2013 DOE Bioenergy Technologies Office (BeTO) Project Peer Review: GASIFICATION

–WBS 3.3.2.1 Advanced Thermochemical Biofuels–

20 May 2013

Jesse Hensley, NREL
Mark Gerber, PNNL

Goal Statement

Project Goal – Improve the performance of mixed alcohol catalysts so that DOE can meet or exceed cellulosic ethanol cost targets

- **Support the development of process designs and catalysts** that lead to the achievement of ethanol cost targets
- **Improve and validate** the performance of catalysts that produce ethanol from biomass-derived syngas

Quad Chart Overview

Timeline

- Project start: 2005
- Project end: 2012
- 100% complete

Budget

- Total project funding
  - $11.8 MM DOE
- FY11 funding
  - $0.8 MM NREL
  - $1.5 MM PNNL
- FY12 funding
  - $0.8 MM NREL
  - $1.6 MM PNNL

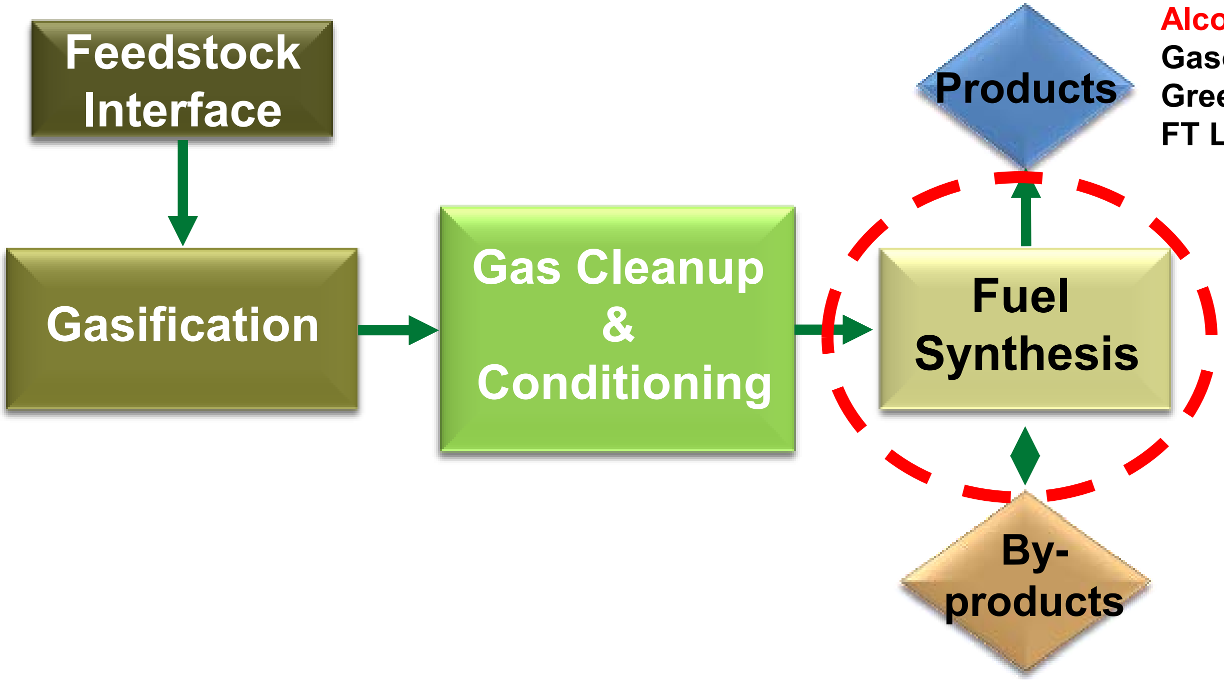
Barriers

- Tt-G fuels catalyst development
  - Low catalyst activity
  - Low selectivity to ethanol
- Process-driven attributes (achieve MESP ≤ $2.05/gal*)
  - Heat management
  - Syngas conversion
  - Syngas compression duty
  - Capital/operating costs
  - Product yield and purity

Partners

- NREL/PNNL
- Project Management via AOP/PMP

Overview: Biomass Gasification for Fuels



Feedstock Interface

Gasification

Gas Cleanup & Conditioning

Fuel Synthesis

Products

By-products

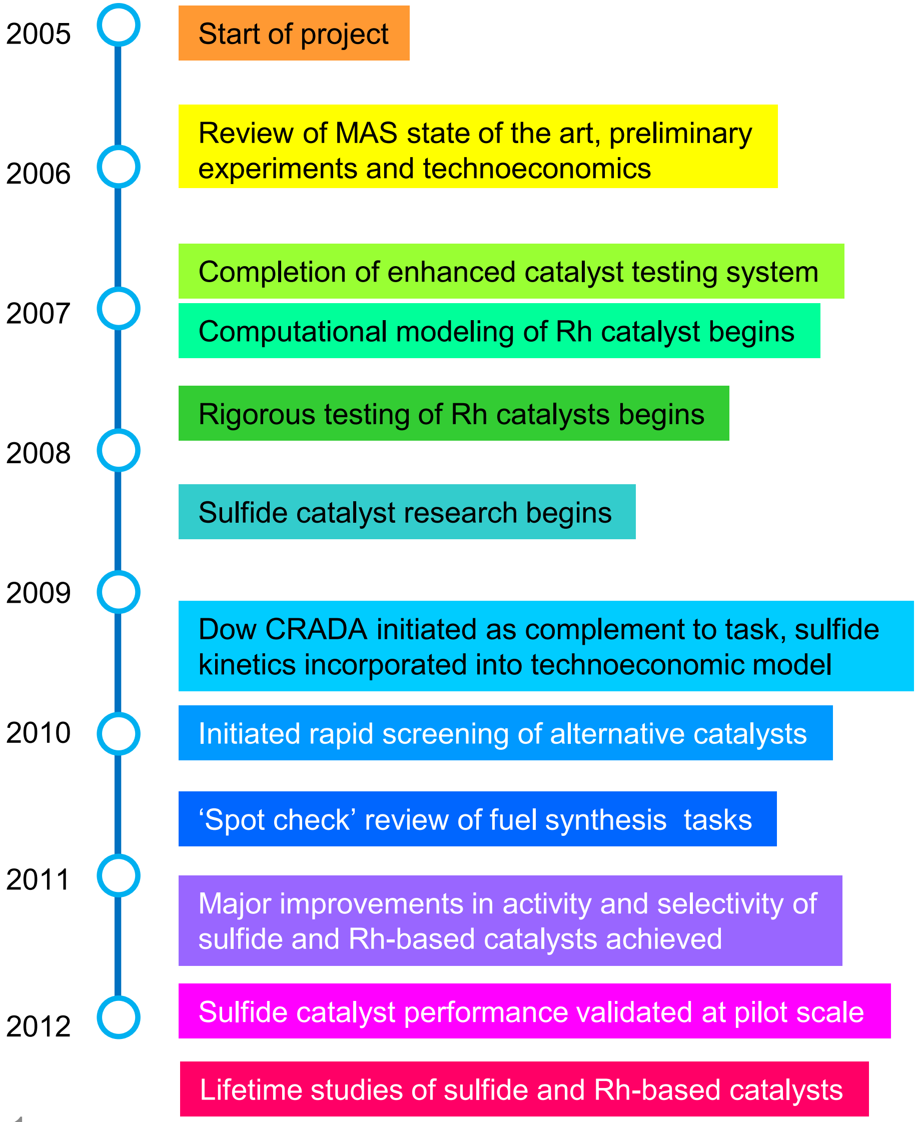
Alcohols
Gasoline
Green Diesel
FT Liquids

More robust catalysts
Higher catalyst yields

Overview: Project Objectives & Timeline

Objectives

- **Monitor and benchmark** the state of the art in mixed oxygenate catalysts
- **Identify and develop** candidate catalysts with the potential for improved performance
- **Provide** performance **information** for technoeconomic modeling of thermochemical biomass to ethanol processes
- **Validate** catalyst performance at the pilot scale



2005

Start of project

Review of MAS state of the art, preliminary experiments and technoeconomics

2006

Completion of enhanced catalyst testing system

2007

Computational modeling of Rh catalyst begins

Rigorous testing of Rh catalysts begins

2008

Sulfide catalyst research begins

2009

Dow CRADA initiated as complement to task, sulfide kinetics incorporated into technoeconomic model

2010

Initiated rapid screening of alternative catalysts

'Spot check' review of fuel synthesis tasks

2011

Major improvements in activity and selectivity of sulfide and Rh-based catalysts achieved

Sulfide catalyst performance validated at pilot scale

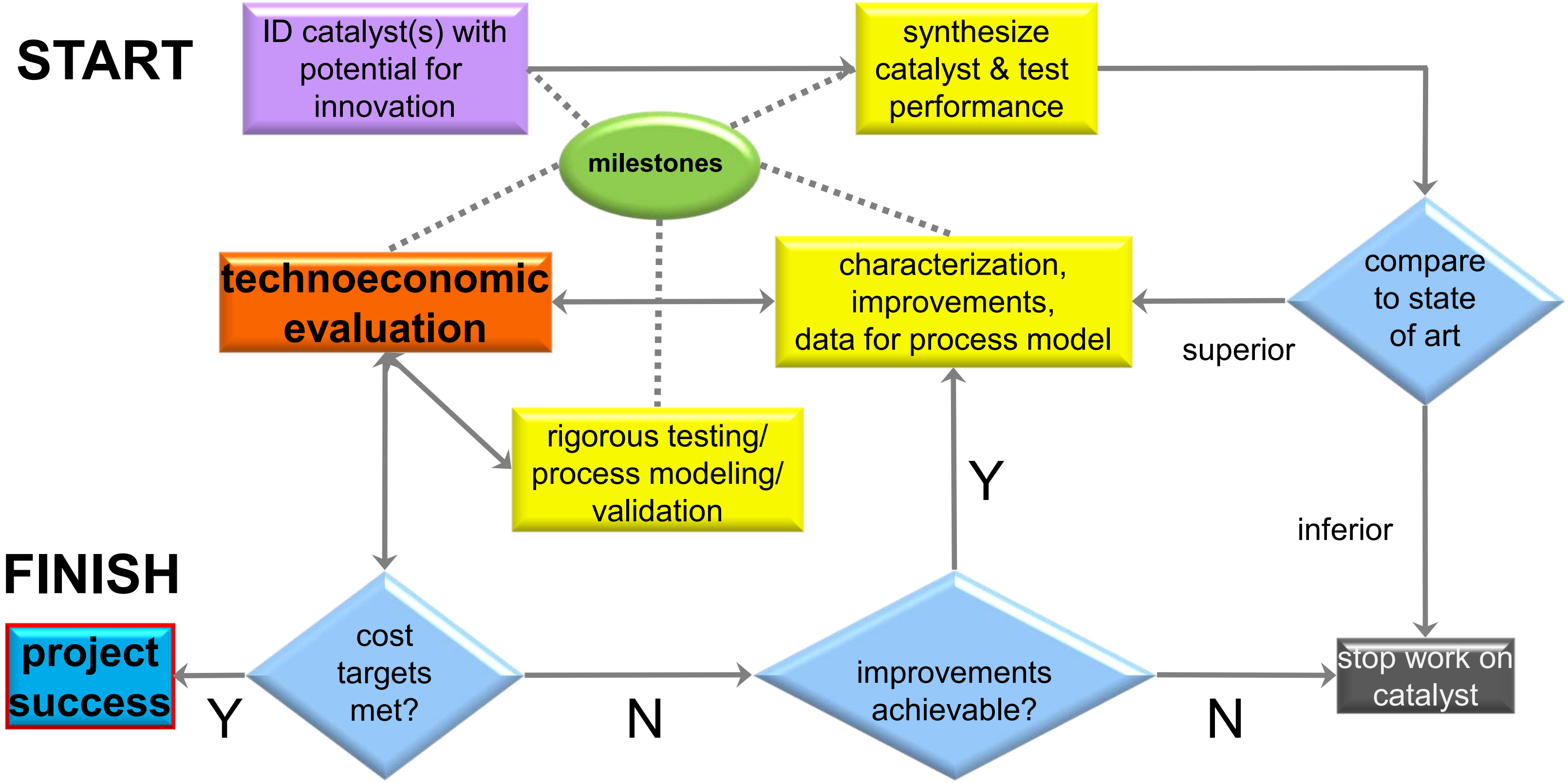
2012

Lifetime studies of sulfide and Rh-based catalysts

Approach

2012 target: modeled MESP of $2.05/gal

conversion cost targets for syngas to ethanol will vary depending on the effects of fuel synthesis on other plant operations



