



U.S. DEPARTMENT OF
ENERGY

Energy Efficiency &
Renewable Energy

Catalytic Upgrading of Biochemical Intermediates

WBS: 2.3.1.100/101/102/103

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Thermochemical Conversion

March 7th, 2017

Project Leads:

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- ORNL

Andrew Sutton - LANL

Mike Lilga, Asanga
Padmaperuma - PNNL

ChemCatBio Structure

Core Catalysis Projects

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

Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL)

Fast Pyrolysis and Upgrading
(PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Recovering and Upgrading Biogenic Carbon in Aqueous Waste Streams
(PNNL, NREL)

Zeolites and Metal Oxide Catalysts

Supported Metal Catalysts

Cross-cutting Discussion Groups

Enabling Projects

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

Catalyst Cost Model Development
(NREL, PNNL)

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

Consortium Integration

- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups

Goal Statement

Project Goal

- Develop and evaluate **several routes for catalytic upgrading of sugars/related intermediates** into hydrocarbon fuels and co-products, including:
 - Ethanol → HC fuels
 - Other fermentation intermediates → HC fuels
 - Sugars/sugar-derived intermediates → HC fuels

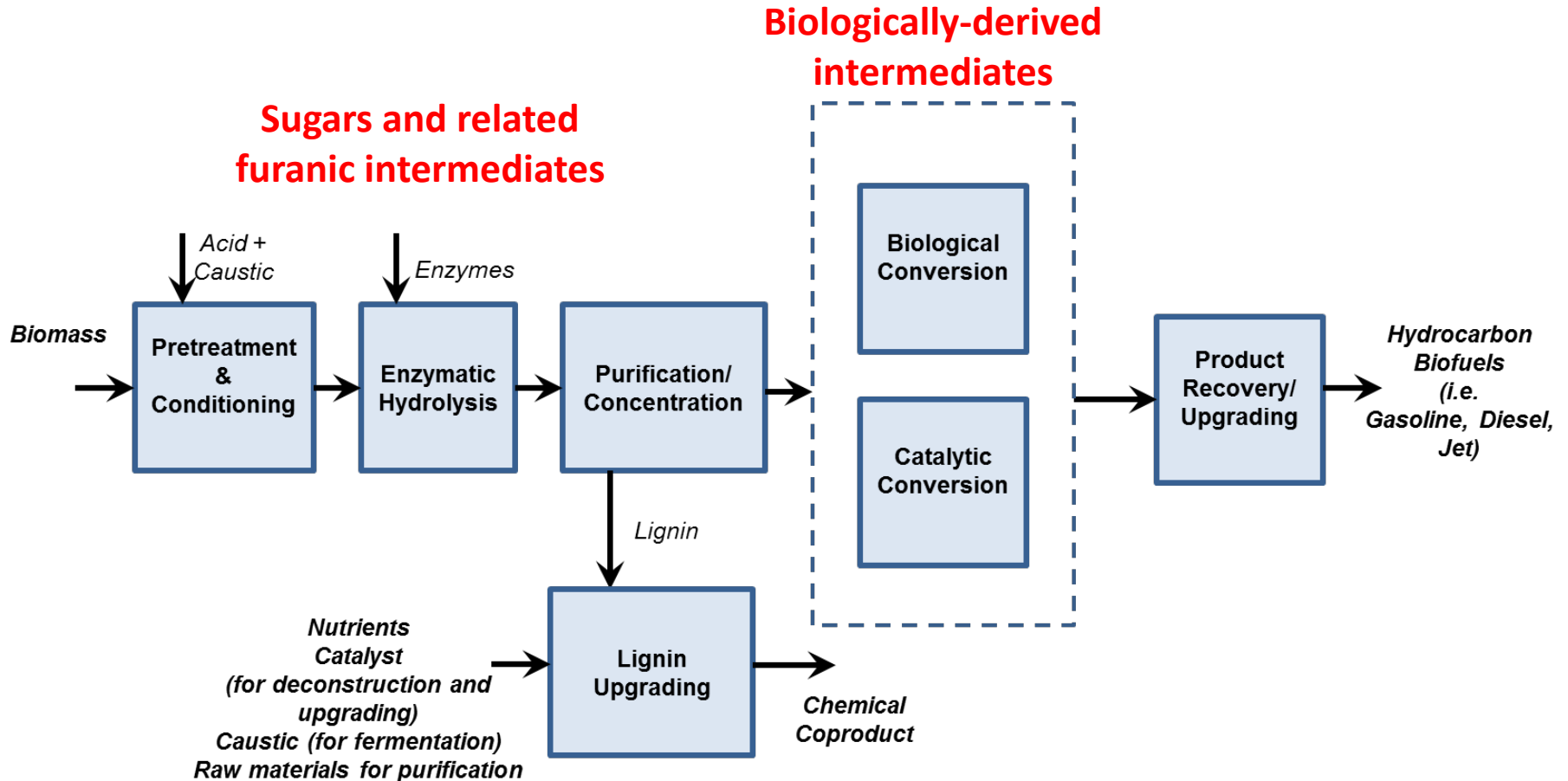
Primary Project Outcome

- 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 that can achieve a **MFSP of \$3/GGE by 2022 with >25% (GGE basis) of the fuel in the jet or diesel ranges**

Relevance

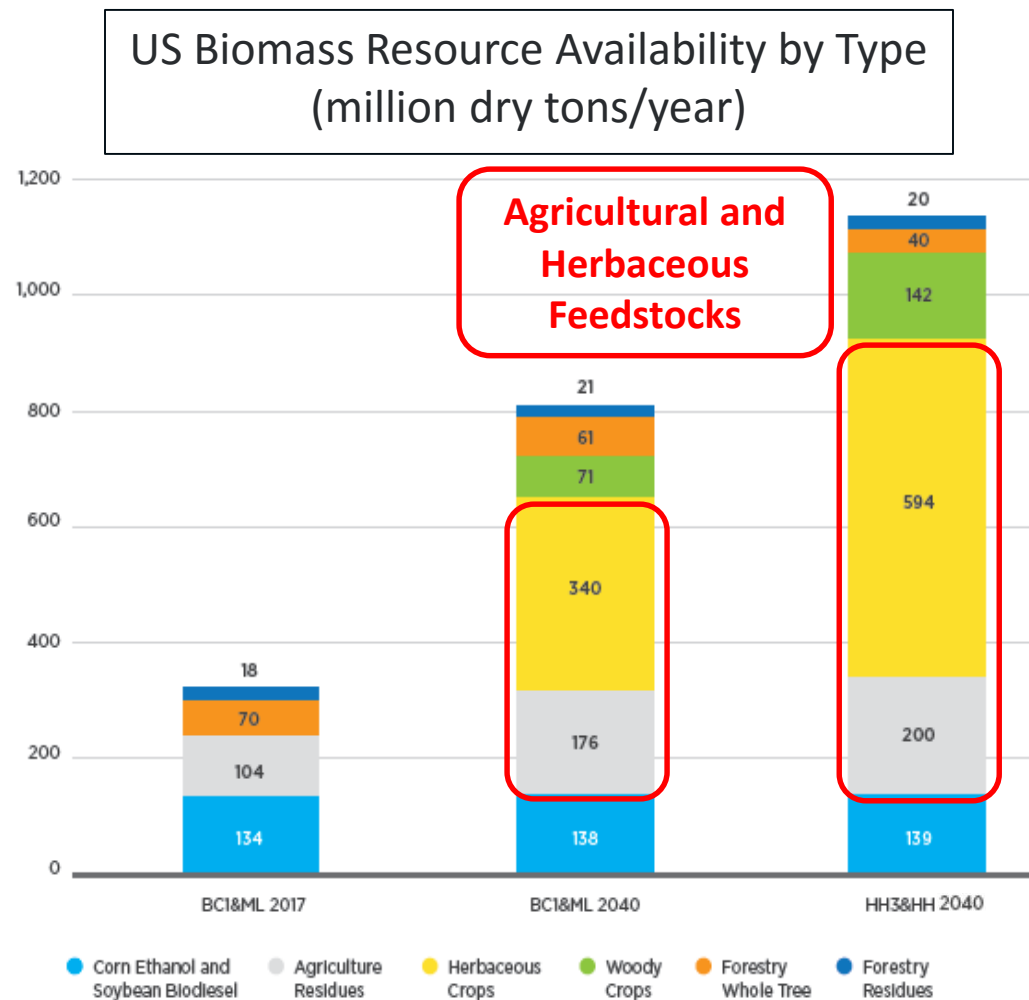
- Facilitate transition of catalytic upgrading of clean sugars/derived intermediates to **biomass sugars/derived intermediates**
 - Numerous companies currently working in this space – most current processes are on clean soluble or easily deconstructed substrates (soluble sugars, starches, etc.)
 - Project provides a **quantitative performance and economic assessment** of several catalytic upgrading approaches using biomass hydrolysis/fermentation intermediates

Process Flow for Biochemically-Derived Intermediates



Why Biochemical Conversion?

- Feedstock characteristics
 - Feedstock types best suited for biochemical conversion will be a large proportion of future feedstock base
- “Clean” streams from mild deconstruction (chemical/enzymatic hydrolysis)
- Intermediate-molecule **specificity**
 - Biological intermediates can be single molecule or a small number of molecules
 - Using different biochemical routes, can generate a suite of fuel and blendstock types, oxygenates, higher-value octane enhancers, etc.



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

- Start: 10/1/2016 (as ChemCatBio collaboration)
- End: 9/30/2019
- Percent Complete: 17%

Budget

	FY15 Costs	FY16 Costs	Total Planned Funding (FY17-Project End Date)
DOE Funded	\$2.6M	\$2.3M	\$6.6M

*FY17 operating budget is \$2.0M

Barriers Addressed & Actions

- CT-H. Efficient Catalytic Upgrading of Sugars/Intermediates
 - Evaluating multiple routes using common feed-streams, systems, and methodologies
- CT-G. Efficient Intermediate Clean-up and Conditioning
 - Identifying feedstock and deconstruction inhibitor effects and mitigation strategies
- CT-J. Process Integration
 - Biochemical deconstruction and biological intermediates with catalytic upgrading

Partners

- **National Labs (FY17 Funding)**
 - NREL: 55%
 - ORNL: 10%
 - LANL: 18%
 - PNNL: 22%
- **Other Collaborations**
 - Ongoing/future collaborations within ChemCatBio

1 – Project Overview

Context and History

- Several independent projects previously developed catalytic upgrading of Biochemical Conversion process intermediates:

ORNL	Direct Catalytic Upgrading of Current Dilute Alcohol Fermentation Streams to Hydrocarbons for Fungible Fuels
NREL	Catalytic Upgrading of Sugars
PNNL	New Catalytic Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels - Levulinic Acid
LANL	Economical Catalytic Routes to Fuels and Chemicals Utilizing Hydrolysates & Fully Bio-Derived Inputs

- A collaborative project began in FY17 within ChemCatBio – focused on biochemically-derived intermediates
 - Catalytic Upgrading of Biochemical Intermediates

Broader 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**
 - Utilize common process intermediates, catalyst/reactor systems, analytical and fuel characterization, TEA, etc.

Utilizing Multiple National Lab Capabilities



Pilot Scale Hydrolysate Production



Batch Microwave Reaction System



Batch Autoclave Reaction System



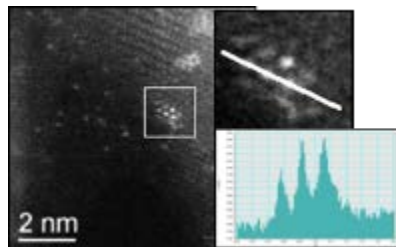
Trickle-Bed Reaction System



Packed-Bed Flow Reactor



Zeolite Synthesis



Atom Scale Characterization



Catalyst Testing: Low and High Pressure



High-Pressure Batch Reactors



High-Pressure Continuous Flow Reactors



High Throughput Catalyst Testing



Multi-batch and 1.4 mL Fixed-Bed Flow Reactors



40 mL



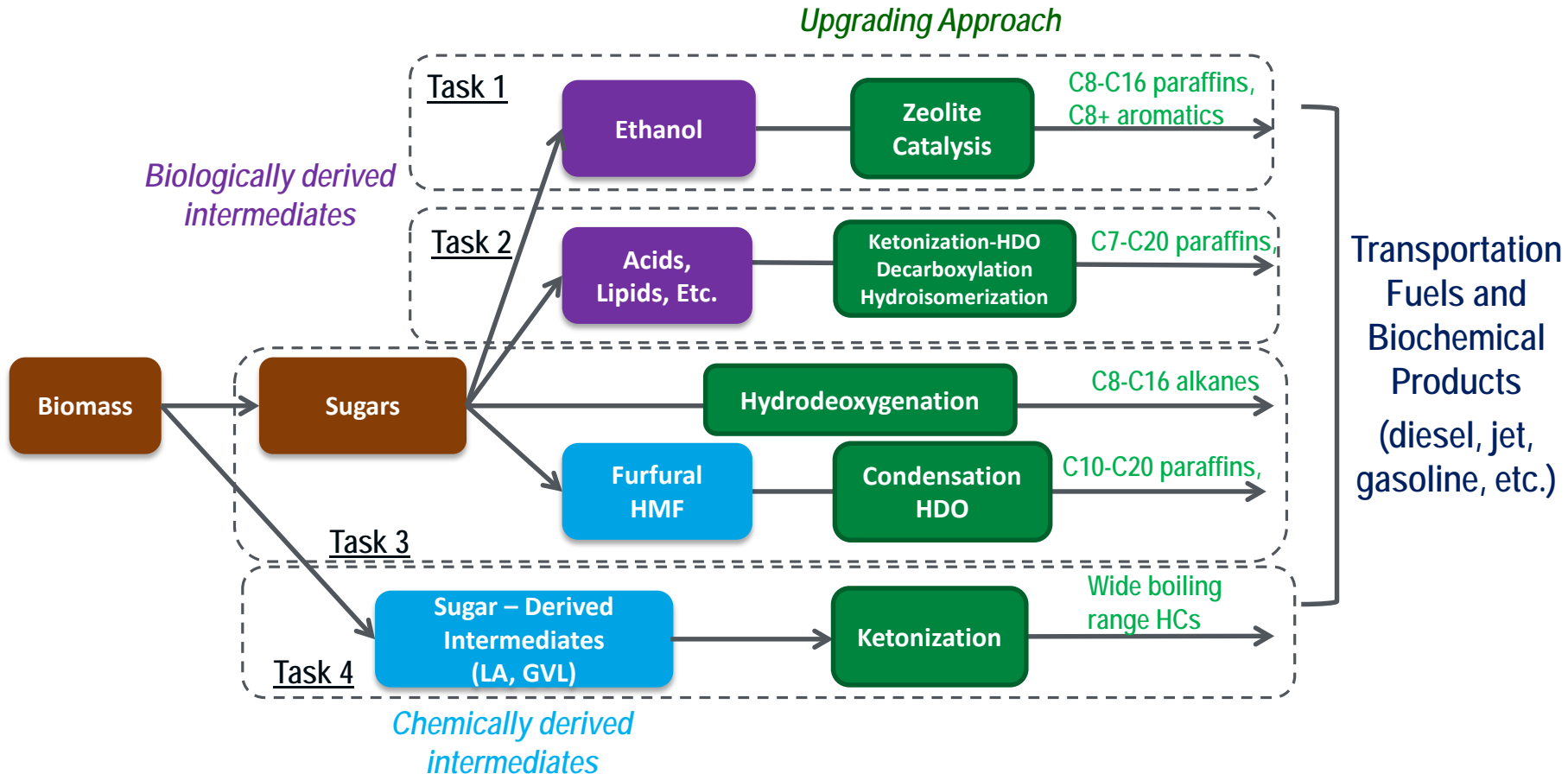
20 liter

Catalytic Upgrading Systems



2 – Approach (Management)

Task Structure



Task 5 – Project coordination; hydrolysate/fermentation broth supply; TEA

2 – Approach (Management)

- Coordinated R&D activities across project tasks
 - Common hydrolysates and fermentation broths
 - Collaborative and shared use of upgrading reactor systems, analytical techniques and capabilities, and fuel assessment capabilities
- TEA incorporated into key milestones and go/no go decisions
 - Q2 FY17 milestone in 2.1.0.100 (NREL Biochemical Platform Analysis) on biochemical catalytic pathways alternatives
 - FY18 go/no go: Initial comparison of routes and potential re-scope
 - FY18 end-of-year milestone
 - FY19 end-of-project milestone
- Reporting status and progress via collaborative work-products
 - Numerous joint milestones and publications (expected)
- Cross-lab communications and coordination
 - Regular teleconferences
 - Periodic in-person meetings

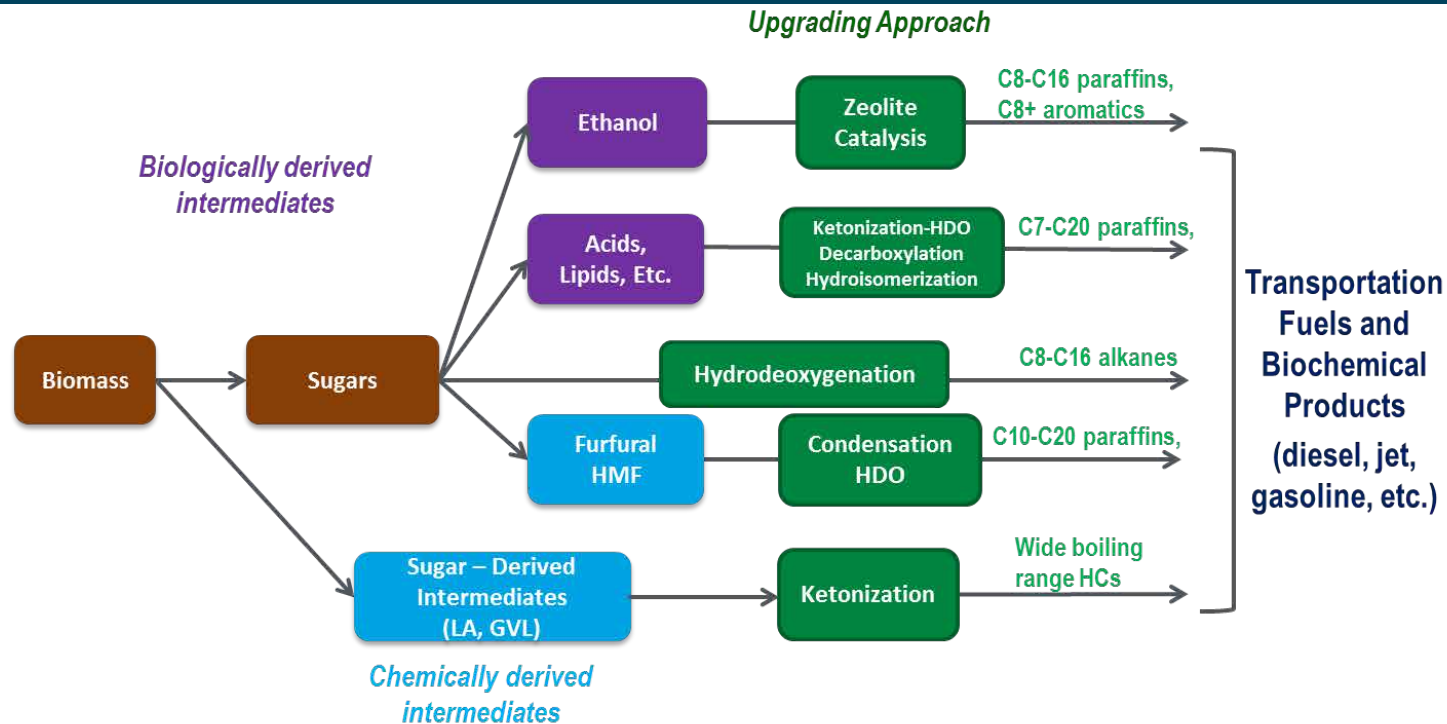
2 – Approach (Technical)

- Multiple catalytic upgrading routes investigated and evaluated in a coordinated manner using common materials, analytical techniques, reactor systems, fuel characterization methods, and TEA tools
- Key Challenges:
 - The **integration of biochemically-derived feed-streams with catalytic upgrading** to hydrocarbon fuels is not well-characterized, with regard to:
 - **Impurities** from relevant feedstocks, deconstruction processes, fermentation media, etc.
 - **Specifications** for biochemically-derived feed-streams
 - Impacts on catalyst cost, formulation, and durability
- Critical Success Factors:
 - Develop and identify catalytic upgrading to HC fuel routes that have commercial relevance and interest
 - Quantify impurity impacts from biochemical deconstruction/upgrading on catalytic upgrading routes (durability, efficiency, selectivity)
 - Define specifications of deconstruction/fermentation streams for catalytic upgrading, including identification of separations/clean-up needs

2 – Approach (Technical)

- Go/No-Go Decision Point (March, 2018)
 - Generation of upgrading performance data on hydrolysates/fermentation products from each route (earlier milestones)
 - Preliminary assessment of fuel properties from each route – as product slate from a single route or in combination with products from other route(s)
 - Initial TEA projections of each upgrading route
 - Re-scoping of project to focus upon route(s) best suited to achieve \$3/gge by 2022 (with lignin co-product valorization)
- End-of Project Milestone (September, 2019)
 - Develop biochemical catalytic upgrading State of Technology with a pathway and targets to achieve a modeled 2022 Minimum Selling Fuel Price of \$3/GGE (2014 \$) with value-added lignin co-products.
 - >25% (GGE basis) in the jet or diesel ranges to show broad fuel-market applicability

3 – Technical Accomplishments/Progress/Results

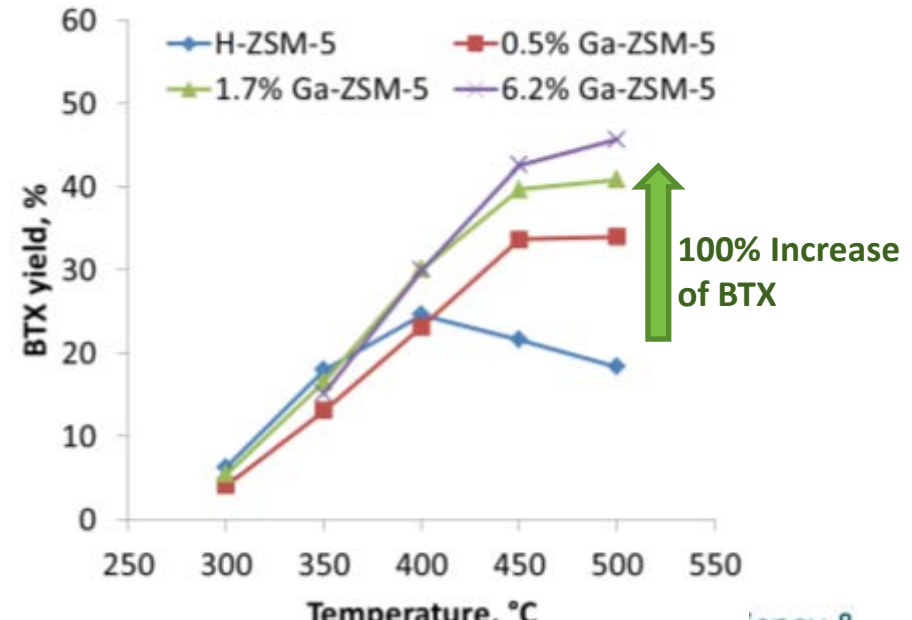
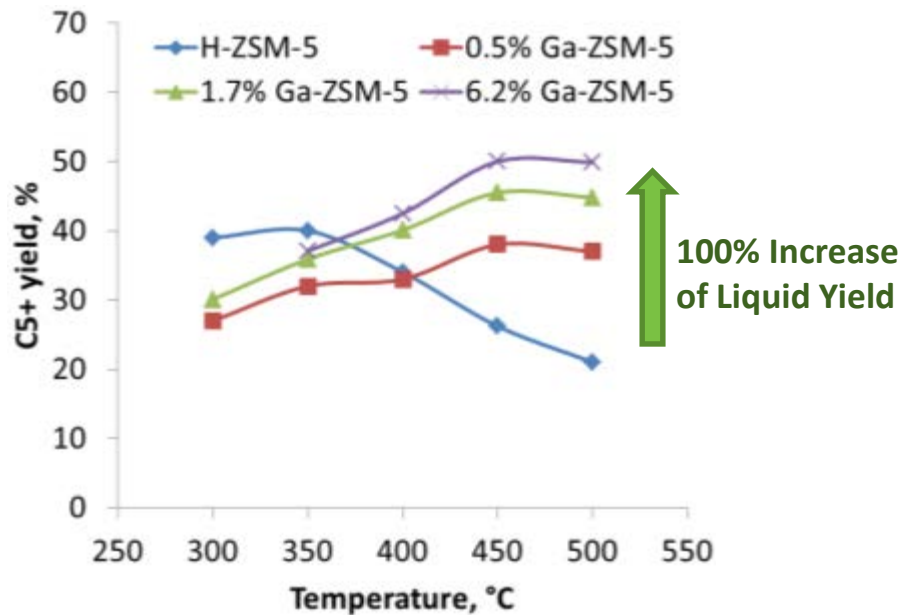


- **Upgrading of biological intermediates (alcohols, organic acids)**
 - Ketonization/HDO to HC fuels
- Sugars to furfural/methylfuran
 - Hydrogenation/Trimerization/HDO to HC fuels
- Biomass/sugars to levulinic acid/ γ -Valerolactone
 - Oligomerization to HC fuels

Technical Accomplishments - Ethanol Upgrading

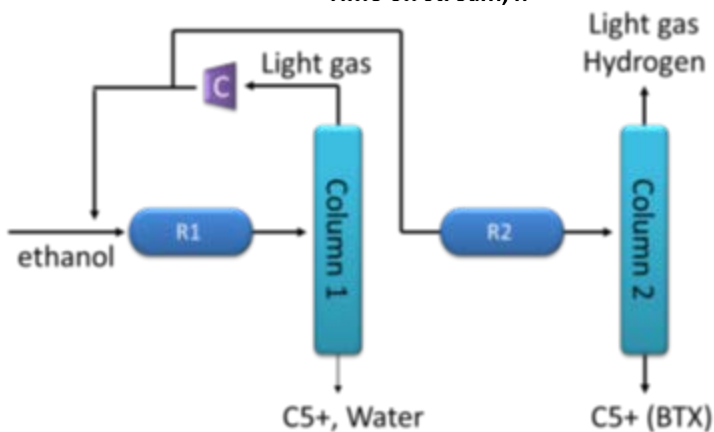
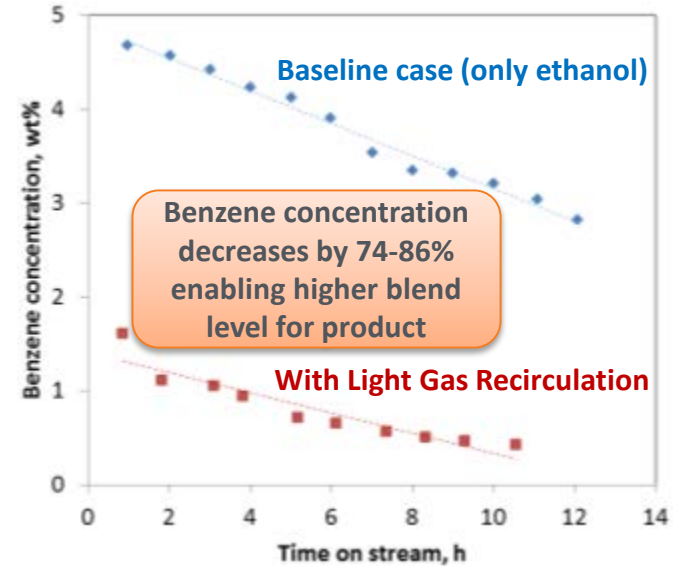
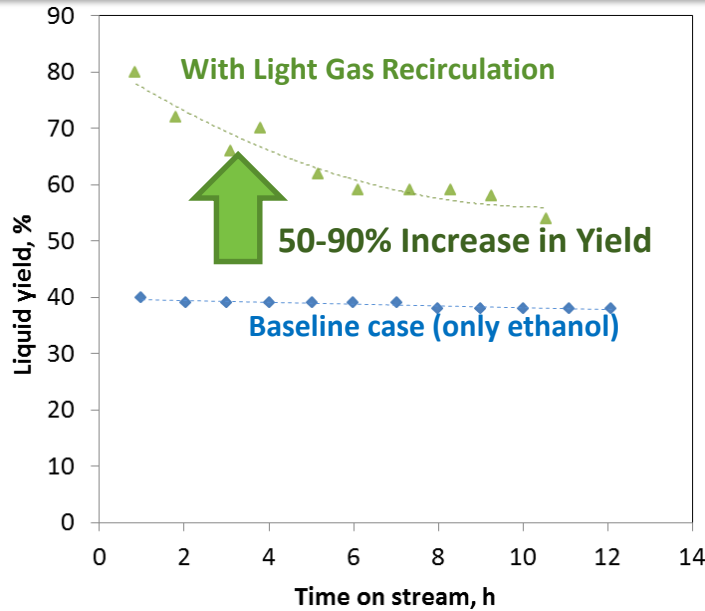
- **Goal:** Increase valuable co-products; increase liquid fuel yield and control benzene to improve fuel quality; facilitate technology transfer to Vertimass for accelerated commercialization.
- **Approach and efforts:**
 - Catalyst development: Ga-ZSM-5
 - Process: light gas recirculation; process integration; optimize operation conditions

Ga-ZSM-5 dramatically increased liquid hydrocarbon yield and BTX. Ethanol upgrading can be a swing operation for producing direct drop-in hydrocarbon fuel and valuable chemicals.



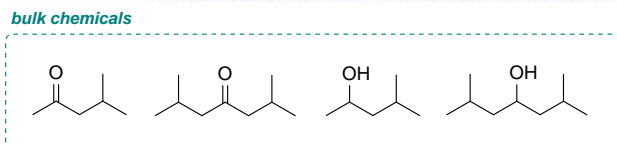
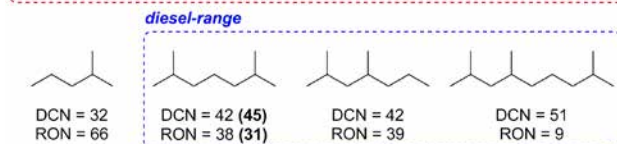
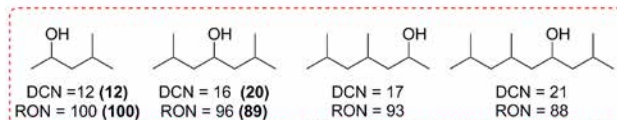
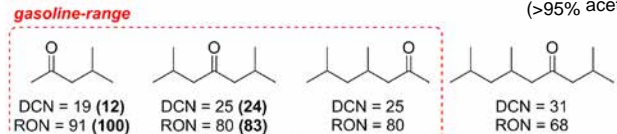
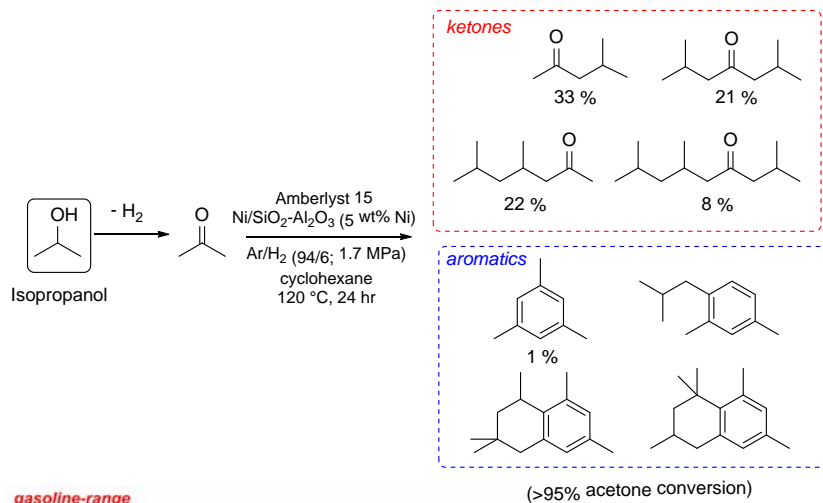
Technical Accomplishments – Ethanol Upgrading

Light gas recirculation (LGR) increases liquid yield by 50-90%, decreases benzene concentration by 74-86%, enabling higher blending level (increase from 18-43%) into gasoline.

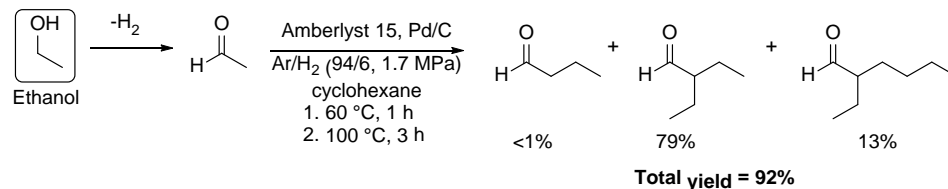


- Liquid HCs increases primarily due to olefin oligomerization; Catalyst deactivation due to coking, regenerable; on-going effort to improve the stability under LGR
- **Integrated process:**
- Remaining light gas (paraffins) on Ga-ZSM-5 selectively to BTX (97% selectivity)
- H₂ produced as co-product, can be used to further optimize fuel composition

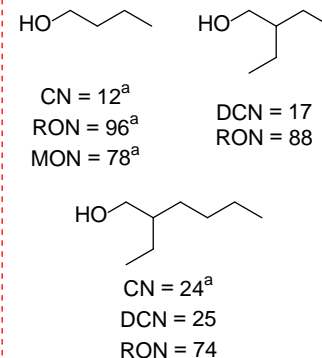
Isopropanol/Acetone



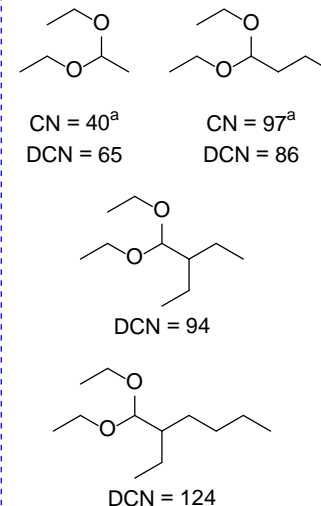
Ethanol



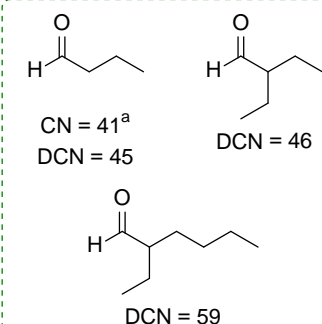
Alcohols



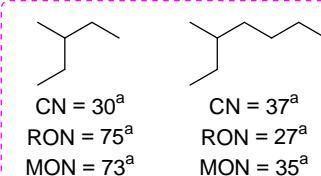
Acetals



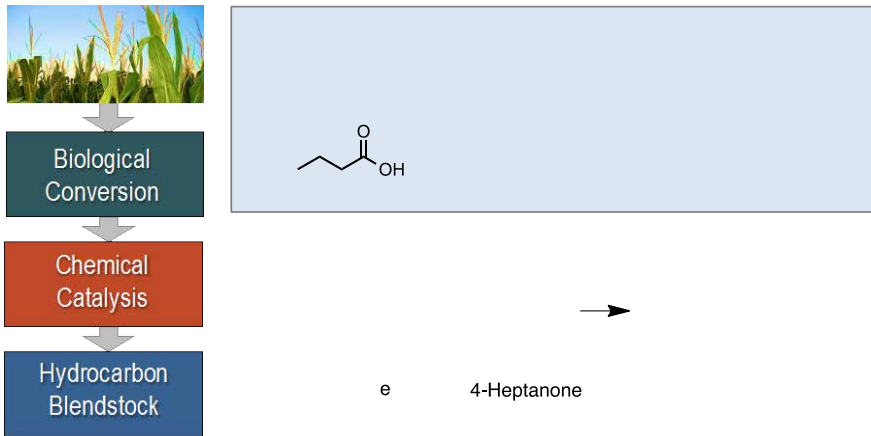
Aldehydes



Alkanes



A wide range of fuel and chemical products can be produced by coupling of biologically-derived intermediates

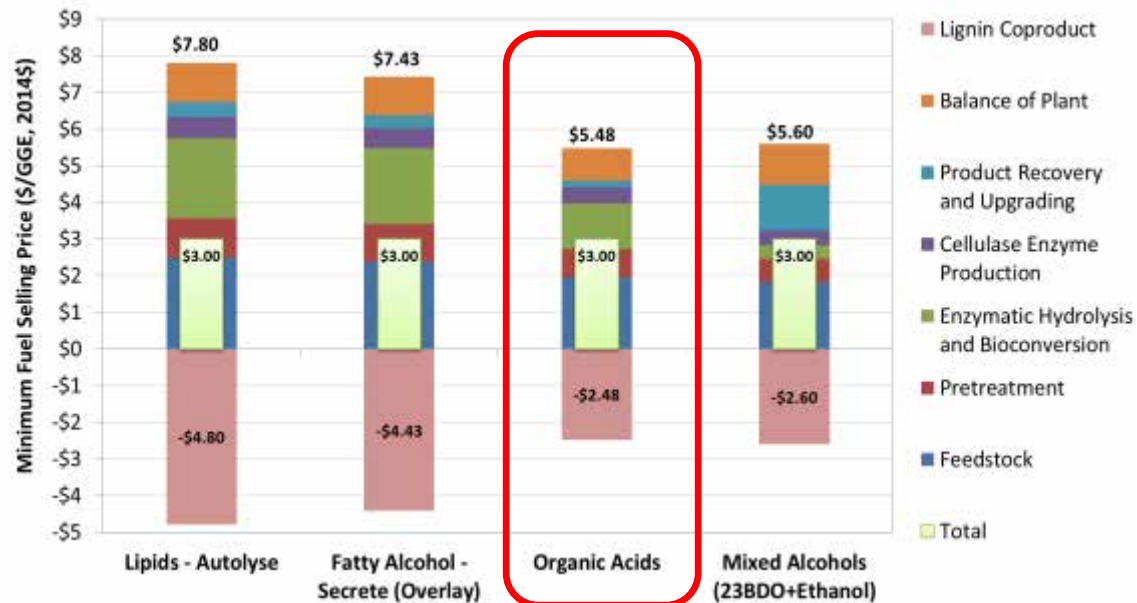


Biomass-to-Fuel Pathway Summary

- **Hybrid Approach:** Mixed sugars anaerobically converted to short chain monocarboxylic acids, followed by catalytic ketonization and HDO to form hydrocarbon blendstock
- **Knowledge Gap:** Mixed acid ketonization poorly studied with model compounds; lack of information regarding bio-derived impurities and target fuel properties

Preliminary TEA for FY16

- **FY16 Q2 NREL TEA Milestone:** Compare preliminary TEA for anaerobic and aerobic biochemical pathways to fuels
- **Targets:** TEA model assumes ketonization + HDO converts 89% of hexanoic acid carbon to fuel blendstock carbon (99% of theoretical)
- **Knowledge Gap:** Experimental data needed to assess mixed acid streams and biobased feeds



FY16 Goals

- Set up continuous reactor for upgrading model and “real” anaerobic acids to hydrocarbon blendstock
- **Q3 Milestone:** Establish baseline performance for the catalytic ketonization and HDO of model anaerobic acids. Target ketonization yields >90% and deoxygenation yields to hydrocarbons >50%.

