

Part I

Introduction

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 (H₂), 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.

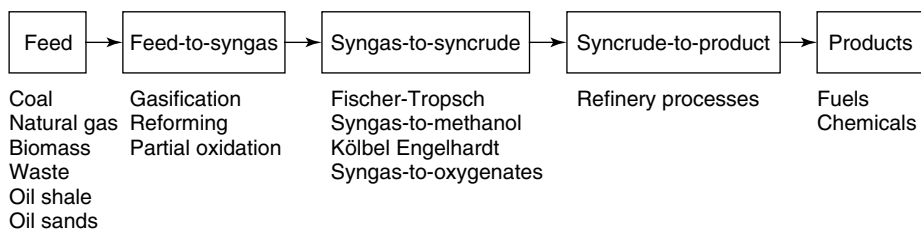


Figure 1.1 Overall indirect liquefaction process for feed-to-liquids (XTL) conversion.

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 asphaltenes 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 $\text{C}_x\text{H}_y\text{O}_z$ -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).

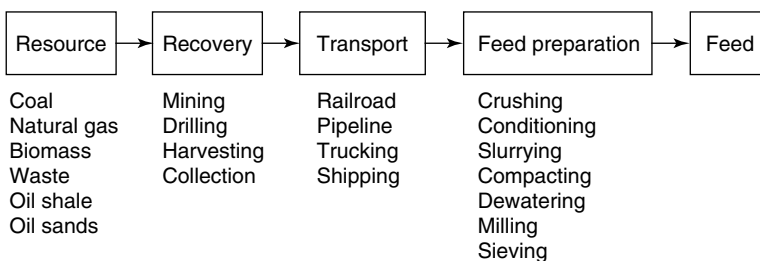


Figure 1.2 Feed logistics and preparation for indirect liquefaction.

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 $\text{H}_2:\text{CO}$ ratio; a $\text{H}_2:\text{CO} > 2$ is typical. When syngas is prepared for Fischer–Tropsch synthesis, steam can be partially substituted by carbon dioxide (CO_2) to lower the $\text{H}_2:\text{CO}$ ratio in the syngas [13].

Adiabatic oxidative reforming produces a syngas with a lower $\text{H}_2:\text{CO}$ ratio; a $\text{H}_2:\text{CO}$ 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
$\text{H}_2:\text{CO}$ ratio in syngas	>2 : 1 to <1 : 1	<1 : 1	~1 : 2

conversion step but also pyrolysis liquids from gasification. The nature of the pyrolysis liquids depends on the feed material, and biomass pyrolysis produces a different product than that produced by coal pyrolysis. The composition of the pyrolysis products also vary with gasifier type, gasifier operation, and the nature of the specific feed. For example, different coals yield different coal pyrolysis products [14]. The syngas composition is also dependent on the gasifier type and operation, with $H_2:CO$ ratios varying from more than 2 : 1 to less than 1 : 1.

Medium-temperature gasification is usually conducted in a fluidized bed and has a gas outlet temperature of 900–1050 °C (lower for biomass as feed). Although the carbon-containing feed is fed countercurrent to the oxidizing agent, as is the case with moving-bed gasifiers, the fluidized bed is well mixed. The temperature profile in the fluidized bed is fairly uniform and it approximates continuous stirred tank reactor behavior. Carbon conversion is therefore lower than that in other gasification types. Some pyrolysis products may be produced during gasification, but considerably less than that produced by using low-temperature gasification. The syngas composition is typically rich in CO and has a $H_2:CO$ ratio of less than 1 : 1.

High-temperature gasification is conducted in entrained flow processes with a gas outlet temperature of 1250–1600 °C. The flow of the carbon-containing feed and oxidizing gas is cocurrent. The principal advantage of this type of gasifier is that it produces a clean syngas that is free of pyrolysis products, thereby simplifying downstream gas cleanup and refining. The syngas is CO-rich and typically has a $H_2:CO$ ratio of around 1 : 2.

From the preceding discussion, it is important to reiterate that the feed-to-syngas conversion step has a direct impact on the associated refinery design. The coproduction of pyrolysis liquids in some gasification technologies increases the volume and complexity of the feed material that has to be refined. This is not necessarily detrimental, and the corefining of pyrolysis liquids may be synergetic.

1.2.3

Syngas Cleaning and Conditioning

Syngas cleaning is required to remove compounds that are Fischer–Tropsch catalyst poisons from the syngas. The most important and universal poison for Fischer–Tropsch catalysts is sulfur, but other species such as nitrogen-containing compounds, oxygen, chlorides, and bromides may also lead to catalyst deactivation. In addition to Fischer–Tropsch catalyst poisons, CO_2 may also be removed during syngas cleaning. The extent of CO_2 removal depends on the syngas cleaning technology employed. The degree of CO_2 removal that is required depends on the optimum gas loop design. Cleaning technologies that remove most sulfur compounds and CO_2 can be selected.

Depending on the feed material, the raw syngas also contains NH_3 . The NH_3 readily dissolves in the aqueous product obtained from cooling the raw syngas and can be removed almost quantitatively by water washing.

When low-temperature gasification technology is employed for syngas generation, the pyrolysis products that are coproduced during gasification need to be recovered during syngas cleaning. The pyrolysis products are mostly heavier organic compounds that can be separated as liquids on syngas cooling. These compounds naturally distribute between the less polar organic liquid phase and the more polar aqueous phase according to their polarity. (An analogous partitioning

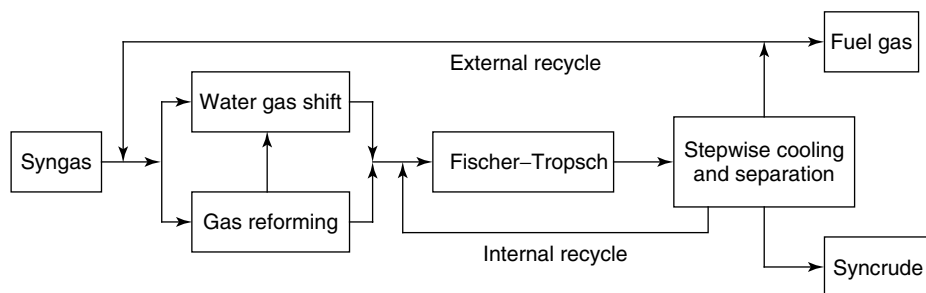


Figure 1.3 Syngas conditioning that may involve one or more of the steps shown: water gas shift conversion, gas reforming, and gas recycle after Fischer–Tropsch synthesis.

of compounds in Fischer–Tropsch syncrude takes place on cooling after synthesis.) The liquid products obtained by condensation likely contain particulate carbon matter from gasification. This has some implications for the further upgrading of these pyrolysis products in the refinery.

Although gas cleaning can be viewed as a feed pretreatment step before Fischer–Tropsch synthesis, gas conditioning also benefits from syngas cleaning.

Syngas conditioning is necessary to adjust the $H_2:CO$ ratio of the synthesis gas to meet the requirements of Fischer–Tropsch conversion. This is performed by a combination of one or more of the following: water gas shift (WGS) conversion, methane reforming, and gas recycle after Fischer–Tropsch synthesis (Figure 1.3).

1.3

Syngas-to-Syncrude Conversion

Once the feed-to-syngas conversion has been completed and the syngas has been cleaned and conditioned, by whatever combinations of technology, the syngas can be converted into syncrude. It was pointed out that Fischer–Tropsch synthesis is not the only syngas-to-syncrude conversion technology, but, in line with the title of the book, it is the only technology that is discussed.

There are basically three syncrude types that are produced commercially, which one can choose from, and it is convenient to classify Fischer–Tropsch synthesis accordingly. The three types of syntheses are iron-based high-temperature Fischer–Tropsch (Fe-HTFT), iron-based low-temperature Fischer–Tropsch (Fe-LTFT), and cobalt-based low-temperature Fischer–Tropsch (Co-LTFT). Syncrude compositions that are representative of each type are given in Table 1.2. Within each syncrude type, there is variation caused by reactor technology, operation, catalyst, and catalyst deactivation. In this respect, syncrude is analogous to crude oil, where the composition of a specific crude oil may vary not only between sources but also within a source between locations and with time [15].

Despite the limited industrial application of Fischer–Tropsch synthesis thus far, there have been a plethora of technologies that were industrially applied (Table 1.3). Many of these are still used commercially. The selection of a catalyst and reactor technology combination is consequently

Table 1.2 Syncrude compositions that are typical of iron-based high-temperature Fischer–Tropsch (Fe-HTFT), iron-based low-temperature Fischer–Tropsch (Fe-LTFT), and cobalt-based low-temperature Fischer–Tropsch (Co-LTFT) syntheses.

Product fraction	Carbon range	Compound class	Syncrude composition ^a (mass%)		
			Fe-HTFT	Fe-LTFT	Co-LTFT
Tail gas	C ₁	Alkane	12.7	4.3	5.6
		Alkene	5.6	1.0	0.1
		Alkane	4.5	1.0	1.0
LPG	C ₃ –C ₄	Alkene	21.2	6.0	3.4
		Alkane	3.0	1.8	1.8
Naphtha	C ₅ –C ₁₀	Alkene	25.8	7.7	7.8
		Alkane	4.3	3.3	12.0
		Aromatic	1.7	0	0
		Oxygenate	1.6	1.3	0.2
Distillate	C ₁₁ –C ₂₂	Alkene	4.8	5.7	1.1
		Alkane	0.9	13.5	20.8
		Aromatic	0.8	0	0
		Oxygenate	0.5	0.3	0
Residue/wax	C ₂₂ +	Alkene	1.6	0.7	0
		Alkane	0.4	49.2	44.6
		Aromatic	0.7	0	0
		Oxygenate	0.2	0	0
Aqueous product	C ₁ –C ₅	Alcohol	4.5	3.9	1.4
		Carbonyl	3.9	0	0
		Carboxylic acid	1.3	0.3	0.2

^aThe syncrude composition is expressed as the total mass of product from Fischer–Tropsch synthesis, excluding inert gases (N₂ and Ar) and water gas shift products (H₂O, CO, CO₂, and H₂). Zero indicates low concentration and not necessarily a total absence of such compounds.

not straightforward. Ultimately, the aim is to produce a specific product slate. One can select the feed-to-syngas and syngas-to-syncrude technologies to yield a syncrude that provides the most efficient feed material to refine to the desired product slate. The analogy with crude oil still holds, since the crude oil basket that is selected for a crude oil refinery, both before design and during operation, also aims to achieve the most efficient conversion of crude oil to the desired product slate [16]. Even so, Fischer–Tropsch synthesis is more versatile, since it is in principle possible to design the Fischer–Tropsch technology (reactor, catalyst, and operation) with a specific refining objective in mind. Unfortunately, in the author’s experience, Fischer–Tropsch technology is developed independent of the ultimate refining objective.

The different technologies for Fischer–Tropsch synthesis are discussed in detail in Chapter 4.

Table 1.3 Fischer–Tropsch technologies that have been applied industrially. The reactor technology, year of first commercial use, and name of the process are given.

Fe-HTFT	Fe-LTFT	Co-LTFT
Fixed fluidized bed (1951, Hydrocol)	Fixed bed (1955, Arbeitsgemeinschaft Ruhrchemie-Lurgi)	Fixed bed (1936, German normal-pressure)
Circulating fluidized bed (1955, Kellogg Synthol)	Slurry bed (1993, Sasol slurry bed process)	Fixed bed (1937, German medium-pressure)
Circulating fluidized bed (1980, Sasol Synthol)	–	Fixed bed (1993, Shell middle distillate synthesis)
Fixed fluidized bed (1995, Sasol Advanced Synthol)	–	Slurry bed (2007, Sasol slurry bed process)

1.4

Syncrude-to-Product Conversion

The product from feed-to-syngas and syngas-to-syncrude conversions is a synthetic crude oil (Table 1.2) that is comparable but different to conventional crude oil. One may therefore argue that it is not necessary to associate syncrude-to-product conversion with a Fischer–Tropsch based XTL process. However, syncrude has some drawbacks compared to crude oil when it is considered as the final product. Crude oil production has to contend with associated gas production, but Fischer–Tropsch syncrude production has to contend with even more product phases. In the case of HTFT syncrude, the syncrude is composed of three different product phases, namely, gaseous, organic liquid, and aqueous. In the case of LTFT syncrudes, there is a fourth phase, namely, organic solids. In fact, less than half of the syncrude from any of the Fischer–Tropsch technologies practised today are available as a liquid organic product. It is only by an upgrading step or proper syncrude refining that more of the syncrude can be transformed into useful products. A Fischer–Tropsch based process without syncrude-to-product conversion is clearly a very inefficient XTL process. The syncrude-to-product conversion step is where the value addition takes place.

1.4.1

Upgrading versus Refining

The difference between upgrading and refining is that upgrading produces intermediate products that must still be refined to produce final products and refining produces final products.

