Contents

Preface *XV*

List of Contributors *XIX*

1 **Renewable Catalytic Technologies – a Perspective** *1*
Rutger A. van Santen

1.1 Introduction *1*
1.2 Economic and Societal Background *1*
1.3 Technology Options *5*
1.4 Process Options for Biomass Conversion *13*
1.5 Conclusions *18*
References *19*

2 **Lignocellulose Conversion: An Introduction to Chemistry, Process and Economics** *21*
Jean-Paul Lange

2.1 Overview *21*
2.2 Introduction *21*
2.2.1 Need for Renewable Energy *21*
2.2.2 Need for Biomass Conversion *22*
2.2.3 Biomass Composition *24*
2.2.4 Fuels and Chemicals Composition *25*
2.2.5 Biomass Deoxygenation *26*
2.3 Chemistry and Processes *26*
2.3.1 Key Reactions of Carbohydrates *27*
2.3.2 Pyrolysis *28*
2.3.2.1 Chemistry *28*
2.3.2.2 Product Applications *30*
2.3.2.3 Processes *30*
2.3.2.4 Alternative Developments *32*
2.3.3 Gasification *32*
2.3.3.1 Chemistry *32*

Catalysis for Renewables: From Feedstock to Energy Production
Edited by Gabriele Centi and Rutger A. van Santen
Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-31788-2

2.3.3.2 Process 33
2.3.3.3 Alternative Developments: Hydrogen Production 35
2.3.4 Hydrolysis 35
2.3.4.1 Chemistry 35
2.3.4.2 Sugar Derivatives 37
2.3.4.3 Process 37
2.3.4.4 Recent Developments 38
2.3.5 Fermentation 39
2.3.5.1 Chemistry 39
2.3.5.2 Process 40
2.3.5.3 Recent Developments 41
2.4 Economics 42
2.4.1 Methodology 42
2.4.2 Fuel Production 42
2.4.2.1 Plant Costs 42
2.4.2.2 Feed Costs 43
2.4.2.3 Manufacturing Costs 44
2.4.3 Process Scale 46
2.4.4 Chemicals Production 46
2.5 Summary and Conclusions 48
References 49

3 Process Options for the Catalytic Conversion of Renewables into Bioproducts 53
Pierre Gallezot

3.1 Overview 53
3.2 Introduction 53
3.3 The Biorefinery Concept 55
3.4 Strategies for Biomass Conversion into Bioproducts 56
3.4.1 From Biomass to Products via Degraded Molecules 56
3.4.2 From Biomass to Products via Platform Molecules 57
3.4.2.1 Identification of Main Platform Molecules 57
3.4.2.2 Selected Examples of Platform Molecule Conversion into Bioproducts 58
3.4.3 From Biomass to Products via New Synthesis Routes 65
3.4.3.1 One-pot Reaction with Cascade Catalysis 65
3.4.3.2 One-pot Conversion into a Mixture of Products 66
3.5 Concluding Remarks 70
References 72

4 Industrial Development and Application of Biobased Oleochemicals 75
Karlheinz Hill

4.1 Overview 75
4.2 Raw Material Situation 75

4.3 Ecological Compatibility *77*
4.4 Examples of Products *78*
4.4.1 Oleochemicals for Polymer Applications *79*
4.4.1.1 Dimer Diols Based on Dimer Acid *82*
4.4.1.2 Polyols Based on Epoxides *83*
4.4.2 Biodegradable Fatty Acid Esters for Lubricants *84*
4.4.3 Surfactants and Emulsifiers Derived from Vegetable Oil Based Fatty Alcohols and Fatty Acids *86*
4.4.3.1 Fatty Alcohol Sulfate (FAS) *88*
4.4.3.2 Acylated Proteins and Amino Acids (Protein–Fatty Acid Condensates) *88*
4.4.3.3 Carbohydrate-based Surfactants – Alkyl Polyglycosides *89*
4.4.3.4 Alkyl Polyglycoside Carboxylate *91*
4.4.3.5 Polyol Esters *92*
4.4.3.6 Multifunctional Care Additives for Skin and Hair *93*
4.4.4 Emollients *95*
4.4.4.1 Dialkyl Carbonate *95*
4.4.4.2 Guerbet Alcohols *96*
4.5 Perspectives *97*
References *97*

