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

Renewable Hydrogen Production from Biomass Pyrolysis Aqueous Phase

March 8, 2017
Thermochem Conversion Review
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Quad Chart Overview

Timeline
- FOA award – CHASE project
- Start: 10/1/2013
- End: 6/30/2017
- 92% complete

Barriers
- Barriers addressed
  - Ct-M. Hydrogen Production
  - Ct-L. Aqueous Phase Utilization and Wastewater Treatment
  - Ct-J. Process Integration - inhibitors

Enabling Technologies
- Novel Technologies, separations

Budget

<table>
<thead>
<tr>
<th></th>
<th>Total Costs FY 12 – FY 14</th>
<th>FY 15 Costs</th>
<th>FY 16 Costs</th>
<th>Total Planned Funding (FY 17-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>448,046</td>
<td>$751,691</td>
<td>$603,502</td>
<td>$331,760</td>
</tr>
<tr>
<td>Project Cost Share (Comp.<em>)</em></td>
<td>174,426 (28%)</td>
<td>182,645 (20%)</td>
<td>165,025 (21%)</td>
<td>$15,554 (20.1%)</td>
</tr>
<tr>
<td>Partners: GIT, UTK, FCE, Pall, Omni</td>
<td></td>
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</tr>
</tbody>
</table>

Partners
- Partners (FY15-16)
  - GIT: Georgia Institute of Technology (36%)
  - University of Tennessee, Knoxville (34%)
  - FuelCellEtc. Inc. (< 1%)
  - Pall Corporation (3%)
  - OmniTech International (1%)
1 - Project Overview

Objectives

• Reforming of aqueous phase organics to hydrogen via microbial electrolysis cell (MEC) technology.

• Develop energy-efficient separations to support MEC.

• Demonstrate improvement in hydrogen efficiency.

• Perform life-cycle analysis.

Figure 2-25: Thermochemical conversion process steps for biomass to biofuels
2-Approach-Management

- Management of multi-partner team
  - Biannual meetings
  - Monthly conference calls/Task
  - IP (Inter-lab NDAs)
  - Quarterly Reports
  - Defining 5 PhD thesis uniquely

Understanding of biooil composition

Biooil pH, instability

Hydrogen requirement

Loss of carbon via aqueous phase

GHG reduction

Produce bio-oil /characterize, analyze aqueous phase (UTK)

Microbial electrolysis of pyrolysis aqueous Phase (ORNL, UTK)

Membrane separations Biocatalyst recovery and recycle (ORNL)

Life cycle analysis Techno-economic Analysis (Omni)

Membrane process modules, supplies (Pall)

Electrolysis cell materials (FuelCellEtc, Sainergy)

Develop oil-water Separation methods (GIT)
2 – Approach (Technical)

• Produce hydrogen from bio-oil aqueous phase organics using MEC
• Investigate separation methods to generate feed for MEC and downstream separations to enable water/biocatalyst recycle

• Critical success factors
  1. Developing biocatalysts capable of utilizing all components of bio-oil aqueous phase
  2. Productivity of H₂
  3. Sufficient recovery of H₂ to upgrade bio-oil

• Challenges
  – Managing toxicity of bio-oil substrates (phenol, benzenediol, furans) and increasing their conversion along with complete utilization of acidic and polar compounds.
  – Improving proton transfer for hydrogen generation
  – Maintaining product specificity at higher scale (prevent CH₄)
  – Minimizing bioelectrochemical losses and achieving high conversion efficiency
  – Developing a continuous process

Milestones achieved:
Converted 99%+ furanic compounds with 77% recovery of hydrogen (03/16)
Developed 130 mL cell and achieved 60% H₂ production recovery (12/16)

Metrics:
  a) H₂ production rate >15 L/L-day
  b) Coulombic efficiency > 60%
3.0 – Technical Accomplishments/Progress/Results

**Objective 1.** Develop a reforming process for efficient conversion of aqueous phase organics to hydrogen via microbial electrolysis.

