Mild, Electroreductive Lignin Cleavage: Optimizing the Depolymerization of Authentic Lignins

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ABSTRACT

Among candidate strategies to depolymerize lignin, electroreduction has promise as a mild, environmentally friendly, low-cost method to cleave lignin's most common linkage, the β-O-4 bond. Much of the prior work on lignin electrolysis has focused on anodic (oxidative) approaches, while most available electroreduction studies have studied lignin model compounds rather than authentic lignin. Here, after optimizing with a model system, we investigated room temperature electroreductive cleavage of four common lignin samples from different pretreatment approaches, including Kraft, Soda, GVL, and Cu-AHP lignin. This mild electrolysis process resulted in solubilization of 45% of the GVL lignin and 60% of the Cu-AHP lignin, affording approximately 17.6 wt% and 19.4 wt% of monomeric materials, respectively. The present work is an encouraging first step toward an electroreductive strategy for lignin depolymerization and upgrading.

KEY WORDS: Electroreduction, Lignin depolymerization, Copper-catalyzed alkaline hydrogen peroxide (Cu-AHP) process, γ-Valerolactone (GVL) pretreatment, Biomass upgrading.

INTRODUCTION

Driven by the imperative to replace fossil-derived products with renewable fuels and chemicals, many studies have focused on lignin, the most abundant aromatic biopolymer on earth, as a low cost, high-energy, and high carbon-content feedstock.[1-3] Numerous homogeneous and heterogeneous catalytic strategies have been explored to depolymerize lignin into smaller fragments amenable to upgrading. However, the typical harsh conditions and/or difficulty of catalyst recovery in these systems make their practical applications challenging.[4, 5] To deconstruct lignin under milder conditions, ideally at ambient temperature and pressure, electrochemical depolymerization is envisioned as a simple, inexpensive, waste-free, and environmentally friendly approach in which only electrons and protons are transferred.[6] Of particular importance is that electrochemical reactions employ electricity, the one major energy mode that does not intrinsically depend on combustion of carbon-based fuels, as it can instead be generated from solar, wind, hydro, or nuclear power.

While electrooxidative depolymerization of lignin has been extensively reported,[6-8] usually involving various types of metal or high-cost electrodes,[9-13] reductive processes have not been as thoroughly studied. Reduction has promise, however, as it increases hydrogen- and decreases oxygen content, thus raising the energy value of the resultant fragments and minimizing oxidative carbon losses.[6] To date, most electroreduction studies have focused on lignin model compounds rather than authentic lignin. In an important recent exception, Chen *et al.*[14] reported electroreduction of wheat straw lignin in alkaline solution using an iron-based alloy as the cathode to produce 28 monomers, six of which were obtained in individual yields as high as 1-3 wt%.

Following up on our previous studies of the biomimetic reductive cleavage of keto aryl ethers[15] and authentic lignin[16] by small organic thiols (Figure 1a), we reported a thio-assisted electroreductive approach involving a pre-electrolyzed disulfide (2,2'-dithiodiethanol). This method achieved over 90% cleavage of β-O-4 dimers in only 1.5 h at room temperature (Figure 1b).[17] Its extension to pre-oxidized poplar lignin released 36 wt% of ethyl acetate soluble fragments and 26 wt% of aqueous soluble fragments, leaving only 38 wt% of insoluble residue after 6 h. Encouraged by these successes, we sought to develop a process that would also electrochemically reduce the disulfide byproducts observed in those earlier studies, with the goal of making the reaction electrocatalytic. Interestingly, substantial cleavage was observed in the

cathodic cell even in control experiments in the absence of sulfur compounds,[17] suggesting a simpler direction for future development.

As described herein, our model studies found that such simple electrolytic conversions take place at ambient temperature and pressure at reasonable rates. Because the properties of lignin vary dramatically depending on their sources, pretreatments, and isolation methods, we optimized and extended this treatment to lignin samples from four common pretreatment methods: kraft,[7] soda,[18] γ-valerolactone/sulfuric acid,[19, 20] and copper-catalyzed alkaline hydrogen peroxide process.[21, 22] These lignins are referred to as Kraft, Soda, GVL, and Cu-AHP, respectively, and their oxidized forms are designated Kraft^{ox}, Soda^{ox}, GVL^{ox}, and Cu-AHP^{ox} hereafter. The present study explores deconstruction of these lignins via simple, mild electrolysis (Figure 1c).

