Lignin Utilization

WBS 2.3.4.100

Principal Investigator: Gregg T. Beckham

Organization: National Renewable Energy Laboratory

2017 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Date: March 7, 2017

Technology Area Review: Biochemical Conversion

Goal Statement

Goal: develop viable processes to produce valuable coproducts from lignin.

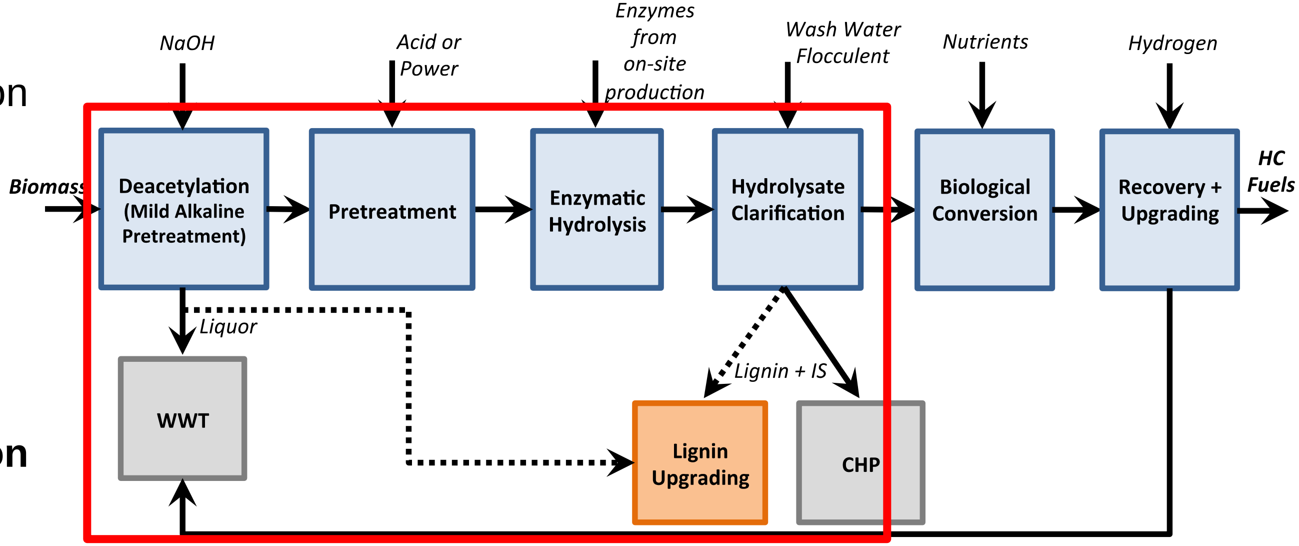
- Contribute to 2022 BETO cost targets of $3/GGE for HC fuel production
- Focus on products with sufficient market size and growth potential to aid bioenergy industry

Aim 1: **Depolymerization**

- Obtain lignin depolymerization products in liquid phase
- Understand impact on carbohydrates

Aim 2: **Upgrading**

- **New upgrading process represents novel foundation for lignin valorization**



Relevance: Lignin utilization will be a major benefit to the U.S. biorefinery infrastructure

- Conduct TEA/LCA to identify cost drivers and data gaps, and to refine process option
- Collaborate with industry and academics for development of tangible lignin utilization processes
- **Outcome:** Demonstrated, scalable processes for converting lignin to valuable coproducts

Quad Chart

Timeline

- Start date: 10/16
- End date: 09/19
- Percent complete: 17**%**

Barriers

- Ct-D: Efficient Pretreatment
  - Developing new lignin-centric pretreatment processes
- Ct-E: Efficient Low T Deconstruction
  - Developing new lignin catalysts
- Ct-H: Efficient Catalytic Upgrading of Aromatics
  - Developing new lignin biocatalysts

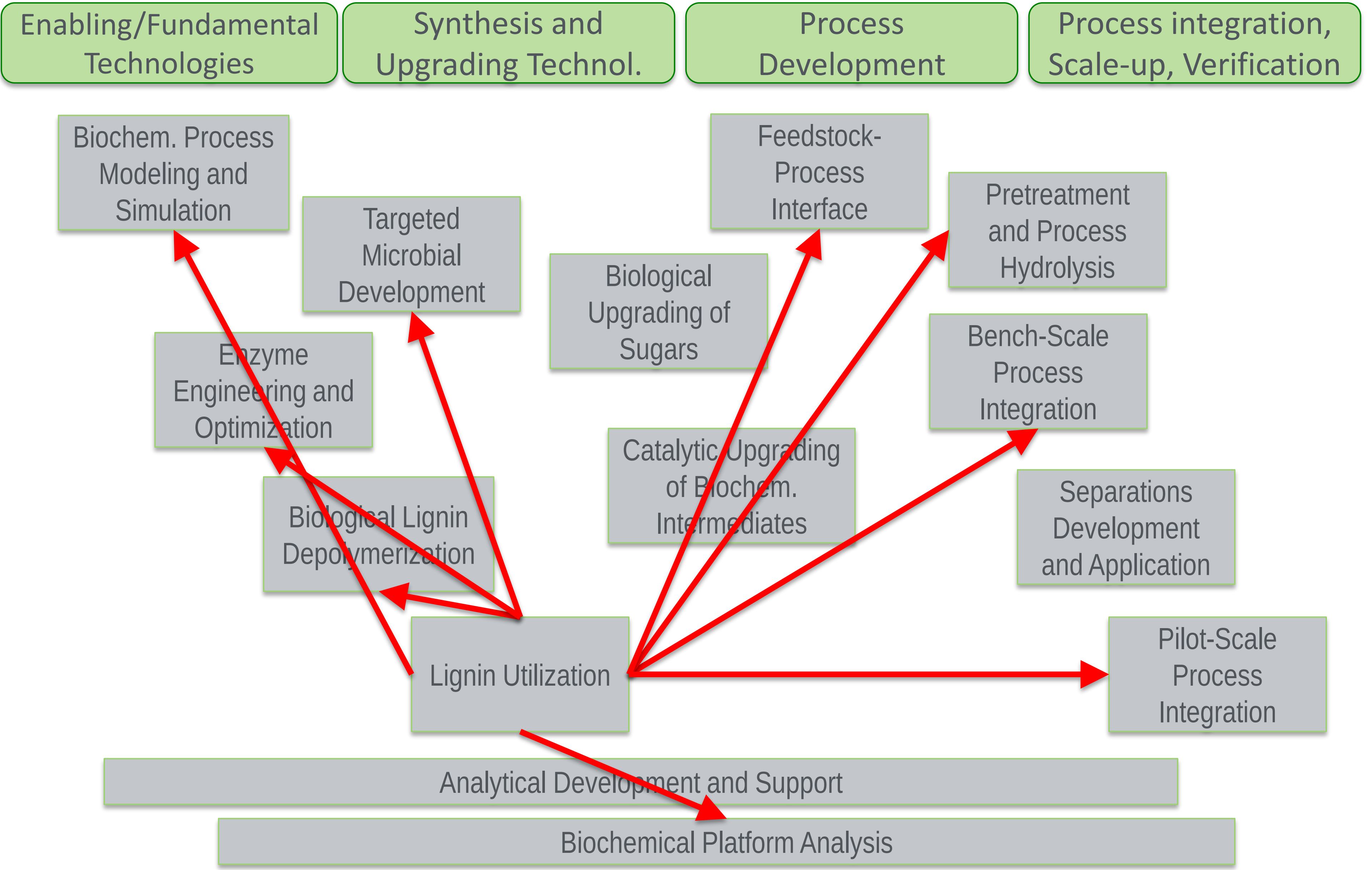
Budget

	FY12–FY14 Costs	FY15 Costs	FY16 Costs	Total Planned Funding (FY17–Project End Date)
DOE-funded	$1,803K	$904K	$1,001K	$4,500K

Partners and Collaborators

- **Industry partners:** Shell Global Solutions, POET, Sustainable Fiber Technologies, RJ Reynolds, CRB Innovations
- **NREL BETO projects**: Biochemical Platform Analysis, Targeted Microbial Development, Feedstock Process Interface, Pretreatment and Process Hydrolysis, Biological Lignin Depolymerization, Biological Conversion of Thermochemical Aqueous Streams, Biochemical Process Modeling and Simulation, Enzyme Engineering and Optimization, Strategic Analysis Platform
- **BETO-funded national lab projects:** Oak Ridge National Laboratory (A. Guss), Idaho National Laboratory (A. Ray), Sandia National Laboratory, Joint BioEnergy Institute (J. Gladden), Separations Consortium
- **Office of Science-funded efforts:** BioEnergy Science Center, C3Bio (EFRC), Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory (R. Robinson, E. Zink)
- **Academic and national institute collaborators:** MIT, University of Georgia, Iowa State University, University of Illinois UC, Colorado School of Mines, University of Oxford, Northwestern University, Purdue University, Swedish University of Agricultural Sciences, University of Portsmouth, University of Tennessee Knoxville, University of Georgia, DTU, NIST

Interaction with Biochemical Conversion Projects



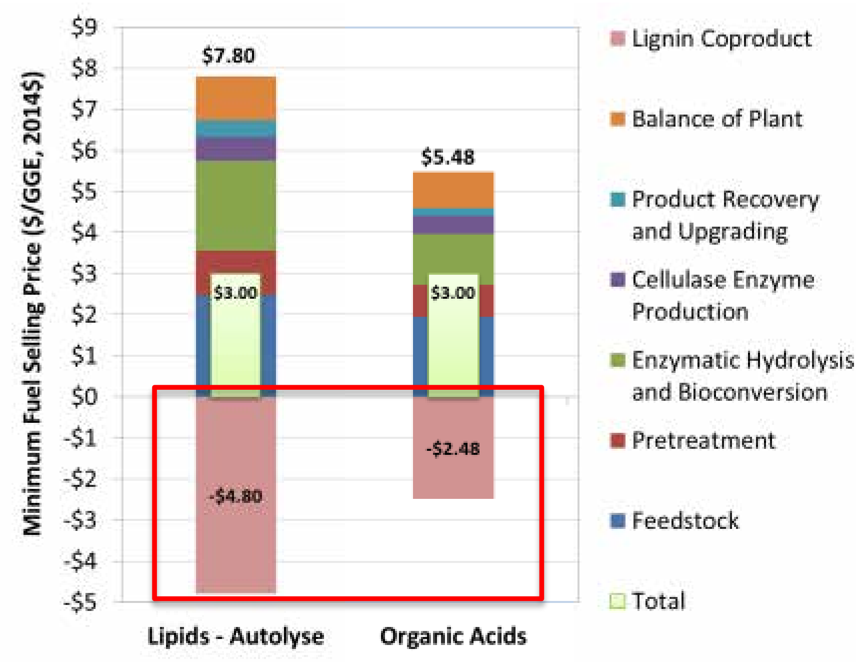
Project Overview

History: Lignin valorization has a long history, restarted at NREL in ~2012

- BETO seed project on lignin depolymerization catalysis
- Identified as a major cost driver for HC biofuels

