U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Development and Process Intensification of Ionic Liquid based Lignocellulosic Conversion Process

March 9th, 2017
Feedstock Conversion Interface Consortium

Seema Singh (PI)
Sandia National Laboratories, Livermore-CA

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Goal Statement

Goal: Examine municipal solid waste (MSW) blends to reduce the feedstock cost and develop promising ionic liquid (IL) based conversion processes to enable high yields of fermentable sugar and bio-based products.

Outcome: Demonstrated economically viable, scalable, efficient conversion processes for biomass fractionation and conversion into fuels and chemicals.

Relevance to BETO:

Directly supports BETO's goal: "Develop commercial viable technologies for converting biomass feedstocks via biological and chemical routes into energy dense, fungible, finished liquid transportation fuels"

Address BTEO's Office Multi-Year Milestone for Feedstocks Supply and Logistics "By 2017, validate efficient, low-cost, and sustainable feedstock supply and logistics systems"

Contribute to 2022 cost targets in biological conversion (supply 285 million dry tons per year to support a biorefining industry).

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Quad Chart Overview

Timeline

Start date: October 1, 2015
End date: September 30, 2017
Percent complete: 65%

Budget

	FY 15 Costs	FY 16 Costs	Total Planned Funding
DOE Funded	$270K	$245K	$764K

Barriers

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

Partners

- Sandia National Laboratories (Seema Singh) 44%
- Idaho National Laboratory (Vicki Thompson) 18%
- Lawrence Berkeley National Laboratory (Ning Sun) 38%

Project Overview

- **Project history**
  - Project started in FY14 as a “seed” AOP between SNL, INL, and LBNL-ABPDU
  - Achieved major milestone in FY14-16 using MSW paper fraction
  - New scope developed in Q1 FY 17 with focus shifted from feedstock blending and conversion to IL process development and intensification
  - Currently on pause
- **Project objective**
  - Identify MSW blends that meet feedstock cost targets.
  - Achieve high yields of fermentable sugars and fuels through the ionic liquid (IL) based process
  - Process scale-up and optimization at the ABPDU
  - TEA based on the scale-up data
- **Team scope**
  - **INL**: Formulate, supply and characterize the MSW blends with the guidance of feedstock cost
  - **SNL**: Develop IL conversion technology, test blends through selected IL-based process, test conversion and fermentability
  - **LBNL**: Process scale-up and optimization, TEA

Approach (Management)

INL
- Formulate MSW blends
- Blends cost

SNL
- Selection of IL process
- Lab scale screening

LBNL
- Process scale-up
- TEA

- Use quarterly milestones to track progress and down-select options
- Phone calls every 3 weeks, site visits once per FY
- Contributions from all partners in managing the project and tracking progress

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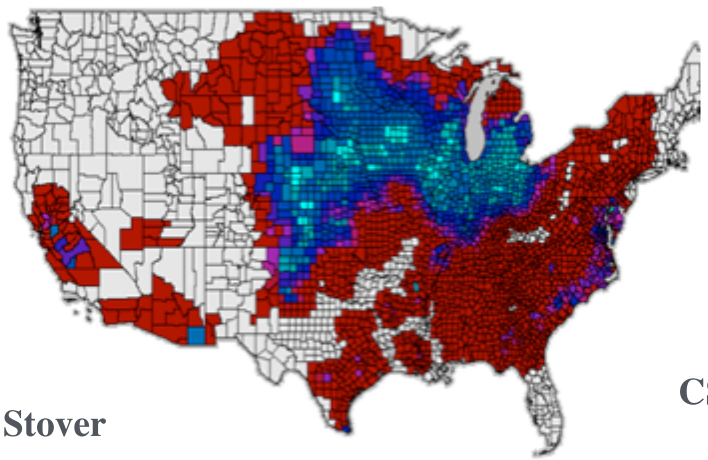
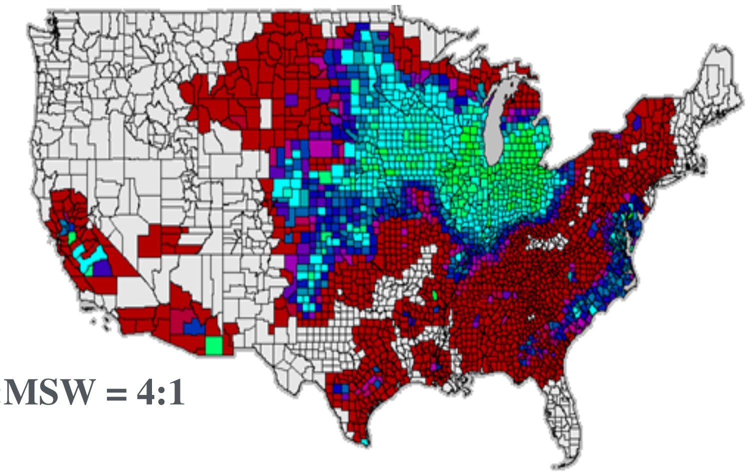
Least Cost Formulation Output for Midwest Corn Stover and MSW Blend

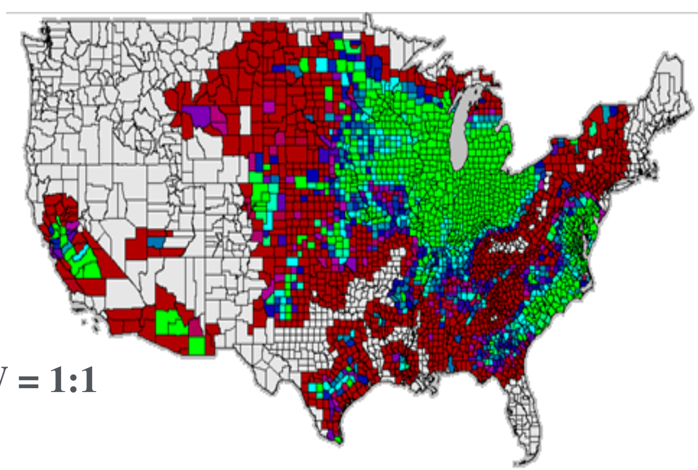
Delivered Feedstock Costs



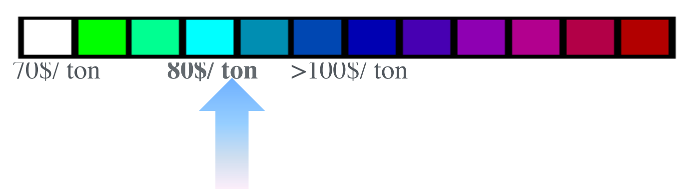
Corn Stover



CS:MSW = 4:1



CS:MSW = 1:1

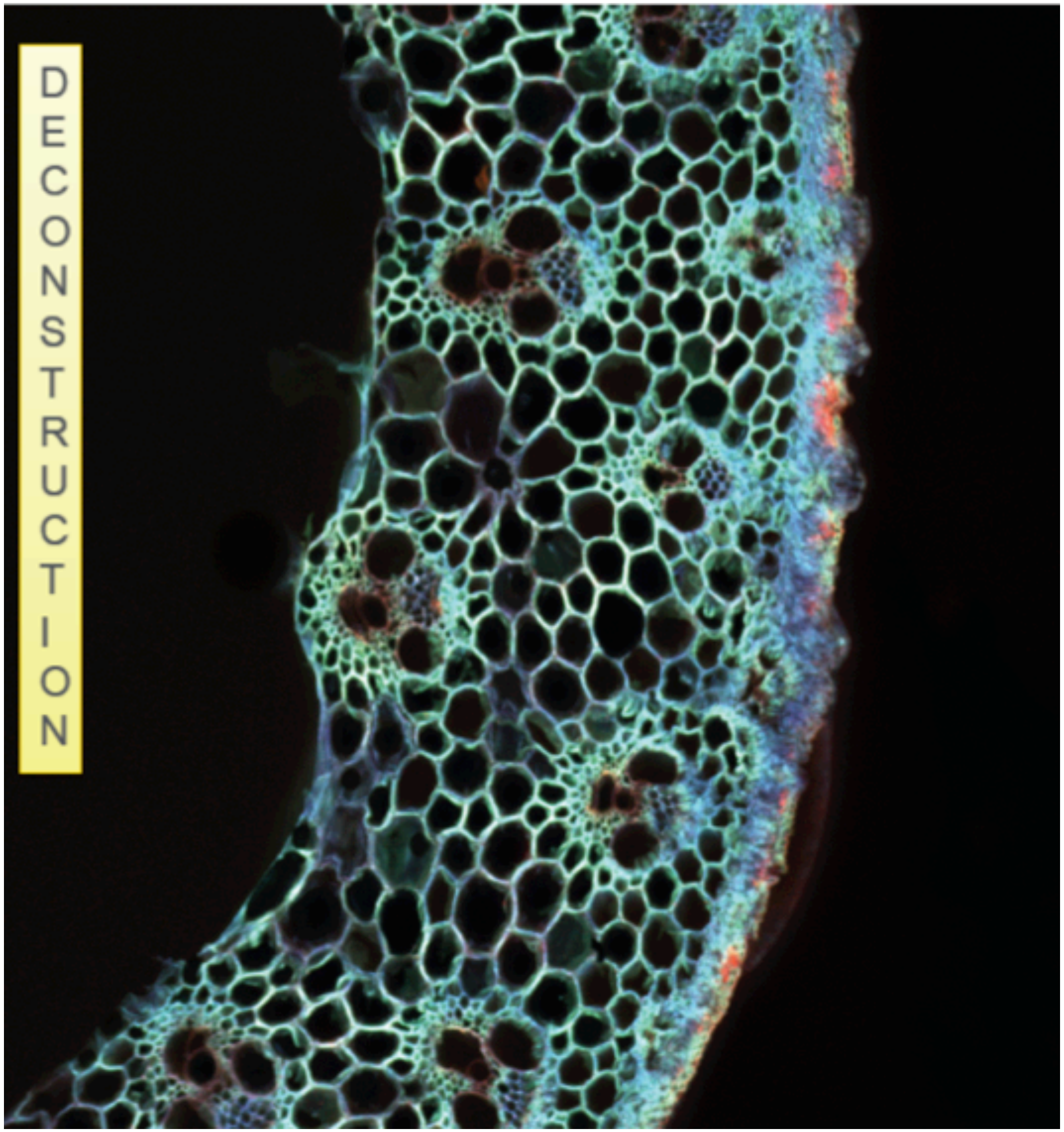


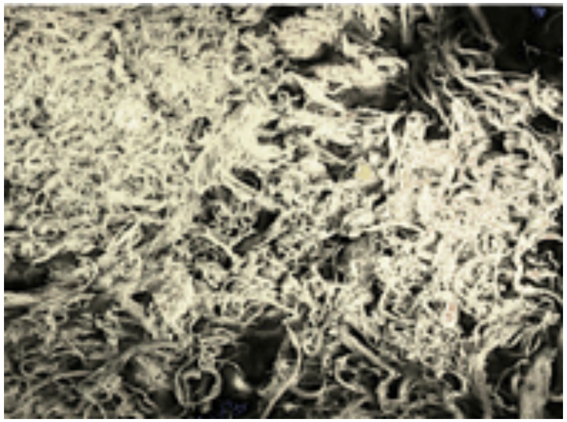
Designer Solvent for Biomass Deconstruction

