

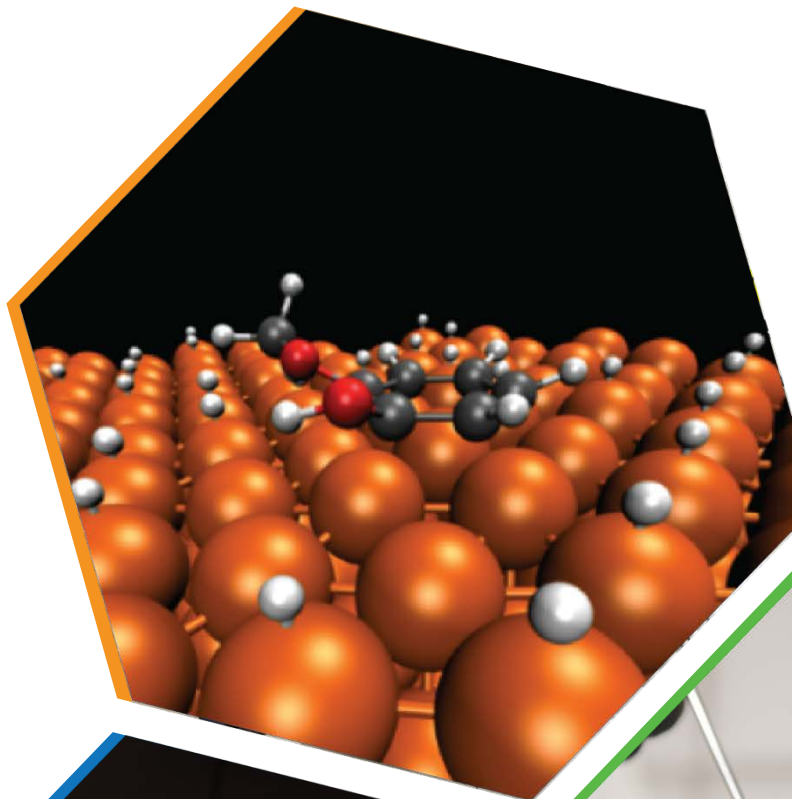


**ChemCatBio**  
Chemical Catalysis for Bioenergy

# Linking Catalyst and Process Development with Techno-Economic Analysis in the Conversion of Biomass to High-Octane Gasoline

Daniel Ruddy

March 7, 2018



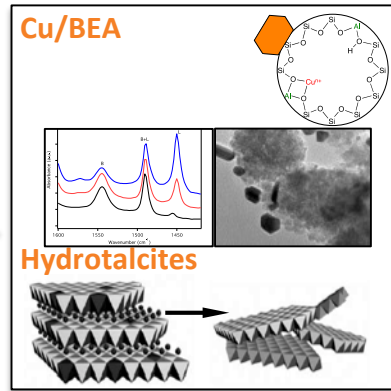
U.S. DEPARTMENT OF  
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& RENEWABLE ENERGY

BIOENERGY TECHNOLOGIES OFFICE

# Coupling Traditional Catalyst Development with TEA

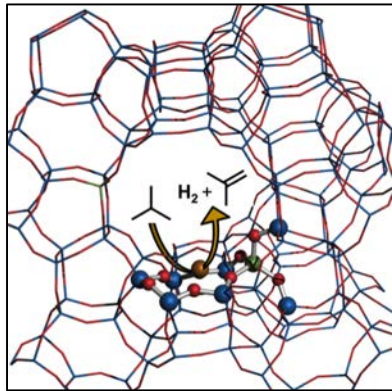
## Synthesis & Characterization



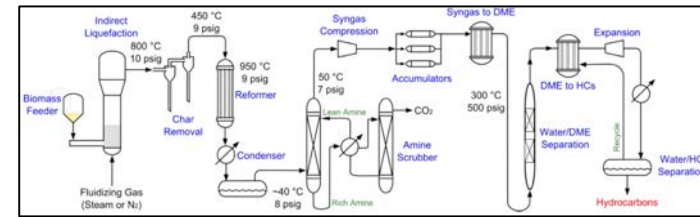
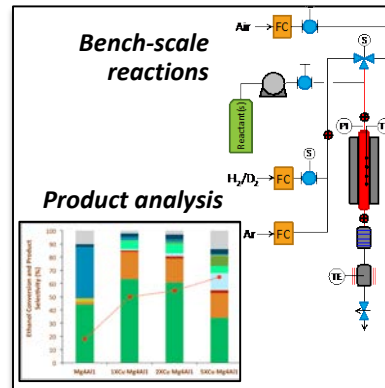
## Technoeconomic Analysis (TEA)



## Theory



## Catalyst Testing

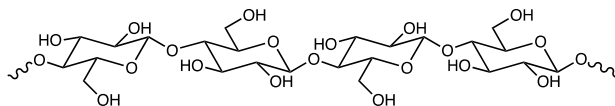


## Catalyst Scaling & Pilot-Scale Testing

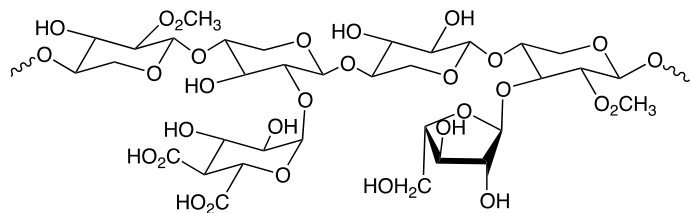
# Biomass Grand Challenge: Complex Functionality

**Biomass -  $\text{CH}_{1.4}\text{O}_{0.6}$**

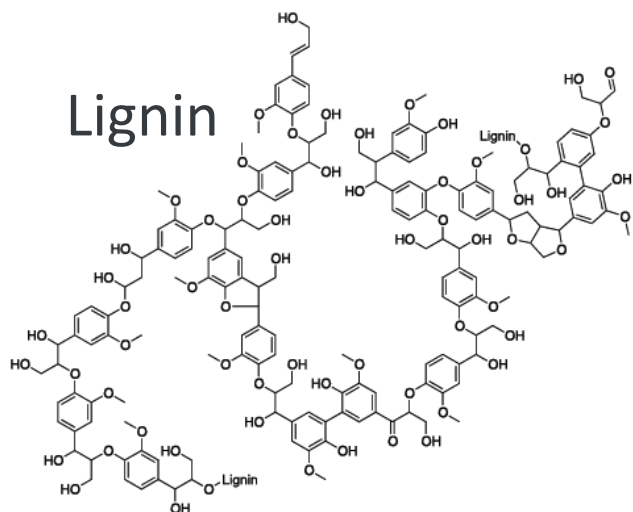
Cellulose



Hemicellulose



Lignin



**Thermochemical Pathways**

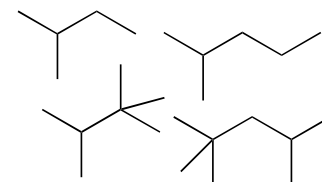
Pyrolysis  
Gasification

**Intermediates**

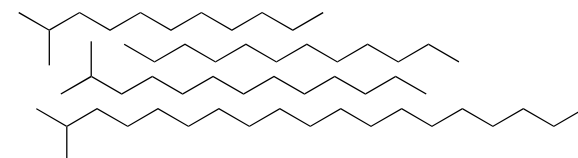
-high yield  
-balanced stability  
and reactivity

**Fuels -  $\text{C}_n\text{H}_{2n+2}$**

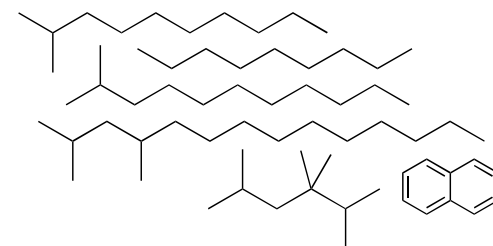
Gasoline



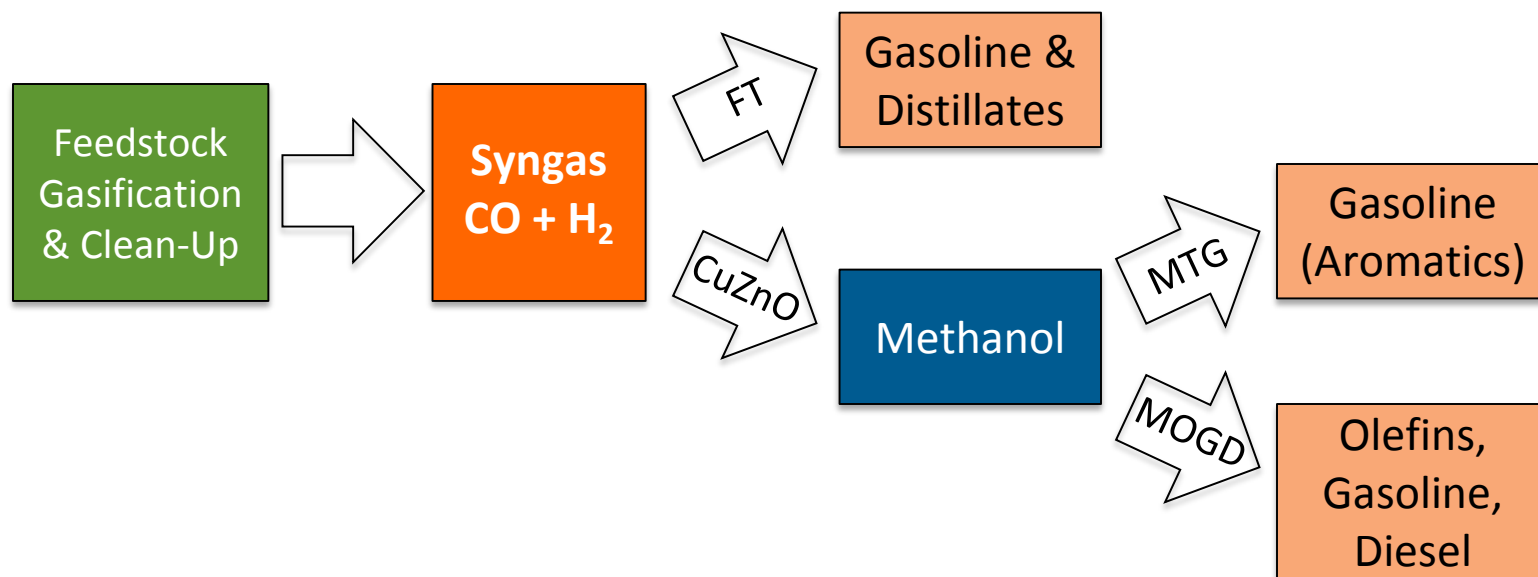
Diesel



Jet Fuel



# Industrially Relevant Syngas-to-Fuels Processes



## *Traditional syngas to hydrocarbon fuels have known drawbacks*

- Fischer Tropsch (FT): Costly catalytic upgrading to produce quality fuels
- Methanol-to-Gasoline (MTG): Capital intensive, high aromatics content
- Mobil Olefins-to-Gasoline-and-Distillate (MOGD): Capital intensive, high number of process steps

