

**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

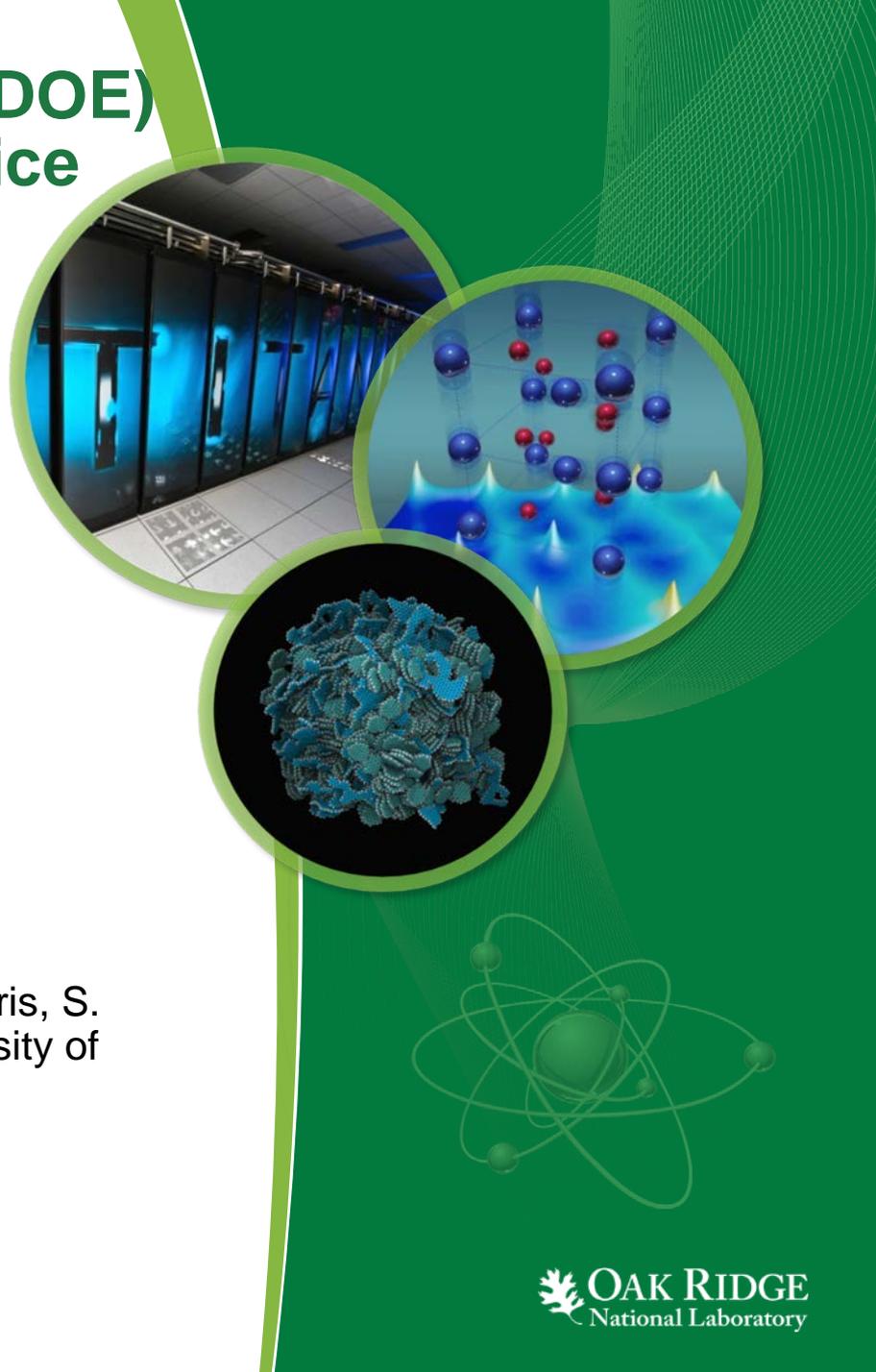
Thermochem Conversion Review

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Oak Ridge National Laboratory

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Industrial Partners: FuelCellEtc., Pall coporation, OmniTech international, Sainergy Tech, Inc.



Quad Chart Overview

Timeline

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

Budget

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

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

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

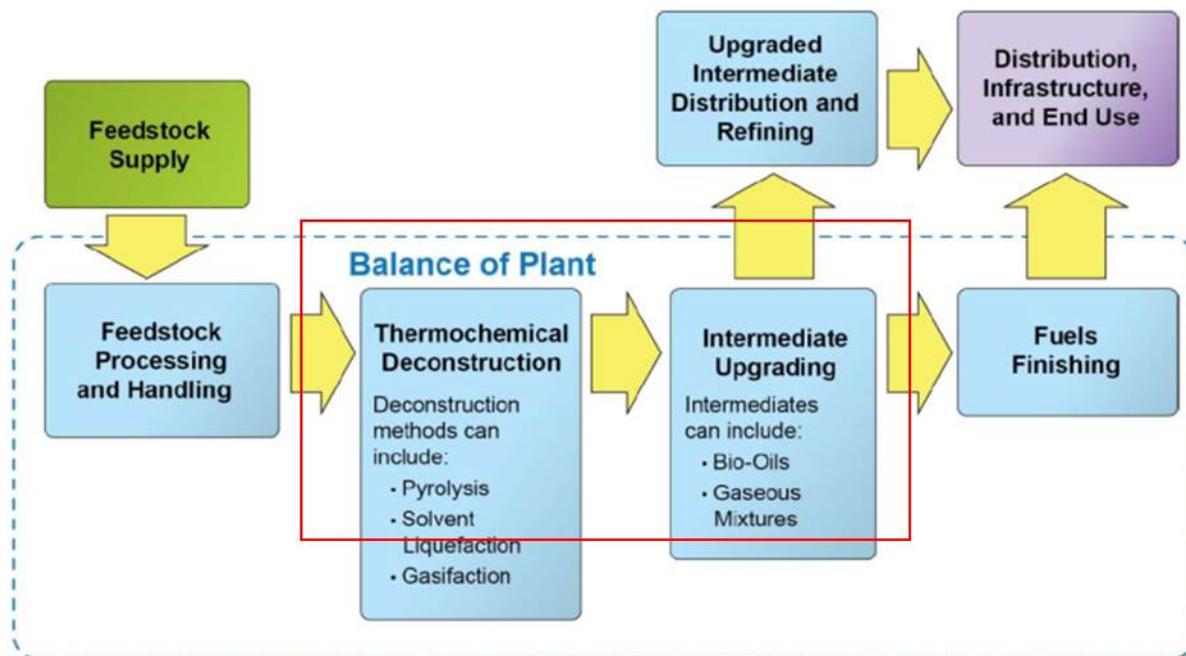
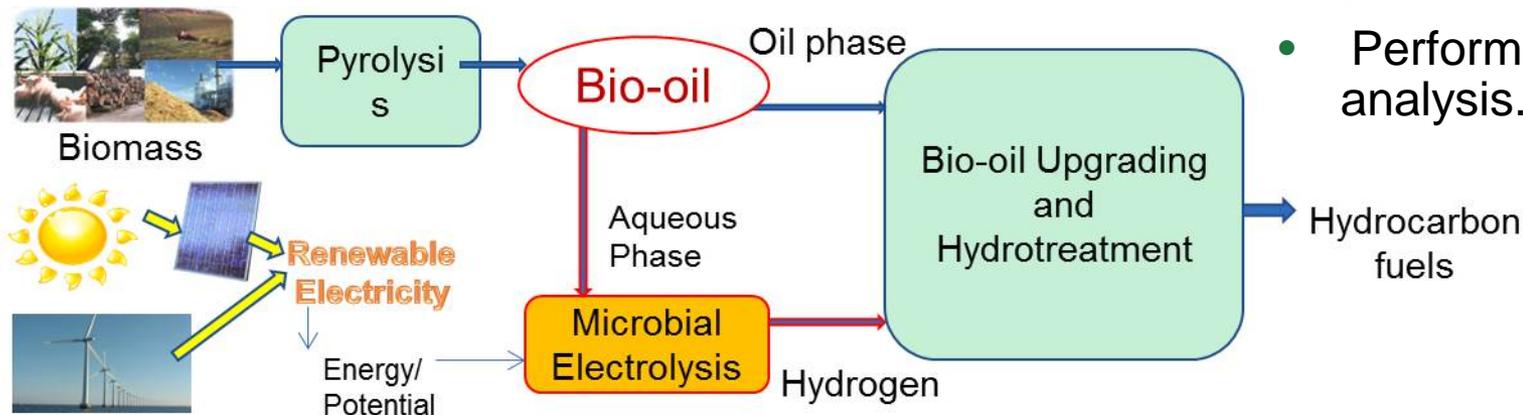


Figure 2-25: Thermochemical conversion process steps for biomass to biofuels



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.

2-Approach-Management

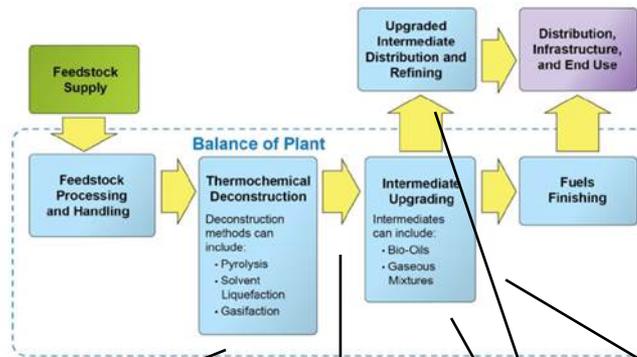


Figure 2-25: Thermochemical conversion process steps for biomass to biofuels

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

Problem

- Understanding of biooil composition
- Biooil pH, instability
- Hydrogen requirement
- Loss of carbon via aqueous phase
- GHG reduction

Solutions

- Produce bio-oil /characterize, analyze aqueous phase (UTK)
- Microbial electrolysis of pyrolysis aqueous Phase (ORNL, UTK)
- Microbial electrolysis of furanic and phenolic Substrates (GIT)
- Membrane separations Biocatalyst recovery and recycle (ORNL)
- Life cycle analysis Techno-economic Analysis (Omni)
- Develop oil-water Separation methods (GIT)
- Membrane process modules, supplies (Pall)
- Electrolysis cell materials (FuelCellEtc, Sainergy)
- Industry partners  RIDGE NATIONAL Laboratory

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-H₂/L of reactor per day for BOAP
 - Maximum productivity using acetic acid as sole substrate = 26 L-H₂/L-day.
 - Delineated mechanisms of conversion of lignin-derived phenolic intermediates to H₂
 - 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% H₂ 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.

Technical Area: Hydrogen Efficiency, subtopic: *Reforming hydrogen from aqueous streams in biomass liquefaction.*

- 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

Carbon, Hydrogen & Separations Efficiency CHASE

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

Conversion of BOAP in MEC

- 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

Conversion of Furanic and Phenolic Compounds

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

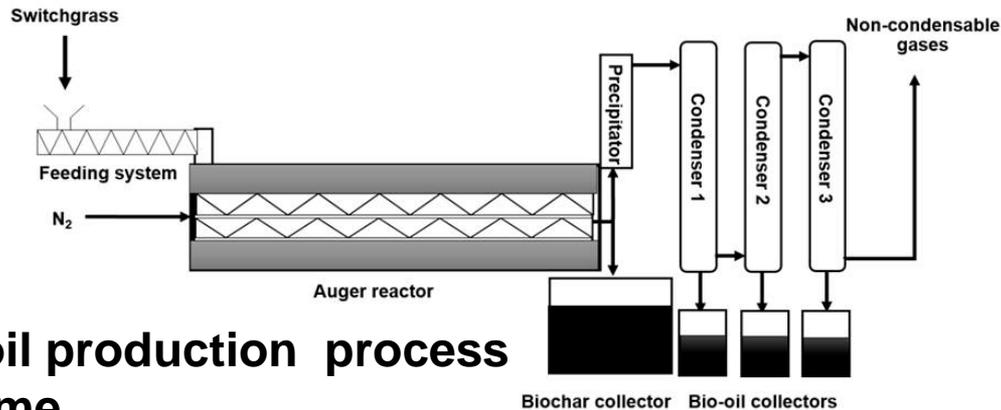
Membrane Separations

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

LCA TEA

- Initiated work on LCA with OmniTech
- Compare 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

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

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

Bio-oil production	Bio-oil yield (wt%)	Bio-char yield (wt%)	Non-condensable gas yield (wt%)
3 rd batch	51	18	31
4 th batch	52	20	28

Completion of Milestones:

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

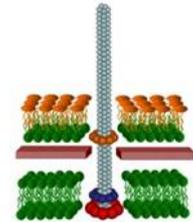
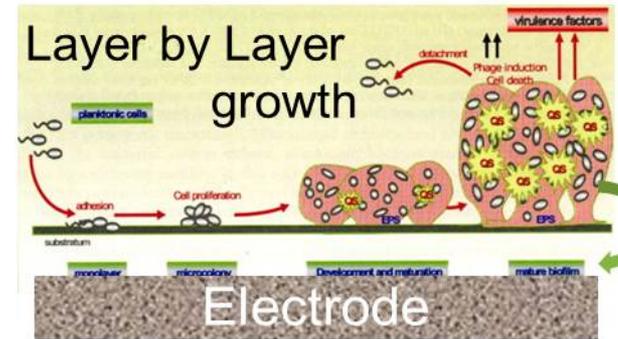
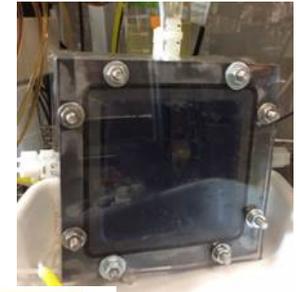
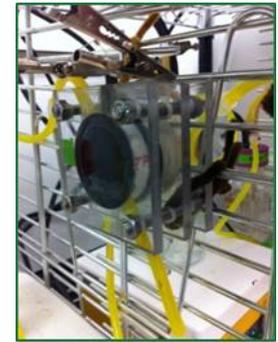
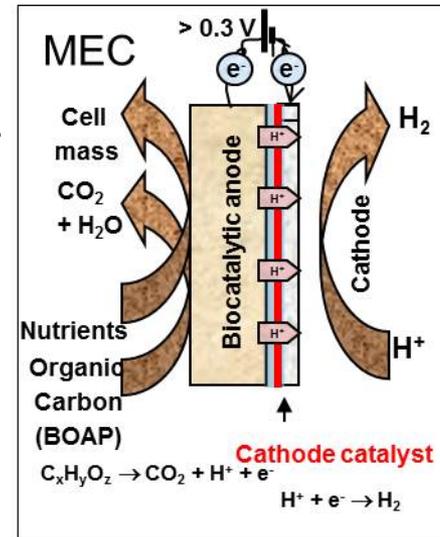
Philip Ye, P. Kim, Shoujie Ren, N. Labbe

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-instability and corrosivity

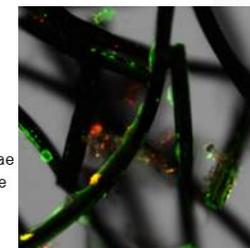
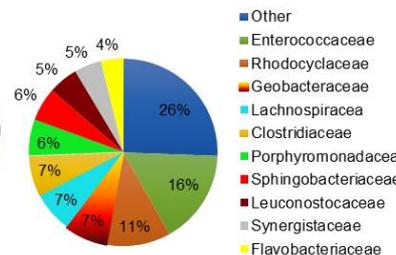
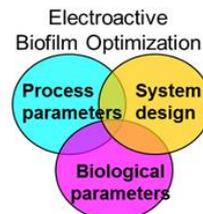


Biological nanowires

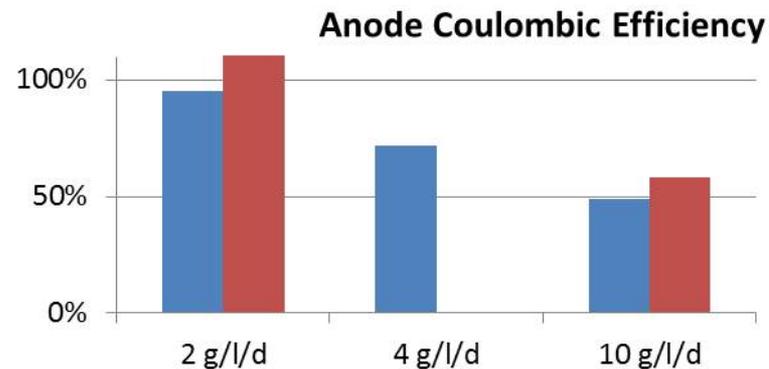
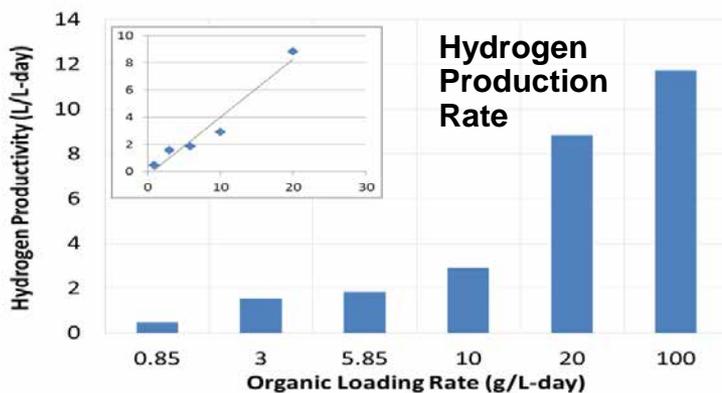
Pathway: Bio-oil Aqueous Phase (boap)

→ electrons + protons (anode) → H₂ (cathode)

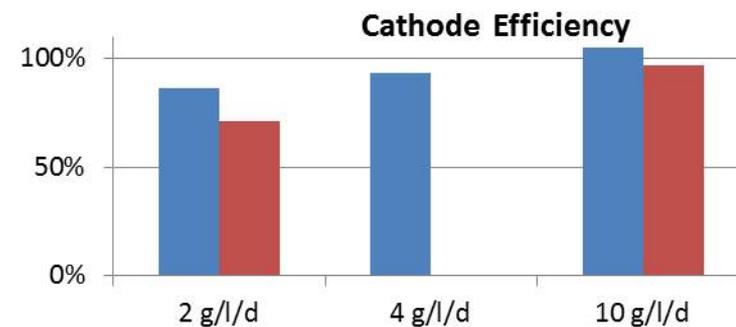
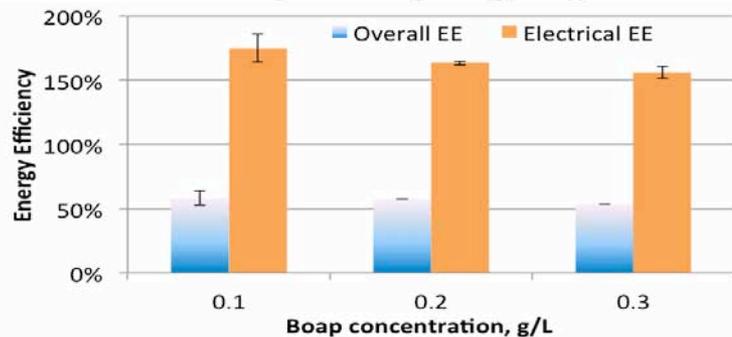
Biotechnol for Biofuels. 2009, 2, 1, 7., Borole, A. P., et al., *Environ Sci Technol*. 2013, 47, 642., Borole, A. P., et al., *Energy Environ. Sci.* 2012, 4: 4813-4834, Borole, A. P., et al. *US Patent* 7,695,834, *UT-Battelle, USA, 2010.*, Borole, A. P. *US Patent* 8,192,854 B2 *UT-Battelle, USA, 2012*, Borole, A.P



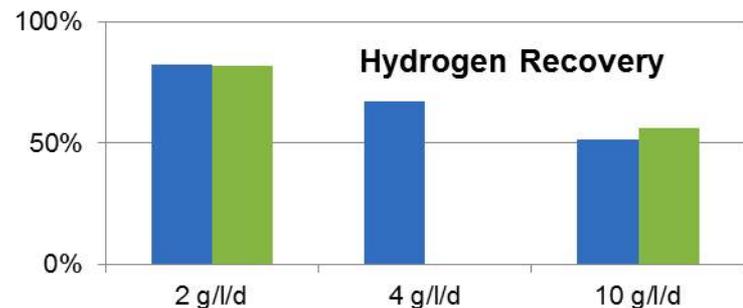
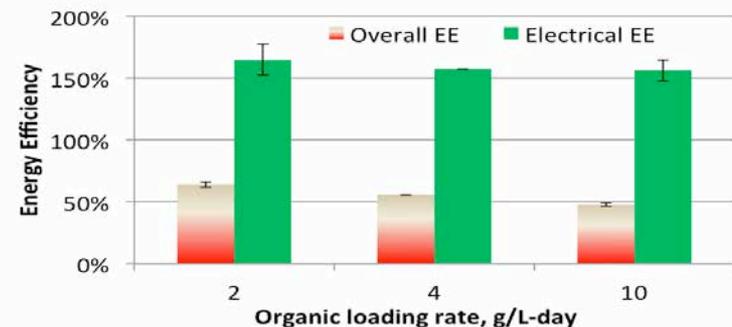
3.d – MEC performance



Batch:



Continuous:

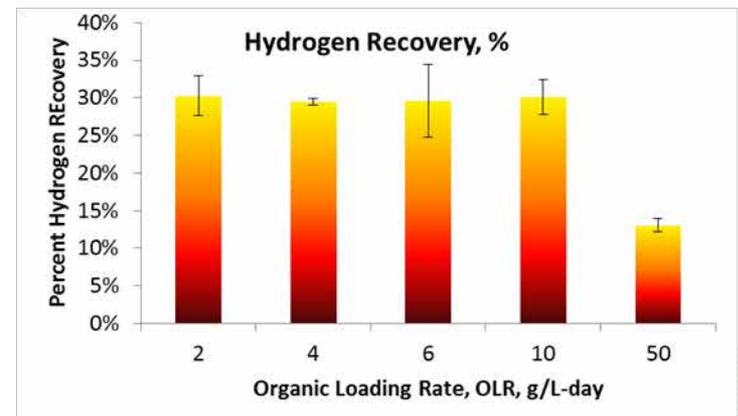
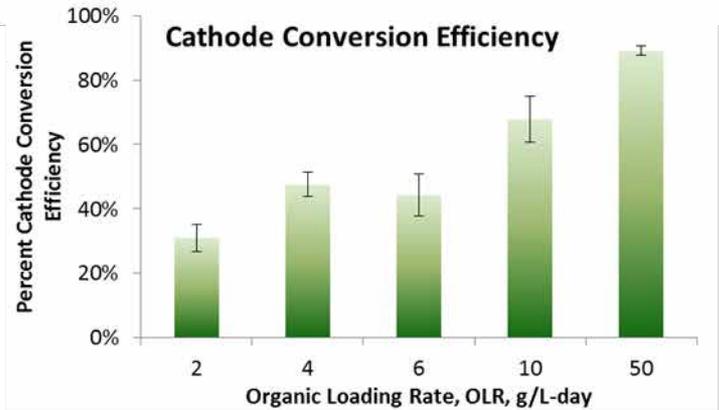
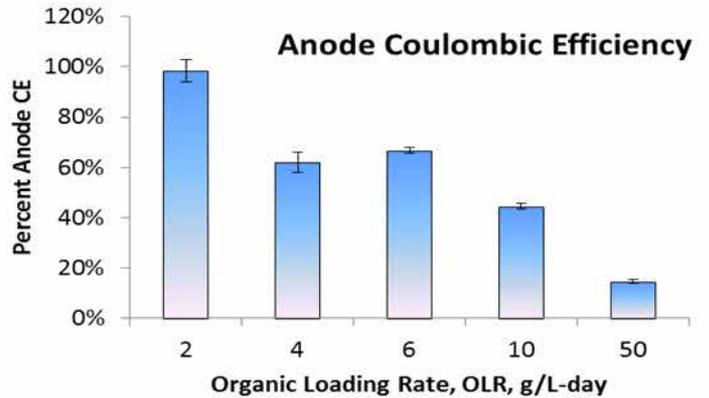
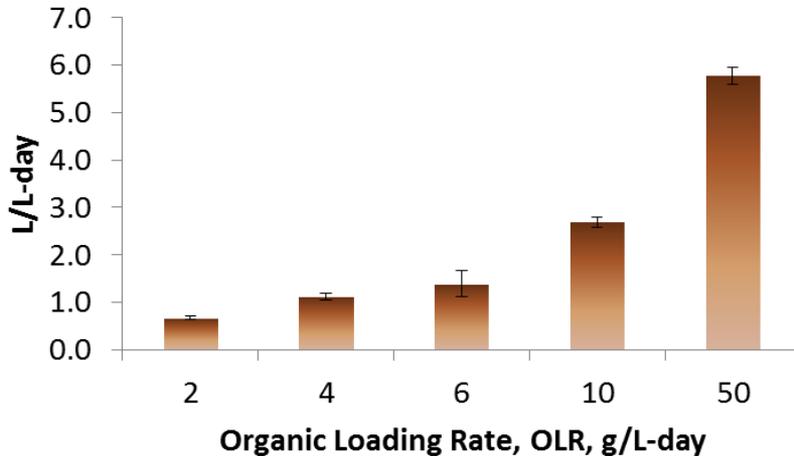


Achieved target performance goals with switchgrass-derived BOAP

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)

