

Contents

Preface xv

Acknowledgments and Conflict of Interest xvii

1 A Brief Introduction of Lignin 1

Yuhe Liao

1.1 Introduction 1

1.2 The Building Blocks of Lignin 3

1.2.1 Interlinkages in Lignin 6

1.2.2 Bioengineering of Lignin 8

1.3 Scope of this Book 10

References 11

2 NMR Characterization of Lignin 15

*Cheng-Ye Ma, Ying Xu, Ling-Hua Xu, Chen Zhang, Ji-Yun Qi and
Jia-Long Wen*

2.1 Introduction 15

2.2 ^1H NMR 17

2.2.1 Sample Preparation and Program 17

2.2.1.1 Sample Preparation of Non-Acetylated Lignin 17

2.2.1.2 Sample Preparation of Acetylated Lignin 18

2.2.1.3 ^1H Program 18

2.2.2 ^1H -NMR Spectra Analysis 18

2.2.2.1 ^1H -NMR Spectra of Non-Acetylated Lignin 18

2.2.2.2 ^1H -NMR Spectra of Acetylated Lignin 19

2.3 ^{13}C -NMR 20

2.3.1 Sample Preparation and Program 21

2.3.1.1 Sample Preparation 21

2.3.1.2 ^{13}C -NMR Program 21

2.3.2 Quantitative ^{13}C -NMR 21

2.3.2.1 Quantitative ^{13}C -NMR of Non-Acetylated Lignin 21

2.3.2.2 Quantitative ^{13}C -NMR of Acetylated Lignin 23

2.3.3 Applications of the ^{13}C -NMR 23

2.4 2D-HSQC (Heteronuclear Single-Quantum Correlation) 25

2.4.1 Sample Preparation and Program 26

2.4.2	Semi-Quantification of Lignin in 2D-HSQC NMR Spectra	26
2.4.2.1	Relative Quantitative Method (Without Internal Standard)	27
2.4.2.2	Relative Quantitative Method (Aromatic Ring as IS)	27
2.4.2.3	Based on the Combination of ^{13}C and 2D-HSQC Technique	28
2.4.3	Assignments of Lignin in 2D-HSQC NMR spectra	28
2.4.3.1	Gramineous Lignin	28
2.4.3.2	Hardwood Lignin	31
2.4.3.3	Softwood	37
2.4.4	Application of 2D-HSQC NMR Technique in the Field of Lignin	37
2.4.4.1	Structure Characterization of Native Lignin from Different Plant Sources	39
2.4.4.2	Structure Changes of Lignin During Delignification and Pretreatment Process	39
2.5	^{31}P NMR	40
2.5.1	Factors Affecting ^{31}P NMR	40
2.5.2	^{31}P NMR Operation	43
2.5.2.1	Detailed Procedures	44
2.5.3	Applications of the ^{31}P NMR	45
2.6	^{19}F NMR	45
2.7	Solution-State NMR of Whole Plant Cell Wall	47
2.7.1	Solution-State 2D-HSQC NMR of Acetylated Plant Cell Walls	47
2.7.2	Solution-State 2D-HSQC NMR of Non-Acetylated Plant Cell Walls	48
2.7.3	Comparison of the Dissolution Methods and Applications of Whole Plant Cell Wall Solution State NMR	49
2.8	Conclusion	49
	References	52
3	Advances in the Molar Mass and Functionality Analysis of Lignin	61
	<i>Oliver Musl and Antje Potthast</i>	
3.1	Introduction	61
3.2	General Aspects	62
3.3	Dissolution of Lignin Samples	64
3.4	Molar Mass Analysis	65
3.4.1	Size-Exclusion Chromatography (SEC)	66
3.4.2	Asymmetric Flow Field-Flow Fractionation (AF4)	68
3.4.3	Detection Systems	69
3.5	Functional Group Analysis	72
3.5.1	Heterogeneity in Functionality	73
3.5.2	Dispersity in Functionality	74
3.6	Analysis of Lignin Composition by Two-Dimensional Liquid Chromatography	76
	References	77
4	Degradative Methods for Lignin Valorization	85
	<i>Elisabetta Borsella, Pietro Colucci, Giuseppe Lembo and Heiko Lange</i>	
4.1	Introduction	85

