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Lignin and Lignans as Renewable Raw Materials

Chemistry, Technology and Applications

Francisco G. Calvo-Flores | José A. Dobado
Joaquín Isac-García | Francisco J. Martín-Martínez

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Chemistry, Technology and Applications

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To our families

Contents

Series Preface **xv**
Preface **xvii**
List of Acronyms **xix**
List of Symbols **xxiii**

Part I Introduction 1

1. Background and Overview **3**
1.1 Introduction 3
1.2 Lignin: Economical Aspects and Sustainability 4
1.3 Structure of the Book 5
References 7

Part II What is Lignin? 9

2. Structure and Physicochemical Properties **11**
2.1 Introduction 11
2.2 Monolignols, The Basis of a Complex Architecture 12
2.3 Chemical Classification of Lignins 16
2.4 Lignin Linkages 17
2.5 Structural Models of Native Lignin 20
2.5.1 Softwood Models 21
2.5.2 Hardwood Models 28
2.5.3 Herbaceous Plant Models 28
2.6 Lignin–Carbohydrate Complex 34
2.7 Physical and Chemical Properties of Lignins 39
2.7.1 Molecular Weight 39
2.7.2 Dispersity Index (*Đ*) 40
2.7.3 Thermal Properties 40
2.7.4 Solubility Properties 41
References 42

3. Detection and Determination **49**
3.1 Introduction 49
3.2 The Detection of Lignin (Color-Forming Reactions) 49
3.2.1 Reagents for Detecting Lignins 50

3.3 Determination of Lignin 55
3.4 Direct Methods for the Determination of Lignin 55
3.4.1 Methods for Lignin as a Residue 57
3.4.2 Lignin in Solution Methods 59
3.5 Indirect Methods for the Determination of Lignin 60
3.5.1 Chemical Methods 61
3.5.2 Spectrophotometric Methods 61
3.5.3 Methods Based on Oxidant Consumption 64
3.6 Comparison of the Different Determination Methods 66
References 68

4. Biosynthesis of Lignin 75
4.1 Introduction 75
4.2 The Biological Function of Lignins 75
4.3 The Shikimic Acid Pathway 76
4.4 The Common Phenylpropanoid Pathway 78
4.5 The Biosynthesis of Lignin Precursors (the Monolignol-Specific Pathway) 80
4.5.1 The Biosynthesis of Other Monolignols 82
4.5.2 The Transport of Monolignols 83
4.6 The Dehydrogenation of the Precursors 85
4.7 Peroxidases and Laccases 86
4.8 The Radical Polymerization 87
4.8.1 Dimerization 88
4.8.2 Quinone Methides 89
4.8.3 Lignification 90
4.8.4 Interunit Linkage Types 91
4.8.5 Dehydrogenation Polymer (DHP) 97
4.9 The Lignin–Carbohydrate Connectivity 97
4.10 Location of Lignins (Cell Wall Lignification) 99
4.11 Differences Between Angiosperm and Gymnosperm Lignins 101
References 103

Part III Sources and Characterization of Lignin 113

5. Isolation of Lignins 115
5.1 Introduction 115
5.2 Methods for Lignin Isolation from Wood and Grass for Laboratory Purposes 116
5.2.1 Lignin as Residue 118
5.2.2 Lignin by Dissolution 120
5.3 Commercial Lignins 127
5.3.1 Kraft Lignin 128
5.3.2 Sulfite Lignin (Lignosulfonate Process) 131
5.3.3 Soda Lignin (Alkali Lignin) 133
5.3.4 Organosolv Pulping 134
5.3.5 Other Methods of Separation of Lignin from Biomass 136
References 136

