

Chaofeng Zhang and Feng Wang

Lignin Conversion Catalysis

Transformation to Aromatic Chemicals



Table of Contents

[Cover](#)

[Title Page](#)

[Copyright](#)

[Dedication](#)

[Preface](#)

[List of Abbreviations](#)

[List of Symbols](#)

[Part I: Book Introduction](#)

[1 Background and Overview](#)

[1.1 Introduction](#)

[1.2 Lignin: A Natural and Sustainable Aromatic
Bank](#)

[1.3 Structure of This Book](#)

[References](#)

[Part II: Lignin Introduction](#)

[2 Lignin Biosynthesis and Structure](#)

[2.1 Lignin Biosynthesis](#)

[2.2 Lignin Structure](#)

[2.3 Chapter Summary](#)

[References](#)

[3 Lignin Isolation, Physicochemistry Properties,
and Chemical Properties](#)

[3.1 Lignin Polymer Physical Properties](#)

[3.2 Lignin Isolation from Lignocellulose and
Technical Lignins](#)

[3.3 Lignin Spectroscopy Properties](#)

[3.4 Lignin Chemical Properties](#)

[3.5 Chapter Summary](#)

[References](#)

[Part III: Lignin Depolymerization: Scientific Questions, Challenges, and Current Progress](#)

[4 Scientific Questions for Lignin Conversion and a Brief Summary of Methods for Lignin Depolymerization](#)

[4.1 Opportunity and Challenges of New Biorefinery Approaches for Lignin Valorization](#)

[4.2 Scientific Questions Involved in Lignin Depolymerization and the Foundation of Strategies](#)

[4.3 Two Different Approaches for the Foundation of Lignin Depolymerization Strategies](#)

[4.4 Classification of Lignin Conversion Methods by Reaction Types](#)

[4.5 Brief Index of Progress of Native/Technical Lignin Conversion](#)

[4.6 Chapter Summary](#)

[References](#)

[Part IV: Review on Lignin Linkages Cleavage Strategies and Mechanisms via an IDA Method](#)

[5 The Inverse Disassembly Analysis Method for Classifying Lignin Conversion Strategies](#)

[5.1 Introduction of Inverse Disassembly Analysis for Lignin Conversion](#)

[5.2 Different Analysis Modes for Lignin Depolymerization](#)

[5.3 IDA Catalogue of Lignin Conversion
Methods Discussed in the Following Chapters](#)

[5.4 Chapter Summary](#)

[References](#)

[6 Direct Lignin C-OAr, ArO-Ar or C-Ar Bonds
Cleavage without First Activation of the Adjacent
Chemical Bonds](#)

[6.1 Brönsted/Lewis Acid + Metal Systems for
the Direct Hydrogenative Cleavage of Ether
Bonds and C-Ar Bonds](#)

[6.2 Base/Organometallic Systems for the Direct
Hydrogenative Cleavage of Ether Bonds](#)

[6.3 Other Heterogeneous Catalytic Systems for
the Direct Hydrogenative Cleavage of C-OAr
Ether Bonds](#)

[6.4 Direct Reductive Cleavage of Ether Bond
with Hydride Reagents](#)

[6.5 Direct Reductive Cleavage of Lignin Ether
Bond with e⁻](#)

[6.6 Chapter Summary](#)

[References](#)

[7 Lignin C-C/C-O Bonds Cleavage via First
Phenolic Hydroxyl Group Dehydrogenation or First
Aromatic Rings Activation](#)

[7.1 Lignin C_{Ar}-C_α/C_α-C_β Bonds Cleavage after
the First Phenolic Hydroxyl Group
Dehydrogenation to the Phenolic Radical](#)

[7.2 Lignin C_α-C_β bonds Cleavage via the First
Single-Electron Transfer \(SET\) of the Aromatic
Ring](#)

7.3 Lignin C_{A-r}-OC/C_{A-r}-C Bonds Cleavage via First Partly-Hydrogenation or Partly-Addition of the Neighbouring Aromatic Ring

7.4 Lignin C(sp²)-C(sp²) σ Bond and C(sp²)-OAr Bonds Cleavage via Adjacent Aromatic Groups Activation or Extra Radicals Attack

7.5 Chapter Summary

References

8 Lignin Linkages Cleavage Beginning with C_αO-H/ArO-H or C_α-OH Bond Heterolysis

8.1 Base-catalyzed C_β-OAr Bond Cleavage Beginning with C_αO-H or ArO-H Heterolysis

8.2 Acid-catalyzed C_β-OAr Bonds Cleavage Beginning with C_α-OH Heterolysis

8.3 Chapter Summary

References

9 Lignin Linkages Cleavage Beginning with C_α-H, C_α-OH, or C_αO-H Bond Non-ionized Activation

9.1 Lignin C_β-OAr Bond Cleavage via a Transfer Hydrogenation or Dehydrogenation-hydrogenation Process Beginning with the First Activation of C_α-H(O-H) to C_α=O

9.2 Lignin C_β-OAr Bond Cleavage in the Dehydrogenation/Oxidation-Hydrogenation (Reduction) Process Beginning with the First Activation of C_α-H(OH) to C_α=O

9.3 Lignin C_α-C_β/C_β-OAr Bonds Cleavage via Multiple Oxidation Process Beginning with the First Activation of C_α-OH to C_α=O