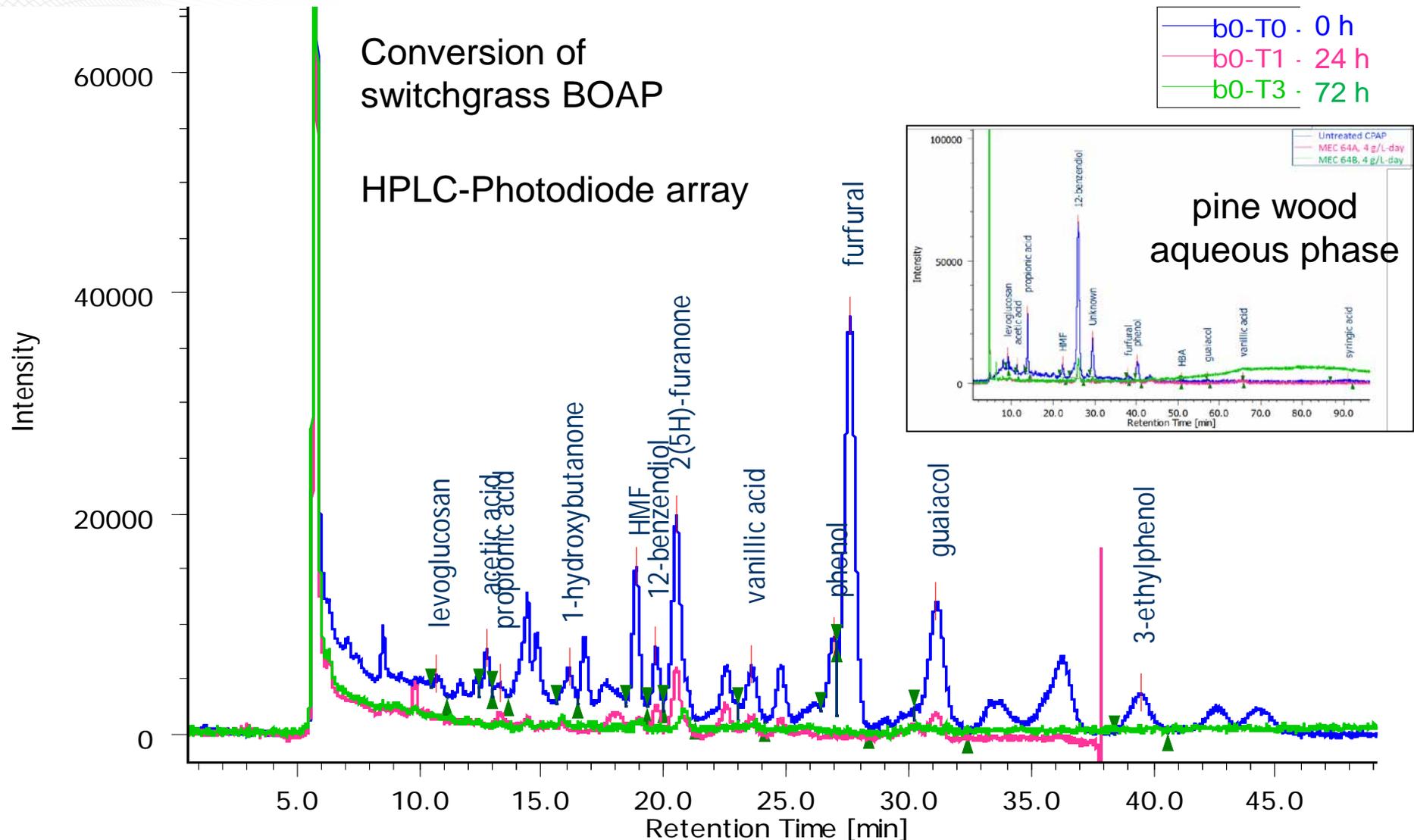
Hydrogen Productivity



Successful demonstration of MEC operation with pine-derived catalytic pyrolysis aqueous phase (**Met Critical Success Factor 1**).

3.f – Technical Achievements

Conversion of Bio-oil Aqueous Phase



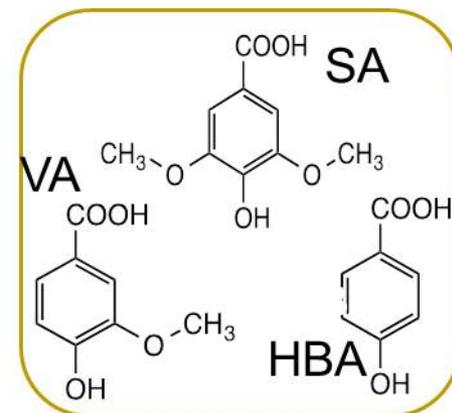
Anode biocatalyst is capable of converting all components of bio-oil aqueous phase, including acetic acid and phenolic acids.

3.g – Technical Achievements - Understanding Mechanism of Furanic and Phenolic Compounds Conversion

Individual Model Compounds Used as Bioanode Substrate

Electron Balance

Parameter	Batch run					
	SA	VA	HBA	FF	HMF	Acetate
Substrate input (mmol) <i>Experimental condition</i>	0.2	0.2	0.2	0.2	0.2	0.48
Substrate electron equivalence (e ⁻ mmol/mmol) <i>Chemical property</i>	36	32	28	20	24	8
Total e ⁻ input (e ⁻ mmol) <i>Substrate input × eeq</i>	7.2	6.4	5.6	4.0	4.8	3.8
e ⁻ recovered as current (e ⁻ mmol) <i>Measured</i>	3.6	0.8	0.4	2.9	2.8	3.2
Anode efficiency (%) <i>substrate → current</i> <i>(COD removal × Coulombic efficiency)</i>	50	12	9	72	56	84
e ⁻ recovered as cathodic H ₂ (e ⁻ mmol) <i>Measured</i>	2.9	0.6	0	2.4	1.9	2.5
Cathode efficiency (%) <i>current → H₂</i>	81	76	NA	83	69	78

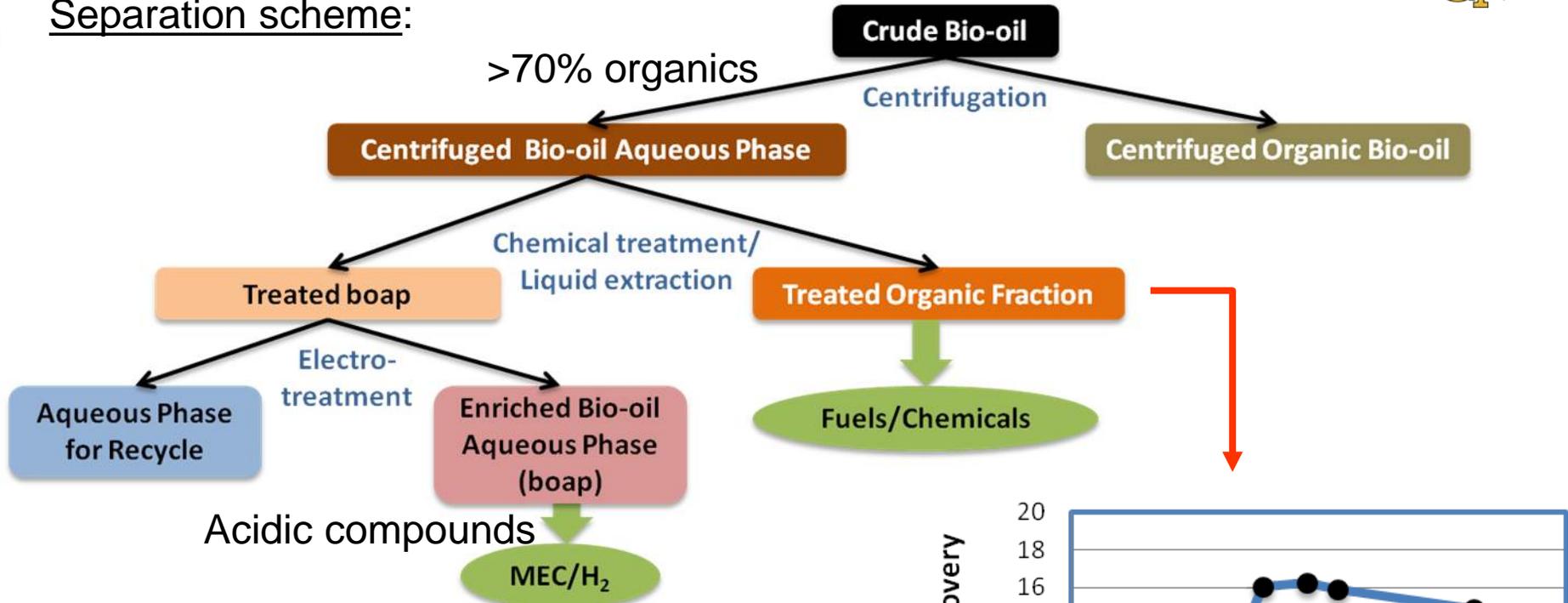


Completed Milestone:
Demonstrate the anodic conversion of furanic compounds

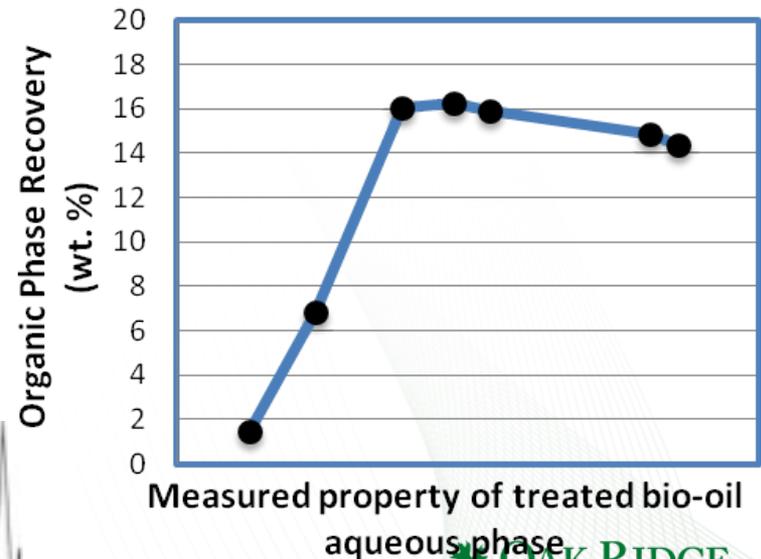
3.h – Technical Achievements Bio-oil separations



Separation scheme:



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



Costas Tsouris,
Sotira Yiacomou, Lydia Park.

