DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

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

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Lignin Utilization

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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 streams 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
  - Co-generation of high purity H_2 generates additional revenue
  - *Industrial Relevance: Phenolic resin market approaching $15 billion/year*
    - *"Green" resins from renewable sources, stable raw materials cost*
    - *Industry interest:*
      - *Dislodging petroleum as a resin precursor*
      - *Environmentally friendly*

Quad Chart Overview

Timeline

- 4/1/2016
- Project end date: April 30, 2020
- Percent complete: 40%

Barriers addressed

Ot-B. Cost of Production.

Technical Targets

Fuel production cost at $3/GGE by 2022

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	11,579	242,244	357,103	861,798
Project Cost Share*	OU: 0 Hexion:0 LU: 0	38,489 1,437 0	56,630 24,667 6,060	122,711 86,156 31,439

•Partners:

Ohio University: 60%

Hexion: 30%

Lakehead University: 10%

Objective

Develop electrochemical processes to convert biorefinery lignin to useful chemicals.

End of Project Goal

Demonstrate 46% conversion of lignin with a path to achieving a 25% reduction in lignocellulosic biofuel cost with the electrochemical conversion process.

1 - Project Overview

- Waste lignin is currently burned by biorefineries as a low-grade fuel
- Lignin's polyaromatic structure makes it an interesting, but underutilized, raw material
- Controlled depolymerization of lignin to useful products has not been demonstrated at high yield by typical catalytic processes
- Electrochemical processes have the advantage that reaction energetics can be precisely controlled by controlling electrode potential
- *We are developing continuous electrochemical reactors to convert lignin to useful chemicals with co-generation of H_2*
- *This approach is innovative because we can achieve significant depolymerization of lignin using inexpensive electrocatalysts (Ni-Co)*
- *Our project is also innovative because we apply statistical analysis to build high confidence in our results*
- Industrial partnership will demonstrate feasibility of a real-world, commercial end-use application for our product streams
- ***This project addresses the high cost of biofuel production by creating additional biorefinery revenue streams from a high-volume waste***

2 – Approach (Management)

OHIO

Electrochemical conversion
Product analysis

HEXION

Product analysis
Resin binder formulations

Lakehead UNIVERSITY

Biorefining Research Institute

Biorefinery TEA

- Management Approach:
  - Team communicates and shares results
  - Analysis is integrated across labs (CEER, Center for Intelligent Chemical Instrumentation, Hexion) to more fully characterize products
  - BRI's expertise in biorefinery economics applied to TEA
  - Hexion's expertise in resin synthesis applied to end-use application

2 – Approach (Technical)

- Develop novel Ni-Co electrocatalysts supported on TiO_2
  - Low-cost, stable under anodic conditions
- Incorporate electrocatalysts onto gas diffusion layer (GDL) support in a continuous flow reactor
  - Standard electrochemical experiments with which Staser has extensive experience
- Conduct comprehensive analysis on product streams to broadly characterize the chemicals generated
- Apply statistical analysis to provide confidence in analytical results
- Potential Challenges
  - Insufficient depolymerization or extent of lignin conversion
  - Inability to adequately characterize product stream
  - Inability to develop a cost-effective process

2 – Approach (Technical)

- Critical Success Factors
  - High rates of lignin depolymerization
  - High yield of aromatic compounds
  - Efficient H_2 production
- Go/No-Go decision point: Generate bio-based phenols at 1.6 V cell voltage, 0.6 V vs. SHE anode potential
- Technical and Economic Metrics (Intermediate Stage)
  - At least 40% conversion of lignin
    - *Chosen based on electrocatalyst improvement and scale-up assumptions from Initial validation*
    - *High conversion is necessary to break down lignin sufficiently for use in resin formulations*
  - At least 67% selectivity toward useful products
    - *Chosen based on early product analysis*
    - *High selectivity toward aromatic units is significant for resin development*
  - At least 26% yield of useful products
    - *Chosen based on early product analysis*
    - *More pure product streams facilitate resin synthesis*
  - 80% faradaic efficiency for H_2 production
    - *Chosen based on typical electrolysis operation*
    - *Efficient H_2 production enhances process economics*
  - These metrics would predict an intermediate stage net biofuel production cost of \$2.67/gge using calculations agreed upon during initial validation

