

Lignin Utilization

Technology Session Review Area: Biochemical Conversion & Lignin Utilization

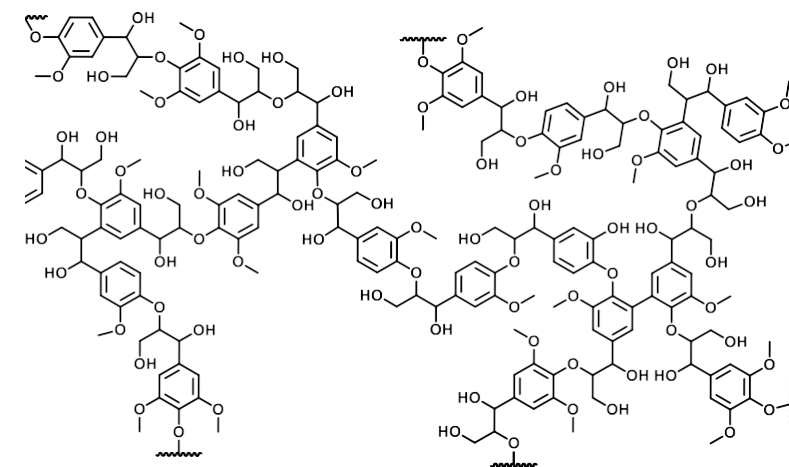
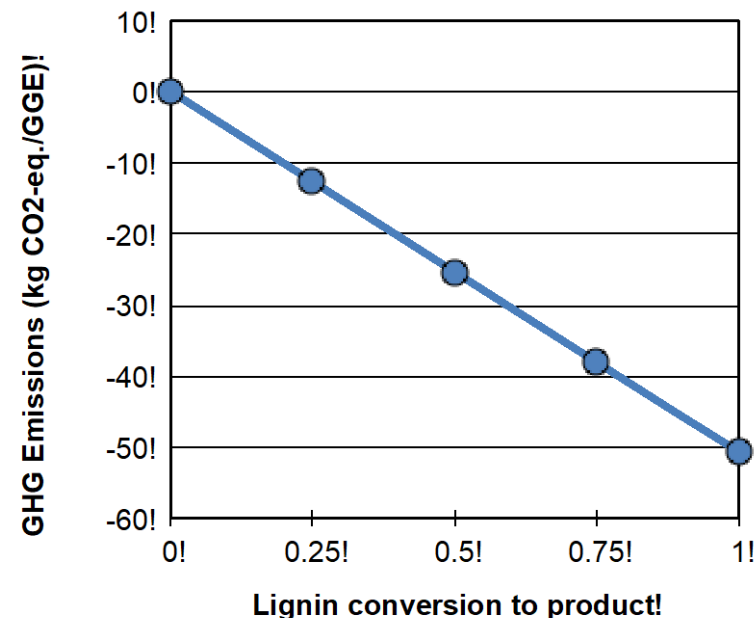
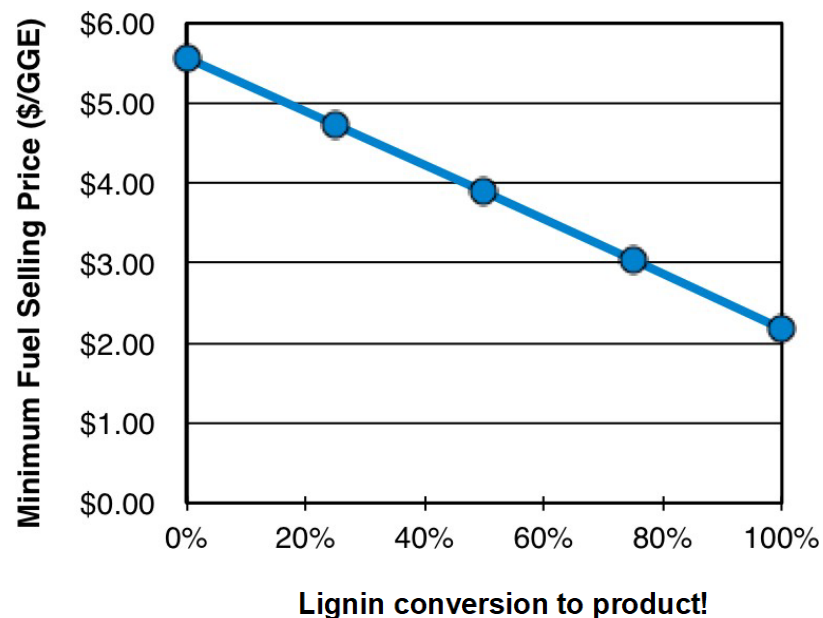
PI: Gregg T. Beckham, National Renewable Energy Laboratory

Goal: Develop industrially-relevant processes and tools for viable lignin valorization – contribute \$2-3/gge to MFSP

- Develop deconstruction catalysts for C–C bonds in lignin
- Provide deconstructed lignin to bioconversion efforts
- Develop lignin analytics and model compound syntheses
- Support lignin projects in the BETO/DOE portfolio (Biological Lignin Valorization (BLV), LigFirst, ORNL project, SepCon, Bioenergy Research Centers, etc.)

Heilmeyer Catechism:

- **Aim:** develop lignin depolymerization catalysts and analytics for accurate process metrics
- **Today:** lignin combusted for heat, C–C bonds are major hurdle, analytics mostly monomers only
- **Important:** lignin key for biorefinery TEA and LCA
- **Risks:** C–C cleavage and quantitative lignin analytics are both challenging



Management

Task 1: Analytics and Synthesis

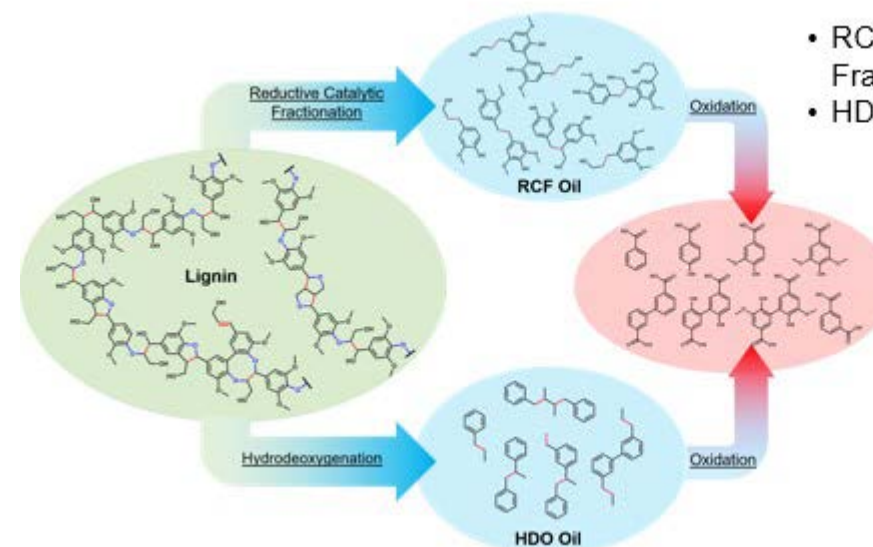
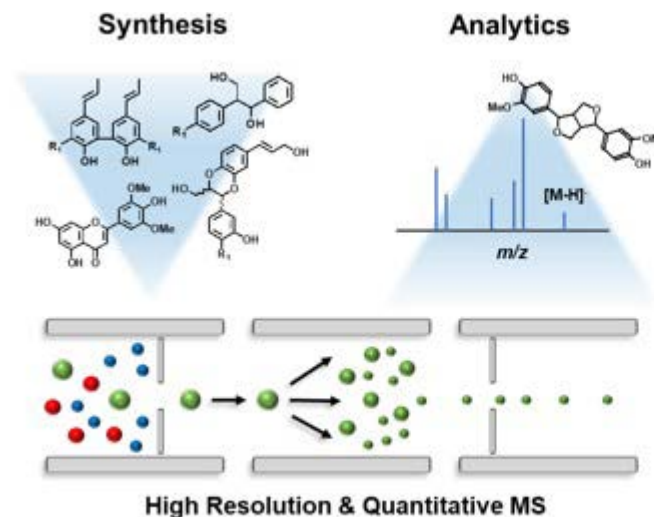
- Experts in synthesis (R. Katahira) and analytics (B. Black)
- Milestones: **lignin characterization tool development, model compound synthesis**
- Collaborate with multiple projects – support BETO lignin portfolio for analytics and models

Task 2: Depolymerization

- Experts in oxidation catalysis (X. Du, C. Palumbo, K. Sullivan) and chemical engineering (J. Kruger)
- Milestones: **usable monomer yield** from **oxidative** catalytic deconstruction processes
- Milestones: **reaction/process engineering, TEA/LCA** with Biochem. Analysis, integration with BLV project

Project organization:

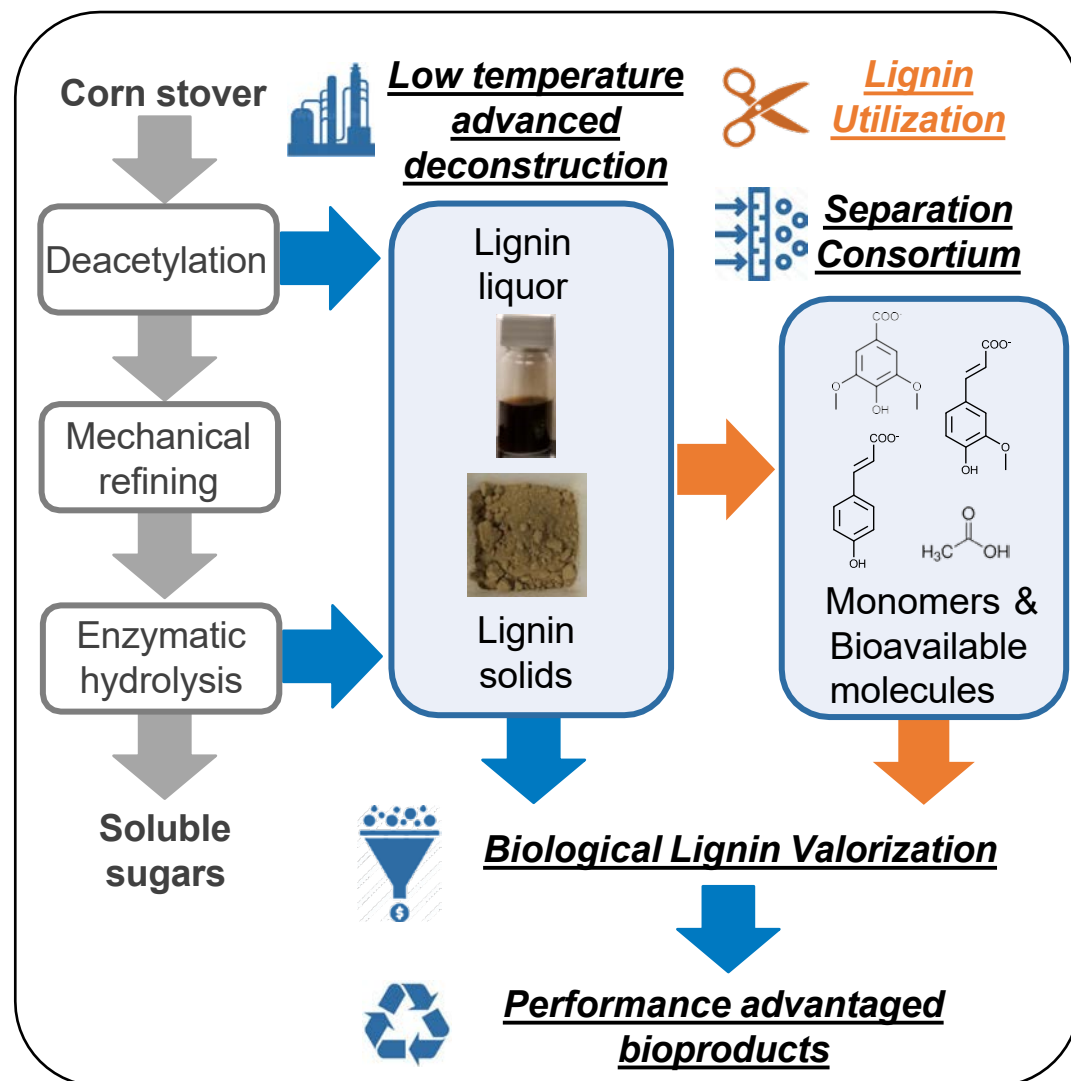
- Monthly meetings for catalysis and analytics
- Monthly 1-on-1 mtgs with PI, staff, postdocs
- *Ad hoc* meetings with Lignin-First Biorefinery Development, Biological Lignin Valorization, SepCon, Analysis, and other projects
- Ops and Project Managers – labs, equipment, reporting, and finances



