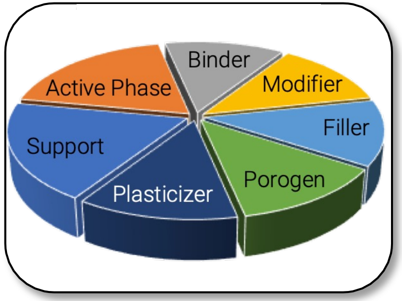
ChemCatBio
Chemical Catalysis for Bioenergy

Perspectives on Engineered Catalyst Design and Forming

Bruce Adkins – Oak Ridge National Laboratory
Frederick Baddour – National Renewable Energy Laboratory
Matthew Greaney – Clariant
June 14, 2023

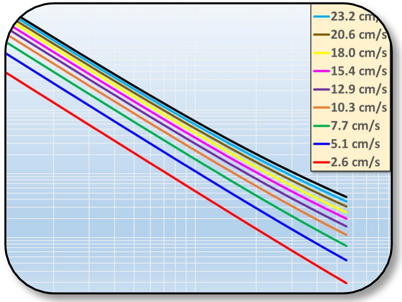
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Run of Show

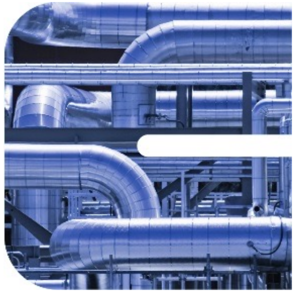


Defining the Catalyst

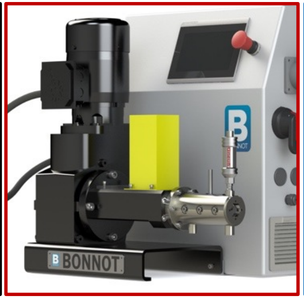
An FCC Case Study



Considerations for Technology Selection & Modeling

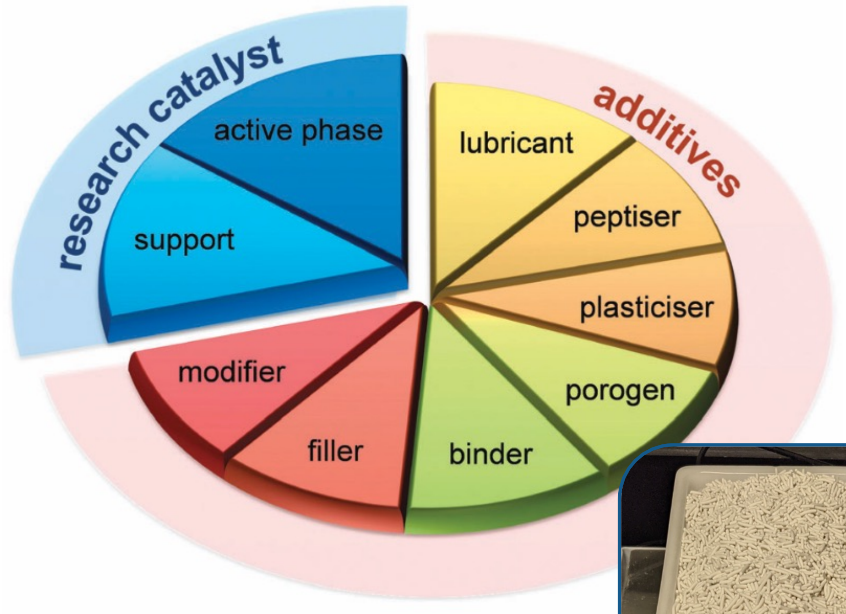


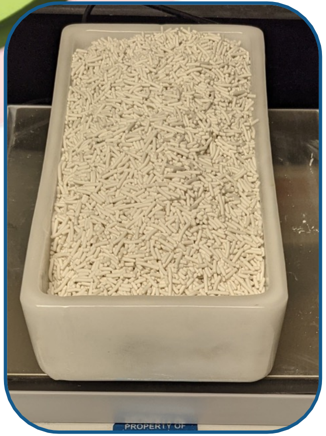
An Industrial Perspective



Engineered Catalyst Development in ChemCatBio

The *Engineered* Catalyst





Mitchell et al., Chem. Soc. Rev., 2013, 42, 6094.

An engineered catalyst is a multicomponent catalyst formulation that possesses additives and structural elements required for operation in a commercial reactor

- Physical: mass/heat transfer
- Chemical: functionality
- Mechanical: strength, attrition resistance

- Simplified requirements for commercialization upon successful identification of promising research catalyst candidates
  - Translation of synthesis methods from bench-scale to multi-ton manufacture
  - Identification of appropriate formulation (left)
  - Powder shaping to macroscopic forms

Catalytic Cracking: The Modern FCC (up to 200 kbpd)

A Technology Race

1933

Houdry Process

- Fixed bed reactors
- Swing regeneration
- Pelleted clay catalyst

1941

Thermofor Cat Cracking (TCC)

- Moving bed reactor
- Continuous flow of catalyst via bucket elevators
- Pelleted SiAl catalyst

1942

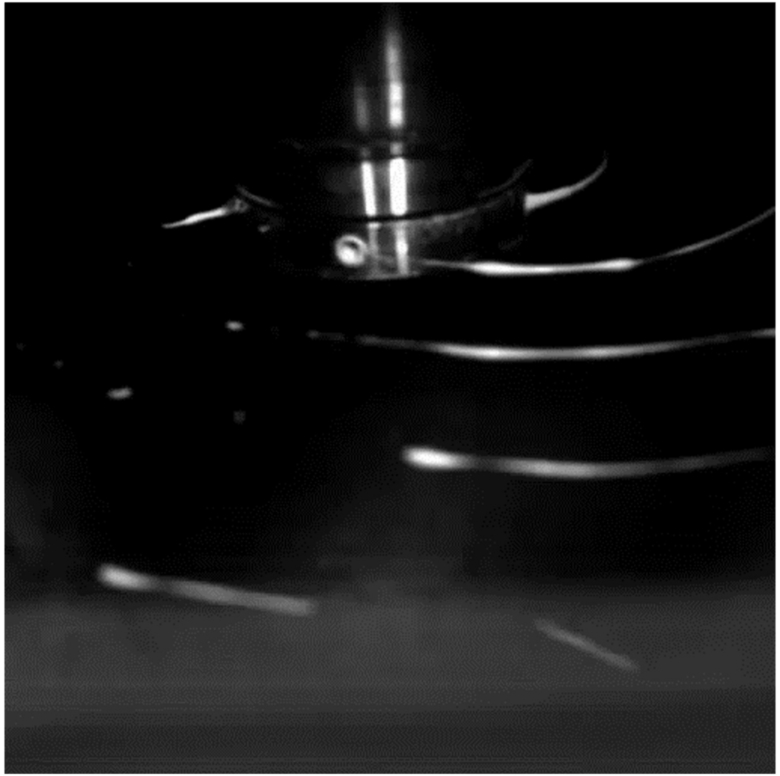
Fluid Cat Cracking (FCC)

