DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

DE-FOA-0001433: MEGABIO: Bioproducts to Enable Biofuels

Alkaline-Oxidative Pretreatment of Woody Biomass for Optimal Co-Product Production

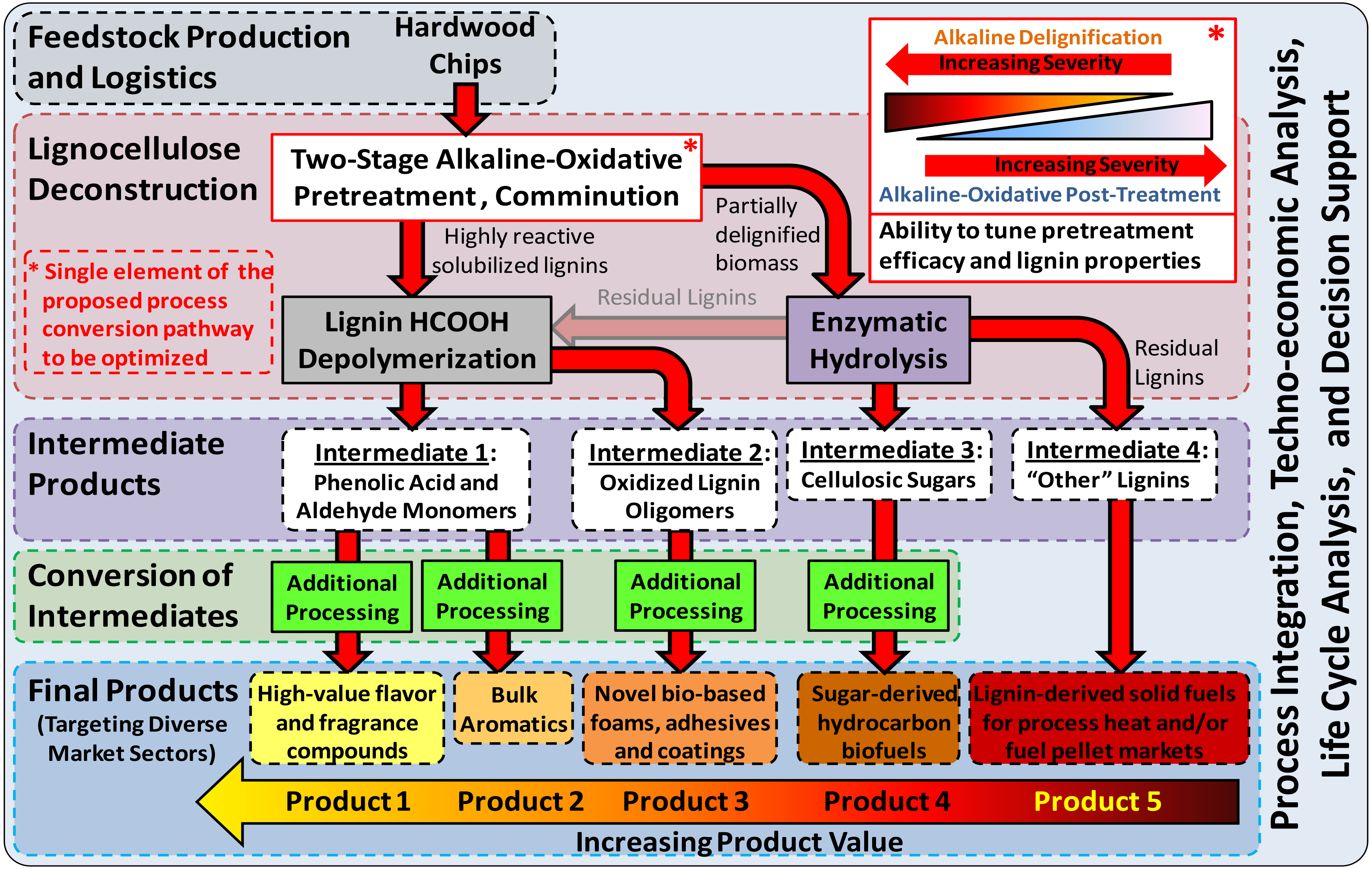
Wednesday, March 10, 2021
Biochemical Conversion and Lignin Utilization

Eric L. Hegg
Michigan State University

Project Overview – Goals and Significance

- **Project Goal:** Optimize our two-stage alkaline-oxidative Cu-AHP pretreatment process to generate from woody biomass both a clean sugar stream for the production of hydrocarbon fuels and lignins that can feed multiple product streams and enable the economic viability of our integrated system.
- **Significance:** Current commercial processes for lignin depolymerization achieve monomer yields of <15%. Our current two-stage alkaline-oxidative Cu-AHP pretreatment process produces a lignin stream that is highly susceptible to depolymerization while simultaneously providing a clean, high-yield sugar stream. Combining the two independent units into an optimized, integrated process could enable the economic viability of a biofuels and bioproducts industry.

Project Overview – Graphical Summary



Project Overview – Background

Copper-Catalyzed Alkaline Hydrogen Peroxide (Cu-AHP) Pretreatment

Raw Biomass

Stage 1
Alkaline Extraction → **(30 °C)**

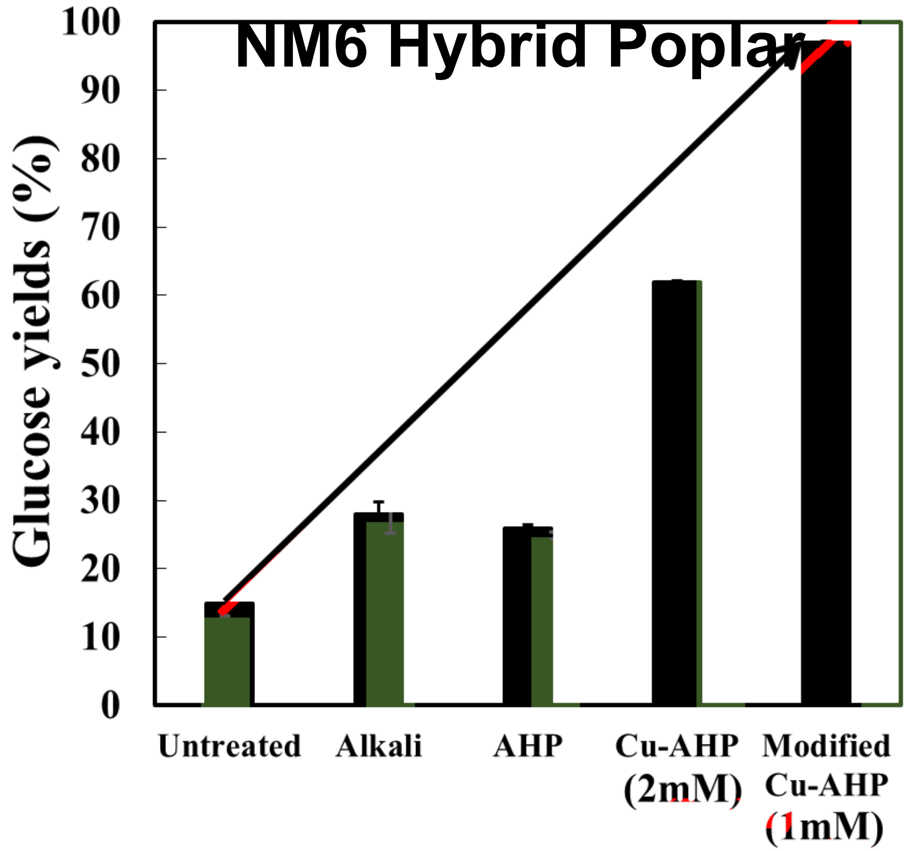
Extracted Biomass

Stage 2
1. NaOH
2. Cu(bpy)
3. H_2O_2

→ **(30 °C)**

Cu-AHP Biomass

Benchmark Cu-AHP process

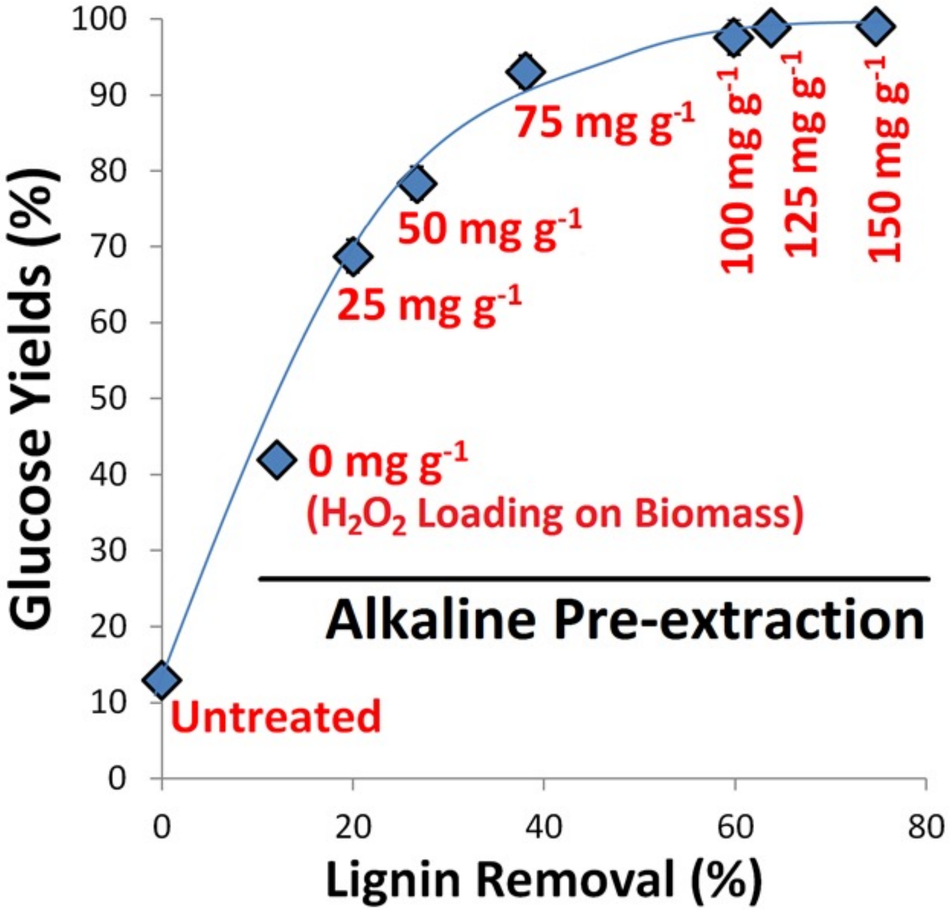


- *Biotechnol. Biofuels* **2013**, *6*, e119
- *Biotechnol. Bioeng.* **2013**, *110*, 1078-1086

