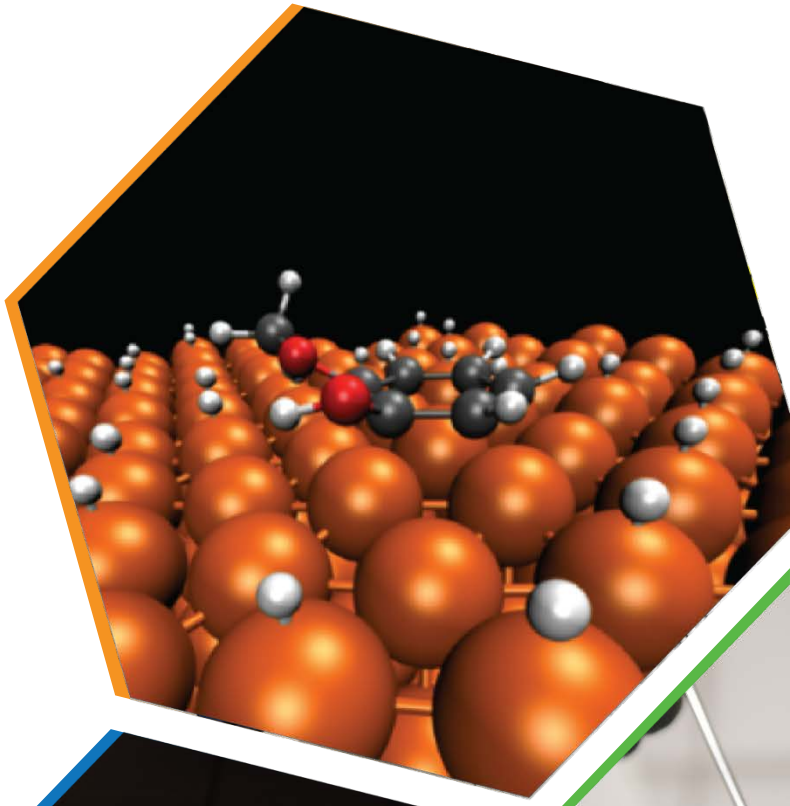
ChemCatBio
Chemical Catalysis for Bioenergy



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

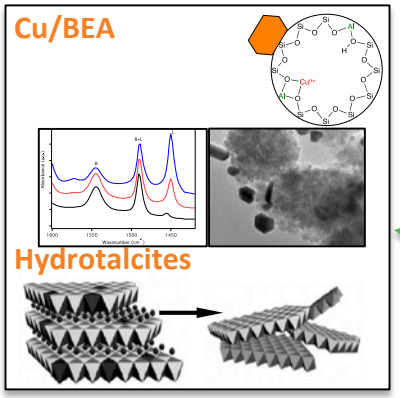
Daniel Ruddy

March 7, 2018

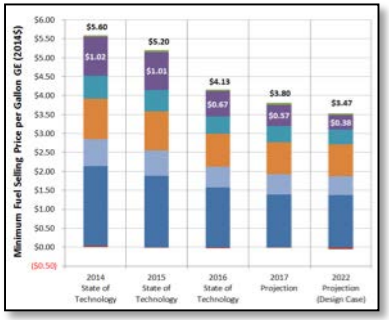
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Coupling Traditional Catalyst Development with TEA

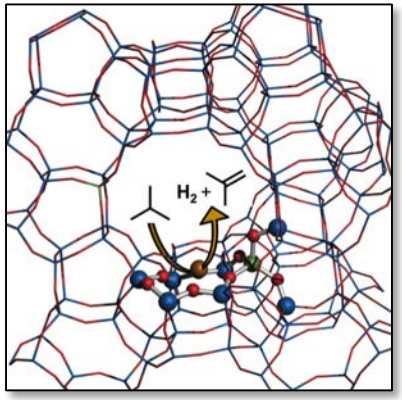
Synthesis & Characterization



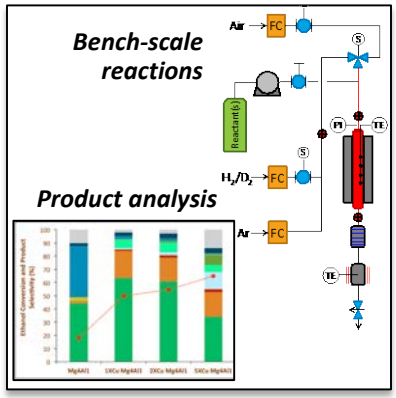
Technoeconomic Analysis (TEA)

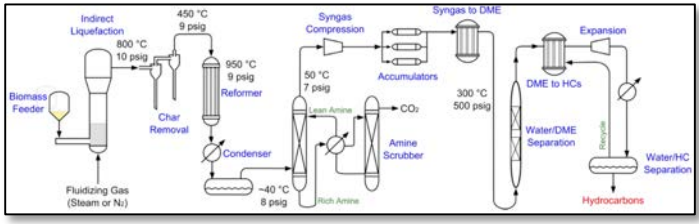


Theory



Catalyst Testing



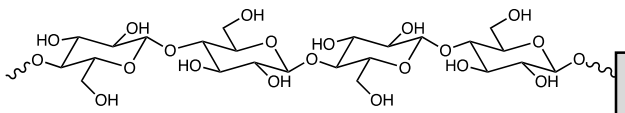


Catalyst Scaling & Pilot-Scale Testing

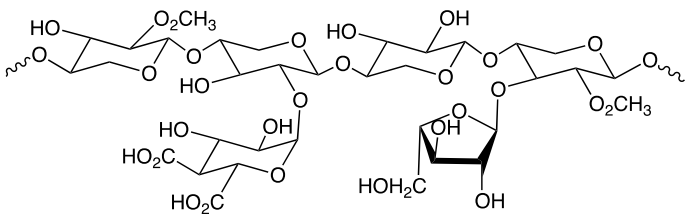
Biomass Grand Challenge: Complex Functionality

Biomass - $CH_{1.4}O_{0.6}$

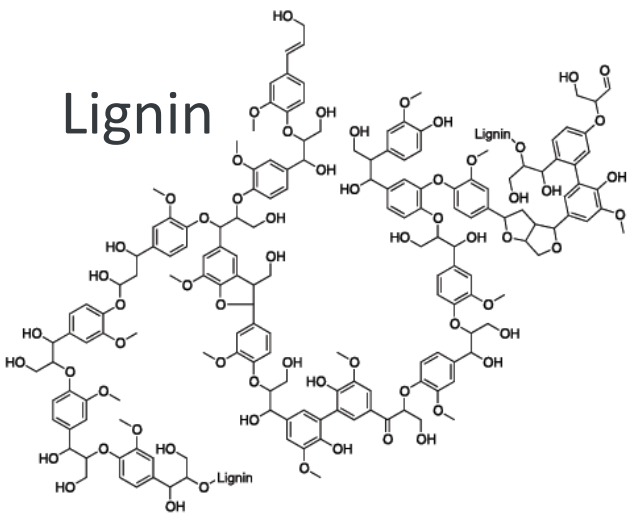
Cellulose



Hemicellulose



Lignin



Thermochemical Pathways

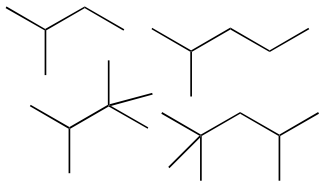
Pyrolysis
Gasification

Intermediates

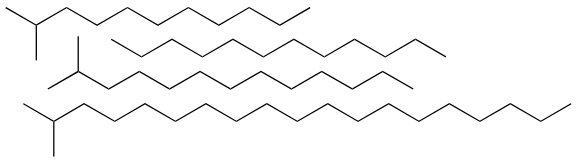
-high yield
-balanced stability and reactivity

