Ionic Liquid Pretreatment

EERE Webinar
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INTRODUCTION - IONIC LIQUIDS

- Salts that are liquid at ambient temperatures.
- Have stable liquid range of over 300 K.
- Very low vapour pressure at room temperature.
- Selective solubility of water and organics.
- Potential to replace volatile organic solvents used in processes
- Often associated with Green Chemistry. Has been a major driving force behind the intense interest in ionic liquids

Industry Drivers: Alternative Solvents for Process Intensification

- There is a need to develop more environmentally benign solvents or use solventless systems
- Such solvents should replace toxic and environmentally hazardous and/or volatile solvents
- Necessary to develop and optimize reactions conditions to use these new solvents and at the same time maximize yield and minimize energy usage.
- Examples include use of solids or involatile liquids rather than volatile, flammable and environmentally hazardous organic compounds (VOC).

Why Consider Ionic Liquids as Green Solvents

- Low melting organic salts (-60 °C)
- Very low vapor pressure (good)
- Non-flammable (good)
- Wide liquid range (300 °C) (good)
- Moderate to high viscosity (bad)
- Solvent properties different from molecular solvents (good and bad)
- Solvent properties can be controlled by selection of anion and cation – hence often termed designer solvents (good)
- BUT – some ionic liquids are toxic to the environment and humans

DESIGNER SOLVENTS - FLEXIBILITY OF CHOOSING FUNCTIONAL GROUPS TO MAKE IONIC LIQUIDS

Alkylammonium
Alkylphosphonium
Alkylnitride
N,*N*'-dialkylimidazolium
N-alkylpyridinium

Halide-based (Cl^-, Br^-, F^-)
Halogeno-based (BF_4^-, PF_6^-)
Halogenoaluminium(III)

NO_3^-, ClO_4^-, HSO_4^-
SO_3^-, $CF_3SO_3^-$
$(CF_3SO_2)_2N^-$
$(CF_3SO_2)_3C^-$

Organic cation

anion

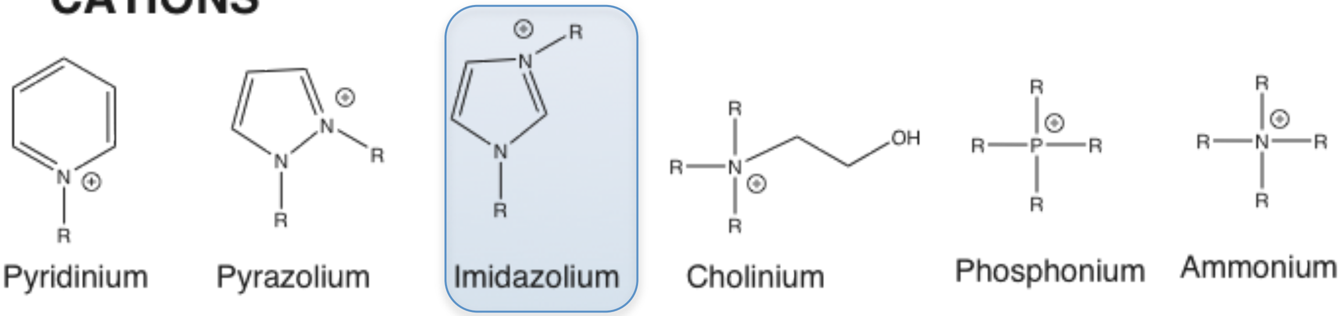
Industrial Processes with Ionic Liquids

Company	Process	IL is ...	Scale
BASF	Acid Scavenging	Auxiliary	commercial
	Extractive Distillation	Extractant	pilot
	Chlorination	Solvent	pilot
IFP	Olefin Dimerization	Solvent	commercial
Degussa	Hydrosilylation	Solvent	pilot
	Compatibilizer	Performance Additive	commercial
Arkema	Fluorination	Solvent	pilot
Chevron Philips	Olefin Oligomerization	Catalyst	pilot
Eastman	Rearrangement	Catalyst	commercial
Eli Lilly	Cleavage of Ether	Catalyst / Reagent	pilot
Air Products	Storage of Gases	Liquid Support	commercial
Iolitec / Wandres	Cleaning Fluid	Performance Additive	commercial

Certain Ionic Liquids (ILs) are Effective Biomass Solvents

Room Temperature, Molten Salts

CATIONS



Cation determines:
- stability
- properties

Water immiscible ⟹ Water miscible

ANIONS

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

$CH_3CO_2^{\ominus}$

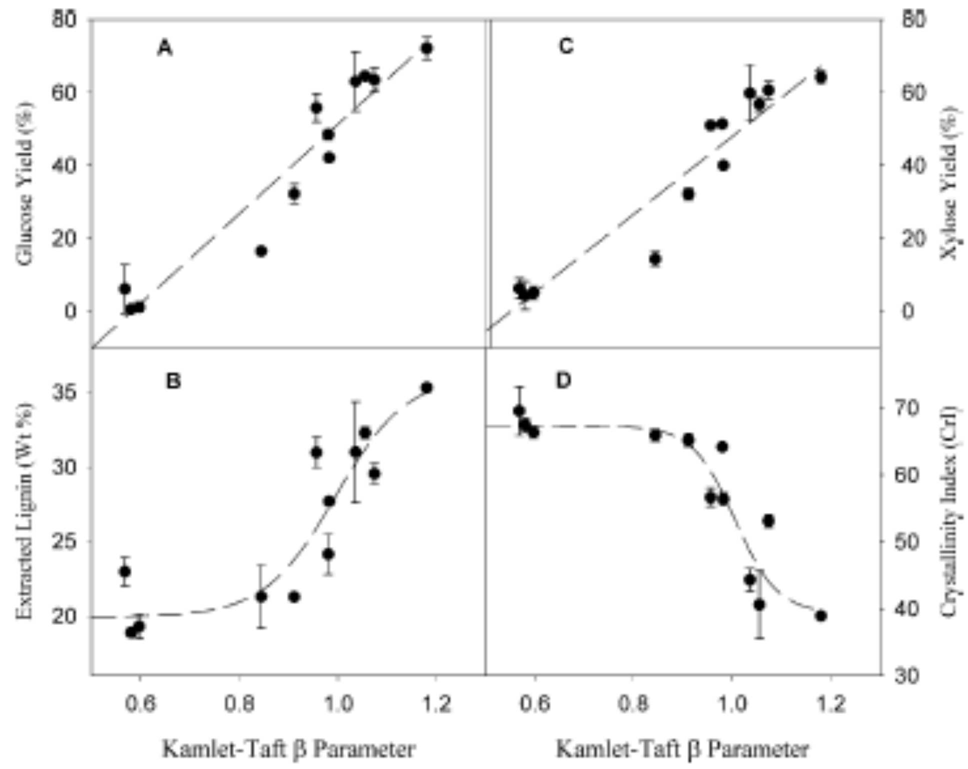
Anion determines:
- chemistry
- functionality

1-ethyl-3-methylimidazolium acetate, abbreviated as $[C_2mim][OAc]$, dissolves > 20 wt% cellulose

Simmons, B. et al., Ionic Liquid Pretreatment, *Chem Eng Prog*, 2010, 3, 50-55

Solvent-Based Predictors of IL Performance on Biomass

- Target: design of task-specific ILs
- Need: method of comparing and determining solvent properties
- Kamlet-Taft parameters is a way of measuring solvent polarity using solvatochromic dyes
- Provides a quantitative measure of:
  - solvent polarizability (π* parameter),
  - hydrogen bond donator capacity (α parameter),
  - hydrogen bond acceptor capacity (β parameter).



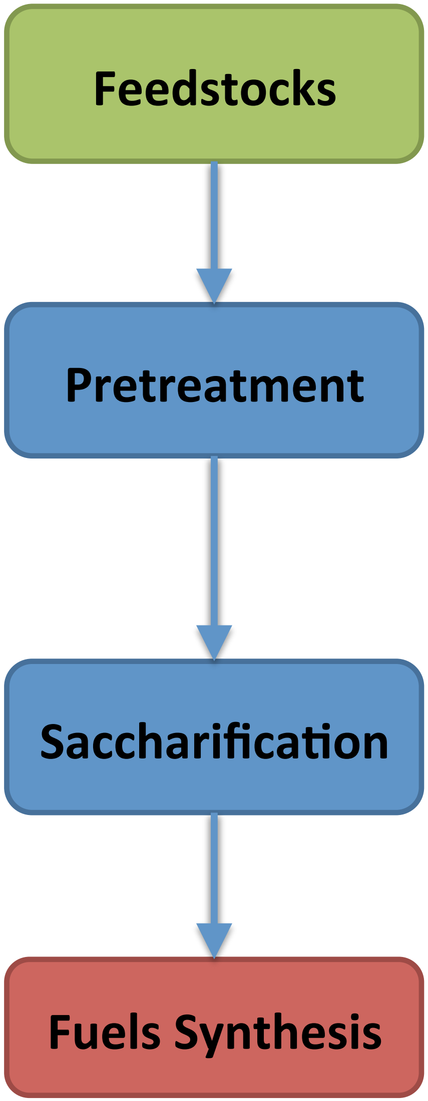
Doherty et al., *Green Chemistry,* 2010, 12(11), 1967-1975.

Establishing an Effective IL Conversion Process Technology

- **Challenge: Current pretreatments are not effective on wide range of feedstocks and/or generate inhibitors**

- **Any upstream unit operation must be integrated with downstream functions**

- **Solution: develop an IL biomass conversion platform that is feedstock agnostic**
  - ➢ **Develop mechanistic understanding of how ILs interact with biomass**
  - ➢ **Explore alternative modes of IL pretreatment that decrease cost**

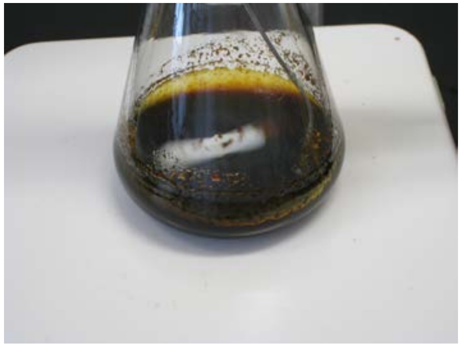


We Have Established an Effective Ionic Liquid Pretreatment Process Baseline

[C_2mim][OAc] **Switchgrass**

Heat

Stir



Anti-solvent

Advantages:

- Increased enzyme accessibility
- Decreased lignin
- Significantly impacted cellulose crystallinity

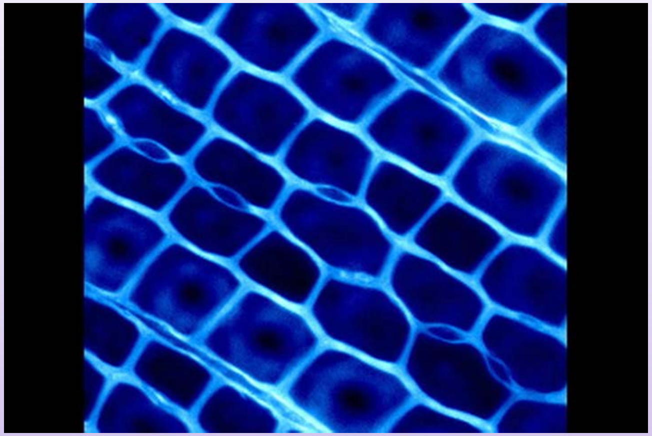
Challenges:

- IL recovery and recycle
- Process integration
- IL cost

UNDERSTANDING IL PRETREATMENT

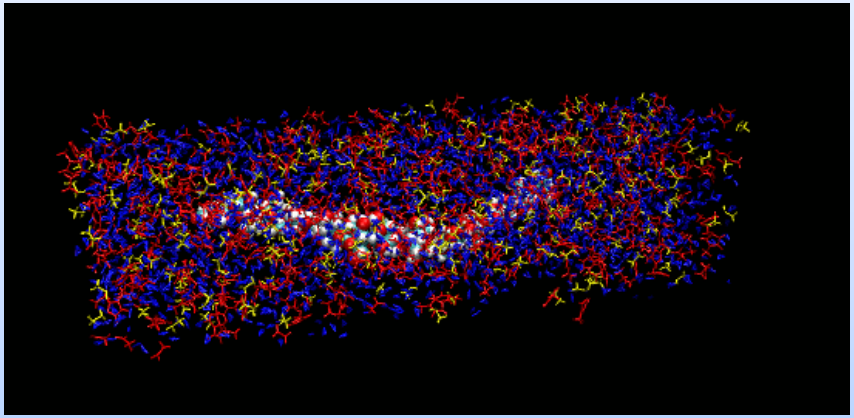
Macroscale: plant cell walls of pine, $[C_2mim][OAc]$, 120 °C

- In situ studies using bright field microscopy
- Rapid swelling of the plant cell walls, followed by dissolution
- Complementary Raman studies indicate that lignin is solvated first, then cellulose



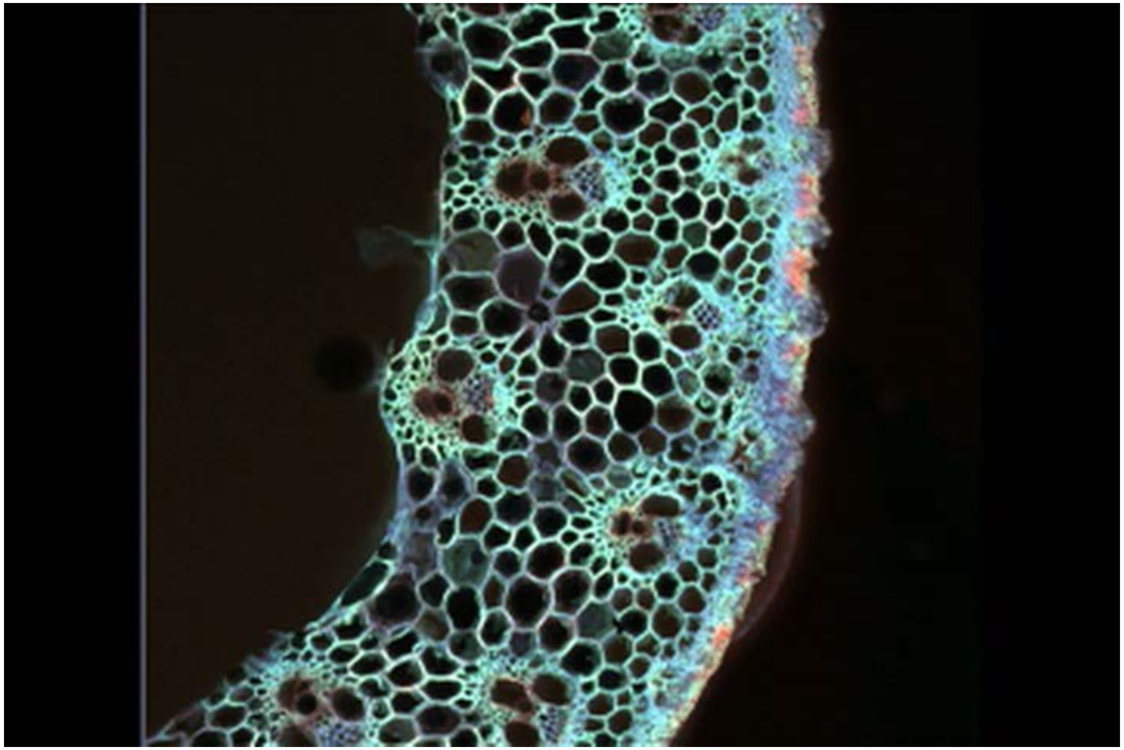
Molecular scale: 20-mer of cellulose; $[C_2mim][OAc]/H_2O$ (w/w) = 50/50

- MD simulations conducted using NERSC resources
- Provides new insight into the mechanism of cellulose solvation in ionic liquids
- Produced new hypothesis on the mechanism of cellulose precipitation



Liu et al., *Journal of Physical Chemistry* (2011), 115(34), 10251-10258.

