Contents

The Next Feedstock Transition  XIII
Preface  XV
List of Contributors  XVII

1  The Industrial Playing Field for the Conversion of Biomass to Renewable Fuels and Chemicals  1
Leo E. Manzer, Jan Cornelis van der Waal, and Pieter Imhof
1.1 Introduction  1
1.2 The Renewables Arena  2
1.3 Renewable Fuels  9
1.4 Renewable Chemicals  18
1.5 Conclusions  22
References  22

2  Selecting Targets  25
Gene Petersen, Joseph Bozell, and James White
2.1 Introduction  25
2.2 Target Selection Can Focus on Specific Structures or General Technologies  28
2.3 Previous Selection Efforts  29
2.4 Corroboration of the Value of Screening Studies  37
2.5 The Importance of Outcomes and Comparisons of Outcomes  38
2.6 Evaluation Processes Can be Comprised of a Variety of Criteria  40
2.6.1 Feedstock and Intermediate Availability  40
2.6.2 Existing Biorefining Infrastructure Dictates Chemical or Biochemical Processes to be Evaluated  41
2.6.3 Market Drivers  42
2.6.4 R&D Drivers  44
2.6.5 Other Screening Opportunities  44
2.6.6 Other Portfolio Opportunities – Biomass Produced Oils  45
2.7 Catalysis Aspects  46
3 The Development of Catalytic Processes from Terpenes to Chemicals 51
Derek McPhee
3.1 Introduction 51
3.2 Strain Engineering for the Production of Terpenes 52
3.3 Terpene Building Blocks of Commercial Interest 55
3.4 Sesquiterpenes as Chemical Building Blocks: β-Farnesene 56
3.5 Polymers 58
3.5.1 Differential Scanning Calorimetry 63
3.5.2 Gel Permeation Chromatography 63
3.5.3 Thermal Gravimetric Analysis 64
3.5.4 Tensile Strength 65
3.6 Lubricants 66
3.7 Conclusions 75
References 76

4 Furan-Based Building Blocks from Carbohydrates 81
Robert-Jan van Putten, Ana Sousa Dias, and Ed de Jong
4.1 Importance of Furans as Building Blocks 81
4.2 Sources of Carbohydrates 82
4.2.1 Storage Carbohydrates 82
4.2.1.1 Sucrose 82
4.2.1.2 Starch 84
4.2.1.3 Inulin 84
4.2.2 Structural Carbohydrates 84
4.2.2.1 Cellulose 87
4.2.2.2 Hemicelluloses 87
4.2.3 Aquatic Carbohydrates 90
4.2.3.1 Macroalgae 91
4.2.3.2 Brown Macroalgae 91
4.2.3.3 Microalgae 91
4.2.3.4 Green Algae 92
4.2.4 Conclusions on Carbohydrate Feedstocks 92
4.3 Carbohydrate Dehydration 92
4.3.1 Introduction 92
4.3.2 Commercial Furfural Production and Applications 93
4.3.3 Furfural Formation from Pentose Feedstock 95
4.3.4 Production Systems of Furfural 99
4.3.5 Heterogeneous Catalysts 101
4.3.6 5-Hydroxymethylfurfural Formation from Hexose Feedstock 105
## 4.4 Conclusions and Further Perspectives 110

References 111

## 5 A Workflow for Process Design—Using Parallel Reactor Equipment

**Beyond Screening** 119

*Erik-Jan Ras*

5.1 Introduction 119

5.2 The Evolution of Parallel Reactor Equipment 120

5.3 The Evolution of Research Methodology—Conceptual Process Design 121

5.4 Essential Workflow Elements 126

5.4.1 Catalyst Testing Equipment 126

5.4.2 Kinetics and Pseudo-Kinetics 129

5.4.3 Statistical Design of Experiments 130

5.4.4 Data Analysis 136

5.4.5 Example of PCA Applied to Catalysis 137

5.4.6 Example of PLS Applied to Diesel Properties 141

5.5 Other Examples of Parallel Reactor Equipment Applied Beyond Screening—Long-Term Catalyst Performance 143

5.6 Concluding Remarks 147

References 147

## 6 Braskem’s Ethanol to Polyethylene Process Development 149

*Paulo Luiz de Andrade Coutinho, Augusto Teruo Morita, Luis F. Cassinelli, Antonio Morschbacker, and Roberto Werneck Do Carmo*

