2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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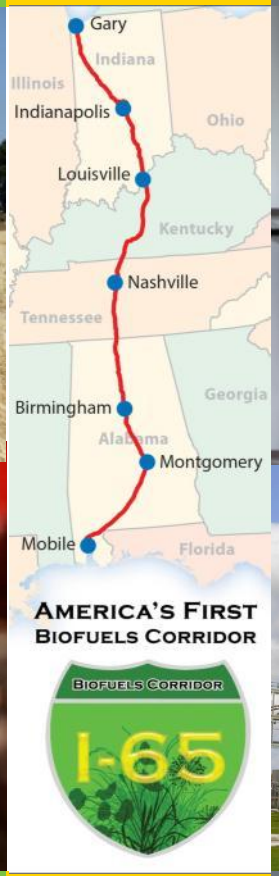

PNNL Fuel Synthesis Catalyst - CRADA with W. R. GRACE

May 21, 2013

Principal Investigators: Richard T. Hallen – PNNL
David G. Ward – W, R. Grace

Technology Area Review: Gasification

WBS 3.3.2.7

Organizations: PNNL/W. R. Grace
Presenter: Jonathan L. Male

Goal/Objective Statement

The objective of this CRADA project was to team with W. R. Grace in the development of improved mixed alcohol synthesis catalysts for the production of alcohol fuels from biomass derived syngas.

- Grace's role was to provided industrial relevant catalysts for testing and evaluation. PNNL's role was to screening and conduct extended testing with the best catalysts, then use the experimental data to construct process models and conduct techno-economic analysis (TEA).
- The goal was to provide feedback from testing and TEA to guide further catalyst development efforts at Grace.
- PNNL also examined the upgrading of the mixed alcohol product to hydrocarbon fuel, and assessed the overall hydrocarbon fuel production costs.

Quad Chart Overview

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Timeline

- CRADA Add. 1
  - Nov 2010 – April 2012
- CRADA Add. 2
  - April 2012 – April 2013

Barriers

- Gt-G: Fuels Catalyst Development
  - Improved yield, carbon efficiency
- Gt-K: Gaseous Intermediates Process Integration
  - Upgrading and fuel production

Budget

- CRADA 1 $312,500 total
  - DOE = $250,000
  - Grace = $62,500
- CRADA 2 $281,250 total
  - DOE = $225,000
  - Grace = $56,250
- Percent spent = 98%

Partners

- W. R. Grace – David G. Ward
- PNNL – Richard T. Hallen
- Project management - PNNL
  - Monthly project updates
  - Quarterly reports
  - Annual reports
  - CRADA closeout report

Project Overview

- A CRADA with W. R. Grace was executed on October 19, 2010 after negotiations with Dow were unsuccessful.
- The research was to support the further development and improve the performance of Grace molybdenum sulfide based mixed alcohol synthesis (MAS) catalysts using PNNL catalyst testing capabilities .
- The CRADA was extended to include upgrading of mixed alcohol product and examination of non-sulfide based catalysts, April 9, 2012 through April 30, 2013.
- PNNL utilized the Avantium Flowrence high throughput catalyst screening system to identify Grace preferred catalyst formulations.
- Catalyst performance data was generated for Grace's catalysts during extended testing in single-tube test stands.

1 - Approach

- Obtain catalyst samples from Grace for testing and evaluation
  - Grace provided preliminary screening results for existing catalyst formulations for the molybdenum sulfide based catalysts as the initial set of baseline catalysts for evaluation at PNNL.
- Conduct additional catalyst screening tests as needed.
  - Sulfided catalysts in single-tube test stand
  - Non-sulfided in Avantium Flowrence high throughput system
- Utilize screening results to down select small subset of catalyst samples for further evaluation, extended testing.
- Utilize TEA to evaluate performance against costs targets for alcohols or hydrocarbon fuels (upgraded).
- Target new catalysts formulations based upon results of analysis (TEA) for evaluation at PNNL.

