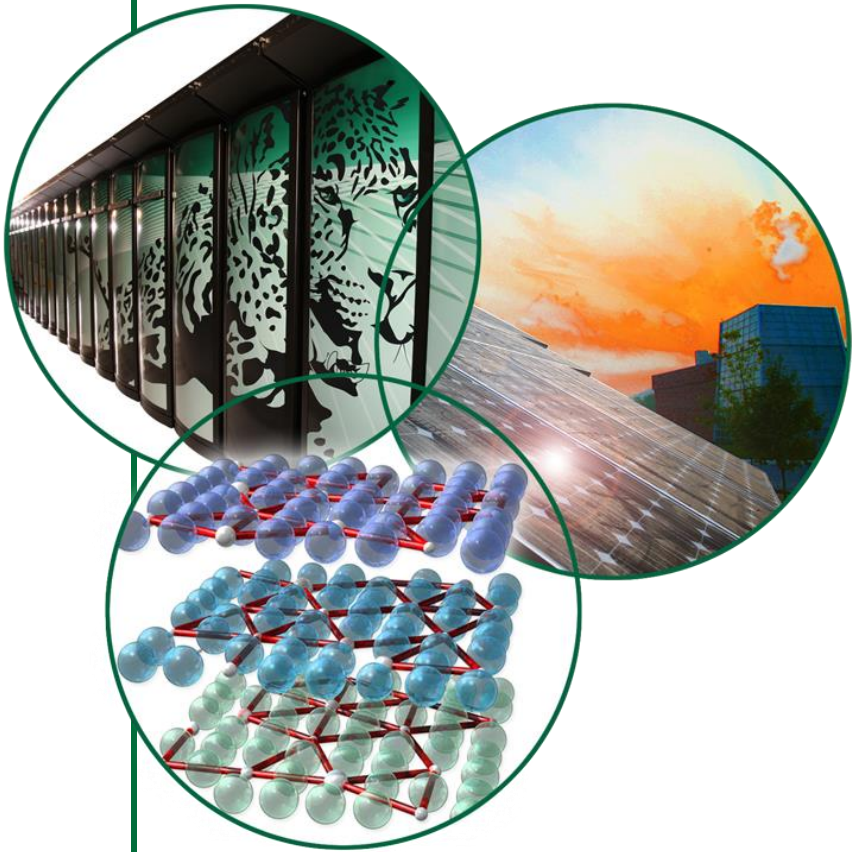
DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Renewable Hydrogen Production from Biomass Pyrolysis Aqueous Phase



March 27, 2015

Thermochem Conversion Review

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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 use of fossil fuels and lower lifecycle greenhouse gas emissions.
  - Investigate separation processes to enable the hydrogen production process.

Quad Chart Overview

Timeline

- FOA award – CHASE project
- 10/1/2013
- 9/30/2016
- 40% complete

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	0.0	$1,697	$446,349	$1,686,954
Project Cost Share (Comp.)*	0.0 **By partner:** GIT UTK FCE Pall Omni	0.0 --------	$174,426 (28.1%) --------- $77,376 $82,257 - $13,794 -	$360,424 ---------- $122,411 $205,193 $4,940 $17,080 $10,800

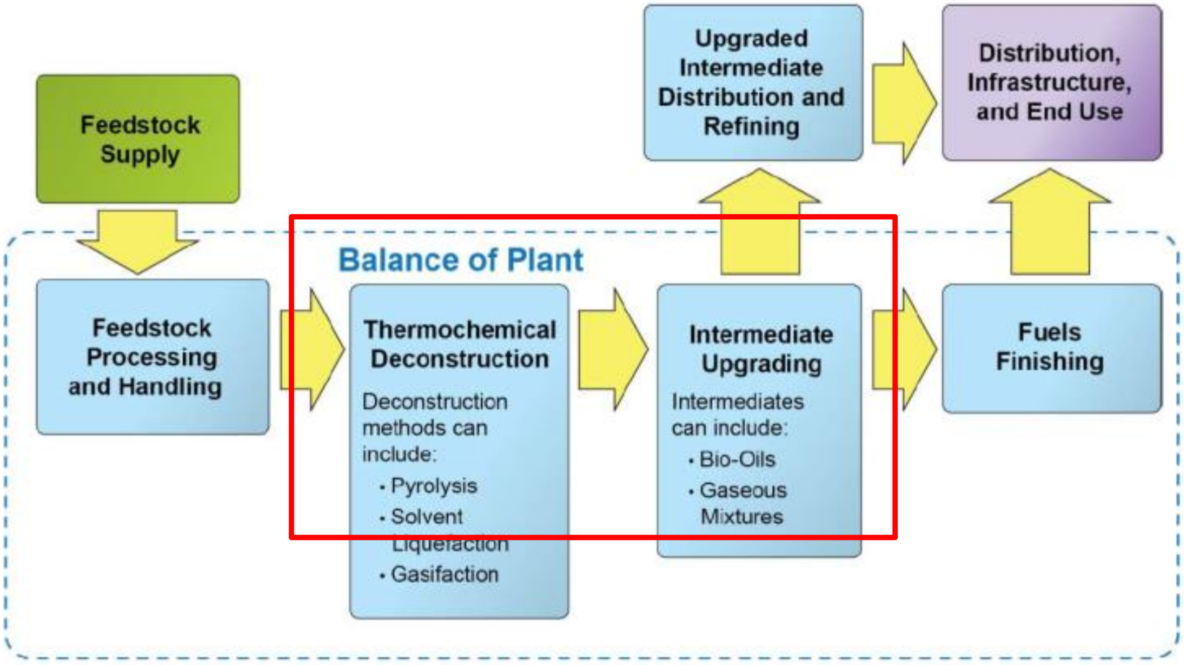
Barriers

- Barriers addressed
  - Tt-M. Hydrogen Production
  - Tt-N. Aqueous Phase Utilization and Wastewater Treatment
  - Tt-O. Separations Efficiency
- Additional barriers addressed
  - Tt-H. Bio-oil Intermediate Stabilization

Partners

- Partners (FY13-14)
  - GIT: Georgia Institute of Technology (40.3%)
  - University of Tennessee, Knoxville (31.3%)
  - FuelCellEtc. Inc. (< 1%)
  - Pall Corporation (6.2%)
  - OmniTech International (< 2%)

1 - Project Overview


Feedstock Supply

Feedstock Processing and Handling

Balance of Plant

Thermochemical Deconstruction

Deconstruction methods can include:
- Pyrolysis
- Solvent Liquefaction
- Gasifaction

Intermediate Upgrading

Intermediates can include:
- Bio-Oils
- Gaseous Mixtures

Upgraded Intermediate Distribution and Refining

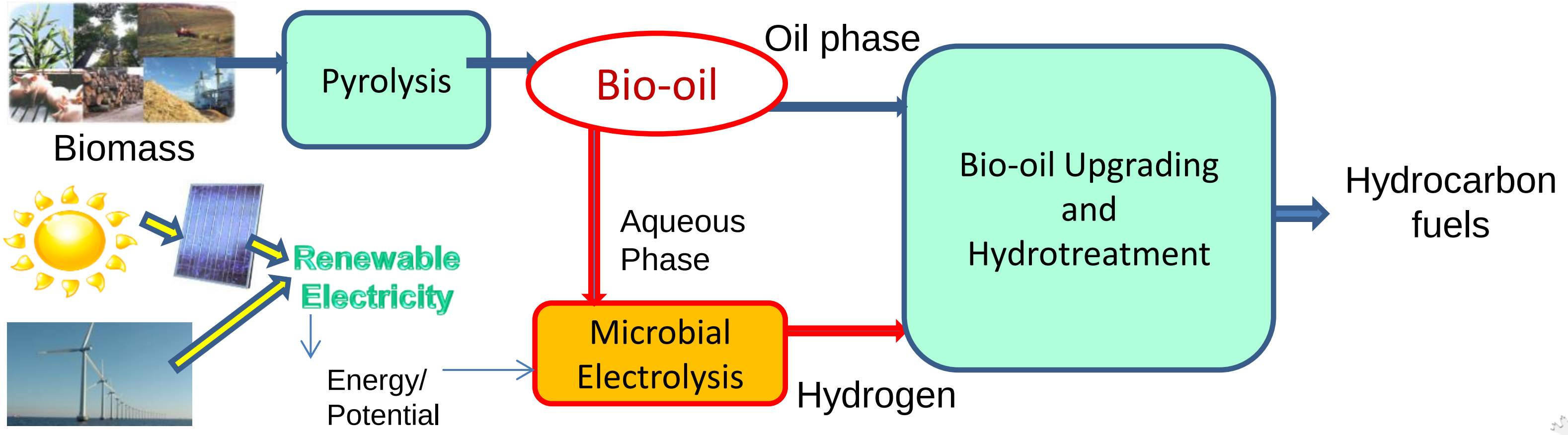
Fuels Finishing

Distribution, Infrastructure, and End Use

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.


