U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

ChemCatBio
Chemical Catalysis for Bioenergy

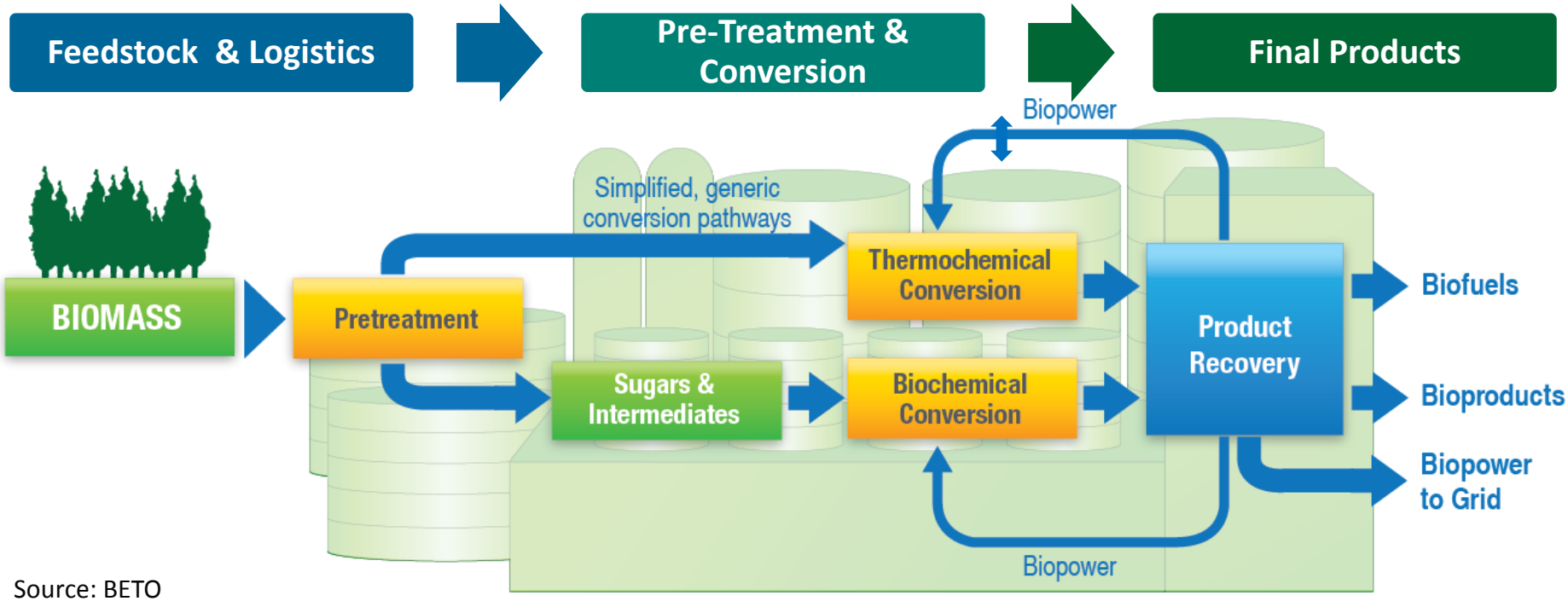
The Chemical Catalysis for Bioenergy Consortium:

Enabling Production of Biofuels and Bioproducts through Catalysis

Josh Schaidle

October 17th, 2017

Catalysis Challenges are Pervasive in Biomass Conversion



Source: BETO

Challenges due to Biomass Composition	Key Catalytic Bioenergy Processes
• High oxygen content → new reactions • Diverse chemical functionalities → competing rxns • High water content → Degradation of cat. supports • Impurities (S, N, alkali metals, Cl, etc.) → Poisoning • Multiple states and compositions (solid, liquid, or gas) • Complex, heterogeneous mixture → difficult to model	• Lignin Deconstruction and Upgrading • Catalytic Upgrading of Biological Intermediates • Synthesis Gas Upgrading • Catalytic Fast Pyrolysis • Catalytic Hydroprocessing • Catalytic Upgrading of Aqueous Waste Streams

Catalyst costs can represent up to 10% of the selling price of biofuel

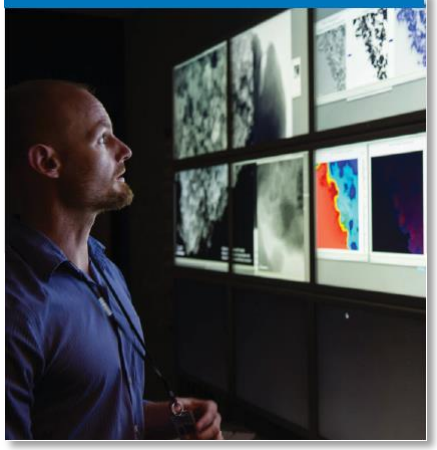
Introducing the Chemical Catalysis for Bioenergy Consortium

ChemCatBio is a national lab led R&D consortium dedicated to identifying and overcoming catalysis challenges for biomass conversion processes

- **Our mission** is to accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals by leveraging unique US DOE national lab capabilities
- **Our team** is comprised of over 100 researchers from seven different national labs

Advanced Synthesis and Characterization

Modeling and Interactive Tools



Multi-Scale Evaluation

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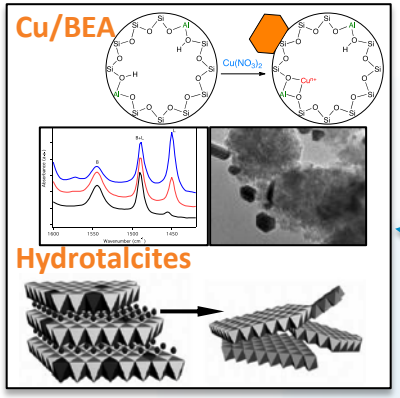
Our Approach