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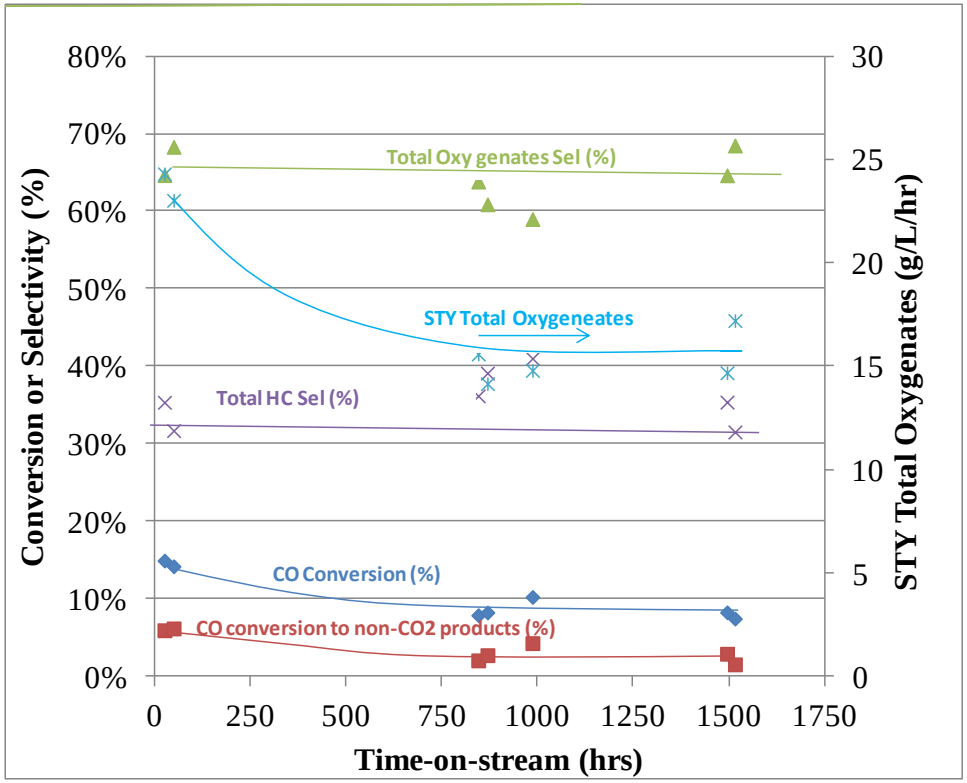
2 – Technical Accomplishments and Results: CRADA 1

Evaluation of Molybdenum Based Mixed Alcohol Catalyst

- Catalyst screening identified the best catalyst formulation for detailed evaluation, Grace-12C selected
- Expanded parametric testing completed for best catalyst formulations

- Grace-12C testing extended over 1500 hours TOS
- Baseline conditions:
  - P=1000 psig, T=325 ˚C, GHSV=1000 hr^{-1}
- Feed Composition:
  - $H_2/CO=1.2$, $CO/CO_2=6.7$, $H_2S=100ppm$
- Parametric studies:
  - T=325-360°C
  - P=800-1200 psig
  - SV=500-4000 hr-1
- Initial catalyst deactivation over ~300 hours TOS

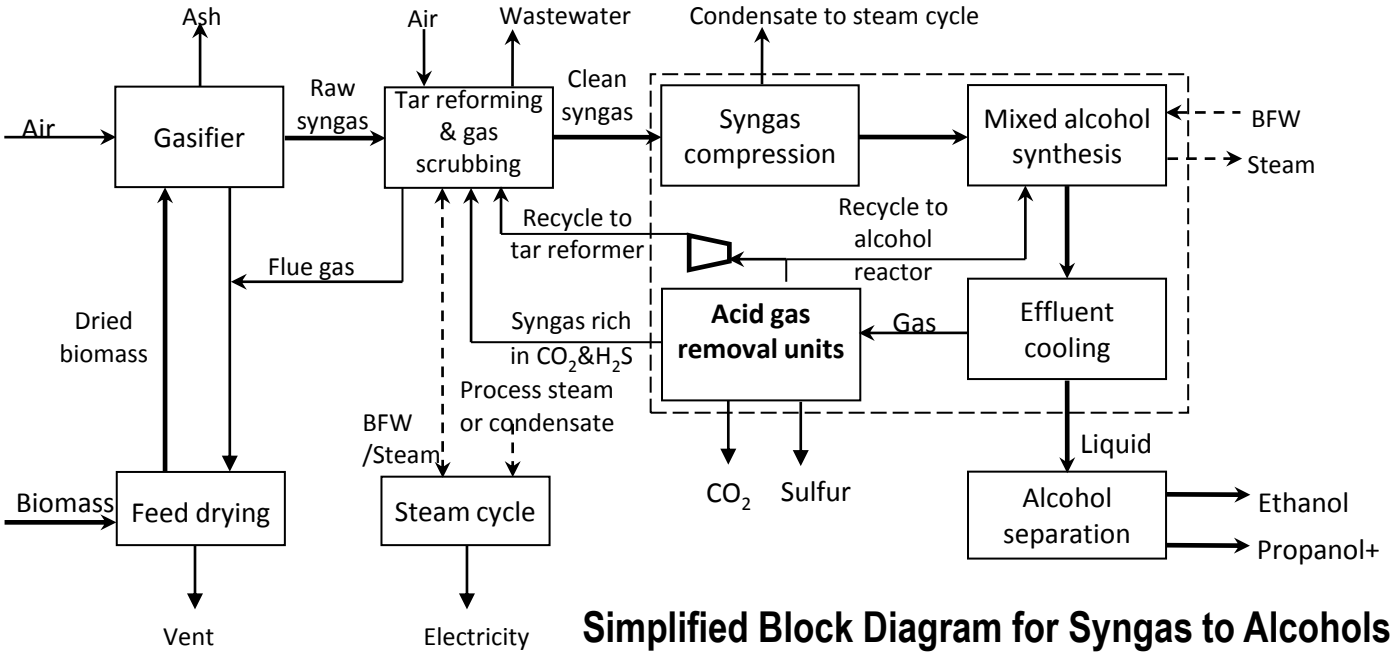


Experimental data generated for techno-economic analysis

Techno-economic Evaluation of Grace Mixed Alcohol Catalyst

Process model developed/adapted for techno-economic analysis (TEA) based on woody biomass gasification and MAS based on Grace catalyst

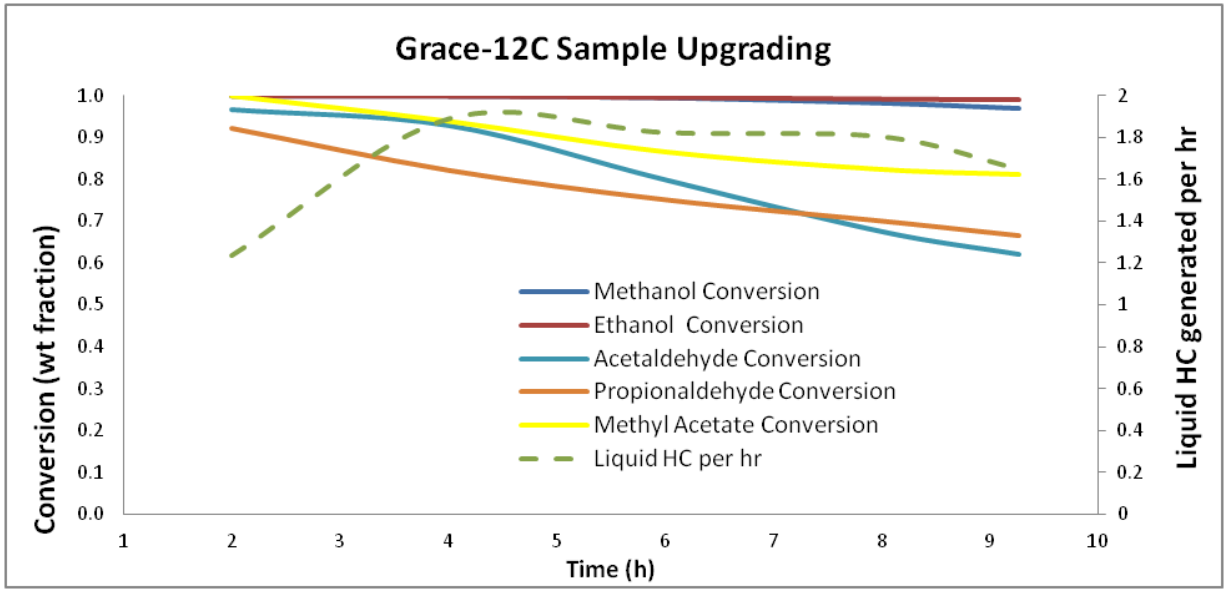
- 2000 dry metric ton/d woody biomass converted to 13 mmgal/yr ethanol and 26.6 mmgal/yr higher mixed alcohols
- Minimum fuel selling price (MFSP):
  - Ethanol as final product and higher alcohols as co-product (heating value) – $7.34/gal ($10.89/gallon gasoline-equivalent (GGE))
  - All alcohols as final product of equal value – $4.01/gal ($5.22/GGE)



Simplified Block Diagram for Syngas to Alcohols

Techno-economic Evaluation of Mixed Alcohol Upgrading

- Feasibility of upgrading mixed alcohols product to hydrocarbon fuel via conventional zeolite catalyzed process like MTG demonstrated
- Experimental data generated for TEA, upgrading validated with an actual sample from extended run with Grace-12C
  - 167,000 gallon/day mixed alcohols converted to 16.7 mmgal/y hydrocarbon fuels. MFSP of hydrocarbon fuel product: $6.80/gal ($6.60/GGE)



Conclusions and Path Forward Identified

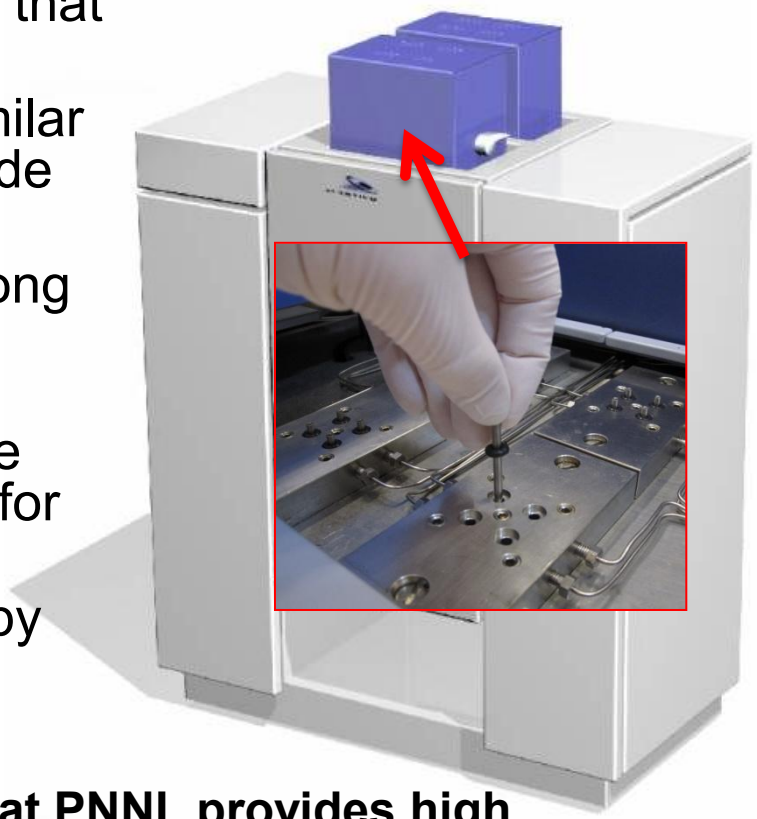
- Molybdenum sulfide catalysts did not meet performance needed
- Expand the screening to other, non-sulfide based catalyst families

Expanded Evaluation to Non-Sulfided Catalysts

Grace, in consultation with PNNL, targeted the synthesis of non-sulfided catalysts formulations for PNNL to evaluate.

