



CHAPTER X

Conclusion

The thesis set out to improve the understanding of Fischer-Tropsch syncrude refining. By first studying current refining practise, crude oil and syncrude could be compared to identify fundamental differences in refining focus and conversion behaviour. This study was followed by a critical evaluation of the compatibility of HTFT and LTFT syncrudes with the chemistry and catalysis of various conversion processes. The recommendations from the technology evaluation provided the foundation for the development of Fischer-Tropsch syncrude based refinery designs to maximise motor-gasoline, jet fuel and diesel fuel production. These designs showed that Fischer-Tropsch refineries could be less complex than 4th generation crude oil refineries for the production of on-specification transportation fuels. It also illustrated the advantage of considering syncrude fundamentals in developing syncrude specific refineries, rather than imposing crude oil design practises on syncrude refinery designs.

1. Introduction

Refining technology is continuously evolving, driven by the changing legislative pressures associated with transportation fuels. The development, commercialisation and licensing of refining technology gave rise to a whole industry. The focus of this industry is on the conversion of crude oil to transportation fuels. Although the production and refining of Fischer-Tropsch syncrude has been around for a long time, very little effort has been devoted to the development and customisation of refining technologies to specifically upgrade syncrude. The designs of commercial facilities for the conversion of Fischer-Tropsch syncrudes to transportation fuels have likewise been based on crude oil refining technologies and know-how. This is not surprising considering the small market share that syncrude refining has; about 250 000 bpd of more than 85 000 000 bpd refining capacity worldwide. However, this does not explain the lack of understanding that permeated the technology selection and the refining technology application for syncrude refining. The premise explored in this thesis, namely that refining of Fischer-Tropsch syncrude requires

significantly different technologies and refinery designs, is a departure from the mainstream practice in the South African synthetic fuels industry.

In the past three decades two distinctly different approaches to syncrude refining emerged. The one approach was to make use of crude oil refining technology for Fischer-Tropsch syncrude refining to transportation fuels, which resulted in complex refineries, such as Sasol Synfuels (Secunda, South Africa) and PetroSA Mossgas (Mossel Bay, South Africa). The other approach was to convert the Fischer-Tropsch syncrude to naphtha and distillate, which could be sold as blending components for transportation fuels or as intermediates for chemical production. This approach was used for the Shell Bintulu (Bintulu, Malaysia) and Oryx GTL (Ras Laffan, Qatar) facilities and resulted in much simpler refineries.

The need to improve our *understanding of refining technology selection and refinery design for processing Fischer-Tropsch syncrude*, proved to be an academically fertile and industrially relevant topic for research.

2. What has been achieved?

2.1. Thesis part 1: Background

In order to develop a better understanding of Fischer-Tropsch syncrude refining, a thorough grasp of crude oil refining was required. This was achieved by studying the feed material, conversion steps and fuel specifications that define the transformation process called fuels refining. The results of this background study have been provided in Chapter II (fuel specifications), Chapter III (crude oil description) and Chapter IV (crude oil refineries). Although these chapters dealt mainly with a review of current literature, the information thus gleaned was interpreted in context to *identify trends for future fuel specifications* (Chapter II, section 5) and *future oil refineries* (Chapter IV, section 4). This is an interpretative contribution, albeit speculative, since it deals with the future that is inherently uncertain.

Literature on Fischer-Tropsch technology is available in two recent books^a on this subject. Rather than rehash information from literature, care was taken to highlight aspects relevant to the present study. Considering that the syncrude composition is dependent on the type of Fischer-Tropsch technology being used and that there are presently six different types

^a Steynberg, A. P.; Dry, M. E. Eds. *Fischer-Tropsch Technology*; Elsevier: Amsterdam, 2004. Davis, B. H.; Ocelli, M. L. Eds. *Fischer-Tropsch synthesis, catalysts and catalysis*; Elsevier: Amsterdam, 2007.

in commercial operation, *syncrude composition was related to Fischer-Tropsch fundamentals* (Chapter V, section 2) to explain differences in the carbon number distribution and compound classes being present. Some of the refining issues related to syncrude composition were anticipated by *comparing crude oil with syncrude and noting fundamental differences in refining focus and conversion behaviour* (Chapter V, section 5).