- CRA consortium
- Fluidizable catalyst particles (~100 um)
    - Crushed catalyst
- **1946:** Spray drying
- **1960:** Zeolites
- **Today:** ~400 units WW, > 10 Mbpd

Co-development of process and catalyst

FCC Catalyst Market (~$3 B) Requires Large Spraydryers

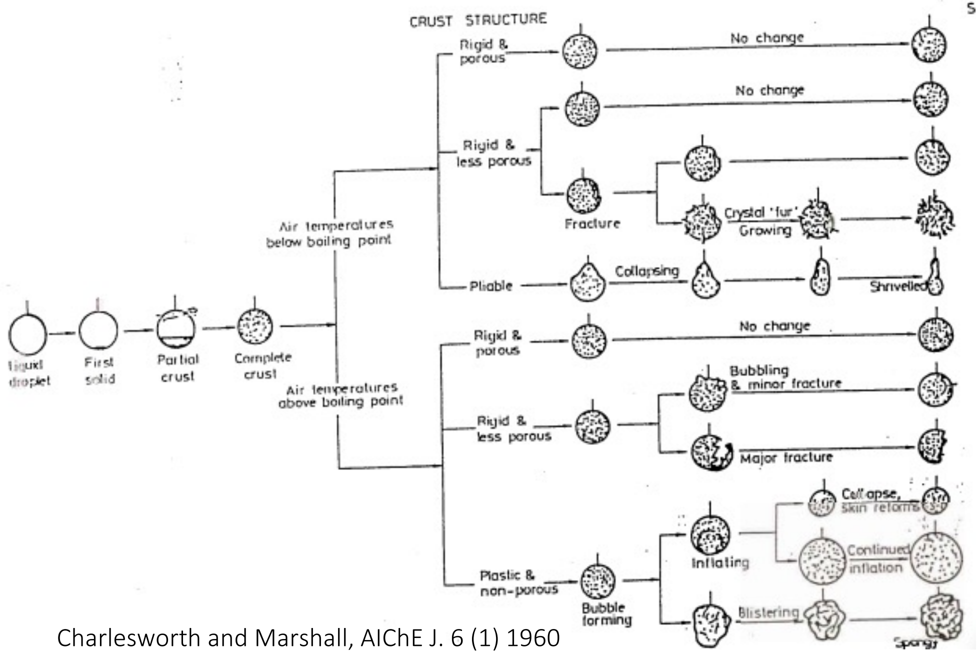
The FCC Catalyst: A Complex Design Challenge



B. Adkins, S. Garner, *"Atomizer Wheel with Improved Nozzle for Rotary Atomizers and Method of Obtaining Microspherical Solid Particles",* US Patent 6,631,851, Oct 2003.

Non-spherical particles WILL BECOME SPHERICAL in the unit: FINES LOSSES, STACK OPACITY, etc

New FCC catalysts can require lots of spray drying R&D to achieve physical property targets at commercial scale



Charlesworth and Marshall, AIChE J. 6 (1) 1960

FCC Catalyst Architecture: Heavily Researched

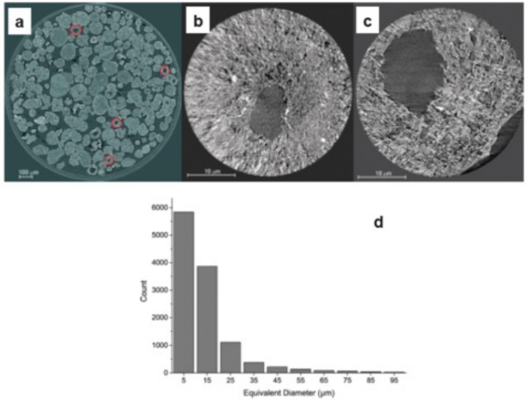


Fig. 24 (a) Single slice of the X-ray micro-tomogram of E-cat particles inside a polyimide tube, which is the circle around the image. The E-cat catalyst particles have a range of shapes and sizes, and some are hollow. Some of them are indicated by the red circles in the image; (b and c) 2D transmission X-ray microscopy images of sections of two E-cat particles showing different sizes of internal voids, which are the dark colored regions in the images; and (d) equivalent diameter of internal voids in the set of E-cat catalyst particles as investigated with X-ray micro-tomography. (Reproduced with permission from ref. 172, Copyright Wiley-VCH, 2014).

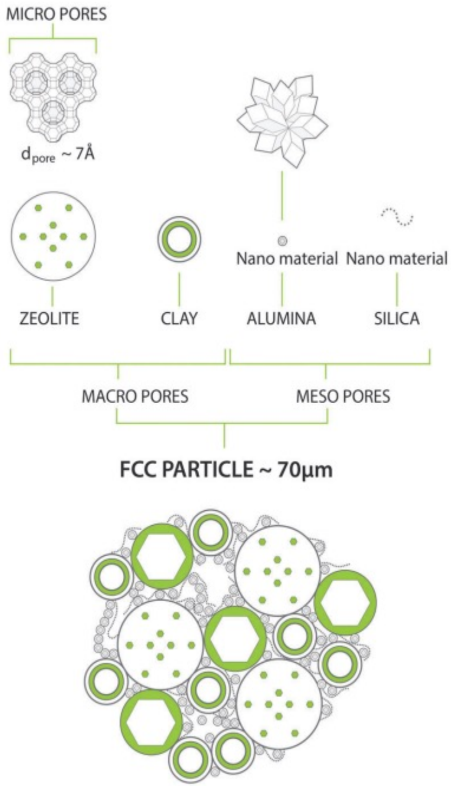


Fig. 7 Typical chemical and structural composition of a FCC particle. Artwork by RSK Communication.