**Progress:**
- Increased hydrogen productivity from 2.0 to 11.7 L-H$_2$/L of reactor per day for BOAP
- Maximum productivity using acetic acid as sole substrate = 26 L-H$_2$/L-day.
- Delineated mechanisms of conversion of lignin-derived phenolic intermediates to H$_2$
- Completed speciation of complex electroactive community (fermentative vs. exoelectrogenic vs. methanogenic)
- Developed advanced separation methods (electro-separations, membrane separations)

**Milestones completed:**
1. 90% conversion of carboxylic acids (06/2015)
2. 16S rRNA - electroactive community (09/2015)
3. Demonstrate TAN removal in MEC (12/2015)
4. 50% conversion of furanic compounds at > 40% coulombic efficiency. (03/2016)
5. Separation of cellular biomass from MEC effluent using membrane system (09/2016)

**Go/No-Go criteria met:**
1. 90% conversion of carboxylic acids (09/2015)
2. Achieve 60% H$_2$ prod. efficiency (12/2016)

**Most important accomplishment:**
- Achieve 60% hydrogen production efficiency from switchgrass BOAP in 100 mL MEC (12/2016)
Goal Statement

• Carbon, Hydrogen and Separations Efficiency (CHASE) Project.


• Goals:
  – Produce hydrogen and improve its recovery from biomass-derived bio-oil aqueous phase to reduce loss of carbon and improve efficiency, while reducing lifecycle greenhouse gas emissions.
  – Investigate separation processes to enable the hydrogen production process.

• Outcome:
  – Demonstrated hydrogen productivity at lab-scale achieving levels required for commercial feasibility, and raised the TRL from 2 to 4.
3.a – Overall Technical Accomplishments

- Initiated work on LCA with OmniTech
- Compared steam reforming with MEC
- TEA analysis for MEC and pyrolysis process started with UTK.
- Complete mass and energy balance for biorefinery MEC
- Complete TEA for MEC

**Bio-oil Production and Characterization**
- 4 batches of oil from switchgrass
- Analysis of the bio-oil organic and aqueous phase
- Switchgrass bio-oil stability analysis

**Oil-Water Separation**
- Phase separation
- pH adjustment
- Centrifugal contactor
- 95% removal of acidic compounds in MEC
- Reached up to 11.7 L/L-day productivity
- Up to 75% COD removal
- 60% efficiency at 100 mL scale
- Effect of size

**Membrane Separations**
- Studied 4 type of membranes using sterile effluent
- Demonstrated potential for separating biomass from aqueous effluent
- Separation of MEC effluent containing *Geobacter*

**Conversion of BOAP in MEC**
- Identification of intermediates from furans and phenolic compounds
- Comparison of batch vs. continuous operation
- Understand inhibition by parent compounds and intermediates
- Bioanode model

**Conversion of Furanic and Phenolic Compounds**

**CHASE**

Carbon, Hydrogen & Separations Efficiency
3.b – Technical Achievements: Bio-oil production

Bio-oil production process scheme

- Feedstock: switchgrass
- Pyrolysis temperature: 500°C, 550°C
- Bio-oil: combined by three condensers
- Batch 3 & 4, 2015-16, 10 kg bio-oil generated
- Generated aqueous phase via water addition to bio-oil (4:1)
- Investigated stability of both fractions

Completion of Milestones:
Production of switchgrass bio-oil, characterization and stability analysis.

