NREL
NATIONAL RENEWABLE ENERGY LABORATORY





Separations Development and Application (WBS 2.4.1.101)

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

James D. ("Jim") McMillan
NREL

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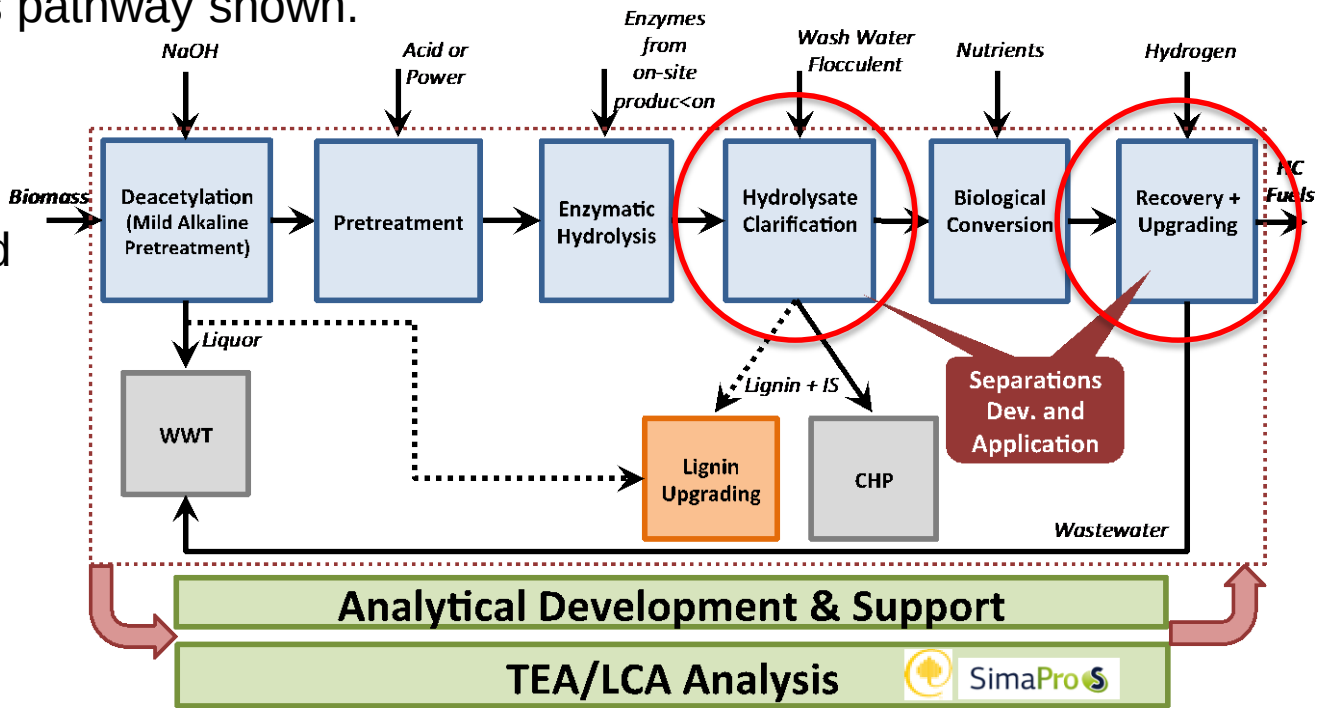
Biochemical Conversion Session

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Project Goal

Overall goal: Define, develop and apply separation processes to enable cost-effective hydrocarbon fuel / precursor production; **focus on sugars and fuel precursor streams**; lipids pathway shown.

Outcome: **Down selected proven, viable methods** for clarifying and concentrating the sugar intermediates stream and for recovering lipids from oleaginous yeast **that pass "go" criteria (i.e., high yield, scalable, and cost effective)**.

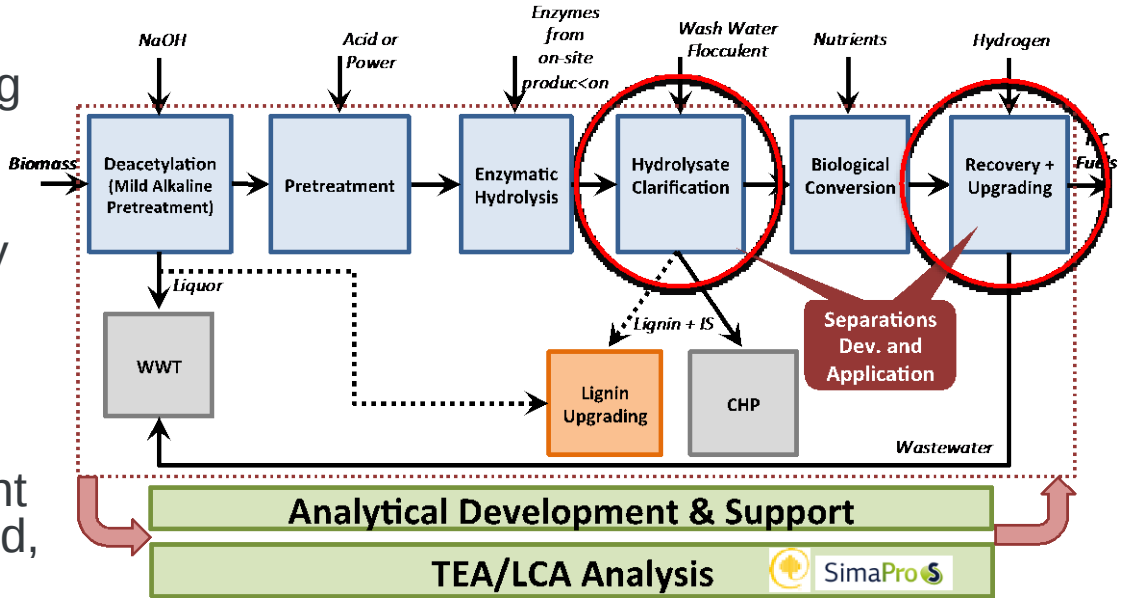


Relevance: **Separations** are key to overall process integration and economics; **often represent ≥ 50% of total process costs;** performance/efficiency can make or break process viability.

Separations this project investigates – sugar stream clarification and concentration, and recovery of intracellular lipids from yeast – **account for 17-26% of projected Minimum Fuel Selling Price (MFSP) for the integrated process**.

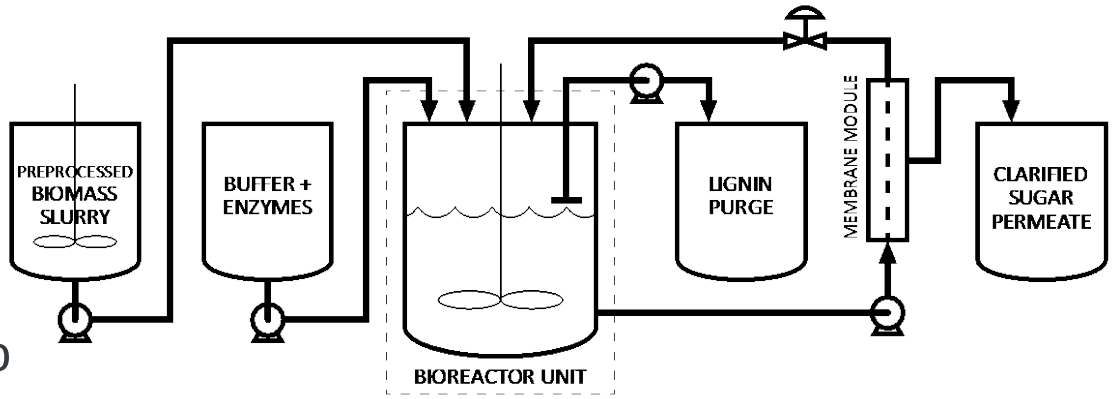
Project Overview

- **Cost driven R&D** to assess/develop/improve key process separations
  - **Sugar stream separations**: S/L, concentrative and polishing
  - **Fuel precursor recovery separations**: oleaginous yeast cell lysis and LLE lipid recovery



