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

ChemCatBio
Chemical Catalysis for Bioenergy

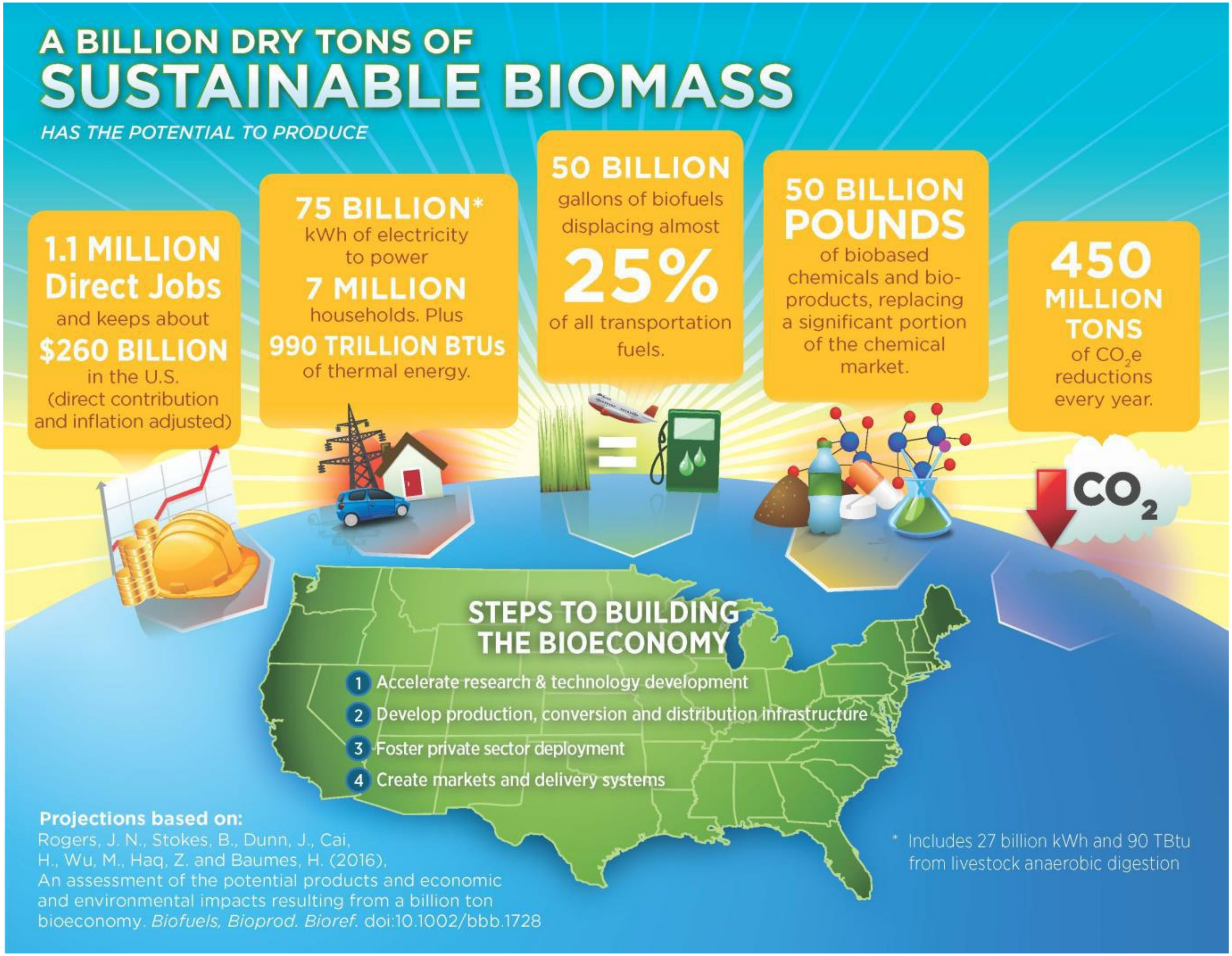
Overview of The Chemical Catalysis for Bioenergy Consortium:

Enabling Production of Biofuels and Bioproducts through Catalysis

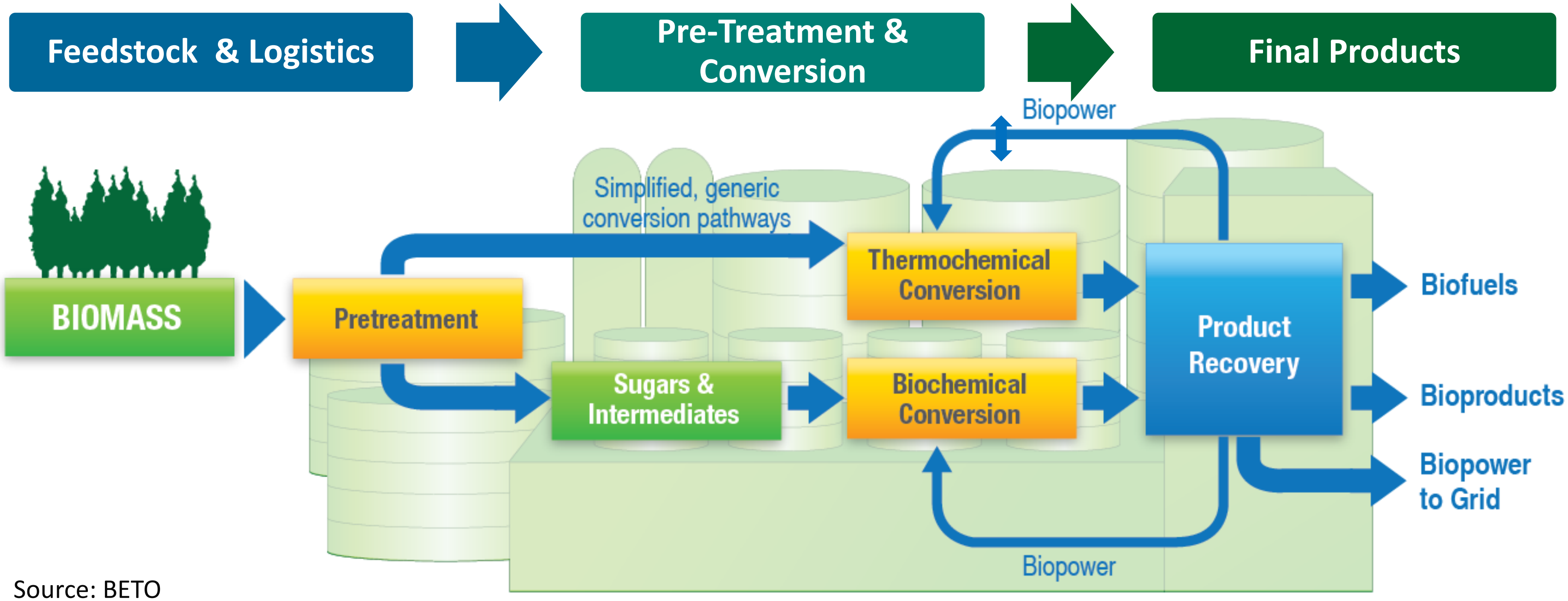
Corinne Drennan, Rick Elander, and Josh Schaidle

December 6th, 2017

Potential Impacts of a Billion-Ton Bioeconomy



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

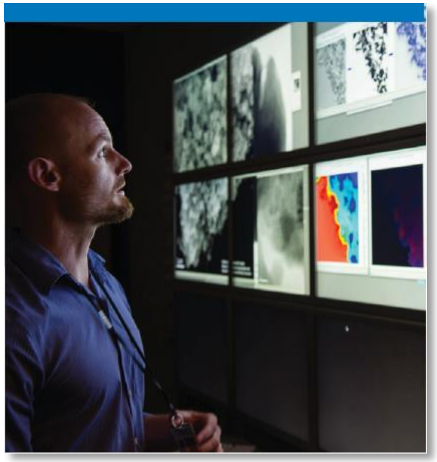
Introducing the Chemical Catalysis for Bioenergy Consortium