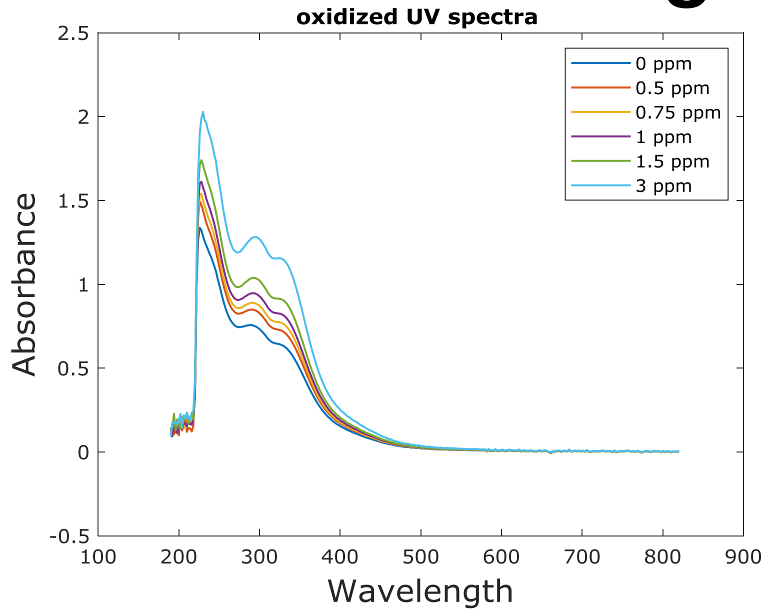
3 – Technical Accomplishments/ Progress/Results

- Intermediate Milestones Achieved:
  - Developed NiCo/TiO_2 electrocatalyst
  - 10 cm^2 reactor, 8 mg/cm^2 catalyst loading, <1 L/hour flow rate, 1.6 V, 120 hours continuous operation
  - H_2 production rate >2 sccm, >98% faradaic efficiency
  - Lignin conversion target (>40% conversion achieved)
  - Yield and selectivity targets (>60% selectivity achieved)
- Key Milestones and Status
  - Electrocatalyst development and down-select: *complete*
  - Demonstration of lignin oxidation with cogeneration of H_2 at <1.6 V in 10 cm^2 test cell: *complete*
  - Development of 200 cm^2 reactor: *ongoing*
  - Formulation of phenol-formaldehyde resins based on bio-aromatics: *ongoing*
  - Techno-economic analysis: *ongoing*

