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Catalysis in the Refining of Fischer–Tropsch Syncrude



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Preface

Fischer–Tropsch synthesis (FTS) has been used on a commercial scale for more than 80 years. Three countries stand out in the history of FTS, namely Germany, the United States of America and South Africa. FTS was developed and commercialised in Germany for strategic reasons. It provided a source of transportation fuels that was independent from crude oil. The strategic advantage of such technology was realised in the USA, but commercial production was short lived. Crude oil was too readily available and too cheap. Nevertheless, initial developments in the field of high-temperature FTS took place in the USA. For much the same reason as Germany, South Africa invested in FTS. It provided a secure source of transportation fuels when its political dispensation resulted in an economic embargo limiting its access to crude oil. Initially the technology for FTS employed in South Africa was of German and US origin, but over the course of more than half a century, considerable experience was gained in the operation of Fischer–Tropsch-based facilities. This ultimately led to improvements in FTS and the development of some new technologies for FTS.

Today, interest in FTS is more global. Many of the oil majors invested in Fischer–Tropsch research. Some of these programmes resulted in demonstration- and even commercial-scale facilities. However, FTS is by no means a mainstream technology yet. Several technologies have been commercialised, which can be broadly classified as 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) synthesis.

The product distribution obtained during LTFT synthesis differs markedly from that obtained from HTFT synthesis. The synthetic crude from LTFT is dominated by *n*-alkanes with a wide carbon number distribution and a sizeable fraction of waxes. The lighter product fraction also contains some alkenes and oxygenates. The synthetic crude from HTFT has a narrower carbon number distribution and is rich in alkenes, the remainder being alkanes, aromatics and oxygenates. Neither of the synthetic crudes contains sulfur- or nitrogen-containing compounds. The composition of Fischer–Tropsch synthetic crude

(syncrude) is consequently different from that of conventional crude oil in a number of respects.

Since the primary hydrocarbons from FT processes contain little sulfur and nitrogen, but are rich in acyclic hydrocarbons, they may be suitable blending components with petroleum-derived fuels. In this way, the overall costs of refining conventional crude oil fractions may be decreased. The integration of FTS with conventional crude oil refining may be an attractive option for improving the efficiency of fuels production from both. FTS also holds promise as an enabling technology for biomass upgrading. Small-scale biomass-to-liquids facilities may overcome the logistic problems associated with the transportation of low energy density biomass. These and other economic and environmental drivers may stimulate interest in FTS and this book is partly justified by our belief that there is indeed a growing interest in FTS.

The main justification for this work is the lack of a general overview of the catalysis that will be needed to convert Fischer–Tropsch syncrude into useful products. Much of the research in the field of Fischer–Tropsch technology has been devoted to FTS. However, the real value addition is not in converting alternative carbon sources into a syncrude, but in delivering final products to the market. Converting syncrude into final products requires catalysts that can convert oxygenates, exploit the reactivity of alkenes and benefit from the low coking propensity of *n*-alkanes. Clearly, the catalysis of Fischer–Tropsch syncrude refining is not the same as that of crude oil refining. Although Fischer–Tropsch syncrude can also be employed for the production of various chemicals, the primary focus of this book is on the catalysis needed for the upgrading of syncrude to transportation fuels.

Alkenes dominate the lighter fractions of Fischer–Tropsch syncrude. The conversion of light alkenes to liquid fuels via oligomerisation is an important part of FT refining. Isomerisation, hydroisomerisation and hydrocracking are equally important reactions for converting *n*-alkanes and *n*-alkenes into fuels and lubricants. Hydrotreating is likewise necessary to ensure that final product specifications are met. The catalysis of these conversion processes will therefore be covered in detail. In this respect, specific attention is given to the conversion of oxygenates and waxes. Other types of catalysis relevant to the refining of Fischer–Tropsch syncrude are also covered, but in less detail. Thus, only a cursory account is provided of FTS and Fischer–Tropsch technology in general, with focus on the aspects that determine the composition of primary products relevant to refining catalysis. Theoretical, engineering and commercial aspects related to FTS have been extensively covered in other books and authoritative reviews and will not be duplicated.

A review of the catalysis in the refining of Fischer–Tropsch syncrude is the main objective of this book. This is the first time that such an extensive study dealing with the upgrading of Fischer–Tropsch syncrude to commercial fuels, lubricants and other products has been undertaken. We hope that this book is a useful, if not overdue, addition to the literature on Fischer–Tropsch technology.

