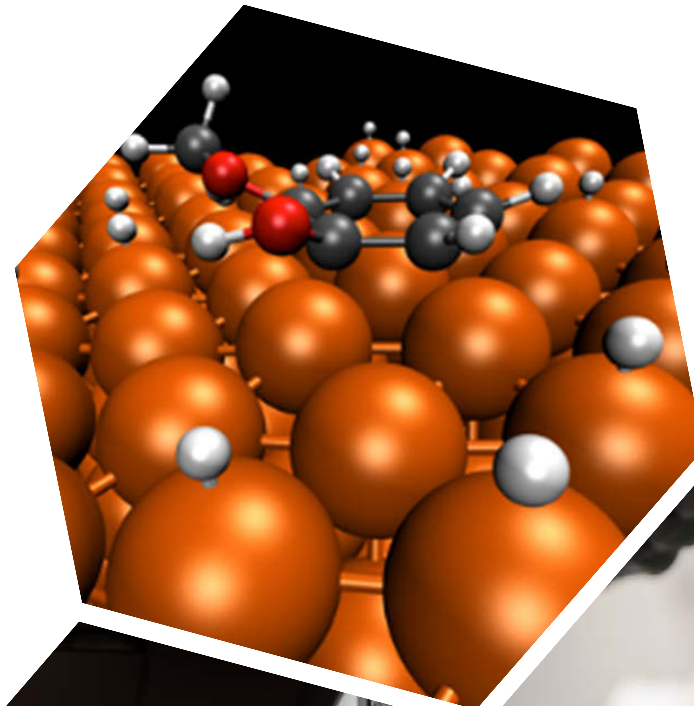
Biomass Ex-Situ CFP Catalyst Design: A Mo_2C Case Study to Evaluate if Trends in Model Compound Reactivity Translate to Real Biomass Feeds

Calvin Mukarakate

TCS 2020

October 5th, 2020

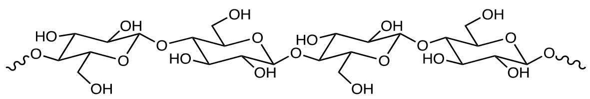


U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

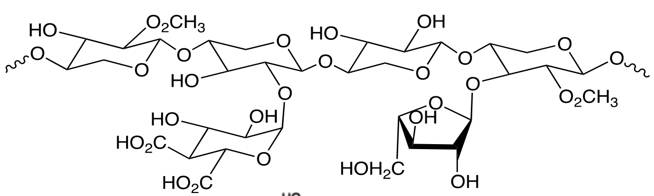
Fast Pyrolysis of Biomass

Pyrolysis of biomass generates hundreds of molecules with different functional groups; water, char and inorganics are also produced

