Low Temperature Advanced Deconstruction WBS 2.2.3.100

Xiaowen Chen

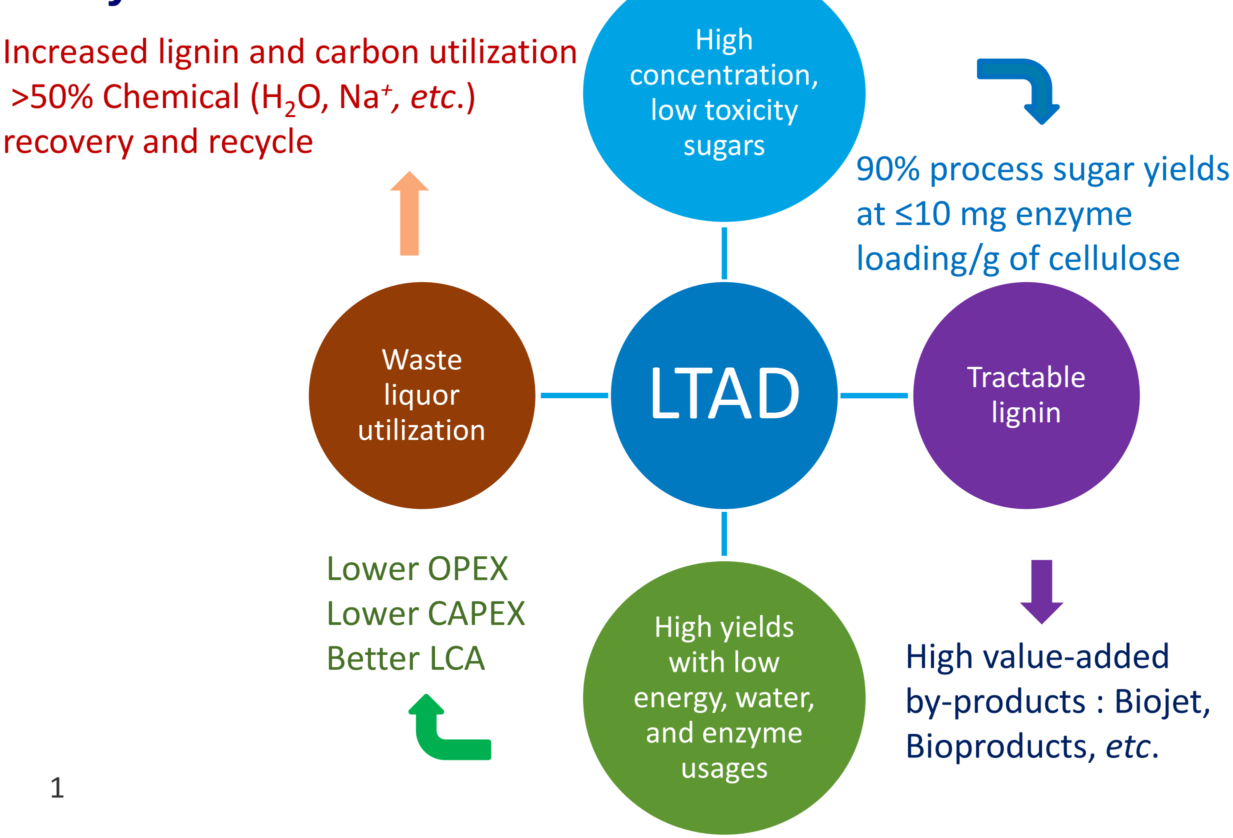
2019 BETO Peer Review Meeting

3/4/2019

Goal Statement

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.

Key Outcomes:



Relevance to Biorefinery Industries:

- Industry relevant and cost effective biomass deconstruction
- Lower cost, higher titer, "cleaner" sugars that enable high TRY in downstream conversions
- Tractable, reactive lignin streams that enable effective lignin utilization
- Water/Chemical recovery that leads to lower OPEX and less environmental and LCA footprints

Quad Chart Overview

Timeline
- Project start date: FY 18
- Project end date: FY 21
- Percent complete: 50%

	Total Costs Pre FY17**	FY 18 Costs	FY 19 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$2.8 MM	$1.5 MM	$1.5 MM	$4.5MM
Project Cost Share				

- **Partners:**
  - **Idaho National Lab, Allison Ray**
  - **Princeton University, Zhiyong Ren**
  - **Washington State University, Bin Yang**

BETO 2018 MYPP Barriers addressed:

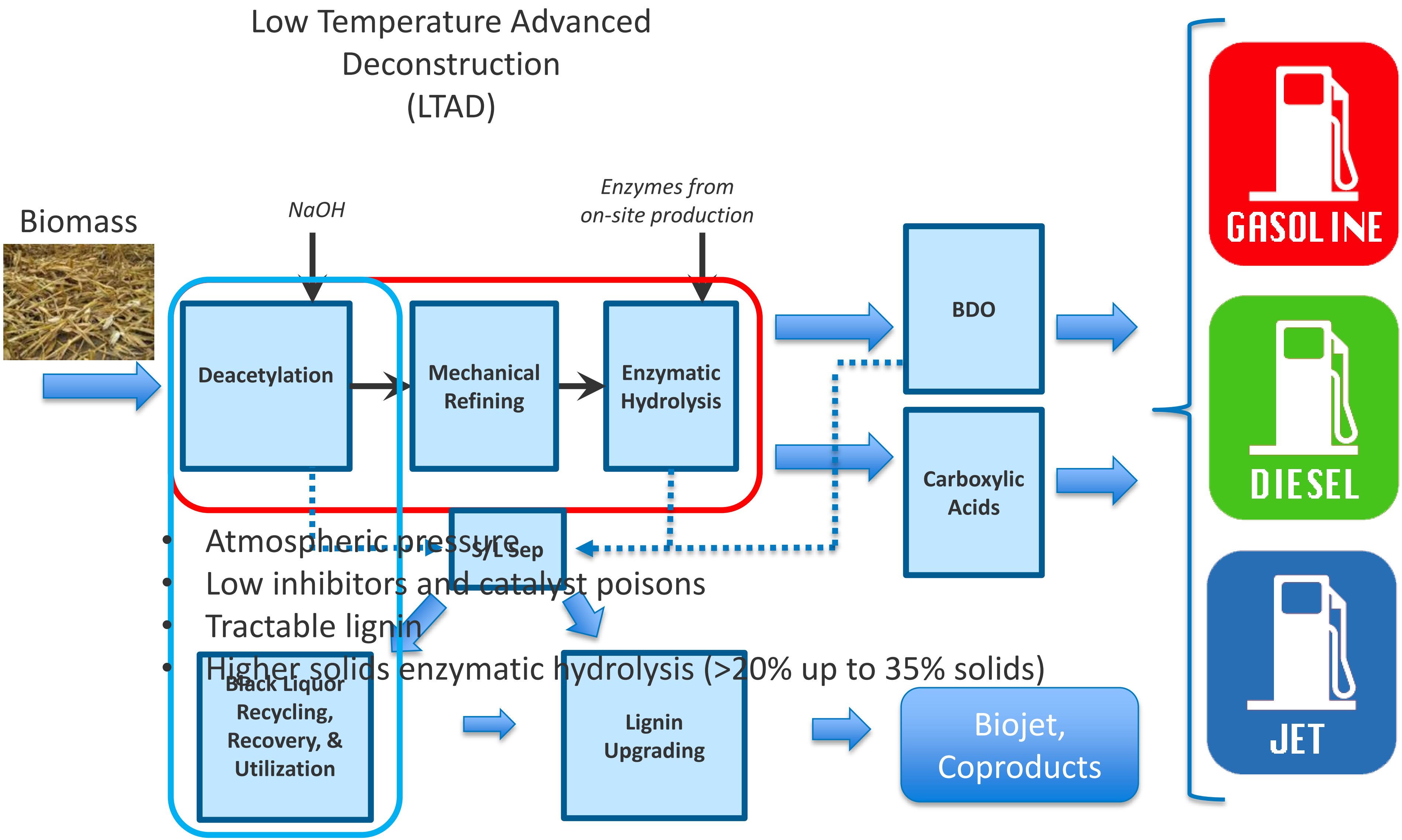
Ct-B. Efficient Preprocessing and pretreatment
DMR- improve sugar yields, sugar and lignin convertibility

ADO-A. Process Integration
DMR- improve reliability of operations and increase on-stream performance

Objective:
Develop industry relevant, cost-effective low temperature deconstruction processes that produce **high yields, low cost and upgradable sugar** and **tractable, reactive lignin** streams from **relevant feedstocks**.

