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Complete List of Authors:	Garedew, Mahlet; Yale University, Yale School of the Environment,; Yale University, Center for Green Chemistry and Green Engineering Lam, Chun Ho; City University of Hong Kong; City University of Hong Kong State Key Laboratory of Marine Pollution Petitjean, Laurene; Yale University, Yale School of the Environment; Yale University, Center for Green Chemistry and Green Engineering Huang, Shuquan; City University of Hong Kong, School of Energy and Environment Song, Bing; New Zealand Forest Research Institute Lin, Fang; Yale University, Center for Green Chemistry and Green Engineering Jackson, James; Michigan State University, Chemistry Saffron, Christopher; Michigan State University, Biosystems and Agricultural Engineering Anastas, Paul; Yale University, School of the Environment; Yale University, Center for Green Chemistry and Green Engineering

Electrochemical Upgrading of Depolymerized Lignin: A Review of Model Compound Studies

Mahlet Garedew, †[a,b] Chun Ho Lam, †*[i,j] Laurene Petitjean, [a,b] Shuquan Huang, [i] Bing Song, [e] Fang Lin, [b,d] James. E. Jackson, [h] Christopher M. Saffron, [f, g] and Paul T. Anastas *[a,b,c]

[a] Yale School of the Environment, Yale University, New Haven, CT, 06511 USA
[b] Center for Green Chemistry and Green Engineering, Yale University, New Haven, CT, 06511 USA
[c] School of Public Health, Yale University, New Haven, CT, 06510, USA
[d] Department of Chemistry, Yale University, New Haven, CT 06520, USA
[e] Scion, 49 Sala Street, Private Bag 3020, Rotorua 3020, New Zealand
[f] Department of Biosystems and Agricultural Engineering, Michigan State University, East Lansing, MI, 48824, USA
[g] Department of Chemical Engineering and Material Science, Michigan State University, East Lansing, MI, 48824, USA
[h] Department of Chemistry, Michigan State University, East Lansing MI, 48824, USA
[i] City University of Hong Kong, School of Energy and Environment, Kowloon Tong, Hong Kong
[j] State Key Laboratory of Marine Pollution, City University of Hong Kong, Hong Kong
† These authors contributed equally

Abstract

A sustainable bio-based future necessitates the utilization of all components of biomass including lignin, which is the second most abundant biopolymer and a source of renewable aromatics. While its use for low value fuel and power production is well established, deriving further value from it via various conversion and upgrading schemes can help enable economically and environmentally sustainable and profitable biorefineries and provide opportunities to implement the Principles of Green Chemistry to minimize negative environmental impacts. As lignin is converted to phenolic monomers, dimers, and oligomers via various conversion methods, electrocatalytic upgrading of these lignin-derived intermediates offers a sustainable way to integrate renewable energy sources such as wind and solar with biomass conversion methods to make valuable products. Using this strategy, abundant low-value lignin intermediates can be used to capture excess renewable electricity in the form of chemical bonds. Furthermore, this process allows for fine tuning of selectivity via the control of electrical potential and avoids elevated temperatures and pressures, further reducing energy inputs. Herein, we present a review of recent electrochemical studies of lignin-derived model compounds. Both oxidative and reductive methods for electrocatalytic upgrading of lignin-relevant monomers are discussed as well as electrocatalytic cleavage of lignin dimers representing specific linkages. Towards framing this technology's future implementation, we also provide a perspective on the main challenges and opportunities in this growing field.

1. Introduction

Petroleum has powered human progress since the industrial revolution, supplying energy, fuels, and chemical raw materials. Use of this fossil resource on a global scale, however, has come at a cost, as reported by the Intergovernmental Panel on Climate Change (IPCC).[1] Rising levels of greenhouse gases (GHG) in the atmosphere[1] are threatening changes in climate and weather patterns through warming the planet, sea-level rise, ocean acidification, and losses in biodiversity and ecosystem services.[2] Environmental damage has also increased due to drilling and extraction in ever more vulnerable sites. Energy dependence and variable access to oil supplies have been linked to global economic and political conflicts. Replacing finite, non-renewable fossil oil with biomass as the source of chemicals and fuels would be a significant contribution to addressing these concerns. Formed by photosynthesis, biomass incorporates carbon extracted from the atmosphere (and thus already in the biospheric carbon cycle) together with energy from sunlight stored in the form of chemical bonds. Thus, the use of fuels and chemicals made from biomass would simply cycle "closed circuit" biospheric carbon rather than adding "open circuit" fossil carbon at rates that increase climate change. As an added benefit of this low-carbon "circular economy", with sustainable cultivation, plant biomass could capture, and to some extent sequester, atmospheric CO_2, helping to offset the environmental impacts of GHG emissions.[3]

Currently, various technologies are used to convert biomass and waste streams to valuable products by thermal, biological, or chemical methods.[4-6] Most commonly, biomass is either directly combusted or its carbohydrate components are fermented to produce ethanol. However, many of these current strategies have lower than desired carbon and energy efficiencies. For example, converting biomass to ethanol using fermentation only utilizes two-thirds of the biomass carbon (cellulose and hemicellulose portions)[7] and at most two thirds of this carbon becomes ethanol because of carbon dioxide co-production. In most scenarios, lignin, one of the three major components of biomass, is burned for process heat or used as a component of largely undigestible animal feed. As the most energy- and carbon-rich component of biomass, and the largest natural source of renewable aromatic compounds, lignin presents itself as a promising candidate for the production of fuels and higher-value chemicals that can displace petrochemicals.[2, 8, 9] It is reported that an estimated 62 million tons of lignin annually could be obtained from biofuel refineries meanwhile, the pulp and paper industry produces close to 50 million tons of lignin as waste each year, of which only 2% is converted to valuable chemical products such as vanillin, while the rest is burned for process heat.[4, 5, 10-12] Considering its abundance and underutilization within the biorefinery context, valorization of lignin along with all other components of biomass is essential for the sustainable operation of biorefineries. Further, the realization of sustainable integrated biorefineries also necessitates the integration of the Principles of Green Chemistry and Engineering[13-16] to avoid unintended environmental consequences and economic burdens.[16, 17]

However, the complex structure of lignin and its resistance to degradation is a major barrier for lignin valorization. Lignin is described as a complex racemic mixture of aromatic polymers produced from the oxidative coupling of three major 4-hydroxyphenylpropanoid monolignols: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.[18-20] The monolignol precursors are proposed to polymerize via random radical coupling at the β position of the side chain to form linkages such as β-O-4, β-O-5, β-β, β-1, and β-5 (Figure 1).[18, 21, 22] In other cases, cross-coupling of two lignin polymers is also proposed whereby free phenolic guaiacyl and syringyl units join together to form, for example, 4-O-5 and 5-5 linkages (Figure 1).[23-25] β-O-4 linkages, the most abundant and dominant types (approximately 45 – 50%), along with other ethers make up roughly two-thirds of lignin's linkages, while C-C bonded units account for the remaining portion.[5, 26] Unlike cellulose or other biopolymers, lignin has no regular repeating pattern;[5, 19, 27, 28] its structure varies widely from species to species, depending on the monolignol subunit distribution and the proportions of the various linkage motifs.[29] For instance, among hardwood, softwood, and grasses, the lignin content and composition vary significantly.[24] Lignin from softwood is primarily made of coniferyl alcohol units; hardwood lignin is mainly made of sinapyl alcohol units while grasses contain all three monolignols.[30] This species-specific heterogeneity in the lignin polymer and the heterogeneous slates of products that are produced upon depolymerization presents one of the major challenges for lignin valorization.[31] Recently, a more linear type of naturally occurring lignin known as catechyl lignin (C-lignin) was discovered, exhibiting a homogenous structure entirely composed caffeoyl alcohol monolignols linked together via benzodioxane linkages.[32, 33] Due to its relatively simple structure and chemistry, this material has been studied recently for its potential valorization to valuable products.[31, 32] In addition to the linkages within the polymer, lignin forms lignin-carbohydrate complexes (LCCs) via various linkages such as benzyl ethers, benzyl esters, glycosidic or phenyl glycosidic, hemiacetal or acetal, and ferulate or diferulate esters.[34] The keys to deriving value from lignin the lie in the effective disruption of LCCs, cleavage of its ether linkages, and valorization of its aromatic fragments through various lignin recovery and conversion methods.[35]

An Overview of Lignin Isolation and Deconstruction.

Lignin isolation and recovery can be achieved via two general routes. The first route includes the solubilization or hydrolysis of cellulose and hemicellulose with subsequent recovery of lignin as a residue.[6, 10, 24, 36] This method is common in ethanol processing plants; an example is dilute acid hydrolysis. The second route entails solubilization of the lignin, allowing the recovery of the insoluble cellulose and hemicellulose. Lignin is then recovered by reprecipitation from the lignin-containing liquor; Kraft, organosolv, soda, and sulfite lignin all fall under this category.[6, 10, 24, 36] More recently, along the lines of the second route, a "lignin-first" strategy for direct upgrading has been developed. This approach involves reductive catalytic fractionation which solubilizes/depolymerizes lignin in one step without additional cross-linking, selectively forming aromatic monomers un high yield.[37, 38]Aside from milled-wood lignin obtained from the Björkman process, which resembles native lignin, lignins obtained from both lignin isolation routes are reported to have altered structure and chemistry to varying degrees which can present additional challenges in downstream lignin depolymerization and valorization.[4, 39, 40] Lignin isolation and recovery methods are beyond the scope of this review but have been extensively reviewed elsewhere.[41, 42]

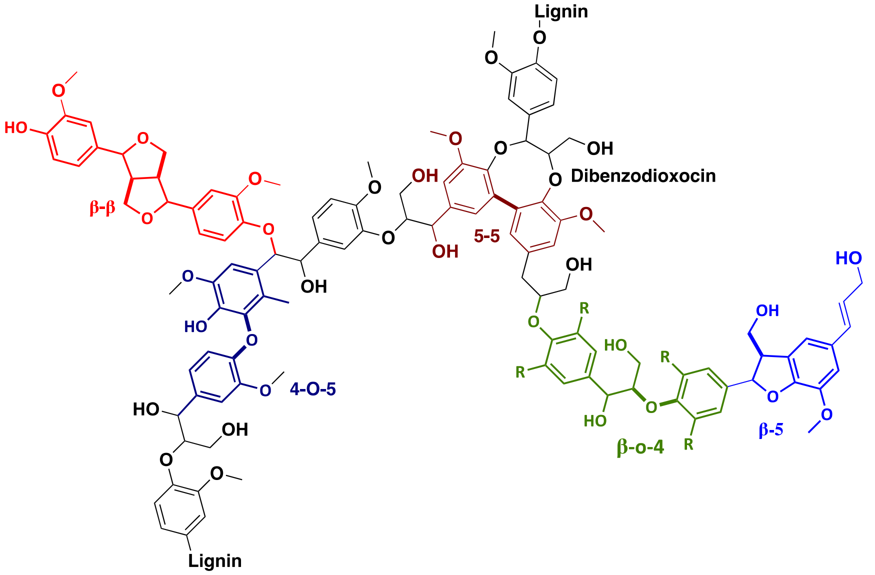


Figure 1. Common lignin linkages β-O-4, α-o-4, 4-O-5, β-5, β-1, 5-5 and β-β.

After recovery, various conversion methods can be used to depolymerize the lignin. For applications in fuel and chemical production, thermal, catalytic, and biological routes have been explored and studied extensively. These methods include thermochemical (pyrolysis, gasification, hydrothermal liquefaction, and microwave assisted), chemical (acid catalyzed, base catalyzed, ionic liquid assisted, sub- or supercritical fluid assisted, oxidative, hydroprocessing, and bioinspired/biomimetic), and biological (bacterial, fungal, or enzymatic) processes.[4, 6, 39, 40, 43-46] Many detailed and outstanding reviews have been recently published that address these advances in lignin conversion and upgrading.[4-6, 26, 39, 40, 47]

2. Scope of this Review

After depolymerization, the aromatic and aliphatic monomers as well as oligomers may need further upgrading into desired high value chemicals or fuels. While methods such as hydroprocessing and biological processing have been explored, electrocatalytic upgrading has also emerged as a greener alternative in recent years. Many reviews on the electrochemical upgrading of aliphatic biomass oxygenates derived from cellulose and hemicellulose have been published and mainly focused on 5-HMF, furfural, levulinic acid, glycerol, and sorbitol. Some reviews have also addressed the catalytic and electrocatalytic upgrading of pyrolysis oil and lignin-derived oxygenated aromatics, mainly focused on guaiacol as a model monomer.[48-56] Our group has recently published a review article on the application of electrocatalysis for direct lignin degradation and upgrading to aromatic fragments, organic acids, and/or complete degradation for hydrogen coproduction.[57] Due et al. have similarly reviewed downstream lignin processing that included electrochemical upgrading of various lignins.[47]

