

“Catalysis in the Refining of Fischer–Tropsch Syncrude”

By Arno de Klerk (University of Alberta, Edmonton, Alberta, Canada) and Edward Furimsky (IMAF Group, Ontario, Ottawa, Canada), RSC Catalysis Series, No. 4, Royal Society of Chemistry, Cambridge, UK, 2010, 294 pages, ISBN: 978-1-84973-080-8, £121.99, US\$205.00, €139.95 (Print version); e-ISBN: 978-1-84973-201-7 (Online version)

<http://dx.doi.org/10.1595/147106711X593717>

<http://www.platinummetalsreview.com/>

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Introduction

“Catalysis in the Refining of Fischer-Tropsch Syncrude” is the fourth book in the Royal Society of Chemistry’s Catalysis Series. Written by Arno de Klerk and Edward Furimsky from the University of Alberta and the IMAF group in Ontario, Canada, respectively, this book provides a review of the somewhat neglected area of refining and upgrading catalysts, rather than the more widely published area of Fisher-Tropsch synthesis itself (1). This book provides an excellent and comprehensive evaluation of the catalytic processes for syncrude conversion to useful products such as fuel and oils.

The book consists of eleven chapters, which are well presented and divided into easily manageable segments. The writing style is very clear and explains the processes concisely and simply. The first two short chapters put syncrude refining into context within the Fisher-Tropsch process as a whole and allow non-specialists to quickly grasp the technology. The remaining chapters take the reader on a logical and well thought out journey through the Fischer-Tropsch production of syncrude; the upgrading of waxes, oxygenates and crude; the catalysis of the refining process; the commercial products obtained during the process; and finally a review of the current patent literature and future perspectives.

Fischer-Tropsch Processes

Fischer-Tropsch is the process whereby synthesis gas (hydrogen and carbon monoxide) is converted into a mixture of hydrocarbons, oxygenates, water and carbon dioxide. The hydrocarbons thus produced can be refined and used in place of more conventional liquid fuels derived from crude oil. Synthetic fuel can be produced by a variety of methods, with gas-to-liquid (GTL), coal-to-liquid (CTL) and biomass-to-liquid (BTL) being the most widespread. An outline of a Fischer-Tropsch facility is summarised in **Figure 1**.

Fischer-Tropsch synthesis has been carried out predominantly using iron- and cobalt-based catalysts

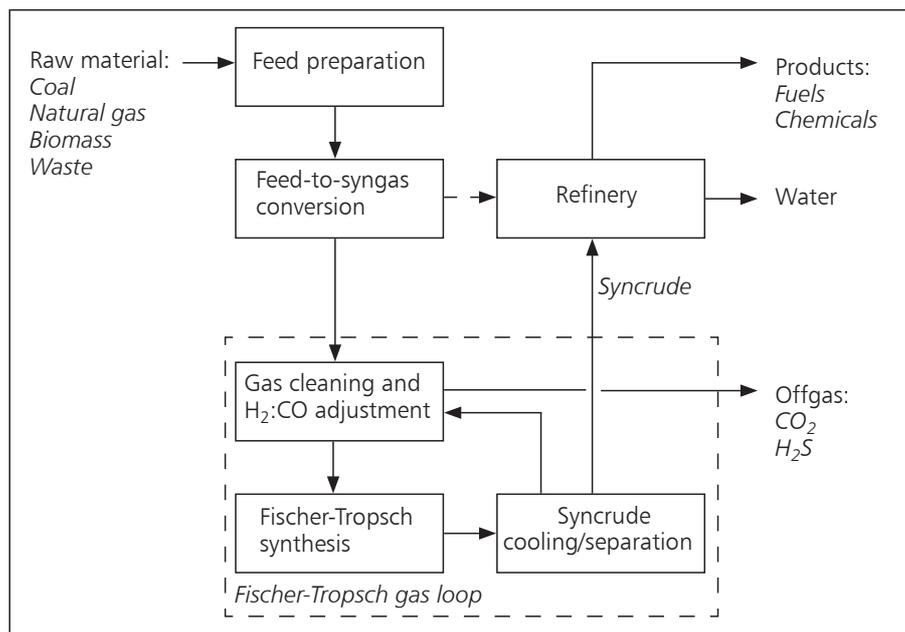


Fig. 1. A simplified flow diagram of a Fischer-Tropsch-based facility (some liquid pyrolysis products may be produced, represented by the dashed line) (Reproduced by permission of The Royal Society of Chemistry)

since the 1930s, having been commercialised in Germany in 1936 to provide transport fuel for the coal rich, oil poor nation. South Africa has since become the largest user of Fischer-Tropsch technology, developed in response to international sanctions that prevented the import of crude oil, and nearly the entire country's diesel is currently produced from coal by this method (2).

