DOE Bioenergy Technologies Office (BETO) 2023 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 during long-term storage and queuing to positively impact downstream processes through reduced chemical and energy input.
  - Enhance anatomical fractionation, co-products
  - Improve feedstock quality, find use for discarded fractions not meeting specification
  - Improve feedstock quality, improved conversion
- Feedstock improvements support BETO sustainable aviation fuel goals
- 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 gate to preserve corn stover
  - 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; characterize value-add components

Project Overview

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

Design a wet feedstock logistics system that takes advantage of moisture and length of storage to not only preserve biomass but also add value.

Value could come in the form of:

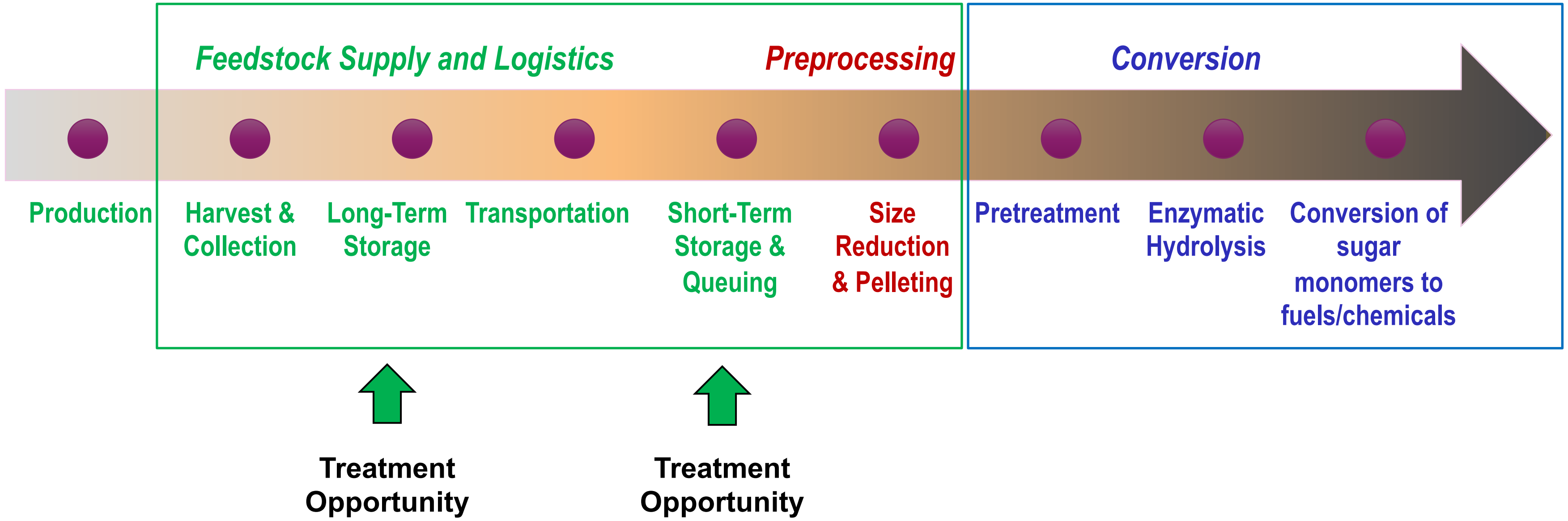
- Enhanced anatomical fractionation
- Reduction in recalcitrance
- Quality improvement

These challenges could be addressed in the storage (long-term or queuing) operation through low severity treatments

Photo of mechanically achieved fractions courtesy of Ling Ding and Rachel Colby, INL

1 - Approach

- A value-add wet storage approach could address feedstock challenges of recalcitrance, quality and variability to improve conversion
  - Utilize the residence time in short- or long-term storage to enhance conversion, develop co-products, or improve quality using low severity (low temp, energy and chemical) treatments



- Feedstock fractionation in combination with value-add storage
  - prior to storage to address quality issues in specific tissues
  - After storage to recover co-products or direct material to tissue-specific conversion

1 – Approach

Using time in storage to address quality issues and develop co-products

1) Opportunity: Mechanical processing of corn stalk alone is insufficient to separate dense fibrous outer rind from amorphous light pith matrix, pectinase treatment to effect delamination
   - Risk: High enzyme cost; Mitigation: Work with analysis AOP (1.1.1.2) to quantify downstream benefits
2) Opportunity: Utilize low severity formic acid treatment to reduce recalcitrance in corn stover
   - Risk: Lignin unaffected by low severity formic acid; Mitigation: Increase severity
3) Opportunity: Utilize in-storage treatment to remove contaminants from underutilized forest residues (bark)
   - Risk: Treated bark unable to meet conversion specifications; Mitigation: Identify alternative uses

Forest product residues

1 – Approach

Project success measured by:

- Support of diversity, equity and inclusion – Supported a female U of Idaho graduate student in chemical engineering, defended December 2022. Thesis title, “The effect of chemical storage pretreatment of loblolly pine bark on pyrolysis conversion.”
- Go/No-Go milestone (completed 3/31/2021) – Determine if active storage can improve corn stover delamination of pith and rind by 20% - **60% Improvement achieved**
- End of Project Milestone (9/30/2023) – Improve critical quality attributes through active storage and queuing to **meet 90% operational efficiency goal**, and **enable cost targets** by reducing process energy requirements

University of Idaho

2 – Progress and Outcomes – Pectinase in queuing to enhance corn stalk tissue fractionation

Goal: Utilize in-storage enzyme treatment to delaminate corn stover rind and undifferentiated matrix (pith)

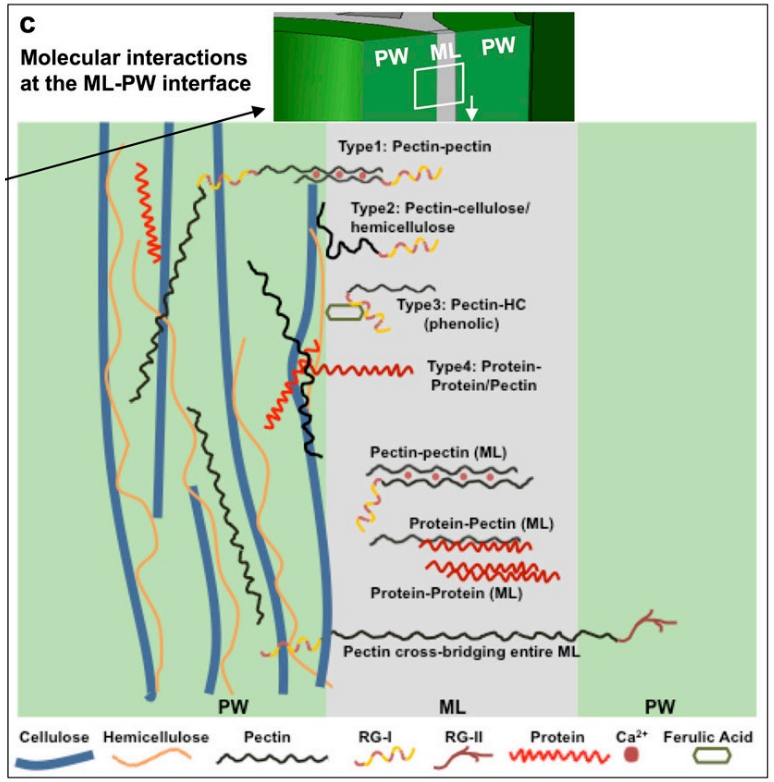
Experimental Matrix:

- Baseline: No enzyme, 55% moisture, 40°C, anaerobic environment of corn stalks
  - Low enzyme, 125 U/g biomass (dry basis)
  - High enzyme, 625 U/g biomass (dry basis)

Impact: Achieve tissue fractionation by delaminating corn stalk and enable histologic tissue-specific processing or co-products

2 – Progress and Outcomes – Pectinase treatment in queuing to enhance corn stalk tissue fractionation

- Middle lamella and the role of pectin. Intercellular space



M S Zamil and A Geitmann 2017 Phys. Biol. 14 015004

2 – Progress and Outcomes – Pectinase treatment in queuing to enhance corn stalk tissue fractionation

