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Edited by Yuhe Liao and Bert F. Sels

# Lignin Chemistry

Characterization, Isolation, and Valorization





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Valorization

*Edited by Yuhe Liao and Bert F. Sels*

## Authors

### *Prof. Yuhe Liao*

Guangzhou Institute of Energy Conversion  
Chinese Academy of Sciences  
Guangzhou, 510640  
China

### *Prof. Bert F. Sels*

KU Leuven  
Faculty of Bioscience Engineering  
Leuven, 3001  
Belgium

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## 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  $^1\text{H}$  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  $^1\text{H}$  Program *18*
- 2.2.2  $^1\text{H}$ -NMR Spectra Analysis *18*
- 2.2.2.1  $^1\text{H}$ -NMR Spectra of Non-Acetylated Lignin *18*
- 2.2.2.2  $^1\text{H}$ -NMR Spectra of Acetylated Lignin *19*
- 2.3  $^{13}\text{C}$ -NMR *20*
- 2.3.1 Sample Preparation and Program *21*
- 2.3.1.1 Sample Preparation *21*
- 2.3.1.2  $^{13}\text{C}$ -NMR Program *21*
- 2.3.2 Quantitative  $^{13}\text{C}$ -NMR *21*
- 2.3.2.1 Quantitative  $^{13}\text{C}$ -NMR of Non-Acetylated Lignin *21*
- 2.3.2.2 Quantitative  $^{13}\text{C}$ -NMR of Acetylated Lignin *23*
- 2.3.3 Applications of the  $^{13}\text{C}$ -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 $^{13}\text{C}$ 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	$^{31}\text{P}$ NMR	40
2.5.1	Factors Affecting $^{31}\text{P}$ NMR	40
2.5.2	$^{31}\text{P}$ NMR Operation	43
2.5.2.1	Detailed Procedures	44
2.5.3	Applications of the $^{31}\text{P}$ NMR	45
2.6	$^{19}\text{F}$ 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

*Oliver Musl and Antje Potthast*

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

*Elisabetta Borsella, Pietro Colucci, Giuseppe Lembo and Heiko Lange*

4.1	Introduction	85
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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
<b>5</b>	<b>Isolation of Native-Like Lignin</b>	<b>139</b>
	<i>Zhiwen Wang, Yiwei Fan and Peter J. Deuss</i>	
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  $\beta$ -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**  
*Qian Xu and Ling-Ping Xiao*
  - 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  $\gamma$ -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**  
*Subhashini, Michal Jeremias and Vineet Singh Sikarwar*
  - 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**  
*Timothy D.H. Bugg, Victoria Sodr , Awatif Alruwaili and Goran M.M. Rashid*
  - 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

*Elena Subbotina, Shannon S. Stahl, Paul Anastas and Joseph S.M. Samec*

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

<b>10</b>	<b>Photocatalytic Conversion of Lignin</b>	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 <sub>β</sub> —O (β-O-4) Bond	269
10.2.1.1	Oxidation of C <sub>α</sub> Hydroxyl into C <sub>α</sub> Carbonyl	269
10.2.1.2	Reductive Cleavage of C <sub>β</sub> —O Bond in β-O-4 Ketone	270
10.2.2	Direct Photocatalytic Cleavage of Lignin C <sub>β</sub> —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 <sub>α</sub> Intermediate	275
10.2.3	Cleavage of C <sub>aryl</sub> —O (β-O-4, 4-O-5) and C <sub>α</sub> —O (α-O-4)	278
10.3	Photocatalytic C—C Bond Cleavage	280
10.3.1	C <sub>α</sub> O—H Bond Activation to Alkoxy Radical Intermediate	280
10.3.2	C <sub>β</sub> —H Bond Activation to C <sub>β</sub> Radical Intermediate	283
10.3.3	Single Electron Transfer to Radical Cation Intermediate	285
10.4	Conclusion and Outlook	286
	References	289
<b>11</b>	<b>Electrochemical Conversion for Lignin Valorization</b>	295
	<i>Qi Zhu, Mahlet Garedeu, 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 <sub>2</sub> O <sub>2</sub> -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
<b>12</b>	<b>Recent Advances in Thermoset and Thermoplastic Polymeric Materials Produced using Technical and Depolymerized Native Lignins</b>	<b>327</b>
	<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
<b>13</b>	<b>Advances in Preparation and Applications of Lignin Nanoparticles</b>	<b>369</b>
	<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
<b>14</b>	<b>Carbon (Nano)Fibers and Carbon Materials from Lignin and Their Applications</b>	<b>401</b>
	<i>Muhammad Muddasar, Anne Beaucamp, Mark Vaughan, Misbah Mushtaq, Mario Culebras, Marina M. Leite, Tadhg Kennedy and Maurice N. Collins</i>	
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

