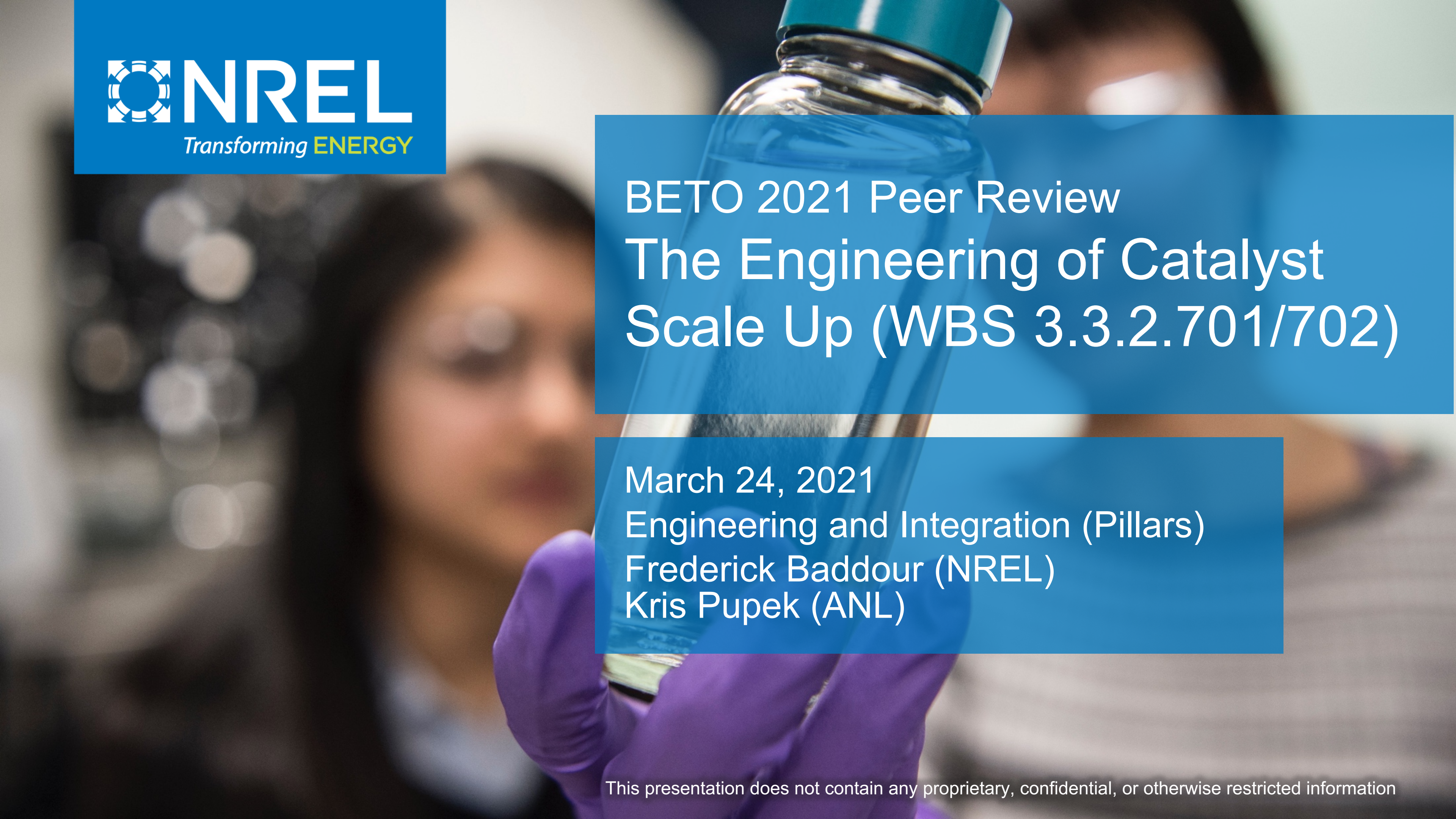


BETO 2021 Peer Review

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***

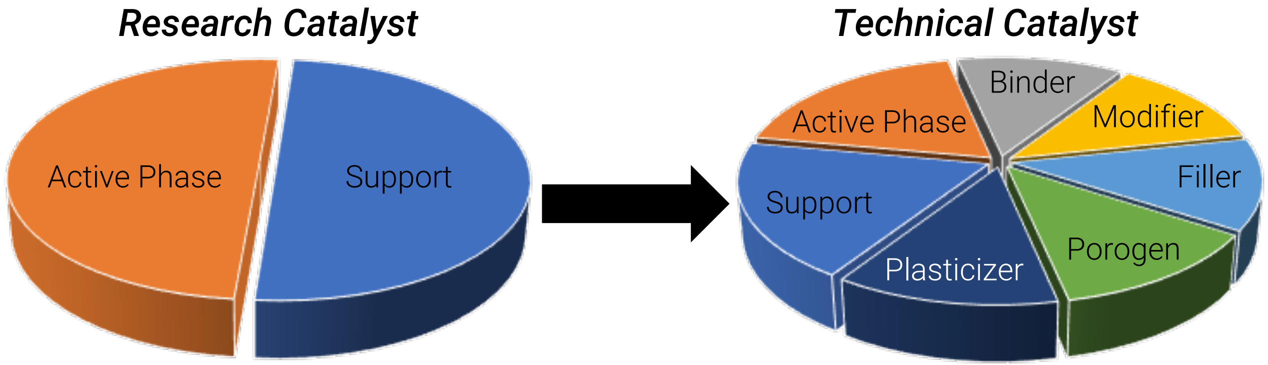
– ***Patented intellectual property*** and publications in ***peer-reviewed journals***

Project Overview

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:***

