NATIONAL RENEWABLE ENERGY LABORATORY

DOE Bioenergy Technologies Office (BETO)

2019 Project Peer Review

Gas Phase Selective Partial Oxidation of Lignin for Co-products from Biomass Conversion

WBS# 2.3.1.501– 33404

Wednesday, March 6, 2019
Denver, CO

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Goal Statement

Goal – Produce phenolic co-products from a biorefinery lignin stream by developing lignin pyrolysis coupled with selective catalytic oxidation to create a valuable, diverse revenue stream to facilitate BETO's $2.50/GGE cost targets

- *Focus on high value **phenolic products** with **large markets** and potential for bio-adoption (support >200 biorefineries at 2000 tonne/day biomass)*

Outcome: A process-agnostic technology to create a revenue stream by producing phenols from biorefinery lignin, thereby enabling cost-competitive fuel production

Conversion Technology	Benchmark on Commercial Catalyst*	NREL State of Technology *		Long-Term Target	Relevance: R&D Challenge
Lignin Pyrolysis	Char Yield 33%	25-50% char	→	15-25% char	Reduce foaming; increase heat transfer; improve operability and gas yields to phenolics
Partial Oxidation of Gas Phase Lignin Pyrolysis Products	Simple Phenols Yield 8%	15% yield (Go/No-Go 10%)	→	25% yield	Tune catalyst metal-oxygen bond strength and process parameters; Balance catalyst acidic and alkylation sites with oxidation sites
	Estimated reduction in MFSP $0.25/GGE*	Reduction of >$0.60/GGE*	→	Reduction of ≥$1.35/GGE*	Improve economics by integrating TEA process design with catalyst development and reaction testing

Quad Chart Overview

Timeline

- Project start date: 10/1/2017
- Project end date: 9/30/2020
- Percent complete: 40%

Budget

	Pre FY17 Costs	FY17 Costs	FY18 Costs	Total Planned Funding (FY19-Project End)
DOE Funded	$0	$0	$304K	$800K

Partners/Collaborators

- **Industry Partners:** Sweetwater Energy, Renmatix, Johnson Matthey, Sumitomo Bakelite
- **NREL BETO Projects**: Co-Products (M. Nimlos), Pretreatment & Process Hydrolysis (M. Tucker), Biochemical Platform Analysis (R. Davis), Catalytic Fast Pyrolysis (J. Schaidle)
- **BETO ChemCatBio Consortia**: Advanced Catalyst Synthesis and Characterization (ACSC), Computational Chemistry and Physics Consortium (CCPC)

BETO MYP Barriers Addressed

Ot-B. Cost of Production

Ct-C. Process Development for Conversion of Lignin

Ct-F. Increasing the Yield from Catalytic Processes

Ct-K. Developing Methods for Bioproduct Production

Developing catalysts and processes to convert lignin to high value phenolic compounds – diversifying biorefinery revenue streams and thereby reducing the MFSP from biorefineries

Objective

Produce phenolic co-products from a lignin stream by developing selective oxidation catalysts for lignin pyrolysis vapors to facilitate BETO's $2.50/GGE cost targets.

End of Project Goal (FY20)

- Demonstrate gas phase partial oxidation of lignin using a bench-scale reactor:
  - >10% phenolics yield for estimated impact of >$0.40/GGE reduction in MFSP
  - Perform detailed analysis of condensed phenols by distillation, GC/MS, GPC, and NMR

1. Overview
2. Approach
3. Progress and Accomplishments
4. Relevance
5. Future Work

1. Overview

Project Overview (1 of 2)

Context and History:

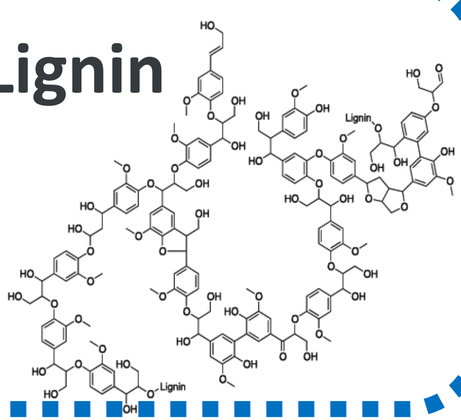
- Project in response to 2017 BETO peer review feedback
  - Opportunity for catalytic pyrolysis to upgrade specific biomass fractions (lignin, cellulose, hemicellulose) to make a narrower product slate

Project Goals:

- Upgrade lignin to simple phenols by developing catalysts to convert lignin pyrolysis vapors via oxidative cleavage
  - Simple phenols used in polycarbonates, epoxide resins, and plastics
  - >10% yield to phenolics on bench-scale by FY20

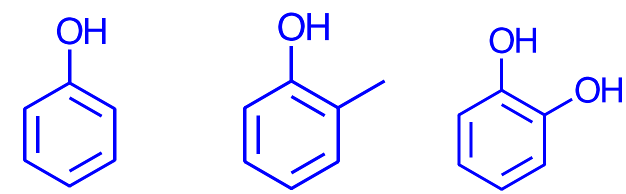
Large market sizes for phenolics could support >200 biorefineries at 2000 tonne/day biomass

Lignin



Pyrolysis
Catalytic upgrading

Oxygenated Aromatics (Simple Phenols)



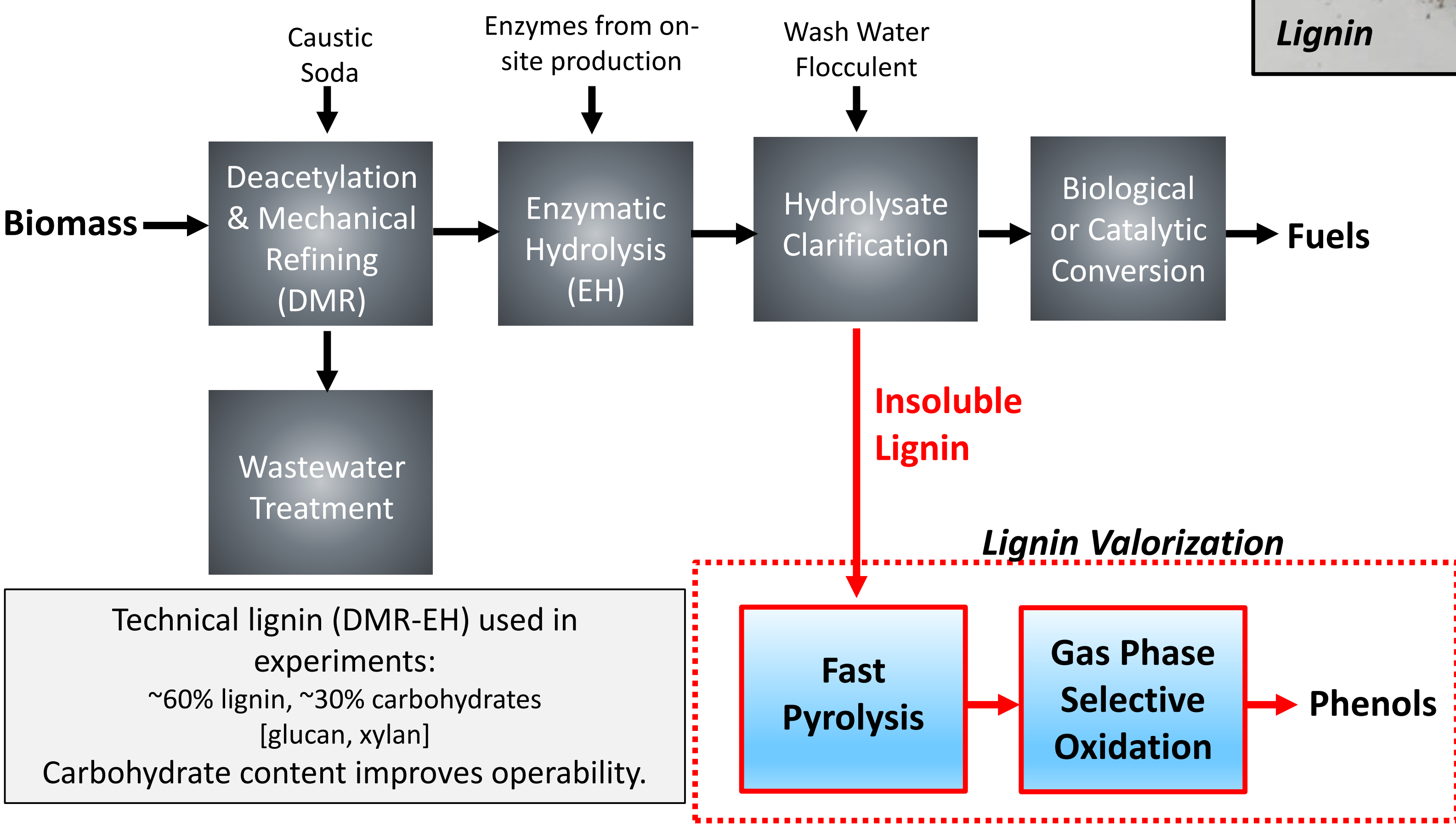
	Phenol	2-Cresol	Catechol
Price ($/kg)	$1-3/kg	$3-5/kg	$5-7/kg
Market Size (kTA)	11,400	3,400	45

Carvajal, J.; Byrne, D. *Chemical Economics Handbook Phenol (686.500)*, IHS, 2014.

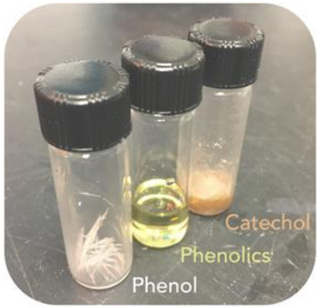
Project Overview (2 of 2)

Simplified Process Flow Diagram

1) Convert C_5/C_6 sugars from biomass to fuels
2) Produce phenols by thermochemically converting lignin pyrolysis vapors via selective oxidation



Technical lignin (DMR-EH) used in experiments:
~60% lignin, ~30% carbohydrates [glucan, xylan]
Carbohydrate content improves operability.



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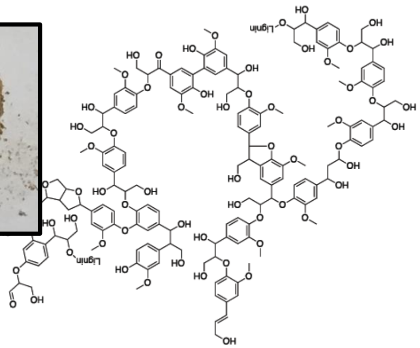
2. Approach

2. Technical Approach (1 of 4)

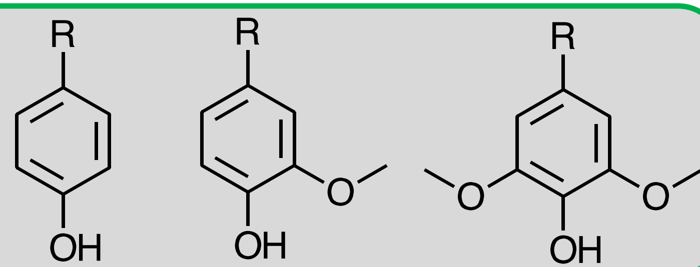
Create phenols from catalytic oxidation and avoid carbon loss to undesirable products.



