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 ² ³

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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
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.)

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

87 g/L BDO
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

CsH₂PO₄ supported on a commercial SiO₂ validated for high butadiene yield

87% butadiene yield at >90%

2,3-BDO conversion under select conditions

10CsH₂PO₄/SA-SiO₂ (Sigma Aldrich SiO₂)


<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cs loading (wt%)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Initial 13BDE yield</th>
<th>Butadiene productivity (g₁₃BDE g₀Cs h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CsH₂PO₄/AA-SiO₂</td>
<td>2.65</td>
<td>157</td>
<td>0.72</td>
<td>0.9%</td>
<td>0.1</td>
</tr>
<tr>
<td>5CsH₂PO₄/SA-SiO₂</td>
<td>2.95</td>
<td>407</td>
<td>0.81</td>
<td>47%</td>
<td>6.4</td>
</tr>
<tr>
<td>10CsH₂PO₄/SA-SiO₂</td>
<td>5.13</td>
<td>337</td>
<td>0.76</td>
<td>61%</td>
<td>5.1</td>
</tr>
<tr>
<td>20CsH₂PO₄/SA-SiO₂</td>
<td>12.4</td>
<td>93</td>
<td>0.46</td>
<td>61%</td>
<td>2.2</td>
</tr>
</tbody>
</table>

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

Experimental validation

Liquid product identification

Epoxide conversion

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

Seonah Kim (NREL), Robert Paton (CSU)

NREL
Price of raw materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Unit price (2018 $/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cesium nitrate</td>
<td>88.33 (Extrapolation)</td>
</tr>
<tr>
<td>Monoammonium phosphate</td>
<td>0.38 (Bulk quote)</td>
</tr>
<tr>
<td>High surface area SiO2</td>
<td>88.39 (Extrapolation)</td>
</tr>
<tr>
<td>Medium surface area SiO2</td>
<td>6.49 (Extrapolation)</td>
</tr>
</tbody>
</table>

Unit catalyst price (raw material + production cost)

Cost of supported CsH$_2$PO$_4$ catalyst can be reduced by increasing production size, developing alternative high surface area support, and minimizing cesium loading.
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

Bio-BDO dehydration

Conditions: 2.0 g 10CsH2PO4/SA-SiO2, 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 CsH₂PO₄ performance and regeneration with hydrothermally stable supports

Mechanistic and material study

Characterize CsH₂PO₄ 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** C₃-C₆ olefin production

**Catalysis Focus**

**Advantages**
- One-step highly selective production of C₃-C₆ 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


(Zhenglong Li, ORNL)
Hierarchical Cu/pillared-MFI for 2,3-BDO to Olefins

Catalyst and Process Improvements
- Maximize C₃-C₆ olefins selectivity
- Enhance catalyst stability — coke resistance

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

2D pillared MFI:
- Reduce coke formation
- Minimize tertiary cracking products, e.g., propene, pentene


Catalyst synthesis: ammonia evaporation
As-synthesized catalyst after calcination: CuO nanoparticles

Majority Cu$^0$, minor Cu$^+$ exists: 300 °C, H$_2$ for 1 hr

Kinga Unocic (ORNL)

Theodore Krause (ANL)
Cu/P-MFI for C₃-C₆ Olefins from 2,3-BDO

Objective: Maximize C₃-C₆ olefins and optimize olefin compositions
- Temperature and H₂/BDO effect

Outcome:
- Final co-product/fuel ratio can be tuned by varying the reaction temperatures
- Tune olefins/fuel composition by varying H₂/BDO ratio in the range of <15
- Optimum C₃-C₆ olefins: above 250 °C
- Tune MEK/olefins ratio by varying reaction temperatures
- H₂/BDO ratio below 15, olefin composition dramatically changes, butenes decrease
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**

- Cu/P-MFI durability testing for 2,3-BDO conversion
- Cu/P-MFI vs Cu/ZSM-5
Conversion of Fermentation Derived 2,3-BDO

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

- **Fermentation broth (NREL)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amount, g/L</th>
<th>Composition</th>
<th>Amount, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellobiose</td>
<td>2.606</td>
<td>BDO</td>
<td>33.013</td>
</tr>
<tr>
<td>Xylose</td>
<td>8.408</td>
<td>Acetoin</td>
<td>20.216</td>
</tr>
<tr>
<td>Arabinose</td>
<td>2.643</td>
<td>Ethanol</td>
<td>0.226</td>
</tr>
<tr>
<td>Glycerol</td>
<td>2.175</td>
<td>Lactic Acid</td>
<td>0.527</td>
</tr>
<tr>
<td>Xylitol</td>
<td>2.986</td>
<td>Acetic acid</td>
<td>0.523</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amount, wt.%</th>
<th>Composition</th>
<th>Amount, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20</td>
<td>Acetic acid</td>
<td>1</td>
</tr>
<tr>
<td>BDO</td>
<td>75</td>
<td>Acetoin</td>
<td>2</td>
</tr>
</tbody>
</table>

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

- Fermentation derived BDO can be converted to C₃-C₆ 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

ORNL
Distillate Production from C$_3$-C$_6$ Olefins

C$_3$-C$_6$ olefins (butenes dominate)

Oligomerization → Hydrogenation → Diesel/Jet

ORNL BDO derived distillate

<table>
<thead>
<tr>
<th></th>
<th>Jet A</th>
<th>BDO derived jet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td>0.775-</td>
<td>0.798</td>
</tr>
<tr>
<td>(g/mL)</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>HHV (MJ/Kg)</td>
<td>46.2</td>
<td>46.7</td>
</tr>
<tr>
<td>Freezing Point (°C)</td>
<td>max -40</td>
<td>&lt;-80</td>
</tr>
<tr>
<td>Aromatics (v/v %)</td>
<td>max 25%</td>
<td>&lt;=25%</td>
</tr>
</tbody>
</table>

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

Butadiene (BD) Product

Acid catalyst (e.g., zeolite, $\text{SO}_4^2-/\text{ZrO}_2$)

Methyl vinyl carbinol (MVC)

In$_2$O$_3$

2,3-butanediol (BDO)

$\text{Cu/Zeolite}$

Methyl ethyl ketone (MEK)

Zn$_x$Zr$_y$O$_z$

$\text{CsH}_2\text{PO}_4$

Expertise in integrated biological and chemo-catalytic processes


Expertise in zeolites for biomass derived oxygenates

US 2017/0356649 A1

$\text{C}_4^+ \text{ olefins}$

Fuel precursor

Expertise in diols and MEK upgrading

US 9,434,659; US 9,517,984; US 9,663,435
A two-step approach for upgrading 2,3-BDO to Olefins fuels precursors

Feedstock: 2,3-BDO in H₂O
- Eliminate need for challenging 2,3-BDO/H₂O separation

Flexible catalysts choice
- non-zeolite catalysts “work”
- No dealumination issue under H₂O environment

Does not require H₂
- 2,3-BDO to C₂-C₆ olefins w/o H₂ is possible
- Still requires H₂ for hydrogenation of olefins to paraffins

PNNL
Mixed oxides catalysts enable efficient conversion of 2,3-BDO/H₂O 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

**Catalysts screening**

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:

Feed: 10 wt. % 2,3-BDO in water, T = 250°C, W/F = 0.6-0.7 g.s.ml⁻¹
Zn$_x$Zr$_y$O$_z$ catalysts are efficient for direct conversion of MEK/H$_2$O into C$_4$-C$_5$ olefins with and without H$_2$

- **ZnxZryOz catalysts**
  - single-step MEK→ C$_4$-C$_6$ olefins
  - (non) aqueous feedstock

<table>
<thead>
<tr>
<th></th>
<th>GHSV (hr$^{-1}$)</th>
<th>Conversion (%)</th>
<th>Olefins Sel. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>93</td>
<td>46.9</td>
<td>14.2</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>603</td>
<td>48.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Zn$<em>x$Zr$</em>{10}$O$_x$</td>
<td>2467</td>
<td>48.2</td>
<td>51.8</td>
</tr>
</tbody>
</table>

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

- Under H$_2$
  - 92% conv.
  - 85% Olefins Sel.

- Under N$_2$
  - 78% conv.
  - 58% Olefins Sel.

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

- Zn$_x$Zr$_y$O$_z$ enable single step upgrading of aqueous MEK to C$_4$-C$_5$ olefins with and w/o H$_2$
Aqueous MEK vs. Pure MEK: H$_2$O inhibits coking but desired olefins production is lower

- MEK upgraded into olefins with and w/o H$_2$O
- Higher olefins yield with pure MEK

- Flexibility in feedstock water content with Zn$_x$Zr$_y$O$_z$ catalysts

- MEK highly diluted in H$_2$O

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

- 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

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

- **OH**
- **OH**
- **O**
- **Acid catalyst**
- **Zr/Zn**
- **OH**
- **OH**
- **Acid catalyst**
- **Zr/Zn**
- **Olefin**
- **Jet and Diesel**

**BDO**

**MEK**

**Co-products**
- e.g. Isobutanol, 2-butanol

- **98% Conv.**
- **82% MEK Sel.**

- **92% Conv.**
- **85% Sel.**

**Oligomerized Olefins:**
- 90% in distillate range
- freezing point < -70 °C

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

**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

- **Contact:** vanessa.dagle@pnnl.gov
2,3-BDO upgrading to Butadiene
A two-step approach for upgrading 2,3-BDO to butadiene

Feedstock: pure 2,3-BDO

\( \text{In}_2\text{O}_3 \) catalyst lifetime advantage

2nd– step MVC to BD is quantitative
In$_2$O$_3$ catalyst for 2,3-BDO conversion to MVC, intermediate to BD

**Background:**
- 40 catalysts screened using high throughput system
- In$_2$O$_3$ chosen: high MVC sel. over MEK
- 2nd step (MVC to BD) is quantitative

**Regeneration improves longevity**

**Better MVC selectivity at lower temperature**

- In$_2$O$_3$ 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
Steaming treatment affects the activity of In$_2$O$_3$ 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$_2$O$_3$ at 300 °C**

- Activity of 1st generation In$_2$O$_3$ is high but surface area is low (8 m$^2$/g)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area (BET) m$^2$/g</th>
<th>Micro Pore Surface Area (T method) m$^2$/g</th>
<th>Pore Volume (BJH method) cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used*</td>
<td>7.5</td>
<td>1</td>
<td>0.09</td>
</tr>
<tr>
<td>Fresh</td>
<td>8.0</td>
<td>0.7</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*after >300 hrs on stream and regenerated 4 times
High surface area In$_2$O$_3$ catalyst for 2,3-BDO conversion to MVC, intermediate to BD

- 2$^{nd}$ generation In$_2$O$_3$ presents high surface higher (>100 m$^2$/g) and higher selectivity to MVC at similar conversion

In$_2$O$_3$ Catalysts screening

- 1$^{st}$ 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

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 C₃-C₆ 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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