4.2	Basics Aspects Regarding Structural Features in (Isolated) Lignins	86
4.2.1	Occurrence and Isolation	86
4.2.2	Standard Means for Elucidating Basic Structural Features of (Isolated) Lignins	89
4.2.2.1	Nuclear Magnetic Resonance (NMR) Spectroscopy-Based Analysis Methods	90
4.2.2.2	Fourier-Transform Infrared Spectroscopy and Raman Spectroscopy	90
4.2.2.3	Size Exclusion and Gel Permeation Chromatographic Methods	91
4.2.3	“Purity” of Isolated Lignins	91
4.2.4	Fractionation of Isolated Lignins for Structurally more Homogeneous Starting Materials	92
4.3	Classic Wet-Chemical Degradation Methods	93
4.4	Catalytic Oxidative Degradation of Lignins	96
4.4.1	Catalytic Chemical Oxidative Degradation	96
4.4.1.1	Metal-Free Oxidations	96
4.4.1.2	Organometallic Catalysts	97
4.4.1.3	Biomimetic Catalysts	100
4.4.2	Enzymatic Oxidative Degradation	102
4.4.2.1	Laccase-Mediated Oxidative Depolymerization	103
4.4.2.2	Peroxidase-Mediated Oxidative Depolymerization	105
4.4.2.3	Technological Advancements to Enable Enzymatic Lignin Degradation	106
4.4.3	Catalytic Chemical Reductive Degradation	107
4.4.3.1	Metal-Free Reductions	107
4.4.3.2	Heterogenic Transition Metal Catalysts	107
4.4.3.3	Organometallic Catalysts	108
4.5	Thermally Induced Lignin Depolymerization	108
4.5.1	Hydro Treatment-Based Lignin Depolymerization	110
4.5.2	Pyrolytic Lignin Degradation	110
4.5.2.1	Torrefaction of Lignin	110
4.5.2.2	Catalyst-Free Pyrolysis of Lignins	113
4.5.2.3	Catalytic Pyrolysis of Lignin	113
4.5.2.4	Advanced Pyrolysis Technologies	115
4.6	Electrochemical Lignin Degradation	115
4.7	Concluding Remarks and Outlook	116
	References	117

5 Isolation of Native-Like Lignin 139

Zhiwen Wang, Yiwei Fan and Peter J. Deuss

5.1	Classical Methods Used for Native-Like Lignin Isolation	142
5.1.1	Mild Alcohol Extracted Lignin	142
5.1.2	Milled Wood Lignin (MWL)	144
5.1.3	Cellulolytic Enzyme Lignin (CEL)	145
5.1.4	Enzymatic Mild Acidolysis Lignin (EMAL)	146
5.1.5	Residual Enzyme Lignin (REL)	147

5.2	Isolation of Lignin with High β -O-4 Content	148
5.2.1	Isolation Under Acidic Conditions	148
5.2.2	Isolation Under Alkaline Conditions	151
5.2.3	Isolation Using Flow-through Extraction	152
5.2.4	Isolation With Alternative Solvents	152
5.2.5	Alternative Resources and Special Lignins	155
5.3	Concluding Comments	155
	References	156
6	Isolation of Lignin in the Biorefinery Process	163
	<i>Qian Xu and Ling-Ping Xiao</i>	
6.1	Introduction	163
6.2	Methods Used to Isolate Lignin from Lignocellulose	164
6.2.1	Organosolv Process	164
6.2.2	Hydrothermal Pretreatment	165
6.2.3	Steam Explosion	166
6.2.4	Ammonia-Based Pretreatment	167
6.2.5	γ -Valerolactone (GVL)	167
6.2.6	Ionic Liquids (ILs)	167
6.2.7	Deep Eutectic Solvents (DES)	169
6.2.8	Acid Treatment	170
6.2.9	Acidic Lithium Bromide Trihydrate (ALBTH) System	172
6.3	Conclusion and Perspectives	174
	Acknowledgments	174
	References	174
7	Gasification and Combined Heat and Power (CHP) from Lignin	183
	<i>Subhashini, Michal Jeremias and Vineet Singh Sikarwar</i>	
7.1	Introduction	183
7.2	Chemical Structure and Composition of Lignin	185
7.3	Sources of Lignin and its Characterization Techniques	186
7.4	Lignin Isolation/Production Process	187
7.5	Lignin Depolymerization and Conversion to Fuel	188
7.5.1	Thermochemical Conversion	192
7.5.1.1	Pyrolysis of Lignin	193
7.5.1.2	Gasification of Lignin	194
7.6	Conclusion	197
	References	198
8	Enzymatic and Microbial Bioconversion of Lignin to Renewable Chemicals	203
	<i>Timothy D.H. Bugg, Victoria Sodr�, Awatif Alruwaili and Goran M.M. Rashid</i>	
8.1	Lignin Conversion by Enzymes	203
8.1.1	Extracellular Peroxidases from White-rot Fungi	203
8.1.2	Bacterial Dye-Decolorizing Peroxidases (DyP)	205