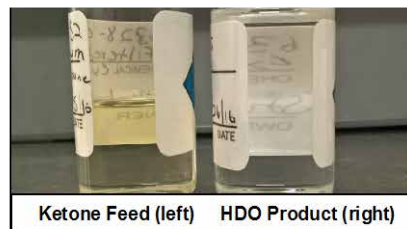
FY16 Findings

- Acid ketonization: Demonstrated near quantitative conversion of C6 acids to mixed organics with ZrO_2
Achieved KET 96% mass yield vs. Milestone 90%
- Mixed organic HDO: Demonstrated quantitative HDO of mixed organics with Pt- Al_2O_3
Achieved HDO 94% mass yield vs. Milestone 50%
- Overall Acid-to-Fuel Conversion: Demonstrated linked KET+HDO of C6 acids to hydrocarbon
Achieved overall 80% C-yield - 2022 target 89%

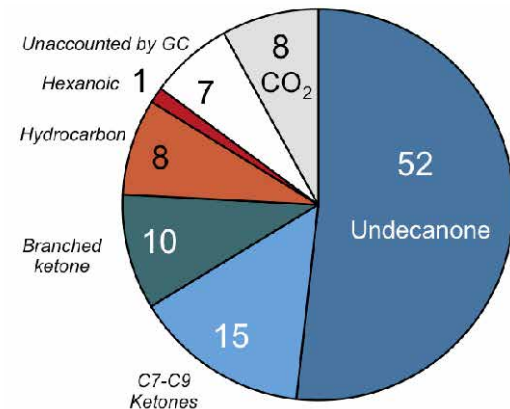
Continuous Packed Bed Rx



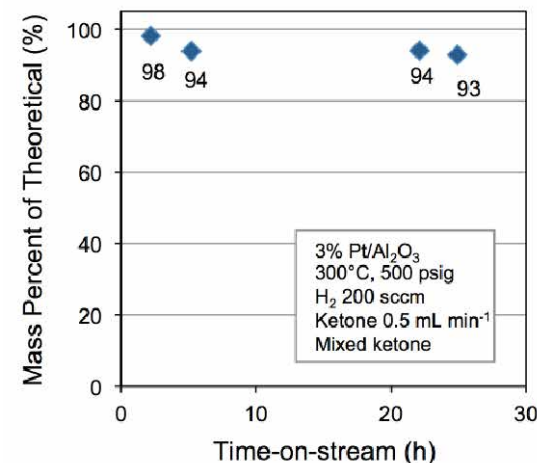
KETONE & HDO Products



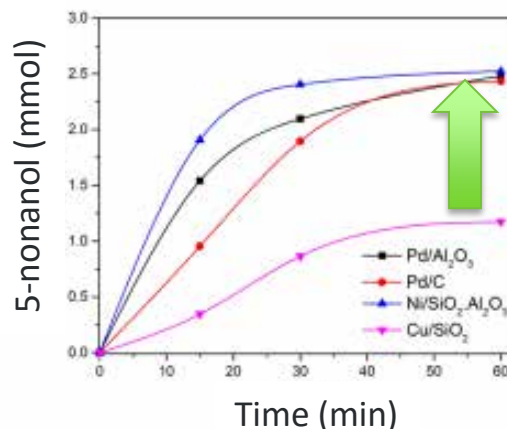
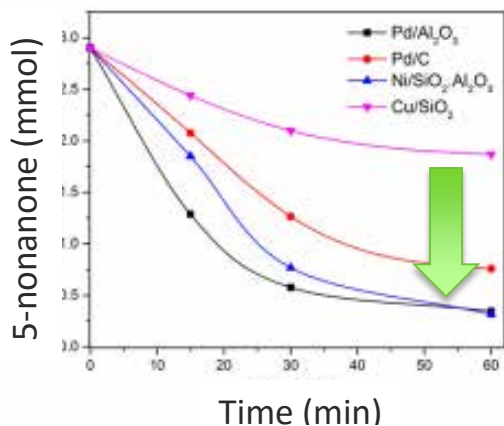
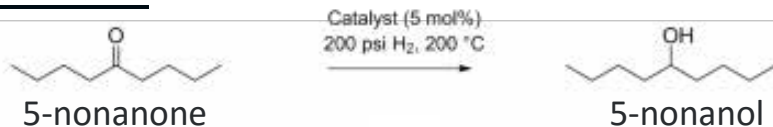
C6 KET Carbon Balance by GC-FID/MS



HDO Mixed Ketone Mass Balance



Batch Reactions



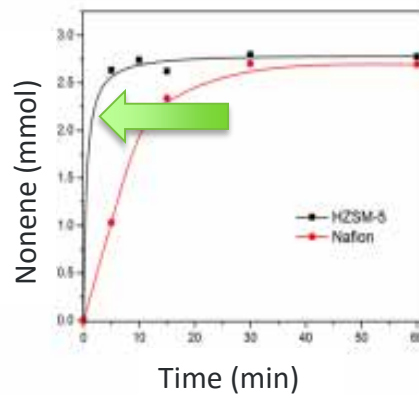
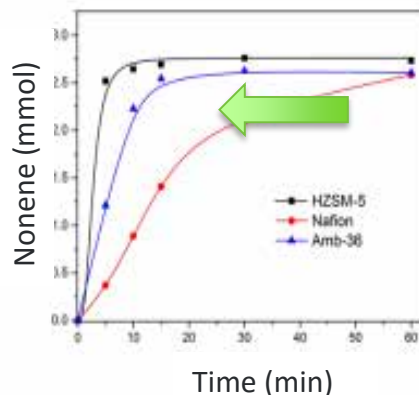
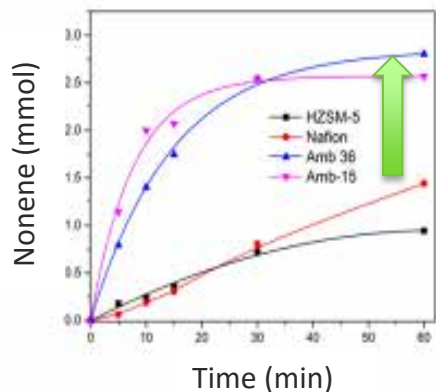
- 5-nonanone: model compound for furan-derived polyketones
- Pd/C, Pd/Al₂O₃ and Ni/SiO₂.Al₂O₃: **≥80% conversion, ≤1 hour**
- Nickel more abundant/cheaper



120 °C

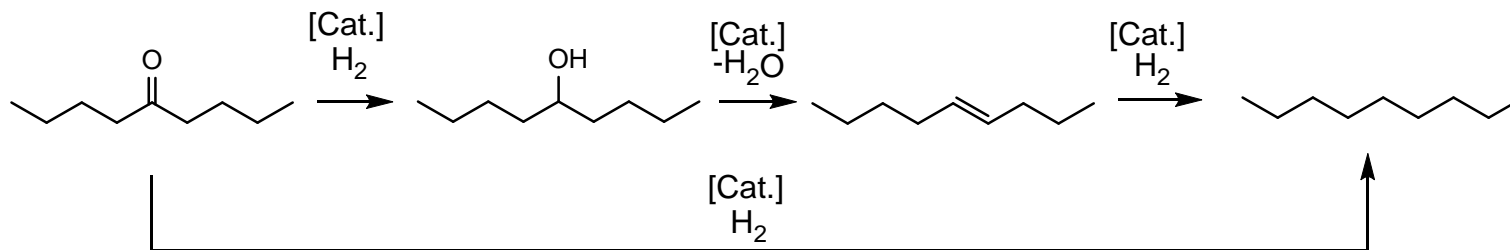
150 °C

190 °C

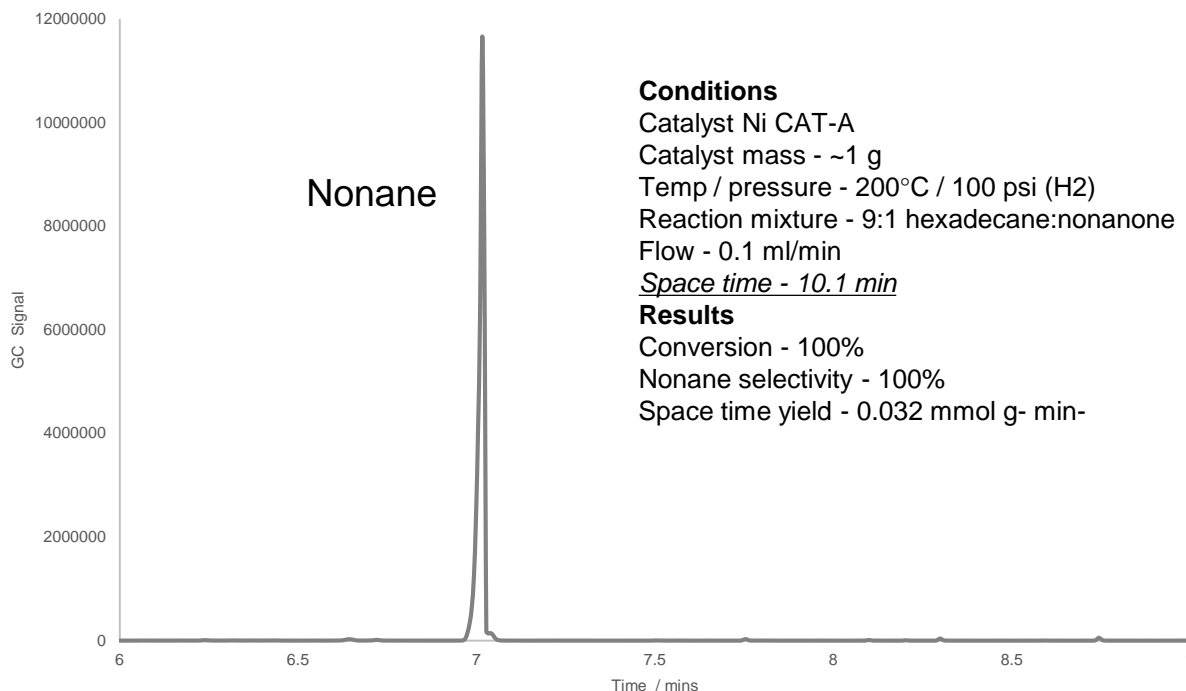


- Solid acid catalysts: Amberlysts, Al₂O₃, ZrO₂, Nafion, Zeolites
- Amberlysts show highest activity at 120 °C
- Zeolite show fastest rate (150 °C and 190 °C), **complete conversion >10 mins**
- Optimized conditions: **near-complete conversion/selectivity**

Continuous Flow Reactions



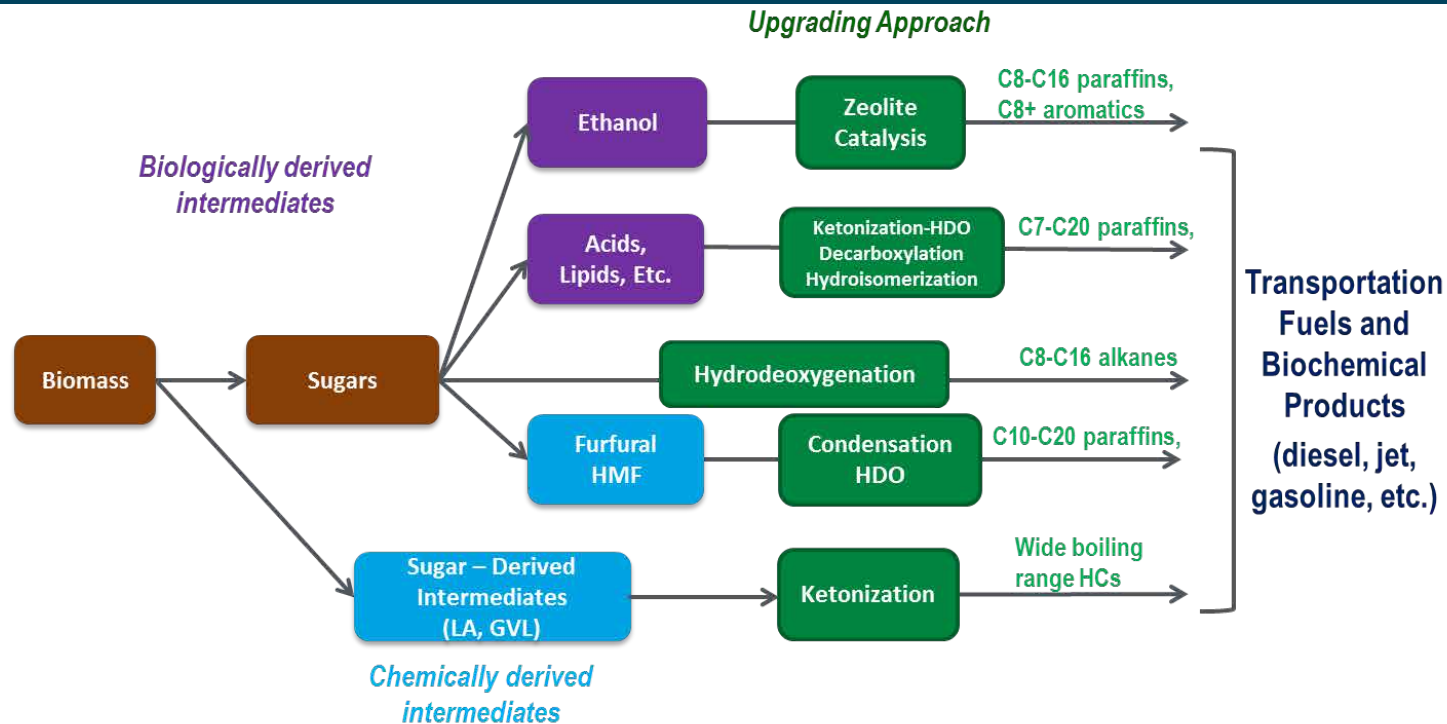
TIC BMR 9 - Space time 10.1 min



- One reactor conversion
- No additional catalyst required
- 10 min space time
- Trying to increase space time yield
- Increasing time on stream
- Applying to other molecules

- **No Acetic acid**
- **No La(OTf)₃**
- **Massive improvement vs. original batch time of 14 hours!**

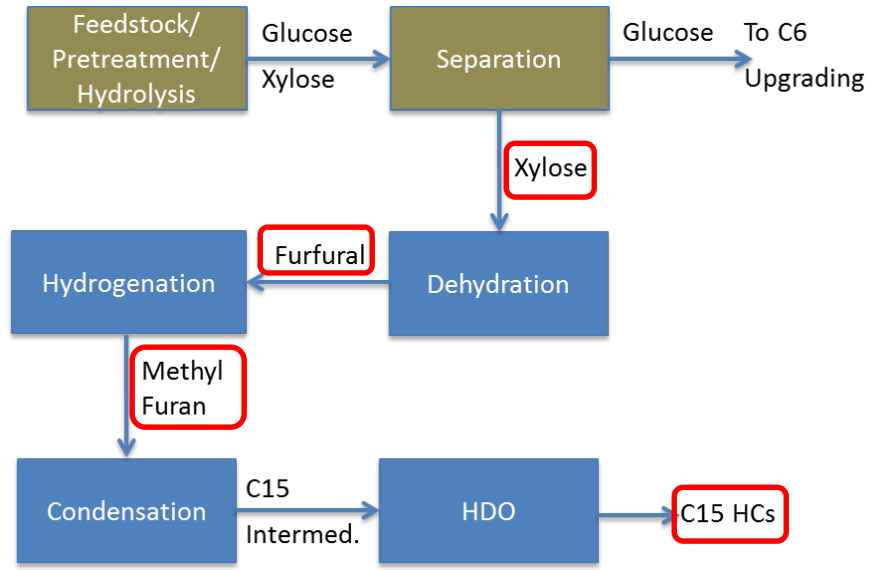
3 – Technical Accomplishments/Progress/Results



- Upgrading of biological intermediates (alcohols, organic acids)
 - Ketonization/HDO to HC fuels
- Sugars to furfural/methylfuran
 - Hydrogenation/Trimerization/HDO to HC fuels
- Biomass/sugars to levulinic acid/ γ -Valerolactone
 - Oligomerization to HC fuels

FY15 milestone: Conduct **initial TEA assessment** for catalytic conversion of carbohydrate intermediates to fuels

- Report describes assumptions, design, and results of a feasibility-level TEA of the pentoses to HC process via furfural production.
- Compared to 3 other NREL designs.
- Results compared favorably with more mature designs for sugars to HC or to succinic acid.