9.4 Lignin C_{α} - C_{β} , C_{Ar} - C_{α} , or $C_{\beta}O$ - C_{Ar} Bonds Cleavage by Inserting an O- or N-containing Fragment after the First Oxidation of C_{α} -OH to $C_{\alpha}=O$

9.5 Embellishing Lignin β -O-4 Linkages Hydrolysis Involving the C_{α} -OH First Oxidation and C_{γ} -OH Transformation

9.6 Lignin C_{β} -OAr Bond Cleavage after the First Activation of C_{α} -H, C_{α} -OH, or $C_{\alpha}O$ -H to $C_{\alpha}\cdot$ Radical

9.7 Lignin C_{α} - C_{β} Bond Cleavage after the First Activation of $C_{\alpha}O$ -H Bond to $C_{\alpha}O\cdot$ Radical via PCET Strategies and LMCT Mechanisms

9.8 Chapter Summary

References

10 Lignin Linkages Cleavage Beginning with C_{β} -H, C_{γ} -H, or $C_{\gamma}O$ -H Direct Activation

10.1 Lignin C-C/ C_{β} -OAr Bond Cleavage Beginning with C_{β} -H Bond Direct Activation

10.2 First $-C_{\gamma}H_2OH$ Activation to $-C_{\gamma}HO/-C_{\gamma}OOR$ Inducing Lignin C-C Bonds Selective Cleavage and Its Derivative Methods

10.3 Lignin C_{β} -OAr Bond Cleavage Beginning with C_{γ} First Sulphonation

10.4 Chapter Summary

References

11 Lignin Linkages Cleavage Considering Fragments Condensation

[11.1 Different Mechanisms of Lignin Fragments Condensation](#)

[11.2 Methods for Restraining Lignin Fragments Condensation](#)

[11.3 Chapter Summary](#)

[References](#)

[Part V: Outcome and Outlook](#)

[12 Summary on Lignin Utilization and Perspectives on Preparation of Aromatic Chemicals](#)

[12.1 Brief Summary on Lignin Utilization as Materials](#)

[12.2 Outlets of Lignin Resources Beyond Aromatic Chemicals](#)

[12.3 Standardized Lignin Substrate and Standardized Products](#)

[12.4 Concluding Remarks](#)

[References](#)

[Index](#)

[End User License Agreement](#)

List of Tables

Chapter 3

[Table 3.1 Typical Method Used for the Lignin Isolation.](#)

[Table 3.2 Different Commercial Organosolv Lignins.](#)

[Table 3.3 Sulfite-pulping Procedures Used to Extract Lignin from Wood.](#)

[Table 3.4 IR-absorption Bands of Lignins.](#)

[Table 3.5 Main \$^1\text{H}\$ Chemical Shifts \(\$\delta\$ \) of Acetylated Spruce MWL and Beech MW...](#)

[Table 3.6 Main \$^{13}\text{C}\$ Chemical Shifts \(\$\delta\$, ppm\). Assignment of Lignin.](#)

Chapter 4

[Table 4.1 A Brief Summary of Main Methods for Lignin Conversion by Reaction...](#)

[Table 4.2 A Brief List of Some Representative Systems for Native/Technical ...](#)

Chapter 5

[Table 5.1 Bond Dissociation Energies of the \$\text{C}_\beta\text{-O}\$ and \$\text{C}_\alpha\text{-C}_\beta\$ B...](#)

List of Illustrations

Chapter 1

[Figure 1.1 The Carbon-Increasing Process Based on the Non-renewable Fossil R...](#)

[Figure 1.2 Lignocellulose \(LC\) from Biomass and its Structural Composition....](#)

[Figure 1.3 Number of Entries Retrieved Using “Lignin” as the Research Topic...](#)

Chapter 2

[Figure 2.1 The Three-step for Lignin Biosynthesis.](#)

[Figure 2.2 Primary and Secondary Metabolic Pathways Leading to the Biosynthe...](#)

[Figure 2.3 The Shikimate-Chorismate Pathway \(from PEP/E-4-P to Chorismate vi...](#)

[Figure 2.4 Common Phenylpropanoid Pathway \(a\) and the Monolignol-Specific Pa...](#)

[Figure 2.5 Chemical Formulas of the Other Monomers of Lignin. *Note: M1monoli...*](#)

[Figure 2.6 Resonance Structures of Monolignols Radicals. *Note: \$R_{H-II} \approx R_{H-II}\$...*](#)

[Figure 2.7 Major Linkages Present in Lignins and Frequencies of Linkages and...](#)

[Figure 2.8 Dehydrogenation of Coniferyl Alcohol and Its Mesomeric Radicals C...](#)

[Figure 2.9 Dehydrogenation of Coniferyl Alcohol and Its Mesomeric Radicals C...](#)

[Figure 2.10 Dehydrogenation of Coniferyl Alcohol and Its Mesomeric Radicals ...](#)

[Figure 2.11 Dehydrogenation of Coniferyl Alcohol and Its Mesomeric Radicals ...](#)

[Figure 2.12 Dehydrogenation of Coniferyl Alcohol and Its Mesomeric Radicals ...](#)

[Figure 2.13 The Formation of Dibenzodioxocin Unit from the 5-5 Linkage.](#)

[Figure 2.14 The \$\beta\$ -1 Cross-coupling Mechanisms and the Corresponding Lignin U...](#)