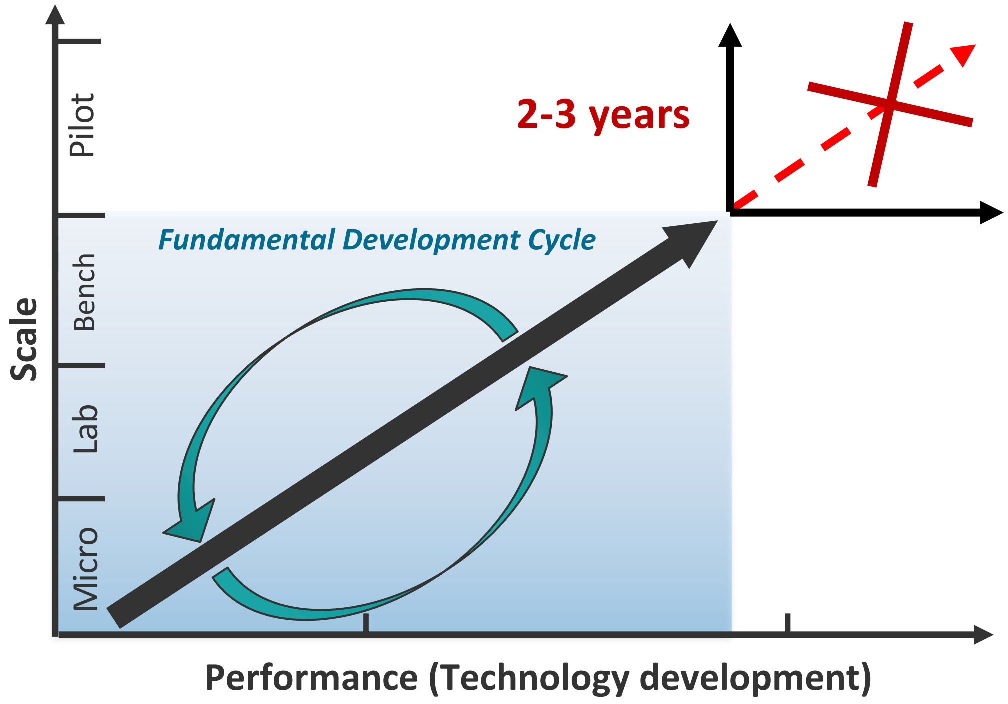
- Gram-to-kilo ***protocol adaptation***
- Determination of ***multi-component formulation***
- ***Shaping powders*** into reactor specific macroscopic forms



Translation of promising research catalysts to viable technical bodies is a non-trivial research challenge

