DOE Bioenergy Technologies Office 2019 Project Peer Review

2.3.4.101 Oxidative Valorization of Lignin (OVL)

Xiao Zhang, PNNL

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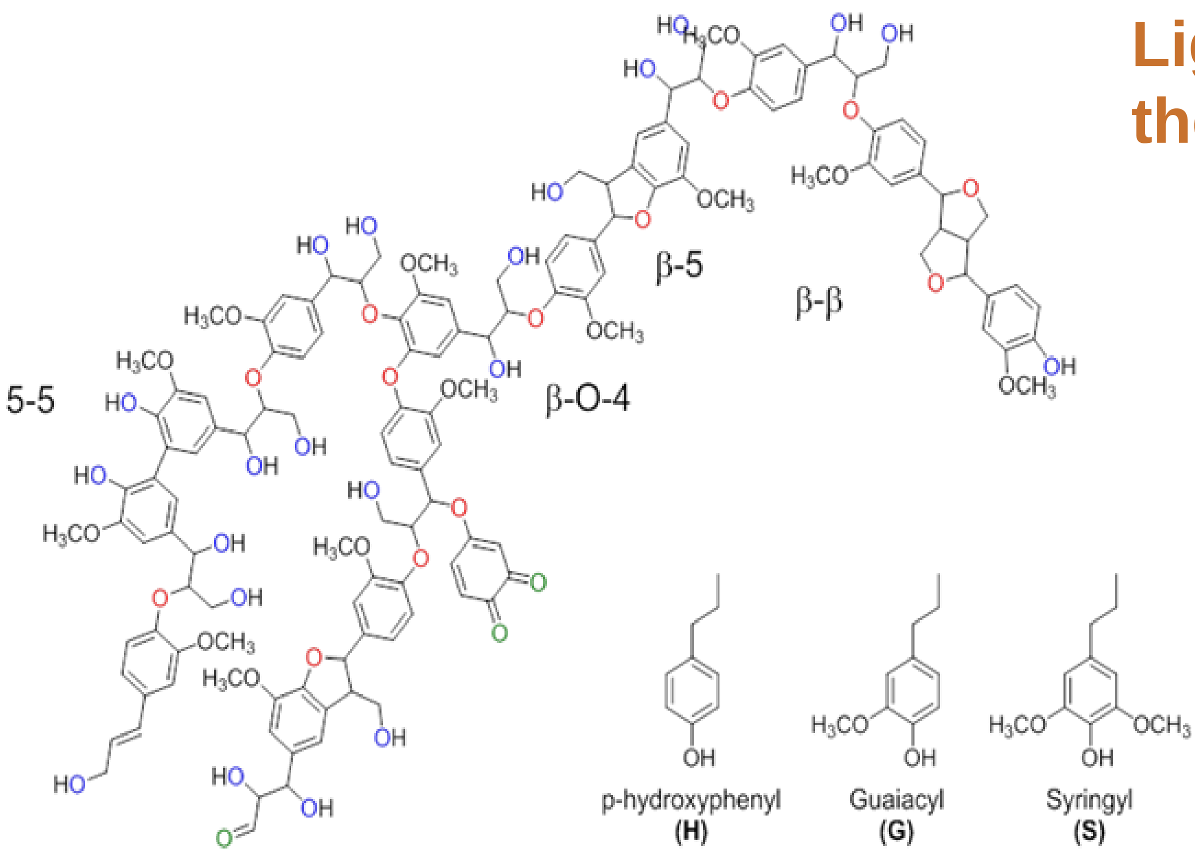
Challenges to economically viable lignin valorization technology

- Complete and efficient depolymerization of lignin
- Production of selective products
- Competition with existing market



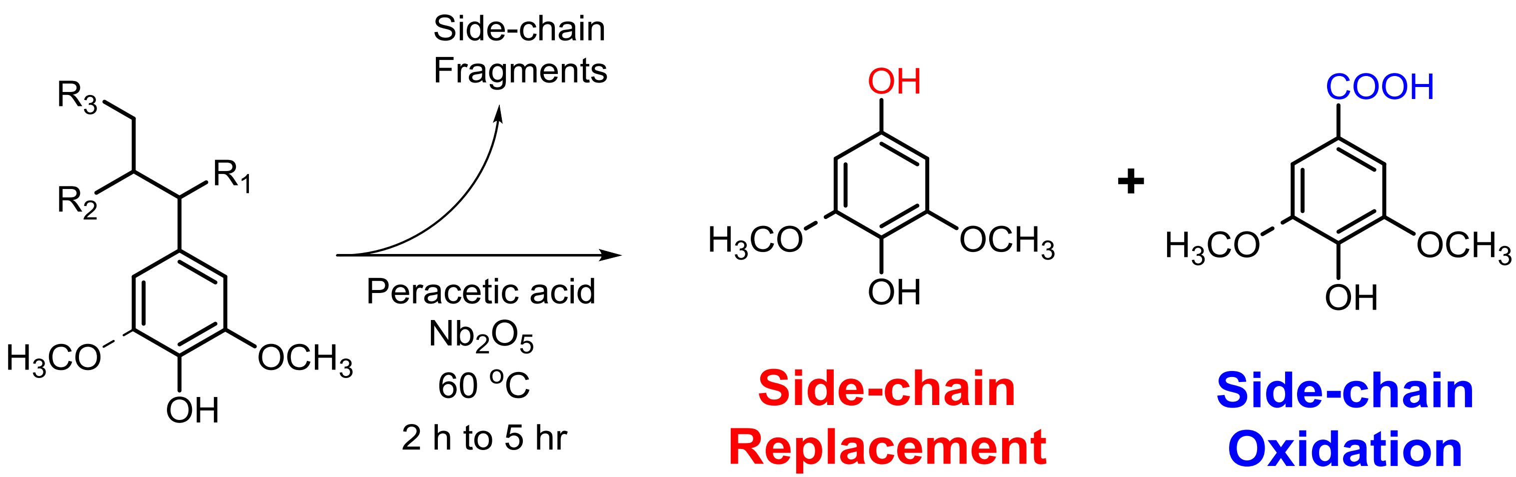
Lignin valorization is the key to the success of biomass refinery

- *Largest renewable source of aromatics.*
- *60+ MT from P&P industry.*
- *225 MT to be generated from biorefineries.*
- *Currently ~1.3 MT lignin based commercial products mostly with low price tag.*

*Need new chemistries and diversified product portfolio

Background:
Oxidative valorization of lignin (OVL):

- A **low capital conversion process** (T< 120°C, ATM) to depolymerize biorefinery lignin developed by PNNL/WSU.
- **Efficient and complete depolymerization** (within hours) of lignin.
- **Selected monomeric phenolic products** with a high yield (~47% wt).
- Applicable to all types of lignin (~ a dozen samples tested).



47% Combined MPC Yield
>85% Selectivity

*Economic cost associated with oxidant and catalyst consumption needs to be determined.

Goal statement

- Demonstrate an oxidative lignin conversion process to:
  - Help significantly reduce cellulosic hydrocarbon fuel cost
  - Generate critical foundational knowledge towards effective and complete depolymerization of lignin by catalytic oxidation technology

- **Specific target:** Overcome key economic barriers associated with:
  - High loading of catalyst(s): i.e. niobium pentoxide (Nb_2O_5)
  - High cost of oxidant: i.e. peracetic acid (PAA)

Baseline: 0.1 g Nb_2O_5 catalyst/g lignin and 1g PAA/g lignin

Quad Chart Overview

Timeline

- Project start date: October 2017
- Project end date: September 2020
- Percent complete: 50%

Barriers Addressed

- **Ct-C. Process Development for Conversion of Lignin:** provides an alternative route for lignin deconstruction and a pathway to produce value added chemicals
- **Ot-B. Cost of Production:** efficacy of various catalysts are tested to enable higher monomer yields to improve cost

Funding and Costs

	Total Cost Pre FY18	FY 18 Costs	FY 19 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	N/A	$167.5 k	$200 k	$400 k
Project Cost Share*				

•Partners: None

Objective

Develop catalytic routes for lignin depolymerization to monomers that are viable feedstocks for advanced/cellulosic biofuels and chemicals.

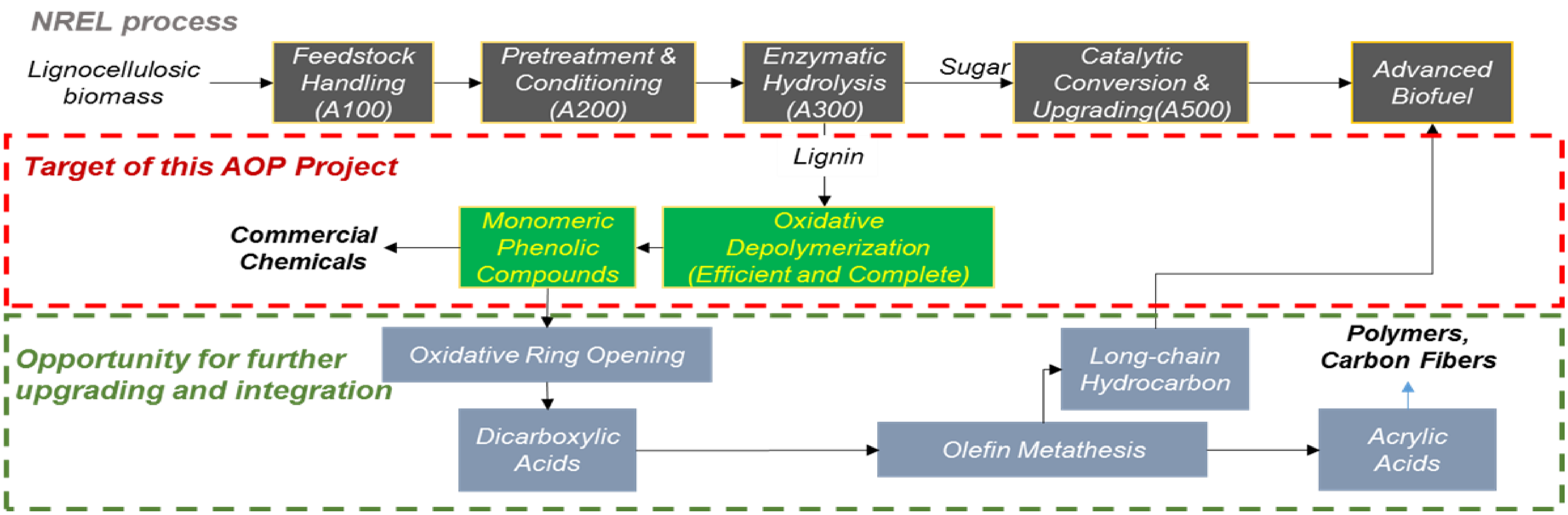
End of Project Goal

By 2020, **demonstrate the techno-economic feasibility of an oxidative lignin valorization technology** that has an overall yield of more than 60% to lignin monomers, while using lower catalyst loading (0.05 g/g lignin, Nb_2O_5 $ equivalent, oxidant concentration (0.2 g/g lignin PAA $ equivalent) and solvent recycle (1 mg acetic acid / g lignin)

Specific tasks towards project goal

1 – Project Overview

- Identify robust (efficient and low cost) **catalysts and optimize chemical reactions** to promote PAA depolymerization of lignin to selected monomeric phenolic compounds (MPC).
- **Elucidate mechanisms** of PAA-catalyst-lignin interactions.
- **Techno-economic analysis** of the oxidative lignin conversion process and its integration with a biochemical based biorefinery (e.g., NREL biorefinery process).



Collaboration and partnership

2 – Approach (Management)

Project Management
(BETO)
Dr. J. Fitzgerald

AOP Team
(PNNL)
Dr. R. Ma
Dr. MV. Olarte
Dr. AB. Padmaperuma
Dr. X. Zhang

Feedstock Supply
(NREL)
Dr. XW. Chen,
Dr. GT. Beckham

Stakeholders dissimilation
DOE, USDA, NSF, FAA

Feedback to NREL Biochemical Conversion Team
Dr. GT. Beckham
Dr. X. Chen

Analytical Support
(PNNL/EMSL)

Industry partners from chemical, automobile and forest products industries

Key milestones identified towards achieving project goal

2 – Approach (Management)

	FY 2018				FY 2019				FY 2020			
KEY MILESTONE	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1) Select one catalyst formulation, 47% MPC products yield, 0.1g catalyst/g lignin and 1 g PAA/lignin (QPM-R)												
2) Complete preliminary TEA (QPM-R)												
3) Demonstrate 25% MPC yield with low catalyst and PAA dosage (0.05 g catalyst/lignin and 0.5 g PAA/lignin) (AM-R)												
4) Elucidation of peracetic acid decomposition kinetics (QPM-R)												
5) Achieve lower oxidant loading, 0.3 g PAA/g lignin with 55% MPC yield (QPM-R)												
6) Deliver updated modeled TEA cost. (AM-R)												
7) Demonstrate 60% yield for lignin depolymerization to MPC, < 0.2 g PAA/g lignin ($ equivalent), 0.05 g Nb_2O_5/g lignin ($ equivalent), recycle = 1 mg acetic acid/g lignin (AM-R)												
8) Lower catalyst and oxidant consumption, 47% MPC yield, 0.05g catalyst/g lignin and 0.5g PAA/lignin, Go/No-Go						3/31/2019						

START DATE

TODAY

Legend: Red is achieved, Green is active and Blue is planned

Screen/identify effective and robust catalysts

2 – Approach (Technical)

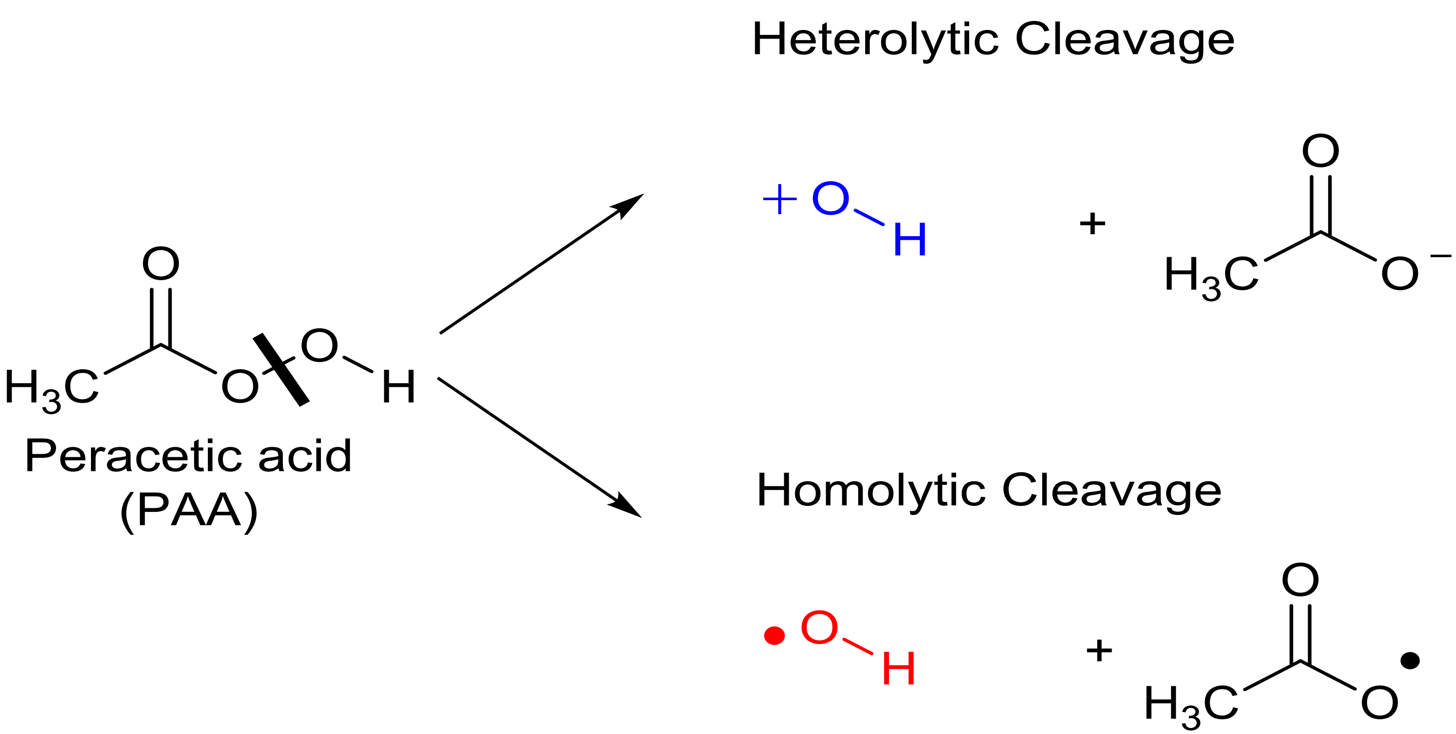
- Screen 32 catalysts (preparations) from four types of catalysts (metal oxide, mixed metal oxides, noble metal, organometallic).
  - Improve oxidation efficiency and reduce oxidant/catalyst cost.
  - Identify alternative oxidant (low cost oxidant).
  - Further improve products selectivity.
  - Two scales: ~ 50mg in COMBI and ~ 1g bench flask.

<u>Objective: Identify a lower cost catalyst while maintaining yield and selectivity of products</u>

Elucidate the mechanism of reaction chemistry to optimize conversion process
2 – Approach (Technical)

- Investigate the role of key reactive species (e.g. HO^+ and $HO^\bullet$) from peracetic acid (PAA) on lignin depolymerization.
- Determine the reactive species formation from PAA/catalysts in different solvents and under different reaction conditions.

<u>Objective: optimize reaction to minimize PAA consumption and maximize products yield and selectivity.</u>



Techno-economic analyses of OVL

2 – Approach (Technical)

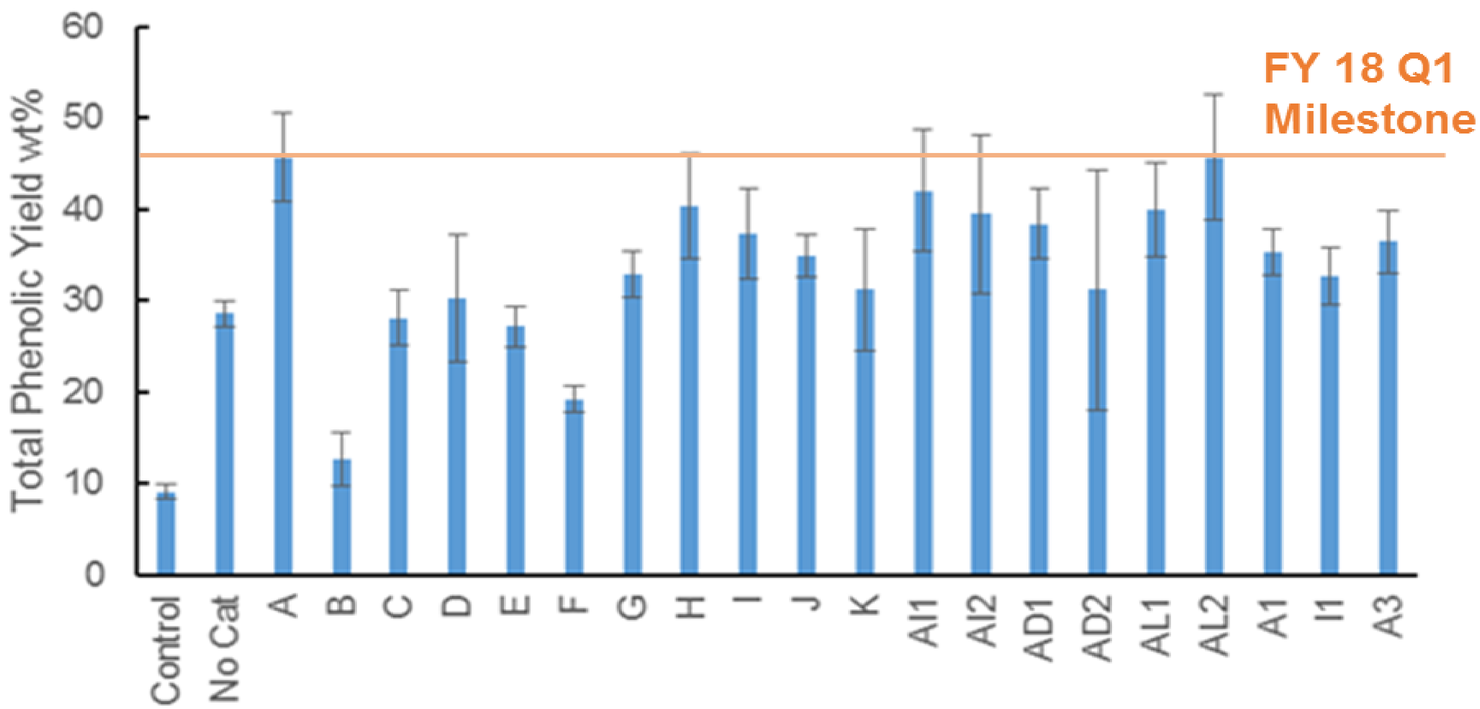
- Implement best analysis practices.
- Inform the catalytic and process development effort which technology aspects are cost drivers and require improvement.
- Evaluate alignment of lignin oxidative technology towards achieving modeled target economic costs for the biochemical platform.

Objective: Develop a techno-economic framework and sustainability metric for the oxidative lignin conversion process and its integration within the biochemical-based biorefinery.

Demonstrate high lignin monomer yields using lower cost catalyst

3 – Technical Accomplishments

- Identified a low cost catalyst preparation from 32 screened that can reach targeted 47% product yields (both COMBI and batch scale, FY18 Q1 & Q2 milestones completed).
- The remaining key cost driver: oxidant consumption by techno-economic analysis (FY18 Q3 milestone completed).

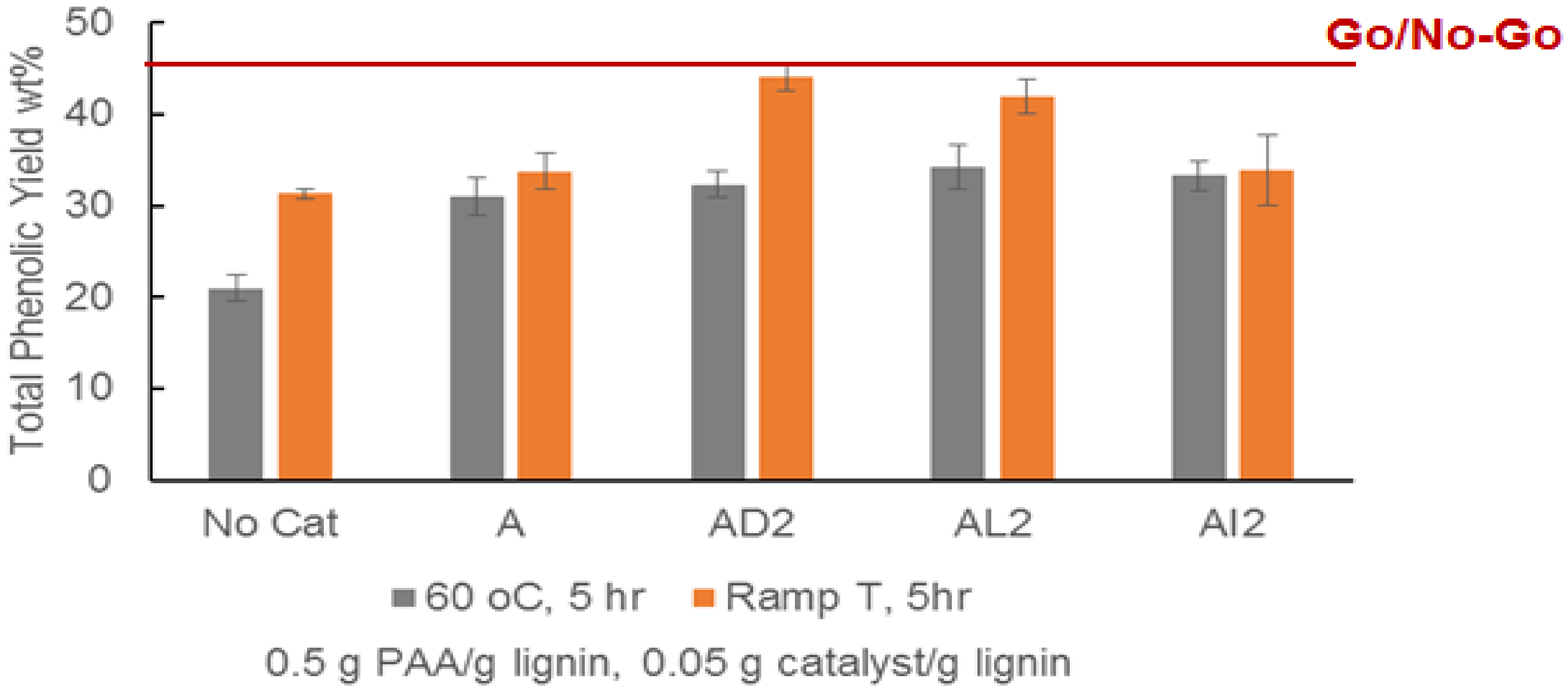


60 °C, 1 g PAA/g lignin, 0.1 g catalyst/g lignin

Demonstrate high lignin monomer yields using lower catalyst and oxidant loadings (both 50%)

3 – Technical Accomplishments

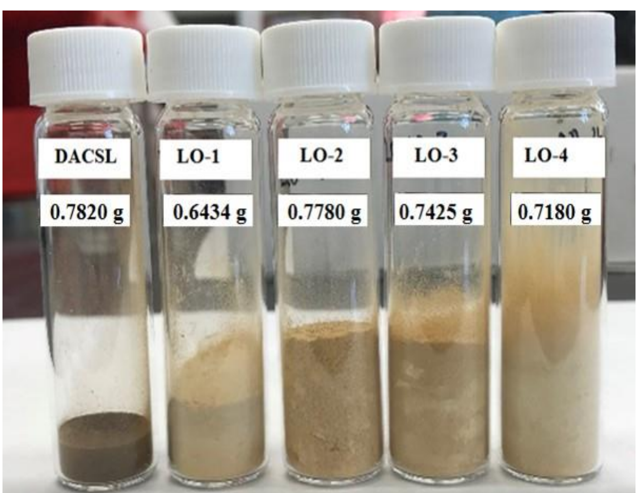
- Demonstrated that lignin depolymerization to MPC can be accomplished with lower catalyst and lower peracetic acid loadings (47% yield, 0.05 g Nb_2O_5 catalyst/g lignin and 0.5 g PAA/g lignin).
- Strengthened confidence to achieve Go/No-go (03/31/2019) target.



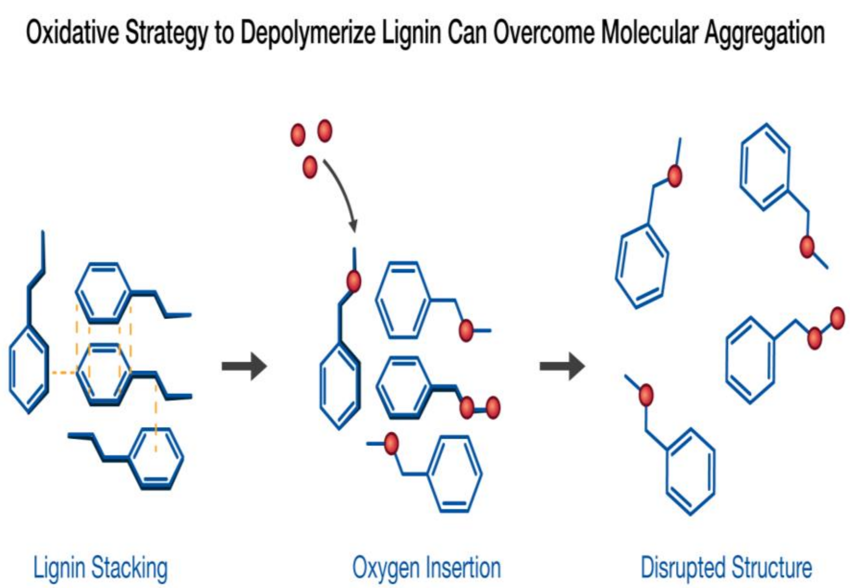
Discover for the first time that PAA can disrupt lignin macromolecular structures: a key factor to efficient depolymerization

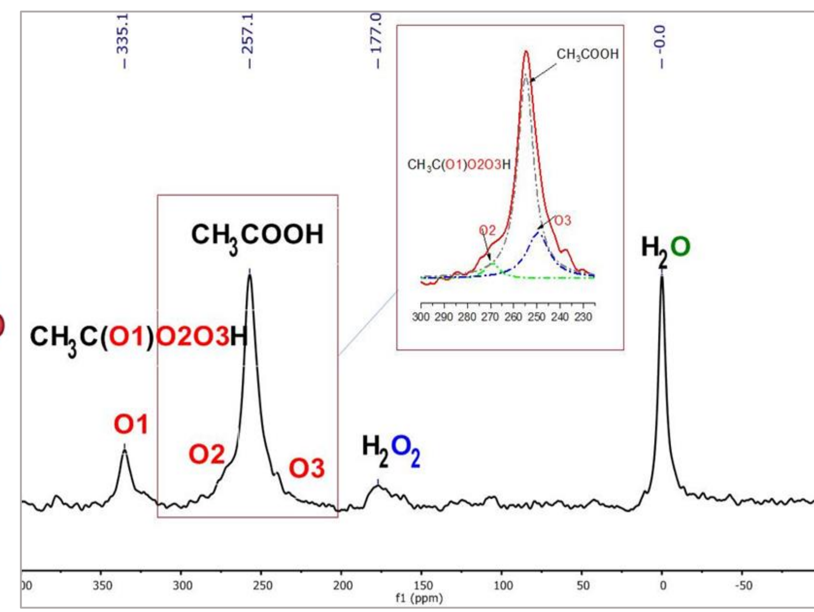
3 – Technical Accomplishments

- Revealed the ability of PAA to disrupt lignin macromolecular structures and facilitate the subsequent depolymerization.
- First to apply a combination of NMR techniques to enable the identification and quantification of HO^+ and $HO^\bullet$ from peracetic acid (PAA).



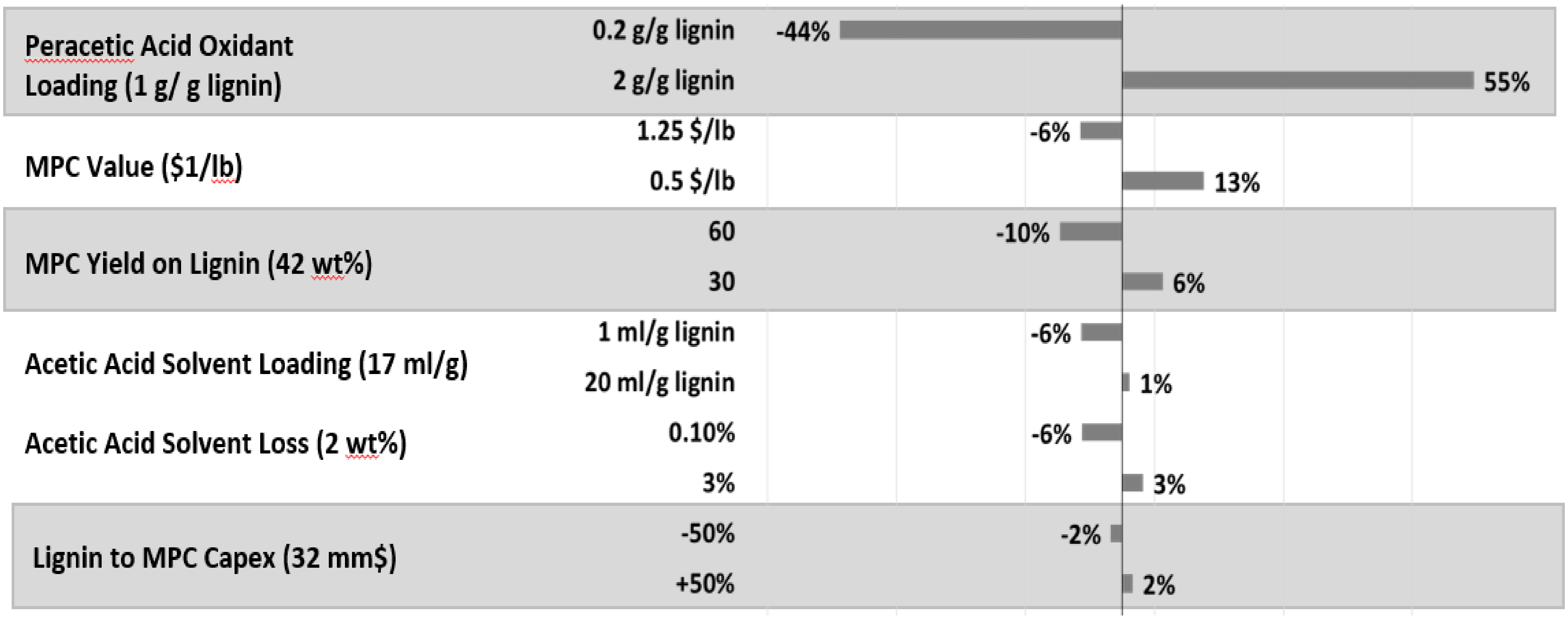
Partially oxidized lignin by 0.2 g PAA/g of lignin treatment of CSL at room temperature for a period over 0-18 hours.





