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

–WBS 3.3.2.8 Dow CRADA–

21 May 2013

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Goal Statement

Project Goal – Improve the economics of ethanol production from biomass-derived syngas through collaborative testing and refinement of process designs

- **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: 2010
- Project end: 2012
- 100% complete

Barriers

- Tt-G fuels catalyst development
  - Low catalyst activity
  - Low selectivity to ethanol
- Process-driven attributes (achieve MESP ≤ $2.05/gal[*])
  - Process optimization
  - Syngas conversion
  - Pilot scale demonstration
  - Impacts of syngas components

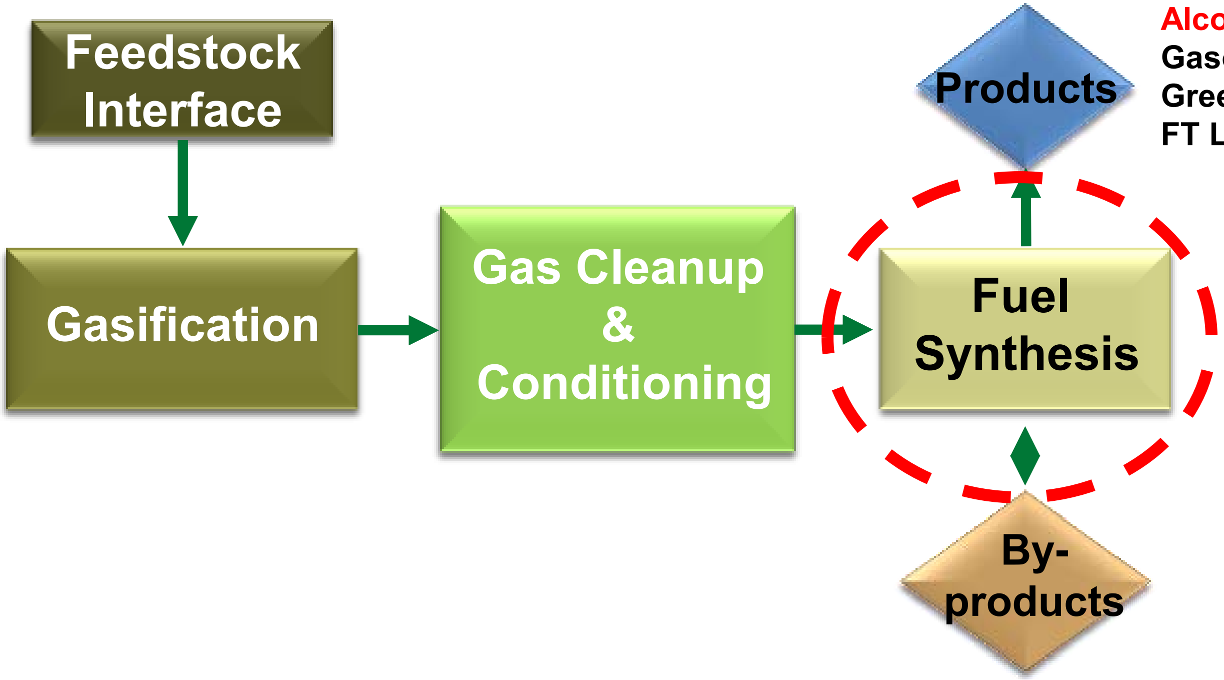
Budget

- Total project funding $1.5 M (DOE)
- FY11 funding $320 k
- FY12 funding $530 k

Partners

- NREL
- The Dow Chemical Company

Overview: Biomass Gasification for Fuels



Feedstock Interface

Gasification

Gas Cleanup & Conditioning

Fuel Synthesis

Products

By-products

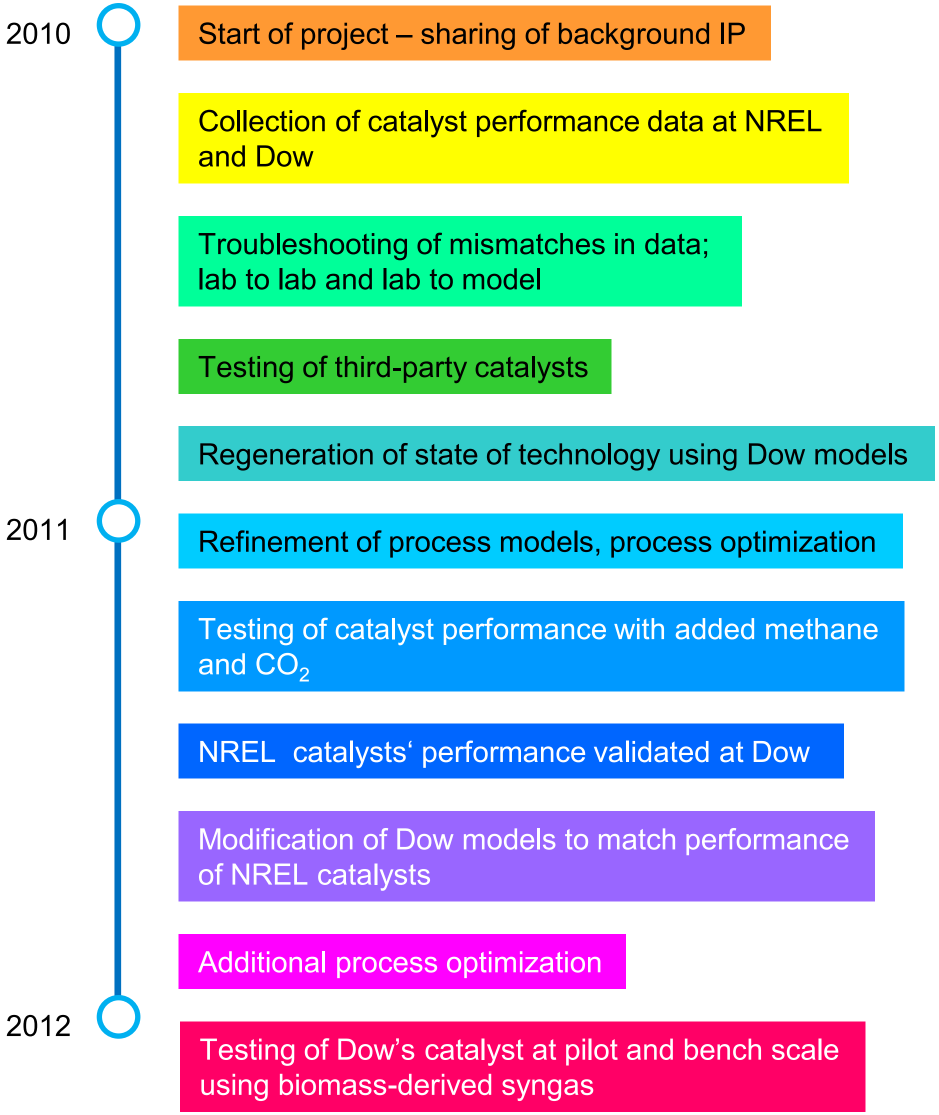
Alcohols
Gasoline
Green Diesel
FT Liquids

More robust catalysts
Higher catalyst yields

Overview: Project Objectives & Timeline

Objectives

- **Improve the economics** of a biomass syngas to mixed alcohol processes
- **Validate catalyst performance** in a variety of reactors at different scales
- **Expand working knowledge** of sulfide catalyst properties and operating ranges
- **Model** catalyst performance



2010

Start of project – sharing of background IP

Collection of catalyst performance data at NREL and Dow

Troubleshooting of mismatches in data; lab to lab and lab to model

Testing of third-party catalysts

Regeneration of state of technology using Dow models

2011

Refinement of process models, process optimization

Testing of catalyst performance with added methane and CO_2

NREL catalysts‘ performance validated at Dow

Modification of Dow models to match performance of NREL catalysts

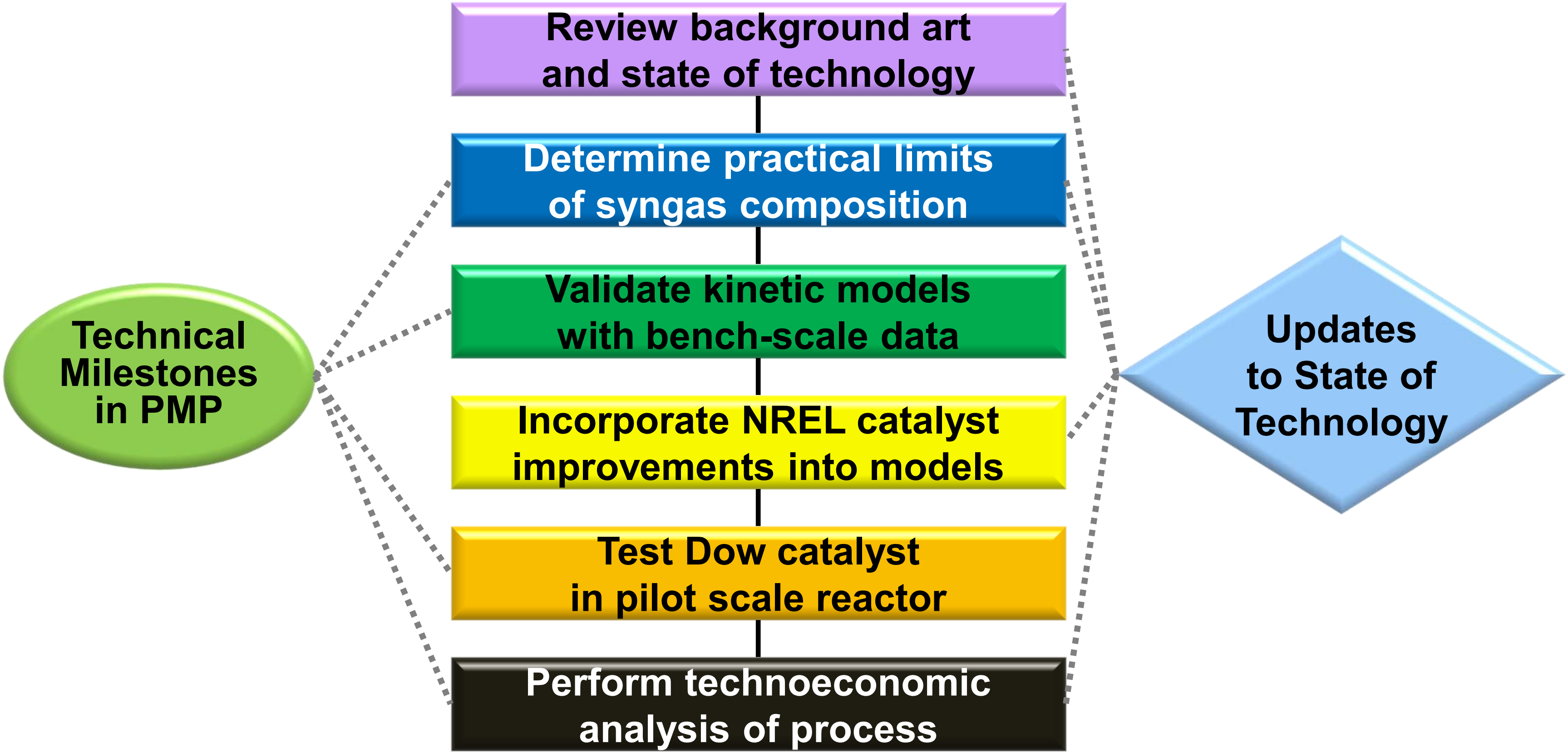
Additional process optimization

2012

Testing of Dow’s catalyst at pilot and bench scale using biomass-derived syngas

Approach

Research driven by CRADA Statement of Work



Technical Milestones in PMP

