2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Enerkem NREL CRADA

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Goal Statement

The goals of this joint CRADA project are:

- Develop the use of carbon dioxide (CO_2) 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

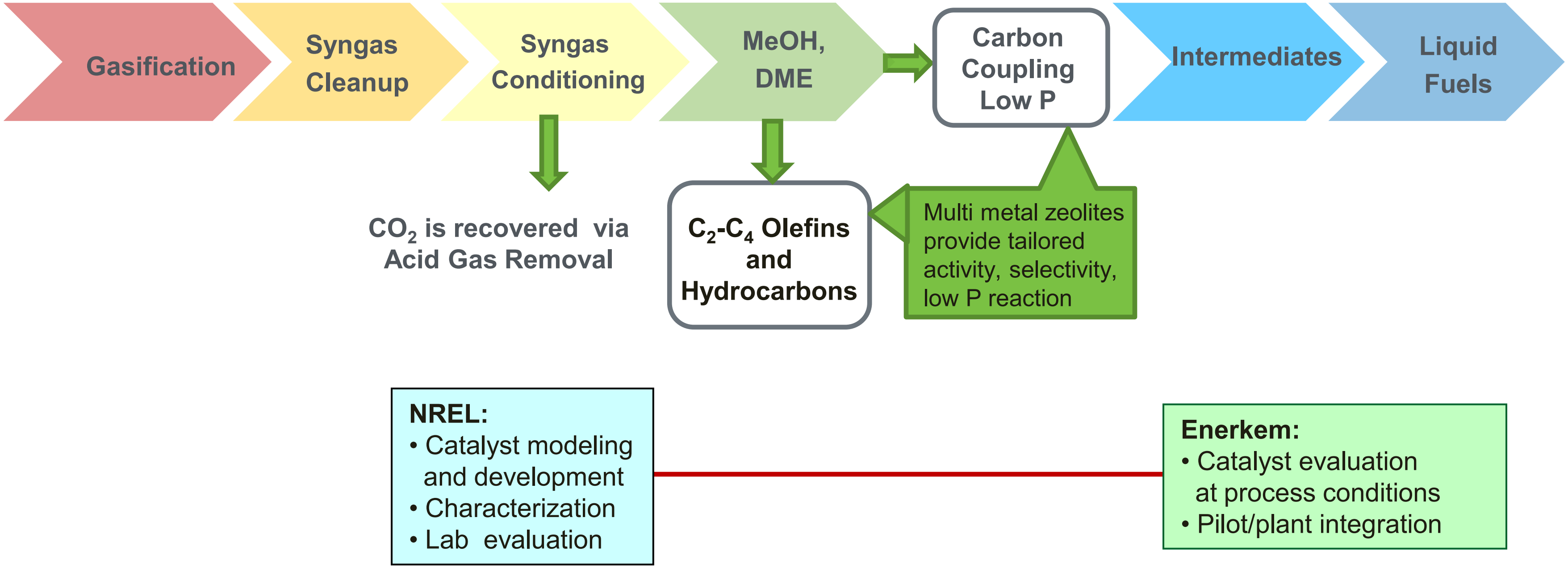
Project management:

- Quarterly reviews with both teams
- Periodic phone calls to asses 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**



