2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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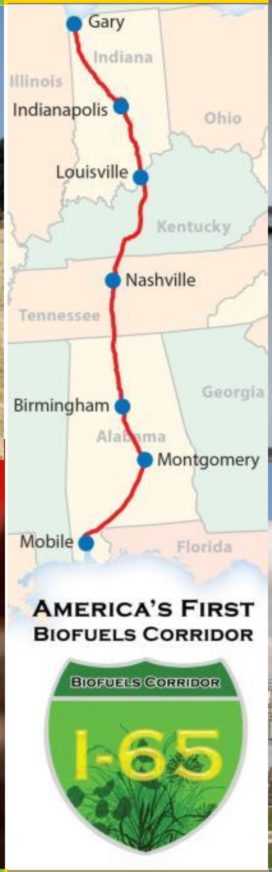

Biochemical Feedstock Supply Interface

May 20, 2013

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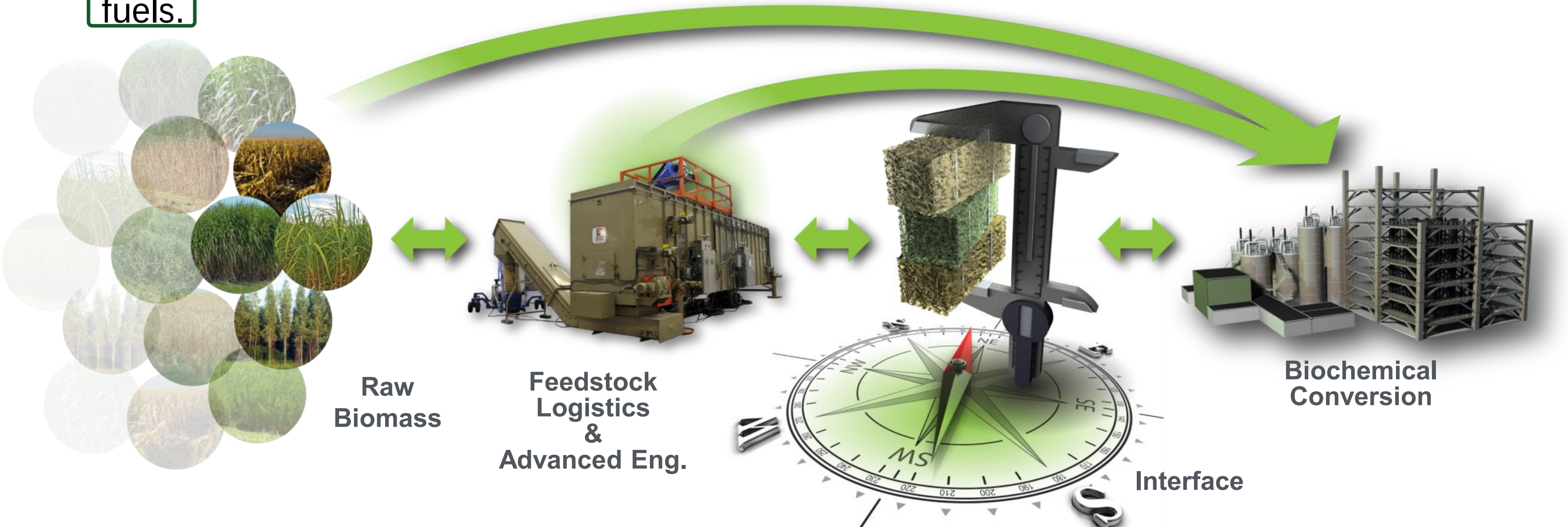
Nick Nagle, NREL

Goal Statement

Goals: Support Biochemical Conversion Pathway: "reducing the cost of converting lignocellulosic biomass to sugars and other fuels intermediates."

1 - Facilitate establishment of pathway(s) toward optimization and cost-reduction; 2 - Develop tools & models to evaluate feedstock costs & quality for BC conversion process (biological, chemical, catalytic upgrading)

- Support development of material performance specifications and rapid characterization tools, which are needed to facilitate effective material conveyance from raw resource to finished fuels.



3 - Integrating technologies & solving key incongruities that require collaboration of FS & BC Platforms

Quad Chart

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Timeline

	INL	*NREL*
Project start:	2005	2006
Project end:	2022	2022

Barriers

- Ft-G Feedstock Quality and Monitoring
- Ft-J Biomass Material Properties
- Bt-B Biomass Variability
- Bt-C Biomass Recalcitrance

Partners

- Idaho National Laboratory (INL)
- National Renewable Energy Laboratory (NREL)
- USDA, Agricultural Research Service
- DOE Regional Feedstock Partnership
- MBI International
- Universities
  - Colorado State University
  - University of Nevada, Reno
  - Swedish University of Agricultural Sciences

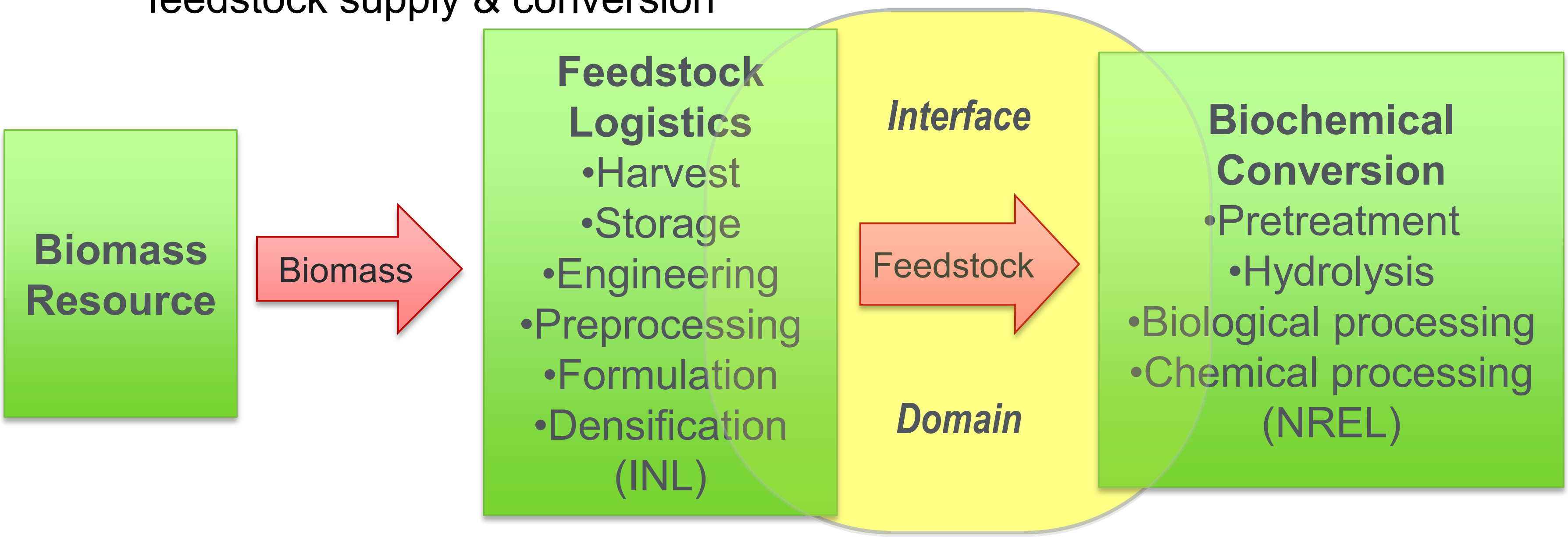
Budgets

	*INL**	*NREL**
FY11	$1,020K ($120K)	$500K
FY12	$1,050K	$800K
FY13	$1,050K	$450K

Total values shown; equipment in ( )
*DOE share: 100%

Project Overview

- Develop & define feedstock specifications (material performance)
  - Produce, characterize & distribute feedstocks, engineered and advanced materials
  - Populate data sets for techno-economic & life cycle analyses
- Develop & deploy analytical screening tools
  - For feedstocks: moisture, ash, lignin, extractive, glucan, xylan, reactivity
- Interface (i.e. cross-cutting) sub-projects & programs
  - Assess preconversion & conversion processes for benefits & costs to feedstock supply & conversion



1 - Project Approach

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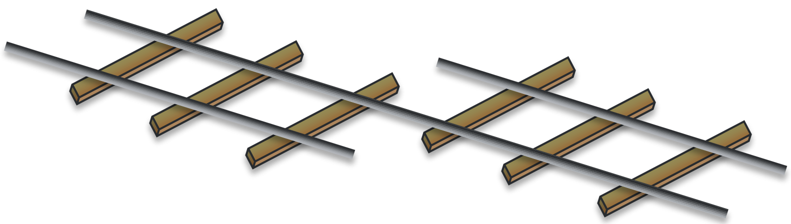
Overall Technical Approach: Focus on bounding variability, determining effect of logistical operations and preprocessing on conversion processes, integrating the requirements of BC conversion and limitations of FS.

- Produce, characterize & share feedstocks (FS consistency)
- Assess preconversion processes for benefits & costs on feedstock supply & conversion
- Assess impact of feedstock quality characteristics/ variability on pretreatment & conversion efficiency, yield & sugars quality
- Continued develop of methods for determine feedstock quality characteristics and variability
- Exchange-point screening tool development: Ash content, Moisture content, Composition, Recalcitrance/Reactivity



Success Metrics

- Meeting or exceeding cost & quality targets for feedstocks & fuels
    - Accomplished by optimizing preconversion operations and feedstock formulations to access full local supply of all low cost resources

1 - Project Approach

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Transition to achieve both cost and volume targets for feedstocks requires new approaches for feedstocks

2007-2012	2013-2022
Single feedstock focus	Blended feedstock from multiple biomass resources
Best Mgmt Practices used to manage feedstock compositional variability	Engineered systems used to control feedstock compositional variability
Minimum feedstock specification	Material performance guarantees
Raw biomass	Engineered formats
Lab-based tool development	Tool development for rapid screening & exchange applications
End product from feedstock conversion - *Ethanol*	End product from feedstock conversion - *Multiple hydrocarbon intermediates*

2 - Technical Accomplishments: The R&D Toolbox

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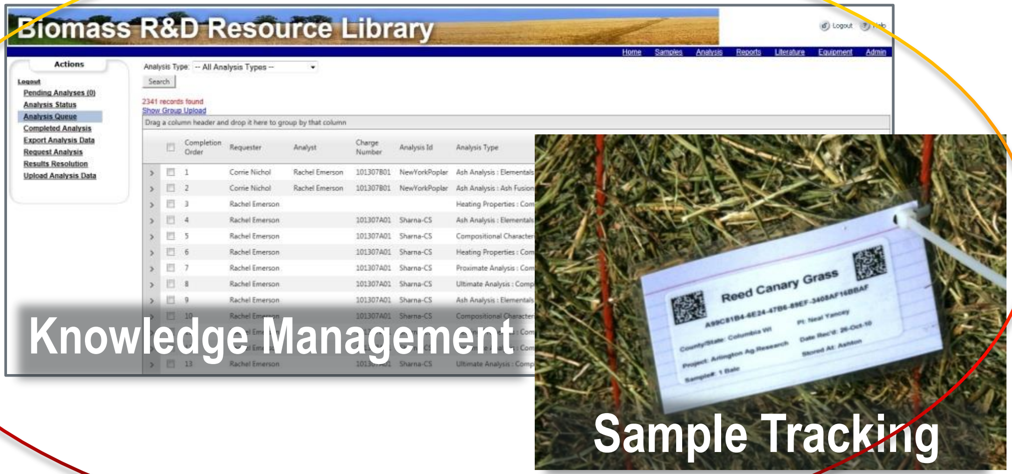
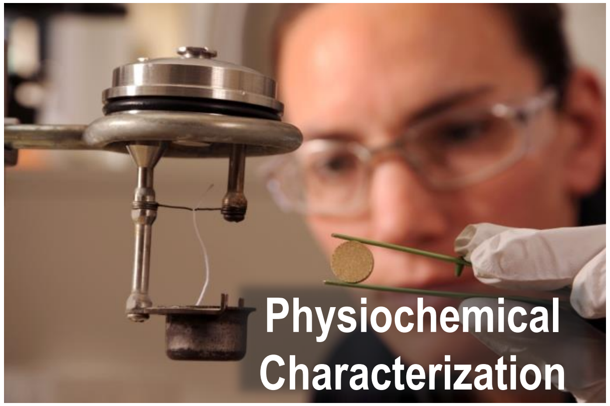
Sample/Data Control and Storage



Preprocessing, Densification and Characterization



2 – Biomass Resource Library

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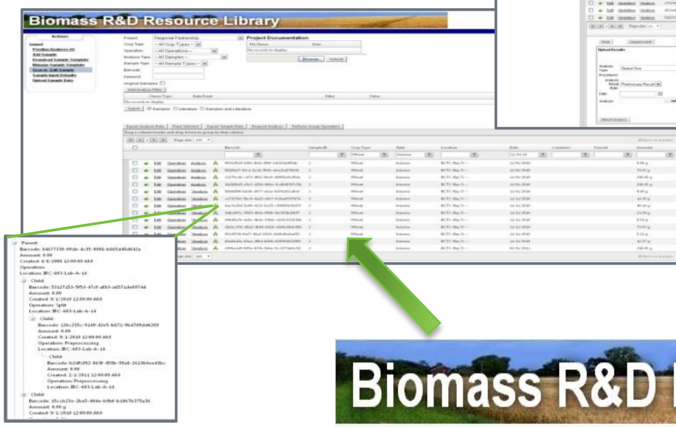
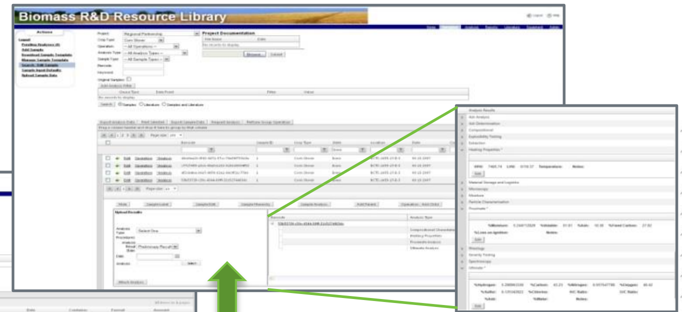
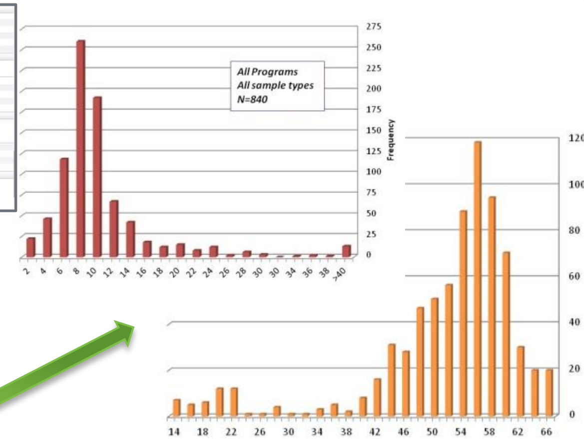
Store and Retrieve Sample Info & Data





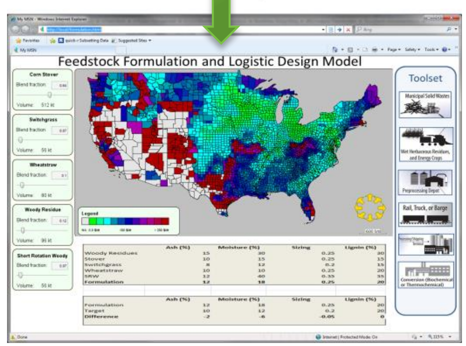
Store & Retrieve Sample Physiochemical Data



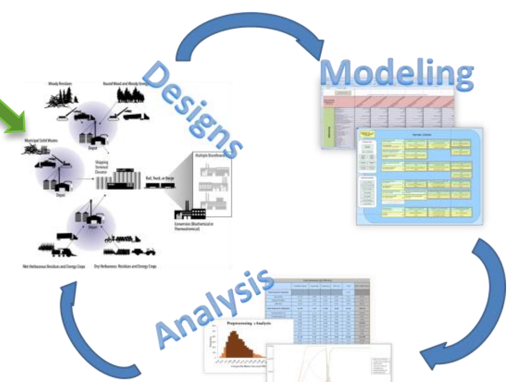
Statistical Analysis

Integrated with KDF

High impact analytics that provides core platforms & Industry with insight & guidance