Fuels - C_nH_{2n+2}

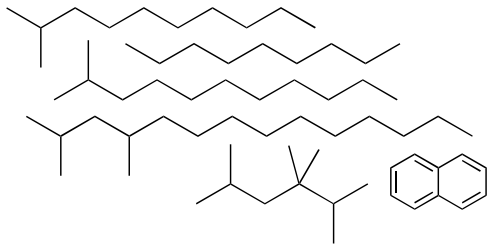
Gasoline



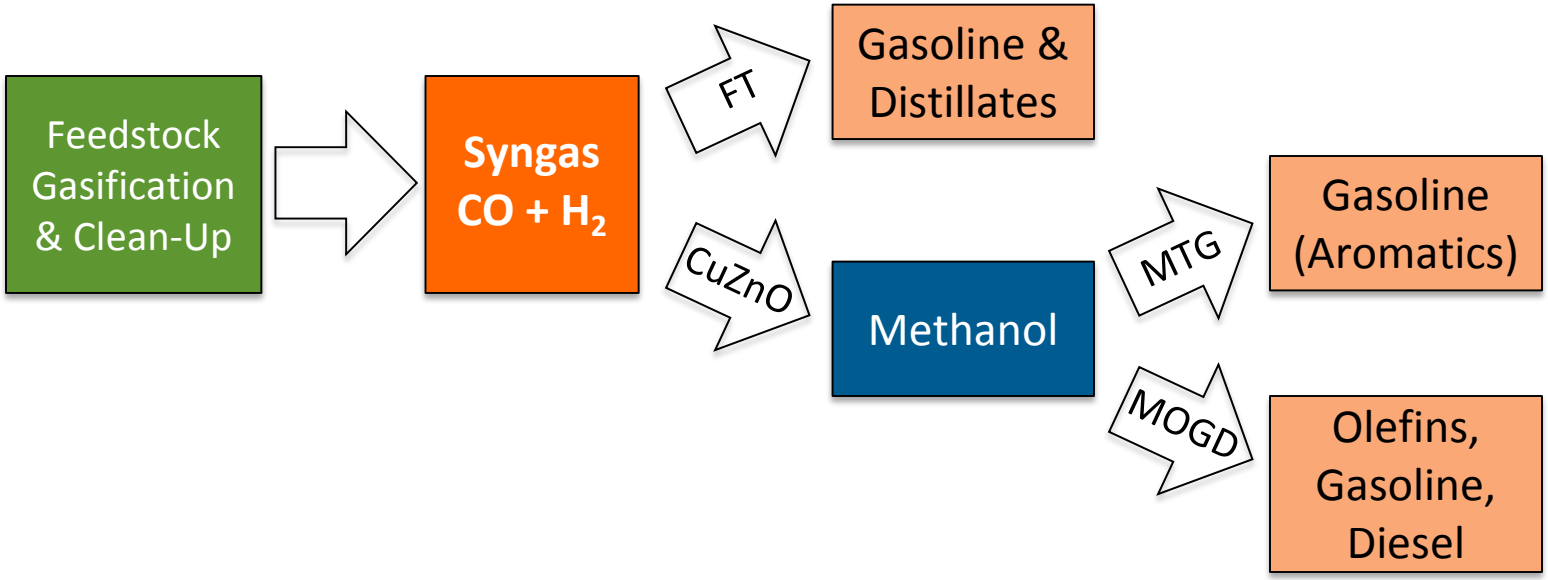
Diesel



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

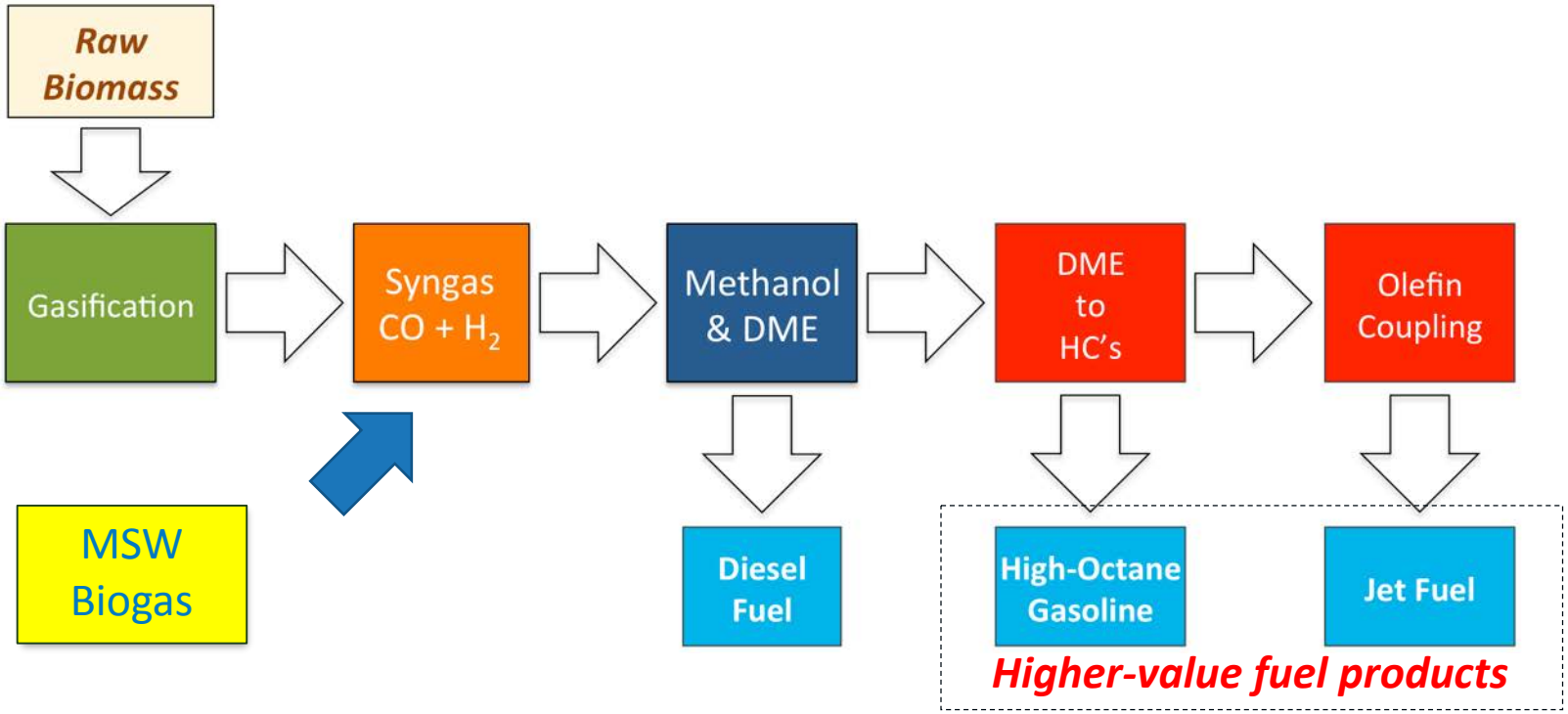
Net cost of production from biomass (2014 $)

- 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_1 intermediates (methanol/DME)

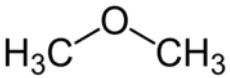
-Non-FT, non-MTG/MOGD route

-Three common fuels from this process

-Balance production of each to meet market needs

Overview: DME-to-hydrocarbons process

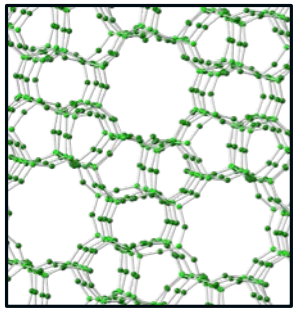
Dimethyl Ether (DME)



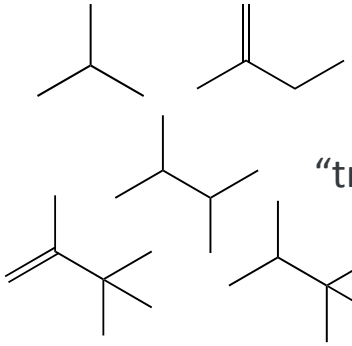
or Methanol CH_3OH

200 °C, 1-30 bar

Large-pore acidic zeolites (H-BEA)

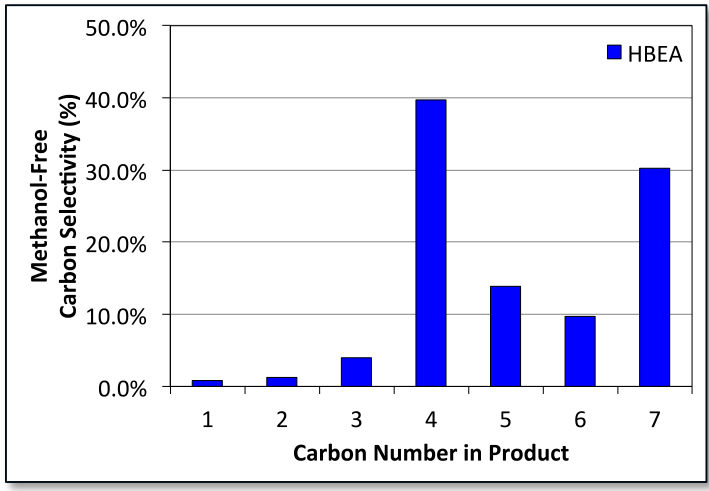


Branched HCs (C_4-C_7)



"triptane" C_7H_{16}

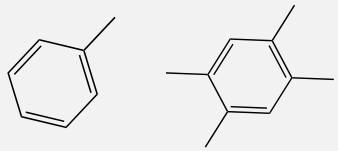
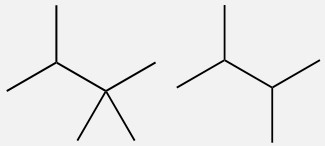
(Ahn et al., *Angew. Chem.*, 2009)
(Ahn et al., US Patent, 2009)
(Simonetti et al., *J. Catal.*, 2011)
(Simonetti et al., *ChemCatChem*, 2011)



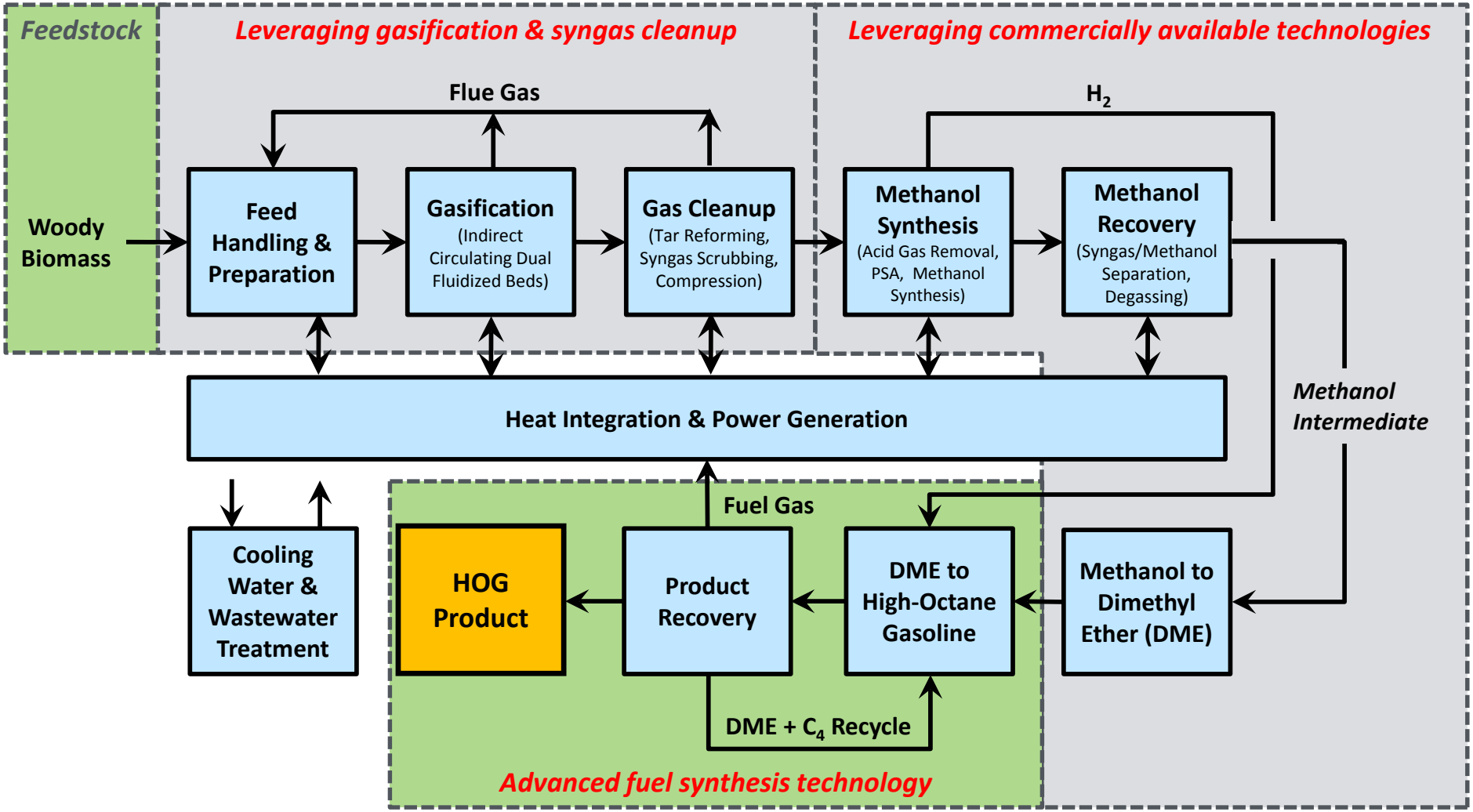
Key points on the technology

- -DME and/or methanol can be synthesized selectively from a number of sources
- -Total product is a *paraffin/olefin mixture* with many C_4-C_8 isomers
  - -Oxygen-free product (except methanol)
  - -Not MTG: Only observed aromatic is hexamethylbenzene (b.p. 265 ^oC)
- -High-octane product is attractive as renewable *refinery alkylate blendstock*
- -C_4-C_8 olefins are *distillate fuel precursors*