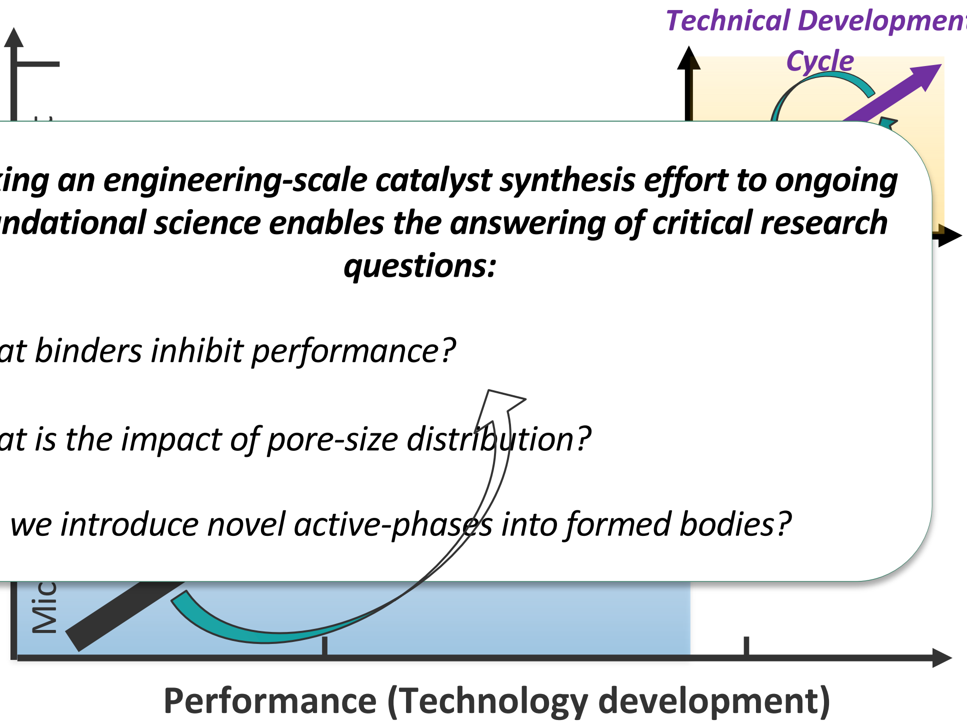
Overview: Coupling Technology Development and Scaling

Simultaneous technology development critical to hitting performance targets at larger scales



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-performance Cu
identified for FY18 tech

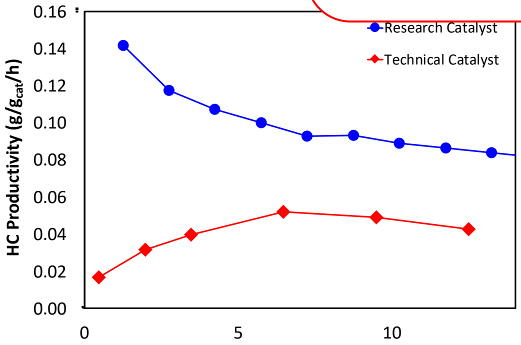
New Prep.

from lab scale

High Cost

Equipment too large for intermediate scale

Time, Cost, Performance, and <u>Value Proposition</u> Negatively Impacted



Requirements for Verification

- ≥10^5 increase in production from gram-scale to 100 kg
- Powder zeolite to formed extrudate

Performance impacted by available commercial extrudate formulation

Market Trends

Product
- 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

Feedstock
- Sustained low oil prices
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H_2
- Closing the carbon cycle

Capital
- Risk of greenfield investments
- Challenges and costs of biorefinery start-up
- Availability of depreciated and underutilized capital equipment

Social Responsibility
- Carbon intensity reduction
- Access to clean air and water
- Environmental equity

NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

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

NREL (3.3.2.701)	**ANL** (3.3.2.702)	Industrial Advisory Board
Frederick Baddour	*Kris Pupek*	*4+ Rotating Members*
• Catalyst Development • Technical Body Formulation • Physical Forming • Performance Evaluation	• Advanced Materials • Nanostructuring • AP and Support Integration • Advanced Characterization	• Equipment selection • Method identification • Review of best practices • Relevant targets

- ***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 **SDI**

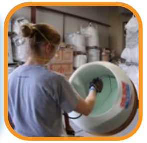
Advanced Synthesis and Characterization

Performance Evaluation

Theory

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

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

2 – Technical Approach: Building a Scale Up Capability

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*

CLARIANT
EVONIK Leading Beyond Chemistry
CABOT
Argonne NATIONAL LABORATORY
ExxonMobil
Pacific Northwest NATIONAL LABORATORY
INL Idaho National Laboratory
OAK RIDGE National Laboratory
Celanese