Least –Cost Formulation Model



Biomass Logistics Model

2 - Bounding Quality Attributes & Variability

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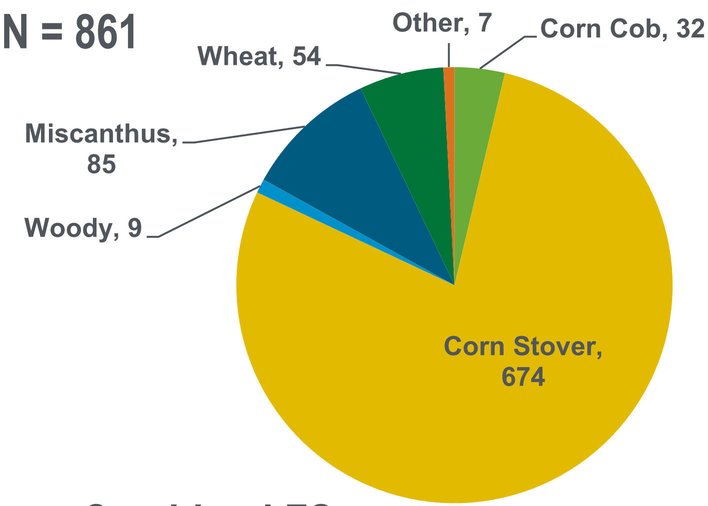
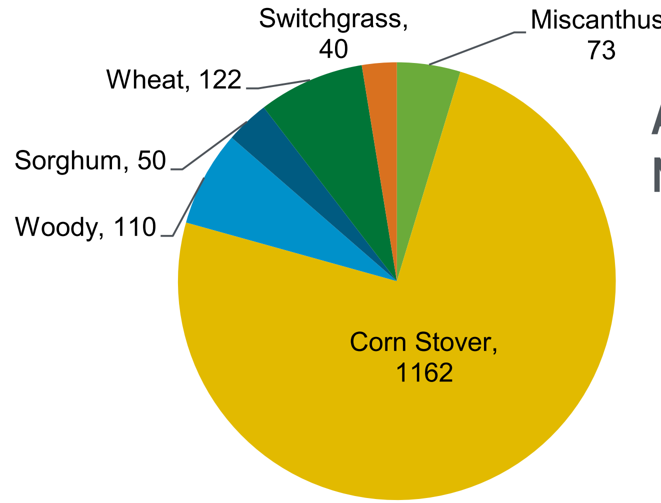
Compositional Analysis

N = 861

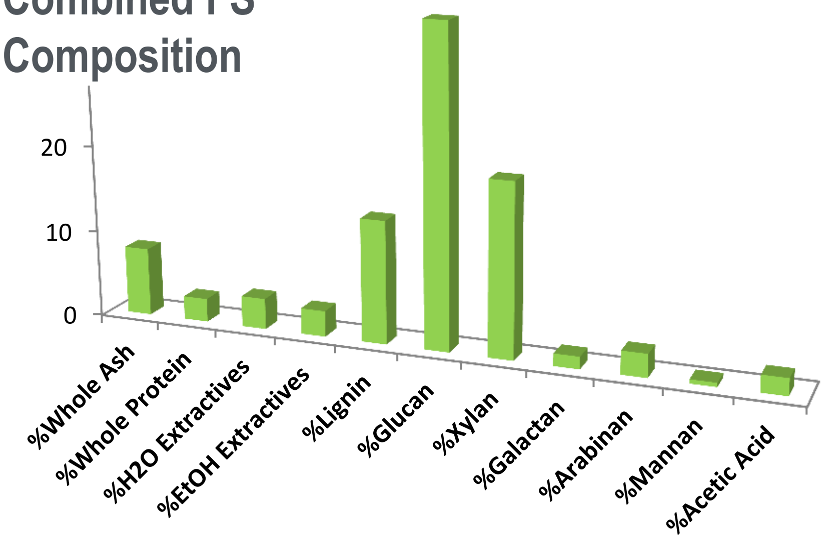


Ash Determination

N = 1557

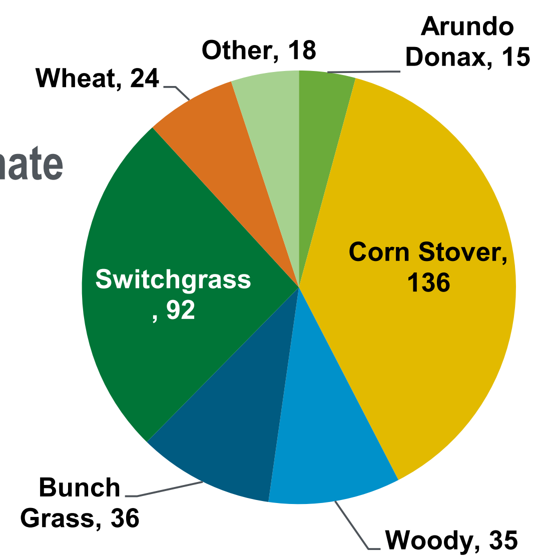


Combined FS Composition



Proximate/Ultimate Analysis

N = 356



2 - Advanced Agronomic Practices: Variability

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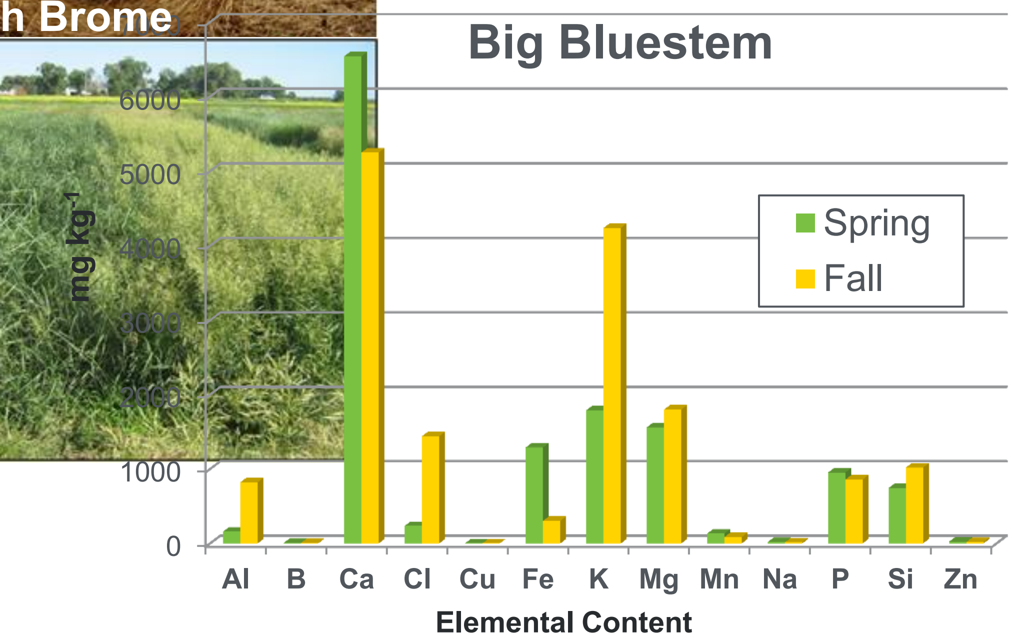
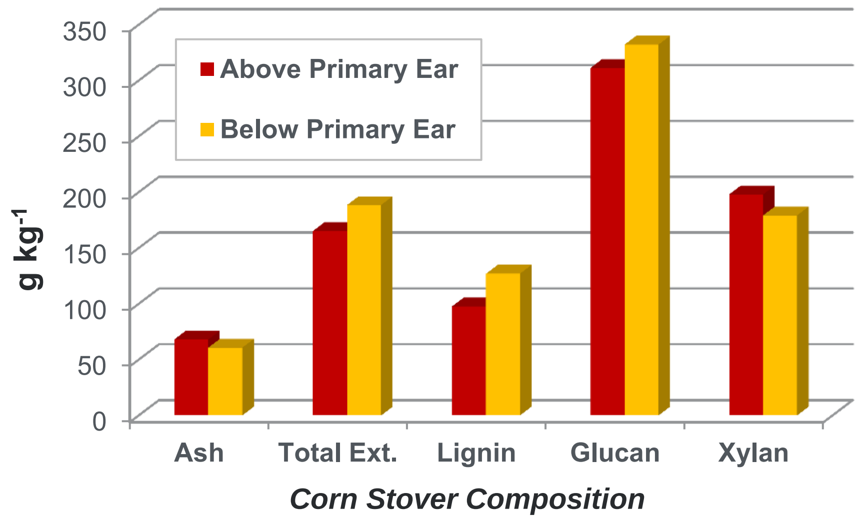
- Understanding impact of delaying harvesting times, "Does Yield and Quality of Big Bluestem and Switchgrass Feedstock Decline Over Winter," *Bioenergy Research*, 2013, accepted.
- Targeted determination of CS variability from eight U.S. location: "Proximate, Ultimate, Calorific and NIR analysis of corn Stover for Eight U.S. Locations" *Bioenergy Research,* 2013, submitted.
- Impact of reduced inputs on plant composition and bioconversion of cool season grasses, "Constraints and Capabilities of No-Till Dryland Agroecosystems as Bioenergy Production Systems," *Agronomy Journal*, 2013,105 (2), 364-376





2 - Advanced Agronomic Practices: Variability

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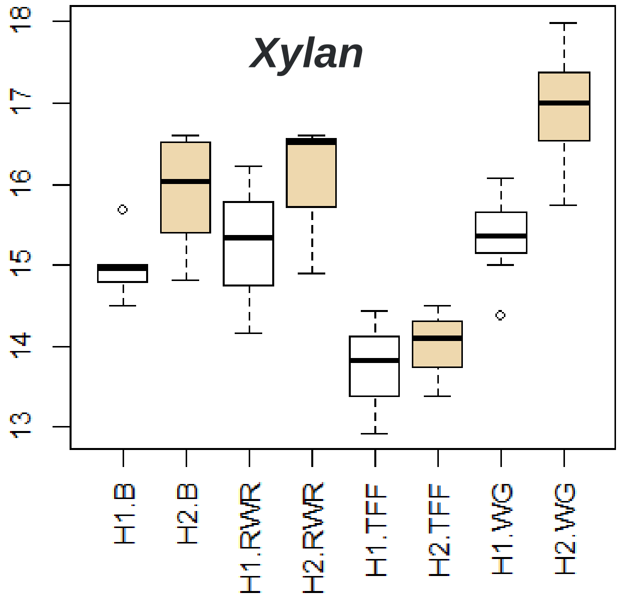
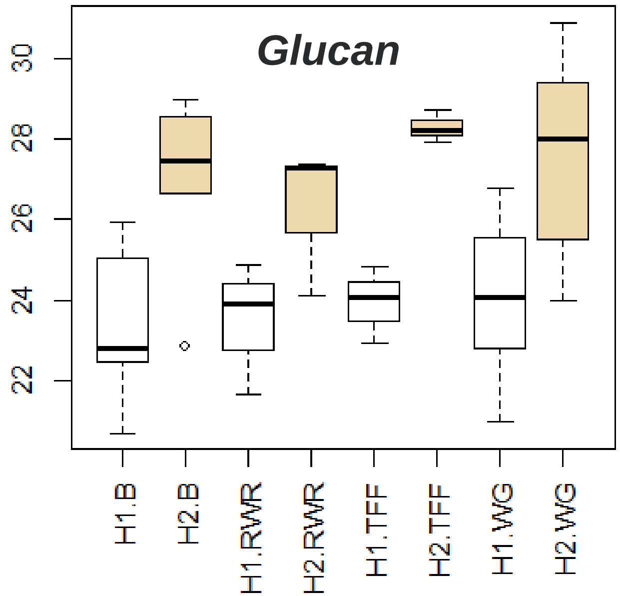




Variability of cool season Grasses (15 species)

4 Grass Families and two harvests:
H1: early June
H2: late June harvest

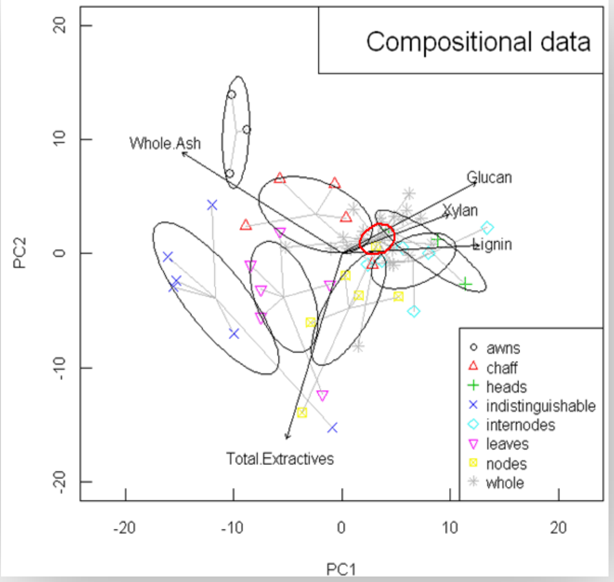
- Multiple factors have an effect on biomass composition
- Variability can not be fully mitigated using best management practices
- Slight changes in composition have significant impact at commercial scale

2 – Advancing Characterization Toolsets

Develop diagnostic tools to screen, characterize and determine the quality characteristics in a cost effective and timely manner.

Why focus on characterization and screening tools?

- Lab-based tools critical to establishing quality attributes and variability
- Rapid screening tools will significantly increase knowledge base
- Exchange-point measurement tools and processing methodologies are critical to mitigating feedstocks variability, ensuring performance guarantees and reducing fuel costs



- Rapid screening: NIR - multivariate analysis (MVA) method used to correlate wet chemistry data
- "Process Relevant" reactivity screening of feedstocks
  - Two step method: ASE 350 dilute acid pretreatment with enzymatic saccharification

2 - NIR Model to Predict FS Composition & Reactivity

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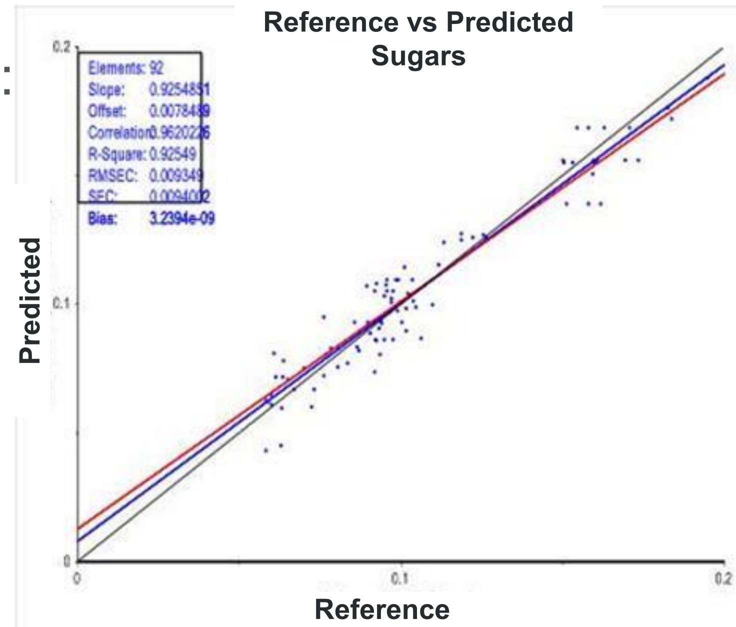
Rapid screening methods provide a high-throughput analysis tool:

•*Provides methodology to determine composition of large number of samples rapidly*

- Multiple predictive NIR models developed:
  - Enhanced corn stover composition
  - Cool season grass composition
  - Wheat composition
  - Mixed feedstocks composition
  - Reactivity* (sugar release)



Herbaceous Feedstock model:

- Corn stover (40)
- Sorghum (40)
- Miscanthus (37)
- Switchgrass (5)
- Rice Straw (8)
- Cool Season Grasses (10)

Spectral treatments	Performance Index & Compositional Components				
	Whole ash	Total Ext.	Lignin	Glucan	Xylan
SNV	87.2	74.5	82.0		
1st derivative				81.2	79.9

2 - High Throughput Reactivity Screening

Goal: Use laboratory-scale equipment to perform “process relevant” reactivity screening of feedstocks

Data must predict performance at larger scales (process relevant)

- Couple FT-NIR for compositional analysis; automated, smaller-scale ASE 350 pretreatment; enzymatic hydrolysis for reactivity screening
- Benchtop reactivity screening for different feedstocks (7) across a range of severity
  - Enzymatically digested PT solids
  - Combined sugar release (Xylose + Glucose) to assess reactivity

Accelerated Solvent Extractor (ASE) 350 system (Thermal Fisher Dionex)

2 - High Throughput Reactivity Screening

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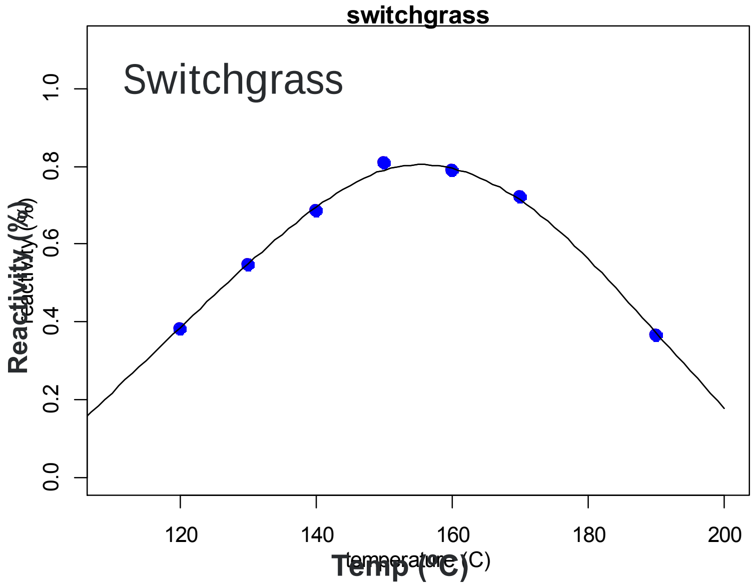
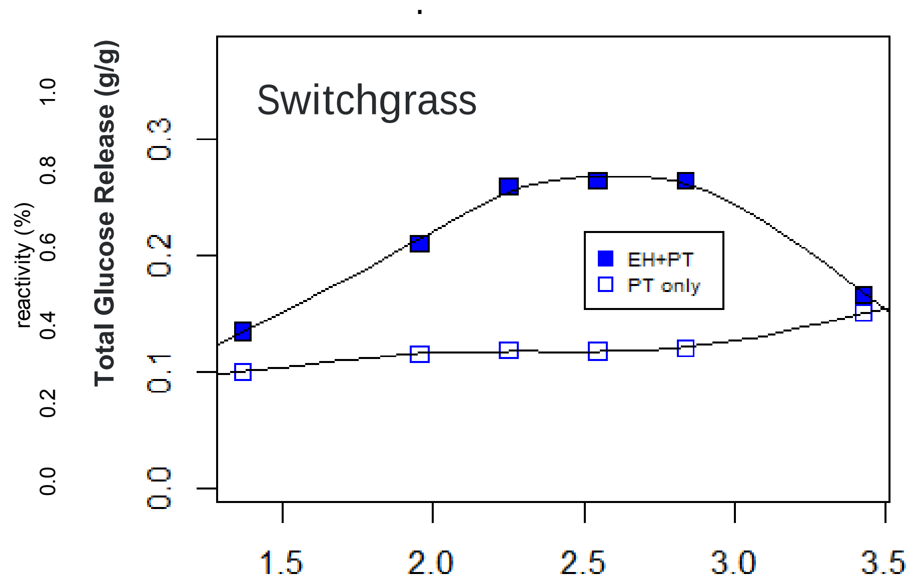
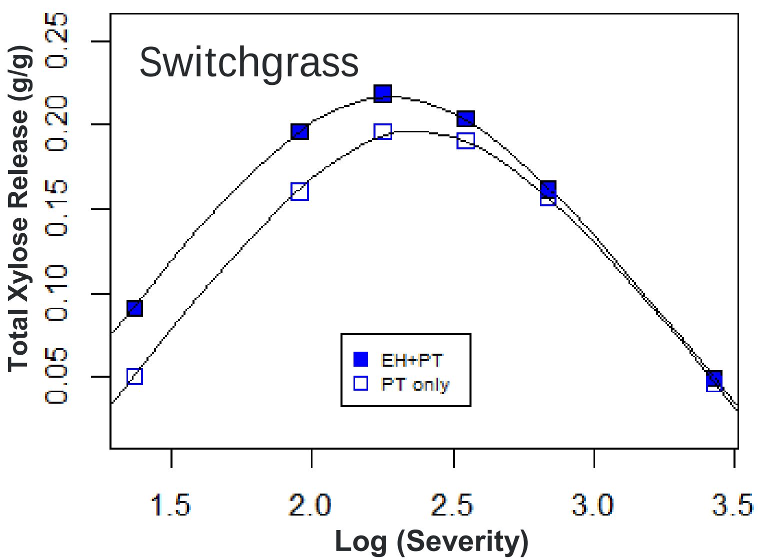






- Pretreatment severity (temperature) affects xylose and glucose yield/ release
- Xylose release during saccharification
- Glucose release during PT
- Xylose release/yield data are more precise than glucose data

3 - Relevance: Spatial Variability

Summary – Corn Stover
Sample Count: 7337
Characterized: 2576

Glucan (n=572)
Mean: 33.95%
Stdev: 3.49%

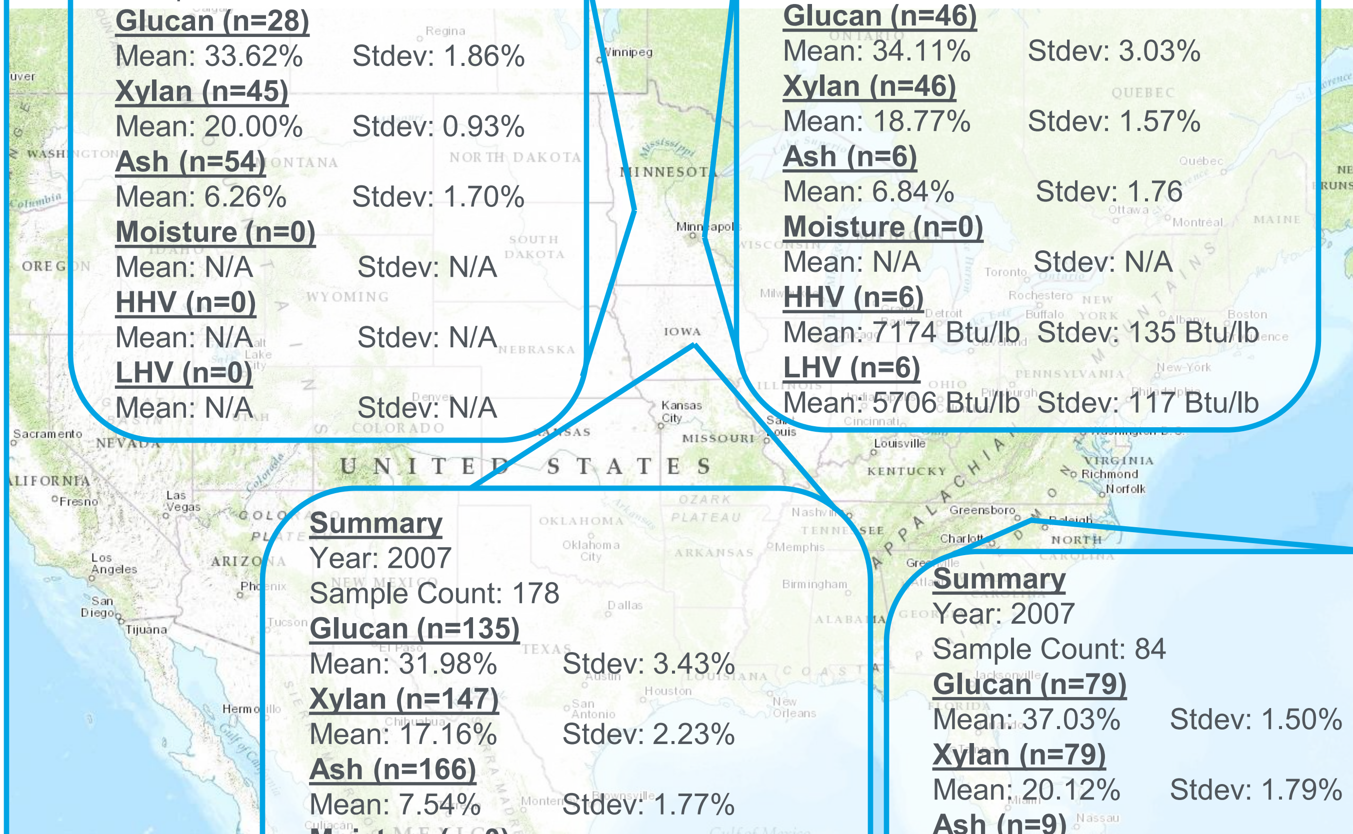
Xylan (n=611)
Mean: 18.74%
Stdev: 2.77%

Ash (n=690)
Mean: 9.552%
Stdev: 7.79%

Moisture (n=507)
Mean: 17.01%
Stdev: 13.07%

HHV (n=136)
Mean: 7318 Btu/lb
Stdev: 466 Btu/lb

LHV (n=133)
Mean: 5911 Btu/lb
Stdev: 544 Btu/lb



Summary
Year: 2007
Sample Count: 65
Glucan (n=28)
Mean: 33.62% Stdev: 1.86%
Xylan (n=45)
Mean: 20.00% Stdev: 0.93%
Ash (n=54)
Mean: 6.26% Stdev: 1.70%
Moisture (n=0)
Mean: N/A Stdev: N/A
HHV (n=0)
Mean: N/A Stdev: N/A
LHV (n=0)
Mean: N/A Stdev: N/A

Summary
Year: 2007
Sample Count: 46
Glucan (n=46)
Mean: 34.11% Stdev: 3.03%
Xylan (n=46)
Mean: 18.77% Stdev: 1.57%
Ash (n=6)
Mean: 6.84% Stdev: 1.76
Moisture (n=0)
Mean: N/A Stdev: N/A
HHV (n=6)
Mean: 7174 Btu/lb Stdev: 135 Btu/lb
LHV (n=6)
Mean: 5706 Btu/lb Stdev: 117 Btu/lb

Summary
Year: 2007
Sample Count: 178
Glucan (n=135)
Mean: 31.98% Stdev: 3.43%
Xylan (n=147)
Mean: 17.16% Stdev: 2.23%
Ash (n=166)
Mean: 7.54% Stdev: 1.77%
Moisture (n=0)
Mean: N/A Stdev: N/A
HHV (n=68)
Mean: 7273 Btu/lb Stdev: 167 Btu/lb
LHV (n=68)
Mean: 5827 Btu/lb Stdev: 157 Btu/lb

Summary
Year: 2007
Sample Count: 84
Glucan (n=79)
Mean: 37.03% Stdev: 1.50%
Xylan (n=79)
Mean: 20.12% Stdev: 1.79%
Ash (n=9)
Mean: 4.39% Stdev: 1.20%
Moisture (n=0)
Mean: N/A Stdev: N/A
HHV (n=9)
Mean: 7323 Btu/lb Stdev: 107 Btu/lb
LHV (n=9)
Mean: 5830 Btu/lb Stdev: 93 Btu/lb

2 - Biomass Variability → Initial FS Specification

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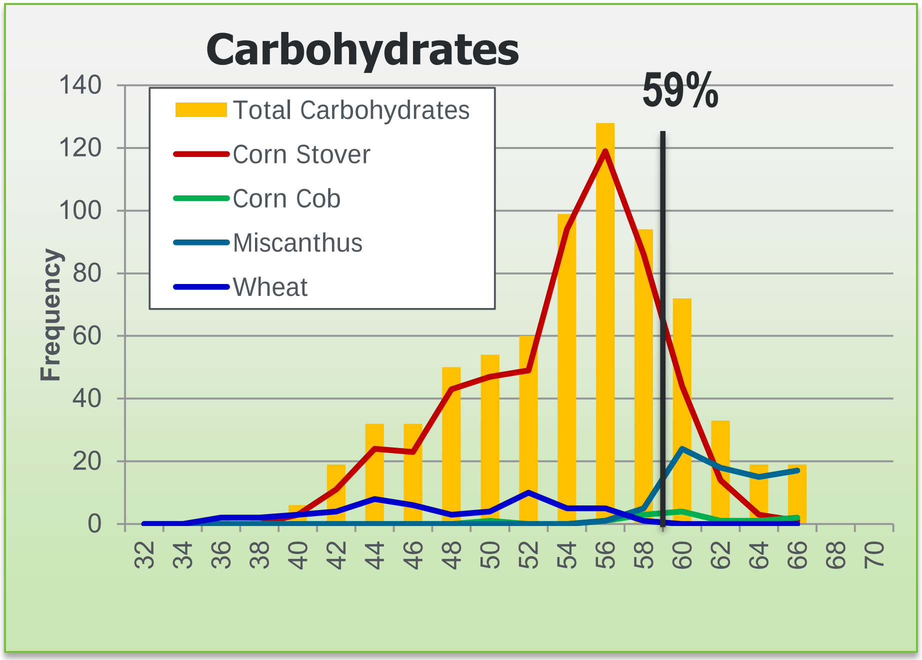
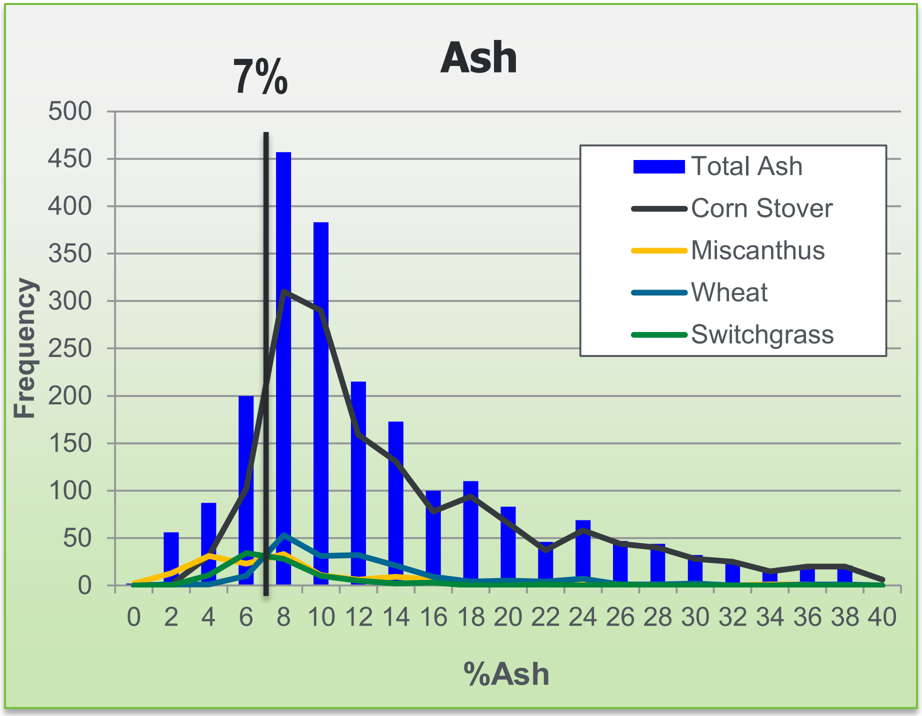
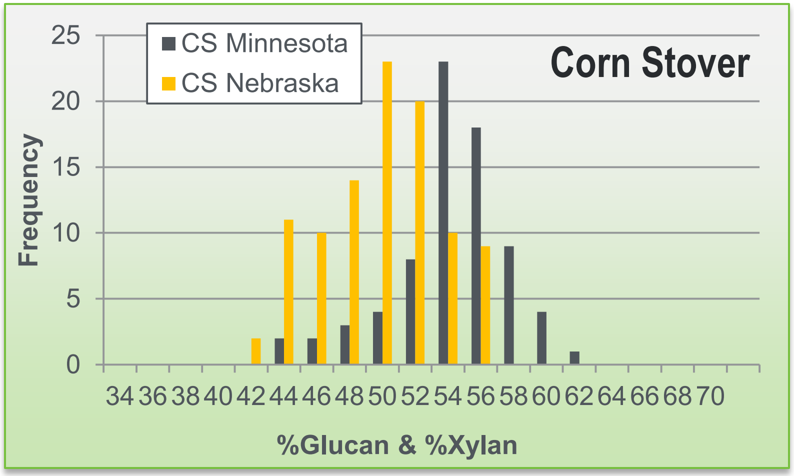


Integrating the needs & requirements of BC conversion with limitations (variability) of biomass





2 - Ash Characterization and Reduction

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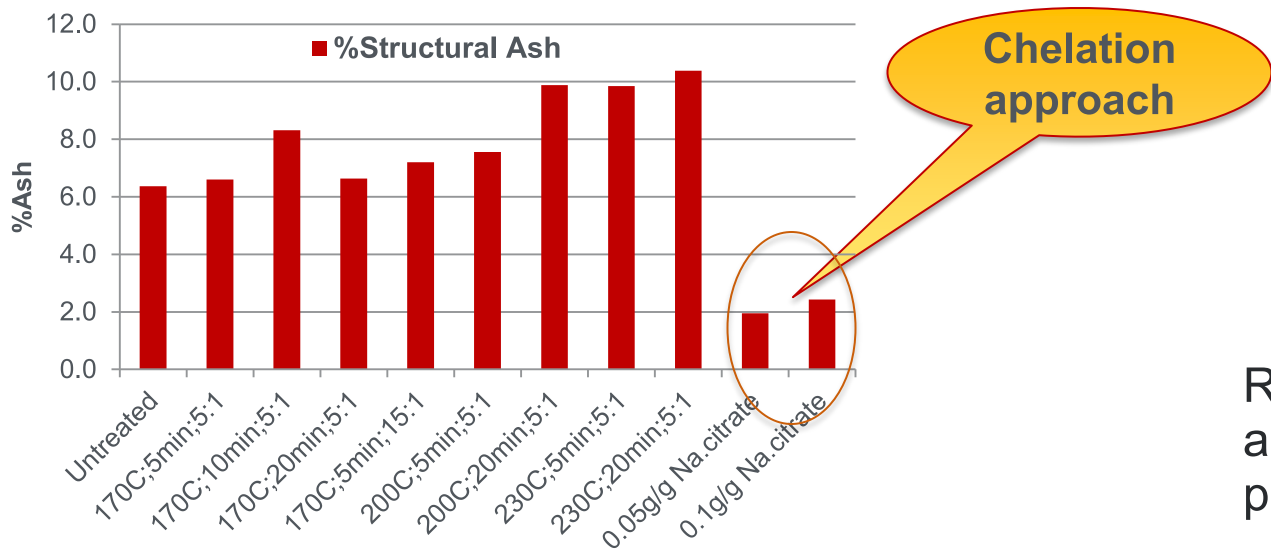
– Evaluate options to reduce physiological ash while maintaining 'intact' feedstock for further conversion, "Chemical Demineralization of Corn Stover," *Environmental Science & Technology*, 2013 draft

Why focus on ash?

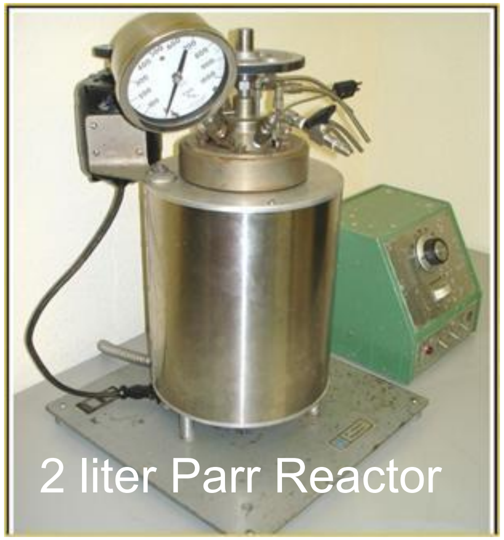
- Affects both BC and TC processes
- Significant waste issue at commercial scale
- Reduces effective acid catalytic capacity
- Increases water treatment cost
- Poison catalysts used for sugar upgrading



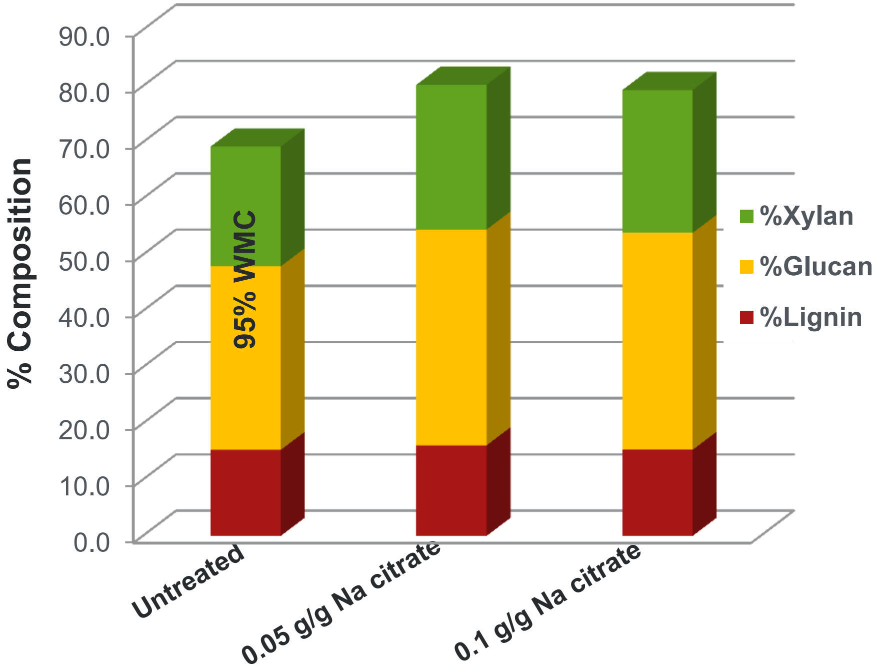
Alkaline Feedstock Deacetylation

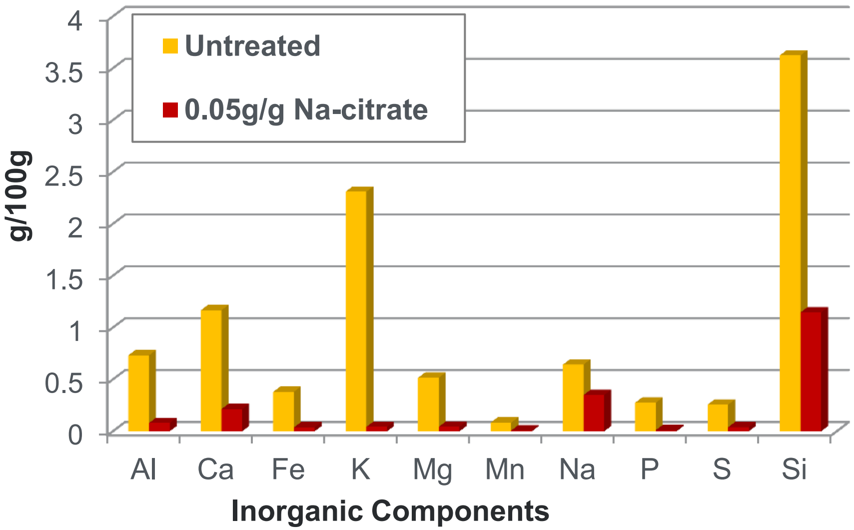
Reduces ash and acetyl content in feedstock prior to pretreatment

2 - Ash Reduction: Mild Hydrothermal Treatment



Performed in collaboration with University of Nevada, Reno





- Extractible inorganics are significantly reduced
- Extractables significantly reduced
- Sugars concentration increase on a wt/wt basis; indicates cellulose and hemicellulose were not degraded

2 - Evaluation of Densified Raw Feedstocks

Evaluate the performance of mechanically-densified FS material relative to conventional formats, "Effect of pelleting on the recalcitrance and bioconversion of dilute-acid pretreated corn stover under low- and high-solids conditions," *Biofuels*, 2013, 4 (3), 271-284.

Solving key incongruities:

- *Does densification render biomass feedstocks more recalcitrant to PT?*
- *Is densification (pelleting) detrimental to sugars and ethanol yield?*

- Corn stover densified using PDU system
  - Two-stage grinding: Vermeer BG 480, (1"); Bliss hammer mill, (1/4" minus)
  - 5 ton/hr Bliss pellet mill (8-10 tons/hr depending on crop type)
    - 10-12% moisture
    - Steam injection ~66ºC to preheat biomass
    - Die temp 98ºC

2 - Measuring the Impact of Densification

INL: Low-Solids (3.3%) PT & SSF

- Chemical analysis of pellets and ¼" grind
- Low-solids pretreatment 121ºC, 30 min, 0.8% H_2SO_4
- SSF of pretreated, washed solids (INL)
- Pore size evaluation (BET)

NREL: High-Solids (25%) PT & EH

- Process relevant conditions
- Chemical analysis of pellets and ¼" grind
- ZipperClave® high-solids pretreatment, 0.8% H_2SO_4
- Enzymatic hydrolysis of washed PT solids
- Reactivity Assessment
- 3 runs/feedstock format

Severity (Log R_0)	Temperature (°C)	Reaction Time (min.)
1.51	125	6
2.07	150	4
2.47	150	10
2.81	175	4
3.29	175	12

ZipperClave Reactor

2 - Corn Stover Xylose Yield

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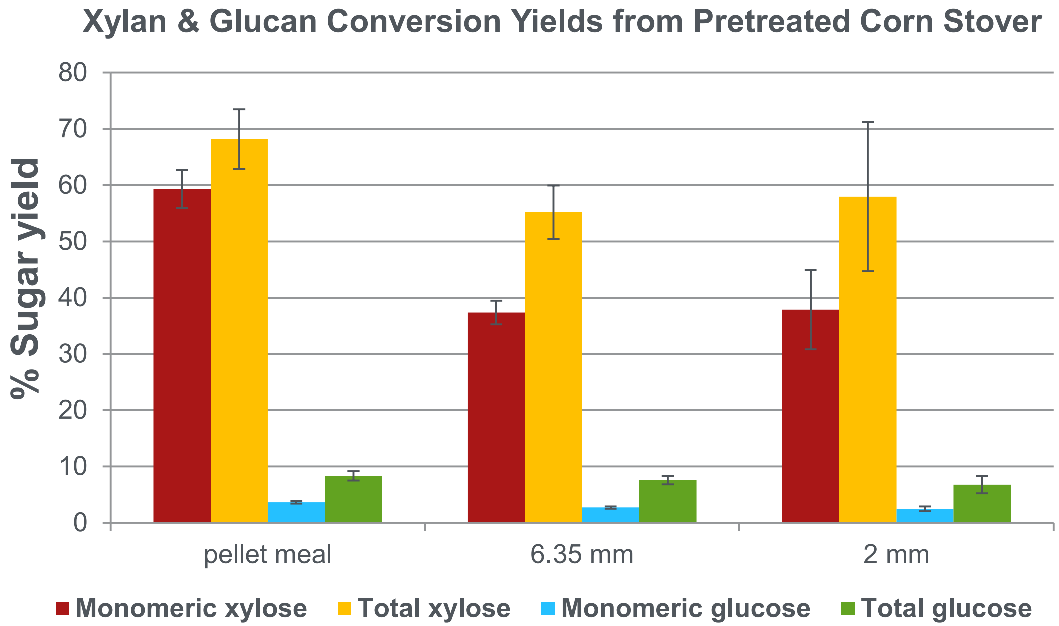
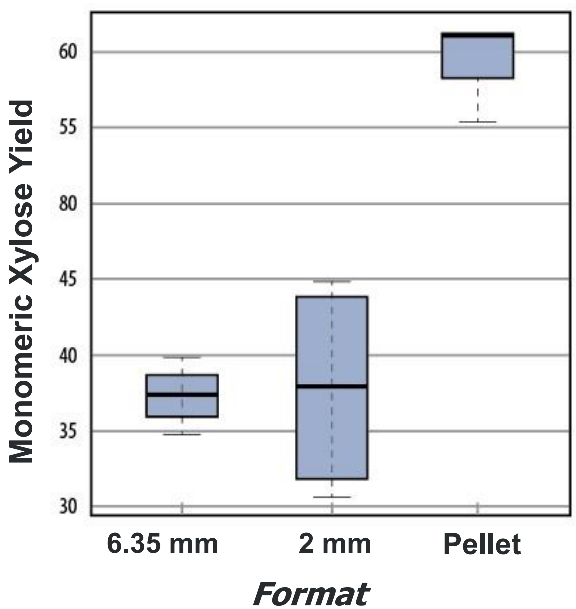
Low-Solids, Dilute-Acid Pretreatment

- Monomeric xylose yields are an important performance parameter for measuring the efficacy of DA-PT



Single point severity testing



Bulk Density: 645 kg/m^3

Monomeric xylose yields were highest for pellets ($p<0.01$), with an average of 59.3% ± 3.4%

2 - SSF Results

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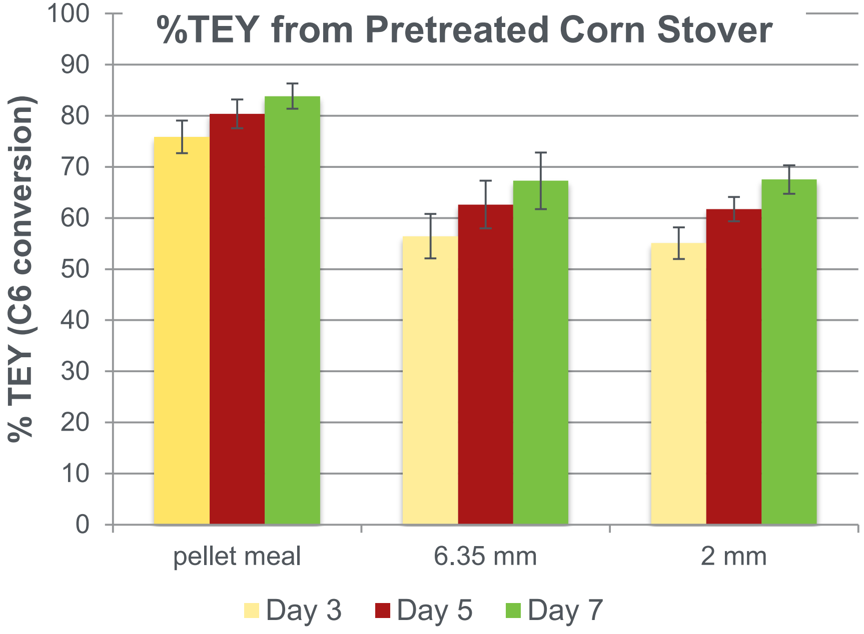
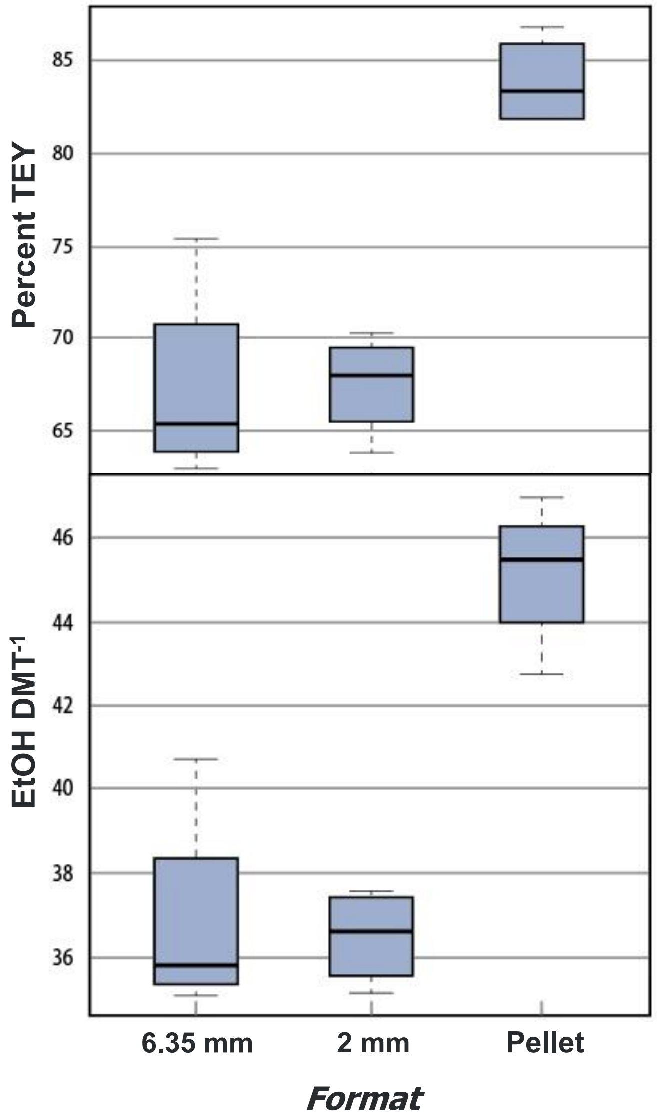
Low-Solids, Dilute-Acid Pretreatment



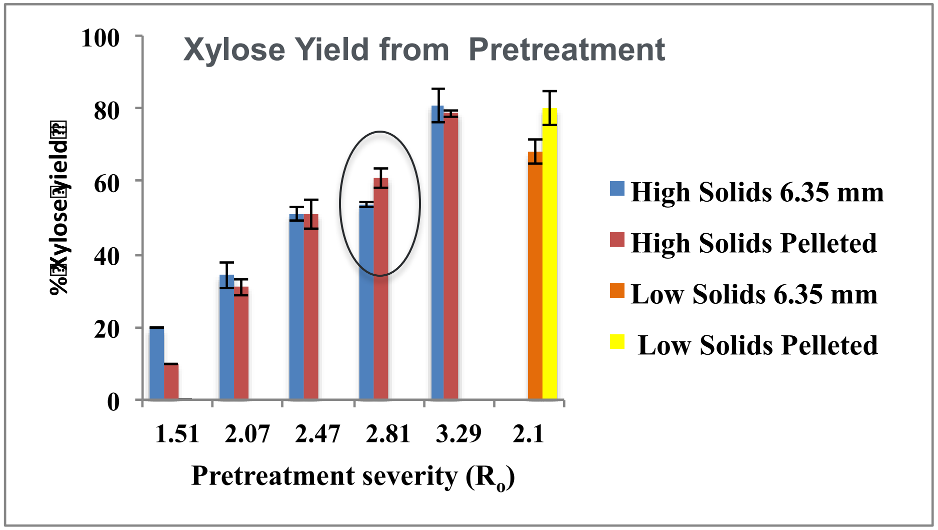


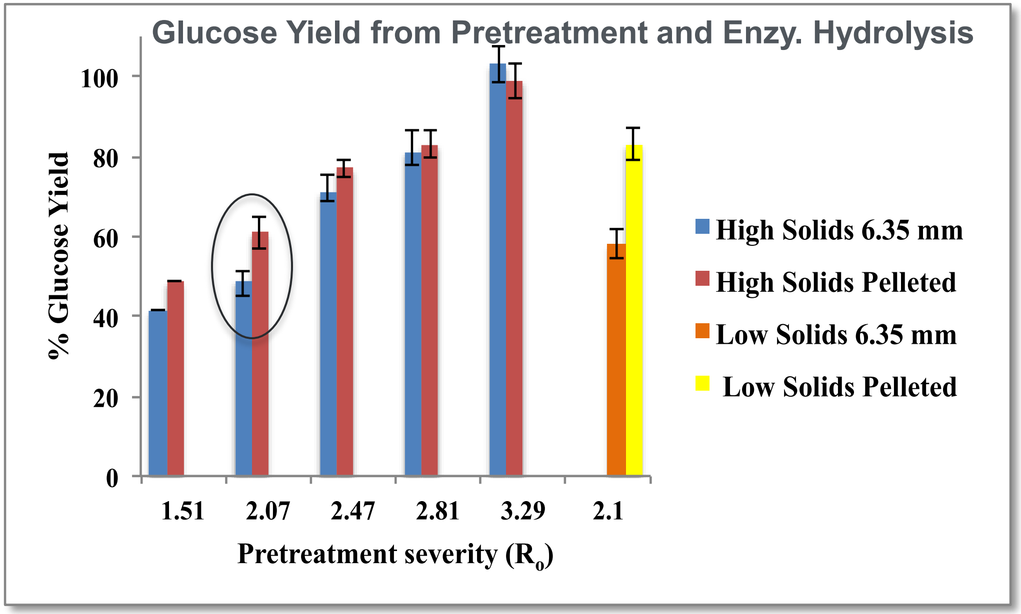
Although pellet composition was slightly reduced in C6 sugars relative to the other formats tested, densified corn stover still achieved significantly higher actual ethanol yields

2 - Comparison of Sugar Yields

Sugar Yields using High and Low-Solids Pretreatment Methodology

- Both methods showed trend of increased sugar release from bioconversion in the pelleted material
- The trend was significant in the low solids method, but not the higher solids loading
- Increased pretreatment severity at higher solids loading is required to achieve similar sugar release observed in the low-solids bioconversion
- Densification was not detrimental to yield in enzym. hydrolysis





2 - High-solids condition: Feedstock Reactivity

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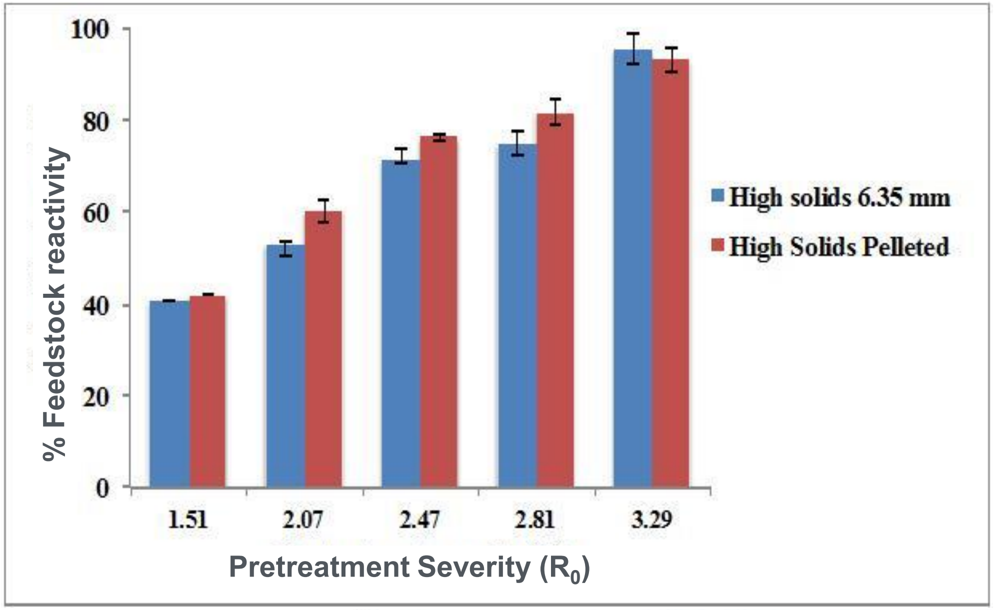
- Reactivity is a measure of biomass recalcitrance representing the combined structural sugar release from both pretreatment and enzymatic hydrolysis

- There was a small, but significant, increase in reactivity for pelleted stover at R_o=2.07, 2.47, & 2.81

Densification did not increase recalcitrance in corn stover pellets



Zipperclave pretreated non-pelleted (left) and pelleted (right) after 175°C/5 min.

3 – Relevance

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Bridge needs and requirement of BC conversion with the limitations of feedstock

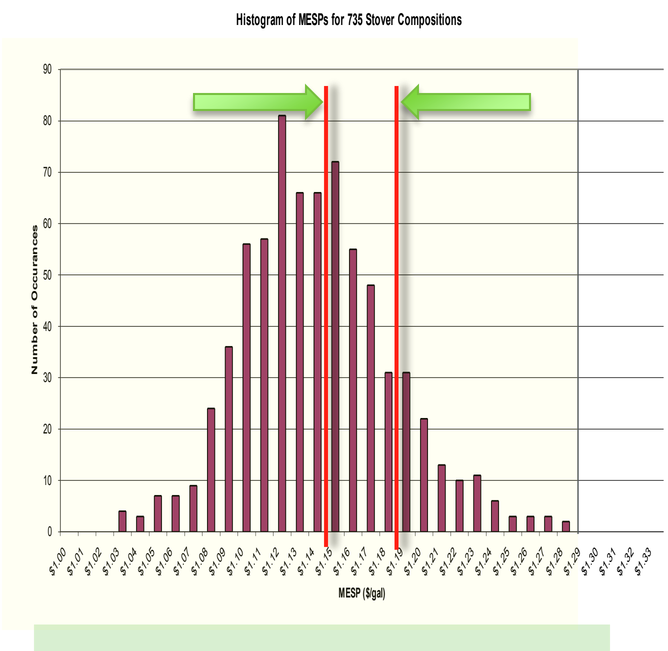
Facilitate conveyance of advanced materials

BC FS Interface supports the cost, quality and volume targets:

- 2017 FS Logistic target to demonstrate feedstock supply and logistics systems that can deliver non-pulpwood feedstock to the conversion reactor throat at required conversion specifications at or below $80/dry ton (DT) ($2011)

- 2022 overall BC Conversion performance goal of $3 per GGE ($2011)
- R&D directly contributes to the understanding limits of FS materials
- Helps guide (navigator) core FS research relative to BC conversion

- Implementation of engineering technologies to reduce variability and risk to provide the lowest fuel costs
- Integration of reduced cost logistics & preconversion operations (transportation, comminution, de-mineralization) with innovative biochemical biomass-to-fuels processes



allenges

Non-linear effects in biochemical conversion complicate predictive tools for optimizing feedstocks

→ *Bounded feedstocks must be tested for initial spec development & model construction/validation*

Rapid screening techniques are not readily adaptable to all FS types and applications

→ *Focused integration of characterization methods & techniques*

Engineering and preprocessing techniques may have inadvertent consequences on BC conversion process

→ *Integration & evaluation of key issues that impact BC conversion processes*

5 – Future Work

Support Biochemical Conversion Pathway: "reduce the overall cost of biomass conversion to sugars by reducing the risk and cost associated with FS production."

1. Develop & define initial feedstock specifications & material performance
   - Produce, characterize & distribute feedstocks, advance – engineered materials
2. Develop & deploy analytical screening tools
   - Moisture, ash, lignin, extractive, glucan, xylan, recalcitrance
3. Interface (i.e. cross-cutting) sub-projects & programs
   - Integrate technologies & solve key incongruities that require collaboration FS & BC Platforms.
4. Assess viability & cost of advanced approaches

2013-2022
Blended feedstock from multiple biomass resources
Engineered systems used to control feedstock compositional variability
Material performance guarantees
Engineered format
Tool development for rapid screening & exchange applications
End product from feedstock conversion - *Multiple hydrocarbon intermediates*

Summary

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- Biomass Resource Library - *High impact analytics that provides core platforms and industry with insight and guidance*
- Capability to fabricate process intermediates using PDU systems - *Multiple formats and intermediates*
- Expanded understanding of quality attributes and variability - *Best management practices is only the first step in reducing variability*
- Novel approaches to mitigating detrimental components investigated – *Method achieved reduce physiological ash content while maintaining sugars*
- Expanded and continued developed robust methods for feedstock compositional analysis & quality characterization - *NIR model development, Reactivity testing, Integrated & validation of methods*
- Navigation and integration of key incongruity that require collaboration of FS & BC platforms – *Engineered material evaluation and determination of impact; validation of bench = pilot- scale characterization methods*
- Future focus – *Interface pipeline for implementation of engineering technologies to reduce variability and risk to provide the lowest fuel costs*

Publications

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Publications and Documents

- A.E. Ray, A.N. Hoover, N. Nagle, X. Chen, and G.L. Gresham, "Effect of pelleting on the recalcitrance and bioconversion of dilute-acid pretreated corn stover under low- and high-solids conditions," *Biofuels,* 2013, 4 (3), 271-284.
- K.L. Kenney, W.A. Smith, G.L. Gresham, T.L. Westover, "Understanding biomass feedstock variability; *Biofuels,* Biofuels Special Focus Issue," 2013, 4 (1), Pages 111-127.
- G.L. Miner, N.C. Hansen, D. Inman, L.A. Sherrod, G. A. Peterson, "Constraints and Capabilities of No-Till Dryland Agroecosystems as Bioenergy Production Systems," *Agronomy Journal*, 2013,105 (2), 364-376.
- R.A. Emerson & Garold Gresham, "Characterization of Advanced Preprocessed Materials (Hydrothermal)," Sept 2102, www.osti.gov/servlets/purl/1060958/
- J.M.F. Johnson, G.L. Gresham, "Do yield and quality of big bluestem and switchgrass feedstock decline over winter," *BioEnergy Research*, 2013, accepted.
- D.L. Karlen, J.M.F. Johnson, G.L. Gresham, A.N. Hoover, R.A. Emerson,K. Cantrell, D. Archer, B. Weinhold, D. Laird, J. Baker, T.E. Ochsner, J. M. Novak, A.D. Halverson, F. Arriaga, D. Lightle and N. Barbour, "Corn Stover Cutting Height Effects on Composition, Proximate, and Ultimate Analysis Parameters," *Bioenergy Research*, 2013, submitted.
- C. Matney, J. Brummer, N. Hansen, K. Gillette, B. Bosley, E. Wolfrum, "Biomass and Forage Quality Tradeoffs of Cool-Season Forage Grasses Related to Harvest Timing and Irrigation," *Agronomy Journal*, 2013, submitted.
- M.T. Reza, R.A. Emerson, M.H. Uddin, G.L. Gresham, C.J. Coronella, "Chemical Demineralization of Corn Stover," *Environmental Science & Technology*, 2013 draft.
- A.N. Hoover, J.S. Tumuluru, F. Teymouri, G.L. Gresham, "Effects of ammonia fiber expansion (AFEX) and pelleting on sugar yields and particle characteristics for corn stover," *Bioresource Technology* 2013, draft.
- N.J. Nagle, E.J. Wolfrum, E.M. Kuhn, G.L. Gresham, A.E. Ray, M.E. Delwiche, N.D. Weiss, C. Radtke, "Evaluation of Ensiling as a Storage Method to Reduce Bioconversion Requirements in Corn Stover," *Biotechnology for Biofuels*, 2013, draft.

Additional Slides

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Abbreviations

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ASE - accelerated solvent extraction
B - bohme grass
BET - Brunauer–Emmett–Teller theory
BC - biochemical
CS - corn stover
DA - dilute acid
EH - enzymatic hydrolysis
Ext - extractives
FS - feedstock(s)
GGE – gallon of gas equivalent
H1- harvest #1
H2 - harvest #2
Indist. - indistinguishable
INL - Idaho National Laboratory
Internd. – internodes
Intg – integration of key issues
MVA - multivariate analysis
NREL - Nation Renewable Energy Laboratory
PC - principle component
PDU - process development unit
PLS PNNL - Pacific Northwest National Laboratory
PT - pretreatment
RWR - russian wildrye grass
Scrn – screening
SNV - Standard Normal Variate
SSF - Simultaneous Saccharification and Fermentation
TC - thermochemical
TFF - tall fescue grass

Presentations

Presentations

- Effect of Pelleting on the Recalcitrance and Bioconversion of Dilute-Acid Pretreated Corn Stover under Low- and High-Solids Conditions. Selected for oral presentation at the 35th Symposium on Biotechnology for Fuels and Chemicals, Portland, OR (April 30, 2013).
- T. L. Westover,., G. L. Gresham (2012). "Rapid Analysis of Ash Composition Using Laser-Induced Breakdown Spectroscopy (LIBS).", AIChe Annual Meeting, Pittsburgh, PA. (Oct. 28 – Nov. 2, 2012).
- A.E. Ray, A.N. Hoover, and G.L. Gresham. Effect of Pelleting on the Recalcitrance and Bioconversion of Corn Stover. Invited EES&T Technical Seminar Series Speaker, Idaho National Laboratory, Idaho Falls, ID (July 20, 2012).
- A.E. Ray & W.A. Smith. Pretreatment and Biochemical Conversion Performance of Densified Biomass. Transforming Biomass into High-Quality, On-Spec, High-Density Feedstocks: Densification Workshop, Idaho National Laboratory, Idaho Falls, ID. (August 23, 2011).
- D. Muth, A. N. Hoover, R. A. EmersonA. D. Hoover, G. L. Gresham "Biomass R&D Library and the Regional Partnership," Proceedings of the 2012 National Sun Grant Meeting: Science for Biomass, New Orleans, LA. (Oct. 2, 2012).

Responses to Previous Reviewer's Comments

1. Project Approach (1-10): Please evaluate the degree to which:

The project performers have implemented technically sound research, development, and deployment approaches and demonstrated necessary results to meet their targets

The project performers have identified a project management plan that includes well-defined milestones and adequate methods for addressing potential risks.

Reviewer comments relative to Project Approach: *The project considers changes in feedstock composition and reactivity as it goes from field to biorefinery and how these changes may impact subsequent conversion. The research looks to be sound. There are many questions related to the feedstock supply interface so this project is really only looking at a small part of the overall area. The "milestones" are not easily grasped, as they are mostly to generate information in broad areas. The management plan will need to account for this in someway. It is not clear how the data obtained in the different studies will be correlated and dovetailed.*

Response: *We are in agreement with the reviewer that the data will require analysis and reduction to provide guidance for stakeholders, industry and partners how best to manage feedstock preprocessing operations (i.e., harvesting, storage, thermal treatment, and densification) for fuel production. The Biomass Resource Library is the cornerstone for linking the many feedstock attributes with the conversion process. The Library system will be used to connect how feedstock attributes are modified/impacted by preprocessing operations, how unit operations influence downstream operations, and how the feedstock characteristics and specifications then impact overall pretreatment performance and conversion.*
The data system, which has just become available online within the last 6 months, provides a mechanism of correlating materials/process intermediates to their attributes and ultimately correlate feedstock specifications to their pretreatment performance. Efforts are underway to allow for multiple approaches to query the data system to highlight both positive and detrimental impacts.

Responses to Previous Reviewer's Comments

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3. Project Relevance (1-10): Please evaluate the degree to which:

The project both identifies with and contributes to meeting the platform goals and objectives of the Biomass Program Multi-Year Program Plan

The project has considered applications of the expected outputs

Reviewer comments relative to Project Relevance: The type of work presented is important but it seems they are a long way from bringing it all together - the work is very scattered. It may be better to narrow the research scope to make more significant progress in a few key areas rather than less progress in many areas.

Response: *The goal in the Interface task is to identify variation within the feedstock formats and its associated impact on the conversion process. A significant portion of early work focused on collection and cataloging of feedstock samples for the INL Biomass Resource Library Database, characterization of these materials and developing new methods for higher-throughput analysis. These tasks were selected as they formed the foundational work required to make assessments and comparisons in feedstocks and changes associated with feedstock processing. The projects described in the presentation were used to demonstrate the efficacy and effectiveness of these tools sets, methodologies and approaches.*

Additionally, as stated above this early work establishes the foundation for future efforts to focus on the impact of harvesting, storage, densification and preprocessing on the many attributes that impact the pretreatment and the bioconversion process.

Responses to Previous Reviewer's Comments

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

4. Critical Success Factors (1-10): Please evaluate the degree to which:
Please evaluate the degree to which:

- The project has identified critical factors, (including technical, business, market, regulatory, and legal factors) that impact the potential technical and commercial success of the project
- The project has presented adequate plans to recognize, address, and overcome these factors
- The project has the opportunity to advance the state of technology and impact the viability of the commercial conversion processes through one or more of the following focus areas:
    i. *Conversion Process Parameters*
    ii. *Environmental Sustainability/Process Parameters*

Reviewer comments relative to Critical Success Factors: This is a diffuse project so success/failure can be viewed in many different ways. The biggest concern is how to tie all the data together (multiple analytical approaches and multiple feedstocks with multiple project objectives). Reproducibility is a big issue in this type of work - but it appears the methods used are satisfactory. The huge diversity in terms of types of feedstocks, harvest times, growing seasons, etc. lead me to believe this type of work could go forever - so how do you extrapolate from one data set to another.

Response: *Extrapolating from one data set to the next can be challenging. However the Biomass Library Database allows for the testing/analysis of multiple large data sets, allowing for a more efficient experimental process. The goal for the multivariate analysis of these feedstock data sets is to identify:*

- *What the driving factors responsible for the variation in these data sets*
- *Determine the reproducibility of these measurements*
- *Develop predictive correlations for new data sets that will allow for hypothesis testing*

Additionally, the INL PDU has the ability to reproduce materials and conditions for feedstocks intermediates and these can be evaluated to test correlations and predictions of feedstock properties.

2 - Add'l Tech Accomplishments: Evaluation of Densified AFEX Materials

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Evaluate the performance of mechanically-densified material relative to preprocessed format, "Effects of ammonia fiber expansion (AFEX) and pelleting on sugar yields and particle characteristics for corn stover, 2013

Low bulk densities of baled and ground biomass pose difficulties to transportation & handling; technologies must be implemented for cost-effective biofuel production

- Corn stover densified using research scale pellet mill
  - 4 and 6 mm corn stover
  - Die speed at 40, 50, 60 Hz
  - With and without preheating to 70ºC

- AFEX treated corn stover
  - 1:1 ammonia : biomass loading
  - 30 min. residence time at 100ºC
  - Moisture content 40%

2 - Add'l Tech Accomplishments: Densification of AFEX Treated Materials

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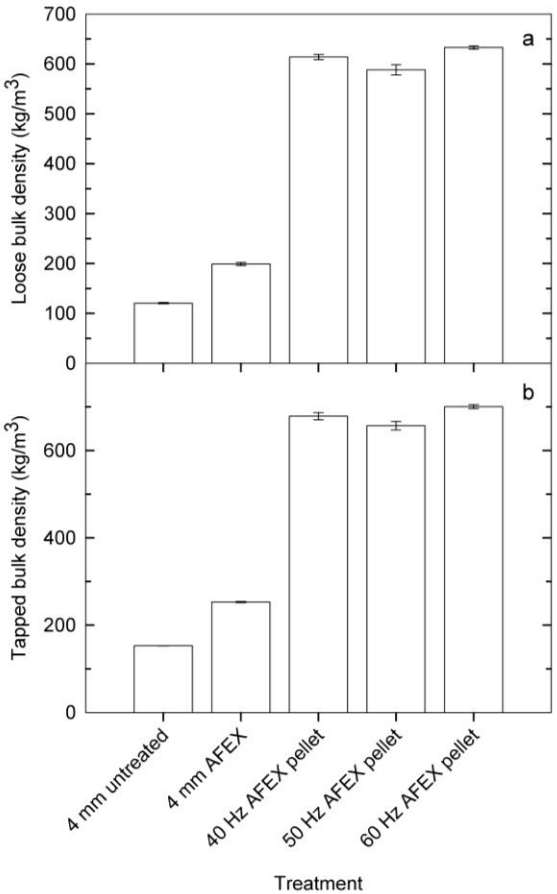
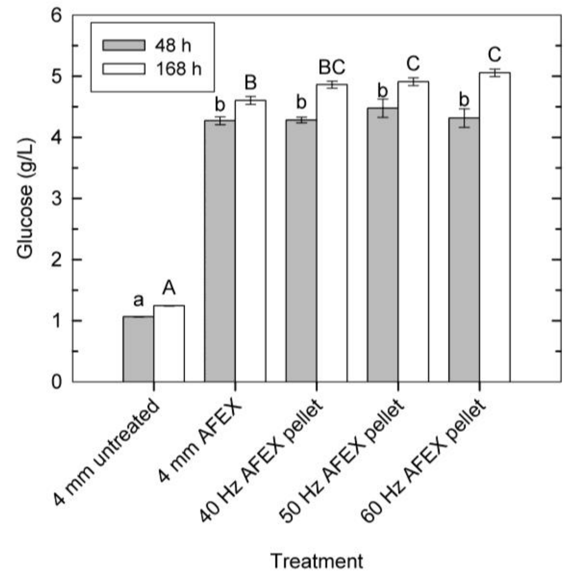
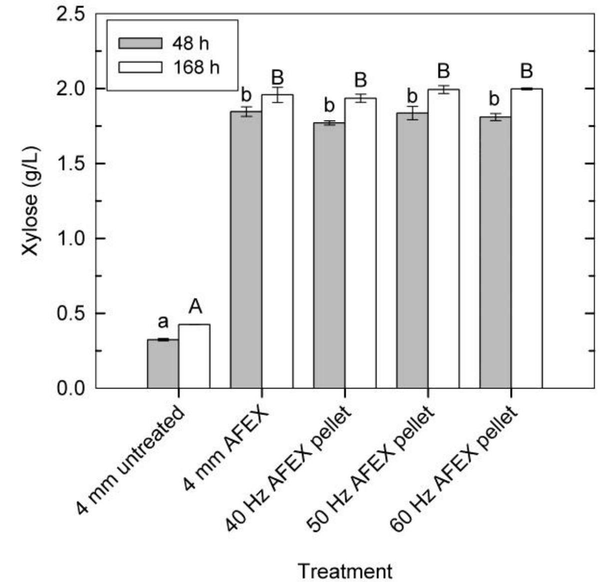




Seed Project; Performed in collaboration with MBI International



Die speed did not have a significant effect on the on physical properties including bulk density and durability

Densification did not have a significant effect on the on conversion efficiency (sugar yields)

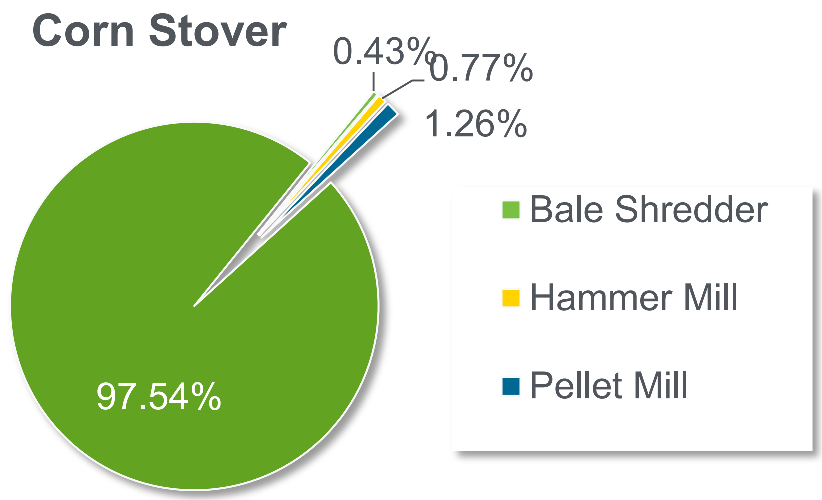
2 – Add'l Tech Accomplishments: Properties of densified Corn Stover

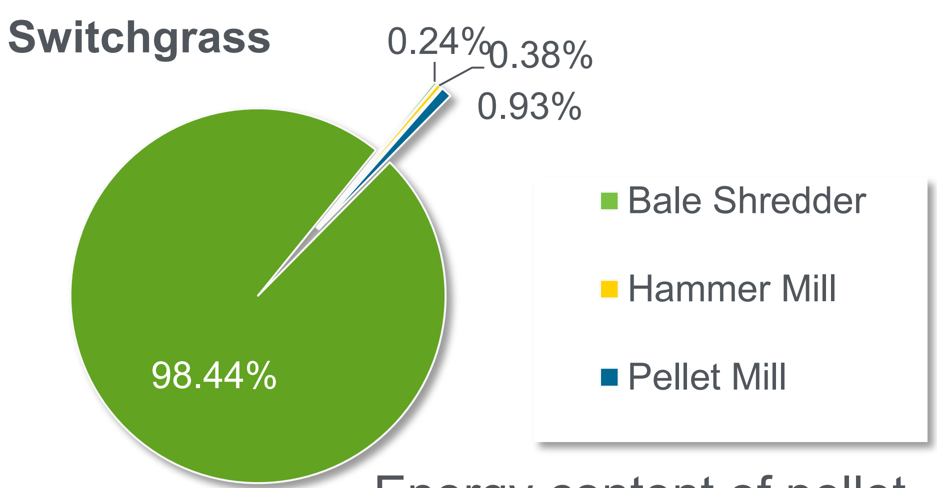
- Moisture content of stover pellets: 11.3%
- Durability: 98.5%
- Bulk Density: 645 kg/m^3 (Coal 1346 kg/m^3)
- HHV of Corn Stover Pellets: 16.55 ± 0.05 MJ/kg
  - (Coal 31.75 MJ/kg)
- Glucan content was lowest for pellets
- Source material (6 mm) had highest xylan content

Format / Screen Size	Glucan	Xylan	Lignin	Structural Ash	Soil	Extractives
Pellet	31.3	20.8	15.7	2.7	1.49	5.4
6.35 mm	33.2	25.1	14.9	2.1	1.06	4.9
2 mm	32.1	21.5	13.8	2.7	0.65	7.3

2 – Add'l Tech Accomplishments: What is the cost of pelleting?

- Energy consumption for 2-stage grinding and pellet mill was recorded for various feedstocks
- Energy consumed for grinding and pelleting represented a small fraction of the energy content of the pelleted material
- Costs cited from literature
    - $51/ton for 6 ton/hr
    - $40/ton at more than 10 ton/hr

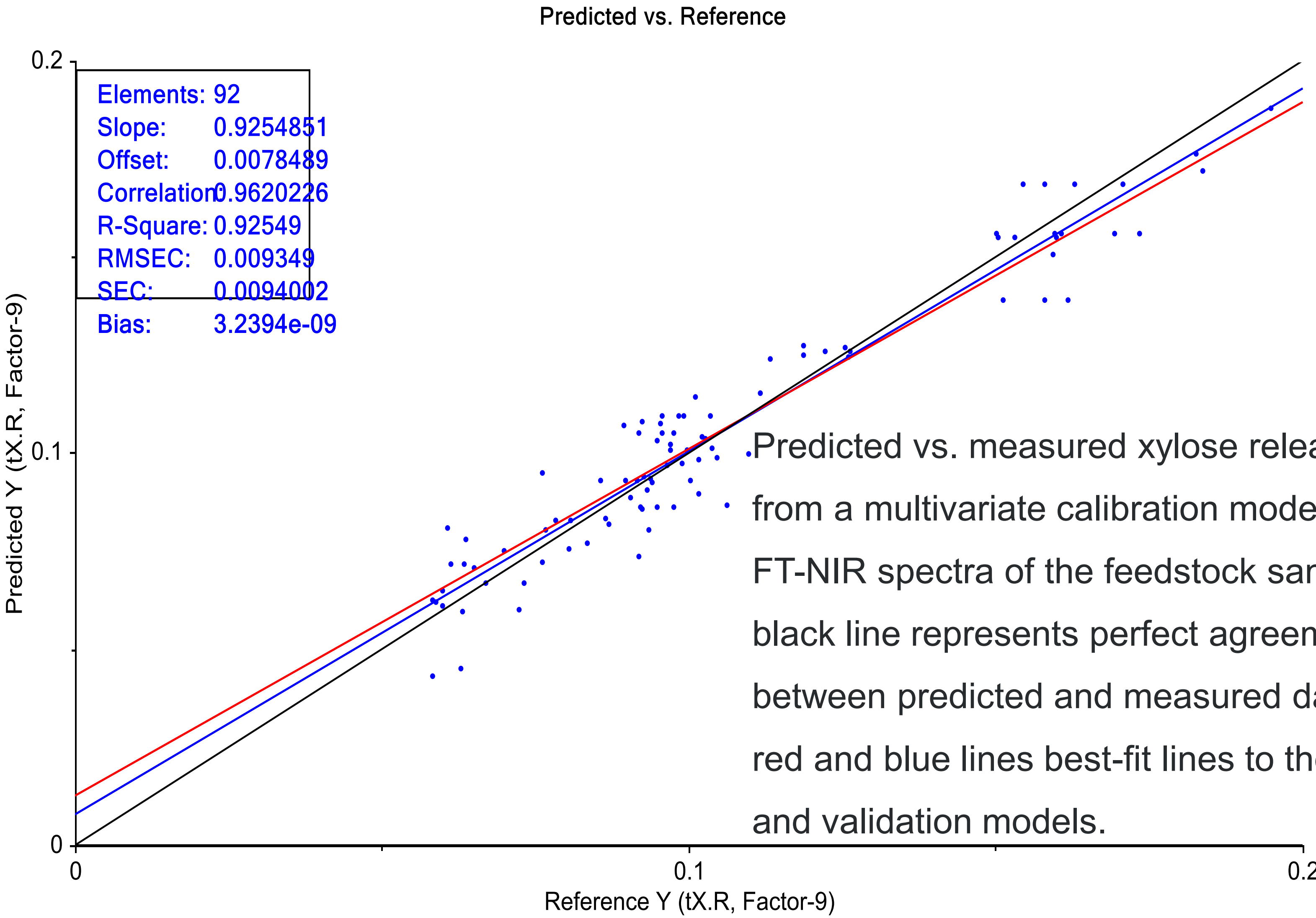




Energy content of pellet

2 – Add'l Tech Accomplishments:

Xylose release from a multivariate calibration model



Predicted vs. measured xylose release (g/g) from a multivariate calibration model based on FT-NIR spectra of the feedstock samples. The black line represents perfect agreement between predicted and measured data, and the red and blue lines best-fit lines to the calibration and validation models.

2 – Add'l Tech Accomplishments:

Xylose yield from a multivariate calibration model

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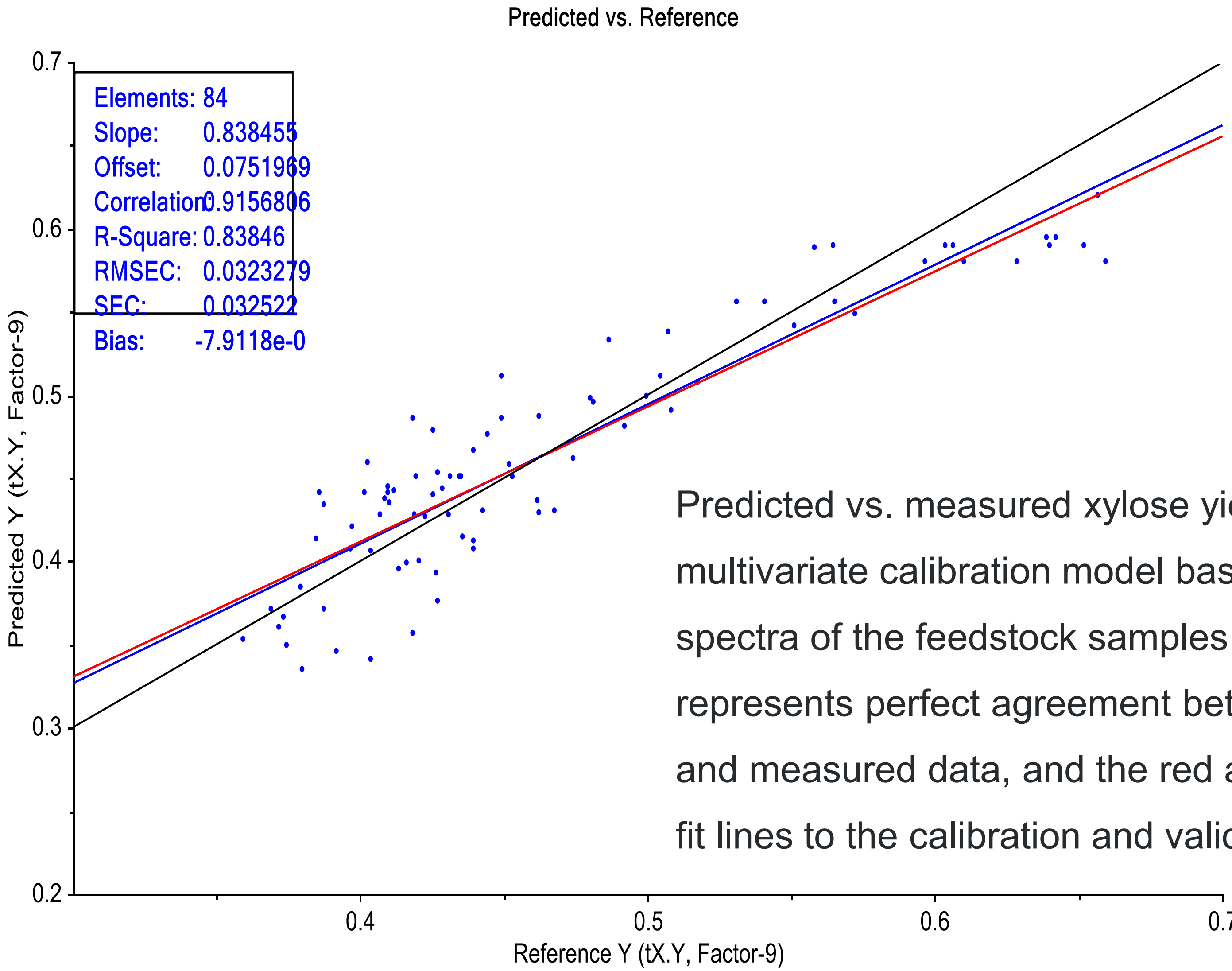

Predicted vs. measured xylose yield from a multivariate calibration model based on FT-NIR spectra of the feedstock samples. The black line represents perfect agreement between predicted and measured data, and the red and blue lines best-fit lines to the calibration and validation models.

