Index

a

accessory enzymes, for lignin oxidation
  bacterial accessory enzymes 209–210
  fungal accessory enzymes 209
acetosyringone 97, 115, 256, 312, 314, 316
acidic lithium bromide trihydrate (ALBTH) system 172–174
acidolysis 16, 92, 93
acid-precipitable lignin (APPL) 207
acid treatment 170, 172–173
aerosol evaporation 370, 373, 387
alkaline oxidation 238–241, 242, 247, 248, 385
alkoxy radical intermediate 280–283
ammonia fiber expansion (AFEX) 167, 168
ammonium dihydrogen phosphate (ADHP) 408
anode materials, lignin-derived 417–420
aromatic alcohol oxidases (AAO) 209
aryl ether linking motifs 140
asymmetric flow field-flow fractionation (AF4) 63, 68–70, 72
atom transfer radical polymerization (ATRP) 347–350, 442, 445, 447, 449
azobisisobutyronitrile (AIBN) initiation 448

b

bacterial accessory enzymes 209–210
bacterial dye-decolorizing peroxidases 205–206
beta-etherase enzymes, for lignin ether cleavage 207, 208
bio-based composite hydrogels 440
biofuel production 45, 188
biomass composition 184
biomimetic catalysts 100–102
biomimetic oxidation 250–251
biorefinery lignin 17, 328, 344
blocked phenolic substrates 103
Bobbitt's salt 237, 238
Brauns' lignin 143, 144
Bruker standard pulse sequence 26
butylated hydroxytoluene (BHT) 310, 377

c

Cannizzaro rearrangement 297
carbazolic copolymers (CzCPs) 272
carbon electrode material characteristics 409
carbon fibers, lignin-based 403–409
carbonization temperature 403, 409, 420
carbon materials
  batteries 416–420
  lignin-derived 402–403

Lignin Chemistry: Characterization, Isolation, and Valorization, First Edition.
Edited by Yuhe Liao and Bert F. Sels.

carbon materials (*contd.*)
lignin-derived activated 412–413
lignin-derived free standing 415–416
sensing 420–422
supercapacitors 409, 412
synthesis routes of 402
template-assisted porous 414–415
thermoelectric devices 422–424
catalyst-free pyrolysis 113
catalytic chemical oxidative degradation
biomimetic catalysts 100–102
metal-free oxidations 96–97
organometallic catalysts 97–101
catalytic chemical reductive degradation
heterogenic transition metal catalysts 107–109
metal-free reductions 107
organometallic catalysts 108
catalytic pyrolysis 113–115
cellobiose dehydrogenase 209
cellulolytic enzyme lignin (CEL) 145–146
cellulose/lignin composite hydrogel 442
chemical shift value, ^{13}C-NMR spectrum of non-acetylated lignin 22
cis,cis-muconic acid/adipic acid 219–220
^{13}C NMR spectroscopy 20
quantitative (*see* quantitative ^{13}C-NMR)
sample preparation and program 21
cobalt-based catalysts 244–246
cobalt–cobalt-based electrodes 310–311
cobalt/manganese catalysts 249–250
cobalt salen ([Co(salen)]) complexes 97
concentration sensitive detectors 69–70
condensed lignin 232
copper catalysts 248
Corynebacterium glutamicum 216, 220
crosslinking, hydrogels 443

d

deep eutectic solvents (DESs) 64, 93, 154, 169–171, 312
densitometry 63
derivatization followed by reductive cleavage (DFRC) 94, 95
dibenzodioxocin 140
direct electrochemical oxidations 252–254
direct photocatalytic cleavage of Cβ–O bond
through β-O-4 ketone intermdiate 273–275
through Cα intermediate 275–277
dispersity, in functionality 74–75
dissolution 51
of lignin samples 64–65
solutions preparation 44
system 40–41
double-enzymatic lignin (DEL), 2D-HSQC spectra of 31, 33
drug delivery application 453–455
dye-decolorizing (DyP) peroxidases 205–206
dye elimination 448, 450–451
DyP-type peroxidases 205