6. Functional and Spectroscopic Characterization of Lignins 145
6.1 Introduction 145
6.2 Elemental Analysis and Empirical Formula 146
6.3 Determination of Molecular Weight 147
6.3.1 Gel-Permeation Chromatography (GPC) 148
6.3.2 Light Scattering 149
6.3.3 Vapor-Pressure Osmometry (VPO) 150
6.3.4 Ultrafiltration (UF) 151
6.4 Functional Group Analyses 151
6.4.1 Methoxyl Group (MeO) 152
6.4.2 Phenolic Hydroxyl Group (OH_{ph}) 152
6.4.3 Total and Aliphatic Hydroxyl Groups (R−OH) 154
6.4.4 Ethylenic Groups (>C=C<) 157
6.4.5 Carbonyl Groups (>C=O) 158
6.4.6 Carboxyl Groups (−COO−) 158
6.4.7 Sulfonate Groups and Total Sulfur Composition ($R\text{-}SO_2O-$ and S) 158
6.5 Frequencies of Functional Groups and Linkage Types in Lignins 159
6.5.1 β-*O*-4′ Linked Units 159
6.5.2 β-5′ Linked Units 160
6.5.3 β-1′ Linked Units 160
6.5.4 α-*O*-4′ Linked Units (benzyl ethers) 162
6.5.5 Condensed and Uncondensed Units 162
6.5.6 Biphenyl Structures 163
6.5.7 4-*O*-5′ Linked Units 163
6.5.8 β-2 and β-6 Linked Units 163
6.5.9 β-β Linked Units 163
6.5.10 Dibenzodioxocin Units 164
6.6 Characterization by Spectroscopic Methods 164
6.6.1 Fourier Transform Infrared (FTIR) Spectroscopy 164
6.7 Raman Spectroscopy 166
6.7.1 Ultraviolet (UV) 167
6.7.2 NMR Spectroscopy 168
6.7.3 Other Spectroscopic Methods 174
References 175

7. Chemical Characterization and Modification of Lignins 189
7.1 Introduction 189
7.2 Characterization by Chemical Degradation Methods 189
7.2.1 Oxidation with Nitrobenzene 190
7.2.2 Oxidation with Cupric Oxide 193
7.2.3 Permanganate Oxidation 195
7.2.4 Mild Hydrolysis 196
7.2.5 Acidolysis 198
7.2.6 Thioglycolic Acid Hydrolysis (Mercaptolysis) 200
7.2.7 Thioacetolysis 200

7.2.8 Thioacidolysis 201
7.2.9 Hydrogenolysis 203
7.2.10 Derivatization Followed by Reductive Cleavage (DFRC) 206
7.2.11 Nucleus-Exchange Reaction (NE) 209
7.2.12 Ozonolysis 212
7.2.13 Pyrolysis 215
7.3 Other Chemical Modifications of Lignins 216
7.3.1 Acylation 216
7.3.2 Alkylation 218
7.3.3 Halogenation 219
7.3.4 Nitration 221
7.3.5 Sulfonation 222
7.3.6 Oxidation 222
7.3.7 Other Modifications of Lignins 225
7.4 Thermolysis (Pyrolysis) of Lignins 227
7.5 Biochemical Transformations of Lignins 227
7.5.1 Biodegradation of Lignin 228
7.5.2 Enzyme-Based Oxidation of Lignin 229
References 230

Part IV Lignins Applications 247

8. Applications of Modified and Unmodified Lignins 249
8.1 Introduction 249
8.2 Lignin as Fuel 252
8.2.1 Combustion in the Paper Industry 252
8.2.2 Heating and Power 252
8.3 Lignin as a Binder 253
8.3.1 Coal Briquettes 253
8.3.2 Packing 254
8.3.3 Pelleted Feeds 254
8.4 Lignin as Chelating Agent 254
8.5 Lignin in Biosciences and Medicine 256
8.6 Lignin in Agriculture 257
8.7 Polymers with Unmodified Lignin 258
8.7.1 Phenol–Formaldehyde Binders 258
8.7.2 Polyolefin–Lignin Polymers 260
8.7.3 Polyester–Lignin Polymers 260
8.7.4 Acrylamide–Lignin Polymers 261
8.7.5 Polyurethane–Lignin Polymers 261
8.7.6 Bioplastics (Liquid Wood) 263
8.7.7 Hydrogels 264
8.7.8 Foams and Composites 265
8.7.9 Conducting Polymers 265

8.8 Other Applications of Unmodified Lignins 267
8.8.1 Lignin in Lead-Acid Batteries 267
8.8.2 Lignin-Based Nanoparticles and Thin Films 267
8.8.3 Lignin in Dust Control 268
8.8.4 Lignin in Concrete Admixtures 269
8.8.5 Lignin as a Dispersant, Emulsifier, and Surfactant 269
8.8.6 Lignin as Floating Agent 271
8.9 New Polymeric Materials Derived from Modified Lignins and Related Biomass Derivatives 271
8.9.1 Modified Lignin in Phenol–Formaldehyde Wood Adhesives 271
8.9.2 Modified Lignins for Epoxy Resin Synthesis 274
8.9.3 Polyurethanes 275
8.9.4 Lignin–Polybutadiene Copolymers 278
8.10 Polymers Derived from Chemicals Obtainable from Lignin Decomposition 278
8.11 Other Applications of Modified Lignins 279
8.11.1 Nanoparticles (NPs) 279
8.11.2 Cationic Amphiphilic Lignin Derivatives 281
8.11.3 Soil Preservation 281
8.11.4 Fertilizers 281
References 281