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

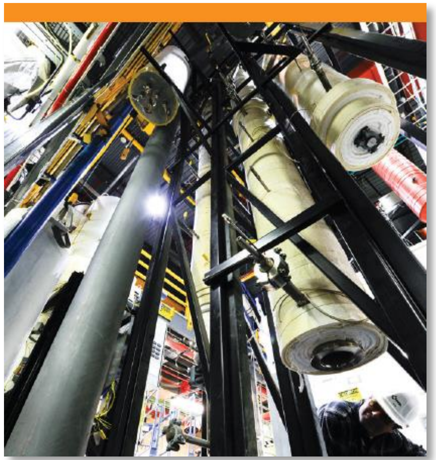
- **Our mission** is to accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals by leveraging unique US DOE national lab capabilities
- **Our team** is composed of over 100 researchers from 7 national labs and has published 84 peer-reviewed manuscripts in the last 2 years

Advanced Synthesis and Characterization

Modeling and Interactive Tools



Multi-Scale Evaluation



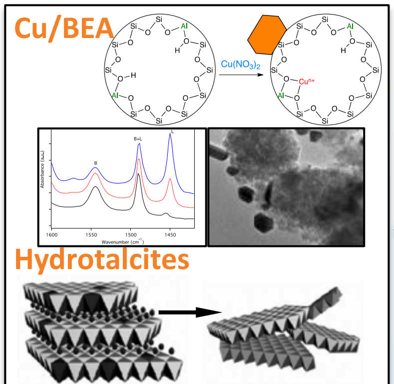
Our Approach

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

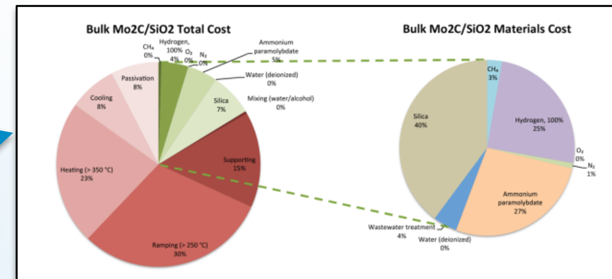
Foundational Science

Applied Engineering

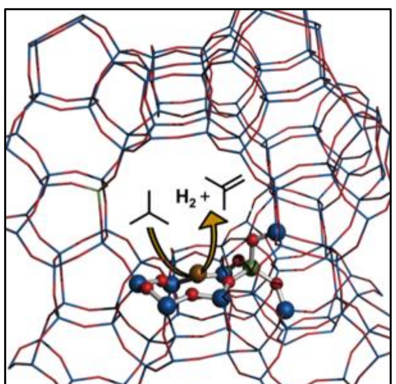
Advanced Synthesis and Characterization



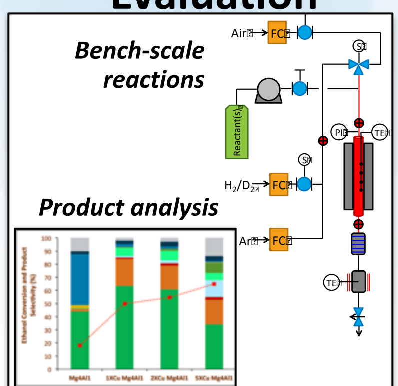
Catalyst Cost Estimation

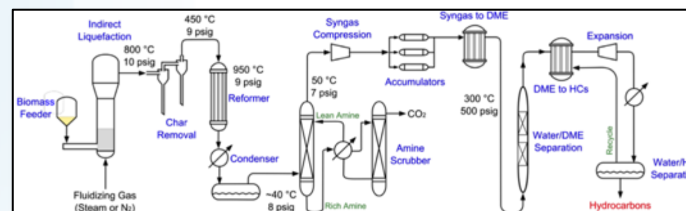


Theory



Performance Evaluation





Catalyst Scaling and Integrated Testing

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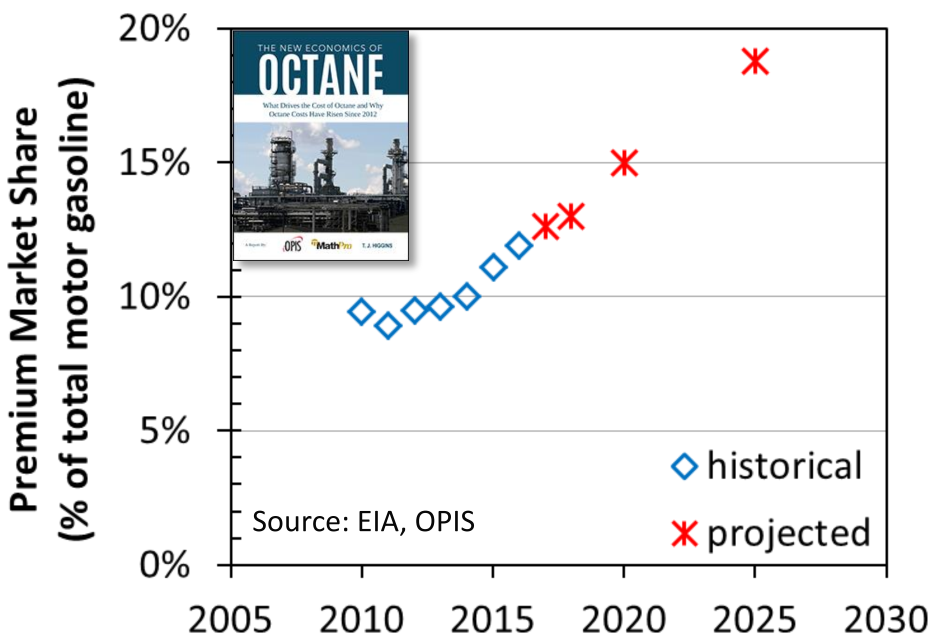
Syngas Upgrading: Market, Opportunity, and Challenge

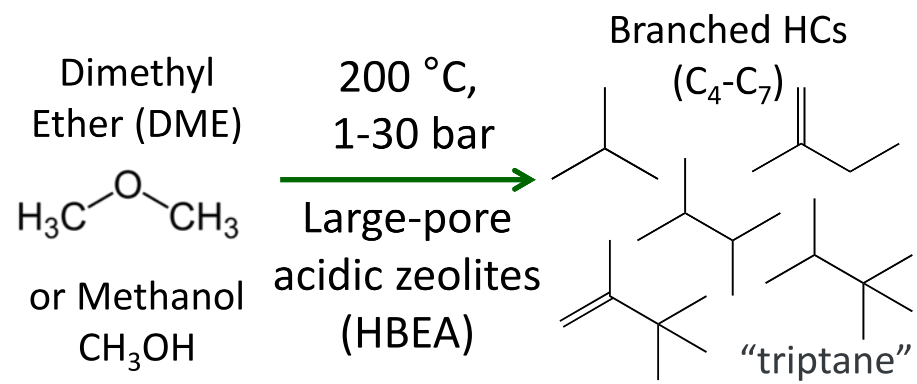
Market Opportunity:

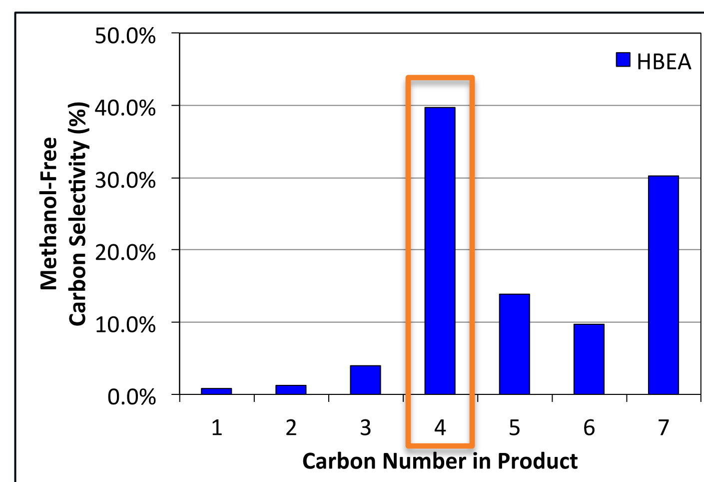
Increasing Demand for Premium Gasoline



Technology Opportunity:

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





Catalysis Challenge:

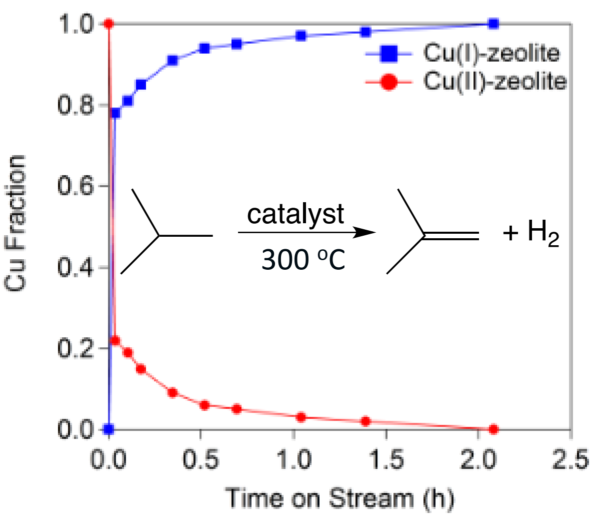
Reactivate and reincorporate light alkane products (isobutane) into the chain growth mechanism, thereby maximizing C_{5+} yield

→ Metal-modified HBEA

Syngas Upgrading: Catalyst Advancements

Active Site

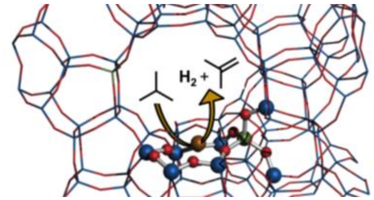
Identified Cu(I) as the active site for i-C_4 dehydrogenation using *in-operando* X-ray absorption spectroscopy

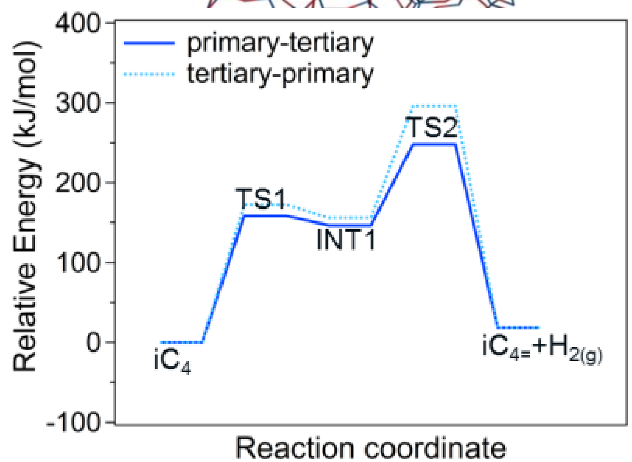


C. Farberow, et al., *ACS Catalysis* 7 (2017) 3662

Reaction Mechanism

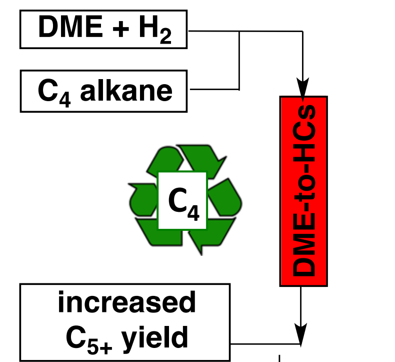
Calculated energetics for 2-step mechanism over Cu(I) active site

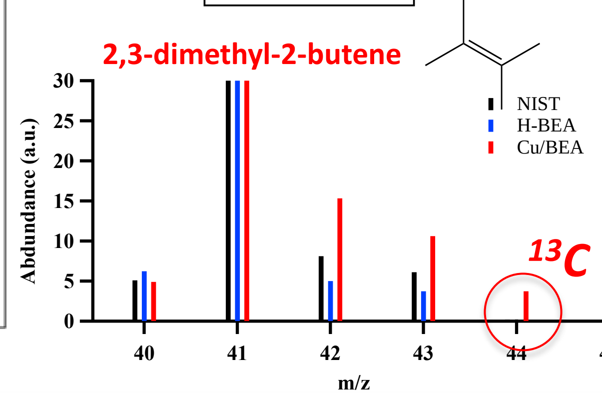




Performance Evaluation

Demonstrated C_4 reincorporation





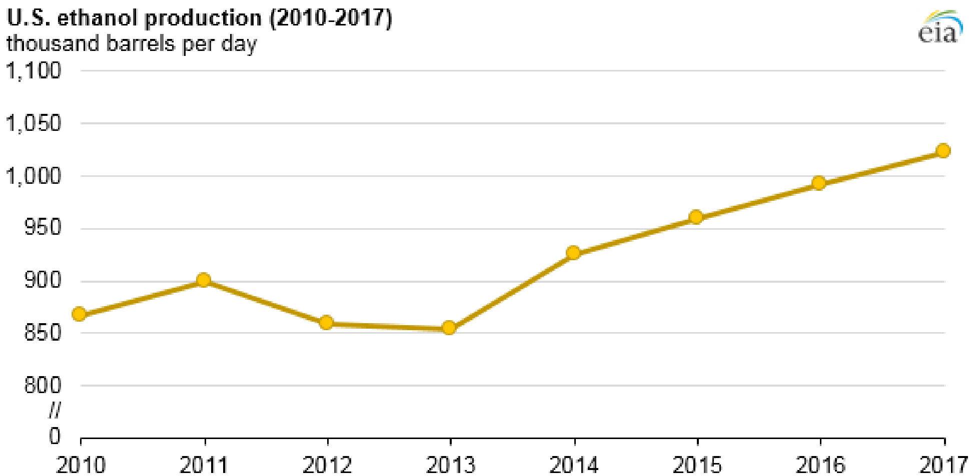
Outcomes:

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

Ethanol Upgrading: Market, Opportunity, and Challenge

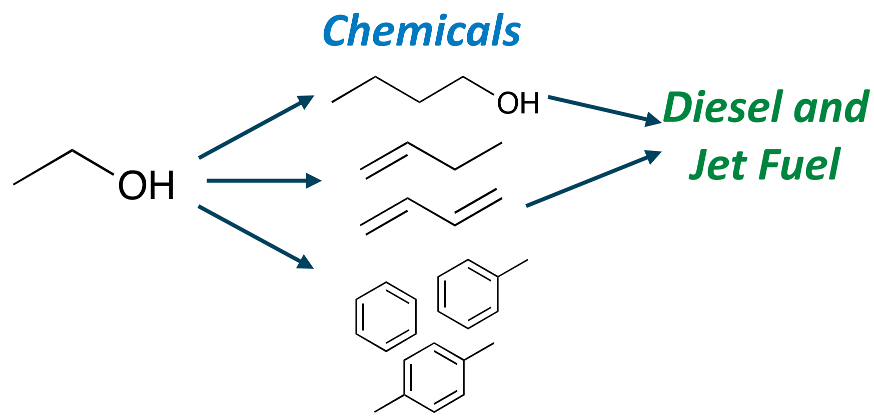
Market Opportunity:

Ethanol as a Platform Molecule for Infrastructure Compatible Fuels and Chemicals



Technology Opportunity:

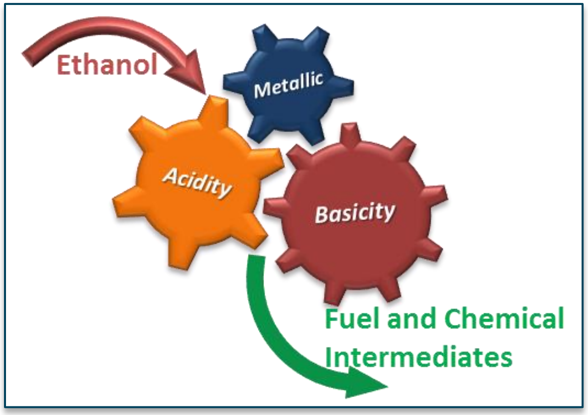
Distillate Fuel Production through High-Value, Large-Market Co-Products



Catalysis Challenge:

Selective conversion to desired products by balancing cascade catalysis

→ Multi-functional catalysts with tailored acidic, basic, and metallic active sites that co-exist at molecular distances



Ethanol to BTX: Catalyst Advancements

Active Site

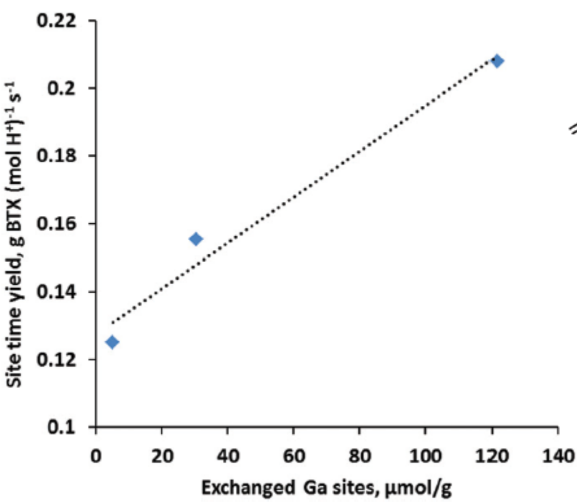
Isolated Ga^{3+} cations are responsible for BTX production

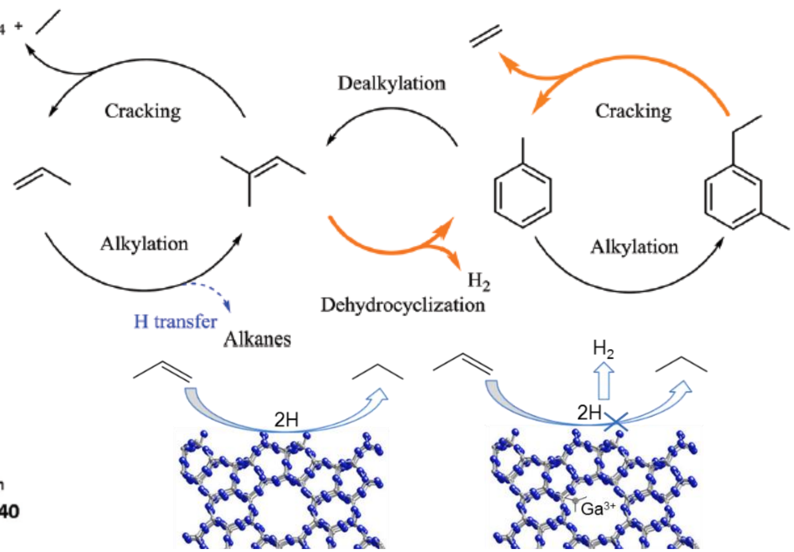
Reaction Mechanism

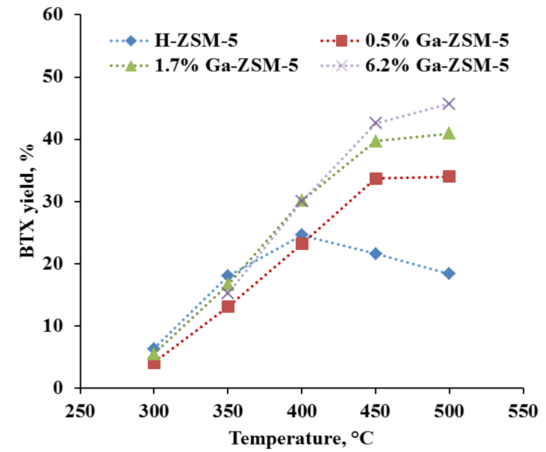
Ga^{3+} promotes the dehydrocyclization and hydrogen desorption steps

Performance Evaluation

BTX production maximized at 450°C/ambient pressure over 6.2% Ga-ZSM-5







Zhenglong Li, et al. *Green Chem* 19 (2017) 4344

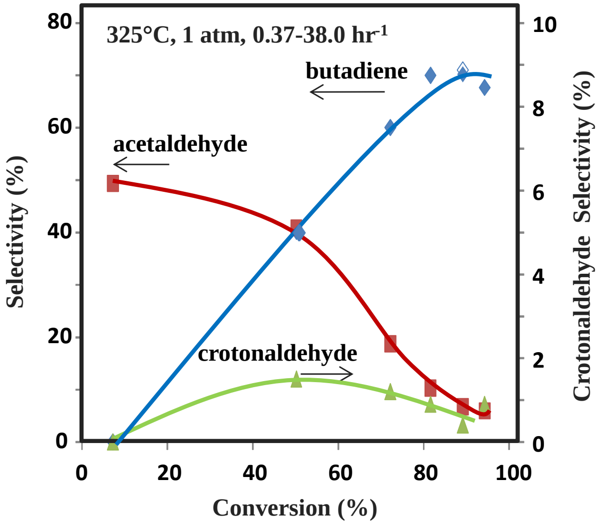
Outcomes:

- Developed a catalyst that doubled the BTX yield compared to H-ZSM-5
- Identified the Ga^{3+} active sites and catalytic function to enable catalyst development to further improve BTX yield

Ethanol to C4's and Fuels: Catalyst Advancements

Reaction Mechanism

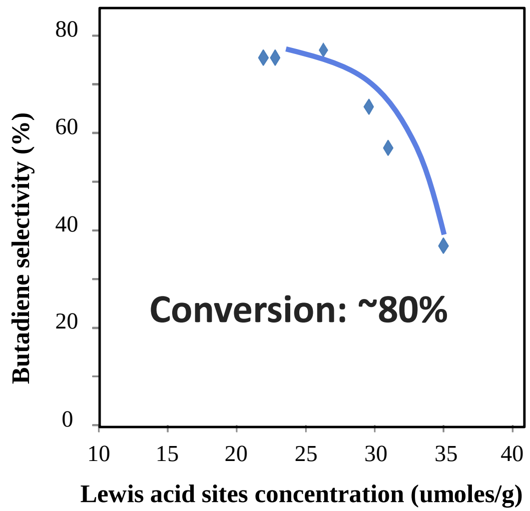
Complex reaction network through acetaldehyde and crotonaldehyde to form butadiene



