

Contents

Preface XIX

Part I Introduction 1

1	Fischer–Tropsch Facilities at a Glance	3
1.1	Introduction	3
1.2	Feed-to-Syngas Conversion	4
1.2.1	Feed Logistics and Feed Preparation	5
1.2.2	Syngas Production	5
1.2.3	Syngas Cleaning and Conditioning	7
1.3	Syngas-to-Syncrude Conversion	8
1.4	Syncrude-to-Product Conversion	10
1.4.1	Upgrading versus Refining	10
1.4.2	Fuels versus Chemicals	11
1.4.3	Crude Oil Compared to Syncrude	12
1.5	Indirect Liquefaction Economics	14
1.5.1	Feed Cost	14
1.5.2	Product Pricing	15
1.5.3	Capital Cost	17
	References	19
2	Refining and Refineries at a Glance	21
2.1	Introduction	21
2.2	Conventional Crude Oil	22
2.2.1	Hydrocarbons in Crude Oil	23
2.2.2	Sulfur Compounds in Crude Oil	23
2.2.3	Nitrogen Compounds in Crude Oil	25
2.2.4	Oxygenates in Crude Oil	25
2.2.5	Metals in Crude Oil	26
2.2.6	Physical Properties	27
2.3	Products from Crude Oil	28
2.3.1	Boiling Range and Product Quality	29
2.4	Evolution of Crude Oil Refineries	31

2.4.1	First-Generation Crude Oil Refineries	32
2.4.2	Second-Generation Crude Oil Refineries	33
2.4.3	Third-Generation Crude Oil Refineries	36
2.4.4	Fourth-Generation Crude Oil Refineries	39
2.4.5	Petrochemical Refineries	43
2.4.6	Lubricant Base Oil Refineries	44
	References	46

Part II Production of Fischer–Tropsch Syncrude 49

3 Synthesis Gas Production, Cleaning, and Conditioning 51

3.1	Introduction	51
3.2	Raw Materials	51
3.2.1	Natural Gas	51
3.2.2	Solid Carbon Sources	52
3.3	Syngas from Natural Gas	53
3.3.1	Natural Gas Cleaning	55
3.3.2	Adiabatic Preforming	55
3.3.3	Steam Reforming	56
3.3.4	Adiabatic Oxidative Reforming	56
3.3.5	Gas Reforming Comparison	57
3.4	Syngas from Solid Carbon Sources	58
3.4.1	Gasification of Heteroatoms	59
3.4.2	Low-Temperature Moving Bed Gasification	60
3.4.3	Medium-Temperature Fluidized Bed Gasification	62
3.4.4	High-Temperature Entrained Flow Gasification	64
3.4.5	Gasification Comparison	66
3.5	Syngas Cleaning	66
3.5.1	Acid Gas Removal	67
3.6	Syngas Conditioning	69
3.6.1	Water Gas Shift Conversion	69
3.7	Air Separation Unit	70
	References	71

4 Fischer–Tropsch Synthesis 73

4.1	Introduction	73
4.2	Fischer–Tropsch Mechanism	74
4.3	Fischer–Tropsch Product Selectivity	77
4.3.1	Probability of Chain Growth	78
4.3.2	Hydrogenation versus Desorption	80
4.3.3	Readsorption Chemistry	81
4.4	Selectivity Manipulation in Fischer–Tropsch Synthesis	81
4.4.1	Fischer–Tropsch Catalyst Formulation	81
4.4.2	Fischer–Tropsch Operating Conditions	83
4.4.3	Fischer–Tropsch Reaction Engineering	84

