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

<table>
<thead>
<tr>
<th>DOE Funded</th>
<th>Total Costs Pre FY17**</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding (FY 19-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11,579</td>
<td>242,244</td>
<td>357,103</td>
<td>861,798</td>
</tr>
</tbody>
</table>

| 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 |

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.

• Partners:
Ohio University: 60%
Hexion: 30%
Lakehead University: 10%
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)

Electrochemical conversion
Product analysis

Product analysis
Resin binder formulations

• 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
    • \textit{Chosen based on electrocatalyst improvement and scale-up assumptions from Initial validation}
    • \textit{High conversion is necessary to break down lignin sufficiently for use in resin formulations}
  – At least 67% selectivity toward useful products
    • \textit{Chosen based on early product analysis}
    • \textit{High selectivity toward aromatic units is significant for resin development}
  – At least 26% yield of useful products
    • \textit{Chosen based on early product analysis}
    • \textit{More pure product streams facilitate resin synthesis}
  – 80% faradaic efficiency for \( H_2 \) production
    • \textit{Chosen based on typical electrolysis operation}
    • \textit{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/TiO₂ electrocatalyst
  – 10 cm² reactor, 8 mg/cm² catalyst loading, <1 L/hour flow rate, 1.6 V, 120 hours continuous operation
  – H₂ 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 H₂ at <1.6 V in 10 cm² test cell: complete
  – Development of 200 cm² 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**
- **Primary Analysis Techniques:**
  - UV-vis spectroscopy with standard addition method
  - FTIR
  - Gel permeation chromatography (GPC)
  - GC-MS
  - HR-MS
- **Provides Information On:**
  - Extent of lignin conversion
  - Product stream composition
  - Co-product H₂ 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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw (Dalton)</th>
<th>Mn (Dalton)</th>
<th>Mz (Dalton)</th>
<th>PDI</th>
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</thead>
<tbody>
<tr>
<td>AD Neat</td>
<td>3254</td>
<td>544</td>
<td>14898</td>
<td>5.983</td>
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<tr>
<td>AD Oxidized</td>
<td>2102</td>
<td>443</td>
<td>8656</td>
<td>4.749</td>
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<td>AE Neat</td>
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<td>554</td>
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<tr>
<td>AE Oxidized</td>
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<td>470</td>
<td>13747</td>
<td>5.919</td>
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<tr>
<td>AF Neat</td>
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<td>5.791</td>
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<tr>
<td>AF Oxidized</td>
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<td>418</td>
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<td>5.422</td>
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<td>AG Neat</td>
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<td>589</td>
<td>15220</td>
<td>5.876</td>
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<tr>
<td>AG Oxidized</td>
<td>2818</td>
<td>463</td>
<td>14061</td>
<td>6.083</td>
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</table>

• 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 \(\rightarrow\) high rates of product stream generation \(\rightarrow\) additional revenue \(\rightarrow\) reduced biofuel cost**
3 – Technical Accomplishments/Progress/Results

• Hydrogen Production

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>Theoretical volume of H₂ (ml/min)</th>
<th>Actual volume of H₂ (ml/min)</th>
<th>Faraday efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.23</td>
<td>2.32</td>
<td>1.04</td>
</tr>
<tr>
<td>250</td>
<td>1.86</td>
<td>1.84</td>
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</tr>
<tr>
<td>200</td>
<td>1.49</td>
<td>1.5</td>
<td>1.01</td>
</tr>
<tr>
<td>150</td>
<td>1.12</td>
<td>1.17</td>
<td>1.05</td>
</tr>
<tr>
<td>100</td>
<td>0.74</td>
<td>0.64</td>
<td>0.86</td>
</tr>
<tr>
<td>50</td>
<td>0.37</td>
<td>0.38</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Ave = 0.99

• H₂ purity = 97% by GC analysis
• Other 3% is a N₂ + O₂ (air) mixture likely due to collection and transfer from the reactor to the GC
• H₂ is an additional product
• Efficient H₂ 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 H₂ 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 H₂ 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 O₂)

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

Since 2017 Merit Review:
• Biofuels Digest, June 25, 2017: