BETO 2021 Peer Review
The Engineering of Catalyst
Scale Up (WBS 3.3.2.701/702)

March 24, 2021
Engineering and Integration (Pillars)
Frederick Baddour (NREL)
Kris Pupek (ANL)
Project Overview: Engineering of Catalyst Scale Up (EOS)

**Project Goal** – Develop a *flexible, engineering-scale catalyst synthesis capability* to produce *scalable and cost effective* next-generation biomass conversion catalysts and mitigate commercialization risk by *enabling large-scale performance evaluation*.

**Approach**
- *Industrially guided* identification and deployment of catalyst manufacturing equipment, processes, and materials
- Develop scalable, industrially relevant *technical catalyst preparatory methods*
- Produce engineering-scale quantities of technical catalysts to *enable large-scale performance evaluation*

**Research Progress & Outcomes**
- Assembled a diverse *industrial advisory board* to oversee development of catalyst scale-up facility
- Demonstrated *reproducible production* of kg-scale quantities of emerging biomass conversion materials from the laboratory to commercial relevance

**Impact**
- A *focused technical catalyst development effort* supporting engineering-scale performance evaluation of novel catalytic materials.
- Rapid prototyping of technical catalyst materials to *reduce scale-up risk*
- *Patented intellectual property* and publications in *peer-reviewed journals*.
The Challenge: A technical catalyst must faithfully reproduce the performance of laboratory preparations and possess the required physical properties for large scale operation.

Developing a technical catalyst from benchtop candidates requires at a minimum:
- Gram-to-kilo protocol adaptation
- Determination of multi-component formulation
- Shaping powders into reactor specific macroscopic forms

Translation of promising research catalysts to viable technical bodies is a non-trivial research challenge.
Simultaneous technology development critical to hitting performance targets at larger scales

2-3 years

Fundamental Development Cycle
Overview: Coupling Technology Development and Scaling

The EOS project seeks to develop a mature technical catalyst development cycle

Linking an engineering-scale catalyst synthesis effort to ongoing foundational science enables the answering of critical research questions:

- What binders inhibit performance?
- What is the impact of pore-size distribution?
- Can we introduce novel active-phases into formed bodies?
Overview: Decoupling Technology Development and Scaling

Challenges in Technology Verification Cycle: Cu/zeolite

- High Cost
- Equipment too large for intermediate scale

Time, Cost, Performance, and Value Proposition Negatively Impacted

Requirements for Verification
- $\geq 10^5$ increase in production from gram-scale to 100 kg
- Powder zeolite to formed extrudate

Performance impacted by available commercial extrudate formulation
NREL’s Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

Market Trends

- Anticipated decrease in gasoline/ethanol demand; diesel demand steady
- Increasing demand for aviation and marine fuel
- Demand for higher-performance products
- Increasing demand for renewable/recyclable materials
- Sustained low oil prices
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H₂
- Closing the carbon cycle
- Risk of greenfield investments
- Challenges and costs of biorefinery start-up
- Availability of depreciated and underutilized capital equipment
- Carbon intensity reduction
- Access to clean air and water
- Environmental equity

Value Proposition

- Coupling engineering-scale synthesis with BETOs conversion pathways can identify, mitigate, and ultimately reduce the risks associated with catalyst scale up.

Key Differentiators

- Dedicated research effort on scale up of pre-commercial catalysts reduces risk of commercial adoption by enabling engineering-scale performance evaluation
- Tight integration of industrial advisory board, conversion pathways, and enabling technologies in ChemCatBio
1 – Management: Highly Integrated Approach

The Engineering of Catalyst Scale-Up Project

<table>
<thead>
<tr>
<th>NREL (3.3.2.701)</th>
<th>ANL (3.3.2.702)</th>
<th>Industrial Advisory Board</th>
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<tbody>
<tr>
<td>Frederick Baddour</td>
<td>Kris Pupek</td>
<td>4+ Rotating Members</td>
</tr>
<tr>
<td>• Catalyst Development</td>
<td>• Advanced Materials</td>
<td>• Equipment selection</td>
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<td>• Technical Body Formulation</td>
<td>• Nanostructuring</td>
<td>• Method identification</td>
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<td>• AP and Support Integration</td>
<td>• Review of best practices</td>
</tr>
<tr>
<td>• Performance Evaluation</td>
<td>• Advanced Characterization</td>
<td>• Relevant targets</td>
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</table>

