

## Contents

**Preface** *xiii*

**List of Abbreviations** *xv*

**List of Symbols** *xviii*

### **Part I Book Introduction 1**

#### **1 Background and Overview 3**

1.1 Introduction 3

1.2 Lignin: A Natural and Sustainable Aromatic Bank 4

1.3 Structure of This Book 6

References 10

### **Part II Lignin Introduction 13**

#### **2 Lignin Biosynthesis and Structure 15**

2.1 Lignin Biosynthesis 15

2.1.1 The Generation of Monolignols 16

2.1.1.1 The Shikimic Acid Pathway 17

2.1.1.2 The Common Phenylpropanoid Pathway and Monolignol-Specific Pathway 18

2.1.1.3 The Biosynthesis of Other Monolignols 20

2.1.2 The Transport of Monolignols 20

2.1.3 The Polymerization of Lignin Monolignols 21

2.1.3.1 The Dehydrogenation of the Precursors 21

2.1.3.2 The Radical Polymerization 21

2.2 Lignin Structure 27

2.2.1 Structure Models of Hardwood Lignin 28

2.2.2 Structure Models of Softwood Lignin 28

2.2.3 Structure Models of Herbaceous Plant Lignin 32

2.2.4 Lignin-Carbohydrate Complex 33

2.3 Chapter Summary 34

References 34

<b>3</b>	<b>Lignin Isolation, Physicochemistry Properties, and Chemical Properties</b>	<b>39</b>
3.1	Lignin Polymer Physical Properties	39
3.1.1	Lignin General Physical Properties	39
3.1.2	Lignin Polymer Physical Properties	41
3.2	Lignin Isolation from Lignocellulose and Technical Lignins	42
3.2.1	Remove Lignin First by Dissolution	43
3.2.2	Remove Cellulose and Hemicellulose First Leaving Lignin Residue	47
3.2.2.1	Promoting Carbohydrate Hydrolysis with Mineral Acid	47
3.2.2.2	Promoting Carbohydrate Hydrolysis or Decomposition with Metal Ion and Oxidant	48
3.2.2.3	Promoting Carbohydrate Hydrolysis or Decomposition with Bio-Enzyme	48
3.2.3	Technical Lignins	49
3.2.3.1	Kraft Lignin	49
3.2.3.2	Sulfite Lignin	50
3.2.3.3	Alkali Lignin	52
3.2.3.4	Steam-Exploded Lignin	52
3.3	Lignin Spectroscopy Properties	53
3.3.1	FT-IR Spectroscopy of Lignin	54
3.3.2	UV-vis Spectroscopy of Lignin	54
3.3.3	Nuclear Magnetic Resonance (NMR) Spectroscopy of Lignin	56
3.3.3.1	$^1\text{H}$ -NMR	56
3.3.3.2	Carbon Spectra ( $^{13}\text{C}$ NMR)	56
3.3.3.3	Two-dimensional NMR Spectroscopy and Solid NMR Spectroscopy	58
3.3.3.4	$^{31}\text{P}$ -NMR	59
3.3.3.5	$^{29}\text{Si}$ -NMR	60
3.3.3.6	$^{19}\text{F}$ -NMR	60
3.3.4	Electron Spin Resonance (ESR) Absorption Spectroscopy	61
3.4	Lignin Chemical Properties	61
3.4.1	Oxidation	62
3.4.2	Hydrogenation	65
3.4.3	Esterification/Acylation	65
3.4.4	Etherification	65
3.4.5	Hydrolysis	65
3.4.6	Alkylation and Phenolation	66
3.4.7	Demethylation	67
3.4.8	Nitration	67
3.4.9	Halogenation	68
3.4.10	Sulfonation	68
3.4.11	Hydroxymethylation	69
3.4.12	Mannich Reaction	69
3.4.13	Nucleus-Exchange Reaction	70
3.5	Chapter Summary	70
	References	71

### **Part III Lignin Depolymerization: Scientific Questions, Challenges, and Current Progress 79**

- 4 Scientific Questions for Lignin Conversion and a Brief Summary of Methods for Lignin Depolymerization 81**
  - 4.1 Opportunity and Challenges of New Biorefinery Approaches for Lignin Valorization 81
  - 4.2 Scientific Questions Involved in Lignin Depolymerization and the Foundation of Strategies 83
  - 4.3 Two Different Approaches for the Foundation of Lignin Depolymerization Strategies 87
    - 4.3.1 Direct Plant Powders or Isolated Lignin Conversion 87
    - 4.3.2 Bottom-up Approach: From Models Conversion to Lignin Depolymerization 88
  - 4.4 Classification of Lignin Conversion Methods by Reaction Types 89
  - 4.5 Brief Index of Progress of Native/Technical Lignin Conversion 99
    - 4.5.1 Definitions of Lignin Conversion and Product Yield 99
    - 4.5.2 Recent Process of Native/Technical Lignin Conversion 99
  - 4.6 Chapter Summary 110
  - References 110

### **Part IV Review on Lignin Linkages Cleavage Strategies and Mechanisms via an IDA Method 131**

- 5 The Inverse Disassembly Analysis Method for Classifying Lignin Conversion Strategies 133**
  - 5.1 Introduction of Inverse Disassembly Analysis for Lignin Conversion 133
  - 5.2 Different Analysis Modes for Lignin Depolymerization 135
  - 5.3 IDA Catalogue of Lignin Conversion Methods Discussed in the Following Chapters 139
  - 5.4 Chapter Summary 145
  - References 145
- 6 Direct Lignin C–OAr, ArO–Ar or C–Ar Bonds Cleavage without First Activation of the Adjacent Chemical Bonds 147**
  - 6.1 Brönsted/Lewis Acid + Metal Systems for the Direct Hydrogenative Cleavage of Ether Bonds and C–Ar Bonds 147
  - 6.2 Base/Organometallic Systems for the Direct Hydrogenative Cleavage of Ether Bonds 155
  - 6.3 Other Heterogeneous Catalytic Systems for the Direct Hydrogenative Cleavage of C–OAr Ether Bonds 161
  - 6.4 Direct Reductive Cleavage of Ether Bond with Hydride Reagents 170
  - 6.5 Direct Reductive Cleavage of Lignin Ether Bond with  $e^-$  178
  - 6.6 Chapter Summary 179
  - References 180

<b>7</b>	<b>Lignin C–C/C–O Bonds Cleavage via First Phenolic Hydroxyl Group Dehydrogenation or First Aromatic Rings Activation</b>	<b>189</b>
7.1	Lignin C <sub>Ar</sub> –C <sub>α</sub> /C <sub>α</sub> –C <sub>β</sub> Bonds Cleavage after the First Phenolic Hydroxyl Group Dehydrogenation to the Phenolic Radical	189
7.1.1	Thermal Systems via the Phenolic Radical	189
7.1.2	Electro/Photo-Electro Systems via the Phenolic Radical	198
7.1.3	Biodegradation Systems via the Phenolic Radical	204
7.2	Lignin C <sub>α</sub> –C <sub>β</sub> bonds Cleavage via the First Single-Electron Transfer (SET) of the Aromatic Ring	205
7.2.1	Biocatalytic Oxidation Systems and the Chemically Mimetic Systems	206
7.2.2	Thermal Catalytic Oxidation Systems via the Aryl Cation Radical	209
7.2.3	Electrocatalytic Systems via the Aryl Cation Radical	213
7.2.4	Photocatalytic Methods via the Aryl Cation Radical	215
7.3	Lignin C <sub>Ar</sub> –OC/C <sub>Ar</sub> –C Bonds Cleavage via First Partly-Hydrogenation or Partly-Addition of the Neighbouring Aromatic Ring	220
7.4	Lignin C(sp <sup>2</sup> )–C(sp <sup>2</sup> ) σ Bond and C(sp <sup>2</sup> )–OAr Bonds Cleavage via Adjacent Aromatic Groups Activation or Extra Radicals Attack	225
7.5	Chapter Summary	230
	References	230
<b>8</b>	<b>Lignin Linkages Cleavage Beginning with C<sub>α</sub>O–H/ArO–H or C<sub>α</sub>–OH Bond Heterolysis</b>	<b>241</b>
8.1	Base-catalyzed C <sub>β</sub> –OAr Bond Cleavage Beginning with C <sub>α</sub> O–H or ArO–H Heterolysis	241
8.1.1	The Mechanism of Base-mediated Lignin Depolymerization	241
8.1.2	Base-promoted Tandem Process for the Cleavage of C <sub>β</sub> –OAr Bond	247
8.2	Acid-catalyzed C <sub>β</sub> –OAr Bonds Cleavage Beginning with C <sub>α</sub> –OH Heterolysis	250
8.2.1	The Mechanism of Acid-mediated Lignin Depolymerization	250
8.2.2	Lignin Acidolysis with Liquid Acid Catalysts	253
8.2.3	Lignin Acidolysis with Homogeneous Metal Salts and Organic Metal Compounds	255
8.2.4	Lignin Acidolysis with Solid Acid Catalysts	258
8.2.5	Acid-promoted Tandem Process for the Cleavage of Lignin C <sub>β</sub> –OAr Bonds	260
8.3	Chapter Summary	263
	References	264
<b>9</b>	<b>Lignin Linkages Cleavage Beginning with C<sub>α</sub>–H, C<sub>α</sub>–OH, or C<sub>α</sub>O–H Bond Non-ionized Activation</b>	<b>277</b>
9.1	Lignin C <sub>β</sub> –OAr Bond Cleavage via a Transfer Hydrogenation or Dehydrogenation-hydrogenation Process Beginning with the First Activation of C <sub>α</sub> –H(O–H) to C <sub>α</sub> =O	277

9.1.1	Homogeneous Catalytic Systems	277
9.1.2	Heterogeneous Catalytic Systems	282
9.2	Lignin $C_\beta$ -OAr Bond Cleavage in the Dehydrogenation/Oxidation-Hydrogenation (Reduction) Process Beginning with the First Activation of $C_\alpha$ -H(OH) to $C_\alpha$ =O	290
9.2.1	Chemical Reduction with Stoichiometric Reductant for the $C_\beta$ -OAr Bond Cleavage in the Pre-oxidized Lignin	290
9.2.2	Thermal Catalytic Hydrogenation Methods for the $C_\beta$ -OAr Bond Cleavage in the Pre-oxidized Lignin	295
9.2.3	Photocatalytic and Electrocatalytic Reduction Methods for the $C_\beta$ -OAr Bond Cleavage in the Pre-oxidized Lignin	297
9.3	Lignin $C_\alpha$ - $C_\beta$ / $C_\beta$ -OAr Bonds Cleavage via Multiple Oxidation Process Beginning with the First Activation of $C_\alpha$ -OH to $C_\alpha$ =O	307
9.3.1	Thermal Catalytic Oxidation Cleavage of $C_\alpha$ - $C_\beta$ Bonds in the Pre-oxidized Lignin	308
9.3.2	Photocatalytic and Electrocatalytic Oxidation Cleavage of $C_\alpha$ - $C_\beta$ / $C_\beta$ -OAr Bonds in the Pre-oxidized Lignin	314
9.4	Lignin $C_\alpha$ - $C_\beta$ , $C_{Ar}$ - $C_\alpha$ , or $C_\beta$ O- $C_{Ar}$ Bonds Cleavage by Inserting an O- or N-containing Fragment after the First Oxidation of $C_\alpha$ -OH to $C_\alpha$ =O	315
9.4.1	Baeyer-Villiger Oxidation Methods	316
9.4.2	Beckmann Rearrangement Methods and Its Derivative Methods	317
9.5	Embellishing Lignin $\beta$ -O-4 Linkages Hydrolysis Involving the $C_\alpha$ -OH First Oxidation and $C_\gamma$ -OH Transformation	322
9.6	Lignin $C_\beta$ -OAr Bond Cleavage after the First Activation of $C_\alpha$ -H, $C_\alpha$ -OH, or $C_\alpha$ O-H to $C_\alpha^*$ Radical	325
9.6.1	The Selective HAT Oxidation Process	326
9.6.2	The Dehydroxylation-hydrogenation Process	328
9.6.3	The Transfer Hydrogenation (Reduction) Process	332
9.6.4	The Redox-neutral Process with First $C_\alpha$ O-H Activation by M=O Species	338
9.7	Lignin $C_\alpha$ - $C_\beta$ Bond Cleavage after the First Activation of $C_\alpha$ O-H Bond to $C_\alpha$ O $^*$ Radical via PCET Strategies and LMCT Mechanisms	341
9.7.1	The HAT Process with the $C_\alpha$ O $^*$ Radical Intermediate	342
9.7.2	The PCET Process with the $C_\alpha$ O $^*$ Radical Intermediate	342
9.7.3	The LMCT Process with the $C_\alpha$ O $^*$ Radical Intermediate	345
9.8	Chapter Summary	349
	References	350
10	<b>Lignin Linkages Cleavage Beginning with <math>C_\beta</math>-H, <math>C_\gamma</math>-H, or <math>C_\gamma</math>O-H Direct Activation</b>	363
10.1	Lignin C-C/ $C_\beta$ -OAr Bond Cleavage Beginning with $C_\beta$ -H Bond Direct Activation	363
10.2	First $-C_\gamma$ H <sub>2</sub> OH Activation to $-C_\gamma$ HO/ $-C_\gamma$ OOR Inducing Lignin C-C Bonds Selective Cleavage and Its Derivative Methods	368

10.3	Lignin C <sub>β</sub> –OAr Bond Cleavage Beginning with C <sub>γ</sub> First Sulphonation	374
10.4	Chapter Summary	376
	References	376
<b>11</b>	<b>Lignin Linkages Cleavage Considering Fragments Condensation</b>	<b>381</b>
11.1	Different Mechanisms of Lignin Fragments Condensation	381
11.1.1	Acid-catalyzed Condensation	381
11.1.2	Base-catalyzed Condensation	382
11.1.3	Radical Condensation and Other Lignin Linkages Transformation	384
11.2	Methods for Restraining Lignin Fragments Condensation	386
11.2.1	Pre-protection of the Active Groups	386
11.2.2	First Transformation of the Active Groups to Promote the Depolymerization	391
11.2.3	In-situ Converting the Active Intermediates and Scavenging the Unwanted Species	393
11.2.4	Catalysts Modification and Design	396
11.2.5	Intensifying the Reaction Systems	397
11.2.6	Employing an “Ideal Lignin” as the Substrates	400
11.3	Chapter Summary	401
	References	402

## Part V Outcome and Outlook 409

<b>12</b>	<b>Summary on Lignin Utilization and Perspectives on Preparation of Aromatic Chemicals</b>	<b>411</b>
12.1	Brief Summary on Lignin Utilization as Materials	411
12.2	Outlets of Lignin Resources Beyond Aromatic Chemicals	412
12.3	Standardized Lignin Substrate and Standardized Products	413
12.3.1	Standardized Lignin Substrate	414
12.3.2	Standardized Products	417
12.4	Concluding Remarks	430
	References	432

## Index 439