Biomass

Pyrolysis

Bio-oil

Oil phase

Aqueous Phase

Bio-oil Upgrading and Hydrotreatment

Hydrocarbon fuels

Renewable Electricity

Energy/ Potential

Microbial Electrolysis

Hydrogen

2 – Approach (Technical)

- Produce hydrogen from biooil aqueous phase.organics using MEC
- Investigate separation methods to generate feed for MEC and downstream separations to enable water/biocatalyst recycle
- **Critical success factors**
  - Developing biocatalysts capable of utilizing biooil
  - Productivity of H_2
  - Sufficient yield of H_2 to upgrade bio-oil
- **Challenges**
  - Overcoming toxicity of biooil substrates (phenolics, furan aldehydes, etc.) and enabling complete utilization/removal of acidic and polar compounds.
  - Product specificity (to avoid methane production in bioanode)
  - Minimizing bioelectrochemical losses and achieving high conversion **efficiency**
  - Developing a continuous process

Go/No-Go criteria:

12 Mo. 80% conversion at 2 g/L-day in MEC

30 Mo. 60% H_2 production efficiency based on organic acids

Metrics:

a) H_2 production rate >5 L/L-day

b) Coulombic efficiency > 50%

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

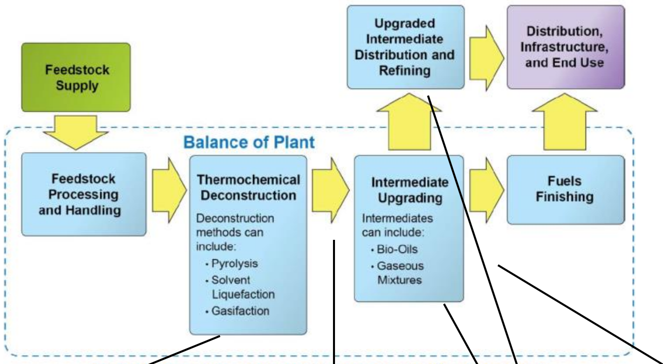


Figure 2-25: Thermochemical conversion process steps for biomass to biofuels

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)

Membrane separations Biocatalyst recovery and recycle (ORNL)

Life cycle analysis Techno-economic Analysis (Omni)

Develop oil-water Separation methods (GIT)

Microbial electrolysis of furanic and phenolic Substrates (GIT)

Membrane process modules, supplies (Pall)

Electrolysis cell materials (FuelCellEtc)

Industry partners

3.0 – Technical Accomplishments/ Progress/Results

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

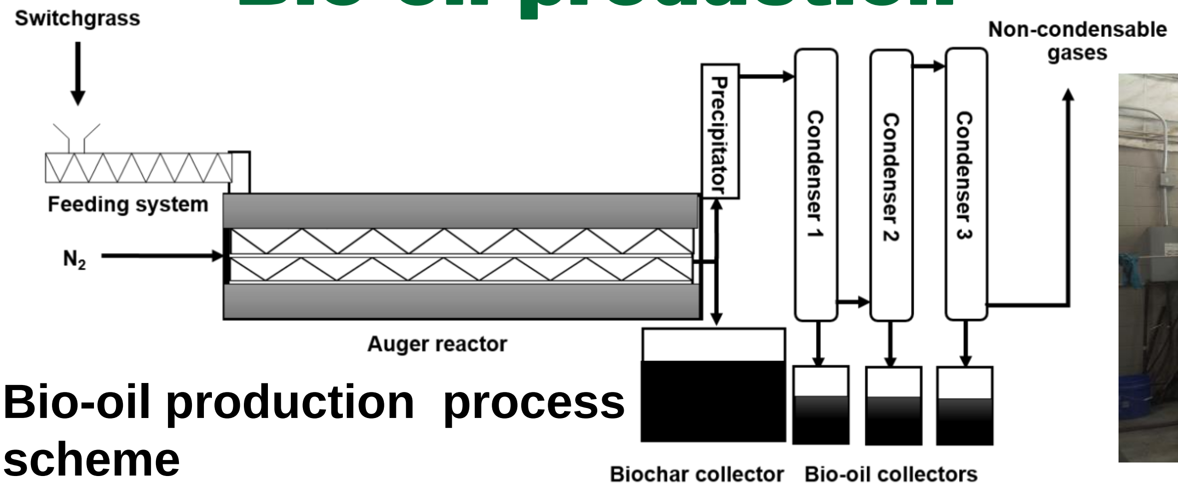
- Progress:
  - Development of electroactive biocatalyst via directed evolution (25 generations)
  - Demonstration of hydrogen production from bio-oil aqueous phase (boap) (5 L/L-day)
  - Demonstrating conversion of phenolic compounds in bioanode (study 5 model compounds)
  - Development of separation methods (electroseparations, membrane separations)

- Milestones completed:

1. Complete set-up of MEC and separations experiments (12/2013)
2. Bio-oil production from switchgrass via pyrolysis (03/2014)
3. Initiate bench-scale membrane separations using Pall system (06/2014)
4. Demonstrate 80% conversion of key boap acids at a rate of 2g/L-day (09/2014). First Go/No-go criteria.
5. Demonstrate the anodic conversion of phenolic acids (12/2014)

- Most important accomplishment:
  - Achieve > 80% conversion of acetic acid and boap at the rate of 2 g/L-day in bioanode (12 Mo. Go/No-Go criteria)

3.a – Technical Achievements: Bio-oil production



Bio-oil production process scheme

Pilot auger pyrolysis reactor at UTK Center for Renewable Carbon

- Feedstock: switchgrass
- Particle size: less than 2mm
- Water content of switchgrass: 7-8 wt%.
- Feeding rate: 10kg/hr
- Reaction temperature: 500°C
- Bio-oil: combined by three condensers
- 1st batch bio-oil: about 10 kg, produced on Jan. 2014
- 2nd batch bio-oil: about 11 kg, produced on Sept. 2014

Products from switchgrass fast pyrolysis

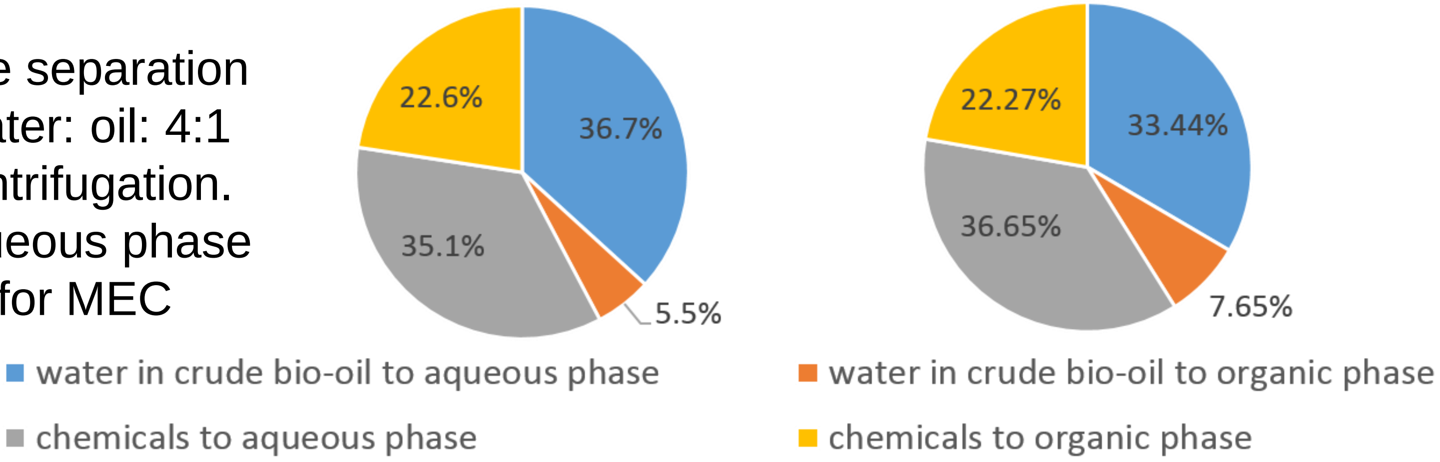
Bio-oil production	Bio-oil yield (wt%)	Bio-char yield (wt%)	Non-condensable gas yield (wt%)
1st batch	50	29	21
2nd batch	54	29	17

Completion of Milestone 2: Production of bio-oil from switchgrass

Philip Ye, P. Kim, Shoujie Ren

3.b – Technical Achievements Bio-oil and aqueous phase characterization

Aqueous phase separation after adding water: oil: 4:1 followed by centrifugation. This bio-oil aqueous phase (boap) is used for MEC studies.



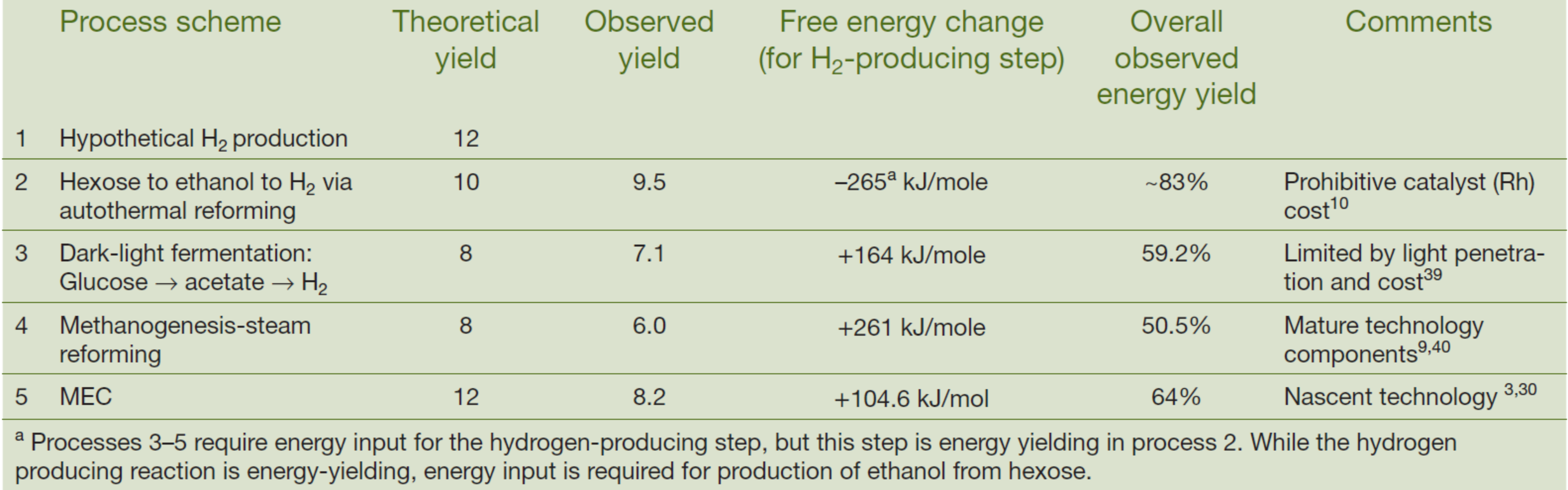
Properties	**Crude bio-oil**	**Aqueous phase**
Water content (wt%)	42.3	91.7
Total solid (wt%)	1.7	Not detected
pH value	2.84	3.02
Density (g/ml)	1.13	1.01
Ash (wt%)	0.31	0.085
Viscosity at 40 °C (cSt)	6.5	0.75
TAN, mg KOH/g	137.3	30.1

Bio-oil and aqueous phase were also analyzed by HPLC-photodiode array detector and GC-MS.