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Abbreviations and Symbols

ASA	Amorphous silica–alumina
ASF	Anderson–Schulz–Flory
ASTM	American Society for Testing and Materials
CFPP	Cold filter plugging point
CN	Cetane number
DO	Decanted oil
EPA	Environmental Protection Agency
FBP	Final boiling point
FCC	Fluid catalytic cracking
FT	Fischer–Tropsch
FTS	Fischer–Tropsch synthesis
GTL	Gas-to-liquids
HDAr	Hydrodearomatisation
HCR	Hydrocracking
HDM	Hydrodemetallisation
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurisation
HFRR	High frequency reciprocating rig (ASTM D6079 test method)
HIS	Hydroisomerisation
HTFT	High-temperature Fischer–Tropsch
HVGO	Heavy vacuum gas oil
HYD	Hydrogenation
IBP	Initial boiling point
IFP	Institut Français du Pétrole
IS	Isomerisation
LHSV	Liquid hourly space velocity
LPA	Liquid phosphoric acid
LSR	Light straight run
LTFT	Low-temperature Fischer–Tropsch
LVGO	Light vacuum gas oil
MAPO	Magnesium aluminophosphate
MEK	Methyl ethyl ketone (2-butanone)
MOGD	Mobil olefins to gasoline and distillates
MON	Motor octane number

MOR	Mordenite
MSA	Mesoporous silica–alumina
MTBE	Methyl <i>tert</i> -butyl ether (2-methoxy-2-methylpropane)
OLI	Oligomerisation
<i>P</i>	Pressure
PAO	Polyalphaolefin
PCP	Protonated cyclopropane
PM	Particulate matter
RFCC	Residue fluid catalytic cracking
RON	Research octane number
SAPO	Silico-aluminophosphate
SLO	Stabilised light oil
SPA	Solid phosphoric acid
SZ	Sulfated zirconia
<i>T</i>	Temperature
TAME	<i>tert</i> -Amyl methyl ether (2-methoxy-2-methylbutane)
TPA	Tungstophosphoric acid
TZ	Tungstated zirconia
ULO	Unstabilised light oil
UOP	Universal Oil Products
VGO	Vacuum gas oil
WGS	Water gas shift
WHSV	Weight hourly space velocity

CHAPTER 1

Introduction

1.1 Overview of Fischer–Tropsch-based Facilities

It has been more than 80 years since the Fischer–Tropsch synthesis (FTS) was first described in the literature.¹ Advances in the development of this technology have been documented in numerous books and review papers dealing with FTS.^{2–20}

During FTS, synthesis gas (H_2 and CO) is converted into a mixture of hydrocarbons, oxygenates, water and carbon dioxide. The hydrocarbon and oxygenate fraction is commonly referred to as a synthetic crude oil or syncrude for short. This syncrude, just like conventional crude oil, has to be refined in order to produce useful products, such as transportation fuels and chemicals. A simplified flow diagram of an FTS facility is shown in Figure 1.1.

In principle any carbon-containing raw material may be employed as feed for synthesis gas production. The nature of the raw material will determine the nature of the feed-to-syngas conversion technology and appropriate feed preparation. When solid feed, such as coal or biomass, is used as raw material, the synthesis gas is produced by gasification. There are various gasification technologies to choose from,^{21,22} and the choice depends on the nature of the feed and also the Fischer–Tropsch technology that has been selected. During gasification, some liquid pyrolysis products may be produced that can be refined with the syncrude, as indicated by the dashed line in Figure 1.1. When natural gas is used as raw material, synthesis gas is typically produced by gas reforming. Impurities in the raw synthesis gas are removed before FTS and synthesis gas conditioning may include processes such as water gas shift (WGS) conversion and CO_2 removal. After FTS, the product is cooled stepwise and separated into different syncrude fractions. Some of the light gases may be recycled and the synthesis gas conditioning steps (gas cleaning and H_2 : CO ratio adjustment), FTS and product cooling are together called the gas loop. The syncrude from FTS forms the feed to the Fischer–Tropsch refinery, where the syncrude is upgraded to intermediate or final products.

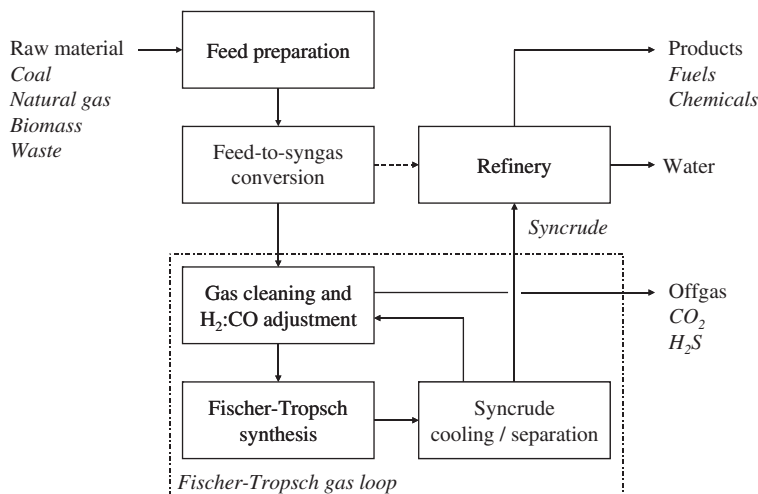


Figure 1.1 Simplified flow diagram of a Fischer–Tropsch-based facility.

