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# Electrocatalytic Cleavage of Lignin Model Dimers Using Ruthenium Supported on Activated Carbon Cloth

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**Abstract:** Biomass lignin is the largest natural source of renewable aromatic compounds, creating an opportunity for its use as a feedstock provided that deconstruction and upgrading methods become available. Lignin valorization is challenging because its complex structure is naturally recalcitrant to biological degradation. Deconstruction of this amorphous cross-linked polymer requires cleavage of aryl ether bonds, which account for more than half of the linkages between lignin's phenylpropanoid building blocks. High temperature cracking of lignin is possible via pyrolysis, but linkages such as 4-O-5 bonds are resistant to thermal degradation. Electrocatalytic hydrogenation offers a mild alternative; operated at low temperature and atmospheric pressure, it cleaves ether bonds while saturating aromatic rings with *in situ* hydrogen. To investigate catalytic ruthenium supported on activated carbon cloth for cleaving 4-O-5 bonds, model compounds that exhibit this linkage were selected, including 3-phenoxyphenol, 4-phenoxyphenol, 3-phenoxyanisole, and 3-phenoxytoluene. The two phenols, 3-phenoxyphenol and 4-phenoxyphenol, were cleaved and hydrogenated to form cyclohexanol. 3-Phenoxyanisole and 3-phenoxytoluene were also cleaved but with lower conversion rate and cyclohexanol yield. Alkaline electrolyte solutions showed the highest cyclohexanol yields for both substrates. Increasing substrate concentrations from 10 mM to 40 mM increased Faradaic efficiency to 25%, while decreasing current density from 100 (33.33 mA cm<sup>-2</sup>) mA to 20 mA (6.67 mA cm<sup>-2</sup>) greatly improved the Faradaic efficiency to 96%.

## Introduction

The development of renewable energy production methods that are efficient, environmentally friendly, and economically viable is essential in addressing the increasing environmental concerns surrounding the use of fossil fuels. As plants store energy from the sun via photosynthesis in the form of chemical bonds between carbon, hydrogen, and oxygen, biomass has the potential to make carbonaceous fuels to store and supply renewable energy.<sup>1-2</sup> Although cellulose and hemicellulose, polymers of simple sugars, have been well studied in terms of conversion to fuel ethanol, lignin is underutilized. This biopolymer is second only to cellulose in abundance and is currently treated as a waste product of the pulp and paper industry and

bioethanol refineries. A complex racemic mixture of aromatic polymers produced from the oxidative coupling of three major 4-hydroxyphenylpropanoid monolignols, lignin is a significant source of natural aromatic compounds.<sup>3-5</sup> This makes it an attractive feedstock for the production of both hydrocarbon fuels and bio-based value-added chemicals. But because of its complexity, lignin is difficult to deconstruct and valorize.<sup>6</sup> Lignin's three dimensional structure is rigid and resistant to deconstruction as its primary function is to provide structure and protect the plant cell wall polysaccharides from biological degradation.<sup>4</sup> This amorphous polymer of carbon and oxygen is bonded at the 4 and 5 positions of its aryl ring and the  $\alpha$  and  $\beta$  positions of its propanoid sidechain, so the depolymerization of lignin is dependent upon the successful cleavage of lignin-specific linkages (e.g.  $\beta$ -O-4,  $\beta$ - $\beta$ ,  $\beta$ -5, 5-5, and 4-O-5).<sup>7</sup> Unravelling this complex polymer and producing valuable monomeric phenols is a challenge to be addressed.<sup>8</sup>

While thermal processes such as pyrolysis can be used to depolymerize lignin,<sup>8-14</sup> some lignin linkages such as 4-O-5 linkages could be resistant to thermal cracking.<sup>15</sup> To this end, various catalytic routes have been investigated specifically for aryl ether bond cleavage using a range of conditions. Early on, Hartwig and coworkers conducted an extensive study of the selective reductive cleavage of various aryl ethers using a nickel carbene complex to form arenes and alcohols at 120 °C and 1 bar.<sup>16</sup> More recently, He et al. conducted kinetic studies of the hydrogenolysis of various lignin-derived dimers (including diaryl ether) to benzene, cyclohexanol, and cyclohexyl phenyl ether on Ni/SiO<sub>2</sub> at 6 bar 120 °C. The reaction rate for the C-O bond cleavage was found to increase as a function of H<sub>2</sub> pressure.<sup>17</sup> Liu et al. was able to achieve complete conversion of diphenyl ethers to cyclohexane with high yields at 200 °C and 2 MPa using a nitrogen doped carbon supported cobalt nitride catalyst.<sup>18</sup> Similarly, Chen et al. later studied the hydrogenation of various lignin-derived model monomers and dimers (including diaryl ethers) over Ru/C at 220 °C and 5 MPa and reported high yield of alkanes as products.<sup>19</sup> Chatterjee et al. investigated diphenyl ether cleavage as a function of hydrogen pressure in supercritical CO<sub>2</sub> at 80 °C using Rh/C and reported that a lower pressure of 0.2 MPa was favorable for monomer formation while 2 MPa favored saturation of the aromatic ring.<sup>20</sup> Park et al. reported the decomposition of 4-phenoxyphenol to cyclohexanol, benzene, and phenol at 200 °C and 10 atm using a catalyst of palladium supported on a phosphoric acid-activated carbon aerogel.<sup>21</sup> The weight ratio of the activating agent (phosphoric acid) and the palladium particle size were reported to have an effect on the conversion and product distribution. More recently, Meng et al. reported on the synthesis of ketones such as cyclohexanone from biomass derived sources (including a 4-O-5 dimer, namely diphenyl ether) using bromide salt-modified Pd/C at the relatively mild temperature of 90 °C and 2 MPa pressure.<sup>22</sup> Zeng et al. and Cao et al. further investigated the cleavage of 4-O-5 diaryl ethers to produce phenols accompanied by the cross coupling reaction in the presence of a pyrrolidine<sup>23</sup> or ammonia<sup>24</sup> to form amine and aniline derivatives using Pd/C at 150/160 °C.