A large fraction of the compounds in bio-oil partition into aqueous phase

3.c - Hydrogen Production: Comparison with Existing Technologies

- Bio-oil steam reforming using Pt-Re or metal catalysts:
  - Low 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:



	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]

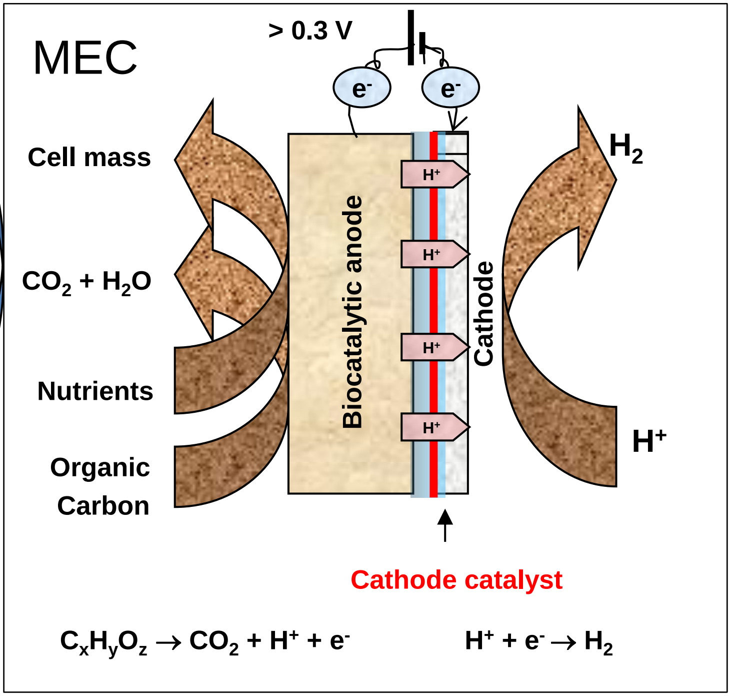
[a] Processes 3–5 require energy input for the hydrogen-producing step, but this step is energy yielding in process 2. While the hydrogen producing reaction is energy-yielding, energy input is required for production of ethanol from hexose.

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

Borole, A. P. (2011). Biofuels, Bioproducts & Biorefining "Improving energy efficiency and enabling water recycle in biorefineries using bioelectrochemical cells." **5**(1): 28-36.

3.d - Microbial Electrolysis

- Pyrolysis derived aqueous phase
  - Potential for loss of carbon
  - Emulsifies with oil phase
  - Makes bio-oil unstable
  - Makes bio-oil corrosive
- Microbial electrolysis
  - Conversion of biooil aqueous phase (boap) organics to hydrogen
  - Anode: Conversion of degradable organics to electrons, protons and CO_2
  - Cathode: Proton reduction to hydrogen at applied potential of 0.3-1V.
  - Uses electroactive biofilms tolerant to inhibitory and toxic molecules in biooil aqueous phase (furfural, hydroxymethylfurfural, phenolics, etc.)

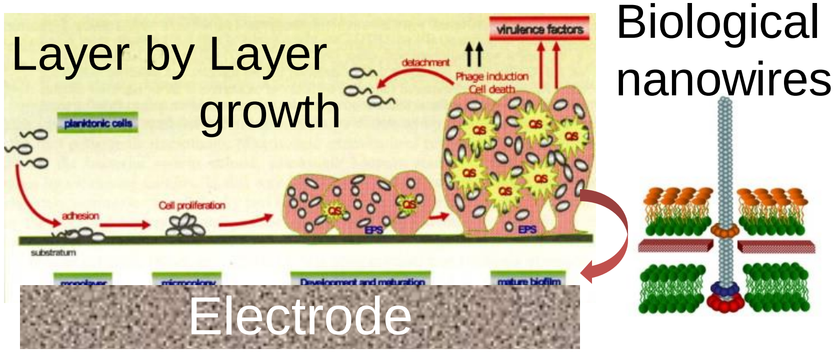


<u>Pathway</u>: Bio-oil Aqueous Phase (boap)
→ electrons + protons (anode)
→ H_2 (cathode)

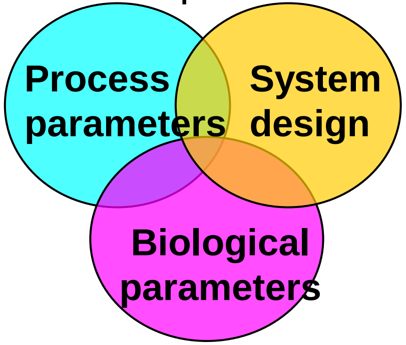
Borole, A. P., et.al., 2009, <u>Biotechnol for Biofuels</u>., *Controlling accumulation of fermentation inhibitors in biorefinery process water using Microbial Fuel Cells,* 2, 1, 7.
Borole, A. P., et al., 2011, <u>Energy Environ. Sci.,</u> *Electroactive biofilms: Current status and future research needs* <u>**4**: 4813-4834.</u>

3.e – Technical Achievements
Anode Biocatalyst Development via Targeted Evolution

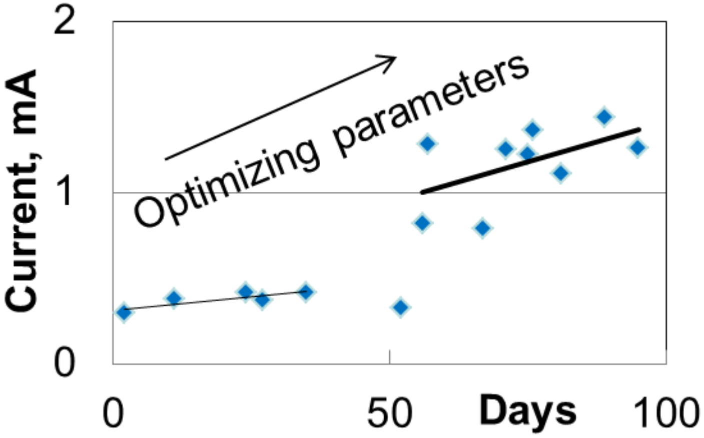
- Growth of anode biocatalyst: Electroactive biofilms
- Biocatalyst density
- Population diversity
- Improving current/ electron production using **boap** via **Targeted Evolution** of biofilms



Electroactive Biofilm Optimization

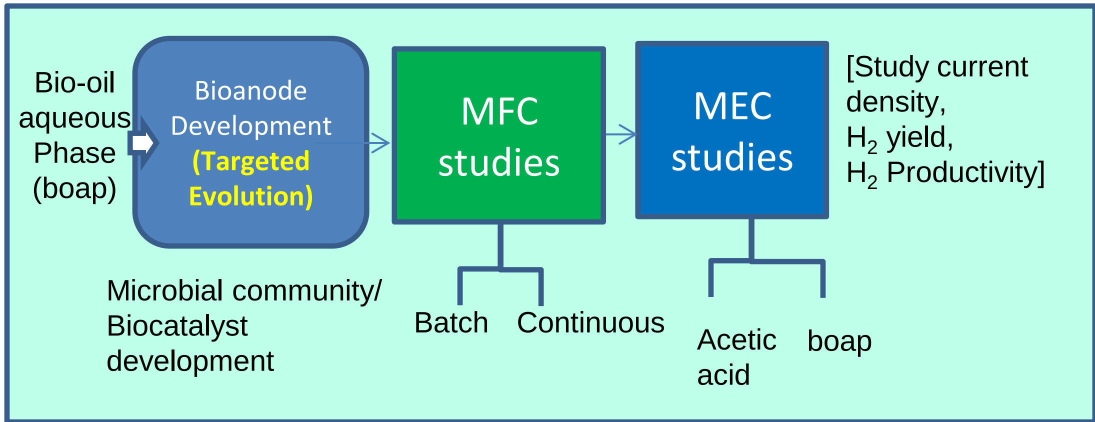


In biofilms



Borole, *A. P.*, *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., 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., Bioresour. Technol. ***2011, 102, 5098.***
Borole, A. P., et al., Biochem. Eng. J. ***2009, 48, 71.***



Bio-oil aqueous Phase (boap)

Bioanode Development **(Targeted Evolution)**

MFC studies

MEC studies

[Study current density, H_2 yield, H_2 Productivity]

