

Contents

Foreword *xi*

Preface *xiii*

1 Role of Biomass in the Production of Chemicals 1

Layla Filiciotto, Evan Pfab and Rafael Luque

- 1.1 Introduction 1
- 1.2 Biomass Valorization 3
- 1.3 Lignocellulosic Biomass 5
- 1.4 Key Biomolecules 6
- 1.5 Solvents 10
- 1.6 Pretreatment of Lignocelluloses 12
- 1.7 Conclusions and Perspectives 15
- References 15

Section I Catalytic Strategies 23

2 Biomass Processing via Acid Catalysis 25

Iurii Bodachivskyi, Unnikrishnan Kuzhiumparambil and D. Bradley G. Williams

- 2.1 Introduction 25
- 2.1.1 Is an Acid the Best Catalyst? 26
- 2.2 Acid-Catalyzed Processing of Cellulosic Polysaccharides 29
- 2.3 Acid-Catalyzed Processing of Lignin 44
- 2.4 Conclusions and Perspectives 47
- References 47

3 Biomass Processing via Base Catalysis 57

Lichen Liu, Maria J. Climent and Sara Iborra

- 3.1 Introduction 57
- 3.2 Aldol Condensation 60
- 3.2.1 Aldol Condensation of Furanic Aldehydes 60
- 3.2.2 Self-Aldol Condensation of Acetone 63

3.2.3	Aldol Condensation Between Alcohols: Guerbet Coupling Reaction	64
3.3	Ketonization Reaction of Carboxylic Acids	65
3.4	Transesterification Reaction	68
3.4.1	Biodiesel Production	68
3.4.2	High Value-Added Chemicals from Transesterification Reactions	70
3.5	Conclusions and Perspectives	73
	References	74
4	Biomass Processing via Metal Catalysis	81
	<i>Sofia Capelli and Alberto Villa</i>	
4.1	Introduction	81
4.2	Synthetic Strategies for Supported Metal Nanoparticles	83
4.2.1	Impregnation	83
4.2.2	Precipitation	84
4.2.3	Sol Immobilization	85
4.3	Furfural	86
4.3.1	Furfural Hydrogenation	87
4.3.1.1	Furfural to Furfuryl Alcohol	87
4.3.1.2	Furfural to Tetrahydrofurfuryl Alcohol	88
4.3.1.3	Furfural to Pentanediols	89
4.3.1.4	Furfural to 2-Methylfuran	90
4.3.2	Furfural Oxidation	92
4.3.2.1	Furfural to Furoates	92
4.4	5-Hydroxymethylfurfural (HMF)	92
4.4.1	HMF Hydrogenation	93
4.4.1.1	HMF to 2,5-Dimethylfuran (DMF)	94
4.4.1.2	HMF to 2,5-Dihydroxymethyltetrahydrofuran (DHMTHF)	95
4.4.2	HMF Oxidation	96
4.4.2.1	HMF to 2,5-Furandicarboxylic Acid (FDCA) Using Monometallic Systems	96
4.4.2.2	HMF Oxidation over Bimetallic Catalysts	100
4.5	Conclusions and Perspectives	103
	References	103
5	Biomass Processing with Biocatalysis	113
	<i>Roger A. Sheldon</i>	
5.1	Introduction	113
5.2	Generations of Renewable Biomass: Advantages and Limitations	113
5.3	Advantages and Limitations of Biocatalysis	116
5.4	Enzyme Discovery and Optimization of Enzyme Performance	117
5.5	Enzyme Immobilization	118
5.5.1	Enzyme Immobilization by Cross-linking Enzyme Molecules	119
5.5.2	Advantages and Limitations of Cross-Linked Enzyme Aggregates (CLEAs)	120
5.5.3	Magnetically Separable Immobilized Enzymes	120

5.6	Enzymatic Hydrolysis of Starch to Glucose	121
5.7	Enzymatic Depolymerization of Lignocellulose	122
5.8	Enzymatic Hydrolysis of Cellulose and Hemicellulose	123
5.8.1	Magnetizable Immobilized Enzymes in Lignocellulose Conversion	124
5.9	Enzymatic Hydrolysis of 3rd Generation (3G) Polysaccharides	124
5.10	Commodity Chemicals from Carbohydrates (Monosaccharides)	126
5.10.1	Fermentative Production of Commodity Chemicals	126
5.10.2	Deoxygenation via Dehydration of Carbohydrates to Furan Derivatives	129
5.10.3	Polyethylene Furandicarboxylate (PEF) as a Renewable Alternative to PET	129
5.10.4	Enzymatic Synthesis of Bio-based Polyesters	131
5.11	Enzymatic Conversions of Triglycerides: Production of Biodiesel and Bulk Chemicals	132
5.12	Conclusions and Perspectives	133
	References	133

