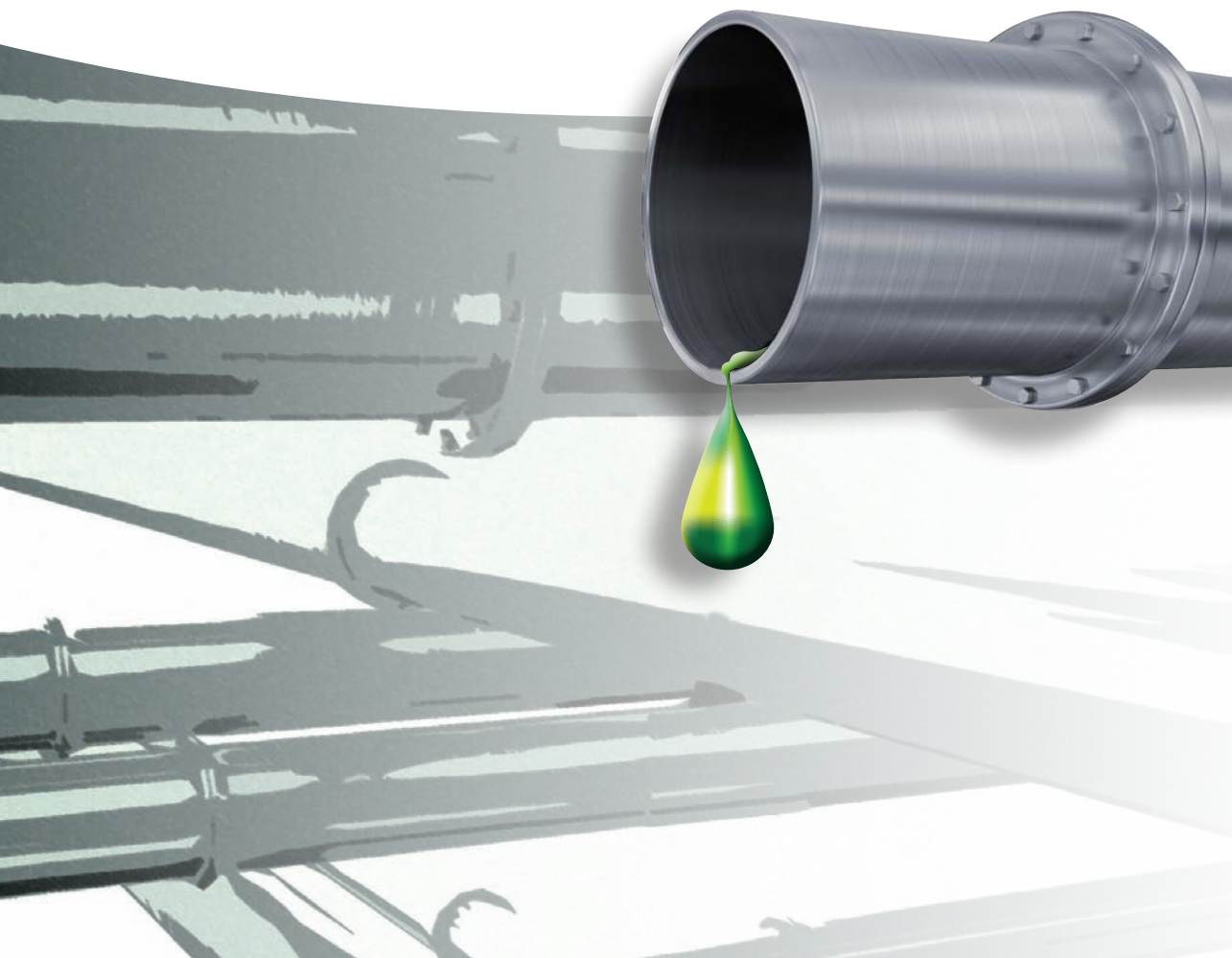


Edited by  
Peter M. Maitlis, Arno de Klerk

# Greener Fischer-Tropsch Processes

for Fuels and Feedstocks





*Edited by*  
*Peter M. Maitlis and*  
*Arno de Klerk*

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# **Greener Fischer-Tropsch Processes for Fuels and Feedstocks**



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## The Editors

**Prof. Peter M. Maitlis**

University of Sheffield  
Department of Chemistry  
Sheffield S3 7HF  
United Kingdom

**Prof. Arno de Klerk**

University of Alberta  
Chemical & Materials Eng.  
9107 - 116 Street  
Edmonton, Alberta T6G 2V4  
Canada

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## Contents

**Preface** *XV*

**List of Contributors** *XVII*

### **Part One Introduction** 1

- 1 What is Fischer–Tropsch?** 3  
*Peter M. Maitlis*  
Synopsis 3
- 1.1 Feedstocks for Fuel and for Chemicals Manufacture 3  
1.2 The Problems 5  
1.3 Fuels for Transportation 6  
1.3.1 Internal Combustion Engines 6  
1.3.2 Electric Cars 7  
1.3.3 Hydrogen-Powered Vehicles 7  
1.4 Feedstocks for the Chemical Industry 8  
1.5 Sustainability and Renewables: Alternatives to Fossil Fuels 8  
1.5.1 Biofuels 9  
1.5.2 Other Renewable but Nonbio Fuels 9  
1.6 The Way Forward 10  
1.7 XTL and the Fischer–Tropsch Process (FTP) 11  
1.7.1 Some History 12  
1.7.2 FT Technology: An Overview 13  
1.7.3 What Goes on? 13  
1.7.4 CO Hydrogenation: Basic Thermodynamics and Kinetics 14  
1.8 Alternatives to Fischer–Tropsch 14  
References 15

**Part Two Industrial and Economics Aspects 17****2 Syngas: The Basis of Fischer–Tropsch 19***Roberto Zennaro, Marco Ricci, Letizia Bua, Cecilia Querci, Lino Carnelli, and Alessandra d'Arminio Monforte*