Pilot auger pyrolysis reactor at UTK Center for Renewable Carbon
Products from switchgrass intermediate pyrolysis

<table>
<thead>
<tr>
<th>Bio-oil production</th>
<th>Bio-oil yield (wt%)</th>
<th>Bio-char yield (wt%)</th>
<th>Non-condensable gas yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd batch</td>
<td>51</td>
<td>18</td>
<td>31</td>
</tr>
<tr>
<td>4th batch</td>
<td>52</td>
<td>20</td>
<td>28</td>
</tr>
</tbody>
</table>

Philip Ye, P. Kim, Shoujie Ren, N. Labbe
3.c - Microbial Electrolysis

• **Concept:**
  - Extract chemical energy as electrons at anode via biocatalysis and generate hydrogen at cathode via electrocatalysis
  - Conversion of biooil aqueous phase (boap) organics to **hydrogen**
  - Anode: Production of electrons, protons and CO₂
  - Cathode: Proton reduction to hydrogen at applied potential of 0.3-1V.
  - Requires **electroactive biofilms** tolerant to inhibitory and toxic molecules in bio-oil aqueous phase (furfural, hydroxymethylfurfural, phenolics, etc.)

• Pyrolysis derived aqueous phase utilization
  - Minimize loss of carbon/energy, reduce bio-c instability and corrosivity

**Pathway:** Bio-oil Aqueous Phase (boap) → electrons + protons (anode) → H₂ (cathode)
Achieved target performance goals with switchgrass-derived BOAP
3.e. Feedstock Specificity for MEC

- Investigated effect of feedstock and pyrolysis process conditions
- Pine wood catalytic pyrolysis aqueous phase as substrate in MEC (courtesy of PNNL/VTT)

Successful demonstration of MEC operation with pine-derived catalytic pyrolysis aqueous phase (*Met Critical Success Factor 1*).
Anode biocatalyst is capable of converting all components of bio-oil aqueous phase, including acetic acid and phenolic acids.
### 3.g – Technical Achievements - Understanding Mechanism of Furanic and Phenolic Compounds Conversion

#### Individual Model Compounds Used as Bioanode Substrate

**Electron Balance**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SA</th>
<th>VA</th>
<th>HBA</th>
<th>FF</th>
<th>HMF</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate input (mmol)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.48</td>
</tr>
<tr>
<td><strong>Experimental condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate electron equivalence (e⁻ mmol/mmol)</td>
<td>36</td>
<td>32</td>
<td>28</td>
<td>20</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td><strong>Chemical property</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total e⁻ input (e⁻ mmol)</td>
<td>7.2</td>
<td>6.4</td>
<td>5.6</td>
<td>4.0</td>
<td>4.8</td>
<td>3.8</td>
</tr>
<tr>
<td><strong>Substrate input × eeq</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e⁻ recovered as current (e⁻ mmol)</td>
<td>3.6</td>
<td>0.8</td>
<td>0.4</td>
<td>2.9</td>
<td>2.8</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>Measured</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode efficiency (%) substrate → current (COD removal × Coulombic efficiency)</td>
<td>50</td>
<td>12</td>
<td>9</td>
<td>72</td>
<td>56</td>
<td>84</td>
</tr>
<tr>
<td>e⁻ recovered as cathodic H₂ (e⁻ mmol)</td>
<td>2.9</td>
<td>0.6</td>
<td>0</td>
<td>2.4</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Measured</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode efficiency (%) current → H₂</td>
<td>81</td>
<td>76</td>
<td>NA</td>
<td>83</td>
<td>69</td>
<td>78</td>
</tr>
</tbody>
</table>

Xiaofei Zeng, SG. Pavlostathis

Completed Milestone: Demonstrate the anodic conversion of furanic compounds
3.6 – Technical Achievements
Bio-oil separations

Separation scheme:

>70% organics

Centrifugation

- Centrifugal separators
- Electro-separations
- Induced phase separation

Acidic compounds

- Methods under investigation:
  - Centrifugal separators
  - Electro-separations
  - Induced phase separation

Costas Tsouris,
Sotira Yiacoumi, Lydia Park.
3.i – Technical Achievements

Bio-oil separations

- Developed an understanding of molecular contribution to TAN
- Conducted mass balance on TAN (acidic groups) in BOAP and employed the knowledge to oil-water separation
- Relationship of pH/pKa-TAN and mixing phenomenon important to extract TAN from bio-oil.