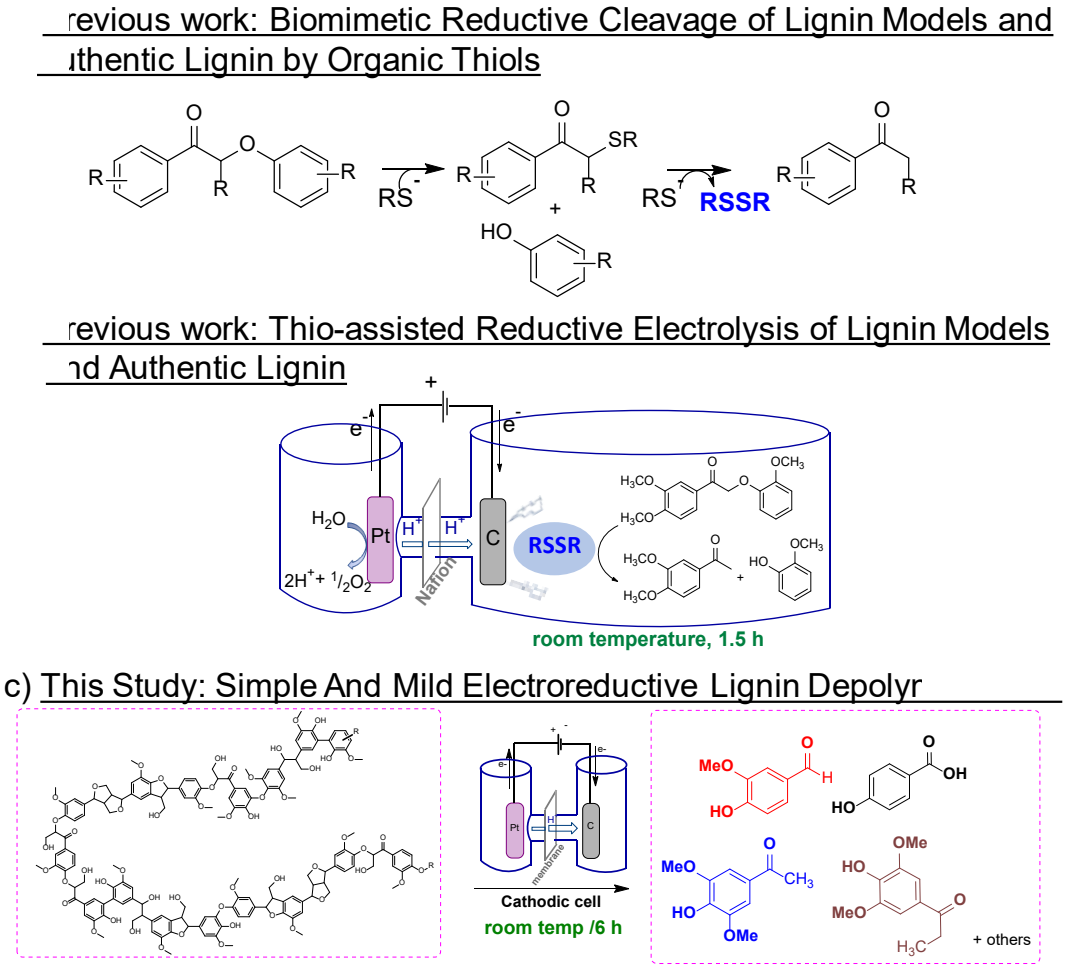


Figure 1. Reductive cleavage of lignin^{ox} into small aromatics at ambient conditions. Our previous works, focusing on the cleavage of β-O-4 model compounds using a) small organic thiols[15] and b)

a thio-assisted reductive electrolysis approach.[16] c) This work, focusing on the depolymerization of four different types of authentic lignin under mild conditions in the absence of sulfur-containing compounds.

EXPERIMENTAL SECTION

Materials

Analytical grade syringic acid, vanillin, *p*-OH benzoic acid, acetosyringone, and propiosyringone were purchased from Sigma-Aldrich. Kraft and soda lignin were provided by Suzano (São Paulo, Brazil) and Green Value (Orbe, Switzerland), respectively; the suppliers indicated that they were from a mixture of hardwoods, but no further detail was available. GVL lignin from hybrid poplar [*Populus nigra L. x P. maximowiczii* A Henry (NM6)] was obtained from the Great Lakes Bioenergy Research Center (University of Wisconsin-Madison, USA), and Cu-AHP lignin from hybrid poplar [*Populus nigra* var. *charkoviensis*×*caudina* cv. NE-19] was produced via copper-catalyzed alkaline hydrogen peroxide pretreatment in our own labs as previously described using 1 mM of copper(II) sulfate and 2 mM of 2,2'-bipyridine.[21]

DDQ Oxidation of Lignin

DDQ-catalyzed oxidation of these four lignins was performed following a previously reported literature procedure.[23] Briefly, a mixture of 3 g of lignin, DDQ (0.3 g; 1.3 mmol), and *t*-BuONO (0.3 g; 2.9 mmol) was solubilized in 42 mL of 1,2-dimethoxyethane/2-ethoxyethanol (v/v = 3:2), followed by heating at 80 °C under an oxygen atmosphere for 14 h. The oxidized lignin product (lignin^{ox}) was precipitated by addition of 200 mL of diethyl ether, isolated by vacuum filtration, washed with additional diethyl ether (100 mL), and dried *in vacuo*.

General Procedure for Cathodic Electrolysis of 2-Phenoxyacetophenone

Reactions were conducted at room temperature for up to 2 h in an H-type electrochemical cell, separated by a Nafion 117 membrane, wherein a platinum wire in 20 mL of pH 8 phosphate buffer was placed in the anode half-cell and reticulated vitreous carbon (RVC, 2 cm^2 immersed) was employed as the cathode. Both half-cells were equipped with magnetic stir bars and were vigorously stirred. The start of the reaction (t = 0) was defined as the time point when substrate (2-phenoxyacetophenone) was added. Briefly, 20 mg of 2-phenoxyacetophenone was directly added

to the cathodic cell and dissolved in a mixture of 10 mL MeOH and 10 mL of one of the various aqueous electrolyte solutions listed in Table 1. After a short period of stirring to achieve homogeneous solution, the 20 mA electric current was applied and continued for the duration of the reaction. Sample aliquots (250 µL) were taken from the cathode cell at timed intervals and diluted with another 250 µL of acetonitrile prior to HPLC analysis.

General Procedure for Lignin^{ox} Electrolysis

In an H-type electrochemical cell, separated by a Nafion 117 membrane and equipped with magnetic stirrers in both compartments, reactions were performed at room temperature with 28 mL of pH 8 phosphate buffer in the anodic cell (platinum wire anode) and 28 mL of NaOH (0.1 M)/methanol (v/v, 1:1) in the cathodic cell (RVC cathode). Sodium chloride (NaCl, 100 mg) was added into the cathodic cell to improve conductivity. Lignin^{ox} (100 mg) was added to the catholyte, and the reaction was then conducted at 20 mA (current density = 10 mA/cm^2) for 6 h. The mixture was transferred to a 50 mL centrifuge tube, where the solvent was removed under a N_2 flow, and the crude product was then solubilized in 20 mL water. The mixture was acidified with 60% H_2SO_4 to pH 2 to precipitate insoluble residue. The precipitate was filtered, washed with water, and dried *in vacuo*, and the remaining filtrate was extracted with ethyl acetate (30 mL × 3). The organic layers were combined, dried with anhydrous Na_2SO_4, and evaporated *in vacuo*. Overall, three fractions were produced and referred to as (1) Ethyl acetate (EA) soluble, (2) Insoluble, and (3) Mass balance (which accounts for the technical losses as well as the aqueous soluble products). A schematic illustration of the reaction work-up is shown in Figure 2.

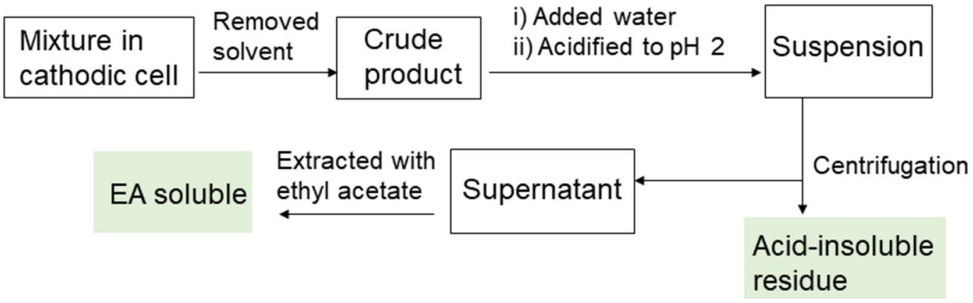


Figure 2. Schematic illustration of the work-up steps for samples taken from the electroreduction of lignin^{ox}. The wt% values of the three components were defined as follows: EA soluble, Acid-insoluble, and Mass balance, where Mass balance was calculated as 100 - (EA soluble wt% + Acid-insoluble wt%).

Characterization of Products

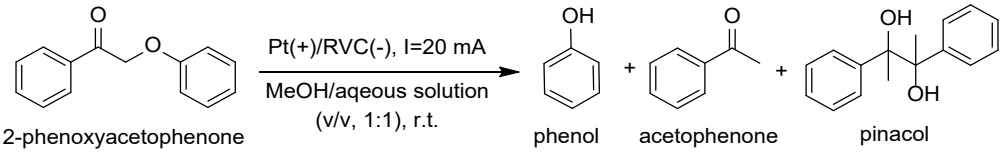
$^{1}H^{13}C$-gradient heteronuclear single quantum coherence (HSQC) was performed (to verify the DDQ oxidation of lignin) at ambient temperature on a 500 MHz Bruker NMR spectrometer equipped with a 5 mm iProbe (BBO probe). Spectra were collected by utilizing the Bruker pulse sequence "hsqcedetgpsisp2.3" with an acquisition time of 63.9 ms (F2, 512 complex points for ^{1}H) and 63.9 ms (F1, 1024 increments for the ^{13}C dimension), using a delay of 1.5 s and 48 scans per increment with spectral widths of 8013 Hz (^{1}H) and 20 kHz (^{13}C). Gel permeation chromatography (GPC) was performed to monitor the molecular weight of lignin^{ox}. Specifically, acid-insoluble products were analyzed by GPC (samples were pre-solubilized in 0.1 M NaOH) using a Waters Ultrahydrogel 250 7.8 x 300 mm column equipped with a Waters Ultrahydrogel 6 x 40 mm guard column. Analyses were performed at 40 °C with a mobile phase of 5 mM NaOH in 80/20 0.1 M aqueous sodium nitrate/acetonitrile at a flow rate of 0.7 mL/min. Polystyrene sulfonic acid and poly(ethylene glycol) were employed as external standards. GC/MS was employed to quantify the EA soluble products on a 6890 Agilent GC equipped with a VF-5ms 30 m x 0.25 mm x 0.25 μm with a 10 m EZ-Guard column and a 5975b single quadrupole MS detector using authentic compounds as standards. Yields of products were reported based on the original weight of lignin^{ox}.

RESULTS & DISCUSSION

Electroreductive Cleavage of Lignin Model Compounds

An ideal system to depolymerize lignin should: 1) be effective under ambient conditions, 2) use inexpensive electrolytes (*e.g.*, NaCl, KCl, etc.) and solvents (*e.g.*, water or simple alcohols such as methanol, ethanol, or 2-propanol), and 3) perform at reasonable rates with high selectivity and the formation of relatively few side products. The electroreduction of 2-phenoxyacetophenone was selected as a model reaction for lignin electrolysis to establish the reaction conditions (Table 1). The electroreductions were conducted at ambient temperature and pressure in a divided cell equipped with reticulated vitreous carbon (RVC) as the cathode and a platinum wire (Pt) as the anode in a mixed solvent composed of methanol and various aqueous solutions (v/v, 1:1).

