DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

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

Wednesday, March 6, 2019
Biochemical Conversion

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Goal Statement

- **Project Goal:** Optimize our two-stage alkaline-oxidative deconstruction 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.

- **Project Outcomes:** (**1**) Identify economically promising conditions for pretreatment through the production of co-products. (**2**) Integrate the individual components of this process using identified conditions into an integrated technology package. (**3**) Identify and mitigate the risks associated with this strategy. (**4**) Achieve a ~25% reduction in the minimum fuel selling price (MFSP).

Goal Statement

- **Relevance to the Bioenergy Industry:** Current commercial processes for lignin depolymerization achieve monomer yields of <15%. In addition to a clean, high-yield sugar stream, our two-stage alkaline-oxidative deconstruction process produces a lignin stream that is highly susceptible to oxidation/depolymerization, potentially achieving monomer yields of >30%. Combining the two independent units into an optimized, integrated process could enable the economic viability of a biofuels and bioproducts industry.

Quad Chart Overview

Timeline

- Project start date: 10/01/2017
- Project end date : 12/31/2020
- Percent complete: 40%

	FY 17 Costs	**FY 18 Costs**	**Total Planned Funding (FY 19-Project End Date)**
DOE Funded		$382,579	$1,417,421
Project Cost Share		$63,516	$386,484

•**Partners: If multiple DOE recipients are involved in the project, please list level of involvement, expressed as percentages of project funding from FY 17-18. [(i.e. NREL (70%); INL (30%)]**

Barriers addressed:

- **Ct-B.** Efficient Preprocessing and Pretreatment.
- **Ct-C.** Process Development for Conversion of Lignin.

Objective

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.

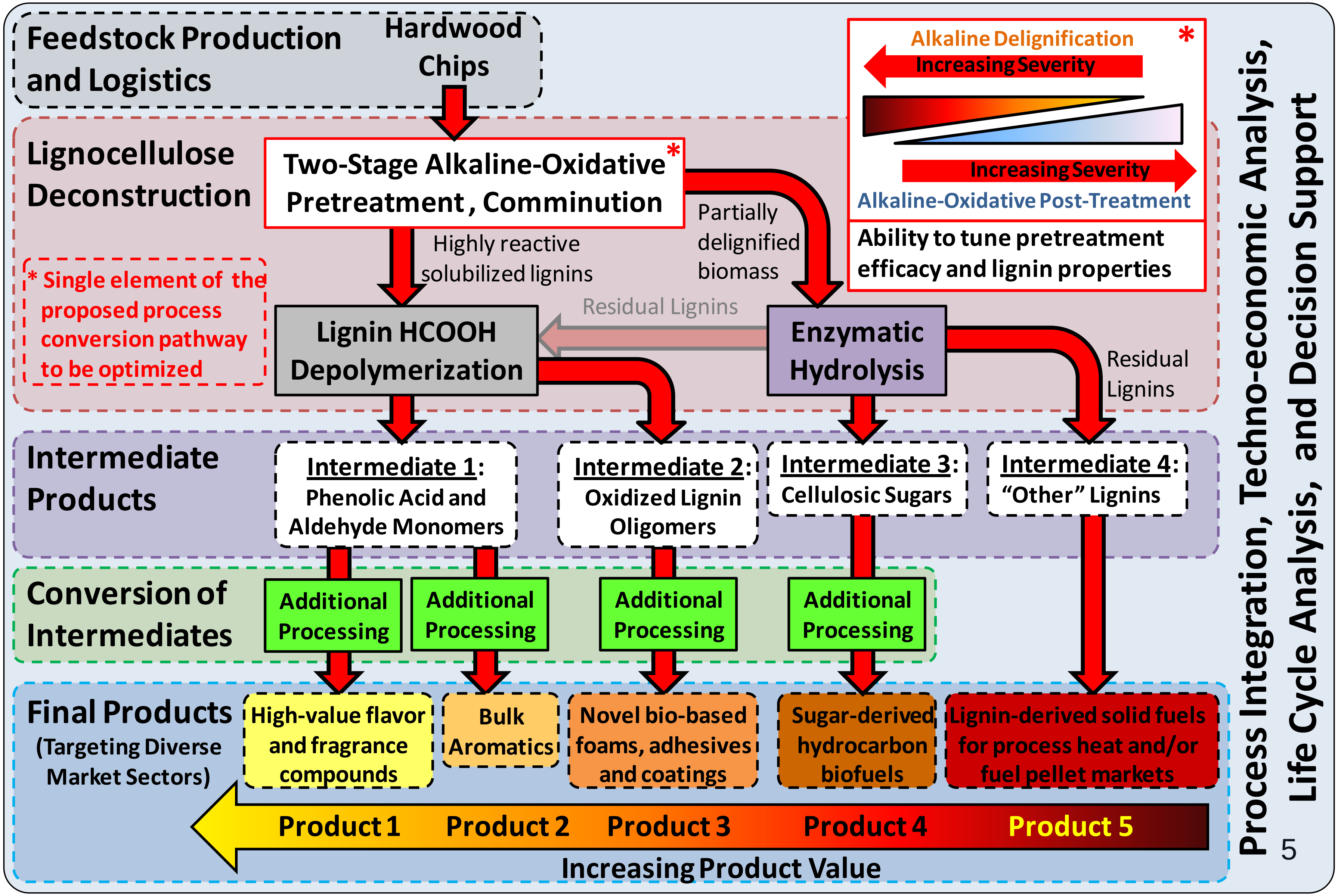
End of Project Goal

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

Partners and Collaborators

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

1 – Project Overview



Feedstock Production and Logistics

Hardwood Chips

Lignocellulose Deconstruction

Two-Stage Alkaline-Oxidative Pretreatment, Comminution *

Highly reactive solubilized lignins

Partially delignified biomass

* Single element of the proposed process conversion pathway to be optimized

Alkaline Delignification *

Increasing Severity

Increasing Severity

Alkaline-Oxidative Post-Treatment

Ability to tune pretreatment efficacy and lignin properties

Lignin HCOOH Depolymerization

Residual Lignins

Enzymatic Hydrolysis

Residual Lignins

Intermediate Products

Intermediate 1: Phenolic Acid and Aldehyde Monomers

Intermediate 2: Oxidized Lignin Oligomers

Intermediate 3: Cellulosic Sugars

Intermediate 4: "Other" Lignins

Conversion of Intermediates

Additional Processing

Additional Processing

Additional Processing

Additional Processing

Final Products (Targeting Diverse Market Sectors)

High-value flavor and fragrance compounds

Bulk Aromatics

Novel bio-based foams, adhesives and coatings

Sugar-derived hydrocarbon biofuels

Lignin-derived solid fuels for process heat and/or fuel pellet markets

Product 1 Product 2 Product 3 Product 4 Product 5

Increasing Product Value

Process Integration, Techno-economic Analysis, Life Cycle Analysis, and Decision Support

1 – Background

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

Raw Biomass

Stage 1

Alkaline Extraction → (30 ºC)

