

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Feedstock Technologies Session

April 5, 2023

Modeling Feedstock Performance and Conversion Operations

1.2.2.103_EE00008910_Purdue University

Michael Ladisch

Purdue University



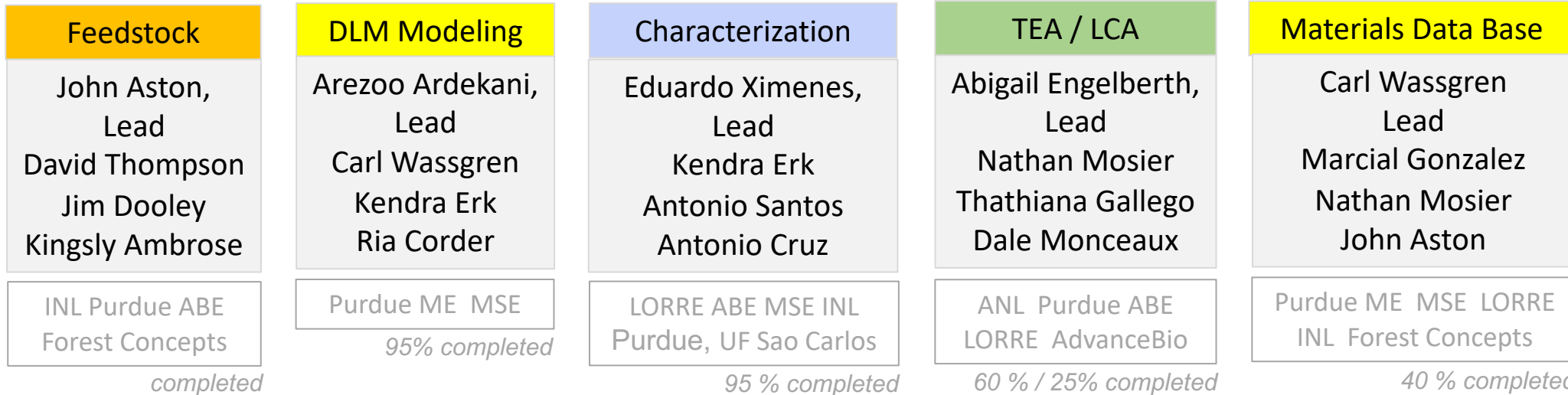
Our Team

1 Approach: Project Coordination, Operations

Michael Ladisch
Project Director

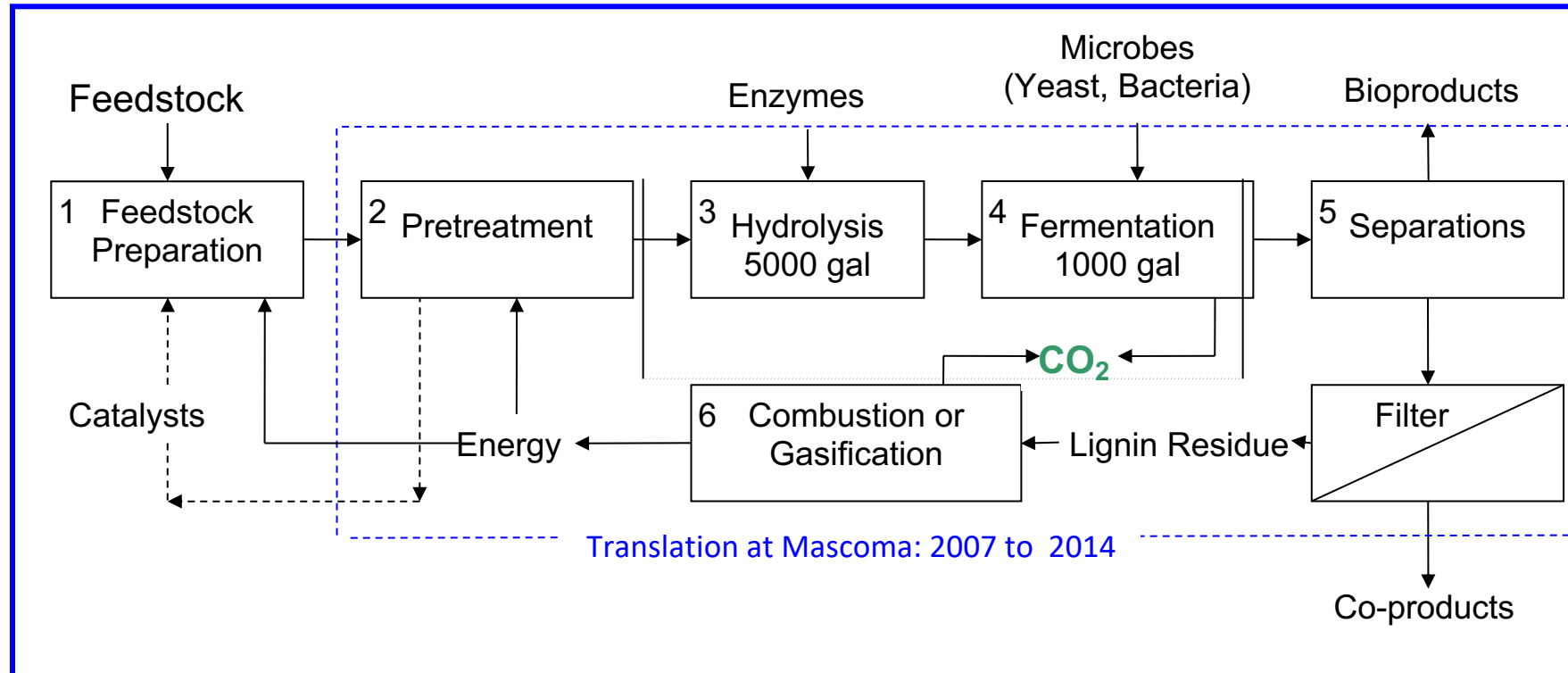
DOE
Elizabeth Burrows
Alexander Jansen
(Clayton Rohman)
(Art Wiselogel)
Mark Elless

Carl Wassgren, Pankaj Sharma
David Thompson, Nathan Mosier
Project Co-Directors



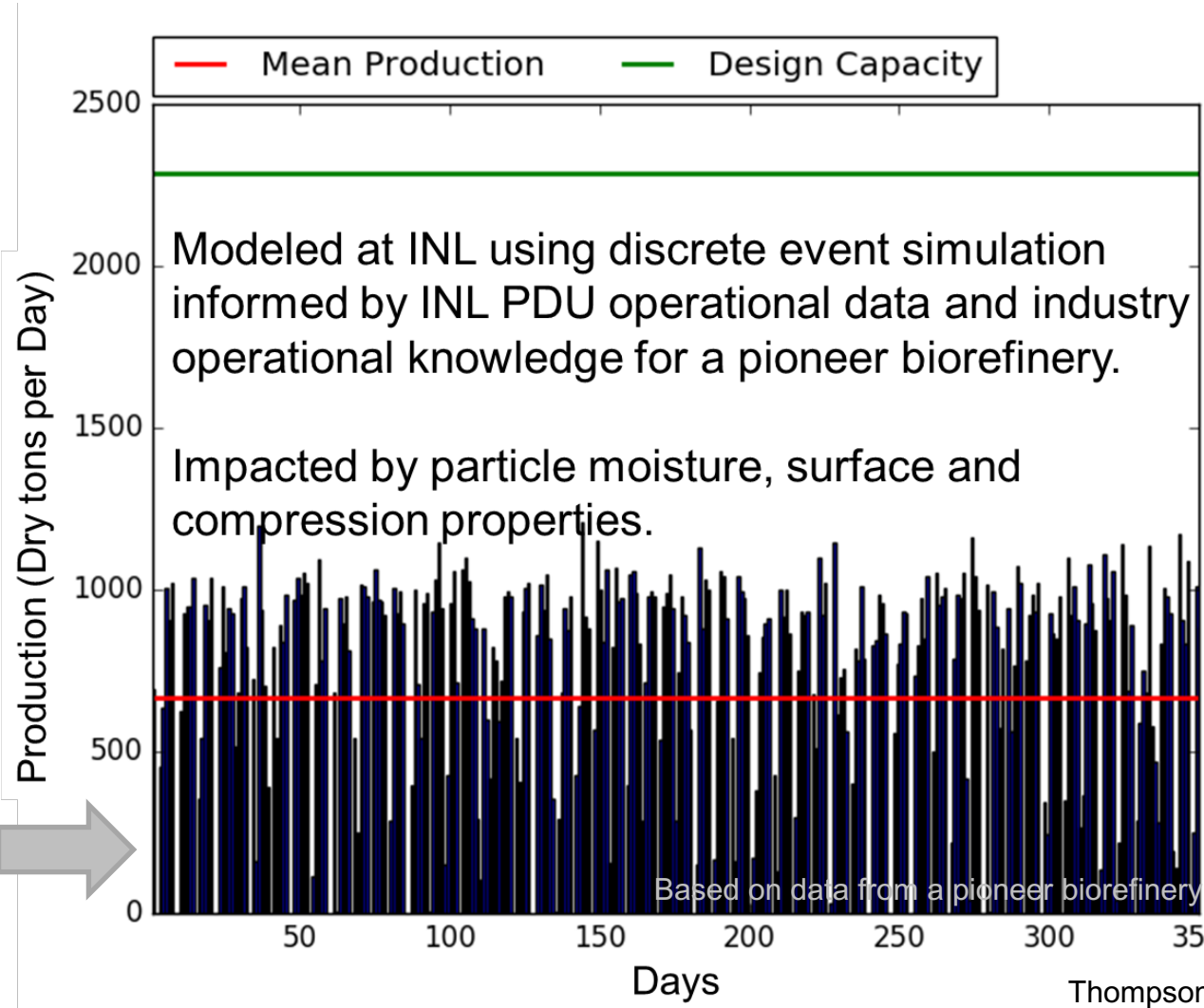
Graduate students and researchers: Luana Assis Serra, Zachary Bebar, Carlos Canizaros, Xueli Chen, Fernanda da Cunha, Diana Ramirez Gutierrez, Rishabh More, Akash Patil, Abhishek Paul, Bjorn Peng, Allison Ray