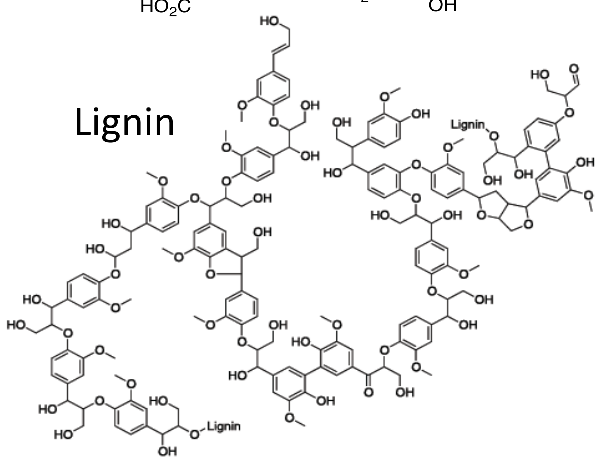
Cellulose



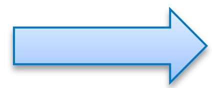
Hemicellulose

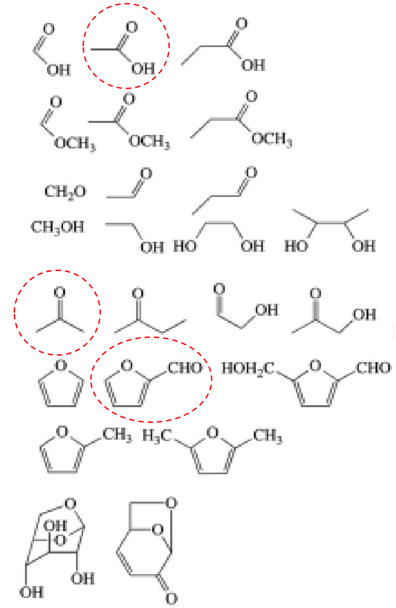


Lignin



500 °C





Organic acids

Esters

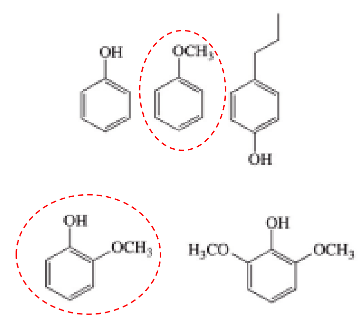
Aldehydes & Alcohols

Ketones

Furan derivatives

Sugars and anhydrosugars

< 50% of the bio-oil has been identified by GCMS



Phenolics and substituted aromatics

In general, new catalysts are evaluated with single model compounds

Mo_2C: Bifunctional Metal-Acid Catalyst

Mo_2C is a single active phase material possessing acidic and metallic-like active sites

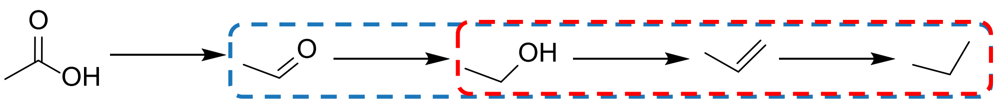
- ❖ Acidic character: Surface –OH (Brønsted acid sites) and Lewis acidic Mo sites
  - ✓ Promote dehydration, alkylation and coupling reactions

- ❖ Metallic like character: Exposed C and Mo sites
  - ✓ Promote hydrogenolysis and hydrogenation

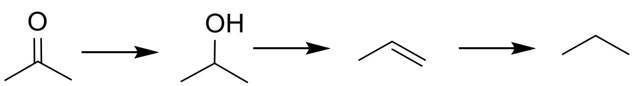
Model Compound Summary

Products from carbohydrate model compounds are consistent with metallic and acidic sites chemistries. Those from lignin model compounds are consistent with metallic site chemistry only

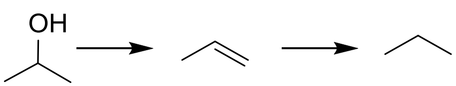
Carbohydrate Model Compounds



***Kumar, et al., Cat. Sci. Tech* 2018, *8* (11), 2938**
***Schaidle, et al., ACS Catalysis* 2016, *6* (2), 1181**



***Sullivan, et al., ACS Catalysis* 2016, *6* (2), 1145-1152**

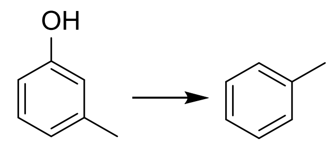


Sullivan, et al., J. Catal. 326 (2015) 82

Hydrogenolysis—Hydrogenation—Dehydration — Hydrogenation

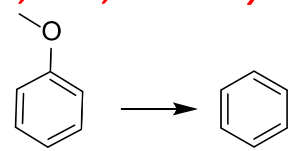
Metallic site chemistry **Acidic site chemistry**