<b>15</b>	<b>Lignin-based Hydrogel: Mechanism, Properties, and Applications</b>	<b>433</b>
	<i>Qiang Wang, Baobin Wang, Jiachuan Chen, Guihua Yang, Lei Zhang, Kefeng Liu, Qimeng Jiang and Pedram Fatehi</i>	
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
	<b>Index</b>	<b>469</b>





## Preface

Utilization of non-renewable fossil resources in the transportation and chemical industry is responsible for the large amounts of carbon dioxide in the atmosphere. Mitigation of such emissions requires disruptive solutions in the area of renewable energy (such as solar and wind) exploitation and utilization, while replacement of fossils with renewable carbon resources will be indispensable. Given its CO<sub>2</sub> conversion capabilities, biomass is such a sustainable feedstock for the production of fuels and chemicals. Processing biomass in biorefineries is a challenging, perhaps under-explored, research activity but also a necessary step to advance biomass conversion field. Besides the carbohydrates, lignin (an aromatic biopolymer) represents the major fraction of the lignocellulosic biomass. Its structure is diverse, hampering quick and easy valorization, and therefore burnt for power and heat today. However, new ideas and advances in lignocellulose biorefinery are focusing on value-added utilization by generating higher-quality primary lignin products for more promising upgrades.

Lignin is a promising carbon feedstock for the production of (oxygen-free) fuels such as bio-jet fuels due to its higher energy density and original cyclic molecular structure, compared to other plant components such as sugars and vegetable oils. Even more, the unique chemical structure of lignin, with its oxygen-containing functional groups, offers opportunities for functional aromatic and cyclic chemicals, as well as for diverse functional materials. Effective and selective conversion of lignin to such high-value products is challenging. This book therefore covers the chemistry of lignin utilization. It starts with an introduction of the state-of-the-art structural characterization and understanding of lignin and its refined lignin fractions, in relation to the lignin's properties. Fractionation of lignin from plant biomass by different (catalytic) biorefinery approaches (including acid and base treatments) to obtain distinct lignin properties is then discussed. The main part of the book discloses a myriad of catalytic conversion of lignin toward high-value chemicals, including biocatalysis, oxidation, photocatalysis, and electrocatalysis, followed by lignin valorization toward functional materials such as thermoset and thermoplastic polymeric materials, nanoparticles, carbon materials, and hydrogels.

Given that it covers analytical chemistry, catalysis, biology, material chemistry, and engineering in the field of biomass conversion, thanks to the interdisciplinary expertise of the contributors; this book may be a valuable and inspiring reference for

students, scientists, engineers, and professionals to motivate them to discover and advance new biorefinery and valorization technologies, with a view on commercial lignin utilization.

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Yuhe Liao  
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Chinese Academy of Sciences (CAS)

Bert F. Sels  
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# 1

## A Brief Introduction of Lignin

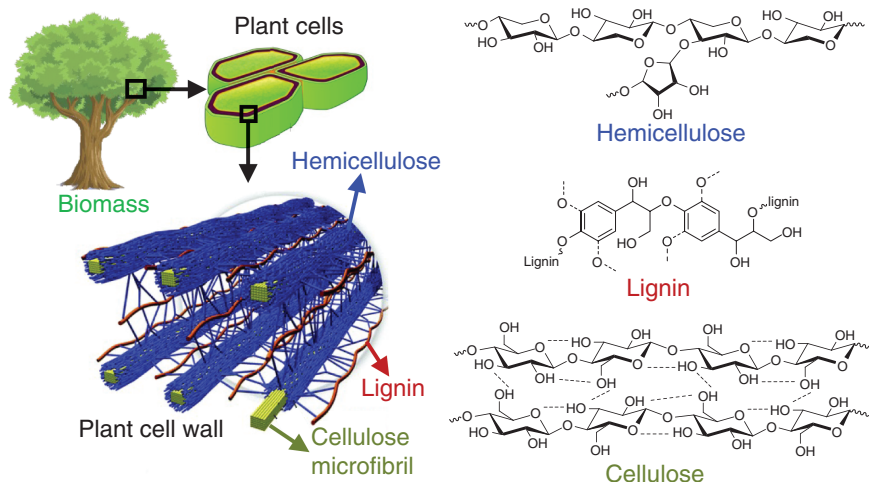
Yuhe Liao

Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, No. 2 Nengyuan Road, Tianhe, Guangzhou, 510640, China

### 1.1 Introduction

To reduce greenhouse gas (GHG) emissions, society should use renewable carbon resources in a sustainable way to produce chemicals, materials, and fuels next to circular use of currently available carbon feedstock. Lignocellulosic biomass has been considered as an abundant, carbon dioxide neutral, and renewable carbon resource [1]. The major compositions in lignocellulosic biomass are three oxygen-containing biopolymers: cellulose (40–60%), hemicellulose (10–40%), and lignin (15–30%), and the minor compositions include proteins, fats, pectins, inorganic matter, and others [2]. Cellulose and hemicellulose are carbohydrate-based biopolymers, whereas lignin is a complex aromatic biopolymer with a high carbon content (Figure 1.1) [3, 4]. Typically, cellulose determines the structure of cell walls in the form of microfibrils. The cross-linked lignin and hemicellulose wrap around the cellulose microfibrils (Figure 1.1). The lignin can provide additional rigidity and cause the cell walls to be hydrophobic and water impermeable. Therefore, these three main fractions are intertwined to yield the complex structure, contributing to biomass recalcitrance, which hampers the effective valorization of lignocellulosic biomass toward high-value products such as chemical and liquid fuels [5].