The 6 Steps for Conversion of Cellulose to Bioproducts



Ladisch, YM Kim, Mosier, 2006, 2010, 2017

Lesson learned: materials handling matters



← Design capacity of a pioneer biorefinery

70% below the design capacity of a pioneer biorefinery

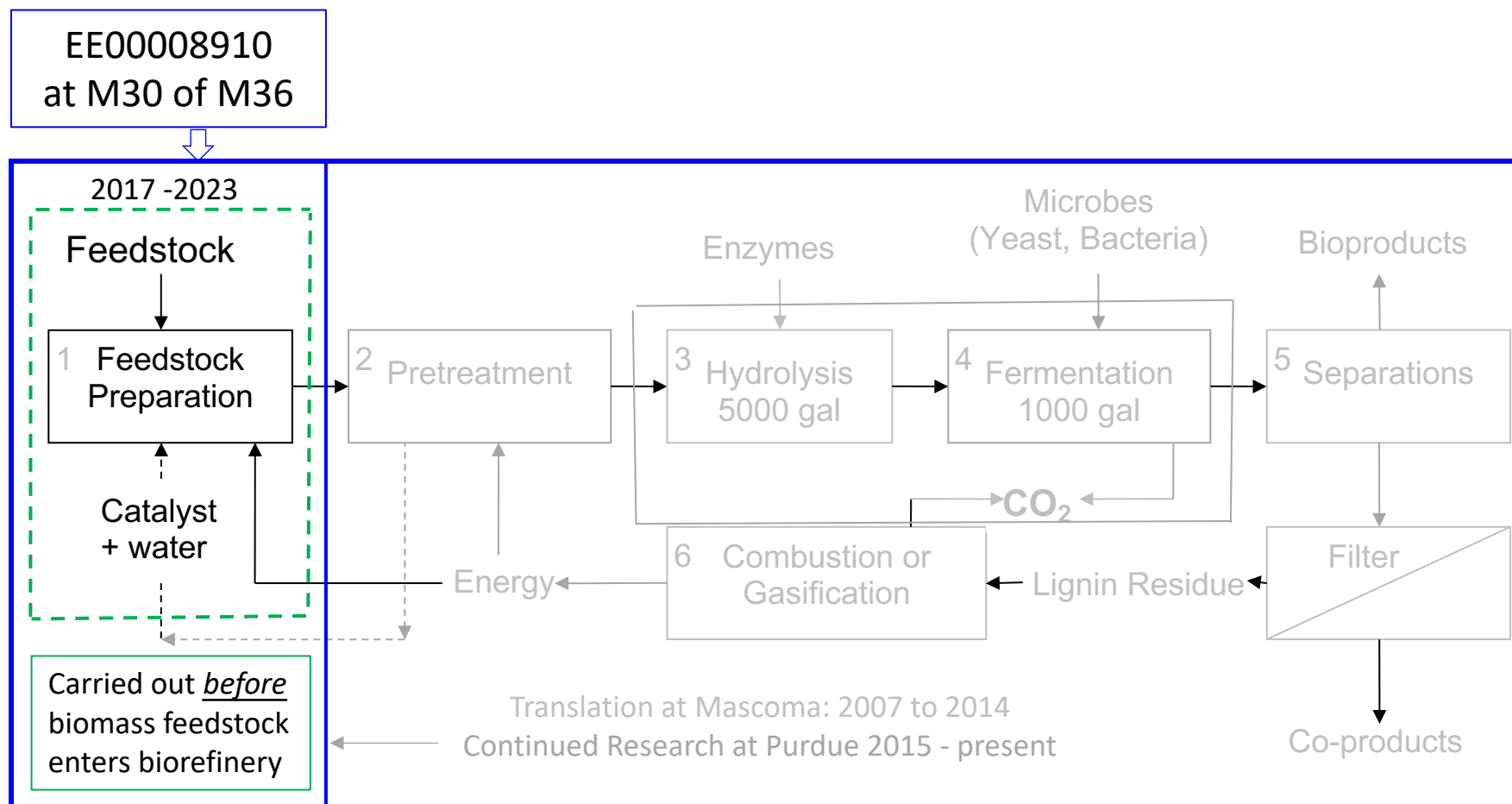
← Attained capacity of a pioneer biorefinery

Due to materials handling (solids)

Thompson, Aston et al., 2018, 2020; Monceaux, 2022

Project Overview

The 6 Steps for Conversion of Cellulose to Bioproducts



Ladisch, Thompson, et al, 2006, 2011, 2017, 2022

Statement of Project Objectives and Specific Aims: EE0008910

Purdue University, INL, ANL, Forest Concepts, AdvanceBio. Project at M30 of M36

Objectives:

Model the formation of an aqueous slurry that may be pumped and processed at high solids loadings i.e., a liquefied form of corn stover, and

relate to chemical and physical characteristics of the biomass material.

The research plan is address research gaps related to the biomass component variability and feedstock conversion interface.

Specific Aims (Technical Objectives)

Investigate characteristics associated with tissue components of cob, stalk, husk, and leaves from corn stover and formation into pellets

Determine how these change during preprocessing into pellets and make high loadings possible before pretreatment

Capture knowledge in dimensionless chemical engineering parameters & mathematical modeling of rheology of flowable slurries of corn stover fractions - before pretreatment – at up to 300 g/L

Formation of highly concentrated, fluid slurries from corn stover would enable transportation of stover as a pumped fluid rather than as a solid material that must be conveyed, resulting in significant savings in pretreatment costs and enhanced operability.

Verification 09032020

Task 1: Verify Overall Approach and Workflow

1 Approach
3 Outcomes

Tasks from SOPO

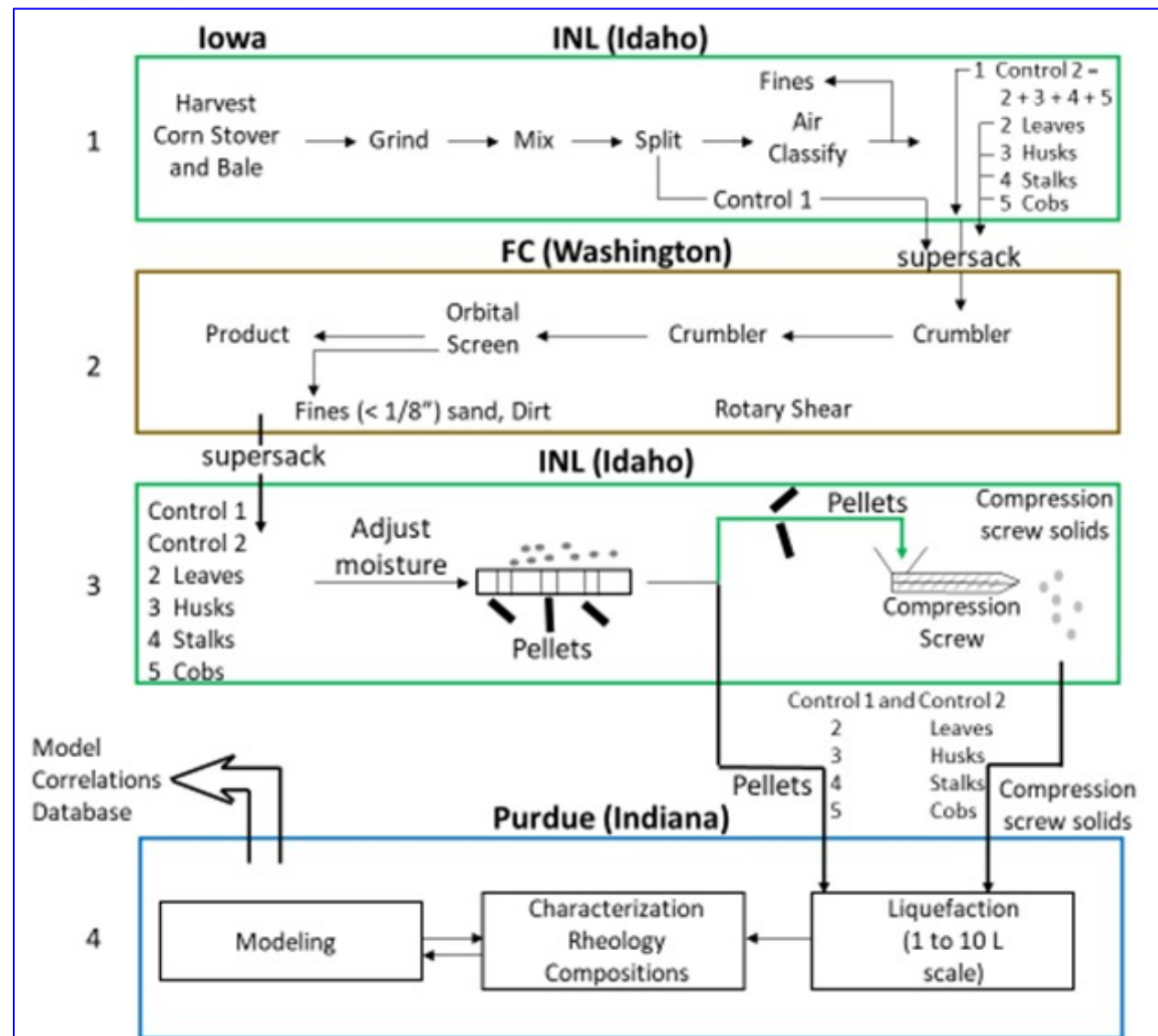
- Task 1:** Verification (completed)
- Task 2:** classification of corn stover components and preparation of pellets (completed)
- Task 3:** computational modeling – Immersed Boundary Method (IB) for biomass slurries (95% completed)
- Task 4:** slurry-forming experiments with fed batch reactors, characterization, data fitted to models (90%)
- Task 5:** techno-economic assessment (TEA) (60%)
- Task 6:** life-cycle analysis (LCA) preprocessing step (25%)
- Task 7:** characterization of optimized materials; dimensionless correlations - materials data base (40%)
- Task 8:** communications, reporting, project coordination

Key elements of the technical scope: (1) verification, (2) corn stover preparation and pelleting, (3) modeling, (4) slurry formation; (5) material characterization; and (6) calculate operational (OpEx) / cap (CapEx) expenses.

