DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Value-added process intensification in the supply chain
W.B.S: 1.2.1.1000

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Feedstock Technologies Session

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Project Overview

Overarching goal:

- Utilize post-harvest physiology and chemistry tools to drive the mechanistic understanding of the biological and chemical reactions that can either degrade or upgrade biomass
  - Application of fundamental knowledge within the working envelope of supply and logistics systems
  - R&D solutions balanced with techno-economic assessments and carbon balances
- Enable real-time learnings and facilitate scale-up to industry

Silage pile with 5% loss over 6 months (Wendt et al., 2018)

Queuing pile at pellet facility
https://www.bruks-siwertell.com/blog/wood-yards-so-much-more-pile-chips

Project History

- **FY15-17: Development of a Wet Logistics System for Corn Stover**
  - Overall project began assessing industrial scale wet storage (i.e. ensiling) at biorefinery rate to preserve corn stover dry matter
  - Funded in response to bale yard fires occurring at Integrated Biorefineries
- 2017 BETO Peer Reviewers suggested the project look beyond storage for stability and explore recalcitrance reduction
  - Resulted in overall change in focus from being a cost-center to value-add
- **FY18-20: Value-added process intensification in the supply chain**
  - 2019 Reviewers stated it was "one of the most relevant projects in the FSL portfolio. Success here will solve several of the most pressing problems around feedstock variability"
- **FY21-23:** Identify storage-assisted quality improvements and physical changes occurring in forest and herbaceous residues to promote delamination ; characterize value-add components

Project Overview

Project goal: Assess opportunities for value-add in the supply chain

Design a feedstock logistics system that utilizes moisture during the residence time in storage to protect and even increase feedstock value (corn stover focus)

- Mismanaged moisture in corn stover continues to negatively impact all unit operations from the field to the reactor
  - Example risk: bale degradation due to excess moisture can result in 30% loss
- Moisture can be used to our advantage by designing logistics systems and operations that are compatible with it
  - Example solution: utilize anaerobic storage where dry baled storage is unlikely

Assess additional opportunities for value-add while improving biomass quality (woody biomass focus)

  - Probe for value-add to increase profitability in low-cost forest residues (FY20)
  - Apply to delamination of woody and herbaceous biomass and MSW (FY21-23)

1 – Management

Engage diverse national laboratory **capabilities** through **collaboration**

- Measure cost impacts with INL Feedstock Supply Chain Analysis team
- Measure impacts of storage treatments through collaboration (e.g. NREL, LANL)

Interaction with BETO promotes **relevance** to DOE and industry

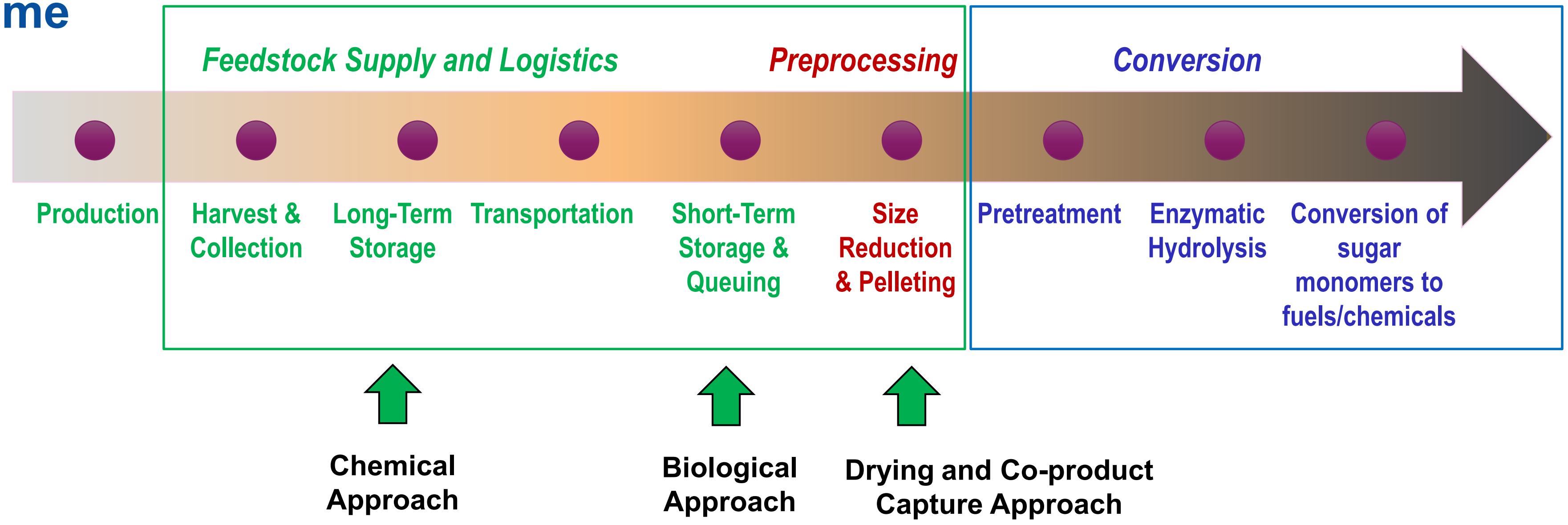
- Annual Operating Plans (AOPs) used to **define research path** and work scope
- Quarterly progress reports and milestones document **step-wise progression** of research
- Quarterly presentations for BETO provide framework for information sharing and **feedback**

Peer-reviewed publications and conference presentations to disseminate results

- Sponsored Research Topic in Frontiers in 2020
  - Storage of Biomass Feedstocks: Risks and Opportunities
  - Review article
  - Perspective article
  - Forest residue, ag residue, waste, and algae covered
- 3 additional manuscripts in preparation

2 – Approach – Value Added Storage

- Addressing the challenge of recalcitrance though value-added, wet storage can be accomplished to improve bioconversion
  - **Physiochemical barriers** in corn stover that necessitate increased temperatures, time, and severity **can be overcome in short- or long-term storage by leveraging the residence time**



- Addressing the challenge of extractives in the supply chain
  - Resins such as diterpenes appear to be a major contributor to plugging in high temperature feed systems

2 – Approach – Value Added Storage

- Long-term storage (>1 month): Promoting chemical impregnation
  - Opportunity: Adding alkali in long-term anaerobic storage to promote chemical impregnation and lignin breakdown for deacetylation and mechanical refining pretreatment
  - Risk: Cost increases in transportation due to moisture
- Queuing (Days to weeks): Promoting biological depolymerization
  - Filamentous fungi: selective and non-selective lignin degraders have been documented to reduce pretreatment severity
  - Opportunity: Application for on-site queuing similar to “seasoning” in pulping industry
  - Risk: Cost increases due to fungal growth resulting in dry matter loss

Success measured by:

- Go/No-Go milestone (completed 3/31/19)
  - Quantified potential for value-added storage reduction recalcitrance by 30%
- End of Project Milestone (completed 9/30/20)
  - Defined costs of a logistics system that preserves corn stover and quality while offsetting costs by $3/ton

3 – Impact

- Alternatives to the dry bale state of technology for high moisture regions or energy crops
  - Provides alternative pathways to manage year-round supply risks
  - Addresses harvest and logistics complications due to waiting for crop dry down
  - Addresses BETO technical barrier: Ft-H. Biomass Storage Systems
- Ability to improve quality in low-cost residues makes them more commercially attractive for conversion entities
  - **Compatible with existing logistics operations** and conversion technology, leading to **quick market entry**
  - Addresses BETO technical barrier: Ft-E. Feedstock Quality
- Transforming storage from a cost-center to value-add
- Provisional patents issue to secure IP and encourage commercial interest
- High impact factor publications targeted to increase additional visibility

4 – Progress and Outcomes – Long-Term Alkali Storage

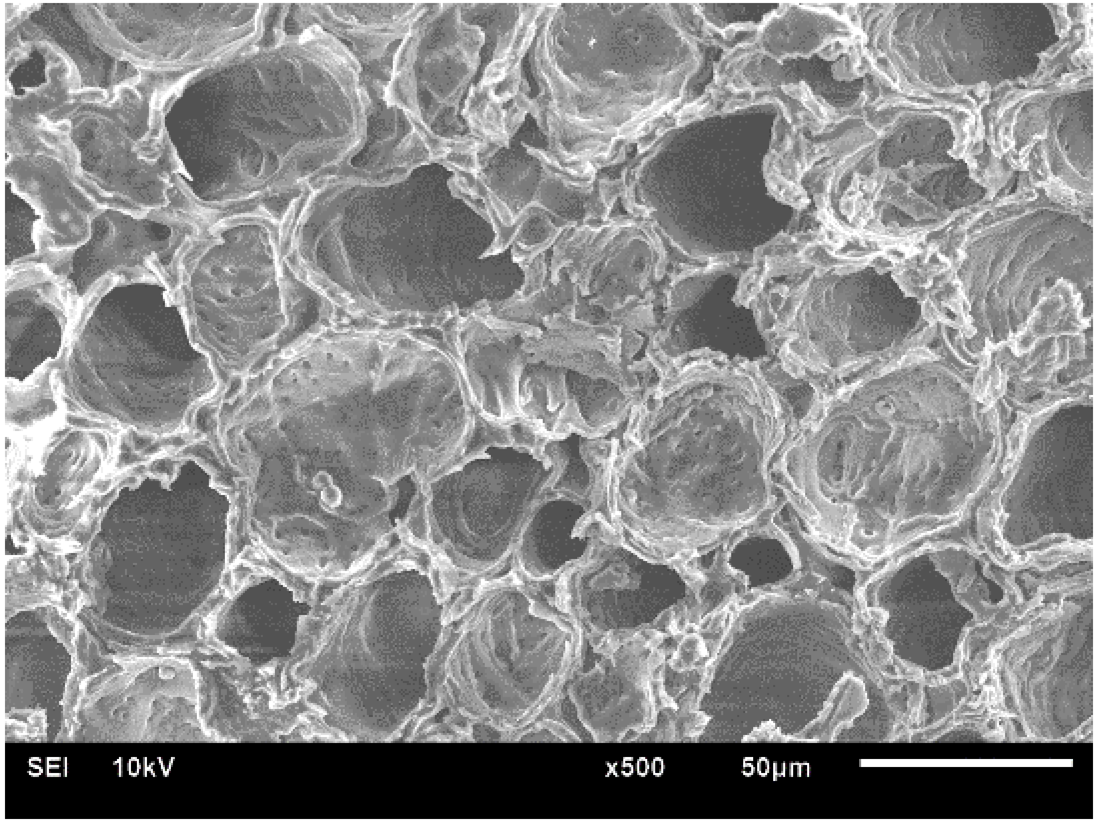
Goal: Understand the range of viable conditions for alkali addition prior to anaerobic storage to reduce recalcitrance