End of Project Goal:
- Achieve over **90% sugar yields** at enzyme loadings of **≦10 mg protein /g** of cellulose.
- Achieve over 50% waste carbon utilization and chemical recovery from pretreatment liquor waste

Project Overview

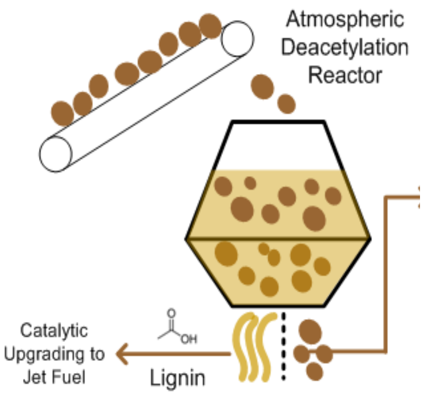


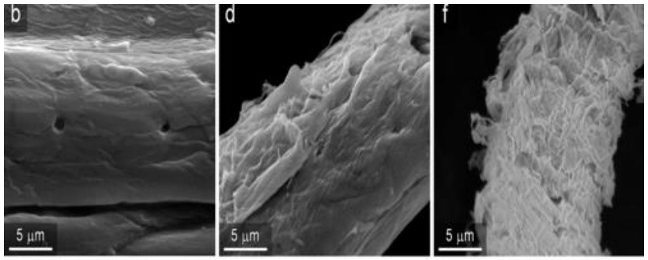
- Atmospheric pressure
- Low inhibitors and catalyst poisons
- Tractable lignin
- Higher solids enzymatic hydrolysis (>20% up to 35% solids)

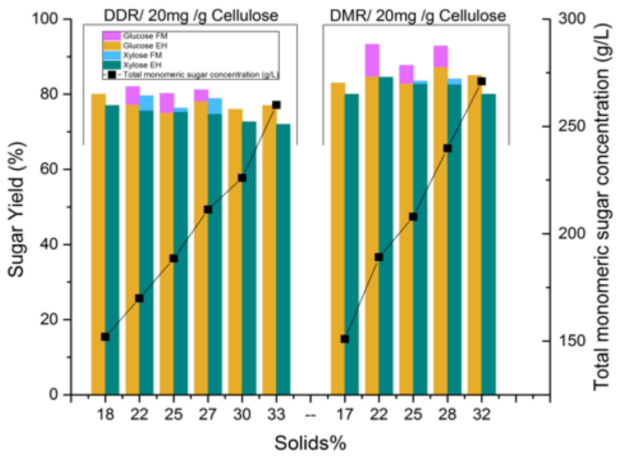
- Chemical/H_2O recovery
- Waste carbon (lignin, acetate, *etc.)* utilization

Project Overview (Continued)

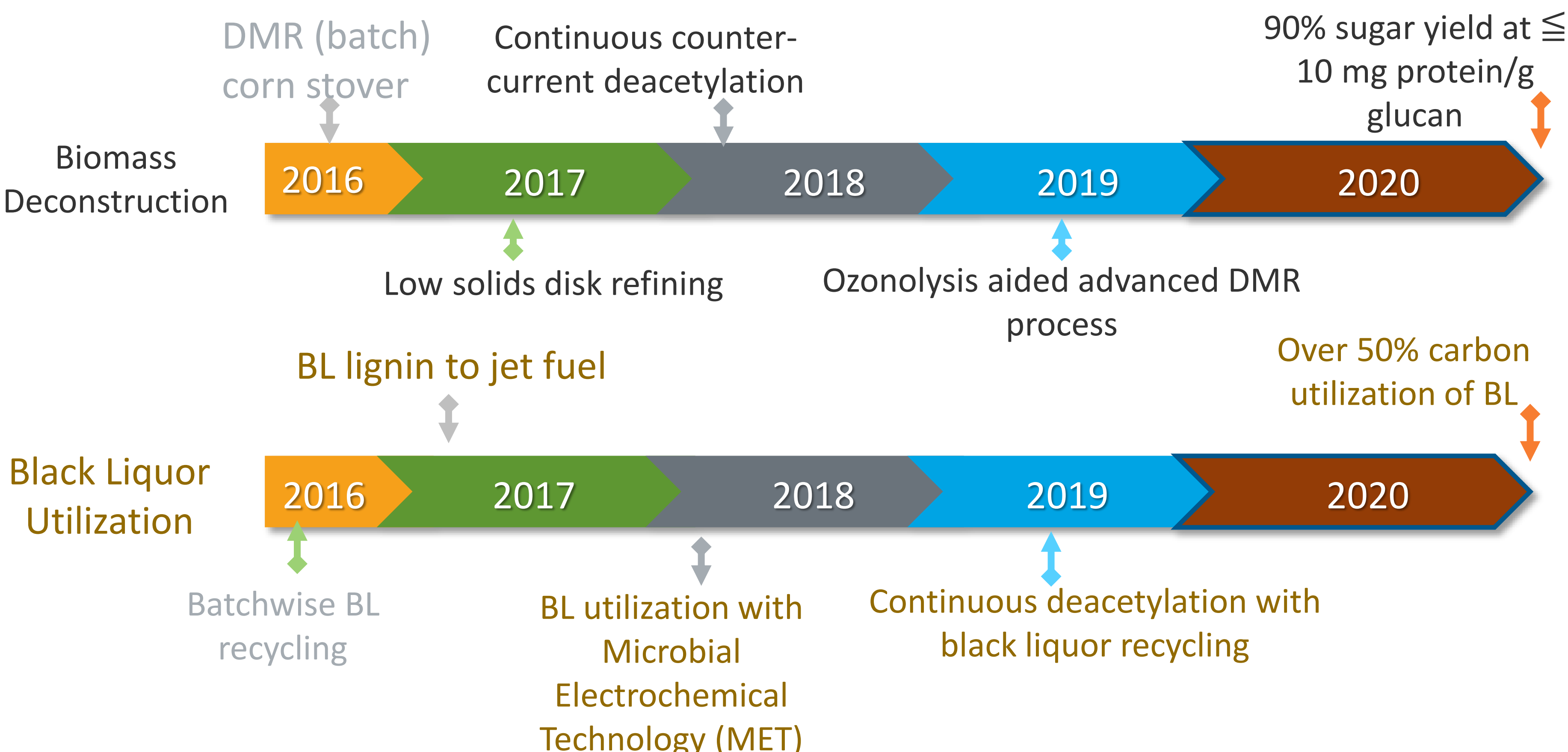
Deacetylation and Mechanical Refining Process (DMR)







Project Overview (Timeline)



Biochemical Conversion Projects - NREL

Agile BioFoundry

Lignin

Feedstock Logistics

Algae

Waste-to-Energy

2.2.3.100 Low Temperature Advanced Deconstruction

CO2

ADO Analysis/ Modeling

Catalysis

ADO Integration Scale-up

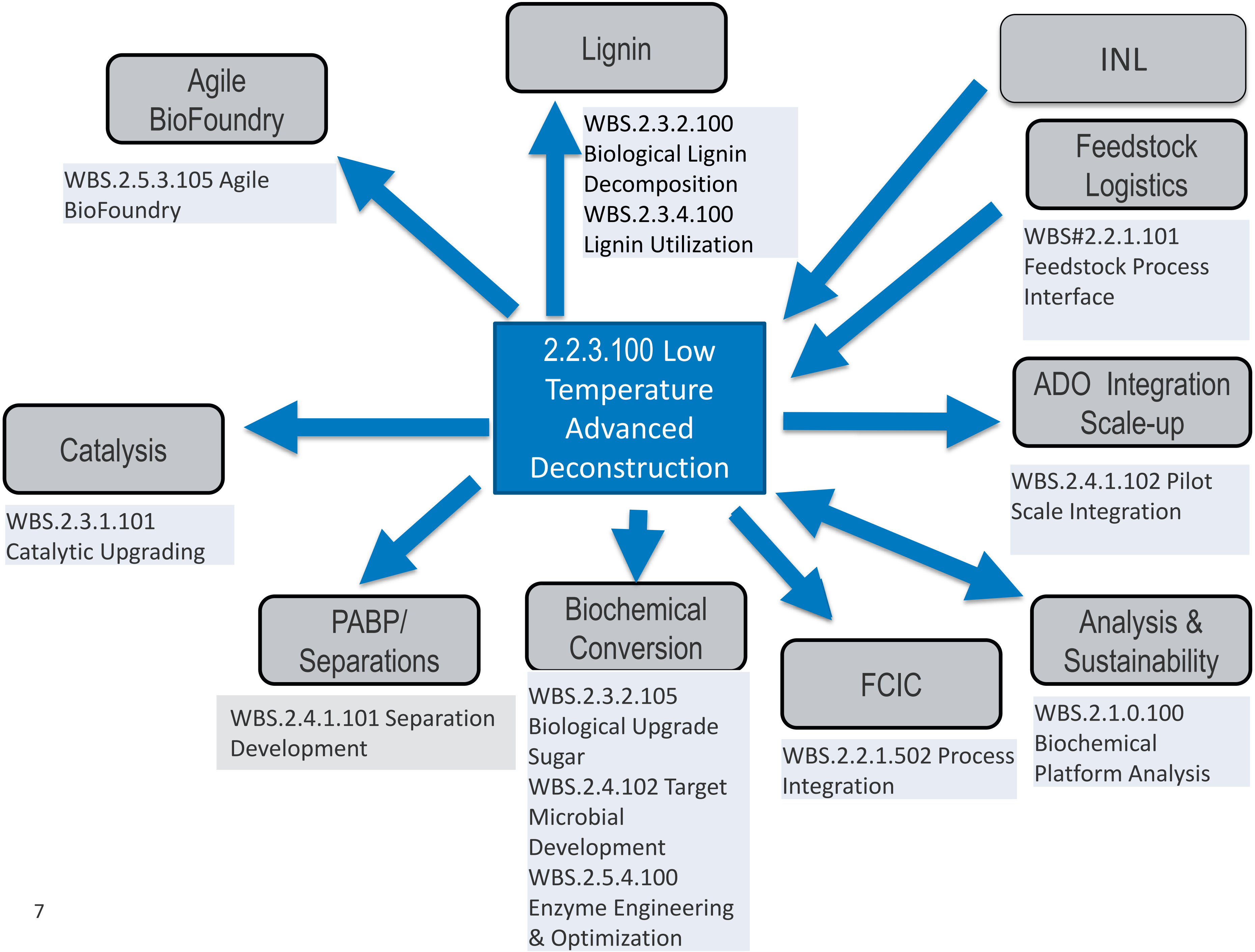
Biochemical Conversion

PABP/ Separations

Analysis & Sustainability

Co-Optima

FCIC


Agile BioFoundry
WBS.2.5.3.105 Agile BioFoundry
Lignin
WBS.2.3.2.100 Biological Lignin Decomposition
WBS.2.3.4.100 Lignin Utilization
INL
Feedstock Logistics
WBS#2.2.1.101 Feedstock Process Interface
2.2.3.100 Low Temperature Advanced Deconstruction
Catalysis
WBS.2.3.1.101 Catalytic Upgrading
ADO Integration Scale-up
WBS.2.4.1.102 Pilot Scale Integration
PABP/ Separations
WBS.2.4.1.101 Separation Development
Biochemical Conversion
WBS.2.3.2.105 Biological Upgrade Sugar
WBS.2.4.102 Target Microbial Development
WBS.2.5.4.100 Enzyme Engineering & Optimization
FCIC
WBS.2.2.1.502 Process Integration
Analysis & Sustainability
WBS.2.1.0.100 Biochemical Platform Analysis

Management Approach

Low Temperature Advanced Deconstruction

Melvin Tucker

- TEA guided research
- Monthly meetings internal to project
- Regular in-person meetings
- Diversified skill sets:
  - Chemical engineering
  - Techno economical analysis (TEA)
  - Biomass/organic chemistry
  - Enzymology
  - Analytical chemistry
  - Automation engineering
  - Microbiology
  - Genetic engineering

Task 1: Advanced DMR Process Development

Nick Nagle

- Develop novel processes to improve current DMR performance
- Develop industry relevant processes to enable rapid deployment

Task 2: Black Liquor Recovery and Recycle

Xiaowen Chen

- Develop novel processes to utilize lignin and polysaccharides in the waste pretreatment liquor (black liquor)
- Develop novel processes to recover chemicals (Na^+ and nutrients), water, and decrease energy usage

Approach (Technical)

Task 1: Develop industry relevant processes:

- continuous counter-current deacetylation
- mechanical refining processes
- feedstocks formats

Task 2: Develop lignin utilization:

- Microbial electrochemical technology (MET) to recover Na^+, water, lignin, *etc.*
- Catalytic upgrading of lignin to biojet

Critical Success Factors	Challenges
High sugar yields at low enzyme loadings	Biomass recalcitrance
Robust/flexible process	Feedstock variability
Mild pretreatment conditions	Biomass sugar degradation
Low energy recovery and recycle	Chemical consumption/recovery
Atmospheric pressure process / non-corrosive chemistry; Lowers CAPEX/OPEX	Reliable continuous operation

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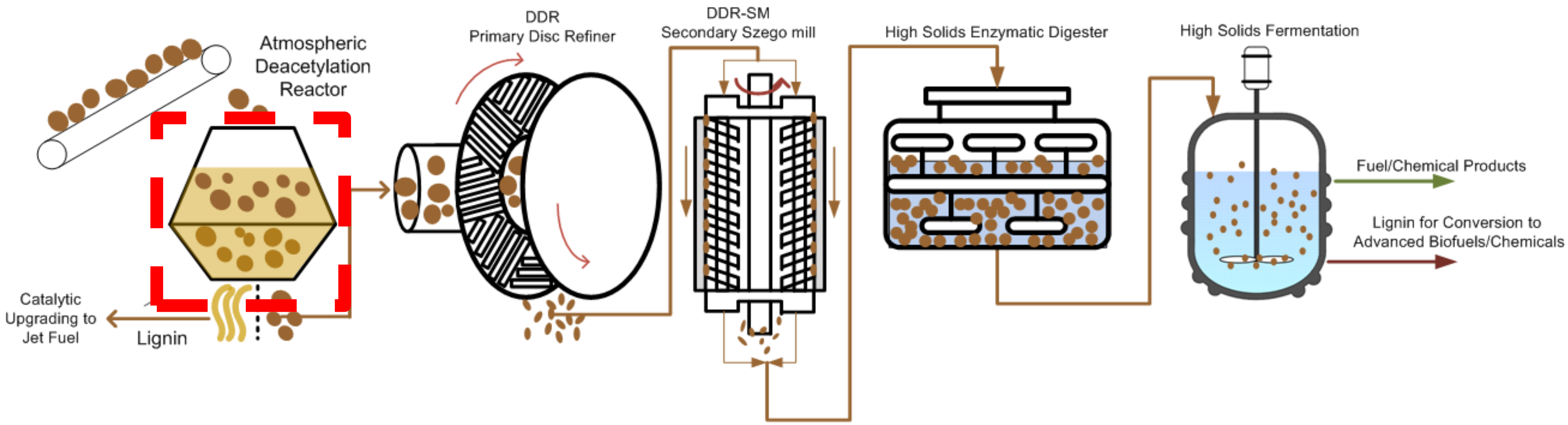
Technical Accomplishments (Deacetylation)



Continuous Counter-Current Deacetylation

Continuous Counter-Current Deacetylation Process (FY18 Q4)

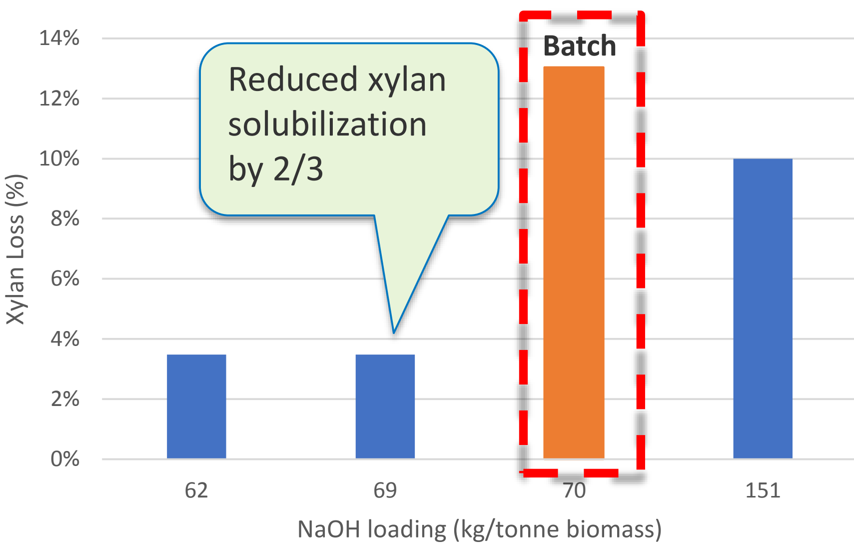
- Key factors affecting continuous deacetylation
  - Residence time
    - Biomass feeding rate
    - Reactor angle
    - Screw speed
  - NaOH loading
    - Biomass feeding rate
    - NaOH feeding rate
    - NaOH concentration

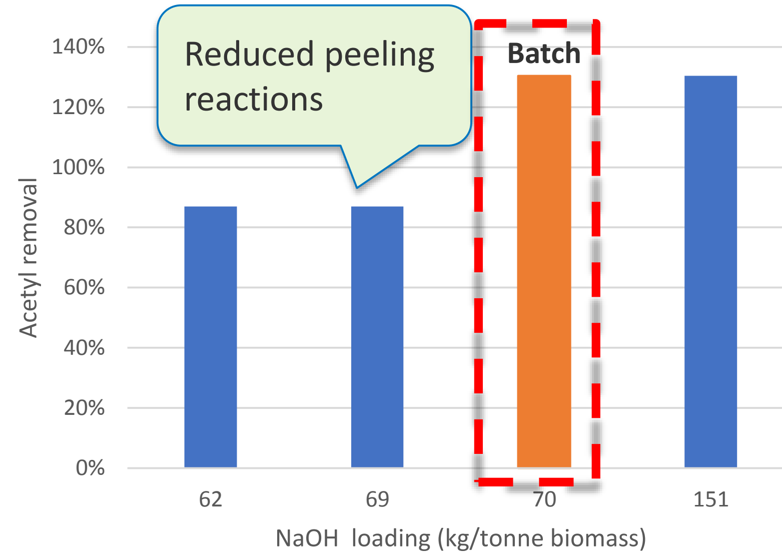
- Previous deacetylation research used batch processes
  - Labor intensive
  - Large reactors
  - Low production rates
- Need to achieve better deacetylation yields
  - Less xylan dissolution
  - Higher lignin removal
  - Less condensation of lignin

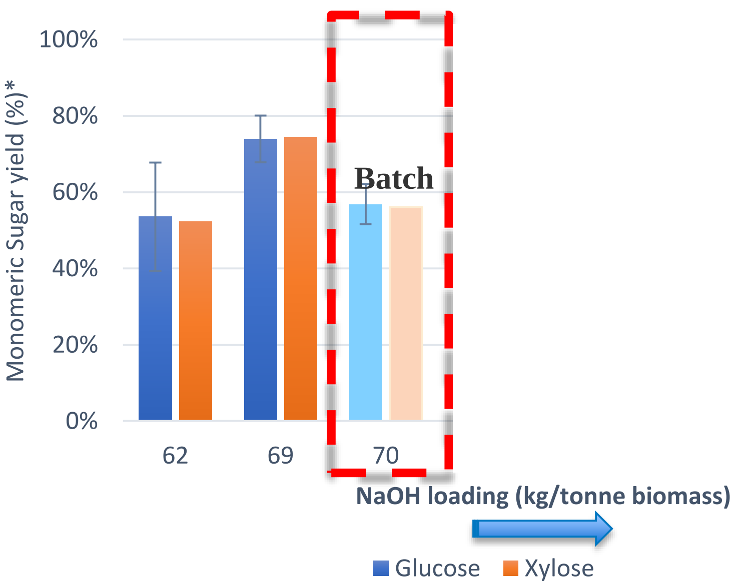
- Hypothesis:
  - **Shorter residence times** with better **mass/heat integration** in the counter-current deacetylation reactor reduces xylan dissolution and also reduces lignin condensation reactions, while keeping/improving deacetylation effects

- Solution:
  - Counter-Current Inclined Shaftless Screw Reactor

Continuous Counter-Current Deacetylation Process (FY18 Q4)





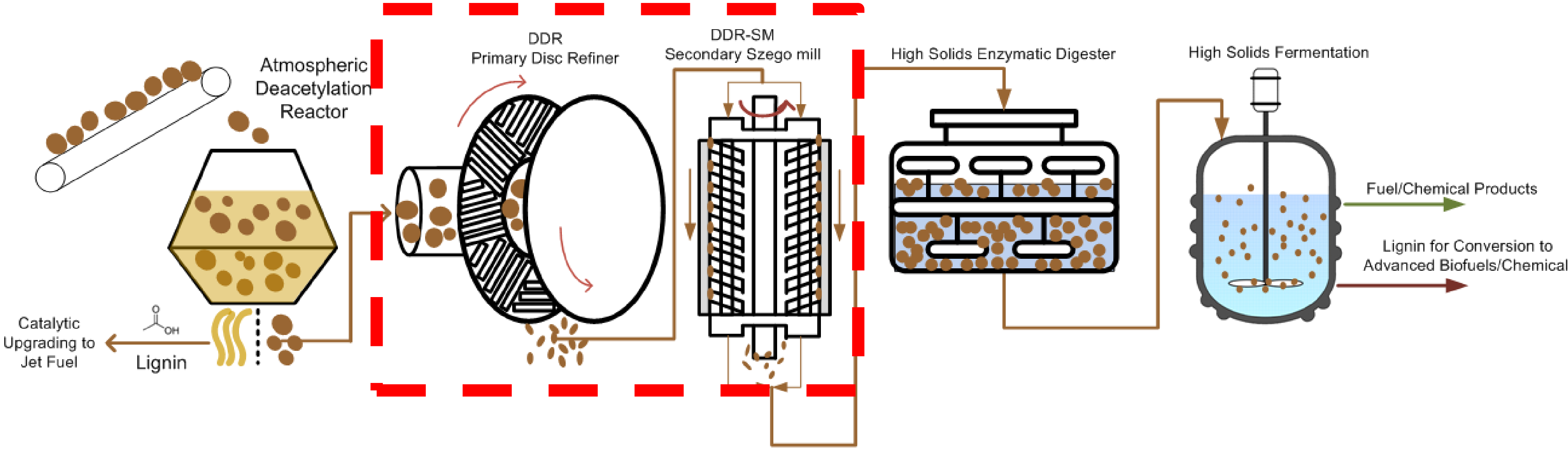


- Glucose and xylose yields increased by 17% and 18% in EH* using counter-current process at similar NaOH loadings
- C5 and C6 sugar hydrolysis show equal effectiveness
- NaOH loadings in excess of 150 kg/tonne biomass show no yield improvements

*8 mg CTec3/g cellulose + 2 mg HTec3/g cellulose, 20% solids, 50°C

Chen and Tucker et al. in preparation

Technical Accomplishments (Mechanical Refining)



Szego mill

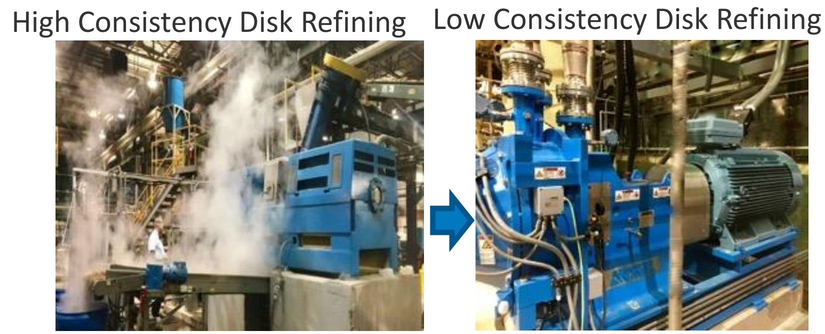
Low consistency disk refiner

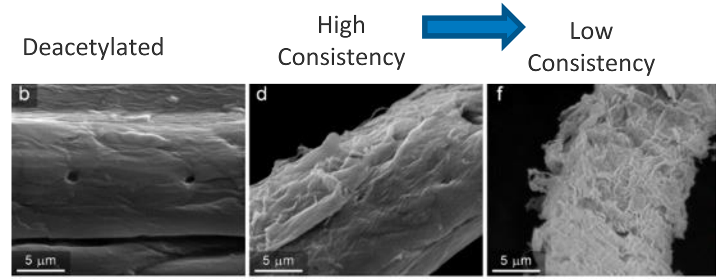
Industry Relevant Refining Processes (FY18 Q1)

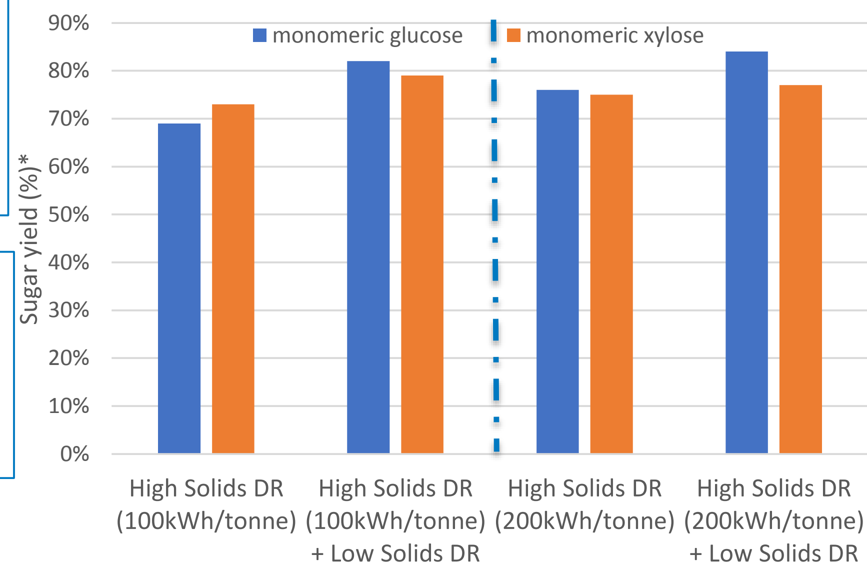
- Challenges:
  - Szego mills are medium (100's kg/h) throughput industrial equipment
    - Vibration issues
    - Noise issues
    - Not widely accepted in fiber industry

- Hypothesis:
  - Low consistency disk refining can further improve biomass digestibility
    - Improved cutting of biomass exposes more reducing ends
    - Breaking fiber bundles into single fibers through fibrillation, thus increasing cellulose accessibility
    - Shive reduction improves homogeneity of refining

- Results:
  - Increased glucose yields by 8-13%
  - Increased xylose yields by 2-6%
  - Similar EH improvements as Szego milling





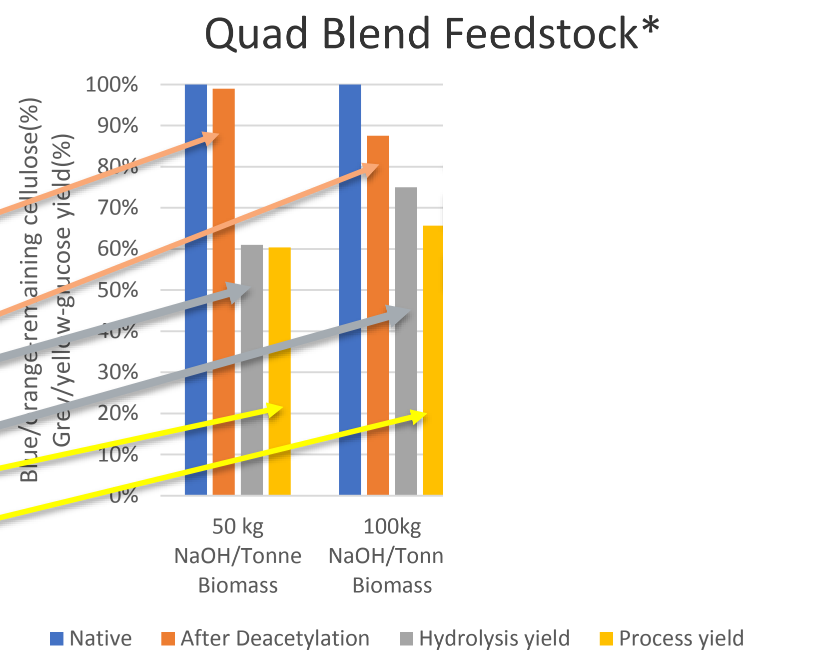


*12 m CTec3/g cellulose + 3 mg HTec3/g cellulose, 20% solids, 50°C

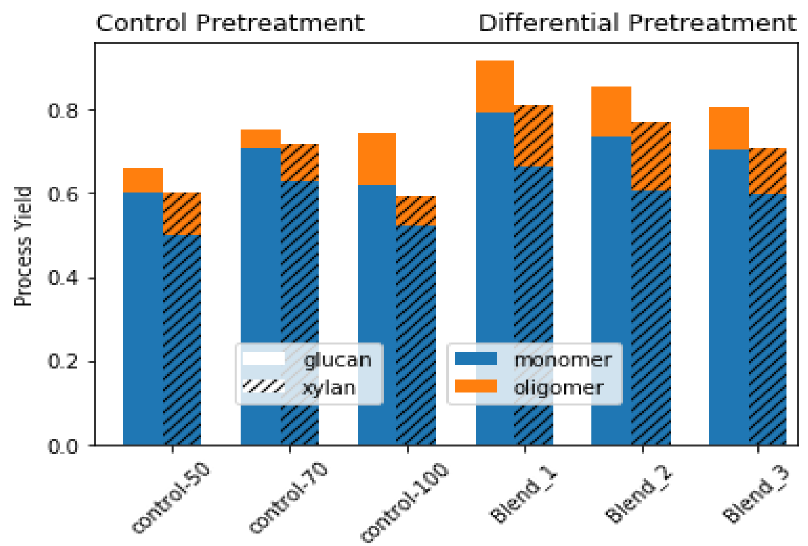
Industry Relevant Feedstocks (Differential Deacetylation)

Challenges:
- Advanced feedstock blends:
  - Meet $86/tonne of biomass in 2022 and $74 in 2030
  - Low and high recalcitrant biomass
- Single pretreatment severity on advanced feedstock blend will lead to reduced sugar yields

	Low severity pretreatment	High severity pretreatment
Low recalcitrant biomass, sp-cs	Good	Degradation products
High recalcitrant biomass, swg	Lower hydrolysis yields	Good
Total yield	LOW	LOW



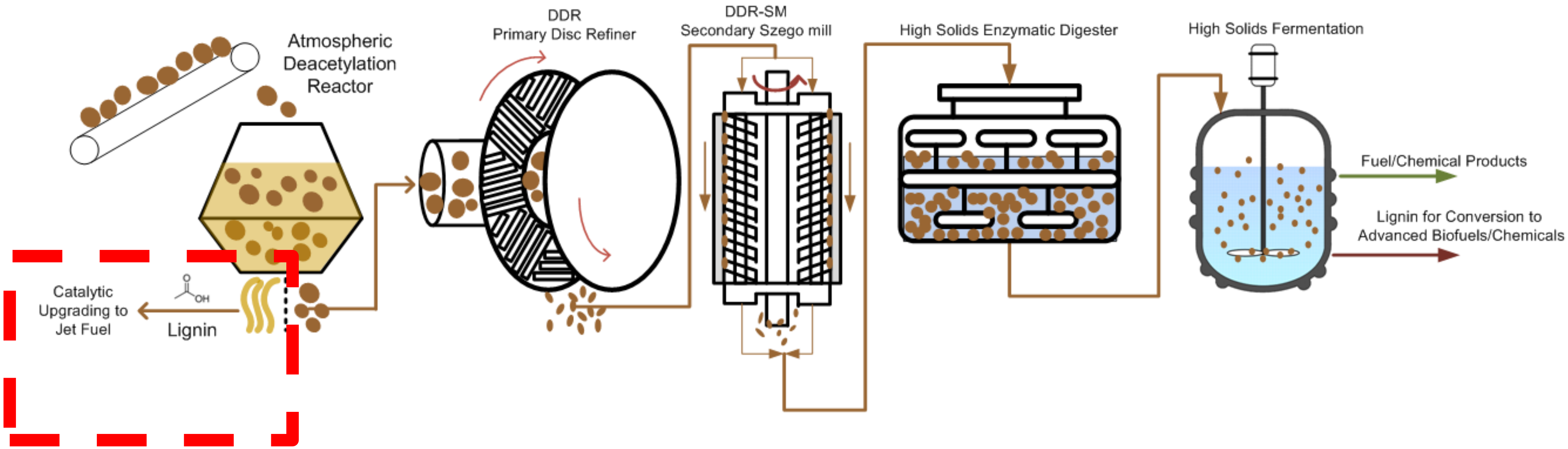
Solutions:
- Differential deacetylation pretreatment
  - Achieve optimum pretreatment severities on different biomass feedstock
  - Enable higher sugar yields and reduce mixing energy



Results:
- Increase overall process monomeric glucose yield by 9% (Blend 1 vs control-70)
- Increase overall total process glucan solubilization yield by nearly 20%

*Quad blend= sp-cs/mp-cs/swg/sorghum

Technical Accomplishments (Lignin / H_2O/ Chemical Recovery)



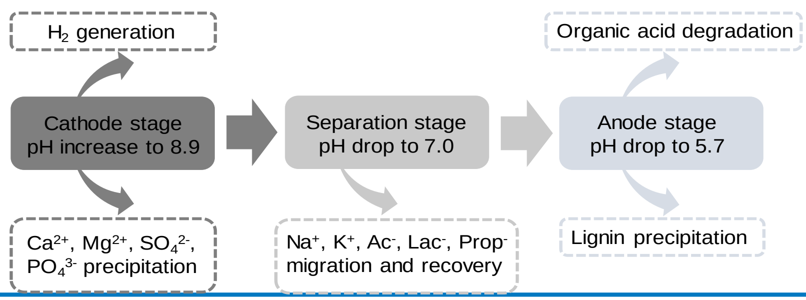
Microbial Electrochemical Technology to Recover Pretreatment Chemicals, Water and Lignin

Challenges:

- DMR black liquor
  - Too dilute
  - Valuable and underutilized lignin, organic acids and sodium
- Conventional Kraft process
  - Expensive recovery boiler/lime kiln
  - Burns lignin and other organics
  - GHG, air pollution and LCA

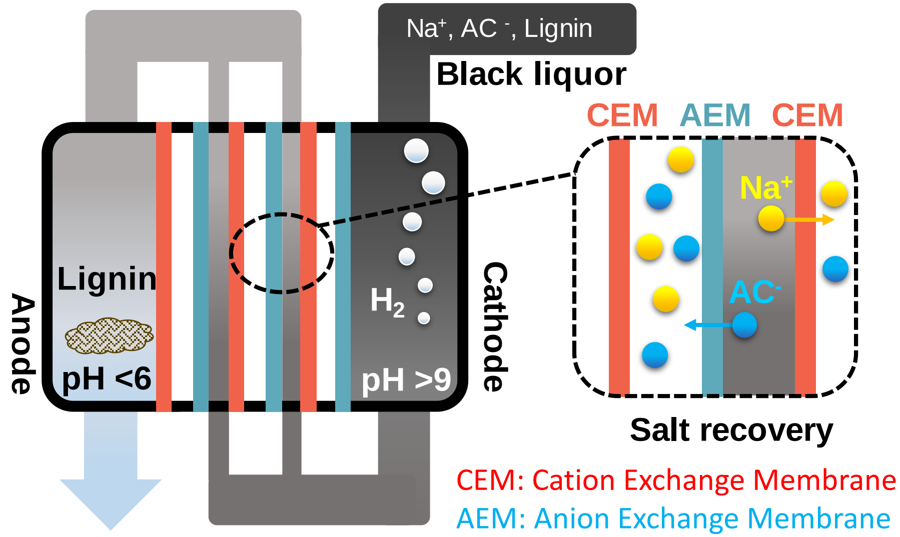
Solutions:

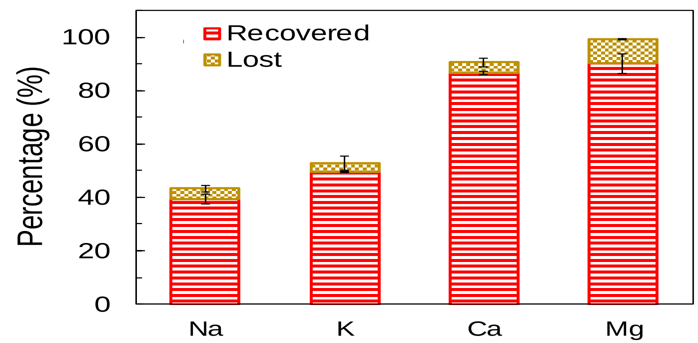
- MET degrades low conc. waste organics
  - Chemical energy -> Electrical potential
  - Salt migration and recovery
- MET precipitates lignin with no added acids

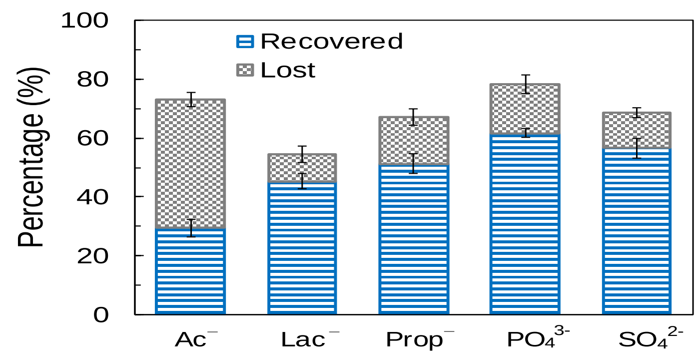


Results:

- Lignin and salt recoveries of ~61.2±2.7% and 92.2±1.6%, respectively.







Chen and Ren et al. Green Chemistry, 2018

Black Liquor Lignin to Jet Fuel*

Challenges:

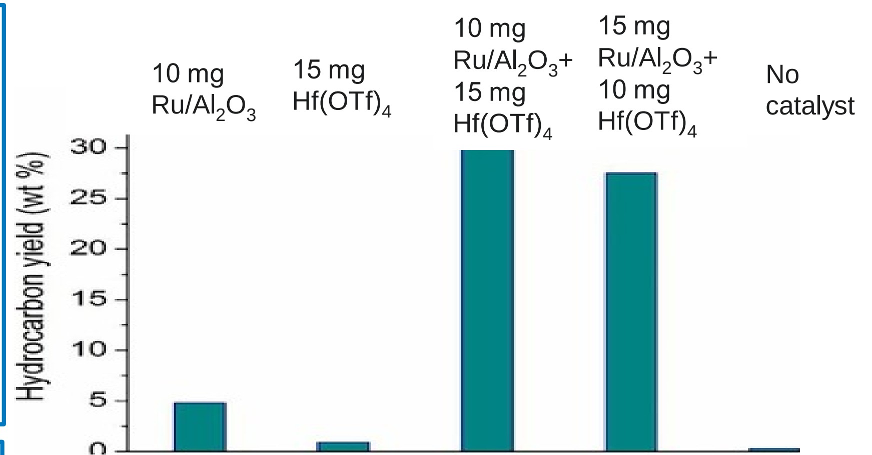
- Lignin's intrinsic heterogeneous robust structure
  - Upgrade/Recovery to single product is very difficult
  - Condensation/Repolymerization
- HDO with acid combined metal as bifunctional catalytic system
  - Most Brønsted acids: less selective
  - Most Lewis acids: water sensitive

Solutions:

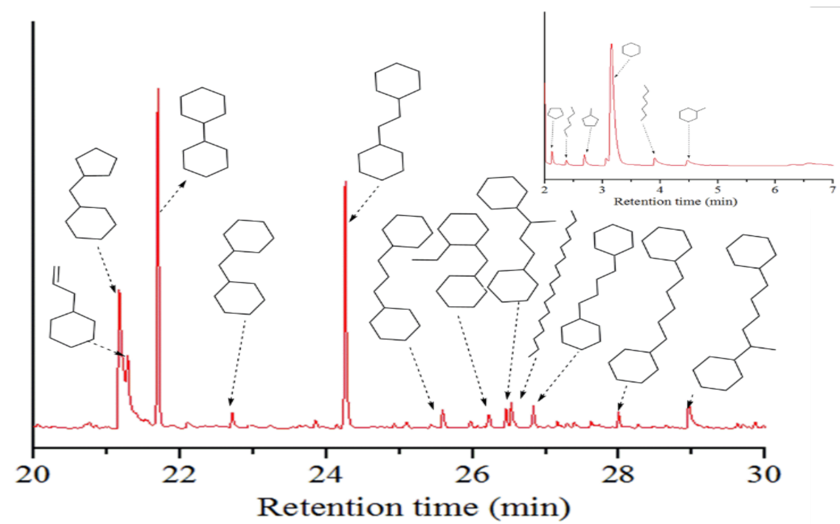
- Super Lewis acid- Metal Triflates
  - Widely used in organic synthesis
  - Water tolerant and thermal stable

Results:

- Near theoretical yields of hydrocarbons were produced from lignin model compounds
- Products mostly alkyl-dicyclohexanes (30%) from lignin in DMR Black Liquor
  - High energy
  - High density



Hydrocarbon yields from DMR lignin in HDO conversion under different conditions. Reaction conditions: lignin (50 mg), *n*-octane (1 mL), *T*=250 °C, *t*=4 h, *P* Hydrogen =4 MPa. in 1 mL *n*-octane containing 10 wt % water as solvent.



*Wang, Yang and Tucker *et al.*, ***ChemSusChem***, 2018, **11**(1)

Relevance

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.

Why is this project important, how is it relevant to BETO and bioenergy industry?

- Biomass deconstruction is the **critical first step of bioconversion** determining intermediate and final product yields!
- DMR - Industry relevant process option - **simple, mild process using existing industrial technologies** for rapid biorefinery deployment
- Directly supports BETO's 2018 MYPP:
  - *"Develop innovative biomass deconstruction approaches to lower the cost of intermediates…"*
- Directly supports BETO's 2022 and beyond goals using higher recalcitrance feedstocks, including industrially relevant and/or economically advantaged, lower costs feedstocks

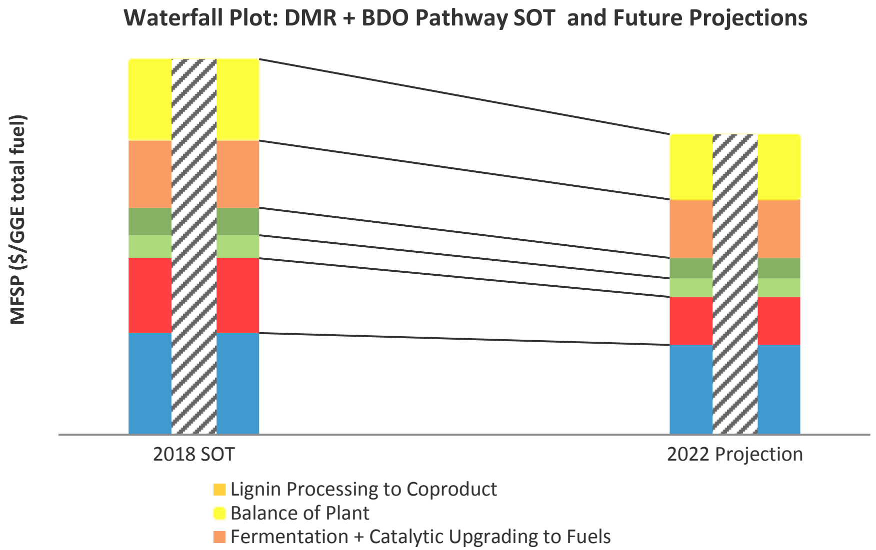
How does this project advance the SOT, contribute to biofuels commercialization?

- Demonstrated **equivalent sugar yields with 60% of the enzyme loadings** used in 2012 demonstration case.
- Demonstrated lignin to **valuable targeted jet fuel molecules**, and **valuable lignin co-products** (muconic acid) via high reactivity lignins from DMR streams.
- Demonstrated higher TRY downstream conversion to 2,3-BDO and carboxylic acids via **high concentration, low toxicity DMR sugar hydrolysates**.

Relevance (continued)

Technology transfer activities

- Published 5 high impact peer reviewed journal articles (Green Chemistry, ACS Sustainable Chemistry and Engineering, *etc*.)
- DMR hydrolysate chosen by Agile Biofoundry (ABF) for microorganisms development
- DMR process may mitigate operational reliability issues of high temperature acid pretreatment for Feedstock Conversion Interface Consortium (FCIC)
- DMR is being implemented in the NREL biochemical pilot plant.



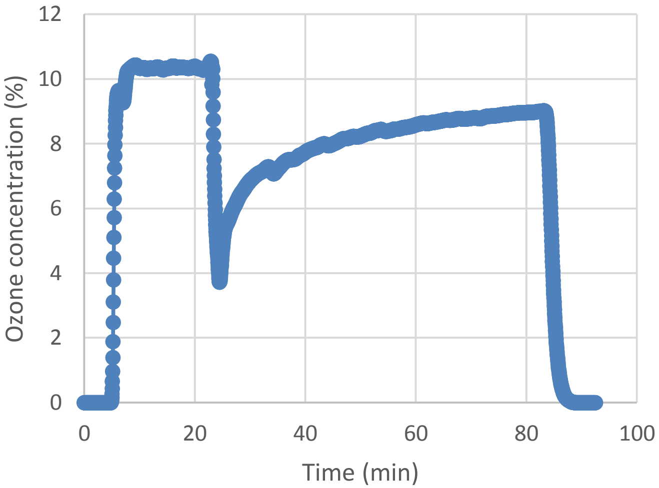
Reduce pretreatment and enzymatic hydrolysis costs by 1/3 by 2022!

Future Work

Develop scalable and cost-effective processes to achieve ≥90% sugar yield with enzyme loadings of ≤10 mg protein/g of cellulose

- Ozonolysis aided advanced DMR process
  - Hypothesis: Ozonolysis could:
    - Improve biomass accessibility
    - Reduce enzyme deactivation
    - Metal catalyst could enhance ozonolysis effect
  - FY 19 Q2 Go/No Go metal catalyst assisted deacetylation TEA milestone report: **Reduce deconstruction costs by 5%**
  - FY 20 Q2 Ozonolysis TEA milestone report: **Reduce deconstruction costs by 15%**
- Continuous counter current deacetylation with black liquor recycling
  - Counter current deacetylation:
    - Improve biomass digestibility
    - Reduce water/chemical usage
    - Reduce sugar losses
    - Improve soluble lignin titers
  - FY20 Q4 TEA milestone report**: Reduce deconstruction cost by 10%**

Ozonolysis system

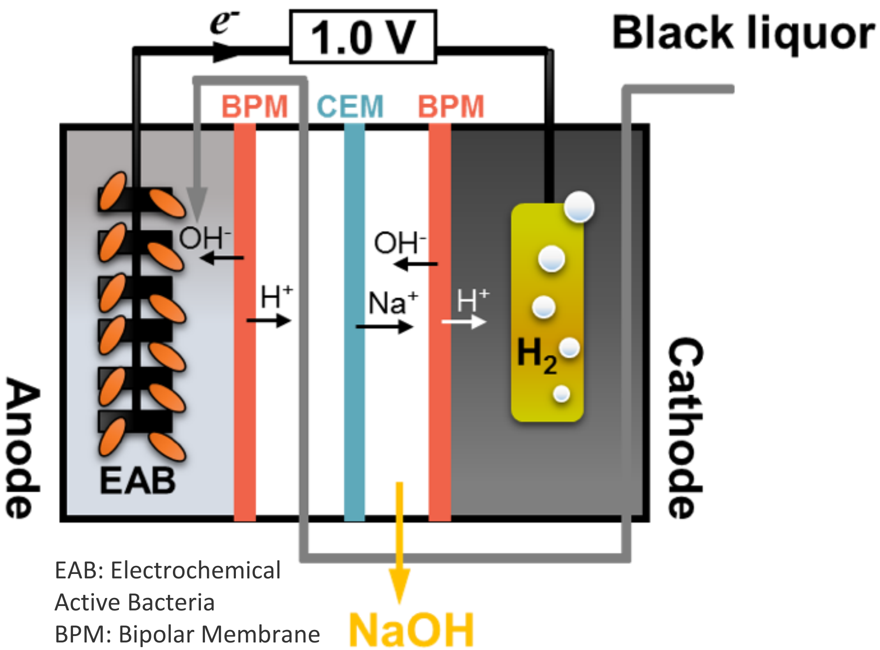


Deacetylated corn stover before and after ozonolysis

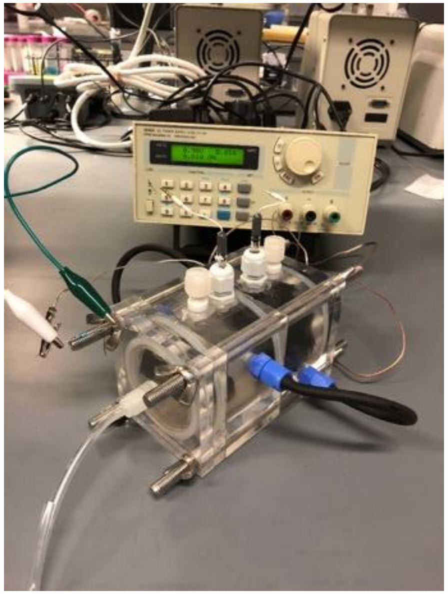
Future Work (continued)

Develop black liquor utilization processes to achieve 50% sodium hydroxide recovery with 50% waste carbon utilization

- Microbial Electrochemical Technologies (MET)
  - Recover pretreatment chemicals
  - Utilize waste carbon
  - Precipitate lignin without chemicals
- – FY 20 Q3 TEA milestone report



EAB: Electrochemical Active Bacteria
BPM: Bipolar Membrane



MET 2.0 system

Summary

Project Overview

- DMR process is necessary for many biological and catalytical pathways
  - High sugar yields and concentrations with low toxicity
  - Tractable/reactive lignin suitable for conversion to fuels/chemicals
  - Simple process design and high operational reliability

Approach

- Develop industry relevant low temperature deconstruction processes
- Develop innovative black liquor carbon utilization/chemical recovery

Technical Accomplishments/Progress/Results

- Improved sugar yields with lower enzyme loadings by
  - Continuous counter-current deacetylation
  - High and low solids (consistency) disk refining
- Black liquor utilization
  - Recovered 90% salts and reduced COD by 60% through MET

Relevance

- Industrial relevance - simple, mild process using existing industrial technologies for possible rapid deployment
- Directly supports BETO's 2018 MYPP: "Develop innovative biomass deconstruction approaches to lower the cost of intermediates…"
- Addresses BETO's 2022 and beyond targets and goals by reducing pretreatment and enzymatic hydrolysis costs

Future Work

- Develop Advanced DMR processes to further reduce enzyme loadings and improve sugar yields (Ozonolysis/metal catalyst/continuous counter-current deacetylation)
- Develop cost-effective black liquor utilization technology (MET 2.0)

Acknowledgments

Funding

- U.S DOE EERE Bioenergy Technologies Office

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- Dan Schell

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- Allison Ray
- Neal Yancey

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- Jason Ren
- Xi Chen

Washington State University

- Bin Yang

DOE

- Ian Rowe

Andritz Inc.

- Antti Luukkonen

Additional Slides

Low Temperature Advanced Deconstruction

Reviewer Comments

- The goals of reducing the severity of pretreatment while at the same time increasing sugar yields/concentrations/recovery are worth pursuing in the context of this project. Primary concern is the understanding of TEA assumptions which were not very clear.

- *We thank the reviewer for this comment and recognize that not enough time was spent covering the assumptions that went into the three different TEA analyses that were presented. The TEA assumptions were unfortunately described by Ryan Davis in his talk for the Biochemical Platform Analysis Project in the Biochemical Conversion session that the Reviewer may not have been able to attend.*

- The project is using a good approach to optimize this particular deconstruction process. It will be interesting to see the TEA's on it as other industry players that looked at disk refiners thought that the electrical demand outweighed the process benefits.

- *Our previous TEA paper (https://biotechnologyforbiofuels.biomedcentral.com/articles/10.1186/s13068-015-0358-0) showed refining energy could not exceed 200kWh/tonne of dry biomass where the break-even point compared to TEA of acid pretreatments. We found deacetylation decreases disc refining energy by 80% to 90%.*

- Technical approach is reasonable. Might want to work towards understanding impact of feedstock variation and type on the efficacy. The critical success factors (technical, market, business) which will define technical and commercial viability.

- *We presented results on several corn stover lots provided by INL over the years, switchgrass and 50/50 corn stover and switchgrass blends. Switchgrass showed higher recalcitrance than corn stover in both DMR and Acid pretreatment. In FY17 and 18, we will continue to evaluate the impact of feedstock variation and type on the efficacy of deconstruction. The main critical success factor for this project was to show that small commercial-scale DMR gave results similar to or better than dilute acid pretreatment. Vendor communications states that small 36-inch disc refiner results are directly scalable to larger commercial scale 42-, 54-, and 60-inch refiners.*

Publications

1)"Microbial electrochemical treatment of biorefinery black liquor and resource recovery"
Xi Chen, Rui Katahir, Zheng Ge, Lu Lu, Dianxun Hou, Darren J. Peterson, Melvin P. Tucker, Xiaowen Chen, and Zhiyong Jason Ren, (2018), *Green Chemistry*, DOI: 10.1039/C8GC02909A.

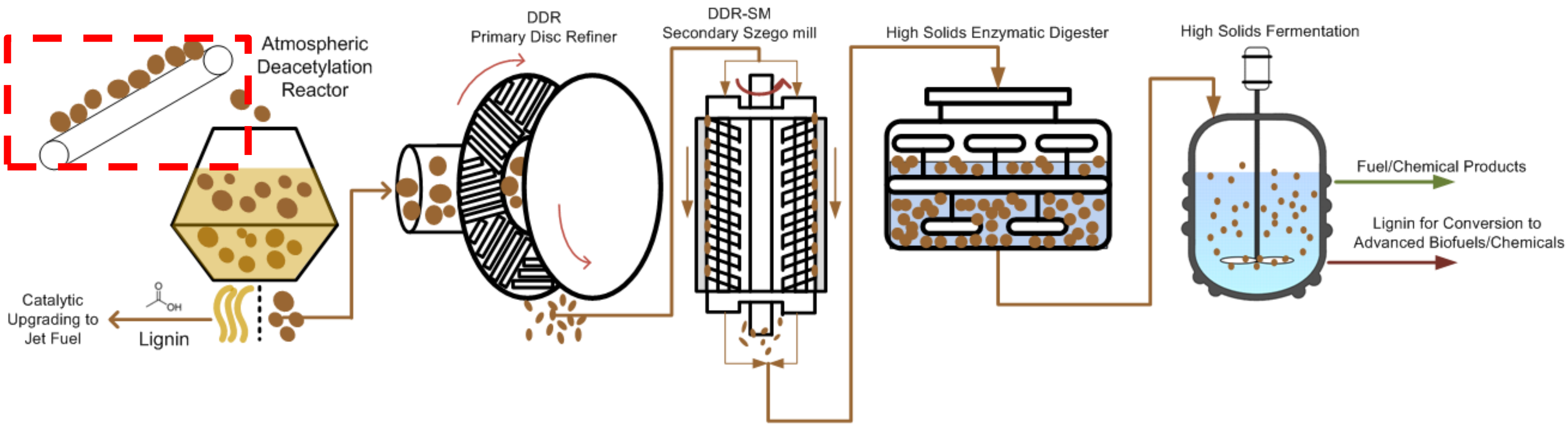
2)"Kinetics and Rheological Behavior of Higher Solid (Solids >20%) Enzymatic Hydrolysis Reactions Using Dilute Acid Pretreated, Deacetylation and Disk Refined, and Deacetylation and Mechanical Refined (DMR) Corn Stover Slurries", Xiaowen Chen, Nathan Crawford, Wei Wang, Erik Kuhn, David Sievers, Ling Tao, and Melvin Tucker, (2019), *ACS Sustainable Chemistry & Engineering*, 7 (1), 1633-1641, DOI: 10.1021/acssuschemeng.8b05391

3) "Recycling of Dilute Deacetylation Black Liquor to Enable Efficient Recovery and Reuse of Spent Chemicals and Biomass Pretreatment Wast", Xiaowen Chen, Erik Kuhn, Nick Nagle, Robert Nelson, Ling Tao, Nathan Crawford, Melvin Tucker, (2018) Frontiers in Energy Research, Vol. 6, DOI=10.3389/fenrg.2018.00051

4) " Kinetic Modelling and Experimental Studies for the Effects of Fe2+ Ions on Xylan Hydrolysis with Dilute-Acid Pretreatment and Subsequent Enzymatic Hydrolysis", Hui Wei, Xiaowen Chen, Joseph Shekiro, Erik Kuhn, Wei Wang, Yun Ji, Mike Himmel, Melvin Tucker, (2018), Catalysts, 8(1), DOI= 10.3390/catal8010039

5)"Unraveling the Role of Peracetic Acid on Efficient Lignin Depolymerization: Disrupt Lignin Packing Structure and Its Interaction with Niobium Based Catalysts", Ma, Ruoshui; Olarte, Mariefel; Job, Heather; Swita, Marie; Jones, Susanne; Burton, Sarah; Cort, John; Bowden, Mark; Chen, Xiaowen; Wolcott, Michael; Zhang, Xiao, submitted to *ACS Sustainable Chemistry and Engineering*

Technical Accomplishments



Corn stover

Switchgrass

Sorghum

Single Pass

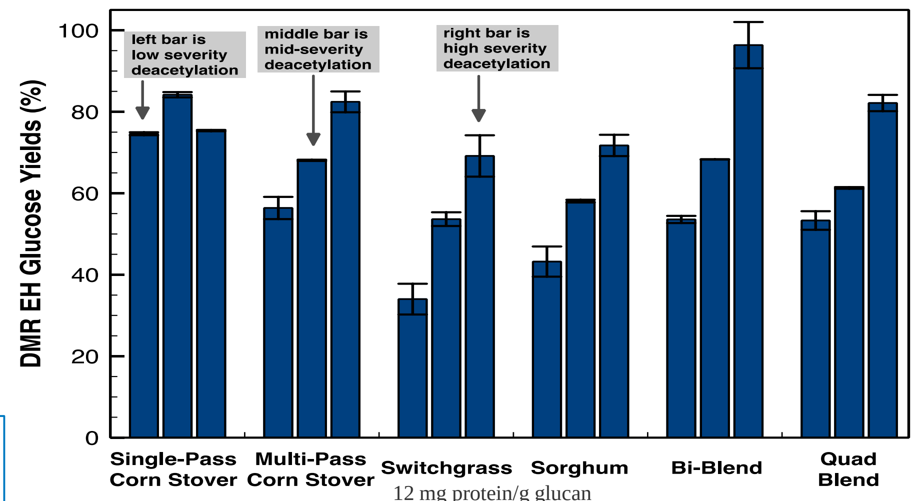
Industry Relevant Feedstocks (Least Cost Formulated Feedstock)

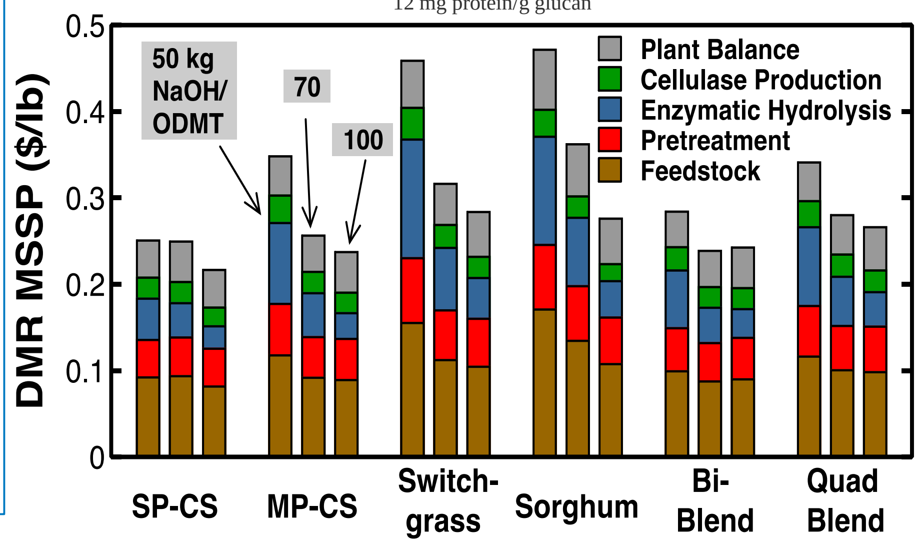
- Challenges:
  - Feedstock variability results in different levels of recalcitrance of biomass

- Solutions:
  - Increasing NaOH loading effectively increased sugar yields thus reducing MSSP
    - Need black liquor recycle/recovery/utilization
  - Differential deacetylation maximized sugar yields and lowered MSSP/MFSP

- Results:
  - Digestibility:
    - SP CS > MP CS > Sorghum > Switchgrass
    - Bi-Blend > Quad Blend
  - Increasing deacetylation severity
    - Increases the sugar yield
    - Decreases the Minimum Sugar Selling Price (MSSP) in most cases
    - Not the optimum method for blend feedstock

	SP-CS (%)	MP-CS (%)	Swithgrass (%)	Sorghum (%)
Bi-Blend	50	50	-	-
Quad-Blend	25	35	35	5





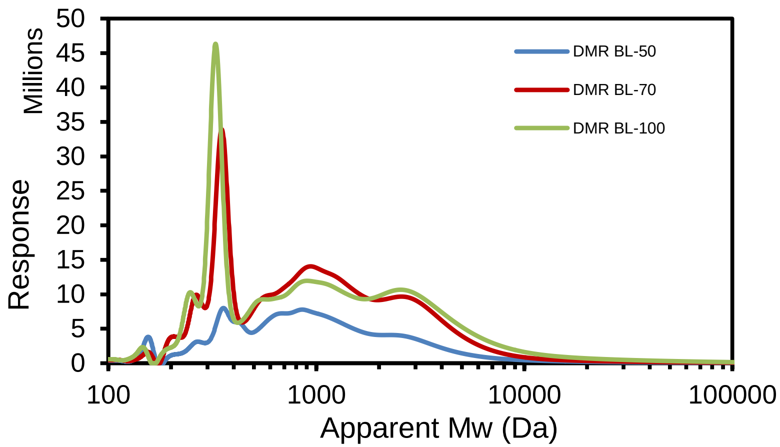
Characterizing of Black Liquor Lignin

Challenges:

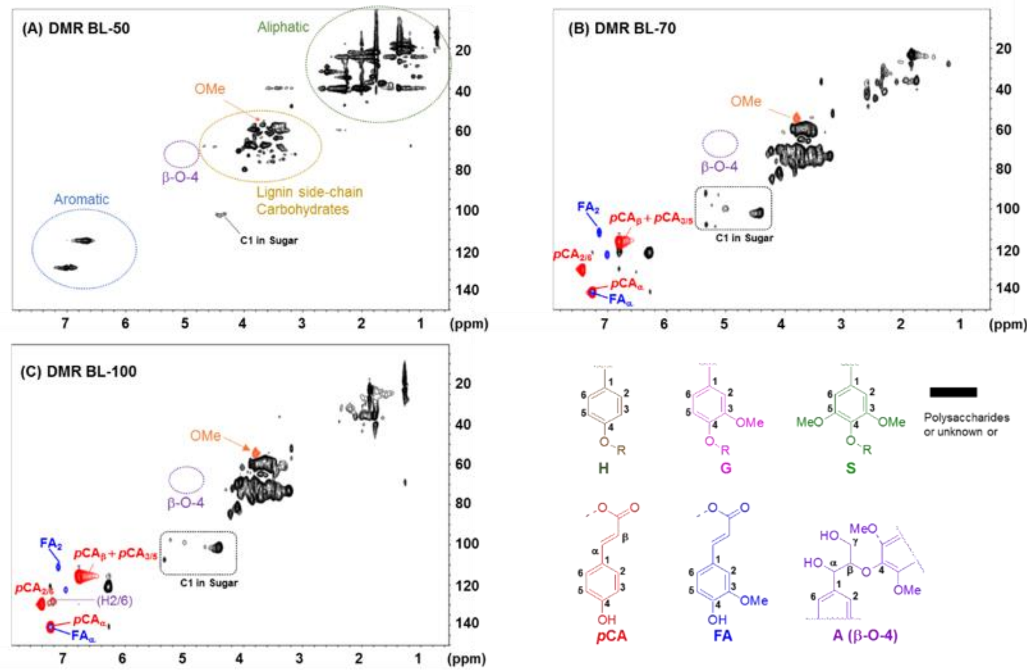
- ○ We are still not very clear about lignin depolymerization and sugar solubilization/degradation kinetics and mechanisms in the deacetylation stage.
- ○ We need to know the structures of lignin moiety and oligosaccharides in the black liquor for upgrading/valorization purpose.

Solutions:

- ○ We use NMR, GPC and TOF MS to characterize the black liquor components.



Sample ID	M_n	M_w	PD
DMR BL-50	570	1900	3.3
DMR BL-70	580	1700	2.9
DMR BL-100	550	2100	3.8



HSQC NMR spectra of three black liquor samples. (A) DMR BL-50, (B) DMR BL-70 and (C) DMR BL-100. H: *p*-hydroxyphenyl, G: guaiacyl, S: syringyl, A: β-aryl ether (β-O-4), *p*CA: *p*-coumarate, FA: ferulate.

Take away messages:

- ○ The mild conditions of deacetylation process **maintain most β-O-4 bonds remaining in solid phase lignin**, which will be essential for downstream process to depolymerize and upgrade the lignin.
- ○ Lignin moiety in black liquor are most **monomers/dimers** and higher Mw fraction (>420 Da) comes from mainly oligosaccharides
- ○ **P-Coumaric and ferulic acids** are the major components found in the deacetylation black liquor, the total amount of extracted PCA and FA in deacetylation are up to 3% of the total weight of biomass.