e

electric double-layer capacitors (EDLCs) 409
electrocatalysts, for lignin depolymerization. *see* lignin depolymerization
electrocatalytic conversion
Faradaic efficiency 299–300
reaction mechanism 297–299
electrocatalytic valorization
acetosyringone 316
guaiacol 315–316
syringaldehyde 315
trans-ferulic acid 316
vanillin 315
electrochemical lignin degradation 115–116
electrochemical membrane reactor (ECMR) 311
electrochemical oxidation 233, 252–257, 297, 307, 313
electrochemical sensors 421–422
electrostatic/ionic interactions 437
enzymatic mild acidolysis lignin (EMAL) 146–148
enzymatic oxidative degradation

enzymatic lignin degradation 106–107
laccase-mediated oxidative depolymerization 103–105
peroxidase-mediated oxidative depolymerization 105–106
enzymes immobilization 106
epichlorohydrin (ECH) 334, 335, 415, 443
epoxy resins
direct epoxidation of technical or fractionated lignins 335
lignin-first/RCF processing 336–337
modification of technical lignins 335
reactive blending with 334–335
1-ethyl-3-methylimidazolium acesulfamate 169

f

Faradaic efficiency (FE) 299–300
Fenton reagent 251
flavin-adenine-dinucleotide (FAD)-containing enzymes 209
^{19}F NMR spectroscopy 45–46
Fourier-transform infrared spectroscopy 90
free radical polymerization 379, 383, 443, 445
functional group analysis 72
dispersity in 74–75
heterogeneity in 73–74
fungal accessory enzymes 209

g

γ-valerolactone (GVL) 167, 169
gasification, of lignin 108, 110, 194–197
gel permeation chromatography (GPC) 91, 92
generally regarded as safe (GRAS) microorganism 215
glyoxal oxidase 209
gold catalysts 249
grafting from approach 342, 347
grafting onto approach 342, 351
grafting to approach 342
gramineous lignin 28–32, 39
graphite anode 255
guaiacol 93, 114, 115, 208, 220, 246, 249, 254, 303–307, 311, 312, 314–316
guaiacyl/syringyl (G/S) ratio 23

h

hard carbon 416, 417
preparation process 418
hard carbon microspheres (HCM) 419
hardwood kraft lignin permeate (HKLP) 407
hardwood lignin 27, 31–37, 42, 87, 99, 107, 113, 405
heavy metal
contamination 451
decontamination, lignin-based hydrogels for 453
heterogeneity, in functionality 73–74
heterogenic transition metal catalysts 107–109
^{1}H NMR spectra
acetylated lignin
sample preparation 18
spectra analysis 19–20
^{1}H program 18
non-acetylated lignin
sample preparation 17
spectra analysis 18–19
H_2O_2-assisted approach 313–314
hydrodeoxygenation (HDO) 107, 114
hydrogels
in agriculture for watering plants and fertilizer 457, 458
atom transfer radical polymerization 445, 447
chemical crosslinking 444
classifications 434–436
crosslinking 443
for energy storage applications 457, 459, 460
free radical polymerization 443, 445
mechanisms of 435–436
networks 440–442
preparation 439–442
RAFT polymerization 447–448
hydrogen bond acceptors (HBAs) 169
hydrogen bond donors (HBDs) 169

hydrogen coproduction approach 314
hydrophobic interaction chromatography (HIC) 75–77
hydrosilanes 107
hydrothermal pretreatment (HTP) 165–166
1-hydroxybenzotriazole (HBT) 103, 206, 251

i

indirect electrooxidation 252, 254–256
industrial pulping 62, 73
in situ tracing method 308
interpenetrating network (IPN) 439
interpenetrating polymer network 440, 445
inverse-gated (IG) decoupling sequence 21
ionic liquids (ILs) 154, 167, 169, 170, 252, 311, 312
iridium (Ir)-based anodes 309

k

Keggin-type polyoxometalates 99
kraft lignin 71, 87, 89, 92, 99, 116, 169, 174, 208, 219, 220, 234, 237, 238, 240, 244–248, 249, 250, 253–255, 270, 309, 311, 312, 315, 316, 327, 330–332, 334, 335, 339, 346, 347, 352, 354, 373, 405