9. High-Value Chemical Products 289
9.1 Introduction 289
9.2 Gasification: Syngas from Lignin 291
9.3 Thermolysis of Lignin 291
9.4 Hydrodeoxygenation (Hydrogenolysis) 294
9.5 Hydrothermal Hydrolysis 295
9.6 Chemical Depolymerization 295
9.6.1 Acid Media Depolymerization 296
9.6.2 Base Media Depolymerization 296
9.6.3 Ionic Liquid-Assisted Depolymerization 297
9.6.4 Supercritical Fluids-Assisted Depolymerization 298
9.7 Oxidative Transformation of Lignin 299
9.7.1 Oxidation with Chlorinated Reagents 299
9.7.2 Oxidation with Ozone 300
9.7.3 Oxidation with Hydrogen Peroxide 300
9.7.4 Oxidation with Peroxy Acids 302
9.7.5 Catalytic Oxidation 302
9.8 High-Value Chemicals from Lignin 302
9.8.1 Vanillin 302
9.8.2 Dimethyl Sulfide and Dimethylsulfoxide 306
9.8.3 Active Carbon 306
9.8.4 Carbon Fiber 308
References 308

Part V Lignans 313

10. Structure and Chemical Properties of Lignans 315

10.1 Introduction 315
10.2 Structure and Classification of Lignans 315
10.2.1 Lignans 316
10.2.2 Hybrid Lignans 319
10.3 Nomenclature of Lignans 319
10.4 Lignan Occurrence in Plants 325
10.5 Methods of Determination and Isolation of Lignans from Plants 328
10.5.1 Lipid Extraction 328
10.5.2 Solvent Extraction 330
10.5.3 Separation by Precipitation 330
10.5.4 Chromatographic Methods 330
10.5.5 Extraction of Polar Lignans from Biological Materials 331
10.6 Structure Determination of Lignans 331
10.7 The Chemical Synthesis of Lignans 332
10.7.1 Generalities on the Asymmetric Total Synthesis of Lignans 332
10.7.2 Dibenzylbutane Lignans 335
10.7.3 Dibenzylbutyrolactone Lignans 337
10.7.4 Cyclolignans (Aryltetralin Lignans) 338
10.7.5 Dibenzocyclooctadiene Lignans 343
References 353

11. Biological Properties of Lignans 369

11.1 Introduction 369
11.2 Biosynthesis of Lignans 370
11.2.1 Pinoresinol Synthase (Dirigent Protein) 370
11.2.2 The General Biosynthetic Pathway of Lignans 371
11.2.3 Other Biosynthetic Pathways of Lignans 372
11.2.4 Biosynthetic Pathways for Neolignans 377
11.2.5 Biosynthetic Pathways for Norlignans 377
11.3 Metabolism of Lignans 377
11.4 Plant Physiology and Plant Defense 383
11.5 Podophyllotoxin 386
11.5.1 Extraction, Synthesis, and Biotechnological Approaches 388
11.5.2 Biological Activities of PPT 389
11.5.3 The Action Mechanism of PPT 392
11.5.4 Congeners and Derivatives (Other Aryltetralin Lactones) 393
11.6 Biological Activity of Different Lignan Structures 397
11.6.1 Dibenzylbutane Lignans 398
11.6.2 Dibenzylbutyrolactone Lignans 401
11.6.3 Dibenzylbutyrolactol Lignans 404
11.6.4 Furanoid Lignans 404
11.6.5 Furofuranoid Lignans 407

11.6.6 Aryltetralin Lignans (No Lactones) 411
11.6.7 Arylnaphthalene Lignans 413
11.6.8 Dibenzocyclooctadiene Lignans 418
11.6.9 Neolignans 422
11.6.10 Hybrid Lignans 423
References 423

Part VI Outcome and Challenges **455**

12. Summary, Conclusions, and Perspectives on Lignin Chemistry **457**
12.1 Sources of Lignin 457
12.2 Structure of Lignin 458
12.3 Biosynthesis and Biological Function 459
12.4 Applications of Lignin 459
12.5 Lignans 461
12.6 Perspectives 462
References 462

Glossary **465**

Index **467**

Series Preface

Renewable resources and their modification are involved in a multitude of important processes with a major influence on our everyday lives. Applications can be found in the energy sector, chemistry, pharmacy, the textile industry, paints and coatings, to name but a few fields.

