NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Use of lignin-based admixture as water reducer (WRA) for tailoring the rheological properties of mortars for 3D-printing.

Fabian B. Rodriguez[1], PhD; Kyle E.O. Foster[1], PhD; Ana Aday[1], PhD; Adewale Odukomaiya[1], PhD; Xavier Fross[1], Rory Schmidt[1], Michael E. Himmel[2], PhD; Michael Griffin[3], PhD.

[1]Building Technologies and Science Center

[2]Bioenergy Science and Technology Department

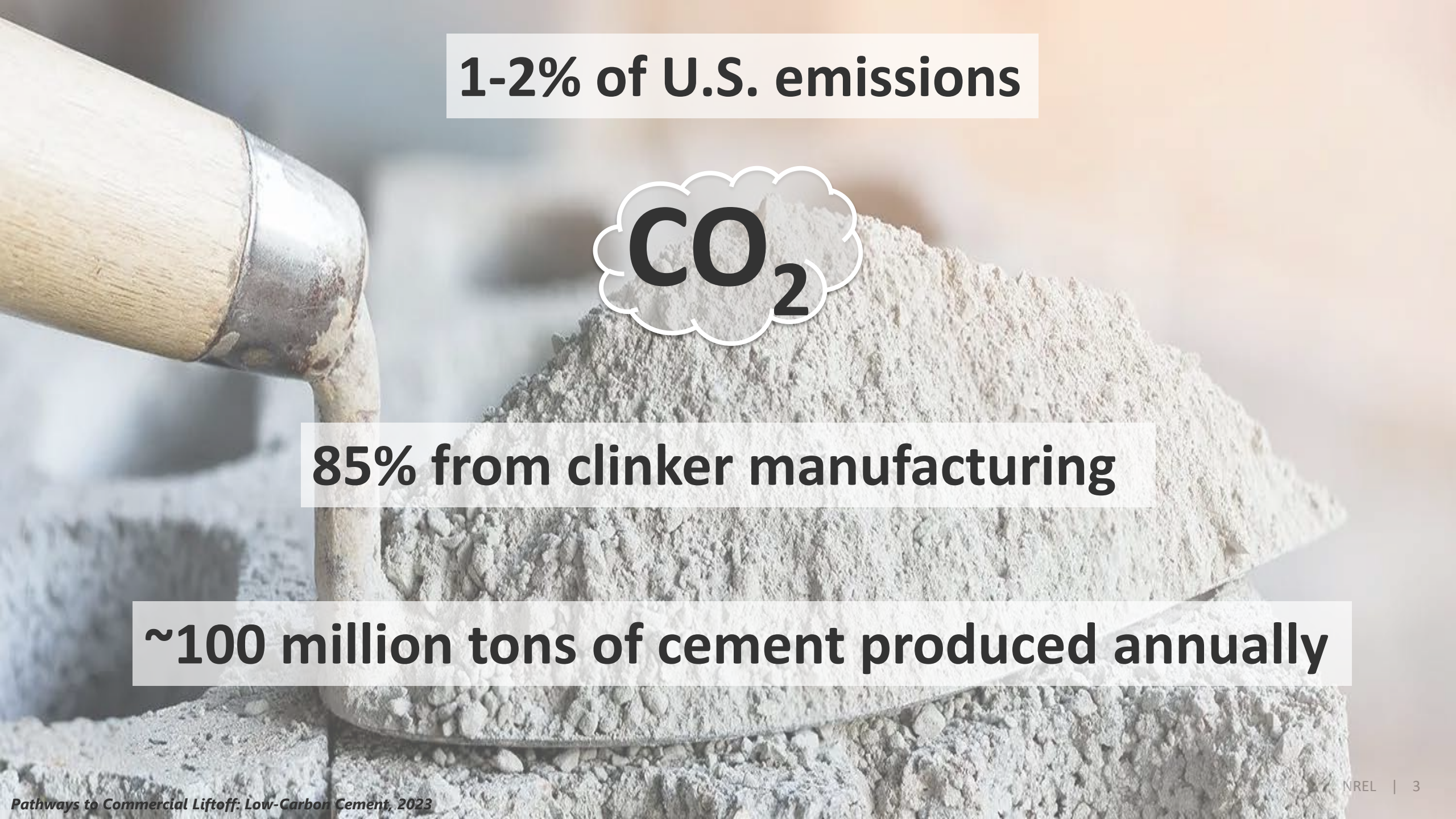
[3]Catalytic Process Development

14th Advances in Cement-based Materials - Advances in Rheology - The American Ceramic Society