The composition and carbon number distribution of syncrude depend on the type of FTS employed (Table 1.1).²³ The gas-phase products from FTS consist only of hydrocarbons, with very little oxygenates. The oil phase contains hydrocarbons and oxygenates. In the oil, the hydrocarbons are dominated by *n*-alkanes and *n*-alkenes. The combined aromatics, cycloalkane and cycloalkene content in the oil varies from 0 to 15%, depending on the type of process. The oxygenate content varies over the same range and the main oxygenate classes are alcohols, carbonyls and carboxylic acids. The concentration of a compound class in a specific fraction may, of course, fall outside the indicated ranges. Low-temperature Fischer–Tropsch (LTFT) synthesis also produces a wax fraction that is rich in *n*-alkanes, and is a solid under ambient conditions. The aqueous fraction obtained from FTS contains mainly short carbon chain oxygenates and very little hydrocarbons. Usually, the primary products from FTS contain practically no sulfur- and nitrogen-containing compounds. Gas cleaning ensures that the synthesis gas contains very little sulfur (parts per billion) and nitrogen; the Fischer–Tropsch catalyst itself is also an excellent sulfur trap. The heteroatom content of Fischer–Tropsch syncrude is consequently limited to oxygen.

1.2 Refining of Fischer–Tropsch Syncrude

Historically, FTS has been used mostly for the production of transportation fuels. Despite some of the positive attributes of syncrude, such as being sulfur free, the primary liquids from FTS cannot be used directly as transportation fuels. Various quality issues must be addressed. For example, syncrude has poor cold flow properties and relatively low thermal and storage stability. Also,

Table 1.1 Syncrude compositions representative of cobalt-based low-temperature Fischer-Tropsch (Co-LTFT), iron-based low-temperature Fischer-Tropsch (Fe-LTFT) and iron-based high-temperature Fischer-Tropsch (Fe-HTFT) synthesis.^a

Product fraction	Carbon range	Compound class	Syncrude composition (mass%) ^{b, c}		
			Co-LTFT	Fe-LTFT	Fe-HTFT
Gas phase					
Tail gas	C ₁	Alkane	5.6	4.3	12.7
	C ₂	Alkene	0.1	1.0	5.6
LPG	C ₃ –C ₄	Alkane	1.0	1.0	4.5
		Alkene	3.4	6.0	21.2
		Alkane	1.8	1.8	3.0
Oil and wax phases					
Naphtha	C ₅ –C ₁₀	Alkene	7.8	7.7	25.8
		Alkane	12.0	3.3	4.3
		Aromatic	0	0	1.7
		Oxygenate	0.2	1.3	1.6
Distillate	C ₁₁ –C ₂₂	Alkene	1.1	5.7	4.8
		Alkane	20.8	13.5	0.9
		Aromatic	0	0	0.8
		Oxygenate	0	0.3	0.5
Residue	C ₂₂ +	Alkene	0	0.7	1.6
		Alkane	44.6	49.2	0.4
		Aromatic	0	0	0.7
		Oxygenate	0	0	0.2
Aqueous phase					
Reaction water	C ₁ –C ₅	Alcohol	1.4	3.9	4.5
		Carbonyl	0	0	3.9
		Carboxylic acid	0.2	0.3	1.3

^aSyncrude composition is affected by factors such as the deactivation state of the Fischer–Tropsch catalyst, operating conditions and reactor technology.

^bThe syncrude composition is based on the total product from FTS, excluding inert gases and water gas shift products (H₂O, CO, CO₂ and H₂).

^cZero values indicate a low concentration and not necessarily a total absence of such compounds.

key performance parameters such as the octane number for motor gasoline need some adjustments. It is therefore necessary to refine the syncrude in order to meet the specification requirements of commercial transportation fuels.

One way of approaching this is to integrate FTS with crude oil refining. This integration can alleviate some problems associated with the use of refinery residues, such as petroleum coke from coking and asphalt from deasphalting. In some specific cases, it may be beneficial to produce sufficient quantities of vacuum residue to be used as the feed for gasification to produce synthesis gas. On the refinery site, the upgraded FTS liquids can be blended with the liquids of petroleum origin. By doing so, one can exploit the blending synergies available to mixtures of Fischer–Tropsch liquids, coal liquids and petroleum liquids.²⁴ For example, due to the low aromatics content of syncrude, blending FTS liquids with similar petroleum-derived fractions can decrease the costs

associated with deep hydrodearomatisation (HDAr) of distillates. This offers some flexibility in response to ever-changing environmental regulations.