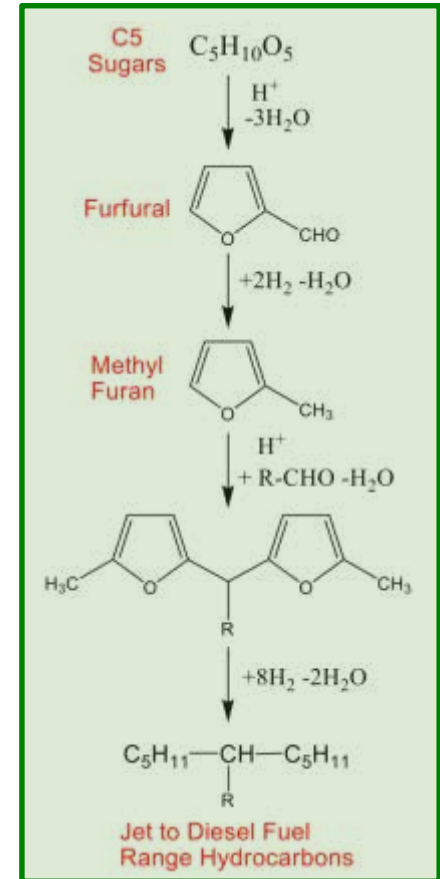
	FY15 Furfural	FY17 Target (Split C5-C6)	Catalytic Des. Rep.	Biological Des. Rep.
MSFP \$/GGE	\$6.22	\$5.03	\$4.05	\$5.10
Yield GGE/dry US ton of feedstock	49	22	78	45
Carbon Retention Efficiencies				
From Hydrolysate (Fuel C/Sugar C)	54%	43%	86%*	50%
From Biomass (Fuel C / Biomass C)	28%	13%	45%	26%
Succinic Acid C /Biomass C		12%		

* Does not include C contribution from natural gas from external SMR hydrogen production, i.e., (Fuel C / Biomass + Natural Gas C)

Demonstrated that at least one of 3 investigated furfural-upgrading routes provides **≥60% overall hydrocarbon yield**

- Furfural yields increased to ~80% from pentoses in corn stover hydrolyzates at up to 11% pentose conc. using biphasic system
- Yields from literature on hydrogenation of furfural to methyl furan (MF) >95% using Cu containing catalysts and 1 bar H₂
- Achieved selective production of MF trimer in high yield (91%) without higher oligomers using macroporous acidic resins. Trimer used without purification in HDO to branched HC.
- Extensive testing identified Pt and Pd on SiO₂/Al₂O₃ as the best catalysts for HDO of MF trimer into mostly C15 paraffins. Fuel properties Cetane 74, BPt 255 °C, Cloud Pt <-80 °C, O <0.2%
- **Passed FY16 Go/No-Go.** MF trimer route had highest overall yield (63%).

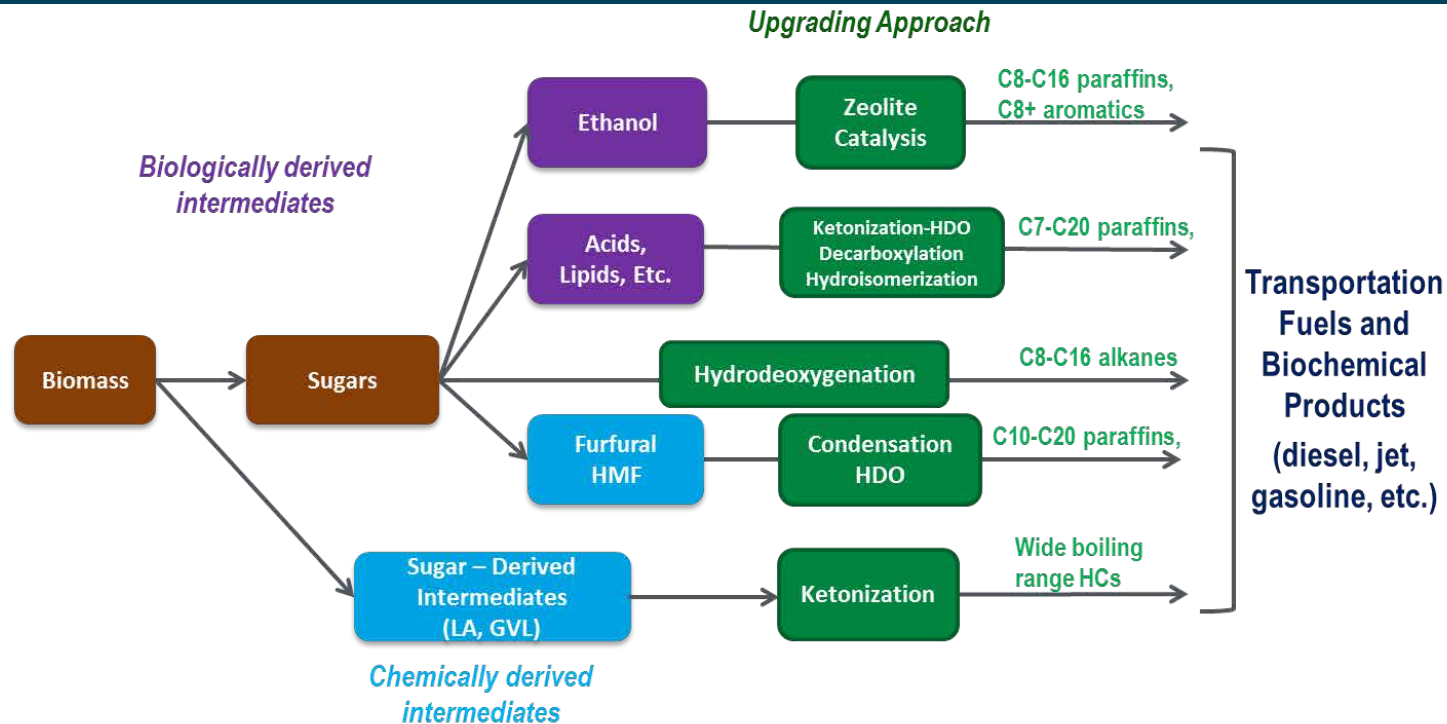
	MF Trimer 2014	MF Trimer 2016
Pentose to furfural	75%	78%
Furfural to methyl furan	95%	95%
Methyl furan to trimer	83%	91%
HDO of trimer to hydrocarbons	93%	93%
Overall Yield	55%	63%



C15 HC product from MF trimer



3 – Technical Accomplishments/Progress/Results

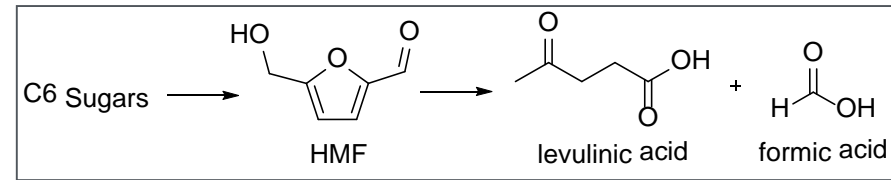


- Upgrading of biological intermediates (alcohols, organic acids)
 - Ketonization/HDO to HC fuels
- Sugars to furfural/methylfuran
 - Hydrogenation/Trimerization/HDO to HC fuels
- Biomass/sugars to levulinic acid/ γ -Valerolactone
 - Oligomerization to HC fuels

Technical Accomplishments – Levulinic Acid/ γ -Valerolactone

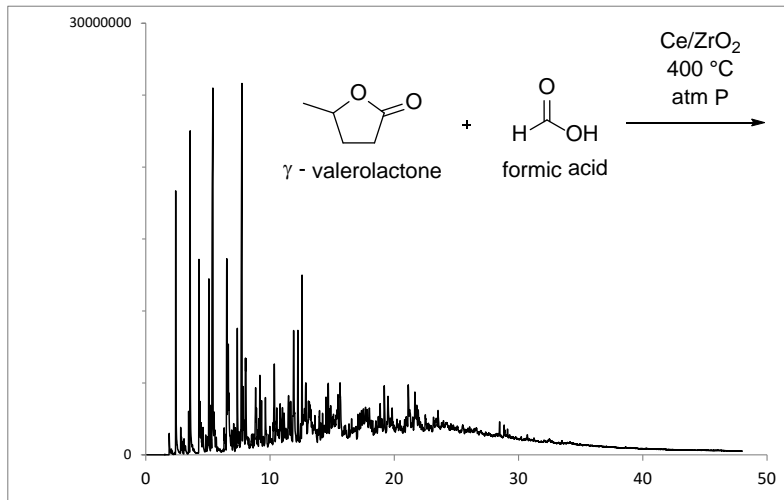
Background: C5 and C6 sugars can be converted to levulinic acid (LA) and γ -valerolactone (GVL)

- C6 sugars dehydrate to one equivalent each of LA and formic acid (FA).
- LA is easily converted to GVL

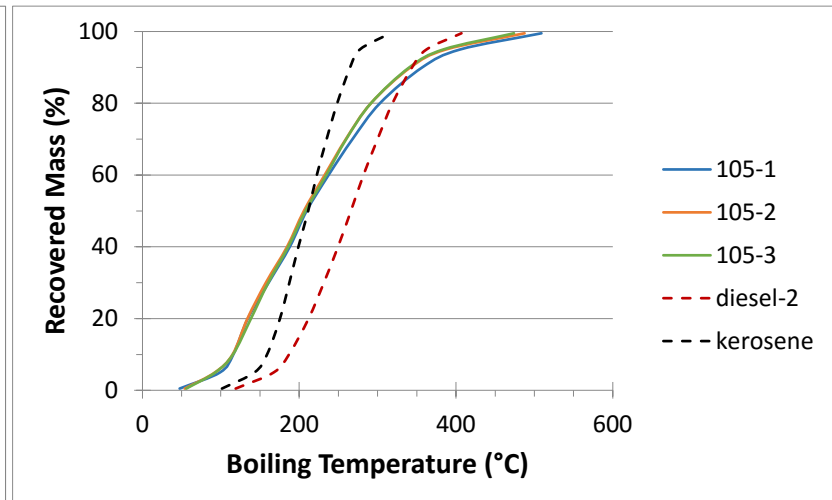


GVL and LA are Oligomerized to Fuel-Range Hydrocarbons

Organic Phase GC/MS Analyses



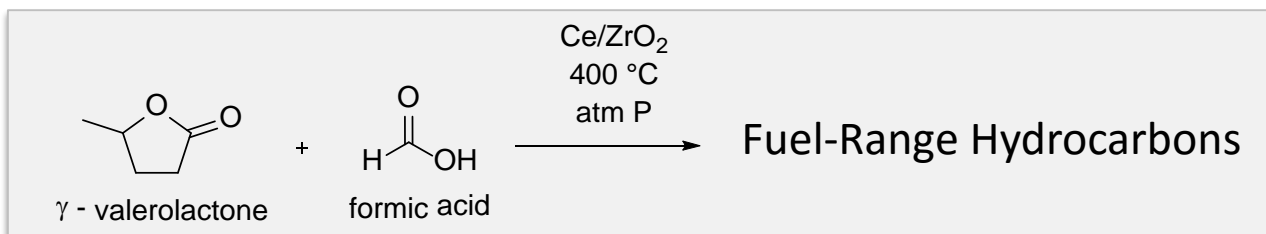
Organic Phase Simulated Distillation



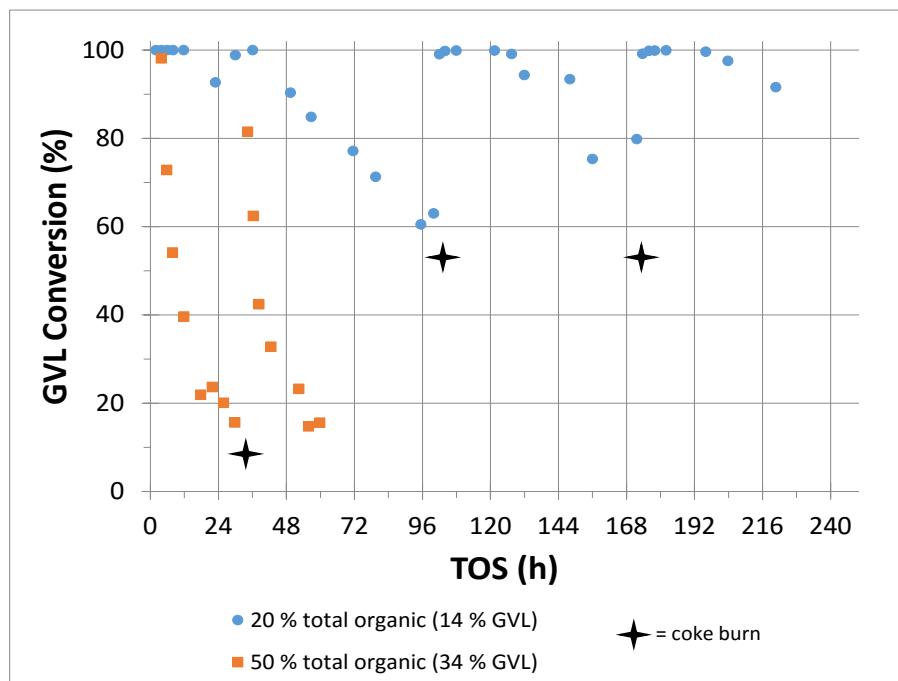
- **Atmospheric processing** gives deoxygenated and oligomerized oil product **in the distillate range**
- Simple reprocessing of the aqueous phase produces additional oil product for a **higher C yield**
- Light ketone products identified by Co-Optima as **high octane components** for gasoline
- Lower GVL WHSV produces a more **deoxygenated oil product** with less C in the aqueous phase
- Excellent mass and carbon balance

Technical Accomplishments – Levulinic Acid/ γ -Valerolactone

Catalyst Lifetime and Regeneration



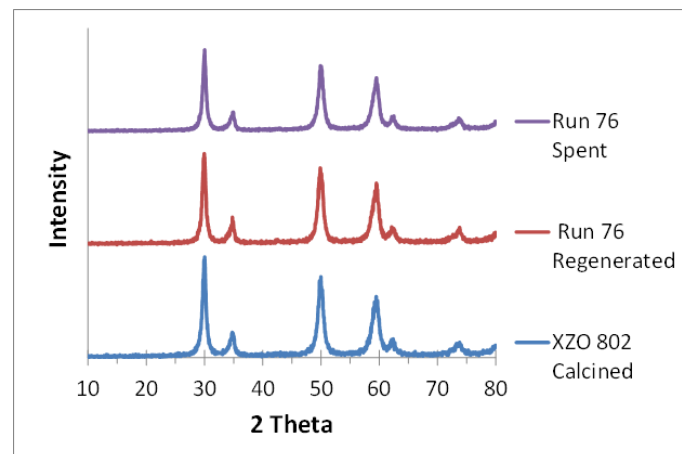
Catalysts are Easily Regenerated
in situ with air at 450 °C



- 20 wt% feed: 14% GVL, 6% FA, 400 °C, WHSV 0.121 h⁻¹ w/rt GVL; (Run 76)
- 50 wt% feed: 34% GVL, 16% FA, 360 °C, WHSV 0.121 h⁻¹ w/rt GVL

Catalysts are Stable
over at least 240 hr on stream

Sample	BET SA (m ² /g)	Pore Vol, cc/g
Fresh 802, Calcined	108.3	0.22
Run 76 Spent	47.7	0.18
Run 76 Regenerated	88.4	0.22



Milestone Name/Description	End Date	Type
NREL will generate and supply up to 20 L of hydrolysate to lab collaborators and up to 4 L of ethanol fermentation broth to ORNL. (NREL, Task 5)	12/31/2016	Quarterly Progress Measure (Regular)

Deacetylated and dilute acid (DDA) pretreated corn slurry generated in Metso 1 ton/day continuous pretreatment reactor



Whole slurry enzymatic hydrolysis in 130 L high-solids at 20% solids (>130 g/L monomer sugar), 40 L of slurry stored



5 L of whole slurry hydrolysate fermented to ethanol using co-fermenting *Zymomonas mobilis* (61 g/L)



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 costs

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 **biomass feedstocks**
 - Approaches and methodologies can be extended to other industry-specific opportunities

Marketability

- ChemCatBio (www.chemcatbio.org) – this project complements the broad, multi-pathway catalysis effort by evaluating catalytic upgrading performance on Biochemical Conversion feedstocks/hydrolysates/fermentation broths
 - ChemCatBio includes an industry outreach and concierge function to leverage the capabilities and expertise of national labs to help solve specific industry problems or develop new, industrially-relevant capabilities

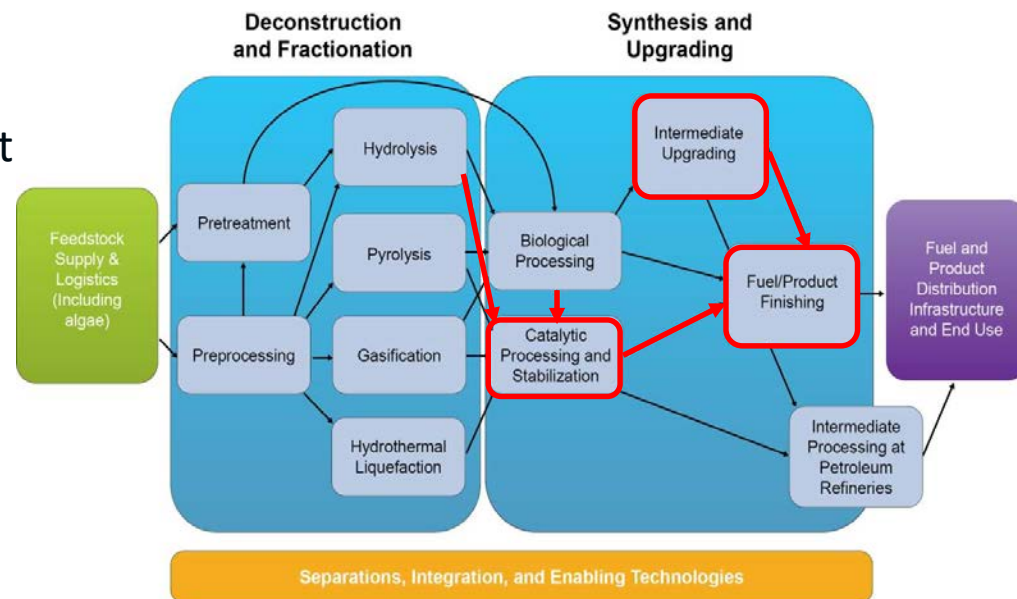


4 – Relevance

Support of BETO's Mission: Conversion R&D Challenges and Barriers (2016 MYPP)