Cu-AHP is promising, but the process economics needs to be improved

Project Overview – Background

Cu-AHP releases a significant fraction of the lignin



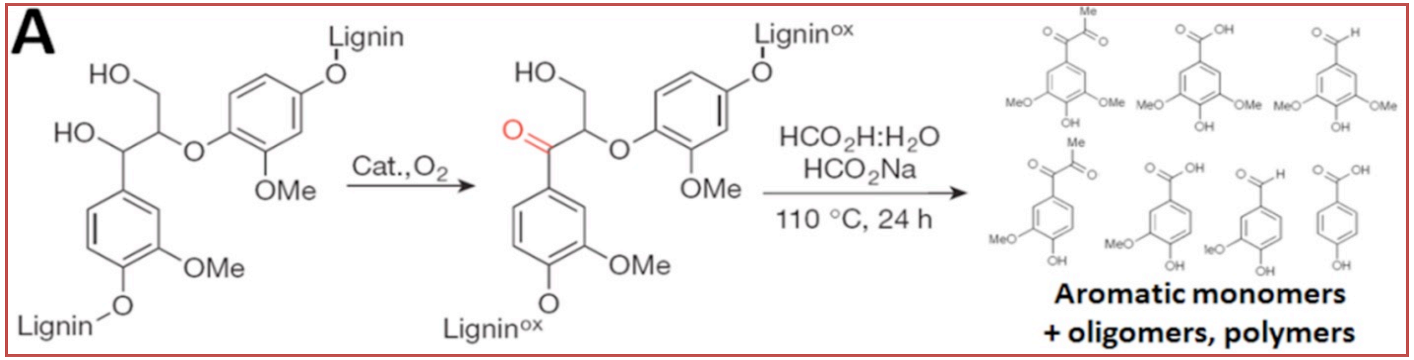
Recovered Lignin

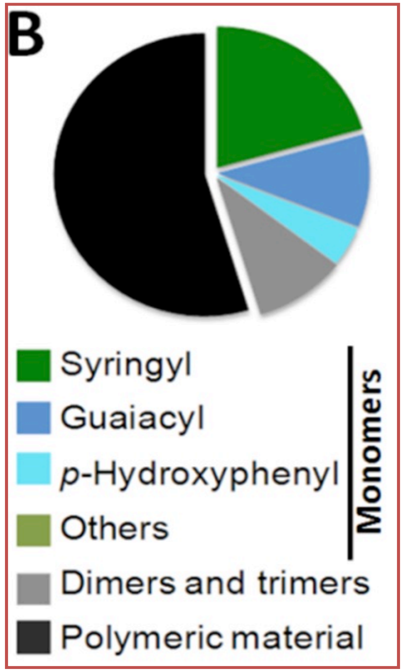
Biotechnol. Biofuels **2016**, *9*, e34

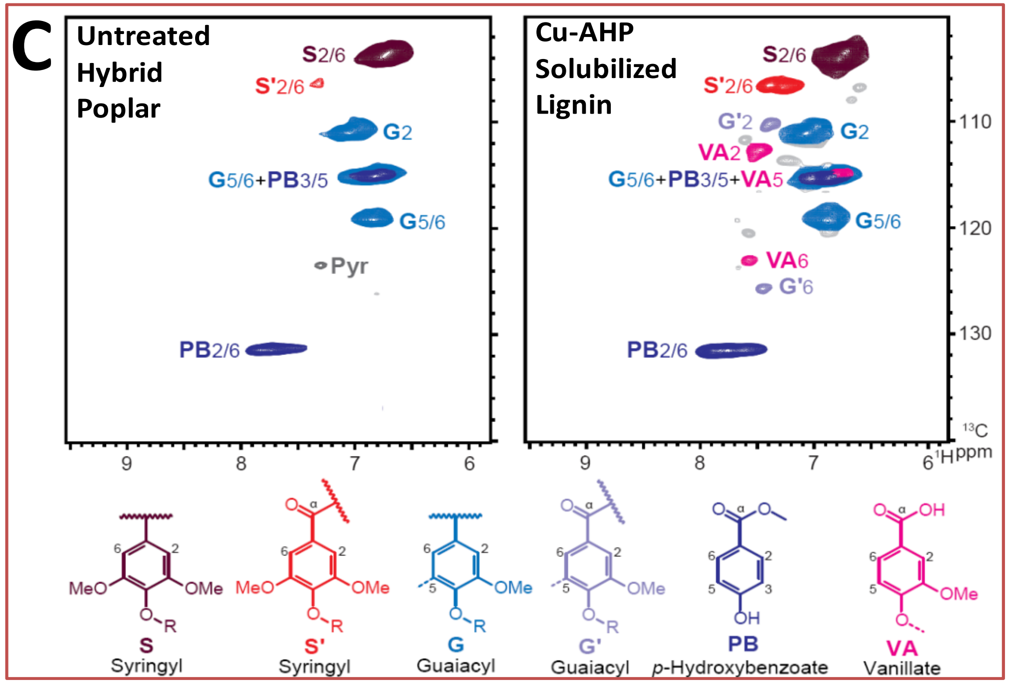
Recovered lignin can aid in the process economics

Project Overview – Background

Oxidation/Depolymerization Process







Nature **2014**, *515*, 249

Cu-AHP lignin is ideal for this depolymerization process

Project Overview – Key Results and Risks

- **Key Results:** (**1**) Identified pretreatment conditions that achieve >90% sugar yields while maintaining high-quality lignin. (**2**) Validated the scalability of our alkaline-oxidative pretreatment technology. (**3**) Developed new, scalable lignin depolymerization strategy and achieved ~30% monomer yields from isolated lignin. (**4**) Demonstrated applications of lignins in polyurethane applications. (**5**) Achieved 40% reduction in the minimum fuel selling price (MFSP) and demonstrated the economic viability of our two-stage Cu-AHP pretreatment process.

- **Risks:** (**1**) Reducing the reaction time to make the process more achievable at pilot- and industrial-scale. (**2**) Fully understanding the reaction mechanisms to further improve this technology. (**3**) Integrating the individual components into a single process.

1 – Management

Objective 1: Optimize and integrate the two-stage alkaline-oxidative deconstruction to yield hydrocarbon fuels and lignin co-products

Objective 2: Determine how pretreatment conditions impact lignin properties suitability for co-products

Objective 3: Apply TEA and LCA) to inform the experimental work and to determine the economic and environmental tradeoffs

Objective 4: Identify and implement strategies to decrease the minimum fuel selling price (MFSP)

Task 1: Initial Validation

Task 2: 1st Stage Alkaline Pretreatment

Task 3: 2nd Stage Alkaline-Oxidative Post-treatment

Task 4: Integration, Scale-Up, and Validation

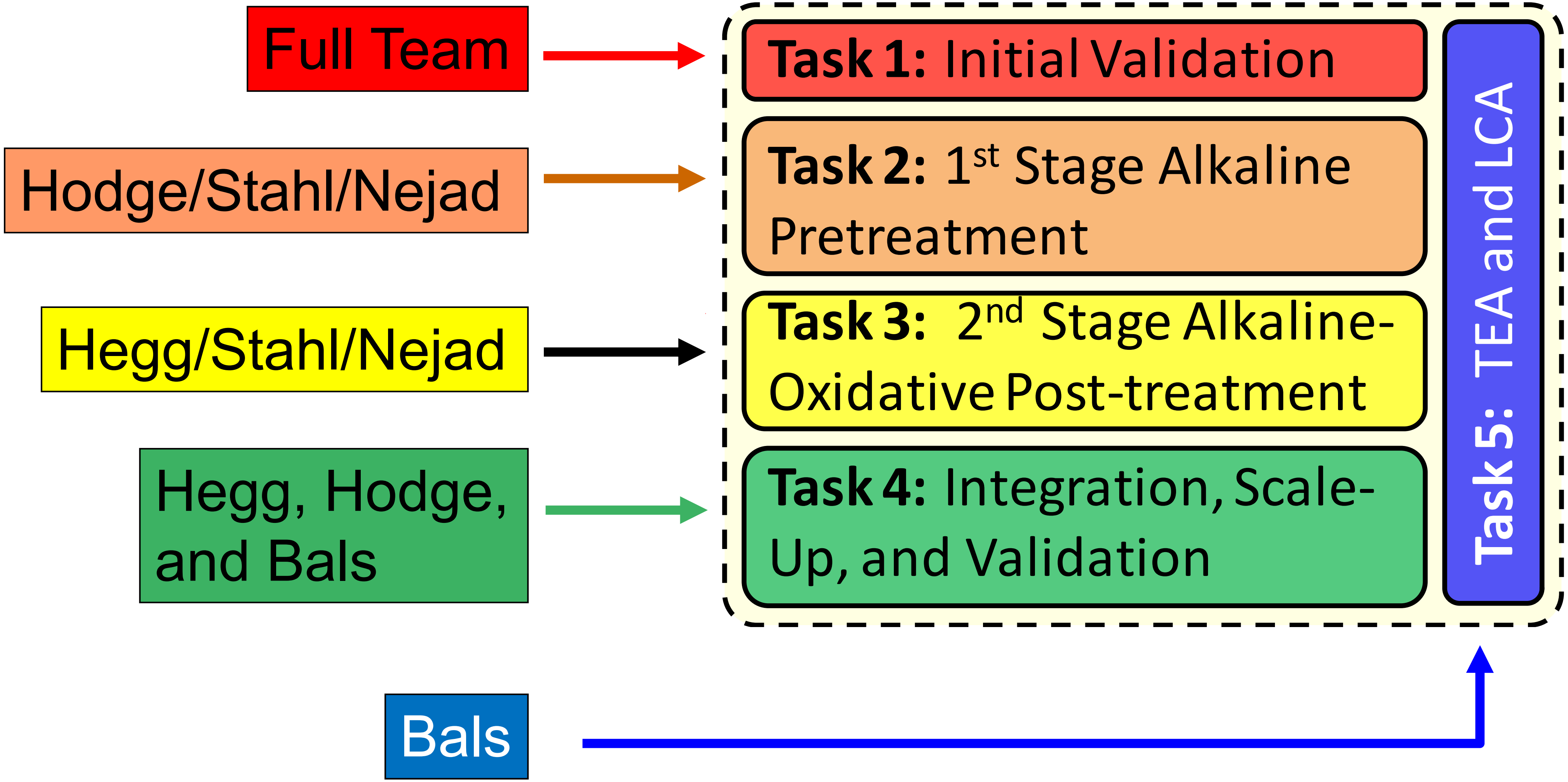
Task 5: TEA and LCA

Outcome 1: Identify conditions for pretreatment and co-product production to achieve target MFSP

Outcome 2: Integrate individual components of this process into an integrated technology package

Outcome 3: Identify and mitigate the risks associated with this strategy

1 – Management



- Multidisciplinary team has expertise in chemistry, catalysis, modeling, engineering, metallobiochemistry, lignin bioproducts, and de-risking.