Review background art and state of technology

Determine practical limits of syngas composition

Validate kinetic models with bench-scale data

Incorporate NREL catalyst improvements into models

Test Dow catalyst in pilot scale reactor

Perform technoeconomic analysis of process

Updates to State of Technology

Technical Approach: Integrate experimentation and technoeconomic evaluation

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

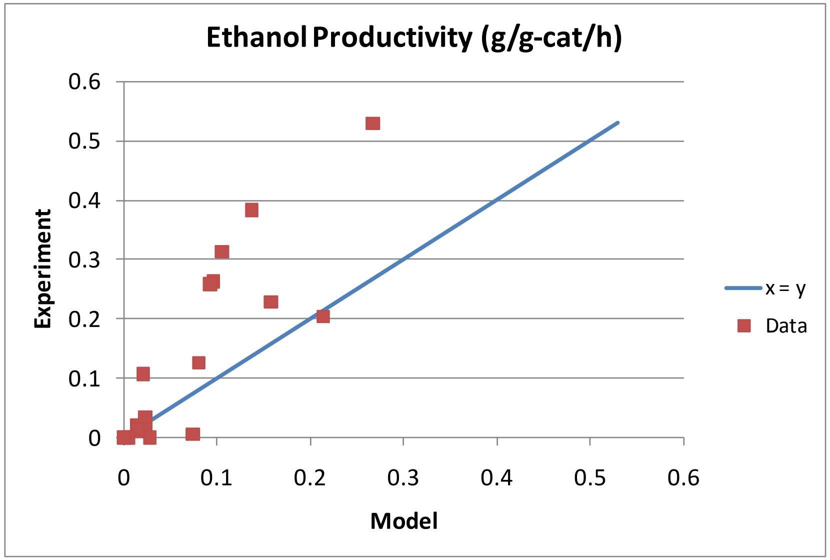
CRADA Partners and Roles

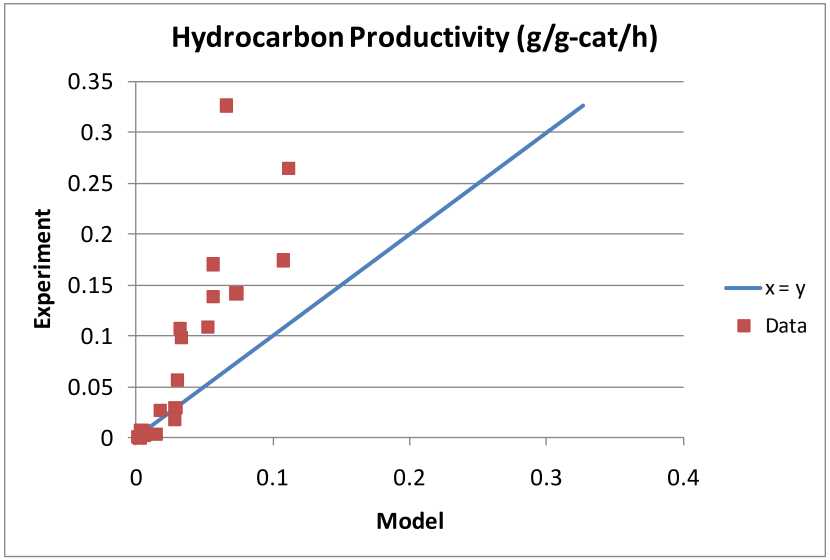
- The Dow Chemical Company
  - Developed and provided catalyst materials
  - Advised in experimental design
  - Provided use of kinetic models and guidance in their implementation and interpretation

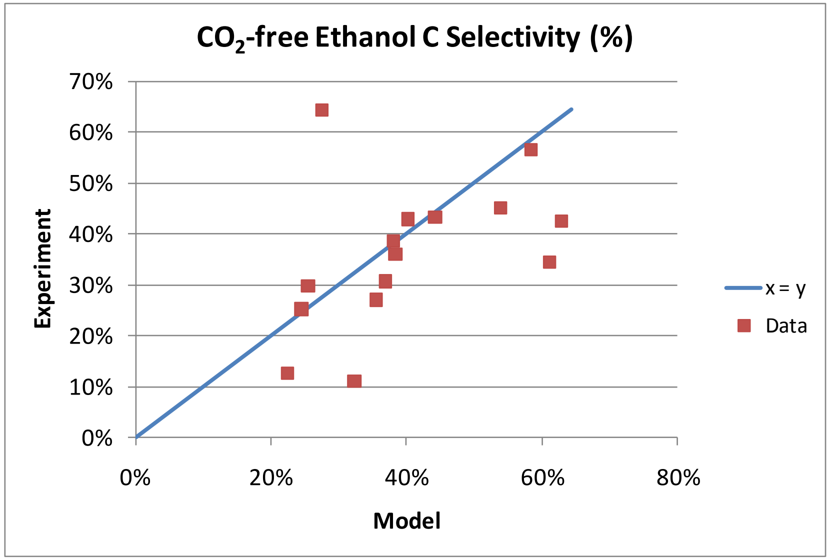
- The National Renewable Energy Laboratory
  - Performed bench- and pilot-scale reactor testing
  - Advised in experimental design
  - Data analysis and interpretation
  - Technoeconomics

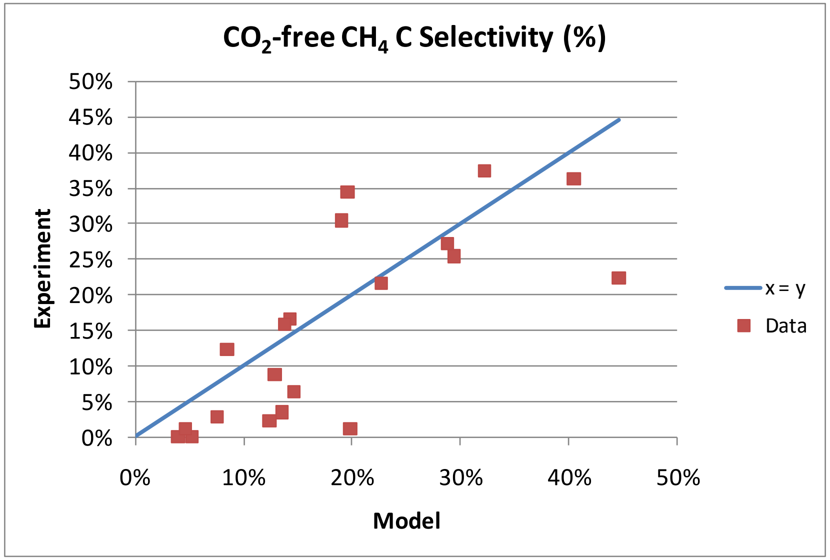
Kinetic Modeling

Validation of Model with Laboratory Data


Ethanol Productivity (g/g-cat/h)


Hydrocarbon Productivity (g/g-cat/h)

