

## 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

*Sofia Capelli and Alberto Villa*

- 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 (DHMTTHF) 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

*Roger A. Sheldon*

- 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

|          |  |     |
|----------|--|-----|
| <b>6</b> | <b>Biomass Processing via Pyrolysis</b>                                | 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,<br>(1R,5S)-1-Hydroxy-3,6-Dioxabicydioxabicyclo-[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 |

|          |  |            |
|----------|--|------------|
| <b>7</b> | <b>Biomass Processing via Thermochemical–Biological Hybrid Processes</b>   | <b>181</b> |
|          | <i>Cristian Torri, Alessandro Girolamo Rombolà, Alisar Kiwan and Daniele Fabbri</i>  |            |
| 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 H <sub>2</sub> , 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, Ketonezation, and Hydrogenation to C <sub>3</sub> –C <sub>6</sub> 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

|          |  |            |
|----------|--|------------|
| <b>8</b> | <b>Biomass Processing via Electrochemical Means</b>  | <b>227</b> |
|          | <i>Roman Latsuzbaia, Roel Johannes Martinus Bisselink, Marc Crockatt, Jan Cornelis van der Waal and Earl Lawrence Vincent Goetheer</i> |            |
| 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        |
| <b>9</b>  | <b>Biomass Processing via Photochemical Means</b>                                     | <b>265</b> |
|           | <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 <sub>α</sub> —C <sub>β</sub> Bond Cleavage                           | 268        |
| 9.3.2     | Strategies for Lignin Oxidation and C <sub>β</sub> —O Bond Cleavage                   | 272        |
| 9.3.3     | Strategies for Ar—O Bond Cleavage   | 278        |
| 9.4       | Conclusions and Perspectives  | 281        |
|           | References  | 282        |
| <b>10</b> | <b>Biomass Processing via Microwave Treatment</b>                                     | <b>289</b> |
|           | <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        |
| <b>11</b> | <b>Biomass Processing Assisted by Ultrasound</b>                                      | <b>315</b> |
|           | <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**

*George Margoutidis and Francesca M. Kerton*

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**

*Tommaso Tabanelli and Fabrizio Cavani*

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**