The industrial approach followed thus far is to construct stand-alone FTS facilities. This implies on-site refining or off-site blending in order to produce marketable transportation fuels. With the continuous developments in catalysis and conversion processes, Fischer–Tropsch refining presents an ever-changing landscape. One can learn a lot by studying older Fischer–Tropsch refinery designs and technologies,²⁵ despite the fact that fuel specifications and engine technology have changed considerably since the first industrial applications of FTS in Germany.

Fischer–Tropsch syncrude can be used, with appropriate pretreatment, in conjunction with any catalytic process that is employed for the conversion of conventional crude oil. Yet Fischer–Tropsch syncrude is in many respects different from crude oil.²⁶ Efficient refining of Fischer–Tropsch syncrude requires a different combination of refining technologies.²⁷ These technologies exploit the unique properties of syncrude (Table 1.1). Fischer–Tropsch syncrude can also be refined to a variety of chemicals.^{28–33}

1.3 Catalysis in Fischer–Tropsch Refining

Although industrial-scale FTS has been practised in conjunction with syncrude refining since its inception, the literature on Fischer–Tropsch refining catalysis is less abundant than that dealing with the catalysis of FTS. The purpose of this book is to address this deficiency and provide an overview of the catalysis relevant to the refining of Fischer–Tropsch syncrude. The focus will be mainly on refining catalysis for the production of transportation fuels, although the catalytic conversion of syncrude to other products will also be touched upon. The main interest is in Fischer–Tropsch-derived materials, but other relevant studies are also included in the discussion. For example, studies using *n*-alkanes and *n*-alkenes, and also branched hydrocarbons, as model compounds have a direct bearing on the catalysis of Fischer–Tropsch-derived feeds.

Three of the most important catalytic conversions in Fischer–Tropsch refining catalysis are (a) oligomerisation (OLI) for the conversion of light alkenes into liquid products, (b) hydrocracking (HCR) for the conversion of heavy alkanes into lighter liquid products and (c) hydroisomerisation (HIS) to introduce some branching into the linear hydrocarbons for applications such as lubricating oil and jet fuel production. The catalysis of these conversions will be discussed in detail. Moreover, the information in the literature on OLI, HCR and HIS is so extensive that a separate book could be written on each topic. It is hoped that the studies that were selected for discussion here will give a good indication of the type of research that is relevant to the upgrading of the Fischer–Tropsch syncrude. Specific attention is paid to the influence of oxygenates, since this is one of the main differentiating features of syncrude compared with crude oil. Other types of catalysis relevant to syncrude conversion are also covered, albeit in less detail.

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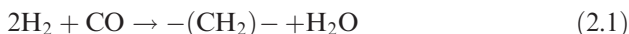
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CHAPTER 2

Production of Synthesis Gas

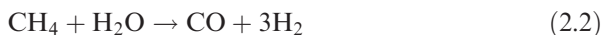
All indirect liquefaction technologies make use of synthesis gas (a mixture of H₂ and CO) as intermediate product. Ideally, synthesis gas, or syngas for short, should make Fischer–Tropsch synthesis (FTS) and other syngas-to-syn crude technologies independent of the raw feed material. This is a commonly held perception, but not entirely true. It is not possible to view FTS independently from the gas loop (Figure 1.1). In the gas loop, the raw synthesis gas has to be purified to remove compounds that may poison the catalyst used for FTS. The synthesis gas composition is also adjusted in the gas loop in order to provide FTS with a synthesis gas feed that has the desired H₂:CO ratio. The optimal H₂:CO ratio depends on the Fischer–Tropsch technology, and although a usage ratio of 2:1 is implied by the generic expression of FTS [Equation (2.1)], the real usage ratio depends on the real product selectivity (Table 1.1). The H₂:CO ratio of synthesis gas is adjusted by making use of the water gas shift (WGS) reaction:



The production of synthesis gas will be considered in the context of the gas loop, with its component parts being discussed separately.

2.1 Synthesis Gas from Gaseous Feed

The steam reforming of natural gas and/or refinery gases has been the most common source of synthesis gas. Although steam reforming is mainly used to produce a hydrogen-rich synthesis gas as a source of refinery hydrogen, it is also useful for applications such as ammonia synthesis and syngas-to-methanol conversion. Theoretically, synthesis gas having a H₂:CO ratio of 3:1 can be produced from steam reforming of methane:



Synthesis gas production from methane is endothermic and a portion of feed material has to be combusted to supply the heat necessary for the reforming

reactions. Neither steam reforming nor the WGS reaction that is needed to adjust the $\text{H}_2\text{:CO}$ ratio proceed to completion.

