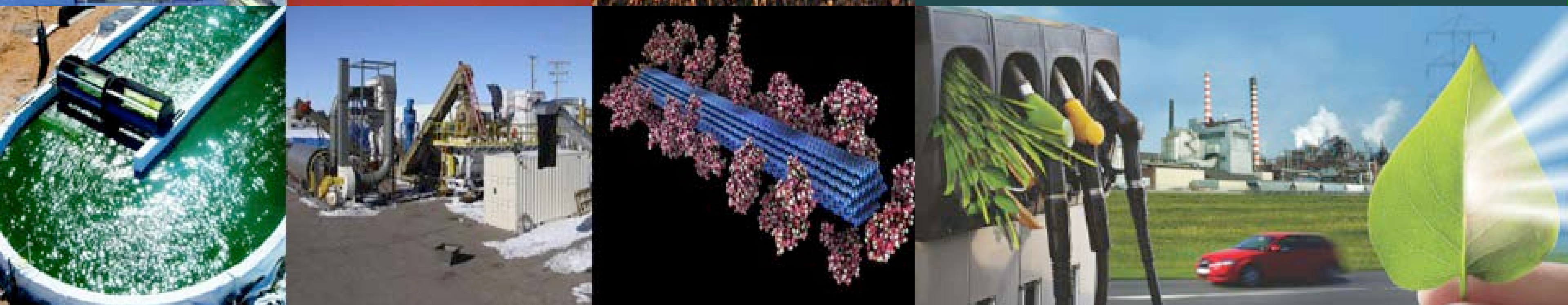


2015 DOE BioEnergy Technologies Office (BETO) Project Peer Review

Date: March 23th, 2015

Technology Review Area: Feedstock-Conversion Interface

Determining the Impact of MSW as a Feedstock Blending Agent (WBS 2.2.1.103-105)

Principal Investigators: Seema Singh (SNL), Vicki Thompson (INL), Todd Pray (ABPDU)

Organizations: Sandia National Lab, Idaho National Lab, Advanced Biofuels Process Demonstration Unit

Goal Statement

- **Goal and outcome**: Identify the optimal blend of municipal solid waste (MSW) to serve as feedstocks for the production of fermentable sugars using an ionic liquid-acidolysis process.
- **Relevance to BETO:** MSW is a promising but nascent feedstock, and the blending of MSW with different types of feedstocks to decrease costs and maximize availability is quickly gaining prominence. Few studies have been carried out to determine the impact of these blended feedstocks on the overall process efficiency of a wide range of platform technologies. This project will:
  - identify MSW blends that meet feedstock cost targets
  - achieve high yields of fermentable sugars through the use of ionic liquids and acidolysis
  - technology will be demonstrated at the 100L scale at the ABPDU at the end of FY15

Sandia National Laboratories

Idaho National Laboratory

ABPDU ADVANCED BIOFUELS PROCESS DEMONSTRATION UNIT

Quad Chart Overview

Timeline

- Start date: October 1, 2013
- End date: September 30, 2015
- Percent complete: 75%

Barriers Addressed

- Ft-A Feedstock availability and cost
- Bt-D Pretreatment processing
- Bt-J Catalyst development

Budget

	Total Costs FY 14–FY 15	Total Planned Funding (FY 14-Project End Date
DOE Funded	$235,600	$500,000

Partners

- Partners
  - Idaho National Laboratories – Vicki Thompson
  - Lawrence Berkeley National Laboratory – Todd Pray

Project Overview

- **Project history**
  - Project initiated in FY14 as a “seed” AOP between SNL, INL, and LBNL-ABPDU
  - Achieved major milestone in FY14 using MSW paper fraction
  - Complementary to other BETO-funded feedstock-conversion interface AOPs (WBS 1.2.2.1)
- **Project context**
  - MSW blends could provide low-cost, nationally available feedstocks suitable for conversion
  - Acidolysis using ionic liquids avoids the use of enzymes
- **High-level objective**
  - To conduct a comparative pretreatment and hydrolysate study to understand and track the impact of MSW as a blending agent with herbaceous (e.g., switchgrass) and agricultural residues (e.g., corn stover) as a function of pretreatment and hydrolysis.

Technical Approach

Substrate: MSW blends produced and distributed by INL

- **Approach**
  - Screen combinations of blends and conversion chemistries at the bench scale
  - Identify parameters for optimal sugar yields
  - Scale-up SNL bench results at the ABPDU
- **Primary challenges:**
  - Effective process controls to identify key optimization parameters
  - Degradation of MSW blends over time
  - Identifying suitable MSW blends that meet cost and performance targets
  - Scaling up process
- **Success factors:**
  - Achieving high yields of sugars from MSW blends
  - Maintain high yields as a function of scale
  - Minimal production of known fermentation inhibitors during process

Management Approach

Critical Success Factors:

•Employ expertise in feedstocks (INL), conversion chemistries (SNL), and process scale-up and controls (ABPDU)

•Leverage experience from two biomass conversion centers

•Work with MSW cost tool to identify optimal blends that are "real world"

•Leverage input and collaborations from other BETO-funded projects feedstock-conversion interface

Management Approach:

•Use quarterly milestones to track progress and down-select options

•Focus on rapid screening and scale-up

•Phone calls every 3 weeks, site visits once per FY

•Contributions from all partners in managing the project and tracking progress

•Divide research in a manner that leverages each partners strengths

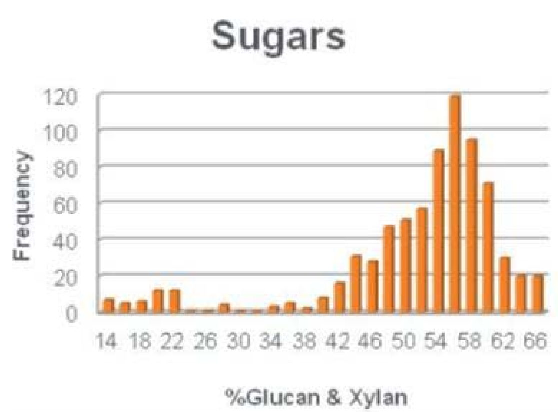
Feedstock Target (INL Biomass Program)

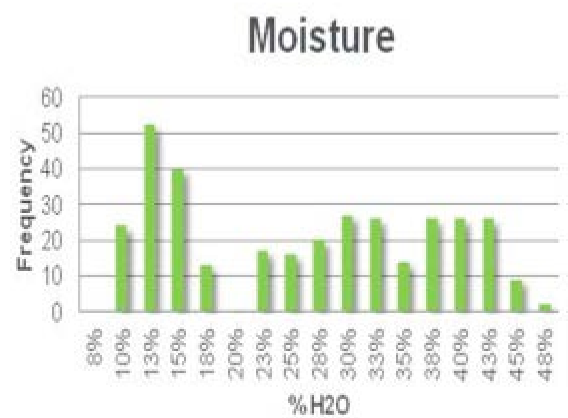
2017 Program Goals

- **Biomass cost $80/ton**
  - Feedstock costs
  - Harvest and collection
  - Transportation
  - Preprocessing
  - Storage
- **Sugar content >59%**
- **Moisture content <20%**
- **Ash content**
  - Biochem <5%
  - Thermochem <1%

