

# Hydrogen and Syngas Production and Purification Technologies

*Ke Liu*  
*Chunshan Song*  
*Velu Subramani*

# Contents

Preface      xiii

Contributors      xv

**1. Introduction to Hydrogen and Syngas Production and Purification Technologies**      **1**

*Chunshan Song*

---

- 1.1 Importance of Hydrogen and Syngas Production      1
- 1.2 Principles of Syngas and Hydrogen Production      4
- 1.3 Options for Hydrogen and Syngas Production      6
- 1.4 Hydrogen Energy and Fuel Cells      8
- 1.5 Fuel Processing for Fuel Cells      9
- 1.6 Sulfur Removal      10
- 1.7 CO<sub>2</sub> Capture and Separation      11
- 1.8 Scope of the Book      11
- Acknowledgments      12
- References      12

**2. Catalytic Steam Reforming Technology for the Production of Hydrogen and Syngas**      **14**

*Velu Subramani, Pradeepkumar Sharma, Lingzhi Zhang, and Ke Liu*

---

- 2.1 Introduction      14
- 2.2 Steam Reforming of Light Hydrocarbons      17
  - 2.2.1 Steam Reforming of Natural Gas      17
  - 2.2.2 Steam Reforming of C<sub>2</sub>-C<sub>4</sub> Hydrocarbons      36
- 2.3 Steam Reforming of Liquid Hydrocarbons      46
  - 2.3.1 Chemistry      46
  - 2.3.2 Thermodynamics      47
  - 2.3.3 Catalyst      52
  - 2.3.4 Kinetics      58
  - 2.3.5 Mechanism      61
  - 2.3.6 Prereforming      61
- 2.4 Steam Reforming of Alcohols      65
  - 2.4.1 Steam Reforming of Methanol (SRM)      65
  - 2.4.2 Steam Reforming of Ethanol (SRE)      77
- 2.5 Carbon Formation and Catalyst Deactivation      106

2.6	Recent Developments in Reforming Technologies	109
2.6.1	Microreactor Reformer	109
2.6.2	Plate Reformer	110
2.6.3	Membrane Reformer	110
2.6.4	Plasma Reforming (PR)	112
2.7	Summary	112
	References	112
<b>3.</b>	<b>Catalytic Partial Oxidation and Autothermal Reforming</b>	<b>127</b>
	<i>Ke Liu, Gregg D. Deluga, Anders Bitsch-Larsen, Lanny D. Schmidt, and Lingzhi Zhang</i>	
3.1	Introduction	127
3.2	Natural Gas Reforming Technologies: Fundamental Chemistry	130
3.2.1	ATR	130
3.2.2	Homogeneous POX	132
3.2.3	CPO	133
3.3	Development/Commercialization Status of ATR, POX, and CPO Reformers	136
3.4	CPO Catalysts	138
3.4.1	Nickel-Based CPO Catalysts	138
3.4.2	Precious Metal CPO Catalysts	142
3.5	CPO Mechanism and Kinetics	146
3.5.1	Ni Catalyst Mechanism and Reactor Kinetics Modeling	146
3.5.2	Precious Metal Catalyst Mechanism and Reactor Kinetics Modeling	147
3.6	Start-Up and Shutdown Procedure of CPO	149
3.7	CPO of Renewable Fuels	150
3.8	Summary	151
	Acknowledgments	151
	References	151
<b>4.</b>	<b>Coal Gasification</b>	<b>156</b>
	<i>Ke Liu, Zhe Cui, and Thomas H. Fletcher</i>	
4.1	Introduction to Gasification	156
4.2	Coal Gasification History	158
4.3	Coal Gasification Chemistry	160
4.3.1	Pyrolysis Process	161
4.3.2	Combustion of Volatiles	163
4.3.3	Char Gasification Reactions	164
4.3.4	Ash-Slag Chemistry	166
4.4	Gasification Thermodynamics	169
4.5	Gasification Kinetics	173
4.5.1	Reaction Mechanisms and the Kinetics of the Boudouard Reaction	174
4.5.2	Reaction Mechanisms and the Kinetics of the Water-Gas Reaction	175

