2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review
WBS 3.2.2.27

TAN Control of Bio-oil

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Bio-Oil Technology Area Review

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Goal/Objective Statement

- **Goal** – Develop conversion enabling technology to remove destabilized components from bio-oil
- **Objective** - Evaluate the application of Resin Wafer Electrodeionization (RW-EDI) technology on acids/salts removal of pyrolysis bio-oil to reduce acidity and improve stability
- Address the R&D barrier of Tt-E. : Bio-Oil Stabilization
- R&D Approach WBS - Bio-oil Characterization, Stabilization and Upgrading in 3.2.2 - Develop cleanup & conditioning processes

Project Quad Chart Overview

Timeline

- Project start date – 10/2012
- Project end date – 9/2014
- Percent complete – 25%

Barriers

- Barriers addressed
  - Tt-E. : Liquefaction of Biomass and Bio-Oil Stabilization

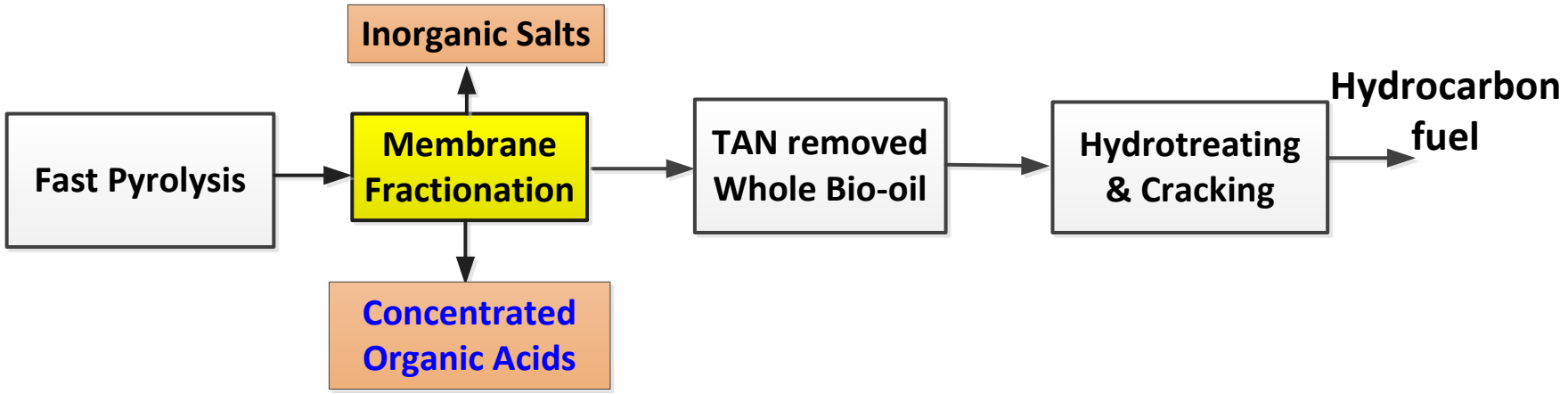
Budget

Total project funding - $200 K
Funding received in FY 2011 - $0
Funding in FY 2012 - $0
Funding for FY 2013 - $200.0 K
ARRA Funding – N/A
Years the project has been funded & average annual funding