Establish an integrated and collaborative portfolio of catalytic technologies and enabling capabilities

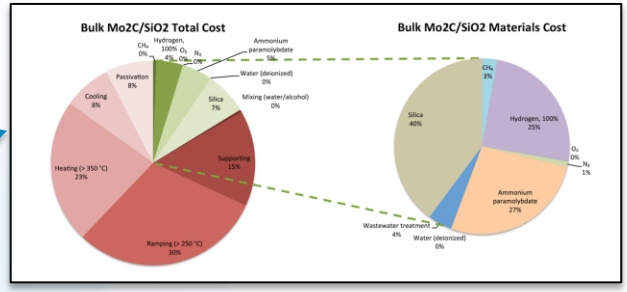
Foundational Science

Applied Engineering

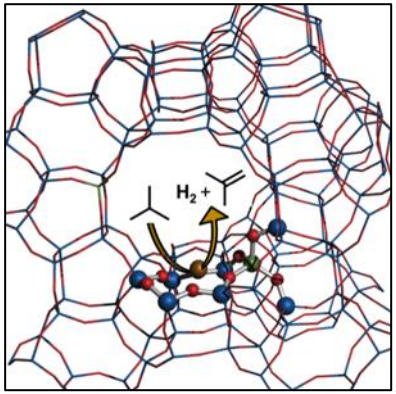
Advanced Synthesis and Characterization



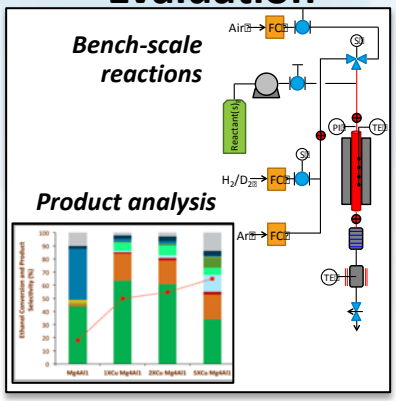
Catalyst Cost Estimation

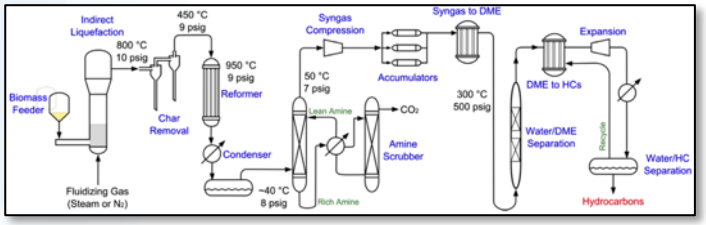


Theory



Performance Evaluation





Catalyst Scaling and Pilot-Scale Testing

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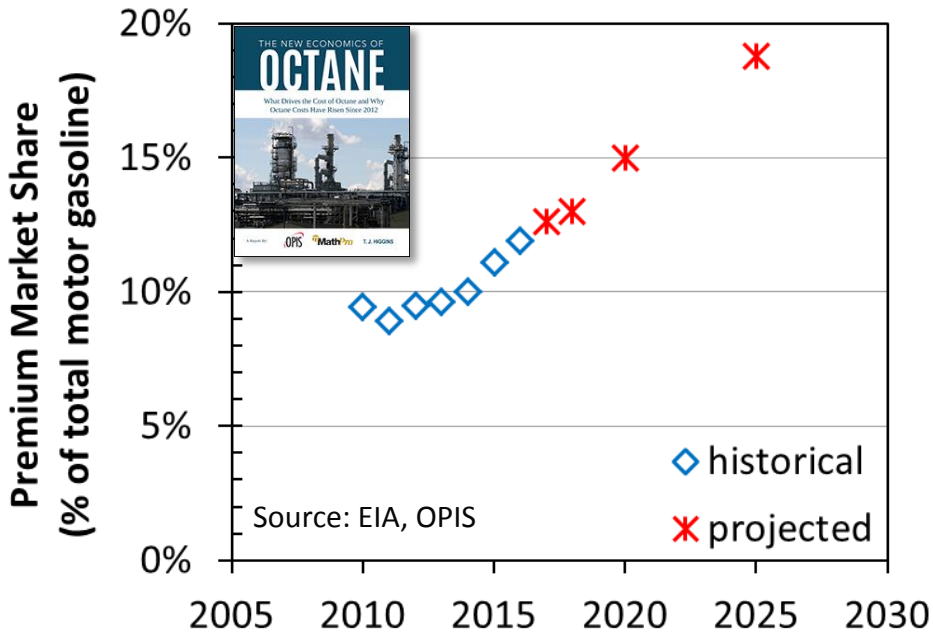
Syngas Upgrading: Market, Opportunity, and Challenge

Market Opportunity:

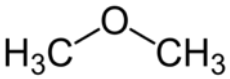
Increasing Demand for Premium Gasoline



Technology Opportunity:

Production of High-Octane Synthetic Alkylate from Biomass-Derived Dimethyl Ether

Dimethyl Ether (DME)

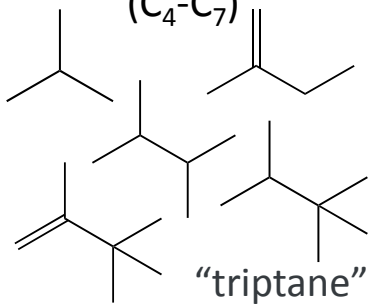


or Methanol CH_3OH

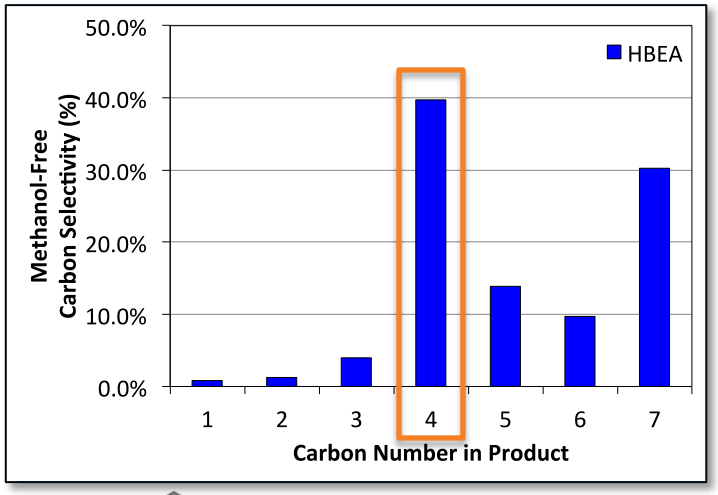
200 °C, 1-30 bar

Large-pore acidic zeolites (HBEA)

Branched HCs (C_4-C_7)



"triptane"



Catalysis Challenge:

Reactivate and reincorporate light alkane products (isobutane) into the chain growth mechanism, thereby maximizing C_{5+} yield

→ Metal-modified HBEA

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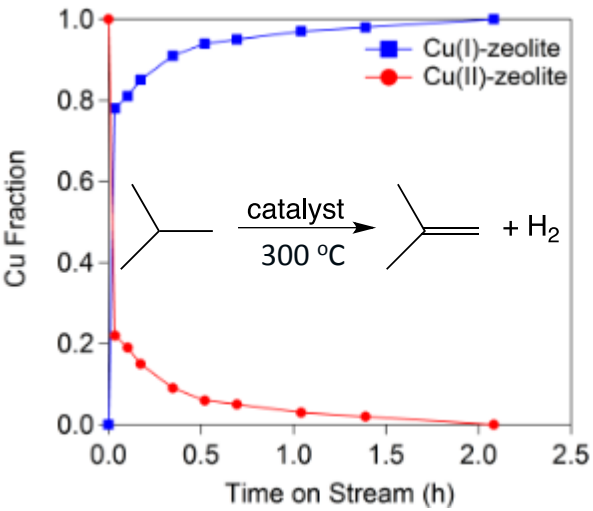
Syngas Upgrading: Catalyst Advancements

Active Site

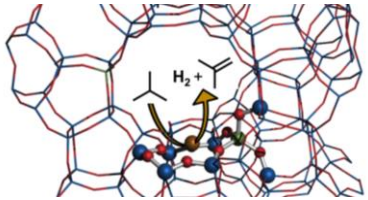
Identified Cu(I) as the active site for i-C_4 dehydrogenation using *in-operando* X-ray Absorption Spectroscopy

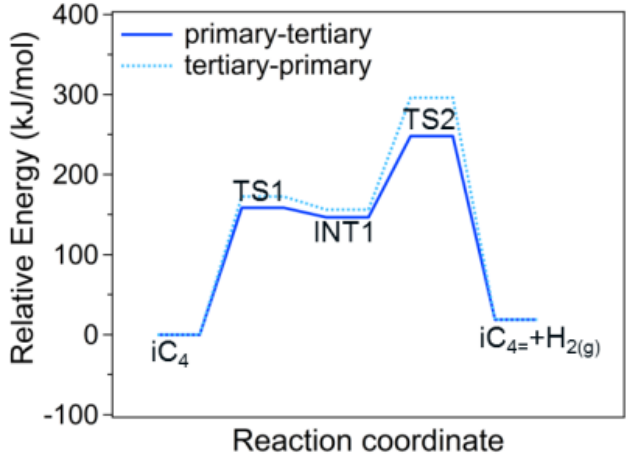


C. Farberow, et al., *ACS Catalysis* 7 (2017) 3662

Reaction Mechanism

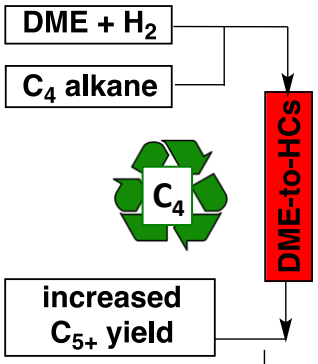
Calculated energetics for 2-step mechanism over Cu(I) active site

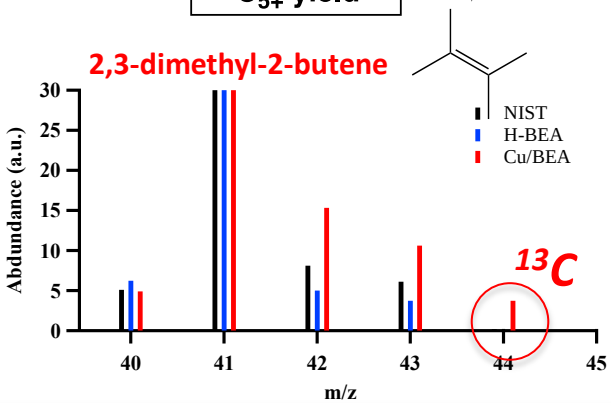




Performance Evaluation

Demonstrated C_4 reincorporation





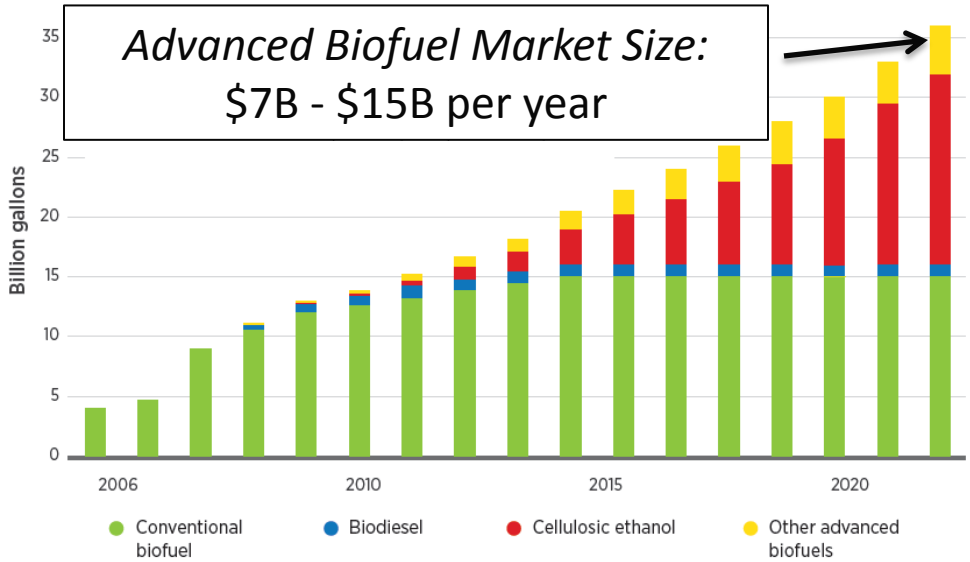
Outcomes:

- Reduced modeled fuel production cost by >$1/gal since 2015
- Identified promising bimetallic formulations for improved performance

Catalytic Fast Pyrolysis: Market, Opportunity, and Challenge

Market Opportunity:

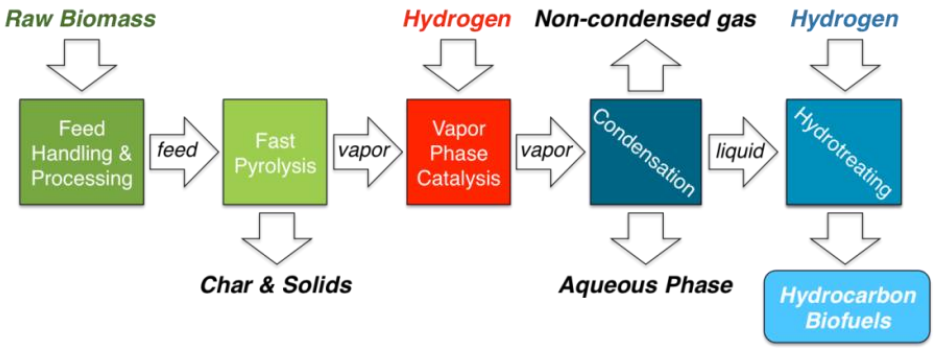
Renewable Fuel Standard Mandates for Advanced Biofuels



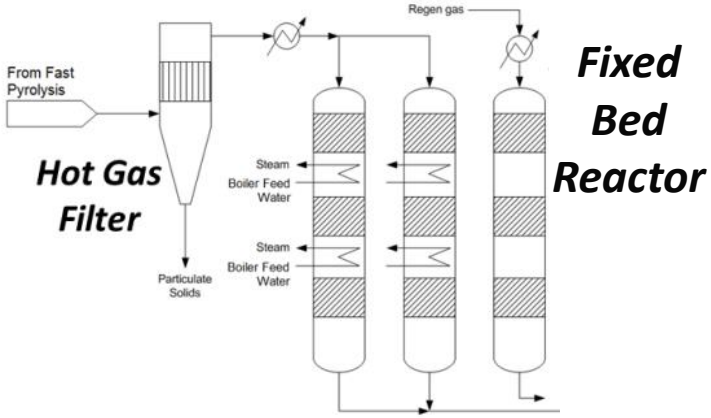
Source: EPA, DOE Billion Ton Study

Technology Opportunity:

Woody Biomass Conversion to Gasoline and Diesel Blendstocks through Catalytic Fast Pyrolysis



D. Ruddy, et al. *Green Chem* 16 (2014) 454



A. Dutta, et al., *Top. Catal.* 59 (2016) 2

Catalysis Challenge:

Improve carbon yields and extend catalyst lifetime

→ Leverage a fixed-bed system with co-fed H_2 operating at near atmospheric pressure over non-zeolite catalysts

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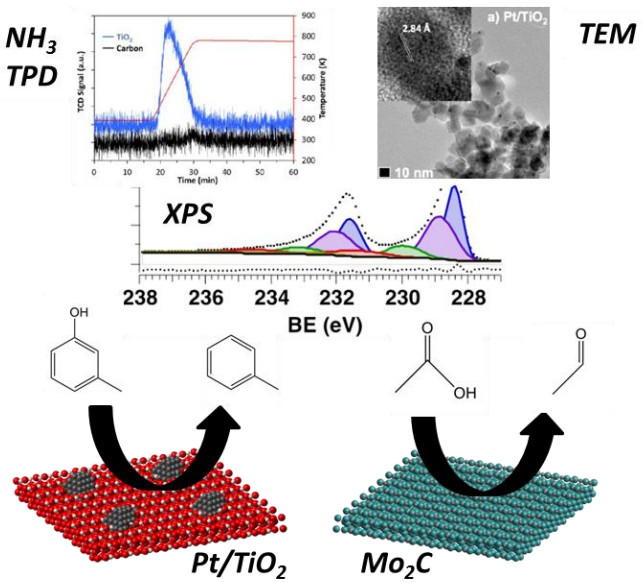
Catalytic Fast Pyrolysis: Catalyst Advancements