Green Solvent:
- Compounds consist of ions (salt)
- Melting point below 100 °C
- Good thermal stability
- Negligible vapor pressure
- Non-flammable

IL Process Advantages:
- ✧ **>** 90% Sugar yield
- ✧ Fast saccharification kinetics
- ✧ Feedstock agnostic
- ✧ Designer solvent- task specificity
- ✧ Process consolidation
- ✧ Can be made cheap

Ionic liquids show excellent solvation properties & enable fractionation





Pretreated biomass that are readily hydrolyzed

LMW Lignin stream for upgrading

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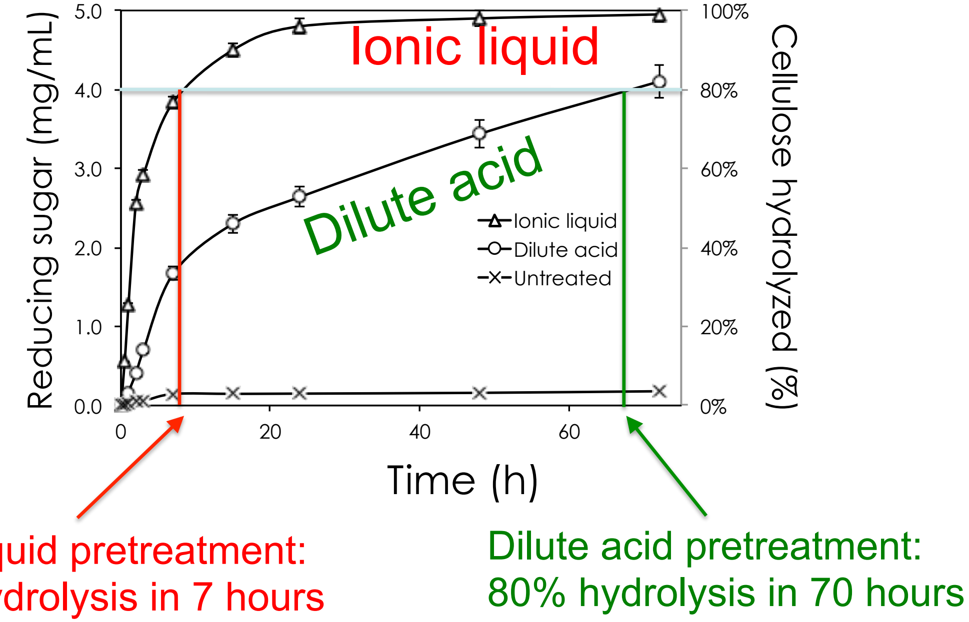
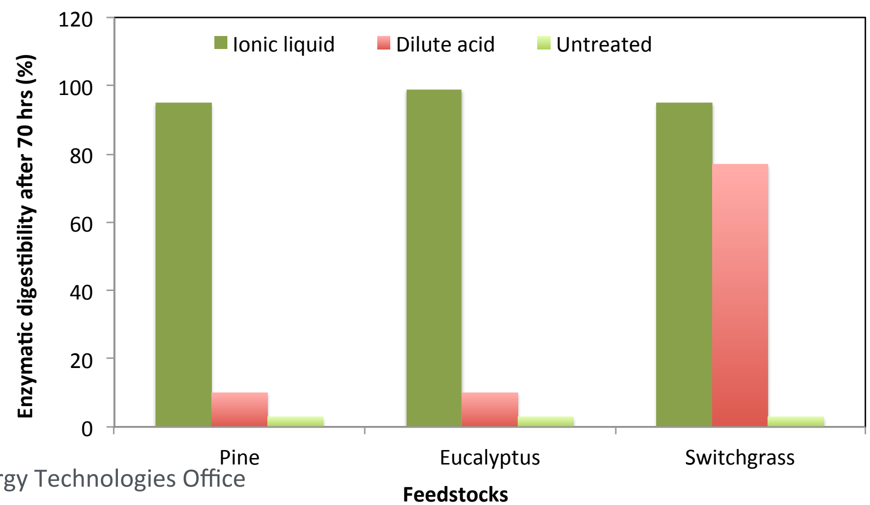
Ionic Liquid Conversion Processes are Efficient & Feedstock Agnostic





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LCF provided MSW Formulations that meet feedstock cost target

No.	Corn stover	Switchgrass	Grass clippings	MSW	Abbr.
1	90		10		CG9:1
2	80		20		CG8:2
3	70		30		CG7:3
4	60		40		CG6:4
5		90	10		SG9:1
6		80	20		SG8:2
7		70	30		SG7:3
8		60	40		SG6:4
9	90	10			CS9:1
10	80	20			CS8:2
11	90			10	CM9:1
12	80			20	CM8:2
13	70			30	CM7:3
14		90		10	SM9:1
15		80		20	SM8:2
16		70		30	SM7:3

MSW: The non-recyclable paper consisted of aseptic and polycoat containers and packaging, food soiled paper, shredded paper and waxed or coated papers and cardboard.