l

laccase-mediated oxidative depolymerization 103–105
laccase-mediator system (LMS) 105, 106, 313
lead/lead oxide based anodes 309–310
light stimuli carbon quantum dots, for sensing applications 420
lignification 6, 37
lignin
  bioengineering 8–10
  building blocks 3–6
  carbon fibers properties 410, 411
  characteristics 376
  characterization 186–188
  chemical structure 185–186
  composition 185–186
  interlinkages 6–8
  nanospheres and nanorods 372
  oxidation via electrochemical combination reactions 256–257
  pretreatment 300–302
lignin analysis
  dissolution 64–65
  functional group analysis 72–75
  molar mass 65–72
  sample history 62
  sample purity 62
  two-dimensional liquid chromatography 76–77
lignin-carbohydrate-complex (LCC) 25, 63, 86, 140, 164, 301
lignin conversion
  biodegradative pretreatment 312
  deep eutectic solvent electrolytes assisted approach 311–312
  H_2O_2-assisted approach 313–314
  hydrogen coproduction approach 314
  ionic liquid 311–312
  mediator-assisted approach 313
  photo-assisted approach 312–313
lignin conversion by enzymes
  beta-etherase enzymes 207, 208
  dye-decolorizing (DyP) peroxidases 205–206
  extracellular peroxidases from white-rot fungi 203–205
  lignin conversion *in vitro* *210*–211
  multi-copper oxidases 206–207
  other lignin-oxidizing enzymes 208
lignin depolymerization 188, 189, 192–197
  cobalt–cobalt-based electrodes 310–311
  iridium (Ir)-based anode 309
  lead/lead oxide-based anode 309–310
  methods 301
  nickel–cobalt-based electrodes 310–311

lignin-derived model compounds 302–309
lignin fibers stabilization and carbonization 408–409
lignin isolation/production process 187–188, 190–192
lignin nanoparticles
  aerosol evaporation 373
  biologically active nanomaterials 386–387
  carrier systems for agriculture and biomedicine 381–382
  composites and applications 379, 380
  emulsifiers for Pickering emulsions 382–383
  gels, adhesives and coatings 379–381
  inherent properties of 373–375
  kinetic biodegradability of 375
  metal and inorganic nanoparticles 384, 385
  pH shifting 373
  polymer composites 379–381
  sensors 383, 384
  size control 375–376
  solvent exchange 370–372
  stabilized and solvent-resistant particles 378
  sunscreens 384–386
  versatile particle morphologies and tailored properties 376–378
lignin oxidation, accessory enzymes for. *see* accessory enzymes, for lignin oxidation
lignin valorization
  isolated lignin fractionation, for homogeneous starting materials 92–93
  purity of isolated lignins 91–92
  structural features in (isolated) lignins
    elucidation 89–91
    occurrence and isolation 86–89
lignocellulose 1, 148, 163, 221, 276
  lignin isolation methods from 164–174
  structure 2
lignocellulosic biomass 61, 163
lignol dimers
  oxidative approach 308–309
  reductive approach 306–307
lignolytic peroxidases 204
lignosulfonate 40, 43, 44, 63, 64, 66, 69, 75, 77, 87, 207, 238, 314, 315, 327, 331, 338, 354, 372, 373, 442
liquid-phase pyrolysis 115
localized surface plasmon resonance (LSPR) 279
lower critical solution temperature (LCST) 437

m

maleic acid hydro fractionation (MAHF) 172
mediator-assisted approach 313
melt spinning 404
  of lignin 405–406
  of lignin-polymer blends 406–407
  precursors via solution 407–408
mesoporous graphitic carbon nitride (mpg-C3N4) 283
metal-free oxidations 96–97, 233, 235
metal-free oxidative depolymerization 233
metal-free reductions 107
metalloporphyrins 100, 102, 250
methyltrioxorhenium (MTO) 97–98, 243
microbial lignin bioconversion
  depolymerized lignin hydrolysates 216–222
  microbial hosts for 213–216
microbial lignin degradation pathways 211–214
microwave radiation 166
mild alcohol extraction 142–143
milled wood lignin (MWL) 19, 31, 113, 144–145
molar mass analysis 65
  asymmetric flow field-flow fractionation (AF4) 68–69
  detection systems 69–72
  size-exclusion chromatography (SEC) 66–68

