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### Publication Date

2020-01-03

### DOI

10.1002/cssc.202000002

Peer reviewed

# Heterogeneous Catalyst Design Principles for the Conversion of Lignin into High-Value Commodity Fuels and Chemicals

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Lignin valorization has risen as a promising pathway to supplant the use of petrochemicals for chemical commodities and fuels. However, the challenges of separating and breaking down lignin from lignocellulosic biomass are the primary barriers to success. Integrated biorefinery systems that incorporate both homo- and heterogeneous catalysis for the upgrading of lignin intermediates have emerged as a viable solution. Homogeneous catalysis can perform selected chemistries, such as the hydrolysis and dehydration of ester or ether bonds, that are more suitable for the pretreatment and fractionation of biomass. Heterogeneous catalysis, however, offers a tunable platform for the conversion of extracted lignin into chemicals, fuels, and materials. Tremendous effort has been invested in

elucidating the necessary factors for the valorization of lignin by using heterogeneous catalysts, with efforts to explore more robust methods to drive down costs. Current progress in lignin conversion has fostered numerous advances, but understanding the key catalyst design principles is important for advancing the field. This Minireview aims to provide a summary on the fundamental design principles for the selective conversion of lignin by using heterogeneous catalysts, including the pairing of catalyst metals, supports, and solvents. The review puts a particular focus on the use of bimetallic catalysts on porous supports as a strategy for the selective conversion of lignin. Finally, future research on the valorization of lignin is proposed on the basis of recent progress.

## 1. Introduction

The world currently relies heavily on natural resources, such as coal, gas, and petroleum, as a source for fuel and chemicals. In fact, 87% of the energy produced in the USA comes from non-renewable sources.<sup>[1]</sup> Much of the petrochemical resources are finite and the development of an alternative infrastructure that relies on renewable resources will be key to the economic and environmental well-being of the world. Plant biomass may relieve the dependence on petroleum by utilizing this abundant source of carbon to create sustainable feedstocks. There are many challenges with achieving this goal, but utilizing all parts

of biomass to their full economic potential may make this a reality. One potential solution is to continue to improve current biorefinery strategies towards integrated catalytic approaches that seek to improve total utilization of biomass waste towards fungible fuels and biochemicals. Lignin, in particular, has rightfully garnered significant attention due to its substantial contribution to biomass, in terms of mass and carbon content. However, its valorization to commercially relevant fuels and chemicals has been relatively challenging compared with carbohydrates due to lignin's high degree of polymerization, diverse spectrum of chemical moieties, and complex structure.


The most promising route for the catalytic conversion of biomass is the development of catalyst systems that can be streamlined into biorefineries to economically achieve high selectivity, conversion, and robustness. At a high level, catalytic processing can be categorized as either homo- or heterogeneous that can be differentiated by the use of catalysts that are either soluble or insoluble in the liquid medium, respectively, during the intended reaction. Both types are useful for processing biomass and biomass-derived intermediates and a combined strategy is often proposed to take advantage of the merits of both.<sup>[2–9]</sup> Homogeneous catalysis for biomass upgrading primarily addresses the challenges of the direct processing of raw biomass feedstocks to drive sufficient biomass deconstruction by solubilization, hydrolysis, and dehydration to liquid chemical intermediates, such as sugars, furfurals, oxo acids, polyols, and depolymerized technical lignins.<sup>[10–12]</sup> However, homogeneous biomass reactions often produce a limited scope of water-soluble intermediates that necessitate subse-

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<https://doi.org/10.1002/cssc.202000002>.

quent separation steps to recover valuable reactive chemical intermediates, while separating them from the catalytic component and contaminants, such as mineral ash, chlorine, and acids. A recent integrated approach of a homogeneous reaction in tandem with a heterogeneous process has achieved an impressive 60% total carbon utilization of biomass to fungible fuels and technical-grade lignin.<sup>[2]</sup> Heterogeneous catalysts can be manipulated to extend chemistries not seen in homogeneous catalysis, although heterogeneous catalysts have issues of their own, when it comes to the surface-active sites of the catalyst interacting with the lignin polymeric structure. In an

effort to enhance the use of heterogeneous catalysts for lignin valorization strategies, the material design principles for the choice of the catalyst(s), supports, and even solvents must be understood to improve both the selectivity and conversion. This review details pertinent material principles to improve the selective conversion of model lignin intermediates or extracted lignin into chemicals and fuels. Whereas some reviews have just focused on homo-<sup>[13,14]</sup> and heterogeneous<sup>[3,15,16]</sup> catalysts, our review has a holistic view of the optimization of material and solvent properties needed for biomass upgrading.

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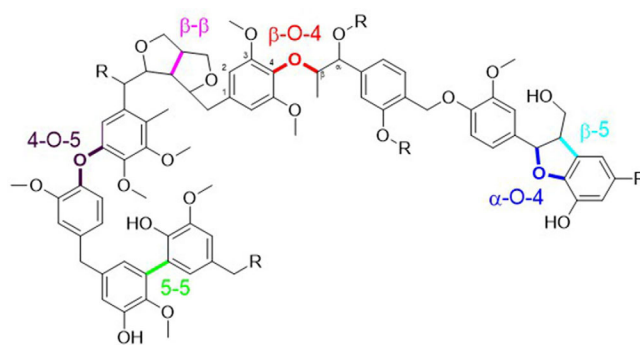
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## 2. Lignin Structure

Biomass can be used to produce energy, food, chemicals, and many other products. Cellulose, hemicellulose, and lignin, in varying amounts, comprise biomass.<sup>[17]</sup> Cellulose is composed of glucose monomers, which make up the largest fraction.<sup>[17]</sup> The next predominant form is hemicellulose, which is comprised of glucose and other sugars, such as xylose and five-carbon monosaccharides.<sup>[17]</sup> Cellulose and hemicellulose are the most frequently used biomass feedstock to produce bio-fuels<sup>[18–22]</sup> and chemicals.<sup>[23–27]</sup> Lignin is the structural component that adds a hydrophobic protective layer in the cell walls of plants.<sup>[28]</sup> Depending on the plant species, the fraction of lignin can vary from 15% in tobacco leaf to over 40% in wood bark and hazelnut shells.<sup>[29]</sup> The structural robustness and complicated network of lignin, consisting of polymeric aromatic groups, renders it an ample resource for value-added chemicals and materials. Thus, current research aims to utilize lignin as a viable feedstock, contrary the common belief that “you can make anything out of lignin, except money.”

The structure of lignin is complicated and can differ, depending on the species,<sup>[30,31]</sup> temperature,<sup>[32,33]</sup> and environmental history of biomass resources.<sup>[34,35]</sup> Some common features of the lignin structure include ether and diethyl bonds, such as  $\beta$ -O-4,  $\alpha$ -O-4, 5-5,  $\beta$ -5, 4-O-5, and  $\beta$ - $\beta$  linkages.<sup>[36–38]</sup> Figure 1 shows a representation of the lignin structure, including the common linkages mentioned above. Most research into the valorization of lignin uses model compounds to optimize the reaction conditions and material properties of the catalysts. Afterwards, the optimized catalysts are applied to raw or extracted lignin, for which further optimization of the



**Figure 1.** Typical structure of lignin, with some common linkages highlighted.

process, scaling, and separation is needed to improve the activity, selectivity, and stability, which can differ from that of model studies significantly.<sup>[39]</sup>

### 3. Pretreatment Methods

The pretreatment method or isolation of lignin from lignocellulosic biomass is a significant factor that can influence the final product distribution and yield. Biomass can either be pretreated by using mechanical or chemical-based methods. The factors that determine the effectiveness of the pretreatment method include the complicated network of lignin around the structure, the crystallinity of cellulose, environmental historical effects, and the integrity of the biomass source. Select mechanical methods include ball milling or grinding, which acts to disrupt the crystallinity and polymeric structure of lignin and the other cellulosic components. Ball milling of biomass undergoes ultrafine grinding to create submicron particles and powders to break up the lignocellulosic structure and allow for extraction. There are many factors that influence the effectiveness of ball milling, including the ball-to-biomass ratio, milling time, and the condition of the biomass (e.g., dry or wet conditions). Despite its use as a possible environmentally friendly alternative to chemical-based methods, the quality of lignin obtained is far inferior to that needed for further upgrading. Ball milling and other mechanical grinding methods are often not used as a stand-alone pretreatment method and are often followed by chemical-based methods for solubilization or separation of the lignin from the milled lignocellulosic biomass framework.<sup>[40–42]</sup>

The chemical-based pretreatment methods are important for preserving the quality of lignin needed for valorization. Chemical methods provide a less destructive alternative to ball milling through which enzymes, solvents, and acid or base chemistry can separate the cellulose, hemicellulose, and lignin fractions. The chemical methods can be divided into biological, acid/base, or solvation chemistry. In biological chemical separation, enzymes or fungi are used to break down the polymer by selective scission of ether or ester bonds.<sup>[43,44]</sup> Biological pretreatments have high selectivity with relatively low process conditions and little to no need for harsh chemicals; this makes them an environmentally friendly and energy-efficient process. The enzymes and fungi can be genetically engineered to produce desired products. However, genetic tools are still under development and need to surpass several milestones before being effective for pretreatment.<sup>[42,44–46]</sup> Despite these advantages, biological pretreatments can take long periods of incubation time, large amounts of space for reactors, and can have prohibitive costs for large-scale applications.