8.1.3	Multi-Copper Oxidases	206
8.1.4	Beta-Etherase Enzymes for Lignin Ether Cleavage	207
8.1.5	Other Lignin-Oxidizing Enzymes	208
8.1.6	Accessory Enzymes for Lignin Oxidation	209
8.1.6.1	Fungal Accessory Enzymes	209
8.1.6.2	Bacterial Accessory Enzymes	209
8.1.7	Lignin Conversion <i>In Vitro</i> by Enzymes	210
8.2	Pathways for Microbial Lignin Degradation	211
8.3	Microbial Lignin Bioconversion by Engineered Bacteria	213
8.3.1	Microbial Hosts for Lignin Bioconversion	213
8.3.2	Conversion of Polymeric Lignin and Depolymerized Lignin Hydrolysates into High-Value Products	216
8.3.2.1	Vanillin	216
8.3.2.2	Polyhydroxyalkanoates	217
8.3.2.3	Triacylglycerol Lipids	219
8.3.2.4	<i>Cis,cis</i> -Muconic Acid (MA)/Adipic Acid	219
8.3.2.5	Pyridine- and Pyrone-Dicarboxylic Acids	220
8.3.2.6	Substituted Styrenes	221
	Acknowledgments	222
	References	222
9	Approaches to the Oxidative Depolymerization of Lignin	231
	<i>Elena Subbotina, Shannon S. Stahl, Paul Anastas and Joseph S.M. Samec</i>	
9.1	Introduction	231
9.2	Metal-Free Oxidative Depolymerization of Lignin	233
9.2.1	Nitrobenzene Oxidation	233
9.2.2	Ozone Mediated Depolymerization of Lignin	234
9.2.3	Other Organic Oxidants	234
9.2.4	Alkaline Oxidation of Lignin	238
9.2.5	Oxidative Catalytic Fractionation of Wood (OCF)	241
9.3	Transition Metal Catalysis for Oxidative Cleavage of Lignin	242
9.4	Rhenium-Based Catalysts	243
9.5	Cobalt-Based Catalysts	244
9.6	Vanadium-Based Catalysts	246
9.7	Other Metals	248
9.8	Biomimetic Oxidations	250
9.9	Electrochemical Oxidative Cleavage of Lignin	252
9.9.1	General Aspects	252
9.10	Direct Electrochemical Oxidation of Lignin	252
9.11	Indirect Electrooxidation of Lignin	254
9.12	Lignin Oxidation via Electrochemical Combination Reactions	256
9.13	Concluding Remarks and Outlook	257
	Acknowledgments	257
	References	258