- **Constant communication** between tasks to ensure efforts remained relevant to pathway needs and adapt to changes
- Monthly meetings to assess performance/material targets, feasibility, and **communicate technical feedback**
- Annual **best practices review** with industrial advisory board members
- **Go/No-go decision point in FY20** to determine if developed methods suitable for meeting the scaling targets of BETO’s conversion pathway projects
1 – Management: Highly Integrated Approach

The Engineering of Catalyst Scale-Up Project

NREL (3.3.2.701)
Frederick Baddour

- Catalyst Development
- Technical Body Formulation
- Physical Forming
- Performance Evaluation

ANL (3.3.2.702)
Kris Pupek

- Advanced Materials
- Nanostructuring
- AP and Support Integration
- Advanced Characterization

Industrial Advisory Board
4+ Rotating Members

- Equipment selection
- Method identification
- Review of best practices
- Relevant targets

Conversion Technologies and ChemCatBio Interfaces

Conversion Pathways
Catalytic Upgrading of Pyrolysis Products (2.3.1.314)
Upgrading C1 Building Blocks (2.3.1.305)

- Identification of materials targets
- Physical property requirements
- Performance evaluation
- Scale requirements

Enabling Technologies
CatCost (2.6.3.500)
CCPC (2.5.1.307)
ACSC (WBS 2.5.4.304)

- Estimation of manufacturing costs
- Predicted material targets
- Advanced characterization
2 – Technical Approach: Context

ChemCatBio/Conversion

- Pioneering scale-up methodologies
- Technical forms of CCB research catalysts
- Fundamental scaling-performance relationships

SDI

Advanced Synthesis and Characterization

Performance Evaluation

Theory

Catalyst Scale-up

- Industry responsive catalyst scale-up
- Production of engineering-scale quantities
- Enable PDU evaluation of next-gen catalysts
- Facilitate effective verification efforts

Enables the fundamental study of technical catalysts to accelerate market deployment of biomass conversion technologies
Establish Industrial Advisory Board

Assembled team of industry advisory board members consisting of members from

- National Laboratories
- Oil and Gas Producers
- Catalyst Manufacturers
- Chemical Producers
- Independent Contractors

Diverse industrial board leveraged to guide scale-up efforts and maintain relevant targets, methodologies, and performance metrics
2 – Technical Approach: Building a Scale Up Capability

- Establish Industrial Advisory Board
- Identify Catalyst Targets
- Phyisco-Chemical Requirements
- Industrial Expert Input and Review
- Equipment Selection
- Assessment of Best Practices
- Methods Development & Review
- Produce 1st-Gen. Scaled Catalyst

Near-term targets identified within Conversion
- Pt/TiO$_2$ (Catalytic Upgrading of Pyrolysis Products)
- Cu-HBEA (Upgrading C1 Building Blocks)

- Process and reactor configuration dictate form and required performance characteristics
- Forming technologies reviewed with advisory board to ensure industrial relevance, feasibility, and equipment requirements
- Academic and patent literature surveyed for best practices
- Develop processing methods with industrial guidance
- Produce baseline technical catalyst at targeted scale
2 – Technical Approach: Staged Scale Up

De-risks conversion technologies
• Enables projects to assess performance at increasing scales
• Go/No-Go decision points ensure performance targets are met at each scale
• Provides a baseline technical catalyst to accelerate commercialization when licensed to technology provider
3 – Impact: Bridging the Scale-Up Gap

**De-risking of catalyst development in BETOs core catalysis projects**

- **Reduces technology commercialization risk** by enabling engineering-scale evaluation of advanced catalyst materials
- **Facilitates manufacturing** hand-off to catalyst toller by utilizing industry standard processing steps
- **Improves commercialization potential** of catalysis technology IP packages

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**Limited to commercial catalysts**
4 – Progress and Outcomes: Equipment Selection

**Initial Material Targets**

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<th>Pt/TiO₂</th>
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**Process Requirements**

- Dry Mixing
- Wet Mixing
- Extrusion
- Drying
- Tumbling
- Calcination

**Upgrading C1 Building Blocks**

<table>
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<tr>
<th>Technical Body Requirements</th>
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<tr>
<td>Extrudate pellets</td>
</tr>
<tr>
<td>Alumina-free binder</td>
</tr>
<tr>
<td>Diameter: 1/16”</td>
</tr>
<tr>
<td>Surface Area: ca. 500 m²/g</td>
</tr>
<tr>
<td>Crush Strength: &gt; 13 N/mm</td>
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</table>

**Initial Scale:** 1 – 10 kg
4 – Progress and Outcomes: Equipment Selection

**Process Requirements**

(1 – 10 kg)