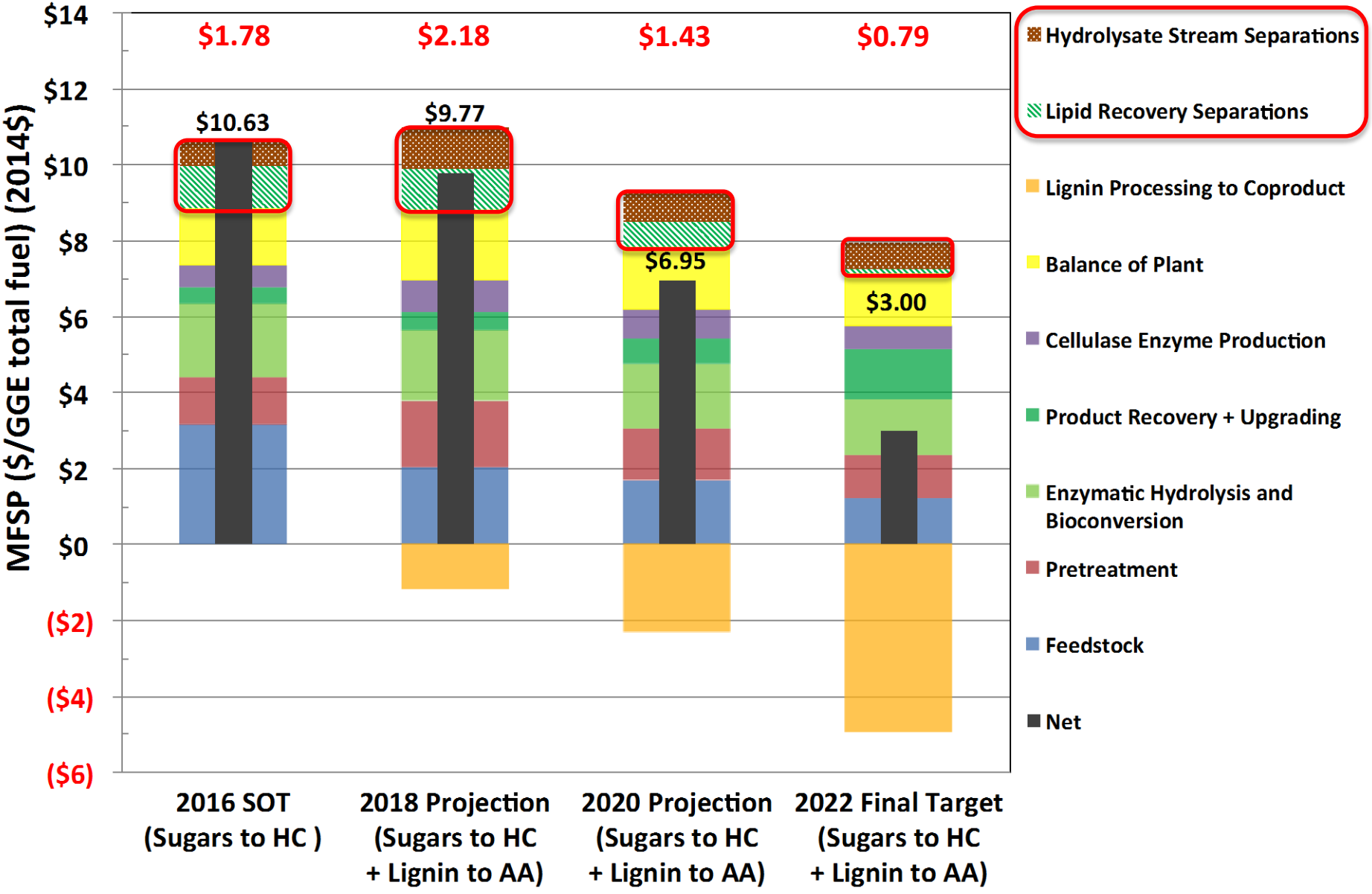
- Identify and characterize effective methods
  - Show capability to pass relevant go/no-go criteria (e.g., high yield, low cost, scalable)

- **Exploit *in situ* separation for process intensification**
  - Enable Continuous Enzymatic Hydrolysis (CEH)



- **Generate performance data** to develop / refine process TEAs and LCAs

Separations Technoeconomic Impact



Quad Chart Overview

Timeline

Start: FY 15 (Oct., '14)

End: FY 17 (Sept., '17; projected)

Percent complete: ~ 80%

Budget

	Total Costs FY 12 – FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY17-Project End Date)
DOE Funded	N.A.	$786K	$701K	$750K
Project Cost Share (Comp)*	--	--	--	--

Barriers

Primary focus on addressing upstream and downstream **separations-related barriers**:

- **Ct-G. Intermediate Cleanup/Condition**
  - Sugar stream clarification, concentration and clean up for biological and catalytic upgrading
  - Recover intracellular lipids from oleaginous yeast
- **Ct-J. BC Process Integration**
  - Incorporate continuous cross flow S/L separation during enzymatic hydrolysis to enable CEH

Partners

Subcontractors

- U. Colorado, U. Arkansas – Initial support for CEH and membrane-based concentration
- Pall Corporation – Pilot scale cross flow filtration
- NSF MAST Center – membrane separations
- Other(s) – Other equipment suppliers, TBD

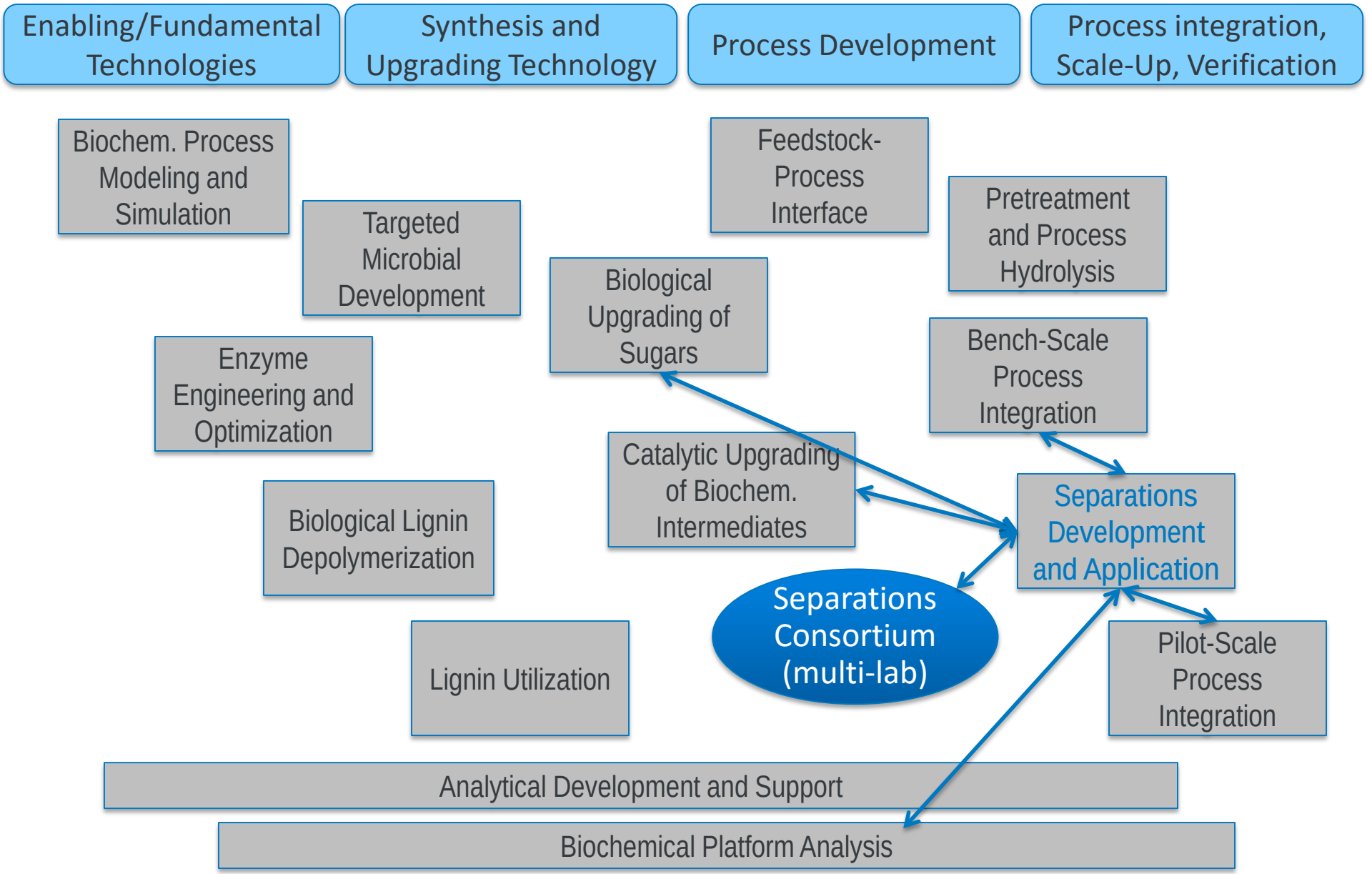
National Laboratories

- LBNL (ABPDU) – Homogenizer data
- ANL – EDI organic acid recovery data

Related NREL projects

- Biochemical Platform Analysis (BPA)
- Biological/Catalytic Sugars Use (BUS/CUS)
- Bench and Pilot Scale Integration (BSI/PSI)
- Separations Consortium (multi-lab, esp. NREL)

Biochemical Conversion Projects—NREL



Approach (Management)

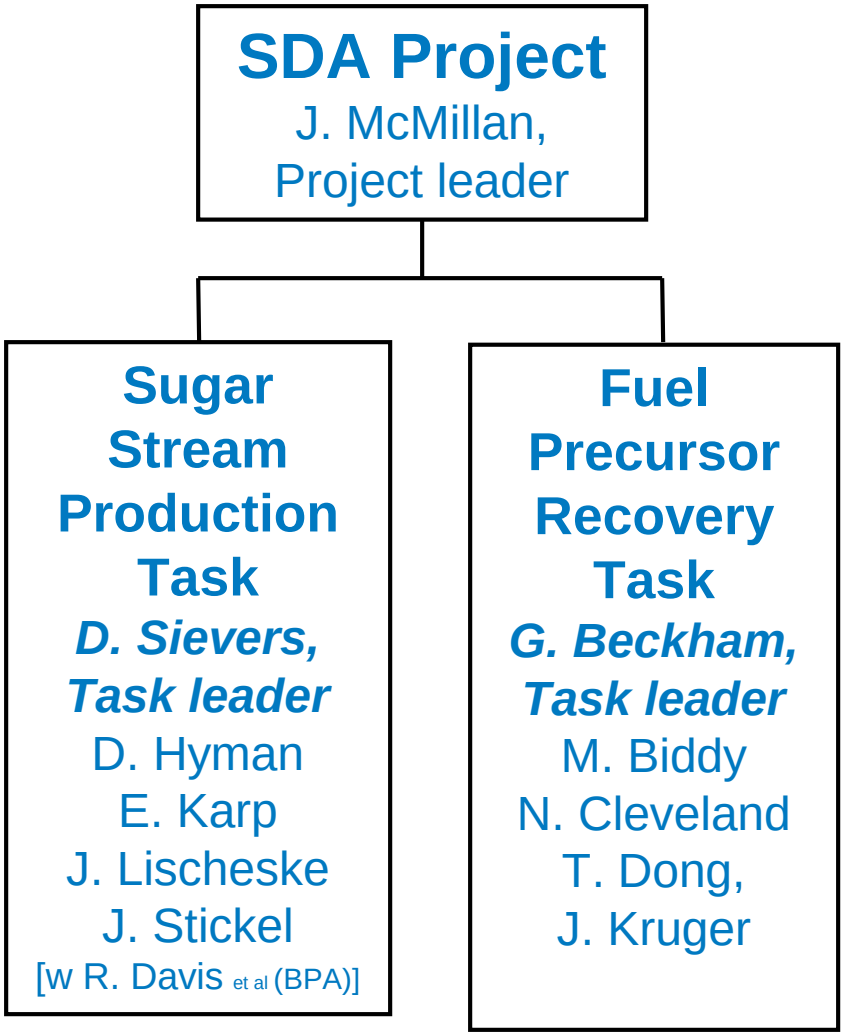
Project managed within NREL's Biomass AOP process, with established progress milestones and go/no-go decision points.