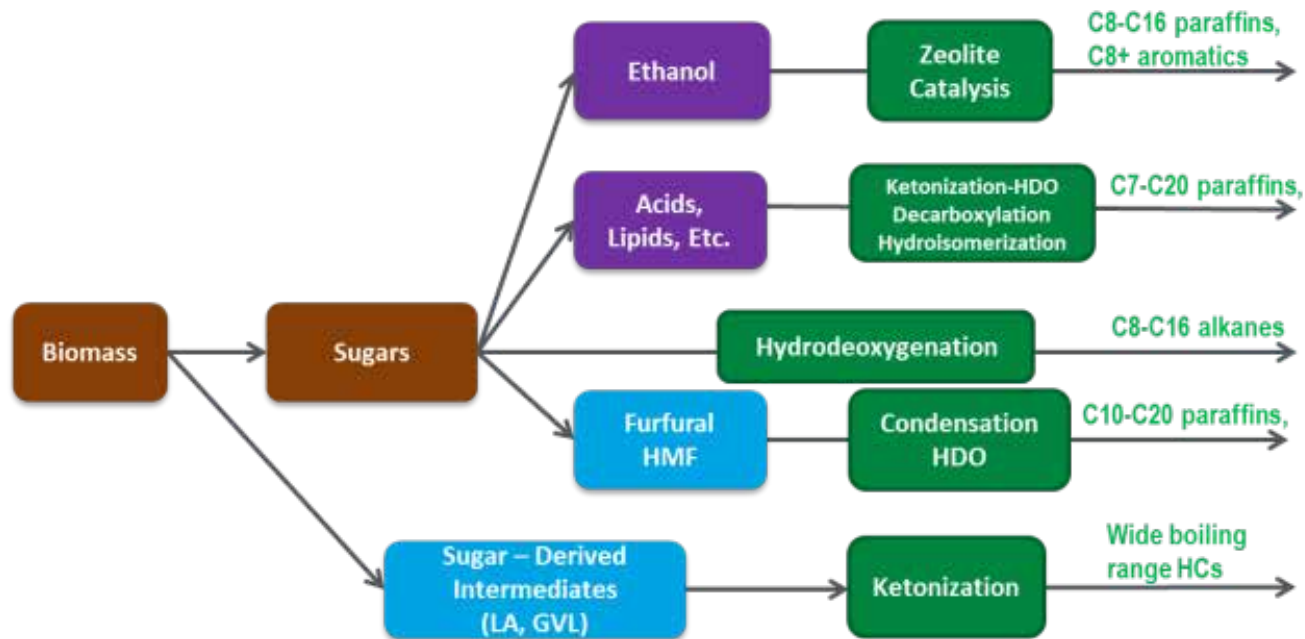
- **Novel, durable catalysts** are needed that are capable of selective **sugars and biological intermediate upgrading**
 - CT-H. Efficient Catalytic Upgrading of Sugars...to Fuels and Chemicals
- **Benchmark catalyst performance** against common Biochemical Conversion feedstocks and hydrolysates/fermentation broths and **identify inhibitory effects** that require mitigation
 - CT-G. Efficient Intermediate Clean-up and Conditioning
- A coordinated approach to **bridge biochemical conversion** feedstocks/hydrolysates/fermentation broths **with catalytic upgrading** of resulting intermediates
 - CT-J. Process Integration

MYPP Pathway: Low Temperature Deconstruction and Catalytic Sugar Upgrading



Adapted from Table 2-21, BETO Multi-Year Program Plan (March, 2016)

5 – Future Work

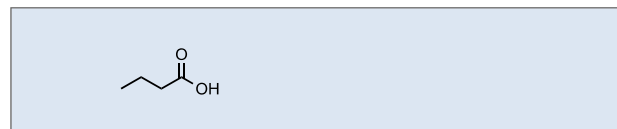
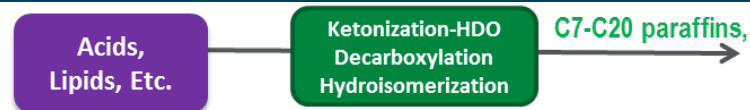


- Focusing on investigation of various upgrading approaches in a comparative manner, leading to identification of **best routes to provide a flexible range of fuel components and properties**
 - Validated by **comprehensive TEA performed in a whole-process context**, using comparative data on relevant, low-cost feed-streams
 - Managed through **comparative data generation** driven toward quantified targets and go-no go decision methodology

5 – Future Work



- FY17 Q4 Milestone - Maximize the product value by increasing jet/diesel fraction (C₈₊ Hydrocarbons) to >30% in the product stream from catalytic conversion of ethanol
 - Mixed with streams from Tasks 2-4 to produce diesel or jet fuels
- Identify optimum drop-in diesel and jet fuels via blending HCs from other routes
- Apply ethanol upgrading technologies other biologically derived intermediates (e.g., aqueous butanol, diols)
- Define effect of impurities
- TEA analysis
- Links to Other ChemCatBio Efforts
 - CCPC, ACSC to understand and improve the catalysts



C8-C12 Branched Alkanes
C9-C15 Branched Cycloparaffins
C5-C3
C5-C5-C5

Ketonization: Modified ZrO₂ acidity through selective doping and improved selectivity

Achieved KET 70% C-selectivity vs. Milestone 60%

Condensation:

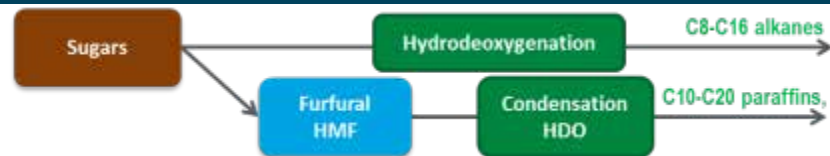
Achieved complete conversion of pentanone to dimers and trimers in batch time-series rxn

Demonstrated C-C elongation step

FY18 Goals

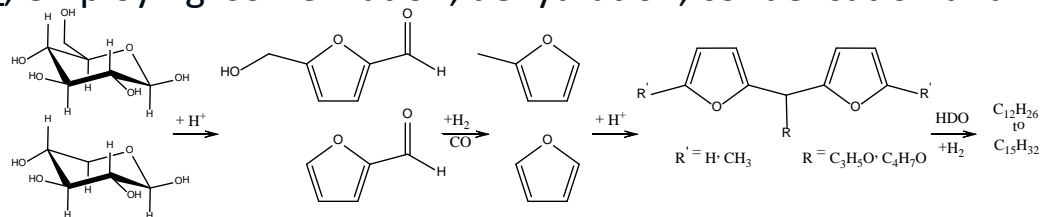
- **Goal 1:** Demonstrate >24 h of ketonization catalyst stability and generate 100 mL of hydrocarbon blendstock for testing through condensation coupling and HDO.
- **Goal 2:** Demonstrate anaerobic acid-to-fuel pathway with “real” mixed acids (with BUS + SEPCON projects)
- **Goal 3:** Identify opportunities with ACSC & CCPC to better understand catalyst performance by evaluating changes in fresh and spent material properties

5 – Future Work



Develop catalytic routes to HC that utilize all sugars in biomass hydrolysates

- Build on the process for making HC from sugars via furfural production to utilize mixed pentose and hexose streams, employing isomerization, dehydration, condensation and HDO reactions.



- **FY17 Q2 milestone**. Demonstrate process conditions for conversion of a mixed sugar stream into furfurals in at least 50% yield for both pentoses and hexoses.

Develop catalytic approaches to combine chain extension and HDO reactions in flow reactions

- LANL will further develop the chain extension steps using sugars or bioderived building blocks and translate and combine the chain extension and HDO reaction within one reactor.
- **FY17 Q4 milestone**. Integrate chain extension and HDO reactions into a continuous flow reactor.

Develop lower cost HDO that operates at lower T and P with lower cost metals

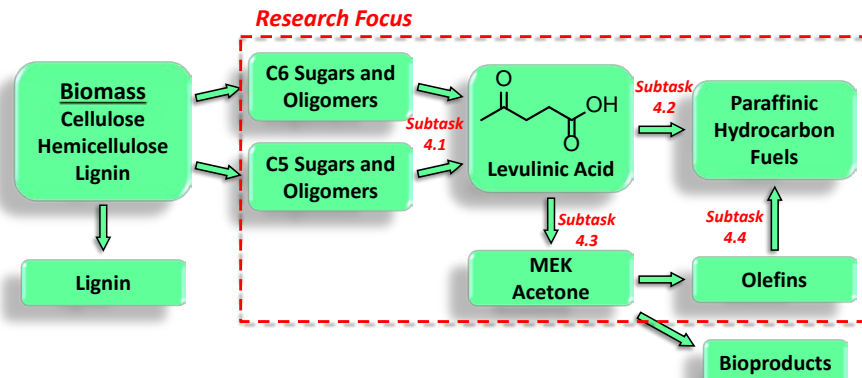
- HDO is a ubiquitous reaction for making HC from biomass – important to many ChemCatBio projects
- HDO is often the most costly step in conversion of biochemical intermediates into HC, requiring costly catalysts, high T, and H₂ at high P
- Work at LANL and NREL will further optimize catalysts to increase catalyst activity, selectivity, and stability while minimizing the cost of the metals used.

5 – Future Work



- Develop improved catalysts for the **direct decarboxylation** of aqueous LA to MEK

- Direct decarboxylation to MEK and acetone demonstrated
- One-step conversion of MEK and acetone to C4 to C6 demonstrated
- Conversion of C4 to C6 olefins to diesel and jet fuel-range hydrocarbons is straight-forward
- Determine the effect of catalyst support, metal, and metal loading



- C. Smith, V.L. Dagle, M. Flake, K.K. Ramasamy, L. Kovarik, M. Bowden, T. Onfroy, R.A. Dagle, Conversion of syngas-derived C2+ mixed oxygenates to C3–C5 olefins over Zn_xZr_yO_z mixed oxide catalysts, Catalysis Science & Technology, (2016).
- V.L. Dagle, C. Smith, M. Flake, K.O. Albrecht, M.J. Gray, K.K. Ramasamy, R.A. Dagle, Integrated Process for the Catalytic Conversion of Biomass-Derived Syngas into Transportation Fuels, Green Chemistry, DOI:10.1039/C5GC02298C (2016).
- V. Dagle & R.A. Dagle, “Process for Conversion of Levulinic Acid to Ketones”, Patent Application filed June 2016.

- Compare performance of LA/GVL derived from different hydrolysates in hydrocarbon production (FY17 Q4 Milestone: >50% yield of LA/GVL from sugars/oligomers)
- Optimize LA/GVL conversion to hydrocarbon fuels
 - WHSV, T, and LA/GVL concentration
 - Maximize carbon yield in the fuel range

5 – Future Work

Project Coordination

- Additional/different hydrolysates routinely available through various Biochemical Conversion project activities
- Fermentation broths (alcohols, diols, organic acid, lipids, etc.) are routinely produced through various Biochemical Conversion project activities
- Continual efforts to identify and utilize appropriate reaction and analytical capabilities across project labs and broadly across ChemCatBio
- TEA activities
 - Q2 FY17 milestone in 2.1.0.100 (NREL Biochemical Platform Analysis) on biochemical catalytic pathways alternatives
 - FY18 go/no go
 - FY19 end-of-project milestone
- Project management and cross-lab communications

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 and instruments
 - Reactor systems
 - Fuel assessment
 - TEA tools and approaches
- Integrated task structure across multiple labs
- Project coordination task
- Go/no-go decision point to re-scope/ focus effort

Accomplishments

- Ethanol Upgrading:
 - Ga-ZSM-5 improves HC and BTX yield; Light gas recirculation
- Organic Acid Upgrading:
 - Alkanes from C4-C6 acids; branched alkanes/ cycloparaffin from C2-C4 acids
- Furfural Upgrading:
 - >60% yield of jet/diesel-range HC from furfural; cont. flow HDO and intermediate coupling
- Levulinic Acid/GVL Upgrading:
 - Oligomerized GVL and LA to fuel-range HCs; catalyst regeneration established
- Project Coordination:
 - Generated hydrolysate and ethanol broth; starting TEA

Relevance

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

Future Work

- Ethanol Upgrading:
 - Increase C8+ HC fraction to >30%
- Organic Acid Upgrading :
 - Increase C6 acid ketonization selectivity to undecanone to > 60%
- Furfural Upgrading:
 - Utilize mixed sugars; chain extension and HDO; lower cost HDO
- Levulinic/GVL Upgrading Decarboxylation of LA to MEK; compare hydrolysates for LA/GVL production
- Project Coordination
 - Comparative TEA Go/No-Go

Acknowledgements



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T. Semelsberger

D. Auberry
C. Drennan
M. Guo
H. Job
S. Lee
M. Swita

Biochemical Platform Analysis Project
Pretreatment And Process Hydrolysis Project
Fuel Performance Group



Energy Efficiency &
Renewable Energy

Additional Slides

Responses to Previous Reviewers Comments (2.3.1.100)

- *“This is a good project with good results, moving on to commercialization. Generally, it is a success story.”*
- *“I would like to see a lot more data on the durability of the catalyst and the impact of organic acids on catalyst life. Very interesting.”*
- *“Although not yet complete, this project looks like it has the potential to be a major success for the BETO portfolio. The use of ethanol as a feedstock can go a long way to allowing existing cellulosic ethanol projects to move toward commercial demonstration, and the ability to handle dilute ethanol streams will have a significant impact on the economics of those facilities. The durability of the catalyst is encouraging, and migration of the industry from ethanol to hydrocarbon drop-in fuels has enormous potential.”*
- *“This is a well-planned, well-executed project which has developed an innovative and promising technology for conversion of ethanol to a fungible hydrocarbon for gasoline. This project was a highlight from the peer review and should serve as a model for other technology projects.”*
- *“Excellent work and excellent progress.”*

PI Response to Reviewer Comments

We have lots of results regarding catalyst durability and impact of organic acids. Due to limited presentation time, not all of this information was presented and some of these tests were from a prior Fiscal Year. These data support the summarized catalyst durability of much greater than 200 hours with regeneration; though they were from shorter runs under a wide variety of conditions. The tested organic acids (such as acetic acid) had no apparent effect on the V-ZSM-5 zeolite and were also converted by the catalyst

Responses to Previous Reviewers Comments (2.3.1.101)

Comment	Response
<p><u>Project Relevance</u> Producing jet fuels from intermediates is very relevant and important research. .</p>	
<p><u>Overall Impressions</u> This is a good project. It is very important to pursue the “combined” biological step to platform chemical followed by further, simple, well understood chemical processing. This project has significant potential, and it is good to see coproduct and downstream chemical production work tied to hydrocarbon fuels production. Commercialization potential for the nanoparticle catalyst will be interesting to observe as the project progresses. It is important that techno-economic analysis (TEA) be considered early with projects like these. While it is clear that the project is interested in working with existing models to support the industry and the BETO portfolio, additional effort should be taken to make sure it happens. The project uses creative approaches to generating hydrocarbons from biomass. It would be good to see use of preliminary TEA to guide and constrain research. This is extremely valuable work investigating alternative conversion chemistries and pathways. There is a lot of potential in the methods being investigated in this program.</p>	<p>We thank the reviewers for their positive comments. We agree with the reviewers that more interaction with the TEA group will be beneficial to the direction of our research, and this will occur as often as is feasible. It is our expectation that these interactions will lead to technical targets that will become the focus of our research. A milestone “Conduct preliminary TEA assessment for catalytic conversion of carbohydrate intermediates to fuels” was completed 6/30/2015. The results of the assessment was that the MFSP for the furfural process compared favorably with more mature designs which were also based on aspirational targets. The feasibility-level model suggested that the cost potential for this pathway was in a similar range to the other pathways, and additional research could enable further cost improvements beyond the MFSP projected thus far.</p>

Responses to Previous Reviewers Comments (2.3.1.102)

- *“This is a good generic platform for research to produce sugars that can be utilized in most biochemical/catalytic processes.”*
- *“This is differentiated work to make products of open chain hydrocarbon molecules. There has been good progress toward demonstrating new reaction pathways. It would be good to see the use of techno-economic analysis and more relevant sugar feedstocks earlier in the experimental work”*
- *“This project may have great potential, but it is disconcerting that so little economic analysis has been done. On first glance, there are several items that could significantly impact commercialization potential that should be evaluated. Given that much of the process is novel, techno-economic analyses should have been performed to help direct the R&D effort. It is strongly recommended that this be completed immediately.”*
- PI Response to Reviewer Comments
- Thank you for the review comments. We presented a flow chart outlining our overall vision to show how the apparently disparate activities we are conducting are actually part of a unified approach to lignocellulose conversion to hydrocarbon fuels. We chose the deconstruction and levulinic acid to hydrocarbon fuels tasks because, in our view, they were the most challenging, yet the most important to demonstrate before the overall vision could be realized. Not to say the oligomer to levulinic acid conversion will be easy, but there is certainly more literature in that area.
- Significant progress has been made since the last review. Flow deconstruction is new and has demonstrated improved performance over earlier batch studies. Discovery that ash components do not transfer to the sugar phase in batch experiments is remarkably significant and is new information. The levulinic acid conversion data is totally new and also remarkably significant. Clearly, there is more to do. But in our opinion, we’ve demonstrated what we said were the hardest parts. Connecting the dots by demonstrating oligomer conversion to levulinic acid and use of the “dirty” levulinic acid in the conversion reactor now become priorities.
- Techno-economic analysis is to be conducted in FY15. The technical challenges we have overcome to bring the technology to the current level have been large. In fact, our course has changed significantly on both the deconstruction and levulinic acid conversion tasks. The levulinic acid conversion work was surprising and could not have been predicted. We understand the importance of TEAs and conduct them regularly to guide research. In this case, however, there was enough uncertainty in process configurations and pathways that we felt an early TEA would not have been a meaningful exercise. We are now at a point, however, where pathways are established enough, and variations (including process/reactor configurations) can be envisioned well enough, that resources can be spent confidently to produce a useful TEA.

Responses to Previous Reviewers Comments (2.3.1.103)

- *“This is a good project and a good alternative for converting sugars to fuels. We need to keep in mind the high cost of large pressure reactors and might want shorter reaction time as a milestone.”*
- *“The project is moving in the right direction to reduce capital and operating costs. I would really encourage a techno-economic analysis (TEA) soon.”*
- *“Catalytic conversion of biomass with limited downstream upgrading has significant potential in the commercial biomass portfolio. The fact that this project utilizes fairly mild conditions and commercially available, inexpensive catalysts is very encouraging.”*
- *“The project uses innovative chemistry to produce hydrocarbons from biomass. Selection of catalysts and conditions was generally driven by economic considerations, but it would be helpful to have a more holistic TEA for some of the proposed pathways. I recommend this group connect with TEA modeling activities at NREL and other labs working on chemical catalysis projects to approach the cost estimates in a consistent way.”*
- *“The project had long reaction times with the potential to be very costly; however, this is a very important activity.”*

PI Response to Reviewer Comments

- We appreciate the reviewers' comments and their understanding of the advances we have made in lowering operating conditions, moving to cheaper catalysts and reaction optimization as we move towards further economic analysis and process flow development. The reviewers note that “successful completion will have a significant impact on state of the technology” and that this project aligns well with BETO's goals. Now that we have developed an efficient and “innovative chemistry to produce hydrocarbons from biomass,” our future work (dependent on continued funding) will aim to encompass all the reviewers' comments regarding scale-up, catalyst reuse, and economic analysis to build robustness and diversity into the continued use and development of hydrolysate as a biomass feedstock.

Publications, Presentations, and Patents (2.3.1.100) – 1

Publications

- Narula, C.K., Li, Z.; Casbeer, E.; Geiger, R.A.; DeBusk, M.; Keller, M.; Buchanan, M.; Davison, B.H.; Heterobimetallic Zeolite, InV-ZSM-5, enables efficient conversion of biomass derived ethanol to renewable hydrocarbons, *Sci. Rep.* 2015, 5, 16039 (this was highlighted in *Science* 2015, 350, 1329).
- Zhenglong Li, Andrew Lepore, Brian H. Davison, Chaitanya K. Narula. Catalytic Conversion of Biomass Derived Ethanol to Liquid Hydrocarbon Blend-Stock: Effect of Light Gas Recirculation. *Energy & Fuels*, 2016, 30 (12), pp 10611–10617.
- Zhenglong Li, Andrew Lepore, Mariam F. Salazar, Guo Shiou Foo, Brian H. Davison, Zili Wu, Chaitanya K. Narula. Selective Conversion of Ethanol to BTX on Ga-ZSM-5. (In preparation)

Presentations

- R. Geiger, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Fuel," ACS Spring Meeting, San Diego, March 25, 2012.
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel," ACS Fall Meeting, Philadelphia, 2012 (abstract published, presentation not made due to travel restrictions).
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel," ACS Spring Meeting, New Orleans, 2013.
- C. K. Narula, B. H. Davison - BETO merit review – May 20-22, 2013, Alexandria, Virginia.
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, C. K. Narula, "Hydrocarbon Blend-Stock from Catalytic Conversion of Biomass Derived Ethanol," North American Catalysis Society Meeting, Louisville, Kentucky, 2013.
- E. Casbeer, J. Szybist, C. Kinchin, M. Keller, Davison, B.H., and C. K. Narula, "Direct Catalytic Conversion of Aqueous Ethanol Streams into Hydrocarbon Blendstock," 35th Symposium on Biotechnology for Fuels and Chemicals, April 29-May 2, 2013, Portland, Oregon.
- E. M. Casbeer, A. W. Lepore, B. H. Davison, and C. K. Narula, "Direct Catalytic Conversion of Alcohols Stream into Hydrocarbon Blend-Stock," American Chemical Society National Fall Meeting, San Francisco, August 10-14, 2014.
- E. Casbeer, R. A. Geiger, B. H. Davison, J. P. Szybist, M. Keller, and C. K. Narula, "Hydrocarbon-Pool Route to Conversion of Biomass Derived Ethanol to Hydrocarbon Blend-Stock," American Chemical Society National Fall Meeting, Indianapolis, September 8-12, 2014.
- Zhenglong Li, Erik M. Casbeer, Brian H Davison, Chaitanya K Narula, "Direct Catalytic Conversion of Ethanol Stream to Hydrocarbon Blend-Stock: Approaches to Increase Liquid Hydrocarbon Production," American Chemical Society National Meeting, Denver, March 22-26, 2016.
- Zhenglong Li, Andrew Lepore, Erik M. Casbeer, Brian H. Davison, and Chaitanya K. Narula, "Hydrocarbon Blend-Stock from Catalytic Conversion of Alcohols," North American Catalysis Society Meeting, Pittsburgh, JUNE 14-19, 2015.

Publications, Patents and Commercialization (2.3.1.100) – 2

Patents and Commercialization

- Technology Licensed to Vertimass, LLC on March 6, 2014
- Currently Vertimass is collaborating with Technip to scale up this ethanol upgrading process
- Patents
 1. Narula, C.K.; Davison, B.; Keller, M.; Zeolitic catalytic conversion of alcohols to hydrocarbons, US Patent 9,535,921, Jan 3, 2017
 2. Narula, C.K.; Davison, B; Keller, M.; Catalytic conversion of alcohols to hydrocarbons with low benzene content, US Patent 9,434,658 Sept. 6, 2016
 3. Narula, C.K.; Davison, B; Keller, M.; Catalytic conversion of alcohols to hydrocarbons with low benzene content, US Patent, 9,278,892 March 8, 2016
 4. Narula, C.K.; Davison, B.; Catalytic Conversion of alcohols having at least three carbon atoms to hydrocarbon blend-stock, US Patent 9,181,493 Nov. 10, 2015
 5. Narula, C.K.; Davison, B.; Catalytic Conversion of alcohols having at least three carbon atoms to hydrocarbon blend-stock, 20160032195, Feb 4, 2016
 6. Narula, C.K.; Li, Z.; Davison, B.H.; Liquid Hydrocarbons from Biomass Derived Ethanol, (Filed)

Publications, Presentations, and Patents (2.3.1.101)

Publications

- Heidi Pilath, Ashutosh Mittal, Luc Moens, Todd Vinzant, Wei Wang and David K. Johnson. “A Route from Biomass to Hydrocarbons via Depolymerization and Decarboxylation of Microbially Produced Polyhydroxybutyrate,” by. Published in “Direct Microbial Conversion of Biomass to Advanced Biofuels” Ed. Michael Himmel, Chapter 19, 383-394, (2015).
- Jared Clark, Heidi M. Pilath, Ashutosh Mittal, Luc Moens, David J. Robichaud, and David K. Johnson. “Direct Production of Propene from the Thermolysis of Poly(β -hydroxybutyrate) (PHB). An experimental and DFT Investigation.” *Journal of Physical Chemistry A* 120 (3), 332-345.
- M.J. Bidy, R. Davis, D. Humbird, L. Tao, N. Dowe, M.T. Guarnieri, J.G. Linger, E.M. Karp, D. Salvachua, D.R. Vardon, G.T. Beckham. (2016). The techno-economic bases for coproduct manufacturing to enable hydrocarbon fuel production from lignocellulosic biomass. *ACS Sustainable Chem. Eng.* 4, 3196-3211

Presentations

- D.K. Johnson, “Conversion of Furfural into Hydrocarbons for Blending in Jet And Diesel Fuels” at the 3rd Frontiers in Biorefining conference at St Simons Island, GA on October 24, 2014.
- D.K. Johnson, “Conversion of Sugars into Hydrocarbons by Decarboxylation and Hydrodeoxygenation” at the Annual AIChE Meeting in Atlanta, GA, on November 16, 2014.
- D. K. Johnson, “Progress in converting furfural into hydrocarbons for blending into jet and diesel fuels” at the Symposium on Biotechnology for Fuels and Chemicals, in Baltimore, MD, April, 2016.
- D.K. Johnson, “Production of advanced biofuels for blending into jet and diesel fuels via furanic intermediates” at the 4th Frontiers in Biorefining conference at St Simons Island, GA on November 8, 2016
- 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.
- D.R. Vardon. *Catalytic upgrading of microbial acids to renewable polymer precursors*. Invited Seminar. Colorado School of Mines, Chemistry Department. September 2016.
- D. Salvachua, E.M. Karp, D.R. Vardon, N.A. Rorrer, A. Mohaghegih, H. Smith, B.A. Black, M.T. Guarnieri, Y.C. Chou, N. Dowe, G.T. Beckham. *Integrated succinic acid production from xylose-enriched hydrolyzates by Actinobacillus succinogenes for downstream biopolymer production*. SIMB Symposium on Biotechnology for Biofuels, Baltimore, MD. April 2016.
- A.E. Settle, K.X. Steirer, K.E. Moyer, G.T. Beckham, D.R. Vardon. *Bimetallic catalysts for the aqueous phase reduction of succinic acid to 1,4-butanediol*. Spring 2016 American Chemical Society Meeting, San Diego, CA. March 2016.

Patents

- D.R. Vardon, T.R. Eaton, A.E. Settle. (2017). Solid catalysts for producing alcohols and methods of making the same. *Provisional patent application. US PTO 62/450,520*.

Publications, Presentations, and Patents (2.3.1.102)

Publications

- Lilga, Padmaperuma, et al., “Ketonization of Levulinic Acid and g-Valerolactone to Hydrocarbon Fuel Precursors”, submitted as invited paper to Catalysis Today

Presentations

- Lilga MA, AB Padmaperuma, and HM Job. 2015. "Catalytic Conversion of Lignocellulosic Feedstocks to Hydrocarbon Fuels." Presented by Asanga B Padmaperuma (Invited Speaker) at 2015 AIChE Annual meeting on November 9, 2015.
- Lilga MA, AB Padmaperuma, D Auberry. 2016. "Conversion of lignocellulosic biomass to hydrocarbon fuels." (invited Talk) 252nd ACS National Meeting, Philadelphia, PA. August 21, 2016

Patents

- “Process for Conversion of Selected Feedstock Compounds to Distillate Range Hydrocarbons”, Michael A. Lilga, Asanga B. Padmaperuma, Provisional Patent Application No. 62/253,007 filed 11/9/2015.

Publications and Patents (2.3.1.103)

Publications

- R. W. Jenkins, C. M. Moore, T. A. Semelsberger, A. D. Sutton. “Heterogeneous ketone hydrodeoxygenation for the production of fuels and feedstocks from biomass” Chem. Cat. Chem. 2017, accepted for publication.
- 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.
- C. M. Moore, R. W. Jenkins, E. Polikarpov, W. L. Kubic Jr., A. D. Sutton “Synthesis of Acetone-Derived C6-, C9 and C12 Carbon Scaffolds for Chemical and Fuel Applications.” Chem. Sus. Chem. Comm. 2016, 9, 3382.

Presentations

- The use of bio-derived molecular building blocks for the simultaneous production of fuels and chemicals – Frontiers in Biorefining, 2016., St. Simons Island, GA.

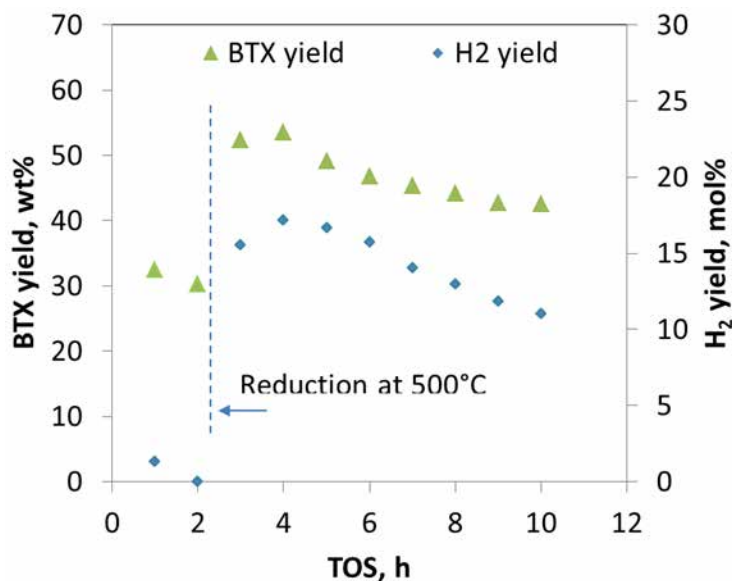
Additional Technical Content

Catalytic Upgrading of Fermentation Derived Alcohols (FY16)

BTX can be selectively produced from ethanol over Ga-ZSM-5. Ethanol upgrading can be in a swing operation for producing direct drop-in hydrocarbon fuel and valuable chemicals.

	WHSV g g ⁻¹ h ⁻¹	CH ₄ +C ₂ H ₆	C ₂ H ₄	C ₃ +C ₄	BTX	H ₂ (mol%)
H-ZSM-5	0.4	5.1	17.5	49.5	26.0	0
	0.8	3.8	17.4	52.4	23.6	0
	1.6	2.8	18.2	53.6	20.5	0
	3.2	2.1	25.7	54.6	16.8	0
Ga-ZSM-5	0.4	11.7	13.1	12.3	55.3	25
	0.8	9.5	18.5	15.3	52.2	25
	1.6	7.5	27.6	17.0	42.9	23
	3.2	4.6	38.9	18.9	29.5	21

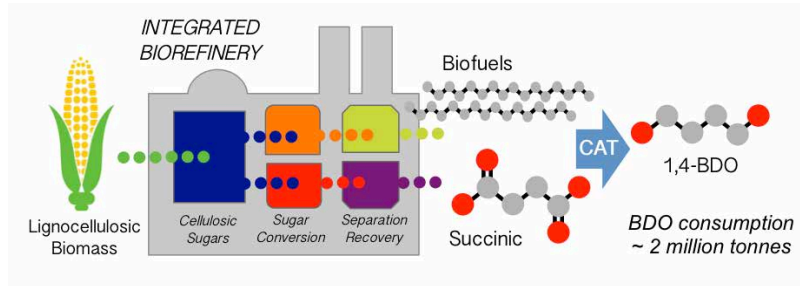
- BTX yield doubled with Ga promotion.
- C₃ and C₄ hydrocarbons, reaction intermediates, further aromatized to BTX on Ga-ZSM-5.
- Addition of Ga onto H-ZSM-5 promotes the recombinative desorption of H₂, hinders hydrogen transfer reactions and light paraffin formation.



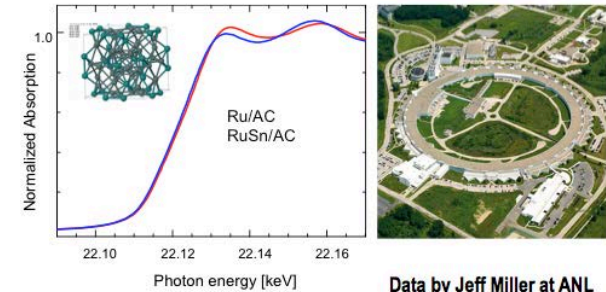
- Physical mixtures of β -Ga₂O₃ and H-ZSM-5 (Ga₂O₃ loading 6% to 50%) perform similarly to H-ZSM-5--- the **external surface Ga₂O₃ particle not contributing to the promotion effect.**
- **Exchanged Ga sites function together with Brønsted acid sites to enhance the BTX production from ethanol.**

Task 2: Short Chain Anaerobic Acids - FY16 Closeout

Succinic Acid to 1,4-BDO with Ru-Sn/AC

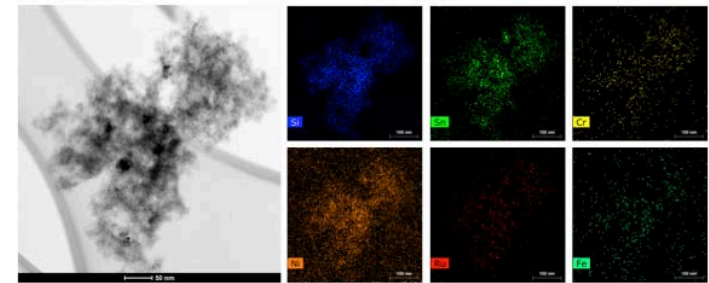


Collaborations with ACSC & CCPC



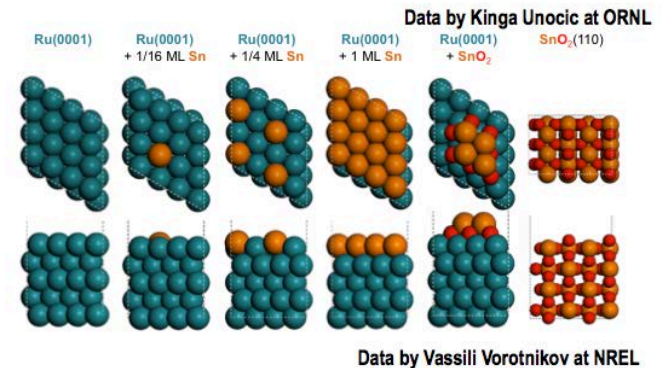
Succinic Scientific Highlights from FY16

- **Metallurgy:** Identified stainless steel leaching as major problem leading to Ru-Sn restructuring; resolved w/silica CVD Rx coating
- **Continuous Performance :** Demonstrated 96 h of complete succinic conversion to yield 71% BDO and 15% THF
- **ACSC & CCPC :** XAS at ANL provided insight into Ru-Sn oxidation state; DFT at NREL supports Ru-Sn lower H₂ affinity; STEM-EDX at ORNL shows onset of Sn migration as Ni lays down



Succinic Closeout Patents & Publications

- **Publication 1:** "Ru-Sn/AC for Aqueous Phase Reduction of Succinic Acid to 1,4-Butanediol" *In prep.*
- **Publication 2:** "Identifying the active surface in bimetallic Ru-Sn hydrogenation catalysts and the role of Sn" *In prep.*
- **ROI:** "Ru-Sn Catalyst for Producing Alcohols from Acids and Ketones"