Georgia
Tech

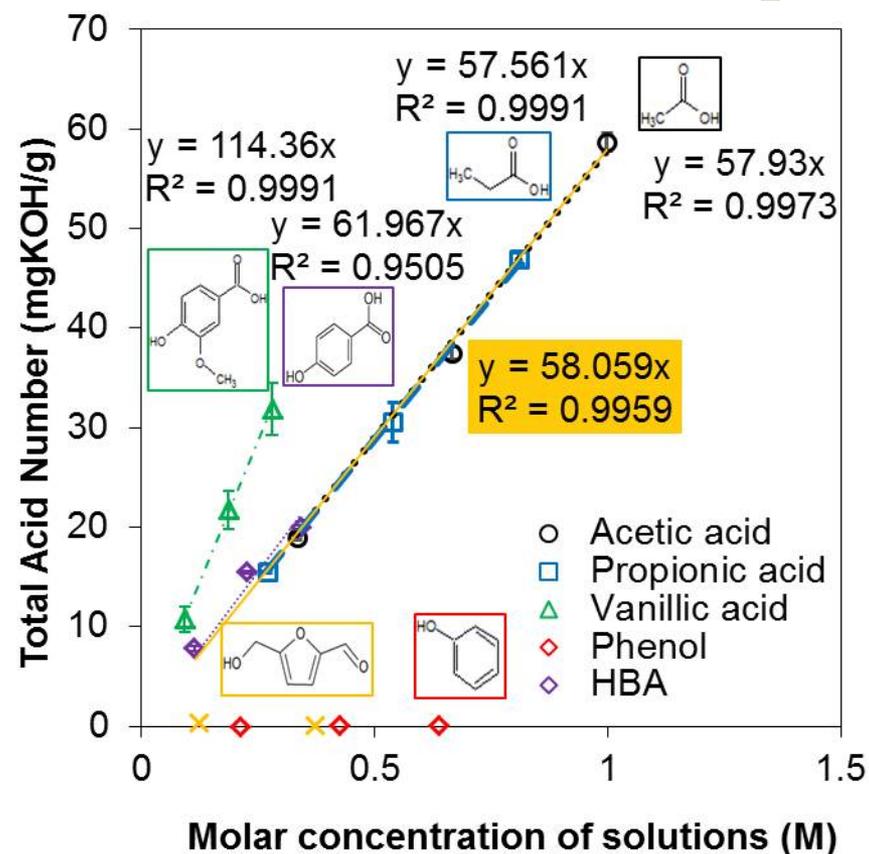
OAK RIDGE
National Laboratory

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.

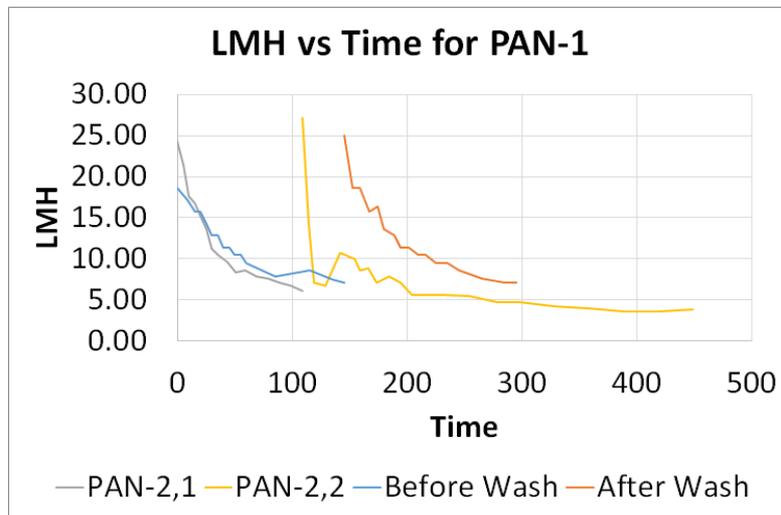
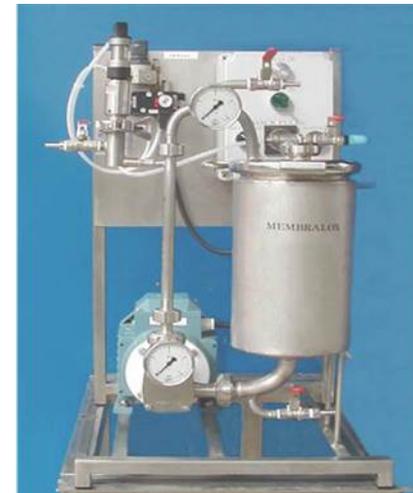


Results show potential of the methodology to be applied for understanding separation of acidic compounds from bio-oil and subsequent increase in TAN during storage.

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 $\sim 1000 \mu\text{m}$

10 % of particles up to 2 μm

50th percentile was $\sim 140 \mu\text{m}$

Filtration Performance

Membrane flux: 40 -60 L/hr- m^2 .

Polymeric membranes better than ceramic zirconia, PVDF better than PAN

Andrew Drake, Ramesh Bhawe, ORNL

Completed Milestone: Develop membrane separation of MEC effluent

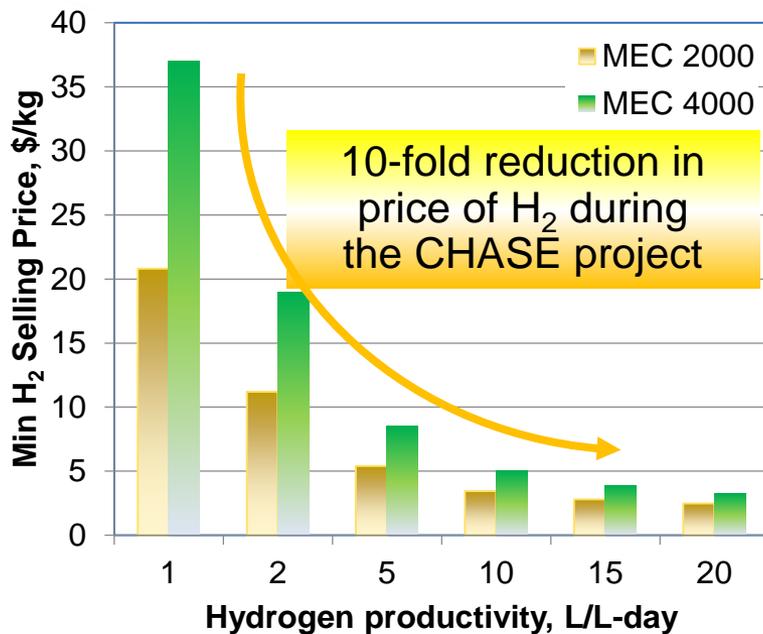
Performance and efficiency metrics for MEC development

	<i>Targets for commercial consideration</i>	<i>Start of Project (Oct 2013)</i>	<i>March 2015</i>	<i>March 2017</i>	
Scale			16 mL	16 mL	130 mL
Hydrogen production rate, L H₂/L-reactor-day	>15 FCTO MEC using sugars: 0.36 L/L-day	1.5	2.0	11.7 ± 0.2 (BOAP) 27 (Acetic acid)	
Anode current density, A/m ²	20	1-2	5	11.5 (BOAP) 27 (Acetic Acid)	
Anode CE	>90%	< 40% [7]	54%	Up to 79%#	62%
% COD removal	> 80%	NA		74.2%	74%
Applied voltage	< 0.6 V	1.0 V [14]	0.9 V	0.8 V	0.75V
Cathode CE	>90% at 0.6V or less	80% with 1 V (acetic acid)	80-96%	Up to 100%\$	85%
Electrical Efficiency	>150%	100%+ with acetic acid		162%	149%
Resistance	< 80 mΩ m ²	36 – 189 mΩ m ² (non-BOAP)	NA (BOAP)	105 mΩ m² (BOAP)	

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



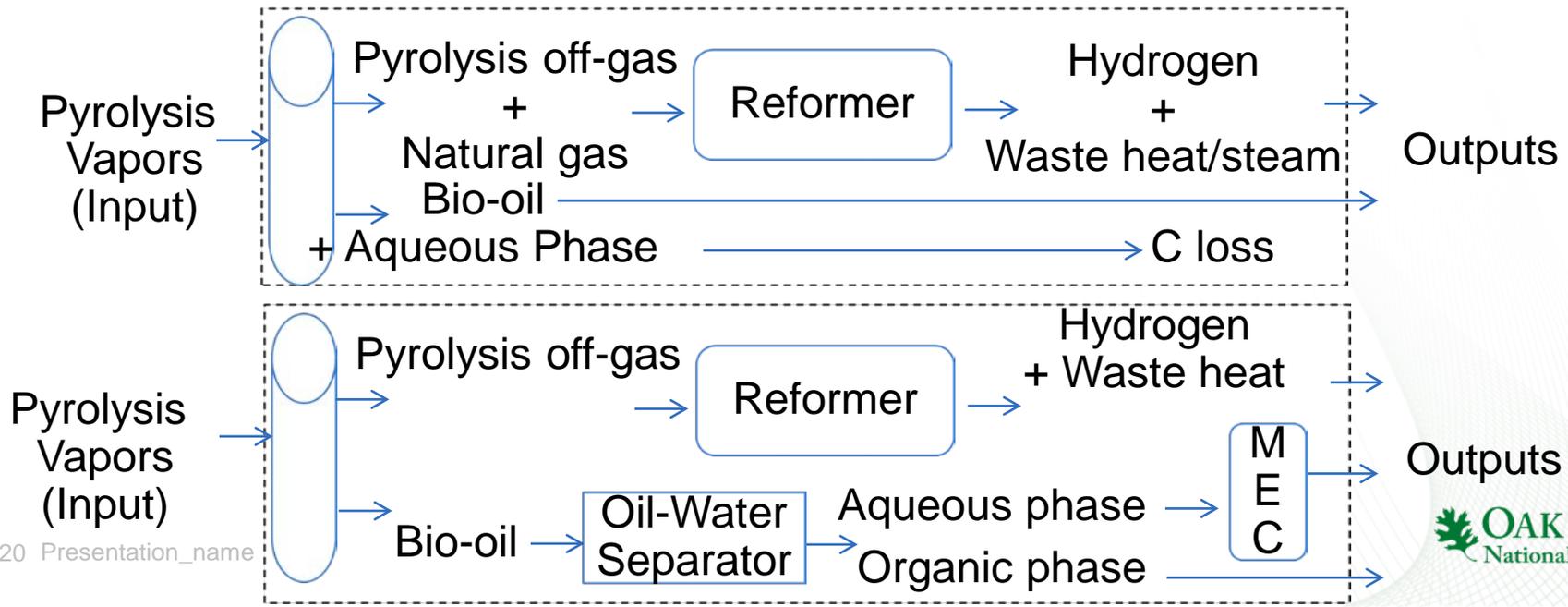
Sensitivity Analysis
H₂ productivity = 20 L/L-day
Capital costs :
\$2000 to \$4000: \$2.5 to \$3.25/kg
Feedstock costs:
(0 to \$ 85/ton): \$ 2.5 to 3.9/kg
Conversion efficiency:
45-57%: \$ 3.9 to \$ 3.6/kg



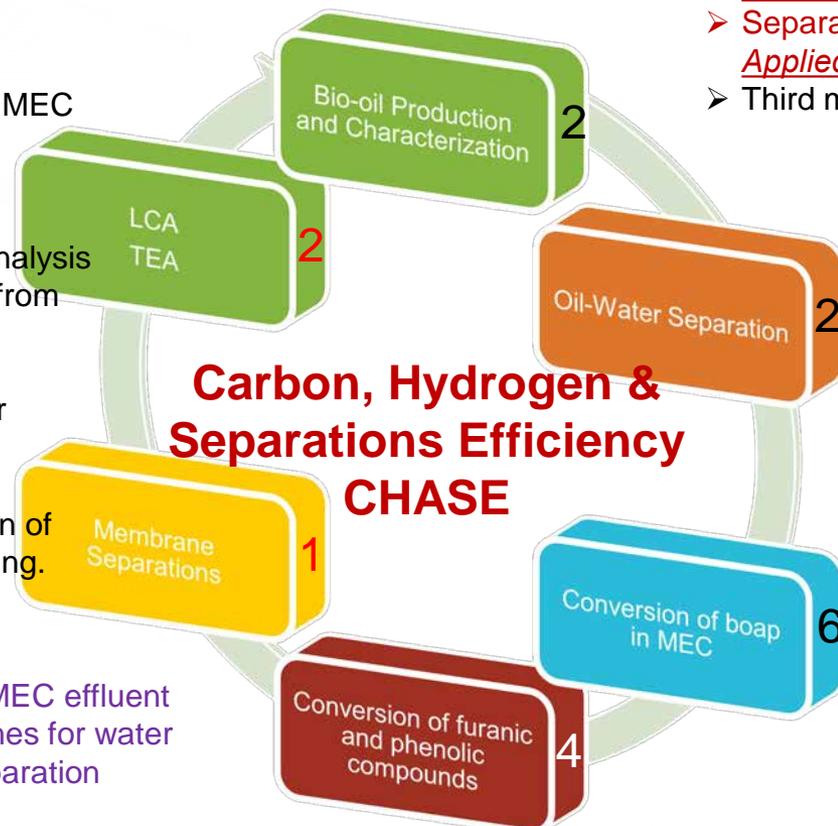
Target performance for application feasibility

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
- BOAP conversion – *Bior. Technol., 2015*
- 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
- Electroactive biofilm enrichment process,
- WTE conversion via biorefinery MEC integration

Carbon, Hydrogen & Separations Efficiency CHASE

- Conversion of phenolic and furanic compounds – *ES&T, 2015*
- Effect of continuous operation in MECs – *RSC Advances, 2016*
- Understand inhibition by parent compounds and intermediates -- *ES&T, 2016*
- Identification of intermediates from furans and phenolic compounds – *Water Res., 2017*
- + modeling manuscript

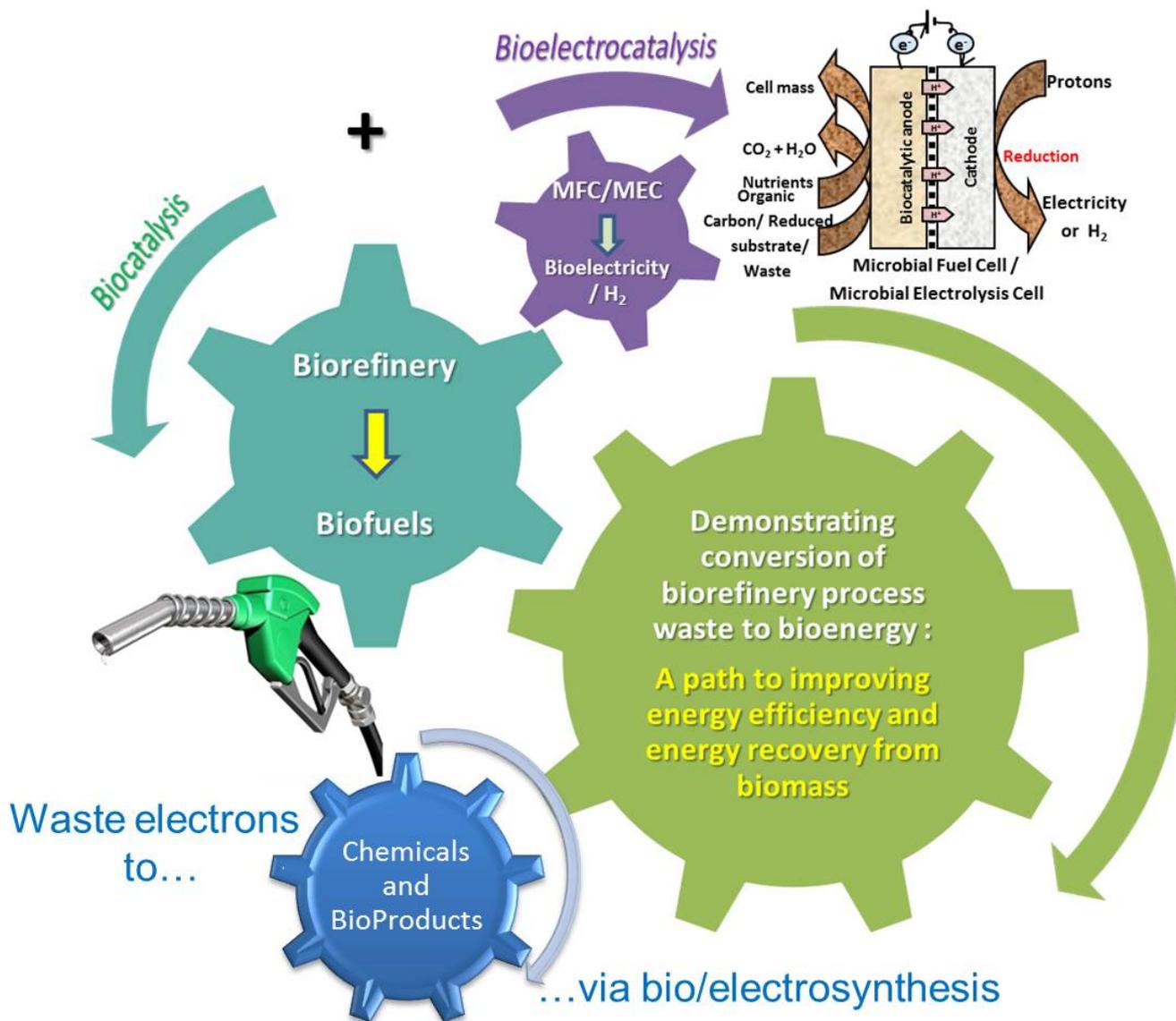
- Report: LCA analysis of MEC in comparison to steam reforming for hydrogen production
- Manuscript: Life cycle analysis of hydrogen production from biomass via microbial electrolysis (planned)
- TEA analysis of MEC for hydrogen production in biorefinery (planned)
- + one more - comparison of MEC with steam reforming.