4.6	Classification of Different Gasifiers	176
4.7	GE (Texaco) Gasification Technology with CWS Feeding	178
4.7.1	Introduction to GE Gasification Technology	178
4.7.2	GE Gasification Process	179
4.7.3	Coal Requirements of the GE Gasifier	184
4.7.4	Summary of GE Slurry Feeding Gasification Technology	186
4.8	Shell Gasification Technology with Dry Feeding	187
4.8.1	Introduction to Dry-Feeding Coal Gasification	187
4.8.2	Shell Gasification Process	189
4.8.3	Coal Requirements of Shell Gasification Process	193
4.8.4	Summary of Dry-Feeding Shell Gasifier	194
4.9	Other Gasification Technologies	195
4.9.1	GSP Gasification Technology	195
4.9.2	East China University of Science and Technology (ECUST) Gasifier	198
4.9.3	TPRI Gasifier	199
4.9.4	Fluidized-Bed Gasifiers	199
4.9.5	ConocoPhillips Gasifier	202
4.9.6	Moving-Bed and Fixed-Bed Gasifiers: Lurgi's Gasification Technology	203
4.9.7	Summary of Different Gasification Technologies	205
4.10	Challenges in Gasification Technology: Some Examples	206
4.10.1	High AFT Coals	206
4.10.2	Increasing the Coal Concentration in the CWS	207
4.10.3	Improved Performance and Life of Gasifier Nozzles	208
4.10.4	Gasifier Refractory Brick Life	208
4.10.5	Gasifier Scale-Up	209
4.11	Syngas Cleanup	210
4.12	Integration of Coal Gasification with Coal Polygeneration Systems	215
	References	216

## 5. Desulfurization Technologies

219

*Chunshan Song and Xiaoliang Ma*

---

5.1	Challenges in Deep Desulfurization for Hydrocarbon Fuel Processing and Fuel Cell Applications	219
5.2	HDS Technology	225
5.2.1	Natural Gas	225
5.2.2	Gasoline	226
5.2.3	Diesel	233
5.3	Adsorptive Desulfurization	243
5.3.1	Natural Gas	244
5.3.2	Gasoline	246
5.3.3	Jet Fuel	256
5.3.4	Diesel	258
5.4	Post-Reformer Desulfurization: H <sub>2</sub> S Sorption	264
5.4.1	H <sub>2</sub> S Sorbents	265
5.4.2	H <sub>2</sub> S Adsorption Thermodynamics	268

5.5	Desulfurization of Coal Gasification Gas	272
5.5.1	Absorption by Solvents	275
5.5.2	Hot and Warm Gas Cleanup	291
5.6	ODS	293
5.6.1	Natural Gas	293
5.6.2	Liquid Hydrocarbon Fuels	295
5.7	Summary	298
	References	300

## 6. Water-Gas Shift Technologies

311

*Alex Platon and Yong Wang*

---

6.1	Introduction	311
6.2	Thermodynamic Considerations	312
6.3	Industrial Processes and Catalysts	313
6.3.1	Ferrocchrome Catalyst for HTS Reaction	313
6.3.2	CuZn Catalysts for LTS Reaction	314
6.3.3	CoMo Catalyst for LTS Reaction	314
6.4	Reaction Mechanism and Kinetics	315
6.4.1	Ferrocchrome Catalyst	315
6.4.2	CuZn-Based Catalyst	317
6.4.3	CoMo Catalyst	317
6.5	Catalyst Improvements and New Classes of Catalysts	318
6.5.1	Improvements to the Cu- and Fe-Based Catalysts	318
6.5.2	New Reaction Technologies	319
6.5.3	New Classes of Catalysts	321
	References	326

## 7. Removal of Trace Contaminants from Fuel Processing Reformate: Preferential Oxidation (Prox)

329

*Marco J. Castaldi*

---

7.1	Introduction	329
7.2	Reactions of Prox	331
7.3	General Prox Reactor Performance	333
7.3.1	Multiple Steady-State Operation	337
7.3.2	Water–Oxygen Synergy	339
7.4	Catalysts Formulations	342
7.5	Reactor Geometries	344
7.5.1	Monolithic Reactors	345
7.5.2	SCT Reactors	346
7.5.3	Microchannel Reactors	349
7.5.4	MEMS-Based Reactors	350
7.6	Commercial Units	352
	Acknowledgments	353
	References	353

**8. Hydrogen Membrane Technologies and Application in Fuel Processing** 357  
*David Edlund*

---

- 8.1 Introduction 357
- 8.2 Fundamentals of Membrane-Based Separations 358
- 8.3 Membrane Purification for Hydrogen Energy and Fuel Cell Applications 363
  - 8.3.1 Product Hydrogen Purity 365
  - 8.3.2 Process Scale 367
  - 8.3.3 Energy Efficiency 368
- 8.4 Membrane Modules for Hydrogen Separation and Purification 369
- 8.5 Dense Metal Membranes 372
  - 8.5.1 Metal Membrane Durability and Selectivity 375
- 8.6 Integration of Reforming and Membrane-Based Purification 378
- 8.7 Commercialization Activities 380
- References 383