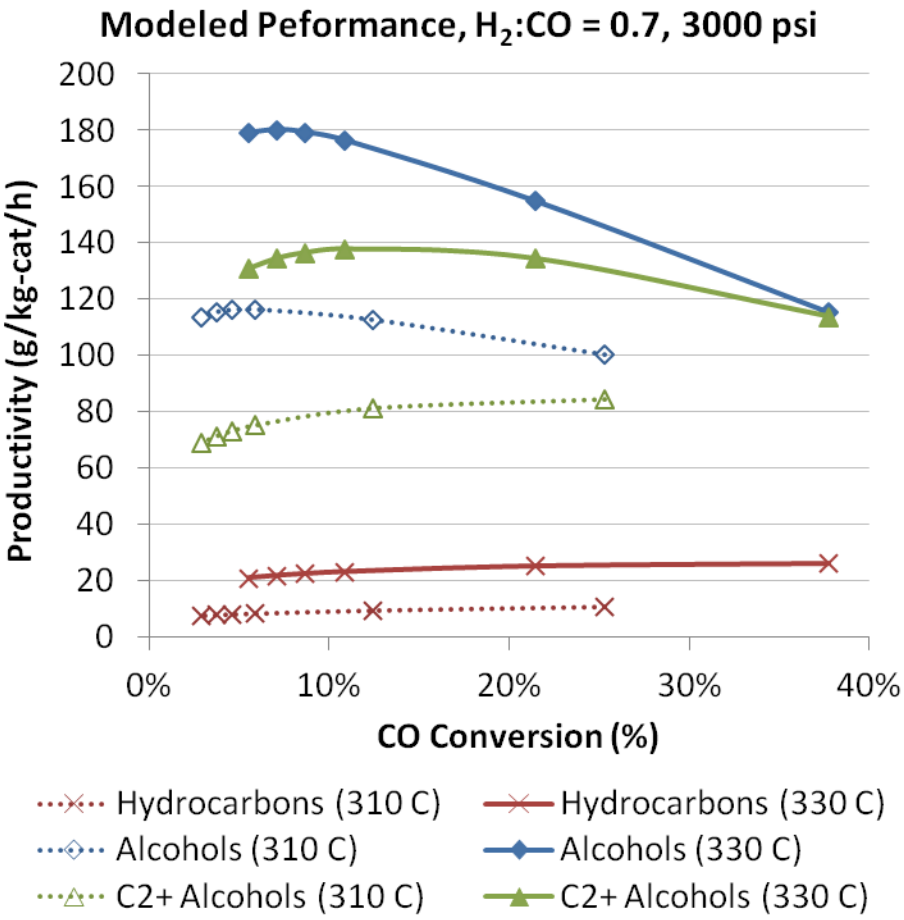

CO$_2$-free Ethanol C Selectivity (%)

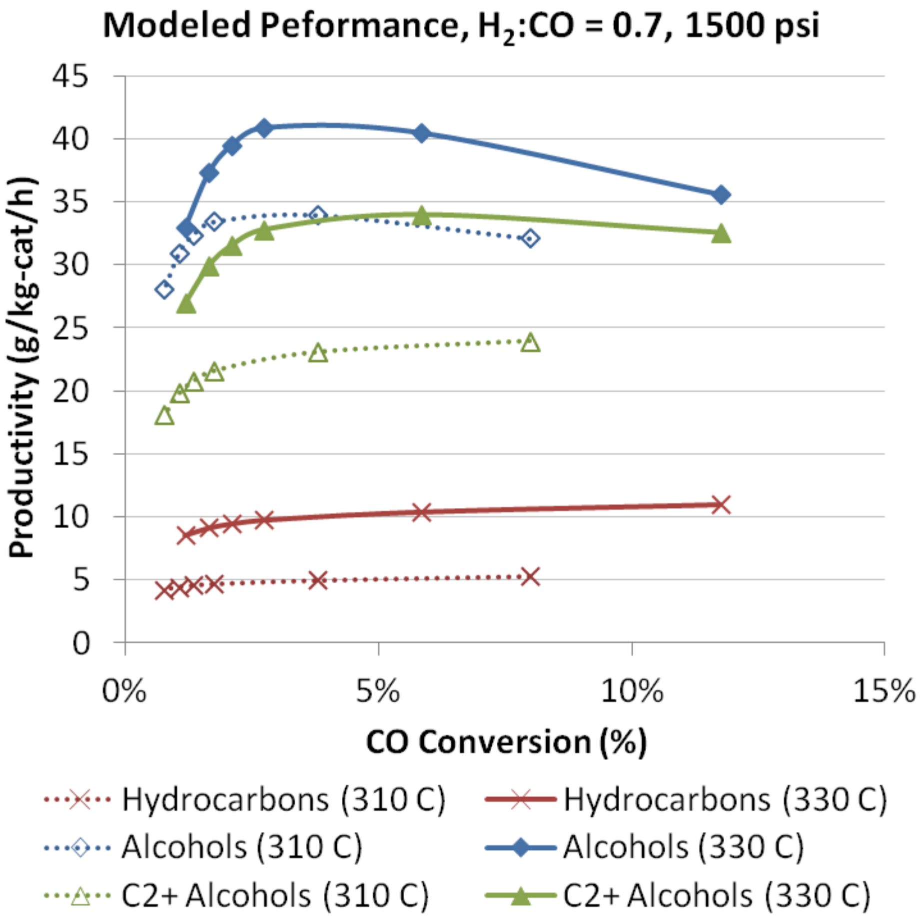

CO$_2$-free CH$_4$ C Selectivity (%)

Original model matched selectivity, under-predicted activity of newer Dow catalysts