Technical Approach: Integrate experimentation and technoeconomic evaluation to achieve cost targets

Management Approach: DOE-approved Project Management Plans detail schedules/milestones/risk abatement

TC Conversion to Cellulosic Ethanol

Rh vs. MoS_2 based catalysts

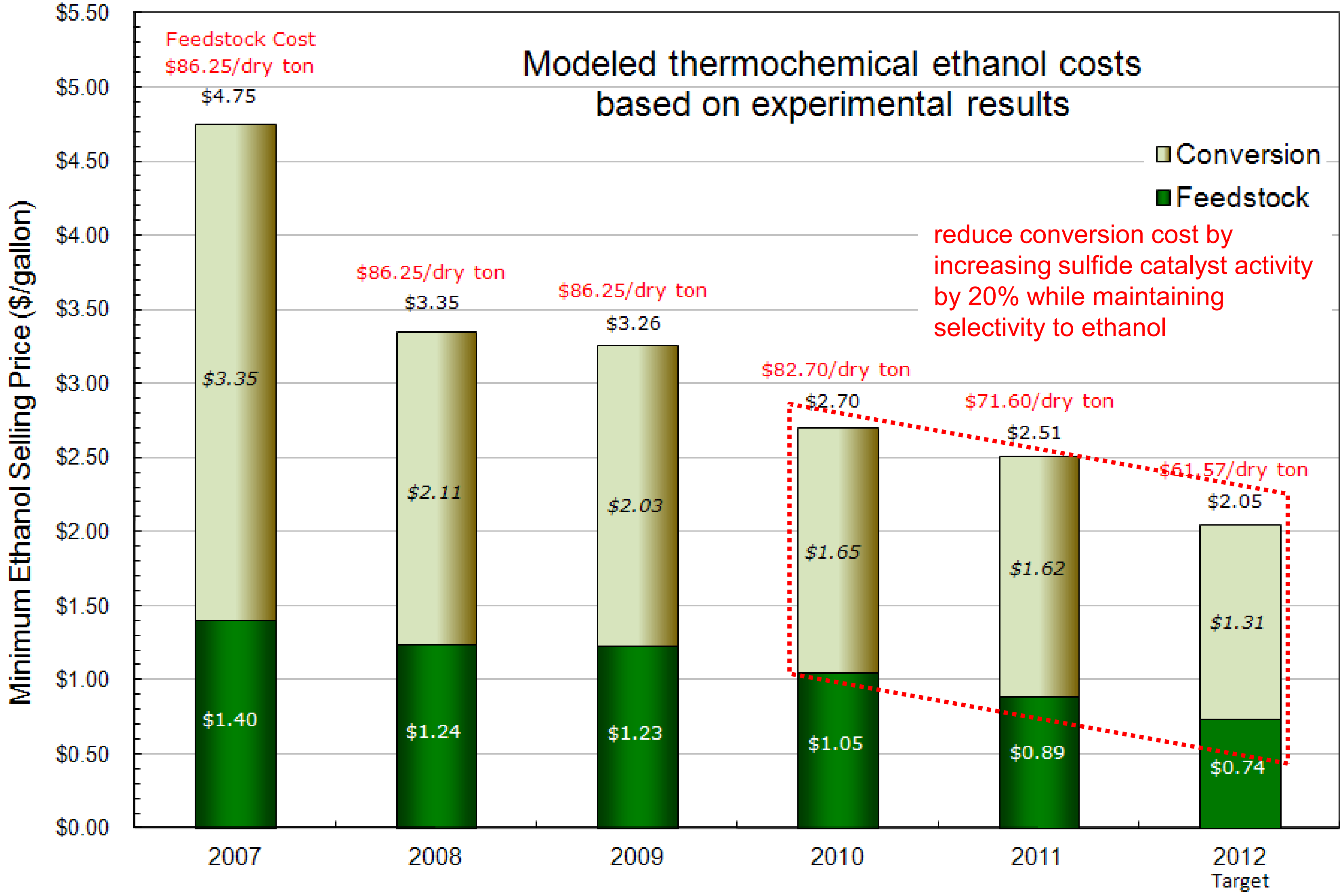
Catalysts chosen for study (refresher from 2011 review)

Performance Metric	**Rh Based (PNNL focus)**	**MoS_2 Based (NREL focus)**
C_{2+} alcohol productivity (g/kg-cat/h)	270-510	200-400
Non-alcohol oxygenate productivity (g/kgcat/h)	500-1100	< 10
Operating Pressure (psig)	500 – 1200	1300 – 3000
Methanol Production (% of condensable product)	< 1%	> 40%
Ethanol Selectivity (CO_2-free basis)	25-35%	25-40%
Light Hydrocarbon Selectivity (CO_2-free basis)	14-25%	5-15%
Sensitivity to bio-syngas contaminants (per literature)	Very low S required	Requires S
Predicted catalyst cost* ($/lb)	100	28

*cost of reclaiming/refurbishing RhMn catalyst or cost of fresh sulfide catalyst less credit from metals recycle

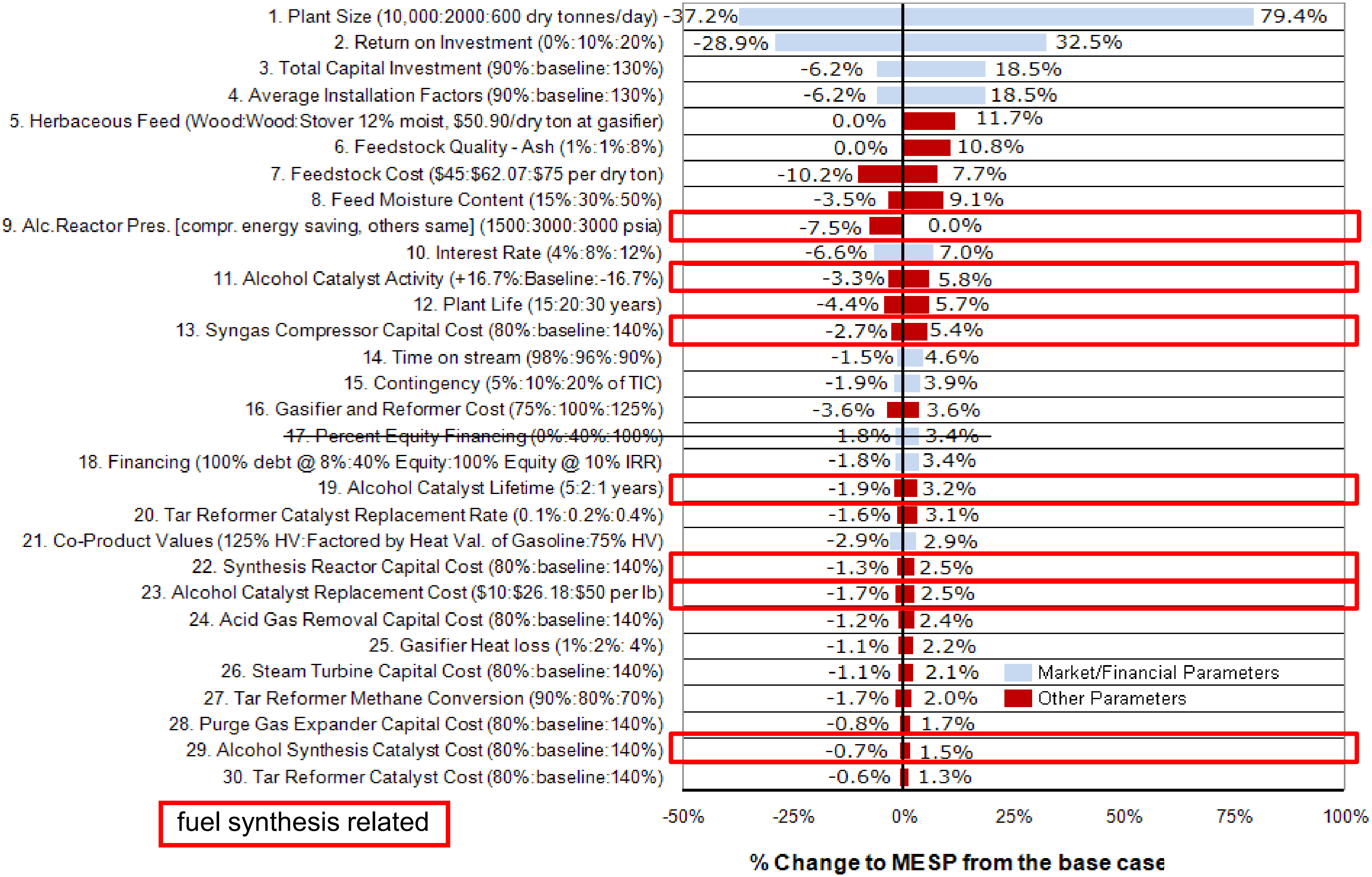
Path to Cost-Competitive Ethanol

Contributions to Cost Reduction


Modeled thermochemical ethanol costs based on experimental results

reduce conversion cost by increasing sulfide catalyst activity by 20% while maintaining selectivity to ethanol

Key Barriers—Informed by TEA



When using the **sulfide catalyst** route, improvements in catalyst *activity* will have the largest impact on process economics

Key Accomplishments:

RhMn-Based Catalysts

- Optimized Rh:Mn:Ir ratios and metal loadings for preferred support utilizing both high-throughput multi-tube tests and single-tube tests
- Completed computational chemistry analyses to explain performance trends, assist catalyst optimization
  - **Identified 2nd parallel reaction pathway to C_2+ oxygenates** that leads to significantly higher STY's and selectivities
  - Showed catalyst metal cluster surface composition different than gross cluster composition - affects catalyst optimization
  - Showed Mn interacts differently with different supports – affects catalyst stability and flexibility in catalyst formulation options
- Completed Long-term (>3300 hr) test with best catalyst
  - Slow deactivation at constant temperature – restored with higher operating temperature
  - Constant selectivity to C_2+ oxygenates over time and without significant temperature effects

RhMn-Based Catalysts

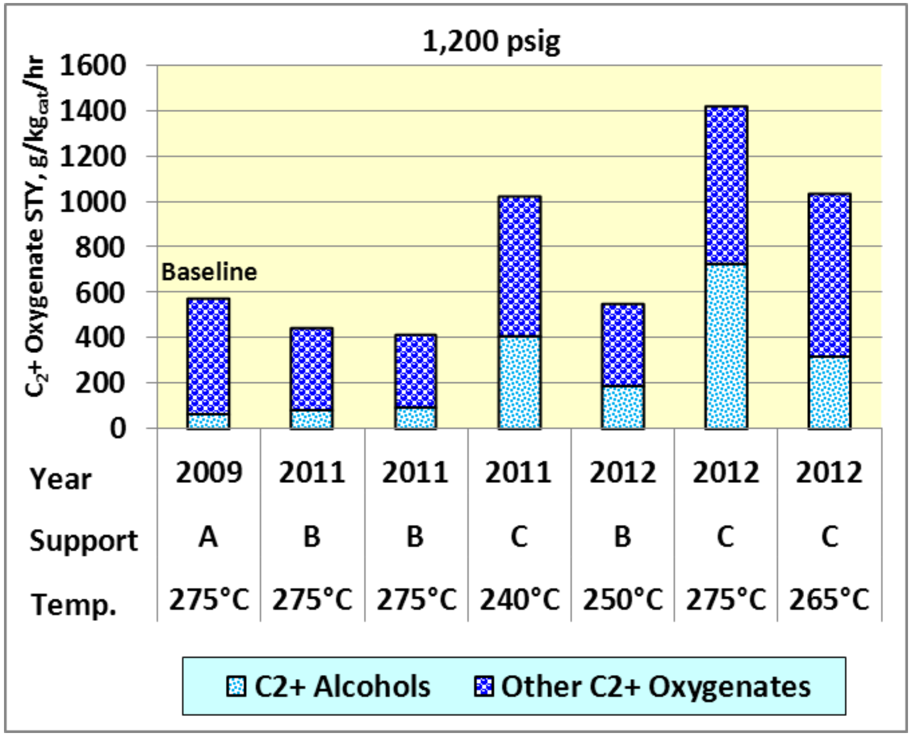
Multi-Tube Flow Reactor Testing

- Multi-tube parallel flow reactor system was used for rapid screening and preliminary evaluation of catalysts
  - Sixteen catalysts in a single test run
  - Approximately 280 catalysts tested in FY12 and FY13
- Screening and parametric evaluation in support of RhMnIr-based catalyst optimization
  - Additional promoters
  - Alternative supports
- Screening for possible alternative mixed alcohols catalysts with combinations of metals with oxygenate and F-T synthesis activity
- Most promising catalysts tested in single-tube reactors to confirm performance under more controlled test conditions.

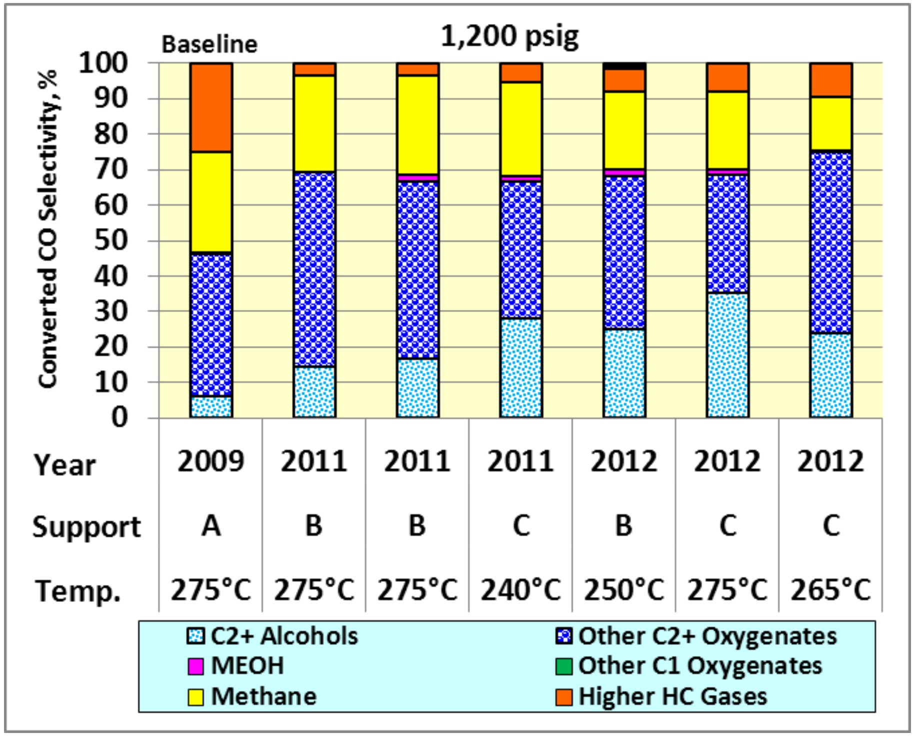
RhMn-Based Catalysts

Catalyst Development—Single Tube Tests

Productivity



Selectivity



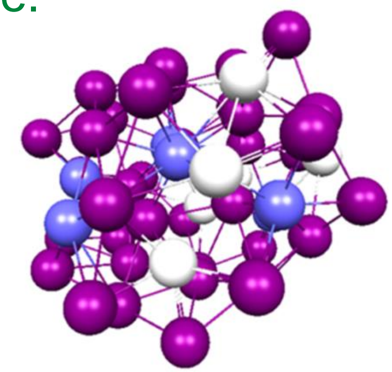
- **Achieved significant improvements in C_{2+} alcohol productivity and selectivity**
- Lower temperature operation now possible with high STYs
- Selectivities of 70-74% are less sensitive to temperature

RhMn-Based Catalysts

Computational Chemistry Contributions

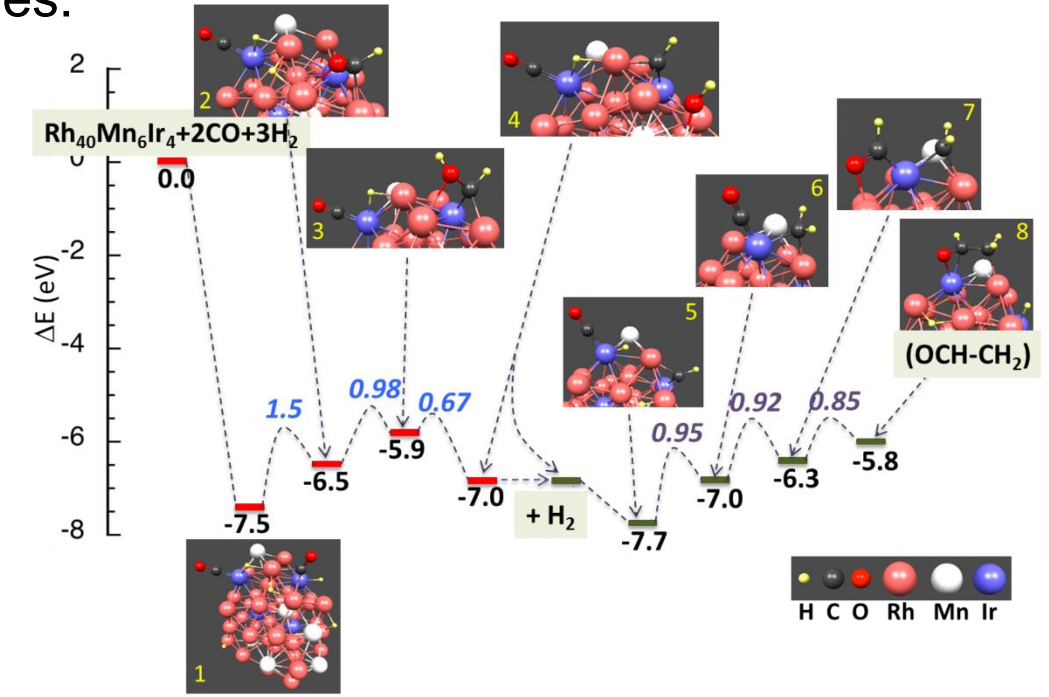
Computational chemistry uses quantum theory and molecular dynamics to understand catalyst cluster morphological changes and interactions with reactants and intermediate species.

Optimized ternary RhMnIr alloy cluster using ab initio molecular dynamics simulations. Ir prefers to stay inside the particle while Mn appears on the particle surface.



Rh (magenta), Ir (blue), Mn (white)

Topics in Catalysis 55(7-10):595-600

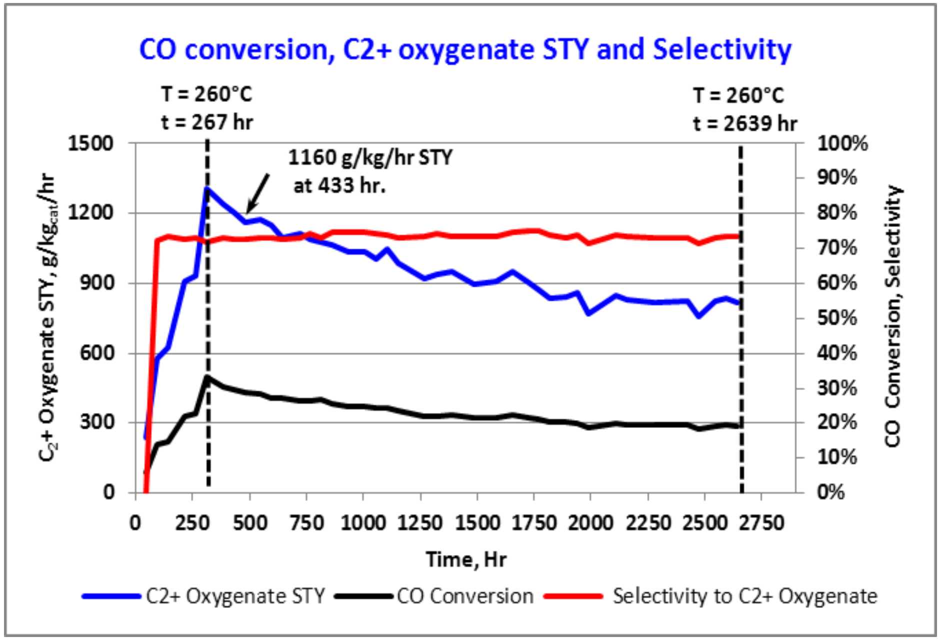


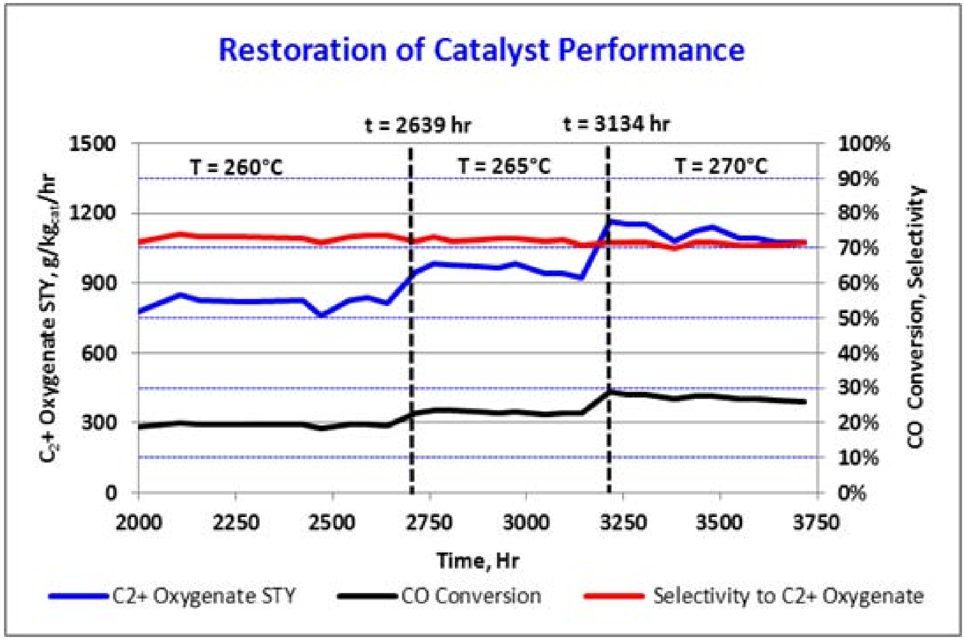
Alternative path leading to adsorbed C_2 oxygenate on RhMnIr alloy cluster showing preferred location and binding energies of adsorbed intermediate species and energy barriers between species.

RhMn-Based Catalysts

Catalyst Stability in Extended Operation

Single –Tube Test (1,200 psi, 1.3:1 H_2:CO, 4% CO_2, 4% N_2, 13,000 L/kg_{cat}/hr)





Operated 2370 h at 260 ° C

- Selectivity to oxygenates was maintained at 73% ±1.5%
- Space time yield of oxygenates, CO conversion gradually decreased over time

Additional Testing at 265 ° C, 270 ° C to evaluate restoring activity

- Activity evaluated for at least 500 hr at each temperature
- 10 ° C increase (to 270 ° C) restored activity to 1160 g/kg/hr
- Catalyst selectivity was unchanged at higher temperature

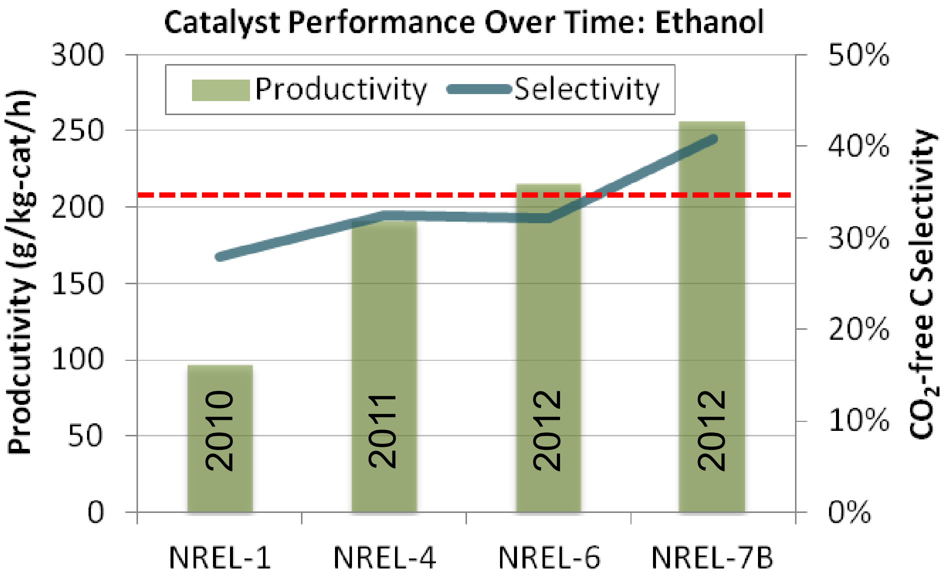
Key Accomplishments:
Metal Sulfide Catalysts

- *Exceeded FY12 technical targets for catalyst activity and selectivity*
  - Met targets at lower than required operating pressure
  - Demonstrated acceptable performance in biomass-derived syngas
  - A major contribution to meeting FY12 Joule target: $2.05/gal ethanol
- Performed detailed compositional and distillation analysis on crude mixed alcohol product
  - Undesired components like aldehydes and sulfides separate from ethanol product with the methanol recycle stream
- Demonstrated long-term stability of catalyst (>4000 h)
- Scaled catalyst synthesis from g to kg per batch with negligible impacts on catalyst performance
  - Pelletized material tested at pilot scale with biomass-derived syngas

Metal Sulfide Catalysts

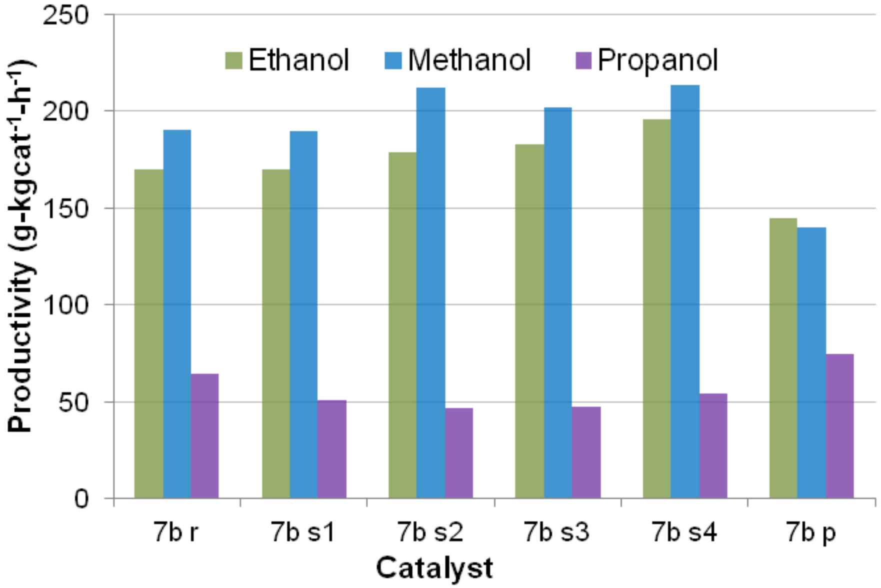
Catalyst Development

Performance



FY12 target productivity

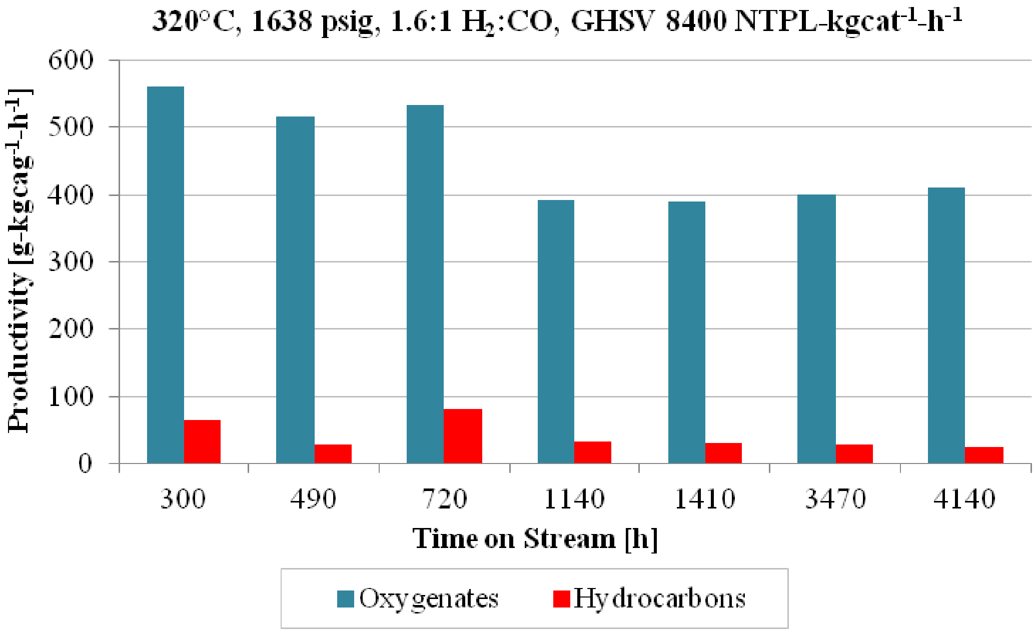
Repeatability



- **Catalyst activity more than doubled while maintaining selectivity**
- Demonstrated ethanol productivity up to 600 g/kg$_{cat}$/h, selectivity up to 55% on catalyst NREL 7B (max observed, not shown in plots above)
- Improved (simplified) synthesis procedures, and demonstrated repeatability and scalability

Metal Sulfide Catalysts

Catalyst Stability in Extended Operation

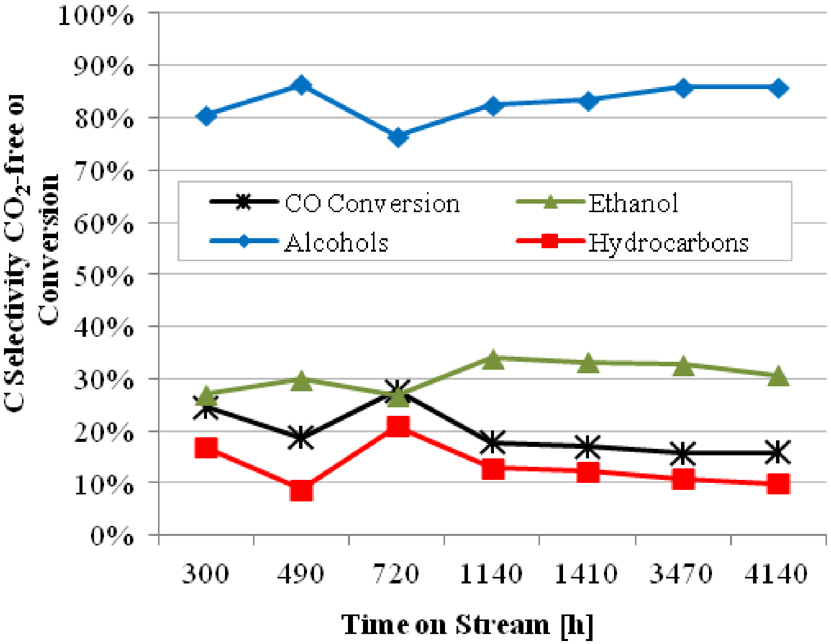


Performance at a ‘baseline’ condition

- T, space velocity similar to design case
- P lower than design case
- H_2S cofed at 100 ppm to maintain sulfide