Different approaches have been developed to overcome the recalcitrance and valorize lignocellulosic biomass over the past decades [2, 6]. Classically, the lignocellulosic biomass is utilized to produce high-quality pulps for paper production. Emerging approaches are conversion of lignocellulose via thermal cracking (e.g. pyrolysis), biocatalysis, chemocatalysis, and integration of them toward chemicals and fuels such as bioethanol, furfurals, and levulinic acid [1, 3, 4, 7–13]. It is clear



**Figure 1.1** General structure of lignocellulose in plant and representative structure of cellulose, hemicellulose, and lignin. Source: From Liao et al. [2].

that these products are usually derived from cellulose and hemicellulose, whereas lignin, either left as a solid residue after conversion of cellulose and hemicellulose (such as via hydrolysis) or extracted from lignocellulose with cellulose and hemicellulose as solid residue, is considered as a waste or a low-value product for energy use. Currently, the pulping and biorefinery processes such as bioethanol production generate more than 50 million tons of lignin annually with ca. 95% used as fuel for heat and power generation due to the recalcitrance of lignin [14, 15]. The utilized 5% of lignin have several applications such as additives, surfactants, and adhesives. Although delignification (i.e. removal of lignin) of lignocellulosic biomass can facilitate the utilization of cellulose and hemicellulose to improve the economics of biorefineries, the value of biomass may not be maximized without utilization of lignin toward high-value products. Techno-economic analysis (TEA) and life-cycle assessment (LCA) have shown that valorize lignin can improve both economics and sustainability of biorefineries [16]. Hence, it is paramount to valorization of lignin with novel strategies to explore the potential of all carbon constituents of lignocellulose.

Over the past years, some progresses were achieved in the aspects of lignin characterizations to reveal the structure of lignin, isolation to obtain lignin with different properties (even native like), and valorization toward chemicals, fuels, and materials with novel approaches. Hence, this book aims to introduce the most recent advancements in these aspects, particularly the valorization methods such as oxidation, photocatalysis, electrocatalysis, and valorization of native lignin. As a preface to the following chapters, this introductory chapter will briefly introduce the structure of lignin from the point of view of monomeric units, inter-unit linkages, and biosynthesis.