Comparing MTG and HOG Pathways

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

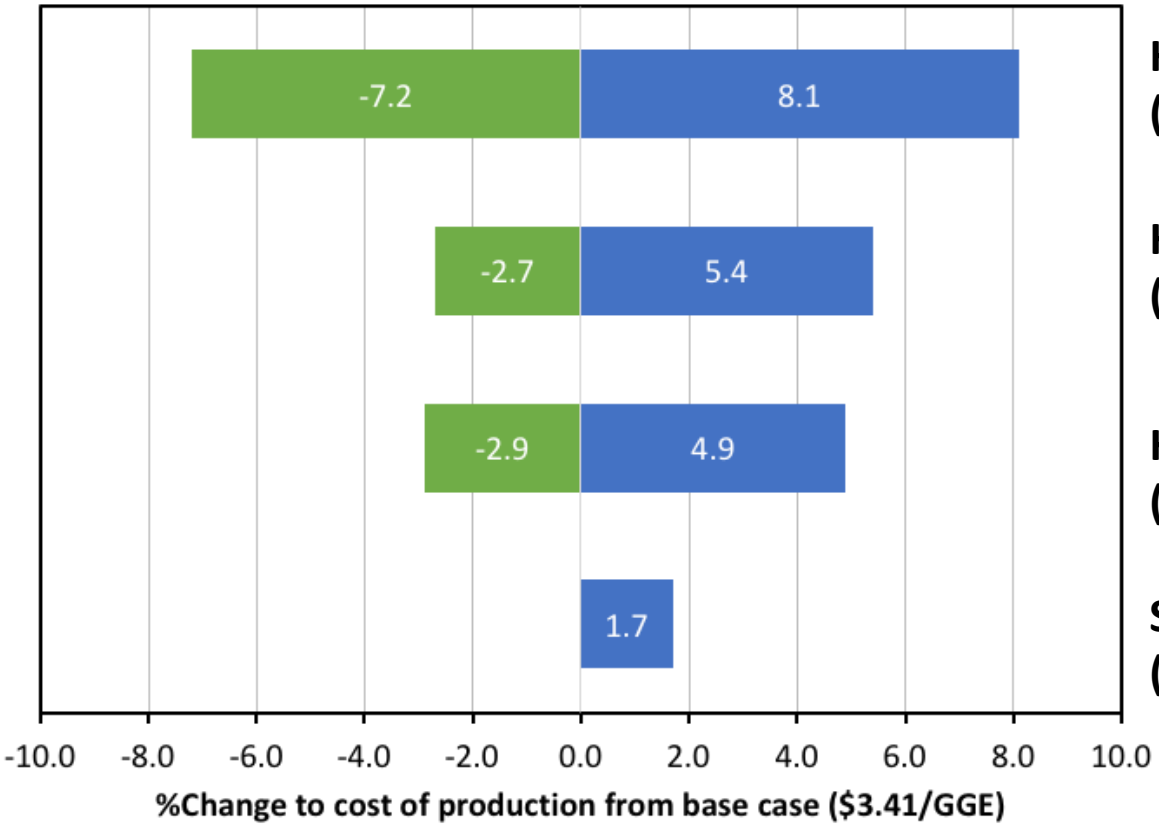
Process Design for Biomass to High-Octane Gasoline



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



HOG Yield (70:65:60 Gal/ton)

HOG Catalyst Cost (50:100:200%)

HOG Synthesis Catalyst Lifetime (5:2:1 year)

Single-Pass DME Conversion (40:40:25%)

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

What limits the performance by HBEA?

Hydrogen Deficiency

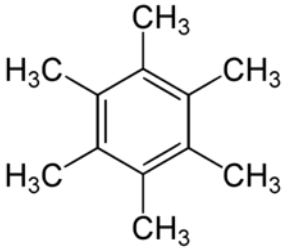
$CH_3OCH_3 \longrightarrow 2\ \text{“}CH_2\text{”} + H_2O$

Need an additional 2H per alkane produced

Yield Loss

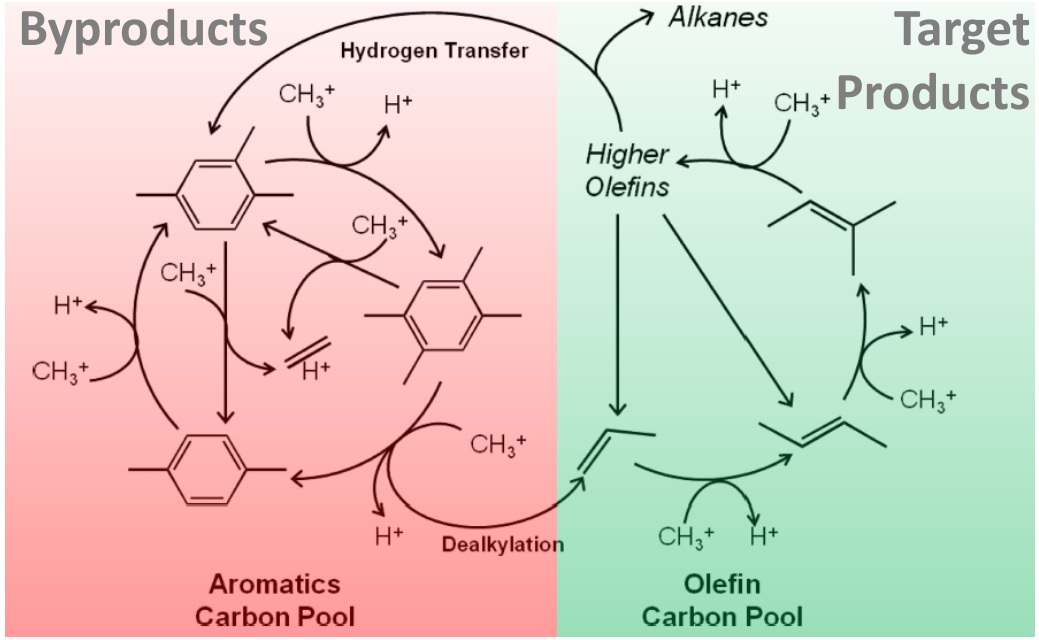
$33\ CH_3OCH_3 \longrightarrow 6\ C_7H_{16} + 33\ H_2O$
$\mathbf{+\ 2\ C_6(CH_3)_6}$

Leads to formation of heavy unsaturated hydrocarbons



“HMB”

Dual-Cycle Mechanism

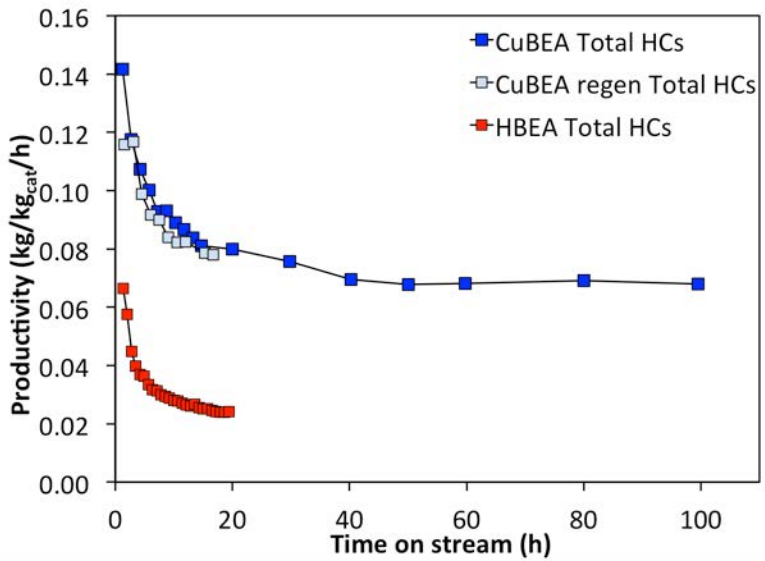


S. Ilias, A. Bhan, *ACS Catalysis*, 2013

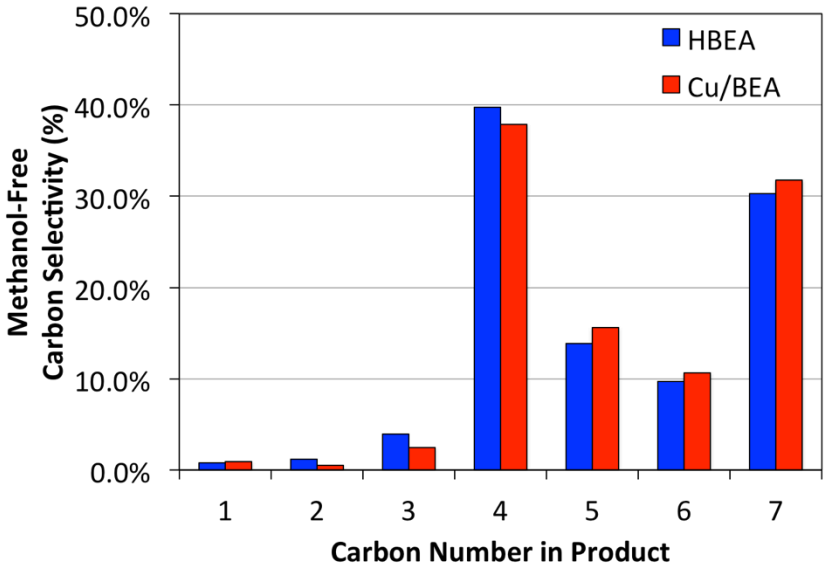
Catalyst Improvements Needed

1. Shift away from aromatic cycle and toward olefin cycle
2. H_2 can be activated and participate in the reaction
   -reduce aromatic formation, maintain C_{5+} selectivity
3. Light alkane products can be reactivated and re-enter the catalytic cycle
   -recycle (to extinction) to maximize C_{5+} yield