Results show potential of the methodology to be applied for understanding separation of acidic compounds from bio-oil and subsequent increase in TAN during storage.
3.j – Technical Achievements
Membrane separation of MEC effluent for water and biocatalyst recycle
– Develop a model system (*Geobacter sulfurreducens*) for studying separations of MEC effluent
– Identified conditions for effluent clean-up
– Evaluated cellular biomass effluent with polymer and ceramic membranes
– Establish long term flux stability over time
– Demonstrated effective fouled membrane cleaning

**MEC effluent particle size preliminary analysis**
Particle size range: 0.1 μm to ~1000 μm
10 % of particles up to 2 μm
50\textsuperscript{th} percentile was ~140 μm

**Filtration Performance**
Membrane flux: 40 -60 L/hr-m\textsuperscript{2}.
Polymeric membranes better than ceramic zirconia, PVDF better than PAN

**Completed Milestone: Develop membrane separation of MEC effluent**
### Performance and efficiency metrics for MEC development

<table>
<thead>
<tr>
<th></th>
<th>Targets for commercial consideration</th>
<th>Start of Project (Oct 2013)</th>
<th>March 2015</th>
<th>March 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td></td>
<td>16 mL</td>
<td>16 mL</td>
<td>130 mL</td>
</tr>
<tr>
<td>Hydrogen production rate, ( \text{L H}_2/\text{L-reactor-day} )</td>
<td>( &gt;15 )</td>
<td>1.5</td>
<td>2.0</td>
<td>11.7 ± 0.2 (BOAP)</td>
</tr>
<tr>
<td></td>
<td>FCTO MEC using sugars: 0.36 L/L-day</td>
<td></td>
<td>27 (Acetic acid)</td>
<td></td>
</tr>
<tr>
<td>Anode current density, A/m²</td>
<td>20</td>
<td>1-2</td>
<td>5</td>
<td>11.5 (BOAP)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27 (Acetic Acid)</td>
<td></td>
</tr>
<tr>
<td>Anode CE</td>
<td>( &gt;90% )</td>
<td>( &lt; 40% ) [7]</td>
<td>54%</td>
<td>Up to 79%#</td>
</tr>
<tr>
<td>% COD removal</td>
<td>( &gt; 80% )</td>
<td>NA</td>
<td>74.2%</td>
<td>74%</td>
</tr>
<tr>
<td>Applied voltage</td>
<td>(&lt; 0.6 \text{ V} )</td>
<td>1.0 V [14]</td>
<td>0.9 V</td>
<td>0.8 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.75V</td>
<td></td>
</tr>
<tr>
<td>Cathode CE</td>
<td>( &gt;90% ) at 0.6 V or less</td>
<td>80% with 1 V (acetic acid)</td>
<td>80-96%</td>
<td>Up to 100%$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85%</td>
</tr>
<tr>
<td>Electrical Efficiency</td>
<td>( &gt;150% )</td>
<td>100% with acetic acid</td>
<td></td>
<td>162%</td>
</tr>
<tr>
<td>Resistance</td>
<td>(&lt; 80 \text{ mΩ m}^2 )</td>
<td>36 – 189 mΩ m² (non-BOAP)</td>
<td>NA (BOAP)</td>
<td>105 mΩ m² (BOAP)</td>
</tr>
</tbody>
</table>

Achieved hydrogen productivity goals required to show commercial feasibility! *(Met 2nd Critical Success Factor)* Elevated technology from TRL 2 to TRL 4
3.m Techno-Economic Analysis (TEA)

- Biorefinery MEC integration
- Utilization of carbonyl compounds in BOAP to generate hydrogen
- MEC capital costs $2000/m³
- TEA model to assess MEC feasibility

Sensitivity Analysis

H₂ productivity = 20 L/L-day
Capital costs:
$2000 to $4000: $2.5 to $3.25/kg
Feedstock costs:
(0 to $85/ton): $2.5 to 3.9/kg
Conversion efficiency:
45-57%: $3.9 to $3.6/kg

