2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Presentation Template

Separations/Separative Bioreactor

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Technology Area Review: Biochemical Conversion

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Organization: Argonne National Laboratory

Goal Statement

- **Pretreatment using new separations platform**
  - Technical feasibility and benefit of using integrated separation platform to optimize the hydrolysis pretreatment process -
    - Low-energy slurry separation
    - No waste gypsum generation and handling
    - Reduce process time
    - Less water usage (1/4 ~1/3 less water)
    - Inorganic acid recycle (Less chemical usage)
    - Recover value-added organic acids
    - Higher sugar titers
    - Favorable conditions for enzyme hydrolysis (removal of toxic by-products from hydrolysis conditioning step)

- Address the R&D barrier of Bt-I : Cleanup/Separation

Quad Chart Overview

Timeline

- Project start date – July 2004
- Project end date – September 2013
- Percent complete – 95%

Barriers

- Barriers addressed
  - Cleanup/Separation
  - Biological Process Integration
  - Co-product

Budget

- Funding for FY11($1,409 K/$0)
- Funding for FY12($750 K / $0)
- Funding for FY13 ($30K / $0)
- Years the project has been funded / average annual funding.

Partners

- ADM for co-product
- Nalco for commercialization
- NREL for hydrolysate

Project Overview

- **Project Background –**
  - Early work at Argonne on HFCS desalination (DOE ITP)
  - Internal work on immobilized enzymes for conversion and recovery (LDRD)
  - Funding initiated by OBP in late FY2004
  - CRADA executed with ADM FY2005
  - License executed with Nalco FY2012
- **Biochemical Platform - Overall Goals and Objectives**
  - Demonstrate the integrated biorefinery for economical production of biobased chemicals and biofuel
    - One-step production and capture of pure organic acids from bioreactor without neutralization during fermentation
    - Demonstration of the separative bioreactor as a platform unit operation for integrated biorefinery
    - **Produce commercial-grade products from sugars**
    - **Minimize capital costs**
    - **Commercial validation of a new separation platform**

Project Overview (cont.)

- **Biochemical Platform- Overall Goals and Objectives**
  - Demonstrate the integrated biorefinery for economical production of biobased chemicals and biofuels
    - Separation of mineral acids after weak acid hydrolysis
    - Recovery and reuse of sulfuric acid
    - Separation of acetic acid to improve enzyme hydrolysis
    - Avoid neutralization, overliming, gypsum production , and calcium inhibition.
    - Separation of liquid hydrolysate from sludge

Approach

Task O – Pilot-scale demonstration of RW-EDI de-acidification of liquid hydrolysate from dilute acid-treated corn stover slurry (FY11)

Task Q – Validation of integrated membrane separation of lignocellulosic pretreatment (FY12)

Task R – Develop fabrication technique for 3rd generation ion-exchange resin wafer (FY13)

Task S - Evaluation of multi-cell RW-EDI stack performance and techno-economic benefits using new generation resin wafer in acids separation of liquid fraction hydrolysate (FY13)

Milestone O: Pilot-scale demonstration of RW-EDI membrane separations for mixed cellulosic sugar acid hydrolysis slurry treatment (09/2011)

- >97% inorganic acid removal from liquid hydrolysate of corn stover

Milestone Q: Determine commercial viability of integrated microfiltration/RW-EDI for acid hydrolysis pretreatment (09/2012)

- Estimate processing cost of removing >97% inorganic and >75% organic acids

Milestone R: Demonstrate an optimized resin wafer fabricated by new fabrication techniques (03/2013)

