Arno de Klerk

Fischer–Tropsch Refining

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The Author

Arno de Klerk
University of Alberta
Chemical and Materials Engineering
Edmonton, Alberta, T6G 2V4
Canada

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To my wife, Chèrie, who loves and supports me so much.

Contents

Preface

Life sometimes takes one on a journey that is quite unanticipated. After graduation, I had dreams of making the world a better place by becoming a forensic scientist. Three years later, life took me down a different path. As a young process engineer the objective changed and I had to console myself with trying to make the world a better place in a different way. Thus started an industrial career in the refining of synthetic liquids.

The energy business is tremendously dependent on the crude oil price, which by all accounts seems to be inherently unpredictable. The crude oil price holds the synthetic liquids industry to ransom, as it fluctuates in response to many global forces. Today, coal-to-liquids and gas-to-liquids are economical processes – tomorrow it may not be. So, it goes on and on, and has been going on for many decades.

When an idealistic individual is confronted with the realities of the energy business and the fickleness of decisions related to the continuous quest for power and money, it can become frustrating. It is not possible to develop technology for the refining of synthetic liquids in phase with the waxing and waning of the oil price. This in turn leads to inefficient refining practices and creates false impressions about the refining of synthetic liquids. Research is not amenable to the stop–start–stop–start cycles dictated by the economic fortunes of the synthetic liquids industry. The wheel has been reinvented many times over, as know-how is lost in times when indirect liquefaction is not economical.

This book is an attempt to present and preserve some of the thinking around the refining of Fischer–Tropsch syncrude in the hope that it will help bridge the stop–start–stop–start interest in indirect liquefaction by Fischer–Tropsch synthesis. There are no other works on this topic, except for the occasional chapter in works on Fischer–Tropsch synthesis. The catalysis related to Fischer–Tropsch refining has been discussed in a recent book by Ed Furimsky and myself that is titled ''Catalysis in the refining of Fischer–Tropsch syncrude.'' There was a deliberate attempt to avoid duplication of effort and overlap with the aforementioned work. This book focuses on the application of catalysis, the processes, the refining technologies, and the refinery design associated with Fischer–Tropsch syncrude.

During the writing of this book, some decisions had to be made. The book also had to deal with shortcomings in the reported literature that could not be overcome by the author's experience in this field. The intent is not to apologize for these decisions and shortcomings but rather to make the reader aware of them.

1) Throughout the book, the International Union of Pure and Applied Chemistry (IUPAC) chemical nomenclature was employed. This may create a slightly unfamiliar feel for many

readers from the industry and maybe even some readers from the academia. It is a common occurrence to refer to paraffins (not alkanes) and olefins (not alkenes). Yet, having waded through a fair bit of the older literature on Fischer–Tropsch in writing this book, one appreciates the value of having a consistent nomenclature. It was too often necessary to scrounge around to establish what compound or mixture has been described by a colloquial term that had been in common use 80 years ago, but is quite unfamiliar at present. As concession and in order to improve readability, commonly used trivial names and terms were provided in brackets with the IUPAC nomenclature. In cases where the trivial name is unambiguous and recognized in IUPAC nomenclature, the more familiar name was adopted, for example, *o*-xylene instead of 1,2-dimethylbenzene.

2) In chemical structures, hydrogen atoms are not indicated unless it improves readability. The symbol "R" denotes an alkyl group or hydrogen and the symbol "M" denotes a metal atom.
3) The Système International d'Unités (SI units) were used, albeit with some exceptions. Temperature is reported in degrees Celsius (°C) and not Kelvin (K). The conversion from degrees Celsius to Kelvin is easy, just add 273.15. Kinematic viscosity is reported in centistokes (cSt) and not square meter per second ($1\ \text{cSt} = 1 \times 10^{-6}\ \text{m}^2{\cdot}\text{s}^{-1} = 1\ \text{mm}^2{\cdot}\text{s}^{-1}$). Not all rates were converted to a per second basis and more familiar time periods were employed for production capacities and flow rates. Since the topic of the book is on refining, it also became clear that the unit of barrels per day (bbl/day) cannot be avoided ($1\ \text{bbl} = 0.158\,987\,3\ \text{m}^3$).
4) In the chapters that discuss transportation fuel specifications, the measurement of fuel properties mainly refers to the American Society for Testing and Materials (ASTM) standard test methods. There are of course equivalent methods from the Institute of Petroleum (IP), International Standards Organization (ISO), and various national institutes. Reference to the one rather than the other implies no value judgment.
5) Transportation fuel specifications are country dependent and are ever changing. No attempt was made to provide an anthology of global specifications, which would in any case become outdated rather quickly. The European motor-gasoline (EN228:2004) and diesel fuel (EN590:2004) specifications were selected as the basis for discussion, with reference to some other specifications, including the World Wide Fuel Charter (WWFC). The same applies to jet fuel, where the DEF-STAN 91-91 Issue 6 has been selected as the basis for discussion. There is no implicit value judgment. The discussion focuses on the fundamentals and the specifications are only illustrative in nature.
6) Refining consists of conversion and separation processes. In the book, there is a definite bias toward conversion processes. This does not imply that separation is less important than conversion, but in many instances the challenge in fuel refining is not efficient separation, but efficient conversion. In petrochemical refining, the roles are sometimes reversed. The bias toward conversion goes hand in hand with the focus.
7) The effort that has been expended in literature to correctly identify and quantify compounds varies considerably. If some compounds or compound classes have not been mentioned in conjunction with a specific topic, it does not necessarily imply that these compounds were not present. In Fischer–Tropsch literature, the oxygenates and especially the aqueous products tend to be ignored or are considered with less care than is bestowed on the organic product. Where possible this bias was rectified, but this was not possible in all instances.