2 – Add'l Tech Accomplishments: Quality Attributes

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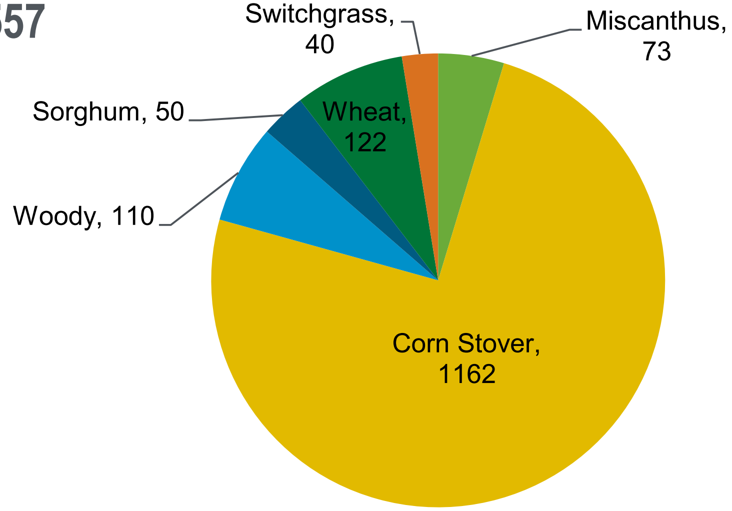
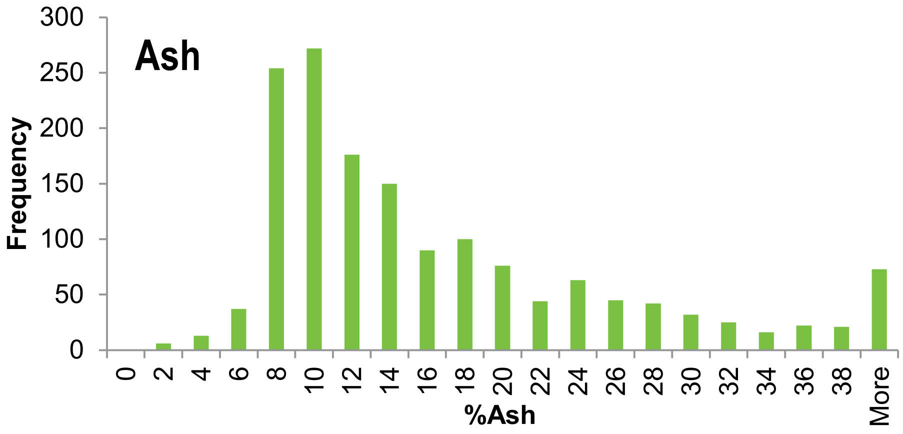
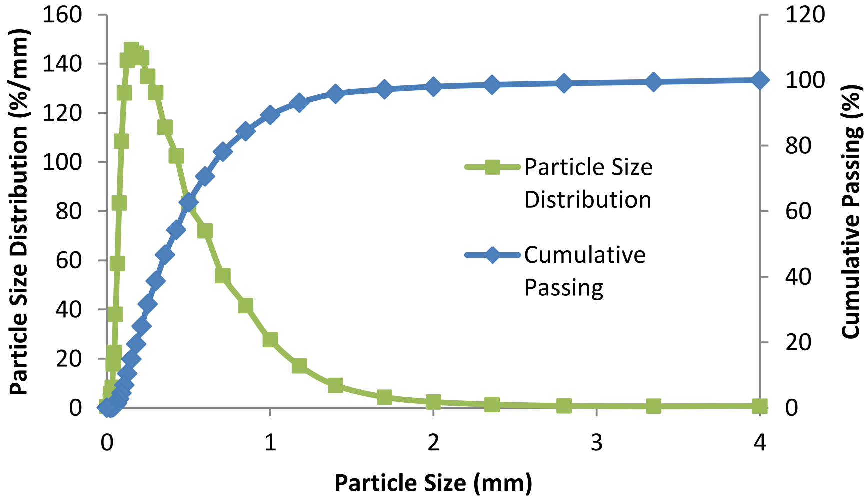
Ash Determination
N = 1557

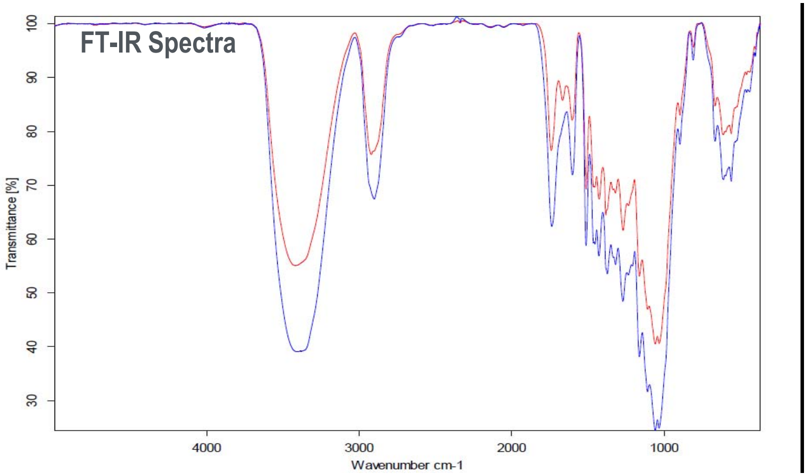




Particle Characterization



Spectral Characterization



2 – Add'l Tech Accomplishments: DOE Biofuel Research Pathways

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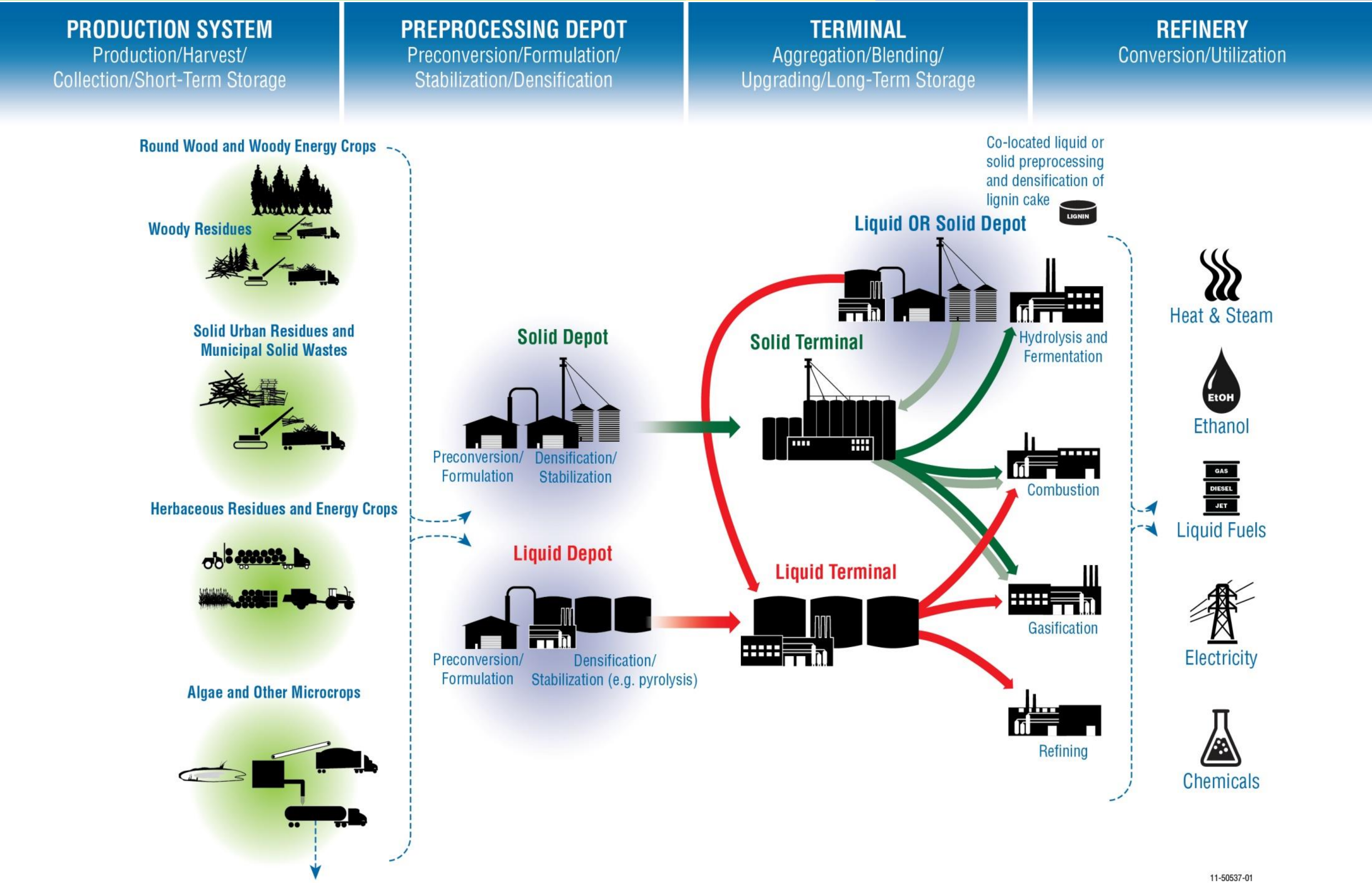

2 - Add'l Tech Accomplishments: Temporal Variability

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Summary – Corn Stover
Sample Count: 7337
Characterized: 2576

Glucan (n=572)
Mean: 33.95%
Stdev: 3.49%

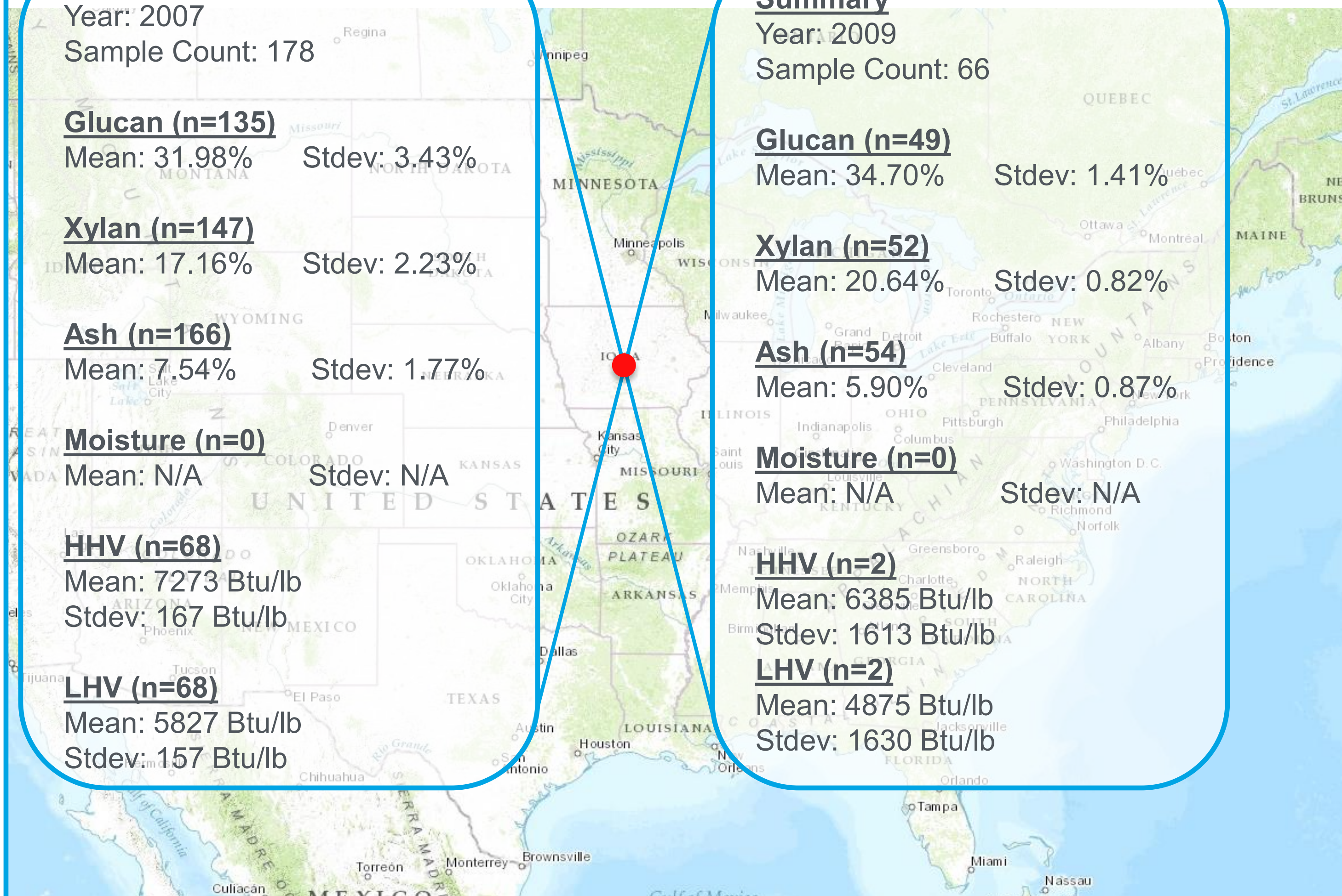
Xylan (n=611)
Mean: 18.74%
Stdev: 2.77%

Ash (n=690)
Mean: 9.552%
Stdev: 7.79%

Moisture (n=507)
Mean: 17.01%
Stdev: 13.07%

HHV (n=136)
Mean: 7318 Btu/lb
Stdev: 466 Btu/lb

LHV (n=133)
Mean: 5911 Btu/lb
Stdev: 544 Btu/lb



Summary
Year: 2007
Sample Count: 178

Glucan (n=135)
Mean: 31.98% Stdev: 3.43%

Xylan (n=147)
Mean: 17.16% Stdev: 2.23%

Ash (n=166)
Mean: 7.54% Stdev: 1.77%

Moisture (n=0)
Mean: N/A Stdev: N/A

HHV (n=68)
Mean: 7273 Btu/lb
Stdev: 167 Btu/lb

LHV (n=68)
Mean: 5827 Btu/lb
Stdev: 157 Btu/lb

Summary
Year: 2009
Sample Count: 66

Glucan (n=49)
Mean: 34.70% Stdev: 1.41%

Xylan (n=52)
Mean: 20.64% Stdev: 0.82%

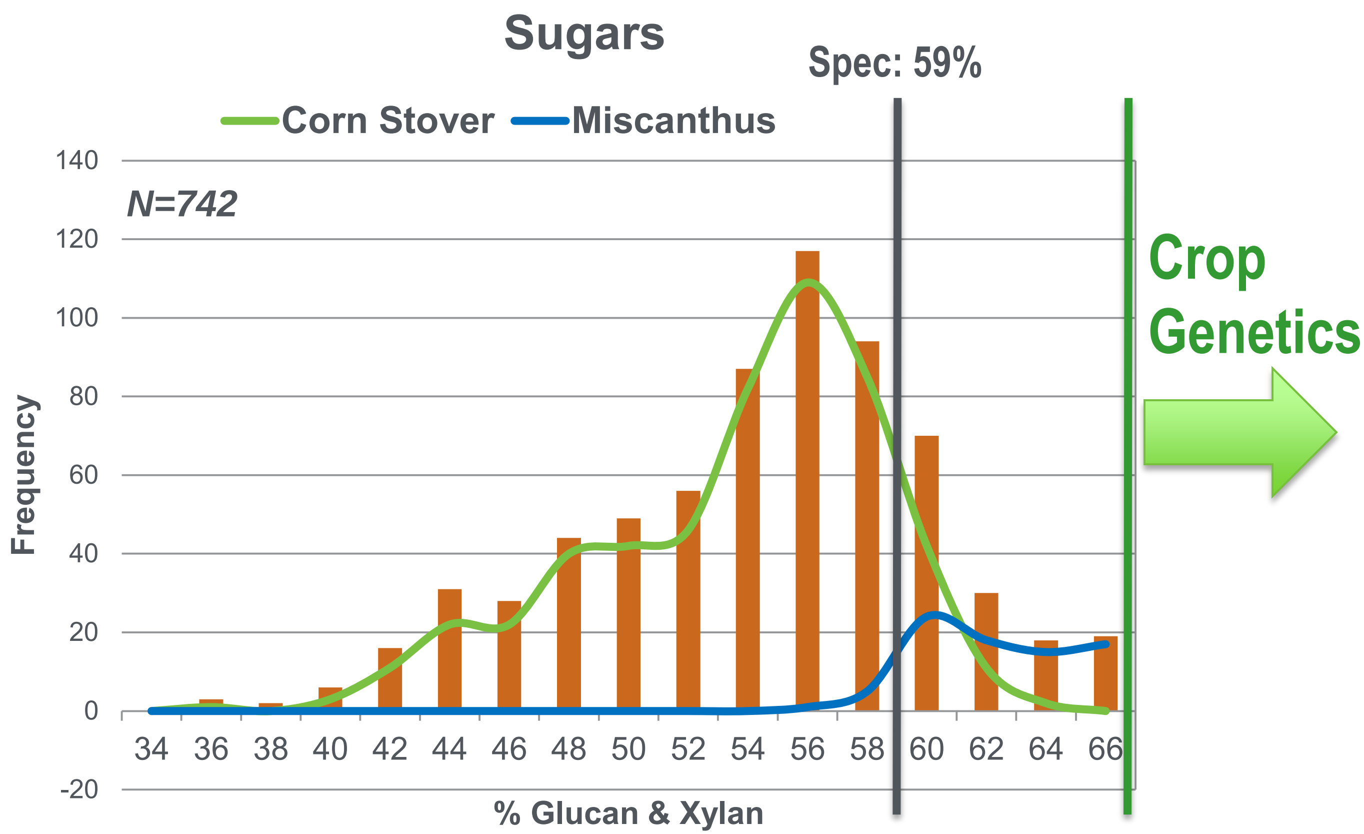
Ash (n=54)
Mean: 5.90% Stdev: 0.87%

Moisture (n=0)
Mean: N/A Stdev: N/A

HHV (n=2)
Mean: 6385 Btu/lb
Stdev: 1613 Btu/lb

LHV (n=2)
Mean: 4875 Btu/lb
Stdev: 1630 Btu/lb

2 – Add'l Tech Accomplishments: Step #1: Feedstock Selection for Sugars



- Selection of optimum feedstock
- Risk: Reliance on specific biomass resources
- Results in boutique feedstocks

