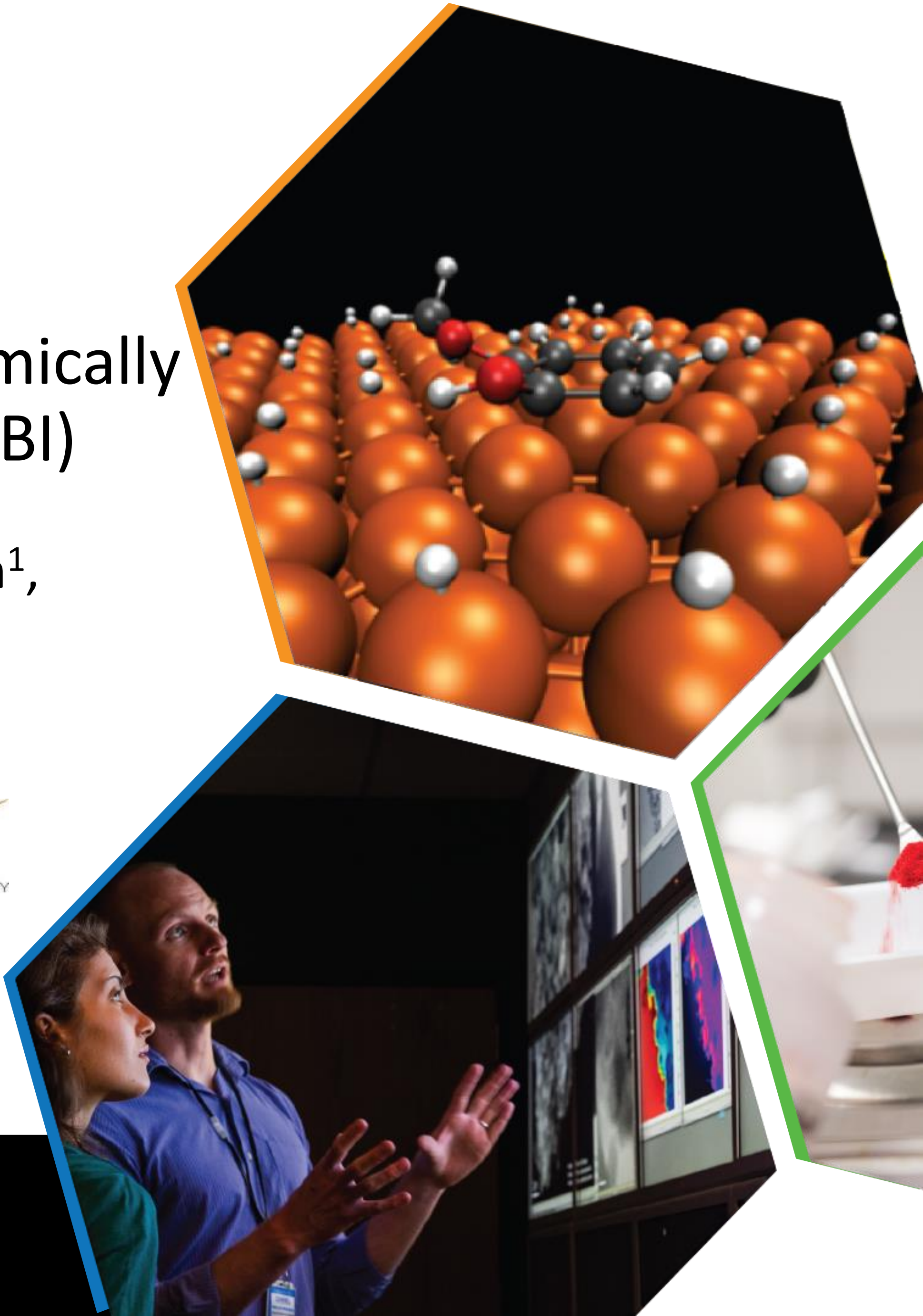
ChemCatBio
Chemical Catalysis for Bioenergy

Catalytic Upgrading of Biochemically Derived Intermediates (CUBI)



R.T. Elander[1], D. Vardon[1], D.K. Johnson[1], Z. Li[2], A.D. Sutton[3], V. Dagle[4], K.K. Ramasamy[4]

[1] NREL National Renewable Energy Laboratory [2] Oak Ridge National Laboratory [3] Los Alamos National Laboratory EST. 1943 [4] Pacific Northwest National Laboratory

March 4, 2019

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

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL, NREL*)

Catalytic Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Electrocatalytic and Thermocatalytic CO_2 Utilization
(NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL, SNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

Catalyst Deactivation Mitigation for Biomass Conversion
(PNNL)

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

Goal Statement

Project Goal

- Develop and evaluate several routes for **catalytic upgrading of biomass-derived sugars/related intermediates** into hydrocarbon fuels and co-products, including:
  - Alcohols/diols
  - Carboxylic acids
  - Sugars and sugar-derived intermediates

Primary Project Outcome

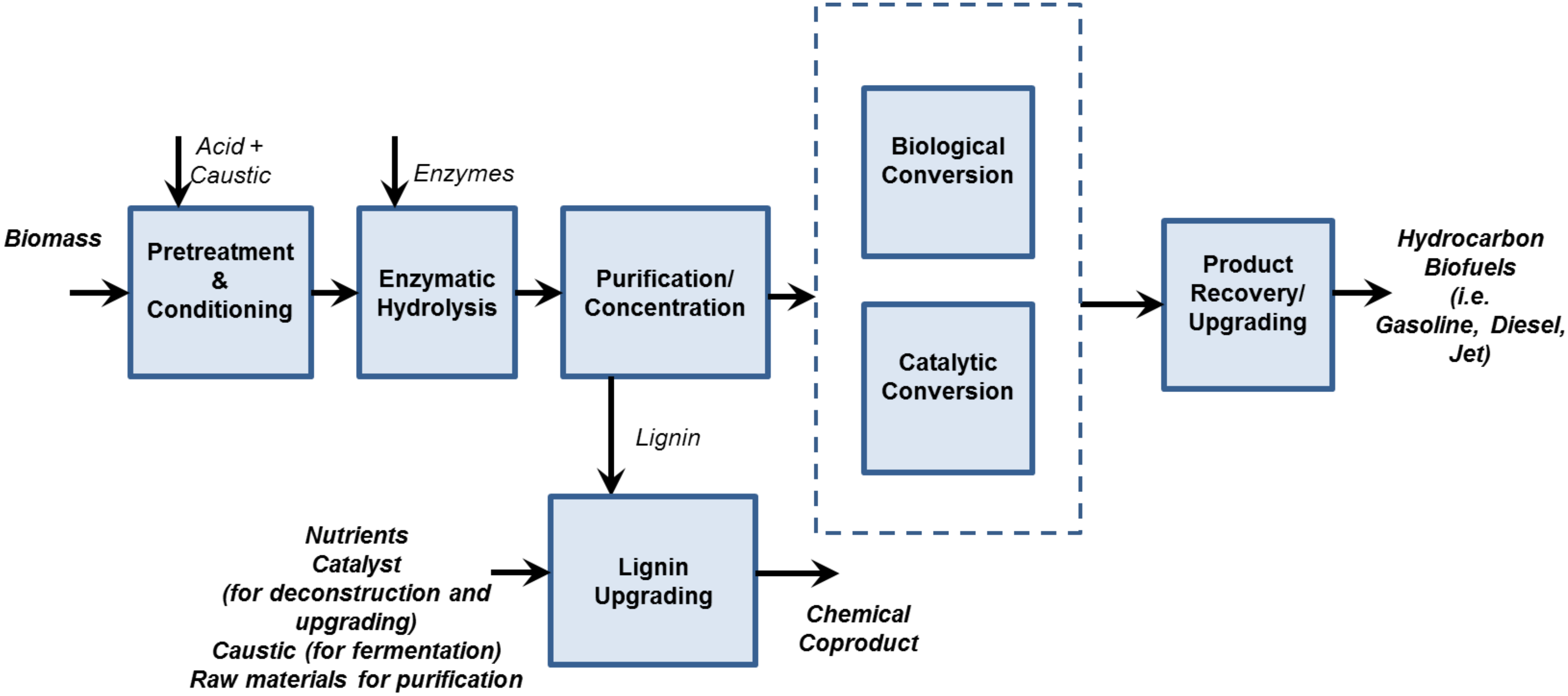
- Select and develop **at least one route** for catalytic upgrading of sugars/related intermediates and/or biologically derived intermediates into fuel blendstocks with conversion performance than can achieve a **MFSP of \$3/GGE by 2022** with **>25% (GGE basis) of the fuel in the jet or diesel ranges**

Relevance

- Facilitate **transition** from catalytic upgrading of **clean sugars** (cane and starch-derived) to **cellulosic sugars**/derived intermediates to enable commercialization
- 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**

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.)



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[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

Quad Chart Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 80% (current 3-year cycle)

	Total Costs Pre FY17**	**FY 17 Costs**	**FY 18 Costs**	**Total Planned Funding (FY 19-Project End Date)**
DOE Funded		$1.63M	$1.79M	$2.23M
Project Cost Share*				

Partners:

NREL (65%)
ORNL (12%)
PNNL (12%)
LANL (11%)

Barriers addressed

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

Objective

Develop and evaluate several routes for catalytic upgrading of biomass-derived sugars/related intermediates into hydrocarbon fuels and co-products, including alcohols/diols, carboxylic acids, and sugars/sugar derived intermediates.

End of Project Goal

Quantify performance of catalytic upgrading performance using biochemical conversion process-derived intermediates in a fully integrated TEA model.

- Describe the relative levels of development of each technology within CUBI, the most promising CUBI pathway(s), and what are the critical remaining research needs to achieve an MFSP of <$3/gge.

1 – Project Overview

Context and History

- Prior to FY17, several independent projects across several national labs were investigating the catalytic upgrading of Biochemical Conversion process intermediates
- A multi-lab core Catalytic Technologies project began in FY17 within ChemCatBio – focused on biochemically-derived intermediates
  - **Catalytic Upgrading of Biochemical Intermediates (CUBI)**

NREL National Renewable Energy Laboratory | Oak Ridge National Laboratory | Los Alamos National Laboratory EST 1943 | Pacific Northwest National Laboratory

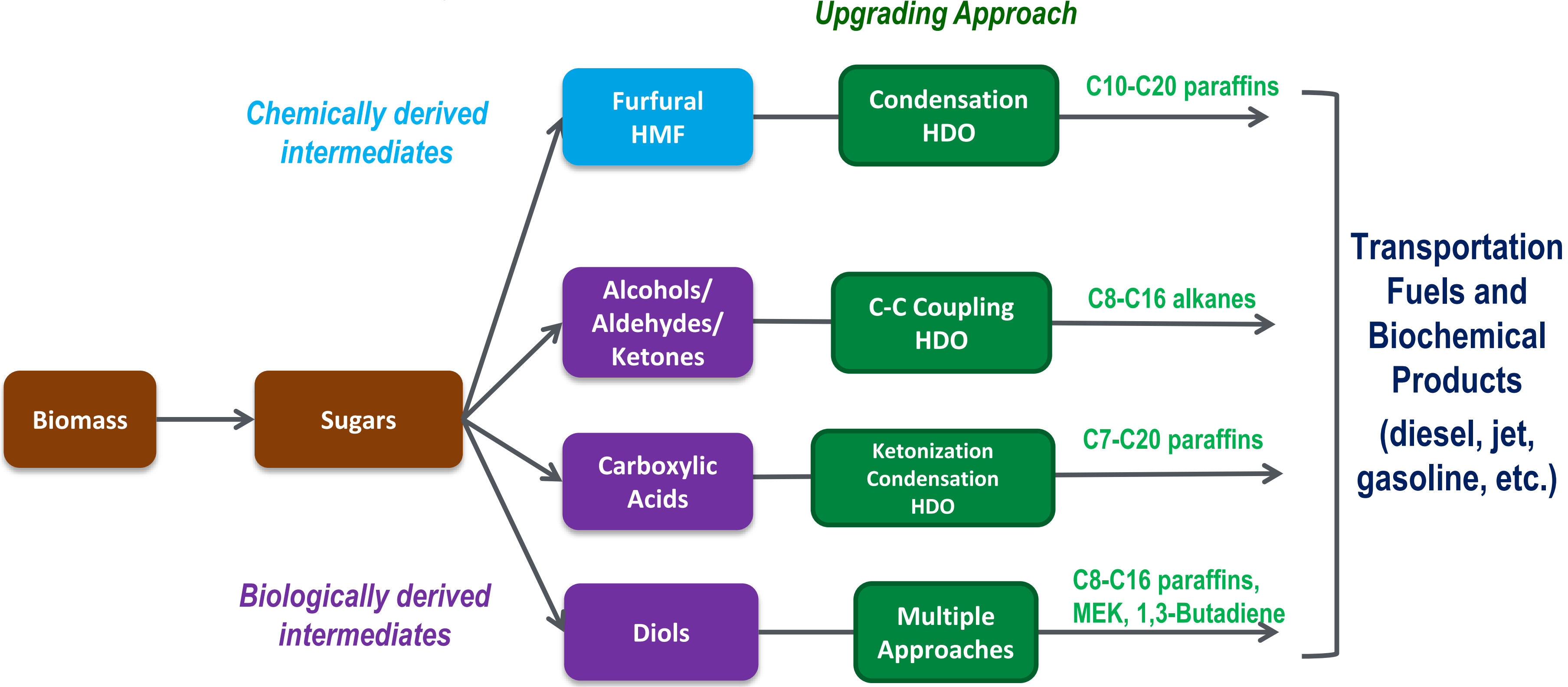
- Eliminated duplicative efforts and ensured a systematic and integrated approach
  - **Common** process intermediates, catalyst/reactor systems, analytical and fuel characterization, TEA, etc. across multiple national labs

Broad Project Impact

- Exploiting the **specificity of intermediate compounds** generated via **biochemical deconstruction** (hydrolysis, dehydration, etc.) and **biological upgrading** (fermentation) to catalytically produce a **range of targeted hydrocarbons**
  - Primary effort within BETO portfolio for “downstream” Biochemical Conversion process development and integration

2 – Approach (Management)

- Project organized according to catalytic upgrading routes being investigated within Biochemical Conversion portfolio



- <u>Task 1</u>: 2,3-butanediol (BDO)
- <u>Task 2</u>: Carboxylic acids
- <u>Task 3</u>: Sugars/sugar-derived intermediates
- <u>Task 4</u>: Hydrolysate/fermentation broth production; techno-economic analysis

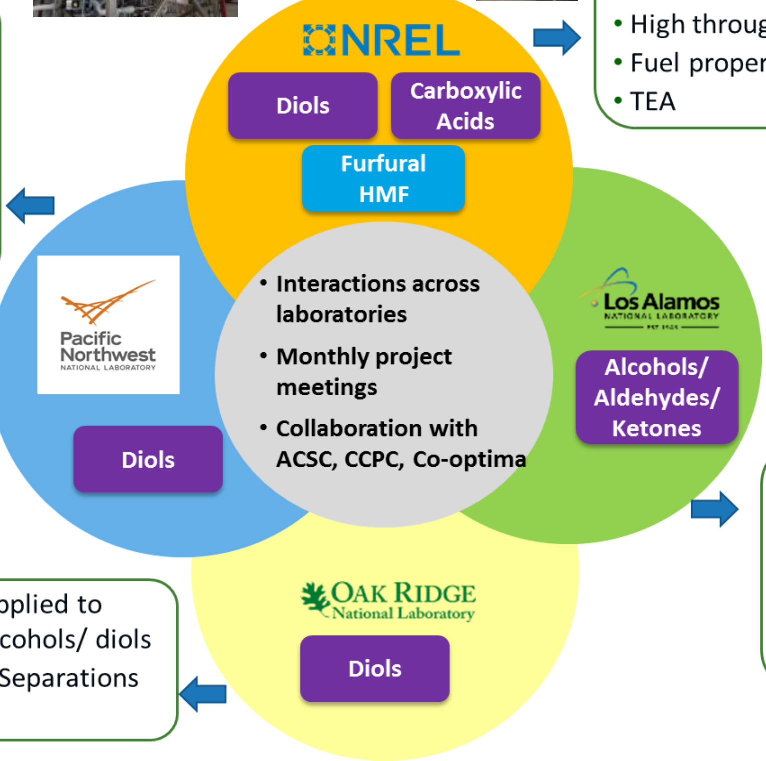
2 – Approach (Management)

Capabilities and Expertise Across Multiple National Laboratories

Pilot Scale Hydrolysate Production

Packed-Bed Flow Reactor

- Hydrolysate/fermentation intermediates
- Catalyst characterization
- High throughput/flow testing
- Fuel property testing
- TEA



NREL

Diols

Carboxylic Acids

Furfural HMF

Pacific Northwest NATIONAL LABORATORY

Diols

Los Alamos NATIONAL LABORATORY

Alcohols/ Aldehydes/ Ketones

OAK RIDGE National Laboratory

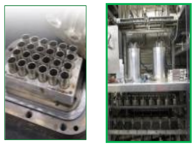
Diols

- **Interactions across laboratories**
- **Monthly project meetings**
- **Collaboration with ACSC, CCPC, Co-optima**

- High-throughput catalyst testing
- Catalyst characterization
- Fuel property testing
- TEA