June 21, 2024

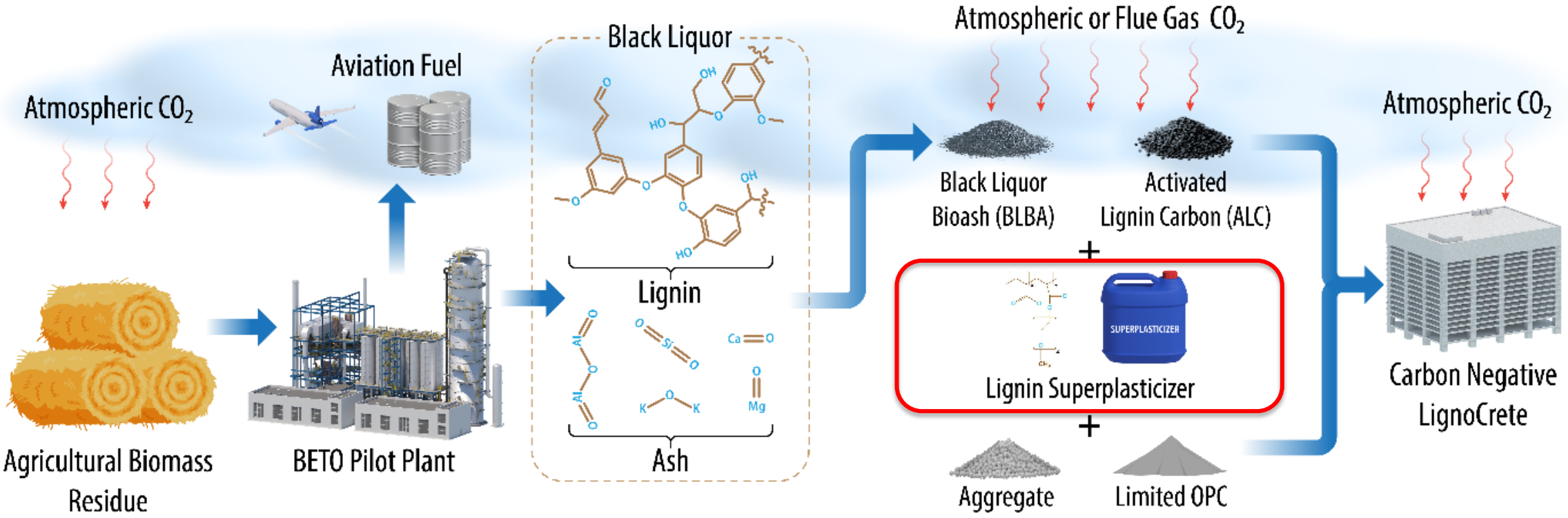
Agenda

1. Background
2. Lignin-admixture production process
3. Experimental program
4. Results
5. Conclusions
6. Future work



Pathways to Commercial Liftoff: Low-Carbon Cement, 2023

Background: Technology Overview

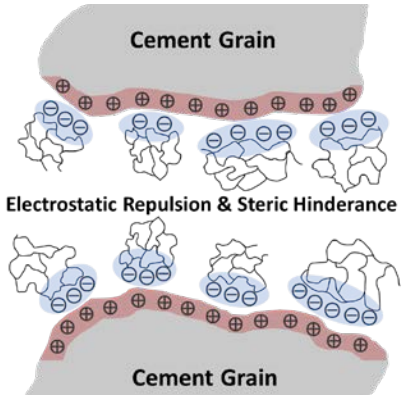


Potential Impact

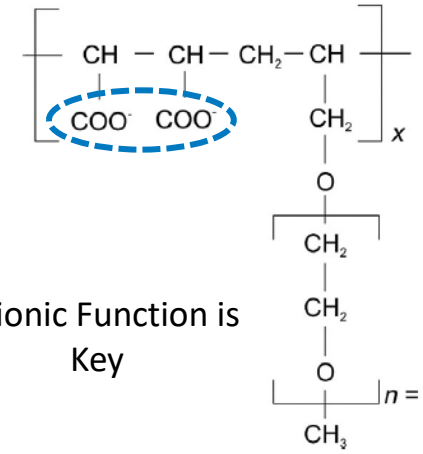
Lignin-based superplasticizers (SPs) can offset petrochemical-derived SPs for additional carbon-negative additives to concrete and provide viscosity modification for additive construction techniques.

Motivation

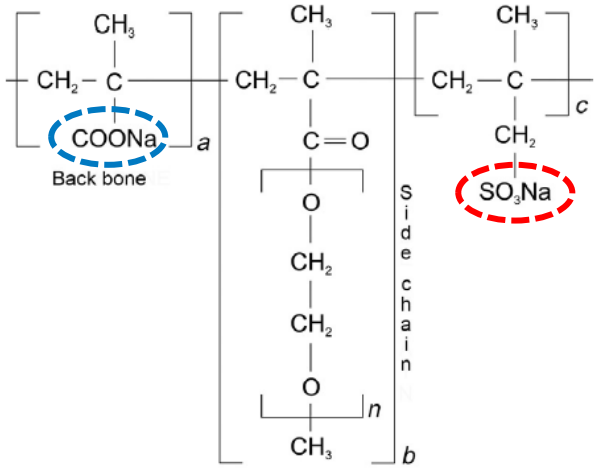
SPs Reduce Water 12–30% & Increase Strength



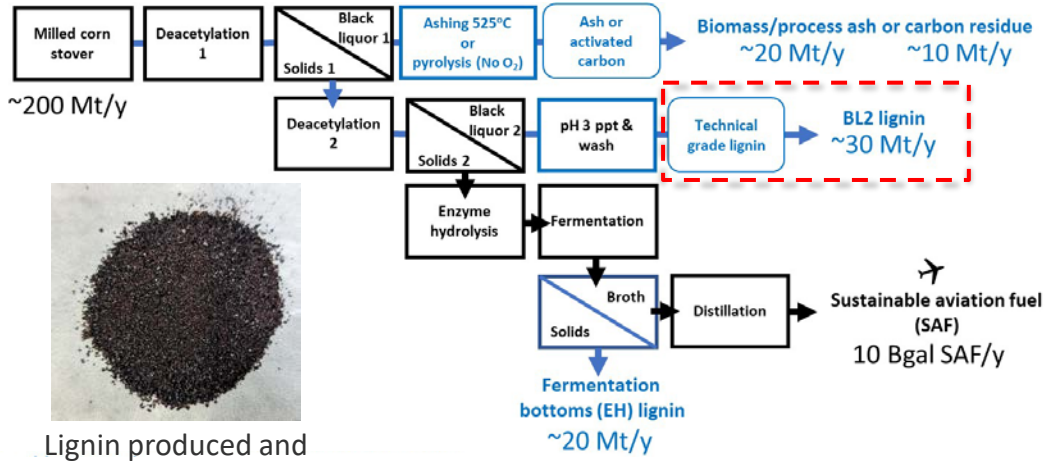
Conventional SPs are Petrochemical-Based