V. Dagle, et al. *App. Catal. B Env.*, in review

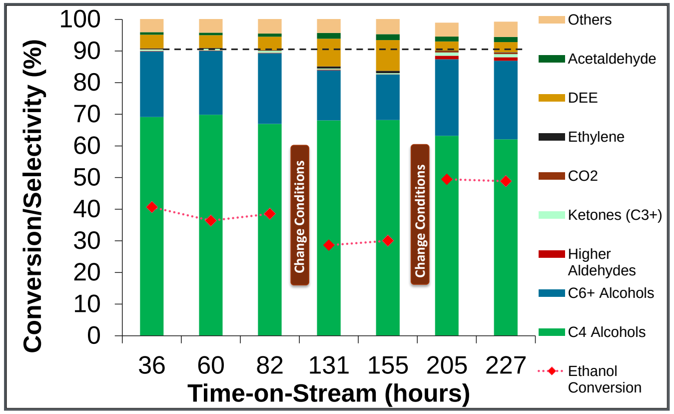
Structure-Function Relationship

Greater Lewis acid site density decreases butadiene selectivity



Performance Evaluation

Cu/Mixed oxide catalyst converts ethanol to C4+ alcohols with 90% selectivity; stable for >200 hours



Outcomes:

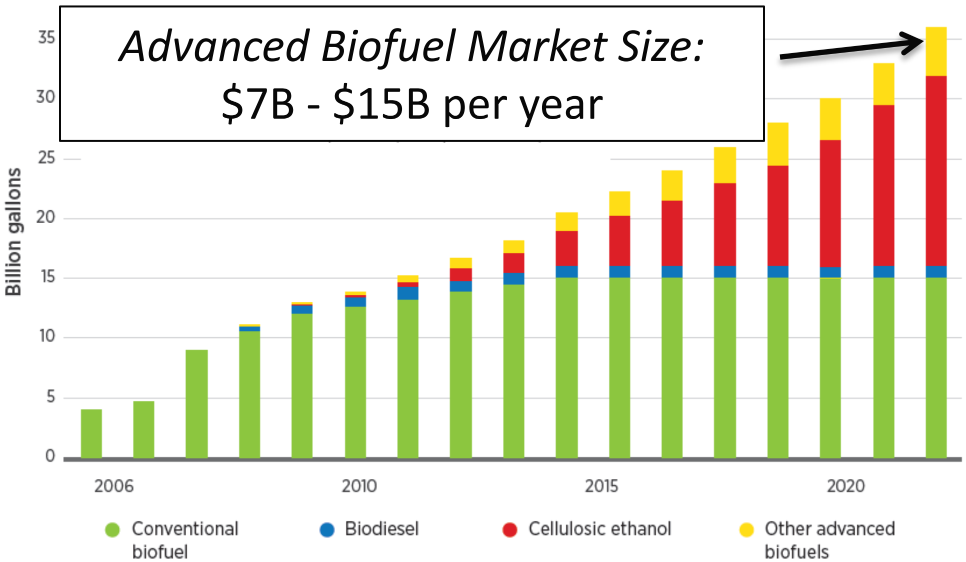
- Developed ethanol-to-butadiene catalyst with 70% yield (patent pending)
- Developed a stable ethanol-to-C4+ alcohol catalyst with high selectivity

Catalytic Fast Pyrolysis: Market, Opportunity, and Challenge

Market Opportunity:

Renewable Fuel Standard Mandates for Advanced Biofuels

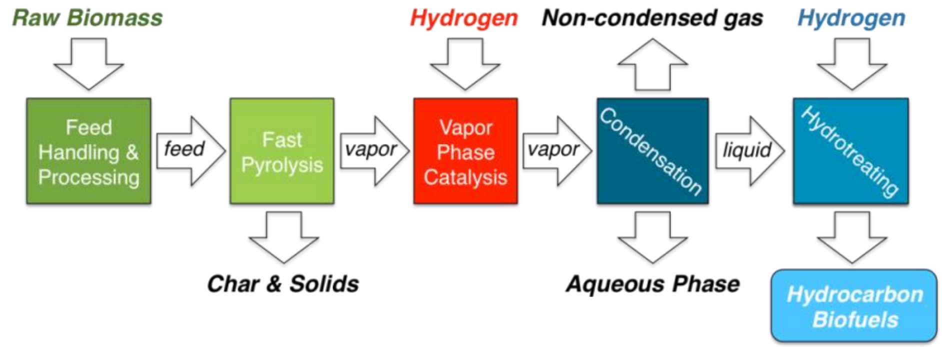
Advanced Biofuel Market Size:
$7B - $15B per year



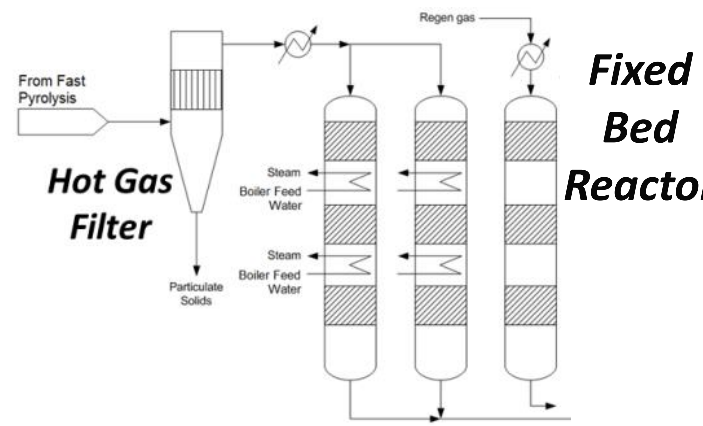
Source: EPA, DOE Billion Ton Study

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

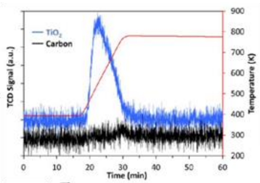
→ Leverage a fixed-bed system with co-fed H_2 operating at near atmospheric pressure over non-zeolite catalysts

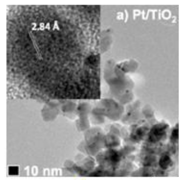
Catalytic Fast Pyrolysis: Catalyst Advancements

Surface Chemistry

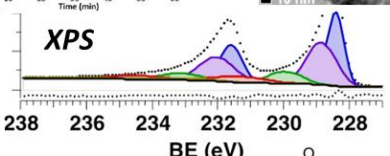
Determined role of acidic and metallic sites for CFP using advanced characterization

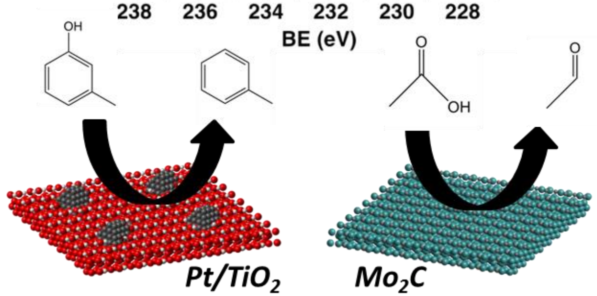
NH_3 TPD





TEM





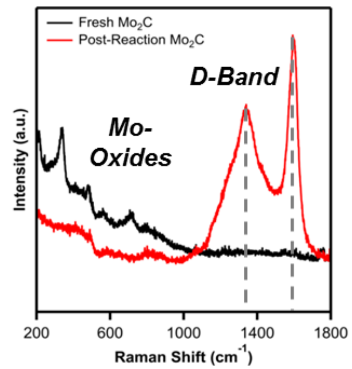
M. Griffin, et al., *ACS Catalysis* 6 (2016) 2715