Cu/BEA for improved DME homologation performance



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



High selectivity to C_4 and C_7

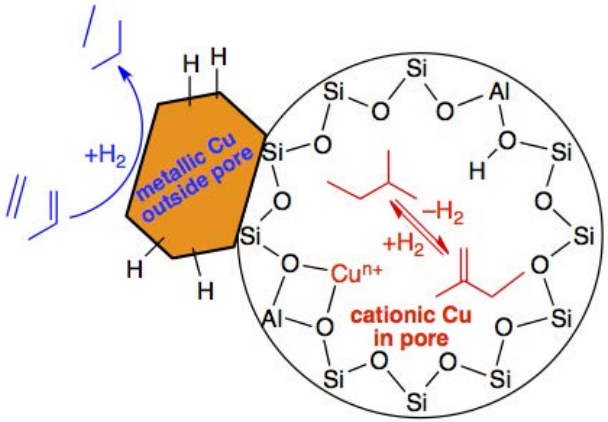
Catalyst	Aromatic cycle	Olefin cycle	%C as HMB
HBEA	23%	77%	13%
HBEA + H_2	21%	79%	7%
Cu/BEA + H_2	8%	92%	4%

- ***Decrease*** **in aromatic (HMB) selectivity for Cu/BEA + H_2**
- **Products from olefin cycle are favored using Cu/BEA + H_2**
- **Cu/BEA catalyst achieves the first 2 goals**

Schaidle, J.; Ruddy, D.; Habas, S.; Pan, M.; Zhang, G.; Miller, J.; Hensley, J. *ACS Catal*, (2015) 5, 1794.

What is the role of Cu?

Cu speciation explored using XAS (Argonne National Lab)

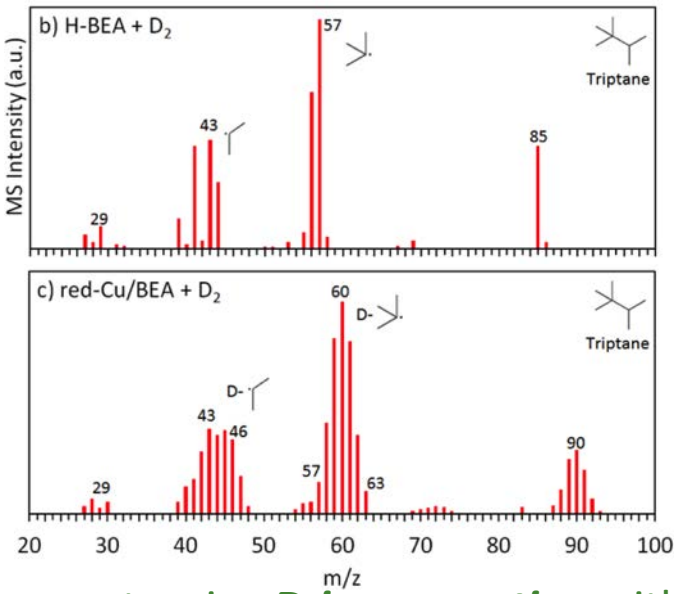


-Observe contributions from ***metallic*** and ***ionic*** Cu

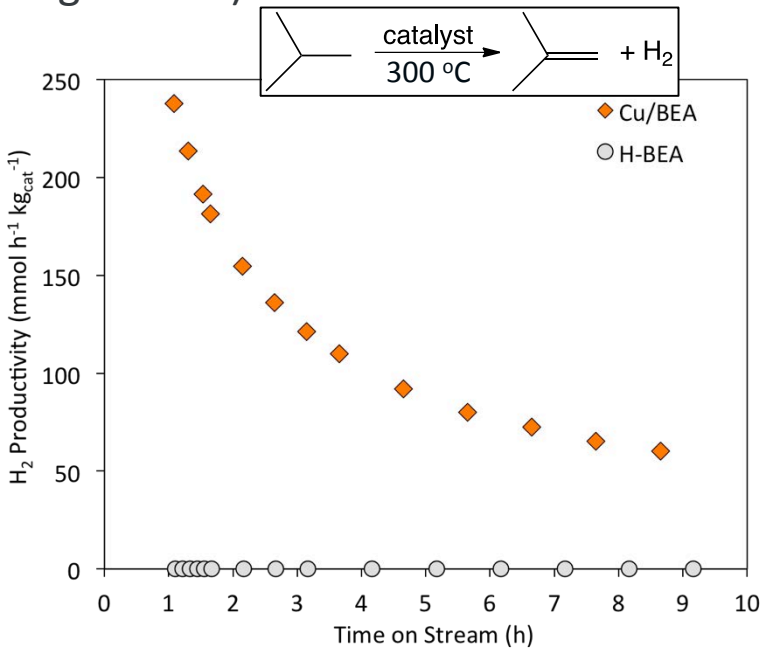
Multi-functional catalysis:

(1) metallic Cu activates H_2, performs ethylene/propylene hydrogenation (increases P:O ratio)

(2) cationic Cu facilitates H-transfer (dehydrogenation)



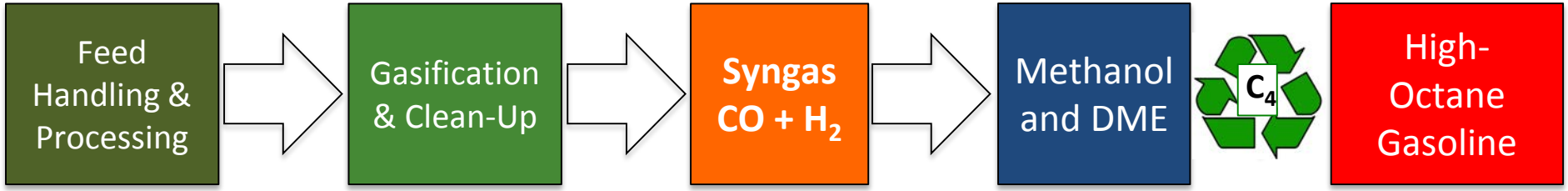
-Observe extensive ***D-incorporation*** with D_2



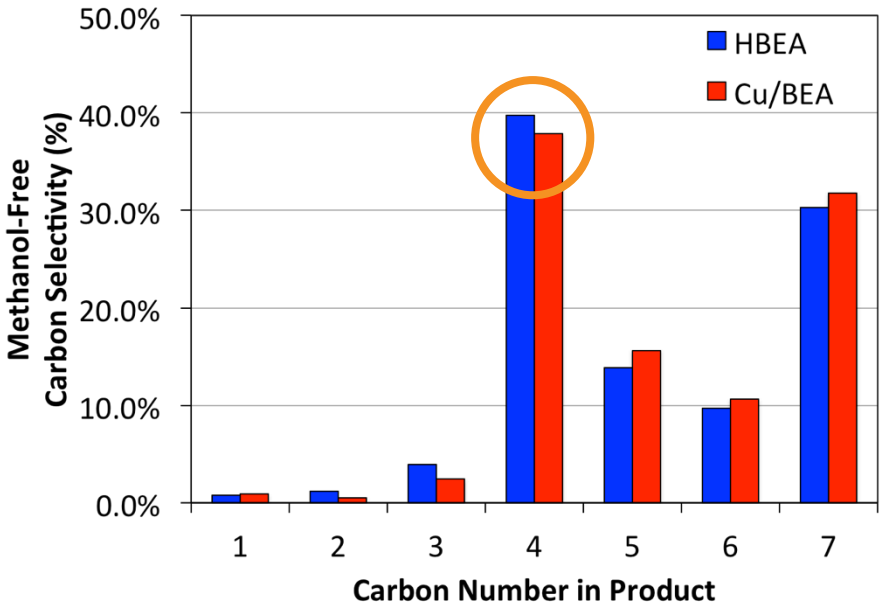
-H_2 ***production*** from C_4H_{10} over Cu/BEA

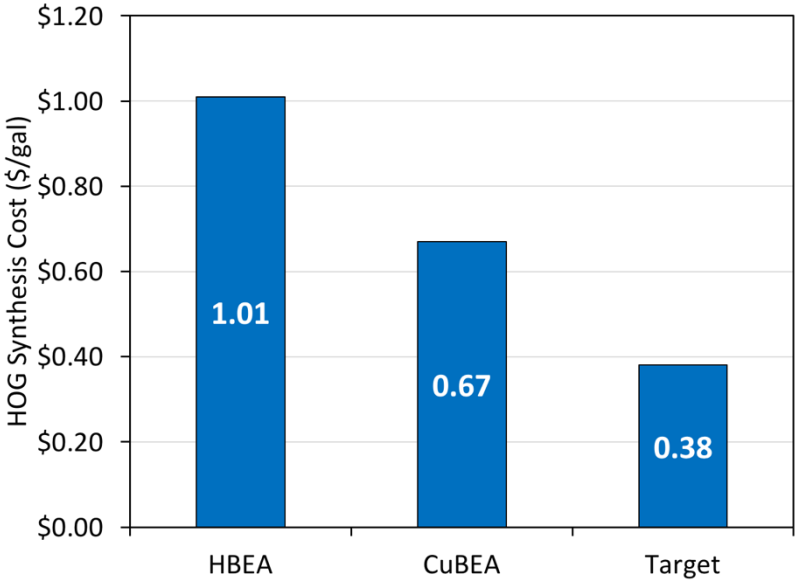
Schaidle, *et al.*, *ACS Catal*, **2015**, *5*, 1794; Farberow *et al.*, *ACS Catal* **2017**, *7*, 3662.