Context: Major component of biomass

- ~15%–30% of biomass
- ~40% of biomass carbon
- Typically slated for heat and power
- Lignin valorization essential for $3/GGE cost target by 2022 (minimum is ~$2.50/GGE) and for economic viability of biorefineries where carbohydrates are used to produce fuels



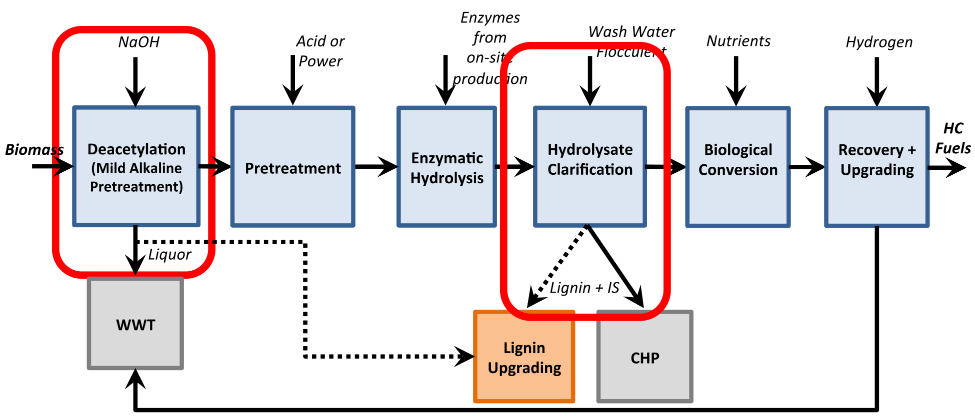
Project Objectives:

- Develop scalable pathway(s) for lignin isolation and upgrading to meet 2022 cost targets
- Conduct integrated process development with carbohydrate utilization projects
- Employ TEA/LCA to develop process options based on bench-scale data

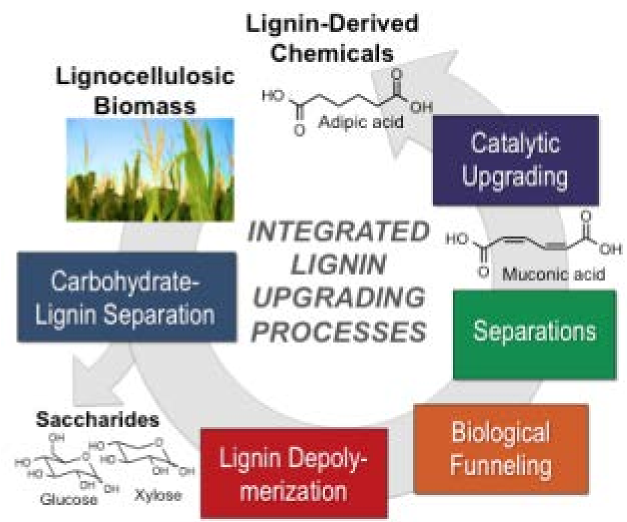
Davis et al., NREL Design Report, 2013
Davis et al. 2016 NREL Milestone

Technical Approach

Aim 1: Obtain liquid-phase intermediates



Aim 2: Use biology and catalysis to upgrade lignin



Approach:

- Obtain lignin in pretreatment and/or post-EH residual solids
- Develop lignin depolymerization strategies

Primary challenges and success factors:

- High yields of stable, liquid, low-MW products
- Analysis of resulting product distributions
- Impact to both carbohydrates and lignin in pretreatment

Ragauskas, Beckham, Biddy, et al., *Science*, 2014

Approach:

- "Biological funneling" to obtain single products
- Targeting adipic acid as a product via muconic acid as an intermediate

Primary challenges and success factors:

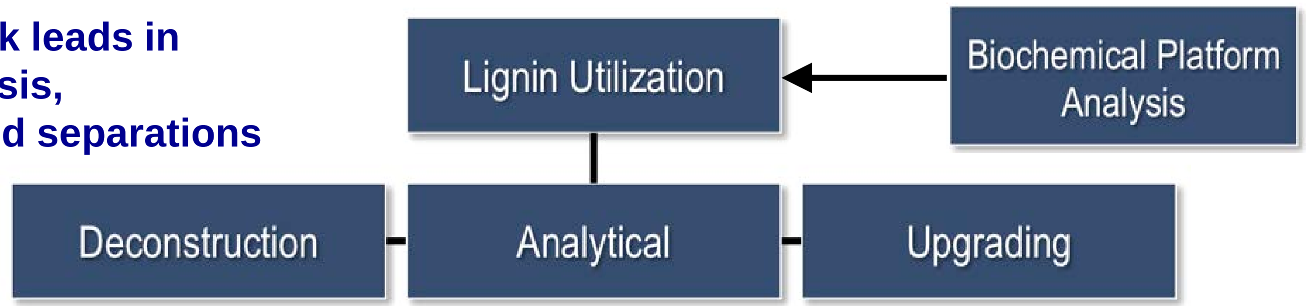
- High yields in the biological step
- Codesign of lignin stream and strain
- Cost-effective separations

Linger, Vardon, Guarnieri, Karp, et al., *PNAS* 2014
Vardon, Franden, Johnson, Karp, et al., *EES* 2015

Management Approach

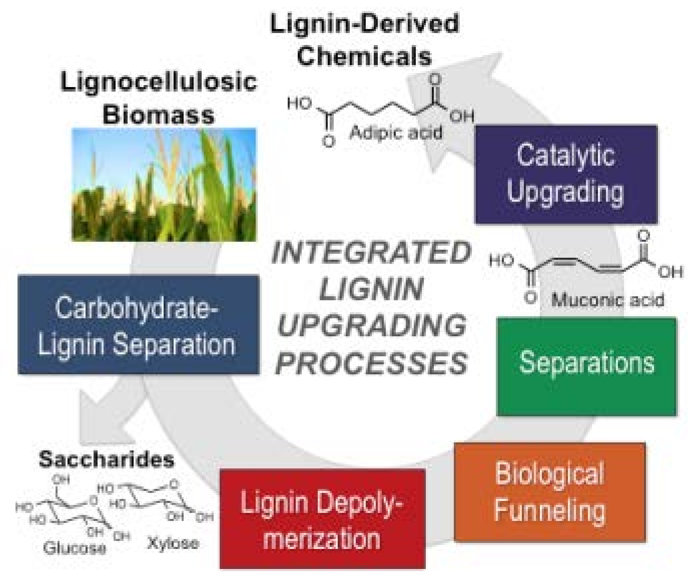
- *Develop simple, integrated approaches and use TEA/LCA and go/no-go decisions to refine options*
- *Employ fundamentals-driven science/engineering approach with an interdisciplinary team*

Experienced task leads in analytics, catalysis, fermentation, and separations



Approach:

- Biological funneling can handle multiple substrates
- Lignin will need to be depolymerized to water-soluble aromatic compounds (oxidation as a catalytic approach)
- Focus on simple, integrated technical solutions
- Work with Pretreatment and Process Hydrolysis (PPH) project for producing high-pH lignin streams for oxidation
- Work with Targeted Microbial Development project for strain engineering and fermentation development
- Work with Separations Consortium for lignin stream conditioning for catalysis



Technical Results – Outline

Isolation to obtain lignin-enriched streams

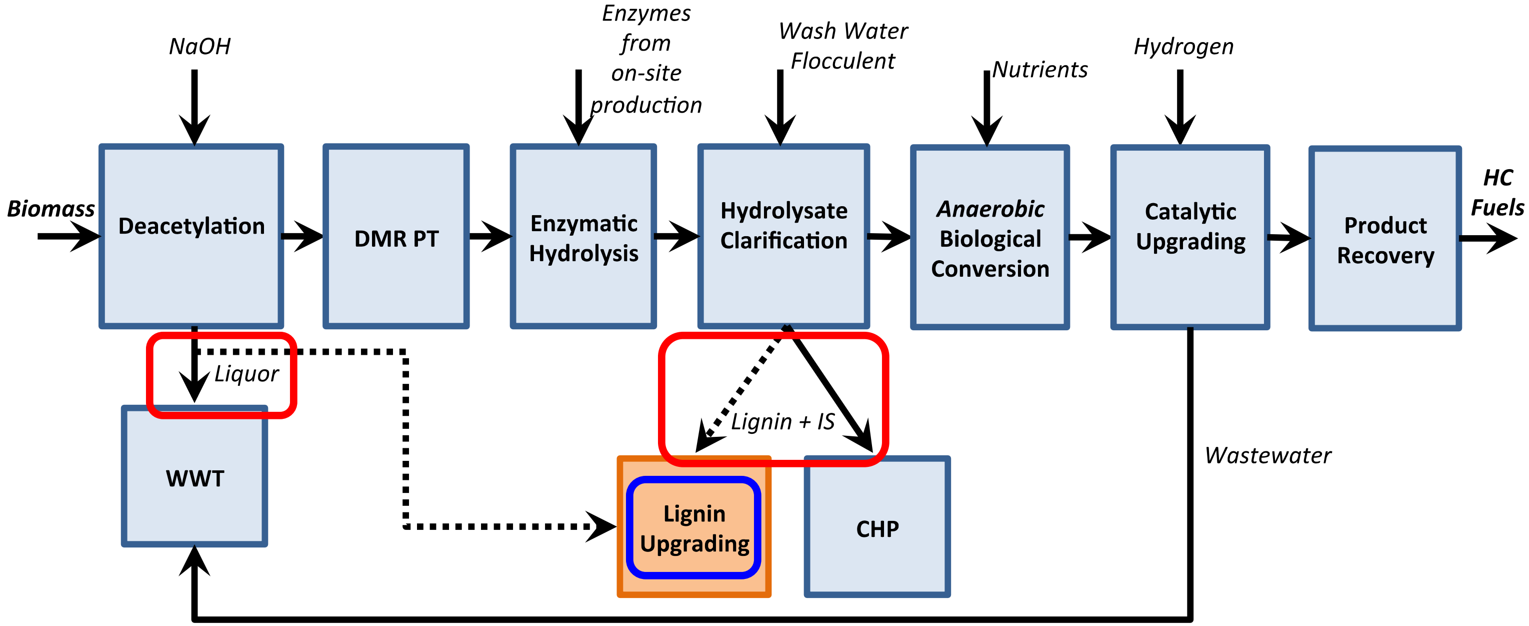
- Deacetylation (**Alkaline Prt**)/ Mechanical Refining (collaboration with Pretreatment and Process Hydrolysis Project)
- Ammonia pretreatment