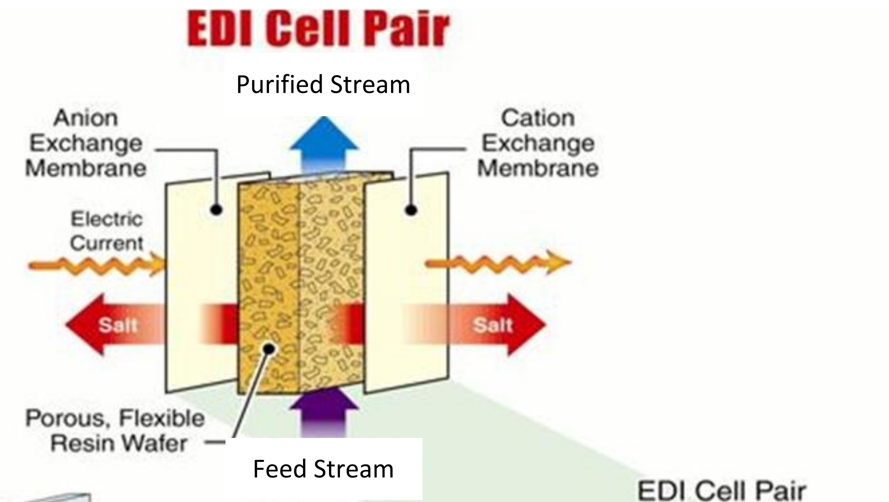
- Improved ionic conductivity

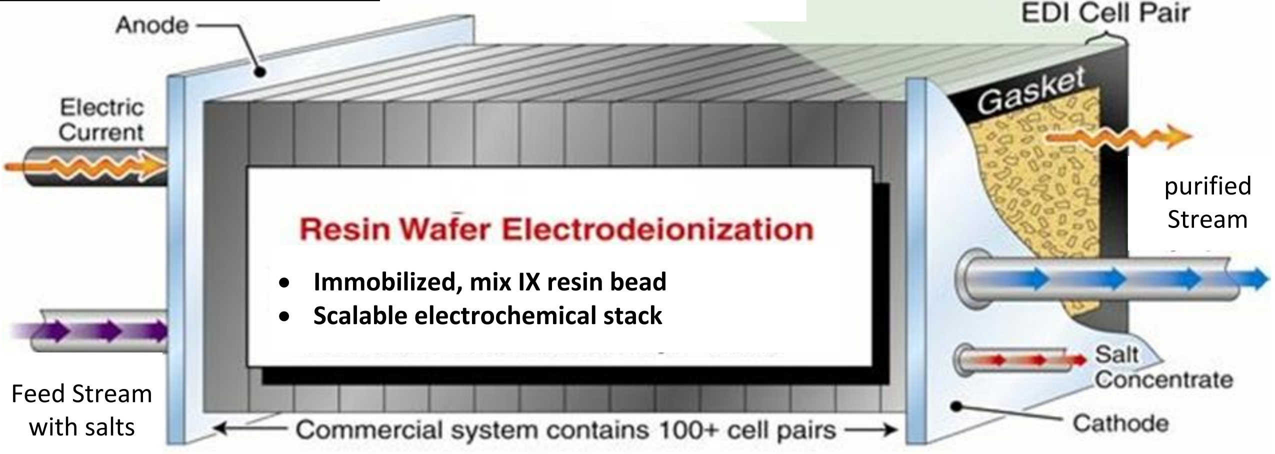
Milestone S: Demonstrate increased acid removal productivity of a synthetic hydrolysate liquid fraction using 3rd G resin wafer and document economic benefits. (09/2013)

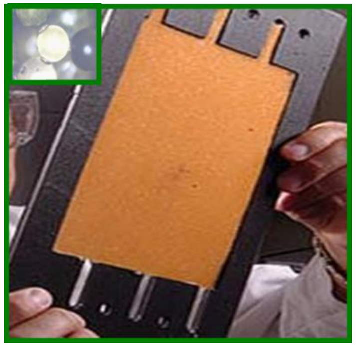
- Electric power consumption <2.0 kWh/lb SA and > 80g/m^2/hour acid removal productivity

Resin Wafer Electrodeionization (RW-EDI)

- Electrochemical Ion-exchange process
- High efficiency & low energy membrane separation for dilute ionic streams
- Easily tuned RW properties enhance performance and consistency
- Special components with desirable chemical properties can be incorporated into the resin wafer
- RW reduces R&D time for new developing applications