The view has been expressed that steam reforming by itself is not the preferred technology for synthesis gas production in large-scale gas-to-liquids (GTL) based on FTS.¹ This view is supported by the poor economy of scale compared with partial oxidation processes and the hydrogen-rich synthesis gas that is well above the usage ratio required by FTS. In partial oxidation processes, such as autothermal reforming (ATR), the energy to drive the reforming reaction is provided by partial combustion of the feed in the reformer. The synthesis gas thus produced typically has an $\text{H}_2\text{:CO}$ ratio in the range 1.6–1.9, which is closer to the usage ratio required by FTS.

It was pointed out that the conversion of natural gas to syncrude, starting with steam reforming, through WGS, CO_2 scrubbing and ending with FTS, may not be accomplished without a negative overall energy balance.² On a global scale, the direct utilisation, in either energy applications or transportation, may be the most efficient use for a high-value fuel such as natural gas. Natural gas inherently has a high H:C ratio, which is degraded when it is employed for syncrude production.

2.2 Synthesis Gas from Liquid and Solid Feed

Synthesis gas may be produced from a variety of solid carbon sources by gasification. Higman and van der Burgt listed various raw materials that have been investigated for gasification.³ These include coal, bitumen–water emulsions, oil sand residues, biomass, heavy petroleum fractions and wastes. Of these, only coal is at present used industrially in conjunction with FTS. Instances where coal can be obtained by low-cost surface mining are of particular importance. Coal gasification is capital intensive and a low raw material cost is necessary to make the construction and operation of such facilities economically viable. Irrespective, gasification of the solid and/or semi-solid feeds to produce synthesis gas, which is followed by WGS and FTS, can be employed to convert a low-value feed material into higher value products.⁴

The composition of the synthesis gas obtained by gasification depends on the feed material. The approximate concentrations of gasification products obtained from a lignite, vacuum residue, asphalt from deasphalting and fluid coke (petcoke) are given in Table 2.1.⁴ The lignite and coke were fed as ~50:50 water slurries, whereas vacuum residue and asphalt were in a liquid form. It is evident that with respect to the $\text{H}_2\text{:CO}$ ratio, vacuum residue and asphalt are more suitable feeds for gasification with FTS in mind. Thus, in order to obtain an $\text{H}_2\text{:CO}$ ratio of around 2:1 from a synthesis gas with a ratio of around 0.4:1, such as the gaseous mixture obtained from lignite in a British Gas Lurgi (BGL) gasifier, the synthesis gas has to be subjected to substantial WGS:

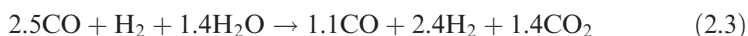
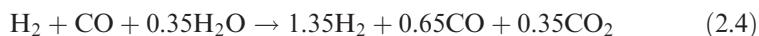


Table 2.1 Composition of clean and dry synthesis gas produced by gasification in British Gas Lurgi (BGL) and Texaco gasifiers employing different liquid and solid feed materials.

Composition	Lignite coal		Vacuum residue	Asphalt	Fluid coke (Petcoke)
	BGL	Texaco ^a	Texaco ^b	Texaco ^b	Texaco ^a
H ₂ :CO ratio	0.4	0.8	1.0	1.0	0.5
H ₂ (%)	26	35	47	47	28
CO (%)	63	45	47	47	54
CO ₂ (%)	3	18	4	4	15
CH ₄ (%)	5	Trace	1	1	Trace
N ₂ + Ar (%)	3	2	1	1	1

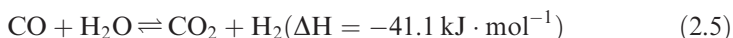
^aFed as a water slurry.^bFed in a liquid form.

Much less extensive WGS is required for gaseous mixtures obtained from vacuum residue and asphalt:



2.3 Water Gas Shift Conversion

The composition of the synthesis gas can be adjusted by employing the water gas shift reaction [Equation (2.5)]. The WGS reaction is reversible. Lower temperatures favour CO₂ and H₂, whereas higher temperatures favour CO and H₂O.



