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

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Coupling Traditional Catalyst Development with TEA

Synthesis & Characterization

Hydrotalcites

Cu/BEA

Theory

Product analysis

Bench-scale reactions

Technoeconomic Analysis (TEA)

Catalyst Testing

Catalyst Scaling & Pilot-Scale Testing

Techno-economic Analysis (TEA)
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

ChemCatBio
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

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

Key points on the technology

-DME and/or methanol can be synthesized selectively from a number of sources
-Total product is a \textit{paraffin/olefin mixture} with many \( \text{C}_4-\text{C}_8 \) isomers
  -Oxygen-free product (except methanol)
  -Not MTG: Only observed aromatic is hexamethylbenzene (b.p. 265 °C)
-High-octane product is attractive as renewable \textit{refinery alkylate blendstock}
-\( \text{C}_4-\text{C}_8 \) olefins are \textit{distillate fuel precursors}
Comparing MTG and HOG Pathways

<table>
<thead>
<tr>
<th>Methanol to Gasoline (MTG) Pathway</th>
<th>High-Octane Gasoline (HOG) Pathway</th>
<th>Advantages of HOG Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="ZSM-5 zeolite catalyst" /></td>
<td><img src="image" alt="Beta-zeolite catalyst" /></td>
<td>Branched HC product, minimal aromatics</td>
</tr>
<tr>
<td>ZSM-5 zeolite catalyst</td>
<td>Beta-zeolite catalyst</td>
<td>Lower severity conditions, lower coking rate</td>
</tr>
<tr>
<td>650 – 950 °F</td>
<td>350 – 450 °F</td>
<td>High octane synthetic alkylate</td>
</tr>
<tr>
<td>315 psia</td>
<td>130 psia</td>
<td>Higher yield (18%)</td>
</tr>
<tr>
<td>RON: 92</td>
<td>RON: 95+</td>
<td></td>
</tr>
<tr>
<td>MON: 83</td>
<td>MON: 90+</td>
<td></td>
</tr>
<tr>
<td>55 gal/ton</td>
<td>65 gal/ton</td>
<td></td>
</tr>
</tbody>
</table>
Process Design for Biomass to High-Octane Gasoline

**Feedstock**

- Woody Biomass

**Leveraging gasification & syngas cleanup**

1. Feed Handling & Preparation
2. Gasification (Indirect Circulating Dual Fluidized Beds)
3. Gas Cleanup (Tar Reforming, Syngas Scrubbing, Compression)

**Heat Integration & Power Generation**

**Leveraging commercially available technologies**

1. Methanol Synthesis (Acid Gas Removal, PSA, Methanol Synthesis)
2. Methanol Recovery (Syngas/Methanol Separation, Degassing)
3. Methanol Intermediate

**Methanol**

- Methanol Recovery
- Methanol to Dimethyl Ether (DME)

**Advanced fuel synthesis technology**

- HOG Product
- Product Recovery
- DME to High-Octane Gasoline
- DME + C4 Recycle

**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 $C_{5+}$ products to increase product yield
- Selectivity to $C_{5+}$ products is more important than conversion

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%)
What limits the performance by HBEA?

Hydrogen Deficiency

\[ \text{CH}_3\text{OCH}_3 \rightarrow 2 \text{ “CH}_2” + \text{H}_2\text{O} \]

Need an additional 2H per alkane produced

Yield Loss

\[ 33 \text{CH}_3\text{OCH}_3 \rightarrow 6 \text{C}_7\text{H}_{16} + 33 \text{H}_2\text{O} + 2 \text{C}_6(\text{CH}_3)_6 \]

Leads to formation of heavy unsaturated hydrocarbons

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

- Decrease in aromatic (HMB) selectivity for Cu/BEA + H₂
- Products from olefin cycle are favored using Cu/BEA + H₂
- Cu/BEA catalyst achieves the first 2 goals

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Aromatic cycle</th>
<th>Olefin cycle</th>
<th>%C as HMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBEA</td>
<td>23%</td>
<td>77%</td>
<td>13%</td>
</tr>
<tr>
<td>HBEA + H₂</td>
<td>21%</td>
<td>79%</td>
<td>7%</td>
</tr>
<tr>
<td>Cu/BEA + H₂</td>
<td>8%</td>
<td>92%</td>
<td>4%</td>
</tr>
</tbody>
</table>

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 H₂, performs ethylene/propylene hydrogenation (increases P:O ratio)

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

-Observed extensive *D- incorporation* with D₂

- H₂ *production* from C₄H₁₀ over Cu/BEA

TEA Motivation to Recycle $C_4$ Product

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

Yield and Cost Impact with $C_4$ Recycle
Why is $C_4$ 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 $C_4$ alkanes

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

### Catalyst Materials and Characterization

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pre-treatment</th>
<th>Site (characterization)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/SiO₂</td>
<td>1% O₂, 500 °C</td>
<td>CuO particles (XRD)</td>
</tr>
<tr>
<td>Cu/SiO₂</td>
<td>1% O₂, 500 °C; 2% H₂, 300 °C</td>
<td>Cu(0) particles (XRD)</td>
</tr>
<tr>
<td>H-BEA</td>
<td>1% O₂, 500 °C</td>
<td>Brønsted acid (NH₃ TPD, pyridine-DRIFTS)</td>
</tr>
<tr>
<td>ox-IE-Cu/BEA</td>
<td>1% O₂, 500 °C</td>
<td>Ionic Cu(II)-zeolite (XAS)</td>
</tr>
<tr>
<td>red-IE-Cu/BEA</td>
<td>1% O₂, 500 °C; 2% H₂, 300 °C</td>
<td>Ionic Cu(I)-zeolite (XAS)</td>
</tr>
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</table>

