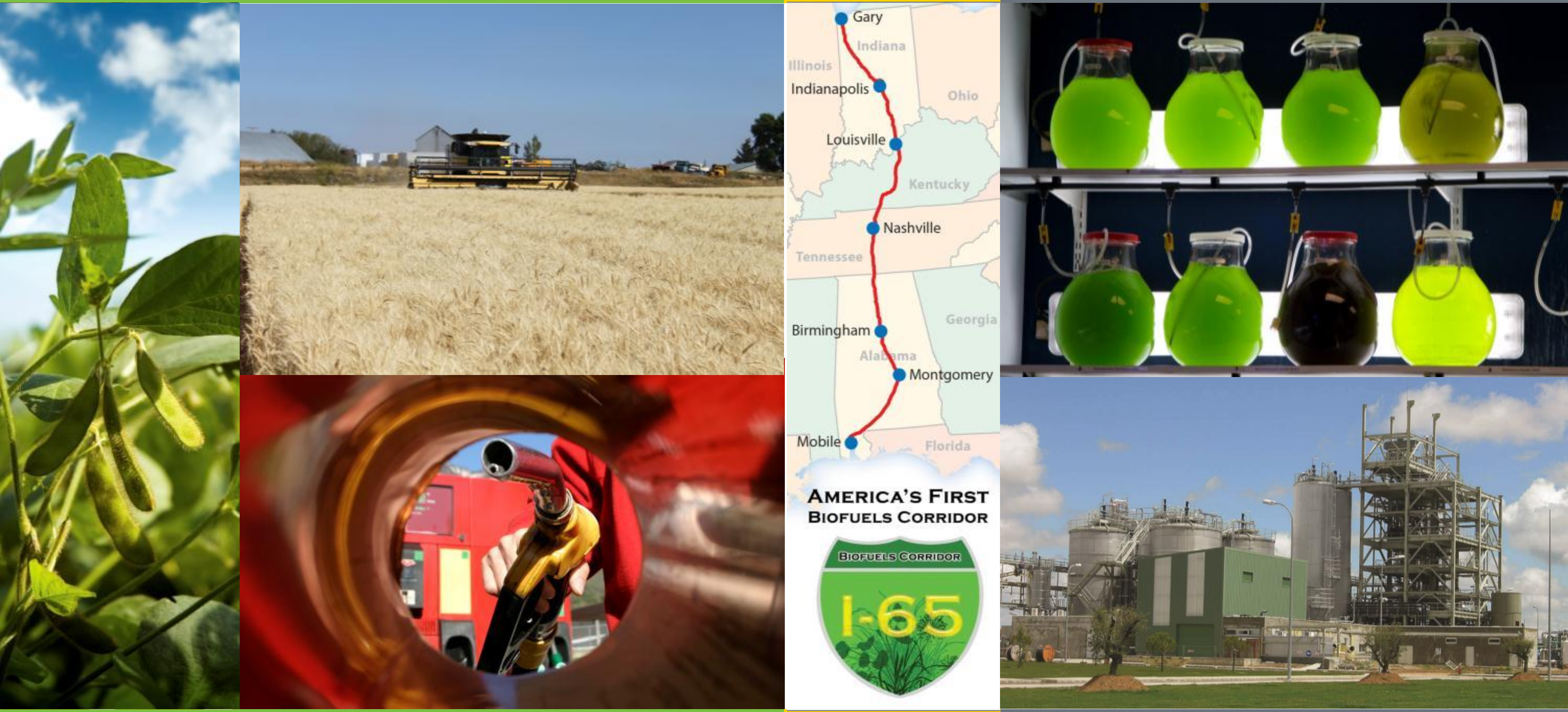
DOE Bioenergy Technologies Office 2015 Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Electrochemical Methods of Upgrading Pyrolysis Oils

Tedd Lister (INL), Mike Lilga (PNNL), and YuPo Lin (ANL)

March 24, 2015

Goal Statement

- Problem: Bio-oil processing through thermal hydrodeoxygenation is an expensive, multi-stage process requiring significant H_2 at high pressure
- Goal: Achieve an electrochemical process to economically hydrotreat pyrolysis oils under mild conditions to a more stable form that can be transported and further upgraded catalytically
- A new innovative process is being developed that could change the way we think about fast pyrolysis bio oil upgrading and provide new processing options not currently possible that will:
  - Increase efficiency (carbon, thermal, etc.)
  - Reduce H_2 demand (EChem hydrogenation, removal of short acids)
  - Reduce GHG
  - Enable access to stranded resources (distributed processing)
  - Contribute to attaining the $3/GGE cost target
- US benefits from:
  - Reduced dependence on foreign oil
  - Sustainable domestic transportation fuel supply
  - Jobs and economic development

Overview

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Thermochemical Conversion SEED

Timeline

- Start: 11/19/2013
- End: 09/30/2017
- Percent complete: 30%

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded (PNNL)	0	0	$310K	$1,280K
DOE Funded (INL)	0	0	$285K	$855K
DOE Funded (ANL)	0	0	$120K	$400K

Barriers Addressed

Tt-H Bio-oil intermediate stabilization

Tt-J Catalytic upgrading of bio-oil intermediates to fuels and chemicals

Tt-O Separations efficiency

Other barriers

Tt-M Hydrogen production

Tt-P Materials compatibility

Tt-N Aqueous phase utilization and wastewater treatment

Partners

PNNL	Michael Lilga	50%
INL	Tedd Lister	35%
ANL	YuPo Lin	15%

University of Arkansas, Fayetteville, AR

Giner Inc., Boston, MA

1 - Project Overview

EC hydrogenation background

- Electrochemical hydrogenation/reduction has a long history and is employed for commercial synthesis
- Hydrogenation of vegetable oils and sugars is established technology
- Recent growth in literature activity demonstrates potential for an electrochemical process (surrogate and separated bio-oil – see additional slides for recent papers)
- No previous EC processing of raw pyrolysis oil
- Project initiated with limited knowledge base to benchmark process (thus a SEED project)

Electrochemistry plays a big role in industrial commodity chemical production

Cl_2 was #6 on the US Top Chemicals Produced list in 2004 at 12.2 M metric tons

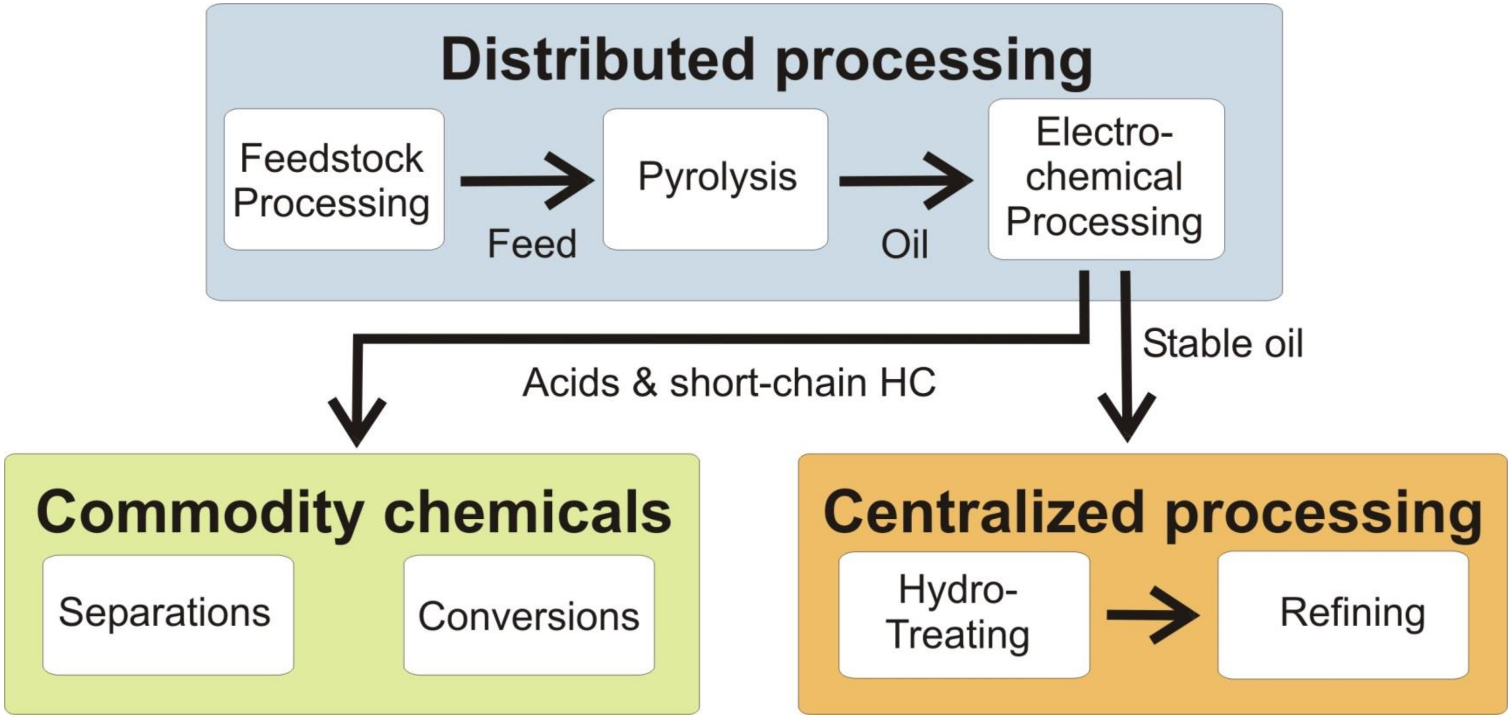
http://pubs.acs.org/cen/coverstory/83/pdf/8328production.pdf