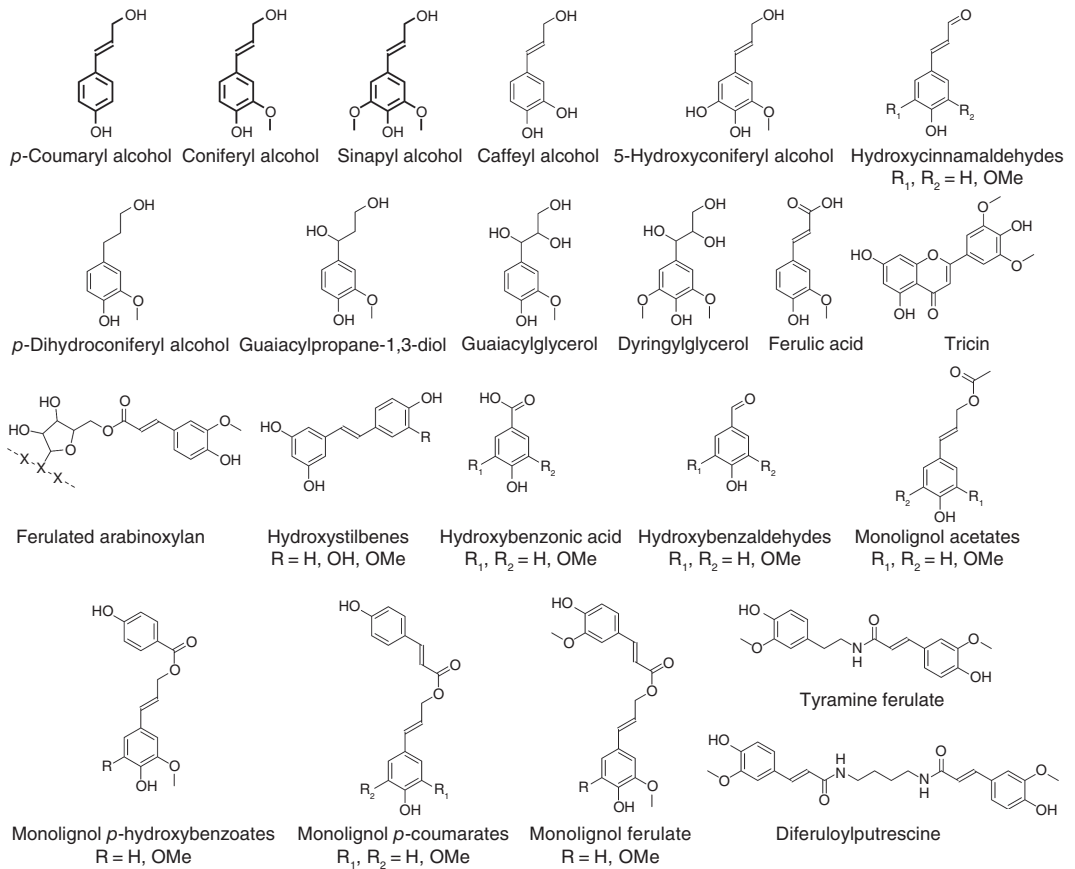
## 1.2 The Building Blocks of Lignin

Lignin, a phenolic biopolymer, is derived primarily from three kinds of 4-hydroxyphenylpropanoids (i.e. monolignols, e.g. *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, Figure 1.2). These monolignols differ in substitution degree of methoxylation on the aromatic ring (i.e. 2 and 6 positions) and incorporate into lignin chain to produce corresponding *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively [17]. Besides, it is found that lignin is derived from numerous other building blocks, such as *p*-coumarates, ferulates, caffeoyl alcohol, *p*-hydroxybenzoates, hydroxycinnamaldehydes, triclin, and hydroxystilbenes [18, 19]. These building blocks are shown in Figure 1.2.

Currently, the only known route to form these building blocks is the phenylpropanoid pathway starting from phenylalanine via multiple steps in all plants with different enzymes [20, 21]. Whereas tyrosine can be an additional starting substrate for grasses. Figure 1.3 overviews the complete pathway of phenylpropanoid pathway for these building blocks. The phenylalanine was first deaminated in the presence of phenylalanine ammonia-lyase (PAL) toward cinnamic acid, which is then hydroxylated toward *p*-coumaric acid in the presence of cinnamate 4-hydroxylase (C4H). While in the case of tyrosine, *p*-coumaric acid can be produced from a shortcut pathway, direct deamination with tyrosine ammonia-lyase (TAL) or PAL [14, 23].

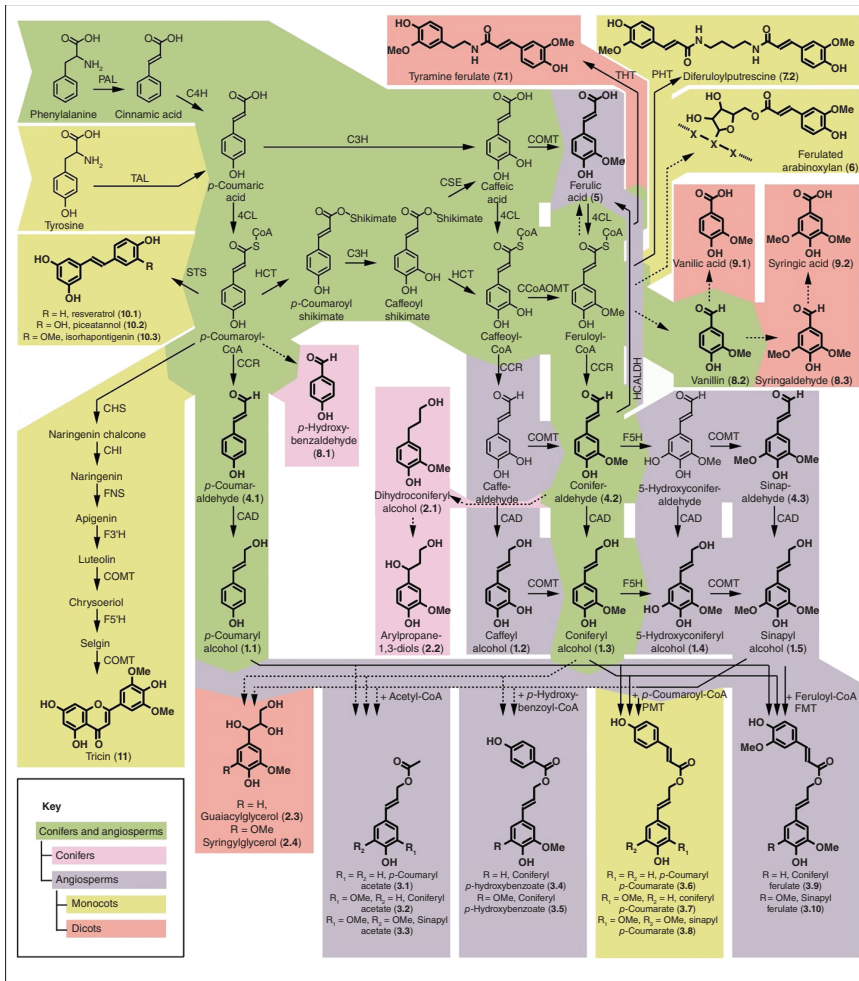
Then, *p*-coumaric acid is enzymatically converted toward either *p*-coumaroyl-CoA via 4-coumarate: CoA ligase (4CL) or caffeic acid through hydroxylation via *p*-coumarate 3-hydroxylase (C3H). *p*-Coumaryl alcohol is produced from reduction of *p*-coumaroyl-CoA via cinnamoyl-CoA reductase (CCR) and cinnamyl alcohol dehydrogenase (CAD). For caffeic acid, methylation via caffeic acid *O*-methyltransferase (COMT) forms ferulic acid, which can be transformed into feruloyl-CoA. Meanwhile, caffeic acid can be converted toward caffeoyl-CoA, which can be further methylated to feruloyl-CoA via caffeoyl-CoA *O*-methyltransferase (CCoAOMT). In addition, conversion of *p*-coumaroyl-CoA in the presence of shikimate/quinic acid hydroxycinnamoyl transferase (HCT) yields *p*-coumaroyl shikimate. Hydroxylation of *p*-coumaroyl shikimate via C3H can produce *p*-caffeoyl shikimate, which can be transformed toward caffeic acid and caffeoyl-CoA in the presence of caffeoyl shikimate esterase (CSE) and HCT, respectively. The shikimate intermediates are currently recognized as the favored substrates for hydroxylation [22].

