NREL
Transforming ENERGY

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Electrocatalytic Oxidation of Lignin Oligomers

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Lignin Utilization

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%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	N/A	N/A	$150k	$600k
Project Cost Share	N/A			

Related Projects: 2.2.3.106 Lignin-First Biorefinery Development, 2.3.1.316 CO_2 Utilization: Thermo- and Electro-catalytic routes to fuels and chemicals, 2.3.1.317 Hybrid electro- and thermo-catalytic upgrading of CO_2 to fuels and C_{2+} chemicals, 2.5.4.304 Advanced Catalyst Synthesis and Characterization

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

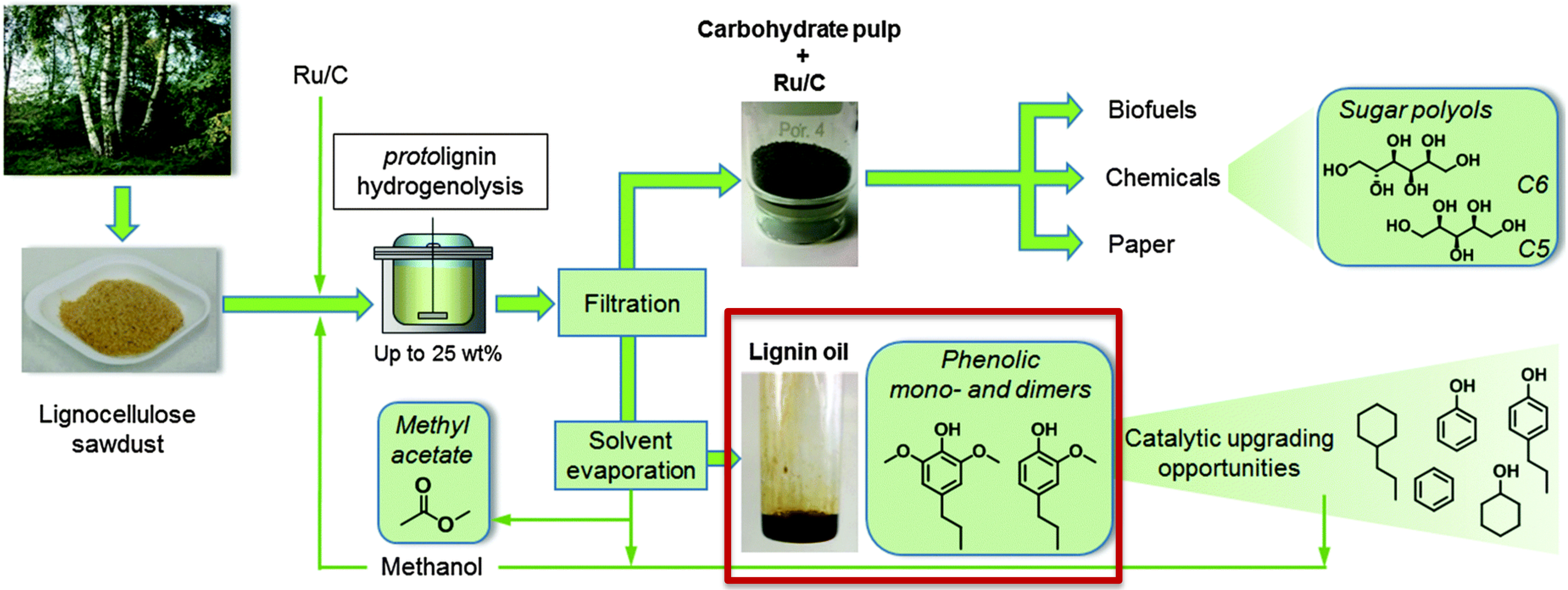
(1) Demonstrate proof-of-concept that C-C linkages in reductive catalytic fractionation (RCF) -derived soluble lignin oligomer streams can be selectively cleaved by electrocatalytic oxidation, thus producing functionalized monomers, and (2) advance the technology by targeting yield improvements

End of Project Goal

By September 2020, achieve >50% monomer selectivity from RCF-derived lignin stream at a maximum applied voltage of 1.5V

Project Overview:
Reductive Catalytic Fractionation (RCF)

Catalytic solvation approach to effectively separate lignin and carbohydrates



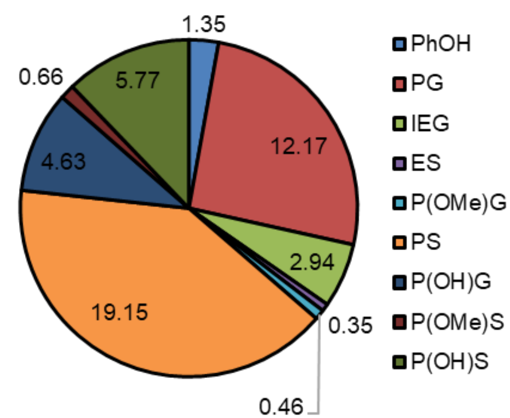
S. Van den Bosch, et al. *Energy Environ. Sci.* 8 (2015) 1748

Opportunity: *Lignin oil comprised of monomers and oligomers that possess rich functionality for use as chemical and material precursors*

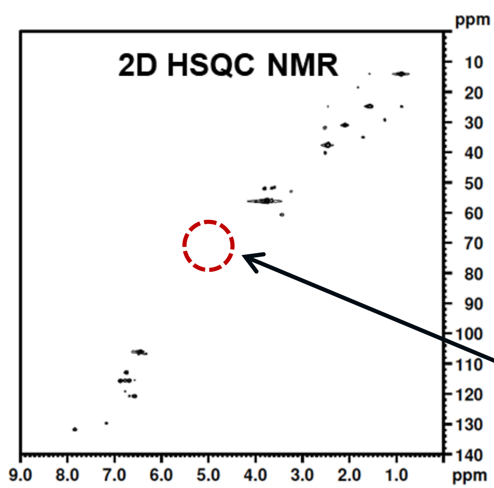
Project Overview: Composition of RCF Lignin Oil

Hybrid Poplar RCF Lignin Oil*

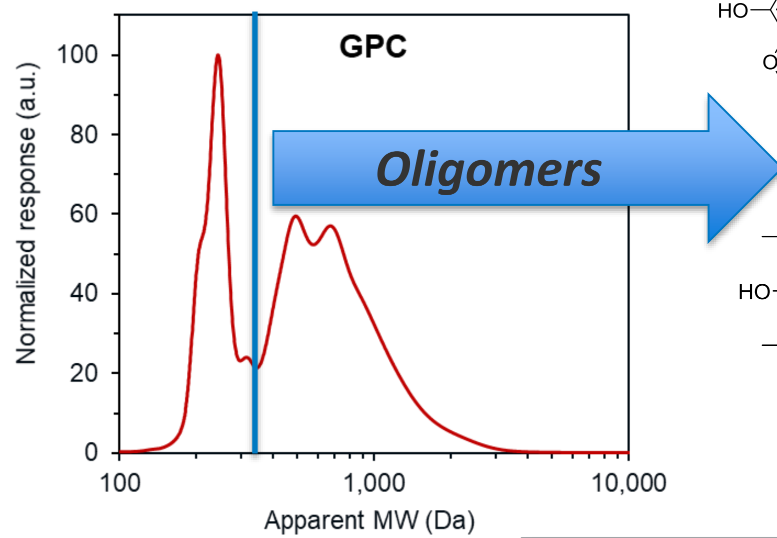
Monomer Yields by GC-FID



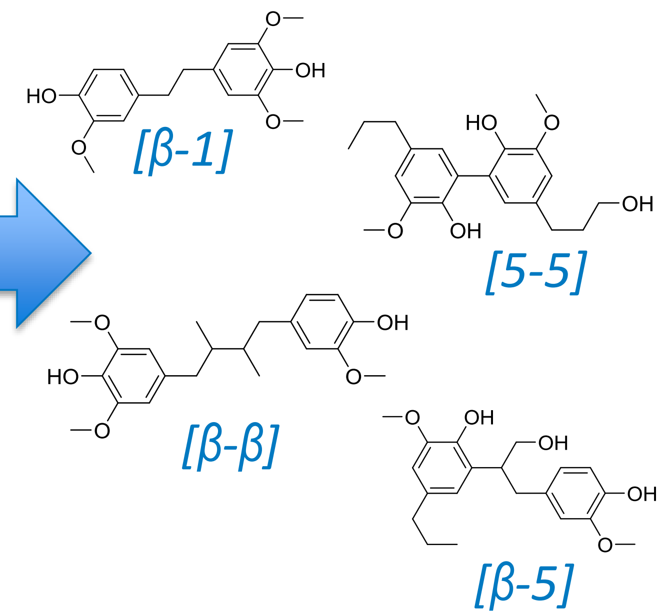
Monomer yields approaching theoretical limits based on ether bond cleavage



Complete disappearance of β–O–4' linkages



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



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

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

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

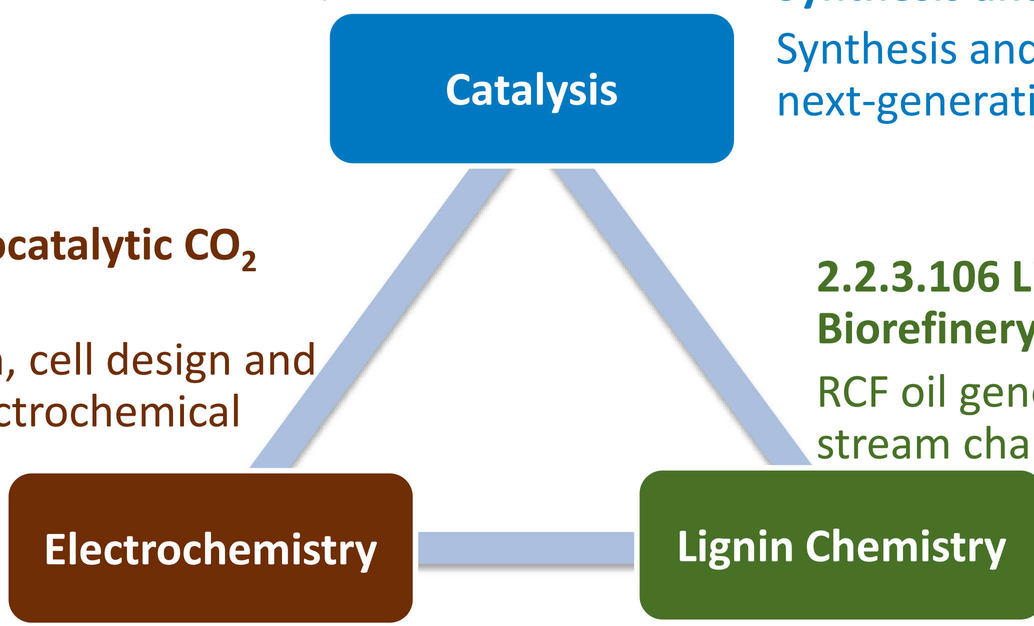
Interactions:

- Biweekly team meetings
- Monthly meetings with each collaborative project

ChemCatBio
Chemical Catalysis for Bioenergy

2.5.4.304 Advanced Catalyst Synthesis and Characterization

Synthesis and characterization of next-generation electrocatalysts



2.3.1.316/317 Electrocatalytic CO_2 Reduction

Electrode preparation, cell design and optimization, and electrochemical evaluation

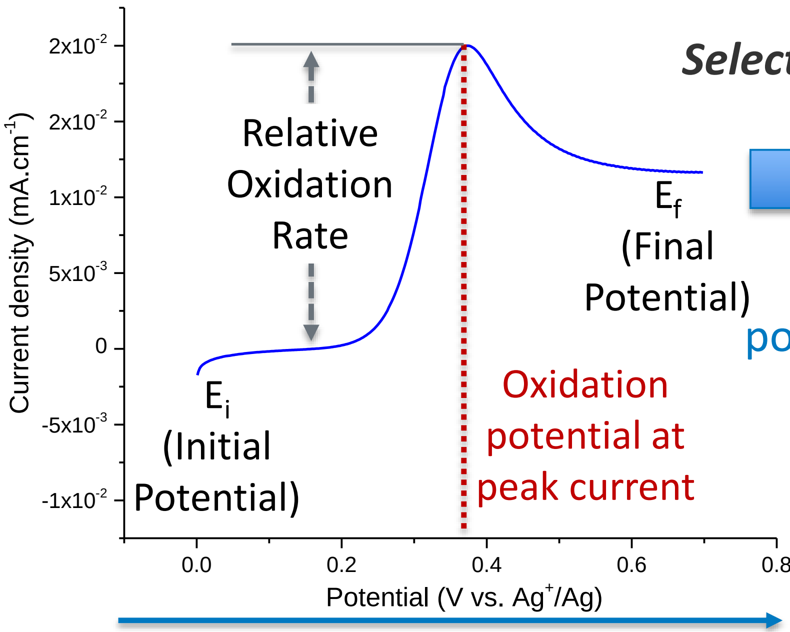
2.2.3.106 Lignin-First Biorefinery Development

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



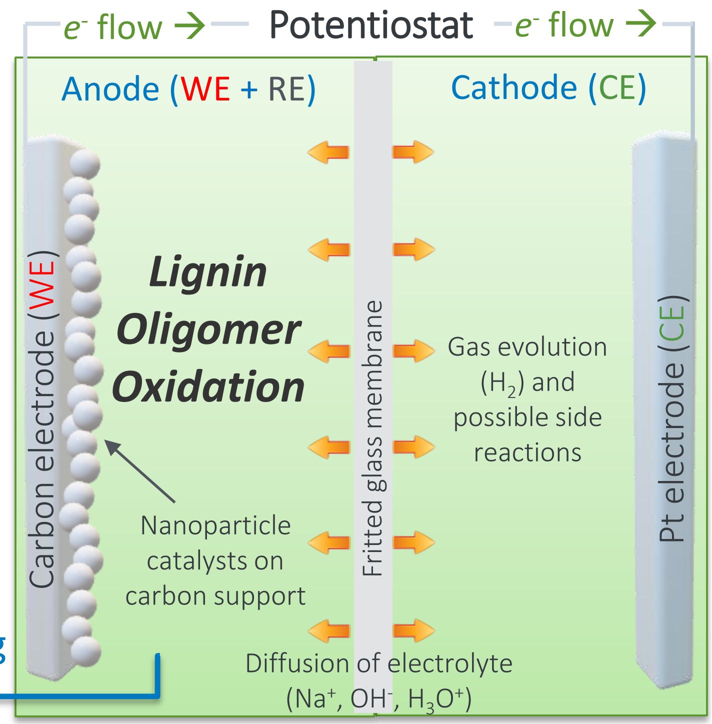
Potential of working electrode (WE) is scanned linearly with time from E_i to E_f

Selection of Operating Conditions

[oxidation potential, solvent, electrolyte, electrode]

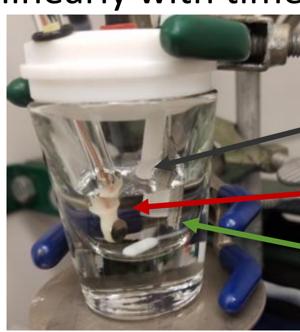
Controlled Potential Electrolysis (CPE)

Bulk electrolysis at a selected potential to generate products for quantification



Liquid sampling for product analysis

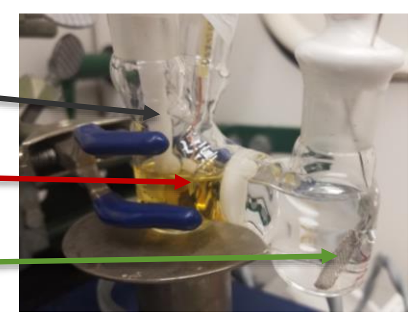
Undivided 3-electrode cell



Reference electrode (RE)

