

# Contents

Preface.....	xiii
Authors.....	xv
<b>Chapter 1</b> Desulfurization.....	1
1.1 Introduction .....	1
1.2 Hydrodesulfurization.....	4
1.2.1 Reaction Mechanism.....	4
1.2.2 Catalysts .....	6
1.2.3 Reactor Configuration .....	7
1.3 Thermodynamic Aspects.....	9
1.4 Kinetics of Hydrodesulfurization.....	10
1.5 Sulfur Removal during Refining .....	13
1.5.1 Thermal Cracking .....	14
1.5.2 Catalytic Cracking.....	15
1.5.3 Hydrogenation .....	18
1.5.3.1 Hydrocracking .....	19
1.5.3.2 Hydrotreating.....	20
1.6 Macromolecular Concepts.....	21
1.7 Sediment Formation and Fouling.....	25
References .....	26
<b>Chapter 2</b> Feedstocks .....	31
2.1 Introduction .....	31
2.2 Natural Feedstocks .....	38
2.2.1 Petroleum.....	38
2.2.2 Natural Gas and Gas Condensate.....	38
2.2.3 Opportunity Crudes.....	39
2.2.4 High-Acid Crudes.....	40
2.2.5 Oil from Tight Shale .....	41
2.2.6 Heavy Oil .....	42
2.2.7 Extra Heavy Oil.....	42
2.2.8 Tar Sand Bitumen.....	43
2.3 Refinery-Produced Feedstocks .....	44
2.3.1 Naphtha .....	44
2.3.2 Middle Distillates.....	45
2.3.3 Residuum.....	46
2.4 Sulfur in Petroleum .....	54
2.5 Sulfur Levels and Legislative Regulations.....	58
References .....	60
<b>Chapter 3</b> Feedstock Evaluation.....	63
3.1 Introduction .....	63
3.2 Feedstock Evaluation.....	67

3.2.1	Elemental (Ultimate) Analysis .....	67
3.2.2	Metal Content .....	69
3.2.3	Density and Specific Gravity .....	70
3.2.4	Viscosity .....	72
3.2.5	Carbon Residue .....	74
3.2.6	Specific Heat .....	75
3.2.7	Heat of Combustion .....	75
3.3	Chromatographic Methods .....	76
3.4	Molecular Weight .....	76
3.5	Other Properties .....	77
3.6	Use of the Data .....	79
	References .....	80
<b>Chapter 4</b>	<b>Desulfurization during Refining .....</b>	<b>83</b>
4.1	Introduction .....	83
4.2	Refinery Configuration .....	84
4.3	Dewatering and Desalting .....	87
4.4	Distillation .....	88
4.4.1	Atmospheric Distillation .....	88
4.4.2	Vacuum Distillation .....	88
4.4.3	Cracking Distillation .....	90
4.4.4	Desulfurization during Distillation .....	91
4.5	Thermal Processes .....	93
4.5.1	Thermal Cracking .....	94
4.5.2	Visbreaking .....	94
4.5.3	Coking .....	97
4.5.3.1	Delayed Coking .....	97
4.5.3.2	Fluid Coking and Flexicoking .....	99
4.5.4	Desulfurization during Coking .....	101
4.6	Catalytic Cracking .....	102
4.6.1	Process Options .....	107
4.6.2	Feedstock .....	107
4.6.3	Catalysts .....	108
4.6.4	Desulfurization during Catalytic Cracking .....	109
4.7	Hydroprocesses .....	111
4.7.1	Hydrotreating .....	111
4.7.2	Hydrocracking .....	114
4.7.3	Desulfurization during Hydroprocessing .....	115
4.8	Deasphalting .....	117
4.8.1	Deasphalting Processes .....	117
4.8.2	Desulfurization during Deasphalting .....	119
4.8.3	Dewaxing Processes .....	120
4.8.4	Desulfurization during Dewaxing .....	122
4.9	Feedstock Modification .....	123
	References .....	124
<b>Chapter 5</b>	<b>Upgrading Heavy Feedstocks .....</b>	<b>127</b>
5.1	Introduction .....	127
5.2	Thermal Processes .....	132

5.2.1	Asphalt Coking Technology (ASCOT) Process.....	132
5.2.2	Cherry-P (Comprehensive Heavy Ends Reforming Refinery) Process.....	133
5.2.3	ET-II Process.....	133
5.2.4	Eureka Process.....	135
5.2.5	Fluid Thermal Cracking (FTC) Process.....	136
5.2.6	High-Conversion Soaker Cracking (HSC) Process.....	136
5.2.7	Tervahl Process.....	138
5.3	Catalytic Cracking Processes.....	138
5.3.1	Asphalt Residual Treating (ART) Process.....	139
5.3.2	Residue FCC Process.....	141
5.3.3	Heavy Oil Treating (HOT) Process.....	141
5.3.4	R2R Process.....	143
5.3.5	Reduced Crude Oil Conversion (RCC) Process.....	144
5.3.6	Shell FCC Process.....	145
5.3.7	S&W FCC Process.....	145
5.3.8	Millisecond Catalytic Cracking (MSCC) Process.....	146
5.3.9	Residuum Desulfurization (RDS) and Vacuum Residuum Desulfurization (VRDS) Processes.....	146
5.4	Solvent Processes.....	147
5.4.1	Deep Solvent Deasphalting Process.....	147
5.4.2	Demex Process.....	149
5.4.3	MDS Process.....	151
5.4.4	Residuum Oil Supercritical Extraction (ROSE) Process.....	152
5.4.5	Solvahl Process.....	153
5.5	Future.....	153
	References.....	154