In the present book, Chapters 3 and 4 provide a good technical overview of and background to the chemistry of Fischer-Tropsch reactions. These chapters concentrate on how different reaction and catalyst conditions affect the composition of the synchrude (Figure 2). Chapter 3 concludes with an examination of current industrial Fischer-Tropsch processes. The message is that this area of chemistry is not just an academic pursuit, but rather a key technology for future energy security and fuel production. The table of production facilities provides a timeline from the first facilities employed by Germany during the Second World War right up to the gigantic Shell 'Pearl GTL' plant in Qatar. This plant began shipments of its GTL Gasoil product in 2011 with full production scheduled for 2012. In Chapter 4, the reader is taken in more detail through the initial processing steps of Fischer-Tropsch synthesis and how the synchrude produced differs from that obtained from conventional crude oil. The differences in chemical composition are vital in understanding

which downstream refining and upgrading processes are required to produce useful commercial products.

Platinum Group Metals in the Upgrading of Fischer-Tropsch Synchrude

Chapter 5 is where the main topic of the book really gets going, it is by far the largest chapter in the whole book with over 120 pages devoted to it. Here the reader is provided with a review of the technical detail behind the catalysis of upgrading Fischer-Tropsch synchrude. The chapter is split into four main sections corresponding to the most widely utilised conversion technologies. These are:

- oligomerisation,
- isomerisation and hydroisomerisation,
- cracking and hydrocracking,
- hydrotreating.

Although this chapter contains the most significant amount of information, it only concerns the upgrading of synchrude rather than the refining. Catalytic reforming, which is an important platinum group metal (pgm) utilising process in refineries, is mentioned in a later chapter.

In terms of pgm usage, all but the oligomerisation section contain numerous references to pgm-catalysed processes. The subsections proceed in a logical fashion, describing first the background and mechanism of each process, then the various catalysts used. The use