- The Avantium Flowrence System is a high throughput, automated catalyst test stand that screens 16 catalyst samples at a time
- Catalyst evaluated side-by-side under similar reaction conditions. Test matrix can include baseline catalysts for comparison.
- Catalyst reduced in-situ as part of week long testing campaign that includes 5 process conditions.
- On-line gas analysis for gases and volatile organic products, liquid sample collected for off-line analysis.
- Screening protocol and results validated by single-tube testing.

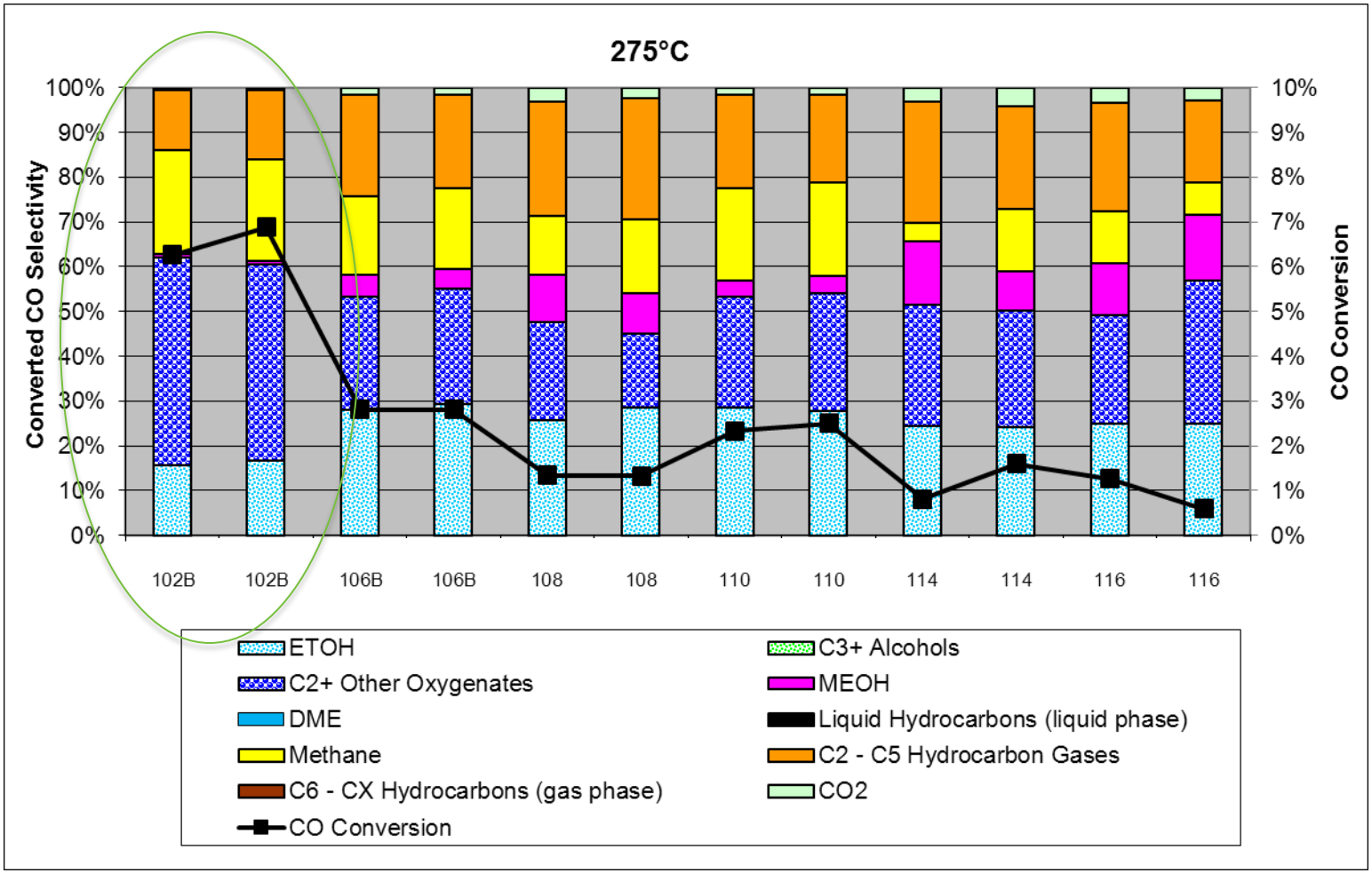
