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Review

Recovery and Utilization of Lignin Monomers as Part of the Biorefinery Approach

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Abstract: Lignin is a substantial component of lignocellulosic biomass but is under-utilized relative to the cellulose and hemicellulose components. Historically, lignin has been burned as a source of process heat, but this heat is usually in excess of the process energy demands. Current models indicate that development of an economically competitive biorefinery system requires adding value to lignin beyond process heat. This addition of value, also known as lignin valorization, requires economically viable processes for separating the lignin from the other biomass components, depolymerizing the lignin into monomeric subunits, and then upgrading these monomers to a value-added product. The fact that lignin's biological role is to provide biomass with structural integrity means that this heteropolymer can be difficult to depolymerize. However, there are chemical and biological routes to upgrade lignin from its native form to compounds of industrial value. Here we review the historical background and current technology of (thermo) chemical depolymerization of lignin; the natural ability of microbial enzymes and pathways to utilize lignin, the current prospecting work to find novel microbial routes to lignin degradation, and some applications of these microbial enzymes and pathways; and the current chemical and biological technologies to upgrade lignin-derived monomers.

Keywords: valorization; depolymerization; laccase; aromatic; pyrolysis; organosolv

1. Introduction

Lignocellulosic biomass includes a wide variety of plant material, such as crops, agricultural residue, and wood. Humankind has utilized biomass throughout history to produce: heat for warmth and cooking; biochemicals, such as the ethanol and lactic acid produced by fermentation; and biofibers, such as those used in clothing and other textiles [1]. Present-day utilization of lignocellulosic biomass instead of petroleum in the production of chemicals and fibers could contribute to the improvement of environmental quality, national security, and rural economic development [1].

One component of lignocellulosic biomass, lignin, has long been viewed as a low-value or waste product in the wood pulping industry. The most common pulping process is the Kraft process, where lignin is dissolved in hot sodium hydroxide and sodium sulfide [2]. The top three pulping processes are the Kraft process, the sulfite process, and the soda lignin process. These three processes produce 60–100 Ktonnes of Kraft lignin, 1 Mtonne of lignosulfonates, and 5–10 Ktonnes of Sulfur-free soda lignin per year, respectively [3]. Typically, lignin is used as a fuel to fire pulping boilers [4]. However, the energy produced through lignin combustion is about sixty percent greater than the demand [5]. Traditionally, only 1%–2% of lignin was isolated from pulping liquors and used for specialty products,

such as dispersants or binders [6]. It follows that lignin has also been combusted as an energy source in the conversion of biomass to ethanol [7].

There is a vast collection of literature on lignin processing, including improving the recovery of lignin from biomass, depolymerization of lignin into monomers by chemical and/or biological means, and upgrading of the depolymerized lignin monomers to industrially relevant chemicals, which have been described in several other recent reviews (Figure 1) [2,5,8,9]. The purpose of this review is to summarize strategies from each of these processing steps and to briefly describe their economic relevance.

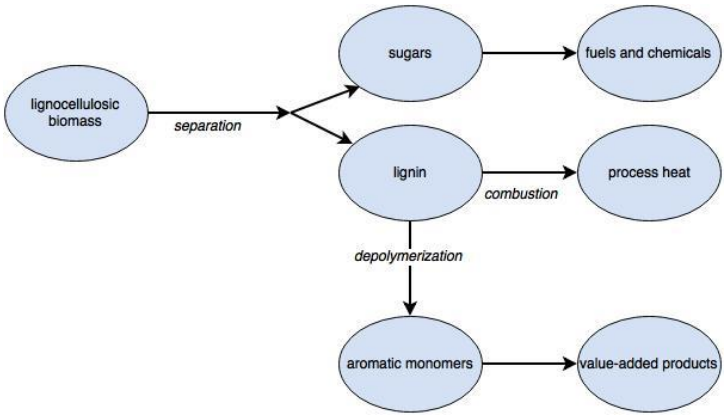

Figure 1. The lignin polymer can be processed via combustion, chemical processing, thermochemical processing, biological processing or a combination of these routes. This review covers chemical, thermochemical, and biological processing of depolymerized lignin to produce industrially relevant chemicals.

2. Lignin Structure and Abundance

Lignin is a stable aromatic heteropolymer that accounts for 10–35 *wt*% of lignocellulosic biomass [8]. Table 1 details the variation of lignin content in various lignocellulosic biomass types. Lignin is the second most abundant terrestrial polymer after cellulose, and it is the only large-volume renewable source of aromatics [10,11]. In nature, lignin functions as a matrix that holds the plant together and provides protection from environmental factors. The properties of lignin that benefit the plant are also the properties that make lignin difficult to access and convert to industrially relevant products. Although the structure and composition of lignin vary from plant to plant, during lignin production, the three primary lignin monomers coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol are subject to polymerization so that the resulting lignin polymer is comprised of three phenylpropanoid monomeric units guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) (Figure 2) [12,13].

Table 1. Lignin content in lignocellulosic crops.

Biomass Category	Biomass Type	Lignin Content (*wt*%)
Softwood	Pine	28 [14]
Hardwood	Poplar	21–27 [15]
	Eucalyptus	29–32 [16]
Herbaceous	Miscanthus	9–13 [17]
	Switchgrass	17–18 [18]
	Corn Stover	18 [19]
	Bagasse	20 [20]

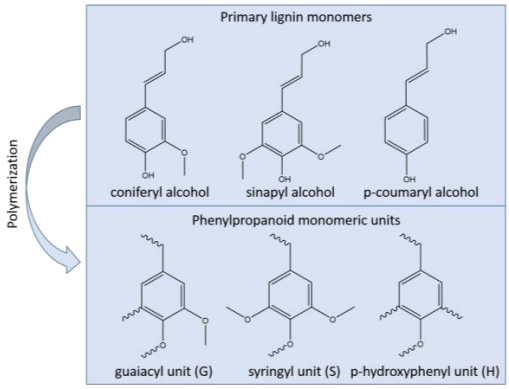

Figure 2. Primary lignin monomers are hydroxycinnamyl alcohols which are known as monolignols. These primary lignin monomers are polymerized. The corresponding phenylpropanoid monomeric units in the lignin polymer are guiacyl units (G), syringyl units (S), and p-hydroxyphenyl units (H), respectively, which can be polymerized at any of the wavy bond positions [12,13].

3. Challenges and Progress in Lignin Recovery

Lignin is recalcitrant and has a heterogeneous structure. In addition, the separation of lignin from biomass can be energy intensive and sometimes requires harsh chemicals. The lignin isolation methods in Table 2 use combinations of acid/base chemistry, high temperatures and pressures, solvents, and catalysts.

3.1. Pulping Processes

Kraft pulping is the dominant pulping process, with about 90% share of the total global production capacity, while less than 10% of pulp is produced by sulfite pulping and less than 5% by sulfur free alkali pulping [2,21]. In the Kraft process, cellulose is isolated from hemicellulose and lignin using sodium hydroxide and sodium sulfide. The heating value of the hemicellulose and lignin in the by-product liquor is high: 14–16 MJ/kg on a dry basis [22]. A chemical produced from the lignin in the black liquor needs to be of sufficient value to compensate for this loss of possible heat energy or only excess lignin should be diverted from process heat production [2].

Table 2. Non-biological lignin recovery methods.

Recovery Methods	Benefits	Challenges	Products
Kraft [23] and sulfite pulping [21]	Well-developed	Harsh chemicals	Cellulose, hemicellulose/lignin
Sulfur free alkali (soda) pulping [24]	Sulfur-free	Lower lignin removal rate	Solid polysaccharides, lignin-rich liquid
Organosolv pulping [25]	Sulfur-free	Has not been adapted to production scale	Varies by process, some organosolv processes can essentially isolate cellulose, hemicellulose, and lignin
Fast pyrolysis [26]	Fast	Undesired char formation	Solid (bio-char), Liquid (bio-oil), and gas
Dilute acid hydrolysis [27]	Highly advanced	Solid product is acid insoluble	Monomeric sugars, Biofine ligneous char (high heating value)
Hydrothermal Fractionation [28,29]	High product selectivity, produces monomeric products	Separation of hydrogen catalyst from the wood residue is challenging	Aromatic monomers, hydrolyzed hemicellulose
Biphasic fractionation [30]	Lower temperatures, near atmospheric pressure	Toxic solvents used in some cases	Hemicellulose degradation products (such as C_5 oligomers, furfural), Cellulose solid, and lignin fragments

Organosolv pulping uses low-boiling, organic solvents (typically sulfur free) for delignification. Commonly used solvents for organosolv are ethanol, methanol, organic acids, and mixed organic solvent–non organic alkali. Organosolv pulping is more environmentally benign than Kraft and sulfite pulping, and it allows for almost complete separation of cellulose, hemicellulose, and lignin. Research activities on organosolv biomass fractionation are increasing, but there is not a full-scale process to date [2].

3.2. Thermochemical Depolymerization of Biomass

Pyrolysis is the heating of biomass in the absence of oxygen. Fast pyrolysis converts biomass to a liquid (bio-oil), gas, and solid (char) product at moderately high temperatures (up to 500 °C). Up to 75% of the pyrolysis product is bio-oil, which contains compounds of similar structure to the original molecules [2]. However, there are a lower number of methoxyl groups on the pyrolytic lignin compared to the native milled wood lignin which is likely caused by demethoxylation of guaiacyl and syringyl moieties to form methanol [31]. The carbohydrate-derived compounds in the bio-oil have a higher affinity for water than the lignin-derived compounds. Therefore, separation of the lignin component can be done with water, controlled deposition, or solvent extraction [2,32–34]. Biomass pyrolysis also produces a solid, known as bio-char, that can be used as a soil amendment for carbon sequestration and to improve crop production [35,36].

3.3. Dilute Acid Hydrolysis

In the dilute acid hydrolysis process known as the Biofine process, shredded biomass is added to dilute sulfuric acid. Then the product is subject to two stages of dilute acid treatment at high temperatures to hydrolyze polysaccharides into their monomeric units. A solid called Biofine char is produced, which has a very high heating value of 26 MJ/kg and is mainly comprised of ligneous type components according to thermogravimetric-Fourier Transform infrared spectroscopy (TG-FTIR). The Biofine process is highly advanced in the processing of polysaccharides. The polysaccharides are converted into levulinic acid, formic acid, and furfural. However, the use of the Biofine char has limited applications because it is acid insoluble [2,27].

3.4. Hydrothermal Fractionation

Hydrothermal fractionation is the heating of wood in hot-compressed water (200 °C and moderate hydrogen pressure) in the presence of a hydrogenation catalyst [2,29]. The main products are the lignin-derived aromatic monomers propyl guaiacol, propyl syringol, guaiacyl propanol, syringyl propanol, and also hydrolyzed hemicellulose, which all remain in the aqueous phase. The advantage of hydrothermal fractionation is good product selectivity. However, it can be difficult to separate the hydrogenation catalyst from the wood residue [2].

3.5. Biphasic Fractionation

Biphasic fractionation can be used to separate the cellulose, hemicellulose, and lignin from each other. Solvents that have been applied to the organic phase include phenol [37–39], cresol [40], lignin-derived phenolic mixtures [41], polyethylene glycol [42–45], and 2-methyltetrahydrofuran [46]. The hemicellulose components can be extracted by the aqueous phase, the lignin components can be extracted by the organic phase, and the cellulose can precipitate as a solid. Although biphasic fractionation is advantageous because it can be carried out at lower temperatures and near atmospheric pressure, the toxicity of some of the solvents could pose a challenge [2].

3.6. Modeling of Lignin Isolation

There is no precise equation for the amount of lignin extracted relative to the "severity" of treatment [47]. In 1987, an equation for the severity was proposed that depended on two parameters:

temperature and time [48]. However, the equation was intended to estimate the impact of the treatment on the hemicellulose fraction of the biomass and not the lignin fraction, and there was no direct correlation between extracted lignin and the severity factor. In addition, the equation was not applicable for temperatures lower than 100 °C and it had limitations for catalyst usage. In 1990 and 2007, the severity factor was modified to reflect the effect of acid and base respectively on the severity factor, but the equation had to be modified by a factor of n depending on whether an acid or base was being used [49,50]. A recent study proposed an improved model that is universal for both acid and base treatments, and shows good correlation for one- and two-shot steam explosion, hot alkali macerations, and Kraft pulping with different types of biomass [47].

4. Lignin Utilization in Nature

In nature, lignin is utilized by specialized microorganisms encoding metabolic pathways that can break down components of lignin. Microorganisms that can break down lignin are able to use it as a carbon and energy source for metabolite production and have an advantage over biological organisms that can only utilize the cellulose and hemicellulose components of lignocellulosic biomass. Throughout this review, the phrases model lignin and lignin model compounds will be used. Researchers often use lignin model compounds when investigating what types of products can be produced using biological or chemical catalysis. Lignin model compounds have similarities to the lignin structure, such as common linkages or common structure seen in lignin. Zakzeski et al. categorize the most commonly researched lignin model compounds into β-O-4 linkage, carbon-carbon linkage, β-5 linkage, α-O-4 and 4-O-5 linkage, and *p*-coumaryl, coniferyl, and sinapyl alcohol [51].

4.1. Lignin Degrading Enzymes

Lignin degrading enzymes must have properties distinct from cellulose or hemicellulose degrading enzymes. Hydrolytic enzymes that can cleave other plant material cannot cleave lignin because of lignin's heterogeneous C-C and C-O linkages [52]. The enzymes responsible for the initiation of lignin polymerization in plants, low potential oxidoreductases, cannot oxidize the non-phenolic aromatic components of lignin [5]. However, some fungal and bacterial species do express enzymes that can break down the bulky and heterogeneous structures of lignin and/or convert smaller lignin-derived molecules into carbon and energy (Table 3) [53,54].

There are four major types of ligninolytic peroxidases: ligninolytic peroxidase (LiP), manganese-dependent peroxidase (MnP), versatile peroxidase (VP), and dye-decolorizing peroxidase (DyP) [5,55]. LiP, originally isolated from *Phanerochaete chrysosporium*, can oxidize molecules with high redox potential, including the moderately activated non-phenolic aromatics that can make up to 90% of the lignin polymer [5,56,57]. Unlike LiP, MnP cannot oxidize non-phenolics, and it is dependent on Mn^{2+} ions. However, MnP can oxidize phenolic model lignin compounds [5,58]. VP can oxidize both non-phenolic and phenolic compounds [5,59]. DyPs are the most recently discovered ligninolytic peroxidases. DyPs are unique because they can oxidize hydroxyl-free anthraquinone [55]. Many dyes are derived from anthraquinone, and therefore, it is present in dye-contaminated wastewater [55]. Anthraquinone is also used in the pulping process as a redox catalyst in papermaking [2]. White-rot fungi produce aryl-alcohol oxidase and glyoxal oxidase, and these oxidases produce hydrogen peroxide for the peroxidases [60,61].

Laccases are another class of enzymes contributing to the degradation of lignin. These copper-containing oxidases are found in bacteria and fungi, reduce molecular oxygen to water, and oxidize a large range of compounds including polyphenols, methoxy-substituted phenols, and diamines [62]. However, laccases are bulky and have non-phenolic sub-units that prohibit direct action on the lignin polymer. Instead, laccases have been shown to depolymerize lignin and lignin-derived molecules by action on smaller mediator molecules such as 2,2′-azino-bis(3-ethylbenzothiazoline)-6-sulphonic acid (ABTS) and hydroxybenzotriazole (HBT) [54,63,64].

Table 3. Major enzyme families involved in lignin degradation.

Enzyme	Function
Ligninolytic peroxidase (LiP)	Oxidizes molecules with high redox potential, including moderately activated non-phenolic aromatics (up to 90% of lignin polymer) [5,56,57]
Manganese-dependent peroxidase (MnP)	Oxidizes phenolic compounds [5,58]
Versatile peroxidase (VP)	Oxidizes both non-phenolic and phenolic compounds [5,59]
Dye-decolorizing peroxidase (DyP)	Oxidizes hydroxyl-free antraquinone and peroxidase substrates [55]
Lacasse	Oxidize aromatics and phenols, take action on smaller molecules in lignin such as ABTS and HBT in order to oxidize non-phenolic aromatics [54,62–64]

4.2. Bacterial and Fungal Pathways of Lignin Utilization

The bacteria Alpha-proteobacteria, gamma-proteobacteria, Firmicutes, and some actinomycetes have been shown to modify or degrade lignin. However, a bioinformatic analysis has shown a higher proportion of lignin-degrading genes in proteobacteria and actinobacteria than in Firmicutes [54,65]. The metabolic pathways for aromatic degradation depend on the microorganism and its environment, particularly its oxygen availability (Figure 3).

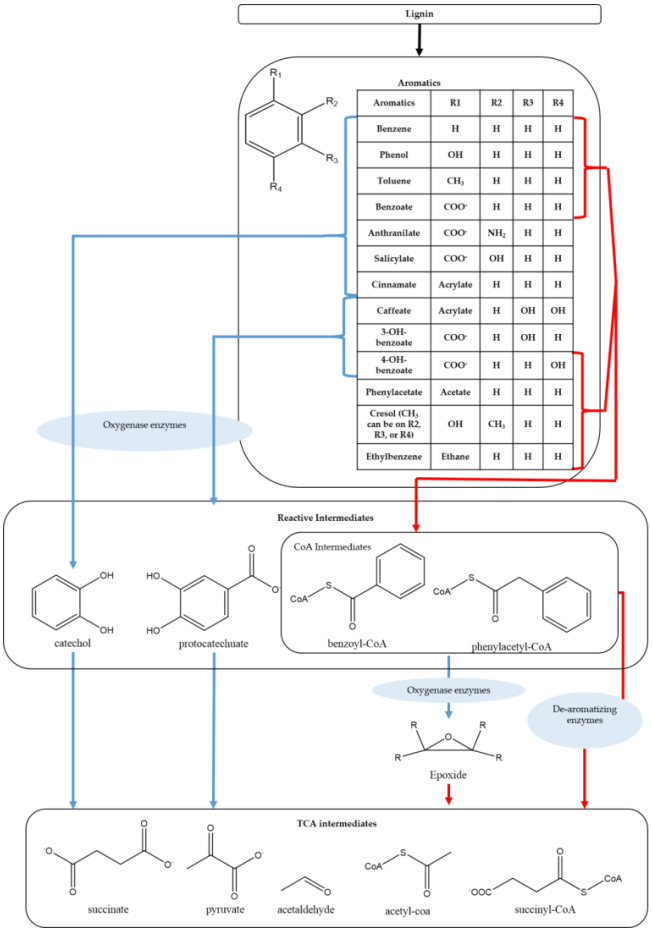

Figure 3. Aromatics can be degraded via aerobic routes (indicated by blue lines) or anaerobic routes (indicated by red lines). In the two far left routes, aromatics are converted to reactive intermediates and then converted to elements of the TCA cycle. In the third route, aromatics are first converted to reactive intermediates, then reactive intermediates are converted into non-aromatic epoxides. Next, the non-aromatic epoxides are converted to TCA cycle intermediates. In the far right route, aromatics are converted into reactive intermediates, then reduced, and finally converted into elements of the TCA cycle. This figure is an adaptation from Figure 2 in Fuchs et al. [9].

4.2.1. Aerobic Degradation

In aerobic degradation, aromatic compounds derived from lignin are normally attacked by oxygenases with the help of O_2 [9,66]. The aromatic compounds are funneled to a few key molecules known as central intermediates, which can then be more easily converted into elements of the tricarboxylic acid (TCA) cycle. Hydroxylated central intermediates such as catechol (1,2-dihydroxybenzene), protocatechuate (3,4-dihydroxybenzoate), and less frequently gentisate or homogentisate, are normally produced from aromatic monomers with the help of bacterial and fungal oxygenases [67–72]. The hydroxylated products are activated for oxidative ring cleavage because they have electron rich functional groups in ortho and para positions. The central intermediates are then converted by ring-cleaving enzymes [73–78].

The β-ketoadipate pathway is a classic example of oxygenation and ring-cleavage. Dioxygen aromatic cleavage can proceed in the ortho position between the two hydroxy groups or in the meta position adjacent to the two hydroxyl groups [9].

Another route to cleaving the aromatic ring, which may be an adaptation of low or fluctuating O_2 environments, is epoxidation of CoA thioesters. In this route, O_2 is used to form a non-aromatic epoxide. Then the ring is cleaved by hydrolysis and the molecule is converted to TCA cycle intermediates. The epoxidation route occurs in bacteria to degrade benzoate, phenylacetate, or compounds that can be broken into these two molecules. The epoxidation route requires monooxygenases in the class I di-iron protein pathway. In the case of benzoate and phenylacetate degradation, the monooxygenases act as epoxidases to catalyze ring epoxidation. The epoxidation of CoA thioesters to degrade benzoate and phenylacetate occur either as the only pathway or as an additional pathway in low oxygen conditions in about 5% and 16%, respectively, of all bacteria that have a sequenced genome [79–89].

4.2.2. Anaerobic Conditions

In anoxic conditions, O_2 can no longer be used as a co-substrate, and the aromatic ring must be reduced, which is a demanding reaction. Reduction of the aromatic ring requires agents with redox potentials that are much more negative than a physiological electron donor could provide. Therefore, the anaerobic pathways use central intermediates with substituents that have an electron withdrawing effect [9].

A common intermediate in the anaerobic breakdown of aromatic compounds is benzoyl-CoA, where the electron-withdrawing substituent is the carboxyl-thioester group. The benzoyl-CoA type molecules can then be reduced by ring-reducing enzymes [9,72,90,91].