10	Photocatalytic Conversion of Lignin	265
	<i>Xuejiao Wu, Shunji Xie and Ye Wang</i>	
10.1	Introduction	265
10.2	Photocatalytic C—O Bond Cleavage	268
10.2.1	Stepwise Photocatalytic Cleavage of C _β —O (β-O-4) Bond	269
10.2.1.1	Oxidation of C _α Hydroxyl into C _α Carbonyl	269
10.2.1.2	Reductive Cleavage of C _β —O Bond in β-O-4 Ketone	270
10.2.2	Direct Photocatalytic Cleavage of Lignin C _β —O (β-O-4) Bond	273
10.2.2.1	Direct Approach through β-O-4 Ketone Intermediate	273
10.2.2.2	Direct Approach through C _α Intermediate	275
10.2.3	Cleavage of C _{aryl} —O (β-O-4, 4-O-5) and C _α —O (α-O-4)	278
10.3	Photocatalytic C—C Bond Cleavage	280
10.3.1	C _α O—H Bond Activation to Alkoxy Radical Intermediate	280
10.3.2	C _β —H Bond Activation to C _β Radical Intermediate	283
10.3.3	Single Electron Transfer to Radical Cation Intermediate	285
10.4	Conclusion and Outlook	286
	References	289
11	Electrochemical Conversion for Lignin Valorization	295
	<i>Qi Zhu, Mahlet Garedew, Bing Song, Yuliang Li and Jason Chun-Ho Lam</i>	
11.1	Introduction	295
11.2	The Mechanism of Electrocatalytic Lignin Conversion	297
11.2.1	Reaction Mechanism	297
11.2.2	Faradaic Efficiency	299
11.3	Lignin Pretreatment to Enable Efficient Electrocatalytic Upgrading	300
11.4	Electrocatalytic Cleavage of Lignin-derived Model Compounds	302
11.4.1	Reductive Approach	302
11.4.1.1	Monomers	302
11.4.1.2	Lignol Dimers	306
11.4.2	Oxidative Approach	307
11.4.2.1	Monomers	307
11.4.2.2	Lignol Dimers	308
11.5	Electrocatalytic Depolymerization of Lignin Polymer	309
11.5.1	Electrocatalysts for Lignin Depolymerization Using Various Electrodes	309
11.5.1.1	Iridium Based Anodes	309
11.5.1.2	Lead/Lead Oxide Based Anodes	309
11.5.1.3	Nickel-, Cobalt-, and Nickel–Cobalt Based Electrodes	310
11.5.2	Combination of Electrochemical and Other Process for Lignin Conversion	311
11.5.2.1	Ionic Liquid and Deep Eutectic Solvent Electrolytes Assisted Approach	311
11.5.2.2	Biodegradative Pretreatment	312
11.5.2.3	Photo-Assisted Approach	312
11.5.2.4	Mediator-Assisted Approach	313

11.5.2.5	H ₂ O ₂ -Assisted Approach	313
11.5.2.6	Hydrogen Coproduction Approach	314
11.6	Electrocatalytic Valorization of Lignin to Biorefinery Aromatics Products	314
11.6.1	Vanillin	315
11.6.2	Syringaldehyde	315
11.6.3	Guaiacol	315
11.6.4	<i>Trans</i> -Ferulic Acid	316
11.6.5	Acetosyringone	316
11.7	Summary	316
	References	317
12	Recent Advances in Thermoset and Thermoplastic Polymeric Materials Produced using Technical and Depolymerized Native Lignins	327
	<i>Kirk M. Torr, Oliver J. Driscoll, Daniel J. van de Pas and Elias Feghali</i>	
12.1	Introduction	327
12.2	Lignin-Based Thermosets	329
12.2.1	Polyurethanes	329
12.2.1.1	Use of Technical or Fractionated Technical Lignins	330
12.2.1.2	Use of Chemically Modified Technical Lignins	331
12.2.1.3	Use of Depolymerized Native Lignin Produced by Lignin-First Biorefining/RCF Approaches	333
12.2.2	Epoxies	334
12.2.2.1	Reactive Blending with Epoxy Resins	334
12.2.2.2	Direct Epoxidation of Technical or Fractionated Technical Lignins	335
12.2.2.3	Modification of Technical Lignins Prior to Epoxidation	335
12.2.2.4	Use of Depolymerized Native Lignins Produced by Lignin-First Biorefining/RCF Approaches	336
12.2.3	Phenol-Formaldehyde Resins	337
12.2.4	Other Polymers	339
12.3	Lignin-Based Thermoplastics	341
12.3.1	Graft Copolymers and Scope	342
12.3.2	Lignin-Copolymer Thermoplastics Using Ring-Opening Polymerization	343
12.3.3	Lignin-Copolymer Thermoplastics Using Radical Polymerization	347
12.3.4	Lignin Thermoplastic Polyurethanes	351
12.4	Perspectives	353
	References	357
13	Advances in Preparation and Applications of Lignin Nanoparticles	369
	<i>Mika H. Sipponen and Liyang Liu</i>	
13.1	Introduction	369
13.2	Preparation Methods	370
13.2.1	Solvent Exchange	370
13.2.2	pH Shifting	373