Anionic Function is Key

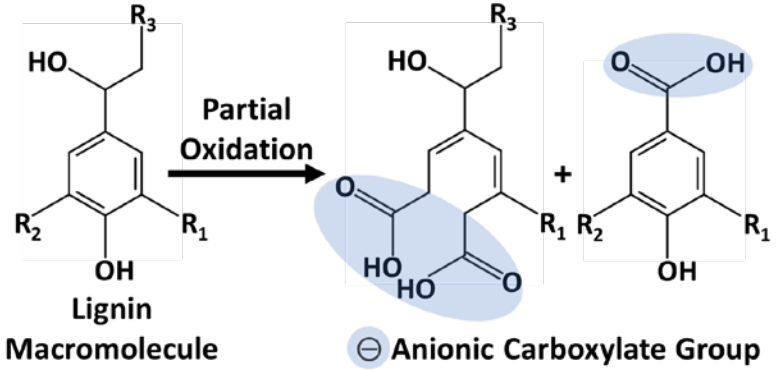


Lignin is a Byproduct from Existing NREL Work

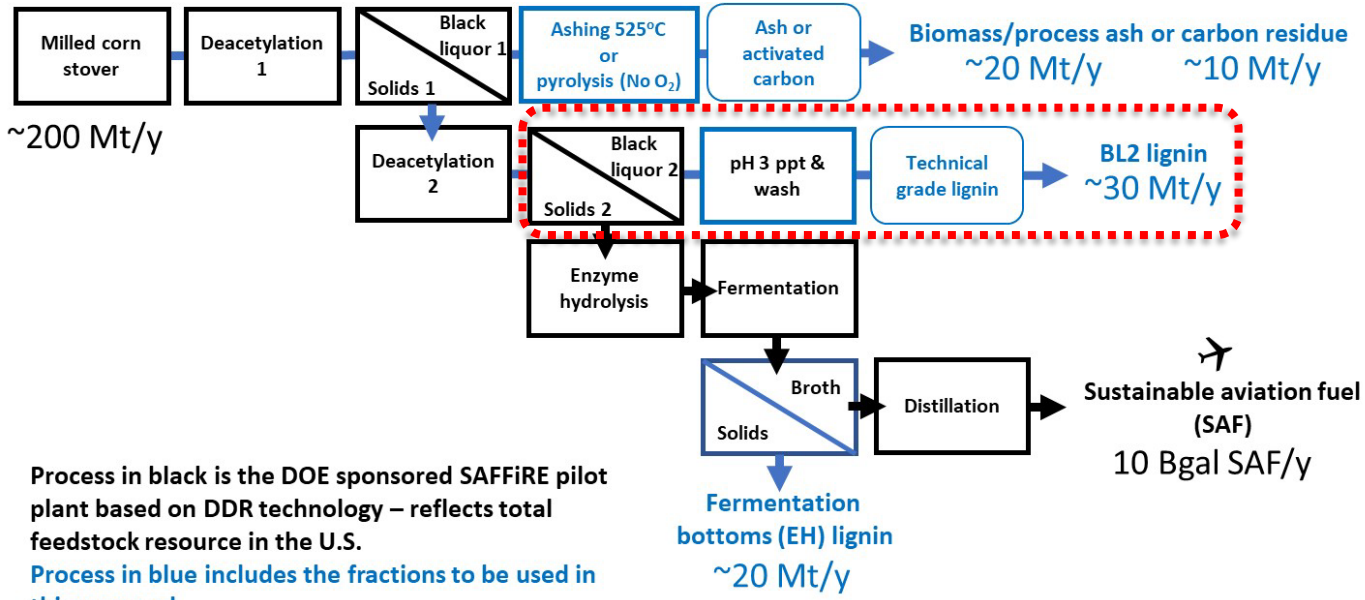


Lignin produced and refined at NREL

Sustainable Chemistry Uses Native Architecture



Production of Technical Lignin



- **Process in black is the DOE sponsored SAFFiRE pilot plant based on DDR technology – reflects total feedstock resource in the U.S.**
- **Process in blue includes the fractions to be used in this proposal**

- Acid precipitation and isolation from black liquor 2 fraction
- 20 L of black liquor yields ~250 g technical lignin

Our Technical Lignin

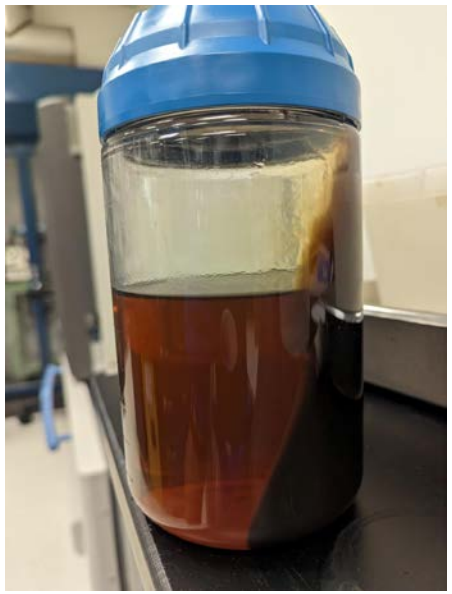
M_n = 680 Da

M_w = 2100 Da

Lignin SPs in the Literature

M_n: 1000 – 25000 Da

M_w: 1600 – 35000 Da

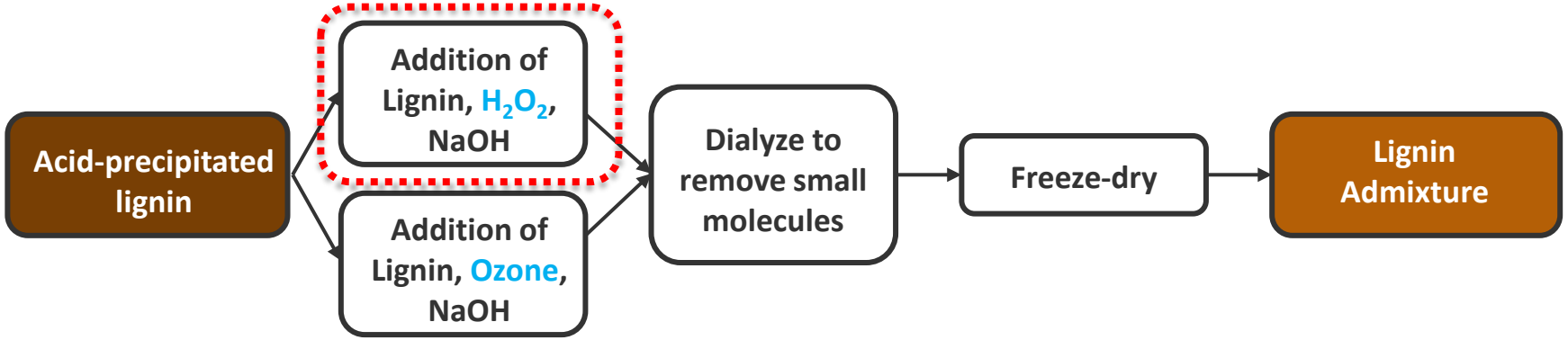


Centrifuge to recover Technical Lignin

Filtered BL2

Technical Lignin

Increasing Carboxylate Content Via Oxidation

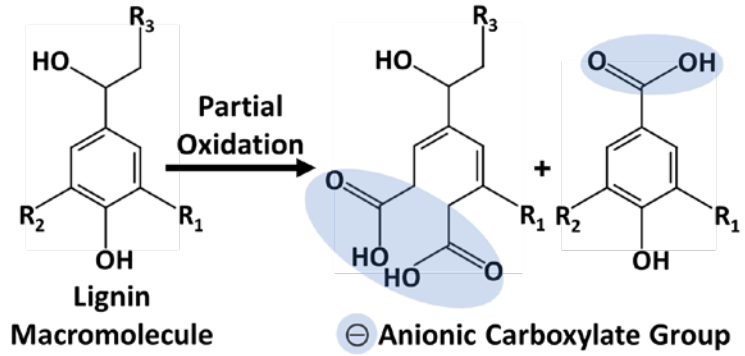


Finding a sweet spot to co-maximize carboxylate content, yield, and molecular weight

- Low MW has been less of an issue than expected (~500 Da)

Removing fragmented acids via dialysis is necessary, but time consuming

- Small molecule acids can hinder the cement reaction outside acceptable conditions



Commercial Polycarboxylate Ether SPs: MW 5 – 20 kDa

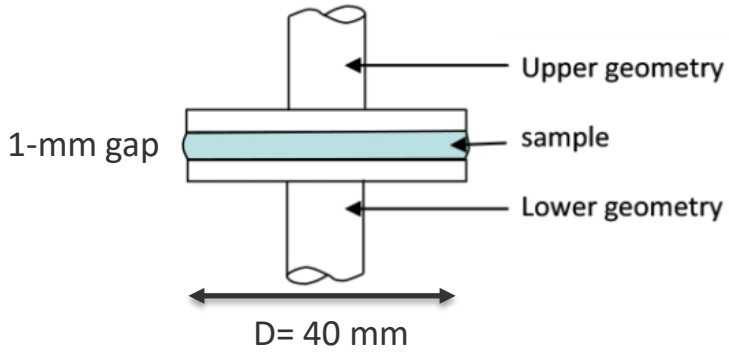
LigWRA material is produced in solution with a solids content ~30%, similar to commercial superplasticizers.

Experimental Program

Assessment of Lignin-based water reducer admixture

- Rheological characterization.
- 3D-printing for printability, buildability evaluation
- Isothermal Calorimetry and Indication of Setting time.