Top Three Challenges

1) Difficulty optimizing separations for processing steps still being refined, i.e., pretreatment and lipid production;
2) Adequately assessing at lab scale methods to be applied at pilot/larger scale;
3) Access to/ability to buy/rent small scale ("table top") systems for testing/optimizing solid-liquid separations, cell disruption, etc.

Critical Success Factors:

1) Develop **scalable, cost effective** methods for sugar S/L sep, conc and clean up; and for cell lysis to enable lipid recovery by LLE
2) Confirm techno-economic viability by demonstrating separation recovery yields ≥ design case targets at CAPEX and OPEX ≤ design case



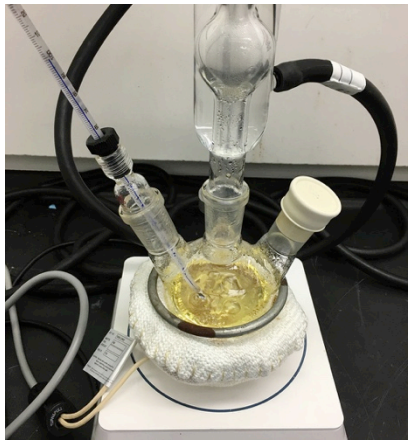
Approach (Technical)

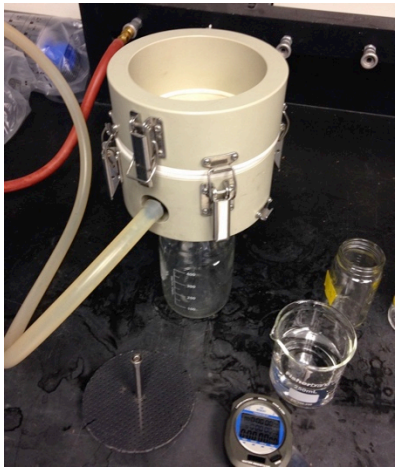
Overall approach is cost-driven R&D: TEA assessment guides research priorities; statistical design of experiments data informs ongoing TEA refinement

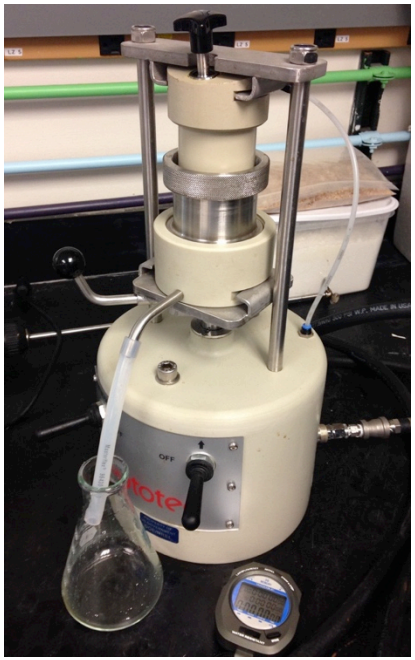
Key metric: Recovery yield (that meets a quality specification) is the most important performance measure for fuel production, followed by CAPEX and OPEX

Where prior relevant data exists, use it to develop initial performance and cost sensitivity information (jointly with BC Platform Analysis) for key separation processes, e.g., filtration and washing to remove solids and recover sugars from post enzymatic hydrolysis slurries.

Where prior data unavailable, use best public info we can find or generate preliminary **bench scale** performance data to inform initial TEA, which then guides R&D prioritization.





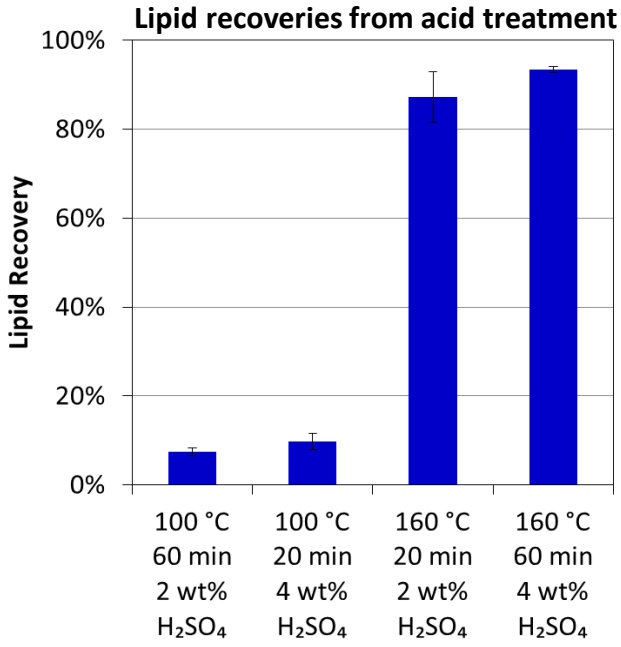


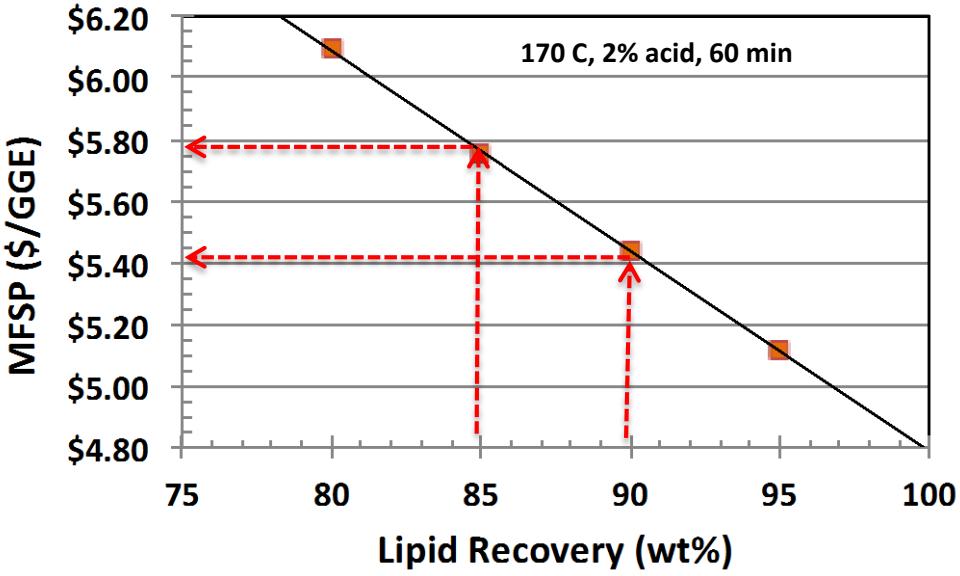
Technical Accomplishments

1. Developed better yeast lysis method (to enable LLE lipid recovery)
2. Quantified slurry filtration perf. variability = f(Reaction Chem)
3. Identified flocculant-based method to clarify post EH slurry
4. Improved TEA for Continuous Enzymatic Hydrolysis (CEH)

Developed Lower Cost Yeast Lysis Method

- **Objective:** Develop **lower cost** cell rupture technique for **lipid recovery** than high pressure homogenization (HPH)
- **Approach:** Downselected from 7 prospective methods spanning physical, thermal, bio/chemical techniques; also assessed relevance of Algal Biomass Program's R&D findings
- **Outcomes**
  1) Acid thermal treatment achieves higher yield lipid recoveries than other methods
  2) Recovery yields exceed 85% minimum target; also higher than HPH (≤ 80%)
  3) Robust, scalable method developed; performed well on several yeast (*L. starkeyi* (ref. strain), *R. toruloides* and *C. curvatus*)
- **Significance**
  1) **Effectively leveraged Algal R&D learnings** to identify method passing go/no-go criteria
  2) Scale up enables recovery of enough lipids to initiate/support hydrotreating experiments
- **Presentation**:
  Kruger *et al*. 2016. AIChE Fall Mtg. 17 Nov. 2016.

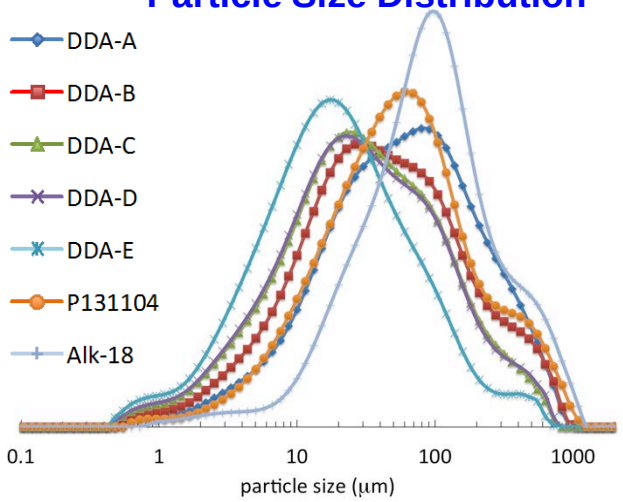




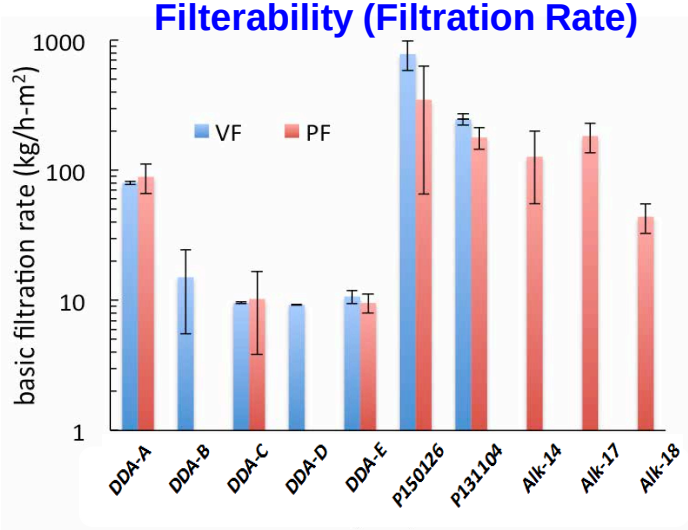
Filtration Performance Highly Variable = f(Rxn Chem)

- **Objective:** Assess variability in S/L separation performance as a function of pretreatment severity
- **Approach:** Bench scale filtration experiments using pretreatment slurries spanning a spectrum of severities and acidic and alkaline chemistries
- **Outcome/Significance:** Filtration performance highly influenced by chemistry and particle size dist (PSD). Must optimize deconstruction to refine quantitative performance data.
- **Reports/Publications:**
  1. Sievers and Kuhn. 2015. SDA FY15 Q3 milestone report (FY15 "BETO dashboard" milestone)
  2. Sievers et al. (2014) Bioresource Technol. **167**: 291-296.

