ChemCatBio
Chemical Catalysis for Bioenergy

Pacific Northwest NATIONAL LABORATORY

DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

CCB DFAs: Low Pressure Hydrogenolysis Catalysts for Bioproduct Upgrading with Visolis

6th March 2019
Catalytic Upgrading

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

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL, NREL*)
- **Catalytic Upgrading of Indirect Liquefaction Intermediates** (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic and Thermocatalytic CO_2 Utilization** (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

- **Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL, SNL)
- **Catalyst Cost Model Development** (NREL, PNNL)
- **Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)
- **Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

- **ChemCatBio Lead Team Support** (NREL)
- **ChemCatBio DataHUB** (NREL)

Quad Chart Overview

Timeline

- Project start date: 01/15/2018
- Project end date: 12/31/2019
- Percent complete: 40%

Barriers Addressed

- Ct-F. Increasing the Yield from Catalytic Processes
- Ct-G. Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded			300K	225K
Project Cost Share			128.6K	96.4K

Objective

Develop a low-pressure and water-tolerant hydrogenolysis catalyst to convert the fermentation derived C5 oxygenate to a high-value monomer.

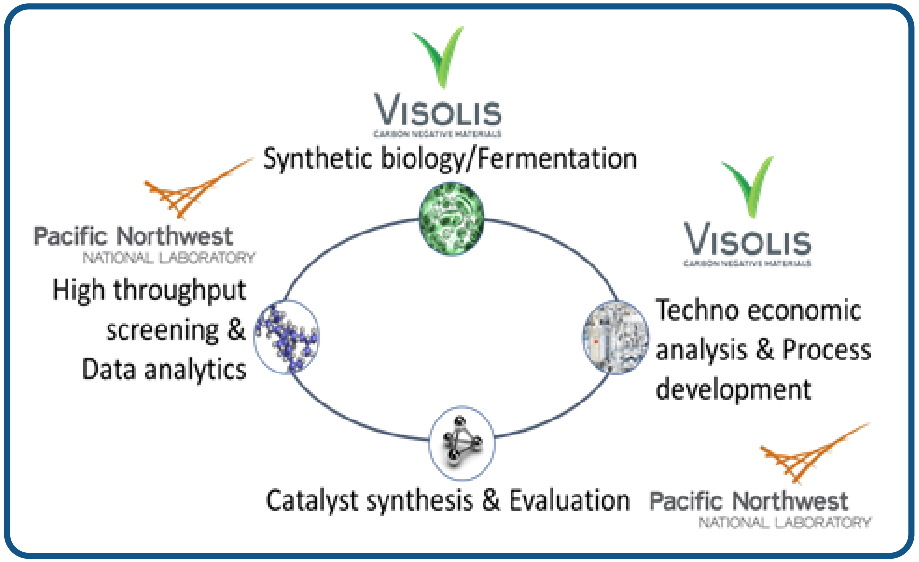
End of Project Goal

Demonstrate stable catalyst with ≥ 80% selectivity to desired product at pressure under 4MPa and complete the techno-economic analysis.

Approach

- Visolis demonstrated demo scale for the production of bio-intermediate (C5 oxygenate) with low projected costs at commercial scale and identified a thermo-catalytic pathway to convert the bio-intermediate to high-value monomer.
  - Preliminary work by Visolis and PNNL demonstrated the conversion of bio-intermediate via hydrogenolysis with a selectivity ~70% at 200°C and 13Mpa.
  - The commercial catalyst identified in the preliminary work requires high hydrogen pressure and demonstrated low catalyst stability.
  - Low-pressure and stable hydrogenolysis catalyst improve the commercial case with major capital cost savings and decreased operating costs.

- Synthetic biology/ fermentation is Visolis core competency.
- PNNL has the demonstrated technical capability in developing hydrogenolysis catalyst and unique catalyst development tools.



Deepak Dugar (President, Visolis Inc.): PNNL's involvement will accelerate the low pressure hydrogenolysis catalyst discovery and the process development cycle.

Approach (Technical)

Testing in High Throughput Analysis

To identify catalyst that can reach >50% selectivity to monomer at ≤13Mpa.