Chlor-alkali electrolyzers

1 – Project Overview

Vision of bio-oil processing using electrochemical stabilization

- Pyrolyzing biomass at distributed sites enables greater accessibility to stranded feedstocks and eliminates the need to transport water (e.g., densifies the intermediate)
- Electrochemical stabilization eliminates the need to have a hydrogen source at a distributed facility



Distributed processing

Feedstock Processing → Feed → Pyrolysis → Oil → Electrochemical Processing

Acids & short-chain HC

Stable oil

Commodity chemicals

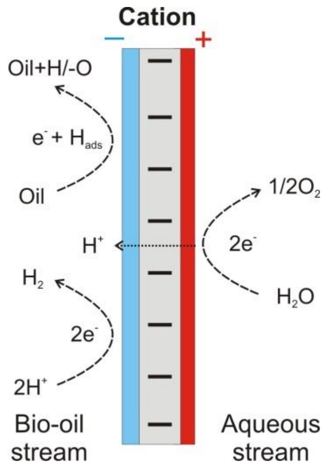
Separations

Conversions

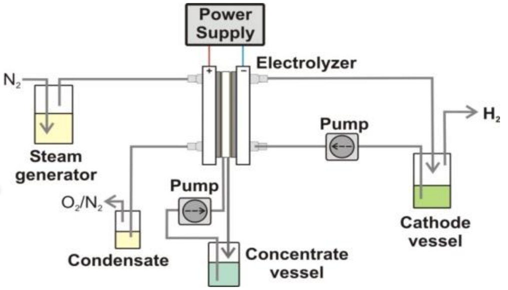
Centralized processing

Hydro-Treating → Refining

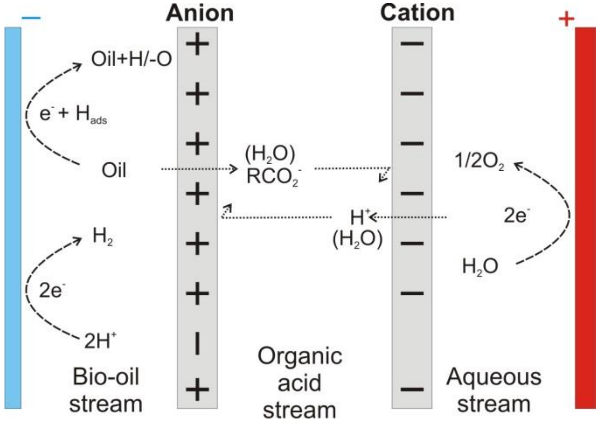
2 - Approach (Technical)



Single Membrane Cell (Cation Exchange)

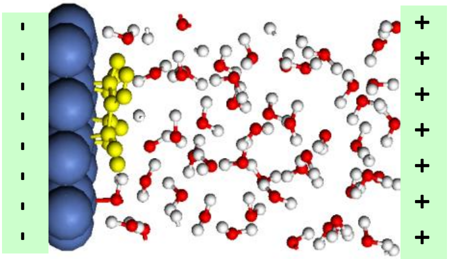


Organic Acid Separations

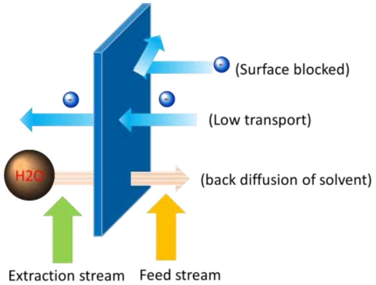


Dual Membrane Cell (Cation and Anion Exchange)

Commercialization



Theoretical Prediction and Experimental Verification



Anion Exchange Membrane Development

2 - Approach (Management)

Critical Success Factors

1) Final process will need to demonstrate:
   - *A favorable impact on cost of processing*
   - *Scalability at the level needed for fuels production*

Challenges

1) Demonstrate bio oil electrochemical hydrogenation (INL)
2) Develop electrode materials with high current efficiency (PNNL)
3) Develop anion exchange membranes resistant to bio oil (ANL)

Mitigation Strategy

1) Utilize the expertise of 3 National Labs to address the immediate challenges
2) Stage the development starting with a simpler cell, then adding complexity
3) Develop more complex elements separately in parallel, then integrate
4) Use Go/No-Gos and TEAs to adjust technology development as needed

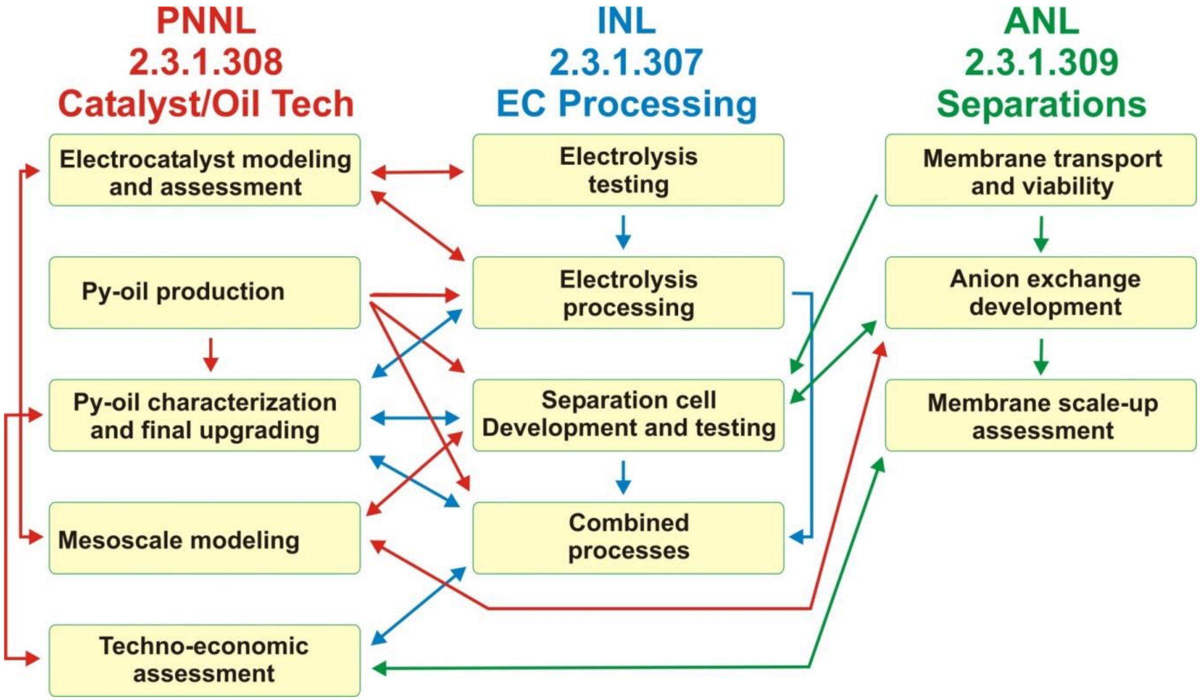
Upcoming Decision Gates

03/31/2015: Demonstrate electrochemical hydrogenation

04/30/2015: Demonstrate enhanced acid separation efficiency on anti-fouling AEM

05/31/2015: Analytical validation of hydrogenation

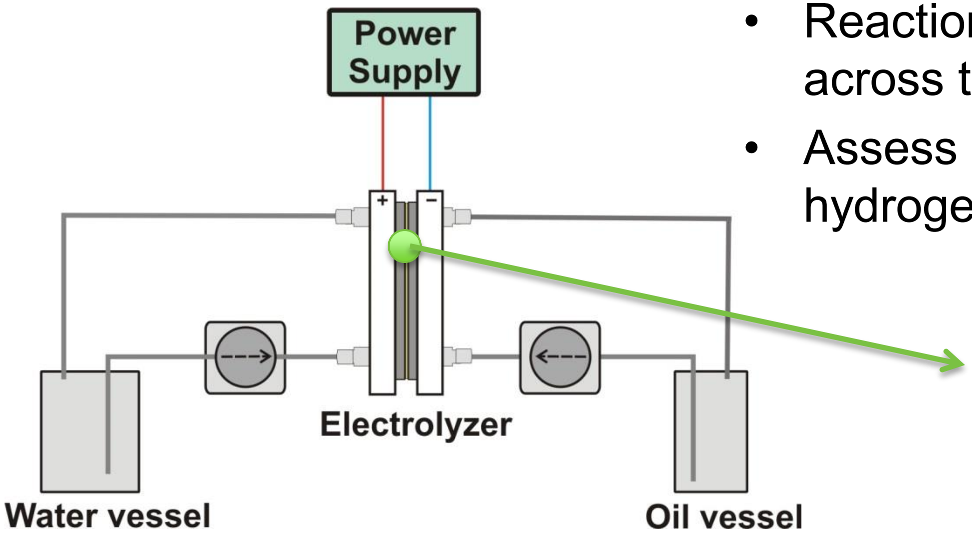
2 – Approach (Management)



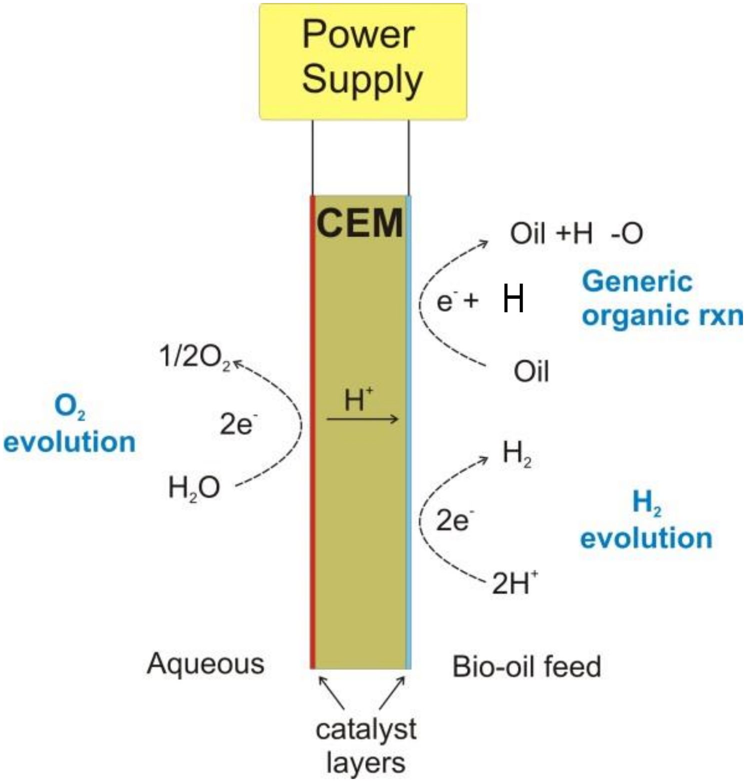
- INL leads the overall effort
  - Subtasks are fully integrated across the 3 labs
- Team meets regularly
  - Inputs and feedback influence experiments and process development
- Quarterly reporting at each lab
- Deep dives with BETO
  - BETO has an active role in project direction

3 – Technical Accomplishments /Progress/Results

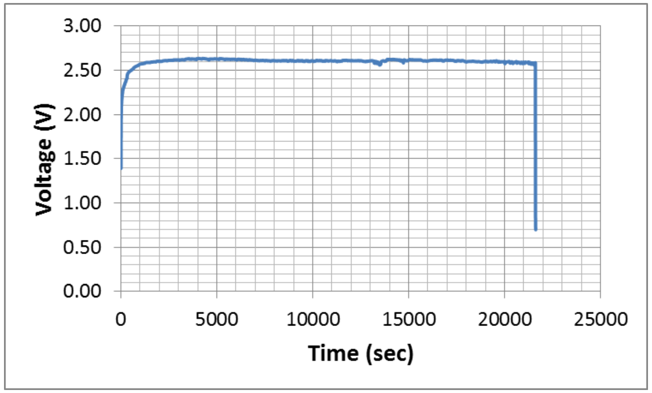
- Reactions are driven by electrical energy applied across the cell
- Assess the potential of electrochemical hydrogenation using mild conditions (T and P)



Electrolysis system



Chemical processes

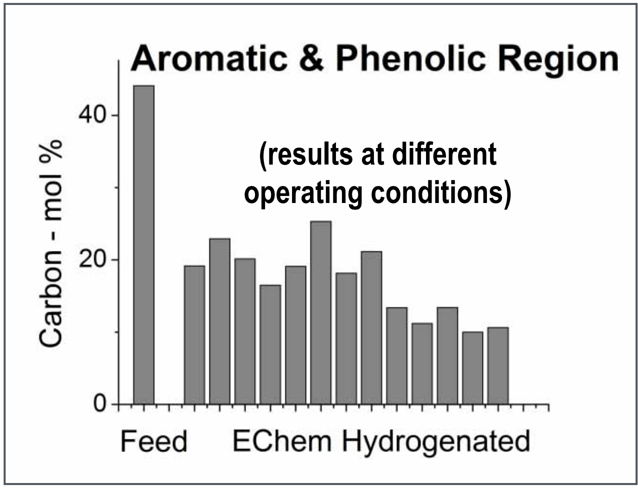


Voltage-time plot in pyrolysis-oil

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

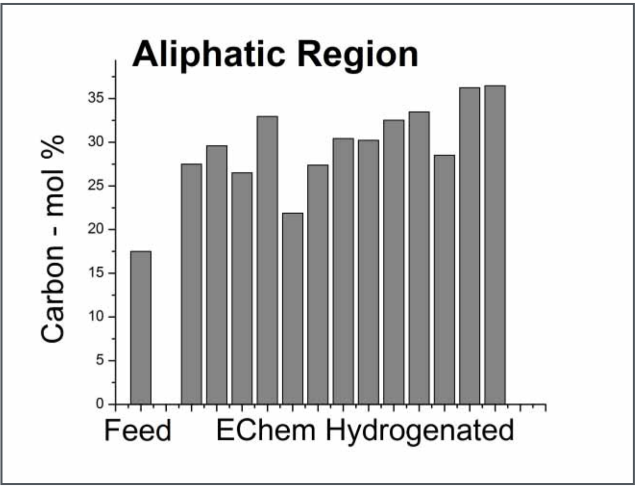
^{13}C NMR Analysis of Electrochemically Hydrogenated Bio-Oil

- ^{13}C NMR suggests electrochemical hydrogenation of phenolics to aliphatic ethers and reduction of carbonyl functionalities

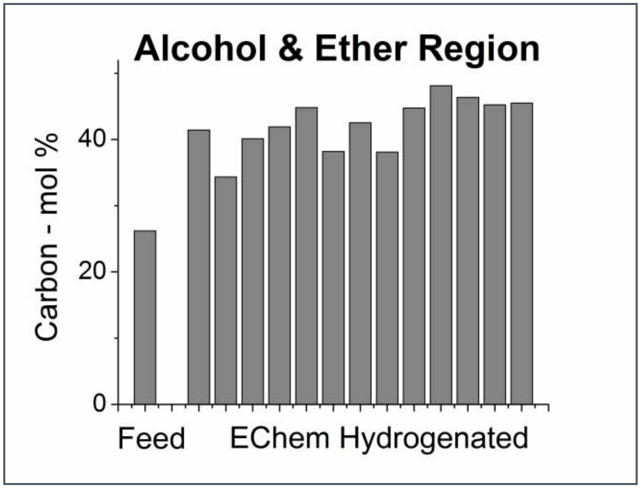


Aromatic & Phenolic Region

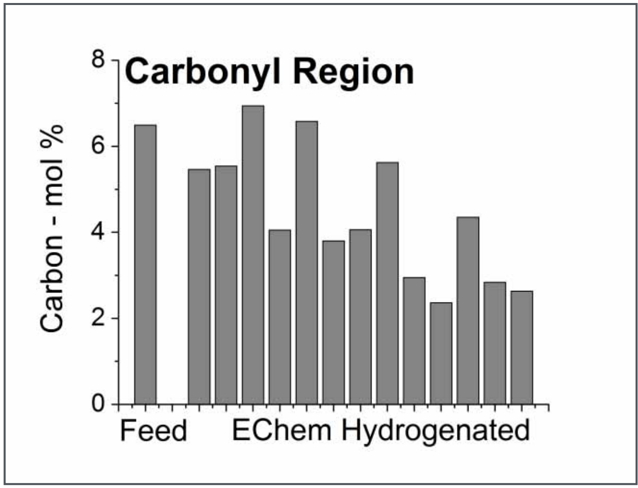
(results at different operating conditions)



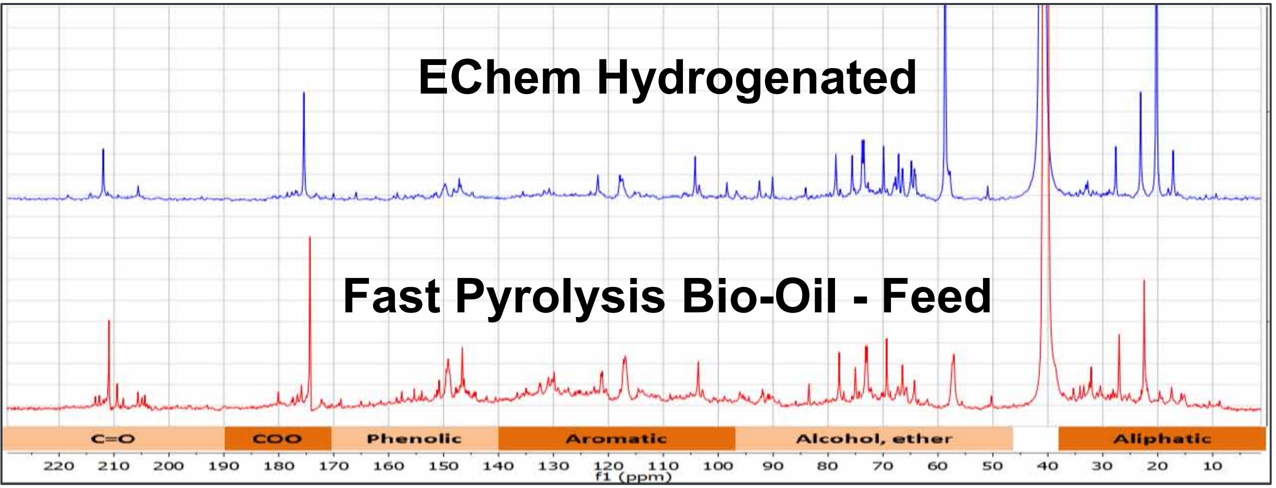
Aliphatic Region



Alcohol & Ether Region



Carbonyl Region



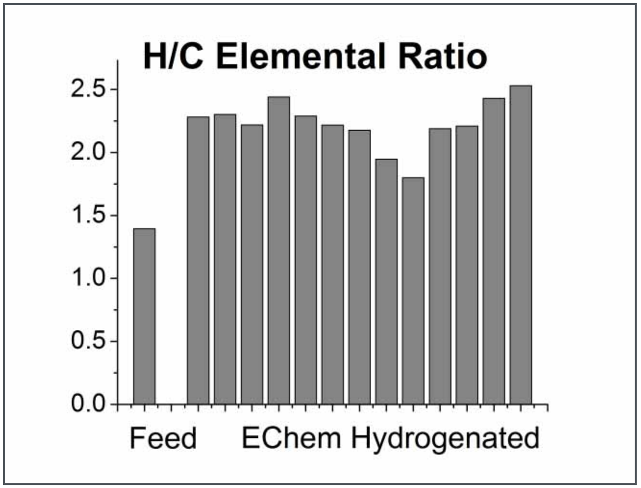
EChem Hydrogenated

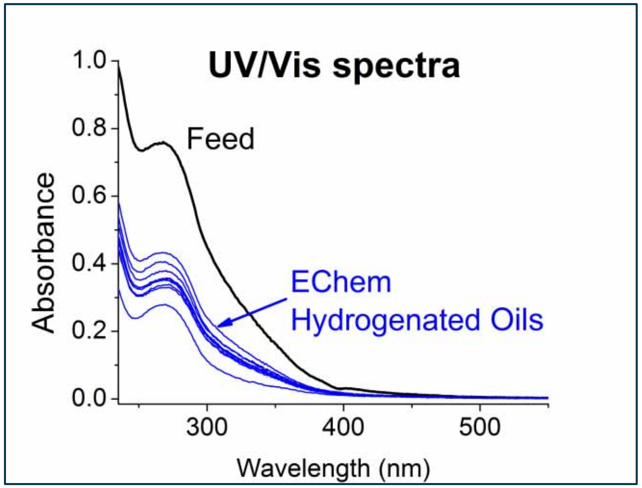
Fast Pyrolysis Bio-Oil - Feed

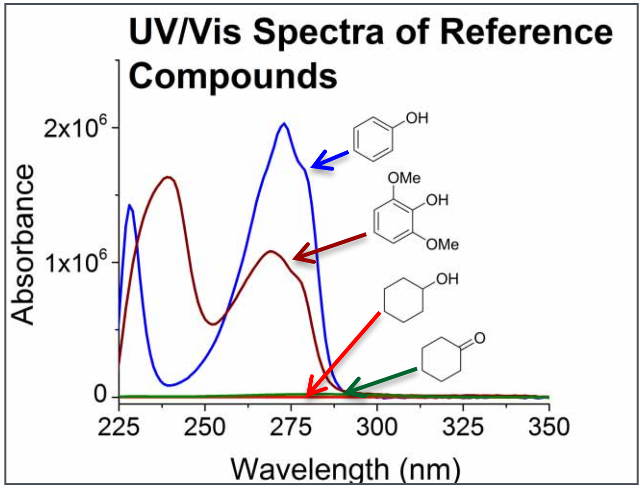
3 – Technical Accomplishments /Progress/Results (cont'd)

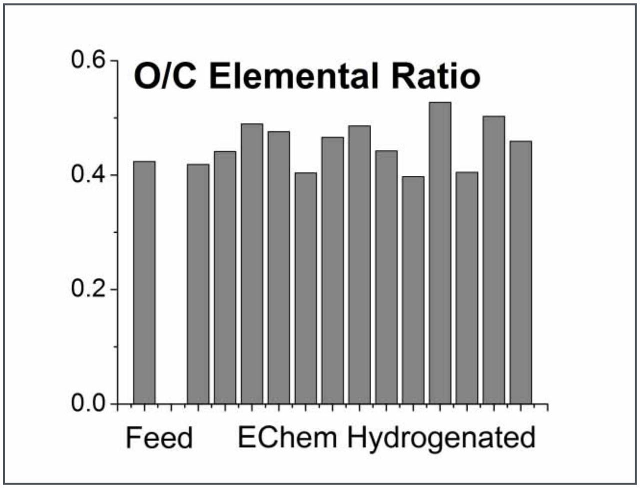
Elemental, TAN, and UV/Vis Analyses of ECH Bio-Oil

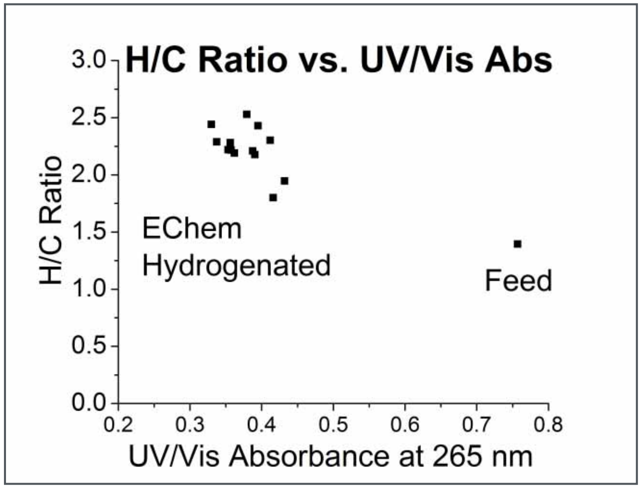
- Analyses are consistent with phenolic aromatic ring reduction

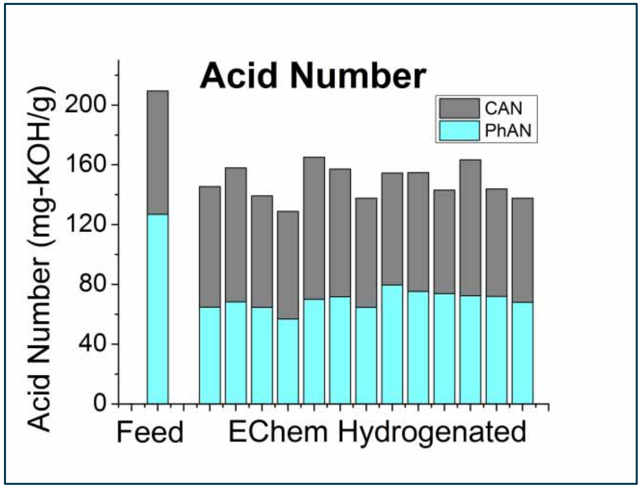








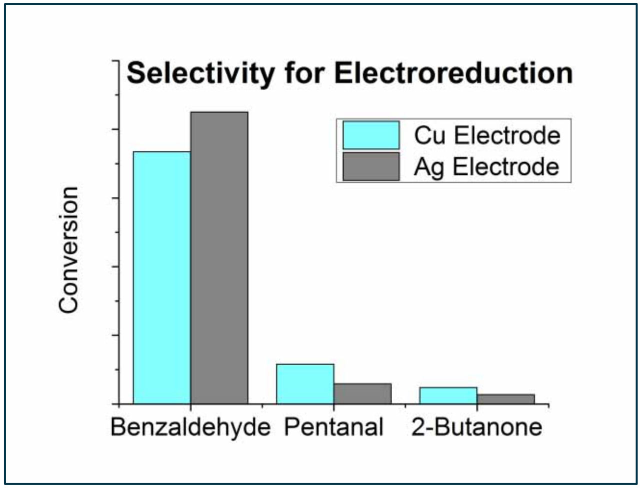




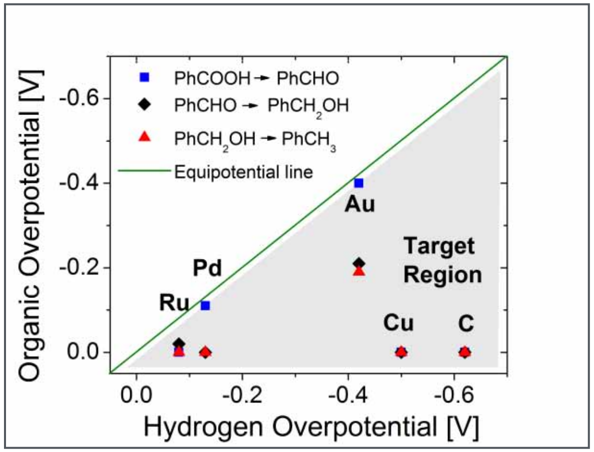
3 – Technical Accomplishments /Progress/Results (cont'd)

Evaluation of New Electrodes Using Theory and Experiments

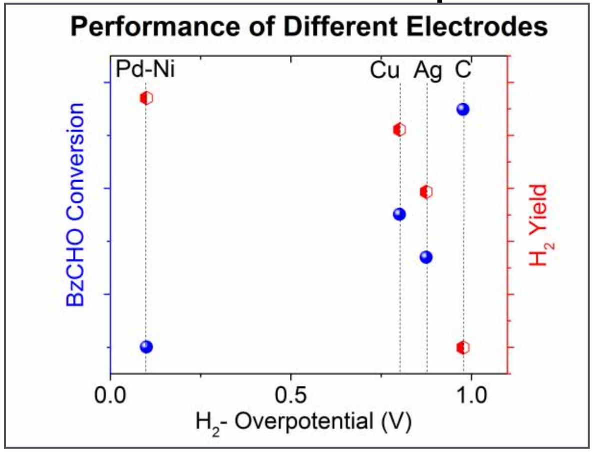
- To favor ECH over H_2 production, electrodes with higher H_2 and lower organic overpotentials are required
  - – Theory – Cu, Au, C are favorable candidates
  - – Experimental – Cu, C, and Ag could be used as new electrodes
  - – Experimental – C had the lowest H_2 production and highest benzaldehyde conversion in agreement with theory
  - – Theory and experiment guide new electrode development
- Aromatic aldehydes demonstrate a higher selectivity for ECH

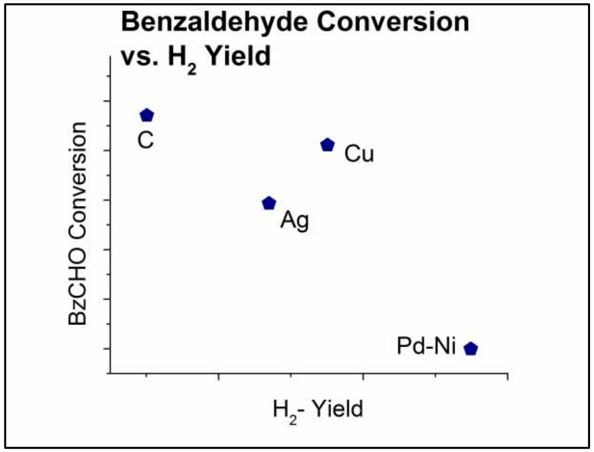


Theoretical Prediction



Experimental Verification



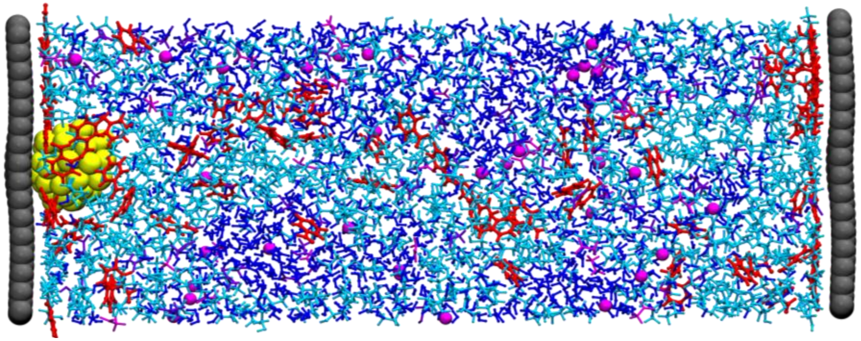


3 – Technical Accomplishments /Progress/Results (cont'd)

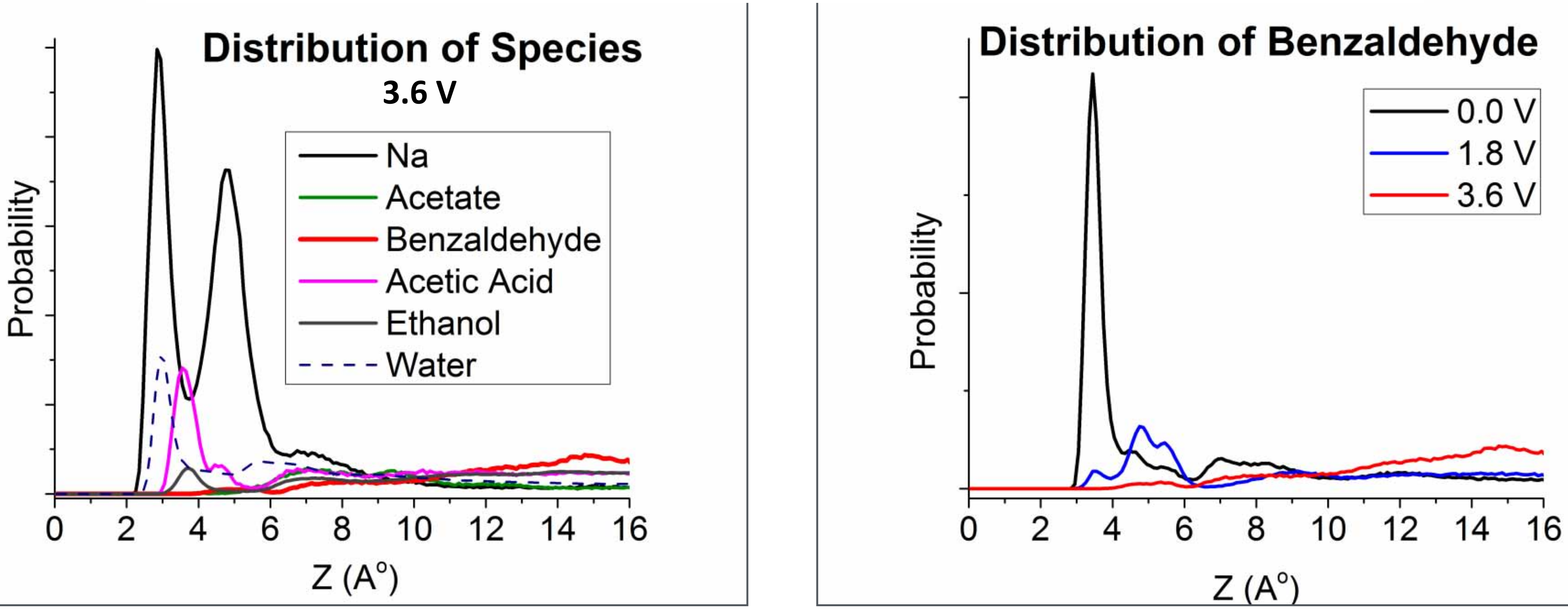
Molecular Dynamics Simulation of the Electrode Surface

- MD describes the environment near the electrode
- Applied potential tends to move organics away from the metal particle
- Analysis will be extended to distribution from the carbon surface (could be different)
- Distribution of phenolics will be determined

MD Simulation Snapshot at 298K, 0 V

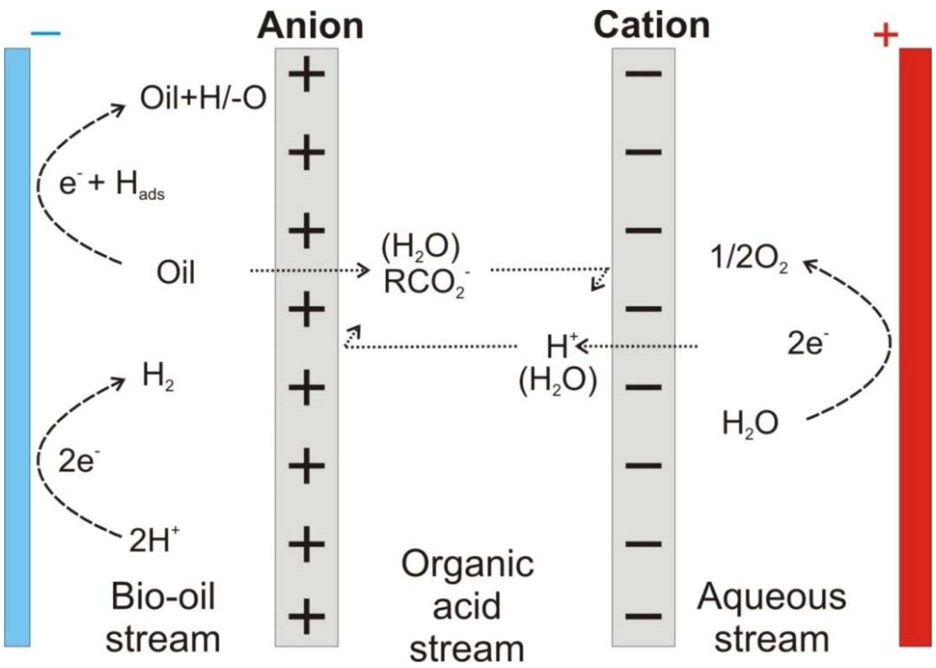


Distribution of Species from the Surface of a Metal Particle

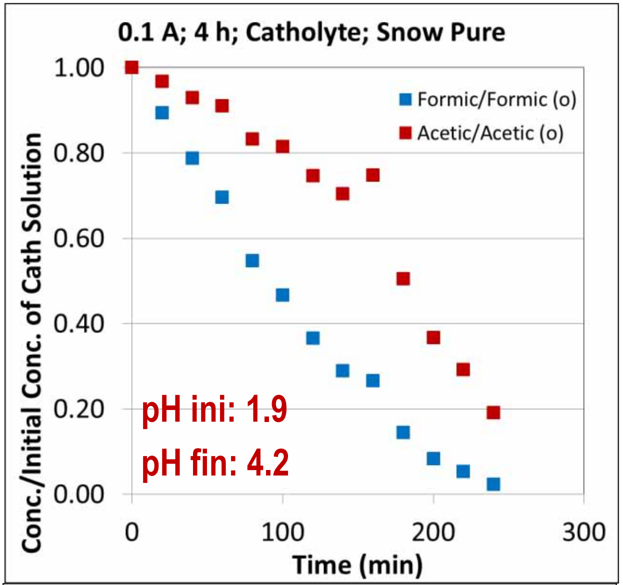


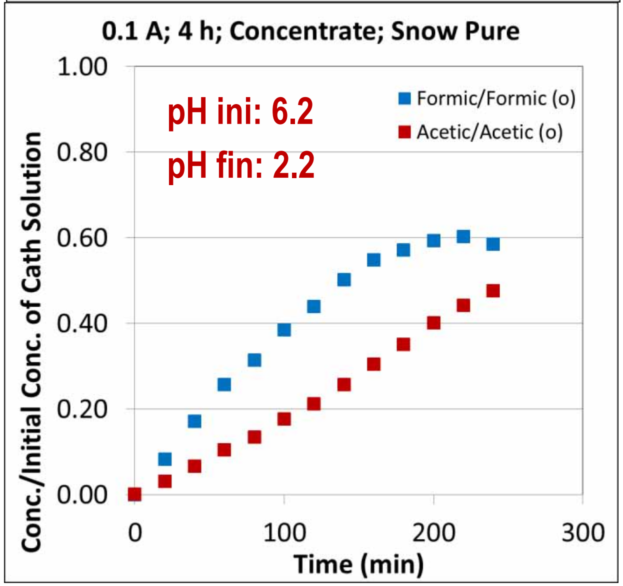
3 – Technical Accomplishments /Progress/Results (cont'd)

Separation-Electrolysis Cell



- Route to TAN reduction
- Electrodialysis cell using alternating AEM-CEM membranes separates organic acids and water
- Will be integrated with hydrogenation system to remove short-chain acids and ash components from pyrolysis-oil





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

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Reversibility of AEM Fouling

Ionic Resistance (ohm-cm^2) of AEM in 0.5 N NaCl solution

						CEM
Soaking Liquid	AHA	ACS	AFN	AXE	AMX	**CMX**
Bio-oil*	17.9	7.0	1.4	1.4	4.2	5.5
Aqueous	7.19	6.1	1.2	1.2	3.8	5.4
Resistance Increase	149%	15%	14%	15%	11%	2%

Soaking Liquid	AMD	AMV	AMT	AXE-M	AMX-M	**Syn. AEM**
Bio-oil*	45.2	3.0	7.5	3.0	3.3	5.8
Aqueous	31.1	2.7	6.4	2.5	2.9	5.6
Resistance Increase	46%	13%	17%	20%	15%	4%

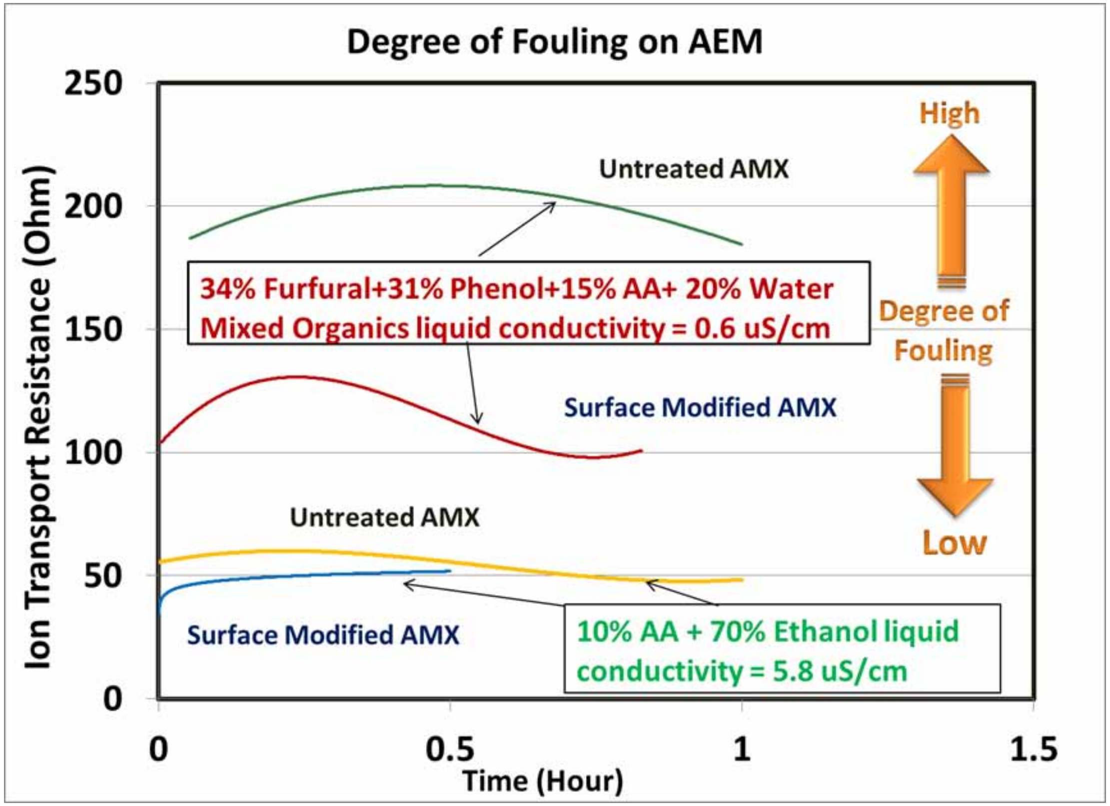
* AEM soaked in bio-oil was washed by 80% EtOH for testing in 0.5 N NaCl solution.

- Cation membrane is not fouled in bio-oil.
- Synthetic AEMs resist organic fouling compared to commercial AEMs, However, its surface coating was not stable. Further improvement is needed.
- Surface modified AMX-M seems have better conductivity after treatment.

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

Fouling and Ion-Transport Property of Surface-Treated AEMs

Electrochemical Fouling Monitoring

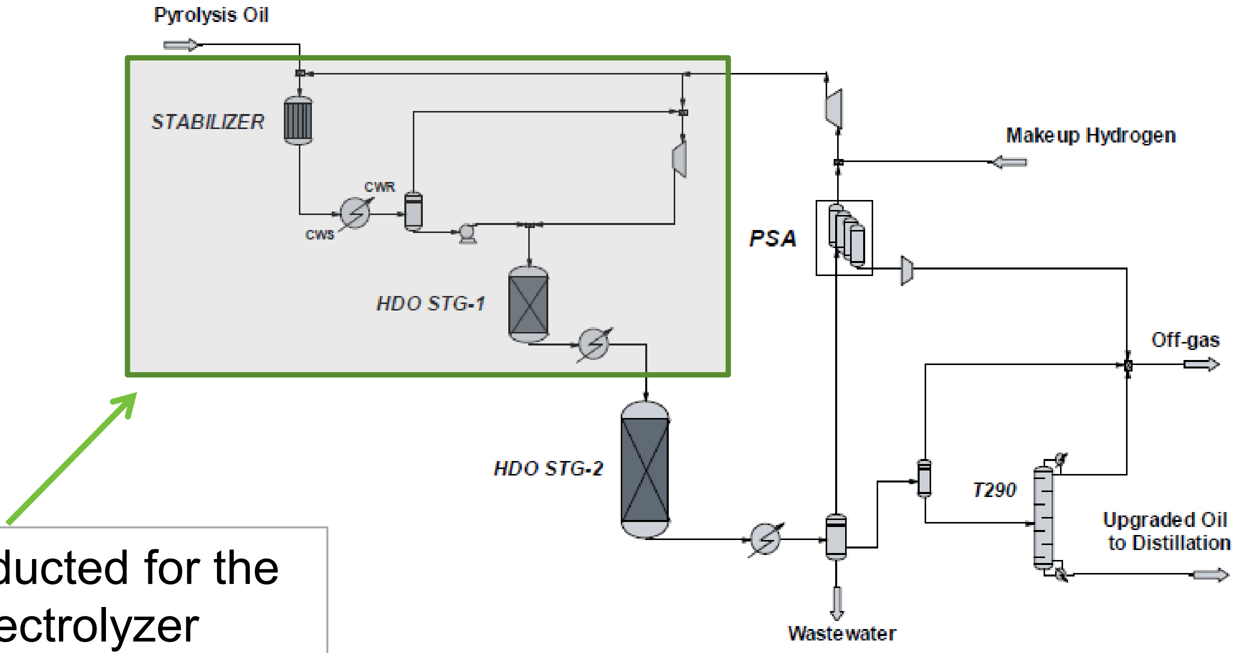


- Resistance of ion transport **increased** in mixed organics - surface fouling?
- Modified surface **decreased** the ion transport resistance – reduce fouling?

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

Preliminary Technoeconomic Analysis

- A high-level TEA was conducted
- As a first pass, the current State Of Technology for thermochemical pyrolysis oil upgrading was used as a basis of comparison
- New experimental results will modify assumptions used in this analysis



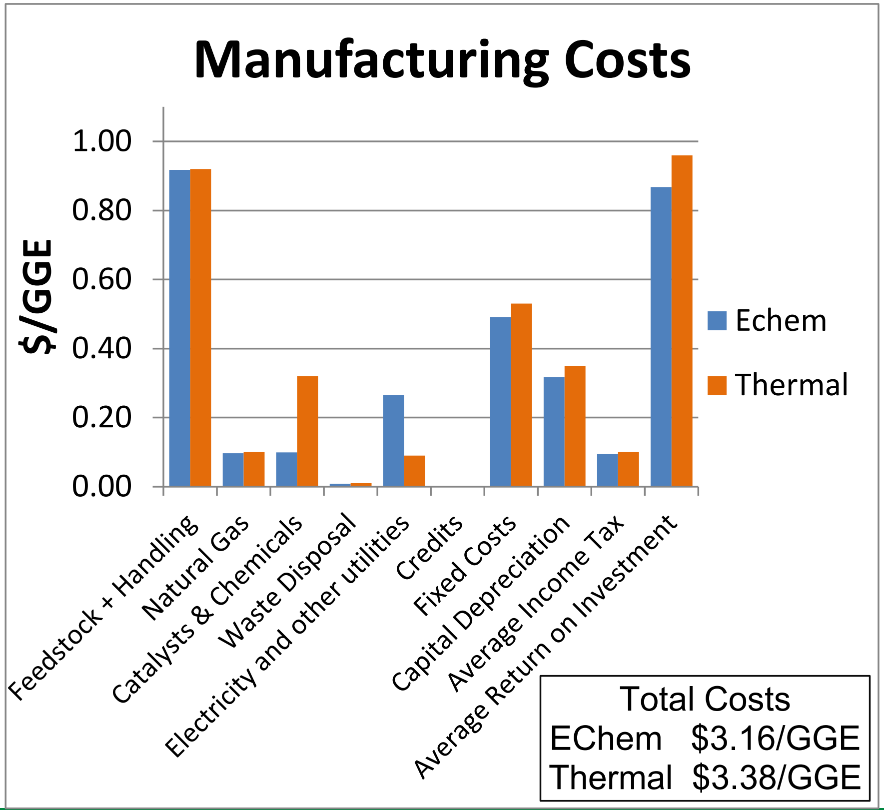
TEA was conducted for the case of the electrolyzer replacing the stabilizer and 1st stage HDO

Figure 6. Bio-Oil Upgrading Process Flow

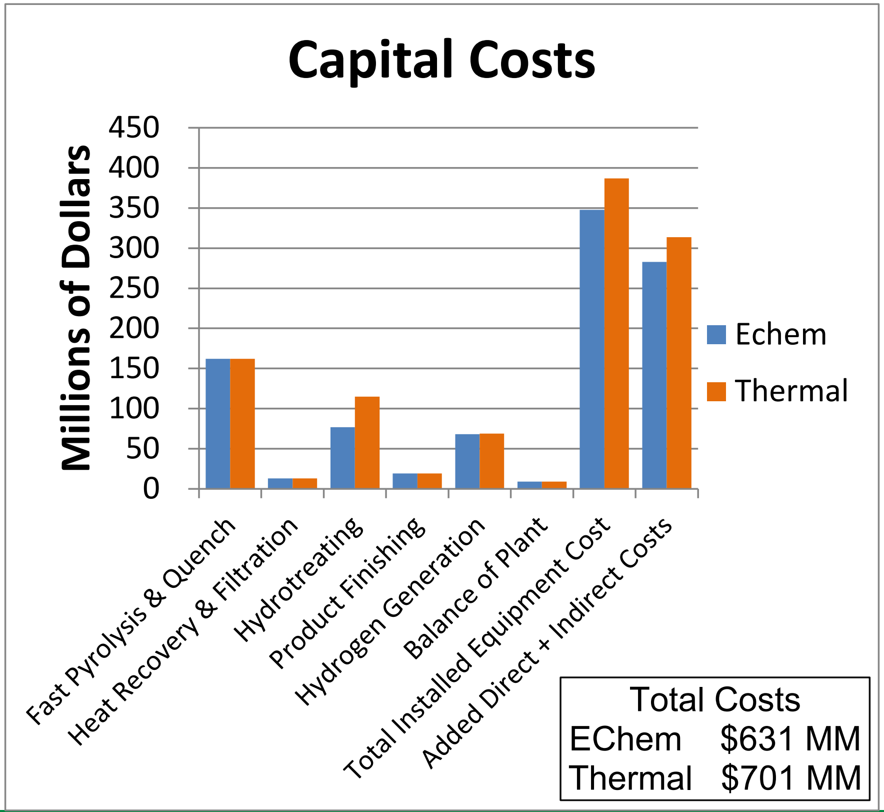
3 – Technical Accomplishments /Progress/Results (cont'd)

EChem and Thermal Costs Compared

- EChem and thermal costs are comparable
- Feedstock the major cost
- Thermal – catalyst cost relatively high; utility cost relatively low
- EChem – catalyst cost relatively low; utility cost relatively high
- Analyses will be updated with new information this FY



Total Costs	
EChem	$3.16/GGE
Thermal	$3.38/GGE



Total Costs	
EChem	$631 MM
Thermal	$701 MM

4 - Relevance

- Electrochemistry provides a method to hydrogenate bio-oils using mild thermal conditions. This provides a method to both stabilize and upgrade pyrolysis oils
  - *Barriers Tt-H and Tt-J*
- Mild electrochemical hydrogenation should stabilize oil to minimize char formation and increase carbon utilization
  - *Thermochem R&D priority*
- By separating chemicals (small organic acids) that are hydrogen sinks during hydrotreating, hydrogen efficiency is increased
  - *Thermochem R&D priority*
- The 2-membrane cell process is expected to decrease acidity and remove organic acids resulting in a less corrosive mixture
  - *Barrier Tt-P*
- Electrochemistry is a scalable method and requires primarily electricity to operate.
  - *This enables "Depot Concept" for energy densification of stranded feedstocks (Advanced Feedstocks Logistics Systems)*
- While this work is ground breaking, electrochemistry is widely used in chemicals production: chlor-alkali, pesticides, hydrogen, etc.

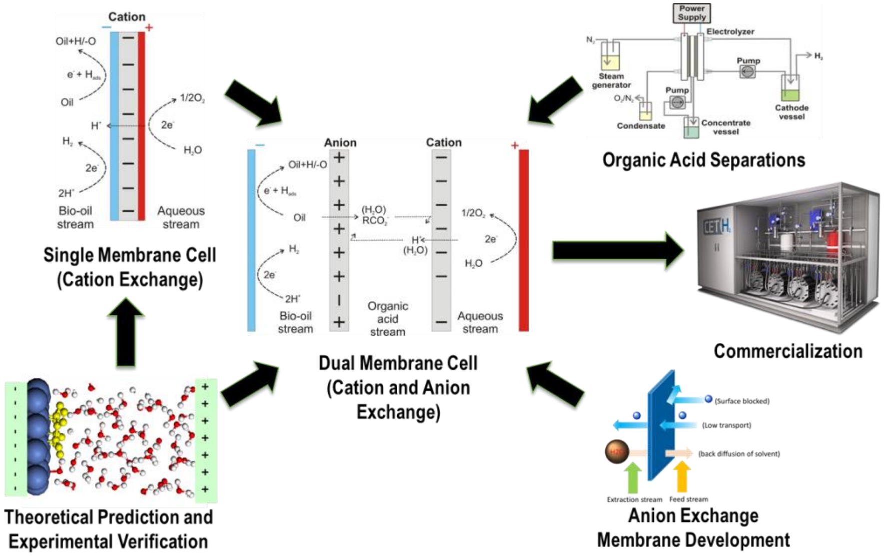
5 – Future Work

1) **Address FY15 Decision points: assess technology and make adjustments**
2) **Develop and refine process as described in activities below**

FY2015	FY2016	FY2017
Demonstrate electrochemical upgrading of pyrolysis-oil	Integration of hydrogenation and separation features	Demonstrate upgrading of other feedstocks
Development of separation cell to enable removal of acids and dewatering	Demonstration of integrated system for upgrading pyrolysis oil	Determine design features of a scaled system
Selection of suitable membranes to perform separations	Develop membrane coating and fouling mitigation protocol to extend membrane lifetime	Investigate co-product usage
TEA tracking of technology	TEA tracking Identify technology gaps and opportunities	TEA assessment of technology
Develop models for understanding of hydrogenation mechanisms	Deepen understanding of hydrogenation and predict desirable electrode compositions	Test improved electrode materials with bio oils

Summary

- Electrochemical processing has great potential for upgrading pyrolysis oil and enabling use of stranded feedstocks
- Project has demonstrated unique phenolic hydrogenation, providing new avenues to bio oil stabilization not attainable by SOT
- Initial assessments have shown processing costs are not significant and could reduce total costs.
- Modeling activities will continue to provide information to guide process decisions
- Work will continue as a team to develop each process “function” in the near term and merge them at a later stage



- Project has developed separation process that will be applied to pyrolysis oils in the near future
- Membrane stability and fouling in bio-oil can be mitigated with membrane composition and use of coatings
- Provisional patent filed 03/23/2015

Additional Slides

Abbreviations

AEM	anion exchange membrane
ANL	Argonne National Laboratory
CAN	carboxylic acid contribution to acid number
CEM	cation exchange membrane
EChem	electrochemistry (process)
ECH	electrochemical hydrogenation
INL	Idaho National Laboratory
NMR	nuclear magnetic resonance (spectroscopy)
PhAN	phenolic contribution to acid number
PNNL	Pacific Northwest National Laboratory
TAN	total acid number
TEA	techno-economic analysis
UV/Vis	ultraviolet visible (spectroscopy)

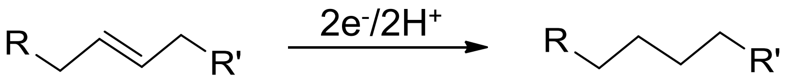
Reactive Groups can be Stabilized by Electrochemical Hydrogenation

Transfer proton + electron to unsaturated organic bonds

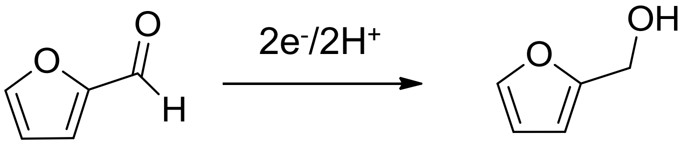
Order of Difficulty

Hydrogenations

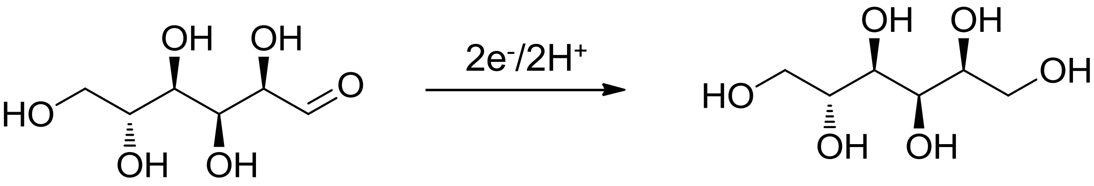
Alkene



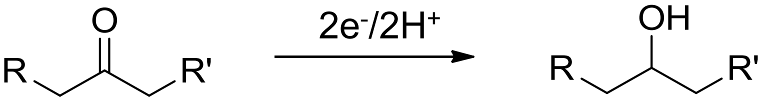
Aromatic aldehyde



Aldehyde

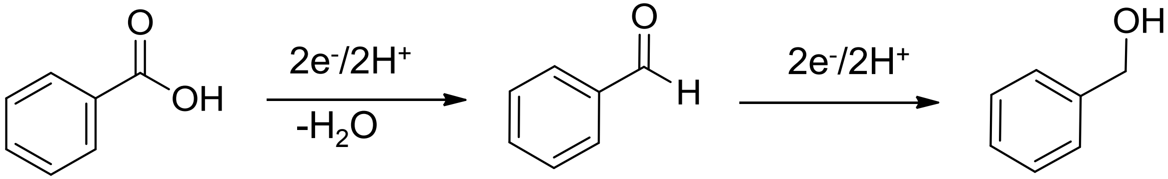


Ketone



Hydrodeoxygenation/hydrogenation

Aromatic acid



Electrolyzers

Stack: series of electrolyzers assembled in parallel

Pressurized electrolyzer stack
Giner Electrochemical Systems

Commercial H_2 electrolyzer system

Papers Relevant to Electrochemical Bio-Oil Hydrogenation (since 2010)

Li et al., Green Chemistry 16 (2014) 844, *A Mild Approach for Bio-oil Stabilization and Upgrading: Electrocatalytic Hydrogenation using Ruthenium Supported on Activated Carbon Cloth.*

Green et al, Green Chemistry DOI: 10.1039/C3GC00090G (2013), *The Electrocatalytic Hydrogenation of Furanic Compounds in a Continuous Electrocatalytic Membrane Reactor. (furfural)*

Saez et al, Electrochmica Acta 91 (2013) 69, *Electrocatalytic Hydrogenation of Acetophenone Using a Polymer Electrolyte Membrane Electrochemical Reactor.*

Xin et al., Chemsuschem 6 (2013) 674, *Electricity Storage in Biofuels: Selective Electrocatalytic Reduction of Levulinic Acid to Valeric Acid or g-Valerolactone.*

Kwon et al., Chemsuschem 6 (2013) 455, *Electrocatalytic Hydrogenation and Deoxygenation of Glucose on Solid Metal Electrodes.*

Li et al, Electrochimica Acta 64 (2012) 87, Aqueous Electrocatalytic Hydrogenation of Furfural Using a Sacrificial Anode

Green et al, Chemsuschem 5 (2012) 2410, *Electrocatalytic Reduction of Acetone in a Proton-Exchange-Membrane Reactor: A Model Reaction for the Electrocatalytic Reduction of Biomass.*

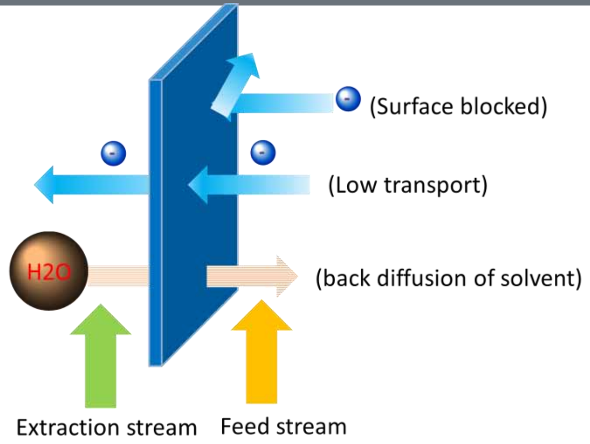
Li et al, Green Chemistry 14 (2012) 2540, *Mild Electrocatalytic Hydrogenation and Hydrodeoxygenation of Bio-oil Derived Phenolic Compounds using Ruthenium Supported on Activated Carbon Cloth.* (guaiacol and similar)

Vilar et al, Applied Catalyst A 372 (2010) 1, *Investigation of the Hydrogenation Reactivity of Some Organic Substrates Using an Electrocatalytic Method.* (aromatic aldehydes and ketones)

Characterization and Improvement of Fouling Resistance in Bio-oil

Considerations of AEM used in Bio-oil

1. Robust - structure stable in bio-oil
2. Mitigatable Organics fouling (Conductivity measurement)
3. Fouling and Ionic transport property in bio-oil (In-situ electrochemical fouling monitoring Technique)
4. Compatibility of the process and extraction streams (e.g. Water back diffusion)



Improve Anti-fouling Resistance in Bio-oil

1. Passivation surface of commercial AEM
    - Poly electrolytes – passivation charge + hydrophobicity
2. Fabricate synthetic AEM
    - Asymmetric
    - Hydrophobic molecules with charged moieties