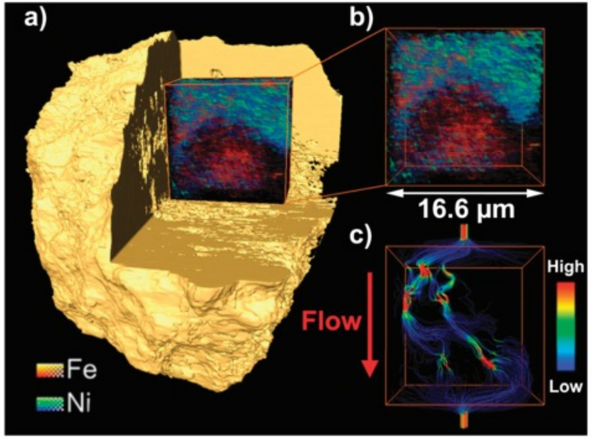


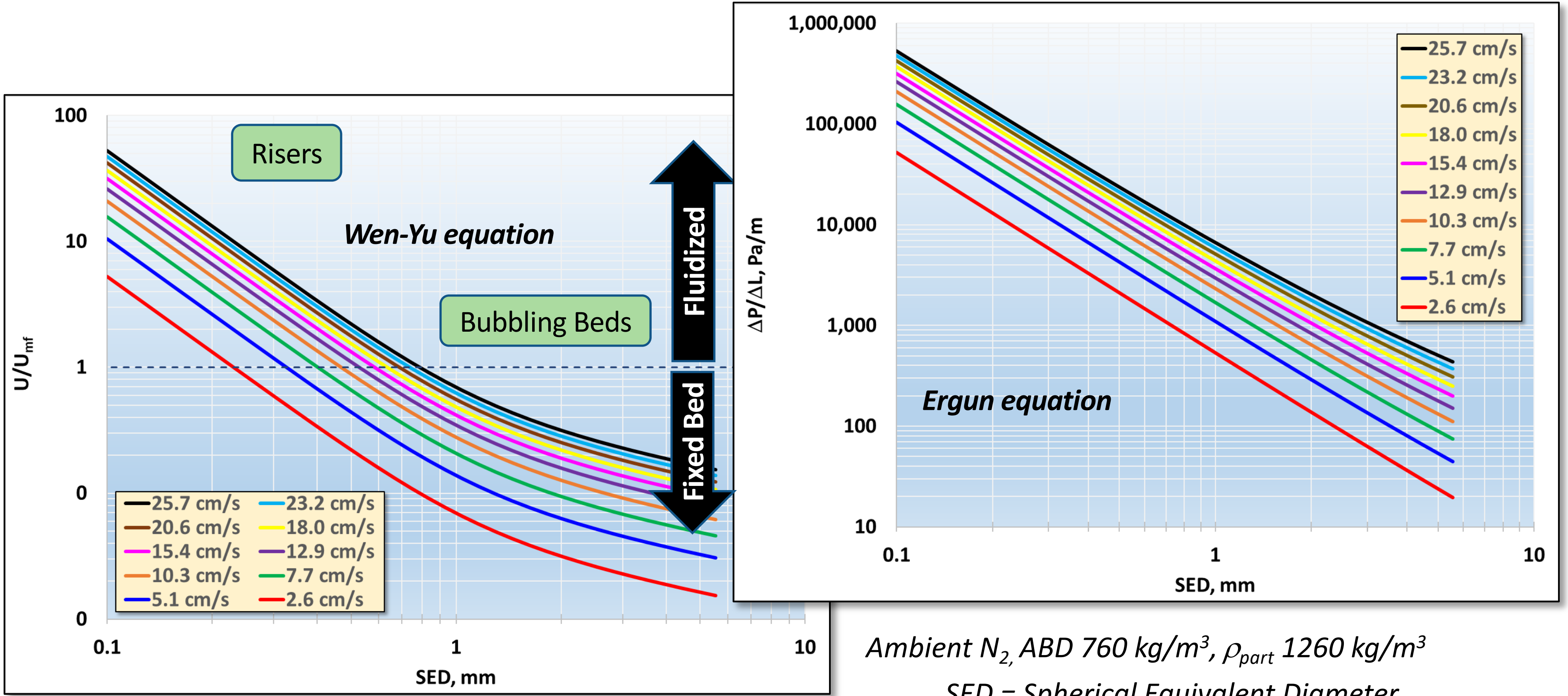
Fig. 23 X-ray nanotomography study of an E-cat catalyst particle, revealing the relative spatial distributions of Ni and Fe and their effect on the macropore structure and accessibility. A sub-volume of 16.6 × 16.6 × 10 μm^3 was selected (b) out of the entire catalyst particle of 44.8 × 52.7 × 51.2 μm^3 in size (a), including the relative Fe and Ni distributions. Permeability calculation was applied on this sub-volume (c). Mass transport through the sub-volume along the selected axis (red arrow) is visualized using the velocity field of the fluid. The streamlines indicate the magnitude of the velocity field where red represents the highest velocity (*i.e.*, where the pore space constriction is the largest) and blue indicates the lowest velocity. (Reproduced with permission from ref. 170, Copyright American Chemical Society, 2015).

Vogt and Weckhuysen, **"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"**, Chem. Soc. Rev., 2015, 44, 7342

Important Considerations for Technology Selection

- Fluid-solid hydrodynamics
  - Set by reactor type (fixed bed, moving bed, fluid bed, riser)
- Intrapellet mass transfer constraints
  - A relative term! Fast vs slow reactions
    - Ratio of diffusion & reaction rates and the *Effectiveness Factor*
    - Fast example: cracking at high temperature → FCC catalyst @ SCT
    - Slow example: resid HDS, WHSV ~ 0.5
- Deactivation rate and regeneration requirements
  - Is the reaction endothermic and powered by coke burn, like FCC?
- Thermal considerations
  - Heat integration
  - Intrapellet heat transfer for highly endothermic/exothermic reactions
  - Frequency and severity of coke oxidation regenerations
  - Fast/large temperature swings (like FCC process)

Fluid-Solid Hydrodynamics: ΔP and U/U_{mf}



Ambient N_2, ABD 760 kg/m³, ρ_{part} 1260 kg/m³

SED = Spherical Equivalent Diameter

Effectiveness Factor η

MATHEMATICAL TREATMENTS OF COUPLED DIFFUSION AND REACTION IN NON-DEACTIVATING AND DEACTIVATING HETEROGENEOUS CATALYSTS

SEPTEMBER 1, 1986

Bruce D. Adkins

Beyond the effectiveness factor: Multi-step reactions with intraparticle diffusion limitations

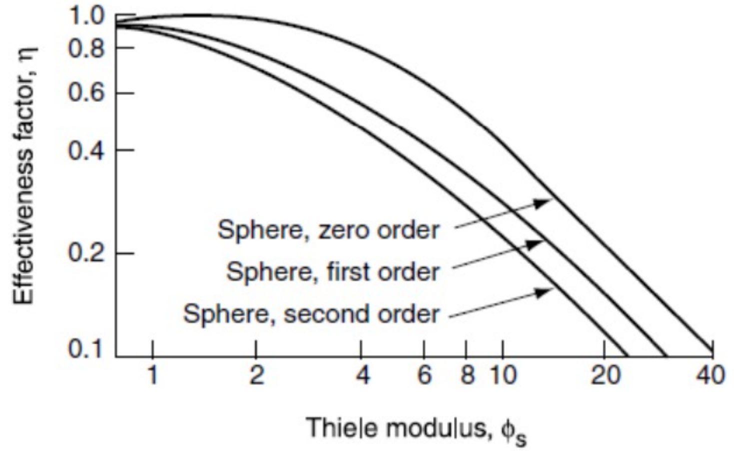
Aaron M. Lattanzi[a,1,*], M. Brennan Pecha[a,1], Vivek S. Bharadwaj[a], Peter N. Ciesielski[a]

[a]*National Renewable Energy Laboratory, Golden, CO, USA*

Preprint submitted to Chemical Engineering Journal *June 25, 2019*

For complex reaction networks, analytical expressions become intractable, in which case combined pellet-reactor modeling can step in!