Techno-economic evaluation confirms oxidant is primary cost driver toward economically feasible lignin oxidation process

3 – Technical Accomplishments



% Change in Minimum Fuel Selling Price from SOT ($8.6/gge)
(numbers at left in parenthesis are the SOT values)

*Optimize oxidative valorization of lignin (OVL) process may help reduce modeled (fuel) cost toward $3/gge

Pacific Northwest NATIONAL LABORATORY

Oxidative valorization of lignin directly supports DOE/BETO mission and goal

4 – Relevance

- Vision 2040: A thriving and sustainable bioeconomy fueled by innovative technologies
- Mission: Developing and demonstrating transformative and revolutionary sustainable bioenergy technologies for a prosperous nation.

Direct Support BETO's

Missions and Goals

Address Out-year Research Target

Address Technical Challenges and Barriers:

- New pathways to deconstruct lignin into tractable streams…
  - Catalysts can funnel lignin into streams of tractable intermediates…

OVL at PNNL

Support BETO Strategic Plan 2016-2022

Interact with Other National Laboratory

- Support BETO 2016-2022 Strategic Plan.
- Strategy: Reduce Cost and Improve Performance
- Substrategy: Develop Robust Technologies To Convert Waste Streams to Fuels and Chemicals

•Synergizing with other national lab's projects on lignin conversion

•Leverage Outcome from other national lab's projects e.g. Feedstocks (NREL, INL)

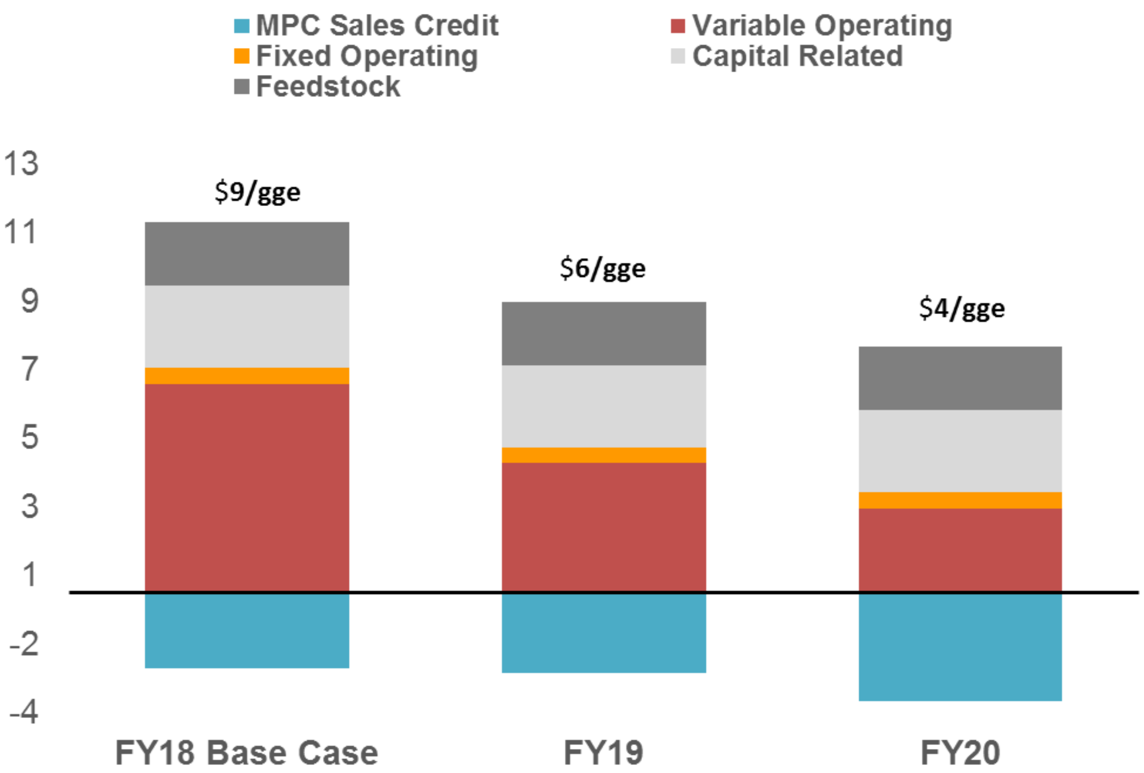
Advancing the state of technology: research efforts resulted in ~28% reduction in FY19 modeled cost

4 – Relevance

Decreasing biofuel cost through lignin conversion to valuable co-products

- Metrics and technical targets identified through data driven TEA.
- Enabled focused research to:
  - Reduce oxidant loading (a major cost driver).
  - Improve lignin conversion
  - Develop less expensive catalysts.
- Significant cost reduction achieved last year.