Project currently at month 30 of 36 month schedule

Workflow

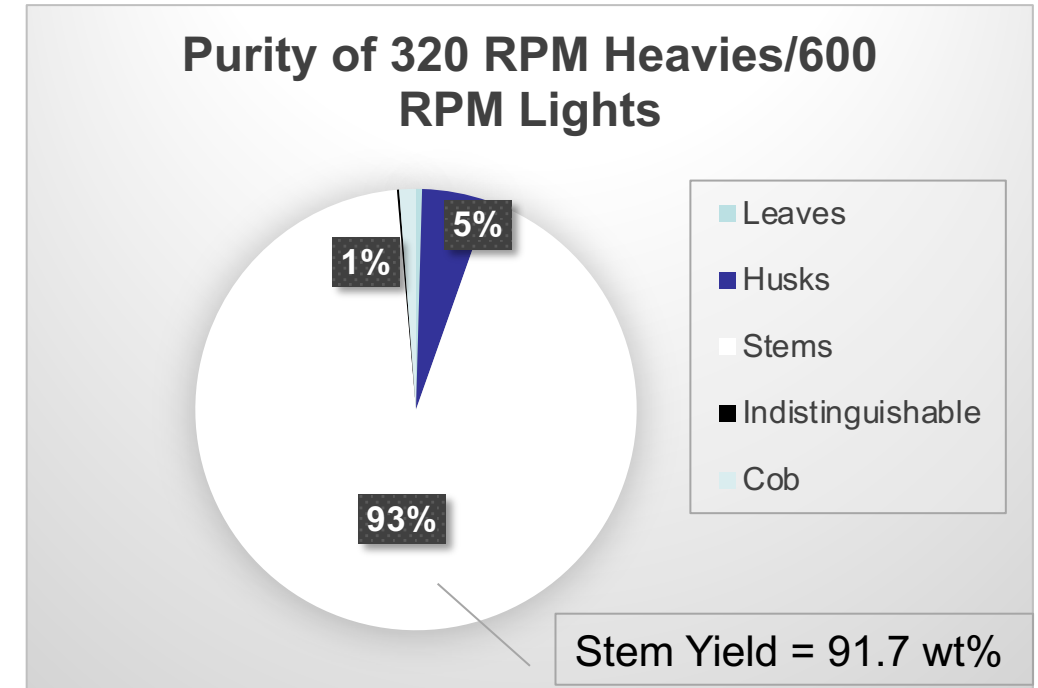
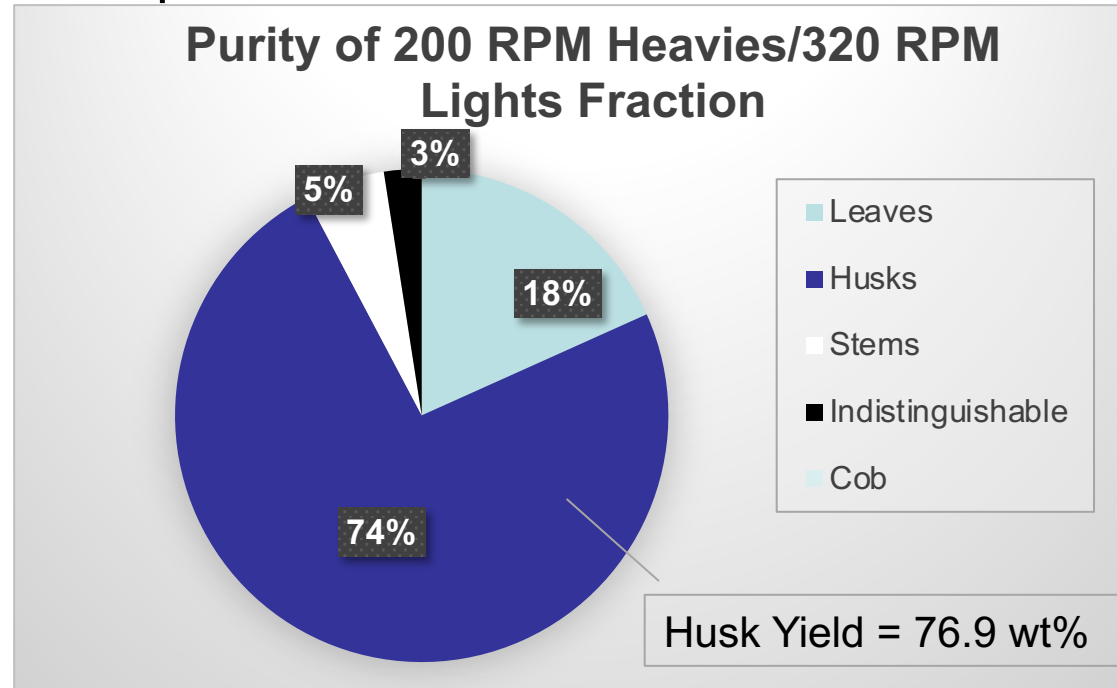
Task 1 is completed



Task 2: Corn stover separated into Anatomical Fractions via Air Classification 75 wt% Target for Purity & Yield

Task 2 is completed

Example:



Aston, Thompson, Dooley, 2021.2022

Data collected from the fractionation of a single bale (1660 lbs).

Separate project showed bale-to-bale variability of ± 10 wt% per fraction, especially for leaf and husk fractions.

Lower rpm of fan corresponds to a lower airflow and therefore separates out light fractions.

Task 2: Bale to Anatomical Fractions at INL

3 Outcomes
4 Impact

Task 2 is completed

Air Fractionation

Fan rpm generates air stream
Fan rpm at 200 to 600 rpm
Bale to bale variability $\pm 10\%$
1660 lbs cornstover processed



Fractionation impacted by

- harvesting method
- moisture content
- air speed (airflow)

Separation into 4 fractions

Aston, Thompson, Dooley, 2021.2022



Cob



Stalk



Husk



Leaf

Impact: Distinct fractions obtained at meaningful scale

Task 3: Modeling of Shear Stress for High Concentration Slurries

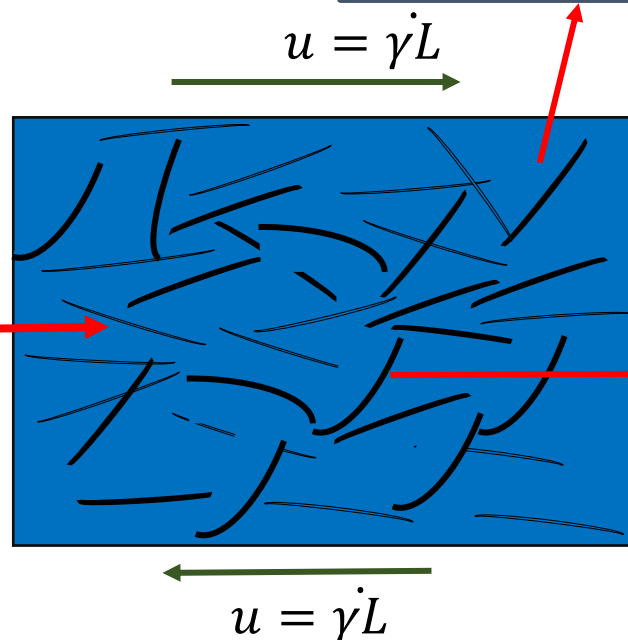
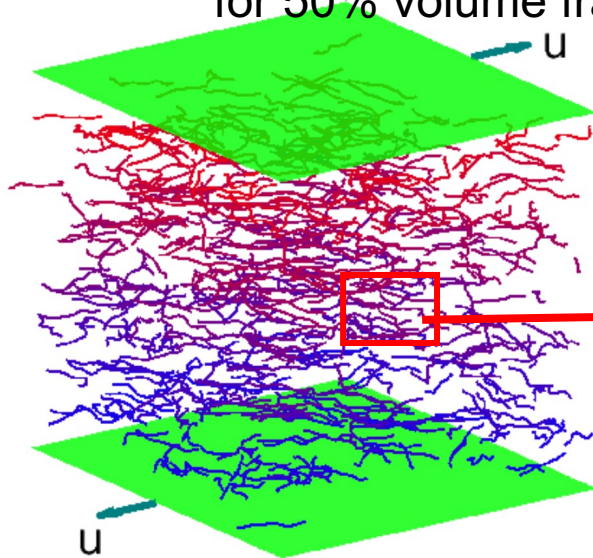
Task 3: 95% completed

Objectives and Specific Aims

- Numerically compare the shear stress at start up with experimental results for corn stover slurries
- Compare steady state shear stress with experiment for corn-stover slurries

Approach

- Develop computational model for fiber suspended in water to predict rheology of corn stover slurries.
- Model suspension viscosity and yield stress for 50% volume fraction



$$\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\mathbf{u} \otimes \mathbf{u}) = -\nabla p + \frac{1}{Re} \nabla^2 \mathbf{u} + \mathbf{f}$$

$$\nabla \cdot \mathbf{u} = 0$$

Solve for fluid velocity, \mathbf{u} Solve for fiber position, \mathbf{X}

$$\frac{\partial^2 \mathbf{X}}{\partial t^2} = \frac{\partial^2 \mathbf{X}_{fluid}}{\partial t^2} + \frac{\partial}{\partial s} \left(T \frac{\partial \mathbf{X}}{\partial s} \right) - B \frac{\partial^4 \mathbf{X}}{\partial s^4} - \mathbf{F} + \mathbf{F}^f$$

Ardekani, More, Erk, 2022, 2023

Task 3: Model gives good fit to experimental measurements

Task 3: 95% completed

Example: comparison of steady state shear stress for corn stover slurries

Dashed line shows experimental fit

Solid lines show numerical fit of Herschel-Bulkley Model:

$$\sigma/\sigma_0 = \tau_y + b * (\gamma/\gamma_0)^c$$

where

τ_y , b and c are fitting parameters

τ_y denotes yield stress of suspension.