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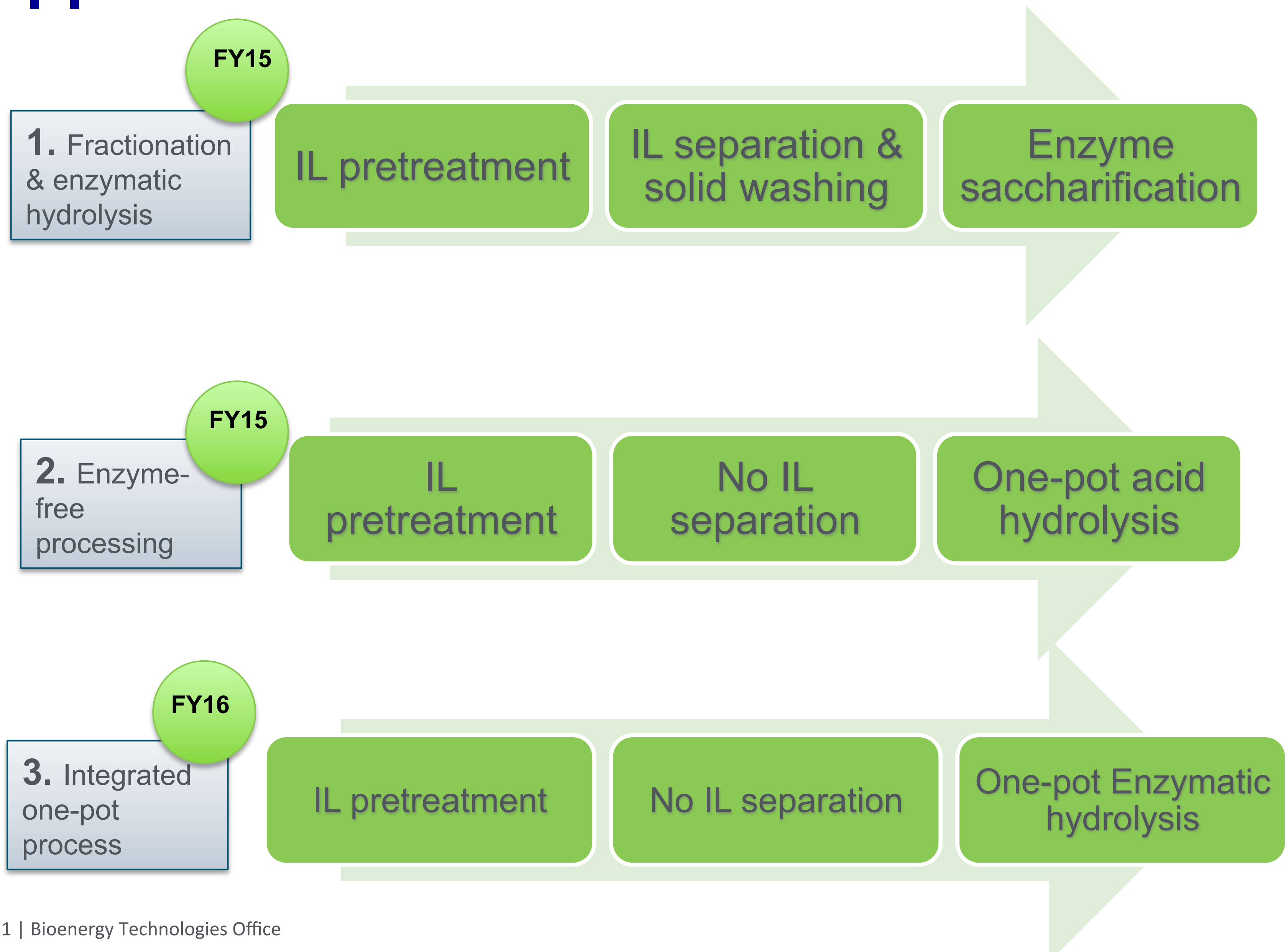
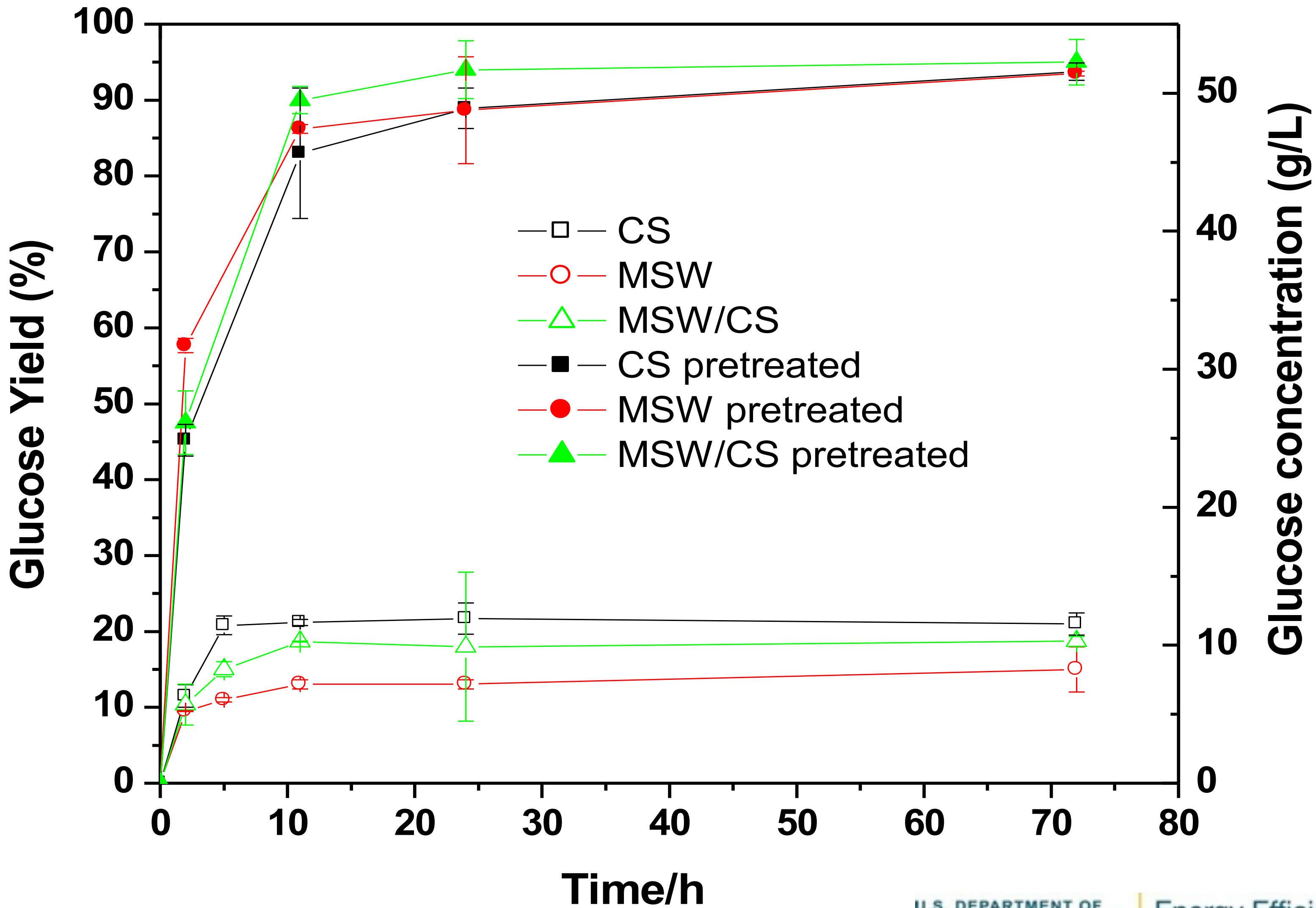
Investigated various IL conversion approaches



Sugar Yield from MSW and MSW:Cornstover Blend Comparable with Cornstover



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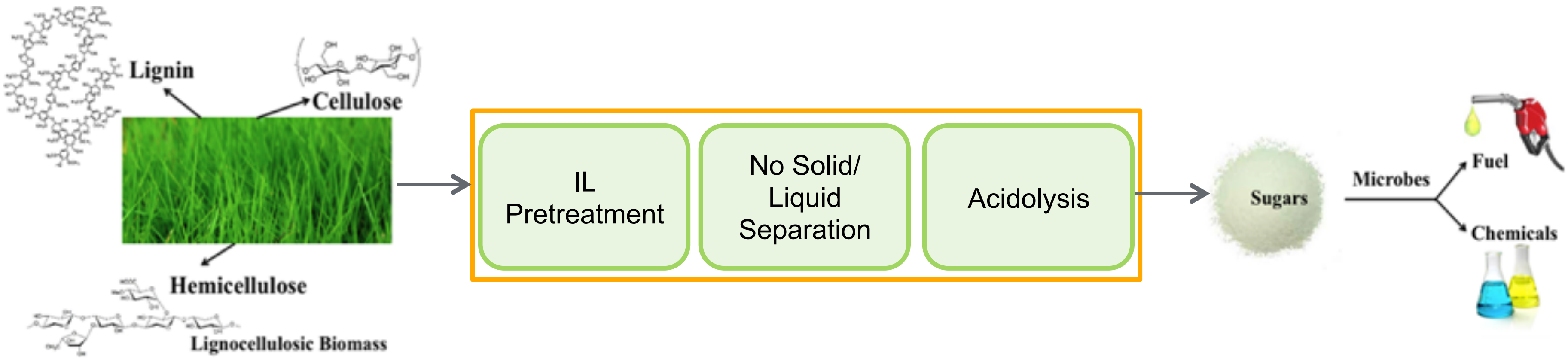
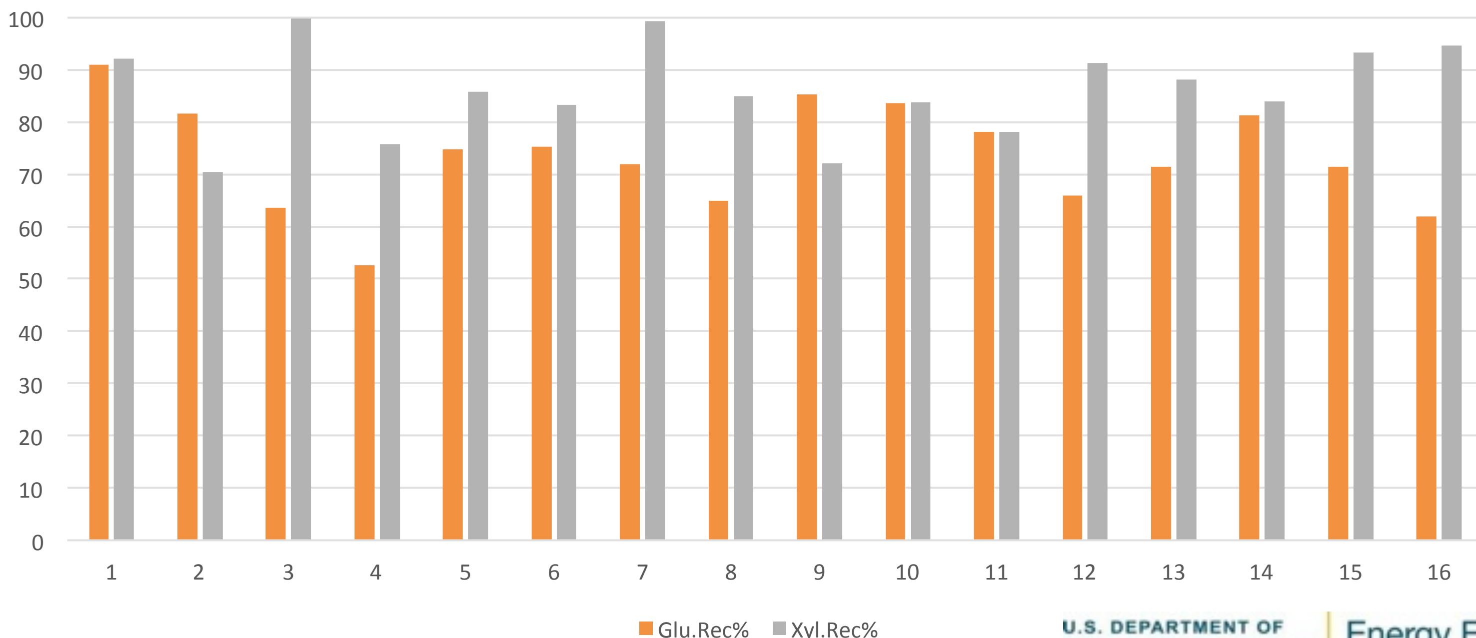
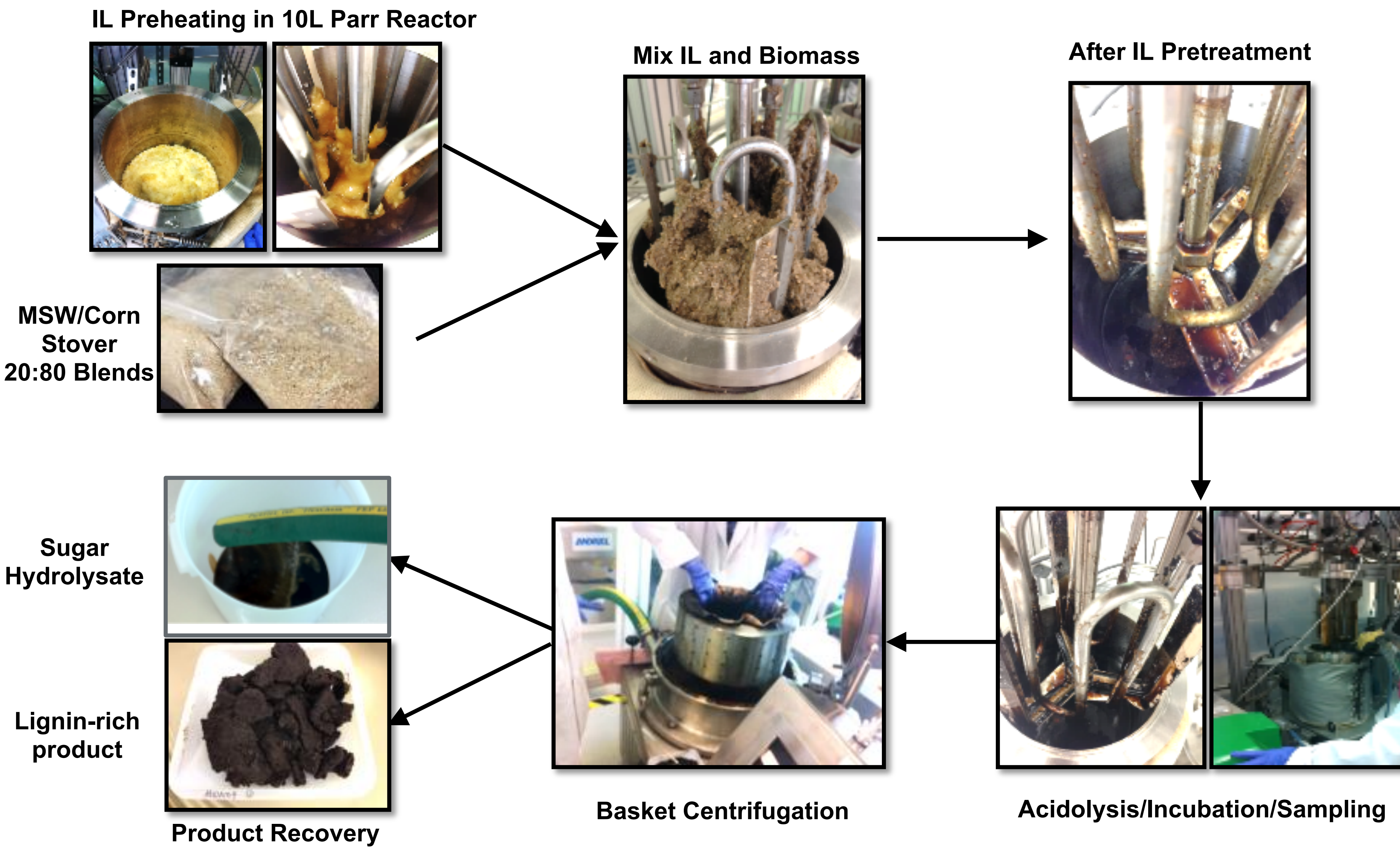
MSW conversion using IL Technology (Enzyme-free)