Acidic pretreatment methods, including sulfuric acid and hydrochloric acid, are used to promote the delignification of biomass. The acidic conditions help to degrade lignin through fragmentation of the  $\beta$ -O-4 aryl ether bonds, leading to depolymerization; however, if the acid environment is sufficiently severe, additional cross-condensation reactions may occur between lignin and sugars that lead to repolymerization and the formation of unwanted pseudo-lignins.<sup>[42,46–49]</sup> At elevated tem-

peratures, the use of acid chemistry accelerates the hydrolysis of cellulose and hemicellulose to produce sugar monomers primarily consisting of glucose and xylose, respectively.<sup>[45,50]</sup> The Klason method uses sulfuric acid to solubilize the cellulose and hemicellulose, while lignin is extracted as the insoluble component.<sup>[51]</sup> The lignin that comes out of the Klason process has undergone changes due to the acidic media and oxygen-containing groups at the benzylic positions.

Alkaline pretreatment uses high-pH reagents, such as sodium hydroxide and ammonia, to delignify biomass. The alkaline conditions promote the solubilization of lignin through saponification of the ester bonds. Alkaline pretreatment is effective at removing lignin, but the relatively higher concentrations of bases used compared with those of dilute acid reactions can lead to significant recovery and treatment costs (as observed by the paper pulp industry). The saponification reactions involved may adversely affect the lignin structure for subsequent catalytic upgrading.<sup>[42,46,52]</sup>

The combination of solvents with dilute concentrations of acid or bases is used to promote the glycolysis or scission of bonds for facile separation of lignin from cellulose and hemicellulose. There are many different chemical methods that utilize solvents, such as the Klason,<sup>[51,53]</sup> Kraft,<sup>[36,54]</sup> organosolv,<sup>[55,56]</sup> and cosolvent-enhanced lignocellulosic fractionation (CELf) strategies.<sup>[57,58]</sup> Each of these isolation techniques utilize solvents with either acids or bases to give unique isolated lignin feedstocks. There are several types of solvents employed to isolate and dissolve lignin, ranging from harsh solvents, such as tetrahydrofuran, ethanol, and benzene, to more green and sustainable alternatives, such as water and ionic liquids.<sup>[59–61]</sup> Ionic liquids consist of liquid salts with anion and cation components that can selectively extract and recover lignin with an antisolvent.<sup>[62]</sup> The use of ionic liquids can separate lignin with little or no structural degradation.

Cosolvent pretreatments, such as organosolv, are effective modifications to dilute acid or base homogeneous processes that employ a combination of organic solvents and water to promote the dissolution and fractionation of biomass into separate lignin, hemicellulose, and cellulose streams.<sup>[50]</sup> Many cosolvent pretreatment methods are also capable of producing high-quality lignin. The extracted lignin contains a minimal amount of ashes and sugars for more effective catalytic upgrading, serving as the primary lignin feedstock to many of the catalytic systems mentioned herein. Cosolvent systems, such as ethanol-water,<sup>[55,63]</sup> methanol-water,<sup>[64,65]</sup> acetone-water,<sup>[66,67]</sup> formic acid-water,<sup>[68,69]</sup> THF-water,<sup>[2,58]</sup> and gamma-valerolactone (GVL)-water,<sup>[8,70]</sup> have been shown to produce high-quality lignin feedstocks. The lignin is precipitated out and has a higher purity and less structural changes than that of acid and base pretreated lignin.<sup>[56]</sup> The CELf method uses THF with dilute acid to remove lignin and solubilize biomass from hardwoods and corn stover.<sup>[57,58]</sup> This method is able to recover over 90% of lignin from maple wood and keep the lignin in a relatively unaltered and pristine form. Once the pristine lignin is separated it will then dissolve in THF to react with the homo- or heterogeneous catalysts. The use of cosolvent pretreatments in tandem with subsequent heterogeneous pro-

cesses are pertinent for a bioeconomic conversion system that fully utilizes the pristine structure of lignin.

Aside from pretreatment methods, there are industrial chemical processes that produce lignin as waste: one of the most prolific is the Kraft pulping process. In the paper industry, lignin is a byproduct of the Kraft pulping process. Lignin is found in the black liquor of the process, which also contains impurities, such as sulfur and sodium.<sup>[54]</sup> Due to the low quality of Kraft lignin, it is often used as an energy source through high-temperature burning.<sup>[71]</sup> Lignin is also a common byproduct of refineries that produce ethanol from the catalytic conversion of cellulose and hemicellulose.<sup>[72]</sup> Lignin isolated from methods, such as CELF, organosolv, Klason, and Kraft, vary in quality and have different properties that require robust catalysts immune to impurities and poisons coupled with depolymerization procedures for adequate retrieval of aromatic products. The advent of searching for valuable catalysts is worthwhile because the structure of lignin lends itself as a reliable renewable source. Valorization strategies discussed in the next section can ensure increasing the profitability of biorefineries by utilizing rationally designed heterogeneous catalysts to convert the lignin byproducts into fungible chemical commodities and fuels.

## 4. Lignin Valorization

The selective depolymerization of lignin by using heterogeneous catalysts can create aromatic monomers or products, such as benzene, toluene, and xylenes (BTX).<sup>[73]</sup> BTX is commonly derived from petroleum and represents a \$100 billion market.<sup>[74]</sup> Additional value-added products from lignin feedstocks include jet fuel,<sup>[75,76]</sup> food additives,<sup>[77,78]</sup> carbon fiber,<sup>[79,80]</sup> hydrogels,<sup>[73,81]</sup> industrial and household cleaners,<sup>[82,83]</sup> and resins.<sup>[84,85]</sup> There are even efforts to design and polymerize extracted lignin mono- and dimers into polymers.<sup>[74,86–88]</sup> For example, thermoplastics can be formed from lignin polymerization.<sup>[89]</sup> Lignin-derived guaiacols and aldehydes were synthesized into triphenylmethane-type polyphenols that could be used to create epoxy thermostats.<sup>[89]</sup>

The majority of lignin valorization research usually starts with studying the effectiveness of developed catalysts for the conversion of model lignin mono-, di-, and oligomers into high-value fuels, chemicals, or materials. After optimization of the process conditions, the catalysts are applied to raw or extracted lignin for which the heterogeneity of the lignin structure and cross-condensation reactions increases the process complexity and significantly influences yields. One of the most viable strategies to overcome some of these challenges is to improve the properties of the catalyst and solvent for which the metal nanoparticle, pore structure, and active-site distributions must be rationally designed to obtain the desired products.

Although herein we primarily focus on catalytic strategies for the conversion of lignin into chemicals and fuels, it is worth mentioning the noncatalytic pathways for lignin valorization, such as the thermal decomposition of lignin through pyrolysis.<sup>[90]</sup> Pyrolysis is conducted at high temperatures under

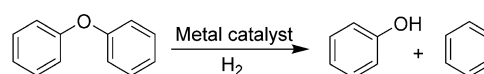
inert conditions, devoid of O<sub>2</sub> or air, to breakdown biomass into bio-oil and other byproducts, such as natural gas. Bio-oil contains many different types of organic compounds, including sugars, aromatics, amines, and alkanes. Due to its complex composition, bio-oil can be used for many different applications, such as transportation fuel, heating oil, electricity generation, and chemicals.<sup>[91–93]</sup> Another thermal decomposition method is hydrothermal carbonization for which water is used as a solvent to produce biochar. The carbonization process can be done at either elevated temperatures, >300 °C, or lower temperatures, <300 °C.<sup>[94]</sup> High-temperature hydrothermal carbonization usually produces high-carbon-content materials, such as carbon nanotubes,<sup>[94]</sup> graphene, and graphite.<sup>[95]</sup> Low-temperature carbonization produces lower carbon content, including sugars and hydrochar. Hydrochar can be further utilized as a precursor for biodiesel and chemical production.<sup>[96]</sup>

## 5. Depolymerization of Lignin

Noble metals are the most commonly used heterogeneous catalysts for the depolymerization of lignin. Very active catalysts include palladium,<sup>[97,98]</sup> ruthenium,<sup>[99,100]</sup> and rhodium,<sup>[100,101]</sup> whereas transition metals, such as nickel,<sup>[102,103]</sup> iron,<sup>[104,105]</sup> and copper,<sup>[106,107]</sup> are frequently used as well. The combination of alloys of metals can promote activity through electronic, interfacial, and synergistic effects. This combination in bimetallic catalysts can have several advantages, such as increased activity and/or selectivity, with conversion rivaling that of precious metals. Some catalyst metal combinations have synergistic natures that may improve activity, selectivity, and/or stability for enhanced depolymerization and valorization through selective scission of carbon–carbon or carbon–heteroatom bonds.<sup>[108]</sup> With more than one metal, the bimetallic catalyst can add complexity because the results can be notably different from that of the monometallic catalyst counterparts.

