

Chaofeng Zhang and Feng Wang

# Lignin Conversion Catalysis

Transformation to Aromatic Chemicals





## **Lignin Conversion Catalysis**



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Transformation to Aromatic Chemicals

*Chaofeng Zhang*  
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**WILEY-VCH**

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## Preface

The development of civilization and human society can be regarded as the changing history of utilization of various resources and materials. In history, drilling wood for fire lightened the glimmer of the development of human civilization, heating water for steam power by burning coal allowed development to catch the train of the steam age, and petroleum utilization built the cornerstone of modern civilization. Each technical revolution based on the utilization of fossil resources promoted the qualitative development of human civilization. However, just as coins have two sides, a large number of fossil resources have been quickly consumed in a short time and the carbon element that has been stored in Earth's crust is concurrently converted into CO<sub>2</sub> gas that enters the atmosphere of the ecosphere where its presence causes corresponding environmental and climate problems. When human society is at a loss about this dilemma, nature has already prepared a solution for us with biomass as the renewable carbon resource. Photosynthesis on Earth can convert CO<sub>2</sub> and water into organic carbon resources and O<sub>2</sub> with renewable solar energy, which produces about 170 billion tonnes of lignocellulose every year. If the renewable biomass resource can be efficiently transformed to the desired chemical stocks with sustainable energy input, the increasing CO<sub>2</sub> concentration will be not a hot potato, primarily because of the potential CO<sub>2</sub>-neutral cycle that transforms solar energy, H<sub>2</sub>O, and CO<sub>2</sub> into chemical stocks and fuels via biomass. Different from the utilization of the fossil resource that can be regarded as the conversion and stitching of small molecules into macromolecules, biomass utilization is more like a process of tailoring and converting natural polymers into corresponding small-molecule chemicals, all of which requires the development of more sophisticated strategies and efficient implementation methods.

Lignin is the third abundant organic carbon resource on the earth. As a precious resource given to mankind by nature, especially for its potential as a treasure house of aromatic chemicals, research on lignin depolymerization and the transformation of its downstream products have drawn much attention from scientists and companies worldwide in the recent decade aimed at harvesting aromatic compounds and hydrocarbon stocks/fuels from this abundant and renewable natural polymer. In November 2020, we received an invitation from Wiley to prepare a book on the topic of lignin conversion/transformation to chemicals. Perhaps it is a coincidence, but our literature retrieval process revealed that the electronic literature on the topic of

lignin can be traced back to the 1920s with the SciFinder database, 100 years from 2020. Thus, it is meaningful to receive the invitation to record the research process of lignin conversion. Before setting a topic line of this book from the complex content of lignin catalytic conversion, we first reviewed previous records to determine the likely readership of the book. We hope that this book is useful for readers in academia, industry, and education at the introductory, advanced, and specialist levels who are interested in wood chemistry or fields of lignin utilization research.

For this reason, Chapter I of the book briefly introduces the structure of the book. In Part II, the basic knowledge of lignin, including lignin biosynthesis, lignin structure, and lignin isolation, physicochemistry properties, and chemical properties are introduced. Then, lignin depolymerization issues, involving scientific questions, challenges, classification of lignin conversion methods by reaction type, and current progress, are discussed in Part III. For the main topic, the critical book aims to provide an overview of key advances in the field of lignin depolymerization to aromatic monomers and more attention is paid to the generalization and summarization of the mechanism of lignin linkage cleavage. It is challenging to systemically summarize all of the strategies via the traditional classification method by reaction types. In Chapter 5 of Part IV, inspired by the retrosynthetic analysis of the natural product to confirm the synthons proposed by Professor Cory, we herein put forward an inverse disassembly analysis (IDA) method to explore the efficient strategies for lignin depolymerization, which can be also used in the classification and discussion of the various methods for lignin conversion viewed from the cleavage order and type of corresponding chemical bonds over various catalytic systems. With  $\beta$ -O-4 linkage as the main lignin mode, we further introduce the lignin depolymerization strategies with the IDA thoughts from Chapter 6 to Chapter 11. Finally, in Part V, exploring lignin depolymerization to aromatic chemicals and how to make lignin depolymerization profitable, we provide some viewpoints for outlets of the lignin resource that highlights the importance of high-value medicine and synthetic block preparation or the utilization of lignin from natural polymer to artificial polymer. To accelerate the lignin utilization from lab to industry application, we discussed the critical roles of the standardized lignin substrate and standardized products, during which we support the idea that funneling and functionalization of a mixture of lignin-derived monomers into a single high-value chemical is fascinating and promising.