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

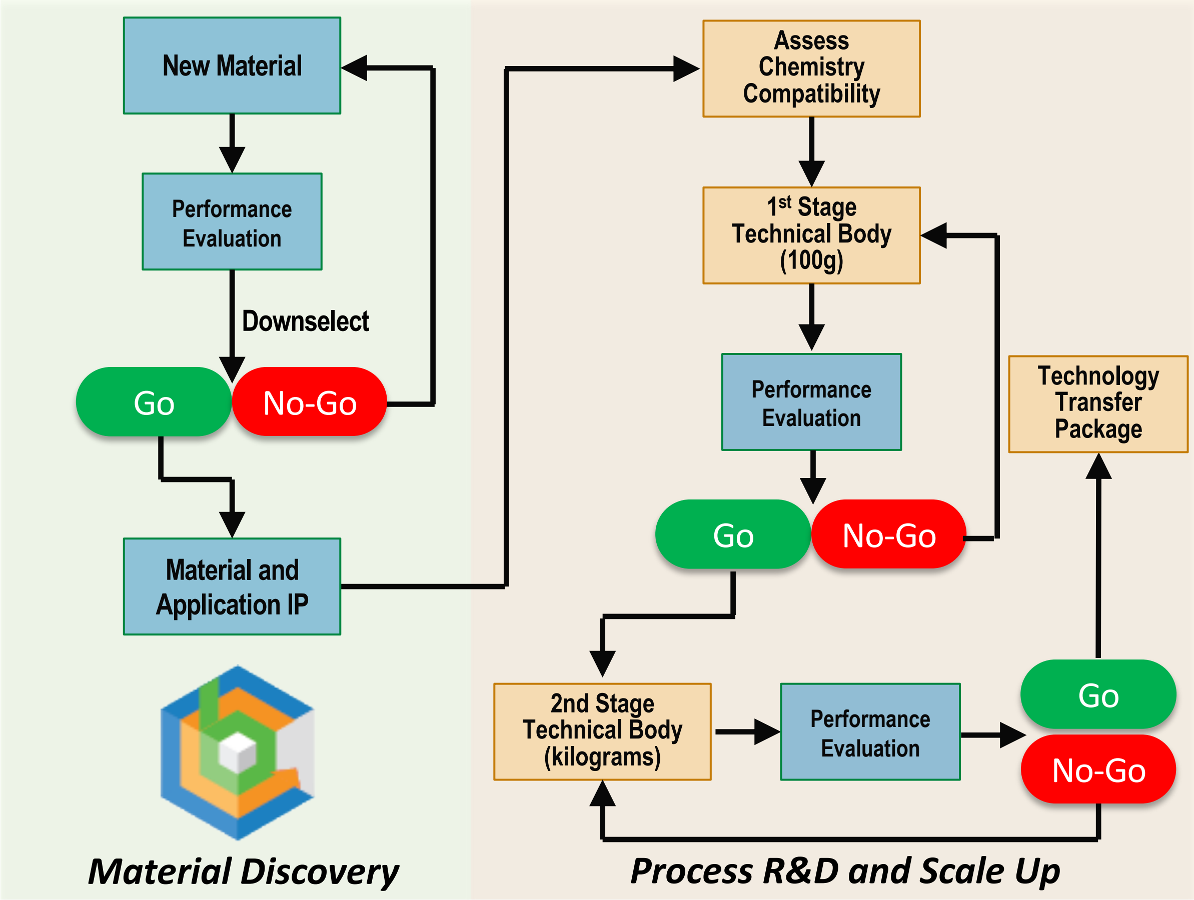
Produce 1st–Gen. Scaled Catalyst

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

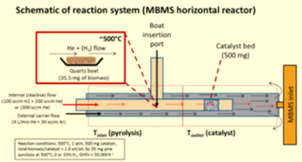


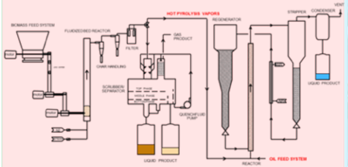
<u>De-risks conversion technologies</u>

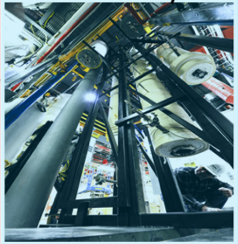
- Enables projects to ***assess performance at increasing scales***
- Go/No-Go decision points ensure performance targets are met at each scale
- Provides a ***baseline technical catalyst*** to accelerate commercialization when licensed to technology provider

