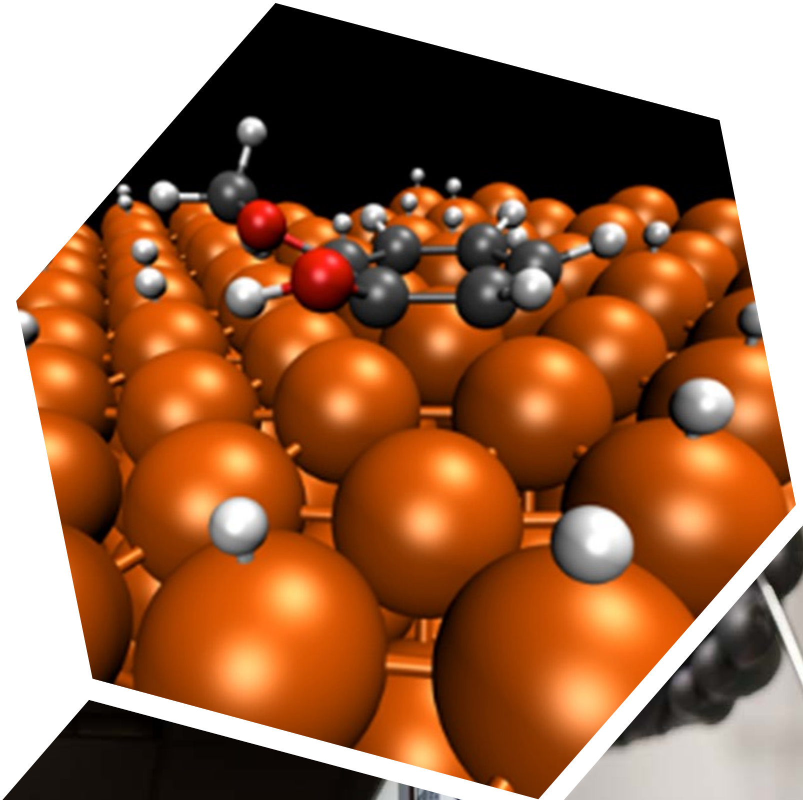
ChemCatBio

Chemical Catalysis for Bioenergy

Pacific Northwest NATIONAL LABORATORY

VISOLIS CARBON NEGATIVE MATERIALS



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

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

BIOENERGY TECHNOLOGIES OFFICE

Develop Low-Pressure Hydrogenolysis Catalyst

Project Goal: Develop hydrogenolysis catalyst that can operate at low-pressures (≤ 5 MPa) and demonstrate conversion of a fermentation-derived C6 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 (Visolis) with commercializing their technology.

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

ChemCatBio Foundation – Fiscal Year 2021

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

Catalytic Upgrading of Biochemical Intermediates
National Renewable Energy Laboratory (NREL), Pacific Northwest National Laboratory (PNNL), Oak Ridge National Laboratory (ORNL), Los Alamos National Laboratory

Upgrading of C1 Building Blocks
NREL

Upgrading of C2 Intermediates
PNNL, ORNL

Catalytic Fast Pyrolysis
NREL, PNNL

Electrocatalytic CO_2 Utilization
NREL

Enabling Capabilities

Advanced Catalyst Synthesis and Characterization
NREL, Argonne National Laboratory, ORNL

Consortium for Computational Physics and Chemistry
ORNL, NREL, PNNL, Argonne National Laboratory, National Energy Technology Laboratory

Catalyst Deactivation Mitigation for Biomass Conversion
PNNL

Industry Partnerships (Phase II Directed Funding)

Opus12 (NREL)

Visolis (PNNL)

Sironix
(Los Alamos National Laboratory)

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

Integrated Work between PNNL and Visolis

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)

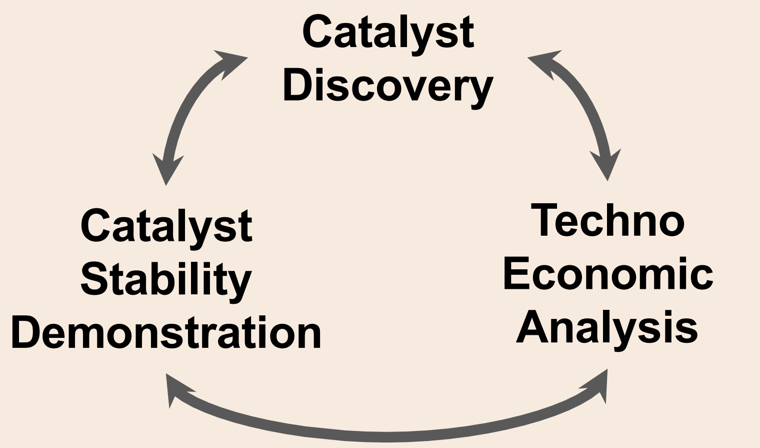
Conduct techno economic analysis to guide the experimental work and develop process flow diagram.

Communication between Stake Holders Enables the Project Success

Inputs

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

Project Structure



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 Go/No-Go:

- Developed the hydrogenolysis catalyst that can operate below 5MPa pressure
- Demonstrated the catalyst lifetime beyond 100 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

Combinatorial Catalysis to Develop Hydrogenolysis Catalyst

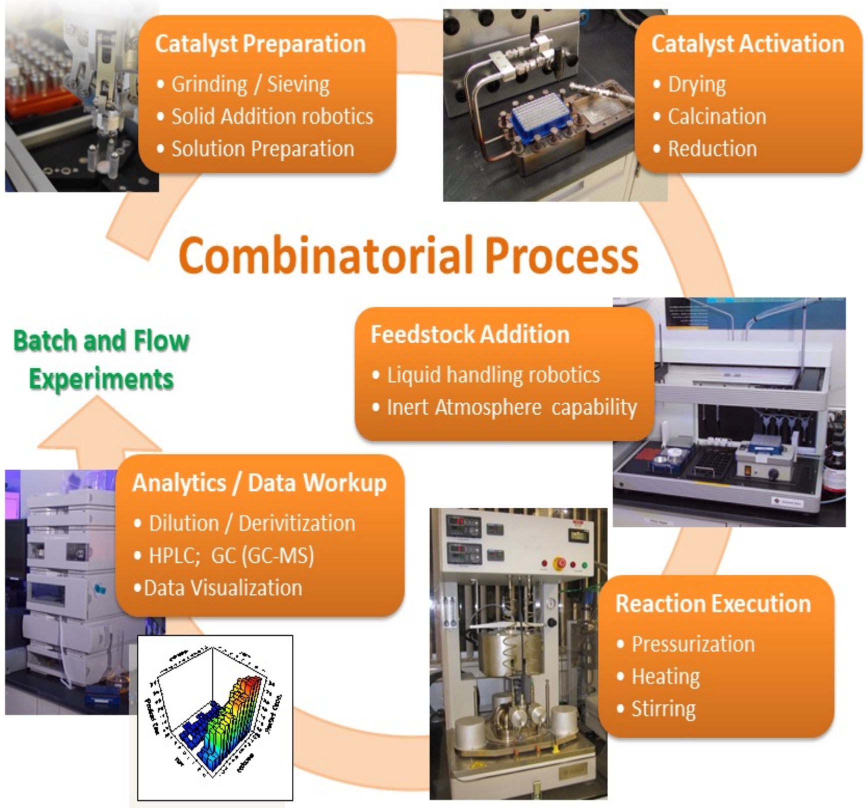
Catalyst Formulation Testing with High Throughput Experimentation: Identify hydrogenolysis catalysts (e.g., support and metal composition) that can operate at pressure below 5MPa.

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

Catalyst Stability and Lifetime Testing: Conduct time-on-stream (TOS) experiments for at least 100 hours to demonstrate catalyst stability and product selectivity at pressure ≤ 5MPa.

TEA and Pilot: Develop and demonstrate a stable hydrogenolysis catalyst at ≥ 80% selectivity at ≤ 5MPa and complete the analysis for pilot plant design based on process and economic analysis.

Phase I Project Duration
Start: March 2018
End: June 2020



2 – Approach (Phase II):
Combinatorial Catalysis to Develop Hydrogenolysis Catalyst

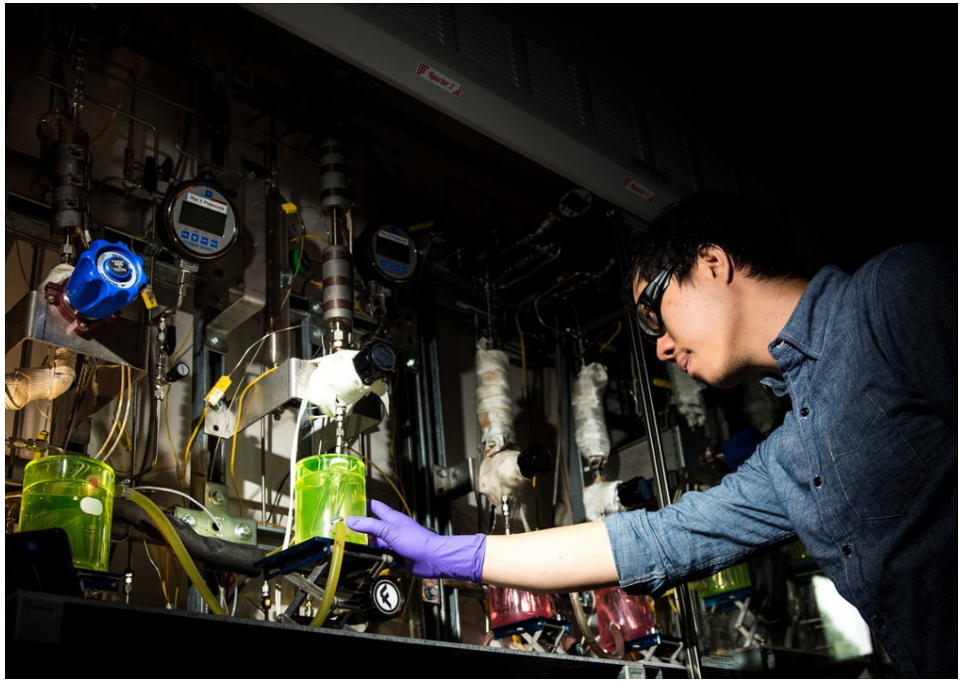
Catalyst Impurity Tolerance: Identify bio-intermediate feedstock impurity tolerance on the low-pressure hydrogenolysis catalyst and develop mitigation protocol.