Microbial community/ Biocatalyst development

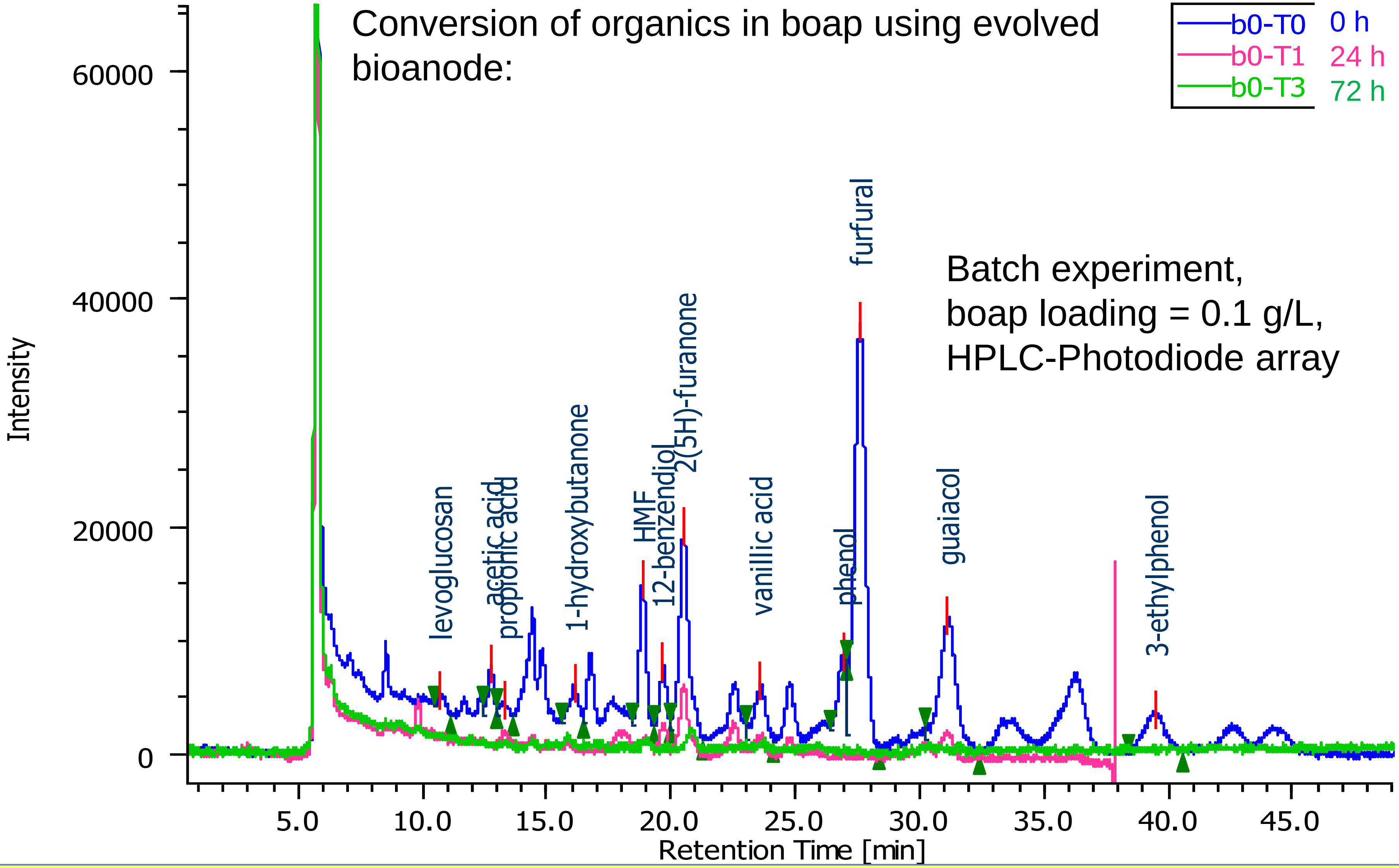
Batch

Continuous

Acetic acid

boap

3.f – Technical Achievements
Conversion of Bio-oil Aqueous Phase

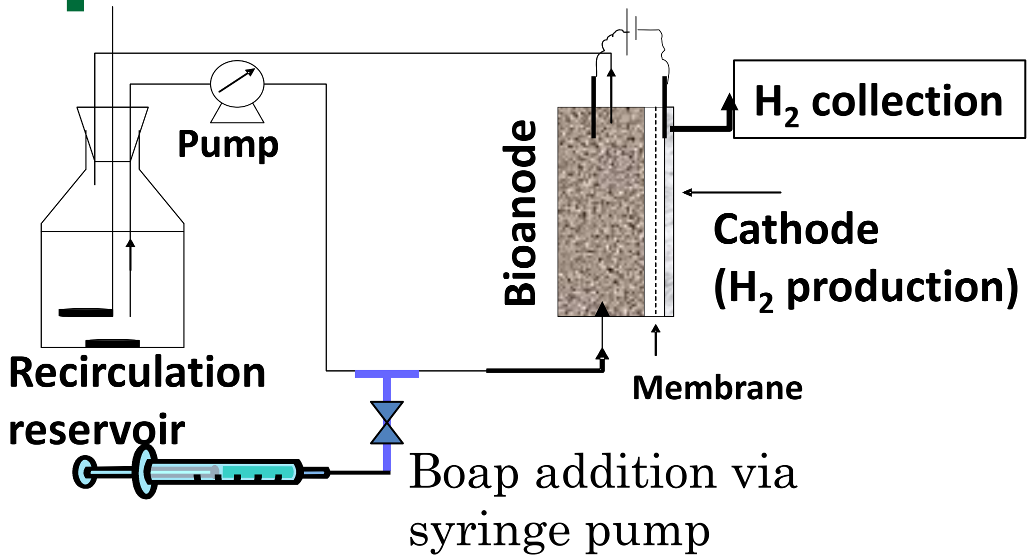


Conversion of organics in boap using evolved bioanode:

Batch experiment,
boap loading = 0.1 g/L,
HPLC-Photodiode array

Successful development of anode biocatalyst for conversion of bio-oil aqueous phase, including removal of acetic acid and phenolic acids.

3.g – Technical Achievements: MEC Operation and Performance


Pump

Bioanode

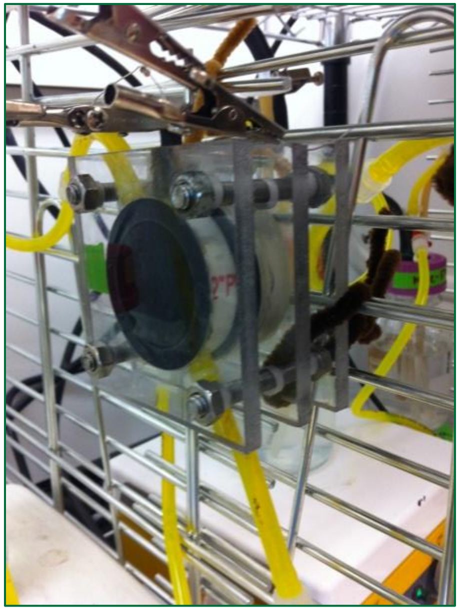
H_2 collection

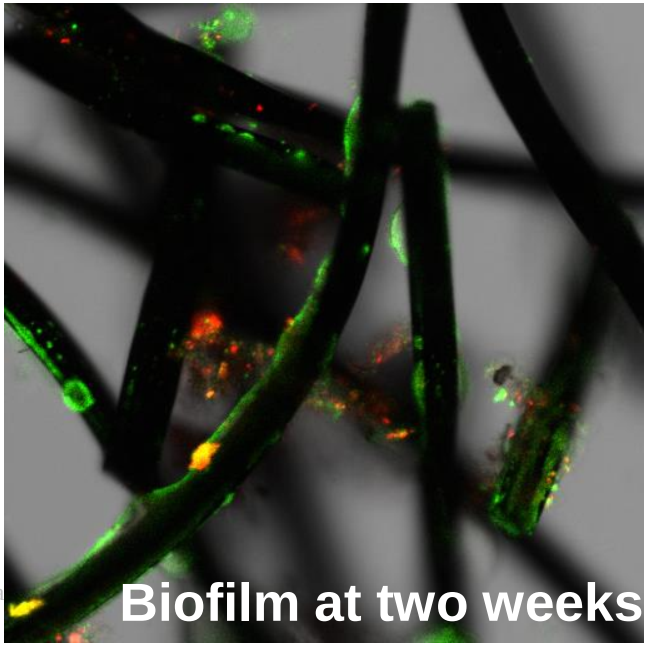
Cathode
(H_2 production)