MULTI-TUBE FLOW REACTORS FOR HIGH THROUGHPUT CATALYST SCREENING



The Catalyst Automated Testing (CAT) Center at PNNL provides high throughput capabilities in the area of catalyst discovery and development.

Catalyst Screening Results: Performance of Catalyst 102B

Duplicate catalyst samples screened and experimental data evaluated



Catalyst activity and selectivity to desired products are key parameters

Single-tube Test Results: Performance of Catalyst 102B

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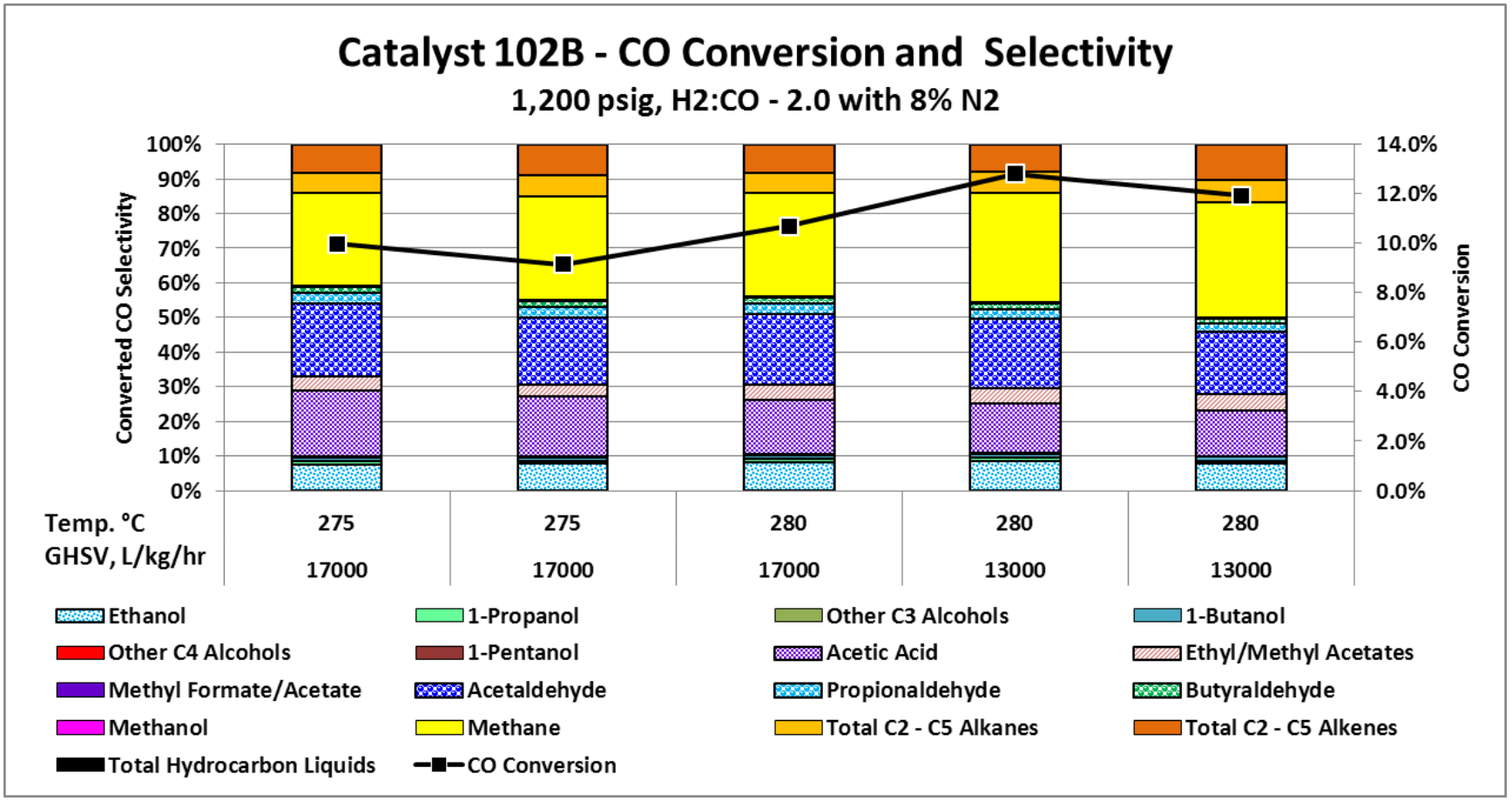
Best catalysts are evaluated in extended single-tube reactor testing