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

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

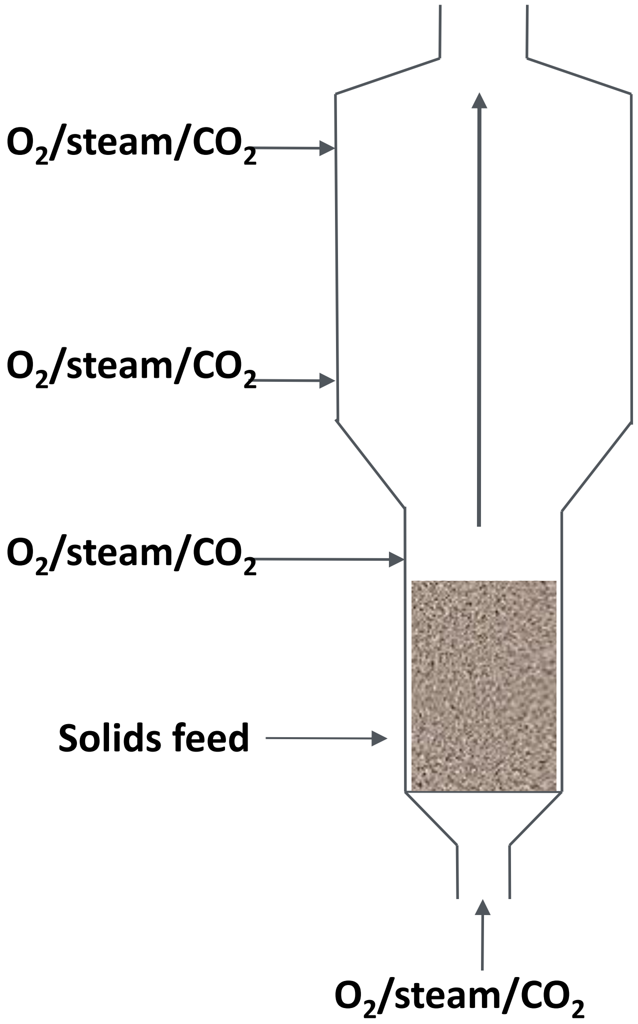
  This reaction is also being studied as part of the CRADA

- CO_2 as reactant for platform chemicals

- CO_2 as source of C for biomass growth

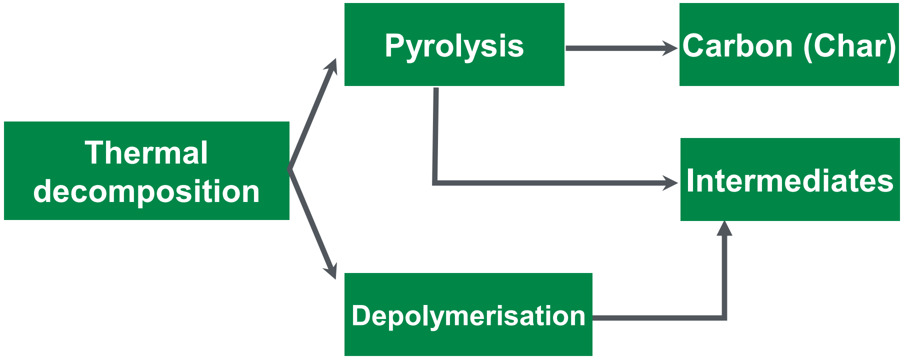
Project Overview

Staged gasification and CO_2 use



Main Chemical Reactions

- Condensation reactions secondary tar
- CO_2 / carbon (char)
- Steam / carbon (char)
- Cracking and steam reforming of intermediates
- Partial oxidation



Thermal decomposition

Pyrolysis

Depolymerisation

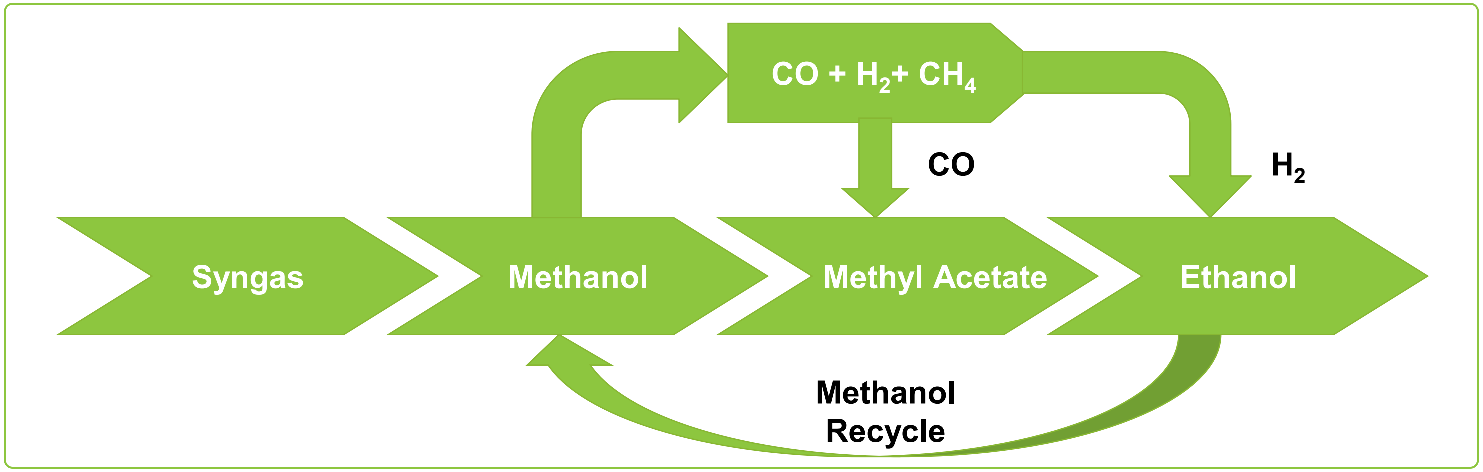
Carbon (Char)

Intermediates

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

Project Overview

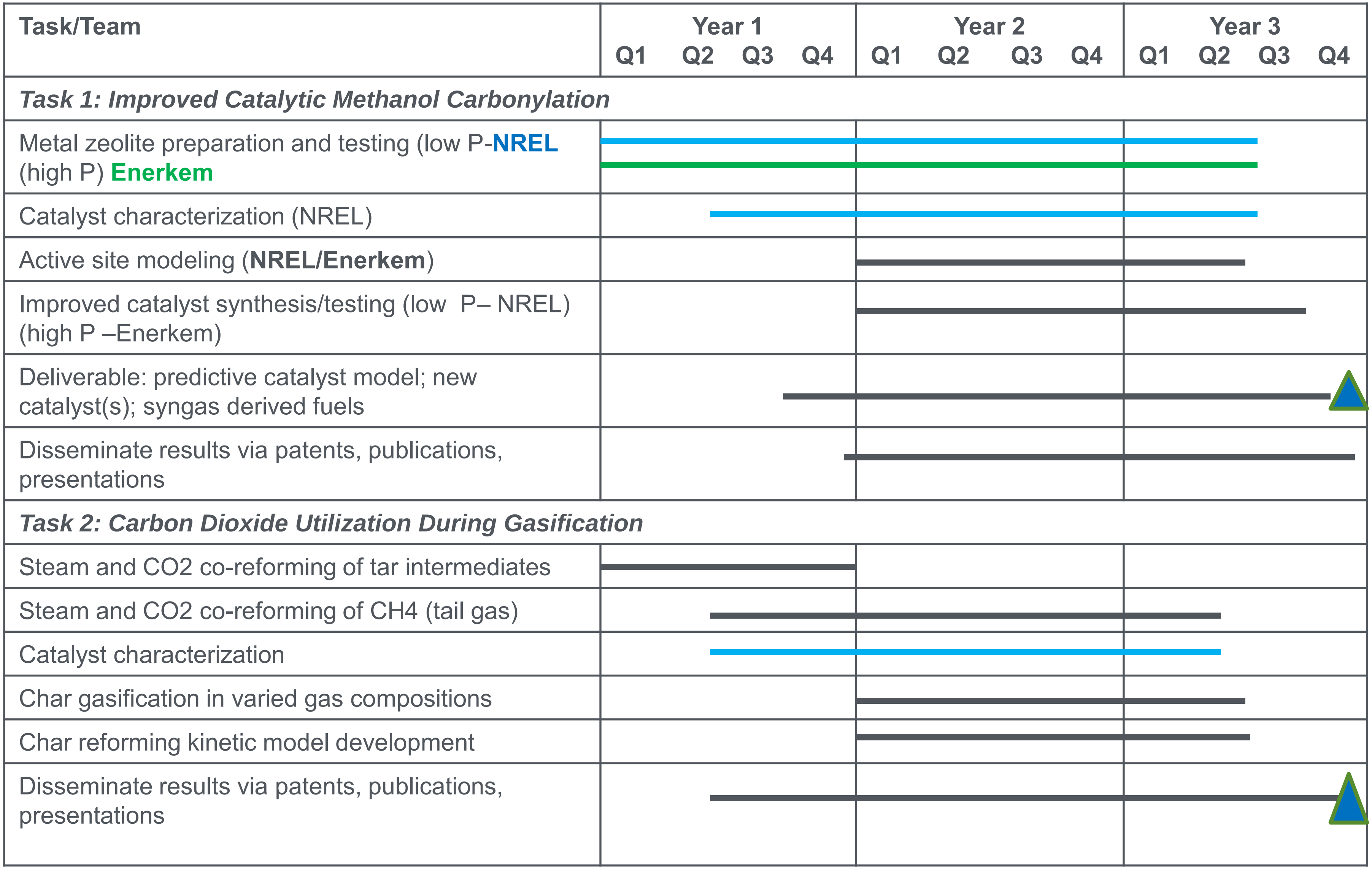
Tail gas co-reforming (CO_2 + H_2O)



- Enerkem converts the syngas to methanol in one pass at 40 % CO conversion;
- The unconverted syngas is separated into a CO-rich stream; a H_2-rich steam and a tail gas that contains the CH_4, and residual CO_2 , CO, H_2 and N_2
- Reforming the tail gas provides additional process syngas and provides the desired H_2/CO ratio. ***The CRADA has been studying the CO_2 + steam co-reforming of CH_4.***

1-Approach

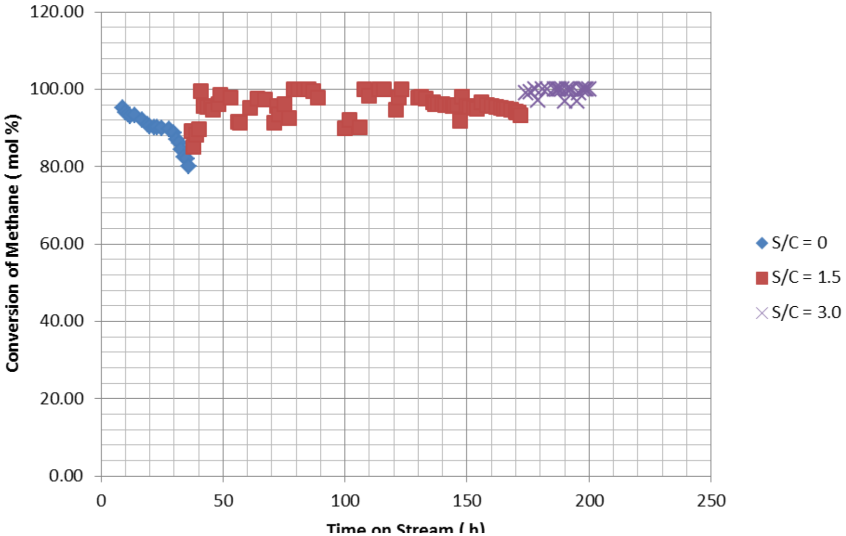
Project Timeline

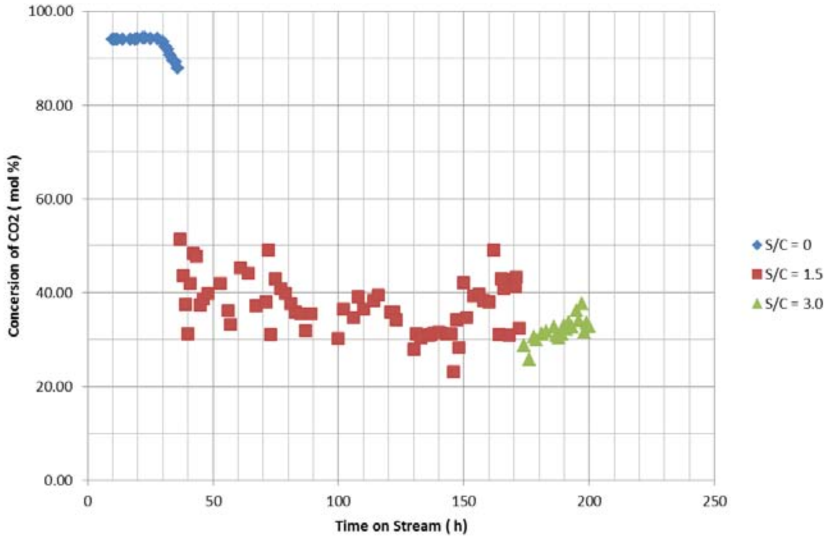


Task/Team	Year 1 Q1	Q2	Q3	Q4	Year 2 Q1	Q2	Q3	Q4	Year 3 Q1	Q2	Q3	Q4
Task 1: Improved Catalytic Methanol Carbonylation												
Metal zeolite preparation and testing (low P-**NREL** (high P) **Enerkem**	━	━	━	━	━	━	━	━	━	━	━	
Catalyst characterization (NREL)		━	━	━	━	━	━	━	━	━	━	
Active site modeling (**NREL/Enerkem**)					━	━	━	━	━	━		
Improved catalyst synthesis/testing (low P– NREL) (high P –Enerkem)					━	━	━	━	━	━	━	