5 Fine Chemicals from Renewables *101*
Herman van Bekkum and Leendert Maat

5.1 Introduction *101*
5.2 Vanillin *103*
5.3 Monoterpenes *105*
5.4 Alkaloids *108*
5.5 Steroids *112*
5.6 Enantioselective Catalysis *113*
5.7 Artimisinine *115*
5.8 Tamiflu *116*
5.9 Final Remarks *117*
References *117*

6 Options for Catalysis in the Thermochemical Conversion of Biomass into Fuels *119*
Sascha R. A. Kersten, Wim P. M. van Swaaij, Leon Lefferts, and Kulathuiyer Seshan

6.1 Introduction *119*
6.2 Biomass as Feedstock for Fuels *120*
6.3 Composition of Biomass *122*
6.4 Biorefinery *125*
6.5 Biomass Pretreatment *126*
6.6 Thermochemical Conversion of Lignocelluloses *127*

6.7 Biomass Gasification *129*
6.7.1 Gasification of Dry Biomass *129*
6.7.2 Catalytic Gasification of Pyrolysis Oil *129*
6.7.3 Chemistry and Catalysis of Gasification *130*
6.7.4 Gasification in Hot Compressed Water *131*
6.8 Liquefaction of Biomass *132*
6.8.1 Non-catalytic Pyrolysis *132*
6.8.2 Catalytic Pyrolysis *134*
6.8.3 Hydrothermal Liquefaction *135*
6.9 Upgrading Pyrolysis Oil to Fuels *136*
6.9.1 Decarboxylation (DCO) *136*
6.9.2 Hydrodeoxygenation (HDO) *137*
6.9.3 Cracking over Zeolites (FCC) *137*
6.10 Hydrolysis *139*
6.11 Underlying Approach for Catalyst Design *140*
6.12 Summary *141*
References *141*

7 Thermal Biomass Conversion *147*
Simone Albertazzi, Francesco Basile, Giuseppe Fornasari, Ferruccio Trifirò, and Angelo Vaccari

7.1 Introduction *147*
7.2 Biomass Resources and Biomass Pre-treatment *148*
7.3 Biomass Combustion *149*
7.4 Biomass Gasification *149*
7.5 Pyrolysis *154*
7.6 Fuels via Thermal Biomass Conversion *158*
7.7 Conclusions *161*
References *161*

8 Thermal Biomass Conversion and NO_x Emissions in Grate Furnaces *163*
Rob J.M. Bastiaans, Hans A.J.A. van Kuijk, Bogdan A. Albrecht, Jeroen A. van Oijen and L. Philip H. de Goey

8.1 Introduction *163*
8.2 Tunable Diode Laser Measurements of Biomass Kinetics *164*
8.2.1 Introduction *164*
8.2.2 Tunable Diode Laser Grid Reactor Experiments *164*
8.2.3 Experimental Setup *165*
8.2.4 Results *166*
8.3 Propagation of Thermal Conversion Fronts *169*
8.3.1 Introduction *169*
8.3.2 Modeling Approach *170*
8.3.3 Experiments *173*

8.4 Gas-phase CFD Modeling of Grate Furnaces *175*
8.4.1 Introduction *175*
8.4.2 Description of the Model *175*
8.4.3 Construction of Look-up Tables for Numerical Simulations and Validation *176*
8.4.4 Application of the Combustion Model on a 2D Grate Furnace *177*
8.5 Conclusions *180*
References *180*

9 Bioethanol: Production and Pathways for Upgrading and Valorization *183*
Stephane Pariente, Nathalie Tanchoux, François Fajula, Gabriele Centi, and Siglinda Perathoner