Cornstover Bale

Air Classification

Cob

Stalks

Leaf/Husk

Pectinase treatment

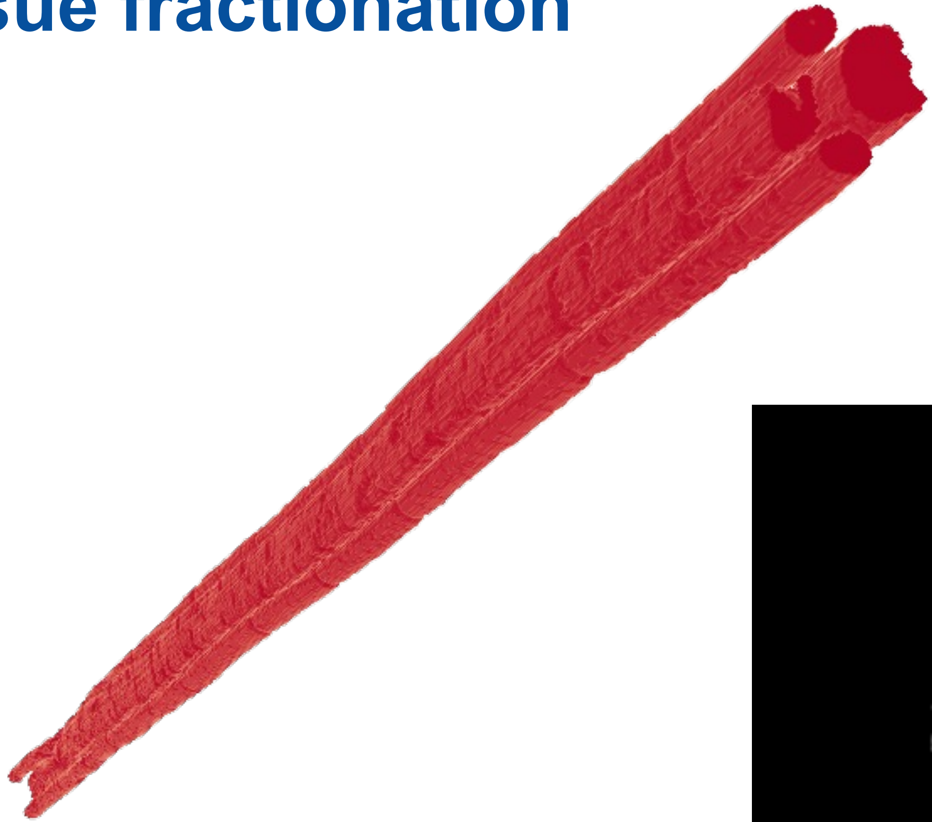
Low-speed milling

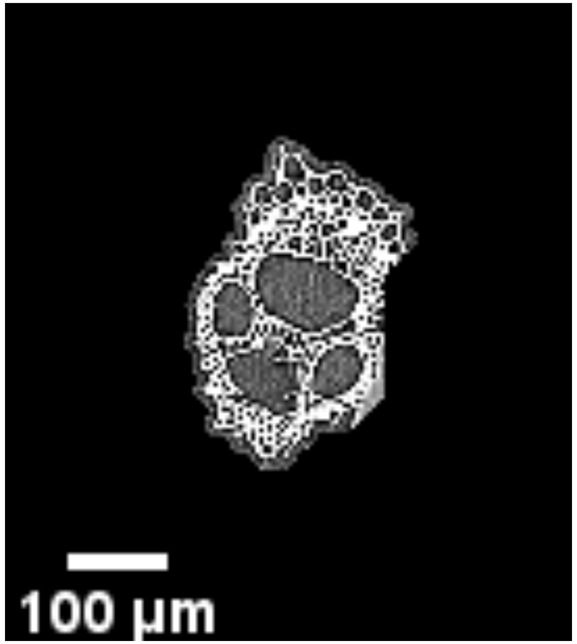
Size separation

- Pectinase treatment: **60% improvement** in pith/rind separation compared to control **met GNG of 20%**
- Rind and pith separate enables use as co-product or tissue-specific processing
- Vascular bundles an unexpected 3rd fraction

2 – Progress and Outcomes – Pectinase treatment in queuing to enhance corn stalk tissue fractionation

- X-ray tomography Micro CT-scan analysis of vascular bundles revealed that each is composed of four circular hollow tubes, ~100 μm in diameter
- In storage treatment permitted separation of not only the pith and rind but also facilitated the recovery of intact vascular bundles
- Anatomical fractionation enables tissue-specific applications/co-products
    - Pith as an absorbent
    - Rind for conversion
    - Seeking applications that could benefit from vascular bundle structure and composition





2 – Progress and Outcomes – Formic acid treatment in queuing/long-term to reduce recalcitrance

Goal: Utilize extended time in storage/queuing to reduce corn stover recalcitrance with formic acid amendment

Experimental Matrix:

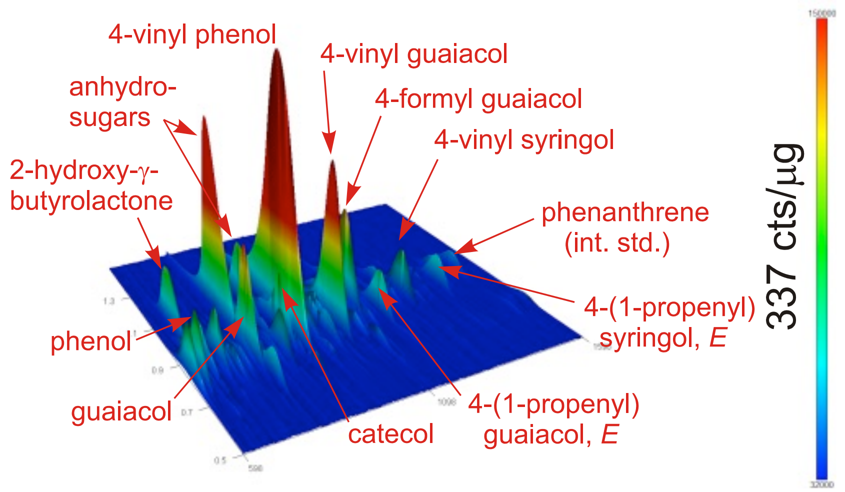
- Baseline: anaerobic storage of untreated stover
- Formic acid at two concentrations (1% & 2.5%, dry basis)