Another group of intermediates in the anaerobic breakdown of aromatic compounds is those with two or more hydroxy groups in the meta position relative to each other. When the hydroxy groups are in the meta position relative to each other, they polarize the ring, which facilitates the reduction of the aromatic compound [9,92]. There have been two main anaerobic routes discovered that degrade aromatics. In the first anaerobic route, aromatic ring cleavage can occur via benzoyl-CoA reduction, driven by ATP hydrolysis and catalyzed by class I benzoyl-CoA reductases [9,93]. It is proposed that the ATP-independent class II benzoyl-CoA reductase recently discovered in *Geobacter metallireducens* and other similar systems could be used as an anaerobic ATP-independent route to aromatic degradation [9,94].

4.3. Application Directed Studies of Lignin Degrading Microorganisms

Specialized microorganisms that contain the enzymes and reaction pathways described above could be harnessed with the following applications in mind: microbial utilization of aromatic-containing waste streams and microbial production of industrially relevant fuels and chemicals from lignin-derived aromatic monomers. There is also an ongoing search for novel enzymes, pathways, and microorganisms, often isolated from unique environments that are suited for use in these applications.

Our knowledge of fungal lignin-degrading enzymes far exceeds our knowledge of bacterial lignin-degrading enzymes. However, fungal systems are typically difficult to manipulate and slow acting. There is a push for utilization of bacterial systems, which are simpler and faster. Tropical soils are depleted of oxygen, limiting fungal growth as well as the oxygen-dependent activities of traditional peroxidases. The unique tropical soil environment was hypothesized to harbor anaerobic lignin degrading bacteria. *Enterobacter lignolyticus* SCF1 was isolated by anaerobically culturing tropical forest soils on minimal media with lignin as the sole carbon source [95]. *E. lignolyticus* SCF1 degraded 56% (*wt*/vol) of the lignin in a lignin/xylose growth medium within 48 h. The *E. lignolyticus* SCF1 enzymes up-regulated in the presence of lignin included: catalase/peroxidase, DyP-type peroxidase, and two glutathione S-transferases (GSTs) [96,97]. As mentioned earlier, peroxidases are a key component of lignin degradation. However, it is still unclear exactly how peroxidases are involved in anaerobic lignin degradation. The presence of GSTs is evidence of a possible β-aryl ether cleavage mechanism in lignin degradation [97].

Several bacteria with aromatic degradation capability have been isolated from termite guts and woodboring beetles [54]. There is some debate on the extent that the microorganisms degrade lignin in vivo compared to the extent that microorganisms degrade lignin in vitro. One metagenomics study of hindgut microflora did not find any lignin degradation genes [98]. However, microflora from the same termite were able to degrade lignin in vitro [99]. In another study on the microflora from *Anoplophora glabripennis* and *Zootermopsis angusticollis*, lignin was depolymerized, demethylated, and ring-hydroxylated. The aerobic reactions required for lignin depolymerization observed in *A. glabripennis* and *Z. angusticollis* indicate that some of the lignin degradation occurs in the foregut rather than in the hindgut, which is mostly anaerobic [99,100].

In order to identify novel lignin degrading microorganisms, a fluorescent transcriptional reporter system was used as a biosensor [101]. This biosensor can respond to specific lignin degradation products such as vanillin, vanillic acid, and p-coumaric acid and was used to screen a DNA library prepared from metagenomes of coal beds. DNA fragments that were enriched were isolated, and the corresponding lignin transformation genes were identified. Recurring subsets of gene functions included: oxidoreductase activity, co-substrate generation (hydrogen peroxide generation), protein secretion, small molecule transport (multidrug efflux superfamily), motility (methyl-accepting chemotaxis proteins), and signal transduction [101]. Oxidoreductase activity, hydrogen peroxide generation, and protein secretion are associated with lignin degradation [54,102]. It was concluded that the small molecule transport systems had a role in regulating microbial responses when exposed to aromatic monomers. The cell motility was proposed to have a role in facilitating optimal positioning, which may be important in environments with microscale physicochemical gradients [101,103]. Signal transduction proteins could play a role in mediating lignin specificity in a microbial community [101].

A study of the structure and biochemistry of *Streptomyces* enzymes gave insight into unique laccase binding capability. SACTE_2871 is found in a *Streptomyces* species isolated from the Pinewood-boring wasp. SACTE_2871 can catalyze O_2-dependent ring opening of catechols. Catechols are often intermediates in the breakdown of lignin-derived molecules. SACTE_2871 can also directly bind to synthetic lignin polymers [5,104]. Similarly, small laccases found in *Streptomyces* species have been found to be able to bind directly to non-phenolic model lignin compounds and rearrange non-phenolic compounds with the help of mediators. The small laccases can also oxidize phenolic β-O-4 linkages [5,105].

Studying the utilization of lignin-derived compounds in nature can be important in tracking the global carbon cycle and monitoring the degradation of pollutants. For instance, the lignin biphenyl component can account for up to 10% of the lignin structure. The biological fate of the lignin biphenyl component is therefore linked with the degradation of lignin. Bacterial biphenyl degradation is well documented in a number of genera and has been reviewed elsewhere [54]. The pollutants benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, and 2-methylnaphthalene are all

aromatic in nature, have structural similarities to lignin-derived molecules, and can be degraded anaerobically [9,106].

The conversion or upgrading of lignin to a higher value molecule could contribute to a more cost-effective biomass processing scheme as discussed further in the economics section. Model lignin-derived compounds can converge via the downstream production of vanillin and vanillic acid before being converted to protocatechuic acid [7]. Extensive research on vanillin production via microorganisms, partially motivated by the global demands for vanillin (12,000 tons/year), has been reviewed elsewhere [107,108].

5. Challenges and Progress in Depolymerization of Isolated Lignin

Even when lignin is isolated, it often needs to be depolymerized into smaller molecules before it can be upgraded. There are five major methods of depolymerization (Table 4): pyrolysis of isolated lignin, catalytic hydrogenolysis, supercritical depolymerization, solvent depolymerization, and alkaline hydrolysis.

Table 4. Non-biological depolymerization methods for isolated lignin.

Recovery Methods	Benefits	Challenges	Products
Pyrolysis of isolated lignin [109–113]	Simple process	Selectivity for specific aromatic compounds is very low; char formation	Aromatic and non-aromatic molecules, char, and light gasses
Catalytic pyrolysis [114–118]	Products are less oxygenated and more stable	Coke deposits on catalysts	Aromatic hydrocarbon containing liquid, char, coke, light hydrocarbons, and oxygenate gasses
Supercritical water [119–123]	Lower concentration of lignin means lower chance of condensation reactions	High cost for process heat; only one-third of lignin product is low molecular weight	Aromatic hydrocarbon containing liquid, char
Supercritical solvent [124–130]	Products have a lower boiling point allowing for easier separation	Mid-high pressure High temperature	Primary product is monomeric substituted cyclohexyl derivatives, negligible aromatics, little to no char
Base-catalyzed depolymerization [12,131]	Oil contains low molecular weight species	Produces around 20% (*wt*/*wt*) desired oil product compared to the total weight of the products (oil, residual lignin, and coke)	Coke (undesired), oil (desired)

5.1. Pyrolysis of Isolated Lignin

Pyrolysis is a simple and fast process to depolymerize lignin. The bio-oils obtained from pyrolysis of isolated lignin are complex mixtures of hundreds of phenolic monomers and oligomers, with no specific compound making up more than 1% of the total product weight. It is known that the products of lignin pyrolysis differ by biomass type. Pyrolysis of hardwood lignin produces both syringol and guaiacol-type phenols, whereas pyrolysis of softwood lignin produces mostly guaiacol-type phenols. Pyrolysis of herbaceous lignin produces a mixture of syringol, guaiacol and phenol types of compounds [132,133]. An investigation of the thermal decomposition of lignin derived from both herbaceous (rice straw and rice husk) and woody (maple) biomass used TG-FTIR and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). There were three mass loss stages observed: the evaporation of water, the evolution of aromatic compounds, and the release of light gasses. It was found that more phenolic compounds, methanol, and methane evolved from maple lignin. Maple lignin was also the most thermally unstable because it formed phenolic compounds earlier than the herbaceous lignin. However, the formation of carbon dioxide was higher in herbaceous lignin than in maple lignin. Py-GC/MS analysis revealed that evolution of phenol-type and aromatic compounds increased with increased temperature due to more demethoxylation and dihydroxylation reactions [133]. Quantifiable phenolic monomers account for up to 17 *wt*% of the pyrolysis oil, [134]

depending on the lignin feedstock. The majority of the compounds in the lignin-derived bio-oil are phenolic oligomers. It has been shown that during pyrolysis of lignin derived from corn stover by organosolv treatment, phenolic monomers and dimers are mainly produced. However, the reactive monomers can rapidly repolymerize [135]. Isolated lignin contains an increased amount of C-C bonds, which is more resistant to thermal depolymerization. Coupled with free radical initiated repolymerization during pyrolysis, isolated lignin could produce over 40% char [136,137]. Approaches to reduce char formation could significantly enhance lignin volatilization.

5.2. Catalytic Pyrolysis of Isolated Lignin

The addition of a catalyst to the pyrolysis reactor can improve product selectivity [118]. For instance, the use of a solid acid catalyst, such as HZSM-5 zeolite, can convert the wide range of phenolic compounds to a smaller number of aromatic hydrocarbons, such as benzene, toluene, and xylene (BTX). Other types of catalysts, such as HY zeolite [138], Al-MCM-41, (CoO/MoO_3) and $Co/Mo/Al_2O_3$ [109,110] have also been tested for lignin pyrolysis. However, these catalysts are less efficient in deoxygenating lignin compared to HZSM-5. Challenges with catalytic pyrolysis of lignin include coke deposits on the catalyst [2,109–113] and low product yield.

In catalytic hydropyrolysis, external hydrogen can help to stabilize reactive free radicals formed during lignin depolymerization and promote hydrodeoxygenation. Hydrocracking also lowers char and coke yields [139]. Under high partial pressure H_2 and in the presence of Ru/C catalyst, Alcell organosolv lignin was converted into cycloalkanes, alky-substituted cyclohexanols, cyclohexanol and linear alkanes [140]. A wide range of supported catalysts, Ru (C, Al_2O_3, and TiO_2), Pd (C, and Al_2O_3), and a Cu/ZrO_2, were also screened for catalytic hydrotreatment of Alcell lignin. It was found that Ru/TiO_2 outperforms other catalysts, yielding a mixture of alkylphenols, aromatics, and catechols [141]. The complex oil mixture formed during catalytic hydropyrolysis is analogous to the bio-oil formed during pyrolysis. However, there is a lower oxygen content in catalytic hydropyrolysis oil, which makes it more stable than pyrolysis bio-oil [114,115]. Incorporating transitional metals into HZSM-5 was beneficial because the bifunctional catalyst has both deoxygenation and hydrogenation abilities. Pyrolysis of steam-explosion hybrid-poplar lignin using 1 *wt*% Pd/HZSM-5 at 1.7 MPa of H_2 produced 44% more aromatic hydrocarbons compared to HZSM-5 as the catalyst. Due to high partial pressure of hydrogen, saturation of the benzene ring occurred and cycloalkanes were found among the products [142].

5.3. Supercritical Water

In the supercritical and subcritical treatment of lignin, there is a lower concentration of lignin compared to catalytic hydropyrolysis of dry lignin, and therefore the probability of undesirable condensation reactions is lower. However, the process heat required for the production of supercritical water is high and the economic viability depends on process heat recovery. Alkali salts have been shown to improve oil production, however, the maximum theoretical yield of low molecular weight products is only one-third of the total lignin weight. The addition of phenol, butanol, and boric acid has been shown to help the depolymerization of lignin and to increase the selectivity of the desired oil product [119–123]. In the case of phenol, butanol, and boric acid addition, products will be biphenyl dimer structures, which can be used as a high boiling solvent. Alternatively, the dimers can be cracked into two aromatic monomers and be partially recycled into the process [2].

5.4. Supercritical Solvents

Supercritical solvents such as ethanol [124–127], methanol [128,129], CO_2/acetone/water [130], and butanol [122] have been used to dissolve isolated lignins at temperatures between 200 and 350 °C and high pressures. Mixtures of alcohols and water have also been utilized at milder pressures [127,143,144]. Lignin solvolysis can be categorized into either base-catalyzed depolymerization or hydrogenolysis. The hydrogen used for hydrogenolysis can come from a variety of

sources, such as external hydrogen supply, a proton donor such as tetralin [144] and formic acid added to the solvent [145,146], or partial reforming of the solvent in the presence of a metal catalyst [129]. When hydrogen donating solvents are used for depolymerization, the presence of a hydrogenation catalyst stabilizes lignin depolymerization products and therefore increases the yield of phenolic monomers. Conversion of birch wood lignin in alcohols (methanol, ethanol and ethylene glycol) using Ni-based catalyst resulted in a phenolic oil with the selectivity of propylguiacol and propylsyringol higher than 90% [147]. Cyclic hydrocarbons (primarily monomeric substituted cyclohexyl derivatives) can be formed from supercritical solvolysis. The lower boiling point of the cyclic hydrocarbons allows for separation and purification at lower temperatures, and the lower temperatures help to prevent repolymerization reactions known to happen at higher temperatures [2].

5.5. Base-Catalyzed Depolymerization

Lignins can be used to produce low molecular weight compounds when subjected to high temperature and pressure in the presence of a base in aqueous or organic solution. This process is known as base-catalyzed depolymerization [131]. A study of the base-catalyzed depolymerization of three different organosolv lignins (acetosolv, acetosolv/formosolv, and formosolv) showed that a higher yield of desired oil product was achieved from base-catalyzed depolymerization of acetosolv and acetosolv/formosolv lignins. Undesired coke production was low in the acetosolv lignin but higher when formosolv was included or used by itself, indicating that formic acid decreased the effectiveness of the catalyst. However, the formosolv oil contained higher amounts of phenolic monomers because the formosolv lignin had the lowest molecular weight. Base-catalyzed depolymerization produces only about 20% (*wt/wt*) oil when compared to the total product that contains repolymerized lignin fragments formed from condensation fragments and a coke by-product [12]. In order to improve the yield of phenolic monomers, boric acid and phenol capping agents were compared in base-catalyzed depolymerization of pruned olive tree branches. When phenol was used as a capping agent, the yields of the phenolic monomers were higher than with no capping agent or with a boric acid capping agent. Boric acid did prevent repolymerization, but the char production was higher compared to the phenolic capping [12].

6. Upgrading of Lignin Monomers

Depolymerized lignin monomers can be further upgraded into industrially relevant chemicals by biological or chemical processing. The chemical processing can be similar to lignin isolation and lignin depolymerization, and sometimes there are not clear distinctions between isolation, depolymerization, and upgrading (as discussed in Section 6.2).

6.1. Progress in Biological Utilization of Depolymerized Lignin Monomers and Lignin Model Compounds

There are two main approaches in the application of microbes to the upgrading of lignin. One approach is a biotransformation in which only a few catalytic steps are utilized from one target reactant to one target product. The other approach is to funnel a number of target reactants through the central metabolism of the microbe and tune the target product based off of industrial relevance. Chemicals produced from lignin-derived substrates or pure compounds known to be present in lignin are listed in Table 5.

Table 5. Biological lignin upgrading.

Molecule Class	Demonstrated Products
Phenolics	Vanillin [107]
Dicarboxylic acids	Muconic acid [148], Succinic acid [53]
Fatty acids	Fatty acid methyl esters (15–18) [149]
Polyhydroxyalkanoates (PHAs)	Short—medium chain length [149,150]
Alpha-hydroxy acids	Lactic acid [53]

6.1.1. Biotransformation

Vanillin can be produced by a number of specialized microorganisms from aromatic molecules such as eugenol [151–157], isoeugenol [157–168], ferulic acid [154,162,169–186], vanillic acid [172,174], and green coconut husk [187]. However, the low titers of vanillin and degradation of vanillin by the microorganisms are problematic [107].

6.1.2. Central Metabolism

Instead of looking at the capability of a microorganism to transform one lignin monomer into one product, microorganisms can be harnessed to utilize multiple substrates, addressing the challenge of the heterogeneous nature of lignin. This funneling strategy was demonstrated by microbial utilization of alkaline pretreated liquor (APL), which contained 35% lignin derived molecules. Both low molecular weight lignins (200–400 Da) and high molecular weight lignins (as high as 30,000 Da) were present [53,148–150]. Fourteen taxonomically diverse microorganisms were tested for their ability to depolymerize lignin, uptake biomass-derived molecules such as aromatic monomers, produce extracellular oxidative enzymes, and accumulate carbon storage products from the lignin derived molecules when grown in APL. *Amycolatopsis* sp., *P. putida* KT2440, *P. putida* mt-2, and *Acinetobacter* sp. were the top lignin converters, demonstrating 15%–20% lignin conversion in nitrogen limiting conditions, and 22%–31% lignin conversion in nutrient rich conditions. These species were also able to utilize a wide molecular weight range of lignin. *R. jostii* could not depolymerize the high molecular weight lignin, but *R. jostii* did convert a high percentage of lignin overall by demonstrating 20% lignin conversion in nitrogen limiting conditions, and 26% lignin conversion in nutrient rich conditions.

It follows that the top lignin converting species consumed the major aromatic monomers in the APL and also produced laccase and peroxidase enzymes. The three Pseudomonads and *Cupriavidus necator* H16 produced high amounts of laccases, 3–6 mU/mL, in nutrient rich conditions. *P. putida* KT2440 produced the most laccase enzymes at day five of the seven-day incubation in nutrient-rich conditions, a total of 6 mU/mL. Although *C. necator* H16 was not a top lignin converter, it produced the most Mn^{2+} independent peroxidases at 6 mU/mL by day two of the seven-day incubation. *Pseudomonas fluorescens* Pf-5, *Rhodococcus erythropolis* U23A, and *P. putida* KT2440 all produced over 3 mU/mL of Mn^{2+} peroxidases. The three Pseudomonads, *C. necator* H16, and *Enterobacter lignolyticus* SCF1 all produced over 2 mU/mL of Mn^{2+} oxidizing enzymes in nitrogen limiting conditions. In nutrient-rich conditions, the three Pseudomonads, *C. necator* H16 all produced over 7 mU/mL of Mn^{2+} oxidizing enzymes with *Pseudomonas putida* KT2440 producing 11 mU/mL.

Four of the five top lignin converters stored carbon as fatty acids or polyhydroxyalkanoates (PHAs) under nitrogen-limiting conditions. *Acinetobacter* sp. was the only top lignin converter that did not store carbon [149]. *P. putida* KT2440 stored 0.25 g/L medium chain length PHAs from APL. As a proof-of-concept, the medium chain length PHAs were subjected to thermal depolymerization and catalytic dehydrogenation to produce hydrocarbons [150].

Other target compounds can be produced by native lignin-utilizing microbes that have been subjected to additional metabolic engineering. For example, *P. putida* KT2440 was engineered to utilize both the protocatechuate and the catechol branches of the β-ketoadipate pathway to produce muconic acid. The engineered *P. putida* KT2440 produced muconic acid from a variety of model aromatic molecules including catechol, phenol, benzoate, protocatechuate, coniferyl alcohol, ferulate, vanillin, caffeate, *p*-coumarate, and 4-hydroxybenzoate. In fed-batch culture, the engineered *P. putida* KT2440 produced muconic acid at a titer of 13.5 g/L from *p*-coumarate in 78.5 h. This muconic acid was purified and converted to adipic acid with a Pd/C catalyst. However, when APL was used as a substrate in shake flasks, only 0.7 g/L muconic acid was produced. While this production represented 67% yield of the two major aromatics detected in the APL (*p*-coumarate and ferulic acid), the titer is much lower than that observed from pure substrates [148]. This is consistent with the use of biomass-derived sugars relative to pure substrate [36]. In this case, the APL contained both aromatic and non-aromatic compounds, and *P. putida* KT2440 did not convert all aromatics at the same efficiency.

Making changes to the catechol and protocatechuate pathways might improve production of target products, such as muconic acid, or change the target products altogether. The position where catechol or protocatechuate are cleaved affects the amount of succinate, acetyl-CoA, and pyruvate produced. For example, when the endogenous catechol ortho pathway in *P. putida* KT2440 was exchanged with the exogenous catechol meta pathway, the pyruvate yield increased from 23.9 ± 3.1 to 31.0 ± 0.9 percent. When the endogenous protocatechuate ortho pathway was replaced by the exogenous protocatechuate ortho pathway, the pyruvate yield increased almost five-fold [53].

6.2. Progress in Chemical Utilization

Lignin can undergo many chemical modifications including, but not limited to, alkylation, acylation, amination, carboxylation, halogenation, oxidation, reduction, nitration, and sulfonation [188].

Figure 4 shows the major thermochemical depolymerization processes in conjunction with the produced products [188]. Zakzeski describes three categories of catalytic lignin transformations: lignin catalytic cracking and hydrolysis, lignin reduction, and lignin oxidation. These processes have been employed with lignin substrates, lignin model compounds, and depolymerized lignin [51].

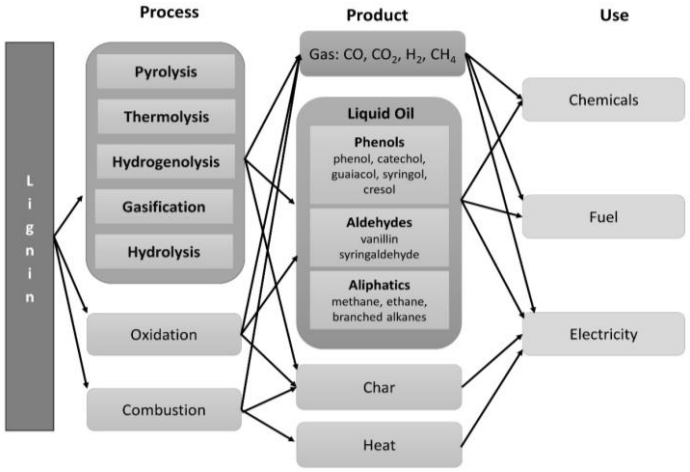

Figure 4. Major thermochemical lignin processes used to depolymerize lignin and the resulting products, as shown by Macfarlane et al. [188].

Liquefaction processes produce monophenolic compounds that can be converted to liquid fuels by hydrodeoxygenation [189]. Monomeric, aromatic-based compounds have also been obtained by steam treatment followed by base-depolymerization to generate two fractions: a monomeric fraction and a dimeric and trimeric fraction [190]. The yield of the monomeric fraction was as great as 15 *wt*% of the initial lignin and included phenolic species such as vanillin, guaiacol, phenol, and catechol. Monomers provide an opportunity for green aromatic-based compounds [190].

Pyrolysis is viewed as one of the most promising thermochemical technologies for lignin utilization [191,192]. The main compounds produced from lignin during fast pyrolysis are gaseous hydrocarbons (i.e., CO_2, CO), volatile liquids (methanol, acetone and acetaldehyde), monolignols, monophenols (phenol, guaiacol, syringol, and catechol) and other monosubstituted phenols [188].

Lignin is the key biorenewable source of aromatic compounds with phenolics, for example, vanillic acid, syringic acid, ferulic acid, syringol, guaiacol, and eugenol attracting the interest of polymer chemists [51,193–196]. They are also valuable building blocks for synthesis of bisphenols [194,197–199], aliphatic-aromatic polyesters [194,199–201], polyethylene terephthalate mimics [194,202], and epoxy resins [194,203–205]. Additionally, there is strong interest in the continued development of polyurethane precursors originating from renewable resources [194].

6.2.1. Cracking and Hydrolysis of Depolymerized Lignin

In lignin catalytic cracking, the β-O-4 linkage is cleaved, and the carbon-carbon bonds are relatively unstable [206]. The zeolite H-ZSM-5 has been used for catalytic cracking of pyrolytic lignin [109,207–210], pyrolytic oil [211], and model compounds obtained from flash pyrolyzed vegetable biomass [212]. Products obtained from catalytic cracking with H-ZSM-5 can include aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, and undesired coke product [51]. Other catalysts such as Pt/Al_2-SiO_2 [213], supported or non-supported Pt-modified superacid catalysts, and metal-loaded large pore zeolites have also been successful in catalytic cracking of biomass derived substrates [109]. In the non-zeolite catalytic cracking, products can include aromatics and phenolic compounds [51].

6.2.2. Reduction of Lignin Model Compounds and Depolymerized Lignin

After the lignin is depolymerized using methods described previously in Section 5, the depolymerized lignin (oil) can be upgraded using similar catalysts. Initial hydrogenolysis or hydrocracking studies of phenol, *o*-cresol, anisole, catechol, syringol, and guaiacol revealed that removal of oxygen for the purpose of increased stability could be done under milder conditions than required for thermal fragmentation and deoxygenation [214–216]. Hydrodeoxygenation of guaiacol has yielded phenol or catechol, although phenol is the preferred product at higher temperatures [214,216]. Depending on the catalyst and temperature, anisole can yield phenol, *o*-cresol, and 2,6-dimethylphenol [214,216]. Further hydrodeoxygenation of the phenol (produced from guaiacol or anisole) can yield benzene and cyclohexane [216]. Excellent conversion of guaiacol and 77% selectivity of phenol was achieved at 598 K, 5 MPa H_2, with a $Co\text{-}Mo/Al_2O_3$ catalyst [216]. Catechol has been shown to be more reactive than phenol itself when subject to hydrodeoxygenation with a $Ni\text{-}Mo/Al_2O_3$ catalyst at 623 K [217]. A mixture of bio-oil model compounds has also been subject to hydrodeoxygenation with Co-Mo and Ni-Mo catalysts, and the catechol component of the bio-oil was converted to phenol [218].

Key conclusions were drawn from studies of hydrodeoxygenation of the lignin-derived phenolic model compounds. Higher temperatures caused rapid deactivation of the catalyst, which was attributed to large amounts of water release, coke formation, and loss of sulfur. However, below 523 K, the catalyst stayed active for 50 h [214]. In addition, the alumina supports for catalysts have shown activity. In fact, when neutral supports such as carbon replaced the alumina, lower activity was observed. However, polycondensation products and coke formation are thought to be associated with the alumina support [218]. When an activated carbon supported Co-Mo catalyst was used instead, there was negligible coke production [219]. The range of lignin-derived model compounds was increased by the hydrotreatment of 4-methylguaiacol, 4-methylcatechol, eugenol, vanillin, *o*,*o*′-biphenol, *o*-hydroxydiphenylmethane, and phenyl ether using a $Co\text{-}Mo/Al_2O_3$ catalyst (523–598 K, 6.9 MPa). Substituted guaiacols and catechols could react to form thermally stable phenols at 573 K [220].

In exploring different iron and molybdenum catalysts on lignin-derived model compounds, it was found that the molybdenum catalysts significantly increased the aromatic bond cleavage, and the iron catalysts only slightly increased the aromatic bond cleavage. Therefore, molybdenum catalysts are better candidates for the production of monophenol and benzene in the hydrocracking process [221]. In order to study the effects of a promoter for the supported molybdenum catalyst, lignin-derived phenolic compounds were subject to hydrodeoxygenation over a $Co\text{-}Mo/Al_2O_3$ catalyst. It was found that 4-propylguaiacol was converted to phenol at temperatures lower than 573 K, but at temperatures greater than 673K, saturated and aromatic hydrocarbons were produced instead. A Ni-Mo catalyst with a more acidic support was shown to have higher dealkylation activity, which resulted in higher yields of cresols and phenol [222].

As mentioned before, the traditional hydrodeoxygenation catalysts discussed above encounter problems with deactivation by coke formation and poisoning by water [51]. With the common problems of traditional catalysts in mind, different metals and supports were tested for hydrodeoxygenation

of anisole. Zirconia and ceria supports were found to be the most effective, and in a comparison of a Ni-Cu/ZrO_2 and Ni-Cu/CeO_2, the former produced mostly aromatics from anisole, and the latter almost fully converted anisole to cyclohexane. In addition, rhodium catalysts performed well for the production of aromatics in some cases [223]. In the interest of using supported platinum-group catalysts, which are known to be more active than sulfided molybdenum catalysts and can be used at lower temperatures, Ru/C and Pd/C were tested for catalytic hydroprocessing of guaiacol. Substrate hydrogenation and loss of aromaticity were observed using both catalysts [224]. Similarly, Pd/C, Pt/C, or Ru/C combined with mineral acids were used to completely hydrogenate and deoxygenate phenols, guaiacols, and syringols to produce cycloalkanes and methanol [225]. Hydrotreatment of pyrolytic lignin with a Ru/C catalyst produced cycloalkanes, alkyl substituted cyclohexanols, cyclohexanol, and linear alkenes [140]. The catalyst types discussed above such as Ru/C are therefore too active for maintaining the aromaticity of the lignin model compounds or depolymerized lignin [51].

In order to try to maintain the aromaticity, guaiacol or catechol was subject to reductive deoxygenation in the presence of α-terpinene and a vanadium or alumina catalyst at atmospheric pressure. Phenol and methyl-substituted phenols were produced at high yield and selectivity [226].