Extracted Biomass

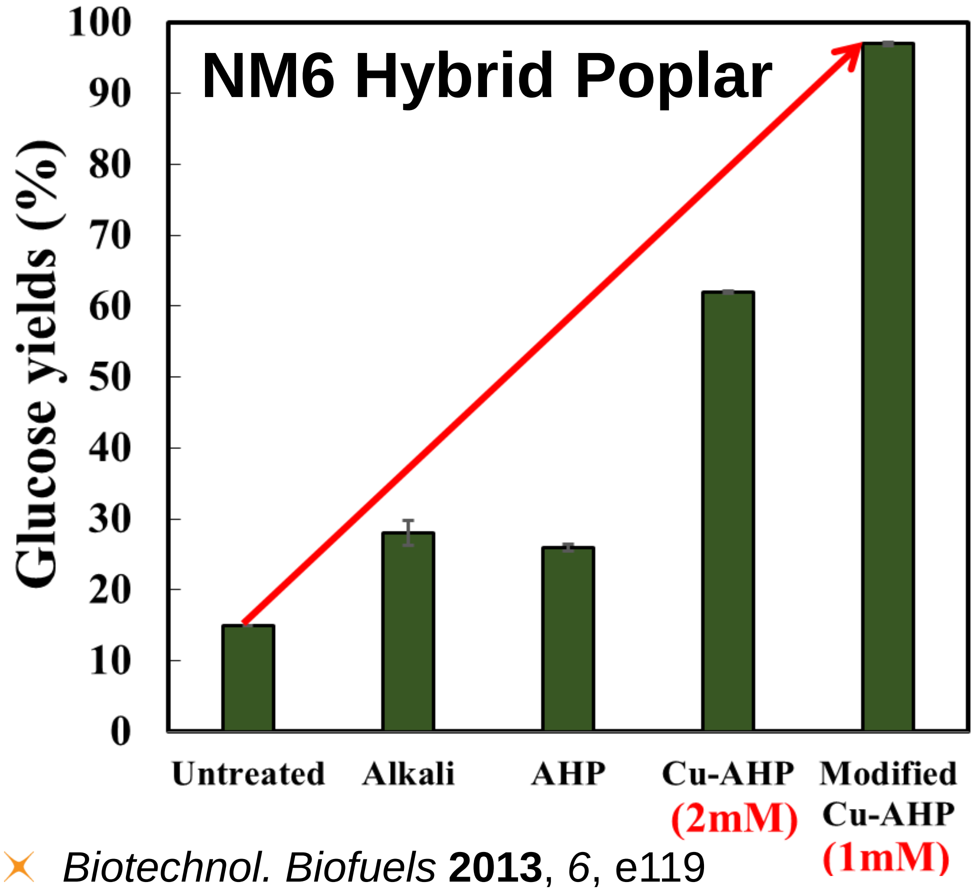
Stage 2

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

→ (30 ºC)

Cu-AHP Biomass

Benchmark Cu-AHP process

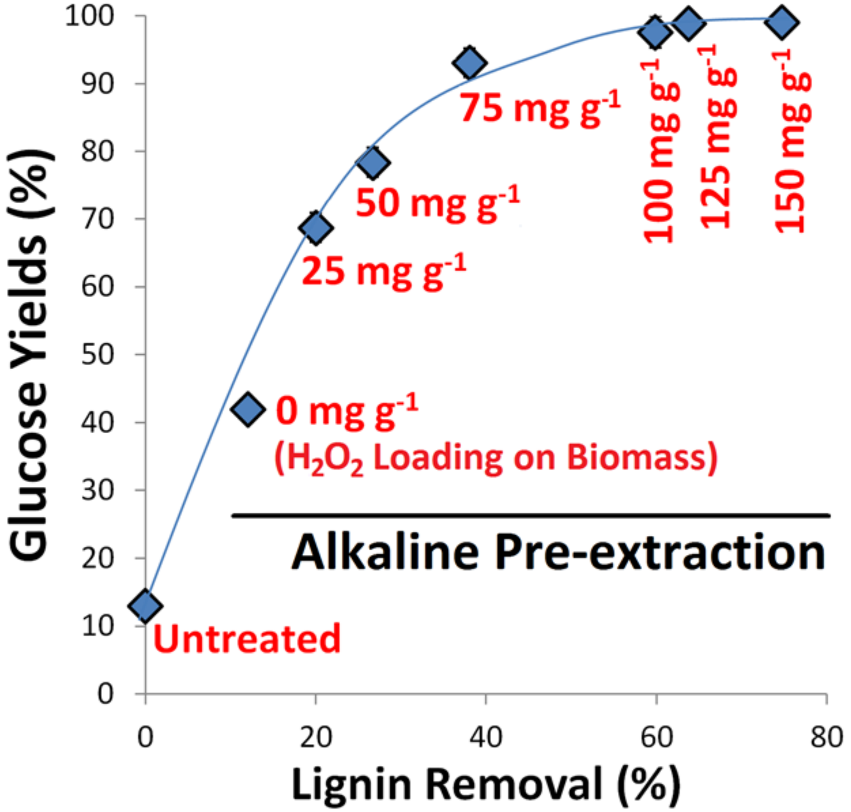


- *Biotechnol. Biofuels* **2013**, *6*, e119
- *Biotechnol. Bioeng.* **2013**, *110*, 1078-1086

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

1 – Background

Delignification of hybrid poplar: Cu-AHP releases a significant fraction of the lignin