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

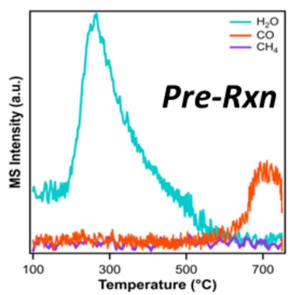
Deactivation Mechanism

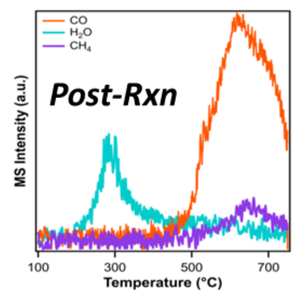
Identified deactivation mechanism using *in situ* spectroscopy

Raman Spectroscopy



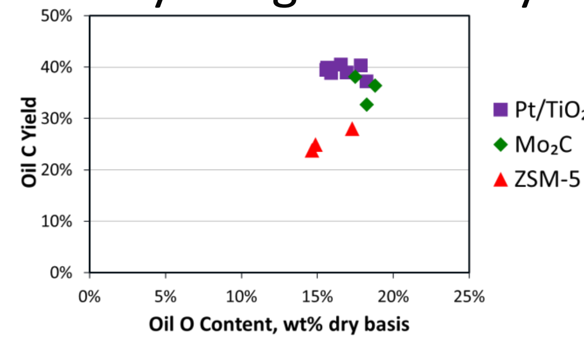
H_2-TPD

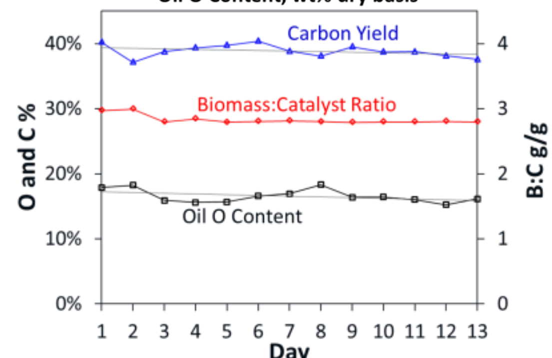




Performance Evaluation

Demonstrated improved oil yields for CFP and catalyst regenerability





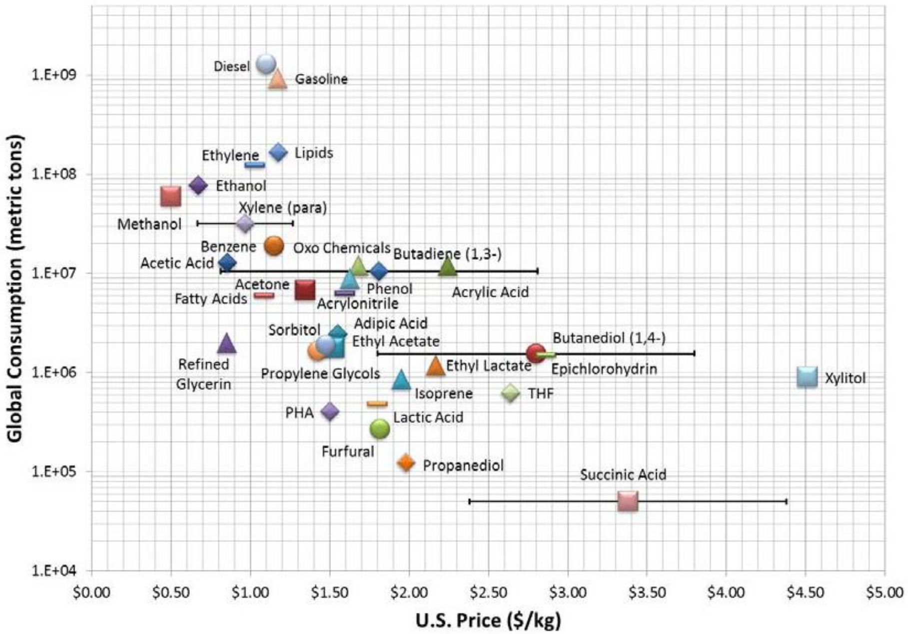
Outcomes:

- 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:

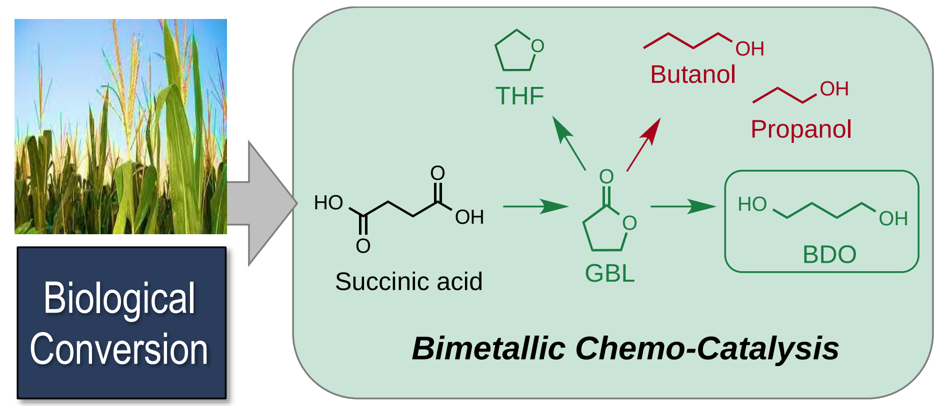
Biomass-Derived Oxygenates as Platform Chemicals



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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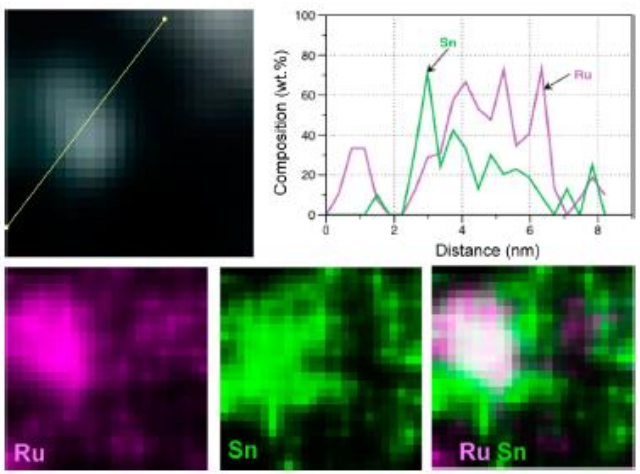
Catalytic Upgrading of Biochemical Intermediates: Catalyst Advancements

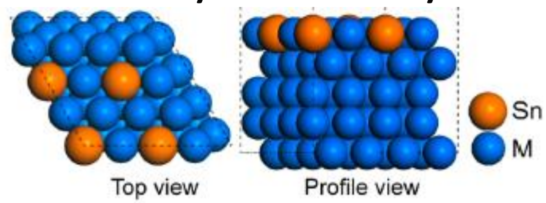
Composition and Morphology

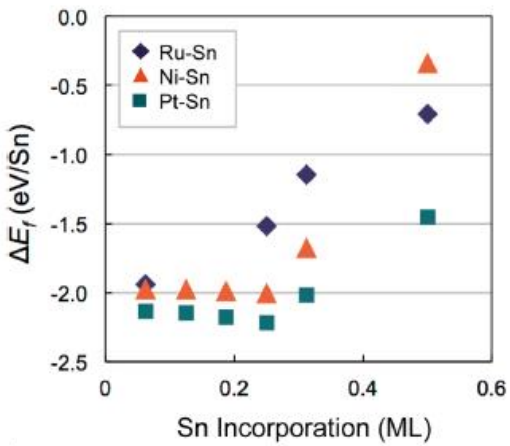
Validated co-location of Ru and Sn using high-resolution scanning transmission electron microscopy