The broad area of renewable resources connects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry …), but it is very difficult to take an expert view on their complicated interactions. Therefore, the idea to create a series of scientific books, focussing on specific topics concerning renewable resources, has been very opportune and can help to clarify some of the underlying connections in this area.

In a very fast-changing world, trends do not only occur in fashion and politics, hype and buzzwords occur in science too. The use of renewable resources is more important nowadays, however, it is not hype. Lively discussions among scientists continue about how long we will be able to use fossil fuels, opinions ranging from 50 years to 500 years, but they do agree that the reserve is limited and that it is essential to search not only for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives to fossil-based raw materials and energy. In the field of the energy supply, biomass and renewable-based resources will be part of the solution alongside other alternatives such as solar energy, wind energy, hydraulic power, hydrogen technology and nuclear energy.

In the field of material sciences, the impact of renewable resources will probably be even bigger. Integral utilisation of crops and the use of waste streams in certain industries will grow in importance leading to a more sustainable way of producing materials.

Although our society was much more (almost exclusively) based on renewable resources centuries ago, this disappeared in the Western world in the nineteenth century. Now it is time to focus again on this field of research. However, it should not mean a *retour à la nature*, but it does require a multidisciplinary effort at a highly technological level to perform research on new opportunities, to develop new crops and products from renewable resources. This will be essential to guarantee a level of comfort for a growing number of people living on our planet. The challenge for coming generations of scientists is to develop more sustainable ways to create prosperity and to fight poverty and hunger in the world. A global approach is certainly favoured.

This challenge can only be met if scientists are attracted to this area and are recognized for their efforts in this interdisciplinary field. It is therefore also essential that consumers recognize the fate of renewable resources in a number of products.

Furthermore, scientists do need to communicate and discuss the relevance of their work so that the use and modification of renewable resources may not follow the path of the genetic engineering concept in terms of consumer acceptance in Europe. In this respect, the series will certainly help to increase the visibility of the importance of renewable resources.

Being convinced of the value of the renewables approach for the industrial world, as well as for developing countries, I was myself delighted to collaborate on this series of books focussing on different aspects of renewable resources. I hope that readers become aware of the complexity, interactions and interconnections, and challenges of this field and that they will help to communicate the importance of renewable resources.

I would like to thank the staff from Wiley's Chichester office, especially David Hughes, Jenny Cossham and Lyn Roberts, in seeing the need for such a series of books on renewable resources, for initiating and supporting it and for helping to carry the project to the end.

Last, but not least I want to thank my family, especially my wife Hilde and children Paulien and Pieter-Jan for their patience and for giving me the time to work on the series when other activities seemed to be more inviting.

Christian V. Stevens, Faculty of Bioscience Engineering
Ghent University, Belgium
Series Editor "Renewable Resources"
June 2005

Preface

This book has grown from a mini-review on lignin that we had published in 2010, by invitation from Sarah Higginbotham (nee Hall) at John Wiley & Sons Publishing Group. From the very outset, it was clear to us that tackling the project as authors of a complete work was the most challenging but nevertheless the most robust way of addressing the issue. Conceiving a whole book appeared to be more complete than the common compilation books where the monograph results from the contribution of various authors coordinated by an editor. In our opinion, although these compilation-type books often result in a series of very specific chapters that provide a collection of review articles of high scientific level, they usually lack a strength thread to unify the entire work.

The specific case of lignin is particularly challenging due to the enormous amount of information available, the abundance of undefined concepts, and the diverse areas of knowledge involved in the topic. Native lignin is studied by botanists for its role in plants and plant cells, by biochemists regarding biosynthesis, by chemists concerned with its structure, and even by engineers dealing with lignin coming from paper mill or biorefineries.

