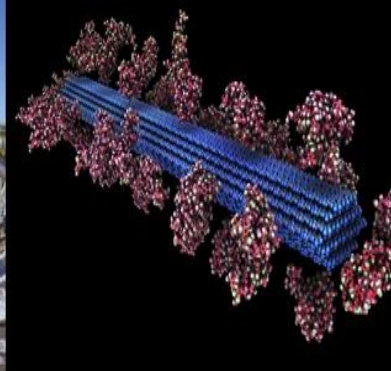




U.S. DEPARTMENT OF
ENERGY

Energy Efficiency &
Renewable Energy



Electrochemical Methods of Upgrading Pyrolysis Oils

March 7, 2017

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Thermochemical Conversion
Session

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Mike Lilga (PNNL)
YuPo Lin (ANL)

Goal Statement

- **Problem:** Bio-oil processing through thermal hydrodeoxygenation is an expensive, multi-stage process requiring significant H₂ at high pressure and temperature
- **Goal:** Achieve an [electrochemical process to economically stabilize pyrolysis oils](#) under mild conditions to a form that can be transported for further catalytic deoxygenation and upgrading
- **Path:** An 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 efficiencies (carbon, hydrogen, thermal, etc.)
 - Reduce H₂ demand (EChem hydrogenation, removal of short acids)
 - 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
- Manufacturing of electrochemical modules

Quad Chart Overview

Timeline

- Start: 10/1/2013
- Merit review: 03/2015
- End: 9/30/2016 (sunsetting)
- 100% complete

Budget

| | Total Costs FY 12 –FY 14 | FY 15 Costs | FY 16 Costs | Total Planned Funding (FY 17-Project End Date) |
|-----------------------------------|--------------------------------|-------------|-------------|---|
| DOE Funded (PNNL) | \$304.9K | \$409.1K | \$360.0K | \$168.7K |
| DOE Funded (INL) | \$231.8K | \$278.5K | \$280.5K | \$105.4K |
| DOE Funded (ANL) | \$120K | \$150K | \$250K | \$40 K |
| Project Cost Share (Comp.)* | | | | |

Barriers

Tt-H Bio-oil intermediate stabilization

- Reduction of reactive functionalities
- Eliminating expensive PM catalysts

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

- Remove functional groups that cause coking
- Stabilized oil offers other processing options

Partners

- INL: 30%
- PNNL: 43%
- ANL: 27%

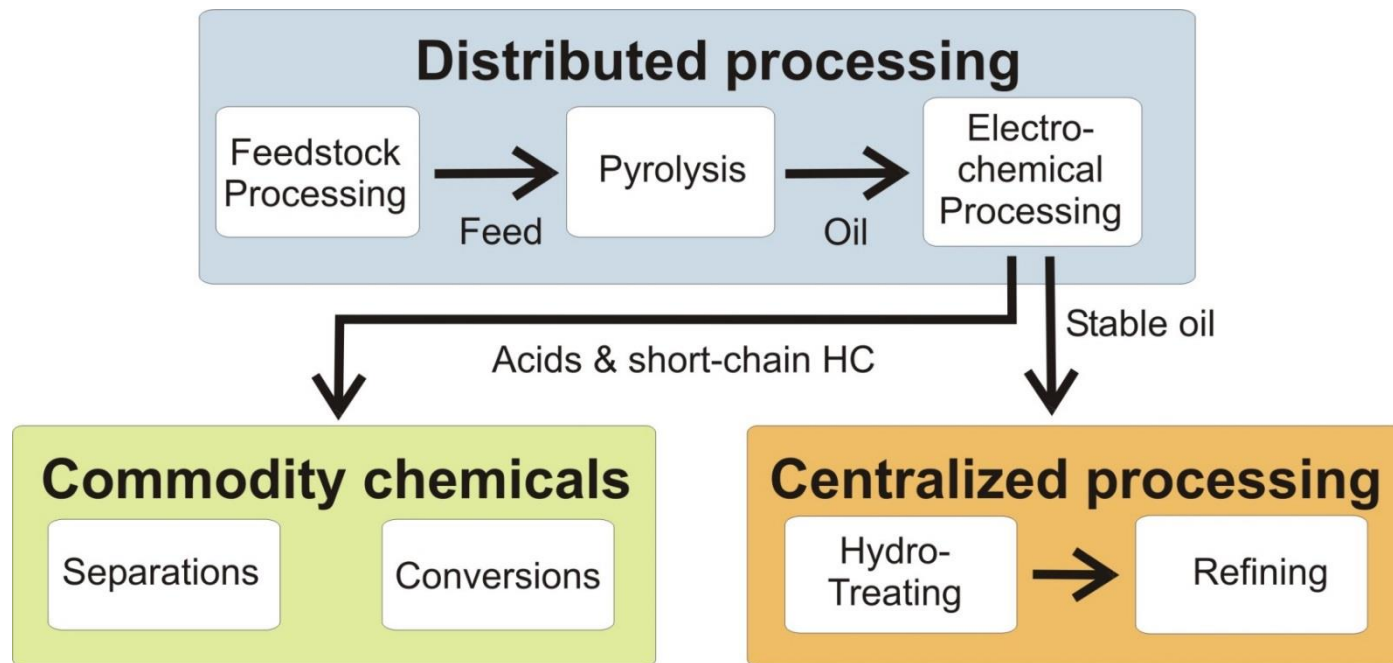
Other interactions/collaborations

- Giner, Inc.
- U. of Arkansas
- Louisiana State U

1 – Project Overview

Vision of bio-oil processing using electrochemical stabilization

- Pyrolyzing biomass at distributed sites enables greater accessibility to stranded feedstocks and densifies the intermediate
- Electrochemical stabilization eliminates the need to have a hydrogen source at a distributed facility
- Electrochemistry scales down well compared to hydrotreaters



1 - Project Overview

EC hydrogenation

Electrochemical reduction (ECR) 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)
- **Raw pyrolysis oils have never been electrochemically treated**
- Project initiated with limited knowledge base to benchmark process (originally a SEED project)



Cathode

Cathode

Anode

Dehydration

Net rxn ←

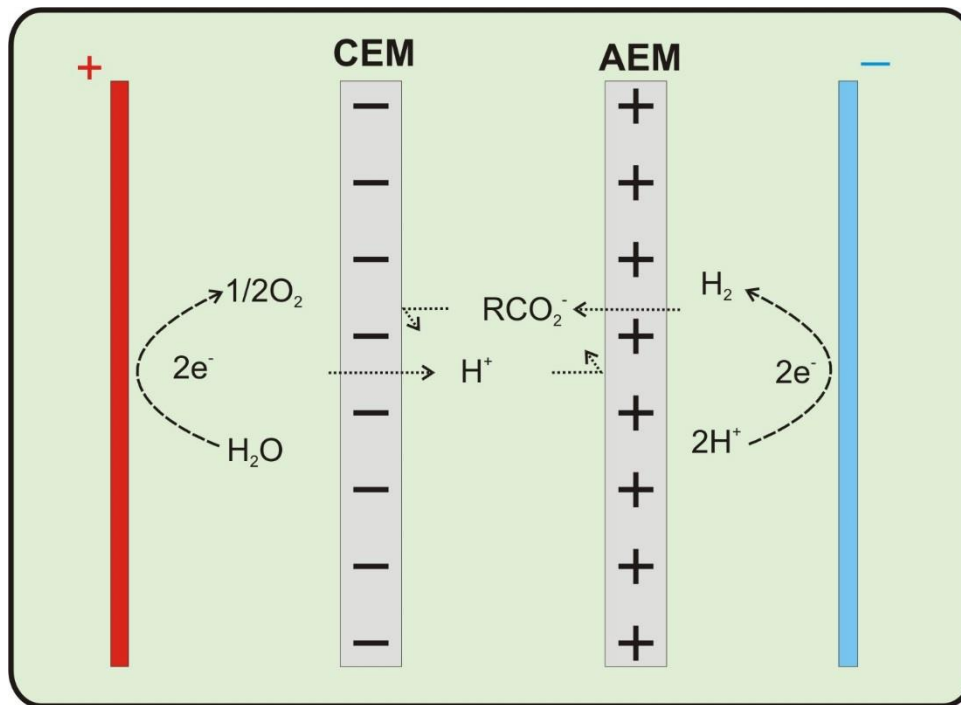
ECR enables bio-oil deoxygenation with formation of O₂ rather than H₂O (use of H₂) or CO₂ (loss of carbon)

1 - Project Overview

Electrochemical separation

Electrodialysis utilizes ion specific membranes to perform separations

- Commercial method used to selectively remove ions from solutions
- Carboxylate anions (such as acetate) are removed from fermentation broths
- Electrolysis reactions occur at anode and cathode of electrodialysis systems

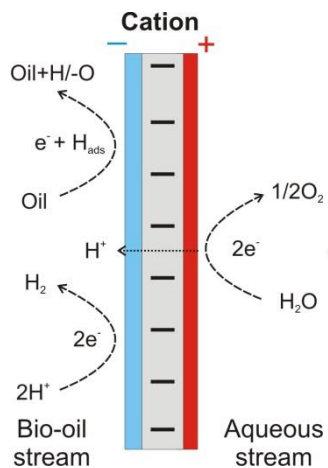


Basic electrodialysis cell

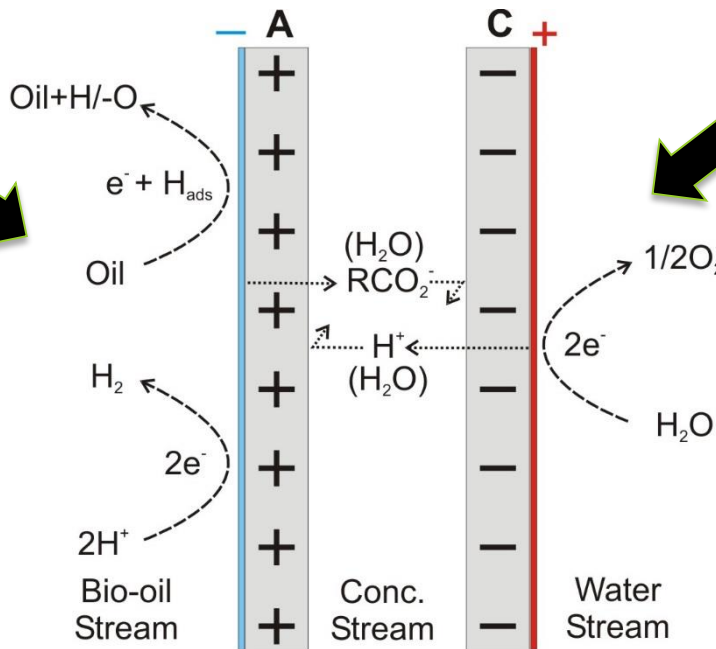
Bio-oil has low conductivity

Must use an alternative cell configuration

2 - Approach (Technical)

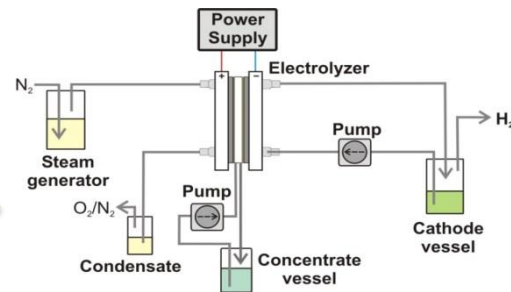


**Single Membrane Cell
(Cation Exchange)**



**Dual Membrane Cell
(Cation and Anion
Exchange)**

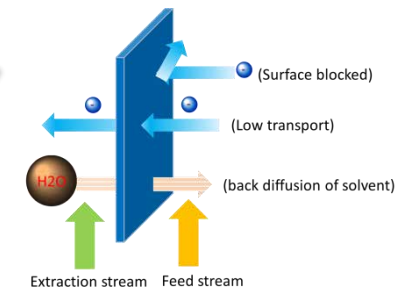
**Techno-economic
Assessment**



Organic Acid Separations



Commercialization



**Anion Exchange
Membrane Development**

**Theoretical Prediction and
Experimental Verification**

2 – Approach (Technical)

Potential benefits

- Process generates hydrogen at the point of conversion using protons in the oil
- Milder temperature and pressure and thus reduced coking
- Separation of short-chain acid molecules leading to better H₂ efficiency
- Consumption of protons should reduce corrosivity

Other secondary benefits are possible

- Excess H₂ (side product) can be used for a mild hydrotreat to complete stabilization
- Can utilize electricity derived from clean sources (solar, wind)
- Highly scalable to provide flexibility for growth

Alternate process options

- Deoxygenation by dehydration of alcohols to olefins
- Alkylation to increase carbons in the distillate range

2 - Approach (Management)

Critical Success Factors

Final process would need to demonstrate:

- *A favorable impact on cost of processing*
- *Scalability at the level needed for fuels production*

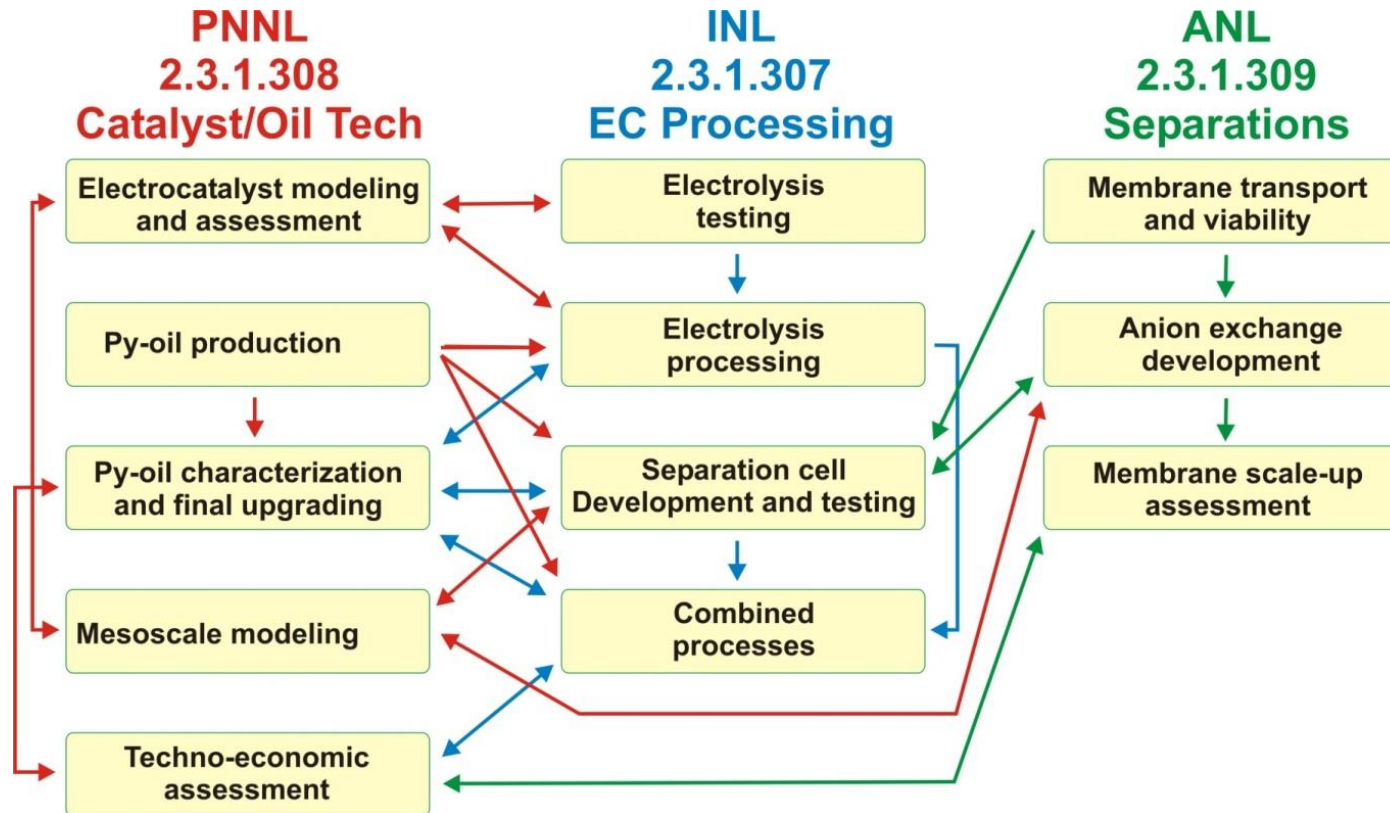
Challenges

- Demonstrate bio-oil electrochemical hydrogenation (INL)
- Develop electrode materials with reasonable current efficiency (PNNL)
- Develop anion exchange membranes resistant to bio-oil (ANL)

Strategy

- Utilize the expertise of 3 National Labs to address the immediate challenges
- Stage the development starting with a simpler cell, then adding complexity
- Develop more complex elements separately in parallel, then integrate
- Use Go/Nogo and TEAs to adjust technology development as needed

2 – Approach (Management)

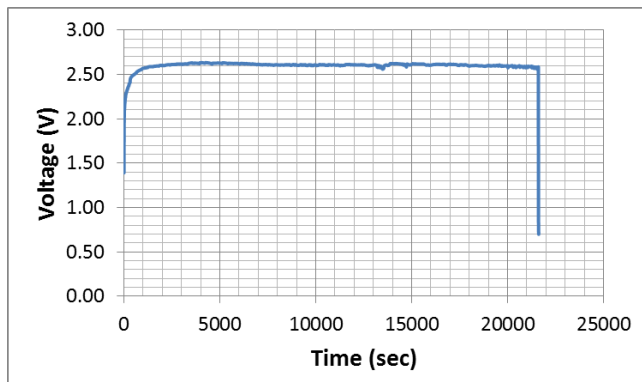
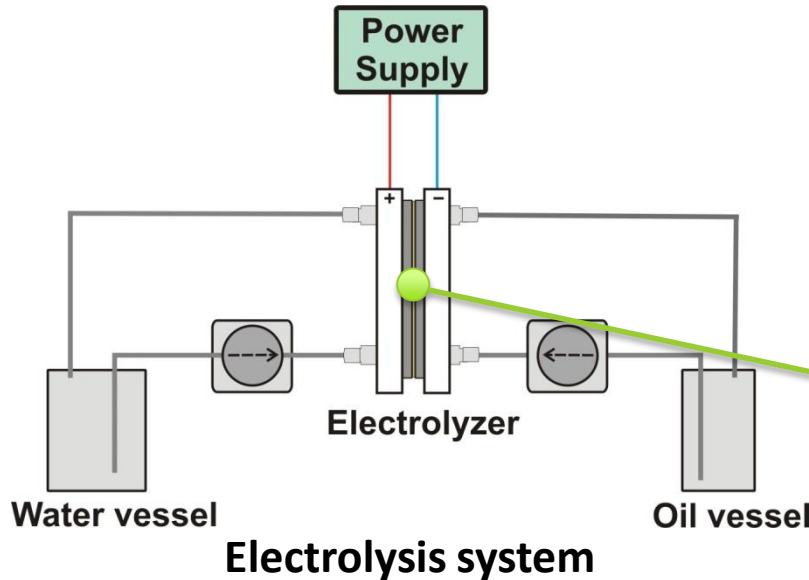