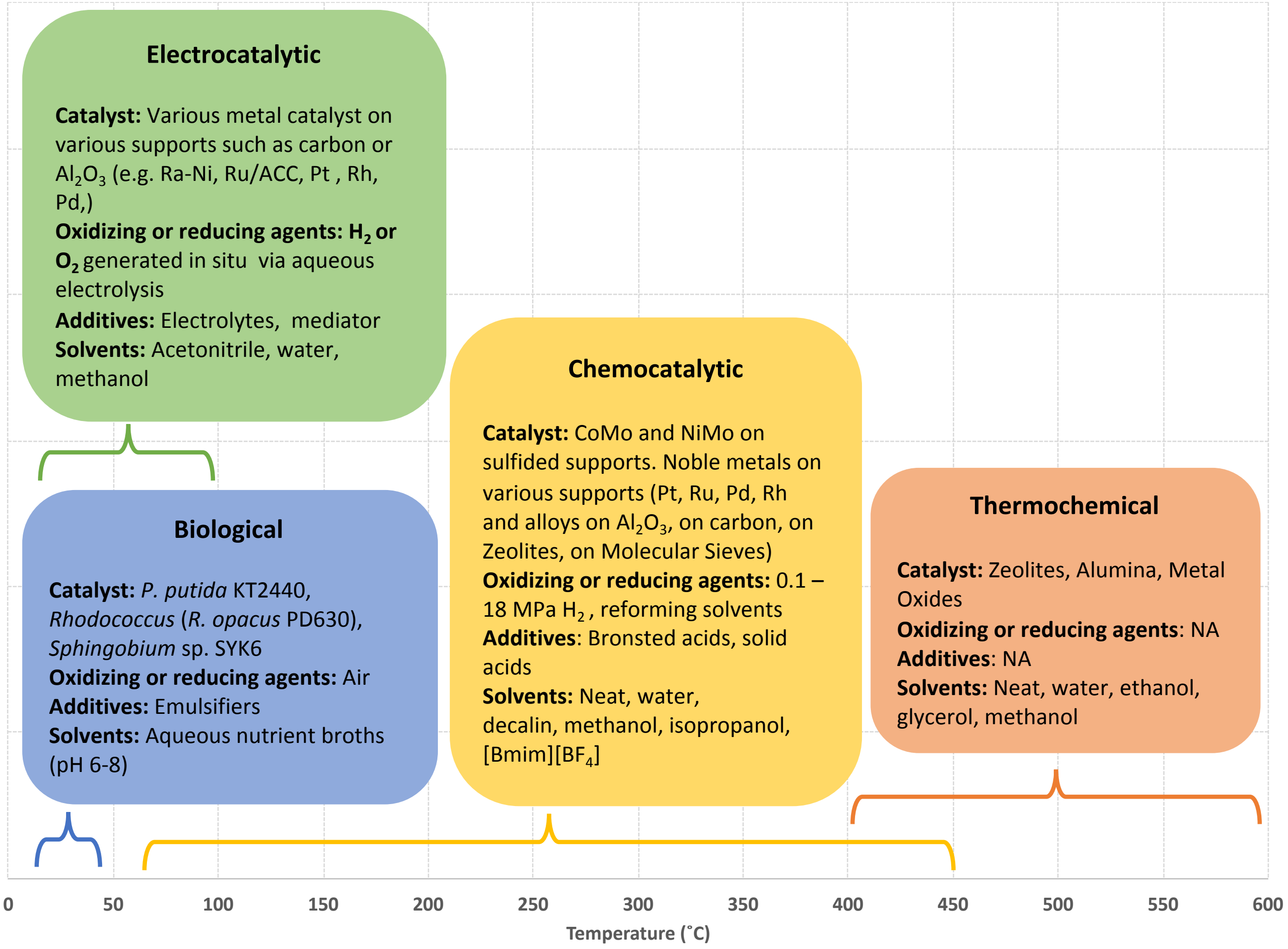
To our knowledge, a standalone review dedicated to electrocatalysis of lignin model compounds has not yet been published. Herein, we build on our previous review and discuss model compound studies that are often utilized as tools to gain more insight into electrochemical upgrading of depolymerized lignins.[58] We start by discussing green and sustainable aspects of electrocatalysis, with a brief overview of mechanisms of electrochemical biomass transformation. We then summarize various upstream methods that are used for lignin depolymerization to understand how electrocatalysis can be integrated with upstream depolymerization schemes. Then, two major areas of lignin model compound electrocatalysis are reviewed in detail: i) electrocatalytic upgrading of aromatic monomers obtained through various lignin depolymerization methods, and ii) electrocatalytic cleavage of lignin model dimers exhibiting lignin-specific linkages. Also discussed are the insights gained via the study of electrocatalytic lignin depolymerization and upgrading reaction mechanisms. Results from different reports are compared to explore points of agreement and difference, with some tentative explanations proposed. Selected reaction examples from each publication are compiled in a reaction summary table (Table 1 and Table 2). For the readers' convenience, examples involving the same substrates, including related studies from the same research group, are displayed in proximity. Finally, challenges and future opportunities are discussed.

3. Green and Sustainable Aspects of Electrocatalysis Compared to other Catalytic Methods

Lignin depolymerization has historically led to complex product mixtures; one strategy for valorization has pursued bulk conversion to fuels. Here, energy content and physical properties are more important than specific chemical composition and purity. Hydroprocessing has thus been extensively explored as a method to hydrodeoxygenate and hydrogenate biomass-derived molecules to valuable chemicals and fuels by increasing their stability and energy density.[59, 60] However, hydroprocessing suffers from challenges that can result in high capital costs and energy demands. These challenges include elevated temperatures, the need to supply pressurized hydrogen (which is often derived from fossil-based sources), and catalyst deactivation due to water and coke formation.[60, 61] Various metal catalysts and supports have been investigated (Figure 2), especially in order to increase selectivity (prevent wasteful excess addition of H_2) and limit catalyst deactivation.[62] Some authors have deemed catalytic lignin-oil upgrading not economically viable with current hydroprocessing technology.[63]

Biotechnology possesses the advantages of operating at mild reaction conditions with high catalytic efficiency and unparalleled selectivity towards targets.[31] Many lignin-derived aromatic monomers, such as phenol, guaiacol, vanillic acid and others can be converted through the action of microbes to two main intermediates: protocatechuate and catechol.[64] These platform compounds can subsequently be further transformed through ring-opening, furnishing a range of dicarboxylic acids and other value-added compounds. Biological catalysis, however, is limited to a narrow range of operating conditions in which the biocatalyst remains active; substrates must be soluble in aqueous media, and catalysts can be inhibited by various substrates or products.[31, 65] The delicate environment required for high biocatalyst efficiency and selectivity can be expensive to maintain. Also if the biocatalyst is difficult to recover and recycle, immobilization strategies may be required. The potential for engineering of biocatalysts to show higher stability and a wider range of desired selectivity, however, is currently under study to broaden their applicability.[31]

Thermochemical methods (fast pyrolysis to fuel-like mixtures or gasification to syngas) occur at modest to high temperatures, typically in the absence of a solvent or oxidant/reductant (Figure 2).[66] Pyrolysis and other thermochemical methods generate a liquid fraction (bio-oil) along with gaseous and solid (char) products.



Electrocatalytic

Catalyst: Various metal catalyst on various supports such as carbon or Al_2O_3 (e.g. Ra-Ni, Ru/ACC, Pt , Rh, Pd,)
Oxidizing or reducing agents: H_2 **or** O_2 generated in situ via aqueous electrolysis
Additives: Electrolytes, mediator
Solvents: Acetonitrile, water, methanol

Biological

Catalyst: *P. putida* KT2440, *Rhodococcus* (*R. opacus* PD630), *Sphingobium* sp. SYK6
Oxidizing or reducing agents: Air
Additives: Emulsifiers
Solvents: Aqueous nutrient broths (pH 6-8)

Chemocatalytic

Catalyst: CoMo and NiMo on sulfided supports. Noble metals on various supports (Pt, Ru, Pd, Rh and alloys on Al_2O_3, on carbon, on Zeolites, on Molecular Sieves)
Oxidizing or reducing agents: 0.1 – 18 MPa H_2, reforming solvents
Additives: Bronsted acids, solid acids
Solvents: Neat, water, decalin, methanol, isopropanol, [Bmim][BF_4]

Thermochemical

Catalyst: Zeolites, Alumina, Metal Oxides
Oxidizing or reducing agents: NA
Additives: NA
Solvents: Neat, water, ethanol, glycerol, methanol

Figure 2: Comparison of operating temperatures for lignin upgrading processes.

By comparison, electrocatalysis has been increasingly explored as a greener alternative method that offers several advantages over the other methods as outlined below:

i. In electrocatalysis, the transfer of electrons between the redox components can be powered by renewable technologies, such as wind turbines and solar photovoltaics.[67] The integration of renewable electricity sources instead of fossil fuel-derived electricity minimizes the environmental impact of the process.[68, 69] This is especially significant as bio-based molecules for energy applications as well as chemical manufacture will not only be made from renewable feedstocks but will also contain clean energy embedded in them.[70]

ii. Catalyst activity and selectivity towards desired high-value products can be achieved by controlling the electrochemical cell potential. Variation of cell potential offers much more delicate control over product selectivity than temperature, further saving on energy inputs often wasted on producing undesired side products.[71]

iii. The activation energy needed to overcome the kinetic barrier of reactions can be supplied by electrical potential instead of thermal inputs.[72, 73] Thus electrocatalysis avoids harsh conditions needed for conventional catalytic conversion and allows for many reactions to be performed at mild temperatures and pressures.

iv. In electrocatalysis, the reagents needed for redox reactions (H_2 or O_2) are derived from the electrochemical water splitting reaction. If there are systems in place to ensure proper wastewater treatment and water recycling, water is indeed considered one of the greenest reagents.[16] These reagents are produced *in situ*; kinetic barriers related to hydrogen dissociation and mass transport limitations of hydrogen gas in aqueous solvents can thus be avoided making it possible to perform reactions without the need for elevated pressures.[74, 75]

v. Electrodes serve as heterogeneous catalysts, so product and catalyst separation challenges are avoided unless the reaction requires the use of a mediator.

vi. Issues with catalyst poisoning by coke formation at elevated temperatures can be avoided in electrocatalysis by using low temperature and low cathodic potential that inhibits adsorption of anionic poisons on the electrode.[74, 75]

vii. Electrochemistry can be integrated with flow chemistry as well as real time monitoring such as *in situ* spectroscopy.[76-78]

viii. Electrocatalysis potentially allows for simultaneous oxidation and reduction reactions to be performed.

ix. Electrocatalytic systems are simple enough to be adapted to decentralized biomass processing facilities, where the biomass can be processed and upgraded near their site of harvest, further reducing costs associated with transporting low-value biomass over long distances to a centralized processing facility.

Using the US as a model, the energy content of non-food grade biomass available in 2030 cannot adequately cover what is spent in the US transportation sector today.[3] This alarming message requires that lignin be repurposed in two directions: i). lignin-to-fuels through energy upgrading to boost biomass' energy content and increase fuel yield, and ii). lignin-to-chemicals in a selective manner to enhance the profitability and the value proposition for decentralized depots and biorefineries. The advantages mentioned herein make a case for electrocatalysis as an ideal methodology to achieve these goals. In a sense, this strategy uses biomass for renewable energy storage and/or utilization for greener chemical transformations to yield needed fuels and high value platform chemicals. However, it is worth noting that there are two main disadvantages with electrocatalytic upgrading of lignin. First, connecting an electrode with the inside of a complex polymer such as lignin is geometrically impossible. Lignin must first be solubilized or fragmented prior to an electrochemical upgrading process. The issue can be circumvented by a variety of degradation methods mentioned in the previous sections, where lignin isolation and destruction are discussed. Second, a supporting electrolyte is required for standard electrolysis, and the supporting electrolyte recovery can be a cumbersome process and an economic burden to the process. This issue can be circumvented by the use of a solid polymer electrolyte to mitigate the need of adding a supporting electrolyte.[79, 80] This strategy has been employed to upgrade biomass fast pyrolysis oil electrochemically.[54]

3.1. The mechanism of electrocatalysis

Electrocatalytic transformation of organic molecules involves electron transfer between the substrates and the catalytic electrode surface.[81] The electron transfer process can occur via three different modes, i) direct electrochemical redox of the adsorbed substrate occurs at the electrode-electrolyte interface; ii) the reactant undergoes a redox reaction at the electrode-electrolyte interface to form an high-energy reactant (an intermediate) that then forms the final product by rearrangement or coupling reactions; or iii) for larger molecules whose adsorption to the electrode surface is impeded by their size, electron transfer between the electrode surface and the reactant is facilitated by a mediator and the redox of the reactant my occur away from the electrode surface (Figure 3).

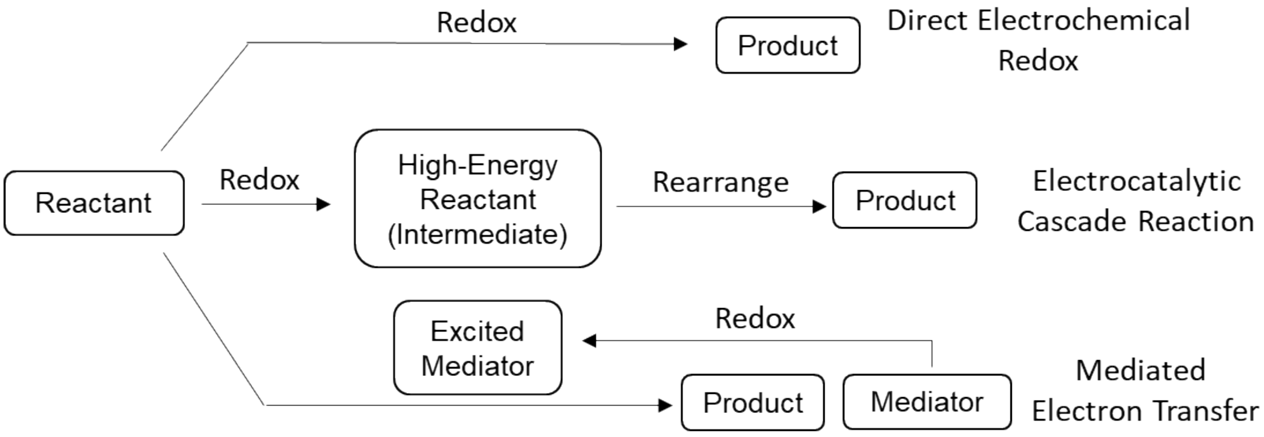


Figure 3: General reaction mechanisms of electrocatalysis for organic transformations

Often electrochemical studies are conducted in batch reactors either in an undivided cell where the anode and cathode are placed in the same compartment or in a divided cell where the anode and the cathode are placed in chambers separated from each other by an ion exchange membrane or a glass frit.[57] Undivided cells are often preferred from a cost perspective, but divided cells are used when the products formed are vulnerable to undesired reactions on the opposing electrode.[57] The reaction selectivity and efficiency can be adjusted by controlling the applied current without altering the electrolyte solvents or electrode catalysts. The applied current is typically reported as current density, which is expressed in mA cm^{-2}. However, many electrodes are not well-defined flat surfaces. Instead, electrodes are often highly porous and oftentimes present as powders. In such cases, geometric electrode area is estimated to calculate current density. In other words, the area used to calculate the current density does not always reflect the electrode's actual surface area.