- Dry Mixing
- Wet Mixing
- Extrusion
- Drying
- Calcination
- Tumbling
- Impregnation

**Equipment Selection**

- High shear / Orbital Mixers
- 1” Screw Extruder
- Bucket/Cement Mixers
- Rotary and Muffle Furnaces
4 – Progress and Outcomes: Equipment Selection

Commissioned 1–10 kg scale catalyst manufacturing equipment

Dedicated in-house equipment for inert processing, thermal treatment, precipitation, physical forming

Ability to optimize translation from research catalyst to technical body

Transferable knowledge for more rapid and simplified contract manufacturing at relevant scales

1” Screw Extruder

High shear / Orbital Mixers

Bucket/Cement Mixers

Rotary and Muffle Furnaces
4 – Progress and Outcomes: Demonstration

**Synthesized 1 – 3 kg batches of TiO\(_2\) extrudate that met specifications of Catalytic Upgrading of Pyrolysis Products project**

<table>
<thead>
<tr>
<th>Technical Body Requirements</th>
<th>NREL Extrudate</th>
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<tr>
<td><strong>Pt/TiO(_2)</strong></td>
<td><strong>Physical Property</strong></td>
</tr>
<tr>
<td>Catalytic Upgrading of Pyrolysis Products</td>
<td><strong>NREL Extrudate</strong></td>
</tr>
<tr>
<td>Extrudate pellets</td>
<td><strong>TiO(_2) Content (%)</strong></td>
</tr>
<tr>
<td>Alumina-free binder</td>
<td><strong>Diameter (mm)</strong></td>
</tr>
<tr>
<td><strong>Diameter:</strong> 0.5 to 3 mm</td>
<td><em><em>Bulk Density</em> (kg/m(^3))</em>*</td>
</tr>
<tr>
<td><strong>Bulk Density:</strong> 600 – 1500</td>
<td><strong>Pore Volume (ml/g)</strong></td>
</tr>
<tr>
<td><strong>Pore Volume:</strong> 0.05 – 0.4</td>
<td><strong>BET Surface Area (m(^2)/g)</strong></td>
</tr>
<tr>
<td><strong>Surface Area:</strong> 20 – 50 m(^2)/g</td>
<td><strong>Crush Strength (N)</strong></td>
</tr>
<tr>
<td><strong>Crush Strength:</strong> 20 – 40 N/mm</td>
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</tbody>
</table>

- 1 mm, 1.6 mm, 3 mm pellets
- Optimized for commercial TiO\(_2\) powder and FSP-derived Pt/TiO\(_2\) nanopowders

Successfully met Go/No-Go Decision criteria of reproducibility (< 5% variation of any spec.)
Synthesized series of 3 TiO₂ extrudates with increasing macroporosity

Rapid synthesis and prototyping facilitates the systematic evaluation of the impact of technical body physical properties on performance
4 – Progress and Outcomes: Impact of Catalyst Forming

**Challenge:** Off-the-shelf HBEA extrudates reduced hydrocarbon productivity by ~50% compared to research powder in methanol to high octane gasoline (HOG) process

- Assess impact of binder in loss of performance

*Prepared HBEA extrudates with varying alumina content in binder (0 – 100%) to enable fundamental study on the impact binder chemistry on the HOG process*

<table>
<thead>
<tr>
<th>Binder</th>
<th>Zeolite:Binder (wt/wt)</th>
<th>Water Content (wt.% of total solids)</th>
<th>Organic Binder Content (wt.% of total solids)</th>
<th>Extrusion Pressure (psig)</th>
<th>Crush Strength of final product (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sipernat 22 LS DISPAL 25F4 Kaolin</td>
<td>70:30</td>
<td>46</td>
<td>0.5</td>
<td>70</td>
<td>11 ± 4</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>38</td>
<td>0.5</td>
<td>200</td>
<td>87 ± 33</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>40</td>
<td>1</td>
<td>150</td>
<td>4 ± 1</td>
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HBEA extrudates with meet the physico-chemical property requirements of Upgrading C1 Building Blocks project *demonstrating the production versatility of the scale-up capability*
4 – Progress and Outcomes: Impact of Catalyst Forming

**Challenge:** Off-the-shelf HBEA extrudates reduced hydrocarbon productivity by ~50% compared to research powder in methanol to high octane gasoline (HOG) process