Partners & Roles

NREL & ISU providing samples

Project Overview

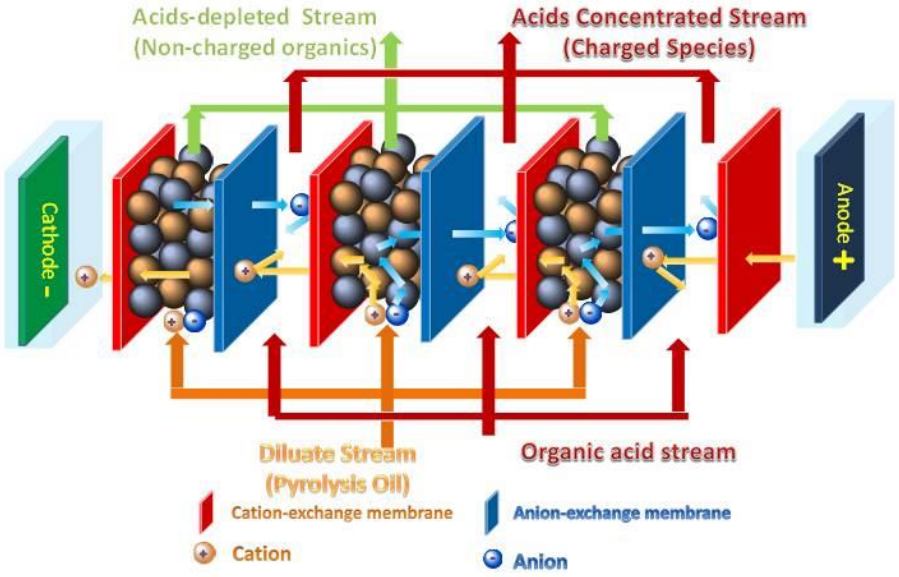


- Mitigate destabilized bio-oil for storage and transport
- Apply membrane selective fractionation to remove charged components from bio-oil – organic acids and mineral salts
- Electrically-Driven Membrane Separation with ion-exchange resin beads
  - Resin wafer electrodeionization (RW-EDI)
    - Pilot-scale demonstration for bioprocessing of organic acids
    - Near commercial technology
- Process challenge of RW-EDI applied on bio-oil
  - Membrane fouling – compatibility with bio-oil; char particles
  - Pressure drop in device due to oil viscosity

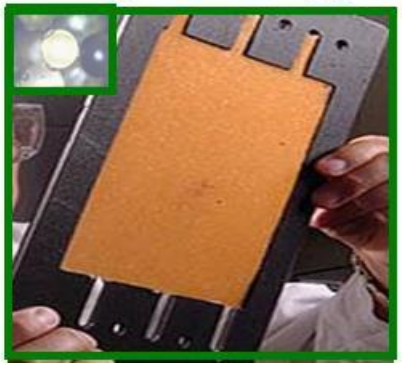
Resin Wafer Electrodeionization

Electrochemical Ion Exchange

- Uses electricity to regenerate ion-exchange resins. No Waste generated!
- Very high utilization of IX capacity (50%)
- A continuous ion exchange process
- Industrially recognized process
- New platform for chemical products separation
- High efficiency & low energy membrane separation for dilute streams



Resin wafer in sealing gasket



Resin wafer Manufacture

ANL's bench-top RW-EDI device

EDI is an enabling device for processing of low conductivity aqueous and/or organic stream

Approach

Task A Fabricate and screen resin wafers for bio-oil desalination performance
Test component compatibility with bio-oil
Task B Evaluate pulse flow microfiltration for pretreatment of bio-oil to remove char
Pretreatment procedure to protect membranes from damaged
Task C Optimize RW-EDI desalination of bio-oil
Develop process operation parameters
Task D Preliminary technical and economic feasibility analysis

Milestone A Resin wafer screening 12/2012
Fabricate resin wafers with optimal composition for bio-oil desalination
Milestone B Evaluation of pulse flow microfiltration for char removal from bio-oil – 4/2013
Evaluate technical feasibility of pulse flow microfiltration for char removal from bio-oil (Due to not enough volume of bio-oil sample received for experiments, the schedule of this task is temporarily pushed back)

Approach (cont.)

Milestone C.1 Demonstrate feasibility of de-acidifying bio-oil with RW-EDI – 7/2013

Demonstrate desalination of bio-oil to achieve pH 5 in the final effluent with > 80% salt removal.

Milestone C.2. Effects of de-acidification and char removal on bio-oil aging and stability-8/2013

Optimize RW-EDI desalination performance. Determine effects of de-acidification and char removal on bio-oil stability.

Milestone D Technical feasibility and preliminary techno-economic analysis - 09/30/2013

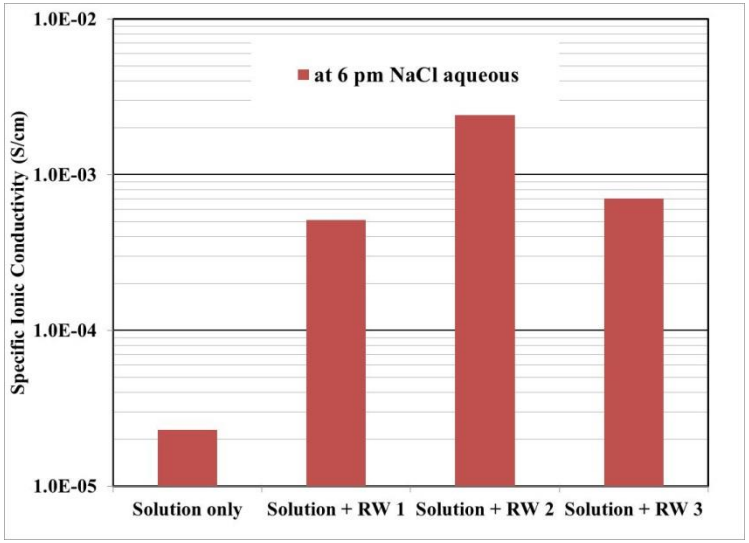
Determine technological viability. Identify potential process upsets in large scale operation. Preliminary process cost will be estimated.

