DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Electrocatalytic Oxidation of Lignin Oligomers

Josh Schaidle, NREL
March 2019
Lignin Utilization

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Goal Statement

**Goal:** Demonstrate *proof-of-concept* that C-C linkages in reductive catalytic fractionation (RCF) derived soluble lignin oligomer streams can be selectively cleaved by electrocatalytic oxidation

- RCF primarily cleaves β-O-4 linkages, thus limiting monomer yield
- Electrocatalytic oxidation could improve monomer yield by >50%
- By 2020, achieve >50% monomer selectivity from RCF-derived lignin stream at a maximum applied voltage of 1.5V

**Outcome:** Develop an *electrocatalytic oxidation process that improves the yield of functionalized lignin monomers from RCF*

- Assess SOT through critical literature review and baseline experiments
- Evaluate existing electrocatalysts with representative model compounds
- Targeted electrocatalyst modifications guided by structure-function relationships
- Assess performance with RCF-derived streams provided from Lignin-First Biorefinery Development project

**Relevance to Bioenergy Industry:** Enables greater value to be extracted from lignin streams by generating functionalized monomers for downstream conversion to chemicals and materials
Quad Chart Overview

Timeline

- Project start date: April 1st, 2018
- Project end date: September 30th, 2020
- Percent complete: 36%

Barriers addressed

**Ct-C: Process Development for Conversion of Lignin**
- Developing electrocatalytic oxidation process to improve monomer yields

**Ct-F: Increasing the Yield from Catalytic Processes**
- Developing electrocatalysts to selectively cleave recalcitrant C-C bonds

Objective

(1) Demonstrate proof-of-concept that C-C linkages in reductive catalytic fractionation (RCF)-derived soluble lignin oligomer streams can be selectively cleaved by electrocatalytic oxidation, thus producing functionalized monomers, and (2) advance the technology by targeting yield improvements

End of Project Goal

By September 2020, achieve >50% monomer selectivity from RCF-derived lignin stream at a maximum applied voltage of 1.5V
Opportunity: Lignin oil comprised of monomers and oligomers that possess rich functionality for use as chemical and material precursors

Project Overview:
Composition of RCF Lignin Oil

**Hybrid Poplar RCF Lignin Oil**

*RCF lignin oil generated and characterized by Lignin-First Biorefinery Project

**Monomer Yields by GC-FID**

- **PhOH**: 0.66
- **PG**: 5.77
- **IEG**: 12.17
- **ES**: 4.63
- **P(OMe)G**: 2.94
- **PS**: 0.35
- **P(OH)G**: 19.15
- **P(OMe)S**: 0.46

Monomer yields approaching theoretical limits based on ether bond cleavage

**Challenge:** Selective cleavage of recalcitrant C-C linkages to improve monomer yield

**Oligomers**

Oligomers make up >50% of RCF lignin oil and are linked by recalcitrant C-C bonds

- **[β-1]**
- **[5-5]**
- **[β-β]**
- **[β-5]**

Complete disappearance of β-O-4' linkages
Project Overview: Value Proposition

**Value Proposition:** Development of a low-pressure, low-temperature, electron-driven process for selective production of functionalized lignin monomers

**Objectives:**
- Establish state-of-the-art and baseline by identifying and evaluating existing electrocatalyst and operating conditions reported in literature
- Utilize standard electrochemical methods to evaluate baseline and next-generation electrocatalysts with representative model compounds to link catalyst composition to performance
- Guide electrocatalyst development by structure-function relationships
- Assess improvements over baseline with RCF lignin oil

**Differentiators:**
- Leveraging NREL’s expertise in catalysis, electrochemistry, and lignin chemistry
- Systematic process evaluation coupled with hypothesis-driven electrocatalyst design
- Close collaboration with Lignin-First Biorefinery team
Management Approach

Focused on effective collaboration to bring together experts in catalysis, electrochemistry, and lignin chemistry

Team members:
• Ken Ngo – Electrochemistry
• Dan Ruddy – Materials Synthesis
• Fred Baddour – Materials Characterization

Interactions:
• Biweekly team meetings
• Monthly meetings with each collaborative project

2.5.4.304 Advanced Catalyst Synthesis and Characterization
Synthesis and characterization of next-generation electrocatalysts

2.3.1.316/317 Electrocatalytic CO₂ Reduction
Electrode preparation, cell design and optimization, and electrochemical evaluation

2.2.3.106 Lignin-First Biorefinery Development
RCF oil generation and process stream characterization
Technical Approach: Utilizing Standard Electrochemical Methods

**Linear Sweep Voltammetry (LSV)**
Rapid method to screen electrocatalysts and identify oxidation events

**Controlled Potential Electrolysis (CPE)**
Bulk electrolysis at a selected potential to generate products for quantification