This set the scene for a detailed discussion of Fischer-Tropsch refineries (Chapter VI), a topic not previously dealt with in a single reference work. The discussion of the refinery designs pointed out syncrude refining peculiarities by *interpreting the design intent*, which is not specified in the literature. The literature review is also valuable in its own right, since it collated the snippets of information on Fischer-Tropsch refining that have not previously been presented together in a single text.

2.2. Thesis part 2: Refining technology and refinery design

The second part of the thesis deals with Fischer-Tropsch refining. It contributes new insights in two fields that until now received scant coverage in literature, namely *refinery technology evaluation in Fischer-Tropsch context* (Chapter VII) and *conceptual Fischer-Tropsch refinery design* (Chapter IX). In both instances the focus was on conversion technology, with limited reference to separation science.

The approach followed in Chapter VII was to evaluate the *compatibility of Fischer-Tropsch syncrude with the chemistry and catalysis* of different conversion processes. The analysis was based on a fundamental understanding of the conversion involved and how it will be affected by the compound classes present in syncrude that are not present in crude oil. The nature and concentration of the olefins and the oxygenates in syncrude were often the differentiating features. Cognisance was also taken of the environmental impact of the conversion technologies, by assessing the waste production, chemicals needed and energy use. The list of technologies that were evaluated transcended the list of refining technologies found in crude oil refining texts, with conversion processes such as double bond isomerisation, aromatic alkylation, metathesis and alcohol dehydration being included in the study. Recommendations were made within each conversion class to indicate preferred technologies. This information is summarised in a compatibility table for Fischer-Tropsch refining technologies (Chapter VII, Table 8).

The chapter on refinery design (Chapter VIII) was necessary to discuss the design process and is not only limited to Fischer-Tropsch refineries. The approach taken is

qualitative and somewhat philosophical, with a clear distinction being made between “real-world” refinery designs and the conceptual design process. Of especial significance was to *highlight the importance of secondary design objectives* in determining the outcome of refinery development. This is not a well-known aspect of refinery design, which is a bit like the law of unintended consequences, and has been illustrated with a “real-world” example (Chapter VIII, Appendix A).

The chapter on conceptual Fischer-Tropsch refinery design (Chapter IX) is the culmination of this study. After the subject matter has been taken apart in Chapters II to VIII, it is put back together again. The insights gained in technology selection and syncrude properties are used to *develop refinery designs for maximum motor-gasoline, jet fuel and diesel fuel* production. Designs were developed for both HTFT and LTFT syncrudes and despite significant differences in these syncrudes, it is shown that neither requires overly complex refinery designs to produce fuels. A total of 16 different fuels refineries were developed and the designs demonstrated that syncrude refineries are often less complex than 4th generation crude oil refineries for the production of on-specification transportation fuels.

A surprising exception was found in the conversion of syncrude to diesel fuel. The refining of on-specification diesel fuel presented a problem on account of a *cetane-density-yield triangle* (Chapter IX, section 5). It could be shown that on a molecular level syncrude is unsuitable for diesel fuel production as defining by current international fuel specifications. This is quite contrary to the expectations created in the media by projects such as Sasol’s Oryx GTL and Shell’s Pearl GTL.

In essence Chapters VII to IX defined a technology roadmap for the refining of Fischer-Tropsch syncrude. The recommendations on technology selection are based on fundamental scientific principles and are therefore logically auditable. The refinery designs that were developed, provide a framework for future project specific refinery designs, as well as an indication to what extent motor-gasoline, jet fuel and diesel fuel production can be maximised. Such an evaluation has not previously been published.

3. Prospects for future study

Refining is a very broad field and the scope of the present investigation leaves much work undone. During the course of this study, some topics were touched on that deserves treatment in their own right. It is hoped that future researchers may take up these suggestions for further study:



a) *Oxygenate refining*. The significant levels of oxygenates (alcohols, aldehydes, carboxylic acids and ketones) present in Fischer-Tropsch syncrude differentiates it from crude oil. Most refining technologies have been developed without paying any attention to the effect of oxygenates on account of their minor role in crude oil refining. A systematic investigation into the effect of oxygenates on different refining technologies will benefit the syncrude refining industry tremendously. Reference to some of the technologies investigated by myself and my co-workers can be found in the thesis, but it still leaves much to be accomplished.

b) *Separation technology*. Separation presents its own set of challenges to the syncrude refiner. The phase behaviour of the hydrocarbon-oxygenate and oxygenate-water mixtures encountered in a Fischer-Tropsch refinery is non-ideal and finding appropriate thermodynamic models to describe it, is challenging. This is made even more difficult by the lack of equilibrium data for such systems.

c) *Syncrude analysis*. The analytical methodologies adopted by the fuels industry are mostly based on crude oil derived petroleum products. Blindly applying these techniques to syncrude is fraught with error. Deficiencies in the characterisation of syncrude have briefly been mentioned in Chapter V and there is much scope for the development of appropriate analytical methodologies for syncrude.

d) *Catalysis of linear α -olefins and 1-alcohols*. Renewed interest in solid phosphoric acid catalysis for syncrude refining was sparked when it was shown that there is a low temperature isomerisation pathway from 1-butene to isobutene during oligomerisation that produced alkylate equivalent products. A different mode of reaction for 1-butene has also been identified for oligomerisation over amorphous silica-alumina catalysts. There are bound to be more reactions and catalysts that have beneficial reaction pathways for linear α -olefins and 1-alcohols. Probing this field may lead to the discovery of more efficient refining technologies for Fischer-Tropsch syncrude.

e) *Metal carboxylates*. The metal containing species in syncrude are mainly metal carboxylates. These species are fundamentally different from the porphyrin-type species in crude oil. The metal carboxylates present in syncrude are usually stable enough to survive low to medium severity conversion processes in the refinery and they are not converted by hydrodemetallisation (HDM) catalysts. Thermal decomposition under more severe operating conditions can potentially cause pressure drop problems. Unfortunately the thermal behaviour of many metal carboxylates of interest to syncrude refining are poorly described.

f) *Catalyst evaluation protocol.* The catalyst testing protocols that have been developed for scale-up and scale-down, are mainly concerned with the influence of hydrodynamics. Hydrodynamics is important, but isothermal catalyst evaluation becomes a dangerous practise when dealing with very exothermic conversion processes, such as is often encountered with syncrude (Chapter V, section 5). The need for adiabatic testing in such situations has been discussed in literature. However, this topic is scantily covered, despite its importance for the selection and evaluation of refining catalysts with syncrude feed materials. Such an investigation should preferably also be extended to the design of appropriate laboratory and pilot-scale reactor systems for such evaluations.

g) *Non-energy refineries.* In Chapter IX reference was made to some literature dealing with the refining of Fischer-Tropsch syncrude to chemicals and the study of non-energy refineries was excluded from the scope of this thesis. It is nevertheless a logical next step in extending the technology roadmap for Fischer-Tropsch refining and should move well beyond the obvious chemicals obtainable by separation from syncrude. Chemicals refining potentially require a different set of conversion technologies that have to be evaluated for their compatibility with syncrude. Furthermore, a proper evaluation of chemicals refining presupposes a thorough understanding of the chemicals market, which is quite different to the transportation fuel market. In this respect it will be especially beneficial to investigate the possibility of producing lubricating oils, fuel additives and other speciality products that have synergy with transportation fuels.

h) *Feedstock integration.* The co-refining of syncrude with feedstocks derived from other sources may prove a fertile ground for improving the efficiency of Fischer-Tropsch technology as basis for fuels and chemicals production. Presently, commercial Fischer-Tropsch facilities are already co-refining coal pyrolysis products and natural gas condensates, while some of the downstream products are blended with crude oil derived materials. The integration of these feedstocks and intermediate products may be achieved in many ways, some of which may be more beneficial than current practice. There are also opportunities for the co-refining of other feed materials, such as crude oil and biomass. Some of these opportunities have been mentioned and many more will undoubtedly become apparent as this field is explored.

Research often unearths more questions than it sets out to answer. The suggested topics for future research are just a fraction of the topics in the field of Fischer-Tropsch refining that deserve attention. In energy research, Fischer-Tropsch refining is still comparatively virgin



territory. The scope for process intensification is huge, with very little having been done in this respect for the integration of syncrude production and refining. Refining catalysis similarly abounds with opportunities. It is hoped that future researchers may derive the same joy from the exploration of the complexity being offered by this topic.