- RCF = Reductive Catalytic Fractionation
- HDO = Hydrodeoxygenation

Management: Project interactions

Projects interchange



We have established a network of lignin-related projects with Lignin Utilization as the central project

- Provide analytics development and support, model compound syntheses, and central lignin valorization platform for:
 - Lignin-First Biorefinery Development
 - Biological Lignin Valorization
 - Low-Temperature Advanced Deconstruction, Feedstock-Conversion Interface Consortium
 - Synthetic Metabolic Pathways for Bioconversion of Lignin Derivatives to Biofuels– ORNL
 - Synthesis and Analysis of Performance-Advantaged Bioproducts
 - Separations Consortium

Risks:

- Oxidative C–C bond cleavage is an inherently challenging reaction
- Oxidative reactions with lignin often lead to undesired side reactions
- Quantitative lignin analytics long pursued, not definitively/generally demonstrated

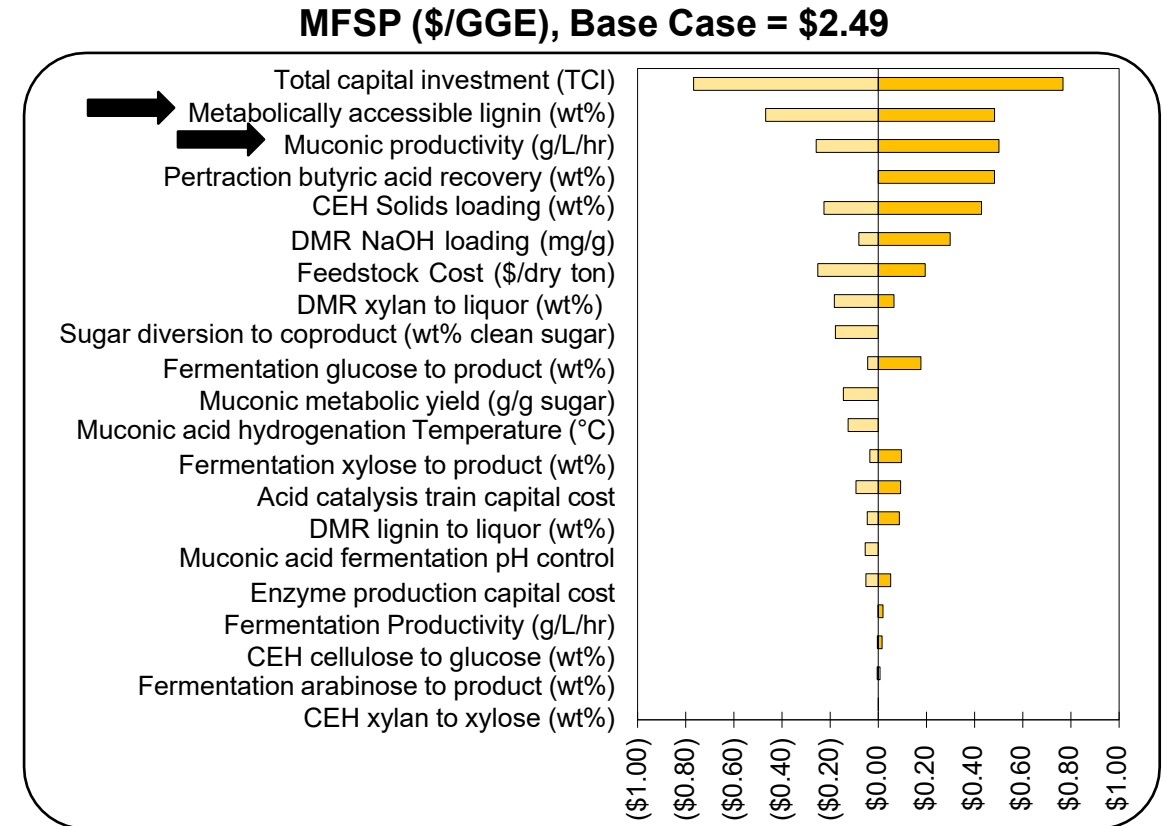
Approach

Overall approach:

- Catalyst development focuses on oxidative catalysis to cleave C–C bonds and produce bioavailable aromatic compounds (SepCon, BLV)
- Analytics and synthesis disseminate methods via Laboratory Analytical Procedures
- Work with Biochem. Analysis project to develop TEA cases towards 2030 for lignin valorization

Major milestones, Go/No-Go Decisions:

- FY20: Screen 15 oxidation catalysts for C–C bond cleavage in model compounds
- FY21 G/NG: 20% above C–O bond cleavage baseline for a catalytic oxidation process
- FY22 (end of project): 60% monomer yield from lignin via C–O and C–C bond cleavage



Goal: Rapidly identify dimeric and oligomeric compounds in lignin samples

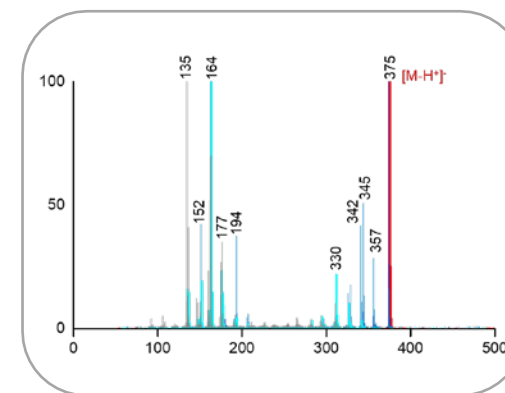
Challenges:

- Existing methods need standards to develop frag. patterns, limited for high-fidelity compound ID
- Existing MS analyses rely on compound libraries that do not include lignin-derived compounds

Approaches:

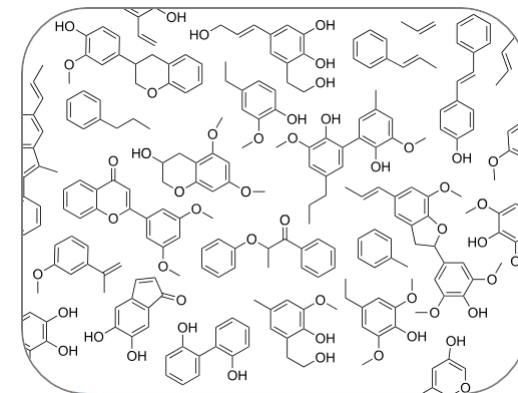
- Determine approaches that can differentiate lignin-derived molecules
- Build on previous modeling efforts¹⁻³ to generate a comprehensive lignin-based compound library
- Pattern match experimental fragmentation data with computational library to rapidly identify compounds

LC-MS optimization for rich data generation

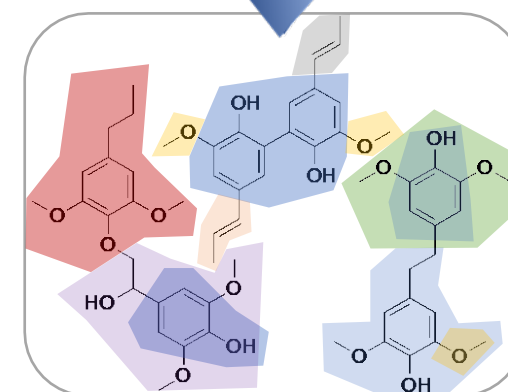


Experimental effort
in LigU

Lignin-based compound library generation



Computational effort
in Biochemical
Process Modeling
and Simulation
(BPMS)



Identification by
substructure matching

Approach: Metal-catalyzed oxidation of lignin

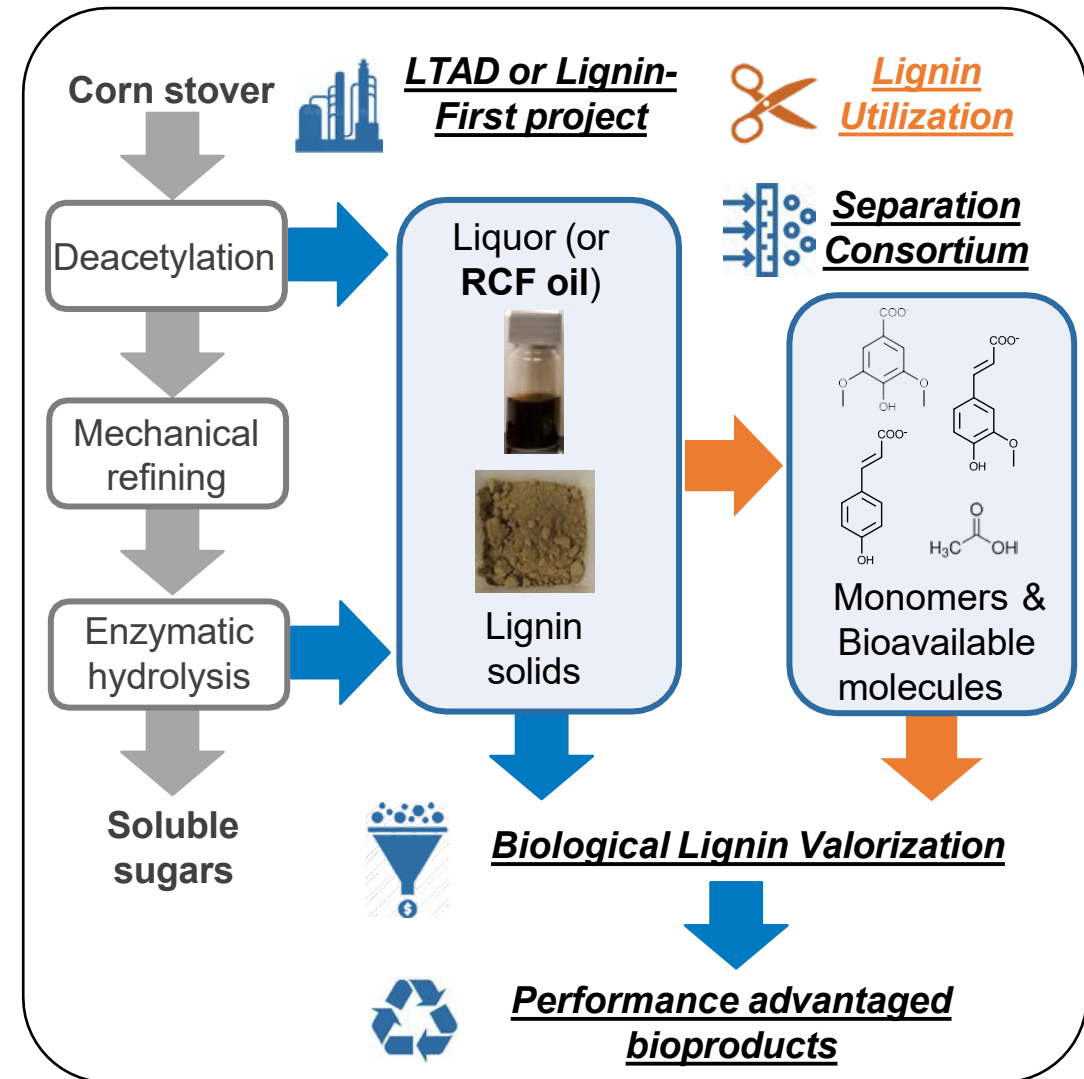
Goal: Develop C–C bond cleavage catalysis to depolymerize lignin oligomers