Experimental Matrix:

- Baseline: Anaerobic storage, 40% moisture, 5% dry matter loss
- Diffusion-based variables probed:
  - Anaerobic vs. Aerobic storage
  - Moisture content: 40% - 60%
  - Alkali addition: low and high loading

Impact: Understand how alkali addition in long term storage can improve carbon retention and begin to depolymerize corn stover

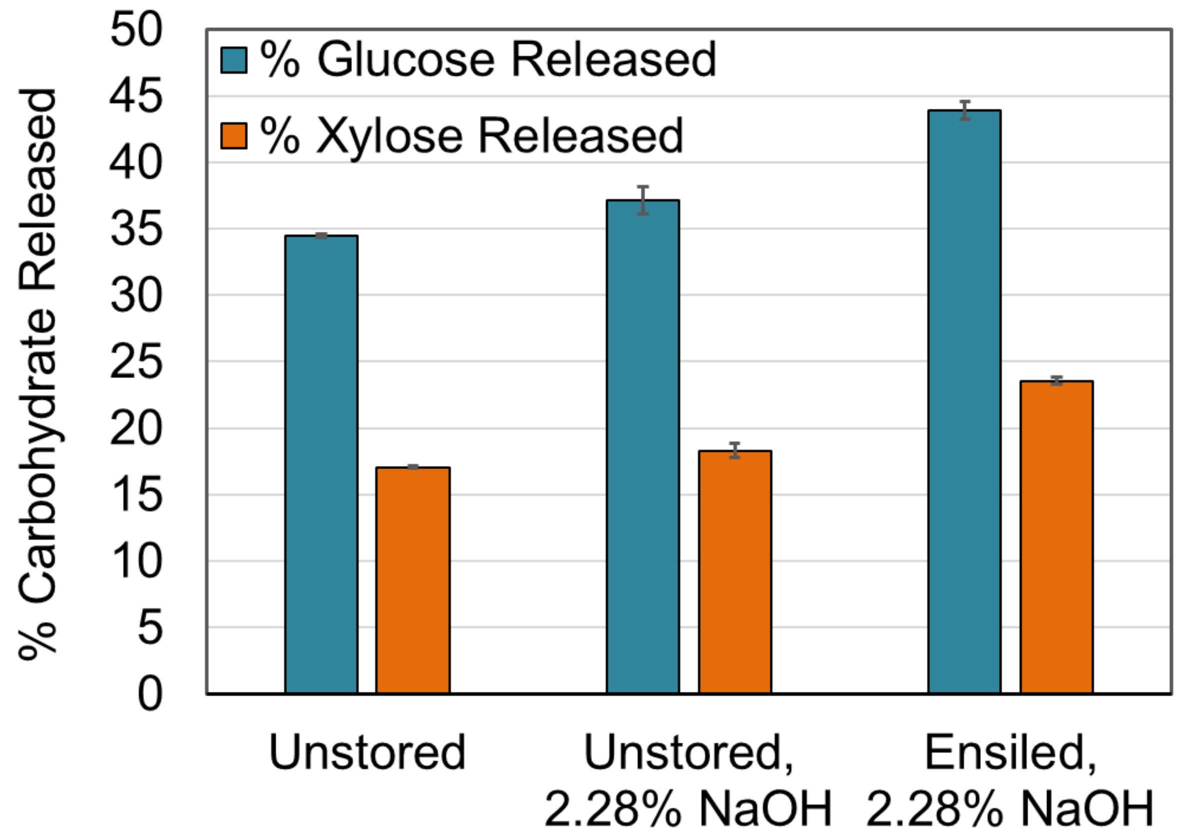
Result: *SEM images show physical changes* (pitting) in corn stover cell walls



Scanning electron microscopy (SEM) image of alkali-treated corn stover parenchyma, 500x magnification

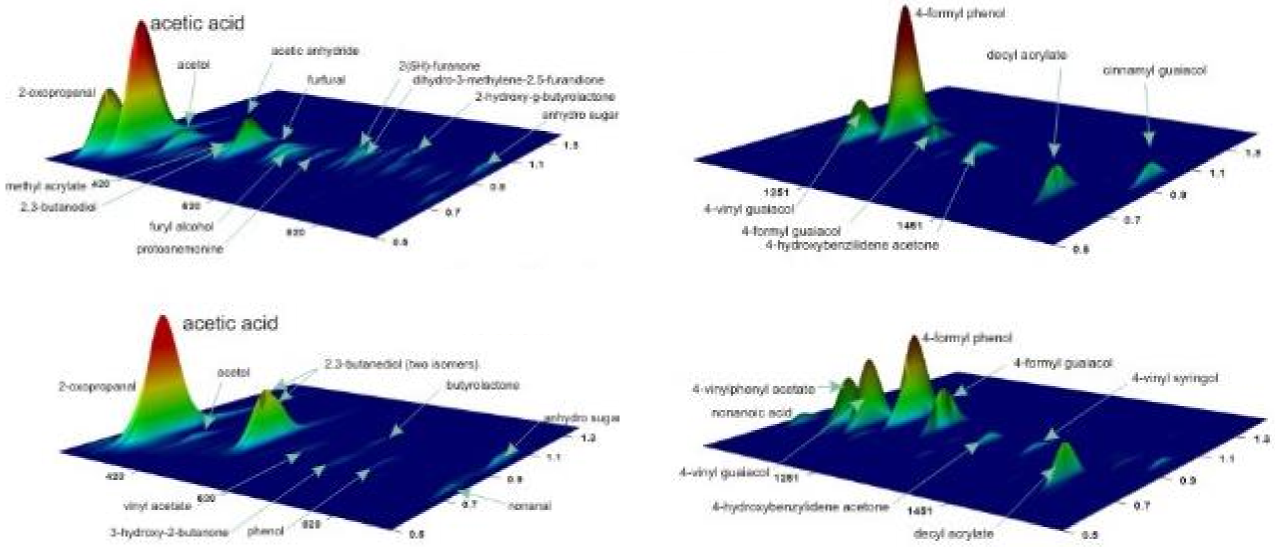
4 – Progress and Outcomes – Long-Term Alkali Storage

- Optimal conditions for reduced recalcitrance were 60% moisture, 2.3% NaOH loading, anaerobic storage
  - 4% dry matter loss observed
- Combined treatment and anaerobic storage results in improved carbohydrate release in enzymatic hydrolysis above alkali addition alone
  - 15% increase in glucose released
  - 22% increase in xylose released



4 – Progress and Outcomes – Long-Term Alkali Storage

- Probing the mechanisms of recalcitrance reduction using pyrolysis coupled with GCxGC/MS
- Stored sample results in:
  - Enhanced 2,3-butandiol release
    - Sugar degradation product
    - Fermentation product
  - Enhanced S and G lignol release
  - Reduced release of acid bridges binding lignin and hemicellulose



4 – Progress and Outcomes – Long-Term Alkali Storage

- Previous sensitivity analysis (Wendt et. al, 2018) indicates yield and bulk density are major cost drivers in transportation
  - Size reduction is also major cost driver in preprocessing costs
- Explored alternative approach based on U Wisconsin design (Cook et. al, 2011)
  - Forage chopping meets size specifications
- Assumed minimal dry matter loss, >5% alkali loading

Self-propelled forage chopper and high dump wagon

Silage tube and bagger

Walking floor trailer

4 – Progress and Outcomes – Long-Term Alkali Storage

- Alternative logistics scenario presented assuming high loading, minimal loss
- Silage tube scenario
  - Exceeds Milestone Target of $3/ton reduction for 2019 SOT
  - Meets Stretch Target of $2.25/ton for 2020 SOT
- Improved carbon retention
  - Experimental results indicate minimal dry matter loss compared to SOT of 5%

Cost Element	Cost ($/dry ton) (2016$)		
	2019 SOT: Two-Pass Stover	2020 SOT: Two-Pass Stover	Silage Tube
Grower payment	$20.13	$20.16	$20.16
Harvest and collection	$18.79	$18.79	$17.28
Storage and queuing	$6.53	$6.74	$21.70
Transportation and handling	$14.98	$13.74	$17.65
In-plant receiving and preprocessing	$20.84	$19.60	$1.16
Dockage	$1.01	$0.89	-
Feedstock Cost Total	**$82.28**	**$79.92**	**$77.95**