Electrocatalytic oxidation (ECO) on the anode occurs via a multistep process (Figure 4). Hydroxyl radicals from water electrolysis adsorb to the metal surface and may even interact with the anode to form metal oxides (Equations 1.1 and 1.2).[82, 83] The interaction of the adsorbed organic substrate with the metal oxide, the adsorbed hydroxyl radicals, and/or free hydroxyl radicals can result in the oxidation of the organic species (Equation 1.3 and 1.4). Parallel to this reaction, dioxygen may be formed via the oxygen evolution reaction (OER) (Equation 1.5 and 1.6).[82, 83] The performance of electrocatalysis is determined by the Faradaic, or current, efficiency, defined as the fraction of charge passed that is allocated to the desired products. On the oxidation side, water oxidation and OER may divert some of the oxidizing current from desired substrate transformations and can affect the reaction's Faradaic efficiency (discussed in section 3.2).

Cathodic reactions such as electrocatalytic hydrogenation and deoxygenation (ECH) also occur via multistep processes, (Figure 4) whereby the electroreduction of water protons occurs on the catalyst surface in the cathode compartment producing chemisorbed hydrogen (Equation 1.7 and 1.8). The organic substrate is also adsorbed on the catalyst surface forming a metal substrate complex (Equation 1.9). The juxtaposition of adsorbed organics and hydrogen moieties on the catalytic metal surface is essentially similar to the scenarios envisioned for classical catalytic hydrogenation of organics; these neighboring partners then interact on the catalyst surface, adding hydrogen to the organic substrate (Equation 1.10). In some cases, oxygen-containing species (e.g. water or alcohols) may be eliminated from the bound complexes. Eventually, the reduced product desorbs from the electrode and is recovered from the bulk electrolyte. Molecular hydrogen also desorbs as gas after being formed via the Tafel and Heyrovsky reactions on the catalyst surface (Equation 1.11 and 1.12).[35, 74, 84, 85] Similar to OER in ECO, this hydrogen evolution reaction (HER) in ECH competes with the substrate transformation and can result in losses in Faradaic efficiency of the system. Various factors pertaining to the catalyst or substrate in turn have been studied and shown to influence (promote or deter) the competing HER or OER reaction vs. the substrate transformations via ECH or ECO reactions.[74, 84, 86]

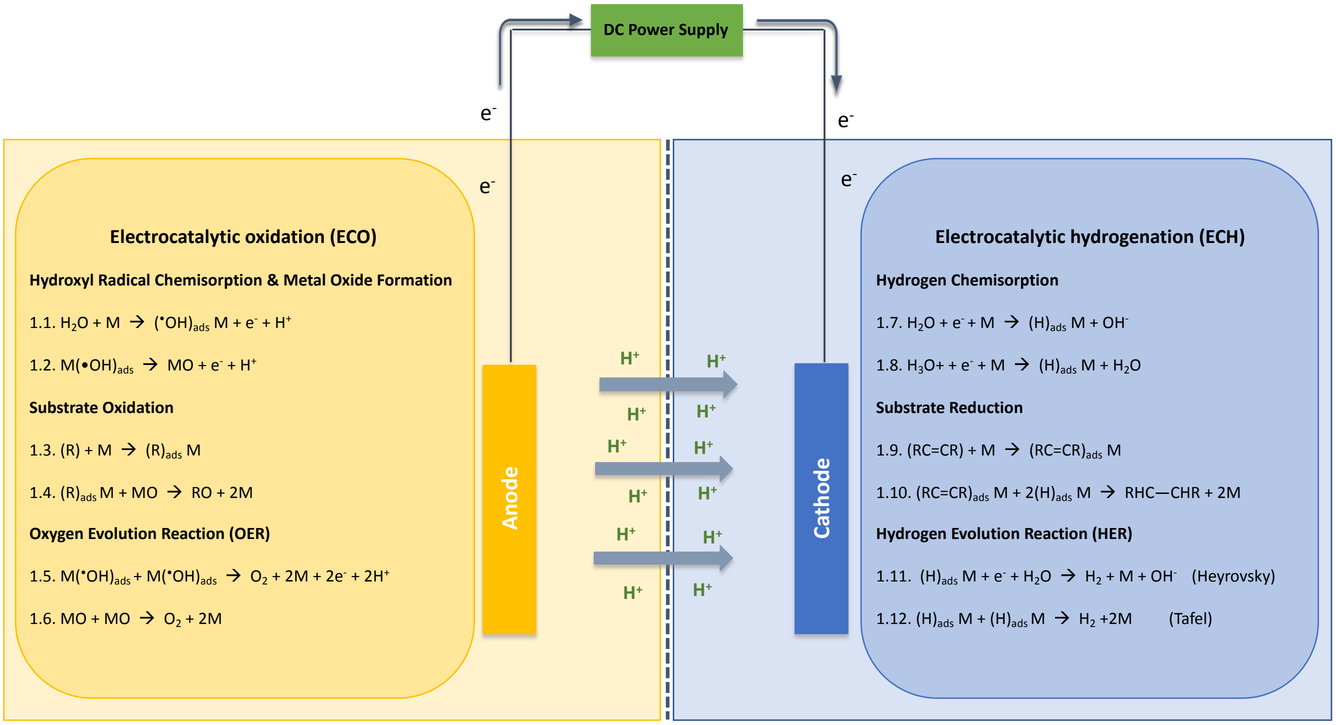


Figure 4: Mechanism of electrocatalytic hydrogenation and electrocatalytic oxidation

3.2. **Faradaic efficiency (or current efficiency)**

When multiple electrochemically active components are present in a reaction medium, electrocatalysis will proceed with any substrates adsorbed to the electrode surface and the selectivity can depend on the substrate redox potential, electrode surface texture, substrate solubility and affinity for the catalyst surface, and applied electrode potentials.[87, 88] When using aqueous electrolytes, the electrochemical redox reactions of water participate but also often compete with the desired organic electrochemical reactions. To assess the number of electrons that were spent on the desired reaction, electrochemists calculate the Faradaic efficiency (a.k.a. current efficiency). The efficiency of an electrochemical process is determined by calculating what fraction of the electrons passed accomplished the desired reaction. This quantity, computed as shown in Equation 2, is formally known as Faradaic efficiency (% F.E.) or current efficiency (% C.E.), and represents the selectivity of electrochemistry for the target reaction.

Current density optimization is often a key finding in any electrocatalysis work. Thus, % C.E. is more than just an indicator of electrochemical efficiency, it is also useful for checking if any undetected byproducts are forming. By carefully monitoring gas evolution (H_2 or O_2), the organic product distribution, and material balances, it is possible to quantify and optimize electron usage while checking for unexpected processes and products. These tools become especially important with increasing substrate complexity, where multiple parallel or sequential reaction pathways are possible.[89]

$$\% \, F.E. = \left(\frac{Mol \times F \times n}{C_{total}}\right) \times 100\%$$

Equation 2. Current Efficiency (% CE) calculation where Mol = moles of product formed; F = Faraday's constant, 96,485 C mol^{-1}; n = number of electrons per reaction; C_{total} = total charge passed.

4. Lignin Depolymerization Pre-treatments to Enable Efficient Electrocatalytic Upgrading

Many methods have been investigated and developed for the deconstruction of lignin to monomers.[90, 91] The high variability in lignin structures, along with the ensuing numerous processes for its valorization, have resulted in the production of an enormous number of individual compounds from lignins.[5, 91-93] Schutyser et al. provide a comprehensive review of the types and yields of products obtained from different lignin depolymerization processes.[94] Understanding depolymerization processes and the ensuing variability in product mixtures is essential to optimize electrochemical upgrading approaches using appropriately relevant aromatic model compounds.[8, 93, 95, 96]

Processes for the valorization of technical lignins can be broadly divided into catalytic oxidative or reductive (including electrochemical) depolymerization, acid/base depolymerizations, thermal depolymerization (such as pyrolysis) and solvolytic depolymerization.[90] In many cases, combinations of these strategies are employed. However, with the goal of producing valuable aromatic components from lignin under mild and green conditions, the selected depolymerization pre-treatment method prior to electrocatalysis should take place in an aqueous environment with minimal organic co-solvent. This avoids solvent recovery, which can be an energy intensive process,[97] between the pre-treatment and electrocatalytic upgrading steps. Thus, supercritical gaseous solvent or ammonia fiber expansion (AFEX) approaches to lignin depolymerization might not be compatible with electrocatalysis because their employment would require an addition of solvent to commence the electrocatalysis. Ideally, the chemical solvent composition between the depolymerization pre-treatment method (assuming solvent is needed) and the subsequent electrochemical upgrading should be the same to enable a single stream, in-tandem upgrading strategy. The current section outlines selected lignin depolymerization pre-treatment methods to enable a smooth transition in subsequent electrocatalytic upgrading of lignin.

Thermal treatment: Pyrolysis strategies, typically performed in the absence of oxygen at temperature ranging from 450-600°C, have been shown to be sensitive to temperature, rate of heating,[98] and the type of technical lignin used,[99-101] yielding gaseous products, char and aromatic monomers (guaiacol, syringol, phenol and substituted phenols), typically in low yields of complex mixtures (~10-40%).[102, 103] The addition of acidic zeolite catalysts during pyrolysis was shown to produce benzene, toluene, and xylenes (BTX) in the product oil,[104, 105] whereas use of a porous material without acidic sites (such as Na-ZSM5) promoted formation of substituted guaiacyl or catechyl aromatics instead.[106, 107] Although pyrolysis is relatively inexpensive compared to other chemical-based treatment, the resulting liquid fraction often has a bi- to tri-phasic composition and whole biomass biooil contains too much acetic acid, which is known to compromise its chemical stability. Pyrolysis of lignin in fluidized bed reactors has been shown to result in melting of the lignin upon pyrolysis and low bio-oil yield compared to whole biomass bio-oil.[108] These qualities make the electrocatalytic upgrading of pyrolysis oil difficult. Nevertheless, some experiments using electrochemical upgrading as a preliminary stabilization strategy have been attempted and the results were deemed promising.[54]

Treatment with organic solvents: Solvolytic lignin depolymerization combines thermal depolymerization with the action of a solvent, which can solubilize lignin and products, while promoting depolymerization.[91] Product selectivity in solvolytic lignin depolymerization is often dictated by the chosen reaction temperature,[109] as well as the biomass source and its pre-treatment.[110] Solvolytic processes have utilized protic solvents (water, methanol, ethanol, and isopropanol) as well as non-protic solvents (THF, dioxane, acetone, tetralin, naphthalene, and others), and allow the recovery of alkylated phenols and guaiacols at low temperatures, whereas higher temperatures tend to furnish unsubstituted phenols or catechols.[91, 111] Water addition promotes the production of less substituted phenolics and catechols.[112] Solvolytic approaches, provided an aqueous system is utilized, would be readily integrated into subsequent electrochemical valorization strategies.

Treatment with base: Deprotonation of hydroxy and phenolic groups can increase lignin's solubility in water. As a result, many lignin depolymerization strategies have investigated the use of bases, which are capable of cleaving the prominent β-O-4 linkage.[113, 114] Typical reaction conditions involve the use of 2-10% NaOH at high temperatures of 240-340°C.[115, 116] Milder reaction conditions, such as weaker bases and lower temperatures (< 300°C) generally provide unsubstituted or substituted methoxyphenols,[117] whereas at harsher reaction conditions, demethylation and demethoxylation reactions occur, and the product composition is shifted to polyhydroxylated phenols.[118] Base catalyzed depolymerization yields remain low (< 20 wt%), typically due to the formation of char by the intermeidates.[113, 114, 119] Strategies to circumvent these issues have included the use of H-donor solvents (ethanol, methanol, phenol, formic acid),[90, 120, 121] as well as capping agents, such as boric acid, *p*-cresol, phenol or 2-naphthol, to trap desired products (phenolate) and active sites in lignin, producing higher yields of the abovementioned products.[90, 122-125] Oxidative lignin depolymerization, which has been reviewed recently,[90, 117, 118, 126-128] has been extensively studied in alkaline solvent systems, with typical reaction conditions including the use of NaOH (0.5 - 4 M), under 2-14 bars of oxygen (as air or O_2) or with H_2O_2, at 120-200°C.[11, 90, 118, 129-131,132,133] Electrochemical approaches under alkaline conditions have succeeded in generating major products vanillin, vanillic acid and acetovanillone, including by producing the oxidant in situ.[128, 134-137] Alkaline oxidative lignin depolymerization generally uses green solvents and oxidants, and offers easy integration with subsequent electrochemical upgrading due to the use of aqueous media already rich in electrolyte and lack of complex reactants/oxidants which might require separation. Homogeneous and heterogeneous catalysts, such as salen complexes,[90, 138] metal salts[139-141] and perovskite-type oxides,[142-144] have also been employed under alkaline oxidative conditions, typically furnishing aromatic aldehydes and acids. As evidenced by the application of electrochemistry in alkaline and alkaline oxidative lignin depolymerization (already reviewed elsewhere[57]), the use of aqueous basic systems can be ideal for further integration with electrocatalytic upgrading.