4.5	Fischer–Tropsch Catalyst Deactivation	88
4.5.1	Poisoning by Syngas Contaminants	89
4.5.2	Volatile Metal Carbonyl Formation	90
4.5.3	Metal Carboxylate Formation	91
4.5.4	Mechanical Catalyst Degradation	92
4.5.5	Deactivation of Fe-HTFT Catalysts	93
4.5.6	Deactivation of Fe-LTFT Catalysts	93
4.5.7	Deactivation of Co-LTFT Catalysts	95
	References	99
5	Fischer–Tropsch Gas Loop	105
5.1	Introduction	105
5.2	Gas Loop Configurations	107
5.2.1	Open Gas Loop Design	107
5.2.2	Closed Gas Loop Design	108
5.3	Syncrude Cooling and Separation	109
5.3.1	Pressure Separation	110
5.3.2	Cryogenic Separation	110
5.3.3	Oxygenate Partitioning	111
5.3.4	HTFT Syncrude Recovery	113
5.3.5	LTFT Syncrude Recovery	114
	References	116
Part III	Industrial Fischer–Tropsch Facilities	117
6	German Fischer–Tropsch Facilities	119
6.1	Introduction	119
6.2	Synthesis Gas Production	119
6.3	Fischer–Tropsch Synthesis	121
6.3.1	Normal-Pressure Synthesis	122
6.3.2	Medium-Pressure Synthesis	125
6.3.3	Gas Loop Design	127
6.3.4	Carbon Efficiency	128
6.4	Fischer–Tropsch Refining	128
6.4.1	Refining C ₃ –C ₄ Crude LPG	129
6.4.2	Refining Carbon Gasoline	130
6.4.3	Refining of Condensate Oil	132
6.4.4	Refining of Waxes	135
6.4.5	Aqueous Product Refining	136
6.5	Discussion of the Refinery Design	137
	References	138
7	American Hydrocol Facility	141
7.1	Introduction	141
7.2	Synthesis Gas Production	142

7.3	Fischer–Tropsch Synthesis	143
7.4	Fischer–Tropsch Refining	145
7.4.1	Oil Product Refining	146
7.4.2	Refining Aqueous Product	149
7.5	Discussion of the Refinery Design	150
	References	151
8	Sasol 1 Facility	153
8.1	Introduction	153
8.2	Synthesis Gas Production	154
8.2.1	Lurgi Dry Ash Coal Gasification	154
8.2.2	Rectisol Synthesis Gas Cleaning	155
8.3	Fischer–Tropsch synthesis	157
8.3.1	Kellogg HTFT synthesis	157
8.3.2	Arge LTFT Synthesis	159
8.3.3	Gas Loop Design	162
8.4	Fischer–Tropsch Refining	163
8.4.1	Kellogg HTFT Oil Refining	163
8.4.2	Arge LTFT Oil Refining	165
8.4.3	Aqueous Product Refining	166
8.4.4	Coal Pyrolysis Product Refining	169
8.4.5	Synthetic Fuel Properties	170
8.5	Evolution of the Sasol 1 Facility	172
8.5.1	Changes in Synthesis Gas Production	172
8.5.2	Changes in Fischer–Tropsch Synthesis	173
8.5.3	Changes in Fischer–Tropsch Refining	174
8.5.4	Changes in Coal Pyrolysis Product Refining	177
8.6	Discussion of the Refinery Design	177
	References	179
9	Sasol 2 and 3 Facilities	181
9.1	Introduction	181
9.2	Synthesis Gas Production	182
9.2.1	Lurgi Dry Ash Coal Gasification	182
9.2.2	Synthesis Gas Cleaning	182
9.3	Fischer–Tropsch Synthesis	183
9.3.1	Gas Loop Design	184
9.4	Fischer–Tropsch Refining	186
9.4.1	Synthol HTFT Condensate Refining	188
9.4.2	Synthol HTFT Oil Refining	192
9.4.3	Aqueous Product Refining	194
9.4.4	Coal Pyrolysis Product Refining	196
9.4.5	Synthetic Fuel Properties	198
9.5	Evolution of Sasol Synfuels	199
9.5.1	Changes in Synthesis Gas Production	201

9.5.2	Changes in Fischer–Tropsch Synthesis	201
9.5.3	Changes in Fischer–Tropsch Condensate Refining	202
9.5.4	Extraction of Linear 1-Alkenes	204
9.5.5	Changes in Fischer–Tropsch Oil Refining	205
9.5.6	Changes in Fischer–Tropsch Aqueous Product Refining	210
9.5.7	Changes in Coal Pyrolysis Product Refining	211
9.5.8	Synthetic Jet Fuel	212
9.6	Discussion of the Refinery Design	212
	References	214
10	Mossgas Facility	217
10.1	Introduction	217
10.2	Synthesis Gas Production	218
10.2.1	Natural Gas Liquid Recovery	218
10.2.2	Gas Reforming	218
10.3	Fischer–Tropsch Synthesis	220
10.3.1	Gas Loop Design	221
10.4	Fischer–Tropsch Refining	222
10.4.1	Oil Refining	222
10.4.2	Aqueous Product Refining	225
10.4.3	Synthetic Fuel Properties	227
10.5	Evolution of the PetroSA Facility	227
10.5.1	Addition of Low-Temperature Fischer–Tropsch Synthesis	227
10.5.2	Changes in the Fischer–Tropsch Refinery	227
10.6	Discussion of the Refinery Design	228
	References	229
11	Shell Middle Distillate Synthesis (SMDS) Facilities	231
11.1	Introduction	231
11.2	Synthesis Gas Production in Bintulu GTL	232
11.3	Fischer–Tropsch Synthesis in Bintulu GTL	233
11.4	Fischer–Tropsch Refining in Bintulu GTL	235
11.4.1	Oil Refining	235
11.4.2	Aqueous Product Treatment	238
11.5	Pearl GTL Facility	238
11.6	Discussion of the Refinery Design	239
	References	239
12	Oryx and Escravos Gas-to-Liquids Facilities	241
12.1	Introduction	241
12.2	Synthesis Gas Production in Oryx GTL	242
12.3	Fischer–Tropsch Synthesis in Oryx GTL	243
12.4	Fischer–Tropsch Refining in Oryx GTL	244
12.4.1	Oil Refining	244
12.4.2	Aqueous Product Treatment	247