Depolymerization of isolated lignin-rich streams (both upstream and downstream)

- Heterogeneous oxidative catalysis

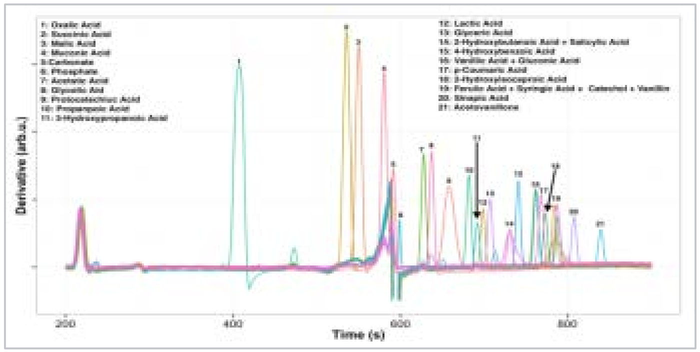
Lignin upgrading to valuable products

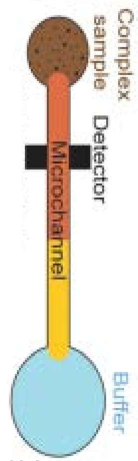
- Biological funneling, separations, catalysis for product upgrading



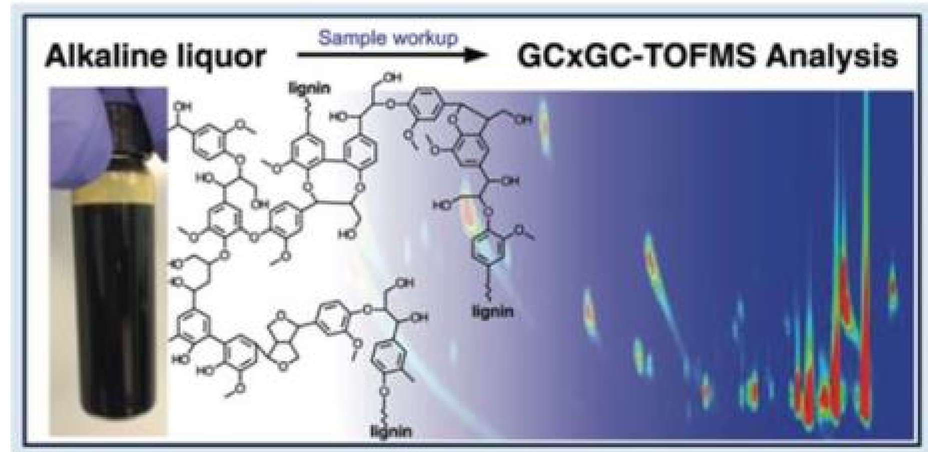
Lignin characterization requires multiple analytics capabilities

Gradient elution moving boundary electrophoresis (GEMBE)



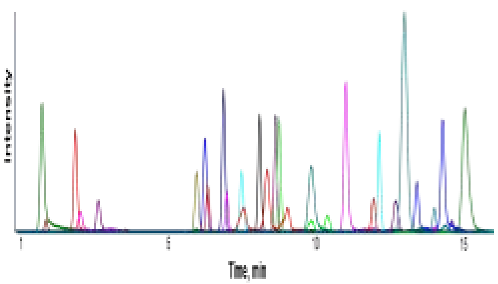


GEMBE: Similar to CE, but a more rapid analysis time
No derivatization necessary



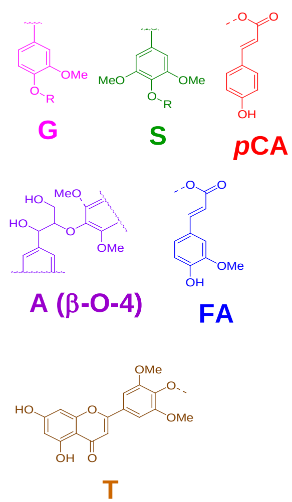
2D GC-MS: Requires ion exchange and derivatization
Enhanced chromatographic resolution and high mass resolution

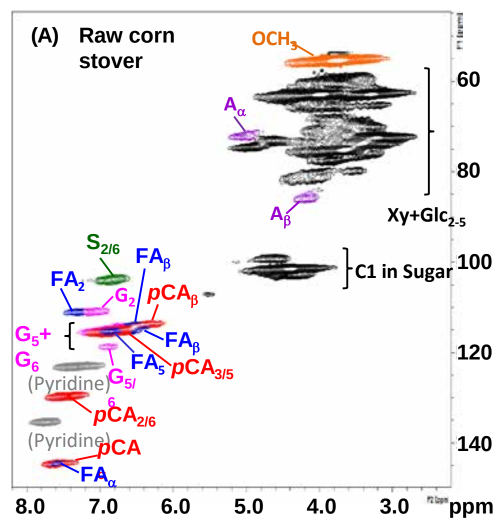
LC-MS



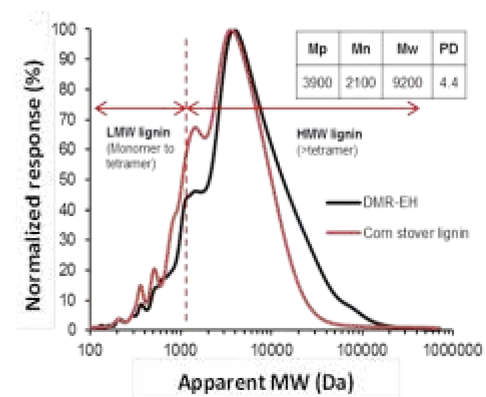
LC-MS: 1 & 2D LC or laser ionization
Low and high mass resolution mass spectrometry
No derivatization necessary

2D HSQC NMR





Aqueous and organic GPC

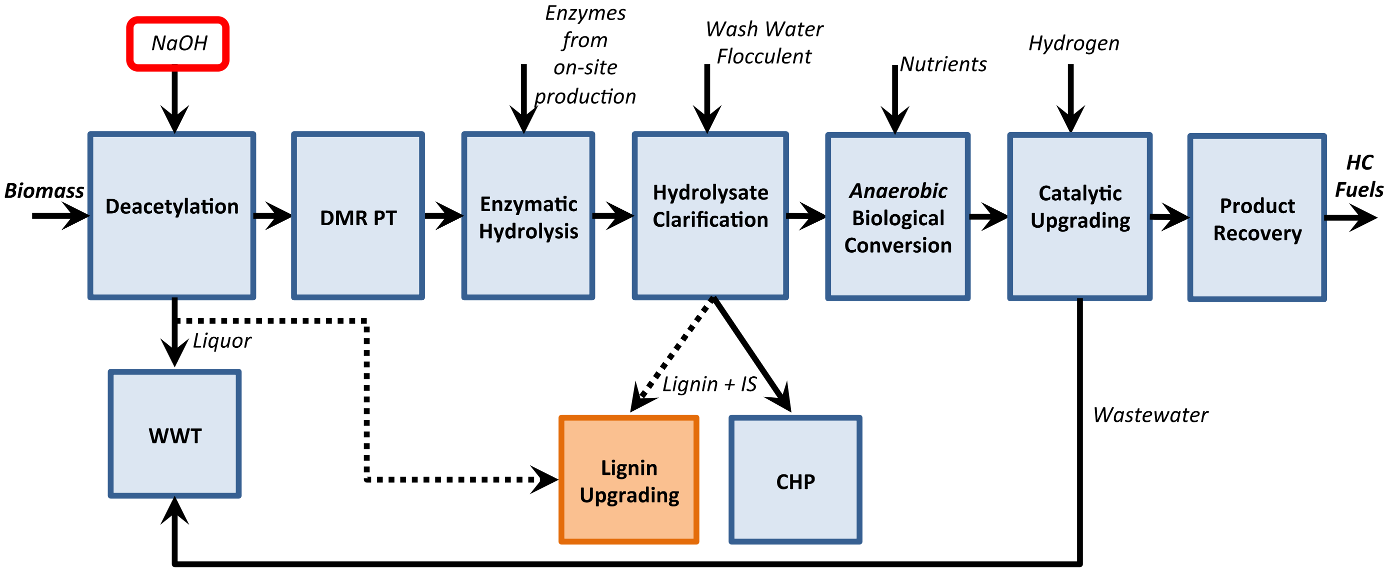


GPC: Aqueous GPC is similar to organic GPC, but no derivatization required; analysis at high pH aqueous mobile phase

Likely process configuration for 2022

Ideal lignin depolymerization strategies would:

- Produce a high-pH, solubilized, fractionated lignin-rich stream for oxidative catalysis
- Employ robust catalysts that can withstand high temperatures and corrosive environments
- Use O_2 as an oxidant to break C-O and C-C bonds
- Produce high yields of water-soluble lignin breakdown products (aromatic monomers)
- Minimize impact to carbohydrate yields



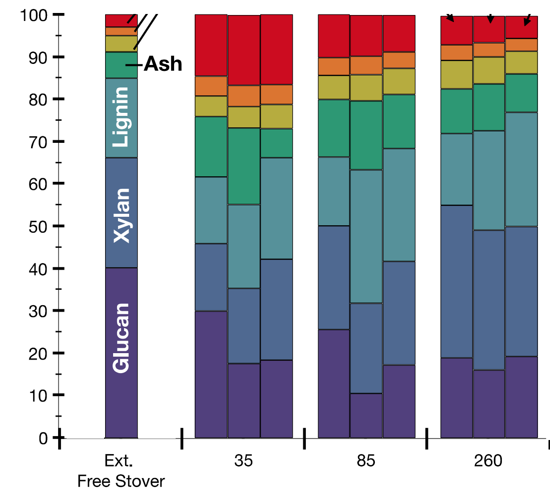
NREL is developing several alkaline processes for fractionation

- These methods produce a high-pH, solubilized, lignin-rich stream
- **To process these streams, we need robust catalysts, a critical target for FY16–FY19**