Synopsis 19

- 2.1 Syngas as Feedstock 19
- 2.2 Routes to Syngas: XTL (X = Gas, Coal, Biomass, and Waste) 21
  - 2.2.1 Starting from Gas (GTL) 23
  - 2.2.2 Starting from Solid Feeds (CTL, BTL, and WTL) 27
- 2.3 Water-Gas Shift Reaction (WGSR) 31
- 2.4 Synthesis Gas Cleanup 34
- 2.5 Thermal and Carbon Efficiency 37
- 2.6 The XTL Gas Loop 41
  - 2.6.1 Gas Loop for HTFT Synthesis with a Coal Gasifier 41
  - 2.6.2 Gas Loop for HTFT Synthesis with a Natural Gas Feed 42
  - 2.6.3 Gas Loop for LTFT Cobalt Catalyst with Natural Gas Feed 43
- 2.7 CO<sub>2</sub> Production and CO<sub>2</sub> as Feedstock 46
- References 49

**3 Fischer–Tropsch Technology 53***Arno de Klerk, Yong-Wang Li, and Roberto Zennaro*

Synopsis 53

- 3.1 Introduction 53
  - 3.1.1 FT Catalyst 54
  - 3.1.2 Operating Conditions 54
  - 3.1.3 FT Reactor Types 54
- 3.2 Industrially Applied FT Technologies 54
  - 3.2.1 German Normal-Pressure Synthesis 55
  - 3.2.2 German Medium-Pressure Synthesis 56
  - 3.2.3 Hydrocol 56
  - 3.2.4 Arbeitsgemeinschaft Ruhrchemie-Lurgi (Arge) 56
  - 3.2.5 Kellogg Synthol and Sasol Synthol 57
  - 3.2.6 Shell Middle Distillate Synthesis (SMDS) 57
  - 3.2.7 Sasol Advanced Synthol (SAS) 57
  - 3.2.8 Iron Sasol Slurry Bed Process (Fe-SSBP) 57
  - 3.2.9 Cobalt Sasol Slurry Bed Process (Co-SSBP) 58
  - 3.2.10 Statoil Cobalt-Based Slurry Bubble Column 58
  - 3.2.11 High-Temperature Slurry Fischer–Tropsch Process (HTSFTP) 58
- 3.3 FT Catalysts 58
- 3.4 Requirements for Industrial Catalysts 59
  - 3.4.1 Activity 59
  - 3.4.2 Selectivity 59
  - 3.4.3 Stability 60
  - 3.4.4 Other Factors 60



3.5	FT Reactors	61
3.5.1	Tube-Cooled Fixed Bed Reactors	61
3.5.2	Multitubular Fixed Bed Reactors	63
3.5.3	Circulating and Fixed Fluidized Bed Reactors	65
3.5.4	Slurry Bed Reactors	68
3.6	Selecting the Right FT Technology	71
3.6.1	Syngas Composition	71
3.6.2	Syngas Purity	72
3.6.3	Impact of Catalyst Deactivation	72
3.6.4	Catalyst Replacement Strategy	72
3.6.5	Turndown Ratio and Robustness	73
3.6.6	Steam Quality	73
3.6.7	Syncrude Composition	73
3.6.8	Syncrude Quality	74
3.7	Selecting the FT Operating Conditions	74
3.8	Selecting the FT Catalyst Type	75
3.8.1	Active Metal	75
3.8.2	Catalyst Complexity	75
3.8.3	Catalyst Particle Size	76
3.9	Other Factors That Affect FT Technology Selection	76
3.9.1	Particle Size	76
3.9.2	Reaction Phase	76
3.9.3	Catalyst Lifetime	77
3.9.4	Volumetric Reactor Productivity	77
3.9.5	Other Considerations	78
	References	78
<b>4</b>	<b>What Can We Do with Fischer–Tropsch Products?</b>	<b>81</b>
	<i>Arno de Klerk and Peter M. Maitlis</i>	
	Synopsis	81
4.1	Introduction	81
4.2	Composition of Fischer–Tropsch Syncrude	82
4.2.1	Carbon Number Distribution: Anderson–Schulz–Flory (ASF) Plots	86
4.2.2	Hydrocarbon Composition	86
4.2.3	Oxygenate Composition	90
4.3	Syncrude Recovery after Fischer–Tropsch Synthesis	92
4.3.1	Stepwise Syncrude Cooling and Recovery	92
4.3.2	Oxygenate Partitioning	94
4.3.3	Oxygenate Recovery from the Aqueous Product	95
4.4	Fuel Products from Fischer–Tropsch Syncrude	96
4.4.1	Synthetic Natural Gas	96
4.4.2	Liquefied Petroleum Gas	97
4.4.3	Motor Gasoline	98
4.4.4	Jet Fuel	99
4.4.5	Diesel Fuel	99

4.5	Lubricants from Fischer–Tropsch Syncrude	101
4.6	Petrochemical Products from Fischer–Tropsch Syncrude	102
4.6.1	Alkane-Based Petrochemicals	102
4.6.2	Alkene-Based Petrochemicals	103
4.6.3	Aromatic-Based Petrochemicals	104
4.6.4	Oxygenate-Based Petrochemicals	104
	References	104
<b>5</b>	<b>Industrial Case Studies</b>	<b>107</b>
	<i>Yong-Wang Li and Arno de Klerk</i>	
	Synopsis	107
5.1	Introduction	107
5.2	A Brief History of Industrial FT Development	108
5.2.1	Early Developments	108
5.2.2	Postwar Transfer of FT Technology across Oceans	110
5.2.3	Industrial Developments in South Africa	110
5.2.4	Industrial Developments by Shell	112
5.2.5	Developments in China	112
5.2.6	Other International Developments	115
5.3	Industrial FT Facilities	116
5.3.1	Sasol 1 Facility	117
5.3.2	Sasol Synfuels Facility	118
5.3.3	Shell Middle Distillate Synthesis (SMDS) Facilities	121
5.3.4	PetroSA GTL Facility	122
5.3.5	Oryx and Escravos GTL Facilities	123
5.4	Perspectives on Industrial Developments	124
5.4.1	Further Investment in Industrial FT Facilities	124
5.4.2	Technology Lessons from Industrial Practice	125
5.4.3	Future of Small-Scale Industrial Facilities	126
	References	128
<b>6</b>	<b>Other Industrially Important Syngas Reactions</b>	<b>131</b>
	<i>Peter M. Maitlis</i>	
	Synopsis	131
6.1	Survey of CO Hydrogenation Reactions	131
6.2	Syngas to Methanol	133
6.2.1	Introduction	133
6.2.2	Synthesis Reaction	134
6.2.3	Mechanism	135
6.2.4	Catalyst Deactivation	136
6.2.5	Uses of Methanol	136
6.3	Syngas to Dimethyl Ether (DME)	137
6.3.1	DME Uses	137
6.4	Syngas to Ethanol	137
6.4.1	Introduction	137

