane. In the $\text{C}_2 - \text{C}_5$ range the 1-olefins makes up 85 %. These results are compared to those obtained when no Mn promotion is used. The Fe spinel gives 19 % methane and 35 % of the total product is 1-olefins in the $\text{C}_2 - \text{C}_5$ range, with the 1-olefins accounting for 70 % of the product in this range.

The same unsupported catalyst is also disclosed by Fiato and Soled (1986a), but is now dually promoted with copper and a group I(a) or II(a) metal. A detailed description of the glycolic acid decomposition method for preparation is also provided. The process using the above mentioned catalyst will produce $\text{C}_2 - \text{C}_{20}$ olefins at preferably $260 - 270^\circ\text{C}$ and $5 - 15$ bar(g). This catalyst and process is also claimed by a patent of Fiato and Soled (1986b), but a different temperature range and pressure range make out the claims. Similarly to the above mentioned Fe catalyst is the Cu promoted Co-Mn spinel claimed by a patent of Soled *et al.* (1992a).

A Fe-Zn based catalyst containing Cu and a group I (typical K) promoter, is claimed by Soled *et al.* (1992b). The catalyst has a Fe:Zn ratio of 5:1 and an alkali metal:copper ratio of at least 2:1. Operating at preferably 250 – 300°C and 5 to 20 bar(g), the catalyst produces liquids with a C₅⁺/C₄- product ratio of at least 4.5/1 (preferable 5/1 to 10/1). The olefin/paraffin ratio is 2.5:1 with the C₂ – C₄ 1-olefin fraction 85 – 93 %. The catalyst was prepared via the glycolic acid decomposition method.

Of the relevant patents obtained most were assigned to Exxon Research and Engineering Company. Just about all of the patents make use of Fe or combinations of Fe and other metals. A couple of these patents are supported iron catalysts (Rao and Goemley, 1982, Wright *et al.*, 1985, Fiato *et al.*, 1985, Bussemeier *et al.*, 1986 and Fiato *et al.*, 1986) in combination with Th, Co, Ti and Zn. K is a preferred promoter with all of the mentioned catalysts.

Literature reveals Mn to be the promoter of choice for olefin promotion. Barrault *et al.* (1983) obtained a maximum in light olefin (C₂ – C₄) formation at a Fe/Mn bulk composition of 1. Das *et al.* (1994) report 70 – 80 % light olefins (C₂ – C₄) without formation of excess methane and CO₂ for a Fe catalyst promoted with 20 mol % Mn and 0.5 mol % K. An olefin to paraffin ratio of 22 to 1 is reported for the C₂ and C₃ fraction by Venter and Vannice (1990) when they tested an Fe-Mn-K catalyst under FT conditions.

Saglam (1989) used an Fe catalyst promoted with Zn and V on a fixed bed reactor. The amount of olefins in the hydrocarbon fraction reached over 80 mol %, while the 1-olefin part of the olefin fraction was over 90 mol %. High linear 1-olefin C % for the C₅⁺ fraction is reported (up to 42 %). Data also shows some selectivity towards alcohols, with carbon percentages as high as 9 % reported. The paper does however not give a breakdown of the alcohols produced, and they might thus only be light alcohols. The addition of Zn separately has been less effective on the olefin selectivity of the catalyst. Operating ranges of 220 to 320°C and 10 to 90 bar(g) were used during the investigation.

Most papers dealing with zeolites for the production of light olefins utilise the ZSM-5 type zeolite. Varma *et al.* (1985) looked at the mixture of Co-Ni-Zr and HZSM-5.

It was concluded that the presence of this zeolite results in:

- A substantial decrease in methane, C₂ and C₃ selectivities,
- A substantial decrease in the olefin/paraffin ratio,
- An increase in C₄ fraction with increased isobutane content,

- An increase in the selectivity of gasoline-range hydrocarbons with excellent yields of aromatics (aromatics is temperature related).

It seems that although the use of zeolites is positive in the sense of distorting the Schulz-Flory distribution, it is less effective for olefin production. In such a two-component catalyst system, olefins produced as primary products of the FT reaction are either further hydrogenated to corresponding paraffins over the FT catalyst, or oligomerised over the HZSM-5 to be converted to aromatics.

2.2.5 Influence of operating conditions on FT process selectivity

Factors influencing the product selectivity of the FT process include the catalyst used and process conditions. This section will briefly discuss the influence of operating parameters such as pressure, temperature, space velocity of the synthesis gas and gas composition on the product selectivity. Van der Laan and Beenackers (1999) give an excellent summary of the general influences of the different operating parameters on the selectivity of the FT process. Table 2.5 is a duplication of this particular summary.

Table 2.5: Selectivity control by process conditions in FT synthesis

Parameter	Chain length	Chain branching	Olefin selectivity	Alcohol selectivity	Carbon deposition	Methane selectivity
Temperature	↓	↑	*	↓	↑	↑
Pressure	↑	↓	*	↑	*	↓
H ₂ /CO	↓	↑	↓	↓	↓	↑
Conversion	*	*	↓	↓	↑	↑
Space velocity	*	*	↑	↑	*	↓

Increase with increasing parameter: ↑

Decrease with increasing parameter: ↓

Complex relation: *

2.2.5.1 Influence of operating temperature on product selectivity:

An increase in temperature results (irrespective of the catalyst type – Fe, Co, Ru, etc.) in an increase in methane selectivity, and thus the probability of chain growth decreases (Dry, 1996). In the temperature range where FT is normally practised, thermodynamics predicts that the products should mainly consist of methane and graphite. The increase in methane selectivity at

higher temperatures may therefore mean that thermodynamic factors start taking over from the mechanistic kinetic factors (Dry, 1990).

Van der Laan and Beenackers (1999) report that some literature indicate an increase of the olefin to paraffin ratio on K promoted precipitated Fe catalysts, while other report a decrease of the olefin selectivity on un-alkalised Fe oxide powder, when increasing the operating temperature. Dry (1990) explains that linear 1-olefins, paraffins, alcohols, aldehydes and carboxylic acids are primary products in the FT synthesis. These products predominate at low temperature, while secondary reactions occur at increased temperature resulting in the formation of ketones and the occurrences of isomerisation.

Xiaoding *et al.* (1987) confirms that the increase of reaction temperature is unfavourable thermodynamically for FT synthesis, methanol synthesis and for higher alcohol synthesis. An upper temperature limit does exist for the synthesis of alcohols, as some oxygenates will not be stable enough and decompose at temperatures above 450°C. Increased temperature does however increase productivity and suppresses possible mass transfer limitations.

2.2.5.2 Influence of pressure on product selectivity:

Dry (1981) reports that most studies show the product selectivity to shift towards heavier products and to more oxygenates with increased total pressure. A change in total pressure will not influence the WGS reaction and skeletal isomerisation, but it will change the equilibrium product distribution for all the other reactions starting from syngas (Xiaoding *et al.*, 1987).

Relating to pressure is the effect of the partial pressure of the different reactants (H₂ and CO). Dry (1981) showed a relation between the methane selectivity as well as an increase in oxygenate (alcohol) selectivity for the Synthol process at increased hydrogen partial pressures. Donnelly and Satterfield (1989) observed more lighter hydrocarbons and a decrease of the olefin to paraffin ratio when increasing the H₂/CO within the reactor. Xiaoding *et al.* (1987) explains that decreasing the H₂/CO ratio will favour CO insertion and C-C chain growth, leading to increased production of higher alcohols and/or hydrocarbons, while the opposite favours the production of lower alcohols and hydrocarbons (also saturated hydrocarbons).

2.2.5.3 Influence of space velocity on product selectivity:

The space velocity will determine the contact time. An increase in space velocity will increase the productivity and may lower the conversion when a reaction is kinetically controlled (Xiaoding *et al.*, 1987). On the other hand, when a reaction is mass transfer controlled, an increase in space velocity will be favourable for the mass transfer of reactants to the core of the catalyst particles and unfavourable for the secondary reactions. An increase in space velocity is normally favourable for the synthesis of higher alcohols.

Kuipers *et al.* (1996) observed an increase of the olefin to paraffin ratio with increasing space velocity, and therefore at lower conversions for a Co based catalyst. The same result was observed by Bukur *et al.* (1990) on a commercial supported Fe catalyst. Van der Laan and Beenackers (1999) show a figure obtained from literature, which indicates that the selectivity to methane and olefins decreases with a decrease of the space velocity, while the selectivity towards paraffins remains unchanged. An increase in the average molecular weight of the products with a decrease in the space velocity is thus observed.

2.3 EXPERIMENTAL

2.3.1 Equipment and procedures

2.3.1.1 Laboratory reactor

A variety of reactor types (fixed bed, bubble column slurry, stirred tank slurry and internal recycle) have been used in the literature for the investigation of FT synthesis and kinetics. Although each reactor type has its advantages and disadvantages, it seems that the stirred tank reactor is most often considered as best suited for fundamental studies. Advantages to this reactor type include (Zimmerman and Bukur, 1990):

- i. Excellent heat transfer characteristics provides for a uniform reaction temperature.
- ii. Intra-particle transport effects can be eliminated using finely ground catalyst particles, with no increase in pressure drop, together with stirring speed adjustments. Van Berge *et al.* (1991) relates this to an obtainable overall effectiveness factor of 1 (Defined as the actual reaction rate divided by the reaction rate in the absence of mass transfer resistance).

- iii. Low H_2/CO feed ratios can be processed without excessive carbon deposition. This means that a wide range of conditions with respect to gas composition and temperature can be investigated.
- iv. Simplified data analysis since the species concentrations and temperature are uniform throughout the reactor.
- v. Control of interphase mass transport by adjustment of the stirring speed.

Uniform concentrations throughout the reactor implies that data obtained at the outlet of the reactor will be representative of reactor conditions. This simplifies any partial pressure calculations of reactant within the reactor. The control over mass transfer via the adjustment of the stirring speed ensures ease of kinetic data interpretation. The disadvantages of the stirred tank slurry reactor are collecting and quantifying the high molecular weight products, which accumulate in the reactor during the synthesis.

General reactor description:

A micro slurry bed reactor was chosen for laboratory experimentation. Figure 2.2 gives a flow scheme of the reactor used for the laboratory experimentation.

Gas enters the slurry reactor by means of a tube, which ensures the release of the gas onto the bottom impeller for dispersion throughout the reactor. Reactor volume is 500 ml. The stirrer with its impellers will ensure complete mixing of the liquid phase, uniform distribution of the catalyst, and high mass and heat transfer rates. A continuous filtering unit within the reactor prevents catalyst loss, while facilitating the draining of product out of the reactor.

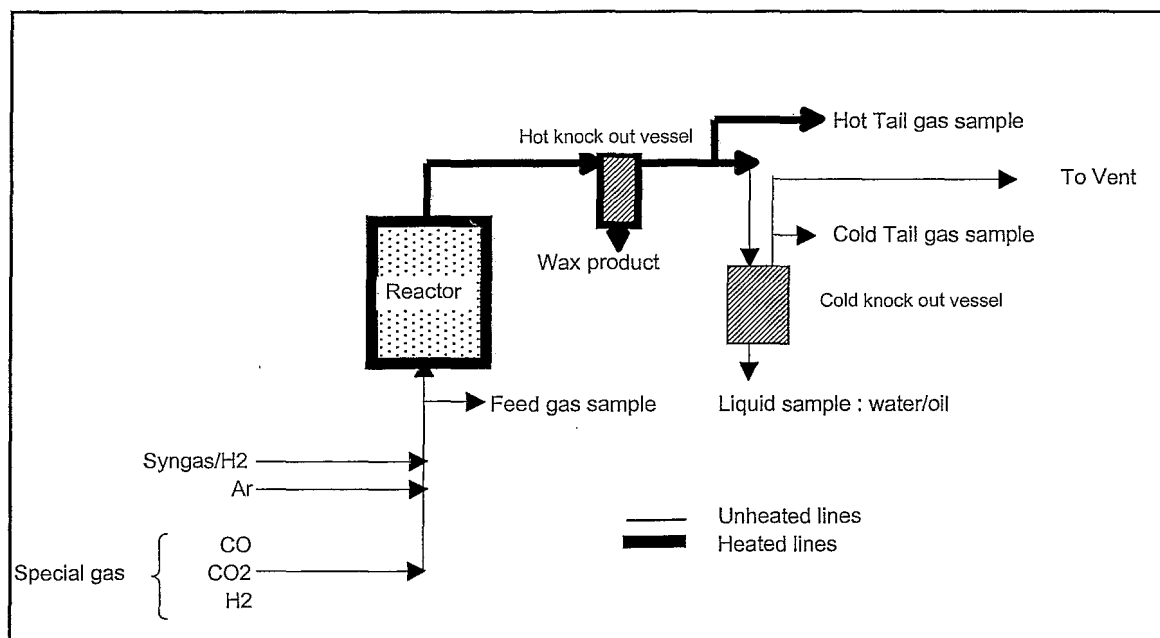


Figure 2.2: Laboratory reactor system flow scheme

Synthesis gas is supplied to the system directly from the Lurgi gasifiers after sulphur removal and purification (known as Arge pure gas – APG). The reactor has the option of adding either H_2 , CO or CO_2 together with the APG (see Table 2.6 for composition) and argon (used as inert tracer gas), which ensures that the desired $H_2:CO:CO_2$ feed ratios can be obtained. Gases not obtained from cylinders are pressurised with a compressor to the pressures needed for the experimentation. Flow of the various gases is controlled with Brooks mass flow controllers, calibrated for the specific applications.

Product and unreacted gas exits the reactor and passes through the hot knock-out vessel (controlled at a temperature of about 180 - 200°C), where higher boiling temperature products (typical wax product and carry over from reactor medium) accumulates. This vessel is followed by the hot gas sample point. This sample point is used for the taking of gas samples that could be quantitatively analysed for product up to C_{15} . From this point onward the lines and vessels are not heated. Gas passes through a water-cooled knock-out vessel (25 – 30°C) where the liquid phase products (water and oil fraction) are drained. This vessel is followed by another ampoule gas sample point for taking cold tail gas samples. These samples enabled the construction of the total mass balance.

The remainder of the gas passes through the backpressure regulator and is released into the venting line system at atmospheric pressure. Temperature can be measured and controlled

automatically on the system, while the pressure control is performed manually using the backpressure regulator. A humidity meter and a Micro-motion mass flow meter are connected to the tailgas.

Table 2.6: Typical Arge pure gas (APG) composition

Component	Mol %
H ₂	58.0
CO	29.0
CO ₂	0.8
CH ₄	12.0
Ar + C ₂ H ₆	0.2

Gas sampling:

Gas samples can be taken of the feed, hot tail and cold tail gas for GC analyses via a sample point. The so-called glass ampoule technique developed at the Engler-Bunte Institute, Karlsruhe University, Germany (Caricato *et al.*, 1993) was used to take the samples. The technique consists of the ampoule sampler where the ampoule is filled with the sample gas, sealing of the ampoule by making use of a portable butane burner and using a modified GC system capable of breaking the ampoule and thus retrieving the gas sample under controlled conditions. Figure 2.3 shows the dimensions of the evacuated glass ampoule (Caricato *et al.* (1993)). The ampoule technique enabled the sampling of excess ampoules, to be stored for extended periods and furthermore isolates the reactor system from the analytical equipment (GC) thereby ensuring that breakdown thereof will not impact on the reactor run directly. This technique results in a single ampoule containing a quantitative sample of all the hydrocarbons from C₁ to C₁₅ as well as possible alternative gases such as Ar, N₂, CO, CO₂, etc.