Lignin isolation via alkaline pretreatment

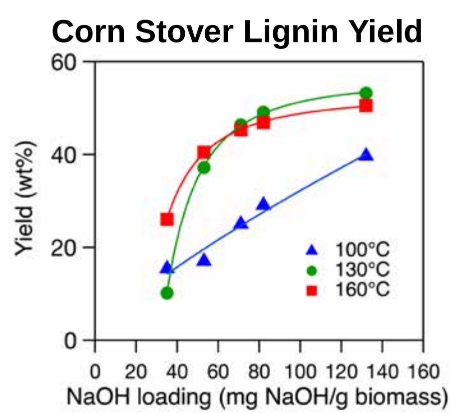
This work ties in closely with mechanical refining pretreatment

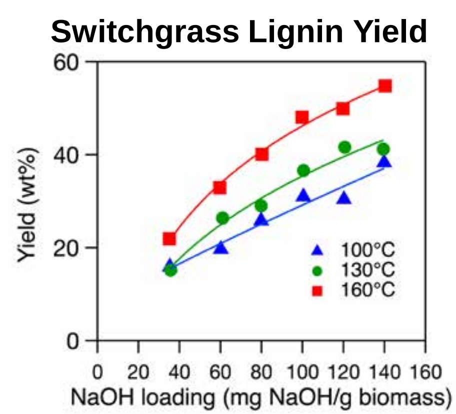
- *Full mass balances, full characterization of resulting lignin streams*
- Cellulose digestibility with industrial enzyme cocktails
- Bench-scale data for TEA/LCA including materials of construction and reactor costs



Objective Function

$$f = \frac{Y_{\text{lignin,bl}}}{Y_{\text{glucan,bl}} + Y_{\text{xylan,bl}}}$$





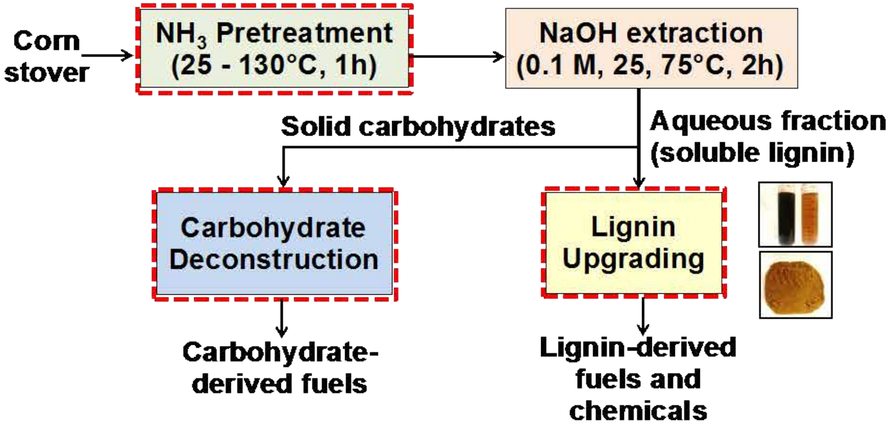
- Work completed with blended/pelleted feedstocks with INL, NREL FI tasks
- Also complete with GM poplar feedstocks (high S lignin)

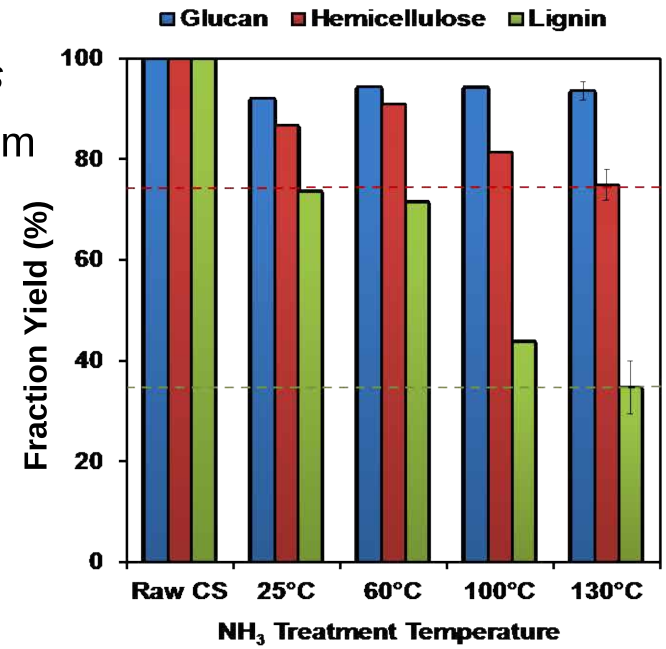
Karp et al., *ACS Sust. Chem. Eng.*, 2014
Karp et al., *ACS Sust. Chem. Eng.*, 2015

Lignin isolation via ammonia pretreatment

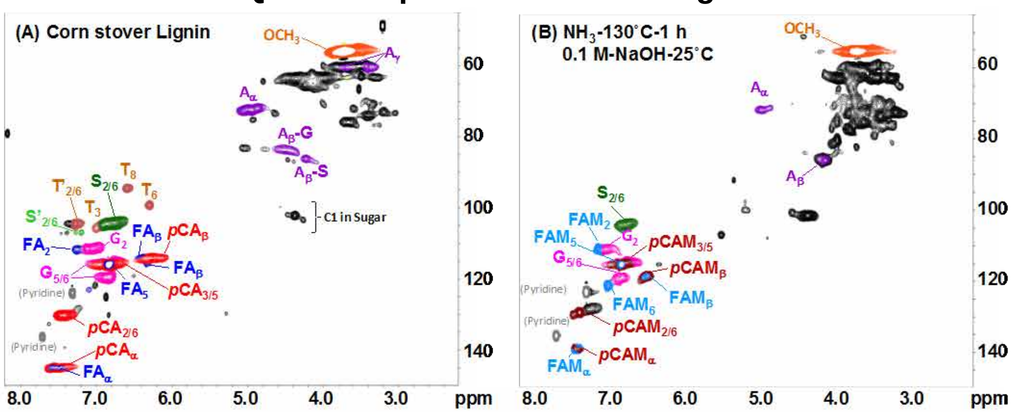
Process-relevant alkaline fractionation of lignin that can "bolted" on to current anhydrous ammonia pretreatments

- *Full mass balances and characterization of lignin streams*
- **Outcome:** Solubilization of > 50% lignin into a soluble form

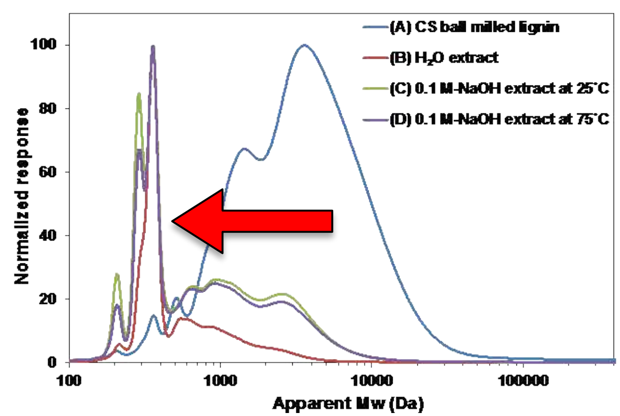




HSQC NMR spectra of Soluble Lignin



GPC Chromatograms of Soluble Lignin

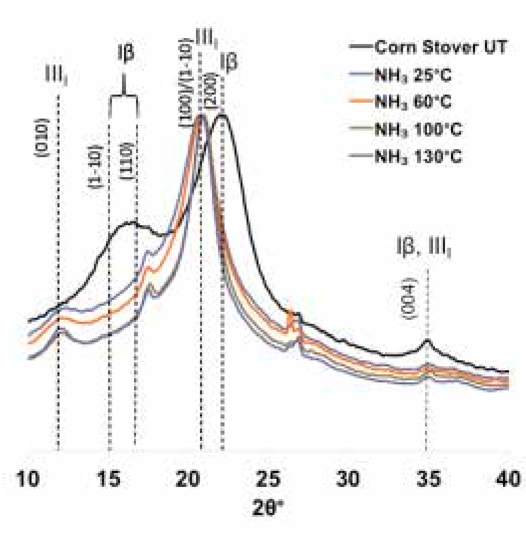


Lignin isolation via ammonia pretreatment

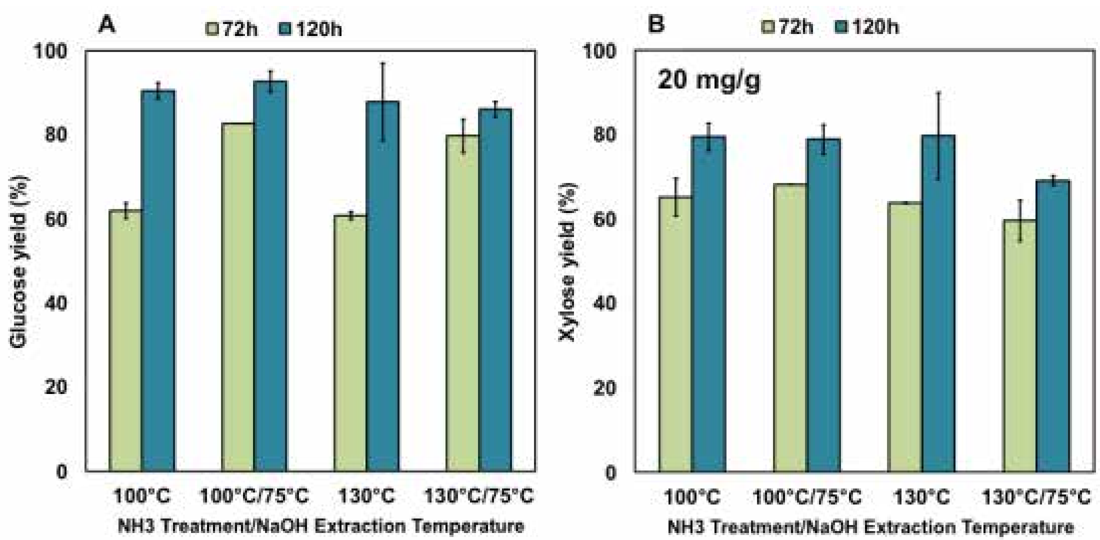
Cellulose digestibility with industrial enzyme cocktails

- Retain >90% of the cellulose and >80% of the hemicellulose in the pretreated solids
- Enhancing enzymatic hydrolysis of biomass by altering its crystalline structure (cellulose I to cellulose III_I)
- ~150 g/L of total monomeric sugars (glucose, xylose, and arabinose) obtained for digestions at 20% solids

X-ray diffractograms of pretreated solids

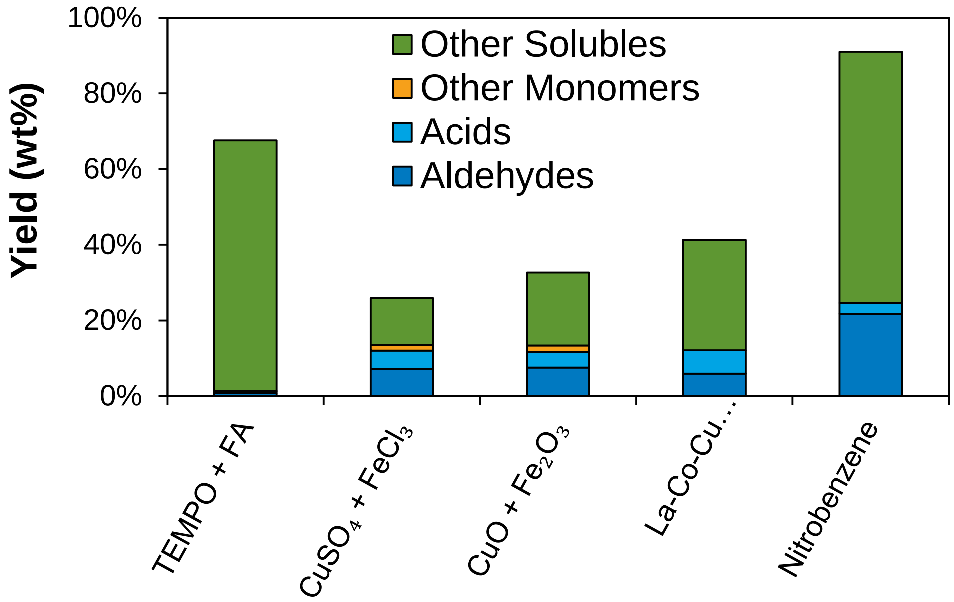


Monomeric sugar yields after enzymatic hydrolysis at 20% solids



Outcome: Two process-relevant pretreatments that are effective for lignin fractionation and produce high-pH lignin streams

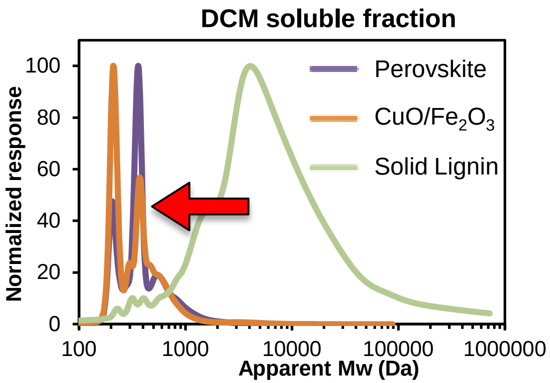
Lignin depolymerization of post-EH lignins



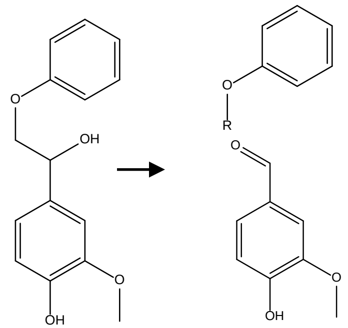
Screened multiple oxidative catalysts at high pH

- Moderate to high lignin solubilization
- High monomer yields
- Side products are mainly non-aromatic acids that will still integrate with downstream processing
- Less expensive catalysts, no H_2
- (Alkaline) aqueous solvent

Products are highly depolymerized



Oxidative catalysis can cleave C–O and C–C bonds



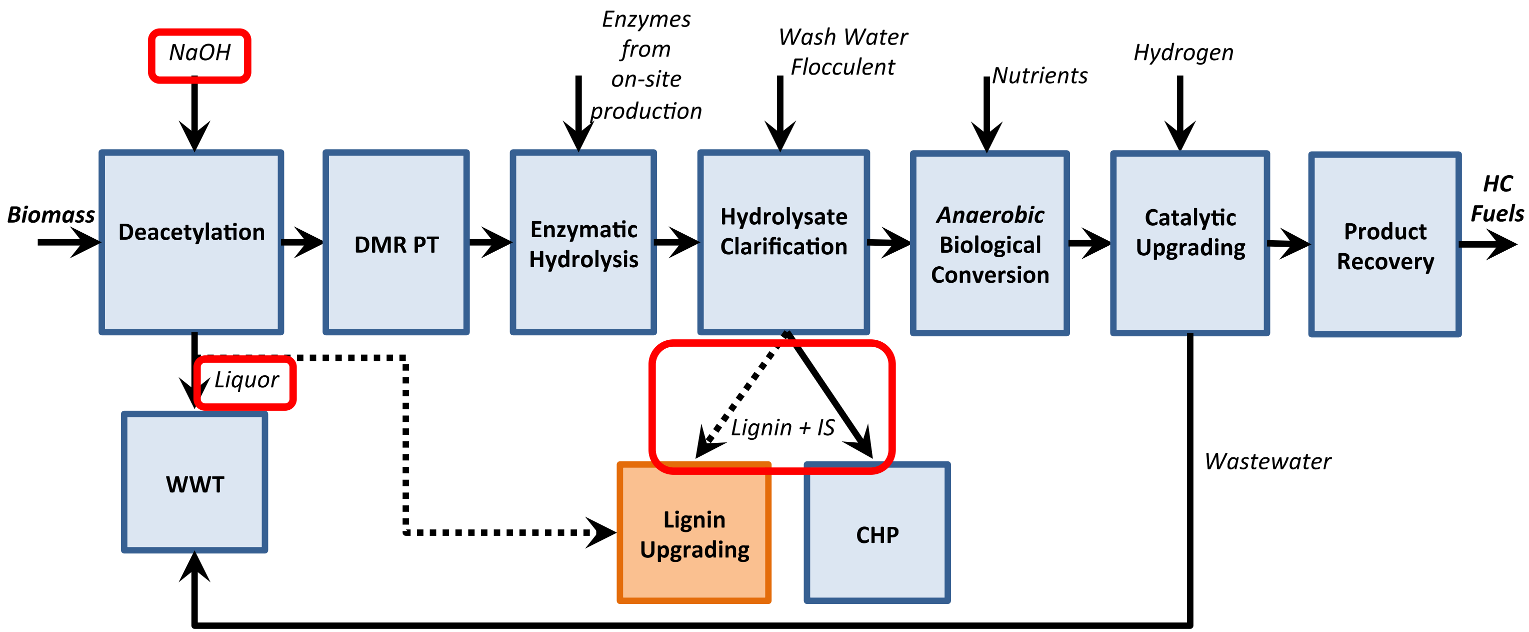
Moving forward with oxidative depolymerization

- Several observed and expected advantages over nonoxidative routes
- Significant space for both fundamental and applied developments

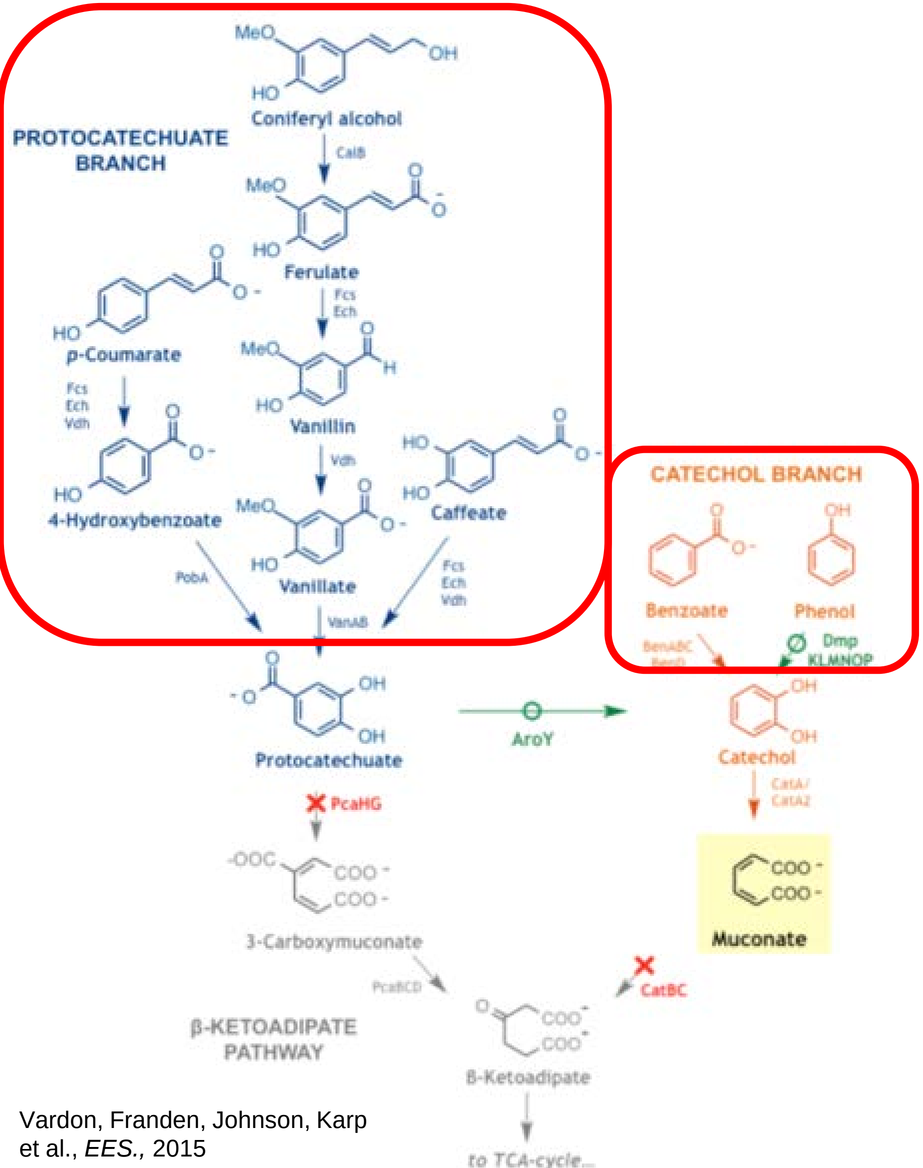
Summary of lignin isolation and depolymerization

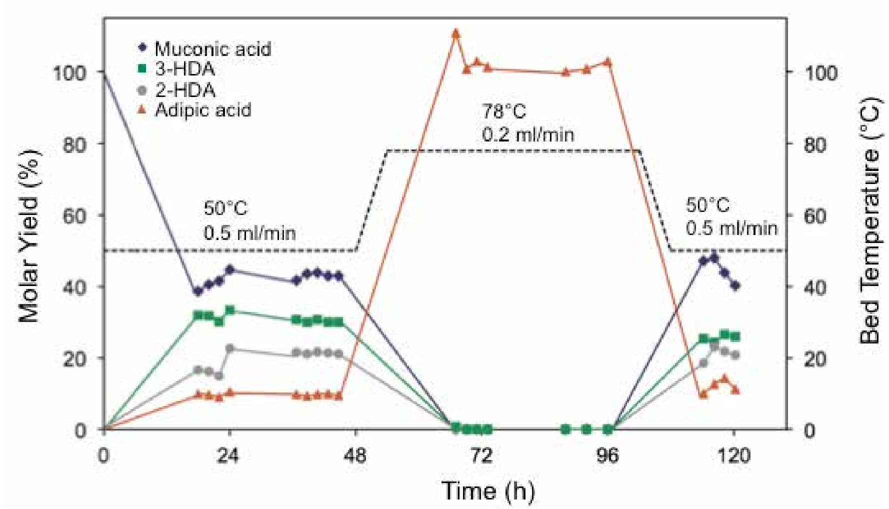
Can partially isolate high-pH lignin stream in pretreatment and isolate remaining solids after enzymatic hydrolysis

- Key target is to understand and design catalysts for enhanced depolymerization of lignin-rich streams, using perovskites as a basis going forward
- Produce water-soluble aromatic monomers for biological upgrading
- Separations are key; working closely with the Separations Consortium



Adipic acid production via biological funneling





Vardon, Franden, Johnson, Karp et al., *EES.*, 2015
Vardon et al., *Green Chem.*, 2016

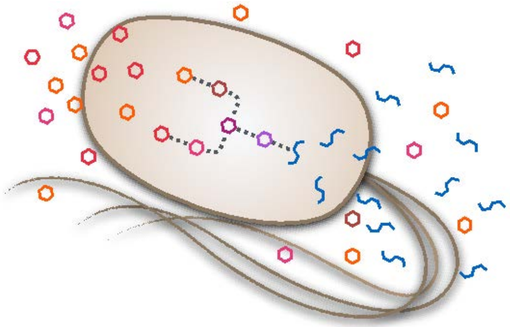
Adipic acid identified as a primary target from lignin from a TEA and LCA perspective

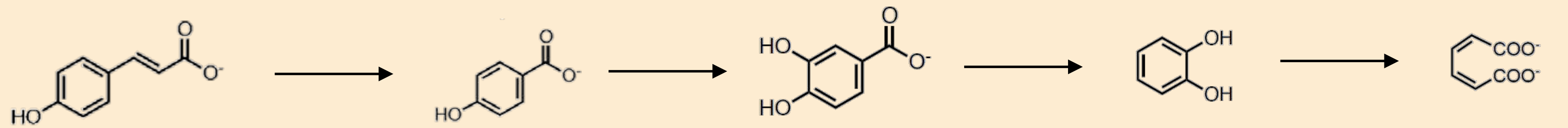
- Combined metabolic engineering, fermentation, separations, and catalysis
- Demonstrated muconic acid production in engineered *P. putida* KT2440
- Achieved >90% recovery and ~100% conversion of muconic acid to adipic acid in flow conditions

Muconic acid production in bioreactors

Bioreactor cultivation enables titer, rate, yield improvements

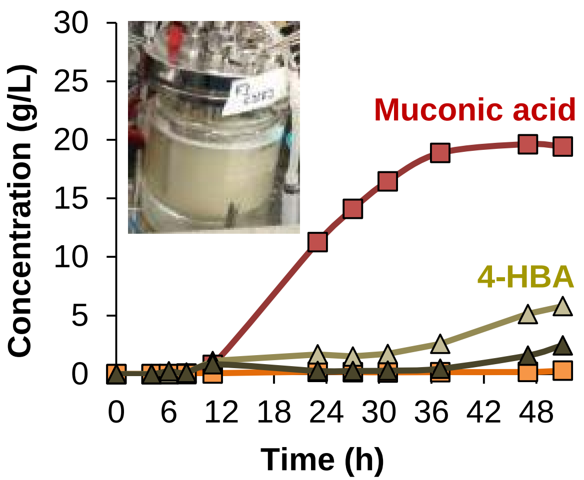
- Collaboration with **Targeted Microbial Development** project
- Achieved **30-52 g/L, 0.6 g/L/h, ~100% yield** on model aromatic compounds
- Conducting multiple-substrate feeding to understand competition
- Strain evolution and optimization ongoing to >**50 g/L, 1 g/L/h, ~100% yield**



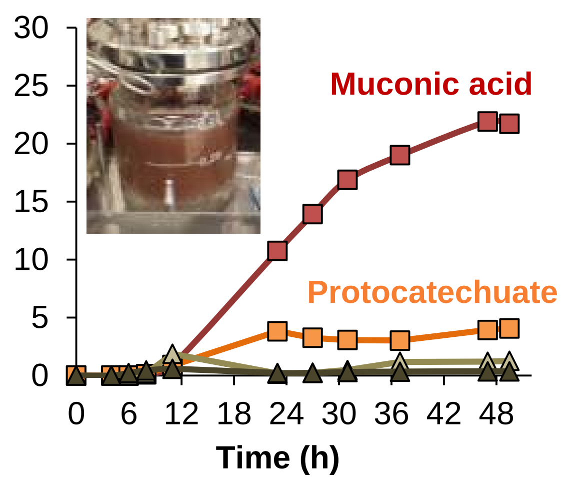


p-Coumarate → **4-Hydroxybenzoate** → **Protocatechuate** → **Catechol** → **Muconate**

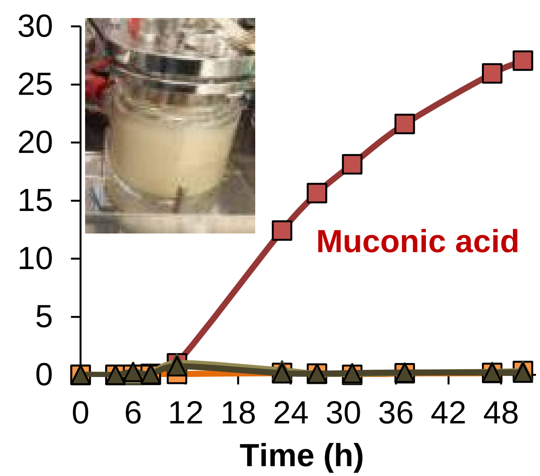
184: EcdBD overexpression



238: Crc Knockout



242: EcdBD + CrcKO



Relevance

Lignin utilization will be essential to achieve 2022 $3/GGE HC fuel cost targets and commercial viability of lignocellulosic biorefineries where carbohydrates go to fuels

- **Overall lignin conversion target: 50% conversion of lignin to adipic acid**
- **Biology target: 50 g/L, 100% yield, 1 g/L/h; Status: 30-52 g/L, 100% yield, 0.6 g/L/h**

Feedstock Variability:
- Working with NREL and INL projects to understand lignin variability

Efficient Pretreatment:
- Developed new fractionation method

Efficient Low T Deconstruction:
- Developing new biological methods to convert heterogeneous lignin compounds to value-added products

Efficient Cat. Upgrading of Aromatics:
- Developing catalysts for lignin depolymerization
- Working with other BETO-funded projects in lignin isolation and scale-up

Process Integration:
- Converting lignin to finished products

Key Stakeholders and Impacts:

- **Industrial and academic research focused on carbohydrate utilization can leverage lignin utilization processes**
- Work will enable adoption of lignin utilization in modern biorefinery designs
- Lignin impacts the **"Whole Barrel of Oil"** initiative
- **Portfolio of chemicals from lignin will diversify and accelerate development of the biomass value chain**
- Significant amounts of peer-reviewed science and IP are being generated from this work (25 papers)
- Methods to upgrade heterogeneous intermediates can be adapted to "waste carbon" valorization projects, including in "aqueous phase utilization" – key MYPP barrier

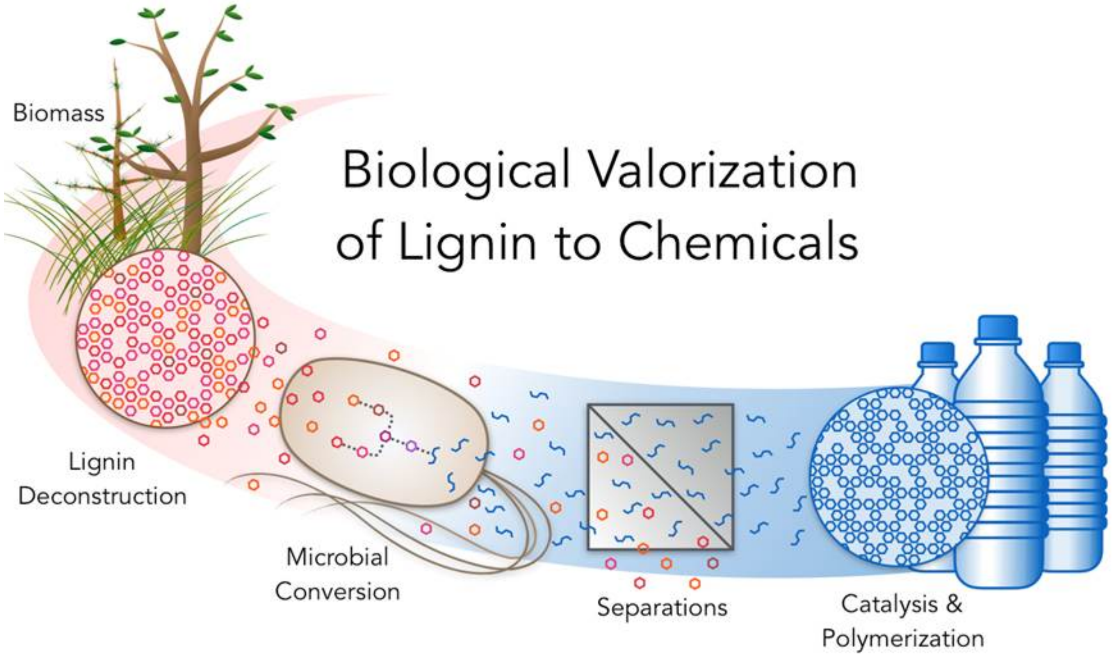
Future Work

Lignin Analytics, Isolation, and Depolymerization

- Continue advancing analytical methods for both polymeric lignin and deconstruction products
- Develop lignin isolation in collaboration with pretreatment/integration projects
- Focus on **catalyst design/reaction** engineering for lignin depolymerization in process-relevant high-pH streams

Lignin Upgrading

- Work closely with Sep. Consortium to condition streams for upgrading.
- Develop *P. putida* strain and bioreactor cultivation with TMD project
- Pursue muconic acid upgrading process integration
- Expand products beyond adipic acid



Integration

- Down-select to a single lignin stream and a catalyst for depolymerization by start of FY20
- Begin scale-up activities for lignin isolation and depolymerization reactor setups

Summary

1) Approach:
   - **<u>Obtain</u>** and **upgrade** lignin to chemicals and/or fuels with fundamentals-driven, interdisciplinary approach underpinned by TEA and LCA
   - Collaborate widely with academic, national lab, and industrial partners including BC Platform tasks

2) Technical accomplishments:
   - Applied **new analytical methods** including GEMBE and GCxGC/TOF-MS to quantify lignin products
   - Demonstrated effective **lignin removal** from biomass via ammonia pretreatment and high-pH extraction
   - Demonstrated initial, effective **lignin depolymerization** using perovskite catalysts in high-pH streams
   - Achieved **30-52 g/L, 0.6 g/L/h, and 100% yield of muconate** from engineered strain of *P. putida*
   - Demonstrated **quantitative conversion of bioderived muconic acid to adipic acid** in a flow reactor

3) Relevance:
   - Coproducts essential to meet DOE hydrocarbon cost targets
   - Addresses Whole Barrel of Oil Initiative and bolsters the biomass value chain

4) Critical success factors and challenges:
   - Heterogeneity, **economic** and **sustainable** production of coproducts, high yields of products needed

5) Future work:
   - Finalize conditions for isolation/deconstruction of lignin by FY19, ramp up scaling of depolymerization
   - Continue development of muconic acid production and conversion

6) Technology transfer:
   - Working with **multiple industry partners** to build commercialization path to lignin utilization
   - **Direct** and **functional replacement** chemicals from biomass

Acknowledgments

- **BETO**: Jay Fitzgerald and Brandon Hoffman

- Mary Biddy
- Brenna Black
- Stuart Black
- David Brandner
- Adam Bratis
- Steve Chmely
- Nicholas Cleveland
- Peter Ciesielski
- Robin Cywar
- Ryan Davis
- Bryon Donohoe
- Rick Elander
- Mary Ann Franden
- Erica Gjersing
- Michael Guarnieri
- Jessica Hamlin
- Chris Johnson
- David Johnson
- Rui Katahira
- Eric Karp
- Jake Kruger
- Eric Kuhn
- Kelsey Lawrence
- Jeffrey Linger
- Lauren Magnusson
- Kellene McKinney
- Bill Michener
- Ashutosh Mittal
- Claire Nimlos
- Marykate O'Brien
- Phil Pienkos
- Heidi Pilath
- Michael Resch
- Nicholas Rorrer
- Davinia Salvachua
- Dan Schell
- Holly Smith
- Matthew Sturgeon
- Derek Vardon
- Shuting Zhang

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy — BIOMASS PROGRAM

External collaborators

- Mahdi Abu-Omar, Clint Chapple, Rick Meilan, Purdue University
- Linda Broadbelt, Northwestern University
- Brent Shanks, Iowa State University
- Alison Buchan, University of Tennessee Knoxville
- Andrea Corona, DTU
- Adam Guss, Oak Ridge National Laboratory
- John McGeehan, Simon Cragg, University of Portsmouth
- Matt Munson, Marc Salit, NIST
- Ellen Neidle, University of Georgia
- Rob Paton, University of Oxford
- Allison Ray, Idaho National Laboratory
- R. Robinson, E. Zink, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory
- Yuriy Roman-Leshkov, MIT
- Jerry Ståhlberg, Mats Sandgren, Swedish University of Agricultural Sciences
- Timm Strathmann, UIUC, CSM

Additional Slides

- Previous reviewer comments from 2011 Peer Review related to lignin
- Previous reviewer comments from 2013 Peer Review on Lignin Utilization Project
- Previous reviewer comments from 2015 Peer Review on Lignin Utilization Project
- Publications
- Patents
- Acronyms
- Techno-economic and life-cycle analysis

Previous reviewer comments regarding lignin (2011)

Lignin Utilization is a new task, but herein are included comments from the 2011 reviews on the Biochemical Conversion platform related to lignin.

- *"Expansion of the approach to lignin might be worth some analysis as it is a quite significant fraction of the total cellulosic biomass available."*

- *"Lignin is a major component of biomass, yet it is given relatively little attention in the Platform work (other than its negative impact on saccharification). This is undoubtedly due to the difficulty in making liquid fuels from lignin, especially via a biochemical process. Our perception is that it is reasonable to begin to expand the work directed at finding value-added uses for lignin (there is one such international project). If successful in this effort, then it seems this would have a major impact on the cost of converting the carbohydrate component to ethanol."*

Previous reviewer comments on Lignin Utilization (2013)

Are there any other gaps in the portfolio for this technology area? Are there topics that are not being adequately addressed? Are there other areas that BETO should consider funding to meet overall programmatic goals?

“Funding for both the biological and the catalytic pathway should include FOAs for higher-value products that will enhance the economic viability of the hydrocarbon platform. Lignin utilization is a key co-product that needs continued research.”

Previous reviewer comments on Lignin Utilization (2013)

- *"Excellent project! Very impressive with great progress in less than a year."*
- *"Overall, this is a strong project that addresses one of the key hurdles to achieve the 2017 and 2022 MYPP goals; namely the utilization of lignin to create value-added products to support replacement of the whole barrel of oil and achieving the $3/gal metric. This project is a good example of the application of fundamentals-driven science and techno-economic analyses."*
- *"Seems like a great project; it is too early to see where this will end up but it has promise. How will this be different from other lignin upgrading efforts? PIs need to keep an eye on development of low-lignin transgenic plants."*
- *"This is a very strong project. The highest and best lignin utilization is an essential component of bioenergy and biochemical production. As the PI mentions, lignin heterogeneity is a major hurdle."*

Previous reviewer comments on Lignin Utilization (2013)

- *"This project tackles a very difficult technical challenge that has been studied extensively. The outcome of using lignin and taking to intermediates to make higher-value chemicals could be significant."*

- *"This is a very relevant and important project that allows low-cost feedstock for fuels and chemicals."*

PI Response to Reviewer Comments:

- We thank the reviewers for their positive comments. Regarding the work on plants with genetically modified lignin, we are currently collaborating with several groups on this topic to understand the influence of less recalcitrant lignins on the lignin removal, deconstruction, and upgrading. The genetically modified lignin feedstocks may offer a dramatic reduction in processing costs and simplify lignin upgrading processes, which certainly could be a revolutionary change in biomass conversion.

Previous reviewer comments on Lignin Utilization (2015)

Project Overview

- lignin upgrading; lignin depolymerization in the liquid phase
  significant benefit to biorefinery infrastructure
  many collaborators
  lignin valorization essential to reduce fuel cost
- Good overview, project gives good history, context, and high-level objectives.
- Isolation and upgrade lignin. Good overview.
  Lignin depolymerization and then upgrading
  Great introduction to context, rational and history
- Lignin utilization great focus. lignin is key to co products and economic viability.
  Simple processes to depolymerize is a good. Start with simple.
  TEA being done a well. good
  Significant partners as part of the team. Impressive team and collaborators.
  -$2 /GGe is target. Where is it now?

Previous reviewer comments on Lignin Utilization (2015)

Project Approach

- lignin in the liquid phase
  need high yields of stable material
  "biological funneling" to single intermediates
  simple integrated approaches/multidisciplinary

- Reasonable project approach. This is project is working with a complex substrate, thus there may be many possible approaches. Need to make sure that they have selected wisely before proceeding. Biological funneling seems to be a new approach and should definately be explored. As one reviewer mentioned you are breaking down very interesting molecules to a simple compound in the cell and then rebuilding, so it might be an entropy battle, sort of reminds you of gasification, bust it all up and rebuild, ehen you might have something already built that you could take advantage of.
  Just make sure that the choice of process to attack is well thought out, bio is probably ok, BCD should make sure of a little more.

- Approach, challenges and CSF well laid out.
  Task structures well defined.

- looking at the two different lignins containing streams from an IBR process is good.

Previous reviewer comments on Lignin Utilization (2015)

Technical Progress and Accomplishments

- alkaline pretreatment processes and others for lignin enriched and lignin-centric processes.
  alkaline pretreated blackliquor
  alternative pretreatments (for example organosolv - but deselected based on economics)
  homogeneous and heterogeneous catalysis
  primary challenge in lignin valorization to co-products is heterogeneity (ie what to do with all the stuff you get) - soil microbes can take those mixtures into key intermediates (acetyl co-A). P putida used to make PHA (under N2 limitation); also muconate then to adipic acid (via catalysis)
- Significant progress has been made for a short-life project (Oct '14). No prior review to report progress against.
- Good work on BCD but I worry about the salt load. You're probably aware of the work at NREL in the 90's on this. There was also an engineering study to look at just how to handle the salt generated by neutralization of the alkaline. I don't think a suitable solution was found. Not clear just why organosolv was rejected. Of course you know that is the process API is using in their demonstration unit.
- Alkaline pretreatments optimizing lignin extraction. Organosolv not economic. Alkaline peroxide pretreatment in analysis DMR lignin extraction from spent solids from DMR or dilute acid
- Lignin upgrading biological funnel -> breaks lignin way down before building up
- Seem to have evaluated logical sources of lignin and a variety of pre-treatment technologies. Pretreatment lignin stream: Post treatment lignin stream; Alkaline pretreatment; looked at pilot scale including continuous pre-treatment. Looked at other pretreatment and eliminated if needed. Looked at DMR stream. Catalyst work has progressed to eliminate Ni. Ability to regenerate catalyst is important Lignin upgrading:

Previous reviewer comments on Lignin Utilization (2015)

Project Relevance

- Biological funneling approach to make multiple products; lignin utilization essential to reach goals
- Relevance is fairly clear: Utilization of lignin is a requirement for even near-term commercial success of most biomass conversion processes. Works toward BETO/MYPP goals.
- Fits the program well. Do not forget about the lignin from the current commercial producers.
- Lignin key to achieving economic targets for HC fuels
- Lignin utilization is critical to the success /economic of making cellulosic material to HC.