Target performance for application feasibility

10-fold reduction in price of H₂ during the CHASE project
3.n Life-Cycle Analysis (LCA)

- Comparison of Steam Methane Reforming (SMR) to MEC process
- Developed PFDs for Hydrogen generation in biorefinery using natural gas + pyrolysis gas vs. BOAP MEC + pyrolysis gas reformer
- Extracted mass balance for SMR from PNNL-25053. Conducted energy balance to complete dataset. Similarly, mass and energy balance for MEC process under way
- Determined baseline LCA for SMR to compare with MEC using SimaPro.
- Collaboration with OmniTech International and UTK
Publications/Patents

- Switchgrass bio-oil production & characterization, *J. Anal. & Applied Pyrolysis*
- Separation of bio-oil components, *J. Anal. & Applied Pyrolysis*
- Third manuscript on stability in preparation
  - Neutralization of pH to separate bio-oil, *Energy & Fuels*
- TAN analysis of BOAP, *Fuel*
- MEC Technology status (*ECS Interface*), MEC impact analysis: *Sustainability*
- Book chapter on biorefinery MXCs
- Effect of flow, RT, on MEC performance – *Biochem. Eng. J.*
- Comparison of batch and continuous bioanode operation in MFCs – *Biochem. Eng. J.*
- Proton transfer in MECs – *Sustainable Energy & Fuels*
- Biocomplexity of anode biofilms – in review
- Effect of redox potential – in preparation…
- + 3 more….
- Provisional Patent for Biorefinery MECs – applied June 2016
- TEA analysis of MEC with steam reforming.

13 Publications + one patent to date + 5 manuscripts in review

Efficiency: < $150k/pub.
4.a Relevance

Demonstrating conversion of biorefinery process waste to bioenergy:
A path to improving energy efficiency and energy recovery from biomass

Waste electrons to...

...via bio/electrosynthesis
4.b Relevance
Integrating the biomass resource into the bio-economy via H₂ carrier → has multiple benefits…

- Fuel Cell H₂ Vehicles
- Renewable Gasoline/Diesel
- Upgrading Bio-oils
- Chemical Building Blocks
- Polymers
- Reducing Agent for Bioproducts

- Biomass
- Electricity
- MEC
- Waste
- Resource Recovery
  Phosphorous, water, nitrogen

Value Added Applications
- Power Generation
- Hydrogen/Natural Gas Infrastructure
- Fuel Cell H₂ Vehicles
- Renewable Gasoline/Diesel
- Upgrading Bio-oils
- Chemical Building Blocks
- Polymers
- Reducing Agent for Bioproducts

Electricity Grid
- Wind
- Solar PV
- Hydrogen Storage/Distribution
- Power Generation
- MEC
- Waste
- Resource Recovery
  Phosphorous, water, nitrogen

Value Added Applications
- Hydrogen Vehicle
- Synthetic Fuels
- Upgrading Oil/Biomass
- CO₂
- N₂
- NH₃
- Electricity
- Waste
- Resource Recovery
  Phosphorous, water, nitrogen
5.a Future Collaborations

- PNNL (MEC conversion of VTT catalytic pyrolysis aqueous phase and product characterization, algal HTL water)
- NREL (TEA spreadsheet - pyrolysis process)
- Iowa State University
  - Aqueous phase from ISU fractionator (Centralized Biorefining)
  - TEA analysis of MEC-SF integration process
- USDA, Peoria
  - Conversion of tail-gas recycle pyrolysis aqueous phase
  - Potential integration of farm-scale pyrolyzer and farm-scale MEC for distributed $H_2$, bio-oil and bio-char.
- Industry
  - Collaboration on Integrated Biorefinery Optimization
  - Integration of MEC into thermochemical biorefinery
5.b – Future Work