Catalytic Upgrading Systems

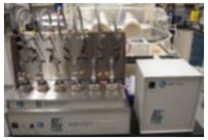
Multi-batch and Fixed-Bed Flow Reactors



- Zeolite expertise applied to biomass derived alcohols/ diols
- Coordination with Separations Consortium

- HDO optimization in flow reactors
- Catalysis-assisted phase separation for aqueous product recovery

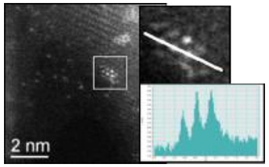
High-Pressure Batch Reactors



High-Pressure Continuous Flow Reactors

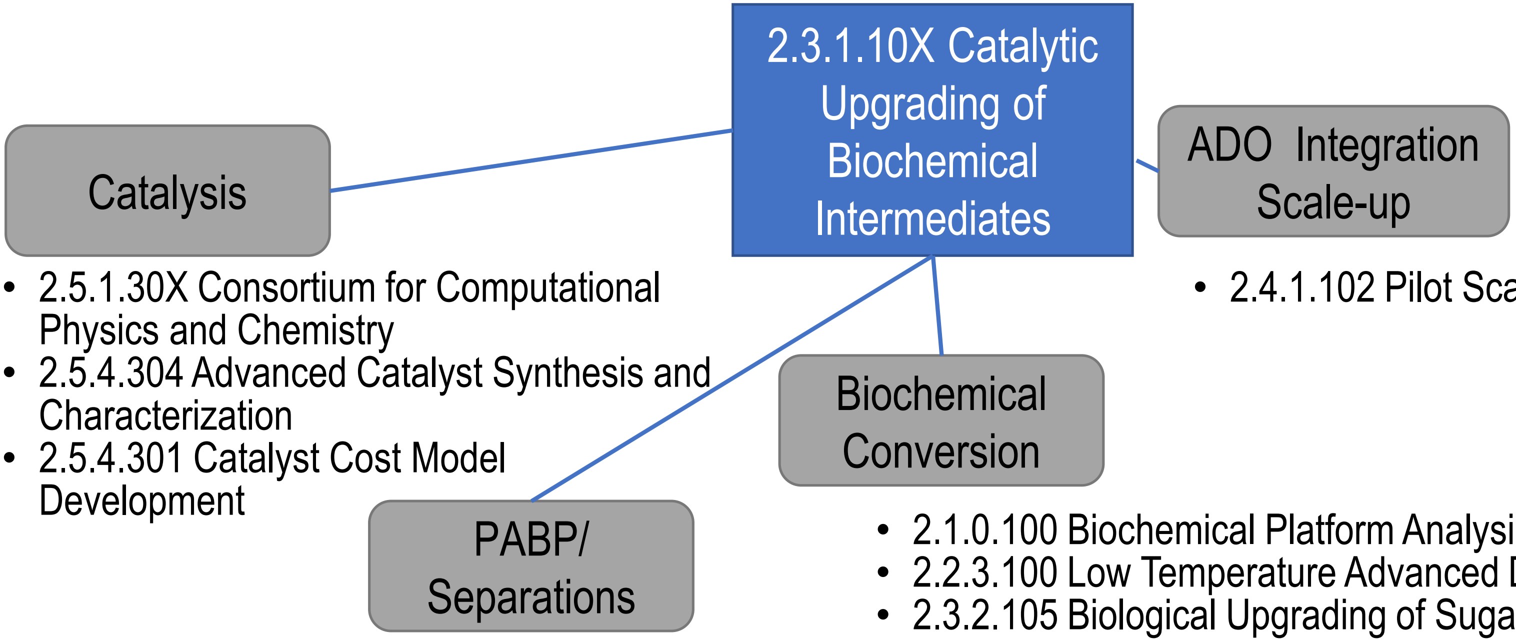
Zeolite Synthesis

Atom Scale Characterization



2 – Approach (Management)

Interactions With Other Projects



2.3.1.10X Catalytic Upgrading of Biochemical Intermediates

Catalysis

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

ADO Integration Scale-up

- 2.4.1.102 Pilot Scale Integration

Biochemical Conversion

- 2.1.0.100 Biochemical Platform Analysis
- 2.2.3.100 Low Temperature Advanced Deconstruction
- 2.3.2.105 Biological Upgrading of Sugars
- 2.4.1.100 Bench Scale R&D

PABP/ Separations

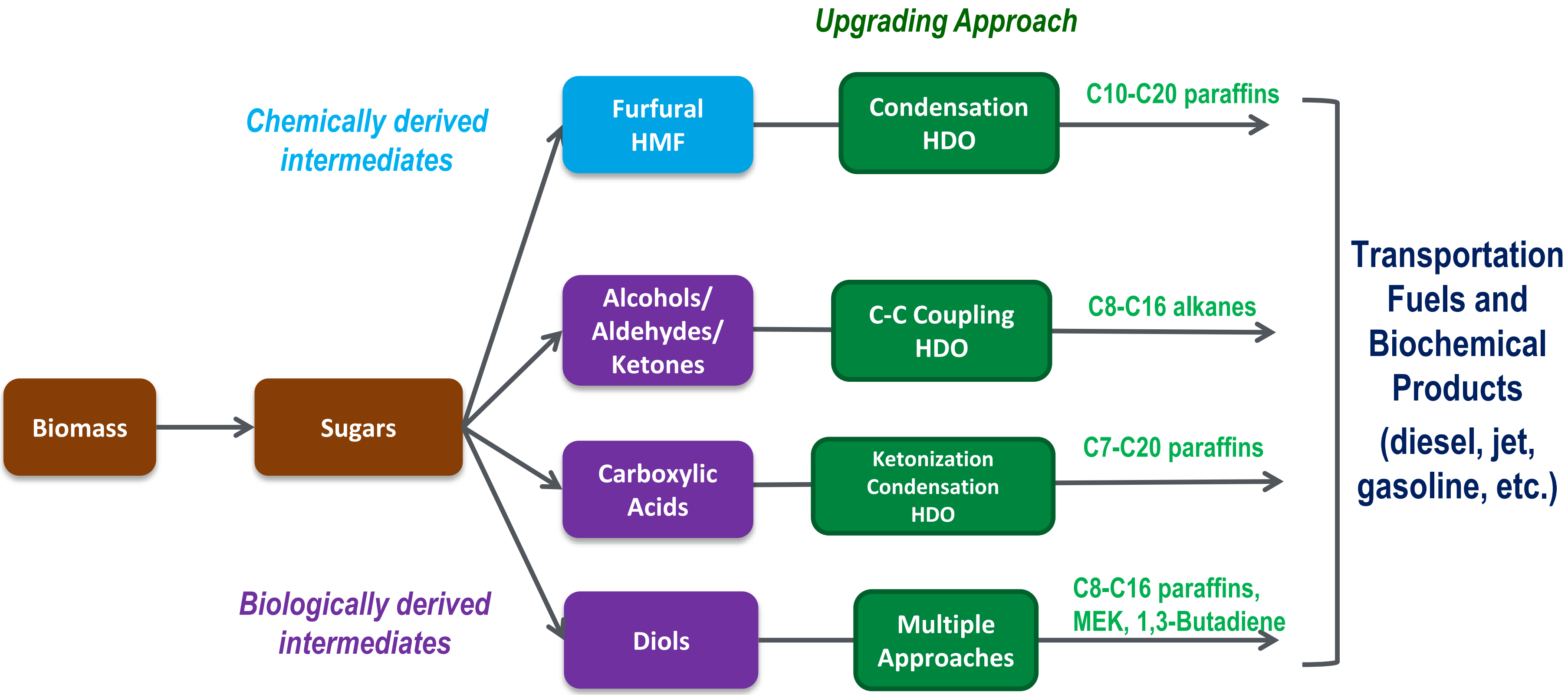
- 2.5.5.50X Separations Consortium

2 – Approach (Technical)

- Multiple catalytic upgrading routes investigated and evaluated in a coordinated manner using common materials, analytical techniques, reactor systems, fuel characterization methods, and TEA tools

Critical Success Factors	Challenges	Strategy
Develop and identify **catalytic upgrading to HC fuel routes** that have commercial relevance and interest .	Numerous biochemical-derived intermediates are potential options, leading to multiple catalytic upgrading routes and approaches.	Coordination with Biochemical Conversion projects to focus on intermediates that are being actively developed and have cost-potential and market size for broad applicability.
Quantify **impurity impacts from biochemical deconstruction/ upgrading** on catalytic upgrading routes (durability, efficiency, selectivity).	Biomass-derived catalyst inhibitors are from multiple sources: • Feedstock • Deconstruction process • Intermediates-production processes	Comparative assessment of pure intermediates and biomass-derived intermediates to determine specific impacts of potential catalyst inhibitors (including water).
Define **specifications for deconstruction/fermentation streams** for catalytic upgrading, including identification of separations/clean-up needs.	Multiple considerations in optimizing various conversion unit operations makes the definition of process-stream specifications challenging to meet overall TEA targets.	Coordinated efforts across projects and multi-lab consortia to focus on critical process-wide considerations: • Feedstock selection/specification • Separations/purification • Fundamental catalyst design/process

3 – Technical Accomplishments



Upgrading Approach

Chemically derived intermediates

Biologically derived intermediates

Biomass

Sugars

Furfural HMF

Alcohols/ Aldehydes/ Ketones

Carboxylic Acids

Diols

Condensation HDO

C-C Coupling HDO

Ketonization Condensation HDO

Multiple Approaches

C10-C20 paraffins

C8-C16 alkanes

C7-C20 paraffins

C8-C16 paraffins, MEK, 1,3-Butadiene

Transportation Fuels and Biochemical Products

(diesel, jet, gasoline, etc.)

- Task 1: 2-3-butanediol (BDO)
- Task 2: Carboxylic acids
- Task 3: Sugars/sugar-derived intermediates
- Task 4: Hydrolysate/fermentation broth production; techno-economic analysis

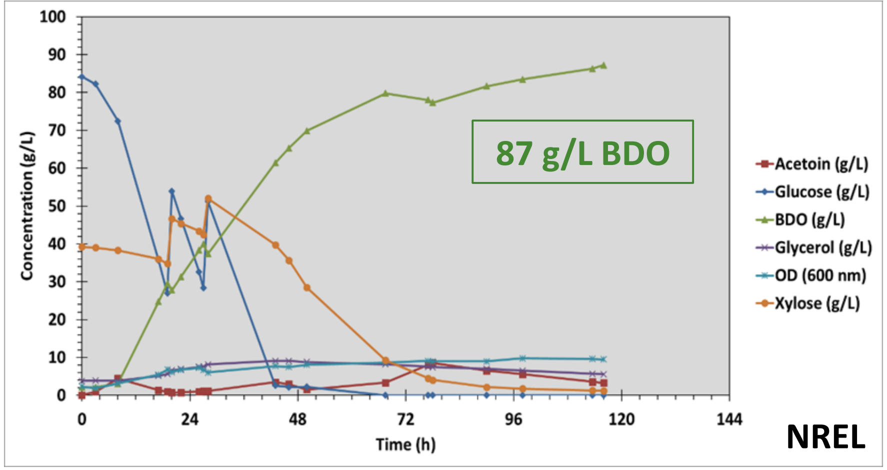
2,3-BDO to Fuel Intermediates and Co-Products

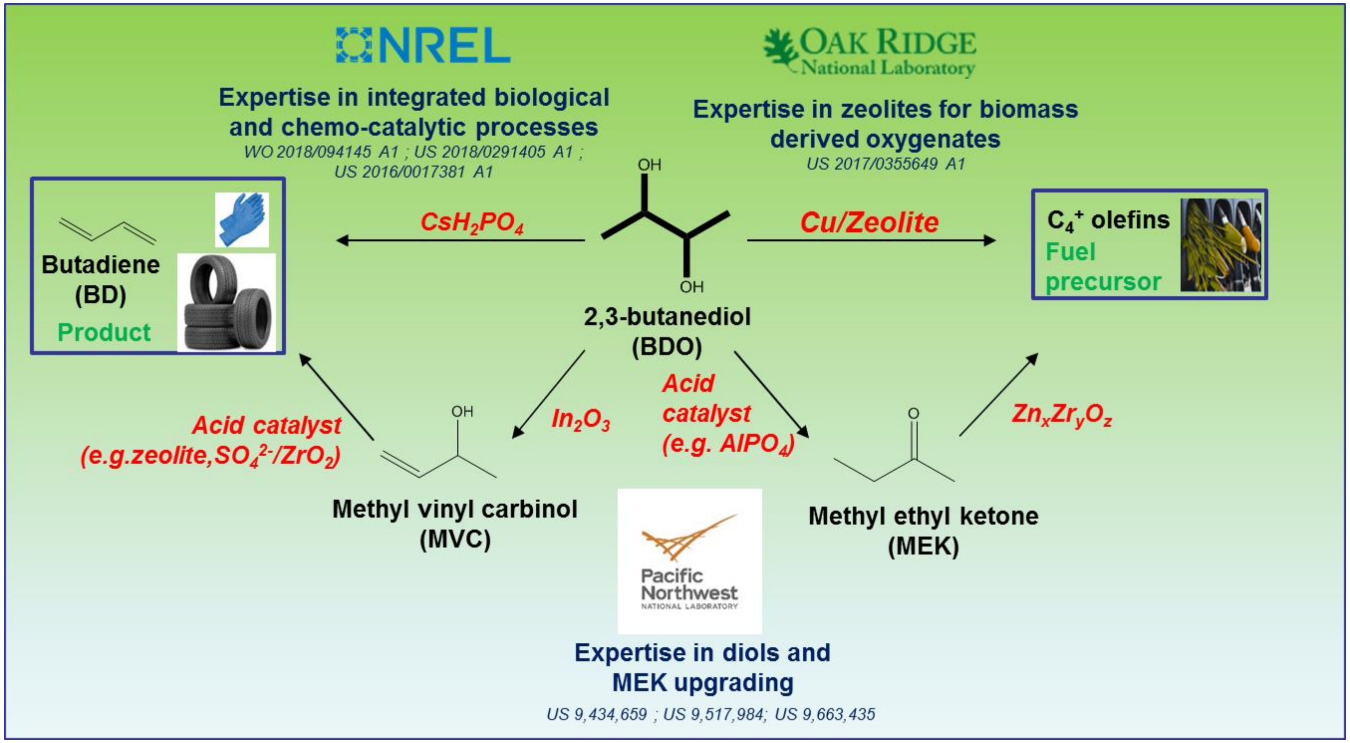
2,3-BDO from Corn Stover Hydrolysate

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





NREL

Expertise in integrated biological and chemo-catalytic processes

WO 2018/094145 A1 ; US 2018/0291405 A1 ; US 2016/0017381 A1

Oak Ridge National Laboratory

Expertise in zeolites for biomass derived oxygenates

US 2017/0355649 A1

Butadiene (BD)

Product

CsH_2PO_4

Cu/Zeolite

C_4^+ olefins

Fuel precursor

2,3-butanediol (BDO)

Acid catalyst (e.g.zeolite, SO_4^{2-}/ZrO_2)

In_2O_3

Acid catalyst (e.g. $AlPO_4$)

$Zn_xZr_yO_z$

Methyl vinyl carbinol (MVC)

Methyl ethyl ketone (MEK)

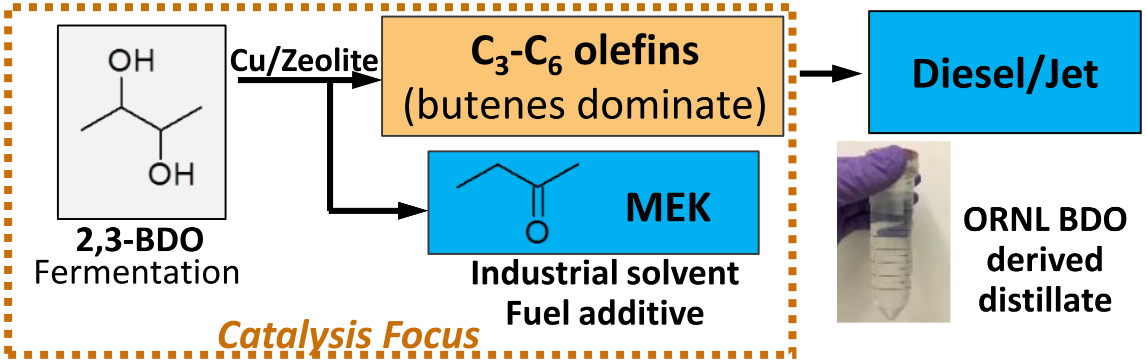
Pacific Northwest NATIONAL LABORATORY

Expertise in diols and MEK upgrading

US 9,434,659 ; US 9,517,984; US 9,663,435

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

BDO to distillate via one-step olefin production



2,3-BDO
Fermentation

Cu/Zeolite

C_3-C_6 olefins
(butenes dominate)

Diesel/Jet

MEK

Industrial solvent
Fuel additive

Catalysis Focus

ORNL BDO derived distillate

Advantages

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

Objective: Maximize C_3-C_6 olefin selectivity via new catalyst design

- ORNL developed a new Cu/Pillared-MFI catalyst, enabling high yield of C_3-C_6 olefins

	Catalyst	Single-pass conversion (%)	C_3-C_6 Olefin Selectivity (%)	Productivity ($g/g_{cat}/h$)	Durability[#] (h)
FY17 baseline	$Cu/SiO_2@ZrO_2$	100	30	0.18	< 5
Current	Cu/P-MFI*	100	90	0.55	>80

*Cu/pillared MFI, 250°C, WHSV=1.0 h^{-1}, 1 atm; #time on stream for each cycle, C_3-C_6 olefin selectivity changes <20%

Outcome:

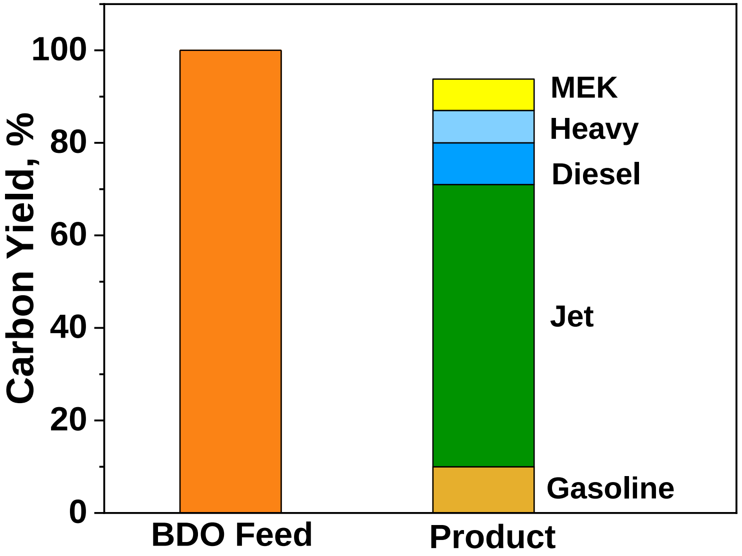
- Cu/P-MFI enables one step high yield of C_3-C_6 olefins with stable performance.
- Set the state-of-the-technology for further development.

