CHAPTER SEVEN
Summary and Conclusions

There has been global renaissance of Fischer-Tropsch Synthesis (FTS) in the energy industry in recent times. The renewed interest in FTS is to a large extent due anticipated decline in crude supply in the near future; and to a lesser extent due to environmental and climate change concerns. FTS provides means to obtain liquid fuels from other carbonaceous resources like natural gas, coal and biomass. Historically, industrial FTS was developed around coal resources. There is a preference for natural gas due to low carbon footprint and increasing discovery of more gas resources. However, for security of supply in liquid fuel, coal remains relevant for FTS especially in emerging economy and coal rich countries. In addition to the traditional use of coal for electricity generation, there are considerations for installation of new coal based FTS plants which are at various stages of completion across the globe. The motivation for this study is maximising coal utilisation for meeting these two energy needs: liquid fuels and electricity. A FTS-electricity poly-generation system is conceived, and the focus of this study has been designed and evaluation of low cost iron and cobalt based catalysts for the FTS section of the system. Despite an overwhelming number of reports on FT catalyst design in the ninety years history of FT technology, there are still enough scope for further contributions in the design of low cost and high efficiency catalysts for this specific FTS operations.

To the catalyst design objective and identify key design parameters, a thorough review of the literature for insight on the chemistry of FTS has been conducted. The literature survey is focussed on the reaction thermodynamics and stoichiometry; product distribution, kinetic expression and mechanism. Despite nine decades of researches on FTS, there still some grey areas on the details of FTS chemistry. Although FTS involves several parallel reactions, for general discussions it is usually represented as: \( n\text{CO} + 2n\text{H}_2 \rightarrow -(\text{CH}_2)_n^- + n\text{H}_2\text{O} \ \Delta H_R (227 \ ^\circ\text{C}) = -165 \ \text{kJ mol}^{-1} \). The product distribution is generally described by ASF law. The ASF law single parameter, \( \alpha \)-model, it shares the simplicity of ideal gas law, but
FTS product selectivities do deviate from ASF law, an indication of over-assumptions in the ASF law. There have been attempts at accounting for the deviations from the ASF law. A two parameter (double-$\alpha$) and other modified ASF law (re-adsorption models) have been proposed.

Chain-length-dependent desorption model suggested by Wojciechowski and co-workers (1985) about two years ago but recently Botes (2008) has given quantitative mathematical treatment which successfully captures nearly all the deviations from ASF distribution law. Specifically, the chain-length-dependent desorption model is able to account for C$_1$ and C$_2$ selectivities in FTS products distribution while others could not. Chain-length-dependent desorption model predicates FTS product selectivity in terms of relative rates of hydrogenation and desorption as chain termination step. There appears more reaction types than the assumed hydrogenation and desorption as chain termination step in the models. Investigations are needed into the intermediates and the elementary steps to paraffin and olefin products. These details will contribute to the goal of unravelling the full mechanism of FTS. Thus with a catalyst design objective, the assumptions of the chain-length-dependent desorption model is a more realistic overview of FTS compared to the assumptions of ASF law.

FTS is considered as polymerisation type reactions involving: chain initiation, propagation and termination steps. Exact details of FTS polymerisation steps are yet to be understood fully. Based on examination of proposed macro kinetics expressions, product distribution models and isotopic studies, there is high level of certainty with findings about pathway of chain initiation step as involving hydrogen assisted CO activation. Also, there are increasing evidences in support of CO insertion as C-C coupling mechanism and oxygenate intermediate pathways to hydrocarbon on both iron and cobalt catalysts. However, more fundamental studies are necessary for more details and clearer picture. FTS is compared with other C-C coupling reactions of CO: isosynthesis, carbonylation and hydroformylation. The comparisons suggest the key chemical units for FTS catalysts design are hydrogenation, acidic and basic sites. Hydrogenation property is critical to high
activity, acidic and basic sites influence product distribution. The identified chemical units for catalyst design constitute the points for performance-properties correlations.