Many of the catalytic studies mentioned here are able to achieve good selectivity and excellent conversion but often utilize either relatively elevated temperatures (120-200 °C) or pressures (1-20 bar), or both, and require hydrogen gas to achieve these transformations. Electrochemical upgrading is an alternative method that can be used for lignin valorization via hydrogenation and deoxygenation at mild temperatures and atmospheric pressure.<sup>25</sup> This method offers certain advantages over conventional catalytic hydrogenation and hydrogenolysis. In electrocatalytic hydrogenation/hydrogenolysis (ECH), the kinetic barrier related to hydrogen dissociation is avoided as the hydrogen needed for reduction is produced *in situ*.<sup>26</sup> Mass transport limitations of hydrogen gas in aqueous solutions are also avoided in ECH.<sup>26</sup> Even catalyst poisoning due to coke formation is prevented due to the cathodic potential that inhibits adsorption of anionic poisons.<sup>26</sup> Furthermore, ECH provides the means to selectively produce specific desired products by controlling cell potential.<sup>27-28</sup>

One drawback of ECH, however, is that hydrogen evolution reactions can compete with organic hydrogenation reactions, lowering the cell's Faradaic efficiency, which is defined as the fraction of charge passed that will be allocated to produce the desired products.<sup>26</sup> The rates of both hydrogenation and hydrogen evolution processes are in turn influenced by several other factors such as: bond strength of the substrate that is being reduced, rate and probability of substrate adsorption (related to substrate concentration and functionalities present),<sup>27</sup> strength of bonding of hydrogen to the catalyst surface,<sup>26</sup> and current density.<sup>29</sup> Investigating the effects of these factors on cell performance for lignin cleavage is needed to evaluate lignin valorization using ECH. *In lieu* of complex lignin polymers, simpler model compounds can be used in studies to advance understanding of electrochemical degradation of lignin.

In this regard, a few studies have explored both electrocatalytic oxidation (ECO)<sup>30-35</sup> and ECH<sup>36-41</sup> for lignin model compound cleavage. The early work by the Menard and Lessard groups especially have investigated both  $\beta$ -O-4 and 4-O-5 bonded model dimers. These include work by Mahdavi et al. where the hydrogenolysis of benzyl phenyl ether model dimers was investigated using Raney nickel to determine the optimum current density, temperature, and substrate concentration.<sup>36</sup> More relevant to the current study, Dabo et al. later studied various transition metal powder catalysts embedded in reticulated vitreous carbon to achieve hydrogenolysis of 4-phenoxyphenol to phenol. Raney Ni, Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> were found to have high hydrogenolysis activity and efficiency. Cyr et al. also investigated Raney nickel and palladium-based catalysts for the hydrogenolysis of mostly  $\beta$ -O-4 model compounds and 4-phenoxyphenol. They reported that an increase in the temperature and lower current density favors the dimer conversion and suppresses hydrogen evolution. A high phenol yield was reported for the hydrogenolysis of 4-phenoxyphenol using Raney nickel.<sup>42</sup> More recently, Song et al. and Wu et al. reported the hydrogenolysis of various aryl ethers using Rh/C<sup>43</sup> and Pt<sup>44</sup> electrodes respectively. These studies of model dimers with lignin-specific linkages have been beneficial in understanding the effectiveness of ECO and ECH for lignin degradation.

As lignin is a byproduct of other industries, utilizing it as a feedstock for biofuels and bioproducts is worthy of consideration. What is needed to de-risk lignin ECH is an understanding of how lignin-specific linkages are cleaved under varying conditions. In this study, first the effectiveness of thermal cracking on a 4-O-5 lignin linked dimer is investigated. Then the efficacy of ECH for the cleavage of this thermally resistant linkage is tested. As ECH's performance towards dimer hydrogenation is impacted by current density, electrolyte type, and nature of the substrates (functional groups and position), variations in these factors are included in this study. The effect of varying solution pH, current density, functional group type and their position is needed to determine whether ECH can be used to valorize lignin-based substrates.

## Experimental

### Model Dimers

To compare the effectiveness of pyrolysis for cleavage of 4-O-5 lignin dimers, approximately 1 mg of 2-phenoxyphenol (**3**) was synthesized (see synthesis procedure in the next section) and subjected to analytical pyrolysis. In parallel to pyrolysis, electrocatalytic cleavage of lignin-specific linkages and overall conversion was studied using the model compounds shown in Figure 1. 4-Phenoxyphenol (**1**), 3-phenoxyphenol (**2**), 3-phenoxyanisole (**4**), and 3-phenoxytoluene (**5**) were obtained from Alfa Aesar (Ward Hill, MA) and were subjected to ECH as representative compounds for 4-O-5 type linked lignins.

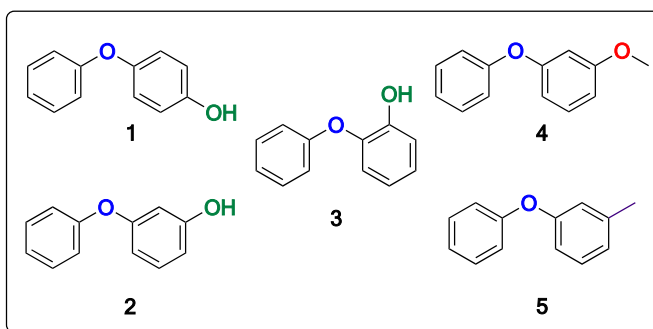


Figure 1. Dimers investigated for analytical pyrolysis and ECH upgrading: 4-phenoxyphenol (**1**), 3-phenoxyphenol (**2**), 2-phenoxyphenol (**3**), 3-phenoxyanisole (**4**), and 3-phenoxytoluene (**5**).

### Synthesis procedure for 2-phenoxyphenol

To a nitrogen flushed round bottom flask, iodobenzene (1.33 g, 12 mmol) and Cu(II)O (0.0203g, 2.5 mol%) were added to a solution of KOH (0.8516 g, 15 mmol) and guaiacol (1.2486 g, 10 mmol) in 10 mL DMSO. The reaction was run at 110 °C for 15 hours. Upon completion, the reaction was quenched with NH<sub>4</sub>Cl (5 mL) and H<sub>2</sub>O (100 mL) and extracted with DCM (200 mL). The DCM layer was then dried with MgSO<sub>4</sub> and concentrated under vacuum. The tan colored crystals were recrystallized from EtOH and vacuum filtered to give a final mass of 0.1964 g, corresponding to a 10% yield.

