

DOE Bioenergy Technologies Office (BETO) 2017 Project Peer Review

Fractionation and Catalytic Upgrading of Bio-Oil
FY13 DE-FOA-000 CHASE

March 2017
Technology Area Review

PI: Daniel E. Resasco
University of Oklahoma

Goal Statement

- Current technologies:
 - low C-retention in fuel range
 - high H consumption.
- Experimental results allow
 - life-cycle analysis (LCA) and
 - techno-economic analysis (TEA)back fed to the experimentalists to refine selection of catalyst and process operations
- ultimate objective is
 - maximizing C efficiency at minimum H utilization.
- This project:
 - effective fractionation, combined with
 - catalytic upgrading for
 - C-C bond formation
 - Hydrodeoxygenationin liquid and vapor phases

Quad Chart Overview

Timeline

- October, 2015
- March, 2017
- 90 % Complete

Partners

- OU 50 %
- INL 25 %
- U. Wisconsin 12.5 %
- U. Pittsburgh 12.5 %

Barriers

Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates

Tt-I. Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals

Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals

Tt-O. Separations Efficiency

Tt-S. Petroleum Refinery Integration of Bio-Oil Intermediates

Budget

| | FY 14-15 Costs to 6/30/15 | FY 15-16 Costs to 6/30/16 | FY 16-17 Costs to 12/31/16 | Total Planned Funding (FY 17- Project End Date |
|--|---------------------------------|---------------------------------|----------------------------------|---|
| DOE Funded | \$1,051,765 | \$684,474 | \$338,364 | \$318,767 |
| Project Cost Share (Comp.)* | \$398,120 | \$232,487 | \$112,329 | \$6,332 |

Approach (Technical)

- **Thermal fractionation:**
 - moderate T and t → most reactive parts
→ small oxygenates
 - Higher temperatures and faster heating
→ mostly phenolic compounds
- **Catalytic upgrading:** Specific catalyst formulations to
 - maximize C retention in liquid phase and minimize catalyst deactivation
 - C-C bond forming and HDO reactions
- **Separation:** Refining of the different fractions
→ supercritical extraction and selective adsorption for purer streams
- **LCA and TEA:** Analysis LCA and TEA helps continuous improvement and feedback

Approach (Management)

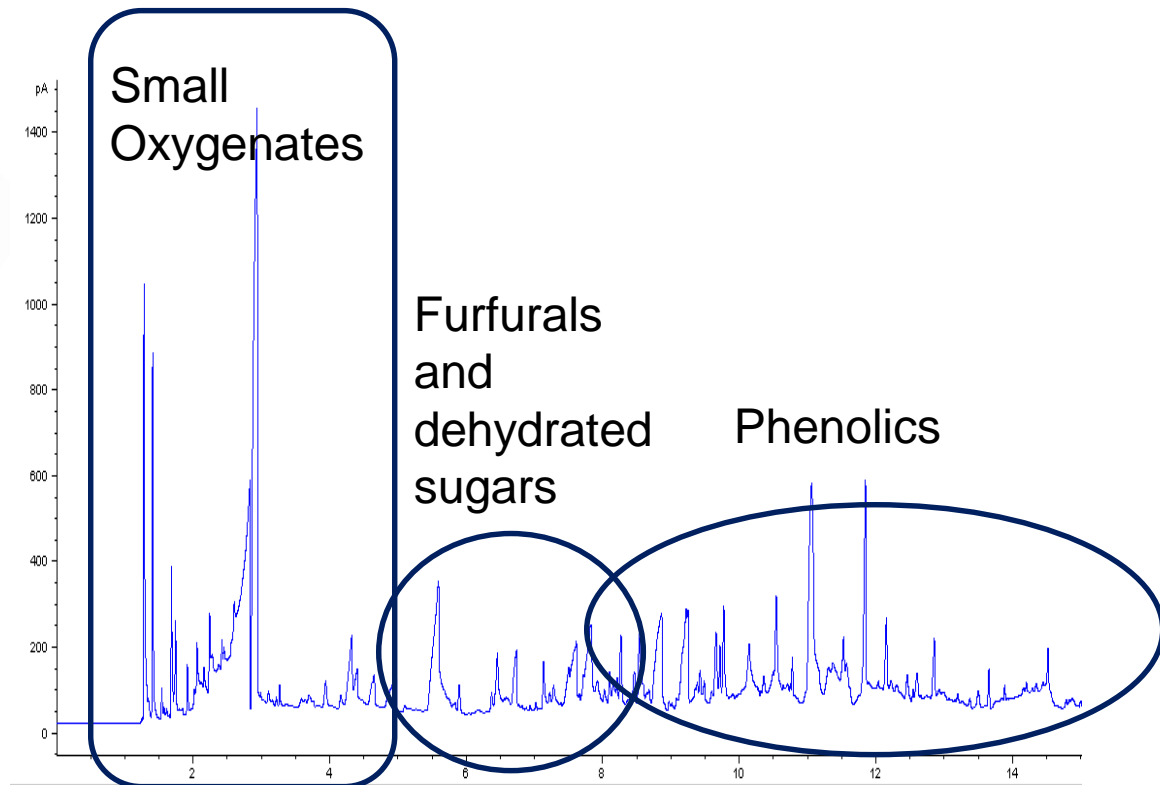
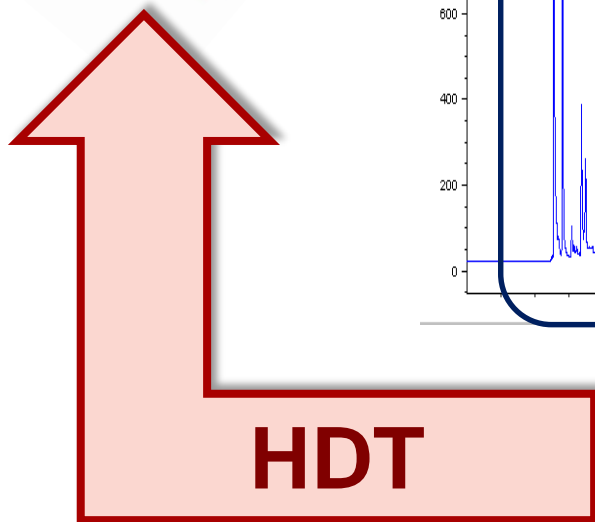
- The outcome of this project will be a series of possible process strategies to produce stabilized liquid projects that could be inserted in a conventional oil refinery.
- The most important challenge is related to process economics
- The current goal is to find thermal fractionation processes, catalysts and catalytic reactors, as well as separation processes that minimize the cost and environmental impacts, maximizing the liquid yield
- The senior personnel of the different parts of the project (thermal conversion, separations, catalysis, LCA, TEA) are responsible of planning, organizing, controlling resources, and procedures to accomplish the established goal

Technical Accomplishments

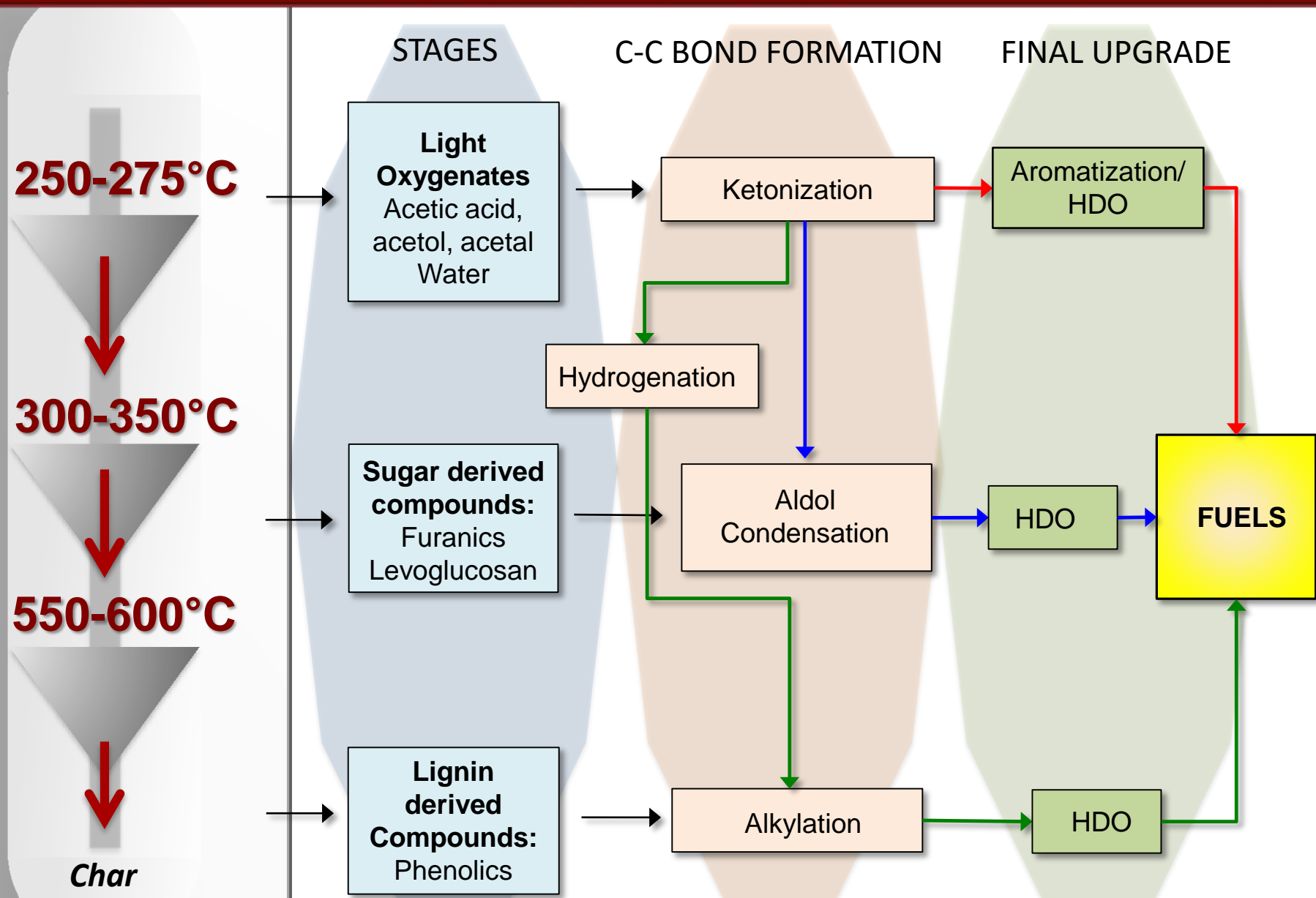
Staged torrefaction/pyrolysis to decrease stream complexity

Low Liquid Yield

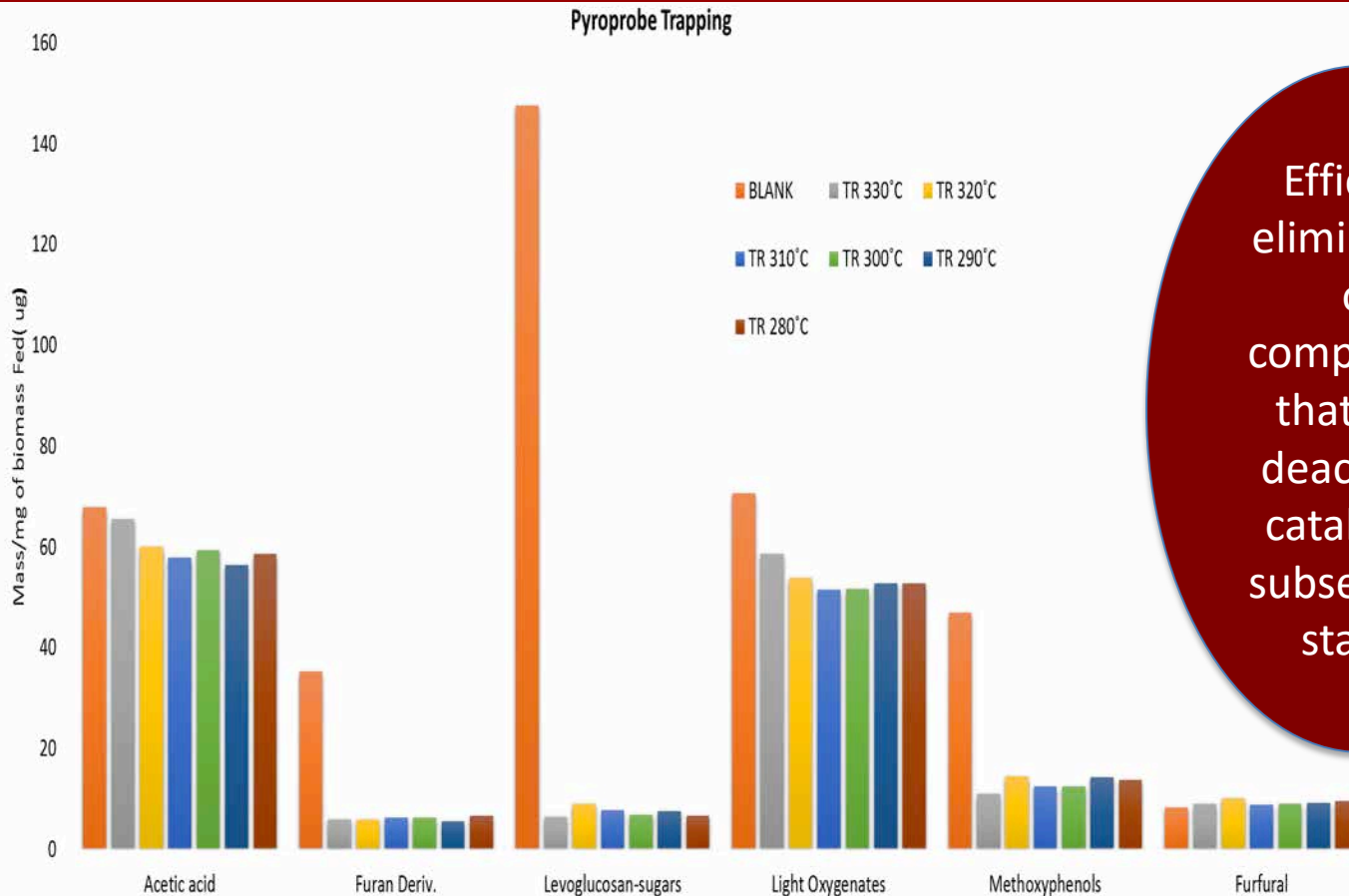
Excessive H_2 Consumption



Multi-stage Pyrolysis + Catalytic Cascade



Activated carbon adsorptive trapping to improve Fractionation efficiency



Efficient elimination of compounds that may deactivate catalyst in subsequent stages

Pyroprobe effluent passing through activated carbon bed shows large reduction in levoglucosan, methoxyphenols.

Upgrade of selected thermal stage streams

Strategies investigated to incorporate two of the most abundant species from thermal stage streams:

acetic Acid / furfural / phenolics

C-C bond forming

(a) Ketonization/hydrogenation/alkylation (1st cycle)

Disadvantage → C loss and H₂ consumption

(b) Direct acylation with acetic acid (2nd cycle)

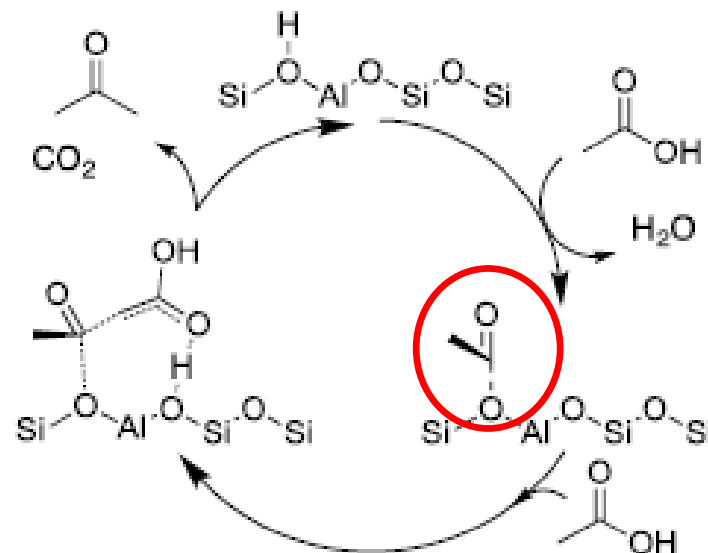
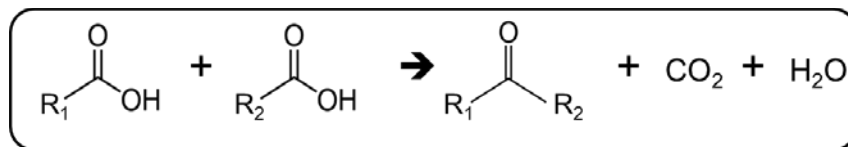
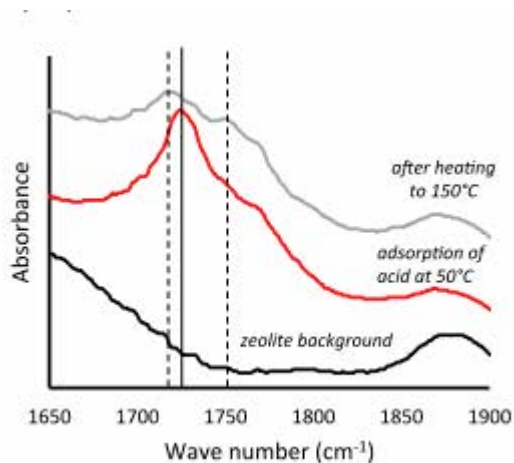
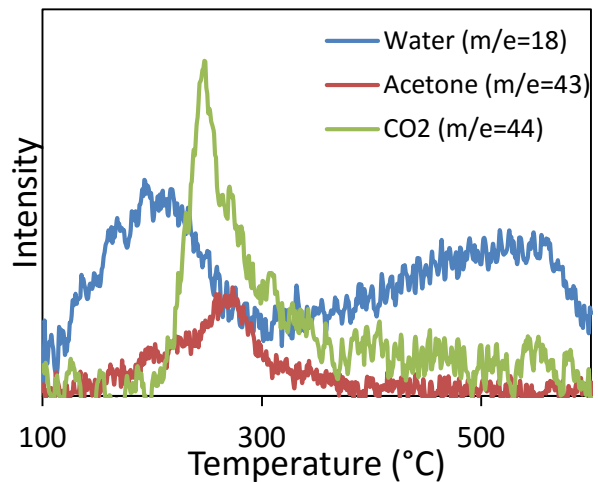
(c) Aldol condensation of acetone/furfural (1st cycle)

Disadvantage → C loss and catalyst deactivation

(d) Formation of cyclopentanone + aldol condensation
(2nd cycle)

HDO reactions

Mechanism of ketonization of acetic acid over HZSM5



1. Surface acyl are formed by dehydration of acid on Brønsted zeolite
2. Dehydration happens at lower temperature than ketonization

Can we pick these surface acyl's ?

New route of acylation → acetic acid acylating agent

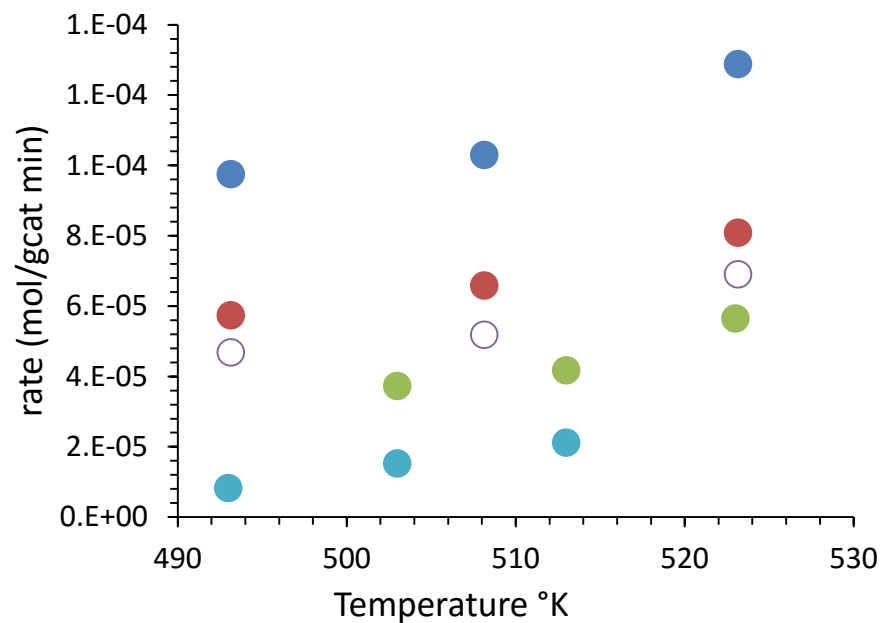
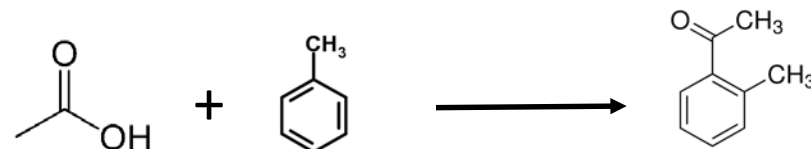
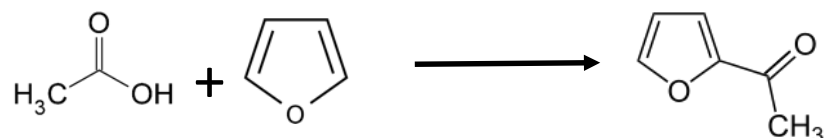
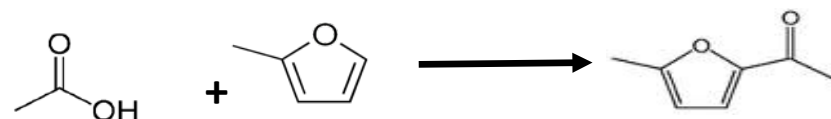
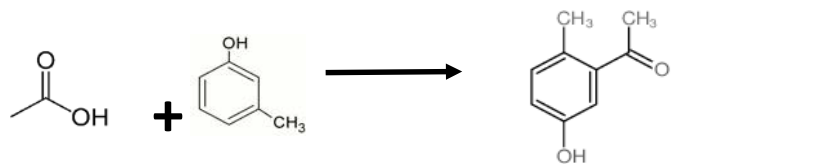
Acylating agent + **Substrate** → **Acylation**

Table 2. Yields for a three-stage torrefaction process of raw oak.

| Species | Yield [wt %] | | | Total [wt %] |
|------------------|-------------------|-------------------|-------------------|--------------|
| | 1st stage, 270 °C | 2nd stage, 360 °C | pyrolysis, 500 °C | |
| H ₂ O | 10.1 | 6.8 | 0.0 | 16.9 |
| acetic acid | 6.9 | 1.9 | 0.5 | 9.3 |
| acetol | 3.1 | 1.9 | 1.8 | 6.8 |
| furan | 0.0 | 0.2 | 0.1 | 0.3 |
| furfural | 1.4 | 4.1 | 0.7 | 6.2 |
| levoglucosan | 0.2 | 7.6 | 4.8 | 12.6 |
| toluene | 0.0 | 0.8 | 0.3 | 1.1 |
| guaiacol | 1.8 | 2.1 | 1.5 | 5.4 |
| cresol | 0.0 | 1.2 | 0.5 | 1.7 |
| CO ₂ | 7.2 | 8.5 | 11.5 | 27.2 |
| char | 0.0 | 0.0 | 12.5 | 12.5 |
| total | 30.7 | 35.1 | 34.2 | 100.0 |

Herron, J. A., Vann, T., Duong, N., Resasco, D. E., Crossley, S., Lobban, L. L., & Maravelias, C. T. (2016). A Systems-Level Roadmap for Biomass Thermal Fractionation and Catalytic Upgrading Strategies. *Energy Technology*.

