

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

During this investigation of an iron based Fischer-Tropsch catalyst for the direct conversion of synthesis gas to valuable chemicals, the following conclusions were reached:

- 1) Optimal calcination conditions for the ChemFT catalyst were identified according to activity and selectivity as 450°C and 16 hours exposure to H₂ flow. Characterisation of the optimum treated Fe/Zn/Mn/Cu/K/SiO₂ ChemFT catalyst showed the phase composition of the catalyst to be ferrihydrite. The surface area of the catalyst is 118 m²/g and the pore volume 0.338 cm³/g.
- 2) The developed catalyst possesses a product spectrum much narrower than normally associated with Fe based catalysts operating at typical low temperature FT conditions. Product selectivity towards the desired alcohol product is much higher (more than double that normally associated with FT catalysts) while similar olefin selectivity is obtainable with much lower paraffin selectivity compared to conventional iron based FT catalysts. Higher hydrocarbon (wax) formation is negligible compared to the liquid product, as is evident from a paraffin growth parameter of around 0.8 compared to values of above 0.9 for typical low temperature FT processes.
- 3) Results have shown that the catalyst possesses a degree of flexibility relating to operating conditions. By manipulating the operating temperature, conversion level and pressure it is possible to increase the selectivity towards olefins and alcohols. Increased reactor temperature cause a decrease in alcohol selectivity, but the olefin selectivity is not influenced much. Temperature increases will result in a lower growth parameter product spectrum (lighter product). Alcohol selectivity is increased with increased reactor pressure while the effect on olefin selectivity is not clear. Increased growth parameters were observed up to 20 bar(g), whereafter it seemed to be stable. Increased synthesis gas conversion does not influence the alcohol selectivity much, but decreases olefin selectivity. The growth

parameter of both products decreased with increased conversion. All the different catalyst behaviour trends could be confirmed with available literature.

- 4) Pilot plant verification of the ChemFT catalyst selectivity showed that there is a good agreement between the laboratory results and those obtained from the pilot plant when recycle is used. Reactant liquid phase concentrations at the point of reaction were suggested to be the cause for differences observed with the pilot plant once-through operation.
- 5) A large amount of literature is available on the topic of FT catalysts and their associated reaction rate equations. Known rate equations have evolved from simple first order rate equations to complex equations which accommodates a wide range of operating conditions and catalyst behaviours. Equations are either empirically formulated or derived by making use of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kind of equations. Generally small amounts of oxygenated products, primarily alcohols, and the CO₂ formed by the Boudouard reaction are neglected.
- 6) This study has shown that existing Fe catalyst reaction rate equations describe the FT kinetics fairly well, but fall short in describing the WGS kinetics of the ChemFT catalyst. A FT reaction rate equation was proposed which accounts for the vacant catalyst sites by incorporating a “1” into the denominator. It was thus proposed that the FT kinetic behaviour of the ChemFT catalyst can be described by:

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^\gamma \cdot P_{CO}}{1 + aP_{CO}}$$

with: $k_o = 58.84 \pm 2.94 \text{ mol/gcat/s/bar}^{A+1}$

$E_{FT} = 77 \pm 4 \text{ kJ/mol}$

$a = 1.09 \pm 0.05$

$\gamma = 0.7$

Evaluation of the FT rate equations showed that the best-suited equations were all based on the hydrogen dependency and can thus easily simplify to a first order equation for the dependence on hydrogen partial pressure. This observation is in line with literature reports of hydrogen dependence at lower conversion levels. The final proposed rate equation suggests that the vacant sites on the catalyst surface (and CO adsorption), and not the competitive

adsorption of water or CO₂ has an inhibiting effect on the reaction rate. The proposed equation presents a more theoretical accurate based equation for the current application.

- 7) The improved WGS reaction rate equation was derived by incorporating the presence of CO₂ adsorption on the catalyst active sites, into the final equation, thereby accounting for any rate inhibiting caused by the presence thereof. The WGS kinetic behaviour of the ChemFT catalyst can be described by:

$$r_{WGS} = \frac{k_o' \cdot e^{(-E_{WGS}/RT)} \cdot (P_{H_2O}P_{CO} - P_{CO_2}P_{H_2}/K_p)}{(1 + a'P_{CO} + b'P_{H_2O} + c'P_{CO_2})^2}$$

with: $k_o' = 419.2 \pm 20.9$ kmol/gcat/s/bar²

$E_{WGS} = 101 \pm 5$ kJ/mol

$a' = 0.98 \pm 0.05$, $b' = 1.19 \pm 0.06$, $c' = 0.54 \pm 0.03$

WGS reaction kinetics is a function of H₂O, CO and CO₂ inhibition. The proposed rate equation takes all of these into account. The presence of different terms and adsorption coefficient values in the FT and WGS rate equation denominators, give strong support towards proving that the two reactions occur on different catalytic sites.

- 8) Activation energies calculated for both reactions falls well within those reported in literature and are also high enough to show that the influence of mass transfer was minimal during the experimental study.

5.2 RECOMMENDATIONS

- 1) Further improvements of the ChemFT catalyst, might see changes concerning the operation conditions of the catalyst. The proposed rate equations are adequate for use in the current ChemFT reactor operating regimes. It is however recommended re-evaluating the equations and the constants thereof when conditions fall outside that reported in this work or if any new promoters are added (or current ones eliminated) in the catalyst preparation formula.
- 2) Although a notable improvement was achieved with the proposed WGS reaction equation, it is still clear that there is room for further investigations towards improving the accuracy

thereof. Such an investigation needs to be undertaken from the point of firstly acquiring knowledge about the catalyst active sites involved. The investigation might be very specific to the ChemFT catalyst, compared to other iron based FT catalysts.

- 3) Literature is available on the kinetics associated with Methanol-Higher alcohol synthesis catalysts. The applicability of this catalyst kinetics to the ChemFT catalyst was not evaluated in this investigation. Further improvements to the ChemFT catalyst alcohol selectivity might necessitate the evaluation of such rate equations. These equations account for the partial pressure effects of the different products in a set of equations, and will thus require much more detailed product analyses.