The next step involved a demethylation. To a nitrogen flushed flask, 1.8 mmol, 0.17 mL of  $\text{BBr}_3$  was added to a solution consisting of 0.2807 g, 1.4 mmol of the first 4-O-5 dimer in 3 mL of DCM. An additional 2 mL of DCM was added to the reaction. The reaction was stirred at  $-70\text{ }^\circ\text{C}$  for one hour and an additional 3 hours at room temperature and monitored with thin layer chromatography (TLC). After completion, the reaction was quenched with 3 mL of  $\text{H}_2\text{O}$  and 6 mL of a 1 M NaOH solution was added. The water layer was extracted and 12 M HCl was added until precipitate formed. This precipitate was dissolved in ethyl acetate and dried over  $\text{MgSO}_4$ . The dried organic layer was concentrated under vacuum to give a final mass of 0.0775 g of tan colored, light crystals for a 30% yield. The reaction was also run on a scale 5.3x the original and gave a final mass of 0.9112 g, corresponding to a 66% yield. Colorless crystals, with flake shape. MS ( $\text{ES}^-$ ): found 185.0600 (M- $\text{H}^+$ ), calculated MS for  $\text{C}_{12}\text{H}_9\text{O}_2$  185.0603.  $^1\text{H}$  NMR (500 MHz, chloroform-*d*)  $\delta$  7.39 - 7.31 (m, 2H), 7.13 (tt,  $J=7.2, 1.1$  Hz, 1H), 7.09 - 6.99 (m, 4H), 6.92 - 6.80 (m, 2H), 5.78 (s, OH).  $^{13}\text{C}$  NMR (126 MHz, chloroform-*d*)  $\delta$  156.87, 147.61, 143.58, 130.02, 124.91, 123.75, 120.76, 119.00, 118.13, 116.30. MS (EI):186.1.

### Analytical pyrolysis of a 4-O-5 dimer

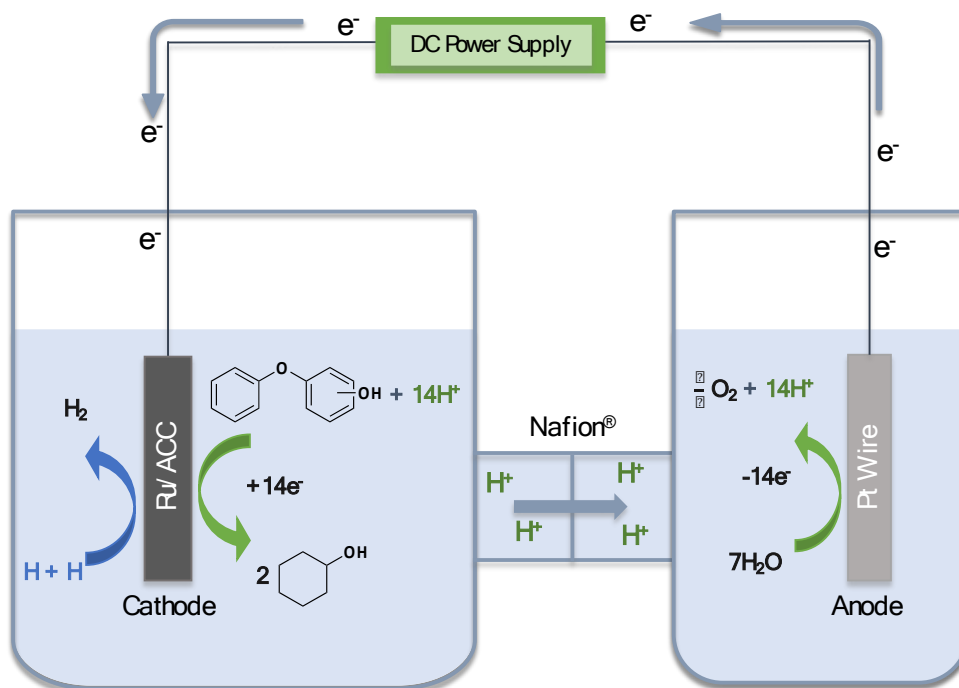
Pyrolysis gas chromatography mass spectrometry (py-GC/MS) was performed to observe the effect of pyrolysis on 2-phenoxyphenol. A CDS pyroprobe 5250 (CDC Analytical Inc. Oxford, PA) coupled with a Shimadzu QP 5050A GC/MS (Shimadzu Corp. Columbia, MD) was used to pyrolyze about a milligram of the dimer sample. Temperature in the pyroprobe was set at  $650\text{ }^\circ\text{C}$  for 20 seconds, while the transfer line temperature and the GC port temperature were both set at  $280\text{ }^\circ\text{C}$ . The GC oven temperature was programmed to increase from  $40\text{ }^\circ\text{C}$  to  $270\text{ }^\circ\text{C}$  at a ramp rate of  $8\text{ }^\circ\text{C}/\text{min}$ . Eluting compounds were identified using the NIST library.

### Catalyst preparation

Zorflex<sup>®</sup> activated carbon cloth (ACC) (Zorflex<sup>®</sup> ACC FM100) obtained from Calgon Carbon Corporation (Pittsburgh, PA) was used to support hexaammineruthenium(III) chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ) which was obtained from Strem Chemicals (Newburyport, MA). As described by Li et al.,<sup>45</sup> ACC was cut into 1.5 x 3.0 cm pieces, agitated overnight in deionized (DI) water, oven dried at  $150\text{ }^\circ\text{C}$ , and soaked in a solution of ruthenium salt ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  (1.01 g) dissolved in ammonium hydroxide (1.96 ml) and water (13.02 ml) to saturate the pores. The ruthenium on activated carbon cloth (Ru/ACC) catalyst was then dried overnight at room temperature, further dried under vacuum for 24 h, and then reduced with molecular hydrogen at  $310\text{ }^\circ\text{C}$  and 500 psi for 12 h in a Parr Reactor model 452HC (Parr Instrument Company, Moline, IL).