Treatment with Acid: Reactions of lignin with soluble or solid Lewis acids, soluble Bronsted acids, acidic ionic liquids, and organic acids have been tested over a wide range of temperatures (140-400°C) and solvents (water, methanol, ethanol, isopropanol, formic acid, dioxane, etc.).[90, 117] In general higher temperatures have been found ot give higher yields of catechol products, while methoxyphenols are obtained at milder reaction conditions.[118] Acid-catalyzed lignin breakage of β-O-4 bonds can occur via the formation of a benzylic cation after dehydration, which can degrade via two pathways, thus either forming aldehydes, or yielding Hibbert's ketones.[145-150] Methodologies including acetal formation, reduction, and decarbonylation have been devised to trap reactive aromatic monomers, such as aldehydes, prior to degradation.[151-155] Catalysts such as polyoxometalates (POMs), Cu, Fe, or Co metal salts, methyl trioxo rhenium (MTO) complexes,[29, 156, 157] as well as metallosalen and metalloporphyrins,[127] in combination with either H_2O_2 or O_2, have been utilized in acidic media (aqueous, mixed aqueous/organic solvents, ionic liquids, or deep eutectic solvents) to effect lignin depolymerization.[128, 134 158]

Treatment with ionic liquids: Dier et al. used 1-ethyl-3-methylimidazolium trifluoromethansulfonate and triethylammonium methanesulfonate with water to convert commercial (alkali and organosolv) lignins through electrochemical production of H_2O_2 to furnish homovanillic acid and vanillic acid as the major products.[158] Most organic-based ionic liquids exhibit high electrochemical windows, and their ionic nature can provide some degree of conductivity. However, the high cost of ILs, together with concerns as to their environmental toxicity and the ongoing debate over their greenness might not make them ideal choices in the field of Green Chemistry.[159, 160] Also, extraction of the aromatic products from ILs could be challenging especially when the aromatic products contain multiple ionic hydroxyl or carboxylic acid groups.

Catalytic approaches: Product distributions in a reductive catalytic approach are dependent on the technical lignin used,[161, 162] the catalyst,[163, 164] the temperature of the process, and whether a terminal reductant is added externally or generated in situ, such as with reforming of solvent systems (water, methanol, isopropanol, formic acid, ethanol, glycerol).[94] In milder reductive catalytic hydrothermal conditions, alkyl-substituted methoxyphenols are obtained,[111, 165, 166] while at harsher reaction conditions, reductive catalytic processes also perform demethoxylation and deoxygenation of aromatics.[167-169] Reductive catalytic depolymerization of lignins evidenced the importance of the preservation of reactive linkages such as the β-O-4 bond during lignin isolation.[162] In addition to novel lignin stabilization strategies during pre-treatment[170], efforts have now evidenced the potential of depolymerizing lignin directly from raw lignocellulose, thereby performing lignin isolation and lignin depolymerization in one step.[37, 171] This strategy, commonly termed lignin-first or reductive catalytic processing, has been performed over a wide range of catalysts (Ra-Ni,[172-175] Pt/C,[176, 177] Ni/C,[178, 179] Pd/C,[180-182] Cu-PMO,[183] Ni-W_2C.AC,[184] and others[38, 185-187]), at 140-250°C, in various solvents (methanol, ethanol, water, dioxane, etc.) and with added pressurized hydrogen or a solvent hydrogen donor. It has proven selective and high yielding, typically furnishing C3-fragmented phenolics.[94] Along with monomeric aromatic products, the process, starting from lignocellulosic biomassfurnishes a carbohydrate solid fraction as well as oligomers and dimers present in the lignin oil.[188] Several studies demonstrated the potential to depolymerize catechyl lignin (C-lignin) through reductive catalytic depolymerization of isolated organosolv C-lignin or through lignin-first valorization of the lignocellulosic biomass.[170, 189-192] In all studies, the major compounds obtained include 4-propylcatechol, 4-(3-

hydroxypropyl)catechol, 4-propenylcatechol and 4-(3-methoxypropyl)catechol. Whereas some instances of reductive catalytic lignin valorization are performed in water, most of the examples utilize protic solvents that would need to be recovered prior to an electrochemical upgrading step. Lignin-first approaches, particularly if performed in water, may introduce polysaccharide-derived small molecules in the lignin oil, including acids, that increase the complexity of subsequent electrocatalytic lignin oil upgrading.

Overall, a wide range of compounds are obtained from lignin depolymerization, which can be rationalized and predicted by assessing the nature of the lignin feedstock, the chosen catalyst, the selected strategy, and corresponding process variables.[90, 94] Typically, product mixtures obtained from lignin are complex, a feature which should be replicated with fidelity in studies that utilize model compounds to explore upgrading strategies. In addition to the wide range of phenolic monomers typically targeted, lignin depolymerization oils also contain dimers and oligomers that are difficult to characterize and quantify.[188, 193] Oligomers found in the lignin depolymerization oil lack the typical aryl-ether linkages, which are degraded during the lignin depolymerization process.[188] These substrates should also be considered in upgrading processes to ensure the full utilization of the lignin biomass.

5. Electrocatalytic Treatment of Lignin-derived Model Compounds

As summarized in section 4, depending on the depolymerization method, the resulting complex lignin oil contains a variety of monomers, dimers, and oligomers.[194] Transformation of such oxygenated aromatics to commodity chemicals and fuels offers potential paths to a sustainable biobased economy. Lignin has a higher energy content than cellulose and hemicellulose but is still significantly lower in heating value than gasoline or diesel. The energy gap between lignin and commodity fuels could be closed by hydrodeoxygenation (HDO) to boost the H:C and C:O ratios for better fuel. Aliphatic and aromatic π-bond hydrogenations are therefore of great interest to the biofuel community. Because of the extra stability induced by the aromaticity, the hydrogenation of aromatic π-bonds typically requires the use of precious metals or harsher reaction conditions. Electrocatalysis can mitigate those energy-demanding needs. ECH of aromatic π-bonds can occur below the boiling temperature of water at atmospheric pressure with or without precious metal catalysts. In general, ECH of oxygenated organics in neutral to basic environments can hydrogenate carbonyl or alkenes functional groups to yield alcohols or alkanes, respectively.[75, 195, 196] However, in acidic environment, the product alcohol group may undergo dehydration to yield alkenes, followed by another ECH treatment to afford alkanes.[197] Alternatively, ECO offers pathways for monomer oxidation to make valuable organic acids, as well as the oxidative cleavage of β-O-4 linkages needed to deconstruct the lignin polymers, oligomers, or dimers that might be found in depolymerized lignin oil mixtures. The following sections comprehensively discuss both oxidative and reductive upgrading of lignin-derived model compounds.

5.1. Electrocatalytic upgrading of monomers

Phenol, guaiacol, and syringol are frequently chosen as model compounds in catalytic studies aimed at lignin upgrading. They are simple, aqueous-friendly, easy to handle, cheap, and they represent substructures that are abundant in the complex lignin matrix and in the product mixtures from various lignin pretreatments. Of these three, guaiacol is most often chosen because of the extra methoxy moiety vs. phenol, while being less complicated than syringol (two methoxy groups) in terms of structure and product mix.

5.1.1. Reductive approach. Li et al. used an activated carbon cloth supported ruthenium (Ru/ACC) prepared by an incipient wetness method to perform ECH on different oxygenated aromatic monomers. Phenol, guaiacol, and syringol were introduced individually into a cathode chamber under constant current electrolysis conditions at 80 °C. For phenol, cyclohexanol was the only main product. However, for guaiacol and syringol, the reaction produced a mixture of aliphatic products that are partially hydrogenated and demethoxylated. In guaiacol's case, *cis*-methoxycyclohexanol was formed 2-3 times more than its *trans*- counterpart. In all cases, no cyclohexane was detected. However, cyclohexane could have vaporized due to its low boiling temperature and poor solubility in ionic solvent.[198] Similarly, as a control experiment during a dimer degradation study, Cyr et al. reported the ECH of guaiacol using a Raney-Nickel cathode, which is the only non-precious porous material that can hydrogenate aromatic π-bonds in ambient conditions; it was found that phenol and cyclohexanol were produced.[199]

Lam et al. studied the ECH of guaiacol and its derived monomers in detail.[195] At 60 °C and atmospheric pressure, guaiacol was demethoxylated and hydrogenated to exclusively yield cyclohexanol with only traces of methoxycyclohexanol formed. The exclusive selectivity for aryl C-O hydrogenolysis triggered a series of mechanistic studies with different substituted alkoxyphenols (3-methoxy, 4-methoxy, 2-ethoxy, and 2-isopropoxy). It was proposed that the aryl–OR ether bond cleavage most likely occurred through a hydroxy coordinated mechanism, where partially hydrogenated guaiacol undergoes demethoxylation to yield phenol before becoming cyclohexanol. An adsorption study was also conducted using phenol and *p*-cresol as competitive substrates to confirm that phenol desorbed from the surface upon its formation, and then re-adsorbed onto the electrode to yield cyclohexanol. As with Li's work, no cyclohexane was detected, which could have been due to vaporization. A similar mechanism applied to syringol, which also underwent demethoxylation to yield a mixture of guaiacol, phenol, and cyclohexanol at a prolonged reaction time.

Zhou et al. also studied ECH of guaiacol using a PtNiB nanoparticle supported on a mesoporous carbon catalyst (PtNiB/CMK3) in a flow fuel cell. The system scored a much higher % C.E. at 86.2% compared to Lam's and Li's ECH work on guaiacol, which were 26% and 30%, respectively. Zhou also showed the system was able to demethoxylate guaiacol to yield phenol. Under optimized conditions, cyclohexanone was observed as the major intermediate instead of phenol, which agrees with Lam's and Li's observations. Overall, Zhou's electrocatalytic system exhibits a much higher % C.E., probably owing to the nanoparticle size and the presence of Pt.

Interestingly, in terms of cathode preparation, the PtNiB/CMK3 is more similar to that of Li's Ru/ACC, as both utilized a highly porous carbon support to maximize the precious metal catalytic performance. However, the product distribution from the PtNiB/CMK3 is similar to that reported by Lam's Raney-nickel cathode, where demethoxylation occurred almost exclusively prior to the full hydrogenation of the aromatic ring. Perhaps the presence of the nickel nanoparticles was responsible for comparable product selectivity between Lam and Zhou's systems or maybe it was the similar current density. Based on the geometric area of the electrodes, Lam's Raney-nickel was applied at 8 mA cm^{-2}, Zhou's at 5 mA cm^{-2}, and Li's at 10–40 mA cm^{-2}. In fact, Li also noted that product selectivity for demethoxylation improved as current density decreases. The control of selectivity by current density is not unprecedented, as glycerol upgrading to different products has been performed with the selectivity tailored by adjusting the current density.[200] The interplay between current density and selectivity towards demethoxylation deserves further investigation.

Song et al. compared ECH and thermal catalytic hydrogenation (TCH) of phenol on carbon-supported platinum and rhenium catalysts (Pt/C and Rh/C). The metal-loaded carbon powder catalysts were made conductive by circulating them inside of a reticular vitreous carbon (RVC) electrode. Both catalysts managed to hydrogenate phenol to cyclohexanol, but Rh/C displayed better yield compared to Pt/C under both ECH and TCH conditions. Notably, they showed that the TCH and ECH of phenolic compounds followed similar routes via hydrogenation, hydrogenolysis, and hydrolysis with similar selectivity. However, ECH rates were higher than TCH when conducted at potentials greater than -0.7 V vs Ag/AgCl due to enhanced hydrogen coverage at the electrode surface. To study the role of hydrogen adsorption, the H_2 from HER was recycled and kept in the ECH reaction chamber. It was found that the turnover frequency (TOF) of phenol hydrogenation in the H_2-recycled ECH reaction matches remarkably well with the TOFs of those reactions conducted individually. This implies that the two hydrogenation processes (TCH and ECH) operated independently from each other.[201] In a subsequent study, several substituted phenolic and dialkyl ether model compounds were subjected to the optimized ECH conditions. For 4-methoxyphenol, only 10% of the products underwent demethoxylation. The selectivity in hydrogenation versus demethoxylation of 4-methoxyphenol is significantly different than that of Lam's, where almost 50% of the 4-methoxyphenol was demethoxylated. While both reaction conditions and the catalyst used are vastly different, the divergence in selectivity must be explored. Notably, Lam[195], Song[201], and Garedew[202] all confirmed that the demethoxylation steps did not occur from the methoxycyclohexanol, but during the aromatic hydrogenation step.

Sanyal et al. did a follow-up study on Song's work by adding Pd/C to the previous Pt/C and Rh/C comparison study. It was found that Pd/C was catalytically inactive for aromatic hydrogenation of phenol.[200, 203, 204] However, when the same set of precious metal catalysts were used for the ECH of the non-aromatic fragment (e.g. carbonyl group of benzaldehyde), Pd/C exhibited the highest activity and the greatest C.E.%, better than that of Pt/C and Rh/C.[200] The results suggest that the most active catalyst for aromatic ring hydrogenation may not display the same pattern of reactivity towards carbonyl groups. Similar aromatic reactivity was reported by Zhao et al., who examined the ECH of phenol with different metal-plated graphite cathodes (M/G).[197, 205] Pt and Rh showed over 50% yield of phenol, while Pd showed only trace conversion products. Plain graphite and nickel were attempted but neither gave any cyclohexanol. Although the catalytic procedures between Zhao and Song are different, their results agreed that Pd is a much less effective catalyst for aromatic π-bond hydrogenation than are Pt and Rh. With Pt/G (Pt on grapgite), Zhao observed cyclohexane formation from phenol in variable amounts. The highest yield of cyclohexane at 30.4% was obtained in optimized acidic conditions. No benzene was observed, suggesting that the cyclohexane was formed from cyclohexanol as opposed to directly from phenol.[197] Later, Sanyal et al. further investigated the influence of particle size on the ECH of aromatic and carbonyl compounds (phenol and benzaldehyde).[204] Interestingly, it was observed that reaction turnover frequency (TOF) of phenol ECH increases as the Pt particle size increases. Across all the particle sizes that were examined, cyclohexanone was the main product, followed by cyclohexanol. This positive correlation between the Pt particle size and the ECH TOF was rationalized by the possibility that more (100) and (111) planes are exposed as the Pt particle size increases, and that those planes were responsible for improved the TOF of ECH of phenol.