ORNL

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

Objective: Demonstrate distillate production from 2,3-BDO

- Via oligomerization of the mixed olefins, followed by hydrotreating



	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%**

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

- Preliminary fuel analysis: **meet Jet A properties**
- Mainly C_8-C_{16}: normal, iso- and cyclic alkanes

Outcome:

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

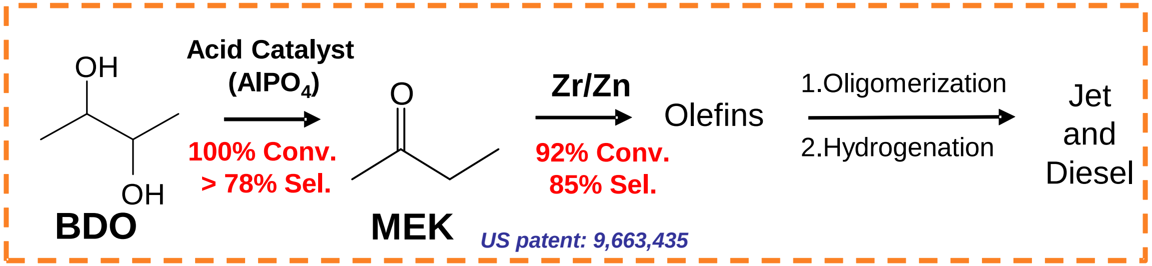
ORNL

2,3-Butanediol Upgrading to Fuel Intermediates

2,3-Butanediol upgrading to fuels via Methyl Ethyl Ketone (MEK) intermediate

Objective:

- Develop a marketable catalyst and process to upgrade 2,3-butanediol (BDO) to **fuels.**



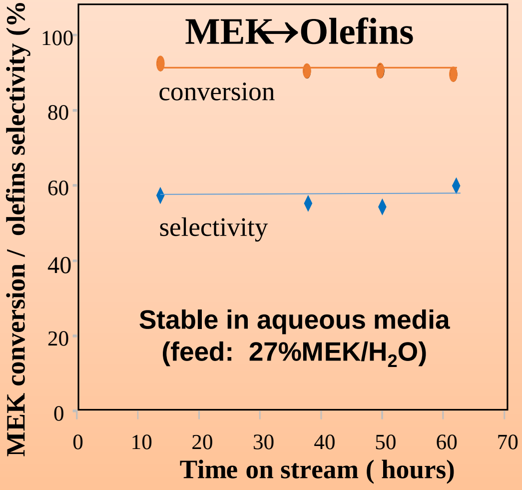
Acid Catalyst ($AlPO_4$): **100% Conv. > 78% Sel.**

Zr/Zn: **92% Conv. 85% Sel.**

1.Oligomerization 2.Hydrogenation

US patent: 9,663,435

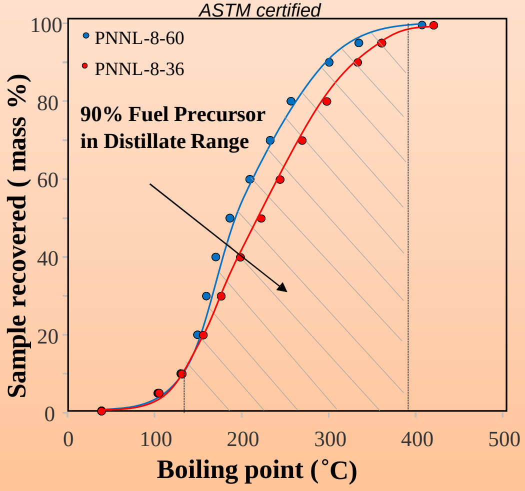
ZnZrO$_x$ Catalyst Stability demonstrated for >60 hr



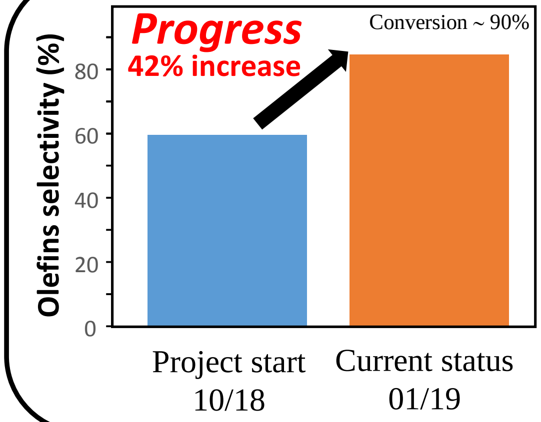
Stable in aqueous media (feed: 27%MEK/H_2O)

T =400°C, GHSV = 550-1300 hr^{-1}, P = 1 atmosphere

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.**



Outcome:

- Stable ZnZrO$_x$ Catalyst
- Operates in aqueous media: BDO/water separation is not needed
- High quality fuel

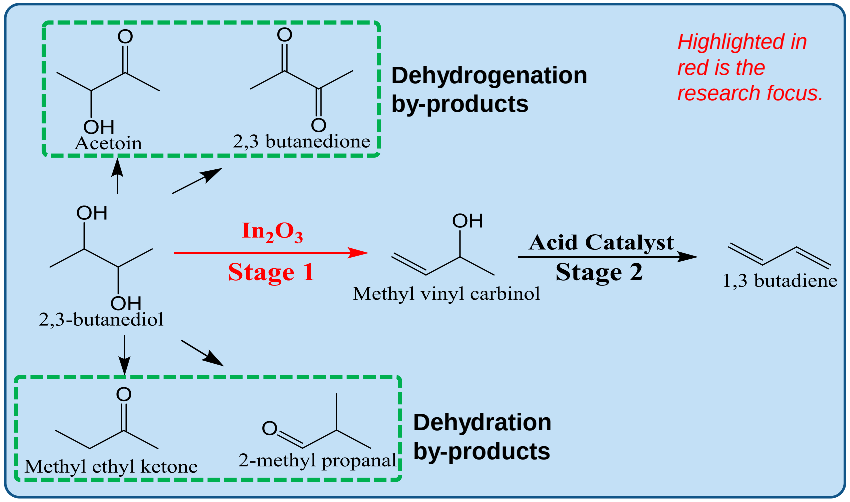
PNNL

2,3-Butanediol Upgrading to Co-Products

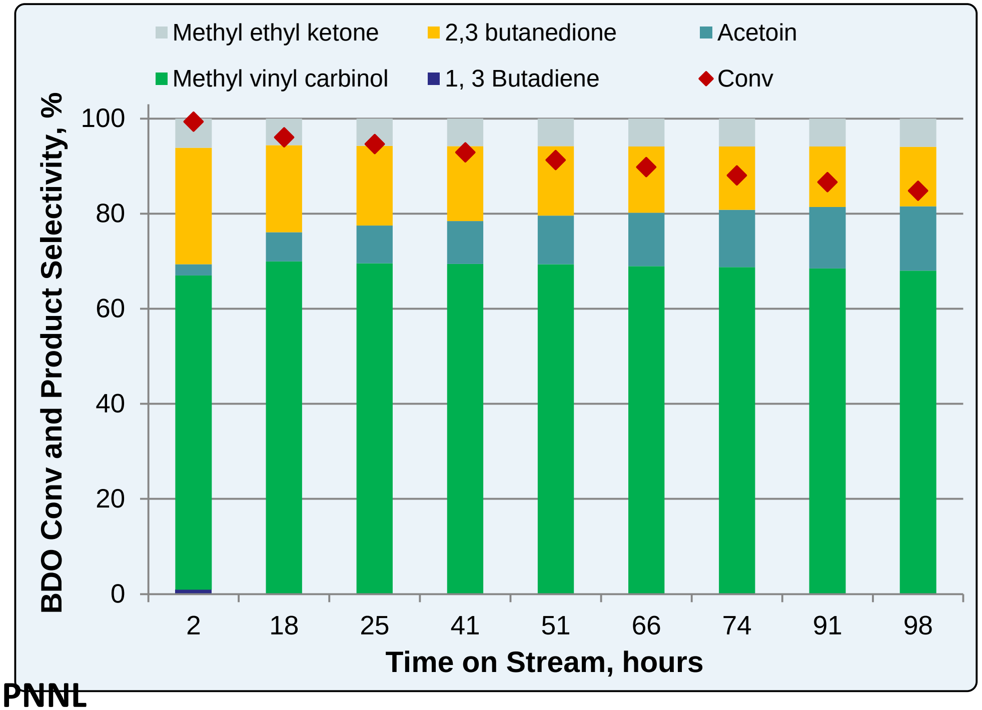
2,3-BDO Upgrading to 1,3-Butadiene (BD) via Methyl Vinyl Carbinol (MVC) Intermediate

Objective:

- Develop a marketable catalyst/process to upgrade 2,3-butanediol (BDO) to **1,3-butadiene (BD).**
  - FY18 focus is on the 1st-stage catalyst (In_2O_3); the second stage MVC to BD is simple and gives high BD yields.



Highlighted in red is the research focus.



PNNL

Outcome:

- BDO-to-MVC (In_2O_3, Stage 1) catalyst is very stable and demonstrated up to 100 hours time on stream.
- In_2O_3 catalyst: ~70% selectivity to MVC was achieved at BDO conversion >90%.
- Regeneration at 450 °C with air completely restores activity of the Stage 1 catalyst (BDO to MVC).

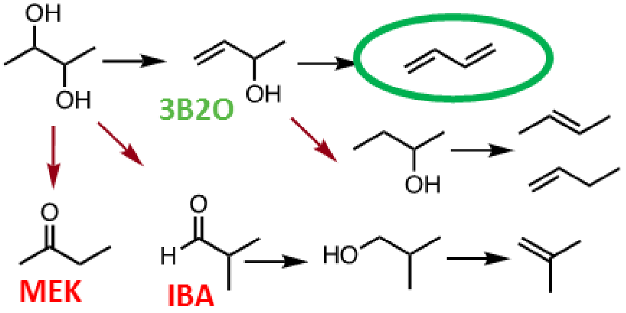
2,3-BDO to Fuel Intermediates and Co-Products

BDO – Single Step Conversion to Butadiene

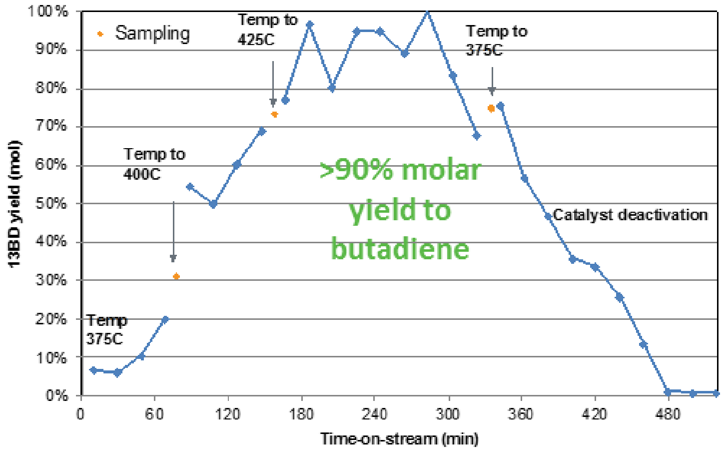
Objective:

- Develop a single step catalytic conversion of 2,3-butanediol (BDO) to **1,3-butadiene (BD).**

Dehydration Reaction Network for 1,3-Butadiene



Validated >90% Butadiene Yield with CsH_2PO_4

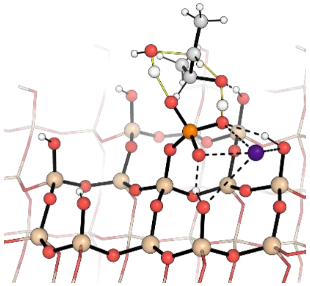


Outcome:

- Recovered BDO from post-fermentation hydrolysate and measured impurities and water content
  - Upgraded model and bio-derived BDO to 1,3-butadiene in yields >50% continuously for >4 h with **CsH_2PO_4/SiO_2** – water content at 10% not a factor
- **Further tuning of catalyst and conditions** allowed for >90% molar yield of butadiene
  - **Steady state coking** can result in the onset of rapid deactivation
  - **Limit to loading support with CsH_2PO_4 -** pore blockage and reduced surface area/activity

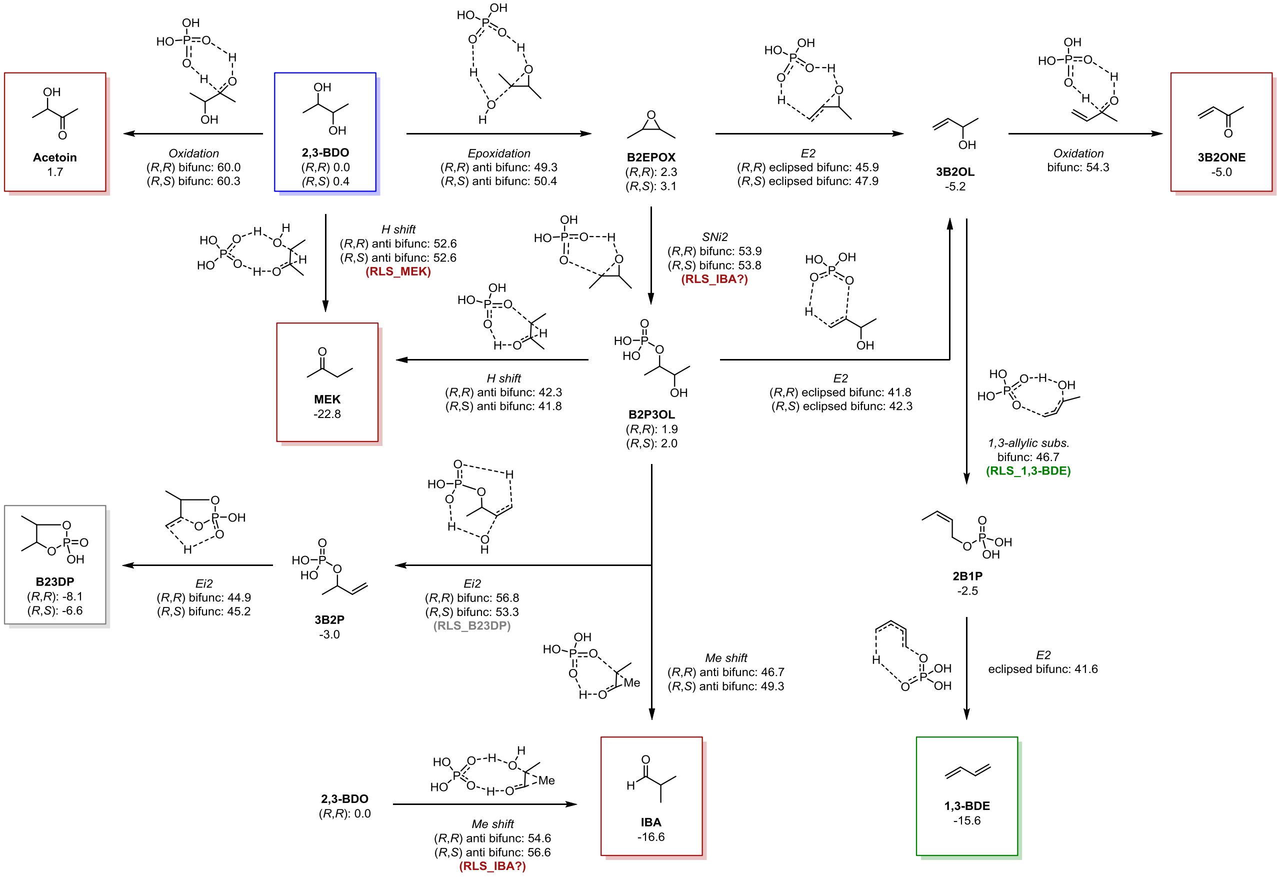
2,3-BDO to Fuel Intermediates and Co-Products

BDO – Single Step Conversion to Butadiene

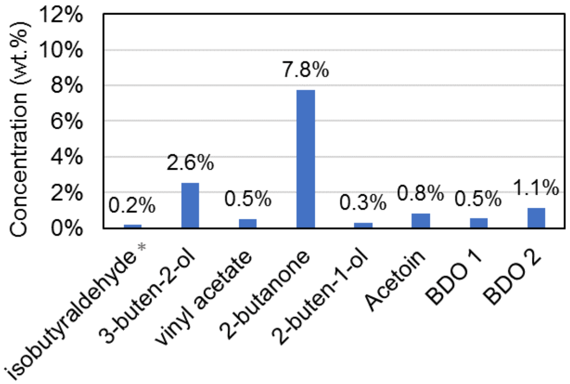


CCPC: Robert Paton and Seonah Kim

Mapping of Reaction Pathways to Explain Selectivity



Characterization of Intermediates & Non-targets



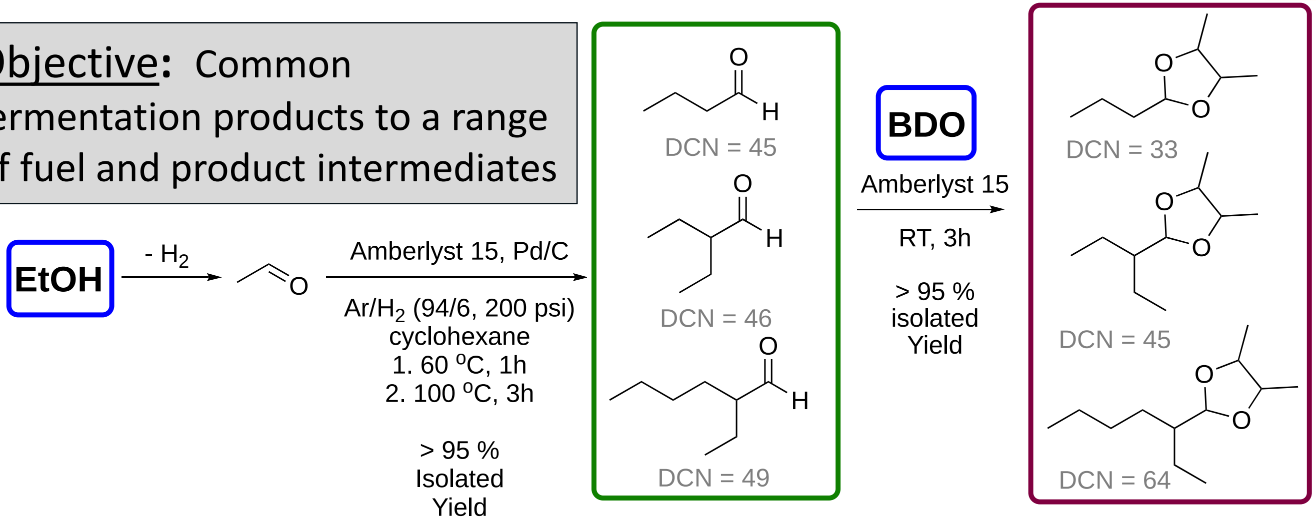
Outcome:

- **Active collaboration with CCPC & ACSC** to evaluate mechanism and catalyst active site
- **Ongoing work to experimentally corroborate** proposed reaction pathways
- **Actively testing catalyst regenerability**, as well as impact of biogenic impurities

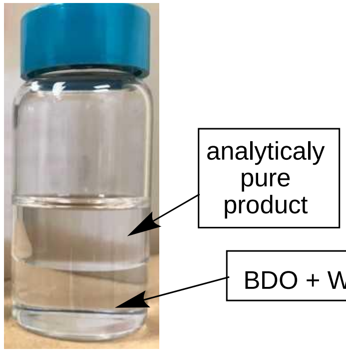
NREL

Ethanol and BDO as Bio-derived Building Blocks

Objective: Common fermentation products to a range of fuel and product intermediates



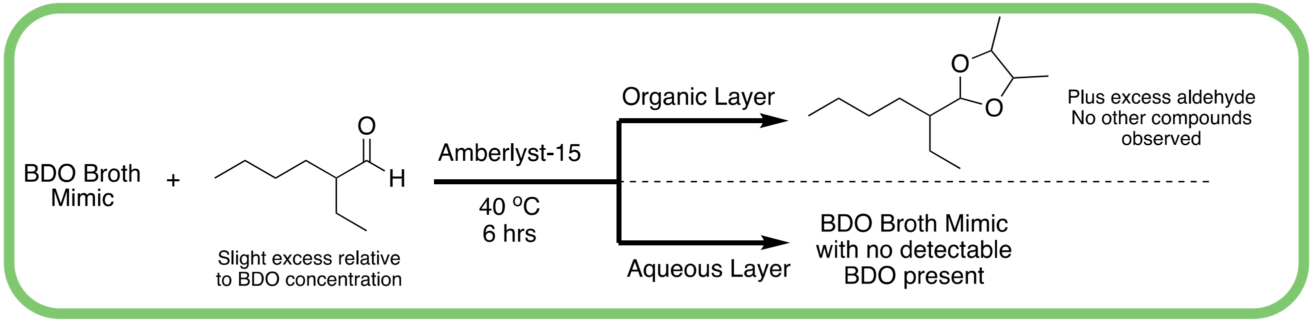
Products Phase Separate



Being adapted for BDO separation and recovery from fermentation broths

Application Towards BDO Separations

Component	Glucose	Xylose	Arabinose	Galactose	BDO	Acetoin	Glycerol	Xylitol	Lactic Acid	Acetic Acid
[g/l]	0.00	4.67	6.23	0.54	82.2	0.00	16.2	2.21	2.09	0.45



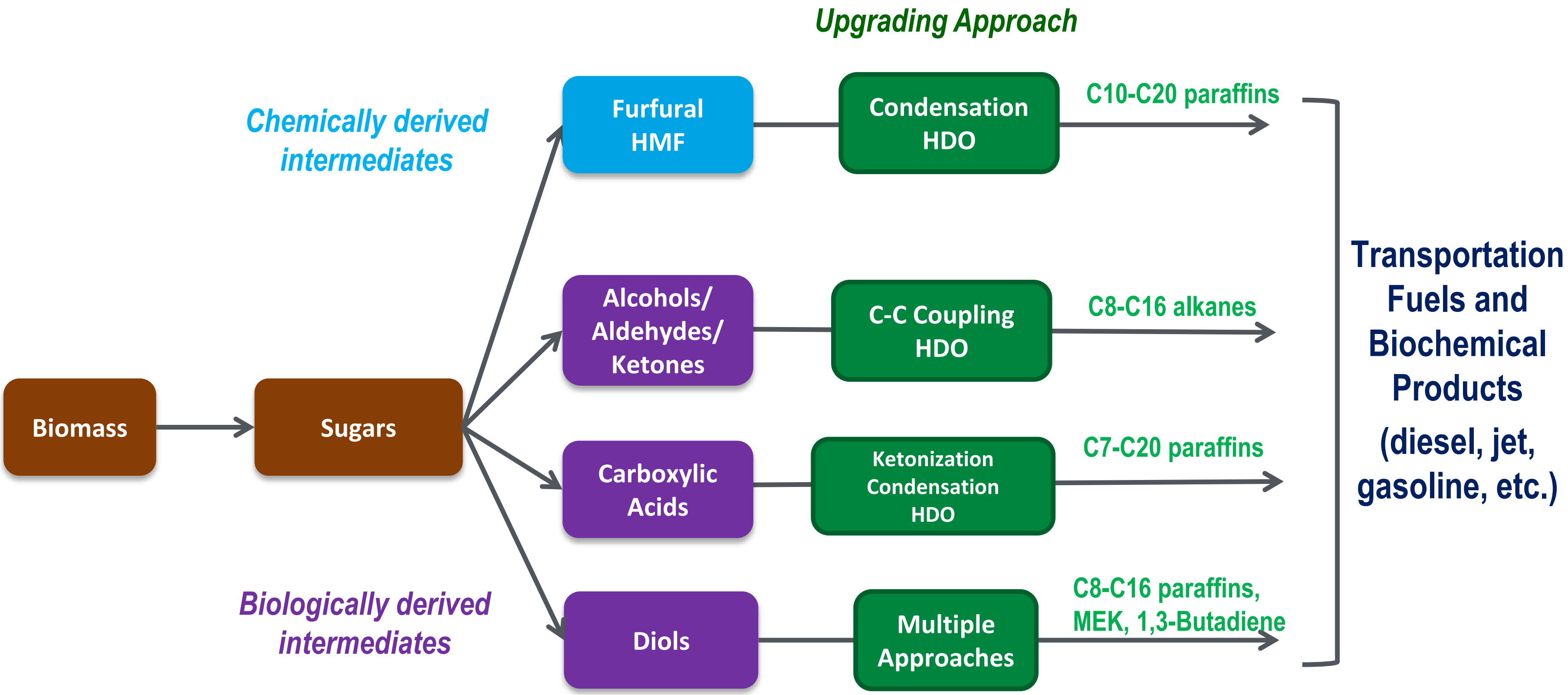
BDO recovery from dioxolanes achievable with mild acid – optimization underway.

Outcome:
- Tunable monomers branched and cyclic fuel intermediates
- New BDO separations approach

Moore *et al.*, Green Chem., 2017, *19*, 169.
Staples *et al.,* Sustainable Energy Fuels, 2018, Advance Article

LANL

3 – Technical Accomplishments



- Task 1: 2,3-butanediol (BDO)
- Task 2: Carboxylic acids
- Task 3: Sugars/sugar-derived intermediates
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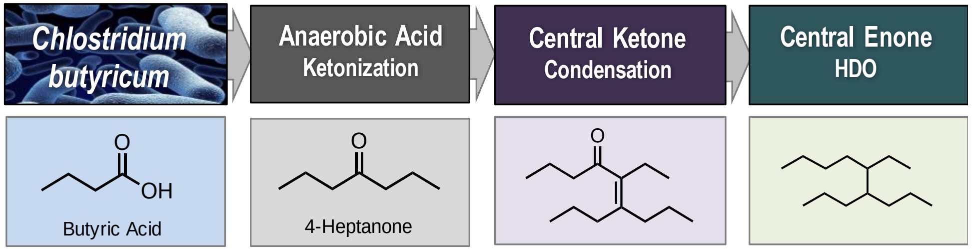
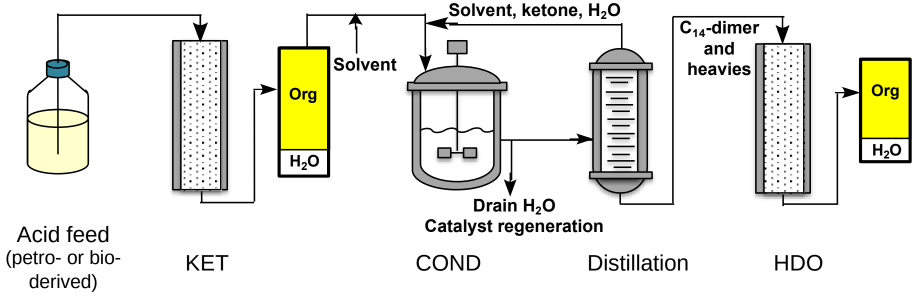
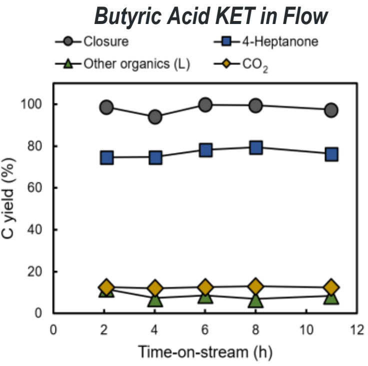
Carboxylic Acids Upgrading

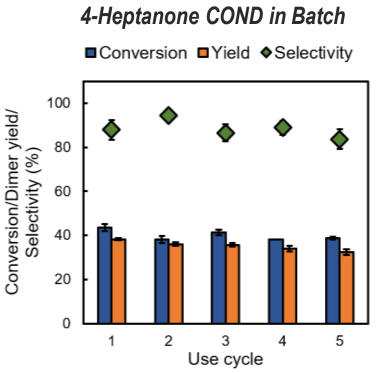
Conversion Scheme for Butyric Acid Upgrading to Hydrocarbons

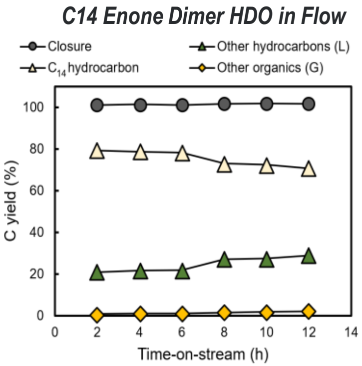




Catalytic Process Development for Individual Reaction Steps







NREL

Objective:

Upgrade C4 acids to diesel hydrocarbon blendstock via ketonization (KET), condensation (COND), and HDO

Generate diesel fuel samples for fuel testing using target C14 HC monomer and complex hydrocarbon mixture

Outcome:

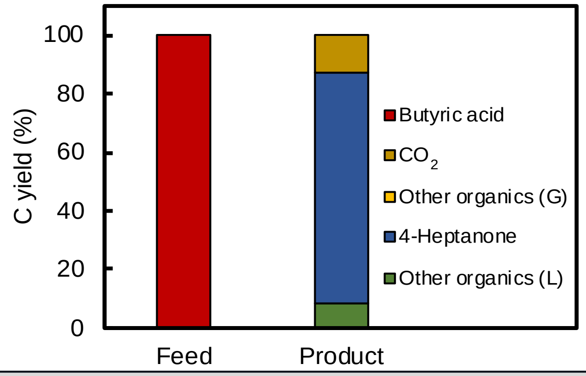
Butyric KET near theoretical carbon balance under complete conversion conditions and stable for >10 hours in flow with **commercial ZrO_2**

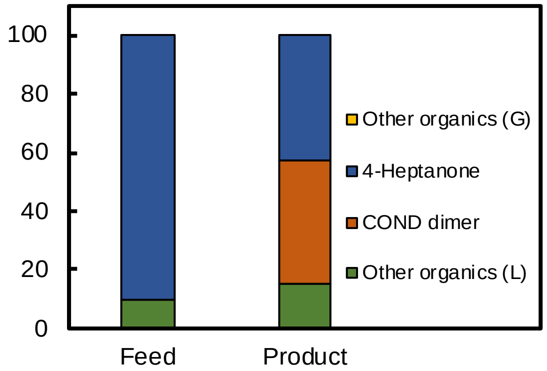
4-Heptanone COND to C14 enone to increase ketone loading (20 wt%), lower catalyst loading (1:5 wt/wt), and show recycle with **commercial Nb_2O_5**

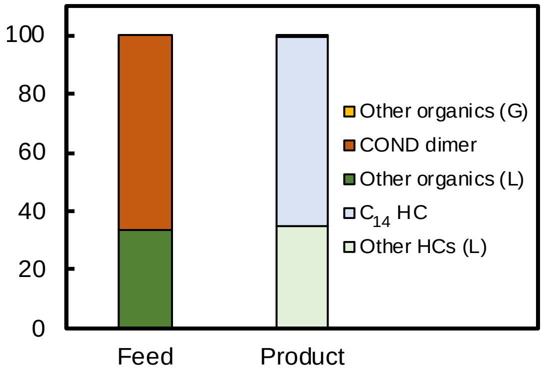
C14 enone HDO complete conversion with >84% selectivity to C14 HC and <2% cracking for >10 hours in flow with **in-house Pt/Al_2O_3**

Carboxylic Acids Upgrading

Objective: Fully Integrated Demonstration of Catalytic Conversion Pathway


Butyric Acid Ketonization


Ketone Condensation


Hydrodeoxygenation

Outcome:

- **Linking all catalytic steps** showed increased HC complexity (67% C14) with full deoxygenation and 84% overall carbon yield to hydrocarbon product
- **Isolated C14 HC has desirable** cetane, low sooting, and cold flow properties
- **Complex HC blendstock was added into diesel** at 20 wt% (**collaboration with Co-Optima**) and reduced soot by 11%