Section II Thermal Strategies 147

6	Biomass Processing via Pyrolysis	149
	<i>Daniele Fabbri, Yunchao Li and Shurong Wang</i>	
6.1	Brief Introduction	149
6.2	Chemicals from Cellulose Pyrolysis	151
6.2.1	General Aspects	151
6.2.2	Levoglucosan	154
6.2.3	Levoglucosenone	156
6.2.4	LAC, (1R,5S)-1-Hydroxy-3,6-Dioxabicyclicdioxabicyclo-[3.2.1]octan-2-one	157
6.3	Chemicals from Lignin Pyrolysis	160
6.4	Pyrolysis of Biomass	161
6.4.1	Levoglucosan	161
6.4.1.1	Effects of Metal Oxides	162
6.4.1.2	Effects of Alkali and Alkaline Earth Metals	162
6.4.1.3	Effects of Acid Impregnation	162
6.4.1.4	Effects of Other Components	163
6.4.2	Levoglucosenone	163
6.4.2.1	Effects of Metal Chlorides	163
6.4.2.2	Effects of Acid Catalysts	163
6.4.2.3	Others	164
6.4.3	Furfural	164
6.4.4	Aromatic Hydrocarbons	167
6.4.5	Phenolic Compounds	169
6.5	Conclusions and Perspectives	170
	References	171

7 Biomass Processing via Thermochemical–Biological Hybrid Processes 181

Cristian Torri, Alessandro Girolamo Rombolà, Alisar Kiwan and Daniele Fabbri

- 7.1 Introduction 181
- 7.1.1 Hybrid Thermochemical/Biological Processing with Single-Strain Microorganisms 183
- 7.1.2 Hybrid Thermochemical/Biological Processing with Microbial Mixed Consortia (MMC) 183
- 7.2 Pyrolysis Products (PyP) from the Microorganism's Standpoint 185
- 7.2.1 What Pyrolysis Can Do for Microorganisms: Yields and Bioavailability of PyP 186
- 7.2.2 Viable Pathways According to Thermodynamics Laws 188
- 7.2.3 Rate of MMC Biological Conversions in Relationship with PyP Treatment 191
- 7.2.4 Toxicity of PyP Toward MMC 193
- 7.3 Conversion of PyP with MMC: Survey of Experimental Evidence 198
- 7.3.1 Syngas Conversion to Methane 203
- 7.3.2 Syngas Conversion to H₂, Volatile Fatty Acids (VFA), and Alcohols 203
- 7.3.3 Conversion of Condensable PyP to Methane 205
- 7.3.4 Conversion of Condensable PyP to VFA and Other Intermediates 206
- 7.4 Feasible Pathways for Producing Chemicals from PyP with MMC 207
- 7.4.1 Hybrid Pyrolysis Fermentation and Extraction of Mixed VFA/Alcohols 207
- 7.4.2 Alkaline Fermentation of Pyrolysis Products to VFA Salts, Ketonization, and Hydrogenation to C3–C6 Mixed Alcohols 209
- 7.4.3 Alkaline Fermentation of Pyrolysis Products to VFA Salts and Polyhydroxyalkanoates (PHA) Production via Aerobic MMC 211
- 7.4.4 Direct Alcohol Production by Means of Fermentation of PyP under High Hydrogen Pressure 213
- 7.5 Conclusions and Perspectives 215
- References 216

Section III Advanced/Unconventional Strategies 225

8 Biomass Processing via Electrochemical Means 227

Roman Latsuzbaia, Roel Johannes Martinus Bisselink, Marc Crockatt, Jan Cornelis van der Waal and Earl Lawrence Vincent Goetheer

- 8.1 Introduction 227
- 8.2 Electrochemical Conversion of Bio-Based Molecules 228
- 8.3 Conversion of Sugars 230
- 8.4 Conversion of Furanics 234
- 8.4.1 5-(Hydroxymethyl)furfural (5-HMF) 234
- 8.4.1.1 5-HMF Oxidation 235