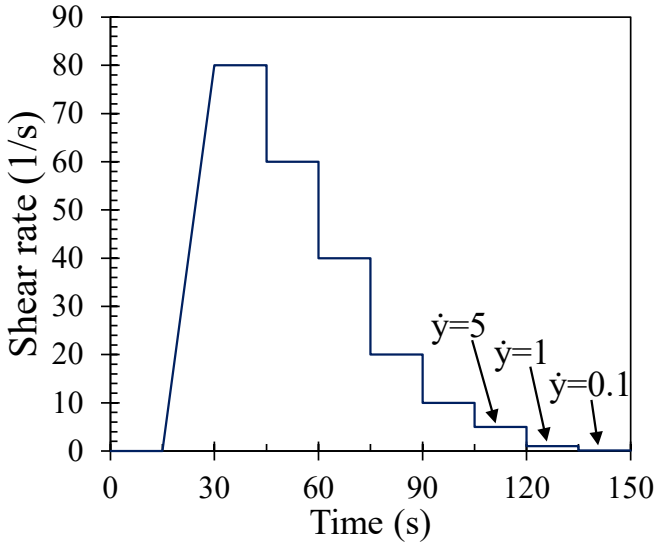
Parallel plates setup



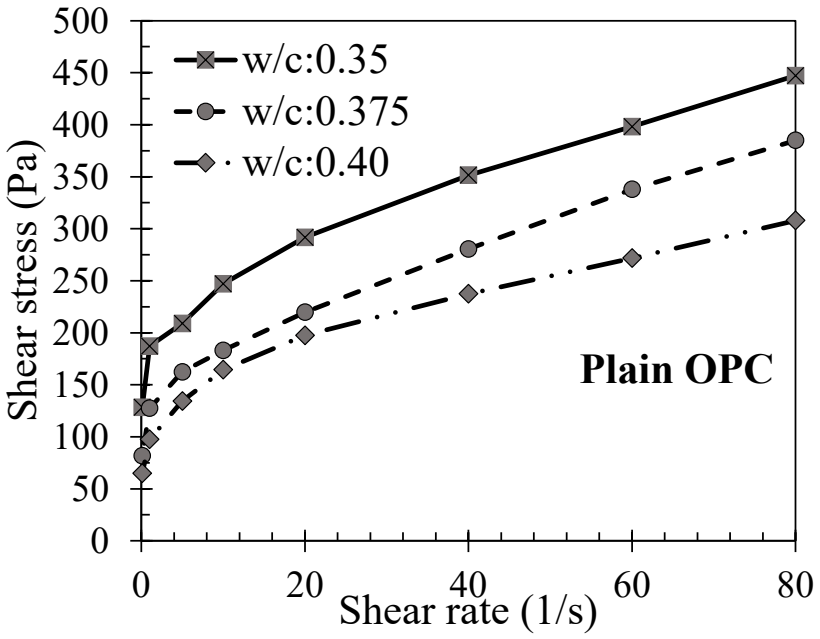
Material tested

- Plain OPC system (Control)
- Commercial WRA (ComWRA)*
- Lignin WRA (LigWRA)*

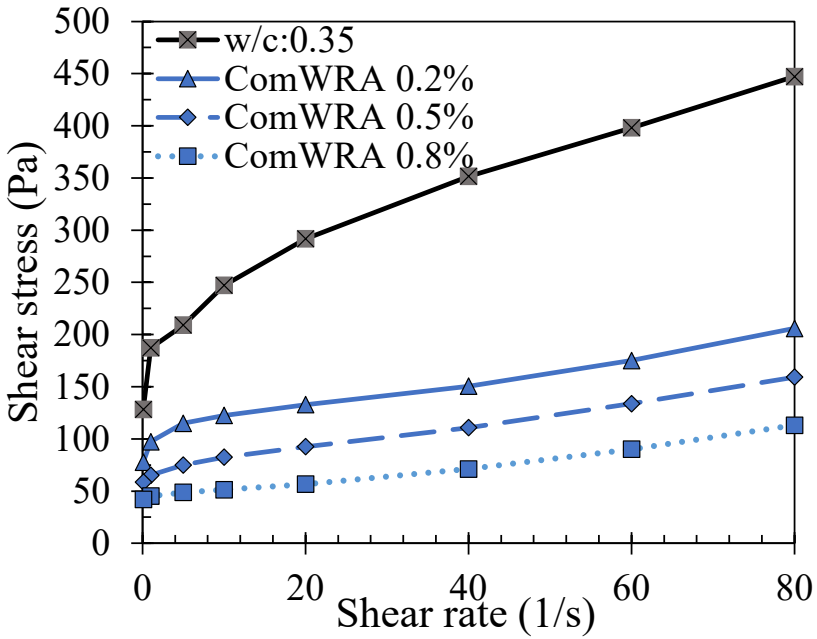
*Admixture dosages: 0.2 wt.%, 0.5 wt.%, 0.8 wt.%



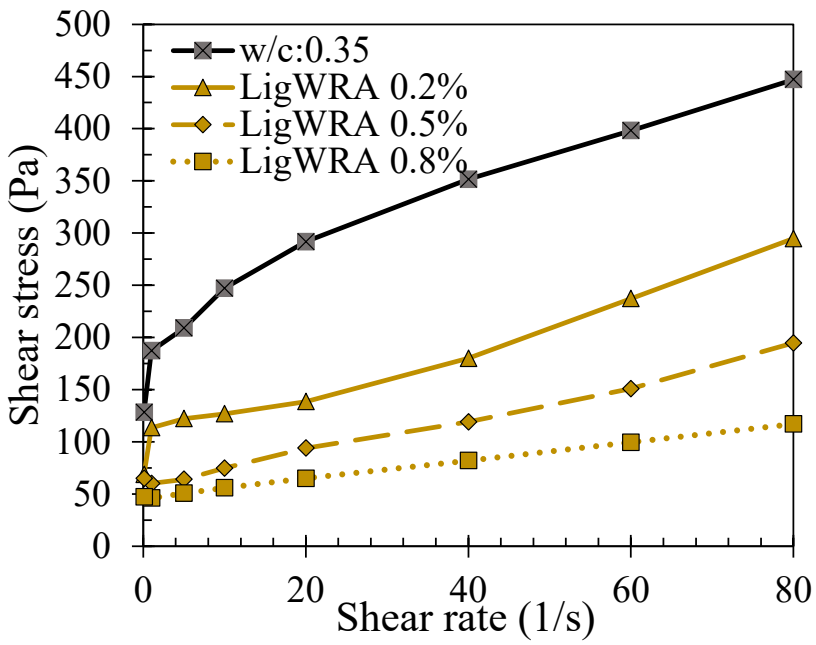
Rheology of Cement Pastes



Commercial WRA



Lignin WRA

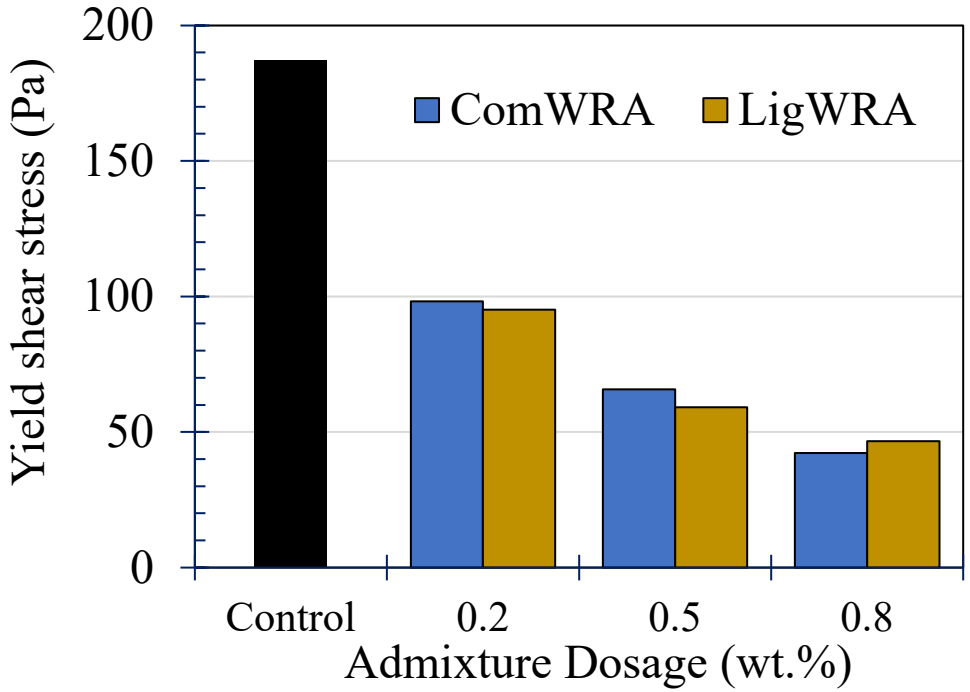


- The use of LigWRA causes a significant change in the shear response of cement pastes in a similar fashion to ComWRA used as reference.

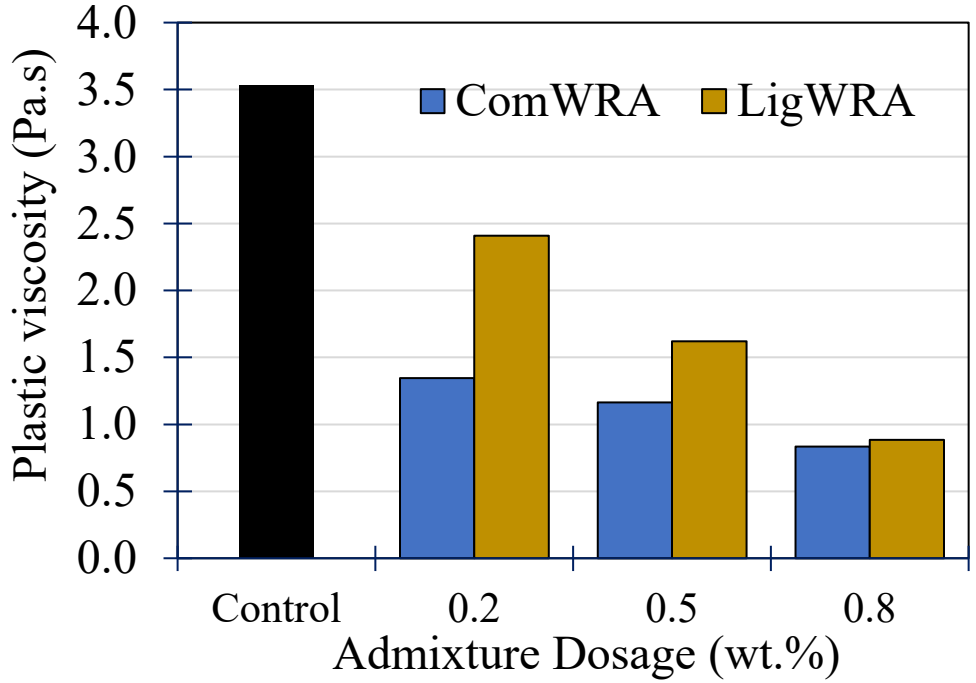
- Bingham model approach is used to determine the yield stress and viscosity of the different mixtures

Rheological Parameters

Yield stress



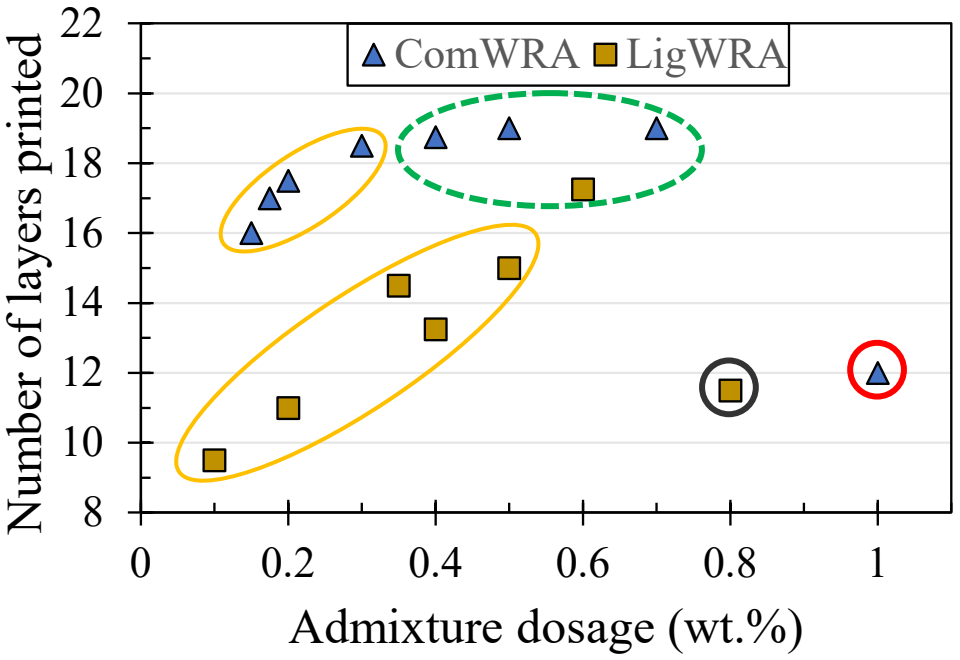
Plastic Viscosity

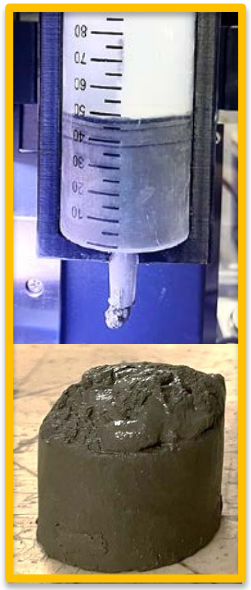


- Yield stress decrease is comparable between ComWRA and LigWRA at different dosages
- Influence of WRAs on the plastic viscosity is more evident on the commercial admixture, while Lignin-based admixture does not have the same effect at 0.2% and 0.5% dosages.

