

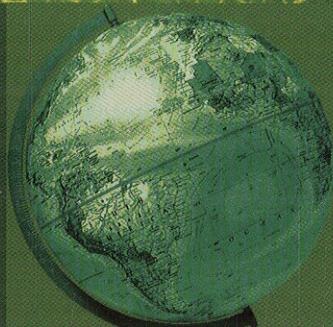
WILEY SERIES IN RENEWABLE RESOURCES

# Thermochemical Processing of **Biomass**

Conversion into Fuels, Chemicals and Power

Robert C. Brown  
Editor

 WILEY



# Contents

<b>Series Preface</b>	<b>xiii</b>
<b>Acknowledgements</b>	<b>xv</b>
<b>List of Contributors</b>	<b>xvii</b>
<b>1 Introduction to Thermochemical Processing of Biomass into Fuels, Chemicals, and Power</b>	<b>1</b>
<i>Robert C. Brown</i>	
1.1 Introduction	1
1.2 Direct Combustion	5
1.3 Gasification	6
1.4 Fast Pyrolysis	7
1.5 Hydrothermal Processing	8
1.6 Hydrolysis to Sugars	9
1.7 Technoeconomic Analysis	10
References	10
<b>2 Biomass Combustion</b>	<b>13</b>
<i>Bryan M. Jenkins, Larry L. Baxter and Jaap Koppejan</i>	
Nomenclature	13
2.1 Introduction	14
2.2 Combustion Systems	15
2.2.1 Fuels	15
2.2.2 Types of Combustor	18
2.3 Fundamentals of Biomass Combustion	23
2.3.1 Combustion Properties of Biomass	23
2.3.2 Combustion Stoichiometry	29
2.3.3 Equilibrium	32
2.3.4 Rates of Reaction	33
2.4 Pollutant Emissions and Environmental Impacts	35
2.4.1 Oxides of Nitrogen and Sulfur	36
2.4.2 Products of Incomplete Combustion	38
2.4.3 Particulate Matter	38
2.4.4 Dioxin-like Compounds	38
2.4.5 Heavy Metals	40
2.4.6 Radioactive Species	40
2.4.7 Greenhouse Gas Emissions	40
References	41

<b>3 Gasification</b>	<b>47</b>
<i>Richard L. Bain and Karl Broer</i>	
3.1 Introduction	47
3.2 Fundamentals of Gasification	48
3.2.1 Heating and Drying	48
3.2.2 Pyrolysis	49
3.2.3 Gas–Solid Reactions	50
3.2.4 Gas-phase Reactions	50
3.3 Feed Properties	51
3.4 Classifying Gasifiers According to Method of Heating	54
3.4.1 Air-blown Gasifiers	54
3.4.2 Steam/Oxygen-blown Gasifiers	56
3.4.3 Indirectly Heated Gasifiers	56
3.5 Classifying Gasifiers According to Transport Processes	58
3.5.1 Fixed Bed	58
3.5.2 Bubbling Fluidized Bed	60
3.5.3 Circulating Fluidized Bed (CFB)	61
3.5.4 Entrained Flow	62
3.6 Pressurized Gasification	63
3.7 Product Composition	64
3.7.1 Char and Tar	67
3.8 System Applications	68
3.8.1 Process Heat	68
3.8.2 Combined Heat and Power (CHP)	68
3.8.3 Synthetic Fuels	74
References	74
<b>4 Syngas Cleanup, Conditioning, and Utilization</b>	<b>78</b>
<i>David C. Dayton, Brian Turk and Raghbir Gupta</i>	
4.1 Introduction	78
4.2 Syngas Cleanup and Conditioning	79
4.2.1 Particulates	81
4.2.2 Sulfur	83
4.2.3 Ammonia Decomposition and HCN Removal	84
4.2.4 Alkalies and Heavy Metals	85
4.2.5 Chlorides	85
4.2.6 Tars	86
4.3 Syngas Utilization	89
4.3.1 Syngas to Gaseous Fuels	90
4.3.2 Syngas to Liquid Fuels	98
4.4 Summary and Conclusions	111
References	115

<b>5 Fast Pyrolysis</b>	<b>124</b>
<i>Robbie H. Venderbosch and Wolter Prins</i>	
5.1 Introduction	124
5.1.1 Fundamentals of Pyrolysis	125
5.1.2 Effect of Ash	128
5.2 Bio-oil Properties	128
5.2.1 Composition and Stability	131
5.3 Fast Pyrolysis Process Technologies	134
5.3.1 Entrained Downflow	135
5.3.2 Ablative Reactor	135
5.3.3 Bubbling Fluidized Bed	138
5.3.4 Circulating Fluidized Bed (CFB)	141
5.3.5 Moving-grate Vacuum Pyrolysis	142
5.3.6 Rotating-cone Pyrolyzer	142
5.4 Bio-oil Fuel Applications	143
5.4.1 Gas Turbines	148
5.4.2 Gasification	149
5.4.3 Transportation Fuels	149
5.5 Chemicals from Bio-oil	150
5.5.1 Whole Bio-oil	150
5.5.2 Fractions of Bio-oil	151
5.6 Concluding Remarks	152
Acknowledgements	153
References	153
<b>6 Upgrading Fast Pyrolysis Liquids</b>	<b>157</b>
<i>Anthony V. Bridgwater</i>	
6.1 Introduction to Fast Pyrolysis and Bio-oil	157
6.1.1 Introduction	157
6.1.2 Bio-oil General Characteristics	157
6.2 Liquid Characteristics and Quality	159
6.3 Significant Factors Affecting Characteristics	159
6.3.1 Feed Material	159
6.3.2 Reactors	164
6.4 Norms and Standards	165
6.5 Bio-oil Upgrading	165
6.5.1 Acidity or Low pH	165
6.5.2 Aging	165
6.5.3 Alkali Metals	166
6.5.4 Char	166
6.5.5 Chlorine	167
6.5.6 Color	167
6.5.7 Contamination of Feed	168
6.5.8 Distillability	168
6.5.9 High Viscosity	168

6.5.10	Inhomogeneity	169
6.5.11	Low H:C Ratio	169
6.5.12	Low pH	169
6.5.13	Materials Incompatibility	169
6.5.14	Miscibility with Hydrocarbons	169
6.5.15	Nitrogen	170
6.5.16	Other Solid Particulates, Excluding Char	170
6.5.17	Oxygen Content	170
6.5.18	Phase Separation or Inhomogeneity	170
6.5.19	Smell	170
6.5.20	Structure of Bio-oil	171
6.5.21	Sulfur	171
6.5.22	Temperature Sensitivity	171
6.5.23	Toxicity	172
6.5.24	Viscosity	172
6.5.25	Water Content	172
6.6	Chemical and Catalytic Upgrading of Bio-oil	172
6.6.1	Physical Upgrading of Bio-oil	172
6.6.2	Catalytic Upgrading of Bio-oil	174
6.6.3	Other Methods for Chemical Upgrading of Bio-oil	180
6.6.4	Hydrogen	182
6.6.5	Chemicals	182
6.7	Conclusions	187
	References	188
<b>7</b>	<b>Hydrothermal Processing</b>	<b>200</b>
	<i>Douglas C. Elliott</i>	
7.1	Introduction	200
7.2	Background	202
7.2.1	Why Hydrothermal Processing?	202
7.2.2	History of Hydrothermal Liquefaction Process Development	202
7.2.3	History of Hydrothermal Gasification Process Development	203
7.3	Fundamentals	203
7.3.1	Subcritical Processing in the Liquid Phase	204
7.3.2	Supercritical Processing in the Vapor Phase	204
7.4	Hydrothermal Liquefaction	205
7.4.1	State of Technology	205
7.4.2	Process Descriptions	205
7.4.3	Product Evaluation	207
7.4.4	Product Utilization	212
7.4.5	Process Mechanism Evaluations	213
7.4.6	Recent Fundamental Evaluations	216
7.4.7	Conclusions Relative to Hydrothermal Liquefaction	216
7.5	Hydrothermal Gasification	217
7.5.1	State of Technology	217