TEA Motivation to Recycle C_4 Product



Yield and Cost Impact with C_4 Recycle

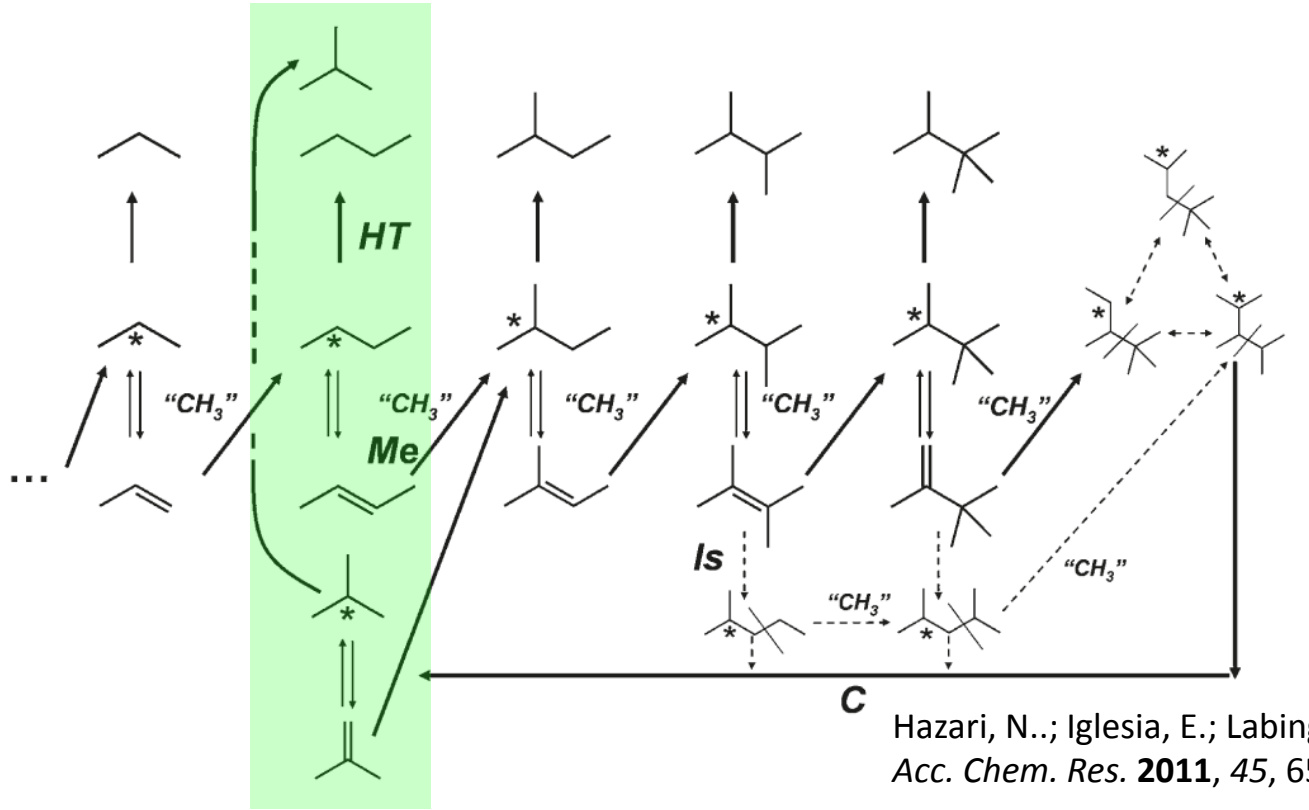




C_4 product recycle is a critical component in the TEA to achieve high yield and lower cost of production

Why is C_4 dehydrogenation difficult?

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



Hazari, N..; Iglesia, E.; Labinger, J. A.; Simonetti, D. A. *Acc. Chem. Res.* **2011**, *45*, 653.

- **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_4 alkanes**

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

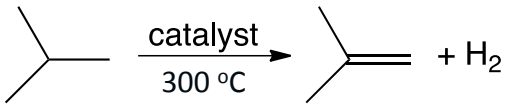
Catalyst Materials and Characterization

Catalyst	Pre-treatment	Site (characterization)
CuO/SiO_2	1% O_2, 500 °C	CuO particles (XRD)
Cu/SiO_2	1% O_2, 500 °C; 2% H_2, 300 °C	Cu(0) particles (XRD)
H-BEA	1% O_2, 500 °C	Brønsted acid (NH_3 TPD, pyridine-DRIFTS)
ox-IE-Cu/BEA	1% O_2, 500 °C	Ionic Cu(II)-zeolite (XAS)
red-IE-Cu/BEA	1% O_2, 500 °C; 2% H_2, 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**

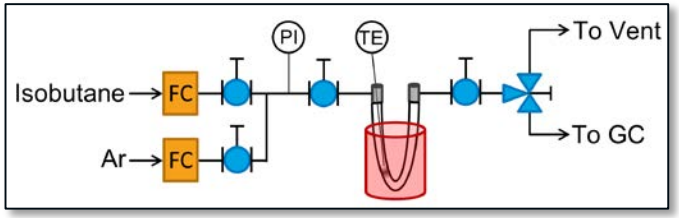
Catalytic Testing

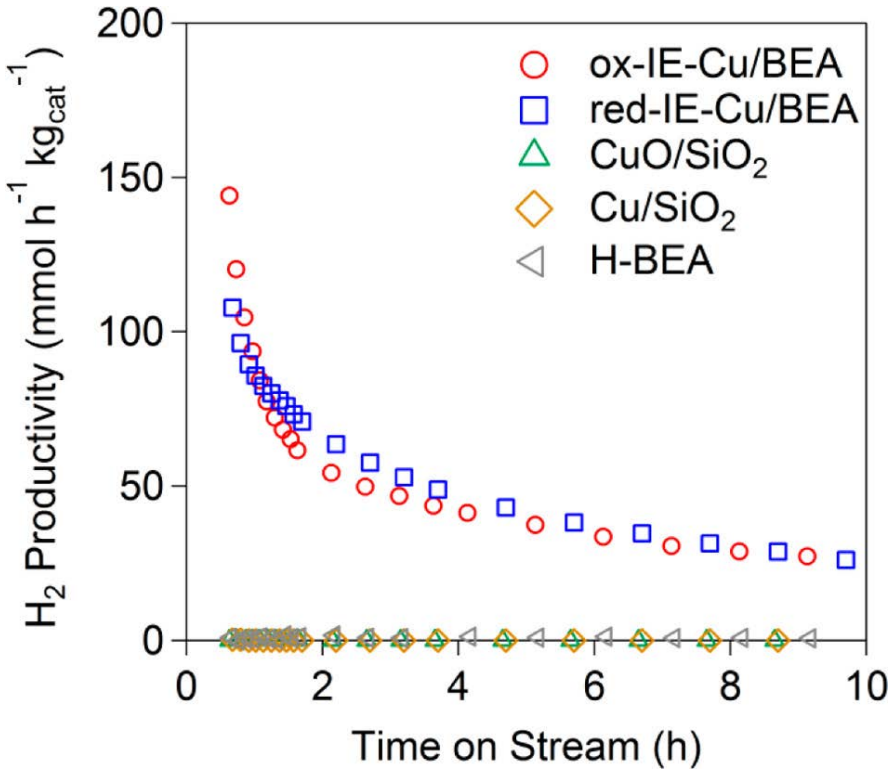
Isobutane Dehydrogenation Reaction



Fixed-bed reactor experiments

- 100 mg_{cat}
- 1% i-butane/He at 7 sccm
- T = 300 °C
- P = 2 atm
- $X_{i\text{-butane}} < 5\%$

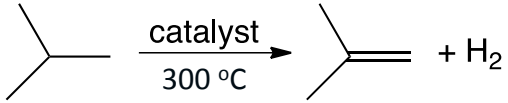




- ***Catalysts containing ionic Cu species exhibit comparable isobutane dehydrogenation activities***
- ***CuO nanoparticles, metallic Cu nanoparticles, and Bronsted acid sites are not active***

Operando XAS (Argonne National Lab)

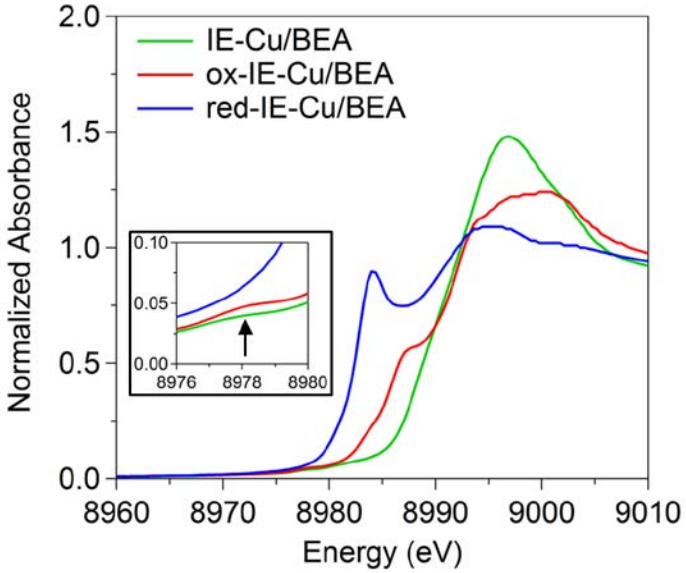
Determine speciation of ionic Cu during isobutane dehydrogenation