Switchgrass undergoing IL pretreatment



- $[C_2mim][OAc]$, 120^{o}C, t = 10 minutes
- In situ studies using bright field microscopy
- Complementary Raman and fluorescence studies indicate that lignin is solvated first, then cellulose

SOLVENT-BASED PREDICTORS OF IL PERFORMANCE

- Target: design of task-specific ILs
- Need: method of comparing and determining solvent properties
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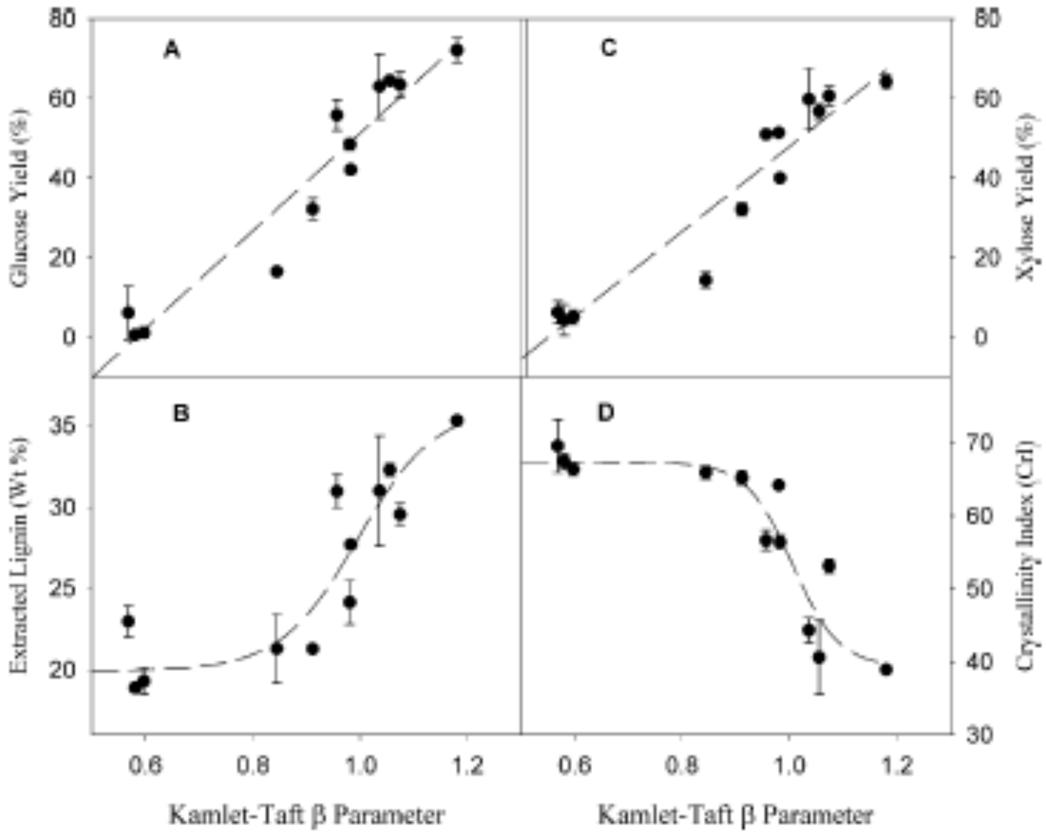
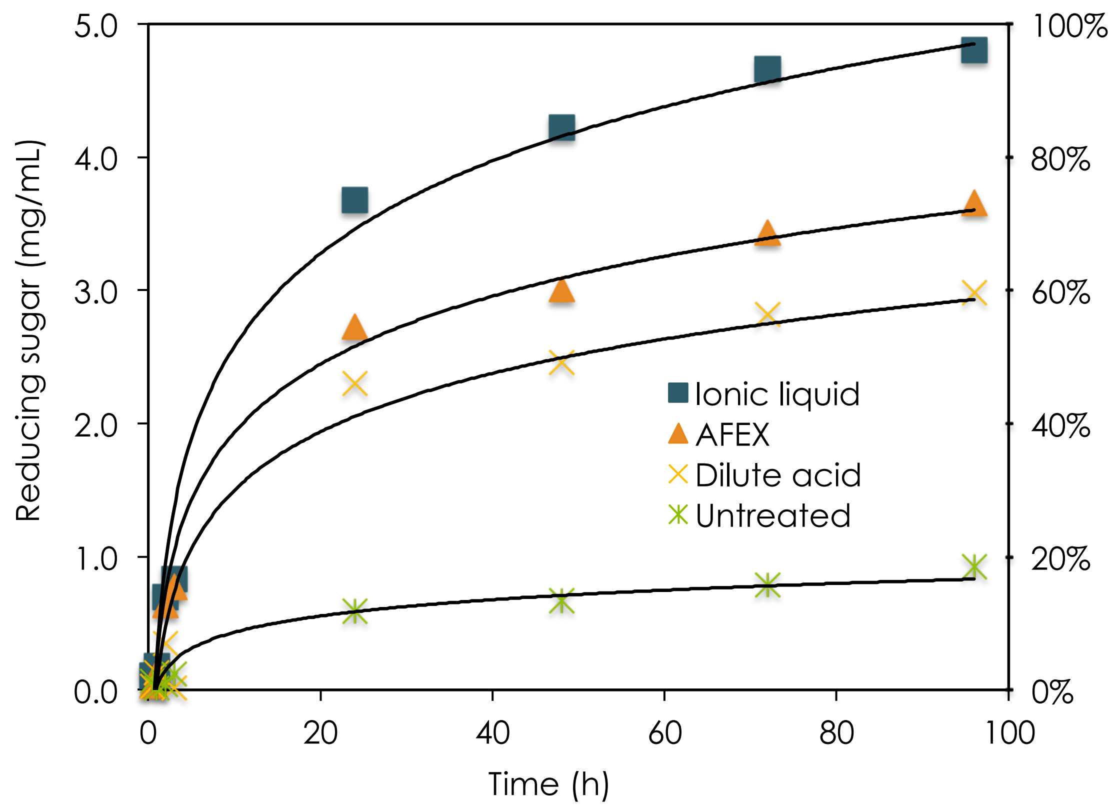


Doherty et al., *Green Chemistry,* 2010, 12(11), 1967-1975.

IL Pretreatment Generates High Sugar Yields

- **Comparative study of leading pretreatment technologies on common feedstock and enzymes (inter-BRC collaboration)**
- **GLBRC: Provided corn stover and AFEX pretreated corn stover**
- **JBEI: Ionic liquid and dilute acid pretreatment of corn stover**
- **Result: Ionic liquid outperforms dilute acid and AFEX**



Novozymes commercial cellulase cocktails:
5g glucan/L biomass loading
50mg protein/g glucan of cellulase (NS50013)
5mg protein/g glucan of β-glucosidase (NS50010)

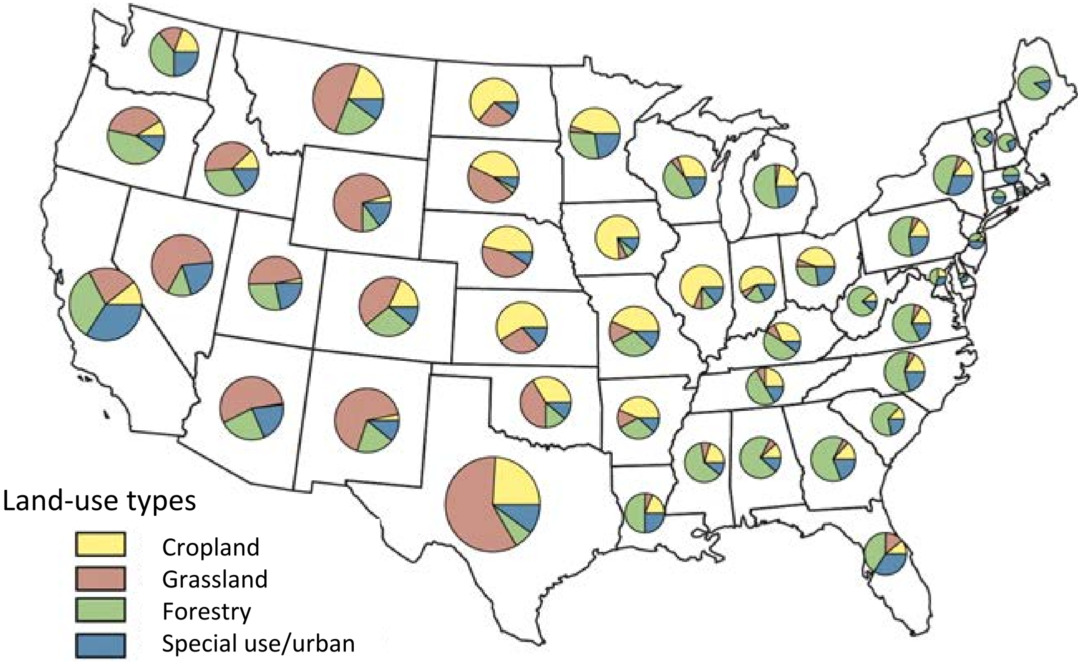
Li et al., *Biores. Tech.* (2011), 102(13), 6928-6936; Li et al., *Biores. Tech.* (2010), 101 (13), 4900-4906

Mixed Feedstocks will be Significant Source of Biomass for Biorefineries

***Mixed feedstocks*: In order to accomplish large-scale utilization of biomass feedstocks for biofuels, a consistent and stable supply of sustainable feedstocks from a variety of sources will be required**

Issues that must be addressed:

- **Impact of blends on conversion efficiency?**
- **What are the most reasonable combinations of feedstocks?**
- **Can we improve energy density?**
- **"Universal Feedstock"?**



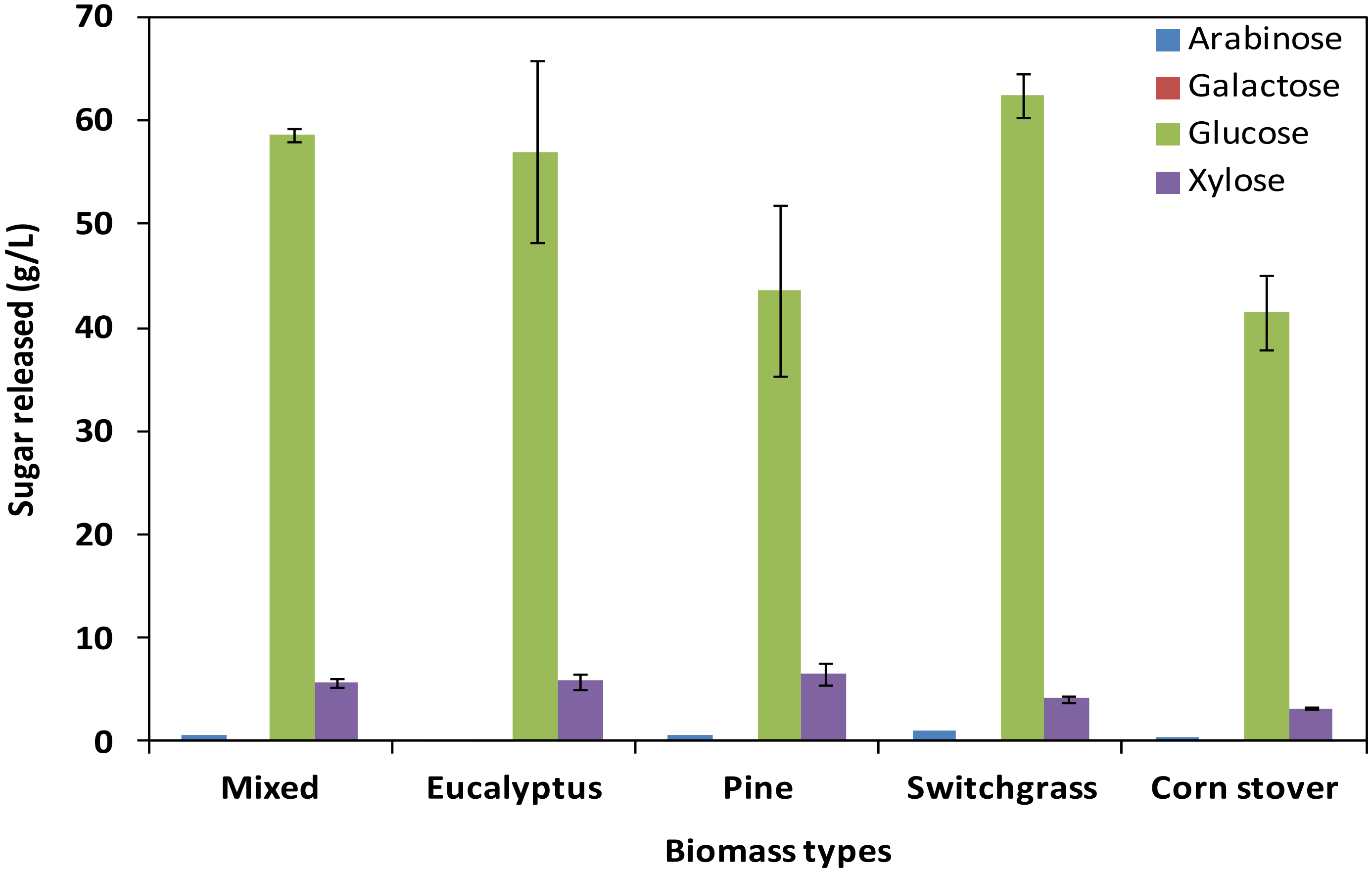
Feedstock availability by type and by state (Lubowski et al. 2005)

Feedstock Densification and Blending

***Densification*: typically involves exposing biomass to elevated pressure and temperature and compressing it to a higher energy density which facilitates the transport, store, and distribute of the biomass .**

Shi et al., *Biofuels,* 2013, 4(1), 63-72.

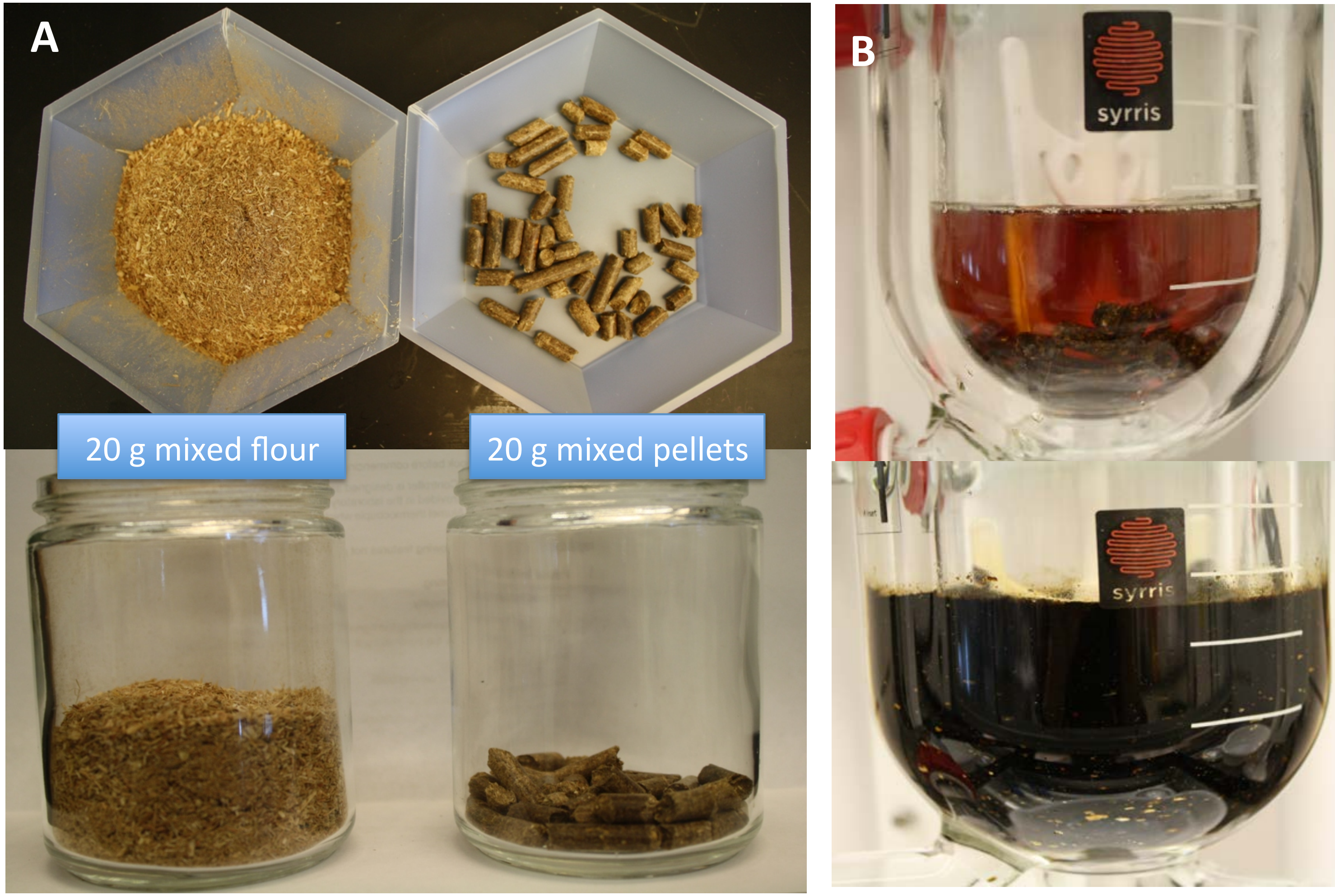
IL Process Generates High Sugar Yields for Single and Mixed Feedstocks



- **Pretreatment: [C_2mim][OAc], 15% solids loading, 160 °C, 3 hours**
- **Saccharification: 15% solids loading, CTec2 @ 40 mg/g glucan loading, HTec2 4 mg/g xylan**
- **Mixed feedstocks appear to perform better than average of single feedstock yields – why?**

Shi et al., *Biofuels,* 2013, 4(1), 63-72.

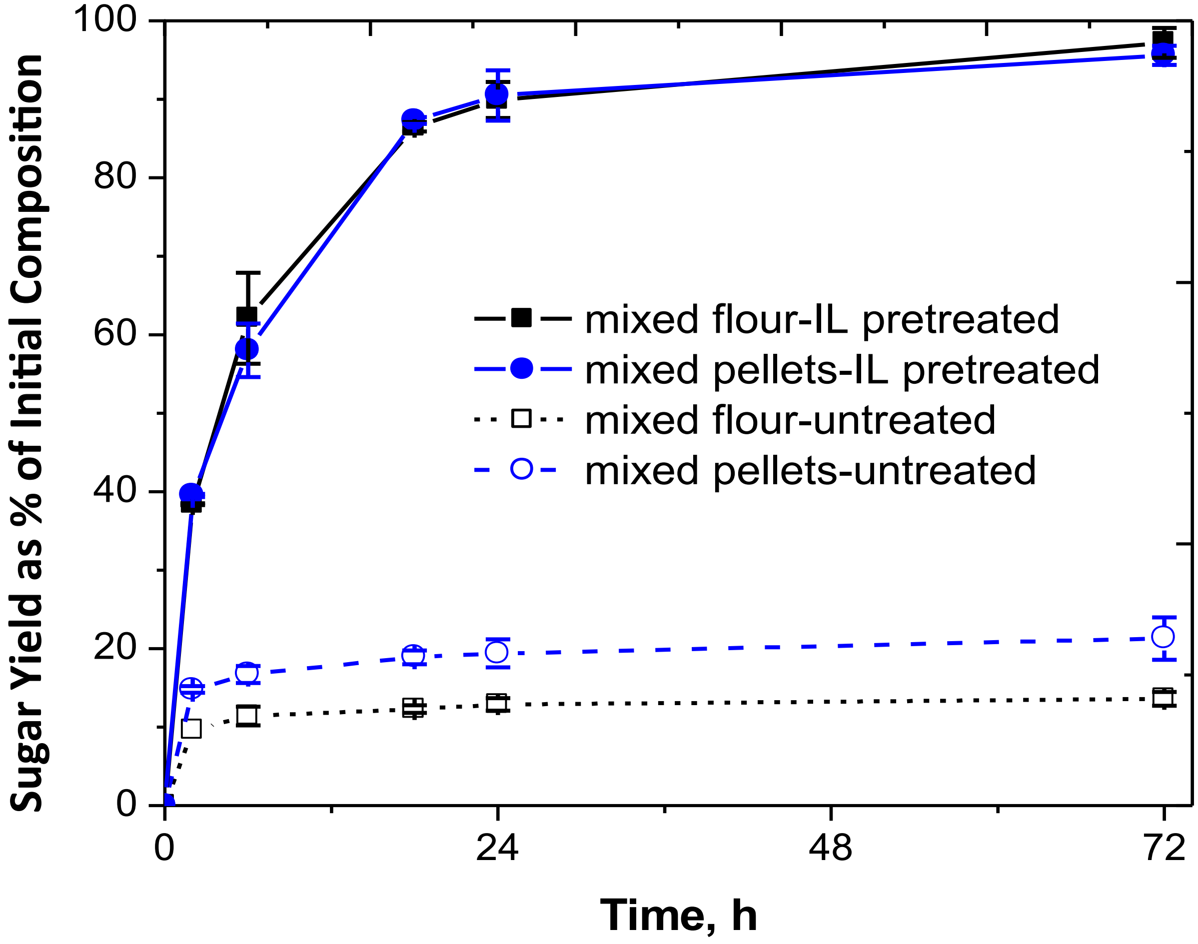
Densified Feedstocks are Effectively Pretreated using ILs



Images of (a) feedstocks before pretreatment and (b) densified feedstocks during IL pretreatment

Shi et al., *Biofuels,* 2013, 4(1), 63-72.

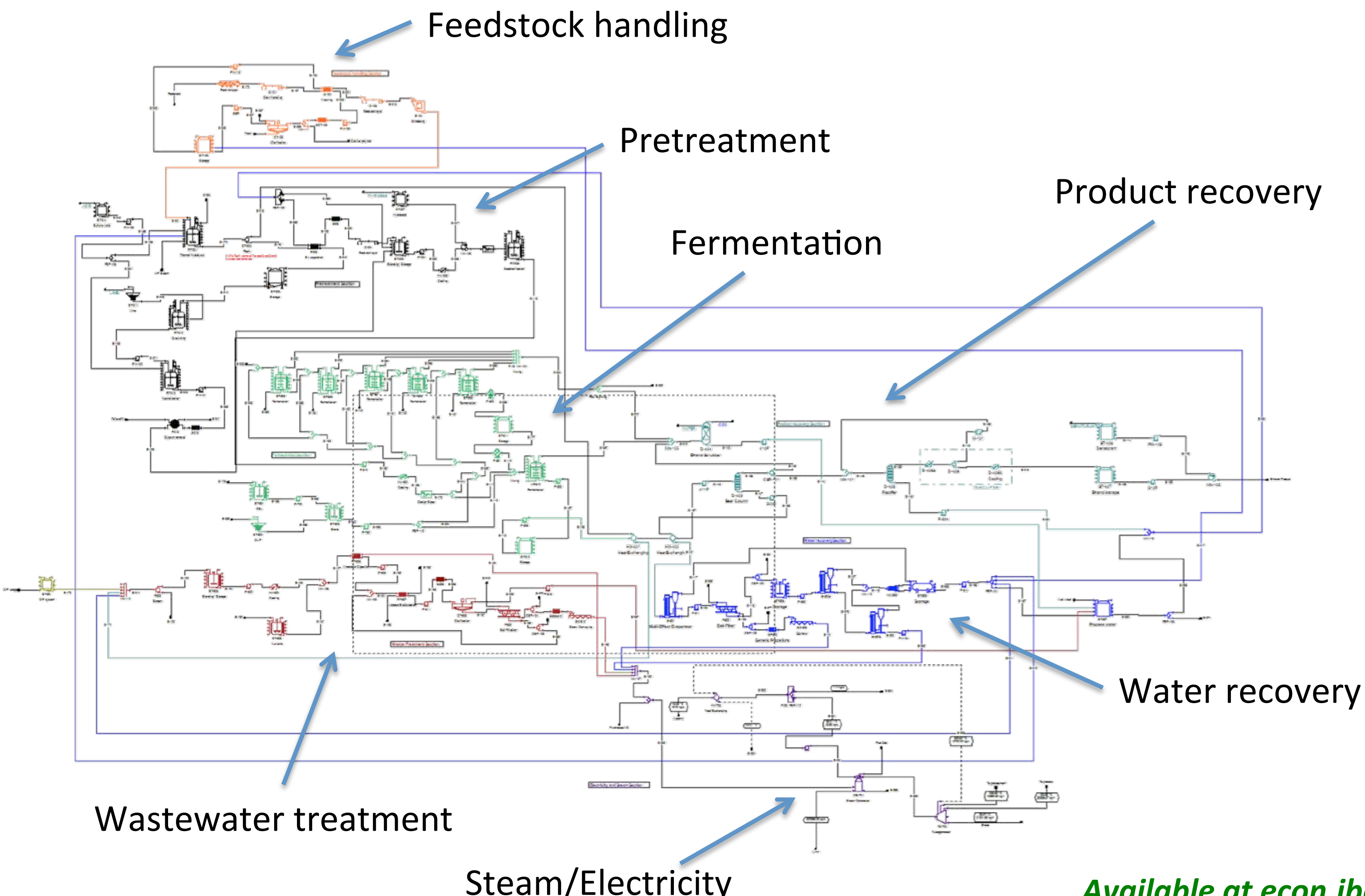
Particle Size and Mixed Feedstocks – No Impact on IL Pretreatment



1:1:1:1 corn stover:switchgrass:eucalyptus:pine. Biomass loading = 20 g/L, with enzyme loading of 20 mg CTec2 protein/g glucan and 0.26 mg HTec2 protein/g glucan

Shi et al., *Biofuels,* 2013, 4(1), 63-72.