The Fischer–Tropsch industry seemingly has come full circle, starting with Co-LTFT and upgrading, moving to Fe-HTFT and Fe-LTFT with refining, and returning to Co-LTFT with upgrading [17, 18]. Yet, this oversimplifies the situation. The German Co-LTFT syncrude was sufficiently upgraded so that it could be blended with coal liquids and crude-oil-derived fuels for use as final products without further refining. The other product fractions were refined to

chemicals. The same is true for the products from the Co-LTFT-based Shell Middle Distillate Synthesis (SMDS) process, where the distillate is blended with crude-oil-derived diesel fuel as a final product, while the rest of the products are refined to *n*-alkane (paraffin) solvents, waxes, and lubricating oils.

All industrial Fischer–Tropsch facilities have at least partial refining for the syncrude-to-product conversion step. It is consequently more appropriate to identify three levels of syncrude-to-product conversion:

- 1) **Upgrading.** In upgrading, all of the products are destined for further refining (not just blending) before becoming final products. The product from an upgrader is a higher quality crude oil and it is marketed as such.
- 2) **Partial refining.** When partial refining takes place, at least some of the products are refined to final products, or are destined for blending (not refining) to produce final products.
- 3) **Stand-alone refining.** All the products from stand-alone refineries are final products, irrespective of whether they are on-specification transportation fuels, commodity chemicals, or speciality products.

In patent literature, there are suggestions on how to upgrade Fischer–Tropsch syncrude into a transportable liquid product [8]. However, philosophically one has to question the use of Fischer–Tropsch synthesis in conjunction with only an upgrader for such a purpose. If the main purpose of an XTL conversion facility is to employ indirect liquefaction to produce a transportable liquid that can be refined elsewhere, syngas-to-methanol synthesis is far more appropriate than Fischer–Tropsch synthesis [1].

1.4.2

Fuels versus Chemicals

The nature of Fischer–Tropsch syncrudes is such that it lends itself to the recovery and refining of some chemicals. The abundance of alkenes (olefins), oxygenates, and *n*-alkanes presents the refinery designer with a smorgasbord of options for both extractive and synthetic approaches to the refining of chemicals [19–25]. The production of chemicals from syncrude will be covered in Chapter 28.

The chemicals that can be produced in an XTL facility are not only limited to those from Fischer–Tropsch synthesis. The feed-to-syngas conversion step, among others, creates opportunities for chemical coproduction too:

- 1) **Chemicals from gasification liquids.** Low-temperature gasification yields pyrolysis products that can contain valuable chemicals typical of the feed source. For example, phenol, benzene, and naphthalene from coal, or methanol from wood.
- 2) **Permanent gases.** ASUs associated with oxygen-blown gasification and gas reforming processes produce nitrogen (N_2) as by-product. In addition, some noble gases, such as argon (Ar), neon (Ne), krypton (Kr), and xenon (Xe), may be separated.
- 3) **Sulfur- and nitrogen-based chemicals.** Hydrogen sulfide (H_2S) and ammonia (NH_3) are recovered during syngas cleaning. Sulfur- and nitrogen-based compounds may also be recovered from gasification liquids.

- 4) **Carbon dioxide (CO₂)**. Depending on the future legislative framework around carbon emissions, the separation and recovery of CO₂ during syngas cleaning and conditioning may be a benefit [26]. Pure CO₂ also has value as a chemical.

Chemicals generally command a higher price than fuels, and from an economic point of view it makes sense to produce as much chemicals as possible. Yet, at this point it is important to add some words of caution. Some of the high-value chemicals that are commercially produced from Fischer–Tropsch syncrude have rather small markets. In the case of linear α -olefins (1-hexene and 1-octene) and some oxygenates (1-propanol), 20–30% of global demand is being satisfied from a single Fe-HTFT facility [22]. The scope for recovery of such chemicals in future facilities is therefore rather limited. Furthermore, the sale of commodity chemicals such as ethene and propene depends on the market associated with downstream petrochemical facilities. Although both gases have large global markets, the market may not be accessible when the Fischer–Tropsch facility has been sited to employ a cheap but remote carbon source as feed.

Historically, investment in Fischer–Tropsch facilities was mainly motivated by energy security and not by economic considerations. As a result, most Fischer–Tropsch facilities were primarily designed to produce transportation fuels. With time, the original motivation and need may dissipate and based purely on economic considerations there may be significant impetus to convert from fuels into chemicals production. A case in point is the Sasol 1 facility in South Africa. It was strategically motivated to produce transportation fuels for the local market, but it was later converted into a petrochemical production facility for economic reasons.

A flexible refinery design that includes the production of both fuels and chemicals has some advantages over a refinery that produces only fuels or only chemicals [27, 28]. This will also become apparent in subsequent chapters, where the conversion of syncrude into fuels and chemicals will be considered.

