Overview of The Chemical Catalysis for Bioenergy Consortium:
Enabling Production of Biofuels and Bioproducts through Catalysis

Corinna Drennan, Rick Elander, and Josh Schaidle

December 6th, 2017
Potential Impacts of a Billion-Ton Bioeconomy

A BILLION DRY TONS OF SUSTAINABLE BIOMASS HAS THE POTENTIAL TO PRODUCE

- 1.1 MILLION Direct Jobs
  and keeps about $260 BILLION in the U.S. (direct contribution and inflation adjusted)
- 75 BILLION* kWh of electricity to power 7 MILLION households. Plus
- 990 TRILLION BTUs of thermal energy.
- 50 BILLION gallons of biofuels displacing almost 25% of all transportation fuels.
- 50 BILLION POUNDS of biobased chemicals and bio-products, replacing a significant portion of the chemical market.
- 450 MILLION TONS of CO₂ reductions every year.

Projections based on:

* Includes 27 billion kWh and 90 TBtus from livestock anaerobic digestion.

ChemCatBio Webinar Series
Energy Materials Network
U.S. Department of Energy
Catalysis Challenges are Pervasive in Biomass Conversion

Challenges due to Biomass Composition
- 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

Key Catalytic Bioenergy Processes
- 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**

- [Image of a researcher performing synthesis]

**Modeling and Interactive Tools**

- [Image of a researcher looking at a computer screen]

**Multi-Scale Evaluation**

- [Image of a laboratory setting]
Our Approach

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

**Foundational Science**
- Advanced Synthesis and Characterization
- Theory

**Applied Engineering**
- Catalyst Cost Estimation
- Catalyst Scaling and Integrated Testing
- Performance Evaluation

---

In line with the webinar series on chemical catalysis for bioenergy, the focus is on establishing a portfolio of integrated catalytic technologies and enabling capabilities. This approach involves:

**Cu/BEA**

Hydrotalcites

**Bench-scale reactions**

Product analysis

**Energy Materials Network**

ChemCatBio Webinar Series
Syngas Upgrading: Market, Opportunity, and Challenge

**Market Opportunity:**
*Increasing Demand for Premium Gasoline*

![Graph showing market share of premium gasoline](image)

- *Historical* (◊)
- *Projected* (×)

Source: EIA, OPIS

**Technology Opportunity:**
*Production of High-Octane Synthetic Alkylate from Biomass-Derived Dimethyl Ether*

- Dimethyl Ether (DME)
- H₃C–O–CH₃
- or Methanol CH₃OH

200 °C, 1-30 bar

Branched HCs (C₄-C₇)

Large-pore acidic zeolites (HBEA)

“triptane”

**Catalysis Challenge:**
*Reactivate and reincorporate light alkane products (isobutane) into the chain growth mechanism, thereby maximizing C⁵⁺ 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

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

**Performance Evaluation**
Demonstrated C$_4$ reincorporation

\[
\text{Catalyst} \xrightarrow{300 \, ^\circ \text{C}} \text{C}_4 \rightarrow \text{H}_2 + \text{H}_2^+ 
\]

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

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**

<table>
<thead>
<tr>
<th>Year</th>
<th>U.S. Ethanol Production (2010-2017) (thousand barrels per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>850</td>
</tr>
<tr>
<td>2011</td>
<td>870</td>
</tr>
<tr>
<td>2012</td>
<td>900</td>
</tr>
<tr>
<td>2013</td>
<td>950</td>
</tr>
<tr>
<td>2014</td>
<td>1,000</td>
</tr>
<tr>
<td>2015</td>
<td>1,050</td>
</tr>
<tr>
<td>2016</td>
<td>1,100</td>
</tr>
<tr>
<td>2017</td>
<td>1,150</td>
</tr>
</tbody>
</table>

## Technology Opportunity:
**Distillate Fuel Production through High-Value, Large-Market Co-Products**

- **Chemicals**
  - Diesel and Jet Fuel

---

## 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

---

[ChemCatBio Webinar Series](https://www.energy.gov/)
[Chemical Catalysis for Bioenergy](https://www.energy.gov/)
[Energy Materials Network](https://www.energy.gov/)
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.

---

**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

**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
**Market Opportunity:**

Renewable Fuel Standard Mandates for Advanced Biofuels

**Catalysis Challenge:**

Improve carbon yields and extend catalyst lifetime

→ Leverage a fixed-bed system with co-fed H₂ operating at near atmospheric pressure over non-zeolite catalysts

**Energy Materials Network**

U.S. Department of Energy
Catalytic Fast Pyrolysis: Catalyst Advancements

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

**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

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

ChemCatBio Webinar Series
Energy Materials Network
U.S. Department of Energy
Catalytic Upgrading of Biochemical Intermediates: Market, Opportunity, and Challenge

**Market Opportunity:**
Biomass-Derived Oxygenates as Platform Chemicals

**Technology Opportunity:**
Hybrid Biological-Catalytic Route for Production of 1,4-Butanediol through Succinic Acid

**Catalysis Challenge:**
Enhance catalyst selectivity to 1,4-BDO and stability under acidic aqueous conditions
→ Bimetallic formulations


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

Process operates under corrosive conditions:
- 170-190°C
- 100-120 bar H₂
- 5wt% succinic acid in water
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

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

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

Ni(acac)$_2$ + 0.5 TOP $\xrightarrow{\Delta}$ solv. Ni Nanocatalyst

**From Laboratory Steps to Unit Ops**

- Dissolution: 20-100°C
- Impregnation: 20-100°C
- Drying: 20-200°C
- Heat treatment: 200-700°C
- Pre-treatment: 200-400°C

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Material</th>
<th>Function</th>
<th>density</th>
<th>MW of precursor</th>
<th>amount</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiW-NiP/SiO$_2$</td>
<td>water</td>
<td>solvent</td>
<td>1</td>
<td>35 mL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ammonium phosphate dibasic</td>
<td>P-source</td>
<td>1.51</td>
<td>0.89 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conc. Nitric Acid</td>
<td>additive</td>
<td>1 mL</td>
<td>1.96 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$ - 6 H$_2$O</td>
<td>metal source</td>
<td>290.79</td>
<td>9.50 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sipernat-22</td>
<td>support</td>
<td>10.00 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials</th>
<th>Quantity (Lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>135830</td>
</tr>
<tr>
<td>ammonium phosphate dibasic</td>
<td>3454</td>
</tr>
<tr>
<td>Conc. Nitric Acid</td>
<td>5860</td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$ - 6 H$_2$O</td>
<td>7606</td>
</tr>
<tr>
<td>Sipernat-22</td>
<td>36868</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Price ($/Lb material)</th>
<th>Price ($)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>677</td>
<td>IHS PEP</td>
</tr>
<tr>
<td>0.462</td>
<td>1597</td>
<td>IHS PEP</td>
</tr>
<tr>
<td>0.089</td>
<td>522</td>
<td>IHS PEP</td>
</tr>
<tr>
<td>1.984</td>
<td>15089</td>
<td>Alfa</td>
</tr>
<tr>
<td>0.874</td>
<td>32227</td>
<td>IHS CEH</td>
</tr>
</tbody>
</table>

**Parameterized scale-up templates**

**Rapid and accurate early-stage catalyst cost estimation**
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)
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
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**
- Single point of contact
- Portfolio management
- Strategic initiatives

**Board of Directors**
- Coordinate activities
- Provide technical guidance
- Identify unique lab capabilities
- Biweekly teleconferences

**Steering Committee**
- Single point of contact
- Portfolio management
- Strategic initiatives

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

**Industry and Academic Partners**
- Single point of contact
- Portfolio management
- Strategic initiatives

**Technical Capabilities Experts**

**Technology Transfer Experts**

**Data Experts**

---

ChemCatBio Webinar Series

Energy Materials Network

U.S. Department of Energy
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

**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)

Cross-cutting Discussion Groups

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