Kinetic Modeling

Using Model to Inform Process Design

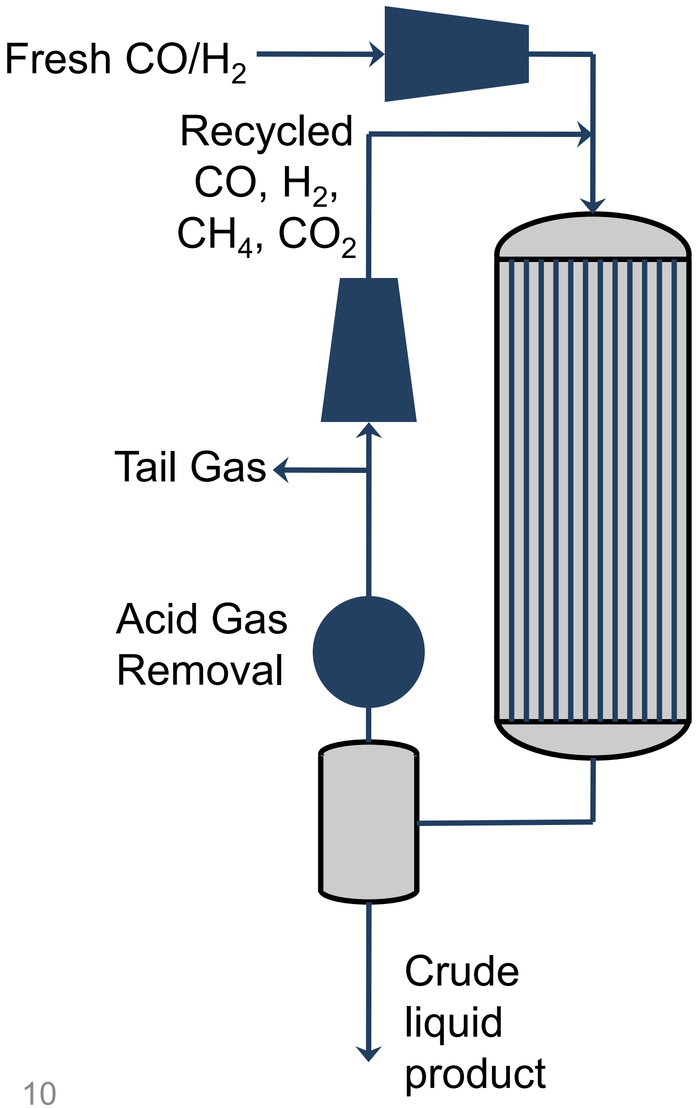




Use of model predictions guided selection of operating T, P, per-pass conversion, desired syngas composition, etc, informing design of upstream processes as well

Kinetic Modeling

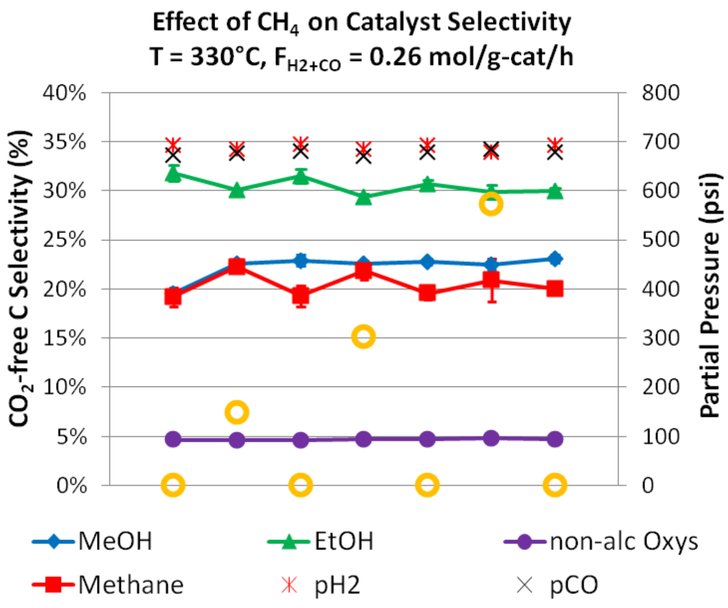
Reactor Design and Acid Gas Removal



- Original design considered acid gas (CO_2) removal from fresh syngas at low pressure
- Kinetic model coupled with process design showed advantages in moving acid gas removal to recycle loop (shown here):
  - Better catalyst productivity (less CO_2 diluting reactant stream)
  - Higher efficiencies in high-pressure Selexol™ CO_2 removal
  - Reduced reactor volume, lower capital cost
  - Advantageous use of native H_2S in fresh biomass syngas
  - Smaller purge of tail gas, higher yield
- Robust evaluation of this option possible through combined expertise and resources at NREL and Dow

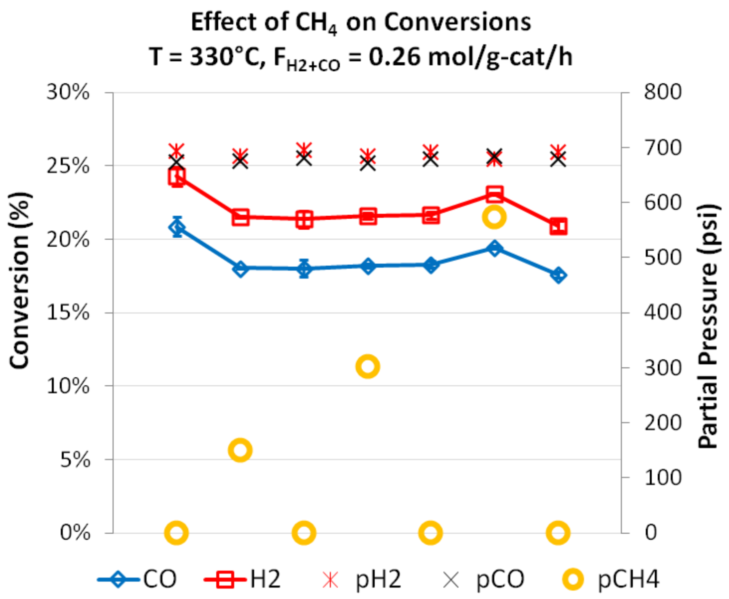
Process Development

Impacts of Other Major Syngas Components

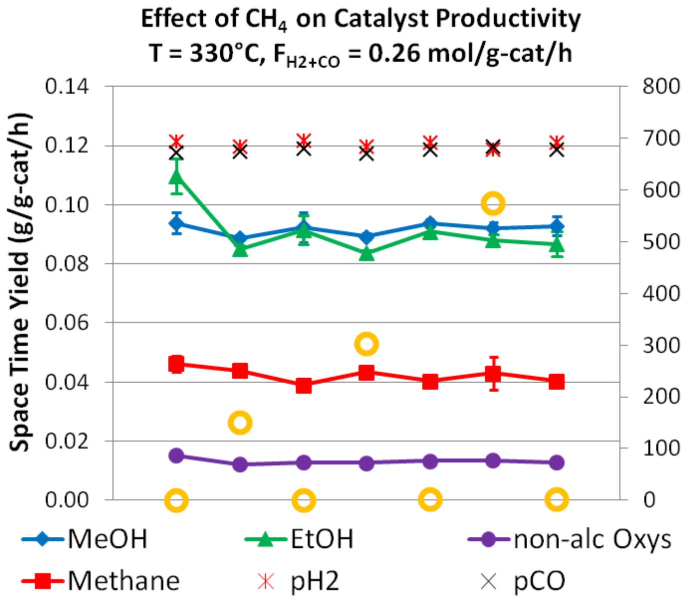


Effect of CH_4 on Catalyst Selectivity
T = 330°C, F_{H2+CO} = 0.26 mol/g-cat/h

- Selectivity and productivity unchanged when methane added to feed (tested to 30% CH_4)
- Thus: CH_4 is an inert diluent on metal sulfides