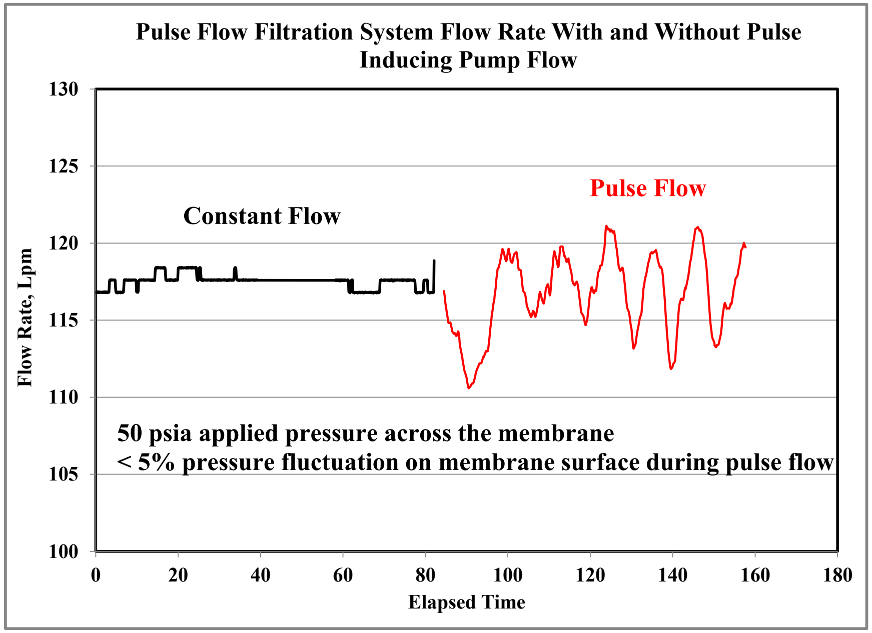




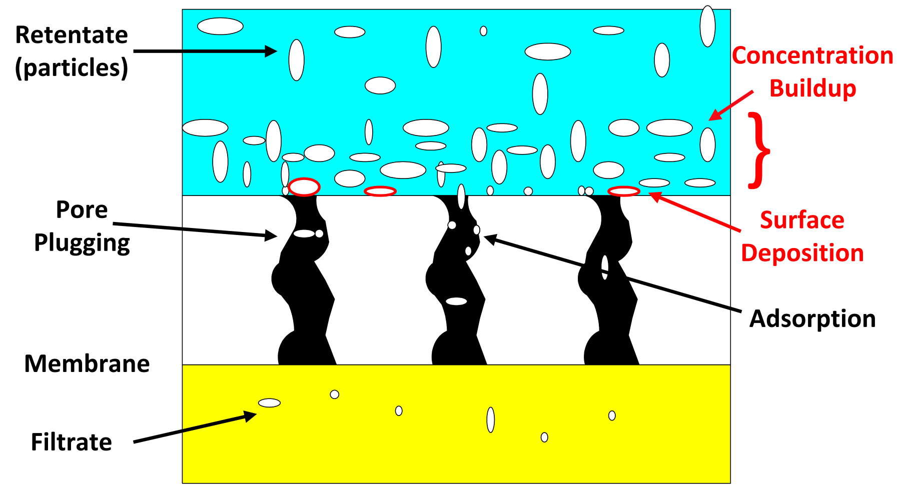
Resin Wafer Used in EDI

Pulse Flow Microfiltration

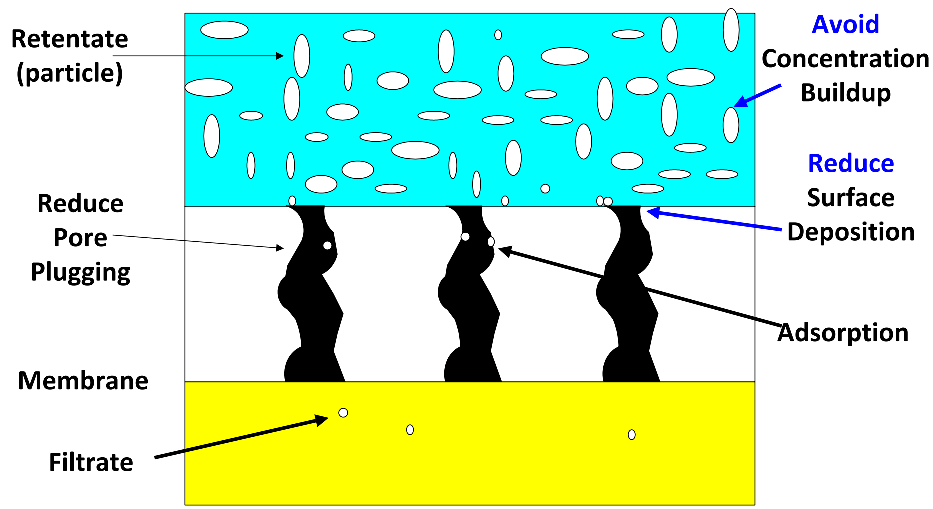
- Proprietary pulse flow generator system
- Low pressure-swing pulse flow
- Mitigate localized deposit buildup
- Reduce permeate flux decline rate
- Extend service time of membrane separation



Fouling Relates to Concentration Buildup Near The membrane Surface



Perturbation of Solutes Near Surface by Pulse Flow to Mitigate/Slow the Fouling relates to Concentration Buildup