Garedew et al. studied the ECH of various guaiacol-derived model compounds including phenol, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol using a Ru/ACC cathode adopted from Li et al. All substrates were upgraded to their corresponding alkylcyclohexanols in moderate yield. Moreover, the increase of alkyl chain length was shown to be a key factor in suppressing the conversion of the model compounds.[202] In Sanyal's work, based on a gas-phase analysis, substituents (e.g. hydroxyl and aldehyde groups) was attributed to decrease the adsorption energy of the substrates on the electrode surface, an effect exacerbated by up to 25% in solution phase.[203, 206, 207]

Recently, Wijaya et al. conducted a comprehensive study of electrolyte and proton concentration effects on ECH of guaiacol and phenol using a stirred slurry reactor with dispersed 5 wt% Pt/C catalyst in the cathode compartment.[208] Comparing different pairs of acid (H_2SO_4), neutral (NaCl), and alkaline (NaOH) catholyte–anolyte combinations, they found that the acid-acid and neutral-acid pairs were the most effective, resulting in the highest conversion and Faradaic efficiencies. While alkaline-acid electrolyte resulted in 0% conversion, presumably because deprotonation of the substrate hinders its adsorption on to the negatively charged cathode surface and/or the instability of the Pt/C catalyst in alkaline medium leads to Pt loss from the carbon support. Aside from the alkaline-acid electrolyte pair, guaiacol substrate could be upgraded to cyclohexanol, cyclohexanone, 2-methoxycyclohexanol, 2-methoxy-cyclohexanone, and phenol along with the methanol byproduct under constant current electrolysis conditions at 50 °C in the other electrolyte pairs. Additionally, the phenol substrate could be upgraded to cyclohexanol and cyclohexanone. Further, mechanistic studies revealed that although the acid dissociated protons could be involved in the reaction, the primary proton supply for ECH reactions comes from water splitting at the anode.[208] In a follow-up study, they compared the conversion, product distribution, and Faradaic efficiency of phenol and guaiacol ECH reactions over Pt/C, Ru/C, and Pd/C catalysts using varying concentrations of the acid-acid and neutral-acid catholyte-anolyte pairs in a stirred slurry reactor. The result showed that Pt/C has superior activity in the acid-acid electrolyte pair, while Ru/C and Pd/C catalysts need neutral-acid catholyte-anolyte pairs to achieve better activities. Pt/C exhibited higher activity than Ru/C and Pd/C, in the acid-acid or neutral-acid pairs, possibly due to enhanced metal dispersion and larger surface area on the Pt/C material compared with the other two. For guaiacol ECH, ring saturation without demethoxylation to produce 2-methoxycyclohexanol was the dominant pathway. However, when Pt/C catalyst was used in neutral-acid electrolyte (0.2 or 0.5 M NaCl -0.5 M H_2SO_4), guaiacol demethoxylation proceeded through aromatic ring hydrogenation to competitively yield cyclohexanol and cyclohexanone. For phenol ECH, all conditions produce cyclohexanol and cyclohexanone, which is similar to most of the reported phenol ECH reactions.[209] Based on the results from these studies, Wijaya et al. concluded that the adsorbed hydrogen atoms on the cathode were mainly responsible for the ECH of guaiacol and phenol.[208, 209] Overall, the slurry reactor configuration allows catalysts to be suspended in the electrolyte, thus possibly offering higher active surface area and effective liquid-solid mass transfer, resulting in superior conversion efficiency.

A slurry reactor configuration could potentially offer many advantages for electrochemical biomass waste valorization. In addition to increasing the active surface area and liquid-solid mass transfer mentioned in Wijaya's studies, facile removal of the solid electrocatalyst coupled with the intrinsically high surface area makes this strategy suitable for industrial applications.[208] Besides, the separation of catalysts from the electrode brings more flexibility for catalyst design. However, in most reported ECH slurry reactors, the reactions only occur if the suspended catalyst particles are in contact with the electrode directly, implying that a large surface area electrode is preferred in order to maximize the electron transfer between the electrode surface and the slurry electrocatalyst. It should be noted that the reaction rate is ultimately dictated by the applied current and by the electron transport between the electrode and the slurry catalyst. [210, 211] Recently, Liu et al. reported a dual-catalyst electrochemical system by adding water-soluble silicotungstic acid (SiW_{12}) into the Pt/C suspension in the cathode chamber. The SiW_{12} acts as an electron transfer catalyst, distributing electrons to every suspended Pt/C catalyst from the electrode. Extremely high conversion efficiency (>99%), working current density (up to 800 mA cm^{-2}), and Faradaic efficiency (>99%) for ECH of phenol, guaiacol, and other bio-oil hydrocarbon compounds were achieved.[212] Compared with most reported current densities (less than 40 mA cm^{-2}) and Faradaic efficiencies (lower than 50%), Liu's work improved the conversion efficiencies of biomass ECH upgrading reactions by almost 20 times in the operating current density and 2-5 times in the Faradaic efficiency.[197, 201, 211, 213-217] Furthermore, complete deoxygenation of phenol to yield cyclohexane (~10%) also was observed when substrates were consumed. In terms of product distributions, phenol was primarily upgraded to cyclohexanol (82.9%), cyclohexanone (0.3%), and cyclohexane (16.8%) in high Faradaic efficiency (90.9%) in less than 10 min under a very high operating current density of 250 mA cm^{-2}. This current density could be further increased to 800 mA cm^{-2} under optimized conditions to give a slightly improved Faradaic efficiency value of 95.3%. For guaiacol, the products consisted of cyclohexane (11.6%), methoxycyclohexane (8.3%), cyclohexanol (56.0%), cyclohexanone (7.6%), 2-methoxycyclohexanone (11.7%), 2-methoxycyclohexanol (4.3%), and phenol (0.5%).[212] Overall, Liu's route provides a great electrochemical system with high Faradaic efficiency, but scaling and application of this system could be hindered by the need to separate the water-soluble electron transfer catalyst (i.e. SiW_{12}) after reactions.

The electrocatalytic transformation of guaiacol and its derived units have been studied by several authors using different electrocatalysts in an aqueous environment. Selectivity between C-O hydrogenolysis and aryl C=C hydrogenation were reported and compared in various conditions. In general, whether guaiacol is converted to phenol or to 2-methoxycyclohexanol from demethoxylation or hydrogenation, respectively, appears to be dictated by the magnitude of the current density. As a general observation, low current density (<10 mA cm^{-2} based on geometric area of the electrode), favors demethoxylation while higher current densities favor full hydrogenation. Several authors have verified that 2-methoxycyclohexanol does not demethoxylate to yield cyclohexanol.[195, 202, 214] Under strongly acidic conditions, cyclohexane is detected, presumably formed from the dehydration of cyclohexanol to cyclohexene, followed by the hydrogenation of the olefin bond (Figure 5).

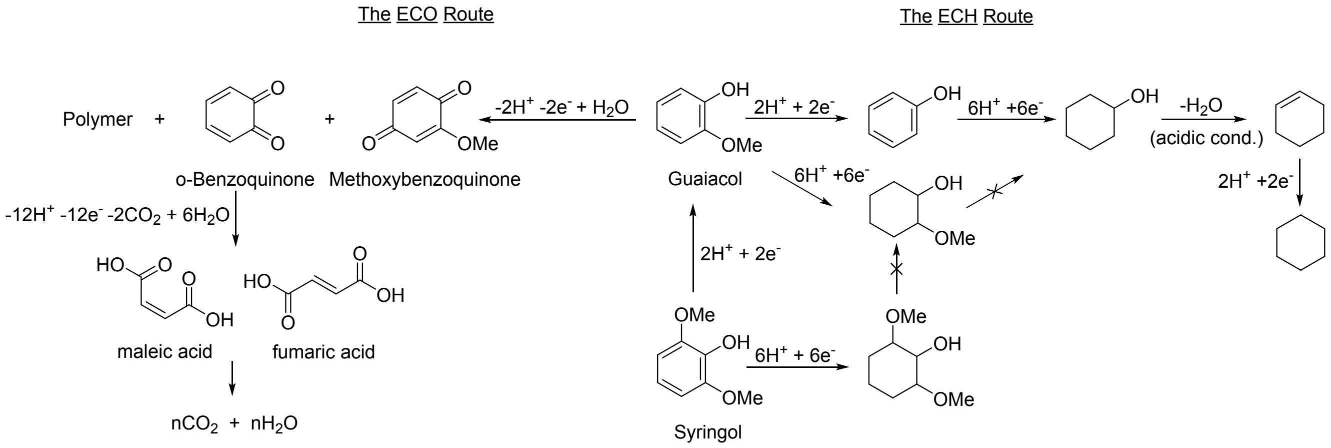


Figure 5. General electrocatalytic redox scheme for reactions of phenol, guaiacol, and syringol.

5.1.2. Oxidative approach. Compared to ECH, electrocatalytic oxidation (ECO) of guaiacol has received less attention. compared to ECH, This imbalance presumably reflects the challenges of collecting the oxidation products and the tendency of phenolic compounds to polymerize on the electrode surface.[218] Electrocatalytic oxidation (ECO) of guaiacol has been investigated on precious metals that have high overpotentials. The tentative mechanisms of oxidative degradation have been proposed, and it was suggested that guaiacol undergoes irreversible 1- or 2- electron transfer to become a phenoxy radical or a phenoxonium cation, which tin an aqueous electroyte may then form *o*-benzoquinone, methoxybenzoquinone, and polymer (Figure 5).[219] It has also been reported that SnO_2 and PbO_2, which favor oxygen atom transfer, can lead to ring-opening products, such as maleic acid before mineralization to CO_2 and H_2O (Figure 5).

As a subsequent mechanistic study to their earlier lignin degradation work, Shao et al. studied the oxidative degradation of guaiacol on titanium supported antimony oxide (Ti/Sb-SnO_2) and lead oxide (Ti/Pb_3O_4) electrodes.[220] Both anodes managed to mineralize guaiacol to CO_2 and H_2O, but their mechanisms are suggested to be different. In an adsorption study of guaiacol using cyclic voltammetry (CV), the current change was examined before and after guaiacol addition. With the Ti/Sb-SnO_2 anode, no current boost was seen upon addition of guaiacol, which indicated only a small fraction of guaiacol was adsorbed on the electrode surface. This implies that the oxidative degradation of guaiacol was achieved via hydroxyl radicals, not on the Ti/Sb-SnO_2 surface. The scenario is much different than that of Ti/Pb_3O_4, which showed a current increase. This suggested that a large amount of guaiacol was adsorbed and degradation most likely took place on the surface. The Ti/Sb-SnO_2, however, was shown to be a more effective catalyst for guaiacol degradation. In both cases, dimerized guaiacol was observed in variable quantity. It is worth noting that quinone and maleic acid were formed as key intermediates during the degradation. If selective termination can be achieved, these intermediates have great potential as platform chemicals. Maleic acid, fumaric acid, and their hydrogenated form, succinic acid, are among the "top 12 as designated platform renewable chemicals" by the US-DOE.[221]

5.2. Electrocatalytic conversion of lignin fragments: lignol dimers

Beyond monomers, dimer degradation and upgrading are also of great interest since degradation of the linkages in lignin is the first step toward valorization. In general, ECH studies have focused most on model compounds that represent lignin's 4-O-5 and α-O_4 linkages, whereas ECO is more commonly applied for β-O-4 bond cleavage. Most ECO of β-O-4 bonds focuses on selective oxidation of the α carbon hydroxy group, which can weaken the bond energy between the α and β carbons by about 40 kJ mol^{-1}.[222] To this end, mild anodic surface-driven or mediated oxidation are frequently explored to selectively oxidize the α carbon hydroxyl group.

5.2.1. Reductive approach. An early study by Mahdavi et al. investigated the ECH of various benzyl phenyl ethers (molecules of α-O_4 linkages) in a mild reductive environment (25 – 40 °C, 1 atm). Using a Raney-nickel electrode in ethanol-water (75:25, 0.1 M NaCl) as the electrolyte, the reaction proceeded with perfect selectivity, first by hydrogenolysis, then by hydrogenation of the monomers, while no direct dimer hydrogenation aliphatic products were observed (Figure 6). The study suggested that ECH was a feasible technique for lignin depolymerization by reducing the C-O linkages with a remarkably high current efficiency of 60 – 80%.[223] Several other groups have looked at the 4-O-5 bond scission using a different electrocatalyst. Park et al. and Wu et al. have also studied the aryl ether dimer cleavage in an undivided system using 4-phenoxyphenol as a model compound on Pd[89] and Pt[224] respectively as active metals. Although their cathodes and systems were prepared differently, both resulted in 60% conversion with phenol as the major product; Wu et al. further demonstrated that adding sodium borohydride ($NaBH_4$) facilitated high conversion (90%).[224] Although the mechanism has not been proven definitively, it appears that the $NaBH_4$ may be protecting the resulting aromatic monomers from anodic oxidation and contributing reducing equivalents (20% of the hydrides needed) to the reduction. Cleavage occurs preferentially to produce aromatic monomers that bear at least one aryl C-O bond. Also, the resulting aromatic monomer survived the reducing and oxidizing power from the cathode and anode, respectively. The selectivity in hydrogenolysis over hydrogenation makes this protocol useful for aromatic chemical production. As discussed earlier, Pt and Rh are highly effective for aromatic π-bond hydrogenation. For the unsymmetrical diaryl-ethers that contain an electron-donating group, such as a methoxy group, next to the ether bond, the cleavage occurred specifically at the C-O bond near the methoxy substituted ring. Similar selectivity was observed for model α-O-4 and β-O-4 dimer $NaBH_4$-assisted cleavage where guaiacol was produced as a result of the selective C-O scission reported by Wu et al.[224]

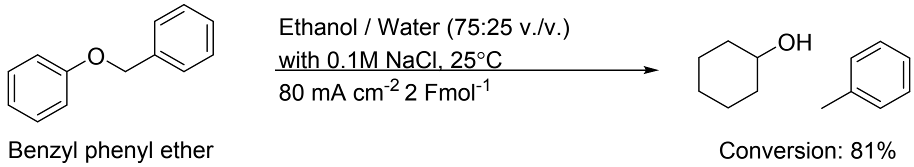


Figure 6. ECH of benzyl phenyl ether using Raney-nickel at 25 °C in 80 mA cm^{-2}. No aliphatic dimer was observed.

Garedew et al. also recently investigated the electrochemical hydrogenation and hydrogenolysis of 4-O-5 model dimers (3-phenoxyphenol, 4-phenoxyphenol, 3-phenoxyanisole, and 3-phenoxytoluene) using ruthenium supported on activated carbon cloth. Complete conversion of 3- and 4-phenoxyphenol to cyclohexanol was reported while hydroxyl group position in relation to the ether bond was found to affect the cyclohexanol yield (3-phenoxy phenol had higher cyclohexanol yield than 4-phnoxyphenol). Substrate concentration and current density were demonstrated to affect Faradaic efficiency and the highest Faradaic efficiency (96%) and high cyclohexanol yield (87%) were reported at 6.67 mA cm^{-2}.[225]

Cyr et al. compared the catalytic performance of Raney-nickel and Pd/C using a β-O-4 dimer, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanol, which yielded guaiacol and α-methylvanillyl alcohol upon hydrogenolysis of the β-O-4 linkage. Both catalysts were in their powder form and were circulated in an RVC electrode. Reactions were performed at a constant current (5 or 20 mA) condition in a 1 M NaOH aqueous solution at different temperature.[199] The extent of hydrogenolysis vs. hydrogenation was studied as a function of temperature and current density. With Raney-nickel, hydrogenolysis and partially hydrogenated product were observed, where monomeric products such as guaiacol, α-methylvanillyl alcohol, phenol, cyclohexanol, and acetovanillone were formed in various quantities (Figure 7). It was shown that higher in temperatures and lower currents favored the hydrogenation process.

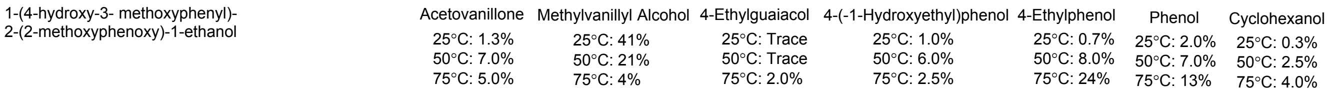


Figure 7. Hydrogenation and hydrogenolysis of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanol in 1 M NaOH at 1 mA cm^{-2} at different temperature and the conversion yield

The Pd/C catalyst, on the other hand, produced only hydrogenolysis products, namely guaiacol and acetovanillone; the ketone hydrogenated to yield α-methylvanillyl alcohol. The exclusive selectivity of hydrogenolysis on Pd/C agreed with Zhao's, Song's, and Sanyal's results that Pd was relatively inert towards aromatic π-bonds. Notably, an unexpected result occurred with the Pd/C catalyst where complete hydrogenolysis occurred even though only half of the theoretical charge was delivered. It was explained that when the α alcohol on the model dimer was oxidized to ketone, the abstracted hydrogens were adsorbed on the Pd surface and then used for the hydrogenolysis of the oxidized dimer.[199] This significant feature of hydrogen-trading could be valuable to hydro lignin upgrading when fully elucidated.

Zhou et al. recently studied the mechanism of the Raney (skeletal) nickel-catalyzed reductive cleavage of β-O-4 aryl ether dimers in an aqueous environment.[196] It was reported the cleavage of the ketone and alcohol dimers both occurred efficiently on the Raney-nickel cathode, but the ketone dimer cleaved roughly twice as fast as the alcohol dimer. More remarkably, even in a reductive environment, the cleavage of the ketone dimer occurred directly at the ether Cα-O bond without reducing the carbonyl group to alcohol as **Error! Reference source not found.**9 shows. (Note: the presence of carbonyl in the acetophenone intermediate could be preserved with an arbitrary low current setting at 5 mA to prevent its reduction).

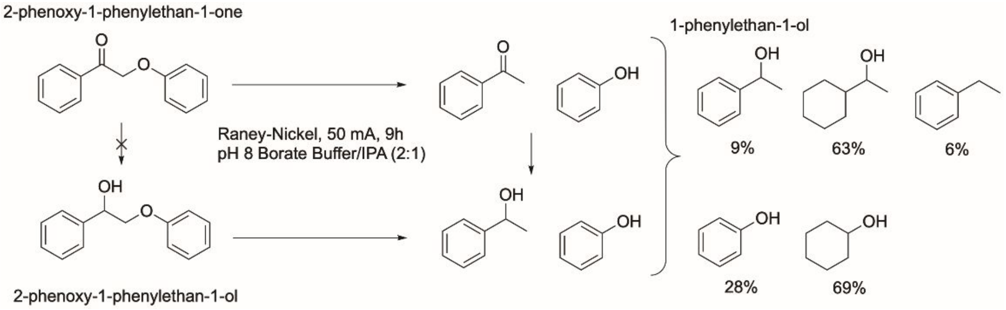


Figure 8. ECH of ether β-O-4 dimers in aqueous environments using a Raney-nickel cathode

5.2.2. Oxidative approach. Shiraishi et al. studied the electro-oxidation of several non-phenolic lignin model monomers, 1-(4-ethoxy-3-methoxyphenyl)ethanol (Et-1G), 1-(4-ethoxy-3,5-dimethoxyphenyl)ethanol (Et-1S), and 1-(4-ethoxyphenyl)ethanol (Et-1H), and the corresponding dimeric β-O-4 model compounds based on those monomers. Using 20 equivalents of 2,6-lutidine as an alkaline catalyst, the α carbon hydroxy group on all monomers were oxidized to carbonyl at around 40% yield.[226] (**Error! Reference source not found.**10)

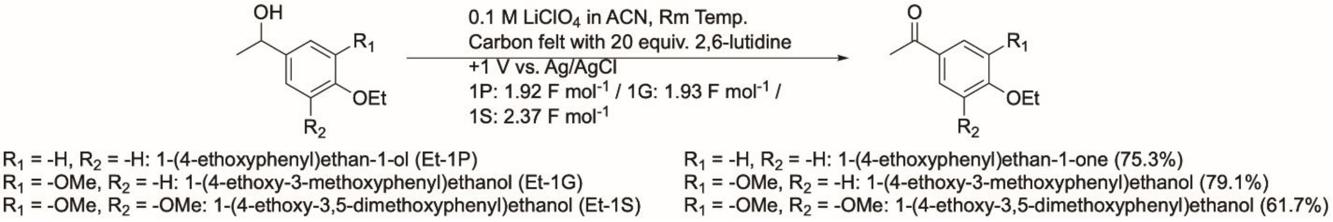


Figure 9. Mediated ECO of various lignin model monomers in 0.1 M $LiClO_4$ at +1 V vs. Ag/AgCl using 20 equiv. of 2,6-lutidine as an alkaline catalyst.

In the subsequent study, Shiraishi expanded the study further with a series of mediators. The oxidative capacity of different mediators on the same set of model compounds was examined with cyclic voltammetry. The study found thar N-hydroxyphthalimide (NHPI) was the most effective mediator to oxidize the α-hydroxy moiety of the Et-1G using 5 equivalents of 2,6-lutidine as a base. NHPI was the sole mediator that showed appreciable yield with good mass balance for selective oxidation of the α carbon hydroxy group (**Error! Reference source not found.**11). Other mediators such as 1-hydroxybenzotriazole (HBT), violuric acid (VLA), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), and 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) yielded little oxidation with poor mass balance.[227]

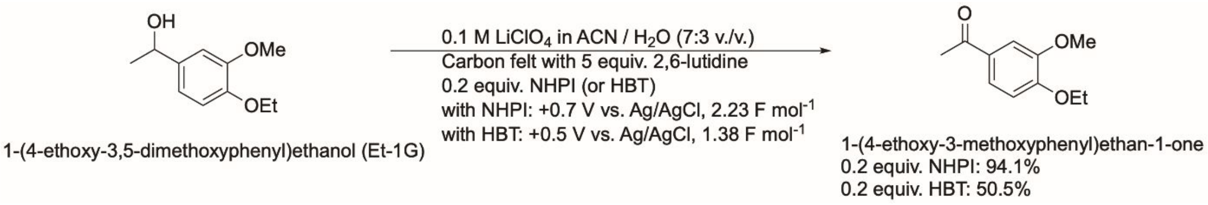


Figure 10. Mediated ECO of lignin model monomers (Et-1G) in 0.1 M $LiClO_4$ in ACN at different working potentials using 5 equivalents of 2,6-lutidine as an alkaline catalyst.

Chen et al. studied the electro-oxidation mechanisms of several β-O-4 bond containing model dimers, 2-phenoxy-1-phenylethanol, 2-phenoxyacetophenone and 2-phenoxy-1-phenylethane by using in situ tracing techniques to investigate the fragmentation pattern of non-phenolic alkyl aryl ether linkages. It was proposed that dimers with C_α-hydroxyl group would selectively be degraded to aldehyde products, otherwise they yield alcohol-containing products (Figure 11). DFT calculations results suggest that the cleavages of either C_β–O or C_α–C_β bonds in dimers are determined by the delocalization of HOMOs.[228]

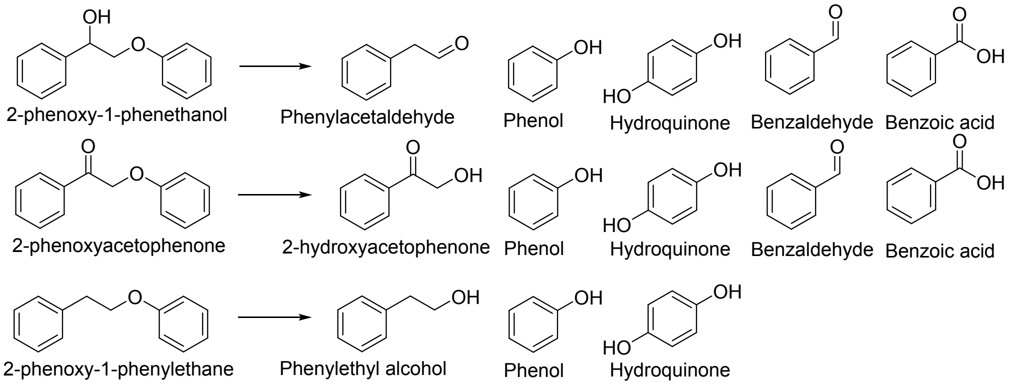


Figure 11. ECO of β-O-4 dimers in aqueous environments using a Pt-sheet cathode. Condition: Two Pt-sheet electrodes (20*20*0.1 mm), and an Ag/Ag^+ non-aqueous reference electrode. Substrate: 0.125 M Electrolyte: 0.1M $LiClO_4$/CH_3CN, room temperature, Scan rate: 0.1 V s^{-1}.

Gao et al. also studied an iodide-mediated electrochemical degradation of various lignin β-O-4 model dimers for the cleavage of the C_β-O bond with different electrodes. Sodium iodide (NaI) was employed at 60 mol% as the mediator using a graphite and a platinum anode (**Error! Reference source not found.**13). Interestingly, the choice of cathode had minor influences on the cleavage. The optimal condition for C_β-O bond cleavage was obtained using a graphite plate as the working electrode and Fe as the cathode in methanol at 0 °C. The cleavage yield is approximately 30 – 40% (after passing 10 F mol^{-1} of charge) and most cleaved products have the α carbonyl methylated from the methanol solvent. The tentative mechanism involves the formation of an epoxy ring that was opened with a methoxide to yield methyl acetal on the α carbon.[229]

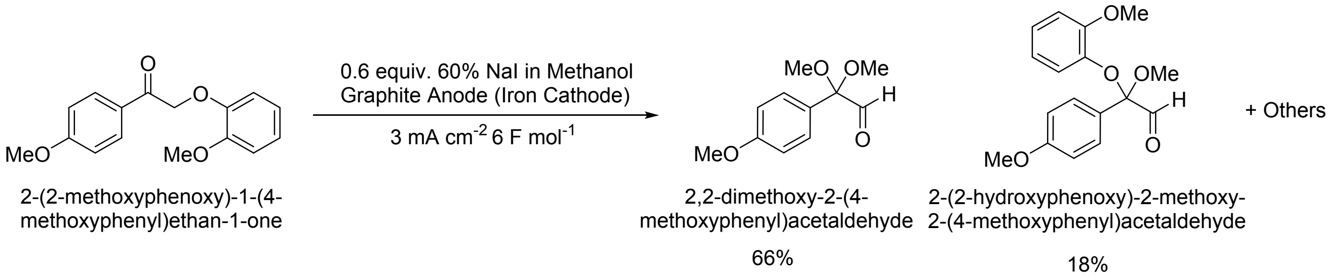


Figure 12. Mediated ECO of a lignin β-O-4 model dimer in methanol at 3 mA cm^{-2} potentials using 60% mol NaI as mediator.

