Contents

Preface			xiii
1	Introduction		
		References	6
		General Literature	6
2	The (Chemical Industry	7
	2.1	A Brief History	7
		2.1.1 Inorganic Chemicals	7
		2.1.2 Organic Chemicals	10
		2.1.3 The Oil Era	11
		2.1.4 The Age of Sustainability	12
	2.2	Structure of the Chemical Industry	13
	2.3	Raw Materials and Energy	16
		2.3.1 Fossil Fuel Consumption and Reserves	16
		2.3.2 Biomass as an Alternative for Fossil Fuels	19
		2.3.3 Energy and the Chemical Industry	21
		2.3.4 Composition of Fossil Fuels and Biomass	23
	2.4	Base Chemicals	35
	2.5	Global Trends in the Chemical Industry	37
		References	39
		General Literature	40
3	Proc	esses in the Oil Refinery	41
	3.1	The Oil Refinery – An Overview	41
	3.2	Physical Processes	42
		3.2.1 Desalting and Dehydration	42
		3.2.2 Crude Distillation	43
		3.2.3 Propane Deasphalting	45
	3.3	Thermal Processes	46
		3.3.1 Visbreaking	46
		3.3.2 Delayed Coking	47
		3.3.3 Flexicoking	48
	3.4	Catalytic Processes	49
		3.4.1 Octane and Cetane Numbers	49
		3.4.2 Catalytic Cracking	51
		3.4.3 Catalytic Reforming	63
		3.4.4 Alkylation	69
		3.4.5 Hydroprocessing	76

vi	Contents
V 2	Contents

	3.5	Current and Future Trends in Oil Refining	91
		3.5.1 Stricter Environmental Regulations	92
		3.5.2 Refinery Configurations	94
		References	96
4	Prod	uction of Light Alkenes	99
	4.1	Introduction	99
	4.2	Cracking Reactions	100
		4.2.1 Thermodynamics	100
		4.2.2 Mechanism	101
		4.2.3 Kinetics	102
	4.3	The Industrial Process	103
		4.3.1 Influence of Feedstock on Steam Cracker Operation and Products	103
		4.3.2 Cracking Furnace	106
		4.3.3 Heat Exchanger	109
		4.3.4 Coke Formation	110
	4.4	Product Processing	111
	4.5	Novel Developments	113
		4.5.1 Selective Dehydrogenation of Light Alkanes	114 116
		4.5.2 Metathesis of Alkenes	118
		4.5.3 Production of Light Alkenes from Synthesis Gas	118
		4.5.4 Dehydration of Bioethanol4.5.5 Direct Conversion of Methane	121
		References	122
		Neterices	120
5		uction of Synthesis Gas	127
	5.1	Introduction	127
	5.2	Synthesis Gas from Natural Gas	129
		5.2.1 Reactions and Thermodynamics	129
		5.2.2 Steam Reforming Process	131
		5.2.3 Autothermal Reforming Process	137
		5.2.4 Novel Developments	139
	5.3	Coal Gasification	142
		5.3.1 Gasification Reactions	142 143
		5.3.2 Thermodynamics	145
		5.3.3 Gasification Technologies5.3.4 Recent Developments in Gasification Technology	140
		5.3.4 Recent Developments in Gasification Technology5.3.5 Applications of Coal Gasification	154
		5.3.6 Integrated Gasification Combined Cycle	154
		5.3.7 Why Gasify, Not Burn for Electricity Generation?	158
		5.3.8 Carbon Capture and Storage (CCS)	150
	5.4	Cleaning and Conditioning of Synthesis Gas	161
	5.7	5.4.1 Acid Gas Removal	161
		5.4.2 Water–Gas Shift Reaction	163
		5.4.3 Methanation	166
		References	168