**Chapter 6 Refining Chemistry..... 157**

6.1	Introduction.....	157
6.2	Cracking.....	158
6.2.1	Thermal Cracking.....	158
6.2.2	Catalytic Cracking.....	160
6.2.3	Dehydrogenation.....	162
6.2.4	Dehydrocyclization.....	162
6.3	Hydrogenation.....	162
6.3.1	Hydrocracking.....	163
6.3.2	Hydrotreating.....	163
6.4	Isomerization.....	164
6.5	Alkylation.....	165
6.6	Polymerization.....	165
6.7	Process Chemistry.....	166
6.7.1	Thermal Chemistry.....	166
6.7.2	Hydroconversion Chemistry.....	174
6.7.3	Chemistry in the Refinery.....	175
6.7.3.1	Visbreaking.....	175
6.7.3.2	Hydroprocessing.....	179
	References.....	181

<b>Chapter 7</b>	Influence of Feedstock .....	185
7.1	Introduction .....	185
7.2	Chemical Composition .....	189
7.2.1	Hydrocarbon Compounds .....	190
7.2.2	Sulfur Compounds .....	192
7.2.3	Nitrogen Compounds .....	193
7.2.4	Oxygen Compounds .....	194
7.2.5	Metallic Compounds .....	195
7.3	Physical Composition .....	196
7.3.1	Asphaltene Separation.....	197
7.3.2	Fractionation.....	198
7.4	Feedstock Types .....	199
7.4.1	Low-Boiling Distillates .....	200
7.4.2	High-Boiling Distillates .....	202
7.4.3	Heavy Feedstocks.....	202
7.5	Feedstock Composition .....	204
7.5.1	Asphaltene and Resin Content .....	205
7.5.2	Metal Content.....	207
7.6	Product Distribution .....	208
7.7	Use of the Data .....	209
	References .....	210
<b>Chapter 8</b>	Desulfurization Methods.....	213
8.1	Introduction .....	213
8.2	Methods for Sulfur Removal .....	214
8.2.1	Hydrodesulfurization .....	217
8.2.2	Extraction .....	218
8.2.3	Desulfurization by Ionic Liquids .....	221
8.2.4	Alkylation.....	223
8.2.5	Desulfurization by Precipitation .....	224
8.2.6	Selective Adsorption .....	225
8.2.7	Oxidative Desulfurization.....	227
8.2.8	Biocatalytic Desulfurization .....	230
8.2.9	Membrane Separation .....	231
8.2.10	Other Methods.....	231
8.2.10.1	Ambient or Mild Conditions without Hydrogen.....	231
8.2.10.2	Elevated Temperatures under Hydrogen without Hydrogenation of Aromatics .....	231
8.3	Molecular Imprinting Technology.....	232
8.4	Future.....	233
	References .....	233
<b>Chapter 9</b>	Biocatalytic Desulfurization .....	241
9.1	Introduction .....	241
9.2	Scale-Up of the Biodesulfurization Technique .....	246
9.3	Nano-Biotechnology and Biodesulfurization.....	258
9.4	Future.....	263
	References .....	265

<b>Chapter 10</b>	Hydrodesulfurization .....	271
10.1	Introduction .....	271
10.2	Process Description .....	274
10.3	Reactor Design .....	281
10.3.1	Downflow Fixed-Bed Reactor .....	282
10.3.2	Radial-Flow Fixed-Bed Reactor .....	284
10.3.3	Upflow Expanded-Bed Reactor (Particulate Fluidized-Bed Reactor) .....	285
10.3.4	Ebullating-Bed Reactor .....	287
10.3.5	Demetallization Reactor .....	288
10.3.6	Reactor Options .....	289
10.4	Catalysts .....	289
10.5	Catalyst Bed Plugging .....	292
10.6	Catalyst Poisoning .....	294
10.7	Process Variables .....	294
10.7.1	Reactor Temperature .....	295
10.7.2	Hydrogen Pressure .....	296
10.7.3	Liquid Hourly Space Velocity .....	296
10.7.4	Hydrogen Recycle Rate .....	297
10.7.5	Catalyst Life .....	297
10.7.6	Feedstock Effects .....	298
	References .....	300
<b>Chapter 11</b>	Desulfurization Processes—Gases .....	303
11.1	Introduction .....	303
11.2	Gas Streams .....	304
11.2.1	Gas Streams from Crude Oil .....	310
11.2.2	Gas Streams from Natural Gas .....	313
11.3	Water Removal .....	313
11.3.1	Absorption .....	314
11.3.2	Adsorption .....	315
11.3.3	Use of Membranes .....	315
11.4	Liquid Removal .....	316
11.4.1	Extraction .....	316
11.4.2	Absorption .....	316
11.4.3	Fractionation of Natural Gas Liquids .....	317
11.5	Nitrogen Removal .....	317
11.6	Acid Gas Removal .....	317
11.7	Enrichment .....	323
11.8	Fractionation .....	323
11.9	Claus Process .....	323
	References .....	326
<b>Chapter 12</b>	Desulfurization Processes—Distillates .....	329
12.1	Introduction .....	329
12.2	Commercial Processes .....	335
12.2.1	Autofining Process .....	336
12.2.2	Ferrofining Process .....	338

12.2.3	Gulf HDS Process .....	338
12.2.4	Hydrofining Process .....	338
12.2.5	Isomax Process.....	340
12.2.6	Ultrafining Process.....	340
12.2.7	Unifining Process .....	340
12.2.8	Unionfining Process .....	341
12.2.9	Other Processes .....	341
12.2.9.1	IFP Prime-D30 Process .....	342
12.2.9.2	MAKfining Process .....	342
12.2.9.3	MQD Unionfining Process .....	343
12.2.9.4	SynSat Process.....	343
12.2.9.5	Topsøe Ultra-Deep HDS Process .....	343
12.3	Gasoline and Diesel Fuel Polishing.....	343
12.4	Biodesulfurization .....	345
	References .....	346
<b>Chapter 13</b>	<b>Desulfurization Processes—Heavy Feedstocks.....</b>	<b>349</b>
13.1	Introduction .....	349
13.2	Process Options .....	353
13.2.1	Asphaltenic Bottom Cracking (ABC) Process.....	354
13.2.2	Aquaconversion .....	355
13.2.3	CANMET Hydrocracking Process .....	355
13.2.4	Chevron RDS Isomax and VRDS Process .....	356
13.2.5	Chevron Deasphalted Oil Hydrotreating Process .....	357
13.2.6	Gulf Resid Hydrodesulfurization Process.....	357
13.2.7	H-Oil Process .....	358
13.2.8	Hydrovisbreaking (HYCAR) Process .....	360
13.2.9	Hyvahl F Process .....	360
13.2.10	IFP Hydrocracking Process.....	361
13.2.11	Isocracking Process.....	361
13.2.12	LC-Fining Process.....	362
13.2.13	MAKfining Process.....	364
13.2.14	Microcat-RC Process.....	365
13.2.15	MRH Process .....	366
13.2.16	RCD Unibon Process.....	366
13.2.17	Residfining Process .....	367
13.2.18	Residue Hydroconversion Process .....	368
13.2.19	Shell Residual Oil Hydrodesulfurization .....	369
13.2.20	Unicracking Hydrodesulfurization Process .....	369
13.2.21	Uniflex Process.....	371
13.2.22	Veba Combi-Cracking (VCC) Process.....	371
13.3	Catalysts .....	372
	References .....	375
<b>Chapter 14</b>	<b>Hydrogen Production and Management.....</b>	<b>377</b>
14.1	Introduction .....	377
14.2	Feedstocks .....	385
14.3	Process Chemistry .....	387

14.4	Commercial Processes .....	388
14.4.1	Heavy Residue Gasification and Combined Cycle Power Generation .....	389
14.4.2	Hybrid Gasification Process .....	390
14.4.3	Hydrocarbon Gasification .....	390
14.4.4	Hypro Process .....	390
14.4.5	Pyrolysis Processes .....	391
14.4.6	Shell Gasification Process .....	393
14.4.7	Steam–Methane Reforming .....	393
14.4.8	Steam–Naphtha Reforming .....	396
14.4.9	Synthesis Gas Generation.....	397
14.4.10	Texaco Gasification Process .....	398
14.4.11	Recovery from Fuel Gas.....	400
14.5	Catalysts .....	400
14.5.1	Reforming Catalysts.....	400
14.5.2	Shift Conversion Catalysts .....	401
14.5.3	Methanation Catalysts .....	402
14.6	Purification .....	402
14.6.1	Wet Scrubbing .....	404
14.6.2	Pressure-Swing Adsorption Units .....	404
14.6.3	Membrane Systems .....	406
14.6.4	Cryogenic Separation .....	406
14.7	Hydrogen Management and Safety .....	406
14.7.1	Distribution.....	407
14.7.2	Management .....	407
14.7.3	Safety.....	408
	References .....	409
	<b>Conversion Factors</b> .....	<b>413</b>
	<b>Glossary</b> .....	<b>415</b>
	<b>Index</b> .....	<b>457</b>