Comparing cresol, m-furan, furan and toluene acylation

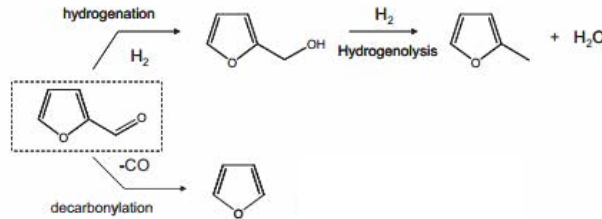


● cresol rate ● m-furan rate ● Furan rate ○ Cresol ring rate ● Toluene rate

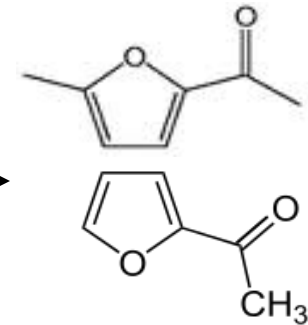
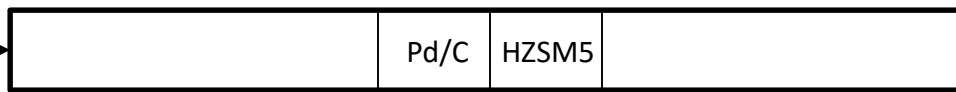
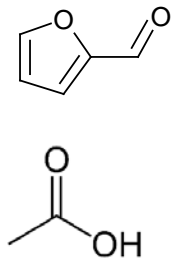
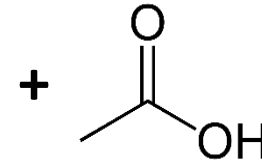
Similar activation energy but varied rate with changing substrate

- Gumidyala, A.; Wang, B.; Crossley, S., Direct carbon-carbon coupling of furanics with acetic acid over Brønsted zeolites. *Science Advances* **2016**, *2* (9), e1601072.

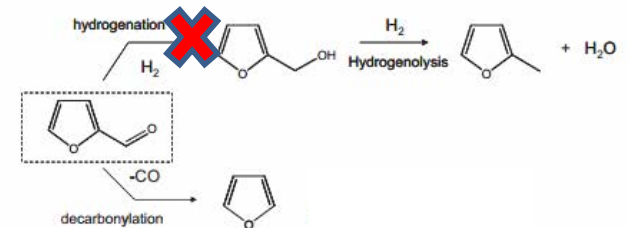
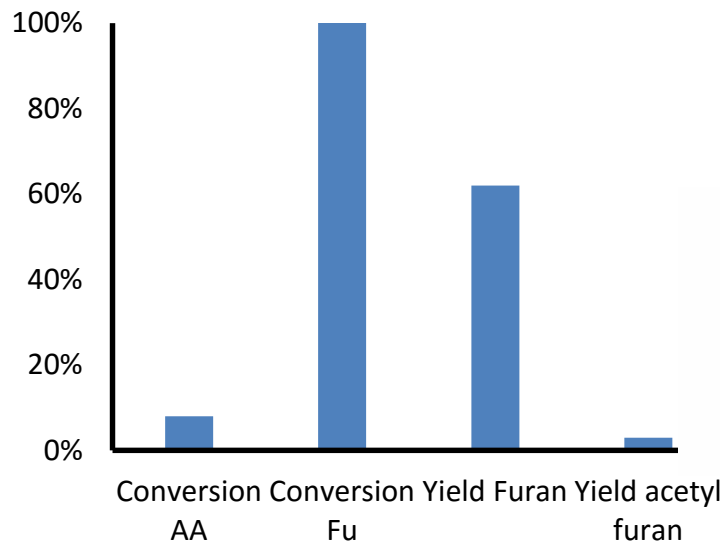
Dual bed reactor with real streams



Scheme 1. Reaction pathways for furfural conversion.



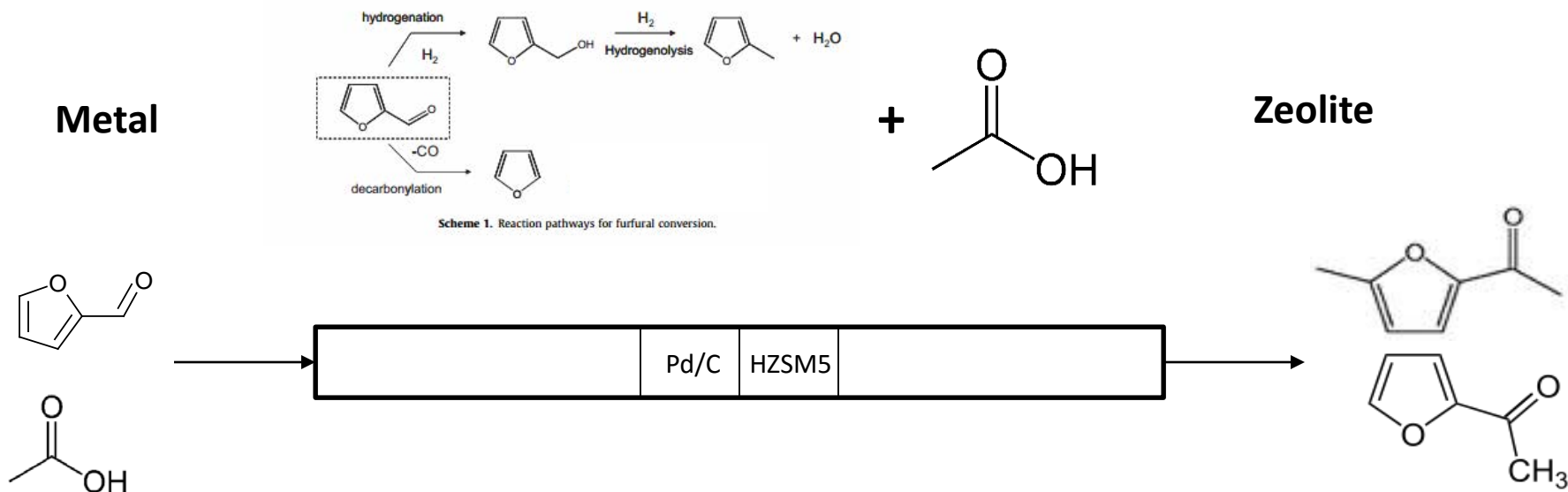
AA : Furfural mole ratio = 1 : 0.8
 Catalyst : HZSM5 (Si/Al =40)
 Catalyst weight : 50 + 50 mg
 Temperature : 250 °C
 In Hydrogen



Scheme 1. Reaction pathways for furfural conversion.

- ❖ Carbon loss in the form of CO and higher barrier for acylation of furan
- ❖ Can we avoid decarbonylation and promote hydrogenation?

Dual bed reactor with real streams



AA : Furfural mole ratio = 1 : 0.15

Catalyst : HZSM5 (Si/Al =40)

Catalyst weight : 50 + 50 mg

Temperature : 300 °C

In Hydrogen

Conversion@ 30min

Furfural = 100%

Acetic acid = 6%

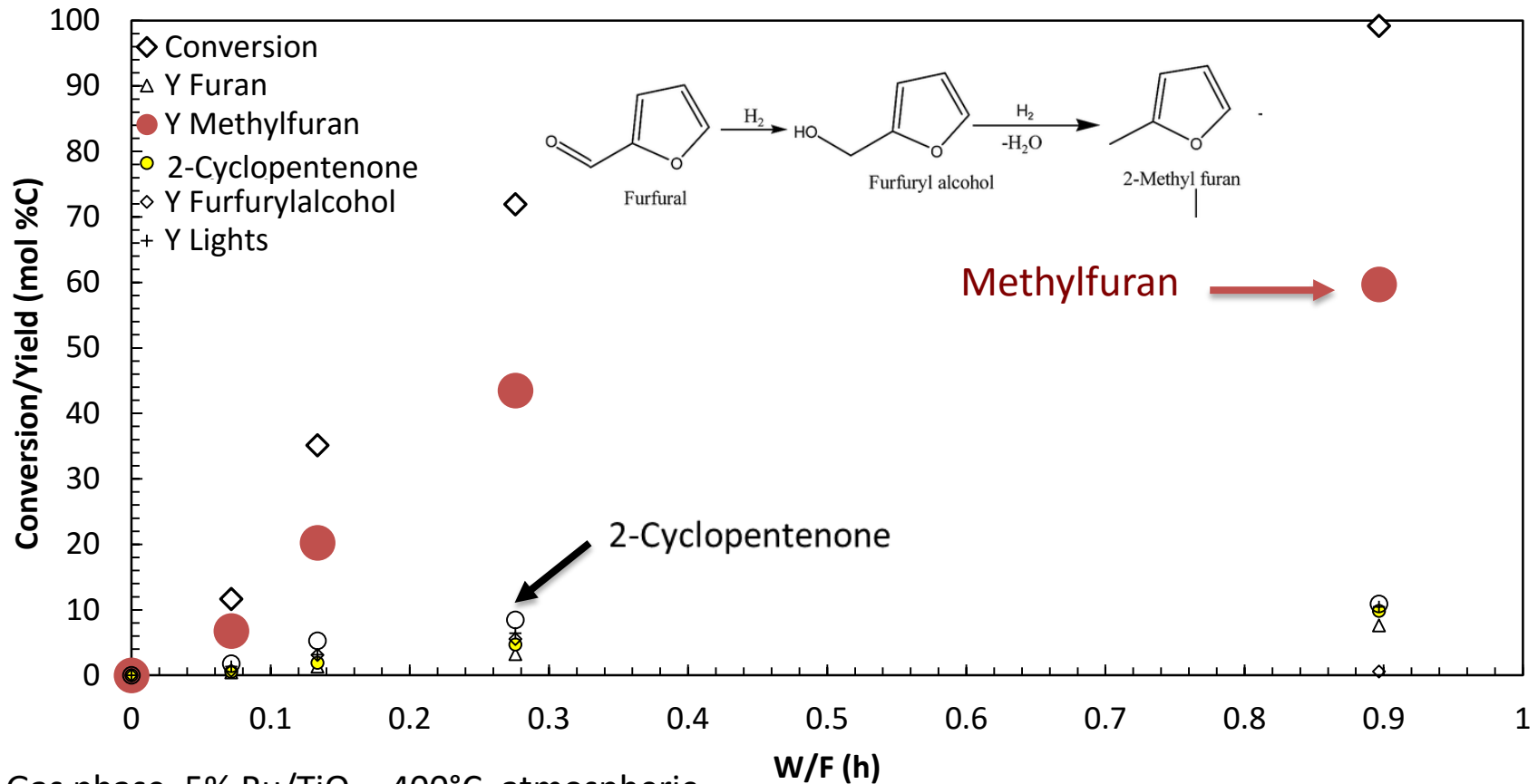
| Yields of products | |
|-------------------------------------|----|
| Furan | 55 |
| m-furan | 32 |
| Acylation and ketonization products | 4 |
| Other products | 9 |

Main products = furan, methyl furan and traces of other products yet to be identified

Traces of acylation and ketonization ?