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As},\ T_s}$$



Zero order $\phi_{s0} = R\sqrt{k_0'' S_a \rho_c / D_e C_{A0}} = R\sqrt{k_0 / D_e C_{A0}}$

First order $\phi_{s1} = R\sqrt{k_1'' S_a \rho_c / D_e} = R\sqrt{k_1 / D_e}$

Second order $\phi_{s2} = R\sqrt{k_2'' S_a \rho_c C_{A0} / D_e} = R\sqrt{k_2 C_{A0} / D_e}$

Coupling Computational Modeling and Experimental Design

Consortium for Computational Physics and Chemistry

The Consortium for Computational Physics and Chemistry (CCPC) is a Bioenergy Technologies Office (BETO) consortium composed of six national labs ***applying multi-scale computational science to enable and accelerate the bioenergy economy.***

CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
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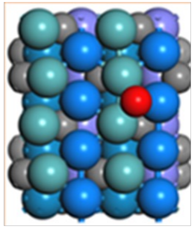
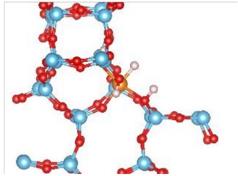
Pacific Northwest National Laboratory · Oak Ridge National Laboratory · National Energy Technology Laboratory · NREL National Renewable Energy Laboratory · Argonne National Laboratory · INL Idaho National Laboratory

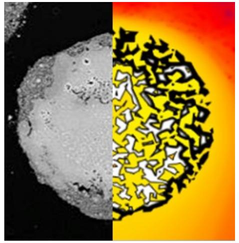
A multi-scale problem… A multi-lab solution

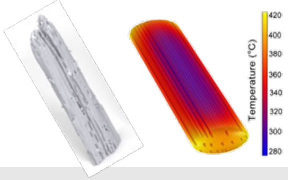
Atomic Scale



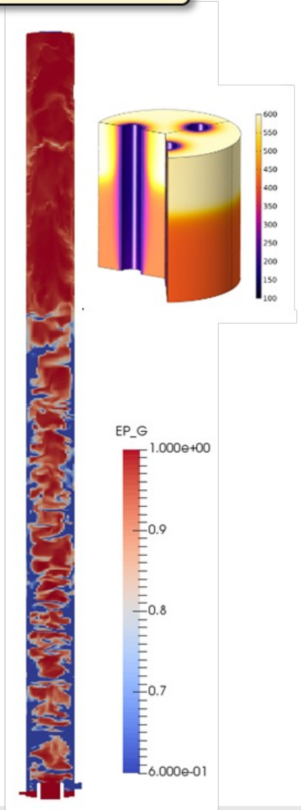


Meso Scale

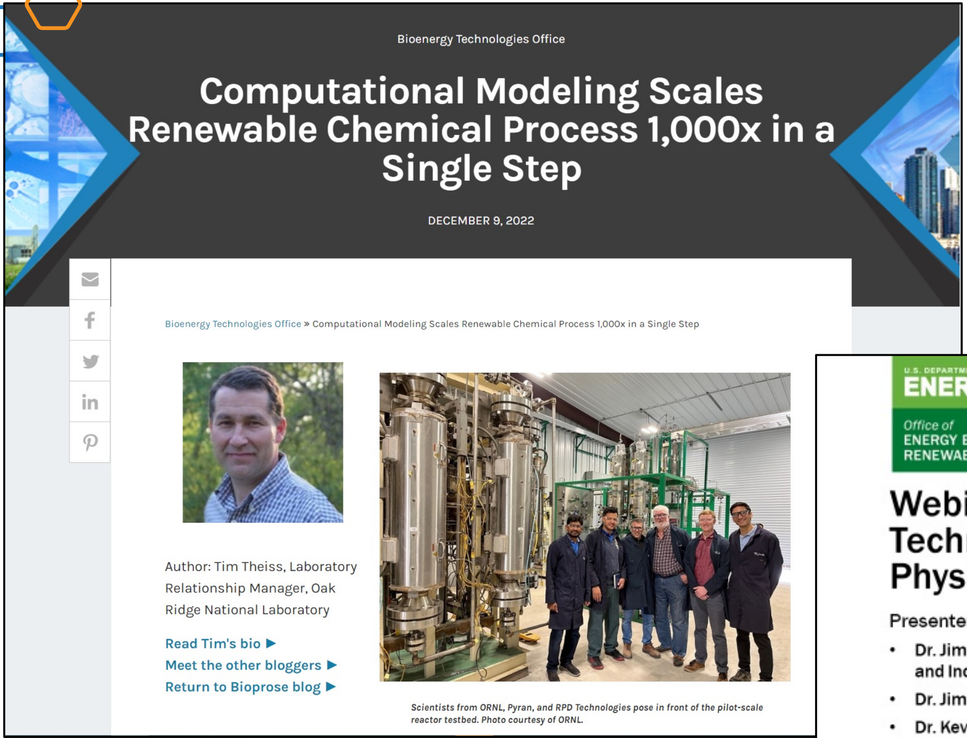




Reactor Scale



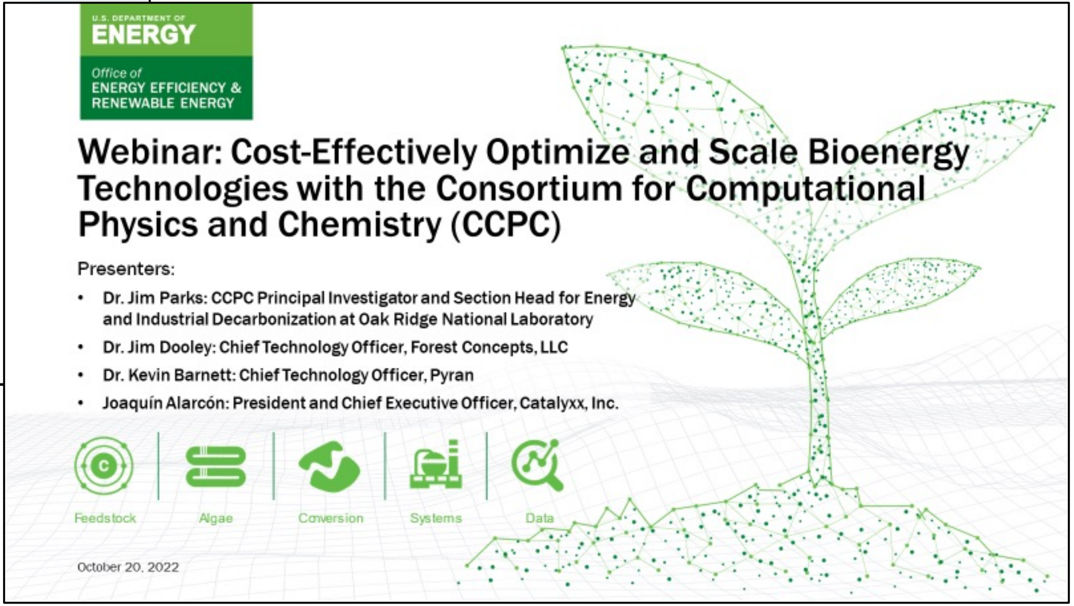
CCPC DFO Program 2021-2022 (Direct Funding Opportunity)



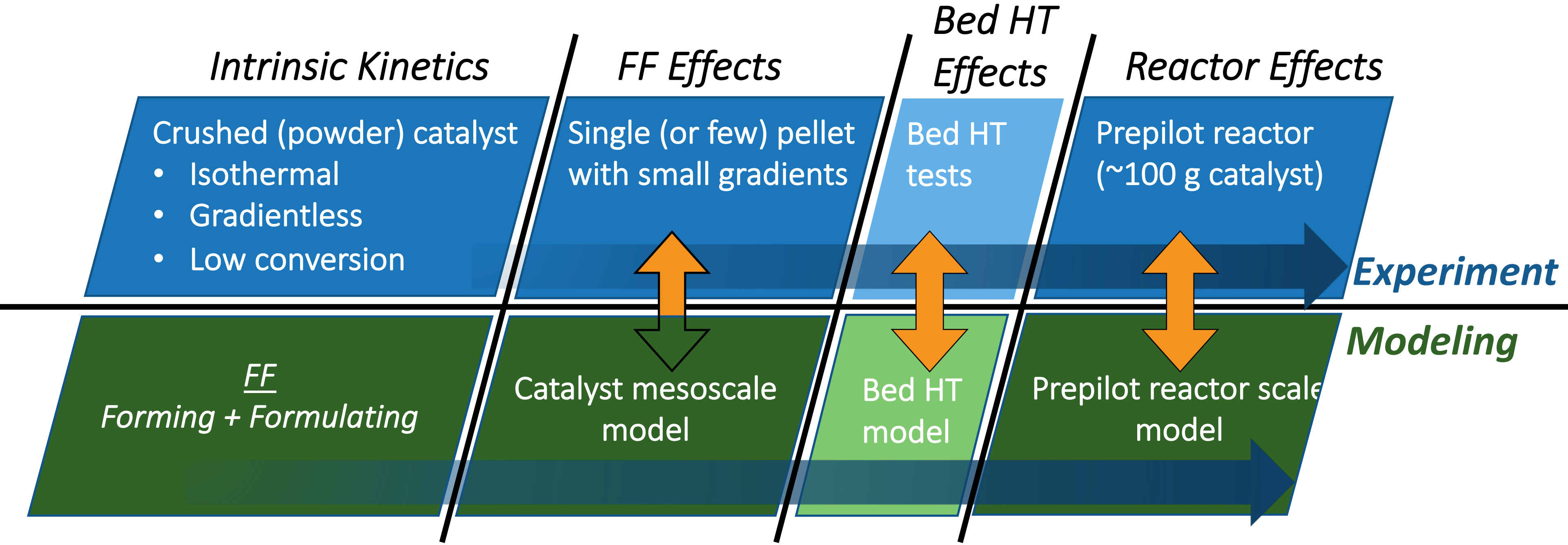
Packed bed deployment

Pyran: 1,5 PDO from furfural

Catalyxx: higher alcohols from EtOH (Guerbet)

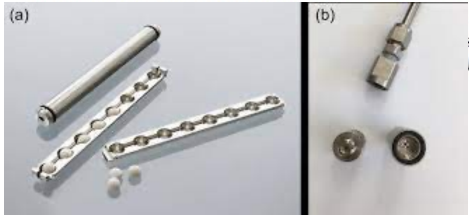


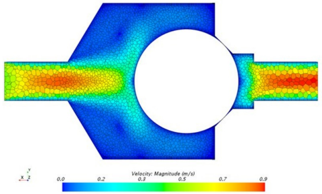
Integrated Computational/Experimental Approach



Characterization of a modular Temkin reactor with experiments and computational fluid dynamics simulations

Gregor D. Wehinger[a,*], Bjarne Kreitz[a], Anton Nagy[b], Thomas Turek[a]





A small, well-mixed reactor for high throughput study of commercial catalyst pills

Edward M. Calverley[a,*], Edward L. Lee[b], De-Wei Yin[a], Thomas J. Parsons[c]

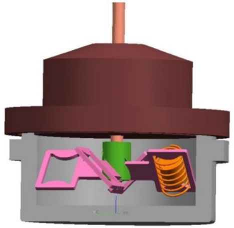
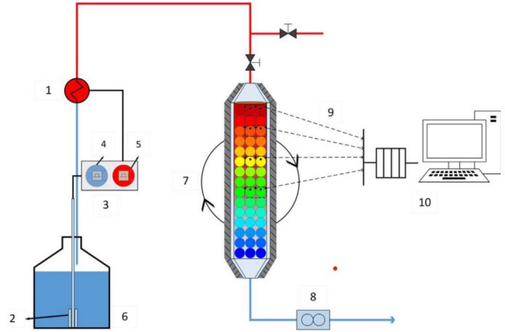


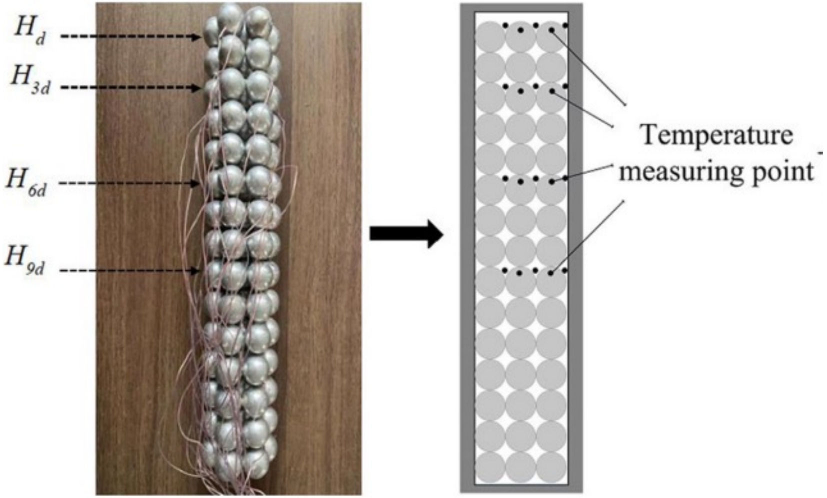
Fig. 5. Schematic of the CSTR for whole catalyst pills.

