CLEMSON UNIVERSITY

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Lignin Fractionation and Valorization: Focusing on both Value and Quality

March 10, 2021 3:50pm

Biochemical Conversion and Lignin Utilization Session

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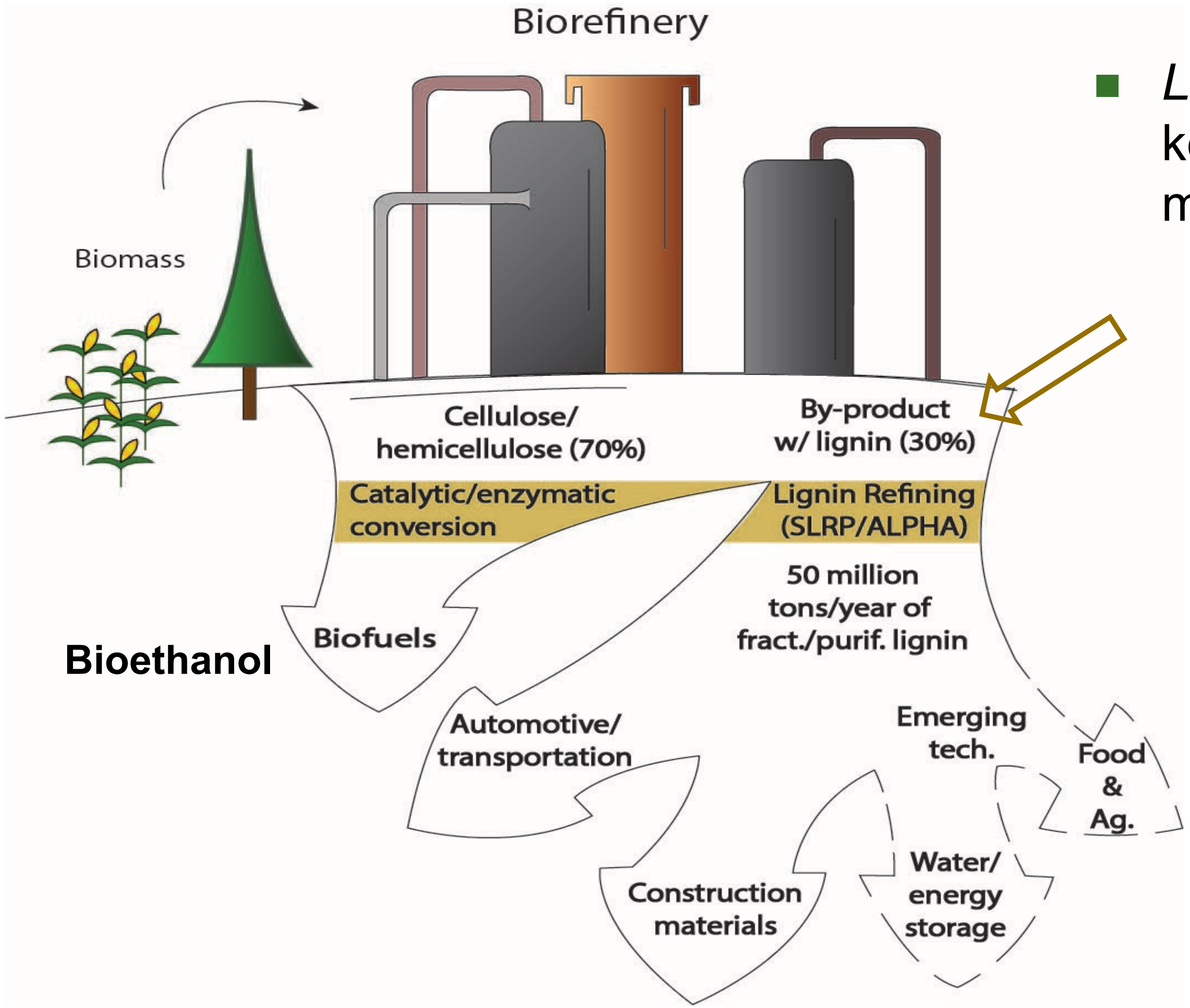
CLEMSON CHEMICAL AND BIOMOLECULAR ENGINEERING

MONTANA STATE UNIVERSITY

MICHIGAN STATE UNIVERSITY

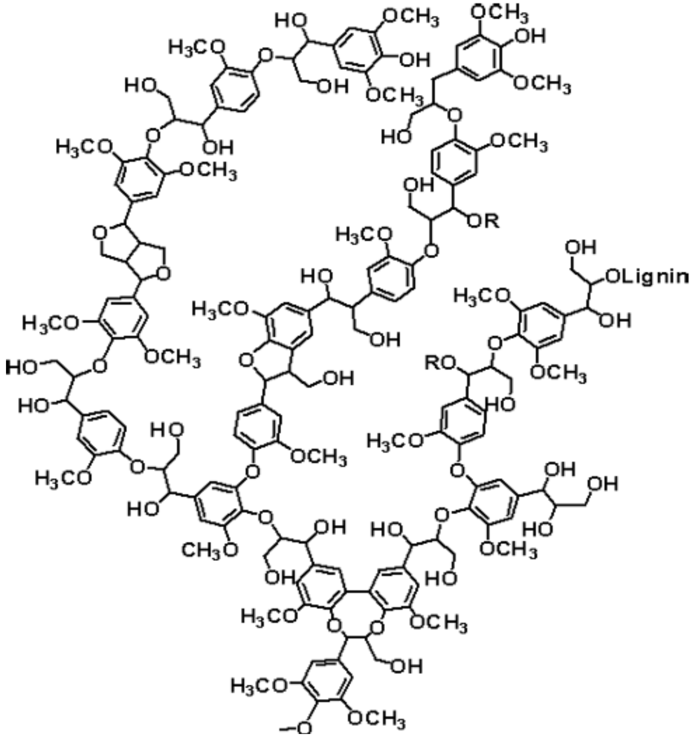
Michigan Tech

The lignocellulosic biorefinery

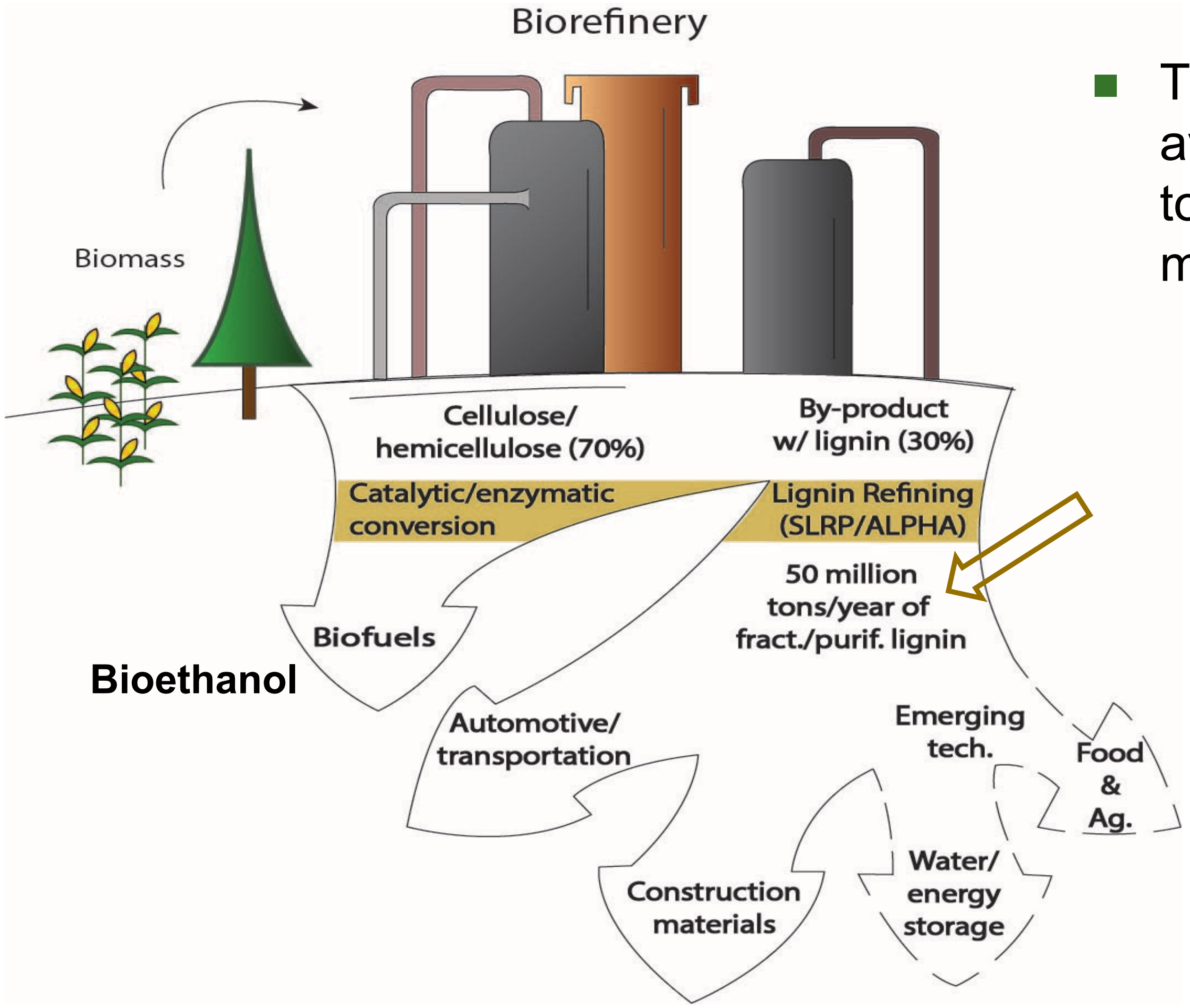


Bioethanol

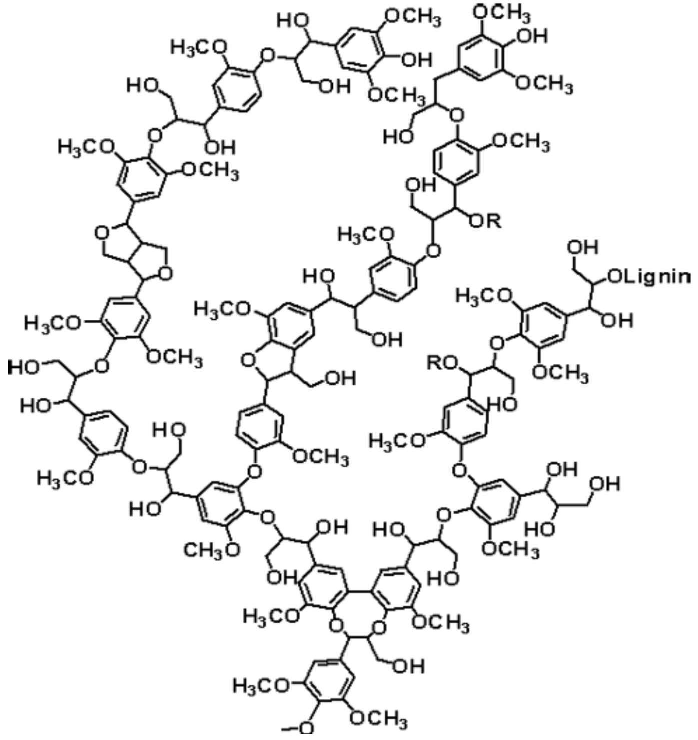
- *Lignin* (20-30% of plant/wood biomass is the key to a successful biorefinery that would make both biofuels and bioproducts



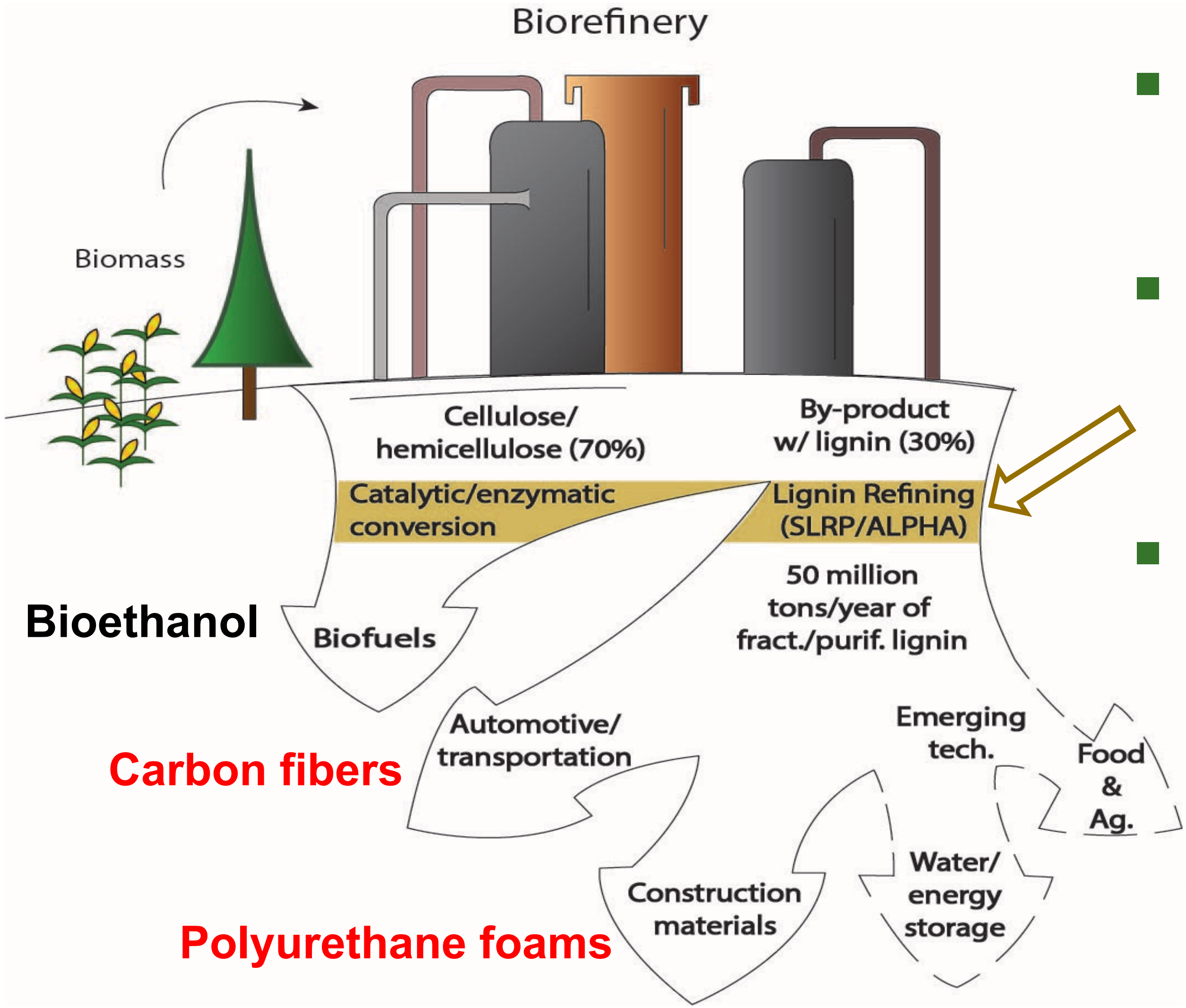
The lignocellulosic biorefinery today



- Today, however, only about 0.2% of the lignin available from lignocellulosics (~50 MM tons/yr) is recovered for nonfuel applications; most is just burned



The lignocellulosic biorefinery: our vision



Bioethanol

Carbon fibers

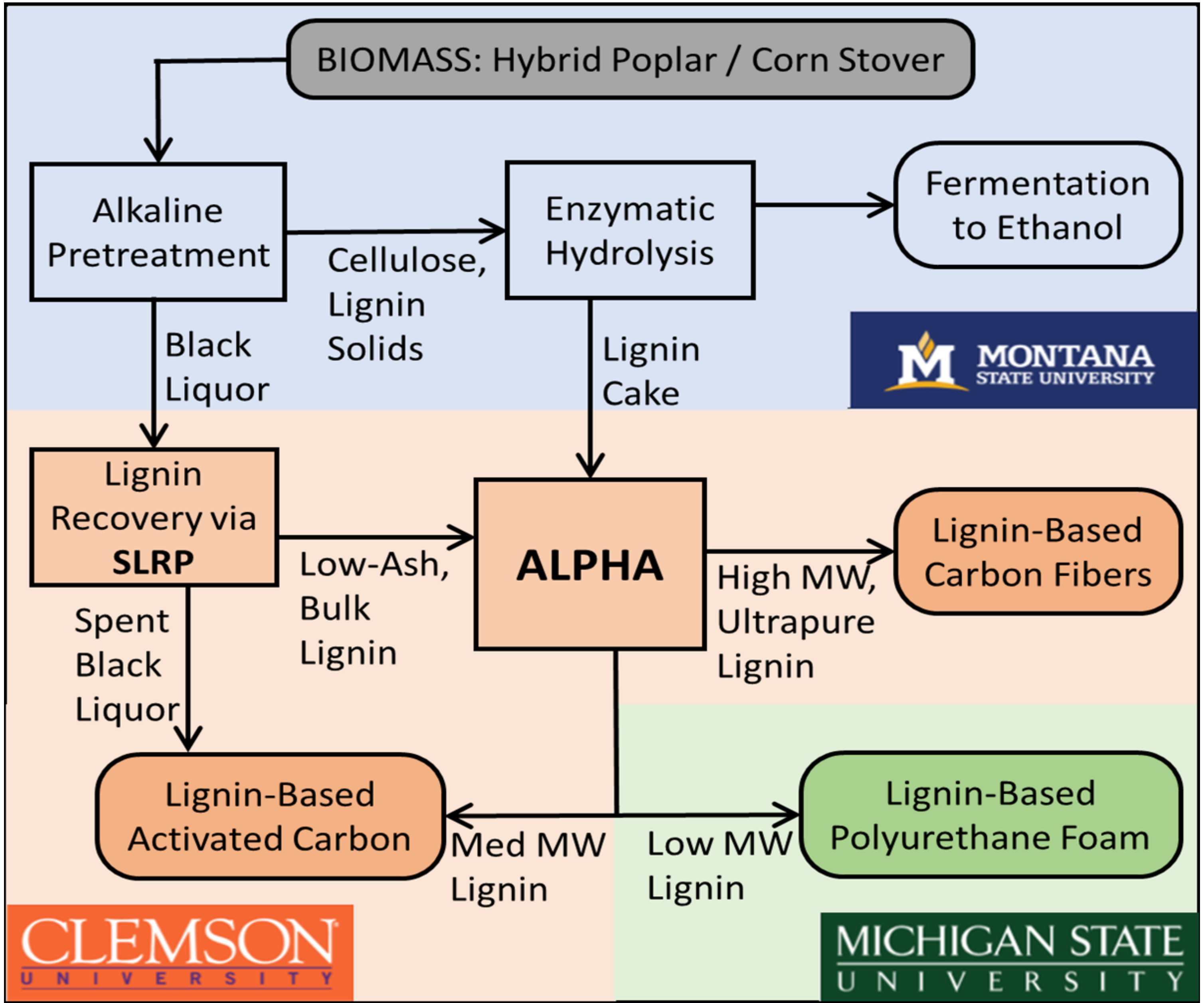
Polyurethane foams

Activated carbon

- We propose the conversion of HP* and CS* lignin into the three, *higher-value, high-volume co-products identified in* **Red** *below*
- The ability to fractionate and clean lignin via the ALPHA process obviates the need for expensive chemical modification of lignin in order to obtain useful properties
- Experts predict that the nascent lignocellulosic ethanol industry will not survive without lignin-based co-products

**hybrid poplar* and *corn stover*

“Lignin flow” from Biomass to Bio-Products



- *Montana State U*: from biomass to raw bulk HP/CS lignin
- *Clemson U*: from raw bulk lignin to ALPHA (A-) lignin of controlled purity, molecular wt
- *Clemson:* from *higher* molecular wt (MW), ultraclean A-lignin to carbon fibers
- *Michigan State U:* from *lower* MW A-lignin to PU foams
- *Clemson:* from lower or higher MW A-lignin to activated carbon (AC)
- *Michigan Tech U:* Continuous assessment of process changes thru TEA/LCA

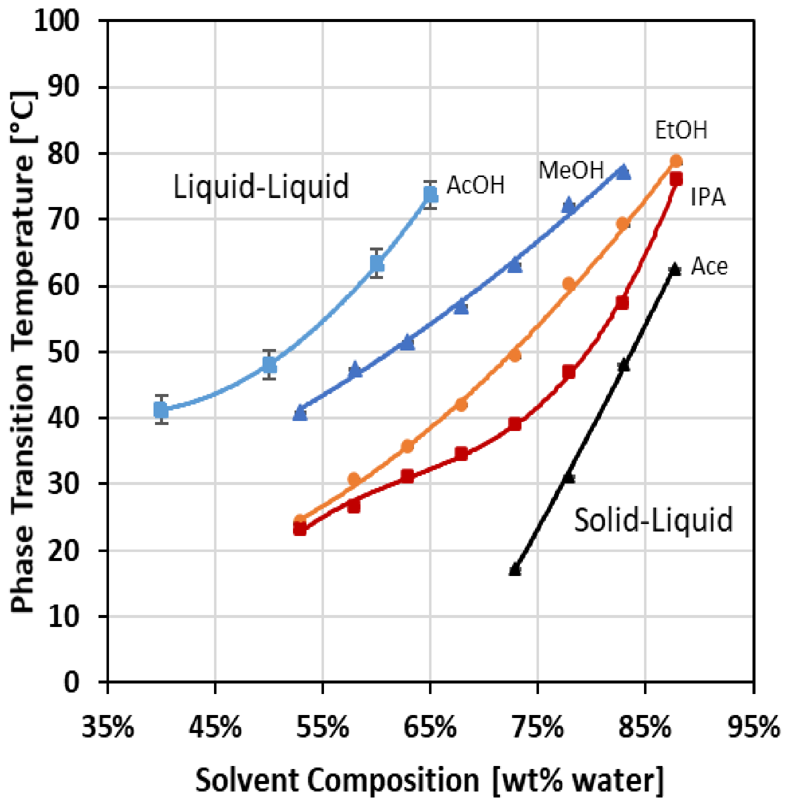
Risk Mitigation Strategies

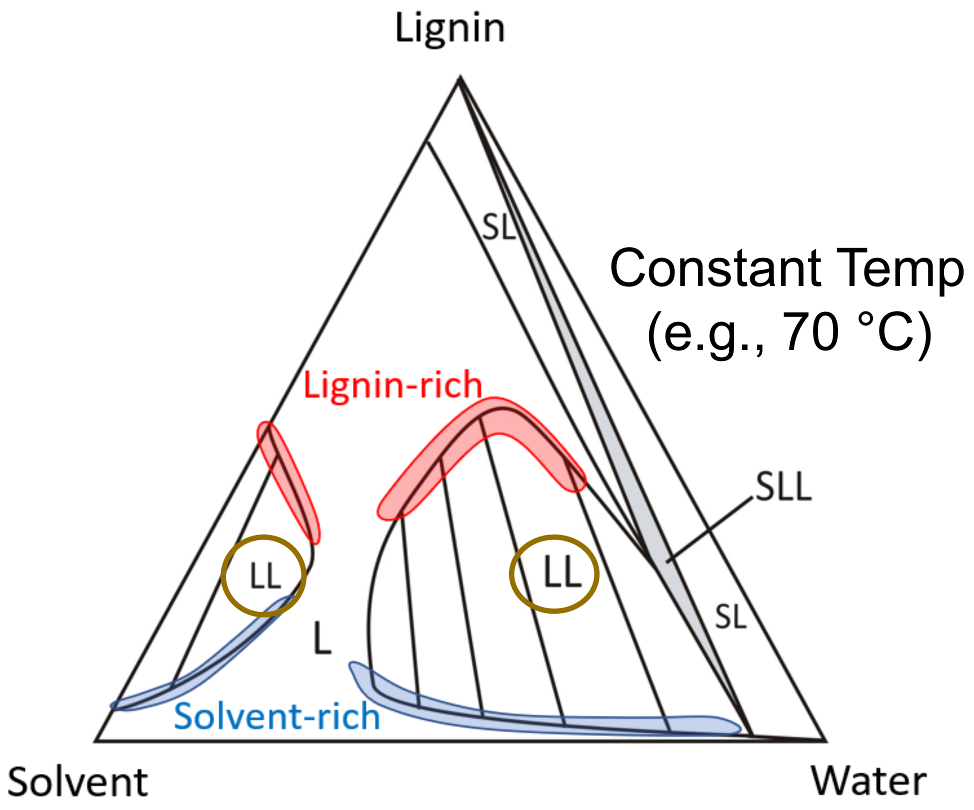
1. The three proposed applications for lignin prefer complementary fractions of the lignin, mitigating the risk of not using most of the lignin.
2. Properties of the lignin fractions (e.g., molecular wt (MW), purity) appropriate for each application overlap to some extent, mitigating the risk posed by one less-than-successful application.
3. A range of aqueous renewable solvents can be used as ALPHA solvents, including acetic acid, ethanol, isopropanol, methanol, and acetone.
4. Lignins from both hybrid poplar and corn stover are being evaluated, as well as from both the alkaline liquor and "cake" portions of these lignins.

Communication with Potential Stakeholders

- *Clemson*: (1) ongoing collaboration with Liquid Lignin Company, inventor and developer of the SLRP process for recovering lignin from alkaline (a.k.a. black) liquor; (2) ongoing collaboration with carbon-fiber manufacturers, in particular Cytek.
- *Michigan State:* ongoing collaboration with Huntsman, one of the largest manufacturers of PU foams in the U.S.

The Enabling Liquid–Liquid Phase Behavior for ALPHA[1]





Constant Temp (e.g., 70 °C)

- Previous work has shown that “ultraclean” lignins of controlled mol wt can be obtained by processing lignin in the liquid–liquid equilibrium region located above the phase-transition boundary
- Depending on the application, either LL region can be used to generate lignin fractions with the requisite properties for materials applications

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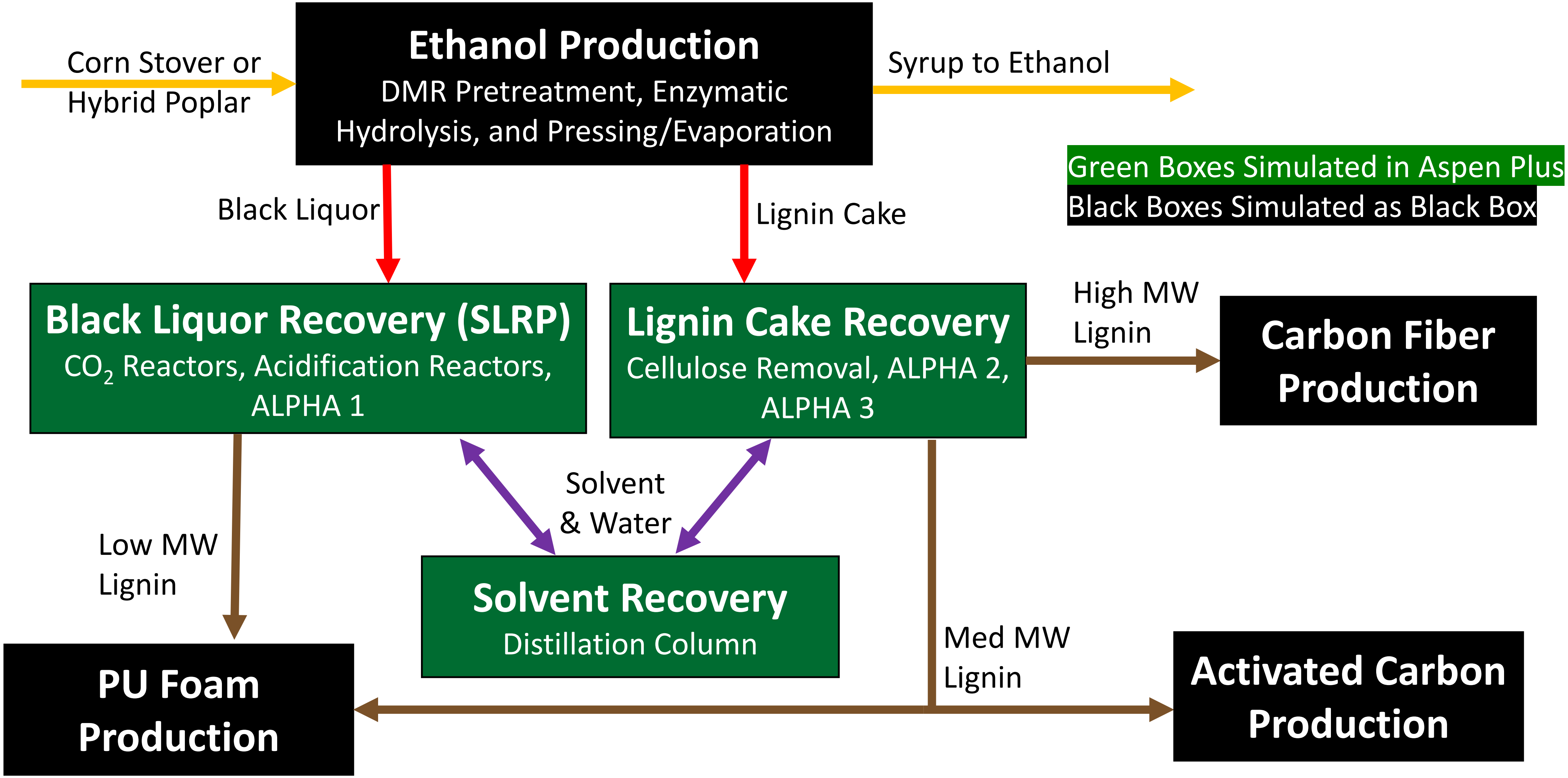
1. Thies et al. Solvent and recovery process for lignin. U.S. Patent 10,053,482; Aug 21, 2018.

Base-Case Process Flowsheet (Aspen Plus)



Corn Stover or Hybrid Poplar

Ethanol Production
DMR Pretreatment, Enzymatic Hydrolysis, and Pressing/Evaporation

Syrup to Ethanol

Green Boxes Simulated in Aspen Plus
Black Boxes Simulated as Black Box

Black Liquor

Lignin Cake

Black Liquor Recovery (SLRP)
CO_2 Reactors, Acidification Reactors, ALPHA 1

Lignin Cake Recovery
Cellulose Removal, ALPHA 2, ALPHA 3

High MW Lignin

Carbon Fiber Production

Solvent & Water

Low MW Lignin

Solvent Recovery
Distillation Column

Med MW Lignin

PU Foam Production

Activated Carbon Production

Key Challenges + Go/No-Go Decision Point

- Challenge 1: Generate the atypical properties in ALPHA lignins (e.g., in MW and metals content) that will produce the desired performance in our proposed bio-products.
- Challenge 2: For a given lignin source, determine the relationship between ALPHA processing conditions (e.g., temperature and solvent/water composition) and lignin properties, such as those delineated above.
- Go/No-Go Decision Point: Lignins with polydispersities (PDIs) <5.0, and containing <0.10% ash and <20% organic impurities, will be generated via ALPHA from hybrid poplar and/or corn stover. *This Go/No-Go was met at project midpoint of Oct 1, 2020.*
- *Q: Why is this Go/No-Go of critical import to the project?* *A:* High PDIs mean poor MW control in ALPHA lignins, high metals create flaws in CFs and consume catalyst in PU foams, organic impurities clog spinnerette during lignin fiber spinning.

Market for CFs, PU Foams, AC from ALPHA Lignins

3 – Impact

- Carbon Fibers: PAN precursor for CFs costs ~$10/lb. TEA-calculated selling cost for ALPHA lignin is dramatically lower, so huge potential if CF properties can be met. Market of 200k tons/yr by 2025 is highly price-sensitive, so would grow significantly if CF could start to compete with glass fibers.

- PU Foams: 4 MM tons/yr, so huge market. Rigid PU foams is focus. 30% of recipe for foams is the much more expensive polyols, so high substitution rates (e.g., 75%) would use almost 1 MM tons lignin/yr.

- Activated Carbon: 3 MM tons/yr. ALPHA produces very high purity AC and reduces/eliminates the conventional acid-washing step. High purity AC opens up food, beverage, medical markets, giving them competitive advantage over conventional AC.

Dissemination of Results

3 – Impact

- Patents. Thies et al. Solvent and recovery process for lignin. U.S. Patent 10,053,482; Aug 21, 2018. Other patent disclosures are in progress.
- Relevant Collaborations. Liquid Lignin Company (combining SLRP and ALPHA processes); Huntsman Corp. (PU foams); wood pulp mills; Cytek (carbon fibers).
- Presentations/seminars/communications. Limited in scope; with international paper companies.
- Special Publications. Invitation "to contribute to a Special Issue of *ChemSusChem* (IF = 7.35) on the topic of *Lignin Valorization: From Theory to Practice*". This and other publications listed at end of talk.

Ultraclean, higher MW A-Lignins for Carbon Fibers -1

- Initial fiber-spinning runs of bulk HP lignin suggested that insoluble species were clogging the spinnerette die (i.e., unstable spinning with multiple breakages)
- So we processed the lignin via ALPHA (Fig. 1). Fig. 2 illustrates our discovery: at high EtOH/H_2O ratios, the metal salts (e.g., Na) concentrate in the "dirty", lignin-rich (LR) phase in the 1st step of ALPHA.
- Thus, we isolate a clean, spinnable lignin in the solvent-rich (SR) phase
- In the 2nd step of ALPHA, at low EtOH/H_2O ratios an ultraclean, spinnable lignin is recovered in the LR phase

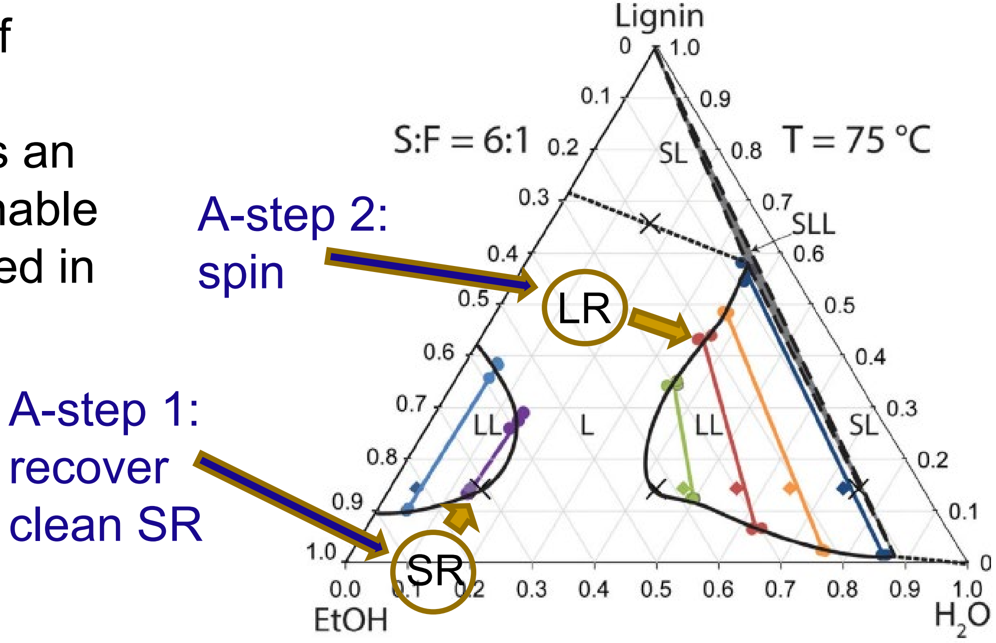


Fig. 1. Quasi-ternary phase diagram for lignin–ethanol–water.