6.4.2	Direct Processes	138
6.5	Syngas to Acetic Acid	139
6.5.1	Acetic Acid Processes	139
6.5.2	Mechanisms	141
6.5.3	Catalyst Deactivation	142
6.6	Higher Hydrocarbons and Higher Oxygenates	143
6.6.1	Isobutene and Isobutanol	143
6.7	Hydroformylation	144
6.8	Other Reactions Based on Syngas	146
6.8.1	Hydroxy and Alkoxy Carbonylations	146
6.8.2	Methyl Formate	146
6.8.3	Dimethyl Carbonate (DMC)	147
6.8.4	Ether Gasoline Additives	147
6.8.5	Hydrogenation	147
	References	148
<b>7</b>	<b>Fischer–Tropsch Process Economics</b>	<b>149</b>
	<i>Roberto Zennaro</i>	
	Synopsis	149
7.1	Introduction and Background	149
7.2	Market Outlook (Natural Gas)	150
7.3	Capital Cost	156
7.4	Operating Costs	162
7.5	Revenues	162
7.6	Economics and Sensitivity Analysis	164
7.6.1	Sensitivity to GTL Plant Capacity (Economy of Scale Effects)	165
7.6.2	Sensitivity to Feedstock Costs	165
7.6.3	Sensitivity to GTL Project Cost (Learning Curve Effect)	166
7.6.4	Sensitivity to Tax Regime	166
7.6.5	Sensitivity to GTL Diesel Valorization	167
7.6.6	Sensitivity to Crude Oil Price Scenario	167
7.6.7	Effects of Key Parameters on GTL Plant Profitability	167
	References	169
<b>Part Three Fundamental Aspects 171</b>		
<b>8</b>	<b>Preparation of Iron FT Catalysts</b>	<b>173</b>
	<i>Burtron H. Davis</i>	
	Synopsis	173
8.1	Introduction	173
8.2	High-Temperature Fischer–Tropsch (HTFT) Catalysts	174
8.3	Low-Temperature Catalysts	176
8.4	Individual Steps	177
8.4.1	Oxidation of Fe <sup>2+</sup>	177

8.4.2	Precipitation of Fe <sup>3+</sup>	180
8.4.3	Precipitate Washing	188
8.4.4	An Environmentally Greener Process	189
8.4.5	Chemical Promoters	189
8.4.6	Copper Promoters	189
8.4.7	Phase Changes	190
8.4.8	Other Iron Catalysts	190
	References	190
<b>9</b>	<b>Cobalt FT Catalysts</b>	<b>193</b>
	<i>Burtron H. Davis</i>	
	Synopsis	193
9.1	Introduction	193
9.2	Early German Work	193
9.3	Support Preparation	194
9.3.1	Alumina Supports	195
9.3.2	Silica Supports	196
9.3.3	Titanium Dioxide Support	201
9.4	Addition of Cobalt and Promoters	202
9.5	Calcination	203
9.6	Reduction	204
9.7	Catalyst Transfer	205
9.8	Catalyst Attrition	205
9.9	Addendum Recent Literature Summary	205
	References	205
<b>10</b>	<b>Other FT Catalysts</b>	<b>209</b>
	<i>Burtron H. Davis and Peter M. Maitlis</i>	
	Synopsis	209
10.1	Introduction	209
10.2	Ni Catalysts	210
10.3	Ruthenium Catalysts	211
10.3.1	Historical	211
10.3.2	Studies on Ru Catalysts	212
10.4	Rhodium Catalysts	217
10.5	Other Catalysts and Promoters	218
	References	218
<b>11</b>	<b>Surface Science Studies Related to Fischer–Tropsch Reactions</b>	<b>221</b>
	<i>Peter M. Maitlis</i>	
	Synopsis	221
11.1	Introduction: Surfaces in Catalysts and Catalytic Cycles	221
11.2	Heterogeneous Catalyst Characterization	222
11.2.1	<i>Diffraction Methods</i>	222

11.2.2	Spectroscopic Methods	222
11.2.3	Microscopy Techniques	223
11.2.4	Molecular Metal Complexes as Models	224
11.3	Species Detected on Surfaces	226
11.3.1	Carbon Monoxide on Surfaces {CO}	228
11.3.2	Activation of CO	229
11.3.3	Transformations of {CO}	230
11.3.4	Hydrogen on Surfaces {H <sub>2</sub> } and {H}	231
11.3.5	Transformations of {H}	232
11.3.6	Reactions of {CO} and {H}	233
11.4	Theoretical Calculations	233
	References	234
<b>12</b>	<b>Mechanistic Studies Related to the Fischer–Tropsch Hydrocarbon Synthesis and Some Cognate Processes</b>	<b>237</b>
	<i>Peter M. Maitlis</i>	
	Synopsis	237
12.1	Introduction	237
12.1.1	A Brief Background: Classical Views of the Mechanism	239
12.2	Basic FT Reaction: Dissociative and Associative Paths	240
12.2.1	Dissociative Activation of CO	241
12.2.2	Associative Activation	242
12.2.3	Dual Mechanism Approaches	244
12.3	Some Mechanisms-Related Experimental Studies	244
12.3.1	The Original Work of Fischer and Tropsch	244
12.3.2	Laboratory-Scale Experimental Results	247
12.3.3	Probe Experiments and Isotopic Labeling	249
12.3.3.1	<sup>13</sup> C Labeling	249
12.3.3.2	<sup>14</sup> C Labeling	251
12.4	Current Views on the Mechanisms of the FT-S	251
12.4.1	The First Steps: H <sub>2</sub> and CO Activation	251
12.4.2	Organometallic Models for CO Activation	253
12.5	Now: Toward a Consensus?	253
12.5.1	Routes Based on a Dissociative (Carbide) Mechanism	254
12.5.2	Routes Based on an Associative (or Oxygenate) Mechanism	255
12.6	Dual FT Mechanisms	256
12.6.1.1	Dual FT Mechanisms: The Nonpolar Path	256
12.6.2	Dual FT Mechanisms: The Ionic/Dipolar Path	258
12.7	Cognate Processes: The Formation of Oxygenates in FT-S	259
12.8	Dual Mechanisms Summary	260
12.9	Improvements by Catalyst Modifications	260
12.10	Catalyst Activation and Deactivation Processes	261
12.11	Desorption and Displacement Effects	262
12.12	Directions for Future Researches	262