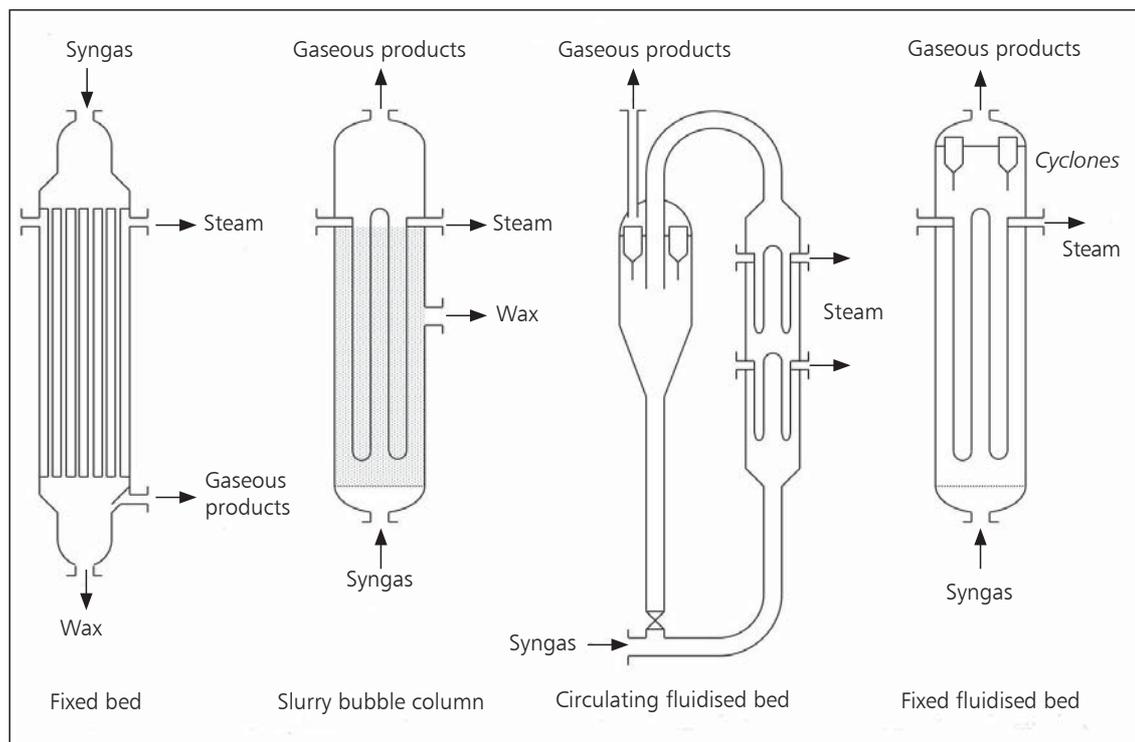


Fig. 2. Fischer-Tropsch reactor technologies in industrial applications (Reproduced by permission of The Royal Society of Chemistry)

of platinum and palladium as promoters in various zeolite, silica-alumina, phosphate and sulfonated zirconia catalysts is given considerable coverage, well illustrated by graphs and tables detailing conversion, yield and selectivity relationships with various feedstocks. The catalytic mechanisms detailed throughout this book are very clear, giving the reader an understanding of the chemistry behind the refining and upgrading processes. The vast range of different temperatures, pressures, feeds, catalysts and other factors are emphasised, giving a good feel for the complexity of syncrude upgrading. The authors compare and contrast these different factors and clearly show the effect of each on the final products.

Each section gives a solid introduction and mechanistic outline to each process, followed by an examination of the commercial aspects and a comprehensive review of the current literature regarding catalyst developments. They conclude with a comparison of the various modes of deactivation for different catalysts and conditions. This is an area often neglected when concentrating on activity, yields and selectivity.

Refining Catalysts

Chapter 8, despite being somewhat shorter than Chapter 5, nevertheless contains an excellent review

of refining catalysts, such as those employed in reforming, a significant area of pgm demand. The first part of the chapter demonstrates the differences between conventional oil refineries and those employing Fischer-Tropsch technology. The generic plant designs illustrated at the beginning of the chapter highlight the major differences in how the various refined fractions are produced and again drives home the message that to produce high quality fuels and oils using Fischer-Tropsch synthesis requires specialised equipment, processes and catalysts to deal with the different chemistries of syncrude and conventional crude oil. The first table in Chapter 8 highlights this further by examining the current conventional conversion processes and their compatibility with Fischer-Tropsch refineries.

There are two subsections dedicated to the use of platinum on acidic alumina and on non-acidic zeolite respectively, highlighting the importance of platinum for the production of synthetic fuels. The higher amounts of oxygenates in Fischer-Tropsch feed have been shown to deactivate the acidic support, although it is very compatible with the non-acidic L-zeolite catalyst (Figure 3). The much lower sulfur content of the feed is a distinct advantage over conventional crude feedstocks.

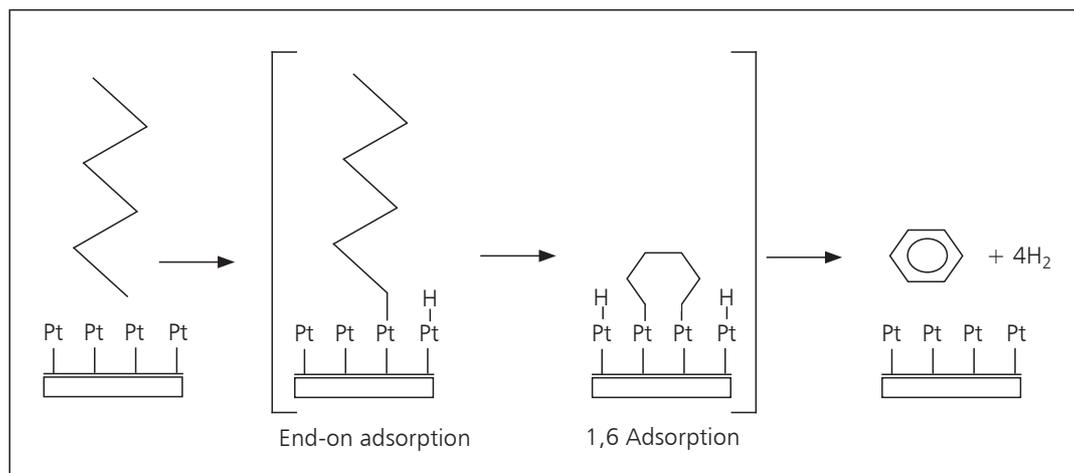


Fig. 3. End-on adsorption of *n*-alkanes on platinum/L-zeolite which results in 1,6-ring closure and aromatisation (Reproduced by permission of The Royal Society of Chemistry)