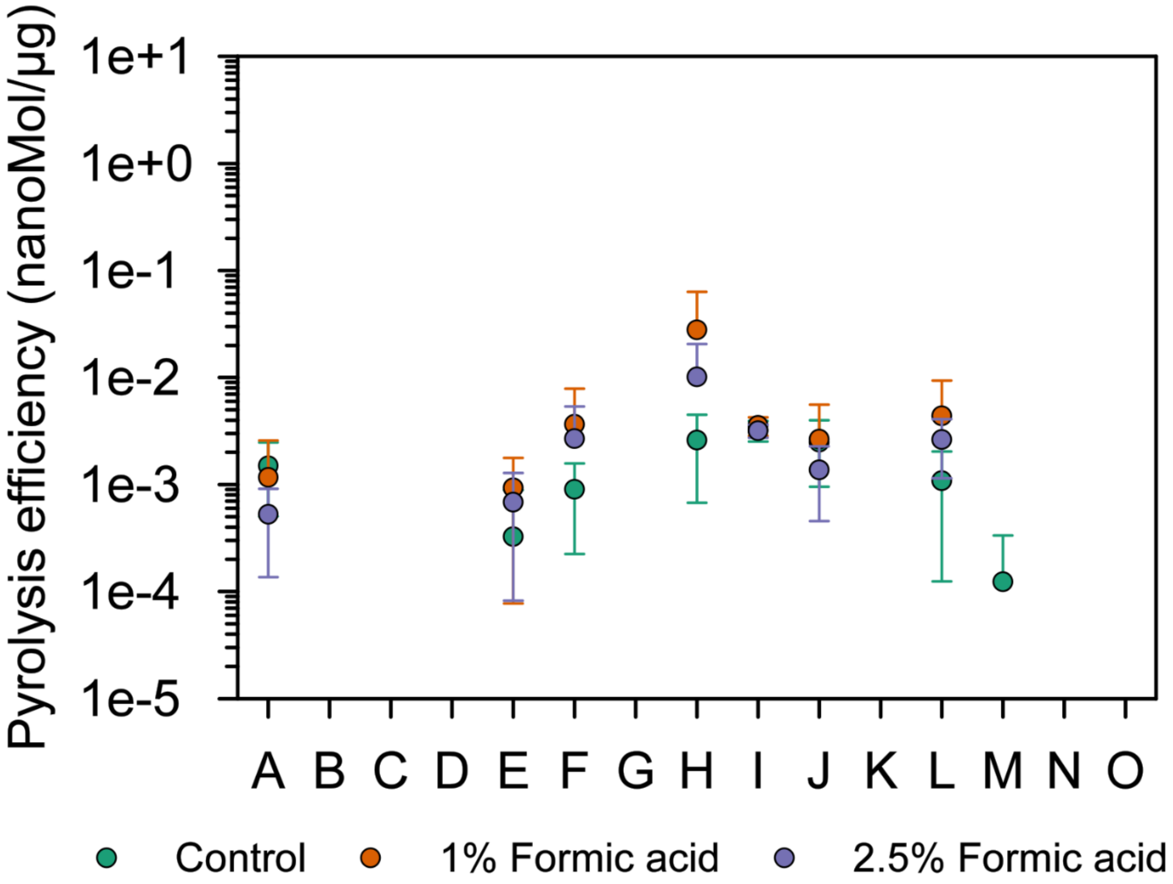
Impact: Formic acid at high concentration delignifies lignocellulosic biomass by cleaving α- and ß-aryl ether linkages. Partial delignification in storage facilitated by low concentrations of formic acid could reduce recalcitrance in thermochemical conversion with minimal input

	Dry Matter Loss	Final pH	Lignin	Extractives	Glucan	Xylan
Control	3.4 ± 1.1	5.3 ± 0.6	16.8 ± 0.2[a]	10.3 ± 0.03[a]	36.3 ± 0.5[a]	20.5 ± 0.4[a]
1% Formic acid	-0.8 ± 0.5	4.3 ± 0.02	15.8 ± 0.03[b]	12.8 ± 0.2[b]	34.9 ± 0.1[b]	20.2 ± 0.2[a]
2.5% Formic acid	0.7 ± 2.4	3.2 ± 0.05	15.8 ± 0.1[b]	12.2 ± 0.3[a]	35.7 ± 0.4[a]	20.6 ± 0.2[a]

2 – Progress and Outcomes - Formic acid treatment in queuing/long-term to reduce recalcitrance

