DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

WBS 2.4.1.101 Continuous Enzymatic Hydrolysis Development (CEHD)

Biochemical Conversion

March 7, 2019

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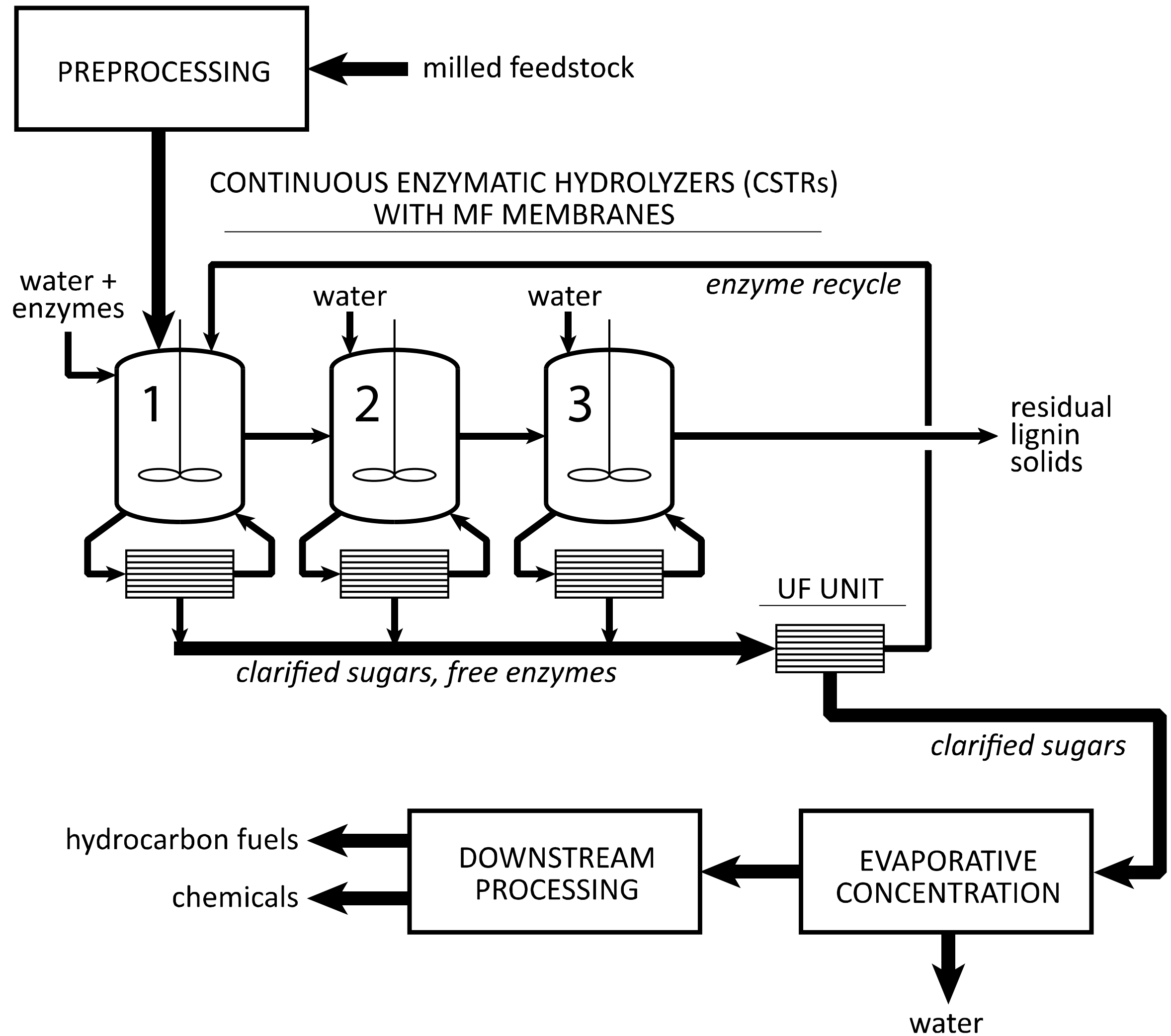
Goal Statement for CEHD Project

Goal: Develop Continuous Enzymatic Hydrolysis (CEH) technology to reduce cost, improve manufacturability of biomass sugar platform

Outcome: One CEH reactor stage (bench-scale) performing at levels commensurate with multi-stage concept feasibility by TEA (e.g., 3–4 units in series operating at insoluble solids (IS) levels ≥ 10 wt%)

Relevance:

+ **Process intensify**: improve rate-limiting enzymatic hydrolysis (EH) step by combining cellulose EH with *in situ* sugars recovery and clarification
+ **Reduce cost**: lower CAPEX by using smaller tanks/reactors; increase capital utilization
+ **Increase biocatalyst efficiency**: recycle and reduced sugar product inhibition improve enzyme usage and efficacy
+ **Enable continuous manufacturing** for lignocellulosic biomass sugar platform



Quad Chart Overview

Timeline

- Project start date: 10-01-2017
- Project end date: 09-30-2020
- Percent complete (50%)

	Total Costs Pre FY17 ($k)	FY 17 Costs ($k)	FY 18 Costs ($k)	Total Planned Funding (FY 19-Project End Date) ($k)
DOE Funded	0	476	530	1,275
Project Cost Share*	n/a	n/a	n/a	n/a

- **Partners**
  - **None (formally)**
  - **Equipment & membrane vendors (informally)**
    - **Koch, Millipore, Pall, Porex, Sefar, Snyder, Texol, Tecweigh, TriSep**

Barriers addressed (MYPP abbreviations)

Primary barriers (Cts): D - Adv. Process Devel.
M - Reactor Design
O - Selective Separations

Secondary/supporting: B - Preprocess/Pretreat
E - (Bio)Catalyst Lifetime
F - Catalytic Process Yield
ADO-A - Process Integration

