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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**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*)

### 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)

*FY19 Seed Project
Quad Chart Overview

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

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.

<table>
<thead>
<tr>
<th>DOE Funded</th>
<th>Total Costs Pre FY17**</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding (FY 19-Project End Date)</th>
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<tbody>
<tr>
<td></td>
<td>200K</td>
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<tr>
<td>Project Cost Share*</td>
<td>86K</td>
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**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.
### Approach (Technical)

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<th>Mixed Metal Oxide Catalyst Development</th>
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<td>Identifying the combination of mixed oxide and promoter material to achieve high conversion and selectivity.</td>
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<th>Shape Selective Catalysts</th>
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<td>Investigate shape selectivity to achieve high selectivity to the p-methyl benzaldehyde over its ortho counterpart.</td>
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<th>Flow Reactor Testing</th>
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<td>Optimize operating conditions and investigate the catalyst lifetime for at least 50 hours time-on-stream and determine regeneration requirements and methods.</td>
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<th>Cost Estimation</th>
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<td>Develop simple cost-benefit analysis for terephthalic acid production via the p-methyl benzaldehyde compared to the traditional process.</td>
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Technical Accomplishments

Background Information:

- 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%.

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.
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.
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.
**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 overall 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.
This research was supported by the DOE Bioenergy Technology Office.

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!

ChemCatBio Team

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Energy Efficiency & Renewable Energy
Bioenergy Technologies Office