3 – Impact: Bridging the Scale-Up Gap

	Microscale Reactor	Bench-Scale Fluid Bed Reactor	Large Bench-Scale DCR System	Pilot-Scale System
Catalyst	1g	500g	2.0kg	100kg
Biomass	25 mg/run	0.5kg/h	3kg/h	30kg/h







Microscale Reactor
- *In-, ex-situ* CFP
- Batch experiments
- Catalyst screening

Bench-Scale Fluid Bed Reactor
- *In-, ex-situ* CFP
- Continuous experiments
- Catalyst screening

Large Bench-Scale DCR System
- *In-, ex-situ* CFP
- Continuous experiments
- Catalyst screening
- Catalyst regeneration
- Hot gas filtration
- Co-processing

Pilot-Scale System
- *In-, ex-situ* CFP
- Continuous experiments
- Catalyst regeneration
- Catalyst screening

Limited to commercial catalysts

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

4 – Progress and Outcomes: Equipment Selection

Initial Material Targets

Pt/TiO_2
Upgrading C1 Building Blocks
<u>Technical Body Requirements</u> *Extrudate pellets* *Alumina-free binder* *Diameter:* 1/16” *Surface Area*: ca. 500 m^2/g *Crush Strength*: > 13 N/mm

Process Requirements

Dry Mixing

Wet Mixing

Extrusion

Drying

Tumbling

Calcination

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

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

High shear / Orbital Mixers

1” Screw Extruder

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

Pt/TiO_2

Catalytic Upgrading of Pyrolysis Products

Technical Body Requirements

Extrudate pellets ✓
Alumina-free binder ✓
Diameter: 0.5 to 3 mm ✓
Bulk Density: 600 – 1500 ✓
Pore Volume: 0.05 – 0.4 ✓
Surface Area: 20 – 50 m^2/g ✓
Crush Strength: 20 – 40 N/mm ✓

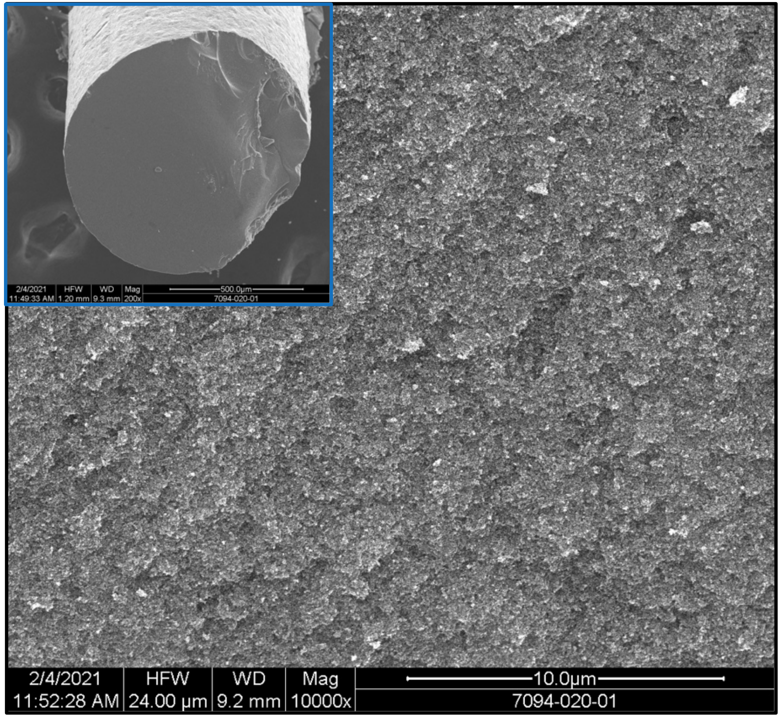
Physical Property	NREL Extrudate
TiO_2 Content (%)	> 99
Diameter (mm)	1.6
Bulk Density* (kg/m^3)	761
Pore Volume (ml/g)	0.34
BET Surface Area (m^2/g)	50
Crush Strength (N)	47 $\pm$ 4

- 1 mm, 1.6 mm, 3 mm pellets
- Optimized for commercial TiO_2 powder and FSP-derived Pt/TiO_2 nanopowders

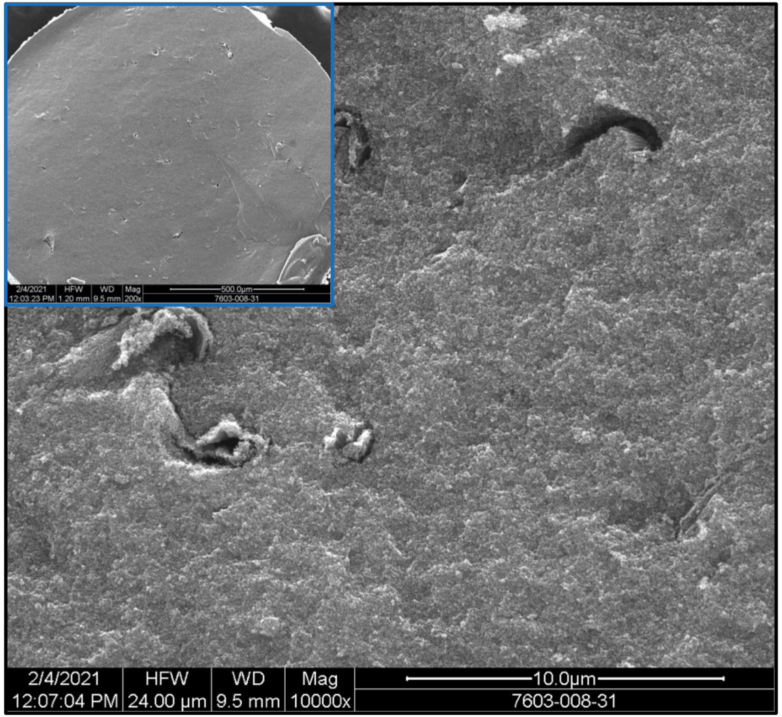
Successfully met Go/No-Go Decision criteria of reproducibility (< 5% variation of any spec.)

4 – Progress and Outcomes: Porosity Control

Synthesized series of 3 TiO_2 extrudates with increasing macroporosity

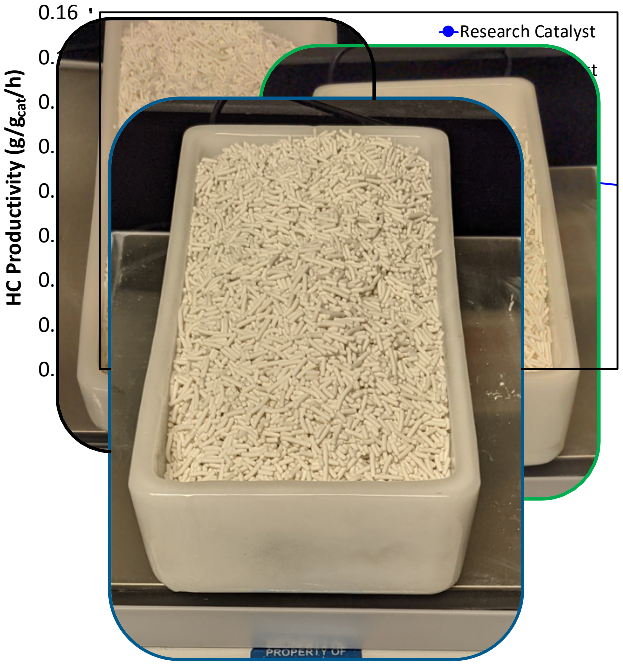


porogen



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

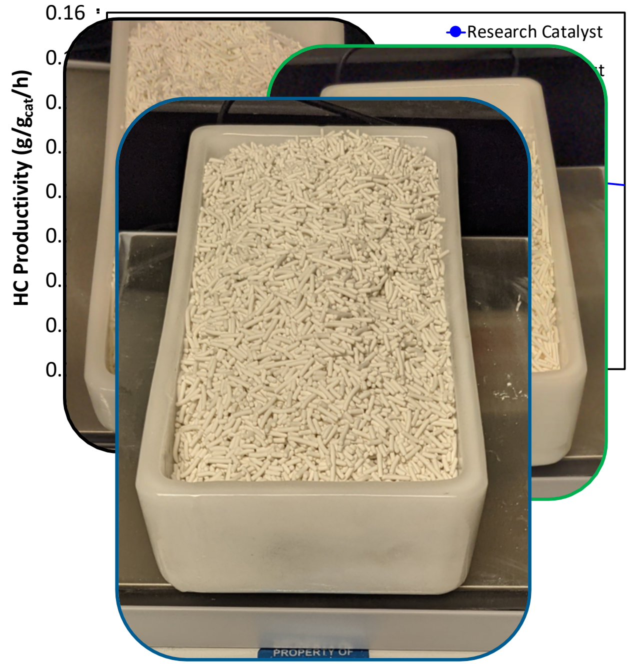
- Assess impact of binder in loss of performance

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

Binder	Zeolite:Binder (wt/wt)	Water Content (wt.% of total solids)	Organic Binder Content (wt.% of total solids)	Extrusion Pressure (psig)	Crush Strength of final product (N)
Sipernat 22 LS	70:30	46	0.5	70	11 ± 4
DISPAL 25F4	70:30	38	0.5	200	87 ± 33
Kaolin	70:30	40	1	150	4 ± 1

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



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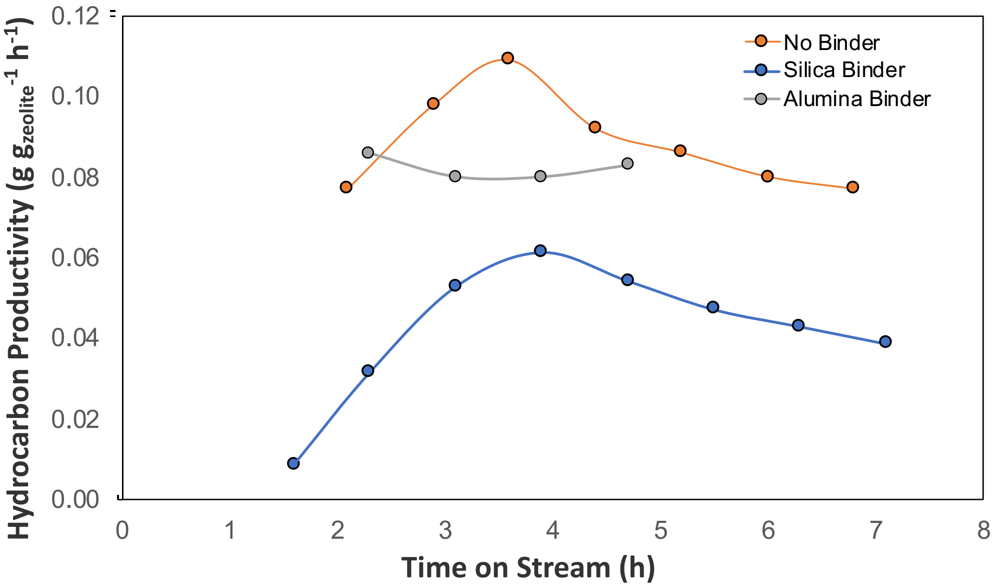
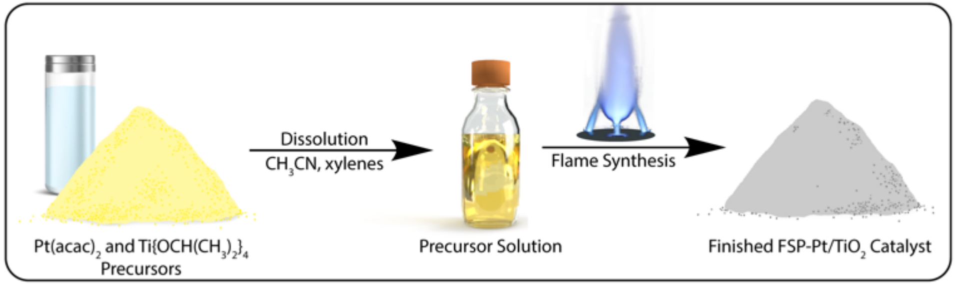


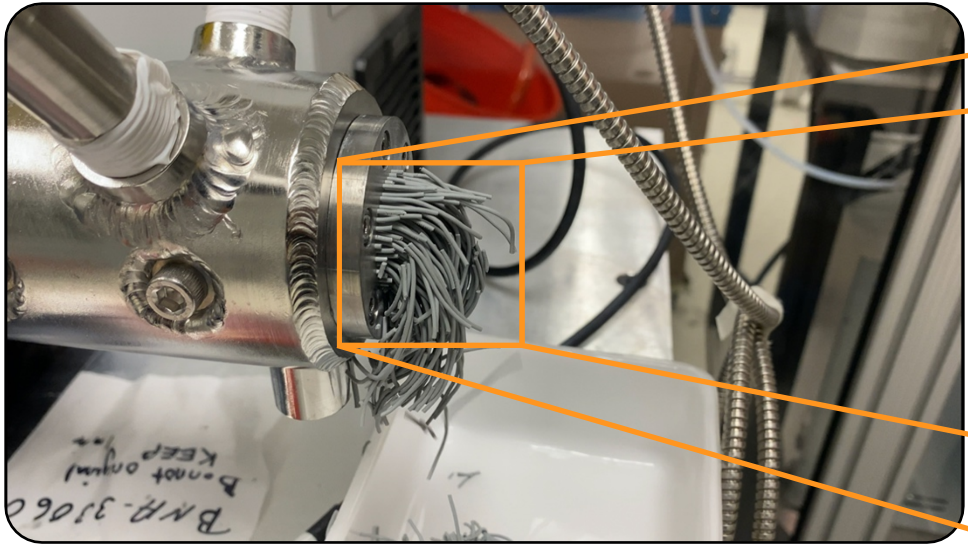
HBEA extrudates with meet the physico-chemical property requirements of Upgrading C1 Building Blocks project ***demonstrating the production versatility of the scale-up capability***

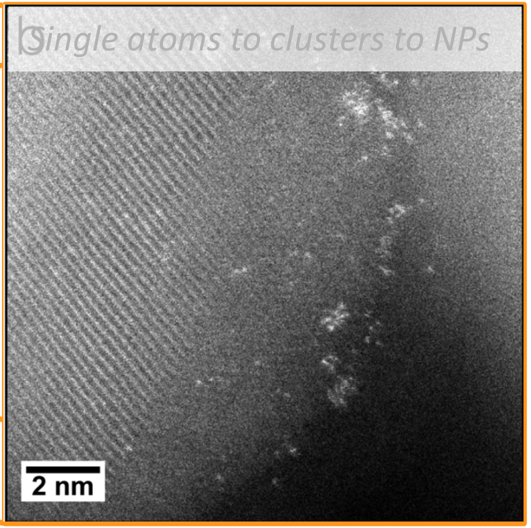
4 – Progress and Outcomes: Emerging Methodologies

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

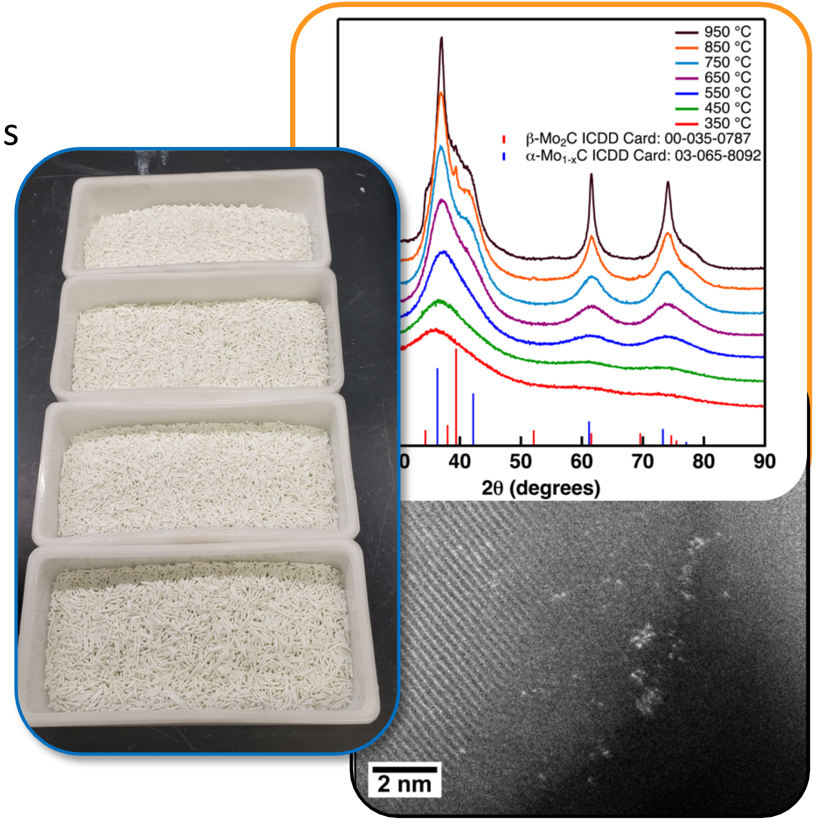




Summary

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



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Quad Chart Overview

Timeline

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

	FY20	Active Project
DOE Funding	$352k	$400k/y

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 α-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.; BETO 2019 Peer Review, Denver, CO, March **2019.**
- 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