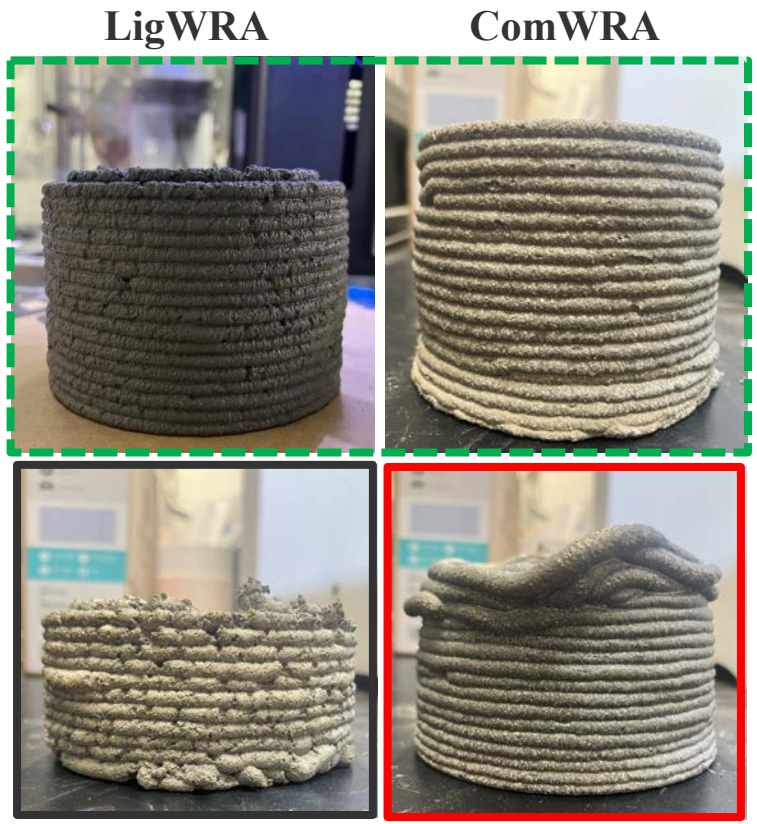
Extrudability and Buildability

Double-wall cylinders



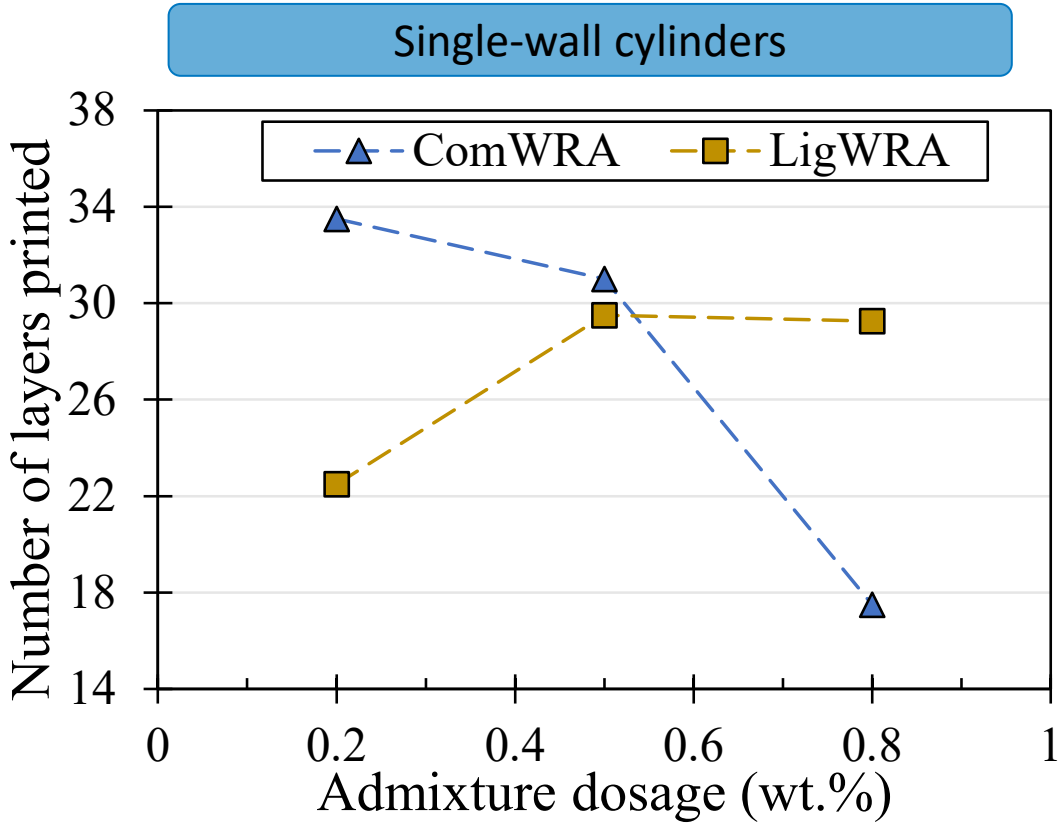


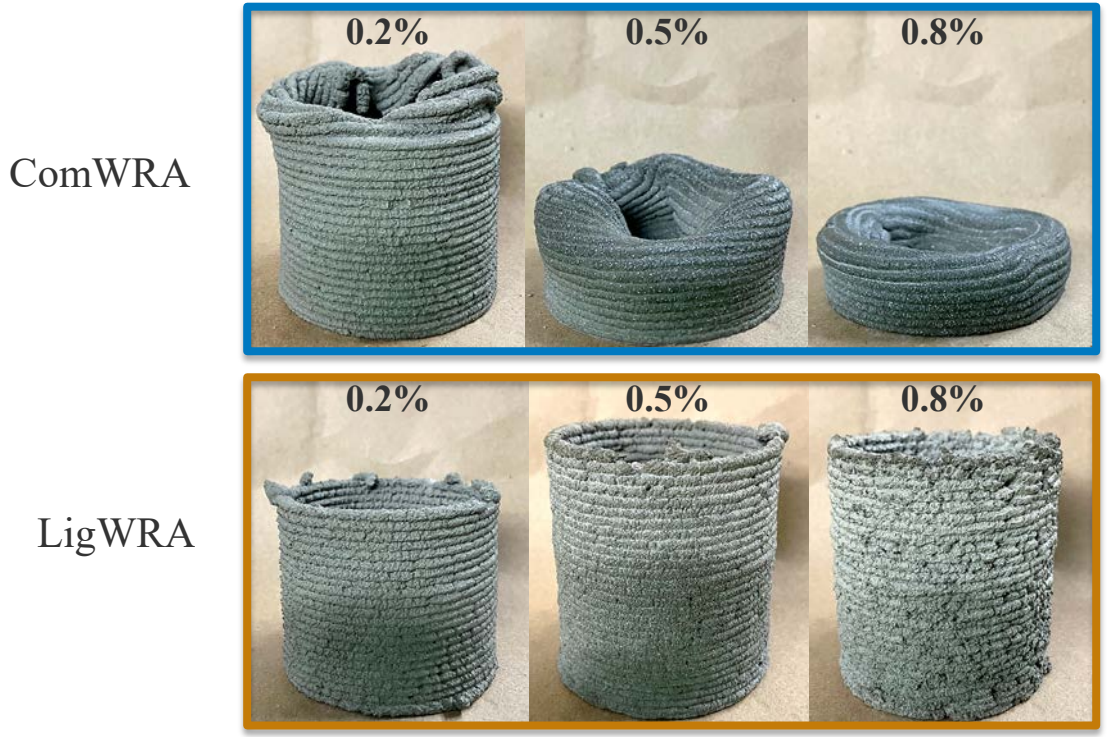
"Dead zone" material



- Lower dosages allow for bleeding of the mixture and clogging due to excessive pressure.
- Appropriate dosages of ComWRA and LigWRA produce continuous flow of material and stable filaments.
- Higher dosages of LigWRA cause a lack of cohesion and breakdown of the filament
- Higher dosages of ComWRA cause instability of the filaments during printing.