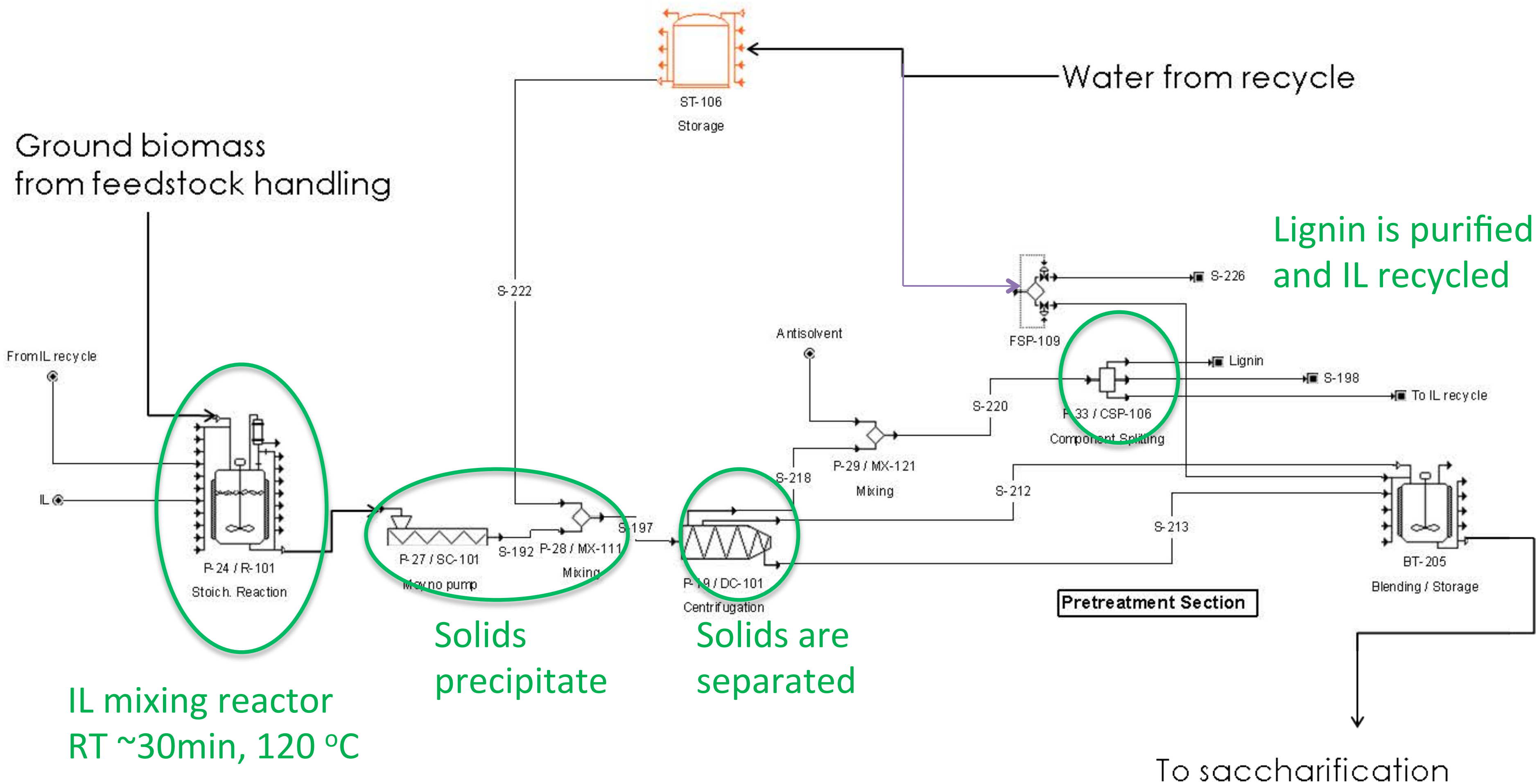
IL Techno-Economic Modeling - Baseline



Available at econ.jbei.org

Klein-Marcuschamer et al., *Biomass and Bioenergy,* 2010, 34(12), 1914-1921

IL Pretreatment Module

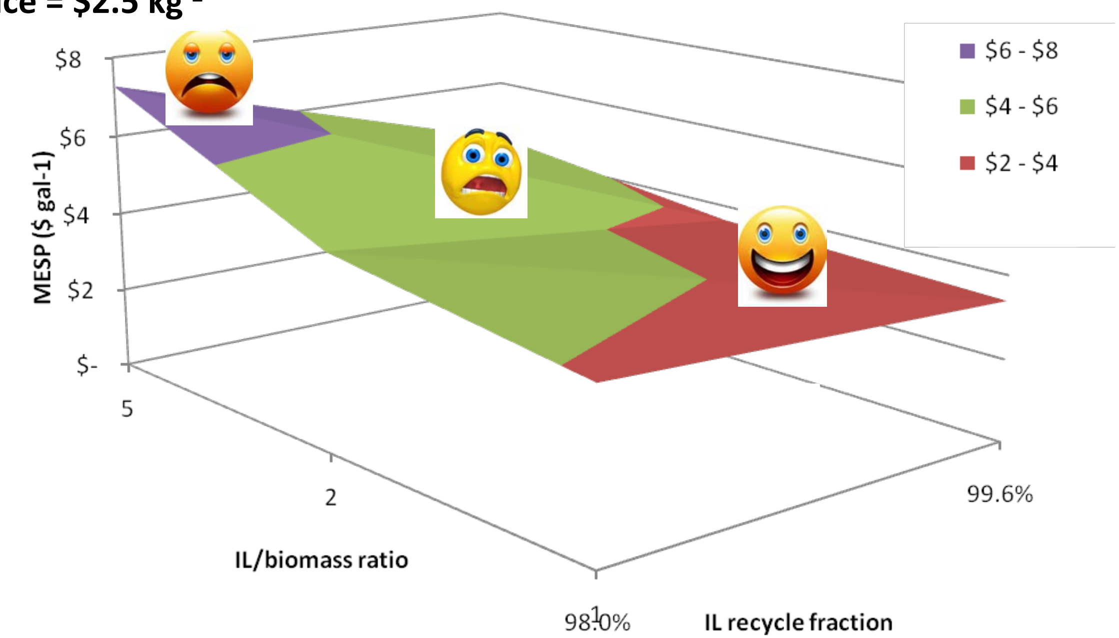


Klein-Marcuschamer et al., *Biofpr*, 2011, 5(5), 562-569

Sensitivity Analysis Highlights Key Opportunities to Improve IL Economics

- IL pretreatment has challenging economics
- Significant swings in IL price based on type and vendor ($1.00-800/kg)
- Key findings to reduce cost:
  - Increase solids loading
    - During IL mixing
    - During saccharification
    - Higher solids loading lowers CAPEX and OPEX
  - Reduce IL price and use
  - Develop efficient IL recycling techniques and technologies
  - Reduce enzyme costs
  - Develop integrated systems approach

IL price = $2.5 kg^{-1}



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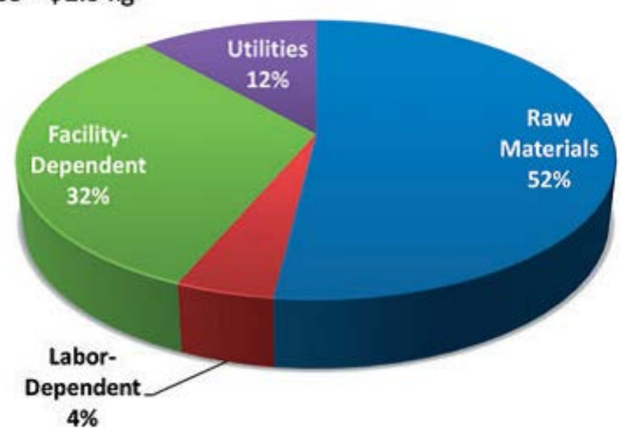

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Developing Solutions to Address Economic and Scientific Challenges

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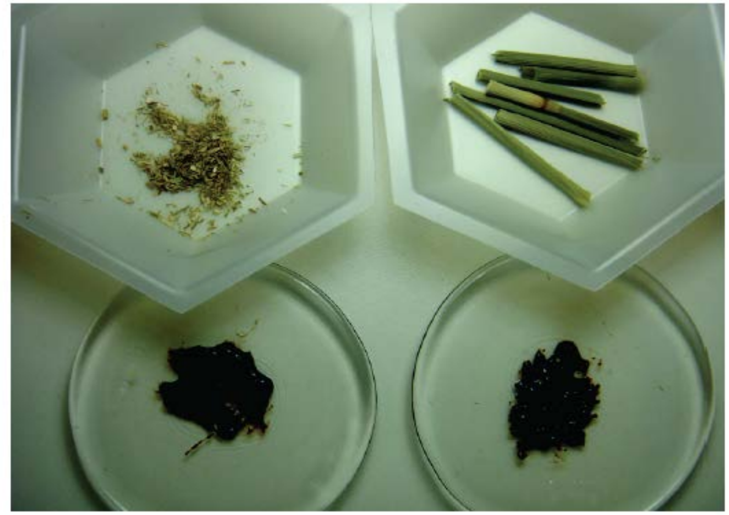
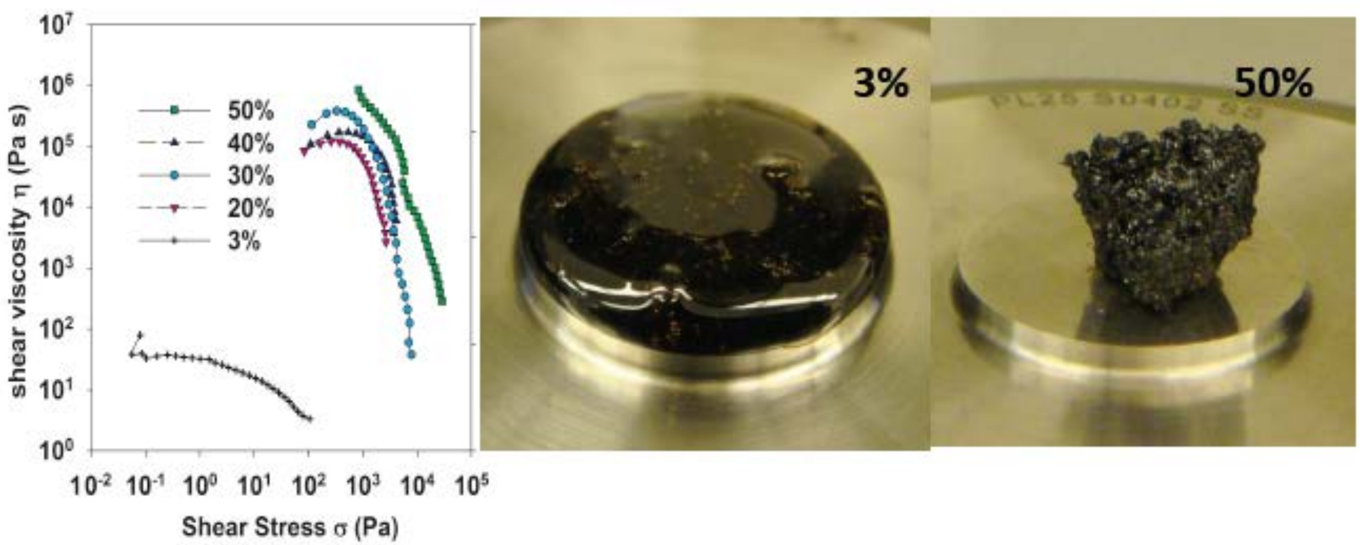
IMPROVING IL PRETREATMENT ECONOMICS - HIGHER BIOMASS LOADING

Benefits of higher biomass loading and larger particle size:

- **Decrease need for comminution**
- **Biorefinery OPEX savings**
- **Impacts harvesting options**
- **May drive to co-solvent options to mitigate viscosity concerns**

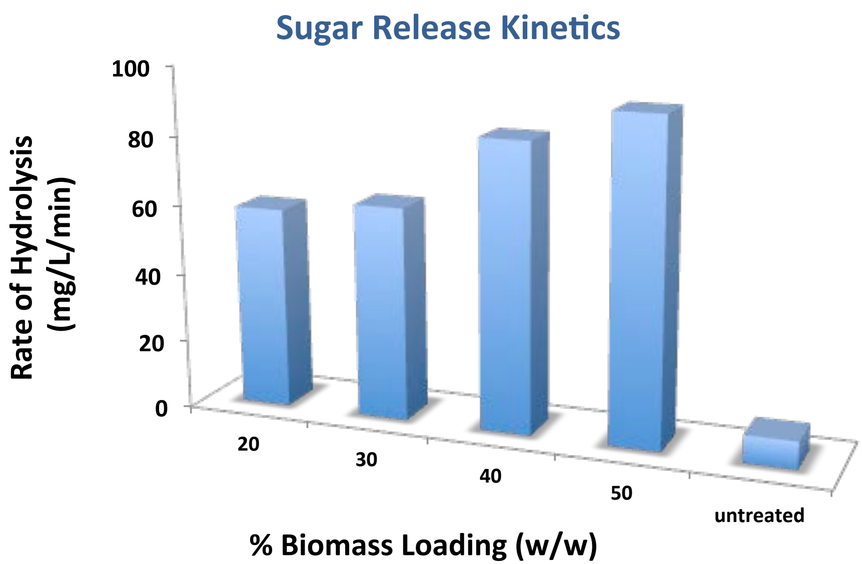


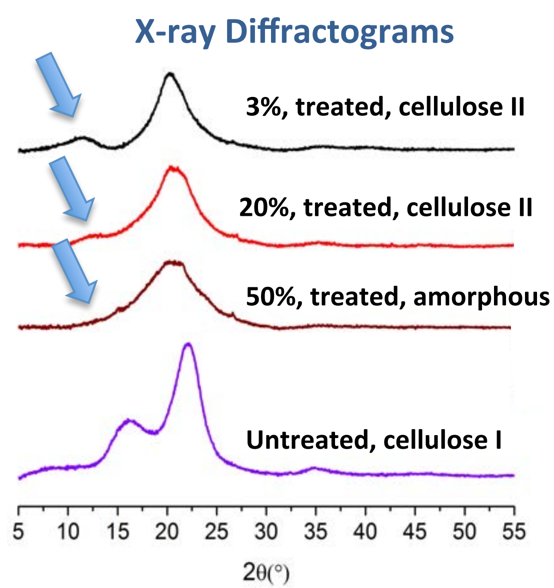


A. Cruz et al., *Biotechnology for Biofuels*, 2013, 6:52.

Unanticipated Benefit of Higher Biomass Loading

- **Surveyed impact of high biomass loading on sugar yields and kinetics**
- **Higher biomass loading yields higher hydrolysis rates**
- **Higher biomass loading generates more amorphous product after pretreatment**





A. Cruz et al., *Biotechnology for Biofuels*, 2013, 6:52.

Developing Solutions to Address Economic and Scientific Challenges

- Increase solids loading
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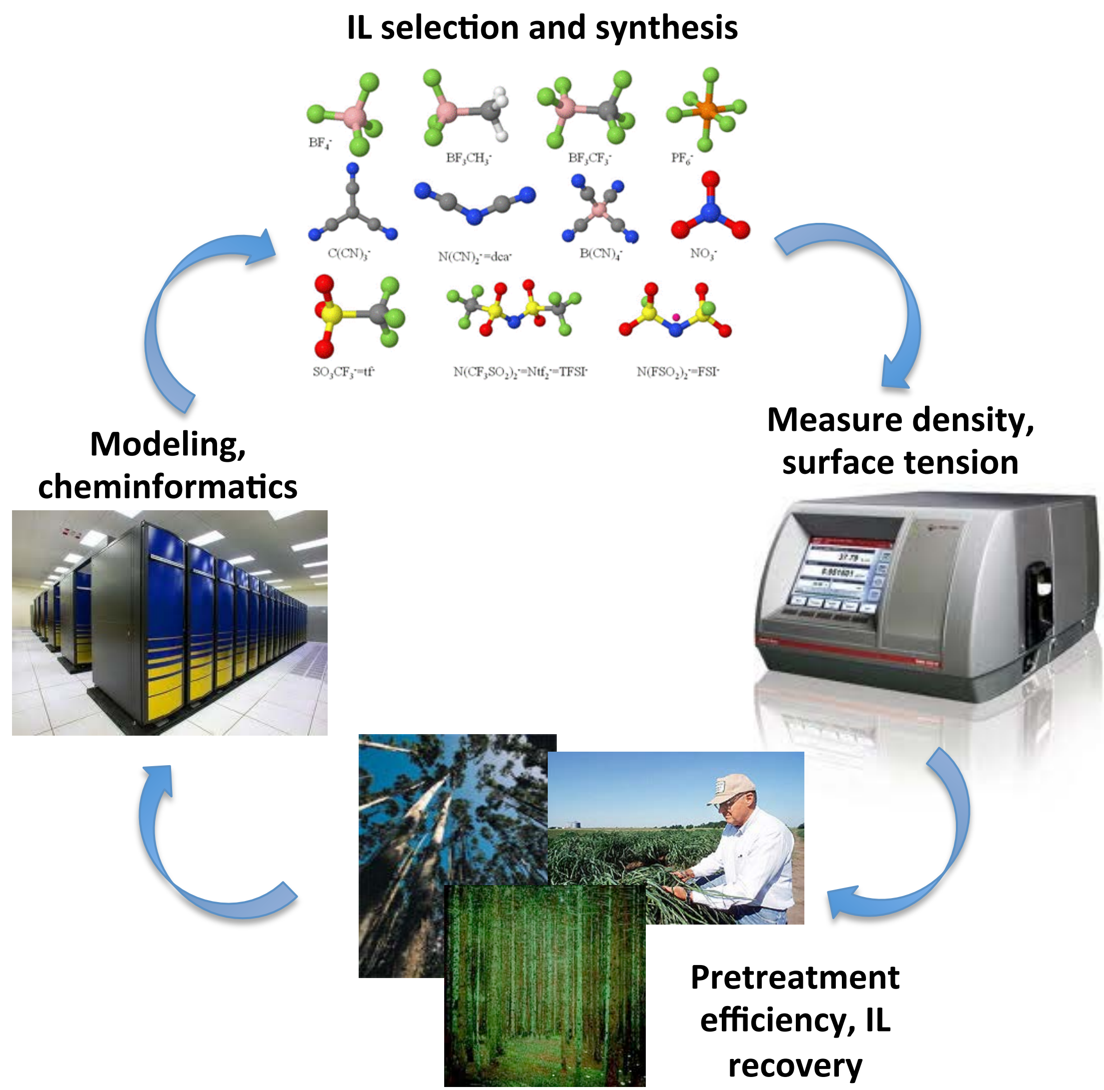
  - Higher solids loading lowers CAPEX and OPEX
- Reduce IL price and use
- Develop better IL recycling techniques and technologies (research phase separation, other ways to extract sugars from IL, etc.)
- Reduce cost of enzymes (they still represent up to 24% of raw material costs)
- Develop integrated systems approach for downstream operations

Discovery and Screening of Low-Cost, High-Performing ILs

- **Challenge: The most effective ILs known to date have limits and are expensive**

- **Solution: Discovery of new ILs with optimal properties**

  - ➢ **Screen new ILs synthesized**
  - ➢ **Determine physicochemical properties and generate cheminformatic training set**
  - ➢ **Evaluate pretreatment performance**



IDENTIFYING AND DEVELOPING COST-EFFECTIVE ILS

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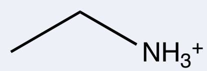
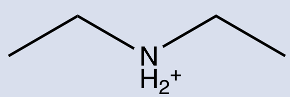
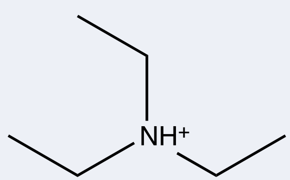
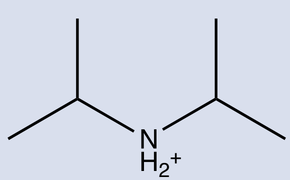
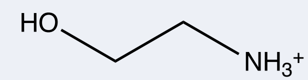
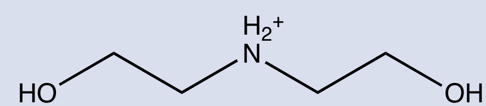
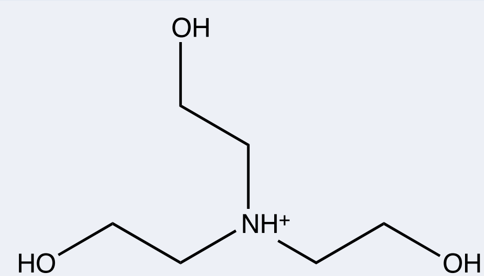
U.S. DEPARTMENT OF ENERGY

Goal: Design, synthesize and screen new ionic liquids that:

1. Compare favorably in performance to our current gold standard [C_2mim][OAc]
2. Do not require anhydrous conditions (operate effectively at 20% H_2O)
3. Compete in cost with commonly used industrial reagents

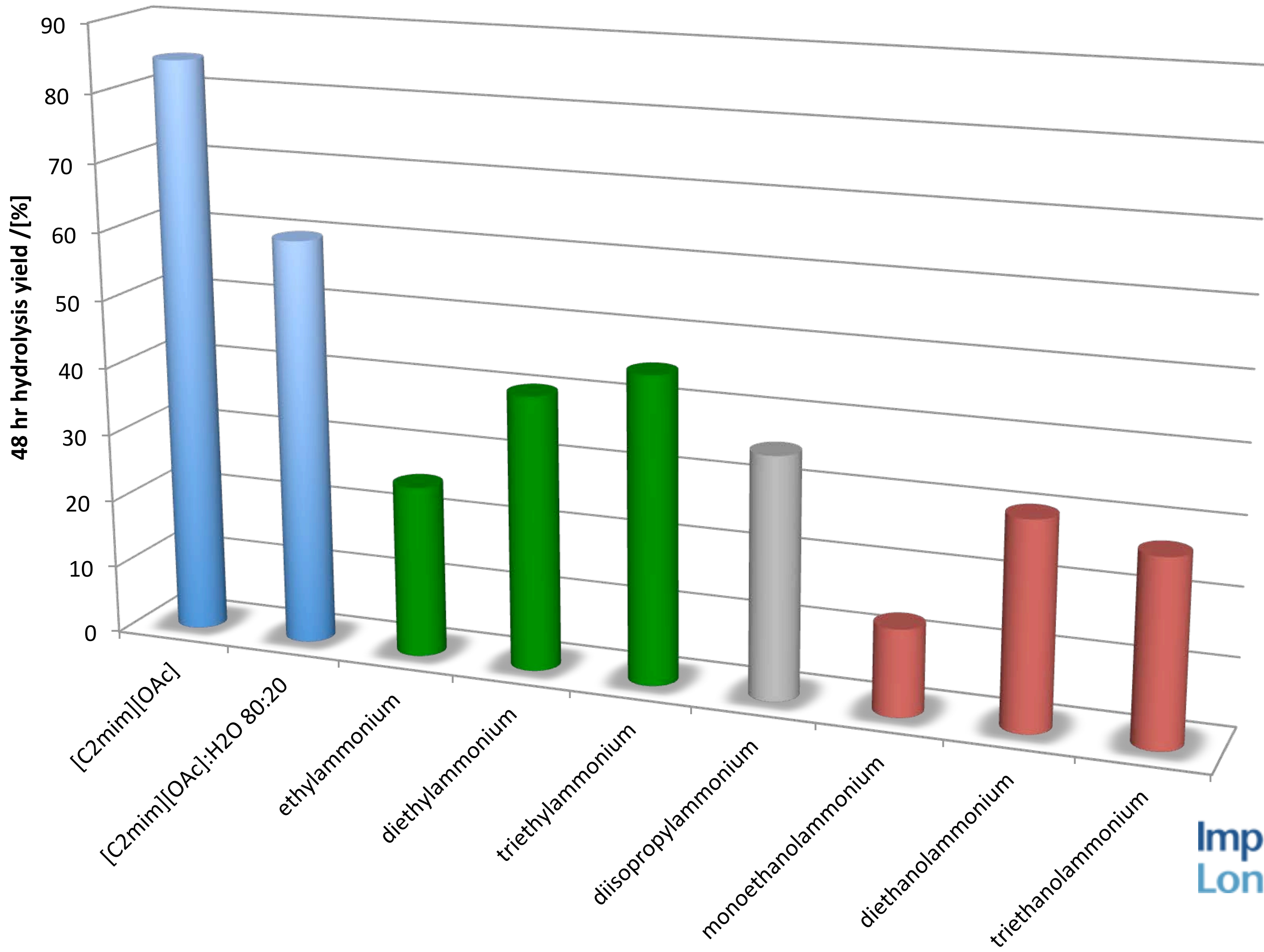
$HSO4^-$ anions (good delignifiers) systematically varied cation, to understand mechanisms.

ethylammonium	
diethylammonium	
triethylammonium	
diisopropylammonium	

monoethanolammonium	
diethanolammonium	
triethanolammonium	

Imperial College London

80:20 Triethylammonium:H_2O mixture is ~80% as effective as 80:20 [C_2mim][OAc]:H_2O……



Pretreatment conditions: 120 ^{o}C, 2 hours, 10% loading
Saccharification conditions: 50 ^{o}C, 1% glucan loading, 72 hours, CTec2 20 mg/g glucan, HTec2 1:10

….AND COSTS $0.75 PER KG VERSUS $20

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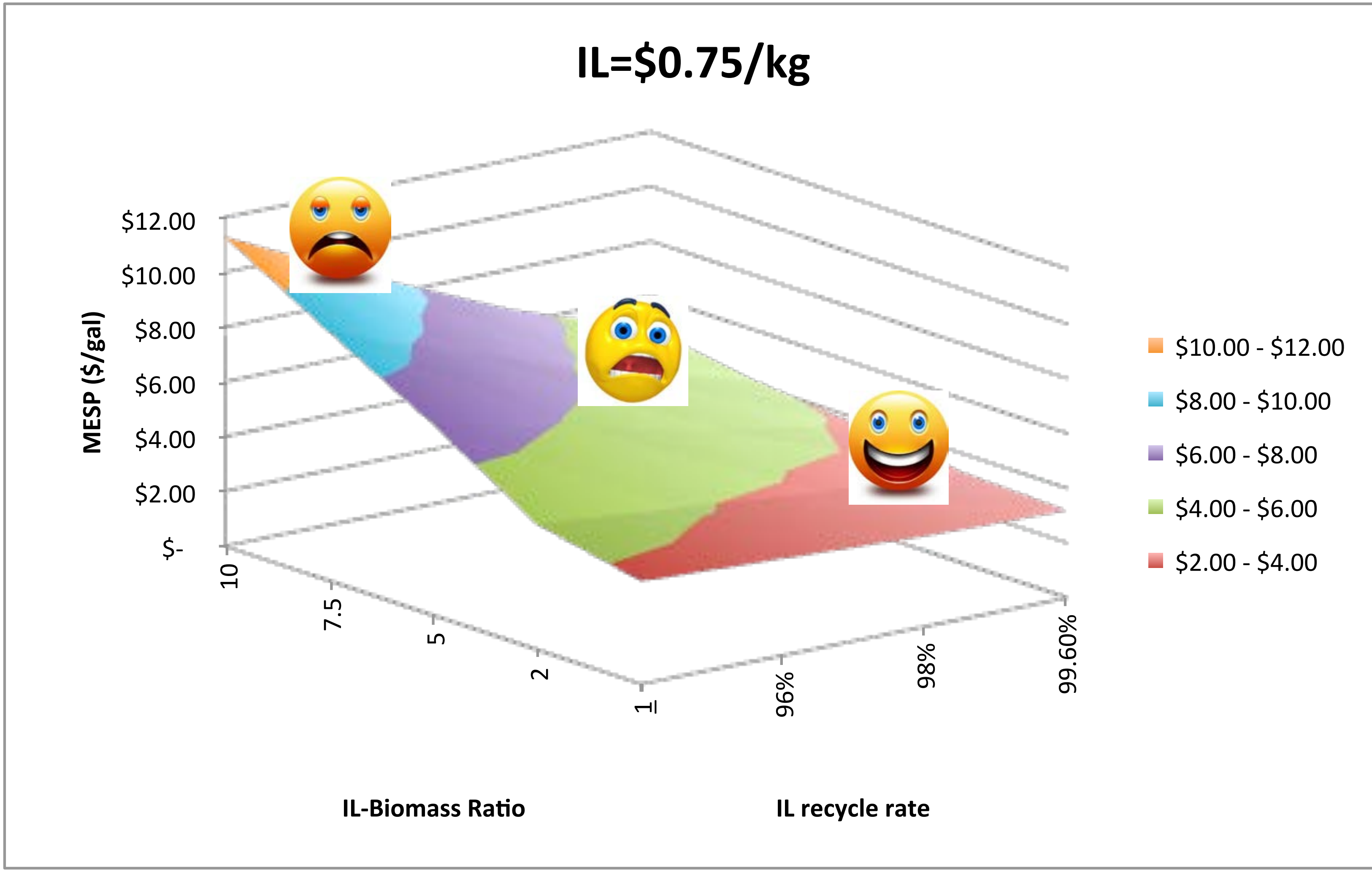
Ionic liquid		Cost /kg
$[C_4C_1im][PF_6]$ (Sigma-Aldrich)	(250g)	$2000
$[C_2mim][OAc]$ (Sigma-Aldrich)	(1kg)	$850
$[(C_8)_3C_1N][Br]$ (Solvent Innovations)	(100T)	$30
$[C_2mim][OAc]$ (BASF)	(best case bulk estimate)	$20
$[C_4mim][HSO_4]$ (BASF)	(best case bulk estimate)	$2.5

TRIETHYLAMMONIUM HYDROGEN SULPHATE	Cost/kg
Raw materials: H_2SO_4 Triethylamine	$0.04 $1.45
Process costs	$0.01
TOTAL COST	**$0.75**