Control: no enzyme, agitated at 50° C

Enzyme: 1FPU (filter paper unit) / g enzyme in agitated reactor (mechanically sheared) at 50° C

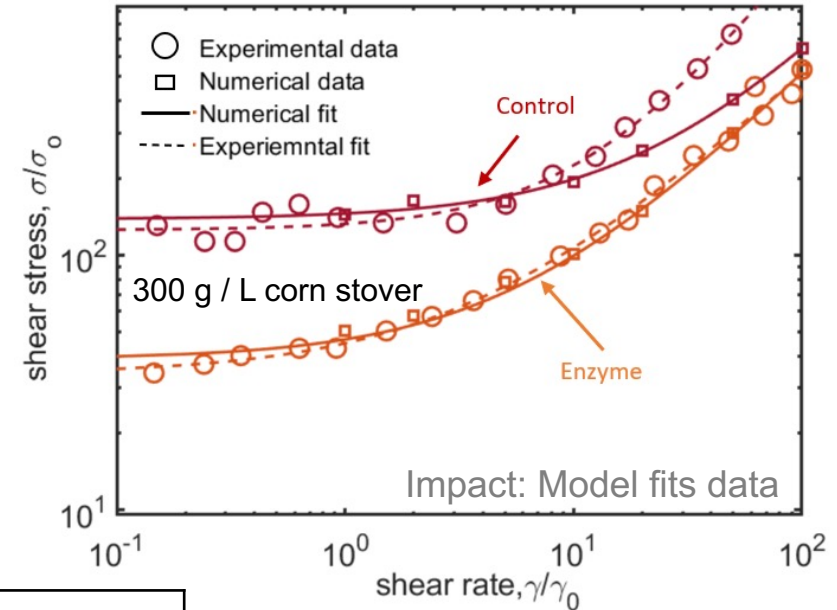


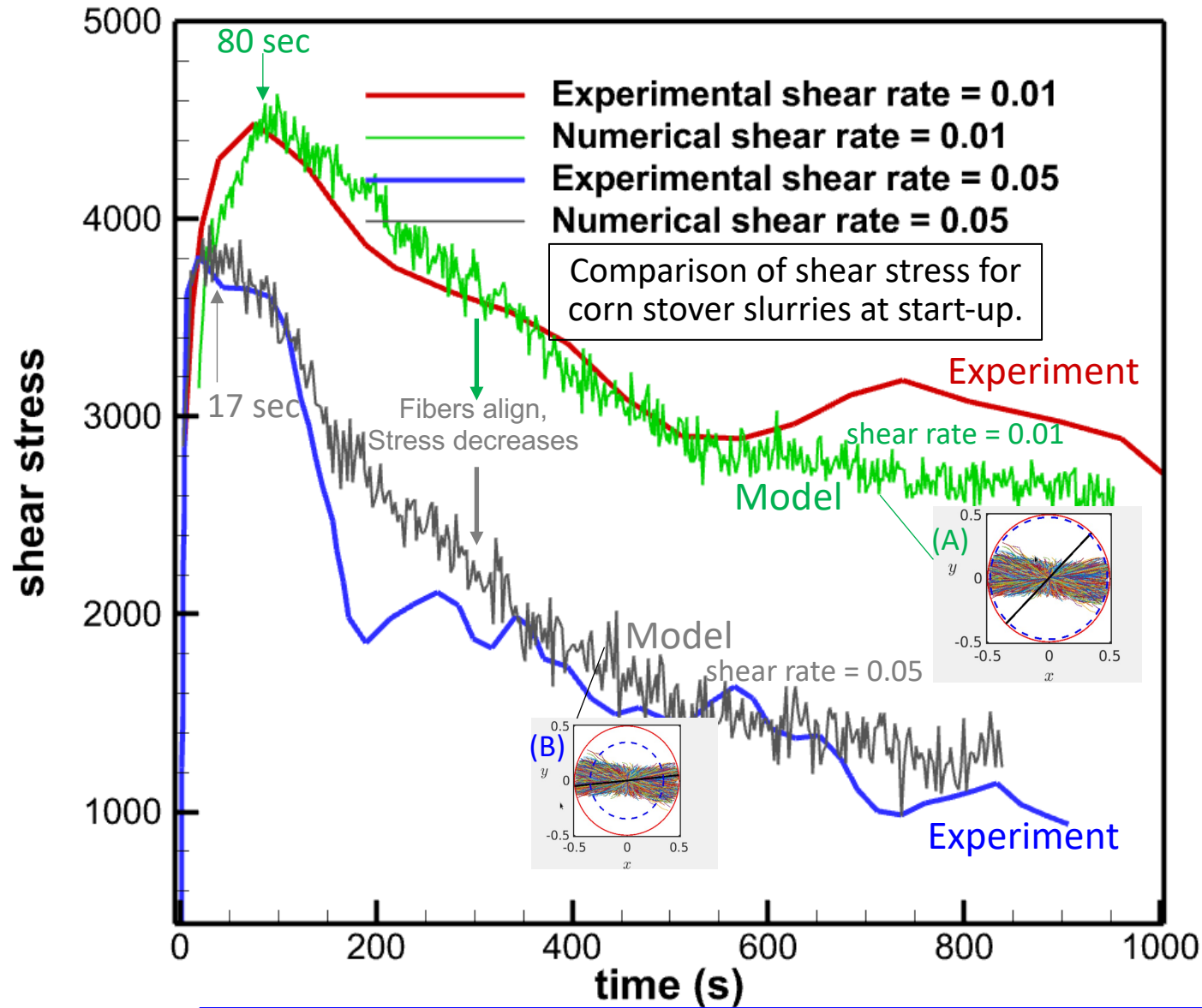
Table . Comparison of Herschel – Bulkley model parameter

| Treatment | Parameter | Numerical | Experimental | % error |
|-----------|-----------------------|-----------|--------------|---------|
| Control | τ_y | 138 | 125 | 10.4% |
| | L ² - Norm | 419.56 | 498 | 15.75% |
| Enzyme | τ_y | 39 | 34 | 14% |
| | L ² - Norm | 378 | 421 | 10.21% |

$$L^2 - Norm = \sqrt{\sum_{K=1}^N \left| \frac{\sigma}{\sigma_0} \right|^2}$$

Task 3: Modeling of Shear Stress for High Concentration Slurries

Task 3: 95% completed



Model predicts - and data show – times when shear stress maxima occur during start-up of mixing of corn stover slurry (17 and 80 sec)

Model: randomly places fiber in domain, and then calculates time dependent shear stress.

As fibers align, shear stress decreases.

As shear rate increases, stress decreases.

| Dimensionless shear rate | Experimental value (dimensionless) | | Numerical (dimensionless) | |
|--------------------------|------------------------------------|--------------------|---------------------------|-----------------------|
| | Max. stress | Time at max stress | Max. stress | Time at max stress(s) |
| 0.01 | 4470 | 79.6 | 4650 | 89 |
| 0.05 | 3380 | 17.7 | 3850 | 24 |