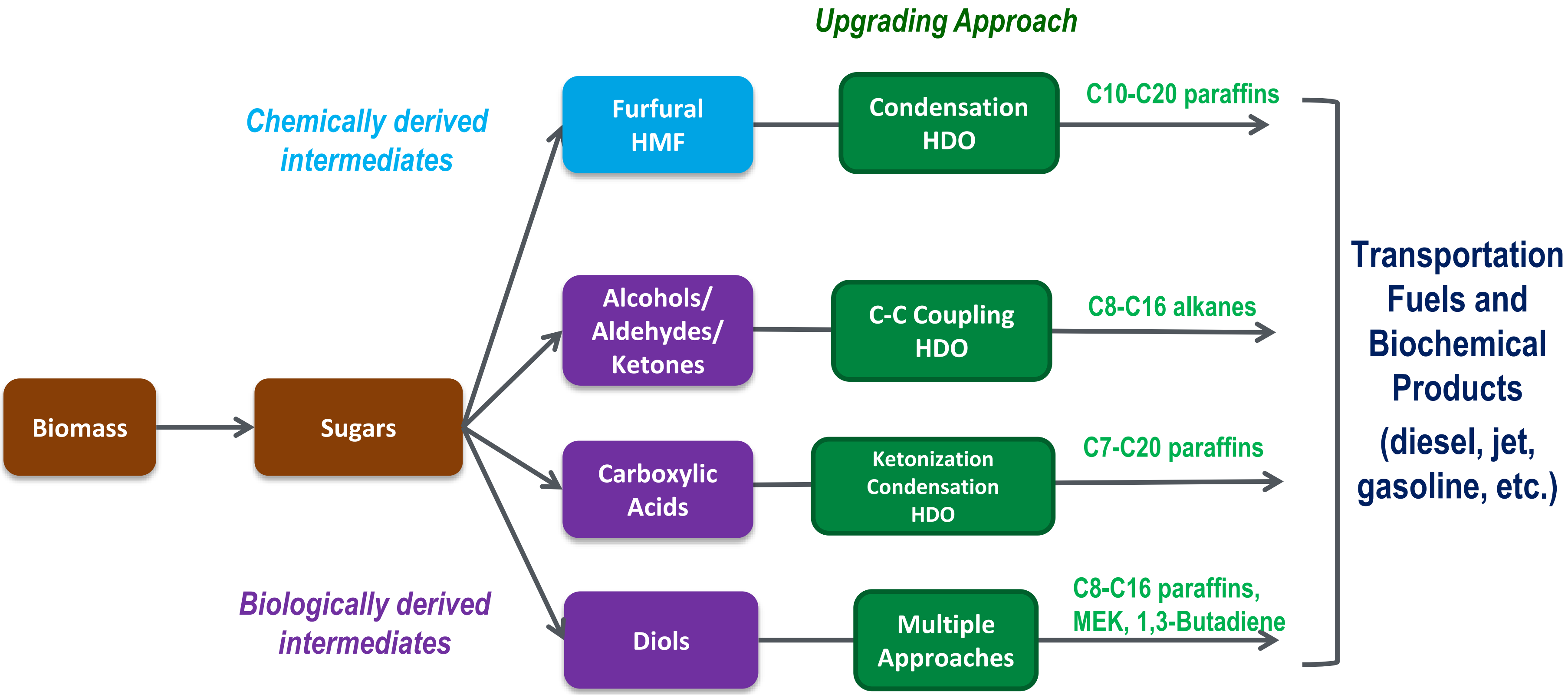
HC Blendstock and Blended Fuel Property Testing

Properties	Blendstock		Diesel and blend	
	Purified C_{14}	Crude C_{14}[a]	Base diesel	Blend
MP (°C)	< -80	< -80	-7.6	-9.5
CP (°C)	< -80	< -80	-7.3	-12
BP (°C)	230	266[c]	333[c]	327
FP (°C)	74.4	ND	55.4	52.1[d]
LHV (MJ kg^{-1})	44	44	45	43
LHV (MJ L^{-1})	34	34	39	37
ν (cSt)	ND	1.53[d]	2.66	ND
Cetane	ND	48[d]	47	46[a]
Sooting index	91	NA	NA	NA
Soot conc.[e]	ND	0.47	1	0.89
ρ (g mL^{-1})	0.78	0.78	0.86	0.85

ND = Not determined. NA = Not applicable. [a]Butyric acid derived blendstock (65% C_{14} purity). [b]Butyric acid derived blendstock (61% C_{14} purity). [c]T90 from simulated distillation profile. [d]Commercial 4-heptanone derived blendstock (83% C_{14} purity). [e]Normalized soot concentration, defined as the concentration of soot measured for a blendstock or a blend normalized to that of the base diesel (NSC = 1).

NREL

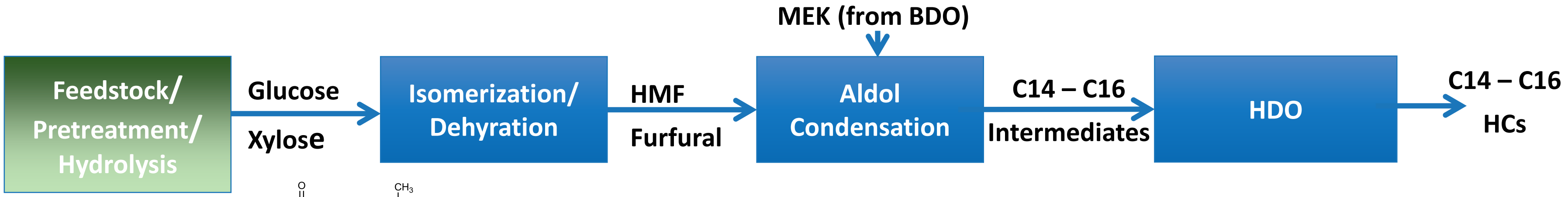
3 – Technical Accomplishments

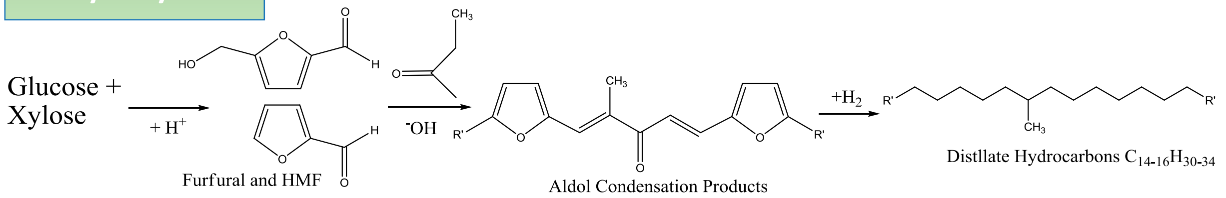


- Task 1: 2,3-butanediol (BDO)
- Task 2: Carboxylic acids
- Task 3: Sugars/sugar-derived intermediates
- Task 4: Hydrolysate/fermentation broth production; techno-economic analysis

Upgrading Furfurals to Distillate Hydrocarbons

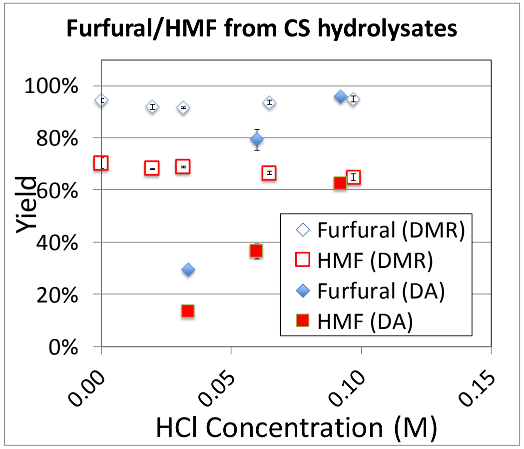
Production of high-cetane distillate via aldol condensation of furfurals followed by HDO

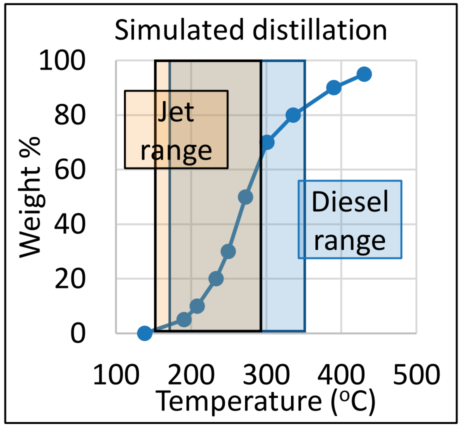




Objective:

- Demonstrate production of furfurals (>50% yield) from mixed C5 + C6 sugars using Lewis/Bronsted acid catalysts.
- Demonstrate >25% (GGE basis) of fuel sample could be blended into jet or diesel fuel (Go/NoGo)





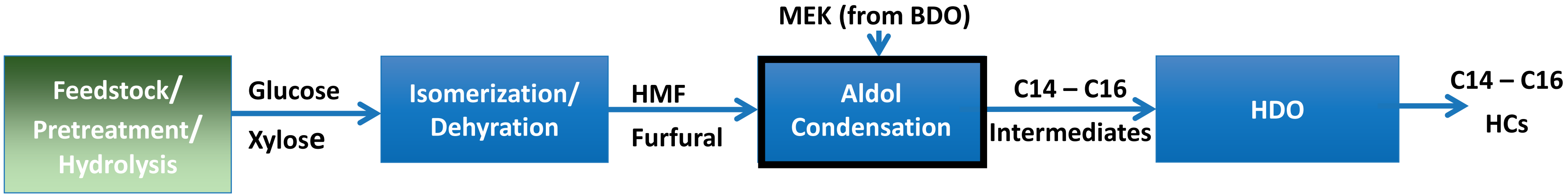
Outcome:

- Furfurals produced in high yield (80%) from corn stover hydrolysates with $AlCl_3$ catalyst, aqueous dioxane, 180 °C, 2 min. Sulfate inhibited $AlCl_3$ catalyst.
- Product had very good fuel properties: Cloud Pt -64 °C, CN 61, 60%/80% in jet/diesel boiling ranges.

NREL

Upgrading Furfurals to Distillate Hydrocarbons

Production of high-cetane distillate via aldol condensation of furfurals followed by HDO



MEK (from BDO)

Feedstock/ Pretreatment/ Hydrolysis

Glucose

Xylose

Isomerization/ Dehyration

HMF

Furfural

Aldol Condensation

C14 – C16

Intermediates

HDO

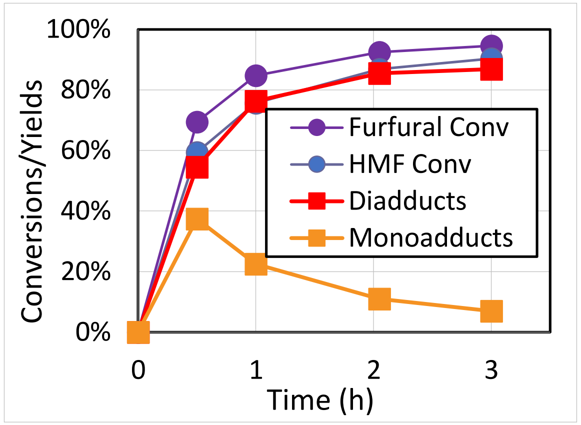
C14 – C16

HCs

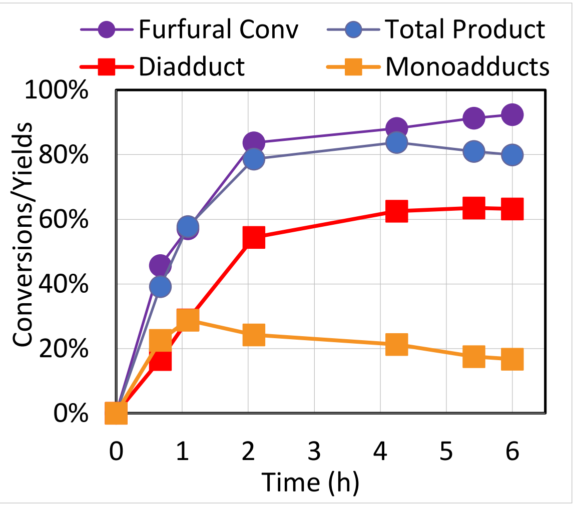
Objective:

- Demonstrate aldol condensation on mixture of furfural and HMF and convert to hydrocarbon product by HDO
- Demonstrate aldol condensation with solid recyclable catalyst with minimal loss of yield/selectivity.

Aldol Condensation of Furfurals Mixture



Amberlyst SAE Resin Catalyst



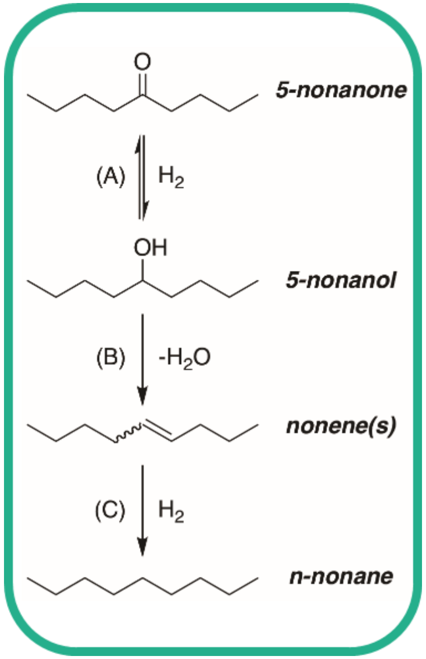
Outcome:

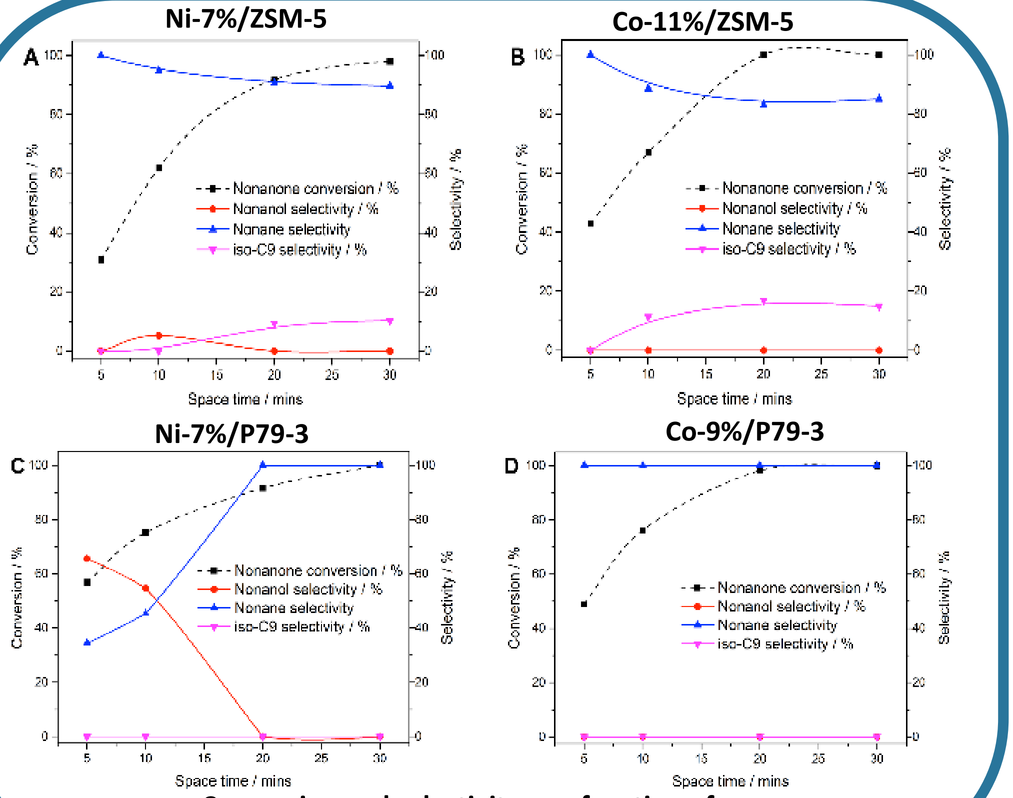
- Aldol condensation of HMF and furfural with MEK using NaOH gave C14-C16 intermediate (diadduct) in high yield
- HDO of intermediate produced HC for Go/NoGo
- Amberlyst A-26 (OH) strong anion exchange (SAE) resin can catalyze aldol condensation, but rate ~½ that of NaOH, probably due to resin's lower alkaline strength.

NREL

Continuous Flow HDO Development

Objective: Demonstrate continuous flow HDO performance for a central ketone intermediate




Ni-7%/ZSM-5 **Co-11%/ZSM-5**

Ni-7%/P79-3 **Co-9%/P79-3**

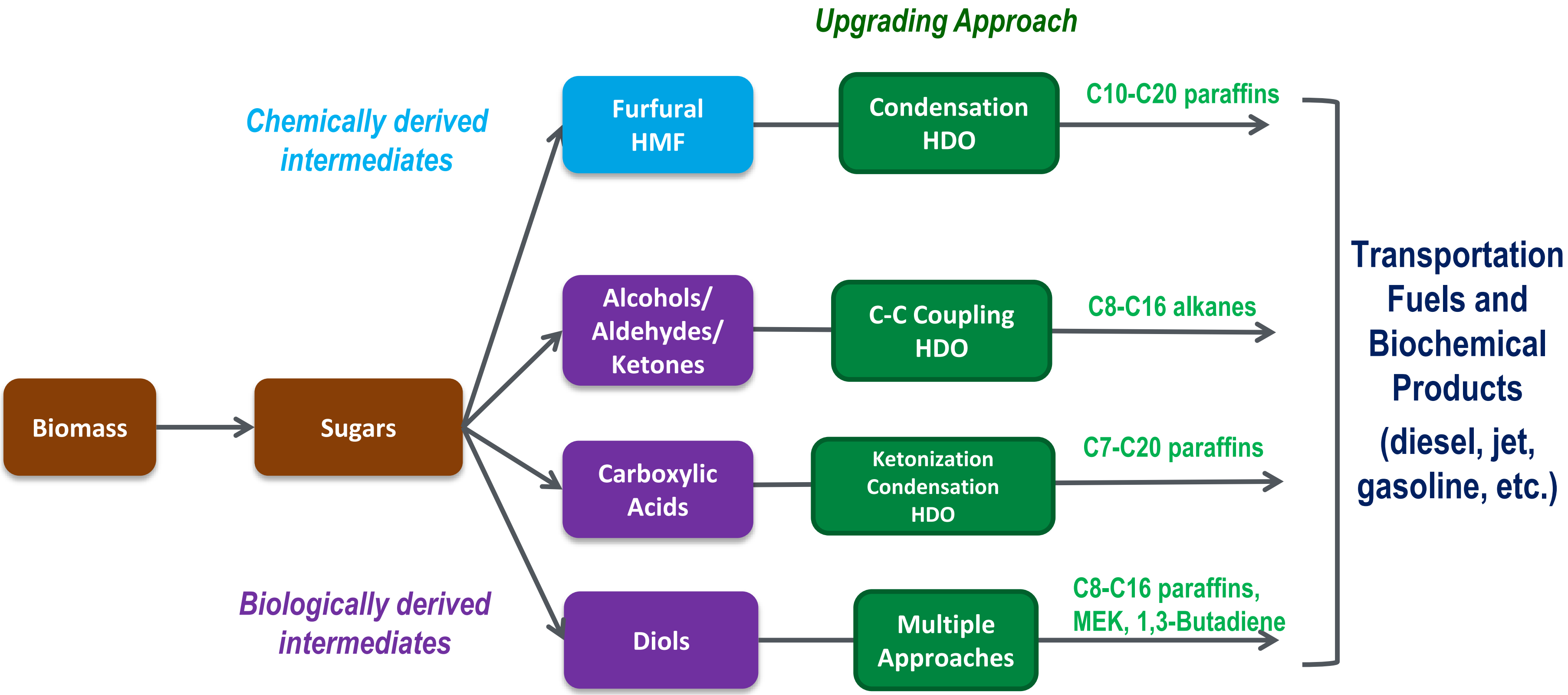
Conversion and selectivity as a function of space time (200 °C, 1.38 Mpa (200 psi) H_2).

Catalyst	Initial Surface Area (m^2/g)	Used Surface Area (m^2/g)	Surface area reduction / %
Ni-7%/ZSM-5	278.10	53.37	80.8
Co-11%/ZSM-5	257.45	102.64	60.1
Ni-7%/P79-3	227.91	196.37	13.8
Co-9%/P79-3	223.28	220.03	1.5

Outcome: Optimized using model system with cobalt catalyst: complete conversion and selectivity to hydrocarbon without isomerization with ~20 min space time. Catalyst lifetime being determined.

LANL

3 – Technical Accomplishments



- Task 1: 2,3-butanediol (BDO)
- Task 2: Carboxylic acids
- Task 3: Sugars/sugar-derived intermediates
- Task 4: Hydrolysate/fermentation broth production; techno-economic analysis

June 2018 Go/No Go Milestone

Determine techno-economic viability to achieve $3/gge when incorporating lignin co-product valorization (opportunities for < $3/gge with partial diversion of sugars/derived intermediates to co-products)

TEA Model Framework

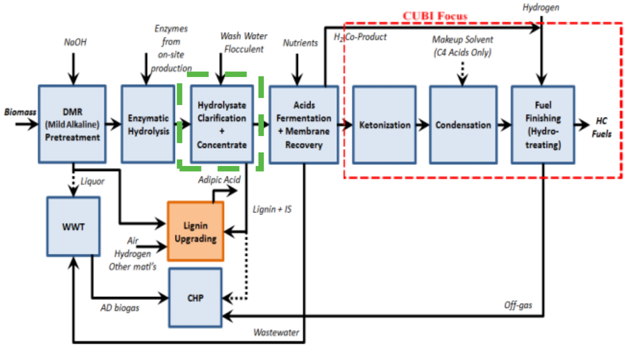
- Deconstruction to sugars
  - Deacetylation and Mechanical Refining (DMR)
    - Enables lignin valorization for biochemical routes
    - Included in 2018 SOT and in new Biochemical Platform Design Report
    - Used for all CUBI cases, with identical process assumptions
- Solid - liquid separation
  - After enzymatic hydrolysis for carboxylic acids and furans routes
  - After fermentation for 2,3-BDO route
- Biological conversion to targeted intermediate OR dehydration to furfurals
- Catalytic upgrading to targeted HC fuel compounds

TEA Summary

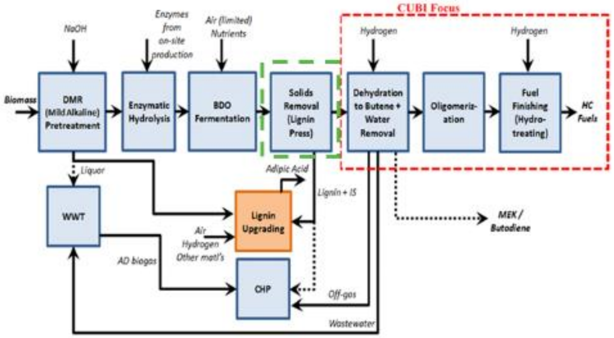
All pathways have routes to $3/GGE

- Sensitivity analysis used to identify areas for catalytic process improvements
- Co-products from catalytic intermediates identify opportunities for < $3/GGE

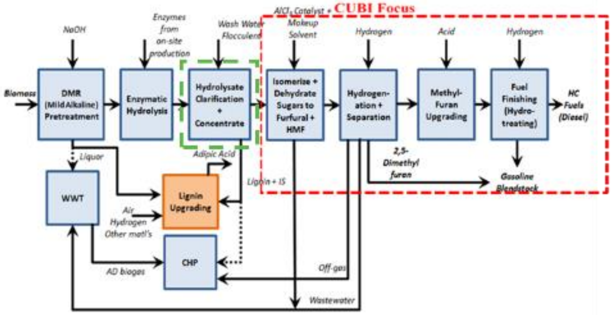
Carboxylic Acid



2,3-BDO



Furfurals



TEA-Guided Future R&D:

- Reduce KET/Cond residence time
- Reduce solvent:ketone ratio
- Utilize lower-cost undoped ZrO_2

- Reduce BDO upgrading temperature
- Improve catalyst stability with fines/ash/ions in feed
- Divert BDO to MEK (example) - opportunity for <$3/GGE

- Reduce isomerization/ dehydration temp.
- Reduce ratio of solvent to aqueous hydrolysate

4 – Relevance

Facilitating transition of catalytic upgrading of biochemically-derived intermediates from clean sugars/intermediates to biomass-derived sugars/intermediates in order to reduce overall process cost

Industry Relevance

- Comparative upgrading data and TEA analysis will inform industry of the relative opportunities for catalytic upgrading of process-relevant, **biochemically-derived intermediates from lignocellulosic feedstocks**
  - Approaches and methodologies can be extended to other industry-specific opportunities for HC fuels components and/or chemical products

Marketability

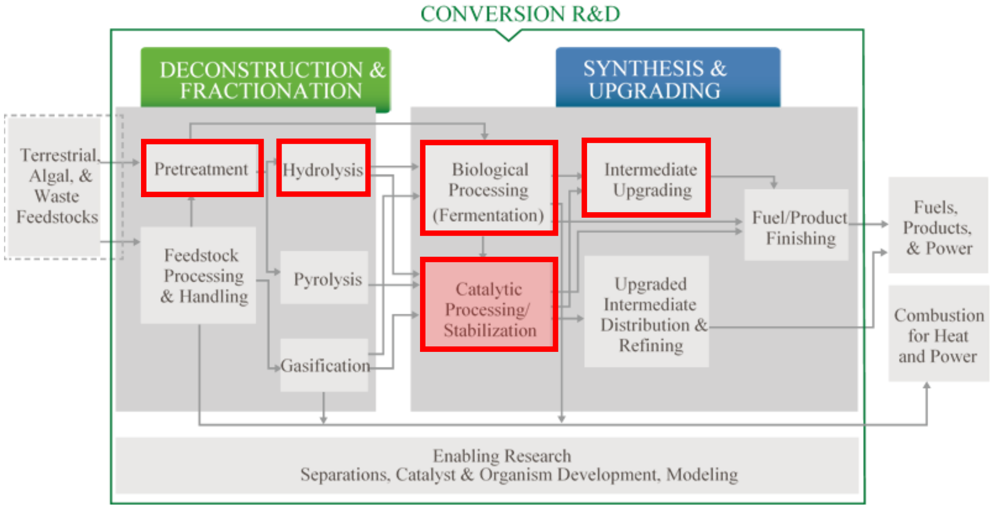
- ChemCatBio (www.chemcatbio.org) has an active industry outreach to leverage the capabilities and expertise of national labs to help solve specific industry problems or develop new, industrially-relevant capabilities

4 – Relevance

Support of BETO’s Mission: Conversion R&D Challenges and Barriers (2019 MYPP)

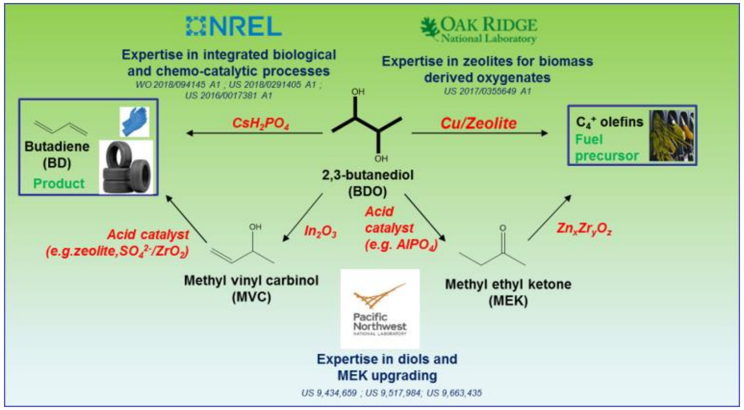
- “Need for both catalysts that are more tolerant of lower-quality feedstocks and for pretreatment and separation processes that eliminate contaminant species”
  - Ct-E: Improving Catalyst Lifetime
- “Need to identify catalysts and process conditions that increase overall yield…by direct improvements to catalyst performance”
  - CT-F: Increasing the Yield from Catalytic Processes
- “Understanding process integration is essential to characterize the interactions between unit operations, identify the impacts of inhibitors and contaminants on processing systems, ….”
  - ADO-A. Process Integration

Low Temperature Deconstruction and Catalytic Sugar Upgrading



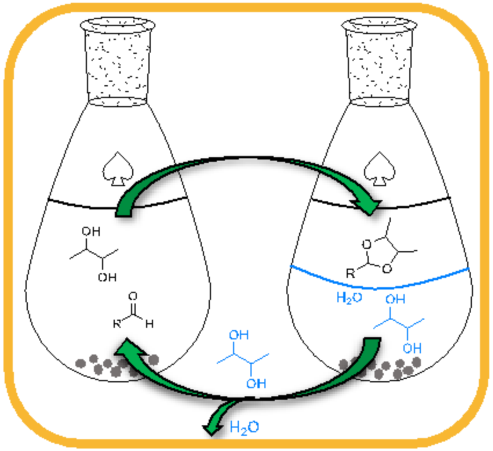
Adapted from Table 2-5, BETO Multi-Year Program Plan (2019)

5 – Future Work



Task 1: Catalytic Upgrading of 2,3-butanediol (BDO)

- Cu/zeolite optimization
  - Structure and mechanism (CCPC/ASCS) – tune olefin composition
- Fuel property optimization (with Co-Optima)
- Tune fuel properties to optimize oligomerization
- BDO to MEK
  - Biogenic inhibitor effect on catalyst performance
  - Impact of actual hydrolysate/fermentation feed
  - NMR investigation of surface species and reaction pathway
- BDO to MVC
  - Synthesize high-surface area In_2O_3 catalyst – MVC selectivity
  - Impact of actual hydrolysate/fermentation feed
  - NMR investigation of surface species and reaction pathway
- Phase separation of dioxylanes from aldehydes and BDO
  - BDO recovery with recycle of aldehydes



FY19 Q2 Milestone:

- Key Catalytic Upgrading Process Improvements
  - Catalyst deactivation modes
  - Improved WHSV, utilize catalyst cost tool
  - New formulations to increase surface area

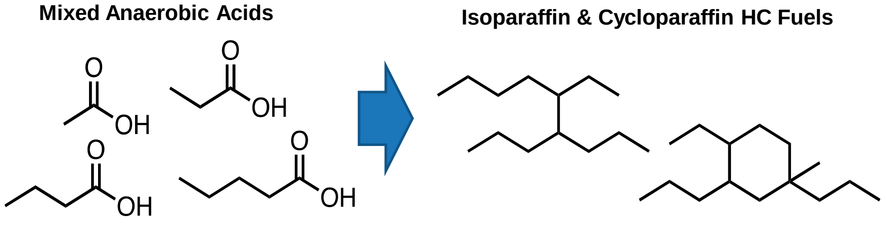
FY19 Q3 Milestone:

- Hydrolysate/Fermentation Inhibitor Assessment
  - Feedstock/hydrolysate derived compounds
  - Fermentation co-products
  - Water – recovery and separations

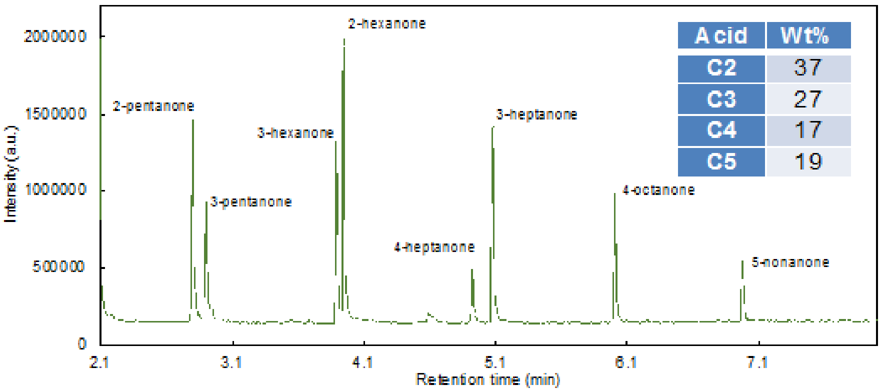
5 – Future Work

Task 2: Catalytic Upgrading of Carboxylic Acids

- Mixed acid (C2-C5) upgrading to address aviation and heavy duty fuel needs
  - Future experimental work to evaluate **mixed acids (C2-C5)** to expand potential feedstocks and upstream organisms suitable for acid-to-fuel pathway
  - **Mixed acids** can expand fuel options by generating **both isoparaffin and cycloparaffin HC** as products since **both central & terminal ketones** are produced as intermediates
  - **Water tolerance and coking** still issues during ketone condensation that will require further understanding of working catalyst surface and effective regeneration strategies



Mixed Acids (C2-C5) Ketonization



Acid	Wt%
C2	37
C3	27
C4	17
C5	19

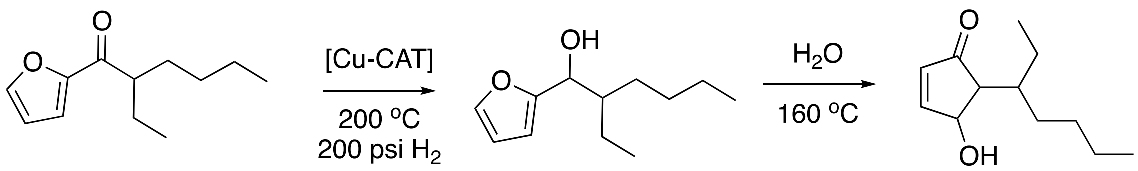
FY19 Q2 Milestone:
- Key Catalytic Upgrading Process Improvements
  - Improve ketone condensation catalyst regenerability by 10% by (i) aqueous treatment fouling coke burn off and (ii) modified burn off conditions (with CCPC)

FY19 Q3 Milestone:
- Hydrolysate/Fermentation Inhibitor Assessment
  - Assess impact of ≥3 impurities by comparing model and bio-derived C4 acid
  - >6 hr TOS for ketonization and HDO
  - Measure impurities at each upgrading step

5 – Future Work

Task 3: Catalytic Upgrading of Sugars/Sugar-derived Intermediates

- Furfurals upgrading
  - Investigate potential for generating **furfurals directly from biomass polysaccharides** without prior pretreatment and enzymatic hydrolysis.
  - Quantify effects **of biomass derived furfurals on heterogenous catalysts** used in producing hydrocarbons, particularly for the **HDO step**.
  - Generate at least 100 mL of hydrocarbons for fuel property testing with greater **emphasis on tests for jet fuel** compatibility.
- Piancatelli furan rearrangements



Increased stability vs. furan

Extendable to a range of LANL aldol products

Analogous to natural products pre-cursors

Defunctionalize to cyclopentane - high S fuel?

FY19 Q2 Milestone:

- Key Catalytic Upgrading Process Improvements
  - Produce biomass furfurals in flow reactor
  - Integrated unit operations for C-C formation and defunctionalization
  - Increase aldol condensation of acetaldehyde yield to ≥80%

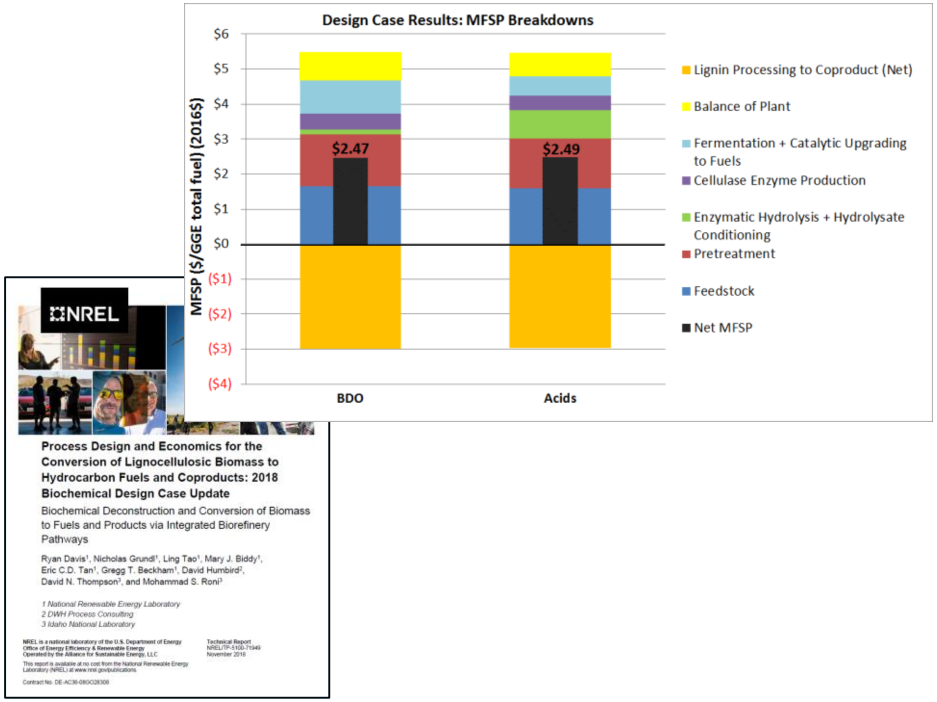
FY19 Q3 Milestone:

- Hydrolysate/Fermentation Inhibitor Assessment
  - Quantify effect of biomass-derived furfurals
  - Catalyst characterization: top 3 poisons
  - Determine tolerance levels for top 3 poisons
- Show that varying MOF properties can improve acetaldehyde coupling to 50% yield

5 – Future Work

Task 4: Hydrolysate/Fermentation Broth production; Techno-economic Analysis

- End-of-project TEA assessment
  - Coordinated with Biochemical Platform TEA assessment for annual State-of-Technology projections
  - Includes catalytic upgrading process configuration and results from CUBI project
  - Use of ChemCatBio Catalyst Cost Modeling tool
  - Describe relative levels of development for each CUBI route; identify leading pathway(s) and remaining research needs to achieve ≤$3/gge



Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update

Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Pathways

Ryan Davis[1], Nicholas Grundl[1], Ling Tao[1], Mary J. Biddy[1], Eric C.D. Tan[1], Gregg T. Beckham[1], David Humbird[2], David N. Thompson[3], and Mohammad S. Roni[3]

1 National Renewable Energy Laboratory
2 DWH Process Consulting
3 Idaho National Laboratory

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Technical Report
NREL/TP-5100-71949
November 2018

FY19 Q4 (end-of-project) Milestone:

- Quantify catalytic upgrading performance using biochemical conversion process-derived intermediates in a fully integrated TEA model.
  - Develop biochemical catalytic upgrading State-of-Technology pathway(s) and targets that achieve a modeled Minimum Fuels Selling Price (MFSP) of $3/gge (2016 $) with value-added lignin co-products (or <$2.5/gge (2016 $) with diversion of a portion of sugars/biological intermediates to co products).

Summary

Evaluate several routes for catalytic upgrading of sugars and sugar-derived intermediates into hydrocarbon fuels and co-products and select routes(s) 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 targeting process intermediates
- Go/no-go decision used to identify catalyst and process improvements

Accomplishments

- 2,3-BDO Upgrading:
  - Multiple routes for fuels and co-products; coordination with enabling ChemCatBio projects
- Carboxylic Acids Upgrading:
  - Focus on C4 acids; integrated demonstration of all catalytic steps with improved yield/selectivity
- Sugars-Derived Upgrading:
  - High yields from hydrolysate-derived furfurals; high cetane distillate via aldol condensation; continuous HDO improvements
- Process Intermediates/TEA:
  - Go/no go identified key areas for process improvement; pilot scale generation of hydrolysates and fermentation intermediates

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

- 2,3-BDO Upgrading:
  - Catalyst/process improvements; inhibitor identification/mitigation; phase separation/recovery
- Carboxylic Acids Upgrading:
  - Catalyst/process improvements; inhibitor identification/mitigation; mixed acids assessment
- Sugars-Derived Upgrading:
  - Catalyst/process improvements; inhibitor identification/mitigation; furfurals from polysacch.; furan rearrangement;
- Process Intermediates/TEA:
  - End-of-project TEA assessment and identify leading routes for ≤$3/gge

Acknowledgements

ChemCatBio
Chemical Catalysis for Bioenergy

CCPC
www.cpcbiomass.org

Energy Materials Network
U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioenergy Technologies Office
Nichole Fitzgerald
Jeremy Leong

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Additional Slides

Responses to Previous Reviewers' Comments

- "The production of biochemical intermediates and their conversion to chemicals and fuels is increasingly recognized as the most promising route for replacing fossil fuels with biomass. This route is the best suited to take advantage of the available biomass and the potential growth in high yield varieties grown specifically for fuels, as outlined in the 2016 Billion-Ton Report."
  - Large-volume feedstocks (herbaceous, ag. residues) as source of hydrolysate sugars
  - Inhibitor effects (from biomass, deconstruction process, fermentation co-products, water, etc.) on catalytic upgrading being characterized; inhibition mechanisms and mitigation strategies being developed

- "The teams have done a great job in exploring the potential routes feasible that will maximize the use of all the carbon versus other approaches. It requires complex chemistry to achieve all the processing steps commercially at economics, but the team has the right approach to narrow the possibilities and should continue to attempt to combine steps into one or two where feasible."
  - Efforts are primarily focused on routes aligned with broader biochemical conversion platform (carboxylic acids, BDO, sugars/furans)
  - Process intensification examples for upgrading routes:
    - Multi-functional catalysts and reaction schemes (BDO)
    - Combining C-C coupling and HDO

Responses to Previous Reviewers' Comments

- "The project has clearly demonstrated the chemistry can work. The focus should begin to shift towards optimizing the process to provide data to the technoeconomic analysis (TEA) by choice of catalyst and reactor conditions. Scale-up to produce sufficient quantities to allow product evaluation should be considered as a next step."
  - Catalyst development and upgrading process development focused on cost reduction approaches (catalyst formulation cost, process intensification, etc.)
  - Switch to BDO as an intermediate driven by upstream TEA considerations
  - Comparative TEA analyses performed based on project results (2018 Go/No Go)
  - Fuel testing of 50 mL samples for product evaluation conducted (2018 Go/No Go)

- "There is significant prior work involving these routes. The next step should be to place these in a commercial context and conduct careful TEA on the same basis. The performance of each of the routes needs to be benchmarked against the prior work both in government and in outside laboratories."
  - Initial TEA analysis being conducted on a comparative basis, including deconstruction and biological production of intermediates
  - Future catalyst performance and TEA is being benchmarked against any relevant commercial approaches (some catalytic upgrading steps use current commercial catalyst formulations)
  - ChemCatBio Catalyst Cost Modeling tool will be used in end-of-project TEA

Responses to Previous Reviewers' Comments

- "Overall, great work—this program's focus on sugar conversions is showing that it can efficiently produce narrow product distributions and also products with high value. This is a result that continues to elude whole-biomass conversion and therefore is a solid step forward. However, technical success is different than commercial or strategic success, and the number of steps required to take sugars all the way to hydrocarbon fuels is concerning."
  - TEA is identifying process intensification opportunities
  - Characterization of inhibitor effects and needed process steps to mitigate inhibitors is underway (FY19 milestone)
  - Catalyst robustness/durability is a key process metric for both conversion performance and accurate representation in TEA models

- "It is possible that the program would contribute to the fuel supply in a more constructive manner if focus was on increasing availability/decreasing costs of fuel additives like antioxidants, octane boosters, multifunctional additives, fuel oil additives, etc. Fuel is not a neat chemical; it is an engineered mixture with numerous components, and if there are components that can be generated more efficiently from sugars than petroleum, that would be most helpful."
  - Fuel testing/analysis has identified properties and fuel component value opportunities from each route
  - Fuel products with specific molecules having targeted functional properties (i.e. jet fuel) have been identified

Publications, Presentations, and Patents

Publications

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- A. D. Sutton, J. K. Kim, R. Wu, C. B. Hoyt, D. B. Kimball, L. A. Silks III, J. C. Gordon, "A Two Step Conversion of Sugars into Branched Hydrocarbons," ChemSusChem, 2016, 9, 2298
- C. M. Moore, O. Staples, R. W. Jenkins, T. R. Brooks, A. D. Sutton "Ethanol Derived Bio-Building Blocks: An Alternative to the Guerbet Reaction" Green Chem., 2017, 19, 169.
- R. W. Jenkins, C. M. Moore, T. A. Semelsberger, A. D. Sutton "Heterogeneous ketone hydrodeoxygenation for the production of fuels and feedstocks from biomass" ChemCatChem., 2017, 9, 2807.
- Li, Z; Lepore, A.; Salazar, M.; Foo, G.; Davison, B.H.; Wu, Z.; Narula, C.K.; Selective Conversion of Bio-Derived Ethanol to Renewable BTX over Ga-ZSM-5, Green Chemistry, 2017, 19, 4344-4352.
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- M.A. Lilga, A.B. Padmaperuma, D.L. Auberry, H.M. Job, M.S. Swita. Ketonization of Levulinic Acid and γ-Valerolactone to Hydrocarbon Fuel Precursors. Catalysis Today, 302 (2018) 80-86. https://doi.org/10.1016/j.cattod.2017.06.021
- D.R. Vardon, A.E. Settle, M.J. Menart, K.X. Steirer, T.R. Eaton, K.A. Unocic, N.S. Cleveland, V. Vorotnikov, K.E. Moyer, W.E. Michener. G.T. Beckham. (2017). Ru-Sn/AC for the aqueous phase reduction of succinic acid to 1,4-butanediol under continuous process conditions. http://dx.doi.org/10.1021/acscatal.7b02015
- O. Staples, C. M. Moore, J. H. Leal, T. A. Semelsberger, C. S. McEnally, L. D. Pfefferle, A. D. Sutton. A simple, solvent free method for transforming bio-derived aldehydes into cyclic acetals for renewable diesel fuels. Sustainable Energy Fuels, 2018, 2, 2742-2746.

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Publications (cont.)

- V. Vorotnikov, T.R. Eaton, A.E. Settle, K. Orton, E.C. Wegener, C. Yang, J.T. Miller, G.T. Beckham, D.R. Vardon. (2019). Inverse bimetallic SnO-Ru catalysts for selective reduction of propionic acid. Submitted.
- R. W. Jenkins, X. Yang, J, Leal, C. M. Moore, T. A. Semelsberger, A. D. Sutton, “Continuous heterogeneous hydrodeoxygenation of bio-derived ketones for fuels and feedstock production” Submitted
- V. Lebarbier Dagle, R.A. Dagle, L. Kovarik, F. Baddour, S. E. Habas, R. Elander. “ Single-step Conversion of Methyl Ethyl Ketone to Olefins over ZnZrOx Catalysts in Aqueous Media” submitted Appl. Catal. A

Publications, Presentations, and Patents

Presentations

- D.K. Johnson. Production of advanced biofuels for blending into jet and diesel fuels via furanic intermediates”, Frontiers in Biorefining Conference, November, 2016, St Simons Island, GA.
- D.R. Vardon. Catalytic upgrading of microbial acids for waste valorization. Invited Seminar. University of Illinois at Urbana-Champaign, Department of Civil and Environmental Engineering. January 2017.
- Elander, R., Johnson, D., Vardon, D., Narula, C., Li, Z., Sutton, A., Lilga, M., and Padmaperuma, A. Catalytic Upgrading of Biochemical Intermediates. Presentation at DOE/BETO 2017 Project Peer Review, Denver, CO, March 7, 2017.
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- A.B. Padmaperuma, D.L. Auberry, and M.A Lilga. Conversion of sugar stream to hydrocarbon fuels over mixed oxide catalysts. North American Catalysis Society Meeting, Denver, CO. June 2017.
- A. D. Sutton, R. W. Jenkins, C. M. Moore, T. A. Semelsberger, O. Staples, W. Kubic. The Use of Bioderived Molecular Building Blocks for the Simultaneous Production of Fuels and Chemicals. ACS Green Chemistry and Engineering Conference, Reston, VA, June 13-15, 2017 (Oral).
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- A.D. Sutton. “Green Gold? Supplanting Petroleum with Renewable Carbon”. Invited talk at Pennsylvania State University (October 12, 2017).
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- R.T Elander, D.K Johnson, D.S. Vardon, A. Li, A.D. Sutton, V. Dagle, M. Lilga. Catalytic upgrading of biochemically derived intermediates from lignocellulosic biomass to advanced biofuels and chemicals. American Chemical Society Spring 2018 National Conference, New Orleans, LA.
- A.D. Sutton, R. Jenkins, W. Kubic, C. Moore, T. Semelsberger, O. Staples. Simultaneously producing fuels and chemicals from bioderived molecular building blocks. American Chemical Society Spring 2018 National Conference, New Orleans, LA
- A.B. Padmaperuma and M.A. Lilga. Catalytic conversion of lignocellulosic feedstock to hydrocarbon fuel intermediates. American Chemical Society Spring 2018 National Conference, New Orleans, LA.
- D.R. Vardon, X. Huo, N.S. Cleveland, J. Stunkel, A.K. Starace, P.C. St. John, S. Kim, R.L. McCormick. Renewable Diesel Fuel via Catalytic Upgrading of Anaerobic Acids. American Chemical Society Green Chemistry Conference, Portland, OR
- J. Alegre-Requena, S. Kim, A.E. Settle, J. Stunkel, D. Robichaud, D.R. Vardon, D.K. Johnson, R. Paton. Experimental and computational studies on catalytic upgrading of biochemical intermediates from biomass. Fall 2018 American Chemical Society Meeting, Boston, MA. August 2018.
- V. Vorotnikov, T.R. Eaton, A.E. Settle, K. McKinney, E.C. Wagner, C. Yang, J.T. Miller, G.T. Beckham, D.R. Vardon. Active surface and mechanism for propionic reduction over Ru-Sn. Fall 2018 American Chemical Society Meeting, Boston, MA. August 2018.
- A. D. Sutton. “Replacing Non-Renewable Carbon with Bio-Derived Alternatives” Yale University, Invited Chemical and Environmental Engineering Seminar, October 19, 2018.
- A.D. Sutton. Catalytic Carbon Chain Extension and Selective Defunctionalization of Bioderived Building Blocks” Andrew D. Sutton, Frontiers in Biorefining, St Simons Island, GA, November 5-8 2018.
- X. Huo, N.A. Huq, J. Stunkel, N.S. Cleveland, A.K. Starace, A.E. Settle, A.M. York, R. Nelson, D.G. Brandner, L. Fouts, P.C. St. John, E.D. Christensen, J.H. Mack, C.S. McEnally, P.A. Cherry, L.D. Pfefferle, T.J. Strathmann, D.Salvachúa, S. Kim, R.L. McCormick, G.T. Beckham, D.R. Vardon. Catalytic upgrading of short chain acids to renewable diesel fuel. Frontiers in Biorefining, St. Simons Island, GA. November 2018.

Publications, Presentations, and Patents

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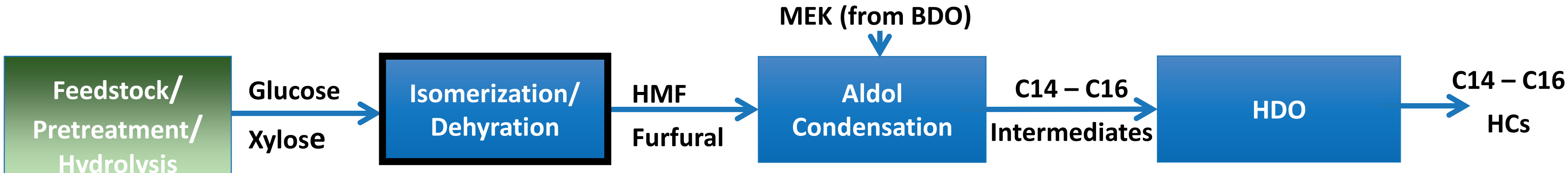
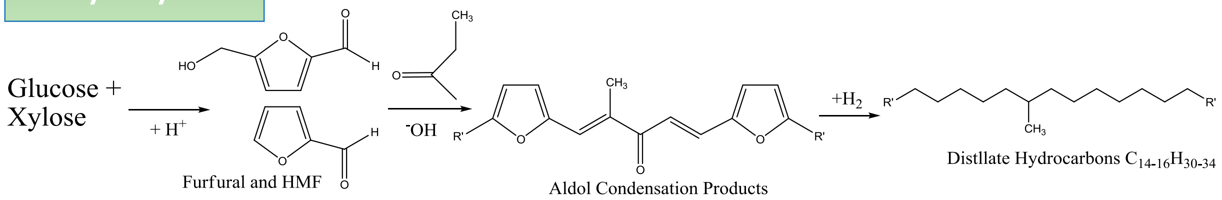
- Synthesis of Fuels and Feedstocks. A. D. Sutton, T. Brooks, R. Jenkins, C. M. Moore, O. Staples, US 9,783,477, October 10, 2017
- Solid catalysts for producing alcohols and methods of making the same. D.R. Vardon, T.R. Eaton, A.E. Settle. US patent application No. 15/828,658 filed on December 1, 2017.
- Conversion of Bioderived Acetone and/or Isopropanol to Aliphatic Hydrocarbons, A. D. Sutton, R. Jenkins, C. M. Moore, U.S. Pat. App. No. 62/327,254, 2017.
- Process for Conversion of Levulinic Acid to Ketones, V. Dagle & R.A. Dagle, US Patent 9,663,435, May 30, 2017.
- Process for Conversion of Selected Feedstock Compounds to Distillate Range Hydrocarbons, M.A. Lilga, A.B. Padmaperuma, US Patent 9,777,224, October 3, 2017
- Catalysts for Conversion of 2,3-butanediol-containing fermentation mixture to hydrocarbons, Z. Li, US 16/059,512, filed on August 9, 2018.