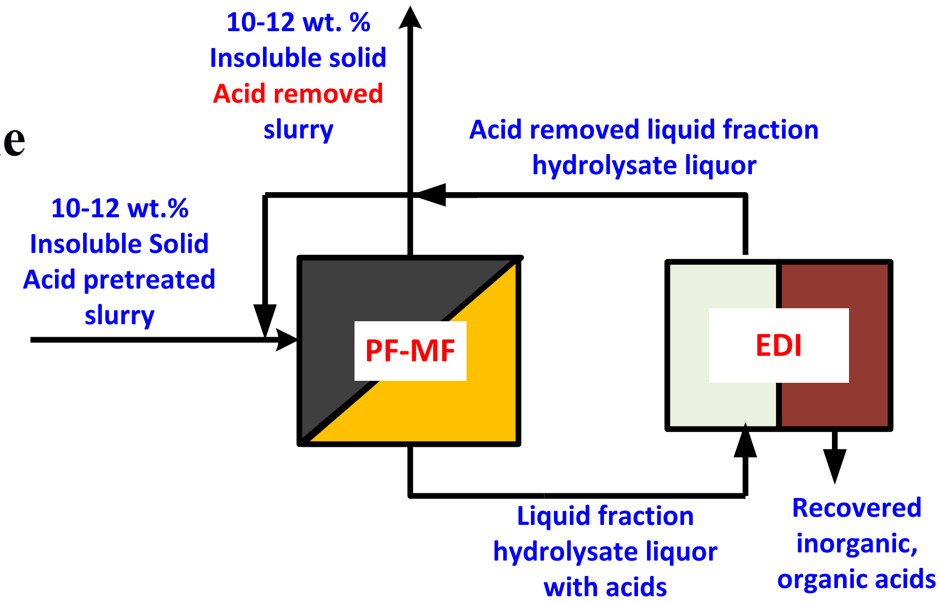


Accomplishment

Task Q - Validation of integrated membrane separation

Process Design of Integrated Membrane

- Integrated Membrane Separation
  - Solid/Liquid + De-acidification
- Continuous acid extraction from hydrolysate sludge
- Avoid solid cake formation
- Avoid extra water addition