[Figure 2.15 Mechanism of 5-Hydroxyconiferyl Alcohol Incorporation into a Gua...](#)

[Figure 2.16 The Coniferaldehyde Coupling with Lignin Fragment to the \$\beta\$ -O-4 L...](#)

[Figure 2.17 The Generation of \$\alpha,\beta\$ Ester Structure from the Quinone Methide I...](#)

[Figure 2.18 Structure Model of Beech Wood Lignin.](#)

[Figure 2.19 2D NMR Spectra Revealing Lignin Unit Compositions. Partial Short...](#)

[Figure 2.20 The Spruce Lignin Model.](#)

[Figure 2.21 Structural Model for Softwood Lignin.](#)

[Figure 2.22 The Spruce Lignin Model.](#)

[Figure 2.23 The Milled Softwood-lignin Model.](#)

[Figure 2.24 Structure Model Reed Stem Lignin.](#)

[Figure 2.25 Five Main Types of LCC Linkages in the Wood.](#)

Chapter 3

[Figure 3.1 Lignin Fragmentation Reaction Taking Place during the Milling of ...](#)

[Figure 3.2 Degradation of Monosaccharide to Dialdehydes in the Periodate Lig...](#)

[Figure 3.3 Main Reactions Involved in the Formation of Kraft Lignin during P...](#)

[Figure 3.4 Structure Model of Lignosulfonate.](#)

[Figure 3.5 Main Reactions Involved in the Formation of Alkali Lignin.](#)

[Figure 3.6 Derivatization of Lignin Hydroxylic Structures with TMPD.](#)

[Figure 3.7 Derivatization of Lignin Hydroxylic Structures with HMDS and Me3S...](#)

[Figure 3.8 Derivatization of Lignin Hydroxylic Structures with Fluorine Reage...](#)

[Figure 3.9 Lignin Oxidation with Nitrobenzene.](#)

[Figure 3.10 Formation of Low-molecular Aliphatic Acids from Ozonolysis of \$\beta\$ -...](#)

[Figure 3.11 Lignin H₂O₂ Oxidation with Broken Down of the Aromatic Ring.](#)

[Figure 3.12 Methylation Reaction in Lignin.](#)

[Figure 3.13 Phenolization Reaction in Lignin.](#)

[Figure 3.14 Demethylation Reaction in Lignin.](#)

[Figure 3.15 Hydroxymethylation Reaction in Lignin.](#)

[Figure 3.16 The lignin Mannich Reaction.](#)

[Figure 3.17 Nucleus-Exchange Reaction in Lignin.](#)

Chapter 4

[Figure 4.1 Lignin Depolymerization to Aromatic Chemicals.](#)

[Figure 4.2 Frequencies of Major Lignin Linkages.](#)

[Figure 4.3 The Solubility of Birch Lignin in Various Solvents Characterized ...](#)

[Figure 4.4 MALDI-TOF Profiles of Dissolved Birch Lignin in 1,4-Dioxane \(A\), ...](#)

[Figure 4.5 Two Different Approaches for the Foundation of Lignin Depolymeriz...](#)

[Figure 4.6 Definitions of Conversion and Product Yield for Lignin \(A\) and Li...](#)

Chapter 5

[Figure 5.1 The Retrosynthetic Analysis of the Natural Product to Confirm the...](#)

[Figure 5.2 Bond Dissociation Enthalpy of Typical Bonds in Lignin Linkages....](#)

[Figure 5.3 Adjacent Functional Group Modification \(AFGM\) Strategy for the Cl...](#)

[Figure 5.4 The \$\beta\$ -O-4 Linkage Model with Atoms Denomination. *Note:* The phenol...](#)

[Figure 5.5 Direct Lignin C-OAr, ArO-Ar or C-Ar Bonds Cleavage without First ...](#)

[Figure 5.6 Lignin C-C/C-O Bonds Cleavage via First Phenolic Hydroxyl Group D...](#)

[Figure 5.7 Lignin Linkages Cleavage Beginning with C _{\$\alpha\$} O-H/ArO-H Heterol...](#)

[Figure 5.8 Lignin Linkages Cleavage Beginning with the Activation of C _{\$\alpha\$} ...](#)

[Figure 5.9 Lignin Linkages Cleavage Beginning with C \$\beta\$ -H, C \$\gamma\$ -H, or C \$\gamma\$ O-H Dire...](#)

Chapter 6

[Figure 6.1 Stoichiometric Reactions for C-O Ether Bonds Cleavage \(A and B\), ...](#)

[Figure 6.2 Acidolysis-hydrogenation Tandem Pathway for Lanthanide Triflate/P...](#)

[Figure 6.3 Step-wise Reaction Profile for Lignin C _{\$\beta\$} -OAr Bond Hydrogenol...](#)

[Figure 6.4 Tandem Catalytic System for the Reductive Fractionation of Woody ...](#)

[Figure 6.5 Hydrogenolysis of Lignin-derived Aromatic Ethers Catalyzed by a S...](#)

[Figure 6.6 Noble-metal Catalyzed Hydrodeoxygenation of Biomass-derived Ligni...](#)

[Figure 6.7 Catalytic Fast Pyrolysis of Lignin over ZSM-5 Zeolite for the Pro...](#)

[Figure 6.8 Direct Hydrodeoxygenation of Woody Biomass into Liquid Alkanes an...](#)

