ChemCatBio
Chemical Catalysis for Bioenergy

Pacific Northwest
NATIONAL LABORATORY

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

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Catalytic Upgrading

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

Project Overview:
Develop Low-Pressure Catalyst

Pacific Northwest NATIONAL LABORATORY

VISOLIS CARBON NEGATIVE MATERIALS

Project Goal:

- Support a biotech start-up company to develop hydrogenolysis catalyst that can operate at low-pressures (≤ 5 MPa) and demonstrate conversion of a fermentation-derived C_6 intermediate to a high value chemical monomer.

Outcome:

- Accelerated catalyst and process development to convert the bio-derived intermediate to a high value monomer.
- Supporting the start-up company with commercializing their technology.

Relevance:

- Risk and cost reduction for bioproduct process commercialization.
- Develop a stable and selective catalyst for biomass conversion R&D.

1 - Approach:
Integrated Work between PNNL and Visolis

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VISOLIS CARBON NEGATIVE MATERIALS

Project Management | Karthikeyan Ramasamy (PNNL) | Deepak Dugar (Visolis)

Develop strategy, coordinate research activities, facilitate regular communications between the team members and communicate with BETO.

Catalyst Synthesis | Senthil Subramaniam (PNNL)

Prepare hydrogenolysis catalyst for combinatorial and flow reactor testing and engineer the catalyst.

Combinatorial Experiments | Mond Guo (PNNL)

Design, plan and conduct combinatorial experiments for catalyst and process parameter identification.

Flow Reactor Testing | Mond Guo (PNNL)

Conduct catalyst testing experiments in flow reactor to develop deactivation kinetics and demonstrate catalyst lifetime.

Intermediate Production | Shylesh Pillai (Visolis)

Generate and purify (as needed) fermentation derived intermediate feedstocks for the hydrogenolysis catalyst development testing.

Techno Economic Analysis | Kedar Cholkar (Visolis)

Conduct techno economic analysis to guide the experimental work and develop process flow diagram.

1 - Approach:
Communication Between Stakeholders Enables the Project Success

Inputs

- External industrial partners
  - ✓ Catalyst development
  - ✓ Process development
- BETO peer review
- Literature information

Project Structure

Catalyst Discovery

Techno Economic Analysis

Catalyst Stability Demonstration

Project Management

- Milestones and Go/No-Go decision
- Communication between PNNL and Visolis
  - ✓ Biweekly team meeting
  - ✓ Year end face to face meeting

Successfully Completed the Phase I/II Go/No-Go:

- Developed the hydrogenolysis catalyst that can operate below 5MPa pressure
- Demonstrated the extruded catalyst lifetime beyond 500 hours with product selectivity >85%

Risk Mitigation:

- Ensure the catalyst developed is industrially relevant and commercially viable
- Coordinated approach to alleviate scale-up and investment risk

1 - Approach:
Combinatorial Catalysis to Develop Hydrogenolysis Catalyst

Catalyst Formulation Testing with High Throughput Experimentation: Identify hydrogenolysis catalysts (e.g., support and metal composition) that can operate at pressure below 5MPa.

Process Optimization in Flow Reactor: Optimize operating conditions (e.g., temperature) as a function of system pressure to achieve ≥ 80% selectivity to desired product at ≤ 5MPa.