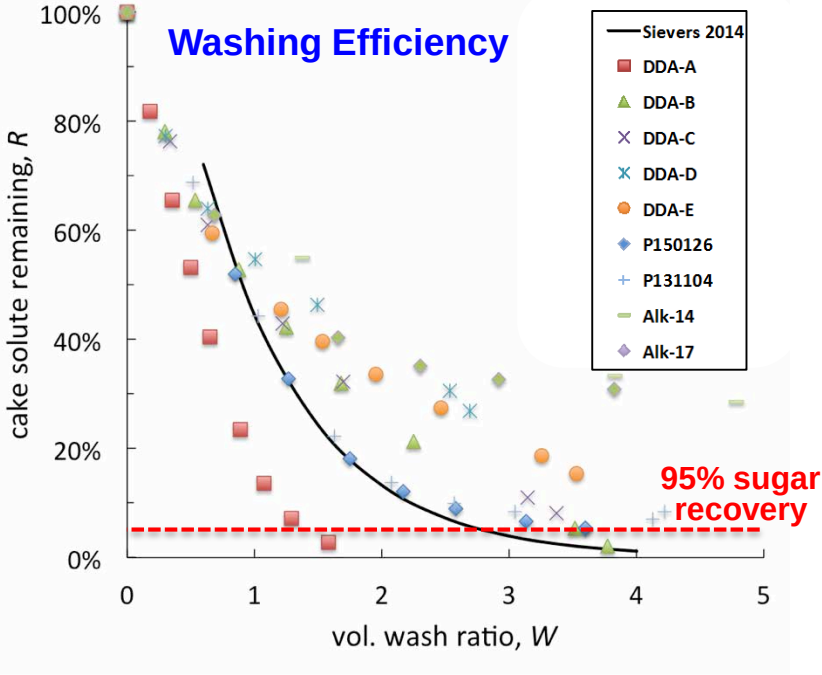
Particle Size Distribution



Filterability (Filtration Rate)

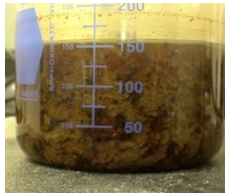


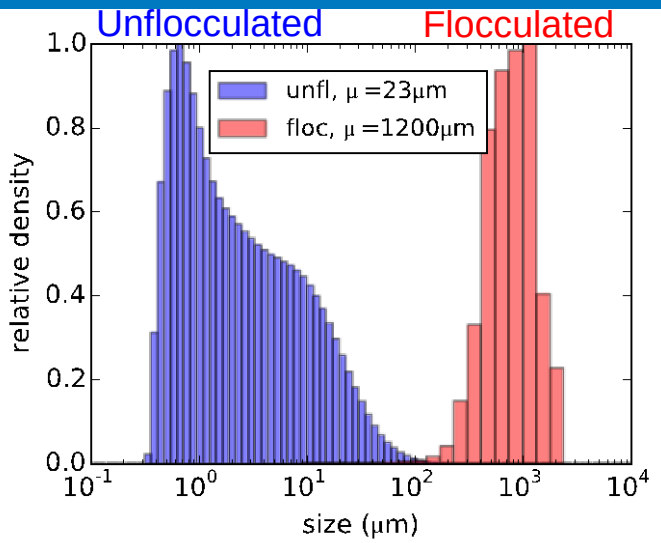
Washing Efficiency

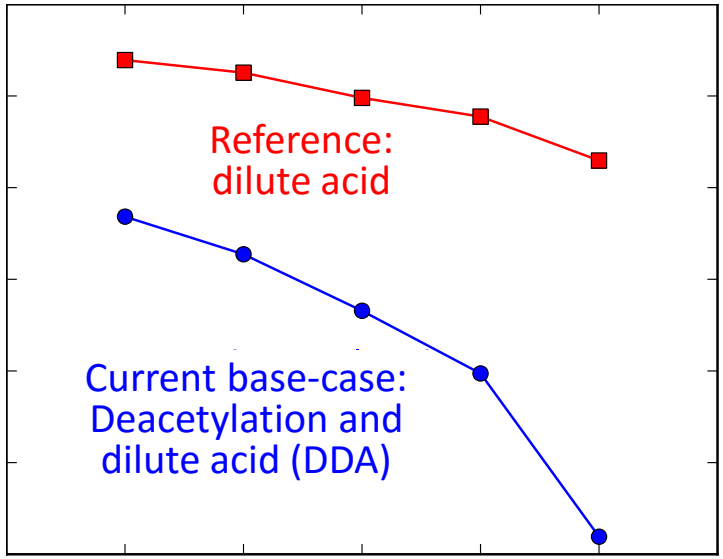


Flocculation-based Method Developed for Post EH Slurry

- **Objective:** Develop process to remove residual solids from post enzymatic hydrolysis (EH) slurry.
- **Approach:** Explore cross flow and pressure filtration ± flocculant on **Deacetylated & Dilute Acid (DDA)** and **Deacetylated & Mechanically Refined (DMR)** hydrolysate slurries post EH
- **Outcomes:**
  1) Poly-electrolyte flocculant improved filterability of both DDA and DMR post EH slurries, although DMR mat'l remains challenging
  2) Substantial improvement using DDA mat'l:
     - ↑ mean particle size 50-fold (23µ →1200µ)
     - ↑ scaled filter capacity 40-fold
- **Significance:** Large potential for savings.
  1) At 95% sugar recovery, MFSP decreased by $3.40/GGE for DDA post EH slurry
  2) Cross flow filtration with Pall unit pending; offers potential "no flocculant" route
- **Publication:**
  Sievers *et al.* (2015). Bioresource Technol. 187: 37-42.

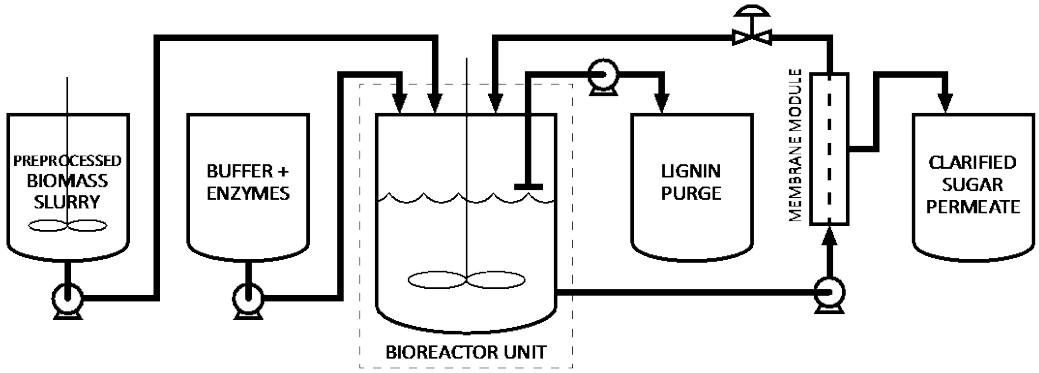


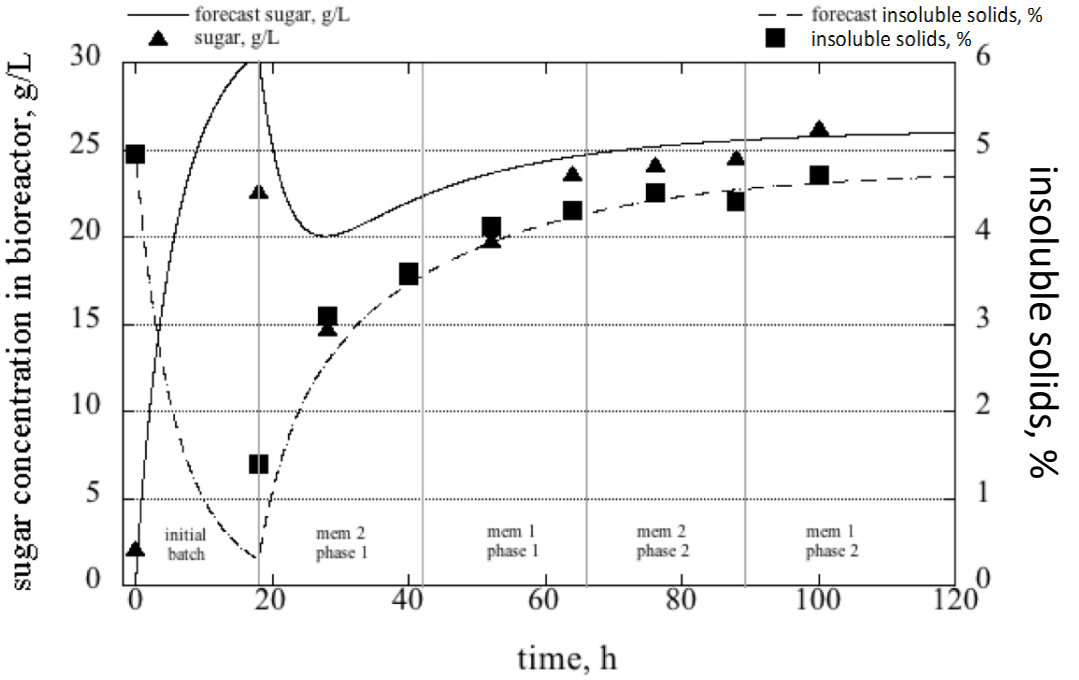




Advanced Continuous Enzymatic Hydrolysis (CEH)