## ECH apparatus and experimental design

A two-chambered electrochemical glass H-cell fabricated by the Department of Chemistry Glassblowing facility at Michigan State University (East Lansing, MI) was used for the experiments. The chambers were separated using a Nafion® 117 membrane obtained from Dupont (Wilmington, DE). Ru/ACC was used as the cathode and platinum wire obtained from Alfa Aesar was used as the anode (Figure 2). Four separate studies were conducted to investigate the different substrates (**1**, **2**, **4**, and **5**), electrolytes (1 M NaOH, 0.2 M HCl or 0.2 M NaCl), substrate concentrations (10, 20, and 40 mM), and current densities (6.67, 16.67 or 33.33 mA cm<sup>-2</sup>) with 0.2 M phosphate buffer used as an anolyte for all experiments. Substrates were directly dissolved in the basic electrolyte. However, since the substrate solubility in acidic and neutral electrolytes was limited, 1 mL of isopropyl alcohol was used to dissolve the substrate prior to mixing with electrolyte. An Instek GPR-11H30D (Instek America Corp., Montclair, CA) power supply provided constant electrical current. To maintain a constant temperature of 80 °C, the entire cell was placed in a heated water bath for all experiments. After the cell setup was completed, a 10-min pre-electrolysis step was performed on the catalyst at 80 mA prior to adding the substrate. After pre-electrolysis, depending on the experiment, the desired amount of substrate was added to 20 mL of each electrolyte, and each experiment was conducted at the desired current density for the desired duration.



**Figure 2.** Two chambered H-cell setup showing reduction of lignin model compound 3-phenoxyphenol to cyclohexanol using Ru/ACC as a cathode and platinum wire as an anode. Adapted with permission from (Garedeu, M.; Young-Farhat, D.; Jackson, J. E.; Saffron, C. M., *ACS Sustainable Chem. Eng.* **2019**, 7 (9), 8375-8386). Copyright (2019) American Chemical Society.<sup>27</sup>

### Sample extraction and analysis

At the end of each experiment, bulk electrolyte samples were saturated with NaCl, acidified to pH 1.0 with concentrated HCl, and extracted in dichloromethane (DCM). The catalyst cloth was placed in 5 mL DCM, sonicated for 10 min, and filtered prior to analysis by gas chromatography mass spectrometry (GC/MS). Samples of the solution were analyzed using a Shimadzu QP-5050A GC/MS (Shimadzu Corp, Columbia, MD). Standards in DCM were used to identify products by retention time and to construct a four-point calibration curve. This curve was used to determine product yields and calculate Faradaic efficiency.

### Calculations

$$\text{Yield}_A = (\text{Moles of A}) / (\text{Initial moles of reactant}) \times 100$$

$$\text{Selectivity}_A = (\text{Moles of A}) / (\text{Moles of total products}) \times 100$$

$$\text{Conversion} = (\text{Moles of reactant consumed}) / (\text{Initial moles of reactants}) \times 100$$

$$\text{Faradaic efficiency} = (\text{moles of isolated product} \times F \times n) / (\text{Total charge passed}) \times 100$$

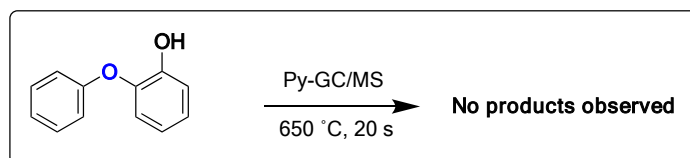
where  $n$  = number of electrons needed to form the product,  $F$  = Faraday's constant, 96485 C mol<sup>-1</sup>

$$\text{Current Density} = (\text{Current}) / (\text{Geometric unit area of catalyst used})$$

## Results and discussion

### Pyrolysis GC/MS of lignin model 4-O-5 dimer

Diphenyl ether dimers such as 4-O-5 bonded compounds, known to be abundant in Kraft lignins, are reported to be resistant to thermal cracking due to their much higher bond dissociation energy (314 kJ mol<sup>-1</sup>) compared to  $\beta$ -O-4 linkages (289 kJ mol<sup>-1</sup>).<sup>15, 39, 42</sup> To investigate the behavior of 4-O-5 bonded dimers during pyrolysis, a model dimer (2-phenoxyphenol) was subjected to analytical pyrolysis at 650 °C for 20 s. The chromatogram shows only the 2-phenoxyphenol (2-PPh) peak with no significant products observed (Figure 3). Lignin depolymerization and upgrading, however, is contingent upon cleaving such bonds so ECH was further investigated herein.

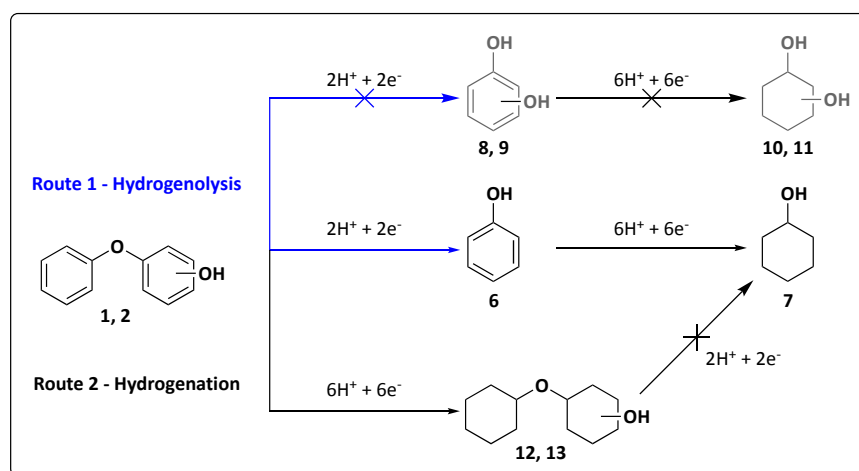


**Figure 3.** Pyrolysis GC/MS products of 2-phenoxyphenol at 650 °C and residence time of 20 s (compounds identified using similarity to the NIST library).



## ECH of lignin model dimers using Ru/ACC

ECH has been investigated and demonstrated to be successful in the conversion of 4-phenoxyphenol to phenol with high conversion using various catalyst materials such as palladium on alumina, palladium on carbon, and Raney nickel.<sup>37-38</sup> ECH of 3-phenoxyphenol (3-PPh) and 4-phenoxyphenol (4-PPh) are investigated here to understand how the hydroxyl group position affects conversion, product selectivity, and Faradaic efficiency. Electrolyte pH and current density were also examined. ECH of both 3- and 4-phenoxyphenol is suggested here to follow two pathways, one via ether bond cleavage to form phenol followed by its hydrogenation to cyclohexanol via a cyclohexanone intermediate (Figure 4, Route 1), the other via hydrogenation of one or both of the aromatic rings followed by C-O bond cleavage (Figure 4, Route 2).<sup>17</sup>



**Figure 4.** Suggested reaction routes for the ECH of 3-phenoxyphenol and 4-phenoxyphenol. Route 1 (hydrogenolysis) could proceed via ether bond cleavage to form phenol followed by ring saturation to form cyclohexanol (products that were not observe are denoted in grey). Route 2 (hydrogenation) could proceed by direct ring saturation followed by possible cleavage of the dimer.

