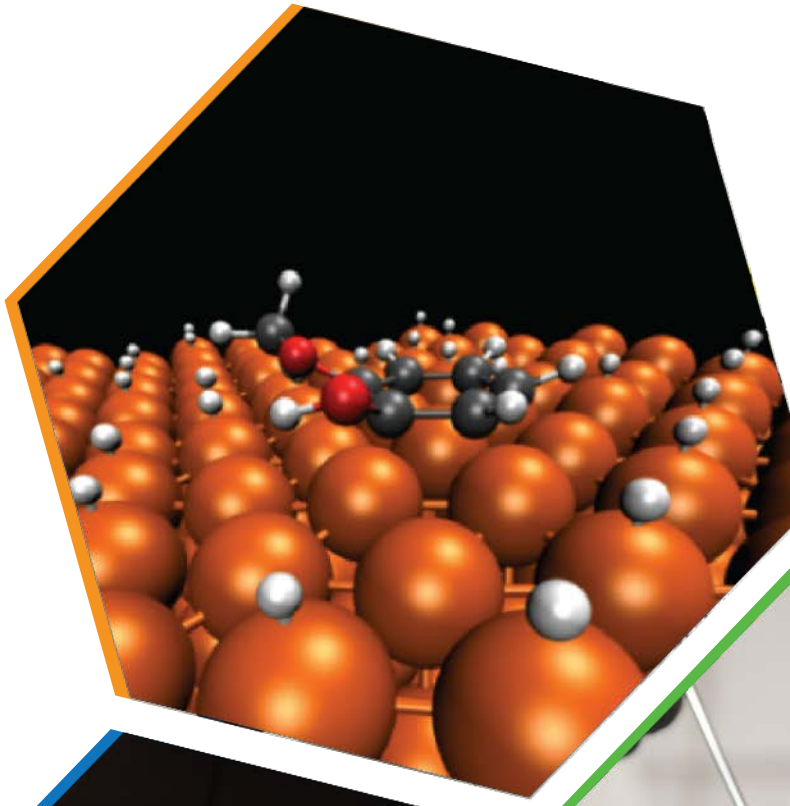
ChemCatBio
Chemical Catalysis for Bioenergy



Technology Options for Catalytically Upgrading Biochemically Derived 2,3-Butanediol from Lignocellulosic Biomass Feedstocks to Advanced Biofuels and Chemical Coproducts

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1 NREL 2 Oak Ridge National Laboratory 3 Pacific Northwest National Laboratory

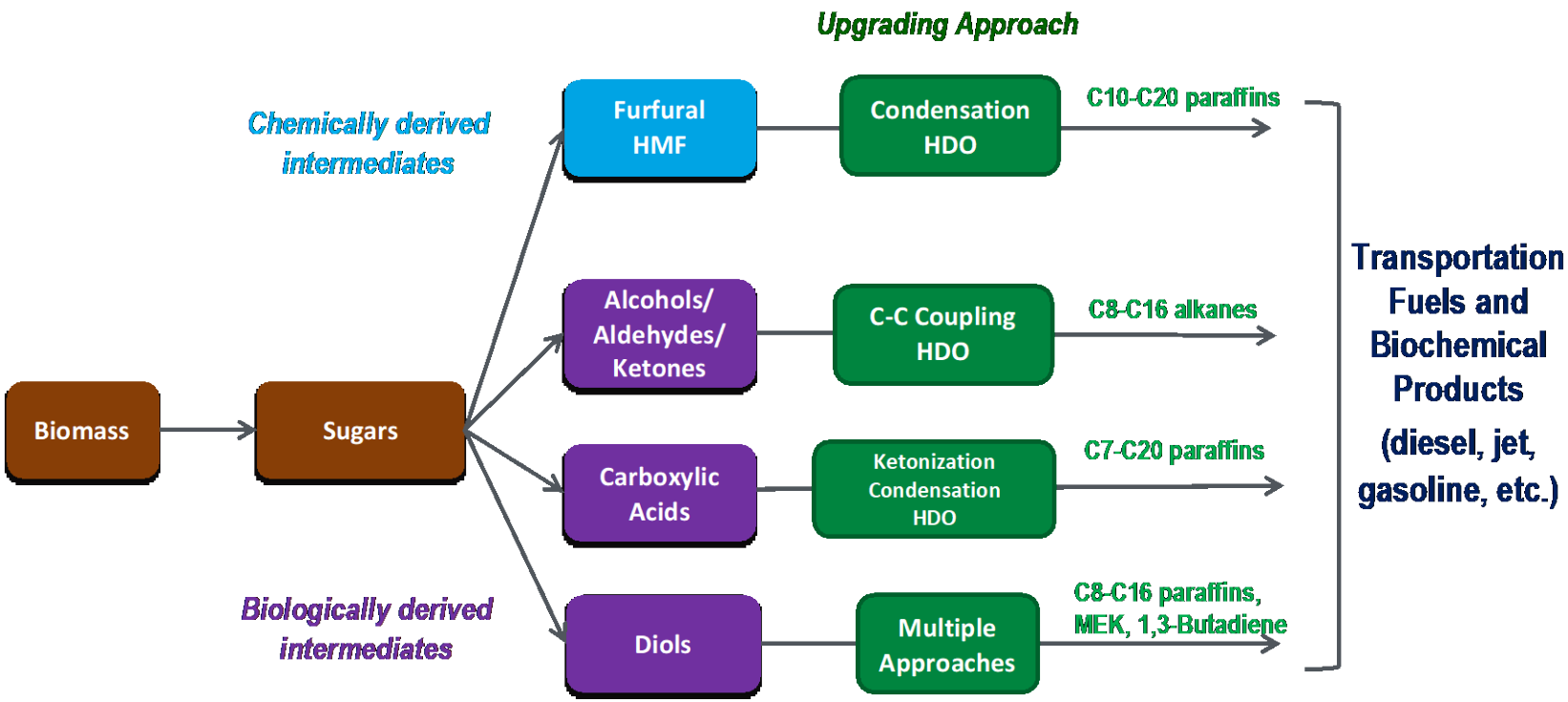
April 24, 2019

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

Project Overview

Catalytic Upgrading of Biochemical Intermediates (CUBI)

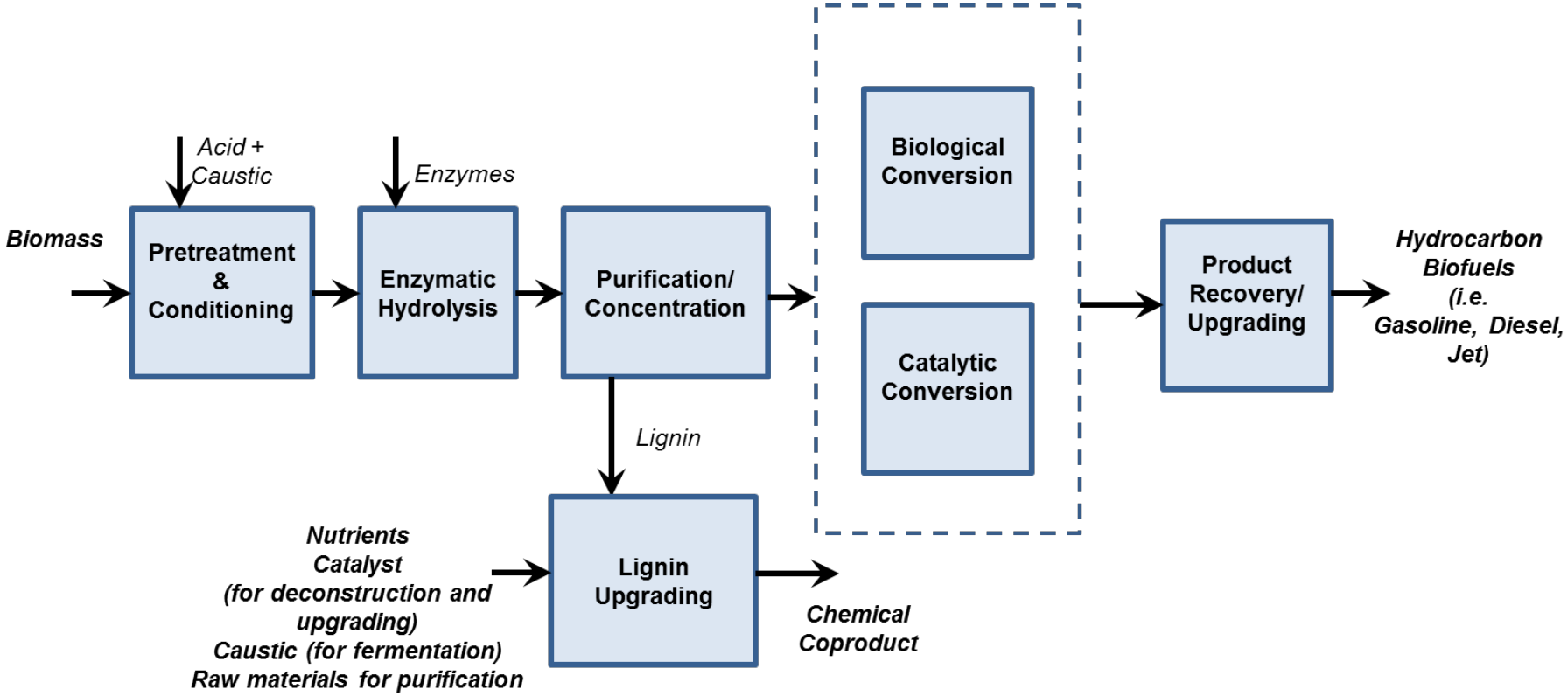
- Multi lab effort to develop and evaluate routes for **catalytic upgrading of biomass-derived sugars/related intermediates** into hydrocarbon fuels and co-products
- Facilitate **transition** from **clean sugars** (cane and starch-derived) to **cellulosic sugars**



NREL NATIONAL RENEWABLE ENERGY LABORATORY · OAK RIDGE National Laboratory · Pacific Northwest NATIONAL LABORATORY · Los Alamos NATIONAL LABORATORY EST. 1943

Process Flow for Biochemically-Derived Intermediates

- Typical biochemical conversion feedstock types are potential **high-volume** biomass sources (> 500 millions dry tons/year by 2040 [1])
  - **Agricultural residues** (corn stover, wheat straw, etc.)
  - **Herbaceous energy crops** (switchgrass, miscanthus, etc.)



[1] 2016 Billion Ton Report, Vol 2 (Jan, 2017), Figure ES-1. https://www.energy.gov/eere/bioenergy/downloads/2016-billion-ton-report-volume-2-environmental-sustainability-effects

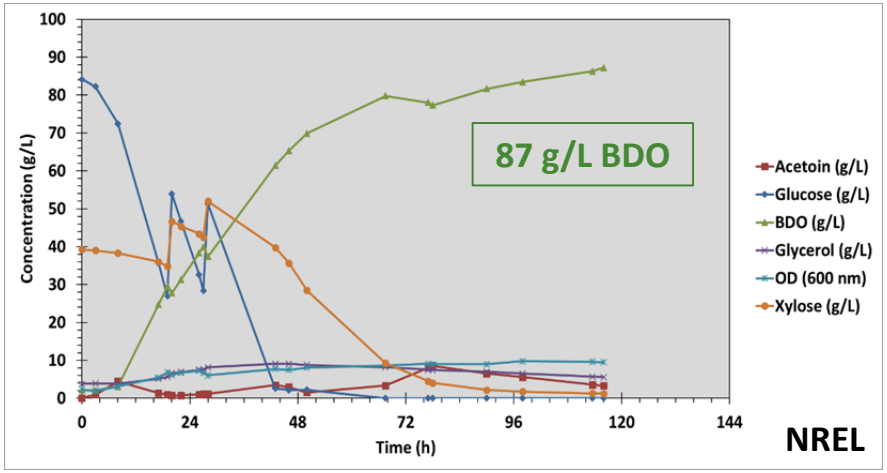
2,3-BDO to Fuel Intermediates and Co-Products

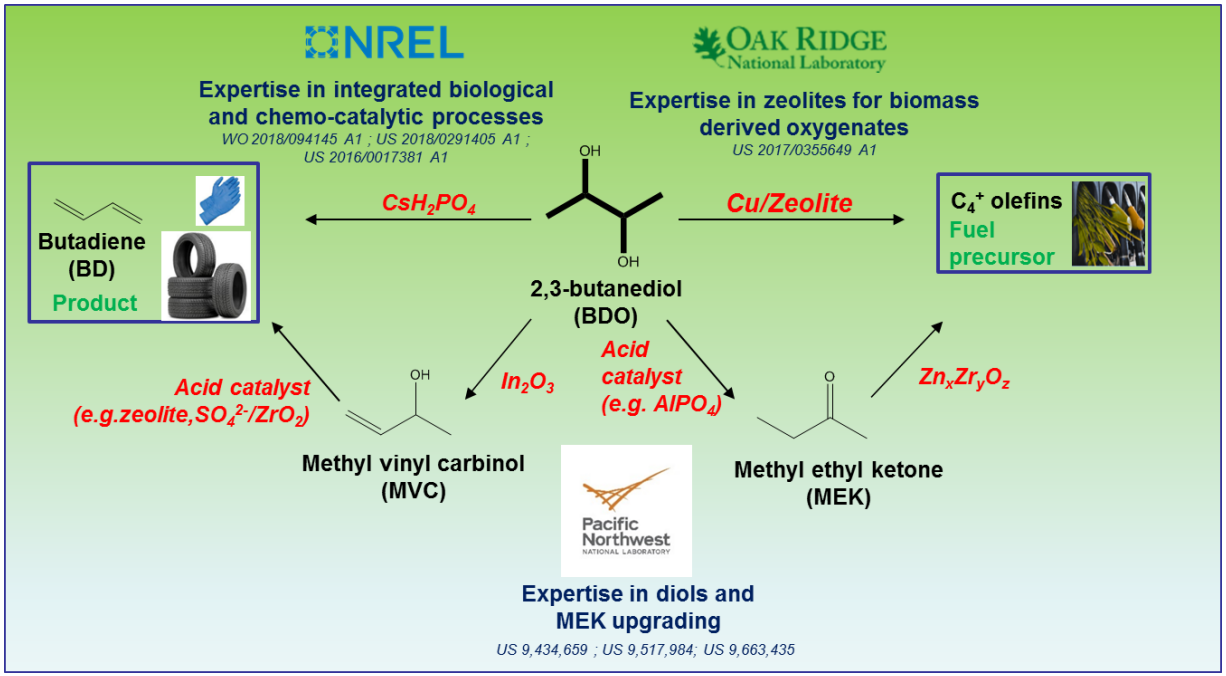
2,3-BDO from Corn Stover Hydrolysate

Advantages:

- 2,3-BDO produced at high titer due to low toxicity
- High distillate yield (~70% C from BDO in distillate)
- Many co-product opportunities: MEK, BD, epoxide, etc.