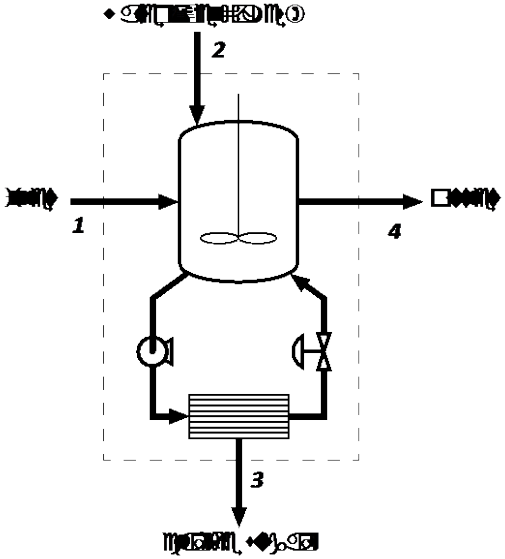
- **Objective:** Improve TEA of CEH, identify MFSP cost reduction targets
- **Approach:** *In situ* UF to remove formed sugars while retaining enzymes and enzyme-bound solids. Expt'l system: 5-L CSTR bioreactor integrated with a UF PVDF HF membrane module
- **Outcome:** More rigorous TEA model confirmed large cost reduction potential if stable operation can be achieved at [IS] ≥ 7.5%; this is FY17 future goal.
- **Significance:** Demonstrated CEH proof-of-concept at 5% [IS], where TEA is similar as for batch EH. CSTRs in series should enable target conversion yields to be achieved.
- **Publications/presentations:**
  1. Malmali et al. (2015). Food Bioprod. Process. 96:189–197.
  2. Wickramasinghe et al. (2015). NAMS Annual mtg, Boston, June.





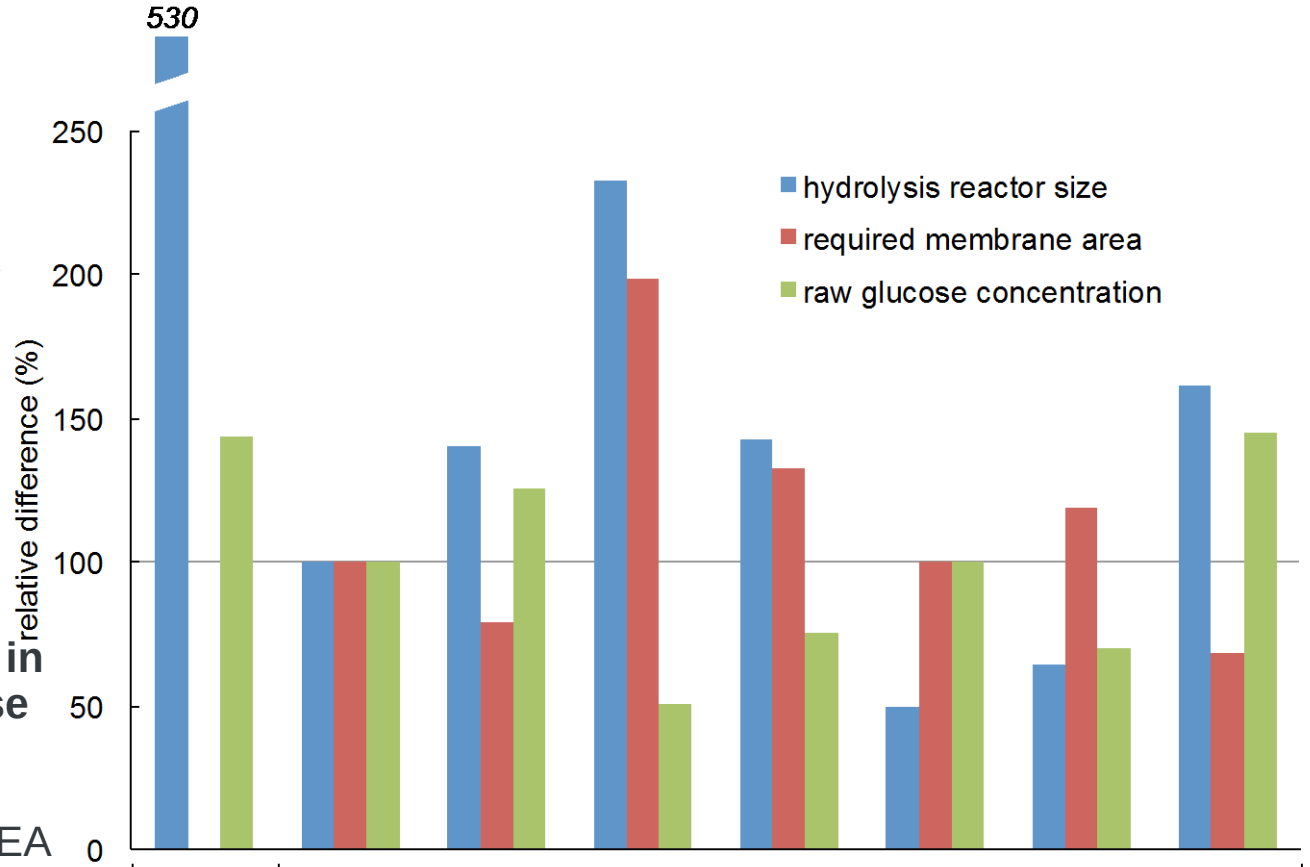
Simulating Multi-CSTR CEH Process

- Modeled single CEH unit



Simulate multiple CEH units in series using Python, then use ASPEN Plus (with BPA) to assess impacts on integrated biorefinery performance and TEA

- Identify key parameters
- Explore cost sensitivities



	batch	*continuous*						
	reference case	base case	3 CSTRs	5 % IS	7½ % IS	20 mg/g enzyme	74% yield	p/f=0.5
total glucose yield[1] (%)	74	90	90	90	90	90	74	90
number CSTRs	*n/a*	4	3	4	4	4	4	4
insoluble solids (%)	13 *initial*	10	10	5	7½	10	10	10
enzyme loading (mg/g)	19	10	10	10	10	20	10	10
permeate/feed ratio[2]	*n/a*	0.8	0.8	0.8	0.8	0.8	0.8	0.5

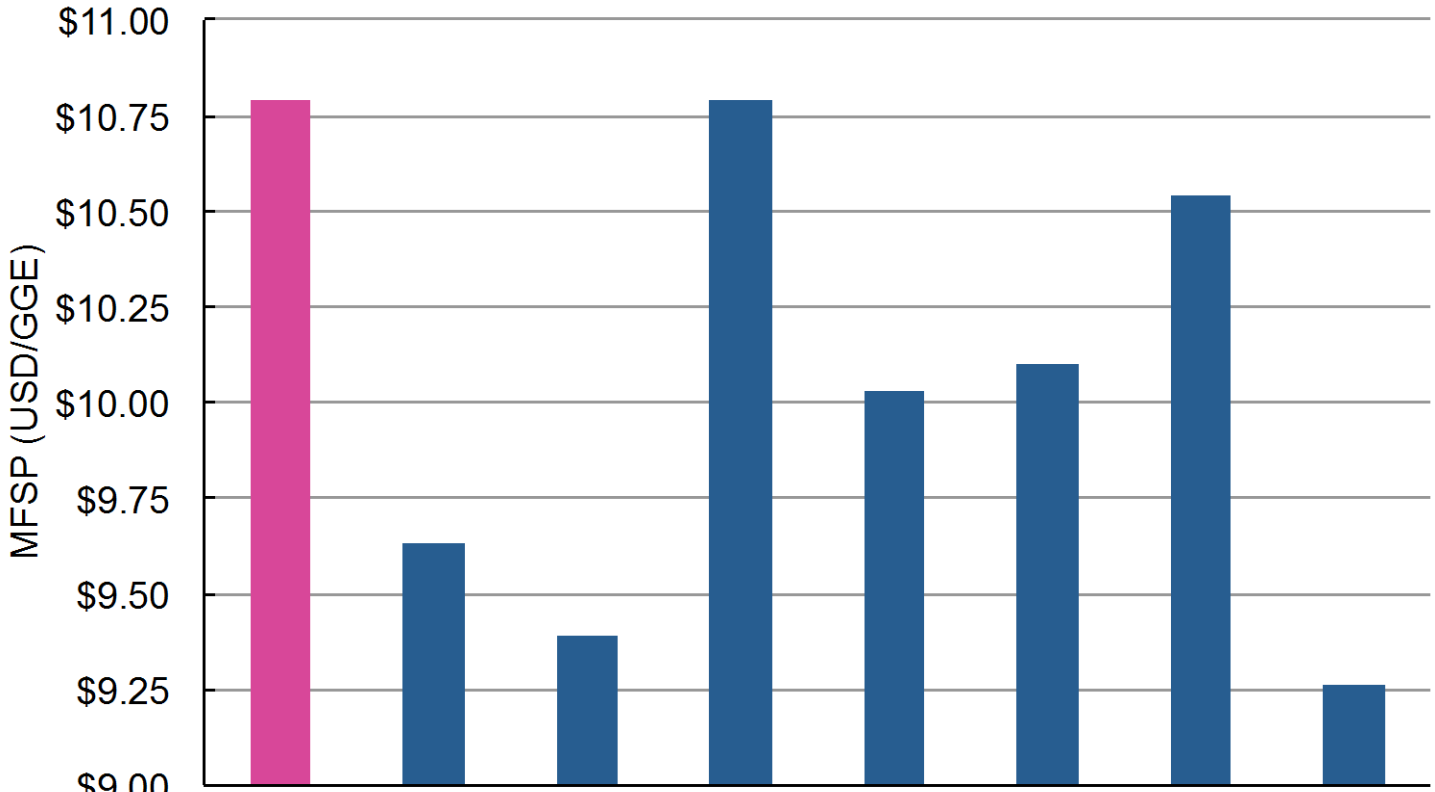
[1] *combined reaction yield and recovery yield in permeate*