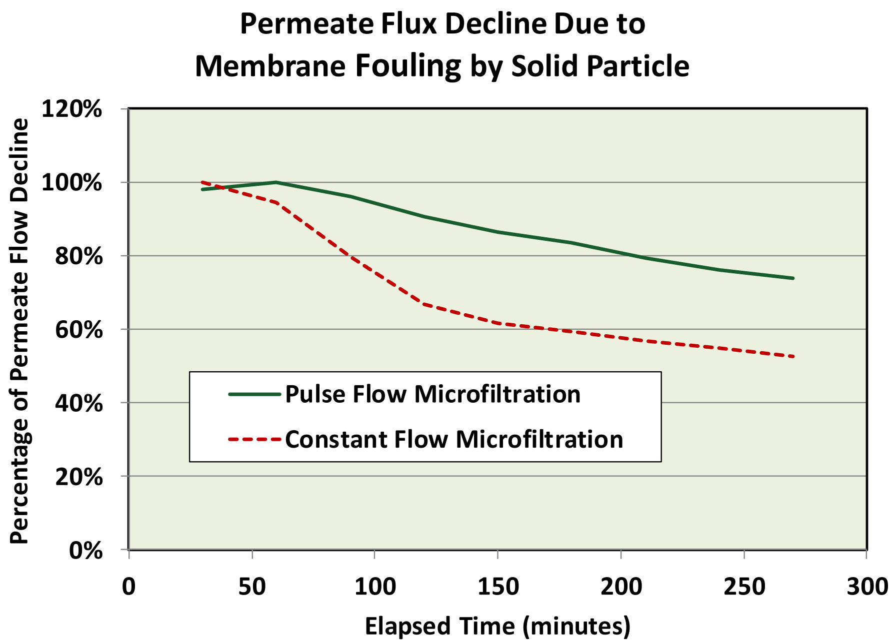
New pulse-flow filtration system

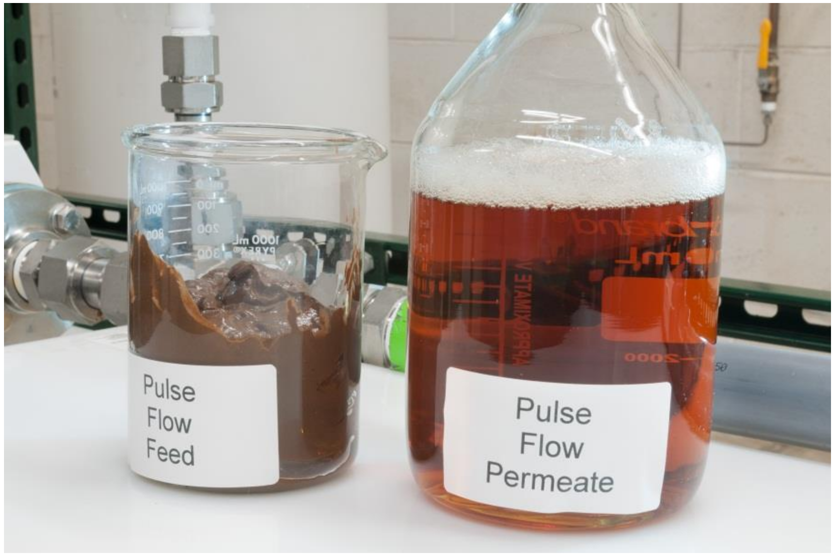
- Proprietary pulse flow generator
- Increase the capability of separating the streams up to 15wt.% solid slurry
- Installed 0.1 um membrane microfiltration

Address barrier of clean & separation (Bt-I)

Accomplishment

Task Q - Validation of integrated membrane separation





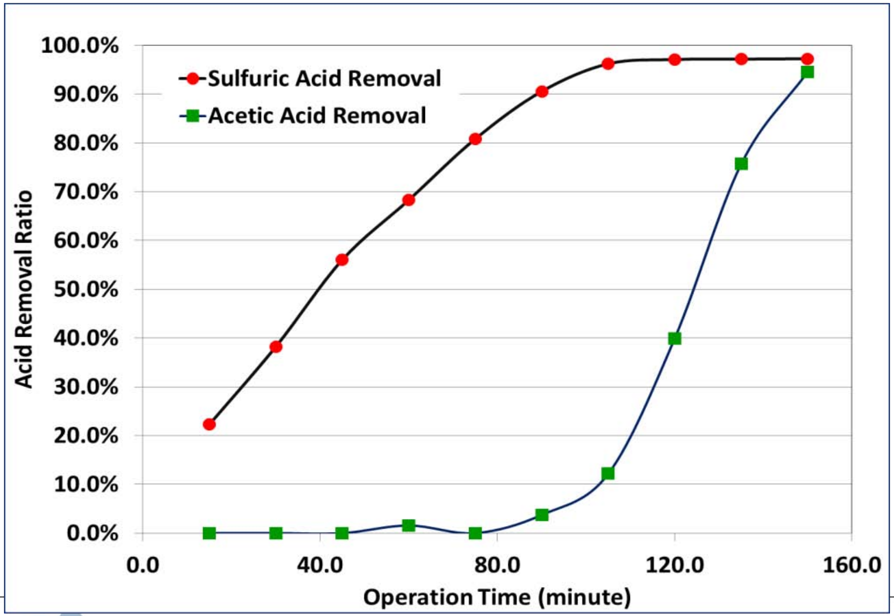
Pulse flow liquid extraction

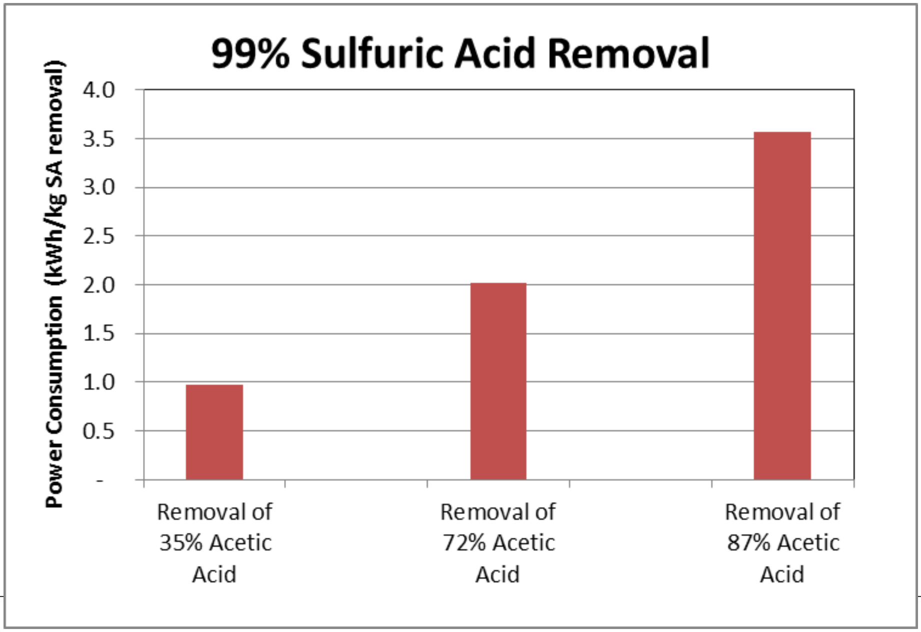
- Pulse flow mode can reduce the permeate flux decline rate
- Average ~ 20% enhanced permeate flux compared to constant flow separation
- Demonstrated feasibility of liquid extraction from 15 wt.% sludge
- Solid deposit on membrane surface can be cleaned
- The permeate liquor can be use directly in RW-EDI de-acidification!

