ChemCatBio
Chemical Catalysis for Bioenergy

Catalytic Upgrading of Biochemical Intermediates (CUBI)
2.3.1.101-104

2021 BETO Peer Review - ChemCatBio

Rick Elander[1], Zhenglong Li[2], Vanessa Dagle[4], Cameron Moore[3], Derek Vardon[1], David Johnson[1]

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March 10, 2021

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Chemical Catalysis for Bioenergy

Biochemical Conversion TEA – Introduction

<u>Biochemical Process Analysis Team</u>
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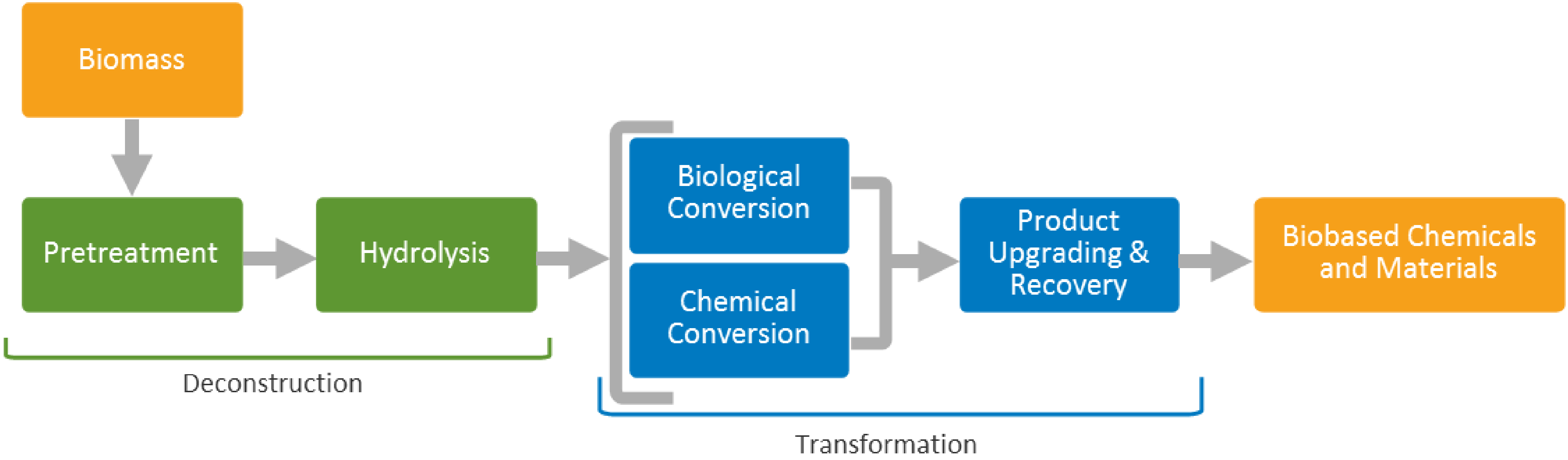
Biochemical Conversion – Process Pathway



Deconstruction

- Thermal/chemical/mechanical pretreatment to reduce biomass recalcitrance
- Enzymatic saccharification to produce sugars
- Depolymerization of lignin

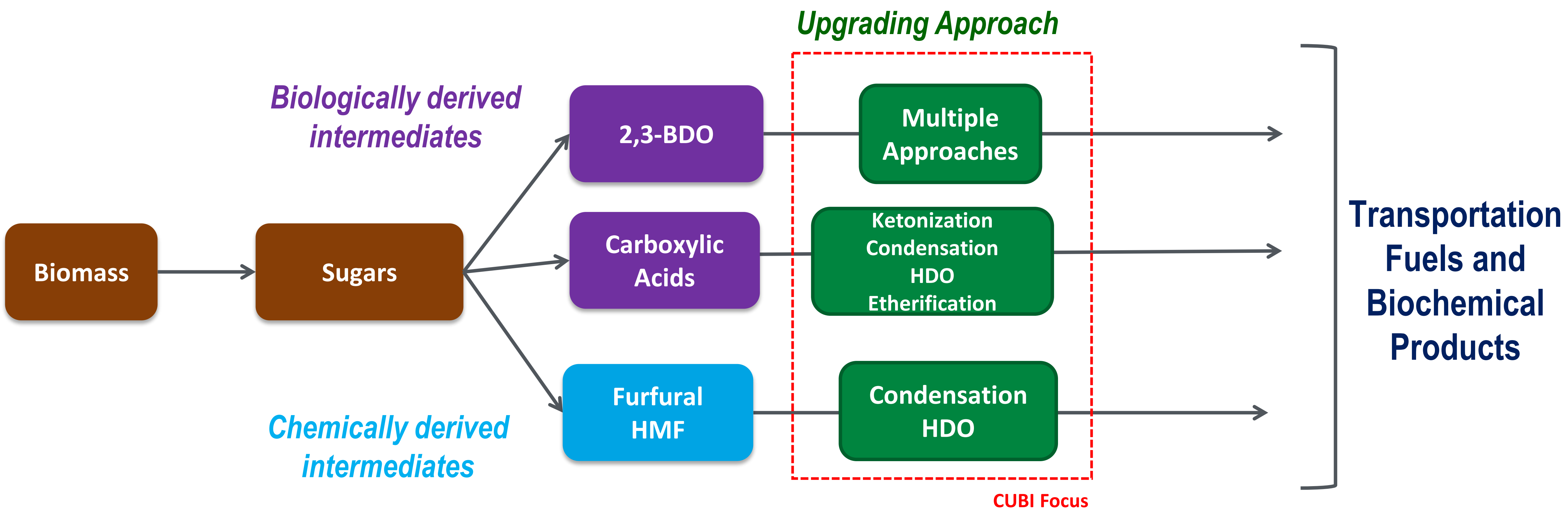
Transformation

- Biological conversion of sugars to upgradeable intermediates for fuel/chemical products
- Catalytic conversion of biological intermediates
- Catalytic conversion of sugars/furans

CUBI Focus

- Biological/catalytic conversion of lignin-derived intermediates

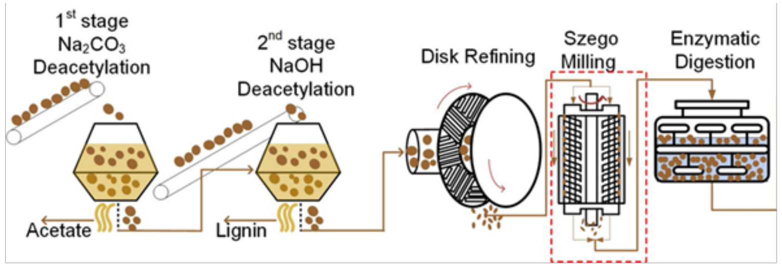
CUBI Overview – Primary Intermediates and Routes

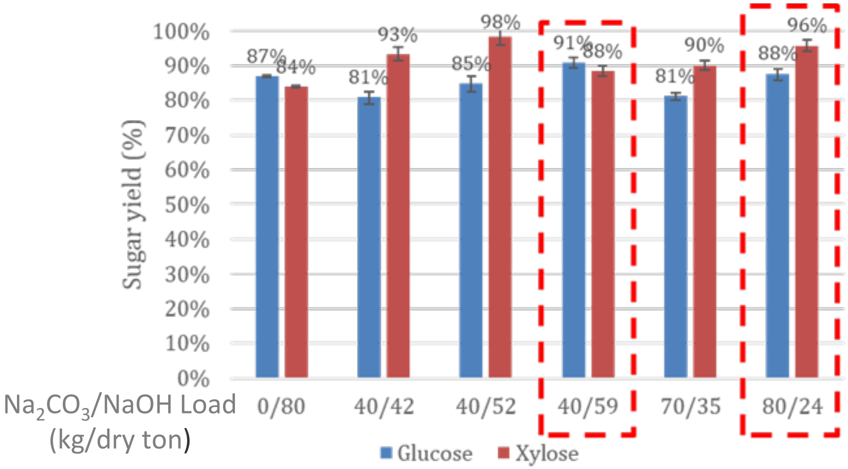


Generation of Biochemical Intermediates

Biomass → Sugars

Atmospheric-Pressure Mild Alkali and Mechanical Refining Pretreatment (DMR) to Improve Operational Reliability



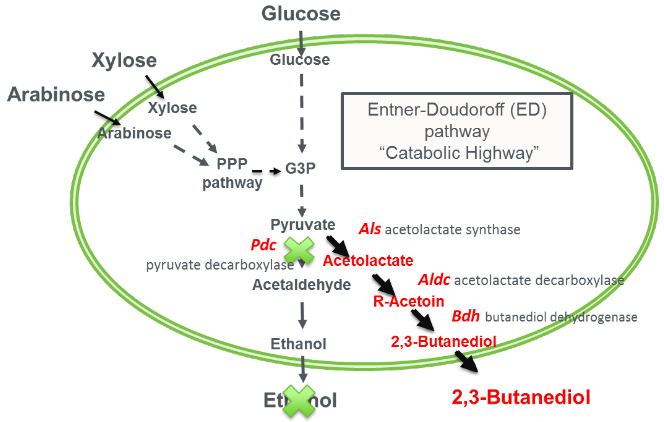


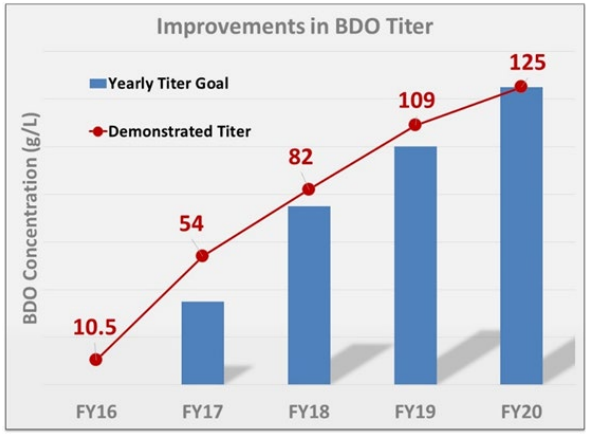
Enzymatic hydrolysis sugar yield (7 day)

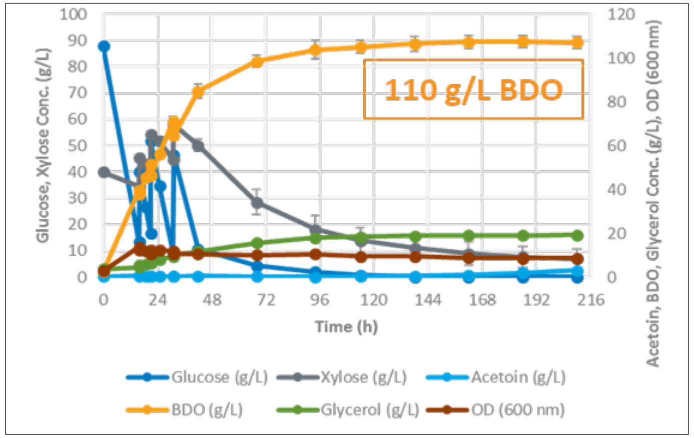
- Solids loading : 20% (w/v)
- Enzyme Loading: 10 mg protein/g glucan (Novozymes Ctec3/Htec3)

Sugars → 2,3-BDO

Fermentation Strain and Process to Achieve > 100 g/L of 2,3-BDO on Mixed C6-C5 Corn Stover Hydrolysate Sugars



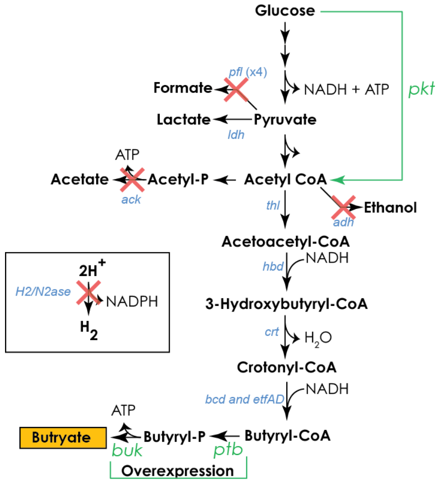


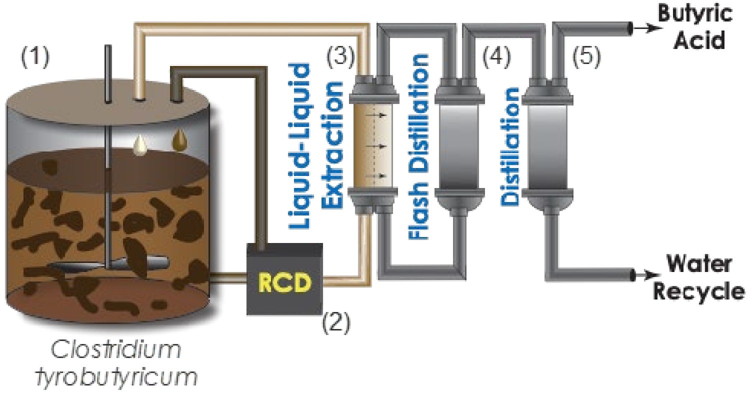


Generation of Biochemical Intermediates

Sugars → **Carboxylic Acids**

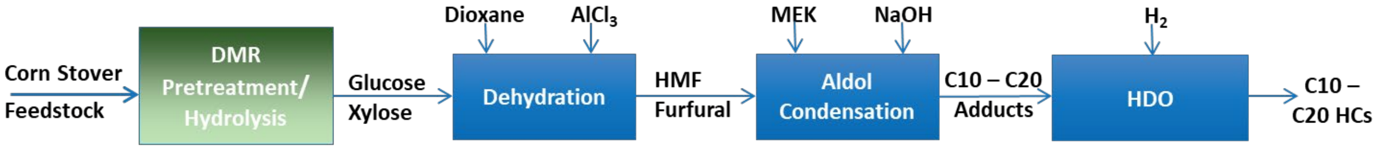
Mixed C6-C5 Corn Stover Hydrolysate Sugars to Produce Butyric Acid with In-situ Product Removal



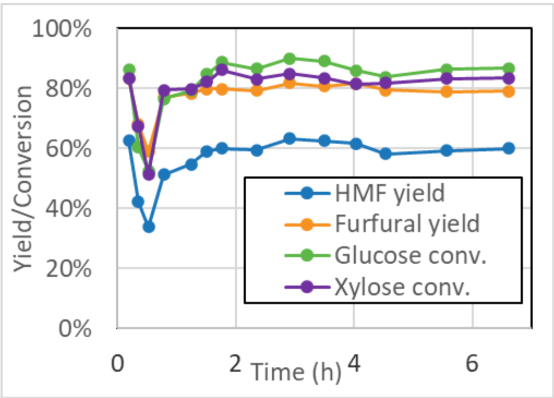


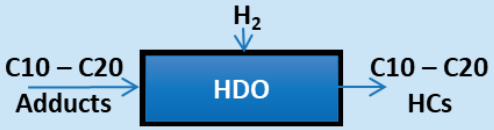
Sugars → **Furfural HMF**

Non-Biological Conversion of Mixed C6-C5 Corn Stover Hydrolysate Sugars to Furans (Furfural, HMF)



Furfurals Production in Flow Reactor from Mixed Hydrolysate Sugars



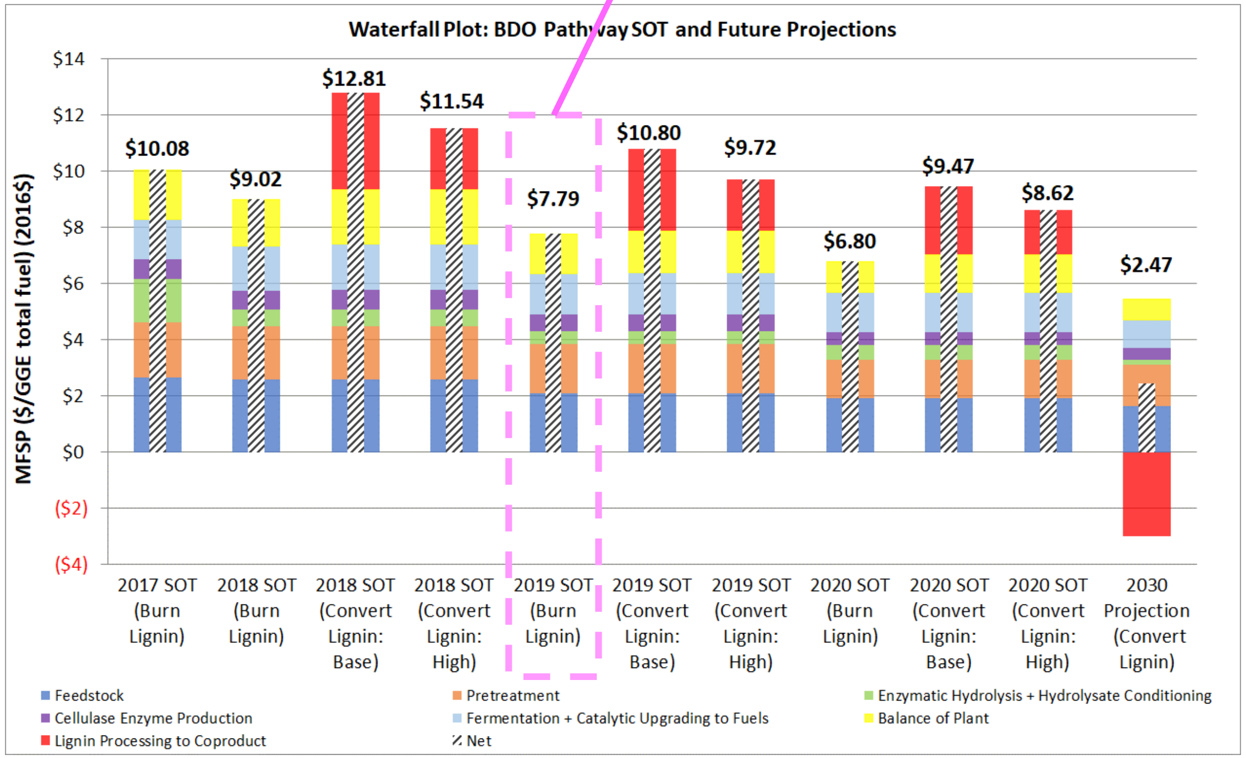


- HDO product (82 mol% yield) from mixed furfural/HMF/MEK aldol product with Pd/SiO_2-Al_2O_3
- Catalysts with acidic silica-alumina supports (MS-13 & -25) needed to produce HCs.
- HC product very good jet/diesel fuel properties Cloud Pt -64 °C, CN 61, 60%/80% jet/diesel BPt ranges

State of Technology Progression for Biochemical Process Routes

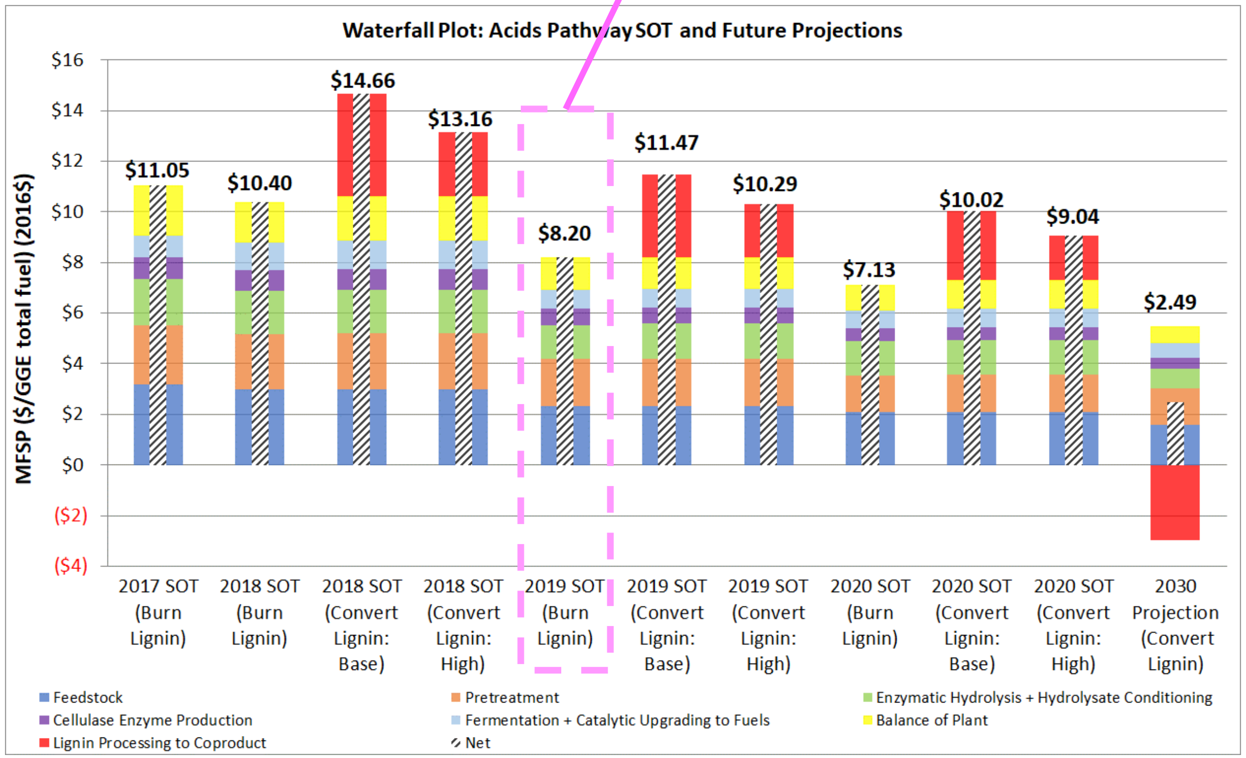
2,3-BDO Pathway

Starting Basis for CUBI Catalytic Upgrading Cost Reduction



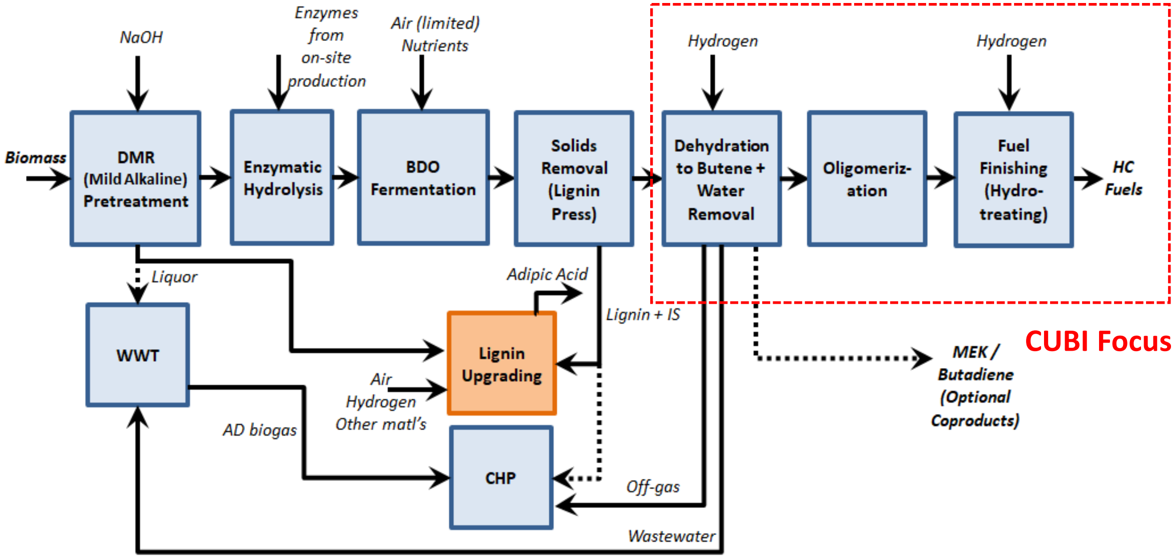
Carboxylic Acids Pathway

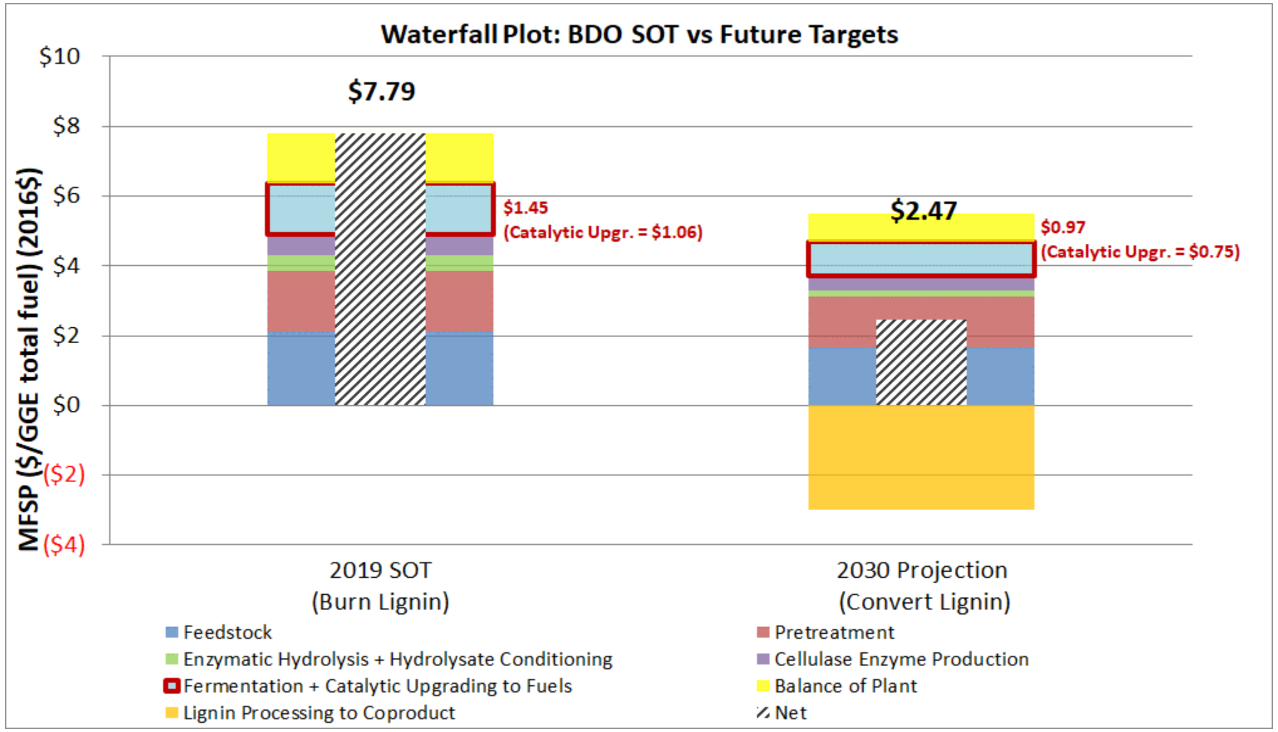
Starting Basis for CUBI Catalytic Upgrading Cost Reduction



2020 Biochemical Conversion State of Technology (Ryan Davis et al., NREL)

CUBI TEA Modeling: BDO (Biological) to Fuels

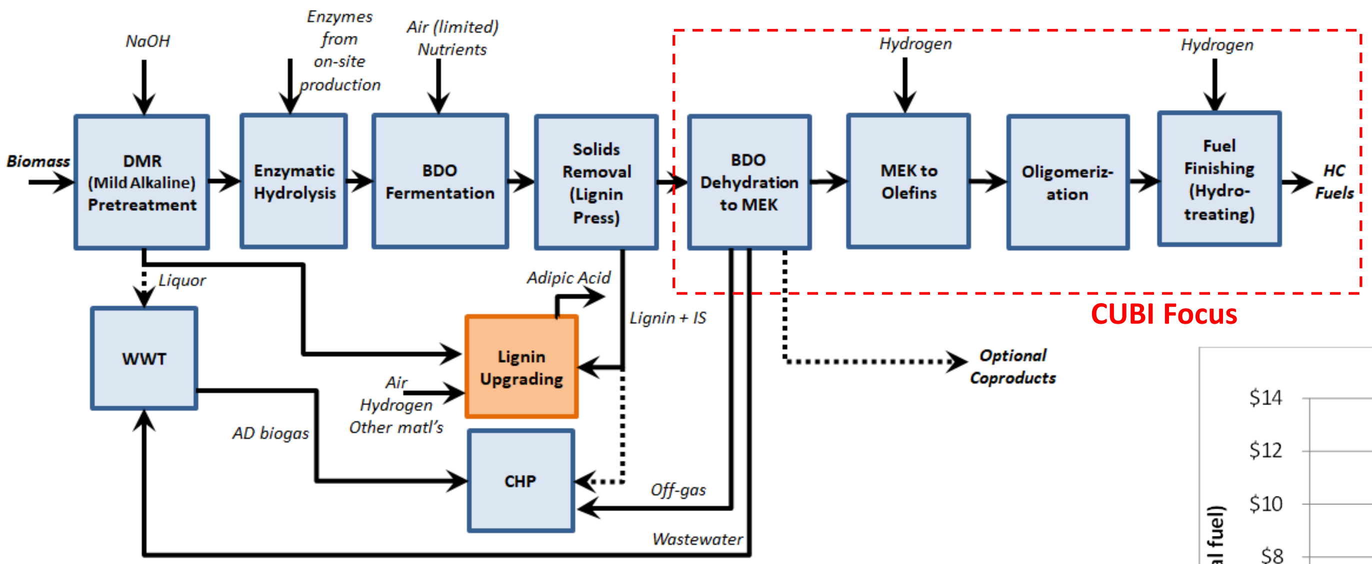


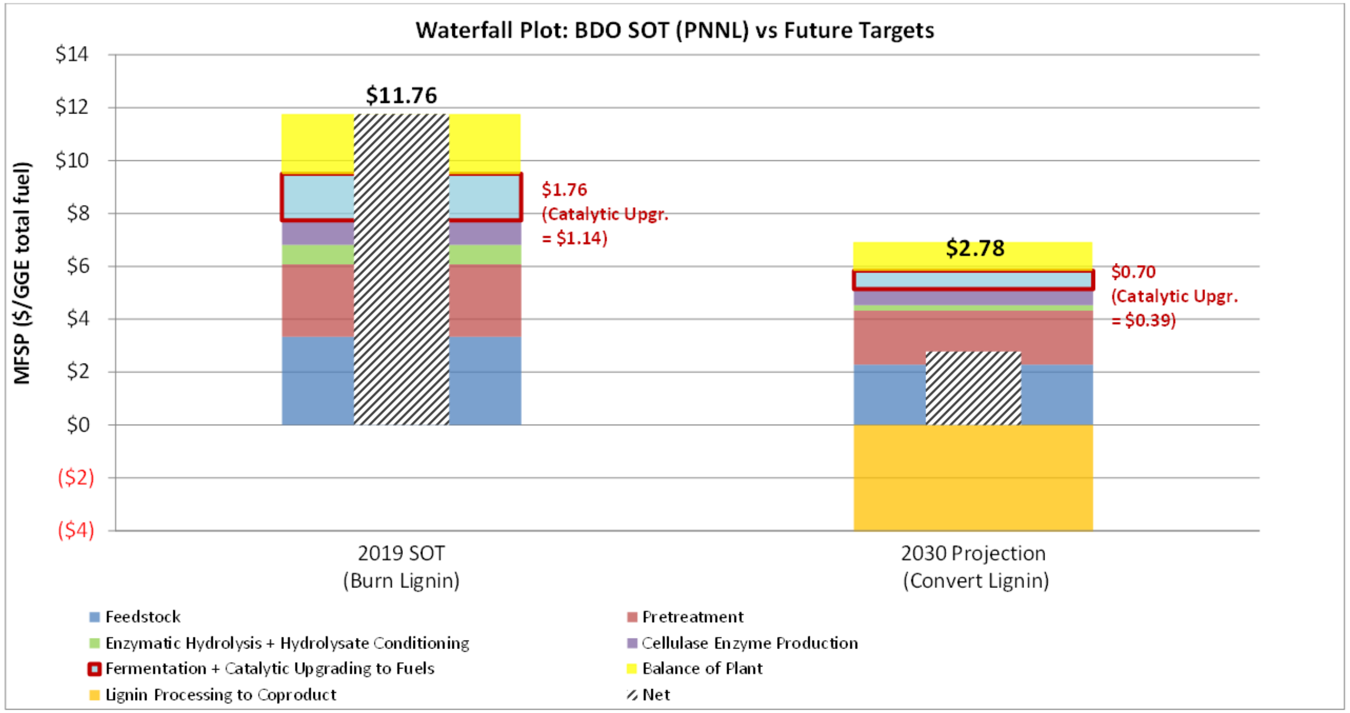


Key Drivers/Risks/Gaps

- Catalyst cost: higher WHSV, robustness/ lifetime
- Reduce energy demands via lower T in BDO upgrading
- Extent of cleanup requirements for clarified BDO (polishing filtration/IX?)
- High water content – more concentrated BDO (Separations Consortium)

CUBI TEA Modeling: BDO (Biological) to Fuels via MEK

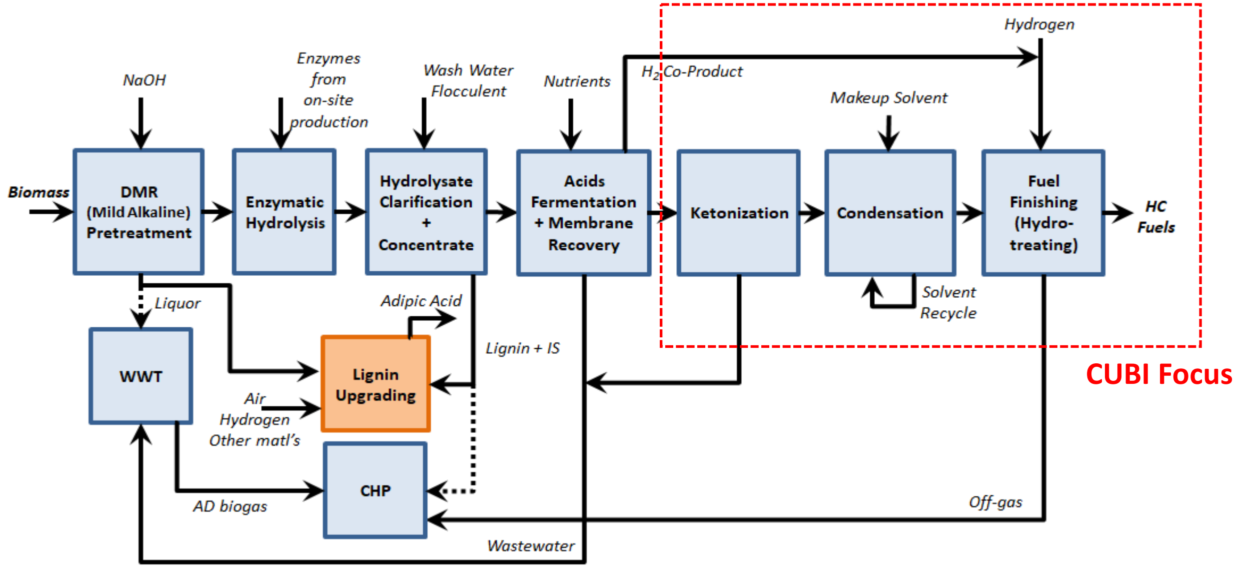


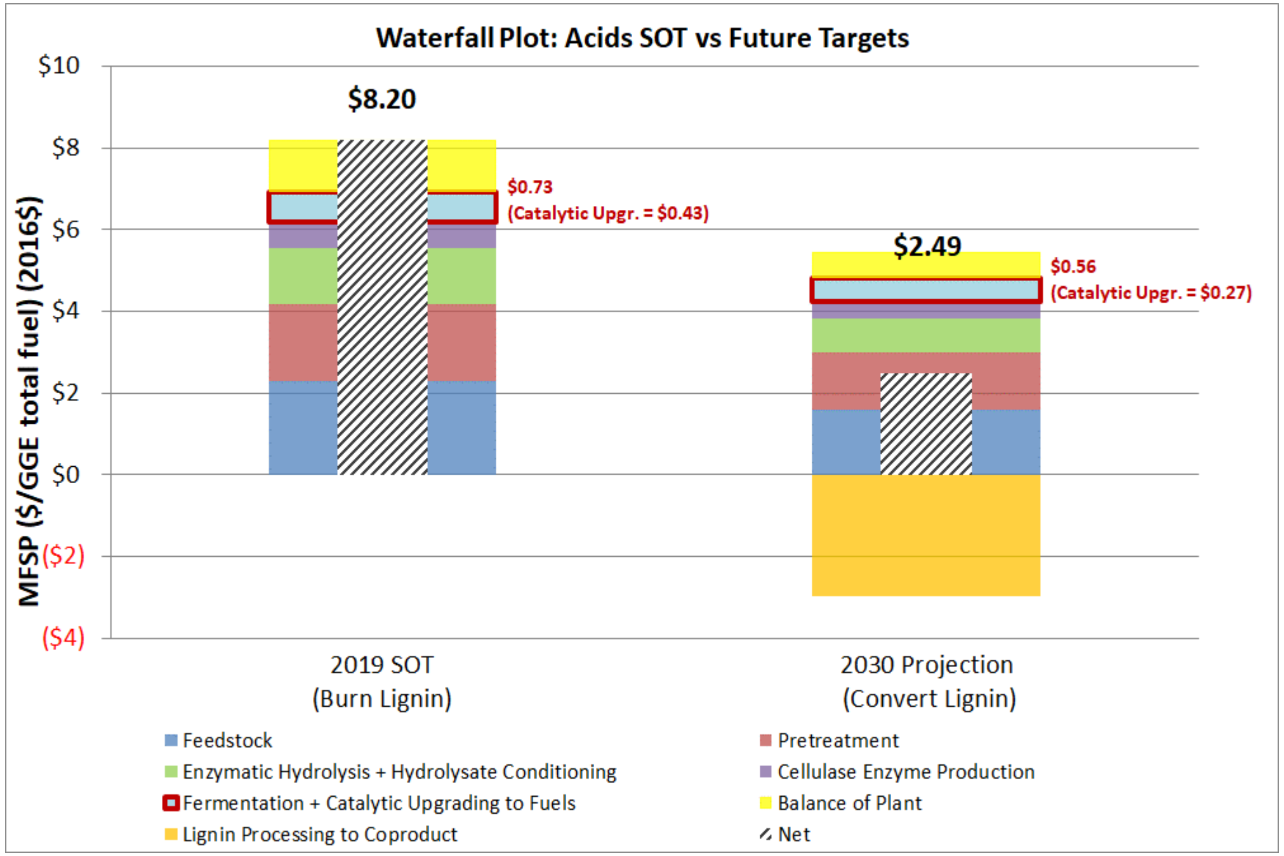


Key Drivers/Risks/Gaps

- Improved carbon yield for dehydration step
- Reduce energy demands/costs via lower T (BDO upgrading) and/or condensed phase upgrading
- Extent of cleanup requirements for clarified BDO (polishing filtration/IX?)
- High water content – more concentrated BDO (Separations Consortium)

CUBI TEA Modeling: Carboxylic Acids (Biological) to Fuels

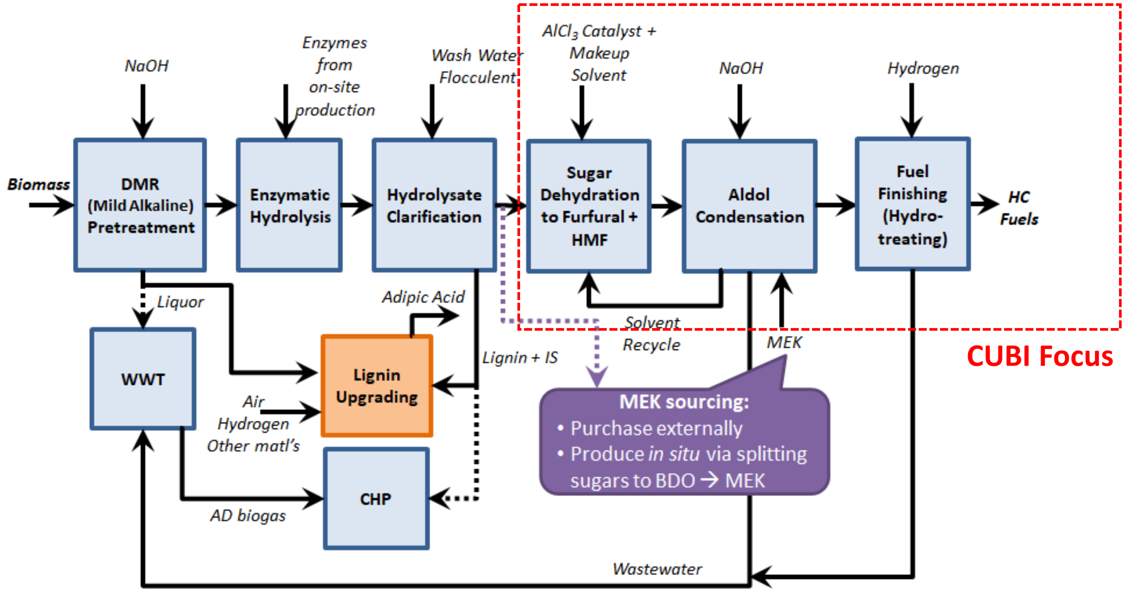


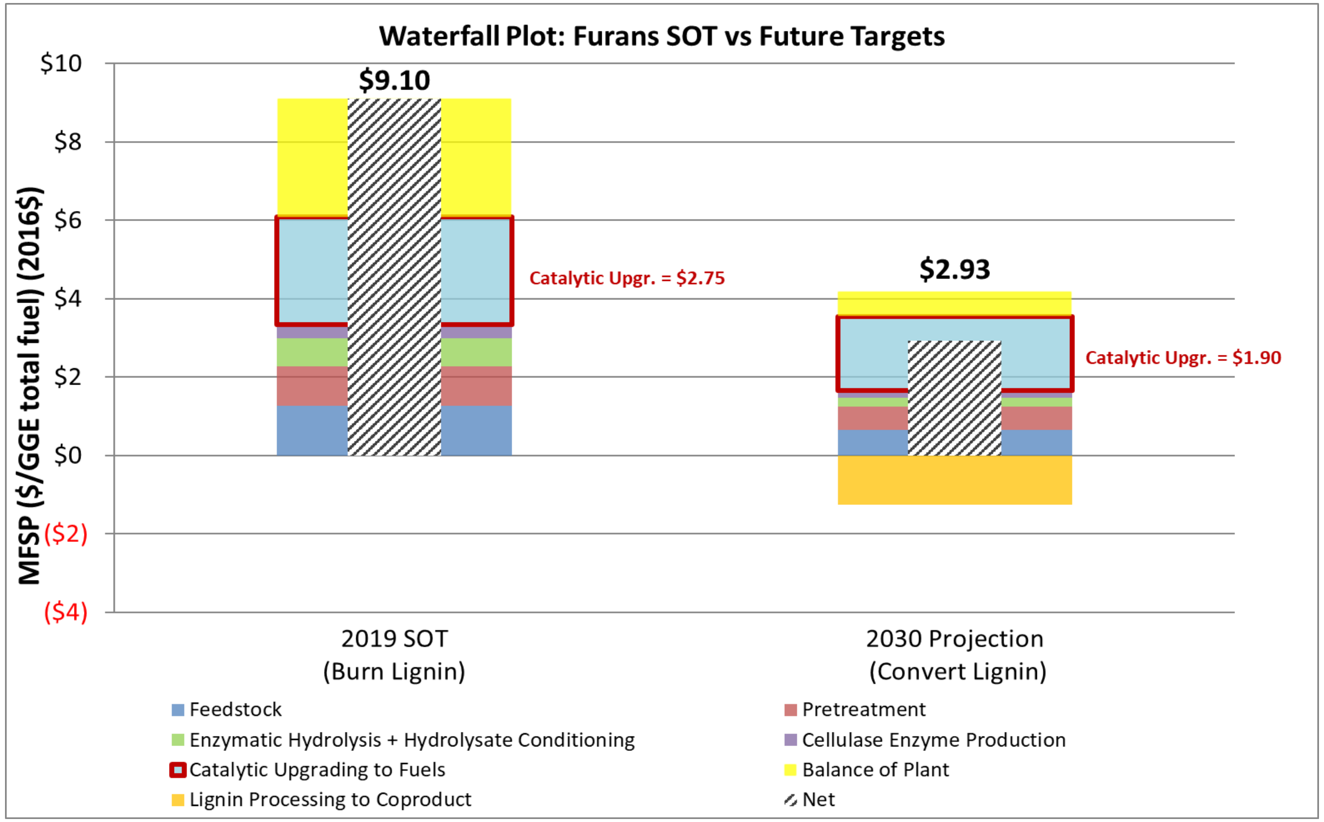


Key Drivers/Risks/Gaps

- Catalyst cost: higher WHSV (ketonization), less costly metallurgy (HDO)
- Reduce energy demands via lower solvent loading (condensation), lower T (ketonization/HDO)
- Condensation operating logistics (catalyst recovery/regeneration in slurry CSTR)

CUBI TEA Modeling: Furfurals (Catalytic) to Fuels



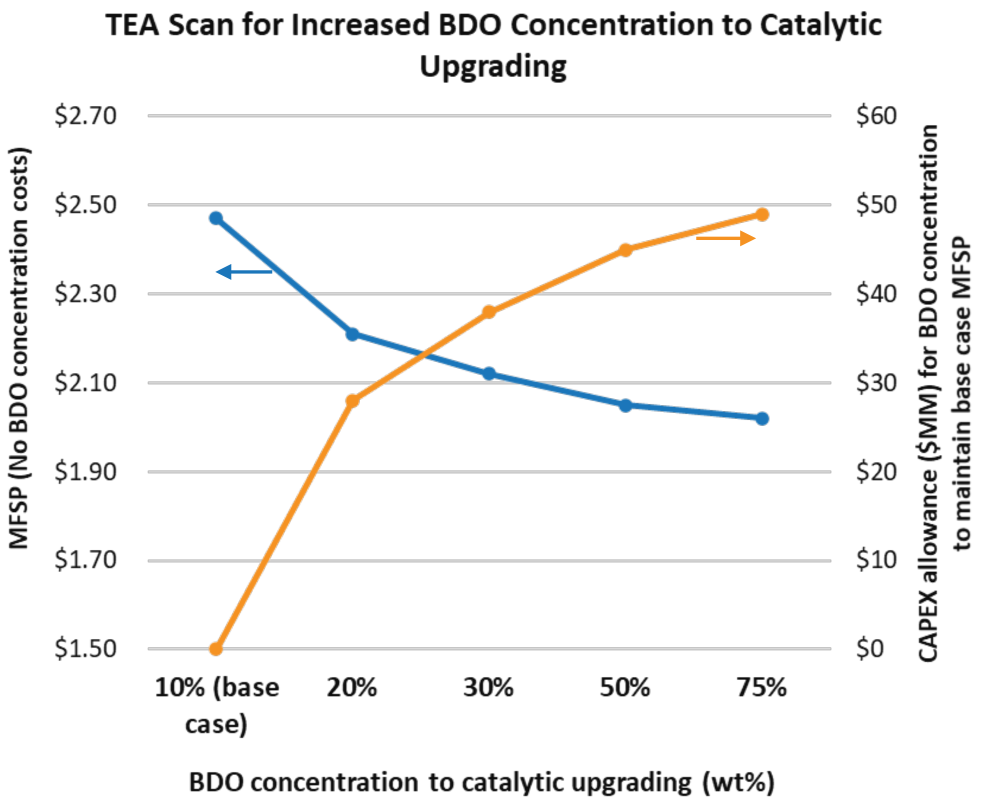


Key Drivers/Risks/Gaps

- Increase conversions/yields; minimize solvent loading (dehydration)
- MEK sourcing - purchased externally (dedicated case) or produced *in situ* (integrated case)
- **High fuel yields** (1.4X) vs BDO/acids pathways (low CO2 production) – but higher opex/energy demands

TEA to Inform Key Process Drivers – Water Removal from Fermentation Broth

TEA Analysis - BDO to olefins route: Effect of reduced water content on MFSP (2030 Design Case)



- A more concentrated BDO stream (especially from 10 wt% to 30 wt%) has a significant impact on projected MFSP
- Analysis allows for determination of allowable costs to achieve original MFSP

Water Removal Technology Evaluation – BDO Fermentation Broth

Technology	Note	Findings
Vacuum evaporation (Baseline)	Near-term consideration (bench scale & pilot plant)	BDO loss, likely part of process but additional processes needed
Membrane separations (Pervaporation dewatering)	Type A membranes: Polymer-GO composites	• SF = 25, • Flux up to 0.5 LMH, • High vacuum (28-29 inHg) required
	Type B membranes: Hydrophobic nanoporous ceramics	• SF = 21, • Flux up to 0.6 LMH, • Very mild vacuum (0-6 inHg) required
Sorbent extraction (BDO-selective)	Hydrophobic MOFs and zeolites	Could separate BDO, glycerol, acetoin Remove other impurities

Michael Hu (ORNL), 2019 CUBI seed project on BDO broth separations

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2 OAK RIDGE National Laboratory
3 Los Alamos NATIONAL LABORATORY EST. 1943
4 Pacific Northwest NATIONAL LABORATORY

March 10, 2021


ChemCatBio Project Structure

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL)
- **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, ANL, ORNL)
- **Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)
- **Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)

Industry Partnerships (Phase II Directed Funding)

- **Opus12** (NREL)
- **Visolis** (PNNL)
- **Sironix** (LANL)

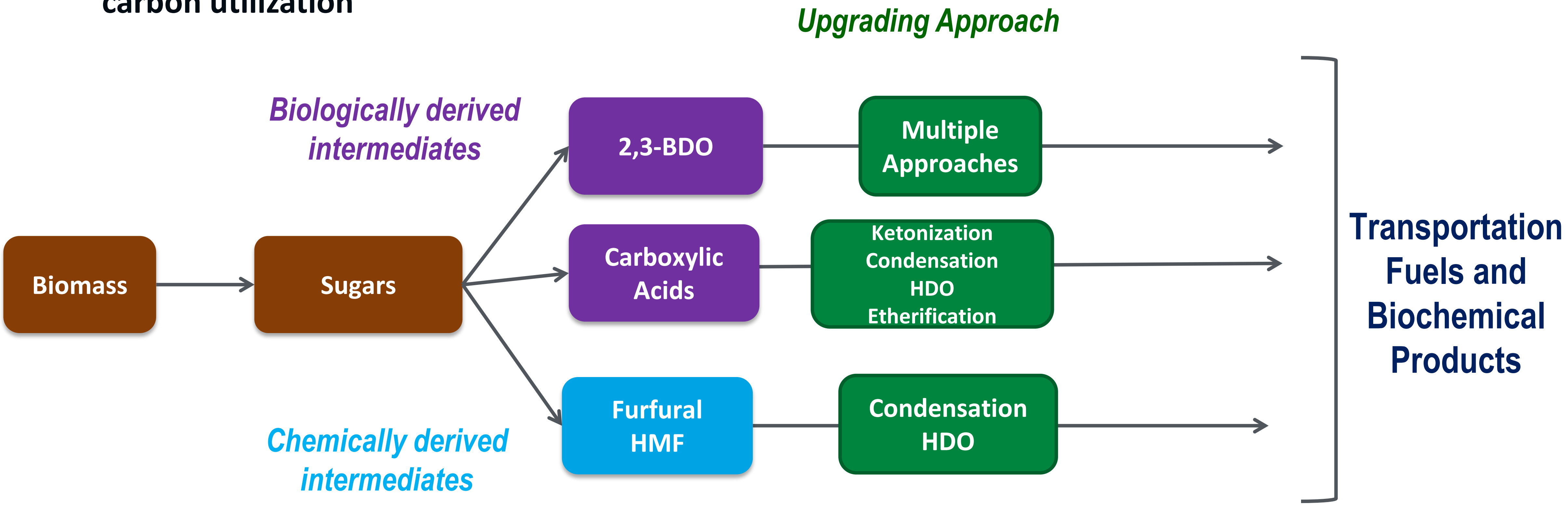
Cross-Cutting Support

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

Project Overview

Project Goal:

- Improve the **catalytic upgrading of targeted biochemically-derived intermediates** to hydrocarbon fuels and chemical co-products by performing focused and integrated R&D for:
  - Development of catalysts with **improved performance and durability**
  - Mitigation of **process-derived inhibitors**, including water
  - Evaluating integrated and intensified processes to **reduce separations requirements** and **improve carbon utilization**



Project Overview

Project Outcomes:

- Achieve **25% to 33% cost reduction** (depending on pathway) in the **catalytic upgrading process area** of an **integrated biochemical conversion process** to enable overall an MFSP of <$2.5/GGE
- **Reduce reliance on lignin co-product valorization** in biochemical conversion processes by demonstrating **large-market chemical co-product opportunities** from biochemical intermediates that can provide >25% of required co-product valorization revenue
  - Example: 2,3-BDO to butadiene, MEK, iso-butanol

Heilmeier Catechism:

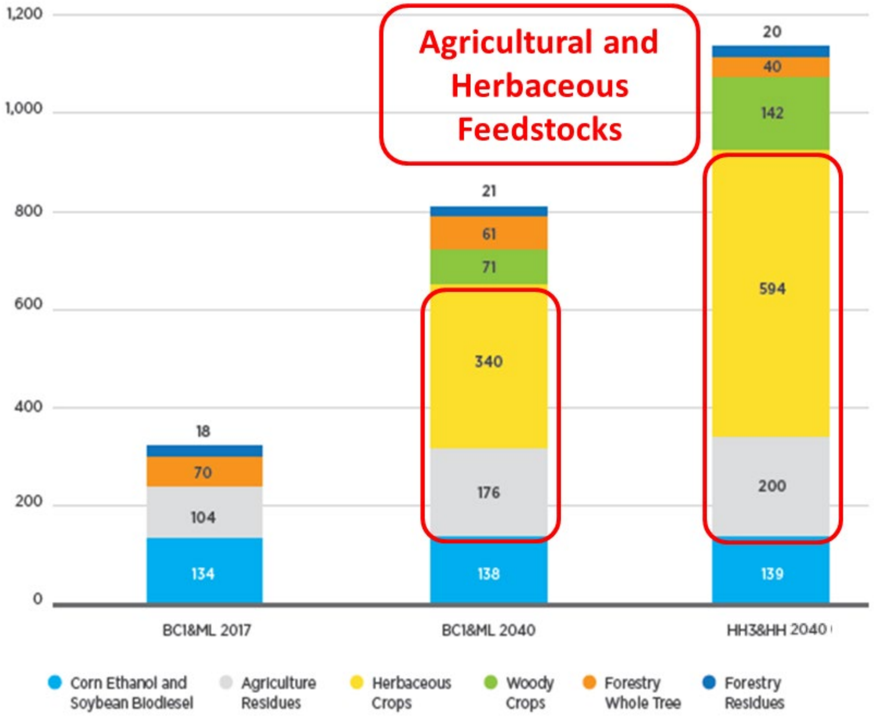
- **What:** Develop and improve catalytic upgrading of biochemical intermediates to fuels and platform chemicals in an integrated process context
- **Today:** Biochemically-derived intermediates used in catalytic upgrading are generally derived from clean sugars with low water content and few inhibitors
- **Importance:** CUBI project is the primary effort within BETO portfolio for “downstream” Biochemical Conversion process development and integration
- **Risks:** Impacts of inhibitors found in real biochemical conversion process streams on catalyst performance/stability/lifetime and how to mitigate is not understood

Project Overview

Key Differentiators

- Facilitate **transition** from catalytic upgrading of **Gen 1 sugars** (cane and starch-derived) to **cellulosic sugars**/derived intermediates
- Focusing on **largest segment** of projected biomass **feedstock resource base** (ag residues and herbaceous energy crops)
- Provide a **quantitative performance and economic assessment** of several catalytic upgrading approaches using **biomass hydrolysis/fermentation** intermediates
- Quantify performance and economic impacts of **biogenic inhibitors**
- Exploit the **specificity of intermediate compounds** generated via **biochemical deconstruction** and **biological upgrading**

US Biomass Resource Availability by Type (million dry tons/year)



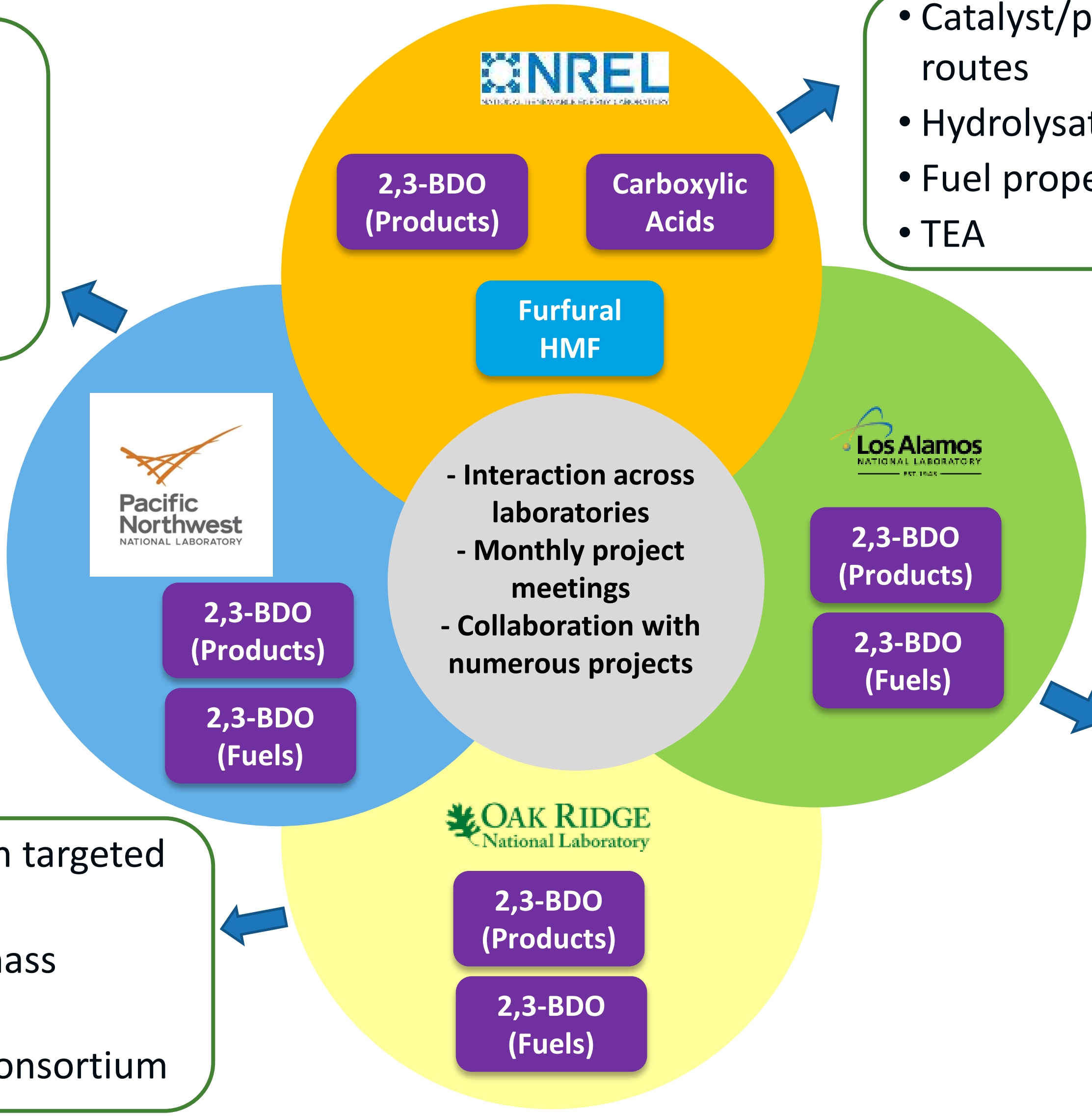
https://www.energy.gov/eere/bioenergy/downloads/2016-billion-ton-report-volume-2-environmental-sustainability-effects

1 - Management

Capabilities and Expertise Across Multiple National Laboratories

- Catalyst/process development on targeted routes
- High-throughput catalyst testing and characterization
- Fuel property testing
- TEA

- Catalyst/process development on targeted routes
- Hydrolysate/fermentation intermediates
- Fuel property testing
- TEA



- Catalyst/process development on targeted routes
- HDO optimization in flow reactors
- Catalysis-assisted phase separation for aqueous product recovery

- Catalyst/process development on targeted routes
- Zeolite expertise applied to biomass derived alcohols/diols
- Coordination with Separations Consortium

1 - Management

Cross-Project Interactions

2.3.1.10X Catalytic Upgrading of Biochemical Intermediates

Catalysis

- 2.5.1.30X Consortium for Computational Physics and Chemistry (ChemCatBio)
- 2.5.4.304 Advanced Catalyst Synthesis and Characterization (ChemCatBio)
- 2.5.4.301 Catalyst Cost Model Development (ChemCatBio)

SDI Integration Scale-up

- 3.4.2.201 Biochemical Pilot Scale Support and Process Int.

Separations

- 2.5.5.50X Separations Consortium
- 2.3.2.107 Separations in Support of Arresting Anaerobic Digestion
- 3.4.2.502 Conversion of 2,3-BDO to Biojet Fuel

Biochemical Conversion

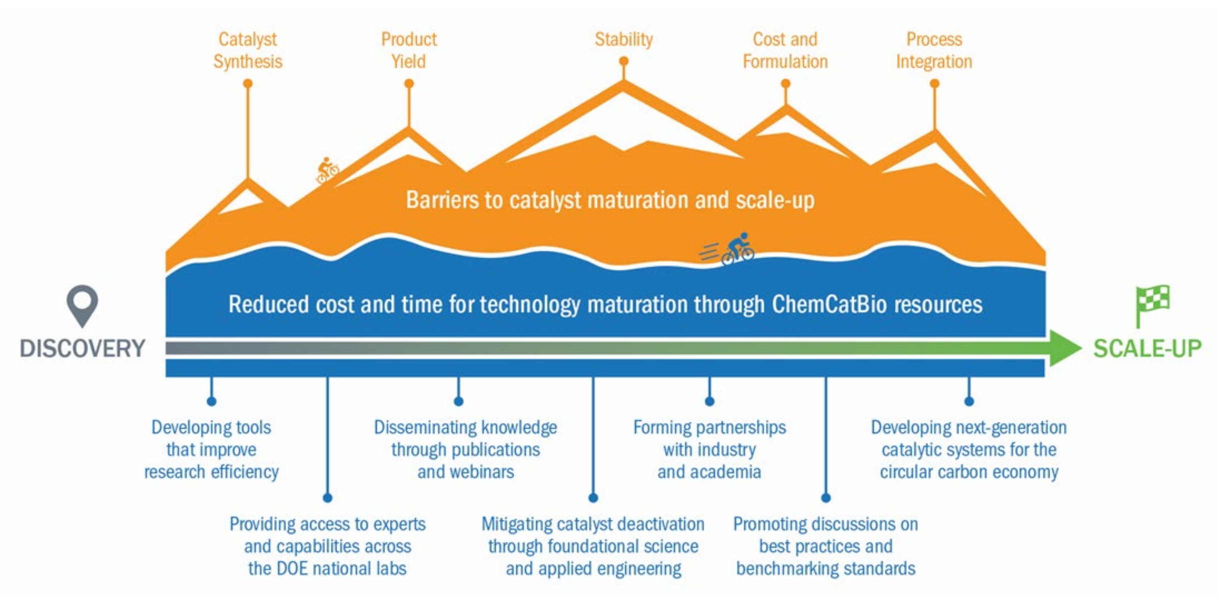
- 2.1.0.100 Biochemical Platform Analysis
- 2.2.3.100 Low Temperature Adv. Deconstruction
- 2.3.2.105 Biological Upgrading of Sugars
- 2.4.1.100 Bench Scale R&D (BDO)

Risk Identification and Mitigation

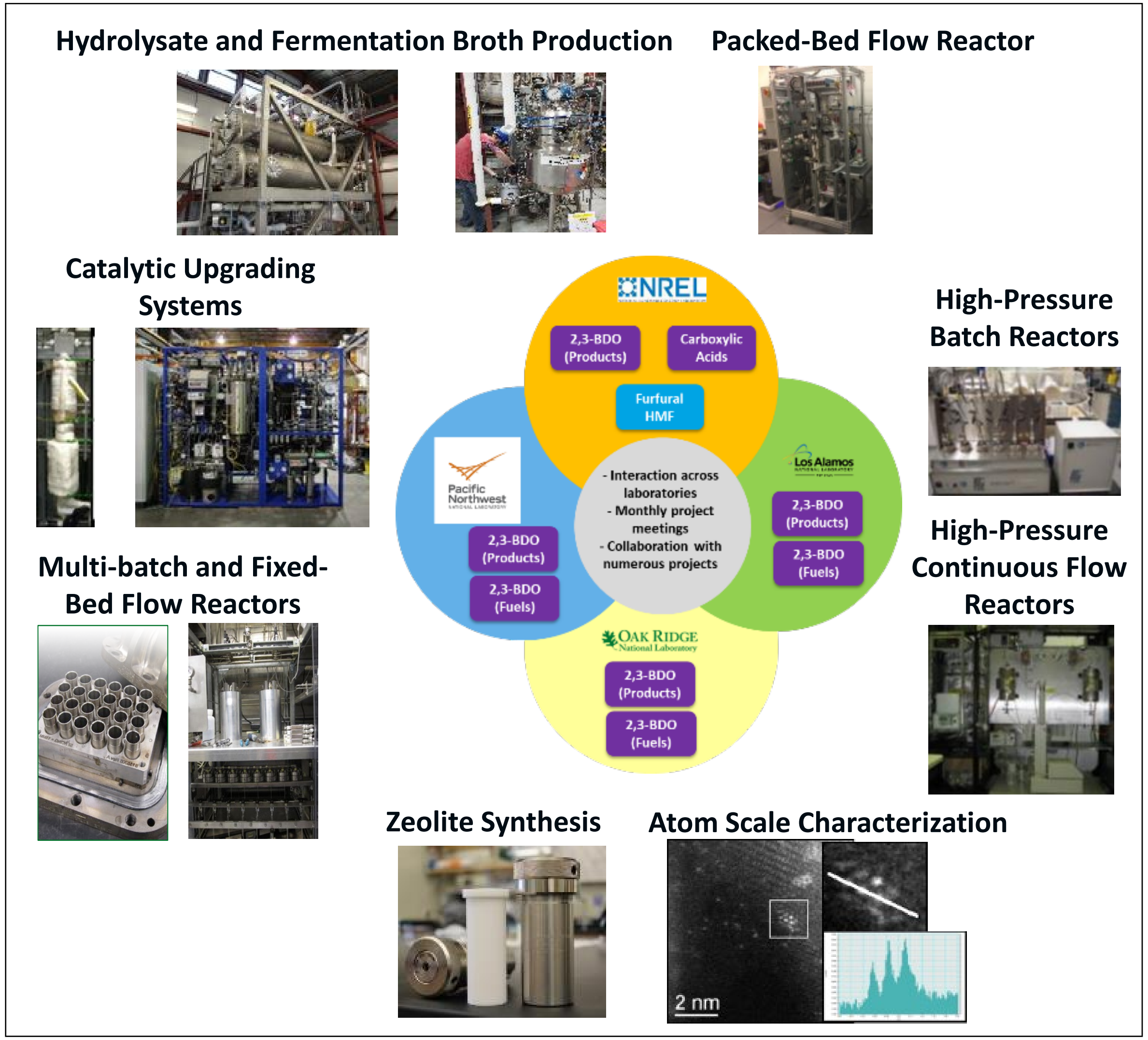
- A primary project focus in FY20-21 is on **process-integration associated risks**
  - Impacts on catalyst performance/stability/lifetime in real biochemical conversion process streams

Identified Risk	Mitigation Approach
Water impacts on BDO upgrading (aqueous fermentation broth)	• Identify costs/process options to remove varying levels of water • Catalyst inactivation characterization • BDO upgrading in gas phase
Catalyst inhibitors from feedstock/hydrolysate/ fermentation broth	• Identification/mechanism of inhibition • Regeneration methods and performance • Upstream process modifications (feedstock preprocessing, pretreatment chemicals, fermentation by-product management)
Excessive coking of the acid metal oxide catalysts for central ketone condensation	• Evaluate impact of temperature and metal oxide acid strength on sustained ketone condensation performance • Validate regeneration strategies following continuous operation

2 – Approach



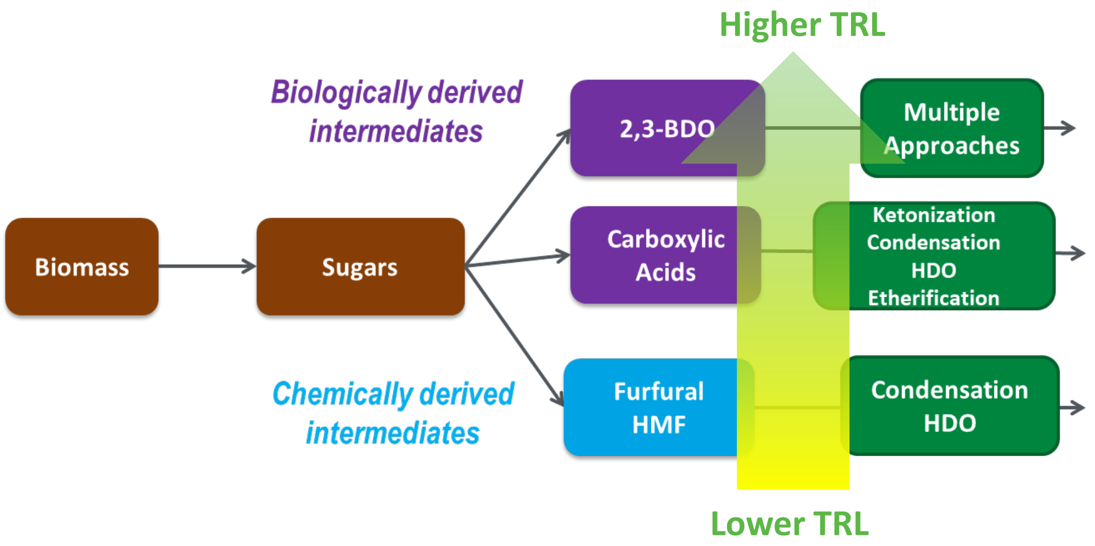
- Advancing catalytic upgrading **process performance and robustness** to produce a range of **targeted, specific fuel** molecules and chemical **co-products**
  - Synthesis, yield, stability, cost, integration
  - Focusing on key risks (inhibitor mitigation)
  - Utilizing experimental and characterization capabilities and modeling tools across 4 CUBI labs and CCB Enabling Projects



2 - Approach

To address **key challenges**, multiple catalytic upgrading routes investigated and evaluated in a coordinated manner using common materials, analytical techniques, reactor systems, fuel characterization methods, and TEA tools

Success factors	Challenges	Strategy
Demonstrate **catalytic upgrading to HC fuel routes** that have commercial relevance and interest	Numerous biochemical-derived intermediates options → multiple catalytic upgrading routes/ approaches	Coordinate with Biochemical conversion projects to focus on intermediates with cost-potential and broad market size applicability
Quantify **impurity impacts from biochemical deconstruction/ upgrading** on catalytic upgrading routes.	Biomass-derived catalyst inhibitors from feedstock, deconstruction unit & intermediates- production units	Comparative assessment of pure & biomass-derived intermediates to identify catalyst inhibitors (including water)
Define **specifications for deconstruction/fermentation streams** for catalytic upgrading, including identification of separations/clean-up needs.	Multiple considerations in optimizing conversion unit operations makes definition of process-stream specifications challenging to meet TEA targets.	Coordinate efforts across projects & multi-lab consortia to focus on critical process-wide considerations: Feedstock selection/specification, Separations/purification, Fundamental catalyst design/process



Biochemical Conversion Pathways

- Pathways identified and selected within broad BETO Biochemical Platform context
- CUBI project is a coordinated effort to develop catalytic upgrading of biochemical intermediates in a collaborative and comparable manner

Go/ No-Go Decision

6/30/2021: Focusing of 2,3-BDO Upgrading Pathways to Fuels and Co-products. BDO upgrading pathway options must achieve the partial cost reduction targets (achieve 30% of the end-of-project milestone target) to continue pathway development in FY21-22.
Focus on BDO pathways.

End-of-project milestone

9/30/2022: Demonstrate improvements consistent with a cost reduction from 25% to 33% (depending on pathway) compared to FY19 SOT in catalytic upgrading of biochemical process-derived carboxylic acids, 2,3-BDO and furfurals intermediates.
For all pathways: BDO, carboxylic acids & furfurals

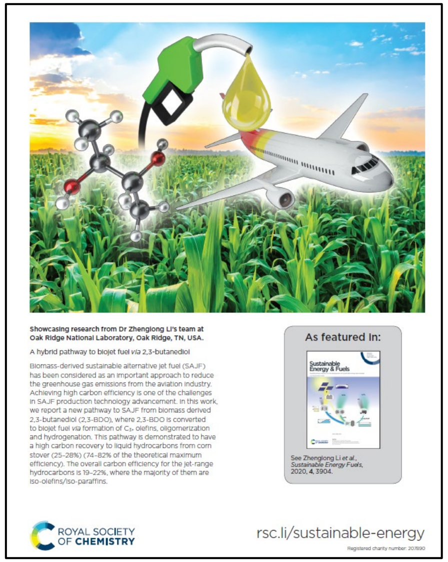
3 - Impact

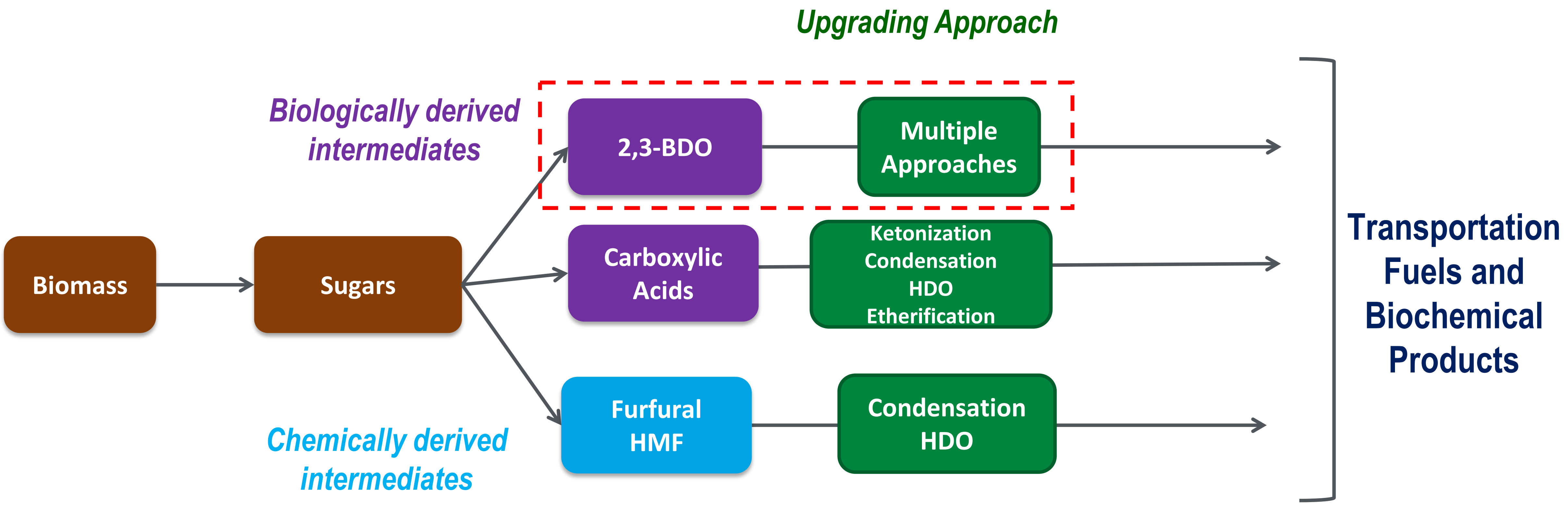
- Documenting improvements in catalytic upgrading area of biochemical conversion design reports and annual SOTs
  - The primary project for catalytic upgrading development and application for BETO biochemical conversion routes

- Numerous impactful publications in major journals – fundamental characterization and process applications
  - 11 peer-reviewed publications (2019-present)
  - 3 patent applications/issued patents (2019-present)

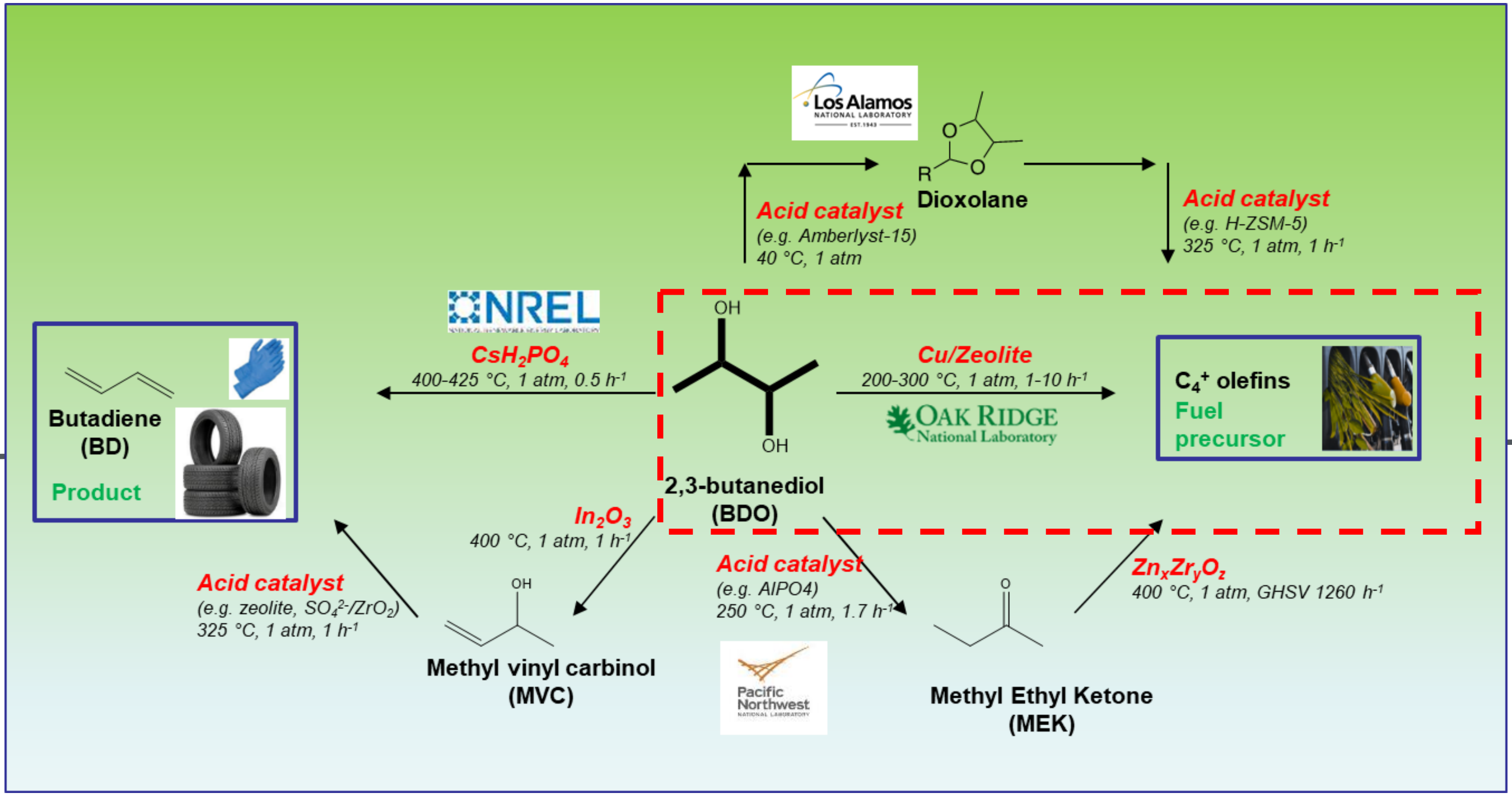
- **Industrial engagement** for catalyst development and process development – utilizing catalytic upgrading technologies developed within project
  - Competitively-awarded TCF and FOA projects with cost-sharing partners for sustainable aviation fuel applications are leveraging DOE/BETO investments

EARTH ENERGY RENEWABLES
FORGE NANO
JM Johnson Matthey Inspiring science, enhancing life
world energy
MATRIC
University of Dayton Research Institute
Southwest
BOEING
LUXFER MEL TECHNOLOGIES




Upgrading Approach
Biologically derived intermediates
Chemically derived intermediates
Biomass
Sugars
2,3-BDO
Multiple Approaches
Carboxylic Acids
Ketonization
Condensation
HDO
Etherification
Furfural
HMF
Condensation
HDO
Transportation Fuels and Biochemical Products

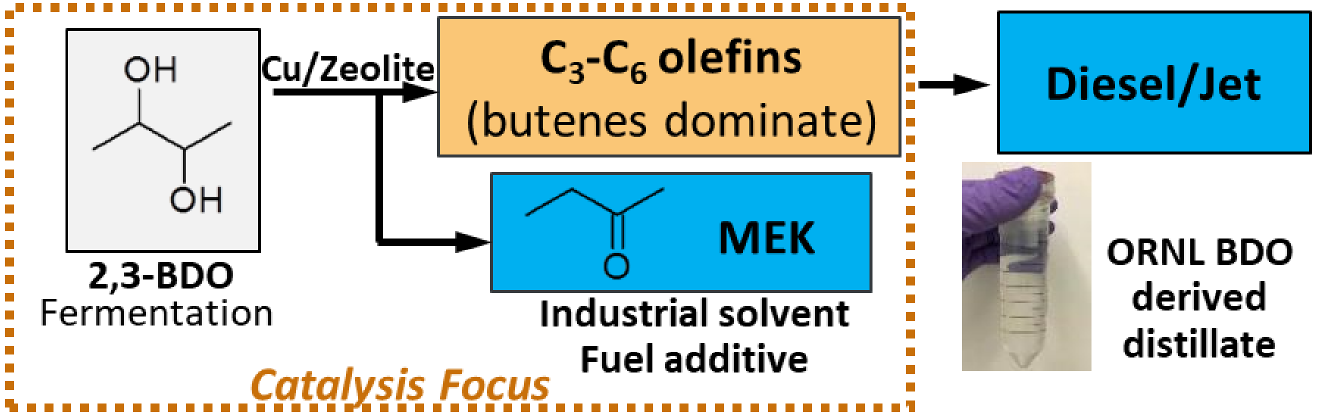
2,3-BDO



Transportation Fuels and Biochemical Products

Progress and Outcomes: BDO to Middle Distillate & Coproduct

Goal: Develop catalyst technology to produce middle distillate and chemical coproducts from biomass-derived 2,3-BDO with high carbon conversion efficiency and catalyst stability

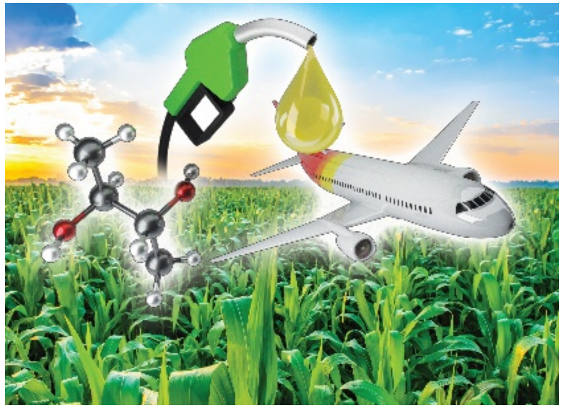


Advantages

- **One step highly selective production of C_3-C_6 olefins**
- **Co-production of MEK**
  - tune the co-product yield
- **High distillate yield**

R&D objectives:

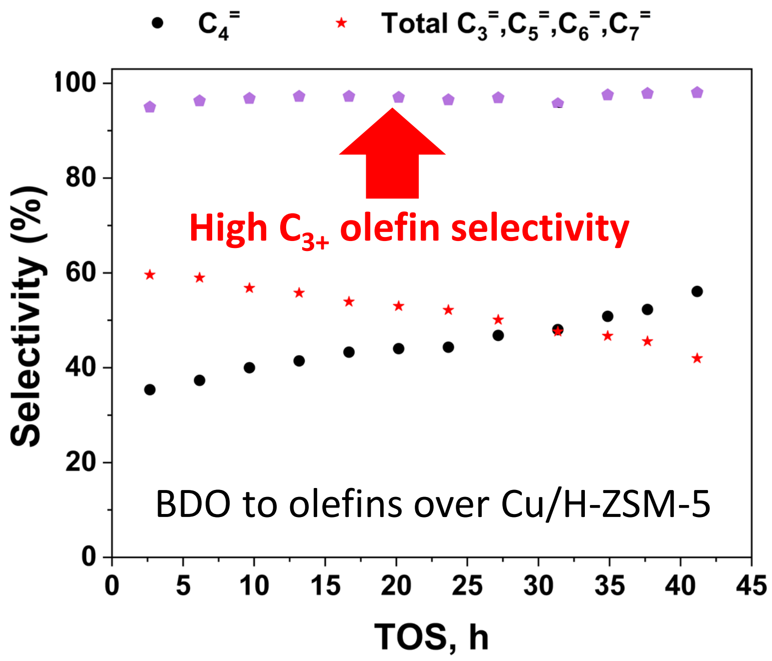
1) **Demonstrate the pathway** of BDO to middle distillate
2) Address **catalyst deactivation** associated with coke formation, impact of water and fermentation impurities for **BDO to olefins step**
3) Advance the state of technology



***Sustainable Energy & Fuels*, 2020, 4, 3904.**

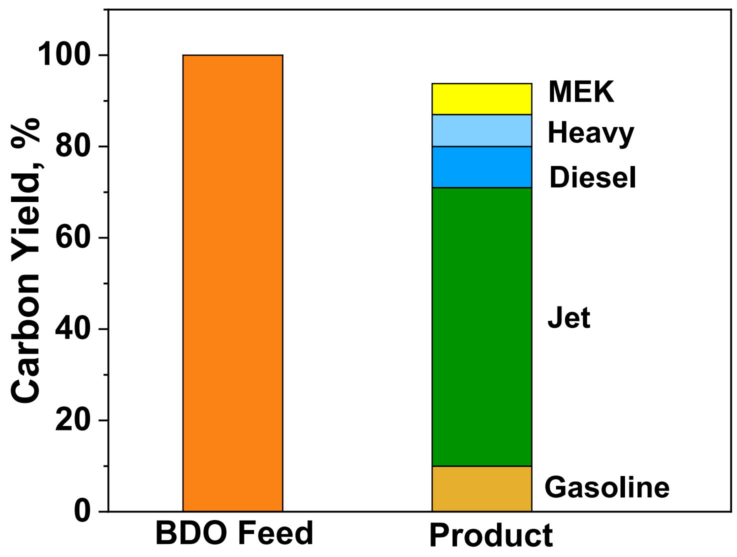
Progress and Outcomes: BDO to Middle Distillate & Coproduct

Goal: Demonstrate BDO conversion to middle distillate and MEK via one-step BDO to C_{3+} olefins

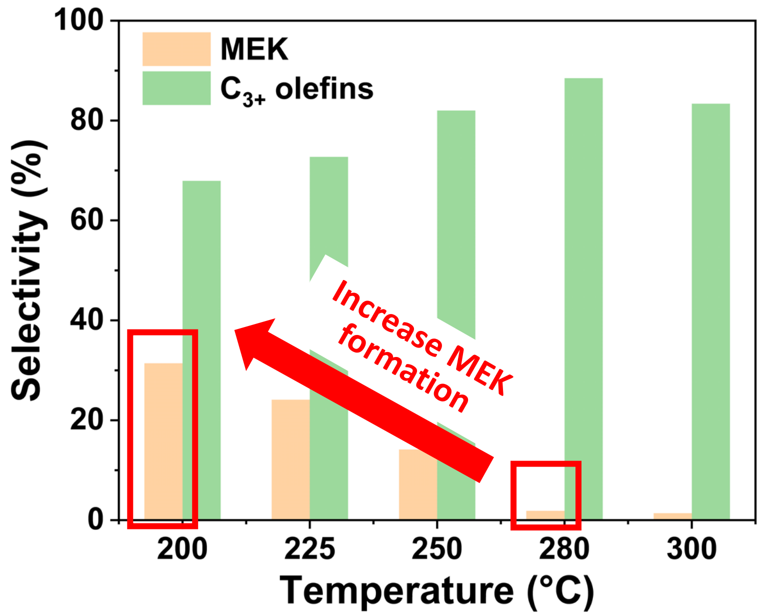


250°C, 1.0 h^{-1} (BDO conversion >97%)

Sustainable Energy & Fuels 2020, 4, 3904.



Carbon conversion efficiency to liquid products



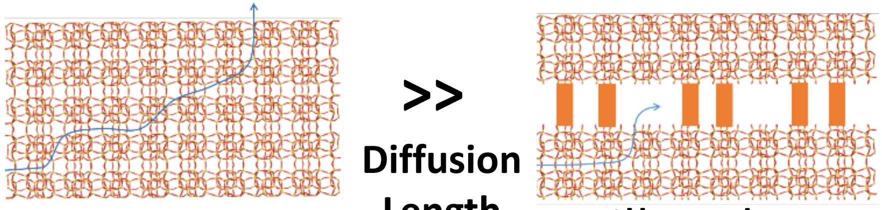
BDO to olefins at varied T, 1.0 h^{-1} (BDO conversion >97%)

Outcomes:

- BDO is selectively converted to C_{3+} olefins (>95%), leading to **high carbon conversion efficiency** into the liquid hydrocarbons (>85%)
- **Coproduction of MEK** can be achieved via tuning reaction conditions (e.g., T, H_2 partial pressure)

Progress and Outcomes: Mitigate Coke Formation for BDO to Olefins

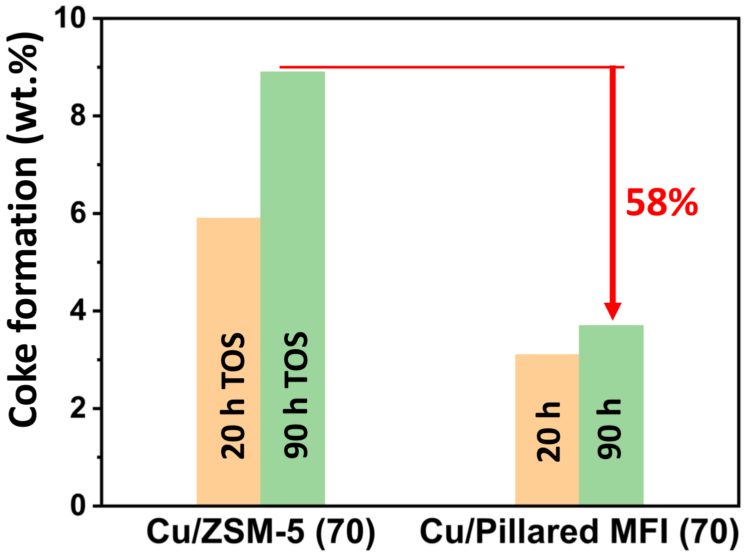
Goal: Cu/Pillared-MFI (P-MFI) to mitigate coke formation and promote butene formation



2D Pillared-MFI Zeolite:

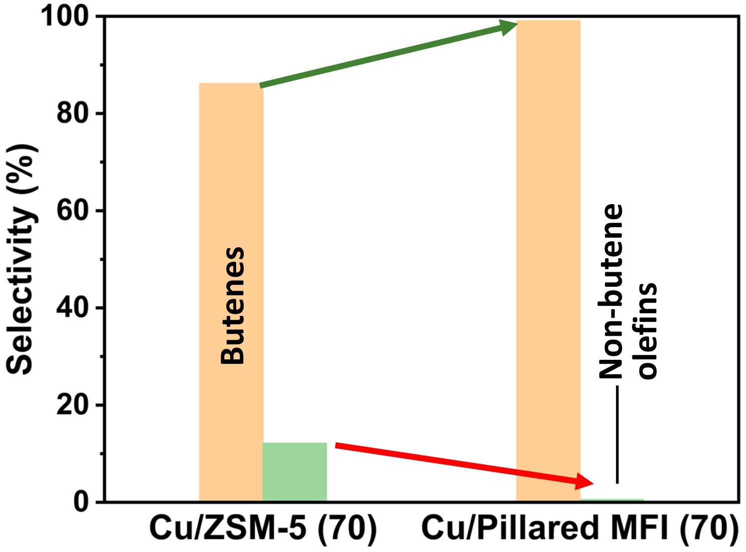
- Reduced diffusion length
- Better mesopore connectivity

Cu/P-MFI reduces coke formation



Coke analysis done by TGA
Reaction: 250 °C, 1.0 h^{-1}

Cu/P-MFI favors butene formation



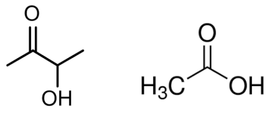
230 °C, 3.3 kPa MEK, 34.5 kPa H_2

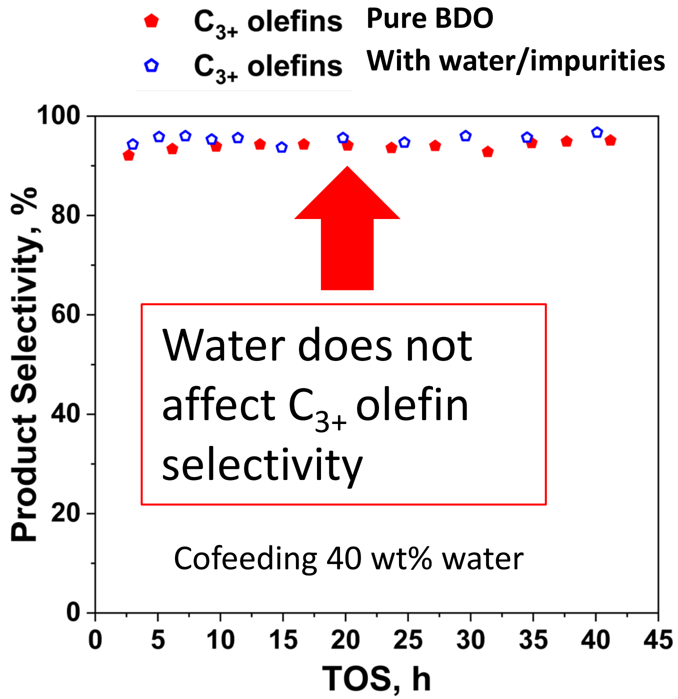
Outcomes:

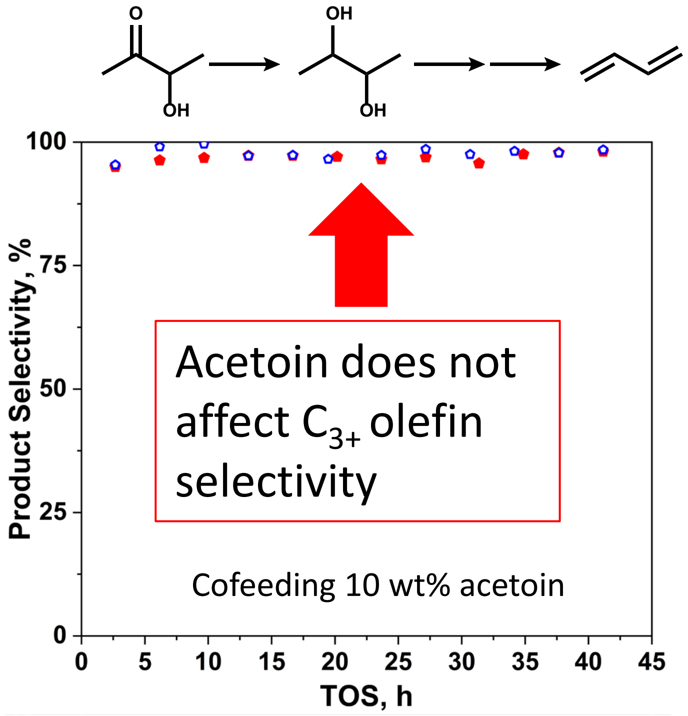
- Cu/Pillared-MFI can **reduce coke formation by >50%** for BDO conversion to olefins
- Unique properties of P-MFI favor **selective formation of butenes** by inhibiting butene oligomerizations and further cracking reactions

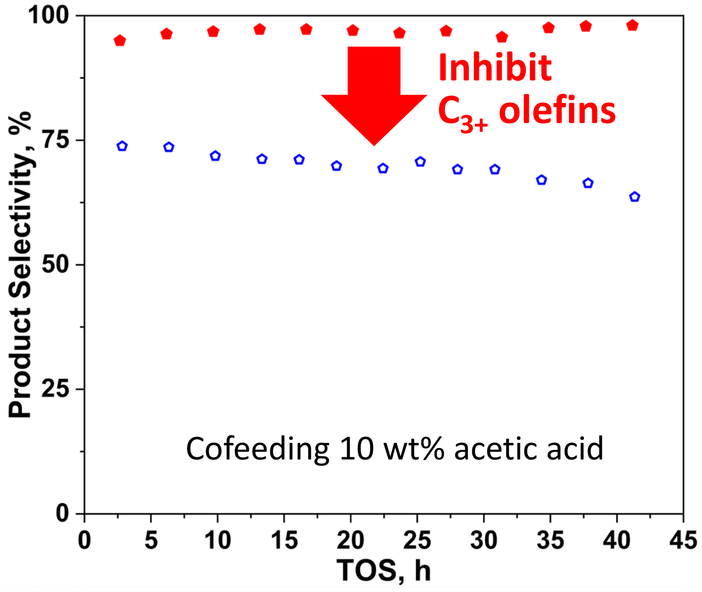
Adhikari and Zhang et al. In preparation

Goal: Evaluate water and fermentation impurities impact on catalyst performance









Cu/H-ZSM-5, 250 °C, 1.0 h^{-1}, 0.22 mL/h liquid flow, 30 cm^3/min H_2, BDO conversion 97-100%

- Presence of ***water does not impact catalyst performance***, allowing ***direct upgrading of aqueous BDO***
- ***Acetoin*** *is* ***converted to butenes to allow high carbon recovery***, not affecting catalyst performance
- ***Acetic acid inhibits*** formation of C_{3+} olefins due to accelerated coking and Cu sintering (ACSC)
- Provide guidance for ***separation R&D*** to mitigate the impact on catalyst

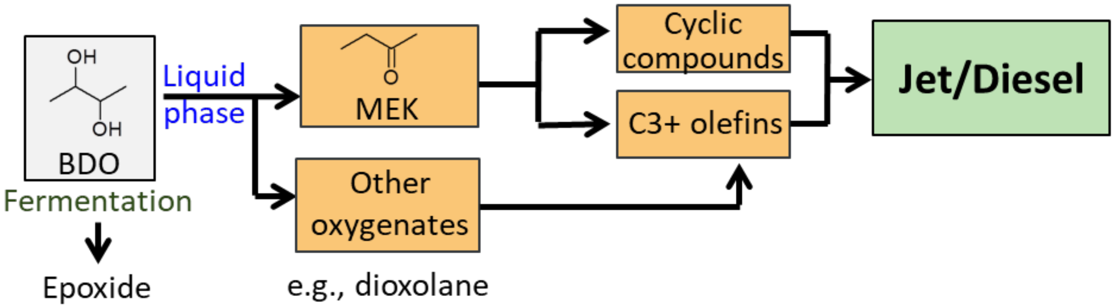
Research Progress Summary and Future Work

Catalysis R&D efforts significantly advance the key BDO to olefin catalyst performance

	Catalyst	Single-pass conversion (%)	C_3-C_6 Olefin Selectivity (%)	Productivity ($g/g_{cat}/h$)	Durability# (h)	BDO Feed	MFSP ($/GGE)
FY17 baseline	$Cu/SiO_2@ZrO_2$	100	30	0.18	< 5	Pure	10.08
Current	Cu/P-MFI*	100	>95	1.80	>100	Pretreated BDO broth	7.79§

*Cu/pillared MFI, 250°C, WHSV=3.0 h^{-1}, 1 atm; #TOS for each cycle, C_3-C_6 olefin selectivity changes <20%; §FY19 SOT

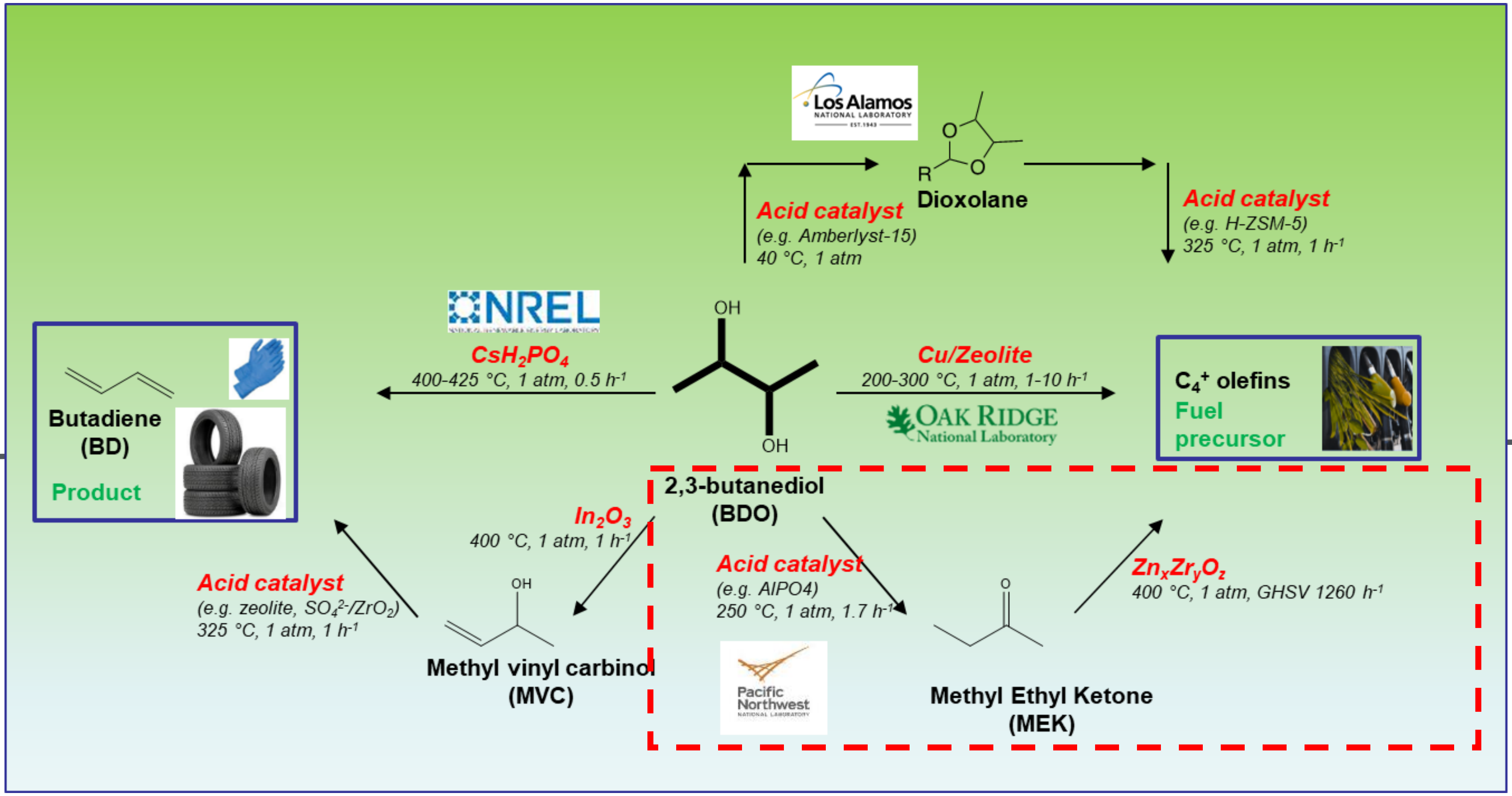
Future catalysis R&D focuses on addressing water separation challenges and diversify the product portfolios



- **BDO liquid phase upgrading to oxygenates**
  - 1st step (BDO to MEK): explore acid catalysts (jointly with PNNL)
  - 2nd step: dioxolane to olefins (with LANL)
- **Collaboration with CDM, ACSC and CCPC to understand catalyst deactivations in hot liquid water** (FY21 Q4 milestone)
- **BDO to value-added co-product epoxide**
  - Explore catalysts and conditions in FY21

4 – Progress and Outcomes

2,3-BDO



Transportation Fuels and Biochemical Products

2,3-Butanediol (BDO) Upgrading to Fuel via Methyl Ethyl Ketone (MEK) Intermediate

Pacific Northwest NATIONAL LABORATORY

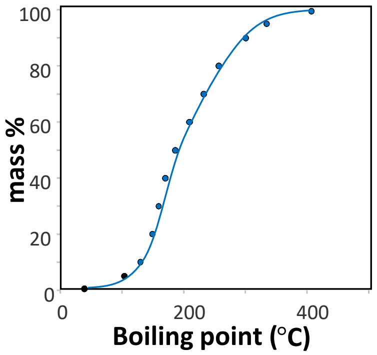
Objective: Develop a marketable catalyst and process to upgrade 2,3-butanediol (BDO) to fuels & Chemicals.

Leverage learning from BES program

Aqueous 2,3-BDO → Acid catalyst → **MEK** → $ZrZnO_x$ → **C_4-C_5 olefins** → Oligomerization / Hydrogenation → **Jet and Diesel**

Typically 10 wt.% BDO/H_2O

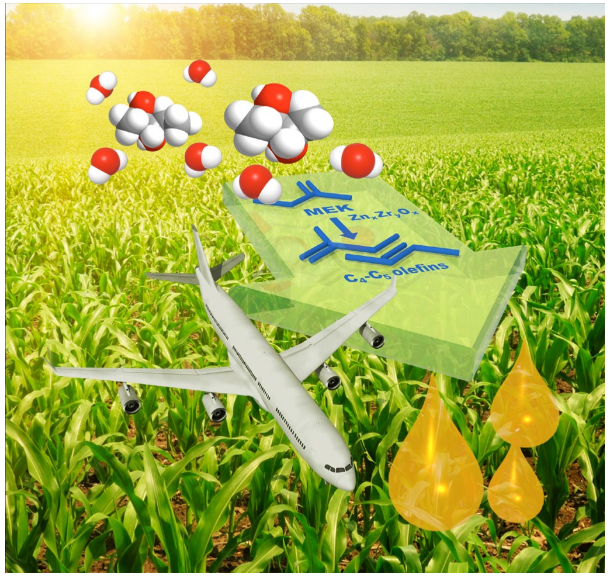
US patent 9,663,435
ChemCatChem , 2019, 11, 3393-3400



SIMDIT, freezing point consistent with PNNL ATJ fuels that have passed AFRL testing and recently certified for jet fuel

2-step process via MEK enables:

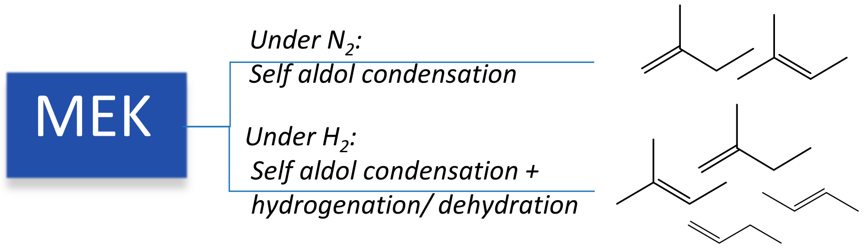
- Co-products diversification beyond MEK
  de-risk credit form lignin to adipic acid
- Operate with aqueous 2,3-BDO feedstock
  (BDO/H_2O separation is energy intensive)
- Operate with or without H_2



ChemCatChem , 2019, 11, 3393-3400
In collaboration with ACSC

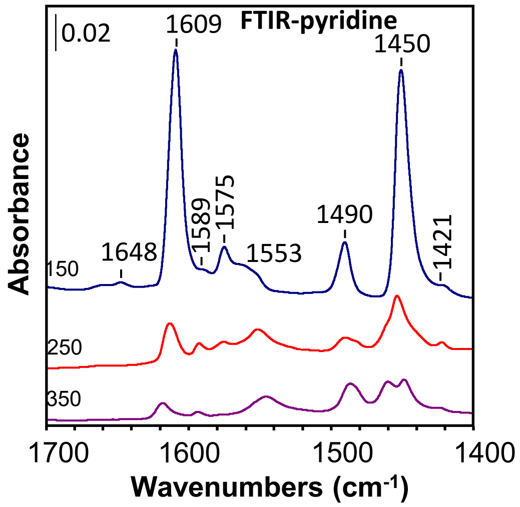
2,3-Butanediol (BDO) Upgrading to Fuel via MEK Intermediate

Progress toward carbon efficiency

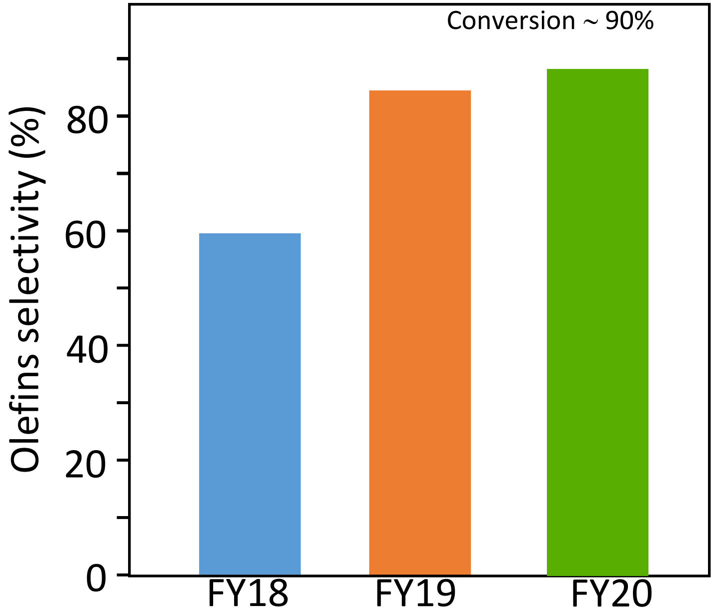


$Zn_1Zr_{10}O_x$ uniqueness:

- Acid properties→ aldol condensation
- Redox properties→ hydrogenation



Increased carbon efficiency



Key findings:

- Demonstrated reaction mechanism
- Discovered olefins product distribution & yield varies with environment (N_2 vs. H_2): Higher yield under H_2
- Improved MFSP (2030 projection) from $3.40 (2018) to $2.78 (2019)

Future work:

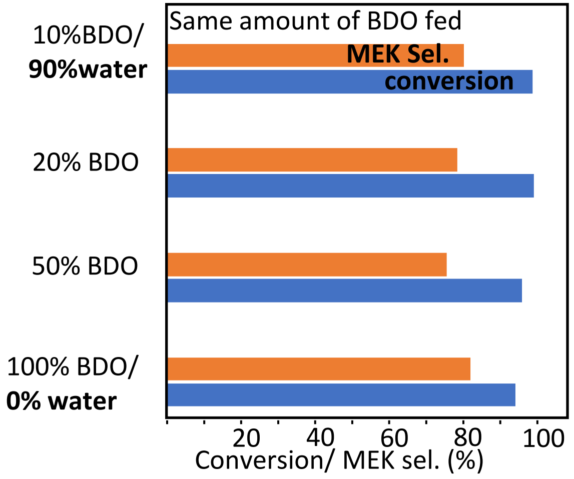
- Update TEA & MFSP in FY21

Outcome: The carbon efficiency of the 2-step BDO to olefins process was improved with >82% olefins selectivity at 90% conversion

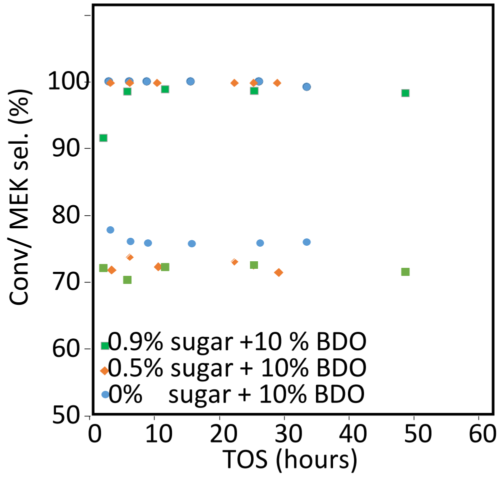
2,3-Butanediol (BDO) Upgrading to Fuel via MEK Intermediate

Progress beyond carbon efficiency to address feedstock risks

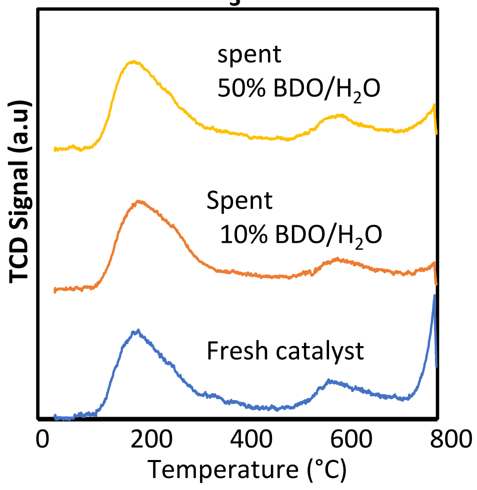
Performance is indifferent to water content

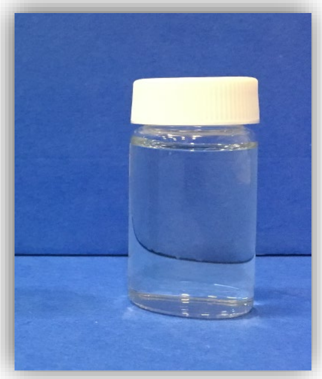


Limited impact of sugars impurities on performance



NH_3-TPD





Clean BDO broth

Impurities (< 2%):
Glycerol
Sugars
Acetoin

Inorganics:
K/Na/P

Key findings:

- Demonstrated water content in the feed does not impact catalytic performance or catalyst structure and surface properties for TOS ≤ 100 hours
- Initiated impurities study:

  acetoin, sugars = limited change is activity

  glycerol = Loss of activity (due to coking)

Future work:

- Investigate the catalytic upgrading of 2,3-BDO to MEK in condensed phase and associated deactivation as needed in collaboration with **CDM**

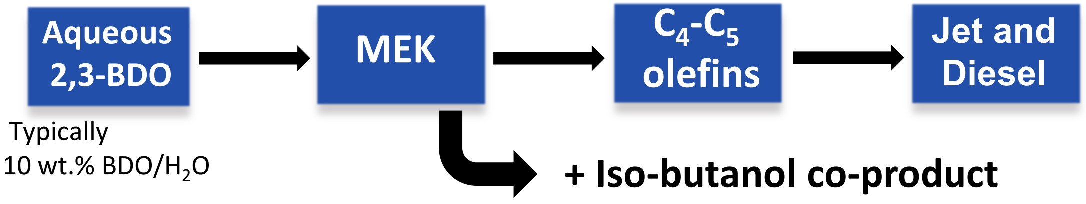
Outcome: The catalytic performance is not affected by the water content (TOS ≤ 100 hours) indicative of process flexibility

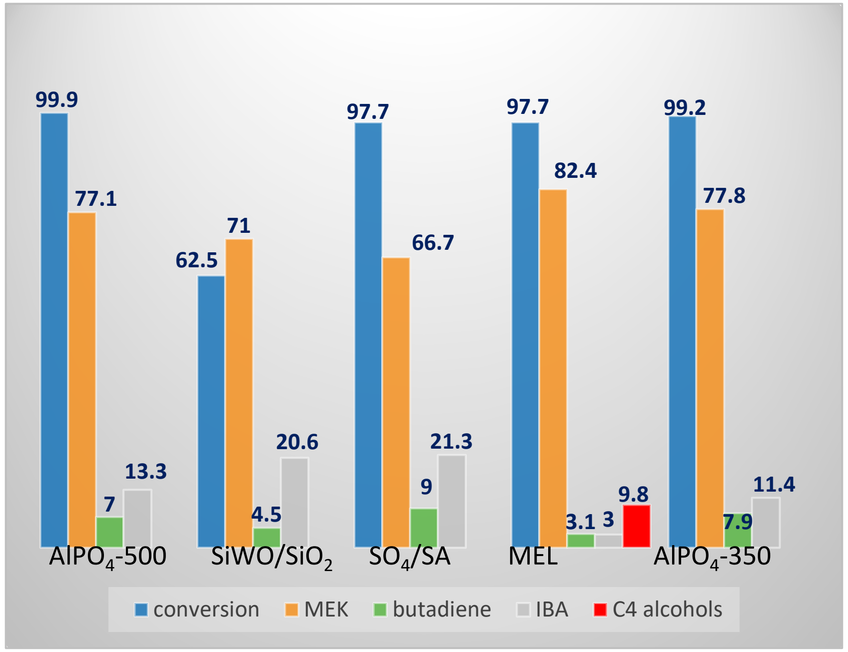
2,3-Butanediol Upgrading to iso-butanol co-product of MEK

Pacific Northwest NATIONAL LABORATORY

Progress beyond carbon efficiency to address lignin risk

This effort is to address FY19 peer review comment: "The overall success of the project is dependent on the success of the lignin valorization projects"





Key Findings:

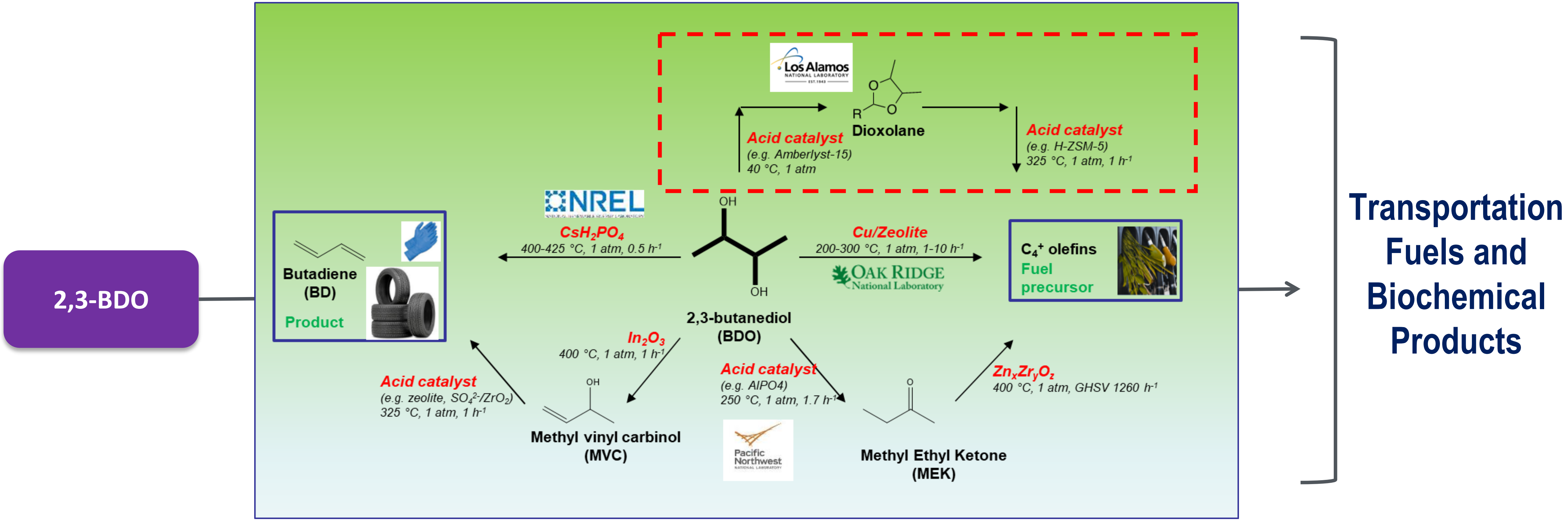
- The 2-step conversion of 2,3-BDO to olefins offers co-product diversification beyond MEK.
- Iso-butanol can be produced along MEK
- Established collaboration with Luxfer-MEL for catalyst development

Future work:

- Catalyst screening & reaction parameters investigation to tune iso-butanol/ MEK ratio
- Collaborate with **CCPC** for understanding the nature of the reaction intermediates and parameters favoring iso-butanol formation

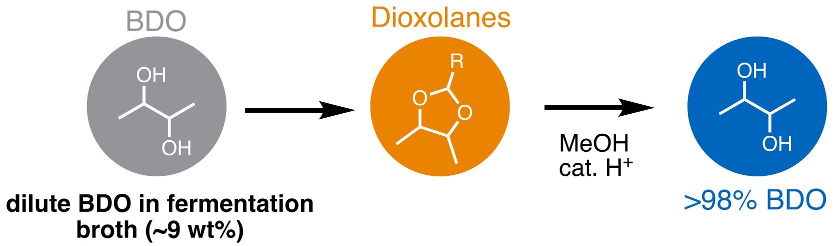
Outcome: Discovered a new pathway for iso-butanol production from 2,3-BDO

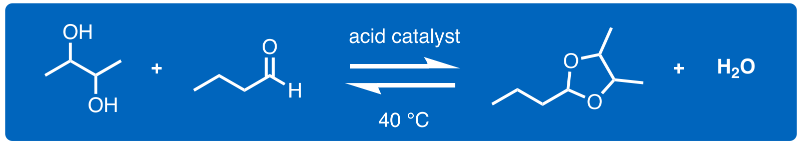
4 – Progress and Outcomes

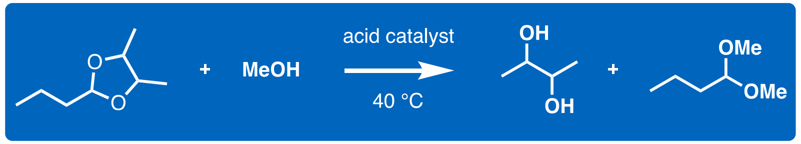


Reactive Extraction of BDO from Fermentation Broth

<u>Objective:</u> Develop a direct catalytic conversion of 2,3-butanediol (BDO) in fermentation broth to dioxolanes to enable separation



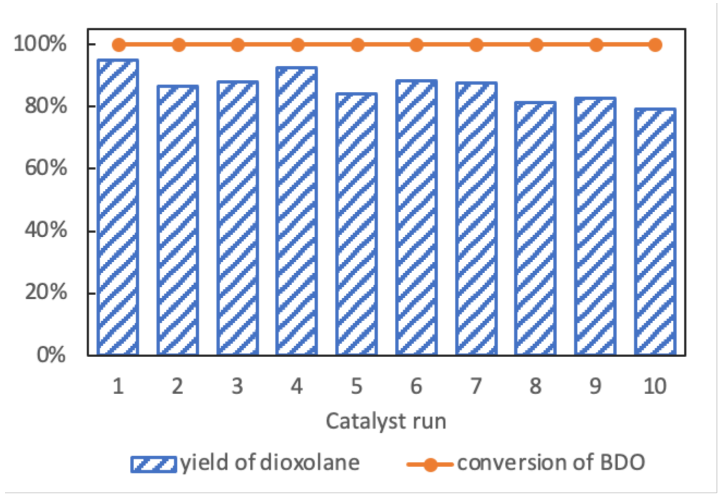




- 1 g scale: 75% isolated BDO yield
- 10 g scale: 90% isolated BDO yield
- >98% BDO purity without chromatography
- Dimethoxybutane (DMB) readily removed along with MeOH via distillation; converted back to butyraldehyde via catalytic hydrolysis

Nafion NR50 recycling experiments: BDO conversion remains high, selectivity slowly decreases

40 °C, pre-treated fermentation broth

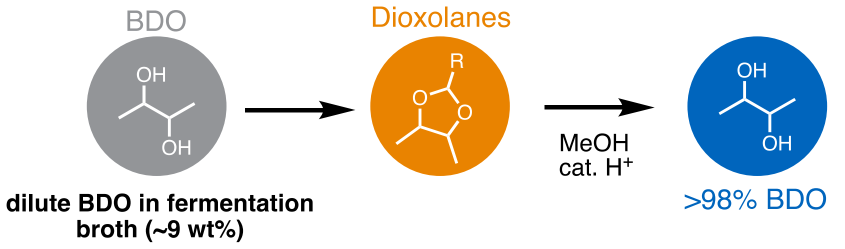


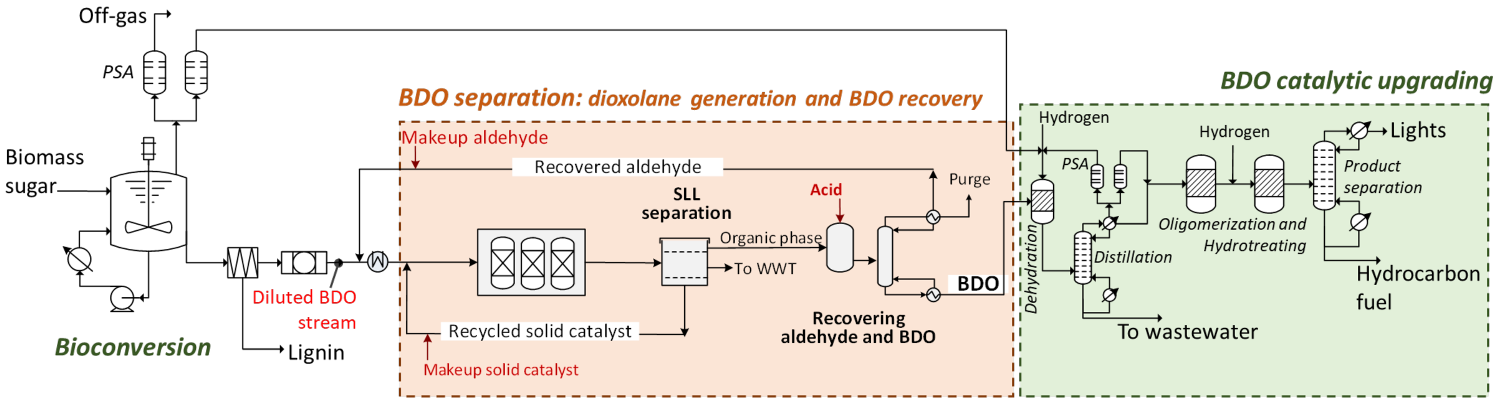
<u>Outcome:</u>

- Recovered BDO from real fermentation broth in >98% purity via reactive extraction and transacetalization
- Pre-treatment of broth increases catalyst lifetime
- Future work: collaboration with SepCon to evaluate pre-treatment strategies to increase catalyst efficiency for dioxolane formation directly in fermentation

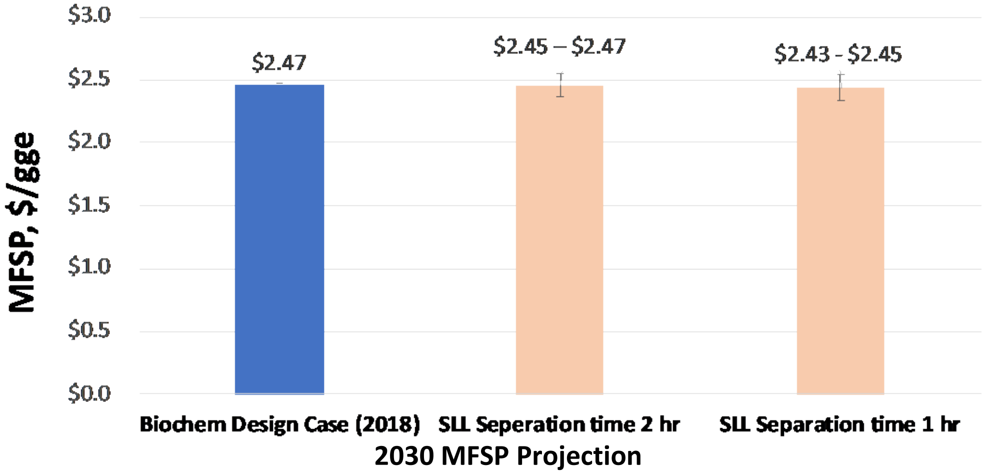
Reactive Extraction of BDO from Fermentation Broth

Objective: Develop a direct catalytic conversion of 2,3-butanediol (BDO) in fermentation broth to dioxolanes to enable separation





Aye Meyer, Steven Phillips (PNNL)

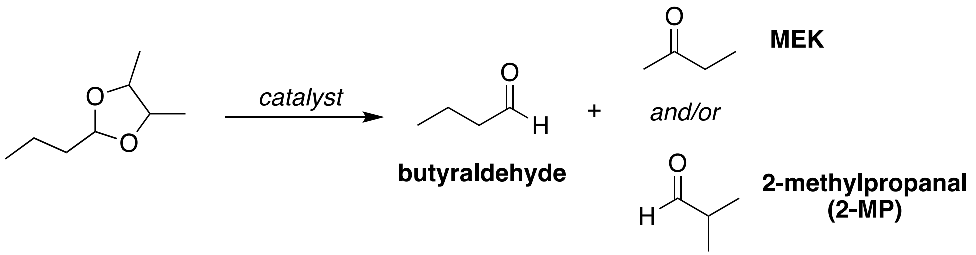


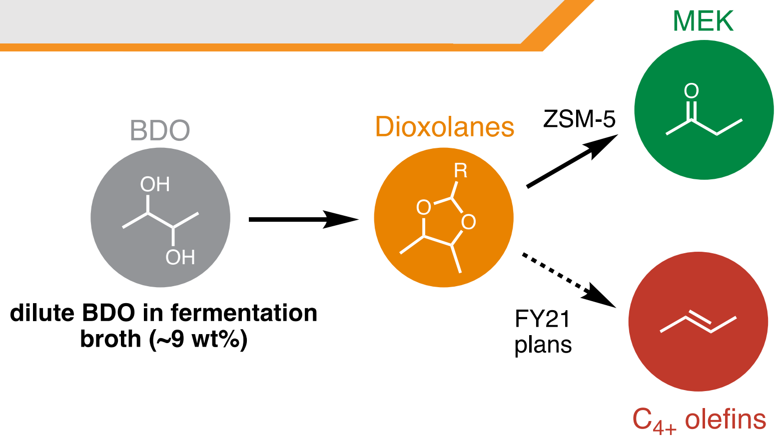
Preliminary TEA

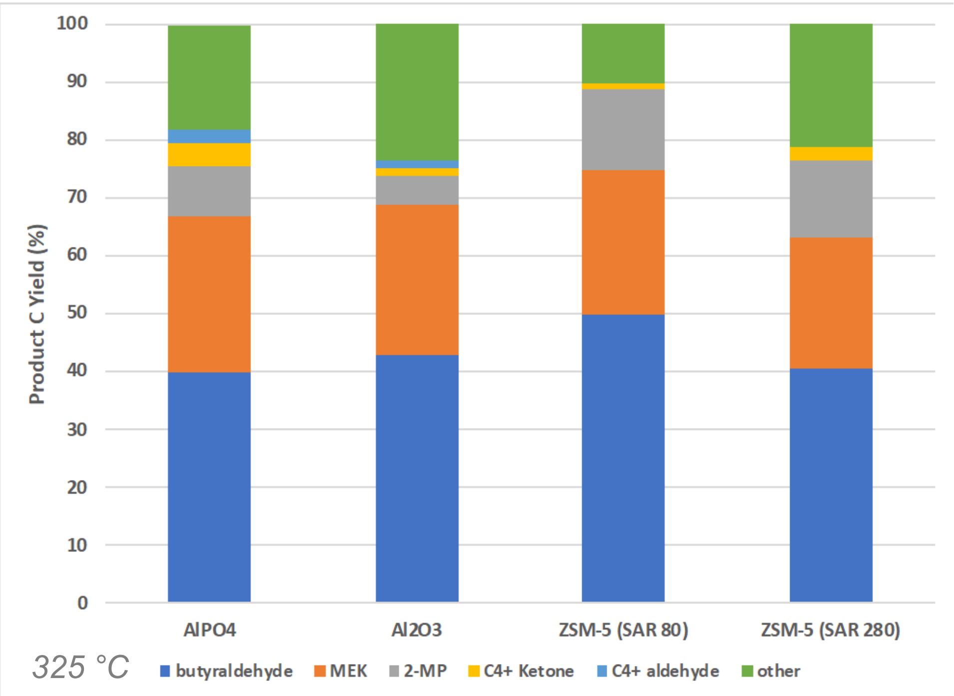
- Biochem design case:
    - Diluted BDO stream going to dehydration reactors
    - Capital and energy intensive to concentrate BDO
- Dioxolane case:
    - ~$10M saved in total capital investment
    - Lower operating costs
    - Quicker separation time and lower acid loading can positively impact MFSP

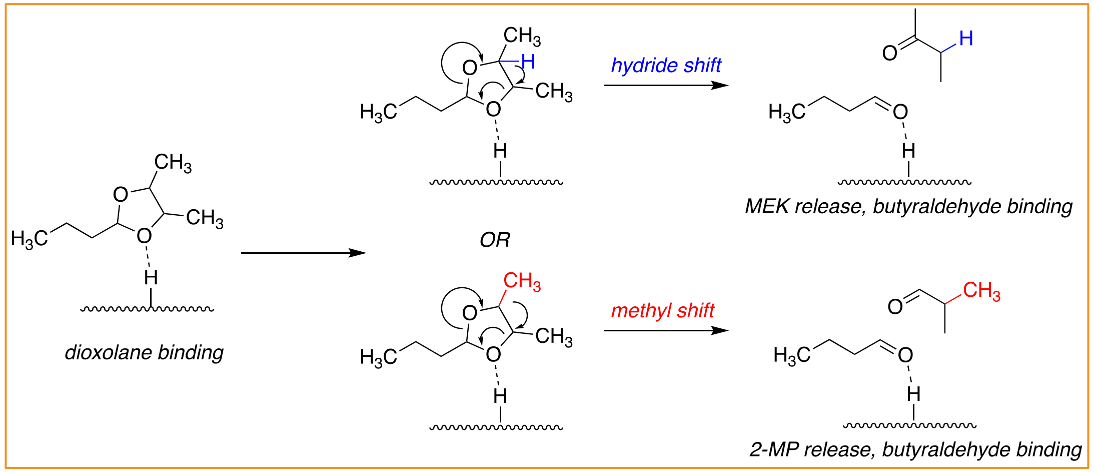
Dioxolane Upgrading to MEK

Objective:
Develop a direct catalytic conversion of dioxolanes to value-added products







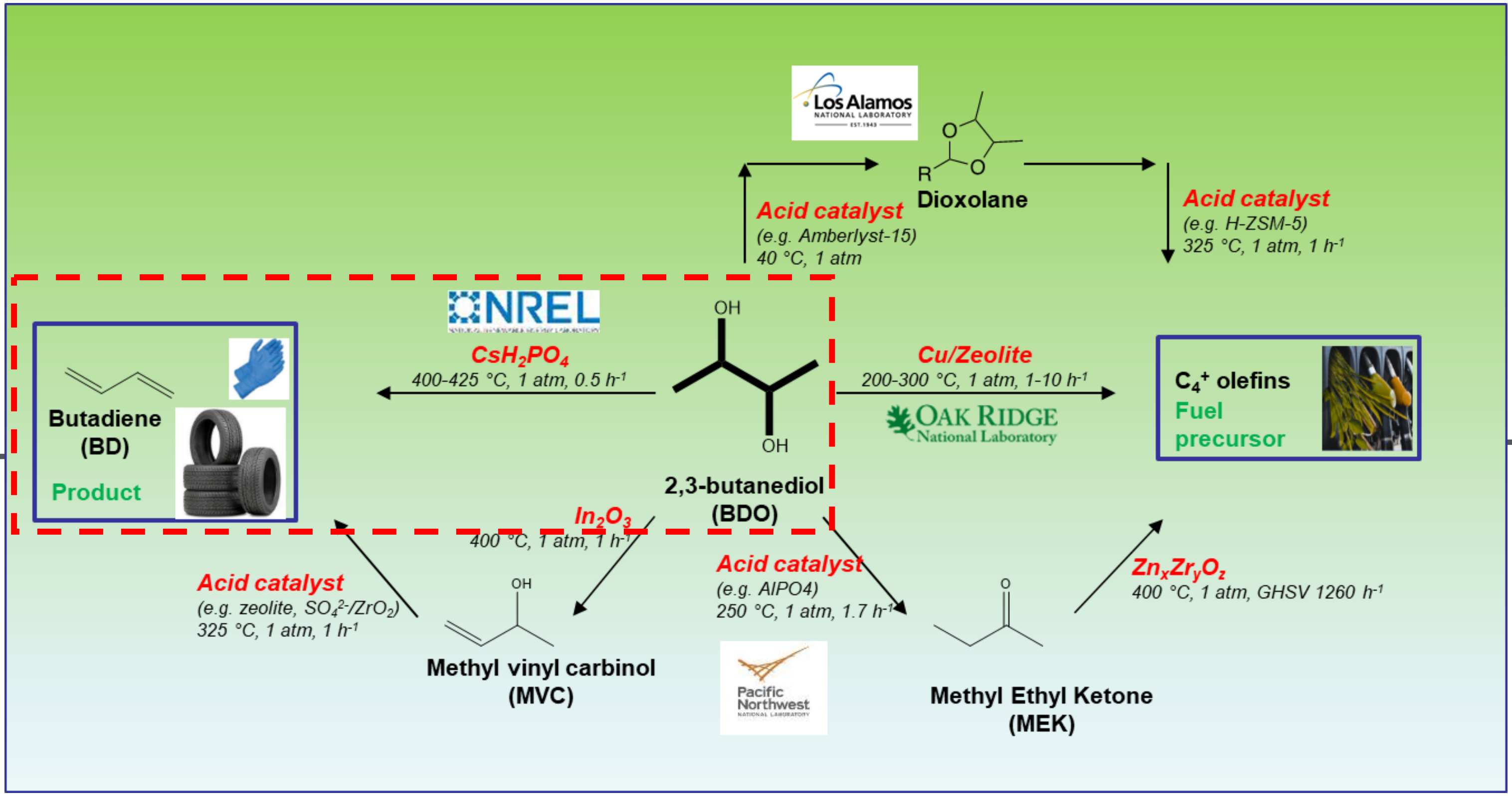


Abraham Martinez, Mond F. Guo, and Karthikeyan K. Ramasamy (PNNL)

Outcome:

- Demonstrated dioxolane upgrading to MEK w/ PNNL; butyraldehyde can be recovered and recycled
- Future work: collaboration with ORNL to evaluate dioxolane to C4+ olefins upgrading pathway

2,3-BDO

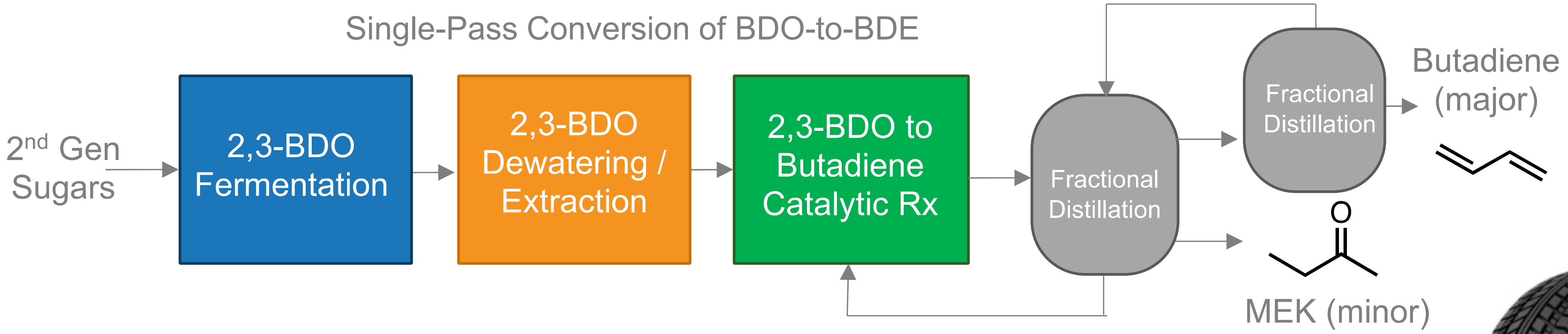


Transportation Fuels and Biochemical Products

Goal to reduce catalytic processing costs during the single-pass conversion of 2,3-BDO to butadiene

2,3-BDO as Precursor for Bio-butadiene

Advance catalytic technology for the single-pass conversion of 2,3-butanediol to butadiene by demonstrating yield, selectivity, and time-on-stream stability that will enable MFSP targets



Research Objectives

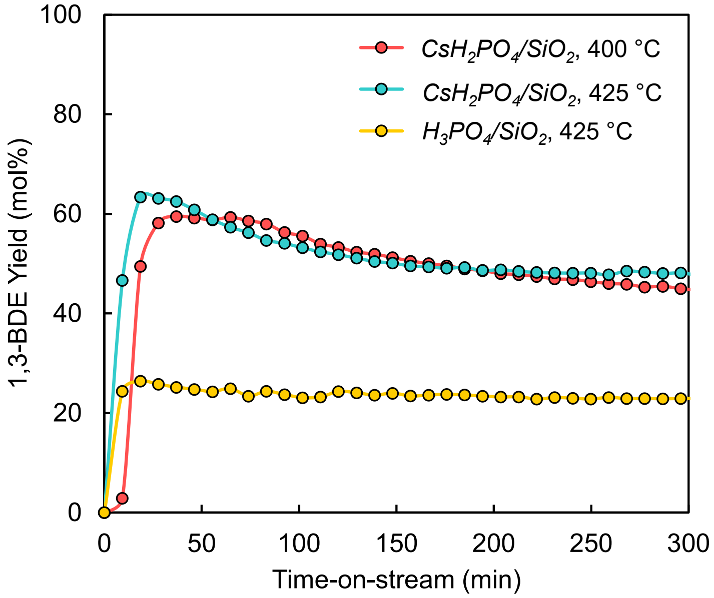
Aim 1) Measure single-pass butadiene yields with leading CsH_2PO_4/SiO_2 catalyst to and with model and bio-derived 2,3-BDO. Evaluate catalyst active site and probe reaction mechanism to inform future catalyst material designs.

Aim 2) Establish baseline and target catalytic process performance parameters to inform TEA and LCA models that integrate fermentation, separation, and catalysis

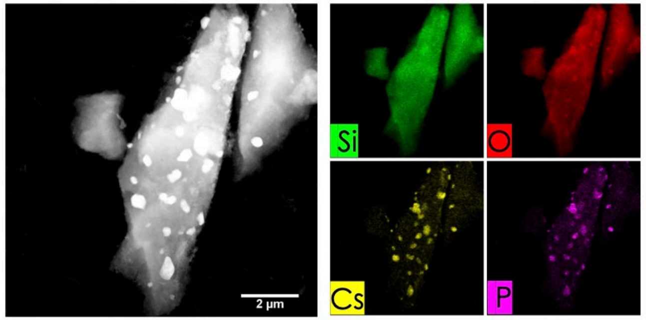
4. Progress and Outcomes

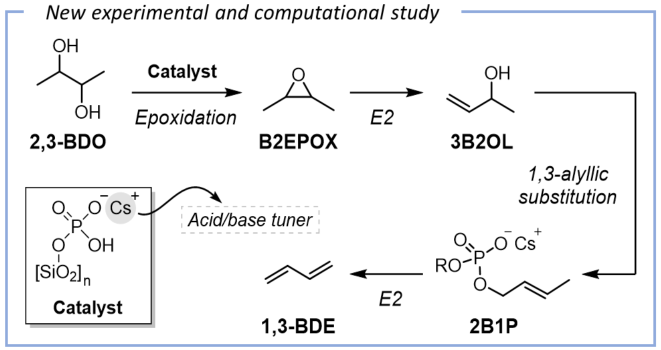
Advanced understanding of single-pass catalyst active site structure and dual dehydration mechanism

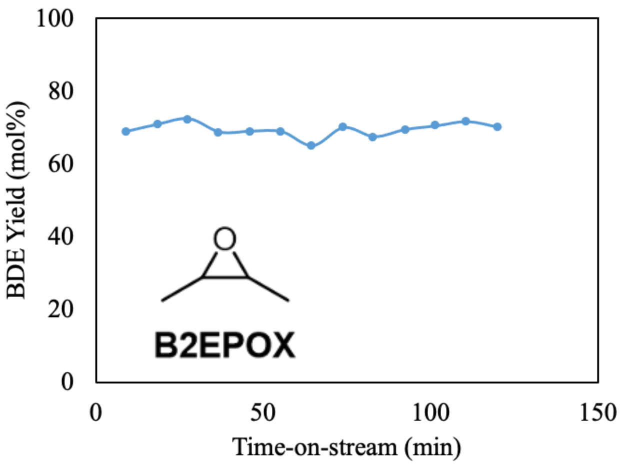
Single-step conversion of 2,3-BDO to 1,3-BDE



Catalyst	Acid NH_3 (umol g^{-1})	Base CO_2 (umol g^{-1})	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
SiO_2	–	–	480	0.75
CsH_2PO_4/SiO_2	28	26	426	0.80
H_3PO_4/SiO_2	95	12	480	0.91







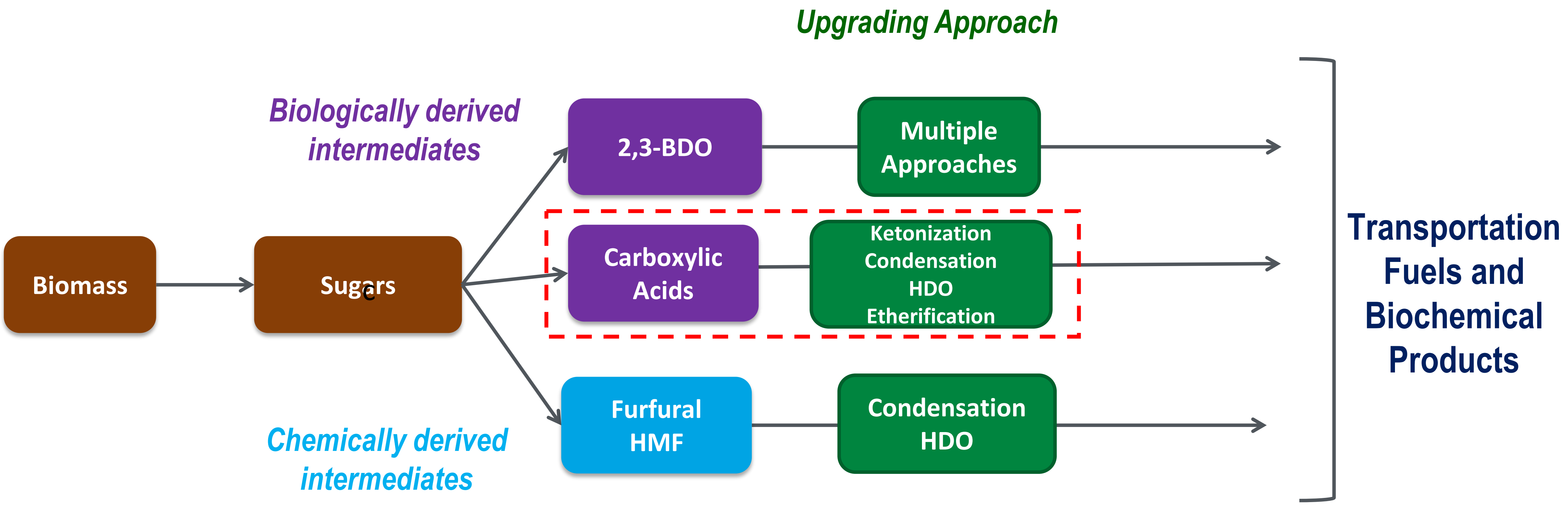
Previous work for single-pass BDE

- Synthesized leading CsH_2PO_4/SiO_2 catalyst to demonstrate >50% single-pass yields of butadiene with model and bio-BDO

Outcomes for active site & mechanism

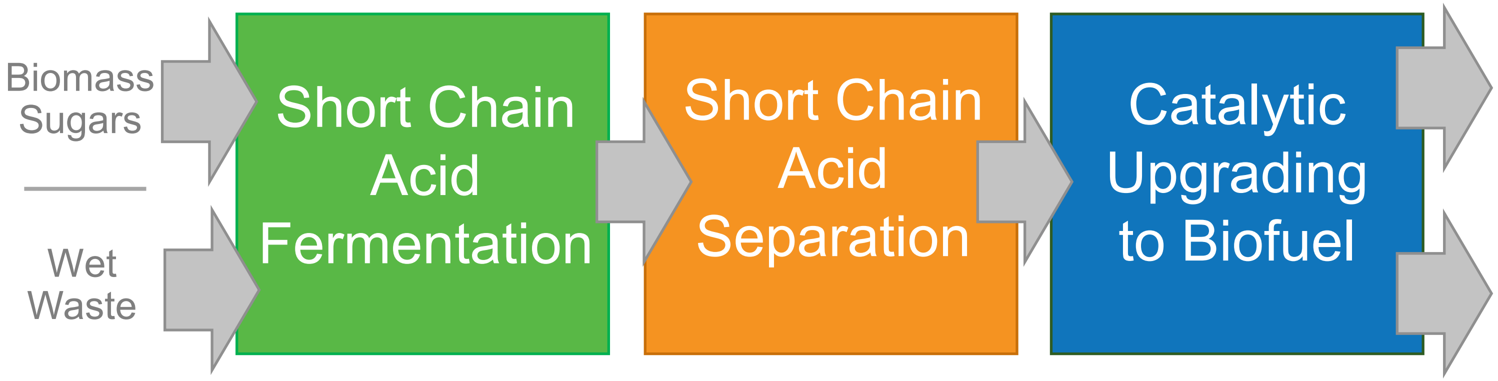
- Worked with **ACSC** to confirm catalyst synthesis results in physical collocation of Cs and P by STEM-EDS, as well as chemical interaction of Cs with PO_4 by 31P-NMR
- Collaborated with **CCPC** to identify epoxide as favorable intermediate, with experimental work with epoxide feed demonstrating comparable butadiene yields to inform future catalyst material active site requirements
- **Upcoming TEA work** planned to establish baseline and target performance metrics based on upstream separations, single-pass catalyst performance, and catalyst material costs

4 – Progress and Outcomes

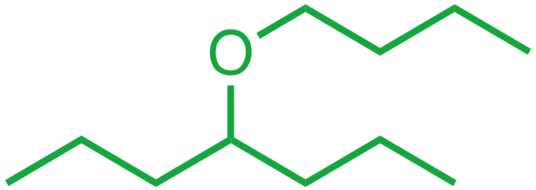


Short Chain Anaerobic Acids for Biofuels

C2-C6 acids can be produced from anaerobic fermentation of lignocellulosic sugars and wet waste and converted to biofuels through C-coupling, reduction, and deoxygenation chemistries

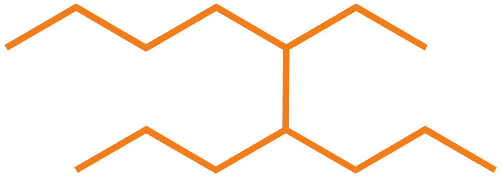


Advantaged Ether Diesel Blendstock



4-Butoxyheptane

Drop-In Hydrocarbons for Diesel & Jet



5-Ethyl-4-Propylnonane

Research Objectives

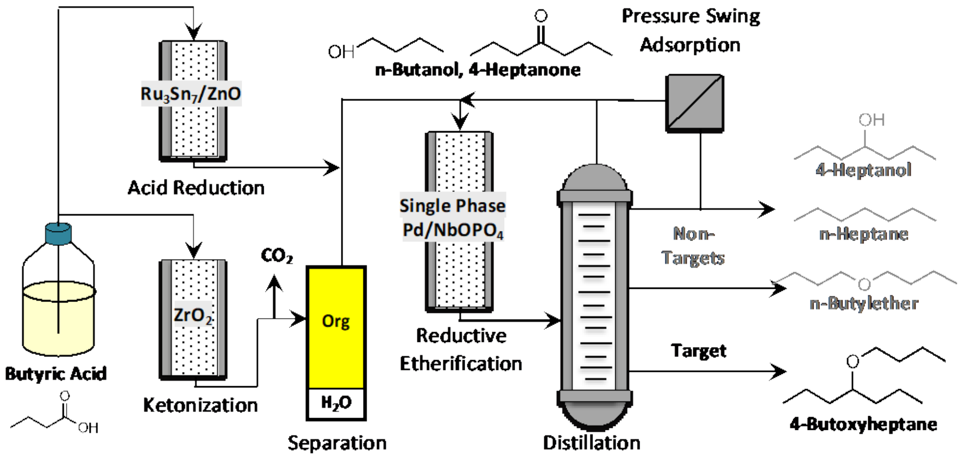
Aim 1) Improve catalyst process yield and stability to reduce cost for producing 4-butoxyheptane diesel blendstock with single-phase catalyst materials

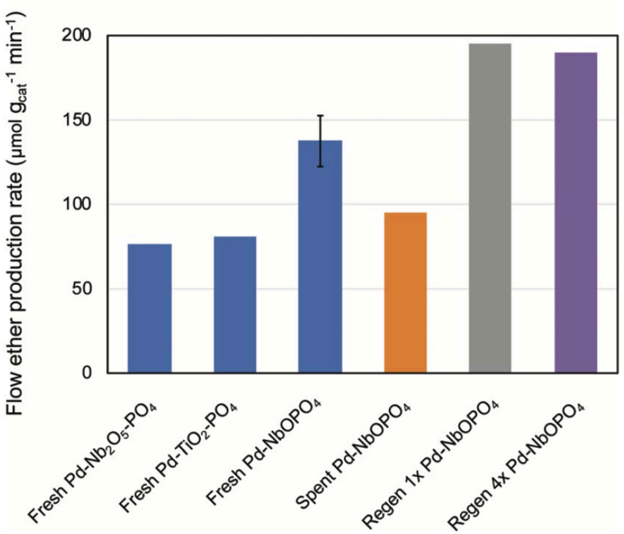
Aim 2) Reduce feedstock cost and GHG footprint for diesel and jet range hydrocarbons with wet waste-derived acids by advancing vapor phase ketonization with biogenic acid feedstocks

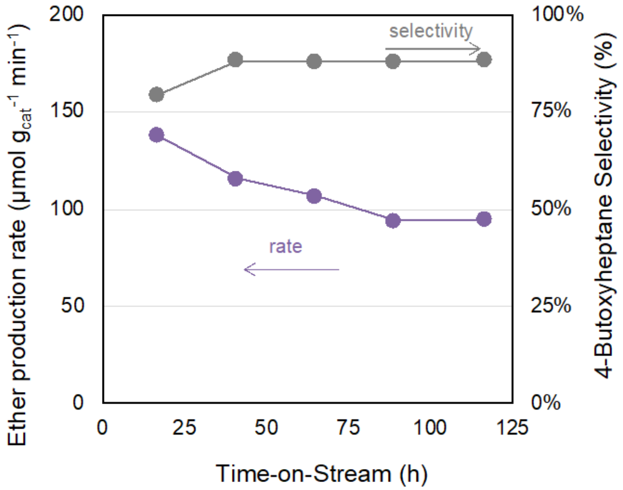
4. Progress and Outcomes

Developed single-phase catalyst to reduce production costs for novel ether diesel bioblendstock

Reductive Etherification Pathway for Ethers







Previous work for 4-butoxyheptane

- Co-Optima identified 4-BH as promising diesel blendstock with 2x cetane and 1/4 sooting; however, co-mixed Pd/C and Amberlyst resin deactivates with TOS

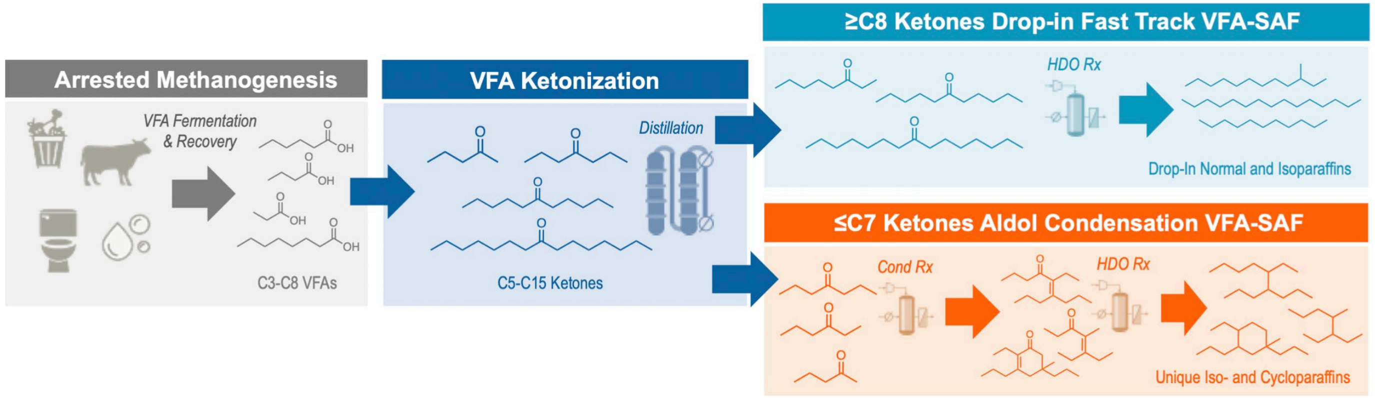
Outcomes for single-phase catalyst

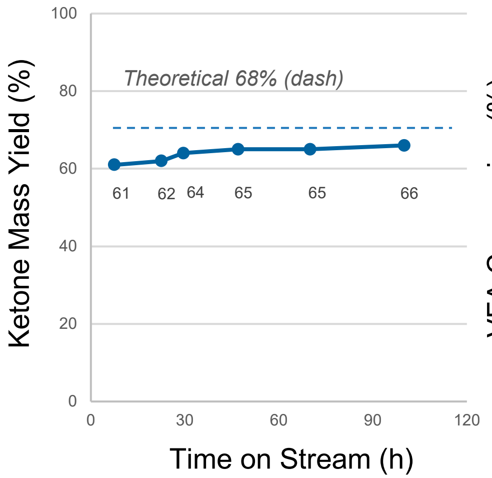
- Synthesized single-phase catalysts with acidic metal oxides for improved thermal stability and regenerability then Amberlyst
- Identified Pd-$NbOPO_4$ as most active single-phase catalysts with 87% selectivity and 58% single-pass yield **TEA confirmed 14% lower 4-BH minimum fuel selling price**
- Demonstrated successful catalyst oxidative regeneration, that also increases Pd size and ether production rate; future work with **ACSC** and **CCPC** to assess why with catalyst structure property relationships

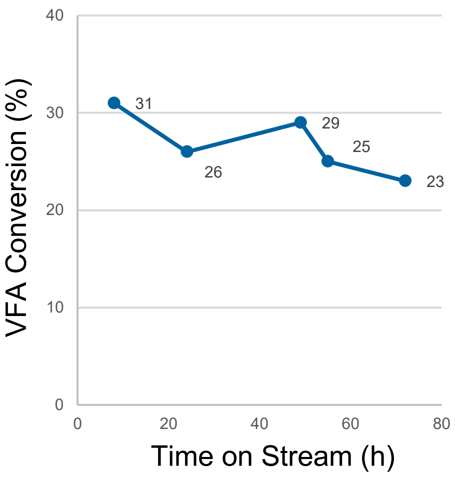
Hafenstine et al (2020) Green Chem. 22, 4463-4472

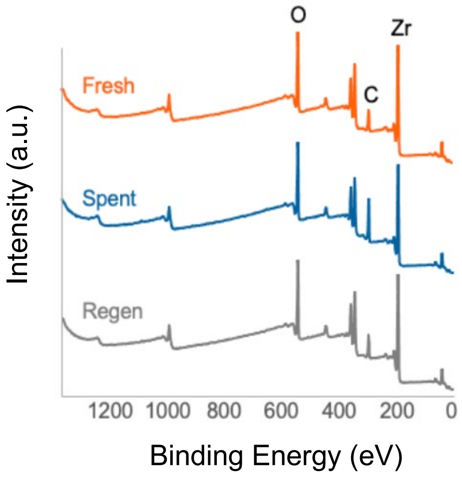
Advanced ketonization of mixed acids derived from wet waste to reduce feedstock costs and GHG footprint

Ketonization and HDO Pathway for Hydrocarbons









Previous work for butyric acid

- Demonstrated near theoretical ketone yields with model & bio-butyric acid; **DOE Biojet** validated ASTM jet fuel properties when upgrading mixed acids

Outcomes for waste mixed acids

- Performed ketonization of food waste-derived mixed C3-C8 acids for 100 h of TOS to confirm near theoretical yields
- Quantified bio-impurities in feed and partial conversion confirmed break-in of <6 h before steady catalyst performance
- Demonstrated that oxidative regeneration restores catalyst activity after 100 h of TOS; **ACSC** confirmed negligible impurity deposition by XPS and STEM-EDS
- **LCA showed 165% lower GHG emissions** relative to fossil jet (Opportunities in Biojet) when diverting food waste from landfills

Huo et al (2019) Green Chem. 21, 5813-5827 Huq et al (2021) PNAS. Accepted

4. Progress and Outcomes

Formed industry partnerships to advance catalytic upgrading of wet waste acids into biojet fuel

Project Partners

Earth Energy Renewables

Forge Nano

Advisory Members

Johnson Matthey — Inspiring science, enhancing life

Southwest

Boeing

2020 DOE Technology Commercialization Fund Award

Goal to advance next-generation catalysts for producing novel biojet fuel molecules derived from wet waste anaerobic acids

Project Team

Earth Energy Renewables

World Energy

MATRIC

University of Dayton Research Institute

Southwest

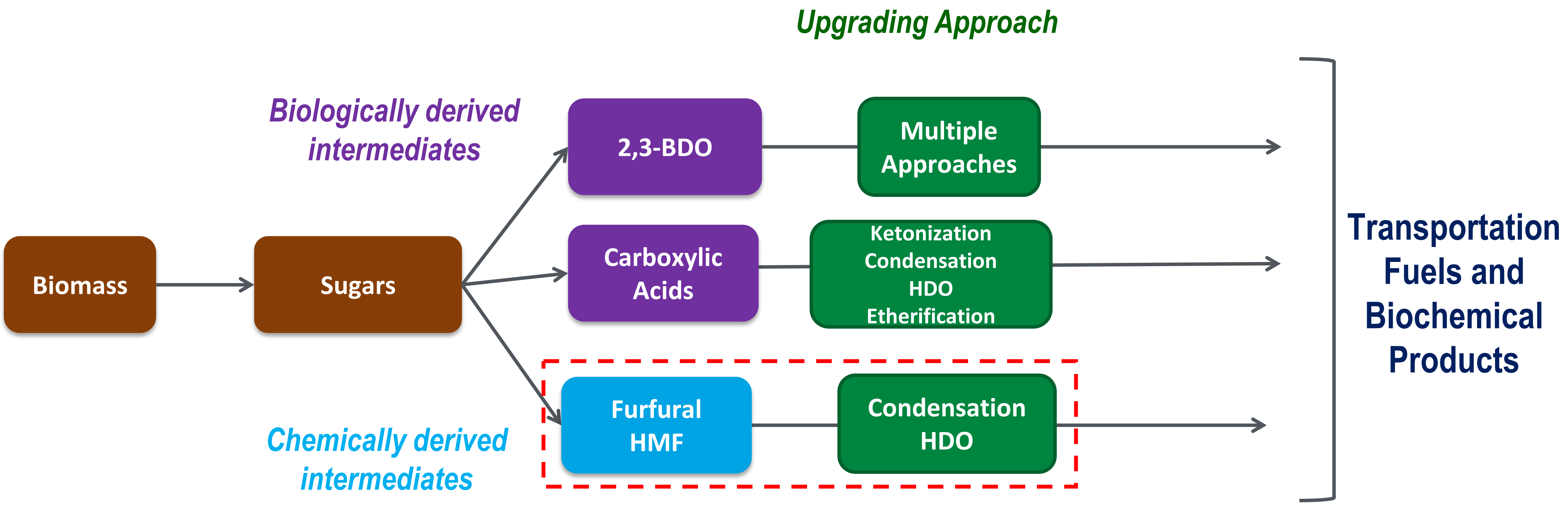
Boeing

2020 DOE Funding Opportunity Announcement Award

Goal to scale the production of net-zero “Fast Track” sustainable aviation fuel derived from wet waste to 30-gpd for ASTM qualification and world’s first flight demonstration

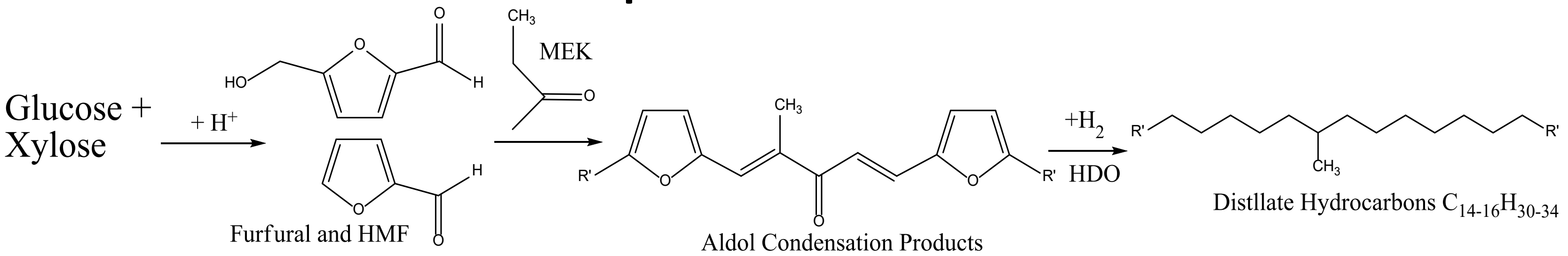
Demonstrated engagement from industry to partner and advance the catalytic upgrading of waste anaerobic acids into sustainable aviation fuel

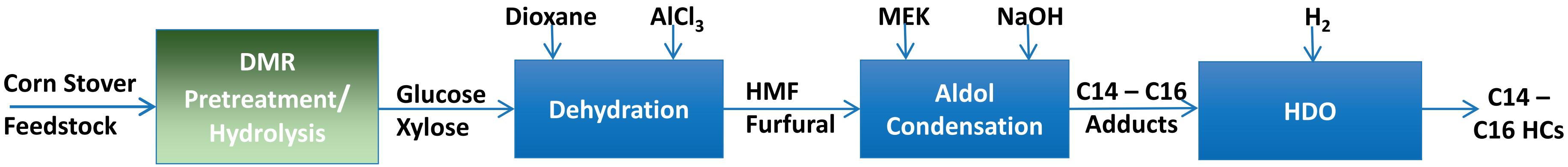
4 – Progress and Outcomes

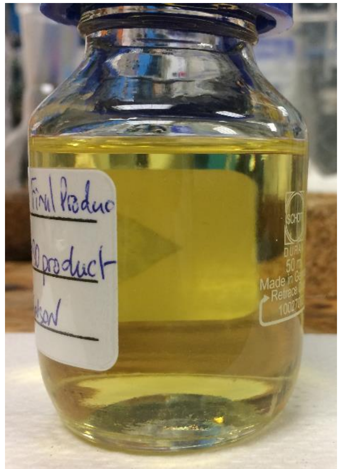


Catalytic Upgrading Furfurals to High Cetane Distillate Hydrocarbons

- **Overview of the conversion process**





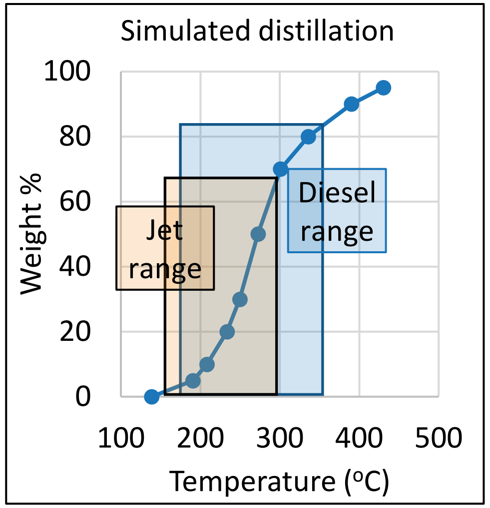


HC product made from model HMF and furfural feed after aldol condensation with MEK and then HDO

- R&D focused on conversion processes shown in blue boxes
  - Dehydration of sugars to furfurals using catalysts that are a mixture of Lewis and Brønsted acids in an organic/aqueous solvent
  - Aldol condensation of furfural mixture with bio-MEK to produce C14-C16 intermediates
  - Hydrodeoxygenation of intermediates to isoparaffins using metal catalysts on silica-alumina supports
- Reactors are flow-through tubular and batch reactors
- TRL level is 2 – 3 with basic bench top research leading to process development research

Hydrocarbon Product Fuel Properties

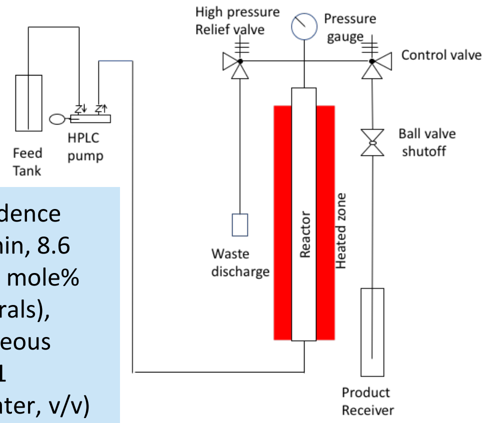
Property	HMF/Furfural Upgraded HC Product	Typical US Diesel
Cloud Point (°C)	-64	-40
Density (g/cm^3)	0.828	0.83-0.86
Higher Heating Value (MJ/kg)	43.6	45.6
Energy Density (MJ/L)	36.1	38.5
Cetane Number (AFIDA)	61.5	Min. 40 Typically 42-45



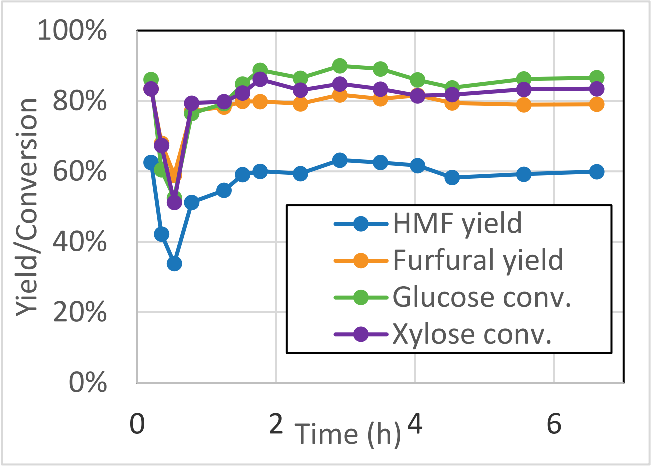
Dehydration of Sugars to Furfurals

Objectives:
- Convert sugars in corn stover hydrolysate into furfural and HMF in a flow reactor
- Increase sugar concentration to decrease solvent amount used.

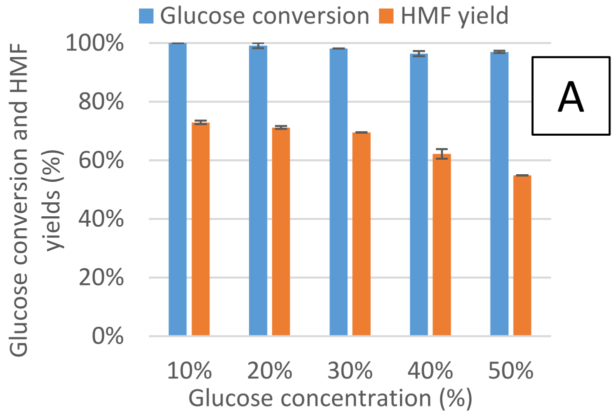
Furfurals Production in Flow Reactor from Corn Stover Hydrolysate



230 °C, residence time 14.6 min, 8.6 mM $AlCl_3$ (3 mole% rel. to furfurals), solvent aqueous dioxane (2:1 dioxane: water, v/v)

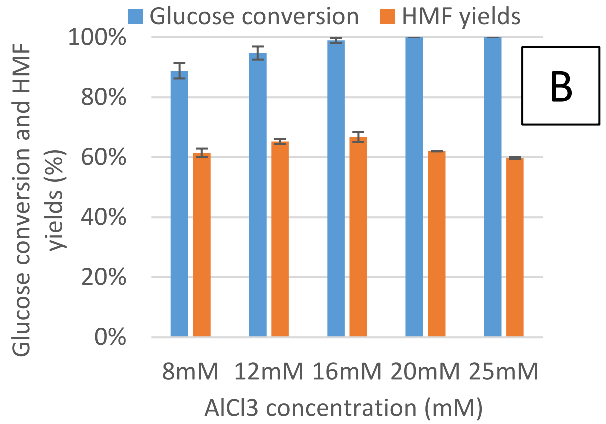


Increasing Glucose Concentration



Dehydration of Glucose to HMF

205 °C, 3 min
Dioxane/H2O (2/1 v/v)
A) 8 mM $AlCl_3$, 25 mM HCl
B) No HCl

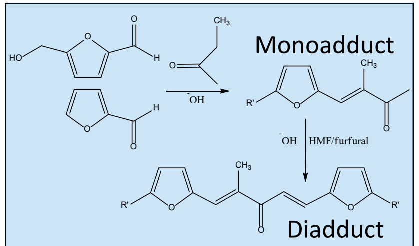


Outcomes:
- Stable operation for 6 h with yields and conversions from hydrolysate very similar to those with pure sugars
- Sugar concentration increased to 30% with little drop off in glucose conversion/HMF yield especially after increasing $AlCl_3$ concentration to 16 mM from 8 mM and eliminating HCl

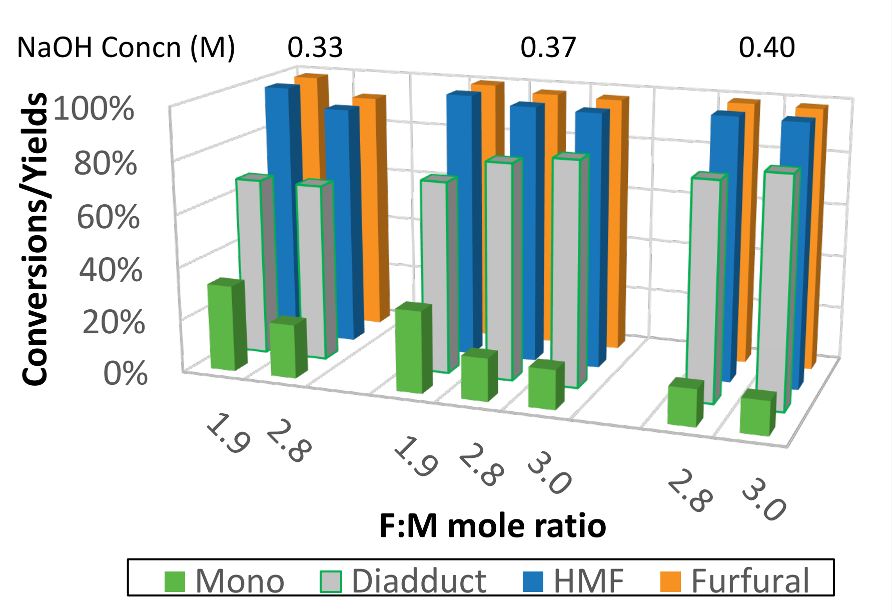
Aldol Condensation and HDO

Objectives:
- Produce aldol condensation intermediates from corn stover hydrolysate furfurals
- Develop better understanding of catalyst roles in HDO of aldol condensation intermediates

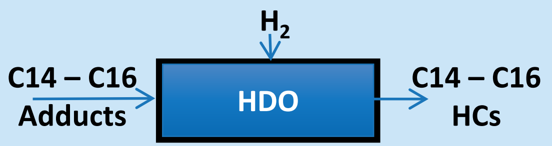
Aldol Condensation with Furfurals from Corn Stover Hydrolysate



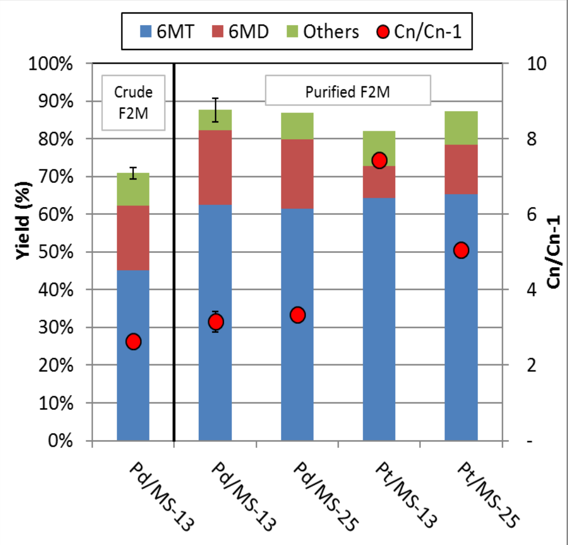
- High concentration furfurals (50 g/L) from CS hydrolysate
- 60 °C, 60 min
- Furfurals: MEK (F:M) mole ratio



Effect of Catalyst on HC Yield



- HDO product (82 mol% yield) from mixed furfural/HMF/MEK aldol product with Pd/SiO_2-Al_2O_3
- Catalysts with acidic silica-alumina supports (MS-13 & -25) needed to produce HCs.
- More C loss (6MD vs 6MT) on Pd catalysts. Larger metal particles appear to favor decarbonylation



6MT = 6-methyl tridecane; 6MD= 6-methyl dodecane
300 °C, 50 bar H_2, 2h, ~2 mole% Pd or Pt

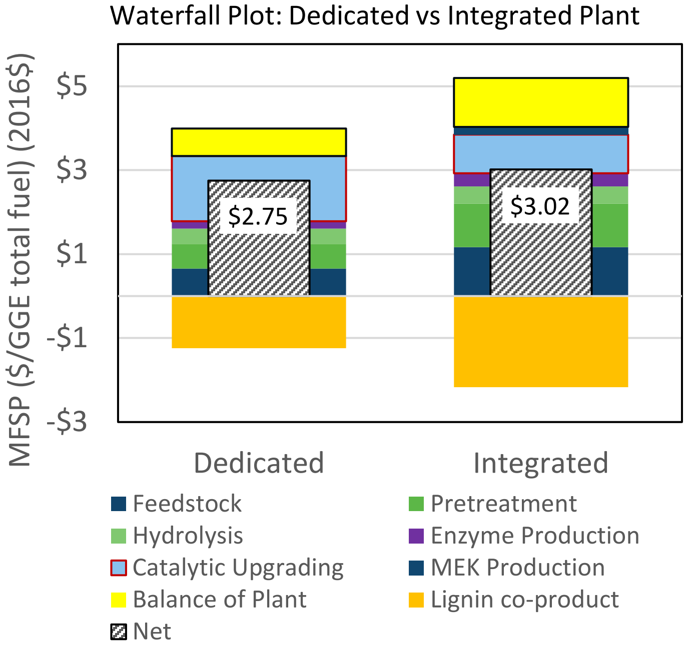
Outcomes:
- Aldol condensation intermediate made with furfurals from corn stover hydrolysate with predominance of C14-C16 diadducts vs C9-C10 monoadducts at higher F:M mole ratio and higher NaOH concn.
- C loss during HDO possibly due to different HDO mechanisms. Appears to be unrelated to support acidity.

TEA and Future Work

Technoeconomic Analysis

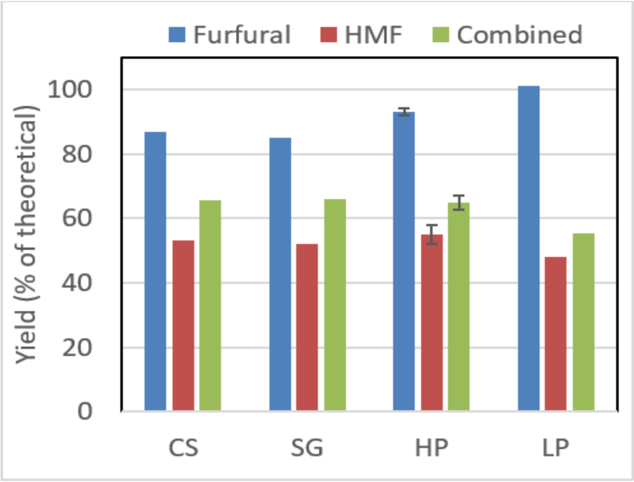
Fuel Yields
- Integrated 61.2 GGE/ton
- Dedicated 108.4 GGE/ton

Decrease Cost by
- Decreasing solvent use
    - Lower dioxane:water
    - Increase sugar concn.
- Increase furfurals yields
- Decrease C loss during HDO
- Better process integration



Direct Furfurals Production from Raw Feedstocks

- Furfurals produced from raw feedstocks without any pretreatment or enzymatic hydrolysis (CS, corn stover; SG, switchgrass; HP, hybrid poplar; LP, loblolly pine).
- 200°C, 5 min, 8 mM $AlCl_3$, 33 mM HCl aqueous dioxane solvent (dioxane: water 2:1 v/v).



Future Directions

- Reduce the MFSP contribution to the catalytic upgrading process by 25% as compared to the 2020 TEA design case. By:
- Investigate furfurals production directly from raw feedstocks. Possibly eliminating pretreatment/hydrolysis costs
- Improving aldol condensation of MEK with biomass hydrolysate derived furfurals
- Decrease C loss during HDO of furfurals-MEK aldol condensation products.
- In out-years, flow reactor time on stream operation will be extended or number of recycles in batch reactors increased.
- At least 1.0 L of hydrocarbon product for fuel performance testing will be generated by end of the 3-year project cycle.
- TEA will be refined based on conversion results and catalyst cost estimates.

Summary

*<u>Goal</u>: Improve the **catalytic upgrading of targeted biochemically-derived intermediates** to hydrocarbon fuels and chemical co-products by performing focused and integrated R&D to achieve **25% to 33% cost reduction** in the **catalytic upgrading process area** of an **integrated biochemical conversion process***

Management

- Integrated task structure
  - Regular, structured cross-lab interactions
  - Shared/complementary capabilities
- Numerous cross-project interactions
  - ChemCatBio enabling projects
  - Biochemical conversion
  - Other BETO consortia
- Early risk identification with structured R&D for risk mitigation

Approach

- Using common/shared:
  - Process materials
  - Analytical methods
  - Reactor systems
  - Fuel assessment
  - TEA tools and approaches
- Critical success factors, challenges, and associated strategies developed
- Go/no-go decision point tied to partial completion of end-of-project milestone and focusing of future efforts

Impact

- Project results used to update TEA design reports and annual SOTs
- Numerous impactful journal articles, patents, webinars, and conference presentations
- Industrial engagement activities with several companies
  - Leveraged TCF and FOA projects

Progress and Outcomes

- 2,3-BDO Upgrading:
  - Catalyst/process improvements; inhibitor identification/mitigation; phase separation/recovery; fuel and co-product targets
- Carboxylic Acids Upgrading:
  - Catalyst/process improvements for reductive etherification for advantaged biodiesel blend stock AND ketonization-HDO for Diesel/jet HCs; mixed acids applications
- Furfurals Upgrading:
  - Furfurals production in flow reactors using high concentration sugars; aldol condensation to achieve intermediate diadducts; detailed TEA design case developed

Quad Chart

Timeline
- Project start date: 10/1/2019
- Project end date: 9/30/2022

	FY20	Active Project
DOE Funding	$2.25M	$7.75 M (3 years: FY20-FY22)

Project Partners*
NREL (60%)
ORNL (18%)
PNNL (11%)
LANL (11%)

Barriers addressed
- Ct-E: Improving Catalyst Lifetime
- CT-F: Increasing the Yield from Catalytic Processes
- ADO-A: Process Integration

Project Goal
Improve the catalytic upgrading of targeted biochemically-derived intermediates to hydrocarbon fuels and chemical co-products by performing focused and integrated R&D to achieve 25% to 33% cost reduction in the catalytic upgrading process area of an integrated biochemical conversion process enable overall an MFSP of <$2.5/GGE (biochemical conversion pathway with lignin co-product valorization)

End of Project Milestone
Demonstrate improvements consistent with a cost reduction from 25% to 33% (depending on pathway) compared to FY19 SOT in catalytic upgrading of biochemical process-derived carboxylic acids, 2,3-BDO, and furfurals intermediates.

Funding Mechanism
FY19 AOP Merit Review (within ChemCatBio)

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ChemCatBio
Chemical Catalysis for Bioenergy

Additional Slides

Responses to Previous Reviewers' Comments

- This project summarizes a broad effort in moving a family of technologies for fuel and co-product production toward commercial development and is driven by TEA-informed decisions that steer the work toward $/GGE targets. The suite of technologies seem very appropriate to the types of feedstocks available. While TEA is helpful for assessing progress toward $/GGE targets, the impact of specific catalytic technologies may be somewhat obscured. Such heavy reliance on co-products may be of concern: it isn't clear if the technologies have been demonstrated yet, and it isn't clear if, e.g., lignin co-product markets are commensurate in size with fuel markets. It would be helpful to make the case for producing fuels + co-products vs fuels alone vs co-products alone.
  - Response: We appreciate the comment on producing value added chemicals to enable biofuels production. We are aware of the market volume challenges for specific co-products. Envisioning the future bioeconomy, there will many co-products via sugars, along with fuel production. The initial MFSP and importance of the lignin conversion process has been determined and presented in Biochemical Conversion session presentations. We will also include more TEA scenarios, including fuels only, co-products only, more than one co-products, etc. For 2,3-BDO upgrading, we envision a flexible process where 2,3-BDO could be converted to either fuels and/or value added chemicals (e.g. butadiene, 1-butanol, isobutanol).

Responses to Previous Reviewers' Comments

- This is a quintessential CCB project; taking in biochemically-derived intermediates and further converting them with chemical catalysis all under the watchful eyes of the TEA team. The bar appears to be set high in all the tasks and the overall impact of the project will be commensurately high at sunset later this year. What's not working: while TEA has been used to indicate that each of the main four pathways has potential to reach the goal of <$3/gge, the actual current value of the $/gge has not been presented. This would provide valuable information.
  - Response: The TEA was conducted within the first 6 months of effort for some upgrading pathways. Significant progress has been made by each catalytic upgrading route within the last 18 months and the TEA will be updated in Q4 FY19 and will further inform opportunities for cost reduction. (*Added note*: The TEA results from the FY19 SOT cases for each route were used in developing the end-of-project milestone metrics for the new 3-year AOP cycle for the CUBI project (FY20-FY22).

Responses to Previous Reviewers' Comments

- Large effort involving many labs and 4 different tasks around a very important topic and many different processes. Very comprehensive work involving many skills and resources. One of the backbone of the consortium. It would be beneficial to have a clear definition of the range of products that are being targeted and the state-of-the-art in many of these processes. The overall success of the project is dependent on the success of the lignin valorization projects. Routes are being evaluated with comprehensive TEA. Need to relate costs not only to catalyst performance but also other factors, such as solvent selection and downstream separation process. The relevance to BETO and potential for technology development is clear.
  - Response: We thank the reviewers for their positive comments. We appreciate concerns regarding the cost dependency on the production of lignin-derived co-products and will show the cost of producing the sugar derived products with and without lignin valorization. TEA analysis will continue to be an important guide to research direction and will include all related costs (solvent selection, downstream processing, catalyst cost). For BDO upgrading route via 2-step process, the co-products are MEK, 1-butanol and isobutanol. The C5 iso-olefins product are used in the synthesis of TAME, a fuel additive. For state-of-the-art for BDO upgrading to fuels, very limited data is available. KSU has demonstrated the conversion of 2,3-BDO to butenes but their work is limited to zeolite catalysts, operating with pure 2,3-BDO and conducted under H2. In addition to zeolites, we have investigated mixed oxides catalysts (e.g. AlPO4, AlZrLa, ZnZrOx) for the BDO to olefins upgrading and demonstrated that using mixed oxides catalysts leads to the formation of a C2-C6 iso-olefins mixture with up to 75% C5 iso-olefins. In addition, we demonstrated that our 2-step process for 2,3-BDO upgrading to iso-olefins fuel precursors can operate without H2.

Publications, Presentations, Patents (2019 – present)

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- Hafenstine et al. (2020). Single-phase catalysis for reductive etherification of diesel bioblendstock. Green Chemistry. 22, 4463-4472
- Mittal, A., Pilath, H.M. and Johnson, D.K., 2020. Direct conversion of biomass carbohydrates to platform chemicals: 5-hydroxymethylfurfural (HMF) and furfural. Energy & Fuels, 34(3), 3284-3293
- Shiba P. Adhikari, Junyan Zhang, Qianying Guo, Kinga A. Unocic, Ling Tao, Zhenglong Li. 'A Hybrid Pathway to Biojet Fuel via 2,3-Butanediol.' Sustainable Energy & Fuels. 2020, 4, 3904-3914. (Back journal cover highlight)
- Yeonjoon Kim, Ashutosh Mittal, Heidi Pilath, Brian Etz, David J. Robichaud, David K. Johnson, and Seonah Kim. Prediction of Hydroxymethylfurfural Yield in Glucose Conversion through Investigation of Lewis Acid and Organic Solvent Effects. ACS Catalysis 2020, 10, 14707−14721. https://dx.doi.org/10.1021/acscatal.0c04245.
- Huo et al. (2021). Towards net-zero sustainable aviation fuel with wet waste-derived volatile fatty acids. PNAS. Accepted.

Publications, Presentations, Patents (2019 – present)

Presentations

- V. Vorotnikov, T.R. Eaton, A.E. Settle, K. Orton, E.C. Wegener, C. Yang, J.T. Miller, G.T. Beckham, D.R. Vardon. Inverse bimetallic catalysts for selective reduction of propionic acid. Spring 2019 American Chemical Society Meeting, Orlando, FL. April 2019
- Z. Li, J. Zhang, S. Adhikari, K. Unocic. "Catalytic Upgrading of Biomass Derived 2,3-Butanediol to Biofuels and Chemicals--2D Pillared Zeolite to Mitigate Coking" ACS National Meeting, Orlando, FL, April 4, 2019.
- S Adhikari, J Zhang, Z Li, "Catalytic Upgrading of Biomass Derived 2,3-Butanediol to Biofuels and Chemicals" Presented by Zhenglong Li - ACS National Meeting, Orlando, FL, April 2019 (Invited)
- Johnson, David. Hydrodeoxygenation of biomass-derived intermediates to paraffins for blending into jet or diesel fuels. Presentation at the ACS Spring 2019 National Meeting Orlando, FL.
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- Johnson, David. Production of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde from biomass hydrolysates as intermediates in the production of hydrocarbons from biomass sugars. Poster presented at the 41st Symposium on Biotechnology for Fuels and Chemicals in Seattle, WA.
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- V. Vorotnikov, T.R. Eaton, A.E. Settle, K. Orton, E.C. Wegener, C. Yang, J.T. Miller, G.T. Beckham, D.R. Vardon. Inverse bimetallic catalysts: Active phases for selective reduction of carboxylic acids. North American Catalysis Society Meeting, Chicago, IL. June 2019.

Publications, Presentations, Patents (2019 – present)

Presentations (continued)

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- S Adhikari, J Zhang, Z Li, “Jet Fuel Production from Bio-derived 2,3-Butanediol using 2D Pillared Zeolite” Presented by Shiba Adhikari – NAM26, Chicago, IL, June 2019
- G.R. Hafenstine, N.A. Huq, X. Huo, J. Stunkel, S.M. Tifft, D.R. Vardon. Conversion, stability, and selectivity improvements through catalyst development for the reductive etherification reaction and implications for bioblendstock production from waste biomass. Fall 2019 American Chemical Society Meeting, San Diego, CA. August 2019.
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- J. V.A. Requena, S. Kim, Y. Guan, X. Huo, J. Stunkel, S. Kim, D.R. Vardon, R.S. Paton. Experimental and computational studies of the production of 1,3-butadiene from bio-2,3-butanediol using SiO_2-supported H_3PO_4 derivatives. Fall 2019 American Chemical Society Meeting, San Diego, CA. August 2019.
- G.R. Hafenstine, N.A. Huq, D.R. Conklin, M.R. Wiatrowski, X. Huo, D.R. Vardon. Waste-to-energy process intensification for reductive etherification production of oxygenated diesel blendstocks. 24th Annual Green Chemistry and Engineering Conference. Virtual. June 2020.

Publications, Presentations, Patents (2019 – present)

Patents

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- Zhenglong Li. (2019) Catalysts for conversion of 2,3-butanediol-containing fermentation mixture to hydrocarbons. U.S. Patent No. 10,300,474 B2. Issued May 28, 2019.
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