- **Synthesized catalyst materials with the specific catalytic functionalities present in Cu/BEA**
  - CuO versus Cu without Brønsted 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

\[
\text{Catalyst} \quad 300 \, ^\circ\text{C} \quad \text{\( \rightarrow \)} \quad \text{\( \rightarrow \)} \quad + \, \text{H}_2
\]

**Fixed-bed reactor experiments**
- 100 mg\textsubscript{cat}
- 1\% i-butane/He at 7 sccm
- T = 300 °C
- P = 2 atm
- \( X_{\text{i-butane}} < 5\% \)

- **Catalysts containing ionic Cu species exhibit comparable isobutane dehydrogenation activities**
- **CuO nanoparticles, metallic Cu nanoparticles, and Bronsted acid sites are not active**
Determining 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**
Comparison of activation energies with previous reports\textsuperscript{1, 2} for Ga- and Zn-modified MFI suggest Cu/BEA should be less active than these.

May improve performance with bimetallic catalysts.

\textsuperscript{1} Y. Sun, T. C. Brown, \textit{International Journal of Chemical Kinetics} (2002) 34, 467

C$_4$H$_{10}$ Recycling during DME-to-HCs

Simulated C$_4$H$_{10}$ recycle to maximize C$_5+$ yield

- **DME + H$_2$**
- **C$_4$ alkane**
- **C$_4$**
- **DME-to-HCs**
- **increased C$_5+$ yield**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (psig)</th>
<th>Co-feed C$<em>4$H$</em>{10}$</th>
<th>Conversion (%)</th>
<th>C$_5+$ Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3</td>
<td>N</td>
<td>20.0</td>
<td>63.4</td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>Y</td>
<td>19.2</td>
<td>63.4</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>N</td>
<td>23.3</td>
<td>68.8</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>Y</td>
<td>19.2</td>
<td>68.3</td>
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Mass spectrum of isobutene product

- **DME + H$_2$ + $^{13}$C-C$_4$H$_{10}$**
  - Minor decrease in yield with co-fed C$_4$H$_{10}$
  - Increased C$_5+$ selectivity with pressure
  - $^{13}$C-isobutene observed in products
  - Confirms dehydrogenation activity over Cu/BEA in the presence of DME + H$_2$
Simulated C₄H₁₀ recycle to maximize C₅⁺ yield

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<tr>
<th>Temperature (°C)</th>
<th>Pressure (psig)</th>
<th>Co-feed C₄H₁₀</th>
<th>Conversion (%)</th>
<th>C₅⁺ Selectivity (%)</th>
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<tbody>
<tr>
<td>200</td>
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</tr>
<tr>
<td>200</td>
<td>3</td>
<td>Y</td>
<td>19.2</td>
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</tr>
<tr>
<td>200</td>
<td>25</td>
<td>N</td>
<td>23.3</td>
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</tr>
<tr>
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<td>25</td>
<td>Y</td>
<td>19.2</td>
<td>68.3</td>
</tr>
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27.7% DME
27.7% H₂
44.6% 1% C₄H₁₀/Ar
WHSV = 0.6 h⁻¹

Mass spectra of C₅ and C₆ products

- Indicates ¹³C-C₄H₁₀ reincorporation into C₅⁺ products
Bioenergy Technologies Office

Process Design for Biomass to High-Octane Gasoline

**Feedstock**
- Woody Biomass

**Leveraging gasification & syngas cleanup**
- Feed Handling & Preparation
- Gasification (Indirect Circulating Dual Fluidized Beds)
- Gas Cleanup (Tar Reforming, Syngas Scrubbing, Compression)

**Heat Integration & Power Generation**

**Leveraging commercially available technologies**
- Methanol Synthesis (Acid Gas Removal, PSA, Methanol Synthesis)
- Methanol Recovery (Syngas/Methanol Separation, Degassing)

**Fuel Gas**
- High-Octane Gasoline Blendstock
- DME + C4 Recycle

**Advanced fuel synthesis technology**

**HOG Product**

**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 C4 reactivation at Cu⁺ sites (not HBEA)
- Recall MOGD at $4.80/gal for gasoline and distillate from biomass
Considering the observed $\text{C}_4\text{H}_{10}$ conversion

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<th>Temperature (°C)</th>
<th>Pressure (psig)</th>
<th>Isobutane Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3</td>
<td>14.5</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>23.2</td>
</tr>
</tbody>
</table>

- 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 $\text{H}_2$
  - Similar to product removal concepts that drive methanol/DME synthesis, condensation reactions, etc.
  - Dehydrogenation inside the zeolite pores at ionic Cu sites near $\text{H}^+$ sites

- Methylation and H-transfer rates of isobutene over HBEA were reported to be 33 and 38 $\mu$mol/mol$_{\text{Al}}$/s
- Our $\text{C}_4\text{H}_{10}$ conversion rate was 7.2 (3psig) and 11.5 (25psig) $\mu$mol/mol$_{\text{Al}}$/s

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%)

- Simple vacuum distillation removes unreacted light C\textsubscript{7}-C\textsubscript{8}
- Carbon numbers are similar to commercial jet fuel (C\textsubscript{8}-C\textsubscript{20})
- No “heavies” (>C\textsubscript{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 + H₂
- 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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Thank you!

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