molecular photocatalysts (MPC) 266
monolignol units 185
monomers
  oxidative approach 307–308
  reductive approach 302–306
multi-angle light scattering (MALS) 70–72
multi-copper oxidases 206–207, 211, 215

n

native-like lignin
  alternative resources and special lignins 155
  cellulolytic enzyme lignin 145–146
  dis/advantage of 142
  enzymatic mild acidolysis lignin 146–147
  evaluation 140, 141
  isolation under acidic condition 148–151
  isolation under alkaline condition 151–152
  isolation under flow-through extraction 152, 153
  isolation with alternative solvents 152–154
  mild alcohol extraction 142–143
  milled wood lignin 144–145
  residual enzyme lignin 147–148
N-hydroxyacetanilide (NHA) 103
nickel–cobalt-based electrodes 310–311
nitrobenzene oxidation (NBO) 95, 233, 257
NMR spectroscopy-based analysis methods 90
nuclear Overhauser effect (NOE) 21

o

oil-in-water (o/w) emulsions 382–383
online viscosity detector 69
organic oxidants 234–238
organometallic catalysts 97–101, 108, 109
organosolv lignin 87, 113, 208, 210, 247–249, 255, 270, 272, 277, 286, 288, 312, 327, 328, 335, 337, 338, 405, 406
organosolv process 164, 165, 188
orthogonal LC systems 76
oxidative approach
  lignol dimers 308–309
  monomers 307–308
oxidative catalytic fractionation (OCF) of wood 241–242
oxidative lignin degradations 94, 309
oxyalkylated lignins 331
ozone mediated depolymerization 234

p

palladium catalysts 249
para-toluenesulfuric acid (PTSA) 149–150
Pb/PbO_2 anode 256, 310
Pd/CeO_2 system 249
pentafluoropyridine (PFP) 46
peralkylation 96
permethylation 96
peroxidase-mediated oxidative depolymerization 105–106
phenol formaldehyde resins 337–339
phenolic hydroxyl groups 23, 40, 42, 167, 281, 282, 377, 379, 384, 385, 443
phenylcoumaran 140
photo-assisted approach 312–313
photocatalytic C–C bond cleavage
  alkoxy radical intermediate 280–283
  Cβ–H bond activation to Cβ radical intermediate 283–285
  single electron transfer to radical cation intermediate 285, 286
photocatalytic C–O bond cleavage
  C_{aryl}–O (β-O-4, 4-O-5) and Cα–O (α-O-4) 278–280
  direct 273–277
  stepwise approach 269–273
photocatalytic lignin conversion 266, 288
pH shifting 370, 373
Pickering emulsions 381–383
plasticization 406
p-nitrobenzaldehyde (NBA) 18
^{31}P NMR spectroscopy

applications of 45
dissolution system 40–41
internal standard 41
operation 43–45
phosphorylation reagent 41–42
program 42–43
polyhydroxyalkanoates 217
polyoxometalate ionic liquid (POM-IL) hybrid catalyst 99
polyoxometalates (POMs) 250
polyurethane (PU) 329–334
lignin thermoplastic 351–353
use of chemically modified technical lignins 331–333
use of depolymerized native lignin 333, 334
use of technical or fractionated lignins 330–331
porous carbon materials 403, 417, 419
P. putida KT2440 strain 215, 219
proton-coupled electron transfer (PCET) 282
p-Toluenesulfonic acid (*p*-TsOH) 170, 172
pulping process 2, 62, 65, 231, 232, 354, 405
pulsed electric field pyrolysis 115
pyridine dicarboxylic acids (PDCAs) 220–221
pyrolysis 93, 108, 110, 112, 117, 189, 193–194
advanced technologies 115
catalyst-free 113
catalytic 113–115
pyrolytic lignin degradation
advanced pyrolysis technologies 115
catalyst-free pyrolysis 113
catalytic pyrolysis 113–115
torrefaction 110–113
pyrone dicarboxylic acids 220–221