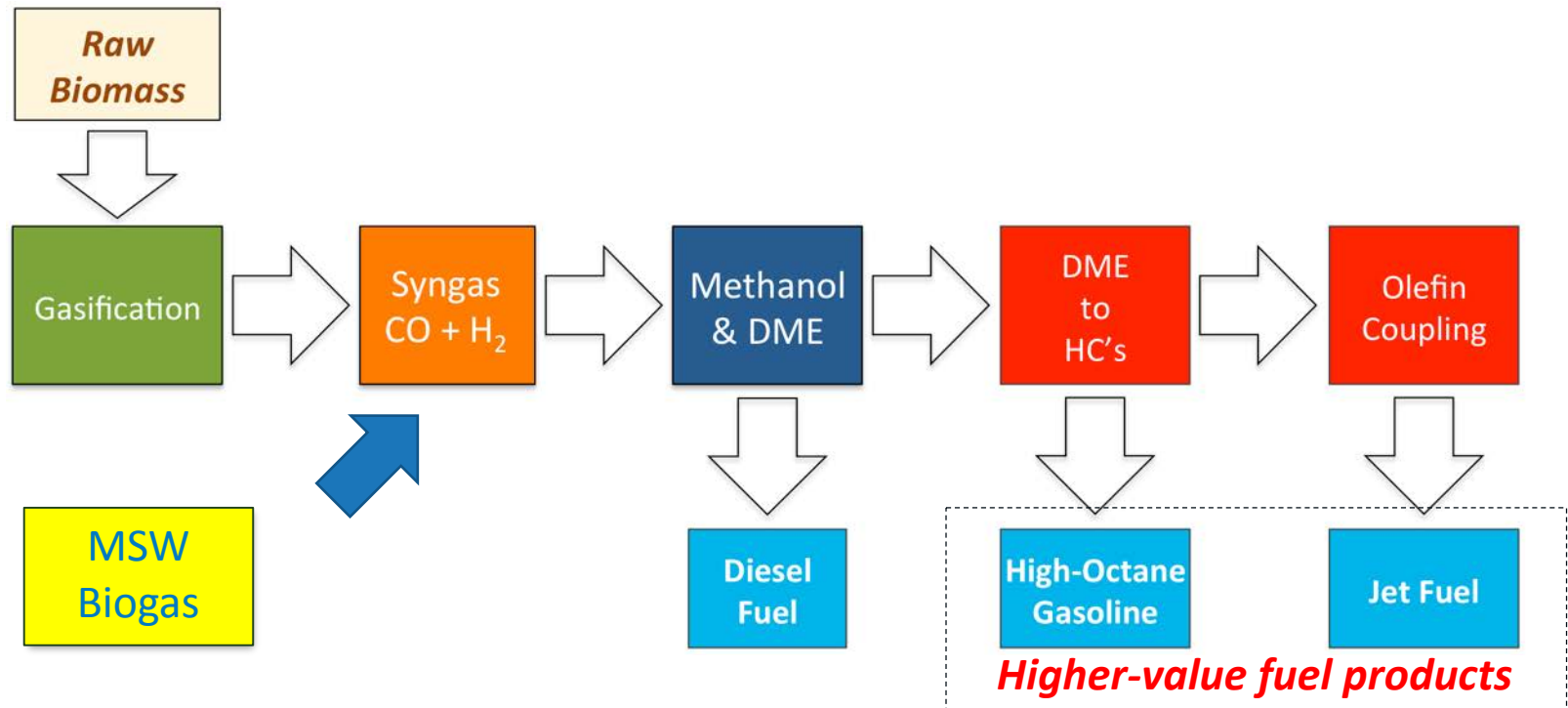
## *Net cost of production from biomass (2014 \$)*

- FT = \$3.82/gal (GGE)
- MOGD = \$4.80/gal (GGE)

***Advanced catalysts and processes are required to produce cost-competitive biomass-derived fuels***

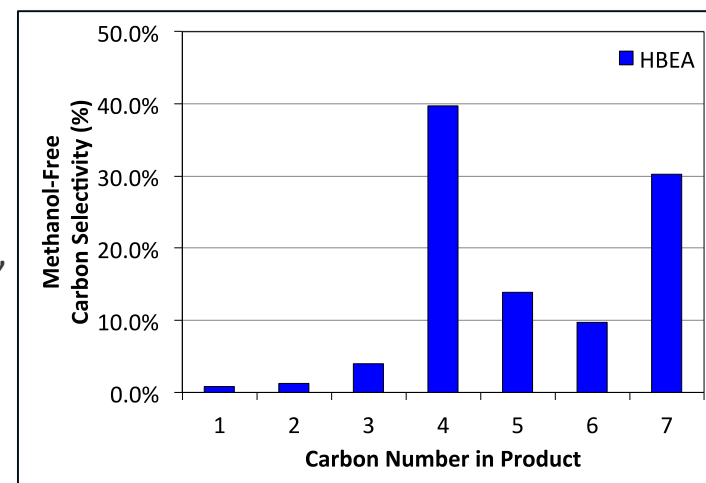
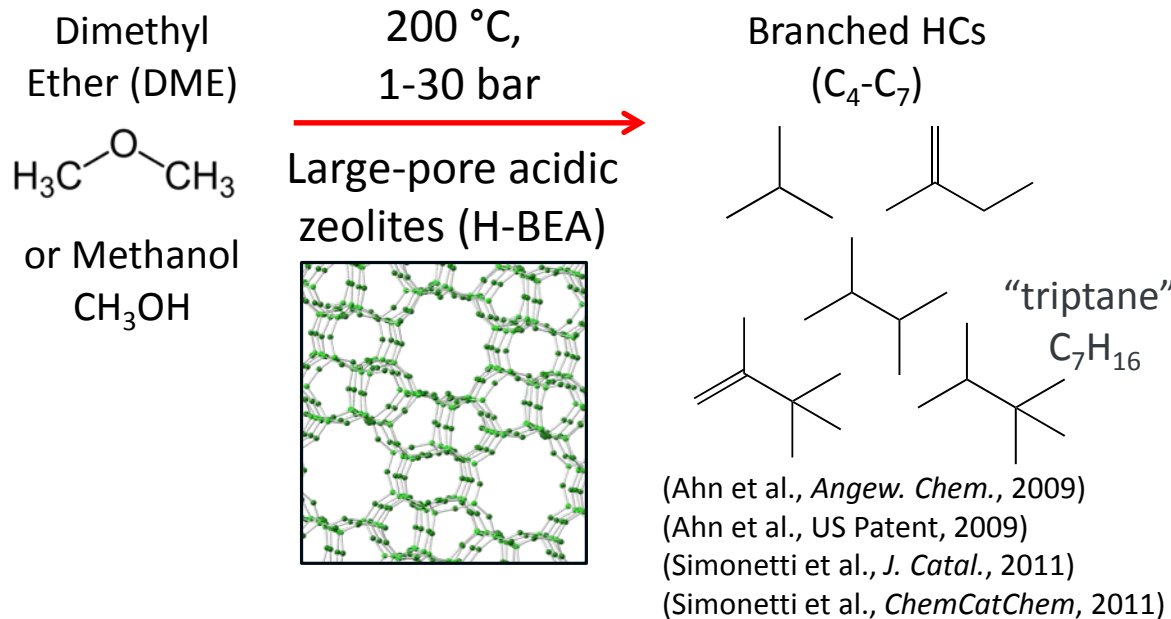
E. Tan, et al., *Biofuel Bioprod. Bioref.* **2017**, *11*, 41.

# A market-responsive biorefinery concept around methanol



- Conversion of C<sub>1</sub> intermediates (methanol/DME)
- Non-FT, non-MTG/MOGD route
- Three common fuels from this process
- Balance production of each to meet market needs

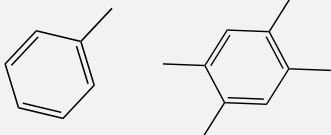
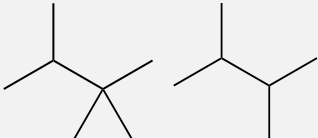
# Overview: DME-to-hydrocarbons process