**Selection of Operating Conditions**

- **E_i** (Initial Potential)
- **E_f** (Final Potential)
- Oxidation potential at peak current

Potential of working electrode (WE) is scanned linearly with time from **E_i** to **E_f**

**Liquid sampling** for product analysis

**Undivided 3-electrode cell**
- Reference electrode (RE)
- Working Electrode (WE)
- Counter electrode (CE)

**Divided 3-electrode cell**
- Anode (WE + RE)
- Cathode (CE)
- Carbon electrode (WE)
- Pt electrode (CE)
- Fritted glass membrane
- Gas evolution (H_2) and possible side reactions
- Diffusion of electrolyte (Na^+, OH^−, H_3O^+)
Technical Approach: Systematic Process Evaluation Coupled with Hypothesis-driven Electrocatalyst Design

Key Challenges: (1) selective cleavage of recalcitrant C-C linkages and (2) lack of foundational knowledge on electrocatalytic lignin oxidation

- Assess state-of-the-art by identifying the most promising existing catalysts and operating conditions reported in literature
- Develop electrochemical evaluation system and protocol and identify suitable solvent/electrolyte system and operating conditions
  - Critical challenges: lignin oligomer solubility and oxidation stability of electrolyte
- Establish baseline performance with model compounds
  - Key metrics: monomer selectivity, yield, and faradaic efficiency
- Design, synthesize, and evaluate next-generation electrocatalysts using insight gained from baseline tests
- Evaluate promising materials with RCF lignin oil

Success Factor: Demonstrate monomer selectivity of 30% at an applied voltage of <1.5V from RCF lignin oil (FY19 Q2 Go/No-Go)
Identified promising electrocatalyst formulations and electrolyte/solvent systems for electrocatalytic lignin oxidation

Electrocatalyst formulations:
- Noble metals: Pt and Pd
- Base metals: Ni, Co, and Cu
- Metal oxides: PbO₂

Electrolyte/Solvent Systems:
- Electrolyte: NaOH (aq), LiClO₄
- Solvents: Methanol (aq), Ethanol (aq), Butanol (aq), Acetonitrile

Selected References:

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Lignin/ Lignin model compound types</th>
<th>Electrolyte</th>
<th>T (°C)</th>
<th>Potential / current density</th>
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<td>Pt</td>
<td>Lignin model compound A</td>
<td>LiClO₄/ CH₃CN</td>
<td>23</td>
<td>1.1 V</td>
<td>4-O-ethylvanillin</td>
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<td>Holzforschung, 2012, 66, 303.</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Bamboo Lignin</td>
<td>1 M NaOH</td>
<td>30</td>
<td>20 mA/cm²</td>
<td>syringaldehyde</td>
<td>6</td>
<td>ChemistrySelect, 2017, 2, 4956.</td>
</tr>
</tbody>
</table>
**Progress:**
**Assess State-of-the-Art**

Identified promising electrocatalyst formulations and electrolyte/solvent systems for electrocatalytic lignin oxidation

*Electrocatalyst formulations:*
- Noble metals: Pt and Pd
- Base metals: Ni, Co, and Cu
- Metal oxides: PbO$_2$

*Electrolyte/Solvent Systems:*
- Electrolyte: NaOH (aq), LiClO$_4$
- Solvents: Methanol (aq), Ethanol (aq), Butanol (aq), Acetonitrile

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![Lignin Model Compound A](image1.png)  
1 h of 1.1 V vs. Ag/AgCl  
40% guaiacol

![Lignin Model Compound B](image2.png)

6 F/mol of charge 1.7 mA/cm$^2$ current  
40% benzoic acid  
< 1% guaiacol
Progress:
Select Operating Conditions

Selected operating conditions for CPE by evaluating Pt, Ni, and Pb/PbO₂ electrodes with LSV in 3 electrolyte/solvent systems

Anodic onset potential ($E_a$, V vs. SCE) and peak current density ($I_p$, mA/cm²)