12.5	Discussion of the Refinery Design	247
	References	248

Part IV Synthetic Transportation Fuels 249

13	Motor-Gasoline	251
13.1	Introduction	251
13.2	Motor-Gasoline Specifications	252
13.3	Motor-Gasoline Properties	253
13.3.1	Octane Number	253
13.3.2	Density	259
13.3.3	Volatility	259
13.3.4	Fuel Stability	261
13.3.5	Alkene Content	261
13.3.6	Aromatic Content	262
13.3.7	Sulfur Content	262
13.3.8	Oxygenate Content	262
13.3.9	Metal Content	263
13.4	Aviation-Gasoline	264
13.5	Future Motor-Gasoline Specification Changes	265
	References	266

14	Jet Fuel	269
14.1	Introduction	269
14.2	Jet Fuel Specifications	270
14.2.1	Synthetic Jet Fuel	271
14.2.2	Fuel for Military Use	272
14.3	Jet Fuel Properties	273
14.3.1	Net Heat of Combustion	274
14.3.2	Density and Viscosity	275
14.3.3	Freezing Point Temperature	276
14.3.4	Aromatic Content and Smoke Point	276
14.3.5	Sulfur and Acid Content	278
14.3.6	Volatility	278
14.3.7	Stability	278
14.3.8	Elastomer Compatibility and Lubricity	279
14.4	Future Jet Fuel Specification Changes	280
	References	280

15	Diesel Fuel	283
15.1	Introduction	283
15.2	Diesel Fuel Specifications	284
15.3	Diesel Fuel Properties	286
15.3.1	Cetane Number	286
15.3.2	Density and Viscosity	290

15.3.3	Flash Point	290
15.3.4	Lubricity	290
15.3.5	Aromatic Content	292
15.3.6	Sulfur Content	292
15.3.7	Cold-Flow Properties	293
15.3.8	Stability	294
15.3.9	Elastomer Compatibility	294
15.4	Diesel Fuel Additives That Affect Refinery Design	295
15.5	Future Diesel Fuel Specification Changes	296
	References	297

Part V Refining Technology 301

16	Refining Technology Selection	303
16.1	Introduction	303
16.2	Hydrotreating	305
16.2.1	Hydrogenation of Alkenes	306
16.2.2	Hydrodeoxygenation	307
16.3	Addition and Removal of Oxygen	308
16.3.1	Dehydration	308
16.3.2	Etherification	309
16.3.3	Hydration	309
16.3.4	Esterification	310
16.3.5	Carbonyl Aromatization	310
16.3.6	Hydroformylation	311
16.3.7	Autoxidation	311
16.4	Alkene Conversion	312
16.4.1	Double Bond Isomerization	312
16.4.2	Metathesis	314
16.4.3	Skeletal Isomerization	314
16.4.4	Oligomerization	315
16.4.5	Aliphatic Alkylation	316
16.4.6	Aromatic Alkylation	317
16.5	Alkane Conversion	319
16.5.1	Hydroisomerization	319
16.5.2	Hydrocracking	320
16.5.3	Naphtha Reforming and Aromatization	321
16.5.4	Dehydrogenation	322
16.6	Residue Conversion	323
16.6.1	Catalytic Cracking	323
16.6.2	Visbreaking	324
16.6.3	Thermal Cracking	324
16.6.4	Coking	326
16.7	Fischer–Tropsch Refining Technology Selection	326
	References	328