- Separation of MEC effluent using membranes for water recycle, in preparation

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

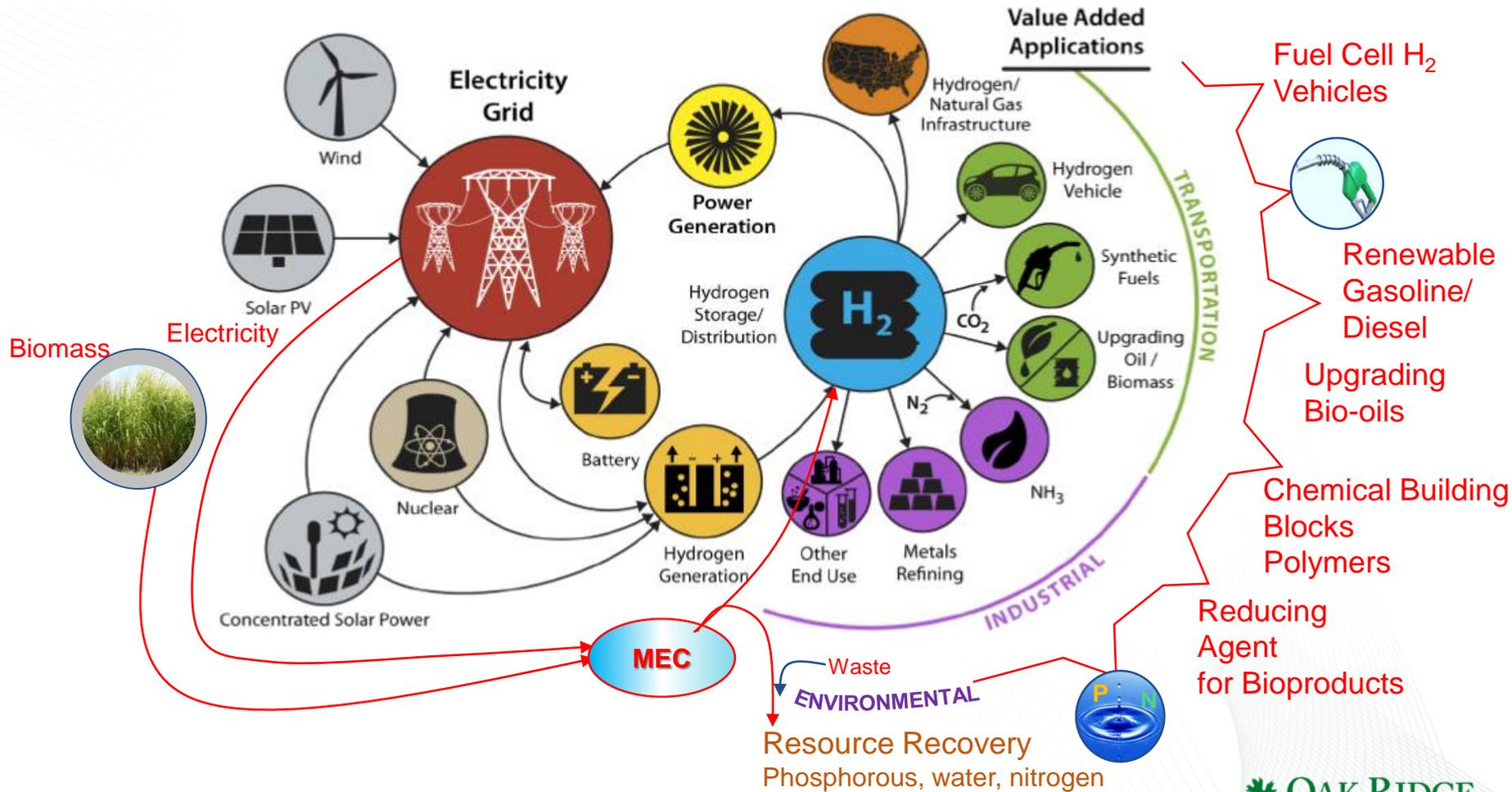
Efficiency: < \$ 150k/pub.

4.a Relevance



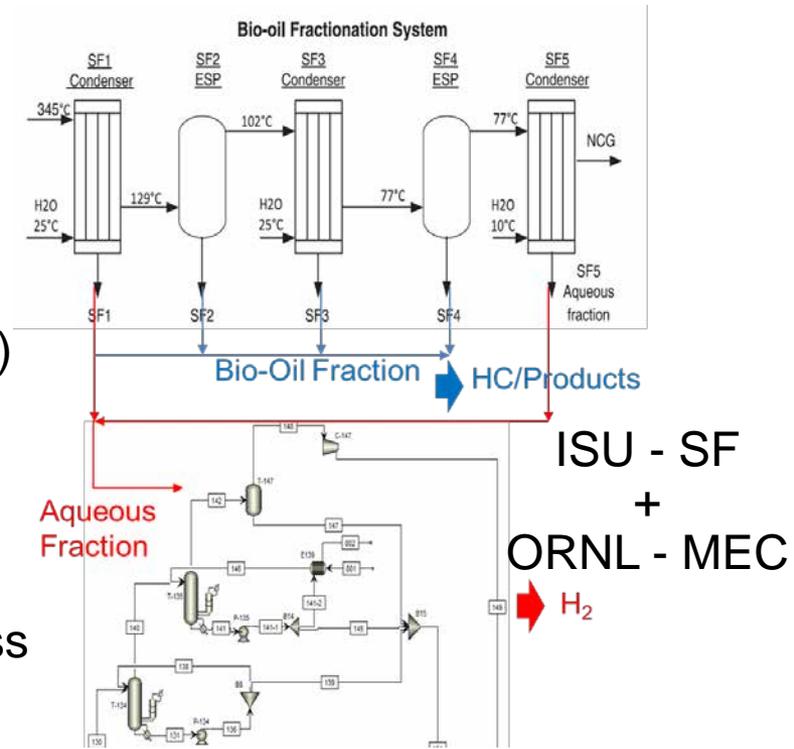
4.b Relevance

Integrating the biomass resource... into the bio-economy via H₂ carrier → has multiple benefits...

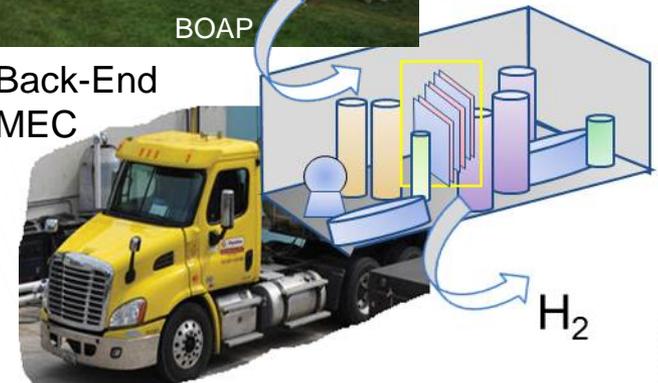


5.a Future Collaborations

- 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 H₂, bio-oil and bio-char.
- Industry
 - Collaboration on Integrated Biorefinery Optimization
 - Integration of MEC into thermochemical biorefinery



Back-End MEC



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 H₂, process recycle and TEA/LCA analysis.
- Accomplished development of an electroactive biocatalyst and MEC to convert boap to H₂ 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 H₂ 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:

Process scheme	Theoretical yield	Observed yield	Free energy change (for H ₂ -producing step)	Overall observed energy yield	Comments
1 Hypothetical H ₂ production	12				
2 Hexose to ethanol to H ₂ via autothermal reforming	10	9.5	-265 ^a kJ/mole	~83%	Prohibitive catalyst (Rh) cost ¹⁰
3 Dark-light fermentation: Glucose → acetate → H ₂	8	7.1	+164 kJ/mole	59.2%	Limited by light penetration and cost ³⁹
4 Methanogenesis-steam reforming	8	6.0	+261 kJ/mole	50.5%	Mature technology components ^{9,40}
5 MEC	12	8.2	+104.6 kJ/mol	64%	Nascent technology ^{3,30}