<table>
<thead>
<tr>
<th>2-phenoxy-1-phenylethanol</th>
<th>Pt disk/ $E_a$ (Ip)</th>
<th>Ni foil/ $E_a$ (Ip)</th>
<th>Pb/PbO₂ foil/ $E_a$ (Ip)</th>
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<tr>
<td>0.1 M LiClO₄ in CH₃CN</td>
<td>1.0 (5.8)</td>
<td>0.79 (27)</td>
<td>No Reaction</td>
</tr>
<tr>
<td>1 M NaOH in H₂O/EtOH</td>
<td>No Reaction</td>
<td>0.35 (70)</td>
<td>0.48 (44)</td>
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<tr>
<td>0.1 M NaOH in H₂O/CH₃CN</td>
<td>1.4 (15.1)</td>
<td>0.69 (17)</td>
<td>0.49 (11)</td>
</tr>
<tr>
<td><strong>1,2-diphenylethanol</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M LiClO₄ in CH₃CN</td>
<td>0.60 (0.26)</td>
<td>0.83 (23)</td>
<td>No Reaction</td>
</tr>
<tr>
<td>1 M NaOH in H₂O/EtOH</td>
<td>No Reaction</td>
<td>0.35 (7.6)</td>
<td>0.49 (23)</td>
</tr>
<tr>
<td>0.1 M NaOH in H₂O/CH₃CN</td>
<td>No Reaction</td>
<td>0.70 (18)</td>
<td>0.49 (13)</td>
</tr>
<tr>
<td><strong>2,2’-biphenol</strong></td>
<td></td>
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<tr>
<td>0.1 M LiClO₄ in CH₃CN</td>
<td>0.67 (4.0)</td>
<td>0.77 (29)</td>
<td>No Reaction</td>
</tr>
<tr>
<td>1 M NaOH in H₂O/EtOH</td>
<td>0.28 (1.4)</td>
<td>No Reaction</td>
<td>0.47 (19)</td>
</tr>
<tr>
<td>0.1 M NaOH in H₂O/CH₃CN</td>
<td>0.28 (1.2)</td>
<td>0.58 (5.7)</td>
<td>0.49 (7.0)</td>
</tr>
</tbody>
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Electrode oxidation at 0.49V vs. SCE
Progress:
Select Operating Conditions

Selected operating conditions for CPE by evaluating Pt, Ni, and Pb/PbO₂ electrodes with LSV in 3 electrolyte/solvent systems

Anodic onset potential ($E_a$/ V vs. SCE) and peak current density ($I_p$/ mA/cm²)

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Pt electrode
LiClO₄ in CH₃CN

$E_a = 1.03$ V
$E_p = 1.18$ V
$I_p = 5.84$ mA.cm⁻¹

Ni electrode
NaOH in H₂O and EtOH

$E_a = 0.352$ V
$E_p = 0.555$ V
$I_p = 69.9$ mA.cm⁻¹

Ni electrode in NaOH/H₂O/EtOH selected as baseline
Progress:
Prepare Electrocatalysts

Synthesized Ni (baseline) and next-generation Ni$_2$P and MoC nanoparticles supported on carbon for CPE experiments

**Critical objectives:**
- Increase active surface area to improve rate of product generation
- Probe effect of bifunctionality and oxophilicity (Ni$_2$P and MoC) on performance

One pot thermal reduction technique with high bp solvent and organic ligands

MoC NPs
- 1-3nm
- Non-spherical shape

Nickel NPs
- ~12nm
- Spherical shape

Mo(CO)$_6$ precursor

Ni(acac)$_2$ precursor

Molybdenum carbide nanoparticles

Nickel nanoparticles
MoC nanoparticles outperformed all other electrocatalysts and demonstrated C-C cleavage of model compounds

2-phenoxy-1-phenylethanol

4.9% conversion

Selected from LSV experiments

Benzaldehyde

3.0%

Phenylacetaldehyde

0.15%

Phenol

1.1%

Toluene

0.52%

Yield

Selectivity

Faradaic efficiency

3 hrs CPE at 0.77 V

20% conversion

1,2-diphenylethanol

Benzaldehyde

2.0%

Toluene

0.40%

Stilbene

12%

Sides products at the Pt cathode

Unknowns

5.6%

3 hrs CPE at 0.70 V

Unknowns

12%

55%
Relevance: High-yield Lignin Conversion is Critical to Achieving BETO cost targets

Developing an innovative electron-driven process to selectively cleave recalcitrant C-C linkages in RCF lignin oligomers, with potential to improve monomer yield from RCF pathway by 50%

• 2018 MYP – "Techno-economic analysis has identified that high-yield conversion of lignin is critical to achieving cost targets."

→ Critical Need: "Development of catalysts and biocatalysts that can selectively cleave bonds between lignin monomers and oligomers"

• This project addresses this critical need by:
  – Demonstrating proof-of-concept for electrocatalytic oxidation of lignin oligomers
  – Advancing state-of-technology by improving selectivity to monomers
    • Selectivity used as a key metric for milestones and Go/No-Go
  – Hypothesis-driven electrocatalyst design
  – Integrating downstream electrocatalysis with upstream RCF
Relevance: Bioenergy Industry

Improving biorefinery carbon utilization by enhancing lignin monomer yield from RCF

- **Potential cost savings** compared to other oxidative approaches due to low-pressure, low-temperature operation:
  - Leverage future low-cost electricity and modularity of electrochemical systems

- **Generate valuable intermediates** from mixed lignin dimer/oligomer streams that currently have near-zero commercial value

IRENA, Renewable Power Generation Costs in 2017
**Future Work:**
Demonstrate Proof-of-Concept with RCF Oil