Catalyst Stability

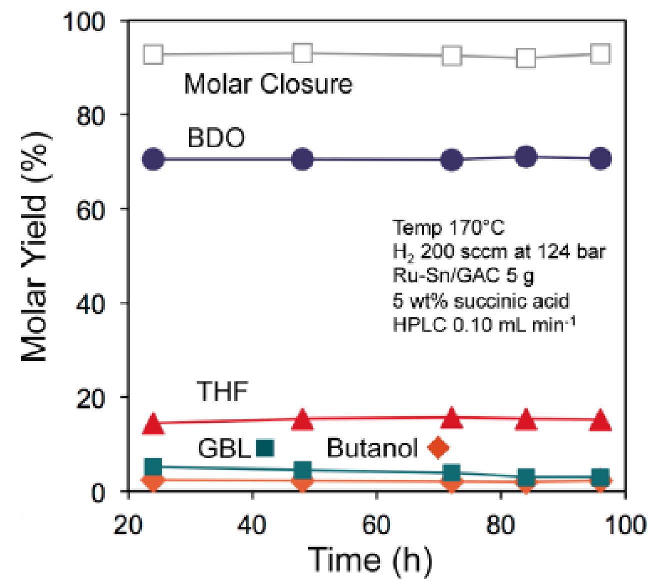
Computationally determined bimetallic catalyst stability





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:

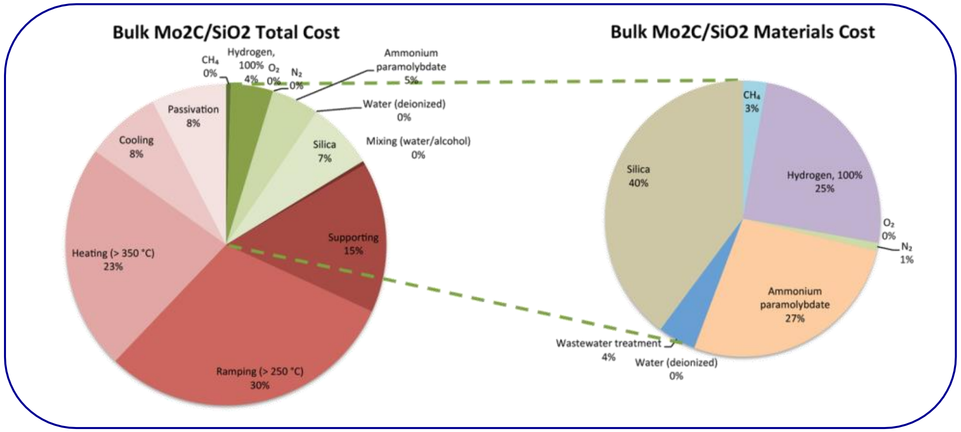
- Identified a Ru-Sn bimetallic catalyst that achieved 71% yield to 1,4-BDO
- Developed computational models to predict stability of bimetallic catalysts

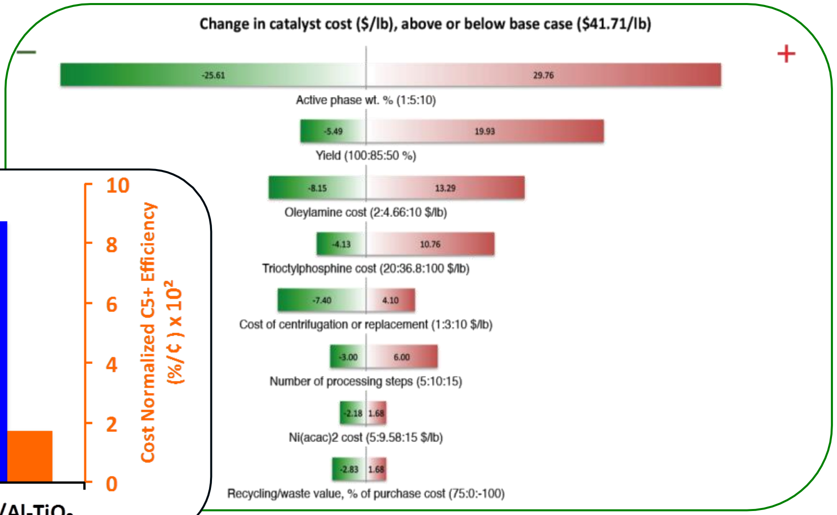
Catalyst Cost Model Development

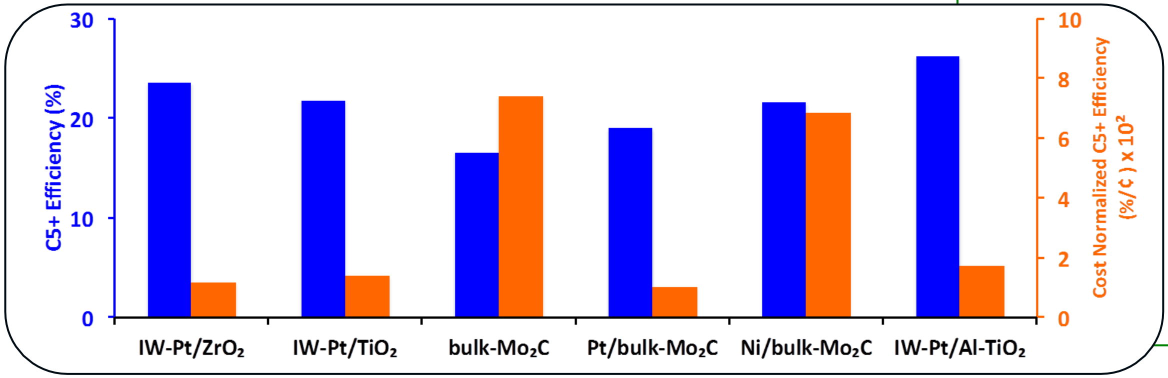
ChemCatBio is releasing a free-of-charge catalyst cost estimation tool

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



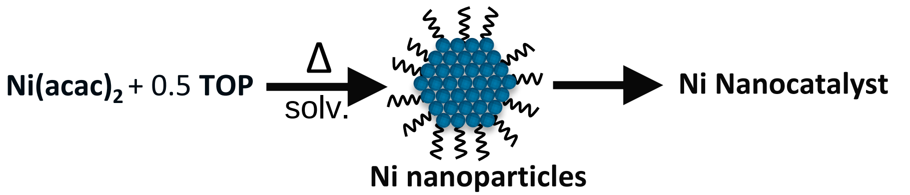




Due for release in 2018 as a downloadable spreadsheet and companion web app

Catalyst Cost Model Development: Approach

Raw materials from grams to tons

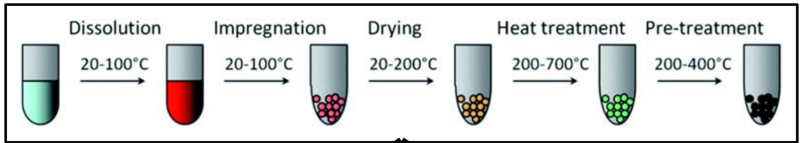


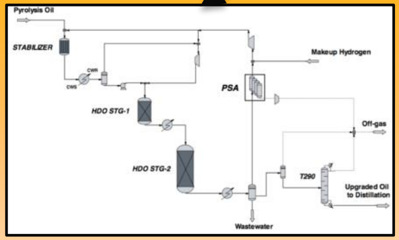
Catalyst	Material	Function	density	MW of precursor	amount	unit
IW-Ni_2P/SiO_2	water	solvent	1		35	mL
	ammonium phosphate dibasic	P-source			0.89	g
	Conc. Nitric Acid	additive	1.51		1	mL
	$Ni(NO_3)_2$ - 6 H_2O	metal source		290.79	1.96	g
	Sipernat-22	support			9.50	g
	Final Catalyst				**10.00**	**g**