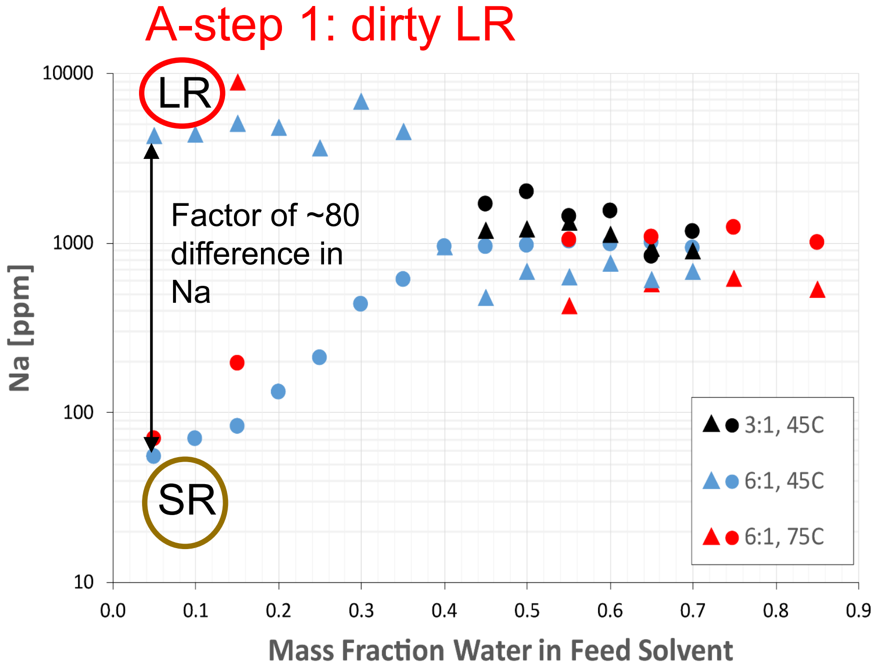


Fig. 2. Metal salts (e.g., Na) are removed in the 1st A-step.

Ultraclean, higher MW A-Lignins for Carbon Fibers - 2

- Lignin fibers were solution-spun from EtOH/H_2O solutions of A-step 2:

(a) Outstanding draw-down ratio (DDR) of 8;

(b) Stable spinning for ~30 min: 5 g of lignin fibers;

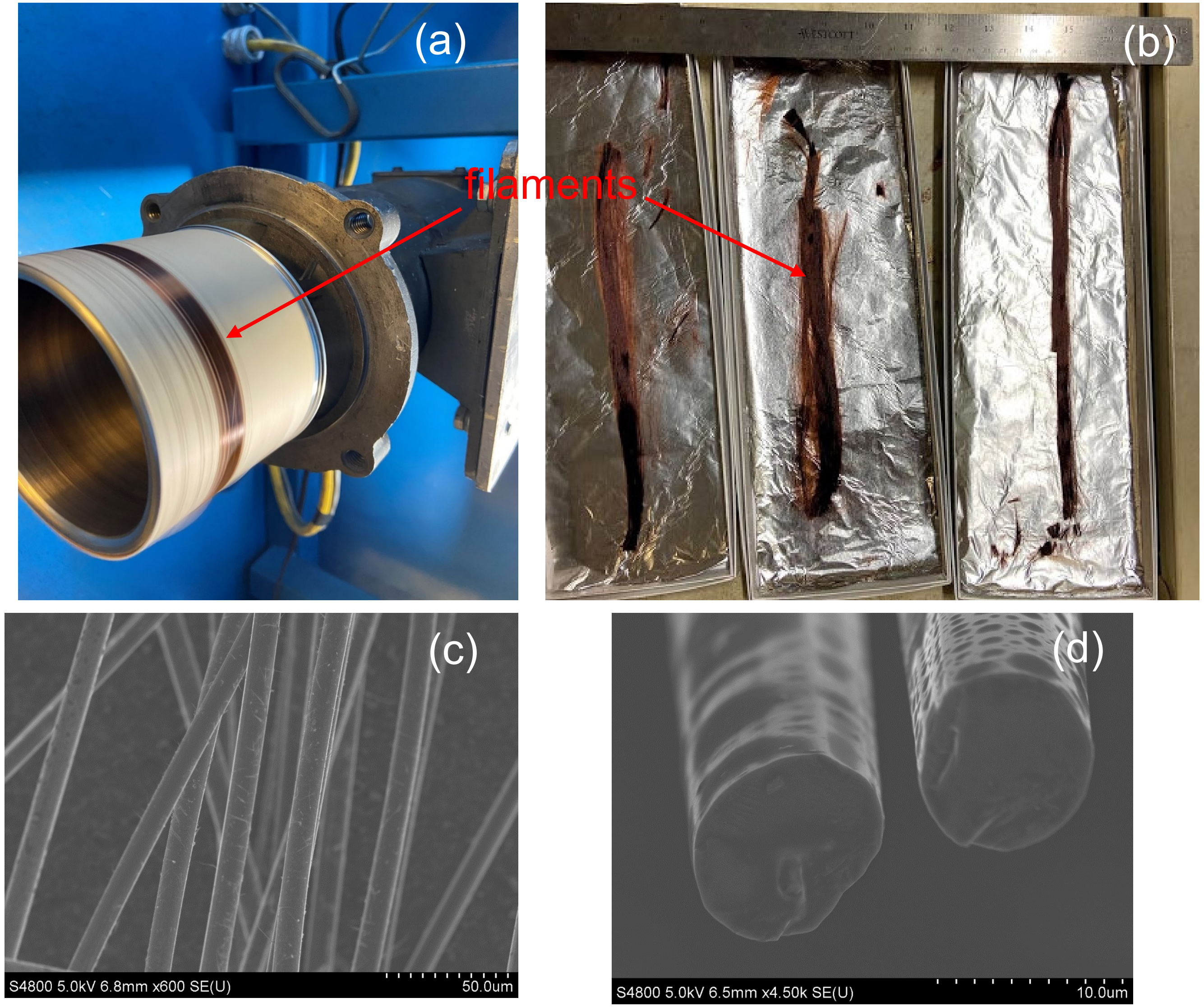
(c) 19±1 µm dia. lignin fibers;

(d) 10±0.5 µm dia. carbon fibers.

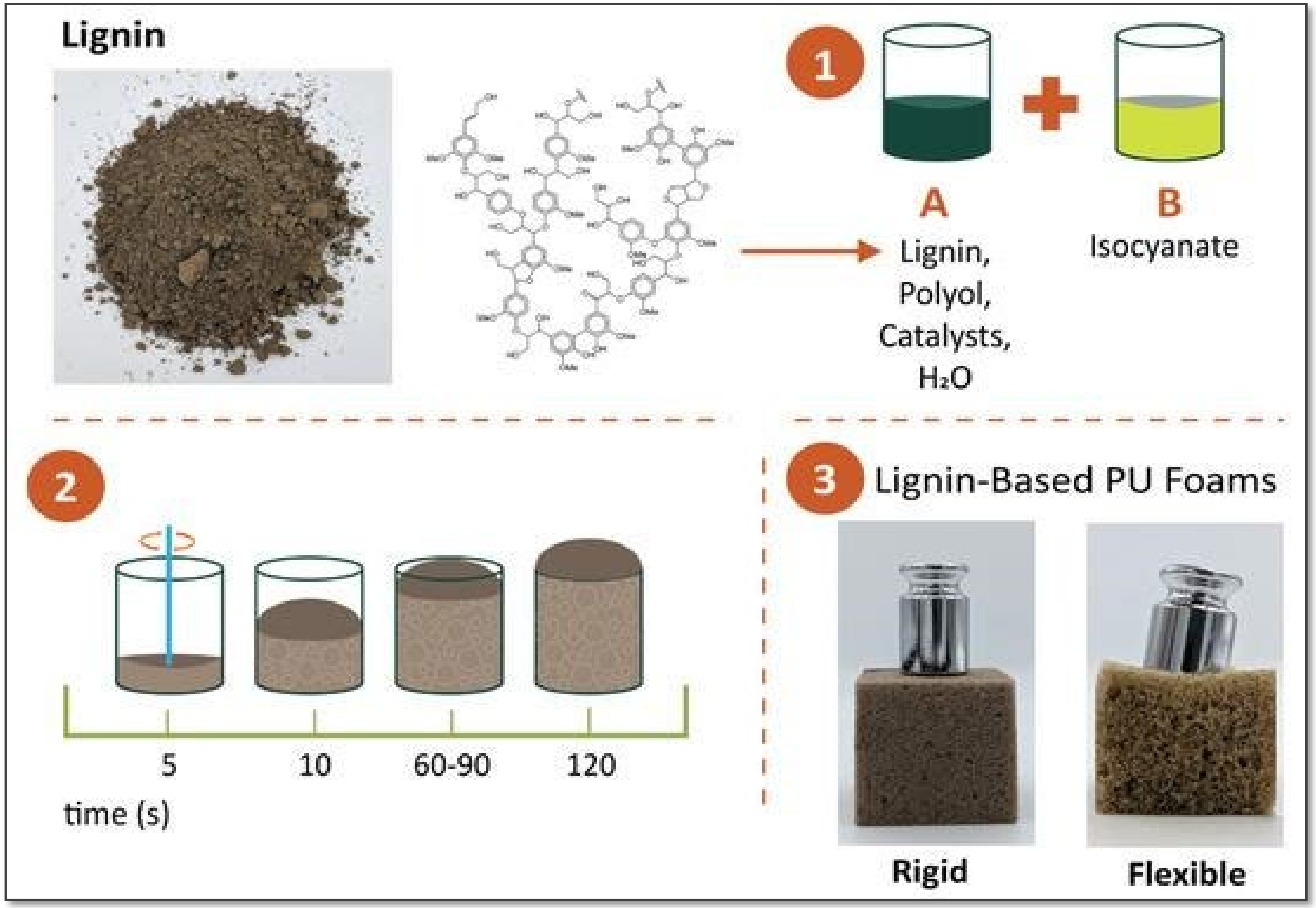
Tensile Strength and Modulus

Pre-cursor	Mw	PDI	Ten Strg (MPa)	Ten Mod (GPa)
Bulk HP lignin	7600	2.9	270	35
A-Lignin	11100	4.4	580	50

- *M18, M27 milestones (>500 MPa, 30 GPa; DDR = 6) were met*



Lower MW A-Lignins for PU Foams -1



- Polyols constitute 30% of the "recipe" for making PU foams
- Lignin as a substitute for the polyols:
  - Lower MW lignins should have higher OH content
  - Effect of lower MW A-lignin on other properties?