- Assess impact of binder in loss of performance

HBEA extrudates with meet the physico-chemical property requirements of Upgrading C1 Building Blocks project **demonstrating the production versatility of the scale-up capability**
Flame-spray pyrolysis (FSP) for tunable Pt speciation

- Industrially deployed at MT/y scale
- One-step synthesis of active phase and support
- Tunable product slate in whole biomass pyrolysis vapor upgrading
Summary

Project Goal – Develop a **flexible, engineering-scale catalyst synthesis capability** to produce **scalable** and **cost effective** next-generation biomass conversion catalysts and mitigate commercialization risk by enabling **large-scale performance evaluation**

- **An industry guided** engineering-scale catalyst synthesis capability can significantly **reduce the economic investment and time** required to verify large-scale performance

- **Responsive engineering-scale catalyst design** enables the **fundamental evaluation** of technical catalyst properties and performance

- **Emerging scale-up methodologies** provide an opportunity for **scalable performance enhancement** over traditional methods
Acknowledgements

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**ANL**
Rongyue Wang  
Kris Pupek  
Joseph Libera

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Quad Chart Overview

Timeline
- Project Start: October 1, 2018
- Project End: September 30, 2021

<table>
<thead>
<tr>
<th>FY20</th>
<th>Active Project</th>
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<tr>
<td>DOE Funding</td>
<td>$352k $400k/y</td>
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</table>

Project Partners
- ANL (WBS 3.3.2.702)

Barriers addressed
- **Ct-G.** Decreasing the Time and cost to developing novel industrially relevant catalysts
- **ADO-D.** Technical Risk of Scaling: Operations must be scaled-up and verified at the pilot-scale

Project Goal
The goal of this project is to create a flexible, engineering-scale catalyst synthesis capability within BETO to develop the critical scientific basis of catalyst scale up required to translate emerging biomass conversion materials from the laboratory to commercial relevance by supporting engineering-scale performance evaluation of novel catalytic materials.

End of Project Milestone
The 3-year goal of this project is to demonstrate a mature technical catalyst development cycle (i.e., the translation of a laboratory-developed research catalyst to a production-ready technical catalyst with targeted physico-chemical properties) by preparing engineering-scale quantities of a 2nd generation technical catalyst for the Upgrading of C1 building blocks project.

Funding Mechanism
FY18 BETO AOP call.
Additional Slides
Publications, Patents, Presentations, Awards, and Commercialization

Papers
• Kumar, A.; Rongyue, W.; Pupek, K.; Libera, J.; Baddour, F. G.; “Synthesis of Tailored Pt/TiO$_2$ Catalysts for Selective Biomass Vapor Upgrading via a Scalable Flame Spray Pyrolysis Route” *In preparation*
• Kumar, A.; Van Allsburg, K. M.; Royappa, A.; Ruddy, D. A.; Baddour, F. G. “Single-Source Precursor Route to Phase-Pure $\alpha$-Molybdenum Carbide.” *In preparation.*
• Van Allsburg, K. M.; Kumar, A.; Baddour, F. G.” Carburization-Free Routes to Molybdenum Carbides with Stoichiometric Phase Selectivity.” *In preparation.*

Patents
• Baddour, F. G.; Kumar A.; Van Allsburg K. M.; Ruddy, D. A.; Habas, S. E. “Metal Carbides and Methods of Making the Same” Application No. 62/993,487

Presentations
• Baddour, F.G.; Johnson Matthey Face-to-Face Billingham, UK, March 2019.
• Baddour, F.G.; Catalyst Manufacturing Consortium, Rutgers University, New Brunswick, New Jersey October 2019.
• Baddour, F.G.; “Synthesis of Nanostructured Catalysts for the Conversion of Biomass to Renewable Fuels and Chemicals”, Boston Regional Inorganic Colloquium, Boston University, Boston, October 2019
Responses to Previous Reviewers’ Comments

• The project team should select 2-3 catalyst compositions which are of the highest interest to the bioconversion platform, understand the reactor design, determine the physical and chemical properties needed for the catalyst, and work with one or more catalyst manufacturers to define what needs to be done to achieve the scale-up goals.

  – This was the approach taken. Pt/TiO$_2$ was targeted for catalytic fast pyrolysis verification support. Reactor design/computational modeling were used to determine extrudate particle size (1 mm) that balanced pressure drop and on-stream time. Equipment was selected with industrial partner support.

  – HBEA was selected as a second target, with the impact of binder chemistry on the methanol to high-octane gasoline process. A systematic study on influence of binder alumina content in Cu-siting and performance is underway in collaboration with the Upgrading of C1 Building Blocks project.