A similar situation involves lignans, where these secondary plant metabolites are studied also by botanists, chemists, and even by professionals in biomedical sciences for the biological properties of these molecules in living organisms. A fairly complete description of the nature, structure, properties, synthetic processes, and applications of this family of compounds is provided.

Given such a complex and multidisciplinary outlook, a thorough review was needed of the existing literature, together with classical references, the brainchild of pioneering authors, as well as recent contributions to the topic in order to provide the reader with a broad view of the most comprehensive knowledge on lignin and lignans. As is inevitable with projects of this scope, the final work might not be as complete as it could have been, but we nevertheless trust that the result is thorough enough to be useful to the scientific community interested in the subject.

Throughout the text, lignin is explained from different perspectives, including its role as a structural component of plants, and how it is produced as a by-product of paper industry and a product of biorefineries. Structural models of this biopolymer are disclosed, as well as the developing process that these models have undergone through the years, parallel to the improvement of structural determination methods, both instrumental and chemical ones. This information will provide the reader with an overall idea of the structure of lignin, its origin, its function, its applications, and its potential. The reader will also learn how to appropriately use the term “lignin,” as the actual lignin depends on the origin of this material.

During the preparation of the book, special effort was made to review the applications and the potential uses of different lignins, with emphasis on the word “potential.” So far, there has been ample academic work on the subject, but the actual results are still relatively modest. Therefore, many topics remain to be developed in the coming years, and they definitely will be, considering the growing importance of renewable raw materials in taking over those of limited availability.

Given our input on lignin, and our experience as authors of the present work, we conclude that this is a highly promising biomaterial, which, in terms of science and technology, still presents many unresolved issues that continue to be investigated. In the literature, terms such as “potential” and "promising" constantly appear, alongside "difficult," "complex," and "underutilized." These modifiers reflect lignin's state of the art. In the coming years, great effort must be needed to ensure lignin the central role as source of raw materials, consumer goods, and much more relevant applications that it deserves. We deeply hope that this book will stimulate further interest and research in this promising biopolymer in its various forms.

Finally, we repeat our appreciation to John Wiley & Sons Publishing Group and its staff for their incalculable help, support, and feedback over the course of the project. Last but not least, we would like to give our special thanks to Dr Ángel Sánchez-González for the design of the front cover, and Mr David Nesbitt for his invaluable work on the revision of the English version of the manuscript and his contribution with the "*Podophyllum peltatum*" illustration.

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List of Acronyms

2D	two dimensional
3D	three dimensional
4CL	4-coumarate CoA ligase
Ac-CW	acetylated cell wall
ADF	acid detergent fiber
AFEX	ammonia fiber explosion
AOAC	Association of Analytical Communities (formerly Association of Official Agricultural Chemists)
AOP	advanced oxidation process
ARP	ammonia recycle percolation
ASAM	alkaline sulfite, anthraquinone, methanol
ASL	alkali sulfite lignin
BADGE	bisphenol A diglycidyl ether
BTX	benzene, toluene, and xylene
C4H	cinnamate 4-hydroxylase
CAGT	coniferyl alcohol glucosyltransferase
CBG	coniferin-β-glucosidase
CD	circular dichroism
CEHPL	chain-extended hydroxypropyl lignin
CEL	cellulolytic enzyme lignin
CK	cytokinins
DAD	photodiode array detector
DAHP	3-deoxy-D-arabinose heptulosonic acid-7-phosphate
DBDO	dibenzodioxocin
DCC	*N*,*N′*-Dicyclohexylcarbodiimide
DCCC	droplet counter-current chromatography
DCG	dehydrodiconiferyl alcohol-4-β-D-glucoside
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DFRC	derivatization followed by reductive cleavage
DHP	dehydrogenation polymer
DIR	dirigent protein
DMAc	*N,N*-dimethylacetamide
DMF	dimethylformamide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DPPH	1,1-diphenyl-2-picrylhydrazyl
EDXA	energy-dispersive X-ray analysis
EMAL	enzymatic mild acidolysis lignin
END	enterodiol
ENL	enterolactone
EPSP	5-enolpyruvylshikimate-3-phosphate