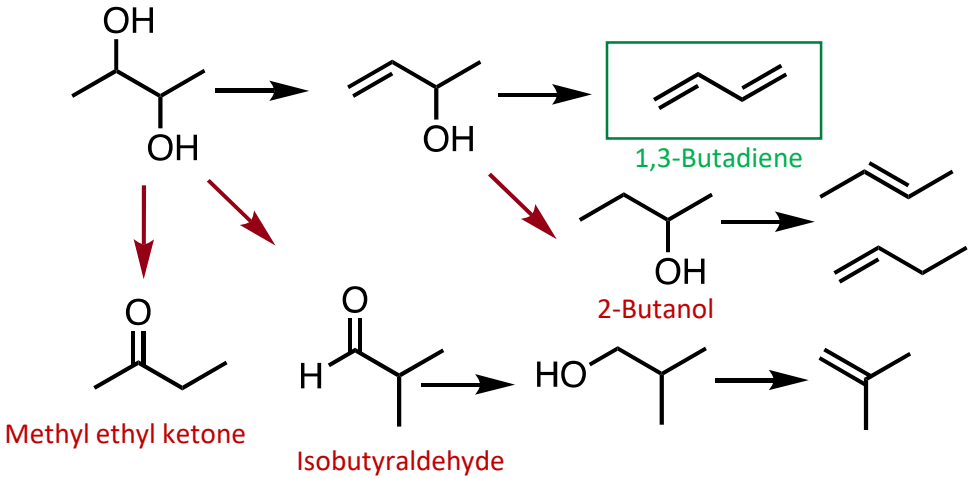
160 L Pilot Fermentation at NREL





Single Step Conversion to 1,3-Butadiene

Research Network for 1,3-Butadiene Production

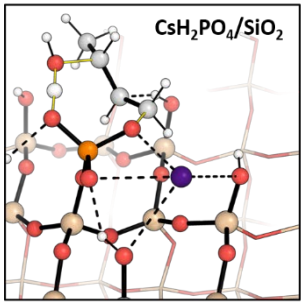


Butadiene large and growing market (USD $16.5 billion 2016; forecast USD $24 billion 2024)[1]

Process Research & Development

Identify requirements for catalyst composition, process conditions, and feed purity specifications for efficient, selective, and economic butadiene

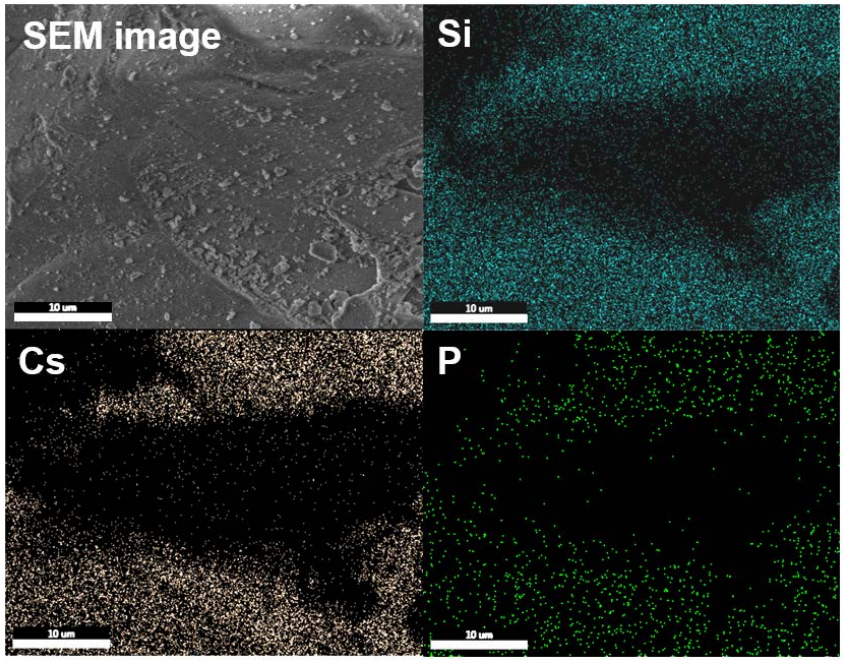
Foundational Science Questions



Understand reaction mechanism, limiting step, catalyst active site structure and properties that govern single step dehydration pathway

[1]Global Market Insights, Inc.

Single Step Conversion to 1,3-Butadiene



CsH_2PO_4 supported on a commercial SiO_2 validated for high butadiene yield

87% butadiene yield at >90% 2,3-BDO conversion

under select conditions

$10CsH_2PO_4/SA\text{-}SiO_2$ (Sigma Aldrich SiO_2)

Conditions: 2.0 g catalyst, 1 atm N_2 carrier gas at 220 sccm, 0.037 mL/min commercial 23BDO, WHSV 1.1 h^{-1}, 425°C

Tsukamoto, D.; Sakami, S.; Ito, M.; Yamada, K.; Yonehara, T. Chemistry Letters 2016, 45 (7), 831-833.

Catalyst	Cs loading (wt%)	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Initial 13BDE yield	Butadiene productivity ($g_{13BDE}\ g_{Cs}\ h^{-1}$)
$5CsH_2PO_4/AA\text{-}SiO_2$	2.65	157	0.72	0.9%	0.1
$5CsH_2PO_4/SA\text{-}SiO_2$	2.95	407	0.81	47%	6.4

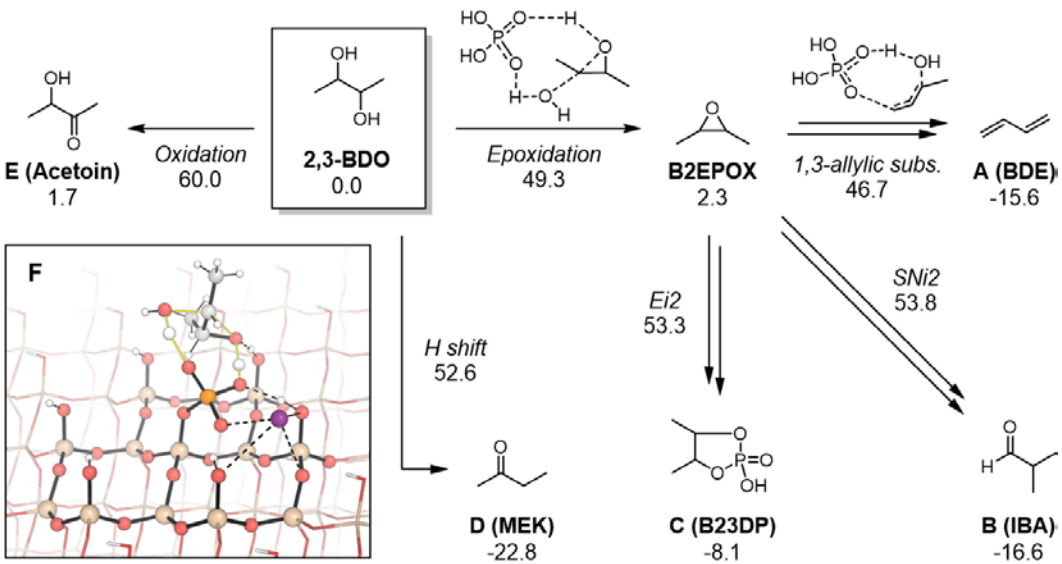
$5CsH_2PO_4/SA\text{-}SiO_2$	2.95	407	0.81	47%	6.4
$10CsH_2PO_4/SA\text{-}SiO_2$	5.13	337	0.76	61%	5.1
$20CsH_2PO_4/SA\text{-}SiO_2$	12.4	93	0.46	61%	2.2

Conditions: 2.0 g catalyst, commercial 2,3-BDO, 1 atm He carrier gas, 372°C, WHSV between 0.60-0.75 h^{-1}.

Single Step Conversion to 1,3-Butadiene

DFT calculations of energetics and TS

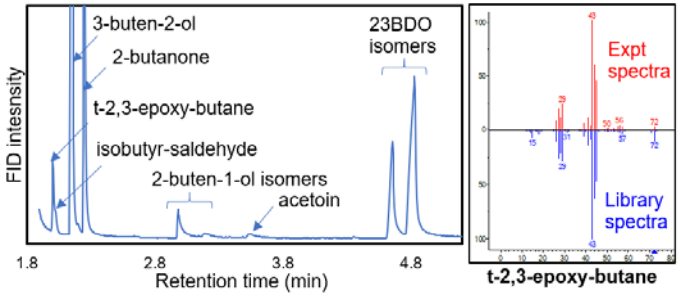
Epoxide identified as potential intermediate to butadiene



Seonah Kim (NREL), Robert Paton (CSU)

Experimental validation

Liquid product identification



Epoxide conversion

P_{B2EPOX} (kPa)	Residence time (s)	13BDE yield[a]	13BDE yield[b]
0.26	0.95	69%	29%
0.43	0.92	62%	30%
0.27	0.48	48%	30%

[a]10CsH_2PO_4/SA-SiO_2. [b]H_3PO_4/SA-SiO_2. Conditions: 2.0 g catalyst, 5 wt% t-2,3-epoxybutane in deionized water, 1 atm He carrier gas, 400°C.

Collaboration with Consortium for Computational Physics and Chemistry (CCPC) identified epoxide transformation as rate limiting step

Single Step Conversion to 1,3-Butadiene

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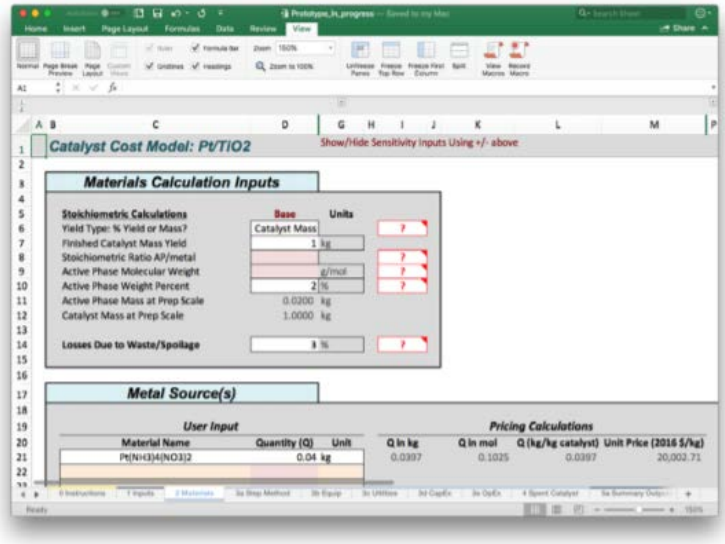
Chemical Catalysis for Bioenergy

Catalyst Cost Model Development (CatCost)