### 5.1. Hydrogenolysis and hydrogenation

Hydrogenolysis uses H<sub>2</sub> to cleave C–C or C–O bonds.<sup>[109]</sup> Scheme 1 shows a model reaction of how hydrogenolysis can occur in diphenyl ether, which is one of the common building blocks in the structure of lignin. The selective use of H<sub>2</sub> to cleave ether bonds has become one of the most used methods for the depolymerization of lignin. This reaction can occur without the use of catalysts; however, the catalyst acts to selectively use H<sub>2</sub> to scission certain bonds. A specified form of hydrogenolysis is hydrodeoxygenation (HDO), through which C–O bonds are cleaved and oxygen is removed as H<sub>2</sub>O. HDO is often employed to remove excess oxygen from the lignin fraction. The presence of high concentrations of oxygen limits the



**Scheme 1.** Hydrogenolysis of diphenyl ether as a model compound for one of the common building blocks in lignin.



use of lignin in fuel and chemicals because of its low energy density. Excess oxygen can also prohibit the storage of biomass because of the high acidity and reactivity.

The selectivity of hydrogenolysis can be enhanced with the use of bimetallic catalysts to increase the activity and yield for the desired product. Zhang et al. employed nickel-based bimetallic catalysts, with ruthenium, rhodium, and palladium, respectively, stabilized by polyvinylpyrrolidone (PVP) to depolymerize extracted wood lignin and 2-phenoxy-1-phenethanol in water.<sup>[100]</sup> Their goal was to perform hydrogenolysis under mild conditions, 130 °C and 10 bar of H<sub>2</sub>, with NiRu, NiRh, and NiPd to determine if the combination of metals changed the performance of the catalyst. A comparison of the mono- or dimer product yields and conversion was made between the monometallic metals, Ni, Rh, Ru, and Pd, and the bimetallic catalysts. After 1 h of reaction time, the monometallic monomer product yields were 0, 0.16, 0.27, and 0.46 wt% for Ni, Ru, Rh, and Pd, respectively, compared with bimetallic catalyst product yields of 0.8, 2.6, and 2.4 wt% for Ni<sub>85</sub>Ru<sub>15</sub>, Ni<sub>85</sub>Rh<sub>15</sub>, and Ni<sub>85</sub>Pd<sub>15</sub>. After 12 h, the monomer product yield increased to 6.4, 3.6, and 4.6 wt% for Ni<sub>85</sub>Ru<sub>15</sub>, Ni<sub>85</sub>Rh<sub>15</sub>, and Ni<sub>85</sub>Pd<sub>15</sub>, respectively. Zhang et al. explored the change in H<sub>2</sub> pressure effects in model lignin compounds by using Ni<sub>85</sub>Ru<sub>15</sub> at 130 °C for 0.5 h.<sup>[100]</sup> The conversion remained constant at higher pressures, but the product yield changed. The monomer yield was higher at low pressures and the dimer yield was dominant at high pressures. It is surmised that the improved synergistic effects between nickel and ruthenium occurred due to the greater concentration of nickel surface atoms and the orientation of the reactants on the surface to prohibit hydrogenation of the aromatic rings.

Optimization of the bimetallic metal ratios must be done to find the best composition for the desired reaction and lignin phenotype. A sort of “goldilocks” zone must be obtained for bimetallic catalysts. Zhai et al. studied the change in selectivity and activity for the hydrogenolysis of organosolv-extracted birch lignin by using different ratios of nickel and iron over activated carbon (AC).<sup>[104]</sup> Lignin was depolymerized by using Ni/Fe ratios of 2:1, 1:1, and 1:2. The 1:1 ratio gave the highest conversion of 20.3% compared with conversions of 17.7 and 14.6% for ratios of 2:1 and 1:2. The 1:1 ratio had the highest selectivity to propylguaiaicol (PG) and propylsyringol (PS) out of the three. The 1:1 Ni/Fe catalyst enhanced the ability to remove the hydroxyl group, whereas the 1:2 and 2:1 ratios mainly formed byproducts, including 4-(3-hydroxypropyl)-2-methoxyphenol (PG-OH) and 4-(3-hydroxy-propyl)-2,6-dimethoxyphenol (PS-OH).

Pd/C will react with benzyl phenyl ether (BPE) to create toluene and cyclohexanol through hydrogenolysis and hydrogenation. If the Pd catalyst is alloyed with W, PdW/C, hydrogenation is significantly limited. The Pd/C catalyst had a 36.5% product yield of cyclohexanol, whereas PdW/C had a 0.4% product yield, and Pd had a 0% product yield of phenol, whereas PdW had a 29% product yield. The bimetallic synergy of Pd and W shows increased conversion to the desired toluene product, while limiting hydrogenation.<sup>[99]</sup> Pt–WO<sub>3</sub>/C showed very similar trends to PdW/C upon reacting with *m*-cresol. Pt/C converted

8.3% of *m*-cresol and had a selectivity of 23% 3-methylcyclohexanone, 7.4% 3-methylcyclohexanol, 5.5% methylcyclohexane, and 62% toluene. If combined with WO<sub>3</sub>, Pt–WO<sub>3</sub> was able to increase the conversion to 61% with 98% selectivity to toluene.<sup>[110]</sup> If tungsten was mixed with the precious metals palladium and platinum, the catalyst became more selective to aromatic products and had significantly less hydrogenation.

Alloying palladium with transition metals was also effective at modulating the hydrogenation behavior of the developed catalyst. Ni/C and NiPd/C catalysts were compared at varying temperatures from 180 to 240 °C. At 240 °C, the Ni/C catalyst had the highest conversion of 79% with a selectivity of 46% to cyclohexanol. NiPd/C increased the conversion from 78 to 96% with the same selectivity towards cyclohexanol. At the lower temperature ranges, NiPd/C had a lower occurrence of hydrogenating the aromatic rings relative to Ni/C with a selectivity towards cyclohexanol of 14% versus 21%, respectively.<sup>[98]</sup>

The hydrogenolysis of raw or extracted lignin can change based on the heterogeneity and irrevocable cross-condensation of the raw lignin. As stated earlier, lignin comes in differing structures and qualities, which can drastically change the depolymerization products. Furthermore, condensation reactions of the aromatic products also prevent efficacy of the reaction. NiFe/C was used to depolymerize organosolv-extracted birch lignin versus a lignin-first approach with birch sawdust biomass.<sup>[111–113]</sup> The lignin-first approach performs depolymerization and conversion in a one pot manner through which lignin is extracted and disassembled to preserve the aromaticity of products. Under the same conditions (Table 1), the organosolv-extracted birch had a lower conversion of 20.3% compared with the sawdust conversion of 39.5%. However, the organosolv extract had higher selectivity towards PG and PS than that of the sawdust.<sup>[104]</sup>

The catalysts commonly used in HDO are Ni,<sup>[114]</sup> Ru,<sup>[115]</sup> Pd,<sup>[99]</sup> Fe,<sup>[105]</sup> Co,<sup>[116]</sup> and W.<sup>[99]</sup> Mono- and bimetallic catalysts of transition and noble metals were used in the cleavage of the C–O bond in BPE.<sup>[99]</sup> The use of tungsten-based catalysts seems to promote the aromaticity of the products formed, limiting hydrogenation. The combination of a noble metal with tungsten is surmised to promote the scission of β-O-4 and α-O-4 bonds, while preserving the aromaticity of the products. The catalyst Ru/C depolymerized BPE into toluene and phenol with a conversion of 94.2% and product yields of 81.4 and 48.6%, respectively. In comparison, W/C converts 79.5% BPE with product yields of 40.3% toluene and 33.8% phenol. The combination of Ru and W bimetallic catalyst synergistically increased the conversion to 99.7% and product yields to 92.6 and 61.5%, respectively, which were higher than those of either monometallic catalyst.<sup>[99]</sup> Each of these reactions were performed under the same conditions, as observed in Table 2. Higher conversion and greater selectivity are some of the major advantages of bimetallic catalysts over monometallic catalysts. Other examples are shown with Pd/C and PdW/C. Pd/C has a conversion of 99.7% of BPE and has product yields of 89% toluene, 0% phenol, and 36.5% cyclohexanol (Table 2). If Pd is alloyed with W, the conversion increases to 100% and the product yields change to 100% of toluene, 29% of phenol, and 0.4% cyclo-