Process Optimization in Flow Reactor

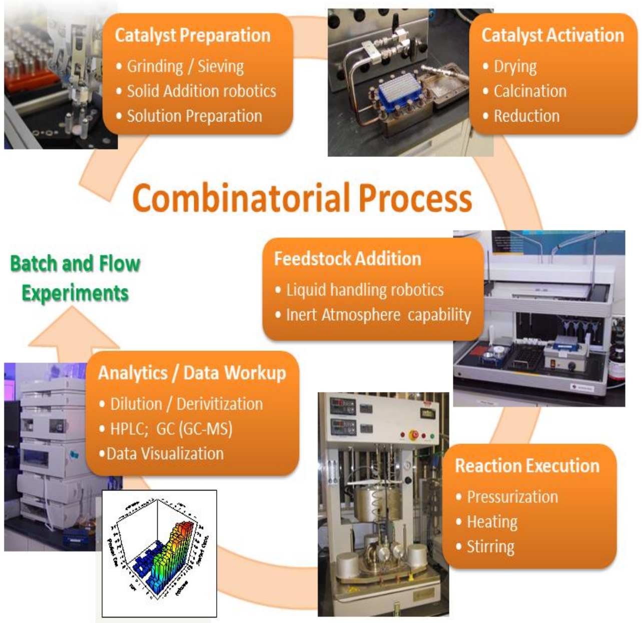
Optimize temperature and residence time as a function of system pressure to identify catalysts that can reach at least 80% selectivity.

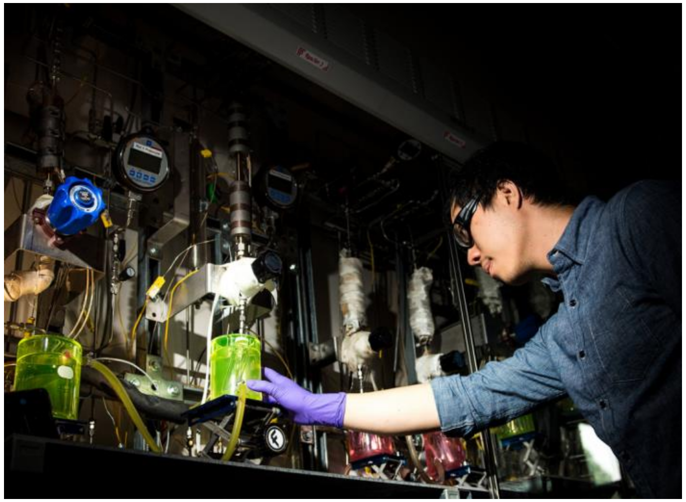
Catalyst Stability and Lifetime Testing

Demonstrate 100-hour time on stream experiment on the selected catalyst and provide catalyst to Visolis for scaled-up testing.

Techno-Economic Analysis and Pilot

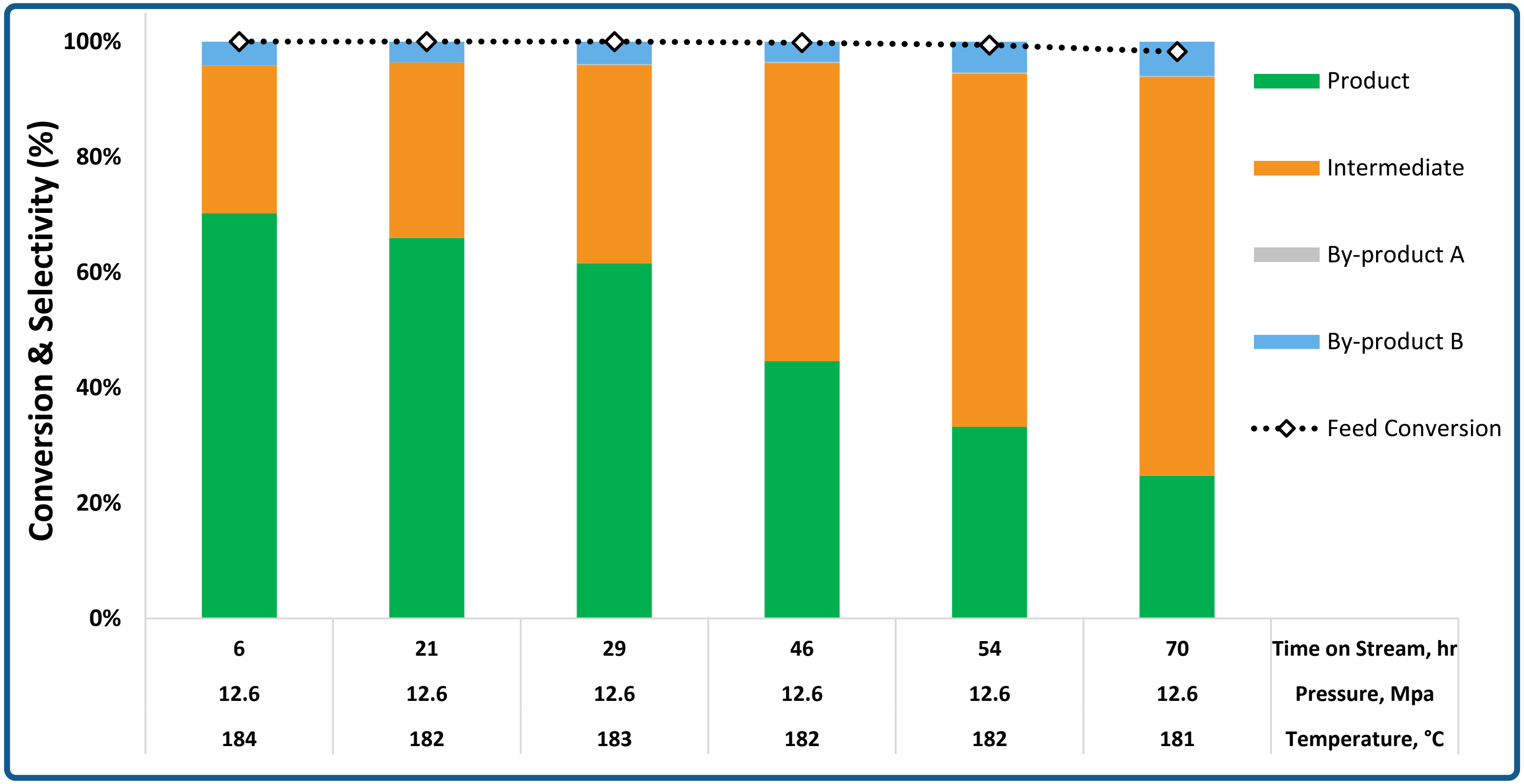
Demonstrate a stable hydrogenolysis catalyst at ≥80% selectivity ≤4MPa and complete the techno-economic analysis.