12.12.1	Surface Spectroscopic Studies	262
12.12.2	Surface Microscopic Studies	262
12.12.3	Labeling and Kinetic Studies	263
12.12.4	Theoretical Calculations	263
12.13	Caveat	264
	References	264

**Part Four Environmental Aspects 267**

**13 Fischer–Tropsch Catalyst Life Cycle 269**

*Julius Pretorius and Arno de Klerk*

Synopsis 269

13.1	Introduction	269
13.2	Catalyst Manufacturing	270
13.2.1	Precipitated Fe-LTFT Catalysts	270
13.2.2	Supported Co-LTFT Catalysts	271
13.2.3	Fused Fe-HTFT Catalysts	271
13.3	Catalyst Consumption	272
13.3.1	Catalyst Lifetime during Industrial Operation	273
13.3.2	Fe-LTFT Catalyst Regeneration	273
13.3.3	Fe-HTFT Catalyst Regeneration	274
13.3.3.1	Fouling by Carbon	274
13.3.3.2	Loss of Alkali Promoter	274
13.3.3.3	Mechanical Attrition	274
13.3.3.4	Sulfur Poisoning	275
13.3.4	Co-LTFT Catalyst Regeneration	275
13.4	Catalyst Disposal	276
	References	277

**14 Fischer–Tropsch Syncrude: To Refine or to Upgrade? 281**

*Vincenzo Calemma and Arno de Klerk*

Synopsis 281

14.1	Introduction	281
14.1.1	To Refine or to Upgrade?	282
14.1.2	Refining of Fischer–Tropsch Syncrude	285
14.2	Wax Hydrocracking and Hydroisomerization	286
14.2.1	Hydrocracking and Hydroisomerization Catalysts	288
14.2.2	Mechanism of Hydrocracking and Hydroisomerization	290
14.2.3	Products from Hydrocracking Conversion	293
14.2.4	Parameters Affecting Hydrocracking	296
14.2.4.1	Effect of Temperature	296
14.2.4.2	Effect of Pressure	297
14.2.4.3	Effect of H <sub>2</sub> /Wax Ratio	298
14.2.4.4	Effect of Space Velocity	300

- 14.2.4.5 Effect of Oxygenates 300
- 14.2.5 Comparative Environmental Impact 301
- 14.3 Olefin Dimerization and Oligomerization 301
  - 14.3.1 Dimerization and Oligomerization Catalysts 301
  - 14.3.2 Mechanisms of Dimerization and Oligomerization 302
  - 14.3.3 Products from Solid Phosphoric Acid and H-ZSM-5 Conversion 304
  - 14.3.4 Parameters Affecting Solid Phosphoric Acid and H-ZSM-5 Conversion 305
    - 14.3.4.1 Effect of Temperature 306
    - 14.3.4.2 Effect of Olefinic Composition 306
    - 14.3.4.3 Effect of Oxygenates 306
  - 14.3.5 Comparative Environmental Impact 306
- References 307

## 15 Environmental Sustainability 311

*Roberta Miglio, Roberto Zennaro, and Arno de Klerk*  
Synopsis 311

- 15.1 Introduction 311
- 15.2 Impact of FT Facilities on the Environment 313
  - 15.2.1 Upstream Impact Assessment 313
  - 15.2.2 Downstream Impact Assessment 315
- 15.3 Water and Wastewater Management 316
  - 15.3.1 Water Produced in FT Facilities 317
  - 15.3.2 Quantities and Quality of Water 318
  - 15.3.3 Water Management Approaches 319
  - 15.3.4 Water Treatment Technologies 321
  - 15.3.5 Benchmark Technology: Water Treatment at Pearl GTL 322
  - 15.3.6 Prospects for Reducing the Water Footprint in CTL 324
- 15.4 Solid Waste Management 325
- 15.5 Air Quality Management 326
  - 15.5.1 The CO<sub>2</sub> Footprint of FT Facilities 327
  - 15.5.2 Is CO<sub>2</sub> a Carbon Feed of the Future? 330
- 15.6 Environmental Footprint of FT Refineries 330
  - 15.6.1 Energy Footprint of Refining 331
  - 15.6.2 Emissions and Wastes in Refining 333
- References 334

## Part Five Future Prospects 337

### 16 New Directions, Challenges, and Opportunities 339

*Peter M. Maitlis and Arno de Klerk*  
Synopsis 339

- 16.1 Introduction 339
- 16.2 Why Go Along the Fischer–Tropsch Route? 341

16.2.1	Strategic Justification	341
16.2.2	Economic Justification	342
16.2.3	Environmental Justification	343
16.3	Considerations against Fischer–Tropsch Facilities	343
16.4	Opportunities to Improve Fischer–Tropsch Facilities	344
16.4.1	Opportunities Offered by Small-Scale FT Facilities	346
16.4.2	Technical Opportunities in Syngas Generation and Cleaning	347
16.4.3	Technical Opportunities in Fischer–Tropsch Synthesis	348
16.4.4	Technical Opportunities in FT Syncrude Recovery and Refining	349
16.4.4.1	Syncrude Recovery Design	349
16.4.4.2	Tail Gas Recovery and Conversion	350
16.4.4.3	Aqueous Product Refining	350
16.5	Fundamental Studies: Keys to Improved FT Processes	351
16.5.1	New Instrumentation	351
16.5.2	New Catalysts and Supports	352
16.5.3	Isotopic Labeling	352
16.5.4	Surface Microscopy	352
16.5.5	Analytical Methods	352
16.5.6	Greener Procedures	353
16.6	Challenges for the Future	353
16.6.1	Hiatus Effect	353
16.6.2	Practical Constraints	354
16.6.2.1	Critical Materials Availability	354
16.6.2.2	Equipment Availability	354
16.6.2.3	Trained Manpower	355
16.6.2.4	Water Availability	355
16.6.2.5	Environmental Requirements, Permits, and Licensing	355
16.6.2.6	Socioeconomic Impacts	355
16.6.3	Politics, Profit, and Perspectives	355
16.7	Conclusions	356
	References	357