[Figure 6.9 Size-dependent Catalytic Performance of Ru Nanoparticles of Ru/Nb...](#)

[Figure 6.10 Lignin Fragmentation over Magnetically Recyclable Composite Co@N...](#)

[Figure 6.11 MOF-based Catalysts for Selective Hydrogenolysis of Carbon–oxyge...](#)

[Figure 6.12 Hydrogenolysis of Aryl Ether Bonds over a Nickel Ni Carbene Cata...](#)

[Figure 6.13 Mechanisms for the Conversion of Aryl Alkyl Ethers to Arenes....](#)

[Figure 6.14 Reaction Mechanism for C–O Bond Hydrogenolysis of DiphenylEther ...](#)

[Figure 6.15 Catalytic C–OAr Bond Hydrogenolysis of Methyl Phenyl Ether with ...](#)

[Figure 6.16 The Role of the Excess Base on the Mechanism of Ni-NHC Catalyzed...](#)

[Figure 6.17 Nickel-catalyzed Reductive Cleavage of Aryl Alkyl Ethers to Aren...](#)

[Figure 6.18 Metal-catalyzed Transformations of Aryl Ethers with Various Nucl...](#)

[Figure 6.19 Hydrogenolysis of Diaryl Ethers over a Heterogeneous Nickel Cata...](#)

[Figure 6.20 Ni-catalyzed Cleavage of Aryl Ethers in the Aqueous Phase.](#)

[Figure 6.21 One-pot Catalytic Hydrocracking of Raw Woody Biomass into Chemic...](#)

[Figure 6.22 Lignin Conversion in Methanol with Ni/AC Catalyst.](#)

[Figure 6.23 Representation of the Ni/AC Catalyst Reduced by H₂_\(a\) and Activ...](#)

[Figure 6.24 Depolymerization of Various Lignin over the Ni/C Catalyst in Met...](#)

[Figure 6.25 Hydrogenolysis of Diaryl Ether C-O Bonds by a Heterogeneous Ni/C...](#)

[Figure 6.26 Hydrogenation of Lignin to Aromatic Chemicals over a Ni-Mo₂C/C C...](#)

[Figure 6.27 Catalytic Lignin Ether Bond Cleavage over the Supported Ru-WO_xC...](#)

[Figure 6.28 Reaction Pathways of \$\beta\$ -O-4 Model Transformation into Monomeric a...](#)

[Figure 6.29 Low-temperature Cleavage of Ethers with Boranes/Metal Borohydrid...](#)

[Figure 6.30 NiCl₂/NaBH₄ in Methanol Achieves the Dealkylation or Debenzylati...](#)

[Figure 6.31 Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with ...](#)

[Figure 6.32 Selective Reductive Cleavage of Inert aryl C-O Bonds by an Iron ...](#)

[Figure 6.33 Rh-catalyzed Reductive Cleavage of the C-O Bond of Acetals and w...](#)

[Figure 6.34 Ni-catalyzed Reductive Cleavage of Aryl ether with Hydrosilane....](#)

[Figure 6.35 Ni-catalyzed Protocol for the Reductive Cleavage of Inert Ar-OR ...](#)

[Figure 6.36 Reductive Cleavage of Aryl ethers with Silane and Base..](#)

[Figure 6.37 Reductive Cleavage of Lignin Model Compounds to Phenols and Prim...](#)

[Figure 6.38 Reductive Degradation of Lignin and Model Compounds by Hydrosila...](#)

[Figure 6.39 Pd-catalyzed Hydrogenolysis of Dibenzodioxocin Lignin Model Comp...](#)

[Figure 6.40 Electrochemical Cleavage of Aryl Ethers Promoted by Sodium Boroh...](#)

Chapter 7

[Figure 7.1 Phenoxy Radical Induce the Cleavage of Lignin C-C Bonds.](#)

[Figure 7.2 Catalytic Oxidation of Syringyl Alcohols to the Corresponding Ben...](#)

[Figure 7.3 Oxidative Degradation of Monomeric and Dimeric Phenylpropanoids w...](#)

[Figure 7.4 The Oxidation Mechanism of Veratryl Alcohol with Co\(salen\) Media....](#)

[Figure 7.5 Catalytic Oxidation of Veratryl Alcohol via a Co/ \[EMIM\]\[DEP\]/OH ...](#)

[Figure 7.6 The Catalytic Oxidation Mechanism of Guaiacyl Models with a Hinde...](#)

[Figure 7.7 Reaction Mechanism Proposed for Alkaline Oxidation of Lignin to V...](#)

[Figure 7.8 Lignin Oxidation Mechanism with \$\text{Cu}^{2+}\$ and \$\text{Fe}^{3+}\$ in NaOH.](#)

[Figure 7.9 Proposed Mechanism of Lignin Oxidation in the Presence of Cu-Subs...](#)

[Figure 7.10 Mechanism of Electrooxidation Cleavage of Lignin Model Dimers....](#)

[Figure 7.11 Cleavage of \$\text{C}_{\text{Ar}}\text{-C}\$ and \$\text{C}_{\text{alkyl}}\text{O-Ar}\$ Bonds by the In-situ Generated ...](#)

[Figure 7.12 High-temperature Electrolysis of Kraft Lignin for Selective Vani...](#)