Technical Accomplishments

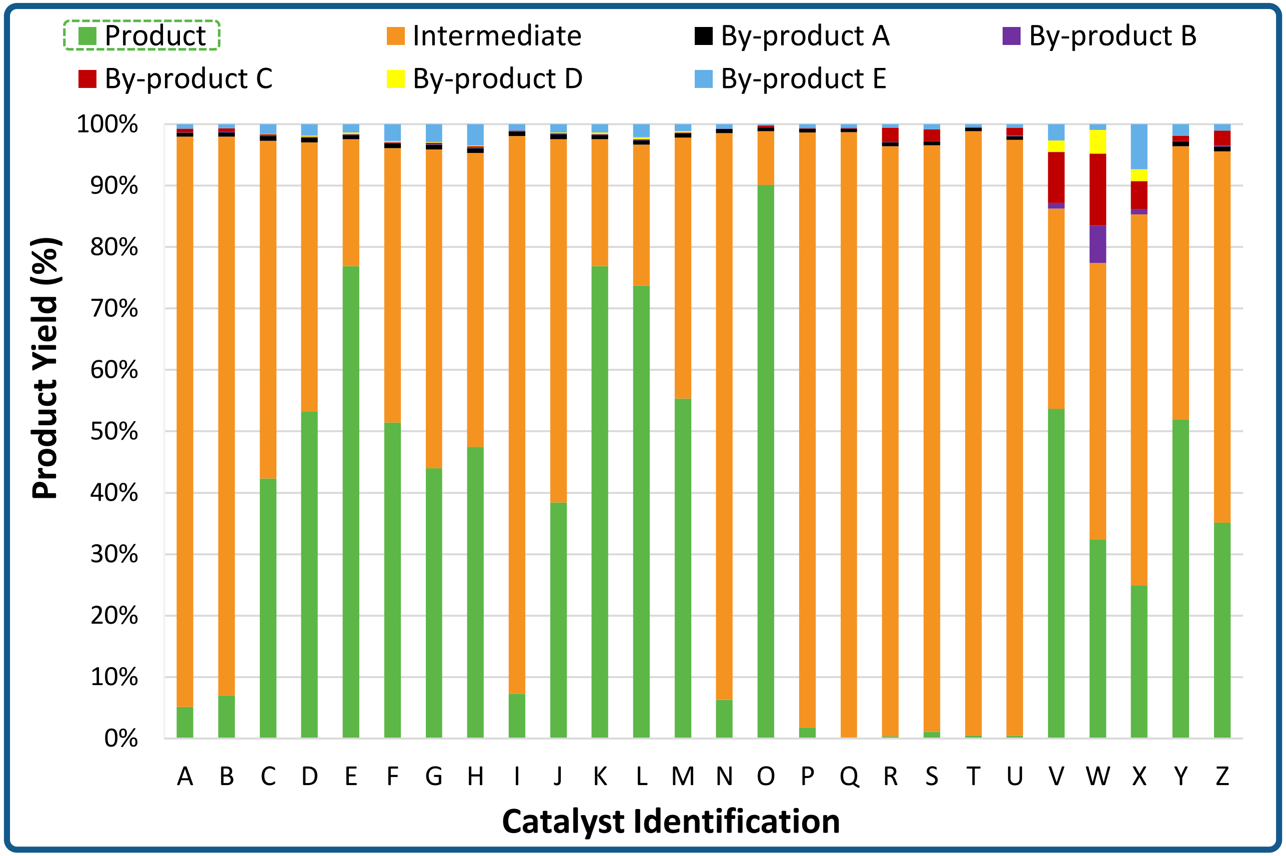
Preliminary Test on Commercial Catalyst



- Operated at high hydrogen pressure (~12.5 Mpa) and temperature (200°C).
- Poor catalyst stability leads to ~20% desired product selectivity within 70 hours of time on stream.