13.2.3	Aerosol Evaporation	373
13.3	Properties	373
13.3.1	Inherent Properties of LNPs	373
13.3.2	Size Control by Different Solvent Systems and Process Parameters	375
13.3.3	Versatile Particle Morphologies and Tailored Properties	376
13.3.4	Stabilized and Solvent-Resistant Lignin Particles	378
13.4	Emerging Applications	378
13.4.1	Polymer Composites, Gels, Adhesives, and Coatings	379
13.4.2	Carrier Systems for Agriculture and Biomedicine	381
13.4.3	Emulsifiers for Pickering Emulsions	382
13.4.4	Sensors	383
13.4.5	Hybrid Particles with Metal and Inorganic Nanoparticles	384
13.4.6	Sunscreens	384
13.4.7	Biologically Active Lignin Nanomaterials	386
13.5	Future Perspectives	387
	References	387

14 Carbon (Nano)Fibers and Carbon Materials from Lignin and Their Applications 401

Muhammad Muddasar, Anne Beaucamp, Mark Vaughan, Misbah Mushtaq, Mario Culebras, Marina M. Leite, Tadhg Kennedy and Maurice N. Collins

14.1	Introduction	401
14.2	Lignin-Derived Carbon Materials	402
14.3	Lignin-Based Carbon Fibers	403
14.3.1	Spinning of Lignin-Based Precursor Fibers	404
14.3.1.1	Spinning of Lignin-Based Precursor Fibers	405
14.3.1.2	Precursors via Solution Spinning	407
14.3.2	Stabilization and Carbonization of Lignin Fibers	408
14.4	Applications of Lignin-Derived Carbon Materials – Supercapacitors	409
14.4.1	Lignin-Derived Activated Carbon Materials	412
14.4.2	Template-Assisted Porous Carbon Materials	414
14.4.3	Lignin-derived Free Standing Carbon Materials	415
14.5	Applications of Lignin-Derived Carbon Materials – Batteries	416
14.5.1	Lignin-derived Anode Materials	417
14.6	Applications of Lignin Derived-Carbon Materials – Sensing	420
14.6.1	Light Stimuli Carbon Quantum Dots for Sensing Applications	420
14.6.2	Strain and Pressure Sensors	421
14.6.3	Electrochemical Sensors	421
14.7	Applications of Lignin Derived-Carbon Materials – Thermoelectric Devices	422
	Acknowledgments	424
	References	425

15 Lignin-based Hydrogel: Mechanism, Properties, and Applications 433

Qiang Wang, Baobin Wang, Jiachuan Chen, Guihua Yang, Lei Zhang, Kefeng Liu, Qimeng Jiang and Pedram Fatehi

15.1 Introduction of Hydrogels 433

15.2 Introduction of Lignin 438

15.2.1 Sources of Lignin 438

15.2.2 Characteristics of Lignin 439

15.3 Lignin-Based Hydrogel Preparation 439

15.3.1 Blending of Lignin in Hydrogel Networks 440

15.3.2 Polymerization of Lignin with Bio-Based/Synthetic Chemicals for Hydrogels 442

15.3.2.1 Crosslinking 443

15.3.2.2 Free Radical Polymerization of Lignin and Monomers 443

15.3.2.3 Atom Transfer Radical Polymerization (ATRP) of Lignin for Hydrogel Production 445

15.3.2.4 Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization 447

15.4 Applications 448

15.4.1 Dye Decontamination 448

15.4.2 Heavy Metal and Other Ion Elimination 451

15.4.3 Drug Delivery Application 453

15.4.4 Lignin-Based Hydrogel for Wound Dressing 455

15.4.5 Lignin-Derived Hydrogel for Agriculture of Watering Plants and Fertilizers 457

15.4.6 Lignin-Derived Hydrogels for Energy Storage Applications 457

15.5 Perspectives and Future Work 460

References 461

Index 469