Erk, Corder, Ardekani, 2022

Task 4: Characterization of Corn Stover Fractions

Objectives

Task 4: 95 % completed

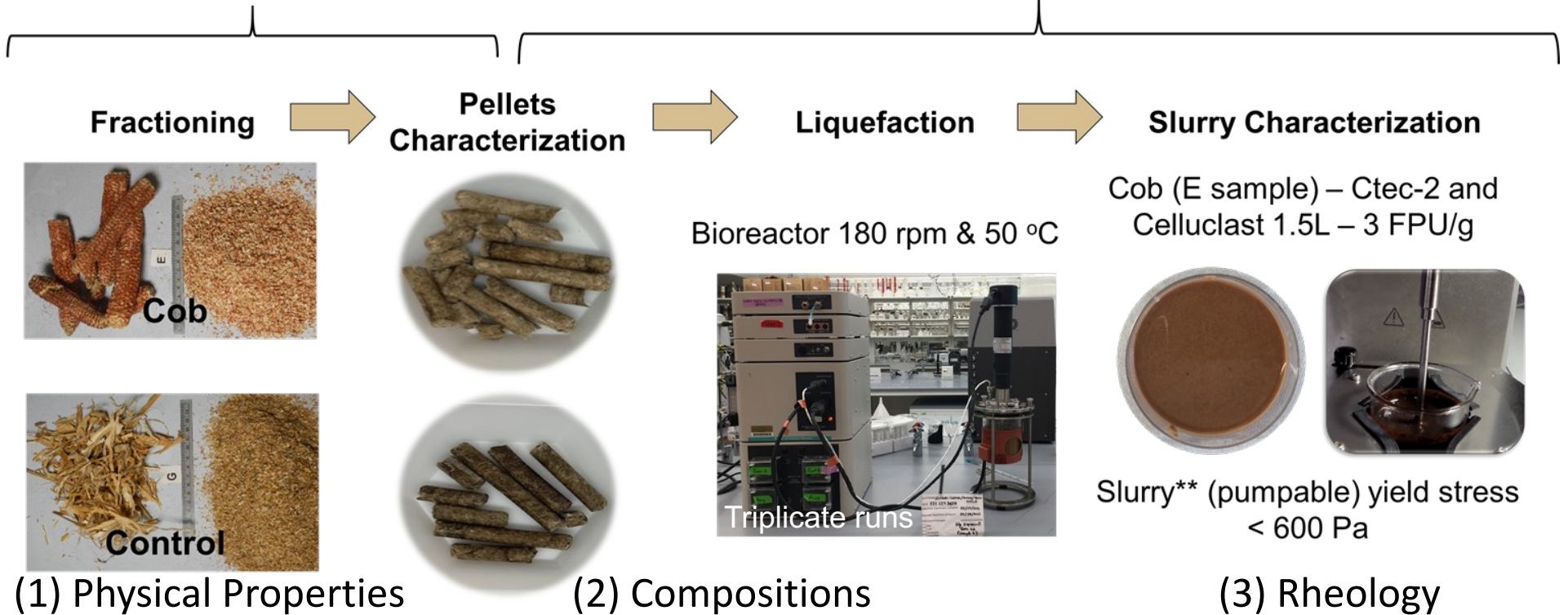
Determine particulate physical properties, compositional analysis, rheological measurements with integration of data obtained into a corn stover particulate database for particles prepared by hammer-milling and rotary shearing, and formed into pellets during course of this project.

Specific Aims



Corn stover

- Leaf
- Husk
- Stem
- Cob
- Unfractionated
- Screened 2mm



Task 4: Characterization of physical properties

2-mm particle size of different fractions prepared by Forest Concepts' rotary shear technology

100% completed



Leaf

Husk

Stem

Cob

Unfractionated
Screened 2 mm

Unfractionated
Control

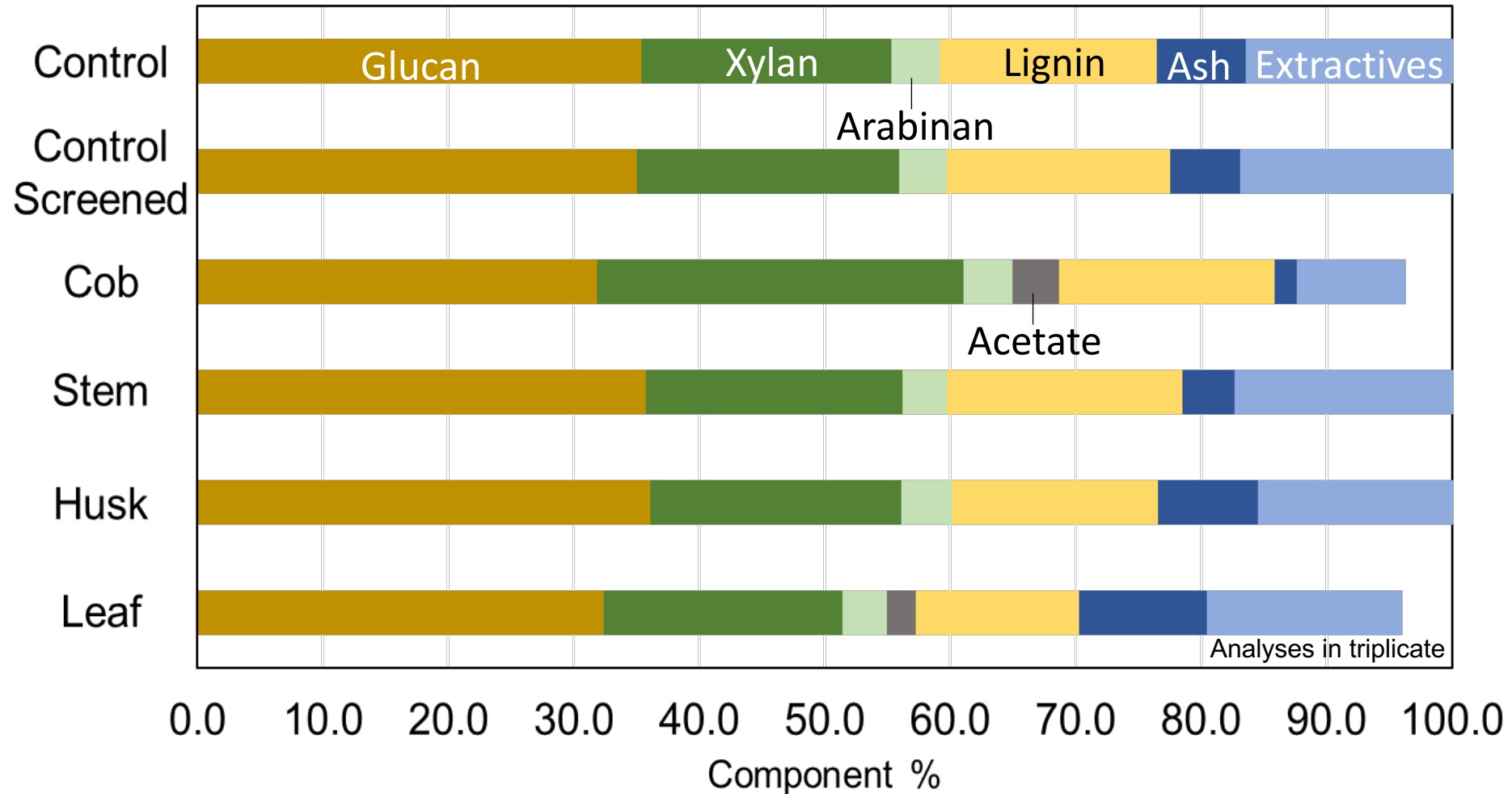
| Material | Moisture MC (%wb) | Particle Size | | Bulk Density | | Yield | | | Comminution Energy | |
|-------------------------------|----------------------|---------------------|---------------------|-------------------------------|--------------------------------|-----------|---------|----------|-----------------------------------|---------------------------|
| | | Initial Xgm (mm) | Accepts Xgm (mm) | Loose (kg/m ³) | Tapped (kg/m ³) | % Accepts | % Fines | % Recirc | Specific E [kWh/odt] (MJ/odMg) | TEA Design E (kWh/odt) |
| A - Leaf | 10.5 | 12.0 | 1.33 | 97 | 124 | 96.7 | 3.3 | 65 | 5.5 (22.0) | 7.3 |
| B - Husk | 8.0 | 6.60 | 1.35 | 91 | 116 | 93.1 | 6.9 | 42 | 7.1 (28.3) | 9.5 |
| C - Stem / Husk | 7.7 | 8.93 | 1.38 | 107 | 134 | 95.4 | 4.6 | 47 | 5.0 (19.7) | 6.7 |
| D - Stem | 7.3 | 13.8 | 1.55 | 134 | 166 | 98.3 | 1.7 | 52 | 7.3 (29.2) | 9.7 |
| E - Cob | 9.5 | 90.4 | 1.78 | 224 | 279 | 99.6 | 0.4 | 63 | 11.1 (44.1) | 14.8 |
| F - Unfractionated / Screened | 7.5 | 8.08 | 1.58 | 107 | 139 | 98.2 | 1.8 | 51 | 4.2 (16.6) | 5.6 |
| G - Unfractionated Control | 7.8 | 8.26 | 1.46 | 112 | 142 | 93.9 | 6.1 | 46 | 6.1 (24.1) | 8.1 |