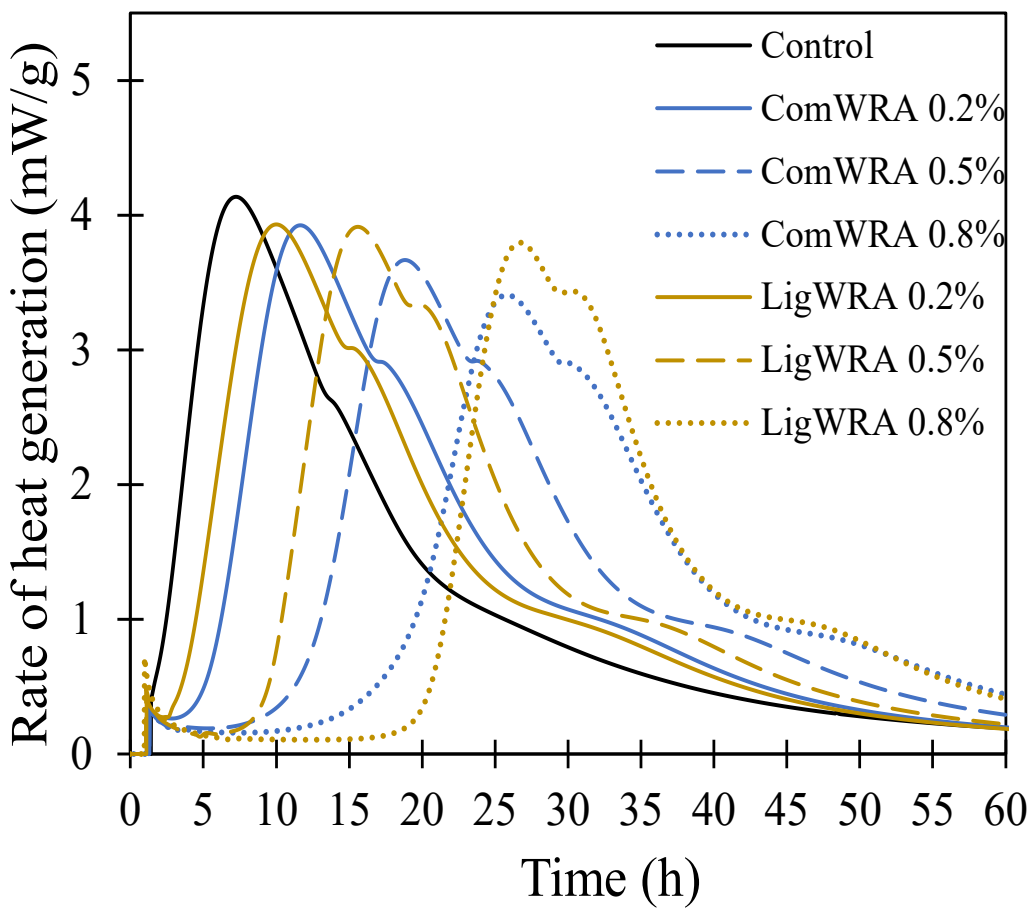
Printability of Single-wall Elements

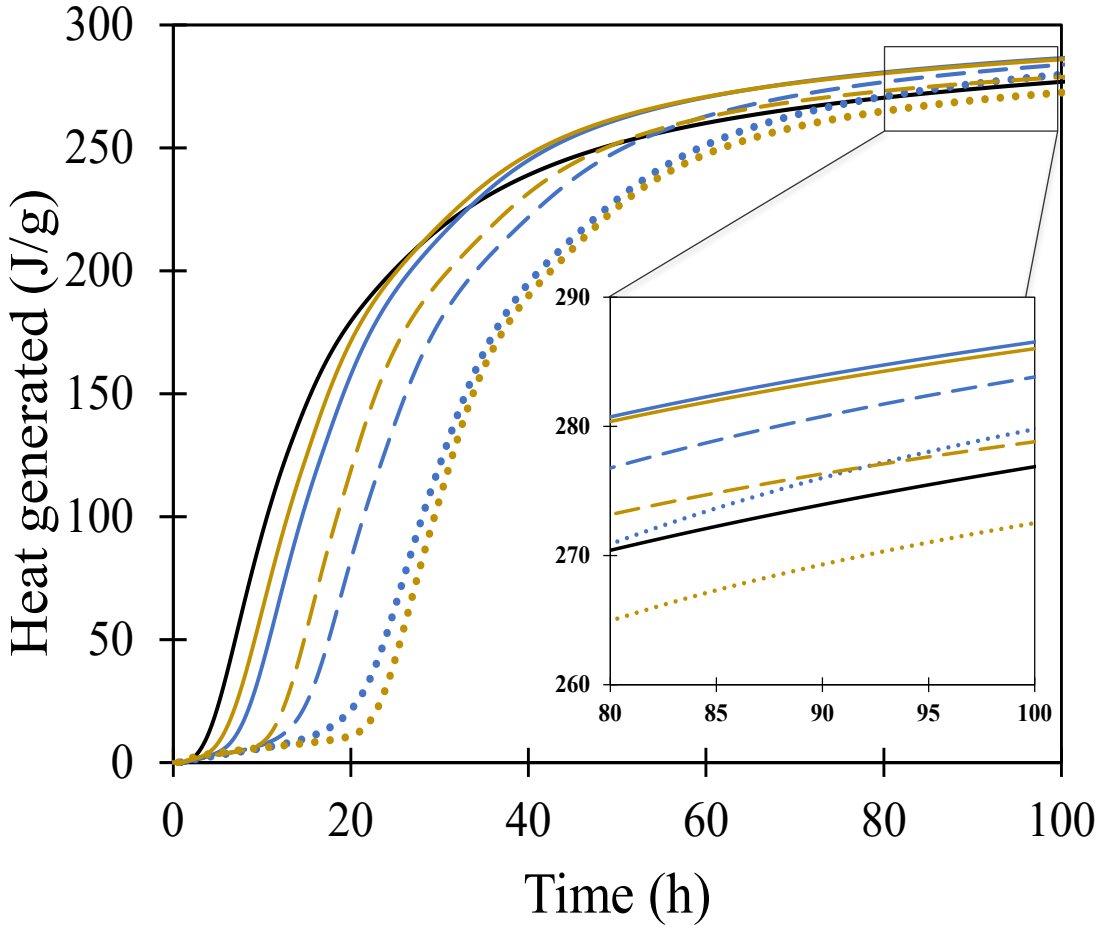




- Satisfactory performance of LigWRA and ComWRA admixtures is achieved at a dosage of 0.5 wt.%.
- However, the mechanisms associated with the failure/limit of the printing process are completely different.