2 – Add'l Tech Accomplishments: Step #2: Sugar Preservation

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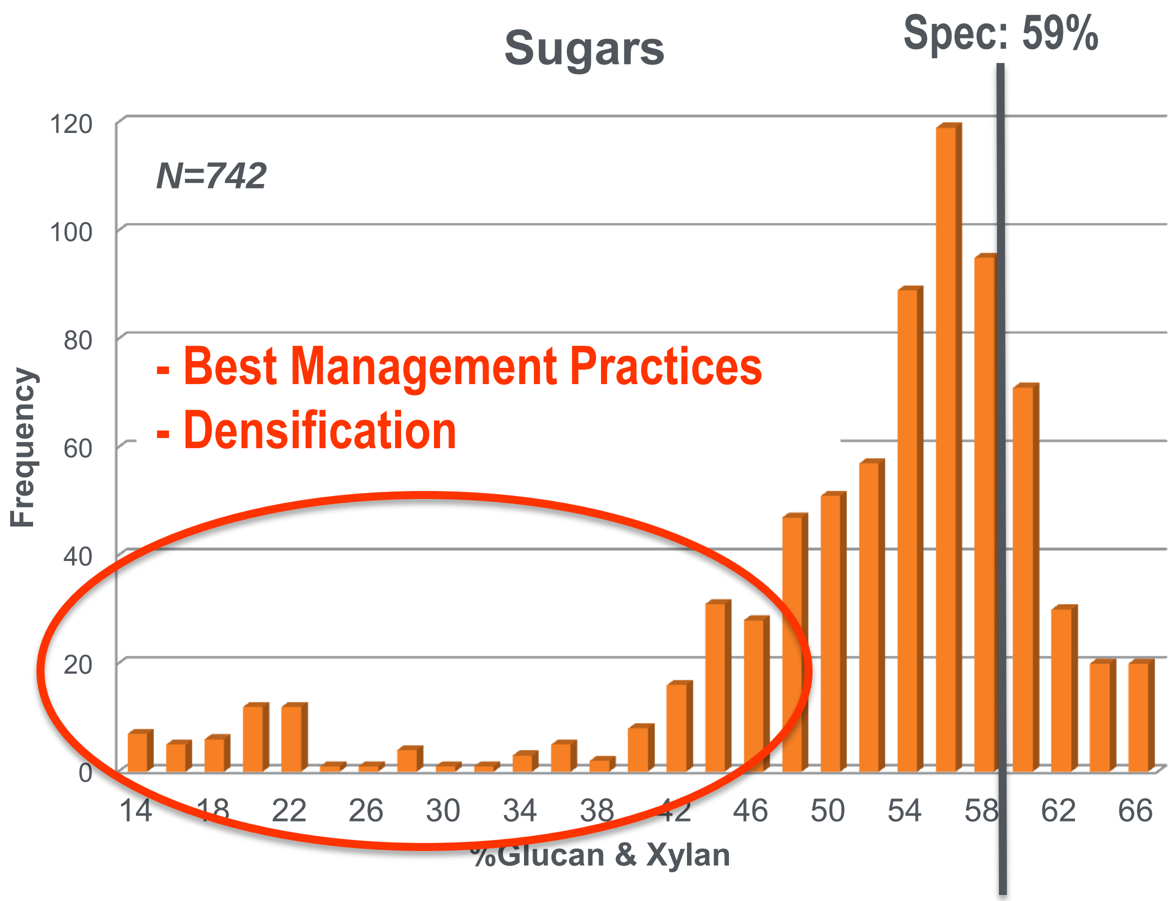
Sugar preservation in storage

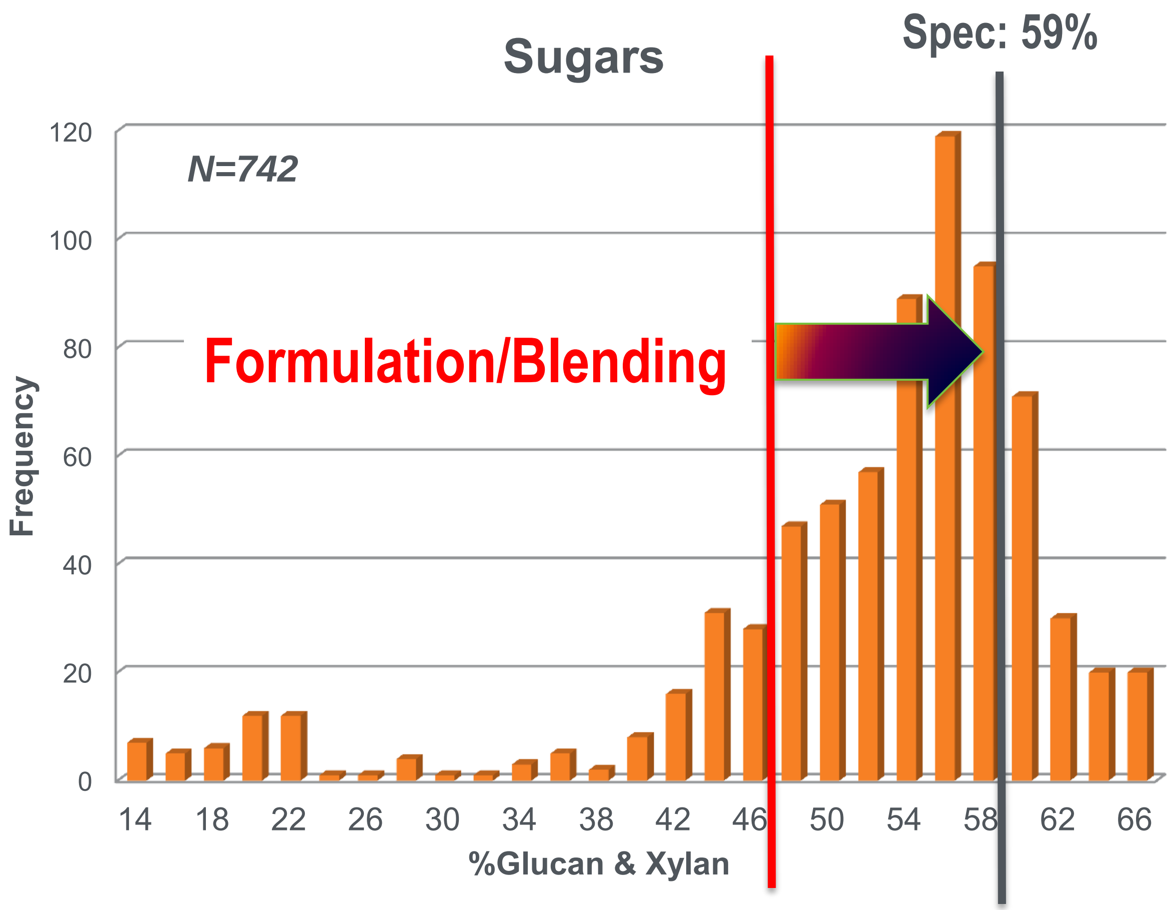
Stabilization through densification



2 – Add'l Tech Accomplishments:
Step #3: Preprocessing to Achieve Sugar Spec

Formulation

- Aggregation – blending of same biomass type to spec
- Blending – multiple resource types to spec
- Amendment – blend with source of cheap sugars



2 - Add'l Tech Accomplishments: Step #1: Feedstock Selection for Ash

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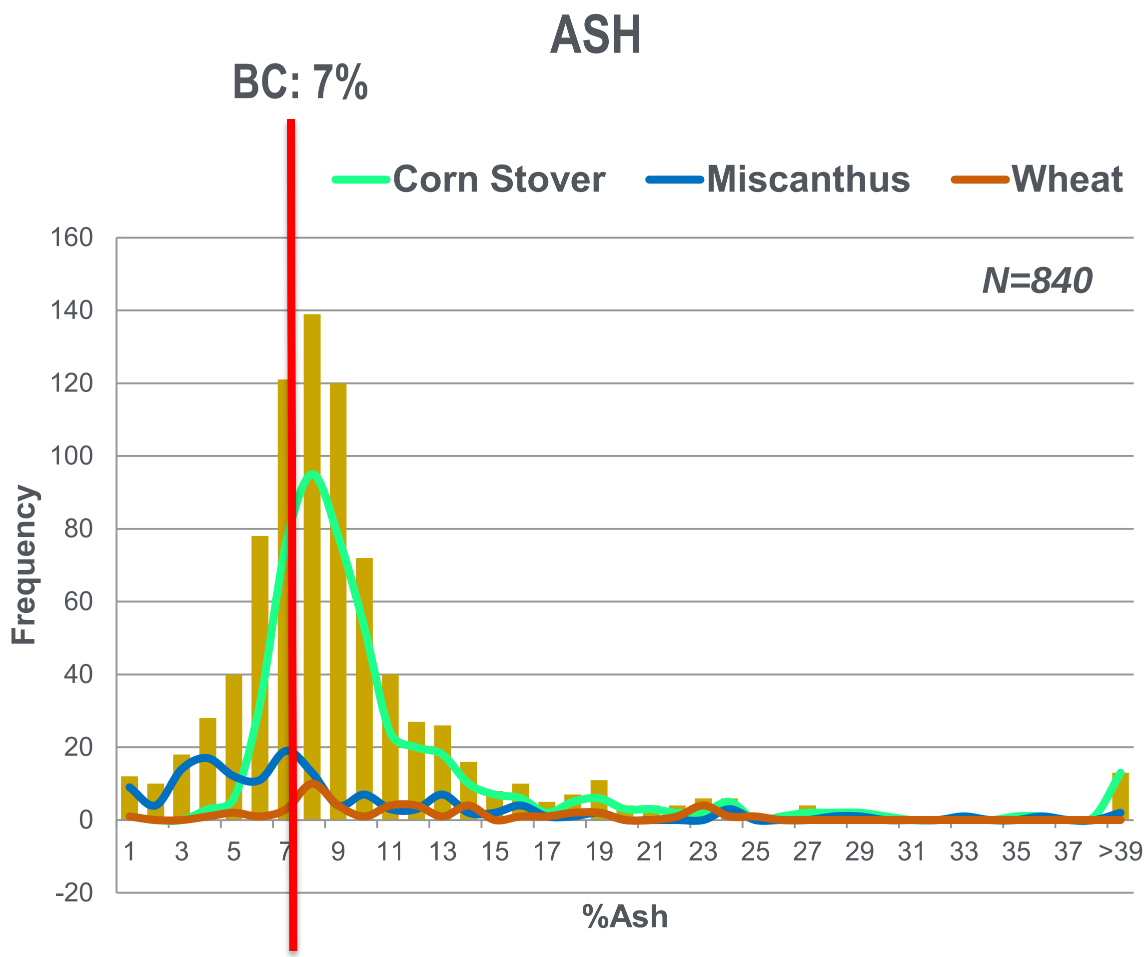
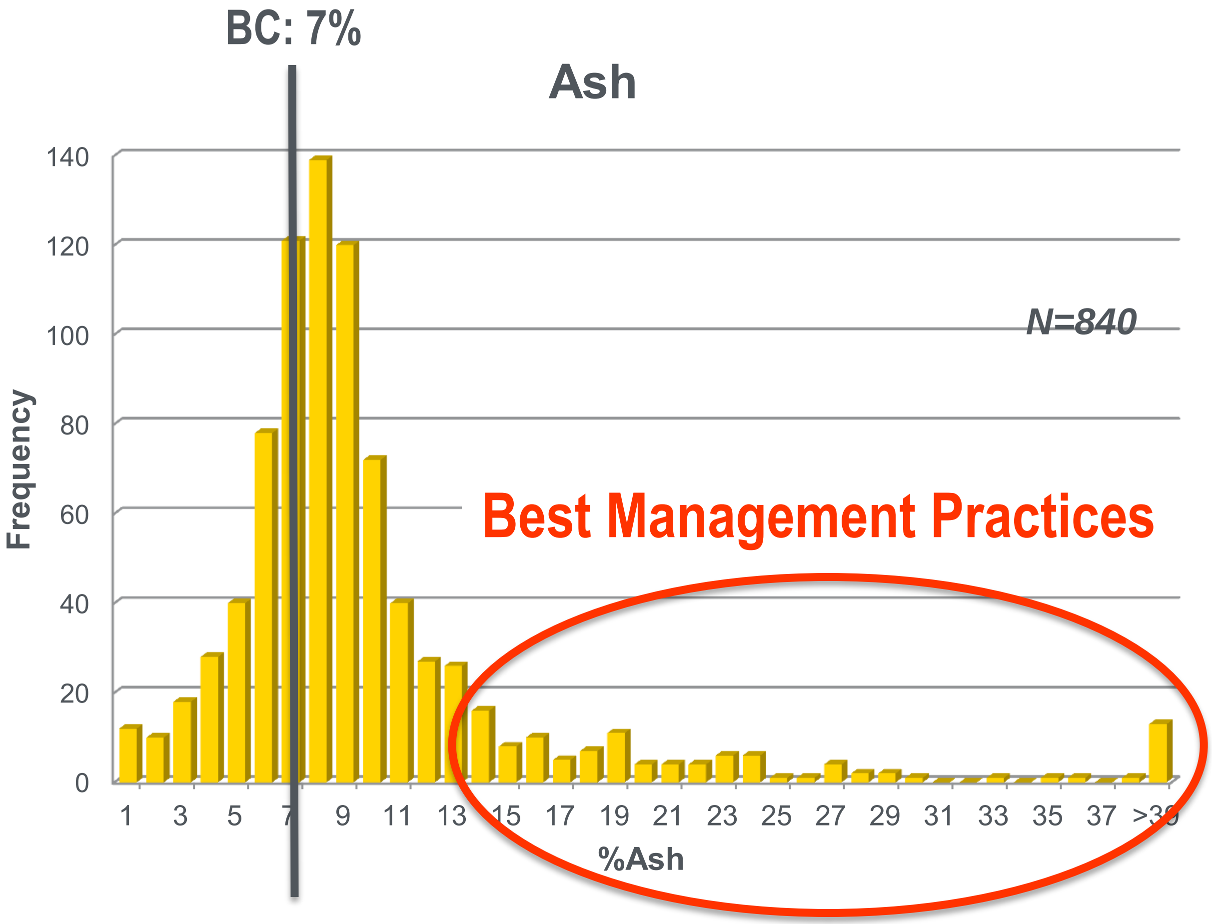


- Selection of optimum feedstock
- Risk: Reliance on specific biomass resources
- Results in boutique feedstocks

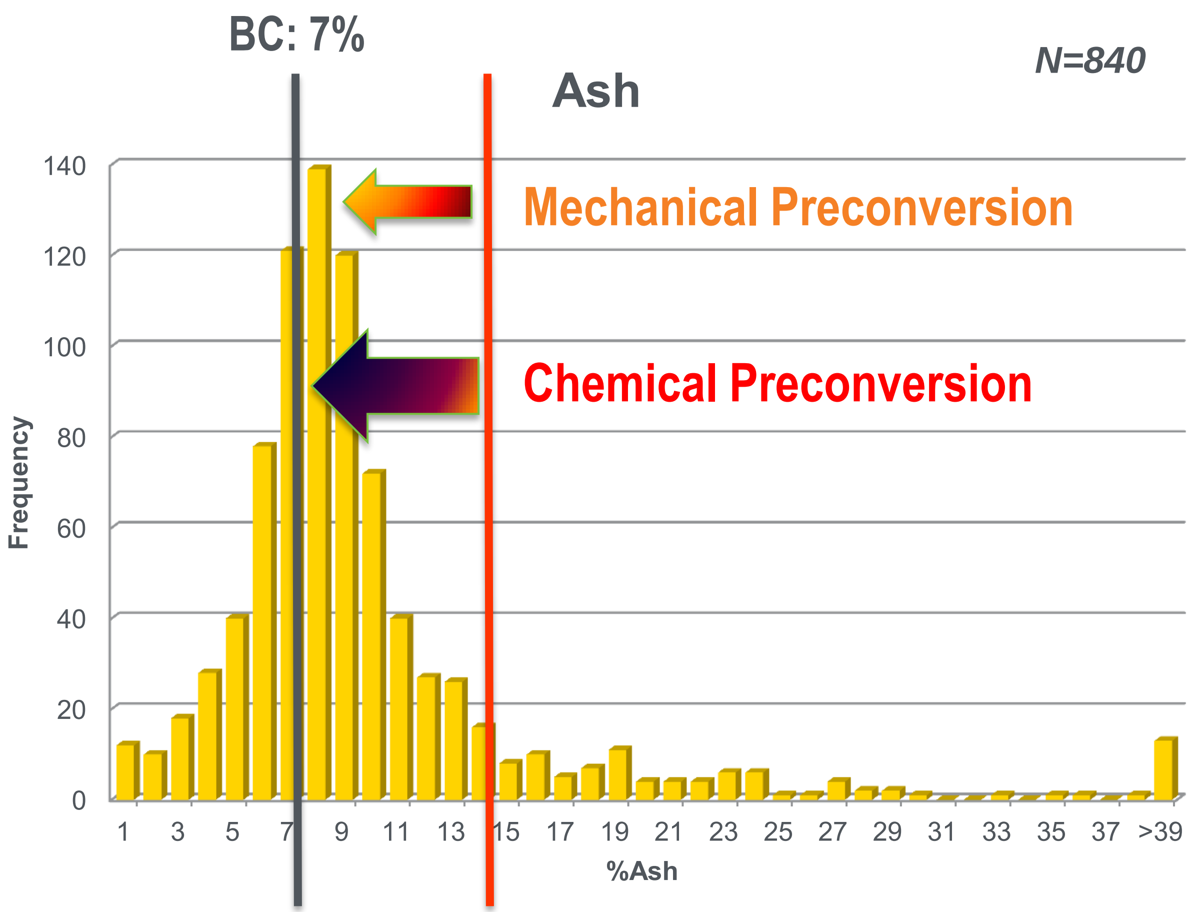
2 – Add'l Tech Accomplishments:
Step #2: Eliminate soil contamination



- Biomass-specific methods
- Biomass-specific equipment

Reduce ash content to physiological levels (5-7 wt%) by minimizing soil contamination

2 – Add'l Tech Accomplishments:
Step #3: Preprocessing to achieve ash spec



Mechanical Preconversion

- Removal of non-structural ash (soil)
- Fractionation & separation of high ash anatomical fractions
- Sieving to remove soil

Chemical Preconversion

- Removal of physiological ash
- Hot water
- Acidic
- Alkaline

Publications

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Publications and Documents

- A.E. Ray, A.N. Hoover, N. Nagle, X. Chen, and G.L. Gresham, "Effect of pelleting on the recalcitrance and bioconversion of dilute-acid pretreated corn stover under low- and high-solids conditions," *Biofuels,* 2013, 4 (3), 271-284.
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- R.A. Emerson & Garold Gresham, "Characterization of Advanced Preprocessed Materials (Hydrothermal)," Sept 2102, www.osti.gov/servlets/purl/1060958/
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