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: Conduct TOS experiment for 500 hours on engineered catalyst and provide engineered catalyst to Visolis to test in 20-gram reactor (scale-up).

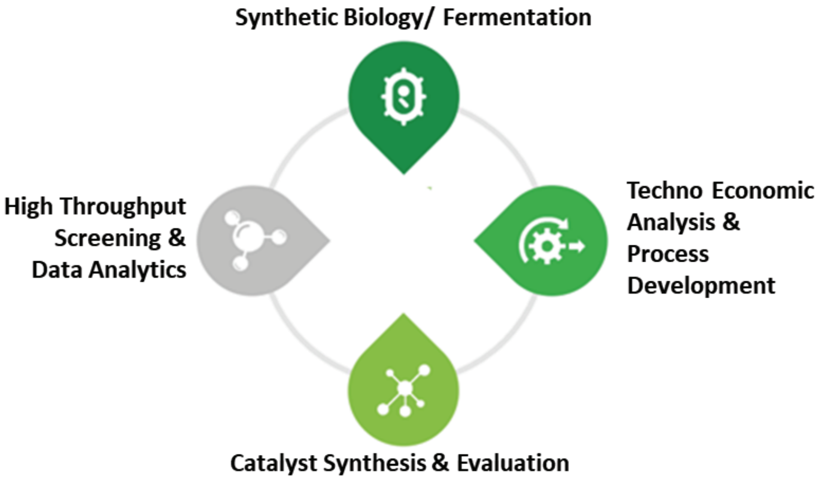
TEA and Pilot: Develop and show a stable hydrogenolysis catalyst at ≥ 80% selectivity under 5 MPa and update the analysis for pilot plant design based on process and economic analysis.

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



Develop Low-Pressure Hydrogenolysis Catalyst

- 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 demonstrated technical capability in developing the hydrogenolysis catalyst and unique catalyst development tools that are beneficial in developing the low-pressure hydrogenolysis catalyst.
- This project will enable the successful catalyst development and commercialization of this technology.

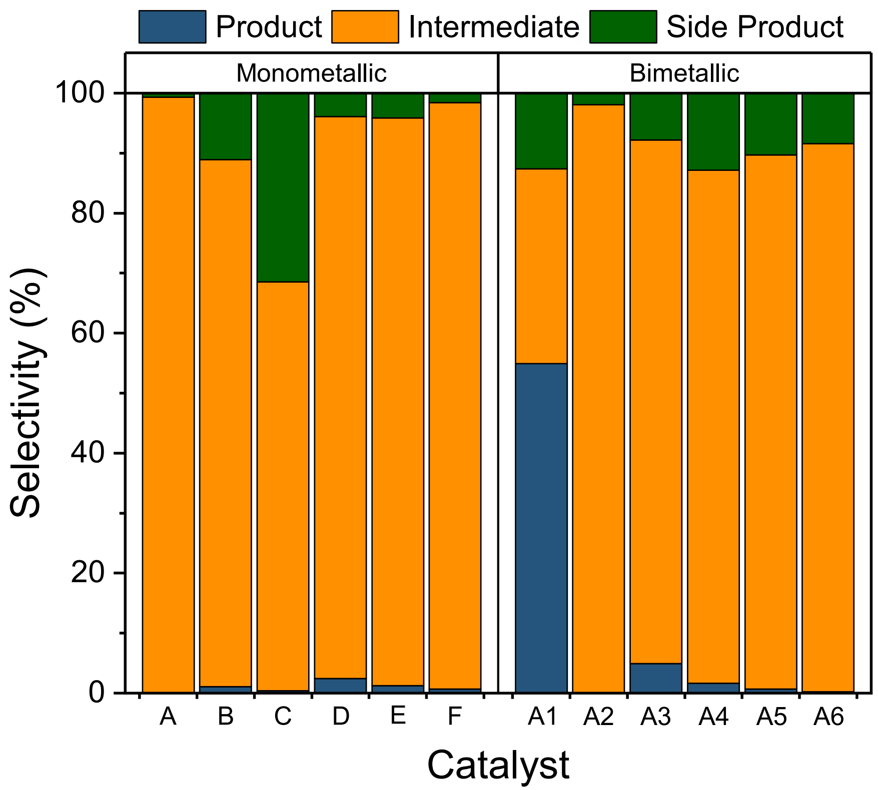


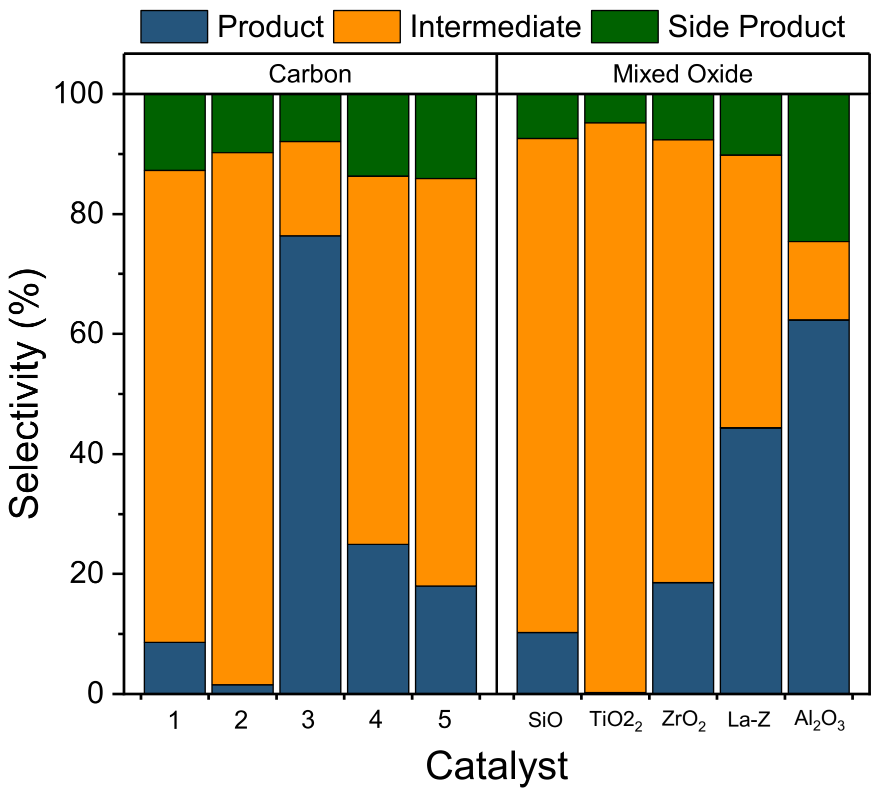
Deepak Dugar (President, Visolis Inc.): *"PNNL's involvement will accelerate the low-pressure hydrogenolysis catalyst discovery and the process development cycle."*

Phase I of this project is successfully completed by demonstrating the hydrogenolysis catalyst at ~5MPa pressure for >100 hours TOS, with product selectivity of >85%.

4 – Progress and Outcomes (Phase I)

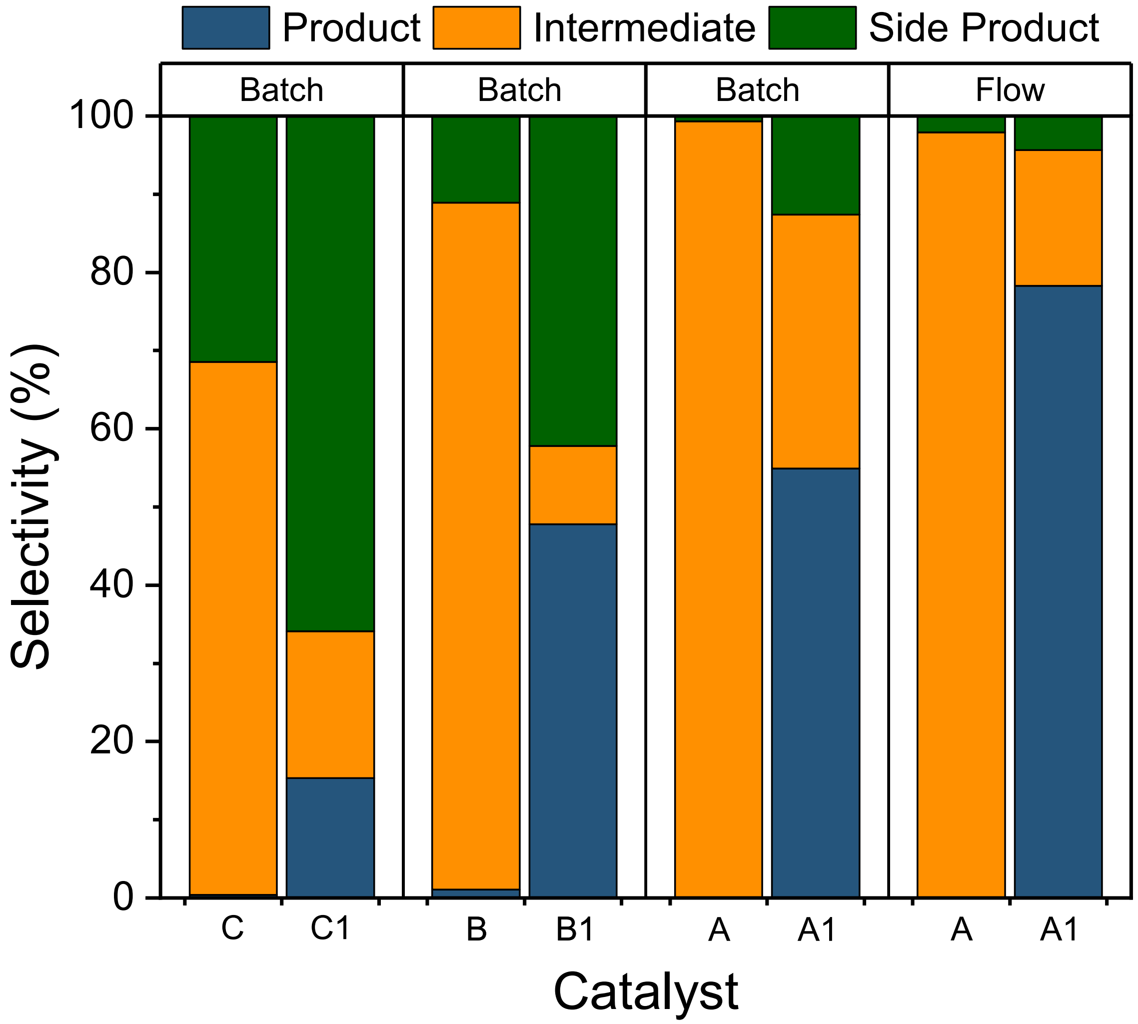
Combinatorial Experiment for Catalyst Screening





- Combinatorial capabilities enable the evaluation of a wide range of metal promoters, supports, and reaction conditions.
- Mono-metallic promoters were found ineffective.
- Identified key synergistic promoter X during an extensive screening of bimetallic formulations.
- Tuning support was allowed for the further improvement of catalytic performance.

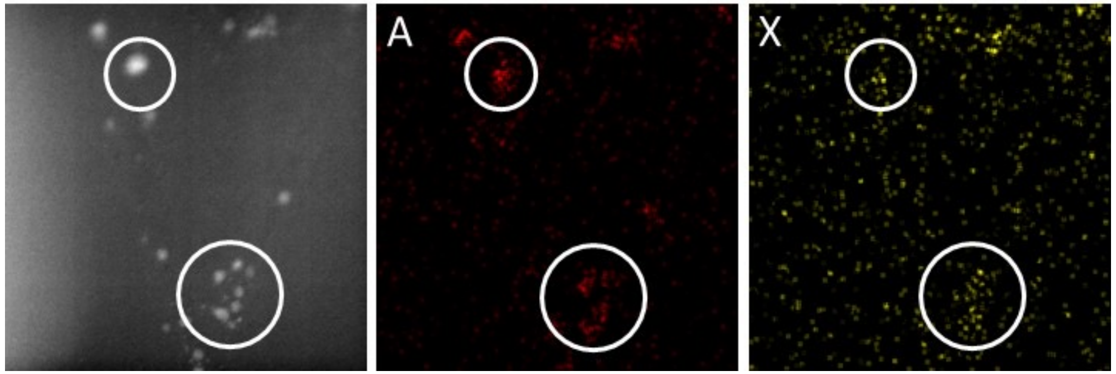
Bimetallic Catalyst Development

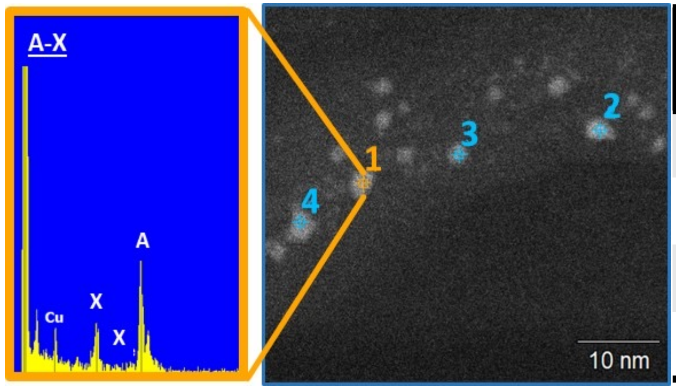


- Mono-metallic catalysts were found to be ineffective for the rate limiting reaction step.
- Identified key synergistic promoter X in an extensive screening of bimetallic formulations.
- Effect was verified for several paired promoters, with A-B being most selective.
- Verification in flow reactor system was demonstrated.

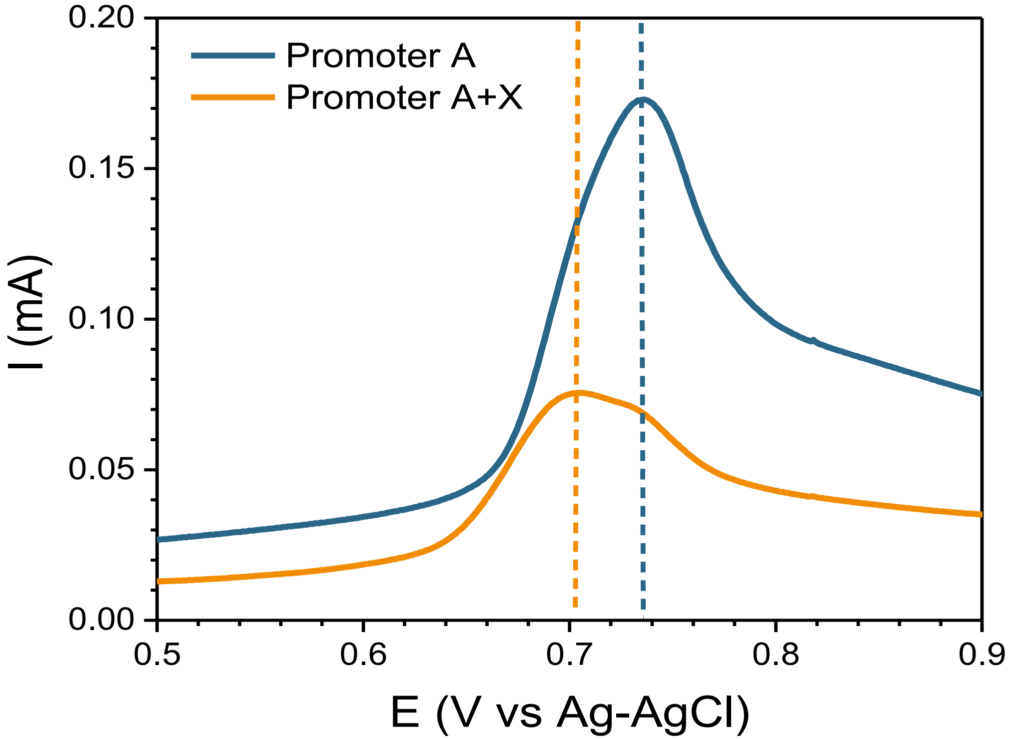
4 – Progress and Outcomes (Phase I)

Effect of Bimetallic Formulation





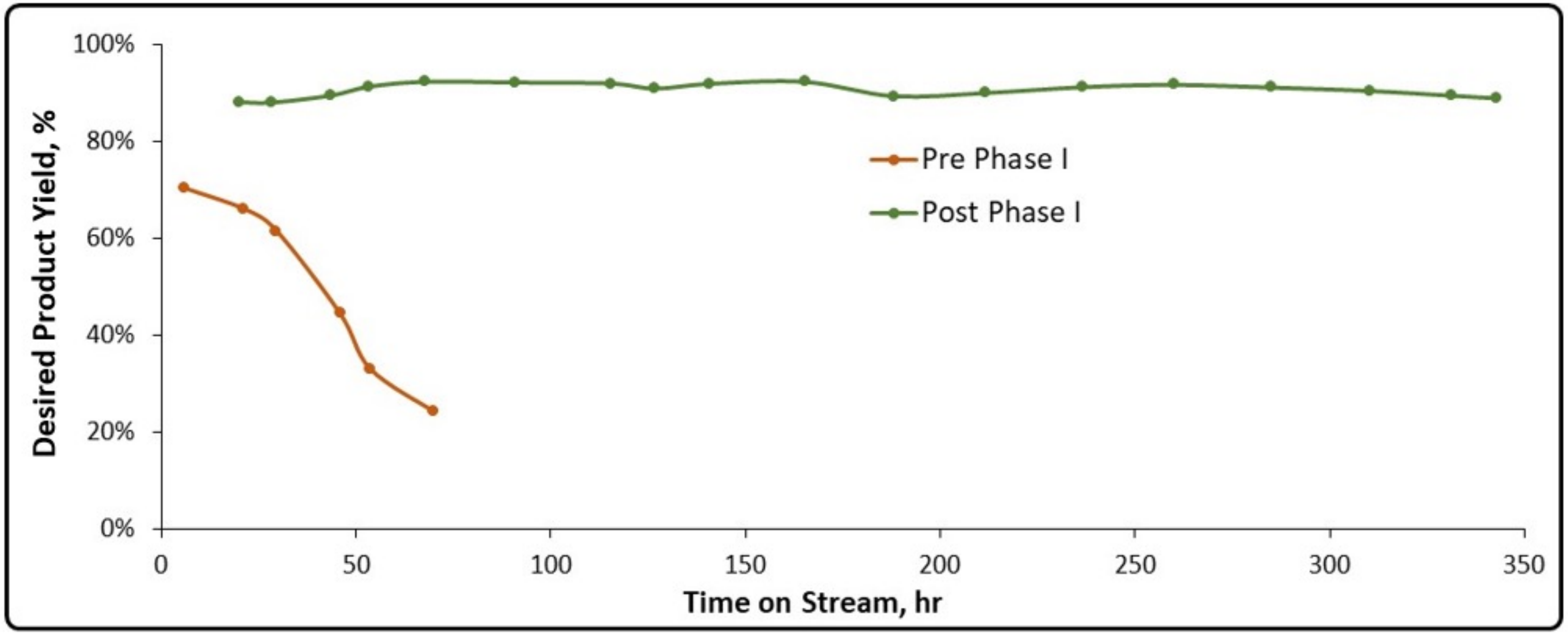
Spot	A	X
1	76.4	23.6
2	72.2	27.8
3	81.0	19.0
4	82.5	17.5



- **TEM Analysis:** Element maps show evidence of co-localization of metal A and X.
- Spot analysis of nanoparticles reveals alloy formation.
- Molar ratio of A and X matches expected alloy distribution from phase diagram.

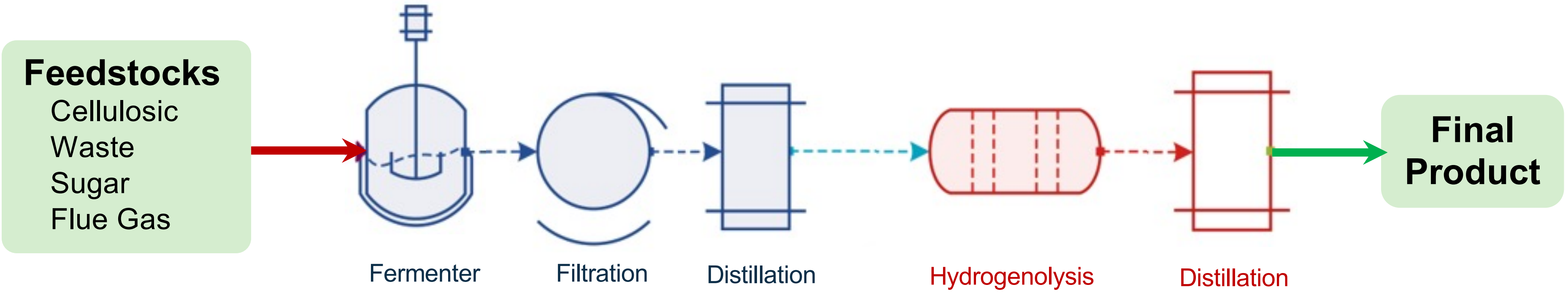
- **CO-Stripping Experiment:** Change in oxidation onset potential with addition of metal A to metal X
  - ✓ Verifies formation of A-X bimetallic alloy
  - ✓ Results in increased electron density on metal A
- Provides explanation for synergistic behavior in experimental results.

Catalyst Stability Demonstration



- Catalyst stability data comparing copper based (Pre-Phase I) catalyst **vs** low-pressure hydrogenolysis catalyst developed during Phase I of the project.
- Copper-based catalyst was tested at **13MPa**, 200°C, and weight hourly space velocity (WHSV) of 0.8 hr^{-1}. Phase I catalyst was tested at **~4MPa,** 145°C, and WHSV of 0.8 hr^{-1}.

Economic Update from Phase I Results



Simplified process flow diagram used in the TEA

Parameter	Pre-Phase I	Post-Phase I	% Reduction	Description
Annual Catalyst Cost ($/ton)	780	620	21	Improved catalyst lifetime and stability
Capital Expense ($/ton)	540	450	16.7	Reduced hydrogenolysis pressure
Operating Expense ($/ton)	1140	950	16.7	Reduction in frequent catalyst maintenance and hydrogen pressure
Total Production Cost ($/ton)	5700	4700	17.5	Improved product selectivity and everything mentioned above

Phase II Work Plan

Start — End

Completed | Future Work

Fiscal Year (FY) 2020 Oct. — 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	Achieve catalyst regeneration and spent-regenerated catalyst performance with greater than 90% of fresh catalyst level.
September 2022	Demonstrate > 500-hour TOS experiment with a product yield > 85% over the engineered catalyst.

Summary

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 the hydrogenolysis catalyst that can operate ≤ 5MPa pressure and demonstrated the catalyst lifetime beyond 300 hours TOS with product selectivity > 85%.
Future Work	▪ Develop an engineered catalyst that is tolerant for feedstock impurities and operate ~5Mpa. Demonstrate the catalyst stability beyond 500 hours TOS. Update the process and economic analysis.

Quad Chart Overview

Timeline

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

	FY 2021	Active Project
U.S. Department of Energy Funding	$200,000	$400,000 (FY 2021-2022)
Visolis	$87,000	$174,000 (FY 2021-2022)

Barriers Addressed

- Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous, and Bio-Oil Intermediates to Fuels and Chemicals
- Ct-J. Process Integration

Project Goal

Develop a low-pressure and water-tolerant hydrogenolysis catalyst to convert the fermentation derived C6 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

Acknowledgement

- **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, a member of the Energy Materials Network.

Pacific Northwest NATIONAL LABORATORY

VISOLIS CARBON NEGATIVE MATERIALS

ChemCatBio Chemical Catalysis for Bioenergy

Energy Materials Network U.S. Department of Energy

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Thank you!

ChemCatBio Team

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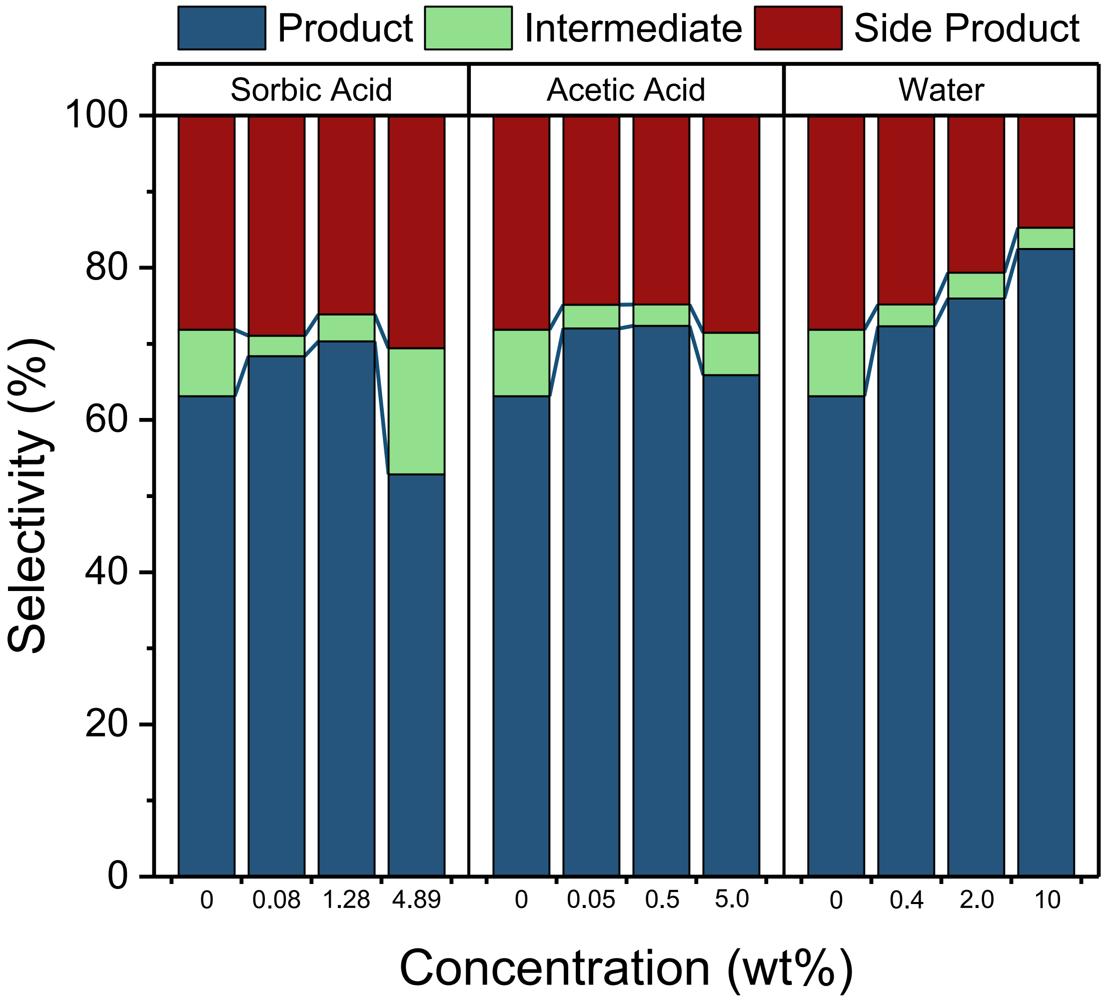
Bioenergy Technologies Office

Impact of Feedstock Impurity on Hydrogenolysis



- Combinatorial experiments were conducted to identify the impact of the impurities.
- Impurities in the form of sorbic acid and acetic acid at concentration below 1% improves the hydrogenolysis performance.
  - ✓ At lower concentration levels sorbic acid and acetic acid might interact with the strong base sites to improve the performance.
- Presence of water in the feed mixture tends to improve the hydrogenolysis performance.
- Flow experiments and catalyst characterization are planned to better understand the influence of these impurities.

2019 Peer Review Response

Lack of technical information in the peer review discussion

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

Potential benefit from the third-party interaction

Visolis is having ongoing discussion with potential suppliers about customized catalyst to be able to scale the material and reaction. This project will access the ACSC and CCPC from the CCB to further develop this catalyst.

Constraints in achieving the high selectivity

The constraint to the selectivity is to manage the right balance between the C-C scission, C=O and over saturation via hydrogenation. We will be comparing to a baseline standard achieved by commercial catalyst.

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