[2] *p/f=1.5 for last CSTR in all cases to encourage diafiltration of sugars*

Multi-unit CEH Offers Large Cost Reduction Potential

TEA results show substantial cost reduction (≥ 50¢/GGE) if CEH can be demonstrated at [IS] ≥ 7.5%

MSFP reductions exceeding $1/GGE are possible if 3 CSTR-membrane CEH "units" in series can be effectively / stably demonstrated at [IS] ≥ 10%



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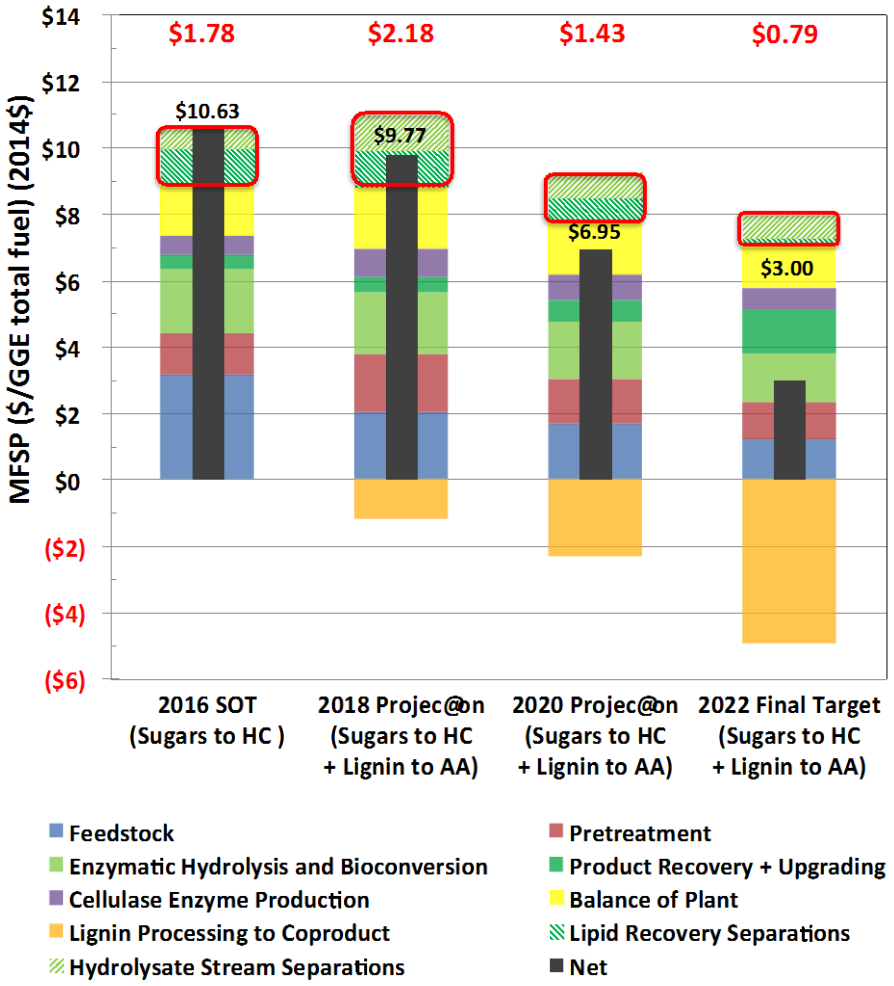
[2] *p/f=1.5 for last CSTR in all cases to encourage diafiltration of sugars*

Relevance

- **Separations often account for ≥ 50% of total production cost;** can make or break techno-economic viability of a process
- **Project R&D targets support BETO's goal** to develop **commercially viable** sugars to biofuels process technologies that achieve **production cost ≤ $3/GGE**
- **This project aligns with MYPP strategic and performance goals** to convert biomass sugars (and other carbohydrate and lignin derivatives) to hydrocarbon fuels, as described in recent reports:
  - *Davis, R. et al. (2013). Design report for biochemical sugars to hydrocarbons target process. NREL/TP-5100-60223*
  - *Davis, R. et al. (2015). Design report for catalytic upgrading of sugars to hydrocarbons. NREL/TP-5100-62498*
- **Reliable, cost effective separation processes required** to enable future year integrated demonstration



Future Work

Status: Project in its 3rd year; beyond FY17, will still need to optimize sugar & product related separations as deconstruction and upgrading processes continue to be improved and downselected/optimized

Future work focused on:

1) Demonstrating scalability of acid treatment lipid recovery;
2) revisiting post EH S/L for optimized DDA- and DMR-based process slurries; and
3) proving CEH operability at higher solids loadings where cost advantages accrue

High-level Gantt chart for FY17:

Date	<----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	--------->
Project Activity	FY17 Q1	FY17 Q1	FY17 Q1	FY17 Q2	FY17 Q2	FY17 Q2	FY17 Q3	FY17 Q3	FY17 Q3	FY17 Q4	FY17 Q4	FY17 Q4
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1. Sugar Stream Production												
Clarification (S/L separation)												
Reburish/validate pilot scale rotary drum												
Pilot testing of post EH S/L, CF v. floc												◆Annual Milestone
Concentration (active FY 15-16)												
Pilot for post EH liquor (after S/L)												☐Proposed FY18 Milestone
Polishing (clean up for catalysis)				◆QPM Milestone (Q1)								
2. Lipid Recovery												
Demo scalability (>85% yield, stretch 90%)							◆QPM Milestone (Q2) (Go/No-go)					
3. Continuous Enzymatic Hydrolysis (CEH)												
Obtain/verify higher selectivity membrane												
Test CEH perf. operability at [IS] 7.5%-12%										◆QPM Milestone (Q3)		

Summary

Overview/Approach: TEA-guided, cost-driven R&D (TEA joint with BPA)

- Leverage prior relevant data, where available, to get started
- Mine literature or develop preliminary performance data where not
- Data informs TEA, which guides R&D prioritization for expt'l design; repeat to refine

Results FY15-16:

- **Sugar Stream Production:** Developed flocculation-based S/L separation (clarification) of difficult post EH lignin-rich fine particulate slurries. Quantified variability of S/L performance as function of pretreatment chemistry and severity. Showed sugar degradation upon conc. prevented using low T / short t evaporation.
- **Fuel Precursor (Lipid) Recovery:** Identified scalable, high yield acid treatment-based method (adapted from algae program). Acid thermolysis achieves ≥ 85% recovery yields and passes go/no-go for this key separation.
- **Process Intensification:** Completed rigorous TEA informed by single CSTR data. Results show substantial potential to reduce cost if CEH can be robustly operated at [IS] ≥ 7.5%, a current year demonstration target.

Relevance: Effective, efficient low cost separations developed in this project are essential to realize an economical sugars-to-hydrocarbon biofuels process.

Future Work: FY17

1) Demonstrate scalability of acid treatment-based lipid (fuel precusor) recovery, producing sufficient quantities of lipids to support lipid hydrotreating experiments.
2) Refine/revisit post EH S/L for optimized DDA- and DMR-based processing.
   - Rebuilt rotary drum filter and new vacuum capable evaporator facilitate verifying scalability of lab results and producing significant quantities of lignin-rich solids for valorization testing;
   - Pilot scale cross flow filtration unit (Pall) enables non-flocculation based method to be tested
3) Prove out CEH at cost effective solids loadings; refine TEA for sugar stream specs. Validate scalability of acid thermolysis lipid recovery and produce materials for hydrotreatment testing.

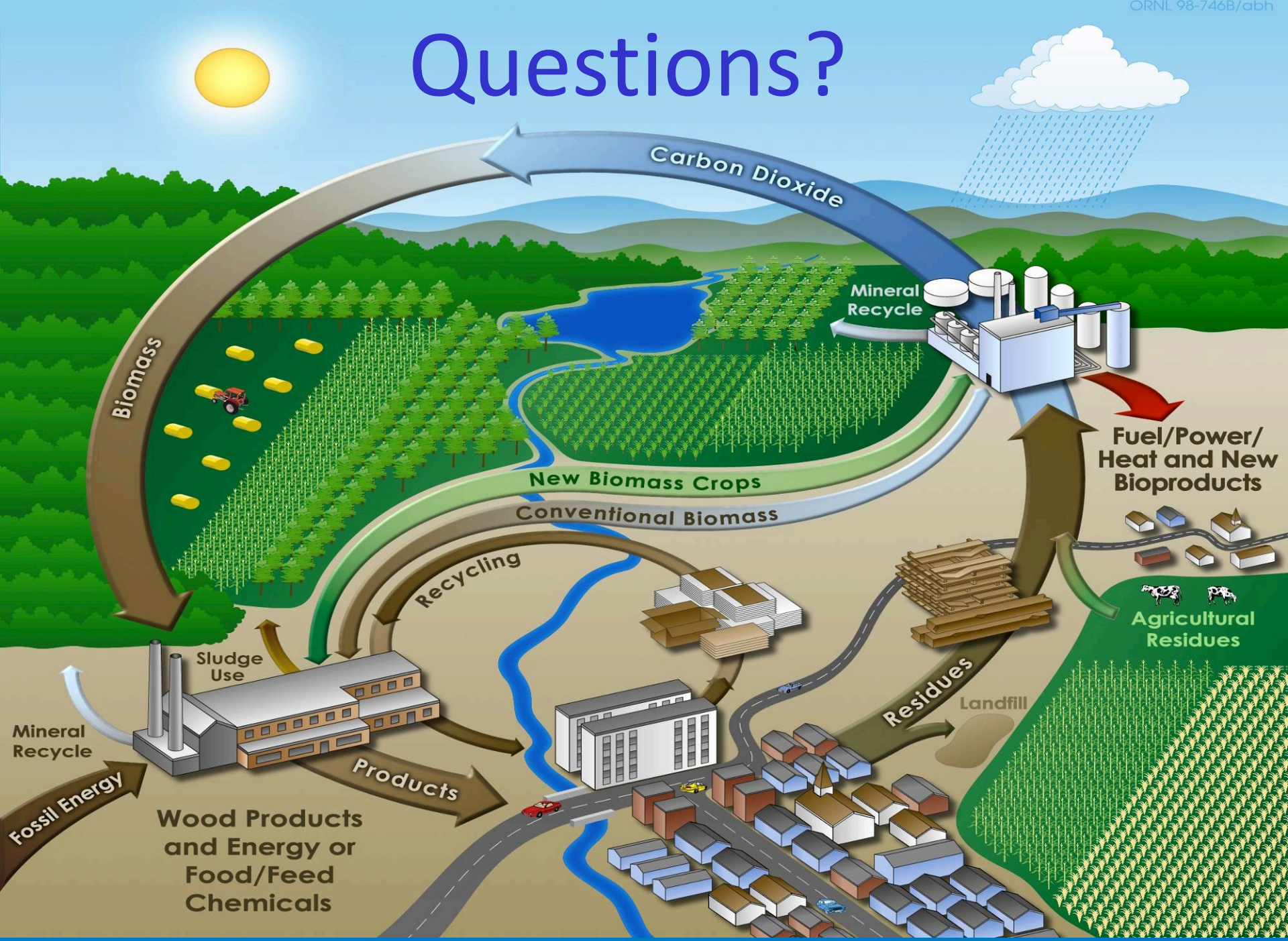
Outyear: Contribute to demo process down select. Separations performance is one key factor to consider when deciding which of the 4 current production scenarios to go forward with.

Acknowledgments

Funding / Oversight: DOE EERE BioEnergy Technologies Office, Prasad Gupte, Project Technology Manager

SDA Project Team (NREL): Gregg Beckham, Mary Biddy, Nick Cleveland, Tao Dong, Eric Karp, Jake Kruger, Jim Lischeske, David Sievers, Jonathan Stickel

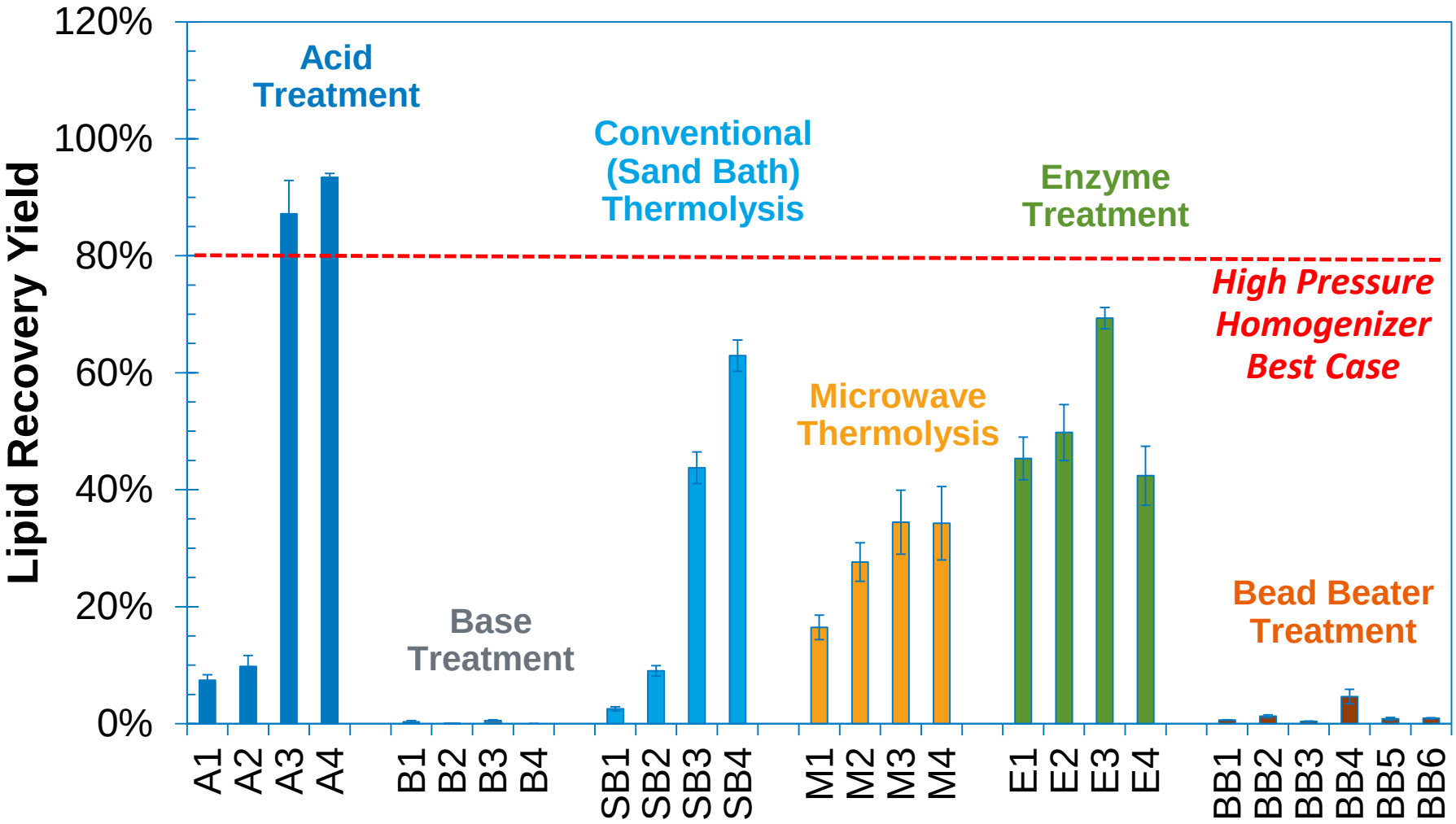
Questions?


ORNL 98-746B/abh
Carbon Dioxide
Biomass
Mineral Recycle
Fuel/Power/ Heat and New Bioproducts
New Biomass Crops
Conventional Biomass
Recycling
Agricultural Residues
Sludge Use
Mineral Recycle
Fossil Energy
Products
Residues
Landfill
Wood Products and Energy or Food/Feed Chemicals

Additional Slides

1. Screening Cell Lysis Methods for Oleaginous Yeast
2. Targets for Improved S/L and Washing Separations
3. Concentration of Clarified Hydrolysate
4. Hydrolysate Polishing for Catalytic Upgrading
5. Publications
6. Presentations

Screening Cell Lysis Methods for Oleaginous Yeast



➔ Acid treatment was only method capable of achieving recovery yields ≥ 85%, the minimum target established for passing the method selection go/no-go

Targets for Improved S/L & Washing Separations

- Using flocculation-assisted S/L filtration to clarify post-enzymatic hydrolysis (EH) hydrolysate slurry

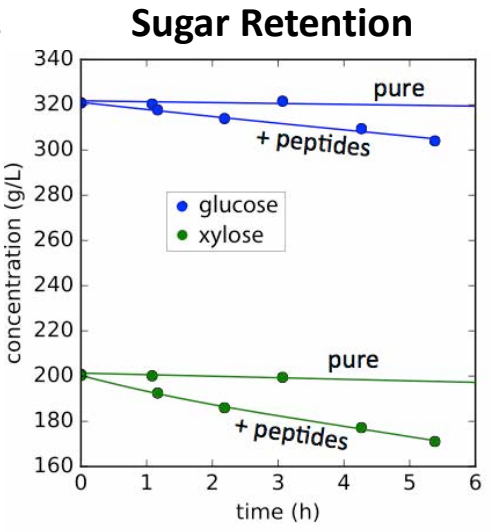
Parameter	DDA hydrolysate	DMR hydrolysate
Sugar retention	95% (SOT and target)	95% (SOT and target)
Wash ratio (L/kg IS)	SOT = 15, Target = 10	SOT= 17.5, Target = 10
Flocculant loading (g/kg IS)	10 (SOT and target)	SOT = 20, Target = 20
Membrane capacity (kg IS/m2-h)	20 (SOT and target)	SOT = 12, Target = 15

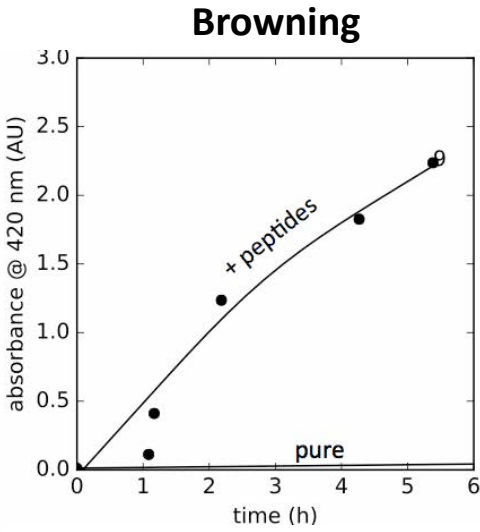
DDA = Deacetylation and Dilute Acid Pretreatment (prior to EH)