Current State of Technology

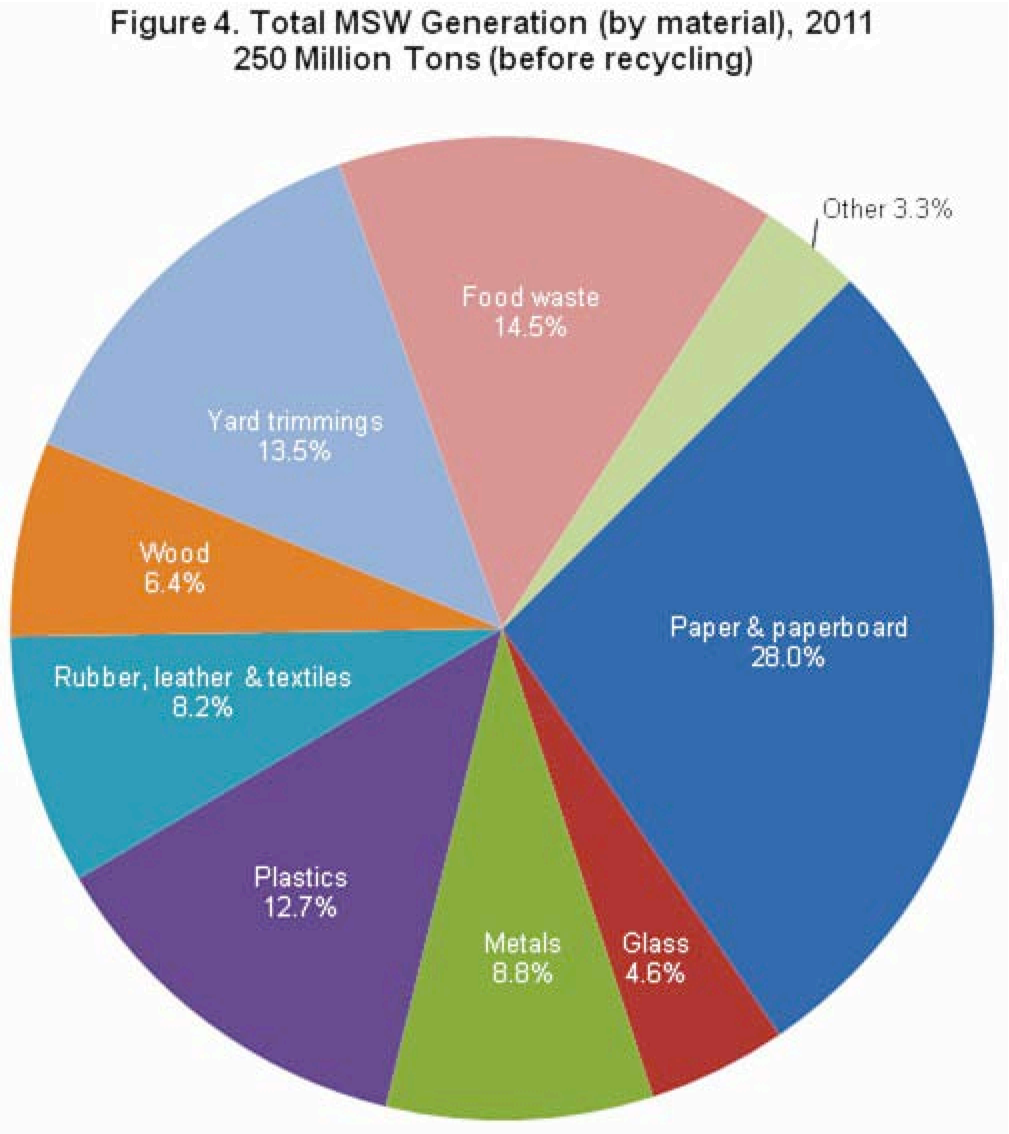
- **Biomass cost $141.70/ton (corn stover)**
  - Feedstock costs $40
  - Harvest and collection $22.20
  - Transportation $11.50
  - Preprocessing $43.60
  - Dockage for not meeting specs $20.10
  - Storage $4.30





Is MSW a Solution?

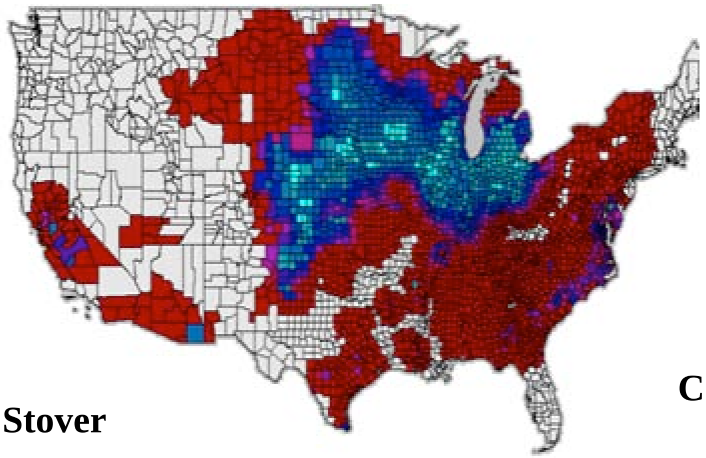
- **Advantages**
  - Low cost
  - Collection infrastructure
  - Under-utilized
  - Distributed generation
  - Renewable
- **Disadvantages**
  - Highly variable
    - Season
    - Year
    - Region
    - "coyote effect"
  - Low quality
    - Sorting
    - Upgrading



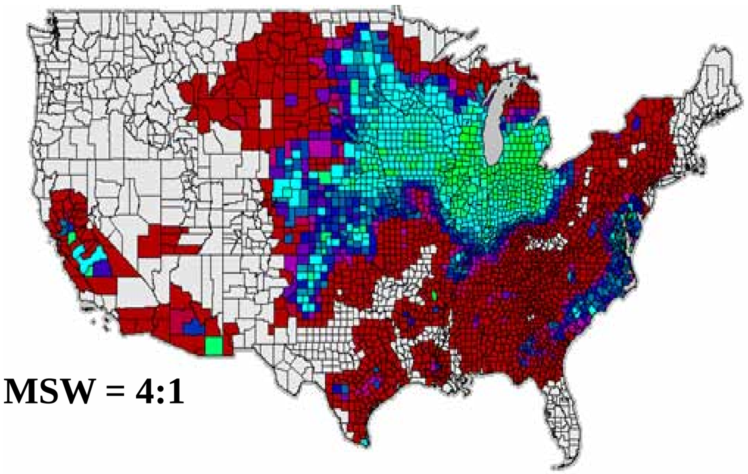
Source: http://www.epa.gov/epawaste/nonhaz/municipal/index.htm

Driving Towards $80/ton Feedstocks with MSW Blends

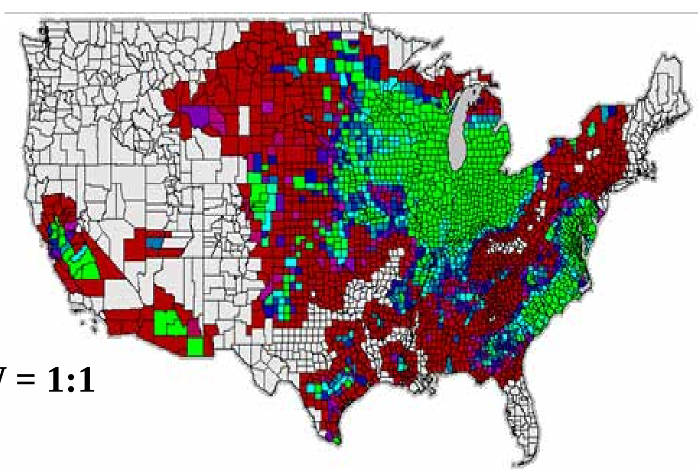
Delivered Feedstock Costs



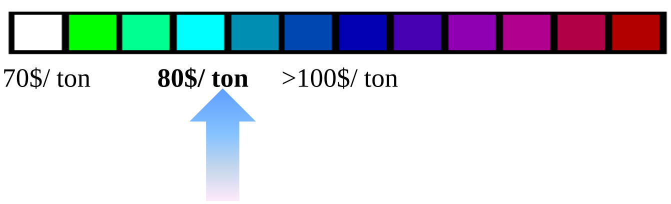
Corn Stover



CS:MSW = 4:1



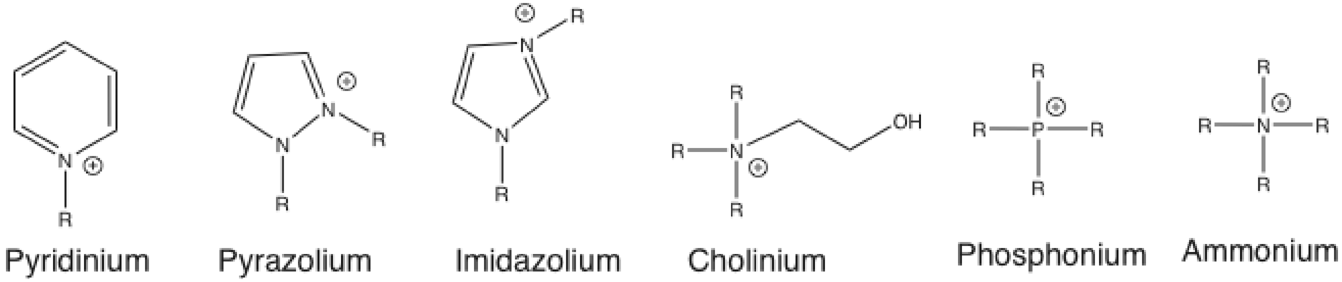
CS:MSW = 1:1



Feedstock Processing using Ionic Liquid

Room Temperature, Molten Salts

CATIONS



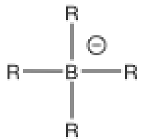
Cation determines:
- stability
- properties

Water immiscible ⇒ Water miscible

ANIONS

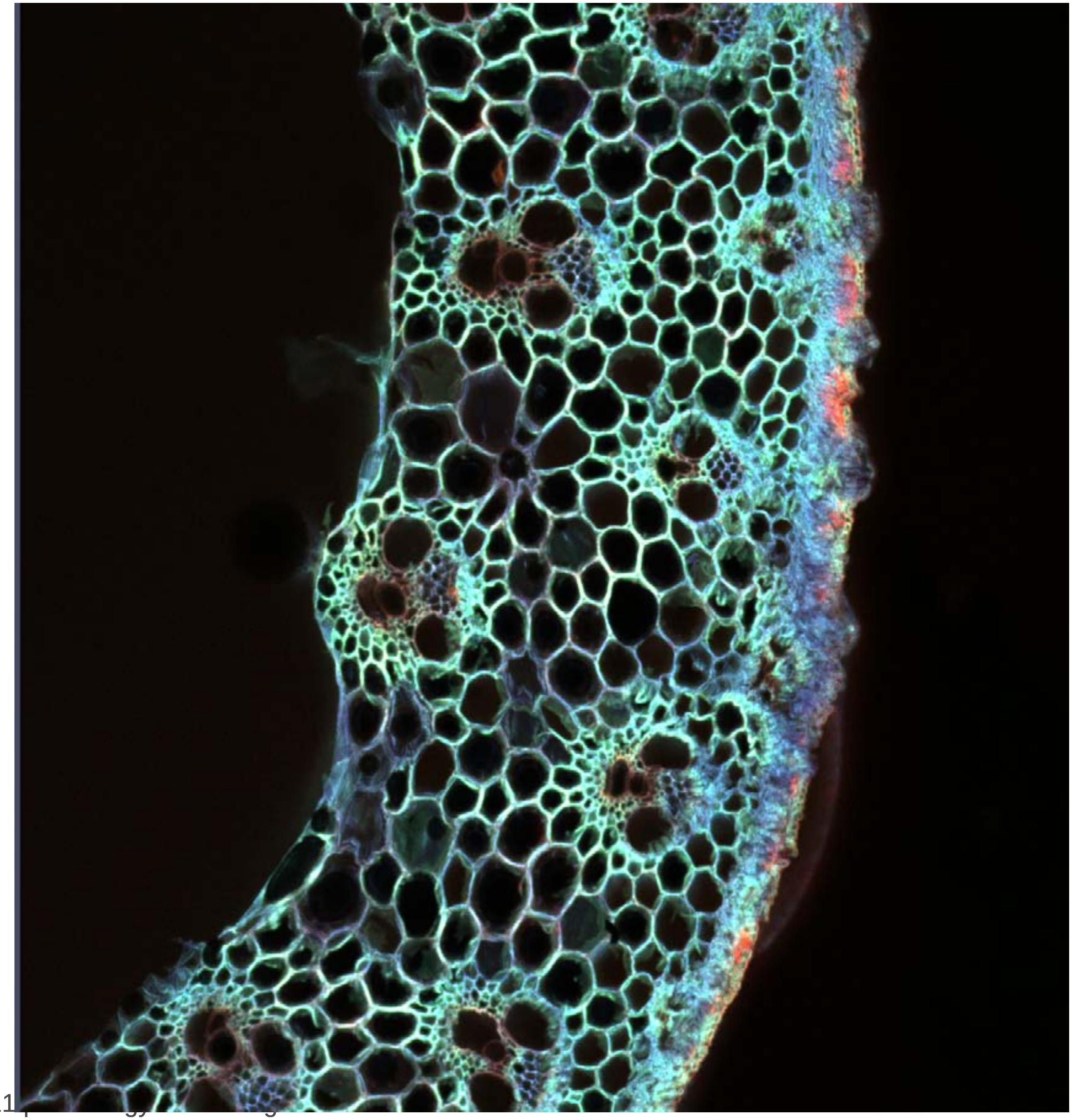
$PF_6^{\ominus}$ $NH(SO_2CF_3)_2^{\ominus}$ $RSO_4^{\ominus}$ $SCN^{\ominus}$ $CH_3SO_3^{\ominus}$ $Cl^{\ominus}$

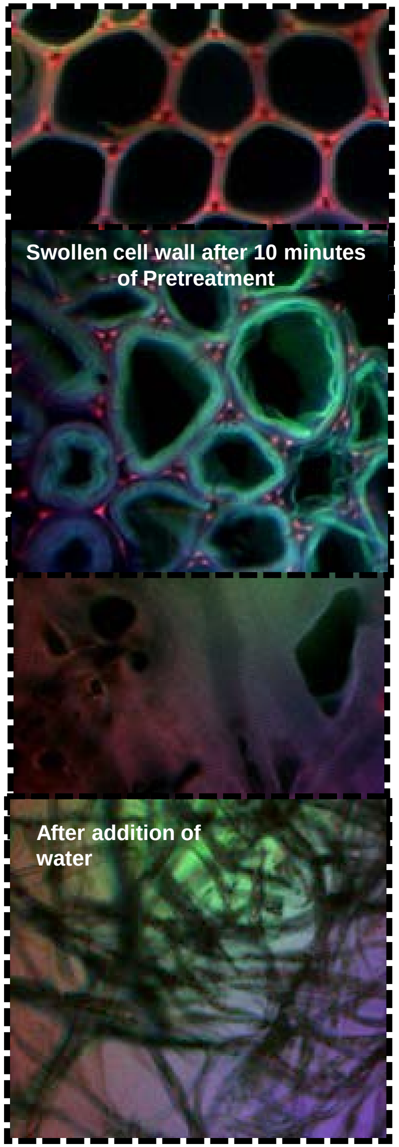
$CH_3CO_2^{\ominus}$



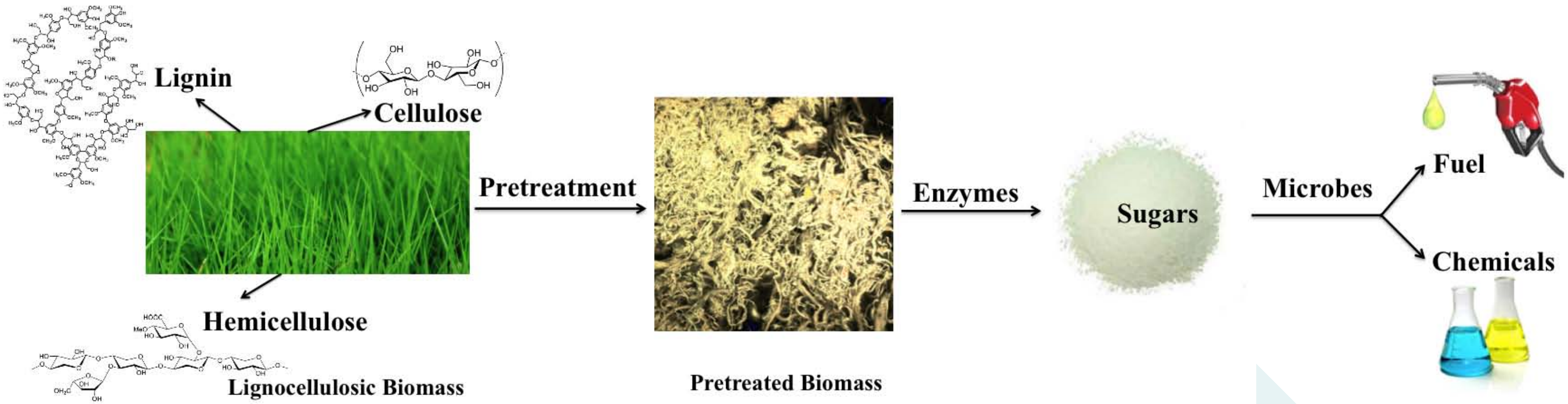
Anion determines:
- chemistry
- functionality

Feedstock Processing using Ionic Liquid





Starting Point (FY14): Comparison of Two Ionic Liquid Process Technologies



IL pretreatment
[C_2mim][OAc], @140°C, 3h, 10% TS)
→ IL separation & solid washing
→ Enzyme saccharification

IL pretreatment
([C_4mim]Cl @140°C, 2h, 10% TS)
→ No IL separation
→ One-pot acid hydrolysis

Comparison of Solids Recovered from Pretreated Feedstocks

Pretreatment using [C_2mim][OAc], @140ºC, 3h, 10% loading)