Reduction of feruloyl-CoA via CCR yields coniferaldehyde, which can be transformed to coniferyl alcohol and 5-hydroxyconiferaldehyde through reduction (via CAD) and hydroxylation (via ferulate 5-hydroxylase, F5H), respectively (Figure 1.3). The main pathway to produce sinapyl alcohol is hydroxylation (via F5H) of coniferyl aldehyde followed by tandem methylation (via COMT) and reduction. Hydroxylation (via F5H) of coniferyl alcohol followed by methylation can form sinapyl alcohol as well. Oxidation of coniferylaldehyde by hydroxycinnamaldehyde dehydrogenase (HCALDH) forms ferulic acid. These synthesized monolignols are transported to the cell wall and integrated into a growing lignin chain.



**Figure 1.2** Lignin building blocks. Three main monolignols (i.e. *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) are shown in bold.





**Figure 1.3** Summary of the metabolic pathway toward lignin building blocks. PAL, phenylalanine ammonia-lyase (PAL); cinnamate 4-hydroxylase (C4H); tyrosine ammonia-lyase (TAL); *p*-coumarate 3-hydroxylase (C3H); caffeic acid *O*-methyltransferase (COMT); 4-coumarate:CoA ligase (4CL); cinnamoyl-CoA reductase (CCR); cinnamyl alcohol dehydrogenase (CAD); *p*-hydroxycinnamoyl-CoA: quinate/shikimate *p*-hydroxycinnamoyltransferase (HCT); caffeoyl-CoA *O*-methyltransferase (CCoAOMT); caffeoyl shikimate esterase (CSE); ferulate 5-hydroxylase (F5H); *p*-coumaroyl-CoA monolignol transferase (PMT); feruloyl-CoA monolignol transferase (FMT); chalcone synthase (CHS); chalcone isomerase (CHI); flavone synthase (FNS); flavonoid 3'-hydroxylase (F3'H); flavonoid 5'-hydroxylase (F5'H); stilbene synthase (STS); hydroxycinnamaldehyde dehydrogenase (HCALDH); hydroxycinnamoyl-CoA: putrescine hydroxycinnamoyl transferase (PHT); hydroxycinnamoyl-CoA: tyramine *N*-hydroxycinnamoyltransferase (THT). Source: Adapted from Vanholme et al. [22].

Next to synthesis of the three main monolignols, *p*-coumaroyl-CoA and feruloyl-CoA can serve as substrates to synthesize other building blocks. *p*-Coumaroyl-CoA can be transformed toward hydroxystilbenes via stilbene synthase (STS) and flavonoids (including tricetin, as identified in grasses) via multistep [24–27]. For feruloyl-CoA, hydroxycinnamides (e.g. tyramine ferulate and diferuloylputrescine) and ferulated arabinoxylan can be obtained from it [28–31]. Besides, hydroxybenzaldehydes (e.g. *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde) and hydroxybenzoic acids (e.g. vanillic acid and syringic acid) can be obtained from them, though the reaction pathway is not clear yet [32, 33].

