U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Biomass Electrochemical Reactor for Upgrading Biorefinery Waste to Industrial Chemicals and Hydrogen

March 7, 2017
Waste to Energy

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Goal Statement

- Goal: *Develop a continuous electrochemical process to convert biorefinery waste lignin to substituted aromatic compounds for resins and resin binders*
- Outcome: *Generate additional biorefinery revenue stream and reduce the cost of biofuels to be competitive with petroleum fuels.*
- Relevance:
  - Lignocellulosic biofuels are not cost-competitive
  - Biorefinery lignin waste can be converted to aromatic compounds to generate additional revenue
  - Catalytic depolymerization of lignin is difficult to control
  - Electrochemical processes can control reaction energetics
  - This project uses *biorefinery waste* as a feedstock to generate aromatic compounds and improve biorefinery economics

Quad Chart Overview

Timeline

- 4/1/2016
- 3/31/2019
- 10%

Project selected as part of the BCU FOA to enable commercialization of biochemical conversion pathways to biofuels.

Budget

	FY 16 Costs	Total Planned Funding (FY 17-Project End Date)
DOE Funded	11,579	1,472,724
Project Cost Share (Comp.)*	16,180	OU: 218,430 Hexion: 112,260 BRI: 37,500

*If there are multiple cost-share partners, separate rows should be used.

Barriers

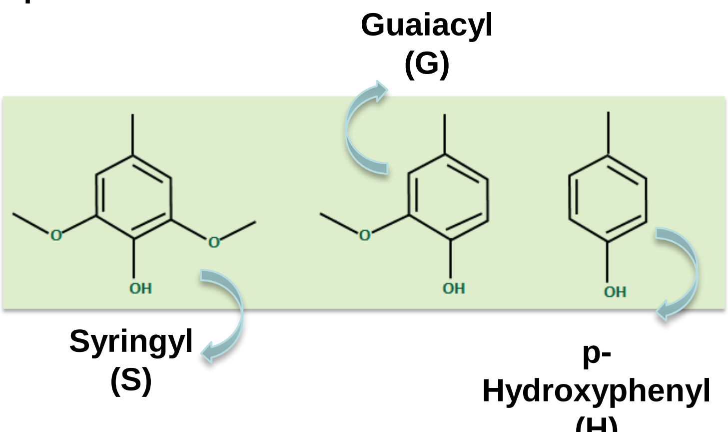
- High-rate conversion of lignin to targeted chemicals.
- Generation of product streams readily applied to resins and resin binders without significant modification.
- Integration into biorefinery with revenue generated to reduce cost of biofuel by 25%

Partners

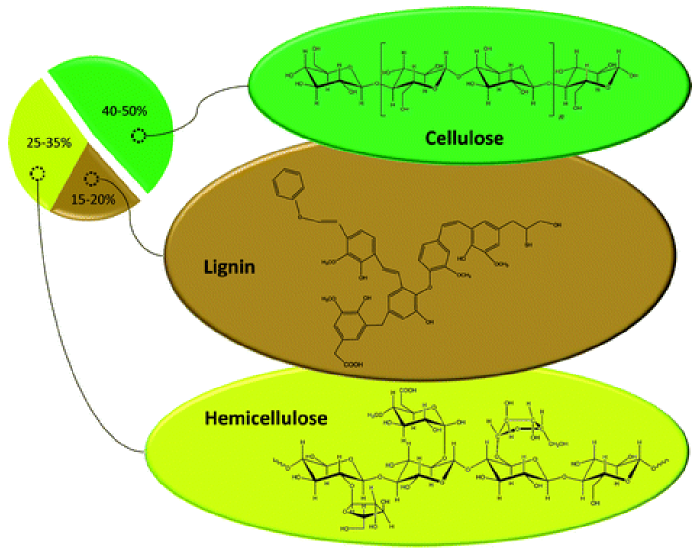
- Hexion, Inc.: resin manufacturer, product stream evaluation
- Biorefining Research Institute: process economics and biorefinery integration
- Ohio University Department of Chemistry: product analysis

1 - Project Overview

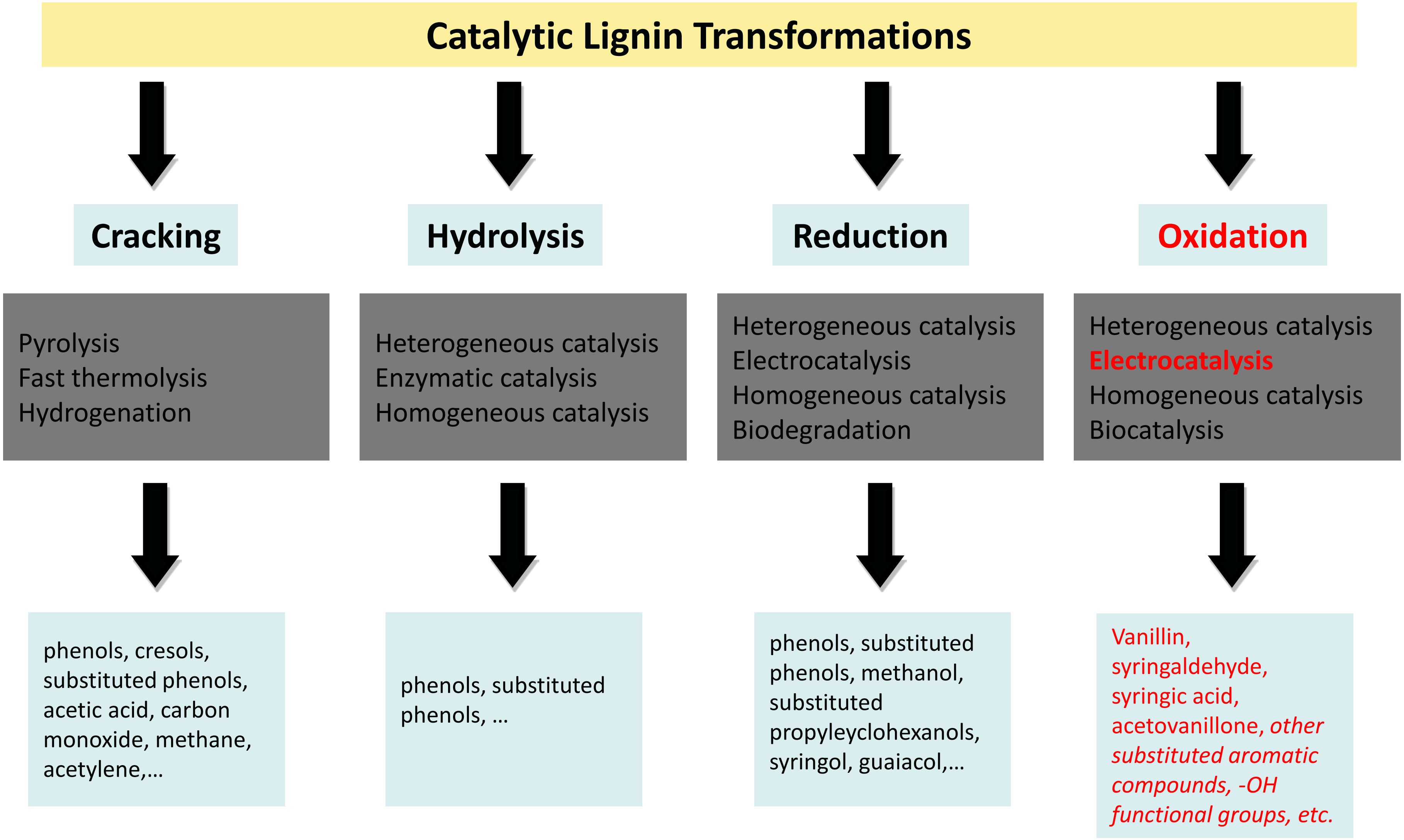
- Biorefineries cannot product biofuel from lignin
- Lignin can be a raw material for aromatics currently sourced from petroleum



The three building blocks of lignin



- We will develop continuous electrochemical processes to convert lignin to resins and resin binders
- *We have demonstrated production of substituted aromatic compounds from lignin using non-precious metal (Ni-Co) electrocatalysts*
- The goal is to apply the continuous electrochemical process to reduce the cost of biofuel by 25%


Catalytic Lignin Transformations
Cracking
Hydrolysis
Reduction
Oxidation
Pyrolysis
Fast thermolysis
Hydrogenation
Heterogeneous catalysis
Enzymatic catalysis
Homogeneous catalysis
Heterogeneous catalysis
Electrocatalysis
Homogeneous catalysis
Biodegradation
Heterogeneous catalysis
Electrocatalysis
Homogeneous catalysis
Biocatalysis
phenols, cresols, substituted phenols, acetic acid, carbon monoxide, methane, acetylene,…
phenols, substituted phenols, …
phenols, substituted phenols, methanol, substituted propyleyclohexanols, syringol, guaiacol,…
Vanillin, syringaldehyde, syringic acid, acetovanillone, other substituted aromatic compounds, -OH functional groups, etc.

2 – Approach (Management)

OHIO

John Staser, PI
Pete Harrington

HEXION

Resin binder formulations

Lakehead UNIVERSITY

Biorefining Research Institute

Biorefinery TEA

- The management approach relies on near-constant communication
  - PI provides regular updates team members through joint conference calls
  - Primary members OU and Hexion meet on-campus regularly for project discussions
  - Graduate students at OU work jointly between Dept. of Chem. Engineering and Dept. of Chemistry on electrocatalytic and product analysis efforts

2 – Approach (Technical)

- Ni-Co electrocatalysts on high surface area carbon and on TiO_2

  - Metal nanoparticles have a higher surface area, which could result in an increased catalytic activity
  - These material have shown good catalytic activity in the oxidation reactions

- We will incorporate these electrocatalysts into the continuous flow electrochemical reactor to oxidize biorefinery lignin
  - We target physical separation of the anode and cathode to generate separate streams; one lignin product stream and another moderate-P hydrogen stream
- We will evaluate product streams via GC-MS, UV-vis and FTIR (in collaboration with OU Dept. of Chemistry and Hexion)
- Hexion will evaluate products for suitability in resin and resin binder formulations

2 – Approach (Technical)

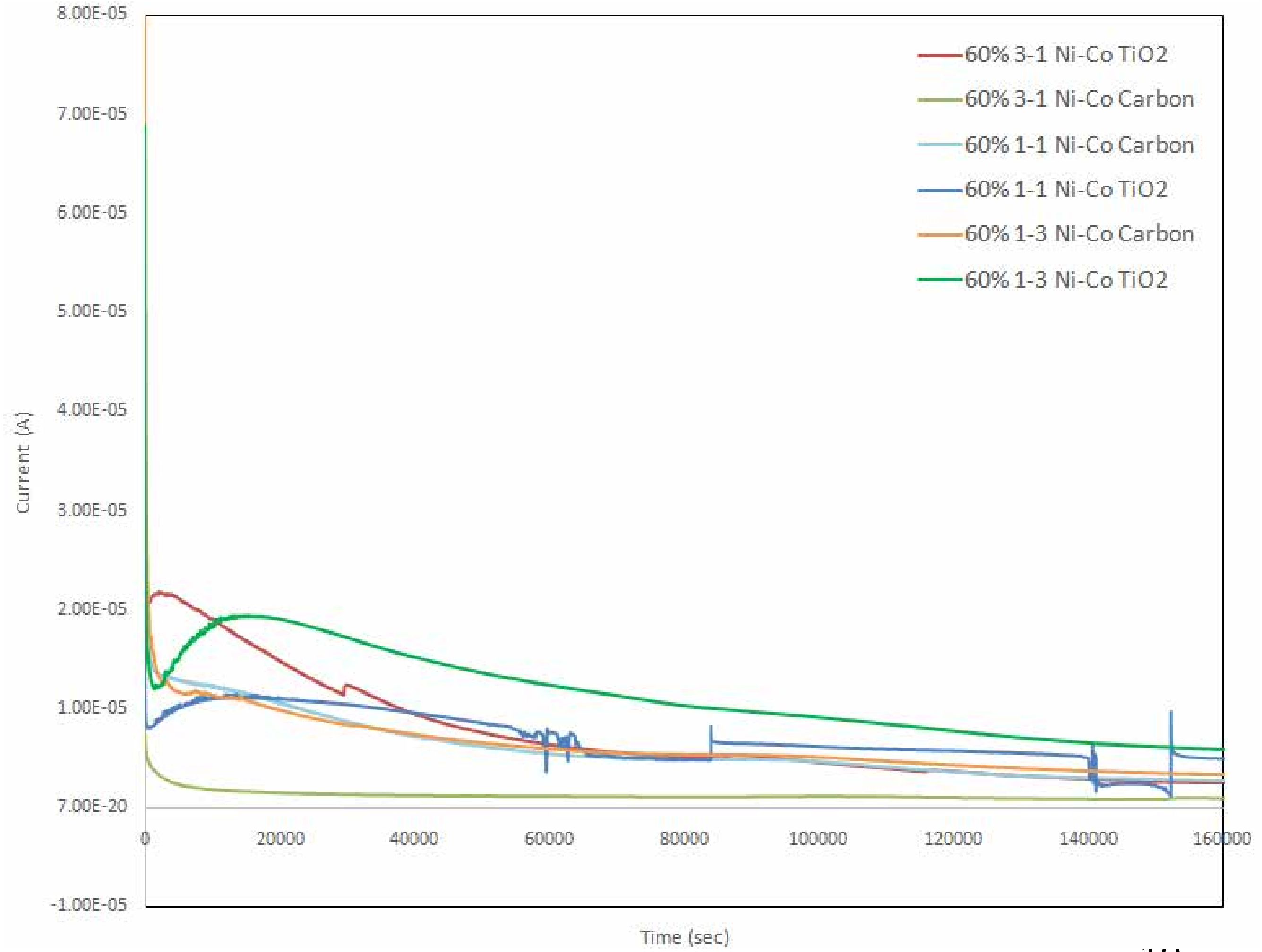
- BRI will scale the reactor and integrate it into the biorefinery concept with economic and market analysis
- Intermediate Go/No Go Decision Point: Achieve 67% mass selectivity (mass of useful product/mass of total product) with 26.6% product purity
- Economic and Technical Metrics
  - Cost of producing biofuel ($/gal)
    - Current process, no lignin upgrading; $2.83/gal
    - Current process, catalytic lignin upgrading; $2.55/gal
    - Benchmark, electrochemical lignin upgrading; $2.99/gal
    - Intermediate, electrochemical lignin upgrading; $2.67/gal
    - Final, electrochemical lignin upgrading; $2.28/gal
  - Achieve the following technical metrics
    - Benchmark mass selectivity; 32%
    - Intermediate mass selectivity; 67%
    - Final mass selectivity; 90%
    - Benchmark product purity; 0.05%
    - Intermediate product purity; 26.6%
    - Final product purity; 42%

2 – Approach (Technical)

- Potential Challenges
  - Poor electrocatalytic activity
  - Low selectivity toward target compounds
- Critical Success Factors
  - Targeting Potential Challenge: Poor Electracatalytic Activity
    - Develop high surface area alloys stable in alkaline media
    - Periodically recover electrocatalyst at reducing potentials to recover any lost activity due to active site poisoning
  - Targeting Potential Challenge: Low Selectivity Toward Target Compounds
    - Control electrode potential to target specific bonds
    - Develop Ni and Co electrocatalysts that are known to favor –OH functionalities on oxidation products
    - Avoid formation of oxygen at anode
    - Control electrochemical reactor residence time to avoid further oxidation of target products

3 – Technical Accomplishments/ Progress/Results

- We have synthesized NiCo electrocatalysts (1:1, 1:3 and 3:1) supported on high surface area carbon and TiO_2 nanowires
- We have successfully demonstrated electrochemical oxidation of lignin on these electrocatalysts

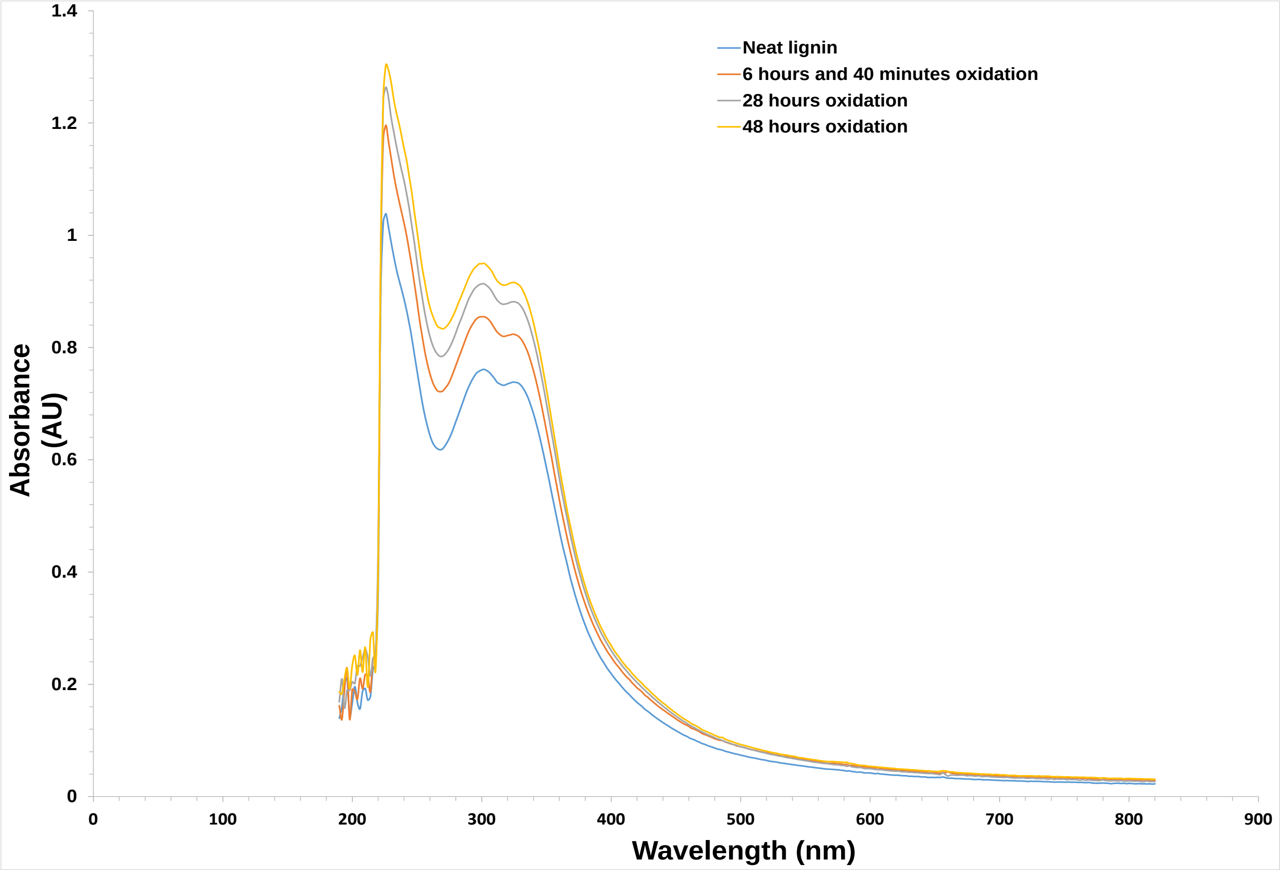


3 – Technical Accomplishments/ Progress/Results

- Per technical targets, we have down-selected two electrocatalysts; 1:3 Ni:Co/C and 1:3 Ni:Co/TiO_2
- We have developed GC-MS procedures to identify oxidation products
- We have determined product purity and mass fraction lignin conversion
  - 1:3 Ni:Co/C, mass selectivity 67%
  - 1:3 Ni:Co/C, product purity 0.62%
- We have also been developing additional analytical techniques to identify changes to lignin during oxidation
- These accomplishments relate to meeting project targets in yield and selectivity of desired compounds
- *Intermediate target for mass selectivity was 67%*
- *Have increased product purity by 10x over benchmark*

3 – Technical Accomplishments/ Progress/Results

- Uv-vis shows increase in phenolic content, functionalization by hydroxyl groups and cleavage of the β-O-4 bond
- Confirms high functionalization of desirable –OH groups via Ni-Co electrocatalysts, targeting metrics for product purity and yield



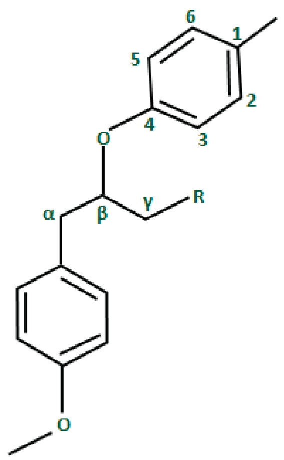
3 – Technical Accomplishments/ Progress/Results (cont'd)

- Accomplishments and Technical Benchmarks
  - We have synthesized target electrocatalysts and down-selected the most promising
  - We have demonstrated high rates of –OH and –CH_3 substituted compound production using these electrocatalysts
  - We have demonstrated Intermediate target mass selectivity
  - We have increased product purity by 10x over the benchmark achievement
  - We have begun testing the continuous flow electrochemical reactor

4 – Relevance

Make Biofuels Cost-competitive by Developing Additional Biorefinery Revenue Streams

- Electrochemical synthesis provides *direct* control of reaction energetics
- Electrochemical processes allow us to target *specific* bond rearrangement (β-O-4 bond for high rates of depolymerization)
- We can control depolymerization pathway and target specific product functionalities



Linkages found in lignin

Linkage	Softwood Lignin (%)	Hardwood Lignin (%)
β-O-4	49-51	65
α-O-4	6-8	-
β-5	9-15	6
β-1	2	15
5-5	9.5	2.3
4-O-5	3.5	1.5
β-β	2	5.5

4 – Relevance

Make Biofuels Cost-competitive by Developing Additional Biorefinery Revenue Streams

- Electrochemical depolymerization of lignin co-generates hydrogen, another useful product
- Project success will impact viability of biomass and biofuels because:
  - It utilizes a current high volume waste biomass as a bioproduct feedstock for increased revenue
  - Process can be directly integrated into the biorefinery to utilize waste *in parallel with* production of biofuels
- Tech transfer/marketability
  - Will work with OHIO's Tech Transfer Office to market the reactor to chemicals companies and biorefineries

5 – Future Work

- Work over the next 18 months will focus on:
  - Developing the continuous flow electrochemical reactor
    - We have begun development of a small-scale continuous flow reactor
    - Will focus on a membrane-based system for higher-P hydrogen and product separation
  - Working with industrial partners to evaluate product streams for application to resins and resin binders
    - Will provide partner Hexion with oxidation product stream from continuous flow reactor
    - Hexion will evaluate product stream in their resin formulations
    - Hexion will also develop new resin formulations based on bioaromatic streams containing some unreacted or partially degraded lignin
  - Integrating the continuous flow reactor into the biorefinery
    - Final deliverable is a techno-economic analysis about the commercial feasibility of this biomass conversion approach
    - We will work with partner Biorefining Research Institute to scale our continuous flow reactor and integrate it into the biorefinery concept
    - We will provide process flow diagrams of the modified biorefinery
    - We will perform a market analysis on the impact of integrating electrochemical conversion processes into the biorefinery

5 – Future Work

- Highlight upcoming key milestones
  - Demonstration of lignin oxidation with cogeneration of H2 at <1.6 V in 10 cm^2 test cell
  - Demonstration of lignin oxidation with cogeneration of H2 at <1.6 V in the 200 cm^2 lab-scale cell at capacities >1 L/h
  - Formulation of phenol-formaldehyde (PF) resins based on bio-aromatics
  - Formulation of bio-aromatic based epoxy resins
- Go/No-Go Point
  - 67% mass selectivity (demonstrated at batch scale)
  - 26.6% product purity (achievable with continuous flow reactor)
- Remaining Budget
  - $1,772,669
  - Sufficient to complete the work

Summary

1. Overview
   - Develop electrochemical process to convert biorefinery lignin waste to industrial chemicals
2. Approach
   - Develop electrocatalysts and a continuous flow reactor to convert lignin-rich biorefinery waste into resins and resin intermediates
3. Technical Accomplishments/Progress/Results
   - Have down-selected electrocatalysts
   - Have demonstrated conversion of lignin to substituted aromatic compounds
   - Have begun developing continuous flow reactor
4. Relevance
   - Utilize waste biomass as raw material for aromatic compounds
   - Generate additional revenue stream for biorefinery
   - Reduce the cost of generating biofuels
5. Future work
   - Design, build and validate electrochemical reactor
   - Formulate resins and resin binders based on bioaromatics and intermediates
   - Generate techno-economic analysis integrating reactor into biorefinery

Additional Slides

Responses to Previous Reviewers' Comments

- N/A

Publications, Patents, Presentations, Awards, and Commercialization

- We have an MTA with a biorefinery company and Hexion to share biorefinery waste and modify that waste by electrochemical processes
- The MTA includes analysis of raw biorefinery waste and biorefinery waste products
- With help from DOE BETO, the Russ College of Engineering and Technology published a story about this project on October 31, 2016. A link to that story can be found here: https://www.ohio.edu/engineering/news/news-story.cfm?newsItem=0C1574BE-5056-A874-1DA7051EF8FCAF27
- Soon after the Russ College published their story, the PI was interviewed by the Ohio University student newspaper (The Post). That story was published on November 17, 2016: http://www.thepostathens.com/article/2016/11/russ-college-biofuel-grant