[Figure 7.13 Degradation of Lignin to BHT by Electrochemical Catalysis on Pb/...](#)

[Figure 7.14 Photocatalytic Chemoselective C–C Bond Cleavage at Room Temperat...](#)

[Figure 7.15 Mechanism of C–C Bonds Cleavage in the Catalytic Oxidation the \$\beta\$...](#)

[Figure 7.16 Proposed Mechanism for Side-chain Cleavage of a Phenolic \$\beta\$ -O-4 L...](#)

[Figure 7.17 Proposed Mechanisms for \$C_{\alpha}\$ -Oxidation \(A\) and Alkyl-phenyl B...](#)

[Figure 7.18 Proposed Mechanism for \$C_{\alpha}\$ - \$C_{\beta}\$ Cleavage of Phenolic \$\beta\$ -1 ...](#)

[Figure 7.19 Lignin \$C_{\alpha}\$ - \$C_{\beta}\$ Bonds Cleavage via the First Generation o...](#)

[Figure 7.20 Proposed Radical Depolymerization Route of a Model Compound of \$\beta\$...](#)

[Figure 7.21 Possible Reactions of the Veratryl Alcohol Cation Radical and a ...](#)

[Figure 7.22 Structures of Porphyrin and Phthalocyanine Catalysts Used for Li...](#)

[Figure 7.23 Single-electron Transfer Mechanism for Oxidation of the \$\beta\$ -1 Lign...](#)

[Figure 7.24 Oxidative Cleavage of Lignin to Aromatic Aldehydes by Metal Salt...](#)

[Figure 7.25 HPA-5 Catalyzed Oxidative Cleavage of Non-phenolic \$\beta\$ -O-4 Bonds \(...\)](#)

[Figure 7.26 Oxidation of Lignosulfonate with Persulphate and Various Metal S...](#)

[Figure 7.27 Oxidation of Lignosulfonate with Nitrobenzene and Metal Salts.](#)

[Figure 7.28 Triarylamine Mediated the Electrochemical Oxidation of Nonphenol...](#)

[Figure 7.29 Regioselectivity of Enzymatic and Photochemical Single Electron ...](#)

[Figure 7.30 Depolymerization Route of \$\beta\$ -1 Linkage via the First One-electron...](#)

[Figure 7.31 Light/Copper Relay for Aerobic Degradation of Lignin Model Compo...](#)

[Figure 7.32 The mechanism for Selective \$C_{\alpha}\$ - \$C_{\beta}\$ Bond Cleavage by Ir ...](#)

[Figure 7.33 Uranyl-Photocatalyzed Hydrolysis of Diaryl Ethers.](#)

[Figure 7.34 Synthesis of Ketones from Lignin-derived Methyl Aromatic Ether....](#)

[Figure 7.35 Palladium-Catalyzed Hydrolytic Cleavage of Aromatic C-O Bonds....](#)

[Figure 7.36 Palladium-Catalyzed Reductive Insertion of Alcohols into Aryl Et...](#)

[Figure 7.37 Cleaving Lignin Ether Bond via First Partly-addition of the Neig...](#)

[Figure 7.38 Ni-catalyzed Reductive Cleavage of Inert \$C_{Ar}\$ -O Bonds with the Ex...](#)

[Figure 7.39 Pd-catalyzed Ether Bond Cleavage and Rearrangement of 4-O-5 Lign...](#)

[Figure 7.40 Methoxybenzenes Oxidation to Benzoquinones Catalyzed by MTO/H₂O₂](#)

[Figure 7.41 Cleavage of a C\(sp²\)-C\(sp²\) \$\sigma\$ Bond between Two Phenyl Groups und...](#)

[Figure 7.42 Functionalized Spirolactones by Photoinduced Dearomatization of ...](#)

[Figure 7.43 Visible-Light Photoredox-Catalyzed C_{Ar}-O Bond Cleava...](#)

[Figure 7.44 Strategy for the Catalytic Activation of C\(aryl\)-C\(aryl\) Bonds o...](#)

Chapter 8

[Figure 8.1 Alkaline Cleavage of \$\alpha\$ -aryl and \$\beta\$ -aryl Ether Bonds in Phenolic Ar...](#)

[Figure 8.2 Competitive Addition of Nucleophiles Hydrosulfide Ion \(a\) or Phen...](#)

[Figure 8.3 Alkali-promoted Condensation Reactions in Phenolic Units with For...](#)

[Figure 8.4 Decomposition of Phenolic Lignin Models over Organic N-bases in a...](#)

[Figure 8.5 Degradation of \$\beta\$ -O-4 Lignin Model Compounds by Solvent-free Grind...](#)

[Figure 8.6 Lignin Depolymerization by Nickel-supported Layered Double Hydrox...](#)

[Figure 8.7 Lignin Depolymerization with Nitrate-Intercalated Hydrotalcite Ca...](#)

[Figure 8.8 Vinylation of Lignin \$\beta\$ -O-4 Linkage with Calcium Carbide through C...](#)

[Figure 8.9 Pathways for the Acid-mediated Cleavage of the Lignin \$\beta\$ -O-4 Linka...](#)

[Figure 8.10 Depolymerization of Lignin Linkage with Hydrogen Iodide.](#)

[Figure 8.11 Selective Ether Bonds Cleavage in Lignins by the DFRC Method.](#)

[Figure 8.12 Degradation of Lignin by Thioacetolysis with Thioacetic Acid.](#)