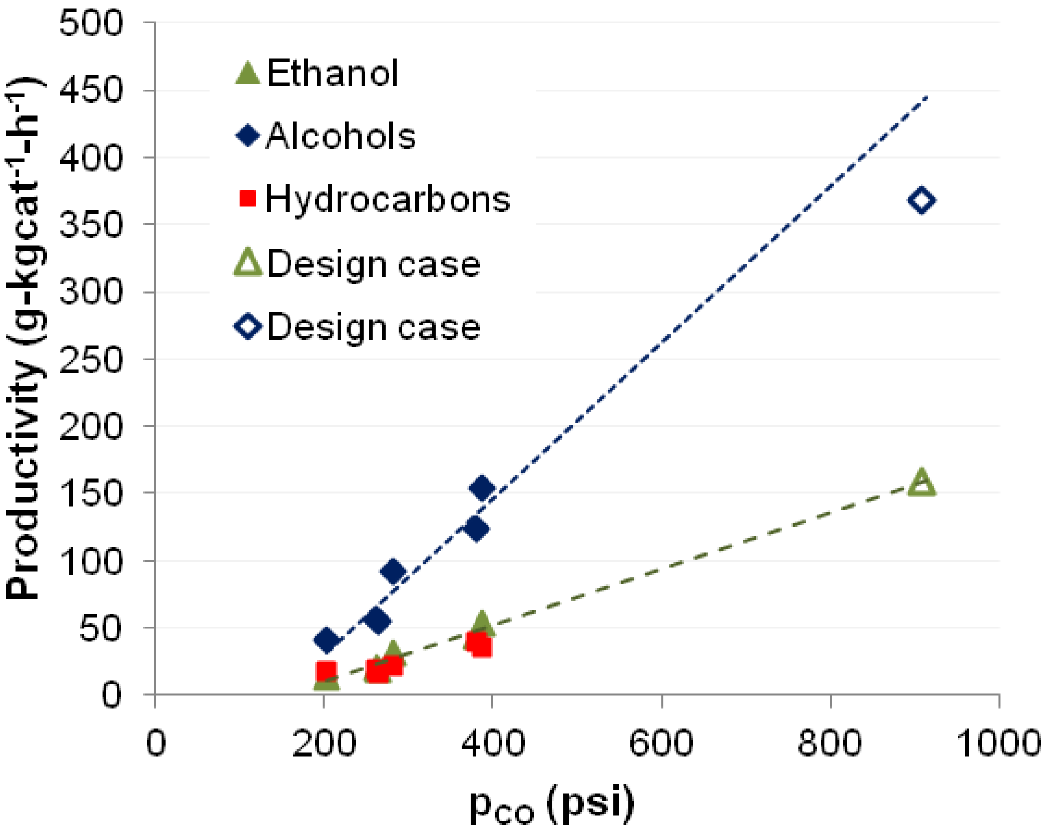
Operated >4000 h with stable performance

- Catalyst put under more ‘stress’ than with typical operation (> 180 different conditions {T, space velocity, feed gas composition} tested in between the shown ‘baseline’ data)
- Selectivity is maintained, turnovers decrease
- Turnovers can be recovered by increasing T or P



Metal Sulfide Catalysts

Pilot Scale Operation

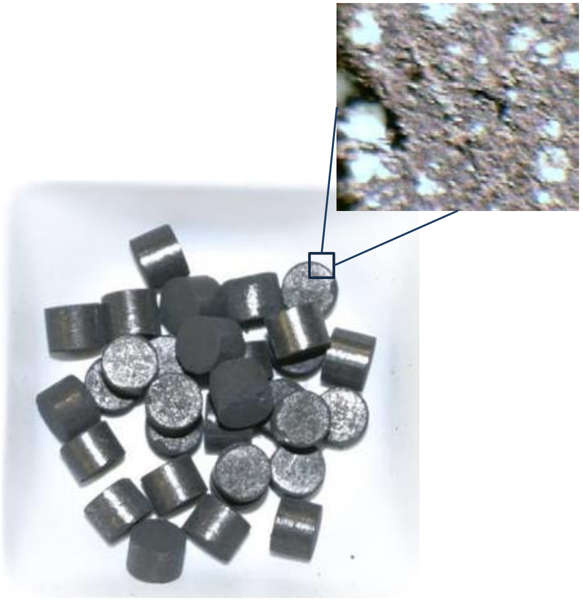


Analysis of Fresh and Discharged samples:

- Possible deposition of iron
- Loss of sulfur (consistent with bottled gas experiments and not greater than usual)
- Minimal loss of surface area

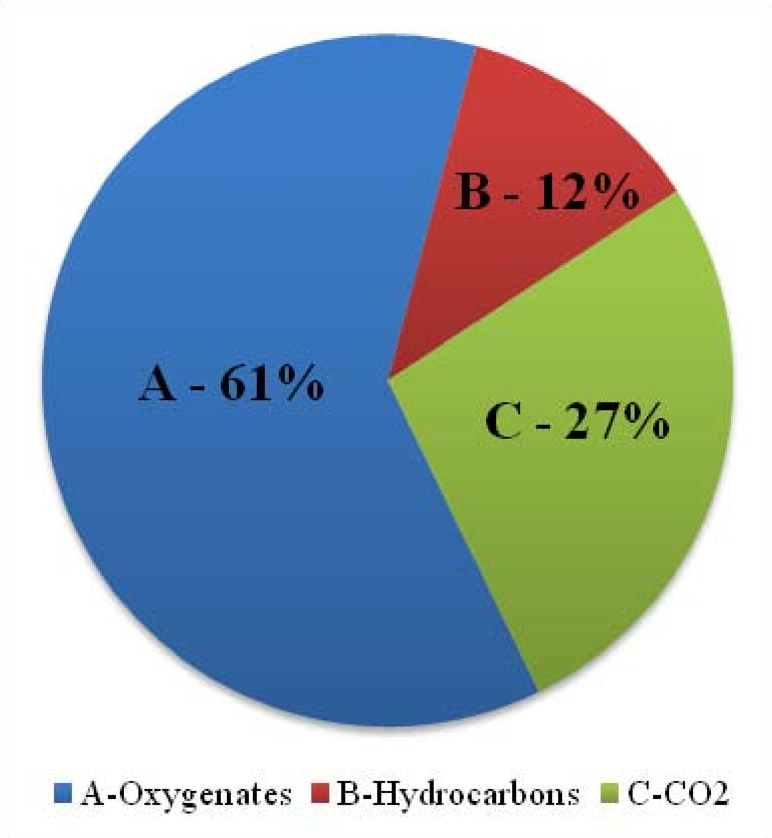
Tested catalyst pellets in a pilot-scale CSTR to max pressure (2000 psi)

- Collected data when feeding biomass and reformed methanol syngas
- Could not reach design pressure with inerts
- Performance trends toward targets

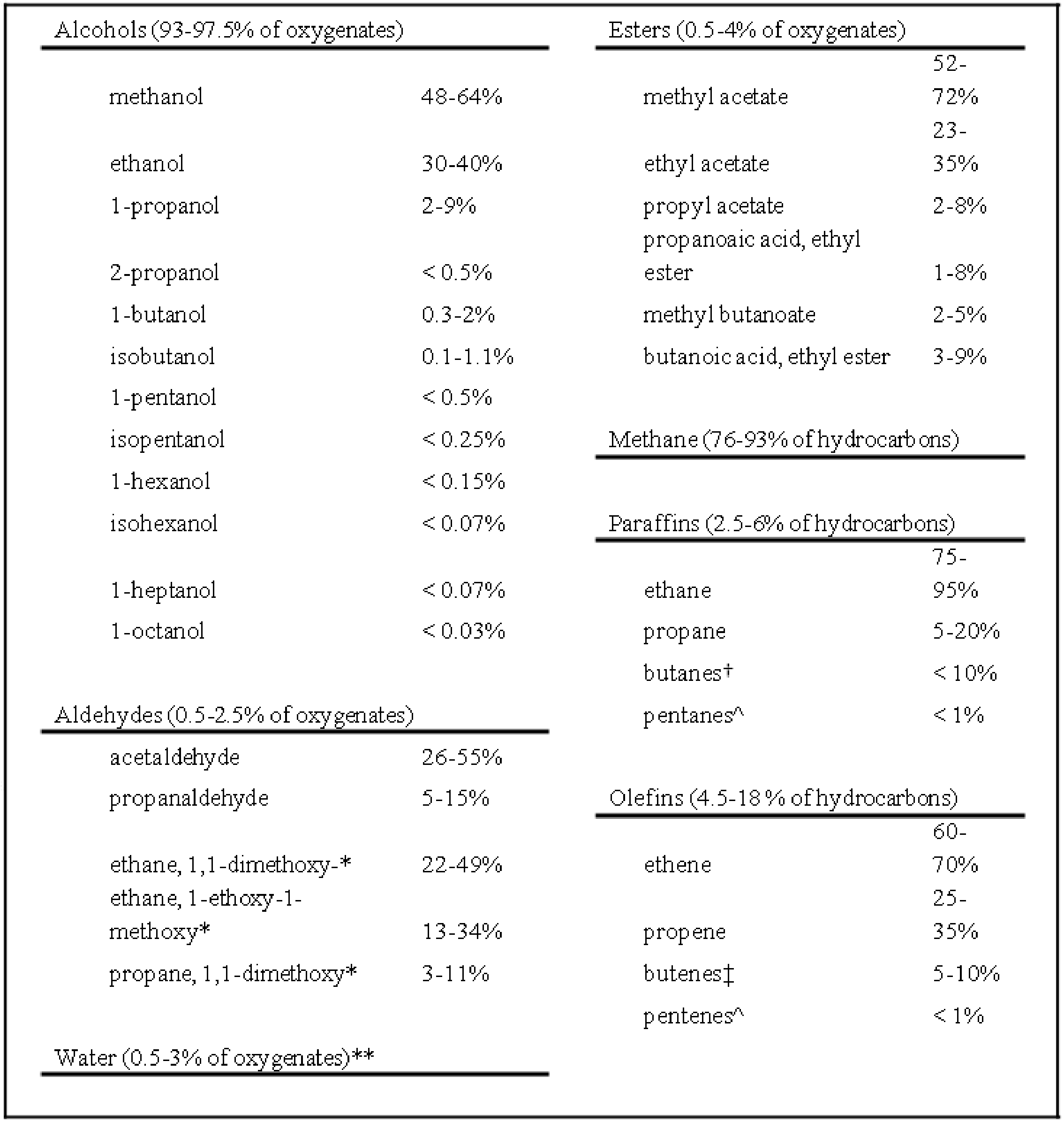


Metal Sulfide Catalysts

Detailed Product Analysis



Median composition of crude product – samples collected over broad range of operating conditions



Alcohols (93-97.5% of oxygenates)	
methanol	48-64%
ethanol	30-40%
1-propanol	2-9%
2-propanol	< 0.5%
1-butanol	0.3-2%
isobutanol	0.1-1.1%
1-pentanol	< 0.5%
isopentanol	< 0.25%
1-hexanol	< 0.15%
isohexanol	< 0.07%
1-heptanol	< 0.07%
1-octanol	< 0.03%

Aldehydes (0.5-2.5% of oxygenates)	
acetaldehyde	26-55%
propanaldehyde	5-15%
ethane, 1,1-dimethoxy-*	22-49%
ethane, 1-ethoxy-1-methoxy*	13-34%
propane, 1,1-dimethoxy*	3-11%

Water (0.5-3% of oxygenates)**

Esters (0.5-4% of oxygenates)	
methyl acetate	52-72%
ethyl acetate	23-35%
propyl acetate	2-8%
propanoaic acid, ethyl ester	1-8%
methyl butanoate	2-5%
butanoic acid, ethyl ester	3-9%

Methane (76-93% of hydrocarbons)

Paraffins (2.5-6% of hydrocarbons)	
ethane	75-95%
propane	5-20%
butanes†	< 10%
pentanes^	< 1%

Olefins (4.5-18 % of hydrocarbons)	
ethene	60-70%
propene	25-35%
butenes‡	5-10%
pentenes^	< 1%

Metal Sulfide Catalysts

Use of Other Alcohols

- Use of alcohols allows one to 'sell the O' in biomass into gasoline pool and improve overall yields
- EPA has granted waivers for Octamix (C_1-C_8 alcohols)
  - Allows sale of other alcohol products
  - Simplifies distillation and lowers operating/capital costs for fractionation
  - Lowers recycle requirements
- No change in fueling infrastructure required
- Using *sulfide catalyst* product as an example:
  - Can blend 9% (vol/vol) with gasoline after removing sulfides, water
  - Can blend 10% (vol/vol) after taking methanol concentration down to 28% (mass/mass) and removing sulfides, water

Octamix requirements:

- Fuel blend ≤ 5 vol% MeOH
- Fuel blend ≥ 2.5 vol% C_2-C_8 alcohol
- Alcohol blendstock ≥ 60 wt% C_2-C_4 alcohol
- Alcohol blendstock ≤ 5 wt% C_7-C_8 alcohol
- Fuel blend ≤ 3.7 wt% O

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."*
  - **Dual technology approach** to producing ethanol from syngas
  - Research and development **guided by technoeconomic feedback**
  - Research is **integrated with other core topic areas** including gasification and syngas cleanup and conditioning
- Project addresses two pathways:
  - M 6.12.1: Produce mixed alcohols from syngas
  - M 6.12.3: Validate integrated process at pilot scale
- Project accomplishments in FY11 and FY12 helped platform to reach its strategic goals:
  - Provided information for improved technoeconomic analysis and benchmarking of today's technology
  - Improved a combination of catalyst activity, selectivity, cost, and robustness to meet technical performance targets
  - **Demonstrated improvements in catalyst performance, scaled synthesis and operation in a pilot plant**

Success Factors

- Rhodium catalysts:
  - **Acceptable selectivity** (>70% of C to C_{2+} oxygenates) and **productivity** (nominally >600g oxygenates/L-cat/h) at operating pressures ≤ 1000 psig *ACHIEVED AT 1100 psig (CO+ H_2 PARTIAL PRESSURE) IN LONG-TERM TEST*
  - Efficient conversion (≥ 95%) of non-alcohol C_2+ oxygenates to alcohols *FUTURE WORK*
  - Acceptable catalyst lifetime (≥ 2 year) *PROBABLE*

- Sulfide catalysts:
  - **Improve activity of catalyst by 20%** to obtain higher space time yields and/or to allow operation of synthesis reactor at lower pressure *ACHIEVED*
  - Acceptable catalyst lifetime (>2 years) *PROBABLE*

Challenges

- Rhodium catalysts:
  - **Additional improvements** to catalyst performance
  - **Efficient conversion** of C_{2+} oxygenates **to higher alcohols**
  - **Maintaining performance at process scale** using commercially acceptable catalyst forms
- Sulfide catalysts:
  - Capture recent catalyst improvements in **predictive models** for commercial designs utilizing lower pressure
  - **Additional** activity and selectivity **improvements**
  - Commercial manufacture of *bulk* sulfides (synthesis scalable but not practiced industrially)
- Market and regulatory:
  - **Price of materials**: feedstock, steel, molybdenum, cobalt, rhodium, iridium, gasoline
  - Product composition: fuel grade ethanol or **Octamix**?

Future Work

This project has been successfully completed

DOE has discontinued R&D on the *Thermochemical Conversion—EtOH via Gasification of Woody Biomass to Mixed Alcohols* Platform

Suggested Future R&D Needs for this Technology:

- RhMn Based Catalyst
  - TEA of current best Rh catalyst for ETOH and mixed oxygenates to provide a basis for developing processes for downstream conversion to liquid HC fuels
  - Further improvements in catalyst performance (consistent with TEA)
  - Catalyst performance in engineered supports (pellet/ extrudate forms)
  - Post process conversion of nonalcoholic oxygenates to alcohols
  - Evaluation of catalyst in an ebbulated bed reactor configuration (heat management)

- Sulfide Based Catalyst
  - Evaluate economics and market barriers for Octamix *in lieu of* fuel-grade ethanol
  - Explore options for product recycle that lead to greater production of C_{2+} alcohols
  - Develop rigorous kinetic models to capture sulfide catalyst improvements, then evaluate TEA with operation at lower pressure
  - Sulfur maintenance and removal
  - Use of supports to increase dispersion of catalytic sites
  - Additional pilot-scale catalyst synthesis and validation of performance

Summary

- Tasks have met all milestones in FY11 and FY12 resulting in *successful project completion*
- Research expanded beyond technical targets to consider long-term catalyst stability and fuel properties
- Parallel research through the Dow CRADA has added industrial process design wisdom for better TEA (discussed separately)
- Future research should include:
  - A TEA for the current best RhMn-based catalyst
  - Further catalyst optimization where opportunities for improvement remain
  - Pilot studies with increasing scale and run time using sulfide-based catalysts
  - Evaluation of expected process configuration and scale effects on catalyst synthesis and performance for RhMn-based catalyst
  - Testing of product alcohol and gasoline blends in engines to confirm suitability as gasoline supplement
- Research has shifted to production of hydrocarbon fuels
  - Knowledge gained from this project with both catalysts is directly transferrable to catalytic hydrocarbon production and warrants further development in this context

Acknowledgements

NREL

Abhijit Dutta
Adam Bratis
Mark Davis
Josh Schaidle
Jack Ferrell
Dan Ruddy
Robert Baldwin
Kristiina Iisa
Kellen Costelow
Jason Thibodeaux
Marc Pomeroy
Mike Sprague
Whitney Jablonski
Matt Yung

Jessica Olstad
Martin Menart
Sarah Paleg
Steve Phillips
Mark Jarvis
Earl Christensen (TT)
Robert McCormick (TT)
Dave Barton (Dow)
Daniela Ferrari (Dow)
Brien Stears (Dow)
Peter Groenendijk (Dow)
Billy Bardin (Dow)
Tara Lovestead (NIST)
Tom Bruno (NIST)

TT – Transportation Technologies Group, NREL

PNNL

Jim White
Don Stevens
Alan Cooper
Heather Brown
Marie Swita
Donghai Mei
Roger Rousseau
Do Heui Kim
Becky Rummel
Chongmin Wang

Vanda Glezakou
Shawn Kathman
Theresa Lemmon
Mark Engelhard
Michel Gray
John Frye
Karl Albrecht

DOE BeTO

PURMET Development

Questions

Additional Slides

Glossary of Terms

AOP	Annual Operating Plan
BET	Brunauer-Emmett-Teller (nitrogen physisorption) surface area analysis
C_{2+}	Indicates molecules containing 2 or more carbon atoms. For example, ethanol is a C_2 alcohol, propane is a C_3 hydrocarbon, etc.
CH_4	Methane
$CoMoS_x$	Cobalt Molybdenum Sulfide catalyst
CRADA	Cooperative Research And Development Agreement
CSTR	Continuously-Stirred Tank Reactor
DMDS	Dimethyl Disulfide ($C_2H_6S_2$)
DOE	Department of Energy
EPA	Environmental Protection Agency
EtOH	Ethanol (C_2H_6O)
FT	Fischer-Tropsch - a type of catalyst that converts carbon monoxide and hydrogen into linear hydrocarbon and alcohol molecules
HC	hydrocarbons
Ir	Iridium
MAS	Mixed Alcohol Synthesis
MeOH	Methanol (CH_4O)
MESP	Minimum Ethanol Selling Price - the sale price of ethanol at which a net present value of zero is achieved for a plant with 20 year life and 10% internal rate of return
Mn	Manganese
MoS_2	Molybdenum disulfide - a material on which many metal sulfide catalysts is based
MYPP	Multi-Year Program Plan
NREL	National Renewable Energy Laboratory
P	Pressure
PMP	Project Management Plan
PNNL	Pacific Northwest National Laboratory
Rh	Rhodium
SOT	State of Technology
STY	Space Time Yield
T	Temperature
TEA	Techno-Economic Analysis - includes mechanical process design, cost and revenue estimates, and sensitivity analysis
TEM	Tranmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Detailed Milestones for FY11, FY12

Due Date	Milestone Type	Milestone Title	Comments
6/30/11	E	Demonstrate sulfide catalyst activity improvements of 15% over the 2010 SOT	Completed
8/31/11	E	Conduct long-term stability tests with RhMnIr based catalysts	Completed
9/19/11	D	Demonstrate ethanol synthesis consistent with modeled performance to achieve an MESP of $1.70/gallon	Completed (note: MESP cost basis changed after this date, value is historical)
9/30/11	D	Achieve 60% converted carbon selectivity to mixed oxygenates on RhMnIr catalyst(s)	Completed
3/31/12	D	Demonstrate mixed alcohol synthesis at the bench scale using biomass-derived syngas from the TCPDU	Completed
1/1/12	E	Begin catalyst screening tests to upgrade a mixed liquid product to gasoline/diesel feedstock	Completed
8/15/12	D	Demonstrate mixed alcohol synthesis for 200h at the pilot scale using biomass-derived syngas from the TCPDU	Completed
9/30/12	D	Achieve 70% converted carbon selectivity to mixed oxygenates on RhMnIr catalyst(s)	Completed
9/30/12	J	Demonstrate ethanol synthesis consistent with modeled performance to achieve an MESP of $2/05/gallon	Completed

path to achieving Thermochemical Conversion Strategic Goals through catalyst improvements and demonstration

Progress Since Last Review

From FY11 review: major challenges/barriers
Those addressed in FY11/12 are indicated in red