Commercial Fischer-Tropsch catalysts are based on iron and cobalt. In addition to these active metals, commercial FT catalysts usually contain additives (promoters, supports) for enhanced activity and sustained performance at different reaction conditions. The additives influence product selectivity of the catalysts. The cost and product selectivities of catalysts have implications on the process economy of the FT technology. Specifically catalyst that will afford intensification and optimisation of electricity and hydrocarbon production from coal is a key objective of this study. Fe-Zn based Fischer-Tropsch catalysts are identified as suitable candidates for coal based electricity-liquid fuel co-production. Effects Cu and Ca promotion on reducibility, carburisation and surface acidity-basicity of the Fe-Zn catalysts are examined using TPR (H₂ and CO) and TPD (NH₃ and CO₂) techniques. Results of the characterisation studies provide prior information on expected catalytic behaviour of the catalysts. Ca promotion enhances carburization however Cu inhibits carburization. Enhanced carburization suggests Ca promoted catalyst will exhibit high olefins/paraffins ratio, increase C₅+ selectivity and decrease methane selectivity. A reverse selectivity is expected for Cu promoted catalyst. Surface acidity and basicity increased in the Ca promoted catalyst, while Cu promoted catalyst showed decreased surface acidity and basicity. The Fe-Zn based catalysts are evaluated for low temperature (180-250 °C) Fischer-Tropsch synthesis (LTFT) using H₂-deficient syngas feed typical of H₂/CO ratio (0.5 – 1.0) from high temperature coal gasifiers. The catalysts display unprecedented low CO₂ selectivity which satisfies the intended optimised poly-generation application objective. Cu and Ca promotion affords wider range of product selectivities of the catalysts at LTFT temperature operation mode. The Fe-Zn based catalysts in this study have relatively lower surface area. Activity of the catalysts can be enhanced by preparation methods that give higher surface area. Moreover, the results obtained in this study show that the common higher CO₂ selectivity of iron compared to cobalt based catalysts can be drastically reduced. This may provide foundation to take full advantage of the lower cost of iron compared to cobalt in FT processes.
Effects of Cu and Ca promotion on reducibility and acid-base properties of alumina supported cobalt catalysts are also examined. Cu enhances reducibility of cobalt phases while its reducibility decreases in the presence of Ca. However both Ca and Cu boost dispersion of the cobalt phases on the support. Cu decreases surface acidity and increases surface basicity of the catalysts. Both surface acidity and basicity increases in the presence of Ca. CO and H\textsubscript{2} adsorption on the supports and catalysts are examined using TPD. This is followed by FT tests of the catalysts. Ca-modification of \(\gamma\)-alumina leads to catalysts with enhanced CO adsorption but decreased H\textsubscript{2} adsorption capacities. Although presence of Ca enhances CO adsorption, it does not translate into increased activity and C\textsubscript{5+} selectivity of the catalyst. Significant proportion of Ca in the catalyst after activation is in undecomposed state of salt. Nature of Ca-phase in the catalysts influences its promotion effect on the catalysts. As opposed to reduction temperature of 350 °C used in this study, calcination/activation temperatures \(\geq 550\) °C may be suitable for a Ca promoted catalyst. Co-Cu based catalysts display higher H\textsubscript{2} adsorption capacity and increased CO adsorption strength. The increased CO adsorption strength is at the expense of lower CO adsorption capacity. This observation is linked with the decoration effect of copper on cobalt particles and oxygenates selectivity of Co-Cu catalysts but constitute a nemesis for hydrocarbon formation. Although the results of Cu and Ca promotion of alumina supported cobalt catalyst from this study do not yield increased activity of the catalysts, it is still possible to exploit the advantage of increased reducibility of cobalt phase with copper promotion. Moreover, CO\textsubscript{2} selectivity of these catalysts is also very low which is suitable for more environmental friendly FT process. Most probably a sequential introduction of the metal precursors on a support, first copper impregnation and calcination followed by cobalt loading will help to circumvent the undesirable decoration effect of copper on cobalt.