Sugar yield after pretreatment at 160ºC 2h, [C_2mim]Cl)



IL Process (Enzyme-free Acidolysis) successfully scaled up to 10 L and sugar yields comparable with bench scale



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Findings from the acidolysis and enzymatic pretreatment-hydrolysis conversion approaches

- Demonstrated potential of MSW as a feedstock blend for biorefinery while maintaining sufficient performance and low feedstock cost
- MSW blending increases solid recovery after pretreatment
- Mass balance analysis show MSW to yield most glucan and xylan
- Acidolysis of MSW Blends yield comparable sugar as enzymatic hydrolysis process
- MSW blending reduced process severity
- MSW blending slightly increases the viscosity of the pretreated slurry

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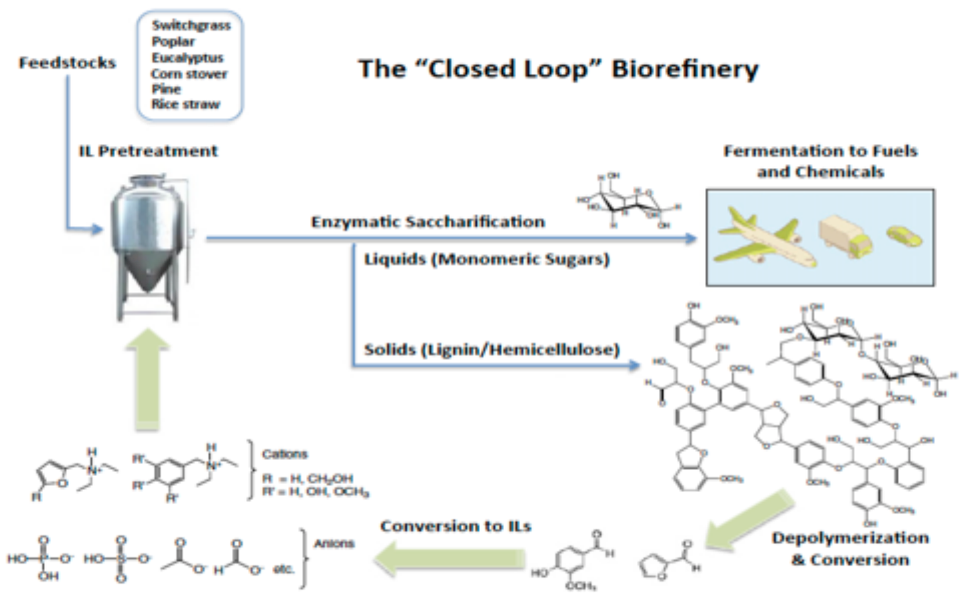
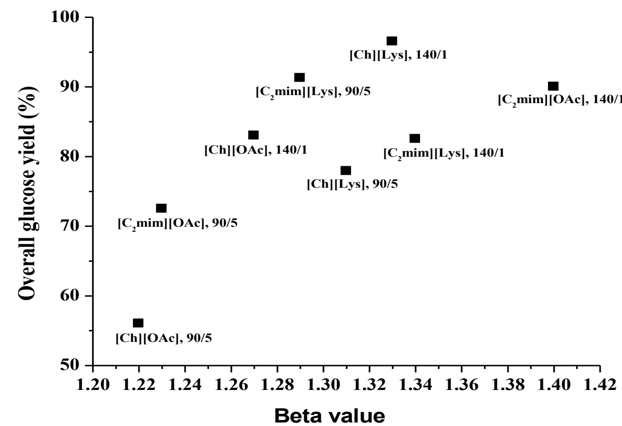
Bionic Liquids: A New Class of Promising Bio-Derived Ionic Liquids





- Lignin derived ILs
- Amino-acid based ILs
- *In-Planta* production of IL

Go/no-go decisions and path forward

- Successfully scaled up enzyme-free acidolysis process

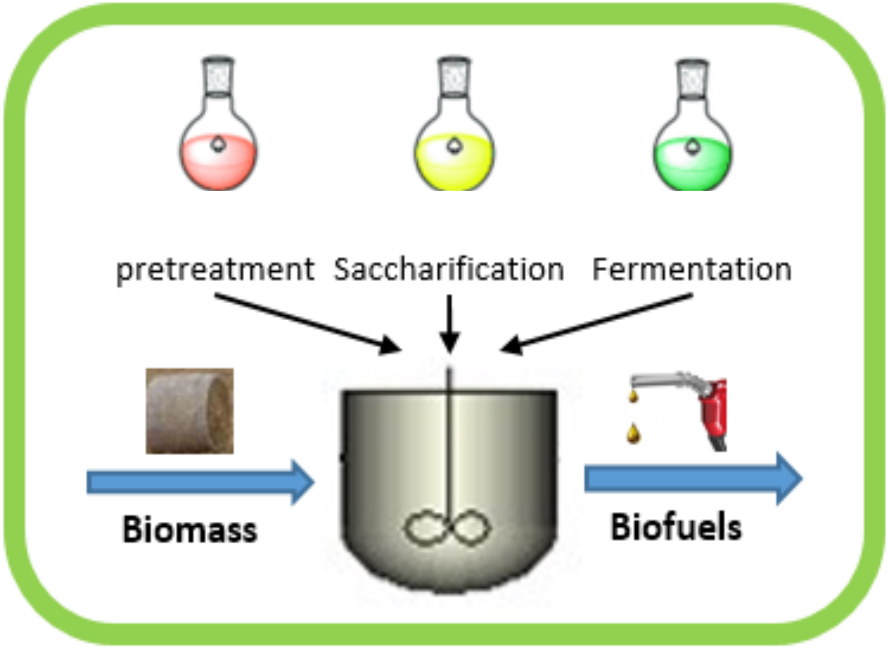
Next step: collaborate on Sep'n Consortia for IL recycle options (sugar extraction platforms).

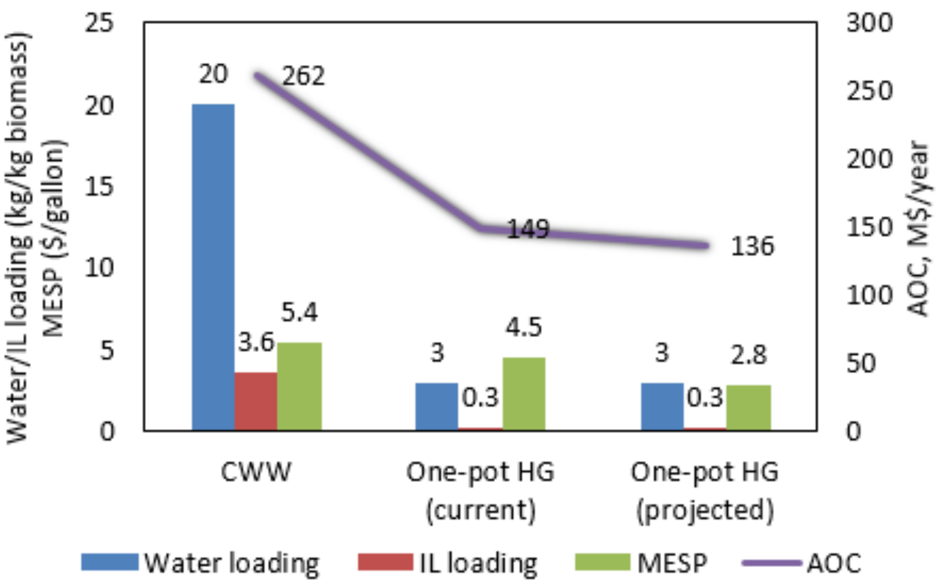
- Enzymatic process

Next steps:

1. Reduce water usage
2. Try bionic Liquids
3. IL recycle on Sep'n Consortia
4. TEA

Demonstrated one-pot process using Bionic IL

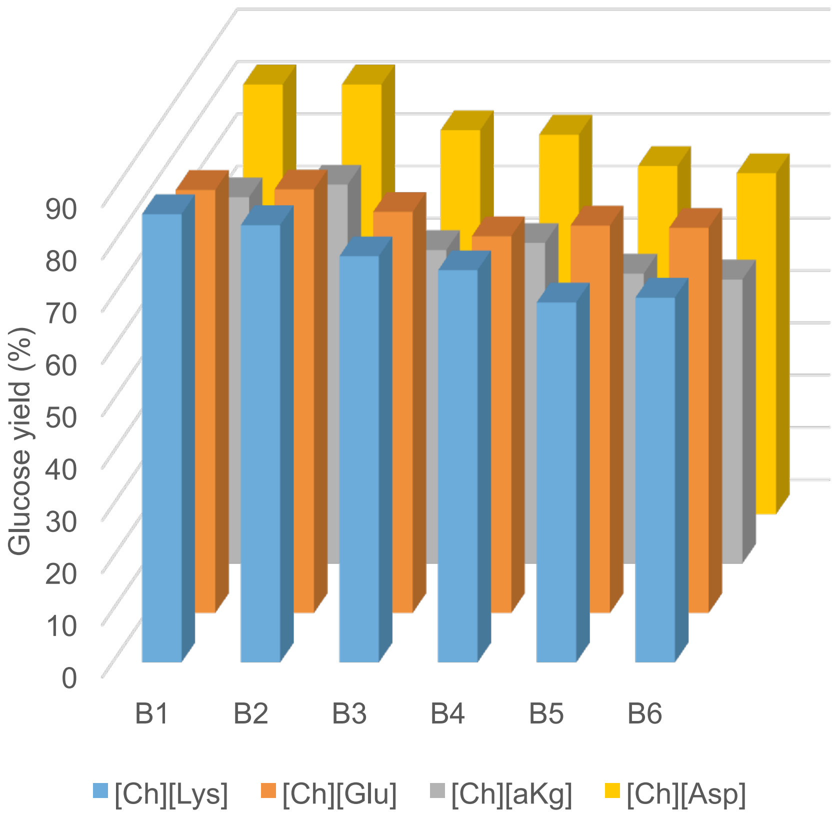


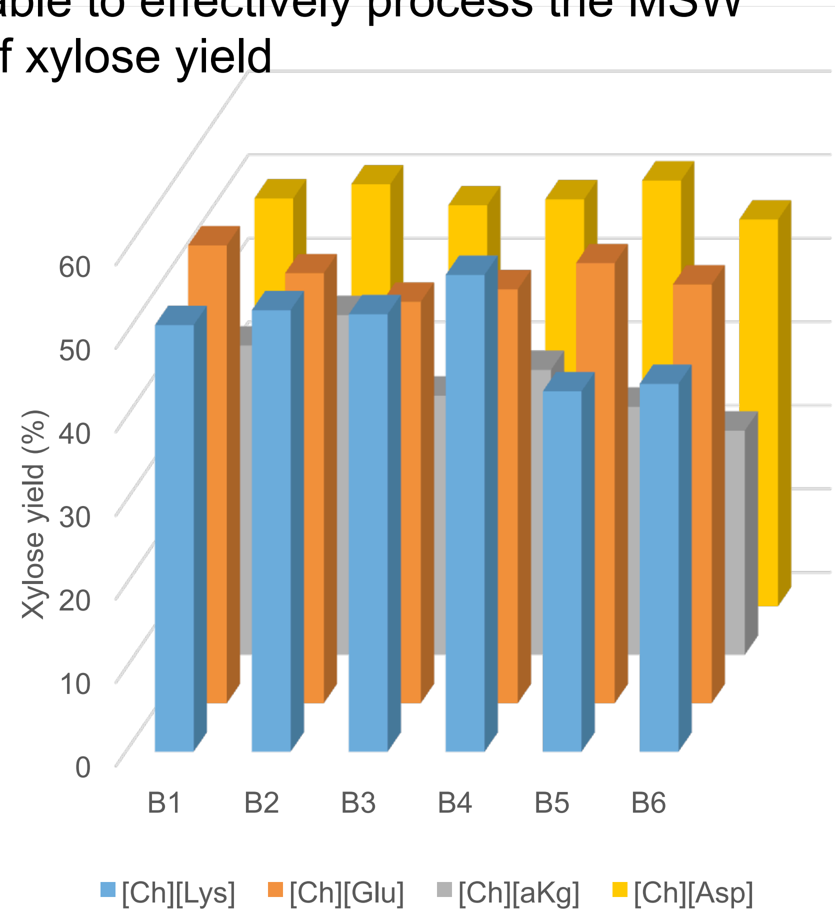


- We have developed several approaches for process consolidation and integration using IL (BER funded project).
- One scenario of process integration was modified and demonstrated for MSW blend conversion to Methyl ketone (BETO funded project).

Efficient Sugar Conversion through the integrated One-pot IL Process

- The sugar yields depend on both types of IL and glucan content of the MSW Blends
- [Ch][Lys], $[Ch]_2[Glu]$, and $[Ch]_2[Asp]$ are able to effectively process the MSW Blends with ~80% of glucose and~50% of xylose yield





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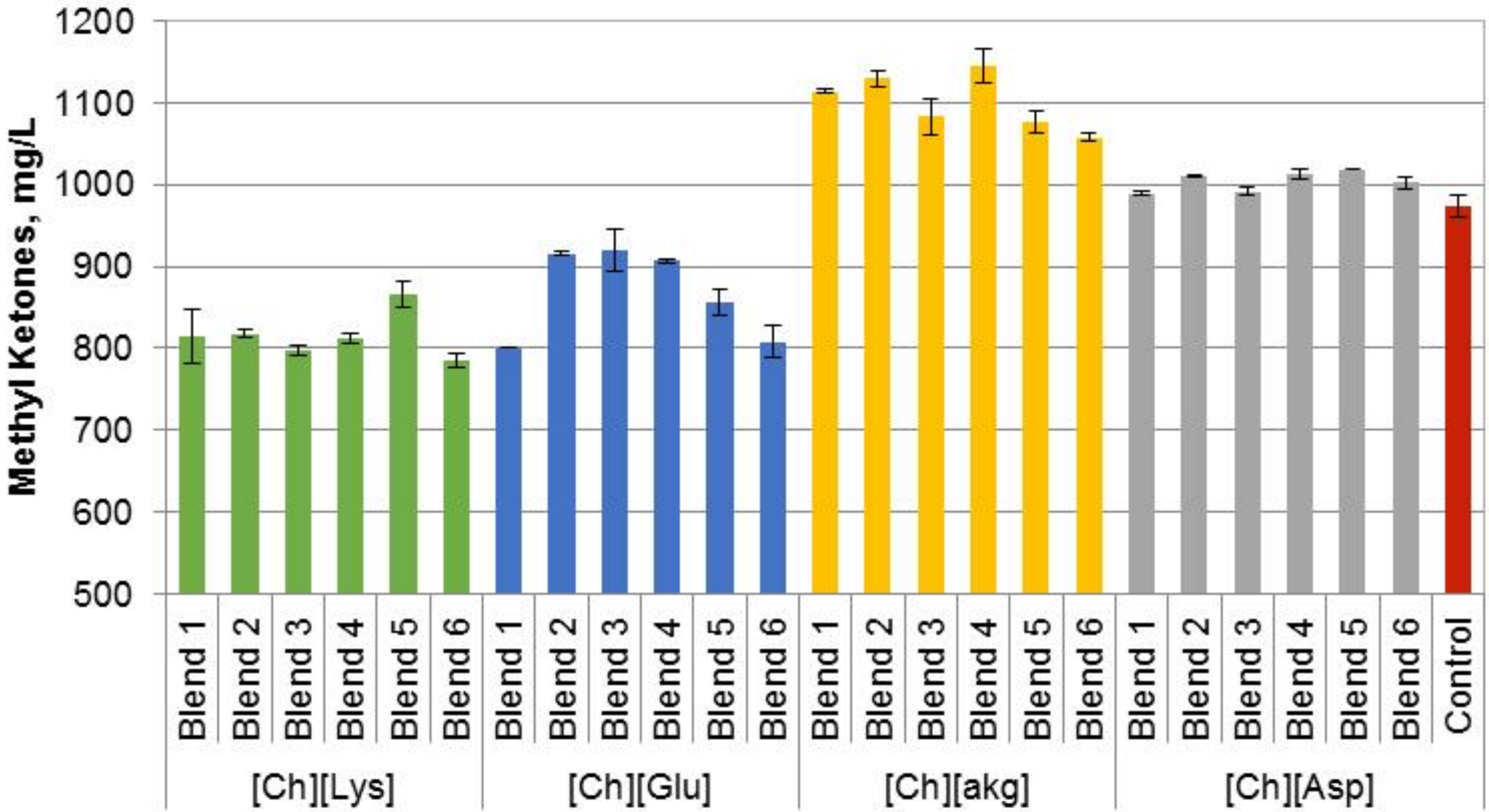
Demonstrated fermentability of sugar from bionic liquid pretreated MSW Blends

Used engineered Escherichia coli to produce saturated and monounsaturated aliphatic methyl ketones (MKs) in the C11 to C15 (diesel) range. MKs have favorable cetane number.