Chemical Engineering Science 151 (2016) 130–138

Heat transfer characteristics of mixed convection in packed beds

Yuelong Qu[a,b], Liang Wang[a,b,c], Xipeng Lin[a,c], Haoshu Ling[a,c], Yakai Bai[a,c], Shuang Zhang[a,c], Haisheng Chen[a,b,c,*]



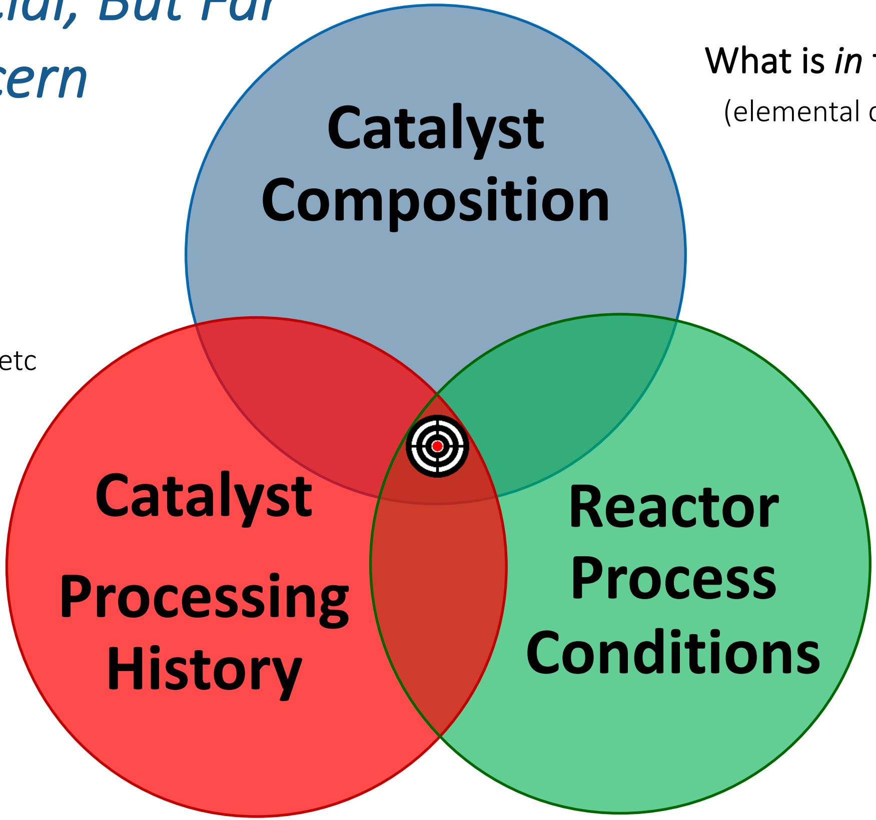


Engineered Catalysts: Considering Shape, Size, and Processing

Composition is Crucial, But Far From the Only Concern

What is *in* the catalyst

(elemental composition)



How it is put together

- Mixing, impregnation, precipitation, etc
- Additives, lubricants, burn-outs, etc
- Forming, shaping, sizing
- Thermal treatments (calcination)

How it is utilized

- reactor type
- reactor scale, dimensions, etc
- temperature, pressure, WHSV
- feed, poisons, etc
- disruptions or runaway potential
- pressure drop (DP, ΔP…)

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Considering Catalyst Form Factors

1. Reactor scale
   - Catalyst loading: need for efficient packing, mechanical strength to prevent attrition
   - Pressure drop: need for uniform flow, avoidance of "hot spots", reduced energy consumption
   - Thermal profile: endo *vs* exo thermic processes, heat management, thermal conductivity

2. Reactor type
   - Fixed bed, fluidized bed, moving bed: can dictate shape, size, & mechanical property needs

3. Phases of matter present
   - Single or multiphase systems: feed, intermediates, products
   - Traditionally, gas phase is most common, but not necessarily for newer trends & technologies

4. Practicality & existing deployed capital assets
   - Economic viability or production
   - Scale & throughput

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Clariant Catalysts: Covering a Wide Range of Applications




CHEMICALS

- Ammonia
- Methanol
- Sour Gas Shift
- Synthetic natural gas
- GTL/Fischer-Tropsch
- Fuel cells
- Oxidation
- Hydrogenation
- Bio-based feedstocks
- Fine chemicals

PETROCHEMICALS

- Steam crackers
- Olefin purification
- Ethylene derivatives
- Styrene & BTX
- On-purpose propylene
- Polypropylene

REFINERY / FUELS

- Gasoline isomerization
- Gasoline from olefins
- Hydrogen plants
- Diesel from olefins
- Diesel dewaxing
- Fuels upgrading
- Fuels from alternative feedstocks

EMISSION CONTROL

- Industrial off-gas treatment
- Exhaust gas treatment for stationary engines
- Zeolite powders for diesel exhaust applications

CUSTOM CATALYSTS tailor-made for specified applications

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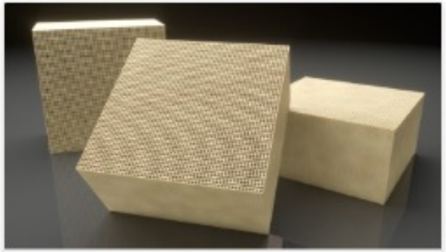
Clariant Catalysts: Covering a Wide Range of Applications

Dehydrogenation

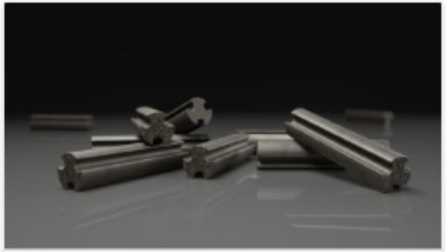


Emission Control, Oxidation & Zeolites

Ethylene & Derivatives

Styrene & MTP

Fuels



Hydrogenation & Custom Catalysts

Polypropylene

SynChem

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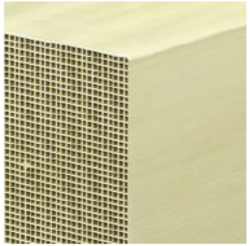
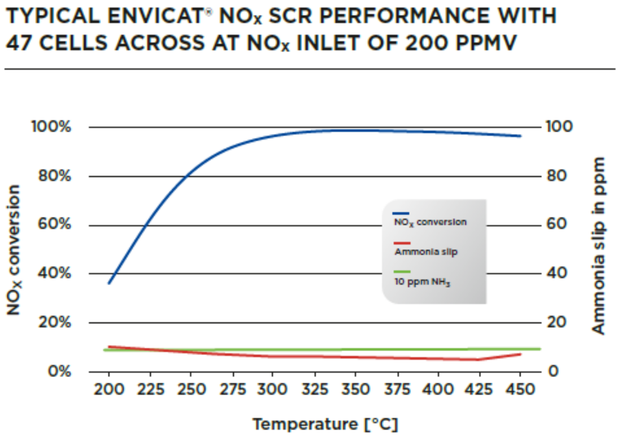
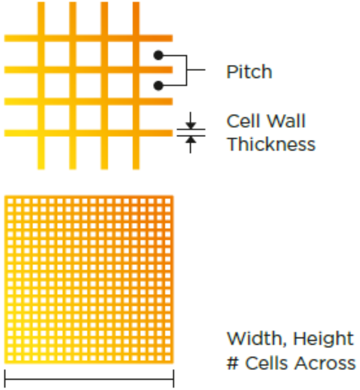
Examples: De-NO_x SCR Using a Wash-Coated Monolith







- Fixed bed
- High WHSV
- No recycle

➢ Honeycomb is extruded & calcined

➢ Active metals are wash-coated

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Examples: Vanadium Phosphates for Maleic Anhydride Production

SYNDANE® LA

Available in different ring sizes - SynDane 3102 LA and SynDane 3122 LA

SYNDANE® 3142 LA

New SynDane shape reduces pressure drop over the catalyst bed

TECHNICAL SPECIFICATIONS

SYNDANE® 3102 LA

Small catalyst rings for short reactor tubes

SYNDANE® 3122 LA

Bigger catalyst rings suitable for wide range of process conditions

SYNDANE® 3142 LA

Proprietary catalyst shape for long reactor tubes with low pressure drop

COMPOSITION SYNDANE® LA SERIES

- Vanadium phosphorus mixed oxide
- Vanadium content > 27 wt %
- Pre-activated
- Specific promoters to decrease by-product formation
- Thermal stability up to approx. 500°C

- Fixed bed
- Thousands of small reactor tubes
- Sensitive to WHSV
- Critical need for thermal management

➢ Shaped catalyst is extruded & calcined

➢ Specific shape is dictated by reactor

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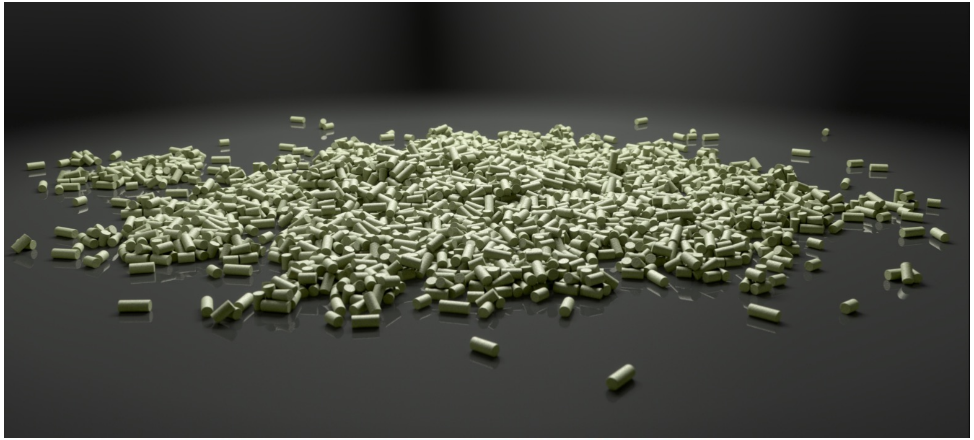
Examples: CrO_x/Al_2O_3 Dehydrogenation Catalyst



- Fixed bed
- Large single train reactors
- >10,000 tons produced/yr
- >4 year catalyst operating life

➢ Al_2O_3 carrier is produced by multi-step process
  - ➢ Forming, extruding calcining & steaming are critical
  - ➢ Texture required

➢ Active components impregnated, but carrier physical properties are key to long-term stability & performance

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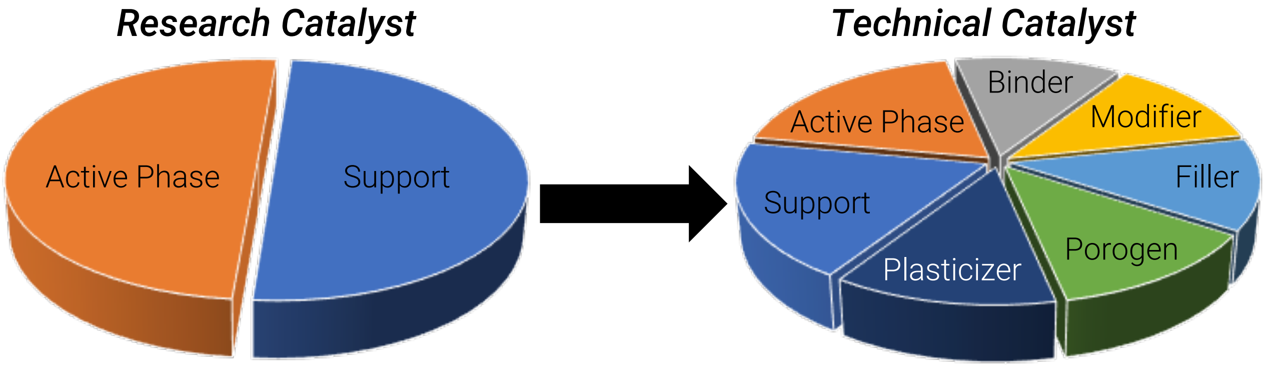
CCB: Approach to Engineered Catalyst Development

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

CCB: Building an Engineered Catalyst 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. Eng. Catalyst

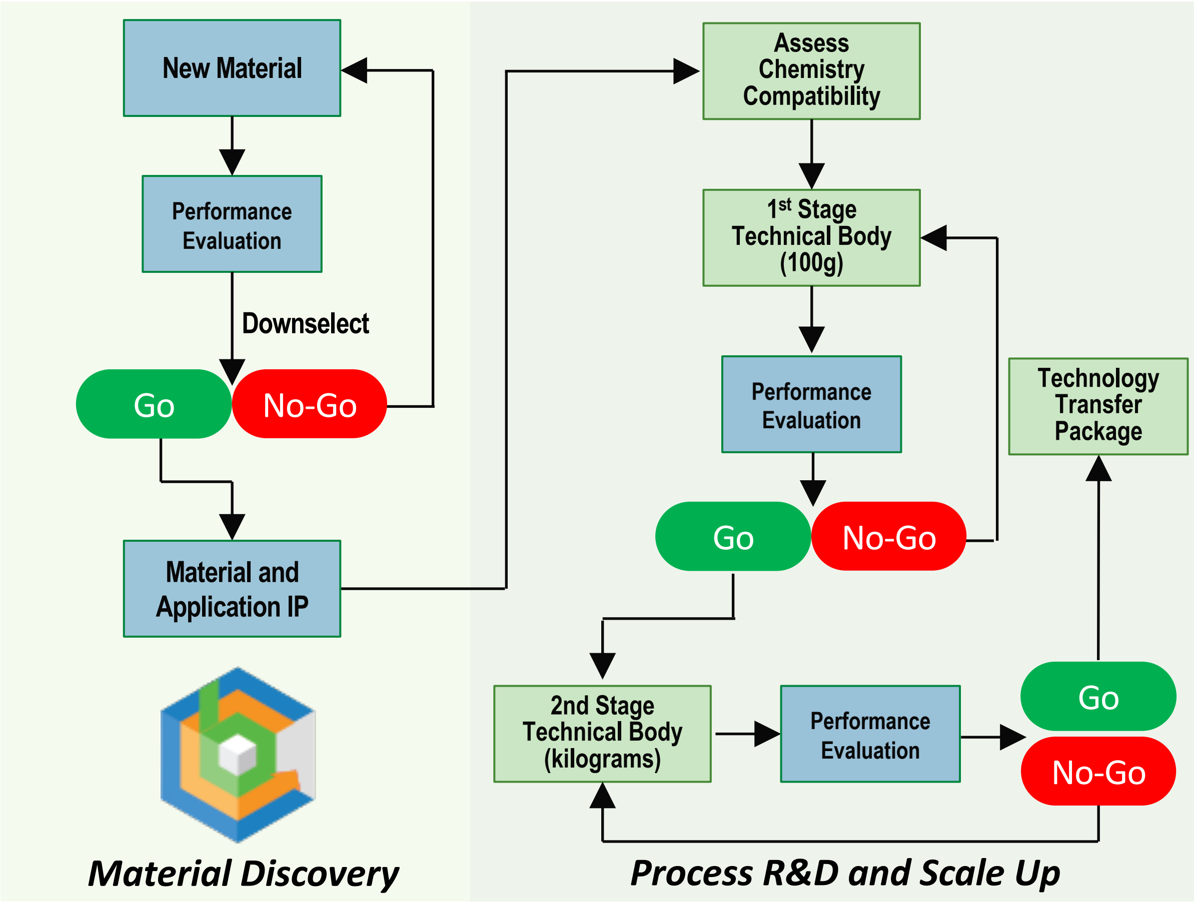
Near-term targets identified within *Conversion*