q

quantitative ^{13}C-NMR
of acetylated lignin 23
applications of 23–25
of non-acetylated lignin 21–23
quinone-methide intermediate 94

r

radical polymerization 86, 347–351, 433, 443
Raman spectroscopy 90, 409
Raney®-nickel cathode 303
reductive approach
lignol dimers 306–307
monomers 302–306
reductive catalytic fractionation (RCF) approach 241, 328, 330, 333, 334, 336–337, 347, 350
relative quantification strategy
aromatic ring as IS 27–28
without an internal standard (IS) 27
residual enzyme lignin (REL) 147–148, 155
reversed-phase chromatography (RPC) 75, 76
reversible addition-fragmentation chain transfer (RAFT) polymerization 447–449
rhenium-based catalysts 243–244
ring opening polymerization 343–347

s

Seebeck effect 422, 423
size-exclusion chromatography (SEC) 66–68, 70, 91, 92
soft templates 414
softwood kraft lignin permeate (SKLP) fibers 408
softwood lignin 27, 37, 71, 87, 107, 241, 403
solar light 265
solution-state 2D-HSQC NMR
of acetylated plant cell walls 47–48
of non-acetylated plant cell walls 48–50
solvent exchange 369–372
solvent-fractionated lignosulfonates 372
solvent fractionation 330, 331, 342, 344, 375, 381
solvent polarity shifting methods 370
spirodienone 25, 140
steam explosion (SE) 164, 166

stepwise approach
oxidation of Cα hydroxyl into Cα carbonyl 269–270
reductive cleavage of Cβ–O bond in β-O-4 ketone 270–273
strain and pressure sensors 421
substituted styrenes 221–222
supercapacitors 403, 457
applications 409, 412–416
supercritical-phase pyrolysis 115
syringaldehyde 94, 99, 115, 217, 239, 242, 246, 249, 254, 256, 310, 314, 315

t

technical lignins 62–64, 70–73, 85, 87, 91, 92, 100, 155, 231, 233, 275, 314, 328–335, 338–341, 347, 351, 354–356, 375, 376, 401
template-assisted porous carbon materials 414–415
thermal catalytic hydrogenation (TCH) 305
thermally induced lignin depolymerization
hydrotreating process 110
pyrolytic lignin degradation 110–115
thermochemical conversion
gasification 194–197
pyrolysis 193–194
thermoelectric devices 422–424
thermoplastics
graft copolymers and scope 342–343
polyurethanes 351–353
radical polymerization 347–351
ring opening polymerization 343–347
thermosets
epoxy resin 334–337
phenol formaldehyde resins 337–339
polyurethane 329–334
thermosetting, classes of 340
thermostabilization process 408
thioacidolysis 16, 92–95, 233
torrefaction of lignin 110–113
transesterification exchange reactions 339
trans-ferulic acid 256, 314, 316
transition metal catalysis 242
triacylglycerol lipids 219
triazabicyclodecene (TBD) 344
triethylammonium methanesulfonate (TMS) 93, 254
two-dimensional heteronuclear single quantum correlation (2D-HSQC) NMR technique
and ^{13}C combination method 28
delignification and pretreatment process 39
gramineous lignin 28–32
hardwood lignin 31–37
^{31}P NMR spectroscopy 40–45
sample preparation and program 26
semi-quantification of lignin 26–28
softwood lignin 37
structure characterization of native lignin 39
two-dimensional liquid chromatography 76–77

u

upper critical solution temperature (UCST) 437

v

vanadium-based catalysts 246–248
vanadium pyrophosphate 248
vanillin 6, 94, 99, 213, 216–218, 238, 241, 247–250, 254, 256, 309–315

w

wet-chemical degradation methods 93–96
white-rot fungi, extracellular peroxidases from 203–205
whole plant cell wall solution-state NMR
acetylated 47–48
advantages and disadvantages 49, 51
non-acetylated 48–50
wound dressing 387, 433
lignin-based hydrogel for 455–457
wound healing 455, 457