4 – Progress and Outcomes – Fungi Enhanced Queuing

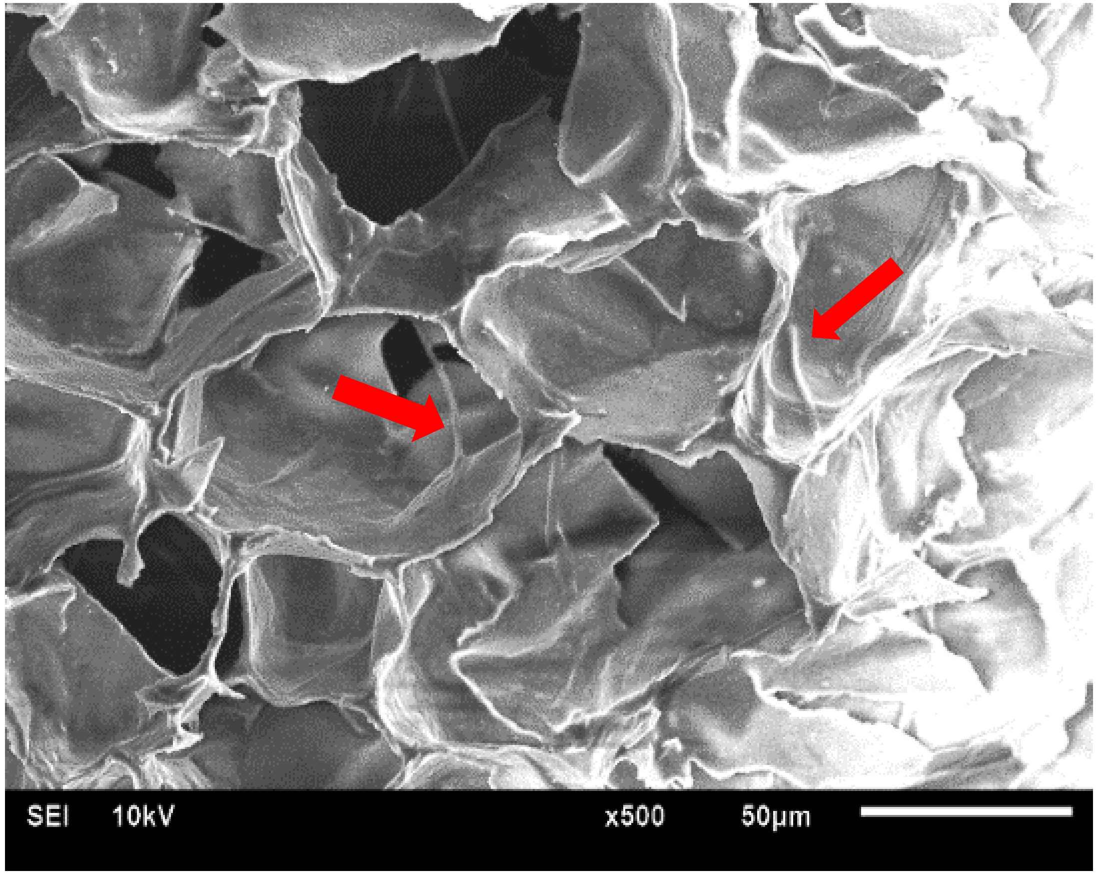
Goal: Understand the range of viable conditions for fungal treatment in queuing piles

Experimental Matrix:

- Baseline: No treatment
- Diffusion- and strain-based variables probed:
  - Selective and non-selective lignin degraders
  - Moisture content: 40% - 60%
  - Residence Time 2 - 4 weeks

Impact: Develop queuing systems that can provide necessary residence time to maintain biorefinery supply while reducing downstream treatment time

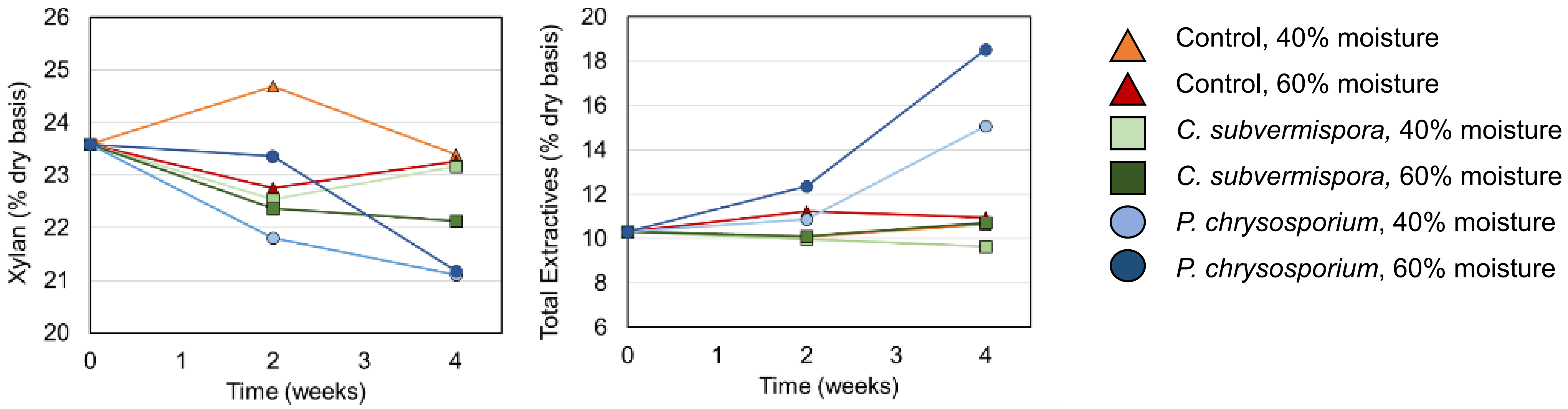
Result: Fungal hyphae attached in cell lumen and visualized by SEM



Scanning electron microscopy (SEM) image of fungal treated corn stover parenchyma, 500x magnification

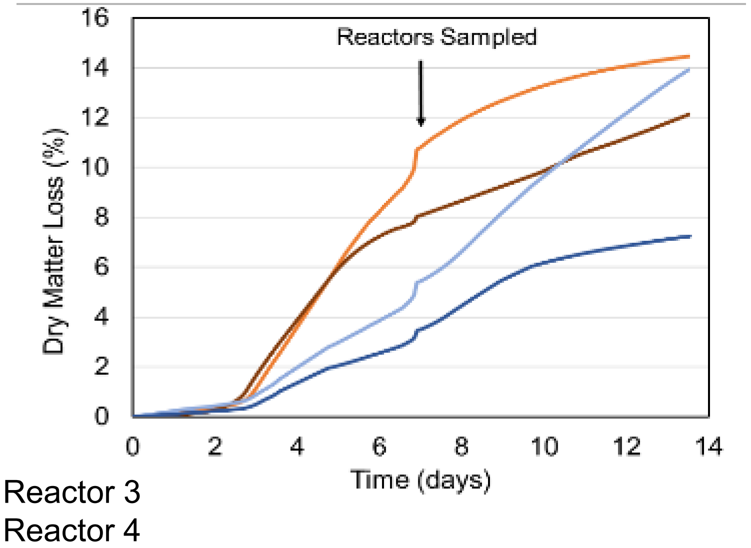
4 – Progress and Outcomes – Fungi Enhanced Queuing

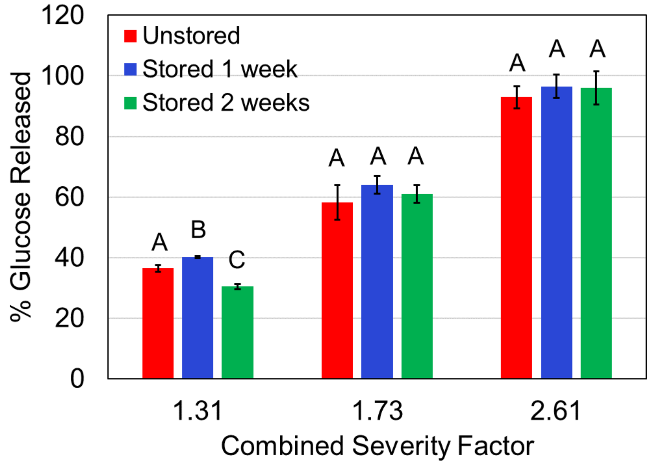
- Higher moisture content needed to support depolymerization
  - Increases soluble lignin, xylan, and arabinan observed
- Dry matter loss and depolymerization must be balanced
  - 2 weeks sufficient time
- *P. chrysosporium* selected for scale-up to demonstrate greatest impact in recalcitrance reduction

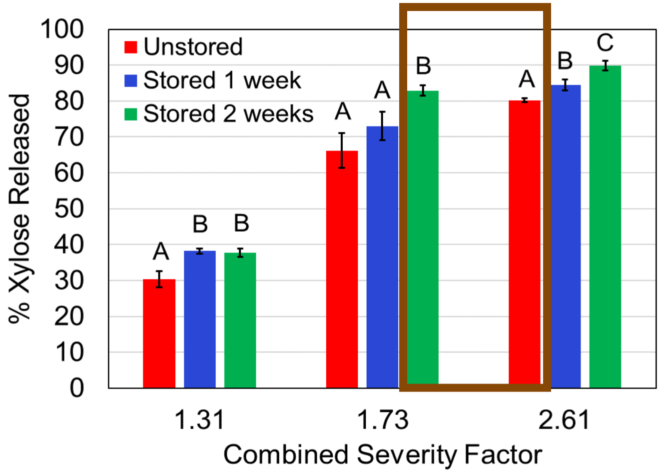


4 – Progress and Outcomes – Fungi Enhanced Queuing

- Real-time degradation rate obtained in storage 100 L controlled storage reactors
  - 60% moisture corn stover inoculated with *P. chrysosporium*
  - Moisture only control
- Dilute acid pretreatment (PT) followed by enzymatic hydrolysis indicated
  - 30% reduction of severity PT possible in xylose
    - Temperature reduction from 160°C to 130°C possible
  - No difference in glucose indicates cellulose microfibrils unaffected by storage

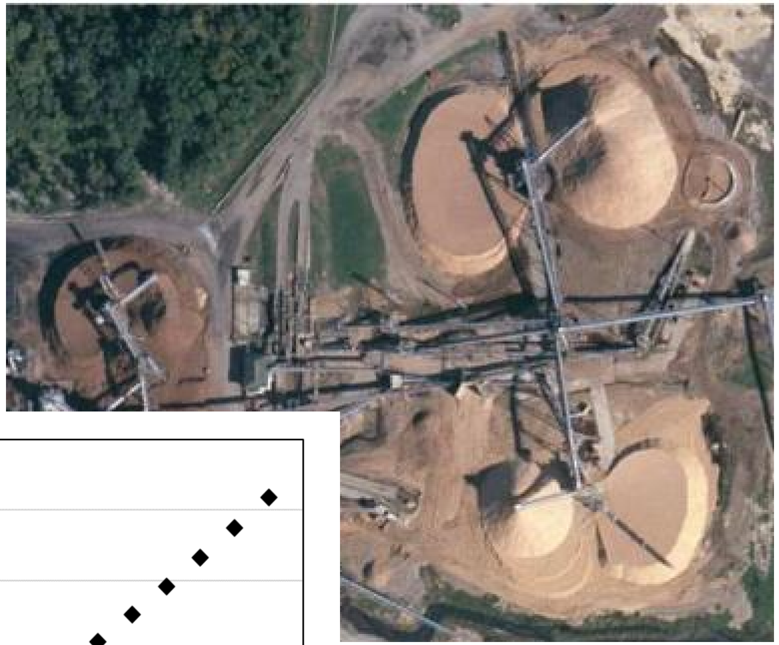


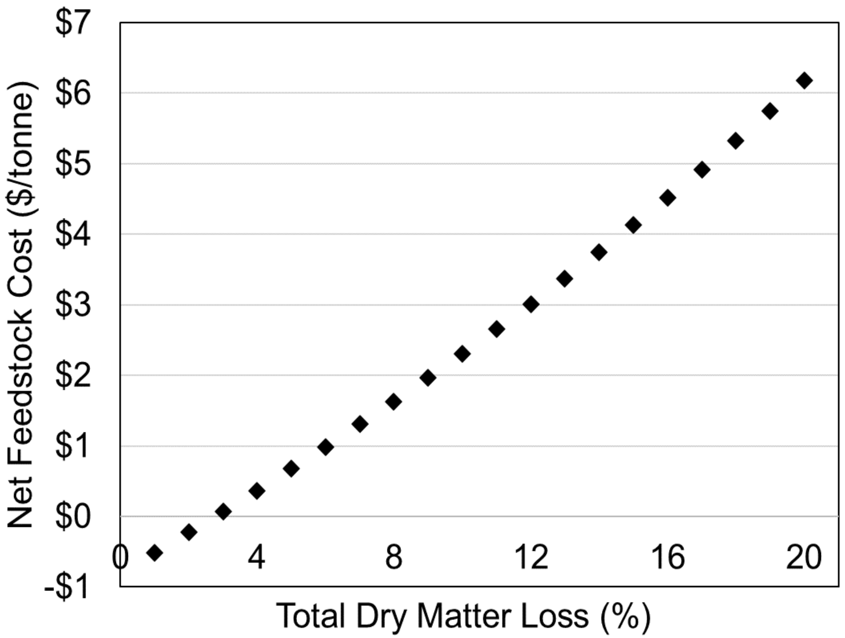




4 – Progress and Outcomes – Fungi Enhanced Queuing

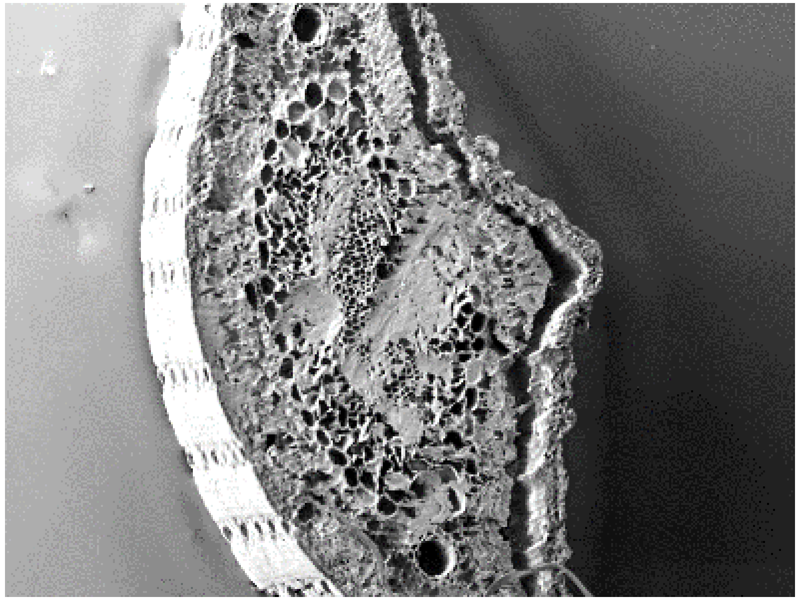
- All dry bale logistics supply chain unit operations preserved until depot co-located with biorefinery
- Active stacking reclaiming queuing pile
  - First in, first out
  - 7- or 14-day residence time
- Result: maintaining 3% dry matter loss of less necessary to under these conditions
  - Suggests dry matter loss must be balanced with recalcitrance reduction, but opportunities exist for lower residence time treatments



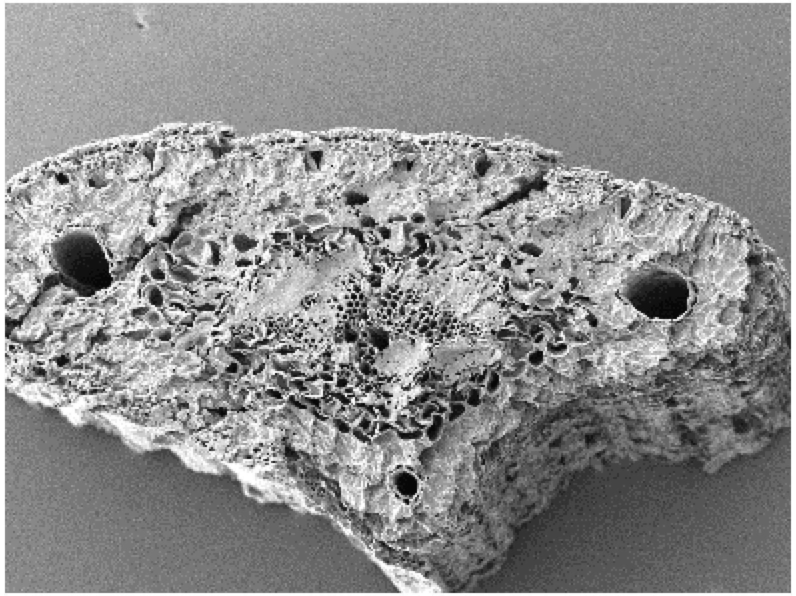


4 – Progress and Outcomes – Value-Added Drying

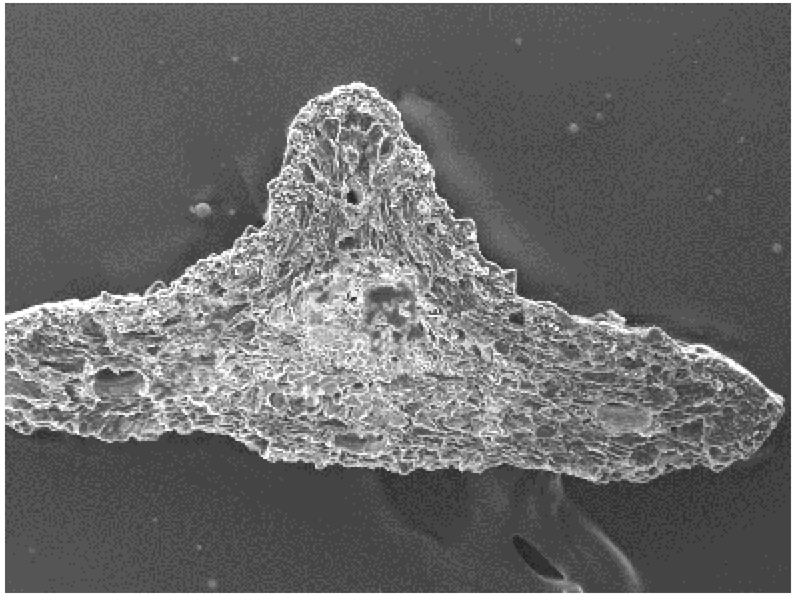
- Assessed pine needles that could be isolated from low-cost residues but do not meet quality specs for conversion
- Drying biomass with Dimethyl-ether (DME) could reduce drying energy by 50%
  - Pore collapse shown in high temperature drying



DME Dried Needles 100x



40°C Dried Needles 100x

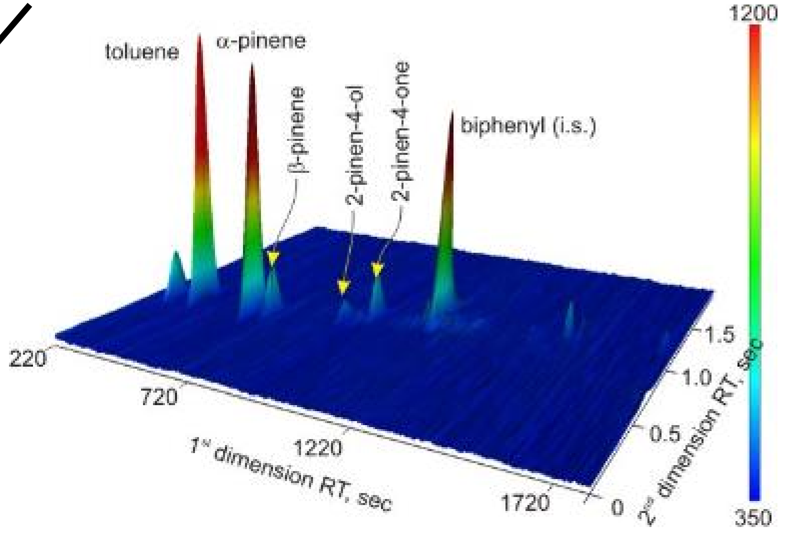


105°C Dried Needles 100x

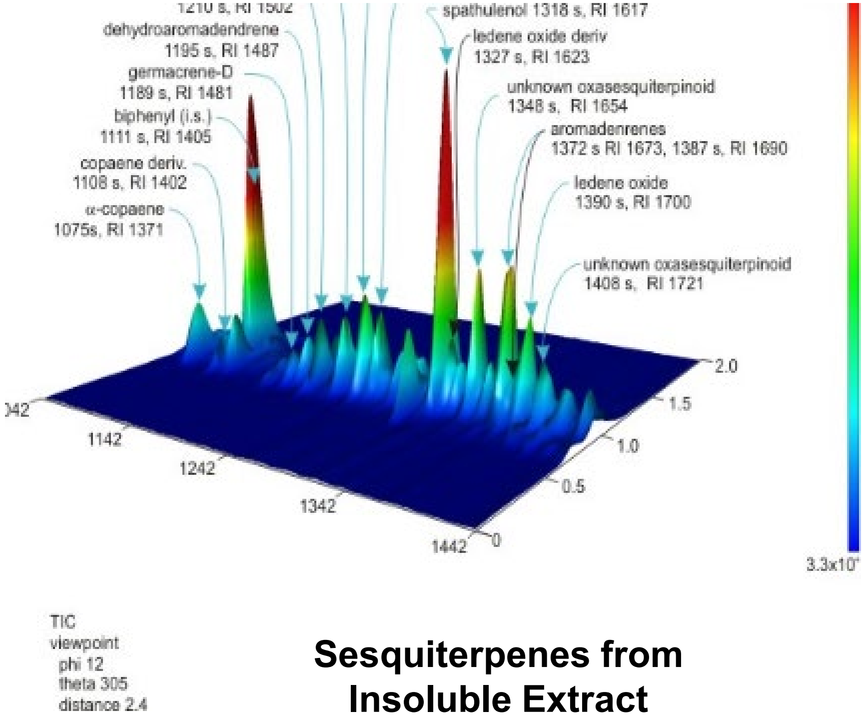
4 – Progress and Outcomes – Value-Added Drying

- Micropyrolysis coupled with GCxGC/MS utilized to characterize extracts
- α-pinene and spathulenol were identified as a value-added co-products
  - Essential oil markets; anti-inflammatory and anti-microbial markets, jet fuel

DME Dried Pine



Diterpenes from Aqueous Extract



Sesquiterpenes from Insoluble Extract

Summary

- Storage can be refocused to become a value-add instead of a cost by utilizing the residence time to perform slow chemical transformations
  - Recalcitrance reduction possible though biological and chemical approaches
  - Compatible with multiple conversion approaches
- Mechanisms of reduced recalcitrance are being probed through multiple methods to gain a fundamental understanding of reactions and impacts
  - Understanding compositional, mechanical, and conversion changes will aid in mechanistic understanding
- Future Goals (FY21-FY23 cycle): The knowledge gained can be applied to numerous conditioning scenarios in woody biomass, herbaceous crops, and MSW
  - Specific anatomical fractions
  - Delamination to influence tissue fractionation
  - Reduction in preprocessing energy requirements

Acknowledgments

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- INL Bioenergy Staff:
  - William Smith, Bradley Wahlen, Michelle Walton, Rebecca Brown, Austin Murphy, Kastli Schaller, Frederick Stewart, Sergio Hernandez, Vicki Thompson, Brad Thomas, Jason Nguyen, Sarah Traynor, Quang Nguyen, Gary Groenewold, Brittany Hodges, Aaron Wilson, Luke Williams
- NREL and LANL Collaborators:
  - Nick Nagle, Xiaowen Chen, Troy Semelsberger, Juan Leal

Quad Chart

Timeline

- Project start date: 10/1/2020
- Project end date: 9/30/2023

	FY20	Active Project
DOE Funding	*$585,000*	*$1,540,347*

Project Partners*

- NREL, PNNL, INL: 1.1.1.2, 1.2.1.1; 1.2.1.2; 1.2.1.5; 3.4.1.202,

Barriers addressed

- Ft-F. Biomass Storage Systems
- Ft-E. Feedstock Quality

Project Goal

Storage is currently a cost-center. This project will transform storage to a value-add operation by utilizing low-severity treatments over the residence time in storage.

End of Project Milestone

Go/No-Go (completed FY19Q2): Achieved 30% reduction in PT severity for fungal-treated stover and >30% increase in sugar yield in alkali-treated corn stover after mechanical refining and EH compared to untreated biomass from the same harvest.

End of Project Goal/Q4 (completed FY20Q4): Demonstrate the ability to offset feedstock costs by $3/ton, which could transform storage from a cost-center to a value-add operation, through the application of low-severity treatments over the long residence time in storage

Funding Mechanism

AOP

*Only fill out if applicable.

Idaho National Laboratory

Responses to Previous Reviewers’ Comments

- Wet storage of biomass is a great area of DOE/BETO to fully understand, most notably the cost implications as potential value addition is balanced against higher handling costs. Understanding of current negative cost state suggests some discussions of the cost development pathway screening to accompany the characterization pathway needs to occur with adjacent FSL projects in the portfolio, perhaps resulting in integration of some concepts to mitigate risks associated with each. Wet storage treatments have the potential to help normalize feedstocks/blends in support of creating fungible feedstock.
- This is one of the most relevant projects in the FSL portfolio. Success here will solve several of the most pressing problems around feedstock variability, at least as to corn stover and other materials with similar qualities. And in turn would encourage the investment in and building of projects to advance BETO objectives according to their MYPP. There was a good explanation of the applications for the development of a full commercial scale storage yard. I am not sure PIs have thought through other indirect impacts that this work could have on other parts of the overall enterprise of a cellulosic biorefinery. With the ability to bale wet material, current SOT in baling operation's costs could be cut by 10% or more; if advanced harvest and baling was used by as much as 50%. Advanced baling methods would also reduce the ash content of corn stover and in turn solve another of the most pressing impacts caused by feedstock variability.
- We thank the reviewers for the supporting feedback regarding this research effort. We agree that moisture-tolerant logistics systems can significantly reduce the unforseen costs that are incurred as a result of delayed baling to facility in-field drying as well as deliver a low-variabilty, fungible biomass feedstock to a biorefinery. Furthermore, the opportunity to transform the unit operation of storage from a cost center to a value-added operation shows significant promise for reducing biomass recalcitrance. We will continue to investigate process intensification approaches for delivering biomass of consistent quality, moisture content, and throughput to a biorefinery, meanwhile realizing the potential for pretreatment during storage. We will also work with our colleagues at INL to advance this technology, specifically by incorporating the undocumented risks associated with delayed baling, assessing the impact of storage treatments on pelleting, and scaling this approach through collaboration with the Biomass Feedstock National User Facility.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Thompson VS, Volk TA, Wendt LM, Editorial: Storage of Biomass Feedstocks: Risks and Opportunities. Frontiers in Bioengineering and Biotechnology. In Press. doi: 10.3389/fbioe.2021.657342
- Smith WA, Wendt LM, Bonner IJ, Murphy JA. Effects of storage moisture content on corn stover biomass stability, composition, and conversion efficacy. Frontiers in Bioengineering and Biotechnology 2020 8(716). doi: 10.3389/fbioe.2020.00716
- Quiroz-Arita C, Murphy JA, Plummer MA, Wendt LM, Smith WA. Microbial heat and organic matter loss in an aerobic corn stover storage reactor: A model validation and prediction approach using lumped-parameter dynamical formulation. Frontiers in Bioengineering and Biotechnology 2020 8(777). doi: 10.3389/fbioe.2020.00777
- Nagle NJ, Donohoe BS, Wolfrum EJ, Kuhn EM, Haas TJ, Ray AE, Wendt LM, Delwiche ME, Weiss ND, Radtke C. Chemical and structural changes in corn stover after ensiling: Influence on bioconversion. Frontiers in Bioengineering and Biotechnology. 2020 8(739). doi: 10.3389/fbioe.2020.00739
- Wendt LM and Zhao H. Review on bioenergy storage systems for preserving and improving feedstock value. Frontiers in Bioengineering and Biotechnology. 2020 8(370). doi: 10.3389/fbioe.2020.00370.
- Nguyen QA, Smith WA, Wahlen BD, Wendt LM. Total and sustainable utilization of biomass resources: A perspective. Frontiers in Bioengineering and Biotechnology. 2020 5;8:546. doi: 10.3389/fbioe.2020.00546.
- Wendt LM, Murphy JA, Smith WA, Robb T, Reed DW, Ray AE, et al. Compatibility of high-moisture storage for biochemical conversion of corn stover: storage performance at laboratory and field scales. Frontiers in Bioengineering and Biotechnology. 2018;6(30).
- Wendt LM, Smith WA, Hartley DS, Wendt DS, Ross JA, Sexton DM, et al. Techno-Economic Assessment of a Chopped Feedstock Logistics Supply Chain for Corn Stover. Frontiers in Energy Research. 2018;6(90).

Publications, Patents, Presentations, Awards, and Commercialization

Presentations

- Wendt LM, Wahlen B, Walton M, Nguyen J, Schaller K, Nguyen Q. Alkali pretreatment of corn stover in storage. 41st Symposium on Biotechnology for Fuels and Chemicals. Seattle, WA. April 28-May 1, 2019.
- Wendt LM, Smith WA, Murphy JA, Robb T. Field demonstration of anaerobic storage for high moisture corn stover. 39th Symposium on Biotechnology for Fuels and Chemicals. San Francisco, CA. April 25-28, 2017.
- Wendt, LM, Murphy JA, Smith WA, Robb T, Nguyen Q, Hartley D. Cost and performance estimates of corn stover in a wet logistics system. Poster Presentation. The 38th Symposium on Biotechnology for Fuels and Chemicals, Baltimore, MD. April 25-29, 2016.