Sannami et al. also investigated a mediated degradation of a non-phenolic lignin β-O-4 model compound (derived from Et-1G). As shown in Figure 13, they studied the chemoselectivity of TEMPO and its derived unit, 4-acetamido-TEMPO (ACT).[230] The choice of solvent had a great influence on product selectivity. Electrolysis in 95:5 CH_3CN:H_2O in the presence of excess 2,6-lutidine, led to small amount of selective oxidation of the α alcohol. However, when the solvent was switched to 10:90 dioxane:H_2O in neutral phosphate buffer, the primary hydroxyl group was oxidized to carboxylic acid instead of the α alcohol. The oxidation of the primary hydroxyl group was also not observed in Shiraishi's NHPI and TEMPO work discussed earlier, using 0.1 M of $LiClO_4$ in CH_3CN. Based on Sannami and Shiraishi's results only, it appears a higher concentration of CH_3CN favors the selectivity of the C-α hydroxy group over the primary alcohol. Interestingly, when the same reaction was performed in 10:90 dioxane:carbonate buffer (pH 10), a mixture of oxidized products of both the primary alcohol and the α alcohol were seen, along with some α-β carbon-carbon cleavage products. Notably, 4-acetamido-TEMPO (ACT) oxidized the α-hydroxy group to carbonyl more effectively than TEMPO (11.1% over 3.0%, respectively) (**Error! Reference source not found.** 14). The enhanced catalytic effect of ACT compared to TEMPO is in agreement with Stahl's earlier TEMPO design work.[231]

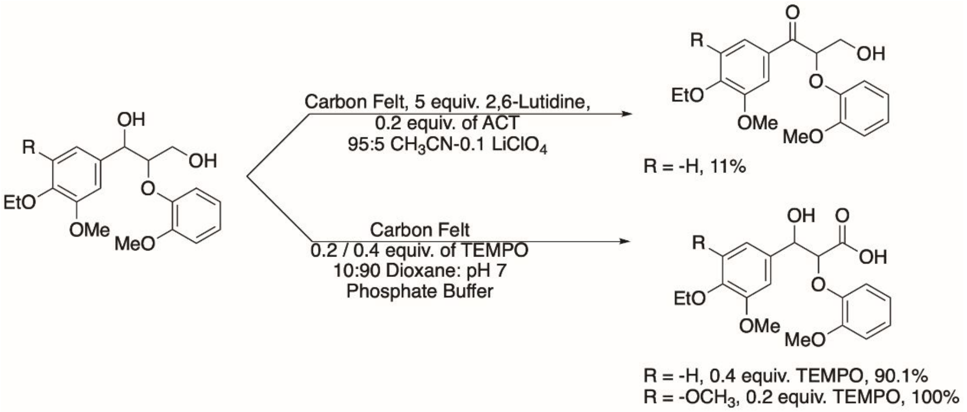


Figure 13. Mediated ECO of a lignin β-O-4 model dimer (derived from Et-1G) in different solvents with TEMPO or its derived mediator.

More recently, Rafiee et al. also investigated the electrochemical oxidation of primary alcohols found in β-O-4 lignin model dimers using TEMPO and ACT and based on CV and chronoamperometry studies they found that ACT had a better performance than TEMPO.[232] Bulk electrolysis in ACT performed at 0.8 V vs. Ag/AgCl indicated that primary alcohol oxidation was favored over secondary alcohol oxidation.[232] Even when stronger base is used, only partial oxidation of the secondary alcohol could be achieved.[232] Overall, after conducting electrolysis of various model compounds, they observed that the primary and secondary alcohols undergo oxidation to form the corresponding carboxylic acids or ketones.[232] While those compounds bearing β-1 linkages (no ether linkage) undergo cleavage of the aliphatic ether unit to form a benzaldehyde and an aliphatic aldehyde fragment.[232] Furthermore, model compounds that bear free phenolic groups also undergo direct electron transfer at the electrode and result in the formation of quinones. Based on these results, they further conducted both CV and bulk electrolysis of poplar lignin in ACT; the results are described in our lignin electrochemical degradation review.[57, 232]

Both Jiang et al. and Wang et al. studied the degradation of 4-(benzyloxy)phenol in [HNEt$_3$][HSO$_4$] (protic) and [BMIM]BF$_4$ (aprotic) ionic liquids, respectively (**Error! Reference source not found.**15).[233, 234] In their studies, 4-(benzyloxy)phenol is degraded into benzaldehyde, para-benzoquinone, and phenylmethanol. Both degradations occurred in the presence of added O$_2$. After gaining one electron, O$_2$ is reduced to become superoxide radical, $O_2^{\cdot -}$, and subsequently becomes hydroperoxyl radical (·OOH) in the presence of protons donated by the model compound, 4-(Benzyloxy)phenol, and then accepted an additional electrons to become H$_2$O$_2$, which becomes available to attack the alkyl-O-aryl bonds in the model compound. The presence of protons in the protic IL improves the formation of H$_2$O$_2$, thereby accelerating the degradation rate of 4-(benzyloxy)phenol.

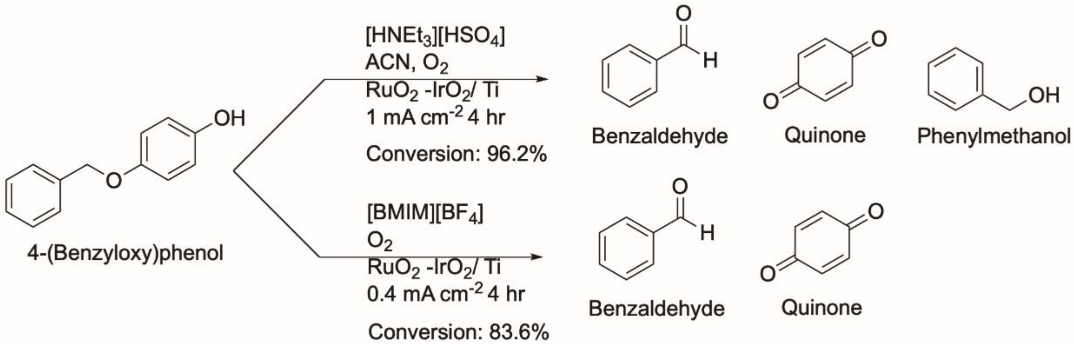


Figure 14. ECO of 4-(Benzyloxy)phenol in different protic and aprotic ionic liquid at varied current density.

Table 1. A summary list of selected representative trials from the recent electrocatalytic studies on lignin monomer model compounds.

Ref.	Feedstock	Catalyst/Working electrode	Electrolyte	I (mA cm^{-2})	Temp. (°C)	Conv. (%)	Duration or Rate	Product Distribution	% C.E.
Wijaya et al.[208]	Guaiacol	Pt/C--Pt	0.2 M H_2SO_4	109	50	37.88	2 h	19.55% Cyclohexanol 30.44% Cyclohexanone 10.79% 2-methoxycyclohexanol 25.46% 2-methoxycyclohexanone 9.52% methanol 4.23% phenol	82.02
			Catholyte: 0.2 M NaCl Anolyte: 0.2 M H_2SO_4	109		36.36		28.00% Cyclohexanol 16.56% Cyclohexanone 26.79% 2-methoxycyclohexanol 18.55% 2-methoxycyclohexanone 8.78% methanol 1.32% phenol	93.99
			Catholyte: 0.2 M NaOH Anolyte: 0.2 M H_2SO_4	109		0		No conversion	0
			Catholyte: 0.2 M H_2SO_4 Anolyte: 0.2 M NaOH	3.63		16.39		5.96% Cyclohexanol 29.65% Cyclohexanone 6.93% 2-methoxycyclohexanol 20.29% 2-methoxycyclohexanone 9.46% methanol 27.71% phenol	27.33
	Phenol	Pt/C--Pt	0.2 M H_2SO_4	109	50	38.95	2 h	23.73% Cyclohexanol 76.27% Cyclohexanone	82.74
			Catholyte: 0.2 M NaCl Anolyte: 0.2 M H_2SO_4	109		39.52		25.67% Cyclohexanol 74.33% Cyclohexanone	92.39
			Catholyte: 0.2 M NaOH Anolyte: 0.2 M H_2SO_4	109		0		No conversion	0
			Catholyte: 0.2 M H_2SO_4 Anolyte: 0.2 M NaOH	3.63		17.80		15.33% Cyclohexanol 84.67% Cyclohexanone	25.49
Wijaya et al.[209]	Guaiacol	Pt/C--Pt	Catholyte: 0.2 M NaCl Anolyte: 0.2 M H_2SO_4	109	50	47.4	4 h	24.6% Cyclohexanol 71.9% 2-methoxycyclohexanol 0.7% 2-methoxycyclohexanone 2.2% Methanol 0.6% Phenol	72.3
			Catholyte: 0.2 M NaCl Anolyte: 0.5 M H_2SO_4			64.7		26.4% Cyclohexanol 25.1% Cyclohexanone 21.1% 2-methoxycyclohexanol 17.0% 2-methoxycyclohexanone 8.4% Methanol 2.1% Phenol	84.3
			Catholyte: 0.5 M NaCl Anolyte: 0.2 M H_2SO_4			39.1		32.2% Cyclohexanol 61.8% 2-methoxycyclohexanol 3.7% Methanol	51.7

Wijaya et al.[209]								2.3% Phenol	
			Catholyte: 0.5 M NaCl Anolyte: 0.5 M H_2SO_4			45.9		44.5% Cyclohexanol 47.4% 2-methoxycyclohexanol 1.4% 2-methoxycyclohexanone 5.8% Methanol 0.9% Phenol	69.4
		Ru/C--Pt	Catholyte: 0.2 M NaCl Anolyte: 0.2 M H_2SO_4	109	50	25.7	4 h	25.7% Cyclohexanol 67.8% 2-methoxycyclohexanol 1.7% 2-methoxycyclohexanone 2.1% Methanol 2.7% Phenol	34
			Catholyte: 0.2 M NaCl Anolyte: 0.5 M H_2SO_4			23.4		21.1% Cyclohexanol 72.8% 2-methoxycyclohexanol 2.3% 2-methoxycyclohexanone 1.5% Methanol 2.4% Phenol	33.0
			Catholyte: 0.5 M NaCl Anolyte: 0.2 M H_2SO_4			34.3		25.0% Cyclohexanol 70.0% 2-methoxycyclohexanol 1.5% 2-methoxycyclohexanone 1.9% Methanol 1.7% Phenol	46.9
			Catholyte: 0.5 M NaCl Anolyte: 0.5 M H_2SO_4			27.4		20.1% Cyclohexanol 72.3% 2-methoxycyclohexanol 3.4% 2-methoxycyclohexanone 1.9% Methanol 2.2% Phenol	35.3
		Pd/C--Pt	Catholyte: 0.2 M NaCl Anolyte: 0.2 M H_2SO_4	109	50	22.6	4 h	18.1% Cyclohexanol 64.8% 2-methoxycyclohexanol 12.6% 2-methoxycyclohexanone 1.5% Methanol 3.1% Phenol	28.3
			Catholyte: 0.2 M NaCl Anolyte: 0.5 M H_2SO_4			16.3		13.7% Cyclohexanol 62.7% 2-methoxycyclohexanol 15.5% 2-methoxycyclohexanone 3.4% Methanol 4.7% Phenol	18.4
			Catholyte: 0.5 M NaCl Anolyte: 0.2 M H_2SO_4			27.9		16.0% Cyclohexanol 66.3% 2-methoxycyclohexanol 12.4% 2-methoxycyclohexanone 2.0% Methanol 3.4% Phenol	33.8
			Catholyte: 0.5 M NaCl Anolyte: 0.5 M H_2SO_4			13.2		17.5% Cyclohexanol 65.3% 2-methoxycyclohexanol 11.0% 2-methoxycyclohexanone 2.4% Methanol 4.0% Phenol	17.7

Liu et al.[212]	Phenol	Pt/C--C	Catholyte: 0.1 M SiW_{12} Anolyte: M H_3PO_4	250	55	>99.9	8.9 min	82.9% Cyclohexanol 0.3% Cyclohexanone 16.8% Cyclohexane	90.9
				800	35	>99.9	11.3 min	80.2% Cyclohexanol 1.2% Cyclohexanone 18.6% Cyclohexane	95.3
	Guaiacol			250	55	94.6	9.2 min	11.6% Cyclohexane 8.3% Methylcyclohexane 56.0% Cyclohexanol 7.6% Cyclohexanone 11.7% 2-methoxycyclohexanone 4.3% 2-methoxycyclohexanol 0.5% Phenol	95.6
Sanyal et. al.[203]	Phenol	RVC - Pd/C	pH 4.6 Acetate buffer	(-0.7V vs Ag/AgCl)	Room temp.	Null	~ 0 h^{-1}	No conversion	Close to 0
	Benzaldehyde					Not reported	~1800 h^{-1}	Phenylmethanol	>95
Sanyal et al.[204]	Phenol	Pt/C (1 wt.% Pt)	pH 4.6 Acetate buffer	115 (-0.7 V vs Ag/AgCl)	Room temp.	Not Reported	60 min	Cyclohexanone (primary) Cyclohexanol (secondary)	Close to 35% current efficiency reported depending on particle size and fractional exposure
		Pt/C (3 wt.% Pt)		125(-0.7 V vs Ag/AgCl)					
		Pt/C (5 wt.% Pt)		115(-0.7 V vs Ag/AgCl)					
		Pt/C (10 wt.% Pt)		150(-0.7 V vs Ag/AgCl)					
Shao et al. [220]	Guaiacol	Ti/Sb-SnO_2	2 wt% of Na_2SO_4 + 5% wt% NaCl	20	Room temp.	97.8	3 h	CO_2	Not Reported
		Ti/Pb_3O_4				96.6			
Li et al.[198]	Phenol	Ru/ACC	0.2 M HCl	40	80	89	2.3 h	Only Cyclohexanol	29
	Guaiacol					75	3 h	53% Cyclohexanol 36% cis-methoxycyclohexanol 11% trans-methoxycyclohexanol	30
	Syringol					58	3.8 h	35% Cyclohexanol 27% cis-methoxycyclohexanol 16% guaiacol 13% 2-methoxycyclohexanone 9% trans-methoxycyclohexanol	29