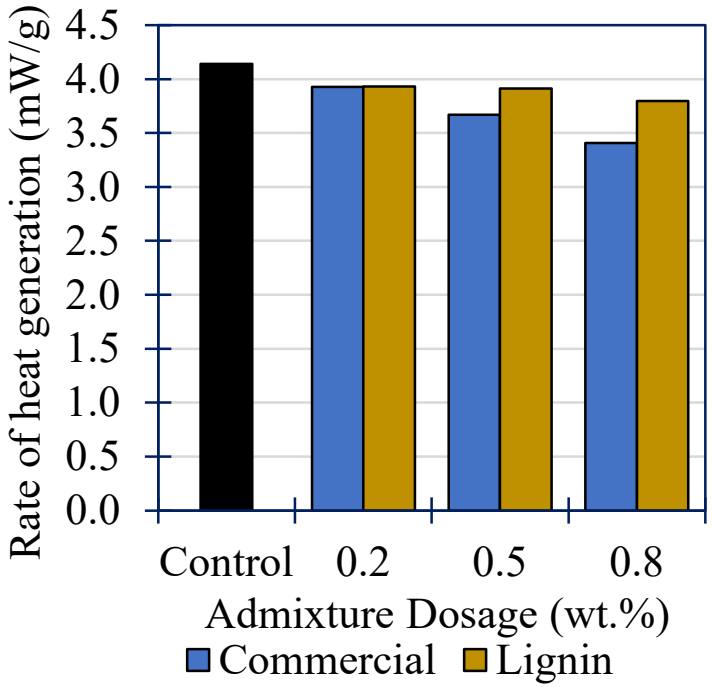
Isothermal Calorimetry

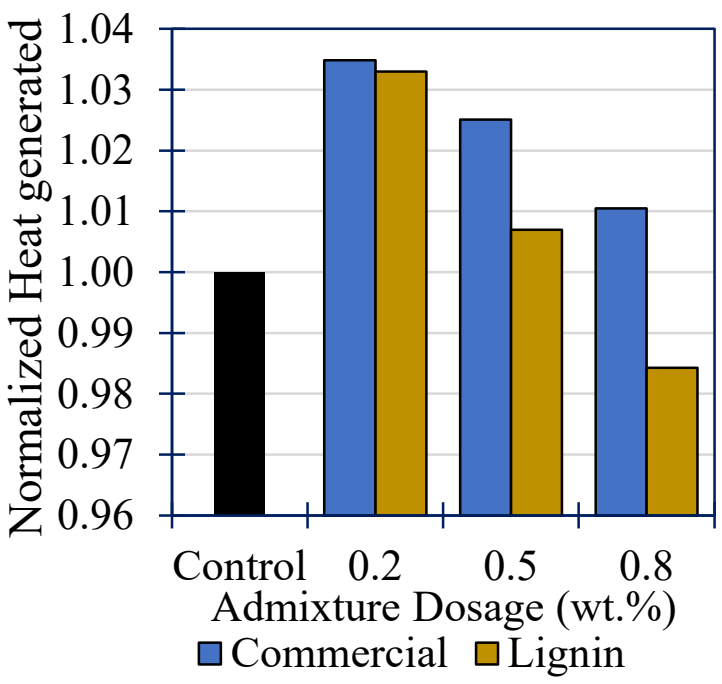


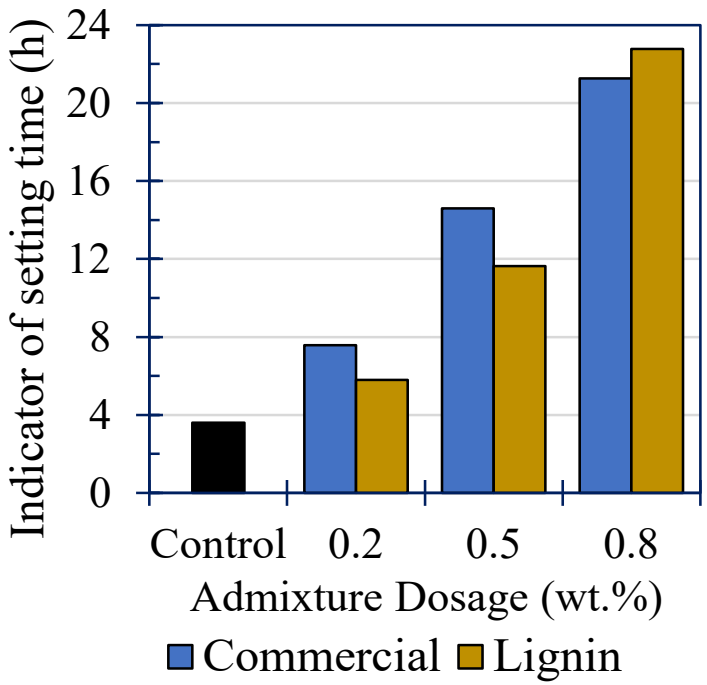


- Clear delay of the hydration process is observed with increase of admixture dosage.
- Still total heat generated is not significantly affected by the use of Commercial or Lignin-based admixture.

Setting time via Isothermal Calorimetry







- Peak of rate of heat generation is comparable between ComWRA and LigWRA for lower dosages.
- Total heat generated is not affected by the addition of lignin-based admixture.
- Increasing dosages of water-reducer admixtures cause a drastic delay in the setting time indicator.

Conclusions

- Preliminary characterization of a lignin-based water-reducing admixture derived from an industrial by-product has shown promising results for application in cement-based systems.
- The use of LigWRA at different dosages influences the rheological characteristics of cement pastes.
- Printability of mortar mixtures with the addition of LigWRA was performed to identify appropriate dosages to produce continuous and stable 3D-printed elements.
- While increasing dosages of LigWRA lower the yield stress and viscosity, it does affect the setting time of cement pastes by delaying the hydration process.
- Maximum rate and cumulative heat of hydration is not affected using LigWRA at different dosages.

Future Work

- Exploration of more direct and efficient approaches to produce lignin-admixture (e.g., ozonolysis) for enhanced carboxylate content and structural characteristics.
- Further characterization of LigWRA according to ASTM C494 (Chemical Admixtures for Concrete)
- Approaches to limit the delay of setting time at appropriate dosages.
- Determination of the effect of LigWRA on the mechanical performance of mortar mixtures.
- Further evaluation of rheological performance including the effects on structural built-up and oscillatory time sweep.
- Assessment of compatibility of LigWRA with other admixtures for concrete such as VMAs and AEAs.

Thank You

www.nrel.gov

NREL/PR-5500-90322

This work was authored by the National Renewable Energy Laboratory (NREL), operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. This work was supported by the Laboratory Directed Research and Development (LDRD) Program at NREL. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.