Challenges:

- C–C bonds difficult to cleave due to their stability
- Phenolic moieties of lignin deactivate catalysis
- Currently no selective methods to achieve high monomer yields through oxidation of lignin

Approaches:

- POM-mediated oxidative cleavage of C–C bonds
- Metal-mediated autoxidation for C–C bond cleavage
- Base-catalyzed depolymerization, with recovery and regeneration of salts



Scientific:

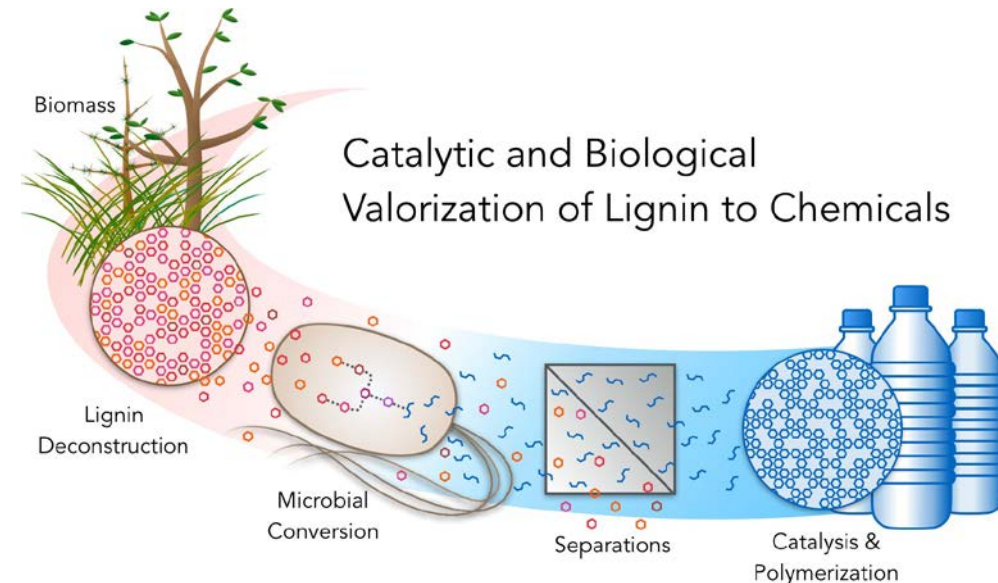
- Monomer yields are limited: C–C cleavage studies will be impactful
- Lignin-related computational pipelines published as open-source online via GitHub
- Developing quantitative methods for lignin analytics and process performance metrics

Industrial:

- Analytics is a common request – multiple Technical Services Agreements & CRADAs
- Partnership with oil major for advice on oxidation catalysis at scale, towards commercially relevant processes
- Focused on both DOE-relevant lignin substrates (DMR-EH) and pulp & paper lignins (Kraft)

Overall:

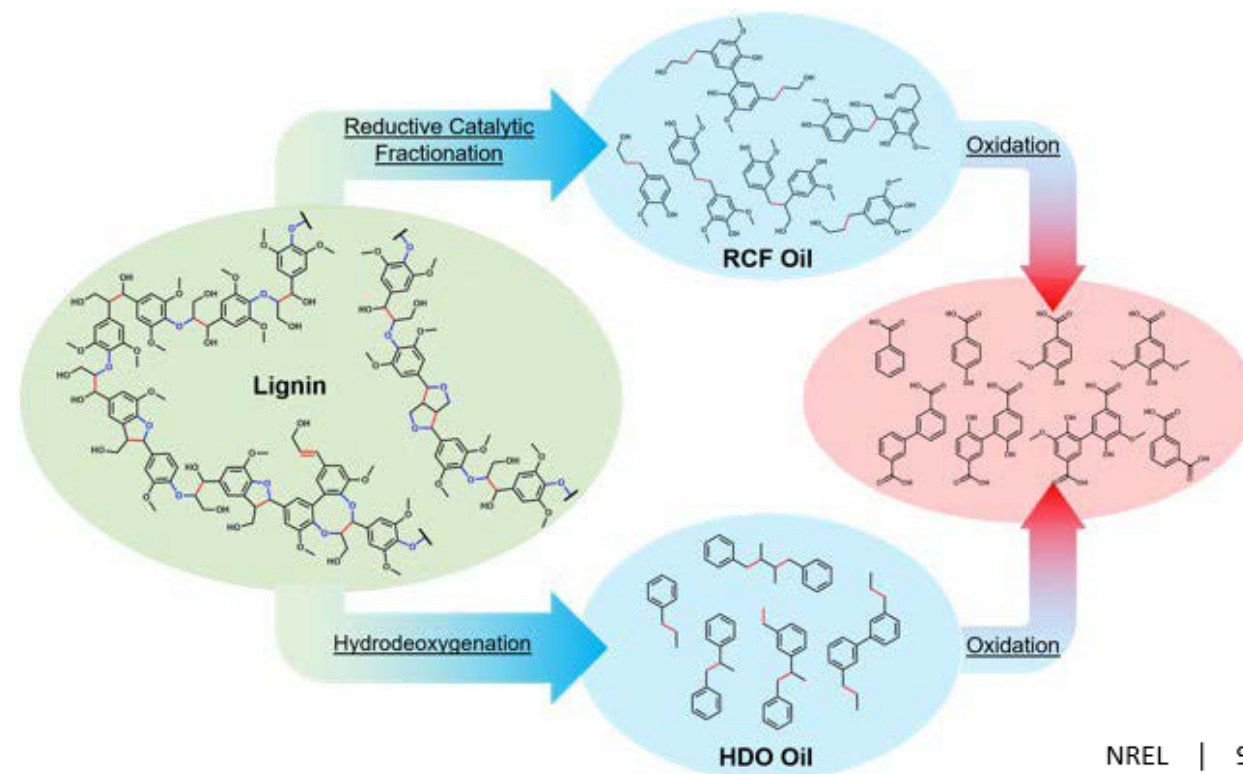
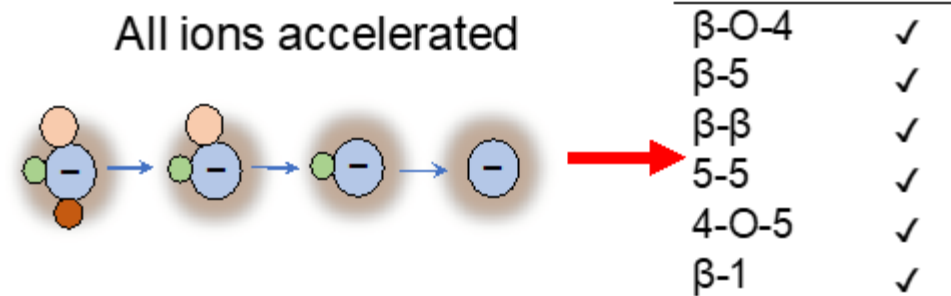
LigU aims to enable quantitative lignin characterization and achieve high-yield deconstruction chemistry for the biorefinery



Progress and Outcomes

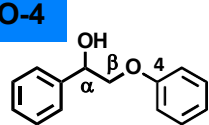
Outline of technical accomplishments and ongoing and future work

- Model compound syntheses
- MS method development for comprehensive lignin characterization
- Computational-experimental pipeline for rapid and quantitative lignin characterization
- Polyoxometalate-catalyzed lignin oxidation
- Metal-catalyzed lignin oxidation
- Base recovery in lignin depolymerization

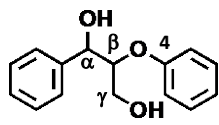


Model compound synthesis

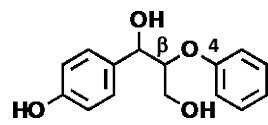
β -O-4



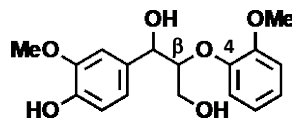
1



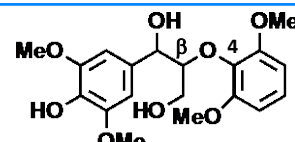
2



3 (HH)

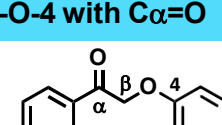


4 (GG)

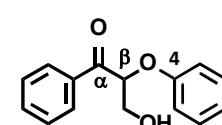


5 (SS)

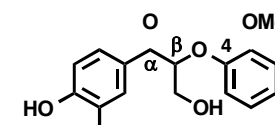
β -O-4 with $C_{\alpha}=O$



6

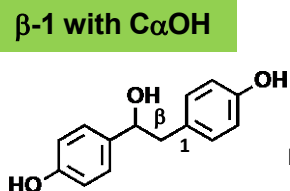


7

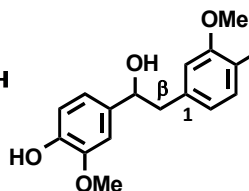


8 (GG)

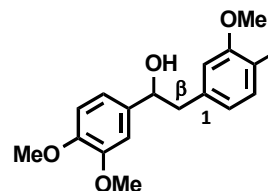
β -1 with $C_{\alpha}OH$



9

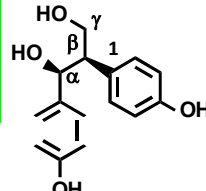


10

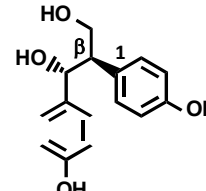


11

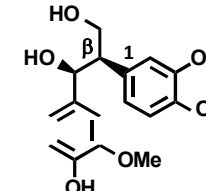
β -1 with $C_{\alpha}OH$ $C_{\gamma}OH$



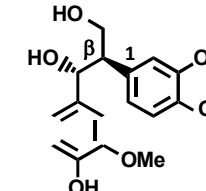
12E (Erythro)



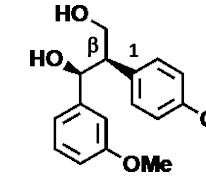
12T (Threo)



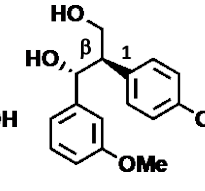
13E (Erythro)



13T (Threo)

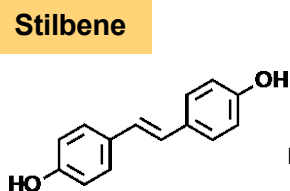


14E (Erythro)

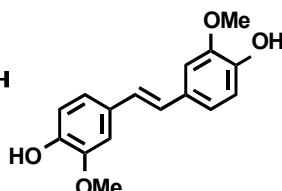


14T (Threo)

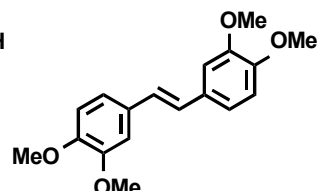
Stilbene



15

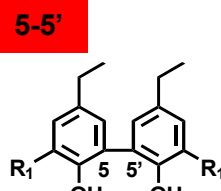


16

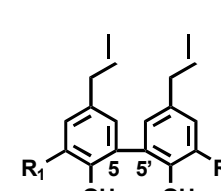


17

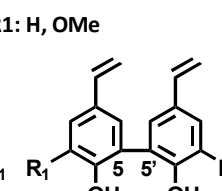
5-5'