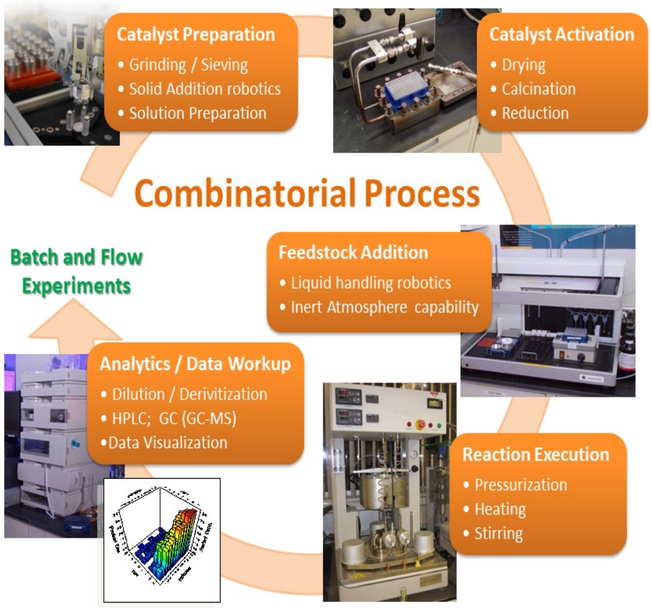
Catalyst Stability and Lifetime Testing: Conduct time on - stream experiments ≥100 hours to demonstrate catalyst stability and product selectivity.

Techno Economic Analysis: Develop and demonstrate a stable hydrogenolysis catalyst at ≥ 80% selectivity at ≤ 5MPa and complete economic analysis.

Phase I Project Duration

Start: March 2018

End: June 2020



1 - Approach:
Impurity Tolerance and Engineered Catalyst

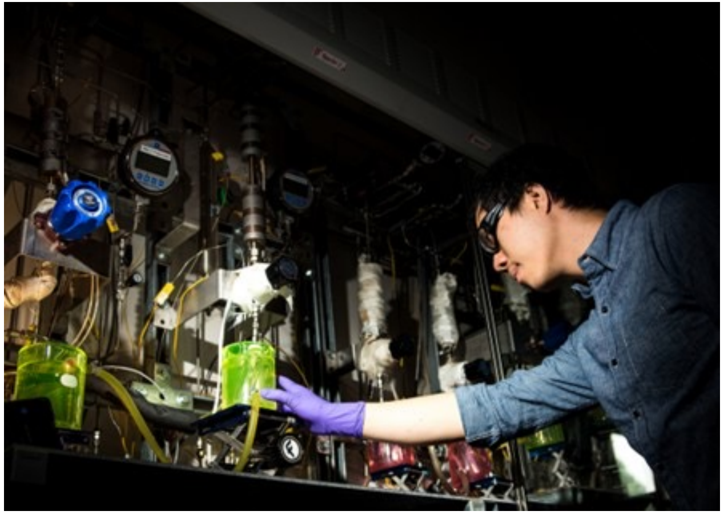
Lowering Pt Group Loading: Reduce the total Pt group metal loading below 1.5% (less than 50% compared to the Phase I catalyst)

Catalyst Impurity Tolerance: Identify bio-intermediate feedstock impurity tolerance on hydrogenolysis catalyst and develop mitigation protocol.

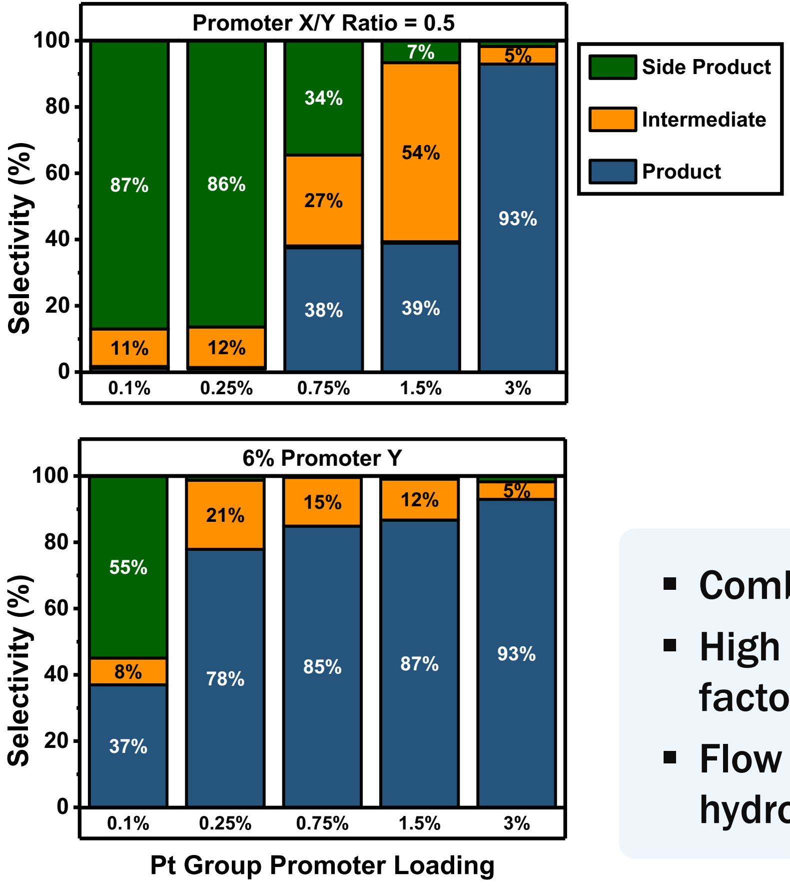
Evaluation of Engineered (pellets) Catalysts: Develop and evaluate extruded versions of the catalyst formulation and demonstrate the catalyst stability and product selectivity.