	FY18 Baseline	FY19 Current	FY20 Target
Catalyst Cost ($/lb)	60	**32.5**	**30**
Oxidant (g/g lignin)	1	**0.5**	**0.2**
wt% Lignin to MPC	42%	**44%**	**60%**

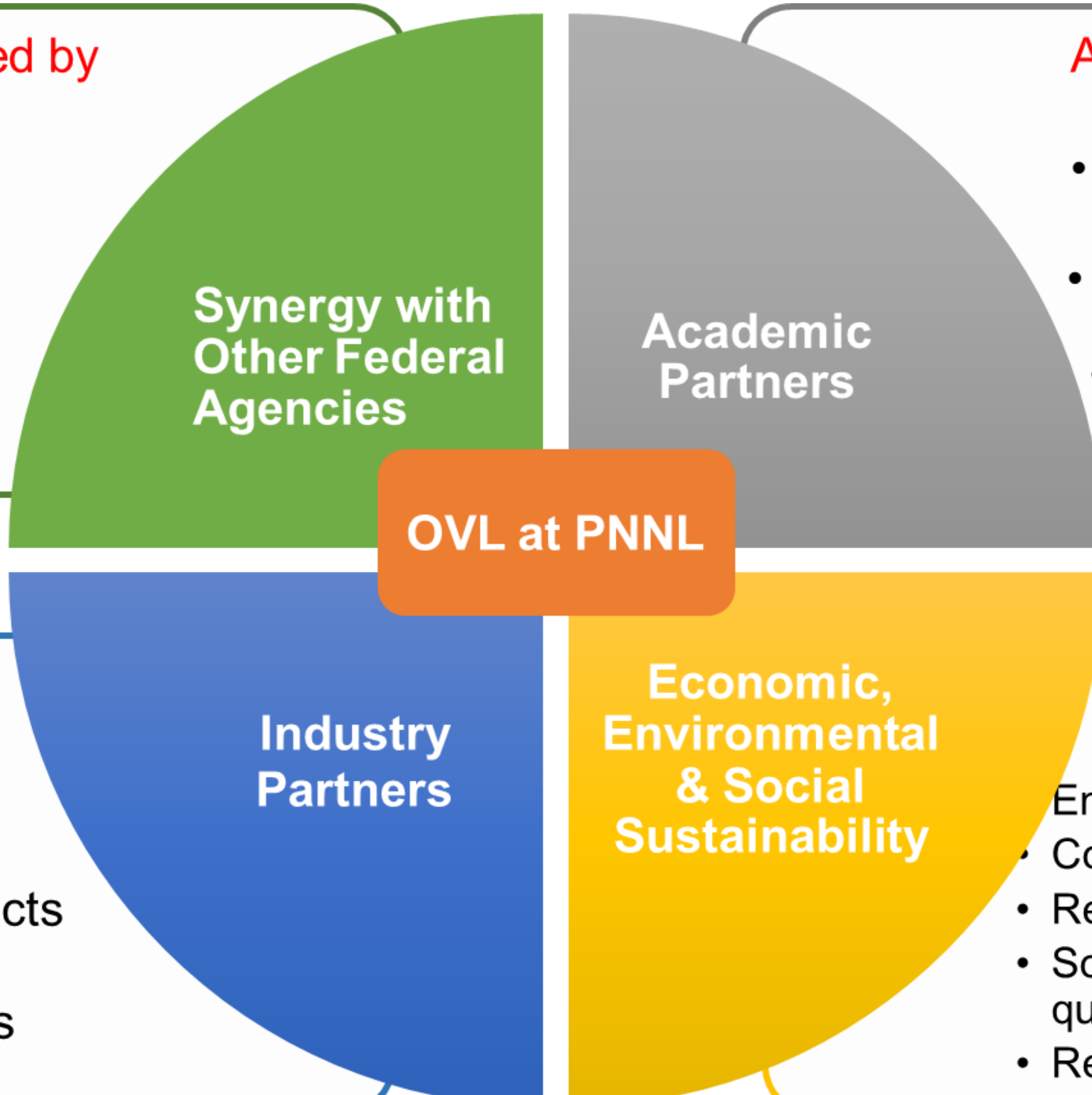


Broader impacts of oxidative valorization of lignin: synergy with stakeholders in biorefinery

4 – Relevance

Projects funded by other federal agencies
- NSF
- USDA
- US DOT
- FAA

Academic/research institutions
- Washington State University
- Auburn University
- University of Wisconsin-Madison
- USDA FPL



Industry
- Chemical
- Forest Products
- Automobile Manufactures

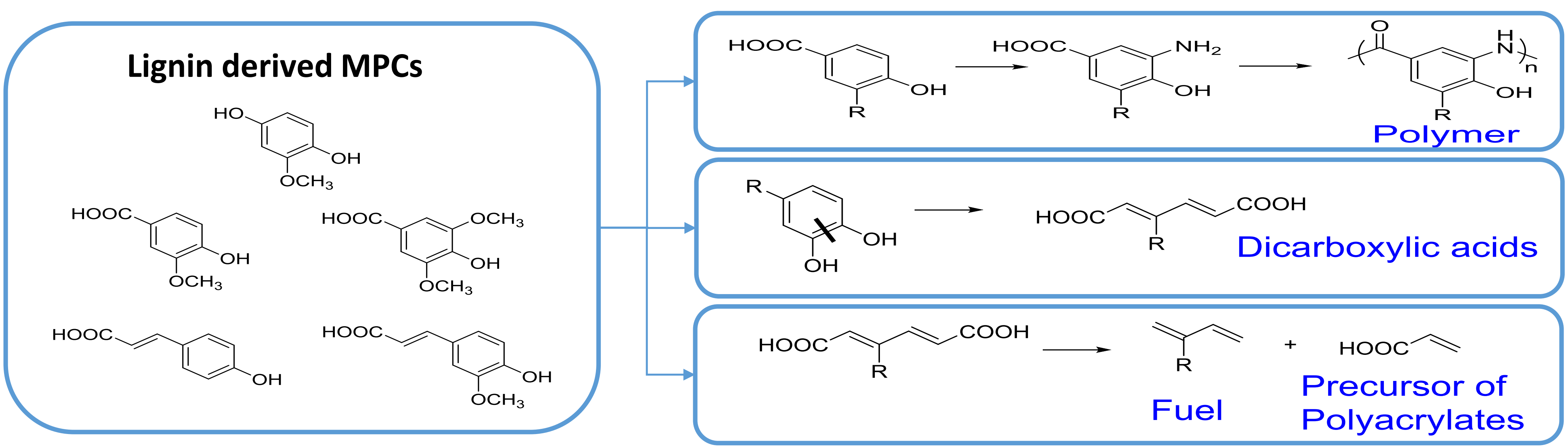
- Environmental impact
- Commercial viability
- Reduce GHG emission
- Soil, water and air quality
- Resource conservation

Advance oxidation valorization of lignin technology and expand new co-products opportunity

5 – Future Work

- Further reduce PAA loading to 0.2g/g lignin.
- Identify alternative oxidant with low cost compare to PAA.
- Optimize reaction conditions to improve MPC yield.
- Monomeric phenolic compounds conversions to biopolymers (with WSU).
- Monomeric phenolic compound upgrading to fuel and acrylates (with WSU).