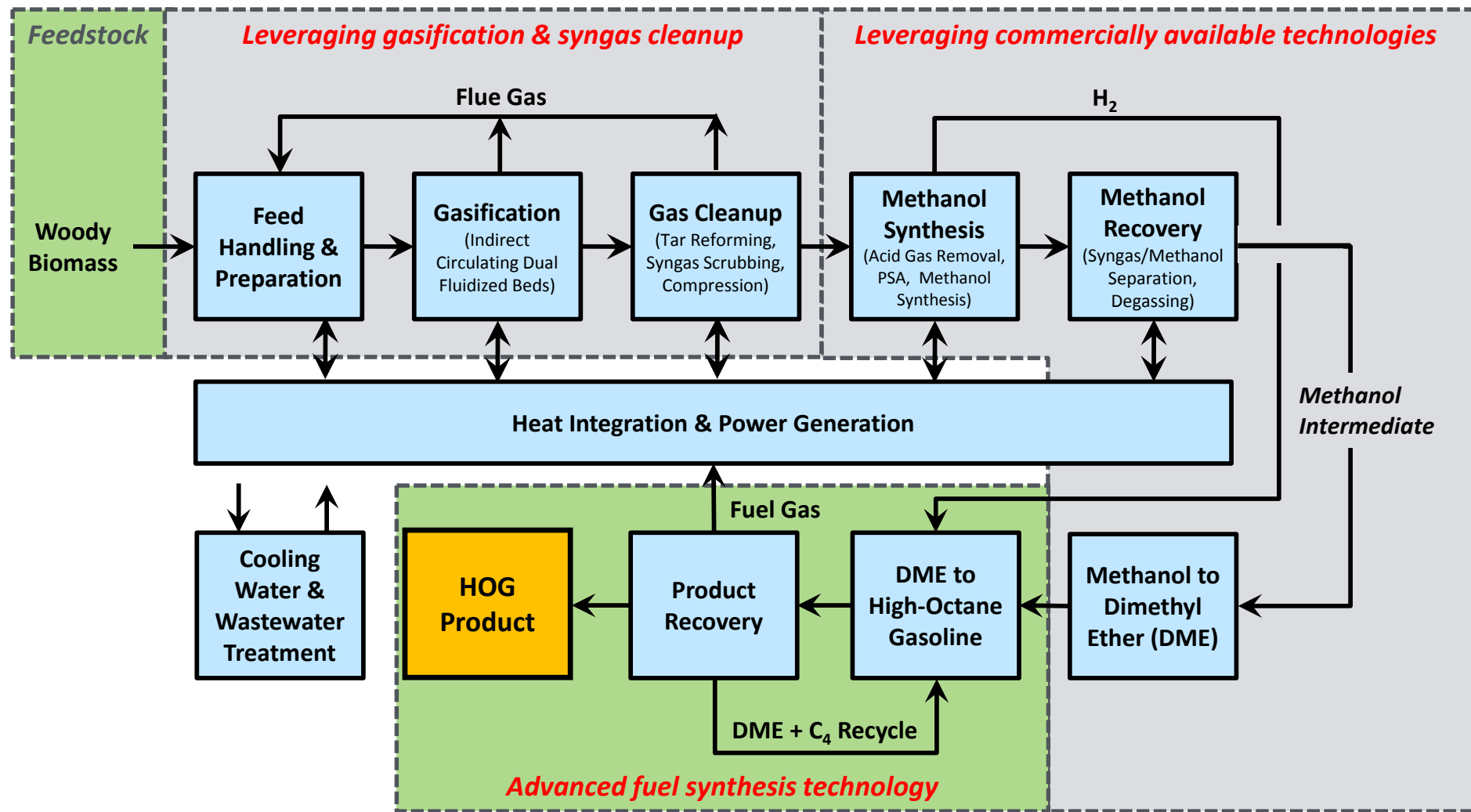
## Key points on the technology

- DME and/or methanol can be synthesized selectively from a number of sources
- Total product is a *paraffin/olefin mixture* with many C<sub>4</sub>-C<sub>8</sub> isomers
  - Oxygen-free product (except methanol)
  - Not MTG: Only observed aromatic is hexamethylbenzene (b.p. 265 °C)
- High-octane product is attractive as renewable *refinery alkylate blendstock*
- C<sub>4</sub>-C<sub>8</sub> olefins are *distillate fuel precursors*

# Comparing MTG and HOG Pathways

Methanol to Gasoline (MTG) Pathway	High-Octane Gasoline (HOG) Pathway	Advantages of HOG Pathway
		<p><b>Branched HC product, minimal aromatics</b></p>
<p><b>ZSM-5 zeolite catalyst</b></p>	<p><b>Beta-zeolite catalyst</b></p>	
<p><b>650 – 950 °F</b></p>	<p><b>350 – 450 °F</b></p>	<p><b>Lower severity conditions,</b></p>
<p><b>315 psia</b></p>	<p><b>130 psia</b></p>	<p><b>lower coking rate</b></p>
<p><b>RON: 92</b></p>	<p><b>RON: 95+</b></p>	<p><b>High octane synthetic alkylate</b></p>
<p><b>MON: 83</b></p>	<p><b>MON: 90+</b></p>	
<p><b>55 gal/ton</b></p>	<p><b>65 gal/ton</b></p>	<p><b>Higher yield (18%)</b></p>

# Process Design for Biomass to High-Octane Gasoline

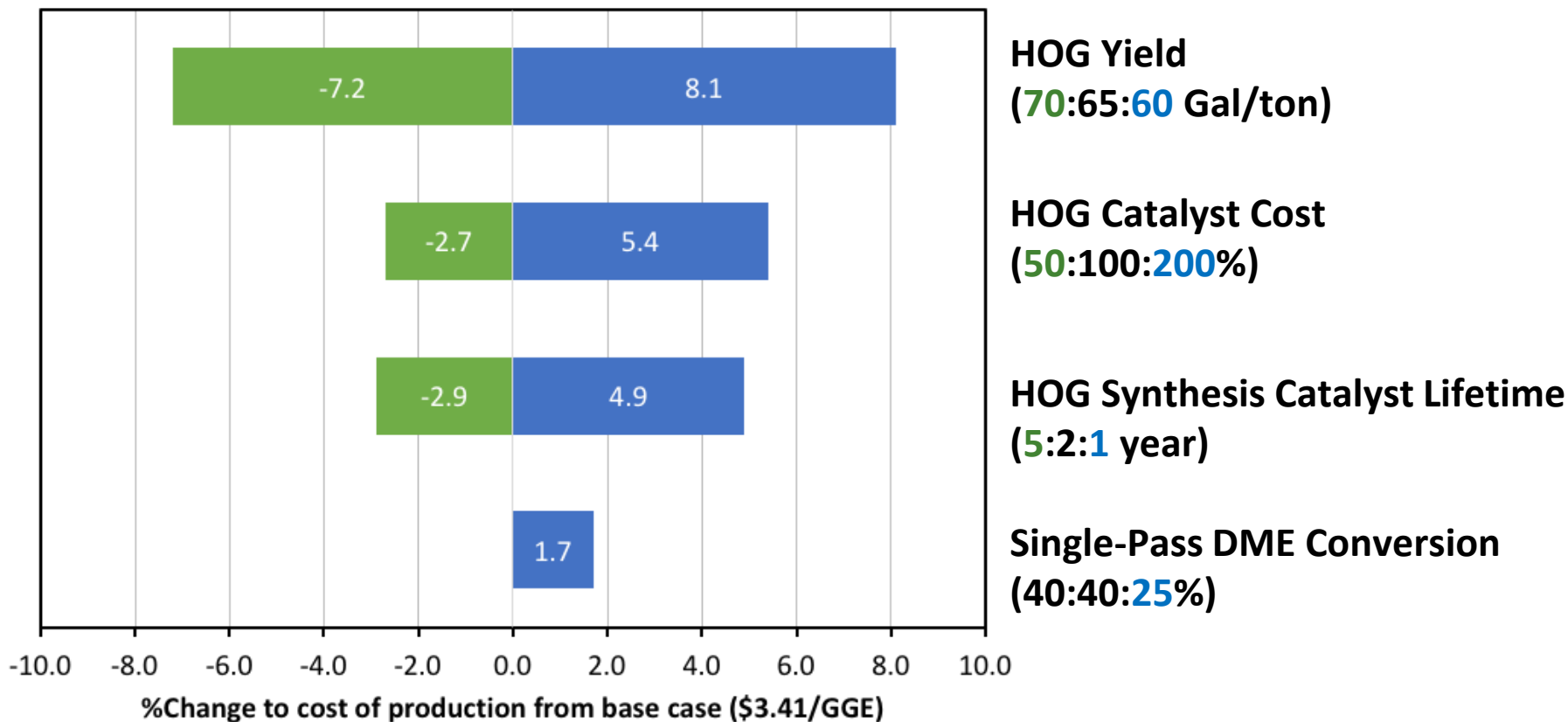


**Long-term targets:** 65 gal/dry-ton biomass; \$3.41/gal

**Near-term values with HBEA catalyst:** 40 gal/dry-ton biomass; \$5.20/gal



# Using the TEA model to aid catalyst development



- Sensitivity analysis highlights the importance of developing an *inexpensive catalyst* with a *long lifetime* that demonstrates *high selectivity to C<sub>5+</sub> products to increase product yield*
- Selectivity to C<sub>5+</sub> products is more important than conversion

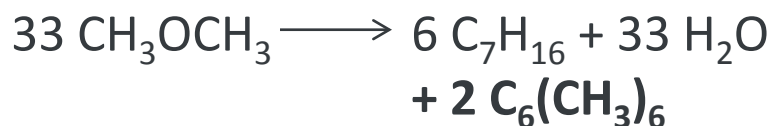
# What limits the performance by HBEA?