Imperial College London

IMPACT OF IL = $0.75/KG

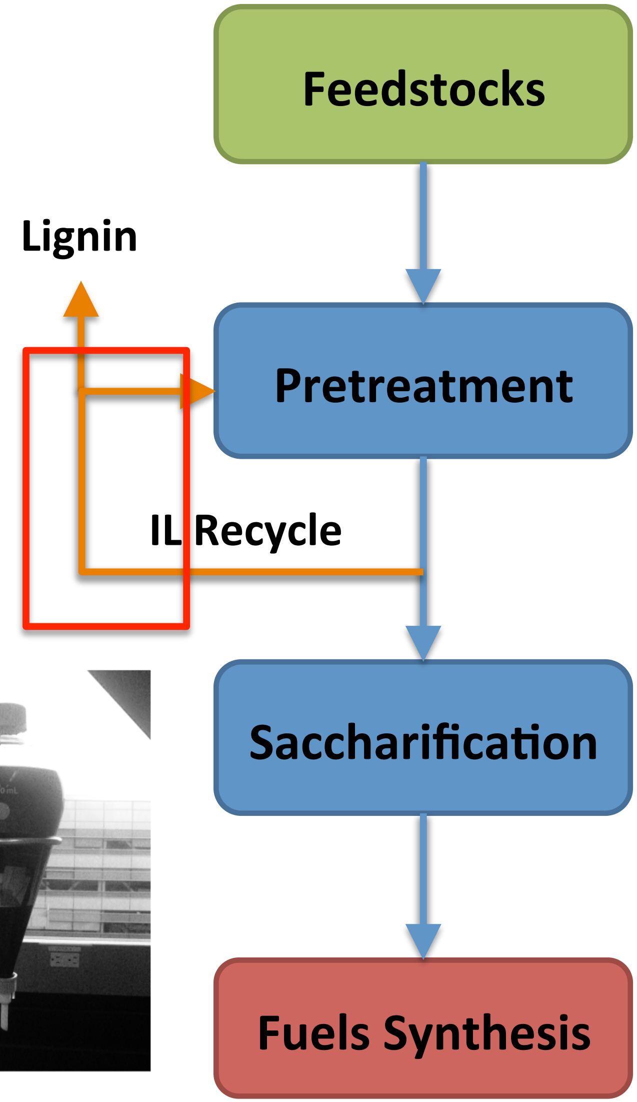


Developing Solutions to Address Economic and Scientific Challenges

- Reduce IL price and use
- Increase the solids loading
  - During IL mixing (as shown in this presentation)
  - During saccharification
  - Higher solids loading mean lower CAPEX and OPEX
- Develop better IL recycling techniques and technologies (research phase separation, other ways to extract sugars from IL, etc.)
- Reduce the contribution of enzymes (they still represent up to 24% of raw material costs)
- Develop integrated systems approach for downstream operations

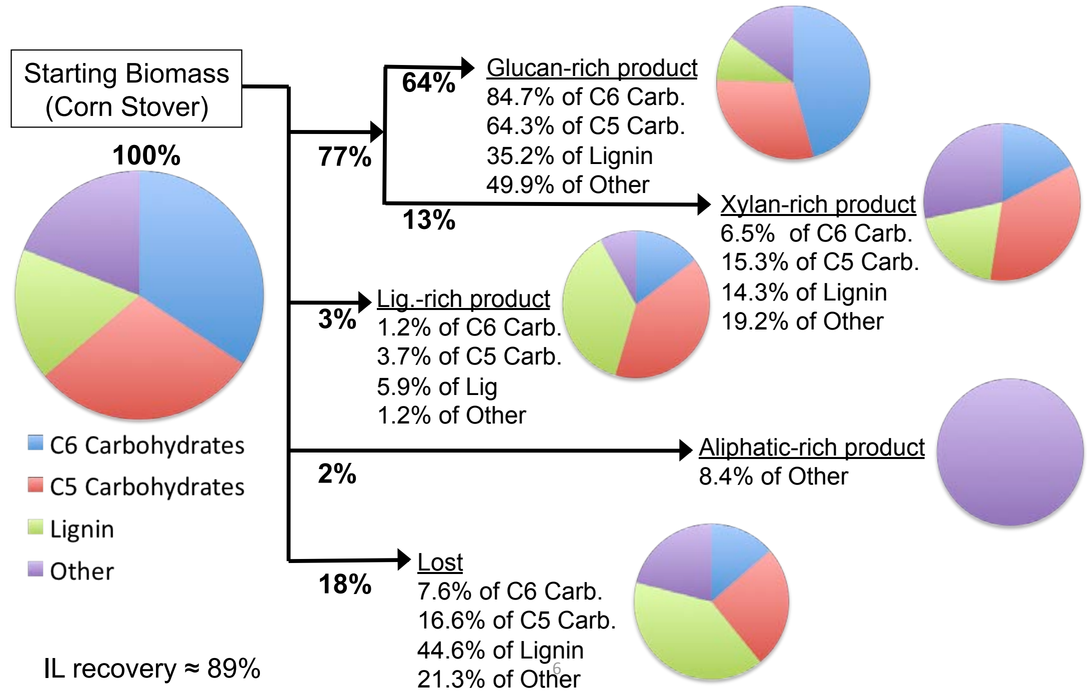
IL Recovery Methods

- **Challenge: Need to recover and reuse ionic liquids after use**
- **Solution: Develop techniques based on liquid-liquid extraction**
  - ➢ **Minimize requirements for energy intensive distillation**
  - ➢ **Generate lignin as a separate product stream**
- **Future directions: evaluate membrane based separations**



Establishing Routes to Efficient IL Recovery and Recycle

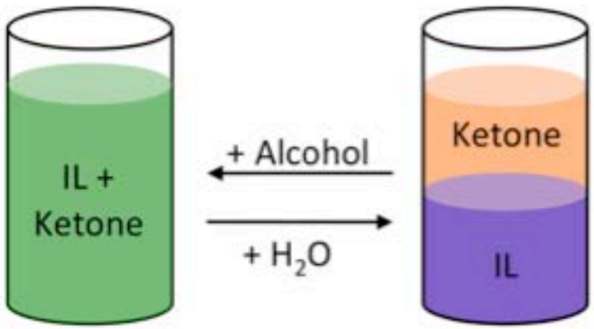
- **Challenge: IL must be recovered and recycled**
- **Solution: Demonstrated ~90% IL recovery and IL maintains pretreatment efficacy.**
    - ➢ **Biomass fractionation can be tailored to desired output streams.**
    - ➢ **<1% IL degraded during pretreatment at these conditions**



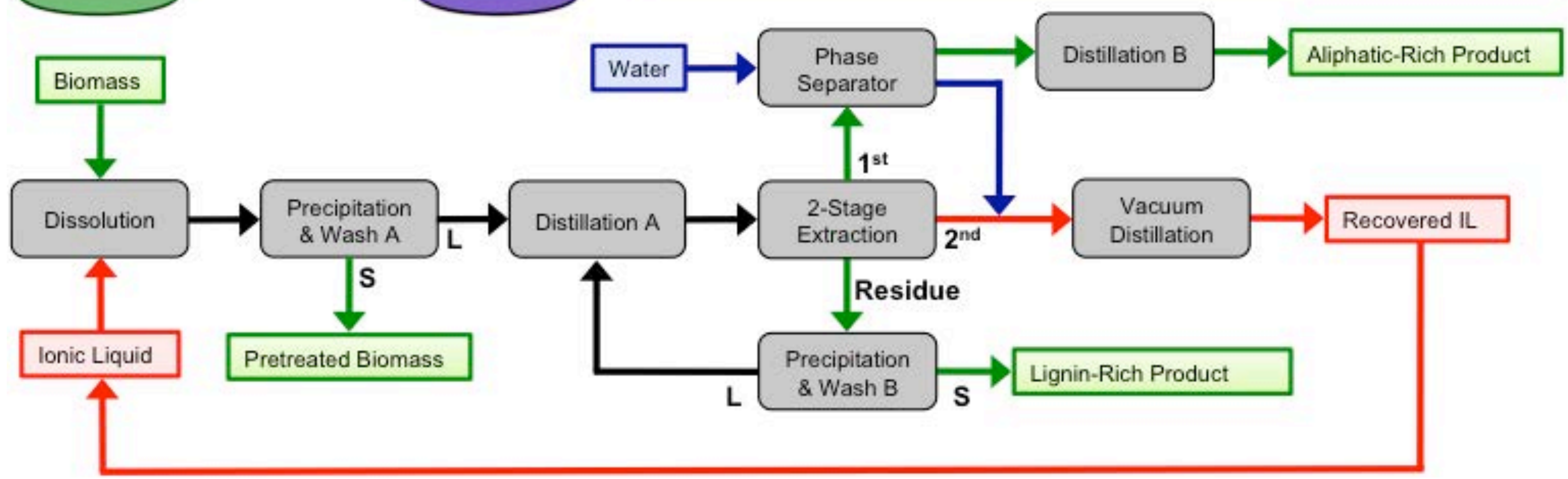
Composition and disposition of corn stover after IL pretreatment utilizing new [C_2mim][OAc] IL for 3 hours at 140 °C. A Xylan-rich product is obtained from a water wash of pretreated solids.

Dibble et al., A facile method for the recovery of ionic liquid and lignin from biomass pretreatment, *Green Chemistry*, 2011,13, 3255-3264.

IL RECOVERY USING WATER-IL-KETONE MIXTURES



Phase switching behavior in a quaternary IL-ketone-water-alcohol system was used to recover IL solutes



Challenges

- Multiple stage process costly and requires distillation
- Energy consumed can be more than the potential energy of some biomass types

Dibble et al., *Green Chemistry*, 2011,13, 3255-3264.

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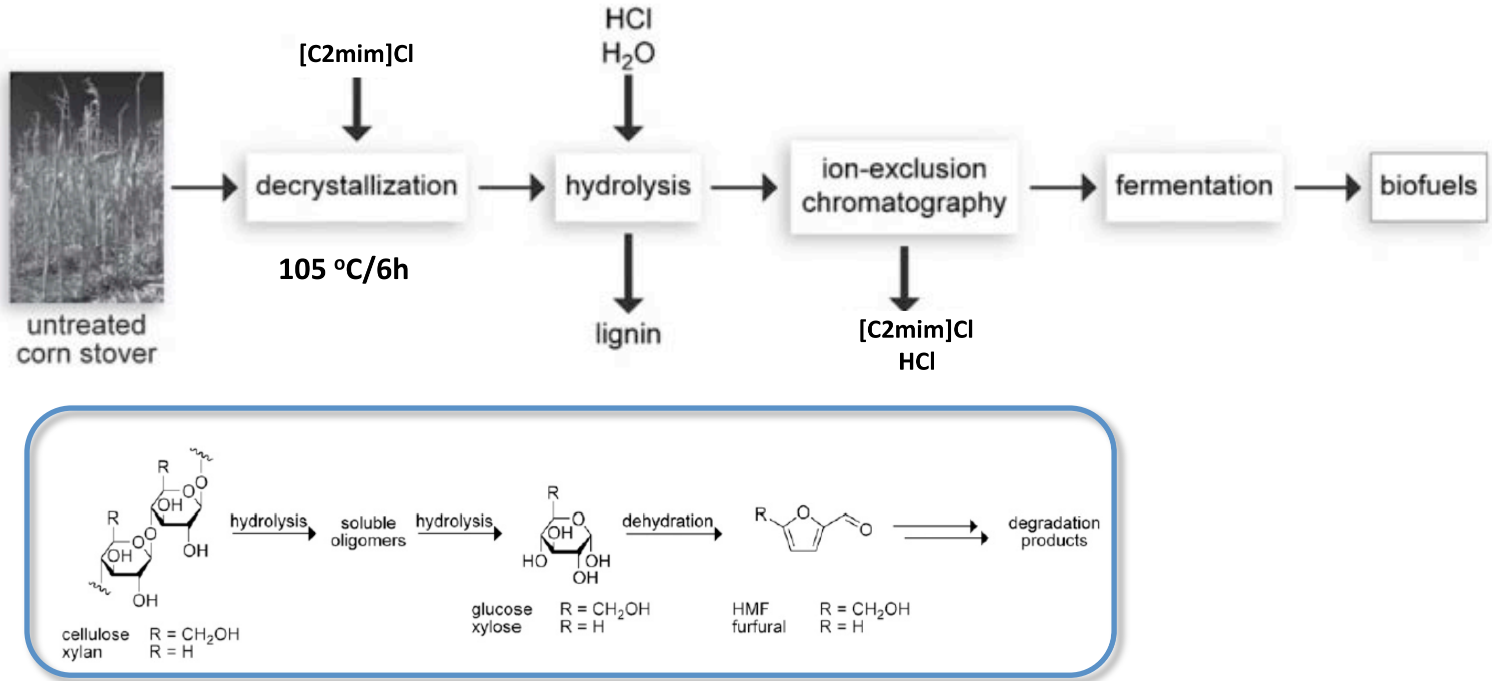
Fermentable Sugars by Acid Hydrolysis

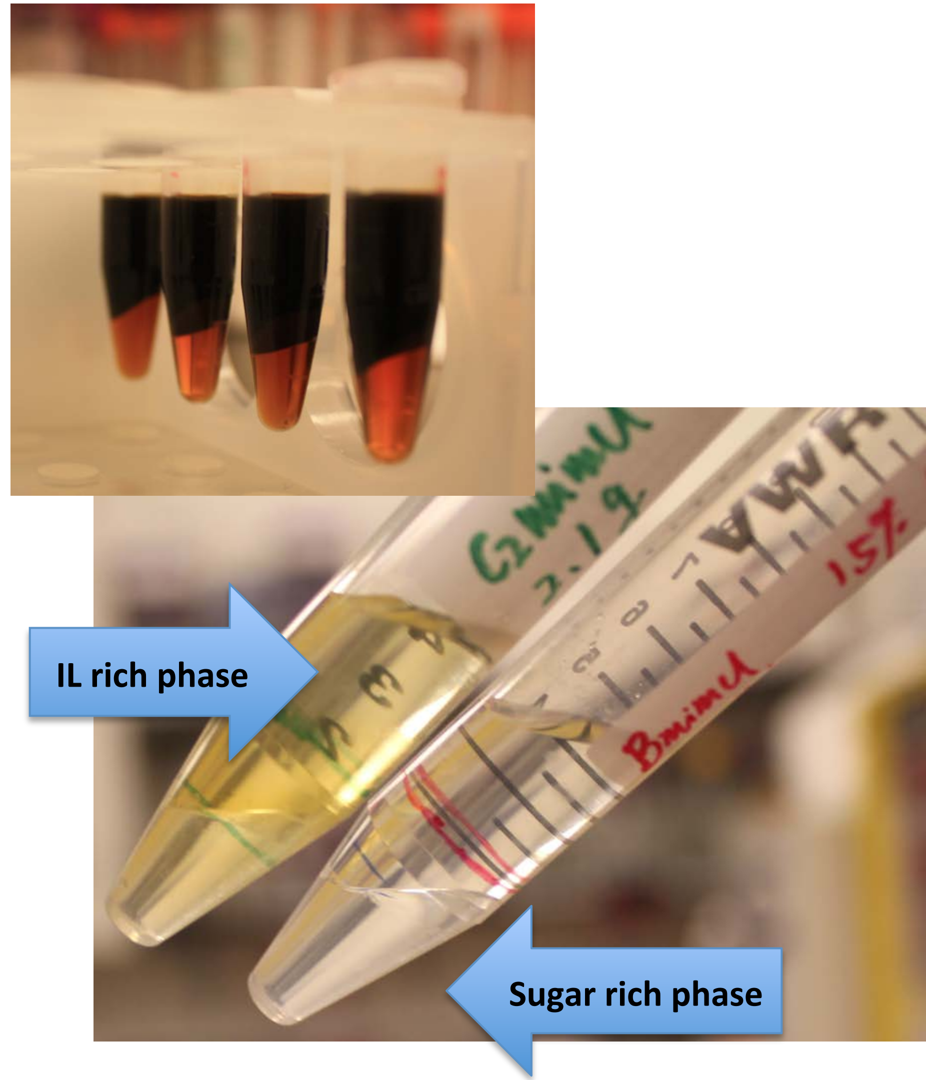


- Directly hydrolyze biomass dissolved in IL with the aid of acid
  - HMF/furfural reduction by titration of water
- Cost effective separation of sugars/products from ILs and IL recycling is a challenge