**Glossary** 359

**Index** 363



## Preface

*And what is a man without energy? Nothing. Nothing at all*  
(Mark Twain)

*Energy and persistence conquer all things*  
(Benjamin Franklin)

This book on Fischer-Tropsch is a study of aspects of energy: how it is produced and transformed today, with special reference to liquid fuels such as those used to drive cars, buses, planes, and other forms of transportation.

We still live in an era of relatively plentiful and cheap fuel, mostly derived from the fossilized organic materials: coal, oil, and natural gas.

New supplies are being discovered all the time and brought into use in quite surprising ways. A good example is natural gas for which it is now estimated that, because of the emergence of techniques such as fracking, the world's reserves may well be enough for around 200 years. This is close to being on a par with coal and much greater than our oil reserves. However, our assets of fossil fuels are limited and, in fairness to the next generations, we must not squander them.

We must learn to use them to buy time until a better and really sustainable source of energy becomes available.

The advantages of natural gas are considerable in comparison to those of coal or oil: it is much easier to clean and much easier to transport from where it occurs in nature to where it is required for work, warmth, and recreation. Compared to oil or coal, the main disadvantage of natural gas is that since it has a large volume for the equivalent energy content, a good pipeline infrastructure or the equivalent is needed.

For deposits that are small, in remote locations, or accumulations that are far from consumers, transportation by pipeline may not be economical. It is for these situations that the Fischer-Tropsch technology is particularly useful, since it enables the conversion into liquid products.

For coal the position is different. Although coal can be transported more simply than gas, cleaning it is a major task and ultimately it must also be converted into a refineable liquid product, before it can be turned into transportation fuels or chemicals. Fischer-Tropsch conversion is again a useful way to achieve this goal.

A considerable problem with all carbon-based fuels is that they produce carbon dioxide when burned. Atmospheric carbon dioxide is a “greenhouse gas,” which when present in large quantities is widely believed to have serious consequences for the climate of our planet.

It can be argued that one should not consider carbon-based fuels and chemicals technology for the future. Unfortunately, at present we have few viable alternatives to fossil fuels on the scale that is required to meet the energy needs of a world population that is already at around 7 billion and still increasing rapidly. Although most of our energy comes from the sun, the direct use of solar power to produce biofuels or to generate hydrogen on industrial scales is still a long way off. In the meantime, we will have to continue to rely on the power of the sun indirectly, via fossil fuels. The question then becomes: even if it is only an interim measure, how can we use our carbon-based resources in the most responsible manner?

The immediate challenge is the efficient transformation of one form of fossil fuel energy into another; in other words, how can we most efficiently transform natural gas, coal, or oil into say diesel or gasoline that we can harness to drive our machines. Even this is a vast task, but it is one that is being tackled very effectively through the Fischer-Tropsch process. That is what this book is about, an up to date review of the fundamental chemical, industrial, economic and environmental aspects of the Fischer-Tropsch process.

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*University of Sheffield, UK*  
*University of Alberta, Canada*  
October 2012

Peter M. Maitlis  
Arno de Klerk

## List of Contributors

**Letizia Bua**

Research Center for Non-  
Conventional Energy  
Eni Istituto Donegani  
via Fauser, 4  
28100 Novara  
Italy

**Vincenzo Calemma**

Eni S.p.A. – Refining & Marketing  
Division  
via Felice Maritano, 26  
20097 S. Donato Milanese  
Milan – Italy

**Lino Carnelli**

Research Center for Non-  
Conventional Energy  
Eni Istituto Donegani  
via Fauser, 4  
28100 Novara  
Italy

**Burtron H. Davis**

University of Kentucky  
Center for Applied Energy Research  
2540 Research Park Drive  
Lexington  
KY 40511  
USA

**Arno de Klerk**

University of Alberta  
Chemical & Materials Engineering  
9107 – 116 Street  
Edmonton  
Alberta T6G 2V4  
Canada

**Yong-Wang Li**

Chinese Academy of Science  
Institute of Coal Chemistry  
Beijing  
China

**Peter M. Maitlis**

University of Sheffield  
Department of Chemistry  
Sheffield S3 7HF  
UK

**Roberta Miglio**

Eni SPA – Exploration & Production  
Division  
San Donato Milanese  
20097 Milan  
Italy

**Alessandra d'Arminio Monforte**

Research Center for Non-  
Conventional Energy  
Eni Istituto Donegani  
via Fauser, 4  
28100 Novara  
Italy

***Julius Pretorius***

Alberta Innovates Technology  
Futures  
250 Karl Clark Road  
Edmonton  
Alberta T6N 1E4  
Canada

***Cecilia Querci***

Research Center for Non-  
Conventional Energy  
Eni Istituto Donegani  
via Fauser, 4  
28100 Novara  
Italy

***Marco Ricci***

Research Center for Non-  
Conventional Energy  
Eni Istituto Donegani  
via Fauser, 4  
28100 Novara  
Italy

***Roberto Zennaro***

Eni S.p.A. – Exploration &  
Production Division  
via Emilia, 1  
20097 San Donato Milanese  
Milan  
Italy

## Part One

### Introduction



## 1

**What is Fischer–Tropsch?***Peter M. Maitlis***Synopsis**

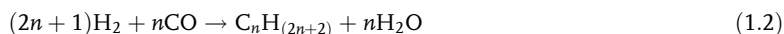
Some of the fundamental and most frequently used terms are explained. Fischer–Tropsch (FT) technology involves the conversion of syngas (a mixture of CO and H<sub>2</sub>) into liquid hydrocarbons. It is a key element in the industrial conversion processes X-To-Liquids (XTL), where X = C, coal; G, natural gas; B, biomass; or W, organic waste. For example, a gas-to-liquids (GTL) process converts natural gas into syncrude, a mixture mainly of long-chain hydrocarbons. The conversion reactions are usually catalyzed by metals (iron, cobalt, and sometimes ruthenium) often carried on oxide supports such as silica or alumina. The liquid hydrocarbons are important sources of transportation fuels and of specialty chemicals. Syngas is now mainly obtained from coal, oil, or natural gas, but will in future be increasingly made from renewable sources such as biomass or organic waste. Since the available reserves of fossil fuels are diminishing, the renewables should provide more sustainable feedstocks in the long term.

## 1.1

**Feedstocks for Fuel and for Chemicals Manufacture**

Syngas, the name given to a mixture of carbon monoxide and hydrogen, is the lifeblood of the chemicals industry and helps to provide a lot of our energy. It can be made from many sources, including coal, natural gas, organic waste, or biomass. The Fischer–Tropsch (FT) process converts syngas catalytically into organic chemicals, mainly linear alkenes and alkanes, which are used as both liquid fuels and feedstocks for making further useful chemicals. Some oxygenates can also be formed (chiefly methanol and ethanol) (see Chapters 4 and 6).

Alkene and alkane formation in the FT-Hydrocarbon Synthesis can be summarized as follows:



**Box 1.1 What its all about: some definitions**

To avoid ambiguity, we will use the following terms with reference to the metal-catalyzed conversion of syngas into organic compounds.

**Fischer–Tropsch process (FTP)** will refer to the overall industrial process wherein the syngas is catalytically converted in a reactor into a mixture of primary (largely but not exclusively linear aliphatic hydrocarbons) and secondary products. Water is also a major primary product. Secondary products that are believed to be formed in the reactor from the primary products include internal alkenes, branched chain and cyclic aliphatics, some aromatics, and some oxygenates such as alcohols.

**Fischer–Tropsch hydrocarbon synthesis** (or FT-HS) will refer to the hydrocarbons (1-*n*-alkenes and *n*-alkanes) that are generally considered to be the primary products of the metal-catalyzed syngas conversion when the reaction is carried out under mild conditions where further secondary reactions are minimized. A subset of the FT-HS, the formation of methane, is sometimes treated separately as **methanation**.

We will use the term **Fischer–Tropsch reaction** (or FT reaction) largely in the discussions on the mode(s) by which the primary products are formed, for example, the kinetics and reaction mechanisms of the FT-HS.

We also introduce two terms. **Sustainable development** is the use of natural resources that “meet present (world) needs without compromising the ability of future generations to meet their own needs” and was coined by the Brundtland Commission. **Renewable energy** is energy that is renewed naturally. It includes traditional biomass (biofuels), hydroelectricity, wind, tidal, solar, and geothermal sources. It excludes raw materials that are depleted in use such as fossil fuels and nuclear power.

Energy has been said to be “the single most important scientific and technological challenge facing humanity in the twenty first century” [1], and we agree. There is the global requirement for more energy, especially as transportation fuels, as populations increase in number and sophistication. In addition, there is also a more specific need for new feedstocks for chemicals manufacture. As we will see, these two needs have features in common. And above all, we recognize the imperative now demanded by Society to produce both fuel and feedstocks in an environmentally acceptable and preferably sustainable manner. We also aim to correct some of the erroneous beliefs and myths present in the energy and chemicals sectors in order that our students, who will be tomorrow’s academic and industrial leaders, have reliable foundations on which to build.

Mankind literally lives off energy. Most of it comes from the sun, indirectly via plants that use carbon dioxide and water to grow. Eventually they die and decay and, very slowly, over geological timescales, are turned into the fossil fuels (coal, oil, natural gas) that we extract and combust to provide heat, light, and other forms of power [2].



**Box 1.2 Fossil fuel resources**

In 2000, global oil reserves were estimated at about 1105 billion barrels; by the end of 2010, new discoveries had increased the proven reserves to 1383 billion or 1476 billion barrels ( $\sim 200 \times 10^9$  tons) if Canadian oil sands and shale oil and gas are included. Similarly, gas reserves were estimated at 109 trillion cubic meters (Tcm) in 1990, 154.3 Tcm in 2000, and 187.5 Tcm in 2010 [3]. Based on the data for current and previous years, the US Department of Energy makes forecasts of the use and the production of energy. Currently, it projects that world consumption of marketed energy will increase from 495 QUAD (quadrillion,  $10^{15}$  British Thermal Units or  $1.055 \times 10^{20}$  J) in 2007 to 590 QUAD in 2020 and then to 739 QUAD ( $\sim 780 \times 10^{20}$  J) in 2035, an overall increase of 49%. Liquids (i.e., largely hydrocarbons) supply a large proportion of world energy consumption, and although their share is predicted to fall somewhat, it will still be around 32% in 2030 [4].

“Unconventional” resources (including oil sands, shale oil and shale gas, extraheavy oil, biofuels, coal-to-liquids, and gas-to-liquids) are expected to become increasingly competitive; world production, which totaled 3.4 million barrels per day in 2007, is forecast to increase to 12.9 million barrels per day and to account for 12% of total world liquids supply in 2035. The proportion of biofuels, largely ethanol and biodiesel, from the United States and Brazil, is forecast to grow slowly.

**1.2****The Problems**

There are two main problems with fossil fuels: the reserves are finite and slowly running out and, since all fossil fuels contain combined carbon, their combustion (oxidation) produces carbon dioxide, which accumulates in the atmosphere and which is likely to have serious consequences for the climate of our planet. Combustion also generates other materials that can harm mankind and the environment, such as CO, oxides of sulfur and nitrogen, and metallic oxide ashes, arising from incomplete oxidation and from impurities in the fuel.

For some end-uses there are many alternatives to fossil fuels, such as hydroelectric and nuclear power and others that are being developed commercially, including solar, wind, tidal, and geothermal power. The latter technologies will play their very important role mainly by providing electric power via large fixed installations. However, they will not have a direct part in providing more liquid transportation fuels or new feedstocks for the chemicals industry.

Why should Fischer–Tropsch be the approach to replace or supplement crude oil as a source of transportation fuels, gasoline (in the United States), or petrol and diesel (in the United Kingdom)? Today transportation fuels from crude oil must undergo extensive cleaning to remove materials containing heteroatoms (N, S, metals, etc.) from the raw feedstocks; if these materials are not removed,

the impurities will quickly spoil and deactivate the catalyst. The amounts of hydrogen and energy needed for this cleaning have steadily increased as the crude oils have become heavier (i.e., more impure) over the years. Today, about 15–20% of the energy in the oil is required to produce environmentally acceptable transportation fuels, and the percentage can only increase as the crude becomes heavier. Thus, the energy advantage of crude oil over other fossil fuels is becoming narrower as time passes. Even today (2012), one is able to convert coal (a very “dirty” material) into transportation fuels in a Fischer–Tropsch process at a cost that is competitive with crude oil.

The environmental properties of the FT-synthesized transportation fuels meet or usually exceed those of crude oil-derived fuels. There are of course a number of other approaches that can be used for converting coal into transportation fuels. For example, the Exxon-Mobil methanol to gasoline process is able to convert coal first into syngas, then methanol, and then gasoline; however, the gasoline obtained by this process is high in aromatics and essentially no diesel range fuels are produced. Another variation converts the coal to low molecular weight alkenes and then further to gasoline and diesel range fuels; however, the diesel that is produced will be multiple branched and have a lower cetane number than the FT diesel.

Environmental concerns today cause governments to provide subsidies to allow renewable fuels to be utilized, as, for example, ethanol in the United States. Even without this subsidy, FT fuels are competitive with the subsidized renewables in some areas. In addition, improvements in gasification procedures are allowing fuels to be obtained from a mixture of renewables and coal so that the FT oil will have the environmental advantage over crude oil.

## 1.3

### Fuels for Transportation

#### 1.3.1

##### Internal Combustion Engines

The form in which the energy is available is important. Although it has been done (e.g., in wartime), it is unrealistic to try and run cars, trucks, or planes on coal, wood, or natural gas. Wikipedia has estimated that there were over 1 billion cars and light trucks on the road in 2010. As motor vehicles are now manufactured in many countries, developed as well as developing, the total must exceed 1.1 billion ( $10^9$ ) quite soon. Almost all of them run on liquid hydrocarbons and it has been estimated that they burn well over 1 billion cubic meters (1 Bcm, 260 billion US gallons, or  $8.5 \times 10^8$  tons) of fuel each year. The engineering has been well worked out so that the internal combustion engines are now extremely efficient for the appropriate fuel. The optimum gasoline has a high proportion of branched chain alkanes (giving a high octane number), while the best diesel has a high component of linear alkanes (with a high cetane number). It should be remembered that it will

be necessary to continue to provide fuel for all the (older) vehicles at present on our roads, as well as those currently being built and planned.

### 1.3.2

#### **Electric Cars**

There is considerable interest in using electricity for transportation and most manufacturers are making electric cars, as they are perceived to cause less pollution in their immediate neighborhoods. However, there are some serious disadvantages. Some of the problems as well as the benefits of the electric car have been amusingly illustrated by Jeremy Clarkson, the presenter of the BBC TV's very popular car show "Top Gear," when he reviewed the projected Mini E being built by BMW [5]. This car works well but requires 5088 lithium ion batteries (weighing 260 kg) and even then has a range of only 104 miles, after which it requires charging for 4.5 h. Eventually, the batteries will need replacing, the cost of which does not bear thinking about. The wide acceptance of electric cars depends on the availability of inexpensive and high-power batteries and also on the availability of national networks of fast-charging stations, which are at present hardly on the drawing board. To get round the problems, many manufacturers add on a liquid hydrocarbon fuel motor to extend both the range and the convenience of electric cars. There are many now available or coming on to the market, for example, the hybrid (electric-gasoline) Toyota Prius or the Chevrolet Volt or Ampera.

There are several serious snags on the way to commercially viable electric cars. Not only are the batteries costly and heavy, but also the lithium they require is difficult to source. The provenance of the electricity for recharging them must also be considered. Thus, the US Energy Information Agency estimates that two-thirds of world electricity is generated from fossil fuels (coal 42%, natural gas 21%, and oil 4%), 14% from nuclear and only 19% from renewables. Furthermore, it has been estimated that the average CO<sub>2</sub> output for electric cars is 128 g/km compared to an average of 105 g/km for hybrids such as the Toyota Prius, when the emissions from coal- and oil-fired electricity-generating stations are included [6]. If we want to minimize CO<sub>2</sub> production by diminishing the use of fossil fuels, given the technology available at present (2012), the nuclear option currently seems the choice for generating sustainable electricity. But that also has serious problems as the disasters at the Chernobyl, Fukushima, and Three Mile Island nuclear plants showed.

### 1.3.3

#### **Hydrogen-Powered Vehicles**

Hydrogen is a very attractive source of power as the only product of combustion is water; unfortunately, large-scale commercial applications are further in the future, even though the science is well known and hydrogen is easily made by splitting water, for example, by electrolysis or solar heating. However, the cost of doing so, in terms of the energy required, makes it very expensive.

Currently, hydrogen is produced mainly by gasification/reforming; thus, hydrogen should be considered a by-product of the petrochemicals industry in the formation of carbon monoxide, for example, from hydrocarbons:



The water-gas shift reaction (WGSR) is then employed to increase the proportion of hydrogen, but this in turn produces carbon dioxide:



Thus, the conventional production of hydrogen today is always associated with the production of  $\text{CO}_2$ .

Perhaps the development of hydrogen-powered fuel cells for cars is a promising direction [7].

One requirement for viable electric or hydrogen-powered transportation systems is the availability of widespread national grids for recharging, the setting up of which will be a mammoth and vastly expensive task. And if the electricity for the grid comes from burning fossil fuels, we have not addressed the sustainability problem – merely moved it sideways to another area.

## 1.4

### Feedstocks for the Chemical Industry

The raw materials for the organic chemicals industry are largely carbon based; in the eighteenth century, the pyrolysis of wood provided useful chemicals. In the nineteenth century, coal tar was exploited as the source of many materials, especially aromatics; while in the twentieth and twenty-first centuries, the feedstocks for many organic chemicals have been derived from oil. To that extent therefore, the supply of feedstocks for chemicals and of fuel for transportation currently run parallel and both depend on nonrenewable resources.

## 1.5

### Sustainability and Renewables: Alternatives to Fossil Fuels

It has been estimated that more solar energy strikes the Earth in 1 h ( $4.3 \times 10^{20}$  J) than is currently consumed by all mankind in a year ( $4.1 \times 10^{20}$  J). That even allows a great expansion of use as there would be more than enough. Thus, there is a continuing search for usable sources of energy that are either from renewable “bio-fuels,” and thus will not deplete our reserves, or that utilize sunlight more directly and do not involve organic intermediates, for example, some form of hydrogen generation by splitting water. The main biorenewables are fast-growing plants, trees, or algae, for example, that can be harvested and burned, directly or indirectly, with the carbon dioxide produced going back to feed more plants.

### 1.5.1

#### **Biofuels**

The best-known commercial example of biofuel manufacture is in Brazil where sugarcane grown on a very large scale is harvested and thereby sugar is extracted and fermented into alcohol that is distilled to be sold in filling stations (as *bioethanol*) to power motor vehicles. Brazil, with a population close to 200 million, has plentiful sunlight, cheap labor, and some government assistance. Prior to the discovery of large offshore oil and gas deposits, it also had the additional stimulus of a lack of home-produced oil fuel. It therefore turned to ethanol to power internal combustion engines, and most Brazilian cars are now able to run on either gasoline or alcohol. Currently, the home-produced ethanol takes care of some 13% of the country's motor fuel needs; the comparable figure is about 4% for the United States [8].

Large amounts of bioethanol, made from maize (corn), are produced in the United States, and ethanol commonly makes up 10% of the fuel at the pump (designated E10). However, it is now recognized that there are major problems with such agriculturally produced fuels. One is that the acreage of arable land needed to grow plants to power transport can seriously hinder the growing of food. This in turn impinges on the cost of food. The energy balance is also more complex than it may appear at first sight since, in addition to sunlight, considerable energy derived from fossil fuels is required to produce the ethanol. Much water is also required, and since water is also a scarce commodity, it must be conserved and recovered, which will also require energy.

It has been calculated that irrespective of crop, one acre of land, pond, or bio-reactor can annually yield enough amount of biomass to fuel one motor vehicle or meet the calorific requirement of several people. This amount of biomass therefore makes only a very small contribution to our present road transport requirements and yet can contribute significantly to global food shortages and rising prices [9, 10]. New technology to make ethanol based on lignocellulose, and which does not depend on food crops, is being actively pursued. Thus, while biomass is used as a renewable fuel, it is not yet the cure-all the world is seeking.

Other forms of biofuels are also known, such as biodiesel made from waste fats (long-chain esters); however, this has not been promoted to the extent of bioethanol and is likely to remain a minor source of energy for transportation.

### 1.5.2

#### **Other Renewable but Nonbio Fuels**

The production of energy by such means that do not involve biointermediates is a very active area of science research. There are many ways to harness solar energy: using photovoltaic cells or solar furnaces, it can be turned directly into electricity. Wind and tidal power can also be similarly harnessed; however, all these sources have the disadvantage that the energy is not continuously produced and the electricity must be stored and cabled to the site where it is needed. Although the

technology to mass-produce solar cells has improved and in some countries (Germany, Japan, Spain, and Israel) electricity from such devices is beginning to make a significant contribution to the national grid, the cost of solar power is currently estimated to be between 10 and 20 times that of power from burning coal. Storage on the scale needed to ensure that power is available nationally even during hours of darkness has also lagged behind. Because fossil fuels are still abundant and inexpensive, non-biorenewables are not likely to play a large role in primary power generation until technological or cost breakthroughs are achieved, or environment-driven carbon taxes are brought in.

## 1.6

### The Way Forward

So, where do we go? If the large-scale use of electric and hydrogen-powered cars is only over the horizon and renewable biofuels will supply a small fraction of our needs for transportation, we must make the best of what we have by improving our tools to deal with our present resources. Since major discoveries of oil and gas and coal are still being made, exact numbers are imprecise, but current best estimates indicate that our planet has enough reserves of oil for about 50 years and of natural gas for perhaps 150–200 years at current consumption levels. Coal is more plentiful and some 100–200 years supply may be available. However, the important factor is how difficult (i.e., how expensive) it will become to extract these fuels: cost is very likely to determine the uses to which fossil fuels will be put in future. The other side of the argument is of course the growth in carbon dioxide. The EIA estimates that annual CO<sub>2</sub> emissions will rise from the 2007 level of about 29.7 billion tons to around 42.4 billion tons by 2035. This 43% increase is likely to have a significant effect on many aspects of our lives, in particular through changes in our climate.

For the twin reasons of conserving our fossil fuels and curbing the increase in CO<sub>2</sub> levels, our primary concern should be in using our resources better and more efficiently. One way to do that is to improve the conversions of the raw materials into conveniently usable fuels and/or chemicals. Doing that is not necessarily straightforward or obvious. Taking natural gas (which is largely methane) as an example, while direct approaches such as partial oxidation of methane to methanol or to higher alkanes may become commercially viable in the future, the best way currently is to reform the natural gas into syngas (CO + H<sub>2</sub>) and then to build on that. The engineering needed for reforming is well established and there are many well worked out reactions making useful products from syngas. One of these is of course the Fischer–Tropsch hydrocarbon synthesis in which the syngas is converted into linear hydrocarbons that can be used either as fuel (diesel) or as chemical feedstocks. Our thesis therefore is that improvements to Fischer–Tropsch are desirable, possible, and necessary and should be developed as soon as practicable. Some other paths that are being followed are outlined in Section 1.7.