For Route 1, the point of cleavage can happen by cleaving the C-O bond from one or both sides of the oxygen (O-hydroxyphenyl or O-phenyl), forming either two moles of phenol (**6**) which is further hydrogenated to cyclohexanol (**7**), or forming hydroquinone (**8**) and resorcinol (**9**) which can be further hydrogenated to the stereoisomers of 1,4-dihydroxycyclohexane (**10**) and 1,3-dihydroxycyclohexane (**11**). The experiments reported here demonstrated that ether bond cleavage was achieved to form the final product cyclohexanol. No hydroquinone (**8**), resorcinol (**9**), 1,4-dihydroxycyclohexane (**10**) or 1,3-dihydroxycyclohexane (**11**) were observed, indicating that for 3-PPh and 4-PPh the cleavage of the C-O bond attached to the hydroxyphenyl ring is favored similar to what was reported by Dabo et al.<sup>38</sup>

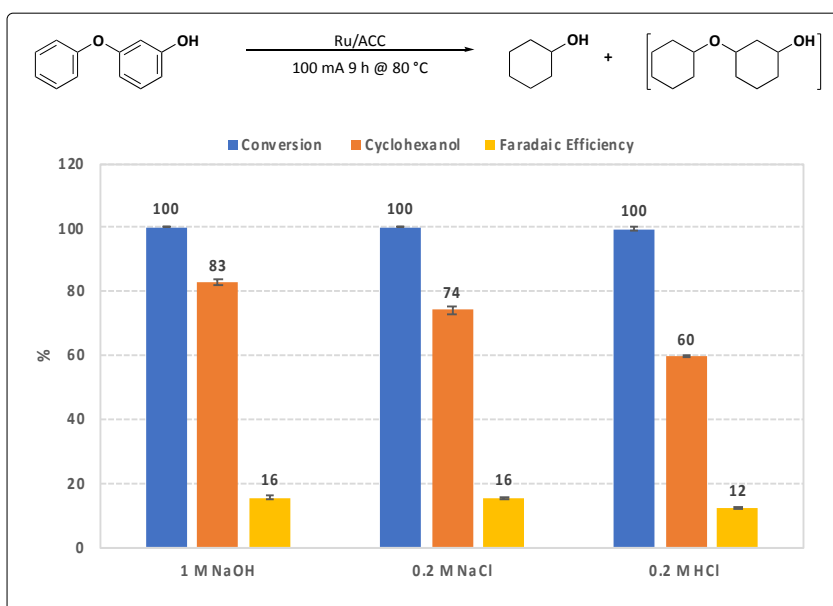
Previous studies suggest that if the hydrogenation of the ring occurs before hydrogenolysis, further C-O bond cleavage to form cyclohexanol will be extremely difficult.<sup>7, 46</sup> Song et al. even demonstrate that when hydrogenation of both rings is achieved for diphenyl ethers, further C-O bond cleavage does not occur.<sup>40</sup> In the current study, what could be the dimer hydrogenation products (4-

cyclohexyloxycyclohexanol (**12**) and 3-cyclohexyloxycyclohexanol (**13**) were observed after ECH of both substrates, though they were only identified by mass spectra matching and were not quantified. Based on reports by Song et al., we believe that further cleavage of the saturated dimers is very difficult and the hydrogenolysis step of Route 2 is highly unlikely. This is the desired result; formation of the hydrogenated dimers is undesirable as selectivity towards these products may lower the degree of lignin depolymerization. To this end, we try to optimize reaction conditions that can improve selectivity towards the hydrogenolysis path (Route 1) that forms the desired products, phenol and cyclohexanol, while improving the Faradaic efficiency of the system.

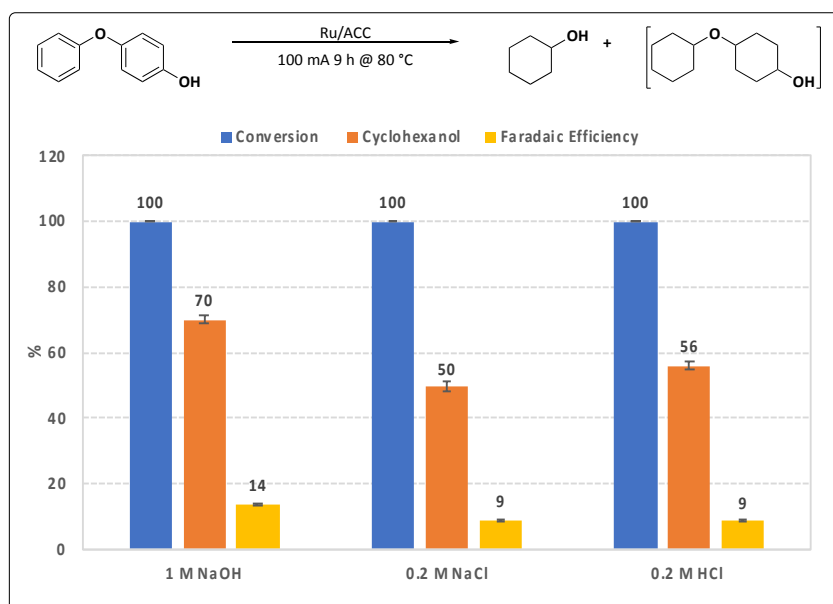
### **Effect of varying electrolyte pH on ECH of 3-phenoxyphenol and 4-phenoxyphenol**

To optimize the ether cleavage of 3- and 4-phenoxyphenol and maximize the cyclohexanol yield, different electrolytes (0.2 M HCl, 0.2 M NaCl, and 1 M NaOH) were investigated. Results from these experiments indicate that after 9 hours, complete conversion of both 3-phenoxyphenol (Figure 5) and 4-phenoxyphenol (Figure 6) was achieved in all electrolytes. The conversion products for all conditions and substrates include cyclohexanol and what could be the saturated dimer cyclohexyloxycyclohexanol (not quantified and only identified via its mass fragments from GC/MS). Furthermore, traces of intermediates such as phenol and cyclohexanone were observed in the 1 M NaOH and 0.2 M NaCl experiments while neither intermediate was observed in the case of the 0.2 M HCl. For both dimers, the cyclohexanol yield was greatest (83% for 3-PPh and 70% for 4-PPh) when using the 1 M NaOH electrolyte that favored the formation of the hydrogenolysis product cyclohexanol (Figure 5 and 6). Since lignin is soluble in basic electrolyte, this result is more relevant and promising for its depolymerization. Adsorption properties of the substrate could be responsible for these differences in selectivity in relation to electrolyte pH. First, since the solubility of both substrates in acidic and neutral electrolytes was limited, the substrates were solubilized in 1 mL isopropyl alcohol (about 0.65 M concentration in 20 mL electrolyte). While isopropyl alcohol helps to solubilize the substrate, it could also be competitively adsorbing to the electrode, reducing the surface coverage by the substrate itself and thus slowing down the rate of conversion. A similar phenomenon was reported by Song et al. in their study of the ECH of diaryl ethers.<sup>40</sup> Second, others have speculated that the mode of adsorption of phenolic compounds could also be responsible for differences in selectivity towards hydrogenolysis products vs. hydrogenation products. If the substrate adsorbs in a planar orientation to the surface, then hydrogenation could be favored resulting in the saturated product. Conversely, nonplanar adsorption via the phenyl hydroxyl group could result in the hydrogenolysis product.<sup>47-48</sup> However this phenomenon might be more of a consequence of functional group types and positions on the phenyl ring (that might influence the orientation and adsorption of the substrate on the electrode surface) rather than the effect of electrolyte pH. When comparing the 0.2 M NaCl and the 0.2 M HCl, higher cyclohexanol yield

(74%) was observed for 3-PPh in NaCl than in HCl (60%) while around 50% cyclohexanol yield was observed for 4-PPh.



**Figure 5.** Observed products, conversion, cyclohexanol yield, and faradaic efficiency for ECH of  $20 \pm 4$  mM 3-phenoxyphenol using 20 mL of the different electrolytes (1 M NaOH, 0.2 M HCl, 0.2 M NaCl) at  $80$  °C, 100 mA ( $33.3 \text{ mA cm}^{-2}$ ), for 9 h. Faradaic efficiency was calculated using only the moles of cyclohexanol measured. The 3-cyclohexyloxycyclohexanol, in square brackets, was only identified (but not quantified) as being a possible product using mass spectra fragments observed and not by injection of the pure compound.

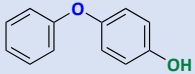
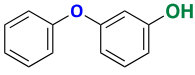
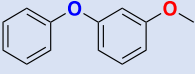
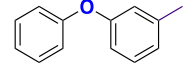
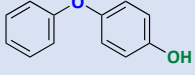
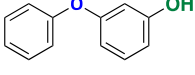
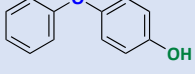
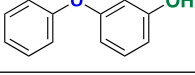


**Figure 6.** Observed products, conversion, cyclohexanol yield, and Faradaic efficiency for ECH of  $20 \pm 4$  mM 4-phenoxyphenol using 20 mL of the different electrolytes (1 M NaOH, 0.2 M HCl, 0.2 M NaCl) at  $80$  °C, 100 mA ( $33.3 \text{ mA cm}^{-2}$ ), for 9 h. Faradaic efficiency was calculated using only the moles of cyclohexanol measured. The 4-cyclohexyloxycyclohexanol, in square brackets, was only identified (but not quantified) as being a possible product using mass spectra fragments observed and not by injection of the pure compound.

### Effect of different functional groups and their position

Aside from differences in selectivity due to electrolyte pH, a comparison of the two dimers showed that the position of the hydroxyl group has an effect on the cyclohexanol yield. It was observed that the hydroxyl group proximity to the ether bond favors cyclohexanol formation. To this end, 3-phenoxyphenol exhibits increased cyclohexanol formation vs. 4-phenoxyphenol, implying that the closer hydroxyl group proximity accelerates cleavage (Table, entry 1 and 2). This could be due to nearby oxygens competing for pi electrons, making the ether oxygen more prone to accepting electrons from the electrode and causing cleavage. A similar phenomenon was observed in previous ECH studies of methoxy substituted phenols (guaiacol, 3-methoxyphenol, and 4-methoxyphenol) by our group.<sup>49-50</sup> Using both Ru/ACC and Raney Ni catalysts, guaiacol showed improved conversion to cyclohexanol compared to 3-methoxyphenol and 4-methoxyphenol.<sup>49-50</sup>

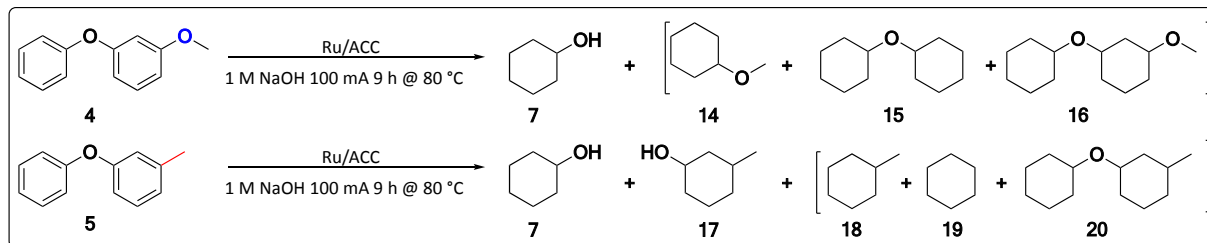
**Table 1.** Conversion and cyclohexanol yield for 4-O-5 dimers with different functional groups and positions.<sup>a</sup>

entry	substrate	compound	electrolyte	conversion [mole %]	cyclohexanol yield [mole %]	Faradaic efficiency [%]
1		<b>1</b>	1 M NaOH	100	70	14 <sup>b</sup>
2		<b>2</b>	1 M NaOH	100	83	16
3		<b>4</b>	1 M NaOH	69	23	3 <sup>c</sup>
4		<b>5</b>	1 M NaOH	67	3	1 <sup>d</sup>
5		<b>1</b>	0.2 M HCl	100	56	9
6		<b>2</b>	0.2 M HCl	100	60	12
7		<b>1</b>	0.2 M NaCl	100	50	9
8		<b>2</b>	0.2 M NaCl	100	74	16

<sup>a</sup> Reaction Conditions: 20 mL of electrolyte (1 M NaOH, 0.2 M HCl or 0.2 M NaCl), substrate concentration of 20±4 mM, at 80 °C, 100 mA, and 9 h. <sup>b,c</sup>Faradaic efficiency calculated only based on moles of cyclohexanol formed, not considering the dimer product. <sup>d</sup>Faradaic efficiency only based on moles of cyclohexanol and 3-methylcyclohexanol formed, not considering the dimer product.