Furthermore, monolignol *p*-coumarates, found in grasses, can be synthesized from *p*-coumaroyl-CoA and monolignols with the action of *p*-coumaroyl-CoA monolignol transferase (PMT), while as found in plants such as *Angelica sinensis*, monolignol ferulates can be obtained from feruloyl-CoA and monolignols with feruloyl-CoA monolignol transferase (FMT) [34, 35]. The three main monolignols and acetyl-CoA can be transformed in the presence of acyl transferases toward  $\gamma$ -O-acylated ester conjugates, acetates, which are found in a large proportion of hardwoods with low levels and in large amount in several plants such as palms, abaca, sisal, and kenaf [36, 37]. Monolignol *p*-hydroxybenzoates, widely found in poplar, aspen, palms, and willow, are the product of three main monolignols and *p*-hydroxybenzoyl-CoA [36, 38]. It should be noted that *p*-coumarate and *p*-hydroxybenzoate are often misinterpreted as H-unit fractions, overestimating the content of H units, which is usually less than 5% and is obtained from monolignol *p*-coumaryl alcohol [14, 36, 39–41]. Caffeyl alcohol was recently found in the lignin of seed coats of some plants such as *vanilla planifolia* and cactaceae species [42–44]. 5-Hydroxyconiferyl alcohol was also identified in seed coats of some plants such as *escobaria* species (*E. dasyacantha*, *E. lloydii*, and *E. zilziana*) [45].

Another two monomers, arylpropane-1,3-diols (guaiacylpropane-1,3-diol in Figure 1.3) and hydroxyphenylglycerols, might be produced from dihydroconiferyl alcohol (in softwoods) and hydroxycinnamyl alcohols, respectively, likely via radical oxidation instead of enzymatical reaction [22, 46, 47].

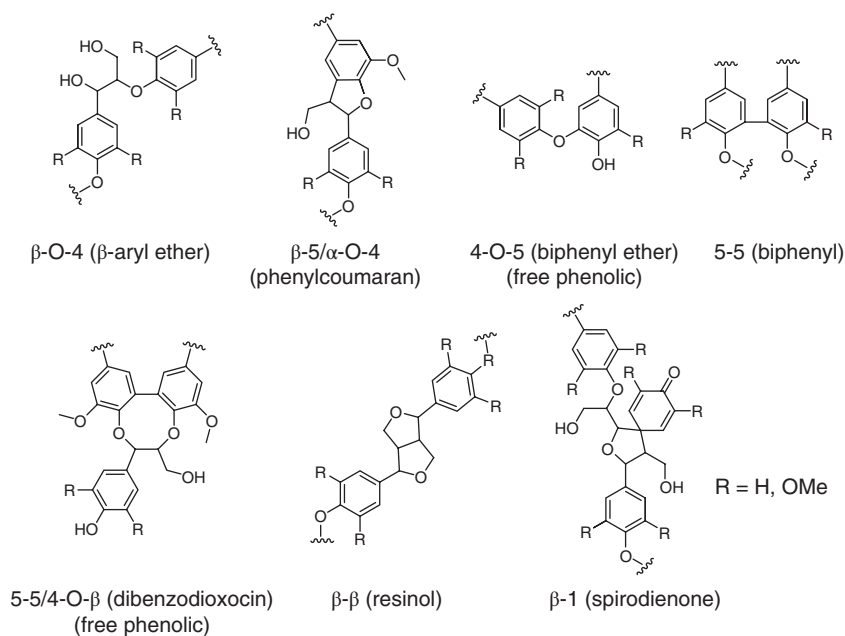
### 1.2.1 Interlinkages in Lignin

Lignin is obtained from polymerization of these building blocks after transportation to the cell wall. In the polymerization process, the phenols are first oxidatively converted via enzymes to form phenolic radicals, which are then subjected to coupling to form a racemic polymer. Peroxidases and laccases are involved in the oxidation step [48]. Hydrogen peroxide is the substrate of peroxidases, while laccases oxidize using oxygen. Lignification is a purely chemical process and not enzymatically determined once the radicals are formed [49].

Generally, the monolignol is first dehydrogenated (i.e. oxidation) to form a phenol radical, which is relatively stable due to the unpaired electron delocalization [40]. Afterward, two monolignol radicals couple to yield a (dehydro)dimer, thereby forming a covalent bond. These monolignol radicals are preferred to couple at their  $\beta$  position, leading to the formation of  $\beta$ - $\beta$  (resinol),  $\beta$ -O-4 ( $\beta$ -aryl ether), and  $\beta$ -5