Binder and Raines. PNAS (2010)

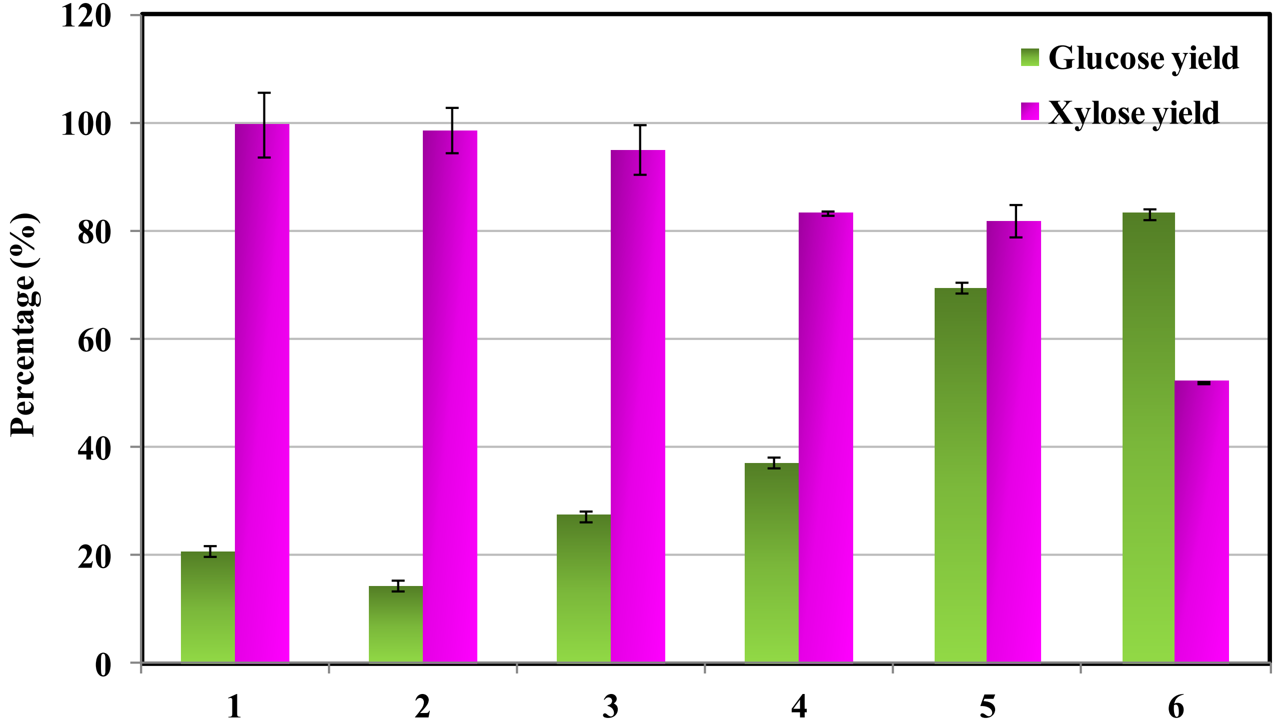
IL Recovery using Aqueous Biphasic (ABP) Systems

- **Expand upon initial results obtained in Years 1-4**
- **Develop process technology based on ABP**
- **Increases IL recovery and recycle**
- **Can be integrated with "one-pot" approach to sugar production**



N. Sun et al., *Biotechnology for Biofuels, 2013, 6:39*.

Higher Pretreatment Temperature Enhances Sugar Yield



- Pretreatment under higher temperature is more efficient for sugar production.
- Xylan is much easier for hydrolysis compared to cellulose. However, with the increase of glucose yield the xylose yield goes down indicating some degradation.
- May indicate that two-stage thermal process is needed to maximize sugar yields.

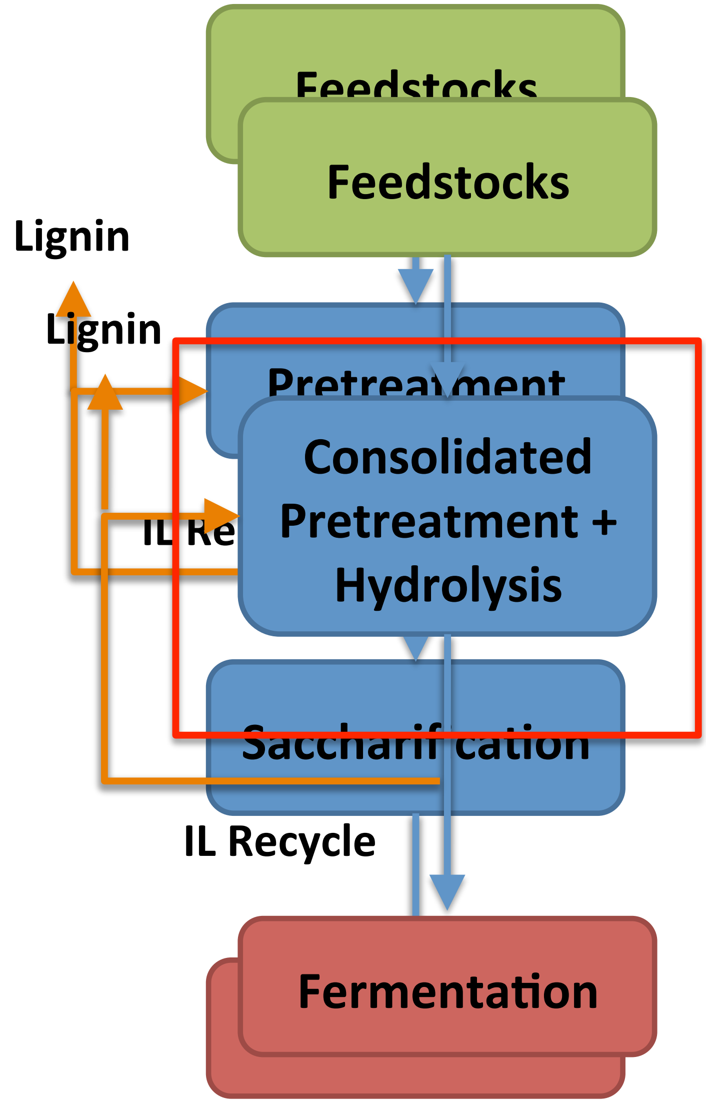
N. Sun et al., *Biotechnology for Biofuels, 2013, 6:39*.

Developing Solutions to Address Economic and Scientific Challenges

- Reduce IL price and use
- Increase the solids loading
  - During IL mixing (as shown in this presentation)
  - During saccharification
  - Higher solids loading mean lower CAPEX and OPEX
- Develop better IL recycling techniques and technologies (research phase separation, other ways to extract sugars from IL, etc.)
- Reduce the contribution of enzymes (they still represent up to 24% of raw material costs)
- Develop integrated systems approach for downstream operations

Alternative IL Process Technologies

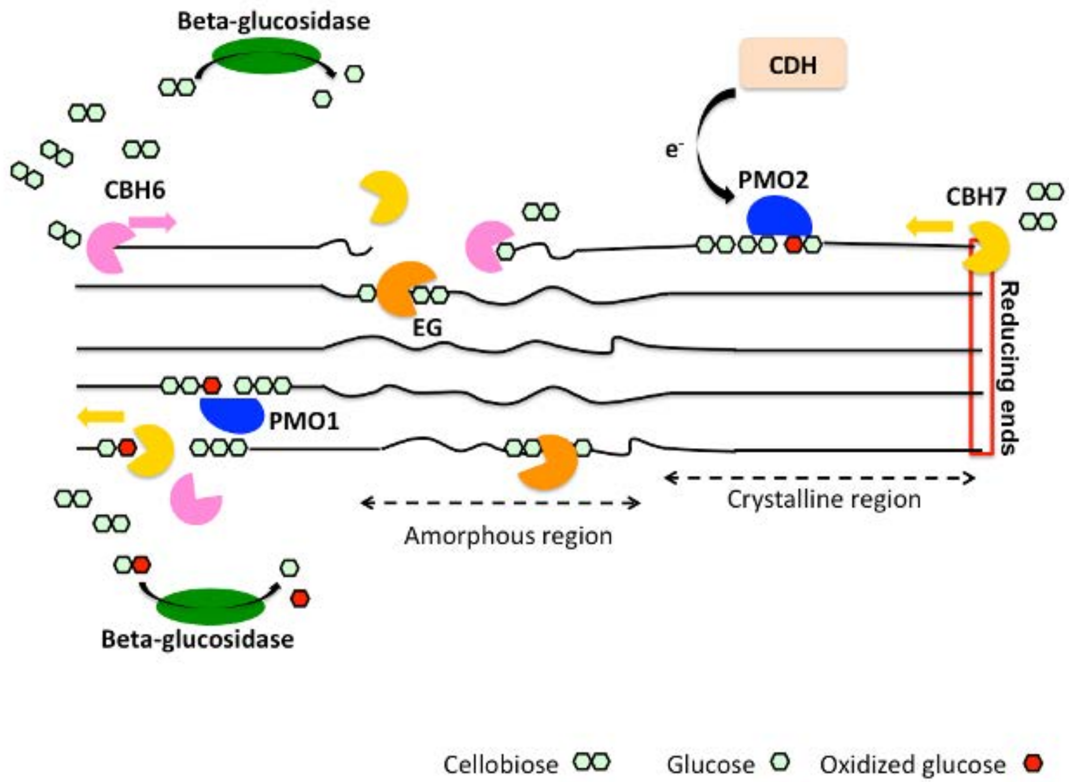
- Challenge: "One-pot" approach requires the development of IL tolerant and thermostable enzymes
- Solution:
  - ➢ Use sequence- and structure-based information as methods to improve stability
  - ➢ Targeted discovery of novel enzymes from microbial communities
  - ➢ Develop enzyme cocktails at high solids loading and relevant processing conditions



Cellulose Hydrolysis to Glucose Requires a Mixture of Enzymes

Enzymes needed to form robust "cocktail":

- **Endoglucanase (EG)**
- **Exoglucanases**
  - ➢ **Cellobiohydrolases (CBH)**
  - ➢ **Cellodextrinases**
- **β-glucosidases**
- **Polysaccharide monooxygenases (PMO)**
- **Cellobiose dehydrogenases (CDH)**



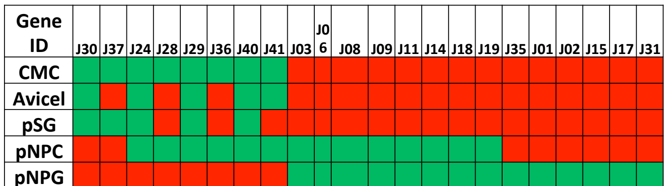
Adapted from Dimarogona et al., 2012

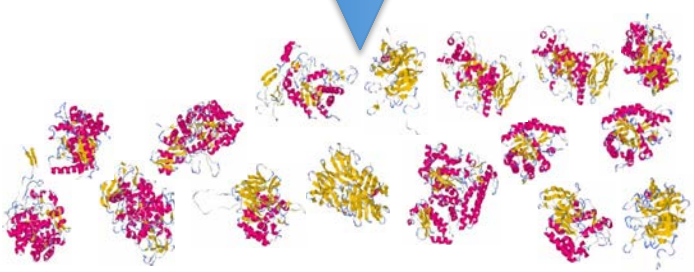
Factors that impact performance:

- **Degree of polymerization**
- **Crystallinity index**
- **Presence of lignin**

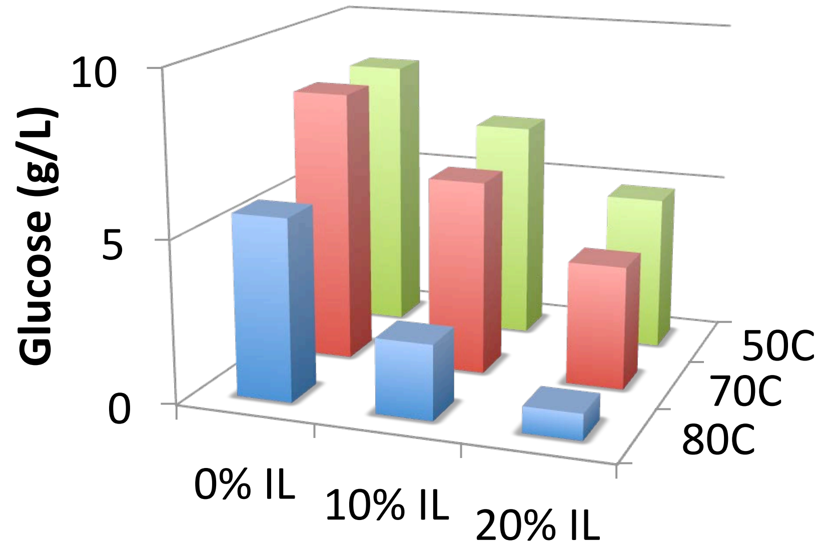
We Have Developed a Cellulase Cocktail that is IL- and Thermo-tolerant