LIGNIN FROM BIOCHEM. PROCESS

Pyrolysis

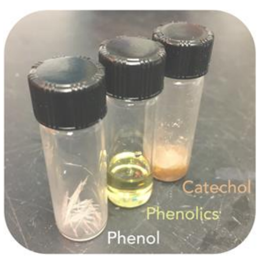
LIGNIN PYROLYSIS PRODUCTS



Catalytic partial oxidation

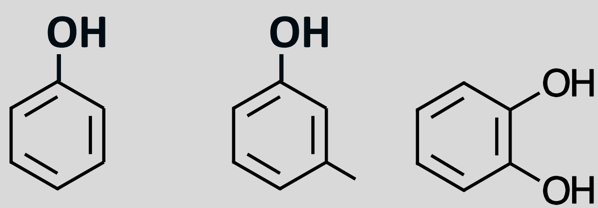
Char
25-60 wt%
(recalcitrant C-C linkages in lignin)

CO and CO_2
>10 wt%
(undesired oxidation products)



SIMPLE PHENOLS

phenol	cresol(s)	catechol
$1-2/kg	$2-3/kg	$5-7/kg
10 Mtons/y	100 ktons/y	45 ktons/y



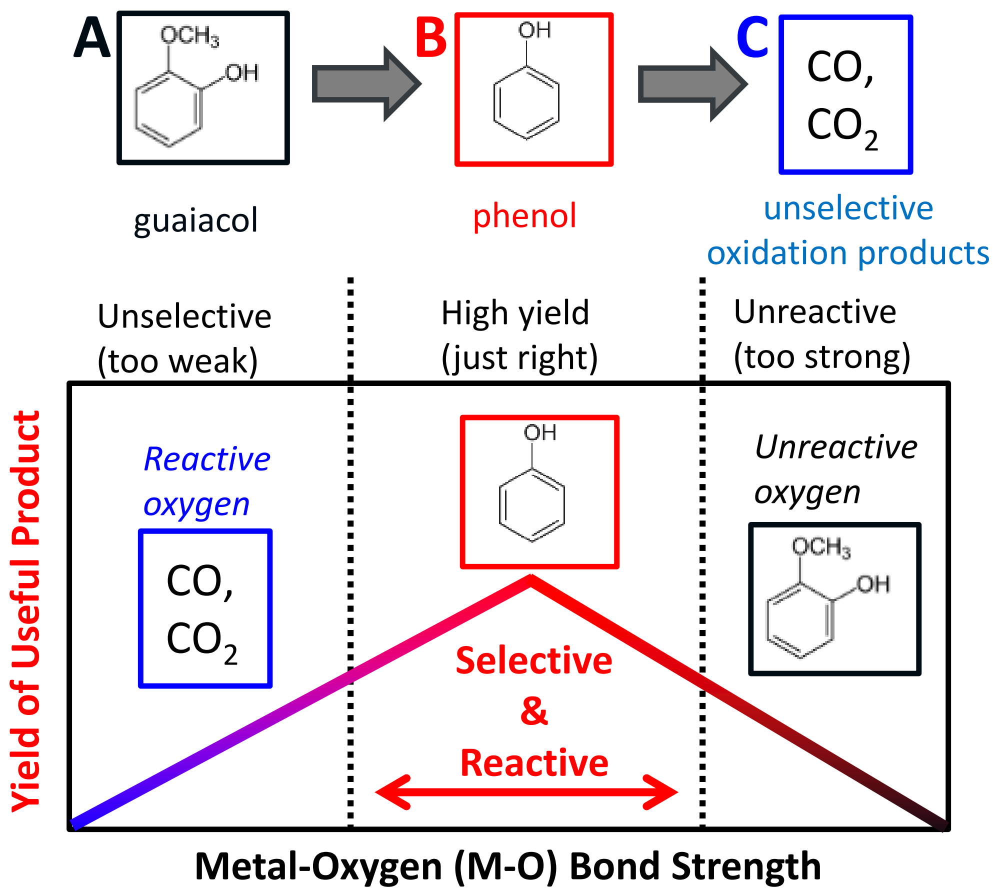
Challenges – Phenol yield is critical for economics; catalyst regeneration; lignin feeding on large systems

Synthesize catalysts with varying surface properties:

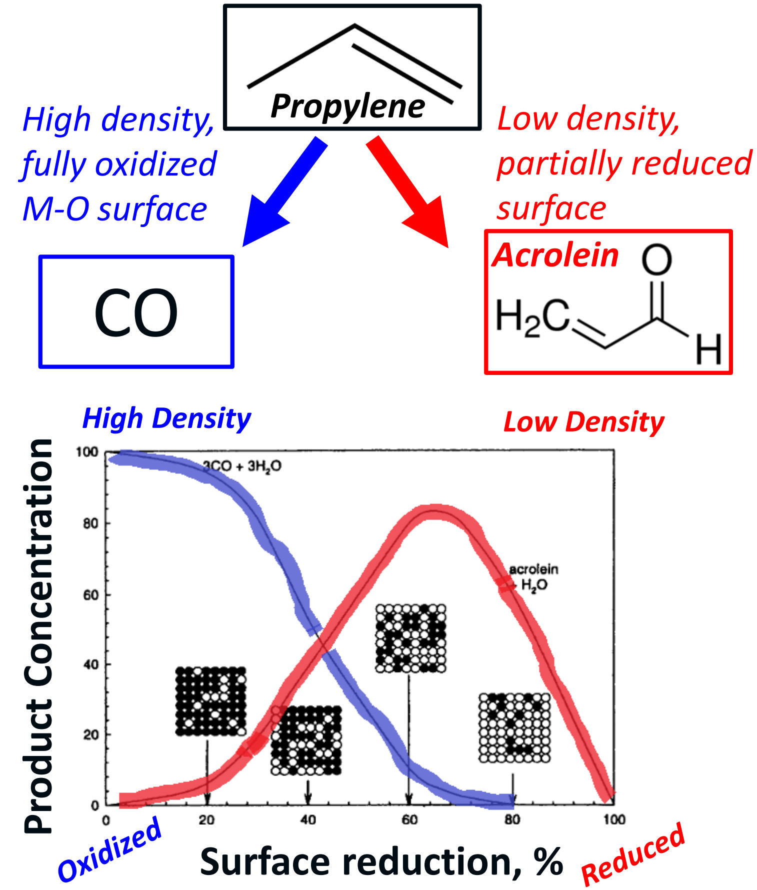
(1) Metal-oxygen bond strength **(2) Active site density**

-Important for parameters for selective oxidation catalysts

1. Metal-oxygen Bond Strength



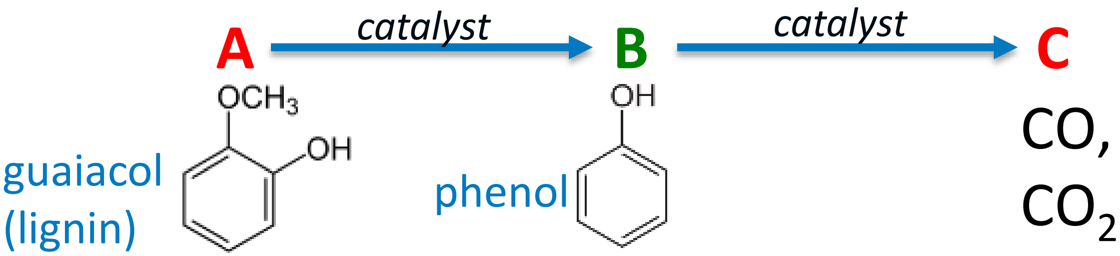
2. Active Site Density

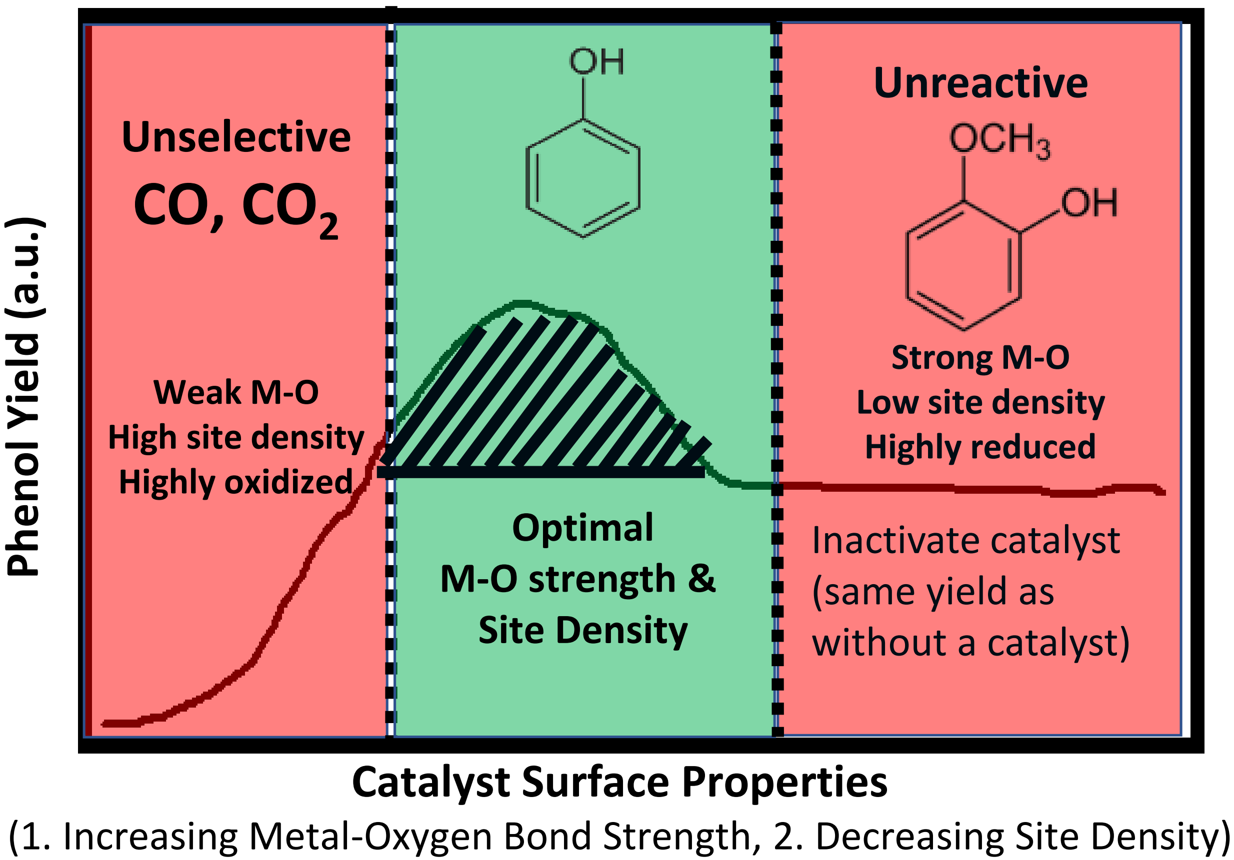


*Grasselli, *Top. Catal* 2002, 79-88. *Chen, J. Catal, 2002, 35-42.*

2. Technical Approach (3 of 4)

Tailor catalyst by changing surface properties to maximize yield of desired product (phenols).