1 – Management

- PI Eric Hegg coordinates administration, performance, and reporting.
- Co-PI David Hodge helps to manage project personnel and coordinate (1) re-focusing and (2) resource reallocation if needed.
- Monthly video conferences facilitate communication.
- Hegg meets other Co-PIs in person at least yearly.
- All Co-PIs are either actively collaborating with or have collaborated in the past with other team members.
- Project builds on previous DOE BER investments in fundamental research (DOE BER Office of Science DEFC02-07ER64494).
  - Patent application filed on the use of metal-ligand complexes during oxidative delignification (Cu-AHP) by PIs Hodge and Hegg.
  - Patent application filed on the lignin depolymerization by PI Stahl.

2 – Approach (Technical)

- Ascertain how reaction conditions for alkaline delignification pretreatment impact sugar yield, lignin yield, and the lignin properties
- Reveal how reaction conditions for catalytic alkaline-oxidative post-pretreatment impact sugar yield, lignin yield, and the lignin properties
- Correlate lignin properties with lignin valorization
- Provide economic and environmental feasibility through technoeconomic and life cycle analyses
- Test several “optimal” design cases based on balancing competing optima (technical, economic, environmental)
- Demonstrate performance of scaled-up process using optimized conditions.

2 – Approach (Technical and Non-Technical Challenges)

- Multiple PI locations.
  - Increased emphasis on communication.
- Lowering the MFSP by using both O_2 and H_2O_2 as co-oxidants during the alkaline-oxidative phase (thereby allowing us to lower chemical inputs while simultaneously increasing sugar yields) has led to a larger percentage of acid-soluble lignin.
  - Indicates that we have partially depolymerized the lignin during pretreatment.
  - The acid-soluble lignin with low molecular-weight might be a challenge for further depolymerization.
  - Acid-soluble lignin provides an opportunity for use directly in to polyurethane applications.
  - Improved separation strategies might needed for optimal recover the lignin fragments solubilized in acid.

2 – Approach (Go/No-Go Decision Points)

- Achieve ≥25% monomer yields from lignin precipitated from alkaline delignification stage (Q9)
  - *Completed. Recovered lignin was also used as feedstock for polyurethane coatings.*
- Achieve a ~25% reduction in the MFSP (Q9)
  - *Completed. A reduction of ~30% was achieved in Q10. In Q12, a reduction of ~40% of the MFSP relative to the base case was achieved.*
- Identify conditions that will achieve ≥30 wt% yield of depolymerized lignin and ≥80% yield of purified sugar without increasing MFSP (Q10)
  - *Completed. Monomer yields of ~30% from isolated lignin and purified sugar yield of >90% were achieved.*
- Complete pretreatment scale-up and validation at ~20-L scale (Q13)
  - *Completed. We validated the successful scale-up of this two-stage alkaline-oxidative delignification technology to the 1.2-kg scale using a 20-L reactor.*

3 – Impact

- **Key technical achievements:**
  - Sugar yields >90%
  - Monomer yields from isolated lignin ~30%
  - Zero VOC, lignin-based polyurethane resins

US 20200332376A1

(19) **United States**
(12) **Patent Application Publication**
Hegg et al.

(10) **Pub. No.: US 2020/0332376 A1**
(43) **Pub. Date: Oct. 22, 2020**

(54) ECONOMICAL METHODS FOR PERFORMING OXIDATIVE CATALYTIC PRETREATMENT OF PLANT BIOMASS USING A HOMOGENEOUS CATALYST SYSTEM

Publication Classification

(51) **Int. Cl.**
C13K 13/00 (2006.01)
C07F 1/08 (2006.01)
C07F 13/00 (2006.01)

- Demonstrated that EERE's mission to enable production of $3/gasoline gallon equivalent of hydrocarbon biofuels from biomass is achievable.
- Supported BETO's mission to develop a "*biomass industry that produces renewable biofuels and bioproducts; enhances U.S. energy security; reduces dependence on foreign oil; provides environmental benefits; and creates nationwide economic opportunities*."

3 – Impact

- **Disseminating the Results:** Four publications in high-tier journals; one patent application; five presentations in scientific conferences; ten invited industry talks; multiple academic seminars.

I&EC research
Industrial & Engineering Chemistry Research
Article
Cite This: *Ind. Eng. Chem. Res.* 2019, 58, 15989–15999 pubs.acs.org/IECR

Integrated Two-Stage Alkaline-Oxidative Pretreatment of Hybrid Poplar. Part 1: Impact of Alkaline Pre-Extraction Conditions on Process Performance and Lignin Properties

Sandip K. Singh,[†] Anthony W. Savoy,[†] Zhaoyang Yuan,[‡] Hao Luo,[‖] Shannon S. Stahl,[‖] Eric L. Hegg,[*,‡] and David B. Hodge[*,†,⊥]

I&EC research
Industrial & Engineering Chemistry Research
Article
Cite This: *Ind. Eng. Chem. Res.* 2019, 58, 16000–16008 pubs.acs.org/IECR

Integrated Two-Stage Alkaline–Oxidative Pretreatment of Hybrid Poplar. Part 2: Impact of Cu-Catalyzed Alkaline Hydrogen Peroxide Pretreatment Conditions on Process Performance and Economics

Zhaoyang Yuan,[†] Sandip Kumar Singh,[‡] Bryan Bals,[§] David B. Hodge,[*,‡,‖] and Eric L. Hegg[*,†]

ACS Sustainable Chemistry & Engineering
pubs.acs.org/journal/ascecg
Research Article

Effective Biomass Fractionation through Oxygen-Enhanced Alkaline–Oxidative Pretreatment

Zhaoyang Yuan, Grace E. Klinger, Saeid Nikafshar, Yanbin Cui, Zhen Fang, Manar Alherech, Shannon Goes, Colin Anson, Sandip K. Singh, Bryan Bals, David B. Hodge,* Mojgan Nejad,* Shannon S. Stahl,* and Eric L. Hegg*

polymers
MDPI

Review

Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives

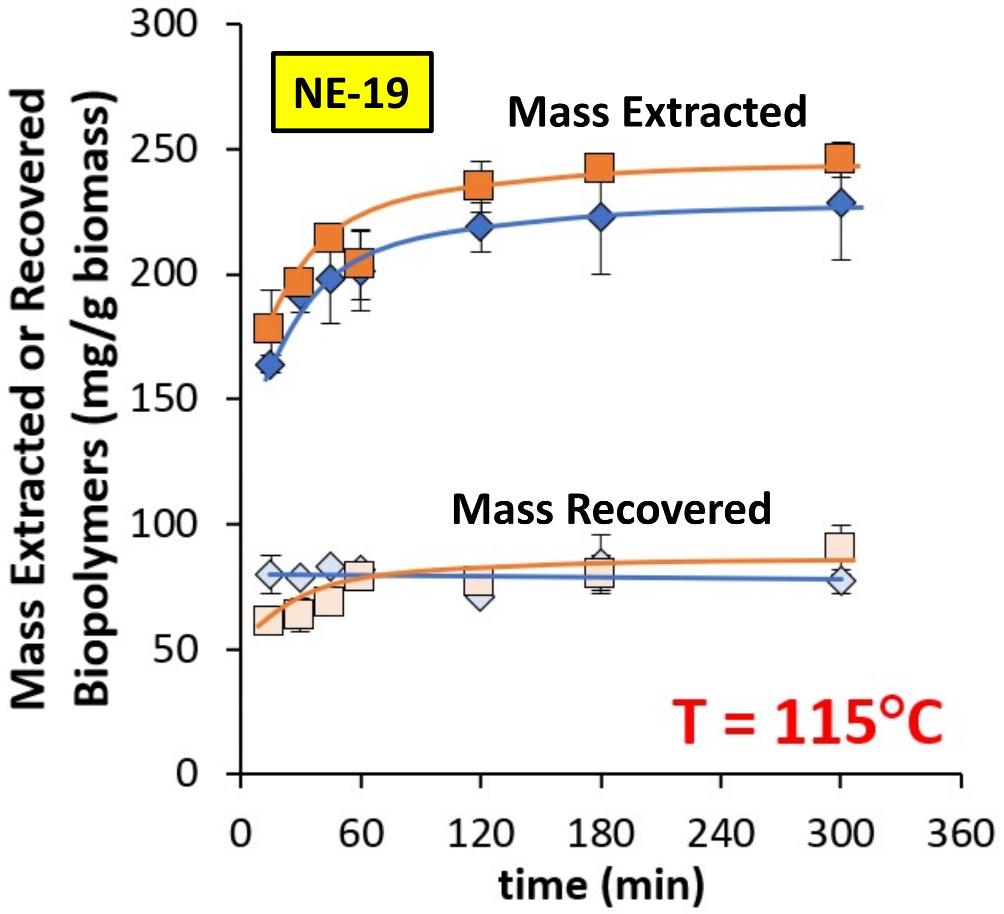
Mona Alinejad [1], Christián Henry [1], Saeid Nikafshar [1], Akash Gondaliya [2], Sajad Bagheri [2], Nusheng Chen [3], Sandip K. Singh [4], David B. Hodge [4,5,*] and Mojgan Nejad [1,2,*]

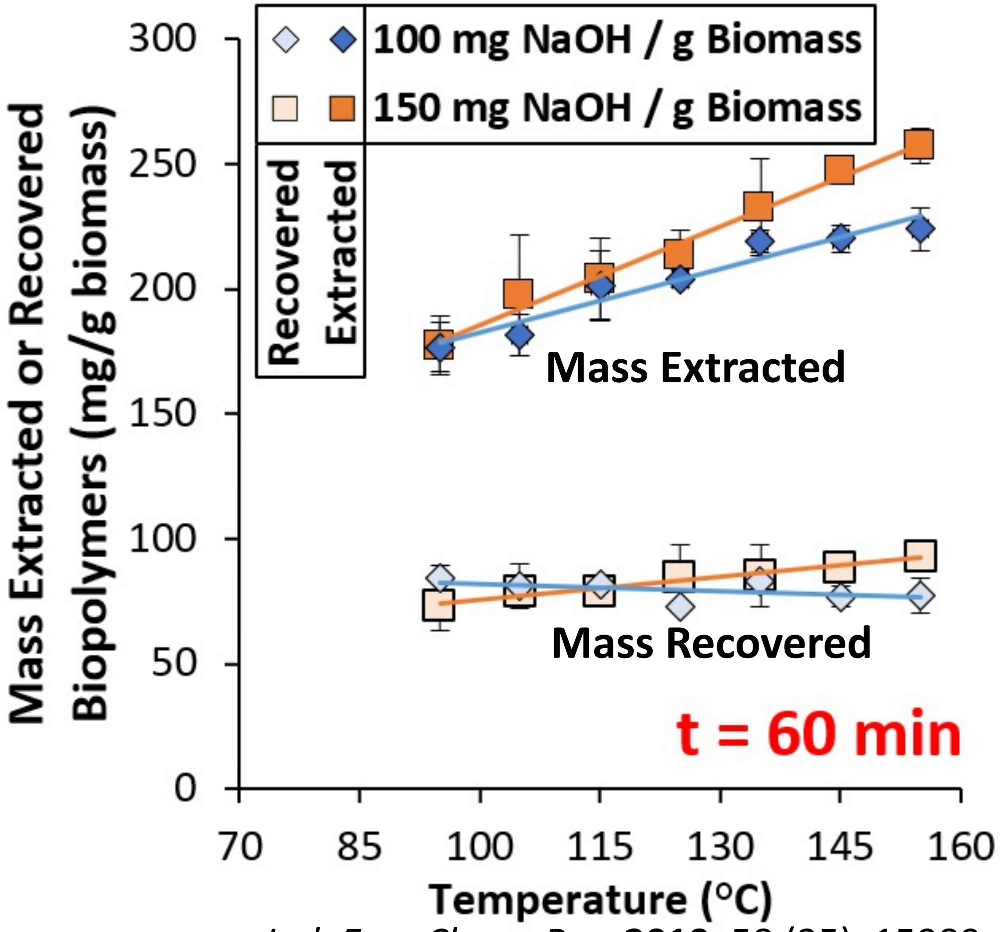
4 – Progress and Outcomes

- Milestone completion is on schedule
- Progress on Tasks is on schedule
  - Task 1 – Validation (also successfully completed our mid-cycle review just over a year ago in December of 2019).
  - Task 2 – Characterize reaction space for alkaline delignification stage (Alkaline pre-extraction).
  - Task 3 – Characterize reaction space for alkaline-oxidative post-treatment (Cu-AHP).
  - Task 4 – Integration, scale-up, and validation.
  - Task 5 – Perform TEA and LCA of the integrated process.

Task 2 – Alkaline Pre-Extraction

- **Task Goals:** Ascertain how alkaline pre-extraction conditions impact sugar yield, lignin yield, and lignin properties, and how changes in lignin properties can be linked to lignin valorization
- **Key Deliverables:** (1) Develop empirical predictive models, (2) identify down-selected set of conditions for future studies, and (3) supply data to Task 5 for sensitivity analysis, TEA, and LCA studies.



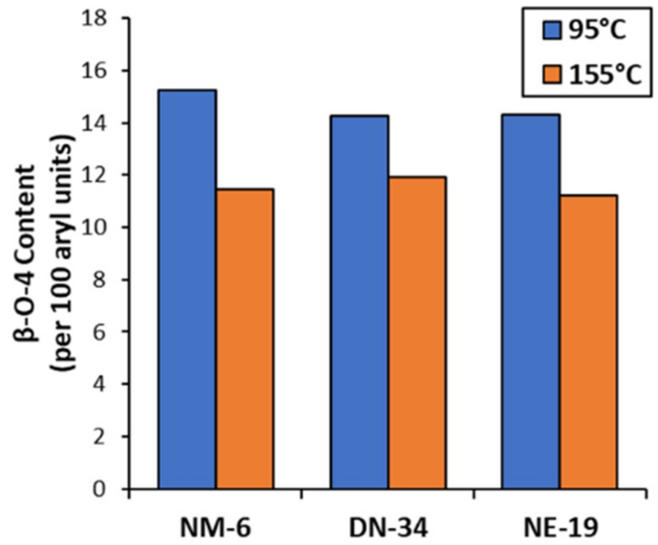


Ind. Eng. Chem. Res. **2019,** 58 (35), 15989-15999.

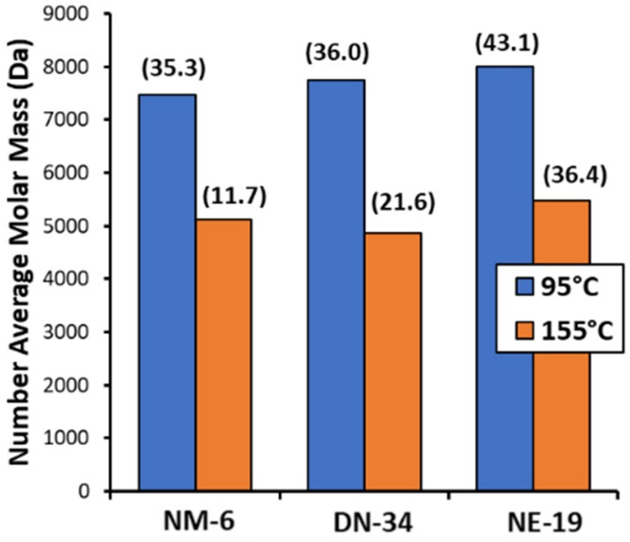
Task 2 – Alkaline Pre-Extraction

Task Accomplishments:

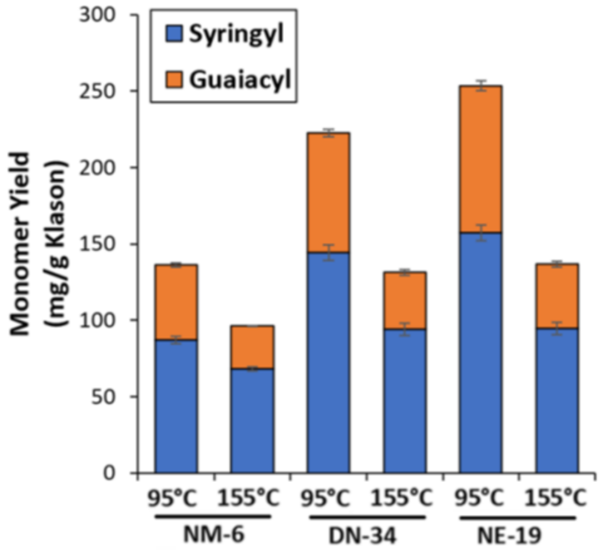
- **Develop correlations** between alkaline pretreatment conditions, lignin properties, and monomer/dimer yields and product distributions to be used in TEA.



^{13}C NMR Results



GPC Results



Thioacidolysis Results

- Extent of delignification correlated to:

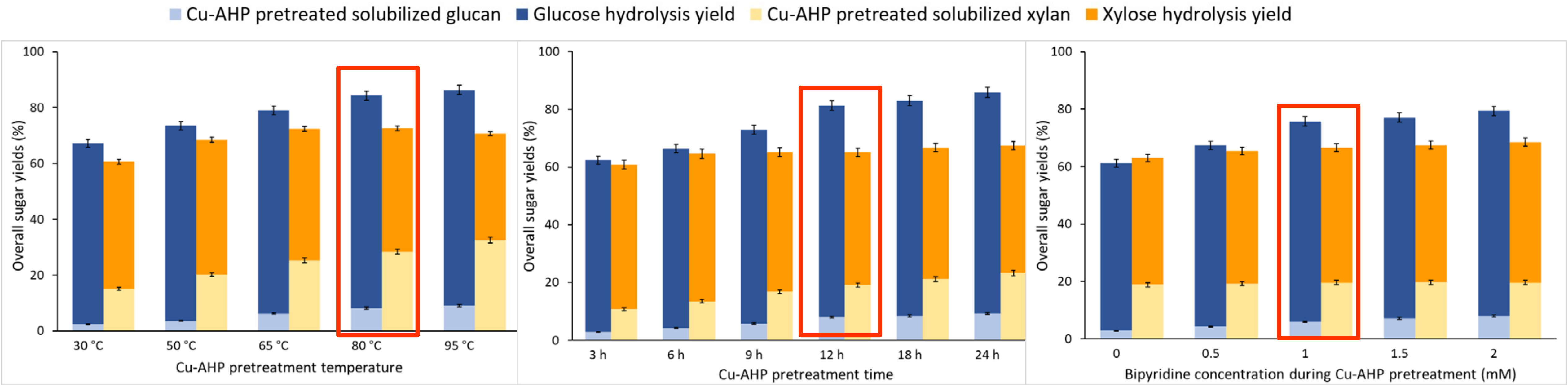
Positive Correlation:
- enzymatic hydrolysis yields
- lignin phenolic hydroxyl content

Negative Correlation:
- aromatic monomer yields
- lignin MW
- lignin solubility in acetone
- β-O-4 content

- No correlations between S/G ratio and transition metal content and any of the other quantified properties for the limited dataset

Task 3 – Alkaline-Oxidative Post-Treatment (Overview)

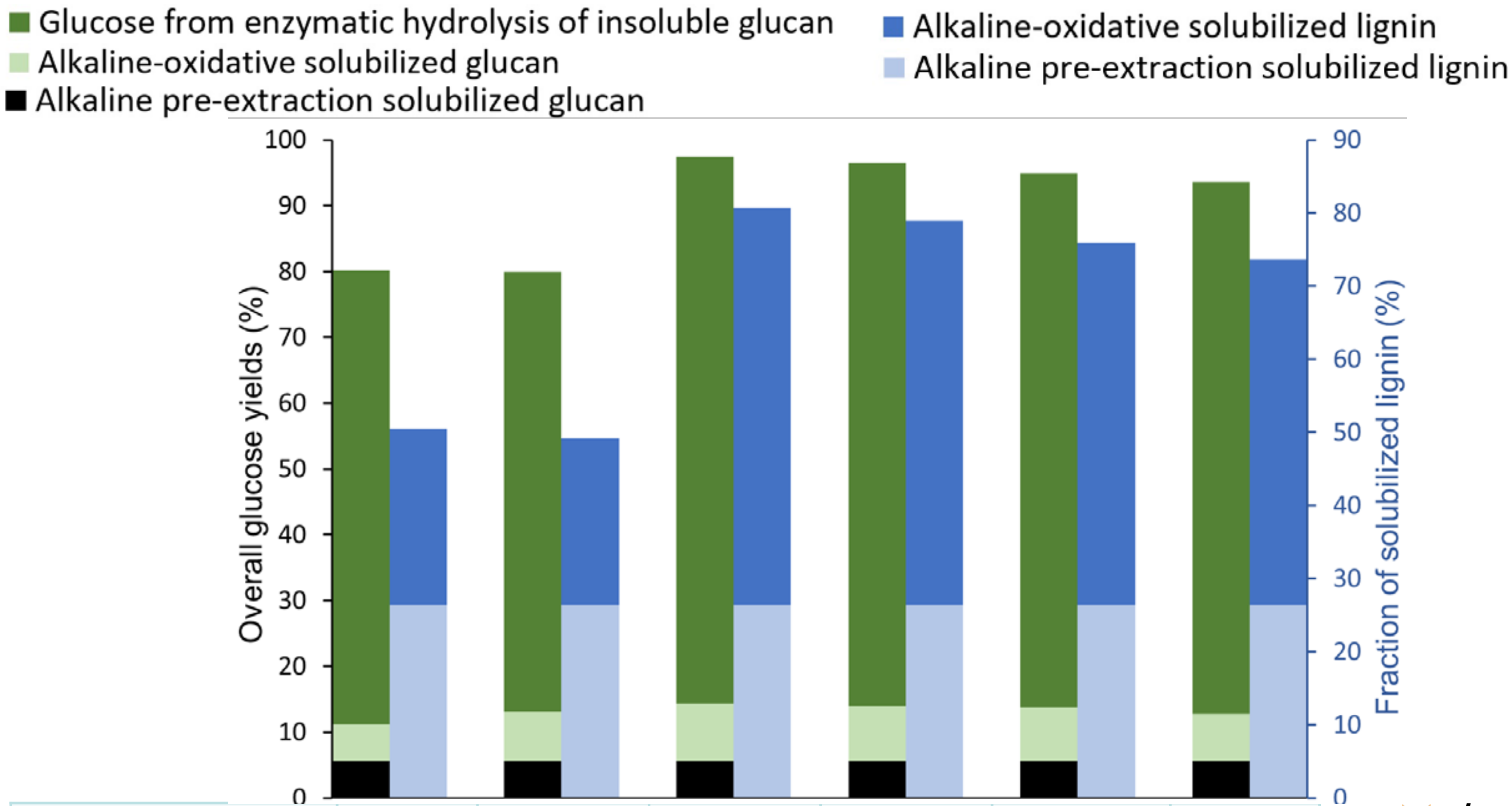
- **Task Goals:** Reveal how reaction conditions for catalytic alkaline-oxidative post-pretreatment impact sugar yield, lignin yield, and the lignin properties, and how these changes in lignin properties can be linked to lignin valorization
- **Key Deliverables:** (1): Assess the feasibility of achieving a ~25% reduction in the MFSP (2) Develop correlations between alkaline pretreatment conditions, lignin properties, and the monomer/dimer yields and product distributions, and (3) Identify conditions that will achieve ≥30 wt% yield of depolymerized lignin and ≥80% yield of purified sugar without increasing MFSP. ✓



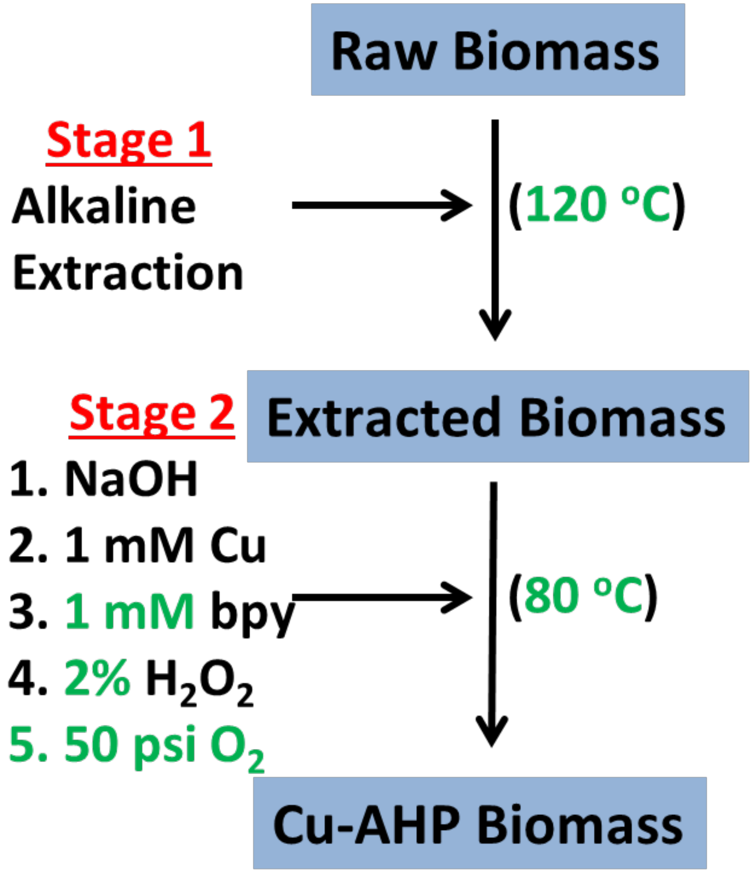
Ind. Eng. Chem. Res. **2019,** 58 (35), 16000-16008.

Task 3 – Alkaline-Oxidative Post-Treatment

- Explored using O_2 and H_2O_2 as co-oxidants for Cu-AHP pretreatment
  - Alkaline pre-extraction: 10% (w/v) solid consistency, 120 ^oC, 1 h, 10% NaOH loading on biomass
  - Cu-AHP post-treatment: 80 ^oC, 12 h, 1 mM $CuSO_4$, 1 mM bipyridine (bpy), and 10% (w/w) NaOH
  - Enzymatic hydrolysis: 15 mg protein/g glucan, 50 ^oC, 72 h



H_2O_2 (%)	8	-	8	6	4	2
O_2 (psi)	-	50	50	50	50	50



- *Ind. Eng. Chem. Res.* **2019**, *58*, 15989-15999
- *Ind. Eng. Chem. Res.* **2019**, *58*, 16000-16008
- *ACS. Sustain. Chem. Eng.* **2021**, *9*, 1118-1127

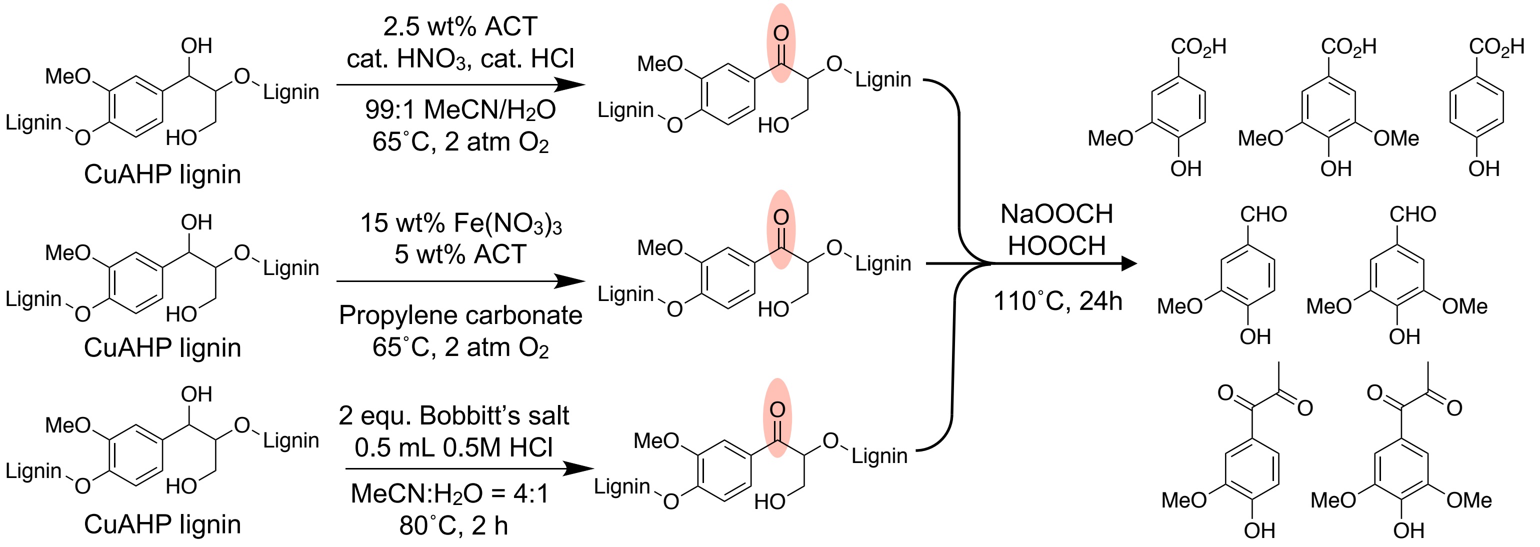
Tasks 2 & 3 – Assessing the Lignin Stream

Previous approaches:

ACT/NO_x Oxidation

$Fe(NO_3)_3$ /ACT Oxidation

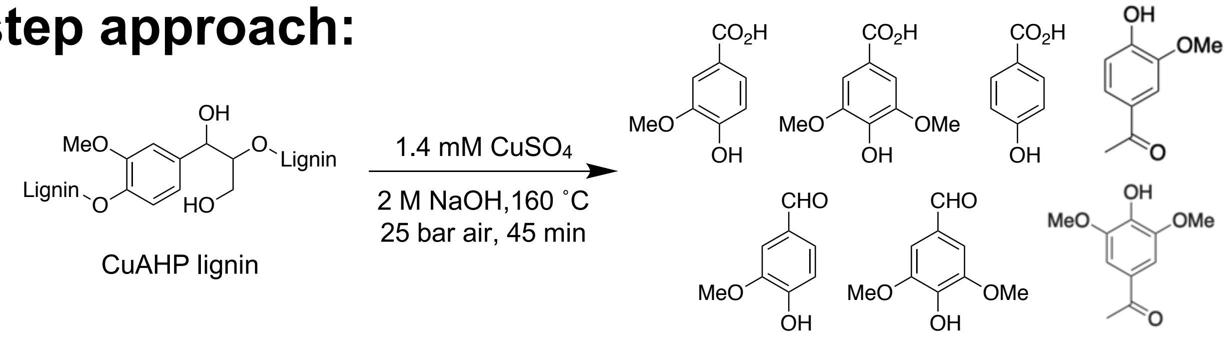
Bobbitt's Salt Oxidation



2-step approaches can achieve monomer yields of up to ~18% (aerobic) with Cu-AHP lignin. Throughput is slow due to long reaction times and scale-up is challenging.