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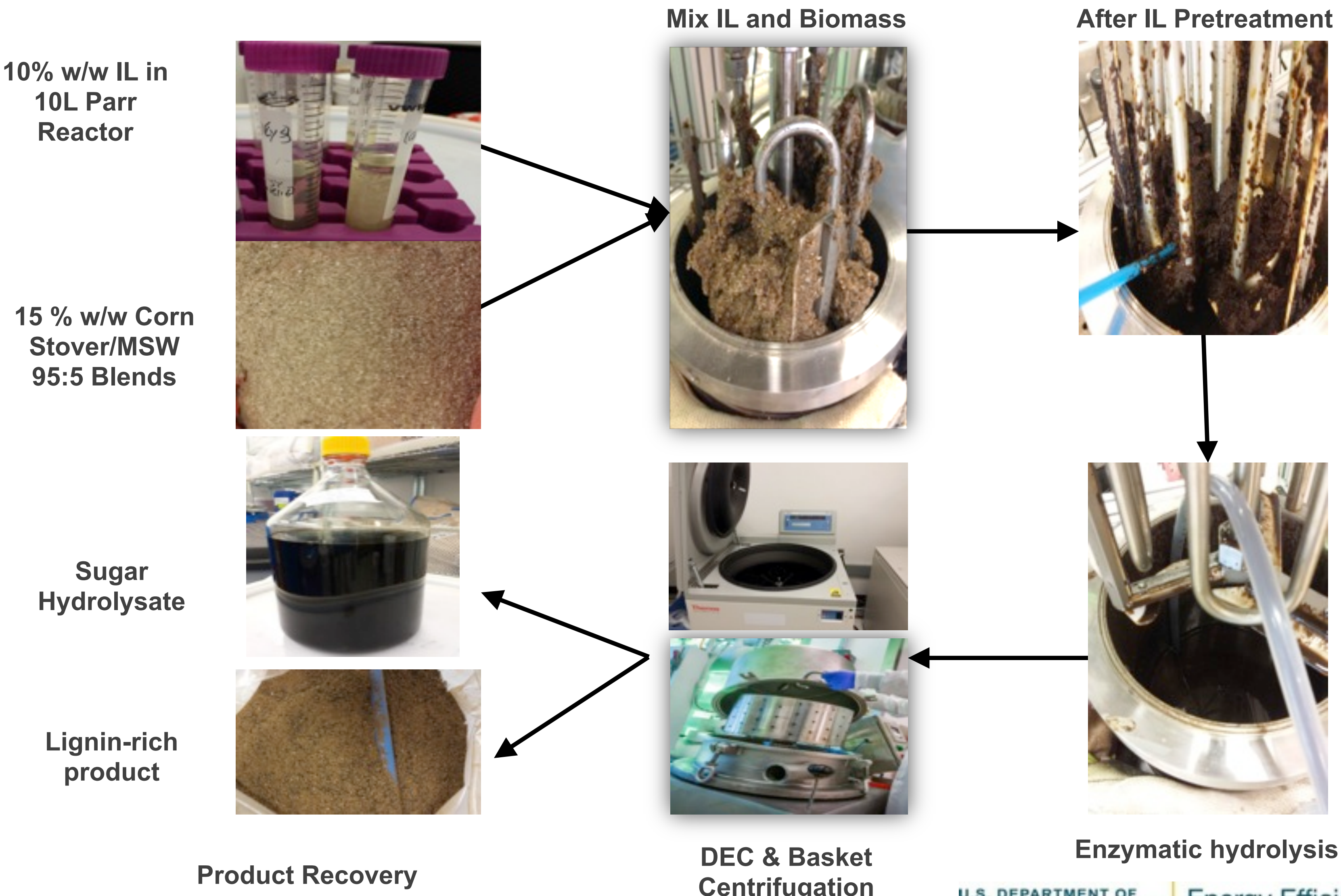
Successfully scaled up the One-pot Bionic IL process to 10 L

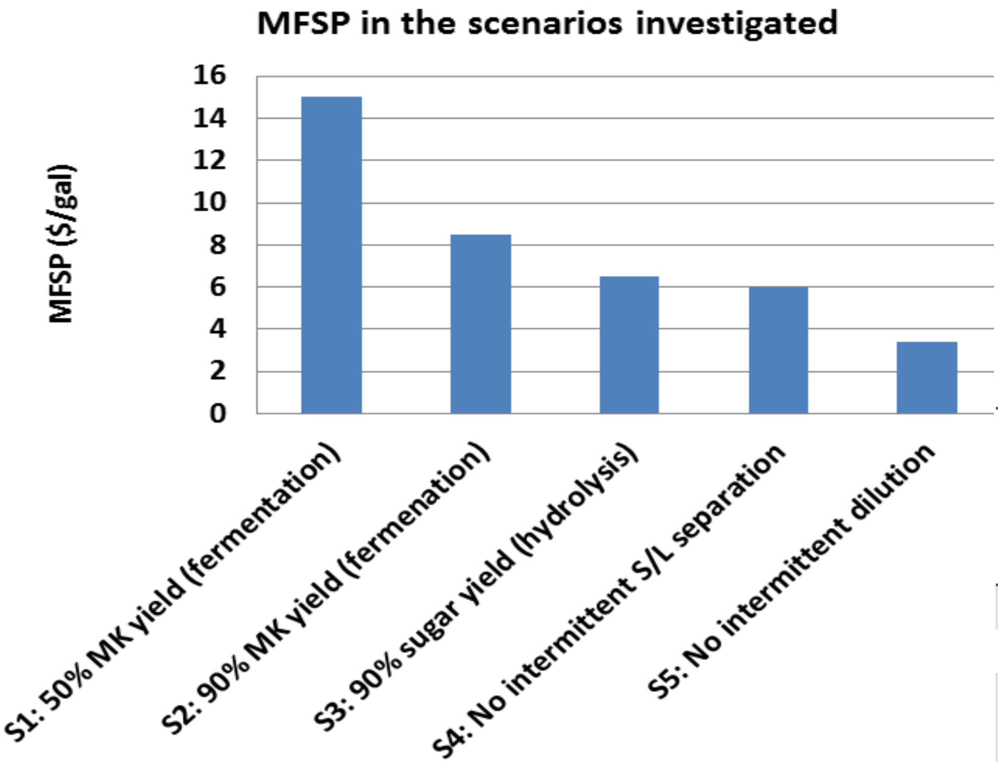


Sugar yields and concentrations are similar between the two scales tested.

		Glucose		Xylose	
	Hydrolysate	Concentration, g/L	Yield, %	Concentration, g/L	Yield, %
250 mL scale	[Ch][Lys]-B2	29.80	83.64	11.30	52.84
6 L scale	[Ch][Lys]-B2	31.94	73.13	11.38	42.55
250 mL scale	$[Ch]_2[Asp]$-B2	33.69	82.21	15.90	50.51
6 L scale	$[Ch]_2[Asp]$-B2	35.10	80.63	12.50	47.17

- Most of the sugars are released within 24
- Xylose yield needs to be further optimized.

TEA of the IL based one-pot process: Key factors are identified for a path-forward to produce cellulosic biofuels cost competitively.



Scenario	Key attributes	Primary operation(s) Requiring advancement
S1	50% of max. yield of MKs	Fermentation
S2	90% of max. yield of MKs	Fermentation
S3	90% yield of sugars (i.e., glucose and xylose)	Hydrolysis
S4	No intermittent separations (such as solid liquid separation)	Fermentation
S5	No intermittent dilution (i.e., prior to hydrolysis and fermentation)	Hydrolysis & fermentation

Technical Achievements -Summary

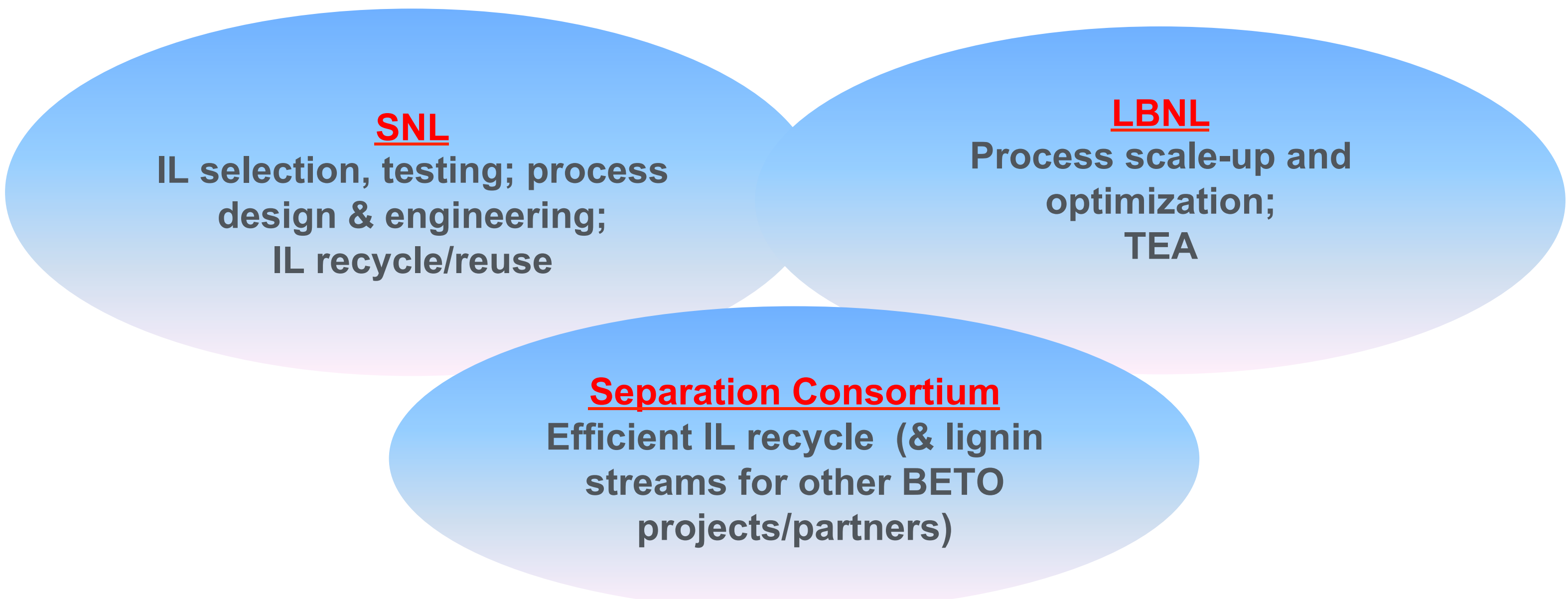
- All the quarterly milestones have been met on time.
- Over 80% of glucose was recovered and medium-chain (C_{11}-C_{17}) methyl ketones were produced using IL conversion technology.
- Successfully demonstrated 200 X scale up of MSW/CS blends for IL-acidolysis (enzyme free process).
- Successfully converted MSW blends to methyl ketones (MKs) using engineered *E. coli* through a one-pot ionic liquid (IL) based approach.
- Successfully scaled up the one-pot process 24X (from 250 mL to 6 L) with similar sugar recovery and comparable MKs production between the two scales.
- Initial TEA has been conducted and the targeted sugar and MKs yields are proposed with the associated minimum fuel selling price (MFSP)

