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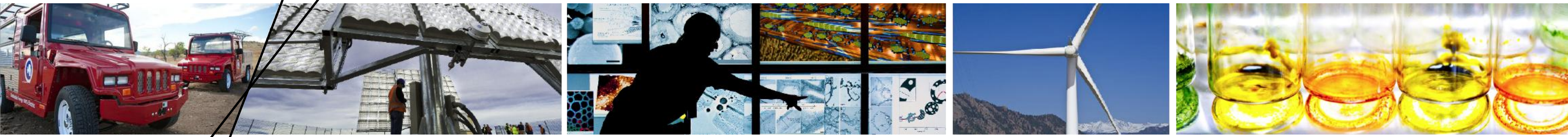
2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Pretreatment and Process Hydrolysis 2.2.3.100



March 23, 2015

Biochemical Conversion Platform

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Goal Statement

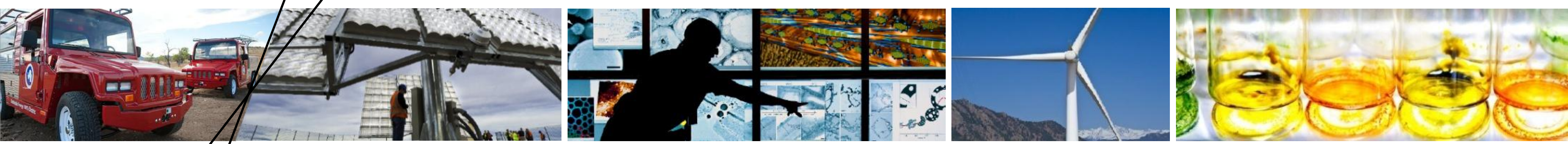
To produce high concentration sugar and reactive lignin streams at high yields and low costs from biomass to meet BETO's 2017 ($5/GGE) and 2022 ($3/GGE) Goals and Targets.

- Reduce enzyme loadings below 10 mg total protein/g cellulose
- High concentration "cleaner" sugar syrups to meet BETO's MYPP
  - Lower toxicity for biological upgrading
  - Lower concentrations of catalyst poisons for catalytic upgrading
- Lignin streams for biological/catalytic upgrading
- Provide hyrolyzate slurries to other projects in Biochemical Platform
- Corn stover, blended, and blended/densified feedstocks to meet BETO's MYTP
- Process scalable to pilot and larger scales
- Re-purpose decommissioned pulp and paper mills

Low cost sugars and lignin streams are essential for biorefinery and U.S. competitiveness.

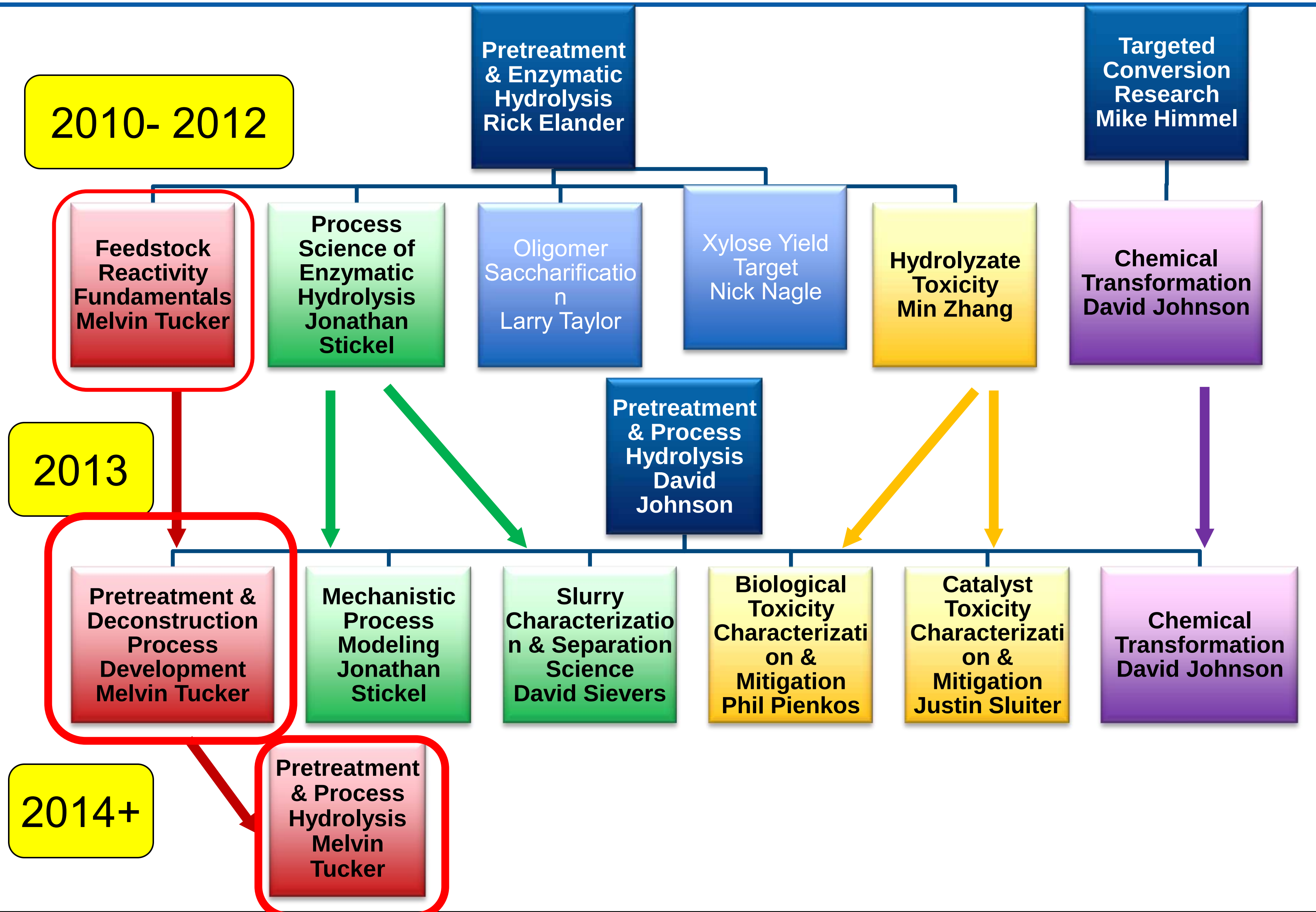
- Essential for cost effective upgrading
- Utilize all carbon
- Increase rural employment opportunities
- Lower petroleum imports
- Decrease carbon footprint.

Project Overview



Pretreatment and Process Hydrolysis

Project Structure



Quad Chart Overview

Timeline

- Project start date: FY10
- Project end date: FY17
- Percent complete: 63%

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$18.8M	$5.6M ($1.2M)	$1.45M	$5.6M (New Funding) (FY15 $1.4M) (FY16 $1.5M) (FY17 $1.6M)
Project Cost Share (Comp.)*				

Barriers

- Bt-A: Biomass Fractionation
- Bt-B: Biomass Variability
- Bt-C: Biomass Recalcitrance
- Bt-D: Pretreatment Chemistry
- Bt-E: Pretreatment Costs
- Bt-G: Cellulase Enzyme Loading
- Bt-K: Biological Process Integration

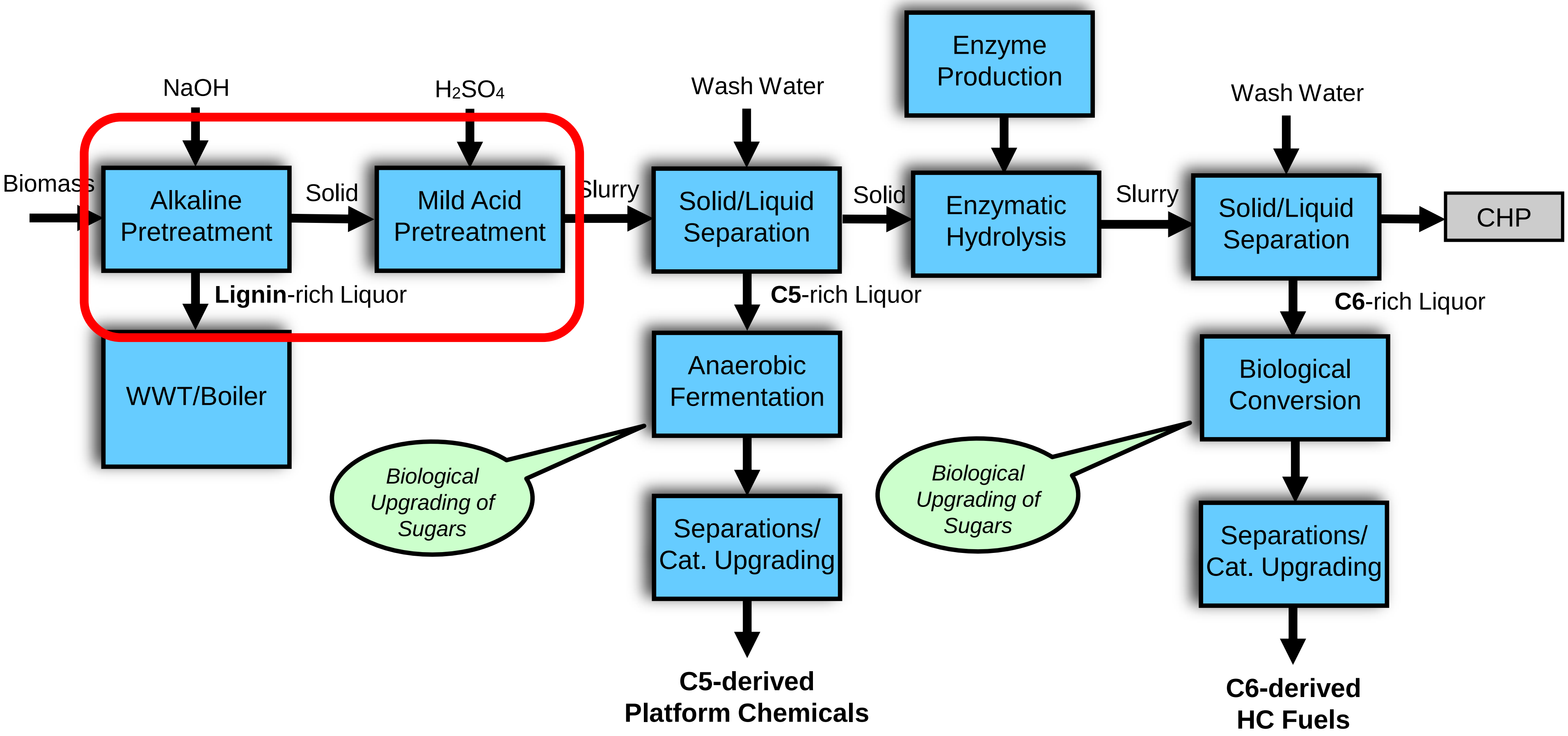
Partners

- Subcontracts
  - Washington State University
  - North Carolina State University
  - U. North Dakota
- Other Collaborations
  - PNNL
  - Andritz Inc.
  - Univ. of Toronto
  - IdeaCHEM,
- The project is managed under the Biochemical Platform at NREL

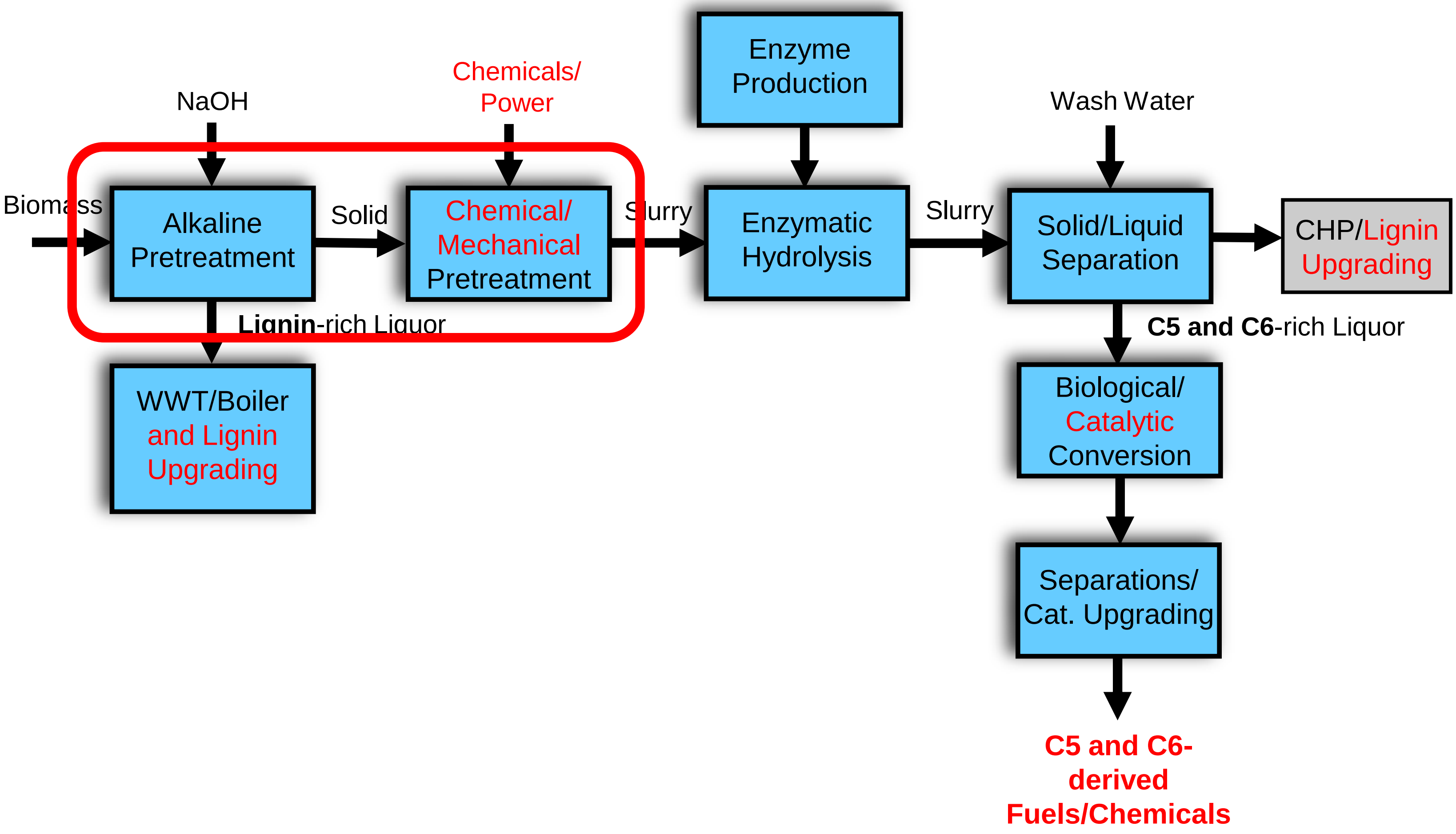
Project Overview

- Continuation from Pretreatment and Enzyme Hydrolysis project
- Focused primarily on lower severity dilute alkali and acid pretreatments
    - Decrease reactor, S/L separations, and OPEX costs
- Investigating NREL's alternative biomass deconstruction options
    - Deacetylation/Mechanical Refining (DMR) process
- Objective of producing high concentration, low toxicity sugar and reactive lignin streams
- Interface with upstream and downstream unit operations:
    - Feed/Process Interface and INL
    - Separations Development and Applications
    - Biological Upgrading (saccharification and fermentation)
    - Lignin Utilization
    - Bench and Pilot Scale Integration
    - Biochemical Platform Analysis

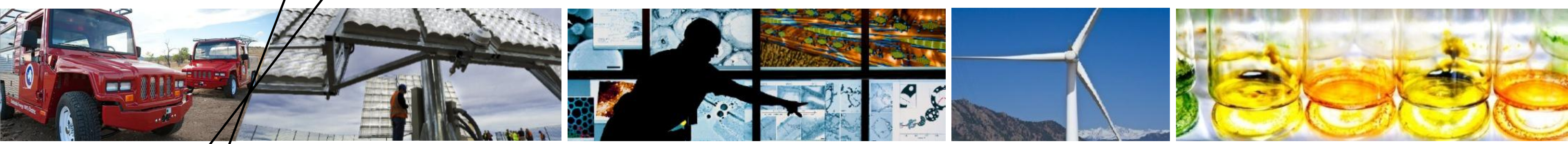
Process Flow Diagram **2017**



Process Flow Diagram **2022**



Project Technical and Management Approaches



Pretreatment and Process Hydrolysis

Technical Approach

- Investigated aqueous phase dehydration of C5 sugars to furfural (FY13 D-Milestone 8/31/2013, TEA analysis)
- High severity pretreatments avoided
  - Loss of C5 sugars, higher inhibitor formation, expensive reactors, difficult S/L separations
- Investigate lower severity pretreatments
  - Lower toxicity, concentrations of salts and catalyst poisons, and pretreatment and EH yields
  - Deacetylation
    - Extracts ~20% biomass, decreases plant equipment sizes, improves yields, lower toxicity
  - Mechanical refining
- Investigate other biomass deconstruction options
  - NREL's DMR process (FY14 Dashboard Milestone 12/31/2013)
    - "Cleaner" sugar and reactive lignin streams for biological and catalytic upgrading
- **Challenges**
  - Effects of blended and blended/densified feedstocks
  - Process must be scalable
- **Critical success factors**
  - Low cost sugars
  - "Clean" sugars upgraded to intermediates at high yields and productivities
  - "Reactive" upgradable lignin stream with low concentrations of catalyst poisons
  - Developed process must reduce energy, water, and chemical usage

Management Approach

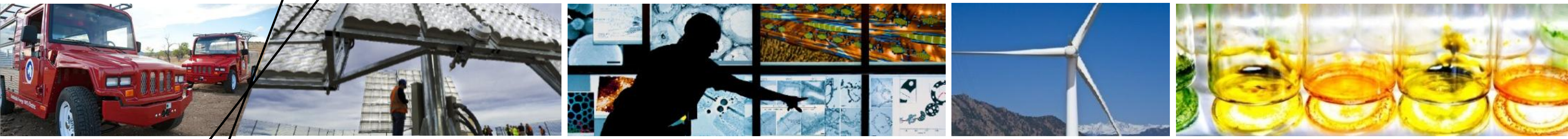
- **Project divided into two tasks**
  - Low severity dilute alkali and acid pretreatments
    - Deacetylation and/or Mechanical refining
  - Deacetylation and Mechanical Refining
    - Dilute alkali deacetylation
    - Mechanical refining
- **Metrified milestones to gauge progress towards meeting BETO's 2017 and 2022 goals and targets with TEA and sensitivity analyses**
  - Two milestones FY13 (one TEA), Four milestones FY14 (one TEA & one Dashboard)
  - Milestones defined with interactions with other Biochemical Conversion projects
- **Incorporate Go/No Go decisions**
- **Research guided by TEA analysis**
- **Challenges**
  - Low pretreatment and EH yields
  - Reduce enzyme loading to <10 mg total protein
- **Critical Success Factors**
  - TEA analysis demonstrate minimum sugar and fuel selling prices that meet BETO goals
  - Process scalable

Out-Year Targeting for R&D

	Design Report Basis	2014 SOT	2015 Projection	2016 Projection	New 2017 Target
Minimum Fuel Selling Price ($/GGE, 2011$)	***$5.10***	**$12.97**	**$10.14**	**$7.43**	**$5.03**
Feedstock Contribution ($/GGE, 2011$)	*$1.76*	$3.88 [1]	$3.20 [1]	$2.47 [1]	$1.87 [1]
Conversion Contribution ($/GGE, 2011$)	***$3.33***	**$9.09** [1]	**$6.93** [1]	**$4.97** [1]	**$3.16** [1]
RDB Fuel Yield (GGE/dry ton)	*45*	18	20	20	22
Succinic Acid Yield (lb/dry ton)	*NA*	197	206	232	270
Feedstock					
Feedstock Cost ($/dry ton) [2]	*$80*	$130	$115	$95	$80
Feedstock Blend	*Blend*	Stover	Stover	Blend	Blend
Pretreatment/Separation					
Solids Loading (wt%)	*30%*	30%	30%	30%	30%
Xylan to Xylose (including conversion in C5 train)	*>73%*	73%	75%	78%	78%
Hydrolysate solid-liquid separation	*No*	Yes	Yes	Yes	Yes
Xylose Sugar Loss (into C6 stream after acid PT separation)	*NA*	5%	4%	2.5%	1%
Enzymes					
Enzyme Loading (mg/g cellulose)	*10*	14	12	10	10
Enzymatic Hydrolysis & Bioconversion – C6 Train					
Total Solids Loading to Hydrolysis (wt%)	*20%*	15%	15%	17.5%	17.5%
Enzymatic Hydrolysis Time (d)	*3.5*	3.5	3.5	3.5	3.5
Hydrolysis Glucan to Glucose	*90%*	77%	85%	85%	90%
Hydrolysis Residual Xylan to Xylose	*>30%*	30%	30%	30%	30%
Glucose Sugar Loss (into solid lignin stream after EH separation)	*1%*	5%	4%	2.5%	1%
Expt'l bioconversion scale/method	*NA*	Bench scale/ Batch	Bench scale/ Fed-batch	Bench scale/ Fed-batch	Pilot scale/ Fed-batch
Bioconversion Volumetric Productivity (g/L-hr)	*1.3*	0.29	0.3	0.35	0.4
Lipid Content (wt%)	*NA*	57%	57%	60%	60%
Glucose to Product [total glucose utilization] [3]	*87% [95%]*	75% [100%]	75% [100%]	78% [100%]	78% [100%]
Xylose to Product [total xylose utilization] [3]	*82% [86%]*	74% [98%]	74% [98%]	76% [98%]	76% [98%]
C6 Train Bioconversion Metabolic Yield (Process Yield) (g/g sugars)	*0.34 (0.28)*	0.26 (0.26)	0.26 (0.26)	0.27 (0.27)	0.27 (0.27)
Intermediate Product Recovery	*97%*	90%	90%	90%	90%
Carbon Yield to RDB from Biomass	*26.2%*	10.4%	11.4%	11.8%	12.5%
Coproduct Production Performance – C5 Train					
Bioconversion Volumetric Productivity (g/L-hr)	*NA*	0.3	1	1.5	2.0
C5 Train Bioconversion Metabolic Yield (Process Yield) (g/g sugars)	*NA*	0.63 (0.59)	0.64 (0.60)	0.66 (0.65)	0.795 (0.74)
Succinic Acid Recovery Efficiency	*NA*	80%	80%	80%	80%
Carbon Yield to Succinic Acid from Biomass	*NA*	8.9%	9.3%	10.5%	12.2%

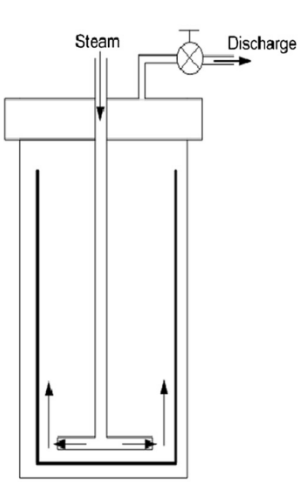
[1] Cost breakdowns to feedstock vs conversion cost contributions are allocated in new target case according to carbon efficiency to RDB fuel vs succinic acid
[2] Feedstock costs based on a 5% "ash equivalent" basis for all years considered, consistent with values provided by INL ash "dockage" costs
[3] First number represents sugar conversion to desired product (FFA), values in parentheses indicate total sugar utilization

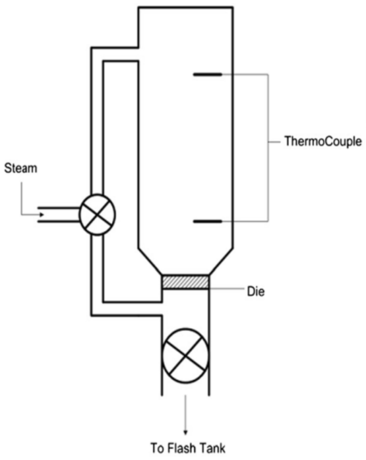
Technical Accomplishments/Progress /Results

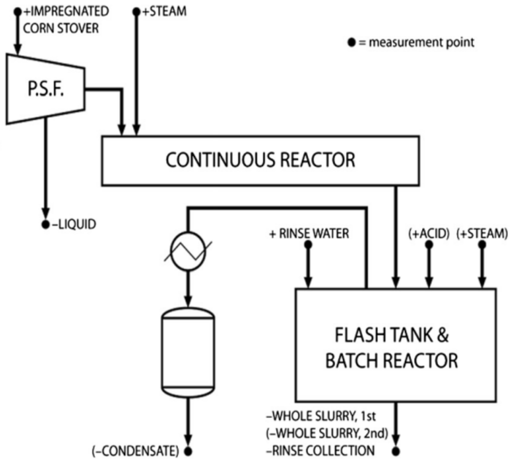


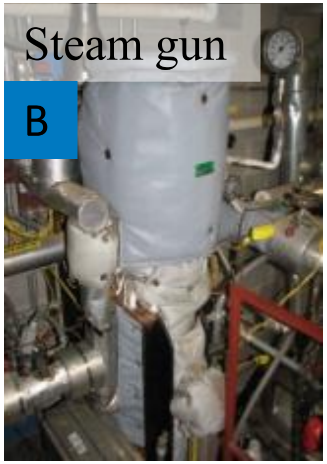
Three Reactor Comparison* in Dilute Acid Pretreatment

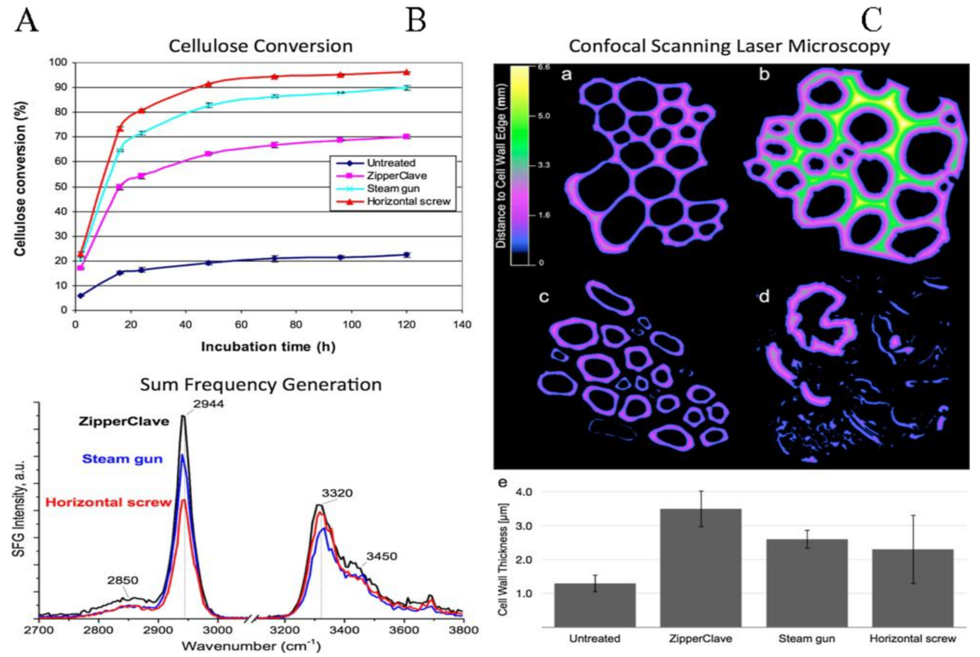
- Utilized same acid impregnated feedstock
- Utilized same pretreatment conditions
  - 160 C, 5 min, 2 wt% H_2SO_4











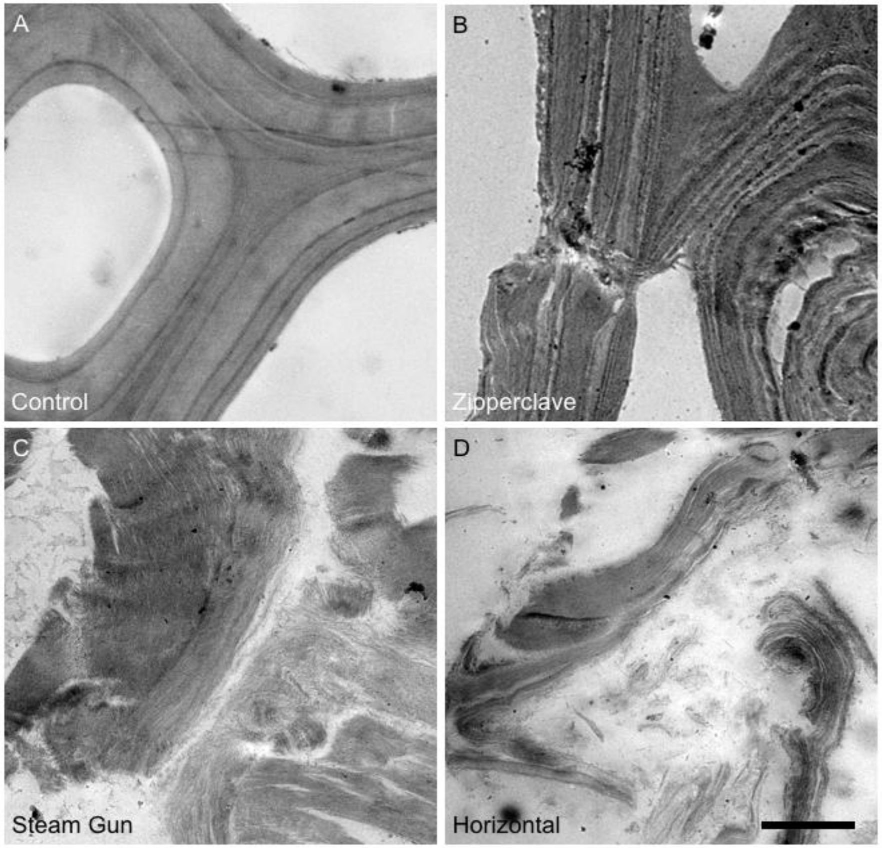
*Wang, W., Chen, X. *et al.*, 2014. *Biotechnology for Biofuels*, 7:47

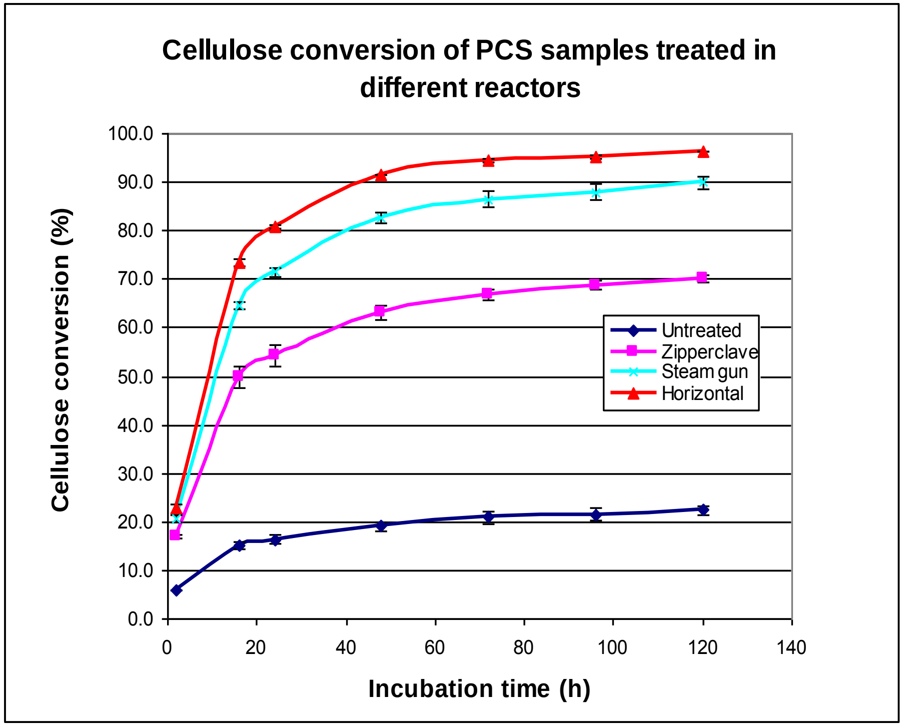
Three Reactor Comparison in Dilute Acid Pretreatment* and Enzymatic Hydrolysis

Increased shear in reactor increases yields

- Xylan to xylose and digestibility yields:
  - Horizontal Screw>Steam Gun > Zipperclave
- Extent of cell wall deconstruction:
  - Horizontal Screw>Steam Gun>Zipperclave

Reactor	Xylan removal (%)
Zipperclave	79
Steam gun	88
Horizontal screw	93





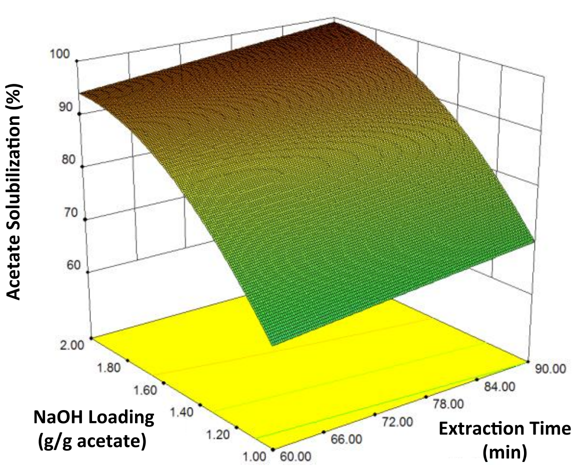
*Pretreatment: 160 C, 5 min, 2 wt% H_2SO_4

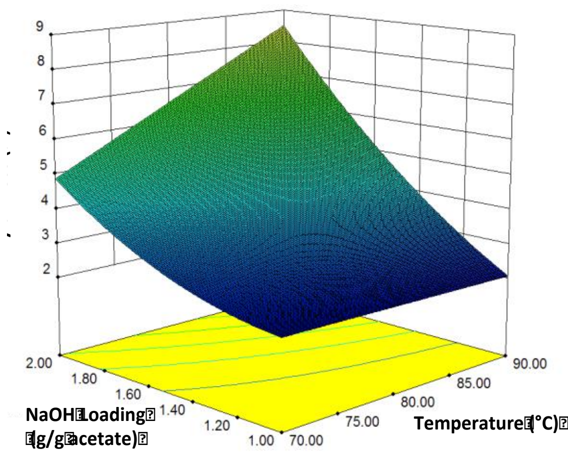
Wang, W., Chen, X. *et al.*, 2014. *Biotechnology for Biofuels*, 7:47

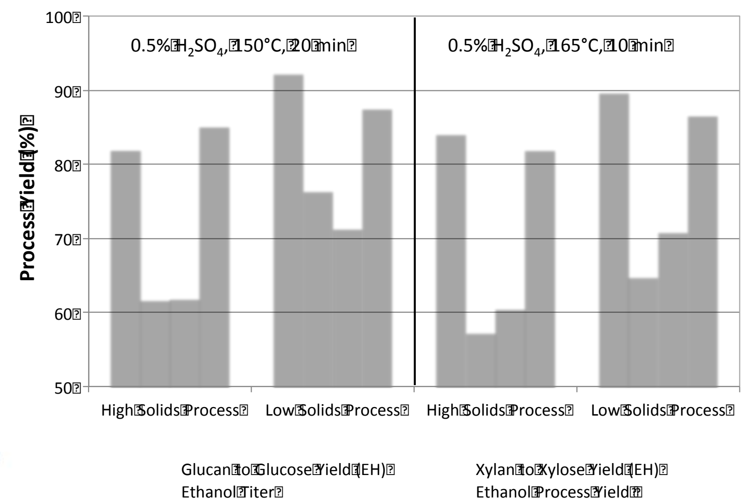
Dilute Alkali Deacetylation Characterization

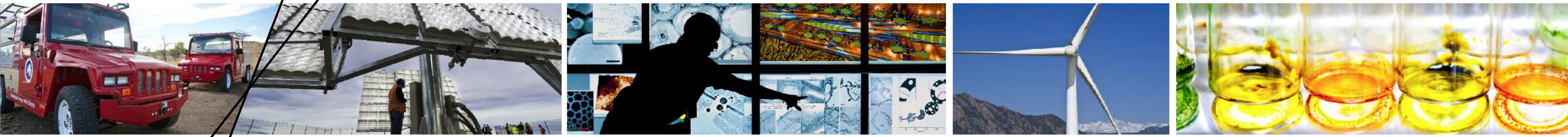
- Evaluated deacetylation process across range of conditions
  - Minimize xylan loss, maintain acetate removal
  - Identify sensitivities to cost drivers
- **Low Solids (Historical) Process**: 1.8 g NaOH/g Acetate loading, 10% solids, 80 C, 2 hours ➔ 80% Acetate, 5% xylan removal
- **High Solids Process**: 1 g NaOH/g Acetate loading, 30% solids, 70 C, 90 min ➔ 70% Acetate, 2% xylan removal

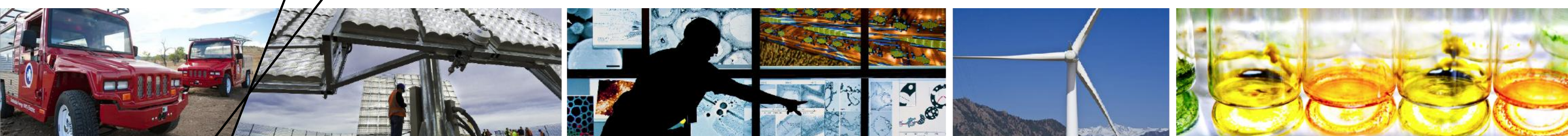
- High solids (30 wt%) deacetylation effective
- Lower temperature deacetylation not as effective in pretreatment
- Lower NaOH loadings remove 70% acetyl content



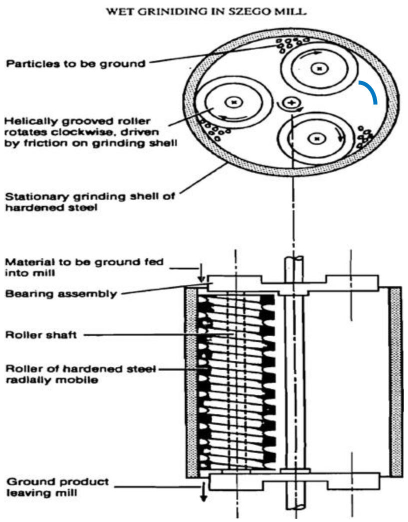








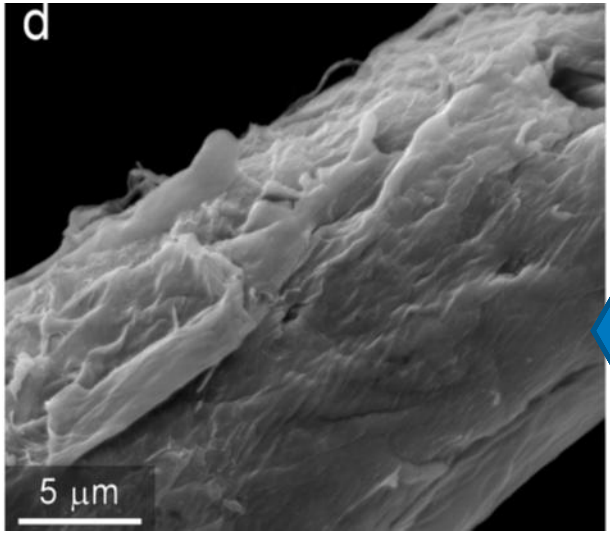
Multi-Stage DMR Process (DR followed by Szego Milling)



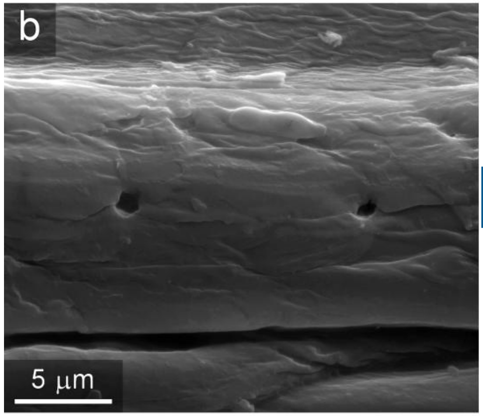
External Fibrillation

Internal Fibrillation

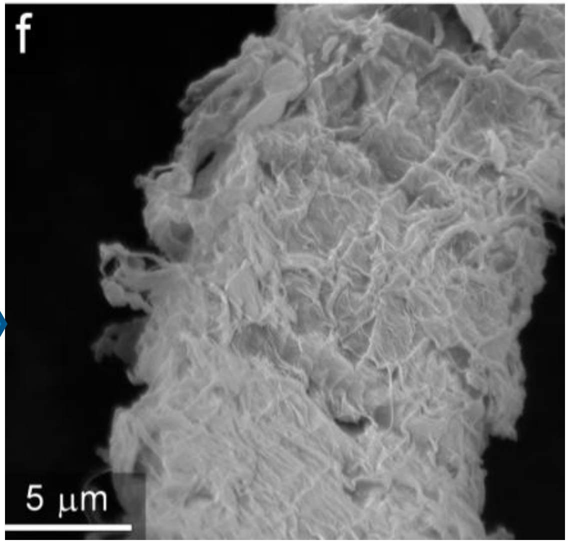
(Chen et al., 2013
Kerekes et al., 2002)



Disk Refining

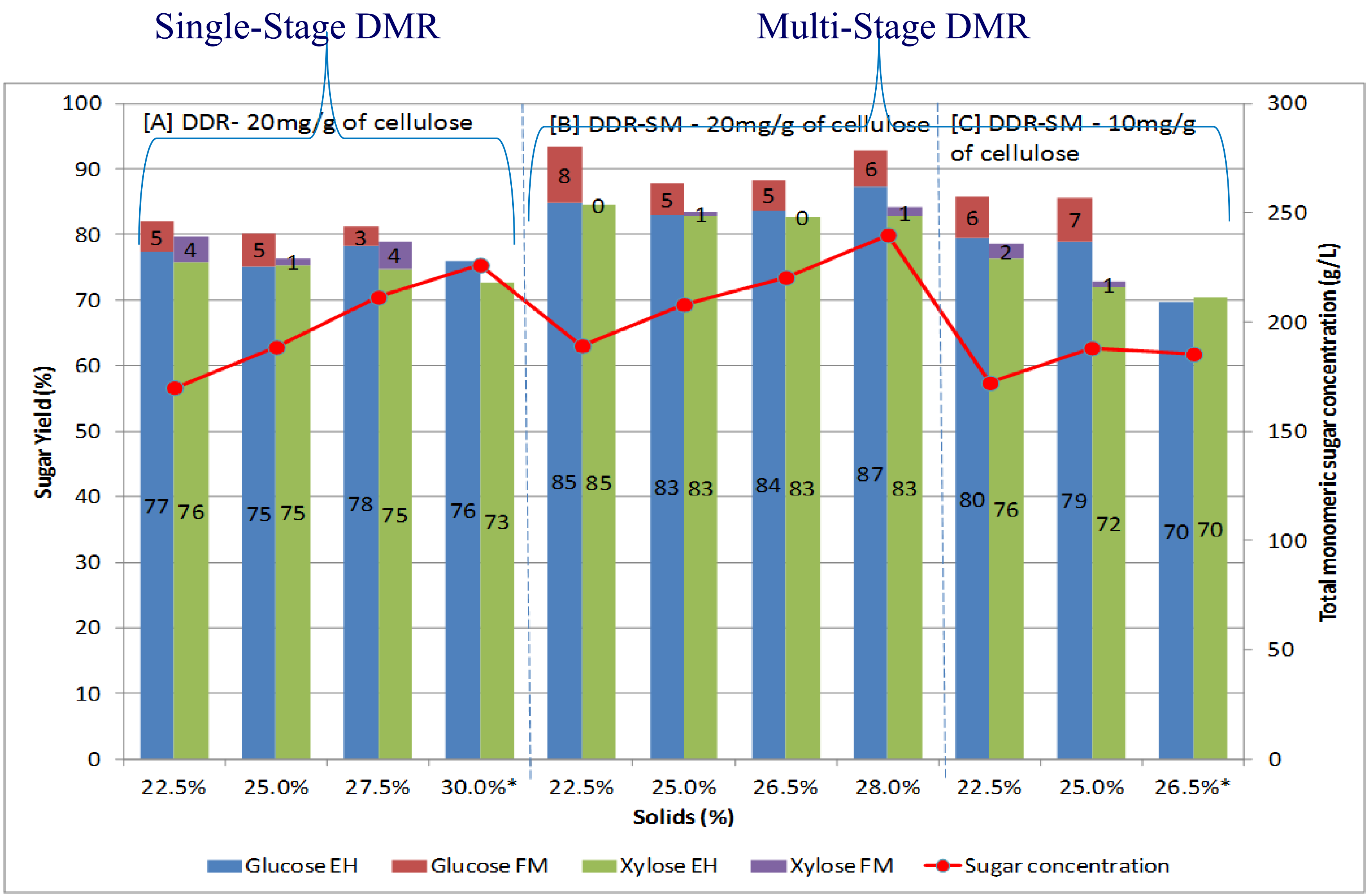


Native Corn Stover



Szego milling

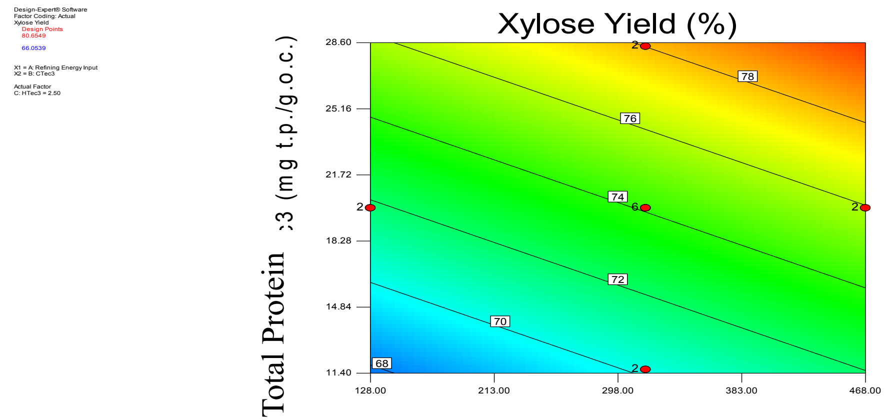
DMR*- Enzymatic Hydrolysis at Higher Solids (22.5-30 wt%)

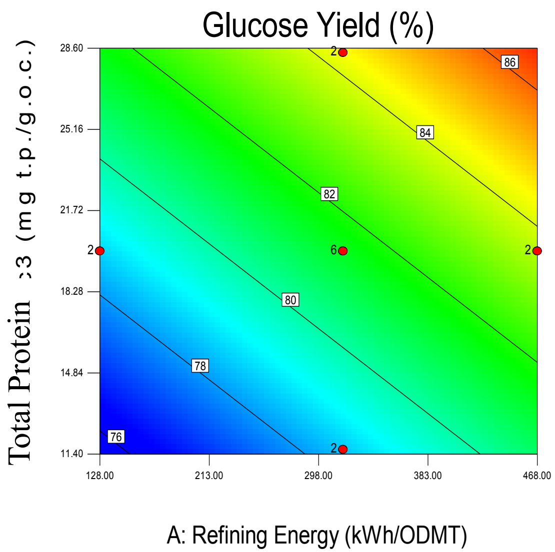


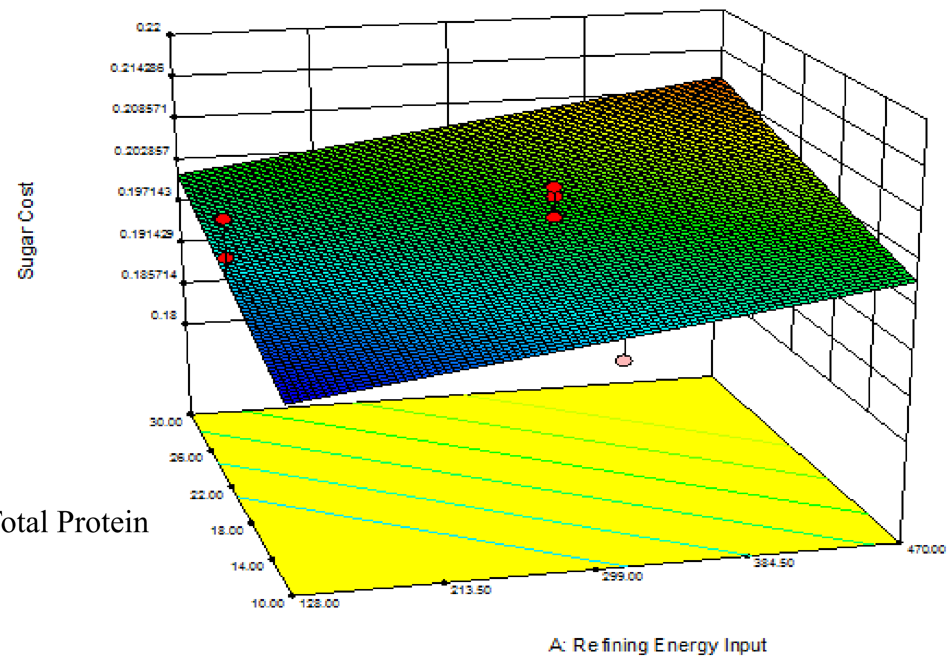
*DMR total refining energy= ~200 kWh/ODMT

TEA of Single-Stage DMR Process

- **Sugar yields increase:**
  - Refining energy increases
  - Total protein loading increases
- **Sugar cost increase as:**
  - Refining energy increases
  - Total protein loading increases
- **<200 kWh/ODMT economical**





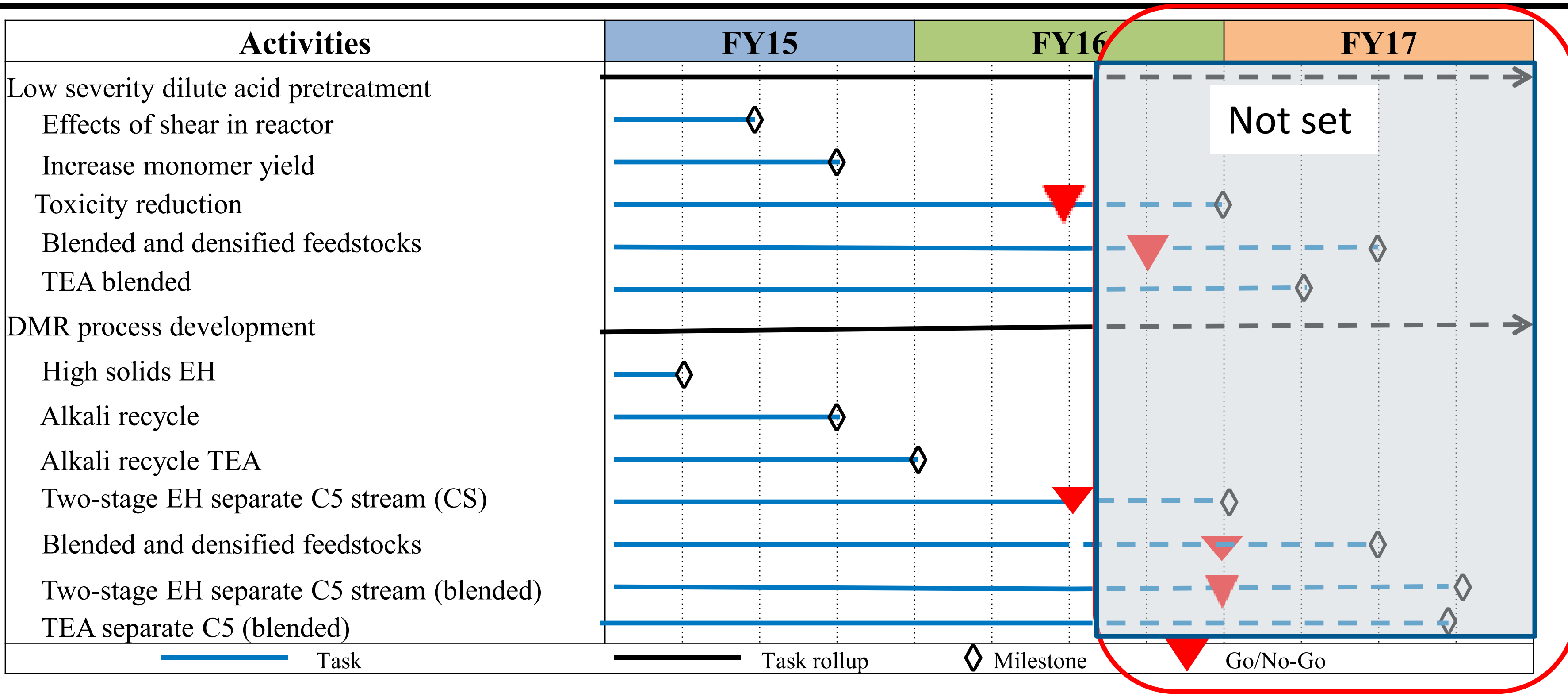


Relevance

Project performs R&D contributing to meeting BETO MYTP strategic and performance goals to develop scalable processes that produce low cost, high concentration sugar and reactive lignin streams to meet 2017 and 2022 goals and targets

- **Approaching BETO's goal of 10 mg protein or less**
- **R&D on blended and blended/densified feedstocks**
- **High concentration "clean" sugars for biological upgrading**
- **Reactive lignin streams for biological/catalytic upgrading**
- **Develop scalable processes**
  - Transfer to commercial scale?
  - Re-purpose shuttered pulp and paper mills?

Future Work



- Lower severity dilute alkali and acid pretreatment of blended and blended/densified feedstocks
    - Separate C5 sugar stream
- DMR of blended and blended/densified feedstocks
    - Recycle TEA to evaluate economic feasibility
    - Separate C5 sugar stream
    - TEA

Summary

- **Project focused on producing low cost, high concentration sugar and reactive lignin streams at high yields to meet BETO's 2017 and 2022 goals and targets.**
- **Demonstrated that shear within biomass reactors increased yields**
- **Showed that biomass deacetylation affects xylan and acetate removal, as well as pretreatment yields**
- **Single-stage DMR alone increased yields without a pretreatment reactor**
  - Deacetylation reduces power consumption
  - TEA showed energy consumption <200kWh/ODMT is economical
- **Two stage DMR increased yields close to 85% even at 10 mg total protein loading**
  - Process produced upgradable high concentration sugar and lignin streams
- **Future work will focus on blended or blended/densified feedstocks for 2017 pilot scale demonstration**
  - Optimize dilute alkali and acid pretreatment of blended or densified feedstocks
    - Lower toxicity and increase monomeric sugar yields
  - Optimize DMR process for blended or densified feedstocks
    - Decrease energy, water, and chemical usage

Acknowledgments

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Thomas Pschorn

University of Toronto

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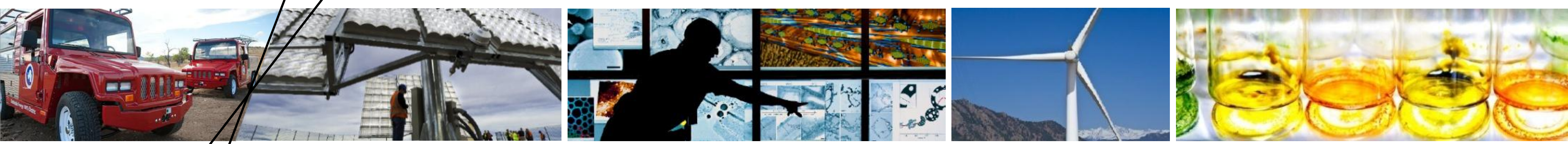
IdeaCHEM

Keith Flanegan

Additional Slides



Pretreatment and Process Hydrolysis

Milestone Schedule for Pretreatment & Process Hydrolysis Project

FY 13/14 Milestones

Type	Title/Performance Measure	Due Date
E	Investigate various co-catalysts in hydrothermal, dilute acid, and alkali pretreatment for the production of furfural/HMF for upgrading to C-10 to C-20 hydrocarbons. Performance measure: Double furfural or HMF yields from 15% to 30%.	7/31/2013
D	**Title:** Scale up promising biomass hydrolysis/deconstruction technology to a continuous reactor to produce intermediates for supply to the Chemical Transformation subtask and other stakeholders for conversion to hydrocarbon fuel molecules. **Performance Measure:** Scale up should be at 200 kg/d scale and achieve soluble upgradable intermediates yields of at least 85% from the xylan component in biomass. TEA	8/31/2013
Dashboard	**Title:** Identify optimal mechanical refining conditions that increase enzymatic digestibility of deconstructed corn stover by at least 20% in sugar release increase over baseline using commercial enzyme preparations. **Performance Measure:** Test 10 different mechanical refining conditions including rpm, roller type, feed rates, and %-solids on energy consumption requirements and enzymatic digestibility of dilute alkali deacetylated corn stover. This optimization would have a large effect on the process efficiency and is expected to beneficially affect the techno-economics of the process.	12/31/2013
Regular	Test 3 different disk refiner plates and at least 10 conditions of rpm, feed rate, and plate gap on energy. Compare results with Szego mill and twin screw extruder.	3/31/2014
Regular	Produce 2 kg each of 3 different deacetylated/mechanically refined/enzyme digested lignin rich corn stover residues for a joint milestone with the Lignin Utilization task for analysis and depolymerization.	6/30/2014
Regular	Determine at least 5 process parameters needed to develop a detailed techno-economic analysis (TEA) of different deacetylation/mechanical refining options. Report TEA and sensitivity analyses based on energyrequirements and enzyme loadings versus pretreatment reactor costs.	9/30/2014

FY15 Milestones

Type	Title/Performance Measure	Due Date
Regular	**Title:** Determine Enzymatic Hydrolysis Glucose and Xylose Yields of DDR solids at High Solids Loadings. **Milestone Description:** Conduct high solids enzymatic hydrolysis on DDR residues produced in a commercial scale disc refiner at 200 kWh/ODMT and Szego milled at 200 kWh/ODMT at solids contents of 22.5, 25, 27.5, 30 wt% insoluble solids in roller bottles with total enzyme loadings of 20mg/g of cellulose.	12/31/2014
Regular	**Title:** Effect of Shear in Steam Explosion Reactor on Pretreatment and Enzymatic Hydrolysis Yields. **Milestone Description:** Perform a set of factorial or surface response experiments consisting of at least 20 bench scale steam explosion pretreatments of corn stover that will maximize pretreatment and enzymatic hydrolysis yields using native and deacetylated corn stover feedstocks over varying acid concentrations, residence times, temperature, and shearing die configurations.	3/31/2015
Regular	**Title:** Determine the Effect of Deacetylation Liquor Recycling on Sugar, Toxicity, and Hydrocarbon Intermediate Yields Using DDR Process Solids and Slurries. **Milestone Description:** Create a deacetylation liquor recycling and chemical makeup process flow diagram and perform recycling of deacetylation liquor up to 5 times using 5 kg corn stover at 10% solids with 0.1N sodium hydroxide at 80C for 2hr in each recycle, draining the liquor using a simple screen solid/liquid separation at the paddle reactor, followed by screw pressing the solids and mixing the recovered squeezed liquor with drained liquor. Dic refine the deacetylated solids from the various recycle experiments. Enzymatically digest the DDR solids at high solids (20 wt% solids or greater).	6/30/2015
Major	**Title:** Assess solid/liquid separation performance of higher severity dilute acidpretreated slurries to Separations Development and Applications Project for Solid/Liquid Separation, Analysis, and Characterization of C5 Sugar Rich Streams. **Milestone Description:** At least five higher severity dilute acid pretreated slurries will be prepared and compositionally characterized by the Analytical Development and Support project (2.5.1.101) and evaluated for their comparative solid-liquid separations performance by the SDA project (2.4.1.101) for possible incorporation into the PSI project's (2.4.1.102) plans for FY17 integrated demonstration.	6/30/2015
Regular	**Title:** Test Six Hemicellulase Enzyme Preparations to Hydrolyze 35% Xylooligomers in Dilute Acid Pretreated and DDR Corn Stover Slurries to Improve Monomeric Xylose Yields. **Performance Measure:** Test at least six commercial and in-house xylanase, xylobiase, hemicellulase and accessory enzyme preparations to hydrolyze at least 35% of the xylooligomers present in dilute acid pretreated and DDR corn stover slurries to improve monomeric xylose yields and to reduce toxicity. Report accessory enzymes needed and monomeric xylose yield performance increases.	6/30/2015
Regular	**Title:** Report in a Techno-Economic Analysis the Effects of Higher Solids Enzymatic Hydrolysis and Deacetylation Liquor Recycling on Sugar and Hydrocarbon Intermediate Production Costs. **Milestone Description:** Construct TEA analysis with Aspen Plus developed models using NaOH and water usage, sugar yields and hydrocarbon intermediate production results from higher solids enzymatic hydrolysis and deacetylation liquor recycle DDR experiments. Prepare a manuscript for submission to a peer reviewed journal for publication of the TEA results.	9/30/2015

Reviewer Comments

- Project: 2.2.1.1 NREL
- Title: *Pretreatment and Enzymatic Hydrolysis*

Presenter: David Johnson
Review Panel: Biochemical Conversion
Presentation Date: Tuesday, May 21, 2013

•

- Reviewer Comments

•

Cost competitive sugars objective applicable to BETO objectives
Timeline reasonable \
Good collaboration
knowledge/application good approach.
considering performance targets leading actual work good approach.
overall project approach solid , follow up by techno economic evaluation logical. $3/gallon cost target?
deployment pathway is reasonable. Looking forward to optimization and recycle
Evolution of tasks based on learning curve and move towards HC is reasonable.

•

Reviewer Comments-2

- goals to produce cost-competitive sugars with partners; pretreatment and enzyme hydrolysis

transition from knowledge development to unit operations applications; performance targets generated for etoh and will generate them for HC. developing strategies for sugars to HC (do you expect them to differ?)

- - capital costs of PT system?

- energy requirements?
- sugar upgrading?

•

Process relevant equipment and process relevant scales
Expanding to HC-based fuels from biomass
2017 Go-No Go on project
Unit operations focus
Looking at modifications for advanced biofuels (e.g., chemical vs. biological pre-treatment)
Changes to Task Structure for 2013 - reflects focus on HC fuels

•

Goal: transition from knowledge development to unit operation applications.

Project management plan is defined and appropriate to actively track progress against milestones and allow for adjustments in RDD&D paths. Milestones could be improved by converting them to SMART goals (i.e. Specific, Measurable, Achievable, Relevant, Timely).
The advanced biofuels work is still in the very early stages of development. Many key variables have been identified (leveraging ethanol work); however, much work remains to establish boundary conditions and refine key assumptions for the production of hydrocarbon fuels.

•

The work to date has been sound. The future work involving conversion of sugars to hydrocarbons is somewhat vague.

•

Reviewer Comments-3

- 2. Technical Progress, Accomplishments, and Goals
- 2) Please evaluate the degree to which:
- The project performers have made progress in reaching their objectives based on their project management plan.
- The project performers have met their objectives in achieving milestones and overcoming technical barriers.
- New project performers have identified viable plans to accomplish their objectives.
- Reviewer Comments
-

cellulosic ethanol
Deacetylation step introduction and scale up resulting positive progress and results.
Evolution of the overall process and process variables good
Sugars
progress on xylooligomers conversion demonstrated.
collaboration of yields with enzymes and hydrolysis developed
progress in enzymatic hydrolysis demonstrated
Haven't seen these kind of results with refining, would like to see the techno-economics piece of this work?
elimination of acid in PT very interesting. Again, techno economics evaluation ?

Reviewer Comments-4

- potential for chemical conversion of sugars. viscosity reduction process to produce more pumpable fluid; deacetylation impact and scale-up allowed for lower severity pretreatment (resulted in less furfural). screw press to remove water after deacetylation (fines issues?); xylooligomers were mainly glucuronic acids and GH-67 discovered (cost benefit of the addition of these enzymes vs leave them out?); development of continuous enzymatic hydrolysis (complex); addition of disc-refining (cost?) but all done at low solids; cost benefit of reaching higher cellulose conversion. evaluating an extruder vs DA pretreatment (is this scaleable?). HC production via catalysts and/or organisms. carbon chain length vs energy content also O-content (decarboxylation is mechanism used by biology to remove O). furans to hydrocarbons (but furans about $3000/ton vs $900/ton for HC fuel). PHA breakdown into HC. estimates that sugar costs about $0.26/kg
- Process slurries - modeling effort

Deacetylation - acetate inhibitory to ethanologens
Continuous enzymatic conversion
Deacetylation with mechanical refining
Microbial inhibitors - ways to mitigate

Tasks seem consistent with needs for improving process/cost analysis
Important to make sure focus is on latest/best technology (e.g., enzyme cocktails)
Where appropriate - focus on mechanism

-

Reviewer Comments-5

- The project performers achieved their objectives with respect to hydrolysis development, unit operation scale-up, and integrated process demonstration for the production of cellulosic ethanol.

•

Mechanical refining results are promising
ID of biological toxicity inhibitors is difficult, will be highly dependent on the exact organism and enzymes in the pathway. The results need to be relevant to commercial processes.

•

Explained very well how, for example, the deacetylation modification was tackled by the different tasks (groups) within the project. Demonstrated how the deacetylation modification resulted in xylooligomers, which could be broken down with some new enzyme cocktails but it was not clear if the advantage of breaking them down would be cost effective with the increased cost of (new) enzymes.

Showed result for deacetylation combined with mechanical processing and how that this could potentially replace acid pretreatment.

Responses to Previous Reviewers' Comments

- Project Approach
- We appreciate the reviewers' comments regarding the applicability of objectives, timeline, collaboration and approach. We expect subtle differences in the development of strategies for utilizing sugars for HC relative to ethanol. Sensitivity of HC producing organisms to inhibitors already appears slightly different to ethanologens from preliminary work looking at the inhibition of these organisms to acetate. A bigger challenge will be the need to reduce sugar costs to meet the BETO HC fuel cost goal ($3/gallon). We agree with the reviewers that estimation of costs and energy requirements will be very important, as will be the identification of viable sugar upgrading strategies.
- Project Relevance
- We agree with the reviewers that feasibility and technoeconomic analyses are essential for the further development of routes from all sugar intermediates to HC, and these are planned to occur in the next year. Statements from the 2012 MYPP were used in the slides describing the goals of the task and relevance of the task, e.g., "Produce sugars and other reactive intermediates to support the 2017 goals for renewable gasoline, diesel, and jet fuel".
- Critical Success Factors
- We agree with the reviewers that staying abreast of the latest developments in pretreatment science and the development of HC pathways will be essential to the success of our program and BETO/DOE's mission. As the pathways from sugars to HC products become better defined, technical targets will be identified and their achievement will become the targets for our research. Overall, the measurable metric will be the cost of producing HC fuels, but the technical targets will be the interim targets we will aim to achieve.
- Technology Transfer and Collaborations
- We agree with the reviewers that greater interaction with process engineers would be beneficial. At NREL their time is highly sought after so we have taken the approach to generate data that can be used in engineering evaluations before involving the engineers. Discussion of specific tech transfer efforts and collaborations may not have given as much time as they warranted during the presentation due to time limitations, however, we are well aware of how important they are to our overall effort. We have numerous subcontractors that make an important contribution to our research effort, and have 3 companies we are working with over the next 2 years that are using the facilities and know-how at NREL.

Responses to Previous Reviewers' Comments (Cont.)

- **<u>Overall Impressions</u>**
- **We agree with the reviewers that more interaction with the TEA people will be beneficial to the direction of our research, and this is planned to occur in the next year. It is our expectation that these interactions will lead to technical targets that will become the focus of our research.**
- **<u>Future Work</u>**
- **We agree with the reviewers that well described and appropriate milestones are essential to the direction of our research. This review occurred just as we were developing milestones for FY14, one of which will be an initial milestone to decrease the cost of producing sugars by 10% by utilizing mechanical refining in conjunction with pretreatment. We agree that the current market cost of furans is much greater than the value of the fuels we are looking to produce. To reach target furfural costs, so that it can be become an intermediate in a fuel production process, will require higher yields and lower feedstock costs than are used in traditional furfural production processes. Again TEA of furfural and PHB processes will be essential and are planned.**
- **<u>Technical Progress, Accomplishments, and Plans</u>**
- **We appreciate that the reviewers recognized the progress made by the task since the last review. We plan to aggressively pursue evaluating the possibility of reducing the severity of or replacing dilute acid pretreatment with some form of mechanical refining. TEA of these options will be essential and will be performed as soon as the data is obtained. In addition TEA of other novel process developments (addition of supplementary enzymes, dewatering, etc.,) will also be performed.**

Publications and Presentations

- "Controlling Porosity in Lignin-Derived Nanoporous Carbon for Supercapacitor Applications", (2014), Ju-Won Jeon, Libing Zhang, Jodie L. Lutkenhaus, Dhrubojyoti D. Laskar, John P. Lemmon, Daiwon Choi, Manjula I. Nandasiri Ali Hashmi, Jie Xu, Radha K. Motkuri, Carlos A. Fernandez, Jian Liu, Melvin P. Tucker, Peter B. McGrail, Bin Yang, and Satish K. Nune, *ChemSusChem.,* DOI: 10.1002/cssc.201402621.
- "Noble-metal catalyzed hydrodeoxygenation of biomass-derived lignin to aromatic hydrocarbons", (2014), Dhrubojyoti D. Laskar, Melvin P. Tucker, Xiaowen Chen, Gregory L. Helms and Bin Yang, *Green Chemistry*, 16, 897-910.
- "A highly efficient dilute alkali deacetylation and mechanical (disc) refining process for the conversion of renewable biomass to lower cost sugars", (2014), Chen, X., Shekiro, J., Pschorn, T., Sabourin, M., Tao, L., Elander, R., Park, S., Jennings, E., Nelson, R., Trass, O., Flanegan, K., Wang, W., Himmel, M., Johnson, D. and Tucker M., *Biotechnology for Biofuels*, 7:98
- "Effect of mechanical disruption on the effectiveness of three reactors used for dilute acid pretreatment of corn stover Part 1: chemical and physical substrate analysis", (2014), Wang, W., Chen, X., Donohoe, B.S., Ciesielski, P.N., Katahira, R., Kuhn, E.M., Kafle, K., Lee, C.M., Park, S., and Kim, S.H., Tucker, M.P., Himmel, M.E., and Johnson, D.K., *Biotechnology for Biofuels* 7, 57.
- "Effect of mechanical disruption on the effectiveness of three reactors used for dilute acid pretreatment of corn stover Part 2: morphological and structural substrate analysis", (2014), Ciesielski, P.N., Wang, W., Chen, X., Vinzant, T.B., Tucker, M.P., Decker, S.R., Himmel, M.E., Johnson, D.K., and Donohoe, B.S. *Biotechnology for Biofuels,* 7, 47.
- "Heterologous expression of xylanase enzymes in lipogenic yeast *yarrowia lipolytica"*, Wang, W., Wei, H., Alahuhta, M., Chen, X., Hyman, D., Johnson, K., Zhang, M., Himmel, M., (2014), *PloS one*, DOI: 10.1371/journal.pone.0111443.
- "Multiscale deconstruction of molecular architecture in corn stover", (2014), Inouye, H., Zhang, Y., Yang, L., Venugopalan, N., Fischetti, R.F., Gleber, S.C., Vogt, S., Fowle, W., Makowski, B., Tucker, M., Ciesielski, P.N., Donohoe, B., Matthews, J., Himmel, M.E., and Makowski, L., *Scientific Reports,* 4.
- "Comparison of transcriptional profiles of Clostridium thermocellum grown on cellobiose and pretreated yellow poplar using RNA-Seq", (2014), Wei, H., Fu, Y., Magnusson, L., Baker, J.O., Maness, P.-C., Xu, Q., Yang, S., Bowersox, A., Bogorad, I., Wang, W., Tucker, M.P., Himmel, M.E., and Ding, S.-Y., *Frontiers in Microbiology* 5: 142.
- Determining the kinetics of sunflower hulls using dilute acid pretreatment in the production of xylose and furfural, (2014), Srinivas Reddy Kamireddy, Evguenii I. Kozliak, Melvin Tucker, Yun Ji, *Green Processing and Synthesis*, 3(1), 69-75. doi: 10.1515/gps-2013-0095.
- "3-D Electron Tomography of Pretreated Biomass Informs Atomic Modeling of Cellulose Microfibrils", (2013), Ciesielski, P.N., Matthews, J.F., Tucker, M.P., Beckham, G.T., Crowley, M.F., Himmel, M.E., Donohoe, B.S., *ACSNano*, 7 (9), 8011-8019. doi: 10.1021/nn4031542.

Publications and Presentations-2

- "Comparison of different mechanical refining technologies on the enzymatic digestibility of low severity acid pretreated corn stover", Chen, X., Kuhn, E., Wang, W., Park, S., Flanegan, K., Trass, O., Tenlep., L., Tao, L. and *et. al.*, 2013. *Bioresource Technology (Impact Factor: 5.60)* 147, 401-408.
- "Recent Development in Chemical Depolymerization of lignin-A Review", (2013), H. Wang, M .Tucker and Y. Ji, *Journal of Applied Chemistry*, Vol. 2013, Article ID 838635, 1-9.
- "Converting Forage Sorghum and Sunn Hemp into Biofuels through Dilute Acid Pretreatment", (2013), S. Reddy Kamireddy, J. Li , S. Abbina, M. Tucker, M. Berti and Y. Ji, *Industrial Crops and Products*, 49, 598-609.
- "Oligomer saccharide reduction during dilute acid pretreatment co-catalyzed with Lewis acids on corn stover biomass", (2013), J. Degenstein, S. Kamireddy, M. Tucker, and Y. Ji, *International Journal of Agricultural and Biological Engineering*, Vol. 6 No. 2, 54-62.
- "Effects and Mechanism of Metal Chlorides Catalysts on Pretreatment and Enzymatic Digestibility of Corn Stover", (2013), S. Kamireddy, J. Li, J. Degenstein, M. Tucker and Y. Ji, *Industrial & Engineering Chemistry Research*, 52(5), 1775-1782.
- "Genomic, Proteomic, and Biochemical Analyses of Oleaginous *Mucor circinelloides*: Evaluating Its Capability in Utilizing Cellulolytic Substrates for Lipid Production", (2013), Wei, H., Wang, W., Yarbrough, J. M., Chen, X., and *et. al.*, *PloS one*, 8(9), e71068.

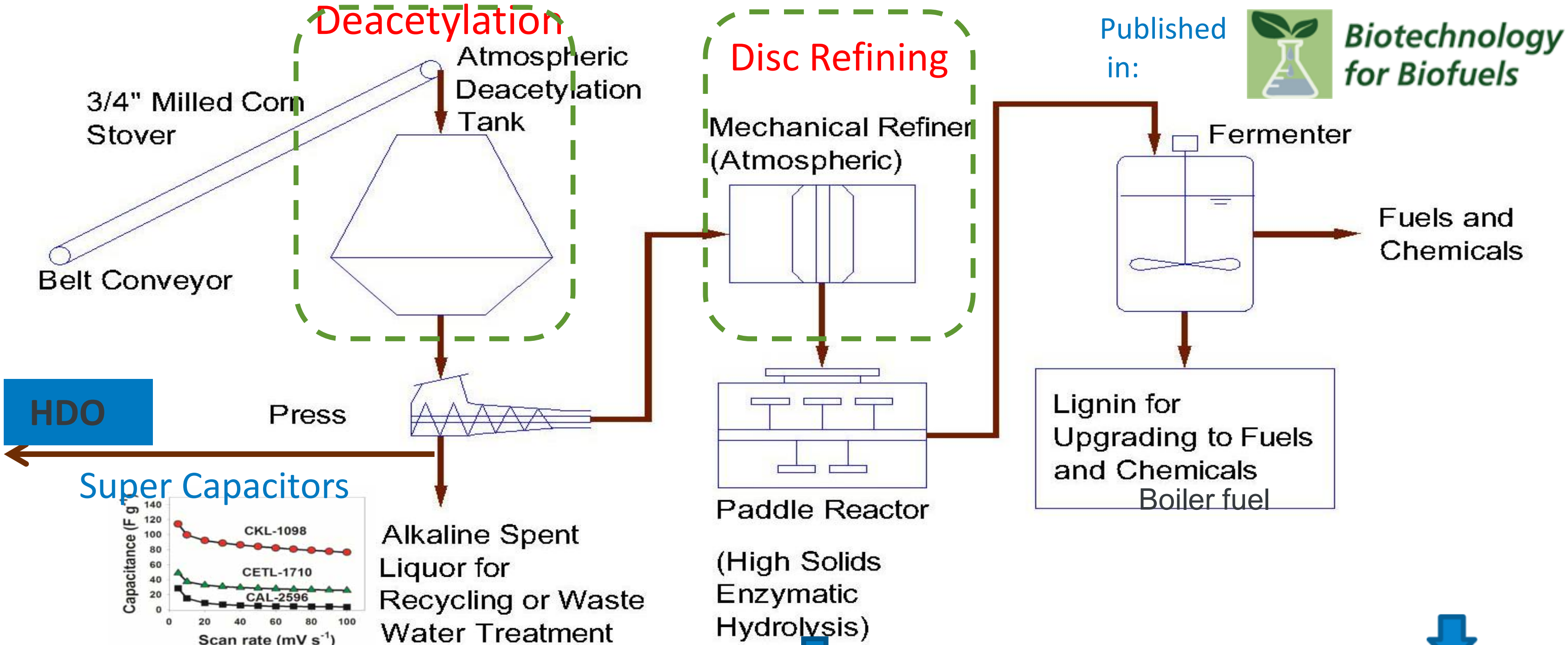
- Book Chapter
  - "Laboratory Pretreatment Systems to Understand Biomass Deconstruction", (2013), Bin Yang and Melvin P. Tucker, in "Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals", Charles Wyman (editor), Wiley Series in Renewable Resources, West Sussex, United Kingdom.

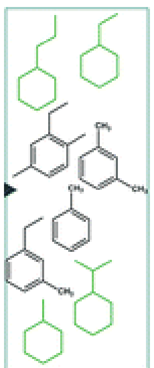
- Presentations
  - "A highly efficient dilute alkali deacetylation and mechanical (disc) refining process for the conversion of renewable biomass to lower cost sugars", Chen, X. and Tucker, M.P., (2014), 5th Biobased Chemicals Commercialization & Partnering, San Francisco, CA
  - "Using furfural as an intermediate for making gasoline, jet and diesel fuel components", Johnson, D.K., Black, S.K., Chen, X., Moens, L., and Tucker, M.P., (2014), 36th Symposium on Biotechnology for Fuels and Chemicals, Clearwater, FL

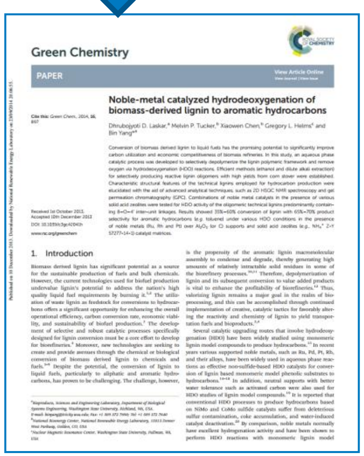
Publications and Presentations-3

- Presentations (continued)
  - Shekiro, J .et al. Dilute Acid Pretreatment of Deacetylated Corn Stover in a Pilot-Scale Pretreatment Reactor At Low Acid Loadings, 2013 AIChE Annual Meeting, San Francisco, CA
  - Shekiro, J. Cost Competitive Cellulosic Ethanol: The National Renewable Energy Lab's Perspective, 2013 AIChE Annual Meeting, San Francisco, CA
  - "Effects of mechanical refining on the enzymatic digestibility of acid pretreated corn stover", Chen, X., Wang, W., Vinzant, T. B., Park, S., Flanegan, K., Tucker, M., November, 2012, AIChE Annual Conference, Pittsburgh, PA.
  - "Upgrading Biomass Derived Lignin for Hydrocarbon Production", Laskar, D. D., Tucker, M.P., Yang, B., November 2012, AIChE Annual Conference, Pittsburg, PA.
- Posters:
  - "Using furfural as an intermediate for making gasoline, jet and diesel fuel components", (2014), Johnson, D.K., Black, S.K., Chen, X., Moens, L., and Tucker, M.P., 36th Symposium on Biotechnology for Fuels and Chemicals, Clearwater, FL
  - "Interactions of ferrous and ferric ions with oxygen and biomass: Impacts on the efficiency of dilute acid pretreatment of biomass", Hui Wei, Xiaowen Chen, Wei Wang, Bryon S. Donohoe, Peter N. Ciesielski, Shi-You Ding, Michael E. Himmel and Melvin P. Tucker, presented at the 35th Sypmosium on Biotechnology for Fuels and Chemicals, Portland, Oregon, April 29-May 2, 2013.
  - "Novel Catalytic Processing of Lignin to Aromatic Hydrocarbons", Dhrubojyoti D. Laskar, Melvin Tucker and Bin Yang, presented at the 35th Sypmosium on Biotechnology for Fuels and Chemicals, Portland, Oregon, April 29-May 2, 2013.
  - "Optimization of Alkaline Extraction for the Removal of Acetic Acid", Joseph Shekiro III, Xiaowen Chen, Melvin P. Tucker, presented at the 35th Sypmosium on Biotechnology for Fuels and Chemicals, Portland, Oregon, April 29-May 2, 2013.
  - "Kinetic studies of dilute acid hydrolysis of acetylated and non-acetylated xylan model compounds", Xiaowen Chen, Joe Shekiro, Jonathan Stickel, and Melvin Tucker, presented at the 35th Sypmosium on Biotechnology for Fuels and Chemicals, Portland, Oregon, April 29-May 2, 2013.
  - "Furfural Production as a By-product of Lignocellulosic Biofuel Process: Experimental and Techno-Economic Analysis", Xiaowen Chen, Ling Tao, Nick Nagle, Erik M. Kuhn, David K. Johnson, and Melvin P. Tucker, presented at the 35th Sypmosium on Biotechnology for Fuels and Chemicals, Portland, Oregon, April 29-May 2, 2013.

Deacetylation and Mechanical Refining Process (DMR)






Green Chemistry

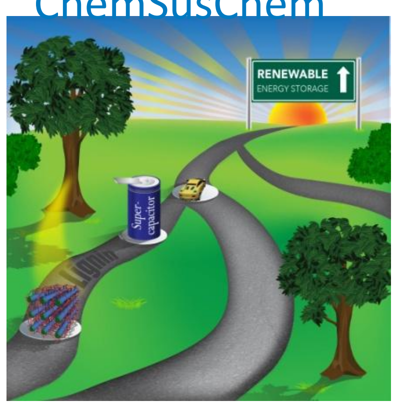
PAPER

Noble-metal catalyzed hydrodeoxygenation of biomass-derived lignin to aromatic hydrocarbons

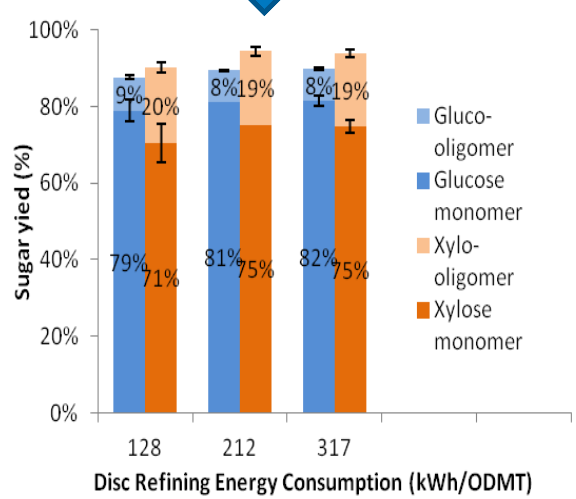
Dhrubojyoti D. Laskar, Melvin P. Tucker, Xiaowen Chen, Gregory L. Helms and Bin Yang

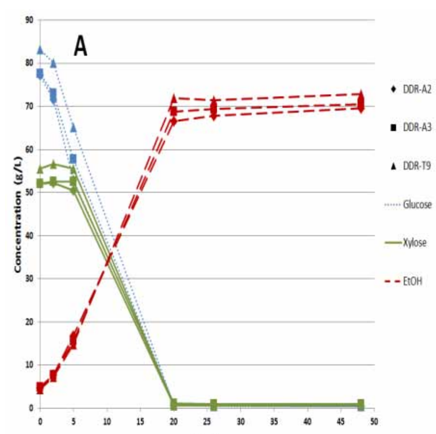
NREL, WSU

ChemSusChem

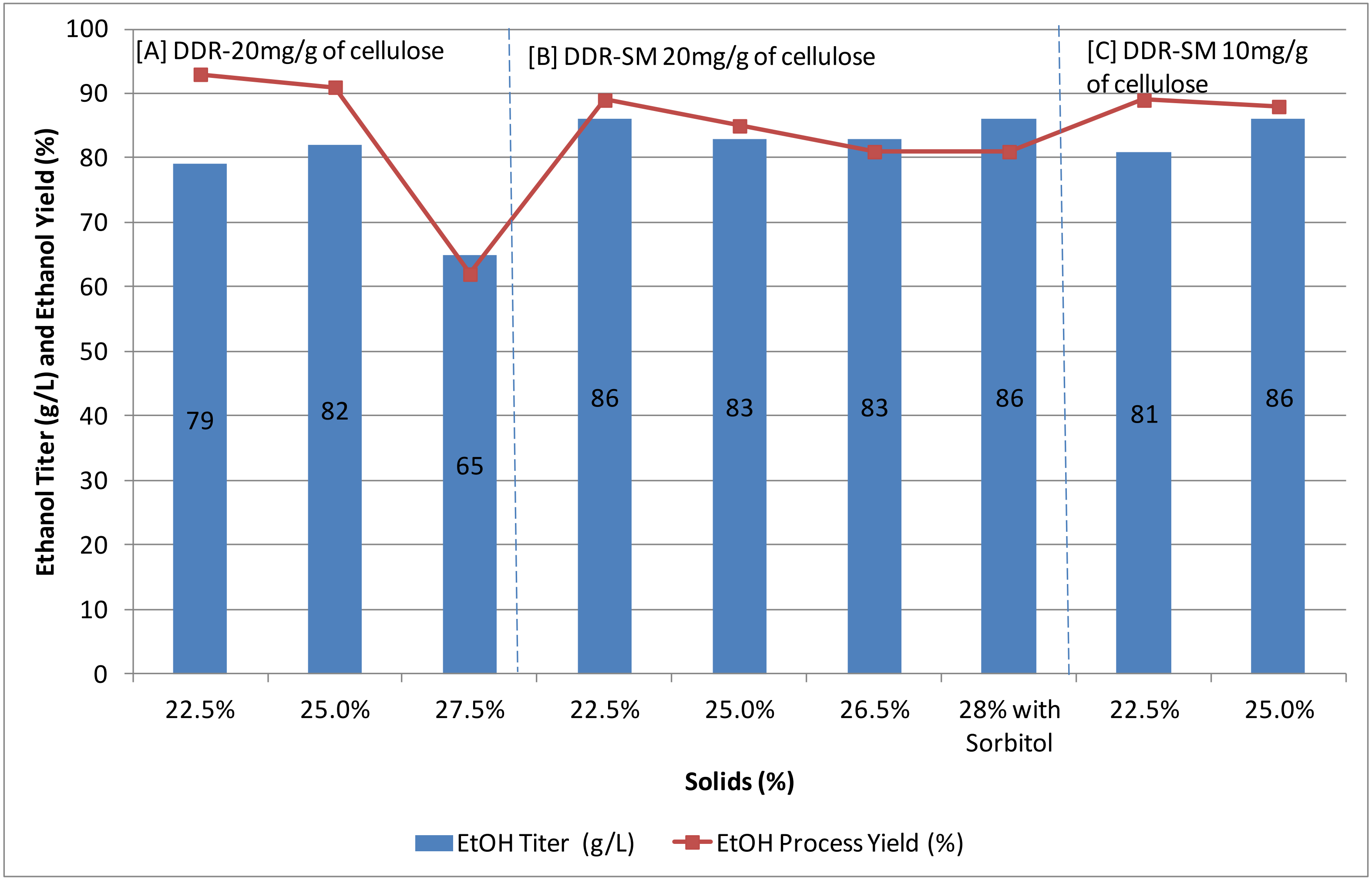


PNNL, NREL,WSU





Fermentation* at Higher Solids (22.5-28%)



Kinetics of Fermentation using DDR-SM substrates at higher total solids (22.5 to 28 wt%)