Analysis in triplicate

Aston, Dooley, Thompson, 2022

Task 4: Characterization of compositions of corn stover fractions

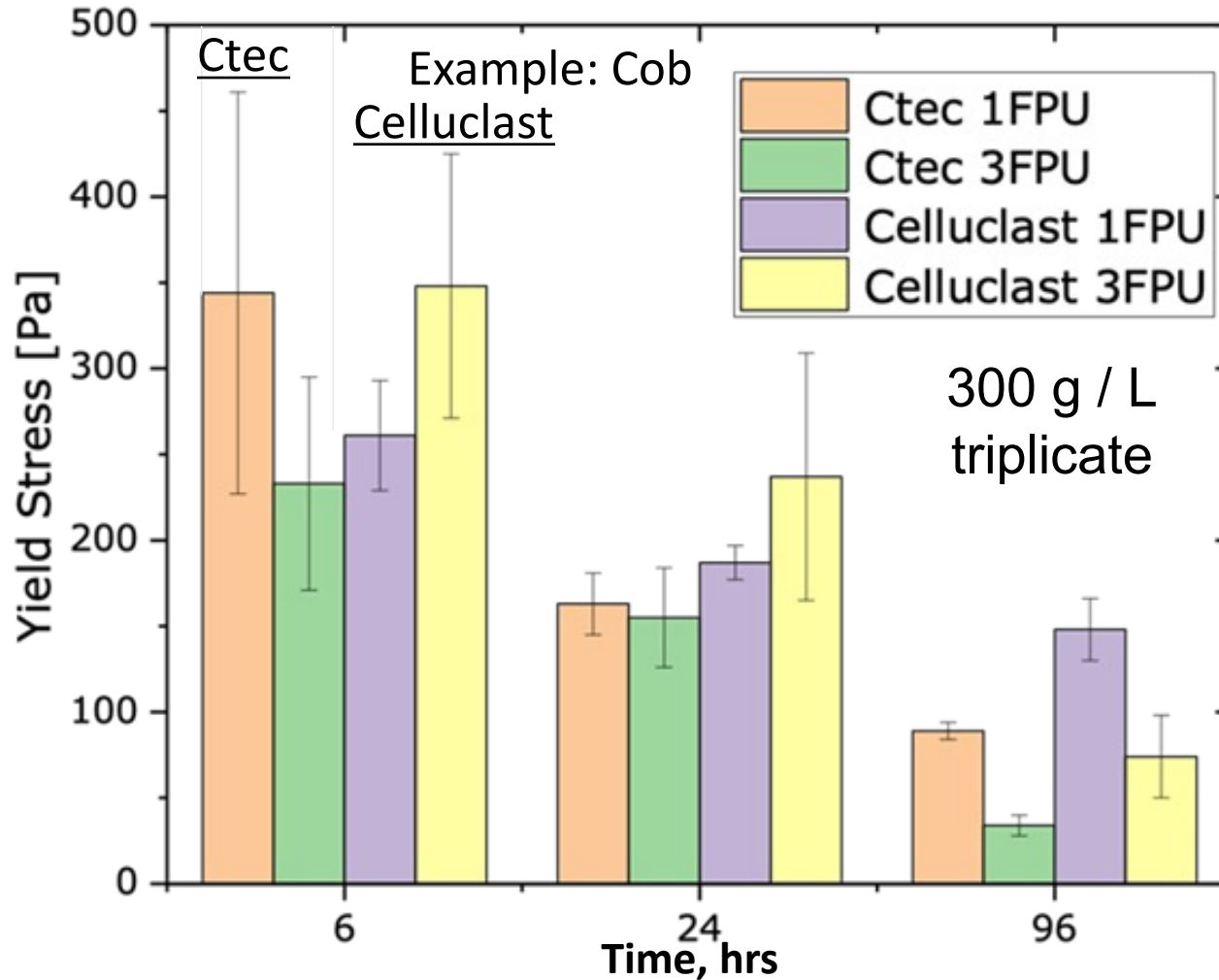
Task 4: 95% completed



Impact: IBM model predicts rheology based on biophysical properties of particles

Task 4: Characterization of rheology for different fractions

Task 4: 95% completed



| Water Absorption Test | | |
|--|------------|------------|
| R = ratio of absorbed water to solid mass | | |
| Sample | t = 10 min | 8 hr |
| 2.2 mm – not fractionated | 1.1 | 4.2 |
| Stem | 1.1 | 4.8 |
| Cob | 1.1 | 4.8 |
| <hr style="border-top: 1px dashed black;"/> | | |
| Not Fractionated | 1.1 | 6.2 |
| Leaves | 1.1 | 6.6 |
| <p>If R > 5; Liquefaction inhibited, with Yield Stresses > 600 Goal: Yield Stress < 200 to 600</p> | | |

Measurements in triplicate Gutierrez, Szeto, Cruz, Erk, Ximenes, 2022

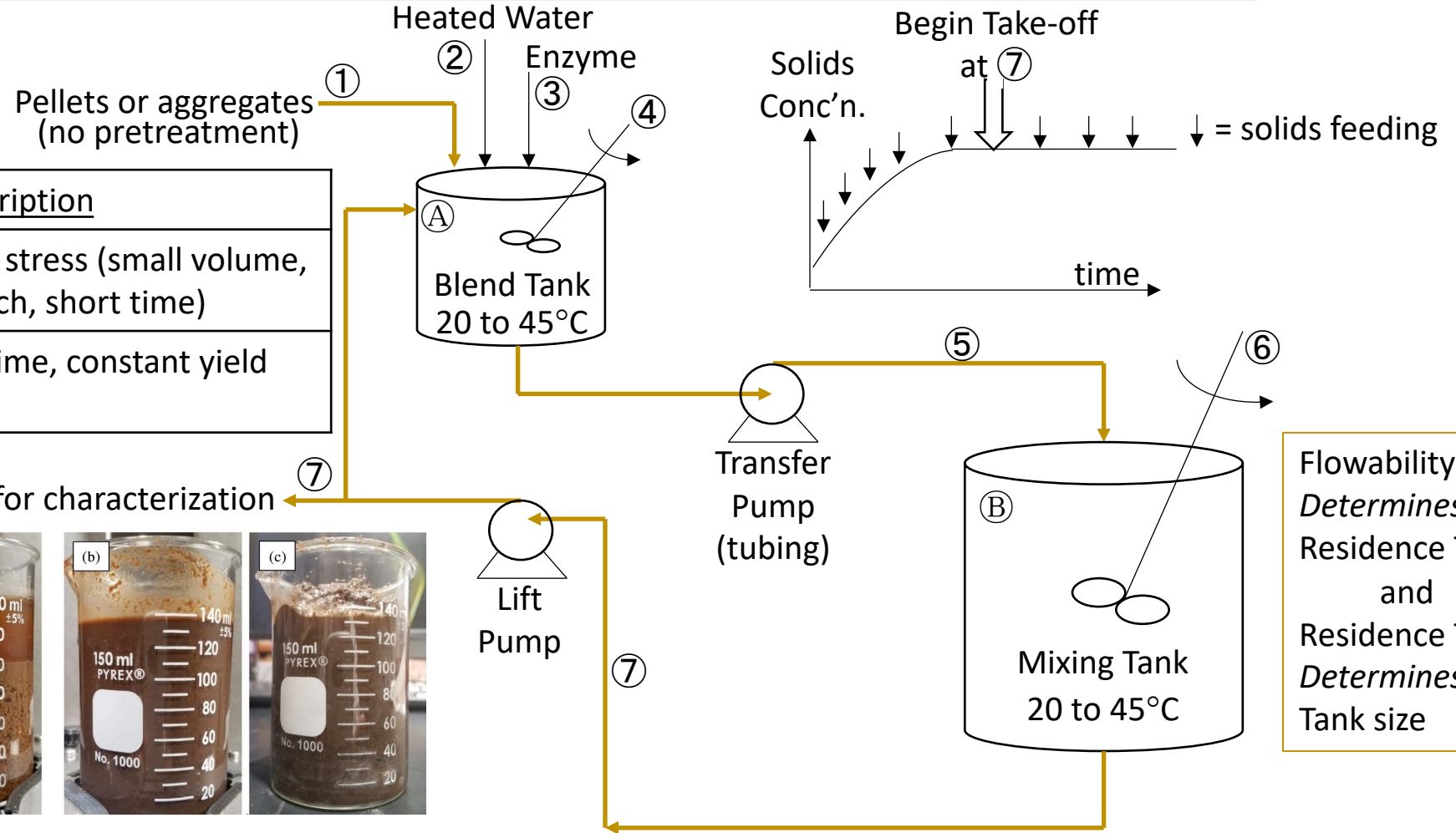
Impact: Water absorption is inversely related to slurry formation at 300 g/L; provides metric for biomass acceptance criteria at plant gate

Task 4, 5: Techno-economic Assessment (TEA)

Process flow before pretreatment

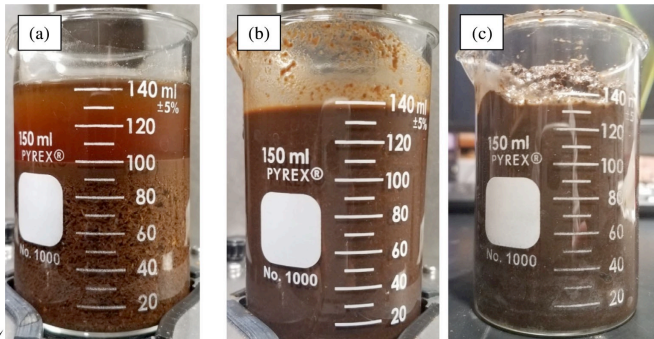
60% completed

| Tank | Description |
|------|---|
| A | design for max yield stress (small volume, small motor fed-batch, short time) |
| B | large volume, long time, constant yield stress |



Corn stover solids

- (a) 10 % w/v
- (b) 20 %
- (c) 30 %



Flowability
Determines
Residence Time
and
Residence Time
Determines
Tank size

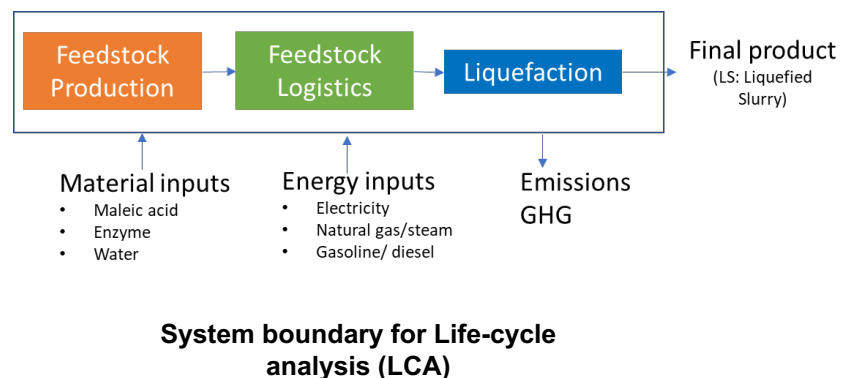
dos Santos, Overton, Kim, Ximenes, Cruz, Mosier, et al, 2021