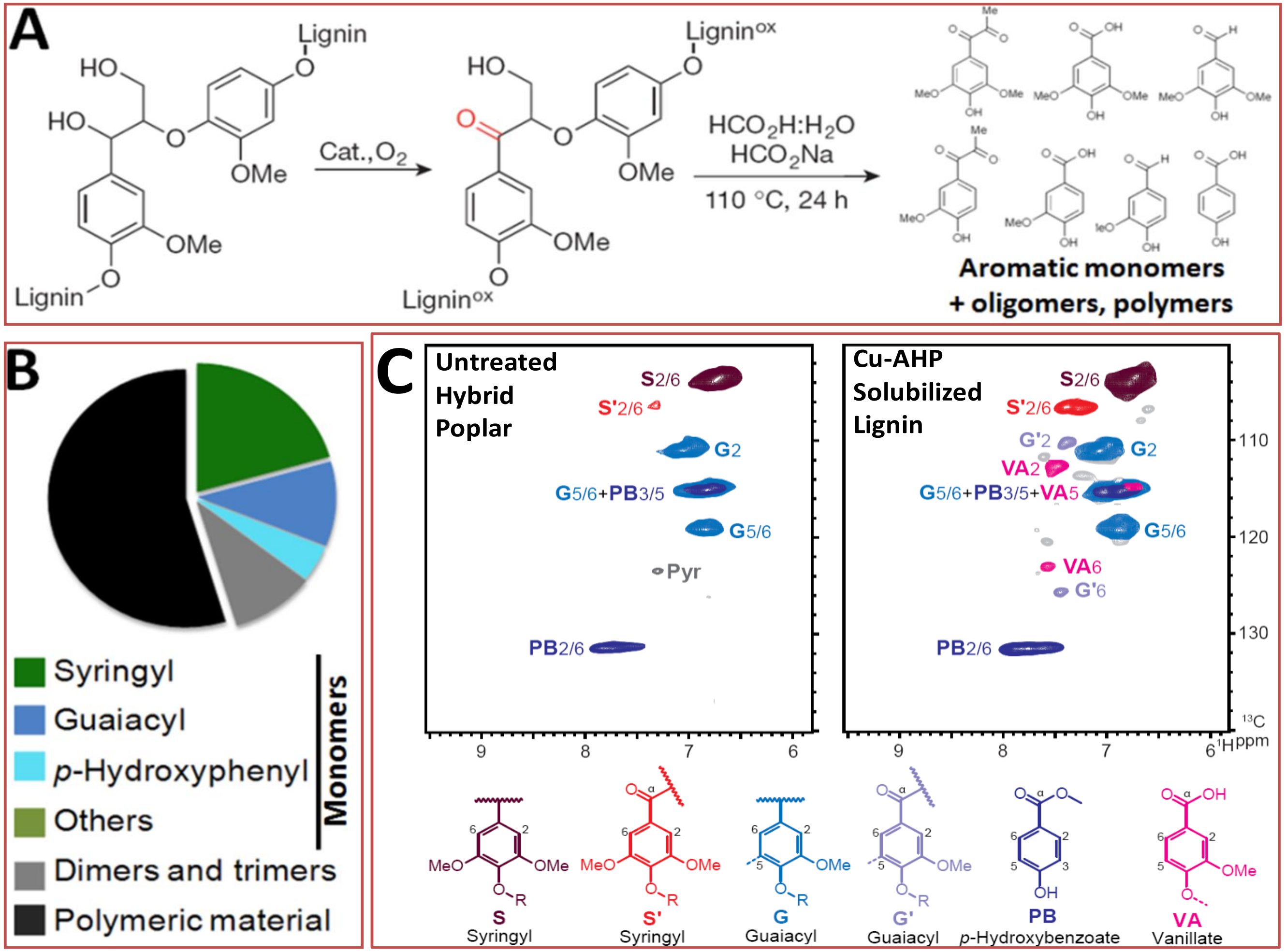
Recovered Lignin

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

Recovered lignin can aid in the process economics

1 – Background

Oxidation/Depolymerization Process



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

Cu-AHP lignin is ideal for this depolymerization process

1 – Project Goals

The overall goals of are project are to optimize our two-stage alkaline-oxidative copper-catalyzed alkaline hydrogen peroxide (Cu-AHP) deconstruction process to generate from woody biomass (hardwoods):

- A clean sugar stream for the production of hydrocarbon fuels
- Lignins that can feed multiple product streams and enable the economic viability of our integrated system.

1 – Project Objectives

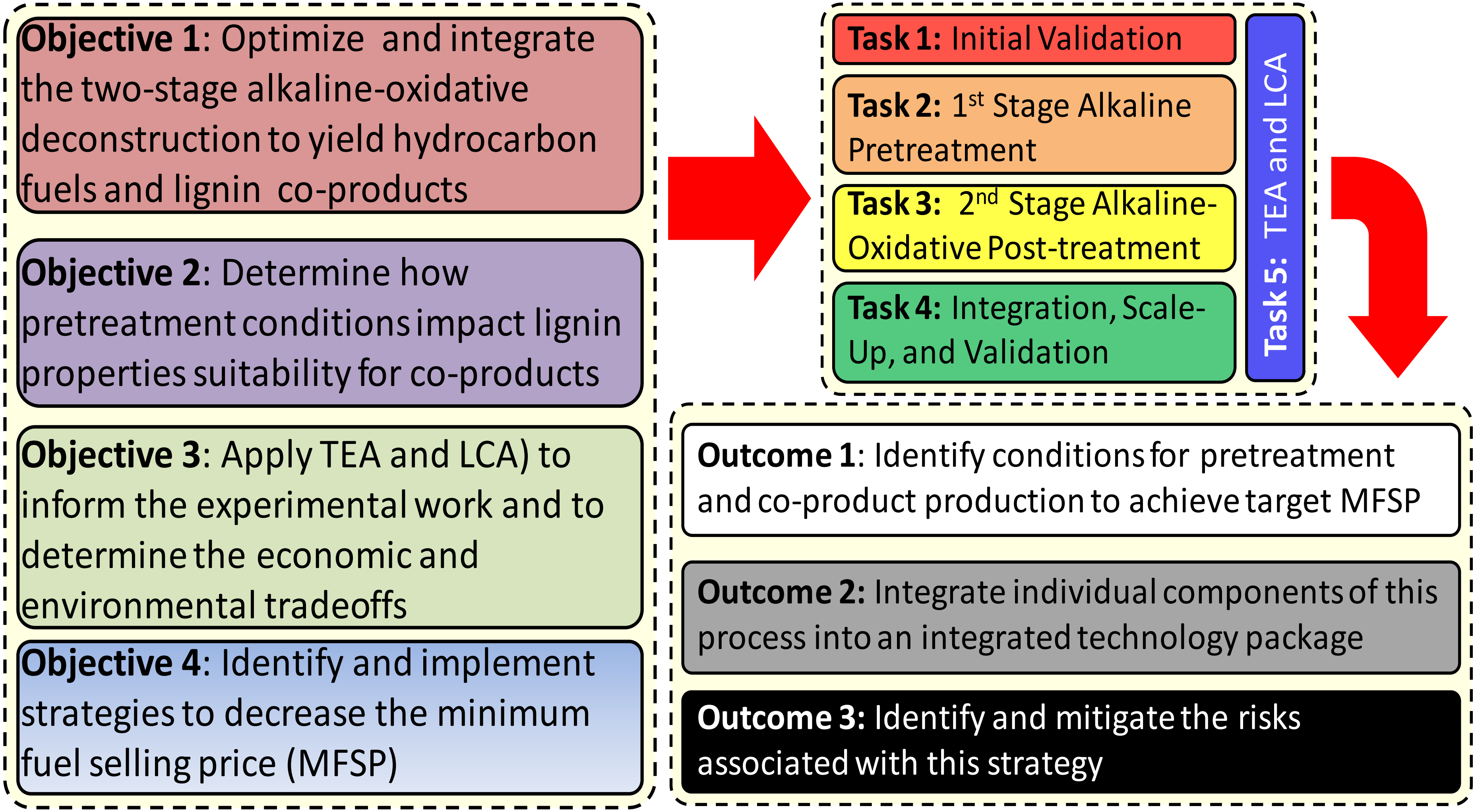
To accomplish these goals, we will:

- Optimize the two-stage alkaline-oxidative deconstruction system to generate both a sugar stream and a lignin stream.
- Reveal how pretreatment conditions impact lignin properties and how these properties can be linked to lignin suitability to co-product applications.
- Employ techno-economic and life cycle analyses to ascertain the tradeoffs between processing costs and environmental costs.
- Identify strategies to decrease the minimum fuel selling price by ~25% relative to our base case, thereby demonstrating that the goal of $3/GGE is attainable.