Accomplishment

Task O - Pilot-scale demonstration of acid removal from hydrolysate liquid fraction of corn-stover

- 25% saving of total water used
- 30-35% fermentable sugar titer increased
- Recycle sulfuric acid
- Enhance stream conditions for enzyme hydrolysis
- Estimated operation cost 9c/gal ethanol to remove 99% Sulfuric acid and 75% Acetic acid
- Address barrier of clean & separation (Bt-I in MYPP)





Accomplishment

Task Q - Validation of integrated membrane separation

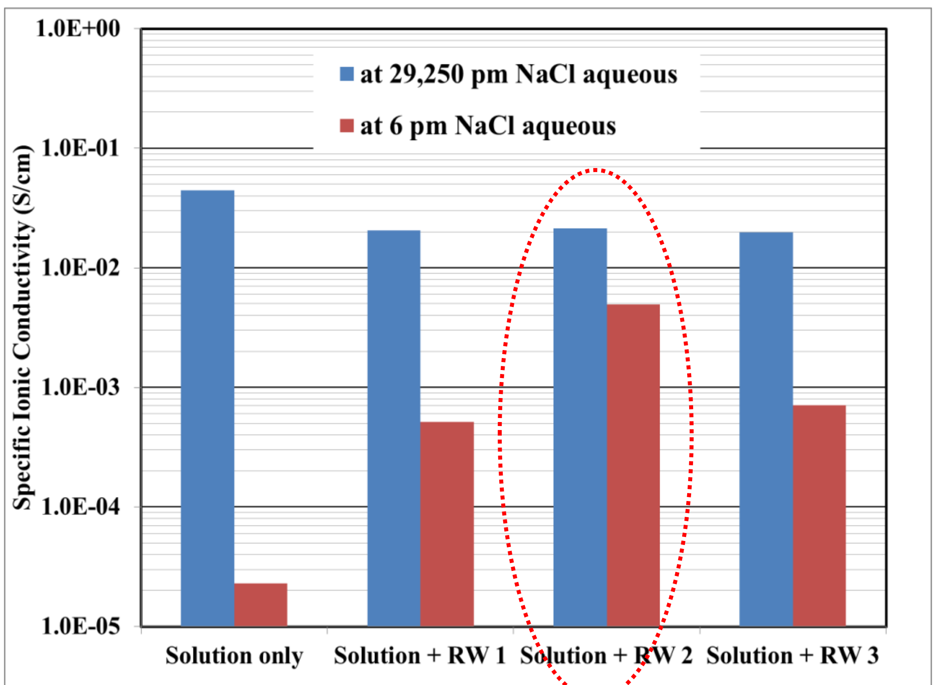
@ Feed Rate (dry ton/day) 2205 Fuel Yield (gallons/dry ton) 72 Annual Fuel Production (MM gallons) 52	99% Sufluric acid removed & 95% organic acid removed ($/gal ethanol)	99% Sufluric acid removed & 76% organic acid removed ($/gal ethanol)	99% Sufluric acid removed & 40% organic acid removed ($/gal ethanol)
Annual Processing Cost of De-acidification using Pulse Flow Microfiltration + RW-EDI	$0.15	$0.11	$0.08