Task 6: Life Cycle Analysis (LCA) Underway, Q9 to Q12, M25 to M36

Task 6: 60% completed

Leveraging material from GREET- LCA modeling tool

TEA Results



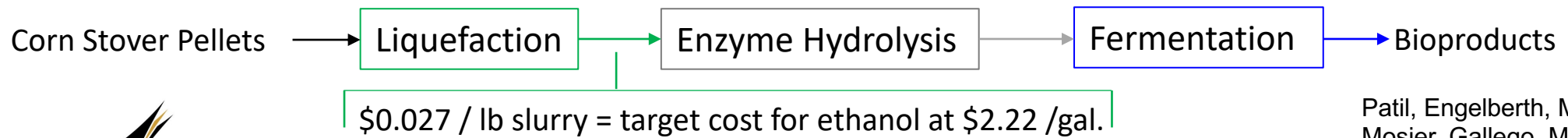
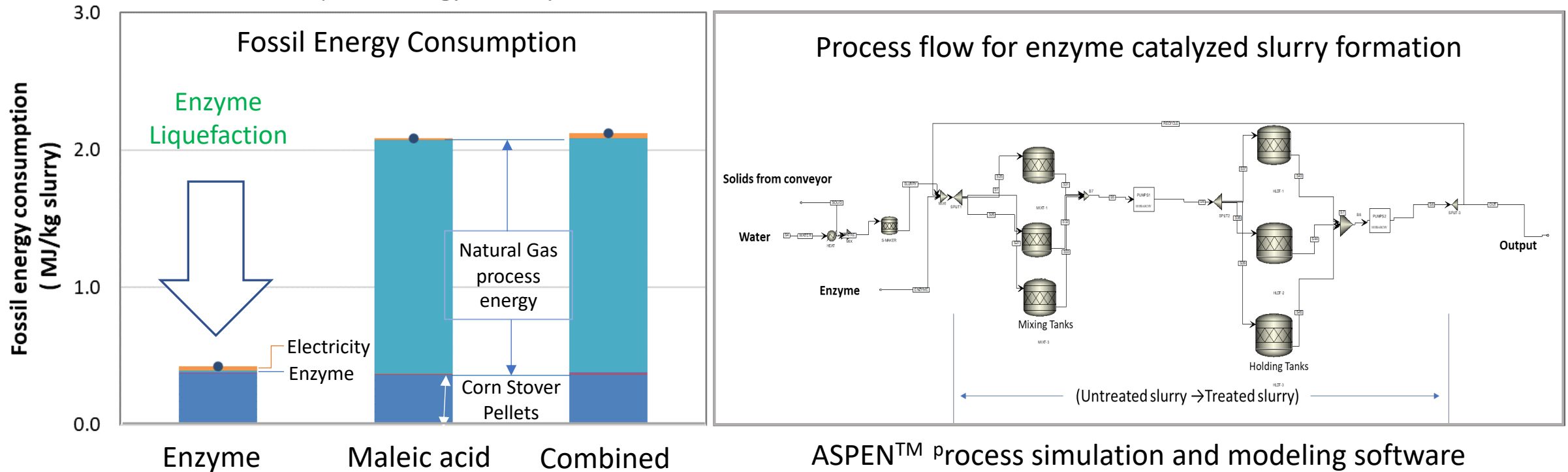
Use material and energy balance starting from corn stover, for a slurry solids loadings of 300 g/L to assess emission energy burdens, and cost prior to the slurry entering a pretreatment step. This TEA/LCA will be focused on the pre-processing steps.

Gallego, Engelberth, Monceaux 2023

Task 6: Technical Assessment and Life Cycle Analysis

60% completed

Framework from DOE 0008256



Patil, Engelberth, Maulik, Ximenes, Mosier, Gallego, Monceaux, 2022

Task 7: Materials Properties Database

1 Approach

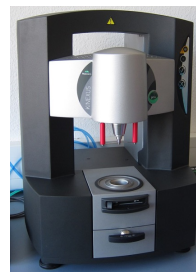
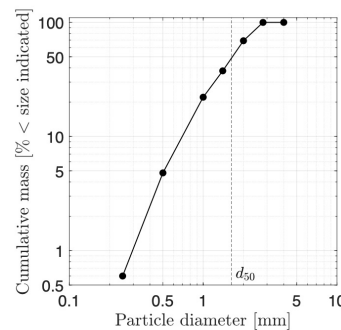
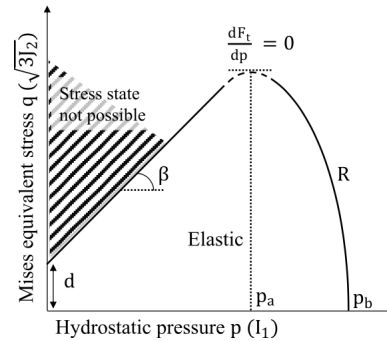
40% completed



receive
pelleted
material



de-aggregate
pellets and
treat to reach
desired moisture
content



store data in a database



Method
Tri-axial Tester
composition by NREL
LAP's

Correlation
Modified Drucker-Prager
Cap (mDPC)
Tabulated Datasets

Particle Level
Measurements
(by sieving)
densities, size, shape

Particle size distributions
Density Correlations
Tabulated Data

Rheology
Fed-batch bioreactors
runs to prepare slurries

IBM model
Rheology correlations
(Ardekani, Erk, this work)
Graphical Comparisons

All measurements in triplicate

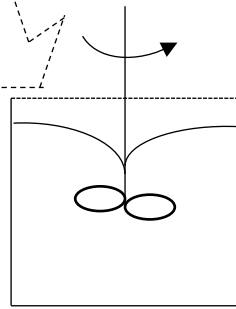
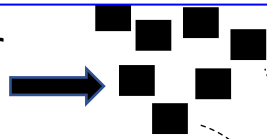
Summary and Overall Impacts: Mechanism, model, method for slurry formation of corn stover fractions

3 Outcomes

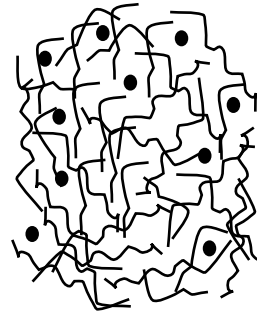
300 g cornstover (pellets)



Professors Rosi and Antonio Cruz, 2022

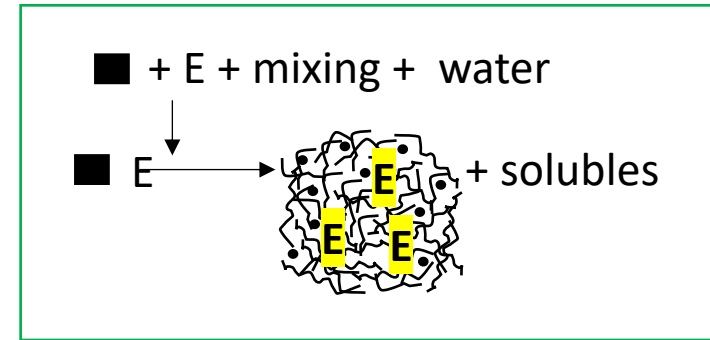


300 g particles

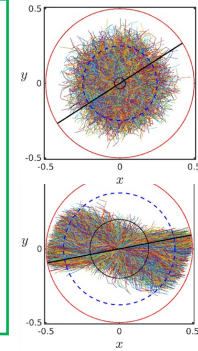


Gutierrez, Assis Serra, 2022

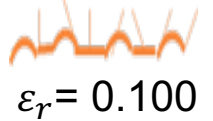
Overall about 85 to 90% completed



Ximenes, Ladisch, 2019

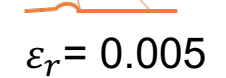


roughness



$\epsilon_r = 0.100$

vs



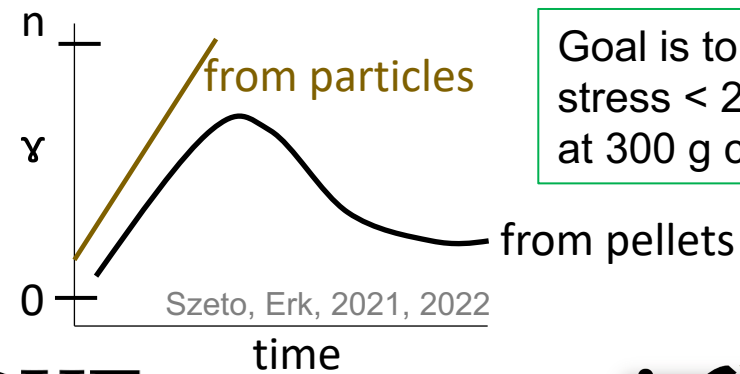
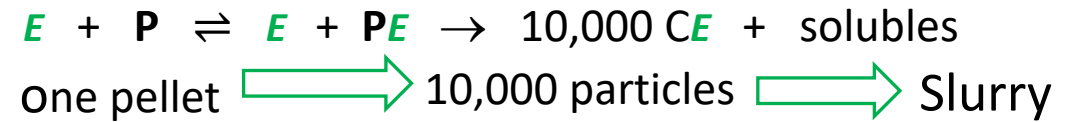
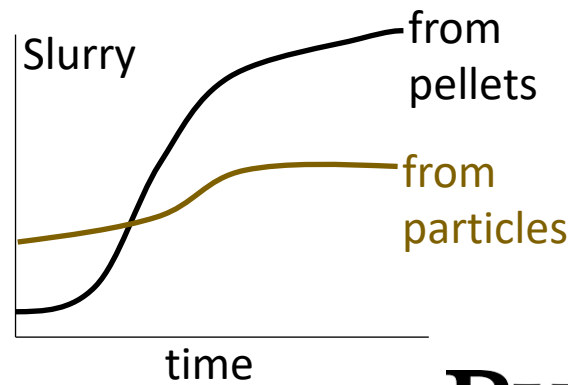
$\epsilon_r = 0.005$

flows better

More, Ardekani, 2022



Number of suspended particles (slurry)



Goal is to decrease yield stress < 200 for slurries at 300 g corn stover / L

Szeto, Erk, 2021, 2022

Overall Project Conclusions and Impacts

3 Outcomes
4 Impacts

Corn stover may be fractionated into readily liquefied materials.