Critical Success Factors

Achieving high phenolic yields is most critical to TEA

Challenges

- High yield and selectivity;
- Lignin feeding on large systems;
- Catalyst regeneration

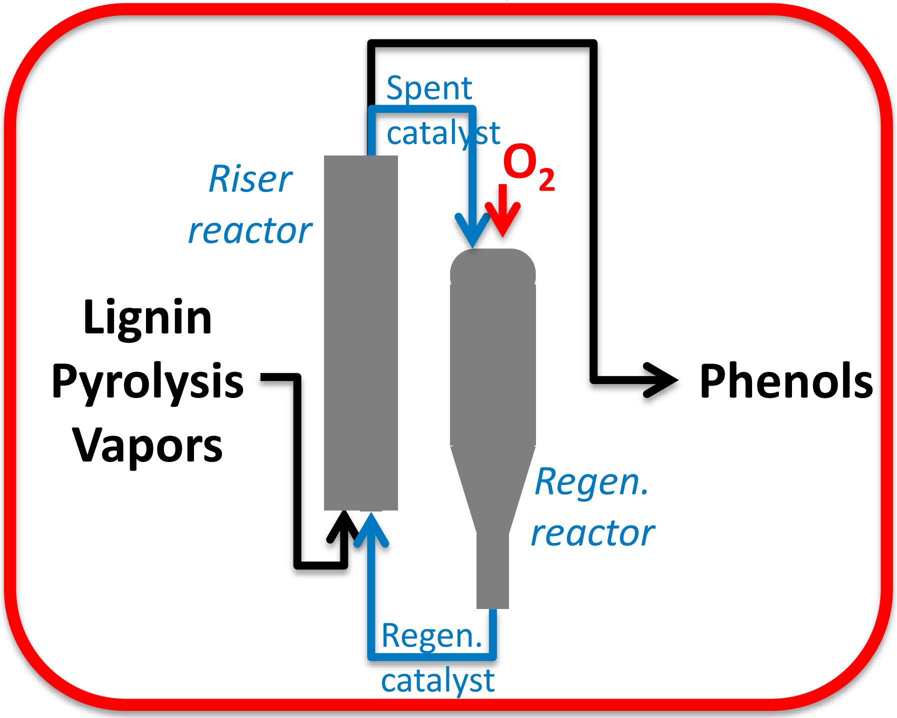
Regeneration: Closing the Catalytic Cycle

Two process options to regenerate and replenish catalyst surface oxygen:

1. Chemical looping (circulating catalyst with regeneration in separate vessel)
2. Co-feed oxidant (O_2 or CO_2)

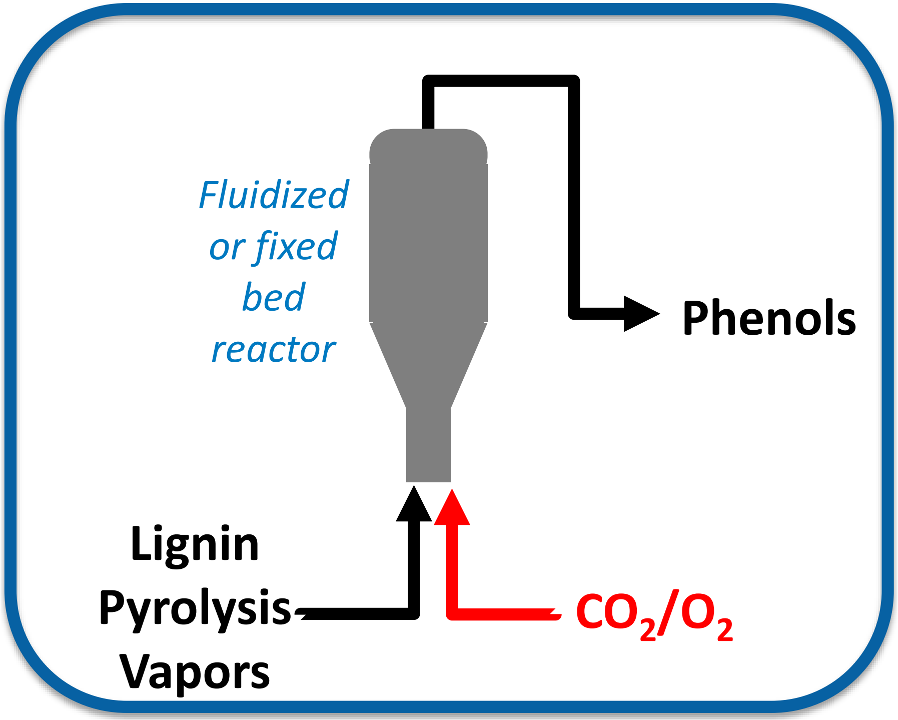
Chemical Looping

(Riser & regeneration reactors; used in industry – fluidized catalytic cracker)



Co-Feed Oxidant

(Fluidized or fixed-bed reactor)

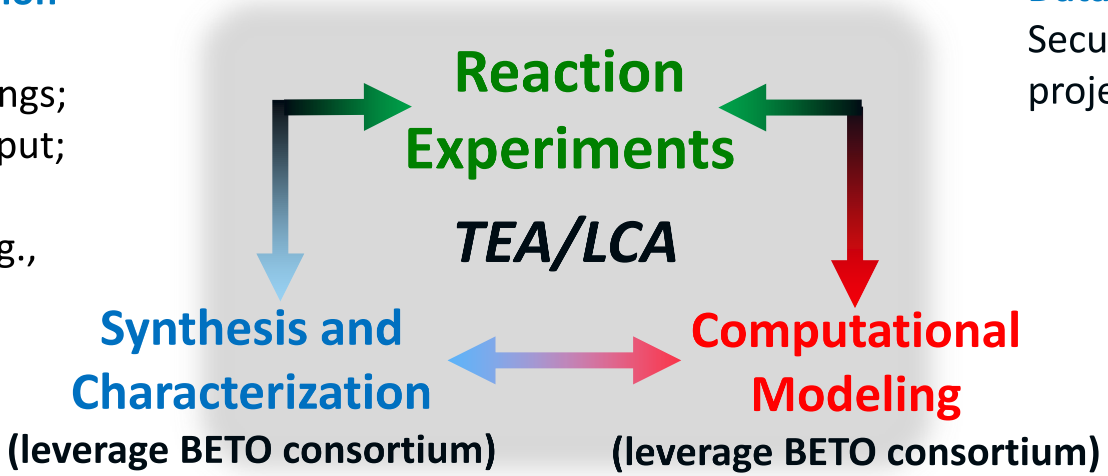


2. Management Approach (1 of 2)

Integrated Approach– Development is accelerated by an iterative, multi-facetted approach to R&D challenges

Project Communication– Biweekly meetings; quarterly DOE meetings; ongoing industrial input; attend meetings for adjacent projects (e.g., CFP, co-products, separations)

Data Management – Secure data folders for all project files



Interdisciplinary Team Members – Expertise in reaction engineering, characterization, synthesis, computation, TEA/LCA, and scale-up

Leverage BETO Projects– Collaborate and leverage BETO ChemCatBio enabling technology consortia for computation (CCPC) and characterization (ACSC), CFP, Co-Products

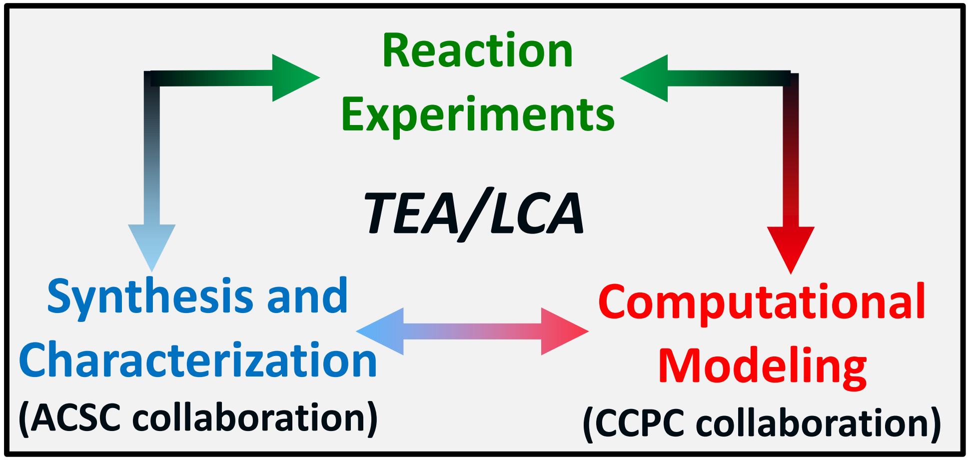
Go/No-Go – Focused on critical success factor – yield of phenolics:
"Demonstrate ≥10% yield of phenolics on lab-scale…" March 2019

- **Surpassed goal (achieved 15% phenol yield on lab-scale)**

2. Management Approach (2 of 2)

Flow Chart for Managing Project Activities

1) Baseline lignin pyrolysis (no catalyst)
2) Benchmark commercial catalyst
3) Use computation to guide initial catalyst synthesis/selection
4) Prepare materials of varying metal-oxygen strength and site density
5) Test catalysts with model compounds and whole vapors
6) Use experimental data with TEA/LCA models
7) Iterate and improve based on findings



Scale-up catalyst and demonstrate on bench-scale

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3. Progress and Accomplishments

3. Progress / Technical Accomplishments (1a of 6)

1. Baseline Pyrolysis: Examine various types of lignin and pyrolysis conditions and their effects on product yields to establish baseline condition(s) and feedstock(s) for experiments.