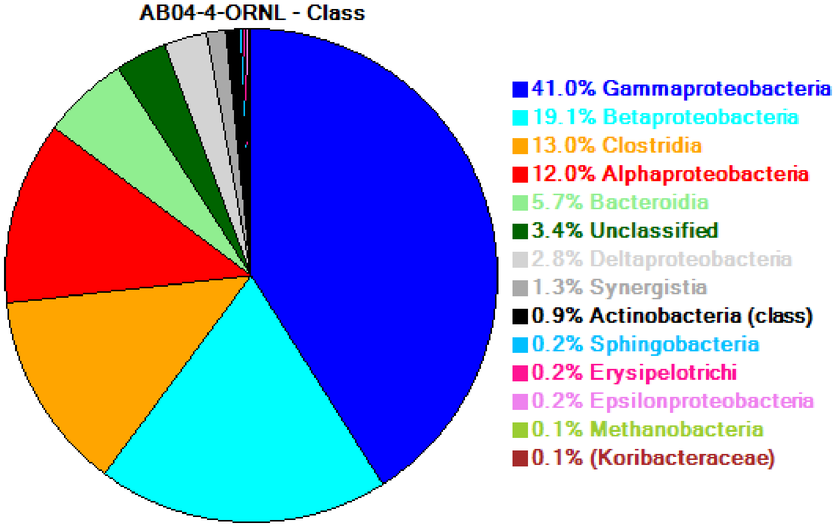
Membrane

Recirculation reservoir

Boap addition via syringe pump



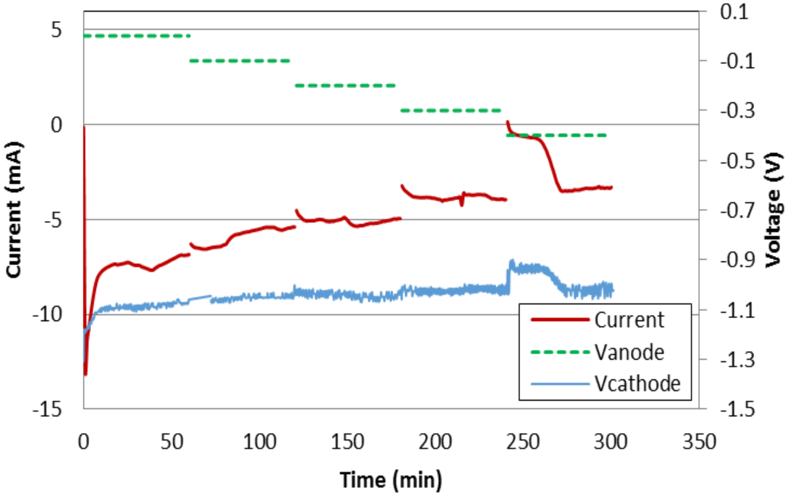




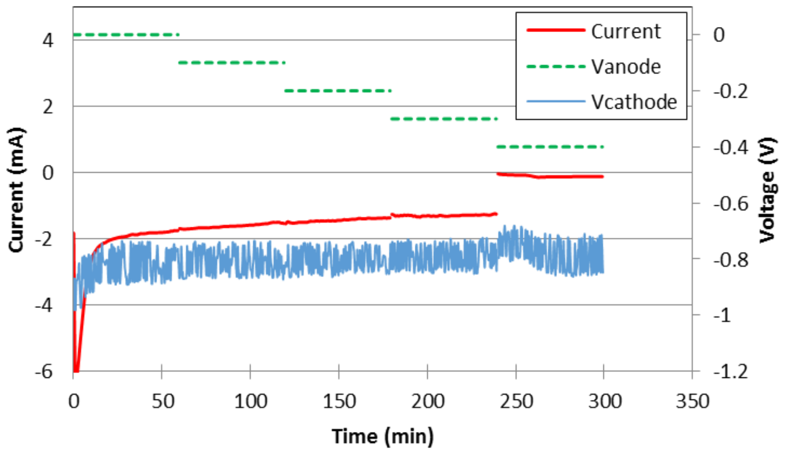
Biofilm at two weeks ***showing initiation of biofilm growth***

3.h – Technical Achievements: Conversion of Acetic Acid and Boap

- Acetic acid conversion in bioanode
  - Continuous addition experiment – 2 g/L-day
    - >80% conversion with > 4 mA current production
    - 0.9 L H_2/L-anode per day



- Boap conversion in bioanode
  - Batch experiment – 1 g/L boap
    - Conversion rate > 5 g/L-anode per day
    - 82.7% conversion in 24 hours
  - Continuous feeding – 2 g/L-day
    - Current production at 1.5 mA ~ 30% conversion

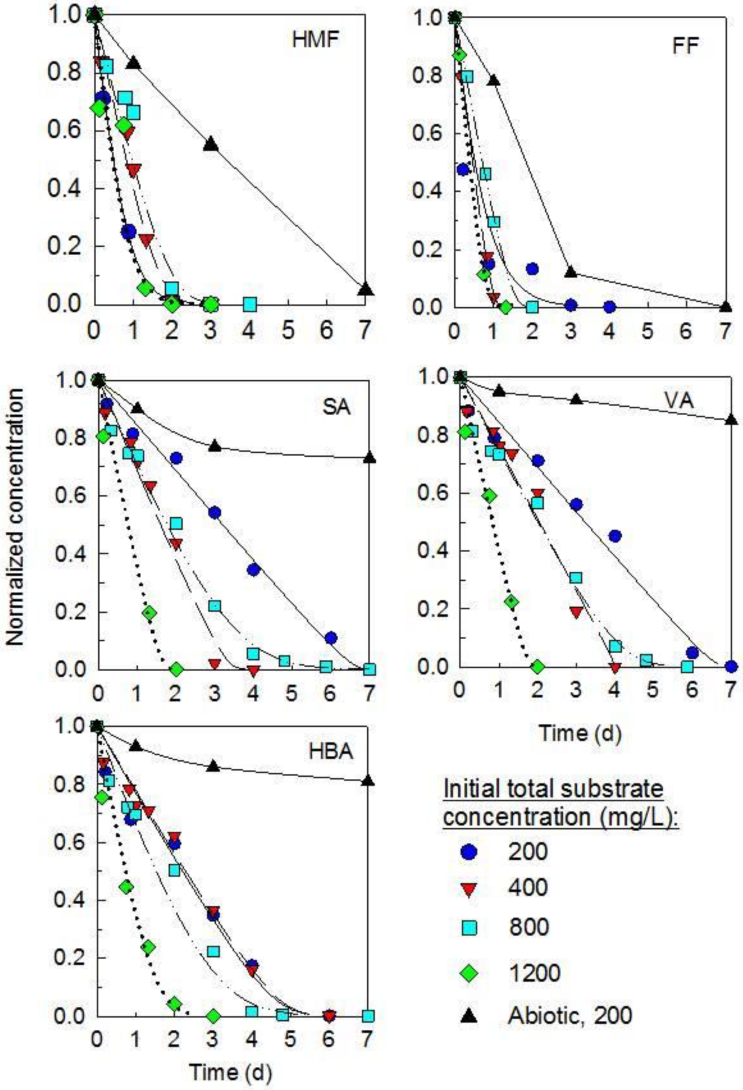


Alex Lewis, UTK

Completed Milestone 4: Demonstrated conversion of major acid component of boap at 2 g/L-day with 80% conversion (1st Go/No-go criteria).

3.i – Technical Achievements - Understanding Conversion of Furanic and Phenolic Compounds in Bioanode

- Investigate inhibition by phenolic compounds and furan aldehydes
- Model compounds:
  - Furfural (FF)
  - Hydroxymethylfurfural (HMF)
  - Syringic acid (SA)
  - Vanillic acid (VA)
  - 4-Hydroxybenzoic acid (HBA)
- Results:
  - No inhibition under 1200 mg/L
  - Served as substrates for anode microorganisms, but conversion limited by accumulation of intermediates.

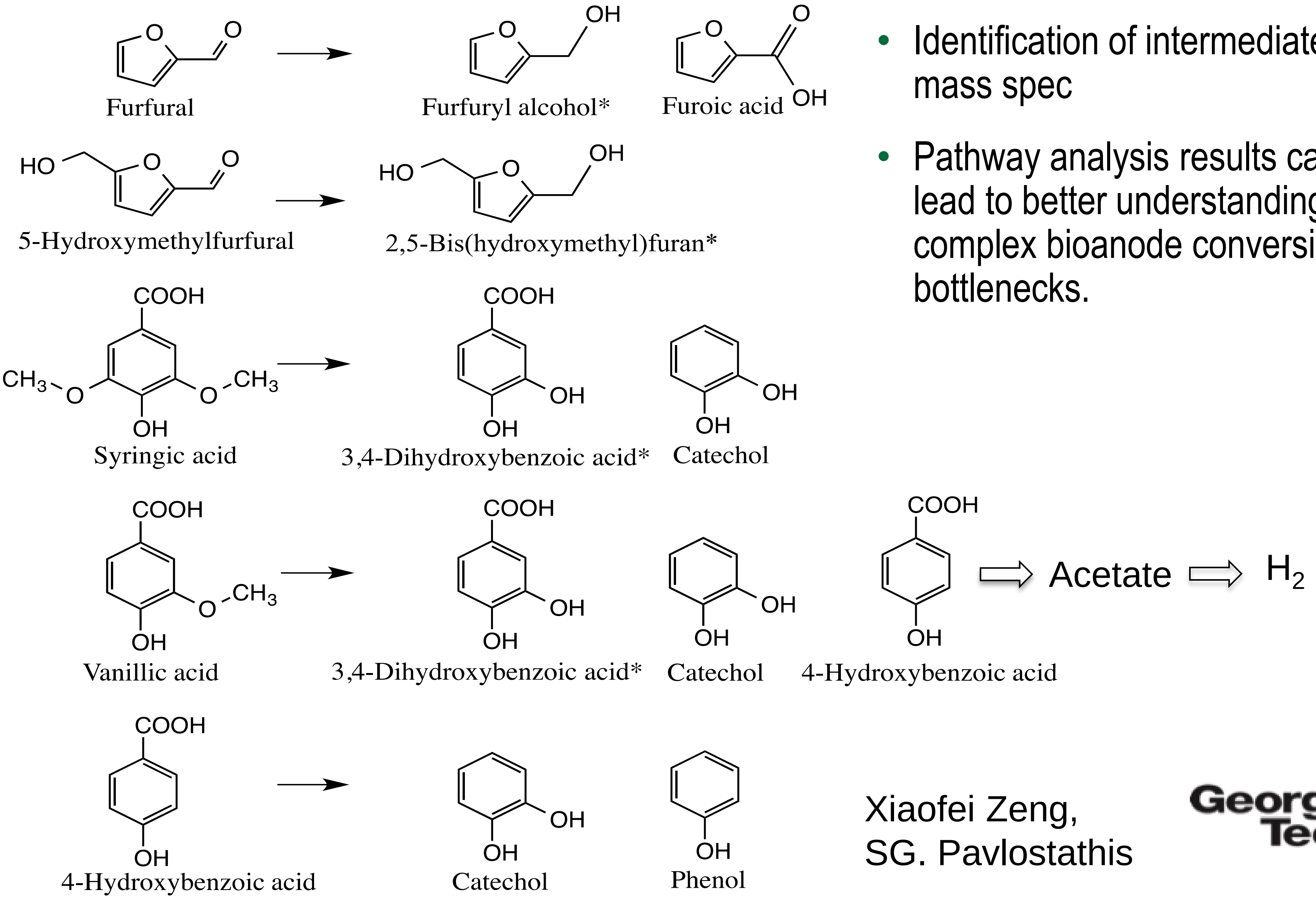


Completed Milestone 5: Demonstrate the anodic conversion of phenolic acids

Xiaofei Zeng, SG. Pavlostathis

3.j – Technical Achievements
Pathways for Conversion of Furanic and Phenolic Compounds in Bioanode