Working Electrode (WE)

Counter electrode (CE)

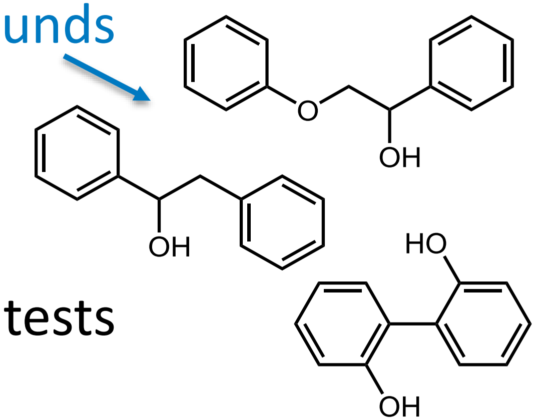


Divided 3-electrode cell

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)*

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

Selected References:

Electrode	Lignin/ Lignin model compound types	Electrolyte	T (°C)	Potential / current density	Primary Product	Yield %	Ref.
Pt	Lignin model compound A	$LiClO_4$/ CH_3CN	23	1.1 V	4-O-ethylvanillin	40	*Holzforschung*, 2012, 66, 303.
Ni	Lignin model compound B	1.5 M NaOH	150	1.7 mA/cm^2	benzoic acid	40	*J. Org. Chem.*, 1991, 56, 7305.
Co	Kraft lignin	3 M NaOH	80	1.9 mA/cm^2	vanillin	1.4	*Beilstein J. Org. Chem.*, 2015, 11, 473.
Cu	Kraft lignin	1 M NaOH	23	70 mA/cm^2	vanillin	< 10	*J. Appl. Electro.*, 2000, 30, 727.
PbO_2	Bamboo Lignin	1 M NaOH	30	20 mA/cm^2	syringaldehyde	6	*ChemistrySelect*, 2017, 2, 4956.

Progress:
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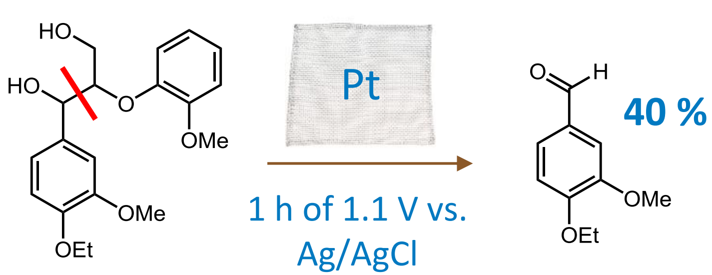
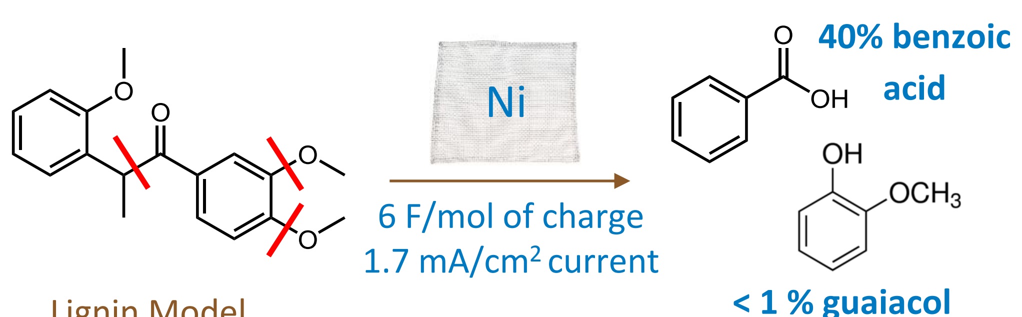


Lignin Model Compound A



Lignin Model Compound B

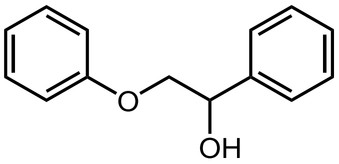
Progress:
Select Operating Conditions

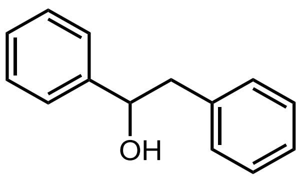
Selected operating conditions for CPE by evaluating Pt, Ni, and Pb/PbO_2 electrodes with LSV in 3 electrolyte/solvent systems

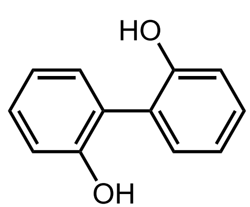
Anodic onset potential (E_a / V vs. SCE) and peak current density (I_p / mA/cm^2)