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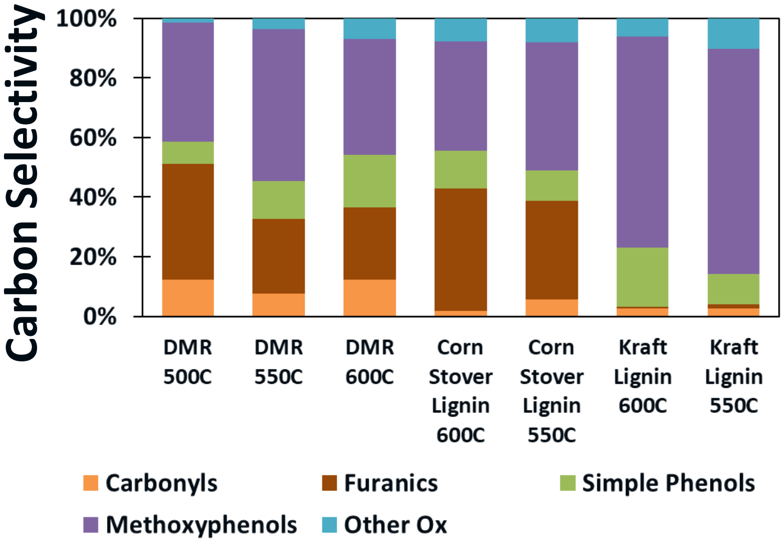
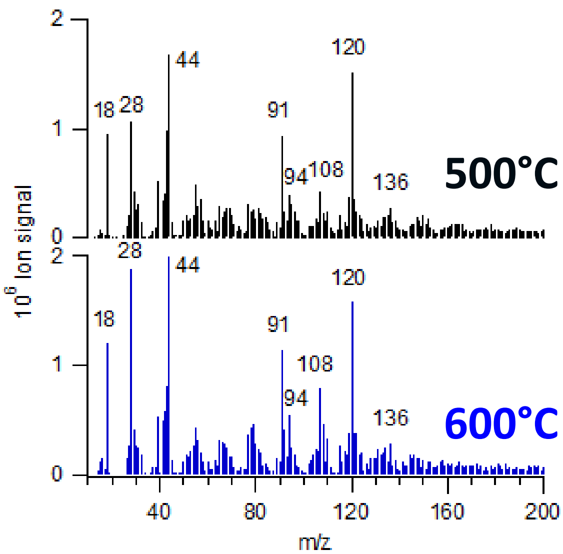
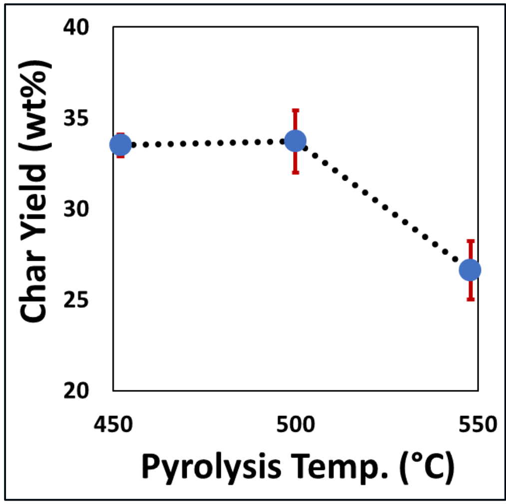
- **Pyrolysis testing of multiple lignins (different processes and biomass sources)**
  - **DMR-EH** (corn stover), corn stover, pine mixed softwoods, Sweetwater, Renmatix, Kraft
  - GC/MS analysis of condensed products
  - MBMS of gaseous products prior to condensation

Pyrolysis Products from Various Lignin Types



Mass spectra and char yields of DMR-EH lignin pyrolysis vapors at varying pyrolysis temperatures





1. Baseline Pyrolysis

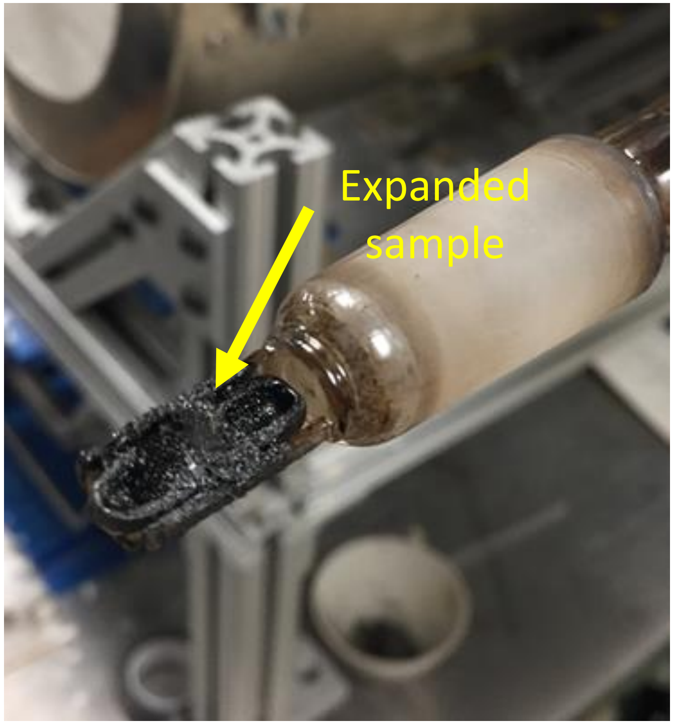
Lignin Pyrolysis (high lignin content, >90%)

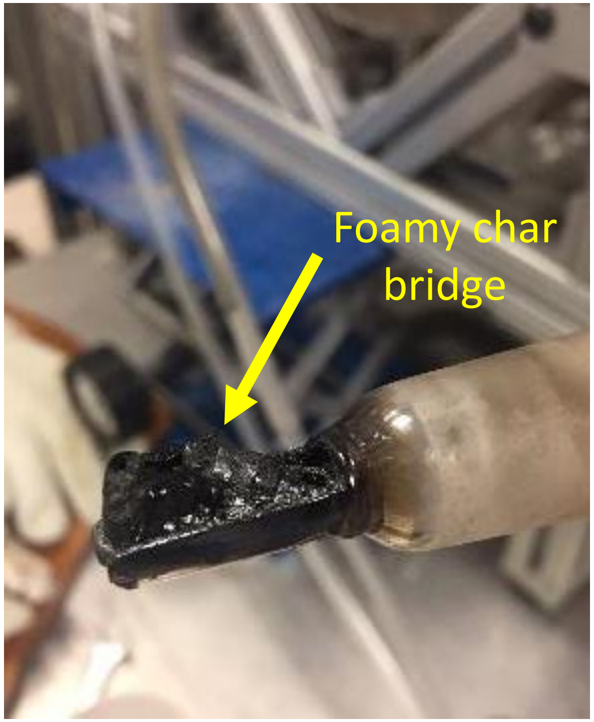
Before pyrolysis

Lignin rests nicely in quartz boat

After pyrolysis

Foamy, sample expansion, forms a char bridge spanning the sample holder and encapsulating the quartz boat



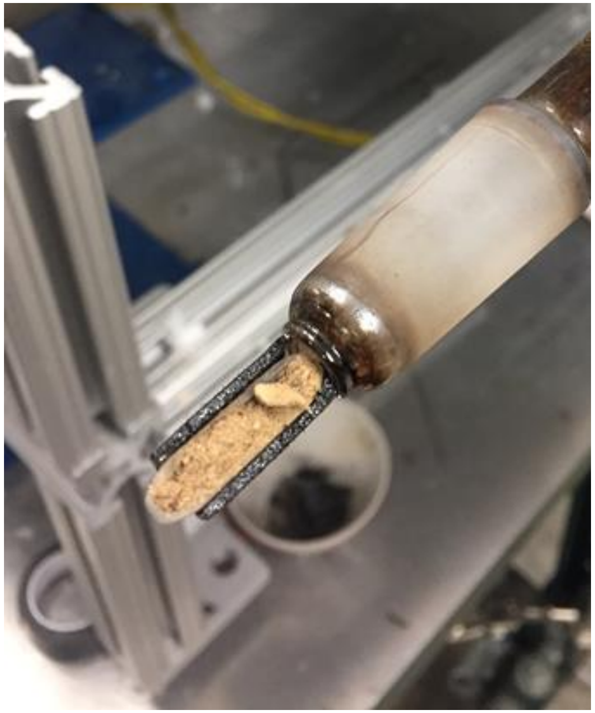


1. Baseline Pyrolysis

DMR Lignin Pyrolysis (60% lignin content)

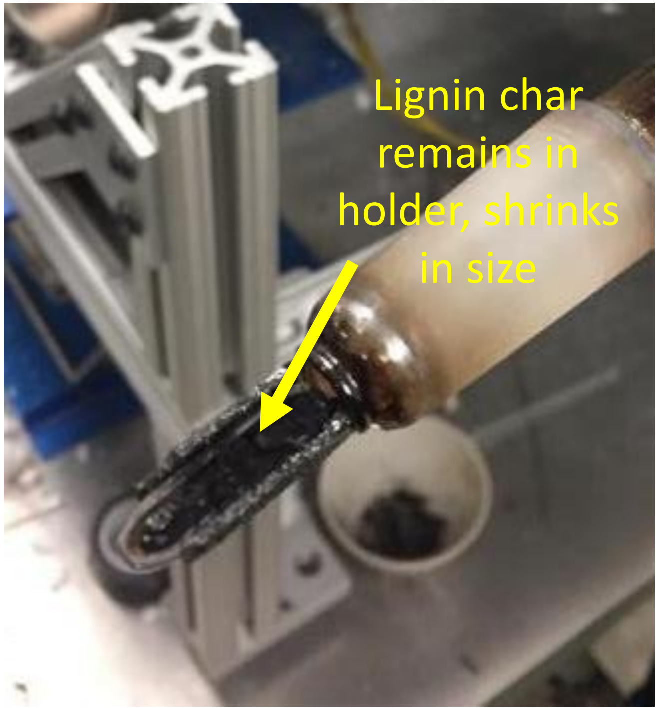
Before pyrolysis

Lignin rests nicely in quartz boat



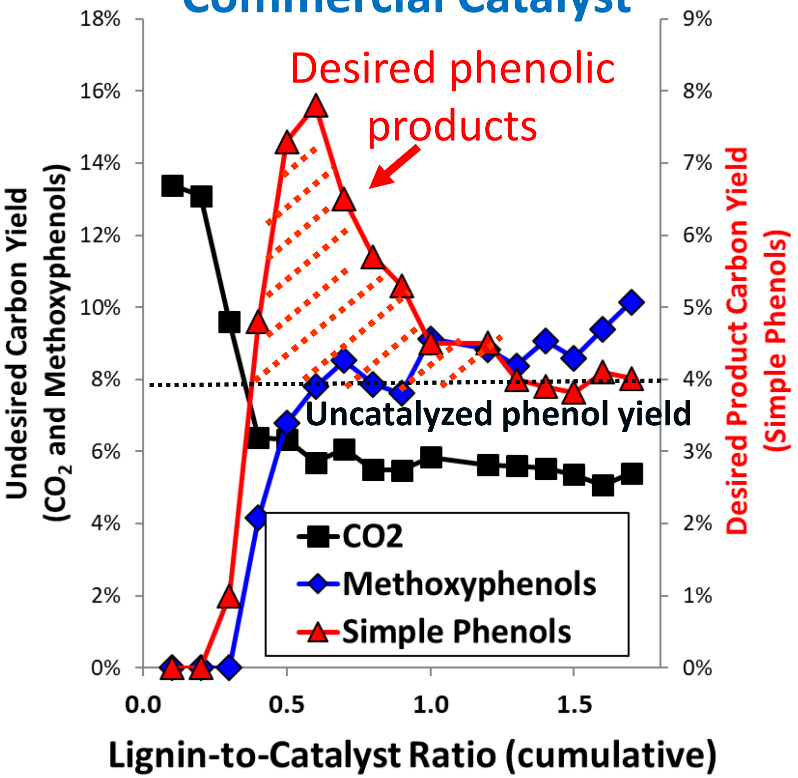
After pyrolysis

No expansion, char remains nicely situated within sample holder



2. Benchmark Commercial Catalyst: A commercial vanadia oxidation catalyst was evaluated for oxidation of lignin pyrolysis vapors to establish a benchmark for phenol yields to compare the NREL-developed catalysts.

Simple Phenol Yields on Commercial Catalyst



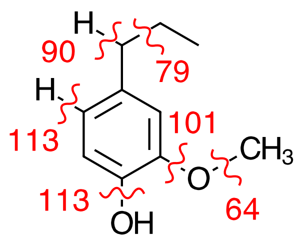
Reaction conditions: Pyrolysis/catalysis of 600°C/ 500°C DMR-EH lignin over V_2O_5 to cumulative lignin:biomass of 1.8.

Baseline carbon yields to simple phenols from DMR-EH lignin pyrolysis:	
4%	**Uncatalyzed (pyrolysis-only)**
8%	**Commercial catalyst benchmark** *(13% based on lignin content of DMR-EH residue)*

- Concept of lignin oxidative conversion to phenolic successfully demonstrated using whole lignin pyrolysis vapors

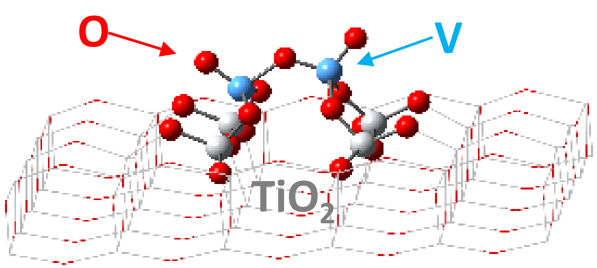
3. Computational Catalysis: Leveraging on-going BETO modeling work with in-project expertise to provide understanding of isolated sites. Reaction pathway for conversion of guaiacol to simple phenols investigated over isolated vanadium species.

BETO consortium



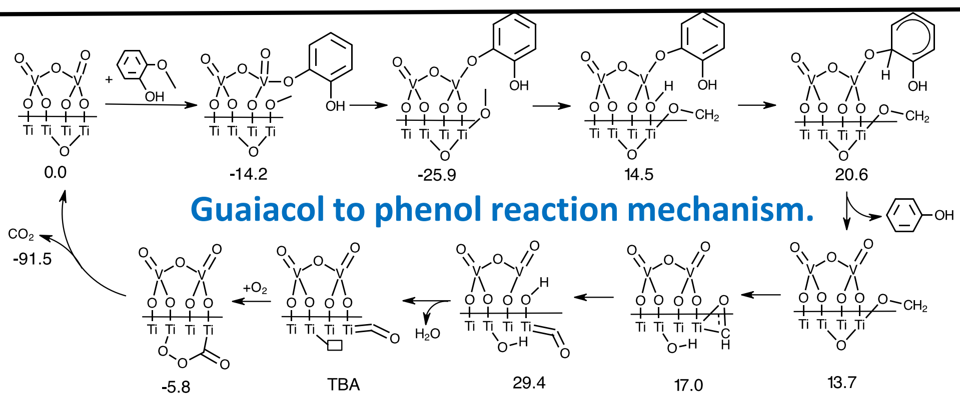
Bond strengths (kcal mol^{-1}) for a lignin monomer.

- Understand bond strengths and opportunities for selective bond cleavage.



Molecular model of V_2O_5/TiO_2: V (blue), O (red), Ti (white) on TiO_2 support.

- Develop models of V_2O_5-supported catalysts on various metal oxides (e.g., TiO_2, SiO_2, Al_2O_3, ZrO_2) and determine relative V-O bond strengths.



Guaiacol to phenol reaction mechanism.

- Explore mechanism(s) for surface reactivity. Established reaction pathway catalytic conversion of guaiacol to phenol was established over isolated vanadium species supported on TiO_2

3. Progress / Technical Accomplishments (4 of 6)

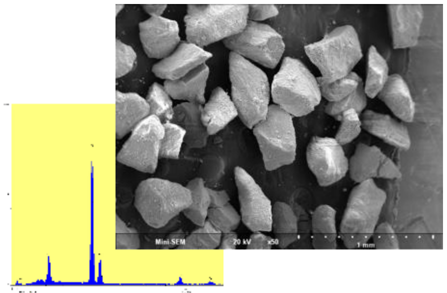
4. Synthesis and Characterization of Catalysts: Successfully synthesized and characterized lignin catalysts with varying metal-oxygen bond strength, active site densities, and molecular structures.

ChemCatBio
Chemical Catalysis for Bioenergy

Optical and SEM images of NREL-synthesized lignin oxidation catalysts

Increasing site density

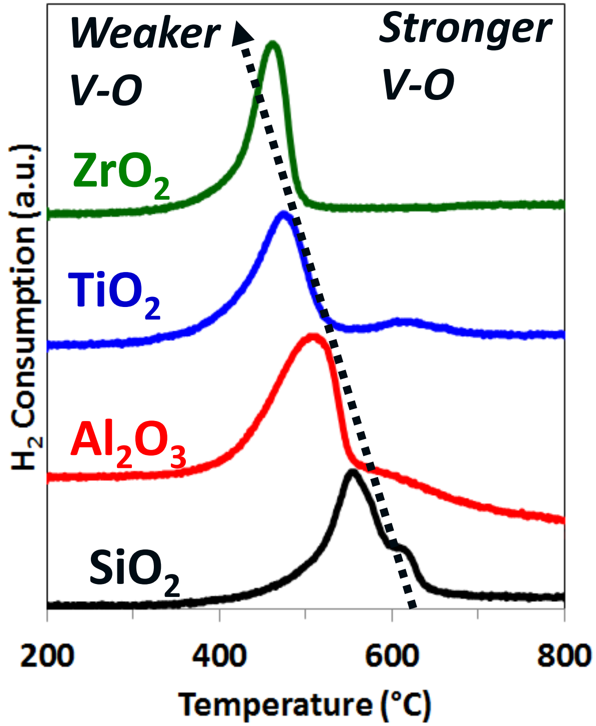
Varying V-O bond strength



SEM EDS of V_2O_5/TiO_2

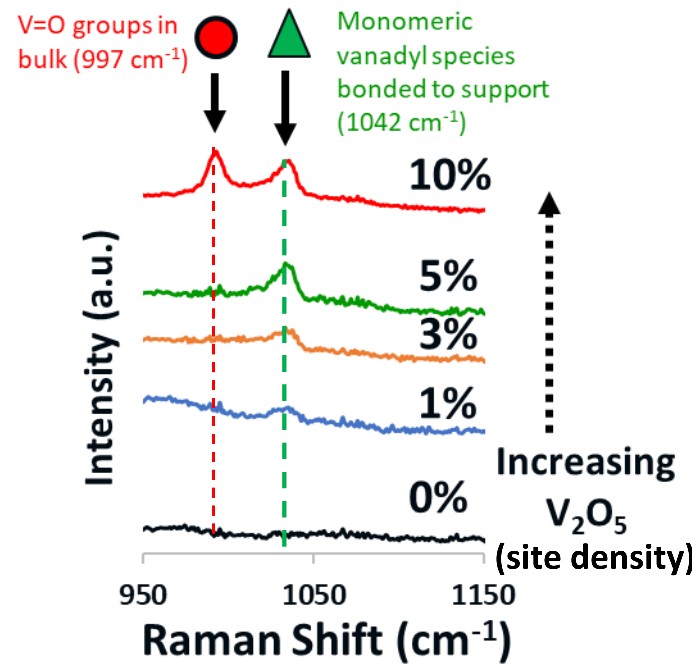
Metal-oxygen bond strength can be tailored.

H_2 temperature-programmed reduction (TPR) of 10% V_2O_5 on different supports showing varying M-O bond strengths



Molecular species change with changing site density.

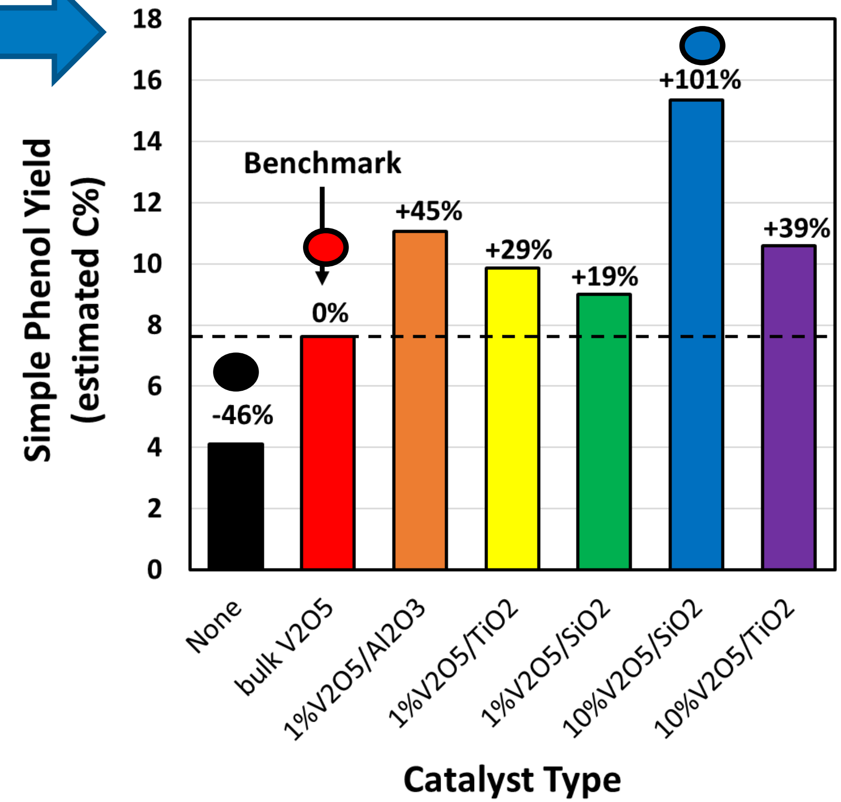
Laser Raman Spectroscopy identified transition from isolated to polymeric vanadyl species with increasing vanadium loading and site density



5. Reaction Testing with Whole Vapors and Model Compounds: 2x improvement in simple phenol yields from DMR lignin as compared to commercial catalyst.