ESR	electron spin resonance
FDA	Food and Drug Administration
FTIR	Fourier transform infrared
G	coniferyl alcohol
GC-MS	gas chromatography-mass spectrometry
GC	gas chromatography
GHG	greenhouse gas
GPC	gel permeation chromatography
H	*p*-coumaryl alcohol
HBS	high-boiling solvents
HDO	hydrodeoxygenation
HDPE	high-density polyethylene
HMR	7-hydroxymatairesinol
HMTA	hexamethylenetetramine
HPA	Heteropoly acids (e.g., $H_3PWO_{12}O_{40}$)
HPL	hydroxypropyl lignin
HPLC	high-performance liquid chromatography
HPSEC	high-pressure size exclusion chromatography
HPSECI	high-pressure size exclusion chromatography infrared
HRMS	high-resolution mass spectrometry
HRP	hydroxyproline-rich protein
HSCCC	high-speed counter-current chromatography
IAT	indulin AT
IM	interference microscopy
IOR	improved oil recovery
IPTES	3-(triethoxysilyl)propylisocyanate
IR	infrared
KL	Klason lignin
LALLS	laser light scattering
LBS	low-boiling solvents
LC-NMR	liquid chromatography-nuclear magnetic resonance
LDPE	low-density polyethylene
LEM	*Lentinus edodes* mycelia
LPF	lignin-modified phenolic resin
LPS	lignin process system
LSA	lignin sulfonic acid, lignosulfonic acid
MAE	microwave-assisted extraction
MDF	medium-density fiberboards
MDI	methylene diphenyl isocyanate
MEKC	micellar electrokinetic capillary chromatography
MOF	metal-organic framework
MPP	mesophase pitch
MSn	multiple-stage mass spectrometry
MWL	milled wood lignin
NADH	nicotinamide adenine dinucleotide
NDGA	nordihydroguaiaretic acid
NE	nucleus exchange
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
NP	nanoparticle

OSB	oriented strand boards
PA66	polyamide 66
PAL	L-Phenylalanine ammonia lyase
PAN	polyacrylonitrile
PE	polyethylene
PEG	polyethylene glycol
PF	phenol formaldehyde
PLCG1	phospholipase C γ1
PLPW	pressurized low-polarity water
PLR	pinoresinol/lariciresinol reductases
PNNL	Pacific Northwest National Laboratory
POM	polyoxometalate
PP	polypropylene
PPG	polypropylene glycol
PPT	podophyllotoxin
PS	polystyrene
PTSA	*p*-toluenesulfonic acid
PU	polyurethane
PVC	polyvinyl chloride
RP	reverse phase
S	sinapyl alcohol
SAA	soaking in aqueous ammonia
SAR	structure–activity relationship
SDG	secoisolariciresinol diglucoside
SEC	size exclusion chromatography
SECO	secoisolariciresinol
SEL	swelled enzyme lignin
SEM	scanning electron microscopy
SHS	switchable hydrophilicity solvent
SIRD	secoisolariciresinol dehydrogenase
TAL	tyrosine ammonia lyase
TAPPI	Technical Association of the Pulp and Paper Industry
TDMP	2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane
TEM	transmission electron microscopy
THF	tetrahydrofuran
TLC	thin-layer chromatography
TOC	total organic carbon
TPA	tonns per annum
TTFA	thallium(III) trifluoroacetate
UDP	uridine diphosphate
UV/Vis	ultraviolet/visible
VCD	vibrational circular dichroism
VPO	vapor pressure osmometry
WG	water-dispersible granules

List of Symbols

δ	NMR chemical shift
$\mathit{Đ}$	dispersity index
ED_{50}	median effective dose
g	contraction factor
IC_{50}	half maximal inhibitory concentration
M_n	average molecular weight
M_w	molecular weight
λ_{max}	The wavelength at which the largest amount of absorption occurs
Log P	partition coefficient
pH	acidity or basicity of an aqueous solution
ppm	parts *per* million
ppu	parts *per* unit
T_g	temperature range of glass transition
rt	room temperature

Part I

Introduction

1

Background and Overview

1.1 Introduction

Surviving on a small planet with limited resources to support our increasing global population is probably the greatest challenge humanity has faced so far. A large part of the problem is that our economy is driven by many technologies that are not sustainable at all. This necessity of developing sustainable technologies capable of addressing such challenges, together with the increasing concern over environmental protection and questions about future availability of petrochemical feedstock have spurred research and development toward new degradable materials from renewable resources, which are more environmentally friendly and sustainable than the currently used petroleum-based materials. Within this context, lignin, which appears as one of the polymeric components in plants, arises as a promising candidate for some of the desirable applications due to its rich chemical structure and its versatility.