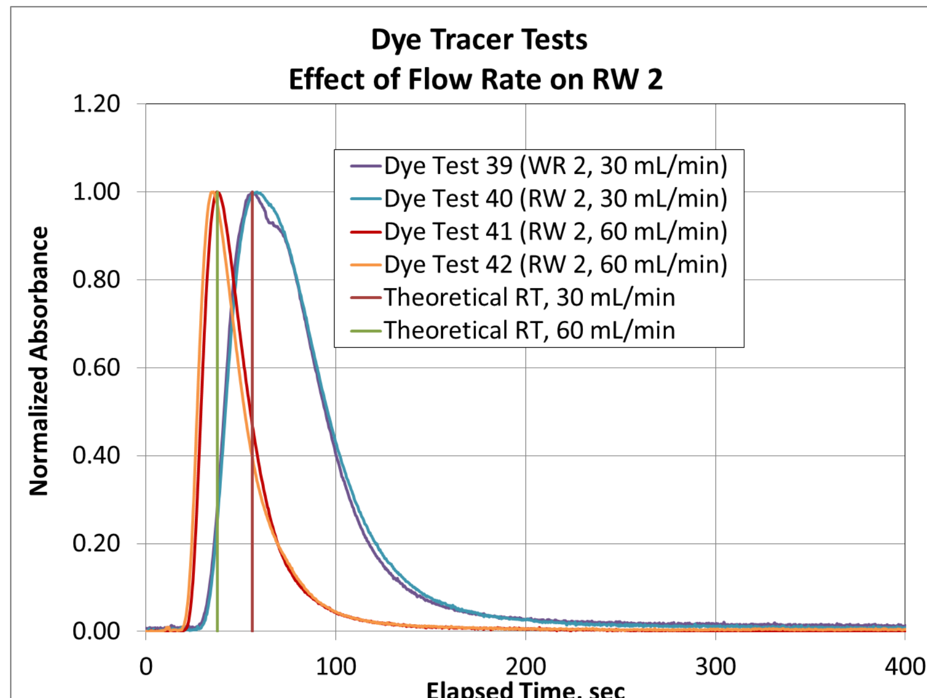
- Direct de-acidification of corn-stover hydrolysate slurry
- Reduce unit operations for de-acidification process
- Avoid expensive hydrolysate liquor filter press process
- Reduce process water usage
- Potential for recycling sulfuric acid to pretreatment step
- Enhance stream conditions for enzyme hydrolysis
- Address barrier of clean & separation (Bt-I in MYPP)

Accomplishment

Task R –Fabrication 3rd generation of ion-exchange resin wafer

- New fabrication technique enhanced flow distribution and ionic conductivity of 3G resin wafer at very dilute ion solution (e.g., 6 ppm NaCl)
  - >200 X improved ionic conductivity, (10X better than 2G RW)
  - Very uniform flow distribution (measured by dynamic dye-tracing system)
- New RW has potential to reduce electric energy
  - Reduce processing cost, energy and economic benefits!





Relevance

- **Biochemical**
  - Conversion R&D
    - Bt-I. Cleanup/Separation:
- **Hybrid (BCITC) advanced biofuels**
    - Bt-l Catalyst Development
- **Demonstrate how the project considers applications of the expected outputs**
    - A more efficient pretreatment process
    - Reduce unit operations needed for pretreatment slurry conditioning
    - Cleaner streams for downstream enzyme hydrolysis
    - Higher sugar titer
    - Avoid acid inhibition
    - Avoid Ca inhibition
    - Reduce wastewater treatment
    - Catalytic conversion

Critical Success Factors

Technical:

Permeate flux decline in filtration separation is an unavoidable phenomena, especially, in dealing with particulate separation.

Pulse flow can reduce the permeate flux decline. We are currently redesigning the pulse flow generator to deliver more effective pulse profile to sustain flux for longer periods

Identify advanced membrane and resin material to further enhance processing efficiency with smaller capital size.

Improving material functionality with nano-materials may bring transformational improvements to the cost and efficiency of bioprocessing. It can also make this platform more effective as a reactor for bio/chemical conversion.

Business: identify commercialization strategy to deploy technologies in biomass feedstock pretreatment /purification for industrial use

We have the right partners for co-products

Looking for the right partners for pre-treatment

Market: select organic acid with a growing market a performance advantage for production in the integrated biorefinery

Partners are selecting advantageous targets

License arrangement leaves us the opportunity to pursue other targets

Future Work

- Demonstrate the increase of de-acidification productivity of a synthetic liquid fraction hydrolysate using 3rd generation resin wafer before the end of FY13. Process target is to reduce electrical power consumption to less than 2.0 kWh/lb SA and increase the de-acidification productivity to more than 80g/m2/hour

- Propose new R&D area in advanced material to enable the catalytic conversion capability of RW-EDI platform

Summary

1. **Technical accomplishments**
   - Pilot-scale demonstration of hydrolysate de-acidification using RW-EDI
   - Demonstrated effective liquid extraction from 15 wt.% corn stover hydrolysate slurry using pulse flow micro-filtration
   - Demonstrated the economic viability of integrated separation of solid/liquid and de-acidification processes that eliminate unit operations and reduce the cost of slurry conditioning
   - Successfully fabricated a 3G resin wafer that significantly enhances ionic conductivity
2. **Relevance** - Addresses the R&D barrier of Bt-I in the cleanup and separation
3. **Critical Success factors and challenges** - The advanced material can significantly strengthen RW-EDI technology for bioprocessing and conversion
4. **Technology transfer** - ANL and Industrial partners, ADM and Nalco have received the 2012 Federal Laboratory Consortium (FLC) Award for Excellence in Technology Transfer

Additional Slides

Responses to Previous Reviewers' Comments

"The choice of ADM as creative partner is a strength but ADM is not a technology partner. If Nalco is on board that would be sufficient but their buy-in in not clear."