**9. CO<sub>2</sub>-Selective Membranes for Hydrogen Fuel Processing** 385  
*Jin Huang, Jian Zou, and W.S. Winston Ho*

---

- 9.1 Introduction 385
- 9.2 Synthesis of Novel CO<sub>2</sub>-Selective Membranes 388
- 9.3 Model Description 389
- 9.4 Results and Discussion 391
  - 9.4.1 Transport Properties of CO<sub>2</sub>-Selective Membrane 391
  - 9.4.2 Modeling Predictions 400
- 9.5 Conclusions 408
  - Glossary 410
  - Acknowledgments 410
  - References 411

**10. Pressure Swing Adsorption Technology for Hydrogen Production** 414  
*Shivaji Sircar and Timothy C. Golden*

---

- 10.1 Introduction 414
- 10.2 PSA Processes for Hydrogen Purification 418
  - 10.2.1 PSA Processes for Production of Hydrogen Only 418
  - 10.2.2 Process for Coproduction of Hydrogen and Carbon Dioxide 422
  - 10.2.3 Processes for the Production of Ammonia Synthesis Gas 425
- 10.3 Adsorbents for Hydrogen PSA Processes 426
  - 10.3.1 Adsorbents for Bulk CO<sub>2</sub> Removal 427
  - 10.3.2 Adsorbents for Dilute CO and N<sub>2</sub> Removal 429
  - 10.3.3 Adsorbents for Dilute CH<sub>4</sub> Removal 432
  - 10.3.4 Adsorbents for C<sub>1</sub>-C<sub>4</sub> Hydrocarbon Removal 432
  - 10.3.5 Other Adsorbent and Related Improvements in the H<sub>2</sub> PSA 434

10.4	Future Trends for Hydrogen PSA	435
10.4.1	RPSA Cycles for Hydrogen Purification	436
10.4.2	Structured Adsorbents	438
10.4.3	Sorption-Enhanced Reaction Process (SERP) for H <sub>2</sub> Production	439
10.5	PSA Process Reliability	441
10.6	Improved Hydrogen Recovery by PSA Processes	441
10.6.1	Integration with Additional PSA System	441
10.6.2	Hybrid PSA-Adsorbent Membrane System	442
10.7	Engineering Process Design	444
10.8	Summary	447
	References	447

**11. Integration of H<sub>2</sub>/Syngas Production Technologies with Future Energy Systems** **451**

*Wei Wei, Parag Kulkarni, and Ke Liu*

---

11.1	Overview of Future Energy Systems and Challenges	451
11.2	Application of Reforming-Based Syngas Technology	454
11.2.1	NGCC Plants	454
11.2.2	Integration of H <sub>2</sub> /Syngas Production Technologies in NGCC Plants	455
11.3	Application of Gasification-Based Syngas Technology	465
11.3.1	IGCC Plant	468
11.4	Application of H <sub>2</sub> /Syngas Generation Technology to Liquid Fuels	477
11.4.1	Coal-to-H <sub>2</sub> Process Description	479
11.4.2	Coal-to-Hydrogen System Performance and Economics	481
11.5	Summary	483
	References	483

**12. Coal and Syngas to Liquids** **486**

*Ke Liu, Zhe Cui, Wei Chen, and Lingzhi Zhang*

---

12.1	Overview and History of Coal to Liquids (CTL)	486
12.2	Direct Coal Liquefaction (DCTL)	488
12.2.1	DCTL Process	488
12.2.2	The Kohleel Process	490
12.2.3	NEDOL (NEDO Liquefaction) Process	491
12.2.4	The HTI-Coal Process	494
12.2.5	Other Single-Stage Processes	495
12.3	Indirect Coal to Liquid (ICTL)	496
12.3.1	Introduction	496
12.3.2	FT Synthesis	498
12.4	Mobil Methanol to Gasoline (MTG)	510
12.5	SMDS	511

12.6	Hybrid Coal Liquefaction	512	
12.7	Coal to Methanol	513	
	12.7.1 Introduction of Methanol Synthesis	513	
	12.7.2 Methanol Synthesis Catalysts	514	
	12.7.3 Methanol Synthesis Reactor Systems	514	
	12.7.4 Liquid-Phase Methanol (LPMEOH™) Process	516	
12.8	Coal to Dimethyl Ether (DME)	519	
	References	520	
<b>Index</b>	<b>522</b>		