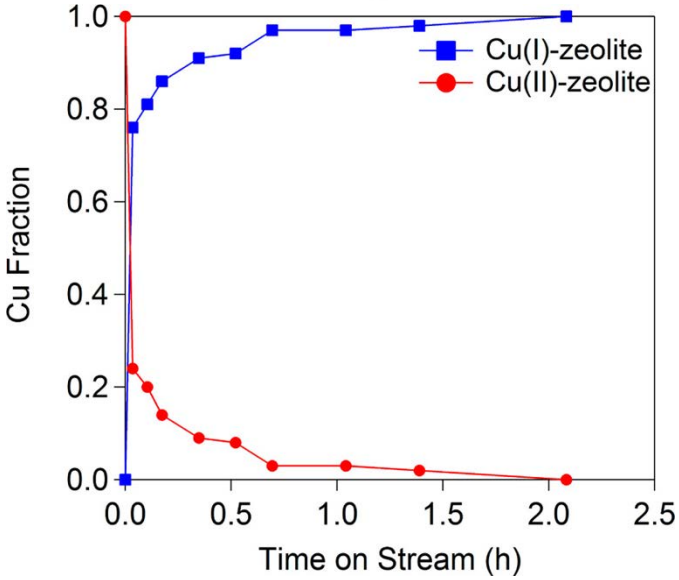


Cu speciation

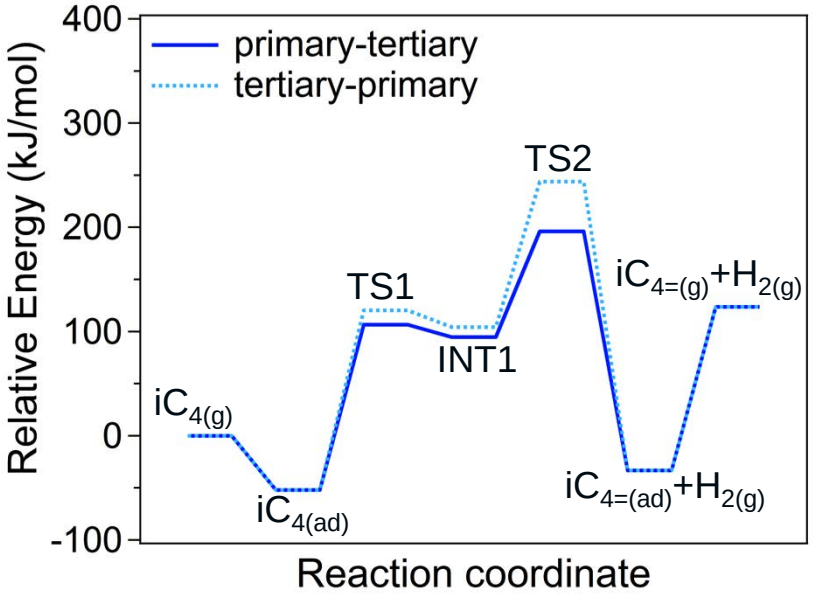
- ox-IE-Cu/BEA is ~80% Cu(I) at 2 min TOS and ~100% Cu(I) by 2h TOS
- red-IE-Cu/BEA remains Cu(I) throughout the experiment
- no metallic copper observed

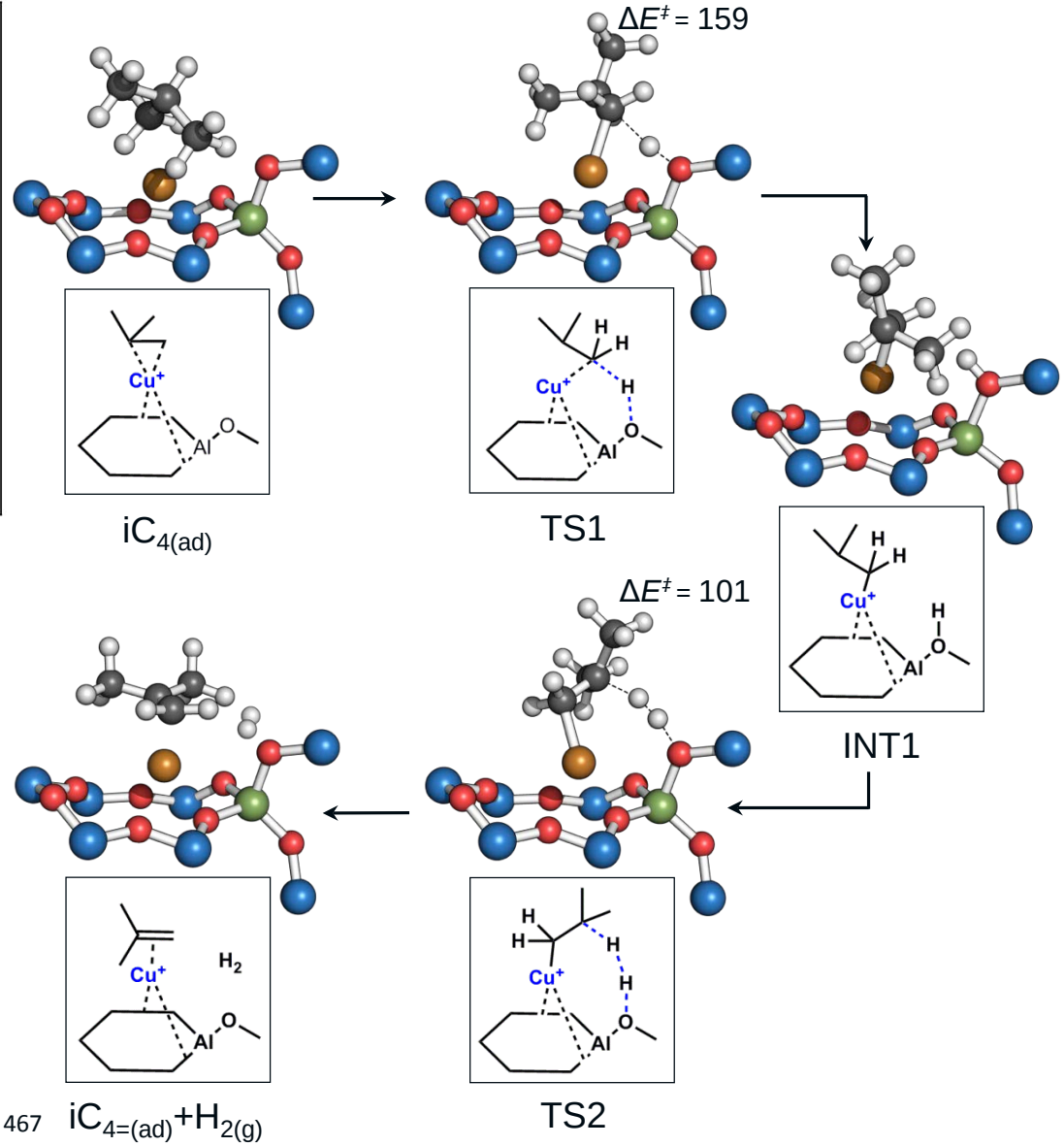
Ionic Cu(I) species are responsible for the observed dehydrogenation activity





Computation: Reaction Mechanism and Energetics



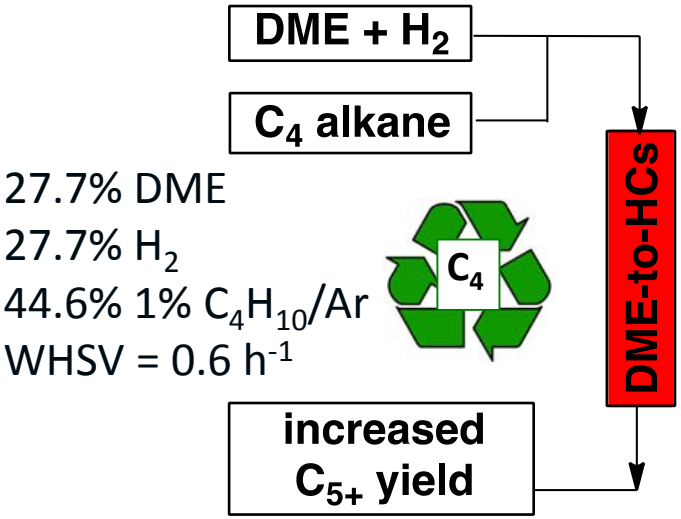


- **Comparison of activation energies with previous reports[1, 2] for Ga- and Zn-modified MFI suggest Cu/BEA should be less active than these**
- **May improve performance with bimetallic catalysts**

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

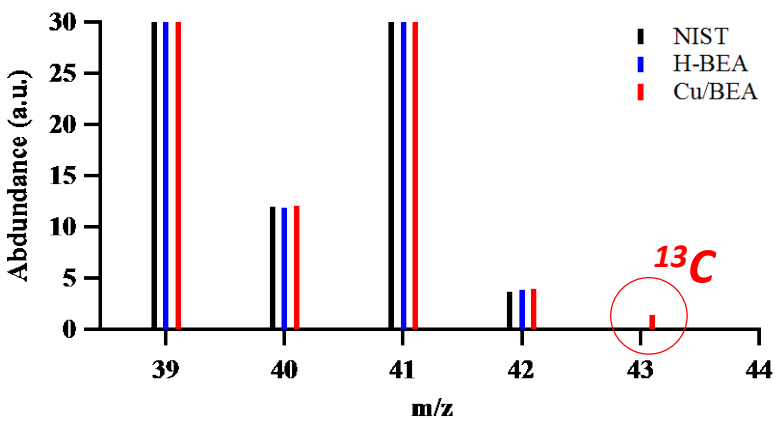
C_4H_{10} Recycling during DME-to-HCs

Simulated C_4H_{10} recycle to maximize C_{5+} yield



Temperature (°C)	Pressure (psig)	Co-feed C_4H_{10}	Conversion (%)	C_{5+} 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

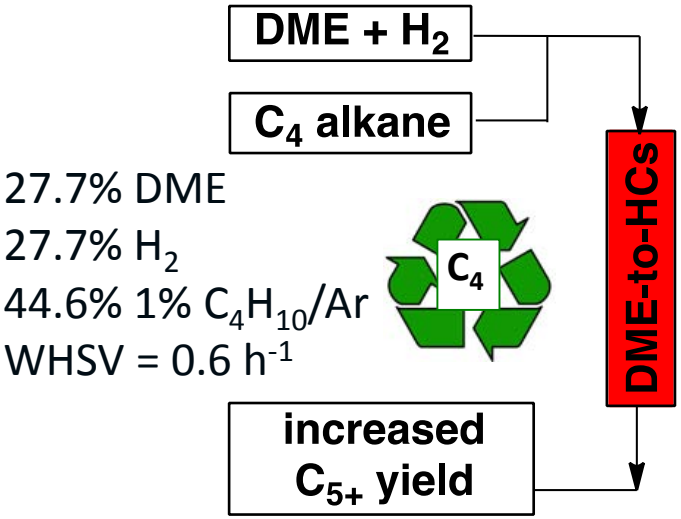


DME + H_2 + ^{13}C-C_4H_{10}

- ***Minor decrease in yield with co-fed C_4H_{10}***
- ***Increased C_{5+} selectivity with pressure***
- ***^{13}C-isobutene observed in products***
- ***Confirms dehydrogenation activity over Cu/BEA in the presence of DME + H_2***