8) The book ‘‘Catalysis in the refining of Fischer–Tropsch syncrude’’ contains an in-depth discussion on the catalysis needed for the refining of Fischer–Tropsch syncrude. It also contains a review of the patent literature on syncrude refining. References to patent literature and catalysis literature have therefore been kept to a minimum. Nevertheless, some discussion of catalysis in the context of refining could not be avoided, since it is critical to the success of syncrude refining.
9) Although every effort has been made to provide a comprehensive discussion of refining, this book is not a general text on oil refining. Process flow diagrams and schematics have consequently not been provided for every technology, and there was a deliberate attempt not to duplicate material readily available in reference texts on crude oil refining. Details related to general issues, such as the pressure and energy balance over fluid catalytic cracking units, were therefore not discussed unless it had a direct bearing on syncrude refining.
10) A number of sections were devoted to the relationship between crude oil refining, transportation fuel specifications, and syncrude refining. Yet, the focus throughout was on Fischer–Tropsch syncrude refining. It was assumed that the reader has at least a superficial knowledge of the conversion processes employed in crude oil refining. If this is not the case, the narrative will be somewhat more taxing to follow, but should still be understandable.

Edmonton, AB, Canada, December 2010 *Arno de Klerk*

Part I
Introduction

Fischer–Tropsch Refining, First Edition. Arno de Klerk.

1
Fischer–Tropsch Facilities at a Glance

1.1
Introduction

Industrial Fischer–Tropsch facilities are currently only used for coal-to-liquid (CTL) and gas-to-liquid (GTL) conversion. The purpose of such facilities is to convert solid or gaseous carbon-based energy sources into products that may be used as fuels or chemicals. Although Fischer–Tropsch synthesis lies at the heart of the conversion, it is actually only a small part of the overall process. The process can be divided into three steps (Figure 1.1): feed-to-syngas conversion, syngas-to-syncrude conversion, and syncrude-to-product conversion. Generically, this is called *indirect liquefaction*, because the feed is first transformed into synthesis gas (syngas) and the syngas is then transformed into products.

From Figure 1.1 it can be seen that the type of feed materials that can be converted in the first step is not restricted to coal and natural gas. The conversion of biomass in a biomass-to-liquids (BTLs) process and waste in a waste-to-liquids (WTLs) process can likewise be considered. Collectively, all of these processes are referred to as feed-to-liquids (XTLs) conversion processes. The raw feed material limits the technology selection for the feed-to-syngas conversion step, but not for the subsequent steps. Once the feed has been converted into syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H_2), the syngas can be conditioned to serve as feed for any syngas-to-syncrude conversion technology. Fischer–Tropsch synthesis is not the only possible technology for the conversion of syngas into a synthetic crude oil (syncrude), but together with syngas-to-methanol conversion [1], Fischer–Tropsch synthesis is industrially the most relevant.

This book deals with the third step in Figure 1.1, namely, the refining of the syncrude into final marketable products, and it specifically deals with the refining of Fischer–Tropsch syncrude as the title suggests. Since methanol is also a product of Fischer–Tropsch synthesis, the refining of methanol as syncrude component is covered too.