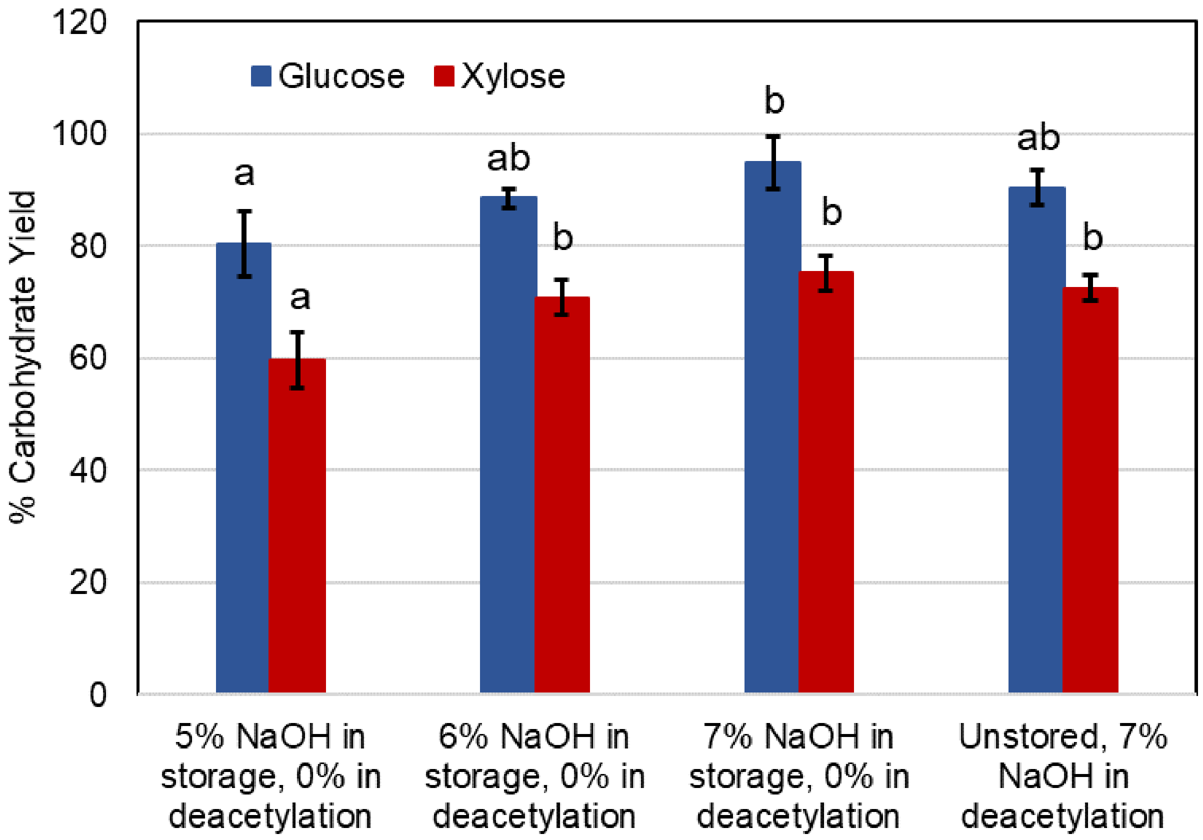
Patent

- U.S. Patent Application Serial No. 16/947,054, filed July 16, 2020, entitled "METHODS OF RECOVERING LIGNIN AND OTHER PRODUCTS FROM BIOMASS", having BEA Attorney Docket Number BA-1050.

Additional Slides

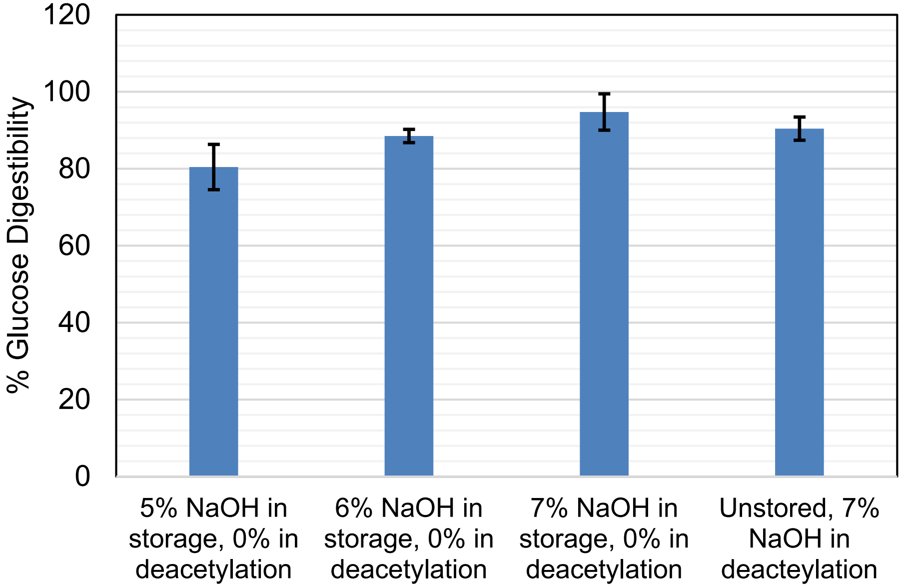
4 – Progress and Outcomes – Long-Term Alkali Storage

- Higher alkali loading assessed (5-7 wt%) with anaerobic storage
- Minimal dry matter loss → carbon retention metrics were preserved
- Hydrolysis differences were not statistically significant
  - Suggest opportunities for impacts in mechanical preprocessing



4 – Progress and Outcomes – Long-Term Alkali Storage

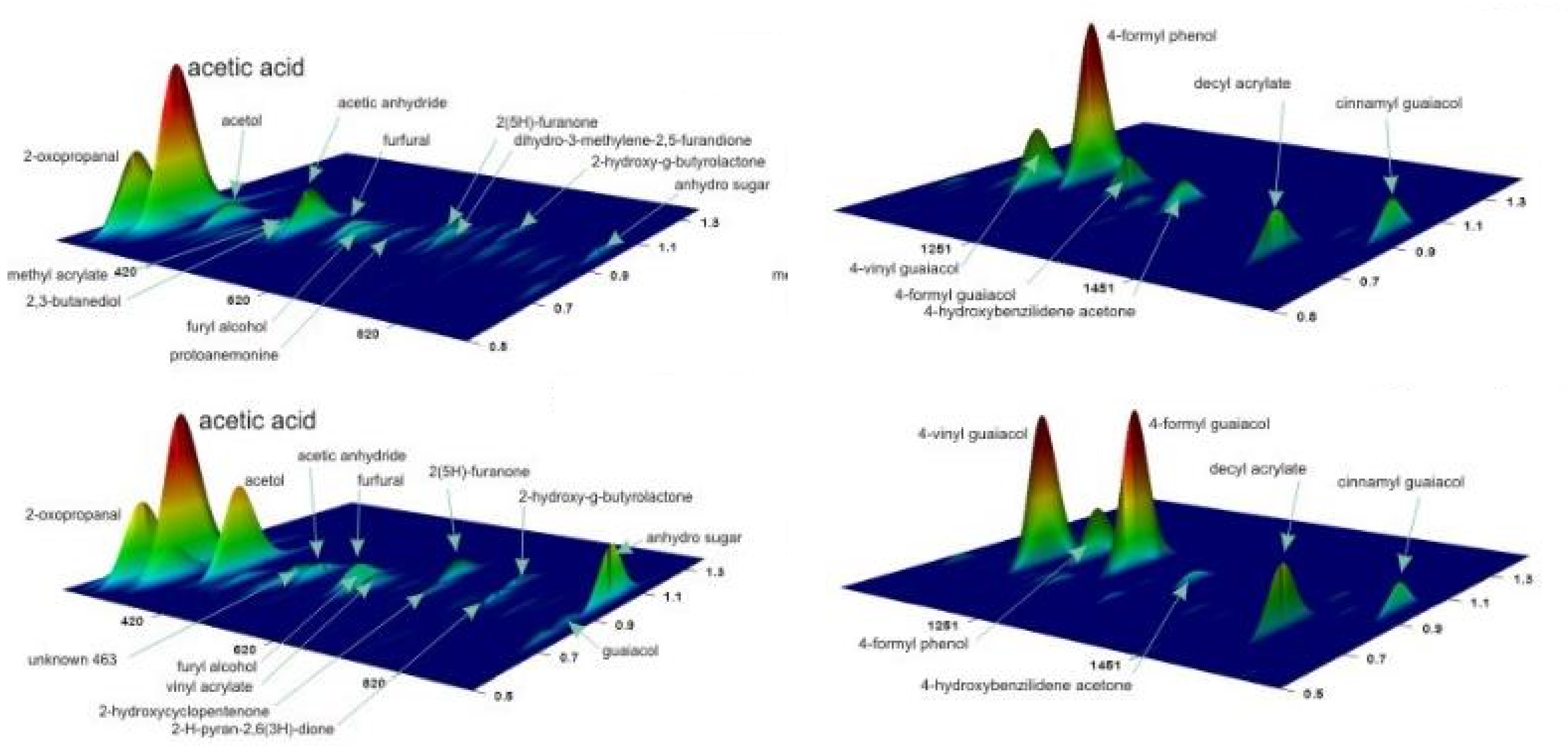
- Bale Wrap scenario in FY19 Q4 TEA relied on significant reduction in sodium hydroxide loading
  - One % point loading reduction = $3.95-$4.11/ton offset ($0.09/gge)
- Bale wrapping meets density targets but has increased storage costs