Lignin Model Compounds

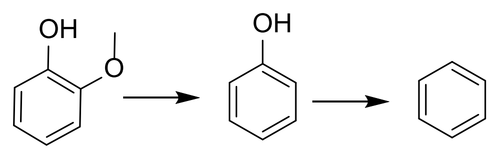


Hydrogenolysis

***Chen, et al., ACS Catalysis* 2017, *7* (2), 1113**



***Lee, et al., Journal of Catalysis* 2014, *319*, 44**



Baddour, et al., *ACS Sus. Chem. Eng. 2017, 5, 12, 11433*

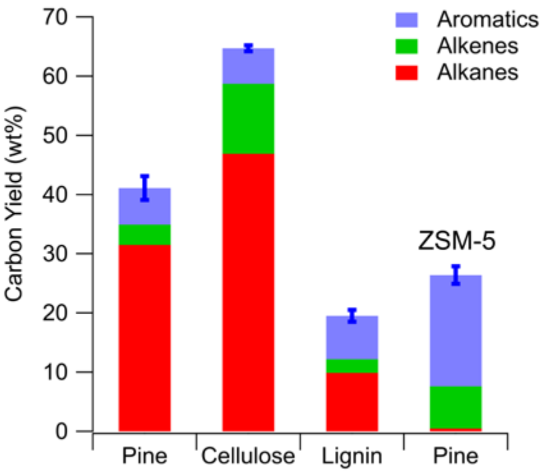
Metallic site chemistry

- Mo_2C regenerated by flowing hot H_2
- Limited alkylation products
- Some hydrogenation of the aromatic ring

Project Objective

Mo_2C demonstrates similar upgrading performance of biomass vapors as model compounds (high conversion)

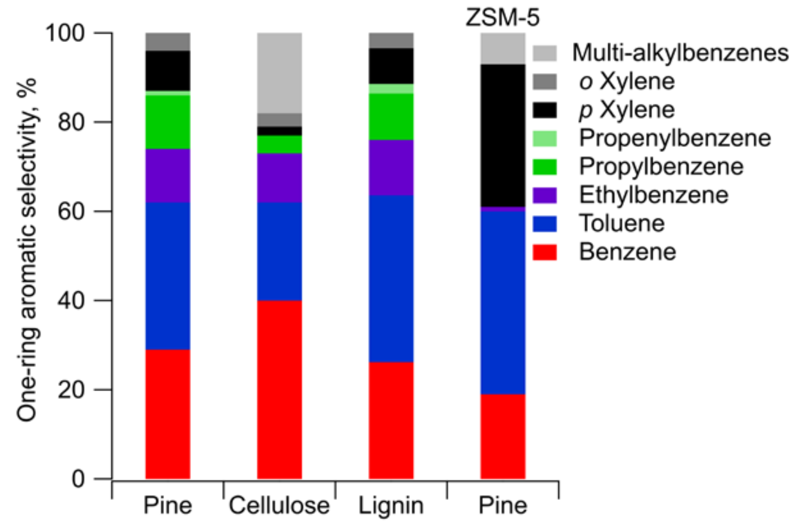
Micro-scale evaluation

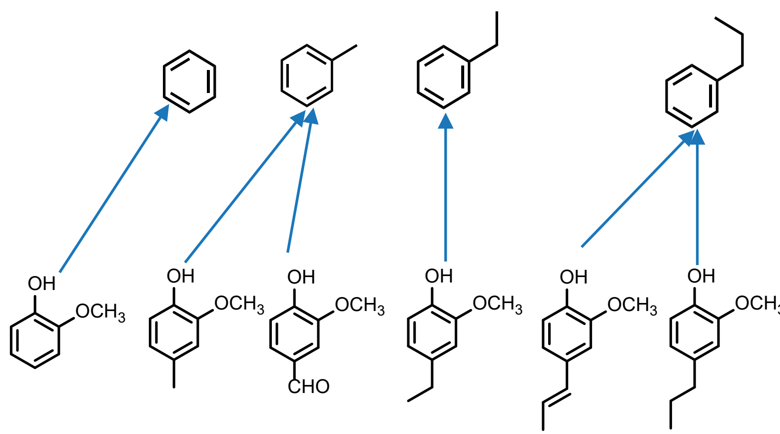


Pyrolysis: 500 ˚C
Upgrading: 400 ˚C
Catalyst: 5mg Mo_2C

Mo_2C (**biomass-to-catalyst ratio: 0.1/pulse**) produces alkanes, 1-ring aromatics and olefins