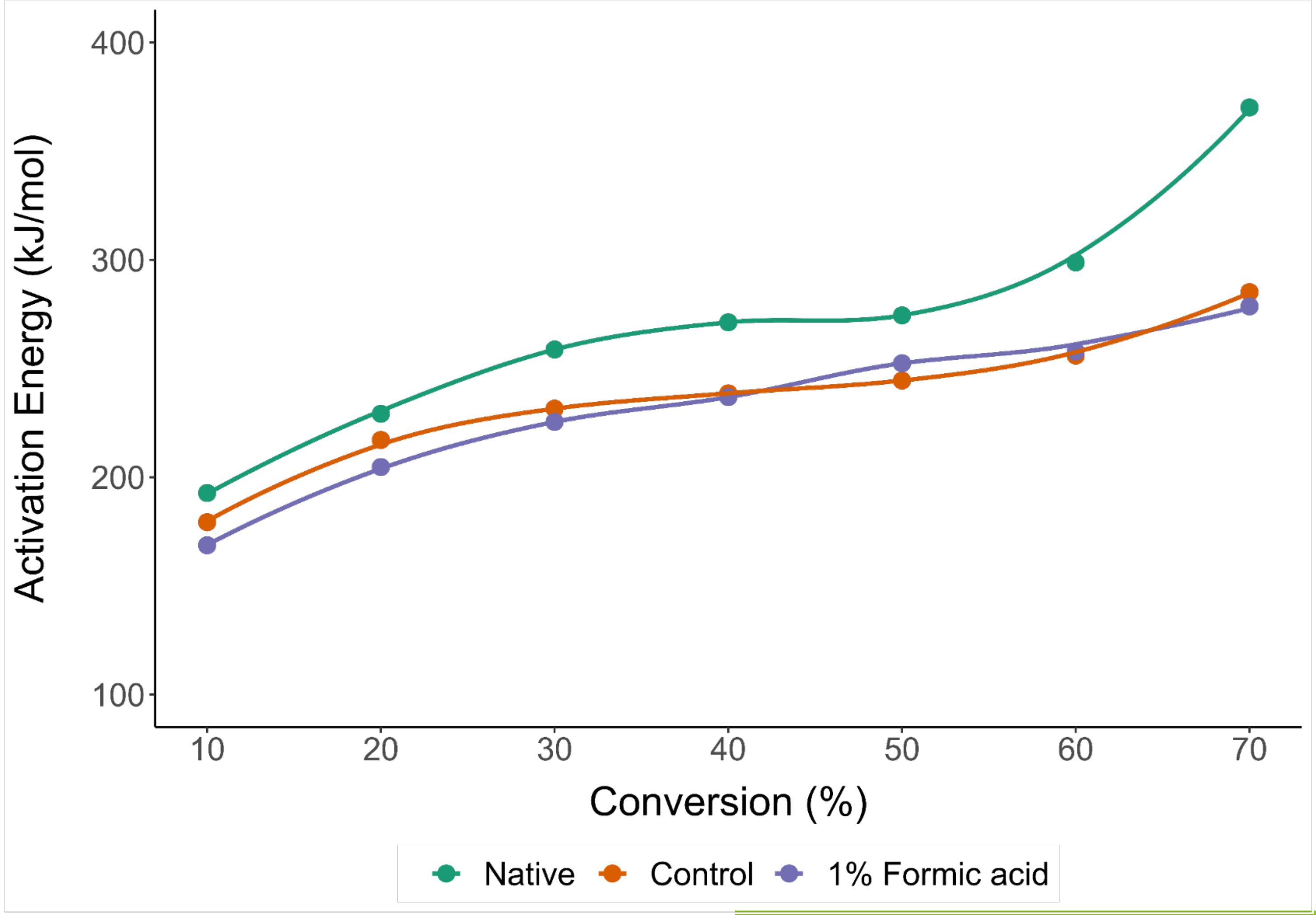
- 2D py-GC-GC/MS of control, 1% FA & 2.5% FA-treated corn stover, pyrolysis at 400, 500 & 600°C.
- Evidence of lignin cleavage in FA-treated corn stover
  - Greater pyrolysis efficiency of lignols at lower temps





2 – Progress and Outcomes – Formic acid treatment in queuing/long-term to reduce recalcitrance

- Formic acid treatment results in a lower activation energy compared to native corn stover
- Formic acid treatment reduces activation energy compared to control below 40% conversion
- Less energy needed to initiate pyrolysis



2 – Progress and Outcomes – Queuing treatments for improved bark utilization

Goal: Improve utilization of bark fraction of forest products residue by **improving quality** or developing a **co-product**

Experimental Matrix: (bark reduced to 2 mm)

- Baseline: Stored without treatment
- Treatments applied: (dry basis)
  - Alkali addition, 4% NaOH
  - Acid addition, sulfuric acid
    - 0.1% Acid
    - 1.0% Acid

Impact: Understand the potential for reduced severity treatment in queuing pile to reduce inorganic element content and increase pyrolysis yields or develop co-products