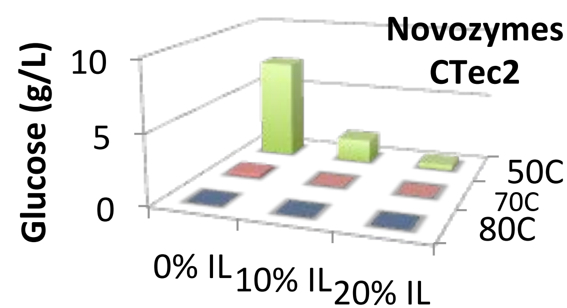
Target genes found in thermophilic compost metagenome expressed and profiled





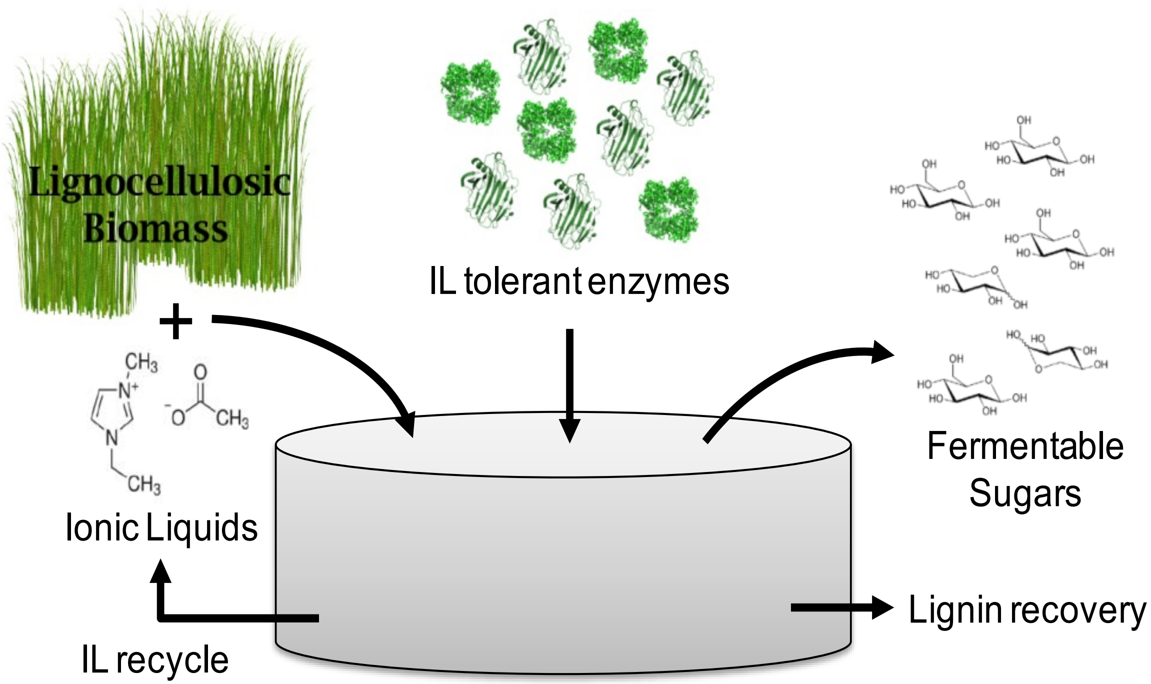
Recombinant thermophilic cellulases from Enzyme Optimization team

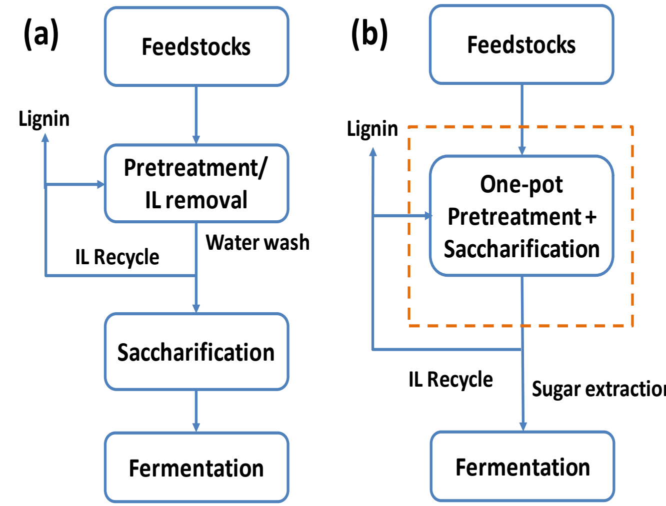


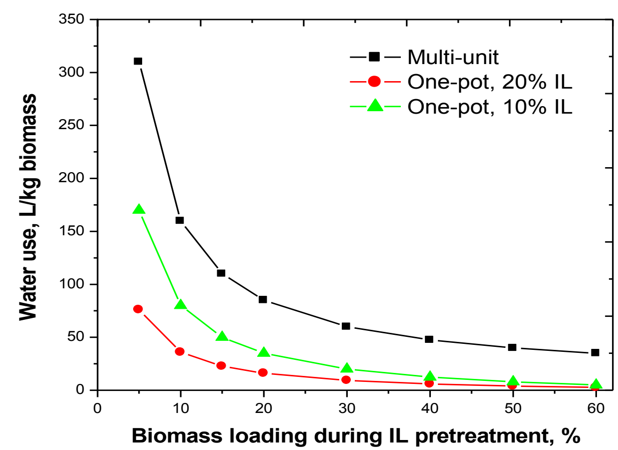


Joshua I. Park et al., A Thermophilic Ionic liquid-tolerant Cellulase Cocktail for the Production of Cellulosic Biofuels, *PLoS ONE*, 2012, 7(5), e37010

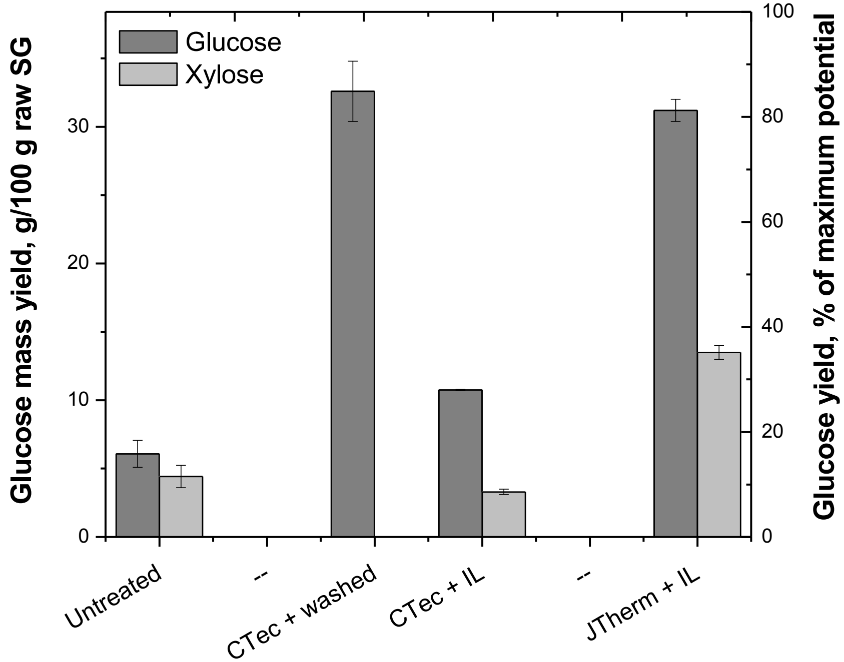
Assembling the Pieces: One-pot Lignocellulosic Processing using JBEI Platform Technologies



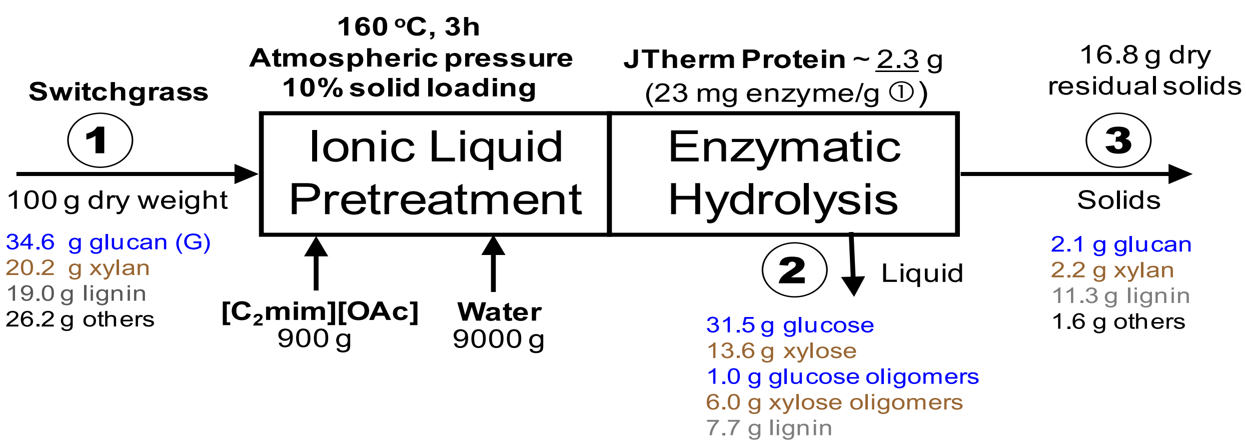




ONE-POT LIGNOCELLULOSIC PROCESSING USING JBEI PLATFORM TECHNOLOGIES



- Wash-free
- No pH adjustment needed
- Glucose and xylose yields comparable to traditional IL pretreatment and saccharification using commercial enzymes
- Selective sugar extraction
- Lignin streams open to recycle and valorization
- Batch mode → continuous mode



Overall yield of glucose from liquid streams = 81.9%

Overall yield of xylose plus xylooligomers from liquid streams = 85.4%

SUMMARY

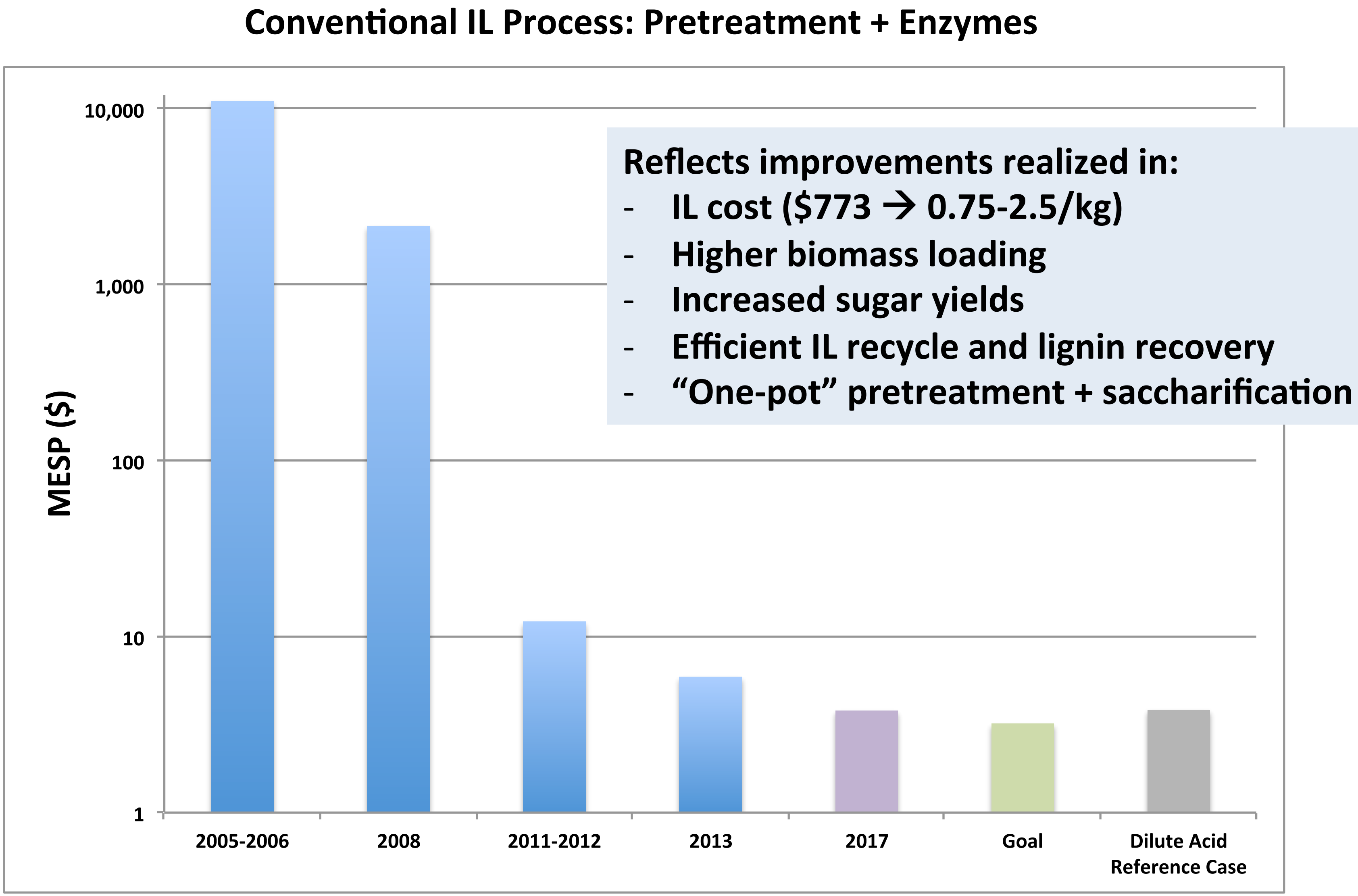
- ILs are a promising pretreatment technology
  - No drop in performance as a function of scale
  - Need to develop an integrated conversion process with all downstream functions tolerant to residual ILs

- ILs provide a unique opportunity to tailor pretreatment and reaction chemistry

- Several challenges remain, primarily around cost of the process
  - Innovations on new IL synthesis routes
  - Cheaper combinations of anions and cations
  - Renewable ionic liquids

- IL pretreatment technology commercialization underway

BENCHMARKING: ECONOMICS



IL Pretreatment and Commercialization

- SuGanit
  - Biochemical conversion platform
  - Uses IL soaking of biomass
  - Hydrolysis using enzyme mixtures
  - Lignin recovery after saccharification
- Hyrax
  - ILs used to solubilize biomass
  - HCl catalysts added to liberate sugars
  - Sugar recovery is a challenge
  - Start-up from lab of Prof. Raines at UW-Mad

Acknowledgments

- JBEI: Seema Singh, Ning Sun, Jian Shi, Kim Tran, Mike Kent, Rich Heins, John Gladden, Ken Sale, Steve Singer
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- INL: Richard Hess, Vicki Thompson