The final chapters examine the commercial products obtained from Fischer-Tropsch syncrude, the current patent literature and future perspectives in this technology. The authors do a very good job of putting the catalysis reviewed in the preceding chapters into a commercial context, whilst showing what the future may hold for this exciting area. The final chapter makes the interesting point that Fischer-Tropsch plants have historically been built to deal with issues of energy security. Going forward it appears that investment will be driven by both the requirement to produce fuels from alternative carbon sources and the price differential between conventional crude and that produced by Fischer-Tropsch technology.

Conclusions

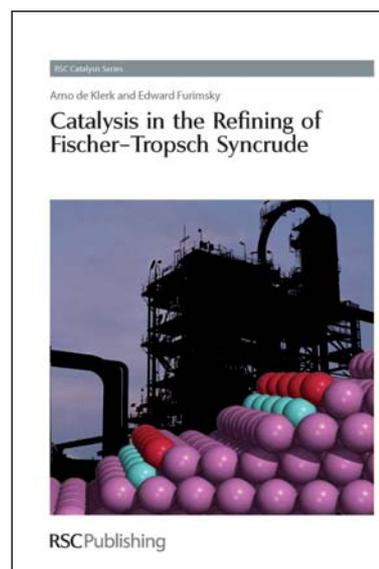
The authors state that a review of catalysis in the refining of Fischer-Tropsch syncrude is the main objective of the book. This objective has been achieved admirably, providing an accessible and comprehensive review of Fischer-Tropsch refining catalysis from the fundamental chemistry to the commercial aspects and applications. The reader is required to have a general understanding of chemistry and catalysis, and the book will appeal both to those looking to gain initial exposure to this topic, and to readers with greater knowledge of the subject. The use of the pgms features strongly throughout the book, dominating the chapters on upgrading and refining syncrude.

Overall, this book will be of interest to a wide audience, from those involved in the academic pursuit of improving the catalysis to those involved with the commercial development of Fischer-Tropsch refining.

It is clearly an exciting area to be involved with and the potential to provide an alternative to conventional fuel sources is something that the authors convey particularly well.

References

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"Catalysis in the Refining of Fischer-Tropsch Syncrude"

The Reviewer



Dr Stewart Brown graduated with an MChem (Hons) and a PhD in Chemistry from the University of Liverpool, UK. He joined Johnson Matthey in 2004 and spent 5 years as a Process Development Chemist, involved in the scale-up of new catalysts and processes for the Emission Control Technologies business unit. In 2009 he transferred to Precious Metals Marketing and is currently a Market Analyst within the Market Research team, focusing on platinum group metal demand from the chemical, electronics, automotive and petroleum refining sectors.

Fischer-Tropsch Synthesis, Catalyst and Catalysis. Melene M. Keyser, Frans F. Prinsloo, in Studies in Surface Science and Catalysis, 2007. 2.12 Catalytic testing. Fischer-Tropsch synthesis is a catalyzed chemical reaction in which synthesis gas (syngas), a mixture of carbon monoxide (CO) and hydrogen (H₂), is converted into gaseous, liquid, and solid hydrocarbons and an appreciable amount of oxygenates (Chadeesingh, 2011). This process is a highly promising, developing option for environmentally sound production of chemicals and fuels from biomass, coal, and natural gas. It is thus not surprising that Fischer-Tropsch technology now occupies a visible place in the energy mix required for sustainable global development. Fischer-Tropsch Refining. Author: Arno de Klerk Promoter: Prof. Philip L. de Vaal Department: Department of Chemical Engineering, University of Pretoria Degree: Philosophiae Doctor (Chemical Engineering). Synopsis. Energy carriers, such as coal, natural gas and biomass, can be converted by Fischer-Tropsch technology into synthetic crude (syncrude). Yet, despite an abundance of literature of Fischer-Tropsch synthesis, there is little literature that deals with the refining of Fischer-Tropsch syncrude. The present study investigated current refining practice for both crude oil and Fischer-Tropsch syncrude in order to identify fundamental differences in their refining focus and conversion behaviour.