6.1 Introduction 149

6.1.1 Overview of Braskem Activities and History 149

6.1.2 Why Renewable Polymers and Why Green Polyethylene? 149

6.2 Ethanol and Brazil 150

6.3 Commercial Plants for Ethanol Dehydration 152

6.3.1 Salgema 100 kty Plant 152

6.3.2 Triunfo 200 kty Plant 153

6.3.3 MEG Plants 154

6.3.4 Announced Renewable Polymer Projects 155

6.4 Legislation and Certification 155

6.4.1 Ethanol Suppliers Code of Conduct 155

6.5 Process Description 156

6.5.1 Reaction 156

6.5.1.1 Catalysts 157

6.5.1.2 Side Reactions 158

6.5.1.3 Fixed Bed, Isothermal Reaction 159

6.5.1.4 Fixed Bed, Adiabatic Reaction 159

6.5.1.5 Fluidized Bed Reaction 160

6.5.2 Removal of Impurities 161

6.5.2.1 Unreacted Ethanol and Oxygenates 161
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5.2.2</td>
<td>CO₂ and Acids</td>
<td>161</td>
</tr>
<tr>
<td>6.5.3</td>
<td>Ethylene Purification</td>
<td>161</td>
</tr>
<tr>
<td>6.6</td>
<td>Polymerization</td>
<td>162</td>
</tr>
<tr>
<td>6.7</td>
<td>Conclusion</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>Acknowledgments</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>163</td>
</tr>
<tr>
<td>7</td>
<td>Fats and Oils as Raw Material for the Chemical Industry</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td><em>Aalbert (Bart) Zwijnenburg</em></td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction—Setting the Scene, Definitions</td>
<td>167</td>
</tr>
<tr>
<td>7.2</td>
<td>Why Fats and Oils Need Catalytic Transformation</td>
<td>168</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Carboxylic Acids</td>
<td>168</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Alcohols</td>
<td>168</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Amines and Amides</td>
<td>168</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Esters</td>
<td>168</td>
</tr>
<tr>
<td>7.3</td>
<td>Catalytic Process Development—Conceptual</td>
<td>171</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Biology or Chemical Routes?</td>
<td>171</td>
</tr>
<tr>
<td>7.3.2</td>
<td>How to Select between Slurry and Fixed-Bed Operations?</td>
<td>172</td>
</tr>
<tr>
<td>7.3.3</td>
<td>How to Choose between Nickel and Palladium?</td>
<td>174</td>
</tr>
<tr>
<td>7.4</td>
<td>Fatty Alcohols: Then and Now, a Case Study</td>
<td>175</td>
</tr>
<tr>
<td>7.4.1</td>
<td>Catalyst Selection</td>
<td>176</td>
</tr>
<tr>
<td>7.4.2</td>
<td>Slurry versus Fixed-Bed Processes</td>
<td>177</td>
</tr>
<tr>
<td>7.5</td>
<td>Conclusion and Outlook: Development Challenges for the Future</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>179</td>
</tr>
<tr>
<td>8</td>
<td>Production of Aromatic Chemicals from Biobased Feedstock</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td><em>David Dodds and Bob Humphreys</em></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>183</td>
</tr>
<tr>
<td>8.2</td>
<td>Chemical Routes to Aromatic Chemicals from Biomass</td>
<td>184</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Process Chemistry</td>
<td>186</td>
</tr>
<tr>
<td>8.2.1.1</td>
<td>Pyrolysis</td>
<td>186</td>
</tr>
<tr>
<td>8.2.1.2</td>
<td>Hydrogenation and Hydrogenolysis</td>
<td>186</td>
</tr>
<tr>
<td>8.2.1.3</td>
<td>Catalytic Reforming</td>
<td>188</td>
</tr>
<tr>
<td>8.2.1.4</td>
<td>Zeolite Treatment</td>
<td>188</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Technology Examples</td>
<td>189</td>
</tr>
<tr>
<td>8.2.2.1</td>
<td>Conversion of Biomass-Derived Sugars to Aromatics including BTX</td>
<td>189</td>
</tr>
<tr>
<td>8.2.2.2</td>
<td>Pyrolysis of Solid Biomass to Aromatic Chemicals</td>
<td>190</td>
</tr>
<tr>
<td>8.2.2.3</td>
<td>Upgrading Bio-Oils to Aromatics</td>
<td>192</td>
</tr>
<tr>
<td>8.2.2.4</td>
<td>Aromatic Chemicals from Other Renewable Raw Materials</td>
<td>192</td>
</tr>
<tr>
<td>8.2.3</td>
<td>Summary</td>
<td>193</td>
</tr>
<tr>
<td>8.3</td>
<td>Biological Routes to Specific Aromatic Chemicals</td>
<td>194</td>
</tr>
<tr>
<td>8.3.1</td>
<td>PTA via PX</td>
<td>194</td>
</tr>
<tr>
<td>8.3.1.1</td>
<td>PX via Isobutanol and Isobutylene</td>
<td>194</td>
</tr>
</tbody>
</table>
8.3.1.2 Valine Pathway to Isobutylene 194
8.3.1.3 Direct Biological Isobutylene Production 196
8.3.1.4 Biological Oxidation of PX to PTA 198
8.3.2 Aromatics via HMF Production 198
8.3.2.1 Preparation of PTA via HMF 200
8.3.2.2 Yield Summary of HMF Routes to PTA 202
8.3.3 Limonene to PTA 203
8.3.4 The Common Aromatic Pathway 203
8.3.4.1 Background 203
8.3.4.2 Other Aromatic Compounds from the Common Aromatic Pathway 210
8.3.5 Other Routes to Aromatic Compounds 215
8.3.5.1 Tetrahydroxybenzene and Pyrogallol 215
8.3.5.2 Phloroglucinol 217
8.3.5.3 Chalcones, Stilbenes, Vanillin and Lignans 217
8.4 Lignin—The Last Frontier 220
8.5 Considerations for Scale-Up and Commercialization 222
8.6 Conclusion 224
References 224