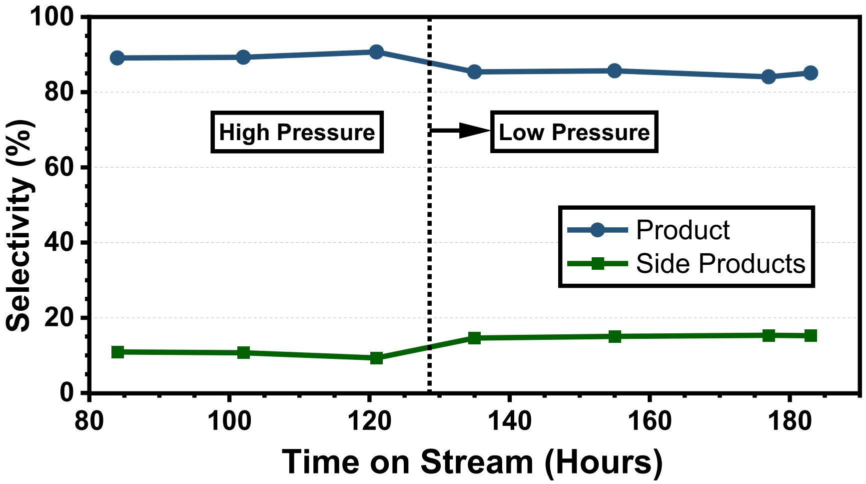
Catalyst Stability and Lifetime Testing: Complete 500 hours time on stream experiment on engineered catalyst in >20mL reactor.

Phase II Project Duration
Start: October 2020
End: September 2022



2 - Progress and Outcomes:
Lowering Pt Group Promoter Loading

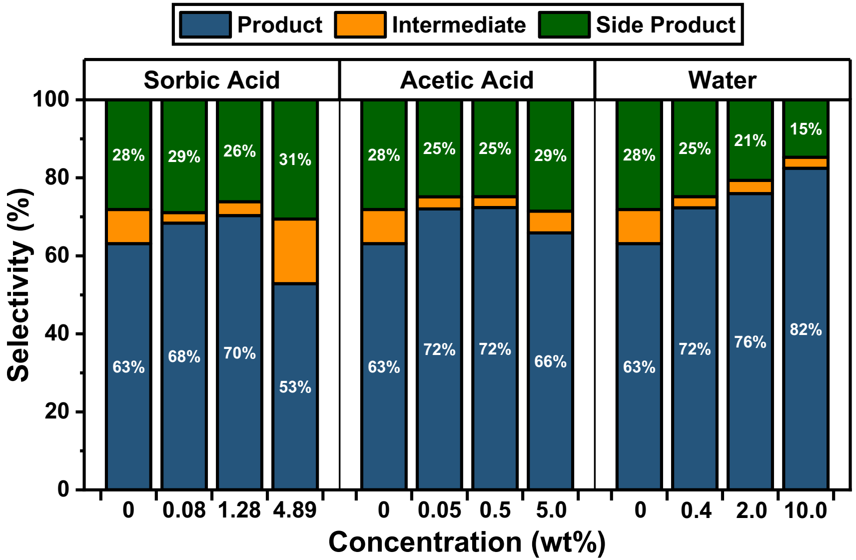




- Combinatorial testing used to lower Pt Group loading
- High ratio of key synergistic promoter identified as key factor in maintaining high yield even at <<1.5% loadings
- Flow reactor testing showed that low pressure hydrogenolysis capability was preserved at <1.5% loading

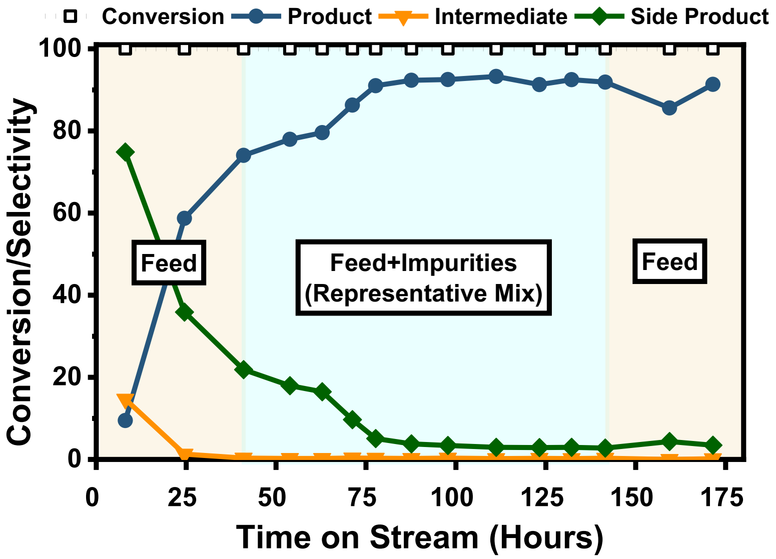
2 - Progress and Outcomes:
Demonstrated High Tolerance to Feed Impurities