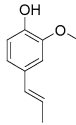
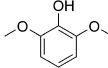
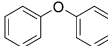
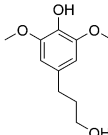
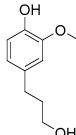
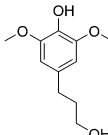
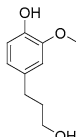
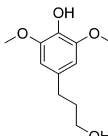
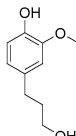

Table 1. Depolymerization of extracted or real lignin.							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion	Feed	Products	Ref.
RuW/AC	260	0.7	10	47.3 %	organosolv poplar lignin	2-methoxy-4-(propenyl)phenol (48.4%)  2,6-dimethoxyphenol (15.8%)  diphenyl ether (18.7%) 	[99]
Ni <sub>85</sub> Rh <sub>15</sub>	130	1	12	3.6 %	organosolv <i>Betula platyphylla</i> suk (birch) lignin	PS-OH (2.2%)  PG-OH (0.7%) 	[100]
Ni <sub>85</sub> Ru <sub>15</sub>	130	1	12	6.8 %	organosolv <i>B. platyphylla</i> suk (birch) lignin	PS-OH (1.4%)  PG-OH (5.0%) 	[100]
Ni <sub>85</sub> Pd <sub>15</sub>	130	1	12	4.6 %	organosolv <i>B. platyphylla</i> suk (birch) lignin	PS-OH (3.3%)  PG-OH (0.9%) 	[100]
Pt/Al <sub>2</sub> O <sub>3</sub>	250	4–6	10	45 %	steam exploded corn stover	toluene (68%) 	[101]






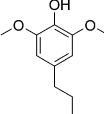
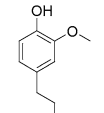
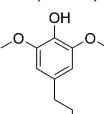
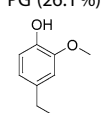
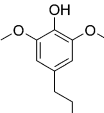
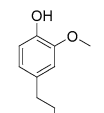
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Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion	Feed	Products	Ref.
Ru/C	250	4–6	8	34 %	steam exploded corn stover	toluene (25%)  methylcyclohexane (23%) 	[101]
Ru/Al <sub>2</sub> O <sub>3</sub>	250	4–6	8	61 %	steam exploded corn stover	toluene (18%)  coumaran (29%) 	[101]
Rh/Al <sub>2</sub> O <sub>3</sub>	250	4–6	10	49 %	steam exploded corn stover	toluene (70%) 	[101]
Ni/C	200	0.1	6	54 %	organosolv birch sawdust	PS (67%)  PG (22%) 	[102]
Ni <sub>1</sub> Fe <sub>1</sub> /AC	200	2	6	20.30 %	organosolv birch lignin	PS (58.9%)  PG (26.1%) 	[104]
Ni <sub>1</sub> Fe <sub>1</sub> /AC	200	2	6	39.50 %	birch sawdust (20% lignin) no pretreatment	PS (23.70%)  PG (11.06%) 	[104]



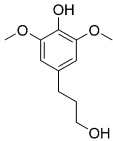
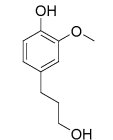
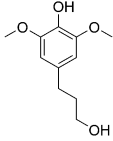




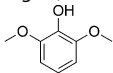
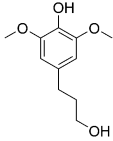
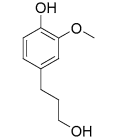
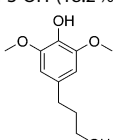

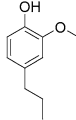
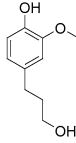
Table 1. (Continued)							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion	Feed	Products	Ref.
Pd/AC	200	2	6	20.10%	organosolv birch lignin	PS-OH (42.9%)  PG-OH (13.8%) 	[104]
Ni/Al <sub>2</sub> O <sub>3</sub>	250	3	3	36%	extracted birch sawdust (19.5 wt% Klason lignin)	PS-OH (21%) 	[111]
Ru/CeO <sub>2</sub>	200	3	6	–	organosolv poplar lignin	phenol (0 wt%) 	[131]
CuCl <sub>2</sub>	200	3	6	–	organosolv poplar lignin	phenol (2.6 wt%) 	[131]
Ru/CeO <sub>2</sub> + CuCl <sub>2</sub>	200	3	6	–	organosolv poplar lignin	phenol (13 wt%)  guaiacol (2 wt%)  syringol (0.5 wt%) 	[131]
Ni <sub>7</sub> Au <sub>3</sub>	170	1	12	14%	organosolv birch sawdust lignin	PS-OH (9.3%)  PG-OH (3.2%) 	[156]
TiN (urea glass)	300	supercritical ethanol	–	61 wt%	P1000 soda lignin	monomer (12 wt%) THF soluble (61 wt%)	[162]
TiN (urea glass)	340	supercritical ethanol	–	51 wt%	P1000 soda lignin	monomer (19 wt%) THF soluble (51 wt%)	[162]
Pd/C + H <sub>3</sub> PO <sub>4</sub>	180	3	3	37%	organosolv birch wood meal lignin	PS-OH (18.2%) 	[163]

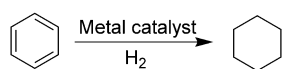
Table 1. (Continued)							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion	Feed	Products	Ref.
Zr-KIT-5	250	in acetic acid	5	11.8%	organosolv corn stover lignin	phenyl acetate (percentage unknown)	[164]
							
Cu <sub>20</sub> PMO <sup>[a]</sup>	310	MeOH	N.R.	48.3%	organosolv candlenut lignin	phenolics, aromatics	[165]
ZnPd/C	150	2	2	100%	β-O-4 synthetic lignin polymer	PG (56%)	[166]
							
						PG-OH (44%)	
							

[a] PMO = porous metal oxides.

hexanol. The Pd/W bimetallic catalyst promoted higher conversion of the ether, promoting hydrogenolysis and increasing the selectivity towards toluene and phenol. The use of tungsten metal typically leads to preferential cleavage of the lower energy aryl ether bonds instead of the higher energy C=C<sup>[117]</sup> bond of the aromatic rings. Coupling tungsten with other metals promotes a synergistic effect, showing that, for selective bond cleavage for aromatic products, the metal–tungsten bimetallic catalyst is more advantageous than that of mono-metallic catalysts.

Hydrogenation is the saturation of bonds by using H<sub>2</sub> to convert C=C or C=O into C–C or C–OH, respectively. Scheme 2 shows an example of hydrogenation in which benzene is converted into cyclohexane. Hydrogenation often occurs as an unwanted side reaction during hydrogenolysis to create different products. The depolymerization of lignin through either hydrogenation or hydrogenolysis requires a delicate balance, which often changes with the process conditions, solvent, and catalyst used. Nevertheless, the hydrogenation of bonds is often utilized to create starting materials for polymers, chemicals, and resins.<sup>[118]</sup> Finding highly selective catalysts can be difficult because many noble metals are excellent at hydrogenation; however, they produce many byproducts that can be difficult to separate.<sup>[119]</sup>

Hydrogenation of the aromatic ring products usually proliferates at higher temperatures. For example, elevated temperatures above 300 °C promoted hydrogenated yields from the depolymerization of P1000 soda lignin.<sup>[162]</sup> Transition-metal cat-



**Scheme 2.** Example of a hydrogenation reaction in which benzene is converted into cyclohexane.

alysts were used in supercritical ethanol at 300 and 340 °C, and in each case, the increase in temperature resulted in increased conversion to hydrogenated products (Table 1). TiN catalyst, made by the urea glass method, increased the monomer yield from 12 to 19 wt%; however, the hydrogenated products increased as well. Although the hydrogenated yields are less than 5% in both cases, there is an increase in yield with an increase in temperature.<sup>[162]</sup> The TiN catalyst was tested against three other types of organosolv-extracted lignin from wheat straw, poplar, and spruce. The monomer product distributions of each lignin source were very similar. Spruce depolymerization gave the highest yield, at 21 wt%, and on the lower end of hydrogenated products.

In addition to temperature, the variation in pressure can also be used to promote or inhibit the hydrogenation of aromatic products. Pressure can have effects on the hydrogenation of the aromatic ring. For model compounds, such as 2-phenoxy-1-phenylethanol (1–20 bar)<sup>[100]</sup> and *p*-cresol (25–89 bar),<sup>[120]</sup> higher hydrogen pressure leads to higher ring hydrogenation. However, if tested with extracted poplar lignin, a higher hydrogen pressure led to more aromatic yield (0–30 bar) and limited hydrogenation.<sup>[121]</sup> In model lignin, hydrogenation and HDO could be competing reactions, whereas in more complex lignin systems other reactions can occur with additional bonds and functional groups that can consume hydrogen. The complexities and heterogeneity of the lignin structure make it difficult to quantify the effect of pressure on hydrogenation because there could be a multitude of reactions occurring at one time.