References

6	Bulk	Chemicals and Synthetic Fuels Derived from Synthesis Gas	171		
	6.1	Ammonia	171		
		6.1.1 Background Information	171		
		6.1.2 Thermodynamics	173		
		6.1.3 Commercial Ammonia Synthesis Reactors	175		
		6.1.4 Ammonia Synthesis Loop	178		
		6.1.5 Integrated Ammonia Plant	180		
		6.1.6 Hydrogen Recovery	182		
		6.1.7 Production of Urea	185		
	6.2	Methanol	191		
	0.2	6.2.1 Background Information	191		
		6.2.2 Reactions, Thermodynamics, and Catalysts	192		
		6.2.3 Synthesis Gas for Methanol Production	195		
		6.2.4 Methanol Synthesis	196		
		6.2.5 Production of Formaldehyde	199		
	6.3	Synthetic Fuels and Fuel Additives	201		
	0.5	6.3.1 Fischer–Tropsch Process	202		
		6.3.2 Methanol-to-Gasoline (MTG) Process	202		
		6.3.3 Recent Developments in the Production of Synthetic Fuels	212		
		6.3.4 Fuel Additives – Methyl Tert-Butyl Ether	214		
		References	213		
		Activities and a second	210		
7	7 Processes for the Conversion of Biomass				
	7.1 Introduction				
	7.2	Production of Biofuels	223		
		7.2.1 Bioethanol and Biobutanol	224		
		7.2.2 Diesel-Type Biofuels	226		
	7.3	Production of Bio-based Chemicals	231		
		7.3.1 Ethanol	232		
		7.3.2 Glycerol	233		
		7.3.3 Succinic Acid	234		
		7.3.4 Hydroxymethylfurfural (HMF)	236		
	7.4	The Biorefinery	236		
		7.4.1 Biorefinery Design Criteria and Products	236		
		7.4.2 Biorefinery Concepts	238		
		7.4.3 Core Technologies of a Thermochemical Biorefinery	239		
		7.4.4 Existing and Projected Biorefineries	243		
		7.4.5 Possibility of Integrating a Biorefinery with Existing Plants	243		
		7.4.6 Biorefinery versus Oil Refinery	245		
	7.5	Conclusions	246		
		References	246		
8	Inon	ganic Bulk Chemicals	249		
Ø	8.1	The Inorganic Chemicals Industry	249 249		
	8.1 8.2	Sulfuric Acid			
	0.2		250		
		•	252		
		8.2.2 SO ₂ Conversion Reactor	252		

		8.2.3 Modern Sulfuric Acid Production Process	254
		8.2.4 Catalyst Deactivation	256
	8.3	Sulfur Production	256
	8.4	Nitric Acid	260
		8.4.1 Reactions and Thermodynamics	260
		8.4.2 Processes	262
		8.4.3 NO_x Abatement	266
	8.5	Chlorine	268
		8.5.1 Reactions for the Electrolysis of NaCl	269
		8.5.2 Technologies for the Electrolysis of NaCl	270
		References	274
9	Homo	geneous Transition Metal Catalysis in the Production of Bulk Chemicals	275
	9.1	Introduction	275
	9.2	Acetic Acid Production	278
		9.2.1 Background Information	278
		9.2.2 Methanol Carbonylation – Reactions, Thermodynamics, and Catalysis	281
		9.2.3 Methanol Carbonylation – Processes	284
	9.3	Hydroformylation	286
		9.3.1 Background Information	286
		9.3.2 Thermodynamics	288
		9.3.3 Catalyst Development	289
		9.3.4 Processes for the Hydroformylation of Propene	292
		9.3.5 Processes for the Hydroformylation of Higher Alkenes	294
	~ .	9.3.6 Comparison of Hydroformylation Processes	296
	9.4	Ethene Oligomerization and More	297
		9.4.1 Background Information	297
		9.4.2 Reactions of the SHOP Process	298
	0.5	9.4.3 The SHOP Process	299
	9.5	Oxidation of <i>p</i> -Xylene: Dimethyl Terephthalate and Terephthalic Acid Production	301 301
		9.5.1 Background Information	301
		9.5.2 Conversion of <i>p</i> -Toluic Acid Intermediate	302
		9.5.3 Processes	305
	0.6	9.5.4 Process Comparison Review of Reactors Used in Homogeneous Catalysis	305
	9.6	9.6.1 Choice of Reactor	306
		9.6.2 Exchanging Heat	308
	9.7	Approaches for Catalyst/Product Separation	308
	9.1	9.7.1 Biphasic Catalyst Systems	309
		9.7.2 Immobilized Catalyst Systems	309
		References	311
10	Hete	rogeneous Catalysis – Concepts and Examples	313
	10.1	Introduction	313
		Catalyst Design	314
		10.2.1 Catalyst Size and Shape	314
		10.2.2 Mechanical Properties of Catalyst Particles	316