Combinatorial Batch

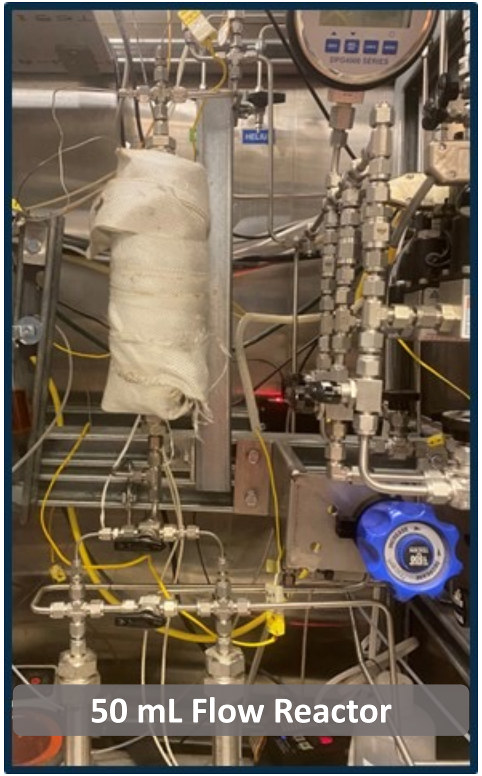


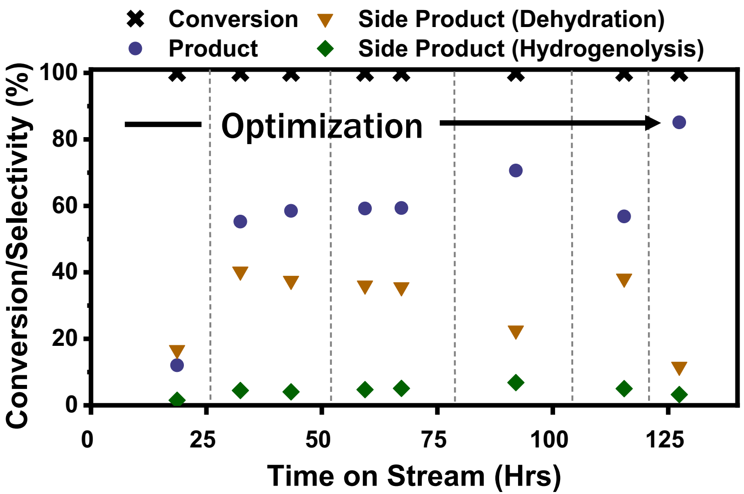
- Organic acid impurities showed little to no impact at reasonable concentrations
- Water content was found to boost selectivity toward product

- Representative feed tested in flow reactor with acid+water impurities
- No significant change to conversion or product selectivity observed



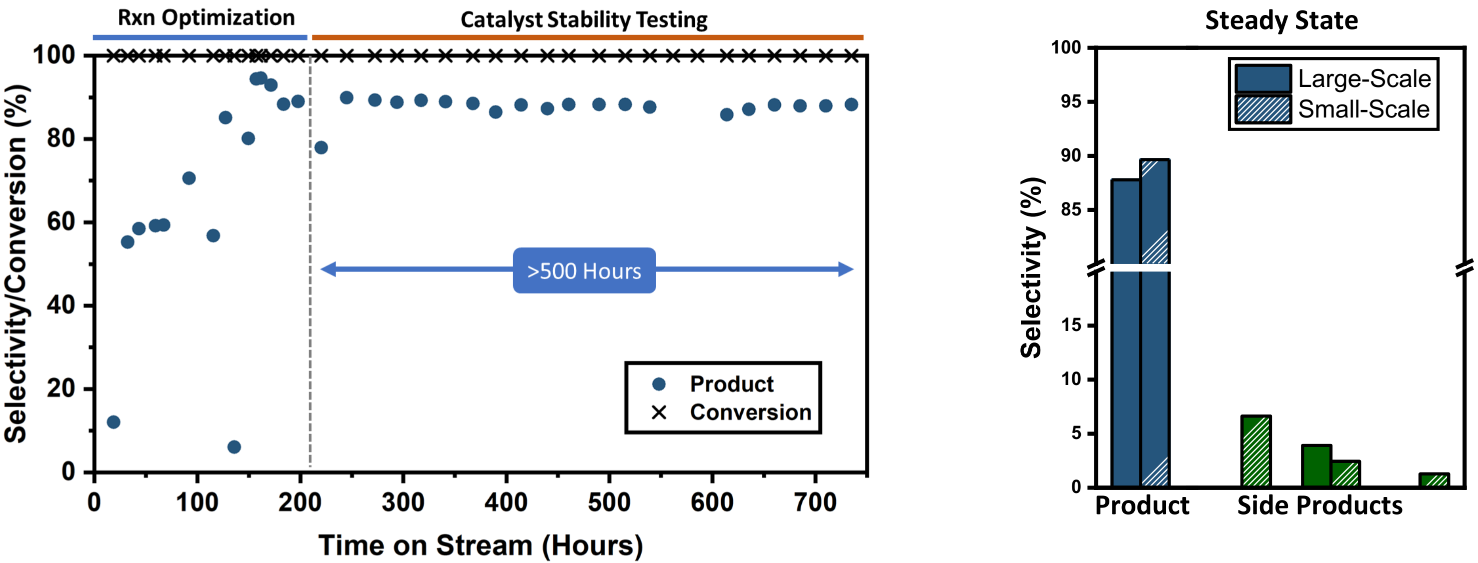
Performed Reaction Scale-up on Engineered Catalyst





