

Contents

Foreword *xi*

Preface *xiii*

Part I Introduction 1

1	Refinery and Petrochemical Processes	3
1.1	Introduction	3
1.2	Petroleum	3
1.2.1	Forms of Petroleum	4
1.2.1.1	Gaseous Petroleum: Gaseous Petroleum Can Be Defined as Natural Gas or Shale Gas	4
1.2.1.2	Liquid Petroleum: Liquid Petroleum Can Be Separated into Light Crude Oil and Heavy Crude Oil	4
1.2.1.3	Solid Petroleum: Bitumen	5
1.2.2	Composition of Petroleum	5
1.2.3	Petroleum Refinery	6
1.2.4	Petroleum Products	9
1.3	Petrochemical Building Blocks	10
	References	16
2	Petrochemical Markets	17
2.1	Introduction	17
2.2	The Market for Ethylene	18
2.3	The Market for Propylene	22
2.4	The Market for C4 Olefins and Diolefins	26
2.5	The Market for Aromatic Compounds	32
2.5.1	The Market for Benzene	32
2.5.2	The Market for Toluene	34
2.5.3	The Market for Xylene	36
2.6	The Market for Synthesis Gas	37

2.6.1	The Market for Ammonia	38
2.6.2	The Market for Methanol	39
	References	40

Part II Olefins and Synthesis Gas 43

3 Olefins and Synthesis Gas Production Technologies 45

3.1	Introduction	45
3.2	Steam Cracking	45
3.3	Light Paraffin Dehydrogenation	48
3.3.1	Process and Catalyst	48
3.3.1.1	Reactor Section	49
3.3.1.2	Product Recovery Section	50
3.3.1.3	Catalyst Regeneration Section	50
3.3.2	UOP C ₃ Oleflex Complex	51
3.3.3	UOP Iso-C ₄ Oleflex Complex	54
3.3.4	UOP C ₃ /C ₄ Oleflex Complex	56
3.3.5	UOP Mixed-C ₄ Oleflex Complex	56
3.4	Heavy Normal-paraffin Dehydrogenation	57
3.4.1	Production of Normal-paraffins	58
3.4.2	Production of LAB	59
3.5	Methanol to Olefins	59
3.6	Syngas Production	62
3.6.1	Removal of Impurities in Raw Natural Gas	63
3.6.2	Conversion of Natural Gas to Syngas	64
3.6.2.1	Steam Reforming	65
3.6.2.2	Partial Oxidation	65
3.6.2.3	Autothermal Reforming	66
3.6.3	Coal Gasification to Syngas	67
	References	72

4 Uses of Olefins and Synthesis Gas 75

4.1	Introduction	75
4.2	Uses of Ethylene	75
4.2.1	Ethylene to Polyethylene	75
4.2.2	Ethylene to Polyvinyl Chloride	77
4.2.3	Ethylene to Monoethylene Glycol	78
4.3	Uses of Propylene	79
4.3.1	Propylene to Polypropylene	79
4.3.2	Propylene to Propylene Oxide	80
4.3.3	Propylene to Acrylonitrile	81
4.4	Uses of Syngas	82
4.4.1	Syngas to Hydrogen	82
4.4.2	Syngas to Ammonia	82
4.4.3	Syngas to Methanol	83
	References	83