Improvements in simple phenol yields	
4%	**Uncatalyzed (pyrolysis-only)**
8%	**Benchmark catalyst**
15%	**NREL-developed catalyst** *(25% based on lignin content of DMR-EH residue)*

Phenol yields from whole vapors from DMR lignin pyrolysis

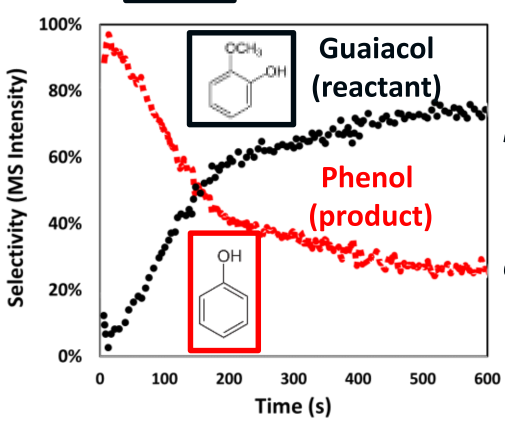


Experiments consistent with computational predictions.

Guaiacol (reactant)

Phenol (product)

+CO, CO_2, H_2O



Model compound reaction experiments in good agreement with computational predictions

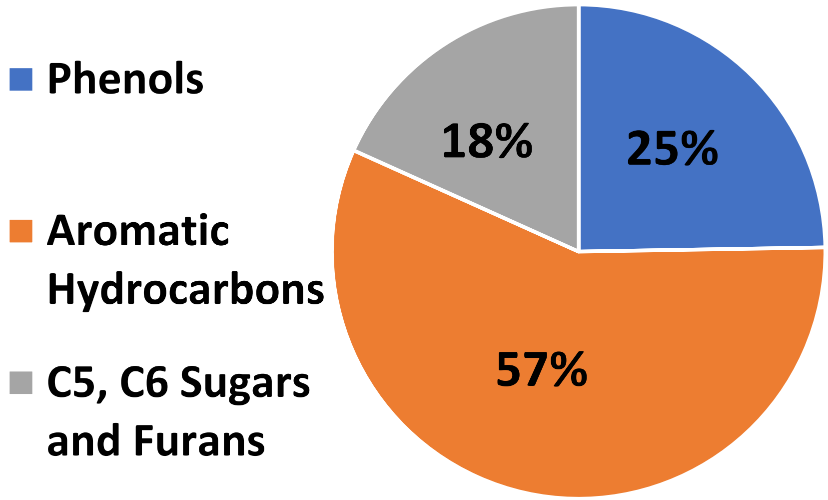
Guaiacol over NREL catalyst on TiO_2 at 450°C.

5. Reaction Testing with Whole Vapors: Condensed Product Composition

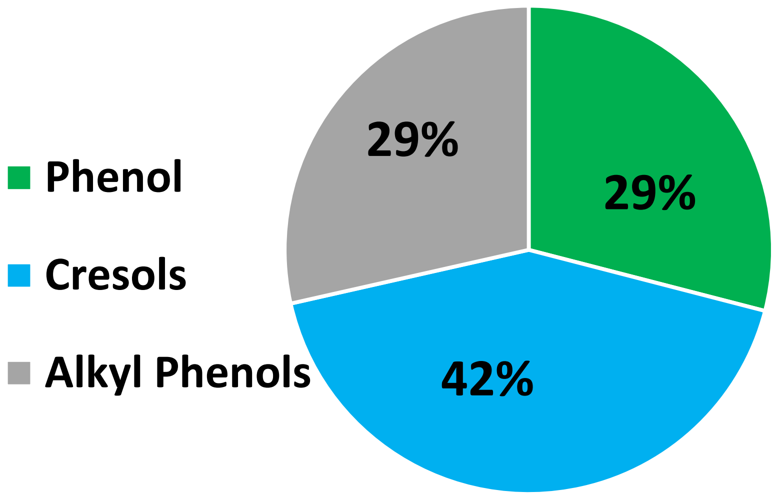
Opportunity to increase phenolic yield by reducing aromatics (catalyst activity)

Opportunity to improve revenue by via higher value phenolics (cresols)

Compositions of Condensed Liquid Product



Distribution of Condensed Phenolic Compounds



Conditions: 1:1 lignin to catalyst ratio, VOx/TiO2 catalyst at 550°C into dry ice condenser; analysis by GC/MS

6 & 7. Establish TEA impact, iterate, and improve: Process modifications and iterations in catalyst design have shown additional opportunities to improve phenol yield.

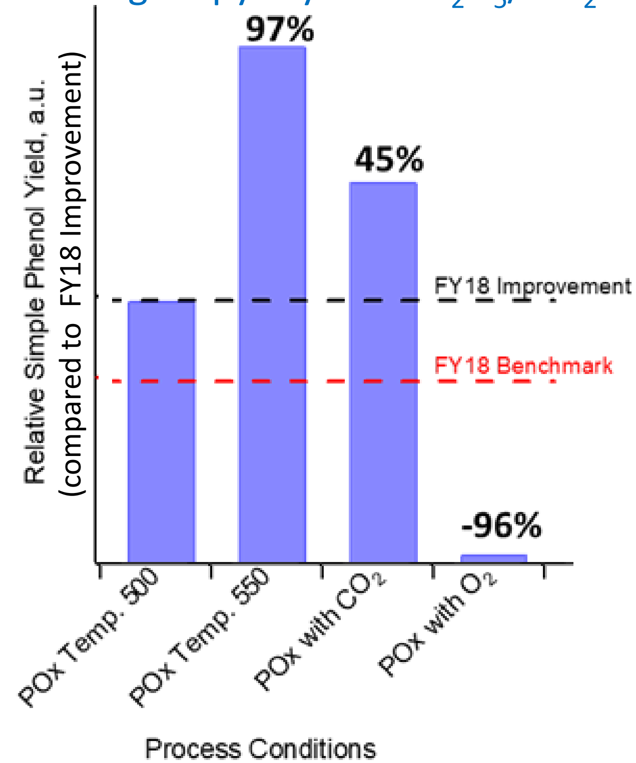
TEA Impact Correlated with Phenol Yield:

Relevant Criteria	Benchmark	Status	Future Target
Lignin conversion to phenolics	8%	**15%**	>25% (10% FY20)
Estimated TEA impact on MFSP reduction	$0.25/GGE	**$0.60/GGE**	>$1.35/GGE

Iterative R&D is assessing the impacts of pyrolysis/catalysis temperatures and oxidant co-feed and have shown significant impact on phenol yields. 2nd-generation catalysts have lowered vanadia loading and achieve dispersed active sites.

Varying Process Parameters (temperatures and oxidant co-feed)

Phenolic yields from whole vapors from DMR lignin pyrolysis on V_2O_5/TiO_2



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4. Relevance

4. Relevance - Addressing BETO Barriers and Goals (1 of 2)

Project Outcomes and Relevance – Reduce biofuel production cost by valorizing lignin via gas phase selective oxidation to make phenolics

- Focus on products with large markets, high value, and potential for bio-adoption
- Novel approach provides portfolio diversification and low-cost route

BETO 2018 MYP Barriers

Ot-B. Cost of Production

Ct-C. Process Development for Conversion of Lignin

Ct-F. Increasing the Yield from Catalytic Processes

Ct-K. Developing Methods for Bioproduct Production

- Developing catalysts for gas phase oxidation to produce high yields of valuable phenols from low-value lignin will reduce biofuel production

Relevant Criteria	Benchmark	Status	Long-Term Target
Lignin conversion to phenolics	8%	15%	>25%
Estimated TEA impact	$0.25/GGE reduction	$0.60/GGE reduction	>$1.35/GGE reduction

BETO Performance Goals (2018 MYP):

By 2030, verify hydrocarbon biofuel technologies that achieve ≥50% reduction in emissions relative to petroleum-derived fuels at **$2.5/GGE MFSP**

↓

- Providing ***early-stage R&D*** to enable verification reduce risk
- ***Identifying viable routes to $2.5/GGE*** through phenolic co-products, combing catalyst and process development

4. Relevance – Addressing Bioenergy Industry (2 of 2)

Industrially-relevant for both established and emerging companies in providing routes to renewably-sourced products to penetrate existing markets and develop new markets.

- Interest from both ***upstream and downstream*** companies (lignin producing biorefineries and phenol consumers)
- ***Market demand*** from existing companies to use renewably-sourced precursors for production of polycarbonates and plastics
  - Create a **cost-competitive** technology for phenol production
  - Focus on products with large markets, high value, and potential for bio-adoption
  - Market size could support >200 biorefineries
- Creates a ***diversified revenue stream*** using low value lignin from biorefineries, economic biofuels/products industry

SWEETWATER ENERGY

Renmatix™

SUMITOMO BAKELITE CO., LTD.

JM Johnson Matthey Inspiring science, enhancing life

Upstream

High value
Large markets

Downstream

Catalyst and chemical producer, and technology licensing

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5. Future Work

5. Future Work (1 of 3)

Challenge #1:

Achieving High Phenol Yield

- Micro/lab-scale experiments have achieved FY20 targets for bench-scale performance (>10% phenol yield)
- Explore opportunities for further improvements in phenol yields and selectivity
  - Catalyst and/or process development
- Future targets and economic biorefineries will require further improvements (25% phenol yield)

Activities

- Continue catalyst development and improve understanding for high phenol yields
  - Lab-scale reactions
  - Site density, support effects, metal-oxygen bond strength, etc.
  - Model compound studies, kinetics, active site titration, characterization
- Assess process conditions in greater detail (T, P, residence time) for further yield/selectivity enhancements

Process development | **Reaction/catalyst development**

Lignin → Lignin Pyrolysis → Gas Phase Selective Oxidation →  Phenols

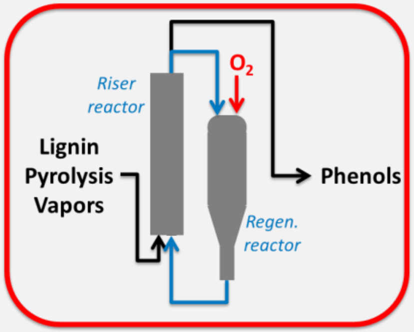
5. Future Work (2 of 3)

Challenge #2:

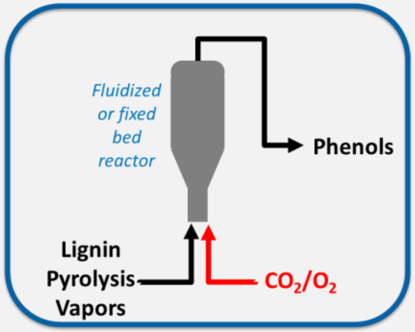
Efficient Catalyst Regeneration

- Catalyst must be capable of extended time-on-stream through economic, efficient regeneration

Chemical Looping
(Recirculating catalyst, riser & regeneration reactors)



Co-Feed Oxidant
(Fluidized or fixed-bed reactor)



Activities

- Explore both regeneration options
  - Chemical Looping
  - Co-Feed Oxidant
- Reaction experiments with varying regeneration conditions
  - Multiple reaction/regeneration cycles
  - Temperature
  - Time
  - Oxidant type
  - Oxidant concentration

Challenge #3:

Bench-scale Lignin Pyrolysis and Feeding

- Scale-up catalyst for use in bench-reactor
- Lignin pyrolysis has posed challenges due to foaming and plugging of reactors

Activities

- Commission bench-scale fluidized bed reactor for lignin pyrolysis experiments
- Scale-up catalyst batch size by 100x for use on bench-scale reactor
  - Characterize large-catalyst batch to ensure consistency with small-catalyst batch
- Utilize DMR-EH lignin in experiments
  - Improved handling for pyrolysis
  - Reduced foaming, expansion, and bridging, attributed to carbohydrate fraction
- Pelletize lignin and explore other sources
  - Successfully used in round-robin lignin pyrolysis study to allow continuous feeding
  - Applicable to multiple types of lignin streams

Summary

Goal: Develop catalysts and process to convert lignin pyrolysis vapors into valuable phenols, adding a diversified revenue stream to enable economic biofuels

-Target: 10% yield to phenolics by 2020 on bench-scale

***-Status: 15% yield to phenolics on lab-scale** (>$0.60/GGE MFSP reduction)*

1) Approach:

- Integrated, collaborative approach to catalyst design for selective oxidation of lignin to produce valuable phenolics
- Develop catalytic materials by varying **bond strength and site density**

2) Technical accomplishments:

- Developed catalysts with 2x improvement in phenol yield over commercial benchmark catalyst
- **Estimated MFSP reduction of >$0.60/GGE since 2017**

3) Relevance to Bioenergy Industry

-Addresses critical technical challenges (adding value to lignin and improve yield of catalytic processes)

-Focus on BETO barriers and performance targets

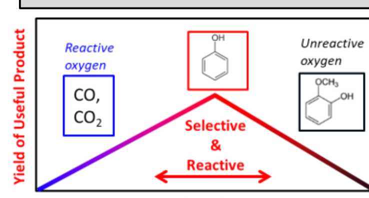
-Renewable, cost-competitive phenols are of interest to industrial partners (upstream and downstream)

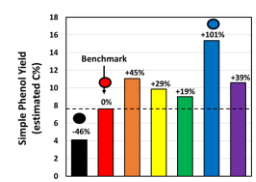
4) Future work:

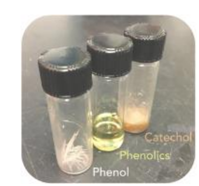
- Improve phenol **yields** (catalyst/process development)
- Determine **regeneration** protocols
- **Scale-up** catalyst and lignin feeding for bench-scale demonstration

Lignin pyrolysis

Catalyst design to achieve high phenol yields and $$$







Acknowledgments

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BETO Consortia Partners

ChemCatBio
Chemical Catalysis for Bioenergy

CCPC
www.cpcbiomass.org

Industrial Partners

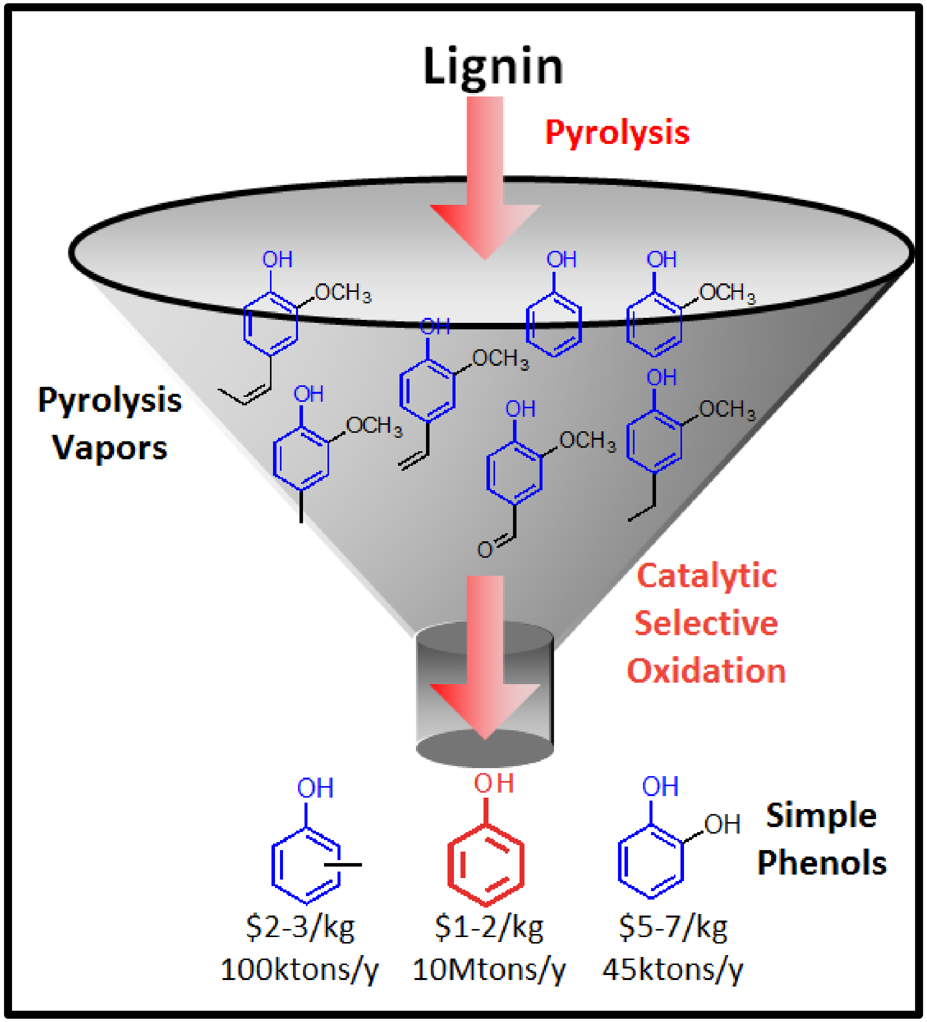
SWEETWATER ENERGY

Renmatix

JM Johnson Matthey
Inspiring science, enhancing life

NREL Biomass Catalysis & Reaction Engineering Group

Additional Slides



Presentations and Publications

Presentations

1. Matthew M. Yung, Mark R. Nimlos, Calvin Mukarakate, "Gas Phase Catalytic Oxidation of Lignin to Produce Phenolic Compounds over Vanadia Catalysts," AIChE National Conference, Pittsburgh, PA, November 1, 2018.

2. Eric Tan, "Techno-Economic Analysis and Life-Cycle Assessment for Gas Phase Catalytic Oxidation of Lignin to Produce Phenolic Compounds," AIChE National Conference, Pittsburgh, PA, October 30, 2018.

3. Matthew M. Yung, Mark R. Nimlos, Calvin Mukarakate, "Lignin valorization by pyrolysis and catalytic oxidation over supported vanadia catalysts," ACS National Conference, Division of Catalysis Science and Technology, Heterogeneous Catalyst Development for Biomass Upgrading, Boston, MA, August 21, 2018. (invited)

4. Matthew Yung, "Lignin Valorization and Thermochemical Biomass Conversion R&D at NREL," Columbia University, Lenfest Center for Sustainable Energy, New York, NY. August 24, 2018. (invited)

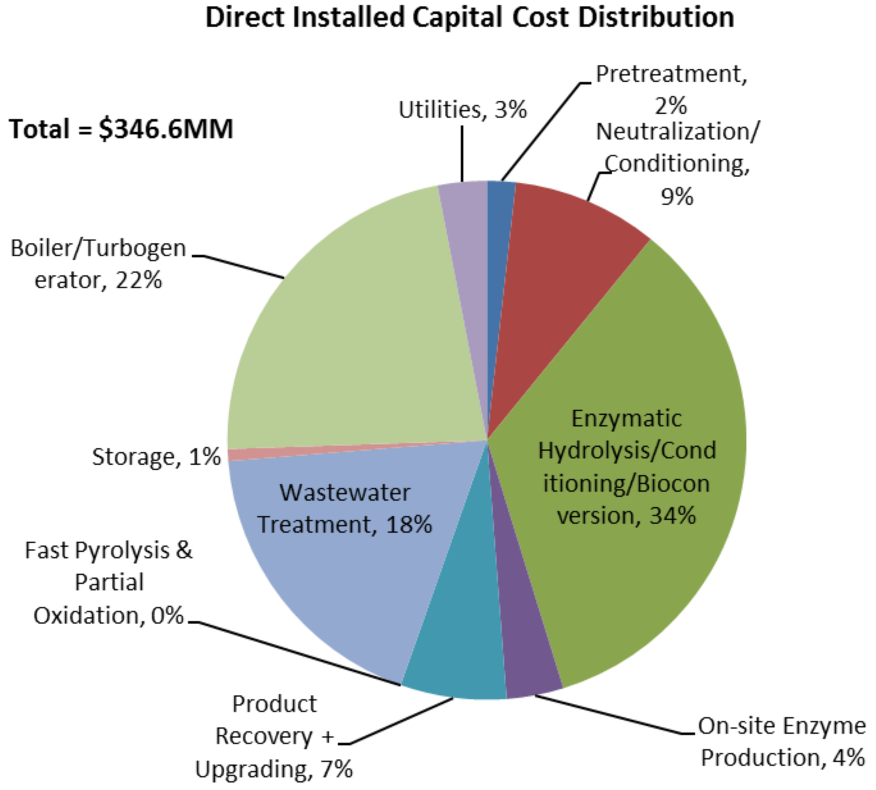
5. Matthew Yung, "Thermochemical Biomass Conversion R&D at NREL: Overview of Current Projects and Catalysis Examples," The City College of New York, Grove School of Engineering, Research Information Series Lecture. August 23, 2018. (invited)