- AOPs/PMPs
- INL led the overall effort: Subtasks were fully integrated across the 3 labs
- Communications: team met regularly: influenced development
- Quarterly reporting at each lab
- Deep dives with BETO

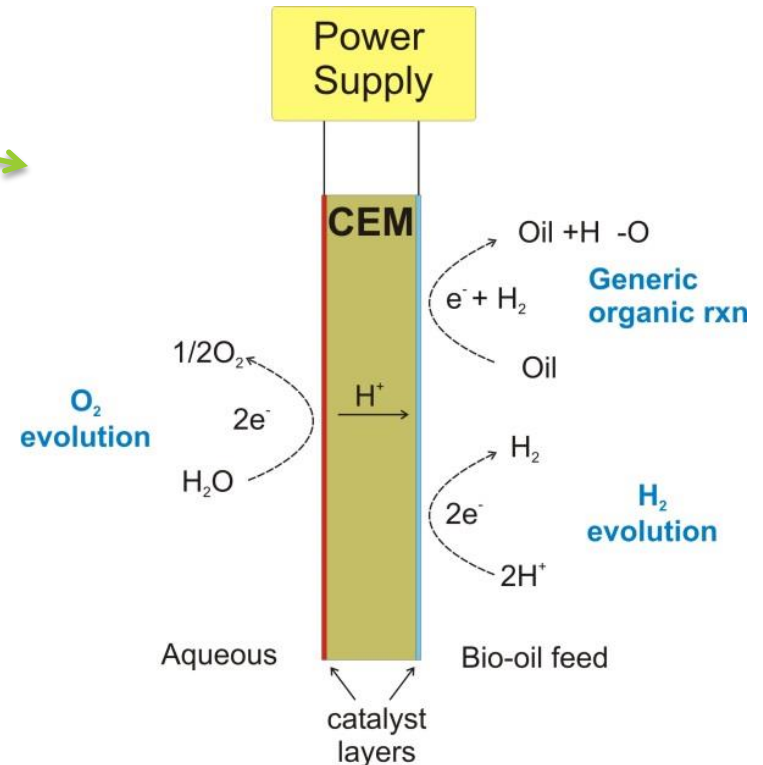
3 – Technical Accomplishments – Single Membrane Cell

Single membrane cell was used to demonstrate electrochemical hydrogenation (ECH)

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



Voltage-time plot in pyrolysis-oil

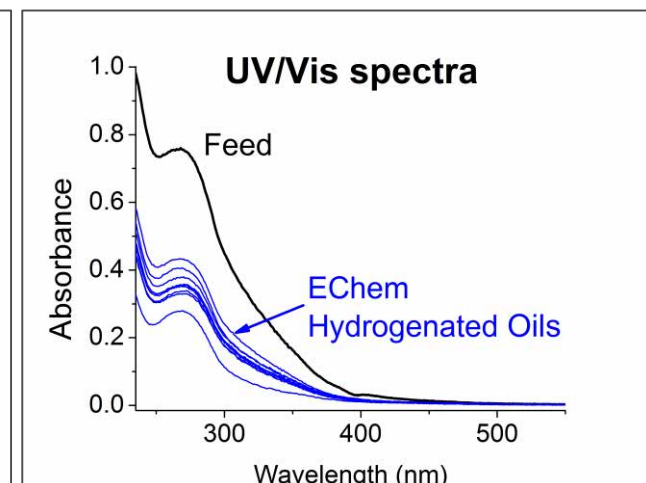
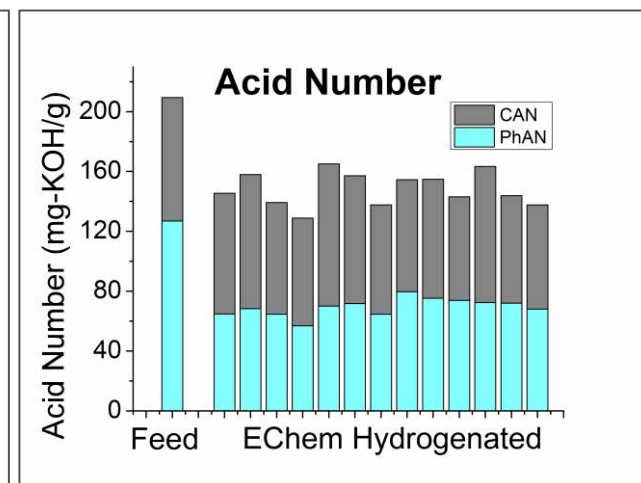
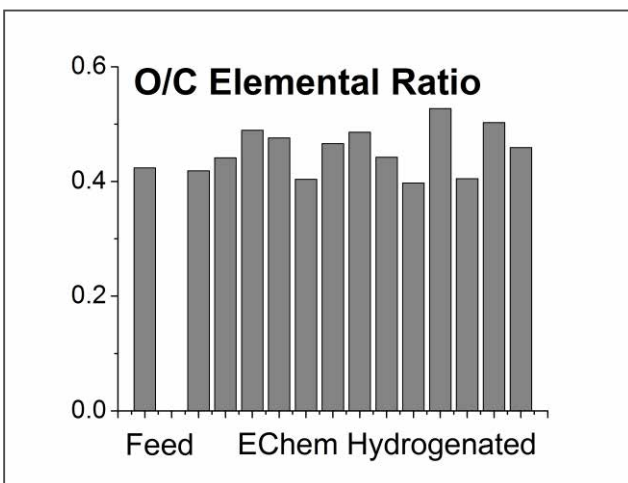
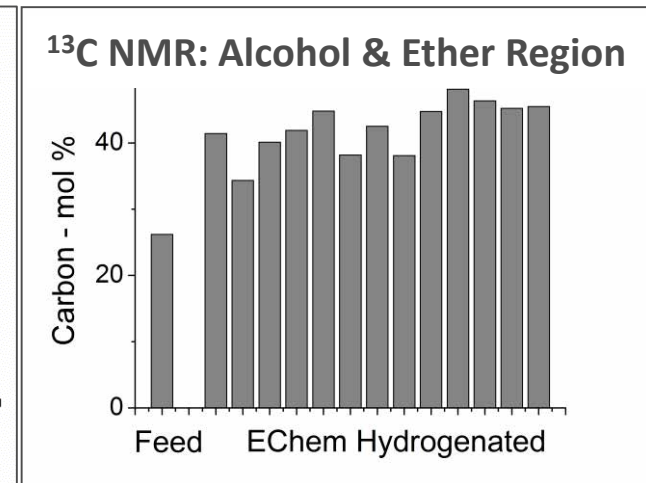
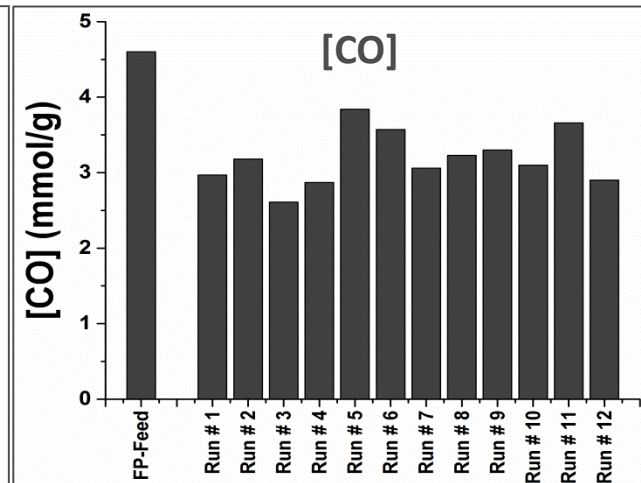
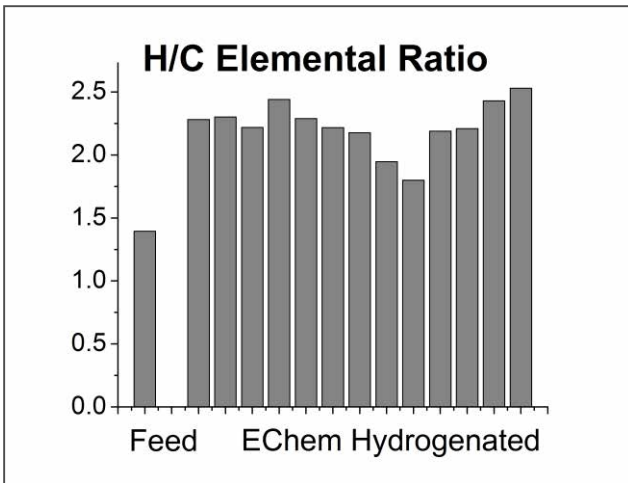


Chemical processes

3 – Technical Accomplishments – Single Membrane Cell

Analyses of ECH bio-oil: elemental, TAN, [CO], ¹³C NMR, and UV/Vis

- ECH leads to:
 - Carbonyl group reduction
 - Phenolic aromatic ring reduction
- Downstream processing:
 - Deoxygenate by simple alcohol dehydration
 - Olefins could be alkylated to improve distillate C yield

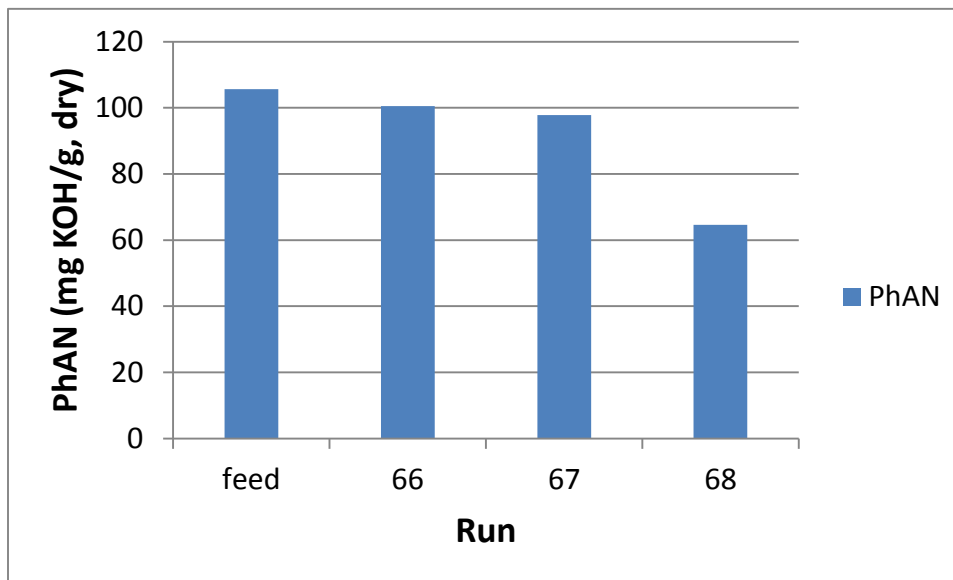


3 – Technical Accomplishments – Single Membrane Cell

Water movement into bio-oil an issue that can be solved

- Water injection through the CEM during bio-oil ECR causes phase separation
- H₂ in the anode or distillation of water slows water addition
- Addition of 5% EtOH to bio-oil feed
 - Prevents phase separation
 - Allows PhAN reduction
 - Literature: used to suppress H₂ evolution
 - Preliminary experiments need further investigation
- Phase separation was not observed in dual membrane cell operation

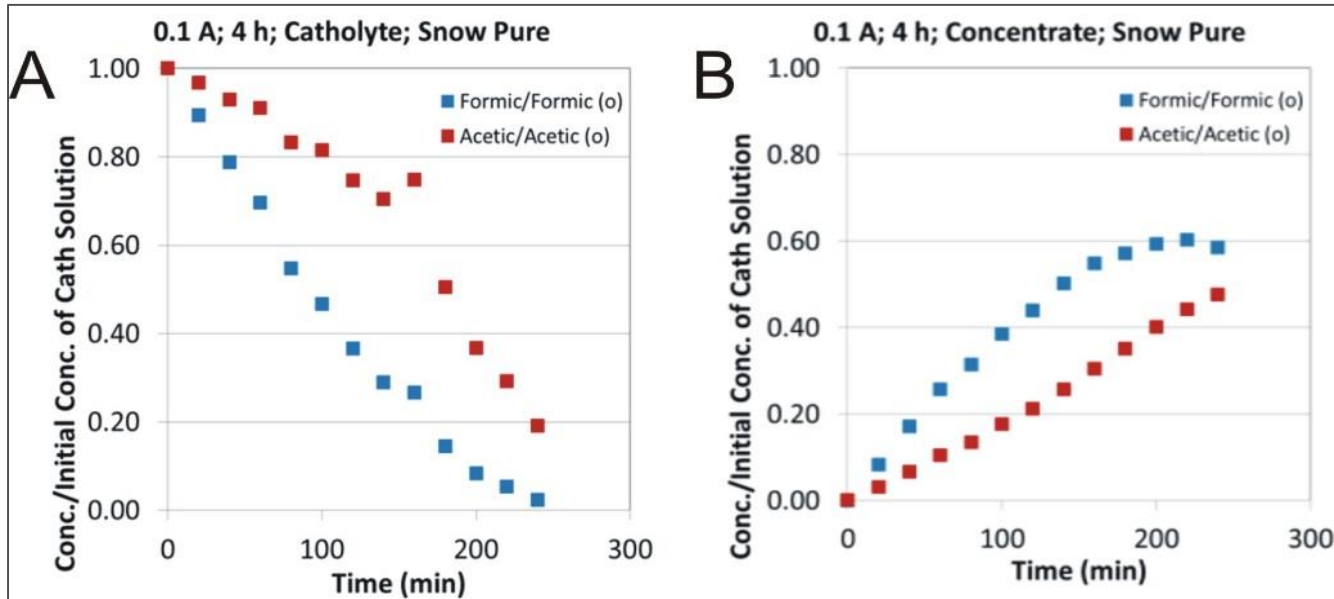
PhAN reduction in experiments with bio-oil containing 5% ethanol



3 – Technical Accomplishments – Acid Separation

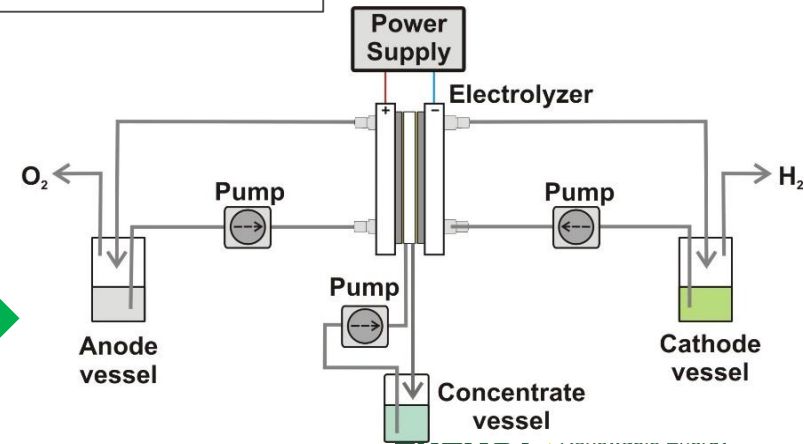
Dual membrane cell demonstrates acid removal from surrogate

Acids removed from catholyte ... and recovered in the concentrate



Ratio of measured to original catholyte concentration for acetic and formic acids as measured by HPLC. Catholyte concentrations measured in (A) and concentrate concentrations in (B).

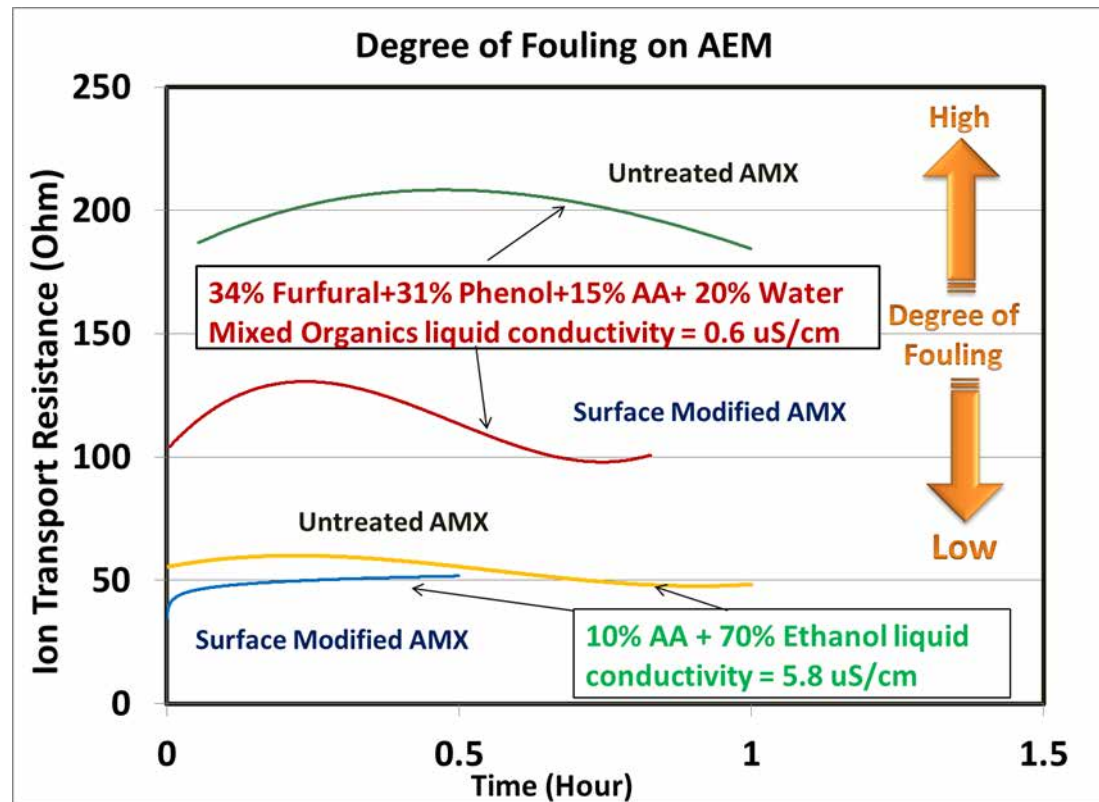
System diagram



3 – Technical Accomplishments – Anion Exchange Membrane

Fouling resistance and ion-transport properties enhanced in surface-treated AEMs

- Ion Transport resistance:
 - Un-modified AEM - Resistance **increased** in mixed organics - *surface fouling*
 - Modified surface AEM - **decreased** ion transport resistance – *reduced fouling*

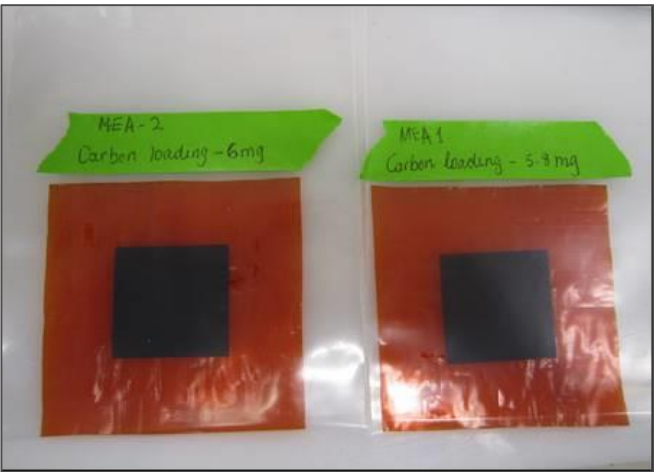


Electrochemical Fouling Monitoring

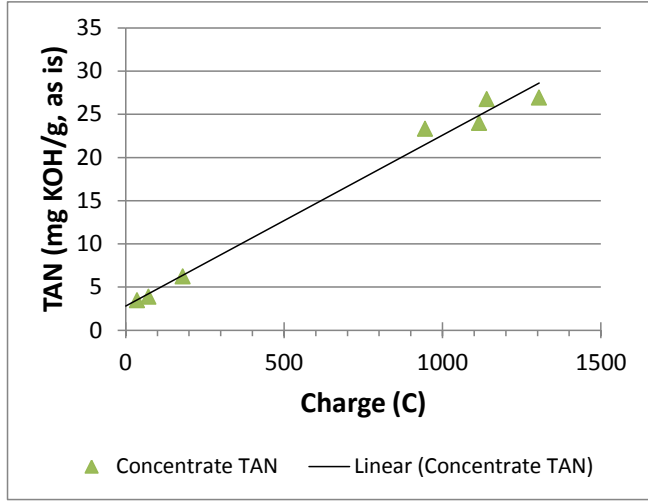
3 – Technical Accomplishments – Dual Membrane Cell

Dual membrane cell removes acids from bio-oil

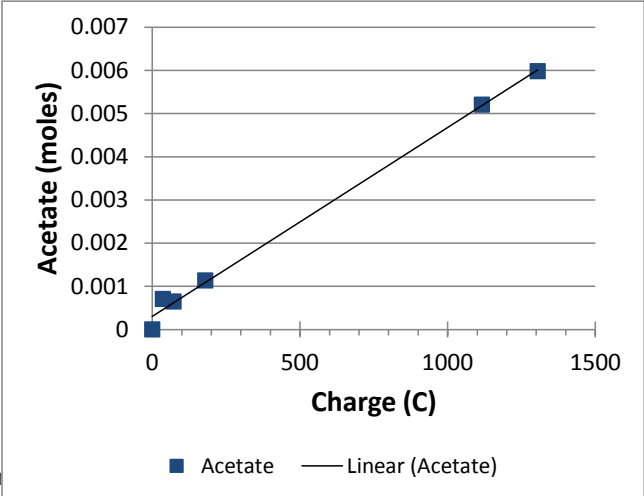
Carbon black MEA on anion exchange membrane



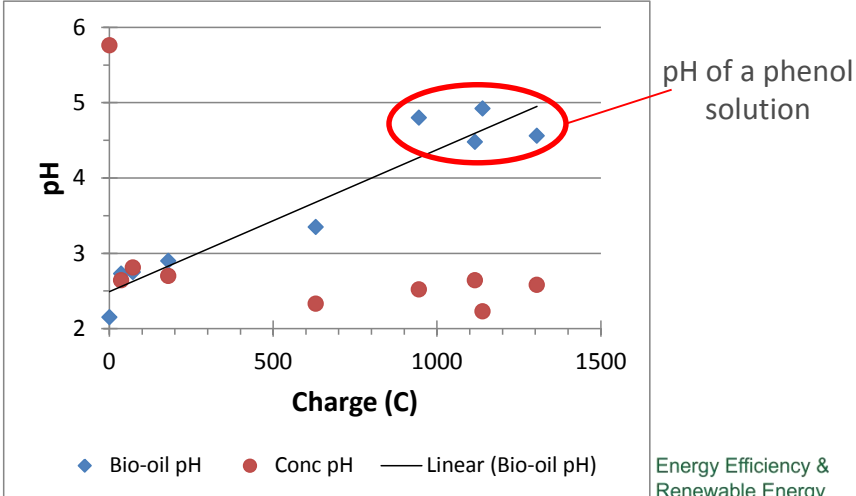
Acetic acid recovered in concentrate stream



Acetate transfers out of bio-oil



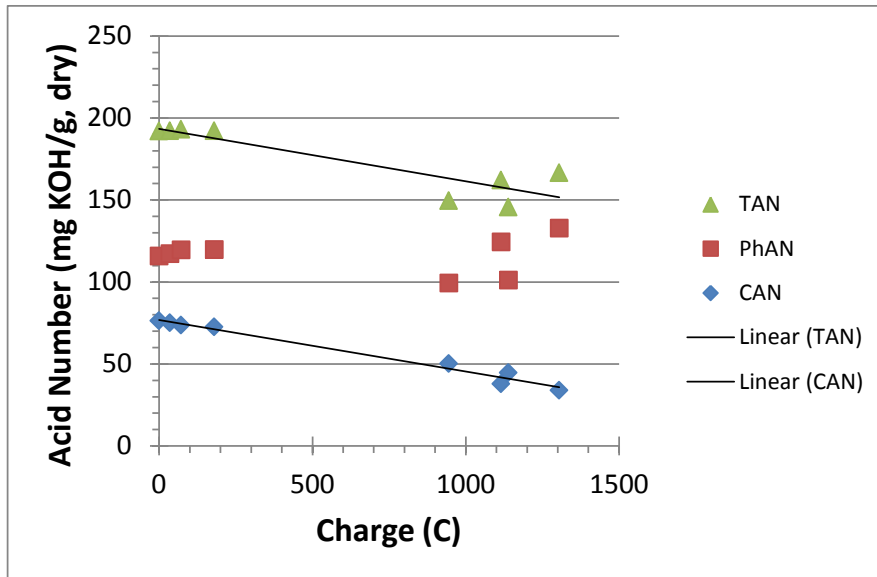
Bio-oil becomes less acidic



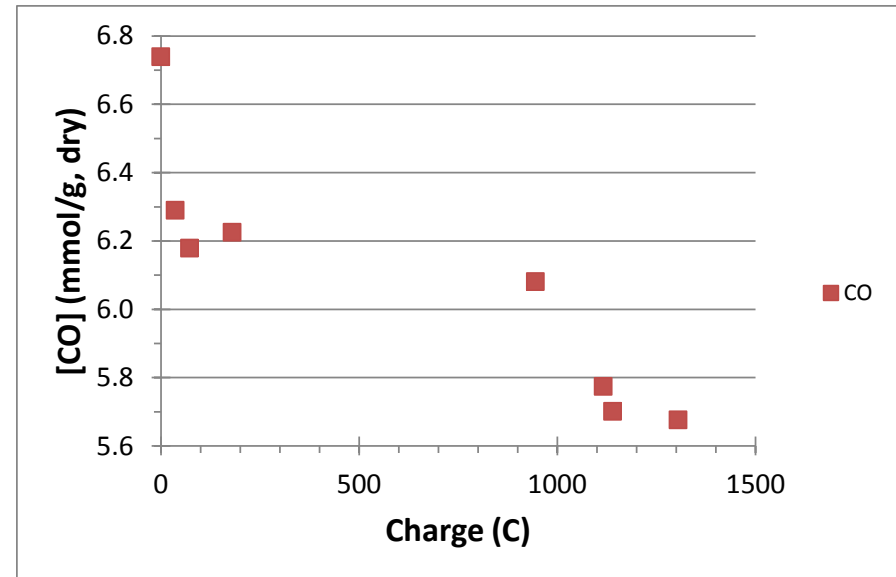
3 – Technical Accomplishments – Dual Membrane Cell

The dual membrane cell decreases TAN and reduces carbonyl groups simultaneously

Bio-oil TAN decreases



Carbonyls are reduced



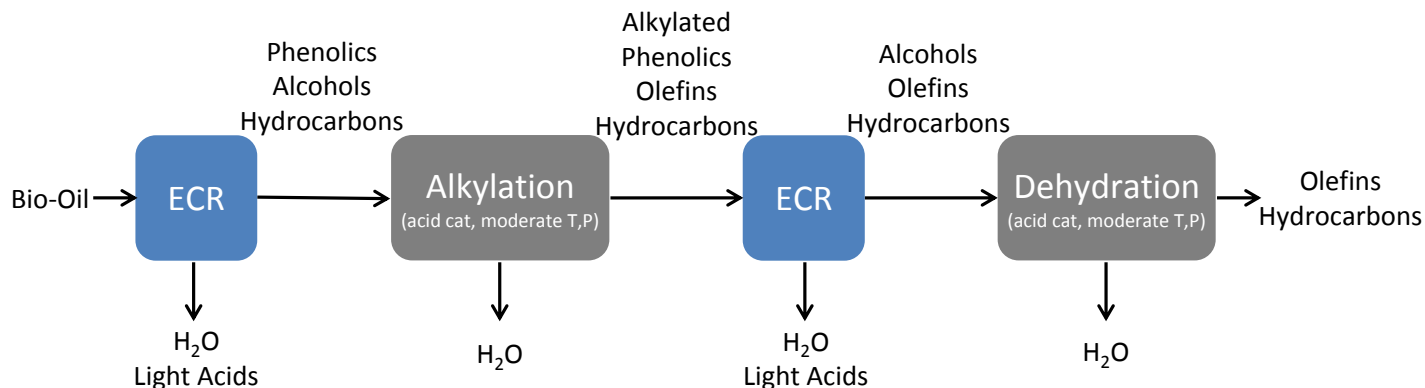
- Commercial carbon MEA (would like to repeat with Pd catalyst)
- Bio-oil is de-acidified and carbonyl groups are reduced
- Charge passed is an order of magnitude lower than in previous experiments so extent of functional group reduction is lower
- PhAN trend cannot be definitively seen in these low charge experiments

3 – Technical Accomplishments - Techno-Economic Update

The process was modeled on a 1/10 scale

- Basis: 2000 metric ton per day biomass to fast pyrolysis unit
 - As described in the 2013 design case (Jones 2013)
- Analysis: Upgrading pyrolysis bio-oil at the 200 metric ton per day scale
- Performance assumptions:
 - Product is a high quality hydrocarbon biocrude with a molar H/C ratio of 2 and an oxygen content of < 1 wt% that can then be finished in a petroleum refinery
 - Residual heat from the pyrolysis combustor is sufficient to drive the endothermic dehydration reactions
 - Purchased hydrogen is used to saturate the olefins when insufficient hydrogen is produced from the ECR

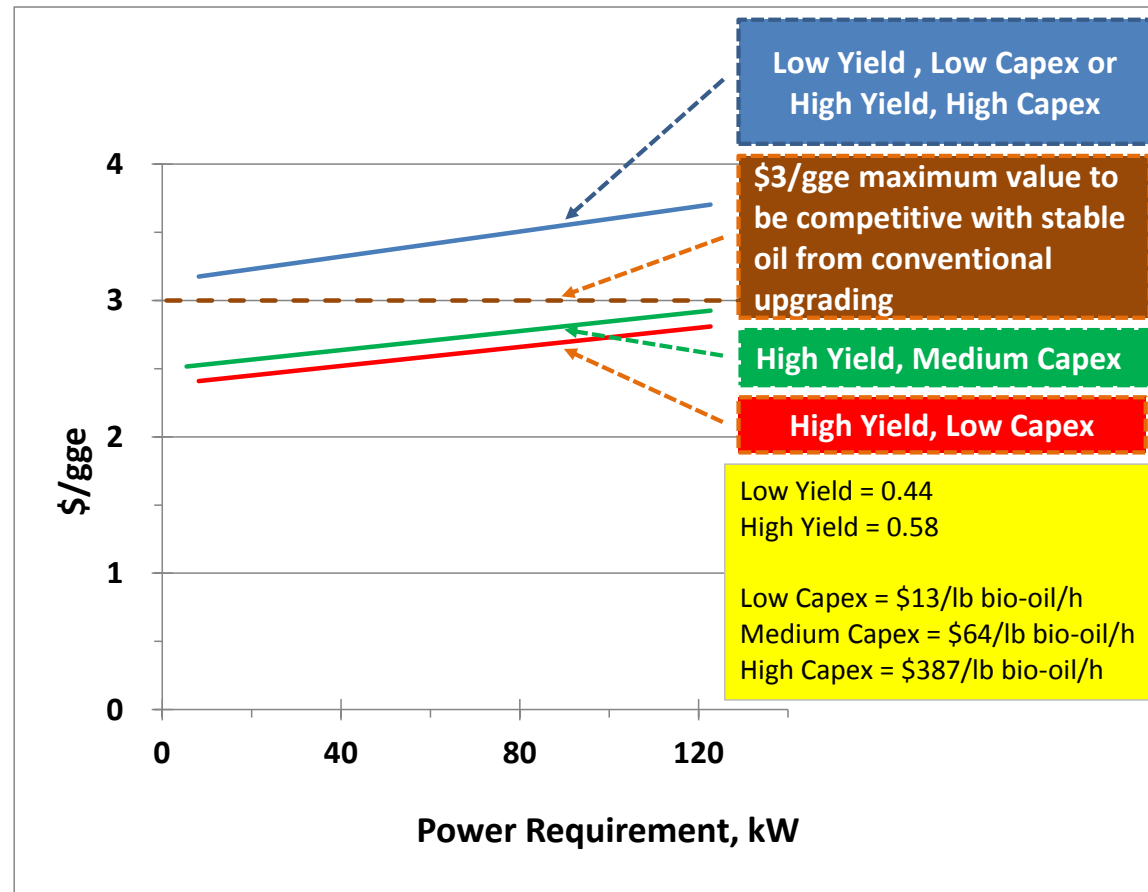
Cathodic Processing:



3 – Technical Accomplishments – Techno-Economic Analysis

Yield and capex are key drivers

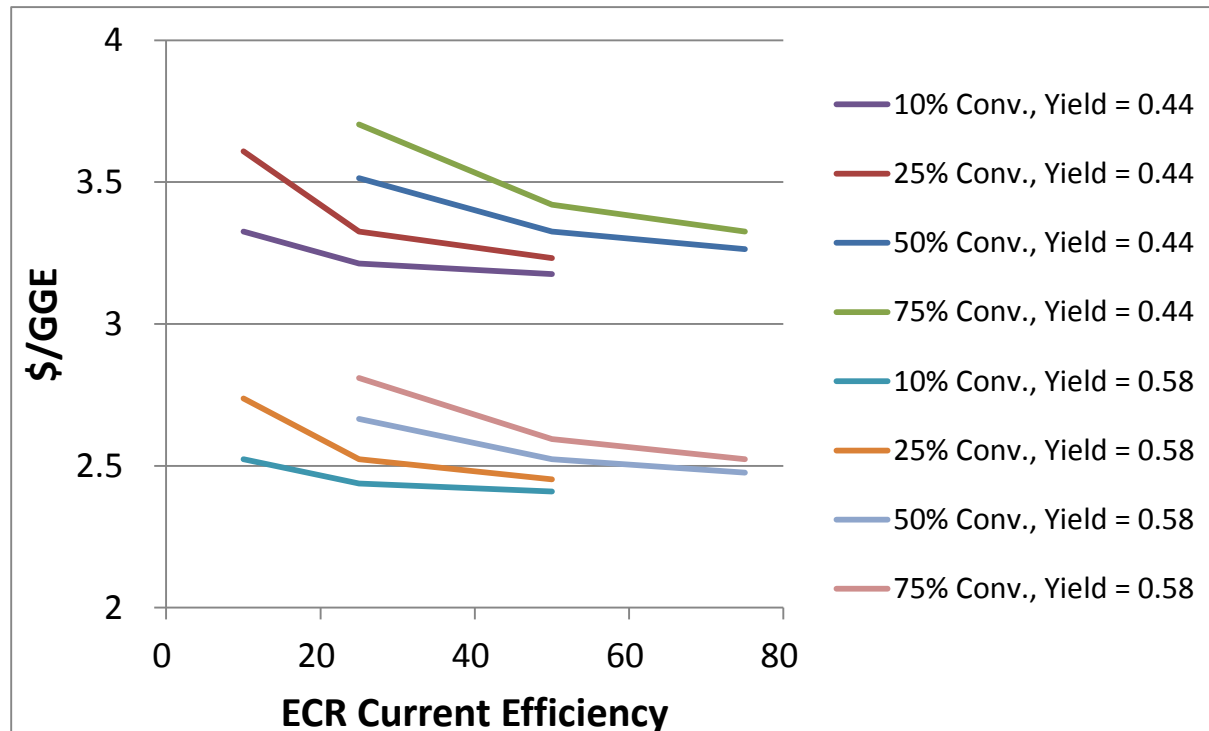
- Costs only slightly influenced by capex in the low to medium yield range.
- Lower yield = 0.44 lb hydrocarbon/lb of bio-oil organics
 - The maximum yield expected from conventional bio-oil HDO over fixed bed catalysts
- Upper end yield = 0.58 lb/lb bio-oil
 - The yield obtainable from the ECR if all the light acids are either transferred to the water phase or converted to hydrogen.
 - Assumes alkylation can incorporate light hydrocarbons into the fuel fraction
- Additional yield increases possible depending on alkylation unit performance



3 – Technical Accomplishments – Techno-Economic Analysis

Current efficiency is important – to a point

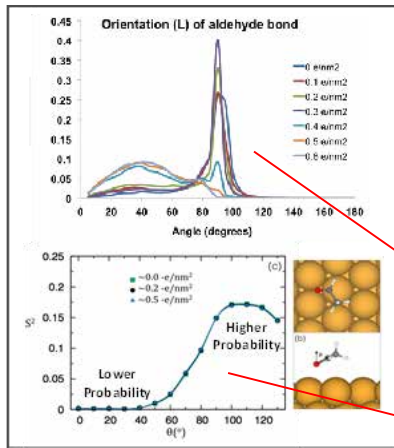
- Current efficiency determines power requirements and hydrogen generation during ECR
- Costs decrease with increasing current efficiency
- There may be a point of diminishing returns
 - Increased current efficiency may not significantly improve process economics.