Corn Stover

72% solid recovery

Corn Stover/MSW mix

80% solid recovery

MSW

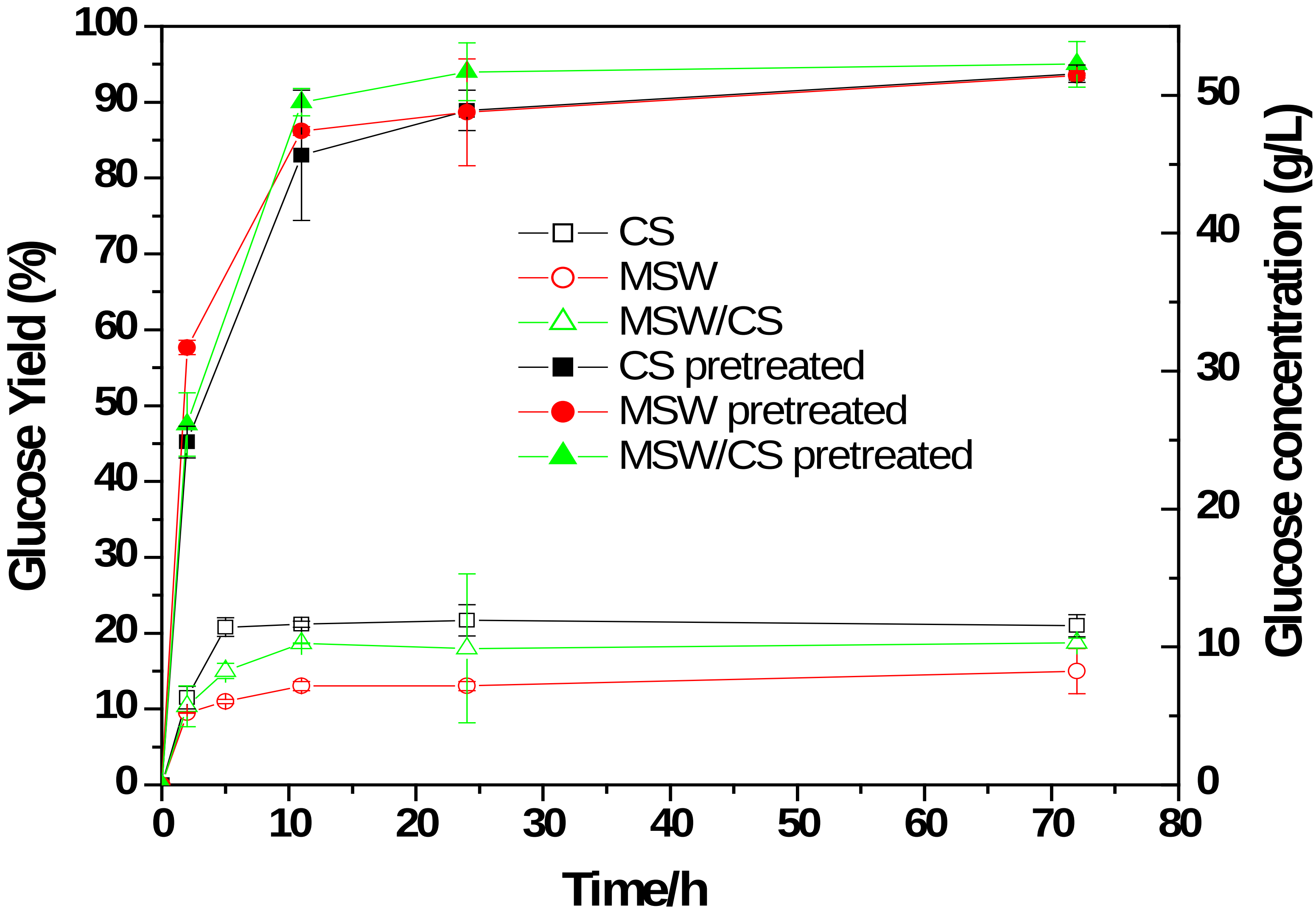
93% solid recovery

Composition of Pretreated Feedstock

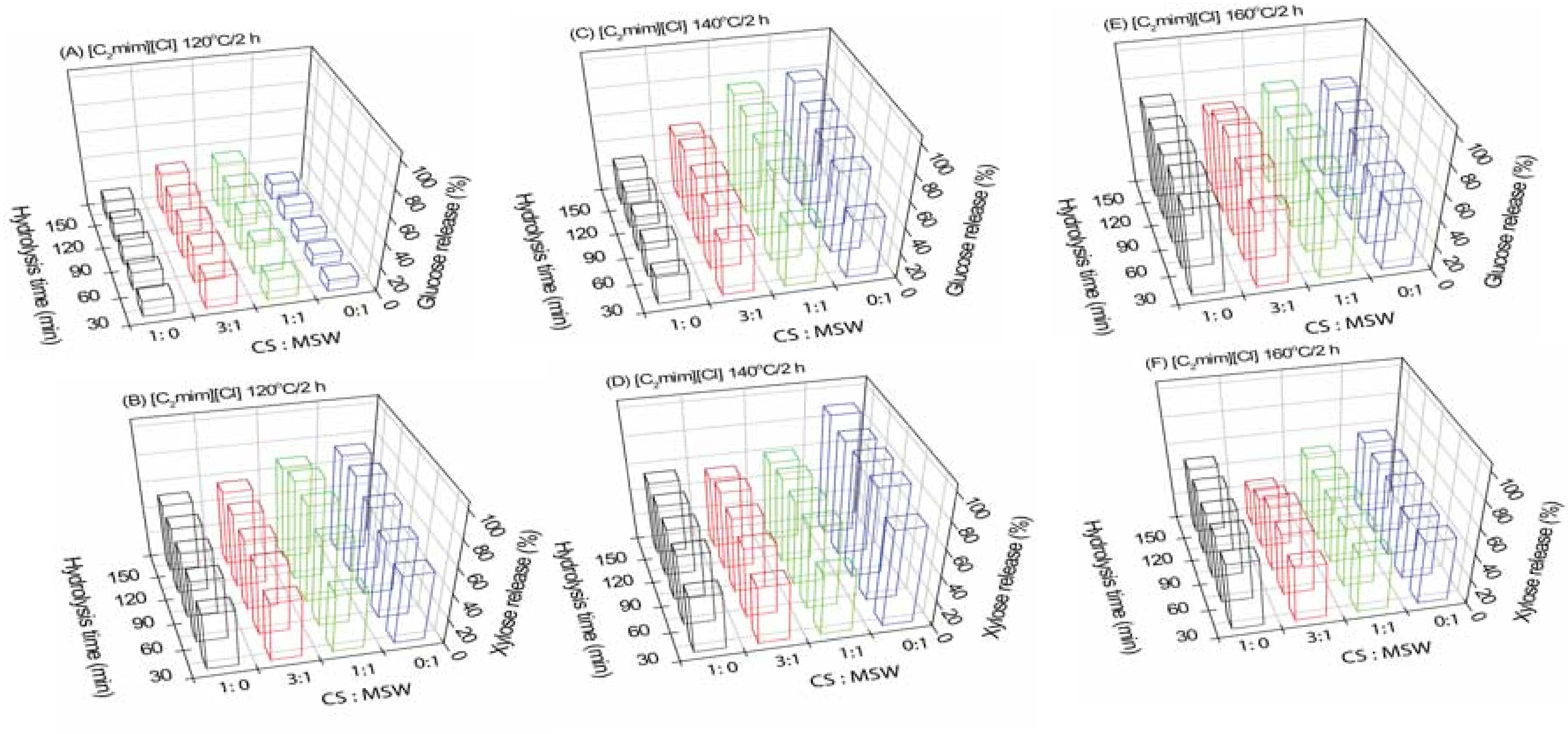
Feedstock		Moisture[b], %	Glucan, %	Xylan, %	Lignin[c], %	Ash[c], %
Corn stover	raw	11.0±0.9	33.2±1.0	20.8±0.04	18.7±1.5	11.9±0.3
	pretreated	87.1±0.3	40.7±4.0	26.2±2.2	5.7±0.8	9.6±0.5
MSW paper mix	raw	5.9±0.3	55.8±5.0	10.0±1.4	11.9±0.3	10.9±1.3
	pretreated	84.4±0.5	52.6±7.2	11.0±1.1	12.0±1.7	6.8±0.3
MSW/CS (1:4)	raw	6.7±0.4	45.5±3.1	17.0±1.0	16.0±0.6	7.5±0.5
	pretreated	85.2±0.1	52.5±6.4	15.3±0.4	8.6±1.2	7.6±0.6

[a] Values represent the average and standard deviation of each component on the basis of dry materials.
[b] Values based on the weight of material as-received for raw feedstock and wet samples for pretreated biomass.
[c] Klason (acid insoluble) lignin based on NREL LAPs.

Sugar Yields after Enzymatic Saccharification from MSW, MSW:Corn Stover, and Corn Stover are Comparable



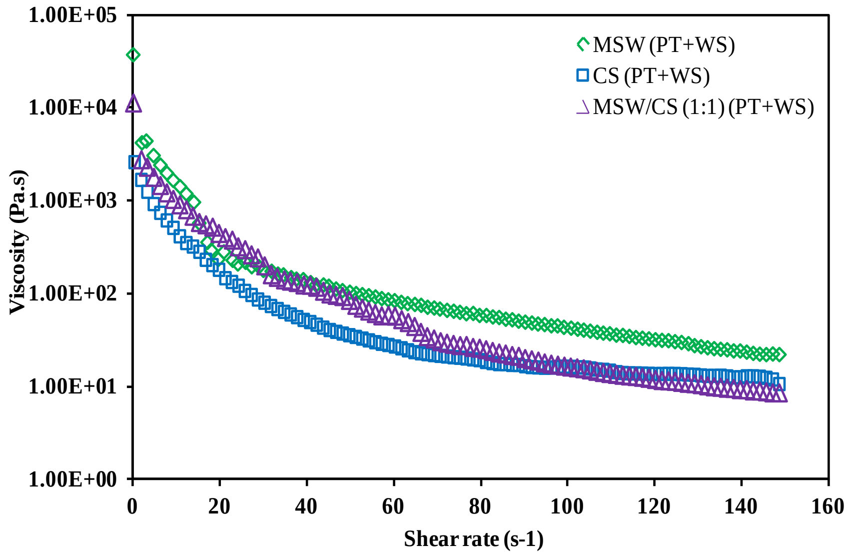
Acidolysis of MSW:CS Blends Generate High Sugar Yields