3 – Technical Accomplishments/ Progress/Results

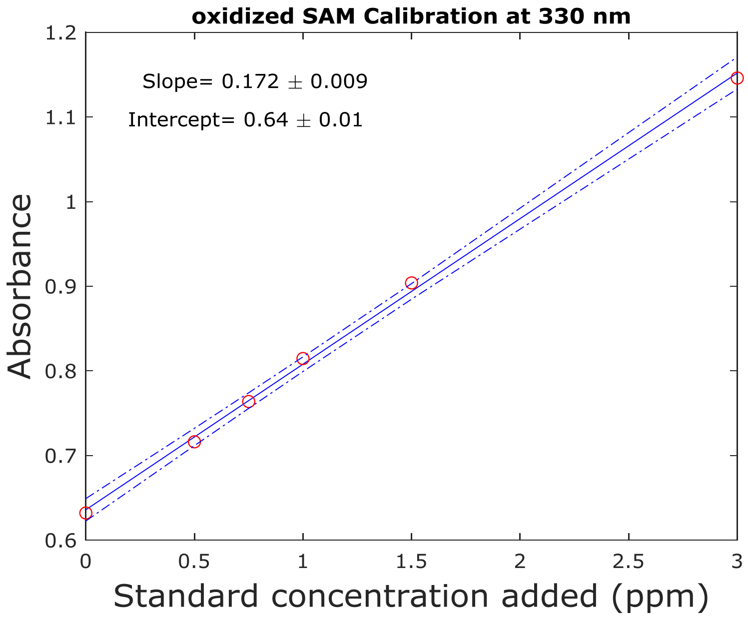
- How do we get here? *Analyze, Analyze, Analyze*
- Analysis of lignin is not trivial
- *Statistical analysis is key to building confidence in our results*
- *This is a novel approach to identification of lignin conversion products*
- <u>Primary Analysis Techniques:</u>
  - UV-vis spectroscopy with standard addition method
  - FTIR
  - Gel permeation chromatography (GPC)
  - GC-MS
  - HR-MS
- <u>Provides Information On:</u>
  - Extent of lignin conversion
  - Product stream composition
  - Co-product H_2 purity

3 – Technical Accomplishments/ Progress/Results



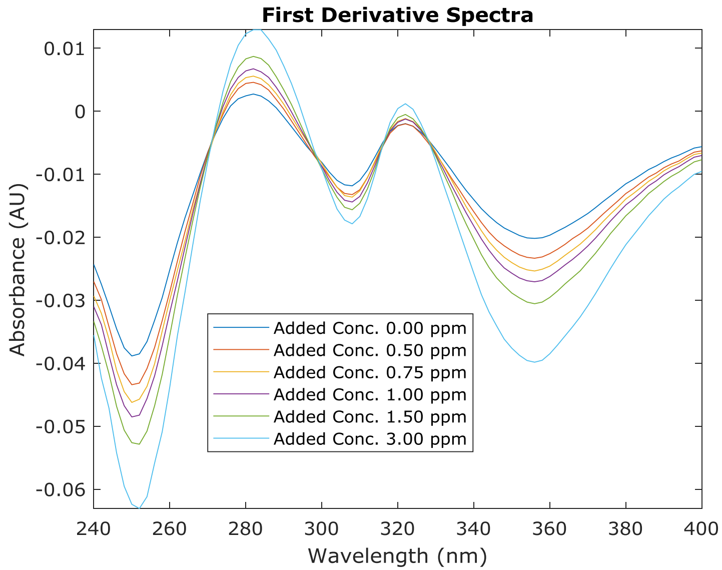
- UV-vis generalized standard addition method
- Add known concentrations of unreacted lignin to product solution (unreacted lignin + oxidation products)
- Analyze peak intensity at 330 nm

- Linearity in peak intensity with neat lignin concentration used to reference amount of unreacted lignin
- How much unreacted lignin do we have to remove so peak at 330 nm reduces to zero intensity (no unreacted lignin condition)