(phenylcoumaran) (dehydro)dimers (Figure 1.4) [50]. These are the most common interunit linkages in lignin. These dimers are further oxidized to form radicals, which then couple with another monolignol radical to increase polymer chain. Usually, the new monolignol radical is coupled exclusively at the  $\beta$  position of the growing oligomer, forming  $\beta$ -O-4 interunit linkage. Therefore,  $\beta$ -O-4 interunit linkage is the most abundant linkage in lignin, and it accounts for 50–80% of total linkages in native lignin [19, 50], while isolation of lignin can decrease the amount of  $\beta$ -O-4 interunit linkage in isolated lignin due to degradation of lignin, and the reduced amount depends on the process conditions [14]. This type of polymerization is termed as endwise coupling, where a monolignol radical is added to the growing lignin polymer (also radical) in one reaction. As the polymerization progresses, two lignin oligomeric phenolic end units are coupled to form 5-5 (biphenyl) and 4-O-5 (diphenyl ether) interlinkages, which are not from the coupling between monomer and oligomer or between monomer and monomer [19, 50]. This is rare for S-unit rich lignin due to the presence of the two methoxy groups, while it is common in G-unit rich lignin as only one methoxy group in the monolignol. Besides,  $\beta$ -1 (spirodienone) linkage is formed by coupling a  $\beta$ -aryl ether dimeric end unit with a monolignol. The possibility of different linkages depends on the type of monolignols and the conditions in the cell wall [50].

The lignin obtained from combinatorial radical coupling is very complex and difficult to valorize and characterize. The composition (i.e. the relative abundance of units), structure, and amount of lignin differ between plant species and within the plant species [51, 52]. Besides, the lignin can vary at different growth stages of plants.



**Figure 1.4** Representative interlinkages in lignin.

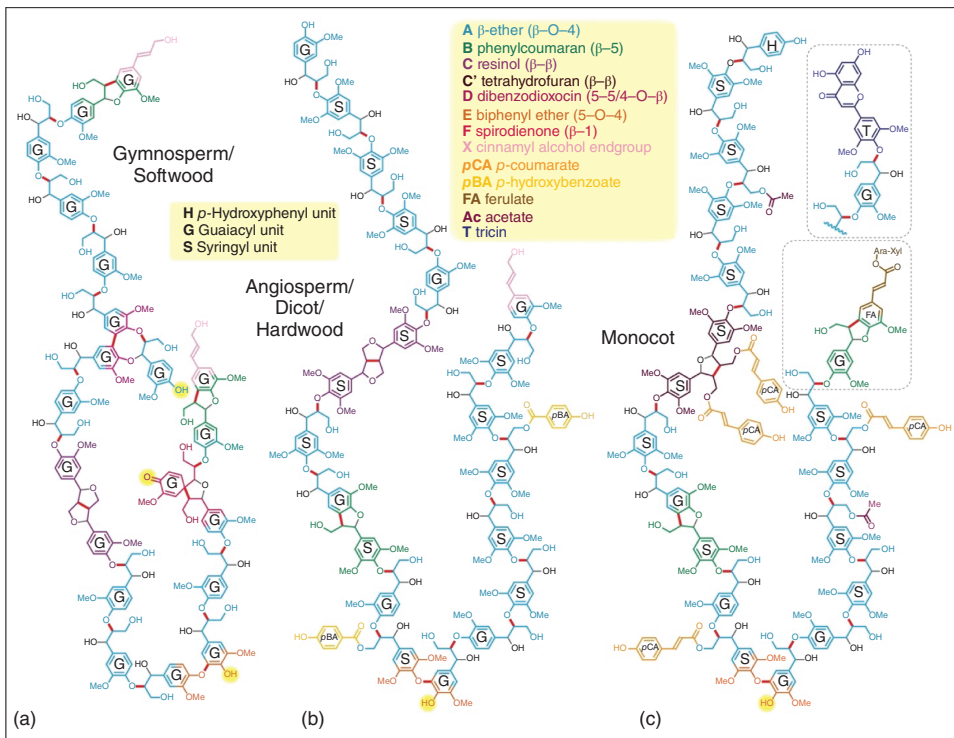
Generally, the lignin in a gymnosperm/softwood is composed of mostly G units, and lignin in angiosperm/dicot/hardwood contains both G and S units with trace amount of H units [19]. The lignin in (commelinid) monocot/grass contains H, G, and S units [19, 53]. The model lignin structure of these three types of plants is displayed in Figure 1.5 [39]. Additional building blocks that have been found in the past are also integrated into the chain of lignin to form new linkages. Indeed, most of the lignin has a very complex structure, but there is an exception for C-lignin, which is obtained from endwise  $\beta$ -O-4 coupling of caffeyl alcohol [42–44]. C-lignin is a linear homopolymer linked with benzodioxane (Figure 1.6) [43]. Therefore, selective depolymerization of C-lignin is easier than other types of lignin as they contain different C–O and C–C interlinkages. For instance, C-lignin can be nearly quantitatively converted into monomeric catechol via hydrogenolysis [54–56]. Besides, 5H-lignin, obtained from coupling of 5-hydroxyconiferyl alcohol, has the same benzodioxane units [43, 45].

Lignin has been hypothesized as a highly branched polymer for a long time, but this is now doubted. It is assumed that lignin chains connected via 5-5 (biphenyl) or 4-O-5 (diphenyl ether) interlinkages can form a Y-branch polymer. However, the yielded structures are mostly free phenolic (which is traditionally hypothesized to be branching points), as identified by 2D NMR recently, and thus the native lignin must be less branched than usually assumed [45, 57]. This was also observed for  $\beta$ -1 (spirodienone) linkage (i.e. free phenolic instead of etherified) [58].