## 5.2. Oxidation

Oxidation processes can be used to selectively break bonds, such as β–O–4, C–C, or aryl ether bonds, in the lignin polymer structure.<sup>[122]</sup> The β–O–4 bond is targeted for lignin depoly-

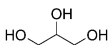
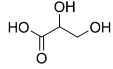

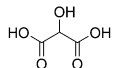
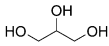
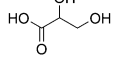

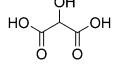
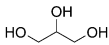
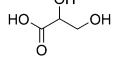

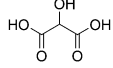
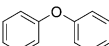


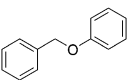


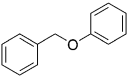


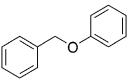


Table 2. Depolymerization of model lignin compounds.							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion [%]	Feed	Products	Ref.
1% Au/G	50	0.3	varied	50	glycerol	glyceric acid 78.5%	[97]
							
						glycolic acid 8.4%	
							
						tartronic acid 10.4%	
							
1% Pd/G	50	0.3	varied	50	glycerol	glyceric acid 80.2%	[97]
							
						glycolic acid 9%	
							
						tartronic acid 10.8%	
							
1% AuPd/G	50	0.3	varied	50	glycerol	glyceric acid 74.3%	[97]
							
						glycolic acid 9.6%	
							
						tartronic acid 11.6%	
							
NiPd/C	240	1	1.5	96	diphenyl ether	benzene (45%)	[98]
							
						cyclohexanol (46%)	
							
Pd/AC	260	0.7	10	99.7	BPE	toluene (89.0%)	[99]
							
						cyclohexanol (36.5%)	
							
Pt/AC	260	0.7	10	89.2	BPE	toluene (60.5%)	[99]
							
						phenol (36.5%)	
							
Ru/AC	260	0.7	10	94.2	BPE	toluene (81.4%)	[99]
							
						phenol (48.6%)	
							

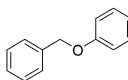


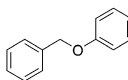


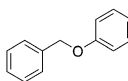


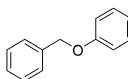


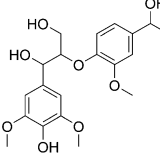

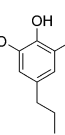
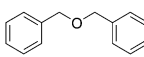








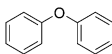


Table 2. (Continued)							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion [%]	Feed	Products	Ref.
W/AC	260	0.7	10	79.5	BPE 	toluene (40.3%)  phenol (33.8%) 	[99]
RuW/AC	260	0.7	10	99.7	BPE 	toluene (92.6%)  phenol (61.5%) 	[99]
PdW/AC	260	0.7	10	100	BPE 	toluene (100%)  phenol (29%) 	[99]
PtW/AC	260	0.7	10	98.9	BPE 	toluene (82.4%)  phenol (50.6%) 	[99]
NiFe/C	200	2	6	100	1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol 	guaiacol (100%)  PS (88%) 	[104]
FeS <sub>2</sub> /AC	250	10	2	98	dibenzyl ether 	toluene (100%) 	[105]
Ni <sub>13.3</sub> Cu <sub>11.8</sub> /Al <sub>2</sub> O <sub>3</sub>	300	1	continuous	70.3	anisole 	benzene (42.2%)  cyclohexane (27.7%) 	[107]
Pt/C	200	3.6	≈3	8.3	<i>m</i> -cresol 	toluene (62%)  3-methylcyclohexanone (23%) 	[110]
WO <sub>x</sub> /C	200	3.6	≈3	0	<i>m</i> -cresol 	none	[110]

Table 2. (Continued)							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion [%]	Feed	Products	Ref.
PtWO <sub>x</sub>	200	3.6	≈3	61	<i>m</i> -cresol 	toluene (98%) 	[110]
ReO <sub>x</sub> /AC	200	3	5	84.5	BPE 	toluene (80.3%)  phenol (62.5%) 	[140]
ReO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	200	3	5	97.4	BPE 	toluene (1.7%)  phenol (20.3%) 	[140]
ReO <sub>x</sub> /SiO <sub>2</sub>	200	3	5	50.3	BPE 	toluene (7.8%)  phenol (9.5%) 	[140]
ReO <sub>x</sub> /CeO <sub>2</sub>	200	3	5	4.7	BPE 	toluene (2.4%)  phenol (3.4%) 	[140]
Pd/C + H <sub>3</sub> PO <sub>4</sub>	250	5	2	100	4-hydroxy-3-methoxyphenylacetone 	propylcyclohexane (71%) 	[157]
Ru/HZSM-5	200	5	4	97	3,3'-oxydiphenol 	cyclohexane (100%) 	[158]
Co/TiO <sub>2</sub>	200	1	2	100	eugenol 	4-propylcyclohexanol 	[159]
NiCuLa/ZrO <sub>2</sub> -SiO <sub>2</sub>	320	17	1	85.6	guaiacol 	cyclohexane (63%) 	[160]
Ni <sub>7</sub> Au <sub>3</sub> /NaOH	100	1	0.5	33.6	2-phenoxy-1-phenylethanol 	phenol (15%) 	[161]

Table 2. (Continued)							
Catalyst <sup>[a]</sup>	T [°C]	P [MPa]	Time [h]	Conversion [%]	Feed	Products	Ref.
Ni <sub>7</sub> Au <sub>3</sub> /NaOH	100	1	15	37.2	diphenyl ether 	phenol (6.5%)  cyclohexanol (12.3%) 	[161]
[a] G = graphite.							

riorization due to the abundance of these linkages in lignin.<sup>[122]</sup> There are many different oxidants that have been employed in lignin oxidation, such as chlorines, nitrobenzene, ionic liquids, and metal catalysts.<sup>[97,106,122,123]</sup> Oxidation is generally performed under mild conditions, which makes it an attractive upgrading option. However, one of the difficulties of oxidation is limiting the reaction to the partial oxidation of bonds.<sup>[124]</sup>

There are several oxidants that can be employed for the oxidation of lignin and one way to differentiate them is by strength: strong and mild.<sup>[106]</sup> Strong oxidants, such as hydrogen peroxide, will disrupt the aromatic ring.<sup>[125]</sup> Mild oxidants, such as air,<sup>[126]</sup> oxygen,<sup>[127]</sup> and nitrobenzene,<sup>[128]</sup> keep the aromatic ring intact. Hydrogen peroxide is highly efficient, inexpensive, and may have industrial applications, but can result in products without an aromatic ring.<sup>[129]</sup> Air is sustainable, very low cost, and green; however, it may not yield the best results. Pure oxygen or oxygen-enriched air is a low cost, green, and sustainable alternative that can give improved results over air, although it presents increased hazards. The improved results may still not be selective enough or have high enough conversions. Nitrobenzene can be used; this has resulted in higher yields and being more selective to aldehydes, while keeping the aromatic ring intact.<sup>[130]</sup> Nitrobenzene is a harmful chemical and may present issues during separations. Oxidants influence product selectivity and yield, which, depending on the situation, will be another variable to consider in the lignin valorization puzzle.

In the process of oxidation, radicals form that can cause the reaction to be reversible. In addition, radicals can cause compounds to polymerize with each other to create products that are not desirable. An additional challenge is to ensure that the product does not overoxidize and break additional bonds. However, if these effects can be minimized, oxidation is a viable pathway to convert lignin into value-added products, such as phenolic monomers.

Phenolic monomers are a value-added product that can be made through selective oxidation of lignin. Lancefield et al. investigated targeting the  $\beta$ -O-4 bond by using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and zinc to oxidize the bond and depolymerize lignin.<sup>[123]</sup> DDQ was able to selectively oxidize lignin  $\beta$ -O-4 model polymers at 80 °C with success of 99% conversion at 20 mol% DDQ and 20 mol% *t*BuONO. The oxidized model compound was then treated with excess amounts of zinc and NH<sub>4</sub>Cl for selective degradation. Selective

degradation gave some good product yields with several model compounds in the 80 to 90% range. Lancefield et al. used both DDQ and zinc to depolymerize birch lignin. The oxidation method produced 5 wt% yield of an isolated phenolic monomer: 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone.<sup>[123]</sup> Oxidation was shown to work under mild conditions (80 °C) in both lignin and model lignin compounds to achieve phenolic products.

Gold, palladium, and Au/Pd over graphite catalysts were used to oxidize glycerol.<sup>[97]</sup> Palladium had a higher activity than that of gold at 50 °C, with double the activity: turnover frequencies (TOFs) of 319.8 and 151.7, respectively. Palladium was slightly more selective to glyceric acid at 80.2% and within 1% selectivity of glycolic acid and tartronic acid. The gold catalyst had an additional byproduct of hydroxypyruvic acid. With the combination of Au/Pd supported on graphite, the catalytic activity was significantly higher than that of either Au or Pd monometallic catalyst. The catalytic activity was 674.8 TOF<sup>-1</sup>, which was more than double that of Pd and more than quadruple that of Au at 50 °C.<sup>[97]</sup> The selectivity of the catalyst was similar to that of the Pd catalyst, with a conversion higher than 50%. The synergy between the two metals markedly helped the catalytic reaction.

The use of multiple catalysts in a tandem fashion to depolymerize and valorize lignin has been applied. Ru/CeO<sub>2</sub> and CuCl<sub>2</sub> were combined to react with organosolv poplar lignin to form phenols. Ru/CeO<sub>2</sub> cleaves the C–O bond through hydrogenolysis, while CuCl<sub>2</sub> oxidizes the C<sub>aryl</sub>–C<sub>α</sub> bond. If used in unison, this produced 13 wt% yield of phenol, with 2 wt% guaiacol and 0.5 wt% syringol. If Ru/CeO<sub>2</sub> was used without CuCl<sub>2</sub>, no phenols were yielded. If CuCl<sub>2</sub> was used without Ru/CeO<sub>2</sub>, only 2.6 wt% phenol was produced.<sup>[131]</sup> This strategy of combining multiple catalysts to perform different cleavages could be a key to unlocking the full potential of lignin.

Partial pressure effects were tested by using Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the catalytic wet air oxidation of sugar cane bagasse. Maintaining a total pressure of 20 bar (1 bar = 10<sup>5</sup> Pa), the oxygen partial pressure was varied from 2 to 5 and 10 bar to see how it would influence the results. A pressure of 5 bar led the highest mass fractions of the aldehydes: vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. In each case, the duration of the reaction would cause a peak for each aldehyde. This indicates that the partial pressure of oxygen has an influence on the maximum yields as a function of reaction time.<sup>[132]</sup>



## 6. Support Effects

It is ideal if the support of a catalyst has a high surface area to maximize the number of active sites available for the reaction.<sup>[133]</sup> The support can also influence the catalytic activity through steric and electronic effects. Almost any material that is thermally stable and relatively inert can be used as a support; however, not all materials are created equal.<sup>[134]</sup> One of the most common supports for biomass upgrading is AC due to its high surface area and microporosity. Expensive noble metals can be easily recovered from spent carbon, which makes it an even more attractive option.<sup>[134]</sup> Some other common supports include  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  is favorable due to its mesopores, high thermal stability, and its ability to be shaped into different structures.<sup>[134]</sup> Additionally, supports may exhibit support effects through which the metal-support interaction can influence the rates of conversion, selectivity, and products.<sup>[135,136]</sup>

Carbon can come in many forms and each form can have different support effects. Carbon nanotubes, oxidized carbon nanotubes, and thermally treated AC were impregnated with nickel and tested for the conversion of guaiacol.<sup>[137]</sup> The carbon nanotubes had the highest conversion followed by the oxidized carbon nanotubes, and AC had the lowest conversion. Hydrogenation was prevalent in all of the supports; the main products were all cyclohexane, cyclohexanol, and methylcyclohexane. The oxidized carbon nanotube catalyst was the only one to have anisole in more than trace amounts in the product; this means that oxidization could have modified the active sites, and thus, limited hydrogenation and promoted hydrogenolysis to a limited capacity. In addition, the oxidized carbon nanotube support had considerable amounts of methoxycyclohexanol, which indicated that not all C–O bonds had been cleaved. The main product of the AC support had methoxycyclohexanol followed by cyclohexanol, which could indicate that hydrogenolysis was inefficient on AC. The carbon nanotube support promoted both hydrogenation and hydrogenolysis. Compared with the oxidized nanotube support, the results indicate that the presence of acid sites is important in the promotion of hydrogenolysis.<sup>[137]</sup> Clearly, certain forms of the carbon support are more suited for depolymerization and aromatic products.

The acidity or basicity of the support can affect the products that are formed. The bimetallic RuW catalyst, with different supports, was used to depolymerize Kraft lignin after it was found to perform better than that of its monometallic counterparts. Neutral AC; acidic ZSM-5; and basic supports MgO- $\text{La}_2\text{O}_3$  (ML), MgO- $\text{CeO}_2$  (MC), and MgO- $\text{ZrO}_2$  (MZ) were used with supercritical methanol in depolymerization. Acidic ZSM-5 produced the lowest amount of methanol-soluble solids at 40 wt% and the highest amount of char at 30 wt%. Neutral AC produced the highest amount of methanol-soluble solids at 82 wt% followed closely by basic ML at 80 wt%, each without any char formation. As the basic supports became more acidic, the methanol-soluble solid yields dropped to 75 and 68 wt% for MC and MZ, respectively. MZ also had some char formation at 4 wt%, which could be attributed to it being the least

basic/most acidic of the basic supports. The number of acidic and basic sites on the surface of each catalyst were tested by using  $\text{NH}_3$  and  $\text{CO}_2$  temperature-programmed desorption (TPD), respectively. ZSM-5 had the highest amount of acidic sites with  $507 \mu\text{molg}^{-1}$  and no basic sites. AC had small amounts of acidic ( $18.6 \mu\text{molg}^{-1}$ ) and basic sites ( $0.6 \mu\text{molg}^{-1}$ ). ML, MC, and MZ each had no acidic sites and decreasing amounts of basic sites from 291 to 188.3 and  $104.7 \mu\text{molg}^{-1}$ , respectively.<sup>[138]</sup> In the depolymerization of Kraft lignin with RuW,<sup>[138]</sup> the more acidic support performed poorly, whereas, as reported by Ma et al.,<sup>[139]</sup> the support with the most Lewis acidic sites was the best. This could indicate that each case is unique in terms of support effects and would need to be determined on a case by case basis.

Some additional examples of the use of supports include Ru/C and Ru/ $\text{Al}_2\text{O}_3$  on steam-exploded corn stover, which led to different conversions and major products.<sup>[101]</sup> Ru/C had a lower conversion of 34% compared with that of Ru/ $\text{Al}_2\text{O}_3$  of 61%. Ru/C led to the formation of 25% toluene and 23% methylcyclohexane, whereas Ru/ $\text{Al}_2\text{O}_3$  led to 18% toluene and 29% coumaran. The carbon support was more selective towards toluene and promoted hydrogenation to form methylcyclohexane as well, whereas the  $\text{Al}_2\text{O}_3$  support preferentially promoted hydrogenolysis to form coumaran and toluene.<sup>[101]</sup> This suggests that the manner of adsorption of the aromatic rings to the supported noble-metal surface plays an important role in selectivity. If the aromatic ring is planar to the support, as in the case with carbon, then it will hydrogenate the ring, but if it is vertical to the support, as in the case with  $\text{Al}_2\text{O}_3$ , then it will cleave bonds through hydrogenolysis.<sup>[101]</sup>

Ruthenium catalysts on various  $\text{NbO}_x$  supports were used in the depolymerization of corn cob lignin. The molar yields of arenes and cycloalkanes were 91.1% for  $\text{Nb}_2\text{O}_5$ , 67.5% for HY-340 (commercial niobic acid), and 69.2% for niobium phosphate from the Companhia Brasileira de Metalurgia e Mineração (NbPO-CBMM). There is a correlation between the selectivity and quantity of Lewis acid sites, which follows the order  $\text{Nb}_2\text{O}_5 > \text{HY-340} > \text{NbPO-CBMM}$ . More Lewis acid sites results in a more selective catalyst towards aromatic products and higher total yield of depolymerized products, including phenolic monomers. There was significantly more hydrogenation with HY-340 and NbPO-CBMM, which indicated that there must be another defining factor. The size and dispersion of Ru particles were investigated; interestingly enough,  $\text{Nb}_2\text{O}_5$  had the highest dispersion and smallest particle size. Large particles can absorb benzene more easily, and thus, lead to greater hydrogenation than that of smaller particles. The smaller particle size of  $\text{Nb}_2\text{O}_5$  binds to the oxygen atom, rather than the benzene ring, and thus, allows for more selective cleavage of the C–O bonds. Ma et al. tested this with *p*-cresol to remove some of the complexities, and if they tested  $\text{Nb}_2\text{O}_5$  with larger Ru particles, they achieved greater hydrogenation and lower conversion.<sup>[139]</sup> Therefore, Lewis acid sites and particle size can have a large influence on Nb-supported catalysts, regarding selectivity and conversion.

Support effects of the  $\text{ReO}_x$  catalyst were tested with seven different supports (AC,  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ , ZnO, and

MgO<sup>[140]</sup> to depolymerize BPE. Acidic ReO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> had the highest conversion of 97.4%, but the selectivity towards toluene and phenol was poor, 1.7 and 20.3% yield, respectively. SiO<sub>2</sub> had a conversion of 50.3% with a very low selectivity towards toluene and phenol. Both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> created many other products, such as 2-benzylphenol, cyclohexanol, and diphenylmethane, which were most likely created through consecutive reactions of radicals. Acidic ReO<sub>x</sub>/AC had a high conversion of 84.5% and yielded 80.3% toluene and 62.5% phenol. The non-acidic and basic catalysts (CeO<sub>2</sub>, TiO<sub>2</sub>, ZnO, and MgO) all had low conversion and limited hydrogenolysis.<sup>[140]</sup>

Pore size is another factor to be considered during the selection of a support. Pores are classified into three major groups: micropores (< 2 nm), mesopores (between 2 and 50 nm), and macropores (> 50 nm).<sup>[141]</sup> Zeolite catalysts have been utilized for lignin depolymerization due their microporous structure, size selectivity, and catalytic activity.<sup>[142,143]</sup> Zeolites have very precise shaped and sizes of pores to allow certain reactants to enter, products to be formed, and/or products to exit from the pores; this can result in highly selective catalysts. However, the active sites are predominantly present inside the micropores, and larger biomass molecules may not be able to access the active site or, if they can, may be significantly limited by mass transfer.<sup>[144]</sup> Although this leads to poor performance, a possible solution is to combine micro- and mesopores to form materials also known as hierarchical zeolites. Hierarchical zeolites allow for bigger molecules to reach more active sites, improve product selectivity for these molecules, and enhance active-site accessibility because the larger molecules are less hindered by mass-transfer properties.<sup>[144]</sup>

HZSM-5 is a common zeolite used in the petroleum industry, and it can be turned into a hierarchical zeolite. Mesoporous and cerium-doped mesoporous HZSM-5 were compared with HZSM-5 in the fast pyrolysis of glucose. HZSM-5 is selective to BTX and, upon testing, had a selectivity of 76.7% and formed 34 wt% coke. Mesoporous HZSM-5 had a selectivity towards BTX of 57.9%, but instead produced more acetaldehyde, furan, and acetone, with selective yields of 16.6, 6.2, and 8.1%, respectively. The cerium-doped mesoporous material had even lower selectivity towards BTX of 39.4%; in turn, it was more selective towards acetaldehyde, furan, and acetone with yields of 25, 12.5, and 9.5%, respectively. In addition to being more selective towards different products, the hierarchical zeolites formed less coke with Meso-HZSM-5 (25 wt%) and Meso-Ce-HZSM-5 (20 wt%).<sup>[145]</sup> The hierarchical catalysts were more selective towards different molecules and produced less coke than that of microporous HZSM-5; this could be attributed to minimizing diffusion limitations. Hicks et al. also used hierarchical HZSM-5 in reactions with model lignin compounds, which enhanced the production of liquids relative to that of the microporous material. Accessibility to the pores in the hierarchical zeolite had a more pronounced role than that of the BET surface area or mesopore size.<sup>[146]</sup> Although pore size is a key component, limitations must also be noted and, depending on the desired products, could be tailored to the reaction.

The support can also play a role in hydrophobicity and -philicity, which can alter the products formed. Lignin exhibits

both hydrophobic and -philic properties and the surface of the catalyst being hydrophobic or -philic can be used to optimize catalytic activity and selectivity.<sup>[147]</sup> Hydrophilic substrates generally attach to hydrophilic surfaces and can be reacted to remove oxygen to become more hydrophobic. The effects of hydrophobicity were tested with CoS<sub>2</sub>-MoS<sub>2</sub> catalysts by adding PVP during catalyst preparation; increasing amounts of PVP increased the hydrophobicity. These catalysts were used to perform HDO on 4-ethylphenol, and the catalyst with no PVP had the lowest conversion of 85.1% and lowest selectivity towards ethylbenzene. As the amount of PVP increased in the catalyst, so did the conversion and selectivity towards ethylbenzene, with the Co-Mo-S-0.4 catalyst resulting in 96.6% conversion and 99.3% selectivity.<sup>[148]</sup> The enhanced hydrophobicity could help prevent sulfur loss and improve the stability of the catalyst, and thus, allow it to perform better.

## 7. Solvent Effects

The solvent used for the chemical conversion of lignin polymers and monomers also plays a role in the desired product distribution. The depolymerization of birch sawdust with Ni/C was tested with many different solvents. Methanol had the highest conversion of 54%. However, the highest selectivity towards PS of 75% was obtained with a mixture of 25% methanol in water. The highest selectivity towards PG of 31% was obtained with 1% methanol in water.<sup>[102]</sup> The solvent effect was also tested for the conversion of BPE with RuW/C. Methanol, 1,4-dioxane, and THF were all solvents that underperformed, with conversions of 5.9, 43.6, and 36.7%, respectively. This performance could be attributed to strong interactions on the surface of RuW/C and the high Lewis basicity of the solvent. Isopropanol, a hydrogen-donating solvent, was shown to have higher conversion than that of other solvents at 62.7%, but it promoted the hydrogenation of aromatic rings. The two best solvents were *n*-hexane and cyclohexane, which were both dipolar aprotic solvents. Cyclohexane had a conversion of 92% and *n*-hexane had a conversion of 99.7%; each with higher product yields to toluene and phenol than that of the other solvents. Neither solvent has Lewis basicity nor is a hydrogen donor, and thus, leads to the best results for BPE hydrogenolysis with RuW/C.<sup>[99]</sup> Many of these solvents were used in BPE depolymerization by ReO<sub>x</sub>/AC. Water had the highest conversion of 99.9% and highest phenol yield of 85.7%; however, the yield of toluene was low, at 41.8%. *n*-Hexane had the highest yield of toluene of 80.3%, along with a high conversion of 84.5% and a high yield of phenol of 62.5%. Cyclohexane also performed well, at 66.5% conversion and yields of 63.1 and 43.9% for toluene and phenol, respectively. Similar to the results with RuW/C, 1,4-dioxane, isopropanol, methanol, and THF did not perform as well as the apolar solvents, *n*-hexane and cyclohexane. For the hydrogenolysis of BPE by ReO<sub>x</sub>/AC, *n*-hexane was the optimized solvent because it had a high conversion and high selectivity towards toluene and phenol.<sup>[140]</sup>

The properties of the solvents used for the reaction medium were also studied with Raney Ni for the hydrogenolysis of diphenyl ether. Four major groups were tested: protic solvents

displaying Lewis basicity, protic solvents displaying no Lewis basicity, aprotic polar solvents, and aprotic nonpolar solvents. The aprotic nonpolar solvents and protic solvents displaying no Lewis basicity have the highest conversions of > 99%, and the products are almost all fully saturated. *n*-Heptane was the only solvent from the groups with no Lewis basicity to have an aromatic product, 1.5% benzene. The two groups with Lewis basicity did not have as high a conversion, ranging from 72.7% 2-propanol to 12.4% methanol. The Lewis basicity reduced hydrogenation, with methanol having the highest selectivity towards aromatic products.<sup>[149]</sup> A comparative analysis of results reported by Wang and Rinaldi,<sup>[149]</sup> for Raney Ni, and Ji et al.,<sup>[99]</sup> for RuW/C, showed the opposite trends for which Lewis basicity promoted hydrogenolysis for Raney Ni, but promoted hydrogenation for RuW/C. These results show that the effect is different for the heterogeneous catalyst used and must be taken into account for the development of processes that influence lignin depolymerization.

Lignin isolated from *Tamarix ramosissima* was depolymerized with several different solvents to see which yielded the best results. The experiments were carried out with MoO<sub>x</sub> catalyst supported on carbon nanotubes under a hydrogen atmosphere. Methanol, ethanol, isopropanol, ethylene glycol, water, and several combinations thereof were screened, with methanol producing the best results. Methanol yielded 33 wt% phenolic monomers, whereas ethanol and isopropanol yielded 21 and 30 wt% phenolic monomers, respectively. Ethylene glycol was lower, at 14 wt%, and interestingly enough, no guaiacyl monomers were formed. Water significantly dropped the yield to 7 wt%, possibly due the lack of lignin solubility, but if combined with ethanol it was able to yield 27 wt% product; however, methanol by itself still yielded the highest monomer yield.<sup>[150]</sup> The ideal solvent choice for lignin valorization will vary between the type of catalysts used and the source and type of biomass feedstock.

The solvent can also be a reactant and can contribute to the formation of additional products. Supercritical ethanol has been shown to react with catalysts and form different hydrocarbons, alcohols, esters, and more. CuMgAl catalysts were used to depolymerize soda lignin with supercritical ethanol, which resulted, in some cases, in greater than 100 wt% yield. The same reactions were carried out without lignin and this yielded many C<sub>4</sub><sup>+</sup> products. The more basic sites the catalyst had, the more products were yielded from ethanol. The combination of copper and basic sites led to the dehydrogenation of ethanol, which produced hydrogen. This additional hydrogen can increase hydrogenolysis and help to facilitate the depolymerization of lignin into monomers with a higher deoxygenated fraction.<sup>[151]</sup> Molybdenum-based catalysts with supercritical ethanol for the depolymerization of Kraft lignin also resulted in yields higher than 100 wt%. The  $\alpha$ -molybdenum carbide catalyst had a high yield of 1.64 g per gram of lignin with no char formation. Ethanol was the best solvent for Kraft lignin conversion over carbide catalysts; water, methanol, and isopropanol were tested and produced low yields.<sup>[152]</sup> The solvent choice is important not only for the solubility of lignin, but it can also play a role as a reactant.

## 8. Caveats and Pitfalls

A large amount of information is presented herein, but not all research in the lignin valorization literature can be compared easily, and some studies fail to characterize the kinetics, mass transfer, and material properties of the catalysts used for depolymerization. Mass-transfer limitations are often overlooked and can be ruled out with additional characterization.<sup>[153,154]</sup> Neglecting mass-transfer limitations may impede accurate comparisons between catalysts, especially those reactions with seemingly high conversion. As mentioned earlier in the discussion of support effects, the pore structure is an important parameter to accurately determine if solubilized lignin is able to diffuse and interact with active sites in the micropores. Zhai et al. compared multiple catalysts near isoconversion conditions for the depolymerization of organosolv birch lignin, and thus, were able to determine if mass-transfer limitations were prevalent.<sup>[104]</sup> The group also studied the influence of reaction temperature and pressure on the conversion and selectivity. Dimitratos et al. effectively tested for diffusion limitations to study the activity of Au–Pd catalysts before mass-transfer limitations prevailed.<sup>[155]</sup> The group varied mass loading and measured conversion and TOFs to test for mass-transfer limits.

A common pitfall for the development of heterogeneous catalysts is the confluence of weight percentages to the actual number and quantity of active sites on the catalyst. The use of weight percentages for the concentration of metals does not easily detail the number of atoms and molar amounts, which can vary for mono- and bimetallic systems. For example, Ji et al. compared 1 wt% Ru (101 amu) with 1 wt% Pt (195 amu), which had comparable performances, although Pt had half the number of atoms.<sup>[99]</sup> This leads to the necessity for some additional characterization, such as dispersion and chemisorption studies, to determine how the number of active sites influences the activity, but, even then, characterization is difficult because adsorbate–metal strength can differ for the two metals and can heavily influence the dispersion and TOF measurements. The calculation of TOF remains a challenge because the adsorbate binding strength and adsorbate orientation can vary from one metal component to the other. Approximations of the binding strength and dispersion can change the value of TOF by an order of magnitude. Therefore, the reader should be aware that it is hard to draw conclusions from the measured conversion values.

Another pitfall is the inadequate characterization of bimetallic synergistic interactions. There needs to be a delineation between whether metals form a solid solution in the form of alloys or core–shells or are two distinct neighboring entities on the surface. A combination of select characterization methods can be utilized to confirm the orientation of the metals, such as adsorption studies, high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDX), X-ray absorption near-edge structure (XANES), FTIR spectroscopy, and/or in situ X-ray photoelectron spectroscopy (XPS). For example, a study by Zhang et al. characterized NiAu by using HAADF-STEM, EDX, HRTEM, XRD, and XANES results.<sup>[156]</sup> This group used iso-

conversion conditions to compare mono- and bimetallic catalysts in the depolymerization of organosolv birch lignin.

Lastly, scaling developed processes from the laboratory to the industrial scale suitable for biorefineries has additional challenges for lignin depolymerization strategies. The quality and structure of extracted lignin can differ from the controlled environment of the laboratory to the same process used in an industrial setting. For example, Deuss et al. compared 27 lignin samples; 18 of the 27 were isolated in the laboratory through organosolv pretreatment, whereas the other 9 were separated by using commercial and industrial processes.<sup>[39]</sup> Overall, the organosolv pretreated lignin in the laboratory had more  $\beta$ -aryl bonds and yielded more phenolic acetyl products upon depolymerization.<sup>[39]</sup> The lignin from an industrial-scale organosolv process incurred structural damage that limited its yield. Thus, scaling complications with pretreatment and depolymerization strategies must be performed carefully to ensure high-quality lignin is maintained, to make fungible chemical products that are competitive against petrochemicals.

## 9. Summary and Outlook

The world has an abundance of lignocellulosic biomass that can be used as a renewable alternative to petrochemical feedstocks. However, most conversion strategies focus on a fraction of the available carbon content by utilizing mostly cellulose and hemicellulose, which is not sufficient for the development of economical strategies to supplant conventional feedstocks. Furthermore, strategies should be developed for the efficient upgrading of the aromatic polymeric structure of lignin. A possible solution is the realization of integrated biorefinery strategies that utilize homogeneous pretreatment methods with heterogeneous catalysis for lignin valorization. However, as this review stressed, the valorization of lignin must take results from materials science with the selection of metals, supports, and solvents to develop successful strategies.

Depolymerization and polymerization through heterogeneous catalytic pathways require further development before lignin valorization is commercially viable. Determining the ideal combination of catalyst metal(s) and support can be difficult, depending on the phenotype of the biomass feedstock, quality of the lignin source, and the desired final products. This review covered many different material design principles, with a particular focus on the use of bimetallics, supports, and solvent effects to modulate the activity and selectivity. The choice and ratio of the metal catalysts are key attributes for the selective depolymerization of the lignin polymeric structure. One can choose from cheap transition metals, such as Ni, W, or Fe, that can be coupled or alloyed with more expensive precious metals, such as Pd or Ru. Alloying of the metals can potentially improve the activity and/or selectivity compared with that of the respective monometallic catalyst components for a desired product. In addition to the type of metal, the catalyst support can influence the activity through steric and electronic effects. Additional factors to consider include the hydrophobicity or -philicity of the support surface, as well as the pore size distributions and acid or base characteristics.

Most studies rely on the optimization of catalyst processes based on model lignin compounds to mimic common linkages in lignin. The ad hoc study of trends is easier to observe due to their simplicity, in comparison with the complicated polymeric structure of raw lignin. However, there are additional factors to consider if dealing with raw lignin, for which the biomass and phenotype source, historical conditions, and pretreatment method must be considered. The polymeric structure of lignin can vary from corn stover, sugar beet bagasse, and birch, and thus, complicate the comparison of heterogeneous catalytic conversion strategies from different laboratories.

Lignin valorization strategies have made many strides in the development of catalytic processes, but additional milestones must be reached before the realization of an economical strategy. There is a need for more fundamental research that can thoroughly characterize and identify trends in how the lignin structure influences conversion strategies. Additional efforts must be made to characterize the lignin polymeric structure from different biomass sources and develop trends on how external factors influence the surface structure. The use of bimetallic heterogeneous catalysts has shown great success in achieving high yields and selectivity and is a promising step in the biomass conversion field. In-depth studies of heterogeneous catalysts will further push the design of better catalysts and integrated processes to help solve many of our chemical and fuel issues.

## Acknowledgements

Funding provided by The Center for Bioenergy Innovation in the Office of Biological and Environmental Research in the U.S. Department of Energy Office of Science.

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** biomass · heterogeneous catalysts · lignin valorization · renewable resources · supported catalysts

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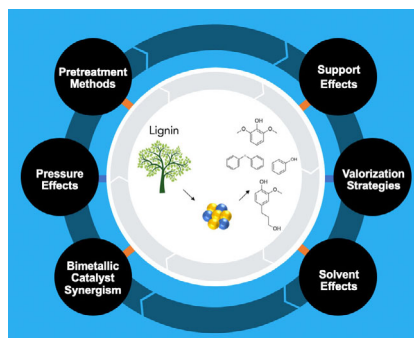
Manuscript received: January 1, 2020

Accepted manuscript online: January 3, 2020

Version of record online: ■ ■ ■, 0000

## MINIREVIEWS

**Observing the complete picture:** Current progress in lignin conversion has fostered numerous advances, but understanding the key catalyst design principles is important for advancing the field. This Minireview aims to provide a summary of the fundamental design principles for the selective conversion of lignin by using heterogeneous catalysts, including the pairing of catalyst metals, supports, and solvents.



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### **Heterogeneous Catalyst Design Principles for the Conversion of Lignin into High-Value Commodity Fuels and Chemicals**