Surface Chemistry

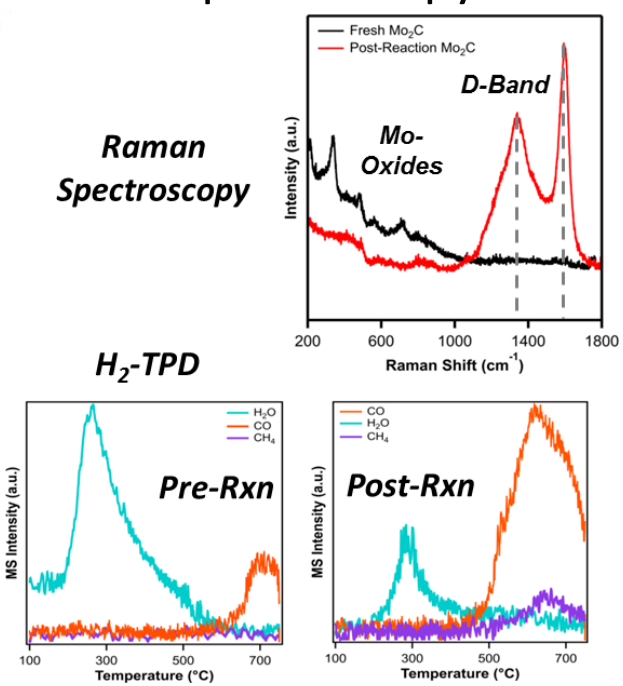
Determined role of acidic and metallic sites for CFP using advanced characterization



M. Griffin, et al., *ACS Catalysis* 6 (2016) 2715
J. Schaidle, et al., *ACS Catalysis* 6 (2016) 1181

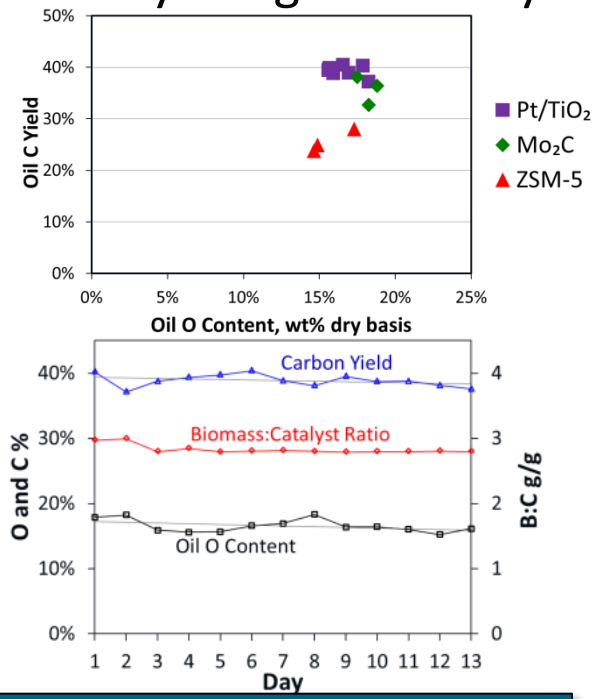
Deactivation Mechanism

Identified deactivation mechanism using *in-situ* spectroscopy



Performance Evaluation

Demonstrated improved oil yields for CFP and catalyst regenerability



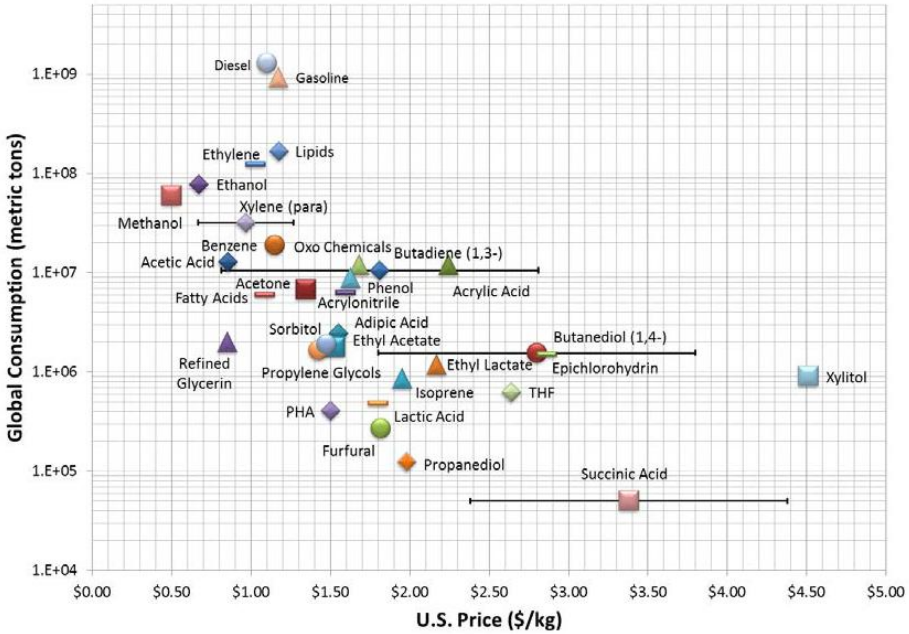
Outcomes:

- Reduced modeled fuel production cost by $0.85/gal since 2016
- Enhanced deoxygenation by tuning metal-acid bifunctionality

Catalytic Upgrading of Biochemical Intermediates: Market, Opportunity, and Challenge

Market Opportunity:

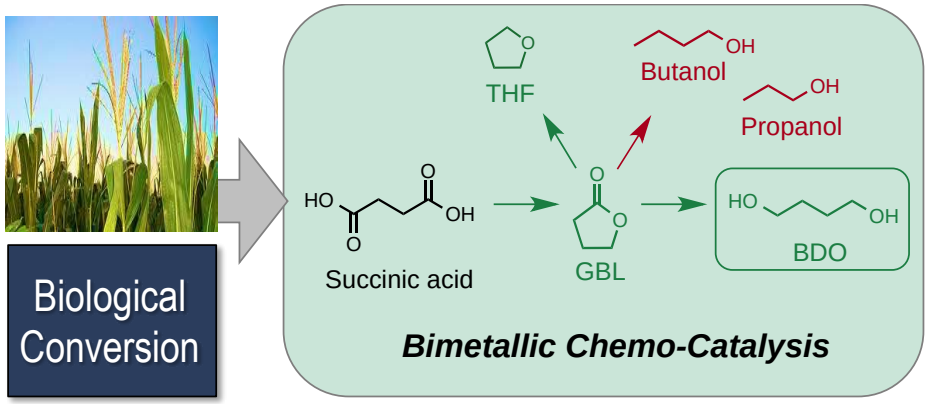
Biomass-Derived Oxygenates as Platform Chemicals



M. Biddy, et al., NREL Technical Report, 2016.

Technology Opportunity:

Hybrid Biological-Catalytic Route for Production of 1,4-Butanediol through Succinic Acid



D. Vardon, et al., *ACS Catalysis* 7 (2017) 6207

Catalysis Challenge:

Enhance catalyst selectivity to 1,4-BDO and stability under acidic aqueous conditions

→ Bimetallic formulations

Process operates under corrosive conditions:

- 170-190°C
- 100-120 bar H_2
- 5wt% succinic acid in water

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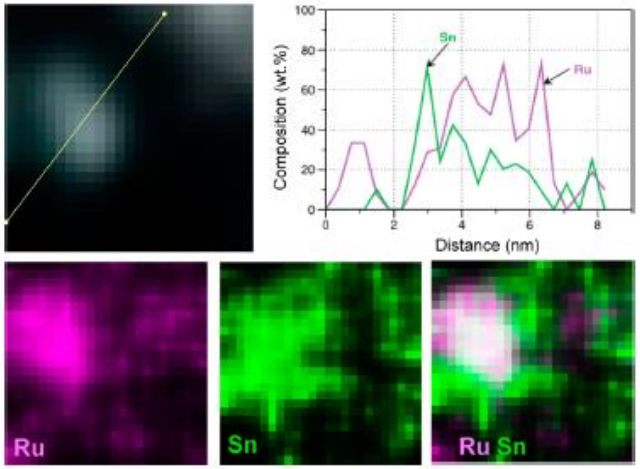
Catalytic Upgrading of Biochemical Intermediates: Catalyst Advancements

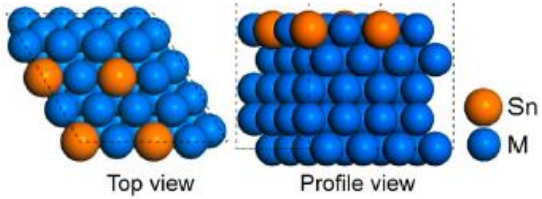
Composition and Morphology

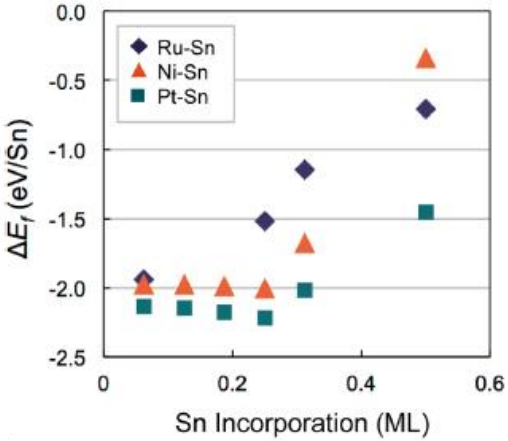
Validated co-location of Ru and Sn using high-resolution scanning transmission electron microscopy



Catalyst Stability

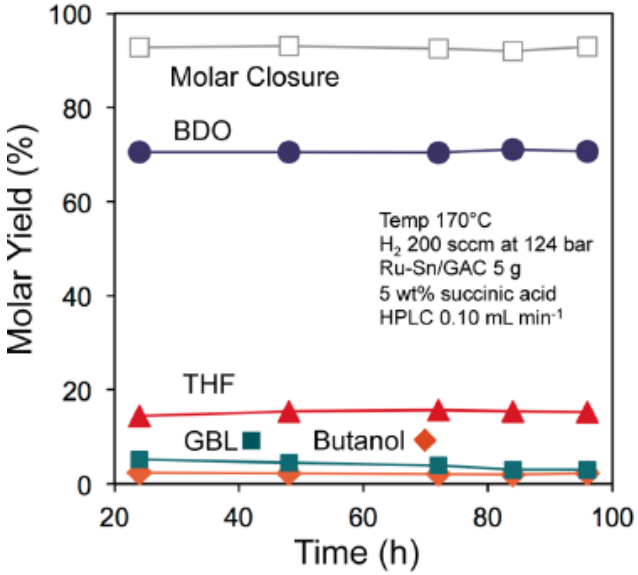
Computationally determined bimetallic catalyst stability





Performance Evaluation

Converted corn stover-derived succinic acid to 1,4-BDO in a flow system



D. Vardon, et al., *ACS Catalysis* 7 (2017) 6207

Outcomes:

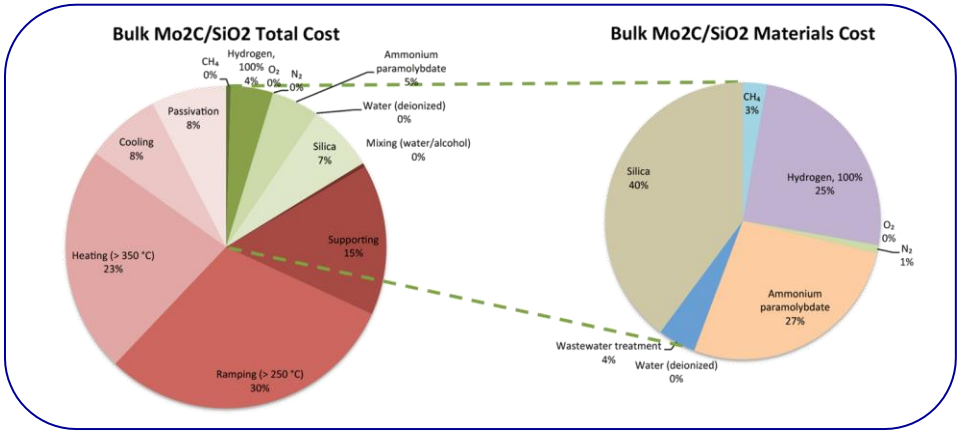
- Identified a Ru-Sn bimetallic catalyst that achieved 71% yield to 1,4-BDO
- Developed computational models to predict stability of bimetallic catalysts

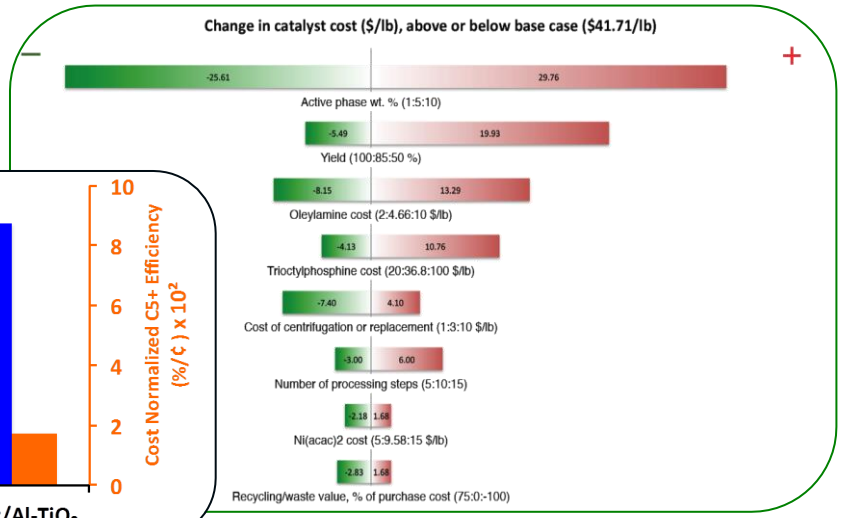
Catalyst Cost Model Development

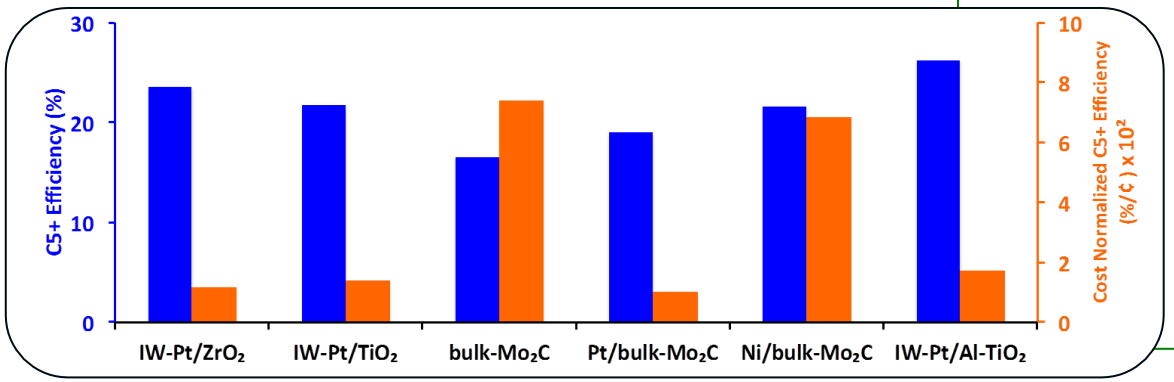
ChemCatBio is releasing a free-of-charge catalyst cost estimation tool

The CCM tool enables:

- Meaningful **cost comparison** for pre-commercial catalysts at bulk scale
- Identification of **major cost drivers** to guide further research
- **Sensitivity/risk analysis** to aid commercialization of new catalysts and processes
- An assessment of the **value proposition** of advanced catalysts early in development







Due for release in 2018 as a downloadable spreadsheet and companion web app

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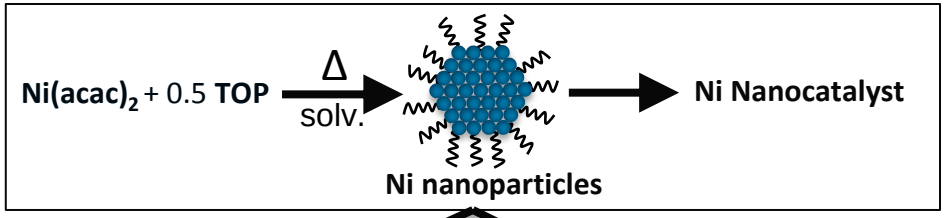
Catalyst Cost Model Development: Approach

Raw materials from grams to tons



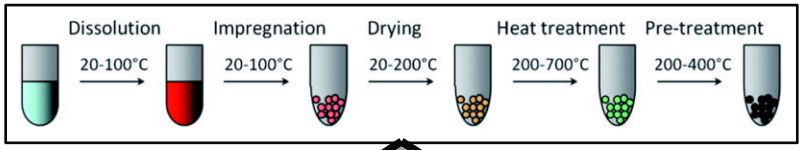
Catalyst	Material	Function	density	MW of precursor	amount	unit
IW-Ni_2P/SiO_2	water	solvent	1		35	mL
	ammonium phosphate dibasic	P-source			0.89	g
	Conc. Nitric Acid	additive	1.51		1	mL
	$Ni(NO_3)_2$ - 6 H_2O	metal source		290.79	1.96	g
	Sipernat-22	support			9.50	g
	Final Catalyst				**10.00**	**g**