8.4.1.2	5-HMF Reduction	238
8.4.2	Furfural	240
8.5	Conversion of Levulinic Acid	244
8.6	Conversion of Glycerol	246
8.7	Lignin Depolymerization	248
8.8	Scale-up of Electrosynthesis of Biomass-Derived Chemicals	248
8.9	Conclusions and Perspectives	254
	References	254
9	Biomass Processing via Photochemical Means	265
	<i>Andrey Shatskiy and Markus D. Kärkäs</i>	
9.1	Introduction	265
9.2	Fundamental Aspects of Photoredox Catalysis	266
9.3	Photochemical Valorization of Lignin	267
9.3.1	Strategies for C _α —C _β Bond Cleavage	268
9.3.2	Strategies for Lignin Oxidation and C _β —O Bond Cleavage	272
9.3.3	Strategies for Ar—O Bond Cleavage	278
9.4	Conclusions and Perspectives	281
	References	282
10	Biomass Processing via Microwave Treatment	289
	<i>Roberto Rosa, Giancarlo Cravotto and Cristina Leonelli</i>	
10.1	Introduction	289
10.2	Microwave–Matter Interaction: Advantages and Limitations in the Processing of Biomass	291
10.3	Microwave Pyrolysis	296
10.4	Microwave-assisted Hydrolysis	299
10.5	Microwave-assisted Extraction of Phytochemical Compounds	303
10.6	Conclusions and Perspectives	306
	References	307
11	Biomass Processing Assisted by Ultrasound	315
	<i>Cezar A. Bizzi, Daniel Santos, Gabrielle D. Iop and Erico M. M. Flores</i>	
11.1	Introduction	315
11.2	Ultrasound Background	316
11.3	Ultrasound-Assisted Biomass Pretreatments	319
11.4	Ultrasound-Assisted Biomass Conversion	322
11.4.1	Thermochemical Conversion Assisted by Ultrasound	323
11.4.2	Biochemical Conversion Assisted by Ultrasound	324
11.4.3	Chemical Conversion (Synthesis) Assisted by Ultrasound	325
11.5	Ultrasound-Assisted Extraction of Value-Added Compounds	326
11.5.1	Ultrasound Contribution to Biomass Extraction Processes	326
11.5.2	Uses of Alternative Approaches for Biomass Extractions Assisted by Ultrasound	328
11.6	Alternative Solvents	331

11.7	Conclusions and Perspectives	332
	References	333
12	Biomass Processing via Mechanochemical Means	343
	<i>George Margoutidis and Francesca M. Kerton</i>	
12.1	Overview and Introduction	343
12.1.1	Background to the Method	343
12.1.2	Properties of a Typical Laboratory Mixer/Mill	346
12.2	Crystallinity Reduction in Biopolymers via Mechanochemistry	348
12.3	Mechanochemical Transformations of Polysaccharides	352
12.3.1	Cellulose Depolymerization	352
12.3.2	Cellulose Modification Toward Composite Materials	355
12.3.3	Transformations of Chitin	355
12.4	Mechanochemical Transformations of Amino Acids, Nucleotides, and Related Materials	357
12.5	Mechanochemical Treatment of Lignin	359
12.6	Biominerals from Mechanochemical Processing of Biomass	360
12.7	Conclusions and Perspectives	361
	References	361
	Section IV Closing Remarks	367
13	Industrial Perspectives of Biomass Processing	369
	<i>Tommaso Tabanelli and Fabrizio Cavani</i>	
13.1	Replacing Existing Petrochemicals with Alternatives from Biomass: An Introduction	369
13.2	Oleochemical Biorefinery: A Consolidated and Multifaceted Example of Biomass Processing	371
13.2.1	Biofuels and Coproduced Chemicals from Oils and Fats	371
13.2.2	Skeletal Isomerization of Unsaturated Fatty Acids for Isostearic Acid Production	379
13.2.3	Bio-based Synthesis of Azelaic and Pelargonic Acids: A Renewable Route Toward Bio-based Polyesters and Cosmetics	382
13.3	From Sugar to Bio-monomers: The Case of 2,5-Furandicarboxylic Acid (FDCA)	385
13.4	From Bioethanol to Rubber: The Synthesis of Bio-butadiene	388
13.5	Conclusions and Perspectives	391
	References	391
	Index	411