Aromatic Selectivity

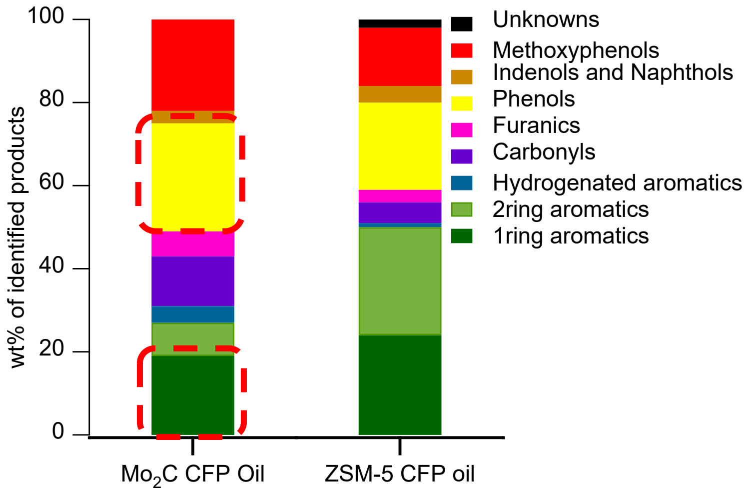




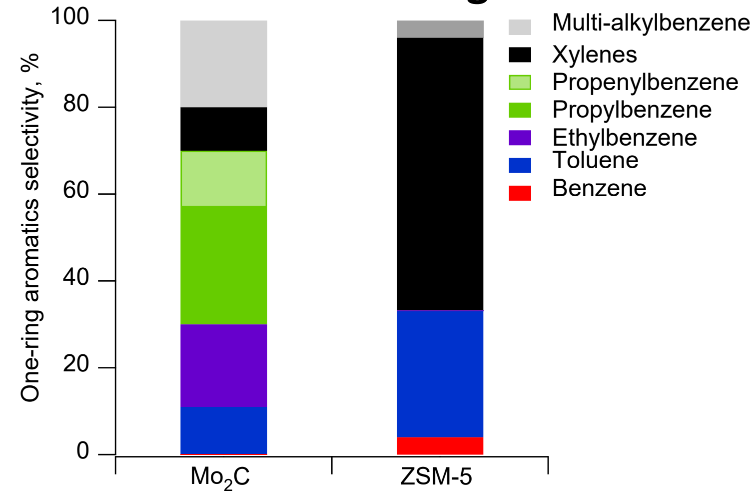
Project Objective

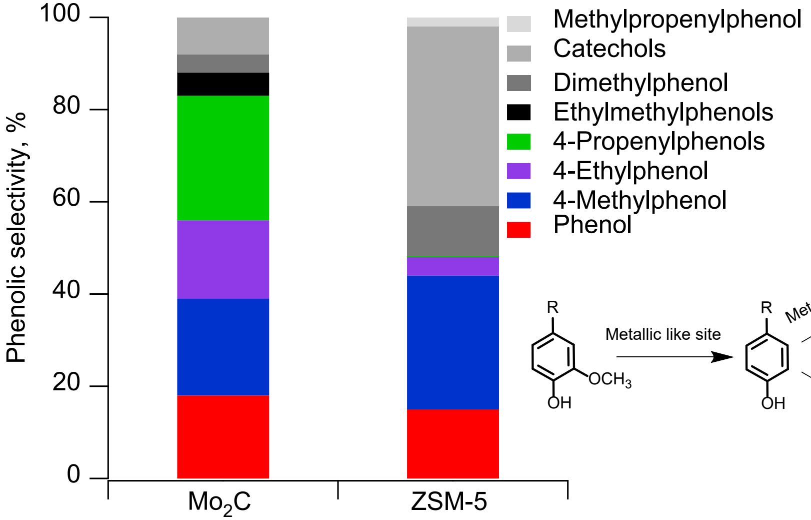
Lignin is upgraded via sequential cleavage of $–OCH_3$, followed by $–OH$ side groups

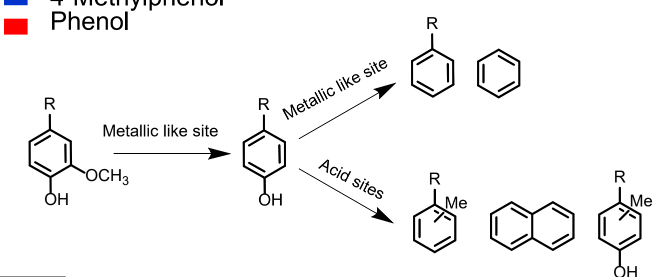
Bench-scale: CFP Oil Composition B:C 2



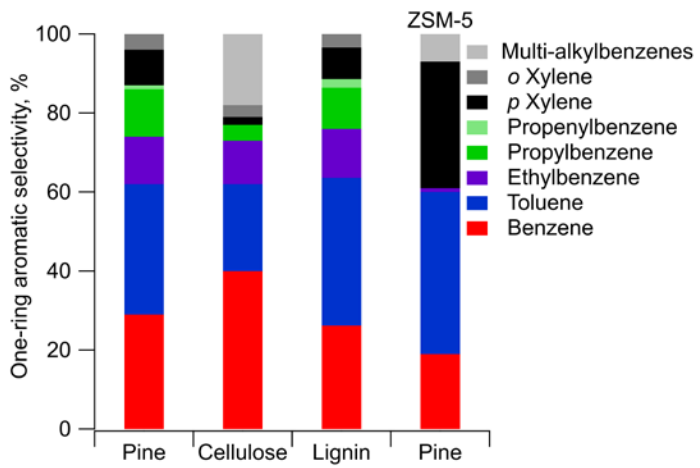
CFP Oil 1-ring Aromatics





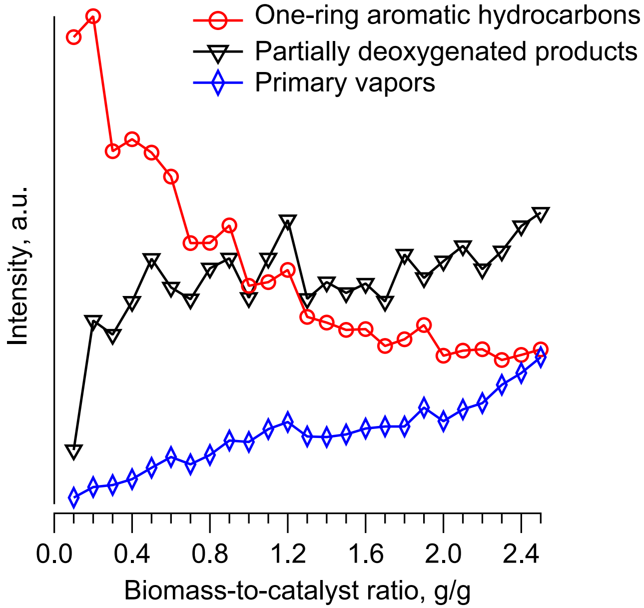


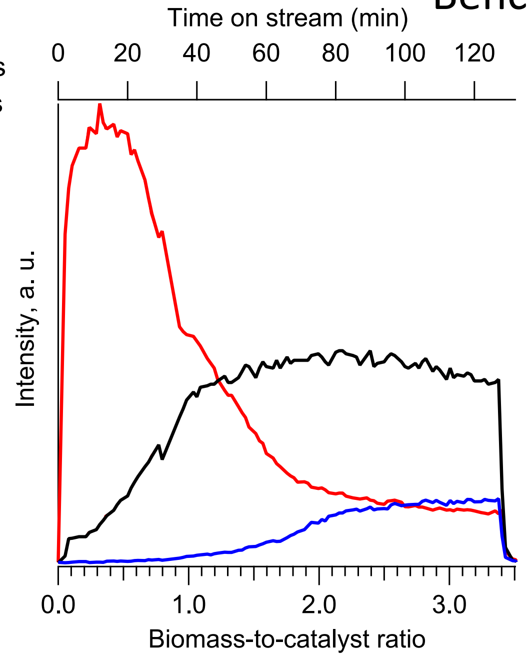
Microscale 1-ring Aromatics



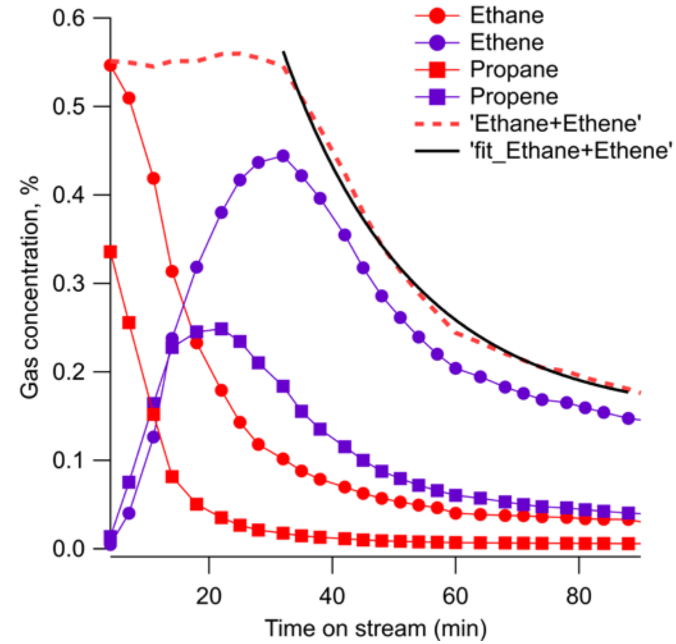
Mo_2C Stability

Micro-scale evaluation



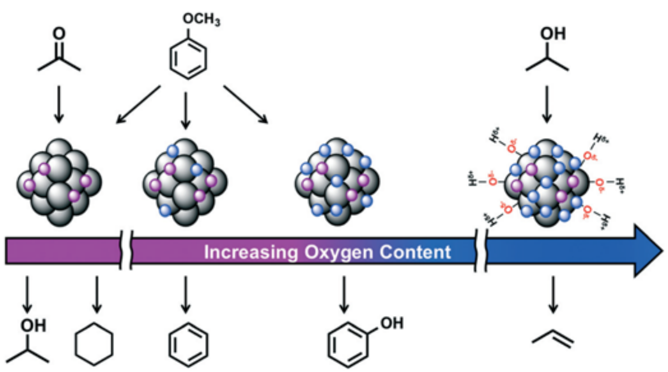


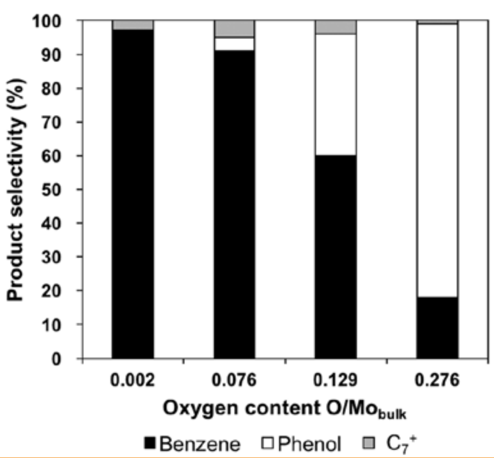
Bench-scale evaluation

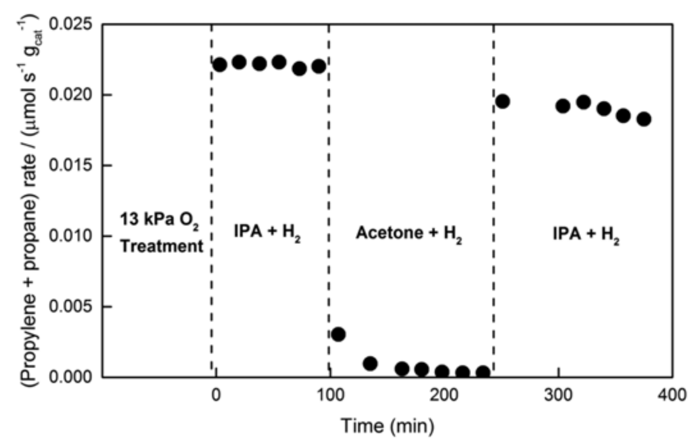