9 Organosolv Biorefining: Creating Higher Value from Biomass 239
E. Kendall Pye and Michael Rushton
9.1 Introduction 239
9.2 Concepts and Principles of Biorefinery Technologies 241
9.2.1 Types of Biorefineries for Biomass Processing 241
9.2.1.1 Biorefineries Employing Thermochemical Treatment of Biomass 242
9.2.1.2 Biorefineries Using Physical and Chemical Pretreatment with Biochemical Processing 243
9.3 Catalytic Processes Employed in Biorefining 245
9.3.1 Catalysis in Biorefineries Employing Gasification and Pyrolysis 245
9.3.2 Catalysts in Anaerobic Digestion Biorefineries 246
9.3.2.1 Catalysts in Non-Thermochemical Biorefineries 246
9.4 An Organosolv Biorefinery Process for High-Value Products 247
9.4.1 Guiding Principles of the Lignol Organosolv Biorefinery 250
9.4.2 Applications and Markets for Organosolv Biorefinery Products 251
9.4.2.1 Native Lignin—Its Properties and Composition 251
9.4.2.2 Lignin from Other Processes 251
9.4.2.3 HP-L™ Lignin—Organosolv Lignin from the Lignol Biorefinery 252
9.4.2.4 Lignin Derivatives 252
9.4.3 HP-L Lignin Properties 253
9.4.4 Current Applications and Market Opportunities for HP-L Lignin 253
9.4.4.1 New Product Opportunities for Lignin Derivatives 254
9.4.4.2 Market Drivers for Commercial Use of HP-L Lignin and Other Bio-Products 256
10 Biomass-to-Liquids by the Fischer–Tropsch Process 265

Erling Rytter, Esther Ochoa-Fernández, and Adil Fahmi

10.1 Basics of Fischer–Tropsch Chemistry and BTL 265
10.1.1 The FT History and Drivers 265
10.1.2 Reactions 266
10.1.3 Mechanisms and Kinetics 268
10.1.4 Products 269
10.1.5 Fischer–Tropsch Metals 270
10.1.6 The Biomass-to-Liquid FT Concept 271
10.2 Cobalt Fischer–Tropsch Catalysis 272
10.2.1 Catalyst Preparation and Activation 272
10.2.2 Catalyst Activity 274
10.2.3 Selectivity 275
10.2.4 Activity Loss 276
10.2.5 Commercial Formulations 277
10.3 Fischer–Tropsch Reactors 279
10.3.1 Reactor Selection 279
10.3.2 Tubular Fixed-Bed 279
10.3.3 Slurry Bubble Column 280
10.4 Biomass Pretreatment and Gasification 282
10.4.1 Pretreatment of Biomass 282
10.4.2 Biomass Gasification 284
10.4.3 Entrained-Flow Gasifier 286
10.4.4 Fluidized-Bed Gasifier 287
10.4.5 Plasma Gasifier 288
10.4.6 Gasification Pilot and Demonstration Projects 288
10.4.6.1 Entrained-Flow Gasifiers 290
10.4.6.2 Fluidized-Bed Gasifiers 291
10.4.6.3 Plasma Gasifiers 291
10.4.6.4 Steam Reforming 292
10.4.7 Syngas Composition 292
10.5 Biomass-to-Liquids Process Concepts 293
10.5.1 Example of Process Flow-Sheet 293
10.5.2 Gas Conditioning and Clean-Up 294
10.5.3 BTL Mass and Energy Balance 295
10.5.4 CO₂ Management 298
10.5.5 Upgrading and Products 299
10.5.6 Production Cost 300
10.6 BTL Pilot and Demonstration Plants 301
10.7 XTL Energy and Carbon Efficiencies 303
11 Catalytic Transformation of Extractives 309
Päivi Mäki-Arvela, Irina L. Simakova, Tapio Salmi, and Dmitry Yu. Murzin
11.1 Introduction 309
11.2 Fine and Special Chemicals from Crude Tall Oil Compounds 313
11.2.1 Sitosterol Hydrogenation and Its Application in Food as a Cholesterol-Suppressing Agent 313
11.3 Fine and Special Chemicals from Turpentine Compounds 317
11.3.1 Isomerization of Monoterpenes and Their Derivatives 317
11.3.2 Oxidation of Monoterpenes 327
11.3.3 Hydrogenation of Monoterpenes 329
11.3.4 Epoxidation of Monoterpenes 330
11.3.5 Hydration of Monoterpenes 332
11.3.6 Esterification and Etherification of Monoterpenes 333
11.3.7 Aldol Condensation of Monoterpene Derivatives 334
11.4 Conclusions 335
11.5 Acknowledgment 336
References 336

12 Environmental Assessment of Novel Catalytic Processes Based on Renewable Raw Materials—Case Study for Furanics 341
Martin K. Patel, Aloysius J.J.E. Eerhart, and Deger Saygin
12.1 Introduction 341
12.2 Energy Savings by Catalytic Processes 343
12.3 LCA Methodology 346
12.4 Case Study: Energy Analysis and GHG Balance of Polyethylene Furandicarboxylate (PEF) as a Potential Replacement for Polyethylene Terephthalate (PET) 348
12.5 Discussion and Conclusions 352
References 352

13 Carbon Dioxide: A Valuable Source of Carbon for Chemicals, Fuels and Materials 355
Michele Aresta and Angela Dibenedetto
13.1 Introduction 355
13.2 The Conditions for Industrial Use of CO₂ 356
13.2.1 Environmental Issue 356
13.2.2 Energy Issues 357
13.2.3 Economic Issues 359
13.3 Carbon Dioxide Conversion 359
13.3.1 Carbonates 359
13.3.1.1 Organic Molecular Compounds 360
13.3.1.2 Synthesis of Acyclic Carbonates via Carboxylation of Alcohols 361
13.3.1.3 Synthesis of Carbonates via Transesterification or Alcoholysis of Urea 364
13.3.1.4 Synthesis of Cyclic Carbonates and Polymers 365
13.3.2 Carbamates and Polyurethanes 366
13.3.2.1 Synthesis of Molecular Carbamates 366
13.3.2.2 Indirect Synthesis of Carbamates 369
13.4 Energy Products from CO₂ 371
13.5 Production of Inorganic Carbonates 373
13.6 Enhanced Fixation of CO₂ into Aquatic Biomass 374
13.7 Conclusion and Future Outlook 378
References 379

Index 387