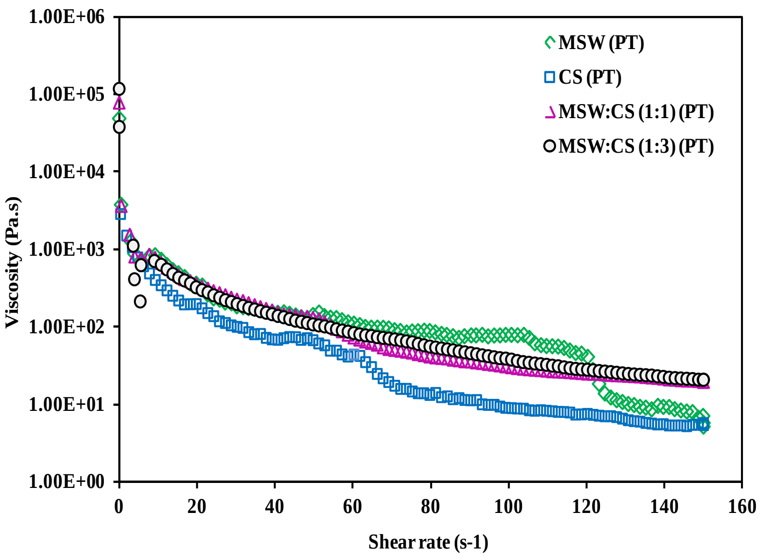
- ❖ **The highest glucose (80.6%) and xylose (90.8%) yields are obtained after pretreatment of MSW at 140 °C for 2 h.**
- ❖ **With more corn stover blended into the feedstock, higher temperature is preferred for glucose production while xylose yields dropped.**

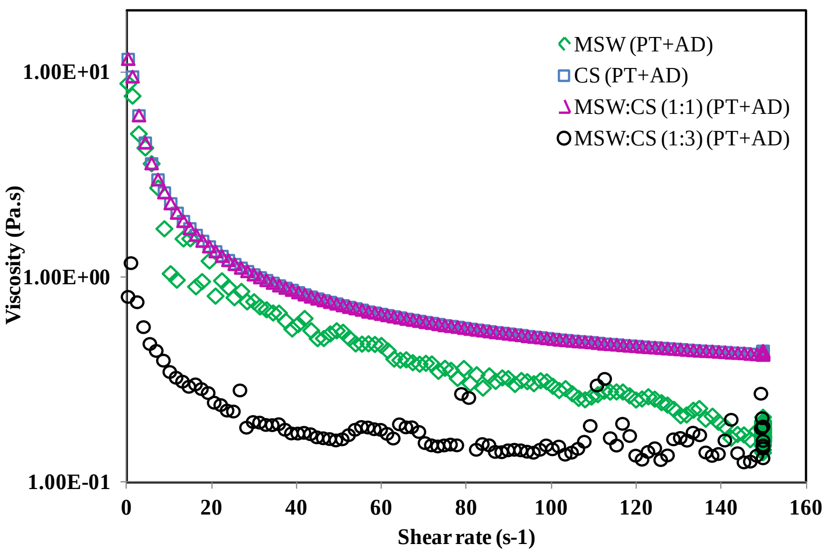
Tracking Viscosity Profiles of the MSW, CS and Blends after Pretreatment & Acidolysis

Enzymatic Process

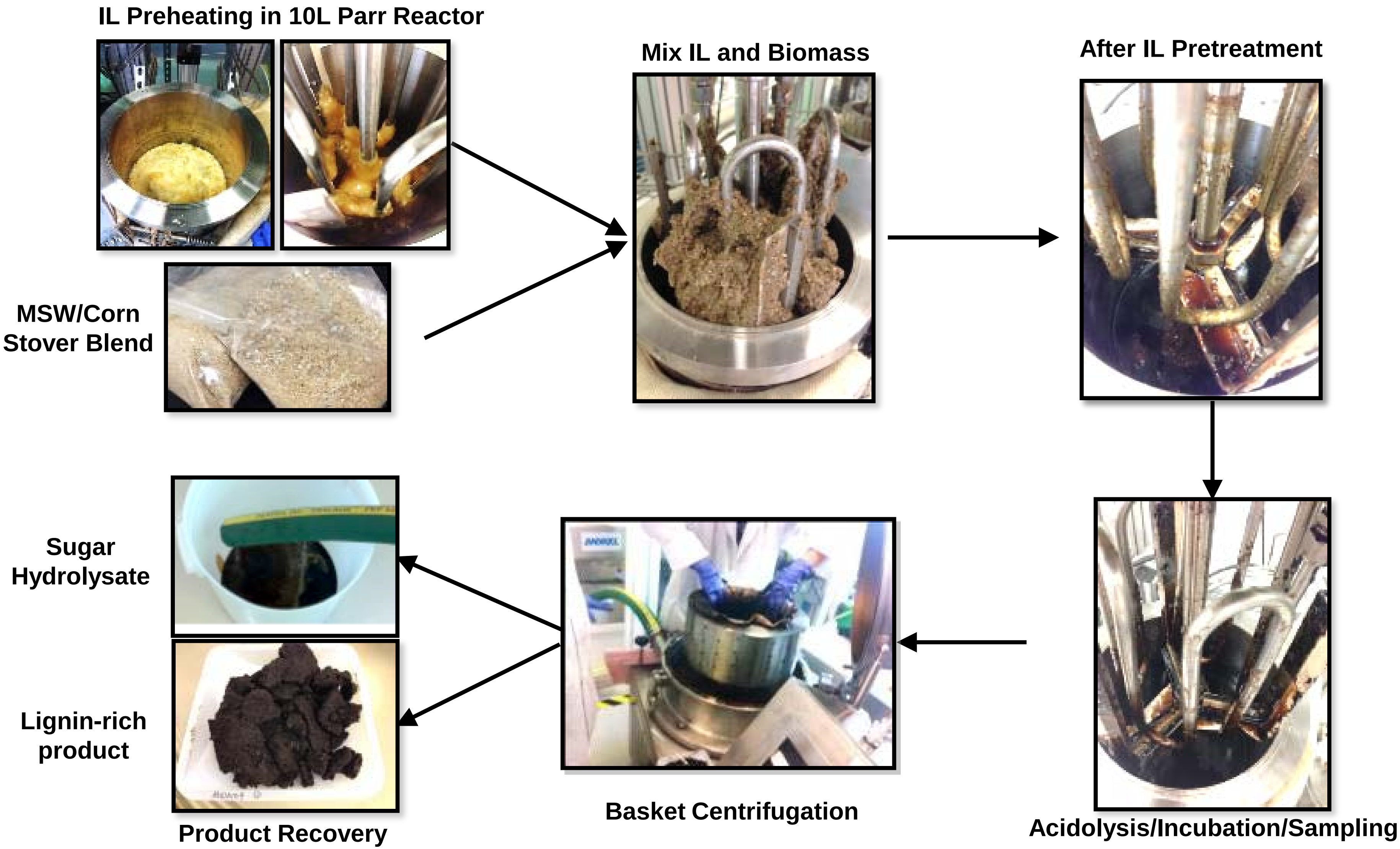


Acidolysis Process

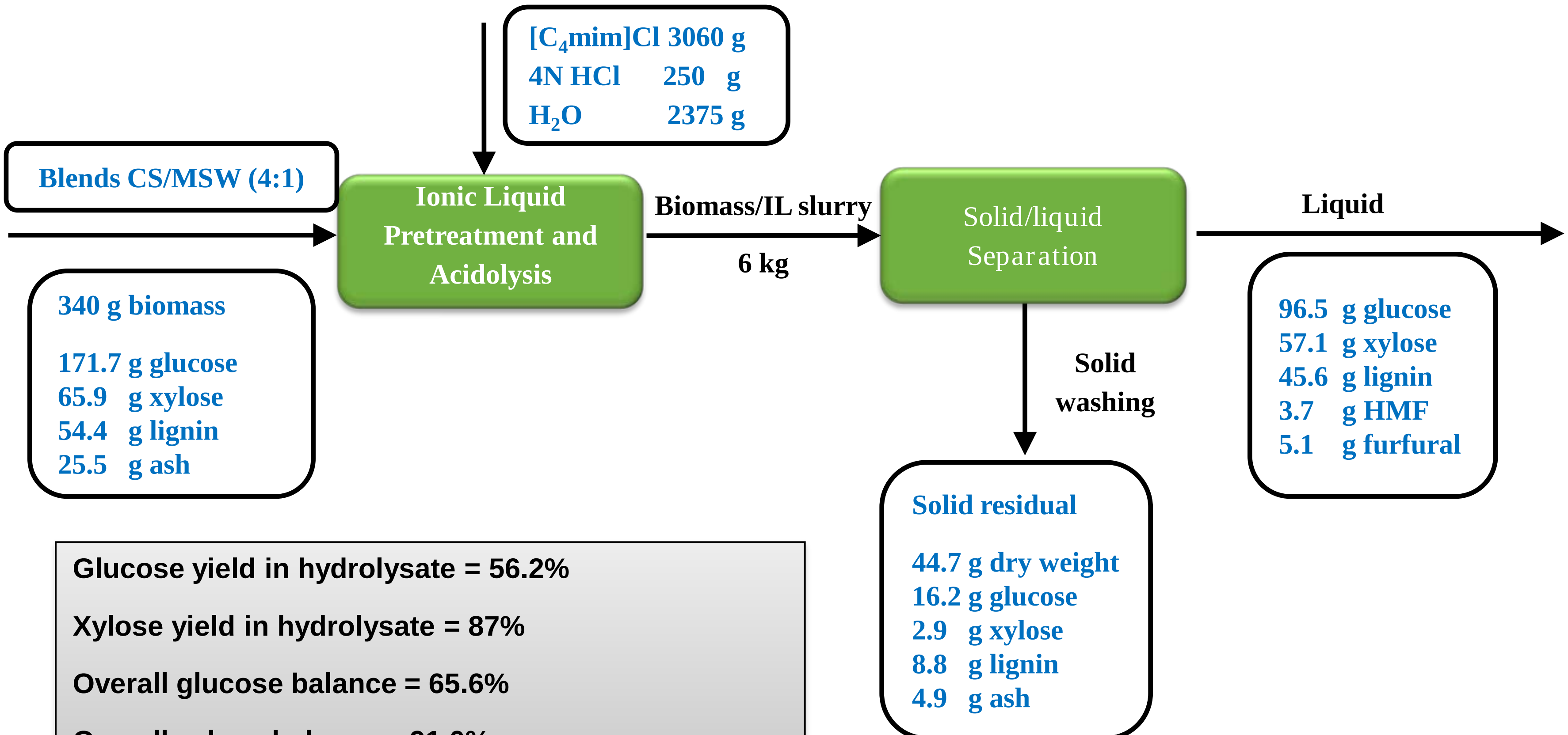




Next Step: Scale-up of Acidolysis Conversion of MSW:CS Blend



Mass Balance for the Scaled Up Acidolysis Conversion of MSW:CS Blend



Glucose yield in hydrolysate = 56.2%

Xylose yield in hydrolysate = 87%

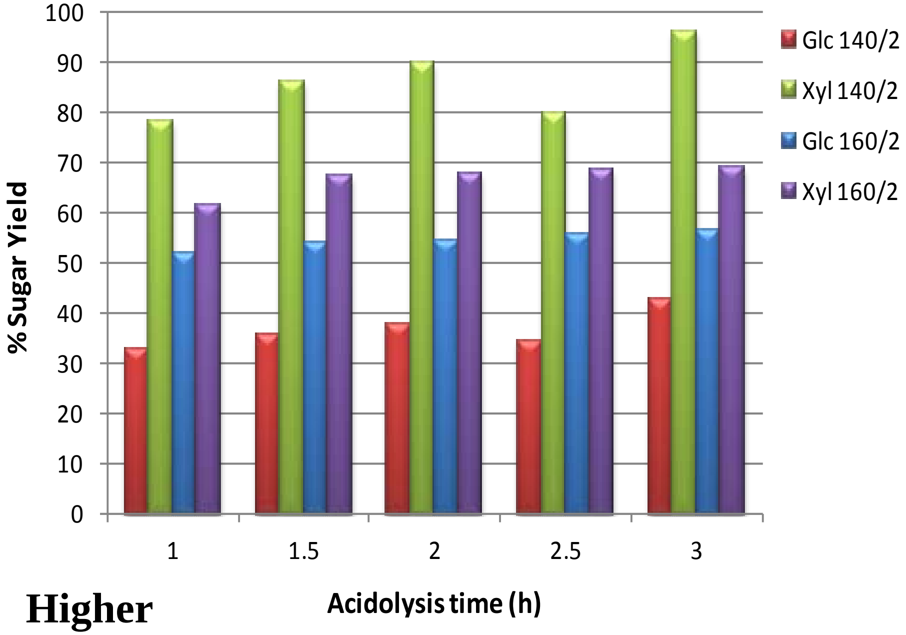
Overall glucose balance = 65.6%

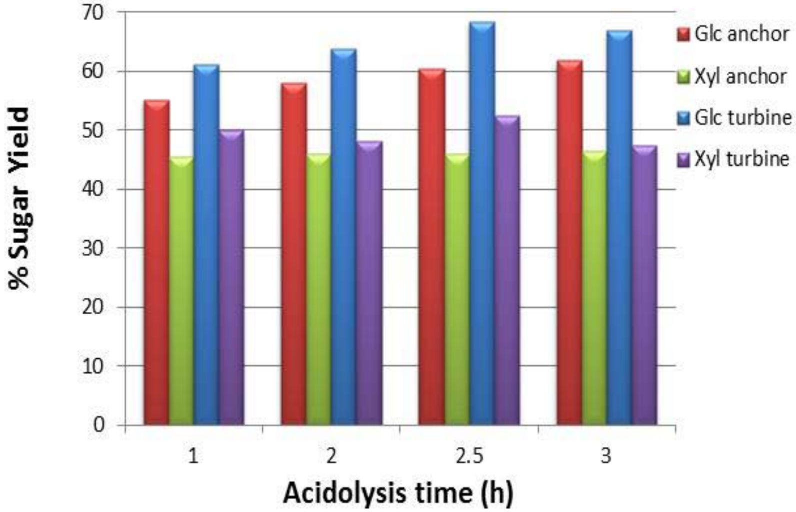
Overall xylose balance = 91.0%

Overall lignin recovery from solid stream = 16%

[C_4mim]Cl Pretreatment @140°C, 2h, 10% TS

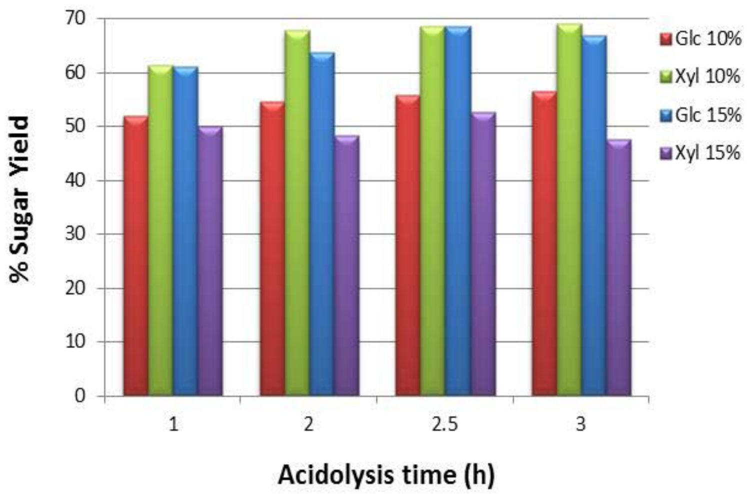
Process Optimization Improves Sugar Yields





Higher temperature results in increased glucose/decreased xylose yields.

Turbine impeller worked better



Under the tested conditions, 15% solid loadings results in higher glucose yield and lower xylose yields.

Publications

- Shi, J., V.S. Thompson, N.A. Yancey, V. Stavila, B.A. Simmons, and S. Singh. 2013. Impact of mixed feedstocks and feedstock densification on ionic liquid pretreatment efficiency, **Biofuels**, 4(1), 63-72.

- Ning Sun, Feng Xu, Noppadon Sathitsuksanoh, Vicki S Thompson, Kara Cafferty, Chenlin Li, Deepti Tanjore, Akash Narani, Todd R. Pray, Blake A. Simmons, Seema Singh, Blending Municipal Solid Waste with Corn Stover for Sugar Production Using Ionic Liquid Process, **Bioresource Technology**, accepted February 2015.

- Jian Shi, Kevin W. George, Ning Sun, Wei He, Chenlin Li, Vitalie Stavila, Jay D. Keasling, Taek Soon Lee, Blake A. Simmons, Seema Singh, Impact of pretreatment technologies on saccharification and isopentenol fermentation of mixed lignocellulosic feedstocks, **BioEnergy Rese**arch, accepted January 2015.

- Chenlin Li, Deepti Tanjore, Wei He, Jessica Wong, James L. Gardner, Vicki S. Thompson, Neal A Yancey, Kenneth Sale, Blake A. Simmons, Seema Singh, Scale-up of Ionic Liquid Based Fractionation of Single and Mixed Feedstocks, **BioEnergy Research**, accepted January 2015.

Presentations

•V. Thompson, A.E. Ray, N. Sun, S. Singh and B. Simmons, 2014. “Assessment of municipal solid waste as a blend feedstock to lower biomass feedstock costs”, Presented at 36th Annual meeting on Biotechnology for Fuels and Chemicals Symposium. Clearwater Beach, FL, April 28.

•Blake Simmons (invited) Renewable Ionic Liquids, 4th Asia-Pacific Conference on Ionic Liquids and Green Processes / 6th Australasian Symposium on Ionic Liquids, Sydney, Australia, September 30, 2014.

•Blake Simmons (invited) Driving the Future: Advanced Biofuels R&D at JBEI, NREL Biomass Seminar Series, NREL, Golden, CO, February 18, 2014.

•Blake A. Simmons (invited). Advances in Biomass Pretreatment at JBEI, Beijing University of Chemical Technology, Beijing, China, December 1, 2014

•Chenlin Li, Deepti Tanjore, Jessica Wong, James Gardner, Julio Baez, Kenneth Sale, Blake A. Simmons and Seema Singh. Scale-up of Ionic Liquid Based High Solid Biomass Deconstruction for Biofuels Production. Oral Presentation for 11th Annual World Congress on Industrial Biotechnology. May 12-15, 2014. Philadelphia, PA.

•Blake A. Simmons (invited) Ionic Liquid Pretreatment: Fundamental Science Enabling Process Engineering Tulane University Seminar Series in Engineering, New Orleans, LA, November 1, 2013.

•Chenlin Li, Deepti Tanjore, Wei He, Jessica Wong, James Gardner, Kenneth Sale, Blake A. Simmons and Seema Singh. Scale-Up Evaluation of Ionic Liquid Based Sugar Production at High Solid Loading. Oral Presentation. AICHE 2013 Annual Meeting. Nov 3-8, 2013, San Francisco, CA.

Future Work

- **Remainder of FY15**
  - Assess other MSW blends identified as meeting cost targets
  - Finalize scale-up process at ABPDU to improve sugar yields
  - Compile overall mass and energy balances, determine hydrolysate composition
  - If possible, screen hydrolysates from optimal blends and process on fermentation to determine any negative (or positive) impacts
- **Potential continuation project in FY16- Proposed R&D Scope**
  - Formulate and screen additional MSW blends with **other terrestrial feedstocks**, specifically **pulp and paper mill residuals and dedicated energy crops,** that meet the $80/ton cost targets
  - **Evaluate renewable, low cost ionic liquids**
  - Carry out **fermentation screens** to **determine impact of inhibitors**
  - Down-select to one conversion pathway based on overall performance and cost **(TEM comparison with NREL 2017 baseline model**) at month 18
  - Optimize and **scale-up selected process to 100L pretreatment** and **300L fermentation**
  - **Focus on biochemical hydrocarbon pathway**

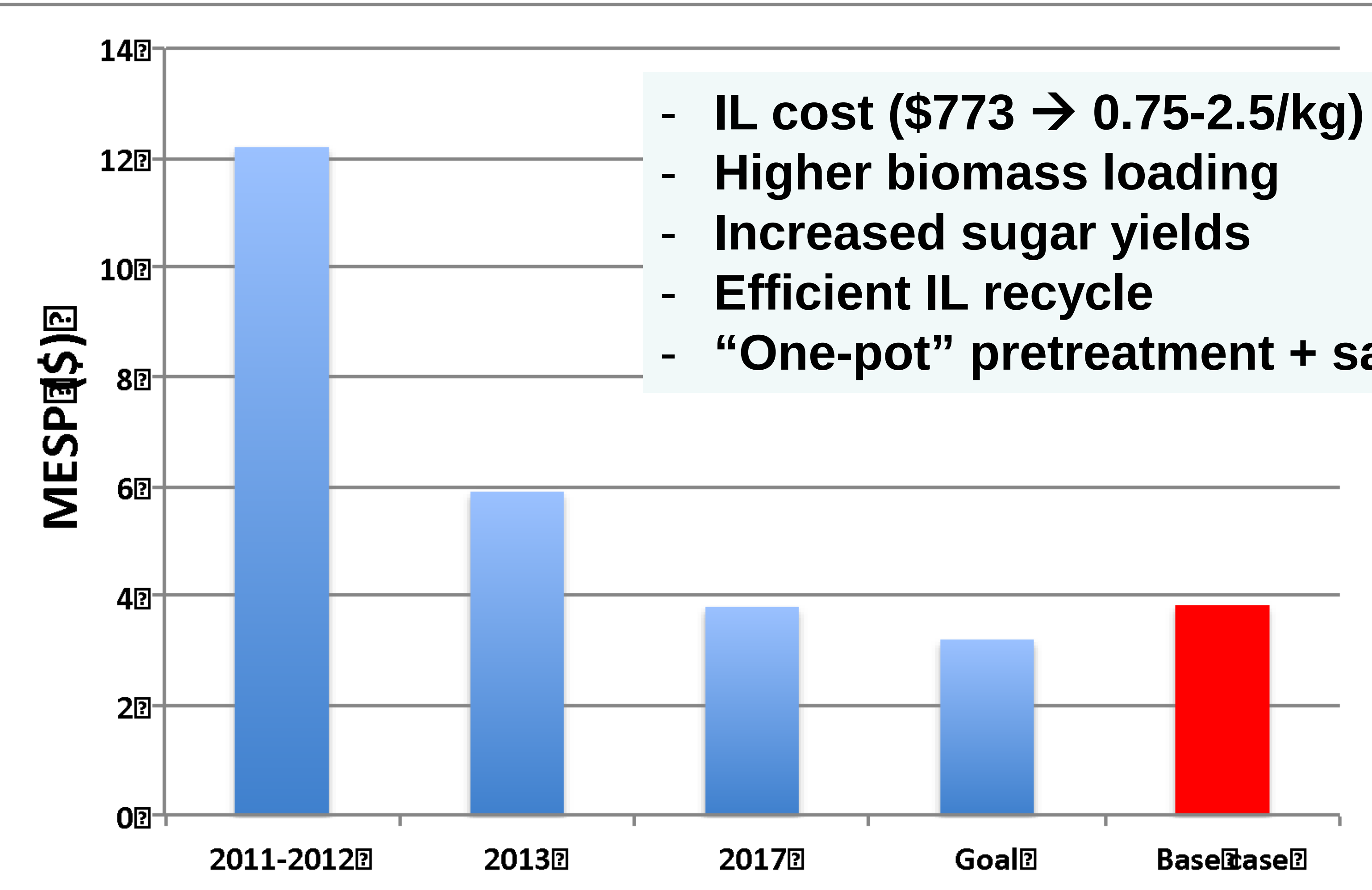
Summary

- Project has met all milestones
- MSW is a growing interest in both the feedstocks and conversion platforms within BETO and the world
- There is a need to understand the impact of these blends on process performance and potential negative impacts on downstream unit operations
- MSW blends must meet cost and performance criteria
- Acidolysis is an approach that can eliminate the need for enzymes altogether, but must be evaluated on an even basis with more mature conversion technologies

Additional Slides

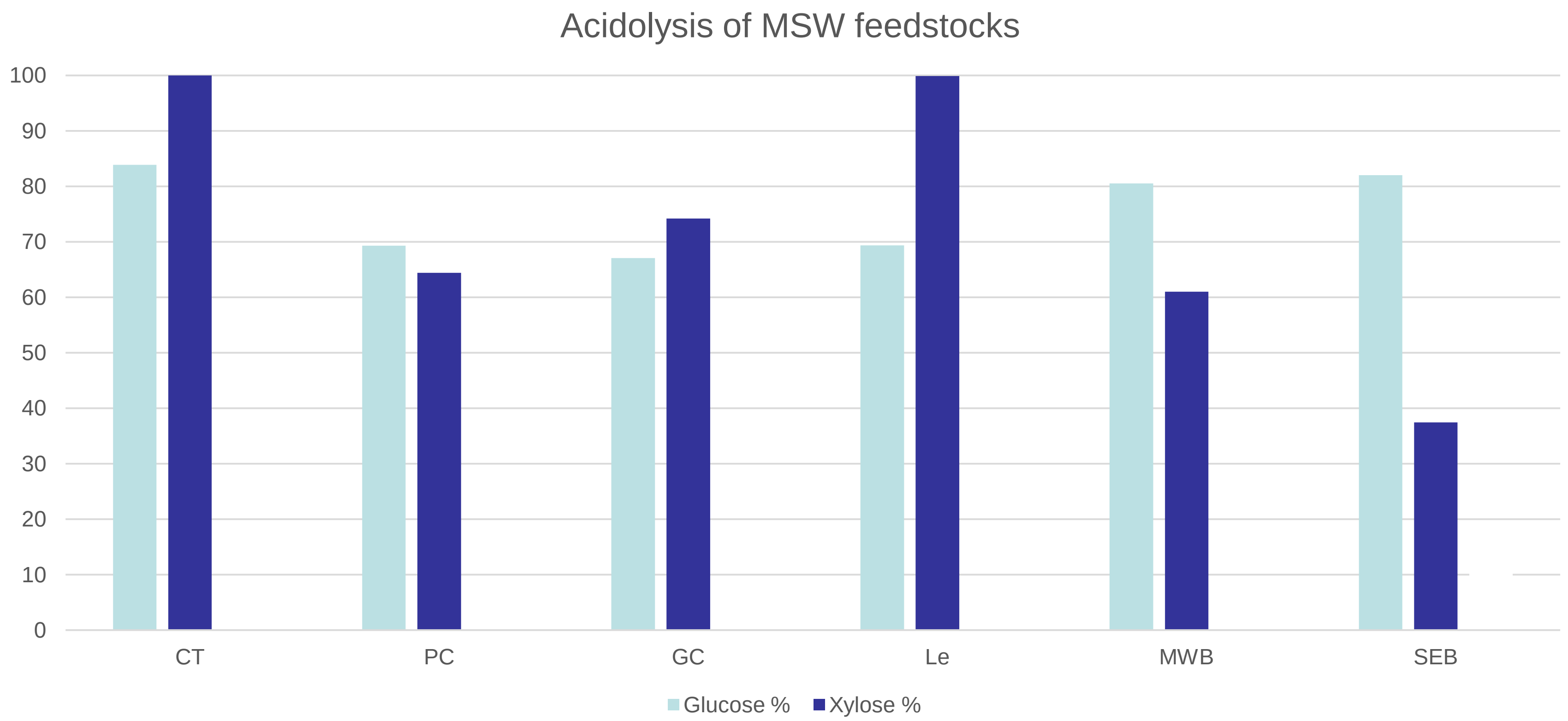
Benchmarking Impact - Economics

Conventional IL Process: Pretreatment + Enzymes



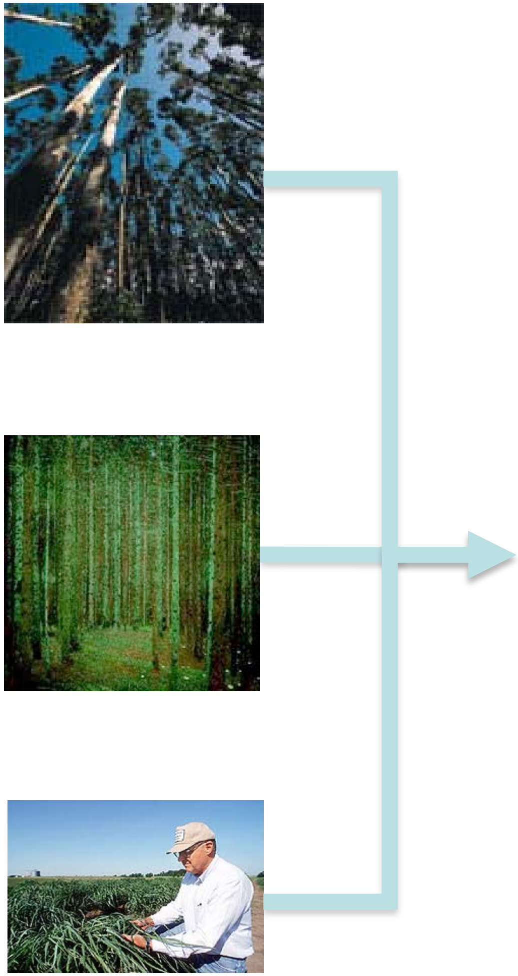
- IL cost ($773 → 0.75-2.5/kg)
- Higher biomass loading
- Increased sugar yields
- Efficient IL recycle
- “One-pot” pretreatment + saccharification

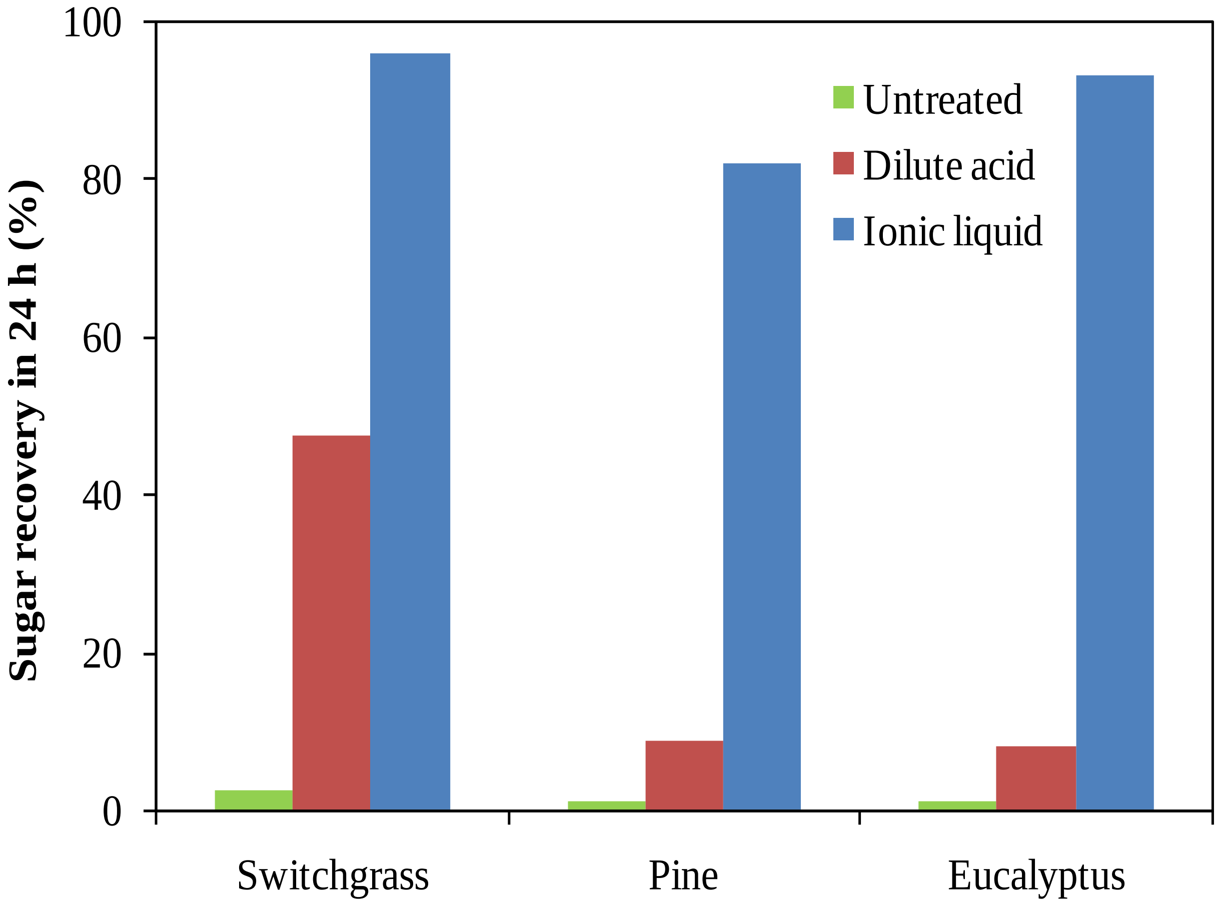
Sugar yield from yard wastes and construction waste



Acidolysis of yard wastes (CT: Christmas tree; PC: Pine cone; GC: Grass clippings; Le: Leaves), Midwest blends and Southeast blends. (Pretreatment: 160 C, 2h, [C_2mim]Cl, 10% biomass loading)

Ionic Liquid Pretreatment is Feedstock Agnostic





Relevance

- MSW is a growing interest in both the feedstocks and conversion platforms within BETO and the world
- There is a need to understand the impact of these blends on process performance and potential negative impacts on downstream unit operations
- MSW blends must meet cost and performance criteria
- Acidolysis is an approach that can eliminate the need for enzymes altogether, but must be evaluated on an even basis with more mature conversion technologies
- Key stakeholders: BETO, industry (e.g., Hyrax, Virdia)
- Cost, performance, and scale-up results generated will help build the business case and enable tech transfer

MSW Blend Matrix Tested

Feedstocks	Ratio	Pret Temp, C	Ionic liquids	Mass loading, %	Glucose yield, %	Xylose yield, %
MSW paper mix (MSWpm)	1	160, 140, 120	[C2mim][Cl]	15%	80.6	90.8
Corn stover (CS)	1	160, 140, 120	[C2mim][Cl]	15%	69.6	52.9
MSWpm/CS	1:1	160, 140, 120	[C2mim][Cl]	15%	79.4	64.1
	1:3	160, 140, 120	[C2mim][Cl]	15%	77.1	51.2
	1:4	160, 140	C2/C4 [Cl]	10%	74.7	94.1
Christmas tree	1	160	[C2mim][Cl]	10%	83.87	97.30
Pine cone	1	160	[C2mim][Cl]	10%	69.33	64.43
Grass clippings	1	160	[C2mim][Cl]	10%	67.05	74.19
leaves	1	160	[C2mim][Cl]	10%	69.39	99.89
Midwest blends	1	160	[C2mim][Cl]	10%	80.53	60.99
Southeast blends	1	160	[C2mim][Cl]	10%	82.04	37.47