17	Dehydration, Etherification, and Hydration	335
17.1	Introduction	335
17.2	Dehydration	336
17.2.1	Reaction Chemistry	339
17.2.2	Catalysis	340
17.2.3	Syncrude Process Technology	341
17.3	Etherification	343
17.3.1	Reaction Chemistry	345
17.3.2	Catalysis	346
17.3.3	Syncrude Process Technology	347
17.4	Hydration	347
17.4.1	Reaction Chemistry	349
17.4.2	Catalysis	349
17.4.3	Syncrude Process Technology	350
	References	350
18	Isomerization	353
18.1	Introduction	353
18.2	Reaction Chemistry	354
18.2.1	Alkene Skeletal Isomerization	354
18.2.2	Alkane Hydroisomerization	356
18.3	Skeletal Isomerization	357
18.3.1	Butene Isomerization Catalysis	358
18.3.2	Pentene Isomerization Catalysis	359
18.3.3	Syncrude Process Technology	360
18.4	Hydroisomerization	360
18.4.1	Butane Hydroisomerization Catalysis	362
18.4.2	C ₅ –C ₆ Naphtha Hydroisomerization Catalysis	362
18.4.3	Heavy Alkane and Wax Hydroisomerization Catalysis	364
18.4.4	Syncrude Process Technology	364
	References	366
19	Oligomerization	369
19.1	Introduction	369
19.2	Reaction Chemistry	372
19.3	Catalysis	374
19.3.1	Solid Phosphoric Acid	375
19.3.2	H-ZSM-5 Zeolite	378
19.3.3	Amorphous Silica–Alumina	380
19.3.4	Acidic Resin	381
19.3.5	Homogeneous Nickel	383
19.3.6	Thermal Oligomerization	384
19.4	Syncrude Process Technology	385
	References	388

20	Aromatic Alkylation	393
20.1	Introduction	393
20.2	Reaction Chemistry	395
20.3	Catalysis	396
20.3.1	Aromatic Alkylation with Ethene	397
20.3.2	Aromatic Alkylation with Propene	399
20.3.3	Aromatic Alkylation with C ₄ and Heavier Alkenes	401
20.4	Syncrude Process Technology	403
	References	405
21	Cracking	407
21.1	Introduction	407
21.2	Reaction Chemistry	410
21.2.1	Thermal Cracking	410
21.2.2	Catalytic Cracking	414
21.2.3	Hydrocracking	416
21.3	Thermal Cracking	419
21.3.1	Syncrude Processing Technology	421
21.4	Catalytic Cracking	421
21.4.1	Catalysis	423
21.4.2	Syncrude Processing Technology	425
21.5	Hydrocracking	427
21.5.1	Catalysis	430
21.5.2	Syncrude Processing Technology	434
	References	436
22	Reforming and Aromatization	441
22.1	Introduction	441
22.2	Thermal Naphtha Reforming	443
22.3	Conventional Catalytic Naphtha Reforming	444
22.3.1	Reaction Chemistry	444
22.3.2	Catalysis	447
22.3.3	Syncrude Processing Technology	449
22.4	Monofunctional Nonacidic Pt/L-Zeolite Naphtha Reforming	450
22.4.1	Reaction Chemistry	451
22.4.2	Catalysis	452
22.4.3	Syncrude Processing Technology	453
22.5	Aromatization	454
22.5.1	Reaction Chemistry	456
22.5.2	Catalysis	457
22.5.3	Syncrude Processing Technology	460
	References	461
23	Chemical Technologies	465
23.1	Introduction	465

23.2	Production of <i>n</i> -1-Alkenes (Linear α -Olefins)	466
23.2.1	Extraction of 1-Pentene and 1-Hexene	467
23.2.2	Extraction of 1-Octene	470
23.2.3	Production of 1-Octene from 1-Heptene	473
23.2.4	Distillate-Range <i>n</i> -1-Alkene Extraction	474
23.3	Autoxidation	474
23.3.1	Autoxidation Regimes	477
23.3.2	Reaction Chemistry	478
23.3.3	Fischer–Tropsch Wax Oxidation	480
23.3.4	Syncrude Process Technology	484
	References	485

Part VI Refinery Design 489

24	Principles of Refinery Design	491
24.1	Introduction	491
24.2	Refinery Design Concepts	491
24.2.1	Characteristic of the Refining Business	491
24.2.2	Complex Systems and Design Rules	493
24.2.3	Refining Complexity	495
24.2.4	Refining Efficiency	496
24.3	Conceptual Refinery Design	497
24.3.1	Linear Programming	497
24.3.2	Hierarchical Design	498
24.3.3	Technology Preselection	498
24.3.4	Carbon-Number-Based Design	499
24.4	Real-World Refinery Design	500
24.4.1	Refinery Type	501
24.4.2	Refinery Products and Markets	501
24.4.3	Refinery Feed Selection	502
24.4.4	Refinery Location	503
24.4.5	Secondary Design Objectives	506
	References	508
25	Motor-Gasoline Refining	509
25.1	Introduction	509
25.2	Gap Analysis for Syncrude to Motor-Gasoline	510
25.2.1	Motor-Gasoline Specifications	510
25.2.2	Carbon Number Distribution	511
25.2.3	Composition and Quality	512
25.3	Decisions Affecting Motor-Gasoline Refining	514
25.3.1	Chemicals Coproduction	514
25.3.2	Fate of C ₂ –C ₄ Hydrocarbons	515
25.3.3	Fate of the Residue and Wax	516
25.3.4	Fate of the Aqueous Product	517

25.3.5	Alkane-Based Naphtha Refining	518
25.3.6	Technology Selection	519
25.3.7	Co-refining	521
25.4	Motor-Gasoline Refining from HTFT Syncrude	522
25.4.1	HTFT Motor-Gasoline Design Case I	522
25.4.2	HTFT Motor-Gasoline Design Case II	526
25.5	Motor-Gasoline Refining from LTFT Syncrude	529
25.5.1	LTFT Motor-Gasoline Design Case I	529
25.5.2	LTFT Motor-Gasoline Design Case II	534
25.5.3	LTFT Motor-Gasoline Design Case III	537
	References	539
26	Jet Fuel Refining	541
26.1	Introduction	541
26.2	Gap Analysis for Syncrude to Jet Fuel	541
26.2.1	Jet Fuel Specifications	541
26.2.2	Carbon Number Distribution	542
26.2.3	Composition and Quality	542
26.3	Decisions Affecting Jet Fuel Refining	544
26.3.1	Fate of C ₂ –C ₄ Hydrocarbons	544
26.3.2	Fate of the Residue and Wax	545
26.3.3	Technology Selection	546
26.3.4	Co-refining	547
26.4	Jet Fuel Refining from HTFT Syncrude	548
26.4.1	HTFT Jet Fuel Design Case I	549
26.4.2	HTFT Jet Fuel Design Case II	552
26.5	Jet Fuel Refining from LTFT Syncrude	553
26.5.1	LTFT Jet Fuel Design Case I	555
	References	558
27	Diesel Fuel Refining	559
27.1	Introduction	559
27.2	Gap Analysis for Syncrude to Diesel Fuel	560
27.2.1	Diesel Fuel Specifications	560
27.2.2	Carbon Number Distribution	561
27.2.3	Composition and Quality	562
27.2.4	Density–Cetane–Yield Triangle	563
27.3	Decisions Affecting Diesel Fuel Refining	564
27.3.1	Fate of C ₂ –C ₄ Hydrocarbons	565
27.3.2	Fate of the Residue and Wax	565
27.3.3	Fate of the Aqueous Product	565
27.3.4	Technology Selection	566
27.3.5	Co-refining	567
27.3.6	Dealing with the Density–Cetane–Yield Triangle	569
27.4	Diesel Fuel Refining from HTFT Syncrude	570

27.4.1	HTFT Diesel Fuel Design Case I	570
27.5	Diesel Fuel Refining from LTFT Syncrude	573
27.5.1	LTFT Diesel Fuel Design Case I	573
27.5.2	LTFT Diesel Fuel Design Case II	576
	References	578
28	Chemicals and Lubricant Refining	581
28.1	Introduction	581
28.2	Petrochemical and Lubricant Markets	582
28.2.1	Petrochemicals	582
28.2.2	Lubricants	584
28.3	Overview of Chemicals Refining Concepts for Syncrude	585
28.3.1	Alkane-Based Refining	585
28.3.2	Aromatics Production	586
28.3.3	Alkene and Oxygenate Recovery	587
28.3.4	Fuels and Chemicals Coproduction	588
28.4	Fischer–Tropsch-Based Petrochemical Refining	591
28.4.1	Alkane Refining	591
28.4.2	Light Alkene Refining	592
28.4.3	Linear 1-Alkene Refining	594
28.4.4	Aromatics Refining	595
28.4.5	Oxygenate Refining	597
28.5	Fischer–Tropsch-Based Lubricant Base Oil Refining	597
28.5.1	Group III Lubricant Refining	598
28.5.2	Group IV Lubricant Refining	599
28.5.3	Lubricant Base Oil Refining	600
	References	601
	Index	603