[Figure 8.13 Acid-catalyzed Mechanism for Hydrolysis of the \$\beta\$ -O-4 Bonds in Io...](#)

[Figure 8.14 Cleavage of Lignin \$\beta\$ -O-4 C-O Bonds Catalyzed by Methyldioxorheni...](#)

[Figure 8.15 Microwave-assisted Fast Conversion of Lignin \$\beta\$ -O-4 Linkage over ...](#)

[Figure 8.16 Proposed Reaction Pathway for the W2C/AC-catalyzed Deconstructio...](#)

Chapter 9

[Figure 9.1 The Mechanism for Ru Catalyzed C-O Bond Cleavage in 2-Aryloxy-1-a...](#)

[Figure 9.2 Mechanism of 2-Aryloxy-1-arylethanol Catalytic Deconstruction by ...](#)

[Figure 9.3 Dehydrogenation and C-O Cleavage by Intermolecular Hydrogen Trans...](#)

[Figure 9.4 Cleavage of the \$\beta\$ -O-4 Linkage with Pincer Complexes.](#)

[Figure 9.5 Binuclear Rh-catalyzed Redox-neutral System for Lignin Depolymeri...](#)

[Figure 9.6 Ru-terpyridine Catalyzed Redox-neutral Depolymerization of Lignin...](#)

[Figure 9.7 Proposed Mechanism of \$\beta\$ -O-4 Ether Bond Cleavage via the \$C_{\alpha}\$ -M...](#)

[Figure 9.8 Proposed Mechanism for the Transformation of \$\beta\$ -O-4 Ether Bond Cle...](#)

[Figure 9.9 Proposed Mechanism of Aryl Propene Formation from Wood over the P...](#)

[Figure 9.10 Proposed Reaction Mechanisms for the Redox Neutral Transfer Hydr...](#)

[Figure 9.11 Pd/C-Catalyzed Redox Neutral Cleavage of the Model I to Products...](#)

[Figure 9.12 Reaction Network for the \$\beta\$ -O-4 Bond Cleavage of 2-Phenoxy-1-phen...](#)

[Figure 9.13 The Optimized \$\beta\$ -O-4 Molecules/Pd\(111\) Structures. In Each Row, t...](#)

[Figure 9.14 \$\text{ZnIn}_2\text{S}_4\$ -catalyzed Photocatalytic Self-transfer Hydrogenolysis of...](#)

[Figure 9.15 The Transformation of Lignin \$\beta\$ -O-4 Models to Benzylamines.](#)

[Figure 9.16 Dehydrogenation/Oxidation-hydrogenation \(Reduction\) Strategies f...](#)

[Figure 9.17 Isolation of Functionalized Phenolic Monomers through Selective ...](#)

[Figure 9.18 Chemoselective Oxidant-free Dehydrogenation of \$\text{C}_\alpha\text{H-OH}\$ in Li...](#)

[Figure 9.19 Nucleophilic Thiols Reductively Cleave Ether Linkages in Lignin M...](#)

[Figure 9.20 The reaction of the LigDFG Enzyme System with AVR.](#)

[Figure 9.21 DFRC Method for Lignin Analysis with \$\text{C}_\beta\text{-OAr}\$ Cleavage.](#)

[Figure 9.22 The Conversion of Birch Sawdust to Aromatic monomers via an Oxid...](#)

[Figure 9.23 Carbon Modification of Nickel Catalyst Ni/MgAlO-C for Depolymeri...](#)

[Figure 9.24 Catalytic Depolymerisation of Oxidized Lignin over TiN-Cu Nanoca...](#)

[Figure 9.25 Two-step Visible-light Mediated Depolymerization Strategies for ...](#)

[Figure 9.26 Selective C–O Bond Cleavage of Lignin Systems and Polymers Enabl...](#)

[Figure 9.27 The One-pot Electrocatalytic Oxidation–reductive Cleavage of \$\beta\$ -O...](#)

[Figure 9.28 Proposed Reaction Mechanism for Photocatalytic C–O Bond Cleavage...](#)

[Figure 9.29 Further Deoxygenation of Aromatic Ketones to Alkyl Arenes over t...](#)

[Figure 9.30 Solar-driven Lignin Oxidation via Hydrogen Atom Transfer with a ...](#)

[Figure 9.31 Fine Tuning the Redox Potentials of Carbazolic Porous Organic Fr...](#)

[Figure 9.32 Visible Light-enabled Selective Depolymerization of Oxidized Lig...](#)

[Figure 9.33 Two-step Oxidation Strategy for \$\beta\$ -O-4 Cleavage.](#)

[Figure 9.34 Possible Reaction Mechanism of the Copper ComplexCatalyzed Oxi...](#)

[Figure 9.35 Oxidative C\(OH\)–C Bond Cleavage of Secondary Alcohols to Acids o...](#)

[Figure 9.36 Cobalt Nanoparticles-Catalyzed Successive C–C Bond Cleavage in A...](#)

[Figure 9.37 Possible Mechanism of Oxidation of Lignin Model Compound in Ioni...](#)

[Figure 9.38 Amine-Mediated Bond Cleavage in Oxidized Lignin Models.](#)

[Figure 9.39 Dual ILs-promoted Photochemical Degradation of Pre-oxidized Lign...](#)