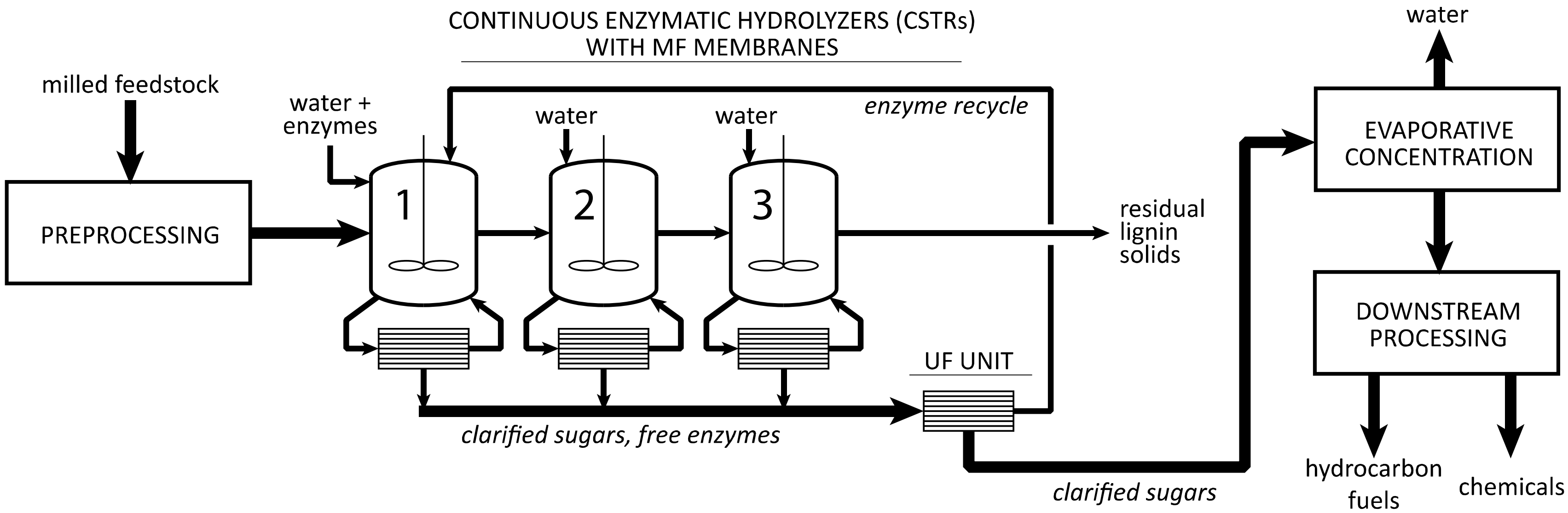
Objective

Demonstrate Continuous Enzymatic Hydrolysis (CEH) process technology at bench / mini-pilot scale. Show extended (≥ 96 h) single CEH reactor stage performance at ≥ 10% insoluble solids level demonstrating potential for multi-stage system to achieve updated 2018 BC design case TEA projections

End of Project Goal (Sept, 2020)

Updated state of technology experimental performance data (based on single) stage and TEA (for multi-stage) CSTR-based CEH, as well as initial literature review and preliminary TEA for alternative approaches to implementing CEH

Project Overview

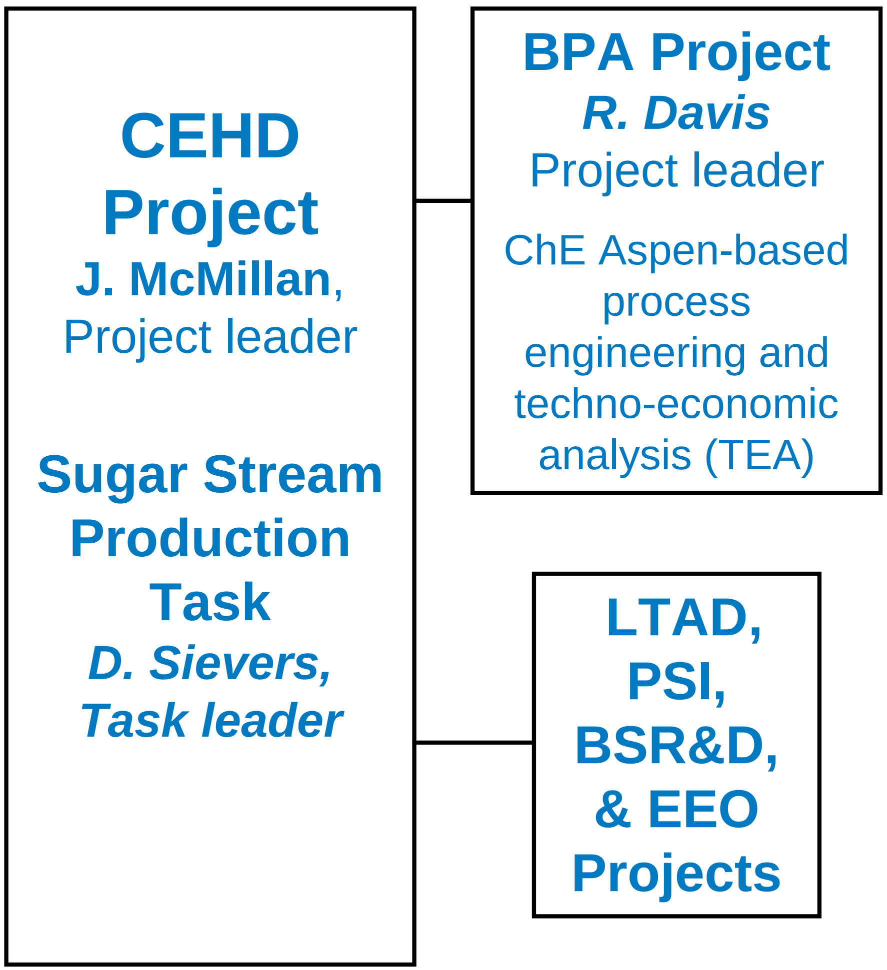


- **Project re-focused/narrowed in 2017 merit review** from broader sugars- and lipids-recovery separations scope to focus on Continuous Enzymatic Hydrolysis (CEH) with *in situ* clarification (S/L separation) of product sugars stream
  – *Responsive to Peer Review feedback to focus on innovation, highest impact R&D elements*
- **CEH processing assumed in updated biochemical design case (Davis *et al*., 2018)** for carboxylic acids production pathway; in this pathway, clarification of produced solubilized sugars essential to enable extractive fermentation.
- **Process intensified CEH processing at high insoluble solids (IS) levels remains to be proven**. Experimental proof of concept so far only demonstrated at low IS (≤ 7.5%), whereas TEAs show operation at higher IS (≥ 8.5%–10%) required for attractive economics.
- Prior TEAs show CEH has **great potential to reduce CAPEX**. Success also will **enable continuous manufacturing** of biomass sugars-based fuels and/or chemicals production.

Approach (Management)

Project managed within NREL's Biomass AOP process, with established quarterly progress milestones and a mid-project go/no-go decision point

- Structured as a single task with scope spanning experiments and modeling
- Staffed by ChE's and research technicians (process R&D and analytical chemistry)
- Primarily interacts with other biochemical platform tasks
  - TEA modeling: **Biochemical Platform Analysis (BPA)**
  - Pretreated feedstocks: **Low Temperature Advanced Deconstruction** (DMR feedstock) and ADO's **Pilot Scale Integration** (DDA feedstock)
  - Enzymes: **Bench Scale R&D** and **Enzyme Engineering and Optimization**

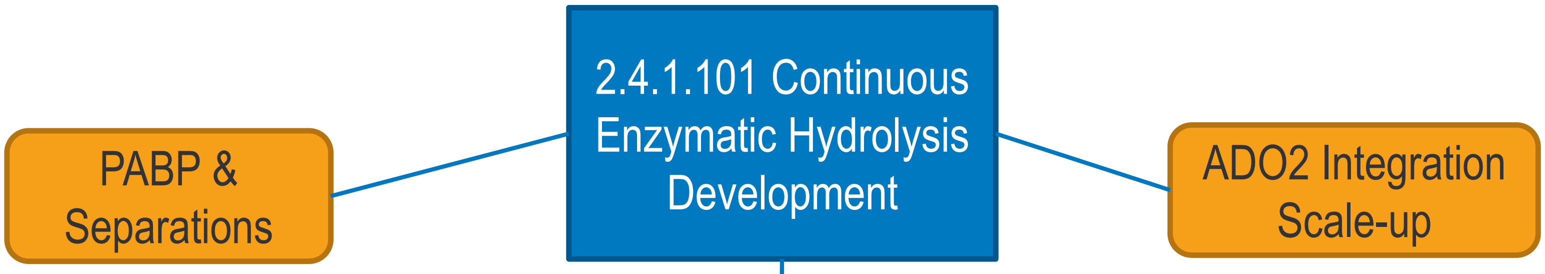


Project Interactions

2.4.1.101 Continuous Enzymatic Hydrolysis Development

- Algae
- Agile BioFoundry
- Lignin
- Waste-to-Energy
- Feedstock Logistics
- Catalysis
- CO2
- ADO Integration Scale-up
- ADO Analysis/ Modeling
- Co-Optima
- PABP/ Separations
- Biochemical Conversion
- FCIC
- Analysis & Sustainability

Project Interactions



- 2.5.5.50X Separations Consortium

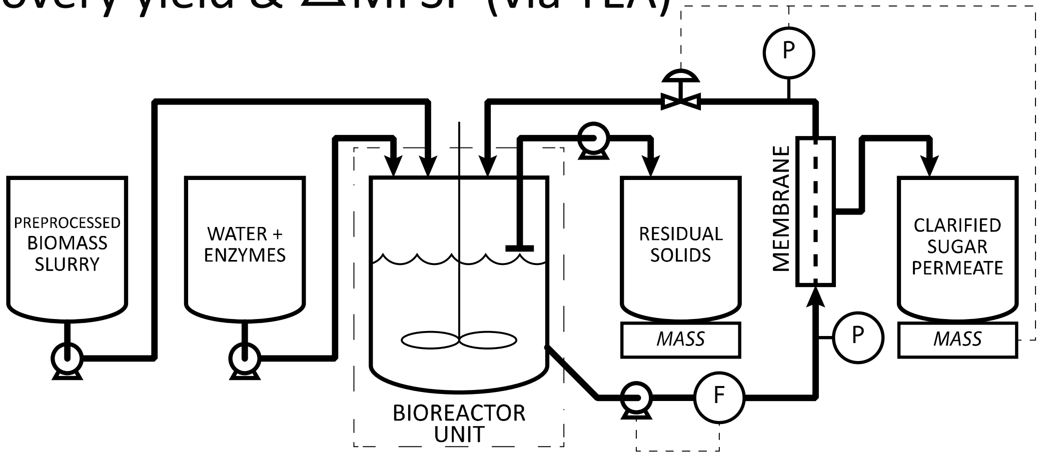
- **2.4.1.102 Pilot Scale Integration**

- **2.1.0.100 Biochemical Platform Analysis**
- 2.2.3.100 Low Temperature Advanced Deconstruction
- **2.4.1.100 Bench Scale R&D**
- 2.5.4.100 Enzyme Engineering and Optimization

Approach (Technical)

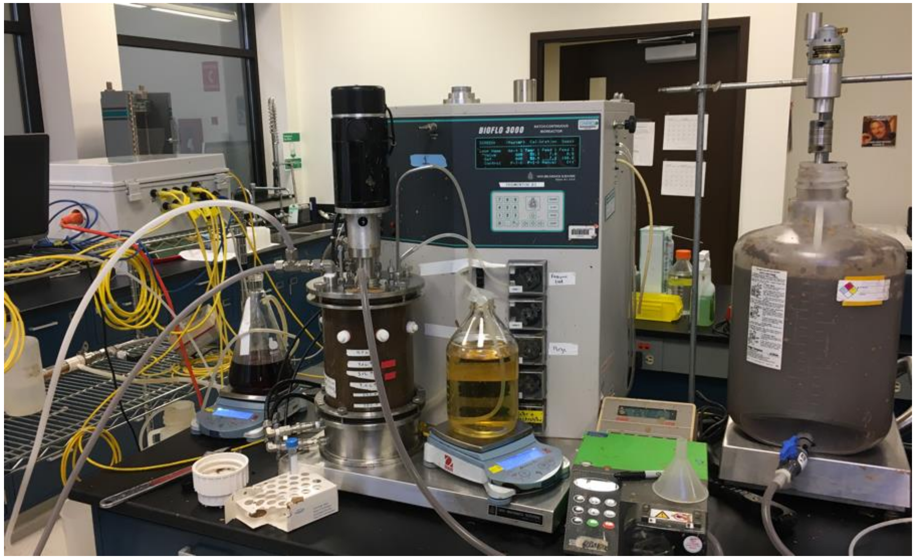
Overall approach: Cost-driven bench/mini-pilot R&D; TEA guides R&D priorities, generated experimental performance data used to refine TEA

Key performance measures: Sugar recovery yield & ΔMFSP (via TEA)



Technical approach:

- Single stage CEH system focus (expts): assess existing equipment capabilities; develop higher IS capable expt'l system
- Evaluate performance: understand sensitivities, key interactions, e.g., trade-offs between IS level, permeation rate and pumping power
- Develop model to simulate multi-stage performance from single stage (and batch) kinetics data (CEH model)
- Demonstrate compelling single-stage CEH performance
- Update TEA (BPA project), show potential to lower MFSP ≥ $0.25/GGE
  - CEHD provides expt'l data and base kinetic model; BPA leads Aspen-based TEA cost assessment



Approach (Technical, continued)

Bench/mini-pilot scale experiments using best available pretreated feedstocks and enzymes. Two pretreatments in play – mechanical refining (DMR) and dilute acid (DDA) – and many enzymes cocktails.

Critical Success Factors	Challenges	Strategy
Develop high IS capable bench/mini-pilot scale experimental system for performance testing CEHD	• Vertical CSTRs limited to operating at IS ≤ 5–7% w/w • Small scale high IS paddle reactors not available; custom fabrication increases $, time	• In-house /vendor testing to identify suitable equipment for high IS capable system • Minimize cost using used equipment
Sustained performance of CEH at IS ≥ 8.5% (10%), with TEA showing potential to lower MFSP ≥ $0.25/GGE (Go/No-go decision point) Subfactors: Membrane performance Enzyme performance Yield attainment	Large expt'l domain size / complexity as many key elements are under parallel R&D: Feedstocks, pretreatments, enzyme cocktails and sugar stream specifications still being defined or downselected	R&D prioritized by platform downselect process; use best pretreated feedstocks and enzyme available at sufficient quantities, e.g., use DDA material until DMR material becomes available

Technical Accomplishments/Progress
(summary)

Experimental

1. Extended bench-scale single-stage CEH performance testing to 7.5–10% IS] using DA PCS pretreated feedstock and Novozymes Ctec3 enzyme prep
2. Identified limits of existing equipment (feeder, reactor, pump around loop that prevent long-term operation of system at higher IS levels (≥ 7.5% IS)
3. Completed bench-scale evaluation of UF membranes for CEH
4. Finished pilot-scale testing of enzymatic hydrolysate clarification by TTF and RVDF (with flocculant) to support comparative TEAs
5. Used in-house and vendor equipment testing to identify/recommend improved bench/mini-pilot equipment to enable higher IS operation (feeder, reactor, pump, back-pressure valve); completed ordering longest lead time equipment

TEA modeling

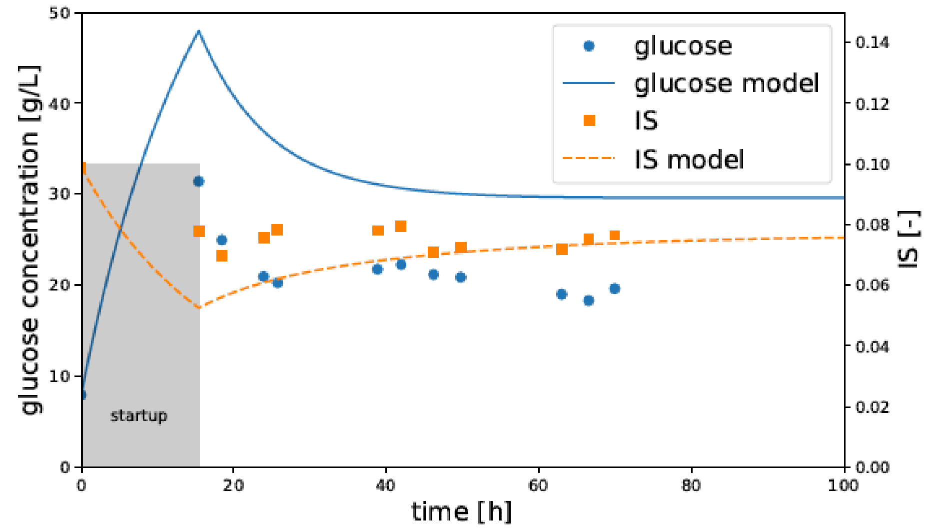
1. Updated CEHD SOT TEA based on updated EH kinetics (using DA PCS + Ctec3)
2. Projected CEH preferable to BEH+TTF or BEH+RVDF (with flocculant) due to potential to achieve higher yields (multi-stage system) and avoid using flocculant
3. Showed viability of preferred 2 sequential membranes CEH system (1° MF, 2° UF)
4. Extended TEA analysis rigor and capabilities by porting model into Aspen Custom Modeler (ACM)

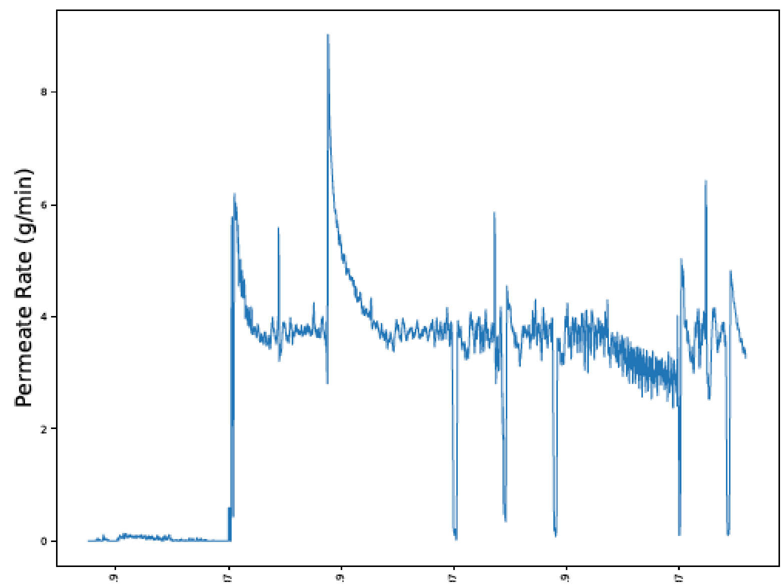
FY17 CEH Experimental Progress

Extended vertical CSTR-based CEH reactor system testing to 5–10% IS, *using DA PCS and Ctec3 enzyme; able to increase operable IS level to ~ 8.5% (vs. 5% previously) but not sustainably*

- ➔ SOT: Achieved 60% single pass conversion at 7.5% IS but struggled to continuously process high IS slurries using this bench-scale experimental system.
- ➔ Identified limitations of existing equipment that make it difficult to maintain stable operation over extended periods (12–24 h) at IS ≥ 5%.
- ➔ ***Reliable CEH operation at IS ≥ 7.5% requires more robust equipment*** *(for feeding, reaction and pump-around loop)*

IS target = 7.5%





FY18 CEH Experimental Progress

Defining New System for High IS Operation

Completed mini-pilot scale testing to evaluate alternative equipment (i.e., horizontal paddle blender reactor, suitable recirculation pump, back pressure valve, membrane unit) capable of maintaining operation at IS levels ≥ 8.5%

System (see photo): Jaygo paddle reactor, rotary lobe pump, Porex MF membrane (0.05 μm nominal pore size), recirculation loop (0.5” ID, target flow 30 ≥ LPM)

Showed: Paddle reactor effective; identified issues with pump and valve; Porex MF membrane unit performed well

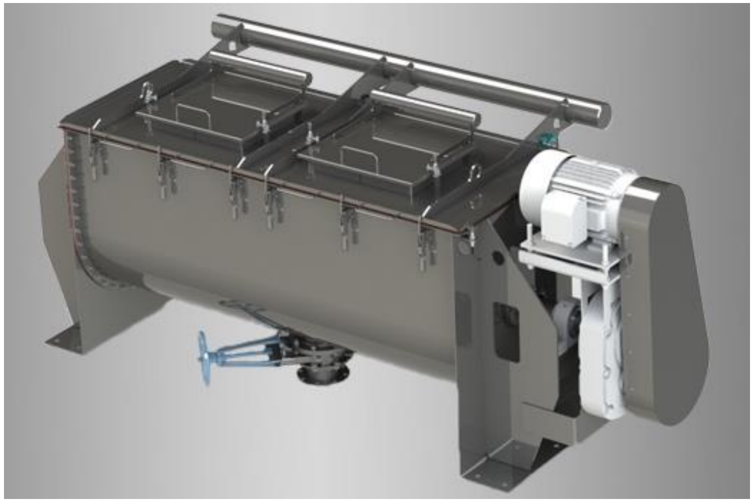
- Achieved favorably high permeation rates (membrane fluxes) using new MF membrane
  - 10% IS slurry: ≥ 90 L/m^2-h
  - 5% IS slurry: ≥ 105 L/m^2-h
- Substantially improved permeate flux performance over dual purpose MF/UF Koch membrane used previously
  - 5% IS slurry: ≤ 50 L/m^2-h

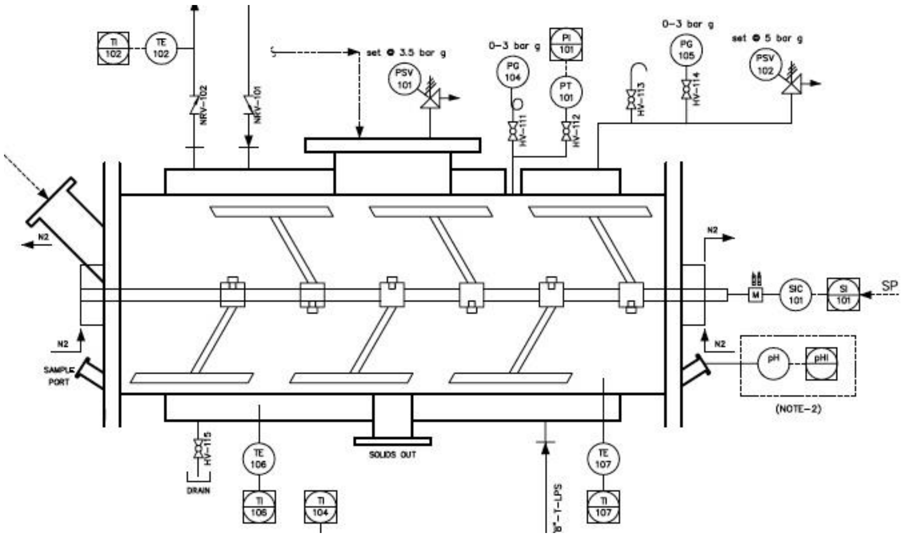
Validated: FY18 Q1 TEA modeling assumption that a slurry permeation rate of 100 L/m^2-h can be achieved

FY18/FY19 CEH Experimental Progress

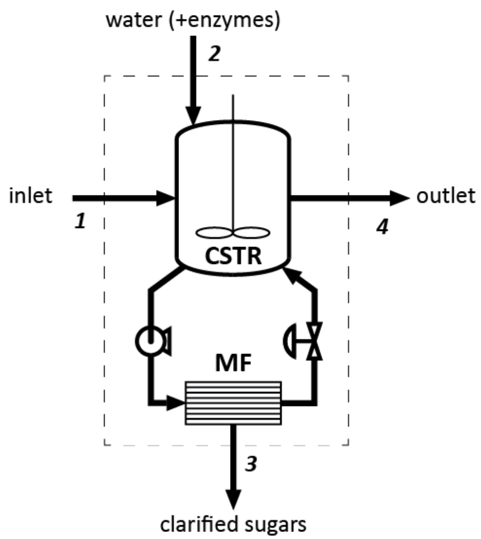
Identified, experimentally evaluated/verified equipment for operating CEH at IS ≥ 8.5%; procurement in progress

- Reactor vessel (new purchase)
  - **Horizontal paddle blender** vendor proposals received, evaluated; expensive and long delivery time (~ 6 months!)
- Feeder/Dispenser (new purchase)
  - **Micro-scale feedstock hopper-feeder** vendor-tested, showed good reliability on partially dried (42% IS) PCS feedstock; difficultly handling as-produced 30% IS PCS material. Scale-down feed handling issue.
  - Less costly, shorter delivery time (~ 2 months)
- Circulation pump (refurbish existing equipment)
  - Rotary-lobe pump tested for membrane loop proved problematic (pump slippage *and* pulsation issues)
  - **DiscFlo pump** – same type successfully used for pilot-scale Pall Cross/Tangential Flow Filtration (TFF) unit
    - Retrofit with VFD motor drive, controller, etc. in progress
- Backpressure valve (reconfigured equipment)
  - Pneumatic pinch-valve for membrane loop tested poorly
  - Fisher VeeBall with new straight-through trim to be tested



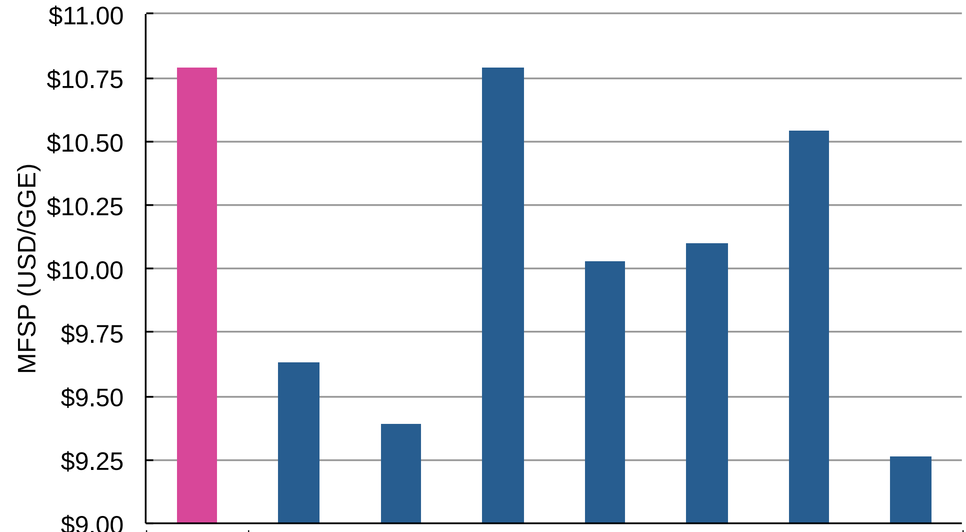


Cost Modeling Multi-stage Process



Model single CEH stage, simulate multiple stages in series using Python, then use ASPEN Plus (with BPA) to assess impacts on integrated biorefinery performance and TEA

- Used to identified key parameters and major cost sensitivities
  – Insoluble solids (IS) level
  – Permeate/feed ratio



	batch reference case	*continuous* 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*

Prior TEA shows:

1) High cost reduction potential (≥ 50¢/GGE) if CEH can be operated at high IS ≥ 7.5%

2) MSFP reductions exceeding $1/GGE possible if 3 CEH stages in series can be effectively / stably operated at IS ≥ 10%

FY17/FY18 CEH Modeling Progress

FY17: Completed comparative TEA of CEH vs. BEH followed by either cross-flow (tangential flow filtration, TFF) or vacuum filtration (rotary drum vacuum filter, RDVF) [based on updated kinetics and pilot scale results using DDA EH slurry]

- ➔ CEH found to be lowest cost option
- ➔ Also see benefit in lignin stream recovery/upgrading to avoid use of polyamide flocculent to enable effective post EH S/L separation (e.g., required for RDVF)

FY18: TEA showed negligible cost impact of modifying CEH scheme to use 2 sequential membranes (i.e., 1° MF at each stage, with 2° UF for combined permeate) [not shown]

Yield drives MFSP reduction

Comparative TEA Results

case	SLS type	MFSP $/GGE	fuel yield GGE/Tonne biomass	total installed CAPEX $MM	net variable OPEX $MM/y	net electricity export kW	SLS water consumption L/kg sugar recovered
reference	vacuum belt filter w/ flocculent	10.79	30.6	500	90	14,588	7.1
TFF	tangential flow diafiltration	11.27	30.6	493	103	-17,771	4.7
CEH	continuous reactive separations	9.63	35.1	520	90	1,076	15.5

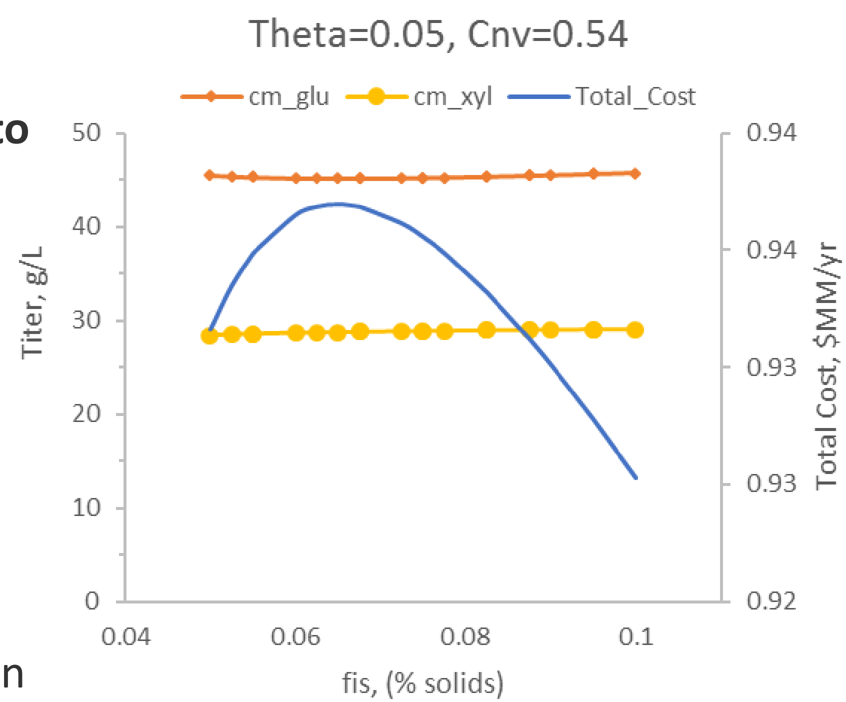
FY18 CEH Modeling Progress, cont'd

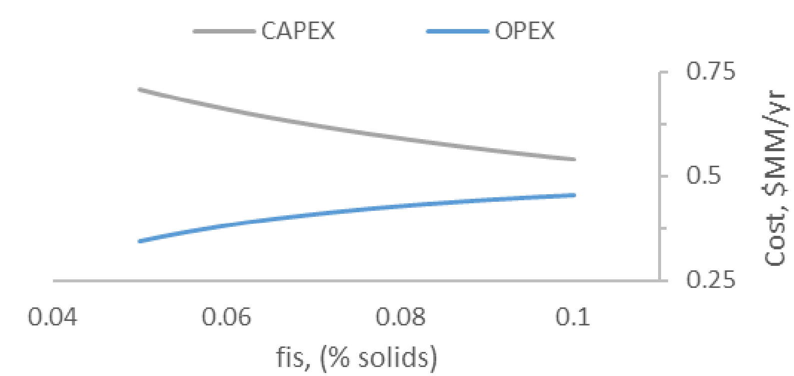
Improved modeling framework by creating ACM-based process model

Successfully ported Python-based CEH model into Aspen Custom Modeler (ACM), verified agreement, tested design space for local minima

Benefits future BC Platform R&D and TEA:

- ACM-based simulations enhance TEA evaluations by reducing cycle time when updating operation parameters if other upstream conditions change; process performance dependencies can be propagated in real-time within the simulation without costly iterations between separate models
- ***These benefits are not task-specific: this ACM framework can/will be applied to advanced TEA platform-wide****, e.g., starting with downstream fermentation process optimization*





Relevance

CEH is an essential component of the acids pathway process detailed in the 2018 biochemical design report:

- *Davis et al. 2018. Process Design and Economics for Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts NREL/TP-5100-71949*

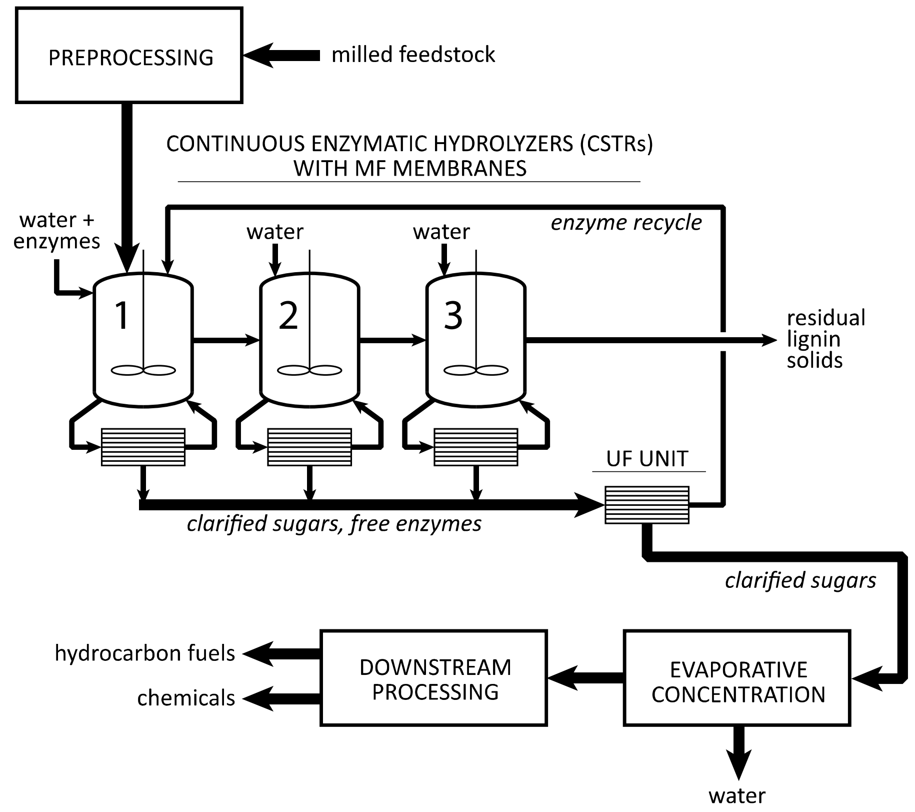
Intensified production of clarified sugars and clean lignin solids streams key to advanced upgrading concepts

– *Avoids flocculent use for this critical separation*

Successful development will provide a continuous biomass sugars manufacturing platform

Supports BETO's goal to develop **commercially viable** sugars to biofuels process technologies that achieve production costs ≤ $2.5/GGE

Aligns with MYPP strategic and performance goals to more efficiently produce and convert biomass sugars and lignin to hydrocarbon fuels and chemicals



Future Work

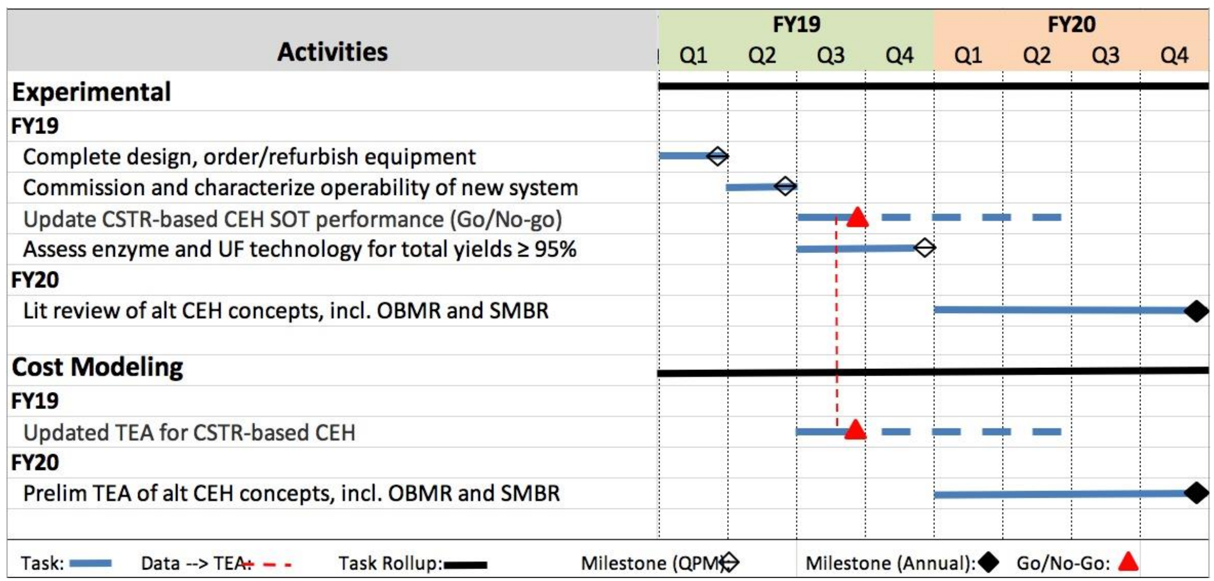
Status: Project in its 2nd year; existing system limitations motivated identifying superior and scalable equipment for improving CEH performance at small scale; procurement in process

Future work: Update CEH State of Technology at higher IS using new system (data & TEA)

Major research elements:

1) Demonstrate CEH at IS ≥ 8.5% and update TEA; achieve compelling performance; pass project's Go/No-go decision milestone
2) Extend CEH performance testing using PCS beyond DA / DDA to DMR pretreated feedstocks
3) Assess/verify ability of UF-recycled enzymes to achieve ≥ 95% cellulose conversion yields (if needed, identify issues hindering this and develop/implement mitigation strategies)
4) Explore other advanced concepts for implementing CEH via both lit. review and preliminary TEA, e.g., Submerged Membrane BioReactor (SMBR) or Oscillatory Baffled Membrane Reactor (OBMR)

Gantt chart FY19-20:



Summary

Overview/Approach: Develop CEH via cost-driven TEA-guided bench/mini-pilot scale R&D

Results FY17-FY19: Generated data, refined CEH model to improve TEA & guide R&D priorities

Experimental:

- **Extended CEH testing to 7.5–10% IS** and updated CEH State of Technology (SOT) (Expt & TEA)
- IDd issues preventing long-term operation at IS ≥ 7.5% in existing system; **IDd equipment to enable high IS operation** (i.e., feeder, reactor, pump, back-pressure valve); ordered equipment; **procurement pending**
- Completed pilot-scale testing of batch enzymatic hydrolysate clarification by TTF and RVDF (with flocculant)

Cost Modeling:

- **Updated CEH SOT TEA** based on updated EH kinetics (using DA PCS + Ctec3)
- **TEA based on pilot-scale data showed CEH preferable** to BEH+TTF or BEH+RVDF (with flocculant) due to **1) higher yields** (assuming 3-4 stages of CEH) **and 2) avoiding use of flocculant**
- **TEA also showed cost equivalency of 2 sequential membrane system** rather than 1 (1° MF, 2° UF)
- **Ported simulation model into Aspen Custom Modeler (ACM)** to extend future TEA analysis capabilities and rigor

Relevance: CEH essential to realize economical clarified biomass sugars-to-hydrocarbon biofuels and chemicals processes. CEH intensifies the rate limiting EH step; reduces CAPEX; enables a continuous manufacturing platform.

Future Work: FY19

1) Assess UF recycled enzymes' ability to achieve total cellulose conversions ≥ 95%
2) Assemble, commission and verify high IS operability of new experimental system for CEH

Outyear: FY20

1) Update CEH performance data and TEA at IS ≥ 8.5% using new experimental system
2) Decision: Extend CSTR-based CEH development or alternative lower TRL concept(s) for CEH
3) Contribute to on-going BC platform demo process down select

Acknowledgments

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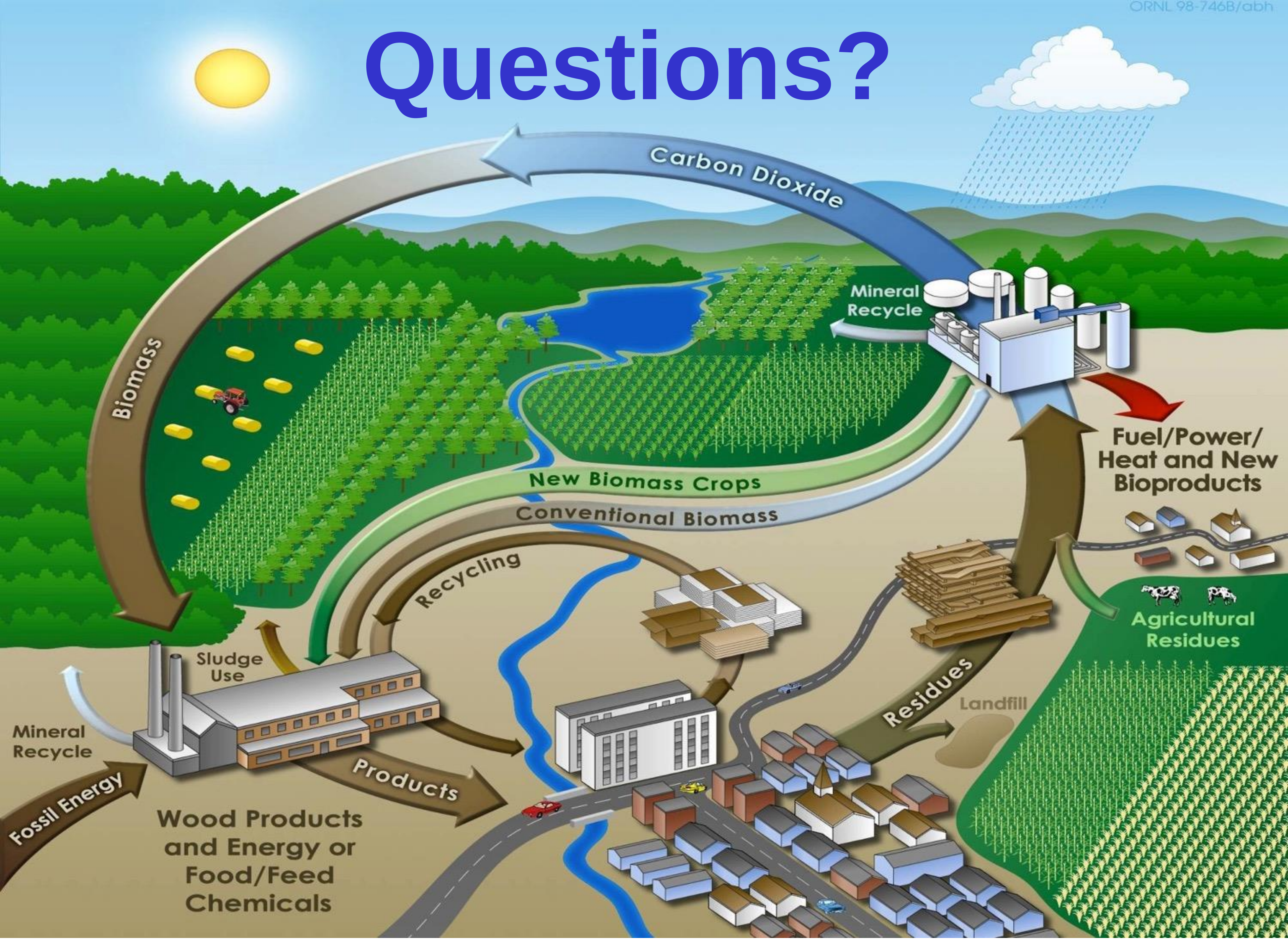
NREL Project Contributors

CEHD: David Sievers, Ben Gallman, Jim Lischeske, Jonathan Stickel

BPA (TEA modeling)**:** Ryan Davis, Nick Grundl

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
Residues
Landfill
Products
Fossil Energy
Wood Products and Energy or Food/Feed Chemicals

Thank You

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Additional Slides

Response to Reviewers' Comments 2017

The re-focusing of the project's scope from broader process separations to development of CEH following 2017 merit review is highly responsive to previous reviewer comments. Rather than continuing to have a research scope spanning broader sugars- and lipids-recovery separations, the project now focuses solely on development of innovative CEH technology that implicitly incorporates *in situ* enzyme recycle and clarification (S/L separation) of the product sugars stream and produces a lignin-rich solids stream not contaminated by polyamide flocculent. This change is consistent with 2017 Peer Review feedback to focus on the most innovative, highest impact R&D elements and to deemphasize further optimization of sugar, lignin and product related separations since many integrated process elements remain incompletely specified and under development (e.g., feedstock, pretreatment method, enzyme cocktail, and specification for produced sugar and lignin streams. The newly created Separations Consortium is focusing on complimentary product recovery related separations rather than production of intermediate sugar and lignin streams like the CEHD project.

Publications & Presentations

1. D.A. Sievers, J.J. Stickel, N.J. Grundl, and L. Tao. 2017. Technical Performance and Economic Evaluation of Evaporative and Membrane-Based Concentration for Biomass-Derived Sugars. ***Ind. Eng. Chem. Res***., **56**, 11584−11592. DOI: 10.1021/acs.iecr.7b02178.

2. D.A. Sievers, E.M. Kuhn, M.P. Tucker, J.D. McMillan. 2017. Effects of Dilute-acid Pretreatment Conditions on Filtration Performance of Corn Stover Hydrolyzate. ***Bioresource Technol***., ***243***, 474–480. DOI: http://dx.doi.org/10.1016/j.biortech.2017.06.144

3. J.J. Stickel, B. Adhikari, D.A. Sievers, J. Pellegrino. 2017. Continuous Enzymatic Hydrolysis of Lignocellulosic Biomass in a Membrane-reactor System. ***J. Chem Technol Biotechnol.***, **93**: 2181–2190. DOI: 10.1002/jctb.5559.

Presentation

1. McMillan, J.D. 2017. Separations Development and Application (WBS 2.4.1.101). Presented in Biochemical Conversion Session of the DOE BETO 2017 Project Peer Review, Denver, Colorado, March 7, 2017. Available a:t https://www.energy.gov/eere/bioenergy/downloads/2017-project-peer-review-biochemical-conversion

Project Gantt Chart FY17-FY20