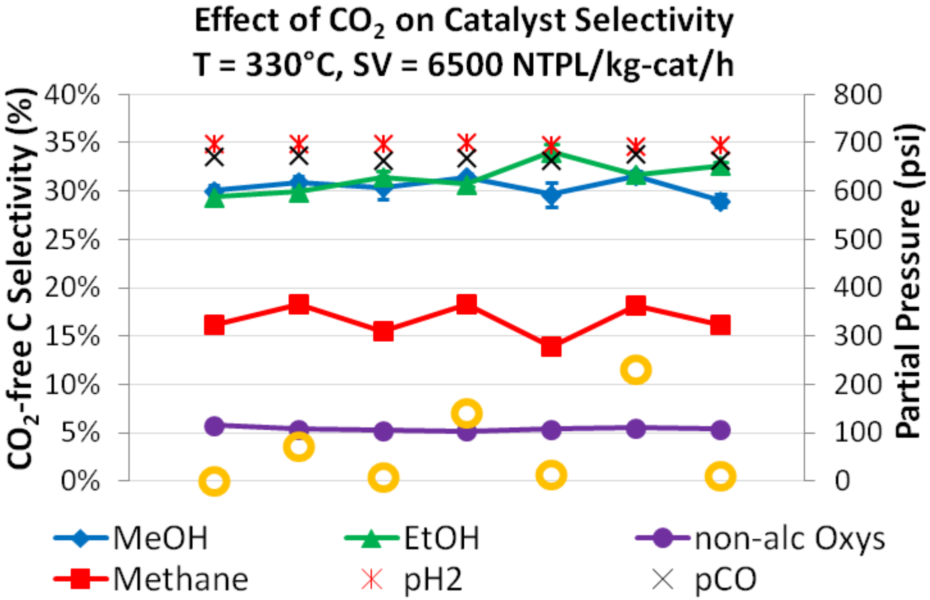
Effect of CH_4 on Conversions
T = 330°C, F_{H2+CO} = 0.26 mol/g-cat/h



Effect of CH_4 on Catalyst Productivity
T = 330°C, F_{H2+CO} = 0.26 mol/g-cat/h

Process Development

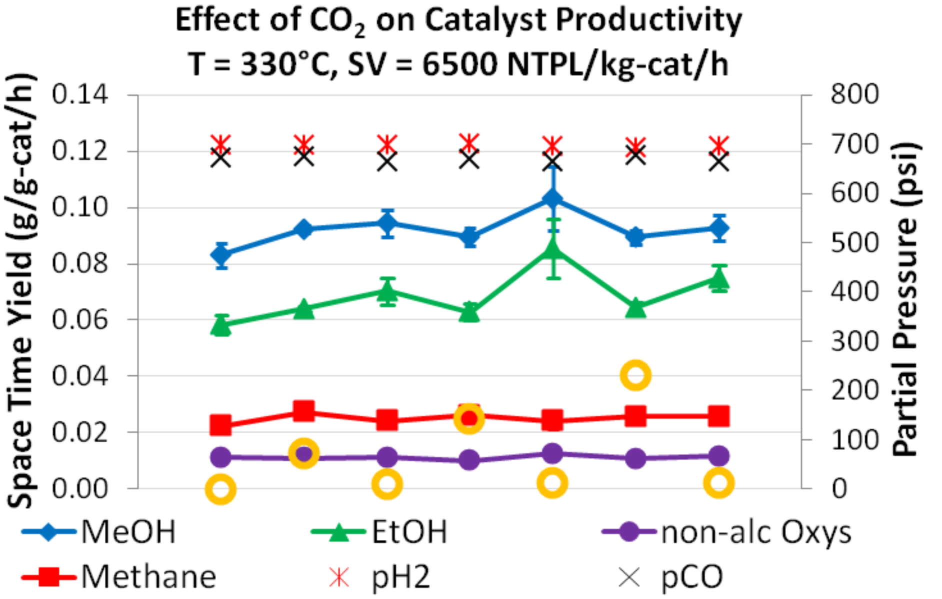
Impacts of Other Major Syngas Components



Effect of CO_2 on Catalyst Selectivity
T = 330°C, SV = 6500 NTPL/kg-cat/h

- Selectivity unchanged with CO_2 in feed up to 15%
- Additional water made via reverse water gas shift
  - May oxidize catalyst
  - Excessive buildup of CO_2 should be avoided (observed odd behavior at CO_2 > 20%)

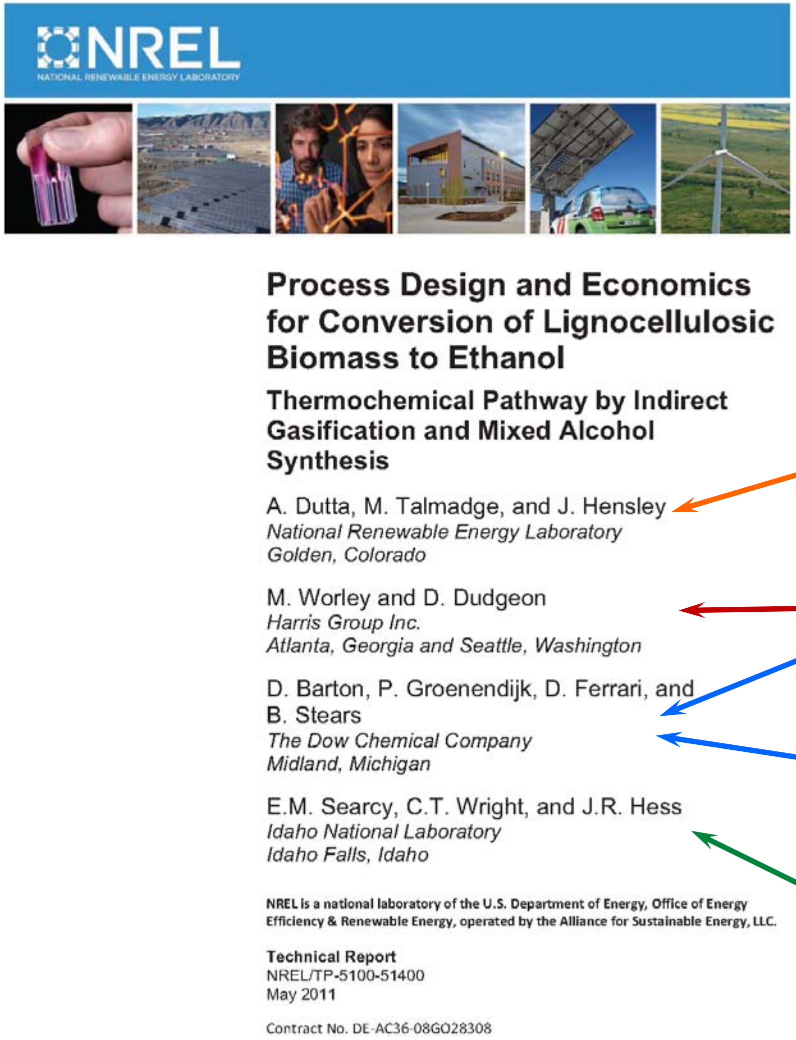
- Catalyst productivity essentially unchanged with CO_2 in feed