Finally, given the complexity of the catalytic conversion of lignin and the multiformity of the catalytic methods, which involves the research fields of different disciplines, the discussion of some relevant catalytic methods for lignin conversion may be omitted because of the limited knowledge reserve of the authors. In addition, if there are any improper points in this book, we encourage readers and experts to constructively criticize and correct them with us.

November 2021, in Dalian

*Chaofeng Zhang*  
*Feng Wang*



## List of Abbreviations

<b>A</b>	AC	Activated carbon
	ACT	4-Acetamido-TEMPO
	AFEX	Ammonia fiber explosion
	AFGM	Adjacent functional group modification
<b>B</b>	BDE	Bond dissociation enthalpy
	BNL	Brauns native lignin
	BTX	Benzene–toluene–xylenes
<b>C</b>	C3H	Coumarate 3-hydroxylase
	C4H	Cinnamic acid 4-hydroxylase
	CAD	Cinnamyl alcohol dehydrogenase.
	CB	Conduction band
	CCoAOTM	Caffeoyl-CoA O-methyltransferase
	CCR	Cinnamoyl-CoA reductase
	CCTC	Contact charge transfer complex
	CDE	CO <sub>2</sub> explosion
	CEL	Cellulolytic Enzyme Lignins
	4CL	4-coumarate CoA ligase
	CoA	Coenzyme A
	COMT	CoA O-methyltransferase
	CP/MAS	It is a combination of cross-polarization sequence (CP) and magic angle transformation technology (MAS).
<b>D</b>	DAIB	Diacetoxiodobenzene
	DBAD	Diisopropyl azodiformate
	DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
	DEPT	Distortionless enhancement by polarization transfer
	DES	Deep eutectic solvent
	DFRC	Derivatization followed by reductive cleavage
	DFT	Density functional theory
	DIPEA	N,N-diisopropylethylamine
	DL	Dioxane (acidolysis) lignins
	DMSO	Dimethyl sulfoxide
	DSPEC	Dye-sensitized photoelectrochemical cell

<b>E</b>	E-4-P	Erythrose-4-phosphate
	EMAL	Enzymatic mild acidolysis lignin
	ESR	Electron spin resonance absorption
	EXAFS	Extended X-ray absorption fine structure
<b>F</b>	F5H	Ferulate 5-hydroxylase
	FA	Formic acid
	FTIR	Fourier transform infrared spectroscopy infrared absorption spectroscopy
<b>G</b>	GFC	Gel-filtration chromatography
	GH	Glucosylhydrolases
	GPC	Gel-permeation chromatography
	GS	Glutathione
	GT	Glucosyl transferases
	G-unit	Coniferyl alcohol, or lignin phenylpropanoid unit with one –OMe connecting with the aromatic ring
<b>H</b>	HAADF-STEM	High angle annular dark-field scanning transmission electron microscopy
	HAT	Hydrogen atom transfer
	HBS	High-boiling-point solvent
	HCT	Hydroxycinnamoyltransferase
	HMBC	Heteronuclear multiple bond correlation
	HMQC	Heteronuclear multiple-quantum correlation
	HPAs	Heteropoly acids
	HPSEC	High-performance size-exclusion chromatography
	HTC	Hydrotalcite
	H-unit	<i>p</i> -Coumaric alcohol, or lignin phenylpropanoid unit without –OMe connecting with the aromatic ring
<b>I</b>	IDA	Inverse disassembly analysis
	ILs	Ionic liquids
	INADEQUATE	Incredible natural abundance double quantum transfer experiment
<b>L</b>	LA	Lewis acid
	LAR	Lignin isolation from lignocellulose with lignin as the residue
	LBD	Lignin isolation from lignocellulose by first lignin dissolution
	LC	Lignocellulose
	LCC	Lignin-carbohydrate complex
	LDH	Layered-double hydroxide catalyst
	LDP	Lignin depolymerization
	LMCT	Ligand-to-metal charge-transfer
	LS	Lignocellulose
<b>M</b>	MALDI-TOF	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
	mCPBA	<i>m</i> -Chloroperbenzoic acid
	MDO	Methyldioxorheniu
	MOF	Metal-organic framework
	MTO	Methyltrioxorhenium