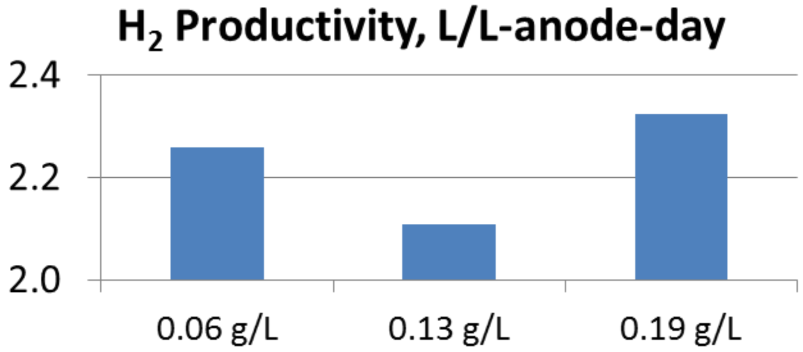
- Identification of intermediates by mass spec
- Pathway analysis results can lead to better understanding of complex bioanode conversion bottlenecks.



Xiaofei Zeng,
SG. Pavlostathis

3.k – Technical Achievements
Further development of MEC

- Production of hydrogen from boap in batch MEC studies.



	Targets for commercial consideration	Start of Project (2013)	February 2015
Hydrogen production rate	>15 L H_2/L-reactor-day FCTO FY20 target for MEC: 4 L/L-day from sugars	< 1 L-H_2/L-reactor-day	**> 2 L/L-day from bio-oil aqueous phase**
Anode current density, A/m^2	20	< 2 for boap	5 for boap
Anode CE	>90%	< 40% [7]	50-54%
Applied voltage	< 0.6 V	1.0 V [14]	0.9V
Cathode CE	>90% at 0.6V or less	80% with 1 V (using acetic acid)	82-96%

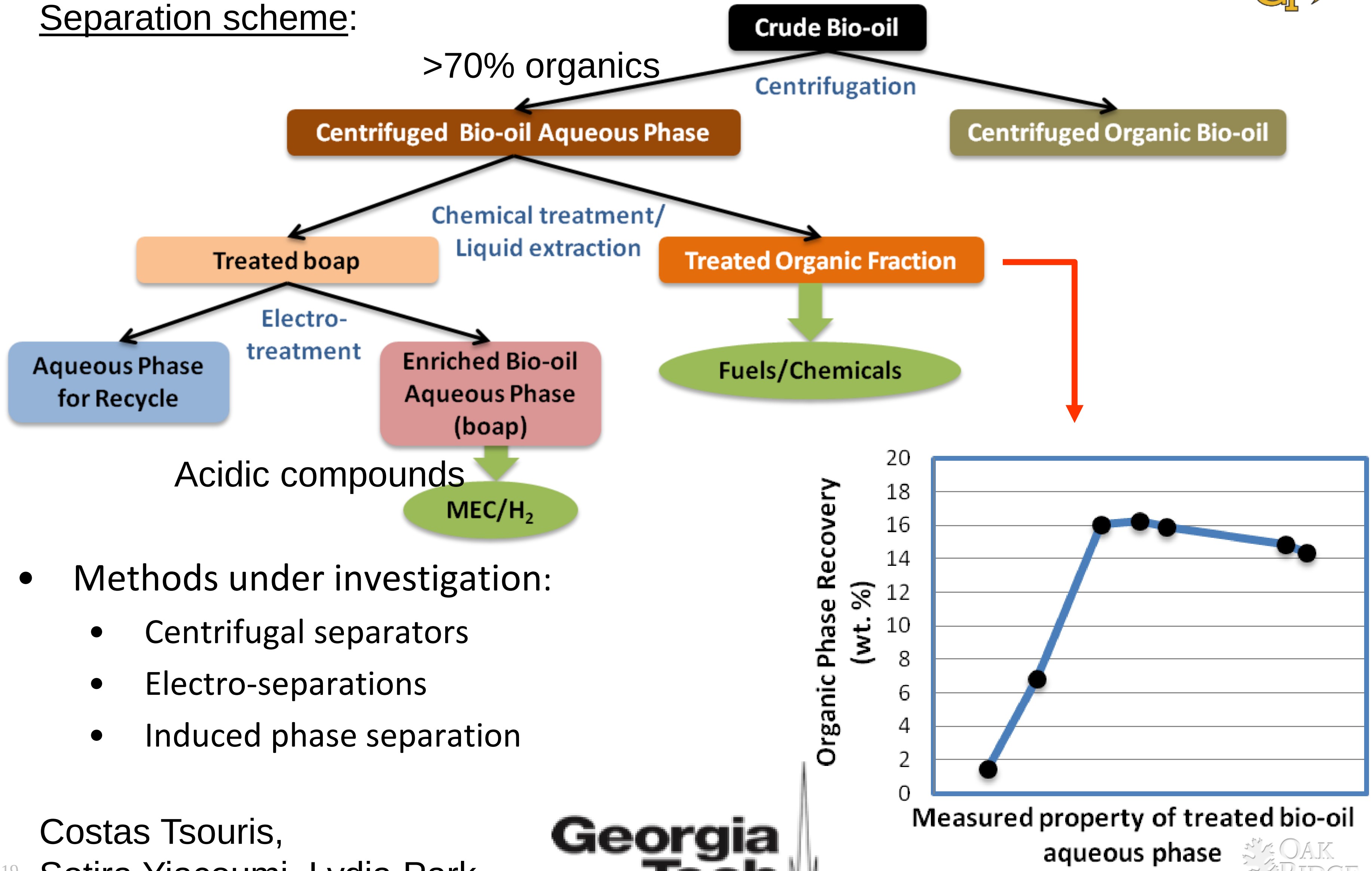
Performance and efficiency metrics for MEC development.

Demonstrated capability of MEC to produce H_2 from boap with high efficiency and productivity.

Alex Lewis, UTK

3.I – Technical Achievements Bio-oil separations

<u>Separation scheme</u>:

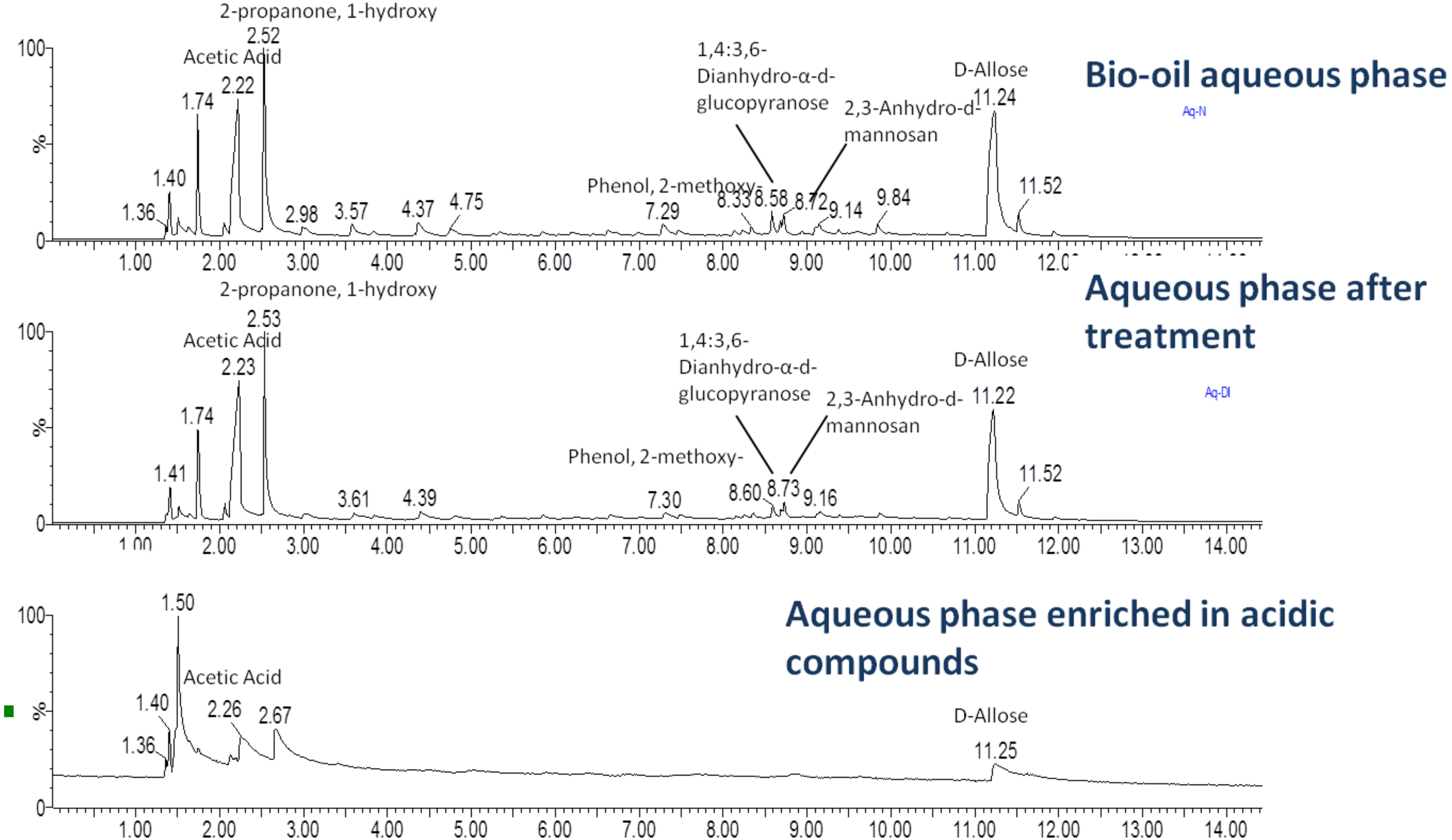


- Methods under investigation:
  - Centrifugal separators
  - Electro-separations
  - Induced phase separation

Costas Tsouris,
Sotira Yiacoumi, Lydia Park.