**Goal:** Achieve lignin monomer selectivity of 30% at an applied voltage of <1.5V from RCF lignin oil (FY19 Q2 Go/No-Go)

**Hybrid Poplar RCF Lignin Oil**

**Controlled Potential Electrolysis**

- **Anode (WE + RE)**
- **Cathode (CE)**

- **Lignin Oligomer Oxidation**
  - Nanoparticle catalysts on carbon support
  - Diffusion of electrolyte ($\text{Na}^+$, $\text{OH}^-$, $\text{H}_3\text{O}^+$)

- **Gas evolution** ($\text{H}_2$) and possible side reactions

- **Electrocatalyst:** MoC/C
- **Electrolyte:** NaOH/EtOH/H$_2$O

**Product Analysis**

- Determine dimer and oligomer conversion and selectivity to monomers
- Analysis with GC-MS, LC-MS, and GPC
- **Critical Metric:** Retain functionality of existing monomers in lignin RCF oil

**Dimers and Oligomers**

**GPC**

<table>
<thead>
<tr>
<th>Normalized response (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

**Apparent MW (Da)**

- 100
- 1,000
- 10,000
Future Work: Hypothesis-Driven Electrocatalyst Development

**Goal:** Develop a mechanistic understanding of the major reaction pathways and leverage this knowledge to guide electrocatalyst modifications

**Target:** 10% increase in lignin monomer selectivity over current state-of-technology

- Probe individual reaction steps with model compounds and reaction intermediates
- Leverage modeling to understand reaction energetics and steric hindrance
- Evaluate carbon spikes as support to enhance reactant accessibility

In collaboration with 2.3.1.317 CO₂ Upgrading (Adam Rondinone, ORNL)
**Future Work: Process Development**

Address critical process questions and challenges identified during proof-of-concept experiments

<table>
<thead>
<tr>
<th>Critical Question/Challenge</th>
<th>Strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side reactions and crossover (anode $\rightarrow$ cathode)</td>
<td>Utilize anion exchange membrane to prevent crossover of lignin compounds</td>
</tr>
<tr>
<td>Impact of OH- and O$_2$ concentration</td>
<td>Perform CPE experiments with varying NaOH concentrations and O$_2$ co-feed</td>
</tr>
<tr>
<td>Role of H$_2$O and EtOH Oxidation</td>
<td>Perform CPE experiments at varying applied voltages</td>
</tr>
<tr>
<td>Electro catalyst stability</td>
<td>• Perform extended CPE experiments with real-time product analysis</td>
</tr>
<tr>
<td></td>
<td>• Characterize spent electrocatalysts</td>
</tr>
<tr>
<td></td>
<td>• Evaluate leaching by analyzing anolyte with ICP</td>
</tr>
<tr>
<td></td>
<td>• Transition to continuous system</td>
</tr>
<tr>
<td>State of MoC electrocatalyst (nature of the active site: Mo vs. C)</td>
<td>Evaluate additional Mo-based catalysts (i.e., MoO$_x$)</td>
</tr>
</tbody>
</table>
Summary

**Goal:** Demonstrate proof-of-concept that C-C linkages in reductive catalytic fractionation (RCF) derived soluble lignin oligomer streams can be selectively cleaved by electrocatalytic oxidation

**Approach and Progress:** Systematic process evaluation coupled with hypothesis-driven electrocatalyst design, resulting in demonstrated cleavage of C-C linkages in lignin model compounds

**Outcome:** Develop an electrocatalytic oxidation process that improves the yield of functionalized lignin monomers from RCF

**Relevance to Bioenergy Industry:** Enables greater value to be extracted from lignin streams by generating functionalized monomers for downstream conversion to chemicals and materials
Acknowledgements

Bioenergy Technologies Office

Team members and contributors:
Ken Ngo
Fred Baddour
Dan Ruddy

Special thanks to all of our collaborators!
Acronyms

- CE – Counter Electrode
- CPE – Controlled Potential Electrolysis
- $E_a$ – Anodic Onset Potential
- EtOH – Ethanol
- ES – Ethyl Syringol
- GC-FID – Gas Chromatography – Flame Ionization Detector
- GC-MS – Gas Chromatography – Mass Spectrometry
- GPC – Gel Permeation Chromatography
- ICP – Inductively Coupled Plasma (Spectroscopy)
- $I_p$ – Peak Current Density
- LC-MS – Liquid Chromatography – Mass Spectrometry
- LSV – Linear Sweep Voltammetry
- 2D HSQC NMR – 2-Dimensional Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance
- PG – Propyl Guaiacol
- PhOH – Phenol
- PS – Propyl Syringol
- RCF – Reductive Catalytic Fractionation
- RE – Reference Electrode
- SCE – Saturated Calomel Electrode
- SOT – State of Technology
- WE – Working Electrode