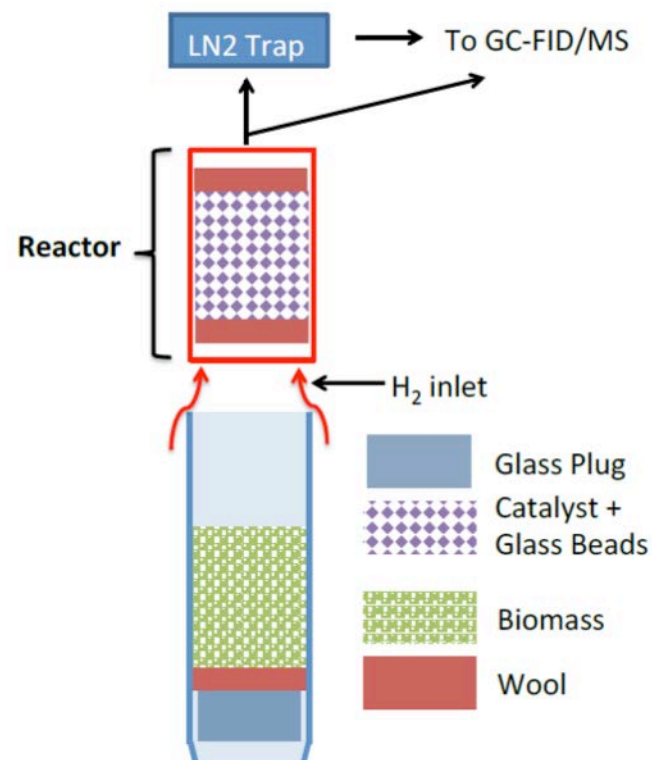
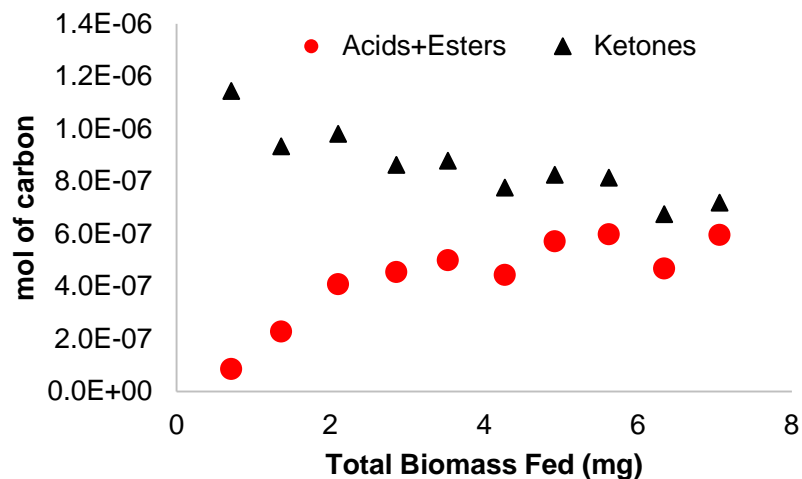
Conversion of furfural in the vapor phase

Ru/TiO₂ is very selective for methylfuran

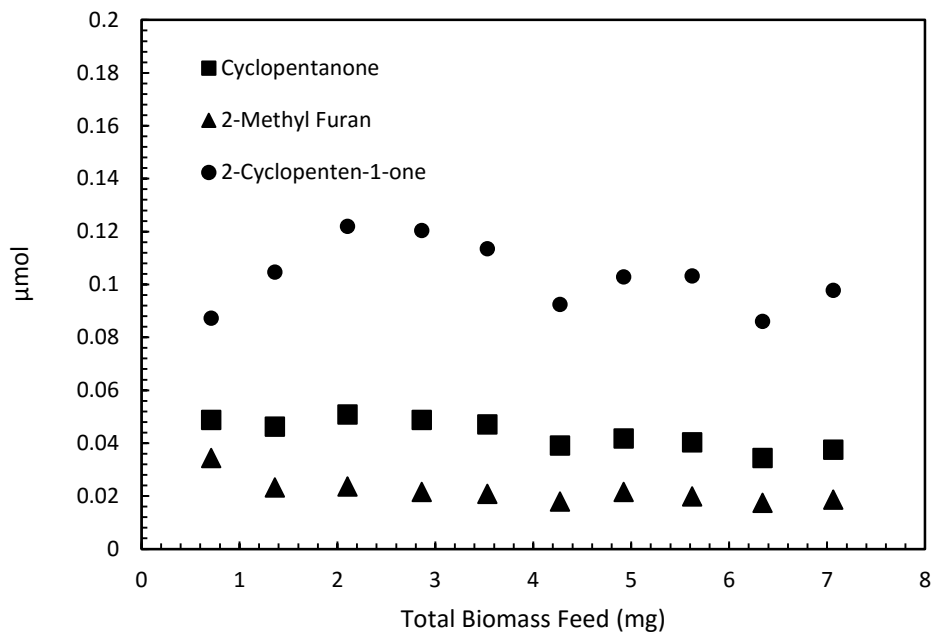


Gas phase. 5% Ru/TiO₂, 400°C, atmospheric pressure, under H₂. Feeding 0.1 mL/h of furfural and 1800 mL/h of H₂.

Selectivity shifts to cyclopentanone with torrefaction vapors

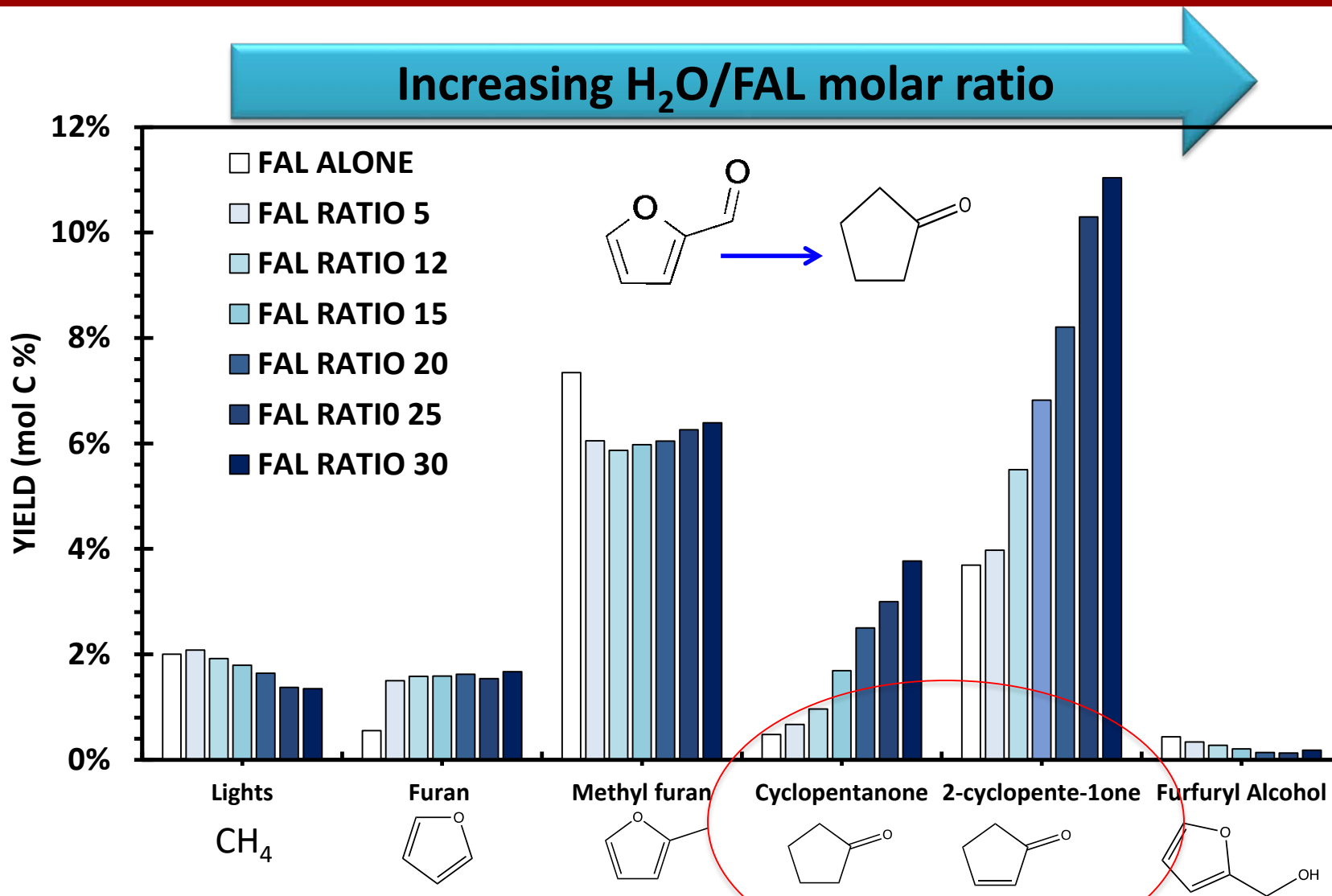


Schematic of pyrolysis/torrefaction coupled with catalytic reactor



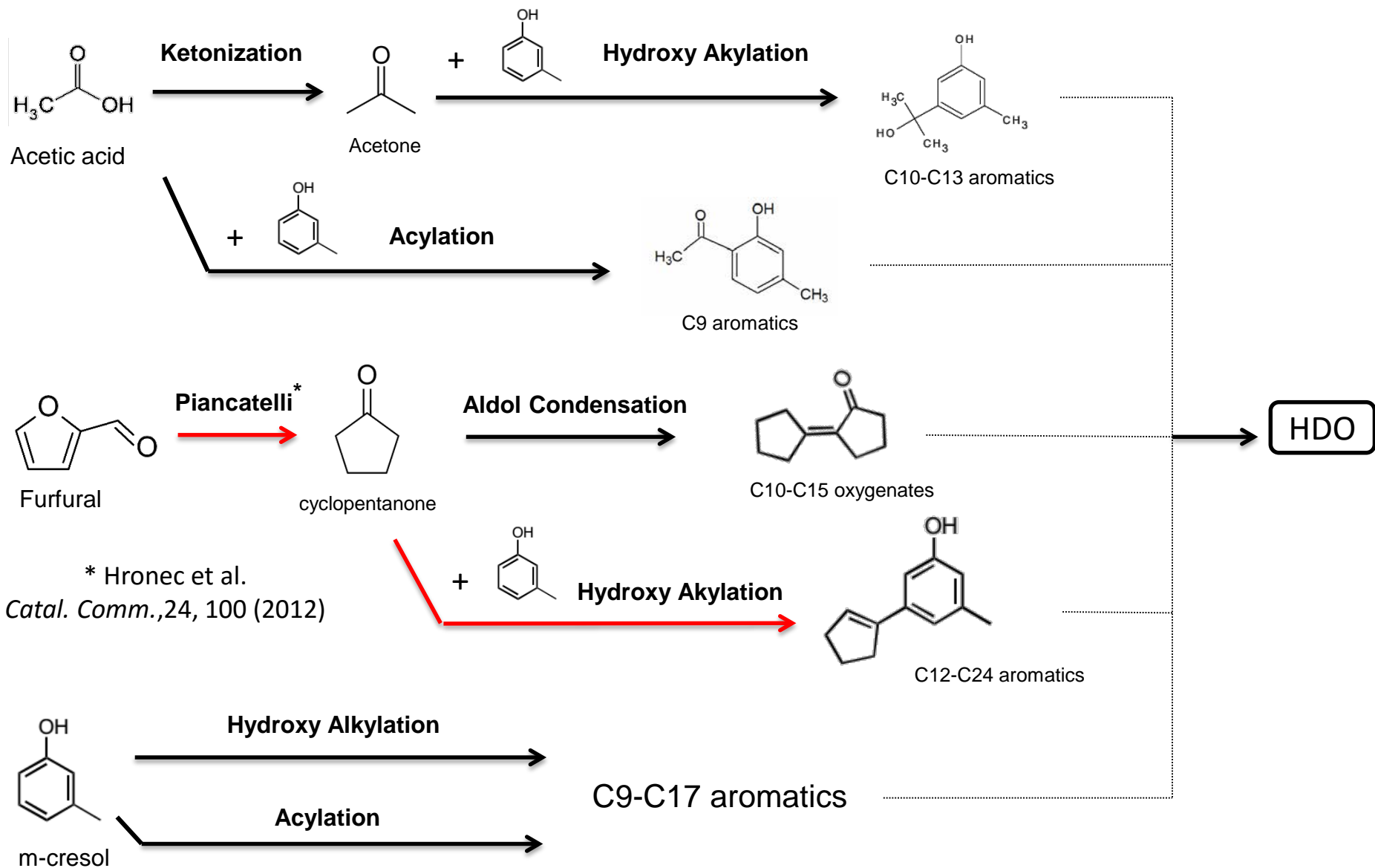
Role of Water !

Water increases furfural conversion and cyclopentanone yield

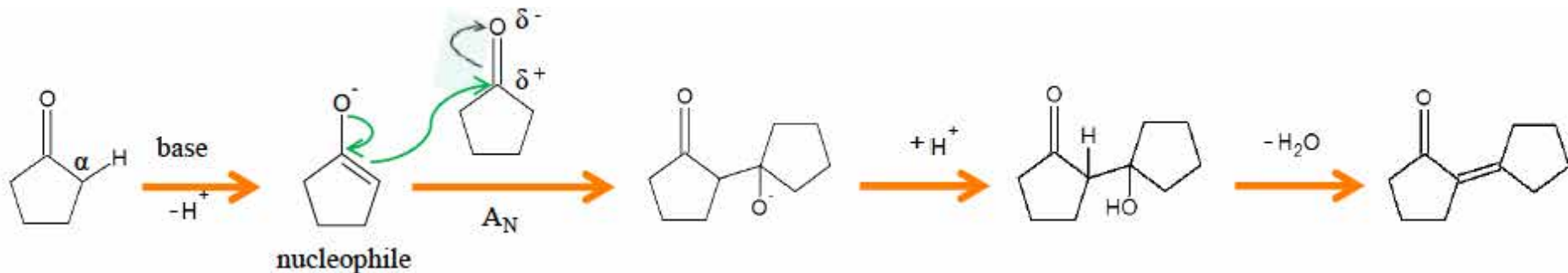


Product Distribution for pure furfural and furfural co-fed with water at different molar ratios over 5% Ru/TiO₂, T= 400°C, P= 1 atm, TOS= 30 mins

Liquid Phase C-C bond forming strategies



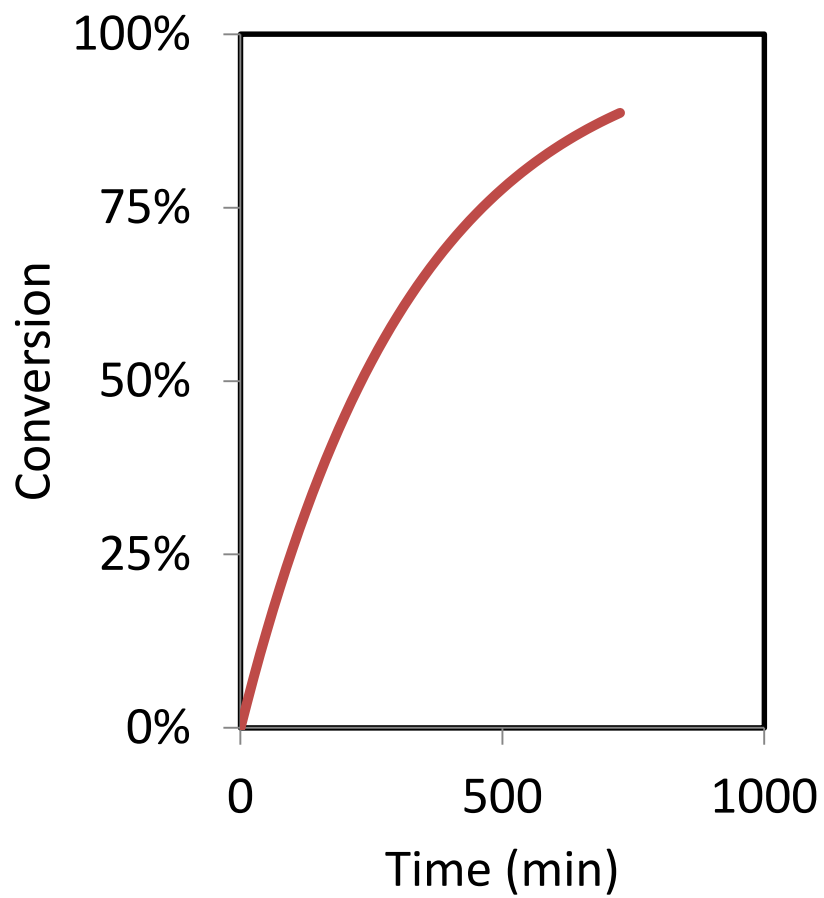
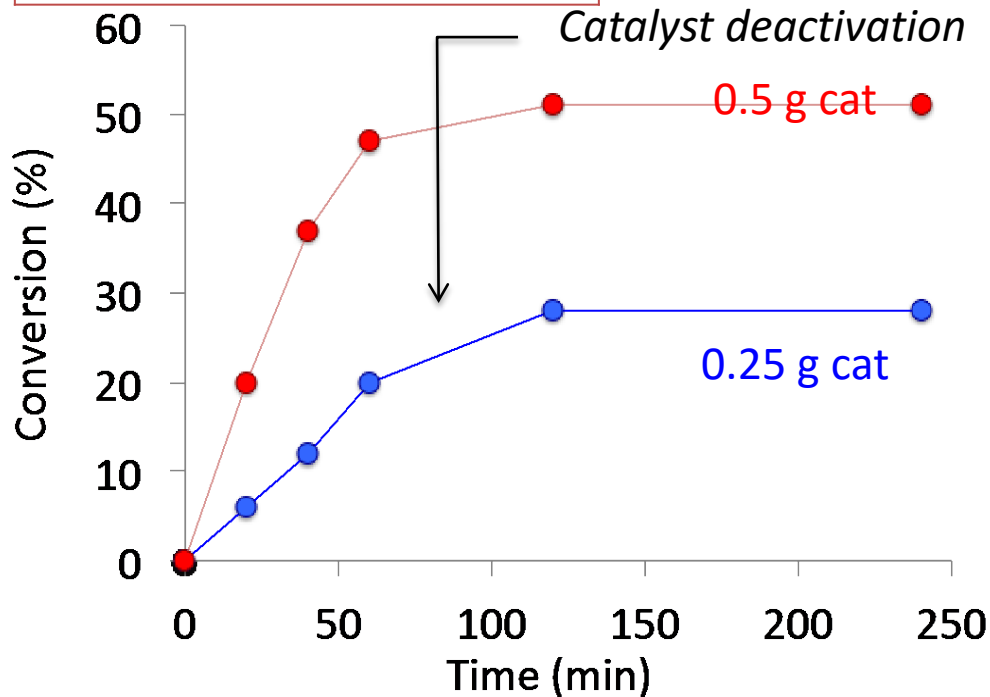
Aldol Condensation of Cyclopentanone



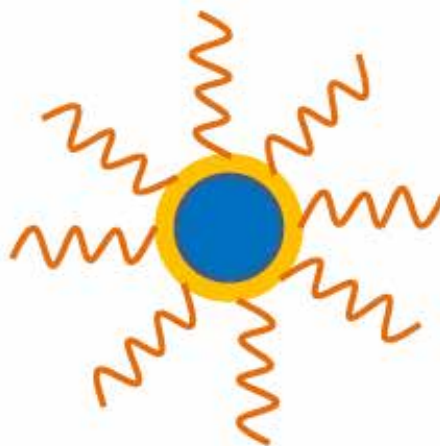
Hydrophobized MgO catalyst

Reactor = Parr
Autoclave
(Batch)

MgO catalyst



Hydrophobized MgO-SiO₂



Conditions: 10 mg dispersed in 5 mL H₂O and stirred at 750 rpm for 10 mins



64%MgO@mSiO₂-16.2%OTS



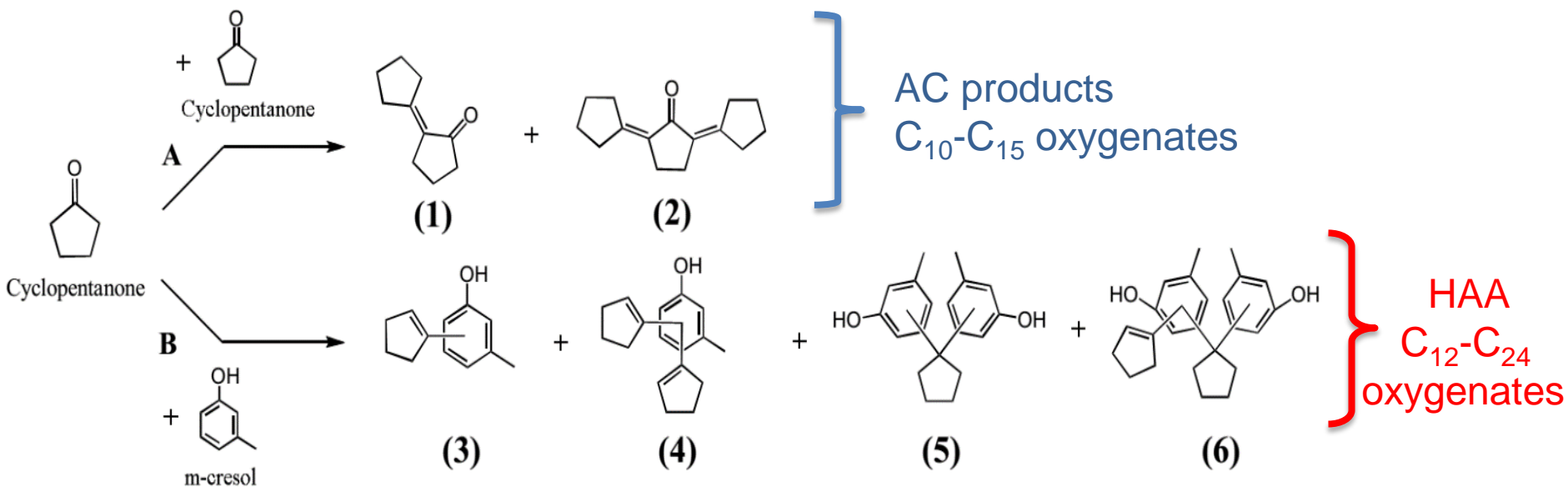
49%MgO@mSiO₂-30%OTS



Hydroxy-Alkylation of cyclopentanone and m-cresol

- **Two Bronsted acid-catalyzed reactions**

- Aldol Condensation : Monomer (1) + Dimer (2)
- HydroxyAlkylation: Monomer (3) + Dimer (4) + Dimer (5) + Trimer (6)



Catalysts:

Amberlyst 36, zeolite beta, etc.

Step 1: C-C bond formation



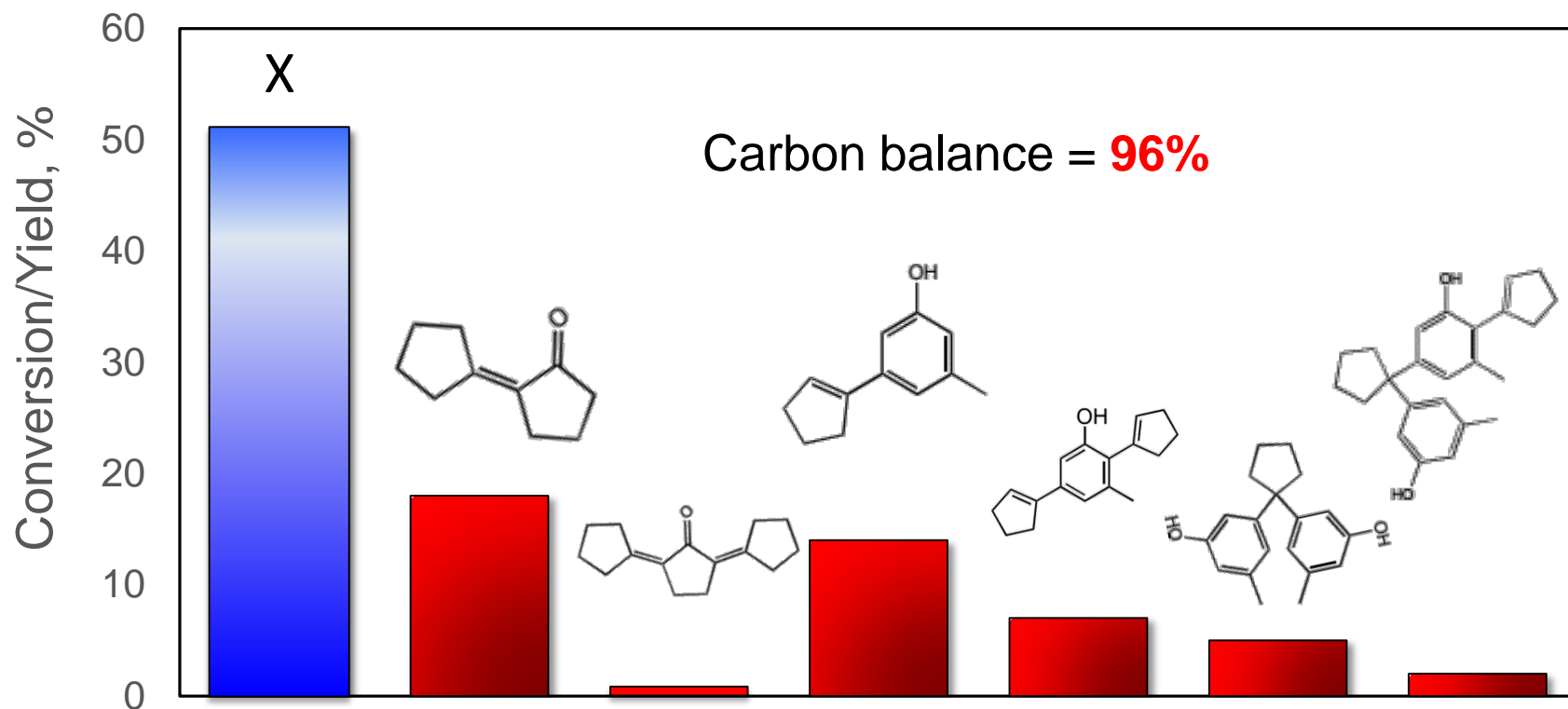
m-cresol/CPO 2:1,

$C_{CPO} = 3M$

Catalyst: 3 g Amberlyst 36

Conditions: 150°C, 12h, 400 psia N₂

- Partial removal of O
- Pre-stabilizing bio-oil
- Forming larger oxygenation via forming C-C bonds



Step 2: Hydrodeoxygenation and Ring Opening

Solvent:

Undecane

Catalyst:

0.5g 2%Pd/Al₂O₃

Reduction:

150°C, 3h

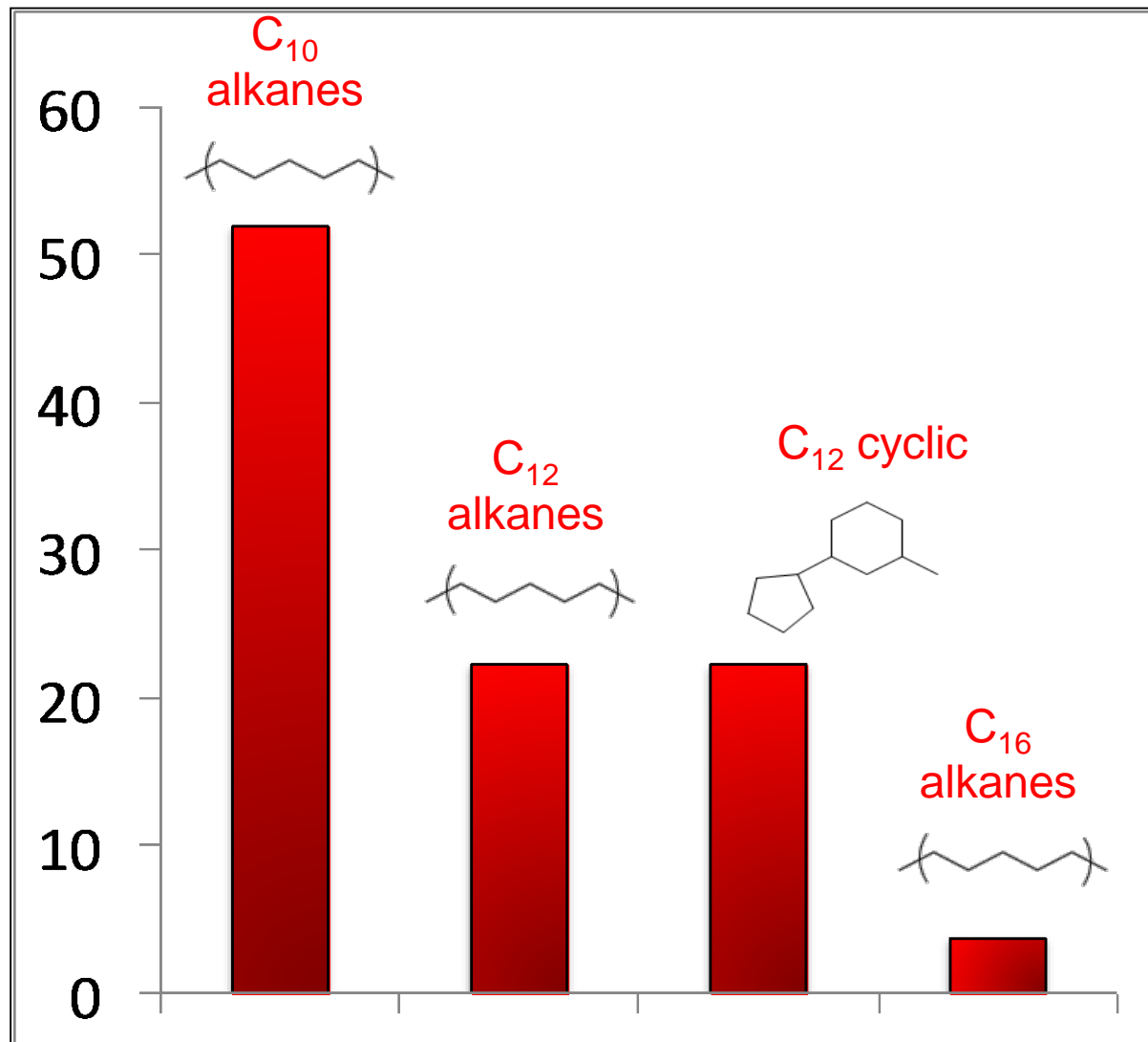
Reaction

Conditions:

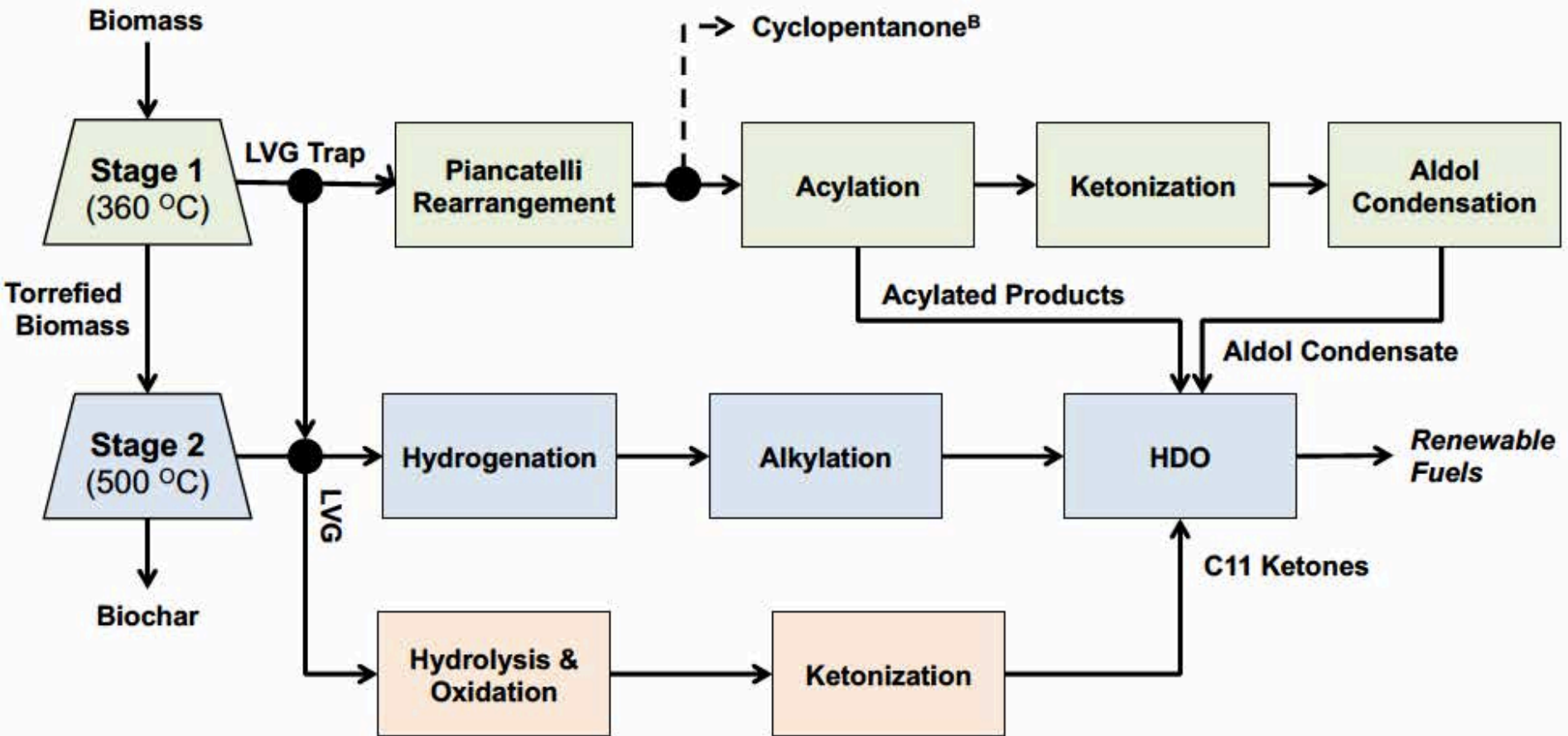
250°C, 12h,

800 psia H₂

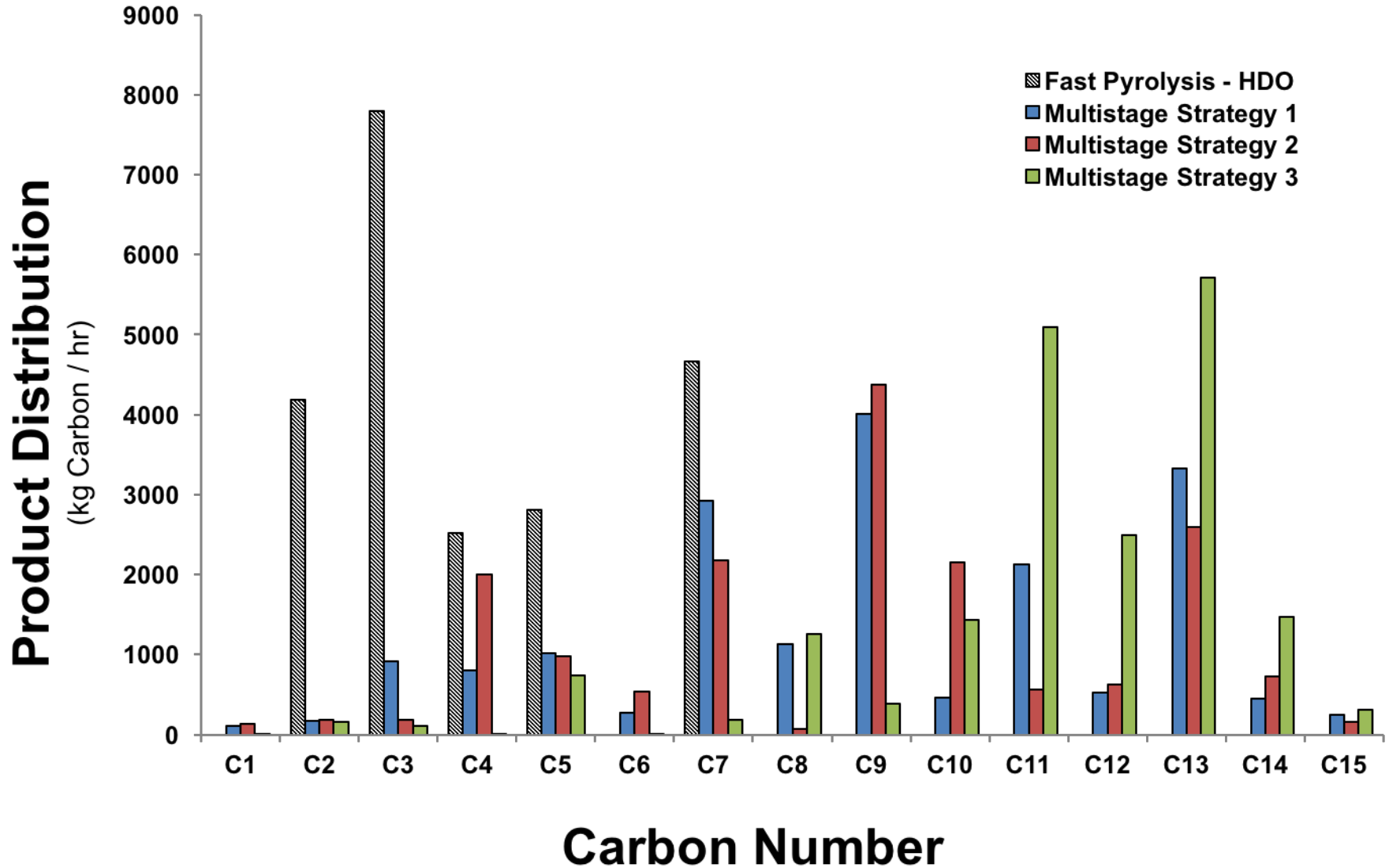
✓ **Carbon
balance = 93%**



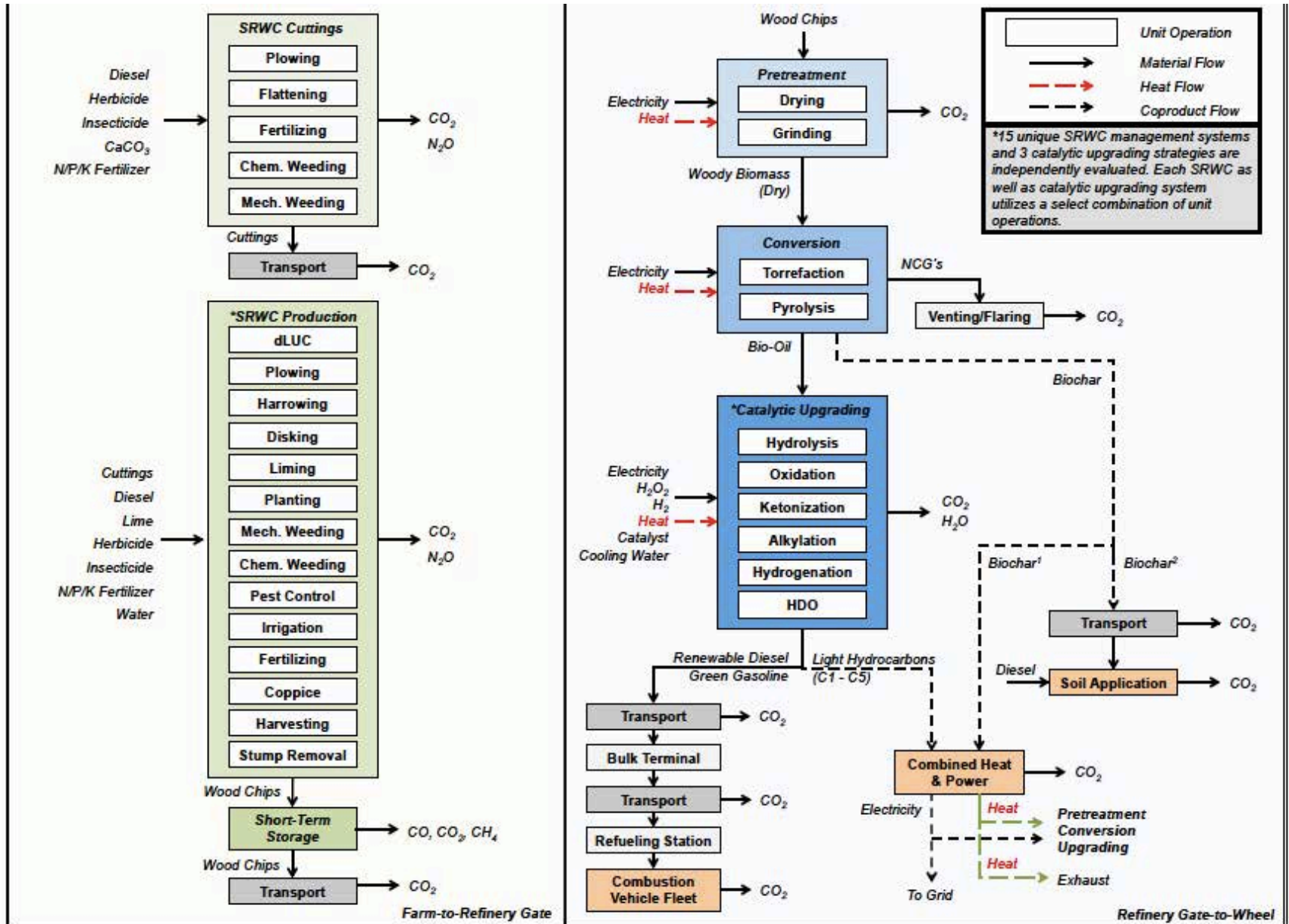
Life Cycle Analysis: Comparing scenarios



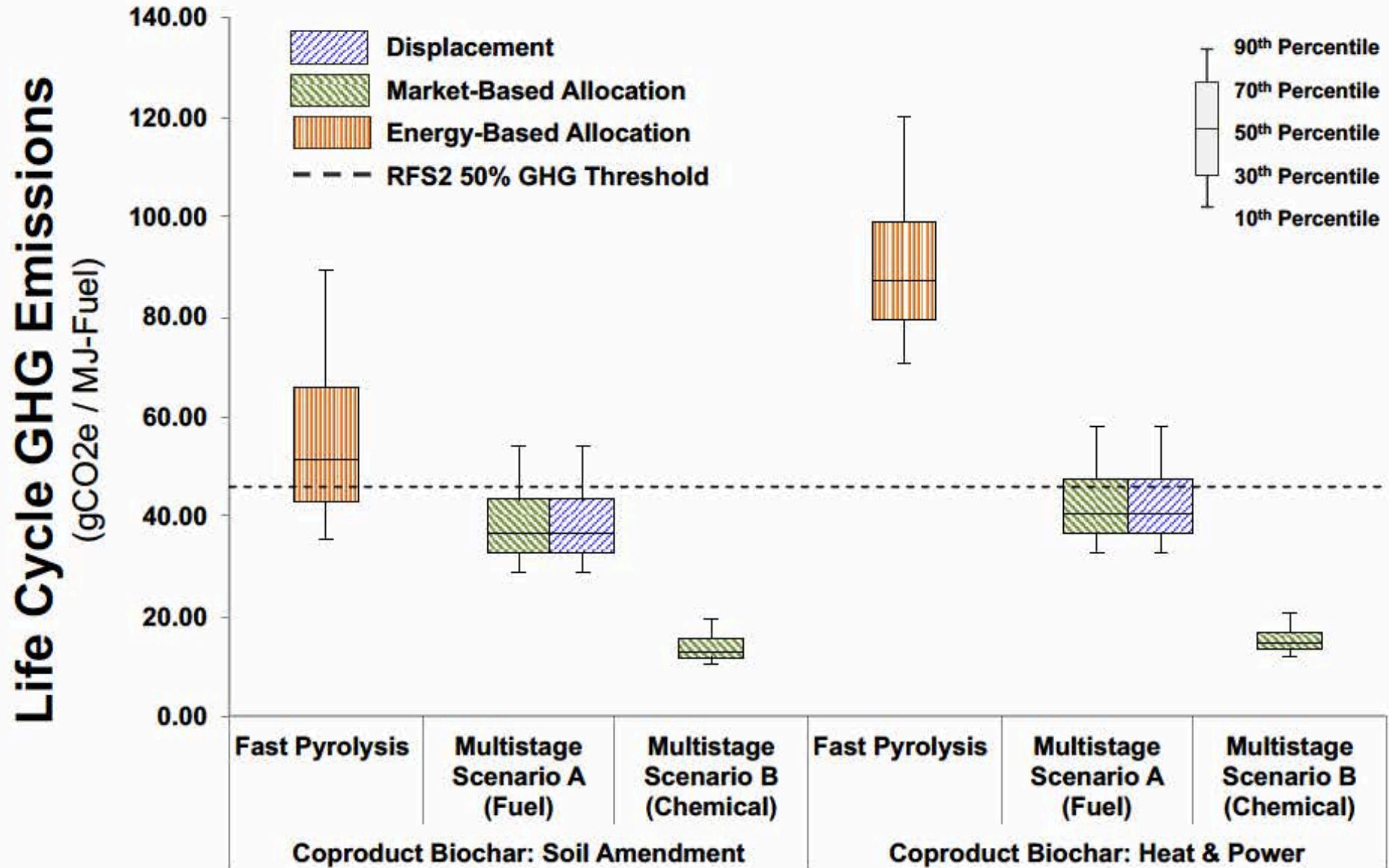
Life Cycle Analysis



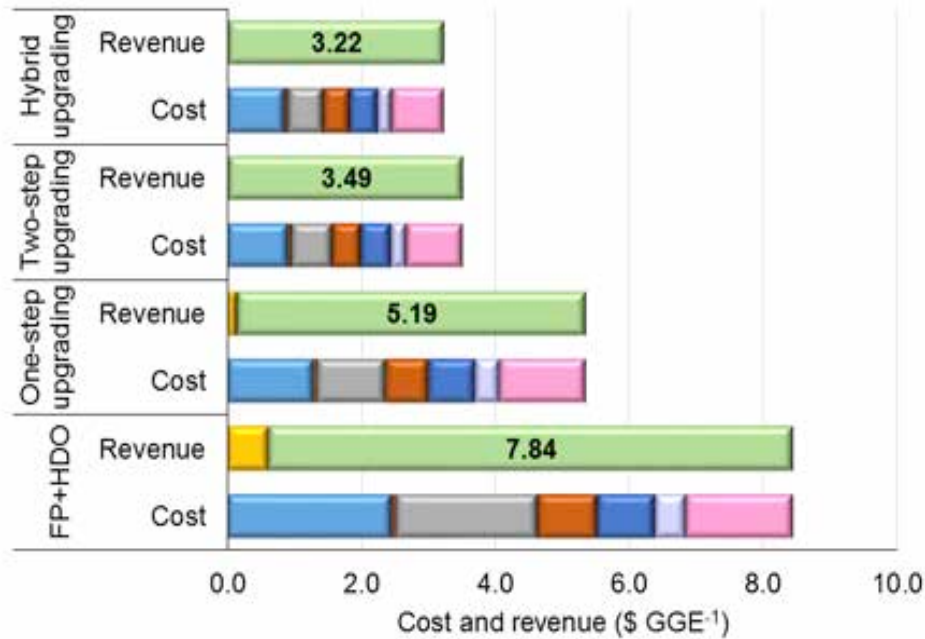
Life Cycle Analysis: Process Overview



Life Cycle Analysis: GHG Emissions

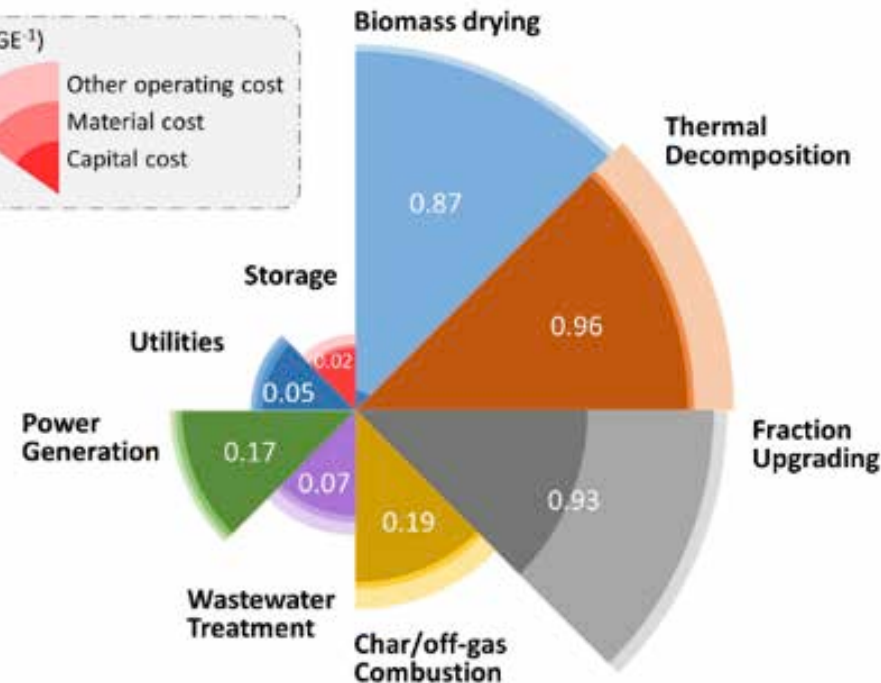
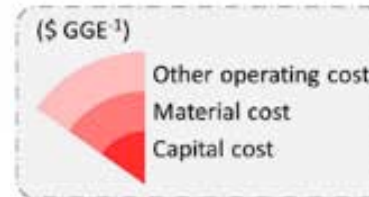


Key trade-offs and cost drivers through detailed TEA



Goal: maximize carbon yield (primary) and minimize H₂ consumption (secondary)

- Carbon yield improvement requires more complex processing, leading to higher capital costs
- Design of thermal decomposition conditions must be done in parallel with fraction upgrading system



Major Findings

- **Acylation and Hydroxyalkylation increase fuel product yields without the C losses previously observed in the path ketonization / alkylation**
- **Similarly, furanic arrangement to cyclopentanone provides another way to maximize product yield via C-C bond forming reactions**
- **Feedstock cost, hydrogen cost, and capital cost appear to be the dominant cost drivers**
- **Multi-stage thermal + catalytic upgrading show better economic performance than the conventional “ fast pyrolysis + HDO”, achieving over 80% GHG reductions relative to petroleum diesel and the highest environmental performance of all the examined design cases, with promising EROI and GHG emissions profile**
- **The net improvements in fuel-grade product yields outweigh the costs of increased process complexity**

PUBLICATIONS

(with direct acknowledgement to this DOE grant)

- Bui, T. V.; Crossley, S.; Resasco, D. E., C–C coupling for biomass-derived furanics upgrading to chemicals and fuels. Wiley-VCH Verlag and Co. KGaA: 2016; pp 431-494.
- Ghorbanpour, A.; Gumidyala, A.; Grabow, L. C.; Crossley, S. P.; Rimer, J. D., Epitaxial growth of ZSM-5@ Silicalite-1: A core–shell zeolite designed with passivated surface acidity. *ACS nano* **2015**, 9 (4), 4006-4016.
- Gumidyala, A.; Sooknoi, T.; Crossley, S., Selective ketonization of acetic acid over HZSM-5: The importance of acyl species and the influence of water. *Journal of Catalysis* **2016**, 340, 76-84.
- Gumidyala, A.; Wang, B.; Crossley, S., Direct carbon-carbon coupling of furanics with acetic acid over Brønsted zeolites. *Science Advances* **2016**, 2 (9), e1601072.
- Herron, J. A.; Vann, T.; Duong, N.; Resasco, D. E.; Crossley, S.; Lobban, L. L.; Maravelias, C. T., A Systems-Level Roadmap for Biomass Thermal Fractionation and Catalytic Upgrading Strategies. *Energy Technology* **2017**, 5 (1), 130-150.
- Resasco, D. E.; Crossley, S. P., Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel. *Catalysis Today* **2015**, 257, 185-199.
- Resasco, D. E.; Wang, B.; Crossley, S., Zeolite-catalysed C–C bond forming reactions for biomass conversion to fuels and chemicals. *Catal. Sci. Technol.* **2016**, 6 (8), 2543-2559.
- A Rozenblit, AJ Avoian, Q Tan, T Sooknoi, DE Resasco - “Reaction mechanism of aqueous-phase conversion of γ -valerolactone (GVL) over a Ru/C catalyst” *Journal of Energy Chemistry*, 25, 1008–1014, 2016

PUBLICATIONS

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- Tuong V Bui, Tawan Sooknoi, Daniel E. Resasco. “Simultaneous upgrading of furanics and phenolics via hydroxyalkylation/aldol condensation reactions” ChemSusChem DOI: 10.1002/cssc.201601251
- “Different Product Distributions and Mechanistic Aspects of the Hydrodeoxygenation of m-Cresol over Platinum and Ruthenium Catalysts” Qiaohua Tan, Gonghua Wang, Lei Nie, Arne Dinse, Corneliu Buda, John Shabaker, Daniel E. Resasco, ACS Catalysis, 5, 6271–6283, 2015
- “Hydride transfer between a phenolic surface pool and reactant paraffins in the catalytic cracking of m-cresol/hexanes mixtures over an HY zeolite” Anh T. To, Daniel E. Resasco, Journal of Catalysis, 329, 57-68, 2015
- “Reaction pathways in the liquid phase alkylation of biomass-derived phenolic compounds” Miguel Angel González-Borja, Daniel E. Resasco, D. AIChE Journal 61 598–609, 2015
- “Tuning the Acid-Metal Balance in Pd/ and Pt/Zeolite Catalysts for the Hydroalkylation of m-Cresol” Felipe Anaya, Lu Zhang, Qiaohua Tan, Daniel E. Resasco, Journal of Catalysis – 328, 173–185, 2015
- “Decoupling HZSM-5 Catalyst Activity from Deactivation during Upgrading of Pyrolysis Oil Vapors” Shaolong Wan, Christopher Waters, Adam Stevens, Abhishek Gumidyala, Rolf Jentoft, Lance Lobban, Daniel Resasco, Richard Mallinson, and Steven Crossley, ChemSusChem., 8, 552-559, 2015
- “Improving the selectivity to C4 Products in the Aldol Condensation of Acetaldehyde over Faujasite Zeolites” L. Zhang, T. N. Pham, J. Faria, D. E. Resasco, Applied Catalysis B, 504, 119–129 2015

PRESENTATIONS

(with direct acknowledgement to this DOE grant)

- Herron, J.A.; Lobban, L.L.; Mallinson, R.G.; Crossley, S.P.; Resasco, D.E.; Maravelias, C.T. Process Synthesis for Biomass Torrefaction. AIChE Annual Meeting, Atlanta, GA, November 16-21, 2014.
- Herron, J.A.; Won, W.; Resasco, D.E.; Maravelias, C.T. A System-level Analysis on Biomass Thermal Fractionation and Catalytic Upgrading Processes. AIChE Annual Meeting, San Francisco, CA, November 13-18, 2016.
- L.M. Petkovic*, D.M. Ginosar, C. Hrbac, S. Lwin, "Fractionation of bio-oils using supercritical fluids," 252th ACS (American Chemical Society) National Meeting, Philadelphia, PA, August 21-25, 2016.
- L.M. Petkovic*, D.M. Ginosar, "Bio-oil fractionation using supercritical fluids," 38th Symposium on Biotechnology for Fuels and Chemicals, Baltimore, MD, April 25-28, 2016.
- L.M. Petkovic*, D.M. Ginosar, "Fractionation of thermally produced bio-oils using supercritical fluids," 250th ACS (American Chemical Society) National Meeting, Boston, MA, August 16-20, 2015.
- G.G. Zaimes, A.W Beck, D.E. Resasco, S.P. Crossley, and V. Khanna, Multistage Torrefaction of Biomass and in Situ Catalytic Upgrading to Hydrocarbon Biofuels and Specialty Biochemicals, American Institute of Chemical Engineers Annual Meeting, San Francisco, CA, November 13-18, 2016.

PRESENTATIONS

(with direct acknowledgement to this DOE grant)

- G.G. Zaines, N. Vora, D.E. Resasco, S.P. Crossley, and V. Khanna, Environmental life cycle evaluation of multistage torrefaction and pyrolysis for biofuel production, American Institute of Chemical Engineers Annual Meeting, Salt Lake City, UT, November 8-13, 2015.
G.G. Zaines, D.E. Resasco, S.P. Crossley, and V. Khanna. Environmental Impacts of Multistage Pyrolysis-Derived Biofuels: Connecting Experimental Studies with Systems-Level Analysis, International Society for Industrial Ecology Meeting, University of Surrey, Guildford, U.K. July 7-10, 2015.
G.G. Zaines, N. Vora, D.E. Resasco, S.P. Crossley, and V. Khanna, Multistage Torrefaction for Biofuel Production: A life cycle inspired assessment of the Climate-Energy Nexus, Association of Environmental Engineering and Science Professors Meeting, New Haven, Connecticut, June 14-16, 2015.