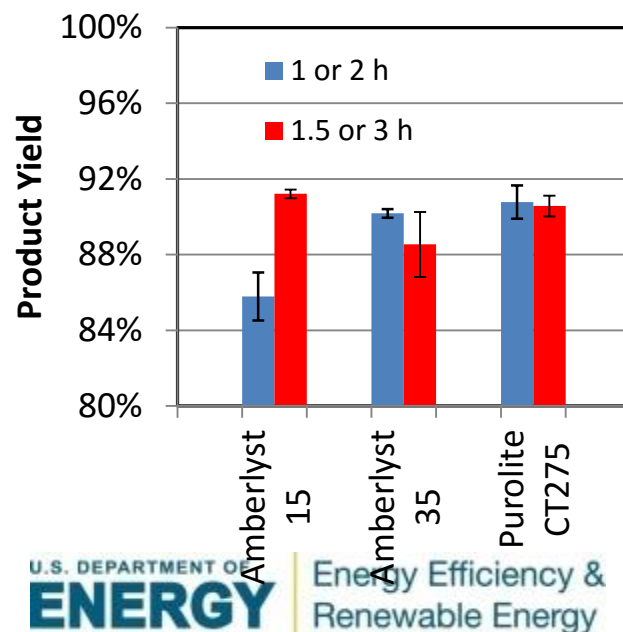
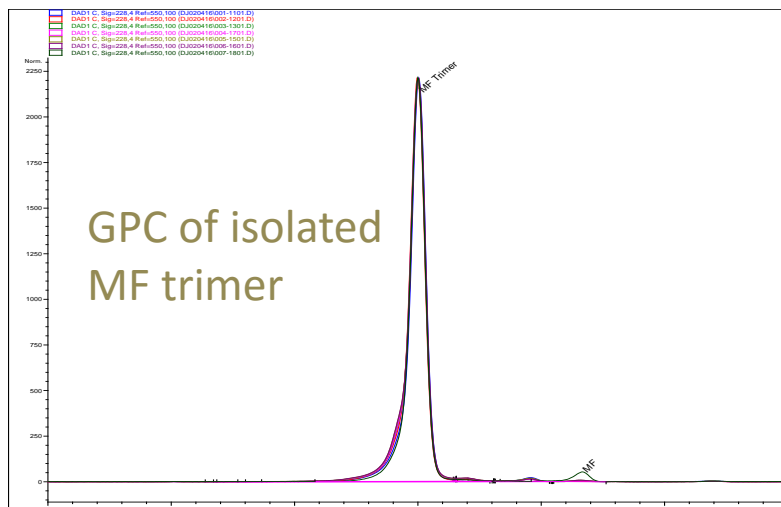
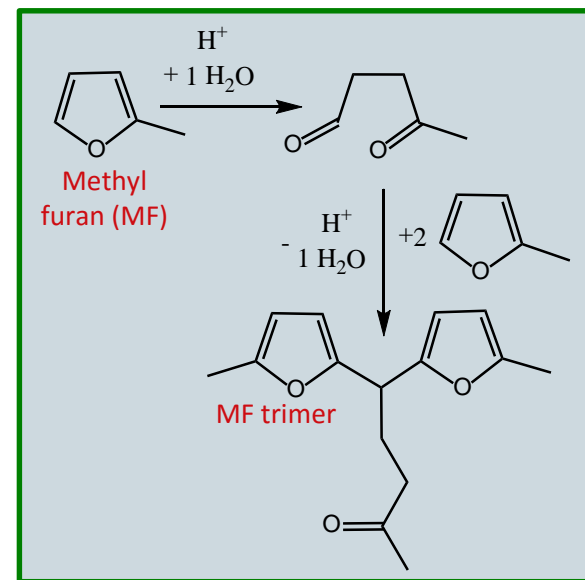


Production of hydrocarbons from furfural-derived intermediates

Acid catalyzed trimerization of methyl furan

Selection of acid resin catalyst and reaction conditions

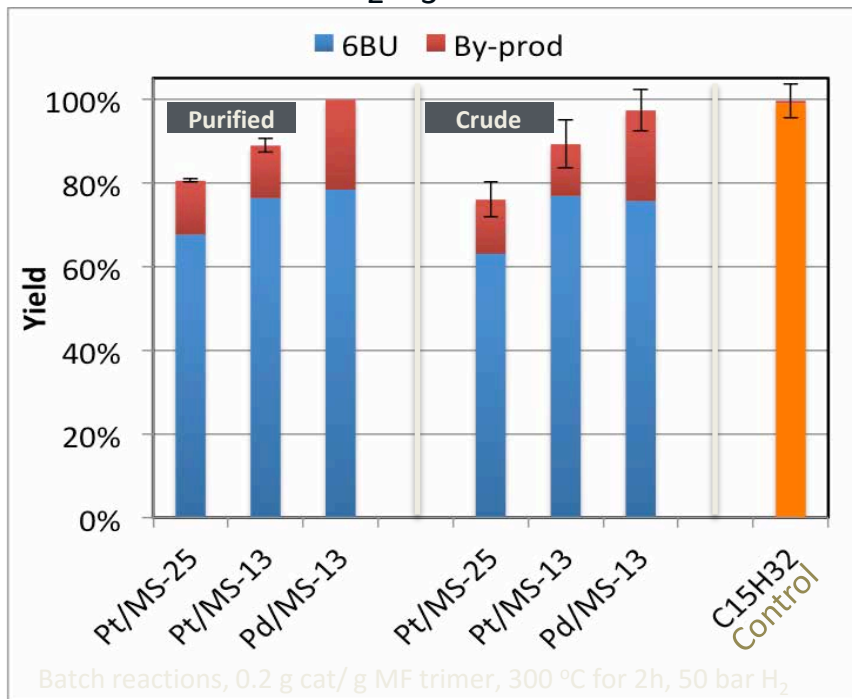
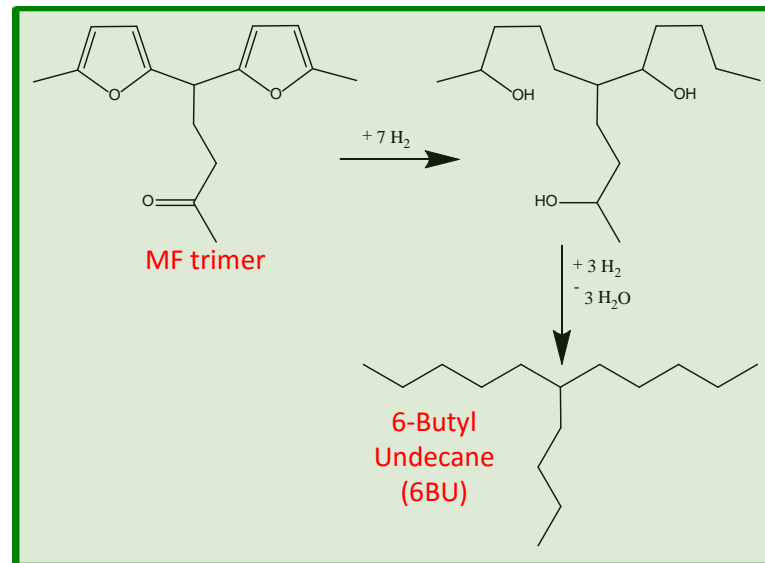
- Macroporous resins more selective for MF trimer. H_2SO_4 and gel resins give more high mol. wt. oligomers
- Batch reactions conducted with MF (25 g) using best macroporous polystyrenesulfonic acid resins at 110 or 130 °C, 1-3 h, 20:1 MF:resin ratio.
- Yields at least 91 mole% at optimum conditions
- Products contain only MF trimer, no higher oligomers (see GPC below)



Production of hydrocarbons from furfural-derived intermediates

HDO of MF trimer

- HDO of MF trimer produced with porous acidic resins equivalent to HDO of distilled trimer
- Tested various HDO catalysts Pt, Pd, Ni, Ru, on SiO₂, Al₂O₃, SiO₂/Al₂O₃, TiO₂, C supports
- Best results with MS-13 (SiO₂/Al₂O₃) support. MS-13 (13% Al₂O₃) has 2X pore diameter of MS-25 (25% Al₂O₃) and higher Bronsted acidity



- Pd higher overall yield than Pt, but Pd gave more cracked by-products
- Pd on Al₂O₃ and C also gave higher total yields than Pt on same supports
- Ni/MS-25 40% 6BU yield
- Ru needed added Sn to decrease cracking
- Pentadecane recovery 99 ± 4%

Experimental – LA Conversion

- Catalysts are Ce- and/or La-doped zirconias
 - Powders are pressed and calcined at 450 °C
 - 60 – 100 mesh
 - 3.5 to 5.5 g catalyst

- Flow Reactors
 - 3/8” diameter
 - 1/2” diameter

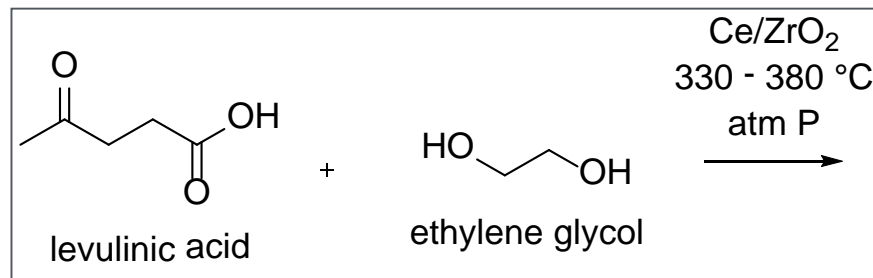
- Experimental Conditions

- 330 to 400 °C
- Atmospheric pressure (N₂)
- Aqueous feed solutions
- Varying WHSV – 0.121 h⁻¹ w/rt LA or GVL typical

MEL ID	Description
XZO 802 *	17% CeO ₂ doped Zr(OH) ₄
XZO 1289/01	17% CeO ₂ doped Zr(OH) ₄
XZO 1290/01	25% CeO ₂ doped Zr(OH) ₄
XZO 892/02	17% CeO ₂ + 5% La ₂ O ₃ doped Zr(OH) ₄
XZO 1291/01	17% CeO ₂ + 5% La ₂ O ₃ doped Zr(OH) ₄
XZO 945/03	10% La doped Zr(OH) ₄

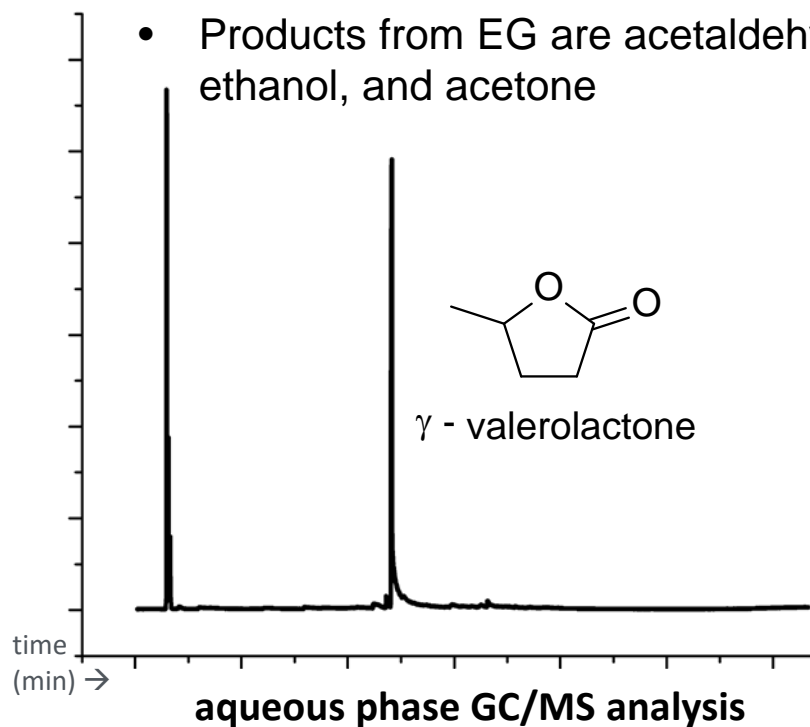
* most of the results shown use this catalyst

Levulinic Acid Conversion to GVL and Polyunsaturated Hydrocarbons



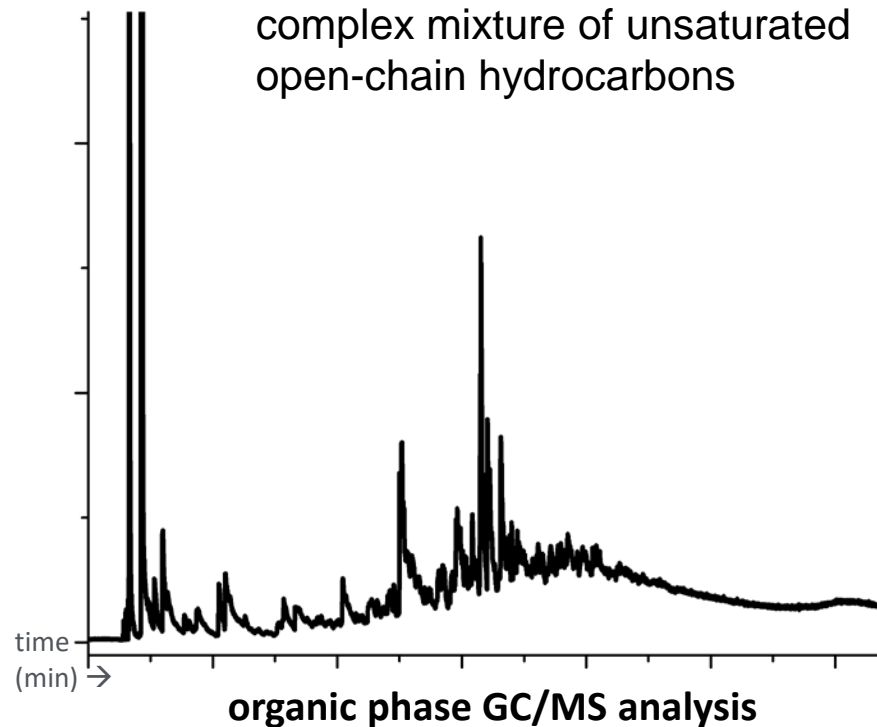
• 330 °C, atm. P

- A single aqueous phase product
- LA is hydrogenated by EG to GVL
- Products from EG are acetaldehyde, ethanol, and acetone

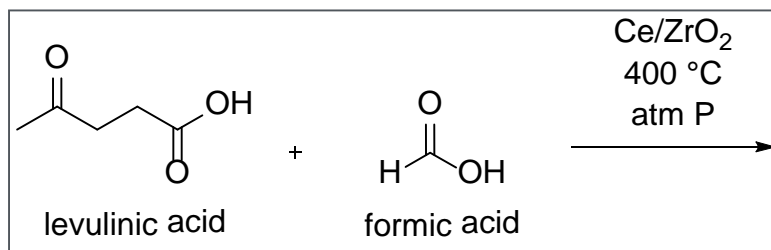


• 380 °C, atm. P

- An organic phase forms
- LA is converted via GVL to a complex mixture of unsaturated open-chain hydrocarbons



LA Catalytic Conversion to Hydrocarbons with Formic Acid

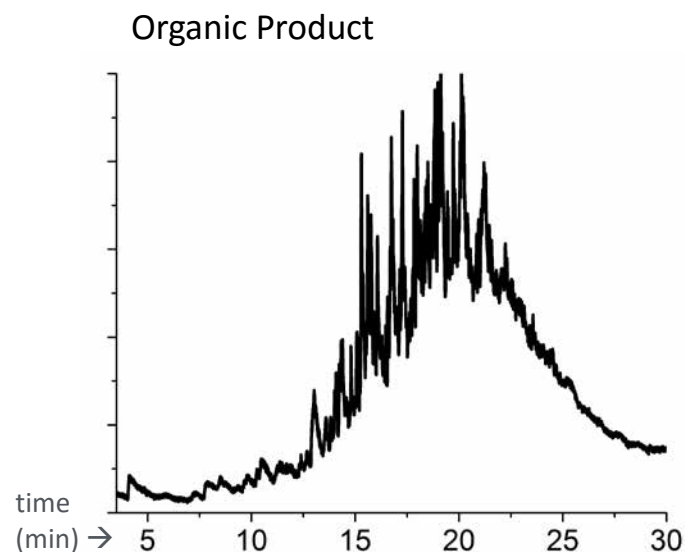
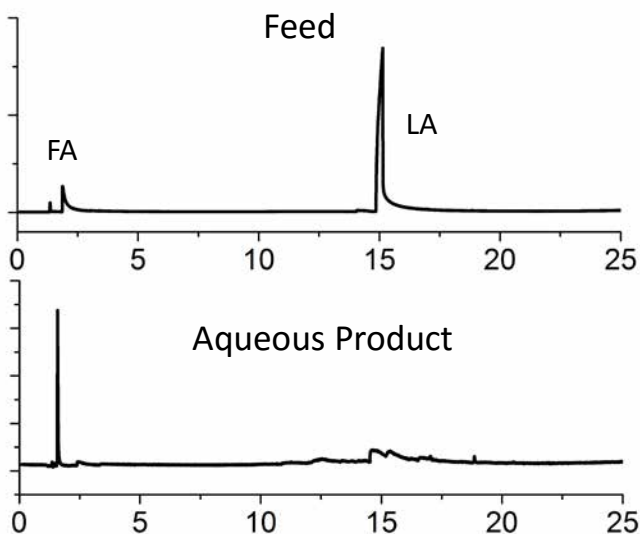
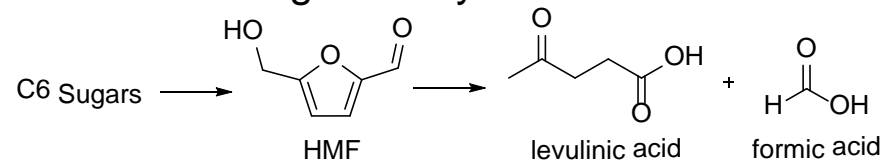