Technical Accomplishments/ Progress/Results

- Completed Task A and reached milestone A
  - Fabricated resin wafer with different compositions and porosities
  - Evaluated compatibility of ion-exchange membranes to bio-oil
- Task B is postponed due to not enough volume of bio-oil sample for test
- Progress in Task C
  - Established data collection procedure to access the influence of TAN on bio-oil stability and aging
  - Completed preliminary tests of process operating parameters
  - Developed process evaluation procedure

Accomplishments/Progress & Results

- Fabricated resin wafers - various cation/anion exchange bead ratios and wafer porosities.
- Characterized wafers properties - ionic conductivity of the resin wafers; porosity
- Evaluated compatibility of ion-exchange membranes in bio-oil



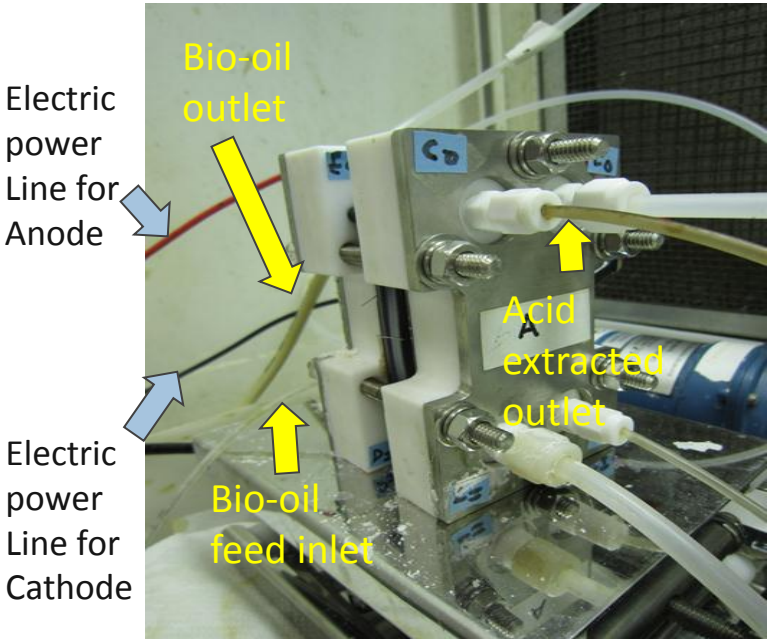
Ionic Resistance (ohm-cm^2) of membranes in 0.5 N NaCl aqueous

Two weeks immersed in	Bipolar (cat+An-EX)	CMX (cation-EX)	AHA (anion-EX)	AFN (anion-EX)	ACS (anion-EX)
Bio-Oil	11.1	5.45	17.9	1.382	5.99
Water	7.1	5.24	7.193	1.209	6.09
Changed %	56%	4%	149%	14%	0%

