2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Enerkem NREL CRADA

May 21, 2013
Esteban Chornet
The goals of this joint CRADA project are:

• Develop the use of carbon dioxide (CO₂) in catalytic reforming and carbon gasification to increase yields and carbon conversion efficiency

• Further develop and improve catalytic carbonylation of biomass derived syngas for carbon-carbon bond formation for the production of fuels and platform chemicals

• Provide comprehensive catalysts and char characterization to understand and improve reactivity reducing Capex and Opex

These goals align with those of the DOE Bioenergy Technologies Office, and with those of the bioenergy industry.
Quad Chart Overview

Timeline
- Project start date: 2011
- Project end date: 2014
- Percent complete: 67%

Barriers

Barriers addressed
- Gt-C. High temperature gas production from biomass
- Gt-G. Fuel synthesis and upgrading
- Gt-K. Gaseous intermediates process integration

Budget

Funding for FY 2012:
$250K NREL, $250K Enerkem

Funding for FY 2013:
$250K NREL, $250K Enerkem

FY 2014 projected budget:
$250K NREL, $250K Enerkem

Years the project has been funded:
$500K average annual funding.

Partners

Interactions/collaborations:
NREL: catalyst development and characterization, gasification kinetics
Enerkem: design of catalytic processes and their plant integration, economics

Project management:
- Quarterly reviews with both teams
- Periodic phone calls to assess progress
- Written quarterly reports
Project Overview:

Biomass-derived synthesis gas => fuels

- Deconstruct biomass all the way to syngas (CO$_2$, CO & H$_2$)
- Decrease Capex and Opex
- **Value proposition:**
  - Use CO$_2$ and improved catalytic approaches

**Diagram:***
- **Gasification**
- **Syngas Cleanup**
- **Syngas Conditioning**
- **MeOH, DME**
- **Carbon Coupling Low P**
- **Intermediates**
- **Liquid Fuels**

**CO$_2$ is recovered via Acid Gas Removal**

**C$_2$-C$_4$ Olefins and Hydrocarbons**

**Multi metal zeolites provide tailored activity, selectivity, low P reaction**

**NREL:**
- Catalyst modeling and development
- Characterization
- Lab evaluation

**Enerkem:**
- Catalyst evaluation at process conditions
- Pilot/plant integration

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Project Overview
Biomass-derived CO$_2$ utilization

- CO$_2$ / steam co-reforming intermediates (char, tar and lower MW HC) during Enerkem’s staged gasification
  
  *The char + CO$_2$ reaction is being studied as part of the CRADA*

- CO$_2$ / Steam co-reforming of CH$_4$ to generate additional syngas
  
  *This reaction is also being studied as part of the CRADA*

- CO$_2$ as reactant for platform chemicals

- CO$_2$ as source of C for biomass growth
Main Chemical Reactions

- Condensation reactions secondary tar
- CO$_2$ / carbon (char)
- Steam / carbon (char)
- Cracking and steam reforming of intermediates
- Partial oxidation

Char impurities and additives (K, Ca, Fe, …) can act as low cost C gasification catalysts to increase conversion by reaction between CO$_2$ and entrained char
Enerkem converts the syngas to methanol in one pass at 40% CO conversion;
The unconverted syngas is separated into a CO-rich stream; a H₂-rich steam and a tail gas that contains the CH₄, and residual CO₂, CO, H₂ and N₂.
Reforming the tail gas provides additional process syngas and provides the desired H₂/CO ratio. The CRADA has been studying the CO₂ + steam co-reforming of CH₄.
## 1-Approach

### Project Timeline

<table>
<thead>
<tr>
<th>Task/Team</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
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<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
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<tr>
<td><strong>Task 1: Improved Catalytic Methanol Carbonylation</strong></td>
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<td>Metal zeolite preparation and testing (low P- <strong>NREL</strong></td>
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<td>(high P) <strong>Enerkem</strong></td>
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<td>Catalyst characterization (NREL)</td>
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<td>Active site modeling ( <strong>NREL/Enerkem</strong> )</td>
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<td>Improved catalyst synthesis/testing (low P – NREL)</td>
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<td>(high P – Enerkem)</td>
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<tr>
<td>Deliverable: predictive catalyst model; new catalyst(s); syngas derived fuels</td>
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<td>Disseminate results via patents, publications, presentations</td>
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<td><strong>Task 2: Carbon Dioxide Utilization During Gasification</strong></td>
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<td>Steam and CO2 co-reforming of tar intermediates</td>
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<td>Steam and CO2 co-reforming of CH4 (tail gas)</td>
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<td>Catalyst characterization</td>
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<td>Char gasification in varied gas compositions</td>
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<td>Char reforming kinetic model development</td>
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<td>Disseminate results via patents, publications, presentations</td>
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2 – Technical Progress: CH₄ and CO₂ conversion during co-reforming

Catalyst ENK3

New formulations show convincing potential for co-reforming with substantial conversions and incorporation of C from CO₂. Project needs to move to pilot.
2 – Technical Progress:
Char gasification

Base line data on char gasification (at 90% C conversion)

<table>
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<tr>
<th>T, °C</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1500</th>
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<td>T, sec</td>
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<tr>
<td>Wood char (B)</td>
<td>4732</td>
<td>1109</td>
<td>326</td>
<td>115</td>
<td>47</td>
<td>21</td>
<td>6</td>
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<tr>
<td>MSW char (C)</td>
<td>1077</td>
<td>485</td>
<td>247</td>
<td>139</td>
<td>85</td>
<td>55</td>
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<tr>
<td>MSW char (D)</td>
<td>1500</td>
<td>750</td>
<td>418</td>
<td>254</td>
<td>165</td>
<td>113</td>
<td>60</td>
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- Conclusion: char, which contains between 7.5 and 15 % of the C in the feedstock is not easy to gasify.
- Catalysts, low cost, are needed, since operating beyond 1100° C is not practical. Goal is to gasify char in < 10 sec
- Identification of additives that enhance reactivity has begun
- Choice of additives and their testing will be pursued in the rest of Year 2 and during Year 3 of the CRADA
Hypothesis: Halide-free conversion of biomass syngas to liquid products can be achieved via carbonylation catalyst development

Enerkem has a functional Methanol => Methyl Acetate => Ethanol gas phase process. *In this CRADA we are exploring strategies to eliminate iodide and thus reduce Capex and Opex maintaining high conversions and selectivities.*

**Strategy 1:** Shape selective catalysts starting from molecular modeling

**Strategy 2:** Supported multi-metals catalysts
Modeling a halide-free active site:

- Constructing a shape selective catalyst and active site that can serve as a substrate for introducing electronic variation via metals addition and acidity changes

- Using modeling package Gaussian with NREL’s supercomputers

- Currently configuring the “catalyst site”

Defined structures with Metal substituted at the acid site and attached to a CO molecule – to promote carbonylation
Supported multi-metal catalysts

- Project started in Year 2 of the CRADA
- Enerkem has:
  - Identified a combination of multi-metals that operated in tandem leads to:
    - Metals Type 1: enhanced activation of CO
    - Metals Type 2: enhanced selectivity to oxygenates
  - Procured kg levels of three catalyst combinations
  - Assembled a functional pilot plant where tests began May 2012. The plant can produce ethanol via the current MeOH => EtOH process and has also an independent reactor system where the new catalytic strategies can be tested
3 - Relevance

• Addresses Thermochemical Conversion R&D Strategic Goal: “Develop technologies for converting feedstocks into cost-competitive commodity liquid fuels such as ethanol, renewable gasoline, jet fuel, and diesel.”
  – Single and dual technology approaches to optimizing biomass carbon utilization from gasification
  – Research and development guided by actual pilot scale validation
  – Research is integrated with other core topic areas including and yet going beyond gasification and ethanol synthesis

• Project pursues two pathways:
  – Feedstock conversion into a clean syngas capturing high C conversion
  – Catalytic strategies to upgrade the syngas into fungible fuels

• Project accomplishments in FY11 and FY12 move us toward strategic goal:
  – Developing improvements in catalyst carbonylation selectivity
  – Improved biomass carbon utilization by reforming process CO₂ to additional syngas
**Technical:**
- Feedstock C conversion into syngas > 95%
- Replace 25% of steam in tail gas reforming
- New catalytic strategies prove that halides are not needed for carbonylation while maintaining yields, for ethanol, > 360 liters/tonne, dry basis

**Fuel & Chemical Pools:**
- Compatibility with existing pools

**Business:**
- Plants converting 100,000 t/y of feedstock can generate profits

**Challenges:**
- Make the char, via inexpensive catalysts, more reactive
- Scale up the co-reforming results
- Stability and Activity of novel catalysts in carbonylation and subsequent conversion to end products

All the above improvements will result in significant Capex and Opex reductions thus impacting positively the production of biofuels
5 – Future Work

Task 1: Enhancing Carbon Conversion via Catalysis

• Understanding the C structures present in char particles comprised of C & ash

• Assessing catalytically modified char reactivity

Task 2: The Biomass Syngas => Methanol Platform: Building Co-products

• Continuing the “halide-free” carbonylation catalyst development and testing

• A new effort will begin developing the Methanol => DME => olefins (C$_2$ and C$_3$) as platform bio-commodities
• CRADA is allowing Enerkem to access the unique expertise existing at NREL on biomass conversion, catalysis and characterization.

• Significant improvements in the biomass => syngas => biofuels space are being made in this CRADA. They enhance reductions in Capex and Opex.

• The results will be useful for the gasification field as a whole and, as well, for the catalysis sector converting syngas into defined fuels.

• Improvements studied cover: co-reforming residual low MW hydrocarbons; char gasification to increase syngas yield; and halide-free carbonylation.

Enerkem is grateful to NREL and DOE for their contribution to this CRADA
• Enerkem will progressively introduce the results of this CRADA into its operations in Edmonton (plant under construction) and in its forthcoming plants in Mississippi and Varennes.

• Major results of the CRADA work will be made available to the public via:
  – Presentations by NREL and Enerkem at selected meetings
  – Publications by NREL’s scientists and engineers participating to the project