New single-step approach:

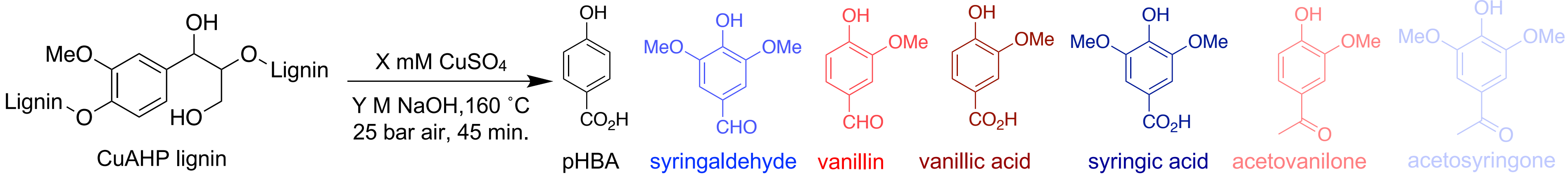
Lignin Oxidative Alkaline Depolymerization (LOAD)



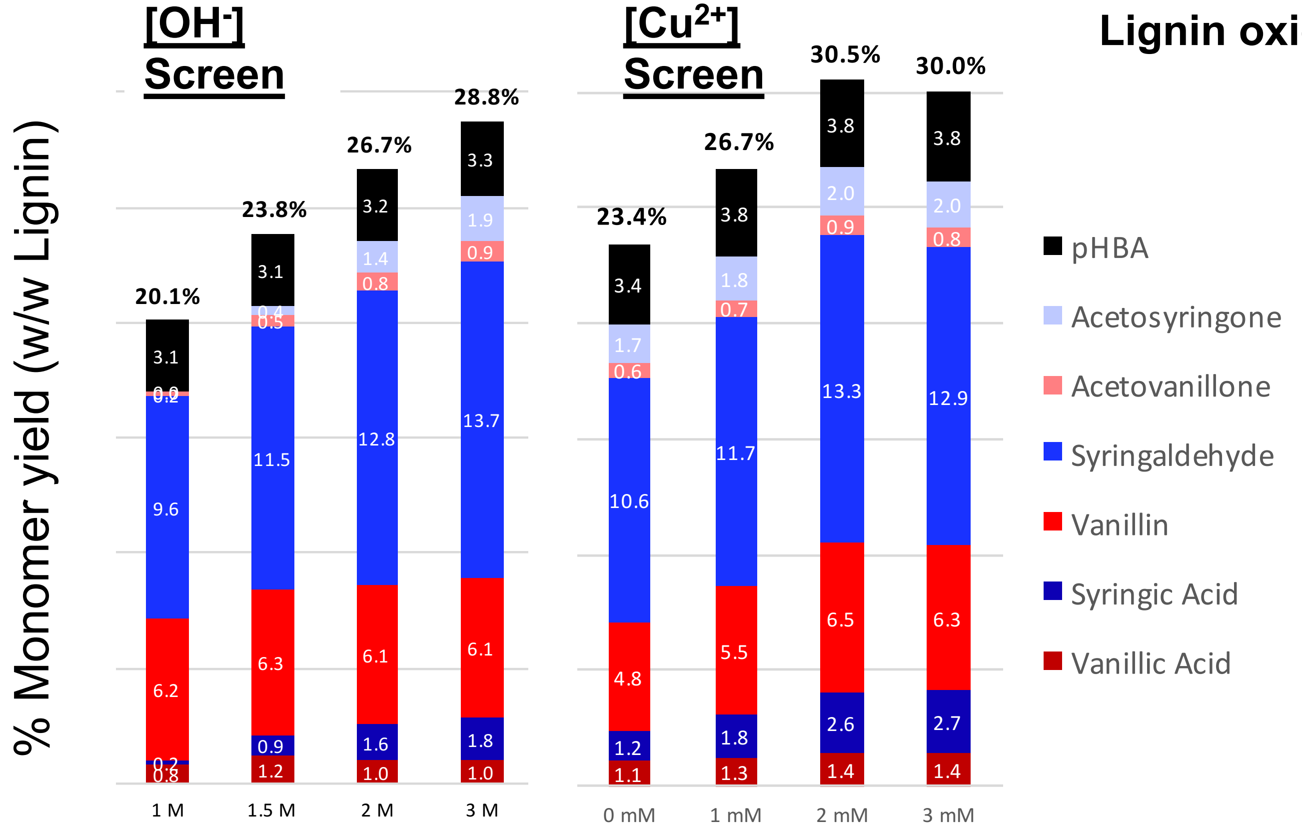
One-step approach can achieve 30% monomer yield with Cu-AHP lignin. Method is easier to scale-up and translate to flow systems due to the solubility of lignin in base and shorter reaction times.

Tasks 2 & 3 – Assessing the Lignin Stream

Key Deliverable: Identify conditions that will achieve ≥30 wt% yield of depolymerized lignin and ≥80% yield of purified sugar without increasing MFSP



Lignin oxidative alkaline depolymerization (LOAD):



X = 1.5 mM $CuSO_4$, Y = [NaOH]

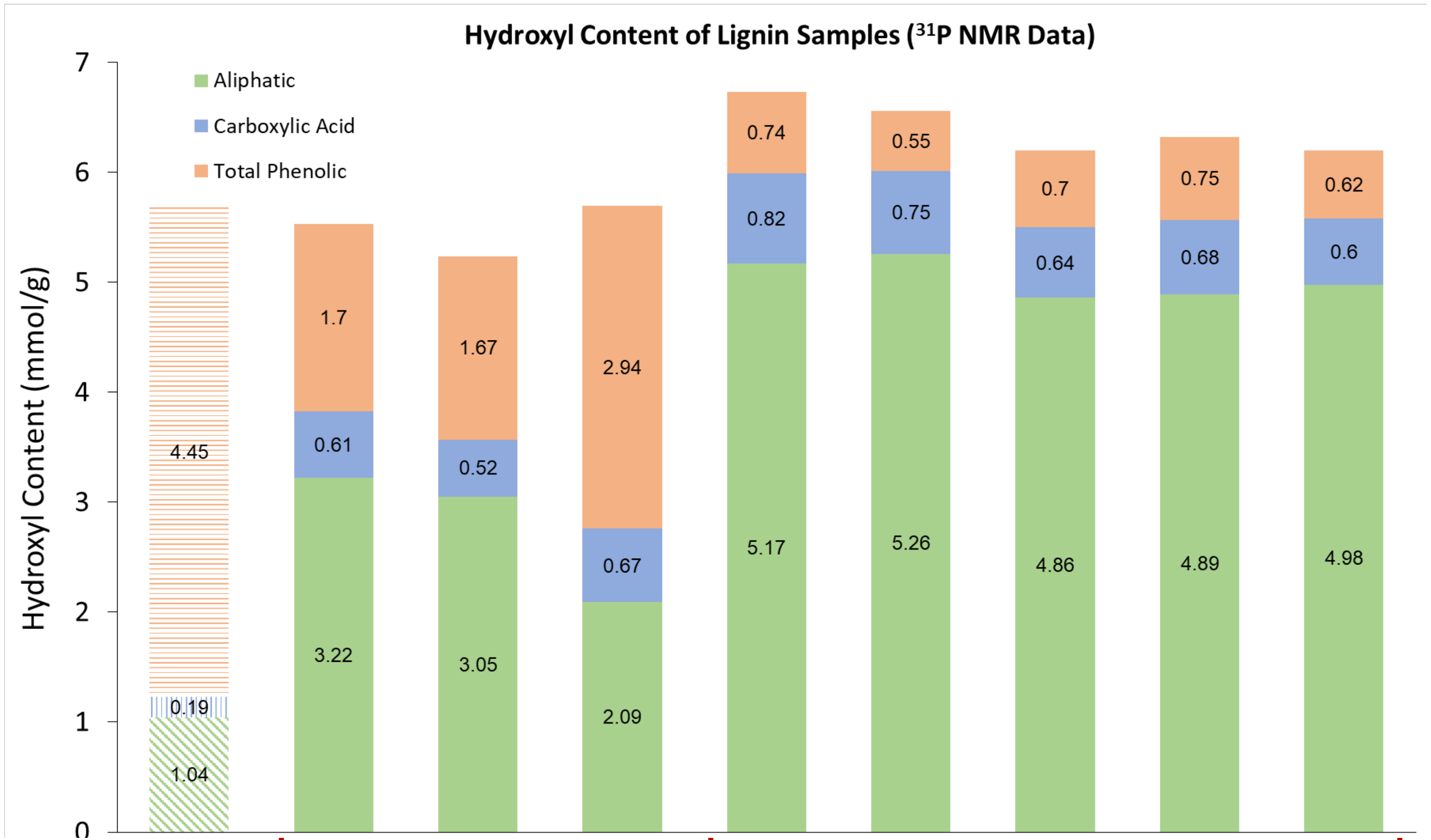
X = [$CuSO_4$], Y = 2 M NaOH

30% yield of lignin monomers achieved using optimized conditions.

Lignin preparation conditions:

- Pre-extraction: 30 ^oC, 10% NaOH (w/w), 1 h
- Alkaline Oxidative Post-Treatment: 30 ^oC, 23 h, 1 mM $CuSO_4$, 2 mM bipyridine, 10% (w/w) NaOH, 10% (w/w) H_2O_2

Tasks 2 & 3- Lignin Valorization into Polyurethanes



Hardwood Kraft Lignin | 170 °C 145 °C 125 °C Alkaline Pre-Extraction Lignin | 8% only 8%/O_2 4%/O_2 2%/O_2 O_2 only

Alkaline-Oxidative Lignin with Varying H_2O_2

(Alkaline pre-extraction was performed at 120 °C)

Tasks 2 & 3- Lignin Valorization into Polyurethanes

- **Key Deliverable:** Formulate lignin-based polyurethane resins for wood coating applications from recovered lignins

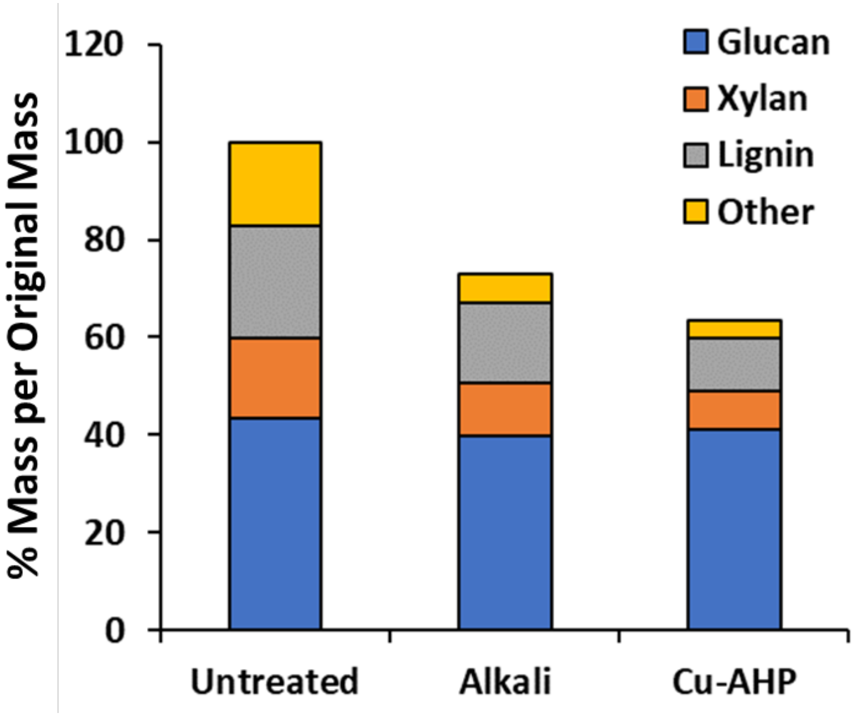
PUD Resin Properties				
Properties	**PU-PEG-200**	**PU-L-125**	**PU-L-145**	**PU-L-170**
Adhesion Strength (Cross-Cut Tape)	5B (0% None)	4B (Less than 5%)	4B (Less than 5%)	4B (Less than 5%)
Pencil Hardness	6H	4H	4H	2H
Water Resistance	99 (0.3)	100 (0.2)	99 (0.3)	99 (0.5)
Solvent Resistance	92 (0.2)	86 (0.3)	82 (0.4)	80 (0.8)

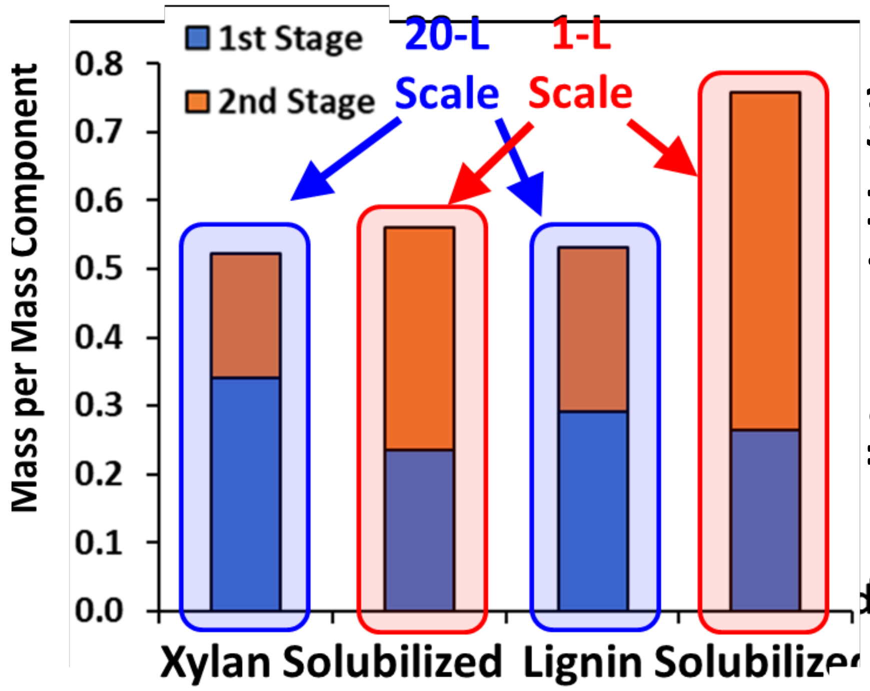
Coated Wood Samples

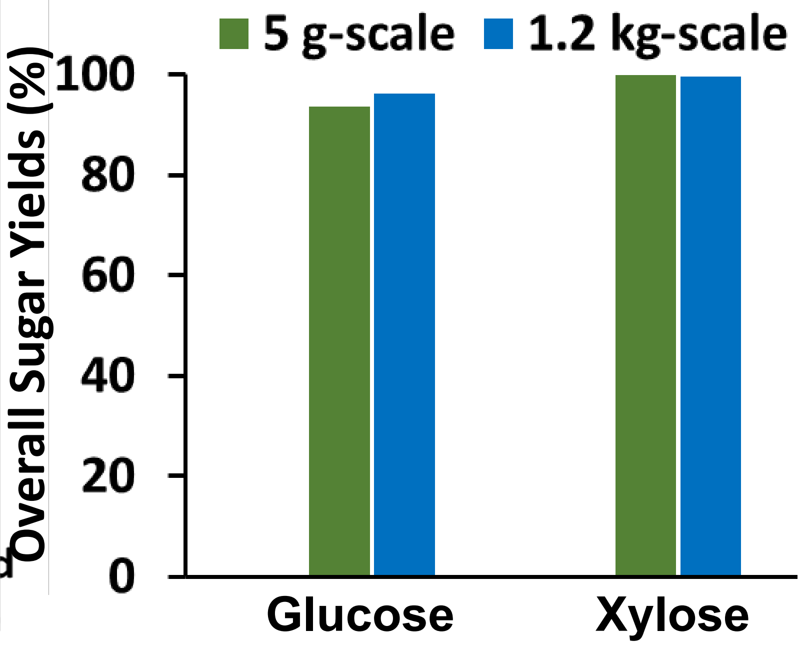
- Zero VOC, lignin-based polyurethane resins were successfully formulated using acetone soluble fraction of alkaline pre-extraction lignins (isolated at 125, 145, and 170 °C).
- Properties of the lignin-based polyurethane resins were very promising.
- Lignin isolated at lower temperatures (125 and 145 °C) had better performance (hardness and solvent resistance) than lignin isolated at higher temperatures (170 °C).

Task 4 – Integration, Scale-Up, and Validation

- **Key Deliverable**: Complete integrated pretreatment scale-up and validation at the ~20-L scale to verify yields and material balances and verify optimization ✓
  - Identified scale-up strategies using different reactor designs.
  - Scaled-up the experiments from 5 g-scale to 1.2 kg-scale using a 20-L batch reactor.
  - TEA results indicate that scale-up of the experiment could further reduce MFSP by 1% compared to the small-scale experiment







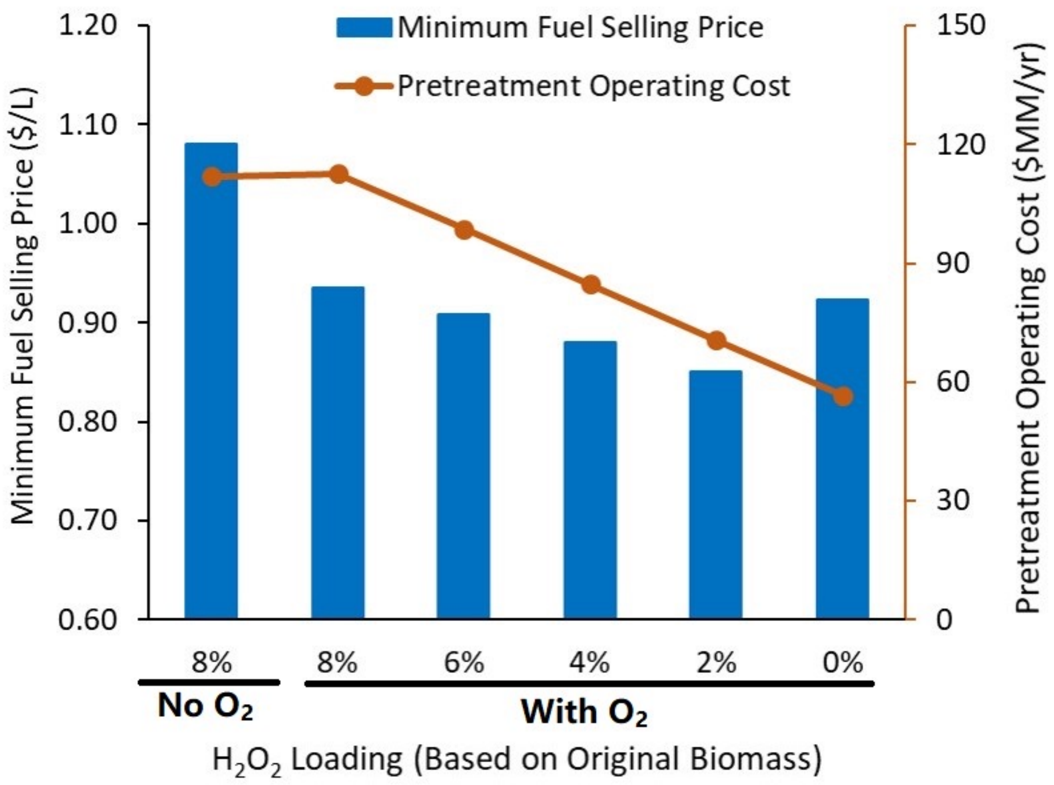
Task 5 – Perform TEA and LCA

- **Key Deliverable**: Complete final techno-economic model using screening conditions with sensitivities and preliminary scale-up cases ✓
- **Key Deliverable**): Complete final life cycle analysis model with sensitivities
- Purpose: Support other tasks in decision making using TEA and LCA
- Method: Use Excel-based models for maximum flexibility as the project continues

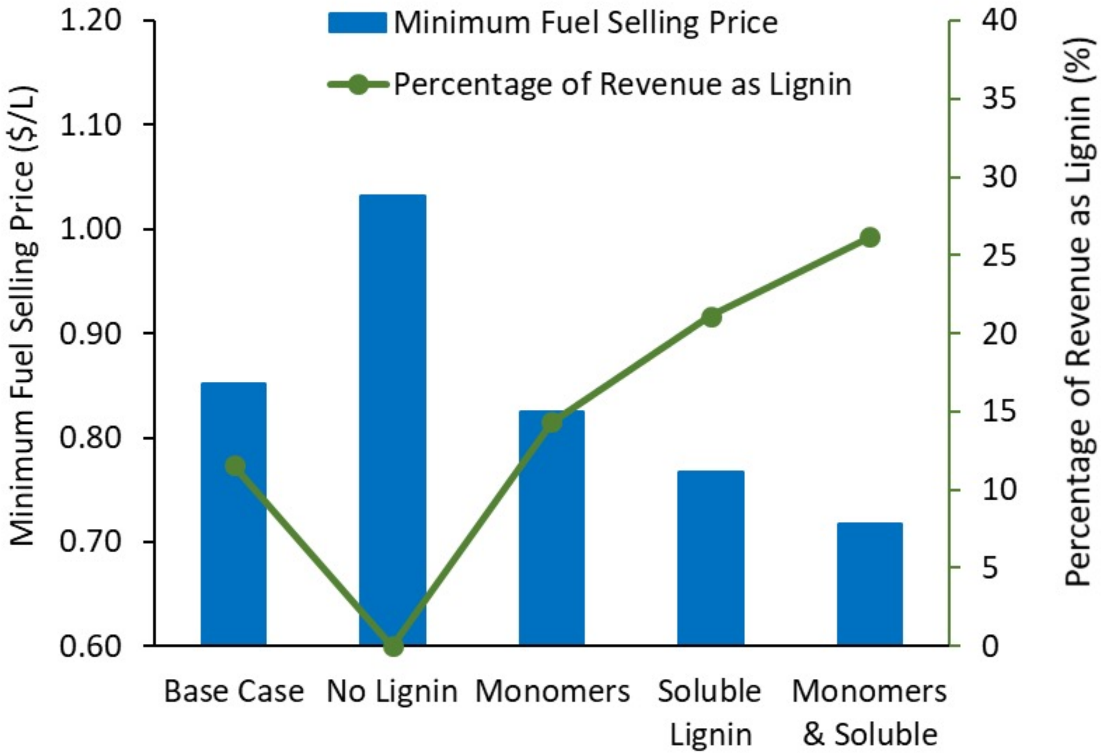
Sources for Economic Model	Sources for Environmental Model
NREL 2015 Model	GREET 2018
Internal Cu-AHP pretreatment model	NREL 2015 Model
Internal hydrolysis model	Literature for bipyridine

- Sensitivity analysis confirms pretreatment inputs, lignin value, and sugar yields as key economic indicators
- CO_2 reduction heavily dependent on whether or not the NaOH is recycled based on the recycle method

Task 5 – Perform TEA and LCA



Change in pretreatment operating cost and minimum fuel selling price (MFSP) as H_2O_2 loading decreases from 8% to 0% in the presence of 50 psi O_2. 8% H_2O_2 loading without O_2 is shown as a reference



Impact of lignin value on MFSP. The base case assumes precipitated lignin is sold as a polyol replacement ($0.80/kg). No lignin assumes all lignin is burned for energy, monomers assumes 16% of the precipitated lignin is sold for monomer production ($2.00/kg) with the remainder as polyol substitute, soluble lignin assumes all soluble lignin is sold as a polyol substitute, and the final condition assumes 16% of all soluble lignin is sold for monomers.

- Current MFSP is $0.85/L ($3.22/gal) gasoline equivalent
- Potential to be reduced to $0.72/L ($2.71/gal) with advanced lignin usage

Summary

- Our two-stage alkaline-oxidative Cu-AHP pretreatment is a promising strategy that effectively generates clean sugar and lignin streams from woody biomass.
- Sugars can be used for the production of hydrocarbon fuels while the lignins can feed multiple product streams
  - Lignin is uniquely susceptible to oxidative depolymerization
  - Lignin is amenable to many polyurethane applications
- Aromatic monomer yields of ~30% could be achieved with the alkaline-oxidative lignin following the depolymerization process. When formulating polyurethane coatings with the lignin isolated from alkaline pre-extraction phase, 85% of petroleum-based polyol could be replaced.
- Enable the economic viability of the biofuels industry.
- Optimization to maximize both sugar and lignin yields while simultaneously reducing chemical inputs has led to a reduction in MFSP by ~40% relative to the base case.

Quad Chart Overview

Timeline

- Project start date: 10/01/2017
- Project end date: 12/31/2021

	FY20 Costed	Total Award
DOE Funding		$1,800,000

Project Goal

Optimize our deconstruction process based on both TEA and LCA analysis for simultaneous high sugar yields and high lignin yields and desired properties for improved valorization.

End of Project Milestone

Achieve a ~25% reduction in the minimum fuel selling price (MFSP) of biofuel generated from woody biomass.

Project Partners

- Eric Hegg (PI) – Michigan State University
- David Hodge (Co-PI) – Montana State University
- Shannon Stahl (Co-PI) – University of Wisconsin
- Bryan Bals (Co-PI) – MBI
- Mojgan Nejad (Partner) – Michigan State U.

Funding Mechanism

- ❖ MEGA-BIO: Bioproducts to Enable Biofuels (DE-FOA-0001433)
- ❖ Topic Area 1: Early TRL (TRL 2-3)
- ❖ FY 2017

Acknowledgments

Montana State

David Hodge

UW

Shannon Stahl

MBI

Bryan Bals

MSU

Mojgan Nejad

Gayle Bentley – Technology Manager
Benjamin Simon – Project Engineer

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Additional Slides

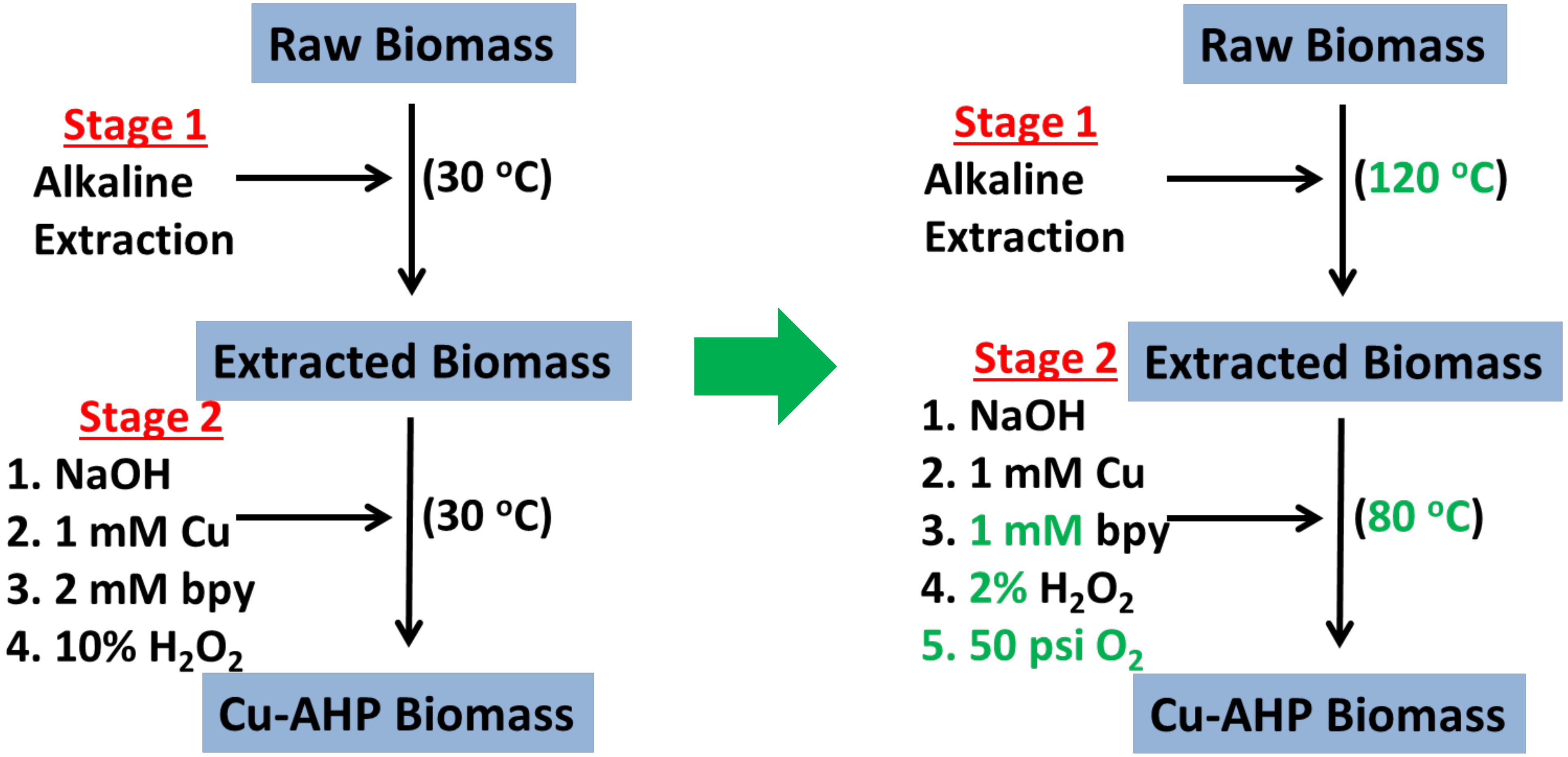
Response to Reviewers' Comments

- "…what is planned to improve sugar and lignin yields…I am concerned the remaining gains will be incremental, and possibly insufficient to meet goals."
  - *O_2 was added as a co-oxidant, thereby allowing us to lower H_2O_2 concentrations, reaction time, and enzyme loading. Overall sugar yields remained >90% while capital and operating costs dropped by ~40%.*
  - *New single step lignin depolymerization process was developed allowing us to achieve 30% monomer yields from recovered lignins.*
- "It is hard to judge whether current performance is on track to industrial relevance."
  - *Current results are very close to a biofuel selling price of EERE's target of $3/gasoline gallon equivalent. A clear path has been outlined to achieve ~$2.70.*
- "No progress reported for Task 4 [scale-up and integration]."
  - *At the time of the previous review, Task 4 was not scheduled to begin. We recently demonstrated scale-up to 20-L scale with no loss of performance.*

Publications & Patents

- Singh, SK; Savoy, AW; Yuan, Z; Luo, H; Stahl, SS; Hegg, EL*; Hodge, DB* "Integrated Two-State Alkaline-Oxidative Pretreatment of Hybrid Poplar. Part 1: Impact of Alkaline Pre-Extraction Conditions on Process Performance and Lignin Properties." *Ind. Eng. Chem. Res.* **2019**, *58*, 15989-15999.
- Yuan, Z; Singh, SK; Bals, B; Hodge, DB*; Hegg, EL* "Integrated Two-State Alkaline-Oxidative Pretreatment of Hybrid Poplar. Part 2: Impact of Cu-Catalyzed Alkaline Hydrogen Peroxide Pretreatment Conditions on Process Performance and Economics." *Ind. Eng. Chem. Res.* **2019**, *58*, 16000-16008.
- Alinejad, M; Henry, C; Nikafshar, S; Gondaliya, A; Bagheri, S; Chen, N; Singh, SK; Hodge, DB*; Nejad, M* "Lignin-based Polyurethanes: Opportunities for Bio-based Foams, Elastomers, Coatings and Adhesives." *Polymers* **2019**, *11*, 1202.
- Yuan, Z; Klinger, GE; Nikafshar, S; Cui, Y; Fang, Z; Alherech, M; Goes, S; Anson, C; Singh, SK; Bals, B; Hodge, DB*; Nejad, M*; Stahl, SS*; Hegg, EL* "Effective Biomass Fractionation through Oxygen-Enhanced Alkaline-Oxidative Pretreatment." *ACS Sustain. Chem. Eng.* **2021**, *9*, 1118-1127.
- Eric L. Hegg, Zhaoyang Yuan, David B. Hodge, Shannon S. Stahl, Bryan D. Bals. "Economic methods for performing oxidative catalytic pretreatment of plant biomass using a homogenous catalyst system." US Patent, Publication No. US 2020/0332376 A1.

Improvement of the Two-Stage Cu-catalyzed Alkaline Hydrogen Peroxide Pretreatment (Cu-AHP) Conditions



- *Biotechnol. Biofuels* **2013**, *6*, e119
- *Biotechnol. Bioeng.* **2013**, *110*, 1078
- *Biotechnol. Biofuels* **2016**, *9*, e34
- *Ind. Eng. Chem. Res.* **2019**, *58*, 15989-15999
- *Ind. Eng. Chem. Res.* **2019**, *58*, 16000-16008
- *ACS. Sustain. Chem. Eng.* **2021**, *9*, 1118-1127