• Scale-up of MEC to 1 L
• Test multi-MEC stack for distributed farm production of H₂ and a stable bio-oil
• Optimize biocatalyst growth for industrial application
• Complete LCA analysis of MEC process
• Complete separation process analysis for optimal feedstock utilization (for downstream MEC and hydrotreating unit ops)
• Complete publication of manuscripts as follows:
  – Separation of oil-water using centrifugal separators and capacitive deionization (2)
  – Membrane separation of MEC effluent
  – Improvements in MEC potential efficiency, Effect of MEC size on performance, Composition-function relationships, omics analysis (4)
  – TEA/LCA analysis (2)
• Identify opportunities for scale-up and integration of MECs into biorefineries
Summary

• **Overview**: Improved hydrogen efficiency via a hybrid biocatalytic-electrocatalytic process (MEC), using a biomass-derived stream, while addressing carbon and separations efficiency.

• Holistic **approach** covering bio-oil production, characterization, conversion of boap to H$_2$, process recycle and TEA/LCA analysis.

• **Accomplished** development of an electroactive biocatalyst and MEC to convert boap to H$_2$ at efficiency > 60%. Demonstrated effective conversion of problematic carbonyl compounds in MEC.

• **Addressed** C, H and separations efficiency and barriers Ct-M, Ct-L, Ct-J **relevant** to BETO.

• **Future work**: Scale the process to modular repeat unit (1-5L) while maintaining productivity at 15 L/L-day and > 60% efficiency.
Extra slides
3.c - Hydrogen Production: Comparison with Existing Technologies

- Bio-oil steam reforming using Pt-Re or metal catalysts:
  - Low $\text{H}_2$ yield (0.1 to 40 %) vs. 64-91% for MEC.
  - High coking vs. no coking in MEC
  - Expensive catalyst vs. regenerable biocatalyst for MEC.

- Bioconversion:

<table>
<thead>
<tr>
<th>Process scheme</th>
<th>Theoretical yield</th>
<th>Observed yield</th>
<th>Free energy change (for $\text{H}_2$-producing step)</th>
<th>Overall observed energy yield</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Hypothetical $\text{H}_2$ production</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Hexose to ethanol to $\text{H}_2$ via autothermal reforming</td>
<td>10</td>
<td>9.5</td>
<td>$-265^a$ kJ/mole</td>
<td>$\sim 83%$</td>
<td>Prohibitive catalyst (Rh) cost$^{10}$</td>
</tr>
<tr>
<td>3 Dark-light fermentation: Glucose $\rightarrow$ acetate $\rightarrow$ $\text{H}_2$</td>
<td>8</td>
<td>7.1</td>
<td>$+164$ kJ/mole</td>
<td>59.2%</td>
<td>Limited by light penetration and cost$^{39}$</td>
</tr>
<tr>
<td>4 Methanogenesis-steam reforming</td>
<td>8</td>
<td>6.0</td>
<td>$+261$ kJ/mole</td>
<td>50.5%</td>
<td>Mature technology components$^{3,40}$</td>
</tr>
<tr>
<td>5 MEC</td>
<td>12</td>
<td>8.2</td>
<td>$+104.6$ kJ/mol</td>
<td>64%</td>
<td>Nascent technology $^{3,30}$</td>
</tr>
</tbody>
</table>

$^a$ Processes 3–5 require energy input for the hydrogen-producing step, but this step is energy yielding in process 2. While the hydrogen producing reaction is energy-yielding, energy input is required for production of ethanol from hexose.

Microbial electrolysis is a high efficiency, high yield, practical alternative available for hydrogen production.

4 - Relevance

• Contributions to BETO MYPP goals:
  – Developed strategy for improving carbon and hydrogen conversion efficiency and demonstrated feasibility of conversion using switchgrass as feedstock (Barriers Tt-M, Tt-N)
  – Initiated investigations into separations technology for extracting acidic compounds from biooil and for water recycle (Tt-O)
  – Address ‘Balance of Plant’ issues: wastewater treatment, minimizing organics in aqueous phase, more efficient carbon and hydrogen usage process recycle
  – Address knowledge gaps in chemical processes via bio-oil characterization, understanding and driving separation and conversion of key problem (acidic/polar) compounds (Tt-H, Tt-L).