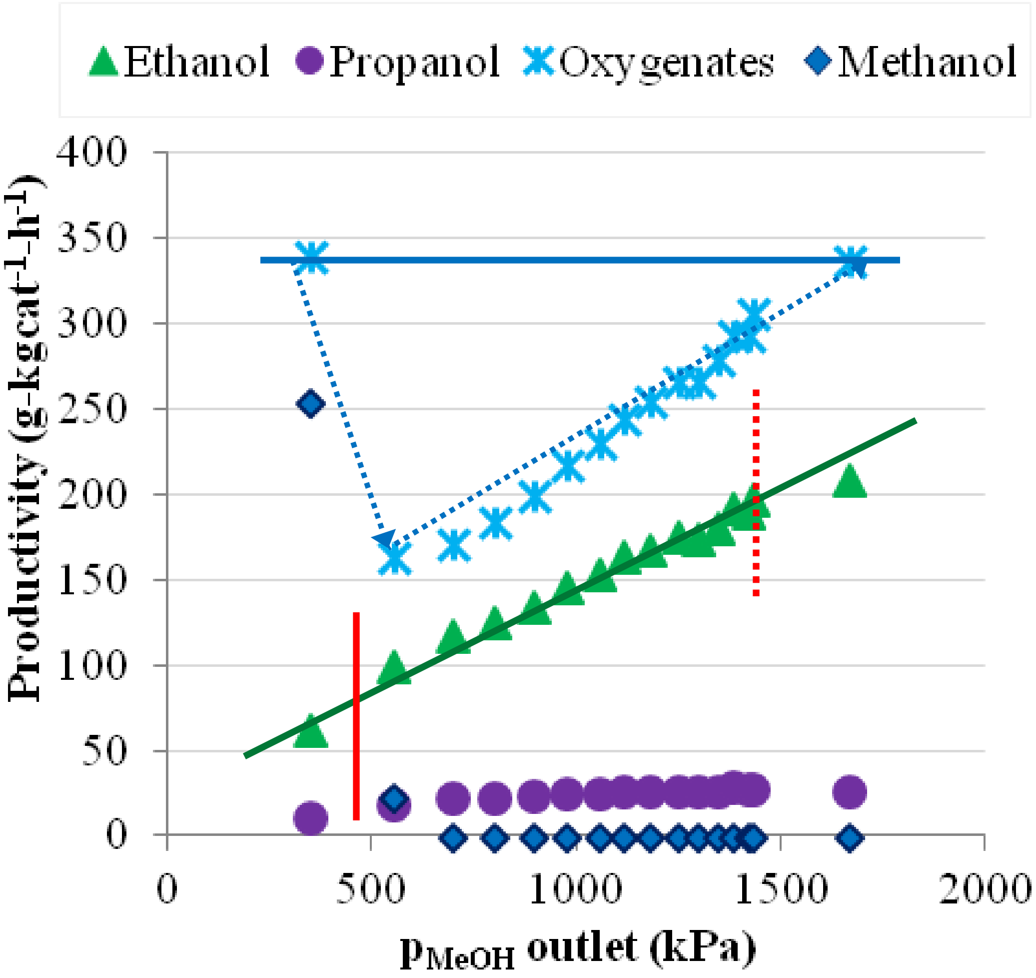
	RhMn-based	**Metal Sulfide**
Selectivity	Reduced selectivity to hydrocarbons	Improve selectivity to EtOH over MeOH
Productivity	Maintained already-high activity at higher C_2+ oxygenates selectivity	Improved total activity of catalyst
Operating costs	higher C_2+ oxygenates selectivity, improved catalyst lifetime	Improved activity at lower operating pressures, improved catalyst lifetime
Capital costs	Adapt to reactor designs that manage heat removal for active catalysts	Improved activity at lower operating pressures
Scale predictions	Kinetic and operating information for techno-economic modeling, pilot testing	Kinetic and operating information for techno-economic modeling, pilot testing

Metal Sulfide Catalysts

Byproduct Recycle

Design report and Joule design considered only partial recycle of methanol due to knowledge at the time (solid line)

There appears to be obvious upside to full recycle, more room for optimization (dotted line)



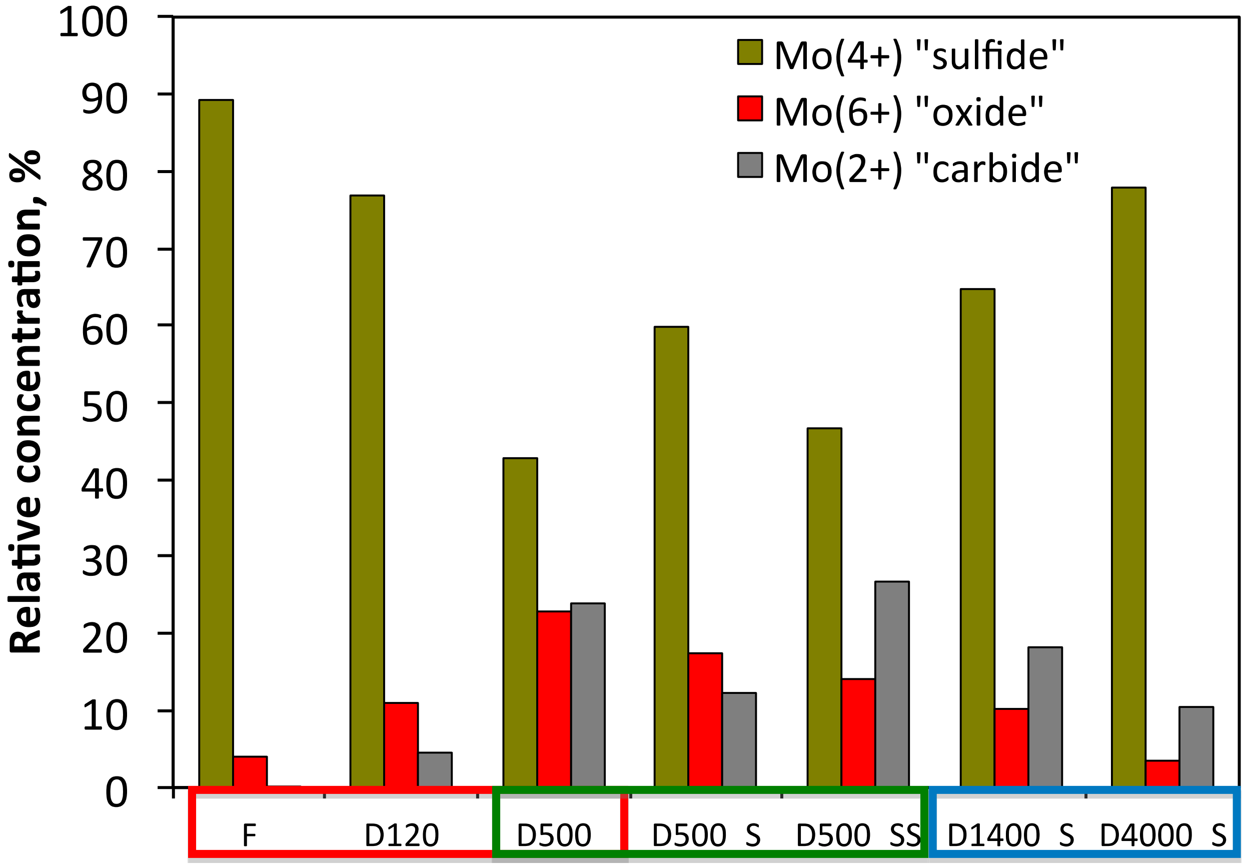
As recycle converges, total oxygenate production returns to max value, but this time without any net production of methanol

Recycling more methanol leads to more ethanol

Note: the rightmost point on the plot is the ONLY condition for which methanol would need to be produced upstream; Moving left to right, the methanol produced is recycled to the reactor inlet

Metal Sulfide Catalysts

Sulfur Maintenance—XPS Surface Analysis



S = H_2S cofeed
SS = DMDS cofeed

1. No S cofeed

- significant S loss
- oxidation observed
- increasing carburization

2. Partial S cofeeds 500 h

- increases Mo-S/Mo-O ratio
- still significant carbide

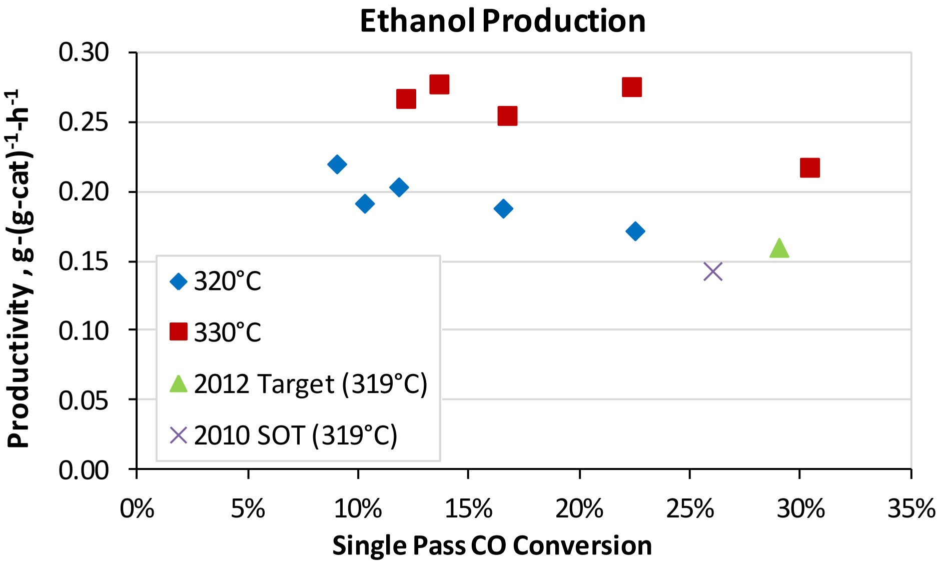
3. S cofeeds >1000 h

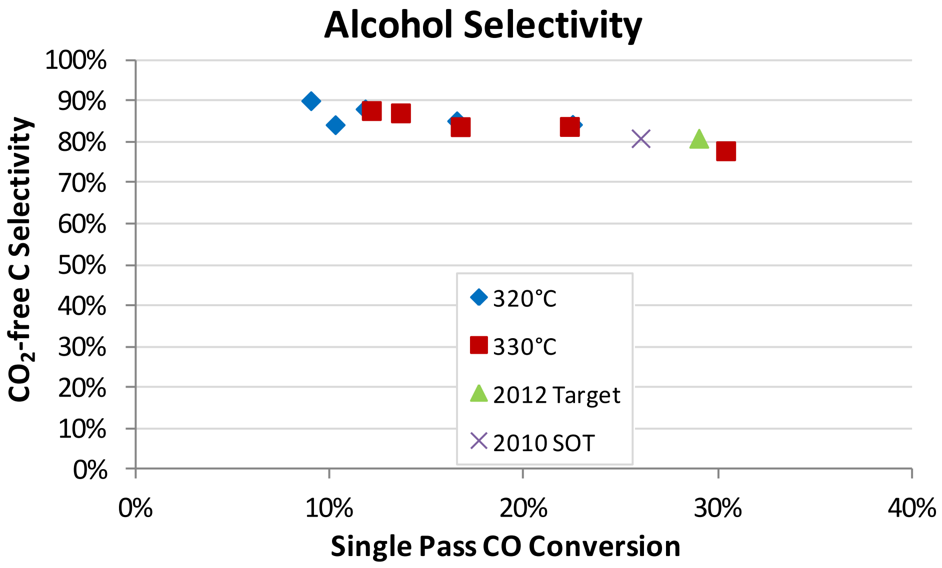
- little oxidation observed
  - resembles F for S,O
- reduction in carbide
- **continuous S feed is key**

Metal Sulfide Catalysts

Achievement of Technical Targets

- MYPP is based on model predictions with synthesis reactors operated at 3000 psi
- For safety reasons, testing capability ≤ 2000 psi
- Can mimic industrial conditions over range of operating flow rates/temperatures (*trends* are equally important to individual values)





- **At similar T, gas compositions, improved catalysts hit targets on trend**
  - **This with catalyst operated at lower than design pressure**
- **Operation at lower flow rate (= lower operating cost) extends trend to higher conversion**

Additional Required Slides for Peer Evaluation

Responses to Previous Reviewers' Comments

Comment – It would be helpful to see more information on the project management plan such as the schedule and milestones. A project management plan was not discussed.

Response – In the FY11 review, our time slot was short and our accomplishments many, so we chose to focus on those for the oral presentation. A detailed breakdown of schedule and milestones was included in the additional slides that only the reviewers received so perhaps this comment was penned during the presentation and not during independent review? For this FY13 review, we've not included milestones as the project is at 100% completion, however, we have provided a chart to show how catalyst performance improvements contribute to the achievement of $2.05 MESP (slide 8).

Comment – It appears that the project is making progress at reducing methane production and increasing ethanol selectivity, although methane production still seems pretty high. Importantly, they have also "hit" the catalysts with various contaminants to see what they do - particularly the sulfur-based catalysts (but have not done the same with the Rh catalysts).

Response – In this review, you will observe that significant progress was made in reducing hydrocarbon formation further. Because the RhMn-based catalysts have a number of challenges that continue to be addressed, we felt that it was a better use of research dollars to move toward performance targets instead of concentrating on catalyst poisoning. Further, many catalysts in use industrially are very sensitive to syngas contaminants (e.g. copper methanol synthesis catalysts), and therefore, we have reason to believe that syngas purification technologies exist for proper syngas cleanup. If this project is renewed or extended, testing the impacts of syngas contaminants is certainly prudent and will be a top priority.

Comment – Demonstrated improved catalyst performance - but hard to gauge/didn't show how this translates in progress toward cost targets.

Response – This detail was left out so as not to be redundant with the TEA task. That task explicitly shows what the impacts of catalyst improvements are to process economics. Therefore, we have focused on showing our technical targets (which feed those cost targets), as the added explanation of TEA would make the presentation very long (and it would repeat information presented the same day of the review).

Responses to Previous Reviewers' Comments

Comment – I was disappointed to learn that they have not tested with actual syngas yet.

Response – Catalysts were tested with real syngas at the pilot scale in FY12. Some details of that test is provided in this presentation.

Comment – I am still not 100% convinced that there is a pathway to hitting the needed combination of catalyst activity and selectivity. I believe this reflects more the challenge being addressed as opposed to the quality of this project.

Response – Please see the results in this review. We've hit our activity and selectivity targets with the sulfide catalysts, and actually exceeded them to the point that our predictive models under-predict the performance we see in the lab.

Comment – Solid, well managed project, just wish DOE were putting this effort into a HC rather than MA synthesis pathway.

Response – As you will probably see, there is little to no emphasis on ethanol pathways in FY13 and beyond. Starting with both syngas and pyrolysis oil, the program is pursuing routes to hydrocarbon fuels.

Publications (FY11 to Present)

- Hensley, JE; Lovestead, TM; Christensen, E; Dutta, A; Bruno, TJ; McCormick, R, **2013**, “Compositional Analysis and Advanced Distillation Curve for Mixed Alcohols Produced Via Syngas on a K-CoMoSx Catalyst” *Energy & Fuels*, accepted—DOI: 10.1021/ef400252x.
- Glezakou, VA; Jaffe, JE; Rousseau, RJ; Mei, D; Kathmann, SM; Albrecht, KO; Gray, MJ; Gerber, MA, **2012**. "The Role of Ir in Ternary Rh-Based Catalysts for Syngas Conversion to C2+ Oxygenates." *Topics in Catalysis* 55 (7-10), 595.
- Dutta, A; Talmadge, M; Hensley, J; Worley, M; Dudgeon, D; Barton, D; Groenendijk, P; Ferrari, D; Stears, B; Searcy, E; Wright, C; Hess, JR, **2012**, “Techno-Economics for Conversion of Lignocellulosic Biomass to Ethanol by Indirect Gasification and Mixed Alcohol Synthesis” *Environmental Progress & Sustainable Energy* 31 (2), 182.
- Menart, MJ; Hensley, JE; Costelow, KE, **2012**, “Thermal Decomposition of Bulk K-$CoMoS_x$ Mixed Alcohol Catalyst Precursors and Effects on Catalyst Morphology and Performance” *Applied Catalysis A-General* 437, 36.
- Dutta, A; Talmadge, M; Hensley, JE; Worley, M; Dudgeon, D; Barton, D; Groenendijk, P; Ferrari, D; Stears, B, **2011**, “Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol” *National Renewable Energy Laboratory: NREL/TP-5100-51400*; http://www.nrel.gov/docs/fy11osti/51400.pdf.
- Hensley, JE; Ferrell, JR, **2013** “Impacts of oxygenate recycle on product composition from a K-$CoMoS_x$ Catalyst” *Applied Catalysis A*, submitted for review.
- Hensley, JE; Ruddy, DR; Pylypenko, S, **2013** “Stability, Lifetime, and Deactivation of K-$CoMoS_x$ Mixed Alcohol Catalysts” *Journal of Catalysis*, to be submitted 6/13.
- Hensley, JE **2013,** “Primary Products and the Mechanisms of Mixed Alcohol and Hydrocarbon Formation on Alkali-Promoted $Co_xMo_yS_z$ Mixed Alcohol Catalysts” *Applied Catalysis A*, to be submitted 8/13.

Presentations (FY11 to Present)

- Ferrell, JR; Hensley, JE, “Mixed Alcohol Synthesis on K-CoMoSx Catalysts: Recycle Studies.” Presented by JR Ferrell at *Western States Catalysis Club annual meeting*, **April 19, 2013**, Provo UT.
- Glezakou, VA; Jaffe, JE; Rousseau, RJ; Gerber, MA; Albrecht, KO; Mei, D; Kathmann, SM, "Mixed Rh Catalysts for Converting Syngas into Alcohols: Insights drawn from atomistic simulations." Presented by VA Glezakou (Invited Speaker) at *24th Biennial ORCS Conference*, **April 19, 2012,** Annapolis, MD. [PNNL-SA-87187]
- Hensley, JE; Ruddy, DR; Schaidle, JA; Ferrell, JR; Thibodeaux, J, “Stability and Lifetime of K-CoMoS$_x$ Mixed Alcohol Catalysts.” Presented by JE Hensley at *American Chemical Society annual spring meeting*, **April 7, 2013**, New Orleans, LA.
- Gerber, MA; Gray, MJ; Albrecht, KO, "Mixed Oxygenate Synthesis: Development of a Rhodium Based Catalyst." Presented by MA Gerber and MJ Gray (Invited Speakers) at *tcbiomass2011*, **September 27, 2011**, Chicago, IL. [PNNL-SA-82757]
- Hensley, JE, “Synthesis, Use, Lifetime, and Deactivation of Sulfide Catalysts for Renewable Cellulosic Ethanol.” Presented by JE Hensley at *Colorado School of Mines, Chemistry Department Invited Speaker Series*, **January 18, 2013**, Golden, CO.
- Menart, M; Hensley JE; Costelow, K, “Thermal Decomposition of Bulk K-CoMoS$_x$ Mixed Alcohol Catalyst Precursors.” Presented by JE Hensley at *American Institute of Chemical Engineers annual meeting*, **October 28, 2012**, Pittsburgh, PA.
- Hensley, JE; Menart, M; Costelow, K; Thibodeaux, J; Yung, M, “Thermal Processing Techniques to Improve Metal Sulfide Mixed Alcohol Catalyst Performance.” Presented by JE Hensley at *American Institute of Chemical Engineers annual meeting*, **October 18, 2011**, Minneapolis, MN.
- Hensley, JE; Costelow, K; Jablonski, W; Thibodeaux J; Yung, M, “Synthesis Techniques for Improved Performance from K/Mo/Co Sulfide Mixed Alcohol Catalysts.” Presented by JE Hensley at *American Chemical Society annual meeting*, **August 29, 2011**, Denver, CO.

Reports (FY11 to Present)

- Gerber, MA; Gray, MJ; Albrecht, KO; Rummel, BL, **2012** “Optimization of Rhodium-Based Catalysts for Mixed Alcohol Synthesis -- 2011 Progress Report,” *PNNL-22078*, Pacific Northwest National Laboratory, Richland, WA.
- Hensley, JE, **2012** “Evaluation of Mixed Alcohol Catalyst Performance with Complete Byproduct Recycle,” *NBC-11138*, National Renewable Energy Laboratory, Golden, CO.
- Hensley, JE; Jablonski, WS; Bain, RL; Carpenter, DL; Smith, KJ; Gaston, KR; Magrini-Bair, KA, **2012** “Pilot Scale Fuel Synthesis Demonstration of Integrated Process,” *NBC-11118*, National Renewable Energy Laboratory, Golden, CO.
- Hensley, JE; Jablonski, WS, **2012** “Bench-Scale Fuel Synthesis Demonstration of an Integrated Biomass to Fuel Process,” *NBC-11050*, National Renewable Energy Laboratory, Golden, CO.
- Gerber, MA; Gray, MJ; Albrecht, KO; White, JF; Rummel, BL; Stevens, DJ, **2012** “Optimization of Rhodium-Based Catalysts for Mixed Alcohol Synthesis -- 2010 Progress Report,” *PNNL-22081*, Pacific Northwest National Laboratory, Richland, WA. (not released)
- Hensley, JE, **2012** “Effects of Sulfur on Catalyst Stability/Performance,” *NBC-11012*, National Renewable Energy Laboratory, Golden, CO.
- Hensley, JE, **2010** “Mixed Alcohol Catalyst Evaluation of Upper Levels of Inert Species,” *NBC-10772*, National Renewable Energy Laboratory, Golden, CO.
- Gerber, MA, Gray, MJ; Stevens, DJ; White, JF; Rummel, BL, **2010** “Optimization of Rhodium-Based Catalysts for Mixed Alcohol Synthesis -- 2009 Progress Report,” *PNNL-20115*, Pacific Northwest National Laboratory, Richland, WA. (not released)
- Hensley, JE; Dutta, A, **2011** “Demonstration of Mixed Alcohol Catalyst Technology Improvement Consistent with the 2011 SOT,” *NBC-10951*, National Renewable Energy Laboratory, Golden, CO.