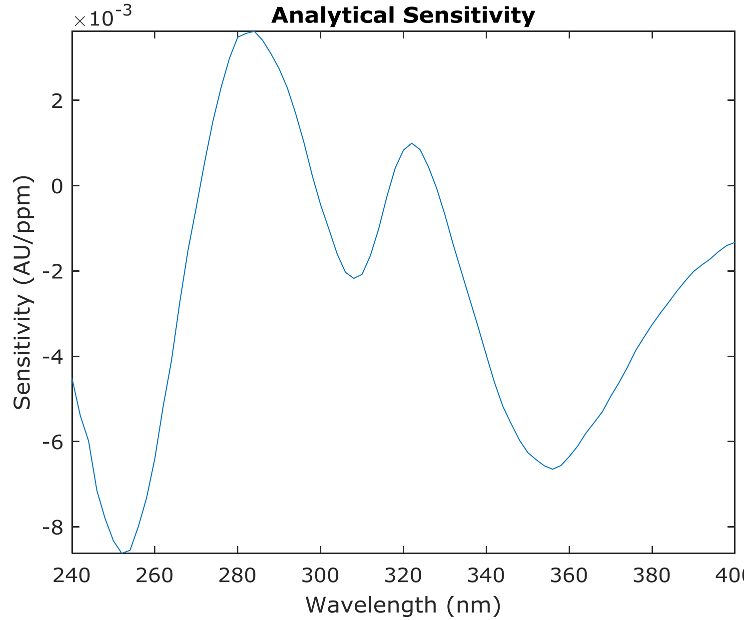


3 – Technical Accomplishments/ Progress/Results

- Generalized Standard Addition Method on UV-vis results



Clear trends with good sensitivity



Electrolysis time (min)	ppm of neat lignin Classical GSAM	ppm of neat lignin Inverse GSAM	Conversion % based on Classical GSAM	Conversion % based on Inverse GSAM
1.28	24.69	24.53	31.62	32.07
2.88	21.98	21.91	39.13	39.32
4	19.31	19.24	46.52	46.72

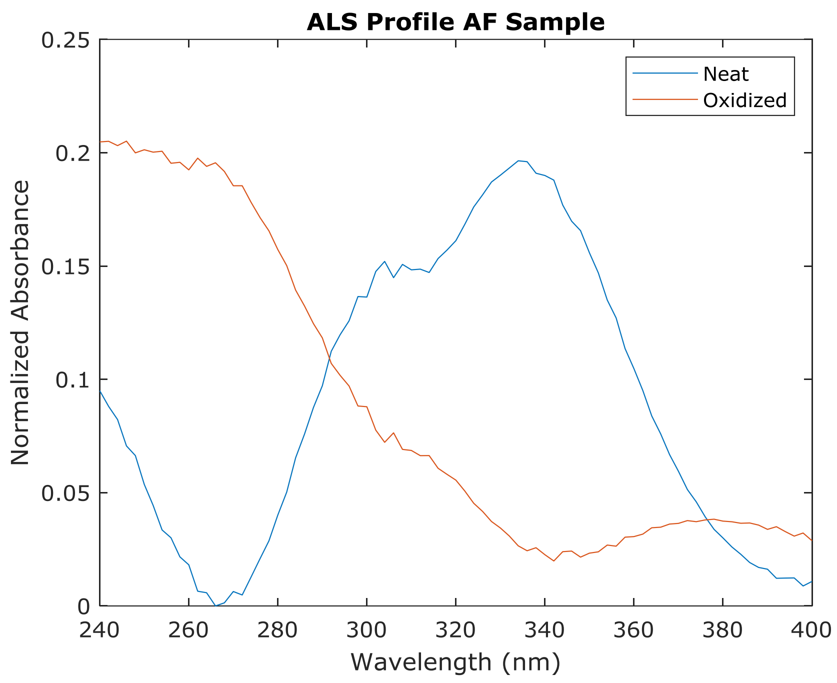
High extents of reaction

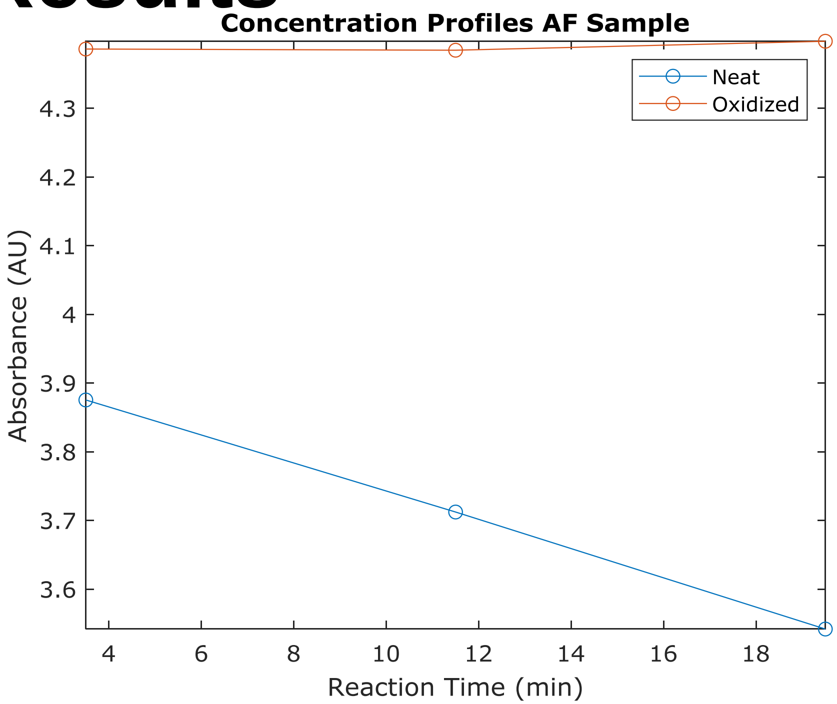
- *Could indicate efficient process*
- *Significant product generation*

Biorefinery revenue – cost reduction

3 – Technical Accomplishments/ Progress/Results

- Correlation between oxidized and neat lignin samples

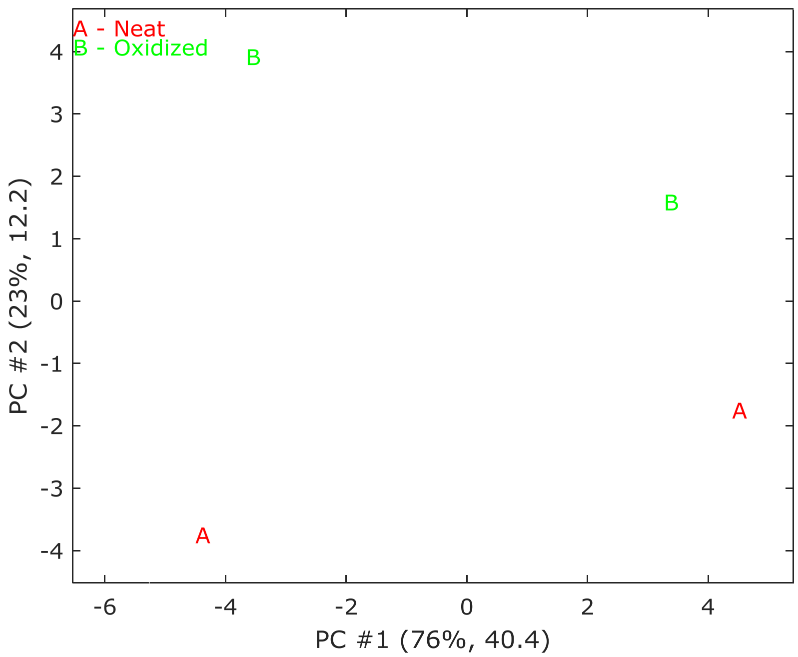


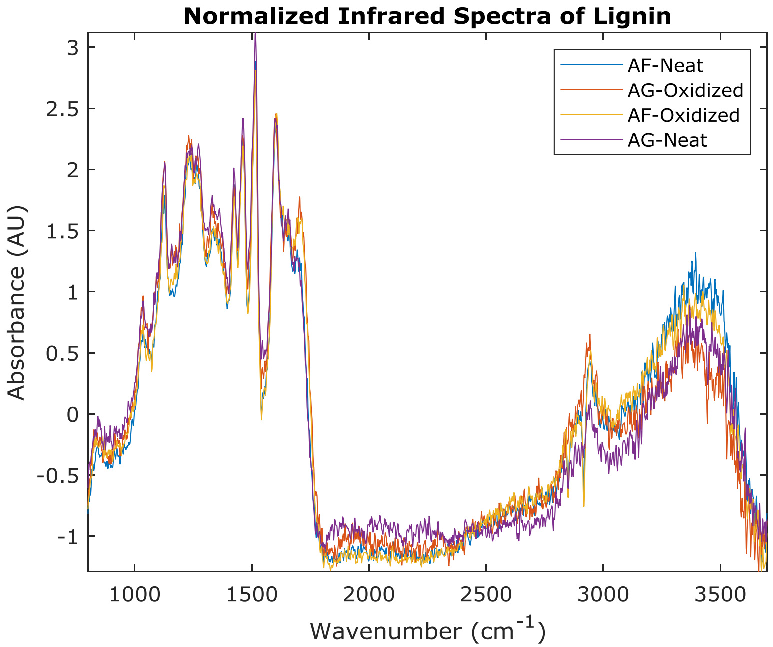


- Preliminary results indicate potential increase in aromatic products
- Key statistical analysis techniques are ongoing to build greater confidence in initial results

3 – Technical Accomplishments/ Progress/Results

- Normalized IR spectra show significant functional group changes





- Significant conversion of C–OH groups to C=O groups
- *C=O more reactive than C-OH*
- *Positive impact on resin synthesis procedures*
- ***More reactive groups → easier resin synthesis → cost impact***

3 – Technical Accomplishments/ Progress/Results

- Depolymerization analyzed by GPC

Sample	Mw (Dalton)	Mn (Dalton)	Mz (Dalton)	PDI
AD Neat	3254	544	14898	5.983
AD Oxidized	2102	443	8656	4.749
AE Neat	3387	554	14372	6.111
AE Oxidized	2784	470	13747	5.919
AF Neat	3306	571	15263	5.791
AF Oxidized	2269	418	12262	5.422
AG Neat	3461	589	15220	5.876
AG Oxidized	2818	463	14061	6.083

- Significant reduction in MW
- Complements UV-vis results
- Trend approaches 2000 MW useful by industrial partner for resin synthesis
- *Further confirmation of extent of lignin depolymerization*
- ***High rates of lignin depolymerization → high rates of product stream generation → additional revenue → reduced biofuel cost***

3 – Technical Accomplishments/ Progress/Results

- Hydrogen Production

Current (mA)	Theoretical volume of H_2 (ml/min)	Actual volume of H_2 (ml/min)	Faraday efficiency
300	2.23	2.32	1.04
250	1.86	1.84	0.98
200	1.49	1.5	1.01
150	1.12	1.17	1.05
100	0.74	0.64	0.86
50	0.37	0.38	1.02
			Ave= 0.99

- H_2 purity = 97% by GC analysis
- Other 3% is a N_2 + O_2 (air) mixture likely due to collection and transfer from the reactor to the GC
- *H_2 is an additional product*
- ***Efficient H_2 production → high-rate co-product generation → additional biorefinery revenue → lower biofuel production cost***

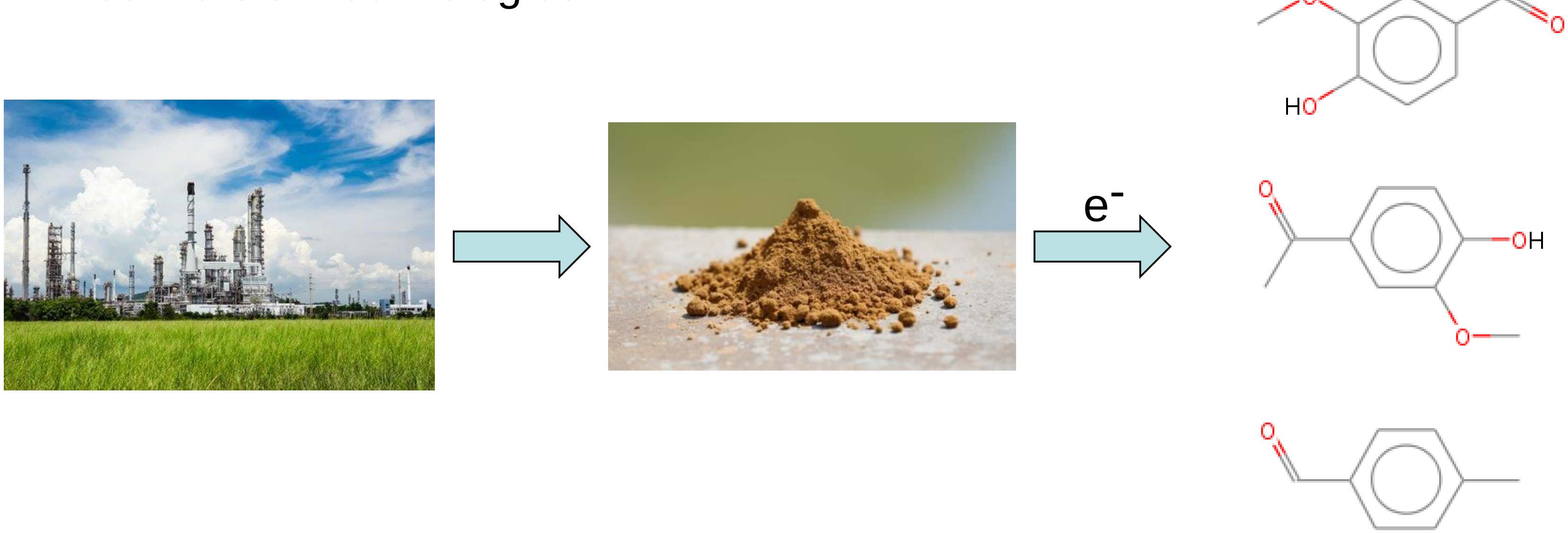
3 – Technical Accomplishments/ Progress/Results (cont'd)

- We have successfully validated a continuous reactor vs. benchmark batch reactor
- Continuous process leads to significantly higher reaction rates and extents of conversion (>40% lignin conversion vs. <1% in benchmark batch process)
- High efficiency (>98% faradaic efficiency) hydrogen production
- Technical Target Benchmark:
  - 40% lignin conversion (**achieved up 46% lignin conversion**)
  - 26% product purity (**achieved 23%**)
  - 67% selectivity (**achieved 68% selectivity**)
  - 0.02 sccm H_2 production (**achieved >2 sccm**)
  - No more than 30 g solubilized lignin remaining after reaction (**achieved 27 g lignin remaining after reaction**)
- No variations/important changes from 2017 Project Review

4 – Relevance

Make Biofuels Cost-competitive by Developing Additional Biorefinery Revenue Streams

- Directly supports BETO’s mission: “Develop and demonstrate transformative and revolutionary bioenergy technologies for a sustainable nation.”
- Addresses Market Transformation: “By 2022, validate successful runs of two biofuels and/or ***bioproducts manufacturing processes*** at pilot scale.”
- Addresses a key component of BETO’s portfolio: R&D on biomass conversion technologies.

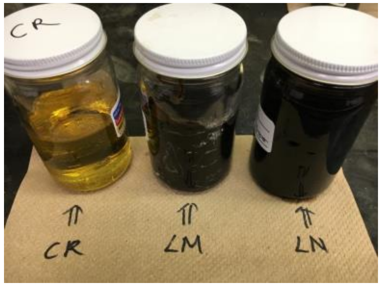


This project develops transformative electrochemical techniques resulting in high rates of lignin conversion and high yields of useful chemicals

4 – Relevance

Relevance to Industry: Provide non-petroleum precursors for phenolic resins; addresses greenhouse gas emissions and petroleum price fluctuations

- Industrial partnership is a key driver for this project
- *Global phenolic resin market expected to grow to $15 billion by 2021*
  - *Industrial partner Hexion has begun formulating resins* ⟹
  - *Could open a new "green" resin market*
  - *Reduces reliance on petroleum*
  - *New high-value uses for renewable biomass*



- *Technology Transfer Potential*
  - *Market commercial-scale electrochemical reactors to:*
    - *Biorefinery companies for on-site conversion of waste lignin to phenolic resin precursors*
    - *Resin, binder and plastics manufacturers for conversion of waste biomass to raw materials at production facilities*

Co-generation of high-purity H_2 can address additional energy needs, including for fuel cells, etc.

5 – Future Work

- Scale up the process to a 200 cm^2 reactor
  - Reduce electrocatalyst loading
  - Increase extent of conversion of lignin and yield of useful products
  - *Optimization of the process (cell voltage, residence time) will be a primary focus going forward*
  - *Optimization starts with factorial design of experiments on 200 cm^2 reactor*
  - *Continue statistical analysis on product streams*
- **Key Milestones/Deliverables**
- Incorporate product stream into resin binder formulations
- Generate process flow diagrams integrating an electrochemical process into the biorefinery concept
- Complete the techno-economic analysis based on further design scale-up using 200 cm^2 reactor data

Summary

1. Overview: *This project focuses on electrochemical conversion of biorefinery lignin to industrial chemicals*
2. Approach: *We have developed a continuous electrochemical process with robust statistical analysis to verify results*
3. Technical Accomplishments/Progress/Results : *We have hit Intermediate milestones on:*
   - » *Reactor scale, flow rate, catalyst loading, operating time*
   - » *Extent of lignin conversion*
   - » *Reaction rate*
   - » *Hydrogen production rate*
4. Relevance: *Supports BETO's mission to develop sustainable bioenergy technologies by directly addressing the cost of lignocellulosic biofuel production (create additional biorefinery revenue)*
5. Future work: *Reactor scale-up and increased extent of lignin conversion, completion of techno-economic analyses demonstrating path toward reduced biofuel cost*

Additional Slides

Responses to Previous Reviewers' Comments

…There are a few other variables (lignin source, catalyst preparation/carrier, power usage/control) for which it would be good to present an understanding of the degree of variability they will give.

- We detect variability in lignin, but it is small and the primary inter-unit linkages (β-O-4) dominate
- Catalyst preparation techniques result in consistent catalyst properties; these are standard and well-understood synthesis procedures
- Power usage/control depends on the applied cell voltage. We operate at <=1.6 V to minimize energy requirements (also avoids unwanted generation of O_2)

The TEA is not as developed as one may want, and I particularly missed an understanding of what the overall market potential is for the proposed enhanced lignin

- Global phenolic resin market expected to grow to $15 billion by 2021
- Over 100 million lbs produced in the US every year
- If phenolic compounds from lignin can compete in price and quality with those derived from petroleum, market is potentially large
- TEA analysis to be updated and expanded as experimental results are generated

Publications, Patents, Presentations, Awards, and Commercialization

Previously Reported:

- With help from DOE BETO, the Russ College of Engineering and Technology published a story about his project on October 31, 2016:

https://www.ohio.edu/engineering/news/news-story.cfm?newsItem=0C1574BE-5056-A874-1DA7051EF8FCAF27

- Ohio University student newspaper (The Post), November 17, 2016:

https://www.thepostathens.com/article/2016/11/russ-college-biofuel-grant

Since 2017 Merit Review:

- Biofuels Digest, June 25, 2017:

http://www.biofuelsdigest.com/bdigest/2017/06/25/things-to-do-with-lignin-the-digests-2017-multi-slide-guide-to-upgrading-biorefinery-waste-to-chemicals-and-hydrogen/

- Mahtab NaderiNasrabadi and John A. Staser, "Continuous Electrochemical Reactor for the Conversion of Biorefinery Lignin to Aromatic Compounds," 232nd ECS Meeting, October 2017.
- Mahtab NaderiNasrabadi and John A. Staser, "Depolymerization of Waste Lignin to Valuable Low Molecular Weight Aromatic Compounds via a Continuous Electrochemical Reactor," 2018 AIChE Annual Meeting, October 2018.