Publications

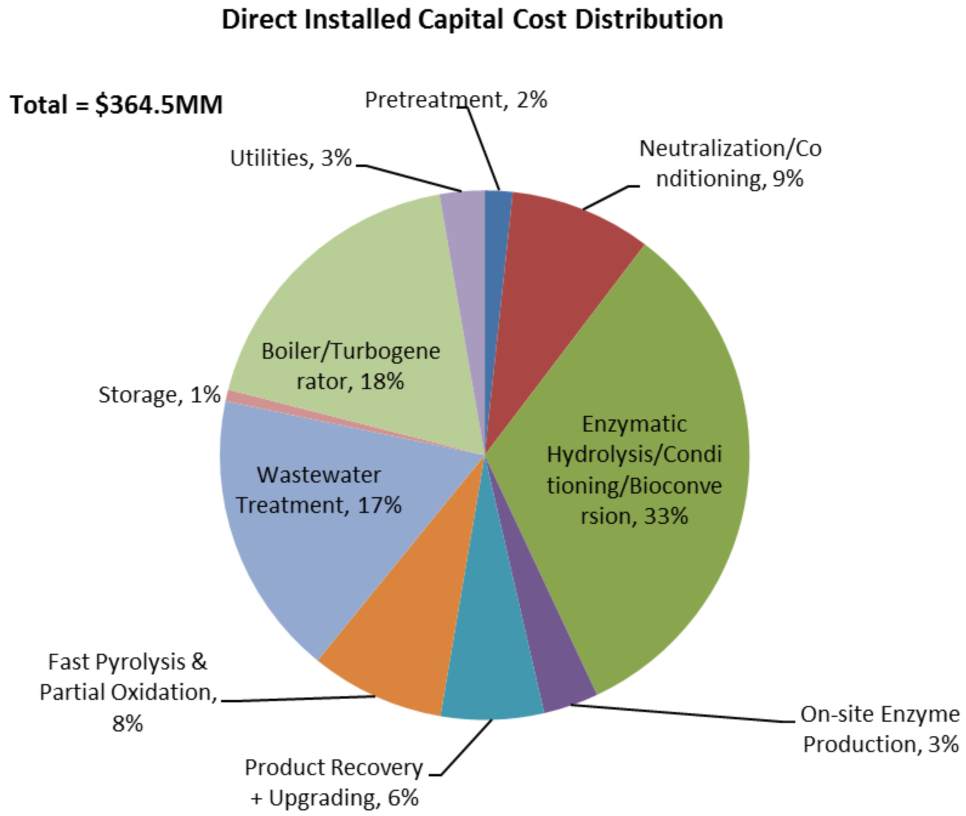
1. "Phenol production via catalytic partial oxidation of lignin pyrolysis vapors: Enabling economic biorefineries by creating revenue streams from lignin," in preparation.
2. "Theory-assisted development of oxidation catalysts for the conversion of lignin pyrolysis vapors into phenolic compounds," in preparation.

TEA: Capital Cost Breakout

Lignin to Heat & Power (no coproduct)



Lignin Valorization (Coproduct: phenols)



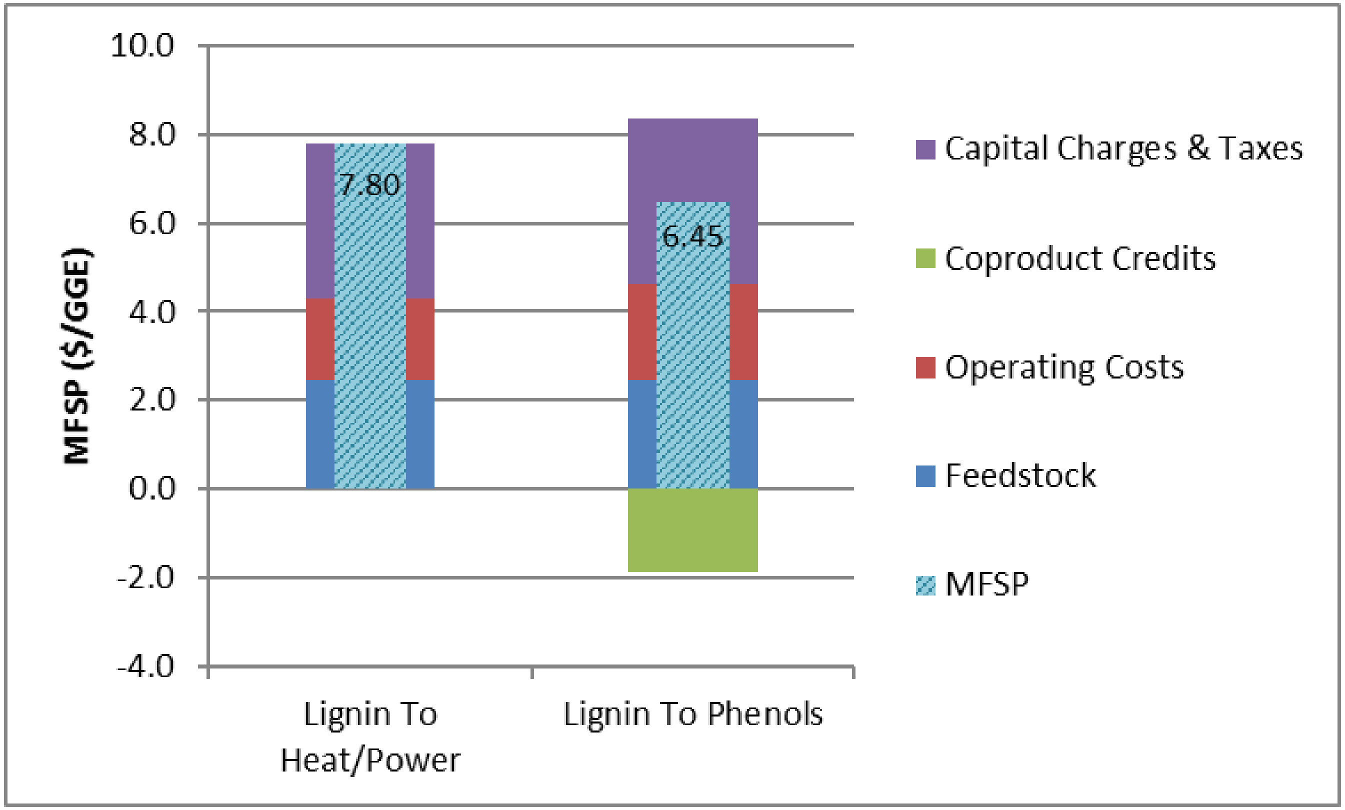
Costs in 2014$

TEA Results

17% MFSP improvement from valorization of lignin

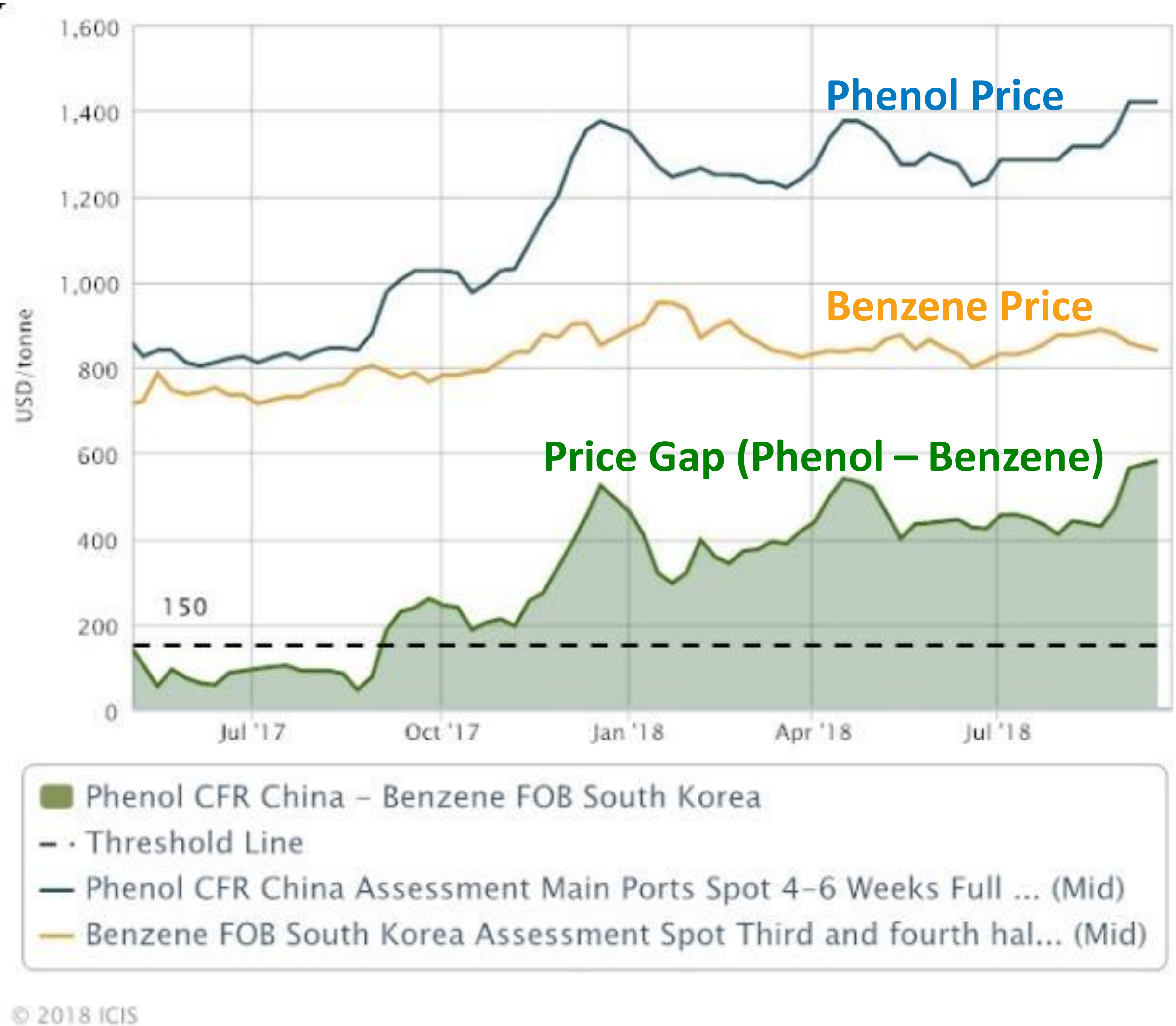
Costs in 2014$

Phenols coproduct value: $1,981/tonne (2010-2014 5-yr average from IHS)



Note: The $7.80/GGE MFSP number for the pathway (via lipids) was presented in the DOE Bioenergy Technologies Office (BETO) 2017 Project Peer Review (March 7, 2017, Denver, CO) (https://www.energy.gov/sites/prod/files/2017/05/f34/Biochemical%20Platform%20Analysis%20Project_0.pdf, see slide 11).

Phenol value and price gap relative to benzene



Higher incentive for integrated phenol producers to produce phenol instead of selling benzene

Lower incentive for integrated phenol producers to produce phenol instead of selling benzene

https://www.icis.com/explore/resources/news/2018/09/26/10261917/china-phenol-import-prices-at-near-4-year-high-on-tight-supply/