Table 1. Screening of the solvent system for electroreductive cleavage of 2-phenoxyacetone



2-phenoxyacetophenone | phenol | acetophenone | pinacol

Entry	Current density (mA/cm^2)	Aqueous solution	Current efficiency
1	10	water, 0.1 M NaCl	48%
2	10	0.1 M NaOH	35%
3	10	1 M NaOH	25%
4	10	pH 9 buffer	33%
5	10	0.1 M NaOH + 0.1 M NaCl	31%
6	5	0.1 M NaOH	72%
7	10	0.1 M HCl	15%
8	10	0.05 M H_2SO_4	20%
9	10	0.1 M H_2SO_4	21%

Note: Current efficiency (CE) was calculated as follows: $CE\% = (\frac{\mathrm{mol}_{\mathrm{prod}} \times F \times n}{C_{\mathrm{total}}}) \times 100$; where $\mathrm{mol}_{\mathrm{prod}}$ is the moles of reduction products (phenol and pinacol); F is the Faraday constant (96,485 C/mol); n is the number of electrons per reaction, and C_{total} is the total charge passed.

Screening was initiated with DI water as the solvent (using 0.1 M NaCl as the electrolyte, Table 1, entry 1) as a reference reaction to monitor the pH changes during the reaction. The starting material, 2-phenoxyacetophenone, was cleaved to phenol (97.3%) and acetophenone (80.6%), in approximately 1 h, and the pH of the solution stabilized at approximately 13. After 1 h, however, the undesired product pinacol, derived from the further reduction of acetophenone, began to accumulate. The timing of pinacol formation corresponded to the near complete consumption of the starting material (Figure 3, entry 1), which agrees with our previous findings in the thio-assisted electrolysis of lignin model compounds.[17] In a more basic solution (0.1 M NaOH, pH=13), the 2-phenoxyacetophenone substrate yielded phenol (> 99%) and acetophenone (77.3%) in only 30 minutes (entry 2, Figure 3), but this was again accompanied by the formation of pinacol near the time when the substrate was completely consumed. Interestingly, neither increasing the NaOH concentration (entry 3), nor utilizing a pH 9 buffer (entry 4), nor employing a combination of 0.1 M NaOH and NaCl (entry 5) significantly altered the reaction profiles, although the pinacol yields did vary somewhat (Figure 3). Not surprisingly, the conversion of 2-phenoxyacetophenone was slower under reduced current (entry 6), but no pinacol formation was detected and encouraging yields of the desired products phenol (> 99%) and acetophenone (77.7%) were still obtained.

Performing the analogous reaction under acidic conditions (entries 7-9, Figure S1) led to dramatically lowered reaction rates and formation of phenol and acetophenone, highlighting the importance of the base. The decreased rate and limited product formation under acidic conditions were likely due to the competitive consumption of electrons by proton reduction to generate H_2. Interestingly, the pH of the reactions initiated under acidic conditions still stabilized at roughly 13 as protons were converted to H_2.

The conditions in entry 2 were selected to depolymerize authentic lignin samples, based on the following considerations: 1) Lignin is poorly solubilized in neutral or acidic media while a high concentration of lignin in the aqueous electrolyte is essential for efficient depolymerization. Hence, lignin electroreduction was conducted in alkaline electrolyte. 2) The ideals of sustainability call for minimal amounts and low cost of added reagents, such as the NaOH employed. 3) High current is desirable to minimize reaction times. Although the model systems showed higher pinacol formation at higher current, the methoxylated aromatic ketones formed in the electrolysis of authentic lignin were much less susceptible to this dimerization,[17] enabling the higher current density of 10 mA/cm^2 to be applied.

Noting the above effects of methoxylation on reactivity, it is natural to look beyond the minimal 2-phenoxyacetophenone to ask about the behavior of other more "lignin-like" models, such as 2-phenoxy-*p*-hydroxyacetophenone or 3-hydroxy-2-phenoxypropiophenone as substrates in our electrolytic conditions. In fact, in prior work[16, 17] these compounds were explored. Briefly, the *p*-hydroxy compound reacts sluggishly, presumably due to deprotonation of the -OH group under the basic conditions, inhibiting reduction at the carbonyl moiety.[16] The hydroxymethyl group in the phenoxypropiophenone had relatively little effect on reaction rate as it was rapidly lost under the basic conditions, presumably via a retro-aldol reaction releasing formaldehyde. The result was formation of only the simple phenol and acetophenone products familiar from the unsubstituted starting material.

