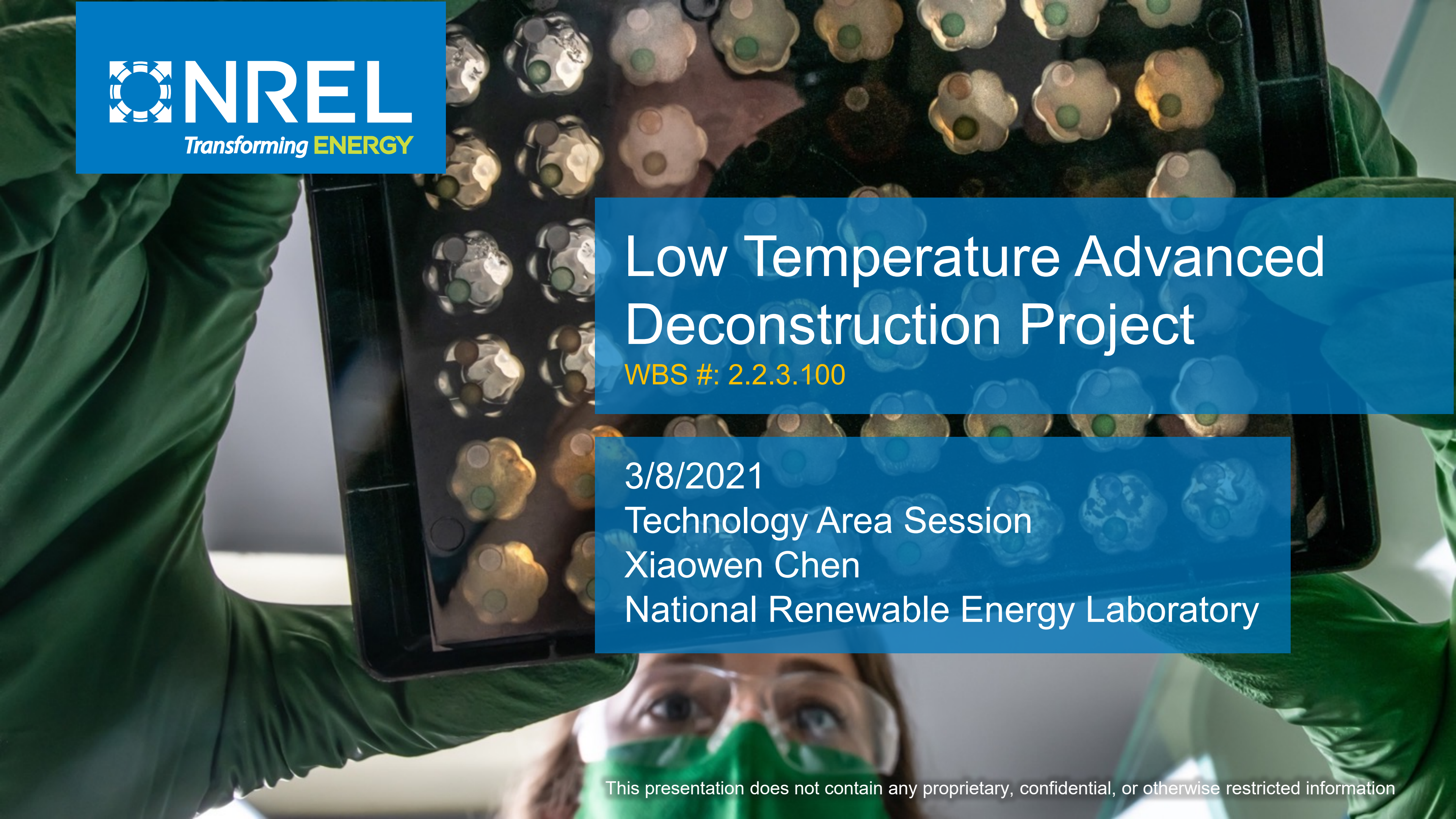


NREL
Transforming ENERGY

Low Temperature Advanced Deconstruction Project

WBS #: 2.2.3.100

3/8/2021

Technology Area Session

Xiaowen Chen
National Renewable Energy Laboratory

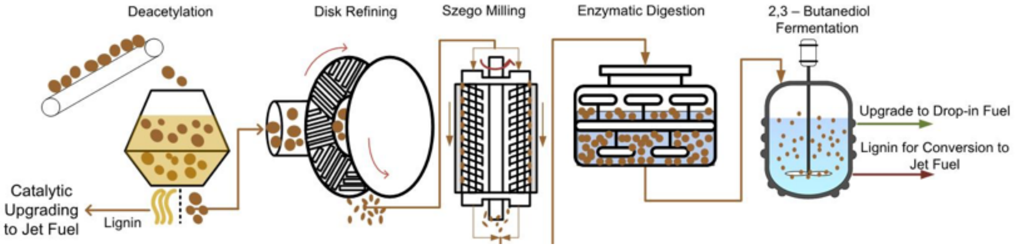
Project Overview

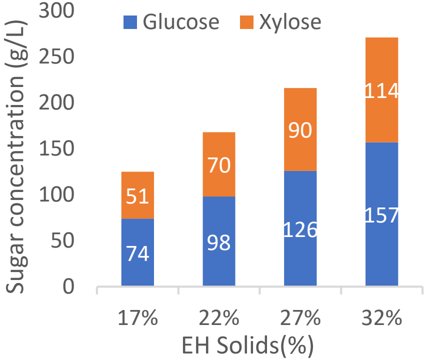
Project Goals: Develop industry relevant and cost-effective low temperature deconstruction processes that produce **high yields, low cost and upgradable sugar** and **tractable, reactive lignin** streams from relevant feedstocks, meeting BETO's 2022 and beyond (2030) targets and goals.

- BETO's Multi-Year Plan (2020) Metrics: "*By 2022, achieve 90% monomeric sugar yield from hydrolysis of deacetylation and mechanical refining (DMR) solids at low (10 milligrams/gram) protein loading using a new DMR-specific enzyme cocktail formulation*".
- Achieve 90% sugar yield at 10 mg/g of cellulose
- Reduce GHG emissions of the DMR process
- Improve overall carbon utilization of the biomass

Project Overview

The Deacetylation and Mechanical Refining Process (2019 peer review meeting)



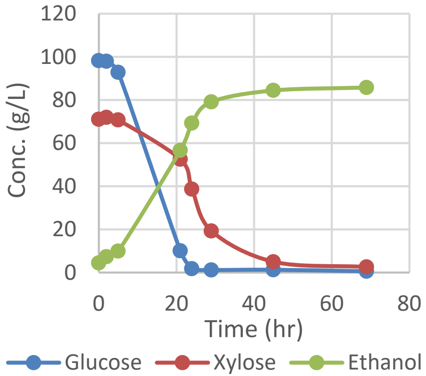


Advantages & Importance

- Low Temp
- Atmospheric Pressure
- No toxic chemicals
- Uses industrial equipment
- ↘ Capital cost
- ↗ Operation reliability
- ↘ Maintenance cost
- Scalable and Industry relevant

- High sugar yield/titer
- Low enzyme loadings
- ↗ Revenue
- ↘ Operational cost

- Highly fermentable
- Reactive Lignin
- ↗ Revenue and value-added products



Market Trends

Product	Gasoline/ethanol demand decreasing, diesel demand steady
Product	Increasing demand for aviation and marine fuel
Product	Demand for higher-performance products
Product	Increasing demand for renewable/recyclable materials
Feedstock	Sustained low oil prices
Feedstock	Decreasing cost of renewable electricity
Feedstock	Sustainable waste management
Feedstock	Expanding availability of green H_2
Feedstock	Closing the carbon cycle
Capital	Risk of greenfield investments
Capital	Challenges and costs of biorefinery start-up
Capital	Availability of depreciated and underutilized capital equipment
Social Responsibility	Carbon intensity reduction
Social Responsibility	Access to clean air and water
Social Responsibility	Environmental equity

NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

Value Proposition

- LTAD project directly supports BETO's mission by:
  - Developing innovative biomass deconstruction
  - Lowering the cost of intermediates
  - Using a simple and mild process with existing industrial technologies.

DMR process differentiates from other process by:

- Produces **high titer clean sugars** to enable subsequent high T/R/Y bioconversion
- Simplifies the deconstruction process and **lowers the requirement and costs for equipment.**
- Produces a **less condensed, sulfur-free lignin.**
- Competitive sugar price (Minimum Sugar Selling Price :~$0.25/lb)

Quad Chart Overview

Timeline

- Starting: 10/1/2018
- Ending: 9/30/2021

	FY20	Active Project
DOE Funding	$1.5M	$4.5M

Project Partners*

- Allison Ray, Vicki Thompson, Idaho National Lab
- Zhiyong (Jason) Ren, Princeton University
- Xiao Zhang, Bin Yang, Washington State University
- Jian Shi, University of Kentucky

Barriers addressed

Ct-B. Efficient Preprocessing and Pretreatment

Aft-J. Resource Recapture and Recycle

Project Goal

Develop industry relevant and cost-effective low temperature deconstruction processes that produce high yields, low cost and upgradable sugar and tractable, reactive lignin streams from relevant feedstocks, meeting BETO's 2022 and beyond (2030) targets and goals.

End of Project Milestone

Achieve at least 90% sugar yields at 10 mg/g cellulose (or less).

Reduce pretreatment cost by 30% compared to FY18 SOT.

Funding Mechanism

AOP project

Management (Project Structure)

ANDRITZ

novozymes

Low Temperature Advanced Deconstruction
PI: Xiaowen Chen (formerly Melvin Tucker)

- Biochemical Platform Analysis (WBS#: 2.1.0.100)
- Enzyme Eng. Optimization (WBS#: 2.5.4.100)
- Bench Scale Integration (WBS#: 2.4.1.100)
- Pilot Scale Integration (WBS#: 2.4.1.301)
- Lignin Utilization (WBS#: 2.3.4.100)
- Feedstock Conversion Interface Consortium

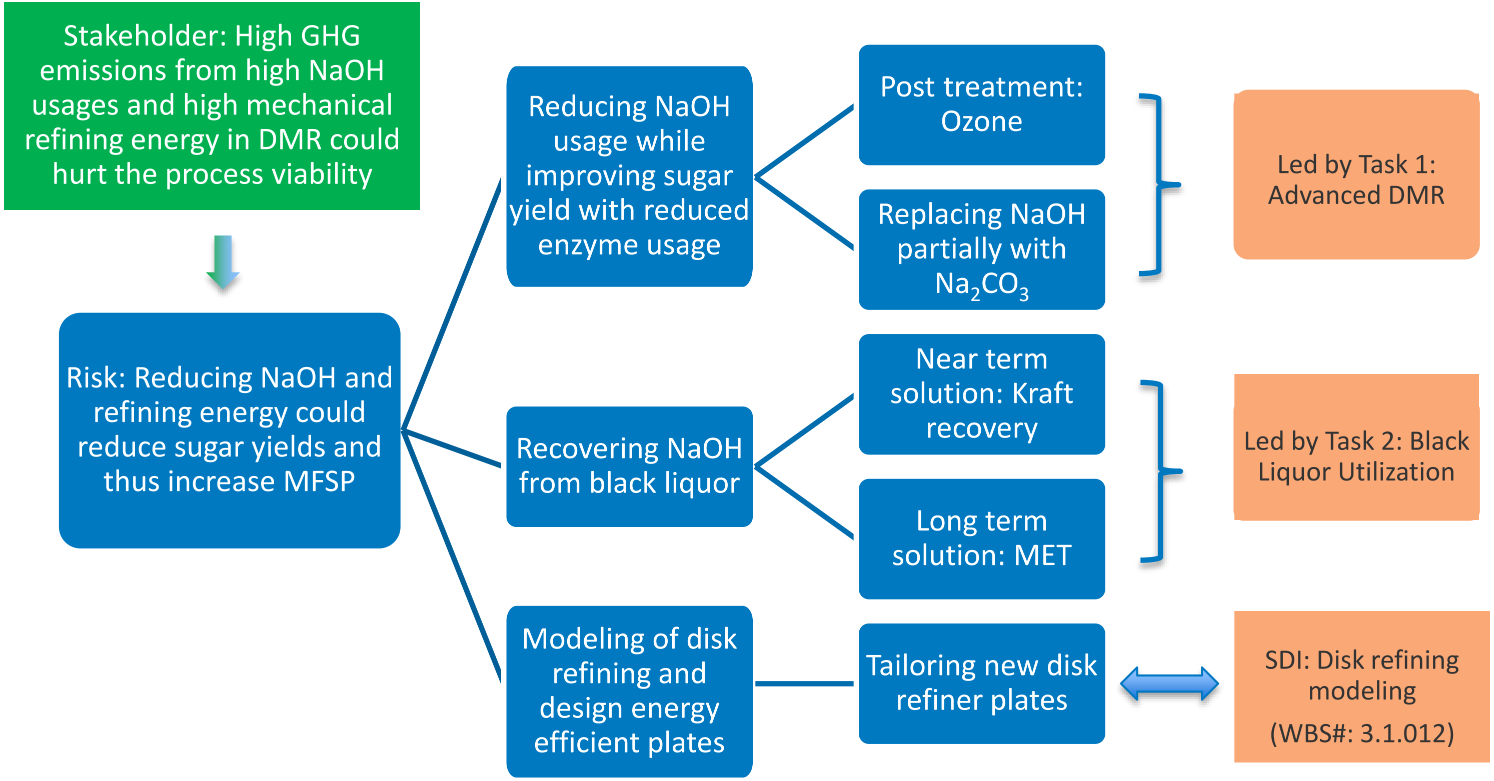
Task 1: Advanced DMR Process Development

- Chemical Engineer: Nick Nagle, Xiaowen Chen, Yudong Li, Dave Sievers — Design/execute/data analysis/modeling of advanced DMR process
- Chemists: Ashutosh Mittal, Rui Katahira, John Yarborough, Darren Peterson — Analyzing/imaging biomass/intermediates/end products

Task 2: Black Liquor Utilization

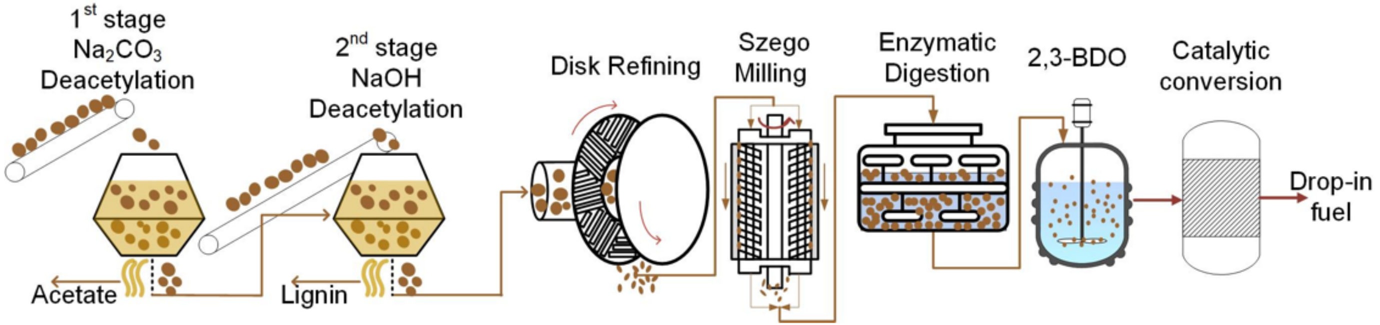
- Chemists/Biologists: Ashutosh Mittal, Wei Wang, Hui Wei, Tao Dong , Robert Nelson — Characterization of black liquor, fractionation of black liquor
- Subcontract: Zhiyong Ren at Princeton University — Develop Microbial Electrochemical Technologies (MET)

Management (Risk Mitigations)

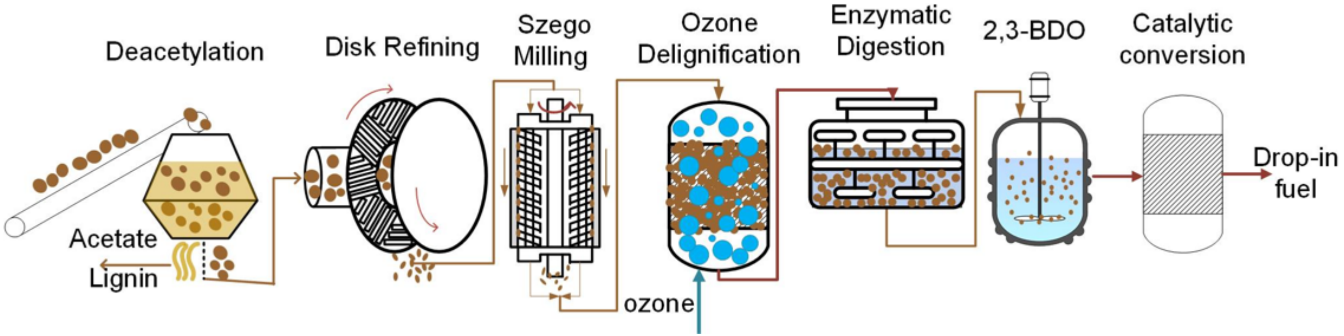


Approach(es)

Approach 1a: 2-stage Na_2CO_3 and NaOH deacetylation: GHG emission reduction while improving sugar yields



Approach 1b: post treatment with ozone delignification to reduce NaOH usage while improving sugar yields

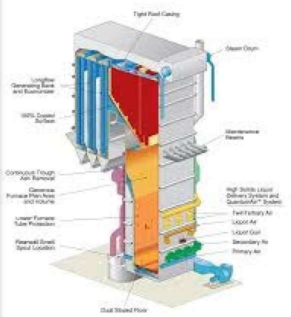


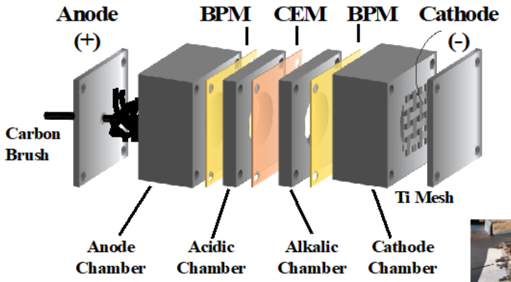
Approach 2: NaOH Recovery

Approach 2: Recovering NaOH from deacetylation waste liquor to further reduce chemical cost and GHG emissions

Benchmarked 4 different NaOH recovery case using TEA tools

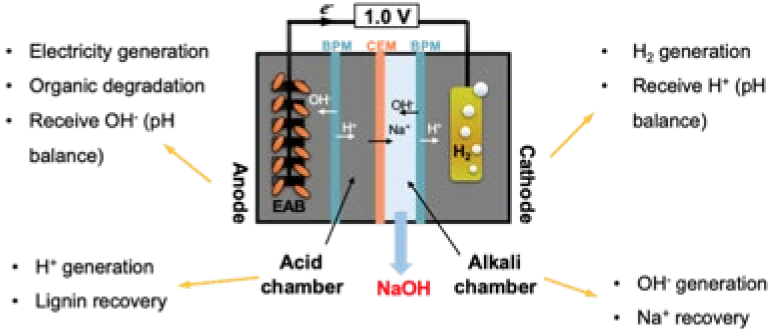
- Addressing 2019 Peer Review (PR) comments
  - Not enough TEA analysis
  - provide competitive benchmarks





Developing novel NaOH recovery technology based on Microbial Electrochemical Technology (MET)

- Addressing PR comments
  - Sodium hydroxide recovery will *be critical* for commercial viability.



Approach 3: Feedstock Variability

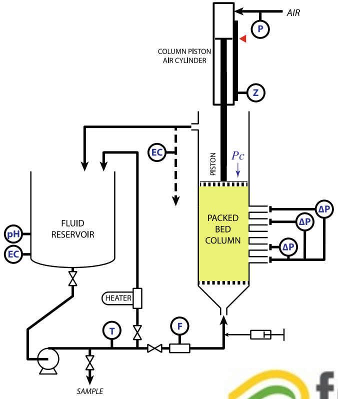
Approach 3: Emphasis on studying feedstock variability through corn stover anatomical fractions, implications on DMR process (2019 PR comments)

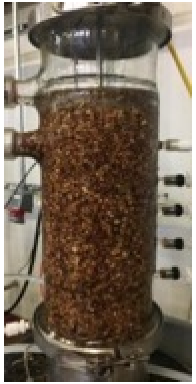
Kinetics and mechanism study of anatomic fractions for DMR and enzymatic hydrolysis

A: cob B: Husks C: Stalks D: Whole Material

Collaborated with FCIC: Task 5

anatomical fraction impact on packed bed permeability and compressibility





Impact

LTAD focuses on developing novel biomass deconstruction processes and improving key process performance by reducing CAPEX and OPEX for advanced biofuel and bioproducts, while reducing GHG emissions to ultimately enable carbon-negative sugar production from agricultural wastes.

Our DMR process provides:

1. a **simple, reliable, and industrial relevant** biomass deconstruction process to produce **low-GHG cost-competitive clean sugars**
2. a **highly-fermentable high concentration sugar stream** to enable high T/R/Y production of biofuel and bioproducts
3. potential to **leverage depreciated and underutilized equipment** from 1st and 1.5 generation ethanol plants as well as from decommissioned pulp mills

Our MET technology provides:

1. solutions for **wastewater treatment in advanced biorefinery industries** and potentially traditional pulp mills by integrating chemical/water recovery, lignin separation, green electricity and H_2 production

Impact

LTAD project contributes to the knowledge base through publication and patent and collaborates with Industries for technology scale-up testing and commercialization.

- Publication impact:
  - 9 peer reviewed journal paper
  - total impact factor of 85.5
  - 2 ROIs
- Presentation:

ABLC2020
Advanced Bioeconomy Leadership Conference
March 25-27, 2020 - Washington, DC

SBFC
Symposium on Biotechnology for Fuels and Chemicals

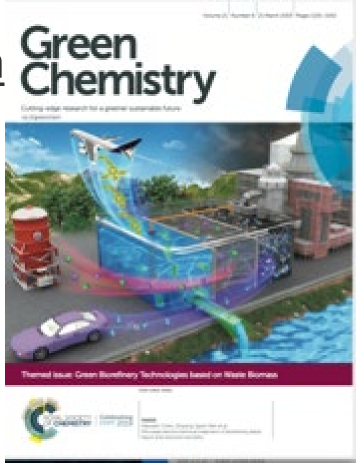
ACS
Chemistry for Life®

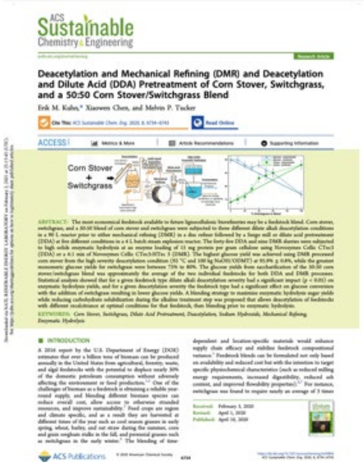
- Industry:

ANDRITZ

novozymes®

ExxonMobil




ACS Sustainable Chemistry & Engineering

Deacetylation and Mechanical Refining (DMR) and Deacetylation and Dilute Acid (DDA) Pretreatment of Corn Stover, Switchgrass, and a 50:50 Corn Stover/Switchgrass Blend

Erik M. Kuhn,* Xiaowen Chen, and Melvin P. Tucker

Progress and Outcomes

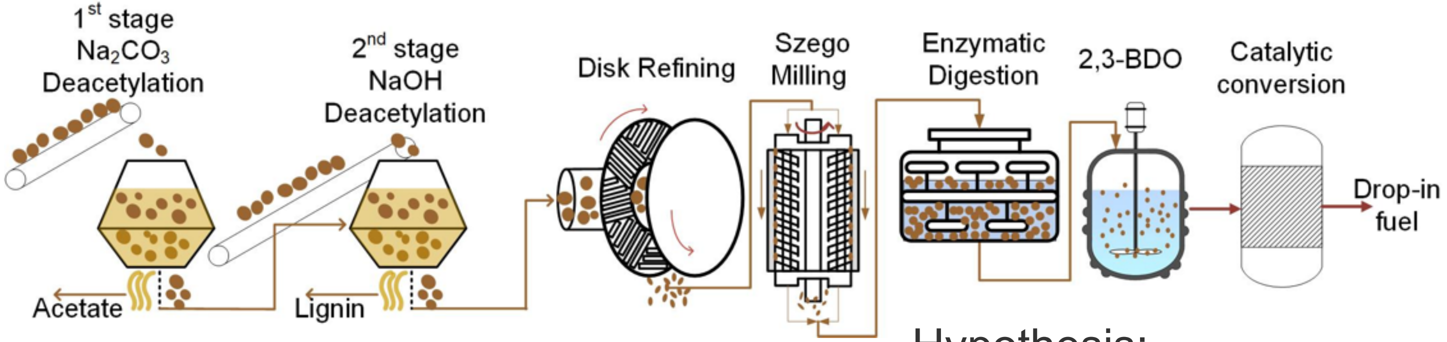
LTAD Major achievements 2019-2021:

- 2022 target glucose yield (90%)
  - Including xylose yield of 88%
  - Using enzyme loadings (10 mg protein/g of cellulose)
- $1/gge reduction of MFSP in FY20 SOT
  - reduces chemical and enzyme usage
  - improved sugar yields
- 22% and 30% reduction in GHG emissions and fossil energy consumption, respectively
- Met/exceeded all required milestones

2-stage Na_2CO_3 and NaOH Deacetylation

Modified DMR Process to Reduce GHG Emissions While Improving Sugar Yields

2-stage Na_2CO_3 and NaOH deacetylation replacing traditional 1-stage NaOH deacetylation



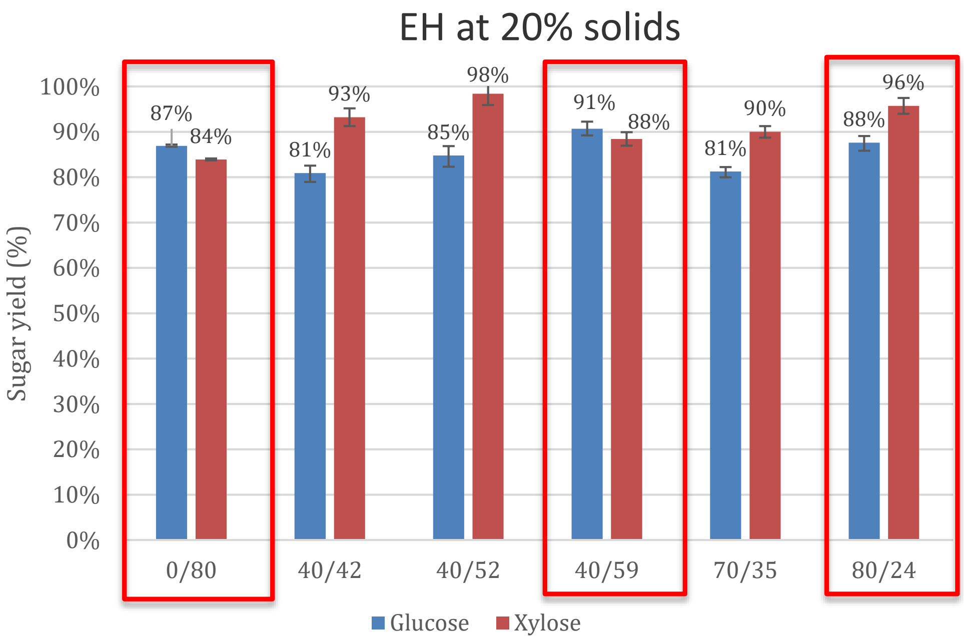
	GHG* (CO_2e/kg)	Fossil Energy (MJ/kg)	Total Energy (MJ/kg)	Cost ($/lb)
NaOH (100%)	2.1	28.9	32.3	0.24
Na_2CO_3 (100%)	0.7	5.93	5.94	0.08

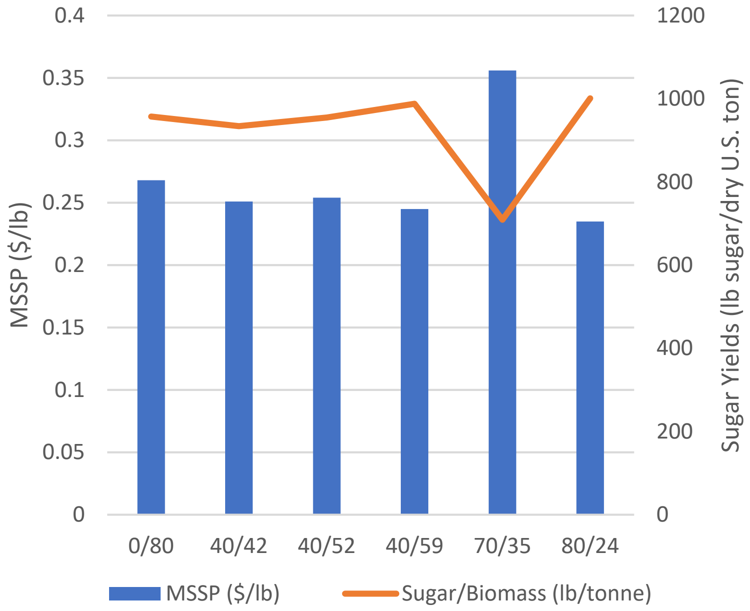
*The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET)

Hypothesis:

- 1st stage deacetylation uses Na_2CO_3 to neutralize acids in corn stover (acetic, formic, lactic acids and etc.)
- We used a reduced amount of NaOH to partially delignify the biomass
- Tested its feasibility and received positive results, leading to extended research in Q4 and incorporated into current 2020 SOT

2-Stage Deacetylated and Mechanical Refining

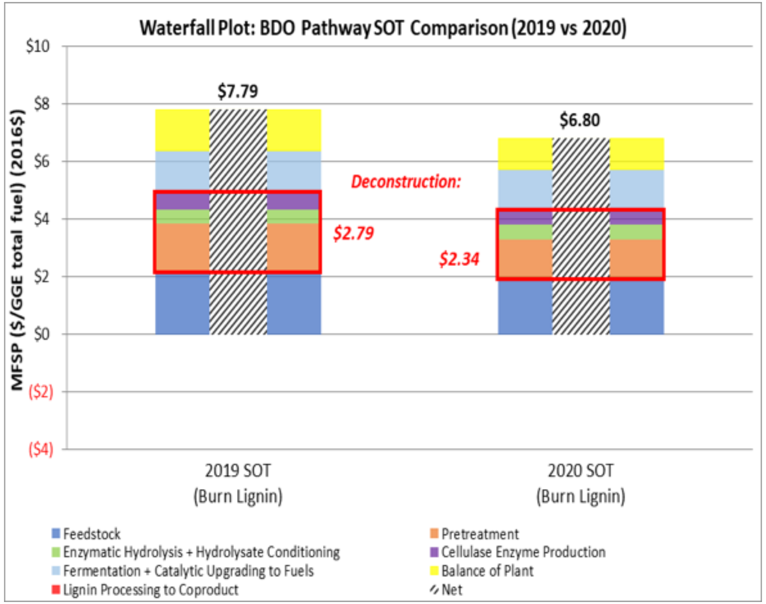


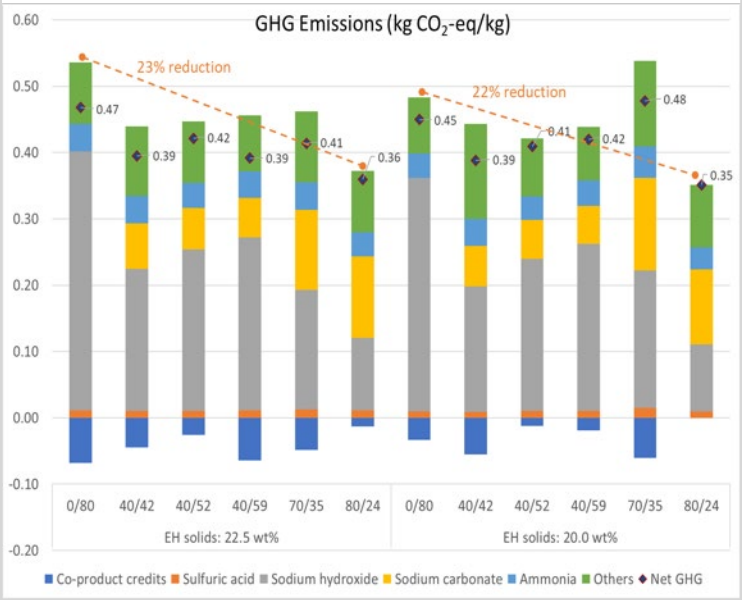


xx/xx : Na_2CO_3 (kg/tonne) / NaOH (kg/tonne) (all loadings based on original biomass weight)
Enzyme loading: 8 mg CTec3/g of cellulose and 2 mg HTec3/g of cellulose

- Achieved target glucose yields (>90%) at 20% solids with an enzyme loading at 10 mg protein/g of cellulose.
- The 80 kg Na_2CO_3 + 24 kg NaOH/ton biomass reduced MSSP by 12%

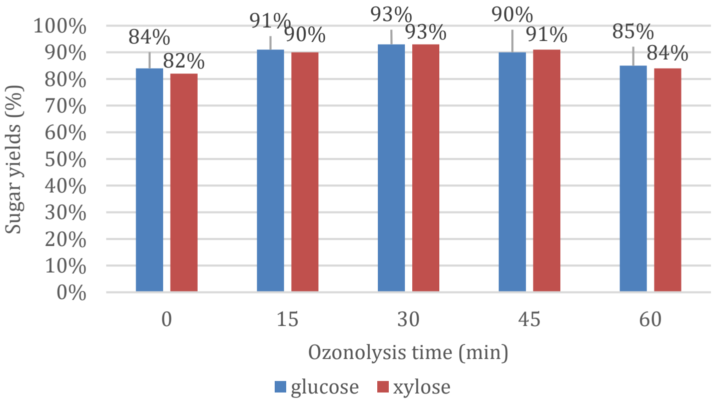
Effect of 2-stage Deacetylation on TEA and LCA

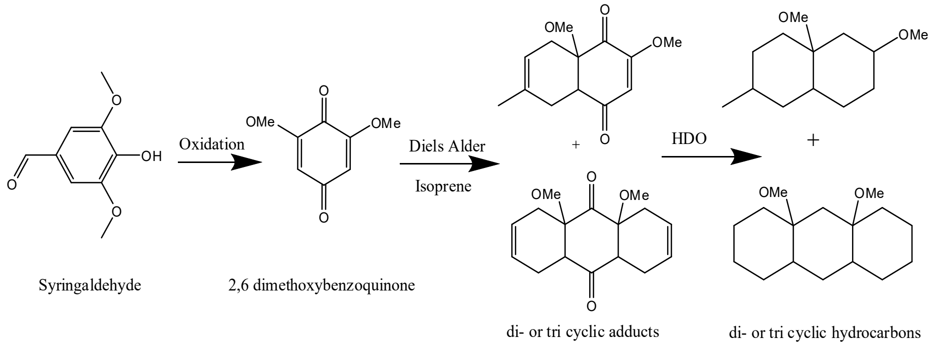


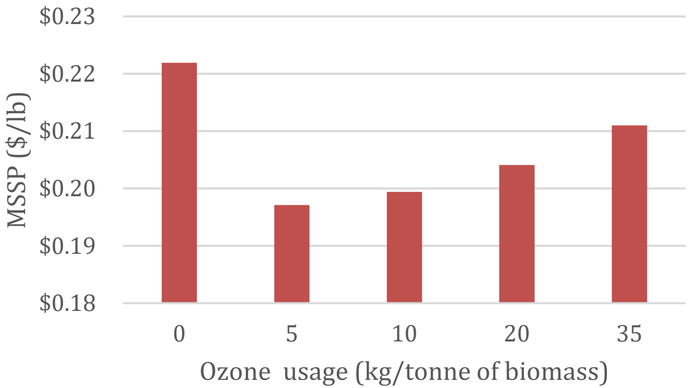


- The 2-stage deacetylation contributes nearly <u>$1/gge reduction on the Minimum Fuel Selling Price (MFSP)</u> in the FY20 SOT.
- The 2-stage deacetylation also reduces GHG emissions of sugar production by up to 23%.

DMR with ozone post-treatment to produce more digestible biomass and upgradable lignin



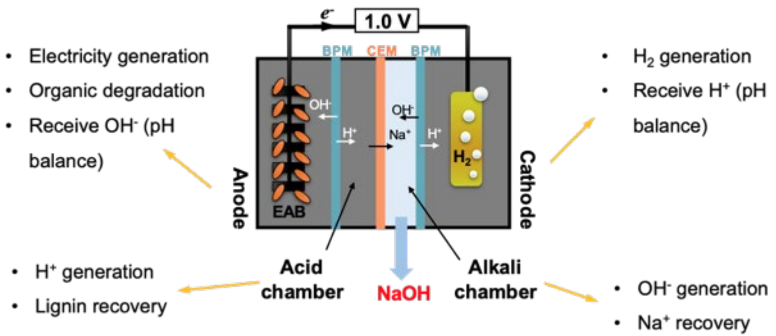


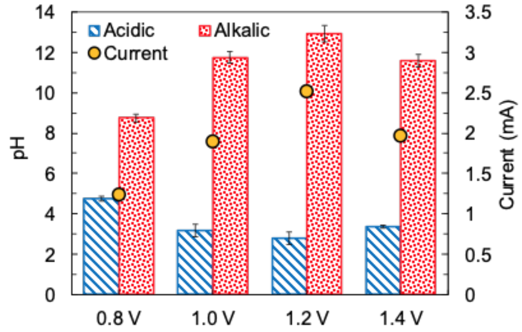


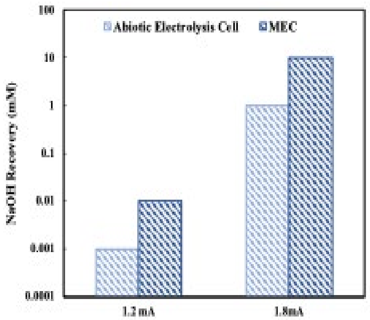
Preliminary TEA analysis. Assumptions: CAPEX is not included; using an older MSSP model (work done in early 2019)

- Increased sugar yields up to 10% and has potentials to substantially reduce MSSP
- Developed a novel pathway to convert ozone oxidized lignin moieties into high energy density jet fuel blendstocks at room temperature
- Considering high electricity cost of current ozone generation (7kWh/kg of ozone), ozone treatment could be a supplemental pathway for the 2-stage deacetylation where renewable electricity is available and more recalcitrant biomass is used

NaOH Recovery by Microbial Electrochemical Technology (MET)

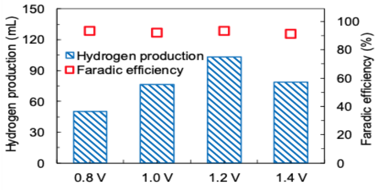


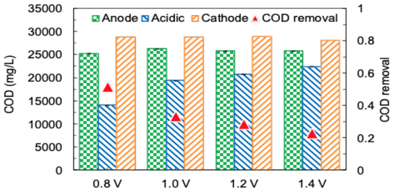




Schematic: Multifunctional MET
- Removal of black liquor COD with lignin recovery
- Recover of NaOH: replenish alkali consumption
- Production of H_2: renewable H_2 for biojet precursor upgrading

NaOH recovery
- 50% electricity savings compared to abiotic electrolysis cells
- up to 10x higher NaOH recovery using MET than the abiotic electrolysis cell

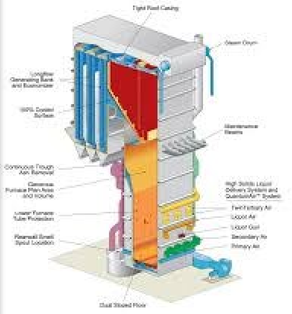




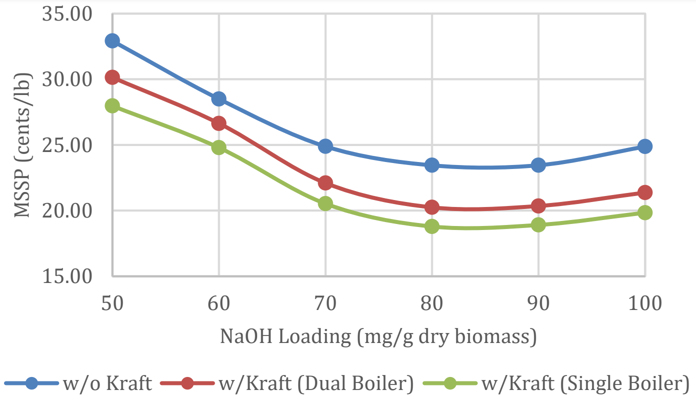
H_2 production and COD degradation:
- Producing H_2 by degrading organic waste matter in black liquor
- Enabling NaOH recovery net-energy negative without the need to burn lignin
- Maximum COD removal > 52%

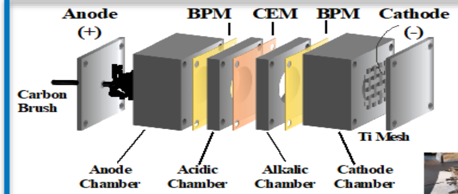
Future research focus
- Elevate current density to 0.5 mA/cm2 cathode area
- Scale up to 1 gallon/day reactor
- Reduce reactor scaling by precipitating lignin /COD

Benchmarking NaOH Recovery Technologies using TEA Analysis

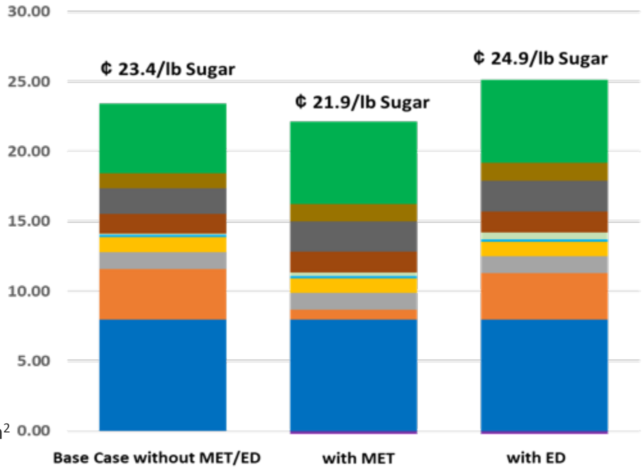


Conventional Kraft Recovery Boiler





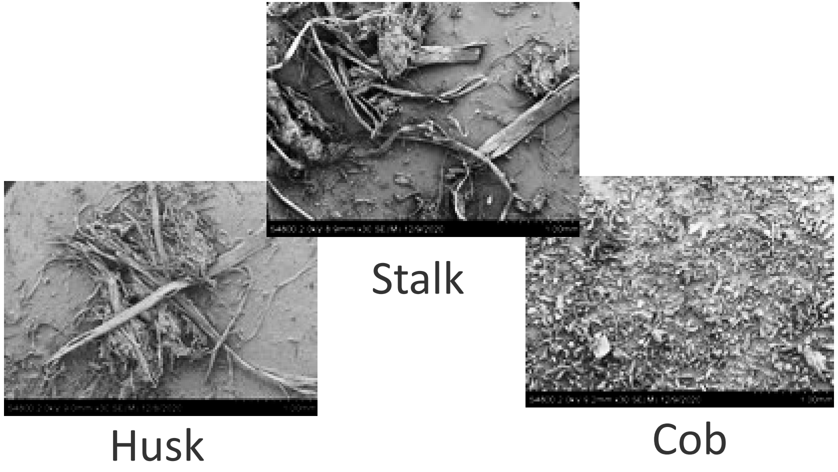
Base vs. MET vs ED (electrodialysis)



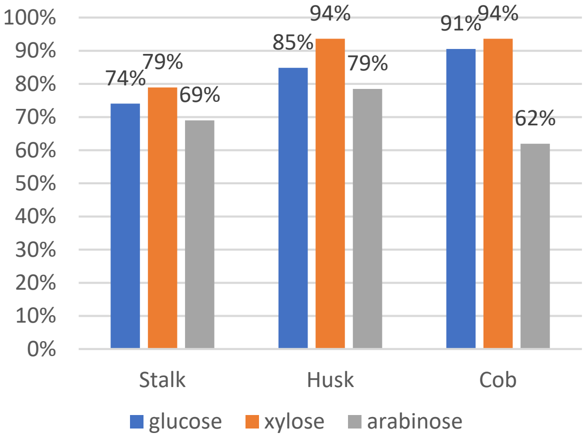
Assumptions: 1. Current density (MET &ED) reach 10 mA/cm^2
2. MET only utilizes acetate in black liquor

- Kraft process could reduce Minimum Sugar Selling Price (MSSP) up to ~20% (Requires burning lignin-short term solution)
- MET reduced MSSP by ~6.7% compared to base case, while ED increased MSSP by ~6.0% (will not burn lignin)
- MET has potential to further reduce MSSP by utilizing biomass extractives

Solving the Feedstock Variability Puzzle through Anatomic Fractions



Fraction	% of each fraction
Stalks	24
Cobs	8
Leaves	26
Husks	18
Other	24

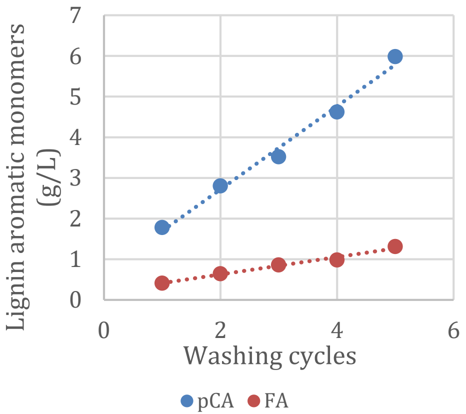


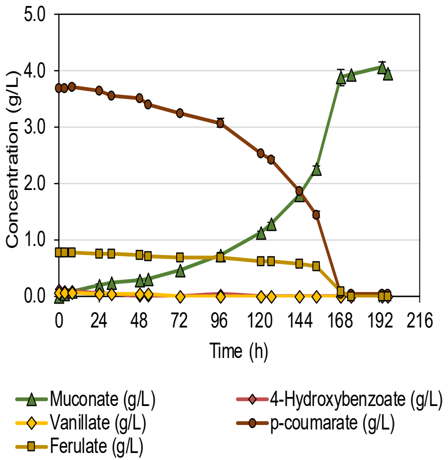
- Digestibility:
  - Cob>Husk>Whole material>Stalk
- DMR material structural disruption:
  - Cob ≥ Husk > Stalk
- Ongoing research: Deacetylation kinetics and mechanism study, permeability and compressibility
- Future work: To maximize corn stover value and minimize operational cost: Air classification followed by differential DMR process

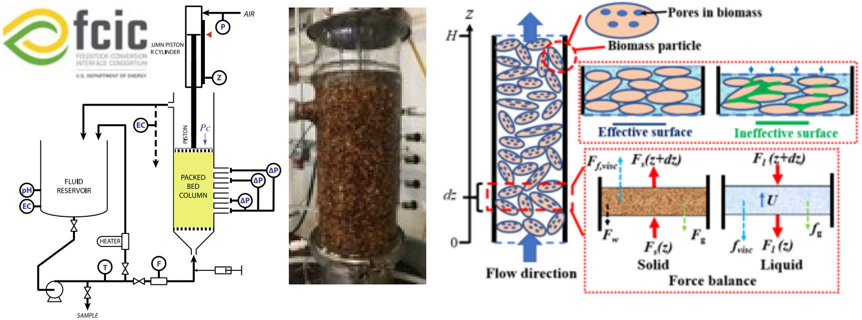
Collaboration with Other BETO Projects

- Continue research on counter current deacetylation in pilot scale shaftless screw reactor. Improved the system by using an automatic feeder.

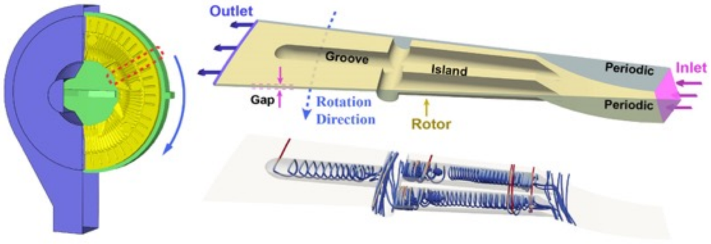
- Collaborated with Lignin Utilization (WBS#: 2.3.4.100) & produced up to 4 g/L of muconate from recycled black liquor solution.







Collaborated with FCIC task 5 on developing mechanistic model to predict feedstock variability, implications relevant to industrial deacetylation process



Collaborated with SDI seed project (WBS: 3.1.1.012) on modeling disk refining of DMR corn stover to predict energy consumptions

Summary

- Management
  - Project milestone design to address BETO's requests for reducing GHG emissions
  - Build a skilled process team
  - Implementation of risk management in multiple tasks
- Approach
  - Two stage Na_2CO_3 and NaOH deacetylation with mechanical refining
  - DMR with ozone post-treatment
  - Novel consolidated NaOH/water recovery & renewable H_2 production through MET
  - Address peer reviews' comments through multiple approaches
- Impact
  - Developed a simple, mild, and industrially relevant pretreatment process
  - 9 Publications (total IF: 85) and 2 ROIs Submitted
  - Collaboration with Andritz, Novozyme and ExxonMobil to scale up the DMR process
- Progress and Outcomes
  - Achieved the 2022 target glucose yield (90%) at the target enzyme loadings as required by 2020 Multi Year Plan (MYP).
  - Reduced MFSP in FY20 SOT by approximately $1/gge.
  - Reduced GHG emissions by up to 23%

Thank you

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This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

NREL Transforming ENERGY

Additional Slides

Responses to Peer Review Comments

Reviewer's Comments in 2019 peer review meeting	How we addressing the comments from 2019-2021
Lack of TEA/LCA analysis results	Worked with BPA team on 3 joint milestone reports on evaluating TEA/LCA results of ozone pretreatment, alkali recovery, and 2-stage deacetylation.
More emphasis should be placed on NaOH recovery, as this will be critical for commercial viability.	We have 5 milestones including a go/no-go milestone to reduce NaOH usage and/or recover NaOH. We also worked very closely with Princeton University on NaOH recovery.
Would be helpful to provide competitive benchmarks to access commercial viability.	We compared commercial NaOH recovery (Kraft) with our FY19 SOT(no sodium hydroxide recovery), FY20 SOT (2 stage deacetylation), FY19 SOT with electrodialysis, and FY19 SOT with MET using TEA analysis tools.
More emphasis should be placed on feedstock variability.	We collaborated closely with FCIC task 2/5/7 to address the impact of feedstock variability on deacetylation kinetics/ biomass packed bed permeability/ hydrolysate toxicity.

- 2020 Q2 G/NG milestone:
  - Introduced for the 1st time 2-stage Na_2CO_3 and NaOH deacetylation
  - Achieved >85% sugar yield with enzyme loading of 10 mg/g of cellulose

Publications, Patents, Presentations, Awards, and Commercialization

Selected journal articles

- Chen, X., et al. (2019). "Microbial electrochemical treatment of biorefinery black liquor and resource recovery." Green Chemistry 21(6): 1258-1266.
- Chen, X., et al. (2019). "Kinetics and Rheological Behavior of Higher Solid (Solids >20%) Enzymatic Hydrolysis Reactions Using Dilute Acid Pretreated, Deacetylation and Disk Refined, and Deacetylation and Mechanical Refined (DMR) Corn Stover Slurries." ACS Sustainable Chemistry & Engineering **7**(1): 1633-1641.
- Kuhn, E. M., et al. (2020). "Deacetylation and Mechanical Refining (DMR) and Deacetylation and Dilute Acid (DDA) Pretreatment of Corn Stover, Switchgrass, and a 50:50 Corn Stover/Switchgrass Blend." ACS Sustainable Chemistry & Engineering **8**(17): 6734-6743.
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Selected conference presentations:

- Chen, X., Biomass Pretreatment, ABLC 2020
- Chen, X., Black liquor recovery, DOE workshop