Effect of CO_2 on Catalyst Productivity
T = 330°C, SV = 6500 NTPL/kg-cat/h

Process Development

Industry-Informed Process Design



NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol

Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis

A. Dutta, M. Talmadge, and J. Hensley
National Renewable Energy Laboratory
Golden, Colorado

M. Worley and D. Dudgeon
Harris Group Inc.
Atlanta, Georgia and Seattle, Washington

D. Barton, P. Groenendijk, D. Ferrari, and B. Stears
The Dow Chemical Company
Midland, Michigan

E.M. Searcy, C.T. Wright, and J.R. Hess
Idaho National Laboratory
Idaho Falls, Idaho

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5100-51400
May 2011

Contract No. DE-AC36-08GO28308

Above analysis and improvements to model parity allowed rigorous design of a biomass to ethanol process

Adjustments to model scale factors showed that BeTO technical targets were achievable by increasing catalyst productivity by 20% (See Advanced Thermochemical Biofuels, W.B.S. 3.3.2.1)

Biomass gasification, reforming, design from NREL

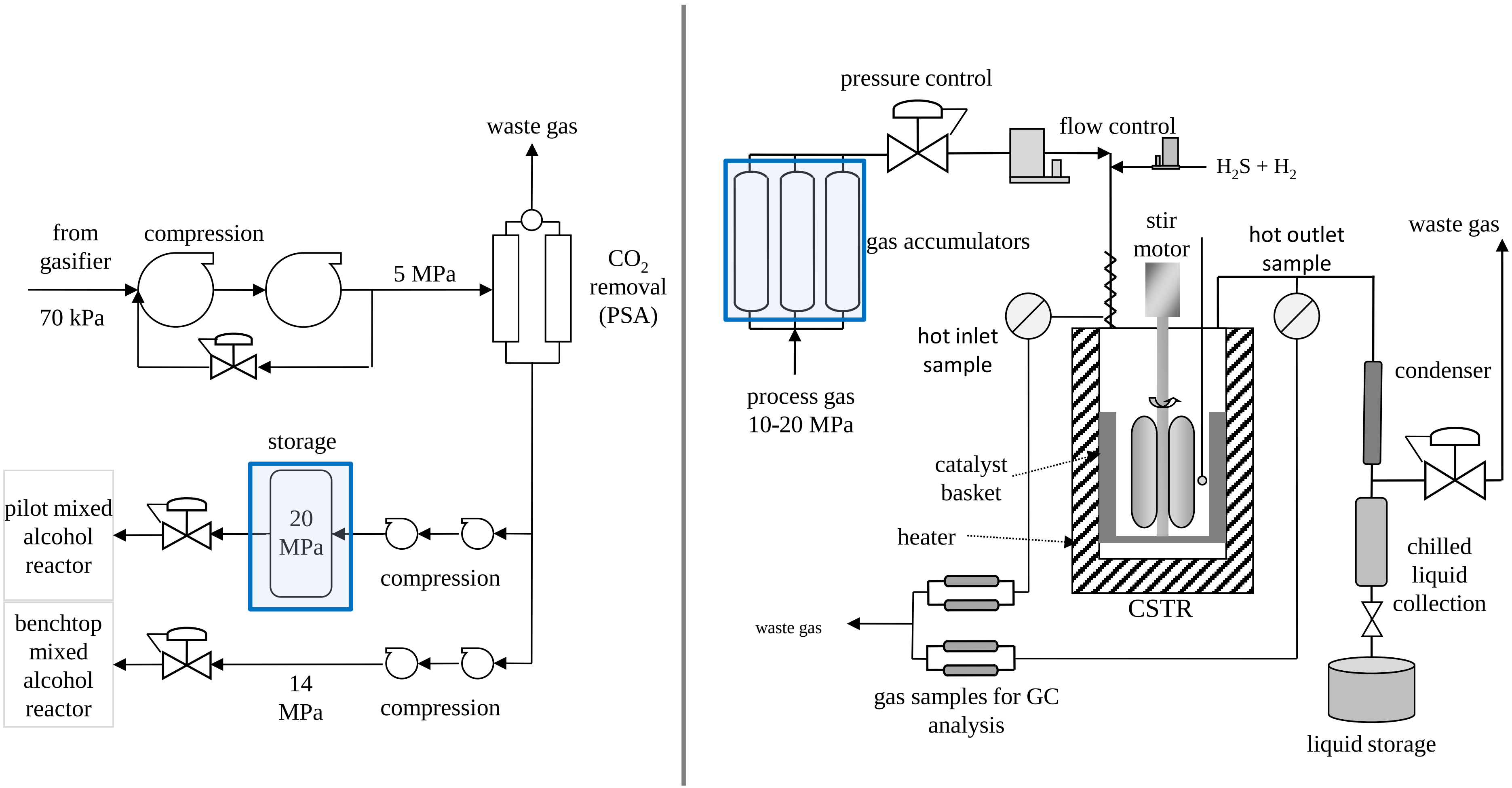
Review and critical input on process design from industry