3 – Technical Accomplishments - Theory

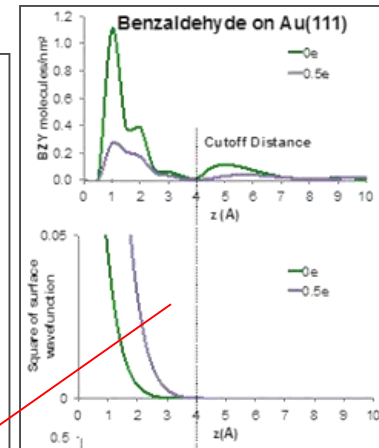
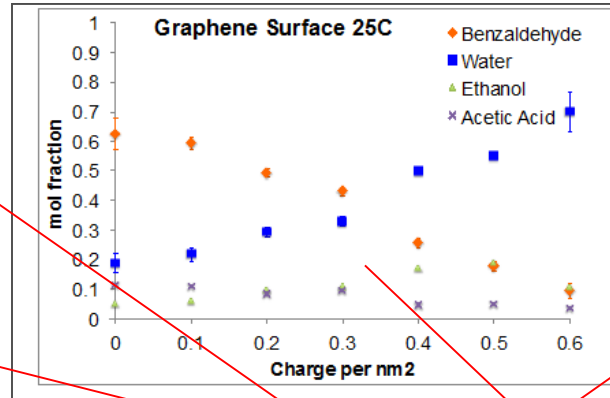
Ab initio molecular dynamics and density functional theory were used to describe electrode processes and reaction mechanisms

Applied potential moves organics away from the electrode



Orientation changes with potential

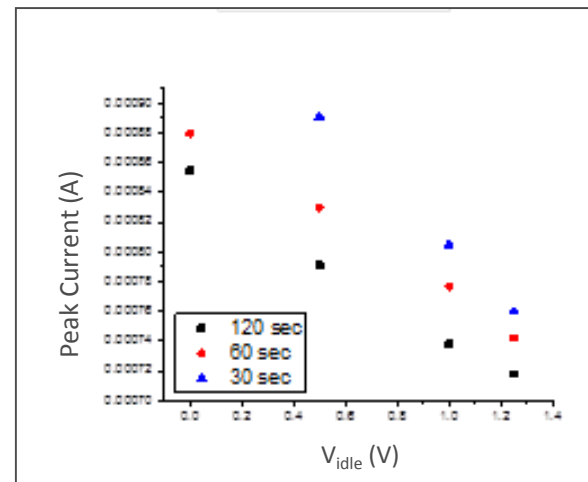
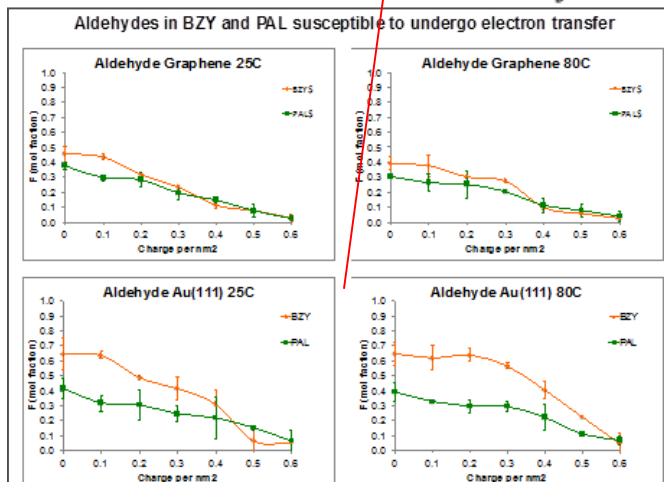
Probability of e⁻ transfer changes with orientation



Only molecules close enough to undergo e⁻ transfer were considered

$$F(q, T) = \left(\int S^2(\theta) L(\theta, q, T) d\theta \right) P(q, T)$$

A Computational First:
The population of molecules susceptible to e⁻ transfer was determined



Experimental results are consistent with theoretical predictions

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*
- Separating small organic acids that are hydrogen sinks during hydrotreating [increases hydrogen efficiency](#)
 - *Thermochem R&D priority*
- The dual membrane cell process [decreases acidity](#) and removes organic acids and may lead to 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)*
- Processing options preserved for producing higher quality fuels
- Tech Transfer/Marketability: [Patent application March 2016](#)

Summary and Lessons Learned

- Project demonstrated **carbonyl and phenolic hydrogenation**, providing new avenues to bio-oil stabilization not attainable by SOT
 - Challenge with water causing phase separation
 - Despite phase separation positive results were observed
 - Results with ethanol were promising
- Project demonstrated a **unique separation process** for bio-oil using membranes in a novel dual membrane cell
 - Removed acid and increased pH
 - Reduced C-O with carbon electrode
 - AEM appears to be the best path if developed further
- TEA shows that with higher yields **fuel production costs below \$3/gge** could be attained and co-produced hydrogen offsets low electron efficiency
 - Must have reasonable capex and good yield
- Modeling has provided **new insights** describing electrode processes that guide process development

Additional Slides

Abbreviations

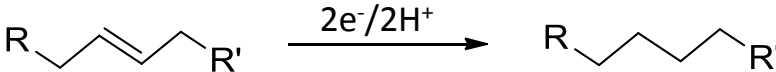
| | |
|--------|---|
| AEM | anion exchange membrane |
| ANL | Argonne National Laboratory |
| CAN | carboxylic acid contribution to acid number |
| CEM | cation exchange membrane |
| EChem | electrochemistry (process) |
| ECR | electrochemical reduction |
| INL | Idaho National Laboratory |
| NMR | 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 ECR

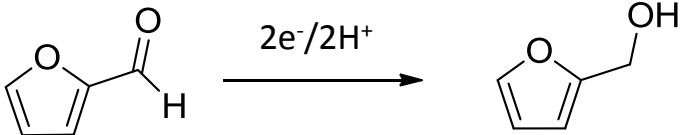
Transfer proton + electron to unsaturated organic bonds

Hydrogenations

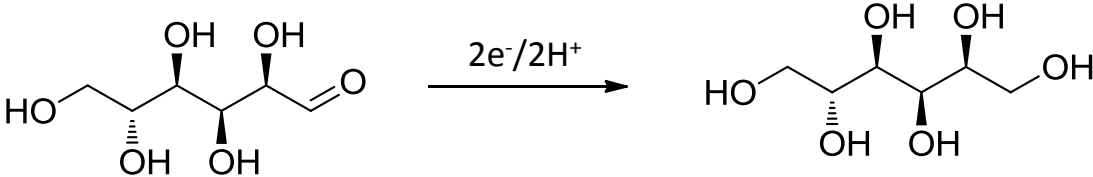
Alkene



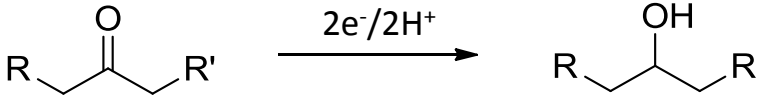
Aromatic aldehyde



Aldehyde

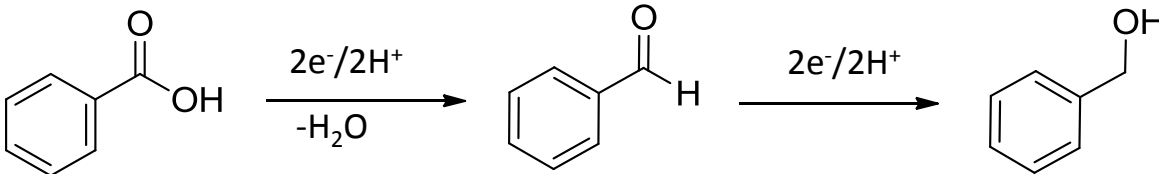


Ketone



Hydrodeoxygenation/hydrogenation

Aromatic acid



Order of Difficulty



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, *Electrochimica 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)*