## Hydrogen Deficiency

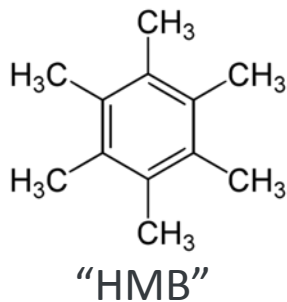


Need an additional 2H per alkane produced

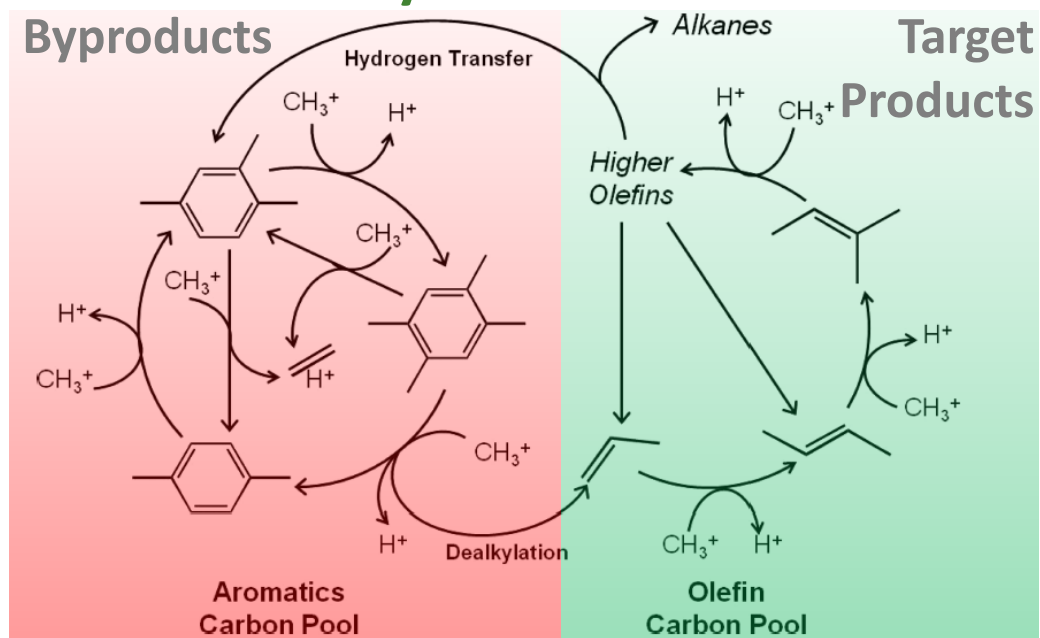
## Yield Loss



Leads to formation of heavy unsaturated hydrocarbons



## Dual-Cycle Mechanism

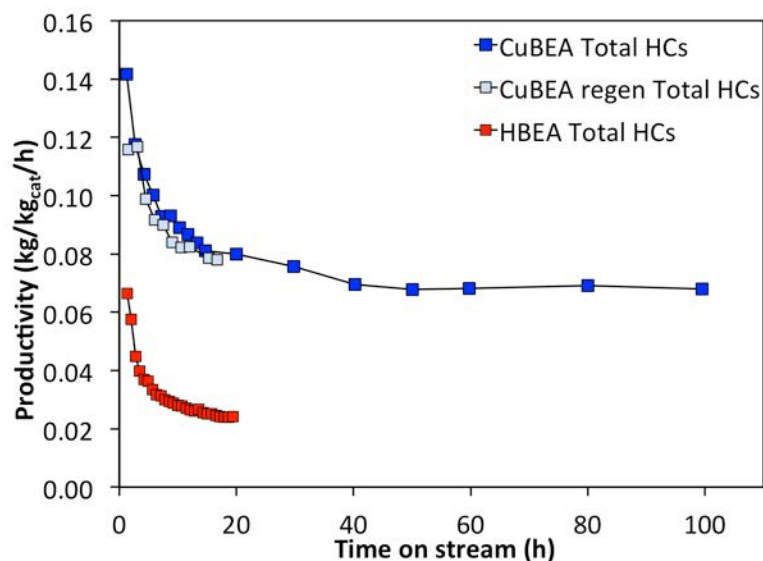


S. Ilias, A. Bhan, *ACS Catalysis*, 2013

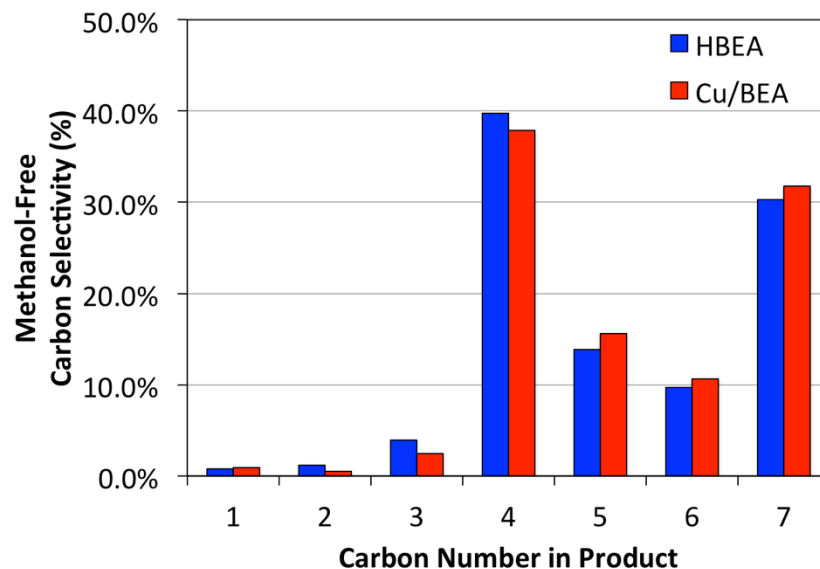
## Catalyst Improvements Needed

1. Shift away from aromatic cycle and toward olefin cycle
2.  $\text{H}_2$  can be activated and participate in the reaction
  - reduce aromatic formation, maintain  $\text{C}_{5+}$  selectivity
3. Light alkane products can be reactivated and re-enter the catalytic cycle
  - recycle (to extinction) to maximize  $\text{C}_{5+}$  yield

# Cu/BEA for improved DME homologation performance



**2-3X increase in HC production rate  
AND extended lifetime**



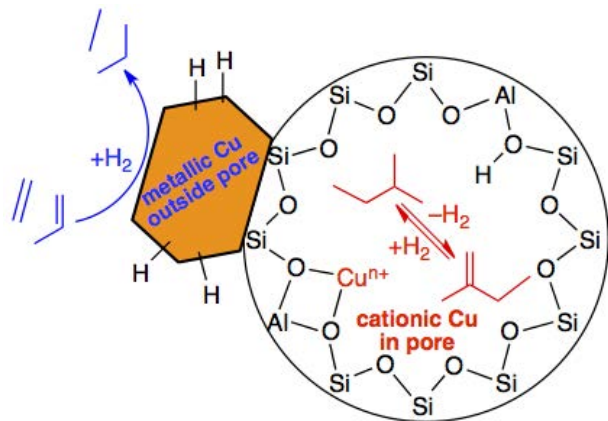
**High selectivity to C<sub>4</sub> and C<sub>7</sub>**

Catalyst	Aromatic cycle	Olefin cycle	%C as HMB
HBEA	23%	77%	13%
HBEA + H <sub>2</sub>	21%	79%	7%
Cu/BEA + H <sub>2</sub>	8%	92%	4%

- **Decrease in aromatic (HMB) selectivity for Cu/BEA + H<sub>2</sub>**
- **Products from olefin cycle are favored using Cu/BEA + H<sub>2</sub>**
- **Cu/BEA catalyst achieves the first 2 goals**

# What is the role of Cu?

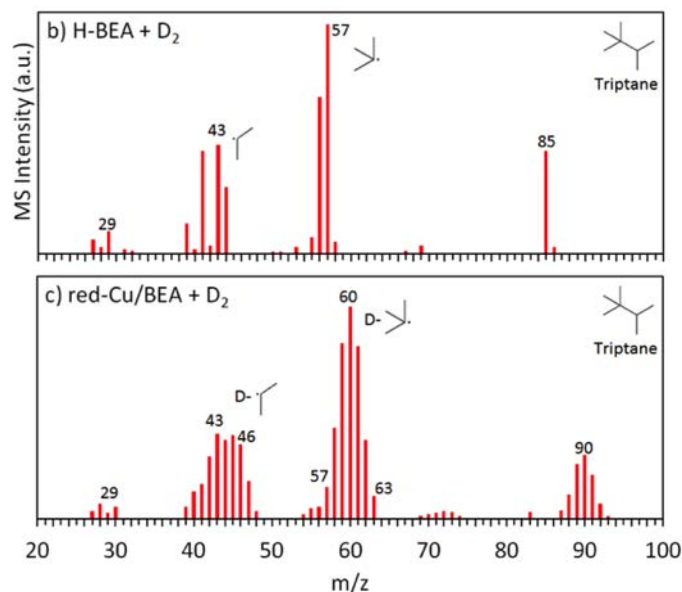
## Cu speciation explored using XAS (Argonne National Lab)



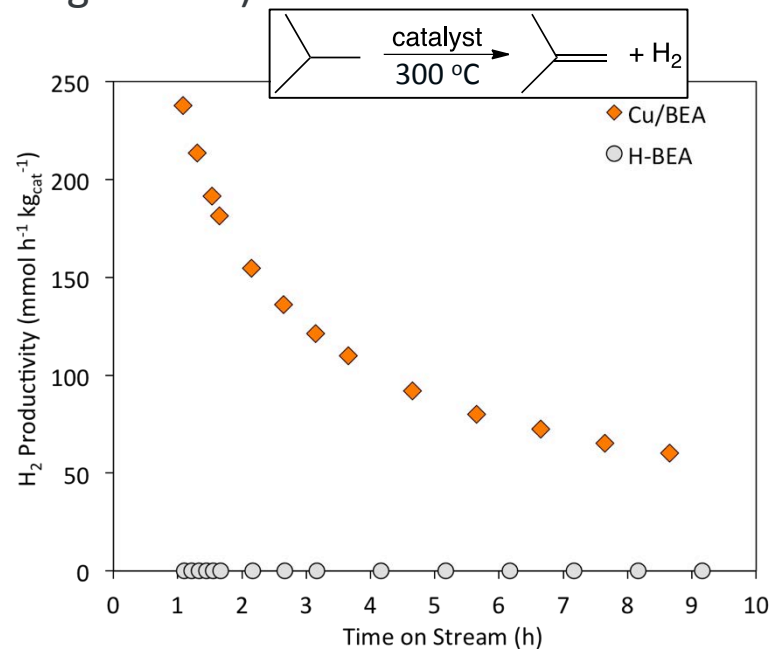
-Observe contributions from **metallic** and **ionic** Cu

### Multi-functional catalysis:

- (1) metallic Cu activates H<sub>2</sub>, performs ethylene/propylene hydrogenation (increases P:O ratio)
- (2) cationic Cu facilitates H-transfer (dehydrogenation)

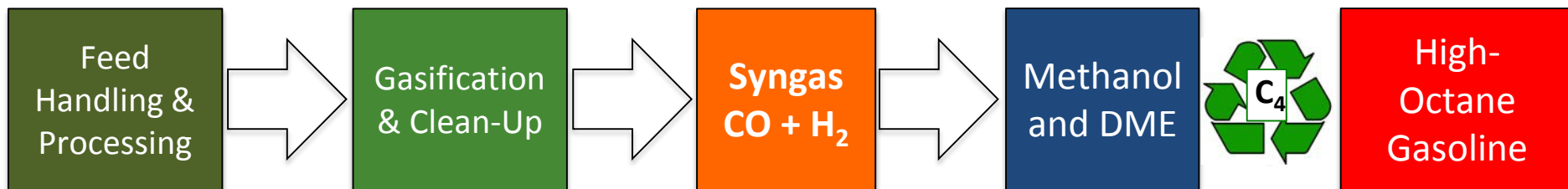


-Observe extensive **D-incorporation** with D<sub>2</sub>

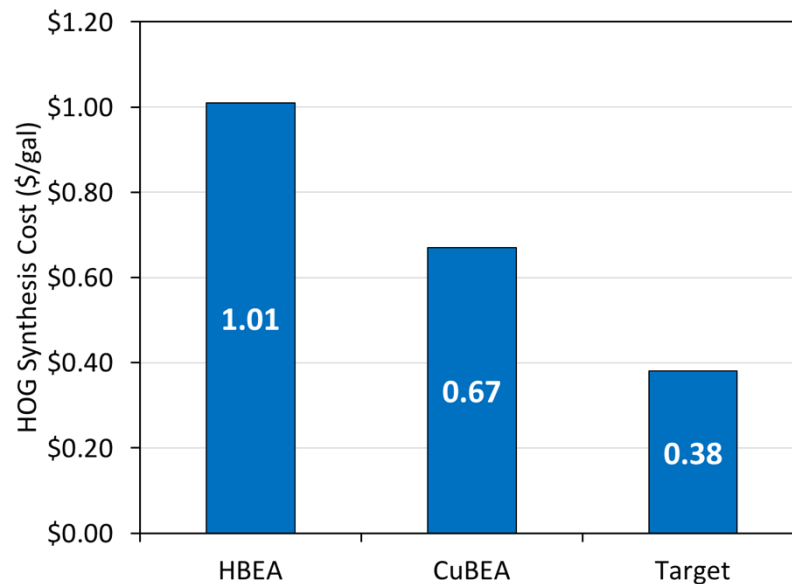
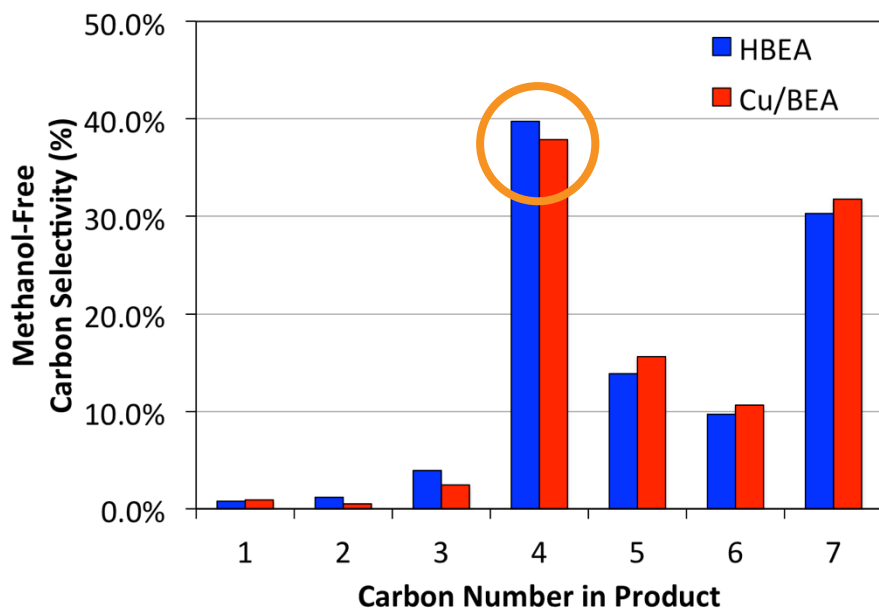


