ChemCatBio
Chemical Catalysis for Bioenergy

Pacific Northwest
NATIONAL LABORATORY

DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

CCB DFAs: Terephthalic Acid Synthesis from Ethanol via p-Methyl Benzaldehyde with LanzaTech

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: 05/15/2018
- Project end date: 06/30/2019
- Percent complete: 50%

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded			200K	
Project Cost Share*			86K	

Barriers Addressed

- Ct-F. Increasing the Yield from Catalytic Processes
- Ct-E. Improving Catalyst Lifetime

Objective

Develop the catalytic conversion of ethanol to chemical intermediates to establish the path for an economical and renewable production of terephthalic acid and phthalic anhydride.

End of Project Goal

Demonstrate conversion of acetaldehyde to methyl benzaldehyde(s) at selectivity greater than 70% with at least 20% selectivity to p-methyl benzaldehyde and complete cost-benefit analysis on terephthalic acid.

Approach

- Ethanol is one of the most versatile, renewable compounds for fuel additives, drop-in fuel, and platform chemicals.
- LanzaTech and PNNL have demonstrated the path for infrastructure compatible jet fuel generation from ethanol.
- Developing the path for high-value / volume chemicals from ethanol will benefit the ethanol-to-fuel program to be cost competitive and help the overall success of the biomass program to enable the bioeconomy.

LanzaTech
capturing carbon fueling growth

Expertise in…
- ❑ Fermentation
- ❑ Process Development
- ❑ Process Economics
- ❑ Commercialization

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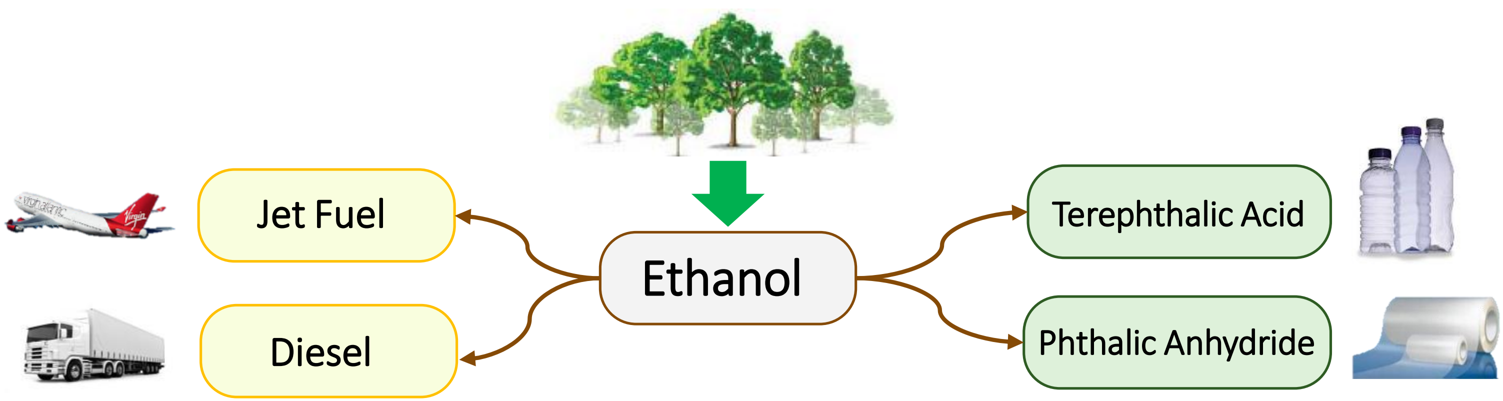
Expertise in…
- ❑ Catalyst Synthesis
- ❑ Catalyst Evaluation
- ❑ Green Chemistry
- ❑ Process Development

Hybrid technology development for the bio-based fuels and chemical production.



Approach (Technical)

Mixed Metal Oxide Catalyst Development

Identifying the combination of mixed oxide and promoter material to achieve high conversion and selectivity.

Shape Selective Catalysts

Investigate shape selectivity to achieve high selectivity to the p-methyl benzaldehyde over its ortho counterpart.

Flow Reactor Testing

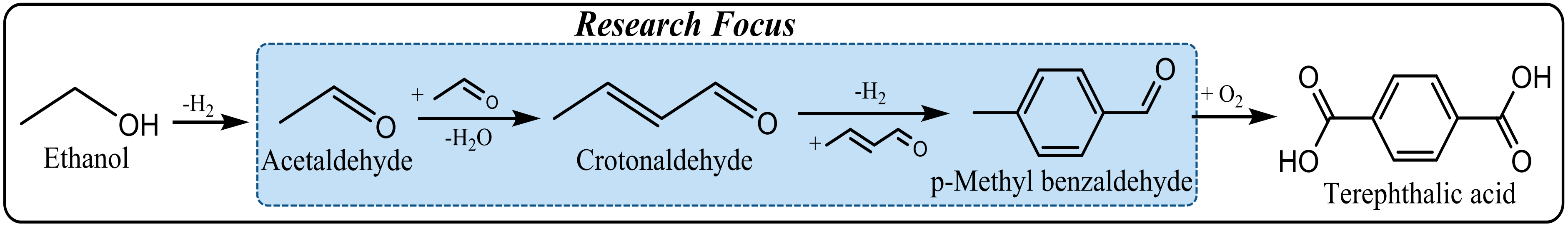
Optimize operating conditions and investigate the catalyst lifetime for at least 50 hours time-on-stream and determine regeneration requirements and methods.

Cost Estimation

Develop simple cost-benefit analysis for terephthalic acid production via the p-methyl benzaldehyde compared to the traditional process.

Technical Accomplishments

Background Information:



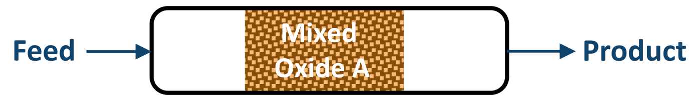
Simplified reaction scheme for the conversion of ethanol to p-methyl benzaldehyde for the terephthalic acid synthesis

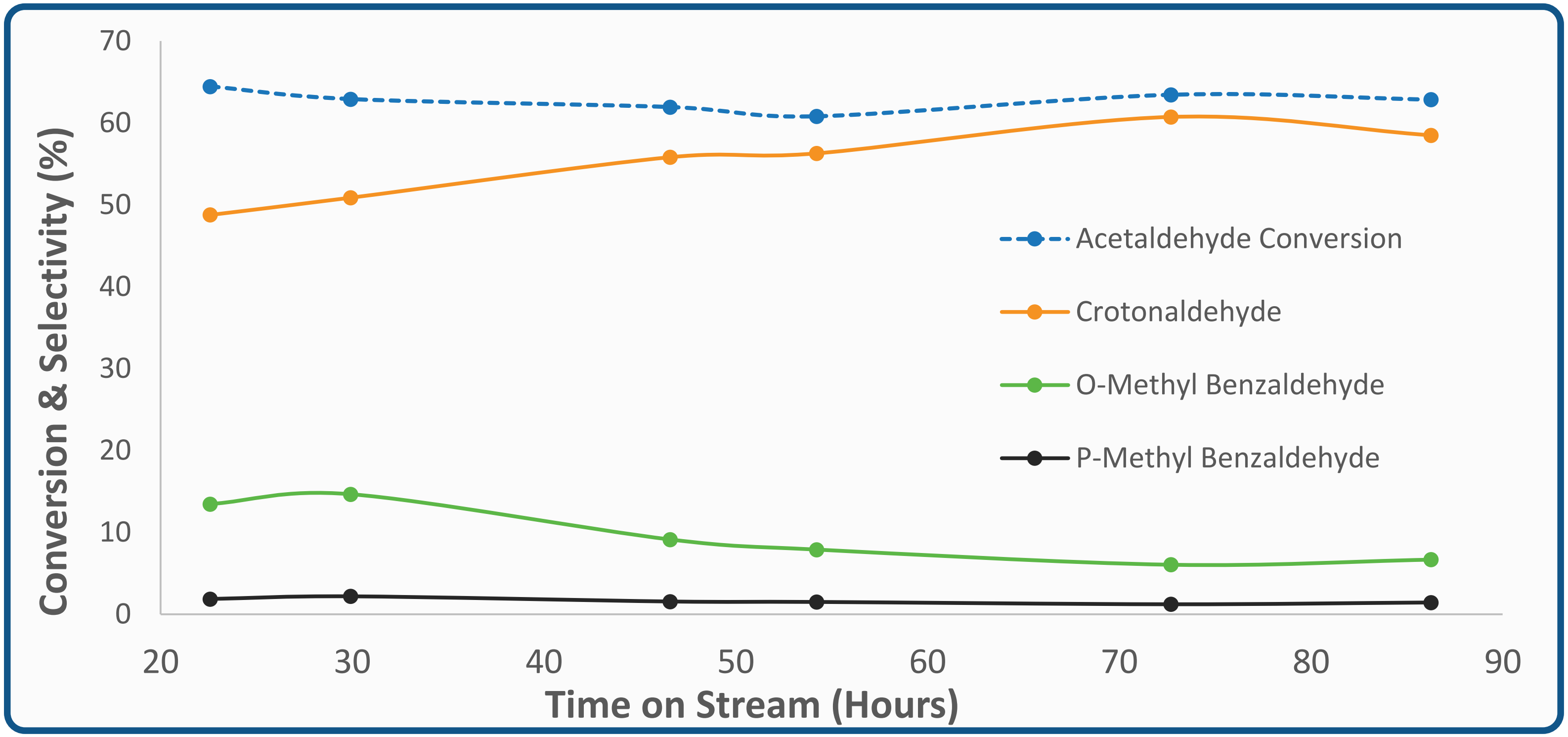
- Very limited work has been reported on the conversion of ethanol/ acetaldehyde to methyl benzaldehyde(s).
- Modified zeolites and hydroxyapatites (Ca-P) were tested for the acetaldehyde conversion to methyl benzaldehyde(s).
- The highest reported yields for the methyl benzaldehyde(s) from the acetaldehyde pathway was between 10-20%.

Source: Moteki, T., et al., ChemCatChem, 2017. 9(11): p. 1921-1929; Zhang, L., et al., ChemSusChem, 2016. 9(7): p. 736-48.

Technical Accomplishments

Single-Bed Acetaldehyde Conversion to Methyl Benzaldehyde

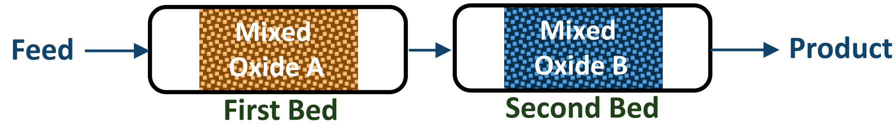


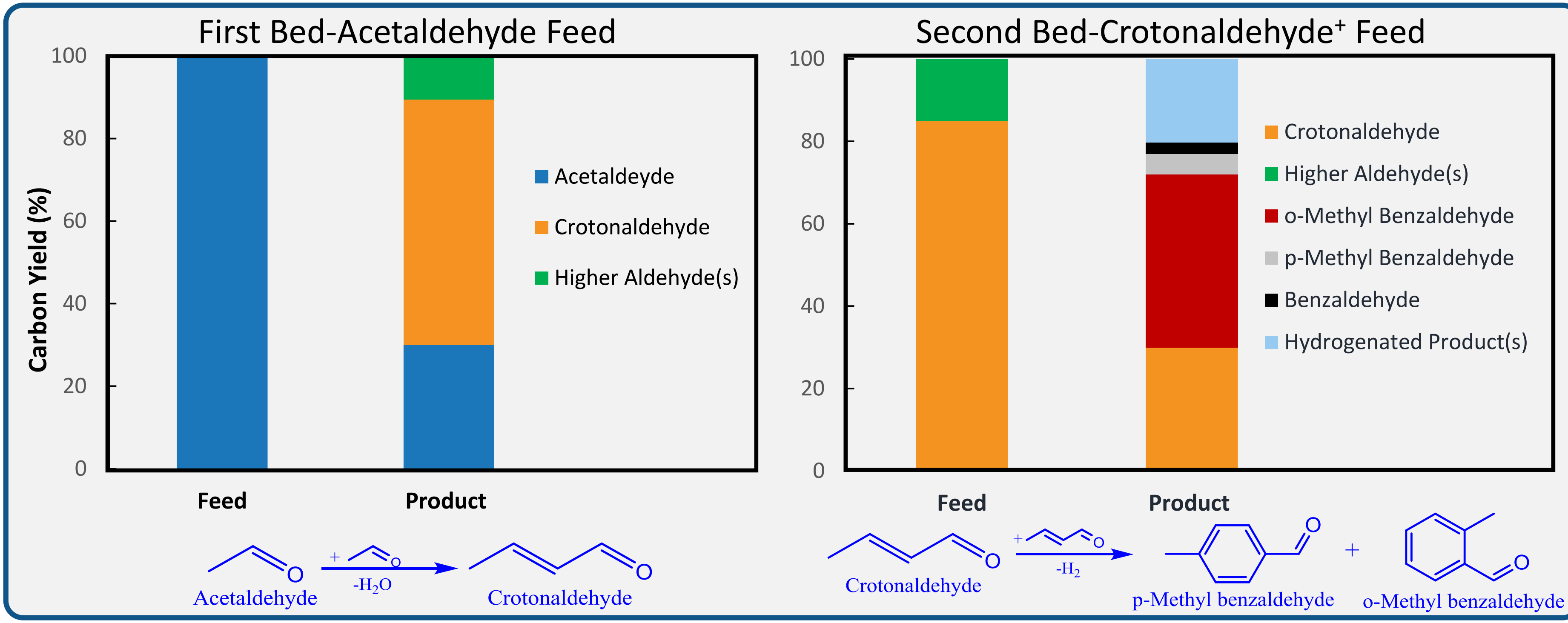


- Product selectivity: 10-20% to methyl benzaldehyde(s); 50-60% to 2-butenal (crotonaldehyde).
- The catalyst lost initial activity with time-on-stream, which reduced the conversion of crotonaldehyde to 2-methylbenzaldehyde.

Technical Accomplishments

Dual-Bed Acetaldehyde Conversion to Methyl Benzaldehyde





- Over all carbon yield around 50% was achieved for the methyl benzaldehyde(s).
- By-product formation from the aldehyde hydrogenation needs to be avoided to improve the overall methyl benzaldehyde(s) selectivity and shape selective catalysis for the higher p-methyl benzaldehyde selectivity.

Future Work

Start — On Track — End

Completed	Future Work

FY18 Jun — FY18 Dec — FY19 Jun

March 2019	Operating condition optimization at which ≥60% selectivity to the methyl benzaldehyde(s).
March 2019	Demonstration of the catalyst stability with 50 hours time-on-stream at 60% selectivity to methyl benzaldehyde(s).
June 2019	Demonstration of 70% overall selectivity to the methyl benzaldehyde(s) and 20% selectivity to p-methyl benzaldehyde.
June 2019	Complete cost-benefit analysis on terephthalic acid and phthalates via methyl-benzaldehyde pathway from experimental data generated from this project.

Summary

Overview	• Conversion pathway for ethanol to chemical intermediates to establish a marketable process for economical production of terephthalic acid and phthalic anhydride.
Approach	• Mixed oxide catalyst development for the acetaldehyde conversion to methyl benzaldehyde(s) and shape selective catalysis to improve the p-methyl benzaldehyde selectivity.
Technical Progress	• Developed a stable mixed oxide catalyst system (dual stage) that converts acetaldehyde to methyl benzaldehyde(s) with over all carbon selectivity over 50%.
Relevance	• Stable catalyst for biological intermediates conversion and approach to bridge biochemical conversion feedstocks with catalytic upgrading.
Future Work	• Demonstration of catalyst stability with 50 hours time-on-stream at 70% selectivity to overall methyl benzaldehyde(s), 20% selectivity to p-methyl benzaldehyde and complete the cost-benefit analysis.

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capturing carbon fueling growth

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Energy Materials Network
U.S. Department of Energy

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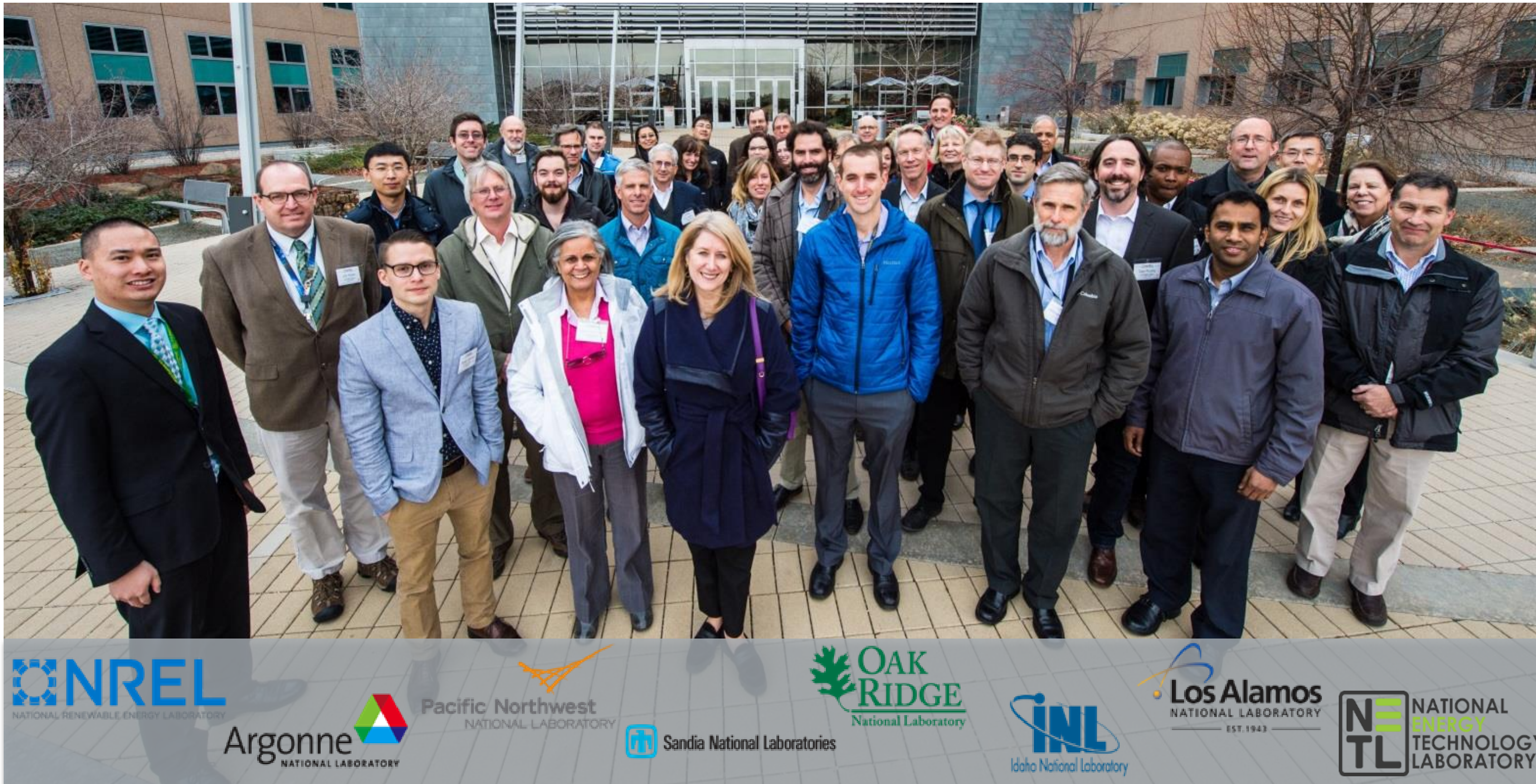

ChemCatBio Team

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