2-phenoxy-1-phenylethanol	Pt disk/ Ea (Ip)	Ni foil/ E_a (I_p)	Pb/PbO_2 foil / E_a (I_p)
0.1 M $LiClO_4$ in CH_3CN	1.0 (5.8)	0.79 (27)	No Reaction
1 M NaOH in H_2O/EtOH	No Reaction	0.35 (70)	0.48 (44)
0.1 M NaOH in H_2O/CH_3CN	1.4 (15.1)	0.69 (17)	0.49 (11)
1,2-diphenylethanol			
0.1 M $LiClO_4$ in CH_3CN	0.60 (0.26)	0.83 (23)	No Reaction
1 M NaOH in H_2O/EtOH	No Reaction	0.35 (7.6)	0.49 (23)
0.1 M NaOH in H_2O/CH_3CN	No Reaction	0.70 (18)	0.49 (13)
2,2'-biphenol			
0.1 M $LiClO_4$ in CH_3CN	0.67 (4.0)	0.77 (29)	No Reaction
1 M NaOH in H_2O/EtOH	0.28 (1.4)	No Reaction	0.47 (19)
0.1 M NaOH in H_2O/CH_3CN	0.28 (1.2)	0.58 (5.7)	0.49 (7.0)

Electrode oxidation at 0.49V vs. SCE







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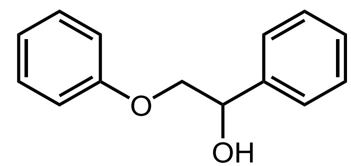
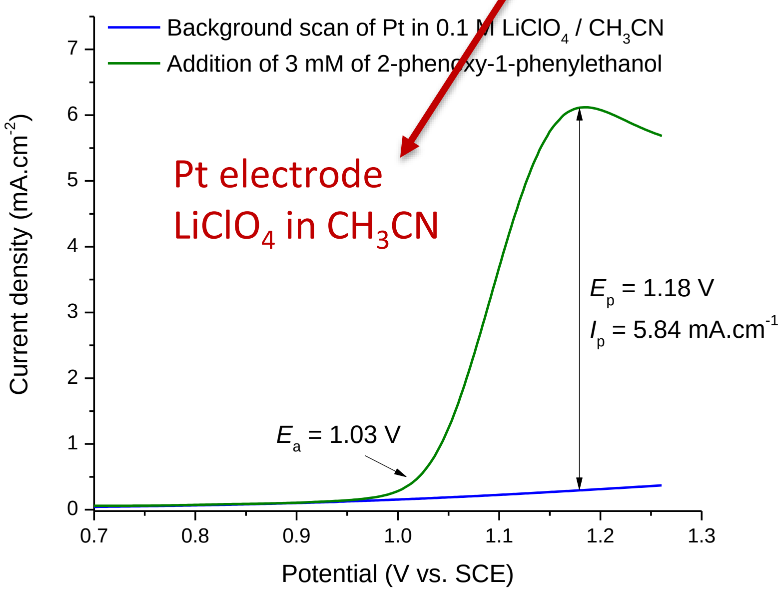
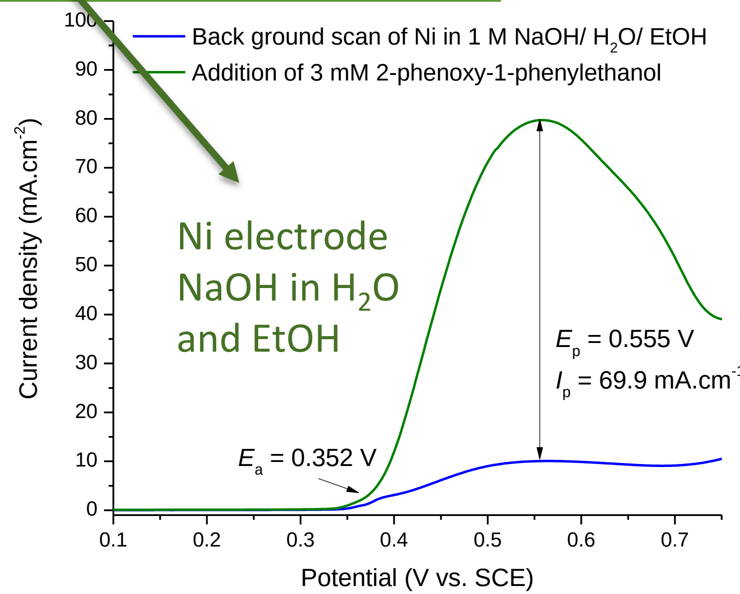






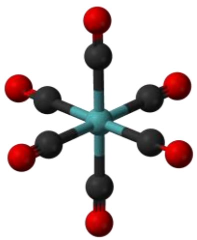
Ni electrode in NaOH/H_2O/EtOH selected as baseline

Progress:
Prepare Electrocatalysts

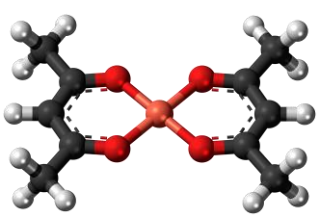
Synthesized Ni (baseline) and next-generation Ni_2P and MoC nanoparticles supported on carbon for CPE experiments

Critical objectives:

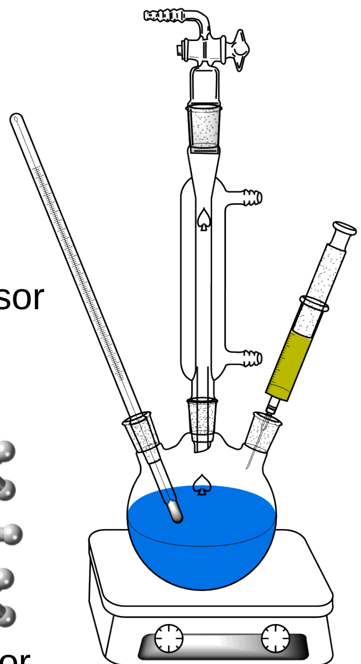
- Increase active surface area to improve rate of product generation
- Probe effect of bifunctionality and oxophilicity (Ni_2P and MoC) on performance