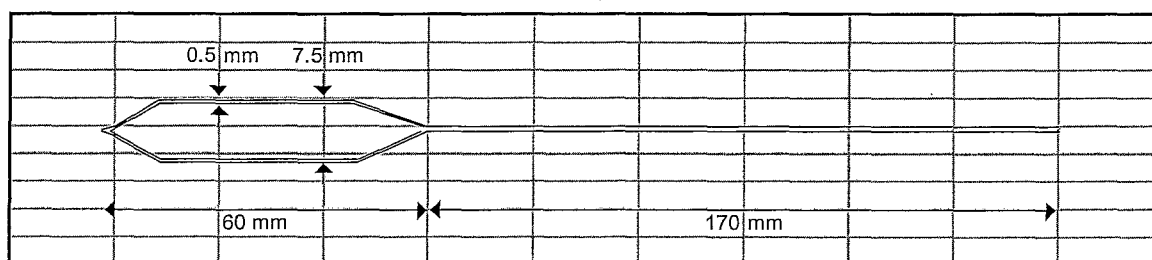


Figure 2.3: Dimensions of evacuated glass ampoule

Reactor operating conditions:

The laboratory reactor can operate at pressures varying from atmospheric to 50 bar(g) at temperatures up to 250°C. To eliminate the influence of the conversion level on the product spectrum/catalyst selectivity, the GHSV was adjusted for the different experiments to a 40 % CO+CO₂ conversion level. Such a conversion level was found to give optimal selectivity results while it is still sufficiently high to relate to a commercial application. Using CO+CO₂ conversion gives an indication of conversion of CO to hydrocarbon products.

Previous work done on the slurry reactor indicated that a stirring speed of 450 rpm is sufficient to eliminate any inter particle transport effects. This result was again confirmed to be true (see Figure 2.4). Further verification of the chosen stirrer speed (450 rpm) was obtained by varying the catalyst particle size.

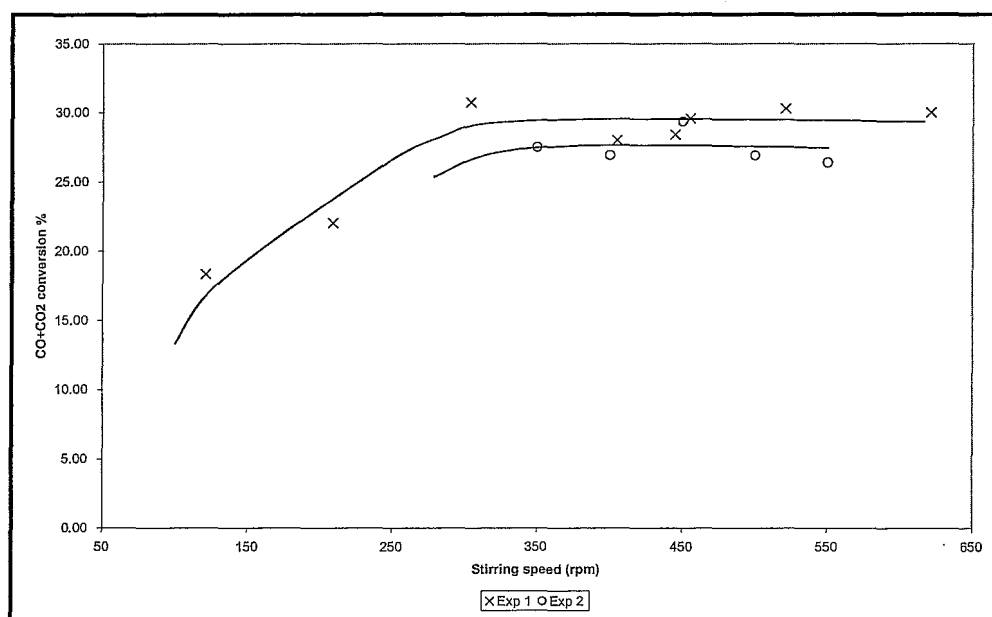


Figure 2.4: Stirrer speed effect on CO+CO₂ conversion

Different sieved catalyst size fractions (< 75, 75 – 150, 150-300 µm) were tested at a stirring speed of 450 rpm. All other reactor-operating parameters (temperature, pressure, GHSV) were kept constant. Similar FT reaction rates were observed, which indicates that the stirrer speed is sufficient to eliminate any interparticle diffusional effects during the kinetic investigation. A catalyst particle size of between 38 and 150 µm was chosen for experimental investigations when using the laboratory micro slurry bed reactor. Figure 2.5 shows the results obtained for experiments performed with different sieved out size fractions of the catalyst.

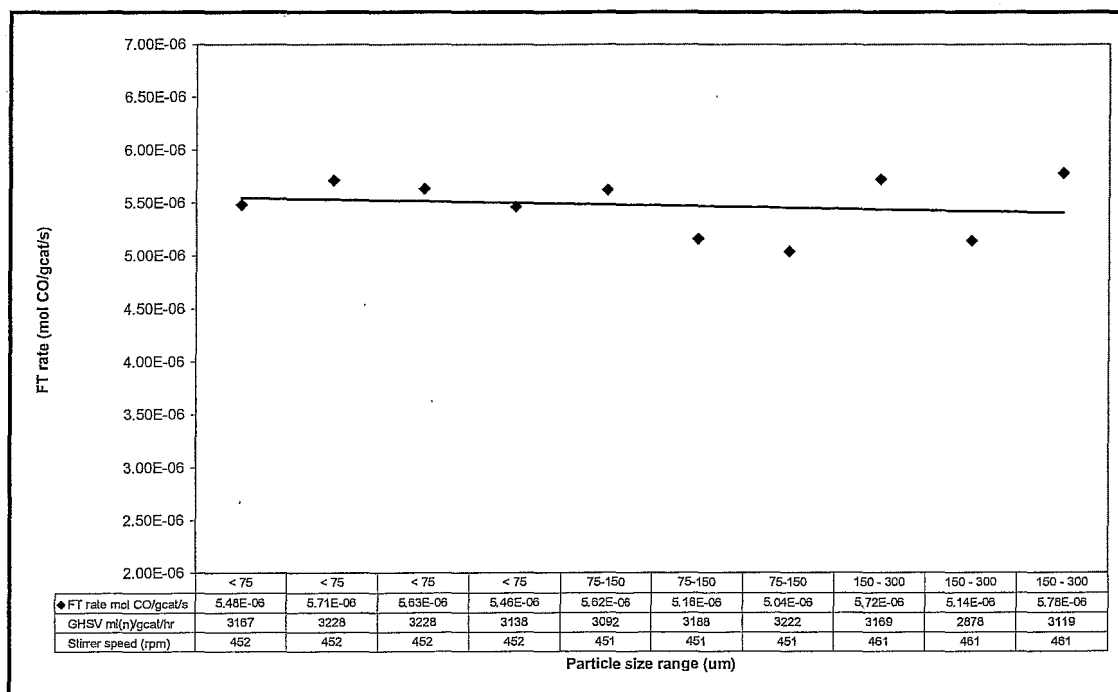


Figure 2.5: Particle size effect on the observed FT reaction rate

2.3.1.2 Catalyst characterisation

i) *Temperature programmed reduction (TPR)* was performed on TPD/TPR 2900 (Micromeritics) instrument. Approximately 0.025 g of sample was exposed to a 10 % H₂ in Ar flow at 45 ml/min with a 10°C/min increase in temperature. The hydrogen consumption was measured as a function of time and temperature.

ii) *The surface area and pore volume* of the samples were recorded on a Gemini (Micromeritics) instrument. Approximately 0.05 g of sample was dried externally at 200°C under a nitrogen flow. This was followed by an in-situ evacuation and analysis. Analysis consisted of placing standard increments of nitrogen into the cell under liquid nitrogen atmosphere, until atmospheric pressure was reached.

iii) *Mössbauer measurements* were performed with a 50 mCi ⁵⁷Co Rh source. The spectrometer was operated in the symmetric constant acceleration mode with 100 μs of a dwell time per channel. Each spectrum was collected over 1024 channels in a mirror image format. All the isomer shift values are reported relative to metallic iron.

2.3.1.3 Gas chromatography analyses

i) *TCD*: Permanent gases (H_2 , Ar, N_2 , CO, CH_4 and CO_2) were analysed on a GC equipped with two thermal conductivity detectors (TCD's), a molsieve 5Å-3 metre column and a Porapak Q column. Ar is used on one of the TCD channels as carrier for H_2 analysis, while He is used on the other to analyse for Ar, N_2 , CO, CH_4 and CO_2 . The GC is able to handle ampoule samples by way of ensuring a vacuum over the system and breaking the gas ampoule into the system, thereby sucking in the gas. Appendix 1 shows typical TCD analyses of the reactor feed and outlet. An experimental error of maximum around 5 % can be expected from chromatography analyses.

ii) *FID*: The analysis of the organic FT products up to C_{15} was done using a Perkin Elmer auto system XL GC equipped with a flame ionisation detector (FID) and modified to handle ampoule samples. The GC was equipped with a Petrocol DH 150 metre column using hydrogen as carrier gas. The ampoule sample was preheated to about 200°C before breakage, to ensure that all sampled hydrocarbons were evaporated. The equipment is fitted with a pneumatic ampoule breaker. Appendix 1 shows typical FID analyses of the reactor feed and outlet with some of the most prominent peaks identified.

iii) *Liquid product*: Liquid samples were separated into water and oil. The oil fraction was analysed using a Petrocol 50 metre column. It was possible to obtain a breakdown of the olefins, paraffins, alcohols, ketones and iso-products from C_1 to C_{30} .

The water fraction was analysed by doing an acid number on it and by using a GC column capable of handling water which gave a breakdown of the compounds present in the sample. An Innowax column gave a breakdown of non-acidic components present (mainly oxygenates), while a FFAP column was used to give a distribution of all organic components present within the water (including organic acids). An acid number is an indication of the acidity of the water product determined by titration with a standard base (0.05M KOH solution) to a phenolphthalein end point.

2.3.1.4 Processing of reactor data

The processing of reactor analysis data will be explained with reference to Figure 2.2, which was a presentation of our micro slurry bed reactor configuration. Gas samples were taken with the

ampoule technique of the feed, cold tail and hot tail. CSTR behaviour of the reactor system simplifies data processing as the hot tail gas composition will be representative of that within the reactor. These gas samples were analysed with TCD and FID gas chromatography. Wax product was drained from the hot pot (set to 180 – 200°C). This product weight is used as part of the mass balances, but due to low wax production and the relatively short testing period it is not possible to have a representative sample of wax for selectivity purposes.

Liquid product consisting of reaction water and oil, was drained from the cold pot (pot was submerged in water and was at about 20°C). The water and oil fractions were separated and sent in for analyses. The oil fraction was analysed with a GC for 1-olefins, internal olefins (Trans-2 and Cis-2-olefins), normal-paraffins, normal-alcohols and ketones, while all the rest of the components present were sorted under iso-olefins and iso-paraffins. A GC analysis was done on the water fraction to determine the amounts of oxygenates (specifically alcohols) present.

Conversions, reactor partial pressures and flows were calculated from the TCD analyses with the help of the argon tracer gas. The data manipulation procedures using data from the GC ampoule technique is fully described by Harms (1996) in an in-house report. The procedure entails that the results from the TCD (feed and cold tail) are used to calculate the absolute flow rates of the permanent gases (H₂, CO, CH₄ and CO₂) entering and leaving the reactor, with the assistance of the internal inert reference gas (Ar gas). This calculation is done by using the following relationship for the molar flow rate of component “i” as a function of known and measurable quantities:

$$n_i^T = \left(\frac{A_i^{TCD} \cdot P_i^C \cdot n_{Ar}^T}{A_{Ar}^{TCD} \cdot P_{Ar}^C} \right) / \left(\frac{A_i^{TCD,C}}{A_{Ar}^{TCD,C}} \right) \dots 2.1$$

With: n_i^T = total molar flow of component i, mol/s
 A_i^{TCD} = peak area of component i in the TCD spectra,
 P_i^C = quantity of i in the reference gas, mole percentage
 A_{Ar}^{TCD} = peak area of Argon in the TCD spectra,
 P_{Ar}^C = quantity of Argon in the reference gas, mole percentage
 $A_i^{TCD,C}$ = TCD peak area of component i in the calibration gas,
 $A_{Ar}^{TCD,C}$ = TCD peak area of Argon in the calibration gas,
 n_{Ar}^T = molar flow rate of Argon, mol/s.

With the above mentioned permanent gases calculated it is possible to use a carbon balance in determining the total amount of hydrocarbons formed. By setting up a carbon balance, with C₃ being representative of the volatile hydrocarbon stream, one obtains:

$$n_{HC}^{T,OUT} = \frac{(n_{CO}^{T,IN} - n_{CO}^{T,OUT}) - (n_{CO_2}^{T,OUT} - n_{CO_2}^{T,IN}) - (n_{CH_4}^{T,OUT} - n_{CH_4}^{T,IN})}{3} \dots 2.2$$

with

$n_i^{T,OUT}$ = total out flow of component "i", mol/s

$n_i^{T,IN}$ = total in flow of component "i", mol/s

TCD analyses cannot directly measure water as well as the volatile hydrocarbons and oxygenates. Traditionally, equations to calculate water flows for FT synthesis, assume that the contribution of the volatile oxygenates to the product stream is negligible and therefore the water flow rate is calculated via an oxygen balance:

$$n_{H_2O}^{T,OUT} = n_{CO}^{T,IN} - n_{CO}^{T,OUT} - 2 \cdot (n_{CO_2}^{T,OUT} - n_{CO_2}^{T,IN}) \dots 2.3$$

This approach will also be followed for the purpose of evaluating the catalyst in this section, although a slightly different approach will be followed for the kinetic study discussed in Chapter 4.

Permanent gases plus the Ar tracer accounted for the total inlet flow of the reactor, while the reactor outlet flow consisted of the water and hydrocarbon flows plus the unreacted permanent gases. Reactor partial pressures could be estimated using the relationship between the specific gas component, total reactor pressure and reactor total outlet flow.

Product distribution (selectivity) data were obtained from TCD, FID and other GC analyses. Figure 2.6 gives a summary of the analyses used to calculate a mass balance and total product distribution. Figure 2.6 furthermore explains the process followed to combine the data obtained from the different analyses. Methane is basically used as tie component between the analysis obtained from the TCD GC and the FID GC, as it is the only component that is accurately measured by both analyses.