1 – Creative Advantage

- Multidisciplinary research team has proven expertise in chemistry, metallobiochemistry, catalysis, engineering, modeling, and lignin bioproducts
- Builds on previous DOE BER investments in fundamental research through Great Lakes Bioenergy Research Center (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 depolymerization of oxidized lignins by PI Stahl.
- Experience in technology de-risking

2 – Approach (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

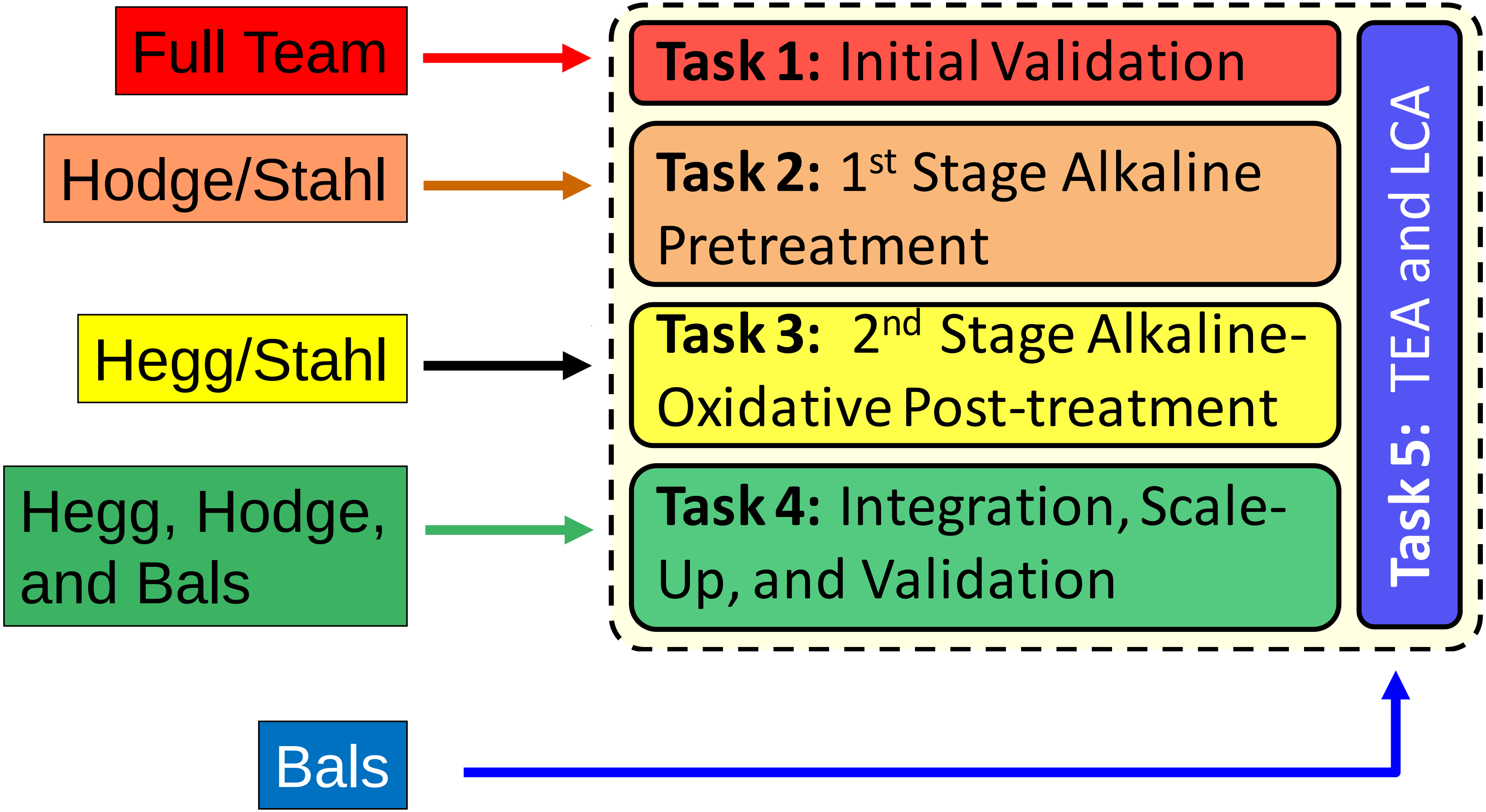
Task 5: TEA and LCA

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

2 – Approach (Management)



Full Team → Task 1: Initial Validation

Hodge/Stahl → Task 2: 1st Stage Alkaline Pretreatment

Hegg/Stahl → Task 3: 2nd Stage Alkaline-Oxidative Post-treatment

Hegg, Hodge, and Bals → Task 4: Integration, Scale-Up, and Validation

Bals → Task 5: TEA and LCA

2 – Approach (Management)

- PI Eric Hegg (Michigan State U.) coordinates the project (administration, performance, and reporting).
- Co-PI David Hodge (Montana State U.) helps to:
  - manage project personnel and collaborators
  - facilitate communication between project participants
  - establish clear accountabilities for delivery of objectives
  - ensure milestones are met and the project is on budget
  - coordinate re-focusing and resource reallocation if needed
- Bi-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

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 techno-economic and life cycle analyses
- Scale-up and demonstrate integrated performance of several “optimal” design cases based on balancing competing optima (technical, economic, environmental)
- Validate performance of the integrated system

Go/No-Go Decision Points

- Achieve ≥25% monomer yields from lignin precipitated from alkaline delignification stage (Q9)
  - If not met, focus will be shifted to utilizing recovered lignins directly as feedstock for polyurethane coatings and/or fuels
- Achieve a ~25% reduction in the MFSP (Q9)
  - If not feasible, shift our focus to optimizing the most promising single-stage pretreatment strategy
- Identify conditions that will achieve ≥30 wt% yield of depolymerized total lignin and ≥80% yield of purified sugar without increasing MFSP (Q10)
  - If not met, reiterate Cu-AHP optimization
- Complete integrated pretreatment scale-up and validation at ~20-L scale (Q39)

Technical and Non-Technical Challenges

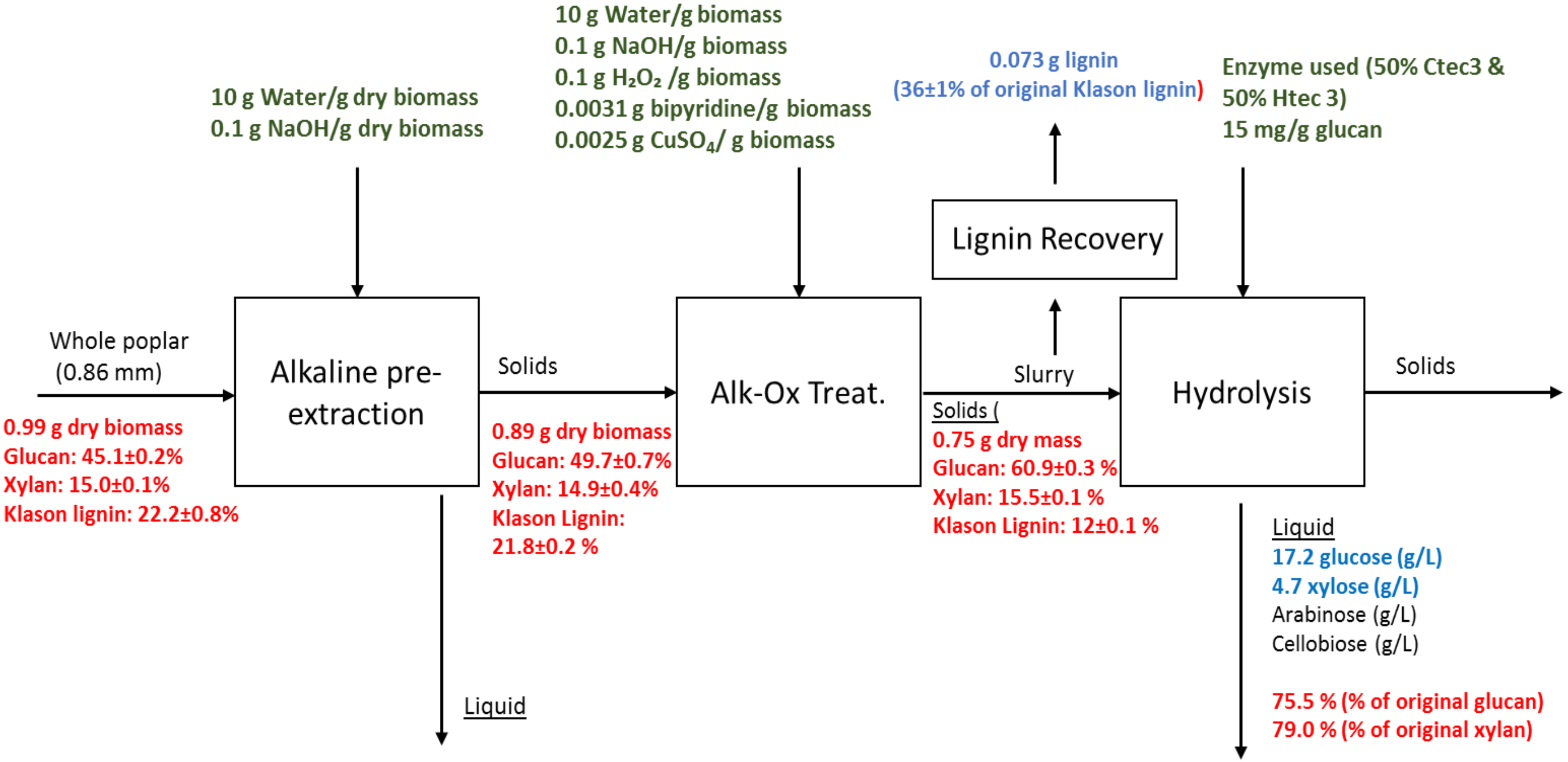
- Multiple PI locations
  - Increased emphasis on communication
  - Increase from bi-monthly team meetings to monthly
- Lowering the MFSP by increasing reaction temperature (thereby allowing us to lower reaction times and chemical inputs) has led to altered lignin properties
  - Re-optimized Cu-AHP reaction conditions (both alkaline delignification stage and alkaline – oxidative post-treatment stage)
  - Improved delignification strategies
  - Increased emphasis on polyurethane applications

3 – Results and Progress

- Suggestions raised by the validation team have been addressed
- Milestone completion is on schedule
- Progress on Tasks is on schedule
  - Task 1 – Validation
  - 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 1 – Validation

- Benchmarked both hydrolytic enzymes and reactors
- Developed SOPs for consistent storage and shipment of pretreated wet biomass



Whole poplar
(0.86 mm)

0.99 g dry biomass
Glucan: 45.1±0.2%
Xylan: 15.0±0.1%
Klason lignin: 22.2±0.8%

10 g Water/g dry biomass
0.1 g NaOH/g dry biomass

Alkaline pre-extraction

Liquid

Solids

0.89 g dry biomass
Glucan: 49.7±0.7%
Xylan: 14.9±0.4%
Klason Lignin: 21.8±0.2 %

10 g Water/g biomass
0.1 g NaOH/g biomass
0.1 g H_2O_2 /g biomass
0.0031 g bipyridine/g biomass
0.0025 g $CuSO_4$/ g biomass

Alk-Ox Treat.

Slurry

Solids (
0.75 g dry mass
Glucan: 60.9±0.3 %
Xylan: 15.5±0.1 %
Klason Lignin: 12±0.1 %

Lignin Recovery

0.073 g lignin
(36±1% of original Klason lignin)

Enzyme used (50% Ctec3 &
50% Htec 3)
15 mg/g glucan

Hydrolysis

Solids

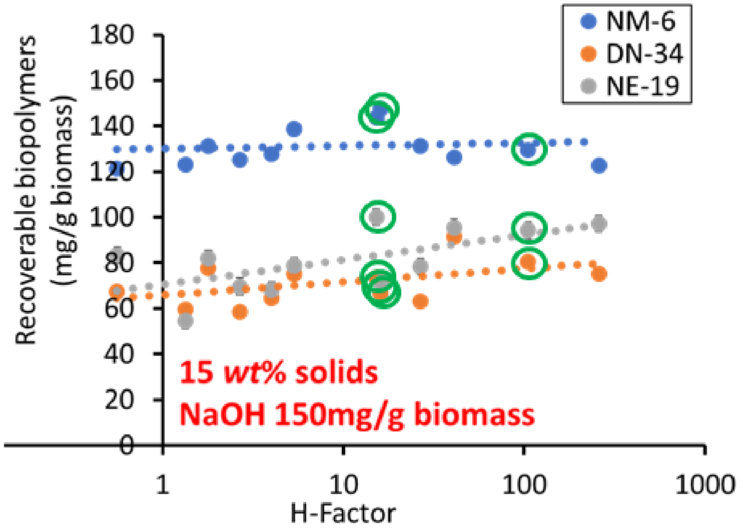
Liquid
17.2 glucose (g/L)
4.7 xylose (g/L)
Arabinose (g/L)
Cellobiose (g/L)

75.5 % (% of original glucan)
79.0 % (% of original xylan)

Validation phase successfully completed 12/31/2017

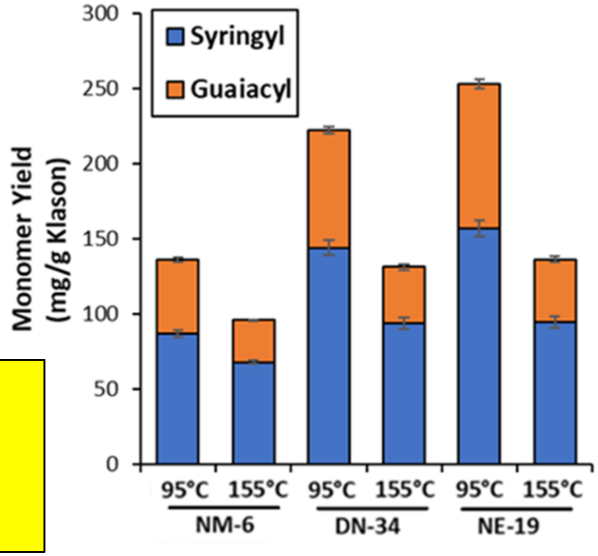
Task 2 – Alkaline Pre-Extraction

- Developed empirical models for delignification, precipitation yields, and composition as a function of severity factor.
- Identified down-selected set of conditions representing diverse levels of delignification, xylan removal, and hydrolysis yields for use in continued optimization work.
- Tested depolymerization of lignin subjected to extremes in H-factor using either (1) thioacidolysis or (2) formic acid and correlated lignin properties with extraction conditions.



H-factor parameter $= \int_o^t e\left(43.2-\frac{16117}{T}\right)dt$

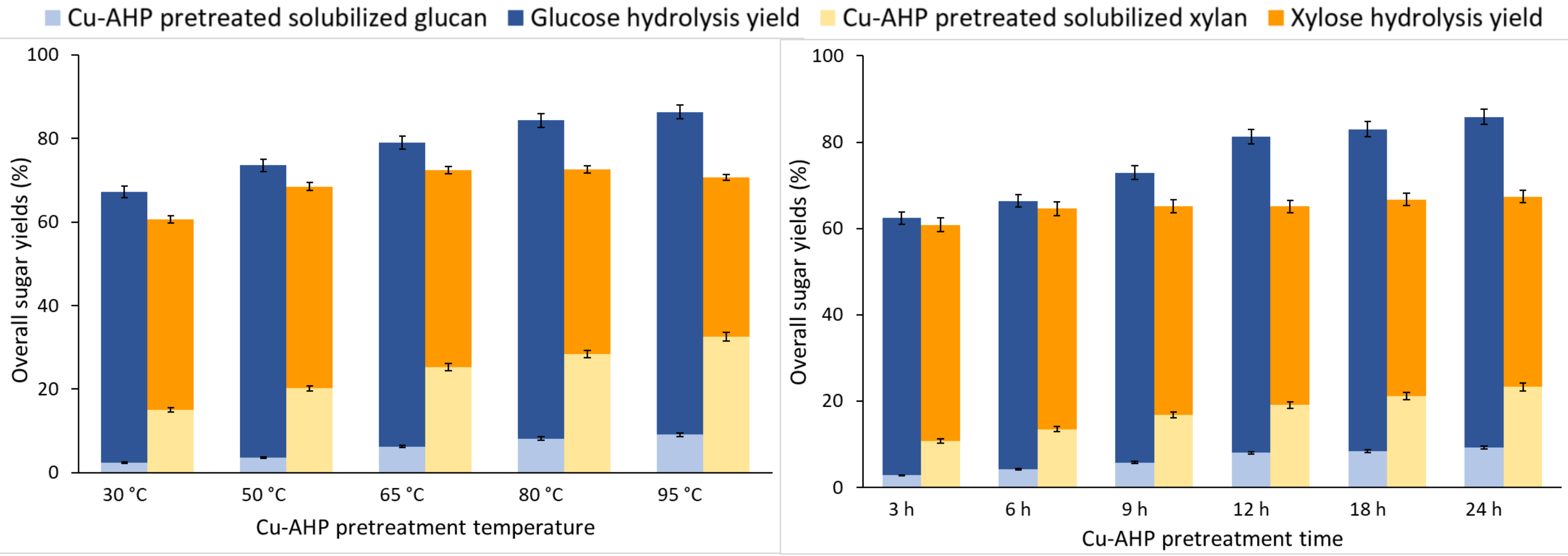
Where T =reaction temperature [K],and t =reaction time [h]



H-factor is a valuable tool to predict effect of pre-extraction conditions

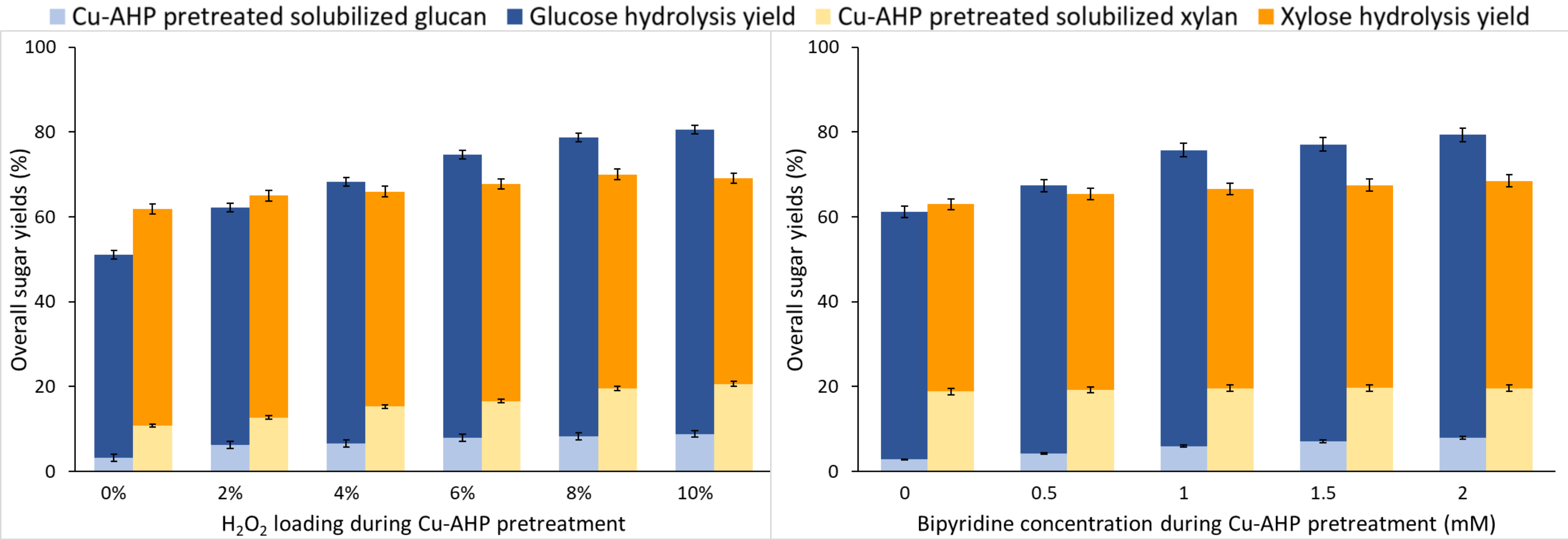
Task 3 – Alkaline Oxidative Post-Treatment

- Screened a number of Cu-AHP conditions
  - Alkaline pre-extraction: 10% solids, 10% NaOH loading on biomass, 120 ºC, 1 h
  - Base case for Cu-AHP: 10% NaOH on biomass, 1 mM $CuSO_4$, 30 ºC, 23 h, 10% w/w H_2O_2, 2 mM bipyridine



Enzymatic hydrolysis: 50 ºC, 15 mg protein per g glucan, pH 5, 72 h

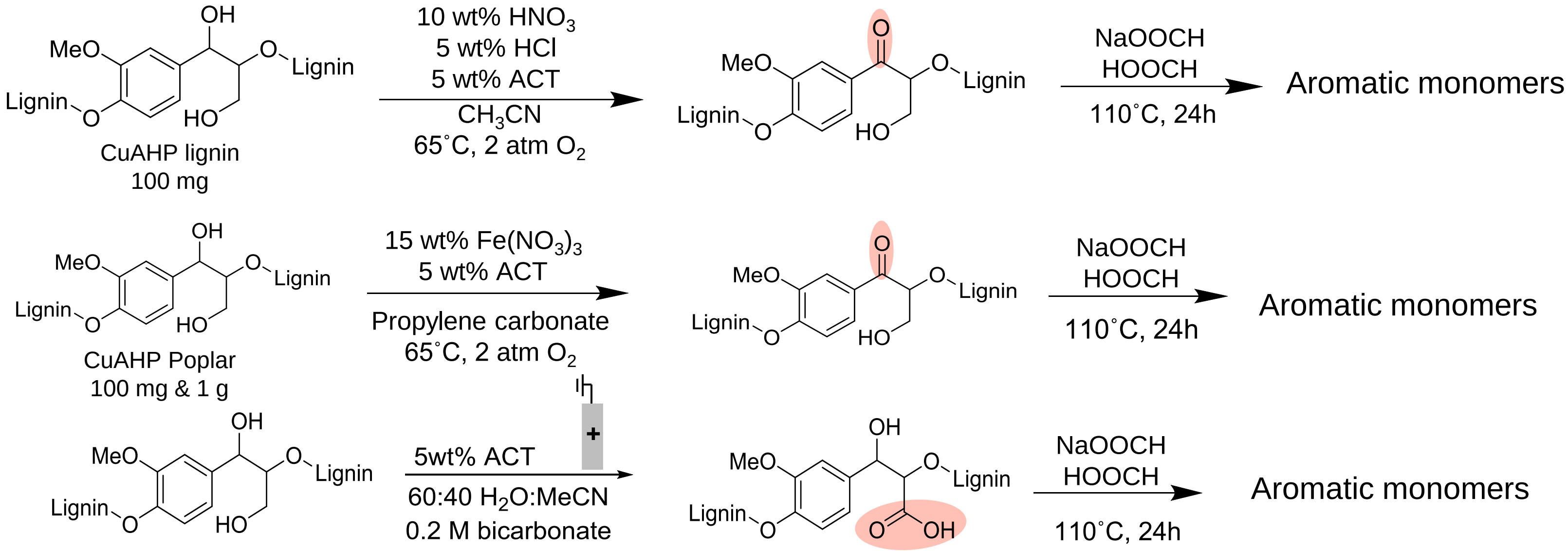
Task 3 – Alkaline Oxidative Post-Treatment



Enzymatic hydrolysis: 50 °C, 15 mg protein per g glucan, pH 5, 72 h

“Optimized” Cu-AHP conditions: 10% NaOH on biomass, 80 °C, 12 h, 6-8% w/w H_2O_2 on biomass, 1 mM $CuSO_4$, and 1 mM bipyridine

Tasks 2 & 3 -- Lignin Oxidation-Depolymerization



NOx/ACT Oxidation

CuAHP lignin
100 mg

10 wt% HNO_3
5 wt% HCl
5 wt% ACT
CH_3CN
65˚C, 2 atm O_2

NaOOCH
HOOCH
110˚C, 24h

Aromatic monomers

$Fe(NO_3)_3$ /ACT Oxidation

CuAHP Poplar
100 mg & 1 g

15 wt% $Fe(NO_3)_3$
5 wt% ACT
Propylene carbonate
65˚C, 2 atm O_2

NaOOCH
HOOCH
110˚C, 24h

Aromatic monomers

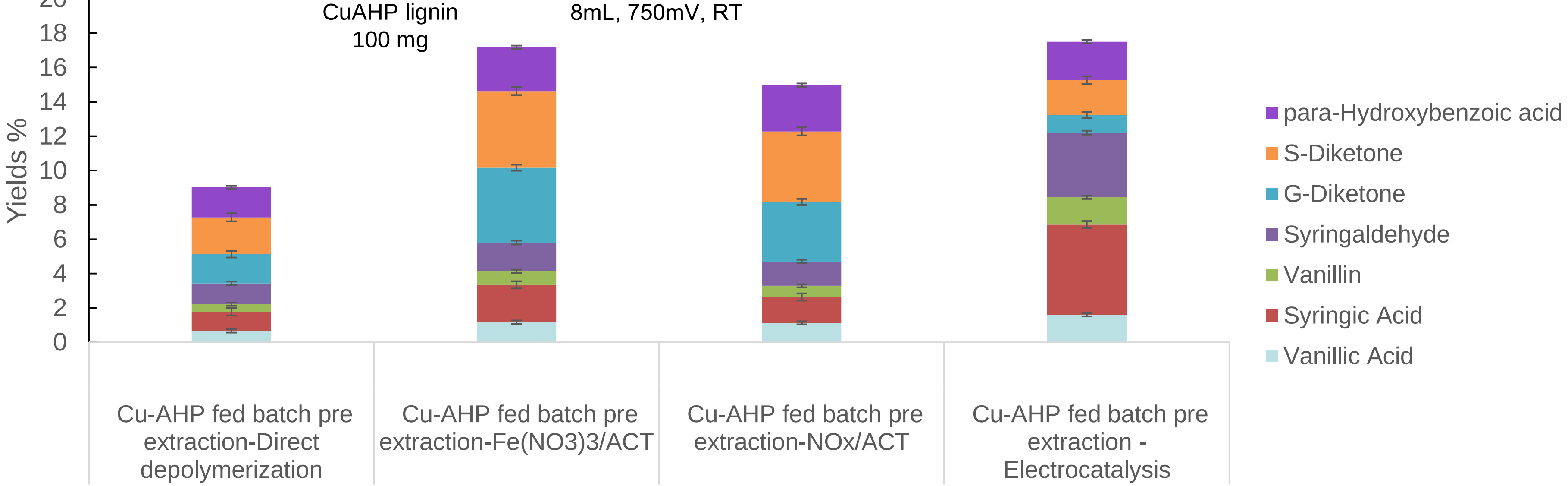
Electrocatalysis Oxidation

CuAHP lignin
100 mg

5wt% ACT
60:40 H_2O:MeCN
0.2 M bicarbonate
8mL, 750mV, RT

NaOOCH
HOOCH
110˚C, 24h

Aromatic monomers



Oxidative depolymerization shows improved monomer yields relative to direct depolymerization

Task 5 – Perform TEA and LCA

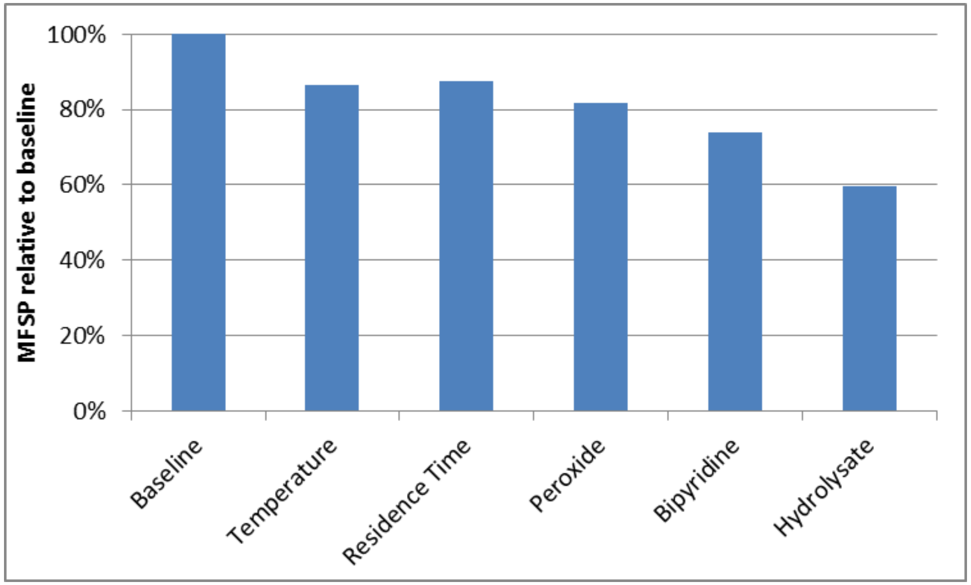
- Purpose: Support other tasks in decision making using economic and environmental analysis
- Method: Use Excel-based models for maximum flexibility as the project continues

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

- TEA model is in use, LCA model to be completed
- Sensitivity analysis confirms bipyridine usage and sugar yields as key economic indicators

Task 5 – Perform TEA and LCA

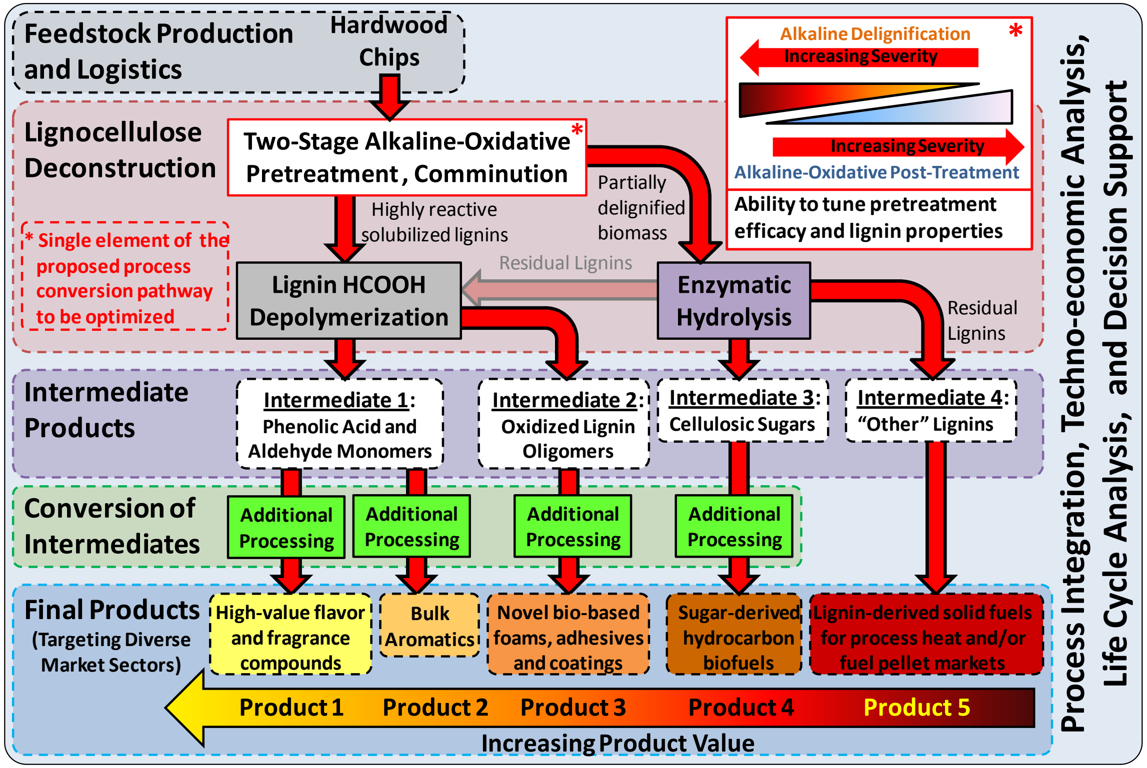
- Increase in lignin usage and pretreatment temperature eliminate electricity coproduct (will impact LCA more than TEA)
- Used TEA analysis to help identify optimal Cu-AHP pretreatment conditions



(Left) Changes to the minimum fuel selling price (MFSP) due to sequential changes in the Cu-AHP pretreatment process. Changes are 1) increasing temperature to 80°C, 2) decreasing residence time to 12 h, 3) reducing H_2O_2 loading to 6%, 4) eliminating bpy usage, 5) recovering solubilized pretreatment sugars during hydrolysis. Assumes constant lignin value.

4 – Relevance

- **Project Goal:** Optimize our two-stage Cu-AHP deconstruction process to generate both a clean sugar stream and lignins suitable for valorization.



Feedstock Production and Logistics

Hardwood Chips

Lignocellulose Deconstruction

Two-Stage Alkaline-Oxidative Pretreatment, Comminution*

* Single element of the proposed process conversion pathway to be optimized

Highly reactive solubilized lignins

Partially delignified biomass

Alkaline Delignification *

Increasing Severity

Increasing Severity

Alkaline-Oxidative Post-Treatment

Ability to tune pretreatment efficacy and lignin properties

Lignin HCOOH Depolymerization

Residual Lignins

Enzymatic Hydrolysis

Residual Lignins

Intermediate Products

Intermediate 1: Phenolic Acid and Aldehyde Monomers

Intermediate 2: Oxidized Lignin Oligomers

Intermediate 3: Cellulosic Sugars

Intermediate 4: "Other" Lignins

Conversion of Intermediates

Additional Processing

Additional Processing

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Additional Processing

Final Products (Targeting Diverse Market Sectors)

High-value flavor and fragrance compounds

Bulk Aromatics

Novel bio-based foams, adhesives and coatings

Sugar-derived hydrocarbon biofuels

Lignin-derived solid fuels for process heat and/or fuel pellet markets

Product 1 Product 2 Product 3 Product 4 Product 5

Increasing Product Value

Process Integration, Techno-economic Analysis, Life Cycle Analysis, and Decision Support

- **Importance & Relevance to Biofuels Industry:** Lignins suitable for depolymerization can feed multiple product streams and enable the economical viability of an integrated biofuels industry.

4 – Relevance

- The project builds on technology developed through the DOE Great Lakes Bioenergy Research Center
- Success will enable us to identify and design scenarios that employ operating conditions and mass allocation of lignin streams with the goal of supporting DOE EERE’s mission to enable production of $3/gasoline gallon equivalent (GGE) of hydrocarbon biofuels from biomass.
- This projects supports BETO’s mission, vision, and activities to “*develop a viable, sustainable domestic biomass industry that produces renewable biofuels and bioproducts; enhance U.S. energy security; reduce dependence on foreign oil; provide environmental benefits; and create nationwide economic opportunities*.”

5 – Future Work

- Continue assessing:
  - Sugar and lignin yields
  - Effect of reaction conditions on lignin properties and monomer yields following lignin depolymerization
  - TEA and LCA of various reaction scenarios
- Scale up, integrate, and validate most promising reaction configurations to ~20 L
- Lower MFSP by ≥ 25%
- Move our two-stage Cu-AHP pretreatment process from TRL-2 to TRL-5

6 – Summary

- Our 2-stage alkaline-oxidative Cu-AHP process is a promising pretreatment 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
- 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 ~26% relative to the base case.
  - Goal is lowering MFSP by ≥ 25% (to ~$3.15/GGE)

Additional Slides

Publications

- Zhaoyang Yuan, Sandip Kumar Singh, Bryan Bals, David B. Hodge*, and Eric L. Hegg*. "Combining Alkaline Pre-Extraction and Copper-Catalyzed Alkaline Hydrogen Peroxide Pretreatment to Enhance Enzymatic Hydrolysis of Hybrid Poplar." *Ind. Eng. Chem. Res.* Submitted.
- Sandip K. Singh, Anthony Savoy, Zhaoyang Yuan, Eric L. Hegg*, David B. Hodge*. "Biorefinery Alkaline Pre-extraction Process for High Efficiency Biopolymers Recovery: Extraction and Properties from Diverse Hybrid Poplar Cultivars " *Ind. Eng. Chem. Res.* Submitted.