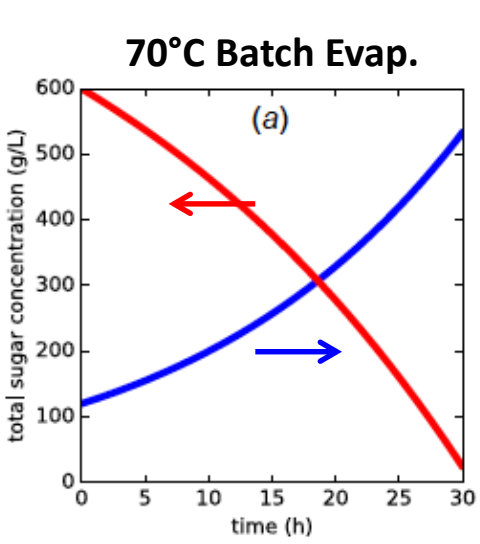
DMR = Deacetylation and Mechanical Refining Pretreatment (prior to EH)

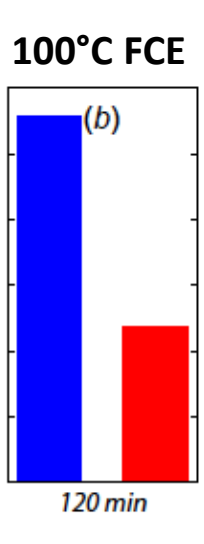
Concentration of Clarified Hydrolysates

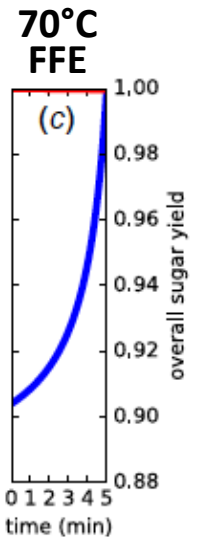
- Assessed evaporation (and membranes) for concentrating clarified hydrolysate, testing both pure sugars and biomass hydrolysates
  - Observed rapid sugar losses, with rate of loss higher for xylose than glucose and exacerbated by peptide addition, higher pH and/or higher T (i.e., putatively seeing Mallaird degradation reactions)
  - Measured sugar degradation rate constants; xylose most labile, degradation rate 3.2x higher than for glucose
- Used results to refine TEA (with BPA) and then simulate operation using potential batch and continuous evaporators
  - Membrane dewatering uneconomical under all examined scenarios (due to high CAPEX, low membrane life)
  - Negligible sugar degradation possible using a continuous falling film / plate evaporator (with mechanical vapor recompression) that enables short residence time







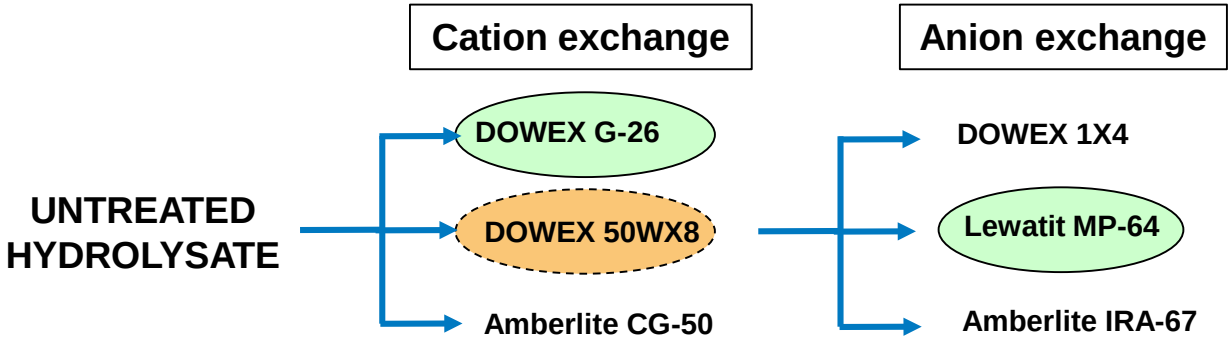




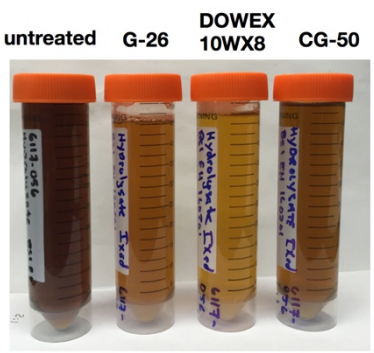
Simulations of 5x concentration: (a) 70°C batch evaporator; (b) 100°C continuous forced recirculation evaporator (FCE); and (c) 70°C continuous falling film/plate evaporator (FFE).

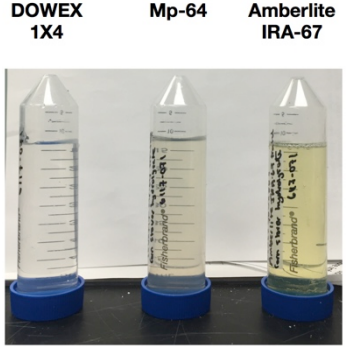
Hydrolysate Polishing (De-ashing) for Catalytic Upgrading

- Initial work to assess ion exchange resin efficacy for "polishing" clarified hydrolysates for catalytic upgrading carried out in FY17 Q1
- 3 cation and 3 anion exchange resins evaluated for removing inorganic cations and anions, furanics, and carboxylates from corn stover-derived hydrolysate
- Goal: Identify resin combination(s) that can achieve ≥ 75% removal of inorganic ionic species as well as ≥ 50% removal of aromatics



- First combination (using DOWEX 50WX8) removed 94% of cations and anions in solution and all detectable furanics and aromatics. However, sugar recoveries were poorer (only 76% glucose, 76% xylose, 91% arabinose and 75% galactose)





- Final combination removed 95% cations and 94% anions in solution and all detectable furanics and aromatics. Sugar recoveries were a bit better (82% glucose, 82% xylose, 91% arabinose and 100% galactose)

➔ **Need to identify resins that can achieve higher/quantitative sugar recoveries**

Publications

SDA publications (FY15-present)

1. Sievers D.A., Lischeske J.J., Biddy M.J., and Stickel J.J. (2015). A low-cost solid-liquid separation process for enzymatically hydrolyzed corn stover slurries. *Bioresour. Technol.*, 187:37–42.
2. Malmali M., Stickel J.J., and Wickramasinghe S.R. (2015). Investigation of a submerged membrane reactor for continuous biomass hydrolysis. *Food Bioprod. Process.*, 96:189–197.
3. Adhikari, B. 2015. Separation challenges and optimizations of sustainable algae and lignocellulose based biofuels (Ph.D. Dissertation, December 18, 2015). University of Colorado, Boulder, CO.
4. Brodeur G., Telotte J., Stickel J.J., and Ramakrishnan S. (2016). Two-stage dilute-acid and organic-solvent lignocellulosic pretreatment for enhanced bioprocessing. *Bioresour. Technol.*, 220:621–628.
5. Crawford N.C., Nagle N., Sievers D.A., and Stickel J.J. (2016). The effects of physical and chemical preprocessing on the flowability of corn stover. *Biomass Bioenergy*, 85:126–134.

Submitted, in review or in advanced preparation

5. Adhikari B., Stickel J.J., Sievers D.A., and Pellegrino J. (2017). Continuous enzymatic hydrolysis of lignocellulose in a membrane-reactor system. In preparation for *Biomass Bioenergy*.
6. Sievers D.A., Kuhn E., McMillan J.D., Tucker M.P. (2017). Effects of Dilute-Acid Pretreatment Conditions on Filtration Performance of Corn Stover Hydrolyzate. In preparation for *Bioresource Technology*.

Presentations

SDA presentations (FY15-present)

1. Crawford N.C., Lischeske J.L., Minot M., Nagle N., Sievers D.A., and Stickel J.J.. Flocculant-aided solid-liquid separation of algal and lignocellulosic biomass slurries. Presented at the 249th ACS National Meeting, Denver, CO, March, 2015
2. Adhikari B., Sievers D.A, Stickel J.J., and Pellegrino J. Development of a membrane-based separation process for the continuous enzymatic saccharification of lignocellulosic biomass. Presented at the 37th Symposium on Biotechnology for Fuels and Chemicals, Sand Diego, CA, April, 2015.
3. Malmali M., Qian X., Stickel J.J., and Wickramasinghe S. R. Continuous Enzymatic Hydrolysis of Biomass in a Membrane Reactor. Presented at the Symposium on Biotechnology for Fuels and Chemicals, San Diego, CA, April, 2015.
4. Wickramasinghe S.R., Malmali M., and Stickel J.J. Continuous enzymatic hydrolysis of biomass in a membrane reactor. Presented at North American Membrane Society Annual Meeting, Boston, MA, June, 2015.
5. Stickel J.J., Crawford N.C., Lischeske J.L., Patton C., and Sievers D.A. Flocculant-aided solid-liquid separation of biomass slurries. Presented at the AIChE Annual Meeting, Salt Lake City, UT, November, 2015.
6. Crawford N.C., Nagle N., Ray A.E., and Stickel J.J.. Flowability of biomass solids: The effects of preprocessing. Presented at the AIChE Annual Meeting, Salt Lake City, UT, November, 2015.
7. Adhikari B., Pellegrino J., Sievers D.A, and Stickel J.J. Membrane-Based Process for the Continuous Enzymatic Saccharification of Lignocellulosic Biomass. Presented at the AIChE Annual Meeting, Salt Lake City, UT, November, 2015.
8. Sievers D.A., Lischeske J., and McMillan J.D. Concentrating Biomass-Derived Hydrolyzates for Production of Fuels and Chemicals Using Thermal Evaporation – Impact on Sugar Quality and Loss. Poster M16 presented at the 38th Symposium on Biotechnology for Fuels and Chemicals, Baltimore, MD, April 2016.
9. Kruger J., Cleveland N., Dong T., Yeap Jl, Beckham G., Biddy M. Lipid Recovery from Oleaginous Yeast. Presented at the AIChE Annual Meeting, San Francisco, CA, November, 2016.

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