-H<sub>2</sub> **production** from C<sub>4</sub>H<sub>10</sub> over Cu/BEA

# TEA Motivation to Recycle $C_4$ Product



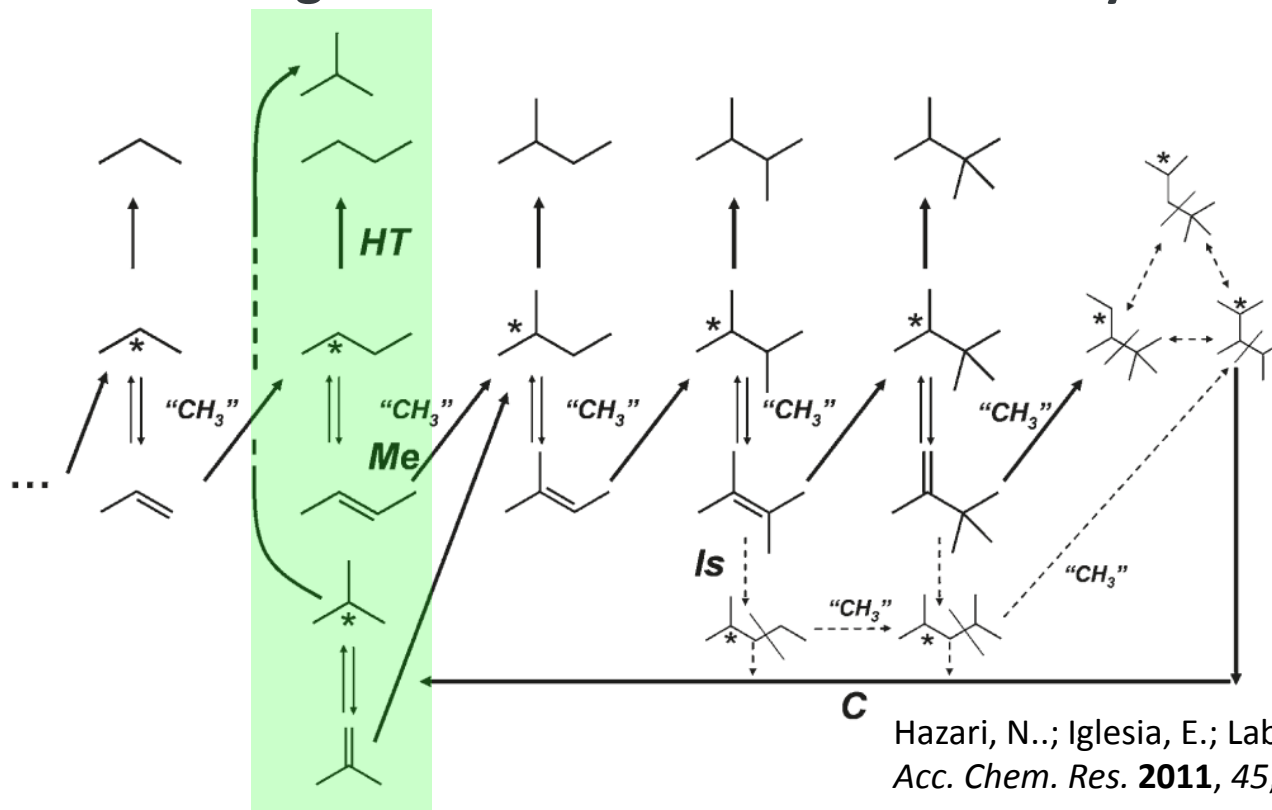
## Yield and Cost Impact with $C_4$ Recycle



*$C_4$  product recycle is a critical component in the TEA to achieve high yield and lower cost of production*

# Why is C<sub>4</sub> dehydrogenation difficult?

## Step-wise chain-growth mechanism for DME-to-Hydrocarbons



- Alkanes are considered terminal products – no re-incorporation over HBEA
- Dehydrogenation of isobutane offers a simple system to probe the ability of a catalyst to reincorporate C<sub>4</sub> alkanes

**Approach:** Combined computational and experimental studies over Cu/BEA

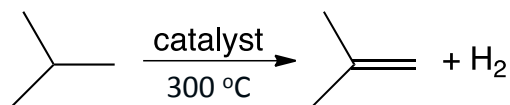
# Catalyst Materials and Characterization

Catalyst	Pre-treatment	Site (characterization)
CuO/SiO <sub>2</sub>	1% O <sub>2</sub> , 500 °C	CuO particles (XRD)
Cu/SiO <sub>2</sub>	1% O <sub>2</sub> , 500 °C; 2% H <sub>2</sub> , 300 °C	Cu(0) particles (XRD)
H-BEA	1% O <sub>2</sub> , 500 °C	Brønsted acid (NH <sub>3</sub> TPD, pyridine-DRIFTS)
ox-IE-Cu/BEA	1% O <sub>2</sub> , 500 °C	Ionic Cu(II)-zeolite (XAS)
red-IE-Cu/BEA	1% O <sub>2</sub> , 500 °C; 2% H <sub>2</sub> , 300 °C	Ionic Cu(I)-zeolite (XAS)

- **Synthesized catalyst materials with the specific catalytic functionalities present in Cu/BEA**
  - **CuO versus Cu without Bronsted acid sites**
  - **Bronsted acid sites only**
  - **Cu(II)-zeolite versus Cu(I)-zeolite with Bronsted acid sites; without metallic Cu**

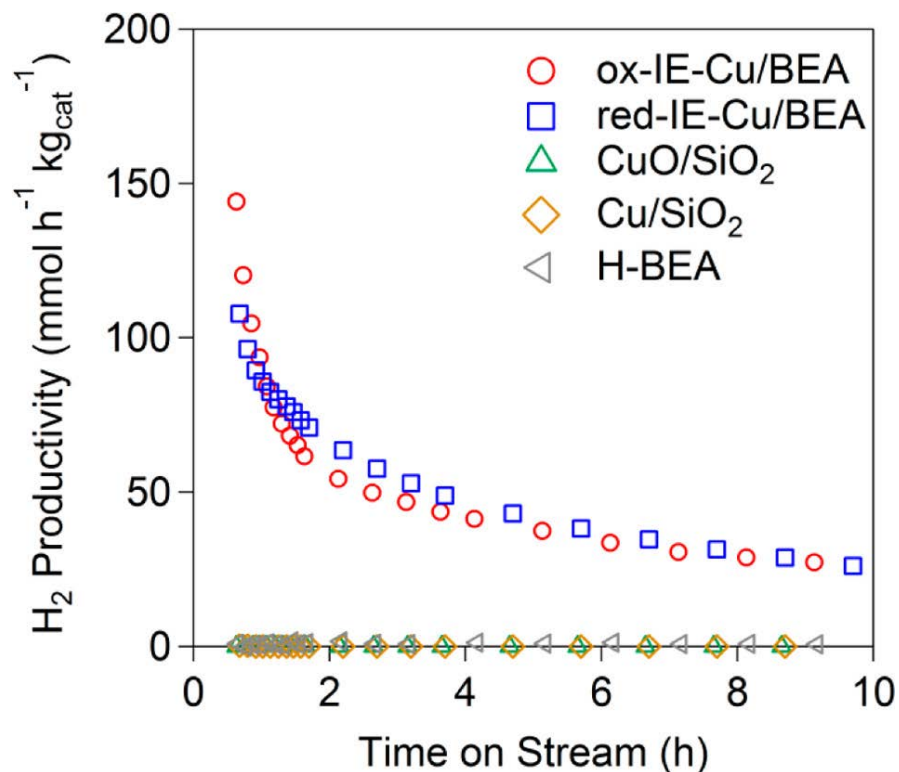
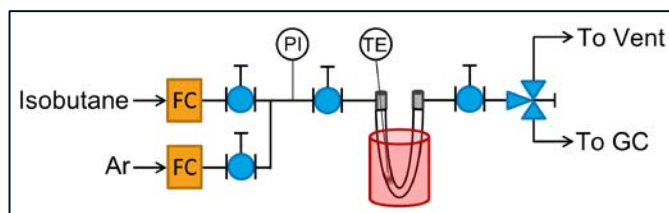
# Catalytic Testing

## Isobutane Dehydrogenation Reaction



### Fixed-bed reactor experiments

- 100 mg<sub>cat</sub>
- 1% i-butane/He at 7 sccm
- T = 300 °C
- P = 2 atm
- X<sub>i-butane</sub> < 5%

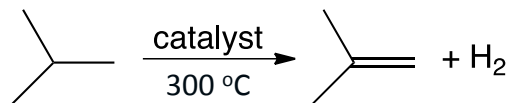


- Catalysts containing **ionic Cu species** exhibit comparable isobutane dehydrogenation activities
- CuO nanoparticles, metallic Cu nanoparticles, and Bronsted acid sites are not active



# Operando XAS (Argonne National Lab)

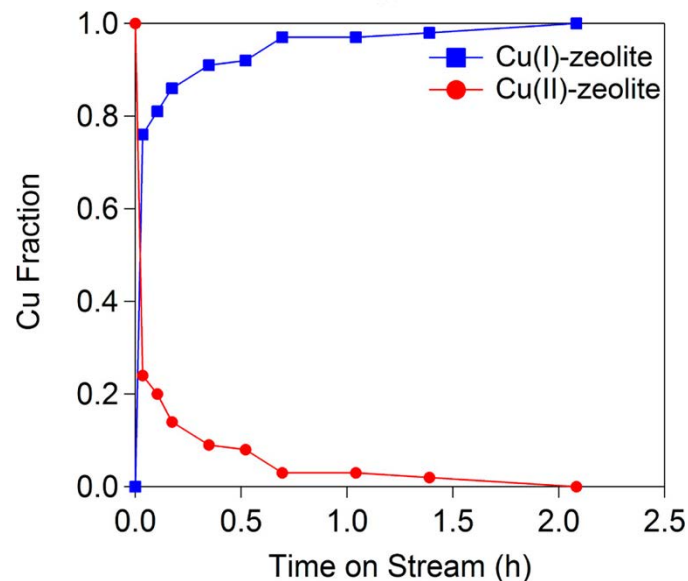
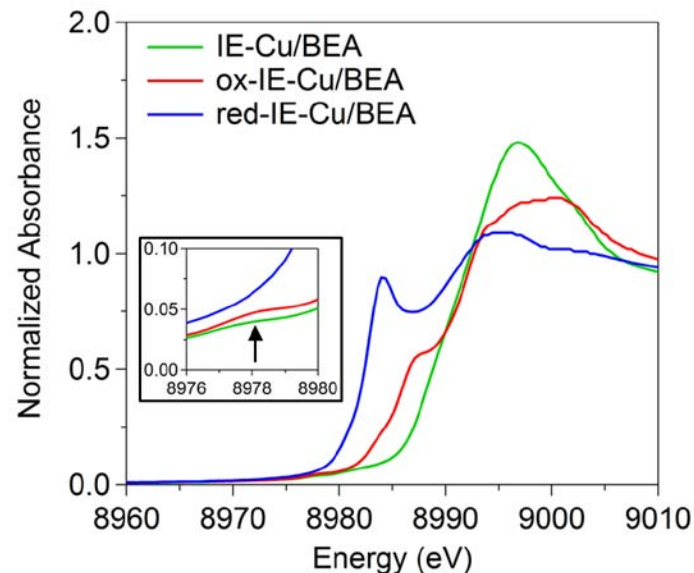
## Determine speciation of ionic Cu during isobutane dehydrogenation



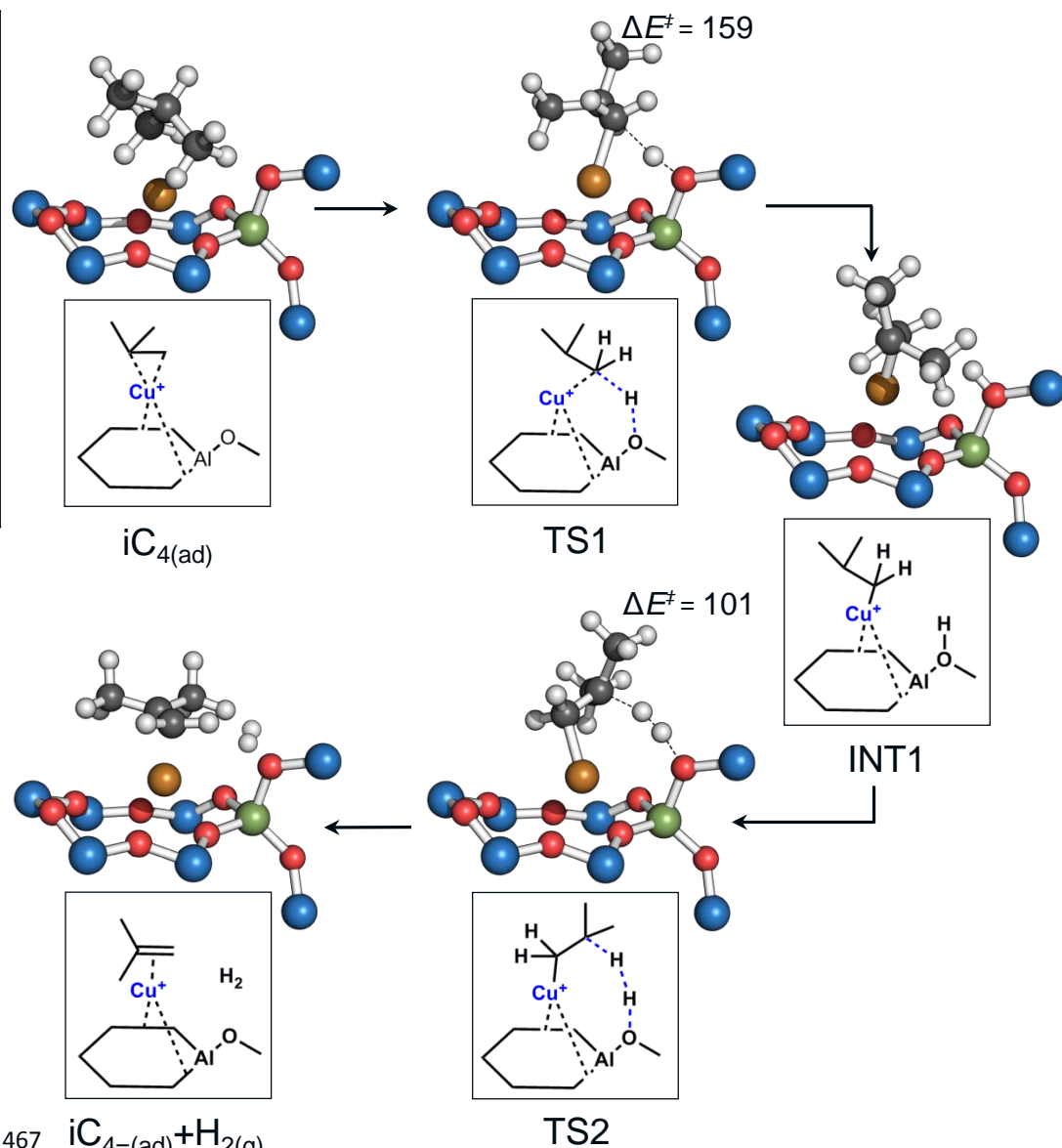
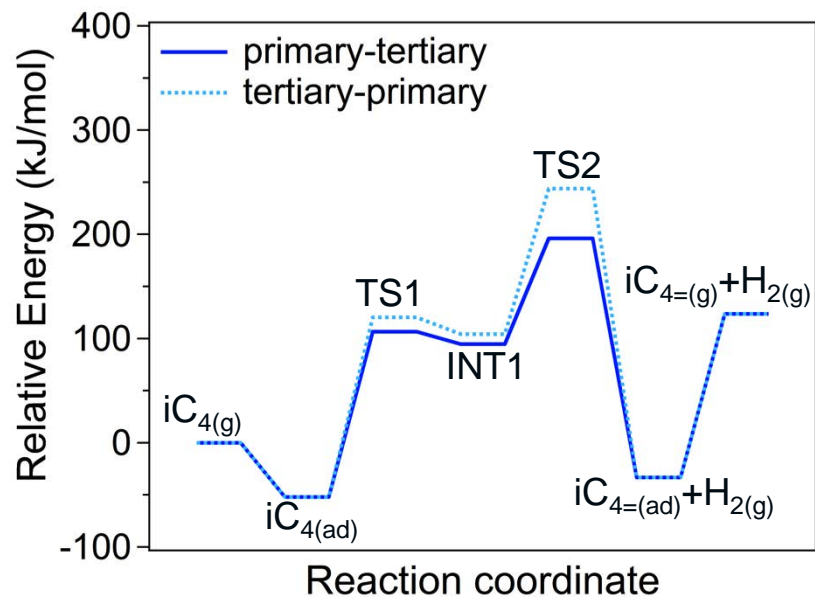
### Cu speciation

- ox-IE-Cu/BEA is ~80% Cu(I) at 2 min TOS and ~100% Cu(I) by 2h TOS
- red-IE-Cu/BEA remains Cu(I) throughout the experiment
- no metallic copper observed

***Ionic Cu(I) species are responsible for the observed dehydrogenation activity***



# Computation: Reaction Mechanism and Energetics

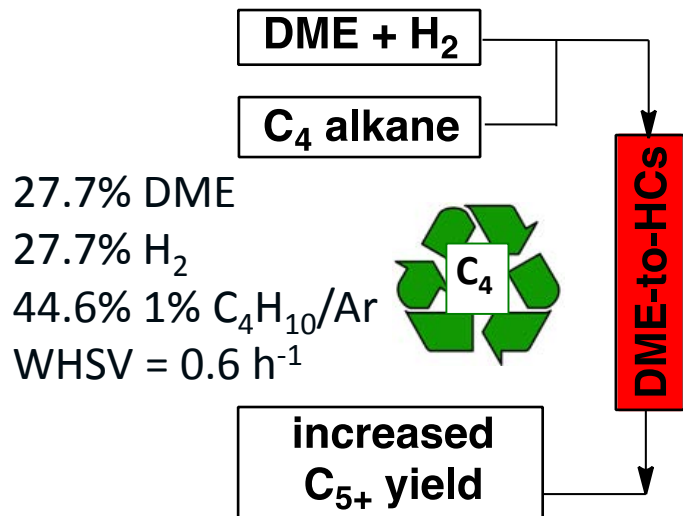


- Comparison of activation energies with previous reports<sup>1, 2</sup> for Ga- and Zn-modified MFI suggest **Cu/BEA** should be less active than these
- May improve performance with bimetallic catalysts

1) Y. Sun, T. C. Brown, *International Journal of Chemical Kinetics* (2002) 34, 467  
 2) M. S. Pereira, A. M. Da Silva, M. A. C. Nascimento, *J Phys Chem C* (2011) 115, 10104

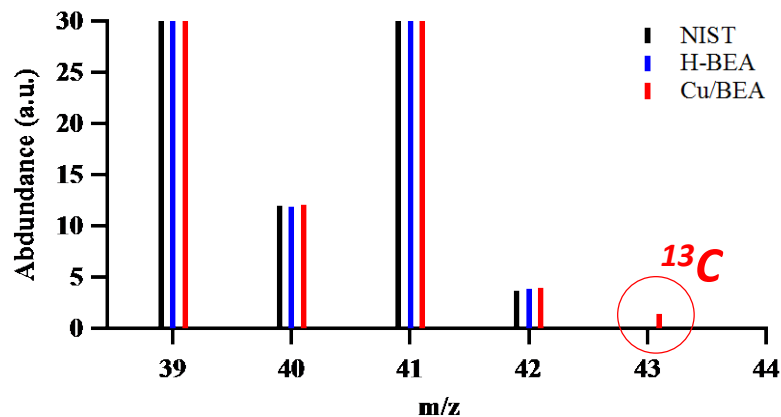
# C<sub>4</sub>H<sub>10</sub> Recycling during DME-to-HCs

## Simulated C<sub>4</sub>H<sub>10</sub> recycle to maximize C<sub>5+</sub> yield



Temperature (°C)	Pressure (psig)	Co-feed C <sub>4</sub> H <sub>10</sub>	Conversion (%)	C <sub>5+</sub> Selectivity (%)
200	3	N	20.0	63.4
200	3	Y	19.2	63.4
200	25	N	23.3	68.8
200	25	Y	19.2	68.3

## Mass spectrum of isobutene product

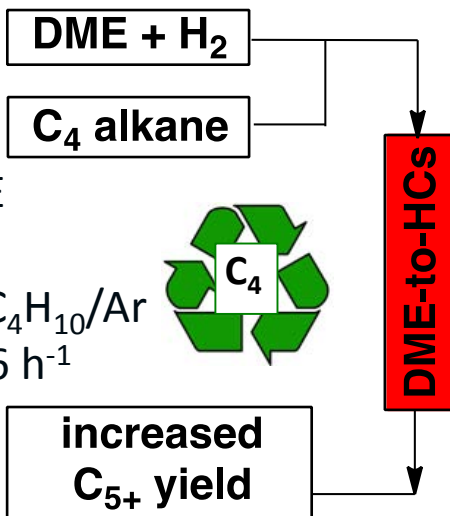


## DME + H<sub>2</sub> + <sup>13</sup>C-C<sub>4</sub>H<sub>10</sub>

- Minor decrease in yield with co-fed C<sub>4</sub>H<sub>10</sub>
- Increased C<sub>5+</sub> selectivity with pressure
- <sup>13</sup>C-isobutene observed in products
- Confirms dehydrogenation activity over Cu/BEA in the presence of DME + H<sub>2</sub>

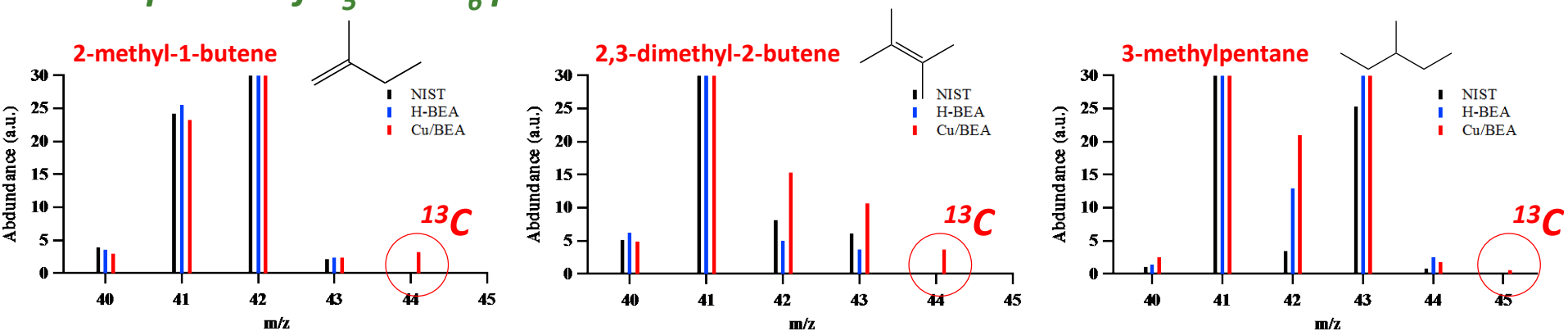
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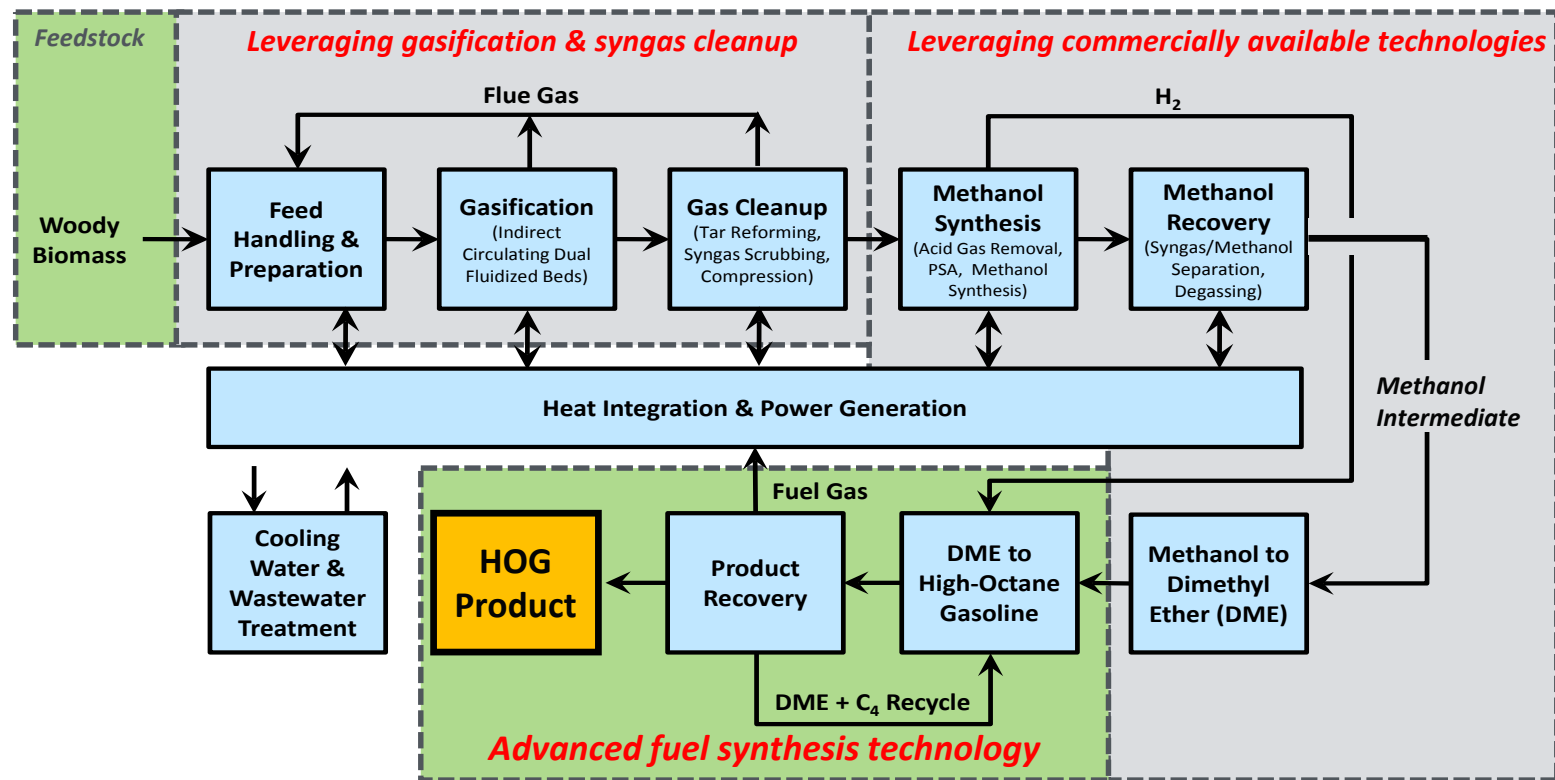
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200	3	N	20.0	63.4
200	3	Y	19.2	63.4
200	25	N	23.3	68.8
200	25	Y	19.2	68.3

## Mass spectra of C<sub>5</sub> and C<sub>6</sub> products



– Indicates <sup>13</sup>C-C<sub>4</sub>H<sub>10</sub> reincorporation into C<sub>5+</sub> products

# Process Design for Biomass to High-Octane Gasoline



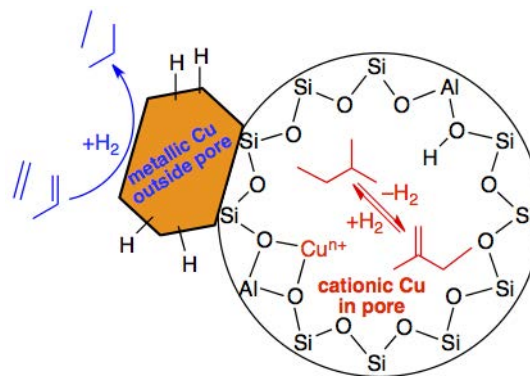
**BEA:** 40 gal/dry-ton biomass; \$5.20/gal

**Cu/BEA:** 56 gal/dry-ton biomass; \$4.54/gal

- 13% reduction versus HBEA catalyst, \$0.66 absolute
- 40% increase in yield per dry ton versus HBEA
- Requires high-productivity Cu/BEA and C<sub>4</sub> reactivation at Cu<sup>+</sup> sites (not HBEA)
- Recall MOGD at \$4.80/gal for gasoline and distillate from biomass

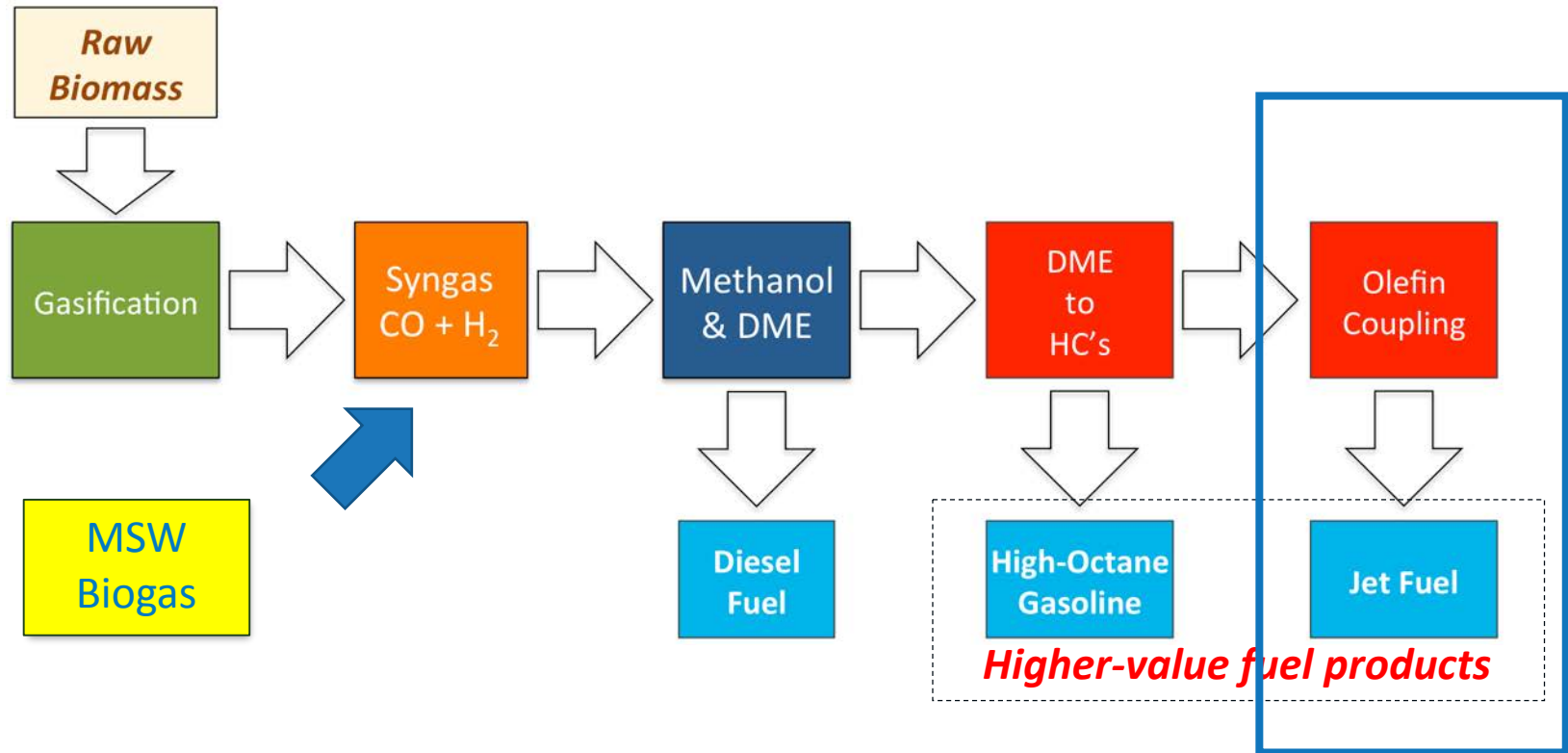
# Considering the observed C<sub>4</sub>H<sub>10</sub> conversion