Pt/TiO_2 (*Catalytic Upgrading of Pyrolysis Products*)

Cu-HBEA (*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

CCB: Staged Approach to Technology Development



<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 engineered catalyst*** to accelerate commercialization when licensed to technology provider

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

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 engineered catalyst

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

High shear / Orbital Mixers

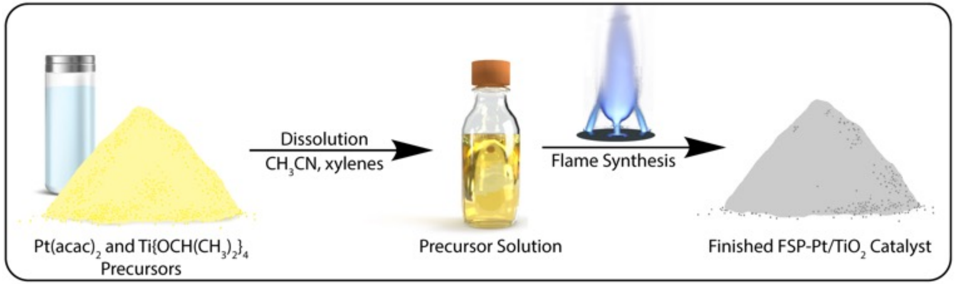
1" Screw Extruder

Bucket/Cement Mixers

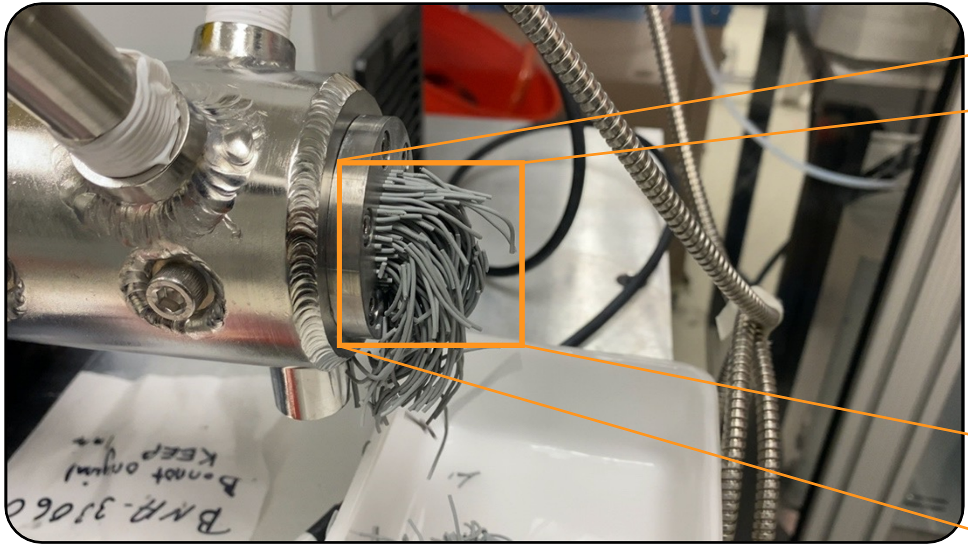
Rotary and Muffle Furnaces

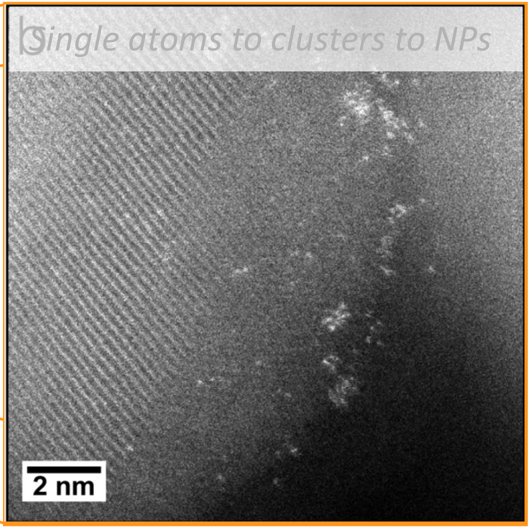
Pipeline for Emerging Methodologies

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

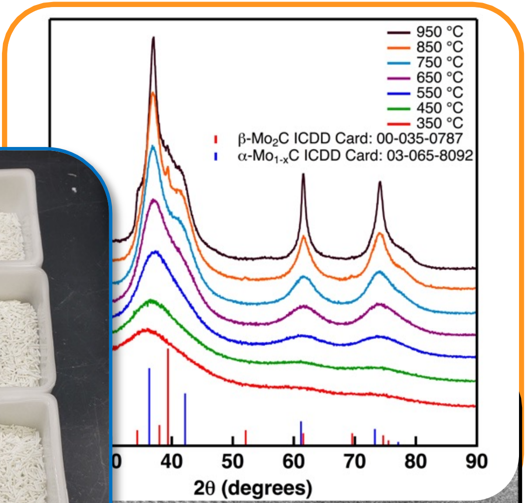


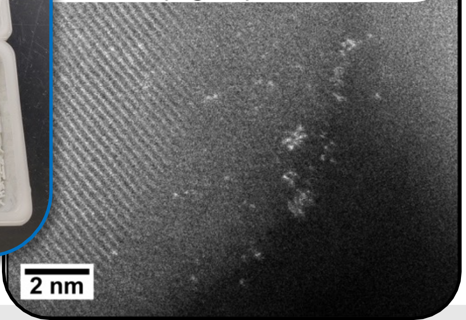


CCB Summary

Developed *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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