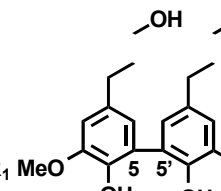
18/19



20/21

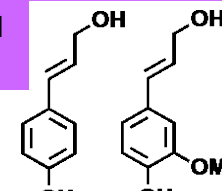


22/23

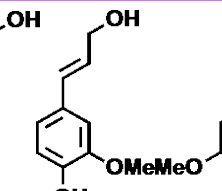


24

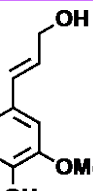
Cinnamyl alcohol



25 (H)

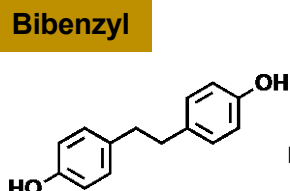


26 (G)

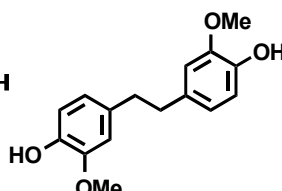


27 (S)

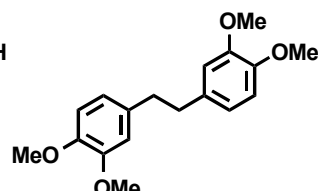
Bibenzyl



28

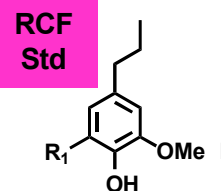


29

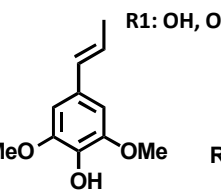


30

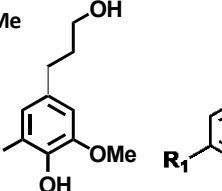
RCF Std



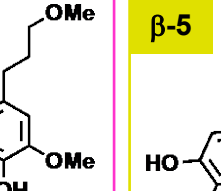
31/32



33

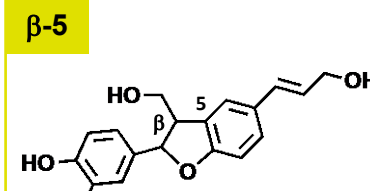


34/35



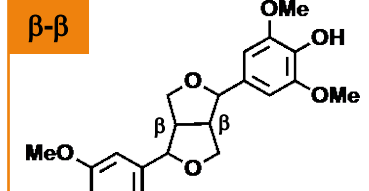
36/37

β -5



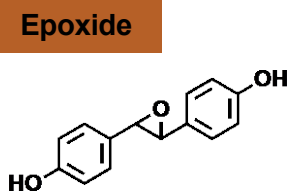
38

β - β

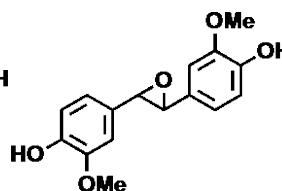


39

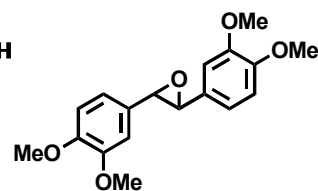
Epoxide



40



41



42

- Prepared 42 models as substrates for catalytic, biological, and stereo-chemically specific lignin depolymerization testing and as analytical standards
- Enabled multiple biological and catalytic studies for lignin valorization across the DOE lignin project portfolio and for many collaborators

Lignin analytics: new MS methods for lignin characterization

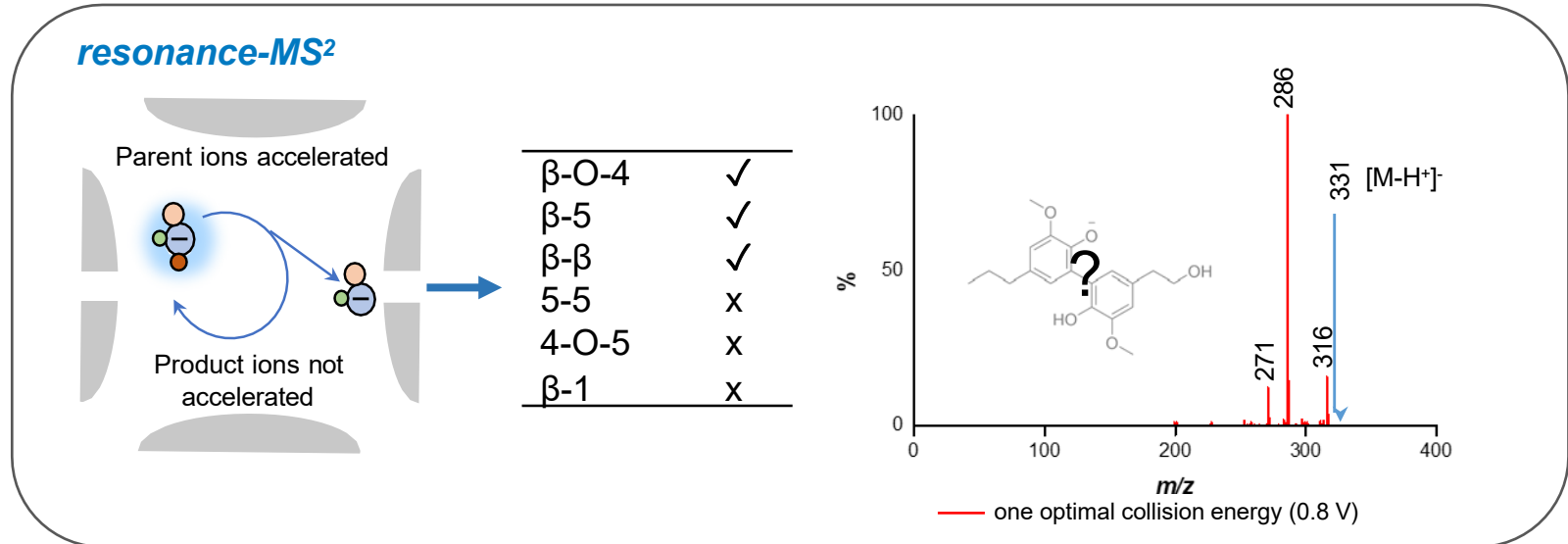
X. Dong, B.A. Black *et al.* in review at *Green Chem.*

Goal: Develop methods that provide improved data for confident lignin oligomer identification

Conventional MS² methods are limited for lignin identification

Tandem MS at a single collision energy

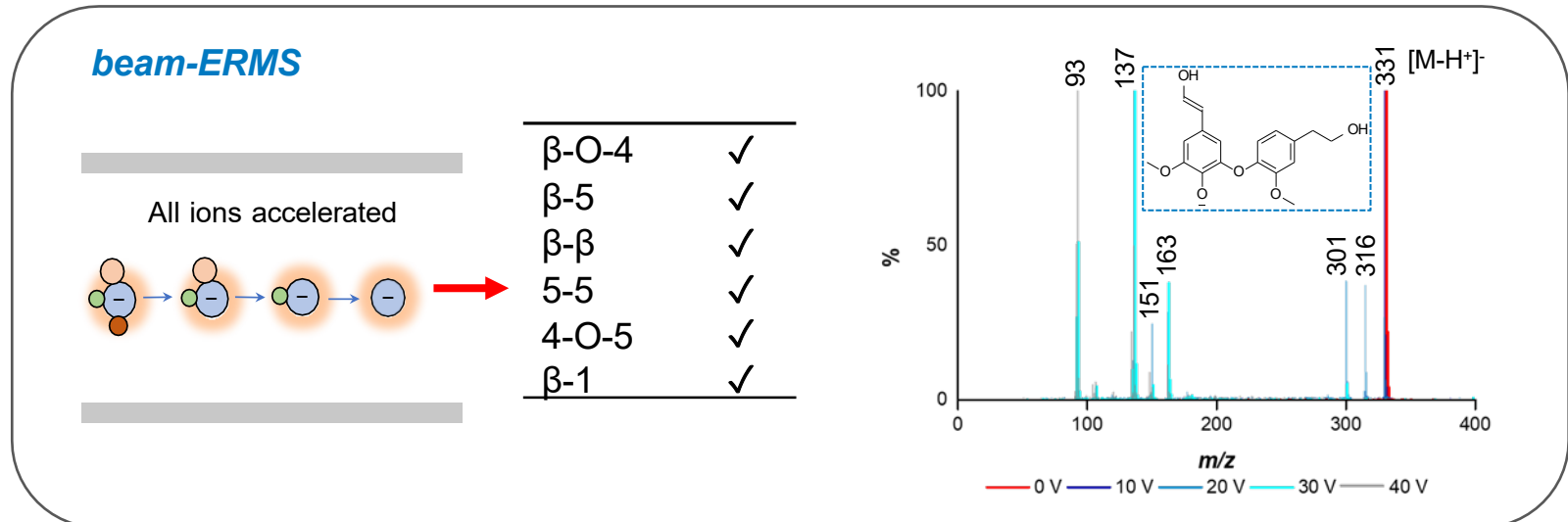
- Results in limited structural information for e.g. 5-5, 4-O-5, and β -1 linkages



Energy resolved MS (ERMS) methods

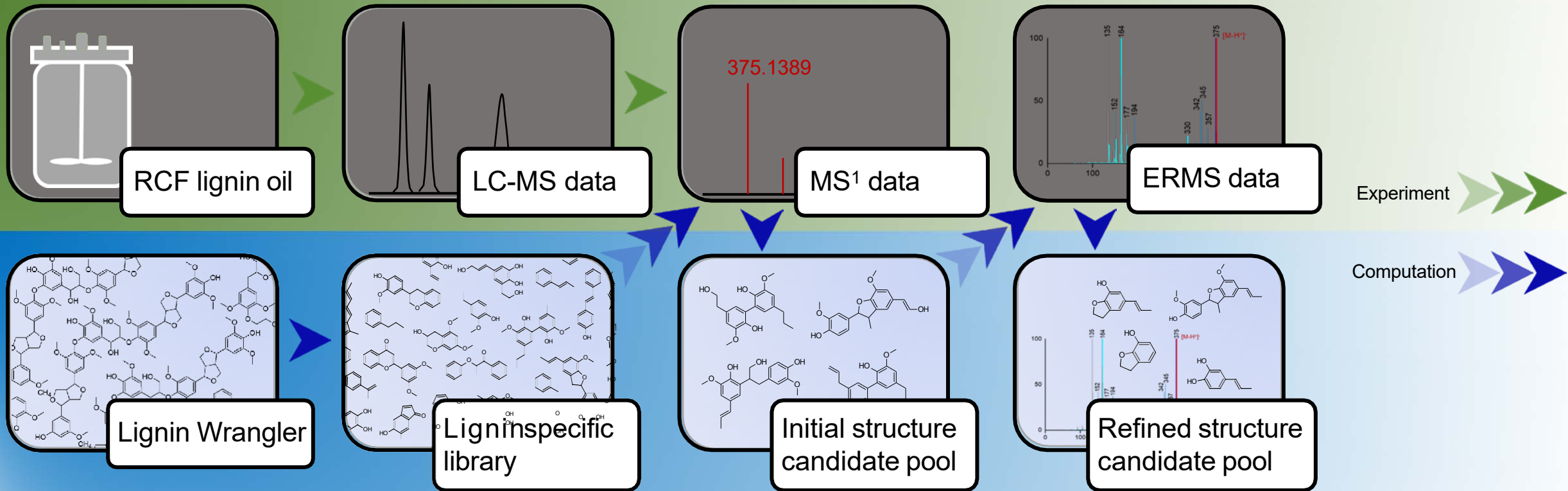
Tandem MS at multiple collision energies