To further understand the effect of varying functional groups, 3-phenoxyanisole (3-PA) and 3-phenoxytoluene (3-PT) were also investigated. Unlike 3- and 4-phenoxyphenol, the solubilities of 3-phenoxytoluene and 3-phenoxyanisole were limited even in the 1 M NaOH electrolyte with isopropyl alcohol cosolvent so conversions were much lower than those observed for 3-phenoxyphenol and 4-phenoxyphenol (Table 1, entry 3 and 4). For 3-phenoxyanisole, a yield of 23% cyclohexanol (**7**) was observed, which is likely a result of ether bond cleavage leading to the formation of phenol and anisole (Figure 7). Further hydrogenation of phenol results in cyclohexanol. It is also possible that hydrogenation and demethylation of anisole can form cyclohexanol. Our group previously reported on this possible pathway, where anisole was completely converted by ECH in two hours to both the demethylation and hydrogenation products (cyclohexanol (**7**) and methoxycyclohexane (**14**)).<sup>50</sup> As such, complete conversion of the anisole intermediate to cyclohexanol and/or methoxycyclohexane is expected in the 9-hour dimer trials reported here. Other products were observed for 3-phenoxyanisole but could not be accurately quantified. Similar to 3-PPh and 4-PPh, the cleavage of the C-O bond from either side of the oxygen is possible, however only products of o-methoxyphenyl bond cleavage were observed for 3-PA. For 3-phenoxytoluene, cleavage appears to happen from both sides of the oxygen to form cyclohexanol (**7**) and the 3-methylcyclohexanol (**17**) stereoisomers. Additionally, the saturated dimer product (**20**) was observed (Figure 7) but was not quantified. The other intermediates such as benzene, toluene, methylcyclohexane, and cyclohexane were not observed, possibly because of their volatility at 80 °C.

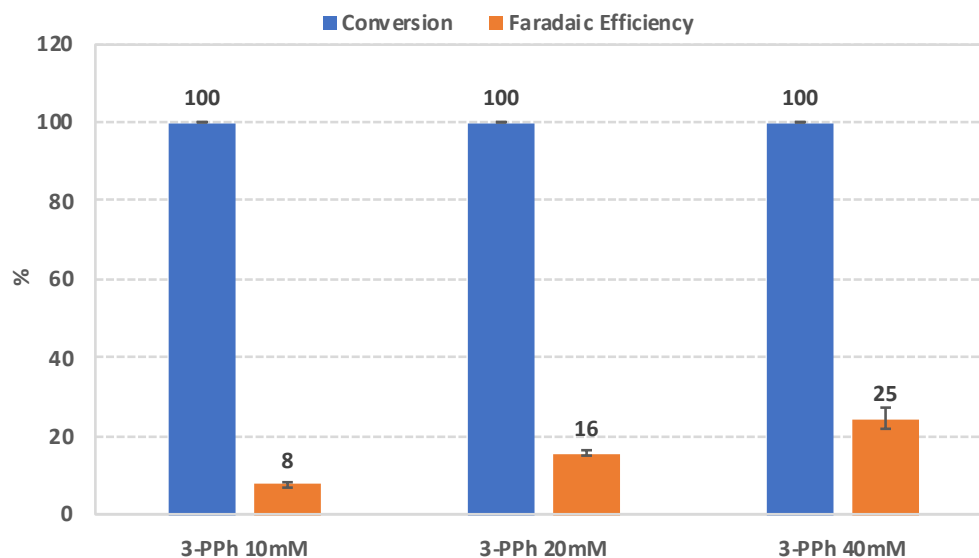
Overall, though ECH was effective at cleaving the ether bonds in all 4-O-5 dimers studied, the nature of the functional groups impacts the conversion and cyclohexanol yield of the reaction. The hydroxyl group on 3- and 4-phenoxyphenol likely assists the adsorption of these substrates on the catalyst surface. However, for 3-phenoxyanisole and 3-phenoxytoluene, no such hydroxyl group is present. Specifically, with 3-PT, since a hydroxyl group is not competing for pi electrons with the ether linkage, the ether oxygen may be less likely to accept electrons from the cathode. Further, the presence of a methyl group can induce steric repulsion from the electrode surface thus decreasing its adsorption enthalpy and resulting in its reduced reactivity.<sup>40</sup> For 3-phenoxyanisole, there is some competition, but its position and the presence of the hydrogen rich methyl group likely limit its competition for pi electrons. The low solubility of 3-PT and 3-PA limits their adsorption, which also lowers their conversion. Future studies should explore the combined effect of several different functional groups to better understand the electrocatalytic conversion of lignin polymers that contain multiple functionalities.



**Figure 7.** Reaction conditions and observed/possible products for the ECH of 3-phenoxyanisole and 3-phenoxytoluene (the square brackets indicate both possible products that were not captured and possible products there were observed and identified by molar mass matching from the mass spectra library and not by injection of pure compounds).