- 1:1 LA : Formic Acid

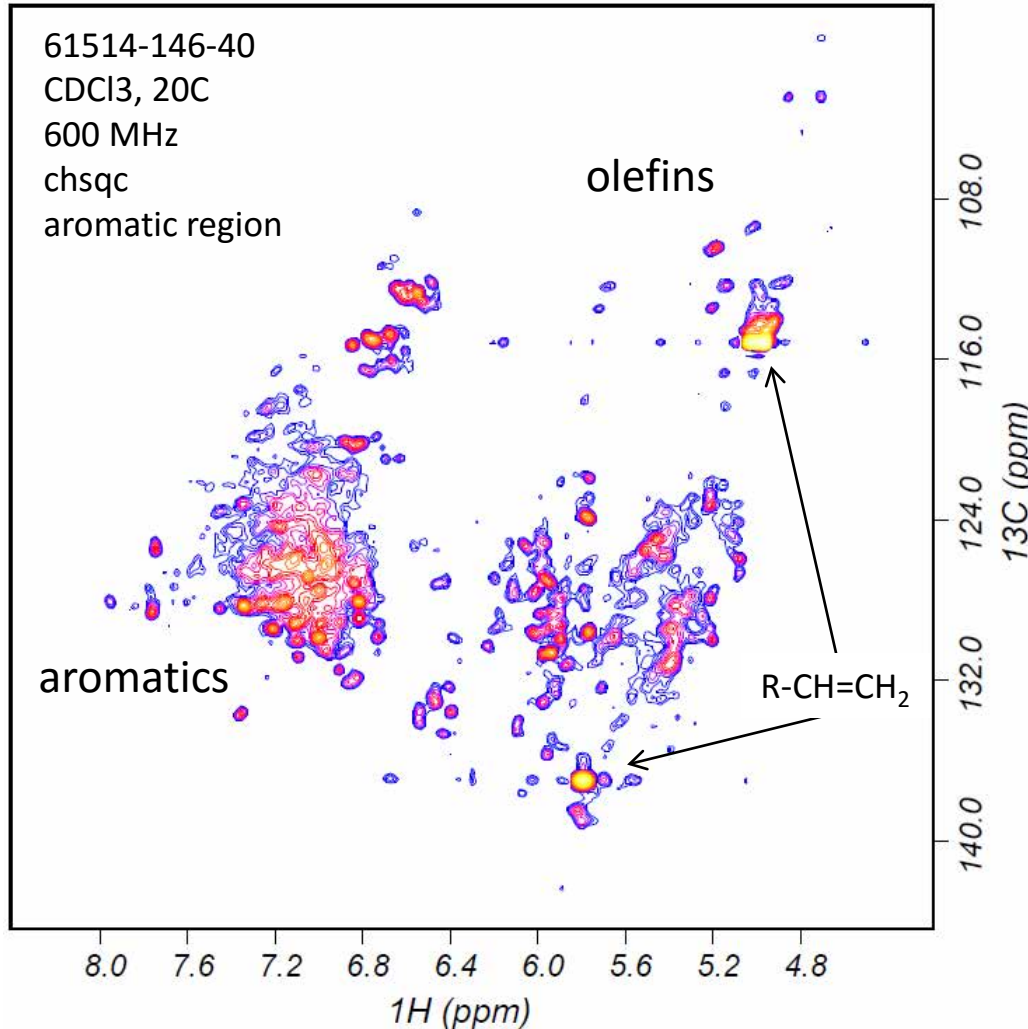
- Unsaturated hydrocarbons produced
- Open-chain products predominate
- Product is partly deoxygenated
- Complete LA and FA conversion

- Significance

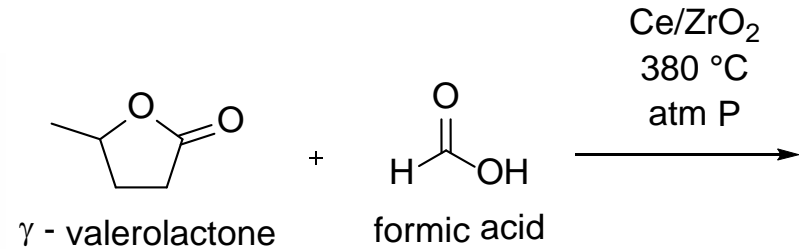
- C6 sugars dehydrate to 1:1 LA:FA



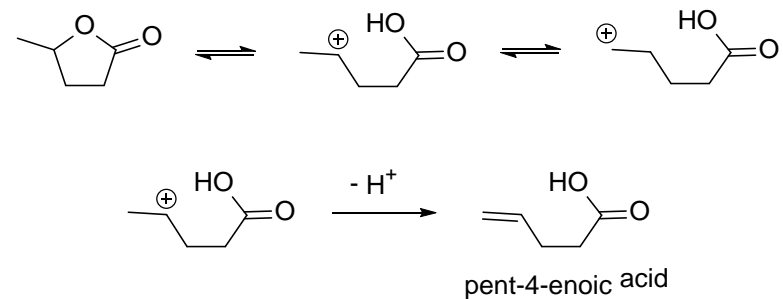
2D NMR of Oils from GVL Conversion



(2D NMR by John Cort, PNNL)



- ▶ 2D NMR spectra of oils shows major presence of *terminal olefins*, consistent with ketonization pent-4-enoic acid, the primary GVL ring-opened intermediate



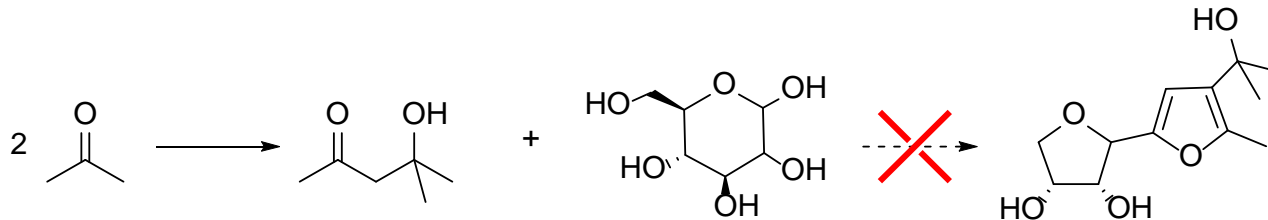
Garcia-Gonzales stumbling block

2,4-Pentanedione is not a fully bioderived precursor:

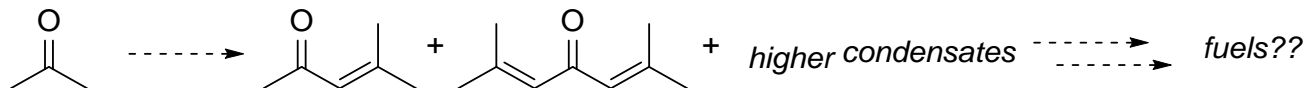
Can we use a bioderived molecule to make a coupling partner?

Acetone produced directly from biomass:

Can we use an acetone condensate for chain extension?

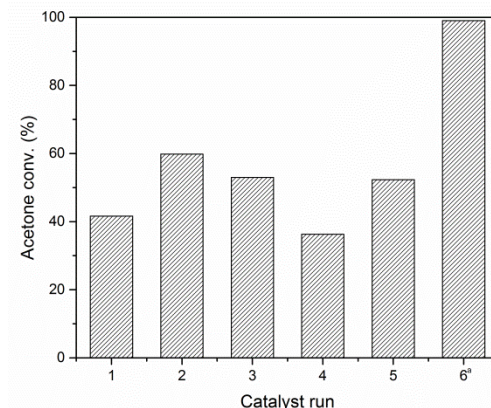
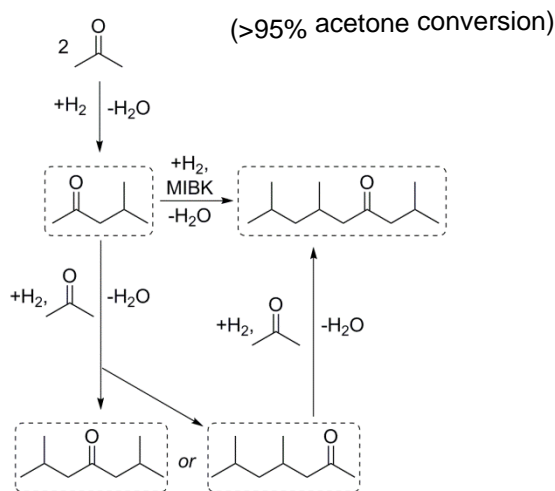
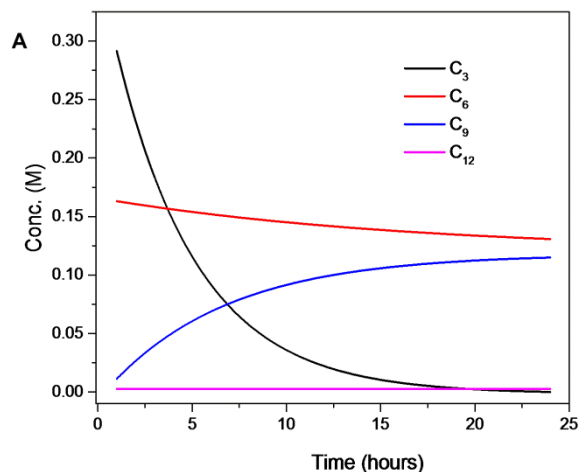
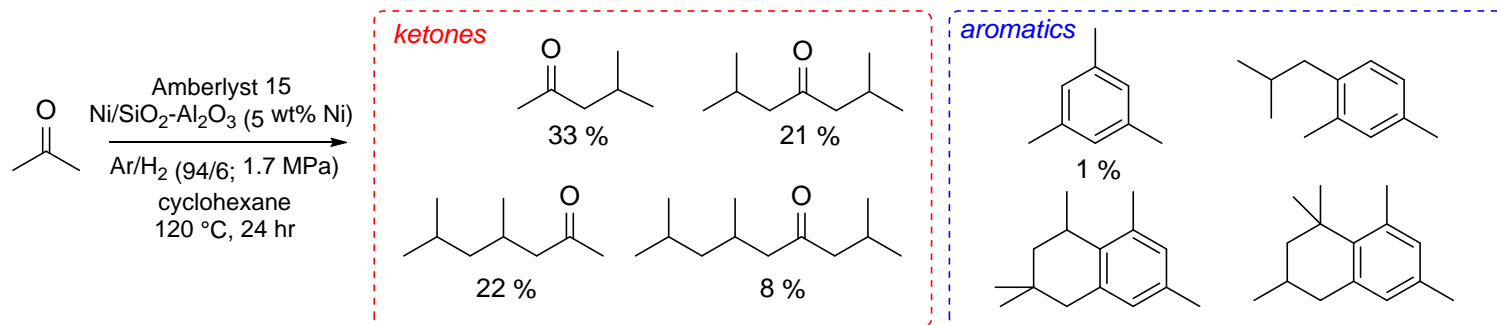


How else can we utilize acetone to produce potential fuels?



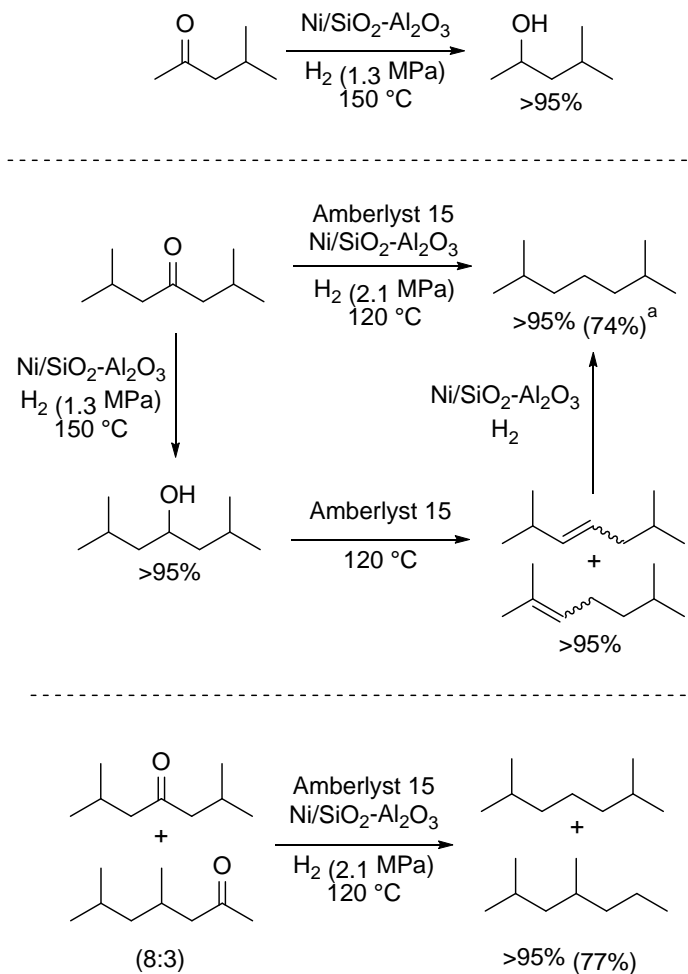
Milder reduction needed

- At low H₂ pressure, acetone is in equilibrium between gas and liquid
- Dilute H₂ enables higher temp. and pressure: full conversion of acetone
- No light products (propene, propane, etc.) observed, good mass balance
- Commercially-available, cheap catalysts used.
- Ideally start from 2-propanol

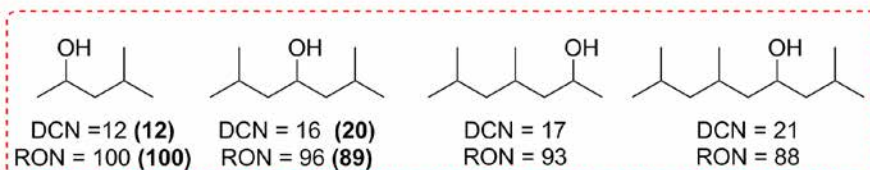
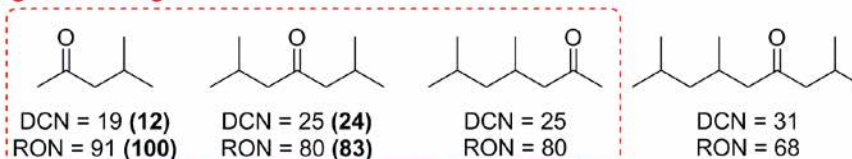


- Catalyst can be recycled w/o loss in activity:
 - Runs 1-5: 1 hour rxn time
 - Run 6: 24 hour rxn time

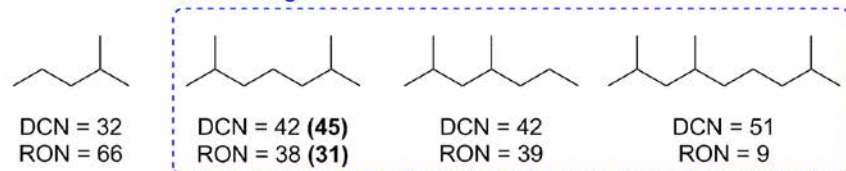
Subsequent defunctionalization



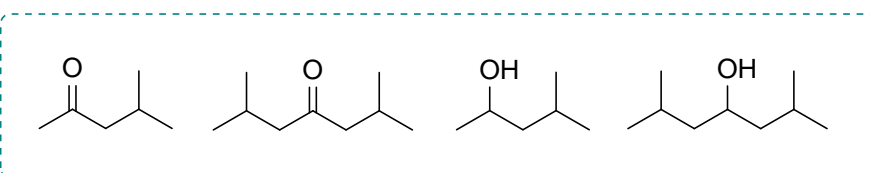
gasoline-range



diesel-range

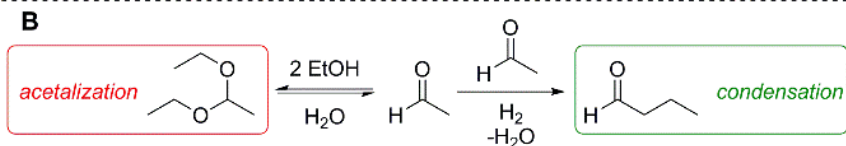
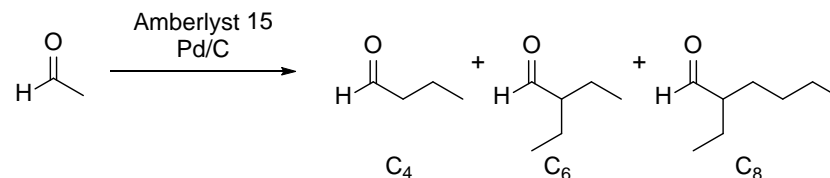
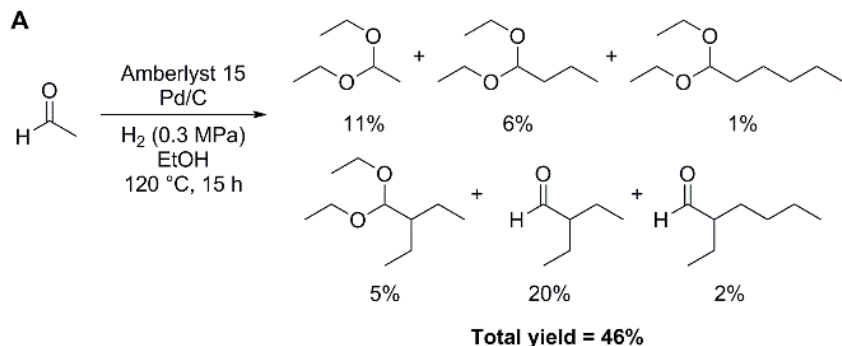


bulk chemicals



Predicted DCN: Energy & Fuels, 2015, 29, 5781.
 Predicted RON: Soc. Automot. Eng., 2005, SP-1972, 203.
 Bolded values: measured using ASTM D6890

Ethanol reduction to acetaldehyde



- Acetals form rapidly in EtOH
- H₂O attempted – no acetals but low conversion
- Aprotic hydrocarbon used – better conversions and selectivity

Entry	Solvent	Temp. (°C)	P (MPa)	Time (h)	Yields (%C) ^a :			
					C ₄	C ₆	C ₈	Total
1	H ₂ O	60	0.2, H ₂	24	<1	2	<1	3
2	H ₂ O	80	0.2, H ₂	24	<1	13	2	15
3	H ₂ O	80	0.3, H ₂	24	<1	10	1	11
4	H ₂ O	120	0.3, H ₂	3	<1	7	1	8
5	H ₂ O	120	0.7, H ₂	3	<1	7	<1	7
6	C ₆ H ₁₂	80	0.3, H ₂	1	9	38	5	51
7	C ₆ H ₁₂	100	0.3, H ₂	1	5	36	5	46
8	C ₆ H ₁₂	120	0.3, H ₂	1	<1	21	4	25
9	C ₆ H ₁₂	40	1.7, Ar/H ₂ ^b	1	5	5	5	15
10	C ₆ H ₁₂	40	1.7, Ar/H ₂ ^b	3	6	9	2	17
12	C ₆ H ₁₂	60	1.7, Ar/H ₂ ^b	1	11	30	3	44
13	C ₆ H ₁₂	60	1.7, Ar/H ₂ ^b	3	7	45	4	56
14	C ₆ H ₁₂	80	1.7, Ar/H ₂ ^b	1	7	47	6	60
15	C ₆ H ₁₂	80	1.7, Ar/H ₂ ^b	3	2	53	8	62
16	C ₆ H ₁₂	100	1.7, Ar/H ₂ ^b	1	3	26	3	32
17	C ₆ H ₁₂	100	1.7, Ar/H ₂ ^b	3	1	34	5	40

Lower yields at higher temperatures