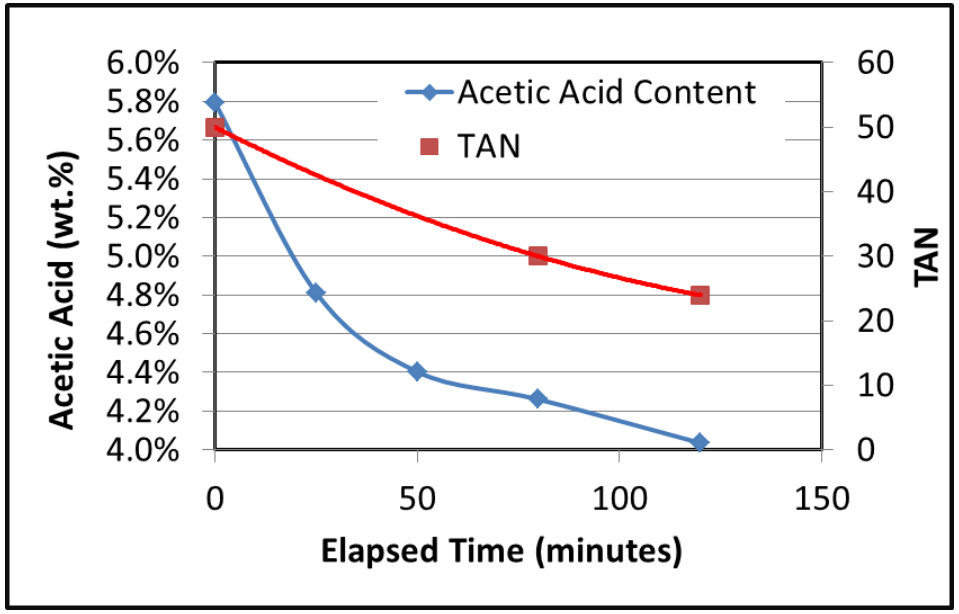
FP bio-oil of Oak

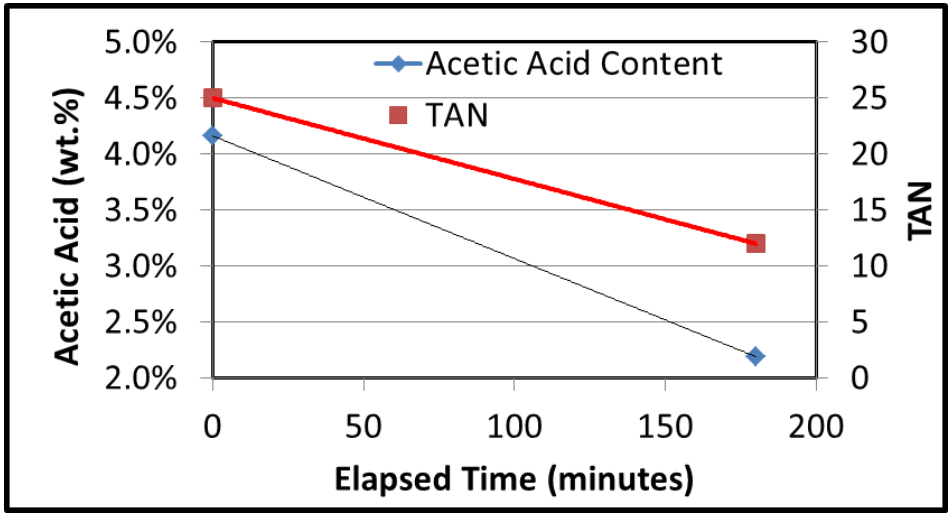
Accomplishments/Progress & Results

- Preliminary evaluation of acid extraction using RW-EDI
- **Without** bio-oil pre-filtration
- 30 – 50 % acid reduced
- Bio-oil kept at 40°C
- Identify operation issues
- Develop clean-in-place method



Exploratory-scale RW-EDI (42 cm^2 membrane area)





Relevance

- Preliminary results show the potential for RW-EDI technology to reduce the TAN of bio-oil. It addresses the R&D barrier of pyrolysis bio-oil stabilizing for conversion technology
- This technology can be applied to the aqueous phase of bio-oil to recover/utilize the carbon (as organic acids) in the aqueous.
- If this technology is demonstrated to be economically viable, it can become an important unit operation to control the bio-oil TAN and recover organic acids as a valuable byproduct. The separate acids can be upgraded into fuels or used to produce hydrogen to improve the carbon as well as hydrogen efficiency

Critical Success Factors

- The critical risks are the membrane fouling and high pressure drop during operation due to the high viscosity of bio-oil.
  - The fouling can be mitigated via the standard clean-in-place procedure
  - Anti-fouling coating on membrane surface is another way to resolve the issues
  - Increase porosity of resin wafer may reduce the pressure. Alternate is to add short-chain alcohol in the crude bio-oil to reduce the viscosity.

- Potential impact -

✓ Acid-free bio-oil will more closely resemble the crude oil, thereby enabling effective and efficient use of petroleum refining technology and processes for bio-oil processing. It can shorten the time to deployment of pyrolysis-based biofuel technology

✓ Organic acids present difficult technical challenges for the different unit operations and upgrading processes used in every pyrolysis-based biomass pathway. This technology can potentially eliminate them as show-stoppers to the economic production of biofuels via pyrolysis routes.

Future Work

- Evaluate the effects of TAN and char contents on bio-oil stability and aging. Determine the threshold level of TAN for corrosion, stability and aging issues.
- Determine technical feasibility to reduce TAN below the threshold level with more than 80% salt removal (milestone C1).
- Assess economic viability
- Perform long-term process operation to assess potential process upsets

Summary

- Relevance : Acid removal from bio-oil can provide an solution to storage and corrosion as well as upgrading challenges
- Approach: We will determine technical feasibility of acid removal using RW-EDI and study the effects of acid on bio-oil stability
- Technical accomplishments: Establish operation parameters and procedure to reduce TAN from bio-oil using RW-EDI; TAN reduction was observed
- Future work: will resolve operation issues and evaluate the effects of TAN on corrosion, stability and aging issues.
- Success factors and challenges: membrane fouling mitigation and reduction of high pressure are the priority.
- Technology transfer: N/A