Why lignin? It improves the

- Flame retardant
- Microbial resistance
- Antioxidant

properties of the PU foam.

And last but not least – it's cheap.

Lower-MW A-Lignins for PU Foams - 2

- ALPHA processing of the bulk lignin, whether from Kraft softwood or hybrid poplar (HP), resulted in a significant lowering of the MW and PDI, and a significant increase in the hydroxyl content of the resultant A-lignin

Lignin ID	S (%)	Ca (%)	Na (%)	Mn (Da)	Mw (Da)	PDI	OH Content
Bio-K-SW	1.98	0.01	0.33	1830	6440	3.5	4.78
A-Bio-K-SW	1.59	0.01	**0.04**	**790**	**1450**	**1.8**	**7.27**
Bulk HP	0.27	0.034	0.33	1700	10200	6	5.02
A-HP	0.21	0.04	0.33	**1150**	**2160**	**1.9**	**6.14**

K=Kraft; SW=Softwood; Bio=Biochoice;
HP=Hybrid Poplar; A=ALPHA

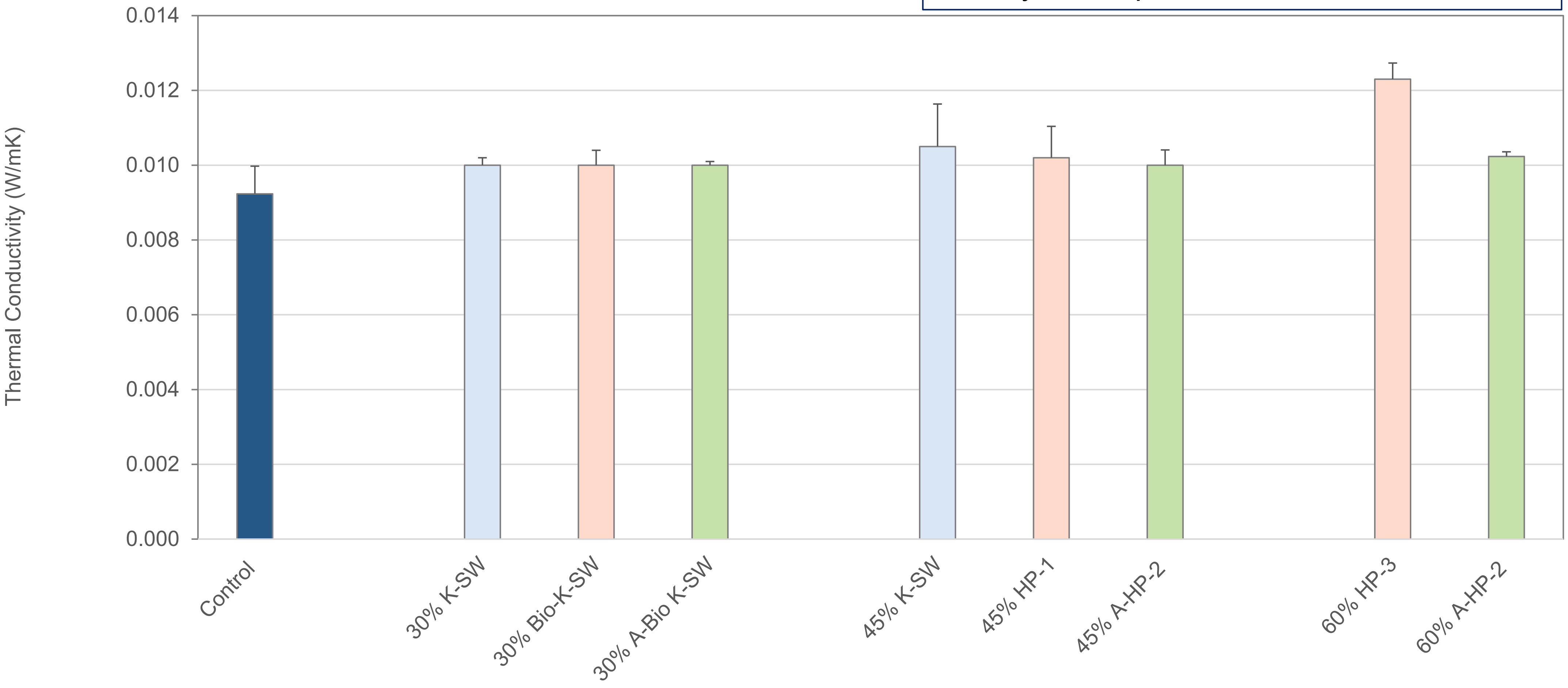
- The effect of A-lignin substitution for polyols on key PU foam properties is shown in the next series of slides →

Lower-MW A-Lignins for PU Foams - 3

- The effect of A-lignin substitution for polyols on key PU foam properties is shown in the next three slides
- 60% substitution of HP lignin for polyols was achieved, with the A-lignin improving several key foam properties.
- *M24 milestone (60% substitution) was met.*
- Compression strength decreased – but ASTM standards were still met

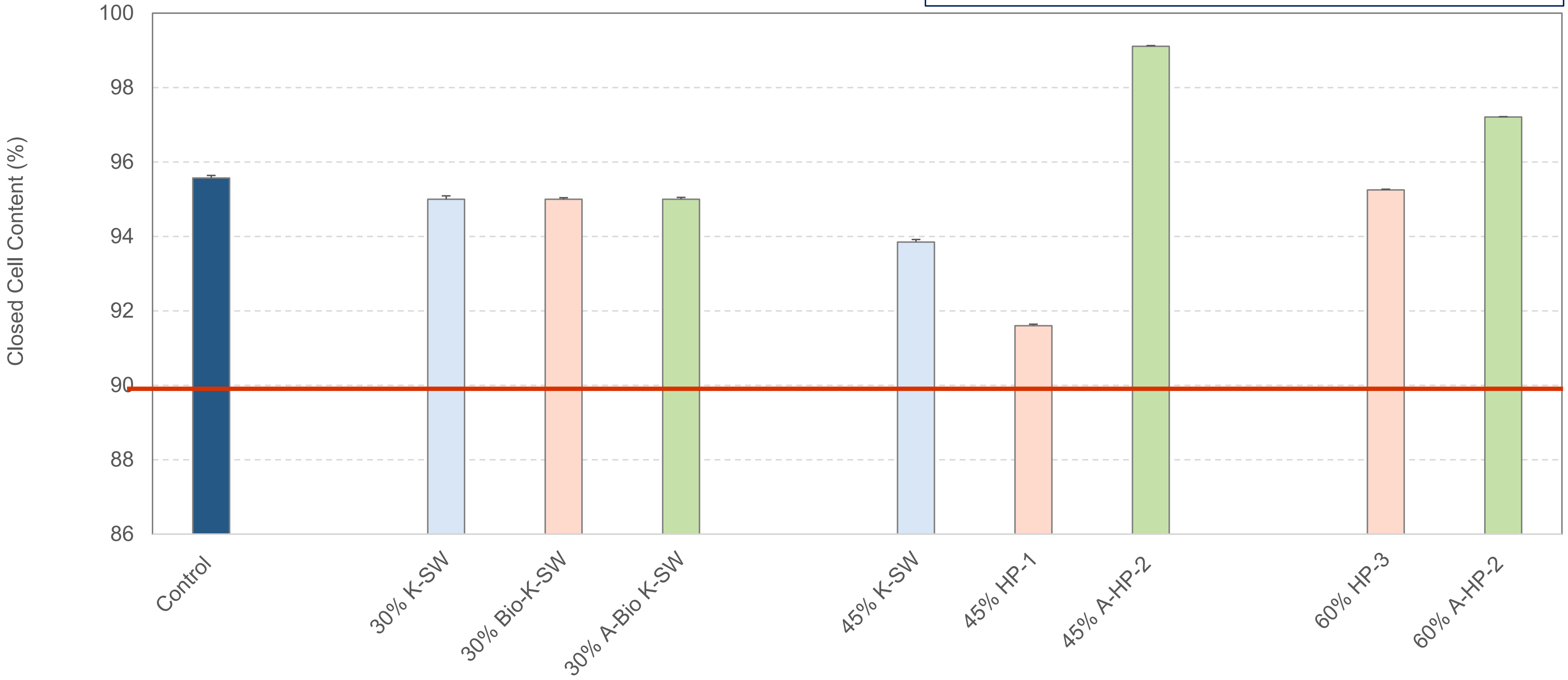
Thermal Conductivity (<0.257) ⬇

K=Kraft; SW=Softwood; Bio=Biochoice;
HP=Hybrid Poplar; A=ALPHA



Closed Cell Content (>90%)