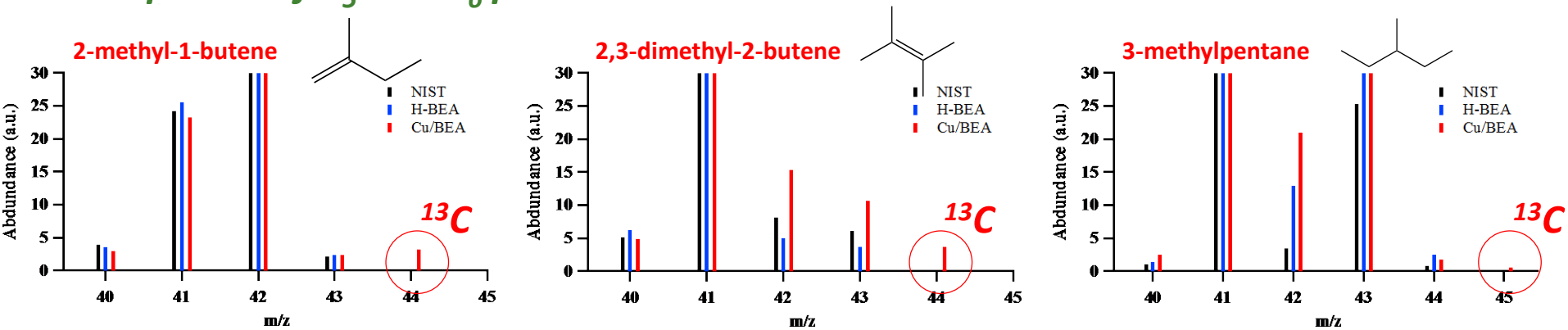
C_4H_{10} Recycling during DME-to-HCs

Simulated C_4H_{10} recycle to maximize C_{5+} yield



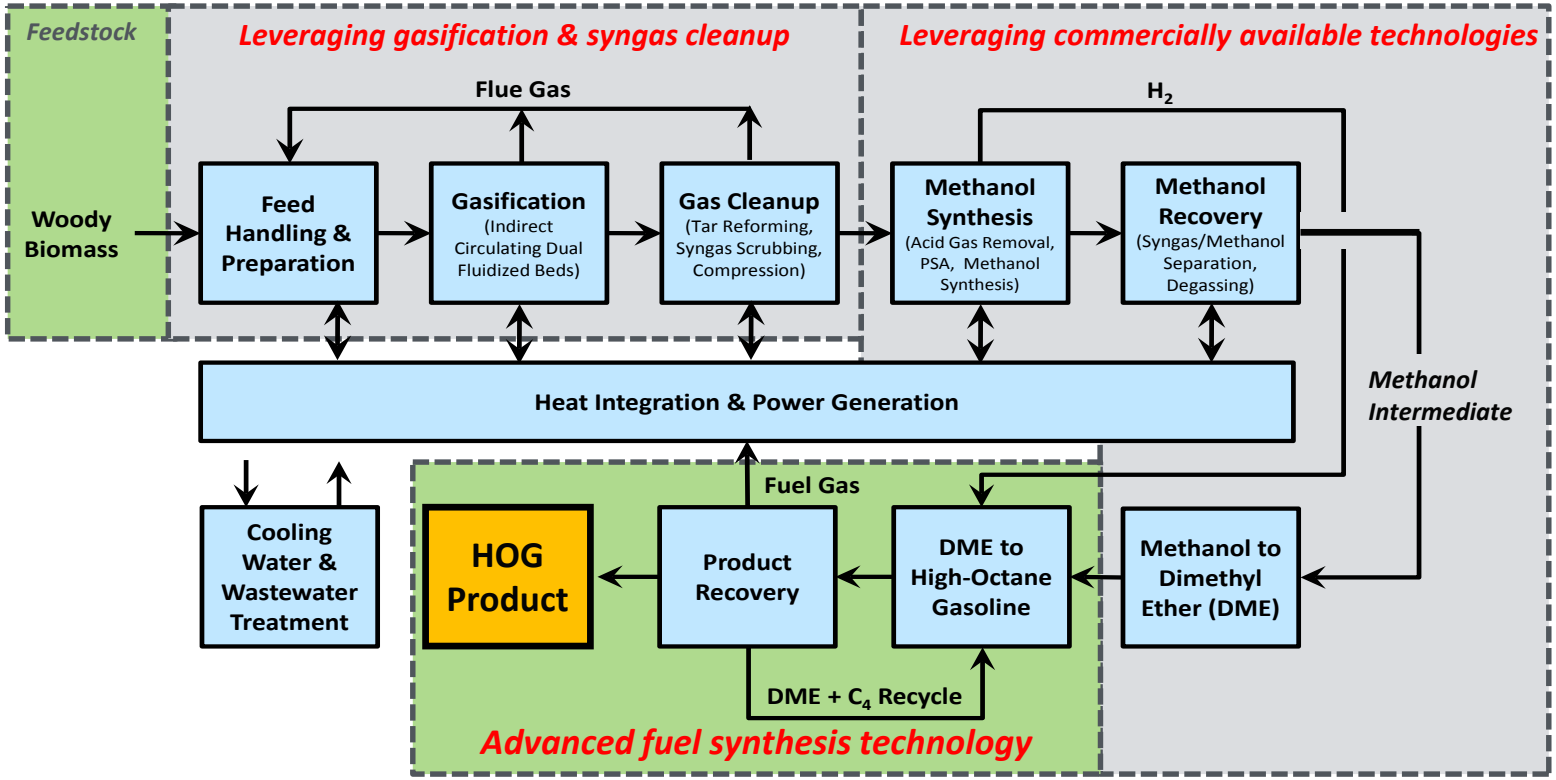
Temperature (°C)	Pressure (psig)	Co-feed C_4H_{10}	Conversion (%)	C_{5+} Selectivity (%)
200	3	N	20.0	63.4
200	3	Y	19.2	63.4
200	25	N	23.3	68.8
200	25	Y	19.2	68.3

Mass spectra of C_5 and C_6 products



– Indicates ^{13}C-C_4H_{10} reincorporation into C_5+ products

Process Design for Biomass to High-Octane Gasoline



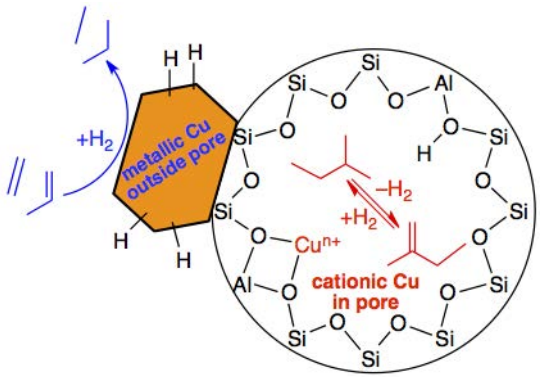
BEA: 40 gal/dry-ton biomass; $5.20/gal

***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_4 reactivation at Cu^+ sites (not HBEA)
- Recall MOGD at $4.80/gal for gasoline and distillate from biomass

Considering the observed C_4H_{10} conversion

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



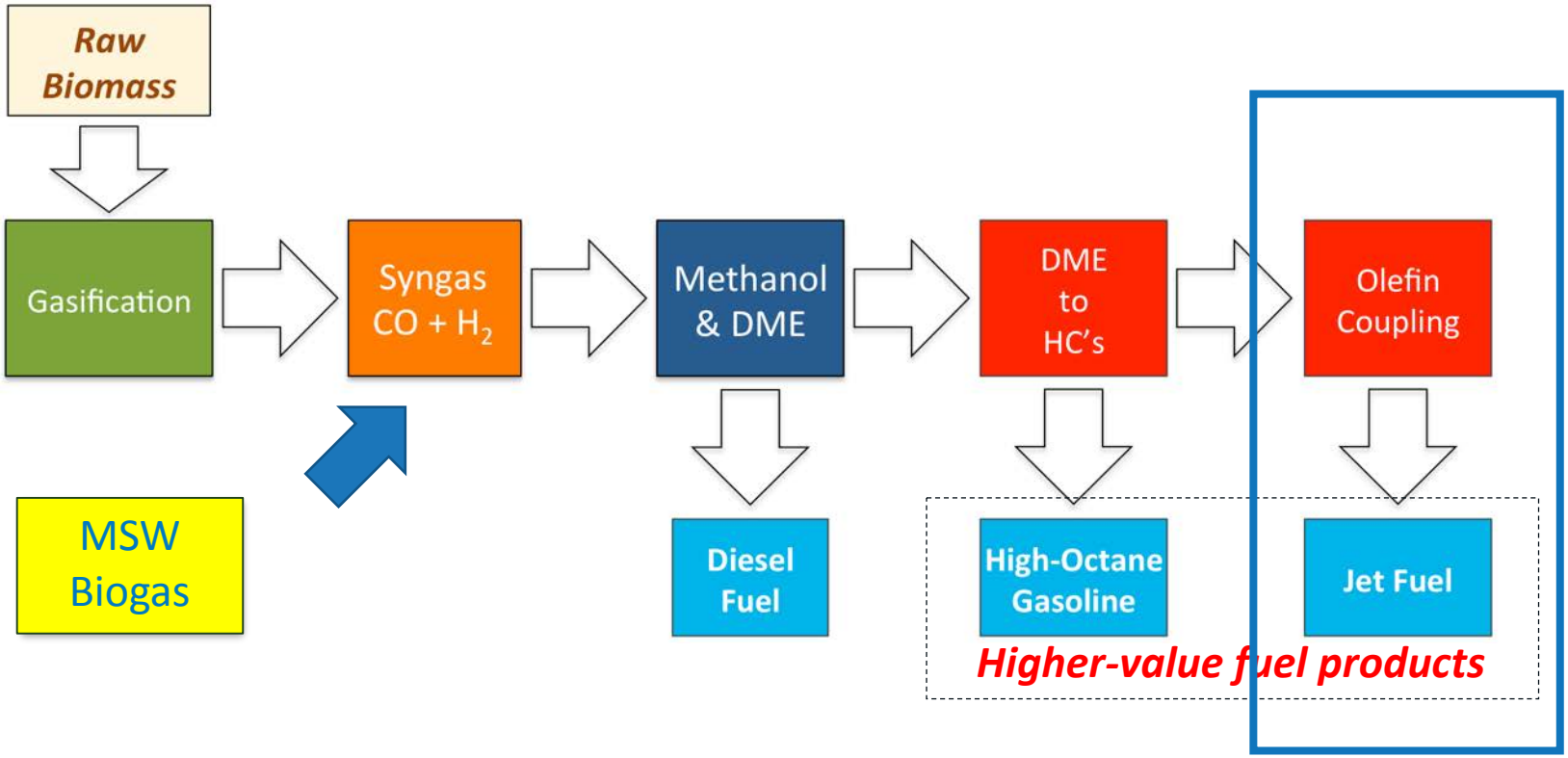
- Conversion values are remarkably high compared to the thermodynamic considerations of isobutane dehydrogenation at 200 °C (< 1% expected)