Deliverable: predictive catalyst model; new catalyst(s); syngas derived fuels				━	━	━	━	━	━	━	━	━ ▲
Disseminate results via patents, publications, presentations				━	━	━	━	━	━	━	━	━
Task 2: Carbon Dioxide Utilization During Gasification												
Steam and CO2 co-reforming of tar intermediates	━	━	━	━								
Steam and CO2 co-reforming of CH4 (tail gas)		━	━	━	━	━	━	━	━	━		
Catalyst characterization		━	━	━	━	━	━	━	━	━		
Char gasification in varied gas compositions					━	━	━	━	━	━		
Char reforming kinetic model development					━	━	━	━	━	━		
Disseminate results via patents, publications, presentations		━	━	━	━	━	━	━	━	━	━	━ ▲

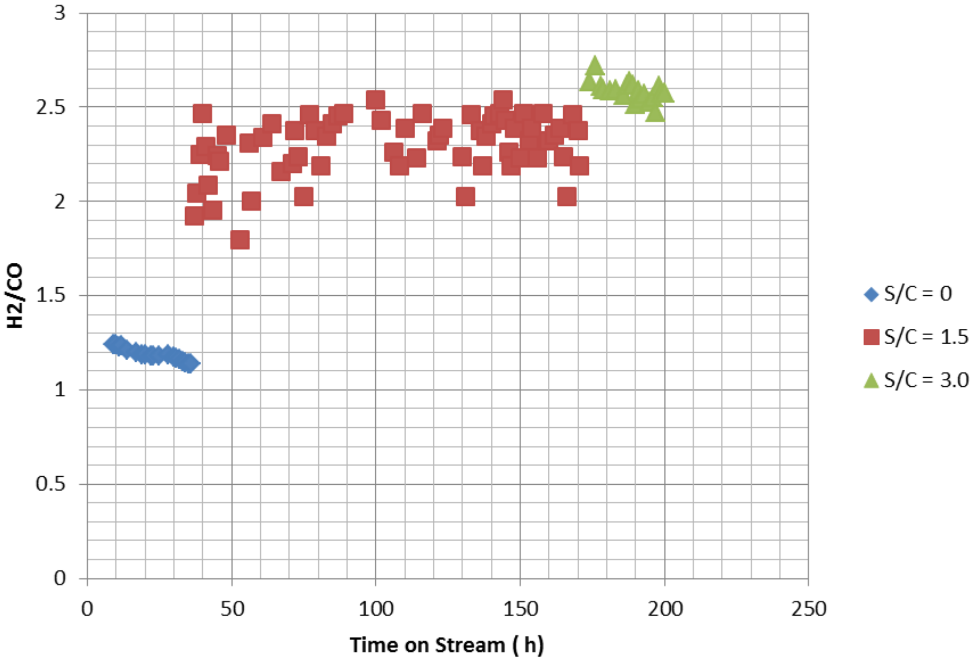
2 – Technical Progress:

CH_4 and CO_2 conversion during co-reforming





Catalyst ENK3



New formulations show convincing potential for co-reforming with substantial conversions and incorporation of C from CO_2. Project needs to move to pilot.