Example Commercial Electrolyzers and Systems

Stack: series of electrolyzers assembled in parallel



Pressurized electrolyzer stack
Giner Electrochemical Systems

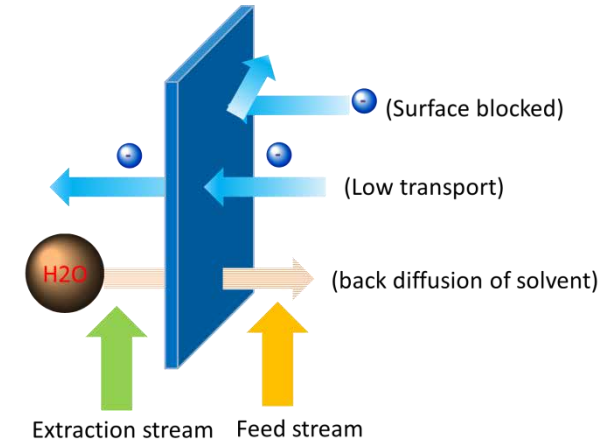


Commercial H₂ electrolyzer system

Characterization and Improvement of Fouling Resistance in Bio-oil

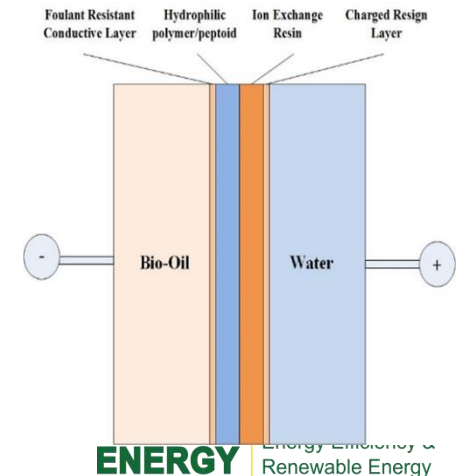
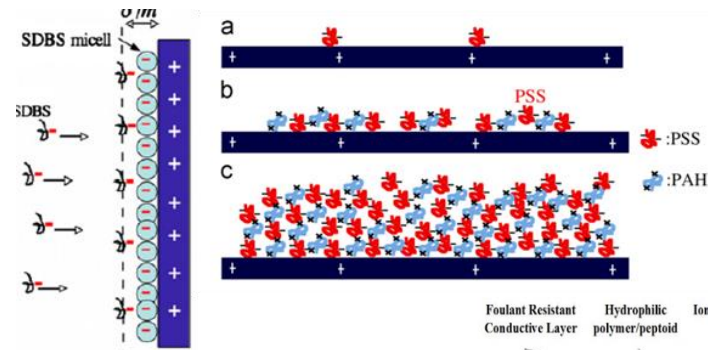
Considerations of AEM used in Bio-oil

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



Reversibility of AEM Fouling

CEM

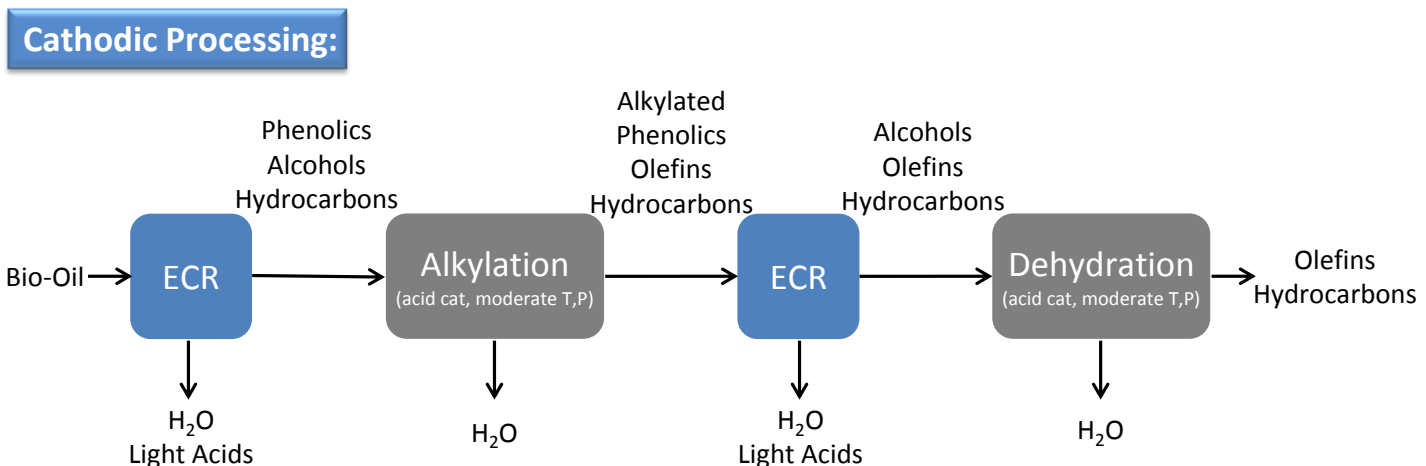
| Ionic Resistance (ohm-cm ²) of AEM in 0.5 N NaCl solution | | | | | | | |
|---|------|-----|-----|-------|-------|-----------------|--|
| Soaking Liquid | AHA | ACS | AFN | AXE | AMX | CMX | |
| Bio-oil* | 17.9 | 7.0 | 1.4 | 1.4 | 4.2 | 5.5 | |
| Aqueous | 7.19 | 6.1 | 1.2 | 1.2 | 3.8 | 5.4 | |
| Resistance 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.

TEA Update

- ▶ Basis: 2000 metric ton per day biomass to fast pyrolysis unit
 - As described in the 2013 design case (Jones 2013).
- ▶ Analysis: Upgrading pyrolysis bio-oil at the 200 metric ton per day scale
- ▶ Performance assumptions:
 - Product is a high quality hydrocarbon biocrude with a molar H/C ratio of 2 and an oxygen content of <1 that can then be finished in a petroleum refinery.
 - Residual heat from the pyrolysis combustor is sufficient to drive the endothermic dehydration reactions
 - Purchased hydrogen is used to saturate the olefins when insufficient hydrogen is produced from the ECR.



TEA - Adjustments from 2013 Design Case

▶ Capital costs:

- Eliminated stabilizer and 1st stage upgrader and auxiliaries capital costs
- Reduce size of 2nd stage upgrader (lower feed flow resulting from reduced water content and removal of small organic acids)
- Eliminated hydrogen plant
- Eliminated distillation and hydrocracking
- Added capital for electrolyzers, fixed bed alkylation and dehydration

▶ Operating costs:

- Eliminated Ru/C catalyst costs for stabilizer and 1st stage
- Reduced catalyst costs for 2nd stage upgrader because of lower fill, and lower activity catalyst (olefin saturation instead of HDO)
- Eliminated natural gas usage
- Added electrolyzer power consumption for 2 ECRs

▶ Scale:

- 2013 design case is based on processing 2000 metric ton/day biomass.
- The ECR system assessed here is 1/10th the design case at 200 metric ton/day biomass.

TEA - Cost Estimation

- ▶ Preliminary capital costs
 - Estimated using literature values for water splitting systems as published by Giner, Inc. and NREL (Cropley 2008, Hamdan 2012, Levine 2005).
- ▶ Scaled for the pyrolysis system
 - Assuming a linear scaling factor.
- ▶ Power consumption and hydrogen production
 - Estimated based on typical carbon type distributions (Venderbosch and Prins, 2010) for a range of light acid and alcohol conversion and ECR efficiencies.
- ▶ Sensitivity analysis
 - Electrolyzer cost, power consumption, membrane replacement cost and rate, purchased hydrogen and fuel yield.
- ▶ Credit
 - 50% of the purchase cost of hydrogen
 - Taken for scenarios predicting excess hydrogen production over that needed to produce a hydrocarbon product with a 2/1 H/C molar ratio.
- ▶ Feedstock
 - \$80/ton was assumed for all scenarios

Publications, Patents, Presentations, Awards, and Commercialization

Patent applications

MICHAEL A. LILGA, ASANGA B. PADMAPERUMA, TEDD E. LISTER, ERIC J. DUFEK, LUCIA M. PETKOVIC and LUIS A. DIAZ-ALDANA, *SYSTEM AND PROCESS FOR ELECTROCHEMICAL UPGRADING OF BIO-OILS AND BIOCRUDES*, Battelle Memorial Institute and Battelle Energy Alliance, [Filed March 23, 2016](#).

Presentations

L.A. Diaz, T.E. Lister, A.B. Padmaperuma, and M.A. Lilga, *Electrochemical Bio-Oil Stabilization as an Alternative for Distributed Processing of Biomass*, [AiCHE 2016 Annual Meeting](#), San Francisco, Nov. 11, 2016.

L.A. Diaz, T.E. Lister, A. Padmaperuma, M.A. Lilga, H. Job, T. Lemmon, and Q. Tran, *Electrochemical Upgrading of Bio-Oil*, Electrochemical Society 229th Meeting, San Diego, June 1, 2016.

T.E. Lister, E.J. Dufek, L. Petkovic and L.D. Aldana, M.A. Lilga and A. Padmaperuma, *Electrochemical Upgrading for Production of Fuels and Chemicals*, Pocatello, Idaho June 24, 2015.

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Publications, Patents, Presentations, Awards, and Commercialization

Presentations cont.

- Lilga MA, AB Padmaperuma, HM Job, TL Lemmon, T Lister, L Diaz Aldana, and LM Petkovic. 2015. "Low temperature electrochemical methods for upgrading bio-oils." 2015 AIChE Annual Meeting, Salt Lake City, UT
- Cantu D, Y Wang, Y Yoon, AB Padmaperuma, MA Lilga, VA Glezakou, and RJ Rousseau. 2015. "Computational Modeling of Electrochemical Bio-oil Upgrading." ACS National Meeting., San Diego, CA
- ACS symposium on "Low Temperature Catalysis" in 252nd ACS Fall meeting (August 21-25, 2016 Philadelphia, Pennsylvania) was co-organized by Asanga B Padmaperuma. One sub-topic of this symposium was electrochemical reduction of bio-oils.
- Cantu D, Y Yoon, MT Nguyen, Y Wang, AB Padmaperuma, MA Lilga, VA Glezakou, and RJ Rousseau. 2016. "Computational Modeling of Electrochemical Bio-oil Upgrading." 252nd ACS National Meeting, Philadelphia, PA.
- Padmaperuma AB, and MA Lilga. 2016. "Electrochemical reduction of pyrolysis oils" 252nd ACS National Meeting, Philadelphia, PA