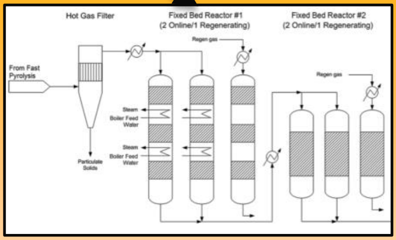
Materials	Quantity (Lb)	Price ($/Lb material)	Price ($)	Source
water	135830	0.005	677	IHS PEP
ammonium phosphate dibasic	3454	0.462	1597	IHS PEP
Conc. Nitric Acid	5860	0.089	522	IHS PEP
$Ni(NO_3)_2$ - 6 H_2O	7606	1.984	15089	Alfa
Sipernat-22	36868	0.874	32227	IHS CEH

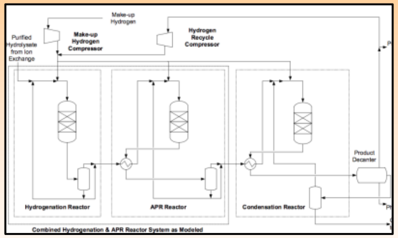
Up-to-date material pricing and industry standard scaling relationships

From Laboratory Steps to Unit Ops





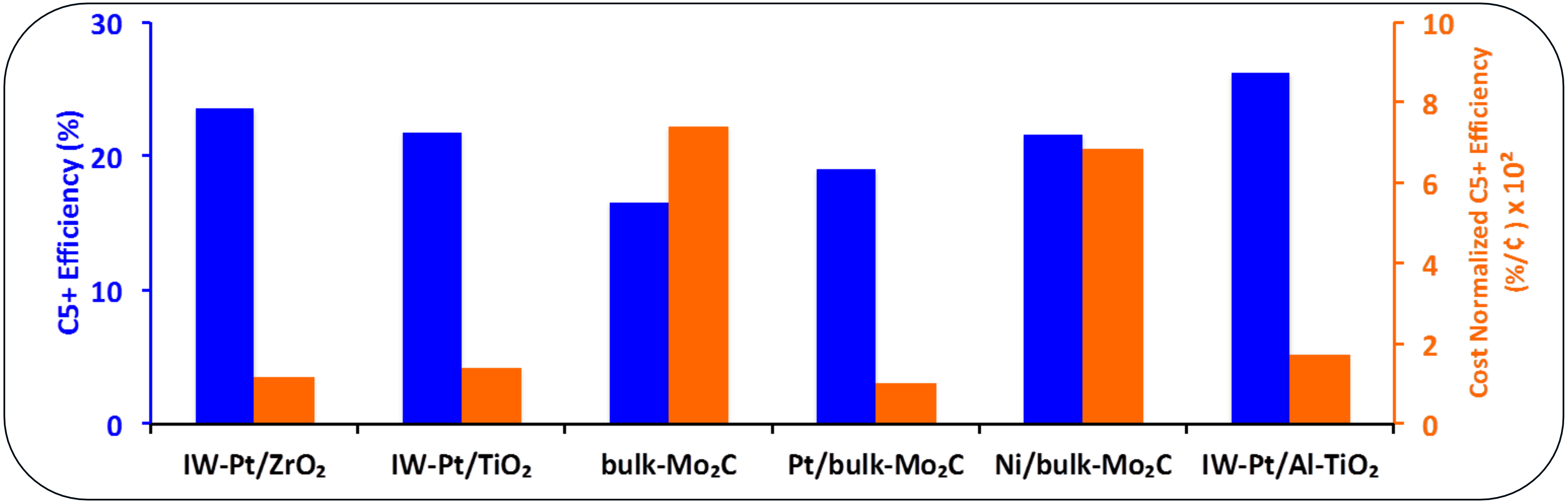




Parameterized scale-up templates

Rapid and accurate early-stage catalyst cost estimation

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

Outreach and Working with Us

- We want to provide **shared value** to the catalysis and bioenergy communities and would appreciate feedback on how to leverage our team and capabilities to create the most value
  - Held Stakeholder Listening Day on June 9th, 2017 in Denver, CO in conjunction with the North American Catalysis Society Meeting
  - Hosted a booth at the TCBiomass Conference in Chicago, IL in September
  - Hosted and visited interested partners to discuss collaboration opportunities
- Numerous **mechanisms to work with ChemCatBio**, including scientist/engineer exchange, post-doc sponsorship, cooperative research agreements/work for others, and funding opportunities
  - Established a single NDA and CRADA across ChemCatBio

Contact us directly at Contact@ChemCatBio.org to learn more

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
  - Hosted in the Division of Catalysis Science and Technology (CATL)

ACS Chemistry for Life®

Upcoming Webinars

ChemCatBio plans to hold one webinar per quarter discussing specific biomass conversion technologies, overarching catalysis challenges, and catalyst development acceleration tools:

- **Q1 2018:** *Linking catalyst and process development with technoeconomic analysis in the conversion of biomass to high octane gasoline*
- **Q2 2018:** *Accelerating the catalyst development cycle: Integrating predictive computational modeling, tailored materials synthesis, and in situ characterization capabilities through the ChemCatBio Consortium*
- **Q3 2018:** *Tutorial: Using the Catalyst Cost Estimation Tool in Synthesis and Scale-up Research*

Acknowledgements

For more information, please visit our website at ChemCatBio.org or email us directly at Contact@ChemCatBio.org

ChemCatBio Team

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

Bioenergy Technologies Office

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

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

ChemCatBio
Chemical Catalysis for Bioenergy

Overview of The Chemical Catalysis for Bioenergy Consortium:

Enabling Production of Biofuels and Bioproducts through Catalysis

Corinne Drennan, Rick Elander, and Josh Schaidle

December 6th, 2017

Management Structure

Bioenergy Technologies Office

Industry and Academic Partners

Board of Directors

- Single point of contact
- Portfolio management
- Strategic initiatives

Steering Committee

- Coordinate activities
- Provide technical guidance
- Identify unique lab capabilities
- Biweekly teleconferences

Team

Industry Advisory Board

- Guide the consortium toward industry-relevant R&D
- Provide a business perspective
- Identify knowledge gaps

Technical Capabilities Experts

Technology Transfer Experts

Data Experts

Board of Directors and Steering Committee Members

Board of Directors

Corinne Drennan
Subsector Lead for Bioenergy Technologies
PNNL

Rick Elander
Biochemical Conversion Platform Manager
NREL

Josh Schaidle
Research Engineer
NREL

Steering Committee Members

Karl O. Albrecht
Senior Research Engineer
PNNL

Frederick G. Baddour
Scientist
NREL

Andrew Sutton
Team Leader – Chemical Energy Storage
LANL

Daniel Ruddy
Senior Scientist
NREL

Susan E. Habas
Senior Scientist
NREL

Ted Krause
Theme Leader, Catalysis and Energy Conversion
ANL

Mariefel V. Olarte
Senior Research Chemical Engineer
PNNL

Jim Parks
Group Leader, Emissions and Catalysis Research
ORNL

Current Project Structure

Catalytic Technologies

Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL)

Catalytic Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Zeolites and Metal Oxide Catalysts

Supported Metal Catalysts

Cross-cutting Discussion Groups

Enabling Capabilities

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups