

Recovering and Upgrading Biogenic Carbon in Biomass-Derived Aqueous Streams

WBS: 2.3.1.310/311

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

Thermochemical Conversion

March 7th, 2017

Project Leads:

Karl Albrecht - PNNL

Calvin Mukarakate - NREL

Robert Dagle – PNNL

Kim Magrini - NREL

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

Challenge: Converting biomass to fuel produces **aqueous streams**

1. These streams contain **expensive biogenic carbon**
2. The carbon is treated as **waste** or processed for **heating gas**

Goal Statement: Develop **separation** and **conversion** technologies for **concentrating** and **valorizing** aqueous phase biogenic carbon into value-added **co-products** to **reduce** modeled biomass-derived fuel **MFSP** by more than 5%.

- Develop liquid-liquid extraction and adsorption, and leverage membrane technology (ANL & NREL) and sorbents from industrial partners to concentrate organics
- Develop catalytic conversion technologies and leverage expertise from PNNL, NREL and industrial partners
- Validate the technologies with TEA, including which co-products to target

Outcome: Demonstrate technologies for redefining aqueous phase carbon from **liability to revenue** generating feedstock.

Quad Chart Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 17%

Budget

	FY15 Costs	FY16 Costs	Total Planned Funding (FY17- Project End Date)
DOE Funded	\$1,902	\$1,920	\$5,250

*FY17 operating budget reduced to \$750k

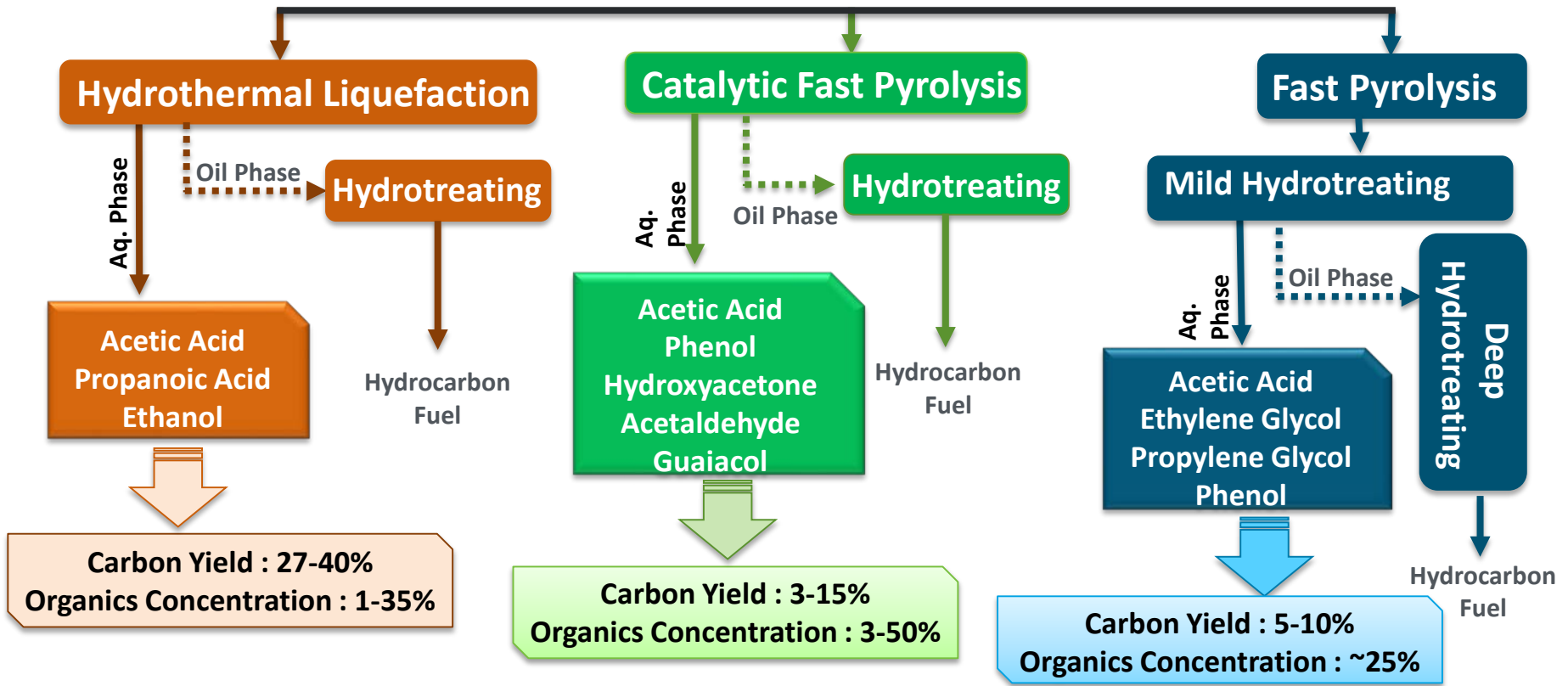
Barriers addressed & Actions

- Ct-L: Aqueous Phase Utilization and Wastewater Treatment
- Ct-M: Cost-Effective Hydrogen Production and Utilization
 - *Recover aqueous carbon; make and sell chemical co-products or H₂; lower MFSP*

Partners

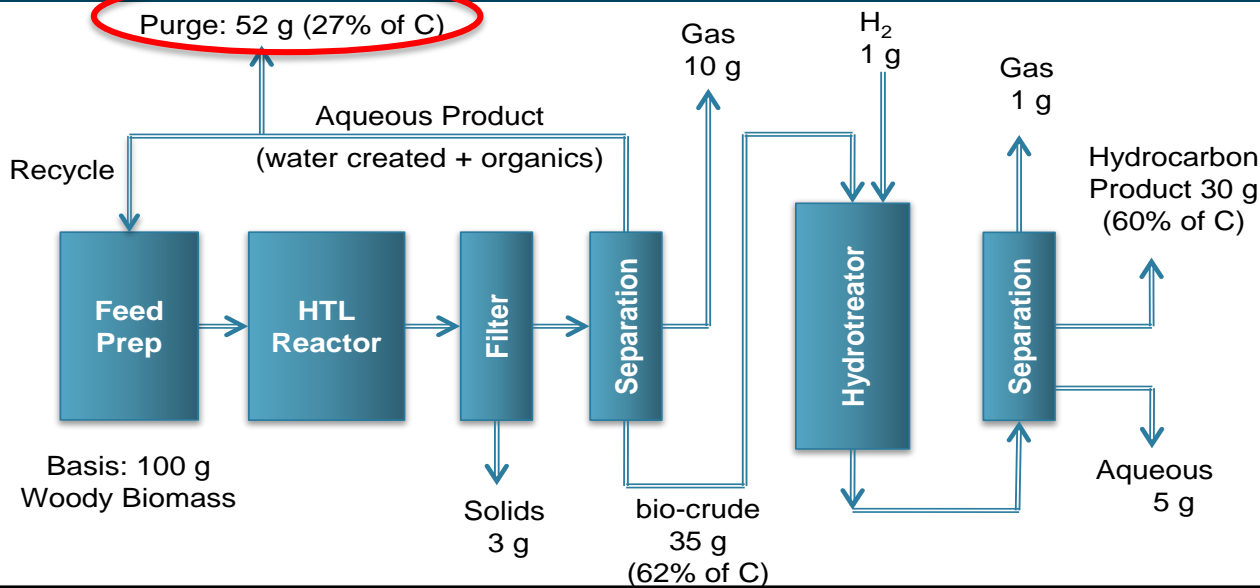
- **National Labs**
 - PNNL (82%)
 - NREL (18%)
 - ORNL and ANL
- **Industry**
 - Johnson Matthey, MEL, W.R. Grace, VTT, Genifuel, SRI International
- **University**
 - Utah State
- **Other Collaborations**
 - USDA

1 - Project Overview: Feedstocks and Processes



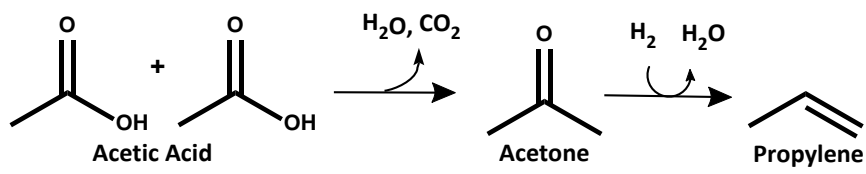
**Significant amounts of biogenic carbon report to aqueous phases
Aqueous phases have diverse chemical compositions**

1 - Project Overview: Example of Impact with HTL

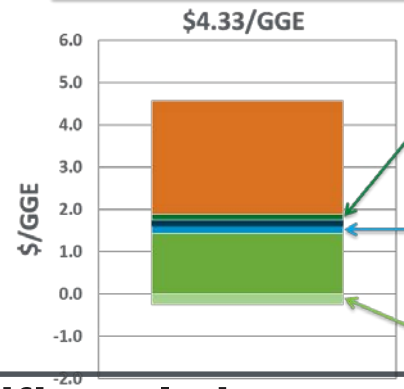


Significant biogenic carbon in aqueous purge

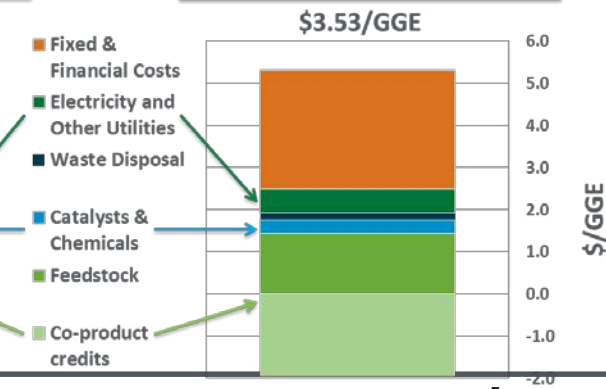
Baseline treatment technology is unproven anaerobic digestion



Anaerobic Digestion



Catalytic Upgrading



1. Recover carbon
2. Convert acids to olefins
3. Lower MFSP 18% (\$0.80/GGE)

Valorizing aqueous phase C significantly improves process economics

Increase Credits: Add valuable co-products (chemicals, hydrogen, more fuel)

Decrease Expenses: Diminish wastewater volume and clean-up costs

2 – Technical Approach



Task 1. Separations

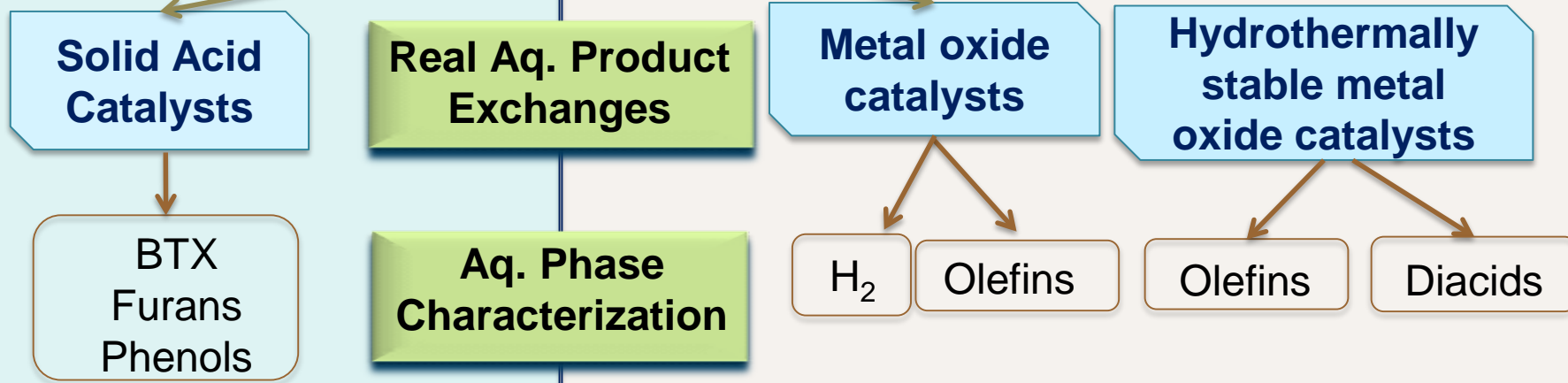
- Membranes
- Sorbents/adsorption
- Azeotropic distillation
- Liquid-liquid extraction
- Activated carbon adsorption

Techno-economic Analyses

Task 2. Thermocatalytic Conversion

Gas Phase Upgrading

Condensed Phase Upgrading



Task 3. Aqueous Phase Options

Compile characterization, TEA, and regulatory data into a single reference document for stakeholders



2 – Management Approach

- Research Strategy and Themes
 - Emphasis on testing **real biomass-generated** aqueous streams
 - Develop **separation methods in parallel** with catalytic process development
 - **Catalyst discovery**: high-throughput testing methods
 - **Catalyst validation** and process development using flow reactors
 - Techno-economic analyses (TEA) to **guide research and set technical targets**
- Project Management Approach
 - ☑ Merit Reviewed AOP – July 2014 & April 2016
 - ☑ Peer Reviewed: 2013, 2015, 2017 – comments implemented to guide research
 - ☑ Quarterly internal milestones – Currently all met and on track to continue
 - ☐ Annual major milestones – Explicit goals to demonstrate progress:
 - ☐ FY17: 75% conversion of oxygenates to olefins; FY18: Industrial stakeholder guiding document completion; FY19: 80% water rejection with membranes
 - ☐ Go/No Go – March 2018: Feasibility demonstration of innovative selective oxidation process: *“Achieve > 5% yield to desired di-carboxylic acids or precursors...”*

Critical Success Factors

Technical: Concentrating and valorizing dilute organics to produce co-products

Market: Technologies that reduce modeled MFSP by at least 5%.

Business: Provide industry with options for reducing wastewater treatment costs

3 – Research Progress

A) Catalytic Fast Pyrolysis (CFP) Aqueous Phase

1. Separation

Distillation + resin adsorption

Recovers phenols from aqueous stream to make resins + polymers

2. Catalytic Conversion

Acid catalyst conversion to form aromatics and furans

B) Hydrothermal Liquefaction (HTL) Aqueous Phase

1. Separation

Liquid-liquid extraction + activated carbon adsorption

Reduces catalyst poisons (dissolved solids and color bodies)

2. Catalytic Conversion

Condensed phase ketonization

Gas phase ketonization + steam reforming

3 – Research Progress

A) Catalytic Fast Pyrolysis (CFP) Aqueous Phase

1. Separation

Distillation + resin adsorption

Recovers phenols from aqueous stream to make resins + polymers

2. Catalytic Conversion

Acid catalyst conversion to form aromatics and furans

B) Hydrothermal Liquefaction (HTL) Aqueous Phase

1. Separation

Liquid-liquid extraction + activated carbon adsorption

Reduces catalyst poisons (dissolved solids and color bodies)

2. Catalytic Conversion

Condensed phase ketonization

Gas phase ketonization + steam reforming

Ex-Situ CFP Separations: Recover Phenolics

CFP with Zeolite

Acetic Acid^s

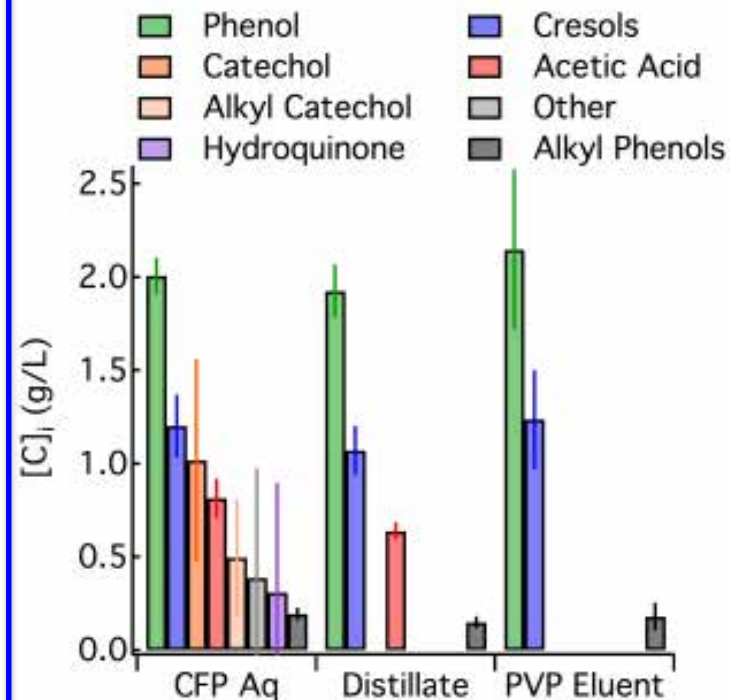


Phenolics
CH₃OH



PVP Effluent
Acetic Acid

To Polymer Synthesis



Goal: Separate phenol and cresols from organics in the DCR aqueous phase product:

Stage 1: Distillation: Phenolics + Acetic Acid / Catechols + Other Split

Stage 2: PVP Resin: Phenolics Dewatering and Separation of Acetic Acid

Stage 3: Remove MeOH and Residual Water from Phenolics

Stage 4: Produce polycarbonates and phenol formaldehyde resins from biogenic phenolics

Overall Recovery 91%, Phenolics Purity > 99%

Wilson, et al. Green Chemistry, submitted

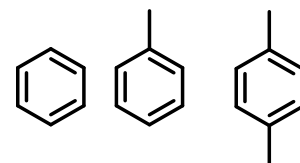
In-situ CFP Catalysis: Acidic Catalysts for Aromatics

Establish baseline experiments to guide future research

- Conduct **state of technology (SOT)** experiments using in-situ CFP aqueous phase¹
- Feed the data in TEA models and compare with design case²

Goals for SOT experiments

- Assess **yield and selectivity** of conversion to **BTX**
- Compare **best** catalysts (HZSM-5 and Ga/HZSM-5)



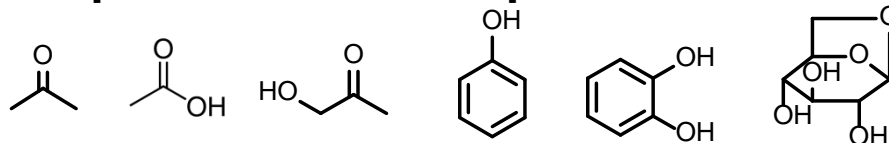
Aqueous phase from catalytic fast pyrolysis*

Carbon: 13.8 wt%

Hydrogen: 8.1 wt%

Water: 67 wt%

Composition of CFP Aqueous Phase*

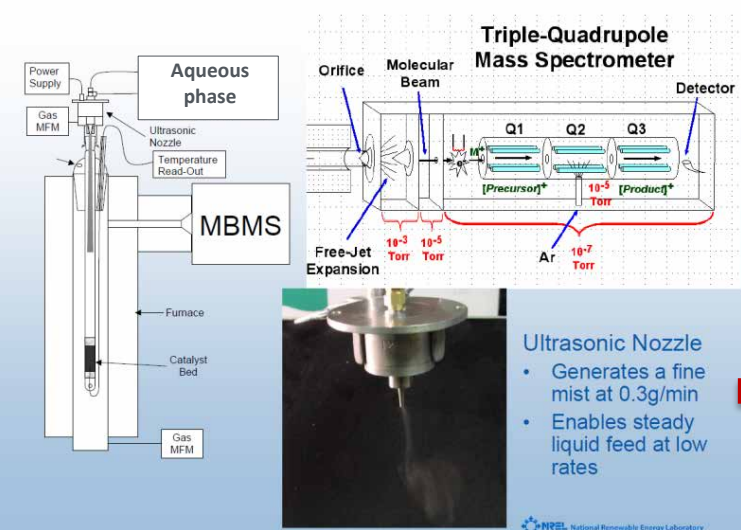


Contain some unreacted pyrolysis products

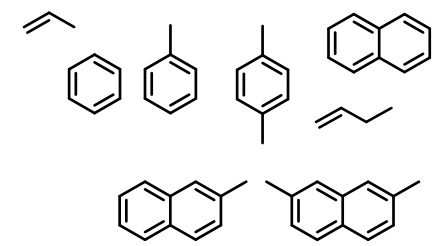
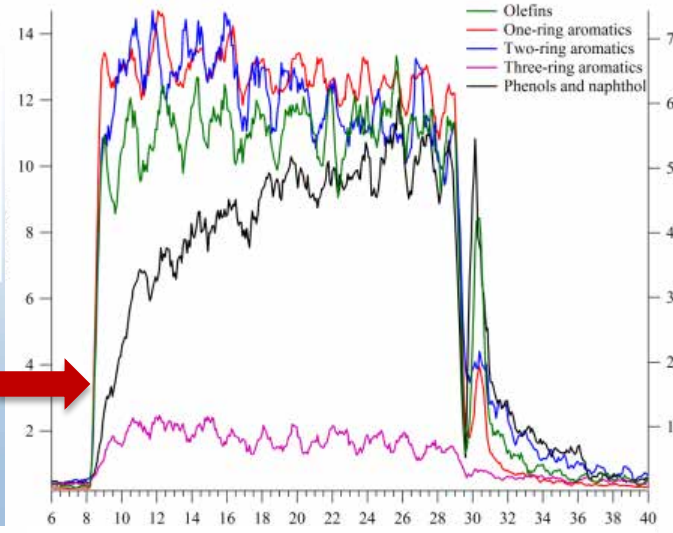
¹ Paasikallio et al., *Green Chem.*, 2014, 16. pp. 3549-3559

² NREL Technical Report NREL/TP-5100-62455, March 2015

In-situ CFP Catalysis: Acidic Catalysts for Aromatics

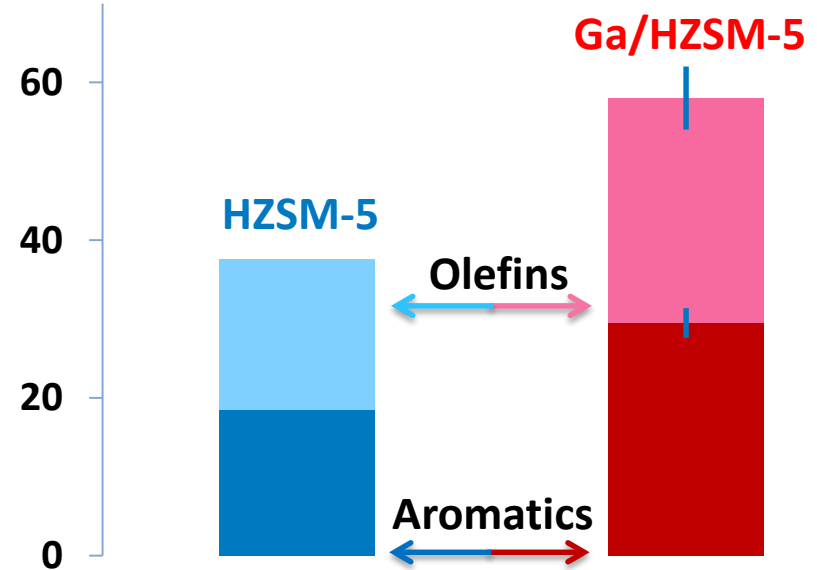


Feed: *in-situ* CFP aqueous phase
T: 500 °C; WHSV: 1 hr⁻¹



Aromatic and olefin products

Product Carbon Yield (%)



- Light organics form **olefins** and **aromatic hydrocarbons**¹ using NREL and Johnson Matthey catalysts
- TEA: Ga/HZSM-5 gave the same overall contribution to MFSP as design case²
- TEA Guidance: Potential to **decrease MFSP by 20 cents/GGE** by focusing on **high value products (furans)** and **removing water**

¹Mukarakate et al., Energy & Fuels., 2017, In press.
²NREL Technical Report NREL/TP-5100-62455, March 2015

3 – Research Progress

A) Catalytic Fast Pyrolysis (CFP) Aqueous Phase

1. Separation

Distillation + resin adsorption

Recovers phenols from aqueous stream to make resins + polymers

2. Catalytic Conversion

Acid catalyst conversion to form aromatics and furans

B) Hydrothermal Liquefaction (HTL) Aqueous Phase

1. Separation

Liquid-liquid extraction + activated carbon adsorption

Reduces catalyst poisons (dissolved solids and color bodies)

2. Catalytic Conversion

Condensed phase ketonization

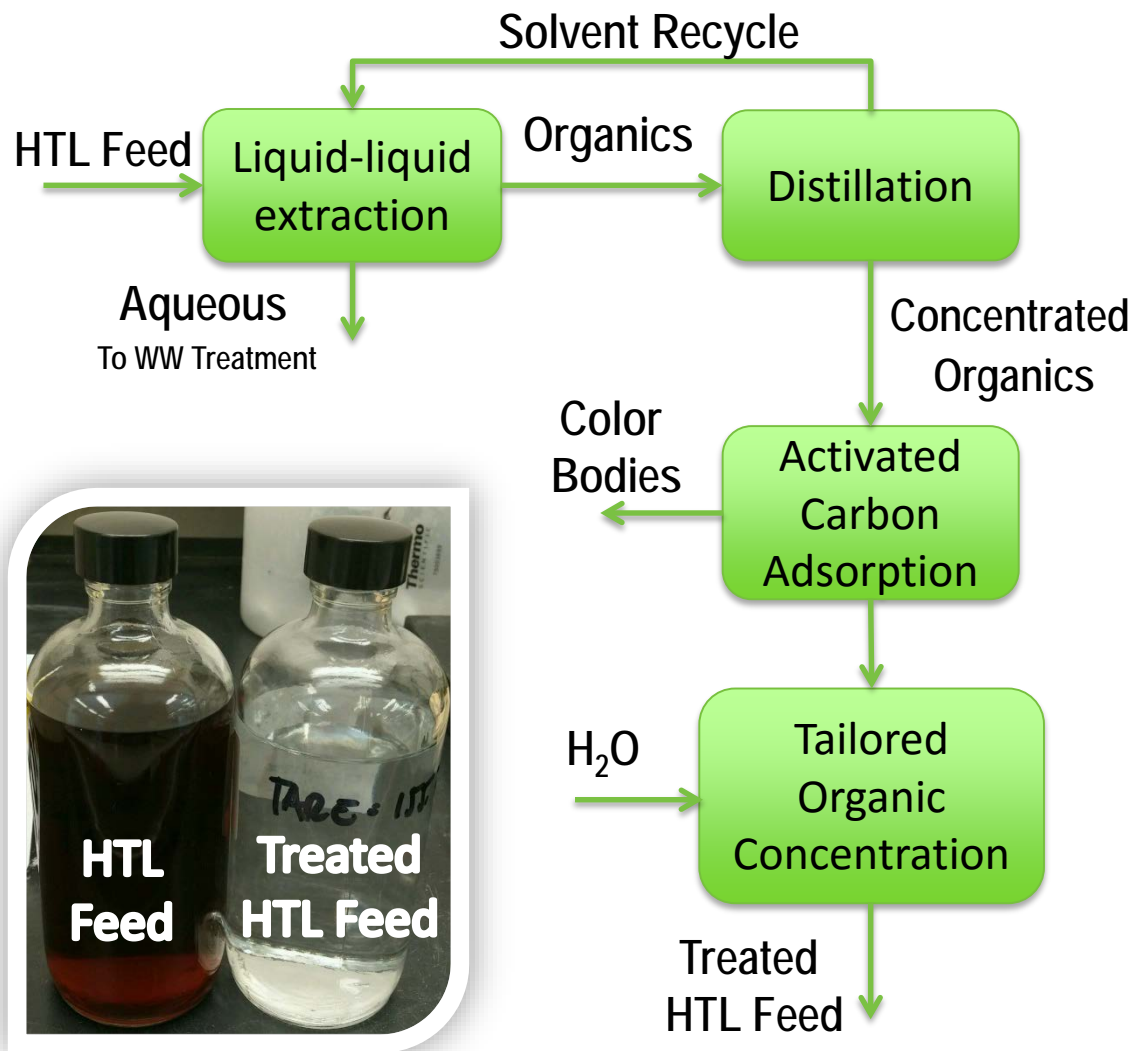
Gas phase ketonization + steam reforming

HTL Separation: Diminish Catalyst Poisons

LC, wt%		
Compounds	HTL Feed	Treated HTL Feed*
Glycolic Acid	1.72	0.19
Formic acid	0.02	0.02
Acetic acid	20.6	9.87
Ethylene Glycol	0.71	0.10
Propylene Glycol	0.03	0.03
Propanoic Acid	3.91	1.65
Ethanol	0.25	0.04
Methanol	1.34	0.00
Methyl Acetate	1.35	0.00

ICP, ppm		
Analytes Name	Real Feed	Treated HTL Feed
Ca	89	27
Mg	60	48
Mn	10	< 2.0
Na	8539	150
P	42	38
S	9	4

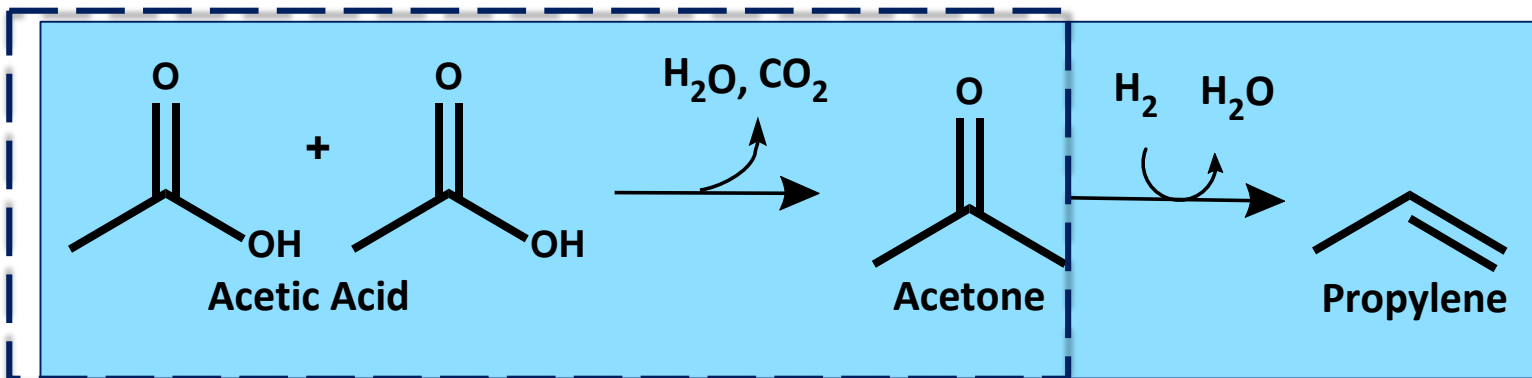
*Tailored to 10% acetic acid for conversion tests on subsequent slides



Extraction + adsorption diminishes dissolved solids and color bodies

HTL Catalysis: Condensed Phase Ketonization

Research Focus



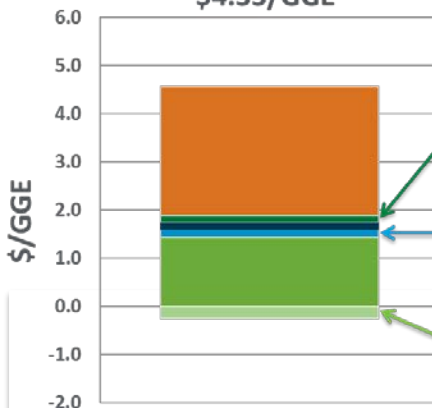
Condensed phase ketonization is the challenging step
Focus: Develop hydrothermally stable ketonization catalysts

TEA Analysis of Process

- Reduces MFSP by 18%
- Includes separation processes
- Includes transportation costs of olefins from plant to buyer

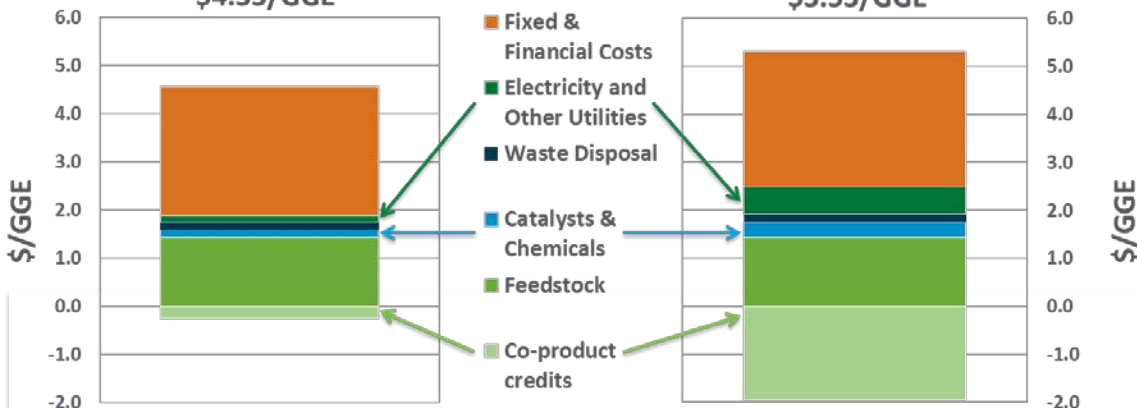
Anaerobic Digestion

\$4.33/GGE



Catalytic Upgrading

\$3.53/GGE

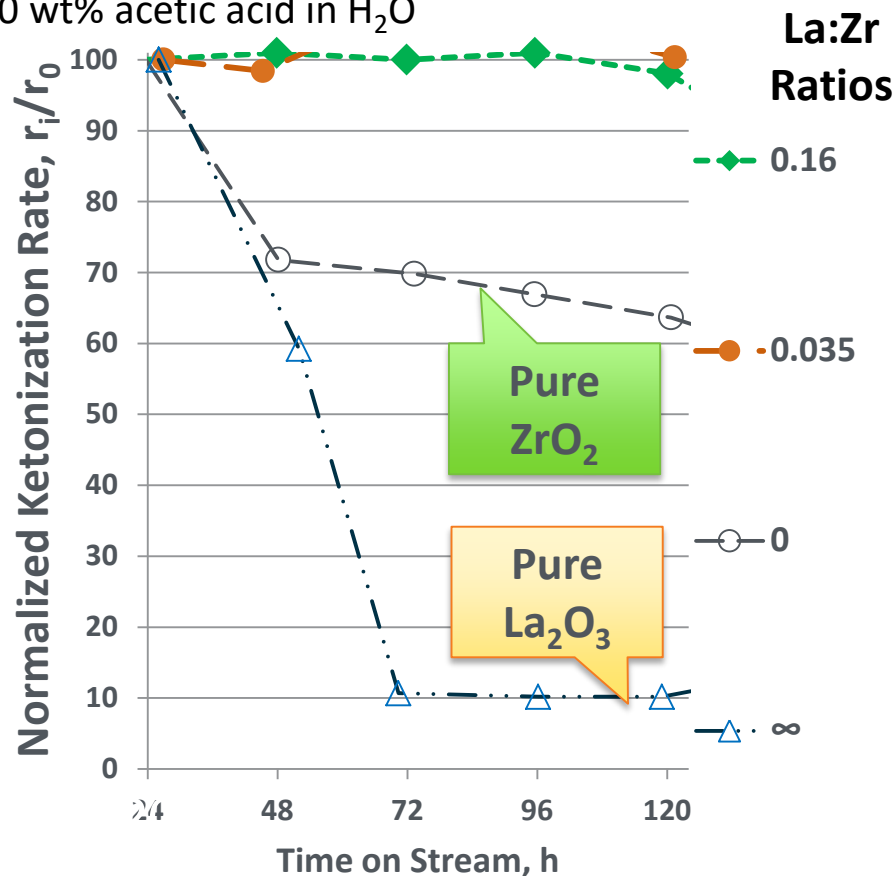
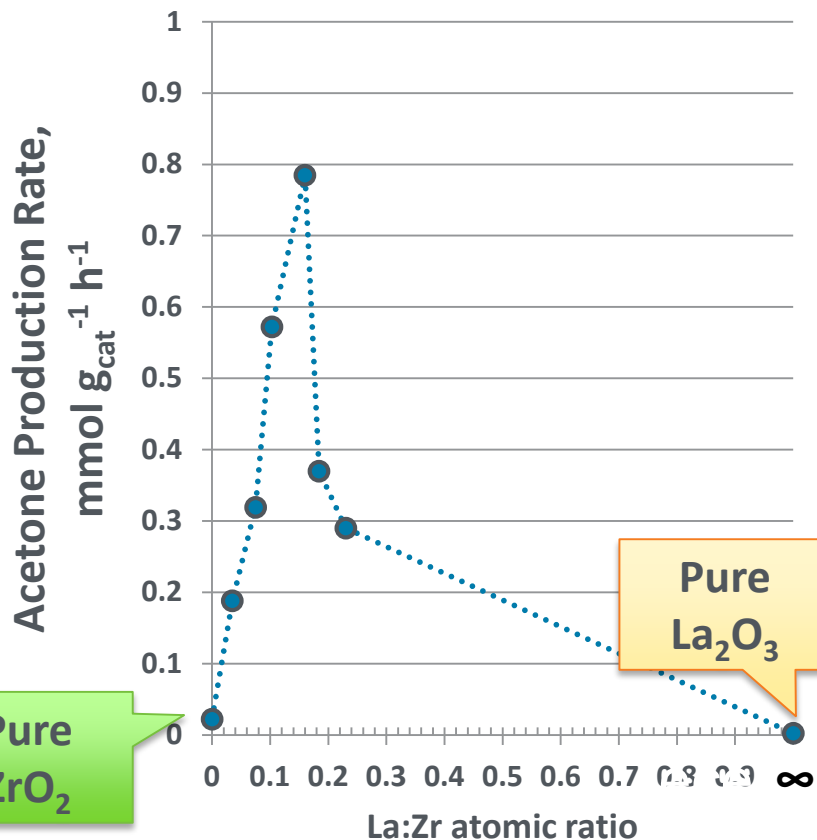


HTL Catalysis: Condensed Phase Ketonization

Reaction conditions:

295°C, 1400 psig, and 10 wt% acetic acid in H₂O

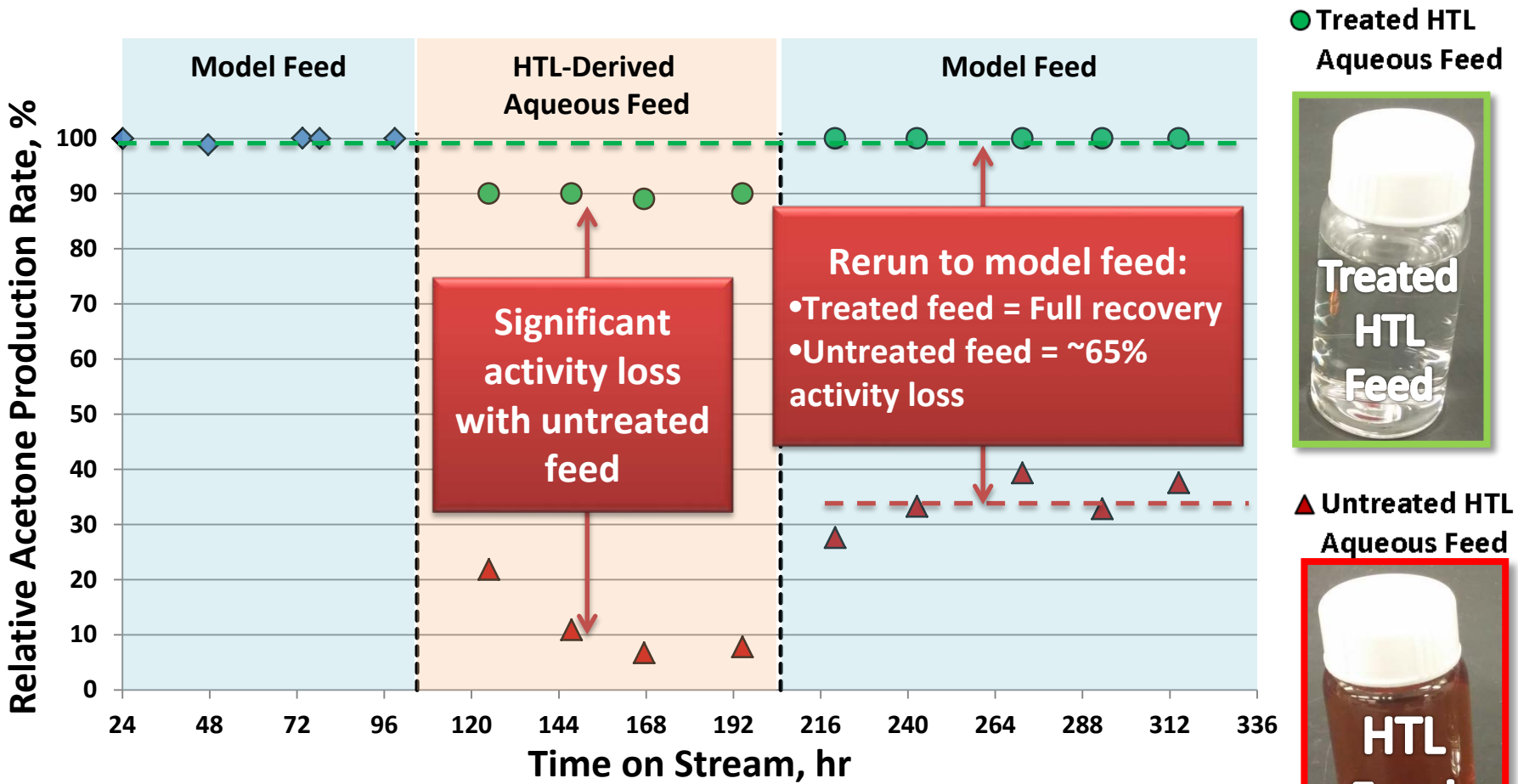
1400+ h on stream demonstrated



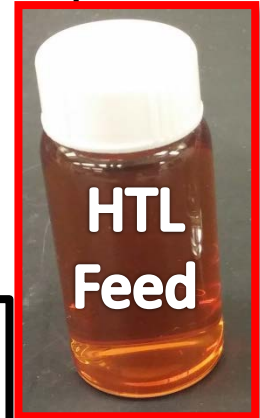
Addition of La₂O₃ to ZrO₂ increases activity ~20x and provides stable activity

HTL Catalysis: Condensed Phase Ketonezation

Reaction Conditions: 295°C, 1400 psig, and 10 wt% acetic acid



▲ Untreated HTL Aqueous Feed

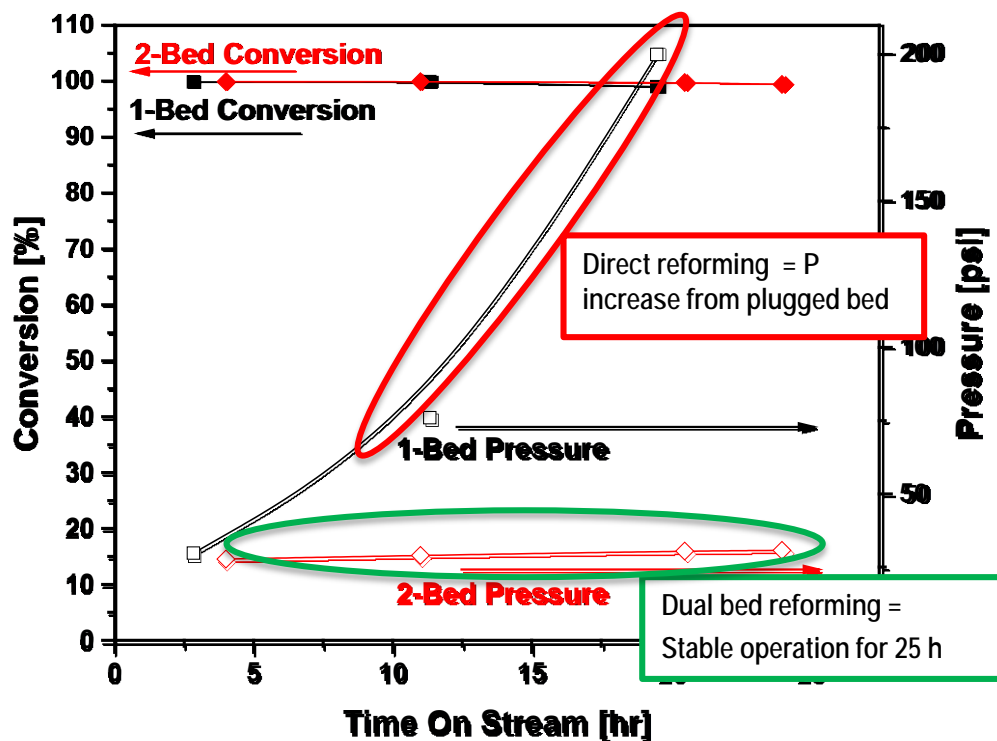
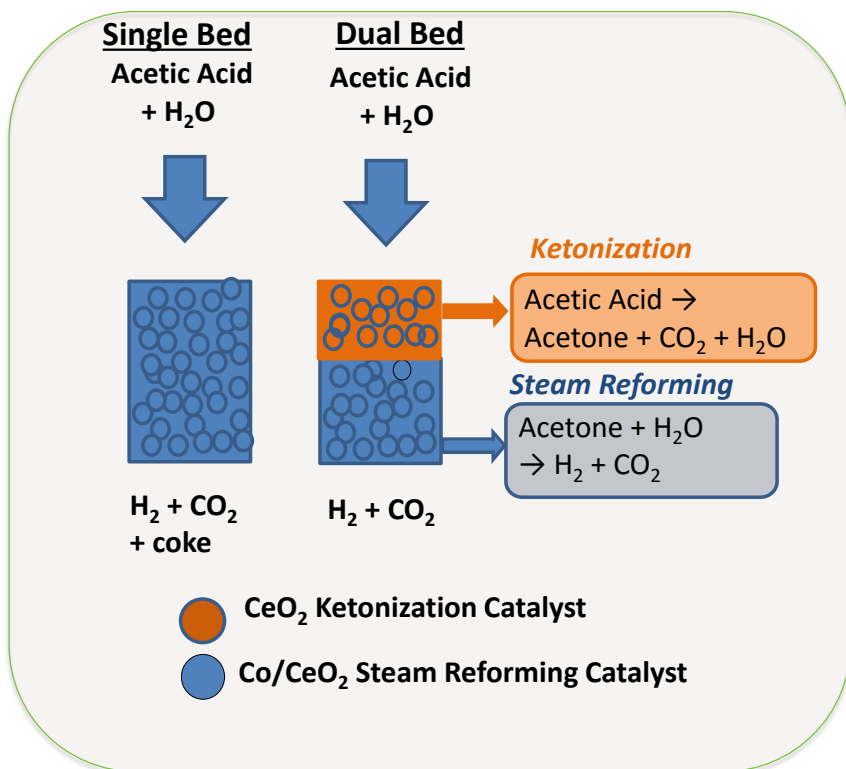


Untreated feed results in activity loss

Liquid extraction + AC adsorption = stable operation

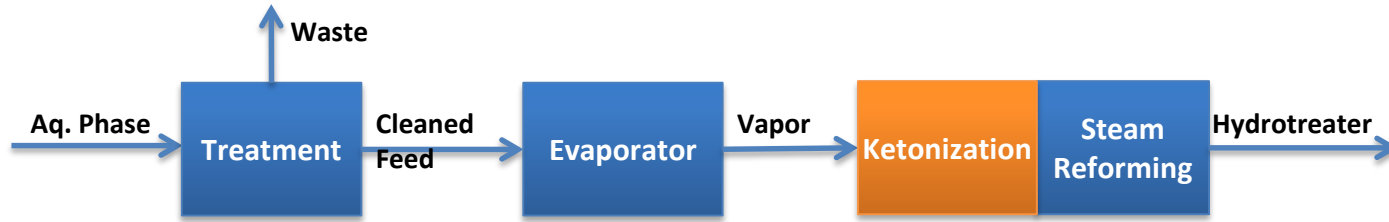
HTL Catalysis: Gas Phase Ketonization + Reforming

- ▶ **Challenge:** Direct steam reforming of organic acids generates coke
- ▶ **Solution:** Dual bed reforming: Ketonize acetic acid to acetone, then steam reform

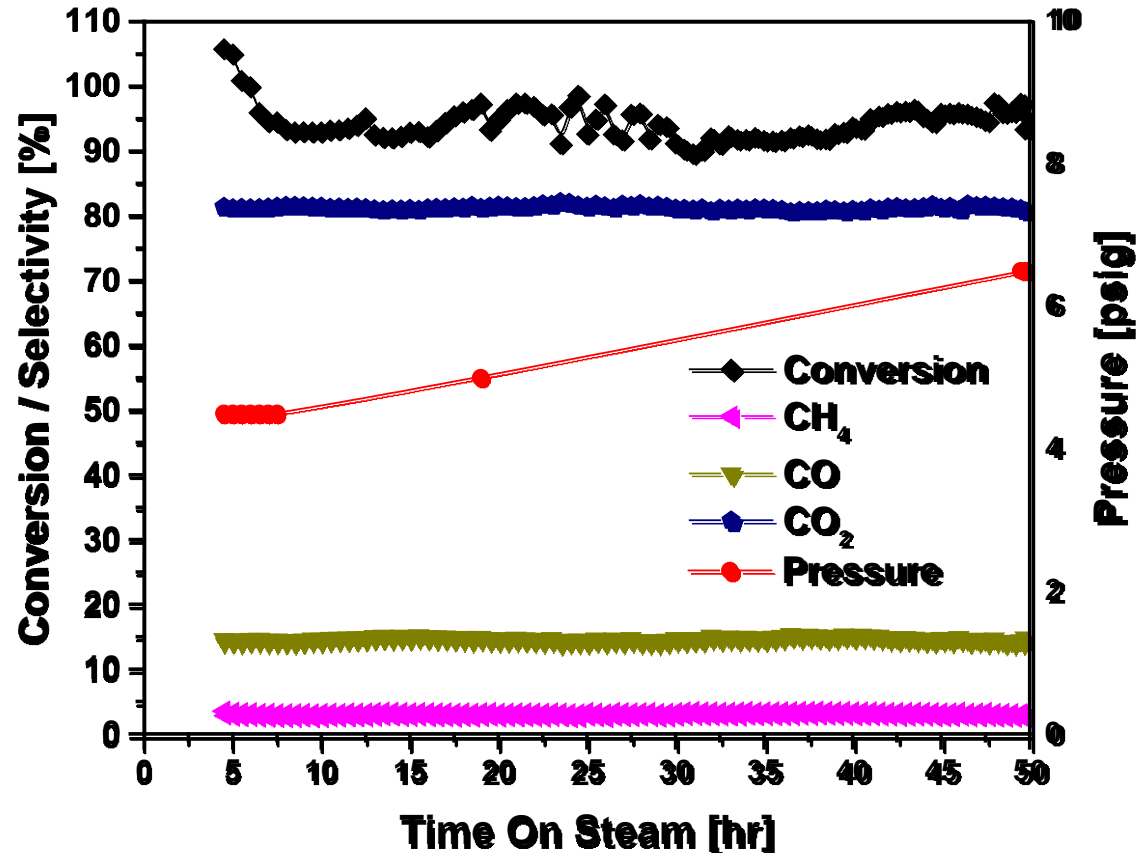
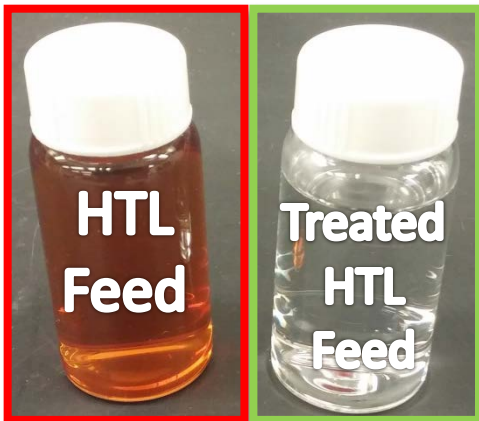


- ▶ **Cobalt catalyst developed.** Conditions analogous to naphtha reforming (450-550°C)
 - More stable and selective to H₂ vs. Ni or Rh catalysts
 - Generate kinetic concentration of CH₄ lower than expected by thermodynamics

HTL Catalysis: Gas Phase Ketonization + Reforming



- ▶ Treated HTL-feed demonstrated for 50 h (consumed all feed)
- ▶ Primary constituents were organic acids
 - Tailored to S/C ratio = 3.5
 - Acetic Acid – 29 wt%
 - Propionic Acid – 5 wt%
- ▶ H₂ yield: 96%



500 °C, 1 atm, 40,000 hr⁻¹, S/C = 3.5 (mol)

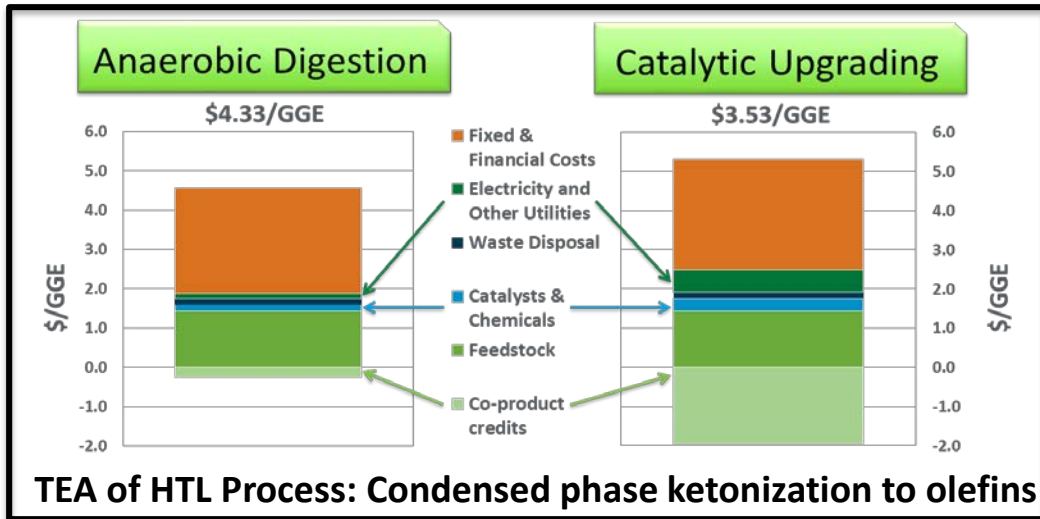
Task 3: Aqueous Phase Options

Aqueous Phase Type	Partner	Analyses Performed/Processes Tested				Notes
		Characterization	Ketonization	Reforming	Zeolite	
FP Aqueous Phase (partially upgraded bio-oil)	PNNL	✓	✓	✓		Home heating oil project, Stable condensed phase ketonization & SR
Wood HTL	PNNL	✓	✓	✓		Separations facilitate ketonization and reforming
Corn Stover HTL	PNNL	✓	✓	✓		Separations facilitate ketonization and reforming
FP Aqueous Phase	NREL	✓				Received early in project, sugar derivatives challenging
Algae HTL	SRI	✓				Short comm in prep with SRI
Catalytic FP	Utah State	✓	✓	✓		Sugar derivatives challenging to separate & process
Catalytic FP	VTT	✓	✓	✓		Sugar derivatives challenging to separate & process
Fast pyrolysis	USDA		✓			Sample just received – testing underway
Algae HTL	PNNL	✓	✓			Low concentration of carbon difficult to recover/utilize
Catalytic FP (2 in. riser)	NREL	✓	✓	✓		Sugar derivatives challenging to separate & process
Catalytic FP (fluidized bed)	NREL	✓			✓	Sugar derivatives challenging to separate & process

Compile characterization, economic and regulatory data into a single document for stakeholders

4 – Relevance

1. We directly support BETO's mission by lowering MFSP \$0.15-0.80/GGE and increasing C yield for numerous conversion pathways



March 2016 MYPP
Ct-L: Aqueous Phase Utilization and Wastewater Treatment:
“...research is needed to...convert the organics present to hydrogen, biochemicals or fuels to improve overall process yield”

2. Our project supports numerous stakeholders at the forefront of bioenergy research

Collaborations with numerous bioenergy stakeholders

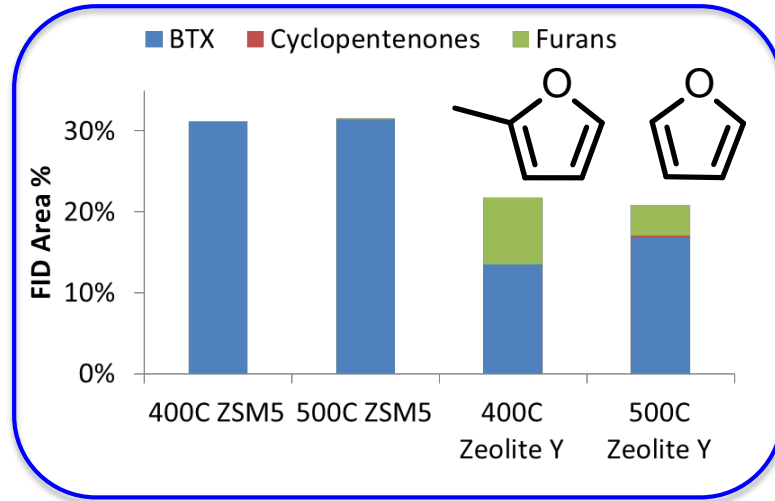
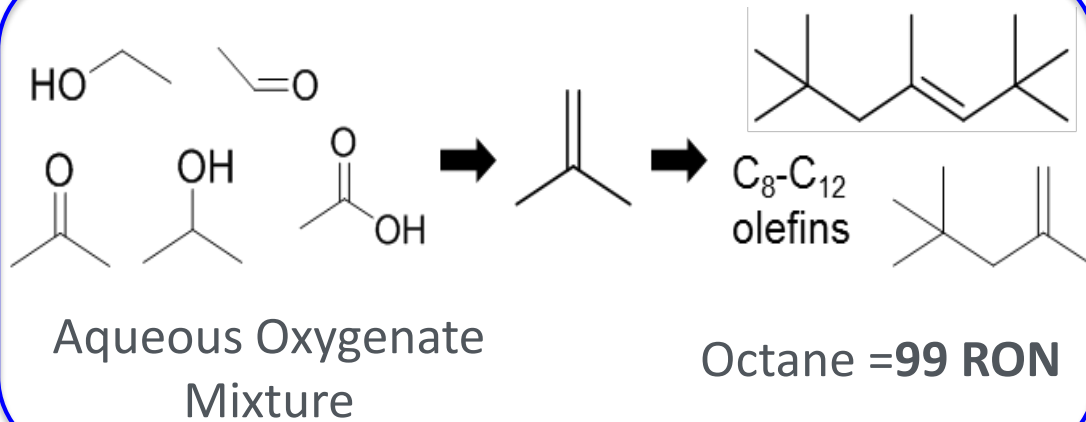
2017 Science Theme Award presented by DOE's EMSL to investigate the hydrothermally stable ketonization catalyst

Research which is attracting external funding

Computational research for more active and stable hydrothermal catalysts

Future Work

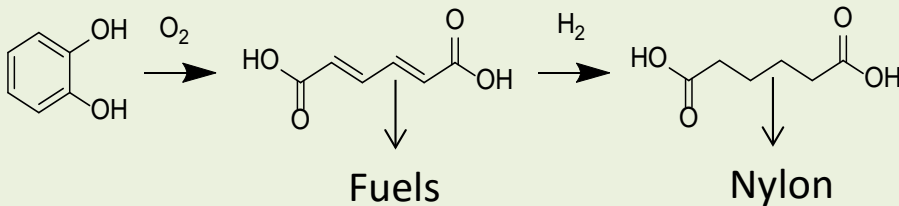
MFSP reduction of 5-20% feasible for all processes



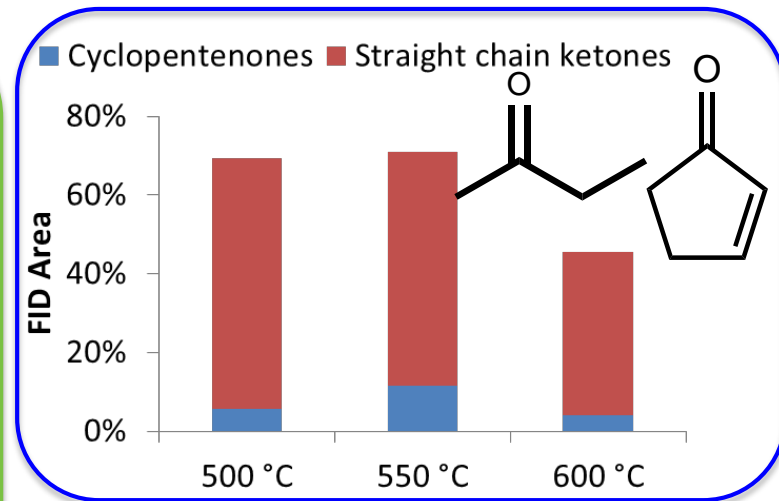
Develop new heterogeneous **gas phase catalysts** for olefins, furans and ketones

Partial Oxidation

Goal: Conversion of refractory aqueous phase compounds to additional chemicals or fuels



Discover new heterogeneous **condensed phase** catalysts for aryl alcohol conversion



5 – Future Work: Major Milestones

Level	Performance Measure	Task	Planned Completion Date
Annual Milestone	Evaluate the yield of olefins for 50 hrs on stream at >75% conversion with the $Zn_xZr_yO_z$ catalyst with an HTL or CFP derived aqueous phase	Conversion	9/30/17
Go/No Go	Demonstrate feasibility of oxidation chemistry: Achieve > 5% yield to desired di-carboxylic acids or switch to complete oxidation investigations to wastewater cleanup	Conversion	3/9/2018
Annual Milestone	Finalize draft of the Aqueous Phase Options Technology guiding document	Aqueous Phase Options	9/30/2018

All milestones on track for timely completion

Summary

1. Waste aqueous phases will be produced by biorefineries
2. We are developing separation and catalytic processing options to convert “waste” aqueous carbon into co-products
3. We will provide economic and regulatory guidance to biorefinery stakeholders through our compiled aqueous roadmap
4. PNNL and NREL are well positioned to perform this work with ready access to biomass-derived streams

We are reducing the technical and economic risks associated with biorefineries through aqueous phase biogenic carbon valorization

Acknowledgments

Funding provided by the U.S. Department of Energy
Bioenergy Technologies Office

Thank you for your attention!

karl.albrecht@pnnl.gov

calvin.mukarakate@nrel.gov

robert.dagle@pnnl.gov

Kim.magrini@nrel.gov

Publications

1. Panisko, Ellen, Thomas Wietsma, Teresa Lemmon, Karl Albrecht, and Daniel Howe. "Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks." *Biomass and Bioenergy* 74 (2015): 162-171.
2. Mei, Donghai, VL Dagle, X Rong, KO Albrecht, and RA Dagle. "Steam Reforming of Ethylene Glycol over MgAl₂O₄ Supported Rh, Ni, and Co Catalysts." *ACS Catalysis* 2016, 6, 315–325.
3. Maddi, Balakrishna,, Ellen Panisko, Karl Albrecht, and Daniel Howe. Qualitative Characterization of the Aqueous Fraction from Hydrothermal Liquefaction of Algae Using 2D Gas Chromatography with Time-of-flight Mass Spectrometry. *JoVE (Journal of Visualized Experiments)*. 2016 Mar 6(109):e53634-e53634.
4. Maddi, Balakrishna, Ellen Panisko, Thomas Wietsma, Teresa Lemmon, Marie Swita, Karl Albrecht, and Daniel Howe. "Quantitative characterization of the aqueous fraction from hydrothermal liquefaction of algae." *Biomass and Bioenergy* 93 (2016): 122-130.
5. Maddi, Balakrishna,, Ellen Panisko, Thomas Wietsma, Teresa Lemmon, Marie Swita, Karl Albrecht, and Daniel Howe. "Quantitative Characterization of Aqueous Byproducts from Hydrothermal Liquefaction of Municipal Wastes, Food Industry Wastes, and Aquatic Feedstocks Grown on Waste." Accepted to *ACS Sustainable Chemistry & Engineering* (2016)
6. C. Mukarakate, R. Evans, S. Deutch, T. Evans, A. Starace, J. Dam, M. Watson, K. Magrini. Reforming Biomass Derived Pyrolysis Bio-oil Aqueous Phase to Fuels. *Energy & Fuels*, 2017, DOI: 10.1021/acs.energyfuels.6b0246.
7. N. Wilson, M. Price, C Mukarakate, R. Katahira, M. Griffin, J. Dorgan and M. Nimlos. Resol Resin from a Biorefinery Waste Stream. Submitted to *Green Chemistry*.
8. Lopez-Ruiz, Juan A., Alan R. Cooper, and Karl O. Albrecht. "Enhanced Hydrothermal Stability and Catalytic Activity of LaxZryOz Mixed Oxides for the Ketonization of Acetic Acid in the Aqueous Condensed Phase". Submitted to *ChemCatChem*.
9. K. Magrini, R. Evans, A. Starace, S. Deutch, D. Lee, C. Mukarakate. Developing and evaluating fluidizable bimetallic reforming catalysts to produce hydrogen from reforming CFP derived aqueous phase, *Applied Catalysis A*, in prep.

Presentations

1. Albrecht, K.O., A.R. Cooper, J.G. Frye, Y. Zhu, D. Mei, S-J. Lee, T.L. Lemmon, H.M. Job. Catalytic Conversion of Organic Compounds in the Aqueous Phase Produced by the Hydrothermal Liquefaction of Terrestrial Biomass. Presented at TCS 2014 on September 2, 2014.
2. Albrecht, Karl O., Alan R. Cooper, John G. Frye, Yunhua Zhu, Donghai Mei, Juan Lopez-Ruiz, Teresa L. Lemmon, Diana N. Tran. "Condensed Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass." AIChE 2015 Spring Meeting. Austin, TX. April 27, 2015.
3. Cai, Qiuxia, Juan A. Lopez-Ruiz, Alan R. Cooper, Karl Albrecht, Jian-guo Wang, Donghai Mei. "Effects of Solvents on Acetic Acid Ketonization over Zirconia Catalysts." North American Catalysis Society North American Meeting. Pittsburgh, PA. June 17, 2015.
4. Albrecht, Karl O., Alan R. Cooper, Juan A. Lopez-Ruiz, Heather M. Job, John G. Frye, Diana N. Tran. "Condensed Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass." NACS NAM. Pittsburgh, PA. June 17, 2015.
5. AR Cooper, KO Albrecht, JA Lopez-Ruiz, JG Frye, and DN Tran. 2015. "Condensed Aqueous Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass ." Presented by Alan R. Cooper at ACS, Boston, MA on August 17, 2015.
6. JA Lopez-Ruiz, AR Cooper, JG Frye, HM Job, and KO Albrecht. 2015. "Development of Hydrothermally Stable Catalysts for the Thermochemical Conversion of Carbon-Containing Aqueous Streams into Fuels and Chemicals ." Presented by Juan A. Lopez-Ruiz at Pacific Coast Catalysis Society Meeting 2015, Richland, WA on September 17, 2015.
7. Juan A. Lopez-Ruiz, Alan R. Cooper, Qiuxia Cai, Donghai Mei, and Karl O. Albrecht. Mechanistic Investigation of Acetic Acid Ketonization over Stable ZrO₂-based Catalysts under Hydrothermal Reaction Conditions. Presented at the 26th Biennial Organic Reactions Catalysis Society Conference. March 30, 2016. Miami, FL.
8. Stephen Davidson, Kurt Spies, Igor Kutnyakov, Vanessa Dagle, Karl Albrecht, and Robert Dagle. "Steam Reforming of Bio-derived Oxygenates: Coupling Ketonization for Greater Stability." TCS 2016: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Chapel Hill, NC. Oral presentation. November 1-4, 2016.
9. Juan Lopez-Ruiz, Luis Estevez, Alan Cooper, Yunhua Zhu, and Karl Albrecht. "Development of ZrO₂-based Hydrothermally Stable Catalysts for the Catalytic Upgrading of Biomass-Derived Aqueous Streams" TCS 2016: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Chapel Hill, NC. Oral presentation. November 1-4, 2016.
10. Balakrishna Maddi, Ellen Panisko, Thomas Wietsma, Teresa Lemmon, Marie Swita, Karl Albrecht, and Daniel Howe. Characterization of Aqueous Byproducts Obtained from Hydrothermal Liquefaction of Industrial and Municipal Waste Streams. TCS 2016: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Chapel Hill, NC. Poster presentation. November 1-4, 2016.
11. A. Starace, R. Evans, E. Palmiotti, K. Magrini and C. Mukarakate. "Valorization of Biorefinery Waste: Catalytic Upgrading of Catalytic Fast Pyrolysis Aqueous Phase to Chemical Intermediates." TCS 2016: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Chapel Hill, NC. Poster presentation. November 1-4, 2016.
12. N. Wislon, M. Price, C. Mukarakate, J. Dorgan, M. Nimlos. Phenols from Catalytic Fast Pyrolysis. TCS 2016: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Chapel Hill, NC. Poster presentation. November 1-4, 2016.

Responses to Previous Reviewers' Comments

- **2015 Peer Review**
- Comment: Once again, there is not enough focus on separations that is required.
- Response: Based on the reviewers' helpful comments, we do plan to add emphasis to our ongoing separations investigations. We are planning to look at liquid-liquid separations using commercially available solvents and lab-scale distillation studies to concentrate organics. Experimental data from our separation studies are planned for implementation into the next updating of the TEA, now that we are beginning to understand the extent to which dissolved solids must be removed for catalyst stability. We are also looking into water separation using sorbents from WR Grace and product separation using a combination of adsorption (on resins) and distillation after water has been removed. We have a FY17Q3 TEA milestone to evaluate the economic viability of these separation techniques.
- **2015 Peer Review**
- Comment: The project is proceeding well, but it faces significant challenges in separations, conversions, and transportation costs.
- Response: The reviewers' excellent suggestion to include transportation costs in our TEA models will be implemented in the next update planned for later this fiscal year. Understanding the value of a chemical as a function of the distance from a potential consumer is extremely important. We plan to implement the transportation cost analysis as a sensitivity analysis to understand the value of the chemical as a function of the distance it must be shipped.
- **FY16 Go/No**
- Go/No Go Description: Demonstrate a modeled 5% reduction in the MFSP of fuel by implementation of a catalytic conversion process to concurrently produce value-added chemicals and/or process H₂ required for bio-oil upgrading.
- Accomplishment: We have demonstrated a lignocellulosic feedstock-based hydrothermal liquefaction (HTL) process will benefit financially from the implementation of technology to convert low molecular weight aqueous phase oxygenates into olefins via ketonization followed by reduction and dehydration reactions. The modeled MFSP decreased 12% from \$3.44/gge for an anaerobic digestion process to \$3.04/gge when utilizing our technology to produce olefins. Included in the modeled costs are all necessary separation and salt removal processes as well as the cost to transport the olefin product to a customer as suggested by reviewers at the 2015 BETO Peer Review. A "Go" was awarded to the project based on the outcome of the modeled technology

Limits of Anaerobic Digestion

HTL (wt%)	HTL Waste H ₂ O Composition	Anaerobic Digestion Limits		
		Stimulating	Moderately Inhibitory	Strongly Inhibitory
Acetic Acid	22.5	0.16 ^b	> 0.24	-
Propanoic Acid	4.1	0.03 ^b	> 0.09	-
Ethanol	0.5	0.16 ^b	> 0.24	-
ICP (ppm)				
Na	6000 - 20000	350	3500 - 5500	8800
K	171	200 - 400	2500 - 4500	12,000
Ca	71	100 - 200	2500 - 4000	8000
Mg	13	75 - 150	1000 - 1500	3000

HTL aqueous waste would need to be diluted to lower the concentration of some inhibitors below acceptable limits. Alternatives to anaerobic digestion are needed.

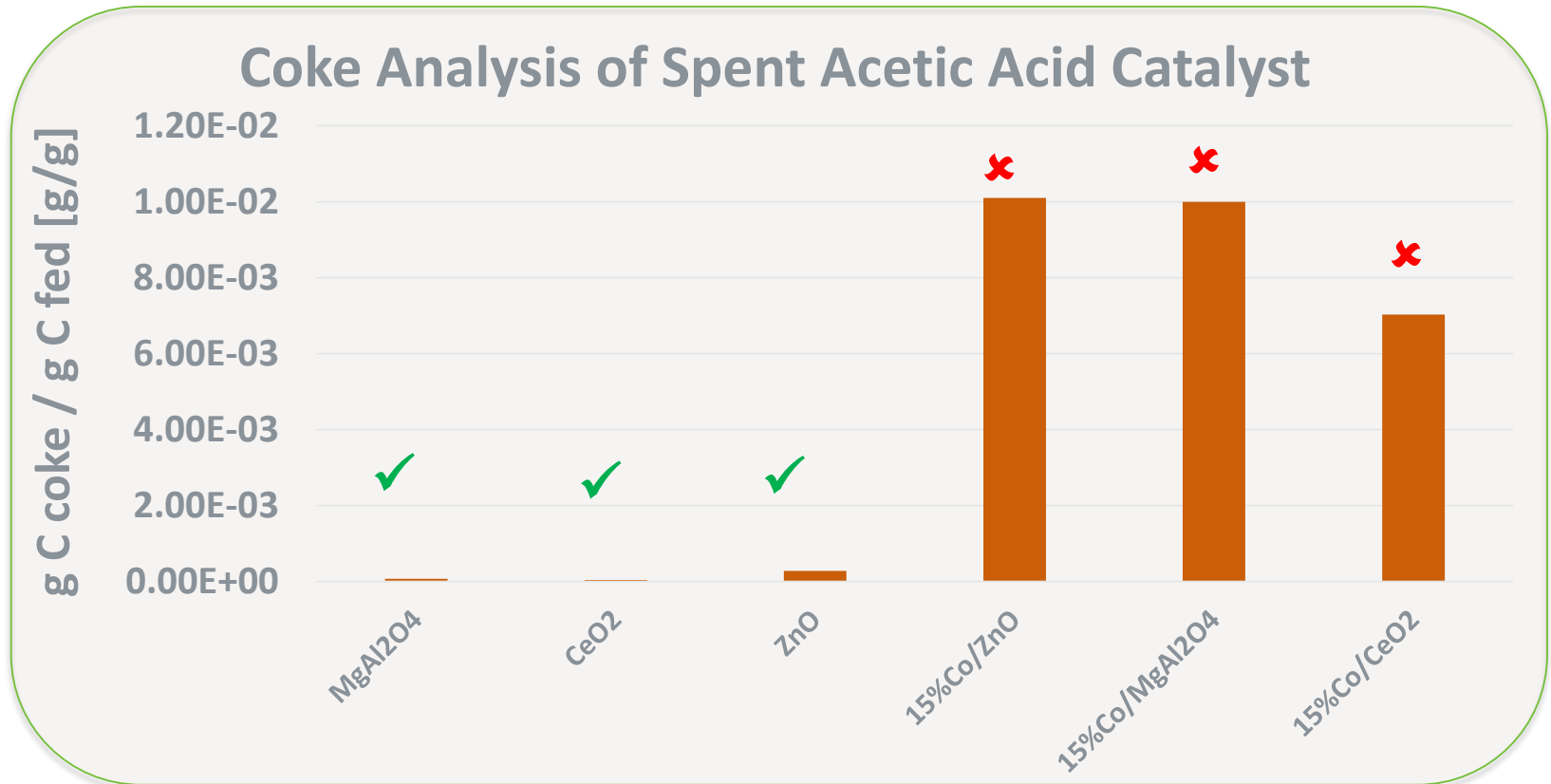
^a L. Appels et al. / Progress in Energy and Combustion Science 34 (2008) 755–781

^b Wang et al./ Biomass and Bioenergy 33 (2009) 848-853

Gas Phase Acetic Acid Steam Reforming - Stability Tests

500 °C, 1 atm, S/C = 3.5 (mol)

Conversion ~ 60%, 150 g carbon fed/g catalyst



- ▶ Negligible coke over oxide supports (ketonization catalysts)
- ▶ Co-supported catalysts promote significantly more coke formation

3b) – TEA of SOT results

- TEA of un-optimized SOT results have the same overall contribution to MFSP as design case*
- However, TEA showed that the modified model has the potential to **decrease MFSP by ~ 20 cents/GGE** by focusing research on:
 - **Reducing capital costs** by concentrating organics (**membranes or sorbents**)
 - **BTX yield improvement** and utilization of olefins
 - Target higher value products: **cyclopentenone, phenol and furans**