Response:

Argonne has a CRADA with ADM to test the technologies on organic acid streams. Based on industrial interest, Nalco signed a license to commercialize the technology and serve as a vendor. The license was executed. We believe that executing the license represents buy-in.

"Seems a major critical success factor that was eluded to but not expanded on is the problems with using actual PT sludges in the recovery system. It appears that a microfiltration system is required, or an alternative to this, to get the system capable of performing. This seems like a major hurdle to implementation."

"Appears difficult to go from synthetic to real samples // microfiltration of slurries to prevent fouling?"

"Have yet to test with full hydrolysate and high solid loading. Biofouling has not been adequately explored especially with fraction from pretreatment reactors with very high solids. Technology may be applicable to waste stream cleanup or dilute sugar solutions but see no reason to believe it will work under OBP projected conditions."

Response:

We agree that the fouling/solids handling is a high priority challenge. We demonstrated that the integrated new pulse flow microfiltration + RW-EDI can performance de-acidification using actual hydrolysate slurry. There is no ion-exchange membrane fouling in the RW-EDI. The solid particle fouling on microfiltration membrane can be cleaned with regular in-place cleaning procedure. Acid removal from dilute sugar has been demonstrated, both at bench-scale and pilot-scale in early project tasks (work with ADM). Using funding outside of OBP, Argonne has evaluated the technology waste stream cleanup and dilute sugars.

Responses to Previous Reviewers' Comments (cont.)

"Technical and commercial challenges have been identified and clear strategies to overcome these developed. Success will also depend on the robustness of this system. What is the anticipated lifetime of the membranes? How will they perform over the long term with complex materials like biomass hydrolysates? In the "non-sterile" environment of a biomass alcohol plant will they be subject to fouling by biofilms?"

Response: Argonne's process economics models are based on a one year service life. Our hands-on experience is that membranes have lasted for thousands of hours of operation without degradation of performance and have been reused for three years or more. In comparison to ED processes, the conductivity of the RW-EDI significantly decreases the likelihood of an electrical-short causing a membrane failure. Argonne has some experience with biofilm formation. It has been handled by using periodic clean-in-place (CIP) procedures using salts, mineral acids, and detergents. The systems are designed for rapid switching to a CIP mode.

Publications, Presentations, and Commercialization

Publications

S. Datta, S.W Snyder, D.J. Schell, C.S Millard, S.F. Ahmad, M.P. Henry, P. Gillenwater, A.T Fracaro, A. Moradia, Z.P. Gwarnicki, Y.J. Lin "Removal of Acidic Impurities from Corn Stover Hydrolysate Liquor by Resin Wafer based Electrodeionization (RW-EDI)", Biomass and Bioenergy, 2012, submitted.

Gurram, Raghu N.; Datta, Saurav; Lin, Yupo J.; Snyder, Seth W.; Menkhaus, Todd J., "Removal of enzymatic and fermentation inhibitory compounds from biomass slurries for enhanced biorefinery process efficiencies", Bioresource Technology vol. 102, 17, p. 7850-7859, 2011.

Presentations

Yupo J. Lin, Saurav Datta and Seth W. Snyder, "Hydrolysate De-acidification Using Electrodeionization", AICHE Annual Fall Meeting, Annual Meeting of AIChE, October 2011

Raghu N. Gurram, Saurav Datta, Yupo J. Lin, Seth W. Snyder, and Todd J. Menkhaus, "Removal of Enzymatic and Fermentation Inhibitory Compounds from Biomass Slurries for Enhanced Biorefinery Process Efficiencies", 33rd symposium on biotechnology for fuels and chemicals, May, Seattle, WA, 2011.

Patents (reduced to practice with project funding)

YuPo J. Lin, Seth W. Snyder, Edward J. St. Martin, "Retention of counter ions in the separative bioreactor", US Patent #8007647, 7/2011

Commercialization

- Executed "work for others" contracts with four industrial partners for organic acids product recovery and solvent deionization using RW-EDI technology, 2011 – 2013.
- Helped industrial partners to deploy RW-EDI technology for commercial demonstration. 2011 – 2013