Corn stover (unfractionated form) readily forms slurries at enzyme loadings of 1 to 3 FPU/g.

Acceptance criteria for corn stover may be based on laboratory measured water absorption

Pellets are needed and fed batch addition required to achieve high loadings

Some tissue fractions form slurries more readily than others (*work in progress*)

Water absorption is a key indicator

Life cycle analysis shows enzyme catalyzed liquefaction has acceptable energy requirement

Impacts:

Slurry formation with fractionated corn stover, achieved before pretreatment, has potential to avoid solids handling challenges experienced in pioneer biorefineries.

Model developed that explains how an aqueous slurry that may be pumped and processed at high solids loadings;

Model, validated with experimental measurements, addresses research gaps at feedstock conversion interface.

Quad Chart Overview

Timeline

- *Project start date: (BP 2); October 1, 2019*
- *Project end date: Sept. 30, 2023*
(approval letter Mar. 21, 2021)

| | FY22 Costed | Total Award |
|---------------------------|-------------|-------------|
| DOE Funding | 450,934 | 1,378,384 |
| Project Cost Share | 77,324 | 346,366 |

TRL at Project Start: TRL 3

TRL at Project End: TRL 4

Project Goal

Model formation of an aqueous slurry that may be pumped and processed at high solids loadings; address research gaps at feedstock conversion interface.

End of Project Milestone

Written report with mathematical model, bulk property database, and dimensionless parameters for high loading slurries of corn stover fractions

Funding Mechanism

DE-FOA-0002029 AOI 2a. 109-58 Energy Policy Act (2005) cooperative agreement CEDA 81.087.

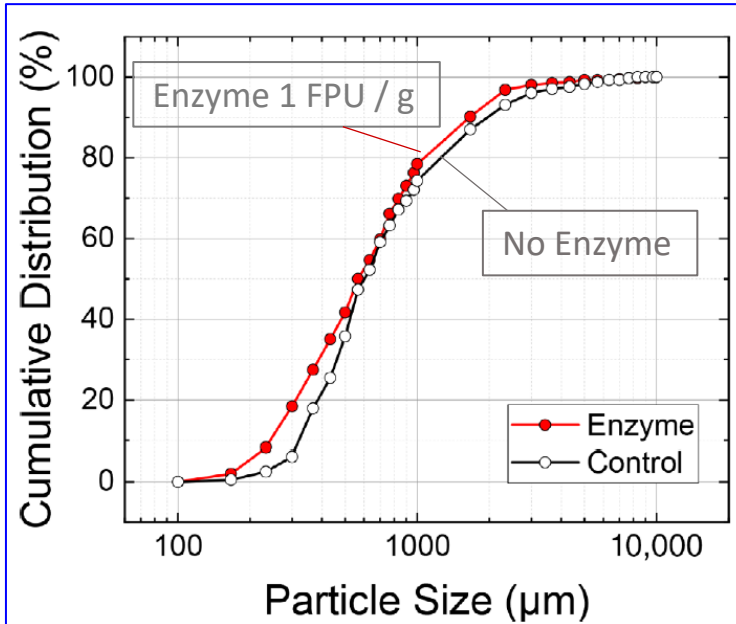
Project Partners

- Partner 1 INL
- Partner 2 ANL
- Partner 3 Forest Concepts
- Partner 4 AdvanceBio

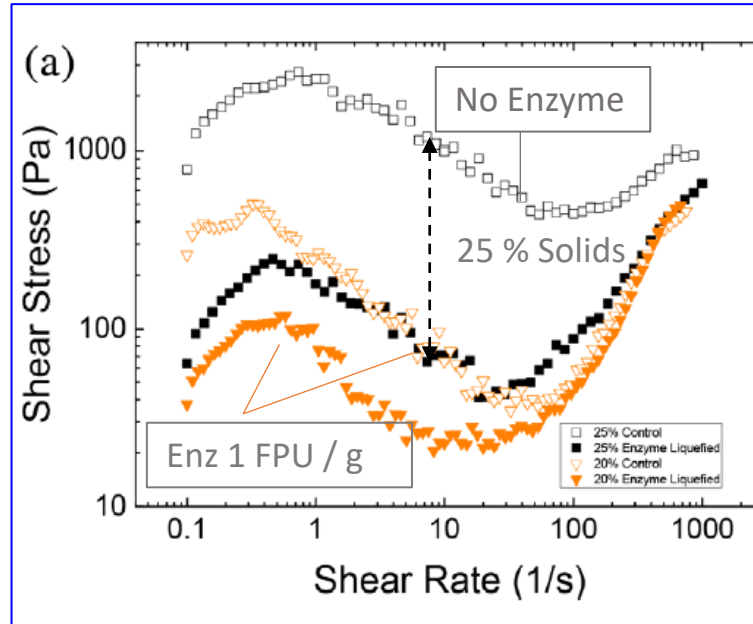
Additional Slides

Rheology shows enzyme reduces shear stress and viscosity > 10 x

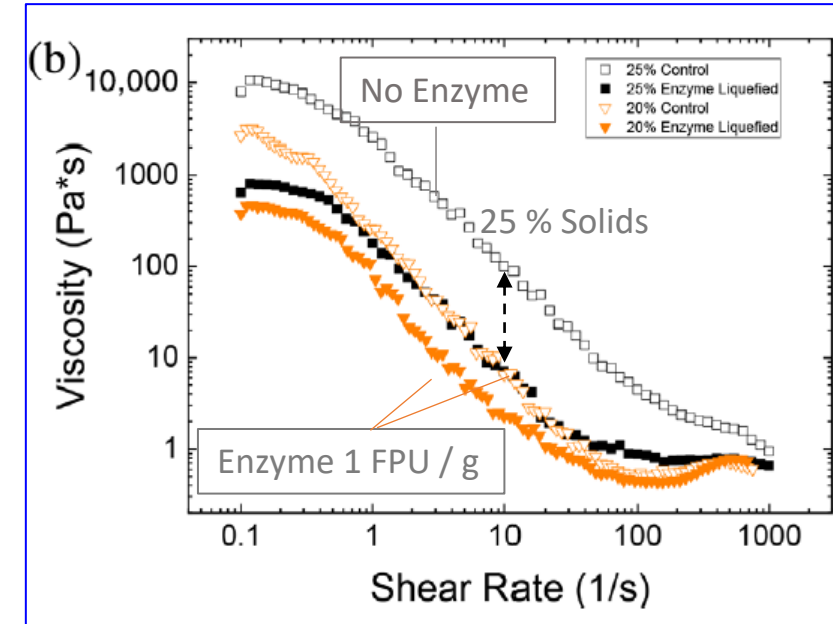
Particle Size Distribution Similar



+ enzyme = 20x lower shear stress



+ enzyme = 10x lower viscosity



Change in particle surface roughness may be a factor

Computational modeling by immersed boundary method (IBM) shows that viscosity increases as large fiber volume to total fiber volume increases.

More, Ardekani et al, 2020; Szeto, Erk et al, 2021

Supporting Publications

from EE0008256

1. Patil, A., A. S. Engelberth, M. R. Ladisch, "Effect of biomass liquefaction on glucose and xylose prices predicted by National Renewable Energy Laboratory biochemical sugar model," *Biofuels, Bioproducts and Biorefining*, 17(1), 1-290 (2023).
2. Serra, L. A., R. G. da Silva Cruz, D. M. R. Gutierrez, A. J. G. Cruz, C. A. T. Canizares, X. Chen, N. Mosier, D. Thompson, J. Aston, J. Dooley, P. Sharma, J. L. De Marco, J. R. M. de Almeida, K. Erk, E. Ximenes, M. R. Ladisch, "Screening method for Enzyme-based liquefaction of corn stover pellets at high solids, *Bioresour. Technol.*, 363, 1-10, doi: 10.1016/j.biortech.2022.127999 (2022).
3. Bordignon, S. E., E. Ximenes, O. M. Perrone, C. da Cost Carriera Nunes, D. Kim, M. Boscolo, E. Gomes, E. X. F. Filho, R. da Silva, and M. R. Ladisch, "Combined Sugarcane Pretreatment for the Generation of Ethanol and Value-Added Products," *Front. Energy Res.*, 10, 1-2, doi:10.3389/feng.2022.834966 (2022).
4. Ximenes, E., C.S. Farinas, A.C. Badino, M.R. Ladisch, "Moving from residual lignocellulosic biomass into high-value products: Outcomes from a long-term international cooperation," *Biofuels, Bioproducts, Biorefining*, DOI: 10.1002/bbb.2179, 15(2), 563-573 (2021).
5. Buffo, M. M., A. L. Z. Ferreira, R. MRG Almeida, C. S. Farinas, A. C. Badino, E. A. Ximenes, M. R. Ladisch, Cellulolytic enzymes production guided by morphology engineering, *EMT*, 149, 1-29 (2021).
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Publications, Patents, Presentations, Awards, and Commercialization

There are none yet for EE0008910 as of Feb 20, 2023