- Suggests that the observed reactivity is *kinetically driven*, presumably through consumption of the products – isobut**ene** and H_2
  - Similar to product removal concepts that drive methanol/DME synthesis, condensation reactions, etc.
  - Dehydrogenation inside the zeolite pores at ionic Cu sites near H^+ sites

- Methylation and H-transfer rates of isobut**ene** over HBEA were reported to be 33 and 38 $\mu mol/mol_{Al}/s$
- Our C_4H_{10} conversion rate was 7.2 (3psig) and 11.5 (25psig) $\mu mol/mol_{Al}/s$

Simonetti, D. A.; Ahn, J. H.; Iglesia, E. *J. Catal.* **2011**, *277*, 173.

A market-responsive biorefinery concept around methanol



-Conversion of C_1 intermediates (methanol/DME)

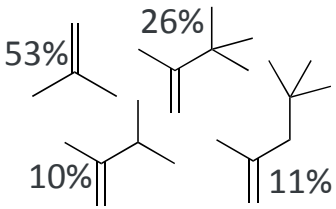
-Non-FT, non-MTG/MOGD route

-Three common fuels from this process

-Balance production of each to meet market needs

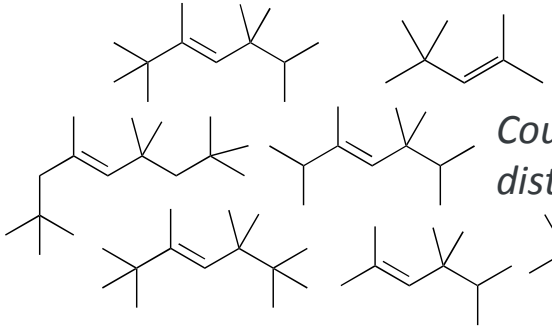
Distillate production from HOG olefins

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

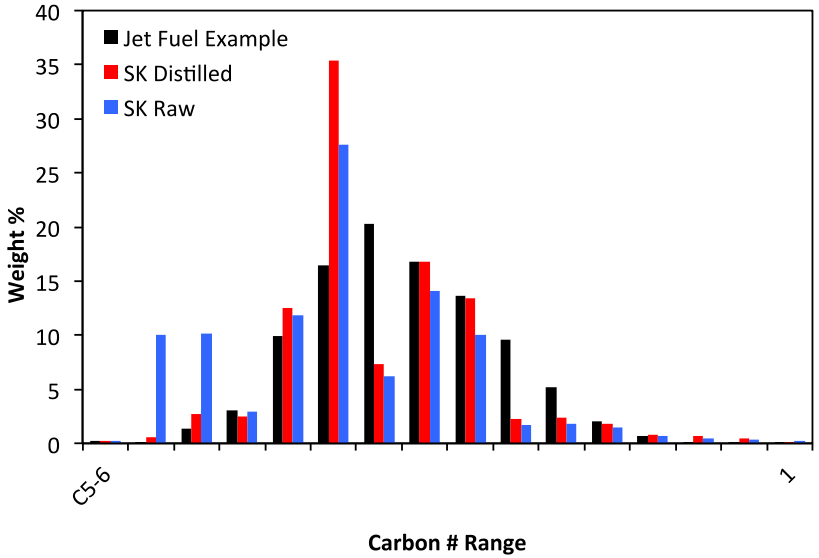


Amberlyst-35 (comm.)

60-100 °C



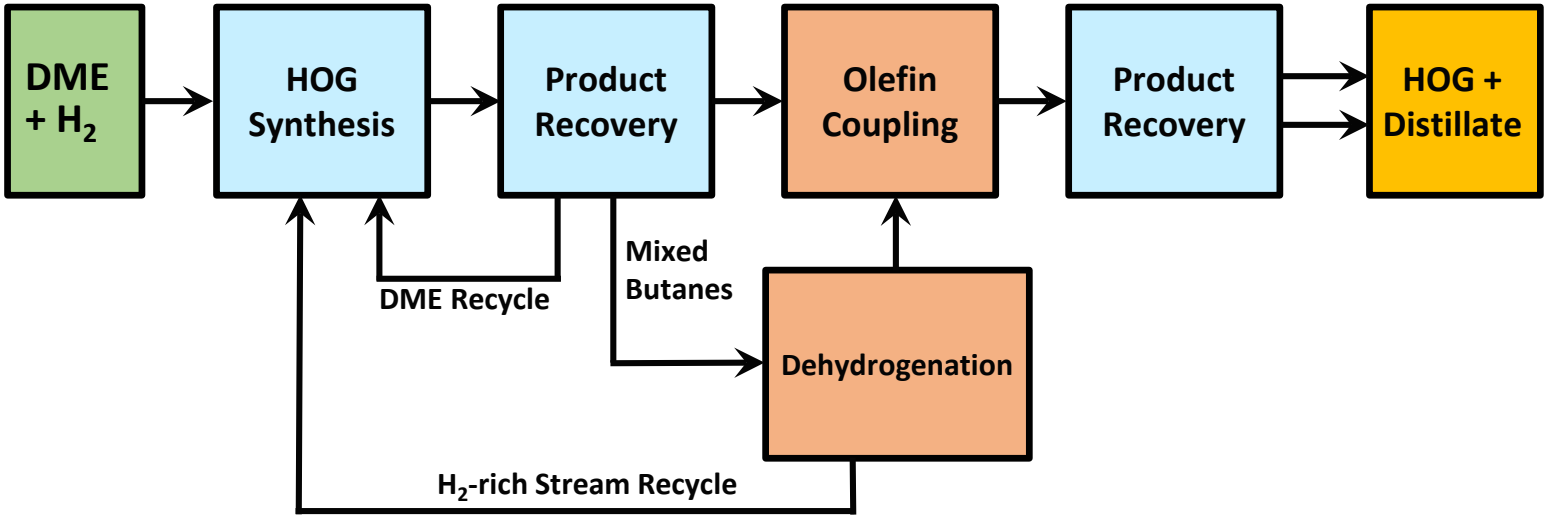
Coupled product in distillate-range



- **Simple vacuum distillation removes unreacted light C_7-C_8**
- **Carbon numbers are similar to commercial jet fuel (C_8-C_{20})**
- **No "heavies" (>C_{22})**

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

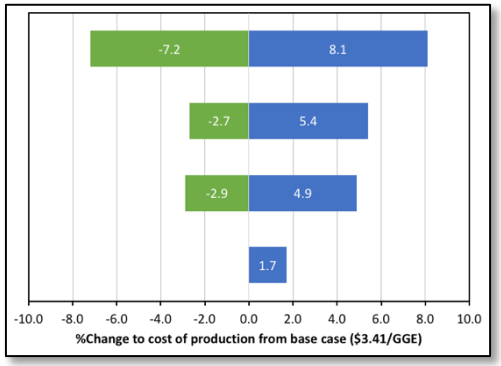
Summary

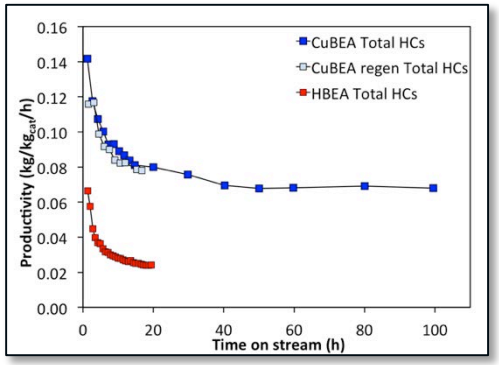
Conclusions

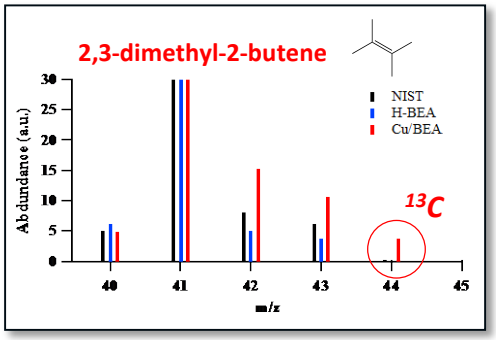
- TEA can be coupled with R&D to direct and understand the value of catalyst improvements
- Developed an inexpensive Cu/BEA catalyst with 2-3X improved productivity and extended lifetime
- Cu/BEA reactivates and reincorporates isobutane in the presence of DME + H_2
- Results in 40% increased yield and 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

Jesse Hensley
Carrie Farberow
Eric Nelson
Gary Grim
Joshua Schaidle
Anh To
Susan Habas
Glenn Powell
Connor Nash
Dan Dupuis
Matt Yung

Technoeconomic Analysis

Eric Tan
Abhijit Dutta

NREL Fuel Property Analysis

Earl Christensen

ANL XAS Collaborators

Ted Krause
Jeff Miller

ORNL TEM Collaborators

Kinga Unocic

U.S. DEPARTMENT OF ENERGY
Bioenergy Technologies Office

DE-AC36-08-GO28308

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

Thank you!

Daniel Ruddy

Dan.Ruddy@nrel.gov

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ChemCatBio
Chemical Catalysis for Bioenergy