Catalyst activity and selectivity are a function of process conditions and catalyst time on stream.

2 – Technical Progress

Title/Description	Due Date	Completed
Complete CRADA	Apr-13	✓
Initiate catalyst testing, existing catalyst formulations	Nov-10	✓
Initiate secondary catalyst testing	Mar-11	✓
Complete testing of new catalyst	Jun-11	✓
Determine optimum catalyst formulation for maximum mixed alcohol production	Mar-12	✓
Determine minimum production cost for MAS with optimum catalyst	Jun-12	✓
Determine hydrocarbon production cost from MAS upgrading	Sep-12	✓

Milestones and deliverables met for project.

Alignment with BETO (from MYPP):

- Gaseous intermediates goal “to develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible, liquid fuels, such as, renewable gasoline, jet fuel, and diesel, bioproducts and chemical intermediates, and bioenergy”
- By 2014, “establish out-year cost goals and technical targets, based on completed techno-economic analysis”
- By 2022, “achieve the overall Program performance cost goal of $3/gge (2011$) via catalytic upgrading of biomass synthesis gas to gasoline and diesel range hydrocarbons”

MYPP Barriers addressed:

- Gt-G. Fuels Catalyst Development
- Gt-K. Gaseous Intermediates Process Integration

4 - Critical Success Factors and Challenges

Critical success factors which will define technical and commercial viability:

1. Improve the overall carbon yield to mixed alcohol products and reduce processing cost for indirect liquefaction processing routes
   - High selectivity and productivity to all oxygenates, low selectivity to methane
   - Potential to reduce fuel production costs by higher value co-products
2. Improve yield of liquid hydrocarbons from mixed alcohol upgrading and reduce overall production costs of drop-in fuels from syngas processes
   - High selectivity to fuel range hydrocarbons, low selectivity to LPG and light naphtha
   - Shift in hydrocarbon distribution to distillate range
   - Reduce fuel production costs by higher value co-products, i.e. p-xylene

Potential challenges to overcome in order to achieve successful project results:

1. Achieve high productivity with low methane yield
2. Achieve long catalyst lifetimes
3. Reduce overall hydrocarbon fuel production costs

The technical feasibility of syngas to hydrocarbon fuels via a mixed alcohol synthesis pathway was demonstrated but significant improvements in the overall conversion processes, and overall economics need to be made to meet future cost targets.

5 - Future Work

- No further work is planned at this time.

Summary

Relevance: Supports the Bioenergy Technologies Office's Multi Year Program Plan (MYPP) transitioning from ethanol to hydrocarbon fuel production

Approach: Economics driven experimental research coupled with sound project management practices

Technical accomplishments: Molybdenum sulfide catalysts exhibit produce mixed alcohol product that can be upgraded to hydrocarbon fuel but costs are high. Non-sulfided catalysts exhibit high productivity and selectivity to C_2+ oxygenates. However, methane yields still above target level.

Success factors and challenges: Improve the overall carbon yield to mixed alcohol products and reduce processing cost for indirect liquefaction routes to hydrocarbon fuels

Technology transfer and future work: CRADA was successfully completed and is closing out

Additional Slides

Responses to Previous Reviewers' Comments

- This project was not peer reviewed in 2011.