Future Work

- Finalize conditions for isolation/deconstuction; ramp up lignin upgrading
- Future work plan is clearly adequate for project goals and includes milestones and quantified metrics. PI has given very good picture of how they intend to work toward these goals and a level of probability of success.
- Good approach, including DAP as that incompases the Poet and Abengoa like materials.
- Good timetable of future work
- Focusing on a couple of options for deconstruction is the right thing to do for the path forward.

Previous reviewer comments on Lignin Utilization (2015)

Overall Impressions

- excellent work with tremendous potential. Could really change the economics of a biorefinery if the lignin is taken advantage of
- Lignin utilization is critical to near-term and mid-term commercial success. This project is making significant progress toward allowing commercial utilization of the lignin stream. Integration with other lignin-related projects is high, which is encouraging and has the potential for a high level of synergy, enhancing probability of success.
- Very timely to get into lignin conversion as the country is about to be producing over 1,000 ton/day of by-product lignin from the three conversion facilities coming on-line. They would all like to have a value add over burning. Could BETO play a role of surveying what the "lignin" is that is coming from these plants, what its variability is with changing feedstocks and process conditions. What do the producers want from DOE? "Lignin" as the mixture comes from the biorefinery is not all the same, what challenges will be faced in converting it.

  Great time to be doing this. Lets take advantage of the timing and not waste any resources or time (not to say that this task is, but lets take a little closer look).

- Very interesting and strategic work. Project seems aligned and connected with other projects and development.

- One comment is that the commercial plants coming on line all use acid pre-treatment, not alkaline. are there any plans to look at acid pretreatment derived lignin. Very interesting research.

Publications

1. M.S. Munson, E.M. Karp, C.T. Nimlos, M. Salit, G.T. Beckham, “Gradient Elution Moving Boundary Electrophoresis enables rapid analysis of acids in complex biomass-derived streams”, in press at *ACS Sust. Chem. Eng.*
2. E.A. Anderson, R. Katahira, M. Reed, M.G. Resch, E.M. Karp, G.T. Beckham, Y. Roman-Leshkov, “Reductive catalytic fractionation of corn stover lignin”, in press at *ACS Sust. Chem. Eng.*
3. T. Elder, L.R. Berstis, G.T. Beckham, M.F. Crowley, “Coupling and reactions of 5-hydroxyconiferyl alcohol in lignin formation”, *J. Ag. Food Chem.* (2016) 64(23), pp. 4742–4750.
4. L.R. Berstis, T. Elder, M.F. Crowley, G.T. Beckham, “The radical nature of C-lignin”, in press at *ACS Sust. Chem. Eng.*
5. E.M. Karp, C.T. Nimlos, S. Deutch, D. Salvachúa, R. Cywar, G.T. Beckham*, “Quantification of acidic compounds in complex biomass-derived streams”, *Green Chem.* (2016) 18, pp. 4750-4760.
6. C.W. Johnson, D. Salvachúa, P. Khanna, H. Smith, D.J. Peterson, G.T. Beckham*, “Enhancing muconic acid production from glucose or lignin via increased protocatechuate decarboxylase activity”, *Metabolic Eng. Comm.* (2016) 3, pp. 111-119.
7. G.T. Beckham*, C.W. Johnson, E.M. Karp, D. Salvachúa, D.R. Vardon, “Opportunities and challenges in biological lignin valorization”, *Curr. Opin. Biotech.* (2016), 42, pp. 40-53.
8. D.R. Vardon, N.A. Rorrer, D. Salvachúa, A.E. Settle, C.W. Johnson, M.J. Menart, N.S. Cleveland, P.N. Ciesielski, K.X. Steirer, J.R. Dorgan, G.T. Beckham, “cis,cis-Muconic acid: Separation and catalysis to bio-adipic acid for nylon-6,6 polymerization”, *Green Chem*. (2016), 18, pp. 3397-3413.
9. J.S. Kruger, N.S. Cleveland, S. Zhang, R. Katahira, B.A. Black, G.M. Chupka, T. Lammens, P.G. Hamilton, M.J. Biddy, G.T. Beckham, “Lignin depolymerization with nitrate-intercalated hydrotalcites”, *ACS Catalysis* (2016), 6(2), pp. 1316-1328.
10. R. Katahira, A. Mittal, K. McKinney, X. Chen, M.P. Tucker, D.K. Johnson, G.T. Beckham, “Base-catalyzed depolymerization of biorefinery lignins”, *ACS Sust. Chem. Eng*. (2016), 4(3), pp. 1474–1486, highlighted as ACS Editor’s Choice.
11. Y.S. Choi, R. Singh, J. Zhang, G. Balasubramaniam, M.R. Sturgeon, R. Katahira, G. Chupka, G.T. Beckham, B.H. Shanks, “Pyrolysis reaction networks for lignin model compounds: Unraveling thermal deconstruction of β-O-4 and α-O-4 compounds”, *Green Chem*. (2016), 18, pp. 1762-1773.
12. S.M. Cragg, G.T. Beckham, N.C. Bruce, T.D.H. Bugg, D.L. Distel, P. Dupree, A.G. Etxabe, B.S. Goodell, J. Jellison, J.E. McGeehan, S.J. McQueen-Mason, K. Schnorr, P.H. Walton, J.E.M. Watts, M. Zimmer, “Lignocellulose degradation mechanisms across the Tree of Life”, *Curr. Opin. Chem. Biol*. (2015), 29, pp. 108-119.
13. E.M. Karp, M.G. Resch, B.S. Donohoe, P.N. Ciesielski, M.H. O’Brien, J.E. Nill, A. Mittal, M.J. Biddy, G.T. Beckham, “Alkaline pretreatment of switchgrass”, *ACS Sust. Chem. Eng.* (2015), 3(7), pp. 1479-1491.
14. A.W. Pelzer, M.R. Sturgeon, A.J. Yanez, G. Chupka, M.H. O’Brien, R. Katahira, R.D. Cortright, L. Woods, G.T. Beckham, L.J. Broadbelt, “Acidolysis of α-O-4 aryl-ether bonds in lignin model compounds: A modeling and experimental study”, *ACS Sust. Chem. Eng.* (2015), 3(7), pp. 1339-1347.
15. C.W. Johnson, G.T. Beckham, “Aromatic catabolic pathway selection for optimal production of pyruvate and lactate from lignin”, *Metabolic Engineering* (2015), 28, pp. 240-247.
16. D.R. Vardon, M.A. Franden, C.W. Johnson, E.M. Karp, M.T. Guarnieri, J.G. Linger, M.A. Salm, T.J. Strathmann, G.T. Beckham, “Adipic acid production from lignin”, *Energy and Environmental Science*. (2015), 8, pp. 617-628.
17. J.G. Linger‡, D.R. Vardon‡, M.T. Guarnieri‡, E.M. Karp‡, G.B. Hunsinger, M.A. Franden, C.W. Johnson, T.J. Strathmann, P.T. Pienkos, G.T. Beckham, “Lignin valorization through integrated biological funneling and chemical catalysis”, *Proc. Natl. Acad. Sci*. (2014), 111(33), pp. 12013-12018.
18. A. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, “Lignin Valorization: Improving Lignin Processing in the Biorefinery”, *Science* (2014), 344, 1246843.
19. E.M. Karp, B.S. Donohoe, M.H. O’Brien, P.N. Ciesielski, A. Mittal, M.J. Biddy, G.T. Beckham, “Alkaline pretreatment of corn stover: Bench-scale fractionation and stream characterization”, *ACS Sust. Chem. Eng.* (2014), 2(6), pp. 1481-1491, featured on cover.
20. M.G. Resch, B.S. Donohoe, P.N. Ciesielski, J.E. Nill, L. Magnusson, M.E. Himmel, A. Mittal, R. Katahira, M.J. Biddy, G.T. Beckham, “Clean fractionation pretreatment reduces enzyme loadings for biomass saccharification and reveals the mechanism of free and cellulosomal enzyme synergy“, *ACS Sust. Chem. Eng*. (2014), 2(6), pp. 1377-1387.
21. R. Katahira, K. McKinney, A. Mittal, P.N. Ciesielski, B.S. Donohoe, S. Black, D.K. Johnson, M.J. Biddy, G.T. Beckham, “Evaluation of clean fractionation pretreatment for the production of renewable fuels and chemicals from corn stover“, *ACS Sust. Chem. Eng*. (2014), 2(6), pp. 1364-1376.
22. M.R. Sturgeon‡, S. Kim‡, K. Lawrence, R.S. Paton, S.C. Chmely, M.R. Nimlos, T.D. Foust, G.T. Beckham, “An experimental and theoretical study of acid catalysis of aryl-ether linkages: Implications for lignin acidolysis”, *ACS Sustain. Chem. Eng.* (2014), 2(3), pp. 472-485.
23. M.R. Sturgeon, M.H. O’Brien, P.N. Ciesielski, J. Kruger, S.C. Chmely, R. Katahira, J. Hamlin, K. Lawrence, T.D. Foust, R.M Baldwin, M.J. Biddy, G.T. Beckham, “Lignin depolymerization by nickel supported layered double hydroxide catalysts”, *Green Chem*. (2014), 16, pp. 824-835.
24. R. Davis, L. Tao, E. Tan, M. Biddy, G.T. Beckham, C. Scarlata, J. Jacobson, K. Cafferty, J. Ross, J. Lukas, D. Knorr, P. Schoen, “Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid Prehydrolysis and Enzymatic Hydrolysis Deconstruction of Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons”, NREL Report, (2013).
25. S.C. Chmely, S. Kim, P.N. Ciesielski, G. Jiminez-Oses, R.S. Paton, G.T. Beckham, “Mechanistic study of a Ru-xantphos catalyst for tandem alcohol dehydrogenation and reductive aryl-ether cleavage”, *ACS Catalysis* 2013.

Patents

Patents:

- Base-catalyzed depolymerization of lignin with heterogeneous catalysts, application 61/710,240 filed on 10/5/2012

- Lignin conversion to fuels, chemicals, and materials, application 14/563,299 filed on 12/8/2014

Acronyms

- BCD: Base-Catalyzed Depolymerization
- CF: Clean Fractionation
- CHP: Combined Heat and Power
- DAP-EH: Dilute-Acid Pretreated, Enzymatically Hydrolyzed feedstock
- DDR-EH: Deacetylated, Disk-Refined, Enzymatically Hydrolyzed feedstock
- LCA: Life-Cycle Analysis
- MW: Molecular Weight
- TEA: Techno-Economic Analysis

Techno-economic and life-cycle analysis

Preliminary TEA shows a pathway to $3/gge with lignin utilization and a massive GHG reduction when targeting adipic acid as a product