Cost Element	Cost ($/dry ton) (2016$) 2018 SOT: Two-Pass Stover	Bale Wrap
Grower payment	$21.71	$21.71
Harvest and collection	$18.79	$18.79
Storage and queuing	$6.53	$16.02
Transportation and handling	$13.52	$13.87
In-plant receiving and preprocessing	$22.65	$16.77
Dockage	$1.01	$1.01
Feedstock Cost Total	**$84.21**	**$88.17**
Alkali Reduction (Acids case)	-	($3.95)
Feedstock Cost Total	**$84.21**	**$84.22**

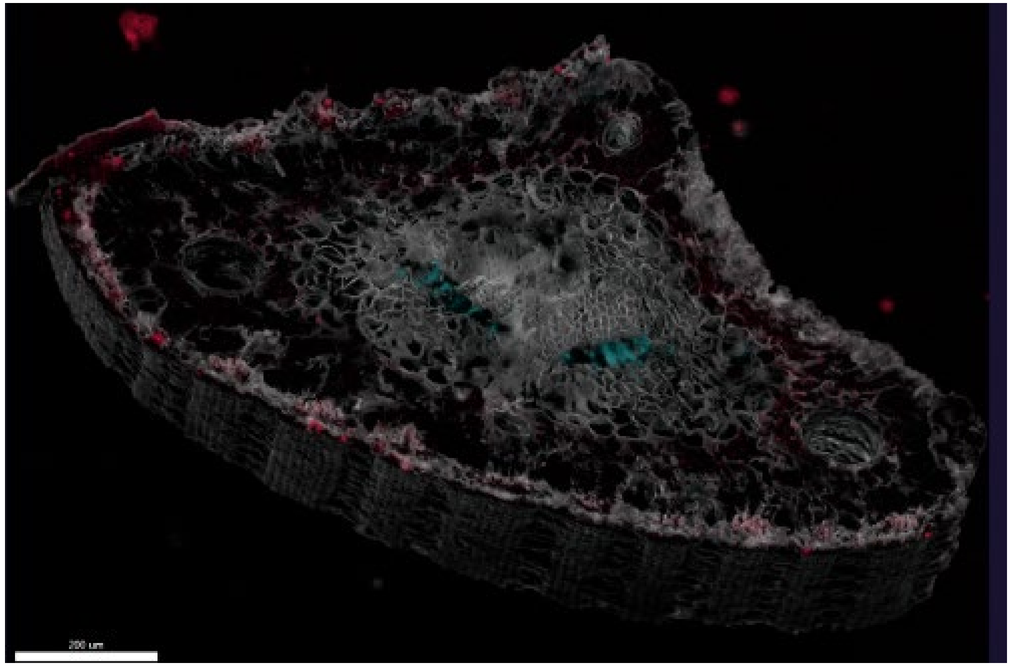
4 – Progress and Outcomes – Fungi Enhanced Queuing

- Stored sample results in:
  - Enhanced acetol and sugar degradation products
  - Enhanced g lignol release

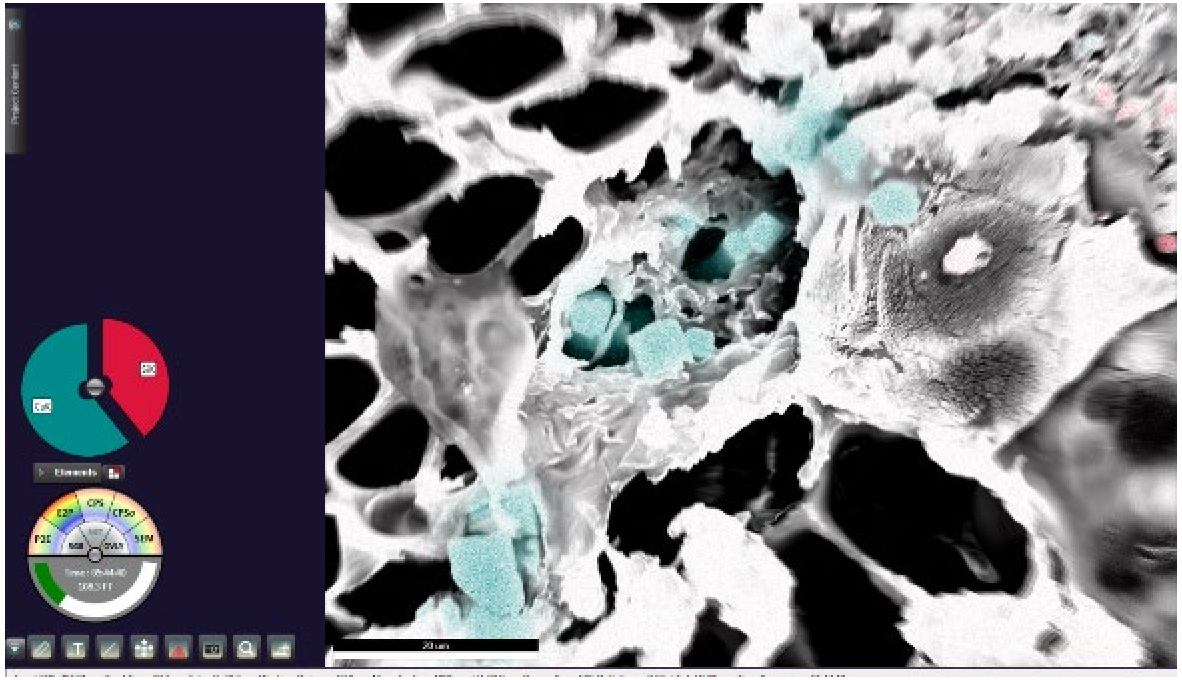


4 – Progress and Outcomes – Value-Added Drying

- 40°C dried samples show inorganic profile consistent with plant physiology
- Silica enriched in epidermis and mesophyl, calcium enriched in phloem
- Path forward: calcium oxalate crystals could be isolated using density-based separation if liberated during fine milling



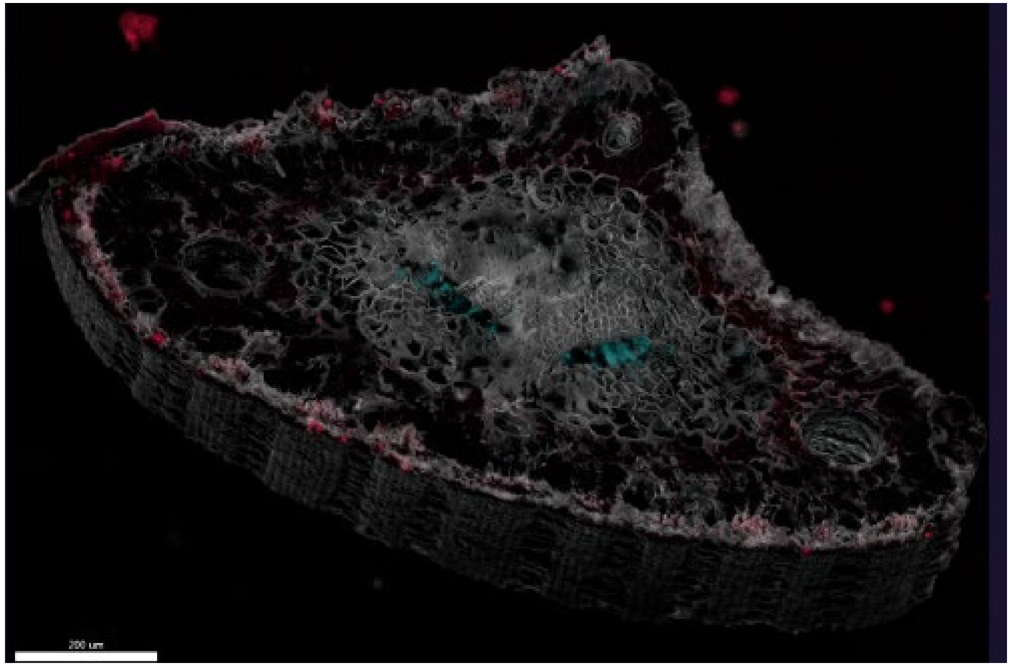
100x Magnification

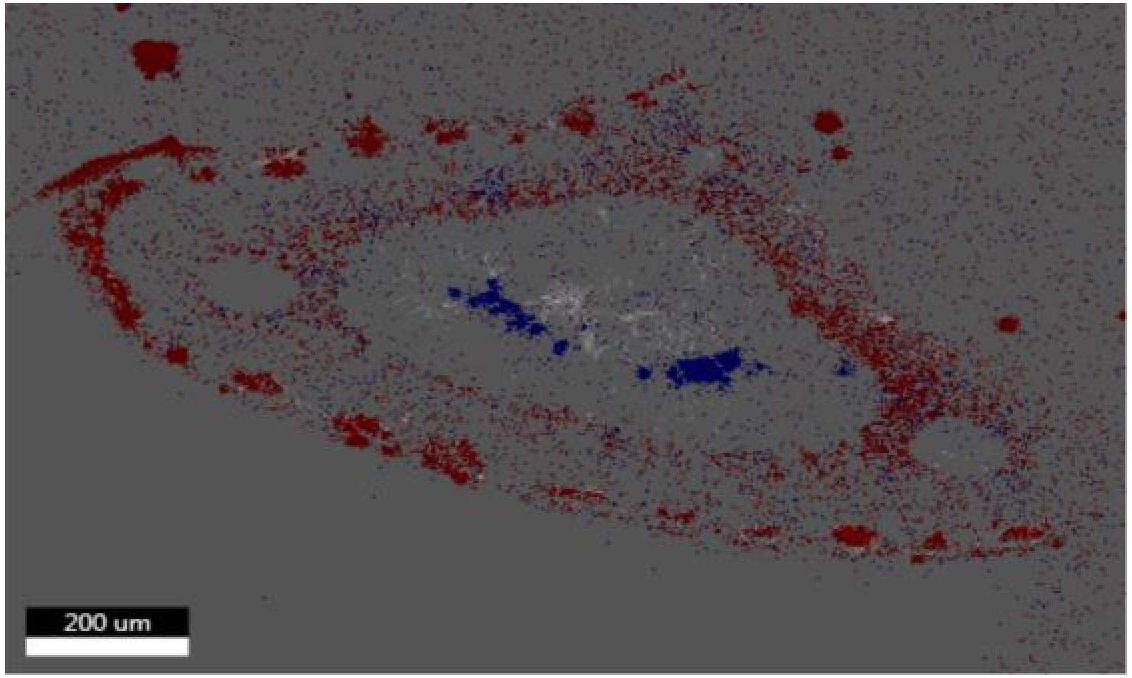


500x Magnification

4 – Progress and Outcomes – Value-Added Drying

- 40°C dried samples show inorganic profile
- Silica enriched in epidermis and mesophyl, calcium enriched in phloem
  - Path forward for isolation of Ca