Technical Accomplishments

High Throughput Catalyst Screening



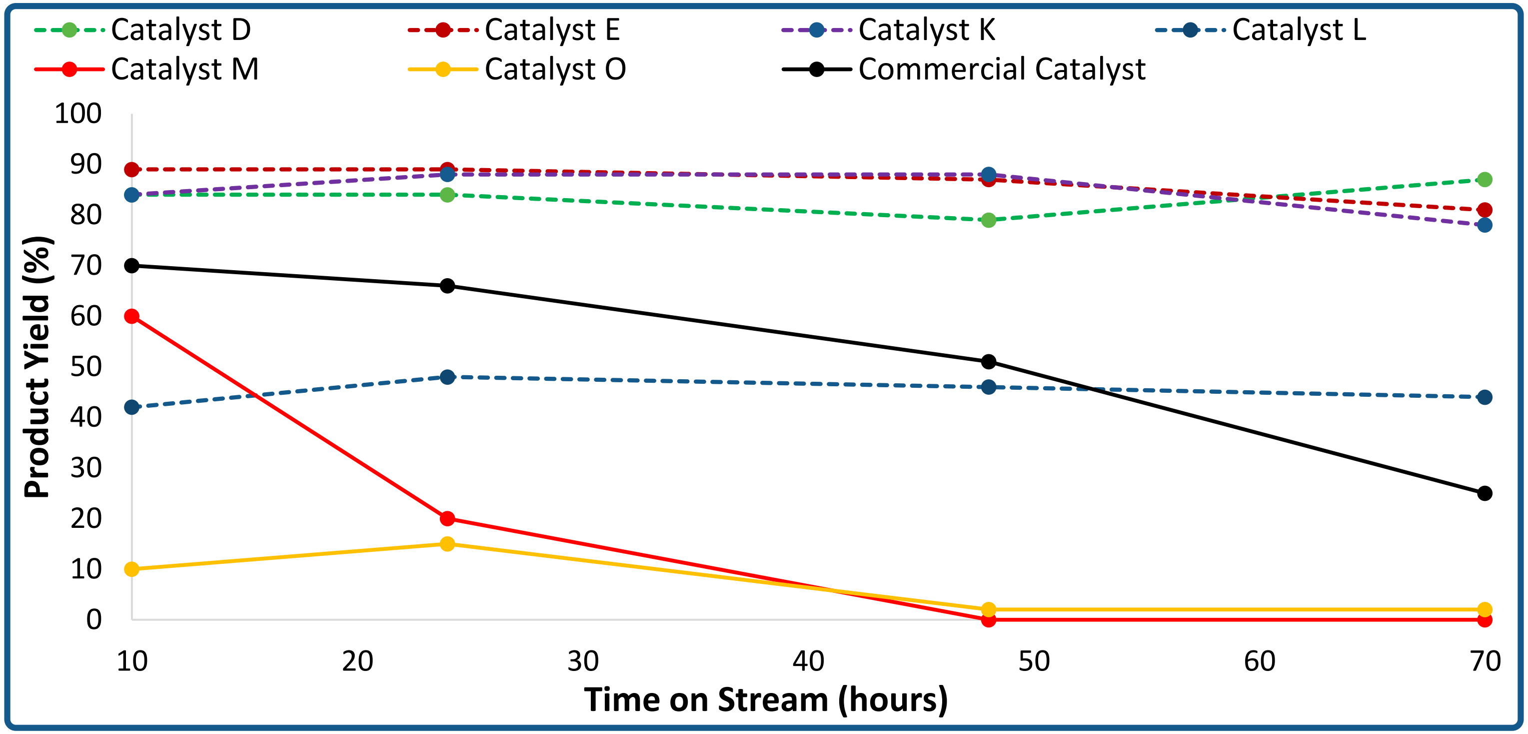
Catalyst Synthesis

Catalyst Testing

- High throughput experiments (>100 catalysts tested) used to select the catalyst compositions and supports for further testing in plug flow reactor.
- Supports with neutral (mild acidic or basic) properties performed better.

Technical Accomplishments

Catalyst Stability Flow Experiment Results



Flow experiments at 150°C (commercial catalyst at 180°C), 12.6Mpa, H_2 to feed ratio of 15.5 and weight hourly space velocity of 0.8hr^{-1}

- Catalysts that deactivate faster tends to produce carboxylic acid intermediate at higher concentration.
  - We hypothesize these acids strongly adsorb on the active sites and deactivate the catalyst.
- Catalysts shown in dotted line are selected for the further study.

Future Work

Start	On Track	End
Completed	Future Work	
FY18 Jan	FY18 Dec	FY19 Dec

March 2019	Operating conditions optimization at which at least 80% selectivity to the product at ≤10MPa pressure.
June 2019	Catalyst regeneration and spent-regenerated catalyst performance with greater than 85% of fresh catalyst level.
September 2019	Demonstration of the hydrogenolysis catalyst at 80% selectivity to desired product under 4MPa pressure.
December 2019	Demonstrate catalyst stability with 100 hour time-on-stream experiment and complete techno-economic modeling.

Summary

Overview	• Low-pressure and water-tolerant hydrogenolysis catalyst to convert the fermentation derived C5 oxygenate to a high-value monomer.
Approach	• High-throughput experiments to screen the potential catalyst and process conditions. Further optimize the selected catalyst to develop the low-pressure hydrogenolysis catalyst.
Technical Progress	• Reduced the pressure requirement from 13Mpa to 7Mpa and demonstrated a stable catalyst beyond 50 hours on stream with product yield around 90%.
Relevance	• Stable catalyst that can operate at low pressure to selectively upgrade biological intermediates and approach to bridge the biochemical conversion feedstocks with catalytic upgrading.
Future Work	• Develop the catalyst that can operate under 4Mpa and demonstrate the catalyst stability beyond 100 hours time-on-stream. Complete the techno economic analysis.

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Thank you!

ChemCatBio Team

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