• Patent applications / Invention disclosures
  – Hydrogen production from pyrolysis-derived aqueous phase (June 2016).
  – Separation of acidic molecules from biooil (in preparation)
4 – Relevance…

• Application in emerging bioenergy industry
  – Establish MEC as core technology for hydrogen production in thermochemical biooil upgrading
  – Potential application for producing hydrogen from fermentation effluent and lipid-extracted algae

• Support of strategic goals (Section 2.2.2.1 of mypp)
  – Use of extracted electrons for increasing efficiency of production of biofuels (butanol) via bioelectrochemical systems (p. 2-71, 2-79 –’yet-to-be-discovered technologies’)
  – Production of biochemicals (1,3-propanediol; 1,4-butanediol)

• Sustainability analysis and communication
  – Consumptive water use, wastewater treatment.
3.j – Technical Achievements
Pathways for Conversion of Furanic and Phenolic Compounds in Bioanode

- Identification of intermediates by mass spec
- Pathway analysis results has lead to better understanding of complex bioanode conversion bottlenecks.

Xiaofei Zeng, SG. Pavlostathis
3.c. Electroactive Biofilm Development via Targeted Evolution

- Microbial consortium capable of converting all class of compounds in BOAP
- Negligible presence of methanogens/archaea
- Reproducibility of consortia in duplicate MECs
- No external mediators and potentially mediator-free operation
- 7-10% **Geobacter**
- Capable of tolerating furanic and phenolic compounds
3.f – Technical Achievements
Conversion of Pine Wood Aqueous Phase

Conversion of pine wood aqueous phase

Anode biocatalyst capable of converting phenol and benzenediol
**GIT Conclusions and Contribution**

**Conversion of Furanic and Phenolic Compounds**
- Promising Coulombic efficiency and H₂ yield by all five compounds utilized
- Two-step biotransformation: fermentation (independent), exoelectrogenesis (dependent)
- Furanic compounds more productive substrates than phenolic compounds

→ Quantitative information on the extent of biotransformation and contribution of individual furanic and phenolic compounds to MEC H₂ production

**Biotransformation Pathways**
- Phloroglucinol vs. benzoyl-CoA pathways
- The extent of biotransformation of phenolic compounds depends on the number and position of hydroxyl (–OH) and methoxy (–O–CH₃) substituents

→ The first study to elucidate biotransformation pathways and rate-limiting steps of phenolic compounds under bioanode conditions
→ Important structure implication on the extent of biodegradation and pathway
GIT Conclusions and Contribution

- **Bioanode Inhibition**
  - Impacted process: exoelectrogenesis, not fermentation
  - Responsible inhibitors: parent compounds >> transformation products; phenolic > furanic
  - Mixture effects: additive, not synergistic

  → **Significant advancement of currently limited understanding of bioanode inhibition**

- **Microbial Interactions**
  - Diverse microbial community: putative exoelectrogens, furanic and phenolic degraders, and other fermentative bacteria
  - Syntrophic (fermenters & exoelectrogens)
  - Competitive (exoelectrogens & methanogens)
  - Operating conditions impact microbial interactions and relative abundance

  → **New insights into microbial interactions in bioelectrochemical systems fed with complex waste streams resulting from the pretreatment of lignocellulosic biomass, which can guide future MEC research and development**
Technical Achievements
Membrane separation of MEC effluent for water and biocatalyst recycle

- Experiments were performed on both anaerobically grown Geobacter and autoclaved samples. Experiments with larger area hollow fiber modules could not be performed in a glove box.

- Among the polymeric membranes evaluated PVDF membranes gave higher flux compared to PAN.

- However, flux values with anaerobic Geobacter were 40-50% lower compared to autoclaved samples. It is believed that Geobacter cell size was considerably smaller (<1 micron) compared to the autoclaved samples with average particle size substantially > 1 micron.