19.19.1

	10.3		r Types and Their Characteristics		316	
			Reactor Types		316	
			Exchanging Heat		319	
			Role of Catalyst Deactivation		321	
			Other Issues		322	
	10.4	-	Selectivity – Zeolites		323	
			Production of Isobutene		325	
			Isomerization of Pentanes and Hexanes		328	
			Production of Ethylbenzene		330	
	10.5		Challenges and (Unconventional) Solutions		334	
			Adiabatic Reactor with Periodic Flow Reversal		334	
		10.5.2	Highly Exothermic Reactions with a Selectivity Challenge – Selective			
	10.0	14	Oxidations		338	
	10.6		th Reactors – Automotive Emission Control		344	
		10.6.1	Exhaust Gas Composition		346	
		10.6.2 Referen	Reduction of Exhaust Gas Emissions		347	
			l Literature		354	
		Genera	I Literature		355	
11	Prod	uction of	f Polymers — Polyethene		357	
11		Introdu			357	
		1.2 Polymerization Reactions			357	
	11.2	-	Step growth Polymerization		358	
			Chain growth Polymerization – Radical and Coordination Pathways		360	
	11.3		enes – Background Information		363	
			Catalyst Development		363	
			Classification and Properties		364	
			Applications		365	
	11.4		es for the Production of Polyethenes		366	
			Monomer Production and Purification		366	
			Polymerization – Exothermicity		367	
			Production of Polyethenes		367	
		Referen	aces		375	
12		duction of Fine Chemicals				
	12.1					
	12.2		Catalysis		380	
		12.2.1	Atom Economy		380	
		12.2.2			381	
		12.2.3			384	
		12.2.4	•		384	
		12.2.5	Biocatalysis	e.	392	
	12.3	Solvent			394	
		12.3.1	Conventional Solvents		394	
		12.3.2	Alternative Solvents		395	

	12.4	Production Plants	398
		12.4.1 Multiproduct and Multipurpose Plants (MMPs)	398
		12.4.2 Dedicated Continuous Plants	406
	12.5	Batch Reactor Selection	407
		12.5.1 Reactors for Liquid and Gas-Liquid Systems	408
		12.5.2 Reactors for Gas-Liquid-Solid Systems	409
	12.6	Batch Reactor Scale-up Effects	411
		12.6.1 Temperature Control	411
		12.6.2 Heat Transfer	411
		12.6.3 Example of the Scale-up of a Batch and Semi-Batch Reactor	412
		12.6.4 Summary of the Scale-up of Batch Reactors	416
	12.7		416
		12.7.1 Thermal Risks	416
		12.7.2 Safety and Process Development	417
		References	419
13	Biote	chnology	423
	13.1	Introduction	423
	13.2	Principles of Fermentation Technology	424
		13.2.1 Mode of Operation	425
		13.2.2 Reactor Types	426
		13.2.3 Sterilization	432
	13.3	Cell Biomass – Bakers' Yeast Production	433
		13.3.1 Process Layout	433
		13.3.2 Cultivation Equipment	434
		13.3.3 Downstream Processing	434
	13.4	Metabolic Products – Biomass as Source of Renewable Energy	435
		13.4.1 Bioethanol and Biobutanol	435
		13.4.2 Biogas	438
	13.5	Environmental Application – Wastewater Treatment	438
		13.5.1 Introduction	438
		13.5.2 Process Layout	438
		13.5.3 Aerobic Treatment Processes	440
		13.5.4 Anaerobic Treatment Processes	443
	13.6	Enzyme Technology – Biocatalysts for Transformations	445
		13.6.1 General Aspects	445
		13.6.2 Immobilization of Enzymes	446
		13.6.3 Production of L-Amino Acids	447
		13.6.4 Production of Artificial Sweeteners	448
		References	452
		General Literature	453
14	Proce	ess Intensification	455
	14.1	Introduction	455
		14.1.1 What is Process Intensification	455
		14.1.2 How to Intensify Processes	457
	14.2	Structured Catalytic Reactors	459
		14.2.1 Types of Structured Catalysts and Reactors	460

Contents	xi
contento	<i>/u</i>

			Monoliths	462
			Microreactors	468
	14.3		unctional Reactors/Reactive Separation	472
			Reactive Distillation	473
			Coupling Reaction and Membrane Separation	477
		14.3.3	1 0	481
		Refere	nces	482
15	Proce	ess Deve	lopment	485
	15.1	Depend	dence of Strategy on Product Type and Raw Materials	485
	15.2	The Co	ourse of Process Development	487
	15.3	Develo	ppment of Individual Steps	489
		15.3.1	Exploratory Phase	489
		15.3.2	From Process Concept to Preliminary Flow Sheet	489
		15.3.3	Pilot Plants/Miniplants	494
	15.4	Scale-1	ıp	499
		15.4.1	Reactors with a Single Fluid Phase	499
		15.4.2	Fixed Bed Catalytic Reactors with One or More Fluid Phases	501
	15.5	Safety	and Loss Prevention	505
		15.5.1	Safety Issues	505
		15.5.2	Reactivity Hazards	511
		15.5.3	Design Approaches to Safety	513
	15.6	Process	s Evaluation	514
		15.6.1	Capital Cost Estimation	515
		15.6.2	Operating Costs and Earnings	523
		15.6.3	Profitability Measures	524
	15.7	Curren	t and Future Trends	526
		Referen	nces	528
		Genera	1 Literature	529
		Magazi	ines	529
Арр	endix	A Che	mical Industry – Figures	531
Арр	endix	B Mai	n Symbols Used in Flow Schemes	535
Inde	Index 5			