### Effect of substrate concentration on ECH of 3-phenoxyphenol

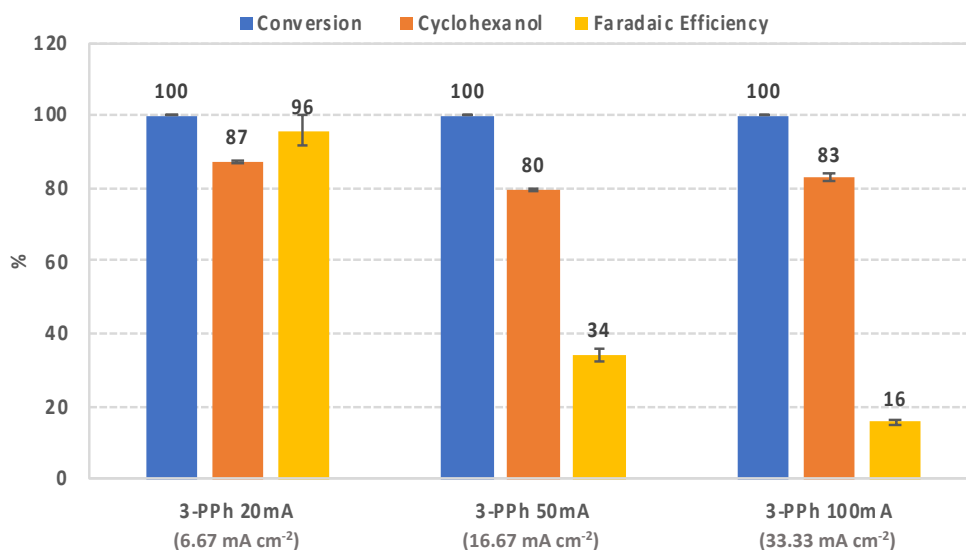
For the studies in the previous sections, the reported Faradaic efficiencies were all lower than 20%. Improving Faradaic efficiency requires the suppression of the hydrogen evolution reactions (HER), which can be achieved by proper control of several parameters. One way of improving the Faradaic efficiency is to increase the rate of substrate hydrogenation by increasing the coverage of the catalyst sites with substrate species. If more active sites are occupied by the substrate species then the likelihood of the chemisorbed hydrogens interacting with these species is increased while the likelihood of chemisorbed hydrogens combining to form hydrogen gas via Tafel and Heyrovsky hydrogen evolution reactions (HER) can be suppressed.<sup>51</sup> To investigate the effect of substrate concentration on the Faradaic efficiency, three different concentrations were investigated. As can be seen from Figure 7, increasing the substrate concentration from 10 mM to 20 mM increased the Faradaic efficiency from 8% to 16%. A further increase of concentration to 40 mM increased the efficiency to 25% (Figure 8). Though improved, this Faradaic efficiency remains modest and merits further investigation.



**Figure 8.** Conversion and Faradaic efficiency for ECH of 3-phenoxyphenol (3-PPh) using different substrate concentrations (10, 20, and 40 mM) in 20 mL 1 M NaOH at 80 °C, 100 mA (33.3 mA cm<sup>-2</sup>), and for 9 h.

### Effect of current density on ECH of 3-phenoxyphenol

To further improve the Faradaic efficiency from 25%, the effect of current density was investigated for the ECH of 3-phenoxyphenol. It was observed that decreasing the current from 100 mA ( $33.33 \text{ mA cm}^{-2}$ ) to 50 mA ( $16.67 \text{ mA cm}^{-2}$ ) increased the Faradaic efficiency from 16% to 34%. Further decreasing the current to 20 mA ( $6.67 \text{ mA cm}^{-2}$ ) resulted in a greatly enhanced Faradaic efficiency of 96% (Figure 9). At lower current density, HER can be suppressed resulting in improved efficiency. After 9 hours, complete conversion was also achieved for all trials, while the cyclohexanol yield was slightly improved by the decrease in current density. This can probably be attributed to the formation of phenol instead of the hydrogenated dimer (cyclohexyloxycyclohexanol) at lower current density. The phenol is further hydrogenated to give higher cyclohexanol yields. In fact, 9% of the phenol intermediate was observed by the end of the 20 mA experiment while less than 1% phenol was observed for the 50 and 100 mA reactions. This shows that 3-phenoxyphenol's selective conversion to phenol vs. the fully hydrogenated, yet undesired, dimer product is favored at lower current density. This has important implications in the selective depolymerization of lignin to valuable products, such as phenols, with high efficiency and low energy inputs.



**Figure 9.** Conversion, cyclohexanol yield, and Faradaic efficiency for ECH of 20 mM 3-phenoxyphenol (3-PPh) using different current densities (6.67, 16.67, and  $33.33 \text{ mA cm}^{-2}$ ) in 20 mL of 1 M NaOH at  $80 \text{ }^{\circ}\text{C}$  for 9 h. Faradaic efficiency was calculated using the cyclohexanol yield (moles) after ECH.

### Conclusions

Analytical pyrolysis of lignin dimers was conducted to identify their resistance to thermal degradation. 2-Phenoxyphenol, a 4-O-5 linked dimer, did not undergo cleavage under pyrolytic cleavage at  $650 \text{ }^{\circ}\text{C}$ .

Consequently, ECH of the 4-O-5 linked dimers 4-phenoxyphenol and 3-phenoxyphenol was investigated in acidic, basic, and neutral electrolytes. Both dimers were cleaved and hydrogenated to cyclohexanol with 100% conversion. ECH of 3-phenoxyanisole and 3-phenoxytoluene resulted in ether cleavage, but the limited solubility of these substrates resulted in lower conversion and formation of lower levels of cyclohexanol. 3-Phenoxyphenol in basic electrolyte showed the highest cyclohexanol yield and Faradaic efficiency of all the substrates, indicating a positive effect of hydroxyl group proximity to the ether bond. Oxygenated functional groups on the aromatic rings in close proximity to the ether linkage appear to accelerate cleavage, possibly because of competition for pi electrons with the ether oxygen. To further improve the Faradaic efficiency, increased substrate concentration and decreased current density were investigated. Though an increase in substrate concentration modestly improved Faradaic efficiency, the greatest improvement was achieved via a decrease in current density to 20 mA ( $6.67 \text{ mA cm}^{-2}$ ), which increased Faradaic efficiency to 96% and cyclohexanol yield to 87%, due to reduced hydrogen evolution. Overall, ECH was demonstrated to be effective in cleaving 4-O-5 type linkages that are often reported to be thermally resistant providing further insight regarding the potential of ECH for lignin depolymerization.

### **Conflicts of interest**

There are no conflicts to declare.

### **Acknowledgements**

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## Synopsis

Thermally resistant 4-O-5 linked lignin model dimers are cleaved to valuable intermediates at mild conditions with high Faradaic efficiency.

## TOC/Abstract Graphic