The representation in Figure 1.1 does not do justice to the complexity of indirect liquefaction. Whole texts have been devoted to aspects of the indirect liquefaction process, such as coal gasification [2, 3], Fischer–Tropsch technology [4–7], and the catalysis of Fischer–Tropsch syncrude refining [8]. This chapter provides only an overview of Fischer–Tropsch facilities. It shows how the component parts are linked together and why they are interdependent. In subsequent chapters, each one of the topics is revisited in more depth, in order to present the detail that is necessary to comprehensively deal with the topic of this book, namely, Fischer–Tropsch refining.

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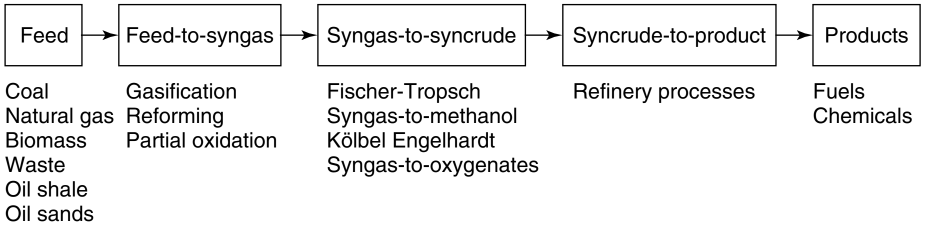

Figure 1.1 Overall indirect liquefaction process for feed-to-liquids (XTL) conversion.

1.2
Feed-to-Syngas Conversion

Feed-to-syngas conversion is an energy-intensive operation and also the most expensive step in indirect liquefaction. Many of the advantages that are related to the feed-to-syngas conversion step do not depend on subsequent processing. It is these advantages that make indirect liquefaction attractive, despite its poorer energy efficiency than direct liquefaction [9–11].

1) **Feed diversity**. One of the major advantages of indirect liquefaction over direct liquefaction is the wide selection of feed materials that can be used. In addition to coal and natural gas, it is possible to employ almost any other carbon source as feed material. The conversion of biomass and waste are attractive concepts, since biomass represents a renewable source of energy and waste conversion represents the beneficial reuse of discarded material. Waste products that can be considered include domestic and industrial waste, for example, discarded plastic containers, old tires, and asphalthenes from carbon rejection processes. However, feed diversity is not the same as feed flexibility. The design of the feed-to-syngas conversion step has to be based on a specific feed slate and it generally has little feed flexibility beyond its designed range of feed compositions.
2) **Mineral rejection**. Indirect liquefaction has the inherent ability to process and separate carbon matter from mineral matter in mineral-containing carbon sources. Oil shales, peat, coal, and oil sands are all mineral-containing carbon sources. Such solid feed materials are typically converted in gasifiers to produce syngas. Once the carbon in these carbon sources has been oxidized to carbon monoxide, separation of the gaseous products from the mineral matter is easily achieved. The physical state of the rejected mineral matter depends on the gasification technology that was employed and it may be a dry ash or a slag.
3) **Heteroatom removal**. Carbon-containing feed material usually contains other elements in addition to carbon and hydrogen. When the feed is converted into a raw synthesis gas, heteroatoms in the feed are also converted into gaseous compounds, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), and ammonia (NH_3). When the raw synthesis gas is purified, these heteroatom-containing compounds are removed to produce a pure synthesis gas, consisting of only carbon monoxide and hydrogen. With the exception of oxygen, all other heteroatoms are therefore removed during syngas purification. The removal of heteroatoms benefits the syncrude refinery, since the syncrude now only contains $C_xH_yO_z$-compounds.

1.2.1
Feed Logistics and Feed Preparation

It is convenient to look at the carbon-containing feed merely as a feed process stream. In the case of natural gas feed that is already available from a pipeline supply, this may be a good approximation, but it is an oversimplification in most other cases. The steps involved in obtaining and preparing feed for indirect liquefaction are more complex (Figure 1.2).

The carbon source is not always concentrated, as it is in the case of a natural nonrenewable resource such as coal. Biomass-derived feed is not concentrated at a single point of origin. Biomass has a low energy density and the feed logistics involved in collecting and transporting the biomass from its origin to the indirect liquefaction facility significantly adds to the cost and complexity of the process. Feed pretreatment and logistics are generally costlier than the direct operating cost of indirect liquefaction to produce Fischer–Tropsch syncrude. It can account for up to a third of the total production cost of the whole facility [12].

For natural gas, the feed logistics may be a significant factor in deciding whether to invest in indirect liquefaction or not. Natural gas can be directly distributed by pipeline as fuel gas, or it can be compressed and distributed as liquefied natural gas (LNG).