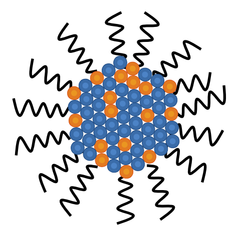


$Mo(CO)_6$ precursor

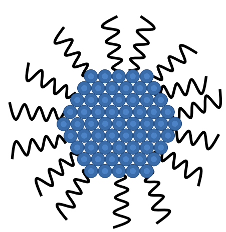


$Ni(acac)_2$ precursor



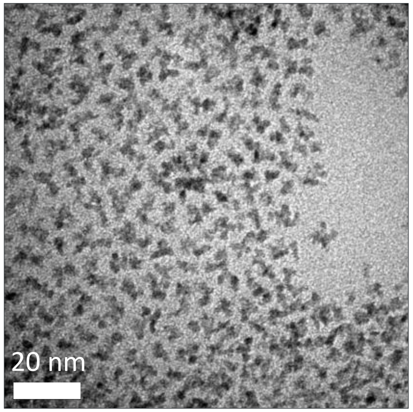


Molybdenum carbide nanoparticles



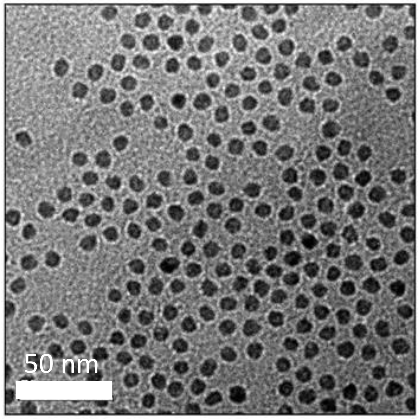
Nickel nanoparticles

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



MoC NPs

- 1-3nm
- Non-spherical shape

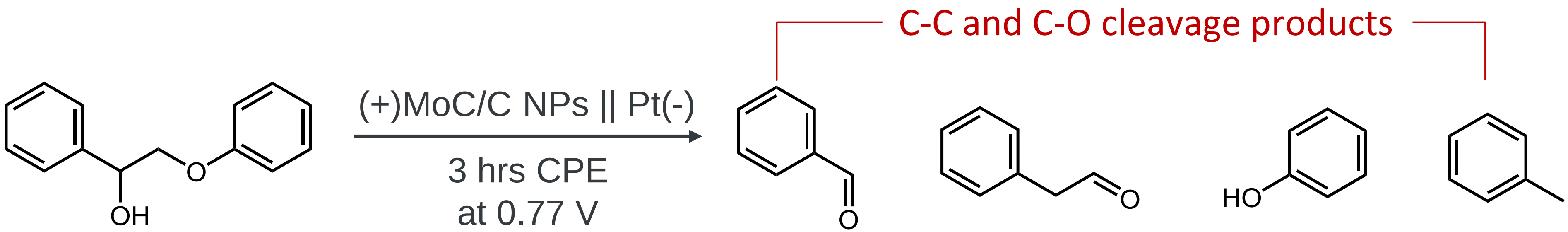


Nickel NPs

- ~12nm
- Spherical shape

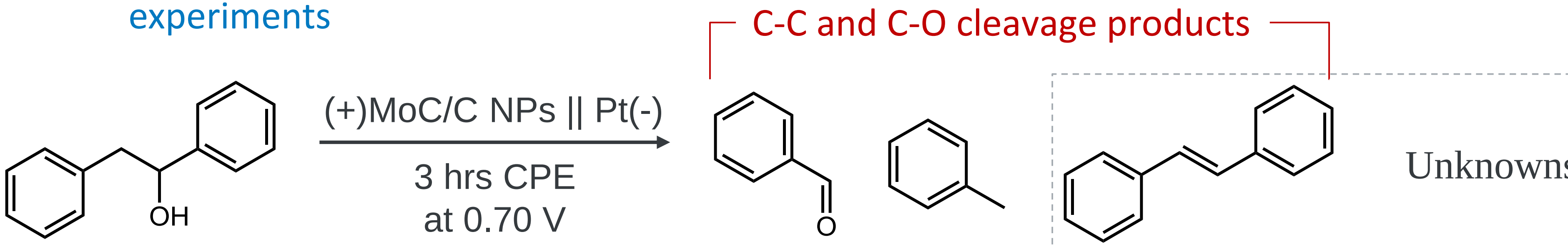
Progress:
Preliminary Proof-of-Concept

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



Selected from LSV experiments

2-phenoxy-1-phenylethanol		Benzaldehyde	Phenylacetaldehyde	Phenol	Toluene
4.9% conversion	*Yield*	3.0%	0.15%	1.1%	0.52%
	Selectivity	63%	3%	23%	11%
	Faradaic efficiency	48%	2%	18%	8%



1,2-diphenylethanol		Benzaldehyde	Toluene	Stilbene	Unknowns
20% conversion	*Yield*	2.0%	0.40%	12%	5.6%
	Selectivity	83%	17%		
	Faradaic efficiency	18%	4%	55%	12%

Side products at the Pt cathode

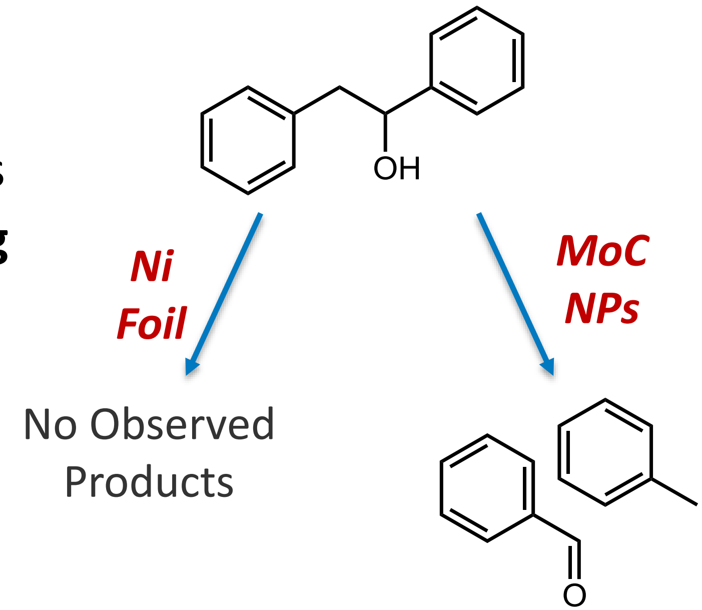
Relevance: High-yield Lignin Conversion is Critical to Achieving BETO cost targets

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

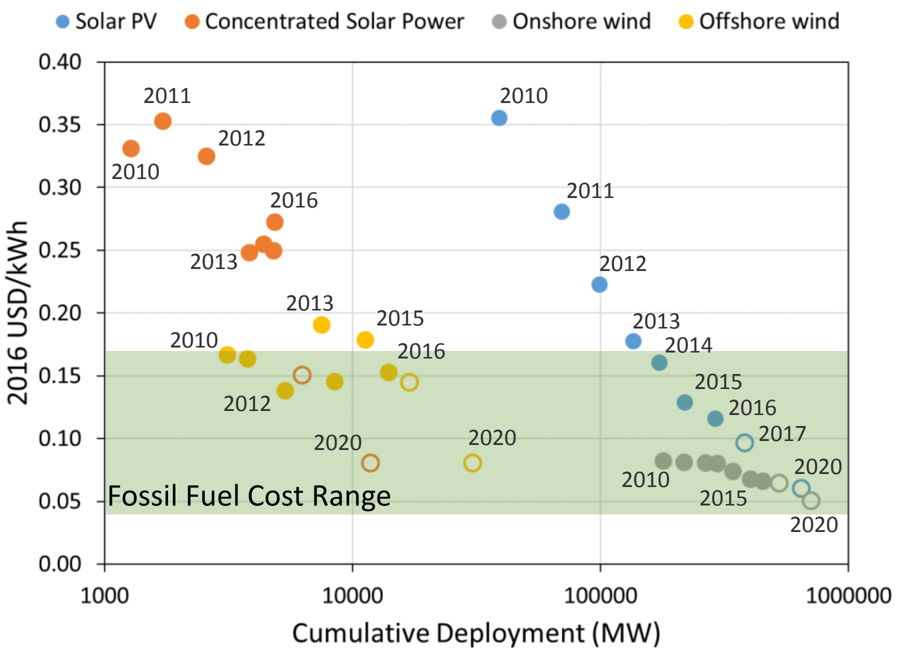


Relevance:
Bioenergy Industry

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

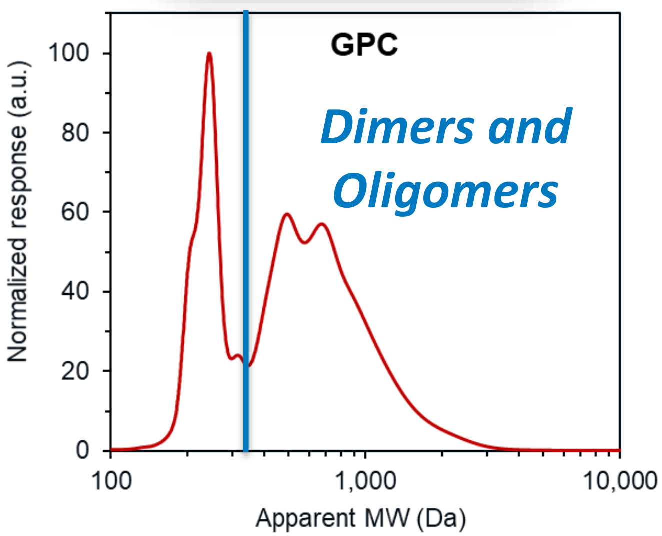


IRENA, Renewable Power Generation Costs in 2017

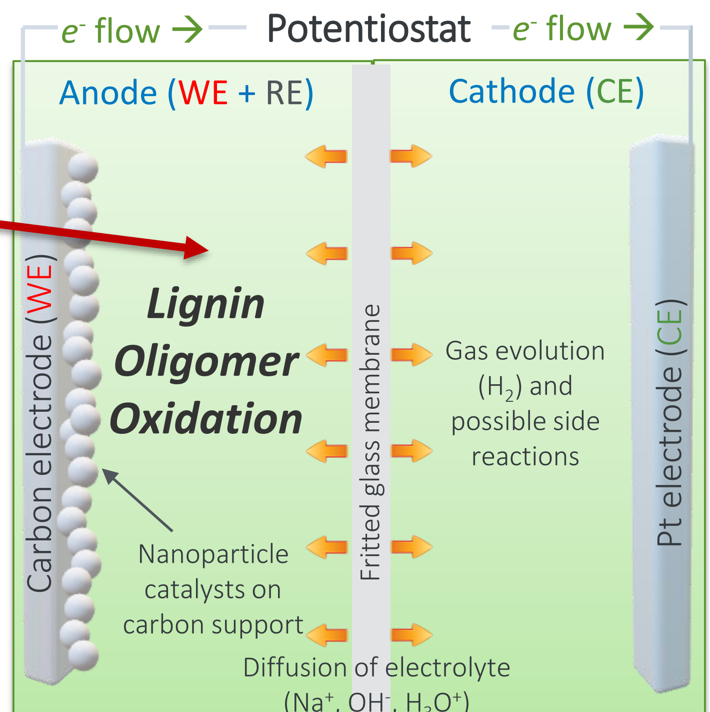
Future Work:
Demonstrate Proof-of-Concept with RCF Oil

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



Electrocatalyst: MoC/C
Electrolyte: $NaOH/EtOH/H_2O$

Product Analysis

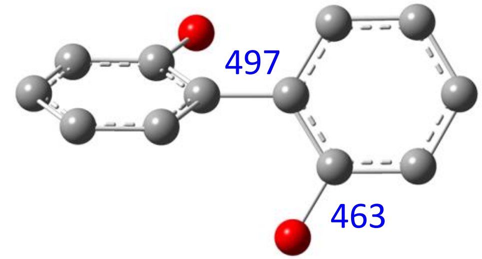
- Determine dimer and oligomer conversion and selectivity to monomers
- Analysis with GC-MS, LC-MS, and GPC
- ***Critical Metric:*** Retain functionality of existing monomers in lignin RCF oil

Future Work:
Hypothesis-Driven Electrocatalyst Development

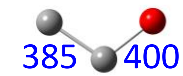
Goal: Develop a mechanistic understanding of the major reaction pathways and leverage this knowledge to guide electrocatalyst modifications

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

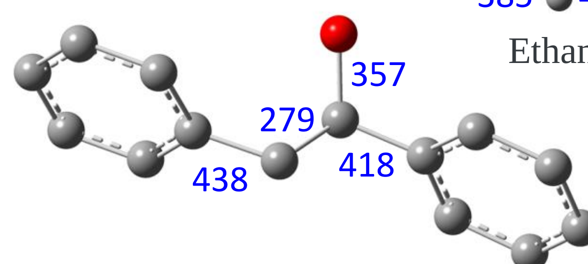
- Probe individual reaction steps with model compounds and reaction intermediates
- Leverage modeling to understand reaction energetics and steric hindrance
- Evaluate carbon spikes as support to enhance reactant accessibility



2,2’-diphenol

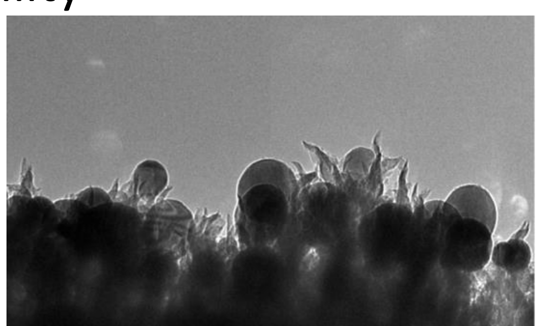


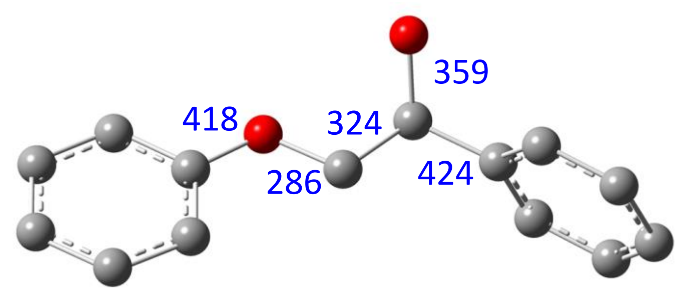
Ethanol



1,2-diphenylethanol

In collaboration with 2.3.1.317 CO_2 Upgrading (Adam Rondinone, ORNL)





2-phenoxy-1-phenylethanol

Future Work:
Process Development

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

Critical Question/Challenge	Strategy
Side reactions and crossover (anode → cathode)	Utilize anion exchange membrane to prevent crossover of lignin compounds
Impact of OH- and O_2 concentration	Perform CPE experiments with varying NaOH concentrations and O_2 co-feed
Role of H_2O and EtOH Oxidation	Perform CPE experiments at varying applied voltages
Electrocatalyst stability	• Perform extended CPE experiments with real-time product analysis • Characterize spent electrocatalysts • Evaluate leaching by analyzing anolyte with ICP • Transition to continuous system
State of MoC electrocatalyst (nature of the active site: Mo vs. C)	Evaluate additional Mo-based catalysts (i.e., MoO_x)

Summary

Goal: Demonstrate **proof-of-concep**t 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

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Thank You

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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