- Increase in fragmentation with beam-configured instruments for maximum structural info
- Allows for ID of lignin oligomers from 6 major linkages



Beam-ERMS methods allow for identification of all lignin oligomers

Lignin analytics: library development and matching algorithm



LigninWrangler: new modular computational-experiment pipeline for lignin analytics

MakeLignin builds on our efforts^{1,2} to generate libraries of **lignin structures** based on kinetics or experimental data

BreakLignin applies chemistry to lignin structures to create a **library of thousands of lignin-derived molecules**

MS2Molecules matches lignin library compounds to MS² data, **identifying likely compound structures** based on fragmentation

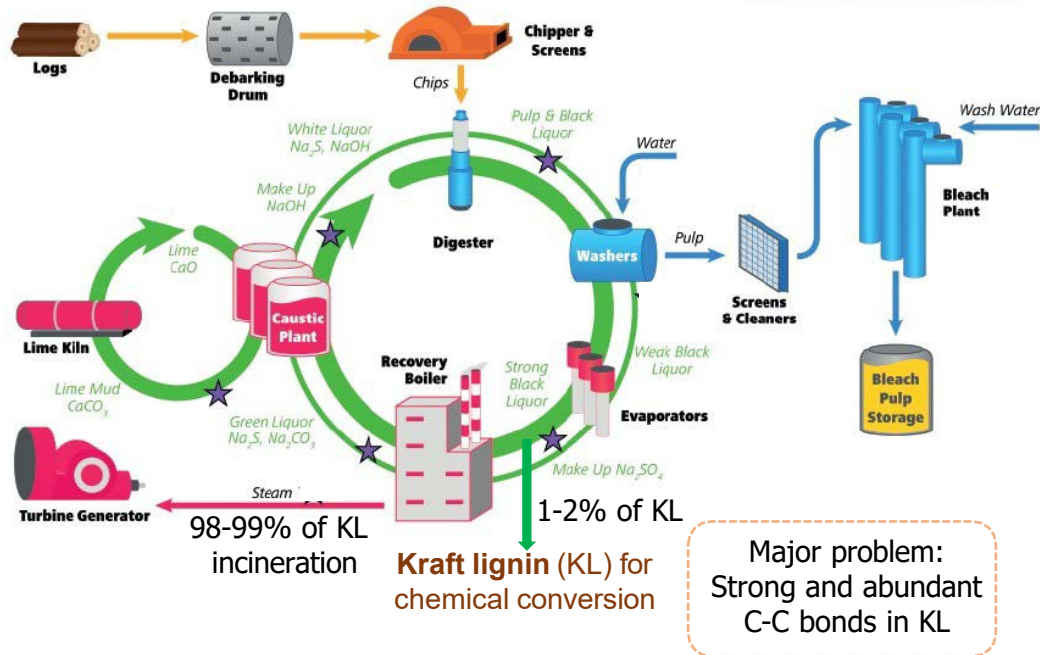
H.B. Mayes, *et al.* in preparation

1. Orella *et al.* *ACS SusChemEng.* 2019
2. Vermaas *et al.* *Green Chem* 2019

Polyoxometalate-based oxidation of Kraft lignin model compounds

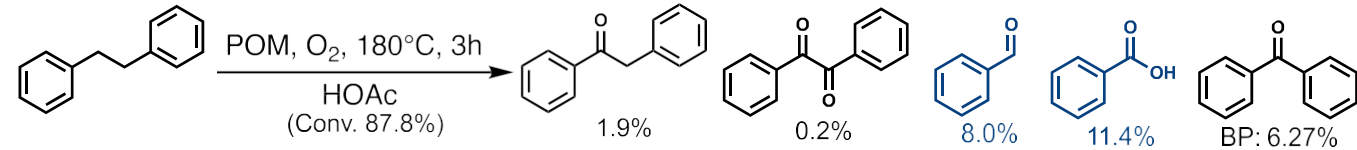
Kraft pulping process¹

Dominated lignin production process
(50 million tons/year)

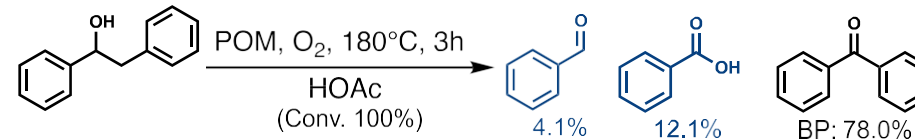


POM catalyzed C-C cleavage of KL model compounds

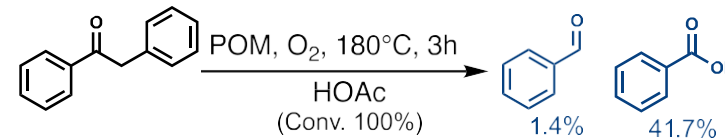
C-C bond



C(OH)-C bond



C(O)-C bond



Polyoxometalate (POM) catalyzed C-C cleavage in lignin model compounds

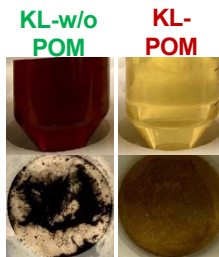
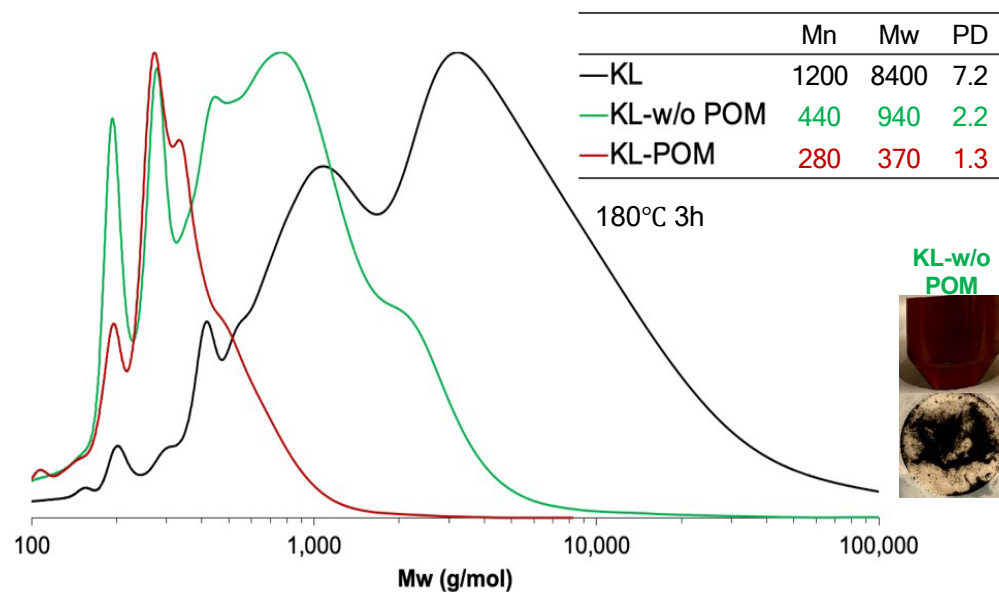
- Both oxidative C-H activation and C(OH)-C cleavage can be achieved by POMs via known mechanisms^{2,3}
- POM catalytic systems have potential to be applied for depolymerization of C-C linkages in lignin
- In acetic acid (HOAc), POM can cleave all types of C-C bonds

1. Metrohm process analytics.

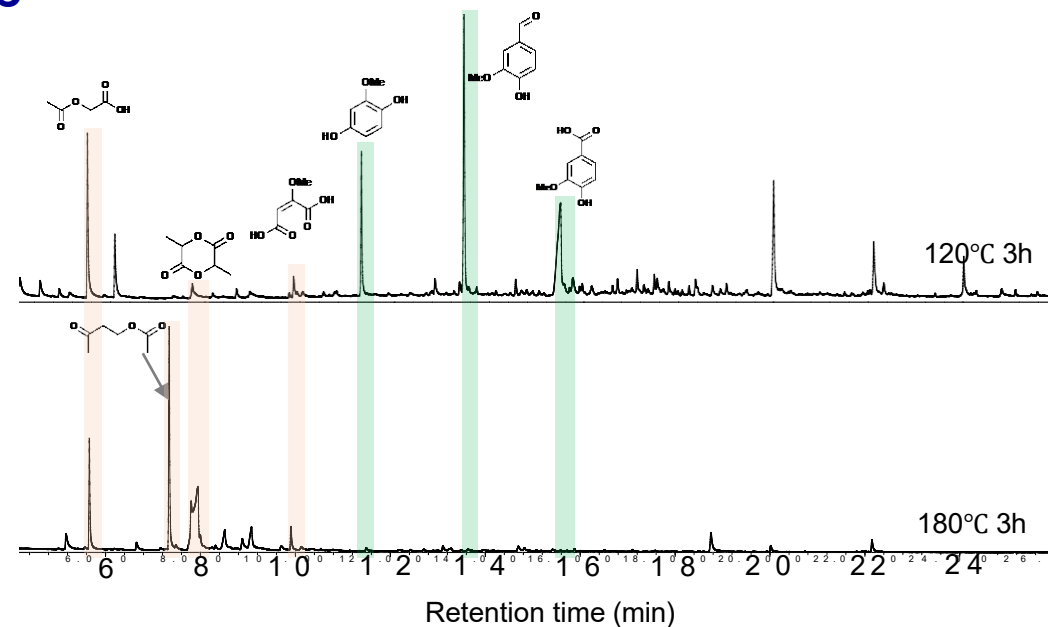
2. Neumann *et al.* JACS. 2001

3. Neumann *et al.* JACS. 2008

GPC



GC



POM-catalyzed Kraft lignin depolymerization

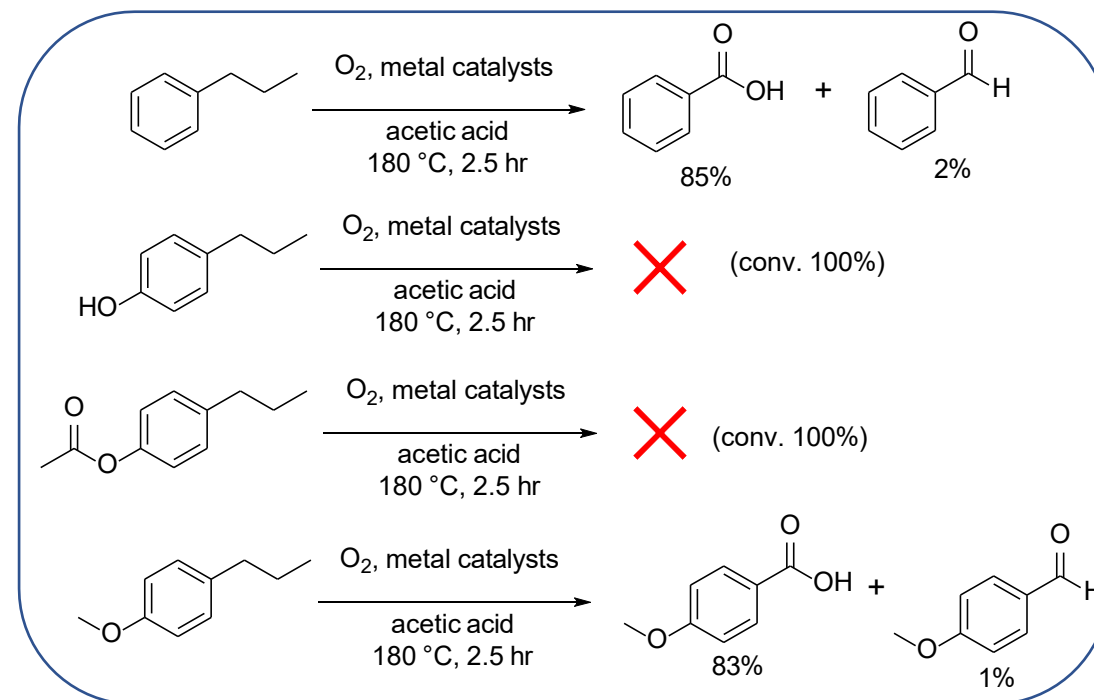
- In HOAc, KL depolymerization extent is considerable – strong effect of temperature on aromatic monomer yields

Current directions:

- Optimizing reaction conditions for model compounds and KL to maximize aromatic products
- Applying advanced MS-based analytics and emerging NMR methods to identify C-C cleavage products in KL

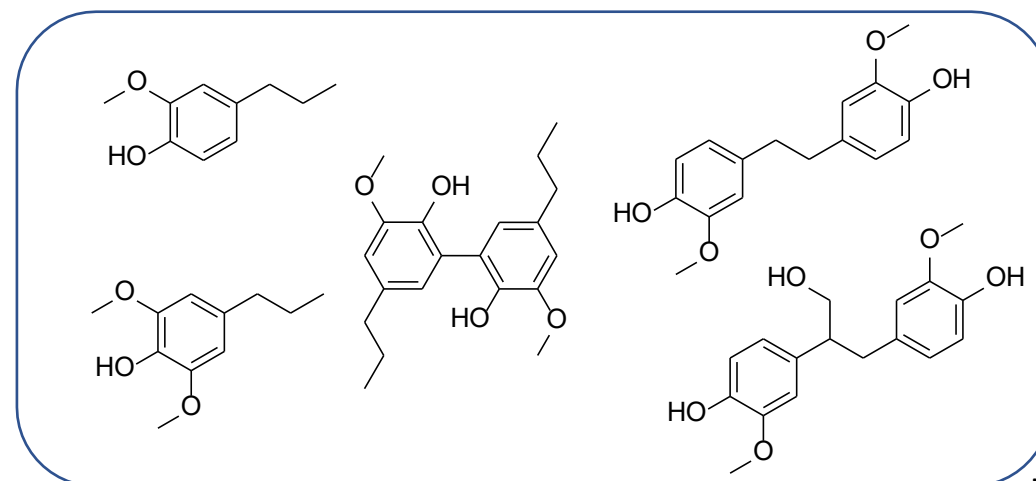
Developing basis for catalytic chemistry with model compounds

- Autoxidation used at scale in petrochemical industry
- **Goal:** apply autoxidation for C–C bond cleavage
- Achieved C–C cleavage product yields up to 85% with propylbenzene and *p*-propylanisole
- Products nearly exclusively benzoic acids (which are readily bio-available compounds)
- Successfully protected phenols through O-methylation, enabling oxidation

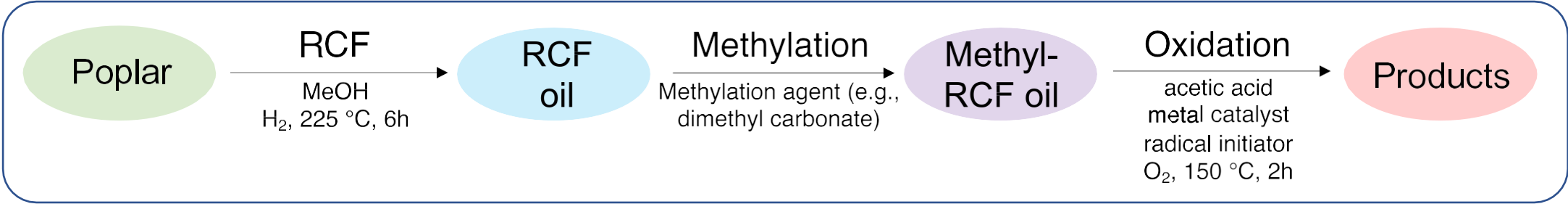


Current directions:

- More realistic model compounds, including G- and S-type monomers, as well as dimers
- Developing detailed mechanistic understanding



Metal-catalyzed oxidation of lignin



Lignin substrates for oxidation catalysis

- Lignin from Lignin-First Biorefinery Development project
- Treat with RCF to obtain C-C dimer- and oligomer-rich substrates

Current directions:

- Optimize depolymerization of RCF oil from pine and poplar lignin

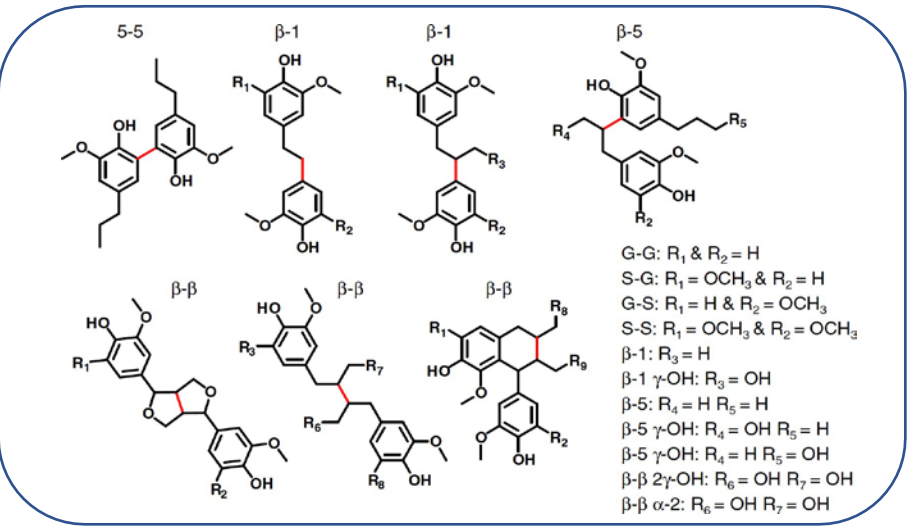
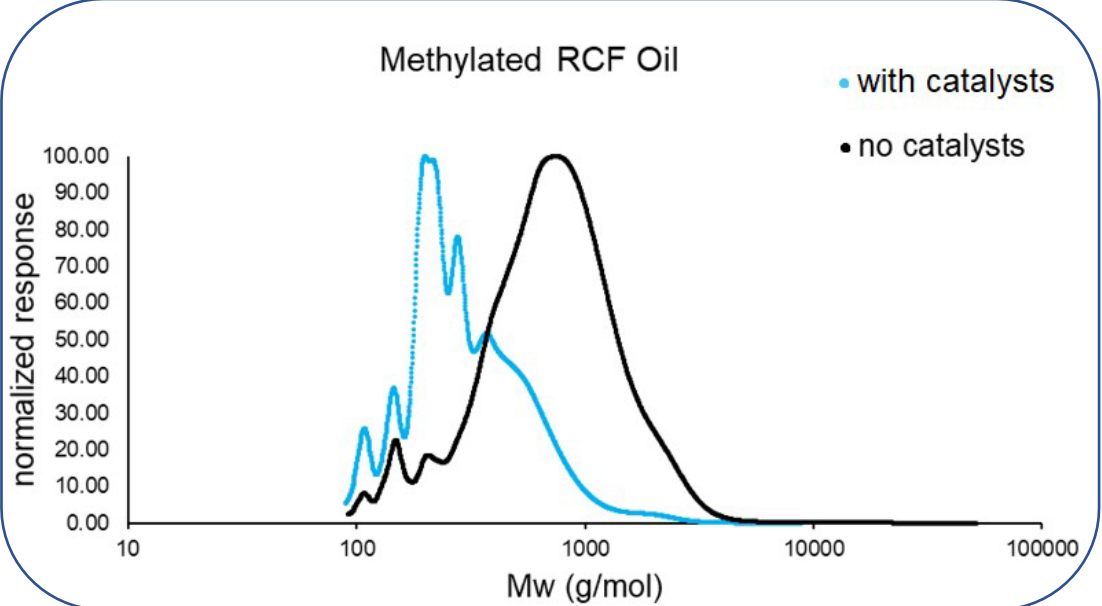
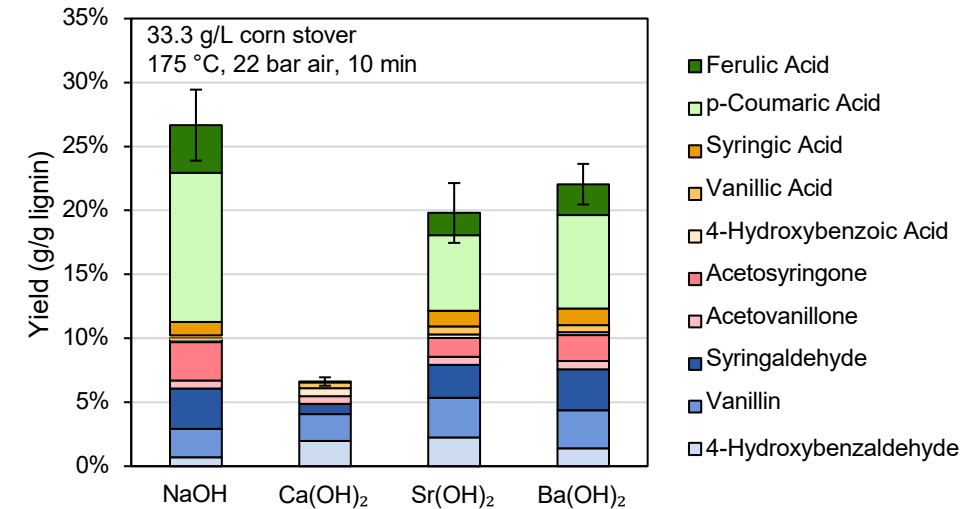
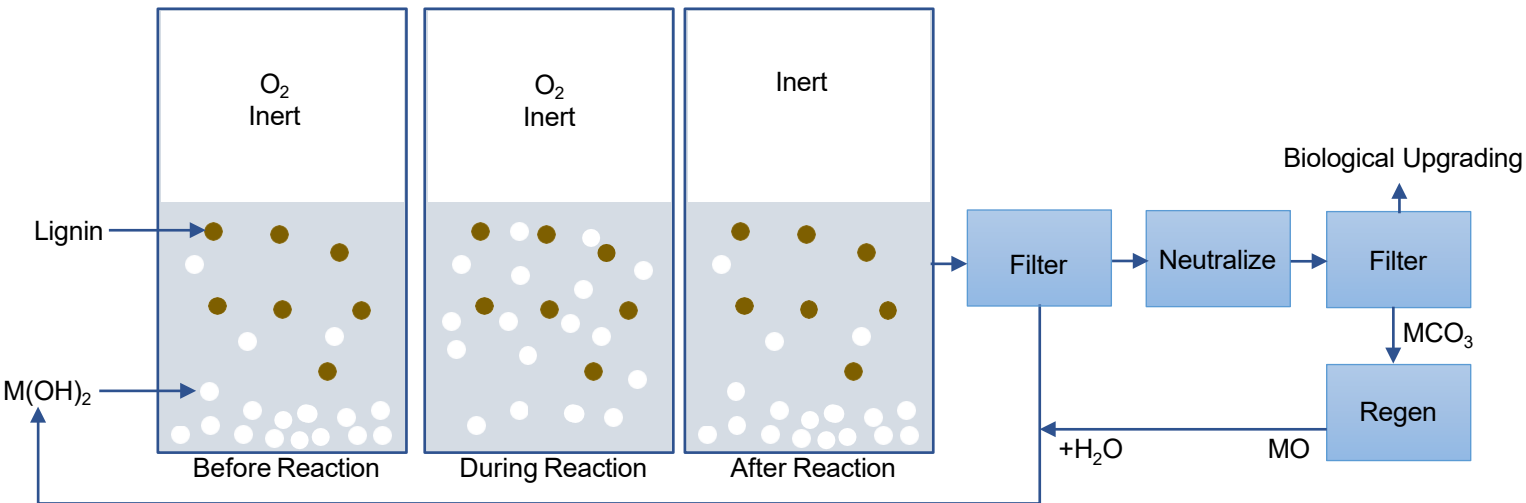


Image from EM Anderson, ML Stone *et al.* Nature Comm. 2019



Base recovery and regeneration in lignin depolymerization



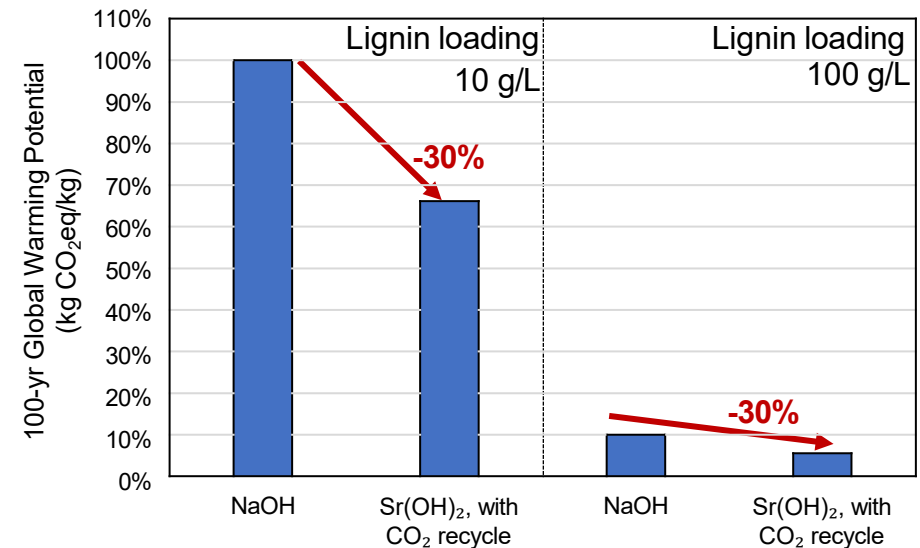
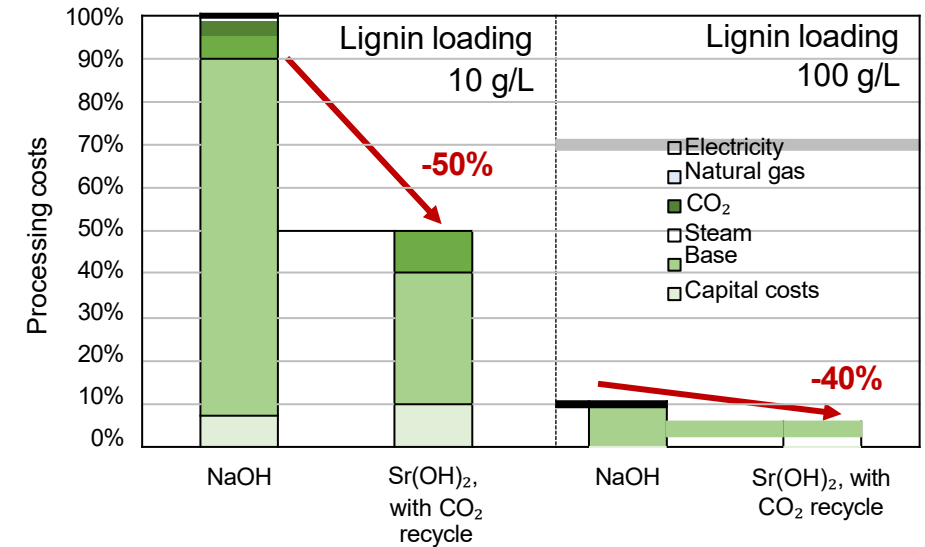
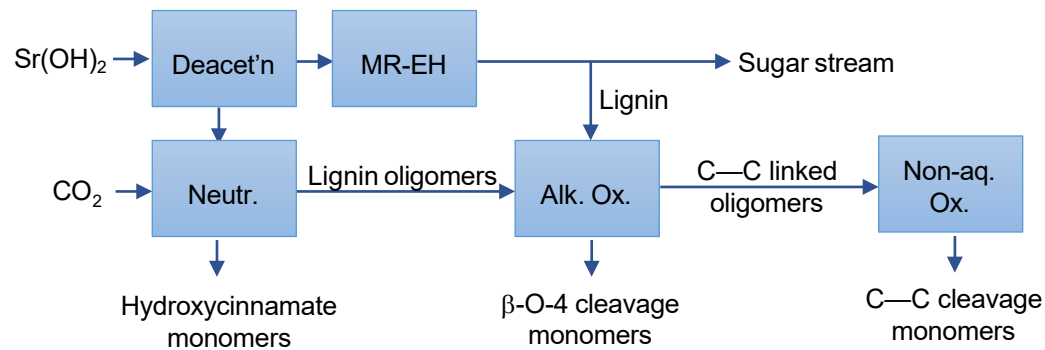
Temperature-reversible solubility of $Sr(OH)_2$ allows high monomer yields and easy recycle of base by filtration and regeneration

- Estimated monomer yields nearing 50 wt%, including deacetylation and alkaline oxidation steps
- Neutralization with CO_2 produces low-salt pH 6 solution, allowing bio-upgrading
- Integrates with ongoing research targeting C-C bond cleavage in base
- **May be able to replace NaOH in deacetylation, BCD, and/or alkaline oxidation**

Base recovery and regeneration in lignin depolymerization

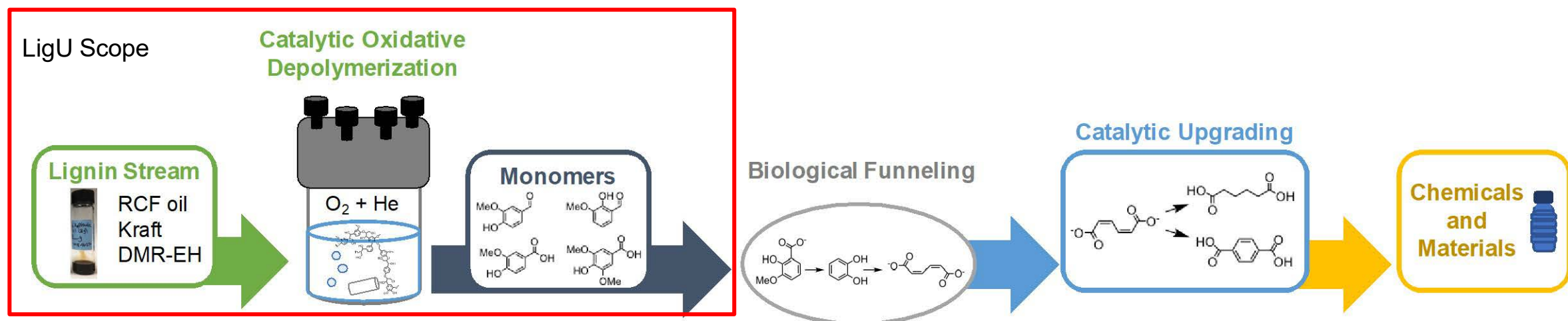
TEA and LCA show that $\text{Sr}(\text{OH})_2$ is more economical and sustainable than NaOH

- Recycle equipment and more expensive base offset by near-elimination of ongoing base purchase and disposal
- Solids loading is major factor
- May enable sequential cleavage of specific lignin bonds to maximize monomer yields within DMR-EH framework
 - Higher base ($\text{Sr}(\text{OH})_2$) loading in deacetylation = release all ester-linked monomers, which degrade under oxidation conditions
 - Aqueous alkaline oxidation or RCF = cleave $\beta\text{-O-4}$ bonds
 - Non-aqueous oxidation = cleave C—C-linked oligomers
- Global warming potential: 30% improvement with Sr
- Cumulative energy demand and ecotoxicity: 15-20% improvement with Sr



Summary

- **Overview:** Focus on 1) increasing the theoretical monomer yield for lignin deconstruction via C-C bond cleavage, 2) developing quantitative lignin analytics, and 3) supporting BETO lignin portfolio
- **Management:** LigU serves as a central hub for lignin valorization projects in the BETO portfolio
- **Approach:** Focus on parallel tracks for lignin deconstruction, employ analysis to identify metrics and milestone targets
- **Impact:** Strategies for technical lignins and DOE-relevant biorefinery lignins
- **Progress and Outcomes:** New computational-experimental pipeline developed for lignin MS-based analytics, two new oxidation methods for lignin deconstruction, recoverable bases demonstrated



Quad charts

Timeline

- Active Project Duration: 10/1/2019 – 9/30/2022
- Total Project Duration: 10/1/2016 – 9/30/2022

	FY20	Active Project (FY20-22)
DOE Funding	\$1,450,000	\$4,350,000

Project Partners

BETO projects: Lignin-First Biorefinery Development (2.2.3.106), Biological Lignin Valorization (2.3.2.100), Separations Consortium (2.5.5.502), Biochemical Platform Analysis (2.1.0.100)

Nat'l labs: Oak Ridge National Laboratory

University collaborators: Northwestern University, University of North Texas, University of British Columbia, Massachusetts Institute of Technology, University of Wisconsin Madison

Barriers addressed

- Ct-C Process development for conversion of lignin
- Ct-F Increasing the yield from catalytic Processes

Project Goal

Develop industrially-relevant processes and tools for lignin valorization

End of Project Milestone

Deliver an oxidation catalyst that can achieve $\geq 75\%$ monomer yield from a realistic lignin stream via C-O and C-C bond cleavage with molecular oxygen as the oxidant in a batch or flow-through system.

Funding Mechanism

Bioenergy Technologies Office FY20 AOP Lab Call (DE-LC-000L071) – 2019

Acknowledgements

DOE Technology Managers Jay Fitzgerald, Sonia Hammache, and Beau Hoffman

NREL Contributors:

Brenna Black, David Brandner, Megan Browning, Nicholas Cleveland, Ryan Davis, Xueming Dong, Xu Du, Rick Elander, Renee Happs, Stefan Haugen, Rui Katahira, Kelsey Kinley, Bruno Klein, Jacob Kruger, Megan Krysiak, Heather Mayes, Joel Miscall, Chad Palumbo, Michelle Reed, Allison Robinson, Wouter Schutyser, Lisa Stanley, Kevin Sullivan, Todd Vinzant

Collaborators:

Linda Broadbelt (Northwestern), Rick Dixon (UNT), Thomas Elder (USDA), Lindsay Eltis (UBC), Adam Guss, Robert Hettich, Josh Michener (ORNL), Yuriy Román-Leshkov, Eric Anderson, Michael Stone (MIT), John Ralph, Shannon Stahl (University of Wisconsin Madison)

Q&A

www.nrel.gov

NREL/PR-2A00-79483

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. 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.

Additional Slides

Responses to previous reviewer comments

- The Lignin Utilization project is tasked with a wide breadth of work that is actually three projects (described as tasks: characterization, deconstruction, and upgrading). Ultimately, the goal is to recover the highest possible yield of usable monomers from lignin, to be upgraded either chemically or biologically to value-added compounds (e.g., muconic acid, adipic acid, terephthalic acid), all to be done from an economically attractive process. Each of these tasks performed to date have demonstrated progress on track with expectations. A new catalyst for C-C bond cleavage has been identified, a more recoverable base to replace sodium hydroxide (NaOH), better understanding of structure, analytical development, and synthesis of model compounds, and pathways to adipic acid and terephthalic acid have been demonstrated. There is still a long way to go in terms of yields, such as additional catalyst identification and development, process integration (chemical and biological), and, importantly, proving out the economics. The project appears very well managed and integrated with other projects such as Biological Lignin Valorization, which will continue to be essential to keep on track.
- This is a well-thought-out and organized team effort with a solid technical approach. Model compound synthesis upfront to evaluate and define the approach is a great first principle approach for the project. There are excellent project results to date, and the team is on track to assist the fuel dollars-per-GGE longer term and help other teams by excellent characterization of products formed for use by the bioupgrading team. Excellent progress on the recovery of monomers from multiple feed materials with the easier-to-recover oxidative bases versus sodium hydroxide. There are minor questions around processes to convert muconate to dimethyl terephthalate (DMT), including iodine, which can be a challenge to remove from wastestreams and any traces could carry through causing issues with processes downstream. Has the team considered other isomerization approaches that might be easier to separate, such as solid isomerization catalysts for fixed-bed operations? Also is there a reason why nickel, which is cheaper than palladium (Pd), is not used in dehydrogenation to DMT? Or is it just for initial proof of concept?
 - The question about use of iodine is a good one. Iodine catalysis is used industrially today, but we are working towards other options for the muconate isomerization in parallel as well, including heterogeneous catalysis strategies, as the reviewer suggests. In terms of the dehydrogenation chemistry to produce DMT, Pd is an initial starting point for this reaction to demonstrate proof of concept, as the reviewer notes.
- This project tackles a key challenge to higher biological utilization of lignin-enriched streams, namely presence of condensed C-C linkages. The approach builds on NaOH-catalyzed lignin depolymerization, now using bases that can be readily recovered and recycled. To facilitate the analysis of lignin products, the team created a library of model lignin compounds, which represents a unique resource that has been made available to other BETO projects. To further demonstrate the applied significance of a base-catalyzed lignin depolymerization process, it will be helpful to report yields of products from the downstream bioconversion step in terms of amount of product per amount of total lignin consumed. The stability of lignin-derived compounds produced by the base-catalyzed process will also be important to verify.
- This appears to have been a broad, effective program that has made significant progress toward its goals while enabling other projects through expansion of the lignin analysis toolbox. The application of analytics and development of a range of model compounds should be leveraged across multiple BETO lignin-related projects.
- The PIs present an important project with direct relevance to the biorefinery. Their effort to generate a reasonable yield of monomers from lignin depolymerization processes that can be used for further biological processing is valuable and addresses a crosscutting challenge to biorefinery development. Improving the clarity regarding certain process steps and the current status of the model versus real lignin work would be helpful.
 - We agree on how to report yields. This is indeed a challenge in many lignin conversion processes, but as discussed at the peer review during the questions, we are attempting to achieve comprehensive mass closures to be able to provide these yield data to the TEA teams in a rigorous fashion.

Publications, patents, presentation, awards, and commercialization

Publications

In preparation:

Jacob S. Kruger, Reagan J. Dreiling, Daniel Wilcox, Katherine Krouse, Camille Amador, David G. Brandner, Kelsey J. Ramirez, Stefan J. Haugen, Bruno Klein, Ryan E. Davis, Rebecca Hanes, Gregg T. Beckham, Lignin Alkaline Oxidation Using Reversibly Soluble Bases.

In review or revision:

Xueming Dong, Rui Katahira, Yanding Li, David G. Brandner, Reagan J. Dreiling, John Ralph, Brenna A. Black*, Gregg T. Beckham*, Energy-Resolved Mass Spectrometry as an Identification Tool for Lignin. In review at *Green Chem*.

Eugene Kuatsjah, Anson C. K. Chan, Rui Katahira, Gregg T. Beckham, Michael E. P. Murphy, and Lindsay D. Eltis*, Elucidating the repertoire of lignostilbene dioxygenases of *Sphingomonas* sp. SYK-6 and their role in the catabolism of lignin-derived aromatic compounds, in revision at *J. Biol. Chem*.

Gerald N. Presley‡, Allison Z. Werner‡, David C. Garcia, Stefan J. Haugen, Caroline B. Hoyt, Rui Katahira, Kelsey J. Ramirez, Richard J. Giannone, Gregg T. Beckham*, and Joshua K. Michener*, Pathway discovery and engineering for cleavage of a β -1 lignin-derived biaryl compound, in revision at *Metabolic Eng*.

Sandra Notonier‡, Allison Z. Werner‡, Eugene Kuatsjah, Linda Dumalo, Paul E. Abraham, E. Anne Hatmaker, Caroline B. Hoyt, Antonella Amore, Kelsey J. Ramirez, Sean P. Woodworth, Dawn M. Klingeman, Richard J. Giannone, Adam M. Guss, Robert L. Hettich, Lindsay D. Eltis*, Christopher W. Johnson*, and Gregg T. Beckham*, Metabolism of syringyl lignin-derived compounds in *Pseudomonas putida* enables convergent production of 2-pyrone-4,6-dicarboxylic acid, in revision at *Metabolic Eng*.

In print:

Laura Berstis, Thomas Elder, Richard A. Dixon, Michael F. Crowley*, Gregg T. Beckham*, Coupling of flavonoid nucleation sites with monolignols studied by density functional theory, in press at *ACS SusChemEng* (2021)

Josh V. Vermaas, Michael F. Crowley*, Gregg T. Beckham*, Molecular lignin solubility and structure in organic solvents, in press at *ACS SusChemEng* (2020).

Morgan M. Fetherolf, David J. Levy-Booth, Laura E Navas, Jie Liu, Jason C Grigg, Andrew Wilson, Rui Katahira, Gregg T. Beckham, William M. Mohn, Lindsay D. Eltis*, Characterization of alkylguaiacol-degrading cytochromes P450 for the biocatalytic valorization of lignin, *PNAS* (2020), 117, 25771-25778.

Thomas Elder*, José Carlos del Río, John Ralph, Jorge Rencoret, Hoon Kim, Gregg T. Beckham, Michael Crowley, Coupling and reactions of lignols and new lignin monomers: A density functional theory study, *ACS Sus. Chem. Eng.* (2020), 8, 11033-11045.

Nicholas E. Thornburg, M. Brennan Pecha, David G. Brandner, Michelle L. Reed, Josh V. Vermaas, William E. Michener, Rui Katahira, Todd B. Vinzant, Thomas D. Foust, Bryon S. Donohoe, Yuriy Román-Leshkov, Peter N. Ciesielski, * Gregg T. Beckham*, Mesoscale reaction-diffusion phenomena governing lignin-first biomass fractionation, *ChemSusChem* (2020), 13, 4495-4509.

Publications, patents, presentation, awards, and commercialization

In print, continued

Erica Teixeira Prates, Michael F. Crowley, Munir S. Skaf, Gregg T. Beckham*, The catalytic mechanism of aryl-ether bond cleavage in lignin by LigF and LigG, *J. Phys. Chem. B.* (2019) 123, 10142-10151.

Josh V. Vermaas, Michael F. Crowley*, Gregg T. Beckham*, A quantitative molecular atlas for interactions between lignin and cellulose, *ACS SusChemEng.* (2019) 7, 19570-19583.

Josh V. Vermaas, Richard A. Dixon, Fang Chen, Shawn D. Mansfield, Wout Boerjan, John Ralph, Michael F. Crowley*, Gregg T. Beckham*, Passive membrane transport of lignin-related compounds, *PNAS* (2019), 116, 23117-23123.

Josh V. Vermaas, Loukas Petridis, Michael F. Crowley*, Gregg T. Beckham*, Systematic parameterization of lignin for the CHARMM force field, *Green Chem.* (2019) 21, 109-122.

Michael J. Orella, Terry Z. H. Gani, Josh V. Vermaas, Michael L. Stone, Eric M. Anderson, Gregg T. Beckham, Fikile R. Brushett,* Yuriy Román-Leshkov*, LIGNIN-KMC: A toolkit for simulating lignin biosynthesis, *ACS Sus. Chem. Eng.* (2019) 7, 18313-18322.

Terry Z. H. Gani, Michael J. Orella, Eric M. Anderson, Michael L. Stone, Fikile R. Brushett, Gregg T. Beckham* and Yuriy Román-Leshkov* Computational evidence for kinetically controlled radical coupling in lignin polymerization, *ACS Sust. Chem. Eng.* (2019) 7, 13270-13277.

Thomas J. Elder*, Jose Carlos del Rio, John Ralph, Jorge Rencoret, Gregg T. Beckham, Radical coupling reactions of piceatannol and monolignols: A density functional theory study, *Phytochemistry* (2019) 164, 12-23.

Josh V. Vermaas, Lauren D. Dellon, Linda J. Broadbelt, Gregg T. Beckham*, Michael F. Crowley*, Automated transformation of lignin topologies into atomic structures with LigninBuilder, *ACS Sust. Chem. Eng.* (2018) 7, 3443-345.

Andrea Corona, Mary J. Bidy, Derek R. Vardon, Morten Birkved, Michael Hauschild, and Gregg T. Beckham*, Life cycle assessment of adipic acid production from lignin, *Green Chem.* (2018) 20, 3857-3866.

Wouter Schutyser, Jacob S. Kruger, Allison M. Robinson, Rui Katahira, David G. Brandner, Nicholas S. Cleveland, Ashutosh Mittal, Darren J. Peterson, Richard Meilan, Yuriy Román-Leshkov*, and Gregg T. Beckham*, Revisiting alkaline aerobic lignin oxidation, *Green Chem.* (2018) 20, 3828-3844.

Wouter Schutyser, Tom Renders, Sander Vanden Bosch, Stef Koelewijn, Gregg T. Beckham, Bert Sels*, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, *Chem. Soc. Rev.* (2018) 47, 10-20.

Publications, patents, presentation, awards, and commercialization

Presentations (2019-2021)

Performance-advantaged bioproducts from lignin, BioEnergy Society of Singapore (via webinar), December 14th, 2020

Efforts towards sustainable performance-advantaged bioproducts and plastics upcycling, Materials Life-Cycle Management Mini-Symposium, University of Delaware (via webinar), October 1st, 2020

Bacterial aromatic catabolism for lignin and plastics conversion, University of Minnesota BioTechnology Institute, March 5th, 2020

Using selective chemical and biological catalysis to upcycle lignin and plastics, ExxonMobil Research and Engineering, October 25th, 2019

Enzymes for lignin and plastics conversion, Enzymes, Coenzymes and Metabolic Pathways, July 23rd, 2019

Engineering non-model cell factories to produce novel polymer precursors, Biomass to Biobased Chemicals and Materials, July 17th, 2019

Challenges and opportunities in plastics upcycling, Plenary Invited Lecture, 26th BioEnvironmental Polymers Meeting, June 5th, 2019

New progresses on biological and catalytic lignin valorization, Great Lakes Bioenergy Research Center and University of Wisconsin Madison, May 13th, 2019

Catalytic valorization of lignin in the biorefinery, 4th Ibero-American Congress on Biorefineries, Plenary Invited Lecture, October 24, 2018

Patent applications (cumulative)

Polyoxometalate catalyzed reductive catalytic fractionation (RCF) oil and Kraft lignin depolymerization: ROI-20-129, pending

Process for Converting CO₂ into Conductive Carbons via Flash Joule Heating: ROI-21-40, pending

Issued patents (cumulative)

Chimeric Enzyme For Conversion of Guaiacol: ROI-16-21

Integrated biological and catalytic conversion for the production of renewable polymer precursors derived from aromatic β -keto adipate pathways: ROI-15-24

Muconate Addition to Industrial Polymers: ROI-15-88

Muconate Separations and Catalytic Upgrading to Adipic Acid: ROI-15-89

Renewable Unsaturated Polyesters and Resins: ROI-16-54