^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

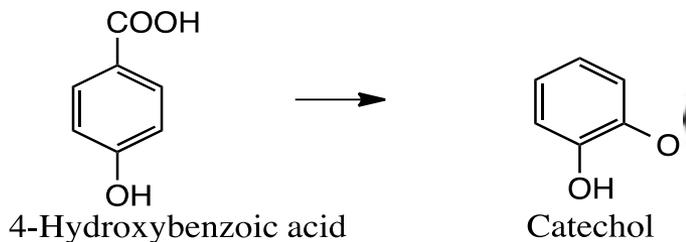
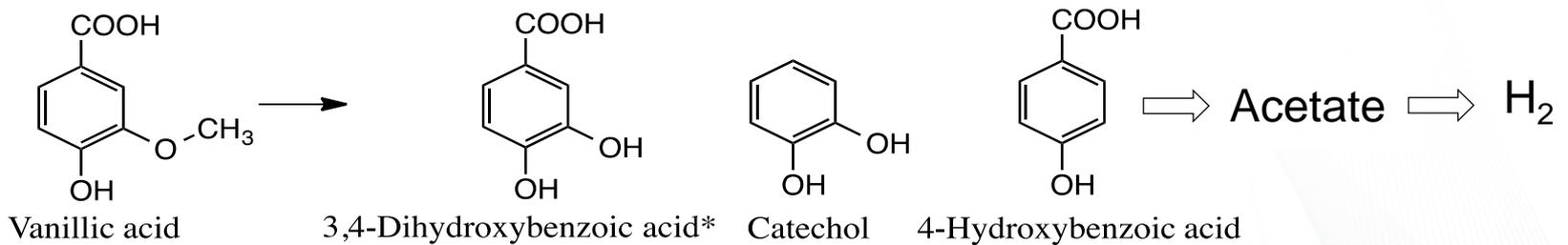
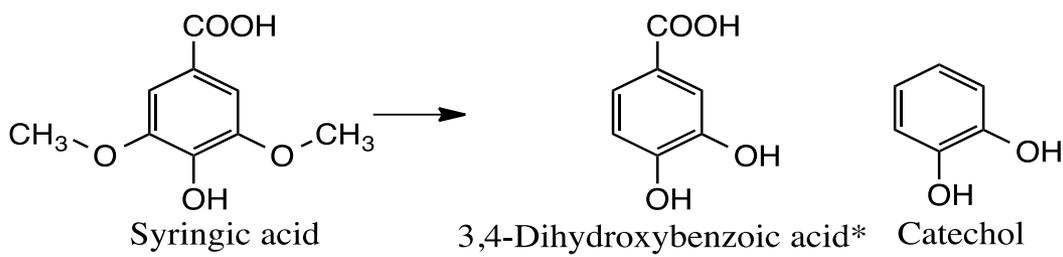
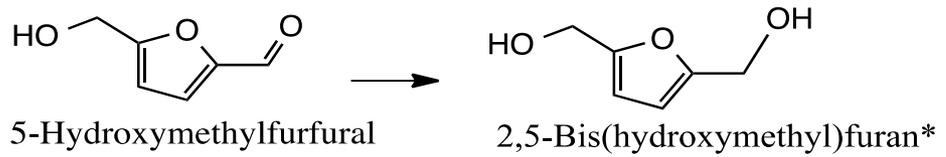
- Contributions to BETO MYPP goals:
 - Developed strategy for improving carbon and hydrogen conversion efficiency and demonstrated feasibility of conversion using switchgrass as feedstock (Barriers Tt-M, Tt-N)
 - Initiated investigations into separations technology for extracting acidic compounds from boap 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.

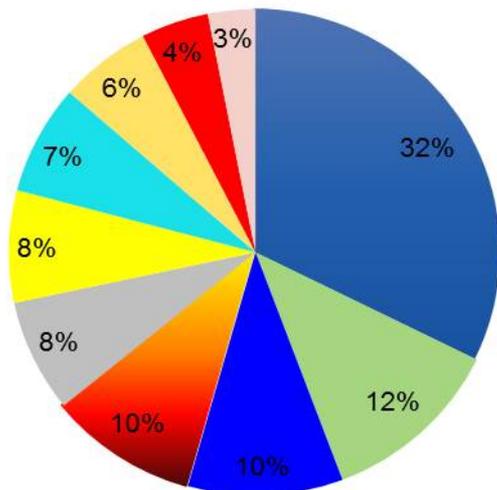
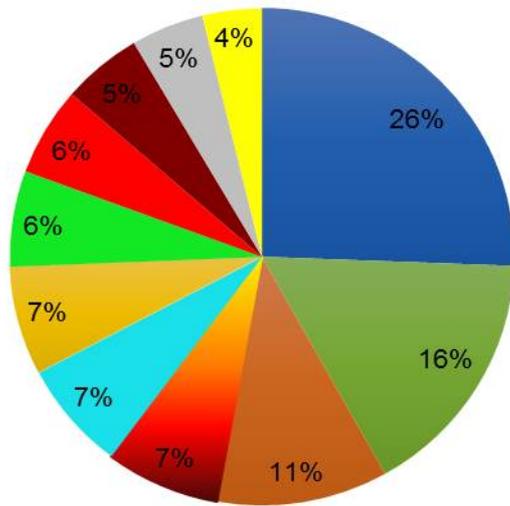
3.j – Technical Achievements

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.

3.c. Electroactive Biofilm Development via Targeted Evolution

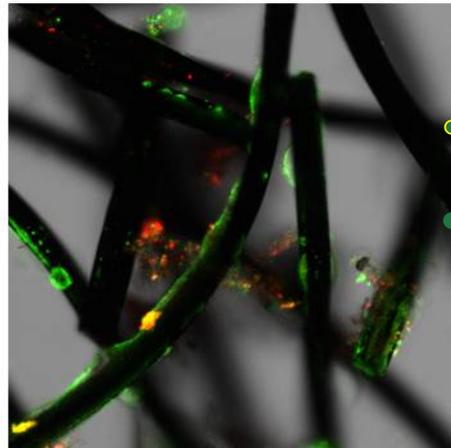


- Other
- Enterococcaceae
- Rhodocyclaceae
- **Geobacteraceae**
- Lachnospiraceae
- Clostridiaceae
- Porphyromonadaceae
- Sphingobacteriaceae
- Leuconostocaceae
- Synergistaceae
- Flavobacteriaceae

- 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

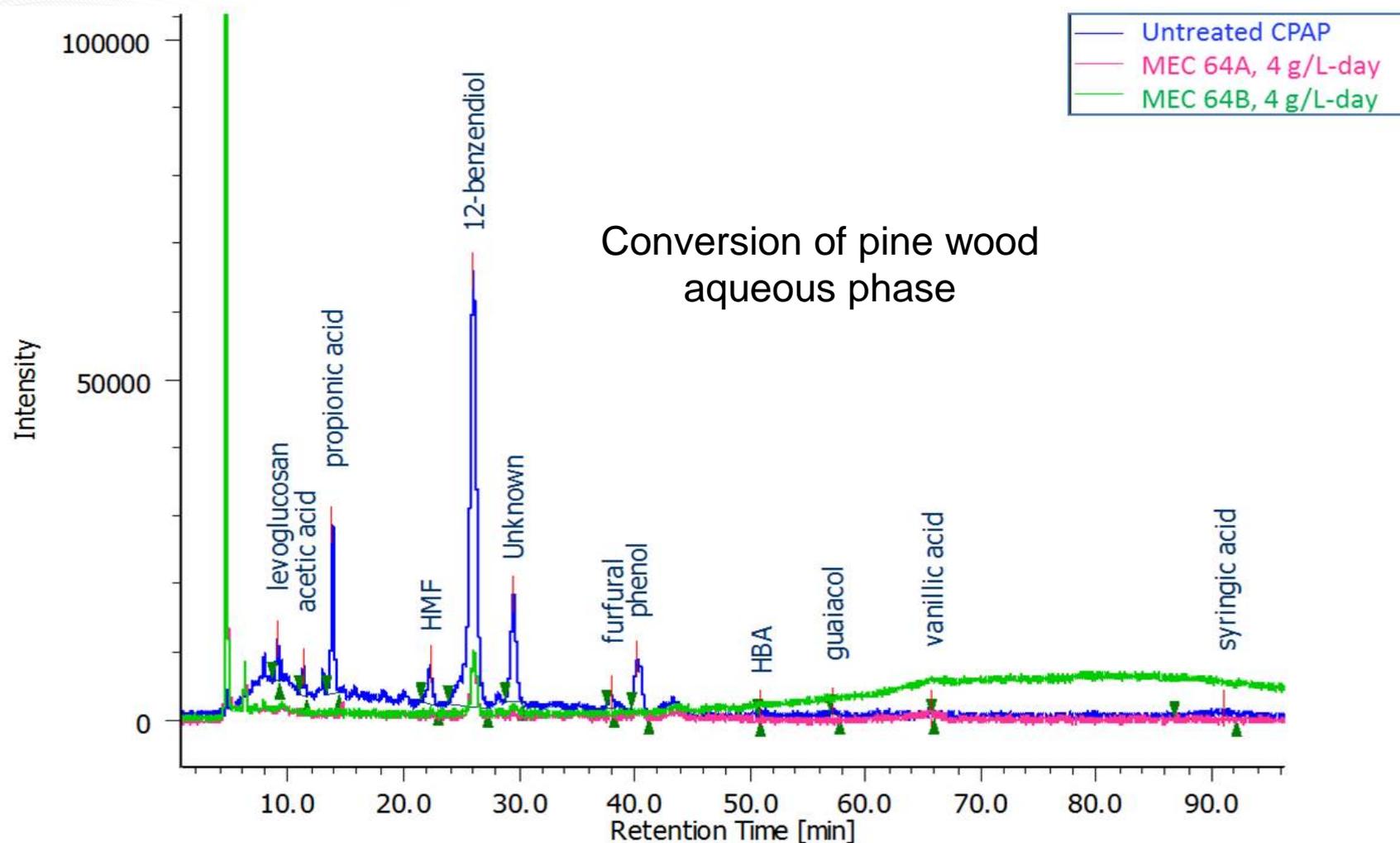
7-10% *Geobacter*

Capable of tolerating furanic and phenolic compounds



3.f – Technical Achievements

Conversion of Pine Wood Aqueous Phase



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.