At very high temperatures (>900 °C), WGS does not require a catalyst, but for most industrial applications it is conducted over a catalyst. Low-temperature catalytic WGS conversion (200–270 °C) employs alumina-supported copper–zinc oxide (Cu–ZnO–Al₂O₃) catalysts. These catalysts are sensitive to sulfur poisoning and the synthesis gas must first be purified (see Section 2.4) to remove acid gases. The sulfur content in the feed should preferably be less than 0.1 µg g⁻¹ for low-temperature WGS catalysts.³ High-temperature catalytic WGS conversion (300–500 °C) employs combined iron oxide and chromium oxide (Fe₂O₃–Cr₂O₃) catalysts, which may include stabilisers and promoters, such as copper oxide.⁵ It is not necessary to remove all the acid gases before high-temperature WGS and catalysts are tolerant of sulfur levels up to 100 µg g⁻¹.³ High-temperature WGS reactors may therefore be operated either as ‘sweet’ shift or as ‘sour’ shift processes. For true ‘sour’ shift, it is best to employ a sulfided CoMo-based catalyst that requires the sulfur to remain in its sulfided state.³ These catalysts can be considered medium-temperature WGS catalysts and typically operate in the range 250–350 °C.⁵ In an FTS gas loop, any sulfur in the synthesis gas must be removed to avoid poisoning of the

Fischer–Tropsch catalyst and there is no need to employ a ‘sour’ shift. It is also possible to make use of noble metal-based catalysts for WGS and numerous examples of noble metal-based WGS catalysts were described in a review paper by Ratnasamy and Wagner.⁵

2.4 Synthesis Gas Purification

An integral part of synthesis gas production is gas purification. Gas purification is mainly required to remove sulfur-containing compounds that are catalyst poisons for Ni-based reforming catalysts, WGS catalysts and Fe- or Co-based Fischer–Tropsch catalysts.

When natural gas is used as a feed material, the natural gas can be desulfurised by hydrotreating, followed by absorption on ZnO.¹ When coal is gasified, the raw synthesis gas from gasification contains, amongst other compounds, sulfur and nitrogen species. The raw synthesis gas can be purified by a cold methanol wash, such as employed in the Rectisol technology,⁶ which has the added benefit of removing the CO₂. Other gas cleaning technologies may also be considered depending on the feed type and synthesis gas purity requirements.⁷

The production of synthesis gas may be accompanied by the co-production of pyrolysis products. Although it does not have a direct impact on FTS or the gas loop configuration, it will affect the design of the gas purification section. The condensable products may be recovered during gas purification and used as feed for chemical extraction, fuel or further refining.

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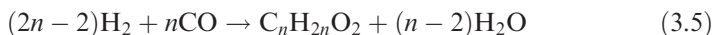
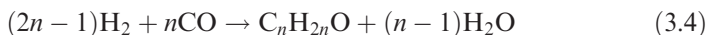
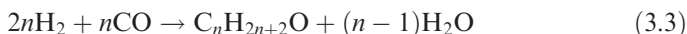
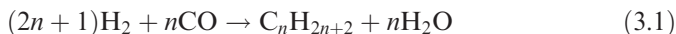
CHAPTER 3

Fischer–Tropsch Synthesis

Up-to-date information on Fischer–Tropsch synthesis (FTS) can be found in recent textbooks.^{1–3} The purpose of this chapter is not to duplicate this literature, but rather to provide a brief overview and to highlight aspects that affect the syncrude composition. The syncrude composition directly influences the catalysis of Fischer–Tropsch syncrude refining and is pertinent to the topic of this book.

3.1 Chemistry of Fischer–Tropsch Synthesis

When synthesis gas is converted over a Fischer–Tropsch catalyst, the following stoichiometric reactions yield hydrocarbons and oxygenates as primary products:



In these reactions, the first two represent the formation of alkanes [Equation (3.1)] and alkenes [Equation (3.2)]. The last three reactions represent the formation of various oxygenates, namely alcohols and ethers [Equation (3.3)], aldehydes and ketones [Equation (3.4)] and carboxylic acids and esters [Equation (3.5)]. Of these, the compounds with functional groups on the terminal carbon are generally considered primary products from FTS.

All Fischer–Tropsch reactions are highly exothermic; an average value for the heat of reaction is around 10 kJ g^{-1} of hydrocarbon product.

3.2 Factors Influencing Fischer–Tropsch Syncrude Composition

The syncrude composition that is obtained from FTS is influenced by many variables. The values in Table 1.1⁴ and Table 3.1⁵ are consequently only indicative of the syncrude compositions obtained from the main classes of FTS that are practised industrially. Factors that significantly affect syncrude composition are the Fischer–Tropsch catalyst type, the reactor technology employed for FTS, Fischer–Tropsch catalyst deactivation and the operating conditions of FTS.