[Figure 9.40 Selective Electrochemical C-O Bond Oxidative Cleavage of \$\beta\$ -O-4 L...](#)

[Figure 9.41 The \$\beta\$ -O-4 Models Transformation via a 'Wedging' Mode.](#)

[Figure 9.42 Chemoselective Aerobic Alcohol Oxidation in Lignin and \$C_{\alpha}\$ -C](#)

[Figure 9.43 Transformation of Lignin Model Compounds to N-substituted Aromat...](#)

[Figure 9.44 \$NH_2OH\$ -mediated Lignin Conversion to Isoxazole and Nitrile.](#)

[Figure 9.45 Introducing N-radical at \$C_{\alpha}\$ Mediated Lignin Aryl Ether Clea...](#)

[Figure 9.46 Nucleophilic Aromatic Substitution for the Cleavage of Aryl C-O ...](#)

[Figure 9.47 From Alkylarenes to Anilines via Site-directed Carbon-carbon Ami...](#)

[Figure 9.48 Selective Utilization of the Methoxy Group in Lignin to Produce ...](#)

[Figure 9.49 \$C_{\beta}\$ -OAr Cleavage of Oxidized Lignin Model Compounds with For...](#)

[Figure 9.50 \$C_{\beta}\$ -OAr Bond Cleavage after the First Activation of \$C_{\alpha}\$ -...](#)

[Figure 9.51 Possible Radical Intermediates for the Degradation Reactions of](#)

[Figure 9.52 Boosting Laccase/HBT-Catalyzed the Cleavage of \$\beta\$ -O-4' Linkage in...](#)

[Figure 9.53 Proposed Pathways for HDO of \$\beta\$ -O-4 Lignin Substrate over Zn\(II\)-...](#)

[Figure 9.54 Zn\(II\)/Pd/C Catalyzed Cleavage and Hydrodeoxygenation of Lignin ...](#)

[Figure 9.55 Catalytic Cleavage of Aryl-ether Bonds in Lignin Model Compounds...](#)

[Figure 9.56 The Potential Dehydroxylation-hydrogenation Strategy for \$\beta\$ -O-4-A...](#)

[Figure 9.57 Solar Energy-driven Lignin-first Approach to Full Utilization of...](#)

[Figure 9.58 Ligand-controlled Photocatalysis of CdS Quantum Dots for Lignin ...](#)

[Figure 9.59 Enhancing Photocatalytic \$\beta\$ -O-4 Bond Cleavage in Lignin Model Com...](#)

[Figure 9.60 Visible-Light-Driven Cleavage of C–O Linkage for Lignin Valoriza...](#)

[Figure 9.61 Catalytic Cleavage of Ether C–O Bonds by Pincer Iridium Complexes...](#)

[Figure 9.62 Multiple Mechanisms Mapped in Aryl Alkyl Ether Cleavage via Aque...](#)

[Figure 9.63 Vanadium-catalyzed Non-oxidative Cleavage of \$\beta\$ -O-4 Linkage.](#)

[Figure 9.64 C–C or C–O Bond Cleavage in a Phenolic Lignin Model Compound: Se...](#)

[Figure 9.65 Overall Mechanistic Proposals for C\(sp³\)–OAr and Ar–C\(sp³\) Bond ...](#)

[Figure 9.66 Catalytic Cleavage of the C-C Bond with an Adjacent Alcohol Grou...](#)

[Figure 9.67 Proposed Mechanistic Cleavage Pathways Schematic BQ-BQH₂ Redox C...](#)

[Figure 9.68 Catalytic Ring-opening of Cyclic Alcohols Enabled by PCET Activa...](#)

[Figure 9.69 Light-driven Depolymerization of Lignin Enabled by PCET.](#)

[Figure 9.70 Photocatalytic C_α-C_β Bond Cleavage in Lignin β-O-...](#)

[Figure 9.71 Selective Lignin β-O-4 C-C Bond Cleavage with a Vanadium Photoca...](#)

[Figure 9.72 Visible-Light-Induced Oxidative Lignin C-C Bond Cleavage to Alde...](#)

[Figure 9.73 Photocatalytic C-C Bond Cleavage and Amination of Cycloalkanols ...](#)

[Figure 9.74 CeCl₃-promoted Photocatalytic Cleavage of C_α-C_β Bond i...](#)

Chapter 10

[Figure 10.1 Lignin Linkages Cleavage Beginning with C_α O-H, or C_β](#)

[Figure 10.2 Photocatalytic C-C Bond Cleavage of β-1 Lignin Models to Aromati...](#)

[Figure 10.3 Photocatalytic Cleavage of C-C Bond in Lignin Models under Visib...](#)

[Figure 10.4 VO\(acac\)₂-catalyzed Oxidative Cleavage of 2-Phenoxy-1-phenyletha...](#)

[Figure 10.5 Pt₁/N-CNTs Catalyze the Electrooxidation of β-O-4 Linkage with C](#)

[Figure 10.6 Retro-aldol Strategies for Biomass C-C Bond Cleavage.](#)

[Figure 10.7 The Transfer Hydrogen-based Retro-aldol Mechanism for the C-C Bo...](#)

[Figure 10.8. Organocatalytic Chemoselective Primary Alcohol Oxidation and Su...](#)

[Figure 10.9 Iridium-catalyzed Primary Alcohol Oxidation and Hydrogen Shuttli...](#)