7.5.2	Process Description	217
7.5.3	Catalytic Hydrothermal Gasification	218
7.5.4	Hydrothermal Gasification in Supercritical Water	221
7.5.5	Conclusions Relative to Hydrothermal Gasification	223
7.6	Pumping Biomass into Hydrothermal Processing Systems	223
7.7	Conclusions of Hydrothermal Processing	226
	References	226
<b>8</b>	<b>Catalytic Conversion of Sugars to Fuels</b>	<b>232</b>
	<i>Geoffrey A. Tompsett, Ning Li and George W. Huber</i>	
8.1	Introduction	232
8.1.1	Overview	232
8.1.2	Desired Targets and Overall Reactions	233
8.1.3	Thermodynamics of Chemistry Conversion	235
8.2	Chemistry of Sugars	238
8.3	Hydrogen from Sugars	242
8.3.1	Overall Reaction and Thermodynamics	242
8.3.2	Reaction Mechanism	244
8.3.3	Aqueous-Phase Reforming	244
8.3.4	Supercritical Reactions – Reforming of Sugars	246
8.4	Sugar to Light Alkanes	249
8.4.1	Overall Reaction and Thermodynamics	249
8.4.2	Dehydration of Sugars	251
8.4.3	Hydrogenation Reactions of Sugars	252
8.4.4	Combined Dehydration/Hydrogenation	254
8.5	Sugars to Oxygenates	254
8.5.1	Targeted Products and Thermodynamics	254
8.5.2	Biphasic Dehydration Reactions (HMF and Furfural Production)	255
8.5.3	Hydrogenation	256
8.5.4	Other Oxygenate Fuels from Sugars	258
8.6	Sugars to Larger Alkanes	261
8.6.1	Overall Reaction and Chemistry	261
8.6.2	C–C Bond Formation	266
8.6.3	Hydrogenation/Dehydration	268
8.7	Sugar Conversion to Aromatics	269
8.7.1	Overall Reaction and Thermodynamics	269
8.7.2	Catalytic Fast Pyrolysis	270
8.7.3	Aromatics from Sugar Fragments in the Aqueous Phase	271
8.8	Conclusions and Summary	271
	Acknowledgements	272
	References	272
<b>9</b>	<b>Hybrid Processing</b>	<b>280</b>
	<i>DongWon Choi, Alan A. DiSpirito, David C. Chipman and Robert C. Brown</i>	
9.1	Introduction	280

9.1.1	Biorefineries	280
9.1.2	Hybrid Thermochemical/Biochemical Processing	281
9.2	Syngas Fermentation	282
9.2.1	Catalytic Conversions of Syngas: Chemical Versus Biological	282
9.2.2	Fermentation of Syngas	282
9.2.3	Microbial CO Metabolism	283
9.2.4	Microbial H <sub>2</sub> Metabolism	288
9.2.5	Microbial CH <sub>4</sub> Metabolism	289
9.2.6	Photosynthetic CO <sub>2</sub> Metabolism	290
9.2.7	Current Industrial Progress of Syngas Fermentation	291
9.2.8	Problems and Future Perspectives	292
9.3	Bio-oil Fermentation	295
9.3.1	Levoglucosan Utilizers	296
9.3.2	Current Status of Levoglucosan Fermentation	297
9.3.3	Future Perspectives	298
	References	299
<b>10</b>	<b>Costs of Thermochemical Conversion of Biomass to Power and Liquid Fuels</b>	<b>307</b>
	<i>Mark M. Wright and Robert C. Brown</i>	
10.1	Introduction	307
10.2	Electric Power Generation	308
10.2.1	Direct Combustion to Power	308
10.2.2	Gasification to Power	308
10.2.3	Fast Pyrolysis to Power	309
10.3	Liquid Fuels via Gasification	309
10.3.1	Gasification to Hydrogen	309
10.3.2	Gasification to Methanol	311
10.3.3	Gasification to Mixed Alcohols	312
10.3.4	Gasification to Fischer-Tropsch Liquids	313
10.3.5	Gasification and Syngas Fermentation to PHA and Co-Product Hydrogen	315
10.4	Liquid Fuels via Fast Pyrolysis	316
10.4.1	Bio-oil Fermentation to Ethanol	316
10.4.2	Bio-oil Upgrading to Gasoline and Diesel	316
10.4.3	Bio-oil Gasification to Liquid Fuels	318
10.5	Summary and Conclusions	319
	References	321
	<b>Index</b>	<b>323</b>