Lam et al.[195]	Guaiacol	Raney-Nickel	pH 8 Borate buffer	8	75	79	6 h	Cyclohexanol	26
Song et al.[214]	Phenol	RVC - Pt/C	pH 5 Acetic acid buffer	0.05	Room temp.	Almost full	46.8 h^{-1}	Cyclohexanol Cyclohexanone	45
		RVC - Rh/C					66 h^{-1}		77
Song et al.[201]	Phenol	RVC - Rh/C	pH 5 Acetic acid buffer	0.05 (-0.6 V vs Ag/AgCl)	Room temp.	100*	3 h 296 h^{-1}	80%* Cyclohexanol 20%* Cyclohexanone	68
	4-Methylphenol					80*	3 h 151 h^{-1}	50%* 4-methylcyclohexanol 30%* 4-methylcyclohexanone	31
	4-Methoxyphenol					80*	3 h 138 h^{-1}	50%* 4-methoxycyclohexanone 25%* 4-methoxycyclohexanol 5%* Phenol + Cyclohexanol	35
Garedew et al.[202]	Guaiacol	Ru/ACC	0.2 M HCl	40	80	90	2 h	28% Cyclohexanol 17% 2-Methoxycyclohexanol	33
	4-Methylguaiacol					73		32% 4-Methylcyclohexanol	Not reported
	4-Ethylguaiacol					59		20% 4-Ethylcyclohexanol	Not reported
	4-Propylguaiacol					63		21% 4-Propylcyclohexanol 33% 2-Methoxy-4-propylcyclohexanol	29
	Eugenol					62		50% 4-Propylguaiacol 6% 2-Methoxy-4-propylcyclohexanol 6% 4-propylcyclohexanol	18
Zhou et al.[235]	Guaiacol	PtNiB/CMK-3	0.2 M $HClO_4$ solution	5	60	98.9	1 h	54.3% Cyclohexanol 36% Cyclohexanone	86.2
	Eugenol					98.7	1.5 h	85.9% 4-propylcyclohexanol 12.1% 4-propylcyclohexanone	84.3
	Syringol					98.6	1.5 h	81.6% Cyclohexanol 11.8% Cyclohexanone	80.2
	Guaiacol	Pt/CMK-3				71.2	1 h	17% Cyclohexanol 72.8% Cyclohexanone	54.7
	Guaiacol	PtNi/CMK-3				11.7	1 h	7.9% Cyclohexanol 56.7% Cyclohexanone	6.3
	Guaiacol	NiB/CMK-3				No reaction	1 h	No Reaction	null

Table 2. A summary list of selected representative trials from the recent electrocatalytic studies on lignin dimer model compounds.

Ref.	Feedstock	Catalyst/Working electrode	Electrolyte	I (mA cm^{-2})	Temp. (℃)	Conv. (%)	Duration or Rate	Product Distribution	% C.E.
Mahdavi et al.[223]	Benzyl phenyl ethers	Raney-nickel	Ethanol/Water (75:25, v/v) with 0.1 M NaCl	80	25	81	2 F mol^{-1}	Toluene Cyclohexanol	81
Cyr. et al.[199]	β-O-4 lignin model dimer: 1-(4-hydroxy-3- methoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanol	Raney-nickel	1 M NaOH	1	25	94	18 F mol^{-1}	6% Unreacted reactant 43% Guaiacol 41% α-Methylvanillyl Alcohol 0.7% 4-Ethylphenol 2.0% Phenol 0.3% Cyclohexanol Trace 4-Ethylguaiacol 1.3% Acetovanillone 1.0% 4-(-1-Hydroxyethyl)phenol	Not reported
					50	Almost full		37% Guaiacol 21% α-Methylvanillyl alcohol 8.0% 4-Ethylphenol 7.0% Phenol 2.5% Cyclohexanol Traces% 4-Ethylguaiacol 7.0% Acetovanillone 6.0% 4-(-1-Hydroxyethyl)phenol	
					75	Almost full		24% Guaiacol 4.0% α-Methylvanillyl alcohol 24% 4-Ethylphenol 13% Phenol 4.0% Cyclohexanol 2.0% 4-Ethylguaiacol 5.0% Acetovanillone 2.5% 4-(-1-Hydroxyethyl)phenol	
Shiraishi et al.[226]	1-(4-ethoxy-3-methoxyphenyl) ethanol (1G)	Carbon Felt with 20 equiv. 2,6-Lutidine	0.1 M $LiClO_4$ in ACN	(+1 V vs. Ag/AgCl)	Not reported	79.1	1.92 F mol^{-1}	1-(4-ethoxy-3-methoxyphenyl)ethan-1-one	85.8
	1-(4-ethoxy-3,5-dimethoxyphenyl) ethanol (1S)					61.7	1.93 F mol^{-1}	1-(4-ethoxy-3,5-dimethoxyphenyl)ethan-1-one	63.9
	1-(4-ethoxyphenyl) ethanol (1P)					75.3	2.37 F mol^{-1}	1-(4-ethoxyphenyl)ethan-1-one	63.4
Shiraishi et al.[227]	1-(4-ethoxy-3-methoxyphenyl) ethanol (1G)	Carbon Felt with 5 equiv. 2,6-Lutidine with 0.2 equiv. of NHPI (mediator)	0.1 M $LiClO_4$ in ACN /H_2O (70/30 v./v.)	(+0.7 vs. Ag/AgCl)	Not reported	94.1	2.23 F mol^{-1}	1-(4-ethoxy-3-methoxyphenyl)ethan-1-one	79.8
		Carbon Felt with 5 equiv. 2,6-Lutidine with 0.2 equiv. of HBT (mediator)		(+0.5 vs. Ag/AgCl)		50.5	1.38 F mol^{-1}		73.0

Gao et al.[229]	2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one	Graphite with 0.6 equiv. KI as mediator Iron cathode	Methanol	3	0	84	6 F mol^{-1}	66% 1-(dimethoxymethyl)-4-methoxybenzene 18% 2-methoxy-2-(2-methoxyphenoxy)-2-(4-methoxyphenyl)acetaldehyde	Not Reported
Wu et al. [224]	Diphenyl ether	Pt with 3 equiv. NaBH$_4$	DMF – 0.2 M TBABF$_4$	17	Room temp.	100	1.75 h	80% Benzene 81% Phenol	Not Reported
	β-O-4 lignin model dimer: 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol	Pt with 4 equiv. NaBH$_4$	0.2 M NaBF4, NMP			Not reported	3 h	65% Guaiacol Numerous Products	
Jiang et al. [233]	4-(Benzyloxy)phenol	RuO$_2$ -IrO$_2$/ Ti	[HNEt$_3$][HSO$_4$] in ACN with O$_2$ bubbled	1	Room temp.	96.2	4 h	Benzaldehyde Quinone Phenylmethanol	14.7
Wang et al. [234]	4-(Benzyloxy)phenol	RuO$_2$ -IrO$_2$/ Ti	[BMIM][BF$_4$] with O$_2$ bubbled	0.4	Room temp.	83.6 95.1 (with 4% H$_2$O)	4 h	Benzaldehyde Quinone Phenylmethanol	Not Reported
Garedew et al. [225]	3-phenoxyphenol	Ru on activated carbon cloth	1 M NaOH	33.33	80	100	9 h	Cyclohexanol	16
	4-phenoxyphenol					100			14
	3-phenoxytoluene					67			1
	3-phenoxyanisole					69			3
	3-phenoxyphenol			6.67		100			96
Zhou et al. [196]	Ketone β-O-4	Skeletal nickel	pH 8 Borate buffer / IPA (2:1)	50	60	>99%	9 h	9% 1-Phenylethanol 28% Phenol 6% Ethylbenzene 63% 1-Cyclohexylethanol 69% Cyclohexanol	Not Reported.
		Reticulated vitreous carbon (RVC)		50		>99%		<1% Acetophenone 21% 1-Phenylethanol 91% Phenol	Not Reported.
	Alcohol β-O-4	Skeletal nickel	pH 8 Borate buffer / IPA (2:1)	50	60	>99%		23% 1-Phenylethanol 35% Phenol 6% Ethylbenzene 54% 1-Cyclohexylethanol 58% Cyclohexanol	Not Reported.
		Reticulated vitreous carbon (RVC)		50		0		No conversion	Not Reported.
Chen et al. [228]	2-phenoxy-1-phenethanol	Pt-sheet	0.1M LiClO$_4$/CH$_3$CN	(1.61 V vs. Ag/Ag+)	Not reported	43.5%	8 h	Phenylacetaldehyde Phenol Hydroquinone Benzaldehyde Benzoic acid	Not Reported.

	2-phenoxyacetophenone			(1.71 V vs. Ag/Ag+)		39.6%		2-hydroxyacetophenone Phenol Hydroquinone Benzaldehyde Benzoic acid	Not Reported.
	2-phenoxy-1-phenylethane			(1.63 V vs. Ag/Ag+)		43.4%		Phenylethyl alcohol Phenol Hydroquinone	Not Reported.

6. **Outlook and Conclusion**

In this review we have summarized the recent literature on electrocatalytic reductive and oxidative upgrading of lignin-derived monomer and dimer molecules. Electrocatalysis offers energetically mild conditions and helps avoid the elevated temperatures and pressures that are often associated with catalytic processes to upgrade lignin-derived aromatic compounds, thus reducing energy input. Most of the electrocatalytic studies covered in this review range between room temperature and no more than 80 °C and were performed at ambient pressure (1 atm). Though not directly addressed by the discussion in this review, upgrading of abundant low-value lignin intermediates via electrocatalysis could capture excess renewable electrical energy in the form of chemical bonds, offering access to valuable fuels and chemicals via green and sustainable, biobased routes. Studies on electrochemical cleavage of dimeric models of lignin linkages also offer some insight into electrochemical lignin depolymerization. Many of the examples reviewed in this article show that generally, ECH serves as an effective strategy to achieve hydrogenolysis of 4-O-5 or α-O-4 type dimers while ECO is more suitable for the cleavage of β-O-4 dimers. For monomers such as guaiacol or phenol, electrooxidation is largely unexplored owing to its tendency to completely mineralize the substrates. Further exploration in this area and control over the extent of oxidation can furnish useful ring opening products such as maleic acid, fumaric acid, and succinic acid.

The studies presented show that efficiency and selectivity are highly sensitive to current density and other parameters such as temperature, catalysts, and solvents used. For practical purposes, product selectivity control is essential, but remains a major issue for many of these transformations. While solvent, temperature, and catalyst integrity all play roles in controlling reaction selectivities, the general observation is that the number of products increases with the size and complexity of the lignin model compounds. The efficiency of electrocatalytic conversions can also be affected greatly by the structural complexity of the molecule as the presence of substituents may electronically or sterically interfere with the molecule's ability to bind and/or undergo redox on the electrode's catalytic surface. Thus, one of the ways to improve product selectivity is to promote the degree of upstream depolymerization pretreatment, where fragmentation and fractionation of the lignin could be sufficiently developed to ensure that electrocatalytic upgrading can proceed specific, well-defined products. The issue of steric hindrances to catalytic binding imposed by substituents can be circumvented by using a small molecule mediator, such as TEMPO to transport the redox electrons to the hindered target redox site. It is also worth noting that studies that can elucidate reaction kinetics through understanding of molecular-level interactions at the electrocatalyst surface and substrate functionalities and substituents at the electrolyte-electrode interface can aid in optimizing selectivity to desired products.

The influence of supporting electrolyte on reaction selectivity has been shown to be relatively minor. This suggests extension to the employ solid polymer electrolyte reactors for lignin upgrading.[79, 80] The use of SPEs could enable continuous flow operation and potentially reduce or eliminate the need for supporting electrolyte. Such non-aqueous flow would then avoid the need for separation of products from aqueous electrolytes, facilitating seamless integration and compatibility of electrocatalysis with upstream depolymerization processes that take place in organic solvents. It has been demonstrated that the selectivity of β-O-4 dimer oxidation can be influenced by the reaction solvent (Stahl's reaction from Figure 13).[232]

Perhaps one of the most important considerations regarding model compound studies pertains to how well the studies herein capture the reactivity and product slates of lignin-derived molecules that are obtained from the various depolymerization processes. When is electrocatalytic upgrading most aptly applied, and when would other methods be preferred. In these studies, while phenol and guaiacol and, in some cases, substituted phenols and guaiacols have been explored, others such as catechols and substituted catechols (derived from C-lignins), lignin polymers, and oligomers have not been addressed. Even more importantly, understanding how aromatic mixtures behave under electrochemical conditions and how selectivity and efficiency are affected by the presence of competing aromatic substrates are other important considerations as most available depolymerization processes lead to complex mixtures rather than single product streams. Despite the wealth of information that can be gained from model monomer and dimer studies, there are limits to their relevance to the electrocatalytic upgrading of raw mixtures from upstream lignin depolymerization processes. Another useful future consideration is to understand how the presence of cellulose and hemicellulose derived aliphatic compounds could affect the product selectivity and reaction efficiency of aromatic upgrading or perhaps how cellulose-derived products may combine with the lignin-derived products. Biomass depolymerization will inevitably deconstruct cellulose and hemicellulose into components that mix with lignin degradation products. Therefore, exploring the electrocatalytic relationship between the cellulose- and lignin-derived substrates is necessary. Until we can control the selectivity of the product, electrochemical upgrading of lignin appears most suitable for a renewable carbon-based fuel precursor production[54] or other chemical enterprises where product purity is less critical than target properties.

Electrocatalytic upgrading of biomass intermediates, especially lignin electrocatalysis technology, is at an early stage of its development and its adoption/implementation at a larger scale requires further investigation. Specifically, its potential for integration with other biomass valorization schemes, its technoeconomics, and environmental merits must be better understood within the context of cradle-to-grave bioenergy and bioproducts systems. Thus, life cycle and technoeconomic analyses of this process are essential components of future research, analysis, and development. Herein, we have assembled and compared the electrochemical studies of lignin-derived monomers and dimers conducted in the last decade with the aim of providing a comprehensive compilation of recent advances in this area and promoting greener and more sustainable pathways to lignin valorization.

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