3.2.1 Fischer–Tropsch Catalyst Type

The main products produced over different Fischer–Tropsch-active metals (Table 3.2) show the effect of catalyst type on product composition.^{6,7} Apart from the main FTS-active metal, Fischer–Tropsch catalysts include various promoters and may be combined with a support. In fact, for the same active metals, the support can have a pronounced effect on conversion and selectivity of the catalyst.⁸

There have been many reports dealing with the two most frequently used Fischer–Tropsch-active metals, namely iron and cobalt. The comparison by Schulz (Table 3.3)⁹ illustrates the significant difference between iron-based

Table 3.1 Selectivity changes during industrial Fe-HTFT synthesis with increasing time on stream, illustrating how catalyst deactivation affects the composition of syncrude. The selectivity values do not reflect water gas shift products (H_2 , H_2O , CO and CO_2) that are also affected by deactivation.

<i>Compound or fraction</i>	<i>Selectivity (%)</i>		
	<i>Start of run</i>	<i>Average</i>	<i>End of run</i>
Methane	7	10	13
Ethene	4	4	3
Ethane	3	6	9
Propene	10	12	13
Propane	1	2	3
Butenes	7	8	9
Butanes	1	1	2
C ₅ and heavier condensate	6	8	9
Light oil	40	35	30
Decanted oil	14	7	2
Aqueous product	7	7	7

Table 3.2 Effect of Fischer–Tropsch active metals and operating range on the nature of the products.

<i>Metal</i>	<i>Temperature (°C)</i>	<i>Pressure (MPa)</i>	<i>Nature of products</i>
Fe	200–250	1.0–3.0	Alkanes, alkenes, oxygenates
	320–340	1.0–3.0	Alkanes, alkenes, aromatics, oxygenates
Co	170–220	0.5–3.0	Alkanes, some alkenes and oxygenates
Ru	150–250	10–100	Paraffin wax
ThO ₂	300–450	10–100	Isoalkanes
Ni	170–205	0.1 ^a	Alkanes, some alkenes

^aAt higher pressures, loss of Ni through Ni(CO)₄ formation becomes too high.

Table 3.3 Comparison of low-temperature Fischer–Tropsch synthesis over potassium-promoted iron-based and cobalt-based catalysts.

<i>Catalysis property</i>	<i>Fe-LTFT</i>	<i>Co-LTFT</i>
Extensive methanation	No	At increasing temperature and decreasing CO partial pressure
Alkali promoters	Essential	No
Monomers	CH ₂	CH ₂ (CO, C ₂ H ₄)
Water gas shift activity	Yes	No
Branching reaction	Static, increases with time	Dynamic, decreases with time
Alkene hydrogenation	No (little)	Extensive
Alkene isomerisation	No (little)	Extensive

low-temperature Fischer–Tropsch (Fe-LTFT) and cobalt-based low-temperature Fischer–Tropsch (Co-LTFT) synthesis. In addition to differences in catalysis listed in Table 3.3, differences in product distributions are also evident (e.g. Tables 1.1 and 3.1). It has further been noted that the Co-LTFT catalysts give a higher conversion rate (depending on synthesis gas conditions) and reportedly have a longer catalyst life. Co-LTFT catalysts are also more active for hydrogenation (HYD) and consequently produce less unsaturated hydrocarbons and oxygenates than Fe-based catalysts. On the other hand, Fe-LTFT catalysts are more easily prepared, cheaper, more robust and more tolerant to poisoning by sulfur.

Details of selectivity control during FTS in relation to catalyst design can be found in the literature, for example the review published by Iglesia *et al.*¹⁰ Valuable insights into the Fischer–Tropsch mechanism in relation to the nature and structure of the catalyst can be found in, among others, publications by Fahey,¹¹ Davis¹² and Maitlis and Zanotti.¹³

3.2.2 Fischer–Tropsch Reactor Technology

There are four main types of reactor technology that have been employed industrially for FTS (Figure 3.1). The high heat release during FTS is a crucial consideration in the design of commercial reactors for FTS. Provision of cooling through steam generation is evident in all of the reactor types. The operating temperature of FTS determines the steam pressure and in this respect a higher operating temperature is beneficial.

Iron-based high-temperature Fischer–Tropsch (Fe-HTFT) processes make use of fluidised bed reactor technology and FTS takes place entirely in the gas phase. The product distribution from FTS does not seem to be significantly affected by the reactor technology *per se*, with similarly operated circulating fluidised bed and fixed fluidised bed reactors yielding similar product distributions.

The same is not true of low-temperature Fischer–Tropsch processes. The product distributions from fixed bed and slurry bubble column FTS are different. This is to be expected, since a fixed bed reactor approximates plug flow behaviour, whereas a slurry bubble column reactor approximates continuous stirred tank behaviour.