2 – Technical Progress:

Char gasification

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

T, °C	800	900	1000	1100	1200	1300	1500
τ, sec							
Wood char (B)	4732	1109	326	115	47	21	6
MSW char (C)	1077	485	247	139	85	55	27
MSW char (D)	1500	750	418	254	165	113	60

- 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

2-Technical Progress:

Carbonylation Catalyst Development

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

2-Technical Progress:

Carbonylation Catalyst Development

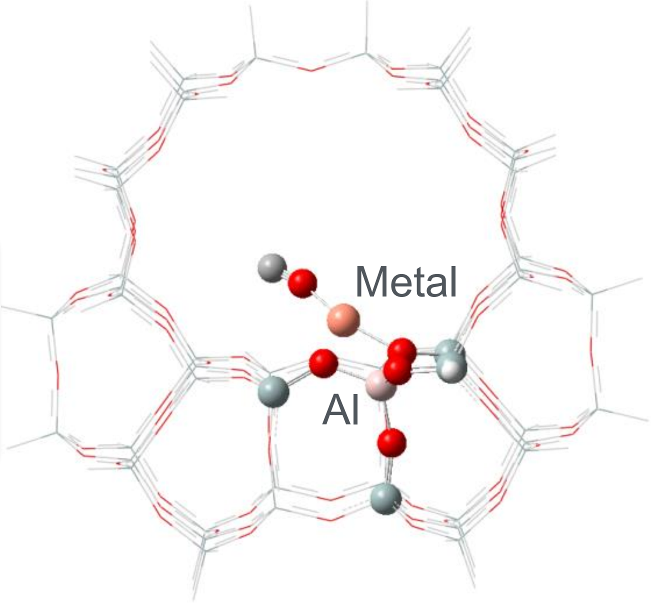
Modeling a halide-free active site:

- 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

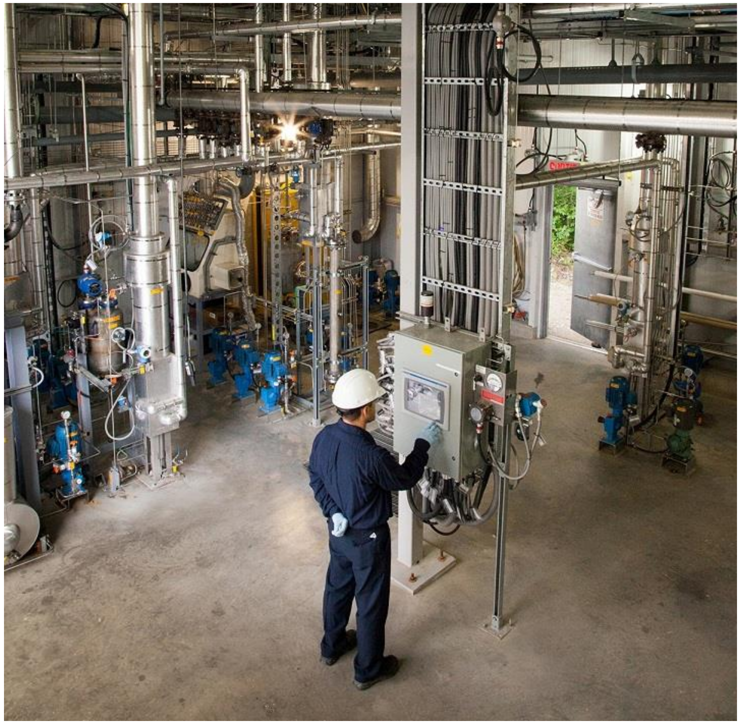


2-Technical Progress:

Carbonylation Catalyst Development

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 CO_2 to additional syngas

4 – Critical Success Factors that lead to commercial viability

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

Summary

- 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

Publications, Presentations, and Commercialization

- 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