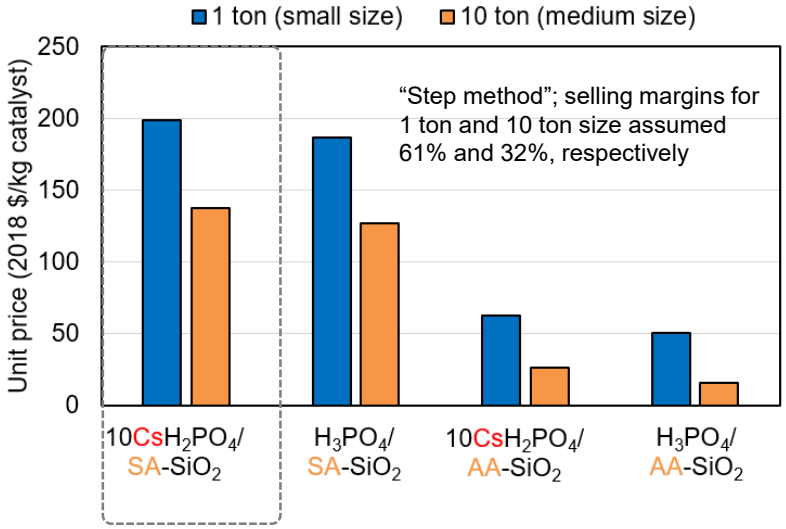


Baddour, F. G.; Snowden-Swan, L.; Super, J. D.; Van Allsburg, K. M. *Org. Process Res. Dev.* **2018**, 22, 12, 1599-1605

Price of raw materials

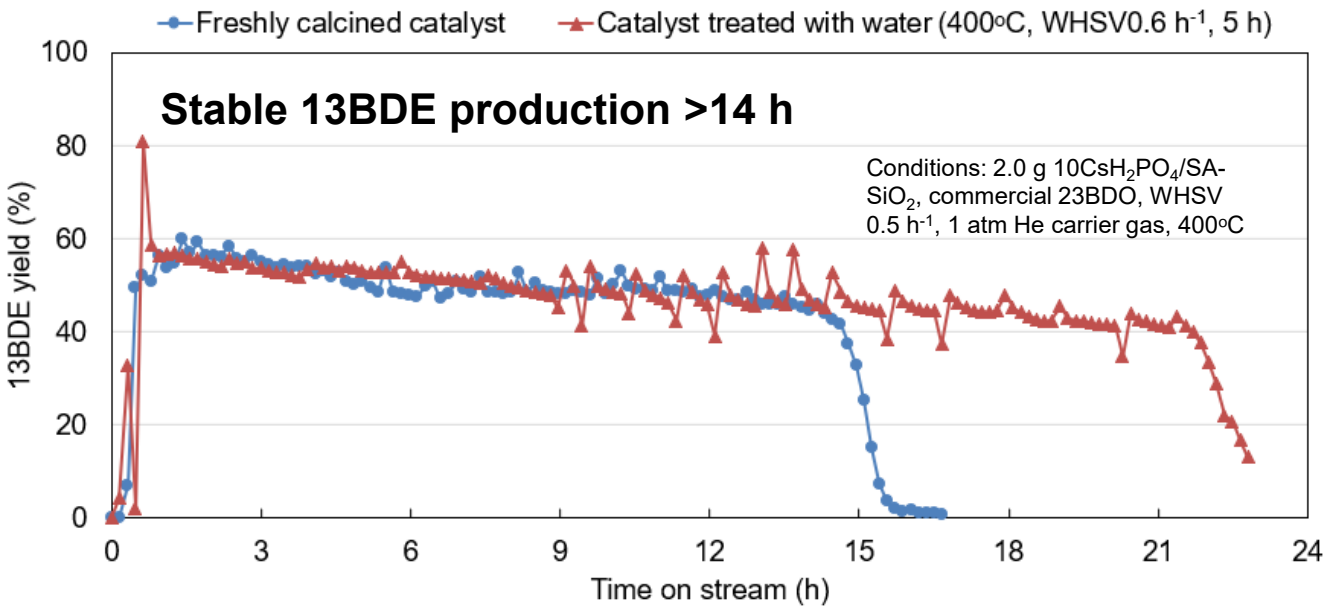
Materials	Unit price (2018 $/kg)
Cesium nitrate	88.33 (Extrapolation)
Monoammonium phosphate	0.38 (Bulk quote)
High surface area SiO_2	88.39 (Extrapolation)
Medium surface area SiO_2	6.49 (Extrapolation)

Unit catalyst price (raw material + production cost)



Cost of supported CsH_2PO_4 catalyst can be reduced by increasing production size, developing alternative high surface area support, and minimizing cesium loading

Single Step Conversion to 1,3-Butadiene



Fresh catalyst

337 m^2 g^{-1}
0.76 m^3 g^{-1}

400°C, WHSV 0.5 h^{-1}, 17h →

Fully deactivated catalyst

185 m^2 g^{-1}
0.47 m^3 g^{-1}

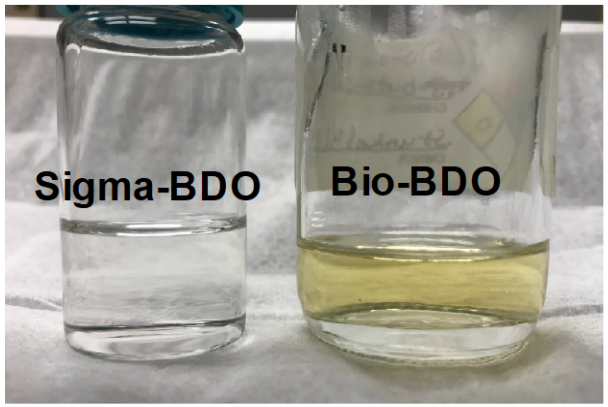
Ex situ, air, 400°C, 24h →

Regenerated catalyst

213 m^2 g^{-1}
0.51 m^3 g^{-1}

Post-catalyst characterization reveals deactivation likely due to coking and support restructuring; initial water exposure may extend time before regeneration

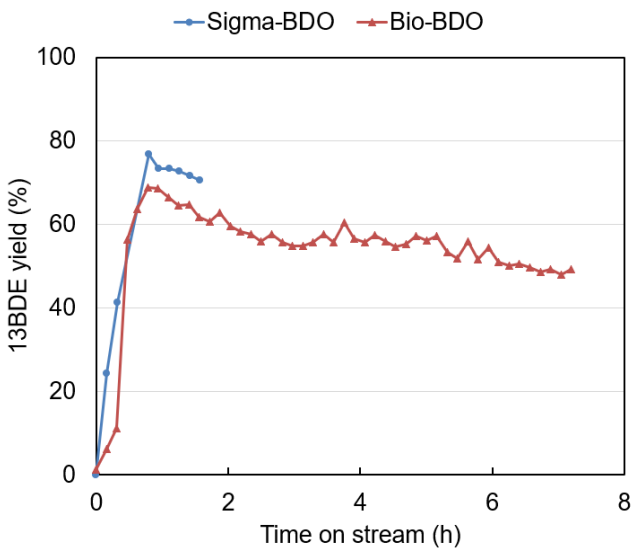
Single Step Conversion to 1,3-Butadiene



Sample	Lactic (g/L)	Acetic (wt%)	Acetoin (wt%)	Glycerol (wt%)	Ethanol (g/L)
Recovered Bio-BDO	ND	1.22	0.14	ND	ND

Mg	Si	P	S	K	Ca	Fe	Ni	Cu	Zn	Mo	Al	Mn
<1	111	10	158	12	3	<1	ND	ND	ND	ND	7	ND

Sample	Water (wt%)
Commercial BDO	1.4
Bio-BDO	8.2



Bio-BDO dehydration

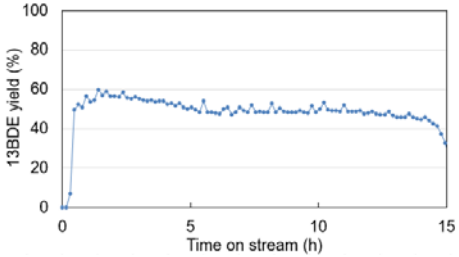
Conditions: 2.0 g 10CsH_2PO_4/SA-SiO_2, 1 atm He carrier gas at 100 sccm, bio-BDO at 0.017 mL/min, WHSV 0.48 h^{-1}, 400°C

Butadiene yield with bio-BDO <10% different from results with commercial 2,3-BDO; Ongoing work to examine long-term impact of impurities

Single Step Conversion to 1,3-Butadiene

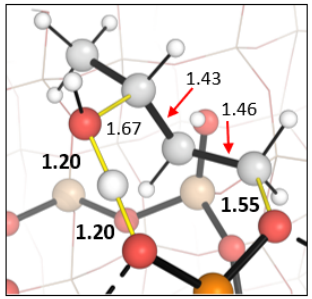
Catalyst and process development

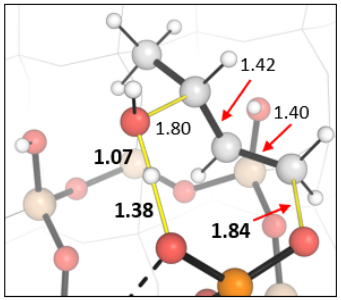
Evaluate CsH_2PO_4 performance and regeneration with hydrothermally stable supports



Mechanistic and material study

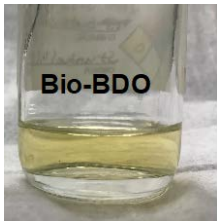
Characterize CsH_2PO_4 acidity and basicity; further understand the role of alkali metal





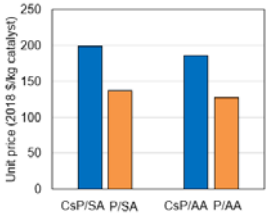
Feedstock specification

Further assess prolonged impact of biomass-derived impurities



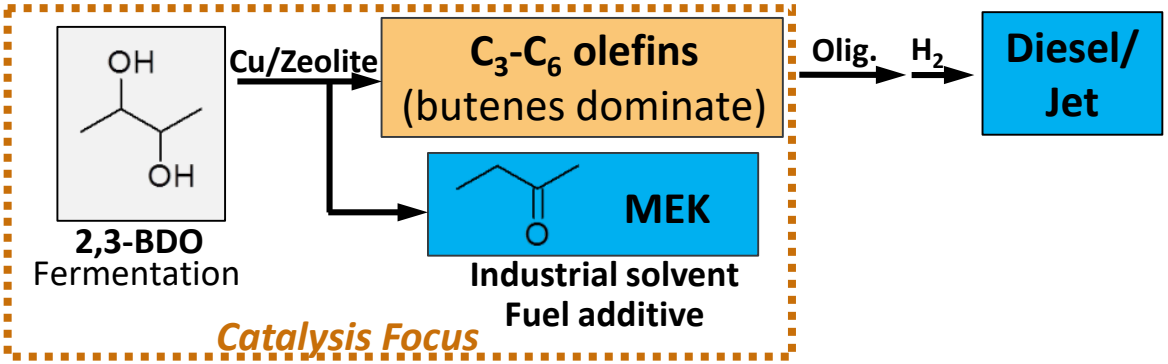
Economics and sustainability

Work with TEA team to assess water separation and catalytic upgrading requirements



2,3-BDO to Distillate and Co-Products

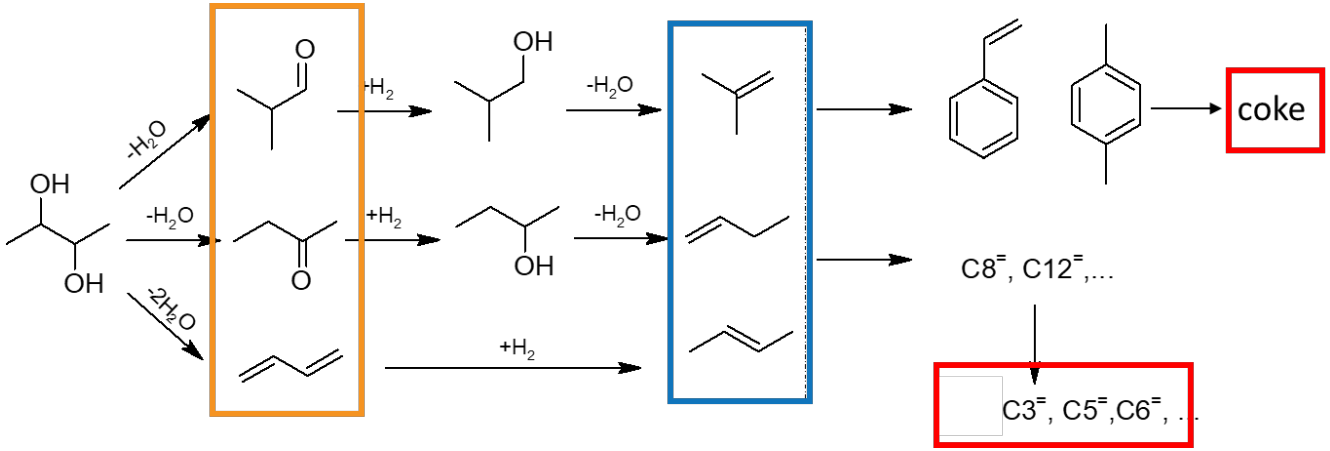
BDO to distillate via ***one-step*** C_3-C_6 olefin production



Advantages

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

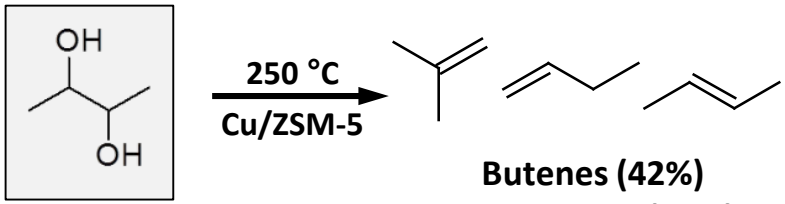
Possible reactions to convert 2,3-BDO to olefins in one step



Journal of Catalysis 330 (2015) 222–237

(Zhenglong Li, ORNL)

Hierarchical Cu/pillared-MFI for 2,3-BDO to Olefins



2,3-BDO

Butenes (42%)
C_3-C_6 olefins (44%)

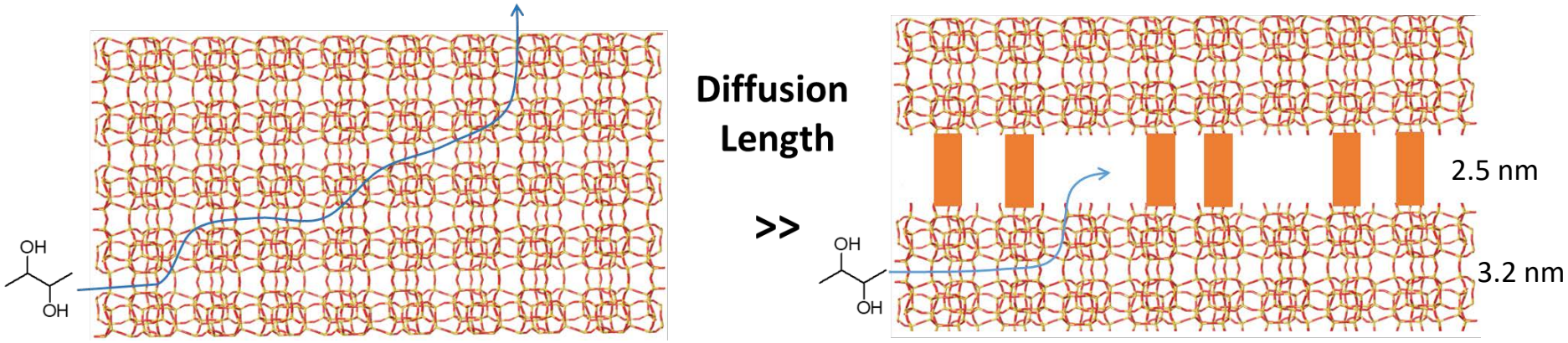
Journal of Catalysis 330 (2015) 222–237

Catalyst and Process Improvements

- Maximize C_3-C_6 olefins selectivity
- Enhance catalyst stability
  —coke resistance

Hierarchical 2D pillared MFI as a potential candidate to mitigate coke formation

Nature, 2009, 461, 246-249.



Microporous ZSM-5

Pillared MFI

2D pillared MFI:

- Reduce coke formation
- Minimize tertiary cracking products, e.g., propene, pentene

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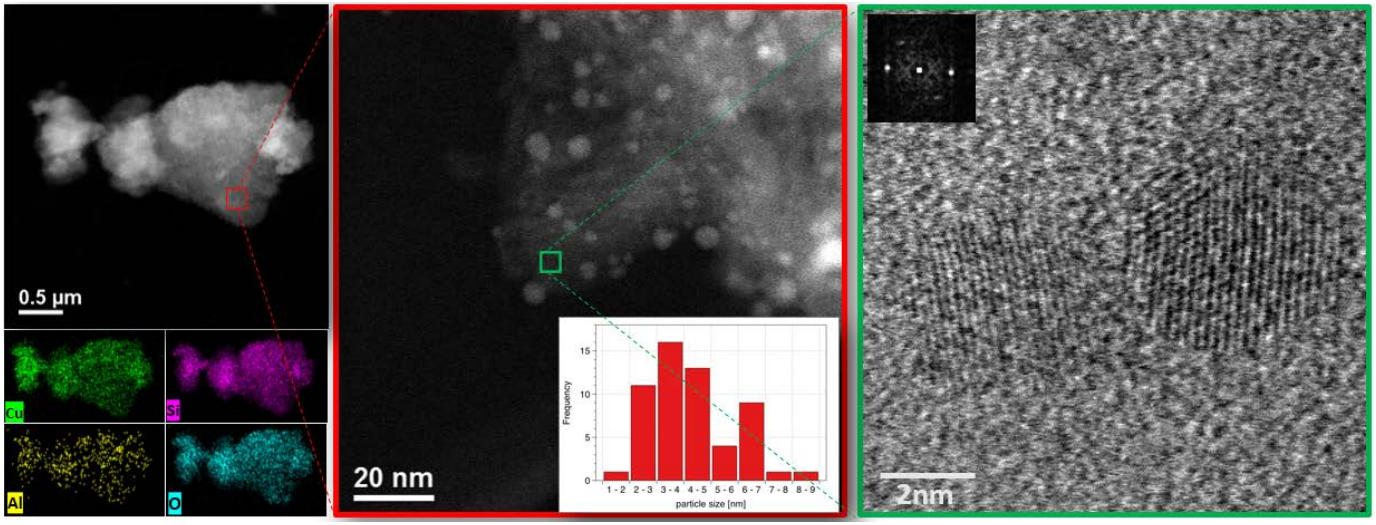
Cu/P-MFI Synthesis and Characterizations (ACSC)

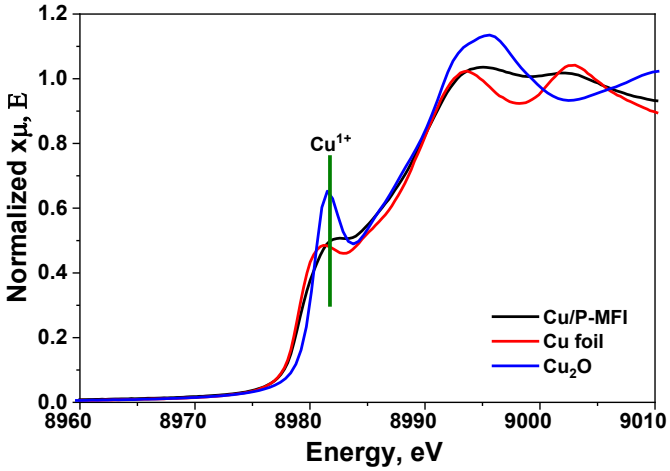
Catalyst synthesis: ammonia evaporation

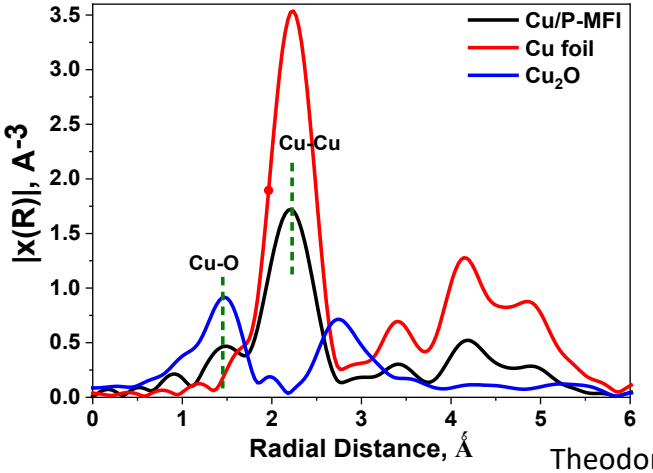
As-synthesized catalyst after calcination: CuO nanoparticles



Kinga Unocic (ORNL)

Majority Cu^0, minor Cu^+ exists: 300 °C, H_2 for 1 hr



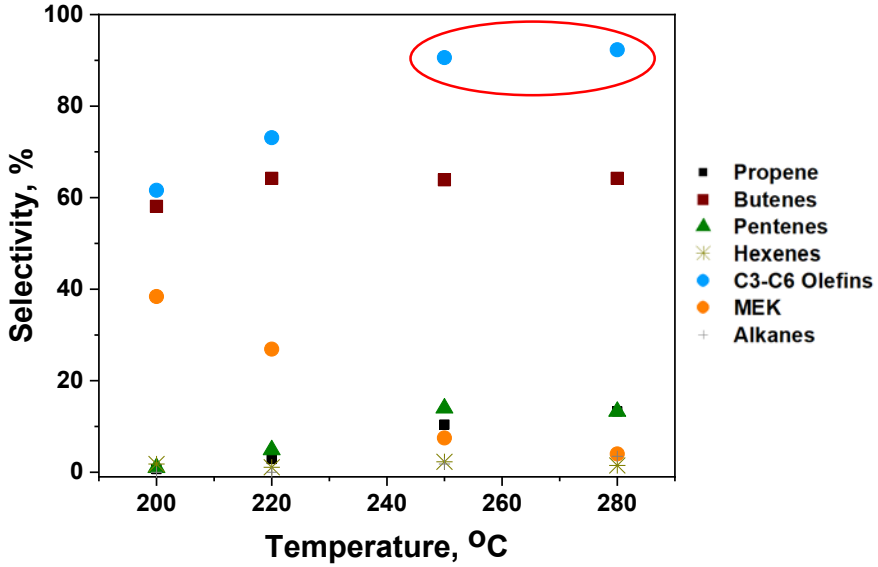


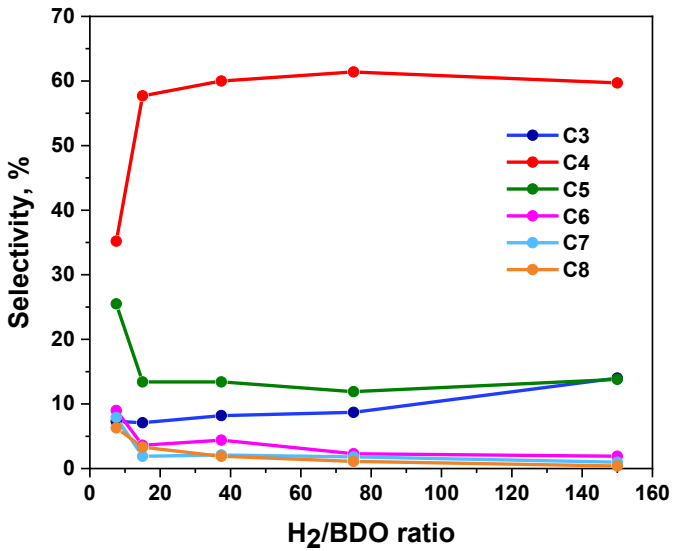
Theodore Krause (ANL)

Cu/P-MFI for C_3-C_6 Olefins from 2,3-BDO

Objective: Maximize C_3-C_6 olefins and optimize olefin compositions

- Temperature and H_2/BDO effect





- Optimum C_3-C_6 olefins: above 250 °C
- Tune MEK/olefins ratio by varying reaction temperatures

- H_2/BDO ratio below 15, olefin composition dramatically changes, butenes decrease

Outcome:

- Final co-product/fuel ratio can be tuned by varying the reaction temperatures
- Tune olefins/fuel composition by varying H_2/BDO ratio in the range of <15

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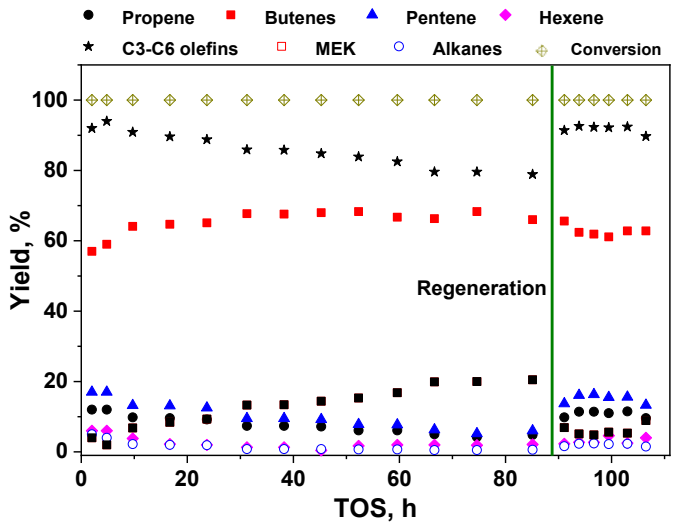
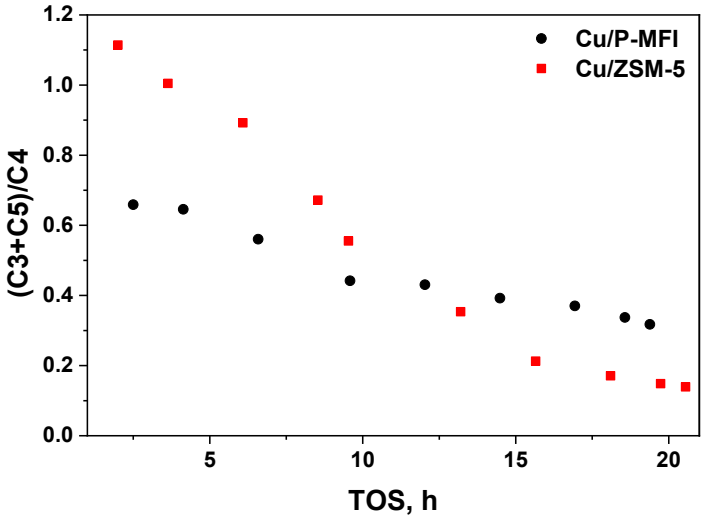
2D Pillared MFI to Mitigate Coke Formation

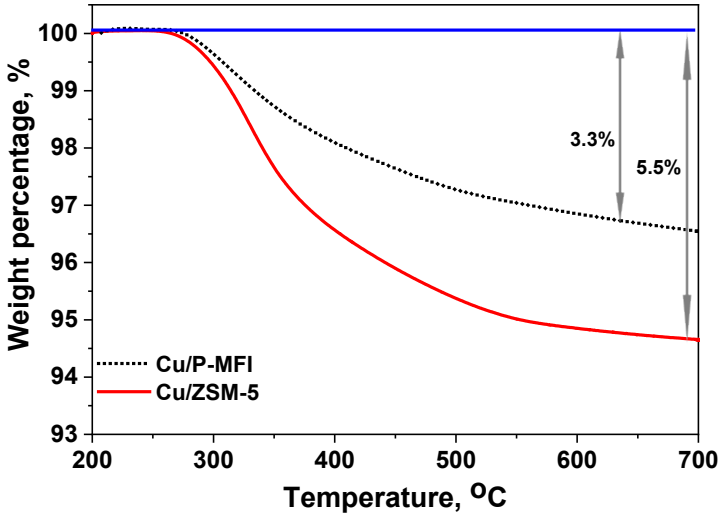
Cu/P-MFI durability testing for 2,3-BDO conversion



- Catalyst can be completely regenerated via calcination under air
  - **Reversible catalyst deactivation**
- 2D pillared MFI vs 3D ZSM-5 (preliminary)
  - Less tertiary products (cracking: C3, C5)
  - Slower change of product selectivity
  - **Better coke resistance**

2D pillared MFI vs 3D microporous ZSM-5





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Conversion of Fermentation Derived 2,3-BDO

Conversion of fermentation derived 2,3-BDO (vacuum distillation)-preliminary

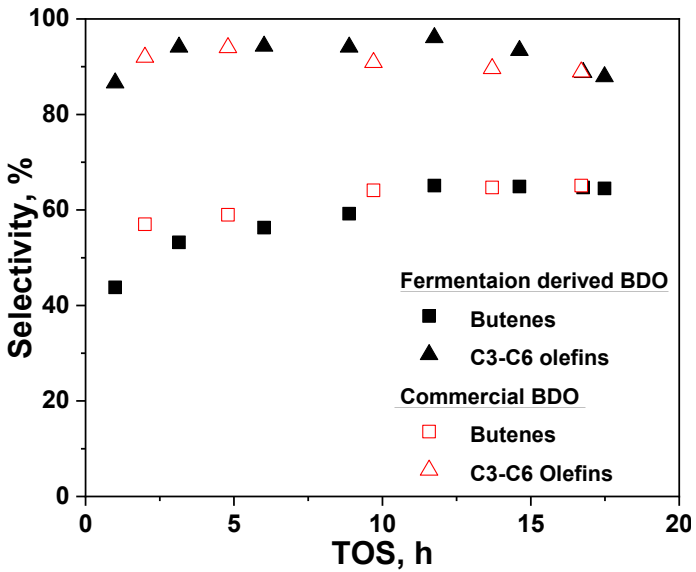
- ***Fermentation broth (NREL)***

Composition	Amount	Composition	Amount
Cellobiose	2.606 g/L	**BDO**	33.013 g/L
Xylose	8.408 g/L	**Acetoin**	20.216 g/L
Arabinose	2.643 g/L	**Ethanol**	0.226 g/L
Glycerol	2.175 g/L	**Lactic Acid**	0.527 g/L
Xylitol	2.986 g/L	**Acetic acid**	0.523 g/L

- ***Primary composition of fermentation derived 2,3-BDO (vacuum distillation)***

Composition	Amount, wt.%	Composition	Amount, wt.%
Water	20	**Acetic acid**	1
BDO	75	**Acetoin**	2

Other impurities: propanoic acid, butyrolactone, and other organics (GCMS)



- Fermentation derived BDO can be converted to C_3-C_6 mixed olefins with selectivity more than 90%
- **Impurities in the vacuum distillation derived BDO have no influence on catalyst performance**
- ***Focus on impurities impact--BDO obtained from different separation approaches***

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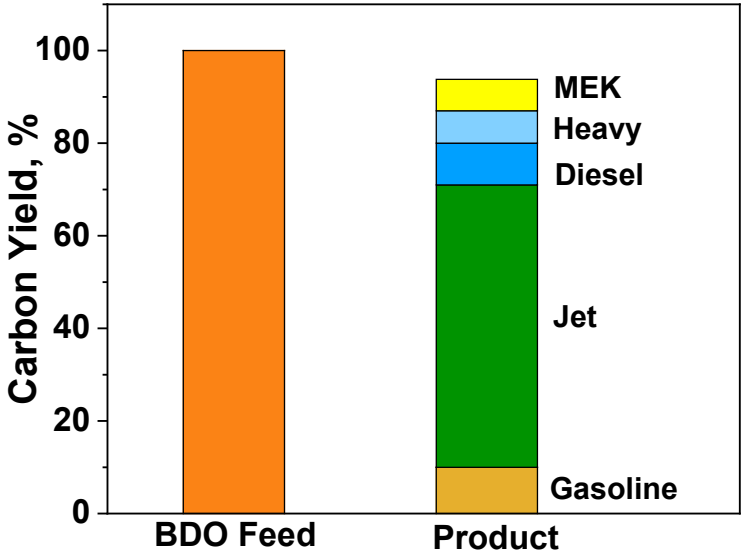
Distillate Production from C_3-C_6 Olefins

C_3-C_6 olefins (butenes dominate) → **Oligomerization** → **Hydrogenation** → **Diesel/ Jet**

ORNL BDO derived distillate

	Jet A	BDO derived jet
Density (g/mL)	0.775-0.84	**0.798**
HHV (MJ/Kg)	46.2	**46.7**
Freezing Point (°C)	max -40	**<-80**
Aromatics (v/v %)	max 25%	**<<25%**



- Preliminary fuel analysis: **meet Jet A properties** (NREL)
- Mainly C_8-C_{16}: iso-paraffinic
- Wide HCs distribution: odd carbon No.

- High overall carbon efficiency:
  - **~94% carbon** in final fuels and products

Outcome:
- BDO derived jet fuel meets preliminary fuel analysis criteria
- High distillate yield can be obtained from 2,3-BDO conversion

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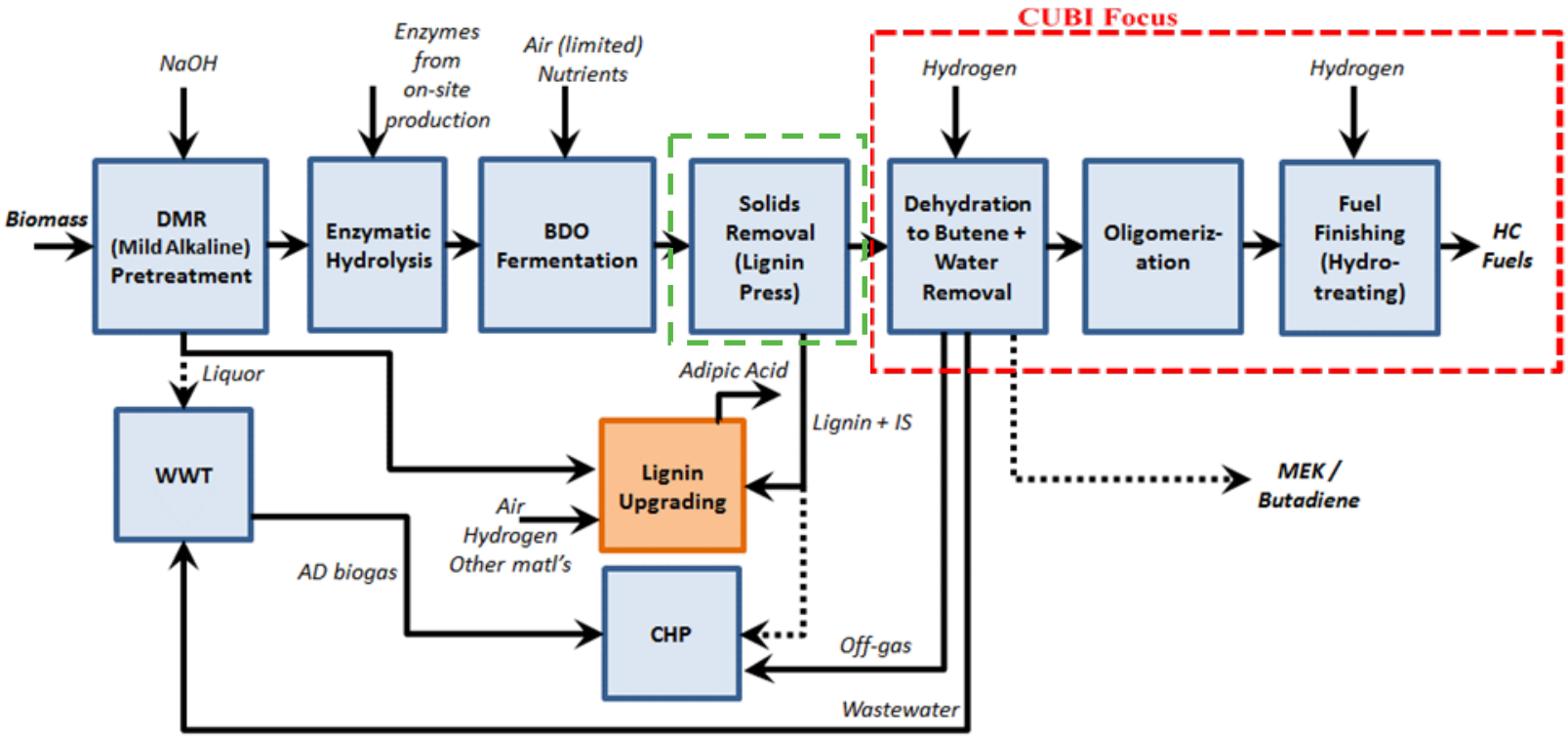
TEA – Guided Future R&D for 2,3-BDO Upgrading

- TEA sensitivity analysis to guide future R&D work
- Design report (NREL/TP-5100-71949) on Conversion of Biomass to Fuels and Products via 2,3-BDO pathway

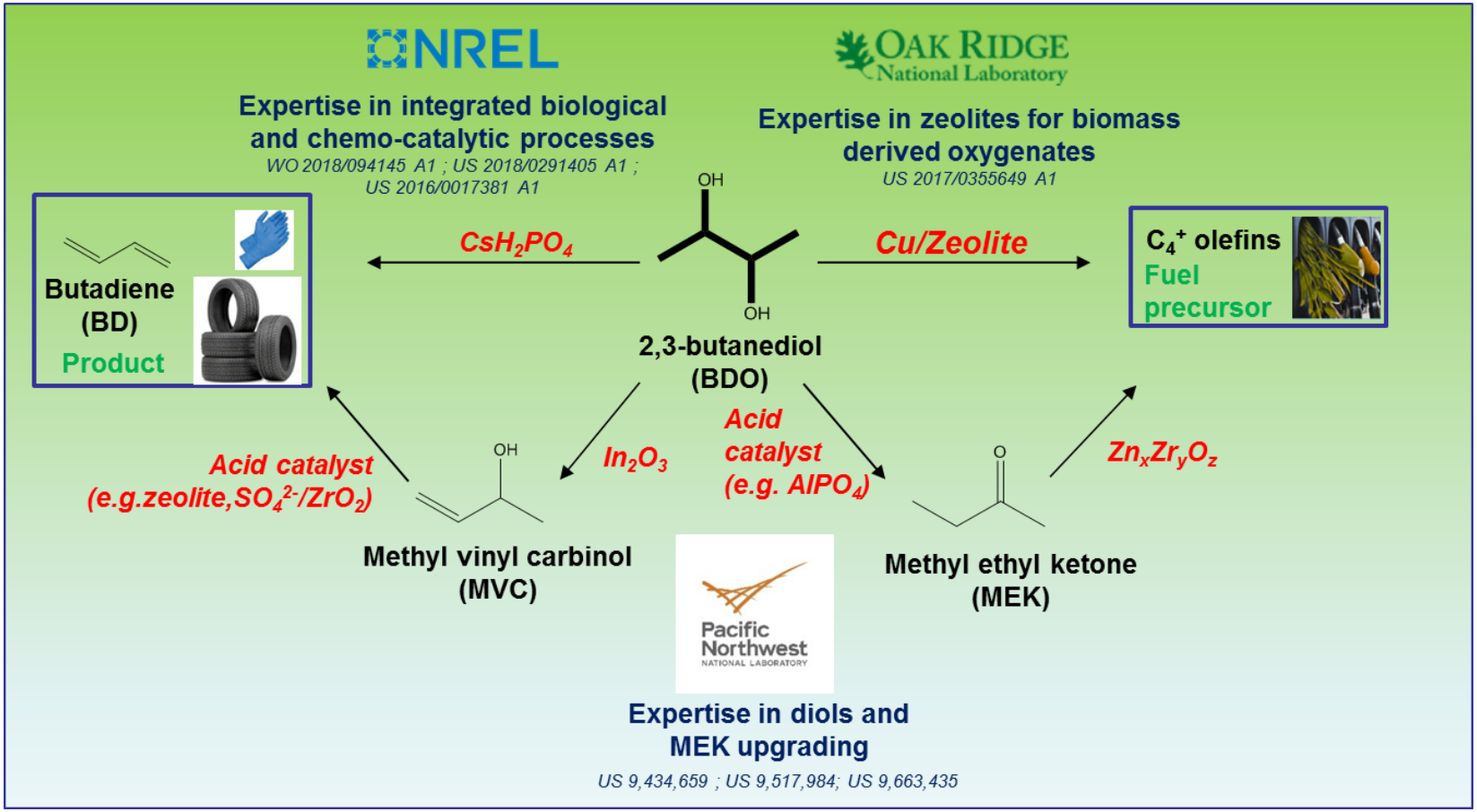


Identified research areas for catalytic process improvements:

- Divert 2,3-BDO to value-added **co-product** (e.g., MEK) for <$3.0/GGE
- **Reduce 2,3-BDO upgrading temperature** for liquid phase upgrading
- Improve **catalyst stability** against impurities to reduce the load of separation

NREL

2,3-BDO upgrading to Fuels and Co-Products



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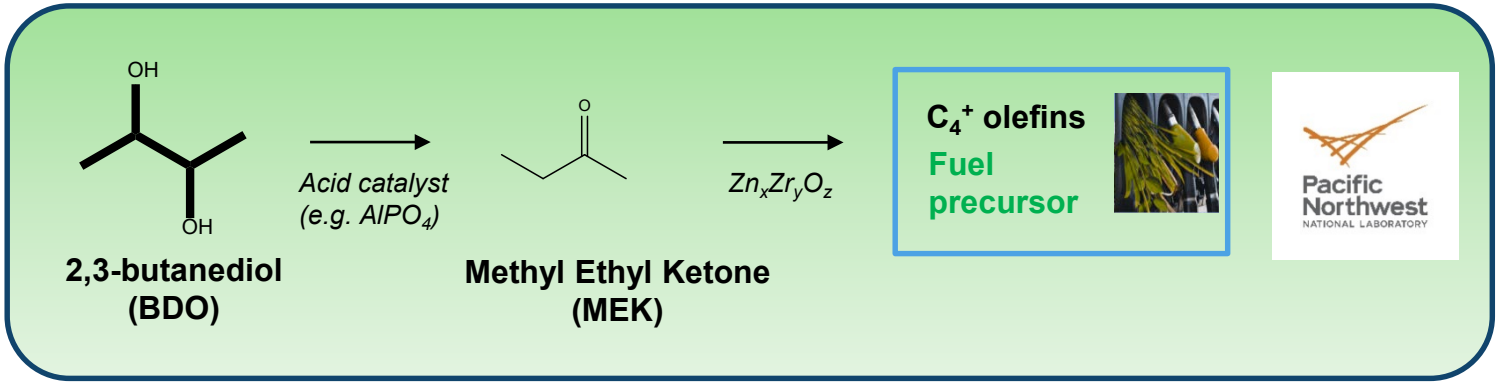
A two-step approach for upgrading 2,3-BDO to Olefins fuels precursors



Feedstock : 2,3-BDO in H_2O

- Eliminate need for challenging 2,3-BDO/H_2O separation

Flexible catalysts choice

- non-zeolite catalysts "work"
- No dealumination issue under H_2O environment

Does not require H_2

- 2,3-BDO to C_2-C_6 olefins w/o H_2 is possible
- Still requires H_2 for hydrogenation of olefins to paraffins

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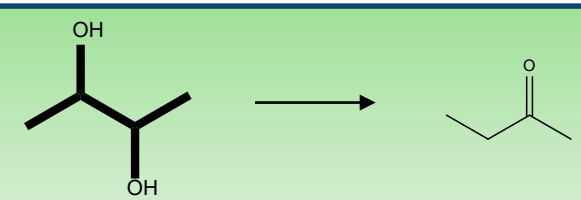
Mixed oxides catalysts enable efficient conversion of 2,3-BDO/H_2O to MEK

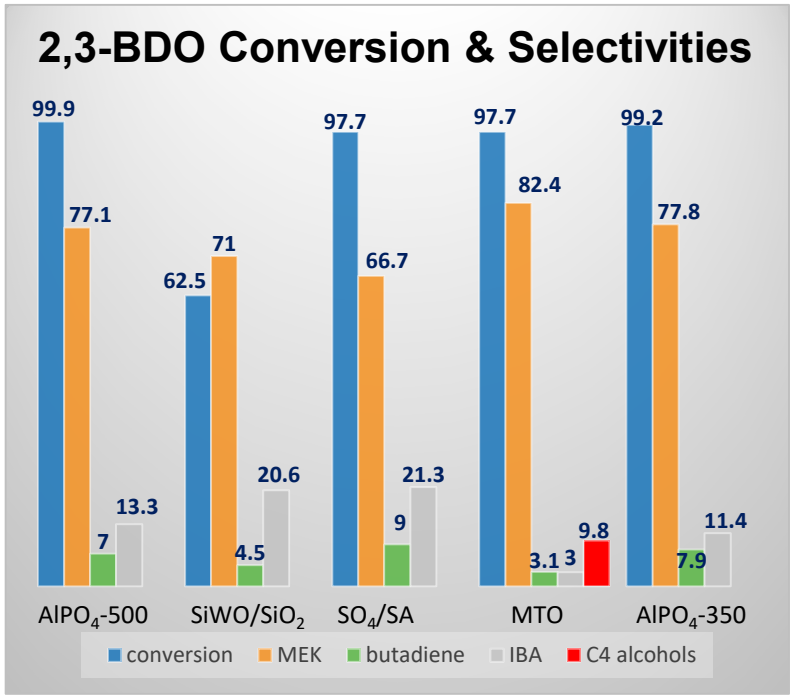
Background:

- Pure 2,3-BDO to MEK: "facile" over zeolites
- MEK sel. ~80-90%
- Isobutyraldehyde (IBA) sel. 10-20%
  → by-product less desired



2,3-butanediol (BDO) → **Methyl Ethyl Ketone (MEK)**

Catalysts screening

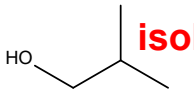


Feed:10 wt. % 2,3-BDO in water, T = 250°C, W/F = 0.6-0.7 g.s.ml^{-1}

- ❑ A mixed oxides catalyst was identified for selective conversion of 2,3-BDO

98% conversion
95% sel. desired products, 82% sel. MEK
3% sel. IBA

- ❑ Opportunity for co-products diversification:



isobutanol

Market: USD 1.18 billion/2022
CAGR: 6%

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$Zn_xZr_yO_z$ catalysts are efficient for direct conversion of MEK/H_2O into C_4-C_5 olefins with and without H_2

❑ ZnxZryOz catalysts

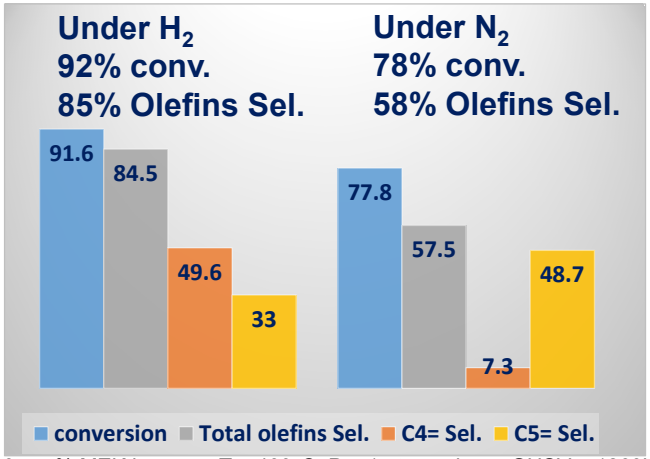
- single-step MEK→ C_4-C_6 olefins
- (non) aqueous feedstock

	GHSV (hr^{-1})	Conversion (%)	Olefins Sel. (%)
ZnO	93	46.9	14.2
ZrO_2	603	48.3	7.4
$Zn_1Zr_{10}O_x$	2467	48.2	51.8

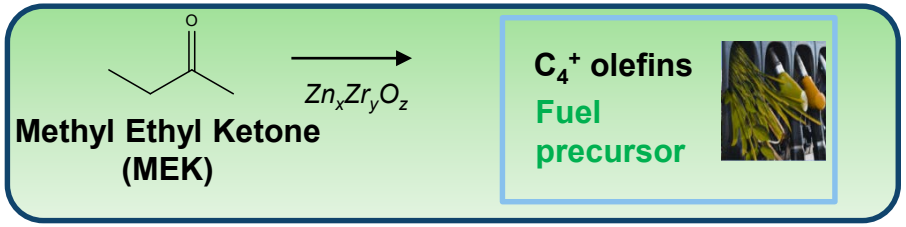
Feed:10 wt. % MEK in water, T = 400°C, P = atmosphere, inert N_2 atmosphere

❑ Operating with H_2 is not required but preferred.

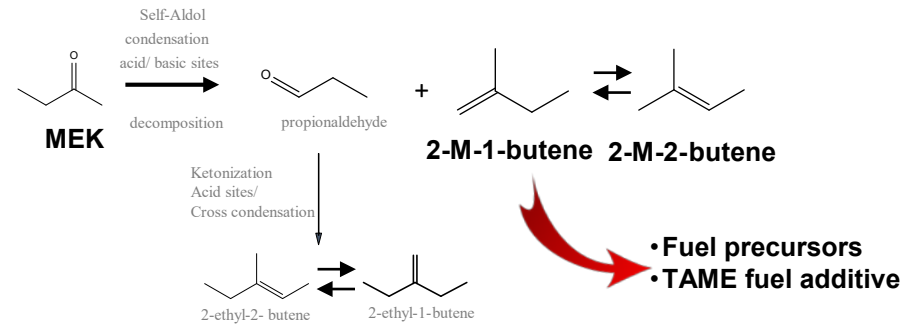
Higher conversion and selectivity
→ higher carbon efficiency



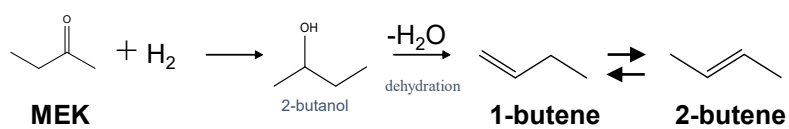
Feed:10 wt. % MEK in water, T = 400°C, P = 1 atmosphere, GHSV = 1260hr^{-1}



Under N_2



Additional pathway under H_2



❑ $Zn_xZr_yO_z$ enable single step upgrading of aqueous MEK to C_4-C_5 olefins with and w/o H_2

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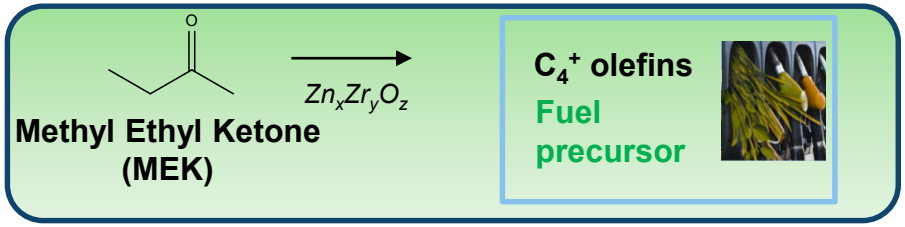
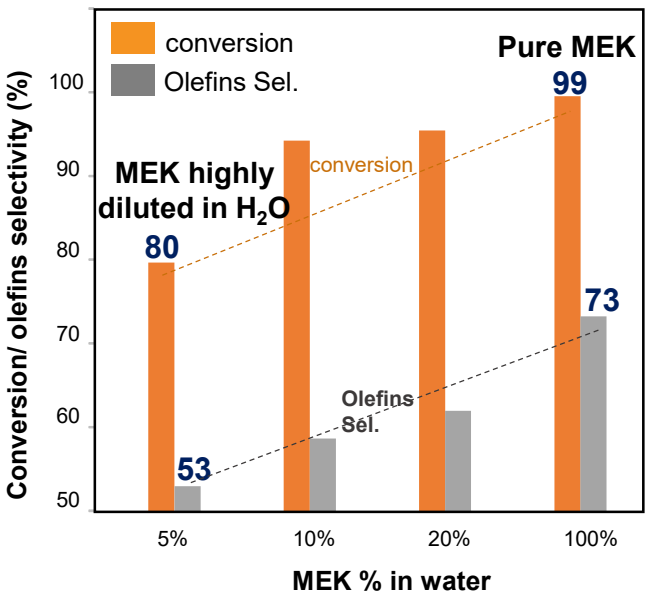
Aqueous MEK vs. Pure MEK: H_2O inhibits coking but desired olefins production is lower

- ❑ Flexibility in feedstock water content with $Zn_xZr_yO_z$ catalysts

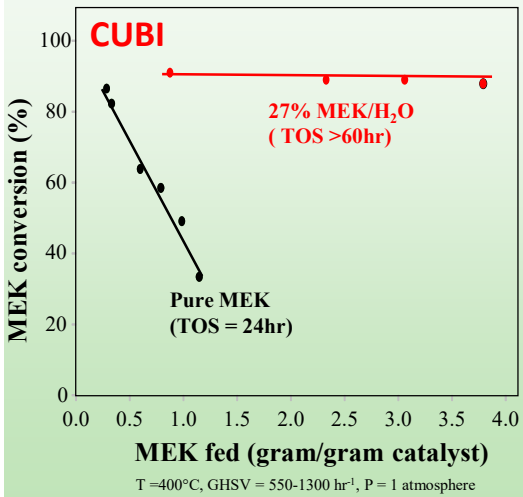
- MEK upgraded into olefins with and w/o H_2O
- Higher olefins yield with pure MEK



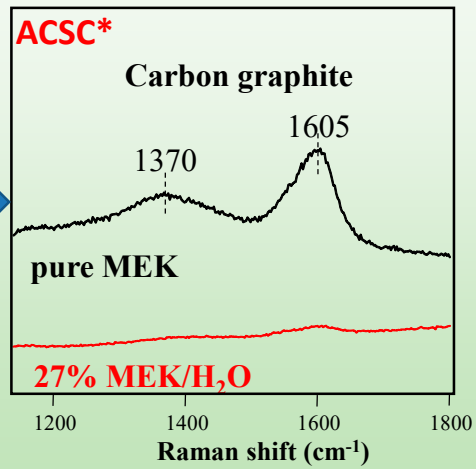


T = 400°C, GHSV= 1300 hr^{-1}, P = 1 atmosphere, inert N_2 atmosphere

$Zn_1Zr_{10}O_x$ Catalyst Stability demonstrated for >60 hr



Coke evidenced by Raman spectroscopy with pure MEK

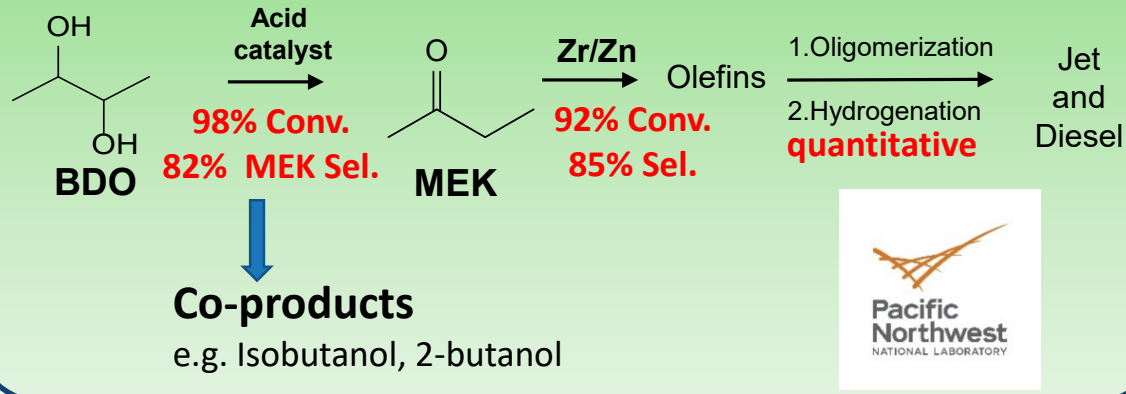


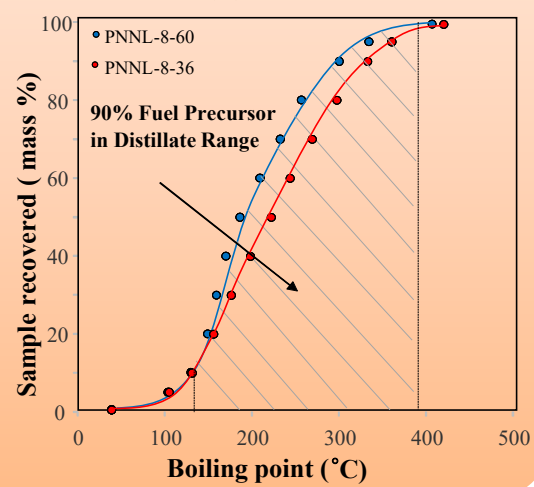
-Deactivation due to coking -Regeneration under air

- ❑ Higher MEK concentration is preferred to obtain higher yield but water helps preventing deactivation due to coking

*ACSC: Advanced Catalysts synthesis and Characterization- enabling project within ChemCatBio

Upgrading of 2,3-BDO to high quality distillate fuels via MEK intermediate





- **This process for 2,3-BDO upgrading to fuels allows high carbon efficiency.**

What's next :

- Testing with real fermentation broth
  - NREL hydrolysate broth 10% 2,3-BDO in water
- Determine impact of impurities on catalyst activity & lifetime
  - glycerol, sugars, acids

- Distillation profile and freezing point are consistent with PNNL ATJ fuels that have passed AFRL testing and recently certified for jet fuel

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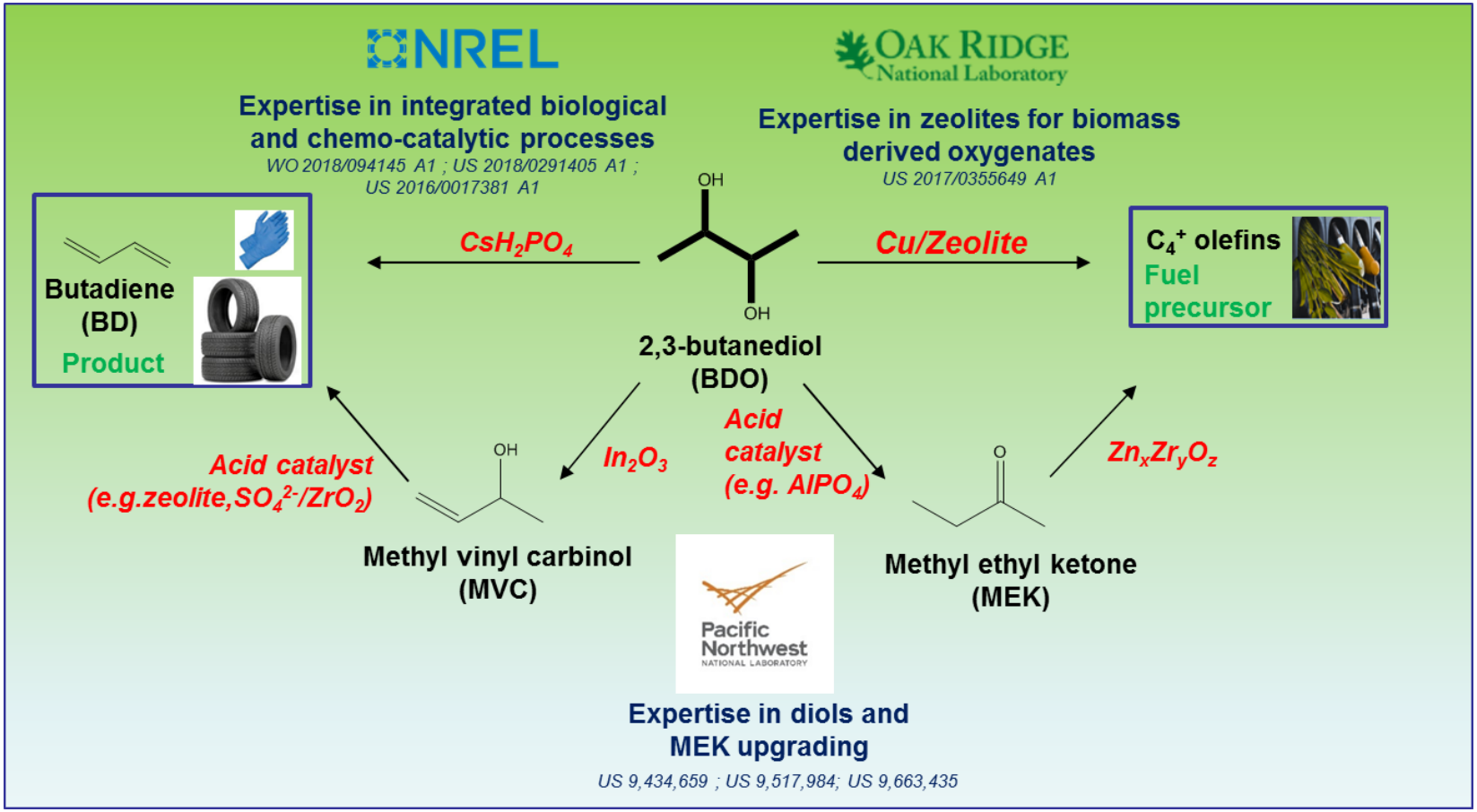
2,3-BDO upgrading to Butadiene



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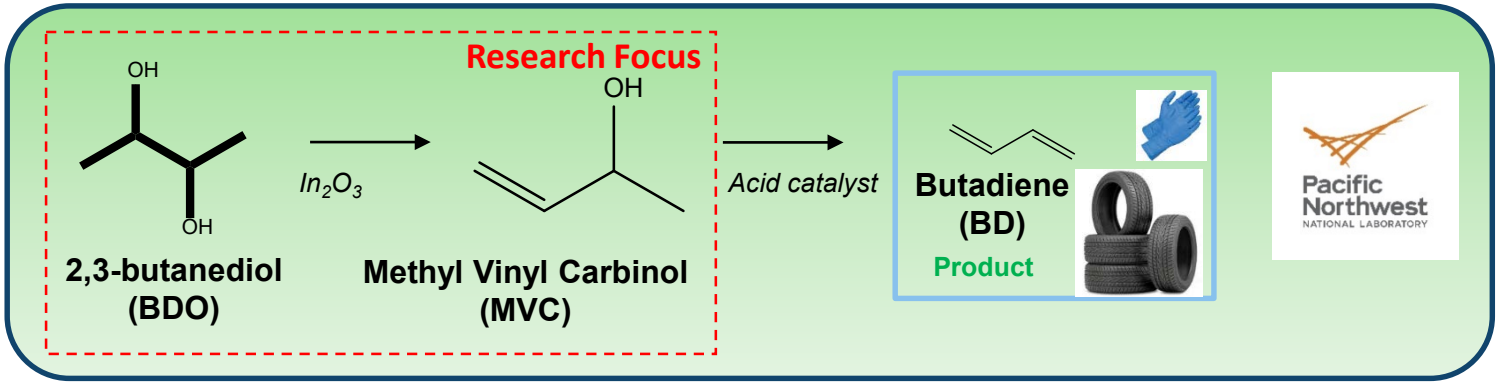
A two-step approach for upgrading 2,3-BDO to butadiene



Feedstock: pure 2,3-BDO

In_2O_3 catalyst lifetime advantage

2nd– step MVC to BD is quantitative

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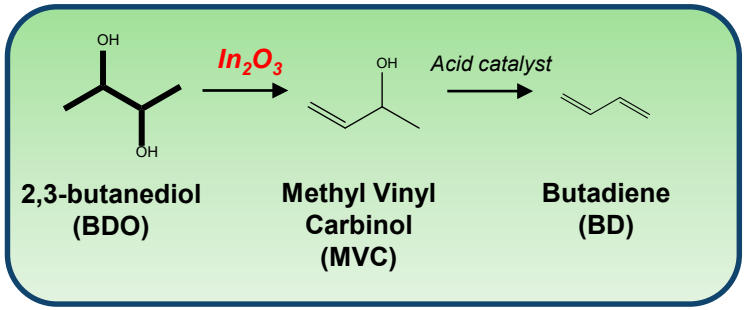
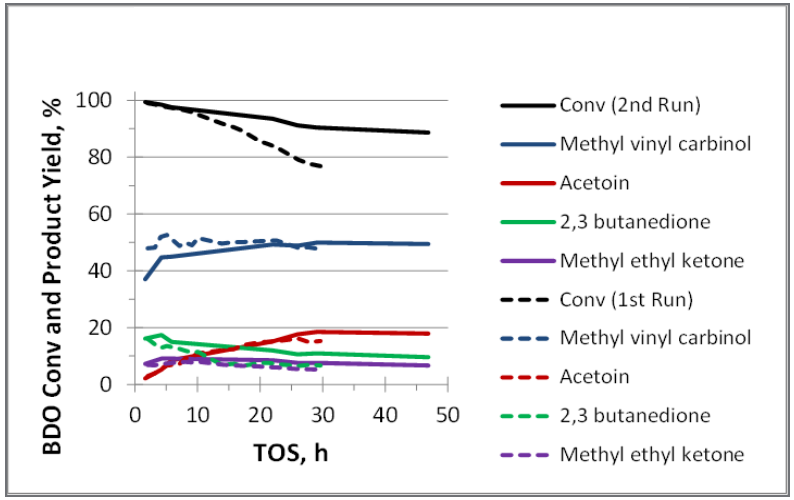
In_2O_3 catalyst for 2,3-BDO conversion to MVC, intermediate to BD

Background:

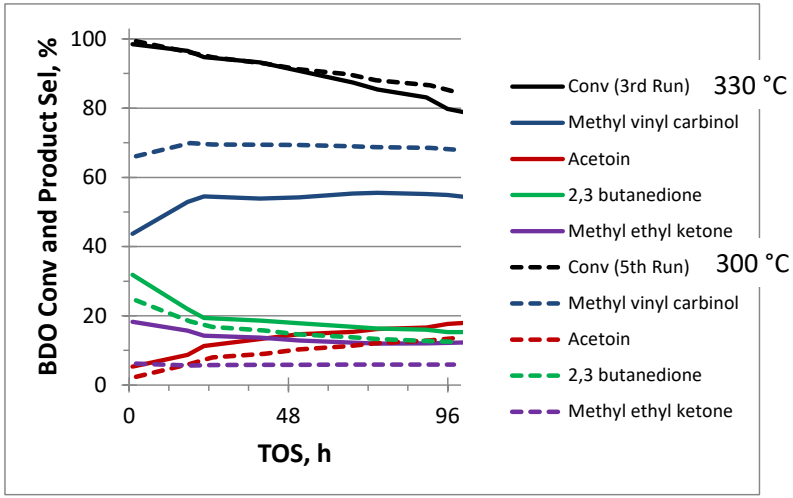
- 40 catalysts screened using high throughput system
- In_2O_3 chosen: high MVC sel. over MEK
- 2nd step (MVC to BD) is quantitative



Regeneration improves longevity



Better MVC selectivity at lower temperature



❑ In_2O_3 catalyst is easily & completed regenerated

- Regeneration under air 450°C

❑ High yield toward desired MVC 70%Sel. at >90% conv

- MEK: only 2-3% Sel.
- Coking occurs at both temperatures

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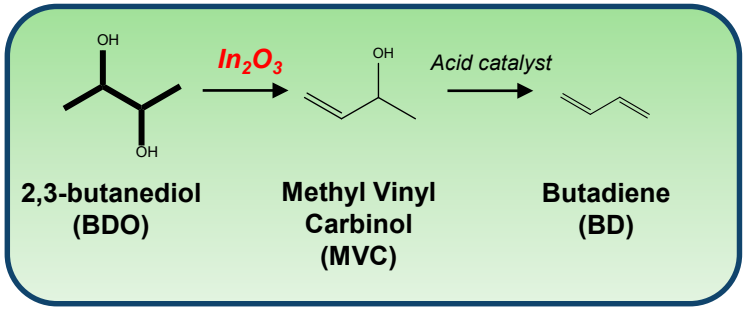
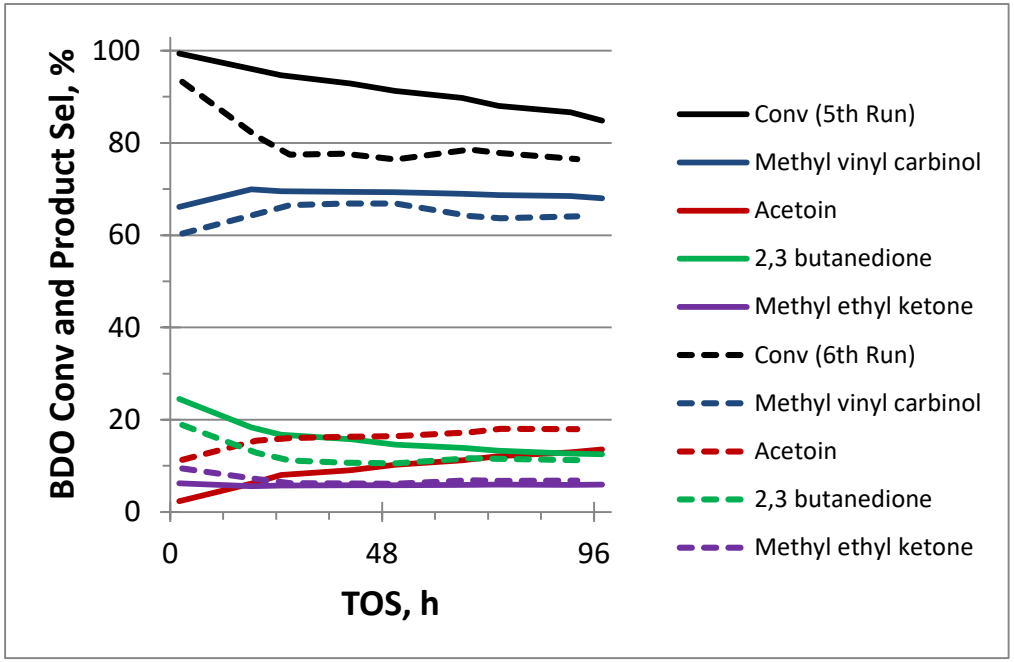
Steaming treatment affects the activity of In_2O_3 for 2,3-BDO conversion to MVC

- Activity and selectivity appear to be closer to steady state following steaming

- Conversion levels off after about 24 h
- High initial activity? Needs to be verified, but might suggest steam could open up or regenerate sites.



BDO dehydration over In_2O_3 at 300 °C



- Activity of 1st generation In_2O_3 is high but surface area is low (8 m^2/g)

Samples	Surface Area (BET) m^2/g	Micro Pore Surface Area (T method) m^2/g	Pore Volume (BJH method) cc/g
Used*	7.5	1	0.09
Fresh	8.0	0.7	0.12

*after >300 hrs on stream and regenerated 4 times

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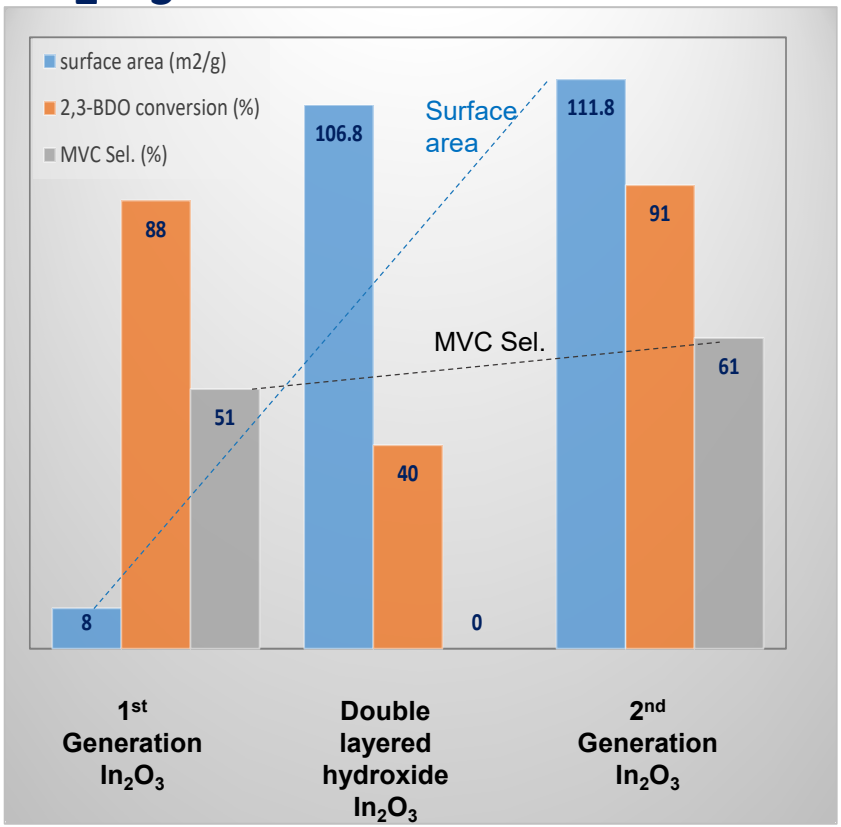
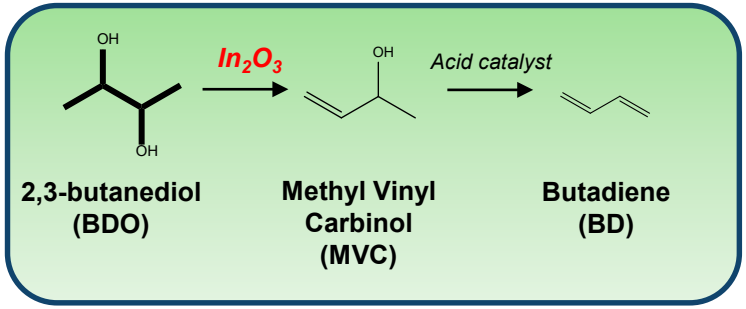
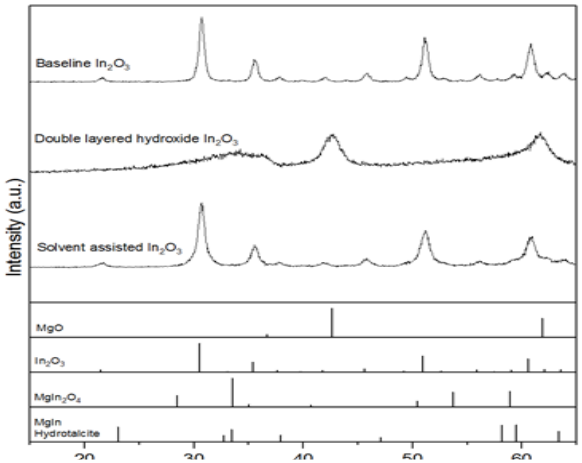
High surface area In_2O_3 catalyst for 2,3-BDO conversion to MVC, intermediate to BD

- **2nd generation In_2O_3 presents high surface higher (>100 m^2/g) and higher selectivity to MVC at similar conversion**

In_2O_3 Catalysts screening

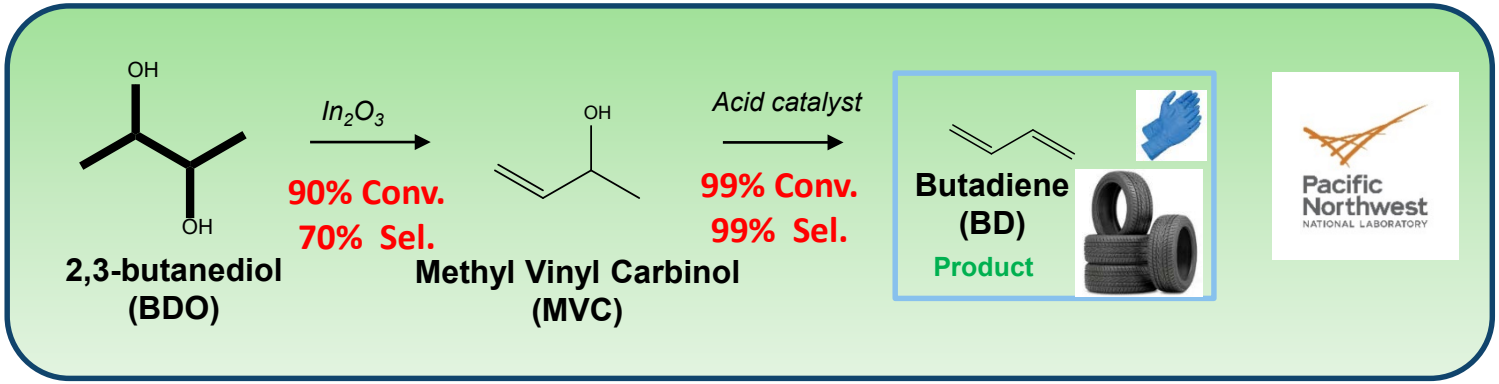






- 1st and 2 nd generations catalysts present same bulk structure

Catalytic upgrading of 2,3-butanediol to butadiene via MVC intermediate



- **This process for 2,3-BDO upgrading to butadiene allows high carbon efficiency.**
- **Catalyst longevity demonstrated for >100 hours**

What's next :

- Testing with real fermentation broth
- Determine impact of impurities on catalyst activity & lifetime
  - glycerol, sugars, acids

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Contact: karthi@pnnl.gov

Summary

Evaluate several routes for catalytic upgrading of 2,3-butanediol into hydrocarbon fuels and co-products with select routes that can achieve $3/gge in 2022

Approach

- Common/shared:
  - Process materials
  - Analytical methods
  - Reactor systems
  - Fuel assessment
  - TEA tools and approaches
- Integrated task structure
- Biochemical Platform leveraging for process intermediates
- Go/no-go decision used to identify catalyst and process improvements

Accomplishments

- Coordination with enabling ChemCatBio projects for advanced characterization, catalyst cost modeling, and computational chemistry
- Validated single step route to butadiene, with insights into reaction mechanism (NREL)
- Developed stable Cu/P-MFI for one-step conversion to C_3-C_6 olefins, which can be upgraded to jet fuel (ORNL)
- Developed 2-step processes for 2,3-BDO upgrading to olefins fuel precursors and butadiene (PNNL)

Relevance

- Addresses key commercialization barriers associated with biochemical conversion streams
- Developing comparative data and TEA on several approaches
- ChemCatBio collaborations and industry outreach

Future Work

- Continued catalyst and process improvements to increase target yields
- Focus on inhibitor identification and mitigation for catalyst lifetime
- Inform upstream separation and recovery efforts for lignocellulose-derived 2,3-BDO

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CCPC
www.cpcbiomass.org

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