Native bark, prior to comminution

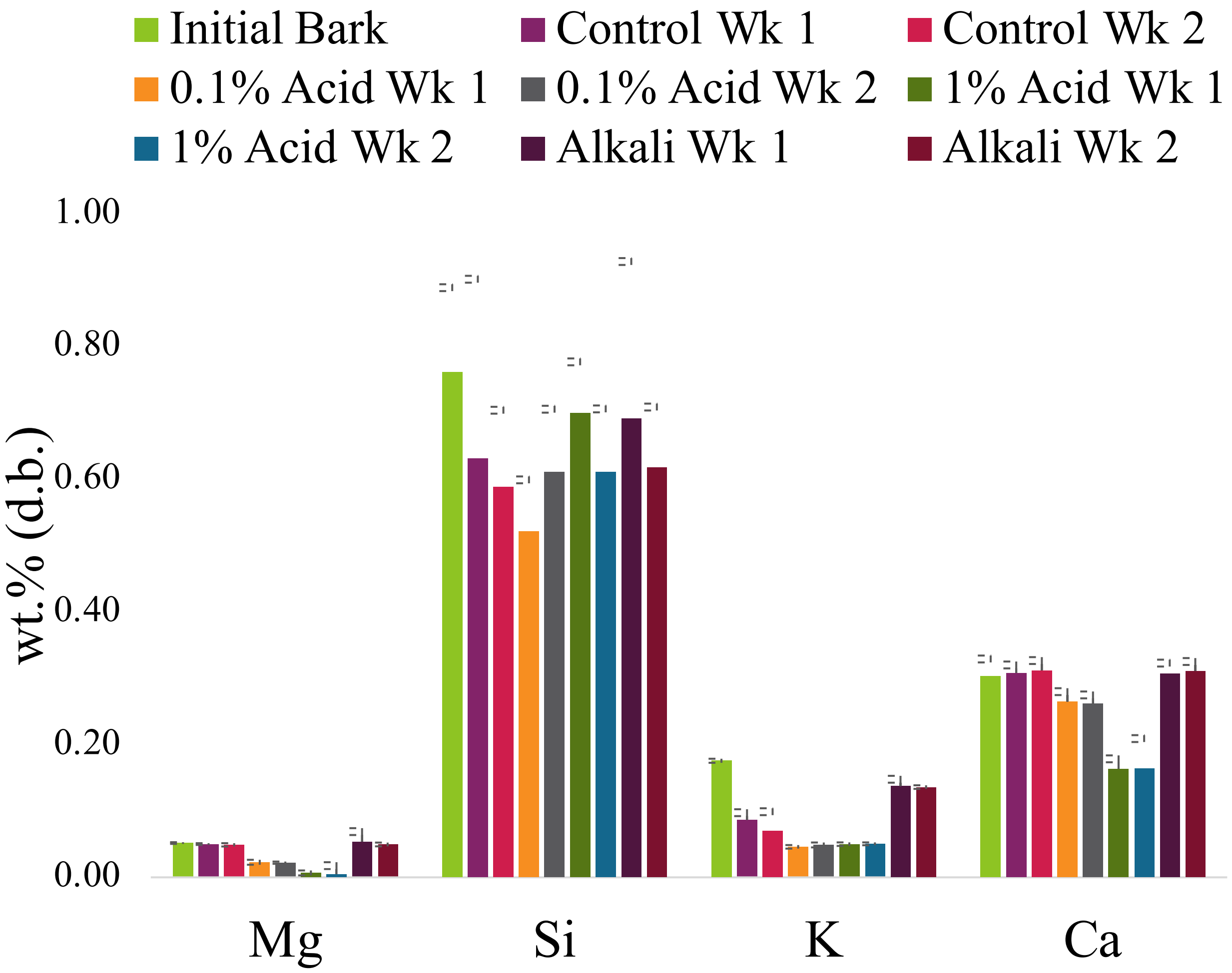
Bark storage reactor

Bark pellet for pyrolysis

Pyrolysis biochar

2 – Progress and Outcomes – Queuing treatments for improved bark utilization

- Acid-treated bark experienced no material loss compared to 3% (dry basis) loss for control
- Maintained or increased higher heating value in storage
- Reduction in ash species
  - Acid treatment **reduced** Ca (up to **45%**), K (up to **72%**) & Mg (up to **80%**)



2 – Progress and Outcomes – Queuing treatments for improved bark utilization

Biochar as a co-product

- Treatments affected biochar quality
  - 1.0% acid improved fuel ratio, energy density and energy yield
  - All treatments improved biochar recalcitrance
- Bark biochar could be a valuable co-product for **soil amendment** and approach to **carbon sequestration**
- 2021 SOT 1st plant analysis discards 23% of biomass not meeting specification. Finding value for bark will improve SOT

Sample	Fuel ratio	Energy densification	Energy yield (%)	R_{50}
Native	2.48	1.42	51.5	0.64
Control	2.01	1.21	36.6	0.66
0.1% Acid	2.03	1.20	39.6	0.75
1.0% Acid	2.76	1.64	60.2	0.78
Alkali	2.28	1.27	49.4	0.93

R_{50} is a measure of recalcitrance and indicates how long carbon could remain in the soil.
Class A ($R_{50} \geq 0.7$) is comparable to graphite/soot
Class B ($0.5 \leq R_{50} \leq 0.7$) intermediate recalcitrance
Class C ($R_{50} \leq 0.5$) comparable to uncharred biomass