3.m – Technical Achievements
Bio-oil separations

- Induced separation of acidic compounds:



Bio-oil aqueous phase

Aqueous phase after treatment

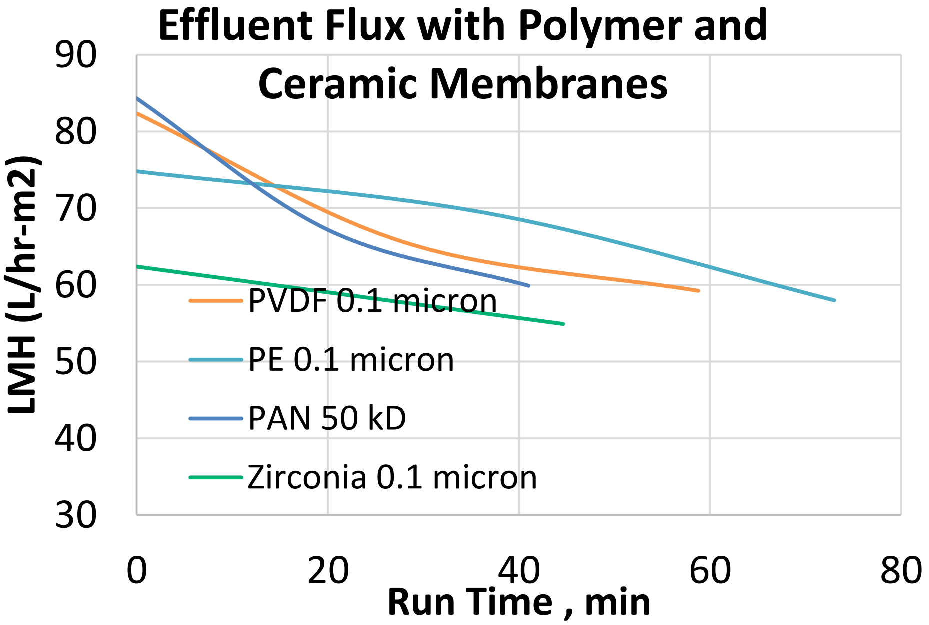
Aqueous phase enriched in acidic compounds

Results show potential of the methodology for separation of acidic compounds.

3.n – Technical Achievements

Membrane separation of MEC effluent for water and biocatalyst recycle

- Evaluate MEC cellular biomass effluent with polymer and ceramic membranes
- Characterize MEC effluent particle size distribution
- Establish long term flux stability over time
- Demonstrate 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

50th percentile was ~140 µm

Filtration Performance

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

Polymeric membranes better than ceramic zirconia.

Tim Mains, Ramesh Bhave, ORNL

Completed Milestone 3: Set-up and initiate membrane separations experiments. Results show potential of membranes to separate biocatalyst from MEC effluent.

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 (p. 2-70 of mypp)
  - Address knowledge gaps in chemical processes via biooil characterization, understanding and driving separation and conversion of key problem (acidic/polar) compounds (Tt-H, Tt-L).
- Invention disclosures
  - Hydrogen production from pyrolysis-derived aqueous phase (February 2015).
  - Separation of acidic molecules from biooil (in preparation)

4 – Relevance…

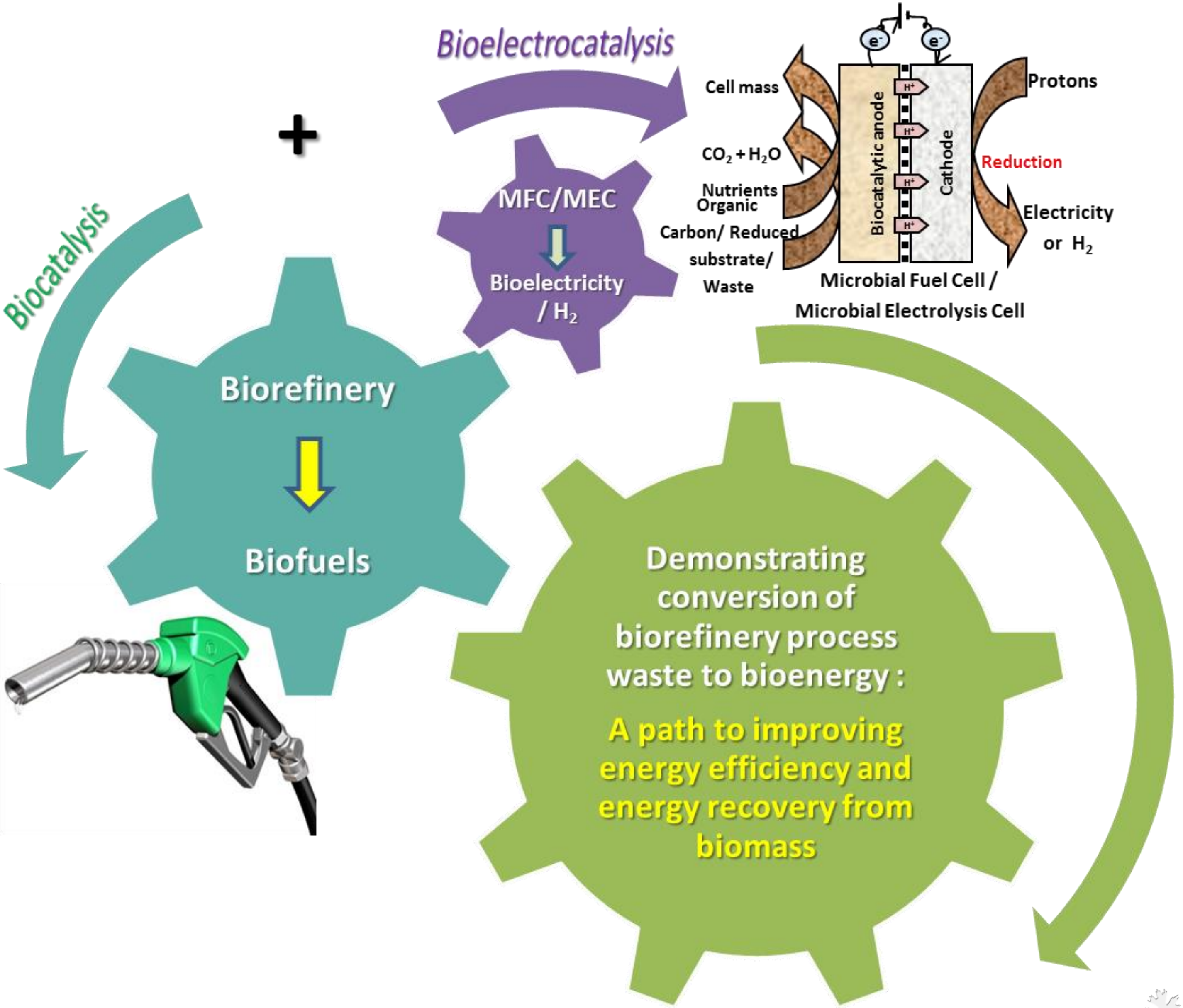
- Application in emerging bioenergy industry
  - Establish MEC as core technology for hydrogen production in thermochemical biooil upgrading
  - Potential application for producing hydrogen from fermentation effluent and lipid-extracted algae
- Support of strategic goals (Section 2.2.2.1 of mypp)
  - 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.

5 – Future Work

- Identify limitations to boap conversion and hydrogen production in MEC via impedance spectroscopy, biofilm diversity analysis and detailed substrate/product characterization
- Increase biocatalyst density to improve H_2 productivity
- Improve substrate conversion in continuous process to improve metrics of hydrogen production (C.2.DL.2, C.1.GN.2)
    - Current density > 10 A/m^2
    - Anode Coulombic efficiency > 60%, 90%+ conversion of major acid (C.1.DL.1)
    - Hydrogen yield > 60%
    - H_2 rate of production > 5 L/L-day (TRL 3, technical feasibility of MEC)
- Develop electroseparation technology for oil-water separation (B.2.ML.1)
- Perform LCA analysis of MEC process (F.1.ML.1)
- Prioritizing thermochemical R&D barriers (p. 2-81 of mypp):
    - Understand the relationship between feedstock quality and conversion (Extend beyond CHASE project feedstock to wood chips and MSW)
    - Strategies for conserving carbon and hydrogen in conversion
    - Enable high-performance separations technologies to improve yields

Summary

- Overview: Focus on improving hydrogen efficiency via a hybrid biocatalytic-electrocatalytic process (MEC), using a switchgrass-derived stream, while addressing carbon and separations efficiency.
- Holistic approach covering biooil production, characterization, conversion of boap to H_2, process recycle and LCA analysis.
- Accomplished development of an electroactive biocatalyst and MEC to convert boap to H_2 at high efficiency. Demonstrated >80% conversion of acidic compounds in MEC.
- Addressed C, H and separations efficiency barriers Tt-M, Tt-N, Tt-O relevant to BETO.
- Future work: Improve boap conversion and develop a continuous process to produce H_2 at > 5 L/L-day and > 60% Coulombic efficiency.