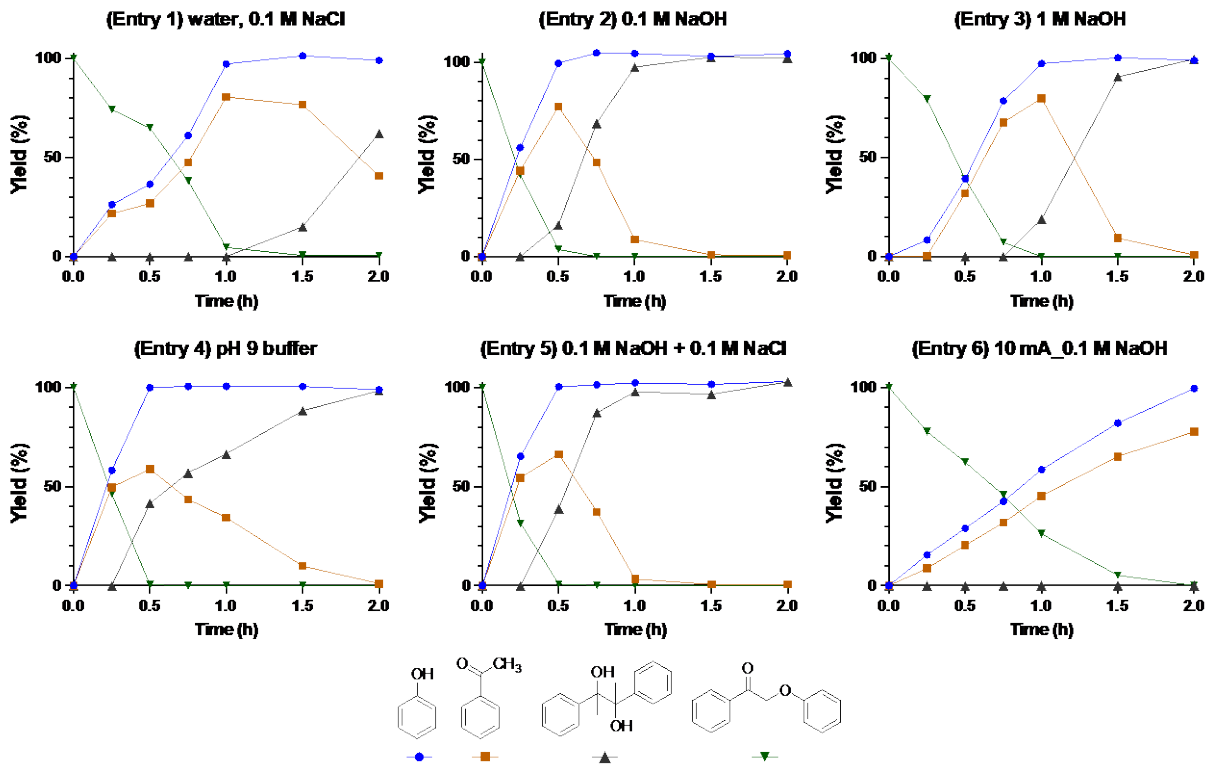


Figure 3. Profiles of electroreduction of 2-phenoxyacetophenone in different aqueous media with an electric current density of 10 mA/cm^2. Note: the maximum theoretical yields of the phenol and acetophenone products are each 100% based on the reaction stoichiometry.

Electroreductive Cleavage of Different Types of Lignin

Our previous study in the thio-assisted electrolysis of lignin revealed the need for oxidation of the α-OH to the corresponding ketone in the β-O-4 linkages, as almost no reaction occurred on the alcohol form (Table S1).[17] Hence, DDQ pre-oxidation of these four lignins was conducted to enable the electrolysis-promoted cleavage of lignin to proceed. Two-dimensional $^{1}H^{13}C$-HSQC NMR spectroscopy validated the oxidation of β-O-4 linkages of lignin, as evidenced by the significant decrease in the correlation peaks associated with the α-OH sites (Figure S2). The pre-oxidized lignins (lignin^{ox}) were then electrolyzed at ambient temperature and pressure for 6 h with a current density of 10 mA/cm^2. Control experiments using identical conditions but in the absence of electric current were also performed (Table 2).

Table 2. Proportions of lignin^{ox} samples divided into EA soluble, Insoluble, and Mass balance fractions after treatment without and with electric current under otherwise identical conditions

Lignin^{ox}	EA soluble		Insoluble		Mass balance	
	No current	10 mA/cm^2	No current	10 mA/cm^2	No current	10 mA/cm^2
Kraft^{ox}	4.0%	11.8%	95.1%	65.3%	0.9%	22.9%
Soda^{ox}	3.5%	6.5%	96.3%	80.2%	0.2%	13.3%
GVL^{ox}	5.1%	19.4%	90.2%	56.2%	4.7%	24.4%
Cu-AHP^{ox}	6.5%	32.0%	92.4%	39.0%	1.1%	29.0%

Note: Results of the electrolysis of non-oxidized (raw) lignins under the same conditions as applied here are provided in Table S1.

Consistent with our previous findings in the electrolysis of Cu-AHP lignin^{ox},[17] electric current was essential to effectively depolymerize the various lignin^{ox} feedstocks. In fact, only 4-6% of EA soluble products were generated from substrates incubated in the absence of current; roughly 90-96 % of the substrate remained inert, regardless of the lignin utilized. In contrast, in the presence of 10 mA/cm^2 current (*i.e.*, 20 mA), the content of EA soluble products increased significantly concomitant with a large decrease in the content of insoluble lignin residue. In particular, as shown in Figure 4, electrolysis of Cu-AHP lignin^{ox} afforded the highest content of EA soluble products (32%) and the lowest insoluble fraction (39%); GVL^{ox} was the second most promising, providing 19.4% and 56.2% of the EA soluble and insoluble fractions, respectively. Kraft^{ox} and Soda^{ox} only showed slight increases in EA soluble products upon electrolysis, consistent with the much higher level of crosslinking expected in these two lignin samples.

GC/MS was then utilized to analyze the composition of the resultant small-molecule products in the ethyl acetate (EA) extracts. Not surprisingly, only small amounts of syringic acid and acetosyringone were found (around 1.4-3.4%) when using Kraft and Soda lignins, in agreement with the corresponding lower yield of the total EA soluble fraction. The harshness of typical kraft and soda processing conditions (~ 175 $^{\circ}$C, pH > 10) can dramatically modify lignin by crosslinking, making these lignin samples refractory to depolymerization. Electrolysis of the more mildly prepared GVL and Cu-AHP lignins afforded significantly higher monomer yields, forming syringic acid, vanillin, *p*-OH benzoic acid, acetosyringone, and propiosyringone as the major products, collectively accounting for 17.6 and 19.4 wt%, respectively (based on the initial weight of lignin^{ox}). The dramatic increase of the monomer yields is presumably the result of a

higher intact β-O-4 content and therefore lower crosslinking in these two lignins compared to Kraft and Soda lignin (Table S2). In a follow-up experiment, the insoluble Cu-AHP lignin residue remaining after electrolysis treatment was further treated with an additional 6 h of current, but only 4.78 wt% of additional EA soluble products were isolated. Thus, prolonged electrolysis time did not significantly enhance yield, presumably because the remaining lignin was more resistant to further decomposition.

GPC provided additional evidence of the limited cleavage of Kraft^{ox} and Soda^{ox} lignin following electrolytic treatment, as suggested by the scant change of weight average molecular weight (M_w), number average molecular weight (M_n), highest-peak molecular weight (M_p), and polydispersity (Figure 5). In contrast, GPC results revealed significant structural changes in the GVL^{ox} and Cu-AHP^{ox} lignins. For instance, electrolytic treatment reduced the M_w of Cu-AHP^{ox} from approximately 25,000 Da to 6,200 Da and decreased the polydispersity from 5.1 to 2.2.

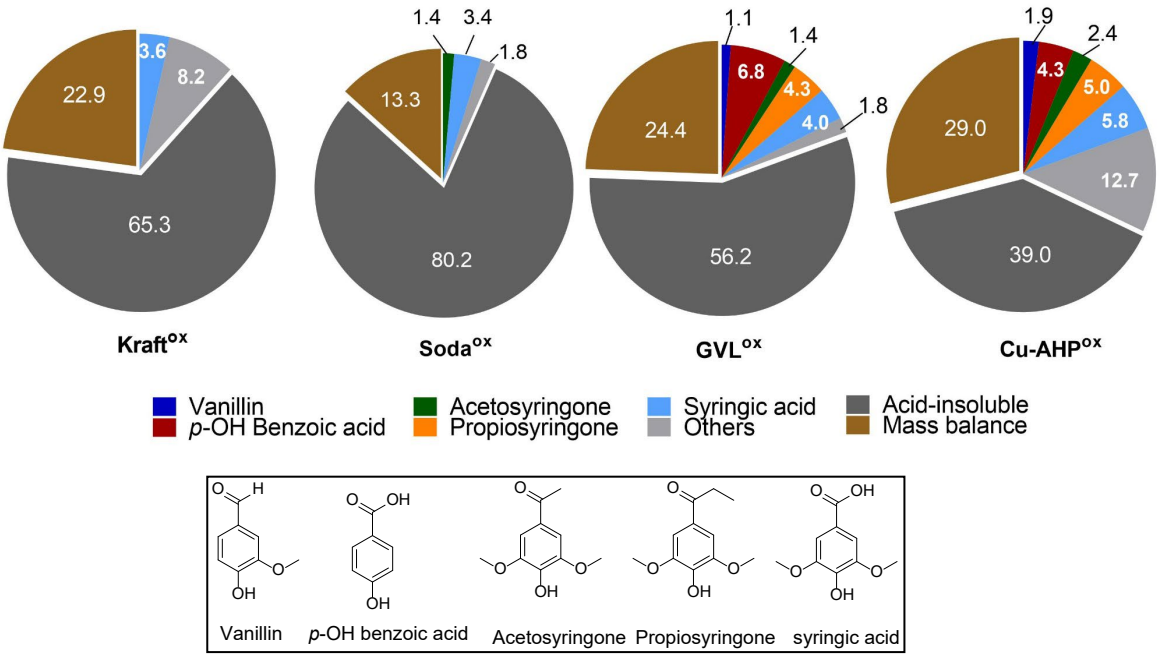


Figure 4. Proportions by weight of the EA soluble, acid insoluble, and mass balance fractions based on the initial weights of the four lignin^{ox} materials after electrolysis. The composition of the EA soluble fraction (upper right sector) is further broken down into the identified (by GC-MS) and remaining unidentified ("Others") substances whose structures were not identified/assigned due to small and overlapping peaks in the GC-MS analysis. Quantification of these materials was based on response factors averaged from the known monomer products. The "Mass balance" sector refers to the sum of unrecovered volatiles, technical losses, and aqueous soluble products.