Fundamentally, on a molecular level, fuel and chemical coproduction makes sense. Some molecules can easily be converted into either chemicals or fuels, but some other molecules have efficient refining pathways to only one of the two products. Forcing the conversion of a molecule into a product that requires a less efficient refining pathway, is inherently wasteful and violates a number of green chemistry principles (prevent waste, maximize atom economy, and increase energy efficiency).

This principle has also been applied to recommend refining technologies for the efficient conversion of Fischer–Tropsch syncrude [29]. The nature of the conversion processes that lead to efficient refining of syncrude is such that the coproduction of fuels and chemicals occurs naturally, often yielding molecules that can be employed either as fuels or as chemicals.

1.4.3

Crude Oil Compared to Syncrude

Some analogies (as well as some differences) between Fischer–Tropsch syncrudes and conventional crude oils have been pointed out. Viewing syncrude as just another crude oil type would simplify the discussion on syncrude-to-product conversion, which then becomes a discussion of crude oil refining. In fact, technologies such as hydrocracking, hydrotreating, and oligomerization that are found in Fischer–Tropsch refineries, are also found in crude oil refineries. Since syncrude and crude oil are both refined to the same products and are subject to the same

Table 1.4 Comparison between the product compositions obtained from Fischer–Tropsch synthesis and those found in a typical conventional crude oil.

Compound class	HTFT	LTFT	Crude oil ^a
Alkanes (paraffins)	>10%	Major product	Major product
Cyclo-alkanes (naphthenes)	<1%	<1%	Major product
Alkenes (olefins)	Major product	>10%	None
Aromatics	5–10%	<1%	Major product
Oxygenates	5–15%	5–15%	<1% O (heavy)
Sulfur compounds	None	None	0.1–5% S
Nitrogen compounds	None	None	<1% N
Organometallics	Carboxylates	Carboxylates	Phorphyrines
Water	Major by-product	Major by-product	0–2%

^aThere is considerable variation between different crude oil types and some crude oils may fall outside the boundaries indicated.

performance criteria, the analogy seems to hold. However, at the detail level the analogy quickly breaks down and some fundamental differences between syncrudes and crude oils can be pointed out (Table 1.4) [30].

From a refining perspective, the following attributes of Fischer–Tropsch syncrude, which are different to that of crude oil, have a significant impact on refinery technology selection and refining approach:

- 1) Multiple product phases
- 2) High oxygenate content
- 3) High alkene content and especially 1-alkene content
- 4) High concentration of linear products (little cyclic compounds)
- 5) Absence of sulfur and nitrogen compounds
- 6) Metal carboxylates.

Conventional crude oil refining technologies can be used with Fischer–Tropsch syncrude, but this often requires feed pretreatment to eliminate compound classes that are not compatible with the technology, or modifications to the technology to deal with Fischer–Tropsch syncrude peculiarities. Direct application of crude oil refining technologies to Fischer–Tropsch derived streams, that is, without pretreatment or modification, generally leads to poor or inefficient operation, and in some cases it leads to complete failure of the technology.

There is a subset of conversion processes that perform well with syncrude [29]. Likewise, there is a subset of catalysts that perform well with syncrude [8, 31]. Not all of these catalysts and conversion processes are commonly found in crude oil refineries. It therefore stands to reason that the design of efficient Fischer–Tropsch refineries will differ from that of efficient crude oil refineries [30, 32]. Taken together, these differences form the justification for this book on Fischer–Tropsch refining.

1.5

Indirect Liquefaction Economics

The economics of indirect liquefaction is strongly affected by three aspects, namely, the cost of the carbon-containing feed material, product pricing, and the capital cost of the indirect liquefaction facility. There is a complex interrelationship between these factors, and what is pertinent to the present discussion is the role of the refinery in the overall economics.

1.5.1

Feed Cost

Superficially, the feed cost is just a significant cost component of the operating cost of a Fischer–Tropsch facility. As such, it influences the economics. To reduce the feed cost, one can make use of a cheap feed source, but feed price is not something that can intrinsically be controlled. What can be controlled is the design of the facility, and through the design the efficiency of feed conversion can be controlled.

Efficiency is a catch-all term that in itself is too broad to provide clear engineering guidance. Control can be exerted over the feed cost through feed selection based on conversion efficiency (not just its price), the carbon efficiency of the design, and the energy efficiency of the design.

- 1) **Feed selection based on the nature of the feed.** Not all carbon sources have been created equally and the feed cost expressed in terms of money per unit energy, or money per unit mass, is insufficient to describe the impact of the feed cost on the economics. It is easier to convert less complex and hydrogen-rich feed materials, such as natural gas, than complex materials, such as coal or biomass, by indirect liquefaction. The feed-to-syngas conversion is easier, there are less by-products, and there is less waste (heteroatoms and mineral matter) associated with the feed material.
- 2) **Carbon efficiency.** The carbon efficiency specifically relates to the percentage of carbon in the feed that is incorporated into the product. By definition, the remaining carbon is lost during the conversion in various ways, ranging from energy production to refining losses. Thus far not much attention has been paid to carbon efficiency, yet carbon efficiency is a measure of the success in performing the transformation from one type of carbon-based energy carrier to another. Ultimately, the aim of indirect liquefaction is not the conversion of a carbon-based feed into energy, but into useful products. The carbon efficiency for a Fischer–Tropsch based CTL facility is around 28–34% (Table 1.5) [9–11, 33, 34]. The values are in agreement with the author's experience in dealing with industrial HTFT-based CTL facilities [35].
- 3) **Thermal efficiency (energy efficiency).** The thermal efficiency is the percentage of the energy in the feed that is converted into energy output as power (electricity) and as products. It generally has a higher value than the carbon efficiency, since some of the energy needed in feed-to-syngas conversion, as well as energy produced during syngas-to-syn crude conversion, can be recovered as steam and converted into power. It has been reported that Fischer–Tropsch based GTL facilities have thermal efficiencies of around 60%, whereas those of CTL facilities are around 50% [33]. This illustrates the impact that the nature of the feed has on the efficiency of the process. However, it is also very much dependent on the

Table 1.5 Carbon efficiencies reported for Fischer–Tropsch based coal-to-liquids facilities, with a coal feed rate around 20 000 tons per day on a dry, ash-free basis.

Carbon efficiency (%)	Technology description			References
	Gasification	Fischer–Tropsch	Refinery	
32 ^a	– ^b	HTFT	Excluded	[9]
33 ^c	Lurgi dry-bottom	HTFT	Included	[10]
28 ^c	– ^b	HTFT	– ^b	[11]
32	Texaco entrained flow	HTFT	Excluded	[33]
34	Texaco entrained flow	LTFT	Excluded	[33]
34	General Electric entrained flow	LTFT	Included	[34]

^aLiquid products' efficiency is based on energy value.

^bData not listed in source reference.

^cLiquid products and pipeline gas counted toward carbon efficiency.

design. For example, thermal efficiencies of 70 and 58%, respectively, have been reported for HTFT based CTL facilities that coproduce substitute natural gas as the major product [9, 10].

The nature of the feed, the carbon efficiency, and the thermal efficiency all have some bearing on each other, but the relationship with each other and the way in which each affects the impact of feed cost on the economics are intricate. Nevertheless, carbon efficiency and thermal efficiency emerge as two critical measures that determine how sensitive the economics will be to feed cost. These two measures affect the economics differently, since it relates feed cost to product pricing in different ways. The product pricing for energy (electricity), fuels, and chemicals is different and not necessarily based purely on either carbon or energy content. Simply put, the value of feed-to-electricity conversion is different to the value of feed-to-products conversion.

The feed cost has to be substantially lower than the price of the products to offset the loss associated with the feed-to-product conversion.

1.5.2

Product Pricing

The product pricing determines the income generated by the Fischer–Tropsch facility. Even if all other variables are held constant, any change in the relative amounts of the products being produced will change the income. This economic reality is well established in crude oil refining, where the refinery design is optimized to produce the highest value product slate that is possible from the crude oil feed selected. The design reflects the anticipated product pricing, but flexibility is built into the design to allow for an imperfect prediction of the future. The flexibility in the refinery design is exploited during refinery operation to respond to changes in product pricing and to keep on optimizing the product slate for maximum income.

The choice of feed-to-syngas conversion technology and Fischer–Tropsch technology for syngas-to-syncrude conversion influences the products that can be produced, but it does not determine the product slate. The output from Fischer–Tropsch synthesis is syncrude, and as with

crude oil refining, the product slate is determined by the refinery design and refinery operation. The Fischer–Tropsch refinery ultimately determines the extent of value addition.

Product pricing is never constant. More importantly, relative product pricing also changes over time. These changes cannot be controlled and are determined by global and local factors. What can be controlled is the design of the facility and through the design the flexibility to respond to changes in product pricing.

- 1) **Feed-to-electricity conversion.** The emphasis that is placed on thermal efficiency, as opposed to carbon efficiency, during XTL design determines the amount of power (electricity) produced relative to the amounts of fuels and chemicals. There is little flexibility that can be built into the design to manipulate this ratio, short of modifying the actual design. The product pricing of electricity is determined by local conditions. Exporting power is usually regulated, regional, and dependent on the local infrastructure for electricity supply and distribution. The decision to export electricity as one of the main products from an XTL facility should not be taken lightly. Electricity is not traded on the global market and it locks the XTL facility into a regional supply agreement and regional product pricing. It is also more likely that the price of electricity is related to the feed cost for the XTL facility. The economics of the feed-to-electricity conversion is therefore linked to the cost effectiveness of XTL versus conventional power generation. The danger of viewing XTL as a power producer should therefore be apparent. Why employ syngas as an intermediate if you want to generate steam to drive a turbine? Philosophically speaking, the main aim of XTL is not power generation, although power generation may be a valuable (inevitable) by-product.
- 2) **Feed-to-products conversion.** A Fischer–Tropsch refinery can be designed to offer product flexibility. The choice between fuels and chemicals has already been discussed (Section 1.4.2). From an economic perspective, this decision is also dependent on the location of the XTL facility, although less so than with electricity generation. The product price must be discounted by the logistic cost of transporting the product to the market. The logistic cost is small if the products are supplied in the local market. Fuels often have the advantage that there is local demand, whereas chemicals may not have this advantage. The product price difference between chemicals and fuels can quickly be eroded if the XTL facility is located far from chemical markets. Furthermore, some chemicals are difficult to transport, and it may be impractical to sell such products as chemicals to a remote market.
- 3) **Crude oil price.** The notion of upgrading syncrude to be sold as a synthetic crude oil has been discussed (Section 1.4.1). In such a case, the product price is directly linked to the crude oil price. The product prices of fuels and chemicals are also influenced by the crude oil price, since it is the main feed cost component in most current petrochemical facilities.

The pricing of energy as a product reveals that price is primarily determined by the nature of the energy carrier or product and not by its energy content. In fact, if this had not been the case, XTL would make no sense at all. It is also important to note that some products have a negative price associated with a disposal cost or tax. In this respect, the product price (value or cost) of CO₂ and water, which are two of the main products from Fischer–Tropsch based XTL, may become an important factor in determining XTL economics.

The difference between produce price and feed cost defines the value addition of XTL and correlates well with the production income and economic viability of XTL facilities.

1.5.3

Capital Cost

There is a large capital cost associated with indirect coal liquefaction based on Fischer–Tropsch synthesis (Table 1.6) [9, 11, 36, 37]. Such processes can be economical if the difference between the product price and feed cost is large enough, although the size of investment required is a serious obstacle to widespread commercial interest. Considering the complexity of a Fischer–Tropsch based CTL facility, the differences in the capital estimates are reasonable.

The breakeven crude oil price for a 50 000 bbl/day crude-oil-equivalent Fischer–Tropsch based CTL facility in 2007 was reportedly around US\$50–70 [34]. These values are in agreement with author’s experience.

The capital cost associated with GTL facilities is less, since the conversion of natural gas into synthesis gas is less complex. From Table 1.6, it is clear that coal preparation and gasification contribute 30% or more of the capital cost, even before taking the cost of utilities, gas cleaning, and air separation into account, which brings the total for syngas preparation to more than 70% of the capital cost for CTL.

Capital cost data for Fischer–Tropsch based GTL are listed in Table 1.7 [38, 39]. There is a significant difference in the estimates, with one being double the other. On the basis of the CTL estimates, one is inclined to accept the higher cost estimate as the more realistic of the two.

Cost data on recent and current GTL construction projects do not clarify the picture. In fact, they highlight an extreme sensitivity to the economic climate and location [40]. The Oryx GTL facility has been completed at a cost close to the lower estimate in Table 1.7. However, the Oryx GTL design employed a new and unproven Fischer–Tropsch technology, which had technical

Table 1.6 Capital cost of Fischer–Tropsch based coal-to-liquids facilities producing 50 000 bbl/day crude oil equivalent liquid products.

Description	Fischer–Tropsch CTL capital cost			
	[9]	[11]	[36]	[37]
Capital cost (US\$/bbl daily capacity, 2010)	81 000	78 000 ^a	97 000	85 000
Capital cost distribution (%)				
Coal preparation and gasification	30	42	30	37
Syngas cleaning and conditioning	11	15	17	20 ^b
Air separation	21	17	17	10
Heat recovery and utilities	15	– ^c	18	16
Fischer–Tropsch, gas recovery, refining	23	26	18 ^d	17

^aProduction of large volumes of liquid petroleum gas and substitute natural gas, which were not counted toward liquid products for calculation.

^bCost of water gas shift reactor included with cost of Fischer–Tropsch synthesis.

^cNot separately listed.

^dRefinery contributed to only 5% of the overall capital cost; the refinery included a hydrocracker, naphtha hydrotreater, distillate hydrotreater, naphtha hydroisomerization unit, and catalytic naphtha reformer.

Table 1.7 Capital cost of Fischer–Tropsch based gas-to-liquids facilities.

Description	Fischer–Tropsch GTL capital cost	
	[36]	[37]
Capital cost (US\$/bbl daily capacity, 2010)	62 000	33 000
Liquid product production capacity (bbl/day)	43 000	34 000
Capital cost distribution (%)		
Syngas generation, including air separation	47	30
Fischer–Tropsch synthesis	15	15
Upgrading and refining	9 ^a	10 ^b
Off-sites, utilities, and other units	29	45

^aRefinery consists of wax hydrocracker, distillate hydrotreater, naphtha hydrotreater, naphtha hydroisomerization, catalytic naphtha reformer, butane hydroisomerization, and aliphatic alkylation unit.

^bRefinery consists of only a wax hydrocracker.

problems during start-up. This prevented the facility from reaching full production capacity and additional capital was required to address the technical problems. The actual capital cost was consequently higher due to the increase in capital spending and reduction in production capacity. The committed capital in Shell’s Pearl GTL project in the same location over time increased to US\$10 billion in 2007 (about US\$70 000 per daily barrel) and further increases were expected [41]. The capital cost of the Escravos GTL facility, using the same technology as Oryx GTL, was reported to have increased to US\$6 billion (about US\$180 000 per daily barrel) [42]. At the close of 2009, it was announced that the wax production capacity at the Sasol 1 site would be doubled at a cost of US\$1.1 billion (about US\$200 000 per daily barrel) [43].

The global economy displayed some extreme behavior during the 2005–2010 period, which is partly responsible for the variance in cost estimates. The only consistent indicator is that the capital cost of Fischer–Tropsch based indirect liquefaction facilities is high. It should be added that this is for facilities based on current commercial technology. There are interesting developments in the field of smaller scale Fischer–Tropsch based designs for BTL. Out of necessity such designs have to make trade-offs to reduce complexity and size. By doing so, some opportunities in process integration and intensification are exploited, which are not seen in larger scale designs. The adage “economy-of-scale” may therefore not hold true.

The cost associated with indirect liquefaction should be evaluated in context. Other competing technologies for the production of synthetic fuels are also capital intensive (Table 1.8) [44]. These values are without the cost of refining.

The capital cost associated with the refining of the Fischer–Tropsch syncrude is small (around 10%) compared to the total capital cost of the indirect liquefaction facility. This has some important implications for refinery design:

- 1) **Maximize carbon efficiency in the refinery.** Any carbon contained in the Fischer–Tropsch syncrude has already required 90% of the total capital cost to produce. Designing a refinery that leaves syncrude unrefined in order to save on the refinery capital cost makes little sense.

Table 1.8 Capital cost estimates of competing technologies for synthetic fuel production.

Synthetic fuel technology	Capacity (bbl/day equivalent)	Capital cost (US\$/bbl daily capacity, 2010)
Direct coal liquefaction	50 000	84 000
Oil shale recovery	50 000	78 000
Oil sands recovery	50 000	66 000
Coal gasification for SNG ^a		
Advanced gasifier design	10 250 ^b	230 000
Underground gasification		
Horizontal coal seams	10 250 ^b	58 000
Steeply dipping coal seams	10 250 ^b	44 000

^aSNG, substitute natural gas.

^bMedium BTU gas, about 60 GJ equivalent.

- 2) **Indirect liquefaction facilities are inherently complex.** Although complex refinery design is not advocated, the complexity of the refinery design has little impact on the overall complexity of the project.
- 3) **Produce final products.** There is a trap in performing incremental economics on a Fischer–Tropsch refinery, since it ignores the significant capital and operating costs associated with the production of the syncrude. For example, if you cannot justify spending 10% more to refine naphtha to a motor-gasoline, how did you justify spending nine times as much on making the naphtha in the first place?

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