***Sullivan, et al., Catal. Sci. Technol.*, 6 (2016) 602**

***Sullivan, et al., ACS Catalysis* 2016, *6* (2), 1145**







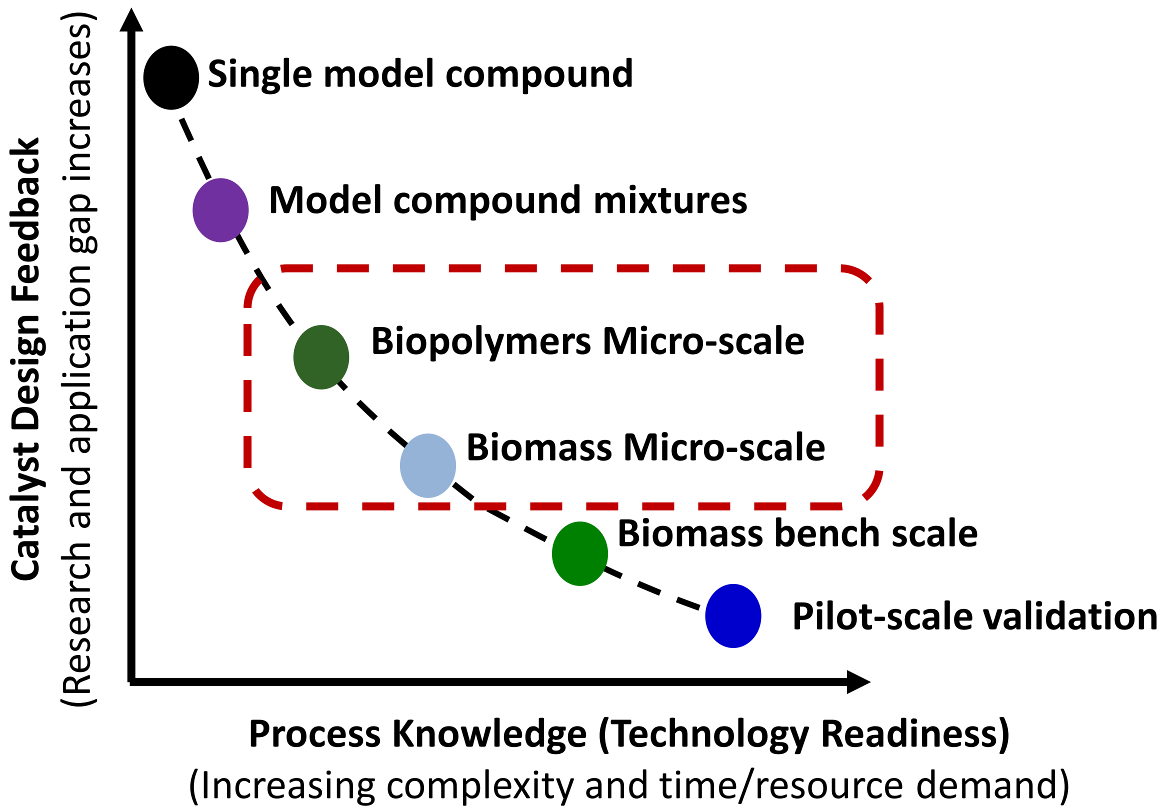
Summary: Model compounds vs Biomass

Can we realistically predict biomass CFP performance based on the model compound data?

Agreement	Disagreement
Metallic site-driven chemistry for phenolics	Acidic site alkylation chemistry
Metallic and acidic sites-driven chemistry for sugars	Aromatic-ring hydrogenation
Product selectivities	Deactivation rates (rapid for biomass)
Catalyst surface modification chemistry: Oxygen adsorption followed by carbon build-up	Regeneration with H_2 (Not sufficient for biomass)

Catalyst Design Guidance for Complex Feeds

Catalyst design for processes with complex feeds will benefit from increased emphasis on micro-scale evaluation with real feedstocks.



Mukarakate, et al., Nature Catalysis, submitted

Acknowledgements

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
Bioenergy Technologies Office

Kellene A. Orton
Mengze Xu
Kristiina Iisa
Richard J. French
Scott Palmer
Connor Nash
Susan Habas
Mark R. Nimlos
Joshua A. Schaidle

NREL/PR-5100-78048

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.