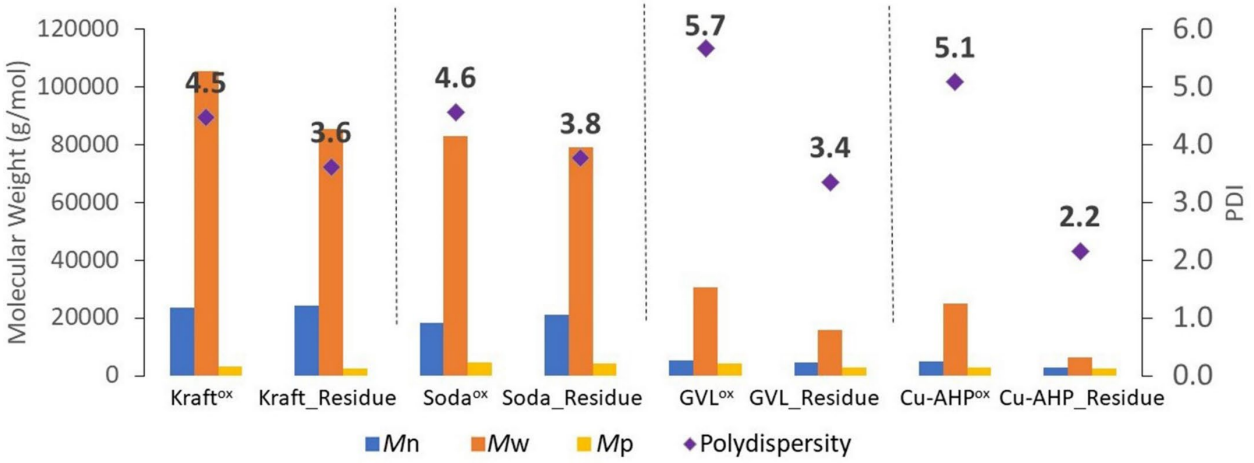


Figure 5. Summary of gel permeation chromatography (GPC) results for the different lignin^{ox} samples before and after electrolysis. Blue bars: number average molecular weight (M_n); orange bars: weight average molecular weight (M_w); yellow bars: highest-peak molecular weight (M_p); purple diamond: polydispersity (PDI).

Discussion

Though anodic oxidative electrocatalytic depolymerization of lignin has been actively explored over the decades,[6, 8] cathodic electrohydrogenolysis has received less attention. In this work, its promise is explored for lignin deconstruction and upgrading to aromatics with alkyl and hydroxy groups commonly found in important chemicals and fuels. Electrolysis of a lignin β-O-4 model compound (2-phenoxyacetophenone) to form phenol and acetophenone provided useful insight into the optimal conditions for subsequent depolymerization work with lignin. The hydrogen evolution reaction (HER) is favored over the electrolysis of the lignin model compound at low pH, consistent with the reduced conversion of 2-phenoxyacetophenone in acidic media (Table 1, entry 7-9). However, conversion of 2-phenoxyacetophenone can be efficiently accomplished in 0.1 M NaOH in the presence of a low-cost inorganic electrolyte (NaCl) and cathode (reticulated vitreous carbon) within a relatively short time (entry 5, 30 minutes), suggesting an encouraging path for the electrolysis of authentic lignin materials.

As noted above, most electrolytic lignin decomposition strategies have focused on the oxidative pathway, generally using commercially available lignin samples (kraft and soda lignin). The depolymerization efficiency commonly depends on the use of traditional catalytic metals (Table 3). As with previous studies on kraft/soda lignin electrolysis, under our conditions, these

two lignin samples in the current system also delivered relatively poor EA soluble fractions (6-11 wt%), with concomitant low monomer yields (< 5 wt%). A comparison of the aforementioned electrooxidative strategies with the electroreductive approach to lignin depolymerization (Table 3) not only showcases the simplicity of the reaction set-up, the requirements of low-cost electrode materials, and the mild reaction conditions for our electroreductive approach, but it also highlights the importance of minimizing crosslinking in the lignin isolation procedure. Thus, once activated by oxidation, lignin prepared using either the GVL or the Cu-AHP process is especially amenable to electroreductive cleavage, releasing the largest amounts of lignin monomers upon electroreduction. Though the β-O-4 linkage, the most abundant linkage in lignin,[1, 7] also appears easiest to cleave, Stahl *et al.* did not observe a correlation between the β-O-4 contents (estimated by 2D HSQC) in different lignin samples and the monomer yields from their formate-based reductive depolymerization process.[24] In our case, however, the lignin samples with higher β-O-4 content, GVL (~46%) and Cu-AHP (~59%), do give higher monomer yields than those with lower β-O-4 contents (theoretical monomer yields were estimated in Table S2).

Table 3. Summary of selected studies on electrolysis of lignin

Lignin	Electrode/Conditions	Major Products	ref
Organosolv	Anode: Ni; Cathode: Pb/PbO_2 35 °C, 1 M NaOH, 30 mA/cm^2	Eight products identified with yields up to 3.6 wt%	Lan *et al.*[10]
Kraft	Anode: Ni foam 1 M NaOH, 5 h	Vanillin, 1.25 wt%	Marino *et al.*[25]
Kraft	Ni electrode, undivided cell in DES	14 monomers identified; total yield ~ 2 wt%	Marino *et al.*[26]
Kraft	Ni foam electrode, 1 M NaOH, 4 h, 35.6-142.2 mA/cm^2	12 monomers identified but with individual yield less than 0.5%	Stiefel *et al.*[27]
Kraft	Ni and Stainless steel electrode, 80 °C, 3 M NaOH, 38 mA/cm^2	Vanillin, 1.0 wt%	Schmitt *et al.*[28]
Soda	Anode: NiOOH; Cathode: Ni 1 M NaOH, rt, 24 h; 6.4 mA/cm^2	14 monomers identified with total yield less than 2 wt%	Di Fidio *et al.*[29]
Kraft	Anode: POM or $FeCl_3$; Cathode: Pt/C electrode 100 °C, 18 h, N_2 protection,	Totally 10 monomers identified, yields not given	Du *et al.*[30]