Electrocatalysis has been researched as a possible route for efficient lignin degradation by hydrogenation [51]. Electrocatalysis of the model lignin compound 4-phenoxyphenol with Raney Ni and Pd supported on alumina and carbon showed high efficiencies of electrohydrogenolysis to phenol [227].

A few studies have been done with homogeneous catalysis of lignin-derived phenolic compounds. A di-μ-chlorobis (η^4-1,5-hexadiene)-dirhodium(I) complex catalyzed the lignin-derived model compounds 4-propelphenol, eugenol, 1,2-dimethoxy-4-propylbenzene, and 2,6-dimethoxy-4-propylphenol. The temperature was 298 K and the medium was two-phase hexane/aqueous [228].

6.2.3. Oxidation of Lignin Model Compounds and Depolymerized Lignin

In the oxidation of lignin model compounds, the goal is to create more complex aromatic molecules, which could be industrially relevant. Although oxidation of lignin historically comes from the pulping industry, this review will focus on upgrading of monomers by oxidation. The Ng/MiO catalysts have been shown to oxidize phenolic, nonphenolic, monomeric, and dimeric lignin model compounds. Vanillyl and veratryl alcohol were oxidized to acids, aldehydes, and quinones (49% yield) and polymeric products [229,230]. In another oxidation study of lignin model compounds, methylrhenium trioxide was used to catalyze the oxidation of isoeugenol or *trans*-ferulic acid in the presence of hydrogen peroxide to produce vanillin [231]. Wet oxidation of ferulic acid was carried out by single metal, bimetal, multimetal, and multimetal oxide alumina or kaolin supported catalysts. Cu-Mn/Al_2O_3 was the most stable catalyst studied and it was the second most active catalyst [232]. An electrocatalysis study carried out the anodic oxidation of lignin model compounds in methanol, and it was shown that the C_α-C_β bond was cleaved [233].

In the study of homogeneous catalysts for oxidation, the idea of biomimicry has been used [51]. Originally iron and manganese porphyrin catalysts were used to better understand the enzymatic degradation of lignin, and it was shown that the iron porphyrin catalysts cleave the C_α-C_β and oxidize lignin model compounds [234].

Metalloporphyrin catalysts are well studied in the selective oxidation of hydrocarbons and therefore are of interest for selective oxidation of lignin and lignin model compounds and have been reviewed by Crestini and Tagliatesta [51,235]. High conversion (67%) was achieved in the oxidation of veratryl alcohol with free and ion-exchange resin-immobilized Fe(TPPS) and Mn(TPPS) complexes using $KHSO_5$ as an oxidant [236]. Several other metalloporphyrin or metalloporphyrin-like catalysts have been used to oxidize lignin model compounds including iron(III) and manganese(III) meso-tetraphenylporphyrin and phthalocyanine complexes [237], iron porphyrin catalysts [238], and trisodium tetra-4-sulfonatophthalocyanineiron(III) [239]. The incorporation of a variety of ring

substituents, the incorporation of axial ligands, and the immobilization of the metalloporphyrin can improve stability, tenability, and recyclability of the catalyst [51].

Simple metal salt-based catalysts have been used for oxidation of lignin and lignin model compounds. Co(II) acetate and Mn(II) acetate were used as catalysts in the single-electron oxidation of a lignin model compound, and it was found that the oxidation occurred primarily by cleavage of the C_α–C_β bond [240].

A well-known example of adding value to lignin monomers involves the oxidative production of vanillin from spent sulfite liquor. A 227,000 kg/year facility was built for this purpose in Thorold, Ontario in 1945 and by 1981 was producing 3.4×10^6 kg/year, accounting for more than half of the world vanillin market [241]. However, the disposal of the waste generated by this process eventually led to this process falling out of favor, with the Thorold plant closing in 1987.

7. Economic Analysis of Lignin Utilization Strategies

The adage that "you can make anything from lignin except money" is well-known in the biofuels and pulp and paper industries. The technological advances reviewed here regarding lignin recovery, depolymerization and upgrading are chipping away at this long-held belief. This establishment of lignin as a source of value appears to be critical to the economic viability of the biorefinery concept. An economic analysis of the utilization of lignocellulosic biomass relies on a number of factors including cost of the biomass feedstock, capital costs, operating costs, and the market size and selling price of the target product(s). The utilization of a lignin "waste" stream in an existing lignocellulosic biomass processing facility could provide an additional source of income for the facility. However, a detailed analysis is needed to determine if the additional income from selling lignin or a lignin-based product would exceed the required capital and operating costs for producing the purified lignin and/or lignin-based product, as highlighted by the example of vanillin production. Since existing lignocellulosic biomass processing facilities often utilize lignin for process heat and electricity, it would also be important to determine what fraction of the available lignin should be diverted to upgrading. The advantage of choosing a platform chemical as a target product is that it provides flexibility. Instead of targeting one product and one application, a platform chemical that can be converted into a variety of downstream products would help with marketability.

Multiple reports have concluded that selling lignin as a co-product contributes to the economic viability of biofuels. A comprehensive 2013 report by the US National Renewable Energy Laboratory (NREL) concluded that achievement of the target value of 3.00 US dollars per gallon of gasoline equivalent fuel required lignin valorization [242]. Kautto et al. modeled the organsolv-based production of ethanol from hardwood with lignin, furfural, and acetic acid as co-products [243]. Consistent with the NREL conclusion, the value of the lignin product was a strong determinant of the minimum ethanol selling price. Specifically, a value of 1.00 US dollars per kg of lignin was required for the ethanol to be sold at market price. Analysis of the production of ethanol from corn stover using ionic liquids for biomass deconstruction concluded that if 65% of the lignin was recovered and sold, a lignin selling price of 2.62 US dollars per kg was sufficient to meet the market price for ethanol [244]. Finally, at least one technoeconomic analysis has included a specific upgrading method for the lignin. Chen and Fu modeled the production of ethanol from corn stover with lignin plastic composite and compressed natural gas as co-products, where the natural gas is produced from the spent fermentation media [245]. This analysis predicted that inclusion of these two co-product streams resulted in a 19% decrease in the ethanol production cost.

Studies have also compared how different lignin utilization strategies impact the process economics, though these have mainly compared the use of lignin to produce steam and electricity to the use of lignin as a soil amendment. Petrou et al. [246] compared corn stover-based ethanol processes in which lignin is burned to produce electricity and steam to processes in which lignin is modified to produce lignosulfonates and/or geomaterial. This study concluded that burning the lignin to produce steam and excess electricity was the top economic performer, but that the scenario

in which lignin was used as a geomaterial was the best in terms of environmental performance [246]. Pourhashem et al. [247] analyzed the production of ethanol from agricultural residues, such as corn stover and barley straw, with the use of lignin as a soil amender, as a coal substitute to produce electricity or for the on-site production of electricity. The use of lignin as a soil amender was deemed the best in terms of both greenhouse gas intensity and capital cost.

As the technologies associated with lignin recovery and upgrading develop, future economic analyses can incorporate these processes and provide additional insight into which routes are the most promising for industrial use.

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Abbreviations

The following abbreviations are used in this manuscript:

TCA	tricarboxylic acid cycle
TG-FTIR	thermogravimetric-fourier transform infrared spectroscopy
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
PHA	polyhydroxyalkanoates

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