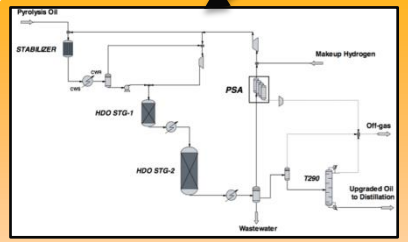
Materials	Quantity (Lb)
water	135830
ammonium phosphate dibasic	3454
Conc. Nitric Acid	5860
$Ni(NO_3)_2$ - 6 H_2O	7606
Sipernat-22	36868

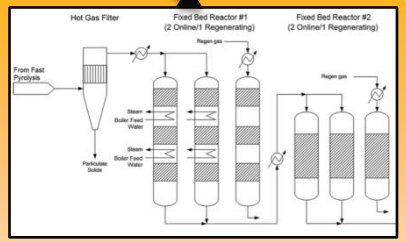
Price ($/Lb material)	Price ($)	Source
0.005	677	IHS PEP
0.462	1597	IHS PEP
0.089	522	IHS PEP
1.984	15089	Alfa
0.874	32227	IHS CEH

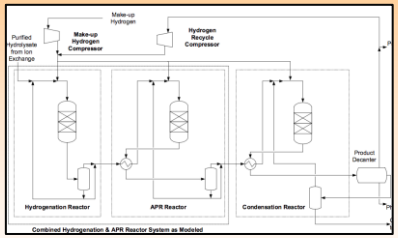
Up-to-date material pricing and industry standard scaling relationships

From Laboratory Steps to Unit Ops









Parameterized scale-up templates

Rapid and accurate early-stage catalyst cost estimation

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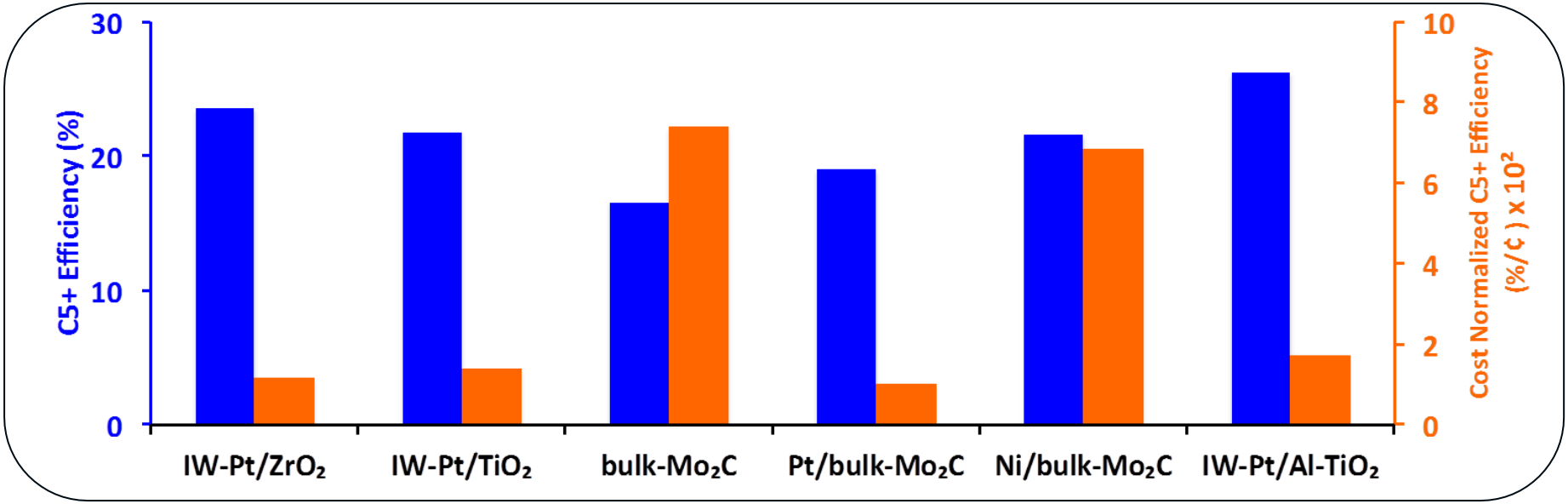
Catalyst Cost Model Development: Value Proposition



- Analysis with the CCM tool enables an early assessment of the **value proposition of a catalyst**
- Catalyst performance metrics (e.g., lifetime, yields, regenerability) can be **normalized by cost**
- Expands **early-stage catalyst design criteria** to include production cost

Announcements and Engagement Opportunities

- Awarded **$4.3M in Directed Funding Assistance** in September for industry to leverage ChemCatBio capabilities to overcome technical challenges in catalyst development and evaluation
  - 9 projects selected with 8 different industry partners
  - Gevo, Visolis, Vertimass, Lanzatech, ALD Nanosolutions, Johnson Matthey, Opus-12, and Sironix Renewables
- Seeking members for our **Industry Advisory Board**
  - Role: Guide the consortium toward industry-relevant R&D, provide a business perspective, and identify knowledge gaps
  - If interested, please contact us at Contact@ChemCatBio.org
- Organizing a **ChemCatBio Symposium at the 255th ACS National Meeting** in New Orleans on March 20th and 21st
  - Abstracts due Friday October 20th
  - Hosted in the Division of Catalysis Science and Technology (CATL)

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Acknowledgements

For more information, please visit our website at ChemCatBio.org
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ChemCatBio Team

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The Chemical Catalysis for Bioenergy Consortium:

Enabling Production of Biofuels and Bioproducts through Catalysis

Josh Schaidle

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