Harvey *et al.*, *Environ. Sci. Technol.* 2012, 46, 1415-1421

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
- Supports BETO sustainable aviation fuel goal of 3 billion gallons by 2030 by addressing feedstock quality and recalcitrance
- Partnership with POET to develop wet logistics system for combined heat & power application
- Patents and provisional patents issued to secure IP and encourage commercial interest
- High impact factor publications targeted to increase additional visibility

Summary

- Storage and queuing can be utilized to add value to feedstocks by taking advantage of the long residence time to perform slow chemical transformations
  - Recalcitrance reduction possible through chemical and biological approaches
  - Address quality issues in specific fractions to positively impact downstream processes or enable co-products
  - Enhance anatomical fractionation of materials that cannot be accomplished mechanically (e.g., delamination of pith and rind).
  - Compatible with multiple feedstocks and conversion approaches
- Bulk wet logistics system provides flexibility to address feedstock quality using low severity treatments not possible in a bale system
- Future Work:
  - Utilize TEA modeling to assess impact of in-storage treatment on operational efficiency and feedstock cost
  - Refine commercial-scale storage models using data from 3,000-ton pile

Quad Chart Overview

Timeline

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

	FY22 Costed	Total Award
DOE Funding	*$546,177*	*$1,755,000*
Project Cost Share *		

TRL at Project Start: 2

TRL at Project End: 3

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

GNG Milestone/FY22 Q2: Determine if active storage can positively impact delamination in corn stover delamination of rind and pith by 20% as measured by bulk anatomical properties.

End of Project Goal/FY23 Q4: Utilize active storage and queuing to manage tissue-level CMAs of biopolymer distribution and AAEM content to address CQA specifications associated with 90% operational efficiency goal meanwhile enabling $86/ton cost targets by reducing process energy requirements

Funding Mechanism

AOP

Project Partners*

- NREL, PNNL, INL: 1.1.1.2; 1.2.1.2; 1.1.2.1: 1.2.1.5; 3.4.1.202

Idaho National Laboratory

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy. INL is the nation's center for nuclear energy research and development, and also performs research in each of DOE's strategic goal areas: energy, national security, science and the environment.

Additional Slides

Response to Reviewers' Comments

- Reviewer: This project is well managed. Advancements uncovered in this project could add substantial value to the biofuels industry. Any preprocessing that could be done at harvest or storage could decrease the thermochemical effort of conversion. This project concept aligns well with the time function in the severity calculation. Annual corn stover harvest occurs in a 4-week window, and the crop spends the rest of the year in long-term storage of queuing. Corn stover markets extend into the cattle feed market as well, so it would be interesting to see if there is benefit of rumen digestion with these ideas. Increasing the demand of corn stover feedstock in the cattle industry will encourage more supply and likely lower the cost of corn stover feedstock in biofuels as baling and storage systems improve. This is an exciting study for biofuel potential. It would be interesting to see if treatment could be done at harvest/baling to help homogenize/stabilize the dynamics in the bale. One disconnect I have is the extremely high moisture content of the studies. Do the project plans include the addition of water at harvest/baling/storage?
- Response: …One reviewer points out an interesting approach on rumen digestibility. Many studies show the promise for anaerobic storage and the production of associated lactic and acetic acids to improve digestibility of herbaceous biomass in the rumen gut. Limited studies exist on alkali-assisted storage providing a similar benefit to rumen digestion, but both calcium oxide and sodium hydroxide have been shown to have a positive benefit. The moisture contents explored in the study represent those in the working envelope of ensiling, as described above
- Reviewer: The project has refocused on value added instead of cost. I think both value added and cost can be considered simultaneously given that the project's ultimate goal is to increase the profit of biomass processing and storage for a facility. It is not clear what exactly the value-added components are and how much value these components can add to the process. Related test/experiment design and sample size need to be clearly defined to address progress and outcomes. In addition to focusing on woody biomass and herbaceous biomass for future goals, I think the scale-up of current study on corn stover can be further explored.
- Response: …We agree that value-added storage and cost reductions go together to impact final profitability. We define the value-added component as anything that can reduce costs downstream in preprocessing or conversion, and an example of this is a credit for reduced temperature in a pretreatment reactor enabled by recalcitrance reduction in storage…