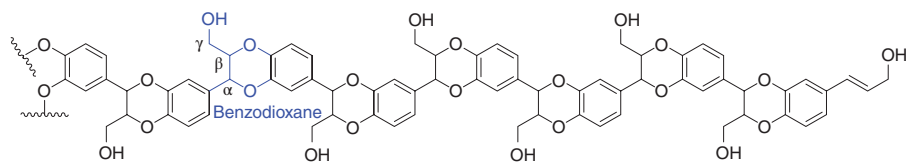
### 1.2.2 Bioengineering of Lignin

As discussed in the previous section, the monolignols are obtained from phenylalanine and tyrosine with the action of different enzymes. Upon genetic modifications of the phenylpropanoid pathway can influence the lignin composition, structure, and amount. For instance, downregulation of the genes of PAL, C4H, and 4CL, which are the enzymes involved in the early stages of phenylpropanoid biosynthesis, can lead to decreased flux, and thus reduce the lignin content in plant [59]. Although low content of recalcitrant lignin can be formed in the plant through this strategy, detrimental agronomic effect can occur as plants need a certain amount of lignin [60].

The favored approach is downregulation or upregulation of enzymes to yield plant lignin, which can facilitate the valorization of biomass (including lignin). For instance, the S/G ratio in angiosperms can be regulated via overexpression or underexpression of the F5H gene [59]. Overexpression of the F5H, when forced by a powerful lignin promoter, can yield linear lignin with extremely high S unit content (98.3%) [61]. The interlinkages in this type of high S lignin only involve  $\beta$ -O-4 and  $\beta$ - $\beta$ , where the  $\beta$ -O-4 linkage accounts for 88.8% (i.e. low content of recalcitrant C–C interlinkage). Depolymerization of this type of linear lignin can produce high monomer yield, such as 78% of monomer was obtained from hydrogenolysis [61, 62]. In contrast, downregulation of F5H can obtain plant lignin with solely guaiacyl unit. Similarly, underexpression of the genes of C3H, HCT, and CSE enzymes, which are related to 3-hydroxylation steps, can produce plant lignin rich in H units [59, 63–67]. However, in the typical wild-type lignin H units are a minor

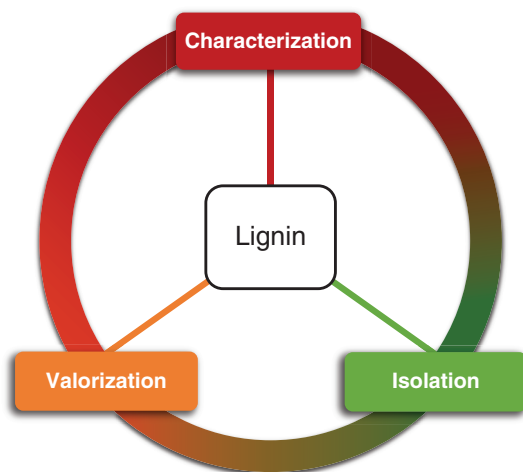


**Figure 1.5** Lignin model structures containing 20 units. (a) A gymnosperm/softwood, (b) an angiosperm/dicot/hardwood, and (c) a (commelinid) monocot/grass. Source: Adapted from Ralph et al. [39].



**Figure 1.6** Representative chemical structural models of C-lignin. It is based on Ref. [43].

fraction. Besides, if chemically labile bonds are introduced into the lignin polymer, it will be easier to degrade lignin [68]. “Zip-lignin” is a successful example in this aspect. It introduces ester bonds, which are more chemically reactive than ether bonds, into lignin chain by acyl transferases [69]. More details about the bioengineering of lignin can be found in the decent reviews [14, 39, 59, 70].



**Figure 1.7** The scope of this book.

### 1.3 Scope of this Book

Besides the inherent complexity as introduced in this chapter, the structure of lignin is modified as the result of depolymerization (i.e. cleavage of linkages) and repolymerization (i.e. formation of new linkages) in most of the biomass processing technologies. Depending on processing technologies and the severity of the process, the structure of the yielded lignin can be varied. From a chemistry and technology point of view, rational utilization of lignin for different applications is determined by three important aspects: (i) characterization of lignin to understand the structure (including linkages), (ii) isolation to obtain lignin with desired properties, and (iii) on purpose valorization of lignin based on the inherent properties (Figure 1.7). Therefore, this interdisciplinary book includes chapters focused on introducing the latest progress in these aspects, and experts from analytic chemistry, organic chemistry, chemocatalysis, biocatalysis, chemical engineering, and material chemistry will contribute to this book. The main focus is valorization of lignin toward fuels, chemicals, and materials.