Satterfield *et al.* directly compared Fe-LTFT in fixed bed and slurry bubble column reactors.¹⁴ Little difference in methane selectivity and carbon number distribution was observed, but the alkene to alkane ratio from the fixed bed reactor was much lower than that from the slurry bubble column reactor. Jager and Espinoza,¹⁵ who compared data from industrial operation of Fe-LTFT in these two reactor types, corroborated these findings. Fixed bed Fe-LTFT was more hydrogenating and produced a syncrude with a lower alkene to alkane ratio. Operation with a fixed bed reactor was also found to be 1.5–2 times less sensitive to sulfur poisoning than operation with a slurry bubble column

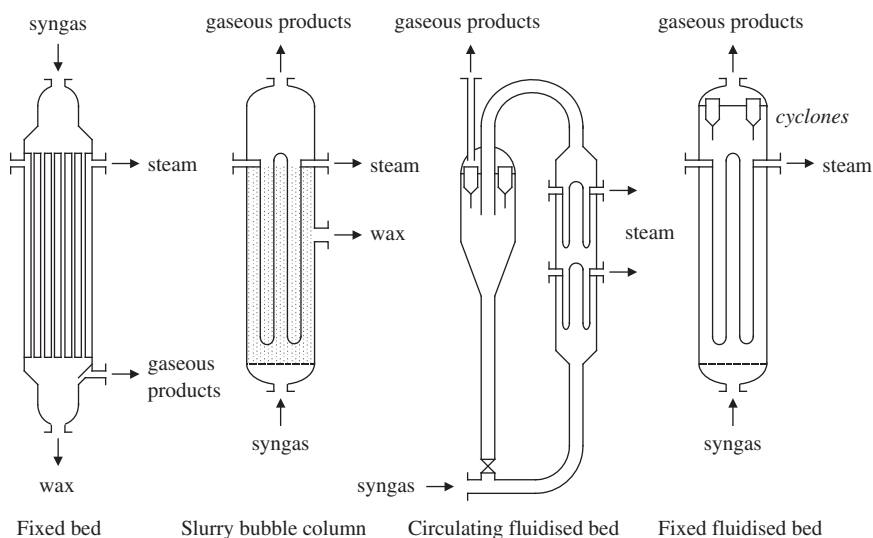


Figure 3.1 Industrially applied Fischer–Tropsch reactor technologies.

reactor. Moderate sulfur poisoning of Fe-LTFT catalysts mainly affects activity and not product selectivity. Slurry bubble column operation led to more productive use of the catalyst. In terms of product produced per unit mass of catalyst, the slurry bubble column reactor could achieve the same productivity with 30% or less catalyst mass than required for a fixed bed reactor.

The reactor technology places different demands on the mechanical strength of the Fischer–Tropsch catalyst. Slurry bubble column operation leads to higher levels of catalyst attrition and care should be taken during Fischer–Tropsch catalyst development to ensure that the working catalyst has sufficient attrition resistance.¹⁶ Catalyst attrition affects the syncrude composition by increasing the level of solids present in the syncrude. It may also contribute to increased levels of dissolved metals in the syncrude.

3.2.3 Fischer–Tropsch Catalyst Deactivation

Syncrude composition is dependent on the age and deactivation history of the Fischer–Tropsch catalyst. As a consequence, the products from FTS may vary with time. These variations can be reduced when fluidised bed and slurry bubble column reactor technologies are employed, since these reactor technologies allow continuous catalyst addition and removal. This is not possible with fixed bed reactor technology, although the impact of such time-dependent changes may be reduced by the parallel operation of multiple fixed bed reactors with different age profiles.

The impact of deactivation on the composition of syncrude is different for the three main classes of Fischer–Tropsch catalysts:

1. An Fe-LTFT catalyst may deactivate until it reaches a stable ‘equilibrium’ catalyst that shows little further deactivation. During the initial period of deactivation, the carbon number distribution becomes lighter with time-on-stream and then stabilises (Figure 3.2).¹⁷ Deactivation is accompanied by a slight increase in alkene and oxygenate (alcohol and carboxylic acid) selectivity. Methane increases and then stabilises at around 3.5% (Figure 3.2) and much of the increase in lighter products is in the C₂–C₄ carbon number range. It was pointed out that Fe-LTFT deactivation is actually beneficial for product refining.¹⁸
2. Co-LTFT catalyst deactivation takes place by various mechanisms.¹⁹ The most prominent of these are poisoning, notably by sulphur compounds, sintering and coalescence of Co crystallites, carbon formation and fouling. Other deactivation mechanisms that may be active include re-oxidation, carbidisation, metal-support reactions, surface reconstruction, leaching of Co and catalyst attrition. It has been found that Co-LTFT catalysts are very sensitive to part per million levels of impurities, even during preparation, which can markedly affect regenerability and deactivation rate.^{16,20} Deactivation with time-on-stream leads to a shift in the carbon number distribution. The relationship between increased methane selectivity and decreased liquid product yield seems to be independent of Co-LTFT catalyst type,²¹ and has a detrimental impact on product refining.²²