	MWD	Molecular weight distribution
	MWL	Milled-wood lignin
<b>N</b>	NCS	N-chlorosuccinimide
	NE	Nucleus exchange
	NHC	N-heterocyclic carbene
	NHPI	N-hydroxyphthalimide
	NMR	Nuclear magnetic resonance spectroscopy
	NPs	Nanoparticles (noble metal)
<b>O</b>	OAT	Oxygen atom transfer
	OMS	Open metal sites
	OPCs	Organic (visible light) photocatalysts
	OSL	Organosolv lignin
<b>P</b>	PAL	Phenylalanine ammonia-lyase;
	PAR	Phenylseleninic acid resin
	PB	<i>p</i> -Hydroxybenzoate
	PCET	Proton-coupled electron transfer
	PDI	Perylene diimide
	PE	Polyethylene
	PEDOS	Partial electronic density of states
	PEP	Phosphoenol pyruvate
	POFs	Porous organic frameworks
	POM	Polyoxometalate
	ppu	Phenylpropanoid units
	PTH	Phenothiazine
<b>R</b>	RCF	Reductive catalytic fractionation
	RSA	Retrosynthetic analysis
<b>S</b>	scMeOH	Supercritical methanol
	SEC	Size-exclusion chromatography
	SET	Single-electron transfer
	S-unit	Sinapyl alcohol, or lignin phenylpropanoid unit with two -OMe connecting with the aromatic ring
<b>T</b>	TAL	Tyrosine ammonia-lyase
	TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
	<sup>t</sup> BuONO	tert-Butyl nitrite
	TDTS	TOF-determining transition state
	TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
	THF	Tetrahydrofuran
	TMSI	1-(Trimethylsilyl)imidazole
	TPA	Terephthalic acid
<b>U</b>	UV	Ultraviolet absorption spectroscopy
	UV–vis DRS	The ultraviolet-visible diffuse reflectance spectrum
<b>V</b>	VB	Valence band
<b>X</b>	XPS	X-ray photoelectron spectroscopy
	XRD	X-ray diffraction

## List of Symbols

$\delta$	NMR chemical shift
$M_n$	number-average molar mass
$M_w$	weight-average molar mass
$\mathcal{D}$	dispersity index, $\mathcal{D} = M_w/M_n$
$\lambda_{\max}$	The wavelength at which the largest amount of absorption occurs
pH	acidity or basicity of an aqueous solution
ppm	parts per million
$T_g$	glass transition temperature
$T_s$	thermal softening temperature
rt	room temperature
$\epsilon$	molar absorption coefficient (UV-vis)