[Figure 10.10 Electrochemical Aminoxyl-mediated Oxidation of Primary Alcohols...](#)

[Figure 10.11 Selective Copper–N-heterocyclic Carbene-catalyzed Aerobic Cleav...](#)

[Figure 10.12 The Transformation of Alcohol\(butanol\)-pretreated Lignin Linkag...](#)

[Figure 10.13 Sequential Catalytic Modification of the Lignin \$\alpha\$ -Ethoxylated \$\beta\$...](#)

[Figure 10.14 The Degradation of \$\beta\$ -O-4 Model Compounds by a TIZ Method.](#)

[Figure 10.15 Multi-steps \$\gamma\$ -TTSA Method for \$\beta\$ -O-4 Linkage Cleavage.](#)

Chapter 11

[Figure 11.1 Lignin Fragments Condensations or New Stable C–C Bond Generation...](#)

[Figure 11.2 Alkaline Cleavage of C \$_{\alpha}\$ -OR Bonds in Phenolic Arylpropane U...](#)

[Figure 11.3 Some Examples of \$\beta\$ -O-4 Lignin Fragments Recondensation Involving...](#)

[Figure 11.4 The Transformation of \$\beta\$ -1 Linkages to Dihydrobenzofuran Structur...](#)

[Figure 11.5 Depolymerization of Lignin by Microwave-assisted Methylation of ...](#)

[Figure 11.6 Production of Phenolic Alcohols from Woody Biomass via an In-sit...](#)

[Figure 11.7 Formaldehyde Stabilization Facilitates Lignin Monomers Productio...](#)

[Figure 11.8 \$\alpha,\gamma\$ -Diol Lignin Stabilization Strategies besides the Formaldehyd...](#)

[Figure 11.9 Mechanistic Insights into Formaldehyde-Blocked Lignin Condensati...](#)

[Figure 11.10 Pre-protection of Lignin: Diol Etherization, Acetylation, and S...](#)

[Figure 11.11 First Transformation of the Active Groups to Promote the Depoly...](#)

[Figure 11.12 Selective Ether Bonds Cleavage in Lignins by the DFRC Method.](#)

[Figure 11.13 The Lignin Depolymerization Strategies with \$\beta\$ -O-4 Fragments Gen...](#)

[Figure 11.14 In Situ Conversion of the Reactive Aldehyde Intermediate in the...](#)

[Figure 11.15 Lewis Acid-catalyzed \$\beta\$ -O-4 Linkage Cleavage with Rh-catalyzed D...](#)

[Figure 11.16 Preventing Lignin Fragments Condensation by Diffusion Control B...](#)

[Figure 11.17 The Reactor Installation with Membrane Separation.](#)

[Figure 11.18 The Normal Lignin Structure and Benzodioxane Structure of C-lig...](#)

[Figure 12.1 The Lignin Polymers Model from the C4H:F5H-up-regular Transgenic...](#)

[Figure 12.2 The Typical Structure Model of the Catechyl lignin.](#)

[Figure 12.3 Schematic Flow of Maleic Acid Promote Sustainable Fractionation ...](#)

[Figure 12.4 Catalytic Hydrogenation Depolymerization of Organosolv \(Methanol...](#)

[Figure 12.5 Hydrogenolysis Monomer Yields of C-lignin over the Pd/C in Metha...](#)

[Figure 12.6 Defunctionalization of Lignin Depolymerization Monomers to Stand...](#)

[Figure 12.7 Catalytic Upgrading of Alkylphenols Derived to Phenol and Olefin...](#)

[Figure 12.8 Proposed Reaction Pathway of Dealkylation, Isomerization, Dispro...](#)

[Figure 12.9 Proposed Mechanism for the O- and C-dealkylation of Ferulic Acid...](#)

[Figure 12.10 Lignin Valorization to Phenol by Direct Transformation of Csp2-...](#)

[Figure 12.11 La\(OTf\)₃ Catalyzed the Selective Transformation of Lignin to Gu...](#)

[Figure 12.12 Lignin Dealkylation to Phenol via Hydrogenation-oxidation-decar...](#)

[Figure 12.13 Reaction Pathways of the Self-Reforming-Driven Depolymerization...](#)

[Figure 12.14 Catalytic Lignin Decomposition to Benzene over the RuW/Zelite ...](#)

[Figure 12.15 Production of Terephthalic Acid \(TPA\) from Lignin-Based Phenoli...](#)

Figure 12.16 A Three-step Strategy for the TPA
Production from Corn Stover L...

Lignin Conversion Catalysis

Transformation to Aromatic Chemicals

Chaofeng Zhang
Feng Wang

WILEY-VCH

Authors

Dr. Chaofeng Zhang

College of Light Industry and Food Engineering
Nanjing Forestry University
159 Longpan Road
210037 Nanjing
China

Prof. Feng Wang

Dalian Institute of Chemical Physics
Dalian Nat. Lab. for Clean Energy
Chinese Academy of Science
457 Zhongshan Road
116023 Dalian
China

Cover Image: Courtesy of Chaofeng Zhang and Feng Wang

All books published by **WILEY-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data: A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche

Nationalbibliothek The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2022 WILEY-VCH GmbH, Boschstraße 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN 978-3-527-34973-9

ePDF ISBN 978-3-527-83501-0

ePub ISBN 978-3-527-83502-7