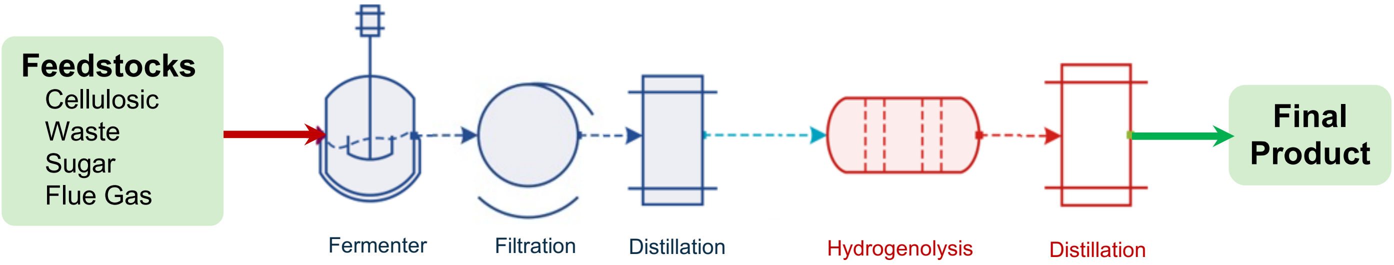
- Carbon extrudates used as engineered catalyst support with 1.5%Pt group loading
- Constructed 50 mL reactor for scale-up experiments
- Optimized temperature and WHSV to minimize side products from over dehydration and incomplete hydrogenolysis

2 - Progress and Outcomes:
Long-Term Catalyst Stability Testing for 500 hours



- Demonstrated continuous performance >500 hours with selectivity >85%
- Total time on catalyst without deactivation >800 hours
- Robust against intermittent operation and sudden H_2 stoppage
- Demonstrated small-scale results to be transferable to larger-scale operation

2 - Progress and Outcomes:
Economic Update from Phase II Results



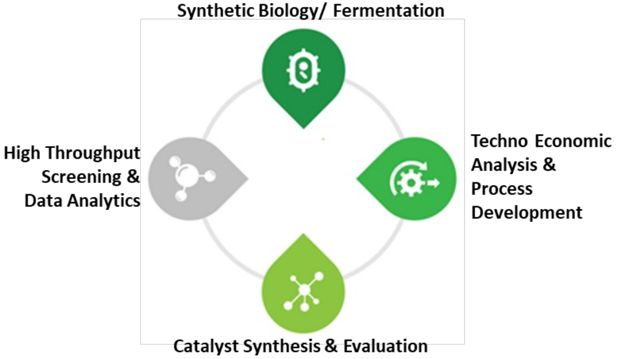
Simplified process flow diagram used in the TEA

Parameter	Pre-Phase I	Post-Phase I	Post-Phase II	% Reduction	Description
Annual Catalyst Cost ($/ton)	780	620	180	76.9	Reduced Pt group metal loading. Improved catalyst lifetime and stability
Capital Expense ($/ton)	540	450	450	16.7	Reduced hydrogenolysis pressure
Operating Expense ($/ton)	1140	950	510	55.7	Reduction in frequent catalyst maintenance and hydrogen pressure
Total Production Cost ($/ton)	5700	4700	4260	25.2	Improved product selectivity and everything mentioned above

Process modelling and economic analysis conducted by Visolis based on the experimental data generated from this project.

3 - Impact:
Accelerating Catalyst Development and Scale-up Activities

- The best hydrogenolysis catalyst identified in the preliminary work by Visolis requires 13MPa pressure and the catalyst was stable for only few hours.
  - ✓ Low-pressure and stable hydrogenolysis catalyst improve the commercial case with major capital cost savings and decreased operating costs.
- Synthetic biology/fermentation is the core competency for Visolis (start-up company).
- PNNL and ChemCatBio's technical capability in developing the hydrogenolysis catalyst and unique catalyst development tools that are beneficial in developing the low-pressure hydrogenolysis catalyst.
- This project enabled the successful catalyst development and commercialization path of this technology.



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

This project has been successfully completed by demonstrating stability of engineered hydrogenolysis catalyst in a scaled-up 50mL reactor for >500 hours TOS, with product selectivity >85%.