9.1 Introduction *183*
9.2 Production, a Short Overview *188*
9.3 Uses as Biofuel *193*
9.3.1 Bioethanol as Fuel Additive *193*
9.3.1.1 Gasoline/Bioethanol Blends *193*
9.3.1.2 Diesel/Bioethanol Blends *195*
9.3.2 Bioethanol and Hydrogen *196*
9.3.3 Bioethanol for Fuel Cells *199*
9.4 Bioethanol Upgrading and Valorization *200*
9.4.1 Conversion into Fuel Components *200*
9.4.2 Conversion into Chemicals *203*
9.5 Conclusions *205*
References *205*

10 Conversion of Glycerol into Traffic Fuels *209*
Tiia S. Viinikainen, Reetta S. Karinen, and A. Outi I. Krause

10.1 Introduction *209*
10.2 Glycerol *210*
10.2.1 Properties, Production and Use of Glycerol *210*
10.2.2 Glycerol from Biodiesel Production *211*
10.3 Etherification of Glycerol with Isobutene *212*
10.3.1 Reaction Scheme *212*
10.3.2 Etherification Catalysts *213*
10.3.3 Process Conditions *214*
10.3.4 Etherification Kinetics *216*
10.3.5 Ethers of Glycerol as Fuel Components *217*
10.4 Improvements to Biodiesel Process *218*
10.4.1 Etherification with Biodiesel Process *218*
10.4.2 Heterogeneous Biodiesel Process *219*
10.5 Reforming of Glycerol *219*
10.5.1 Aqueous Phase Reforming *220*

10.5.2 Steam Reforming *220*
10.6 Future Aspects *220*
References 221

11 Catalytic Transformation of Glycerol *223*
Bert Sels, Els D'Hondt, and Pierre Jacobs

11.1 Introduction and Scope *223*
11.2 Catalytic Dehydration of Glycerol and Acrolein Formation *224*
11.3 Etherification of Glycerol via Catalytic Dehydration *226*
11.3.1 Glycerol Oligomerization *226*
11.3.2 Reaction of Glycerol with Alkenes *228*
11.4 Catalytic Oxidation of Glycerol *231*
11.4.1 Electrochemical Oxidation *231*
11.4.2 Gas-phase Catalytic Oxidation *233*
11.4.3 Selective Oxidation with Molecular Oxygen on Pt/Bi Catalysts *234*
11.4.4 Selective Oxidation with Molecular Oxygen on Gold-based Catalysts *237*
11.4.5 Selective Oxidation with Oxidants Differing from Molecular Oxygen *240*
11.5 Catalytic Hydrogenolysis of Glycerol *241*
11.5.1 Heterogeneous Catalytic Hydrogenolysis of Glycerol *241*
11.5.2 Homogeneous Catalytic Hydrogenolysis of Glycerol *248*
11.6 Glycerol Reforming and Hydrogen Production *249*
11.7 Miscellaneous Oxidation Reactions *250*
11.8 Conclusions *251*
References 252

12 Catalytic Processes for the Selective Epoxidation of Fatty Acids: More Environmentally Benign Routes *257*
Matteo Guidotti, Rinaldo Psaro, Maila Sgobba, and Nicoletta Ravasio

12.1 Introduction *257*
12.2 Non-catalytic Epoxidation Systems *259*
12.3 Homogeneous Catalytic Systems *260*
12.4 Chemoenzymatic Epoxidation Systems *260*
12.5 Heterogeneous Catalytic Systems *261*
12.6 Epoxidation of FAMEs Over Titanium-based Catalysts: The Skills in Milan *264*
12.6.1 Epoxidation of Pure C_{18} Monounsaturated FAMEs *265*
12.6.2 Epoxidation of a Mixture of FAMEs from Vegetable Sources *266*
12.6.2.1 HO Sunflower-, Coriander-, and Castor-oil FAME Mixtures *266*
12.6.2.2 Soya-bean Oil FAME Mixture *269*
12.7 Conclusions *270*
References 270

13 Integration of Biocatalysis with Chemocatalysis: Cascade Catalysis and Multi-step Conversions in Concert *273*
Tom Kieboom