Upgrading Furfurals to Distillate Hydrocarbons

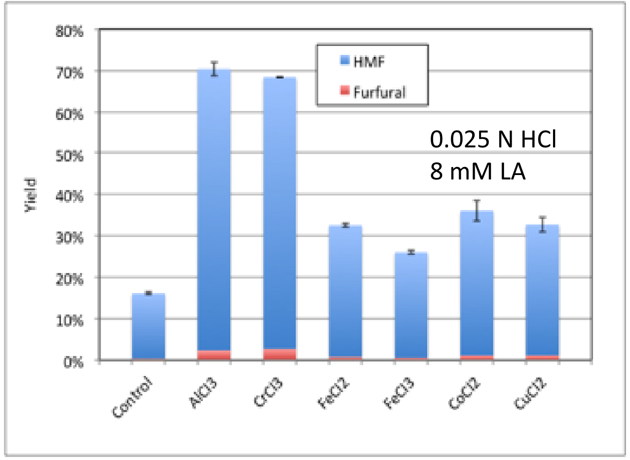
Production of high-cetane distillate via aldol condensation of furfurals followed by HDO





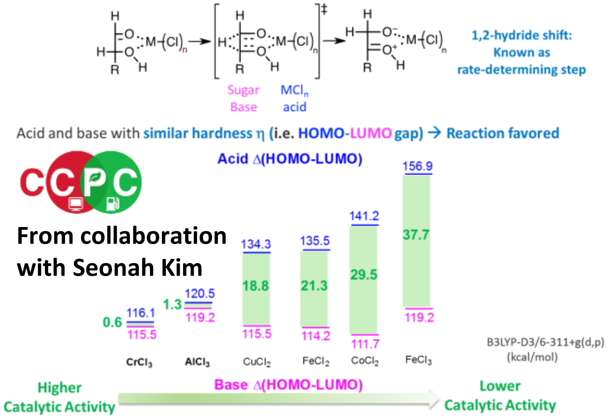
- Conversion of glucose to HMF catalyzed by Lewis acids at low HCl concentrations
- Molecular dynamics simulations show catalysis conforms to hard-soft acid-base theory
- 1,4-Dioxane co-solvent found to give much higher yields of HMF than water-immiscible solvents (shaded in figure).

Conversion of Glucose to HMF with Lewis Acids (LA)



0.025 N HCl
8 mM LA

Lewis Acid Reaction Mechanism



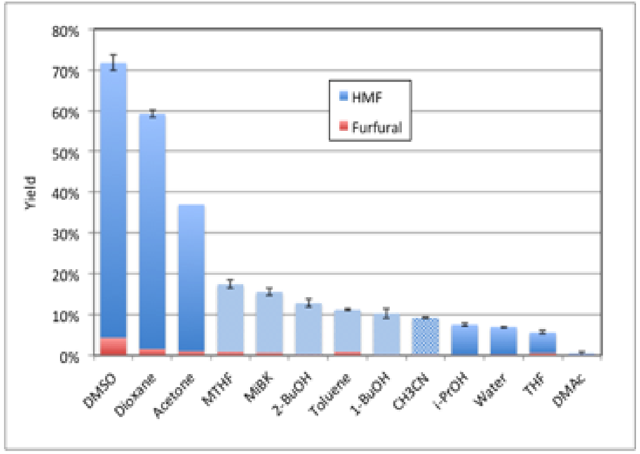
1,2-hydride shift: Known as rate-determining step

Acid and base with similar hardness η (i.e. HOMO-LUMO gap) → Reaction favored

From collaboration with Seonah Kim

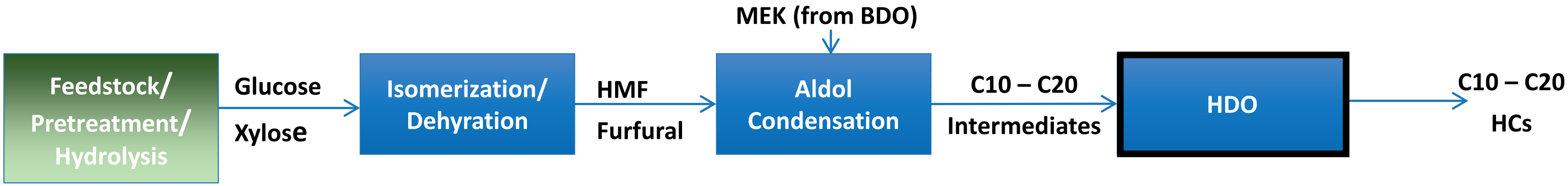
B3LYP-D3/6-311+g(d,p) (kcal/mol)

Effect of Solvent on Glucose to HMF Conversion



Upgrading Furfurals to Distillate Hydrocarbons

Production of high-cetane distillate via aldol condensation of furfurals followed by HDO



MEK (from BDO)

Feedstock/ Pretreatment/ Hydrolysis

Glucose

Xylose

Isomerization/ Dehyration

HMF

Furfural

Aldol Condensation

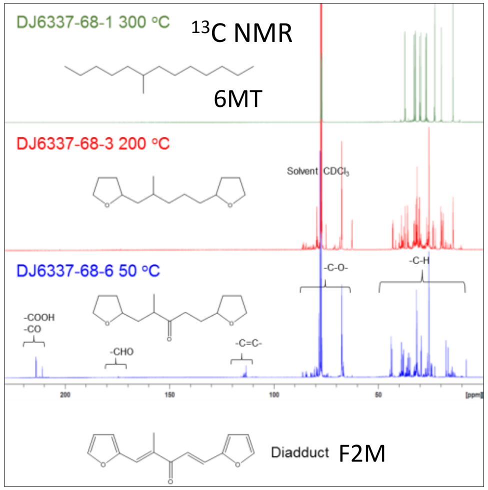
C10 – C20 Intermediates

HDO

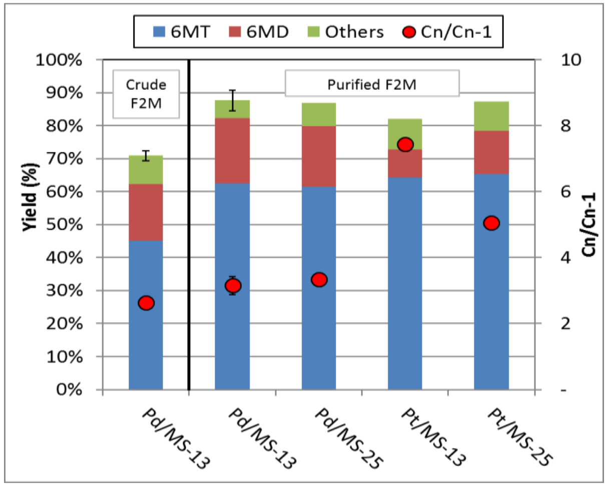
C10 – C20 HCs

- HDO of aldol condensation products give isoparaffins excellent for blending in jet or diesel.
- Catalysts with acidic silica-alumina supports (MS-13 & -25) needed to produce HCs.
- Pd and Pt catalysts have proven to be the best so far.
- Loss of C during HDO of F2M and model 1,12-dodecandiol is not explained by support acidity, but is more likely due to the nature or dispersion of metal on catalyst surface.

NMR shows HDO Mechanism

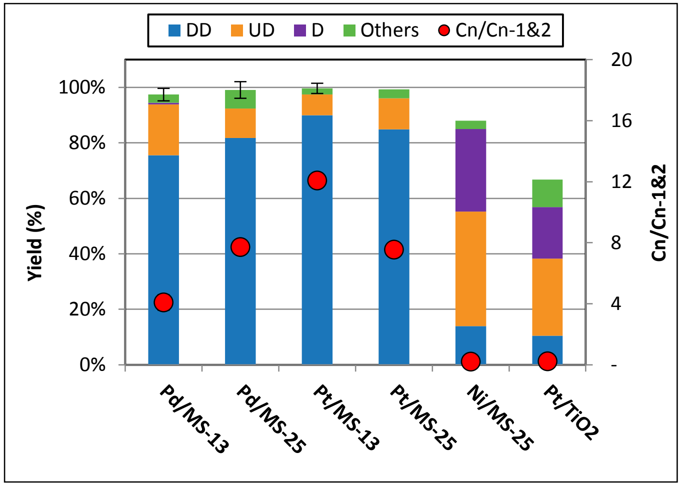


Effect of Catalyst on HC Yield from F2M



6MT = 6-methyl tridecane; 6MD= 6-methyl dodecane

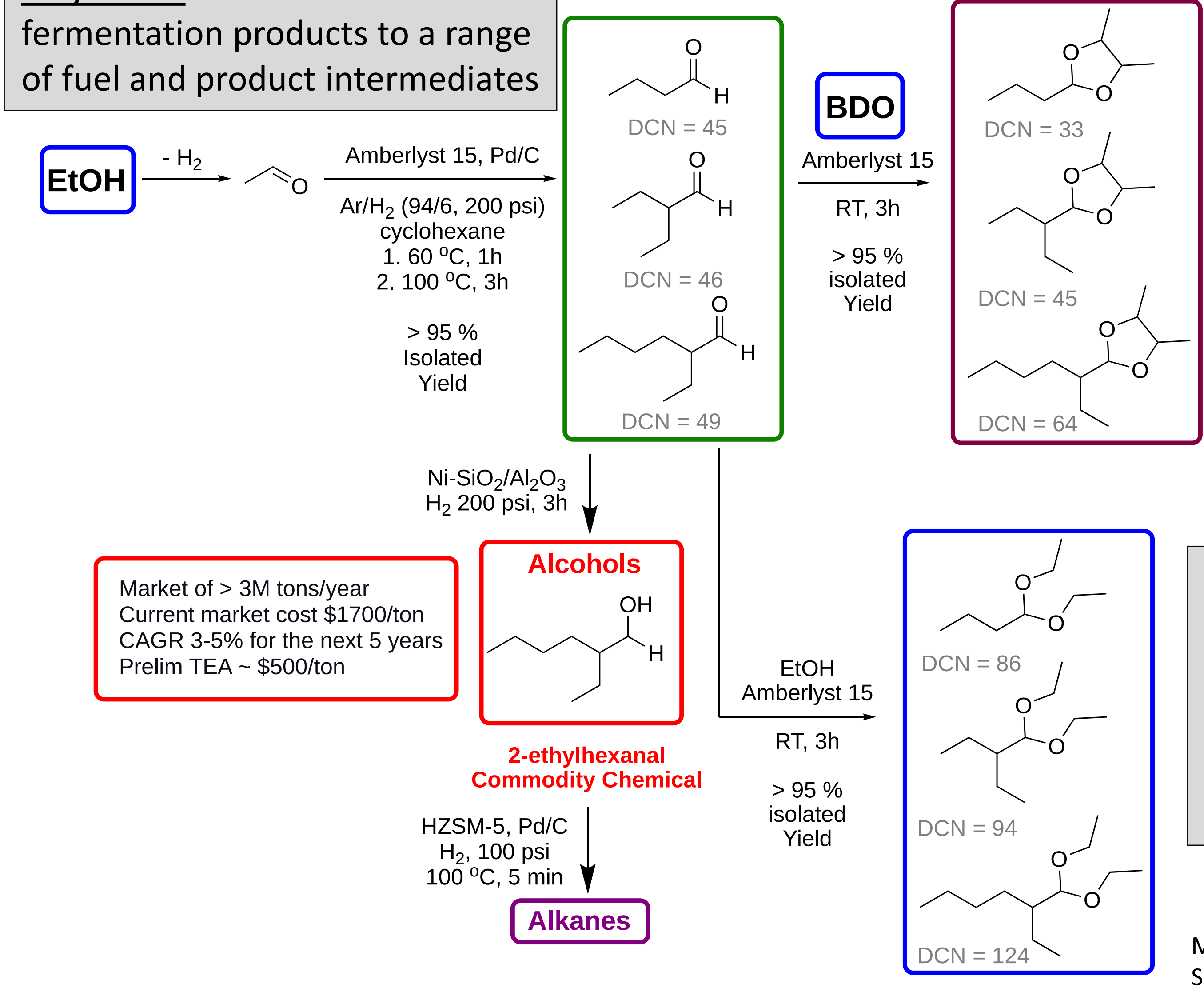
Effect of Catalyst on HC Yield from $C_{12}H_{24}(OH)_2$



DD = dodecane; UD = undecane; D = decane

Ethanol and BDO as Bio-derived Building Blocks

Objective: Common fermentation products to a range of fuel and product intermediates



EtOH

- H_2

Amberlyst 15, Pd/C

Ar/H_2 (94/6, 200 psi)
cyclohexane
1. 60 ^oC, 1h
2. 100 ^oC, 3h

> 95 %
Isolated
Yield

DCN = 45

DCN = 46

DCN = 49

BDO

Amberlyst 15

RT, 3h

> 95 %
isolated
Yield

DCN = 33

DCN = 45

DCN = 64

Ni-SiO_2/Al_2O_3
H_2 200 psi, 3h

Alcohols

Market of > 3M tons/year
Current market cost $1700/ton
CAGR 3-5% for the next 5 years
Prelim TEA ~ $500/ton

2-ethylhexanal
Commodity Chemical

HZSM-5, Pd/C
H_2, 100 psi
100 ^oC, 5 min

Alkanes

EtOH
Amberlyst 15

RT, 3h

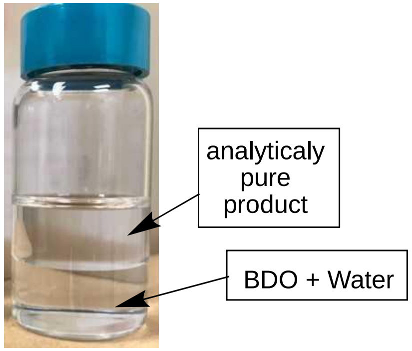
> 95 %
isolated
Yield

DCN = 86

DCN = 94

DCN = 124

Products Phase Separate



Being adapted for BDO separation and recovery from fermentation broths

Outcome:

- Tunable monomers branched and cyclic fuel intermediates
- Potential chemical co-product targets identified

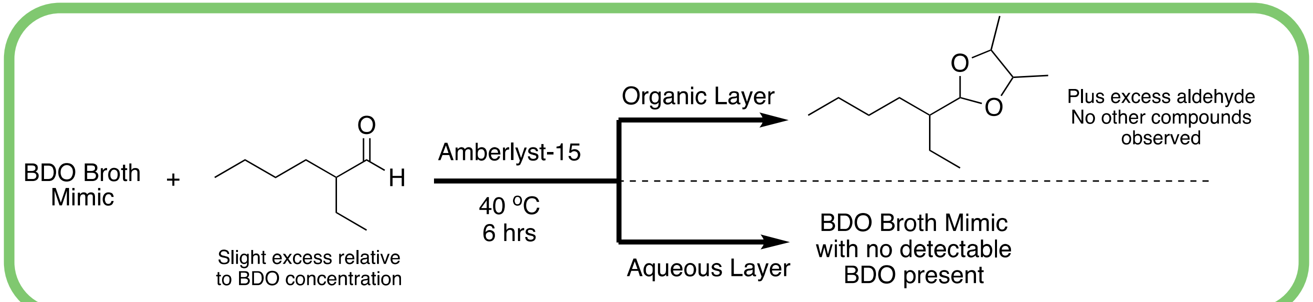
Moore *et al.*, Green Chem., 2017, *19*, 169.
Staples *et al.,* Sustainable Energy Fuels, 2018, Advance Article

LANL

BDO Separation Approach Using Dioxolanes

Objective: Isolation of BDO using phase separation approaches

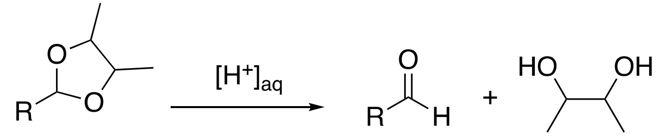
Component	Glucose	Xylose	Arabinose	Galactose	BDO	Acetoin	Glycerol	Xylitol	Lactic Acid	Acetic Acid
[g/l]	0.00	4.67	6.23	0.54	82.2	0.00	16.2	2.21	2.09	0.45



Slight excess relative to BDO concentration

Plus excess aldehyde
No other compounds observed

BDO Broth Mimic with no detectable BDO present



R = alkyl, aryl etc.

Aldehydes can be removed by distillation to isolate BDO

Butryaldehyde b.p. 74.8 °C BDO b.p.177 °C

Optimization On-Going

NREL BDO Broth received – real trials underway

Outcome:
- Several aldehydes facilitate BDO selective separation
- Recovery of BDO achievable using mild acid