4 - Summary:
Overall Phase II Timeline

Start		End
Fiscal Year (FY) 2020 Oct.	Completed	FY 2022 Sept.

March 2021	Evaluate the impacts of feedstock-based impurities on the product yield and develop mitigation strategies.
September 2021	Reduce the Pt group metal loading ≤ 1.5% in the catalyst and show the product yield > 85%.
March 2022	Develop and evaluate extruded versions of the catalyst formulation and demonstrate the catalyst stability.
September 2022	Demonstrate > 500-hour TOS experiment with a product yield > 85% over the engineered catalyst.

Quad Chart Overview

Timeline
- Project start date: 10/1/2020
- Project end date: 9/30/2022

	FY 2022	Total Award
DOE Funding	$200,000	$400,000 (FY 2021-2022)
Visolis	$87,000	$174,000 (FY 2021-2022)

TRL at Project Start: 3

TRL at Project End: 4

Project Goal
Develop a low-pressure and water-tolerant hydrogenolysis catalyst to convert the fermentation derived C_6 oxygenate to a high-value monomer and demonstrate the chemistry with engineered catalyst.

End of Project Milestone
- Cost-effective catalyst that maintains performance at lower pressure (<5Mpa) for long TOS.
- Stable catalyst that is tolerant to minor impurities and recycles.
- Engineered catalyst (extrudates) that is easily scalable.

Funding Mechanism
Directed Funding Assistance through ChemCatBio

Project Partners
Visolis Inc.

4 – Summary

Visolis is working with their commercialization partner for scale-up

Overview	▪ Develop a low-pressure and water-tolerant hydrogenolysis catalyst to convert the fermentation derived C6 oxygenate to a high-value monomer.
Approach	▪ High-throughput experiments to discover potential catalyst composition and process conditions. Transition to the flow reactor setup to optimize and demonstrate the stability of the catalyst.
Impact	▪ Support the start-up company (Visolis) to commercialize their technology by developing a stable catalyst and by reducing the scale-up risk.
Progress and Outcome	▪ Developed an engineered hydrogenolysis catalyst that is tolerant for feedstock impurities and operate ~5Mpa. Demonstrate the catalyst stability beyond 500 hours TOS while maintaining product selectivity above 85%
Future Work	▪ Visolis is working with industrial entities to scale-up toward commercialization

Acknowledgements

- **PNNL:** Mond Guo, Heather Job, Kuan-Ting Lin, Senthil Subramaniam, Michel Gray, Asanga Padmaperuma
- **Visolis:** Deepak Dugar, Shylesh Pillai, Lin Louie, Mustafa Bootwala, Brain Lee, Kedar Cholkar
- **BETO:** Sonia Hammache, Andrea Bailey, Trevor Smith, Nichole Fitzgerald

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This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN)

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Thank You!

2022 Peer Review Responses

Lack of technical information in the peer review discussion

We are not able to provide detailed technical information during the peer review presentation due to the constraints of confidentiality with a commercial partner. Once the novelty is protected by patent, our goal is to document and make available to the public all the information in the data management hub operated by ChemCatBio consortium.

Addressing Catalyst Stability

Long-term catalyst performance is one of the major focus areas as it is critical to successful commercialization. All flow experiments were conducted for at least 100 hours time on stream, with several experiments addressing key areas of which may potentially negatively stability, including low conversion, intermittent operation, low H_2 partial pressure, and high residence times.

Applicability of project to BETO

The successful outcome of this catalyst development will facilitate the adoption of other biomass conversion technologies that are under BETO portfolio. This project supports the CCB's objective to identify and overcome challenges in hydrogenolysis catalysis and make an impact in converting biomass and waste resources into renewable chemicals.

Abbreviations and Acronyms

- BETO: Bioenergy Technologies Office
- FY: Fiscal year
- NREL: National Renewable Energy Laboratory
- ORNL: Oak Ridge National Laboratory
- PNNL: Pacific Northwest National Laboratory
- TEA: Techno-economic analysis
- TOS: Time-on-stream
- WHSV: Weight hourly space velocity