13.1 Overview *273*
13.2 Introduction *274*
13.2.1 Human's Chemistry *274*
13.2.2 Nature's Chemistry *275*
13.2.3 Bio-chemo Integration *276*
13.3 Types of Cascades *277*
13.3.1 Bio-bio Cascades *278*
13.3.2 Chemo-chemo Cascades *280*
13.3.3 Bio-chemo Cascades *281*
13.4 Technologies for Cascades *289*
13.4.1 Catalytic Methods *291*
13.4.2 Reactor Design *292*
13.4.3 Compartmentalization *292*
13.4.4 Medium Engineering *293*
13.4.5 Cell Factory Design *294*
13.5 Conclusions *295*
References *296*

14 Hydrogen Production and Fuel Cells as the Bridging Technologies Towards a Sustainable Energy System *299*
Frank A. de Bruijn, Bert Rietveld, and Ruud W. van den Brink

14.1 Introduction *299*
14.1.1 The Hydrogen Energy Chain *300*
14.1.2 Hydrogen Sources and Production *300*
14.1.3 Use of Hydrogen in Stationary and Mobile Applications *301*
14.2 Hydrogen Production from Natural Gas *301*
14.2.1 Conventional Hydrogen Production *302*
14.2.1.1 Hydrogen Production from Natural Gas *302*
14.2.1.2 Hydrogen Production from Other Feedstocks *304*
14.2.2 Hydrogen Production with CO_2 Capture *305*
14.2.2.1 CO_2 Capture *306*
14.3 Novel Processes for Hydrogen Production with CO_2 Capture *307*
14.3.1 Hydrogen Membrane Reactors *307*
14.3.2 Sorption-enhanced Reforming and Water-gas Shift *310*
14.4 Conclusions and Catalytic Challenges *313*
14.4.1 Electrochemical Hydrogen Production and Conversion *314*
14.4.1.1 Kinetics of the Electrochemical Hydrogen–Oxygen Processes *314*
14.4.1.2 Hydrogen Production by Water Electrolysis *315*
14.4.1.3 Proton Exchange Membrane Fuel Cells *319*
14.4.1.4 Solid Oxide Fuel Cells (SOFCs) *326*
References *333*

15 **Pathways to Clean and Green Hydrogen** *337*
Gert J. Kramer, Joep P. P. Huijsmans, and Dave M. Austgen

15.1 Introduction *337*
15.2 Energy Resource Availability *339*
15.3 Modes of Hydrogen Production and Distribution *340*
15.4 The Cost of Hydrogen Fuel *341*
15.4.1 Case Definition *342*
15.4.2 Results *343*
15.5 "Clean Hydrogen" and the Scope for CO_2 Reduction *345*
15.5.1 Scope *345*
15.5.2 Hydrogen versus Gasoline and Diesel *347*
15.6 Coal and Biomass *348*
15.7 Conclusions *349*
References 349

16 **Solar Photocatalysis for Hydrogen Production and CO_2 Conversion** *351*
Claudio Minero and Valter Maurino

16.1 Introduction *351*
16.2 The Photocatalytic Process *354*
16.2.1 Quantum Yield *357*
16.2.2 Catalyst Related Losses *360*
16.2.2.1 Carrier Thermalization *360*
16.2.2.2 Charge Separation *361*
16.2.2.3 Active Charge Separation *362*
16.2.2.4 Passive Charge Separation *362*
16.2.2.5 Mediated Charge Separation *366*
16.2.3 Surface-related Losses *367*
16.3 Photoelectrochemical Cells *371*
16.4 New Materials *372*
16.4.1 Crystal Structure and Activity *373*
16.4.2 Visible Sensitization *375*
16.5 Conclusions *377*
References 379

Conclusions, Perspectives and Roadmap *387*
Gabriele Centi and Rutger A. van Santen

1 Introduction *387*
2 Driver for a Biomass Economy *388*
3 Main Issues and Perspectives on Bioenergy and Biofuels in Relation to Catalysis *389*
3.1 Biofuels *389*
3.1.1 First Generation Biofuels *390*

3.1.2 Second (or Next) Generation Biofuels *392*
3.2 Biorefineries *394*
3.3 Use of By-products Deriving from Biomass Transformation *399*
3.4 Biomass as Feedstock for Chemical Production *400*
3.5 Use of Solar Energy *403*
4 Conclusions *405*
References *411*

Index *413*