Mass balances			
IN:	Feed	Gas	TCD FID
OUT:	Hot Tail	Gas	TCD
	Cold Tail	Gas	FID
	Cold condensate	Oil	GC
		Water	GC
	Hot condensate	Wax	GC
From TCD:	CH ₄ in feed - mol/time		
	CH ₄ in hot tail - mol/time		
To relate TCD to FID:			
Assume that:	CH ₄ in TCD feed = CH ₄ in FID feed		
	CH ₄ in TCD hot tail = CH ₄ in FID cold tail		
FID → Area % = Mass % → mol %			
With CH ₄ mol flow relate to total flow of feed and Cold tail → get mass flow → get netto product (mass/time)			
Oil mass/time relate to analysis mass % to get mass/time			
Water mass/time relate to water GC analysis (mass %) to get mass/time			
Wax mass/time relate to analysis (mass %) to get mass/time			
Balance:			
IN =	Feed gas	$\left\{ \begin{array}{l} \text{H}_2 \\ \text{CO} \\ \text{CH}_4 \\ \text{CO}_2 \\ \text{H/C} = \text{FID Feed} - \text{CH}_4 \end{array} \right.$	
OUT =	gas	$\left\{ \begin{array}{l} \text{H}_2 \\ \text{CO} \\ \text{CH}_4 \\ \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{H/C} = \text{FID CT} - \text{CH}_4 \end{array} \right.$	
	+ Hot condensate Wax (as drained)		
	+ Cold condensate oil (as drained)		
	+ Cold condensate water (as drained)		
Total product distribution			
Exclude CO ₂ formed and water (Alcohols in water are used)			

Figure 2.6: Construction of a mass balance and product distribution from experimental data

2.3.2 Development of new ChemFT catalyst

Discussed literature on Fe catalysis indicates that catalyst activity can be enhanced by the inclusion of an alkali metal such as K, while catalyst reducibility is enhanced by the inclusion of Cu into the catalyst. Chain growth probability can be controlled through the addition of K. The combination of these three metals would thus constitute a relative cheap Fischer-Tropsch catalyst with high activity. This proven combination formed the basis of the ChemFT catalyst development.

Both Zn and Mn are seen as olefin promoters while Mn can further improve catalyst lifetime. Mn is also associated with Co based alcohol catalysts. The combination of these two metal promoters unexpectedly seems to form a synergistic effect that enhances both olefin and higher alcohol selectivity under Fischer-Tropsch conditions.

In-house development work on the ChemFT catalyst has shown the catalyst crystallite size to be dependent on the Mn levels of the catalyst. The presence of Mn caused the mean crystallite size to decrease (Motjope, 2001). Such a decrease in crystallite size will favour the formation of primary products. Figures 2.7 and 2.8 show transmission electron microscopy (TEM) images of the ChemFT catalyst, with and without the presence of Mn. Figure 2.7 clearly shows smaller crystallites, which result in more homogeneous catalyst crystallite dispersion. A binder added to a precipitated catalyst will enhance attrition resistance during operation in a commercial slurry bed reactor. Such a binder is SiO_2 .

The final catalyst was developed over a period of time. The final composition was the result of an experimental program that statistically evaluated the different promoter influences and the levels thereof (H. Dlamini *et al.*, 2001, Van Zyl, 2001). The development of the catalyst itself does not fall within the scope of this investigation, although the characterisation of the final catalyst will be given to enable a broader understanding of catalyst and product differences compared to traditional FT process catalysts. Table 2.7 shows the desired composition of the developed catalyst.

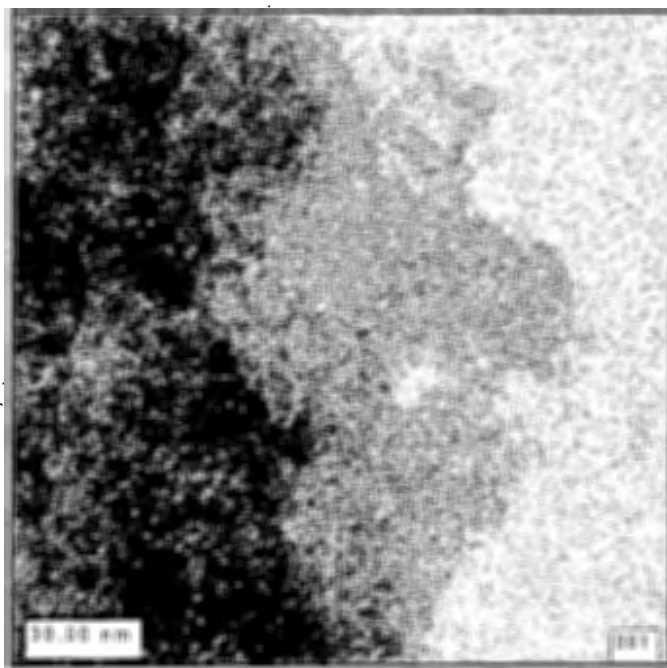


Figure 2.7: TEM image of ChemFT catalyst prepared containing Manganese



Figure 2.8: TEM image of ChemFT catalyst prepared without Manganese

Table 2.7: ChemFT catalyst elemental composition

	Desired chemical composition
Mass % Fe	50.0
Zn/100 Fe	10.0
Mn/100 Fe	25.0
Cu/100 Fe	2.0
K ₂ O/100 Fe	2.0
SiO ₂ /100 Fe	5.0

2.3.3 Preparation of ChemFT catalyst

2.3.3.1 Preparation

The catalyst developed for the production of chemicals via the FT process and used in this investigation was prepared using a continuous precipitation method. This method of preparation was chosen, as it can be scaled-up for commercial application. The method of preparation also allows for a satisfactory degree of control over preparation variables such as temperature and pH. Pilot plant scale equipment was used for the preparation, necessitating the preparation of fairly big batches (~ 20 kg per batch).

Preparation of the final catalyst entailed the following steps (also see Figure 2.9 and Appendix 2 for a detail description of the different steps):

- Fe(NO₃)₃, Zn(NO₃)₂, Mn(NO₃)₃, KNO₃ and Cu(NO₃)₂ were dissolved in distilled water.
- FeC₂O₄ was dissolved separately in dilute HNO₃. This solution was added to the other metal salt solution and the volume of the solution adjusted to obtain the desired Fe concentration.
- The solution was heated up to 70°C.
- A solution of ammonia (25 % NH₃ in H₂O) was co-fed with the metal solution into a precipitation vessel with the feed adjusted such that the precipitation pH was about 8 and the temperature 70°C.
- The precipitate was filtered and washed to the desired conductivity, followed by the re-slurrying of the precipitate. The elemental composition of the slurry was determined via inductively coupled plasma atomic emission spectroscopy.
- Zn, K and Cu were re-added to the slurry in order to obtain the target promoter levels.
- SiO₂ was added to the slurry as binder.
- The catalyst was spraydried to obtain spherical particles.
- Finally the catalyst was calcined.

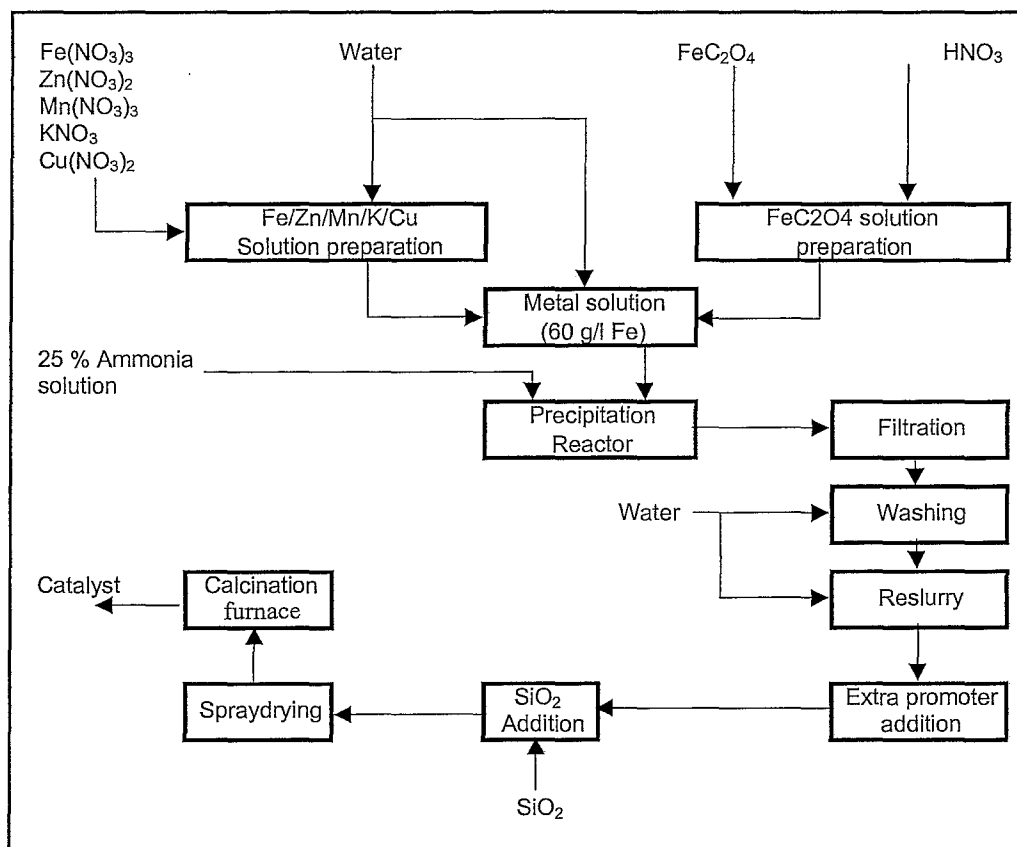


Figure 2.9: Diagram of preparation procedure

2.3.3.2 Calcination of catalyst

Small samples of the prepared catalyst were calcined in an electrically heated furnace (under air) at different temperatures and duration, in an effort to obtain the optimum calcination conditions for the prepared catalyst. Samples were calcined at 400°C for 5 hours and 16 hours and at 450°C, 500°C, 600°C and 700°C for 16 hours.

2.3.3.3 Reduction and conditioning of catalyst (activation)

The catalysts calcined at different temperatures were subjected to various reduction and conditioning procedures. These include in-situ and ex-situ reductions as well as high and low pressures and temperatures. Ex-situ reduction was used in high temperature cases where reactor limitations make in-situ reduction impossible. The chosen method ensured a satisfactory degree of reduction for the completion of the kinetic study of the catalyst. Final optimisation of the

reduction and conditioning method for this catalyst will form part of future experimental programs. Hydrogen was used as the reductant for all the experiments.

In-situ reduction of the catalyst:

20 g of the calcined catalyst was suspended in 350 g of hydrogenated FT synthesis wax and loaded into a slurry bed micro reactor. Pressure was increased to 20 bar(g) under an Ar atmosphere, during which time the reactor temperature was adjusted to 240°C. Reduction took place at 20 bar(g) and 240°C by introducing hydrogen at a space velocity of 6000 ml(n)/gcat/h. Ar was continuously fed at 10 % of the hydrogen flow, as a safety precaution against hydrogen supply interruptions. 16 hours was allowed for reduction. After the 16-hour reduction period, the reactor temperature was decreased to 200°C, while still under hydrogen. It took about an hour for the reactor to cool to 200°C. At 200°C, synthesis gas (APG) was introduced into the reactor at a GHSV of about 3000 ml(n)/gcat/h, while the hydrogen flow was closed. Ar was used at 10 % of the synthesis gas flow as an inert tracer for gas chromatography analyses. An hour after the introduction of the synthesis gas the reactor temperature was increased to 240°C.

The reduction procedure for experiments at 45 bar(g) synthesis pressure was similar to that of the 20 bar(g) experiments up to the conditioning step of 200°C. At this point synthesis gas was introduced at a GHSV of 6000 ml(n)/gcat/h (higher flow facilitates the increase in reactor pressure). After an hour at these conditions the reactor pressure and temperature were increased to 45 bar(g) and 240°C. The synthesis gas GHSV was decreased to 4000 ml(n)/gcat/h upon reaching synthesis conditions. Ar was used at 10 % of the synthesis gas flow as an inert tracer gas.

Ex-situ reduction of the catalyst:

20 g of the calcined catalyst was loaded into a quartz tube. Reduction was done at 1 bar(g) and 340°C for 16 hours with a hydrogen space velocity of 2000 ml(n)/gcat/h. After the reduction time the catalyst was unloaded into a small amount of molten wax under an Ar atmosphere to prevent re-oxidation. The balance of wax (350 g minus the mass used for unloading of catalyst) was melted in the slurry bed reactor. Ar was used to de-gas the molten wax and to ensure an inert atmosphere within the reactor when the cube of reduced catalyst was added.

The reactor was pressurised to 20 bar(g) and temperature of 200°C with Ar. Upon reaching these conditions synthesis gas was introduced at a GHSV of about 2000 ml(n)/gcat/h. After an hour, the reactor temperature was increased to synthesis temperature (240°C). Ar was used at 10 % of

the synthesis gas flow as an inert tracer gas. High pressure experiments (45 bar(g)) followed the same procedure as described under in-situ reduction.

2.4 RESULTS AND DISCUSSION

2.4.1 ChemFT catalyst characterisation

2.4.1.1 Catalyst composition

Results from the chemical analysis performed on the 38 to 150 micron catalyst fraction are presented in Table 2.8. The Fe content was determined via a titration technique, the K, Mn, Cu and Zn with atomic adsorption and the SiO₂ by means of inductively coupled plasma atomic emission spectroscopy.

Table 2.8: ChemFT prepared catalyst elemental composition

	Desired chemical composition	Actual composition
Mass % Fe	50.0	44.8
Zn/100 Fe	10.0	11.4
Mn/100 Fe	25.0	22.1
Cu/100 Fe	2.0	2.2
K ₂ O/100 Fe	2.0	2.0
SiO ₂ /100 Fe	5.0	4.8

2.4.1.2 Characteristics of calcined catalysts

Fresh catalyst samples:

Results obtained for the phase composition, surface area and pore volume are summarised in Table 2.9 for the fresh catalysts calcined at different conditions. Catalysts calcined at 400 and 450°C show the phase composition to be ferrihydrite (Fe³⁺), while calcination above 450°C results in the transformation of small particles of ferrihydrite to large particles of hematite (α -Fe₂O₃). Schwertmann and Cornell (1991) report that the conversion of ferrihydrite to hematite takes place under mild heating. After calcination at 700°C the catalyst still contains small quantities of ferrihydrite. This suggests that there is a limiting factor in the transformation of ferrihydrite to hematite. In-house research on similar catalysts has shown that Mn assists in the stabilisation of small particles of iron oxide (Dlamini and Gibson, 1998). Lee *et al.* (1991) also observed the stabilising effect of Mn.

Table 2.9: Fresh ChemFT catalyst characterisation results

Calcination conditions	Surface area (m ² /g)	Pore volume (cm ³ /g)	Mössbauer phases
400°C for 5h	106.0	0.312	Ferrihydrite (100 %)
400°C for 16h	113.0	0.354	Ferrihydrite (100 %)
450°C for 16h	118.0	0.338	Ferrihydrite (100 %)
500°C for 16h	79.6	0.310	Ferrihydrite (67 %) Hematite (33 %)
600°C for 16h	39.1	0.262	Ferrihydrite (31 %) Hematite (69 %)
700°C for 16h	27.7	0.222	Ferrihydrite (23 %) Hematite (77 %)

The influence of calcination temperature and time can best be seen in Figure 2.10. The drop in surface area as shown on Figure 2.10 can be ascribed to sintering that occurs during calcination (Motjope and Breedts, 2000). The catalyst shows a 25 % loss in surface area at a calcination temperature of 500°C and more severe loss at 600°C. A gradual loss in pore volume was observed with increase in calcination temperature, especially at temperatures of 600°C and above. The relationship between average pore diameter, surface area and pore volume is:

$$\text{average diameter} = \frac{4(\text{pore volume})}{\text{surface area}} \dots 2.4$$

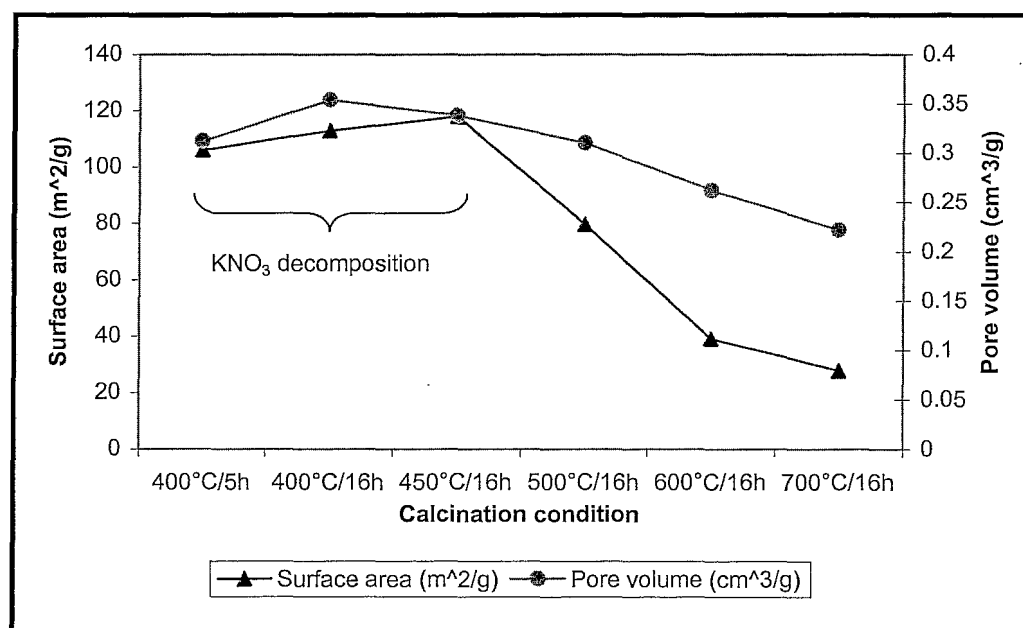


Figure 2.10 Temperature influence on catalyst surface area and pore volume

A notable decrease in surface area decrease together with a less notable pore volume decrease would result in an increase of the average pore diameter. This could be explained as a result of sintering where especially the small pores are reduced in volume by calcination due to collapse of pore walls at high temperature. Hence the change in total surface area is larger than the change in total pore volume.

Rüede (1980) showed similar results during an in-house investigation on commercial fixed bed Fe catalyst. It was found that calcination above 500°C changed the physical (surface area and pore volume) and the chemical (activity and selectivity) properties of the catalyst. Areas decreased from 298 m²/g for the standard catalyst to 253 m²/g (500°C), 198 m²/g (600°C), 105 m²/g (700°C), and less than 1 m²/g (900°C). The pore volume also showed a decrease, which was quite substantial above 700°C (from 0.65 cm³/g -> 0.59 cm³/g -> 0.45 cm³/g -> 0.003 cm³/g).

The small initial increase in area and pore volume as observed on Figure 2.10 can be attributed to the decomposition of the KNO₃ present in the catalyst after preparation. Extending the calcination time from 5 hours to 16 helped to completely decompose this nitrate. 450°C seems to be adequate for the decomposition of NH₄ nitrates (confirmed by TGA analyses).

The TPR spectra show that calcination temperatures below 600°C have similar reduction profiles. Reduction of Fe³⁺ to Fe²⁺ (the first peak), and Fe²⁺ to metallic iron (the second peak) is expected from this catalyst. The hydrogen consumption profiles show a temperature maximum during the reduction process. The observed peak maxima are reported in Table 2.10. Figure 2.11 shows the TPR spectra of the 450°C/16 hours-calcined catalyst. Peaks due to Zn, Mn, Cu cannot easily be detected with a TPR analysis, but the influence thereof might contribute to the shift in peak maxima temperatures observed for higher calcination temperatures.

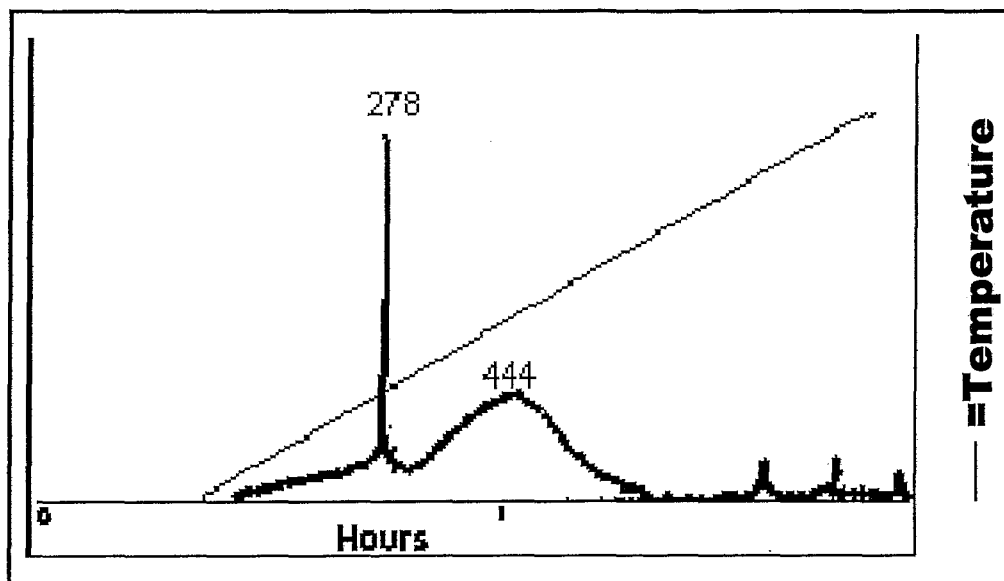


Figure 2.11: TPR spectra 450°C/16 hours calcination

Table 2.10: Results of TPR analysis for ChemFT catalyst

Calcination Temperature (°C)	Peak maxima (°C)
400	284, 447
450	278, 444
500	280, 458
600	310 – 325, 507

Spent catalyst samples:

Mössbauer spectra can be used to differentiate between different metal phases present within a catalyst. Mössbauer spectra of the catalysts calcined at the various temperatures and exposed to FT synthesis conditions for periods shown in Table 2.11 are shown in Figure 2.12 (Motjope and Breedts, 2000).

Table 2.11: Time spent catalysts were under synthesis conditions

Calcination T and time	Time on line (h) under synthesis conditions
400°C/5h	169.7
400°C/16h	141.7
450°C/16h	118.6
500°C/16h	141.8
600°C/16h	141.7

All of the catalysts have been subjected to the same reduction conditions. The phases and the intensity thereof are summarised in Table 2.12. All spectra were fitted with superposition of quadrupole doublets and magnetic sextuplets. It is generally accepted that Fe based catalysts are unstable during FT synthesis as they are converted to Fe carbides (Mdleleni and Dlamini, 2000). It was also seen here that most of the metallic iron is converted into Fe carbides irrespective of the pre-treatment conditions.

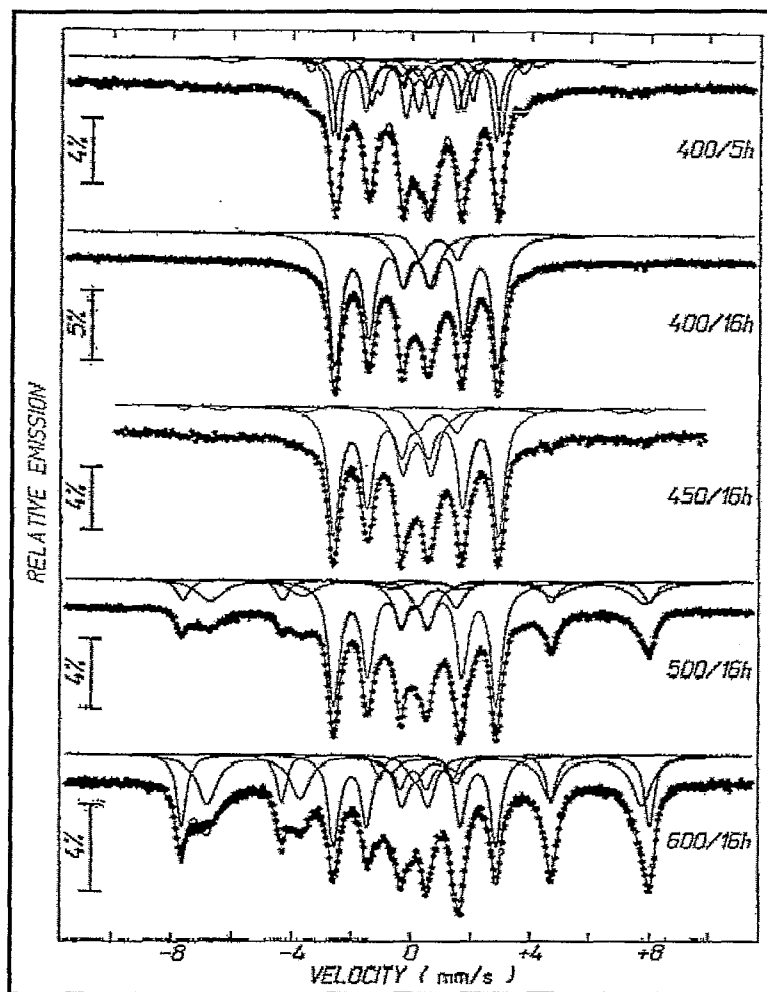


Figure 2.12: Mössbauer spectra of spent catalysts (calcined at 400 to 600°C)

Table 2.12: Phases and intensity of spent catalyst samples recorded at 298 K.

	RA (Intensity)*	Phase
400°C/5h	47.3	χ' -Fe _{2.5} C
	24.6	ϵ' -Fe _{2.2} C
	6.2	Fe ₃ O ₄
	11.1	Fe ²⁺
	11.8	Fe ³⁺
400°C/16h	75.8	ϵ' -Fe _{2.2} C
	7.1	Fe ²⁺
	17.1	Fe ³⁺
450°C/16h	66.2	ϵ' -Fe _{2.2} C
	6.8	Fe ₃ O ₄
	7.4	Fe ²⁺
	19.6	Fe ³⁺
500°C/16h	52.8	ϵ' -Fe _{2.2} C
	28.8	Fe ₃ O ₄
	6.8	Fe ²⁺
	11.6	Fe ³⁺
600°C/16h	30.9	ϵ' -Fe _{2.2} C
	52.7	Fe ₃ O ₄
	6.1	Fe ²⁺
	10.3	Fe ³⁺

*Abundance in % of Fe error in each amount of phase 2 %.

The Mössbauer spectra of the 400°C /5 hour calcined catalyst show the presence of χ' -Fe_{2.5}C in addition to ϵ' -Fe_{2.2}C, Fe₃O₄, Fe²⁺ and Fe³⁺ observed with the other catalysts calcined at 16 hours. The 400°C/16 hours-calcined catalyst was the exception, since it does not contain magnetite (Fe₃O₄).

The ϵ' -Fe_{2.2}C carbide phase seems to increase with a decrease in calcination temperature at the expense of magnetite. Together with this the Fe²⁺/Fe³⁺ decrease with the increase in Fe carbides; this effect is however reversed for temperatures above 450°C. More of the Fe³⁺ is reduced to Fe₃O₄ but further reduction of Fe₃O₄ to α -Fe (assumed to further convert to Fe carbides) seems to be difficult most probably because of sintering of the Fe particles during calcination at the increased temperatures. This is confirmed by TPR results (Table 2.10), which show a shift in

peak position for the reduction of Fe^{2+} to $\alpha\text{-Fe}$ at higher temperatures for catalysts calcined at temperatures above 450°C . From this discussion it seems that the results suggest that calcination temperatures below 500°C may be essential to accelerate the solid state transformation of magnetite to metallic iron and eventually to Fe carbides that are known to be the active phase for FT synthesis.

The $\epsilon'\text{-Fe}_{2.2}\text{C}$ phase seems to be converted to $\chi'\text{-Fe}_{2.5}\text{C}$ at longer reaction times. This observation agrees with previous studies on Fe based catalysts (Jung and Thomson, 1992; Dictor and Bell, 1986) in which are suggested that during FT synthesis, $\alpha\text{-Fe}$ can be converted to $\epsilon'\text{-Fe}_{2.2}\text{C}$ which can further transform to $\chi'\text{-Fe}_{2.5}\text{C}$ with the release of unreactive carbon leading to eventual catalyst deactivation. XRD analysis of the catalyst confirms structural characteristics as far as the presence of spinels are concerned, but falls short in identifying the actual composition of the spinels.

2.4.2 Synthesis results from laboratory reactor

Results are presented firstly of the micro reactor experiments performed on the catalysts calcined at various temperatures. These tests consisted of in-situ and ex-situ reduction of the catalysts and synthesis tests at 20 bar(g) and 240°C . Ex-situ reduction was used in high temperature cases where reactor limitations make in-situ reduction impossible. The influence of calcination temperature is used to conclude on optimal conditions for the catalyst preparation. The influence of synthesis operating conditions such as temperature, pressure and conversion on the selectivity and performance of the optimal calcined catalyst is shown. Obtained results are compared to those found from literature Fe-based FT catalysts.

In this study the selectivities obtained from the different experiments will be related to the growth parameter and thus the chain growth probability towards the different products. The ability of a catalyst to catalyse chain propagation versus chain termination, determine hydrocarbon product selectivities in the FT synthesis (Bartholomew, 1990). The hydrocarbon product distribution is described by a chain polymerisation kinetic model ascribed to Anderson, Schulz and Flory, called the Anderson-Schulz-Flory (ASF) model. This model is given by equation 2.5:

$$\ln\left(\frac{W_n}{n}\right) = (1-\alpha)^2 \alpha^{n-1} \dots 2.5$$

with n the number of carbon atoms in the product, W_n the weight fraction of product containing n carbon atoms and α (alpha) the chain growth probability. A low growth parameter predicts lighter (short chain) products, while long chain carbon products are associated with high growth parameters. The chain growth probability is influenced by reaction conditions and catalyst properties. Several researchers under various reactor conditions and on different FT catalysts reported an effect known as the “double alpha” (Huff and Satterfield, 1984). This effect entails a change in the slopes of ASF plots at a carbon number of about 10, resulting in an increased growth parameter for the C_{10}^+ products. Alpha-one values in this investigation will thus present the growth parameter for C_3 - C_7 products with alpha-two values referring to the growth parameter of C_{10}^+ products.

2.4.2.1 Effect of calcination temperature on catalyst performance

(a) Temperature range 400 to 600°C (reduced in-situ)

Appendix 3 gives the synthesis results for the catalysts calcined at temperatures ranging from 400 to 600°C and tested at 20 bar(g) and 240°C synthesis conditions. Synthesis gas flow rates were adjusted to achieve CO + CO₂ conversions in the order of 40 %. Periods with similar conversion levels (not possible for low activity 600°C catalyst) are used for comparison to show the influence of calcination temperature on the catalyst performance as far as activity and selectivity is concerned.

Activity:

The hydrocarbon production rates (mmol CO + CO₂ converted/gcat/h as indication of catalyst activity) are presented in Figure 2.13. Figure 2.13 shows that the 400°C (16 hr), 450°C and 500°C calcined catalysts show similar activity, but a sharp drop in activity is seen for the 600°C calcination temperature. This result can be related to the decrease in surface area observed for the 600°C calcined catalyst when compared to the lower temperature catalysts. Activity calculated per surface area of the fresh catalysts will thus be similar. Looking at activity it would seem that 400 - 450°C calcination for 16 hours would be adequate in obtaining the optimal activity.

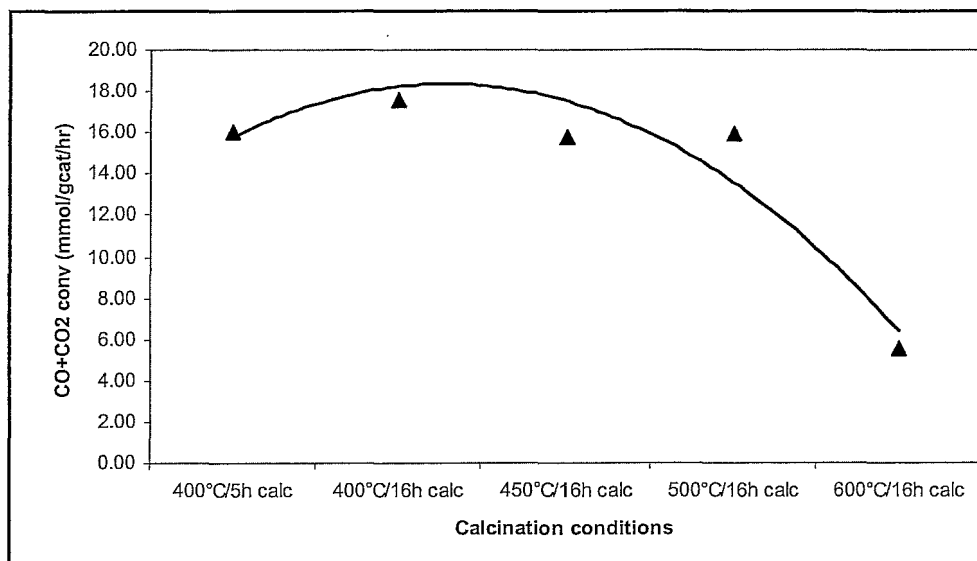


Figure 2.13: Calcination temperature influence on catalyst activity (range 400 to 600°C)

Rüede (1980) reports that higher temperature (above 500°C) calcined catalysts have lower initial activity. This conclusion could not be verified for this experimental program, as the initial activities were not compared and the time spans of the experiments were too short for deactivation evaluations. The above mentioned report also concluded that calcination in general stabilises the catalyst against deactivation. The catalyst calcined at 900°C was however completely inactive.

Observations that the duration of calcination has little or no influence on the performance of the catalyst serves as proof that differences between the 400°C catalyst calcined at 5 hours and at 16 hours observed is the result of non-homogeneous calcination (discussed under Section 2.4.1.2). The latter would therefore allow the presence of undecomposed nitrates resulting in a catalyst with probably similar activity but a different selectivity.

Selectivity:

1-Olefins and alcohol selectivities will be used as measures of comparison for the different catalysts, as these two product groups form the focus of the unique product spectrum of the ChemFT catalyst under investigation. The bulk of the alcohol product is present in the liquid oil fraction of the reactor product. This oil fraction is an easily recoverable product fraction, and therefore the alcohol fraction will be used as a convenient measure of alcohol selectivity.

1-Olefins are split between gas and liquid phase. The overall 1-olefin and alcohol content expressed as a mass percentage of C₁-C₃₀ (product range goes only to about C₃₀) total products will be used for comparison purposes. Figure 2.14 compares the 1-olefin and alcohol content at the various calcination temperatures, while Figure 2.15 shows the 1-olefin and alcohol yields in the oil fraction for the catalyst calcined at different temperatures.

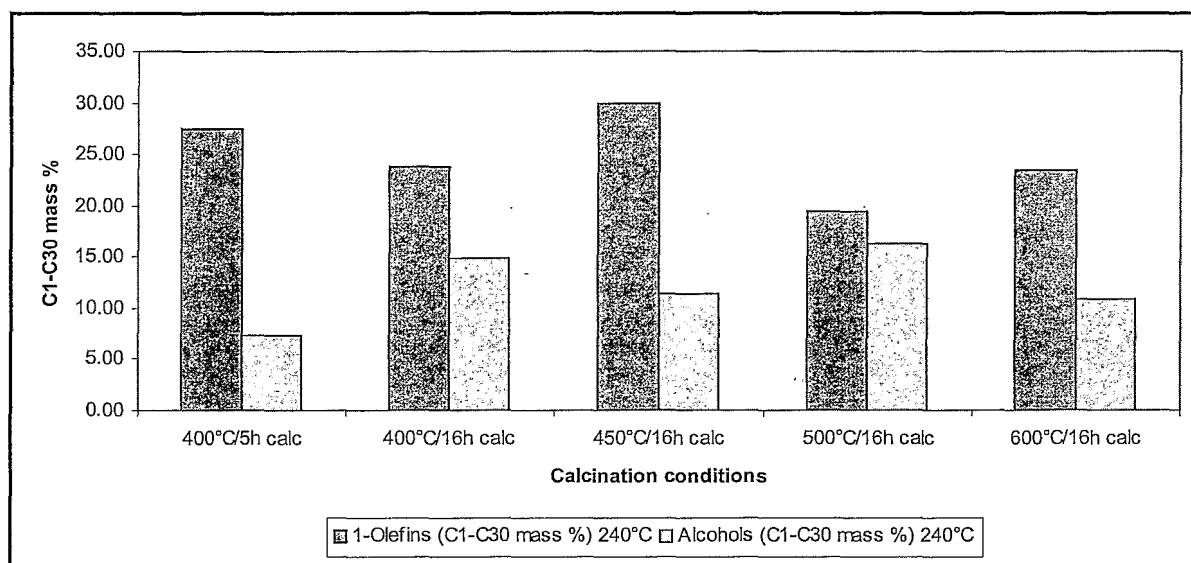


Figure 2.14: 1-Olefin and alcohol total selectivity comparison (calcined at 400 to 600°C)

Results from Figure 2.14 do not show a clear trend for either 1-olefins or alcohols when the normal GC analytical error of around 5 % is taken into account. It can however be argued that the alcohol optimum will be between 400 and 500°C if calcined for 16 hours, while a slight decrease for 1-olefins above 450°C calcination temperature is observed. From Figure 2.15 an increase towards alcohol selectivity can be seen with increased calcination temperature up to 500°C, thereafter the yield drops. The 1-olefin yield again show little variance at the different calcination temperatures, but the same drop above 500°C can be seen, which relates to the inactivity of the catalyst at the high calcination temperature. (as discussed in figure 2.13).

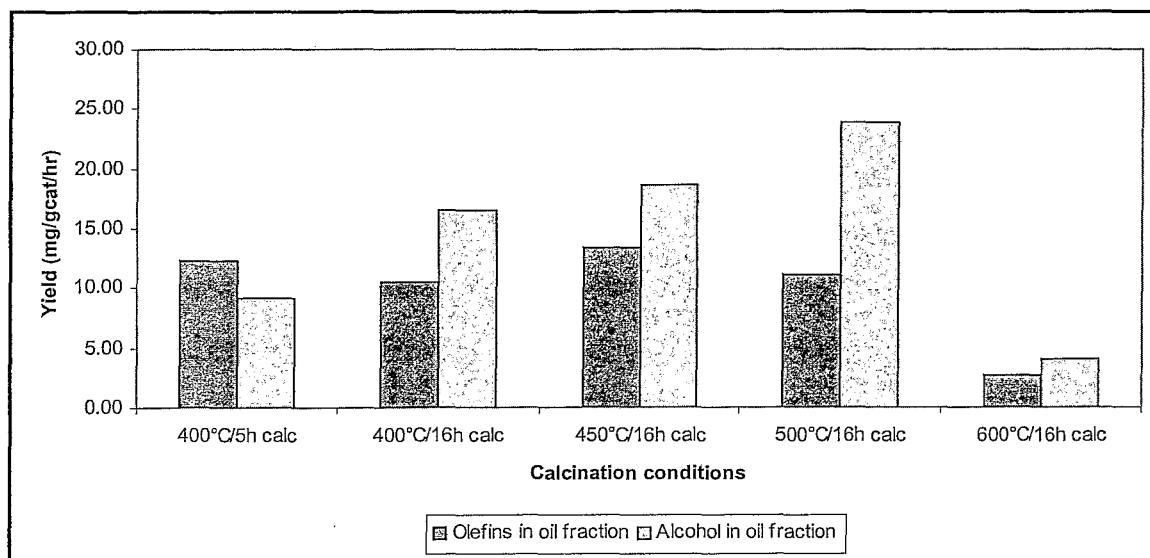


Figure 2.15: Olefin and alcohol yields comparison (calcined at 400 to 600°C)

Table 2.13 gives a summary of the CO₂ formation of the various catalysts (extracted from Appendix 3 data). The CO₂ formation is an indication of the WGS activity of the catalyst, with increased formation indicating an increased WGS activity. A trend towards an increase in the WGS activity with increased calcination temperature can be seen. Newsome (1980) showed the Fe₃O₄ phase to be the active phase for WGS on a ferrochrome catalyst. From characterisation data presented in Table 2.12 an increase in this particular phase can be seen after synthesis when the calcination temperature is increased. This indicates that Newsome's observation also holds true for this particular catalyst.

Table 2.13: Influence of calcination temperature on CO₂ formation (range 400 to 600°C)

Catalyst description	400°C/5 hrs calc	400°C/16 hrs calc	450°C/16 hrs calc	500°C/16 hrs calc	600°C/16 hrs calc
% CO (of total reacted) converted to CO ₂	33.60	37.61	39.30	42.30	38.30

Calculated growth parameters (alpha-1 shown in Appendix 3) vary between 0.65 and 0.69 for the C₃-C₁₀ range of alcohols when the catalysts were calcined between 400 and 500°C, but show a marked increase to 0.78 for the 600°C calcined catalyst. It seems that increased calcination temperature contributes to the formation of longer chain alcohol products. The catalyst does however lack activity compared to the others, and will thus have a fairly low yield of long chain alcohols.

(b) Calcination up to 700°C – reduced at higher temperatures ex-situ

TPR results (Table 2.10) suggest an improvement in activity if the catalysts calcined at higher temperature were to be reduced at increased temperatures. Catalyst calcined at 450°C, 600°C and 700°C were reduced at 340°C. The high temperature reduction needed to be performed ex-situ due to reactor temperature design limitations. Appendix 4 gives the results obtained for the 450°C, 600°C and 700°C calcined catalysts reduced ex-situ at 340°C and 1 bar(g).

Figure 2.16 shows a graphic comparison of the influence of reduction temperature. It can be seen that the 450°C catalyst shows a slight increase in activity when reduced ex-situ at increased temperature. Treating the 600°C calcined catalyst to the higher reduction conditions did however not show similar results. The 700°C calcined catalyst has increased activity compared to the 600°C catalyst. Also notable is that the growth parameter (α -1) value for the 450°C calcined catalyst increased from 0.69 to 0.77 for the alcohols, while that of the 600°C calcined catalyst did not change.

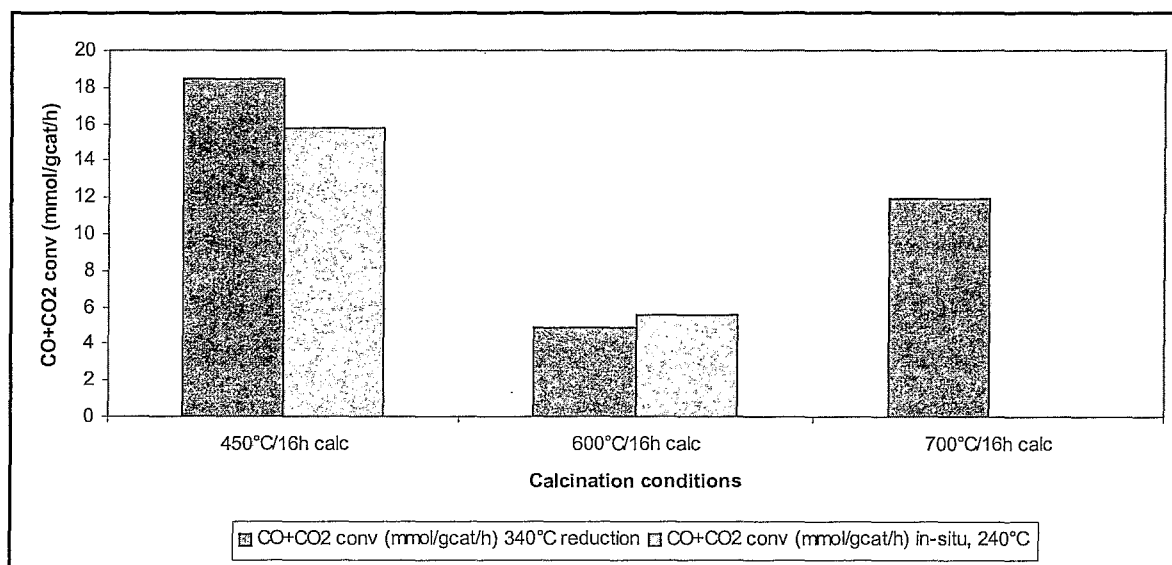


Figure 2.16: Higher temperature reduction influence on activity and selectivity

Probably the most pronounced effect as far as selectivity is concerned is that of the methane selectivity. Catalysts reduced ex-situ at higher temperatures showed lower methane selectivity (although slightly lower conversion levels were used). Very high acid numbers were obtained on the water products, which indicate higher selectivity towards acid production. Both these observations are shown in Figure 2.17.

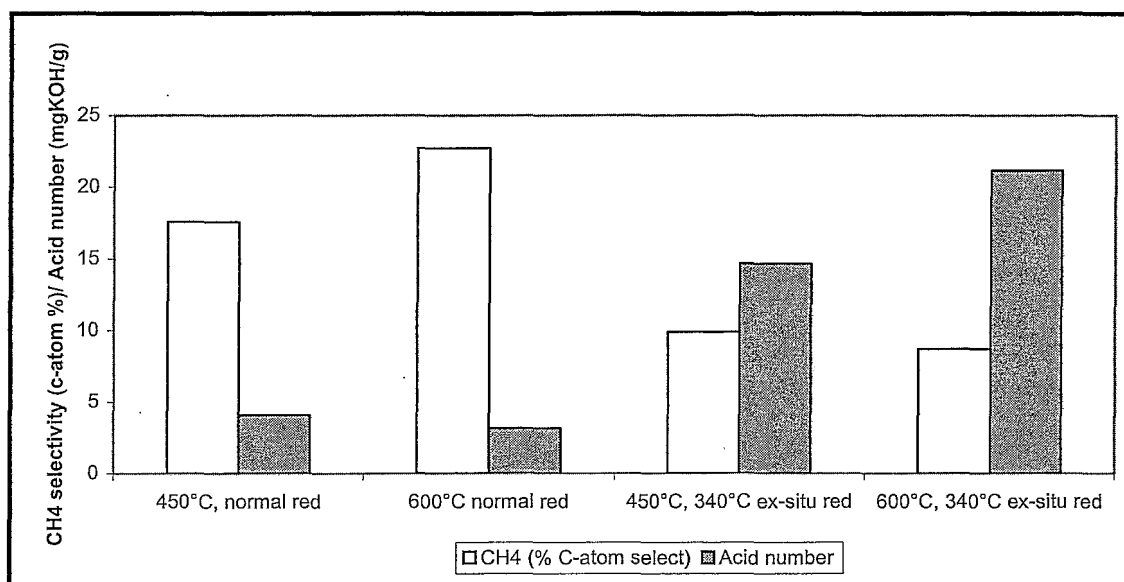


Figure 2.17: Reduction temperature influence on methane selectivity and acid number

Changes due to the higher reduction temperatures on high temperature calcined catalysts appear to be:

- A marked decrease in methane selectivity,
- Increased overall olefin selectivity for 600 and 700°C calcined catalysts,
- Increased alcohol selectivity for the 450°C calcined catalyst,
- 450°C calcined catalyst alcohol growth parameter increased from 0.69 to 0.77 (overall alcohol selectivity rise from 11 to 20 % - lower conversion level used), while the higher temperature calcined catalyst growth parameter stays at 0.78.
- Increased acid number (indicating higher selectivity toward acid production).

The effects observed here could not only be due to the higher reduction temperature used, but also because of the different reduction pressure used. The higher temperature reduction was done ex-situ at 1 atm, while the normal reduction takes place in-situ at 20 bar(g). It is thus expected that different catalyst phases and therefore possibly different selectivity characteristics will be observed due to different P_{H_2}/P_{H_2O} ratio effects experienced at the different reduction pressures. The investigation of reduction conditions and influences will form part of future research programs.

2.4.2.2 Effect of operating temperature in the range 220°C to 280°C on ChemFT catalyst performance

The effect of temperature on the 450°C calcined catalyst was investigated. Reduction was done in-situ at 240°C and 20 bar(g) pressure, before the operating temperature was varied between 220 and 280°C at a operating pressure of 45 bar(g). This specific range was chosen as it falls within the typical temperature range for LTFT. Increasing the operating temperature at a specific gas space velocity shows an expected increase in activity. Figure 2.18 shows the activity obtained at operating temperatures of 220, 240 and 280°C in terms of moles CO converted to hydrocarbon products. It can be seen that temperatures below 220°C will result in very low activity, which will not be economical for commercial operation.

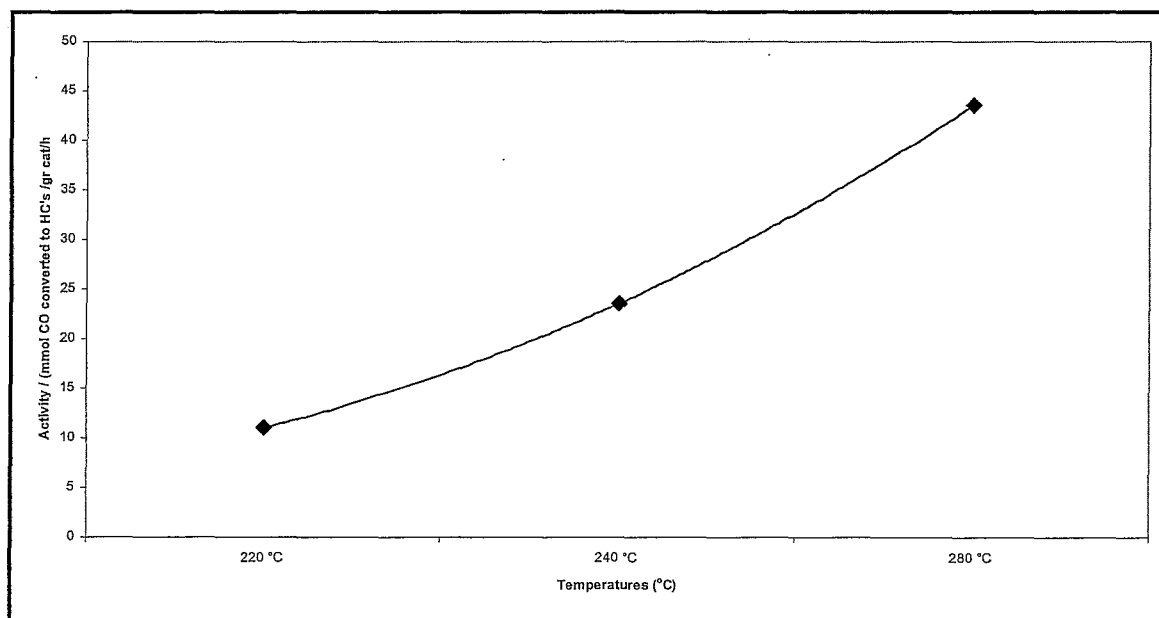


Figure 2.18: Operating temperature influence on catalyst activity (range 220°C to 280°C)

In-house research has shown the activity of a precipitated Fe catalyst operated in a fixed bed to double with a 30°C increase in operating pressure (Shingles, 1970). Similar results were seen with fused Fe catalysts tested in a Berty reactor with a doubling of activity when the temperature was increased from 300 to 310°C, and again at around 340°C (Engelbrecht, 1986).

The influence of temperature on catalyst selectivity with regard to alcohol and olefins, is shown in Figures 2.19 and 2.20. Results shown in these figures were obtained by adjusting the synthesis

gas feed rate to obtain CO+CO₂ conversion levels of around 40 % at the different operating conditions (the 220°C point is not shown due to its low activity).

The alcohol selectivity seems to be constant up to 240°C, whereafter a gradual decrease can be seen. This decrease is accompanied by a shift towards lighter molecular mass products as depicted by the decrease in the growth parameter (α -1) from around 0.67 at 230 and 240°C to 0.56 at 280°C. The effect of temperature on the olefin selectivity is less pronounced, although a decrease is seen for the 280°C data point.

Dry (1981) reports that for fused Fe catalysts used in a fluidised bed application, both the olefinitiy of the products and the alcohol and acid selectivity decreased with increased operating temperature. However the olefin selectivity of a precipitated Fe catalyst operating in a fixed bed reactor under near differential conditions (low conversion) did not show much change with increased temperature. A shift away from heavier products was observed for both the fluidised and fixed bed reactor applications. This observation is in agreement with that of Shingles (1970) where a 23°C increase in operating temperature halved the hard wax selectivity of the precipitated Fe catalyst.

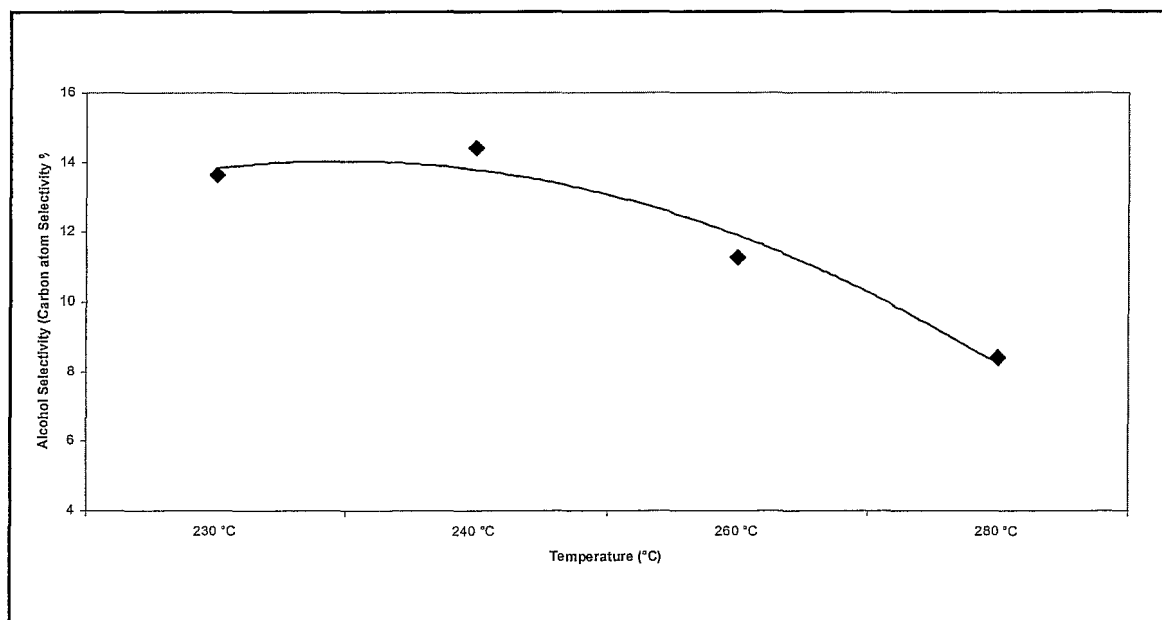


Figure 2.19: Operating temperature influence on alcohol selectivity of ChemFT catalyst

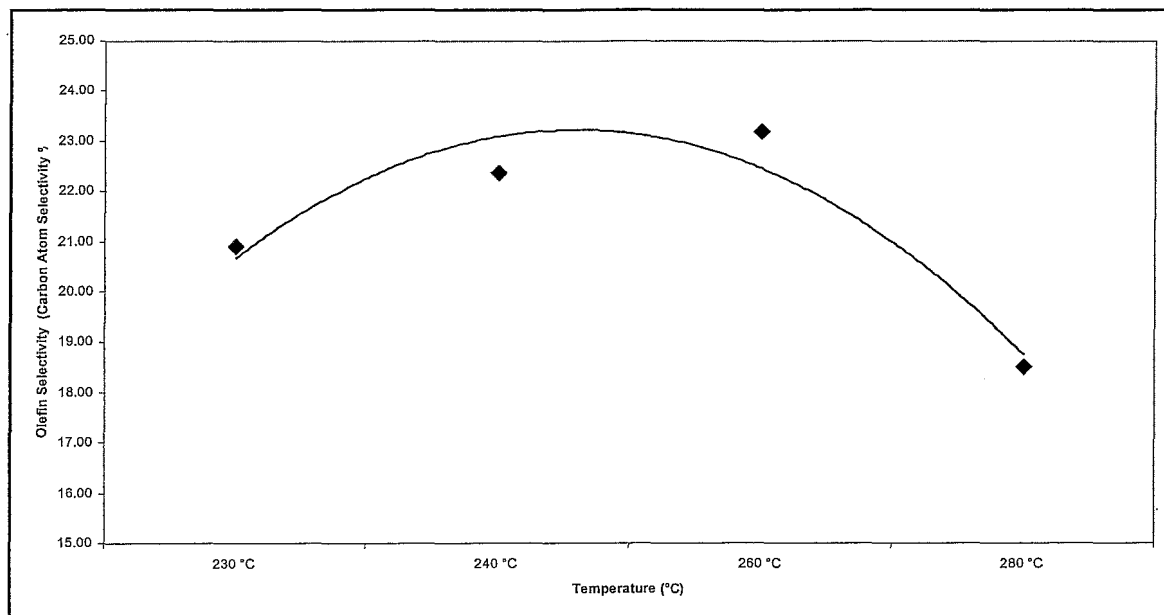


Figure 2.20: Operating temperature influence on olefin selectivity of ChemFT catalyst

From the above it can be concluded that an operating temperature of 240°C gives an optimal compromise between activity and product selectivity. This chosen temperature is in agreement with current commercial Fe slurry reactor operations and also compares with typical temperature ranges observed in literature Fe catalyst investigations.

2.4.2.3 Effect of operating pressure in the range 10 to 65 bar(g) on catalyst performance

The influence of operating pressure on the ChemFT catalyst product selectivity was obtained by adjusting the synthesis gas feed rate to ensure similar conversion levels (40 % CO+CO₂) at the different reactor pressures. The reactor was operated at 240°C during the pressure influence investigation. The laboratory reactor used for this investigation is limited to 50 bar(g) operation. A 65 bar(g) experimental point obtained from pilot plant operation is thus added to broaden the scope of the data. Figures 2.21 and 2.22 show the influence of pressure on the alcohol and olefin selectivity respectively.

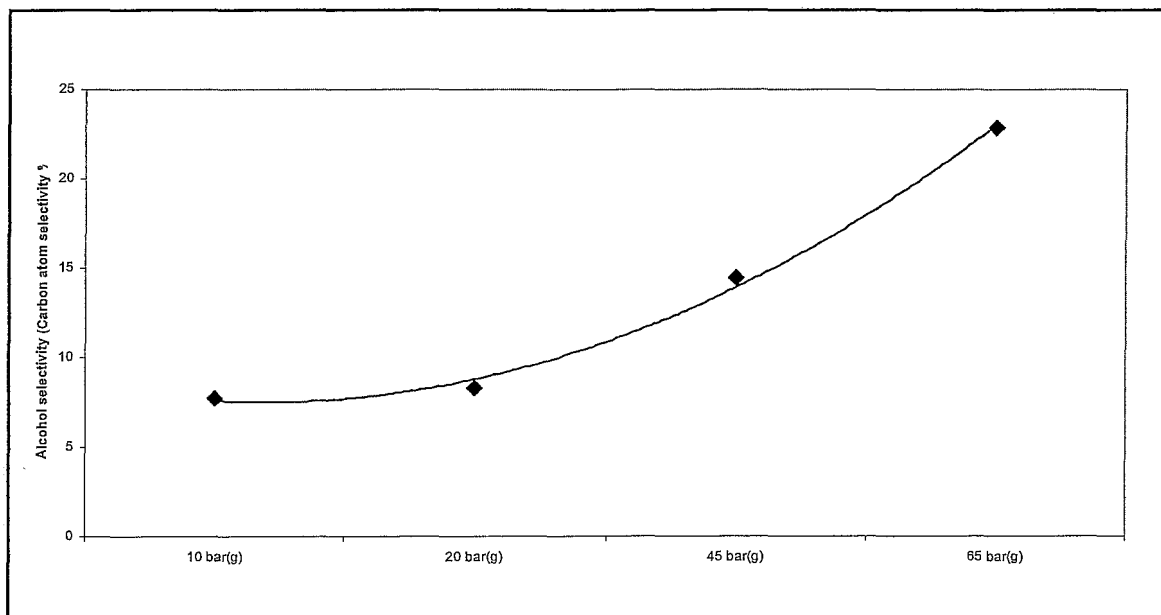


Figure 2.21: Operating pressure influence on alcohol selectivity of ChemFT catalyst

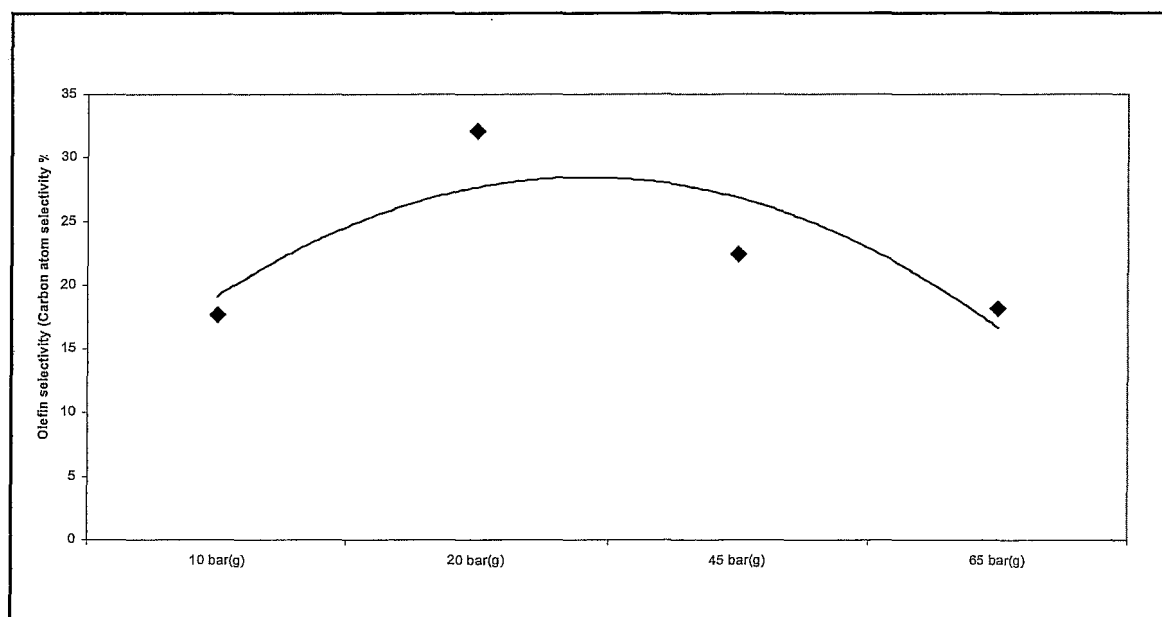


Figure 2.22: Operating pressure influence on olefin selectivity of ChemFT catalyst

The investigation shows a clear increase in alcohol selectivity with increased reactor pressure while the effect on olefin selectivity is not as clear. The growth parameter of both products increases from 10 to 20 bar(g) (for alcohols from 0.6 to 0.68 and for olefins from 0.52 to 0.58), but seems to stay constant towards the higher pressures.

Anderson (1952: as referred to by Dry, 1981) investigated the effect of increasing the operating pressure from 8 to 21 bar(g) on the selectivity of precipitated and fused Fe catalysts. The average

molecular mass decreased slightly for the precipitated catalyst, but increased over the fused catalyst. The yield of oxygenated products increased with increased pressure in both cases, but the olefinity of the fused catalyst was not influenced by pressure. These results obtained for the fused catalyst is in agreement with results from Schlesinger (1964: as referred to by Dry, 1981) where the pressure was increased to 103 bar(g) with a nitrated fused Fe catalyst. Precipitated Fe catalyst results from both fixed and slurry bed reactor operation obtained by Hall (1952: as referred to by Dry, 1981) show increased molecular mass and oxygenate production with decreasing olefinity when increasing the pressure from 20 to 40 bar(g). These results are in agreement with those of Anderson reported earlier.

Dry (1981) concluded that most of the results indicate that increasing the total pressure will result in increased growth probability and oxygenates (alcohols and acids), with little effect on the olefinity of the products. The somewhat stable growth parameters observed for the ChemFT catalyst selectivity investigation at high pressures does not seem to agree with the general conclusion of the effect of pressure on Fe catalyst selectivity.

Work performed on a precipitated iron catalyst by Lox and Froment (1993) led them to conclude that the growth probability (indicated by the growth parameter) is almost independent of the total pressure and the hydrogen partial pressure, but it increases with increasing CO partial pressure. Total pressure increase will thus increase the partial pressure of a desired reactant, which will in turn relate to the selectivity obtained.

Results used for the ChemFT catalyst show an increase in CO partial pressure from around 1 bar(g) to 2.75 bar(g), 5.33 bar(g) and finally to 16 bar(g), which might therefore suggest that the growth parameter needs to increase. H_2/CO reactor ratios for the 20+ bar cases are however similar as the conversion levels were kept similar, and could therefore conceal the selectivity effect.

Xiaoding *et al.* (1987) explains that decreasing the H_2/CO ratio would favour CO insertion and C-C chain growth, leading to increased production of higher alcohols and/or hydrocarbons, while the opposite favours the production of lower alcohols and hydrocarbons (also saturated hydrocarbons). The observed results do show that although an increased overall alcohol selectivity was obtained, the growth probability parameter thereof decreased. This indicates the formation of more lower-alcohols. It can thus be speculated that a specific CO partial pressure

(relating to greater CO coverage of the active catalyst area) would be necessary in conjunction with that of the hydrogen to maximise the effect of increased hydrogen partial pressure into possibly increasing the higher alcohol selectivity.

Reactor pressures of 45 and 65 bar(g) result in increased alcohol selectivity with acceptable growth probability parameters (above 0.65). Due to reactor limitations, 45 – 50 bar(g) reactor pressure is seen as optimal for laboratory investigations.

2.4.2.4 Influence of synthesis gas conversion on ChemFT catalyst performance

Varying the GHSV can vary the synthesis gas conversion. The change in conversion will be due to the change of the gas residence time within the reactor. Figures 2.23 and 2.24 show the influence of conversion (CO+CO₂ conversion %) on alcohol and olefin selectivity.

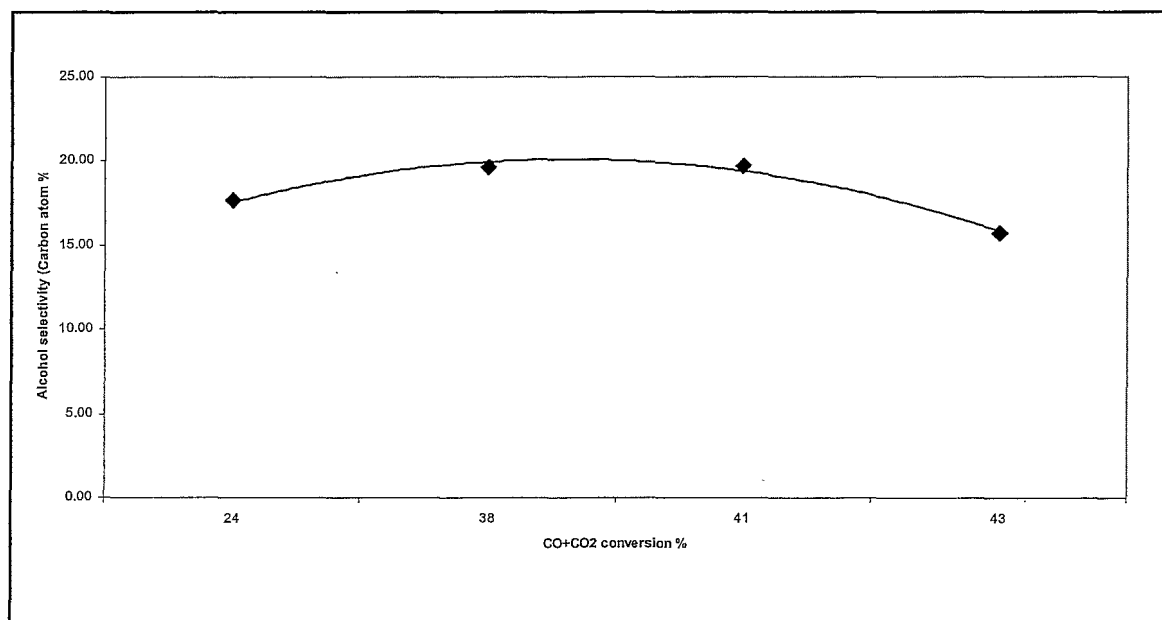


Figure 2.23: Influence of conversion on alcohol selectivity of ChemFT catalyst

The influence of conversion on the alcohol selectivity is not very clear from Figure 2.23, but there does seem to be a slight maximum in the range of 38 to 41 % CO+CO₂ conversion. A slight decrease in growth parameter is also observed with increased conversion, with a growth parameter (α_1) value of about 0.7 at 24 % conversion decreasing to about 0.66 at the 43 % conversion level. This observation suggests a shift towards shorter chain alcohols with increased conversion. This is in agreement with Xiaoding *et al.* (1987) who states that lower conversion

and therefore higher gas space velocity is normally favourable for the synthesis of higher alcohols.

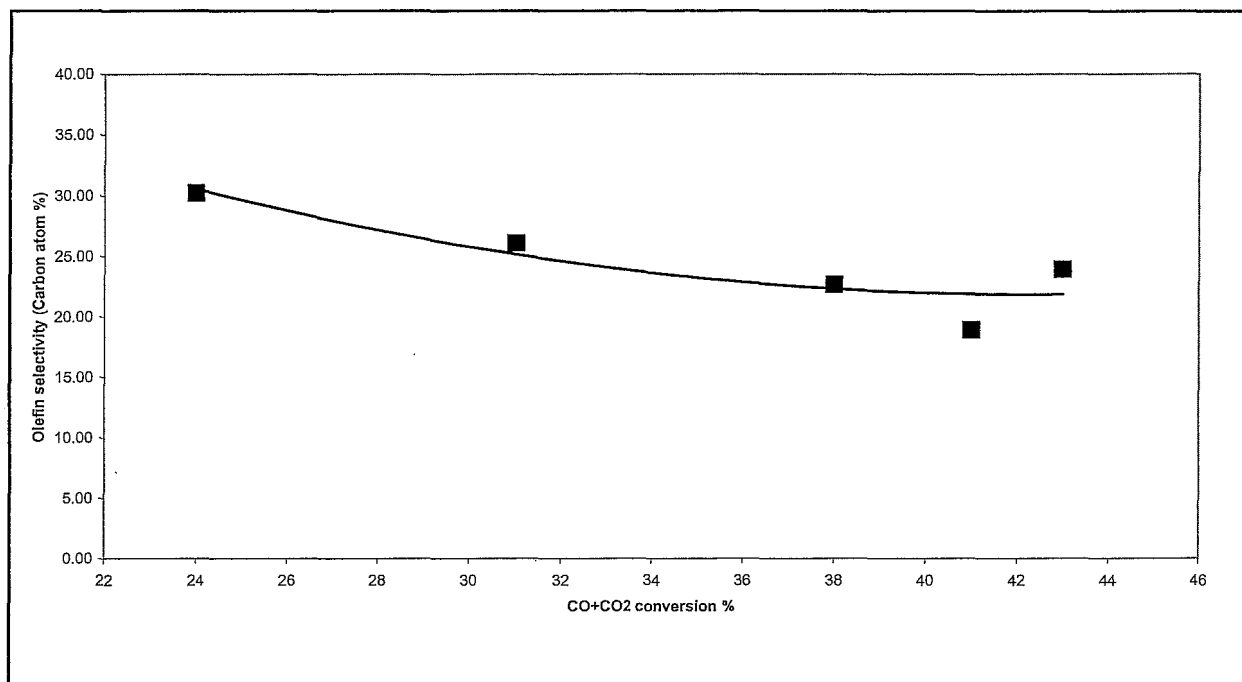


Figure 2.24: Influence of conversion on olefin selectivity of ChemFT catalyst

Figure 2.24 shows a decrease in the olefin selectivity with increased conversion levels. A similar decrease in the olefin growth parameter ($\alpha-1$) was observed with the value changing from about 0.6 at the low conversion levels to 0.54 at the 43 % conversion. Higher conversion is the result of increased residence times of reagents and products in the reaction zone which as a result increase the possibility of secondary reactions such as hydrogenation and isomerisation of products such as olefins (Dry, 1981). Conversion will determine the availability of reactants within the reaction zone / at the catalyst active sites. Dry (1981) concludes that the extent at which olefins and oxygenates are produced must be dependent on the availability of vacant catalyst sites. Such availability depends on the degree of CO conversion.

A CO+CO₂ conversion in the order of 40 % will be an adequate evaluation point of the catalyst performance. Such a level of conversion will also be suitable for commercial scale-up of the process with a satisfactory compromise between selectivity, chain growth probability and reactor size.

2.4.3 Analysis of product spectra and selectivity towards alcohols and olefins

2.4.3.1 Choice of catalyst and operating conditions

From the above mentioned results, the catalyst calcined at 450°C for 16 hours was chosen as the typical ChemFT catalyst and will thus be used for comparison to traditional FT catalysts. The catalyst was reduced in-situ at 240°C. Product spectra obtained at 240°C and 20 bar(g) as well as 45 bar(g) synthesis conditions will be used.

2.4.3.2 Overall product spectra comparison

Dry (1999) published a typical product distribution for low and high temperature FT synthesis processes obtainable with Fe-based catalysts. Table 2.14 compares the product spectrum obtained from the 450°C/16 hours calcined ChemFT catalyst tested at 20 and 45 bar(g) to that given by Dry (1999).

Most notable is the fact that the ChemFT catalyst has a higher selectivity towards methane formation. The ChemFT product spectrum compares better with that of high temperature FT as both catalysts do not produce a noticeable amount of very long chain hydrocarbons (wax – boiling temperatures above 350°C). None of the aromatics associated with HTFT catalysts are however produced by the ChemFT catalyst. Furthermore, the ChemFT catalyst shows higher selectivity towards alcohols.

The catalyst results in a product spectrum much narrower than normally associated with Fe based catalysts operating at these conditions. Products from the ChemFT catalyst consist mostly of linear 1-product with very little branching. 1-Olefins comprise more than 85 % (20 bar(g)) and more than 75 % (45 bar(g)) of the C₅ – C₁₂ olefin fraction.

Table 2.14: Selectivity data comparison of ChemFT to typical iron-based FT processes

C atom %	Dry, 1999	Dry, 1999	ChemFT catalyst	
	LTFT 20 bar(g) 230-240°C	HTFT 25 bar(g) 350°C	20 bar(g) 240°C	45 bar(g) 240°C
C1	3.0	8.0	18.2	19.1
C2 – olef	0.5	4.0	5.3	2.3
C2 – par	1.0	3.0	8.8	11.2
C3 – olef	1.5	11.0	9.7	8.1
C3 – par	1.5	2.0	4.6	7.5
C4 – olef	2.0	9.0	6.1	4.9
C4 – par	2.0	1.0	4.3	5.7
C5 - C6	7.0	16.0	13.3	12.6
C7 - 350°C	26.5	36.0	20.5	12.7
+350°C (waxy products)	51.0	5.0	0.0	0.0
Oxygenates as alcohols	3.8	2.8	8.3	14.4
Oxygenates as acids+ketones	0.2	2.2	0.9	1.6
% breakdown (C5-C12 cut)				
% total paraffins	29.0	13.0	49.6	59.2
% total olefins	64.0	70.0	37.8	25.5
% aromatics	0.0	5.0	0.0	0.0
% oxygenates	7.0	12.0	12.5	15.4

Table 2.15 shows typical analyses of the liquid product oil fraction breakdown obtained for the ChemFT catalyst compared to that of a more standard LTFT (Fe/Cu/K) catalyst. The LTFT catalyst operating conditions is comparable with that of the ChemFT catalyst.

This fraction of product shows that at similar conversion levels the chemical production catalyst has half the amount of internal olefin product and more than double the selectivity towards the desired alcohol product. Similar olefin selectivity is obtainable with much lower paraffin selectivity. The iso-products consist mainly of linear products. The total breakdown of the results of Table 2.15 can be seen in Appendix 5.

Table 2.15: Liquid product oil fraction analyses (C number < 32):ChemFT and LTFT Fe-catalyst processes

Mass %	ChemFT 20 bar(g) 240°C	ChemFT 45 bar(g) 240°C	LTFT – 20 bar(g) 240°C
1 – Olefins	18.98	7.45	19.85
Int-olefins	4.17	4.08	8.98
n-Paraffins	32.31	37.17	49.70
Alcohols	32.34	41.09	13.20
Ketones	1.81	1.17	1.01
Iso-products	10.35	9.04	7.22

Table 2.16 shows the ChemFT catalyst product selectivity with regard to the valuable chemical ranges. The table was constructed using data of Table 2.14 and Appendix 6.

Table 2.16: ChemFT product according to carbon number ranges

	ChemFT, 20 bar(g), 240°C			ChemFT, 45 bar(g), 240°C		
C-atom %	Olefins	Paraffins	Oxygenates	Olefins	Paraffins	Oxygenates
Total product	34.74	56.04	9.22	22.39	61.67	15.95
Breakdown of product fraction						
C ₅ +	39.31	35.91	48.27	31.41	29.61	27.11
C ₉ – C ₁₁	8.08	9.26	9.77	3.11	5.42	4.75
C ₁₂ +	4.84	8.50	4.81	1.19	4.91	1.82
Total product yield (g/gcat/h)	0.24			0.41		

Results from Tables 2.15 and 2.16 show that the catalyst possesses a degree of flexibility relating to operating conditions. By manipulating the operating temperature and pressure it is possible to increase the selectivity towards olefins and alcohols. It can also be seen that the higher pressure (45 bar(g) condition) improves the overall alcohol selectivity, but the breakdown of this fraction does however show a shift towards lighter alcohols (also see Section 2.4.2.3). The ChemFT process would fit in-between traditional high temperature and low temperature iron FT processes, taking into account the operating conditions (temperature and pressure) and product selectivity (see Figure 2.25).

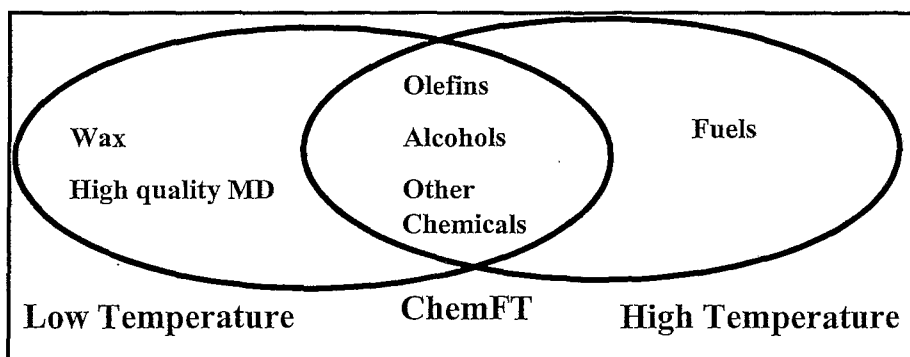


Figure 2.25: ChemFT process relative to LTFT and HTFT

Table 2.17 shows a comparative summary of the suggested ChemFT technology to that currently employed by Sasol in the field of iron based catalysts. Presently fuels and chemicals are often obtained via hydrocracking of heavy FT products or through a complex separation and transformation process of lighter FT products. It would thus seem that a niche exists for a process with lighter “clean” product spectra, maximising chemical value of primary products.

Table 2.17: Sasol iron-based catalyst processes comparison

Process:	LTFT	ChemFT	HTFT
Reactor technology	Fixed bed / Slurry bed	Slurry bed	Sasol advanced Synthol reactor
Operating conditions	230 – 240°C, 20 bar(g)	240°C, 45 – 65 bar(g)	350°C, 25 bar(g)
Catalyst: Type:	Precipitated	Precipitated	Fused
Composition:	Fe/K/Cu/SiO ₂	Fe/Mn/Zn/K/Cu/SiO ₂	Fe/Na/K/Al/SiO ₂
Preparation:	Batch precipitation	Continuous precipitation	Batch
Main products	Wax (to middle distillates through hydrocracking)	Chemicals: Olefins, alcohols, paraffins (max ~ C ₃₀)	Olefins (difficult separation), Petrol, Diesel

Selectivity data from the ChemFT catalyst for the production of alcohols and olefins can be compared to that of other catalysts discussed in Section 2.2.3 and 2.2.4 for the production of either alcohols or olefins. Most notable from the alcohol catalysts are the extreme operating conditions compared to that of ChemFT. The alcohol catalysts operated in a pressure range of 60 – 300 bar(g) and temperatures ranging from 250 – 450°C. These alcohol catalysts also show relatively low productivity compared to the ChemFT catalyst. Only IFP reported catalyst data

obtained at 120 bar(g) and 250°C showing higher total product yield (2645 vs 1644 g/lcat/h) (see comparison of Table 2.18). From this comparison it can be seen that the IFP catalyst is primarily an alcohol production catalyst reported to be in the C₁-C₄ alcohol range. The modified MeOH catalyst shows a little bit of C₅+ alcohol selectivity, but its low activity/yield compares poorly with that of the ChemFT catalyst. MeOH is the primary alcohol produced with the modified MeOH catalyst, comprising 70 wt% of the alcohol product.

Table 2.18: ChemFT vs. literature reported alcohol catalysts

Catalyst	Modified MeOH catalyst (Hofstadt <i>et al</i> , 1981)	Rh-based catalyst (Ichikawa, 1985)	IPF Cu/Co promoted catalyst (Sugier and Freund, 1978 and 1981)		ChemFT	
Operating conditions	100 bar(g), 350°C	0-300 bar(g), 150 – 450°C	60 bar(g), 250°C	120 bar(g), 250°C	20 bar(g), 240°C	45 bar(g), 240°C
Total production (g/lcat/h)	198	-	1302	2645	962	1644
EtOH production (g/lcat/h)	19	49	501	978	29	113
Alcohol C# range reported	C ₁ -C ₄	C ₂	C ₁ -C ₄	C ₁ -C ₄	C ₁ -C ₁₅	C ₁ -C ₁₅
Total alcohol selectivity as wt % of total product	78	-	90-95	95	11.2	21
C5+ OH wt% of total alcohols	Negligible	Not reported	None reported	None reported	40	21

Section 4.2.4 showed that increased temperature improves catalyst activity, while alcohol selectivity is improved with increased operating pressure. Very comparable results are thus obtained with the ChemFT catalyst at much more moderate conditions. High-pressure equipment is very capital intensive, therefore making the ChemFT process economically more attractive than reported alcohol processes.

Reported olefin processes prefer lower operating pressures (normally less than 20 bar(g)) and higher operating temperatures (about 250°C) than that of the ChemFT process. Olefin selectivity of the ChemFT catalyst is about half of that reported by Soled and Fiato (1985) and Das *et al.* (1994). Selectivity towards 1-olefins within the olefin fraction is reported to be above 75 %, which compares well with the ChemFT 85 + %. Das *et al.* (1994) reports growth parameters of between 0.64 and 0.72. The ChemFT process growth parameters range from 0.60 to 0.66, indicating a fairly similar carbon distribution within the olefin fraction.

2.4.3.3 Analysis based on AndersonSchulz Flory distribution

As discussed in Section 2.4.2 the growth parameter relates to the selectivity of the FT process and is described by the ASF model. The ChemFT products will still be bound by the ASF product prediction, despite its product spectrum. The associated ASF distribution of the ChemFT catalyst is shown in Figure 2.26.

The growth parameters obtained for a typical ChemFT catalyst can be compared to those of typical low and high temperature FT Fe catalysts. Alpha-1 values represent the growth parameter of C₃-C₇ products with alpha-2 values referring to the growth parameter of C₁₀⁺ products. It must however be noted that it is generally not easy to obtain accurate analytical measurements of alcohols when produced in smallish quantities compared to the olefins and paraffins. Table 2.19 is however an attempt to compare commercial growth parameter information of the different catalysts to that of the ChemFT developed catalyst.

Table 2.19: Growth parameter comparison of ChemFT to commercial LTFT and HTFT processes

Catalyst	Alpha 1 (C ₃ -C ₇)				Alpha 2 (C ₁₀ ⁺)			
	Olefins	Paraffins	Alcohols	Total product	Olefins	Paraffins	Alcohols	Total product
LTFT Fe catalyst	0.60	0.74	0.73	0.70	0.67	0.94	0.78	0.90
HTFT Fe catalyst	0.65	0.72	0.2-0.35	0.63	0.67	0.84	- *	0.72
ChemFT catalyst	0.60	0.68	0.67	0.64	0.66	0.82	0.75	0.74

* not calculated due to small amounts of these products

Table 2.19 indicates that the growth parameters of the ChemFT and HTFT catalysts compare well as far as olefin and paraffin selectivity is concerned. However comparing the alpha-1 value for the alcohols, a much higher value can be seen for the ChemFT alcohol product, indicating the synthesis of higher alcohol products. The overall product alpha value of the ChemFT catalyst has a notable lower alpha-2 value compared to that of the LTFT catalyst, indicating much less or little wax formation.

It can be concluded from all the above discussions that the ChemFT catalyst differs from the conventional FT iron catalysts as far as selectivity and typical process conditions are concerned. The growth parameter comparison will classify the ChemFT catalyst as having HTFT catalyst selectivity, but with an improved higher alcohol selectivity. The ChemFT catalyst has a tailored

selectivity to ensure more products with higher associated chemical value. It can thus be expected that the known FT iron rate equations would not be adequate for this specific catalyst. The next chapter will focus on the pilot plant verification of the catalyst product selectivity.

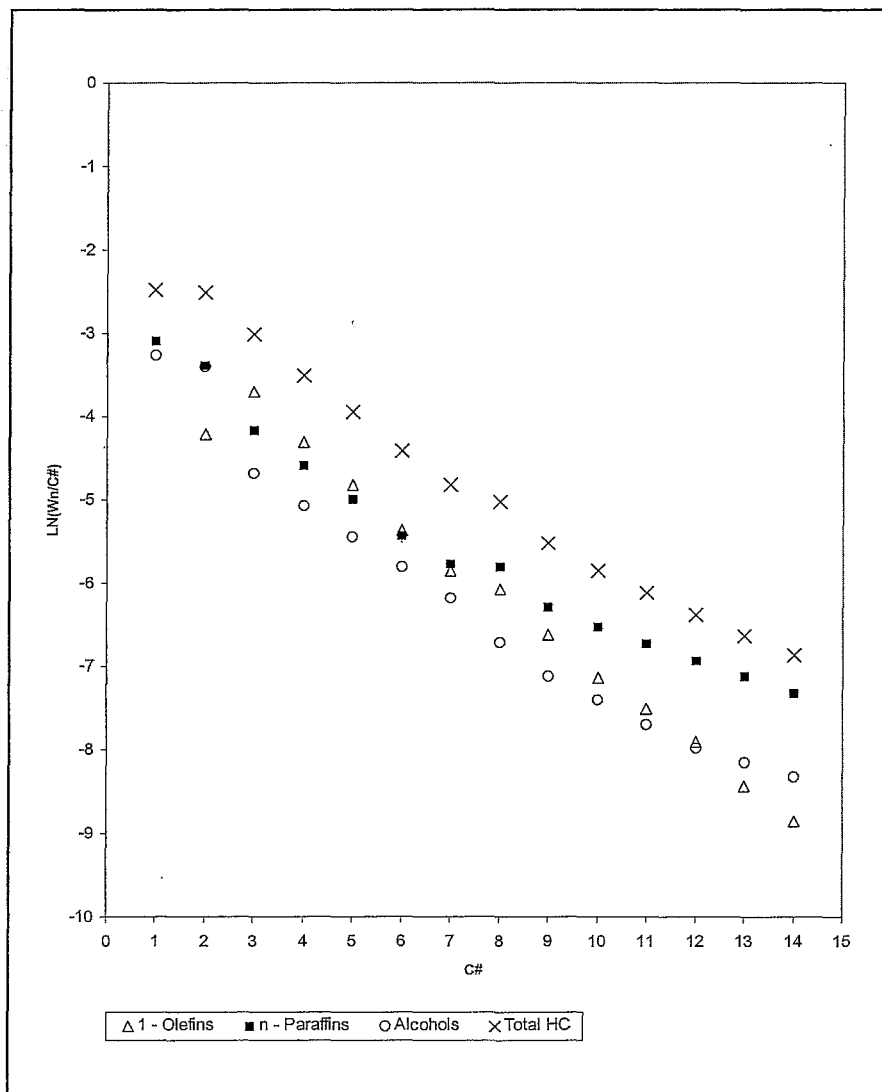


Figure 2.26: Anderson-Schulz-Flory distribution of the ChemFT products

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