MFC/MEC

Bioelectricity / H_2

Biorefinery

Biofuels

Demonstrating conversion of biorefinery process waste to bioenergy :

A path to improving energy efficiency and energy recovery from biomass

Additional Slides

Focus: Hydrogen

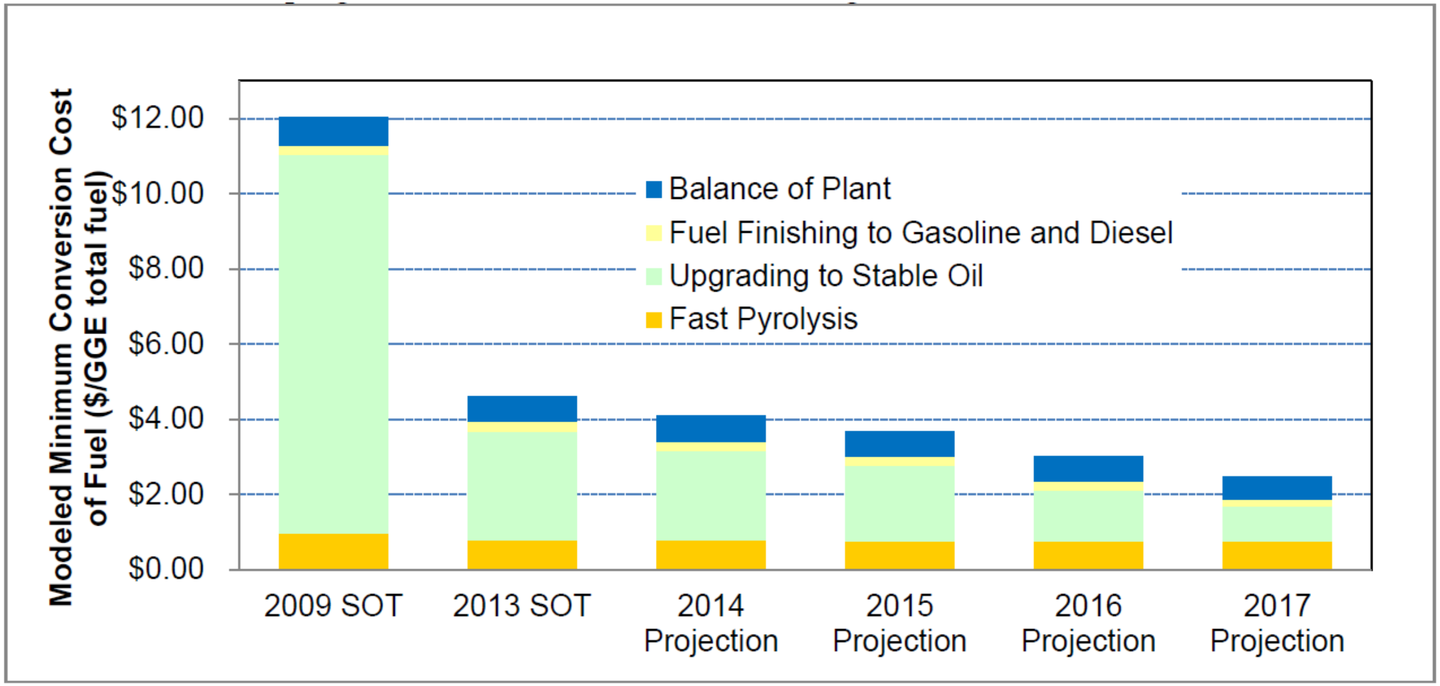


Figure 2-27: Conversion of woody feedstocks to renewable gasoline and diesel-finished fuels via fast pyrolysis

Ref: BETO Multi-year Program Plan

Hydrogen production expenses:
Capital costs: 18% for natural gas reformer
Operating Expenses: cost of natural gas, steam.

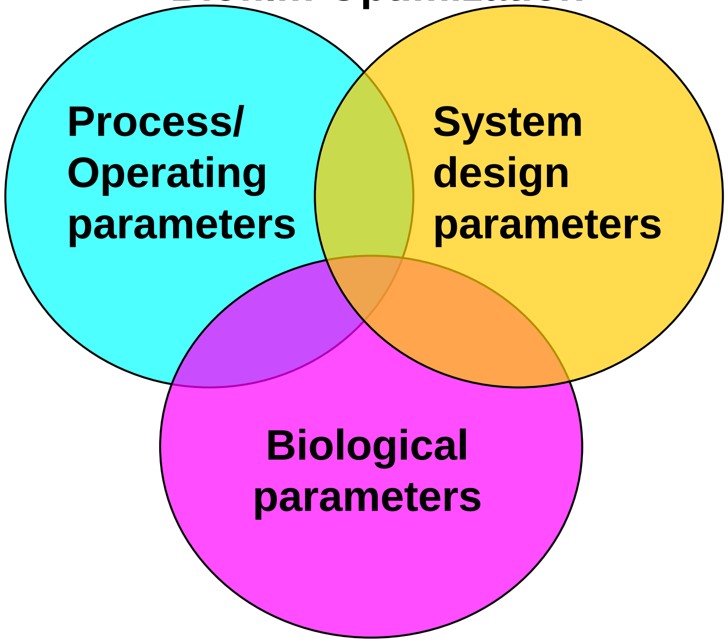
Minimizing natural gas use has potential to minimize operating expenses, while meeting GHG emission goals to meet Renewable fuel standard (RFS2).

3. - Biooil and boap characterization…

Classifications	Major compounds	Concentration in aqueous phase(g/L)	Method
Carboxylic acid	Acetic acid	11.96	HPLC
	Propionic acid	1.89	HPLC
	Vanillic acid	2.69	HPLC
Sugars	Levoglucosan	15.33	HPLC
Furans	Furfural	1.01	HPLC
	HMF	0.54	HPLC
	2(5H)-Furanone	1.17	GC
Alcohols	1,3-propanediol	1.84	GC
	1-hydroxybutanone	1.35	GC
Aldehydes and ketones	Cyclohexanone	0.07	GC
	3-methyl-1,2-cyclopentanedione	0.46	GC
Phenols and alkyl phenols	1,2-benzendiol	1.77	HPLC
	Phenol	1.8	HPLC
	2-methoxyphenol	0.25	GC
	2-methyl-4-methyphenol	0.07	GC
	2,6-Dimethoxyphenol	0.26	GC
	3-ethylphenol	0.56	GC
	Sum	43.01	

Electroactive Biofilm Optimization

1. Batch vs. flow system
2. External resistance
3. Redox potential
4. Shear rate / liquid flow rate
5. pH
6. Substrate loading
7. Temperature
8. Aerobic vs. anaerobic
9. Ionic strength



1. Electrode spacing
2. Presence of membrane and type of membrane
3. Relative anode:cathode surface area
4. Electrode surface area to volume ratio
5. Electrode properties: conductivity, hydrophilicity, porosity, etc.
6. Type of cathode (oxygen diffusion)

1. Source of inoculum
2. Pure culture vs. consortium
3. Gram-positive vs. Gram-negative

Biofilm parameters (Dependent variables)

1. Biofilm growth rate
2. Specific rate of electron transfer
3. Ability to synthesize redox-active mediators
4. Ability to grow nanowires and perform DET
5. Relative exoelectrogen population
6. Characteristics of EPS layer
7. Extent of substrate mineralization
8. Substrate specificity

Borole AP, Reguera G, Ringeisen B, Wang Z, Feng Y, Kim, BH, 2011, **Energy Environ. Sci**. (Review paper)
Electroactive Biofilms: Current Status and Future Research Needs, 4:4813-4834

MEC optimization is a complex process, requiring system design, process and biological parameter optimization.

Publications, Patents, Presentations, Awards, and Commercialization

- Invention disclosures:
  - Hydrogen production from pyrolysis-derived aqueous phase (submitted February 27, 2015).
  - Separation of acidic molecules from bio-oil
- Publications/Manuscripts:
  - Lewis A., Ren S., Ye X., Kim P., Labbe N., Borole A. P., Production of hydrogen from switchgrass-derived bio-oil via microbial electrolysis. In preparation for submission to Biores. Technol.
  - Zeng X., Borole A. P., Pavlostathis S. G. Hydrogen Gas Production from Furanic and Phenolic Compounds in a Batch Microbial Electrolysis Cell. In preparation for submission to Environ. Sci. Technol.
  - Ren et al., Comprehensive characterization of bio-oil and its organic and aqueous fractions derived from switchgrass pyrolysis, manuscript in preparation.
  - Park L.K.-Y.; Ren S.; Yiacoumi S.; Ye X.P; Borole A.P.; Tsouris C., "Liquid Extraction of Bio-oil Components," in preparation.
- Presentations
  - Kyoung Eun Park, *Liquid-Liquid Extraction of Bio-Oil Components*, an oral presentation at AIChE Meeting November 2014, Session: **Sustainable Chemicals: Advances in Innovative Processes**
  - Alex Lewis, *Hydrogen Production from Biomass Via Microbial Electrolysis*, an oral presentation at AIChE Meeting November 2014, Session: **Fundamentals of Hydrogen Production.**
  - Shoujie Ren, *Characterization of Aqueous Phase Bio-Oil Derived from Switchgrass Pyrolysis*, an oral presentation at AIChE Meeting November 2014, Session: **Thermochemical Conversion of Biomass II**
  - Xiaofei Zeng, *Conversion of Furanic and Phenolic Compounds to Hydrogen Gas in a Microbial Electrolysis Cell*, an oral presentation at AIChE Meeting November 2014, Session: **Recovery of Value-Added Co-Products from Biorefinery Residuals and Effluents**
  - Abhijeet P. Borole, *Recovery of Bioelectricity and Hydrogen from Biorefinery Effluents*, an oral presentation at AIChE Meeting November 2014, Session: **Integrating Industrial Waste into Biorefineries**