All raw materials, including natural gas, require some form of feed pretreatment before they are suitable for conversion into syngas. The nature of the pretreatment is directly linked to the method of syngas production. It is prudent to select the syngas production technology with this in mind, since feed pretreatment can be a significant cost component.

1.2.2
Syngas Production

All syngas production technologies involve some form of partial oxidation (Chapter 3). It is convenient to consider the production of syngas from gaseous and solid carbon sources separately. Irrespective of the feed, the syngas production technology must be compatible with the feed and it should ideally be selected to meet the syngas requirements of the syngas-to-syncrude conversion technology. As rule of thumb, one aims for a H_2:CO ratio of around 2 in the syngas. The exact H_2:CO ratio that is required depends on the Fischer–Tropsch technology and the design of Fischer–Tropsch gas loop. The H_2:CO ratio can also be adjusted during syngas conditioning (Section 1.2.3).

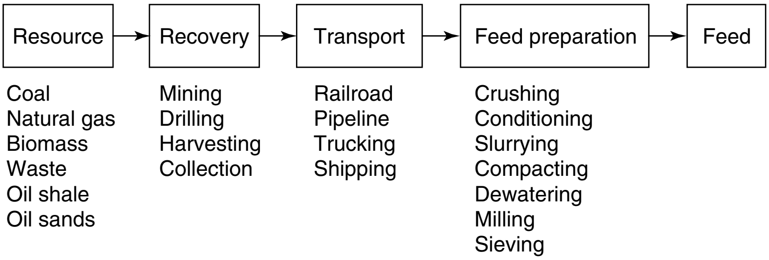

Figure 1.2 Feed logistics and preparation for indirect liquefaction.

Natural gas is already gaseous and it has no associated mineral matter to contend with. The two main conversion technologies for feed-to-syngas conversion are steam reforming and adiabatic oxidative reforming.

Steam reforming is the dominant process for hydrogen production in refineries, and it is able to convert hydrocarbon feed materials ranging from natural gas to heavy naphtha. A steam reformer is essentially a reactor that consists of a fired heater with catalyst-filled tubes placed in the radiant zone of the fired heater. The heat needed for reforming, which is an endothermic conversion, is externally supplied by burning a fuel in the fired heater. The feed consists of a mixture of hydrocarbons and steam (H_2O). The syngas thus produced has a high H_2:CO ratio; a $H_2:CO > 2$ is typical. When syngas is prepared for Fischer–Tropsch synthesis, steam can be partially substituted by carbon dioxide (CO_2) to lower the H_2:CO ratio in the syngas [13].

Adiabatic oxidative reforming produces a syngas with a lower H_2:CO ratio; a H_2:CO ratio in the range 1.6–1.9 is typical. The feed consists of a methane-rich hydrocarbon source, an oxidant (air or oxygen), and, in some instances, steam. The heat needed for reforming is directly supplied by combustion of part of the feed. This allows for a more compact design than a steam reformer. However, in the case of oxygen-fired reformers, it has the disadvantage of requiring an associated air separation unit (ASU), which is not required by a steam reformer.

Solid feed materials have to be gasified in order to produce syngas. Gasification processes can be classified in terms of gas outlet temperature or reactor properties. These two classifications go hand in hand (Table 1.1) [3].

Low-temperature gasification typically employs a moving bed and has a gas outlet temperature of 425–650 °C. The carbon-containing feed is fed from the top and the oxidizing gas is fed at the bottom. In this countercurrent flow arrangement, the hot ash at the bottom of the bed preheats the oxidizing gas before it enters the gasification zone. Gasification takes place in the middle of the bed. As the hot syngas produced in the gasification zone moves upward through the bed, it preheats and devolatilizes the carbon-containing feed at the top of the bed. Much of the heat recovery therefore takes place in the gasifier. Owing to the lower temperature in the top layer of the gasifier, pyrolysis liquids are coproduced during low-temperature gasification. This is an important distinguishing feature of low-temperature gasification that has implications for downstream refining. The refinery receives not only syncrude from the syngas-to-syncrude

Table 1.1 Classification of gasification technologies for feed-to-syngas conversion and their main attributes.

Attribute	Gasification technology		
	Low temperature	**Medium temperature**	**High temperature**
Temperature of syngas (°C)	425–650	900–1050	1250–1600
Reactor technology	Moving bed	Fluidized bed	Entrained flow
Particle size of feed (mm)	6–50	6–10	<0.1
Oxidant demand	Low	Moderate	High
Steam demand	High	Moderate	Low
Pyrolysis products in gas	Yes	Possibly	No
H_2:CO ratio in syngas	>2 : 1 to <1 : 1	<1 : 1	~1 : 2