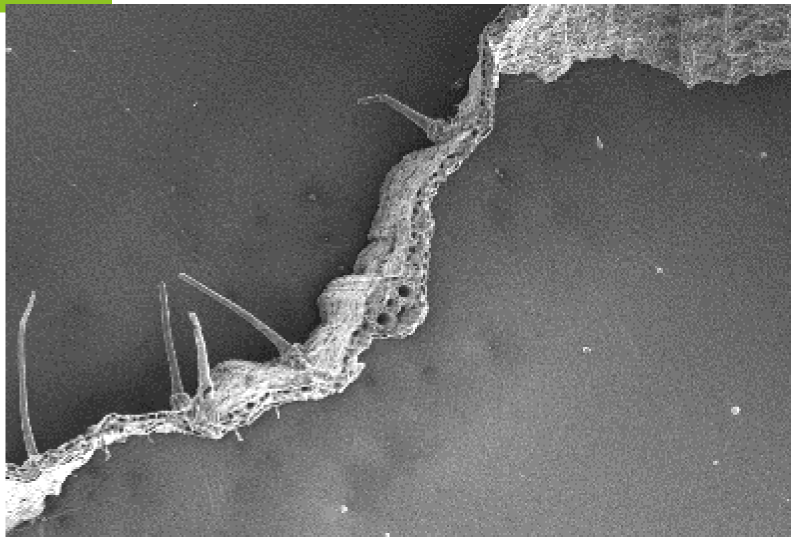
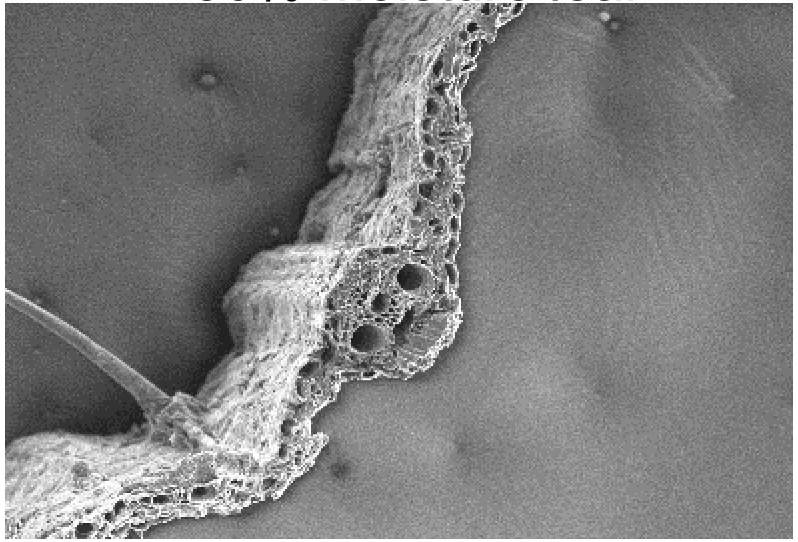
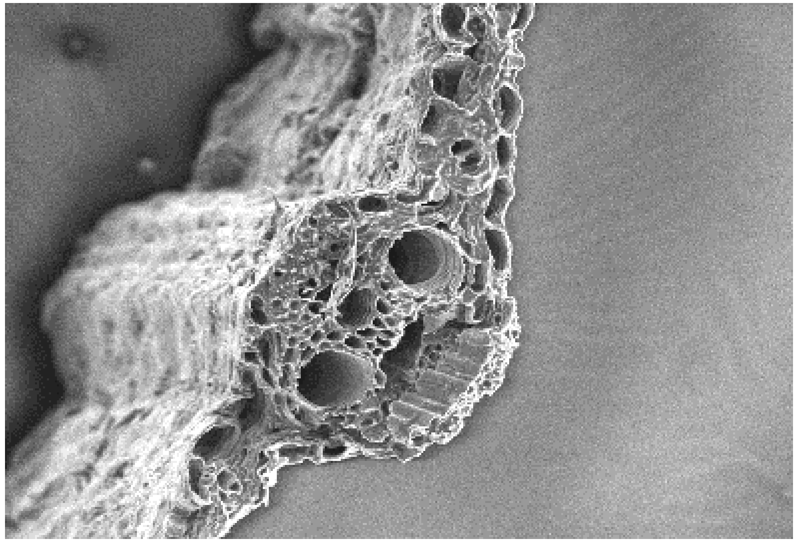


100x

- 91% Unallocated (667169 Pixels)
- 2% CaK/SiK (13670 Pixels)
- 7% SiK/CaK (49273 Pixels)

Stover SEM Images

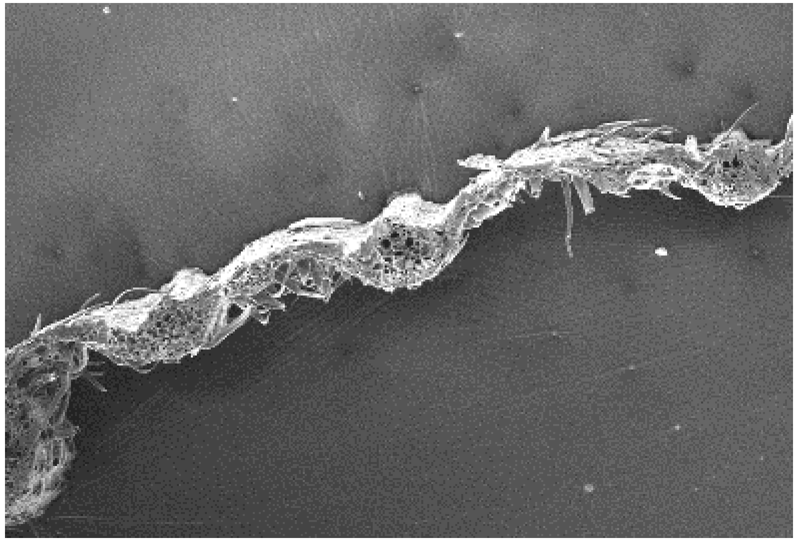
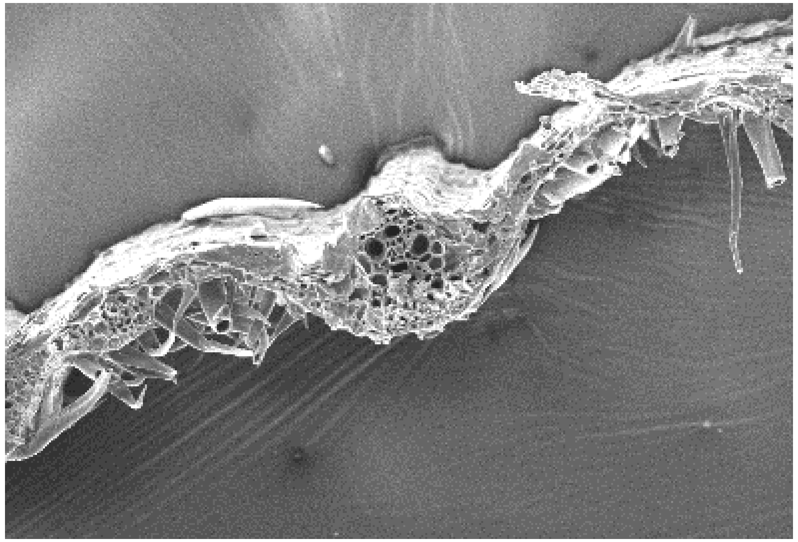
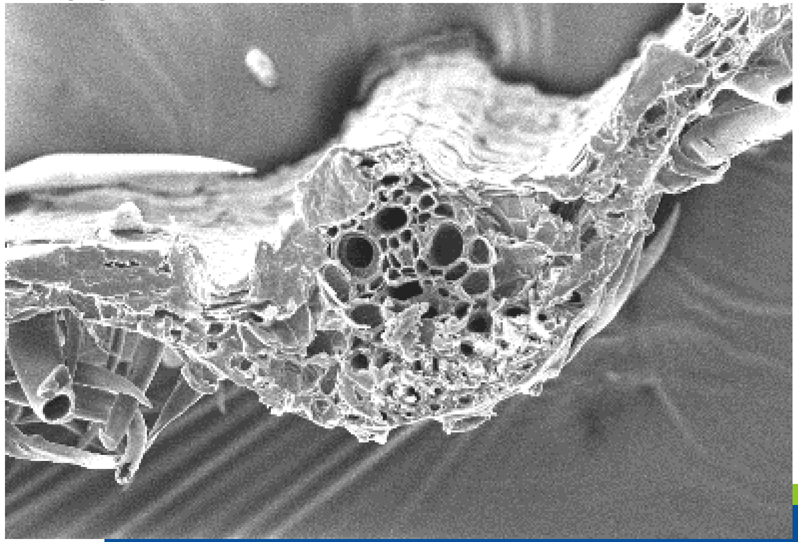
~30% moisture leaf

50x

100x

200x

~15-18% moisture leaf