Expand new co-products opportunity

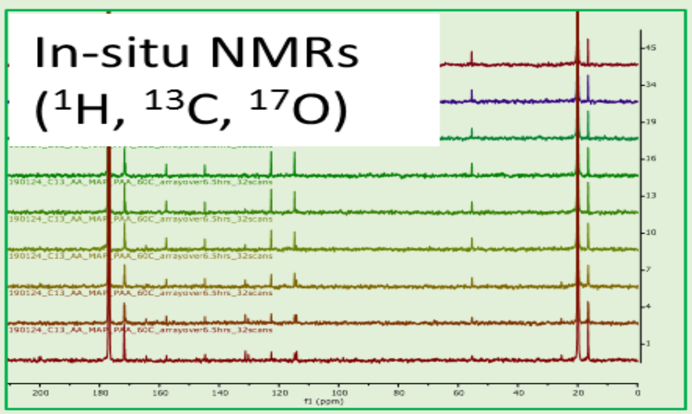


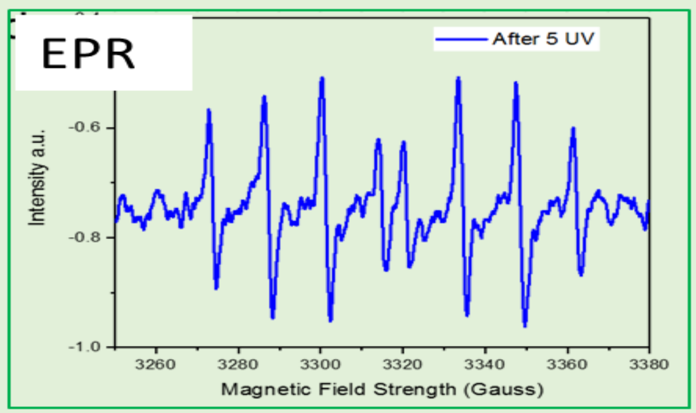
Delineate reaction mechanism to optimize OVL process and complete TEA analyses

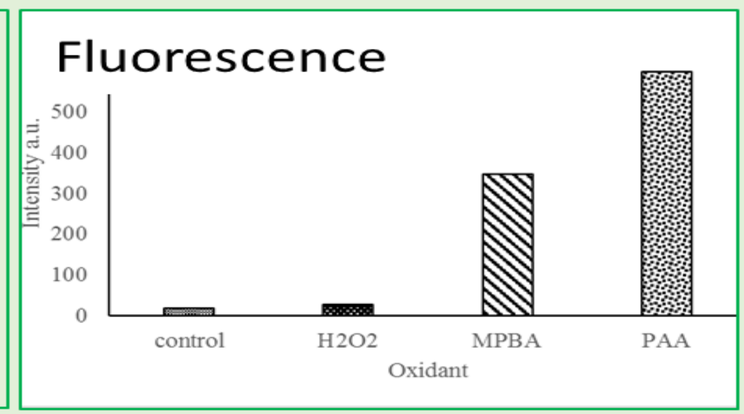
5 – Future Work

Key to the success: maximize the formation and stability of HO$^+$ during depolymerization

- NMR to detect and quantify HO$^+$ during PAA-catalyst interaction
- EPR to differentiate HO$^+$ and HO•.
- Thioamide based fluorescence method to monitor [HO$^+$] during reaction.
- Understand the factors influencing reactive species formation (catalysts, solvent, temp).







Outcome:

- Deliver an efficient and cost competitive lignin valorization technology enabling a commercially viable lignocellulosic biomass to hydrocarbon conversion process

Future project milestones

5 – Future Work

- Batch scale testing to verify and confirm the performance of the selected catalyst/solvent systems based on the findings of the previous quarters to reduce modeled cost *(FY19)*.
- Further improve MPC production toward 60% conversion yield of MPC with low oxidant cost *(FY19)*.
- Test the lignin oxidation process on different types of lignin streams from other labs to confirm technology robustness *(FY19 & FY20)*.
- Upgrade lignin derived monomeric phenolic compounds and dicarboxylic acids to specialty chemicals and hydrocarbon fuel to produce value-added commercial products *(FY20).*
- Conduct detailed Techno-economic evaluation (TEA) and life cycle analyses (LCA) of the oxidative lignin conversion process and its integration with a biochemical-based bio-refinery to analyze economic feasibility of the whole technology *(FY20)*.

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Summary

Overview

Oxidative valorization of lignin (OVL) presents a promising approach to convert biorefinery lignin to marketable chemicals.

Approach

- Screen low cost catalyst, optimize chemical reactions
- Elucidate mechanisms of PAA-lignin-catalyst interactions
- Conduct techno-economic analysis to provide guidance

Technical Progress

- Reduced both catalyst and oxidant cost by ~ 50% while maintaining product yield and conversion efficiency
- Established new techniques to investigate PAA-lignin-catalyst interactions
- Gained new understanding of PAA interaction with lignin

Relevance

- New pathways toward sustainable biofuel/bioproducts production
- Efficient and cost effective technology toward lignin depolymerization
- Synergy with stakeholders in biorefinery development

Future Work

- Further reduce process cost and improve product yield
- Upgrade lignin-derived monomeric phenolic compounds
- Complete TEA: OVL process and its integration with a biochemical-based bio-refinery

Thank you

BETO
Jay Fitzgerald (BETO)

NREL
Xiaowen Chen (NREL)
Gregg T. Beckham (NREL)

PNNL
Ruoshui Ma
Sue Jones
Heather M. Job
John R. Cort
David W. Hoyt
Corinne Drennan
Mariefel V. Olarte
Marie S. Swita
Eric D. Walter
Mark Bowden
Asanga B. Padmaperuma

Additional Slides

Responses to Previous Reviewers' Comments

New project with a start date of 10/01/2017

Publications, patents, presentations, awards, and commercialization

Publications

- Ma R., M.V. Olarte, H.M. Job, M.S. Swita, S.B. Jones, S.D. Burton, and J.R. Cort, et al. 2019. "Catalytic Oxidative Lignin Depolymerization by Peracetic Acid." *In preparation.* PNNL-SA-140523. Manuscript in preparation

Presentations

- Ma R., M.V. Olarte, H.M. Job, and X. Zhang. 08/21/2018. "Oxidative valorization of lignin." Presented by R. Ma at Post Graduate Symposium - Lightning Talks, Richland, Washington.
- Ma R., M.V. Olarte, H.M. Job, and X. Zhang. 08/08/2018. "Catalytic Oxidation of Biorefinery Lignin to Value-Added Platform Chemicals." Presented by R. Ma at Gordon Research Conference-Lignin, Easton, Massachusetts. PNNL-SA-137676.
- Ma R., M.V. Olarte, H.M. Job, and X. Zhang. 06/24/2018. "Catalytic Oxidation of Biorefinery Lignin to Value-Added Platform Chemicals." Presented by R. Ma at American Chemical Society Northwest Meeting. Richland, Washington. PNNL-SA-135881.