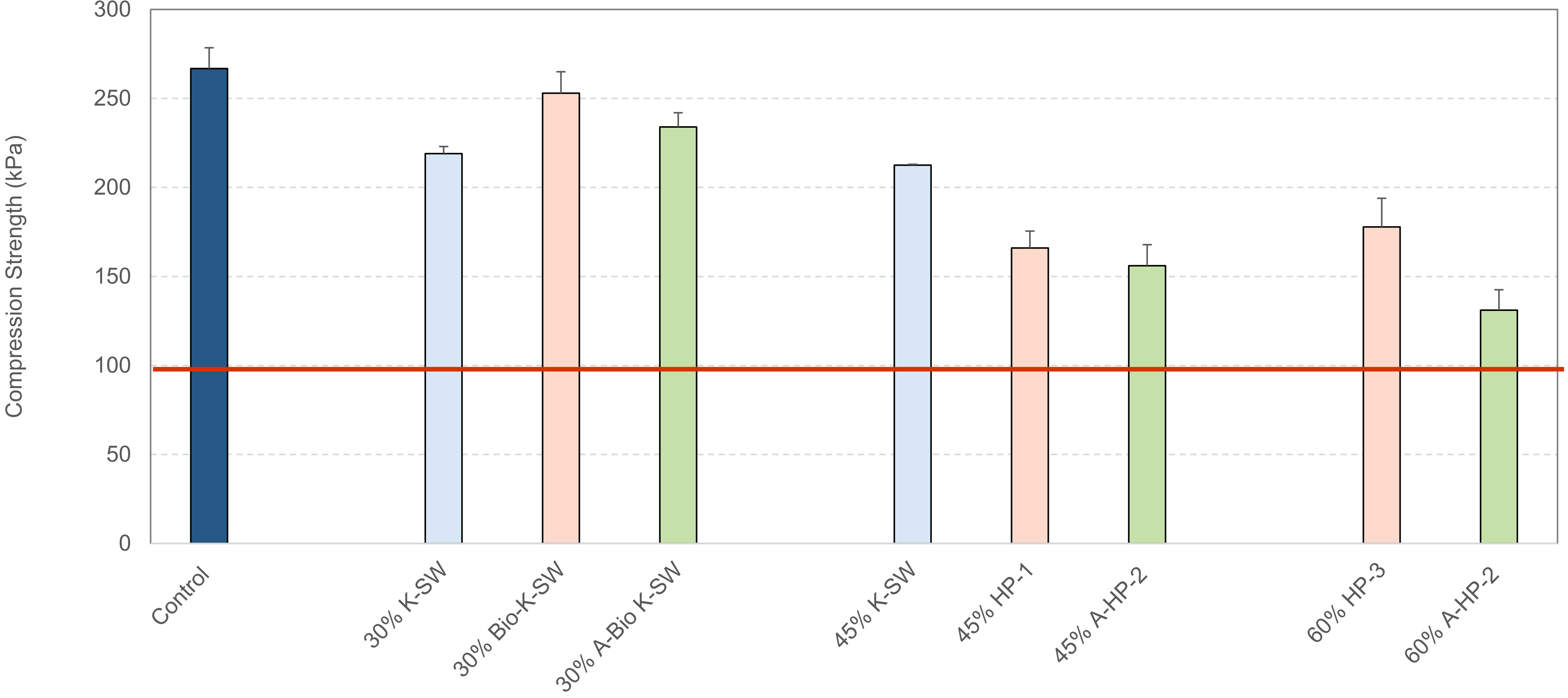
K=Kraft; SW=Softwood; Bio=Biochoice;
HP=Hybrid Poplar; A=ALPHA



Compression Strength (>104KPa)

(But still meeting ASTM standard)

K=Kraft; SW=Softwood; Bio=Biochoice;
HP=Hybrid Poplar; A=ALPHA



Activated Carbon (AC) from A-Lignins -1

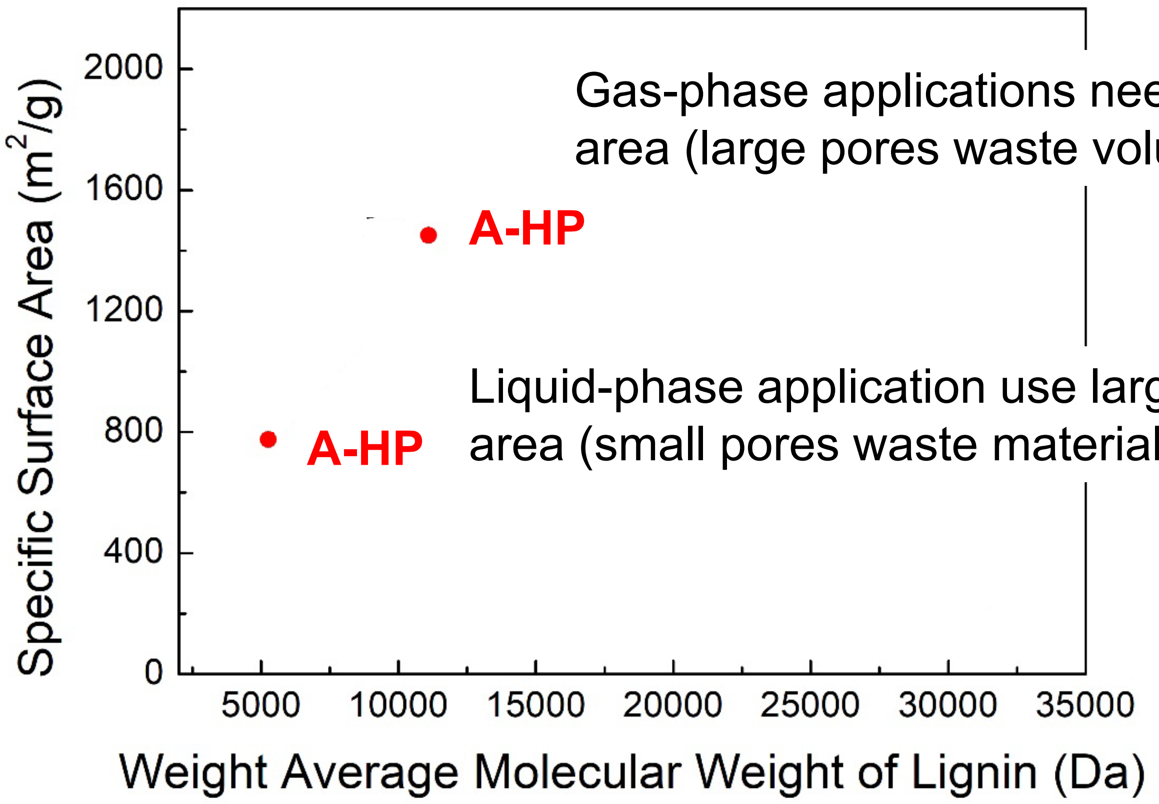
AC can be synthesized from any biomass source; the source determines the AC properties (e.g., *surface area, pore size, purity)*

- Conditions traditionally used to tailor AC properties:
  - Biomass source
  - Pretreatment washing
  - Activation agent (e.g., $ZnCl_2$)
  - Activation concentrations
  - Carbonization temperature (ramp, hold)

- Hypothesis: ALPHA lignin properties can be tailored → AC properties can be tailored.
- ALPHA lignin is a refined biomass having controlled molecular functionality; this should result in an AC with controllable and more uniform properties

Activated Carbon (AC) from A-Lignins -2

- ALPHA processing was used to control the surface area of the AC through MW control of the parent A-HP lignins. A doubling of the MW almost doubled the surface area of the AC product.

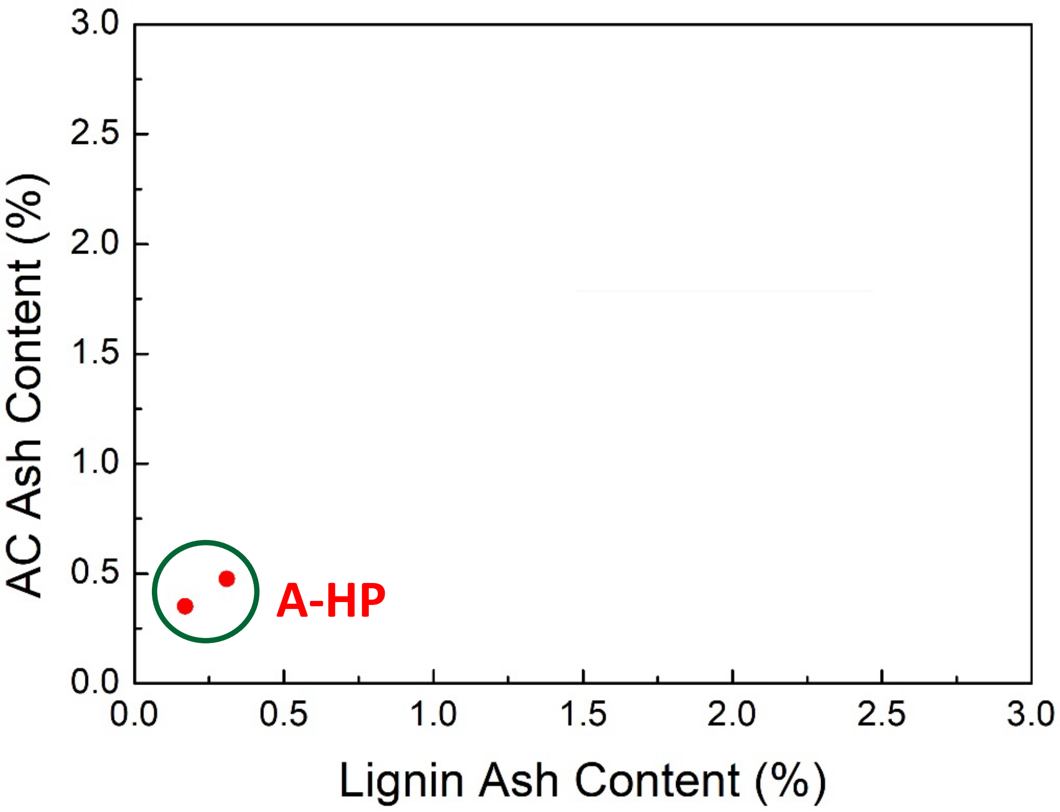


Gas-phase applications need smaller pores / high surface area (large pores waste volume)

Liquid-phase application use large pores / low surface area (small pores waste material)

Activated Carbon (AC) from A-Lignins -3

- Higher purity (e.g., low ash, metals content) feed (ALPHA lignin) leads to higher purity AC (e.g., low ash, metals content).
- ALPHA brings ash levels down to the levels required for specialty, high-purity ACs.



- Our experience indicates that ALPHA is a highly efficient method for cleaning lignins before conversion to ACs, using far less water than traditional acid-washing techniques
- *1st M27 milestone met: <0.5% ash and >1200 m^2/g surface area*
- *2nd M27 milestone met: 60% of bulk HP lignin converted to on-spec AC; 80% of lignin carbon converted to AC.*

Summary for Higher-Value Bioproducts from ALPHA Lignins

1. We propose the conversion of hybrid poplar (HP) and/or corn stover (CS) lignins into three higher-value bio-products, namely carbon fiber, PU foam, and activated carbon (AC). The metric target of >50% conversion of lignin carbon to bio-products (ref: DE-FOA-0001916, Topic Area 6 Lignin Valorization, page 14) has been met, with an overall >60% conversion at project midpoint.
2. The team led by Clemson, including Montana State, Michigan State, and Michigan Tech, starts with raw biomass (wood chips/corn stover) and finishes by producing the three final bio-products.
3. ALPHA (A)-HP lignins of high purity and mol wt with excellent spinnability were converted into carbon fibers <20 µm in dia. Additional, significant property (e.g., strength) increases with lignin MW are expected.
4. A-HP lignins have reached the 60% lignin-for-polyol substitution plateau in PU foams, while meeting all ASTM standards for rigid PU foams.
5. AC with very low ash (<0.5%) content and good surface area (almost 1500 m^2/g) have been generated from A-HP lignins, creating new product opportunities.
6. TEA analysis indicates a highly competitive $0.21/lb cost for ALPHA lignin when EtOH is used as the ALPHA solvent and $0.38/lb for Acetic Acid. GHG savings of 24% for polyol–lignin substitution.

Quad Chart Overview

Timeline

- 10/1/2018
- 3/31/2022

	FY20 Costed	Total Award
DOE Funding	$564,252	$1,795,216
Project Cost Share	$121,496	$448,804

Project Partners*

- Liquid Lignin Company (formerly Lignin Enterprises, LLC)

Project Goal

Exploit the novel liquid–liquid phase equilibrium that exists between lignin and aqueous renewable solvents to fractionate and clean crude bulk lignins for conversion to high-value bioproducts, including carbon fibers, PU foams, and activated carbon.

Include a concise, clear project goal statement (examples in notes section)

End of Project Milestone

>50% of the lignin carbon contained in the lignin-rich process feedstock streams being fed to co-product generation will be converted to co-products, thus meeting the Topic Area 6 metric for DE-FOA-0001916.

Funding Mechanism

DE-FOA-0001916, Topic Area 6 (Lignin Valorization), proposals due 6/27/2018.

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments - 1

Verbatim Highlights from Go/No-Go Review of 1 Oct 2020 (PI additions in parentheses)

- Key Observations and Recommendations:
  - **Carbon Fiber:** Lignin-derived CF with a tensile strength of 0.6 ± 0.1 GPa relative to the intermediate target value of 0.5…were demonstrated. (Ca vs. Na) was an important project learning that can be applied in the future…for the lignin fraction feeding the CF process.
  - **Polyurethane Foam:** The demonstrated 60 wt% lignin replacement of petroleum-based polyol met the intermediate (no, M24) target value of 60 wt%. Equivalent or improved foam properties relative to the control foam made with 100% petroleum-based polyol were demonstrated. It was also noted that…sodium metal acts as a catalyst for polyisocyanurate production…(and can)…improve the PU thermal properties…Thus, the lignin fraction feeding the PU process could serve as a process sink…for sodium metal coming from the biomass feedstock.
  - **Activated Carbon:** The estimated AC surface area of 1,451 m^2/g…met and exceeded the intermediate target value of 1,000 m^2/g. Additionally, the project team demonstrated the ability to tune AC pore size and ash content by controlling the physical characteristics of the lignin fraction fed to the AC process.
  - **Carbon Utilization:** Calculated carbon utilization for the overall process increased from 59.6% at the initial verification to > 60% at the intermediate verification. Both cases met and exceeded the FOA metric target of > 50%.
- Additional Observations:
  - Supply chain disruptions resulting from quarantine created a delay in acquiring the equipment needed to generate the required quantities of pretreated biomass to feed the other task areas in the project. However, through resourcefulness and innovation, the project team was able to generate sufficient quantities of high, medium, and low molecular weight lignin fractions to demonstrate intermediate performance metrics…

Responses to Previous Reviewers' Comments - 2

Verbatim Highlights from Go/No-Go Review – Key Observations and Recommendations (cont'd)

– The project team identified producing sufficient quantities of pretreated biomass to feed the tasks for the three end products (CF, PU, and AC) as a bottleneck during budget period 2. Options such as acquiring more student workers, increasing equipment capacity, etc. were discussed during the verification to help address this bottleneck during the next budget period.

– Achieving the target of <300 ppm total metals in lignin fractions produced from hybrid poplar proved to be one of the most technically challenging aspects of the project during budget period 2. However, the project team increased their knowledge around which specific metals (e.g. sodium) need to be controlled for achieving end product performance targets, particularly for the CF product. In particular, the project team was able to meet intermediate CF performance targets despite much higher levels of total metals (especially calcium) in hybrid poplar lignin than observed in softwood Kraft lignin...

– The verification team recommended performing more market research around AC pricing as a function of AC characteristics to better understand the potential value proposition of AC produced by the envisioned commercial process. Commercial partners could…help guide project research.

– The verification team recommended updating the process model by the final verification as more process details (especially around product recovery and purification) are established to make the process model more representative of the envisioned commercial facility. Lignin yield was identified as a specific parameter that should be further investigated…since it was identified as the primary cost driver in the sensitivity analysis around lignin processing costs. …lignin yield values reported in the NREL design cases may be more aspirational than the experimental yield values demonstrated to date in this project.

Publications, Patents, Presentations, Awards, and Commercialization

1. Thies et al. Solvent and recovery process for lignin. U.S. Patent 10,053,482; Aug 21, 2018.
2. Kulas, D. G.; Thies, M. C.; Shonnard, D. R. Techno-Economic Analysis and Life Cycle Assessment of Waste Lignin Fractionation and Valorization using the ALPHA Process, submitted to *Green Chemistry,* Jan 2021.
3. Tindall, G. W.; Temples, S. C.; Becsy-Jakab, V. E.; Hodge, D. B.; Thies, M. C. Melting Lignins to Form a Processable, Polymer-Rich Phase in the Presence of Aqueous Renewable Solvents, submitted to *Chem Commun.,* Feb 2021.
4. Tindall, G. W.; Becsy-Jakab, V. E.; Hodge, D. B.; Thies, M. C. Ultraclean, ALPHA-processed Hybrid Poplar Lignins for Carbon Fibers, submitted to *Green Chem., Feb 2021.*
5. Henry, C.; Nejad, M. Evaluating Suitability of a Wide Range of Technical Lignins for Partial Polyol Replacement in the Formulation of Low-Density Rigid Polyurethane/Polyisocyanurate Foam, submitted to *Molecules,* Feb 2021.
6. Patent disclosure to Clemson University, Feb 2021.
7. Tindall, G. W.; Chong, J.; Miyasato, E.; Thies, M. C. Fractionating and Purifying Softwood Kraft Lignin with Aqueous Renewable Solvents: Liquid–Liquid Equilibrium for the Lignin–Ethanol–Water System. *ChemSusChem* **2020,** *13,* 1-9.
8. Design and construction of mini-pilot Sequential Liquid Lignin Recovery and Purification (SLRP) unit in collaboration with Liquid Lignin Company. Unit completion slated for mid-summer. To be used for both research support and for commercial trials.