Relevance

- Directly supports BETO's goal: "Develop commercial viable technologies for converting biomass feedstocks via biological and chemical routes into energy dense, fungible, finished liquid transportation fuels"
- Address BTEO's Office Multi-Year Milestone for Feedstocks Supply and Logistics "By 2017, validate efficient, low-cost, and sustainable feedstock supply and logistics systems"
- Project metrics and technical targets are driven by TEA
  - Reduce MFSP through improvement of the sugar/fuel yields, elimination of S/L separation, and elimination of intermittent dilution.

Future Work (FY17): Development and Process Intensification of IL based Lignocellulosic Conversion Process

Goal: To develop and demonstrate an ionic liquid (IL) based lignocellulosic conversion process for fuels or chemical intermediates production that is both scalable and economically viable. The target is to make progress to meet $3/GGE by maximizing product yields and decreasing IL conversion costs.



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Overall Summary

- **MSW is a growing interest in both the feedstocks and conversion platforms within BETO to meet feedstock cost target and IL based technology shows unique advantages for biomass conversion.**

- **There is a need to understand the impact of these blends on process performance, potential negative impacts on downstream unit operations and further investigate IL based processes.**

- **Successfully demonstrated high yields of sugar (>80%), subsequent conversion into fuel (methyl ketone) and >20X scale up in an integrated one pot process.**

- **Initial TEA has been conducted and key factors have been identified to reduce MFSP.**

- **The project directly support BETO's goal and address BTEO's Office Multi-Year Milestone**.

- **Future work will focus on development and demonstration of economically viable and scalable IL based conversion process for fuels and chemicals and include process intensification to meet $3/GGE cost target.**

Additional Slides

Publications and Presentations

Publications:

- N. Sun, F. Xu, N. Sathitsuksanoh, V. S. Thompson, K. Cafferty, C. Li, D. Tanjore, A. Narani, T. R. Pray, B. A. Simmons and S. Singh, Bioresource Technology, 2015, 186, 200-206.
- Li C, Liang L, Sun N, Thompson VS, Xu F, Narani A, He Q, Tanjore D, Pray TR, Simmons BA, Singh S (2017) Scale-up and process integration of sugar production by acidolysis of municipal solid waste/corn stover blends in ionic liquids. Biotechnol Biofuels 10 (1):13.
- Liang L et al. Conversion of municipal solid waste blends using ionic liquids: feedstock convertibility and process scale-up. Submitted to Bioenergy Research 2017/01
- Yan J et al. Conversion of municipal solid waste to methyl ketone using ionic liquid based process in preparation

Conference:

- F. Xu, N. Sun, N. Sathitsuksanoh, V. S. Thompson, C. Li; D.Tanjore, T. R. Pray, B. A. Simmons, S. Singh. Impact of municipal solid waste paper mix as a blending agent on enzymatic hydrolysis and acidolysis SIMB Symposium on Biotechnology for Fuels and Chemicals. April 27-April 30, 2015, San Deigo, CA.
- C. Li; L. Liang, N. Sun, F. Xu, V. S. Thompson, A. Narani, Q. He, T. Luong, D.Tanjore, T. R. Pray, B. A. Simmons, S. Singh. Scale-up and process integration of sugar production by acidolysis of single and mixed feedstocks in ionic liquids. SIMB Symposium on Biotechnology for Fuels and Chemicals. April 27-April 30, 2015, San Deigo, CA.
- L Liang, N Sun, C Li, Q He, T Luong, F Xu, M Somma, N D'Alessio, V S. Thompson, B A. Simmons, S Singh, and T R. Pray. Scale-Up and Process Integration of Municipal Solid Waste Conversion Process. 38th Symposium on Biotechnology for Fuels and Chemicals. April 25-April 28, 2016, Baltimore, MD.
- J Yan, L Liang, Q He, T Luong, F Xu, C Li, V S. Thompson, Ee-Been Goh, H R. Beller, B A Simmons, T R Pray, S Singh, and N Sun Conversion of Municipal Solid Waste to Methyl Ketone Using Ionic Liquid Based Process. 2016 AIChE Annual Meeting, November, 2016, San Francisco, CA

FY17 Milestones

Q1	Complete pretreatment process optimization studies at bench scale with different low cost ionic liquids (ILs). (SNL)
Q2	Complete initial scale-up (>2L scale) at the ABPDU for pretreatment and hydrolysis. (LBNL) Evaluate the hydrolysate quality for fermentation at shake flask scale using a C5/ C6 utilizing microbe. (SNL)
Q3	Demonstrate an integrated pretreatment-saccharification-fermentation process. (SNL) Complete scale-up of the integrated process developed by SNL and optimize the process to achieve high titers for both sugars and fuels. (LBNL)
Q4	Demonstrate the reuse of the recycled ILs (obtained from Separation Consortium AOP) and compare the efficiency with fresh IL. (SNL) Complete TEA based on mass balances obtained at ABPDU and IL recycling data generated from Separation Consortium AOP. (LBNL)

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Acronyms

- IL: Ionic Liquid
- TEA: Techno-Economic Analysis
- MSW: Municipal Solid Waste
- WW process: Water Wash process
- NRP: Non Recyclable Paper
- LCF: Least Cost Formulation
- LMW: Low Molecular Weight

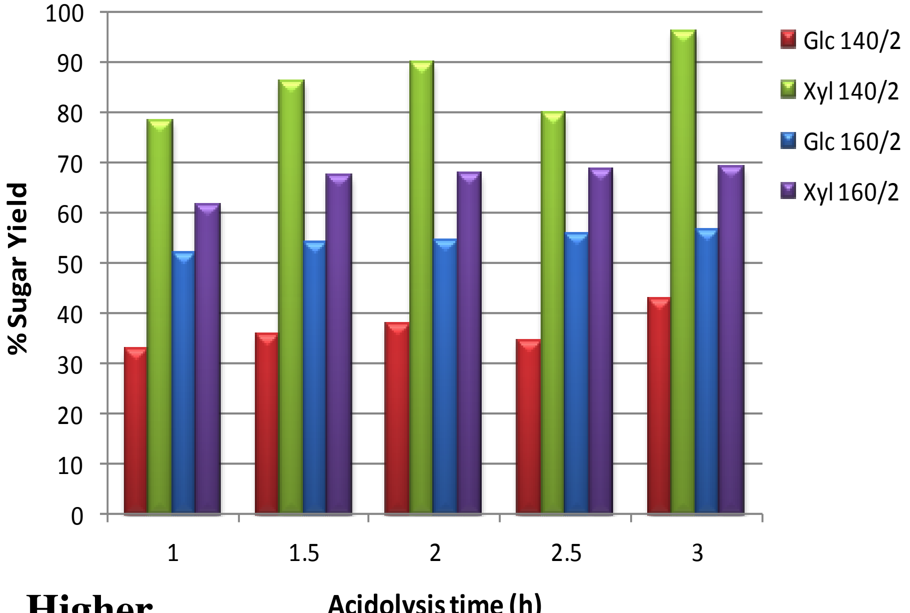
Solid Recovery from Pretreated Feesdtock

Corn Stover
72% solid recovery

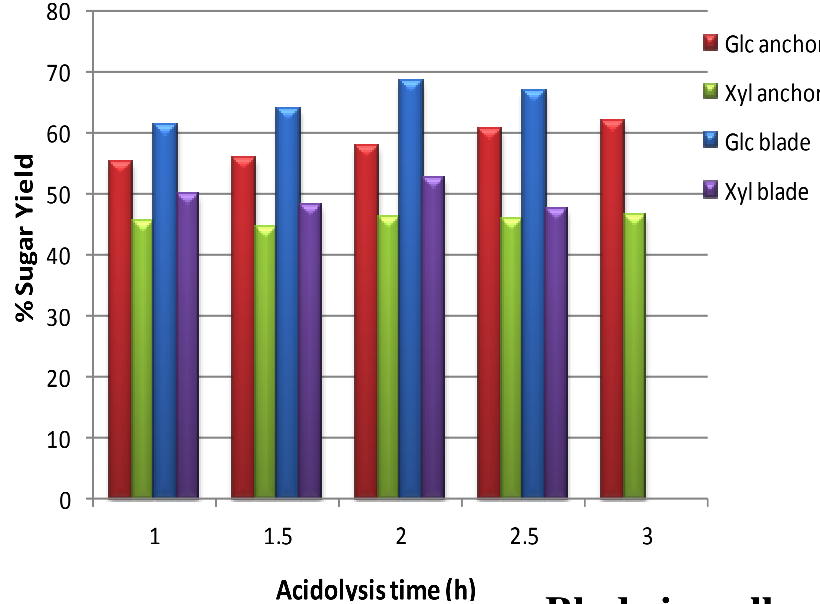
Corn Stover/MSW mix
80% solid recovery

MSW
93% solid recovery

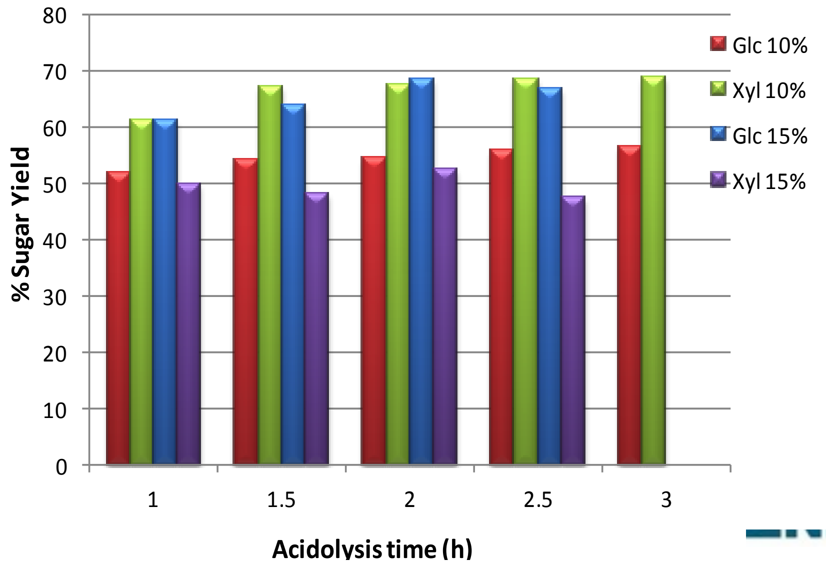
Process Optimization to Improve Sugar Yields



Higher temperature results in increased glucose/ decreased xylose yields.



Blade impeller worked better



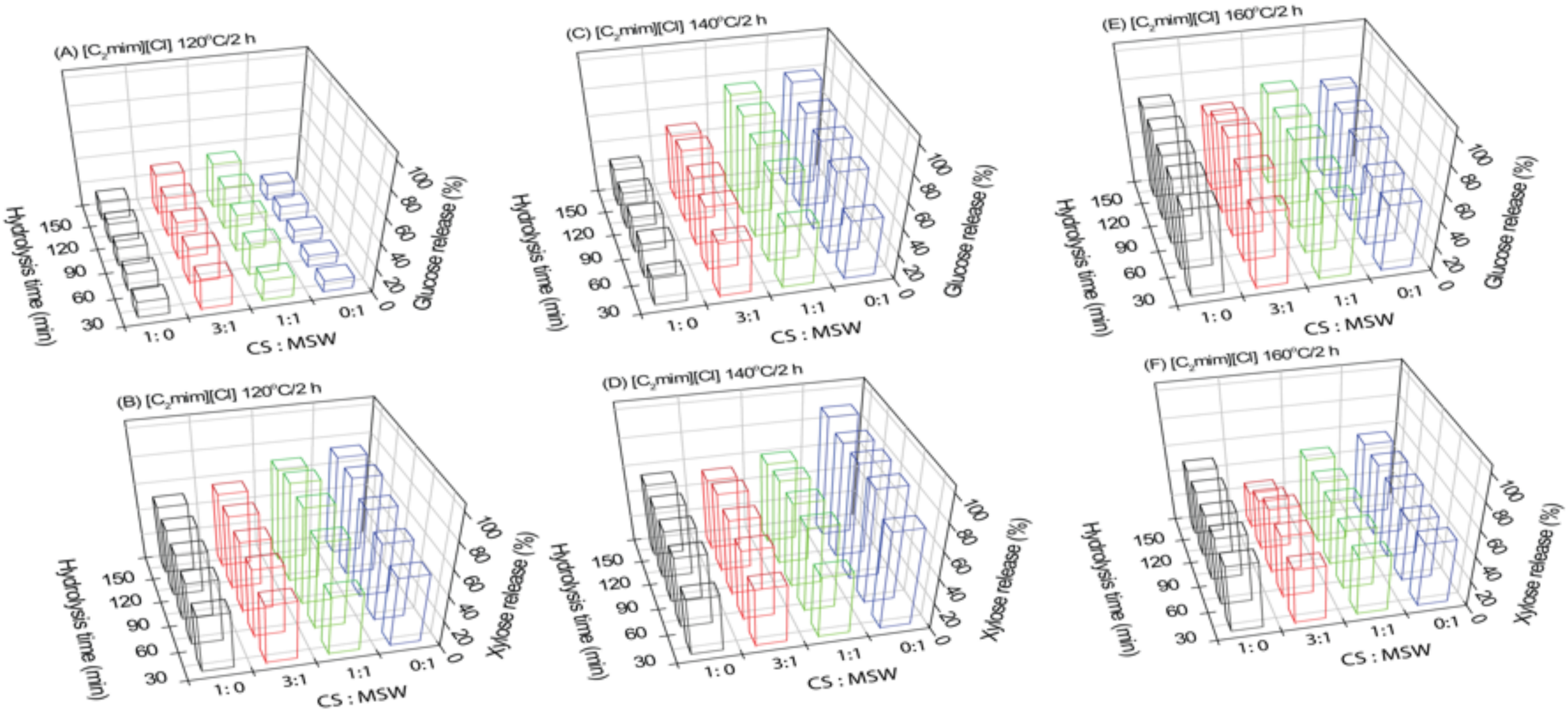
Under the tested conditions, 15% solid loadings results in higher glucose yield and lower xylose yields.

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.

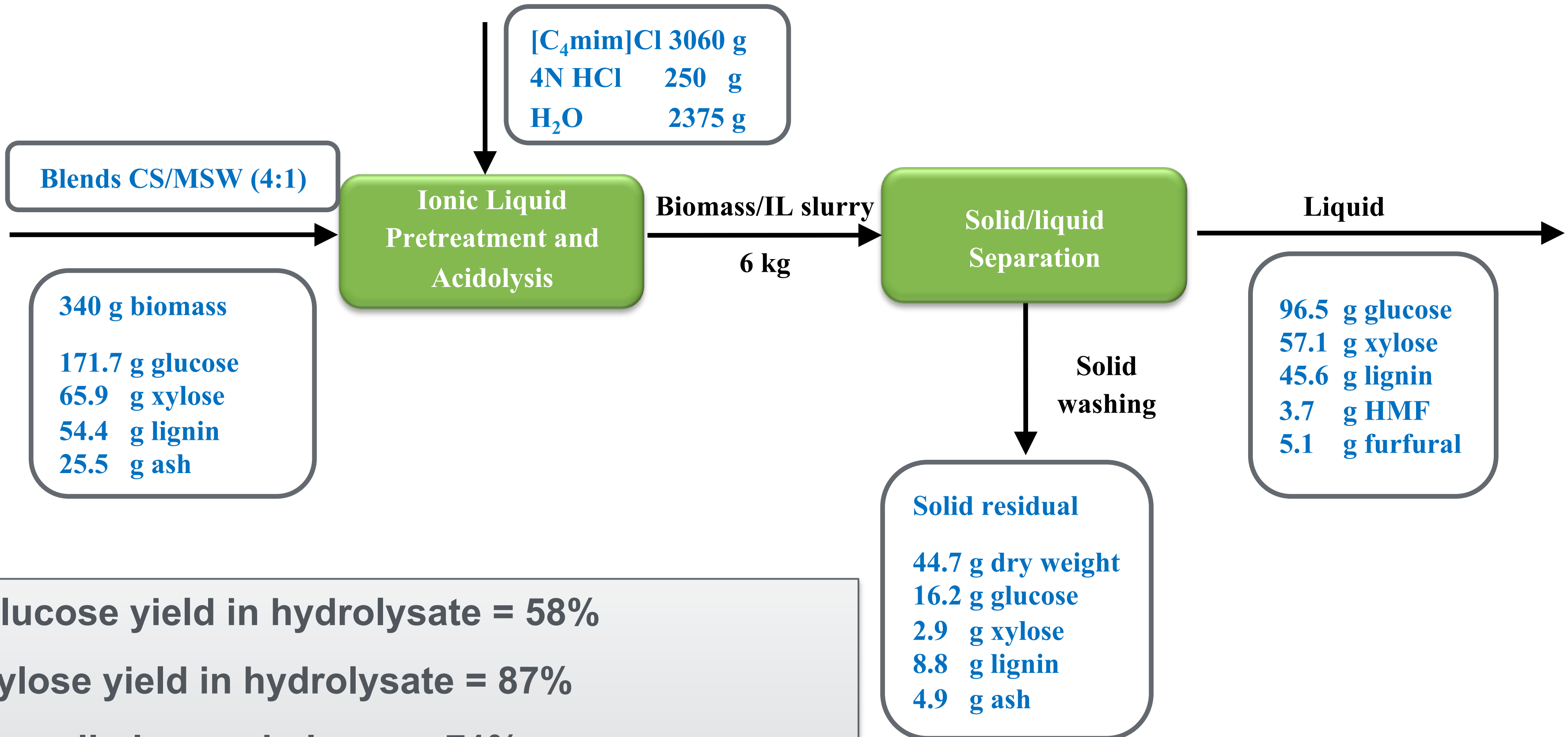
Acidolysis of MSW:CS Blends yield comparable Sugar as Enzymatic Hydrolysis Process



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

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

ABPDU ADVANCED BIOFUELS PROCESS DEMONSTRATION UNIT



Glucose yield in hydrolysate = 58%

Xylose yield in hydrolysate = 87%

Overall glucose balance = 71%

Overall xylose balance = 99%

Overall lignin recovery from solid stream = 16%

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

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