## **Part I**

### **Book Introduction**



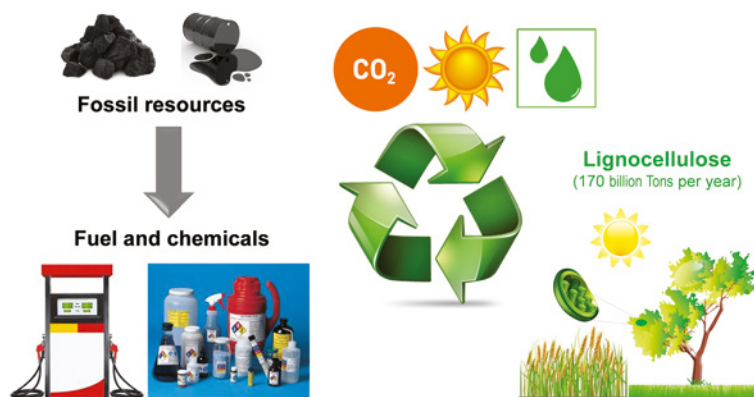
# 1

## Background and Overview

### 1.1 Introduction

The world currently is relying more and more on non-renewable fossil resources. In 2019, the global primary energy consumption reached 583.9 EJ (1 EJ=10<sup>18</sup> J) [1] and the 84.3% of this energy consumption was from traditional fossil fuel resources: coal, natural gas, and crude oil. Besides fuel production and energy output from these resources, billions of tons of additional fossil resources are transformed into chemicals and materials to support the explosive development of human civilization. However, this represents the negative side of a double-edged sword because the immoderate utilization of fossil resources has released billions of tons of CO<sub>2</sub> into the atmosphere within the last century. This CO<sub>2</sub> release has considerably exceeded the capacity of the earth's ecological cycle and therefore caused global climate problems such as global warming and problems deriving from global warming. Against this background of ecological problems, carbon peaking and carbon neutrality have become topics of concern to all those concerned with the future of humanity. Meanwhile, increasing awareness of dwindling fossil resources and the ever-increasing need for more chemical feedstock and energy supply has led to extensive research into more efficient and sustainable methods to meet these demands. To make the carbon cycle more efficient and controllable, optimizing existing technologies and reducing dependence on fossil resources will be insufficient and therefore utilizing sustainable carbon resources is an important and promising option to help address the problem.

As one kind of carbon and solar energy storage form, biomass is any organic matter that is renewable over time and it is only renewable organic carbon resource in nature. Biomass is generally plant-based and includes agricultural residues, forestry wastes, and energy crops [2]. Every year, global photosynthesis can produce about 170 billion tons of lignocellulose (LC) by capturing the low concentration CO<sub>2</sub> from the atmosphere, immobilizing the carbon, and releasing O<sub>2</sub> [3]. However, besides the timber industry and papermaking, only a small proportion of biomass carbon resources is utilized to prepare chemicals. The rest of biomass carbon is primarily



**Figure 1.1** The Carbon-Increasing Process Based on the Non-renewable Fossil Resources Compared with the Carbon-neutral Cycle Connecting Solar Energy,  $H_2O$ , and  $CO_2$  with Chemicals/Fuels via Biomass. *Source:* Zhang and Wang [38].

used to generate heat and power or abandoned. However, biomass is still the fourth largest source of energy in the world after oil, coal, and methane, supplying 10% of the world's primary energy. Considering another perspective, we can reduce millions of years of fossil resources generation if we can efficiently transform the renewable biomass resource to the desired chemical stocks with an acceptable  $CO_2$  release during their preparation [4–12]. This would reduce the concern regarding increasing  $CO_2$  concentration, primarily because  $CO_2$  released during further utilization of chemicals prepared in this way originates from  $CO_2$  in the modern-day atmosphere. It can be a perfect  $CO_2$ -neutral cycle that transforms solar energy,  $H_2O$ , and  $CO_2$  into chemical stocks and fuels via biomass (Figure 1.1).

## 1.2 Lignin: A Natural and Sustainable Aromatic Bank

Aromatic chemicals are important bulk chemicals widely used in the chemical industry for the production of polymers, solvents, medicines, pesticides, and many other materials. With the rapid development of economic and industrial globalization, the demand for aromatic chemicals is increasing sharply every year. At present, aromatic chemicals are primarily obtained through petroleum catalytic reforming or steam cracking followed by a complex functionalization process.

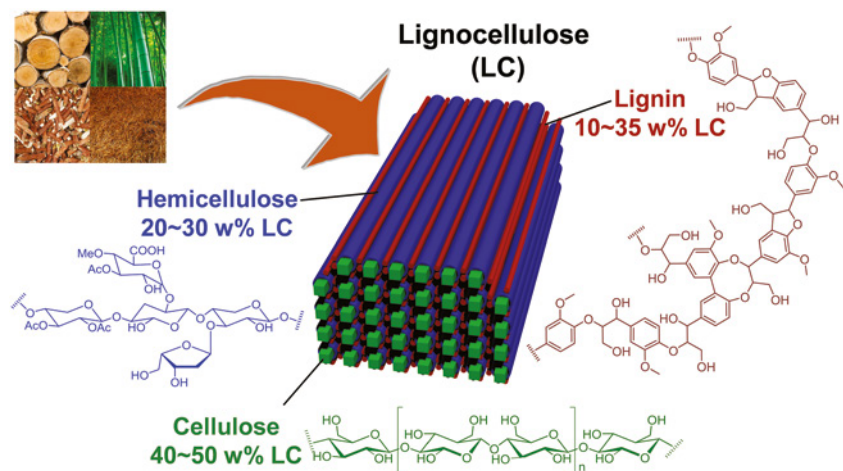
These chemical feedstocks are obtained primarily from fossil resources (coal and oil) formed by the photosynthesis of ancient plants. Ancient plants used solar energy to convert  $CO_2$  into biomass, then the residue of animals and plants in food webs were transformed to fossil resources after millions of years underground.

The technical revolution based on the utilization of these fossil resources to produce power and chemicals promoted the development of human society. However, it is now clear that the inherent non-renewability of fossil resources and tough environmental protection requirements have begun to affect the sustainable production of aromatic chemicals [13]. Therefore, the development of new technologies to



replace or supplement fossil resources to prepare aromatic chemicals has become increasingly important [2, 14–16]. In the past decades of research, people have successively developed methane aromatization [17], methanol aromatization [18], CO<sub>2</sub> conversion [19], C<sub>2</sub> compound synthesis [20], and other routes. However, using these low-carbon substrates as a raw material to obtain aromatic hydrocarbon monomers with high selectivity is still a serious challenge [21].

Lignocellulose (LC), with an annual production of around 170 billion tons, is the most abundant biomass form [3]. The potential use of non-edible lignocellulosic biomass for the production of value-added chemicals could provide an attractive alternative for fossil-based processes is therefore of great significance. As shown in Figure 1.2, LC comprises three main components: hemicellulose, cellulose, and lignin. Among them, hemicellulose (20–30 w% of LC) and cellulose (40–50 w% of LC) are the polymers of C<sub>5</sub> and C<sub>6</sub> sugars (Figure 1.2) [22] that can be further converted to the low-carbon alcohols, aldehydes, ketones, or acid. These compounds can be used in some biomass-based reforming processes to obtain aromatic hydrocarbon compounds, as exemplified by the BioFormPX project from the Virient Company. Additionally, the C<sub>5</sub> and C<sub>6</sub> polymers or their monomers can be transformed to furan-based chemicals or other low-carbon chemicals, which can also be used in C<sub>6</sub> aromatization via a typical 4+2 Diels-Alder reaction [23–25]. At the same time, lignin (10–35 w% of LC) is a complex three-dimensional amorphous polymer, consisting of various methoxylated phenylpropanoid units, which can be regarded as a potential resource to replace fossil resources to directly prepare functionalized aromatic chemicals and non-aromatic hydrocarbon stocks/fuels [14, 26–28]. Therefore, the direct conversion of lignin in LC is a more attractive process. However, the current paper industry and, more recently, biorefineries produce large quantities of lignin that is currently considered almost a by-product, not to mention the transformation of the more complex native lignin. Not only from an economic standpoint but also from a sustainability perspective, the misuse or even nonuse of



**Figure 1.2** Lignocellulose (LC) from Biomass and its Structural Composition.

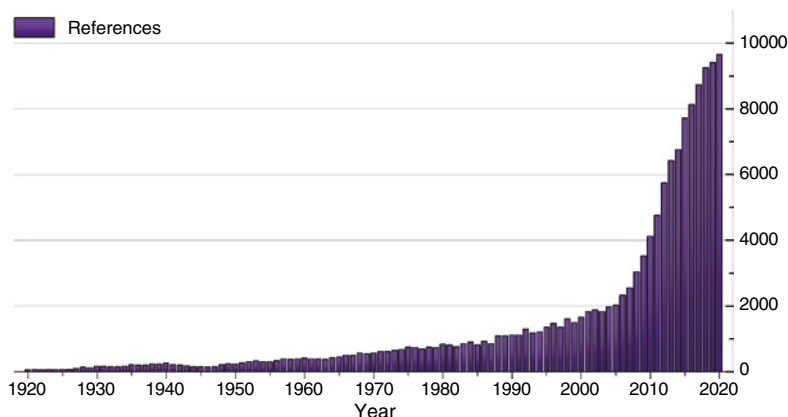
lignin appears to be a colossal mistake. Lignin, whether as native lignin from plants or partially transformed by industrial separation procedures, is a complex material with great potential by itself or as a source of chemicals. In a world where raw materials are in constant demand, having a renewable source such as lignin should be considered a gift from nature to technology [29].

Unlike other bio-platform molecules with a distinct structure, lignin structures are much more complex. The key issue for the lignin transformation/depolymerization lies in the development of strategies with highly selective and active catalysts to effectively cleave the ubiquitous C–O/C–C bonds [2, 14, 16, 30] while leaving the aromatic benzene rings unconverted. Although lignin research can be traced back to 1819, when the Swiss botanist A. P. Candolle (1778–1841) first used the term lignin [31] from the Latin word *lignum* meaning wood, and various non-catalytic and catalytic methods have been explored to cleave the various lignin C–C or C–O linkages bonds from the 1920s [29], it remains a big challenge to selectively convert lignin extracts, or even original lignin, to aromatics. For detailed reasons, this can be attributed to the much more complex mechanism caused by disturbing the lignin structure with various targeted linkages, combined with other factors such as transformations of lignin structure and different condensation modes of lignin fragments. With the development of lignin depolymerization in the last decade, many efficient methods and strategies have been reported for lignin utilization to prepare chemicals and materials [2, 14, 16, 32–35]. To better make use of lignin to prepare aromatic chemicals, it is necessary to summarize the existing catalysts and processes. Based on the obtained knowledge about lignin conversion regimens, we can update the catalysts and develop new routes for lignin efficient conversion.

The critical target of this book is to provide an overview of key advances in the field of lignin depolymerization to aromatics. Unlike previous review work, which classified the research by the lignin substrate (native lignin, kraft lignin, organosolv lignin, etc.), cleavage methods (oxidation, hydrogenation, etc.), or main products (arenes, phenol, acid, etc.), we provide a brief introduction to lignin, past technologies, and new catalytic methods or strategies for lignin depolymerization to monomers and then pay more attention to the relationships among the lignin depolymerization strategies/methods, catalysts, and mechanisms viewed from cleavage order and type of corresponding chemical bonds over various catalytic systems [36, 37]. Based on this summary of reported processes and their results, we hope to partly pull off the lid of the black box of lignin depolymerization.

### 1.3 Structure of This Book

The structure, reactions, and utilizations of the lignins have been studied for about two centuries from 1819 [31]. Lignin has been widely used in the preparation of various functional materials, chemicals, fuels, medicines, polymers, and others. As shown in Figure 1.3, entering the term “lignin into the SciFinder database by the end of December 2020 generated more than 140,000 entries over the last 100 years. Furthermore, the ever-increasing growth curve displays that about half of them



**Figure 1.3** Number of Entries Retrieved Using “Lignin” as the Research Topic in SciFinder from 1920 to 2020.

(76554) have been published in the last 10 years and over 8000 references were reported in each of the last four years, reflecting the fact that lignin is a popular and evolving topic. As a star molecule, lignin and its utilization have drawn much attention from academia to industry worldwide.

One important utilization approach is to efficiently depolymerize the natural lignin polymer to easily-handled monomers as this is a precondition of lignin utilization to prepare chemicals that may be potential alternatives to fossil resources. In recent decades, many attempts have been carried out to achieve this target [2, 12, 14, 16, 37]. Given the complexity of lignin structure, numerous strategies and methods taking varying approaches from different research fields have been developed to effectively degrade lignin into monomer chemicals by targeting linkages and chemical bonds cleavages. These include the traditional methods of pyrolysis, gasification, liquid-phase reforming, supercritical solvolysis, chemical oxidation, hydrogenation, reduction, acidolysis, alkaline hydrolysis, and alcoholysis, as well as the newly developed redox-neutral process, biocatalysis, and combinatorial strategies. Therefore, there is a strong demand to summarize this research, providing a research history to show the connections among different research published in different periods and also providing an overview of current research into lignin depolymerization, which may provide useful suggestions for this vigorous research field.

Although it is quite a challenging project to give a systematic summary of so much research from different research fields with different backgrounds, it is possible using a viewpoint that is not just based on the reaction types or what kinds of catalyst are needed to achieve lignin depolymerization. Classifying the related strategies/methods and establishing their connections needs to come from a deeper perspective. Taking the perspective of a detailed discussion of mechanisms, this book examines the science and technology of lignin depolymerization conversion by using a multidisciplinary approach. About 2000 bibliographical references have been compiled to provide the reader with a complete and systematic overview of research into lignin depolymerization to produce chemicals, mainly aromatic

chemicals. To handle such a vast amount of information about different lignin conversion strategies/methods, this book is divided into several parts that give a wide vision of the science and technology of lignin.

Considering that not all readers are professionals in the field of lignin research, we added some brief introductions about lignin near the beginning of the book (Part II, Chapter 2, and Chapter 3). In Chapter 2, we briefly introduce the biosynthesis of lignin from monolignols generation to their transport and then polymerization to the lignin molecule. Then, we provide an introduction of the lignin structure, viewing from the lignin linkages, linkages generation mechanism, structure models of different kinds of protolignin, and lignin-carbohydrate complex. In Chapter 3, after a brief introduction about the lignin polymer physical properties and methods to isolate lignin from lignocellulose, we present a basic introduction about the spectroscopy properties for the lignin structure characterization. At the end of Chapter 3, lignin chemical properties related to pre-chemical modification are discussed.

Next, focusing on lignin depolymerization, Part III, Chapter 4 first provides a discussion about scientific questions regarding lignin conversion and new biorefinery approaches. Next, we summarize scientific questions focusing on the topic of lignin depolymerization to aromatic monomers. Then, two different approaches for the foundation of lignin depolymerization strategies are introduced: direct lignin conversion and the bottom-up approach. To provide a macro-level understanding of the research field of lignin conversion, the classification of lignin conversion methods by reaction types is summarized. Then, as an important complementary issue, a brief list of systems for lignin/models conversion based on the catalysts is provided and targeted to provide knowledge about the catalyst/reagent that can be used in the lignin conversion via corresponding reaction types. The chapter concludes with summary of systems recently reported for native/technical lignin conversion.

Part IV, Chapters 5 to 11, comprises the main part of this book. As discussed in Chapter 4, multitudinous methods have been developed to depolymerize lignin to provide aromatic monomers. It is hard work to systemically summarize all of these strategies. Facing this question in Chapter 5, inspired by retrosynthetic analysis of the natural product to confirm the synthons and synthetic equivalents, we put forward an inverse disassembly analysis (IDA) method to explore the efficient strategies for lignin depolymerization. The IDA method, which can be used in the classification and discussion of various methods of lignin conversion, considers the cleavage order and type of corresponding chemical bonds over various catalytic systems. Then, to generalize as many lignin conversion methods with various routes and intermediates as possible, four thinking modes based on the IDA for lignin conversion are emphasized: (1) tailoring mode; (2) wedging mode; (3) protection mode; and (4) cascaded mode. With the  $\beta$ -O-4 linkage as the main lignin model, we further introduce the lignin depolymerization strategies with the IDA method from Chapters 6 to 11.

In Chapter 6, we firstly review the stoichiometric reactions and catalytic systems for the direct cleavage of ether bonds with a strong nucleophile or a strong electrophilic reagent. Then, modifying and updating the above methods, Brönsted/Lewis acid and metal systems, base/organometallic systems, and other heterogeneous

catalysts used in the direct hydrogenative cleavage of C–OAr ether bonds are systematically introduced. In addition, for the direct reductive cleavage of ether bond, a brief review of the lignin conversion methods with hydride reagents, and the  $e^-$  species from chemical conversion or surface of the cathode or semiconductors is provided.

In Chapter 7, lignin depolymerization strategies beginning with the first activation/transformation of the neighboring lignin phenolic hydroxyl group or aromatic rings to the active radicals are summarized, which includes the following strategies: (1) lignin  $C_{Ar}$ –C bond cleavage of after the first phenolic hydroxyl group dehydrogenation to the phenolic radical; (2) lignin C–C bond cleavage *via* the first single-electron transfer from the aromatic ring; (3) lignin C–O bond cleavage of *via* the first semi-hydrogenation/addition of one aromatic ring to a cyclohexenyl ether; and (4) lignin C–O or C–C bond cleavage *via* the first inserting a cleavage reagent (metal catalyst center or extra radical) between the target bond with the assistance of the aromatic rings conjoint groups.

In Chapter 8, strategies for lignin linkages cleavage beginning with  $C_{\alpha}O$ –H/ArO–H heterolysis or  $C_{\alpha}$ –OH bond heterolysis are summarized, which is mainly focusing on the lignin alkaline hydrolysis, acidolysis, and their corresponding tandem processes.

In Chapter 9, strategies for lignin catalytic depolymerization which begin with the activation of  $C_{\alpha}$ –H,  $C_{\alpha}$ –OH, or  $C_{\alpha}O$ –H bonds via a non-ionized route are mainly summarized. The first cleavage of  $C_{\alpha}O$ –H and  $C_{\alpha}$ –H bonds to a  $\beta$ -O-4 ketone intermediate can weaken the  $C_{\beta}$ –OAr bond and make a slightly stronger  $C_{\alpha}$ – $C_{\beta}$  bond, but with an active  $C_{\beta}$ –H. Therefore, focusing on this molecule intermediate, the lignin depolymerization strategies of catalytic transfer hydrogenation, dehydrogenation/oxidation-hydrogenation (reduction), and the multiple oxidation process are first summarized. Given that the Baeyer-Villiger oxidation and Beckmann rearrangement can be used in the cleavage of C–C bonds in lignin linkages that contain a ketone substrate site, the corresponding strategies and their derivative methods are then summarized. In addition, the first oxidation of  $C_{\alpha}$ –OH can promote lignin hydrolysis, so an embellished  $\beta$ -O-4 linkage hydrolysis method involving the  $C_{\alpha}$ –OH first oxidation and  $C_{\gamma}$ –OH transformation is discussed. In addition to the first cleavage of  $C_{\alpha}O$ –H and  $C_{\alpha}$ –H bonds to  $C_{\alpha}=O$  at the beginning of the  $\beta$ -O-4 model transformation, some catalytic strategies beginning with the  $C_{\alpha}$ –H or  $C_{\alpha}O$ –H activation to the corresponding active radical intermediates can also lead to the cleavage of the lignin fragments. The first activation of  $C_{\alpha}$ –OH(–H) to a  $C_{\alpha}^{\bullet}$  radical intermediate can reduce the bond dissociation enthalpy (BDE) of the  $C_{\beta}$ –OAr bond for the following self-cleavage of  $\beta$ -O-4 linkage. Additionally, the first activation of  $C_{\alpha}O$ –H bond to the  $C_{\alpha}O^{\bullet}$  via a hydrogen atom transfer (HAT), proton-coupled electron transfer (PCET) oxidation, or redox-neutral ligand-to-metal charge transfer (LMCT) process can lead to the selective cleavage of  $C_{\alpha}$ – $C_{\beta}$  bonds.

In Chapter 10, lignin cleavage strategies beginning with  $C_{\beta}$ –H,  $C_{\gamma}$ –H, or  $C_{\gamma}O$ –H direct activation are summarized. These mainly describe some photocatalytic strategies with direct activation of  $C_{\beta}$ –H bonds that introduce the cleavage agent  $O^*$ , leading to the cleavage of the  $C_{\alpha}$ – $C_{\beta}$  bonds in  $\beta$ -1 and  $\beta$ -O-4 linkages, and some retro-aldol strategies with first  $-C_{\gamma}H_2OH$  activation to  $-C_{\gamma}HO/-C_{\gamma}OOR$  ( $R=H$  or alkyl).

In Chapter 11, the main topic is promoting the lignin linkages cleavage with considering the potential lignin fragments condensation. After a summary of the potential lignin fragments condensation mechanism, we briefly introduce the developed methods for restraining the potential condensation of lignin fragments. The methods are divided into six categories as follows: (1) pre-protection of the active groups to inhibit the condensation; (2) first transformation of the active groups to promote the depolymerization; (3) in-situ converting the active intermediates and scavenging the unwanted species; (4) modifying and designing the catalysts; and (5) intensifying reaction systems; (6) employing “ideal lignins” as the substrates.

Finally, in Part V (Chapter 12), we first briefly introduce the research process of lignin utilization to prepare versatile materials. Then, considering the steps from lignin depolymerization to aromatic chemicals and the issue of how to make lignin depolymerization profitable, we provide our viewpoint for the outlets of lignin resources and emphasize the importance of high-value medicine and synthetic block preparation or the lignin utilization from natural polymer to artificial polymer. To accelerate the lignin utilization from lab to industry application, we discuss the critical roles of standardized lignin substrate and standardized products, during which we hold the idea that funneling and functionalization of a mixture of lignin-derived monomers into a single high-value chemical is fascinating and promising.

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