Kraft	Ni electrode, 160 °C, 3 M NaOH, 10 mA/cm^2	Vanillin, 5.5 wt%	Zirbes *et al.*[31]
Kraft	Anode: Pt; Cathode: RVC, r.t, 0.1 M NaOH, 10 mA/cm^2	Vanillin, 3.6 wt%;	Current work
Soda	Anode: Pt; Cathode: RVC, r.t, 0.1 M NaOH, 10 mA/cm^2	Acetosyringone (1.4 wt%) and syringic acid (3.4 wt%);	Current work
GVL	Anode: Pt; Cathode: RVC, r.t, 0.1 M NaOH, 10 mA/cm^2	Five major identified products with total yield of 17.6 wt%	Current work
Cu-AHP	Anode: Pt; Cathode: RVC, r.t, 0.1 M NaOH, 10 mA/cm^2	Five major identified products with total yield of 19.4 wt%	Current work

Relative to conventional chemical lignin deconstruction approaches, simple reductive electrolysis has been explored here as an alternative, low-waste method for ether cleavage and monomer release. Advantages of this process include:[32] 1) reactions can be powered by renewable electricity sources and technologies; 2) generation of H_2 and O_2 from water splitting could potentially be employed in multiple reactions simultaneously; 3) compared to reagent-based reactions, isolation of products and catalysts is simplified (unless mediators are required in the system) as electrodes are effectively heterogeneous catalysts, easily separated from products by physical removal; and 4) reactions can be easily monitored as they don't require special pressure vessels. A disadvantage is that the simple and effective β-O-4 cleavage presented here is predicated on prior oxidation at the alpha CHOH site. While the DDQ/*t*-butyl nitrite/O_2 reagent combination is effective for this research study, it would not be a practical component in a large-scale integrated process. Ideally, the electrochemical cell's anode could affect the needed oxidation, but development of this complementary half-reaction would be a subject for future work. Similarly, considering the current study's complicated product mixtures, another future direction is to explore the tuning of product selectivity via variation of the electrical potential.[32, 33] Overall, the present work is an encouraging first step toward effective reductive electrolytic lignin depolymerization and upgrading.

CONCLUSION

Encouraged by our previous successes in thio-assisted reductive depolymerization of lignin and lignin models, we investigated four common lignin samples from different pretreatment approaches, including Kraft, Soda, GVL, and Cu-AHP lignin, to explore deconstruction of these lignins via simple, mild electrolysis. Informed by optimization of a model system, the process developed here resulted in solubilization of 45% of the GVL lignin and 60% of the Cu-AHP lignin. Among the four lignin feedstocks explored as substrates for electroreductive cleavage, Cu-AHP proved the most productive in releasing small-molecule organic fragments. This finding is consistent with the lower cross-linking density in this feedstock compared to lignins isolated via the more traditional soda and kraft procedures. A preliminary reagent-based oxidative activation was necessary to enable these reactions in the present work. However, one can envision a strategy that couples activation via anodic oxidation, followed by the reductive cleavage demonstrated herein, to release valuable small-molecule aromatic products from lignin. Ongoing work will explore the product selectivity/separation challenges and the opportunity for such a combined oxidation/reduction approach to lignin valorization.

Conflicts of interest

The authors declare no conflict of interest.

Supporting Information

The Supporting Information is available free of charge online.

Profiles of electroreduction of 2-phenoxyacetophenone in different aqueous media (Figure S1); 2D HSQC spectra of original lignins and DDQ-oxidized lignins (Figure S2); GPC traces of oxidized lignin (lignin^{ox}) and their residues after the electrolytic process (Figure S3); GC/MS spectra of the ethyl acetate soluble fractions from the electrolytic reductive cleavage of different types of lignins (Figure S4); Electrolysis of raw GVL and Cu-AHP lignins with a current density of 10 mA/cm^2 for 6 h (Table S1); Estimated β-O-4 content in different lignin samples based on the 2D HSQC analysis (Table S2).

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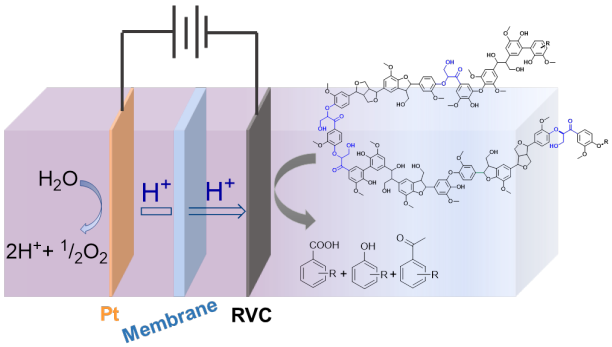

Synopsis:

Pre-oxidized lignin undergoes reductive electrolytic cleavage at ambient conditions over a simple carbon cathode to produce monomeric products.