For more than 100 years, scientists and engineers have made efforts to effectively remove lignin from wood when extracting cellulose in the pulping process.[1]

In 1819, the term "lignin," from the Latin word *lignum* meaning "wood" [1], was used for the first time by the Swiss botanist A. P. Candolle (1778–1841). Later, in 1839, A. Payen first described this "encrusting material" in wood. It took, however, about 20 years to accept the term "lignin" to refer to a material as it is currently understood [2].

An understanding of its chemical composition began in 1875, when Bente [3] demonstrated that the noncellulosic constituent of wood, namely lignin, was aromatic in nature. It was further characterized by Benedikt and Bamberger [4] in 1890, who described the methoxy group as typical of lignin chemical structure. Later in 1960, Brauns [5] stated: '*the lignin building stone has a phenyl propane structure that may be regarded as proven, but how the stones are linked together in proto-lignin is still a mystery*'. In addition, in 1920, Klason [6] postulated that lignin was an oxidation product of coniferyl alcohol, which was demonstrated in 1968 by Freudenberg [7].

[1] Lignocellulosic fibrous material prepared by chemically or mechanically separating cellulose fibers from wood, fiber crops, or waste paper.

Lignin and Lignans as Renewable Raw Materials: Chemistry, Technology and Applications, First Edition.
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Table 1.1 The most common plant phenolic compounds listed according to the count (content) of carbon atoms[a]

Composition	Count of carbons	Types of phenolic substances
C_6	6	Simple phenols, benzoquinones
C_6-C_1	7	Phenolic acids/aldehydes
C_6-C_2	8	Acetophenones, benzofurans
C_6-C_3	9	Phenylpropanoids, benzopyranes (coumarins)
C_6-C_4	10	Naphthoquinones
C_6-C_5	11	Ageratochromenes (prekocens)
$(C_6)_2$	12	Dibenzofurans, dibenzoquinones, biphenyls
$C_6-C_1-C_6$	13	Dibenzopyranes, benzophenones, xanthones
$C_6-C_2-C_6$	14	Stilbenes, anthraquinones, phenanthrenes
$C_6-C_3-C_6$	15	Flavonoids, isoflavones, chalcones, aurones
$C_6-C_4-C_6$	16	Norlignans (diphenylbutadienes)
$C_6-C_5-C_6$	17	Norlignans (conioids)
$(C_6-C_3)_2$	18	Lignans, neolignans
$(C_6-C_3-C_6)_2$	30	Biflavonoids
$(C_6-C_3-C_6)_n$	n	Condensed tannins (flavolans)
$(C_6-C_3)_n$	n	Lignins
$(C_6)_n$	n	Catecholmelanines

[a]Adapted from refs [10–12].

Beyond this historical perspective on early years of lignin research, the rising interest on lignin today has made this natural polymer to go from a waste-side product to a promising source for chemicals, polymers, and many other applications. Lignin is the second most abundant natural polymer together with cellulose, and hemicellulose [8], which are the major sources of nonfossil carbon that make a special contribution to the carbon cycle [9]. Lignin is by far the most abundant substance composed of aromatic moieties in nature (see Table 1.1), and the largest contributor to soil organic matter.

Furthermore, lignin is an important component of secondary cell walls in plant cells, and it helps to maintain the integrity of the cellulose/hemicelluloses/pectin matrix that provides rigidity to the plant. Also, it provides internal transport of nutrients and water, and protects against attack by microorganisms. Apart from this key role in plants, lignin is also obtained from paper industry and other methods. Actually, the many different sources and types of lignin makes it more accurate to refer generically to “lignins” when referring to this multifaceted material. Its diversity also implies that interest in lignin arises from fields of knowledge as diverse as botany, chemistry, chemical engineering, economy, ecology, and so on. Therefore, a general vision about lignin should come from a multidisciplinary approach.

From an ecological viewpoint, lignins are of general significance to the global carbon cycle, since they represent an enormous reservoir of bound organic carbon. However, despite this potential, lignins are a fairly unused renewable raw material that is now gaining the attention of industry, which will make them materials of immense economical importance [13].

1.2 Lignin: Economical Aspects and Sustainability

One-third of the world’s land surface is covered by forest, accounting for 3×10^5 million m^3 of timber, of which some $2.6 \times 10^9 m^3$ are harvested annually. Just for comparison, such a vast amount is twice