Temperature (°C)	Pressure (psig)	Isobutane Conversion (%)
200	3	14.5
200	25	23.2



- Conversion values are remarkably high compared to the thermodynamic considerations of isobutane dehydrogenation at 200 °C (< 1% expected)
- Suggests that the observed reactivity is *kinetically driven*, presumably through consumption of the products – isobutene and H<sub>2</sub>
  - Similar to product removal concepts that drive methanol/DME synthesis, condensation reactions, etc.
  - Dehydrogenation inside the zeolite pores at ionic Cu sites near H<sup>+</sup> sites
- Methylation and H-transfer rates of isobutene over HBEA were reported to be 33 and 38 μmol/mol<sub>Al</sub>/s
- Our C<sub>4</sub>H<sub>10</sub> conversion rate was 7.2 (3psig) and 11.5 (25psig) μmol/mol<sub>Al</sub>/s

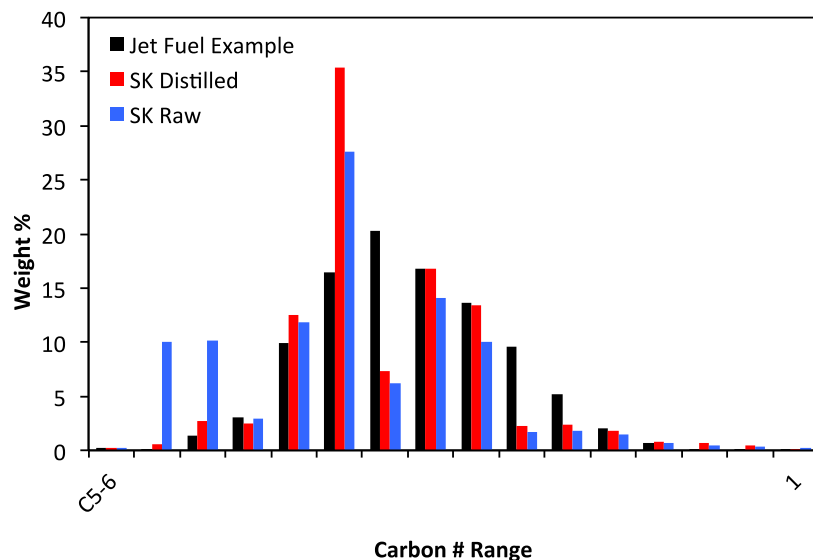
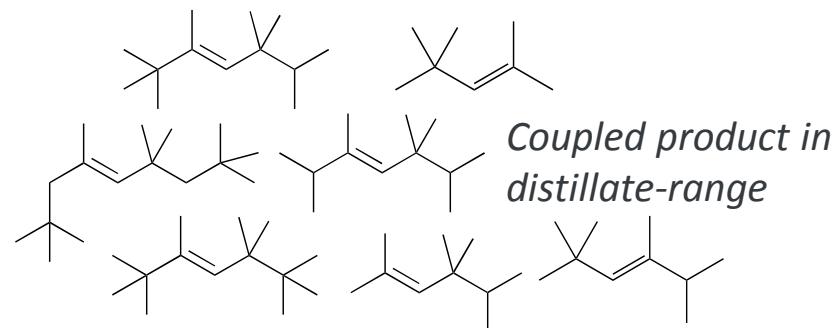
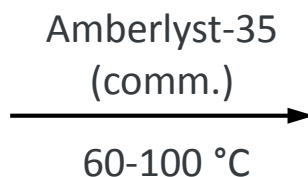
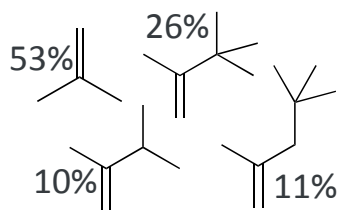
# A market-responsive biorefinery concept around methanol



- Conversion of C<sub>1</sub> intermediates (methanol/DME)
- Non-FT, non-MTG/MOGD route
- Three common fuels from this process
- Balance production of each to meet market needs

# Distillate production from HOG olefins

Representative olefin mix from DME-to-HC (mol%)

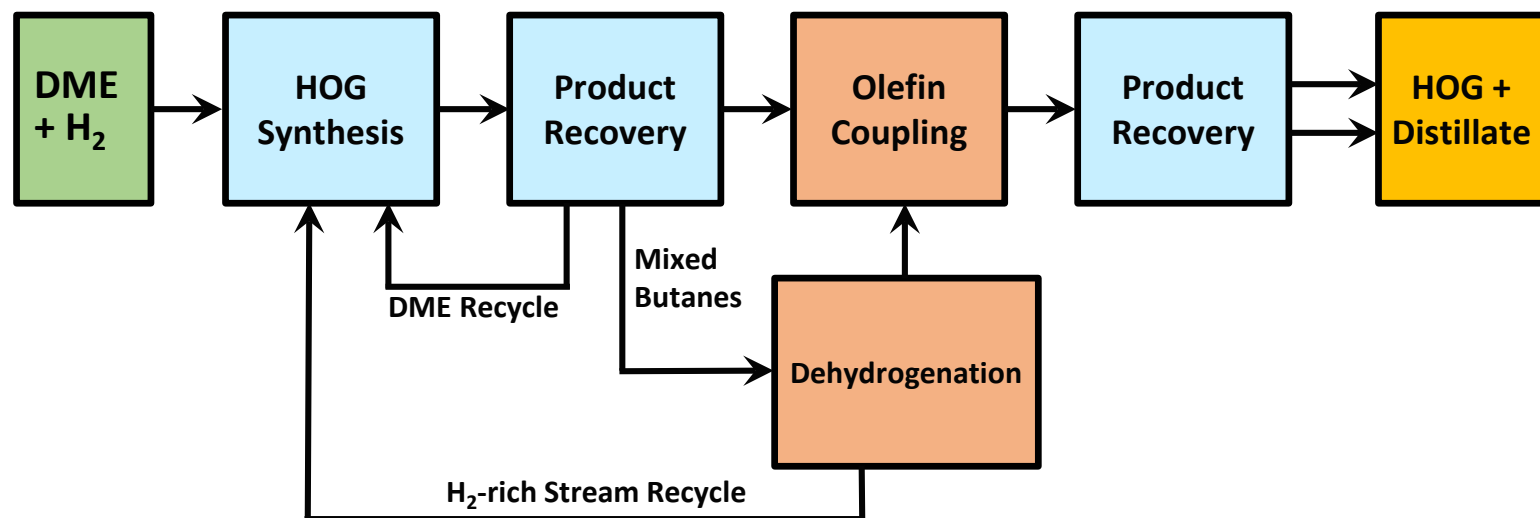


- Simple vacuum distillation removes unreacted light C<sub>7</sub>-C<sub>8</sub>
- Carbon numbers are similar to commercial jet fuel (C<sub>8</sub>-C<sub>20</sub>)
- No "heavies" (>C<sub>22</sub>)

*Product meets ASTM specifications for density, viscosity, heat of combustion, freeze point, distillation curve*



# Incorporating Distillate Production into the TEA model



**HOG only (Cu/BEA):** 56 gal/dry-ton biomass; \$4.54/gal

**HOG and Distillates:**

29 gal-HOG/dry-ton biomass

20 gal-jet/dry-ton biomass

\$4.71/gal

- Slight decrease in total yield, minor increase in cost vs HOG-only
  - Adding additional cap-ex to convert only a portion of the product
  - Distillate yield is limited by paraffin:olefin ratio in HOG product
- Recall MOGD at \$4.80/gal for gasoline and distillate from biomass

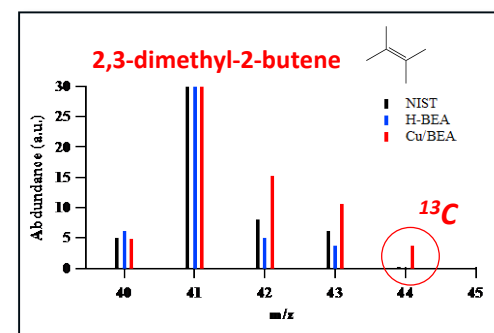
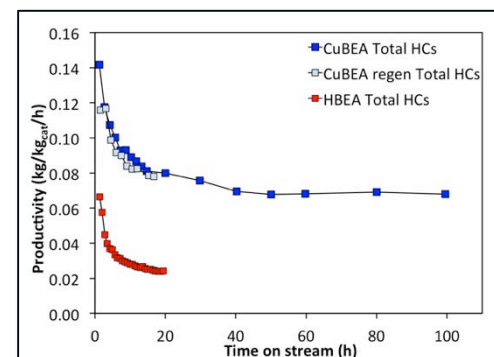
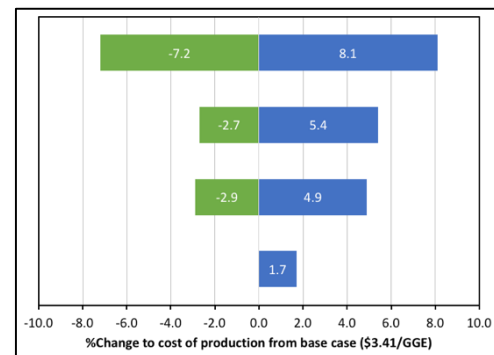
# Summary

## Conclusions

- TEA can be coupled with R&D to direct and understand the value of catalyst improvements
- Developed an inexpensive Cu/BEA catalyst with 2-3X improved productivity and extended lifetime
- Cu/BEA reactivates and reincorporates isobutane in the presence of DME + H<sub>2</sub>
- Results in 40% increased yield and 13% reduced cost versus HBEA in the process model
- Distillates can be produced, but with additional cost

## On-going R&D

- Computation suggests Zn(2+), Ga(3+) should be more active for isobutane dehydrogenation than Cu(1+)
- Developing bimetallic catalysts to control P:O ratio in HOG product
  - Control HOG fuel properties and distillate yield



# DME-to-Fuels Research Team

## ***Catalyst Development Team***

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## ***Technoeconomic Analysis***

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## ***NREL Fuel Property Analysis***

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Bioenergy Technologies Office

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Chemical Catalysis for Bioenergy



**Energy Materials Network**

U.S. Department of Energy

# Thank you!

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