Part III Aromatics 85

5	Aromatic Production Technologies	87
5.1	Introduction	87
5.2	Aromatic Production	87
5.2.1	Reforming Technology	88
5.2.1.1	Semi-regenerative Reforming	91
5.2.1.2	Cyclic Reforming	91
5.2.1.3	CCR Reforming	91
5.2.1.4	High-pressure vs. Low-pressure Consideration	94
5.2.2	Aromatic Transalkylation and Disproportionation Technology	95
5.2.2.1	Selective Toluene Disproportionation Process	99
5.2.3	Isomerization of Aromatics	100
5.2.3.1	Reaction Mechanism	100
5.2.4	Toluene Methylation	103
5.2.5	Aromatization of Light Naphtha/Hydrocarbons	105
5.2.5.1	Mechanism	106
5.2.6	Catalytic Cracking	107
5.2.7	Production from Pyrolysis and Coking	111
5.2.7.1	Steam Cracking/Pyrolysis Gasoline	111
5.2.7.2	Coke-oven Benzole	113
5.2.7.3	Biomass Pyrolysis	115
5.3	Summary	119
	References	119
6	Uses of Aromatics	121
6.1	Introduction	121
6.2	Polymer Production from Basic Aromatic Building Blocks	121
6.2.1	Ethylbenzene and Styrene Production	122
6.2.2	Cyclohexane to Nylon 6, Nylon 6,6	123
6.2.2.1	Adipic Acid Production	124
6.2.2.2	Caprolactam Synthesis	125
6.2.2.3	Properties of Nylon 6 vs. Nylon 6,6	128
6.2.3	Production of Cumene	128
6.2.3.1	Bisphenol A production	130
6.2.3.2	Production of Nitrobenzene	130
6.2.3.3	Production of Aniline	131
6.2.3.4	Production of MDI and Poly-MDI (PMDI)	131
6.2.3.5	Production of Toluene Diisocyanate (TDI)	131
6.2.3.6	Production of Polyurethane	132
6.2.3.7	Alkylbenzenes and Alkylbenzene Sulfonates	132
6.2.3.8	Maleic Anhydride from Benzene	133
6.2.3.9	Dichlorodiphenyltrichloroethane (DDT) from Benzene	133
6.3	Resins and Chemicals Production	133
6.3.1	Unsaturated Polyester Resins Synthesis	138
6.3.2	Alkyd Resin Synthesis:	139

- 6.3.3 *p*-Xylene Oxidation to Terephthalic Acid 139
- 6.3.4 Poly(ethylene terephthalate), PET, and Poly(ethylene naphthalate), PEN 141
- 6.4 Summary 142
- Acknowledgments 142
- References 143

Part IV Industrial Separation 145

- 7 Adsorption 147**
 - 7.1 Principle of Adsorption 147
 - 7.2 Adsorbents 148
 - 7.2.1 Zeolite Adsorbents 148
 - 7.2.2 Zeolite Synthesis 150
 - 7.2.3 Forming Zeolite Powders into Usable Shapes 152
 - 7.2.3.1 Pelletization of Zeolite Powder to Extrudate Adsorbent 153
 - 7.2.3.2 Accretion of Zeolite Powder to Bead Adsorbent 153
 - 7.3 Bulk Liquid-Adsorptive Separation 154
 - 7.3.1 Modes of Liquid-Adsorptive Separation 154
 - 7.3.1.1 Adsorption Isotherms 156
 - 7.3.1.2 Pulse-Test Procedure 156
 - 7.3.1.3 Breakthrough Procedure 157
 - 7.3.1.4 Simulated Moving-Bed Operation: Sorbex Technology 158
 - 7.3.2 Liquid-Adsorptive Separation Processes 159
 - 7.3.2.1 Equilibrium-Selective Adsorption 159
 - 7.3.2.2 Rate-Selective Adsorption 166
 - 7.3.2.3 Shape-Selective Adsorption 168
 - 7.3.2.4 Ion Exchange 169
 - 7.3.2.5 Reactive Adsorption 170
 - 7.4 Commercial Bulk Liquid-Adsorptive Process 170
 - 7.4.1 Parex 170
 - 7.4.2 MX Sorbex™ 173
 - Acknowledgment 174
 - References 174
- 8 Distillation 179**
 - 8.1 Introduction to Distillation 179
 - 8.2 Principles and Systems 181
 - 8.2.1 Vapor-Liquid Equilibrium (VLE) Theory 181
 - 8.2.2 McCabe-Thiele Diagram 182
 - 8.2.3 Factors for VLE-Based Distillation Design 184
 - 8.2.3.1 Relative Volatility 184
 - 8.2.3.2 Activity Coefficient 185
 - 8.2.3.3 Solubility 185
 - 8.2.3.4 Azeotropes: Maximum Concentration Limit 185
 - 8.2.3.5 Surface Area 186

8.2.4	Operating Modes of Distillation	186
8.2.4.1	Batch vs. Continuous	186
8.2.4.2	Tray vs. Packed Column	187
8.3	Distillation Columns and Trays	188
8.3.1	Flow Within the Distillation Column	188
8.3.2	Multicomponent Distillation	189
8.3.3	Tray Types: Sieve, Valve, Bubble-Cap	190
8.4	Distillation Packing Materials	192
8.4.1	Random Packing	193
8.4.2	Structured Packing	194
8.5	Commercial Examples	195
8.5.1	Crude Oil Distillation	195
8.5.2	Extractive Distillation	198
8.5.3	Azeotropic Distillation	198
8.5.4	Dividing Wall Column Distillation	198
8.5.5	Reactive Distillation	200
	References	200
9	Membranes	203
9.1	Principle and Background	203
9.2	Types and Preparation of Membranes	204
9.2.1	Polymeric Membranes	205
9.2.1.1	Fundamentals of Polymeric Membranes	205
9.2.1.2	Preparation of Polymeric Membranes	207
9.2.2	Inorganic Membranes	213
9.2.2.1	Introduction to Microporous Crystalline Inorganic Membranes	214
9.2.2.2	Preparation of Microporous Crystalline Inorganic Membranes	215
9.2.3	Mixed-matrix Membranes	218
9.2.3.1	Introduction to Mixed-matrix Membranes	219
9.2.3.2	Preparation of Mixed-matrix Membranes	221
9.3	Membrane Modules	223
9.4	Membrane Reactors	225
9.5	Commercial Applications of Membranes	227
	References	235
10	Absorption	241
10.1	Introduction to Absorption	241
10.2	Acid Gas Removal	243
10.3	Chemical Solvent	245
10.3.1	Amines Process	246
10.3.1.1	Monoethanolamine (Primary Amine)	248
10.3.1.2	Diethanolamine (Secondary Amine)	248
10.3.1.3	Methyldiethanolamine (Tertiary Amine)	248
10.3.2	Benfield™ Process	249
10.4	Physical Solvent	251
10.4.1	Solvent Selection	252

10.4.1.1	DMEPG (Dimethyl Ether of Polyethylene Glycol, $(\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{CH}_3))$	252
10.4.1.2	MeOH (Methanol, H_3COH)	253
10.4.1.3	PC (Propylene Carbonate, $\text{C}_4\text{H}_6\text{O}_3$)	254
10.4.2	Flow Schemes	254
10.4.3	Selexol™ Process	255
10.5	Additional Commercial Uses of Absorption	257
10.5.1	Glycol Dehydration	257
10.5.2	Organics from Air (Air Stripping)	259
	References	259

11 Extraction Technology 261

11.1	Introduction	261
11.2	Extraction Processes	261
11.2.1	Liquid–Liquid Extraction (LLE)	261
11.2.2	Supercritical Fluid Extraction (SCFE)	263
11.2.3	Liquid–Liquid Extraction vs. Supercritical Fluid Extraction	264
11.3	Solvents	264
11.3.1	Selectivity	264
11.3.2	Recoverability	265
11.3.3	Immiscible	265
11.3.4	Density	265
11.3.5	Chemical Stability	265
11.3.6	Loading Capacity (L_a)	265
11.4	Extractors	266
11.4.1	Simple Extractor	266
11.4.1.1	Sieve-tray Column	266
11.4.1.2	Packed Column	267
11.4.2	Mechanical Extractors	268
11.4.2.1	Rotary and Reciprocal Extractors	268
11.4.2.2	Centrifugal Extractors	268
11.4.3	Simple Extractors vs. Mechanical Extractors	269
11.5	Industrial Extraction	269
11.5.1	Hydrometallurgy Extraction	269
11.5.1.1	Zirconium/Hafnium Separation	270
11.5.1.2	Uranium/Plutonium Separation	272
11.5.2	Hydrocarbon Extraction	272
11.5.2.1	<i>m</i> -Xylene/Xylene Isomer Separation	272
11.5.2.2	Sulfolane Process	274
11.5.2.3	Merox Process	277
11.6	Summary	280
	Acknowledgments	280
	References	281