  We agree that the work should be expanded to woody biomass and even MSW. Scale-up of the alkali study to 10 kg has been accomplished, and further scale-up is warranted but not planned at this point. Scale-up of the anaerobic storage approach in a production setting of 500 tons was presented in the FY 2017 and FY 2019 BETO Peer Reviews. However, fieldwork was not pursued after this time due to the guidance of the previous administration to focus on low-technology-readiness-level research.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Groenewold. G.S., C.J. Orme, C. Stetson, R.M. Brown, L.M. Wendt, Aaron D. Wilson. Extraction of Terpenoids from Pine Needle Biomass using Dimethyl Ether Extraction. alkali treatment and anaerobic storage in corn stover enhances reactivity and surface energy properties. Manuscript under review.
- Wendt, L.M., B.D. Wahlen, T.A. Semelsberger, J.H. Leal, C.D. Pilgrim, M.R. Walton, J.A. Nguyen, H. Zhao. Combined alkali treatment and anaerobic storage in corn stover enhances reactivity and surface energy properties. Manuscript under review.
- Wendt, L. M.; Wahlen, B. D.; Groenewold, G. S.; Hodges, B. D. M.; Pilgrim, C.; Walton, M. R.; Murphy, J. A.; Smith, W. A.; Zhao, H., Molecular and structural impacts of fungal depolymerization of corn stover to reduce pretreatment severity. Sustainable Energy & Fuels 2022, 6 (23), 5400-5413.
- Wendt, L. M.; Wahlen, B. D.; Walton, M. R.; Nguyen, J. A.; Lin, Y.; Brown, R. M.; Zhao, H., Exploring filamentous fungi depolymerization of corn stover in the context bioenergy queuing operations. *Food and Energy Security* 2021.
- Thompson, V.S., T.A. Volk, L.M. Wendt. 2021. Editorial: Storage of Biomass Feedstocks: Risks and Opportunities. Frontiers in Bioengineering and Biotechnology. doi: 10.3389/fbioe.2021.657342.
- Wendt, L.M., B.D. Wahlen, M.R. Walton, J.A. Nguyen, Y. Lin, R.M. Brown. 2021. Screening of Alkali-Assisted Storage Conditions to Define the Operational Window of Deacetylation within Storage Systems in the Bioenergy Supply Chain. Biofuels, Bioproducts and Biorefining. doi: 10.1002/bbb.2288.
- Wendt, L.M. "The Effect of Biological and Chemical Pretreatments During Storage on Corn Stover Physiochemical Properties and Reactivity." Ph.D. Dissertation, University of Idaho, 2021c. ProQuest Dissertations Publishing. 28411704

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- 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

Publications – Manuscripts in Preparation

- Asif Hasan Rony, G Groenwold, BD Wahlen, WA Smith, LM Wendt, Influence of storage assisted dilute formic acid pretreatment of corn stover on the pyrolytic kinetics and material stability
- Asif Hasan Rony, BD Wahlen, WA Smith, LM Wendt, Pectinase treatment of corn stalk at the refinery gate to enable tissue fractionation of pith and rind and recovery of intact vascular bundles
- Kymberly Bowlby, BD Wahlen, H Zhao, LM Wendt, Impact of alkaline and acid pretreatment on pine bark pyrolysis products
- Kymberly Bowlby, “The effect of chemical storage pretreatment of loblolly pine bark on pyrolysis conversion,” Master’s Thesis, University of Idaho 2023

Publications, Patents, Presentations, Awards, and Commercialization

Presentations

- Lynn Wendt, The Role of Long-Term Storage to Reduce Risk of Feedstock Loss and Facilitate Recalcitrance Reduction. November 2022. International Bioenergy & Bioproducts Conference (IBBC), Providence, RI
- Rony, A.H.; Wahlen, B.D.; Wendt, L.M.; Smith, W.A., Novel Enzymatic Treatment to Enhance Delamination of Corn Stalk for Efficient Separation of Pith and Rind. 2022 AIChE Annual Meeting, Phoenix, Arizona.
- Wendt, L.M., B.D. Wahlen. T.A. Semelsberger, J.H. Leal, C.D. Pilgrim. M.R. Walton. Combined Alkali Treatment and Anaerobic Storage in Corn Stover Enhances Reactivity and Surface Energy Properties. Oral Presentation. American Institute of Chemical Engineering (AIChE) Annual Meeting. November 2021.
- 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.

Publications, Patents, Presentations, Awards, and Commercialization

Patents

- Nguyen, Q., L.M. Wendt. *In storage delignification of biomass*. U.S. Patent No. 11420992, granted August 23, 2022.
- Wahlen, B.D., A.H. Rony, W.A. Smith, Wendt L.M., Method for separating corn stalk into anatomical fractions, isolation of vascular bundles. Provisional patent application no. 63/383,986, filed November 14, 2022.
- Stetson, C.C., H. Lee, C.J. Orme, R.M. Brown, V.S. Thompson, L.M. Wendt, C.L. Williams, A.D. Wilson. Methods of removing water from a solid porous material via solvent-driven pore displacement. Provisional patent application no. 63/379,268, filed October 12, 2022.

Other

- Lynn Wendt named Associate Editor for Frontiers in Industrial Microbiology, Fuels and Chemicals section

KAS method for estimating activation energy

Model-free kinetics using KAS method.

A) untreated native corn stover;

B) Untreated control, stored corn stover;

C) 1% formic acid treated stored corn stover;

D) Activation energy plot of each corn stover treatment calculated from KAS plots.