Mixed alcohol process kinetic model from Dow

Feedstock handling and costs from INL

Performance Validation

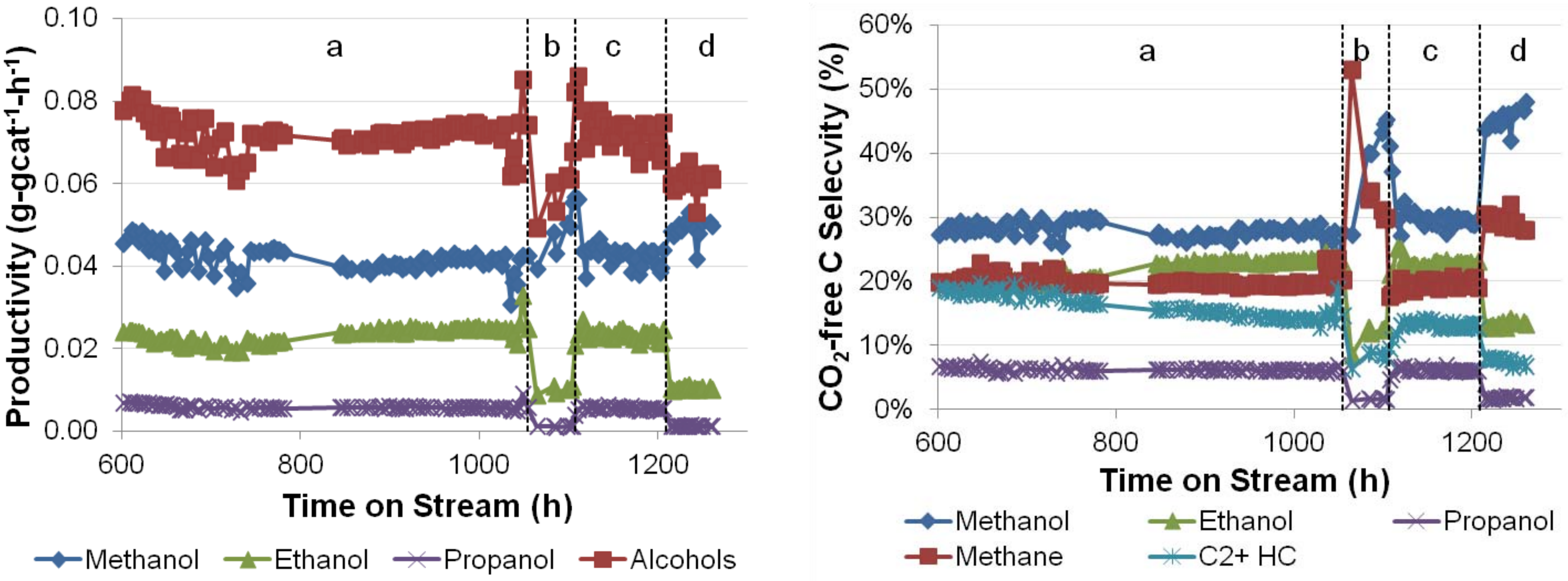
Integrated Operation in Biomass-Derived Syngas



Pilot Scale Gasification and Tar Reforming (not shown) integrated with acid gas removal, compression, and fuel synthesis (above)

Performance Validation

Bench Operation in Biomass-Derived Syngas



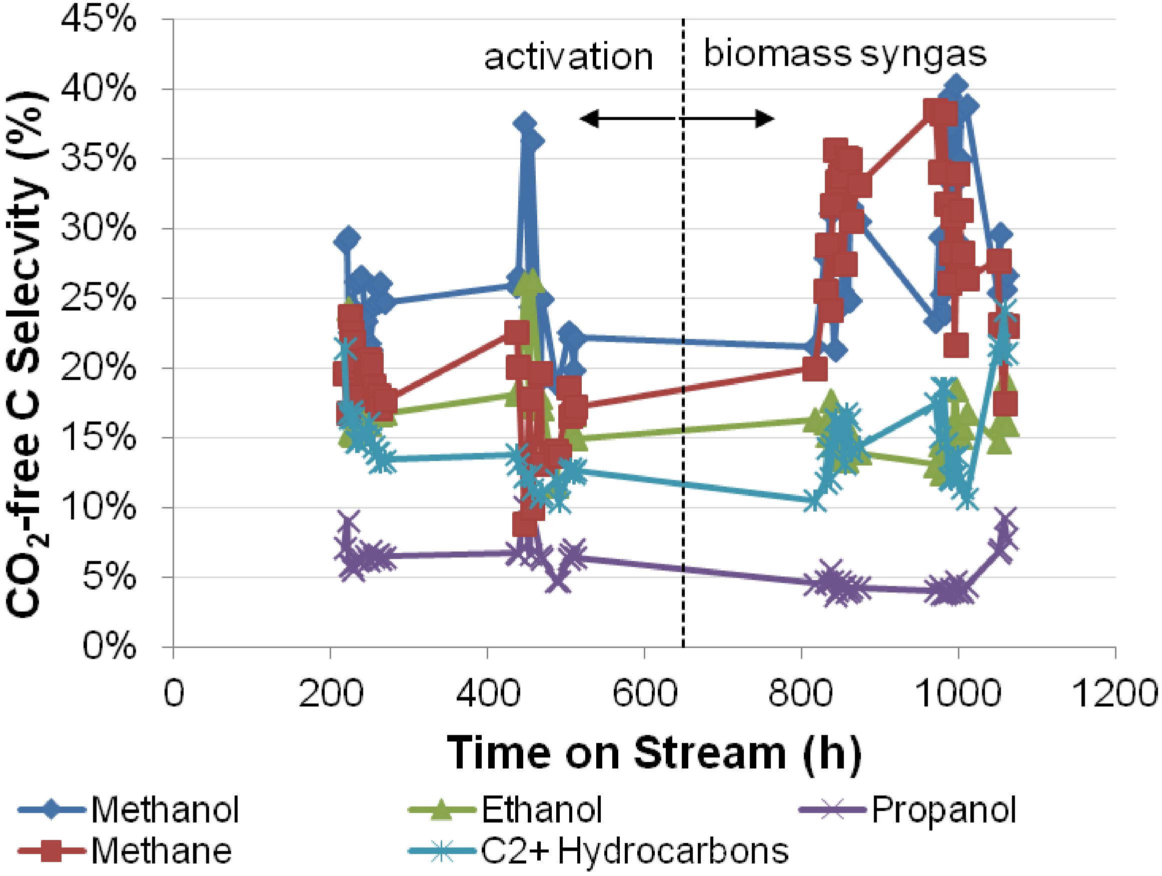
a,c – bottled syngas, 1.2:1 H_2:CO; **b,d** – biomass syngas 8:1 H_2:CO, 20% CO_2

- Observed large drop in productivity when feeding biomass syngas
- Due to differences in syngas composition (H_2:CO ratio, high CO_2), impossible to distinguish between effects of feed composition or something specific to ‘biomass’ syngas
- Based on model predictions, suggest that large increase in CH_4, MeOH selectivity due to high H_2:CO ratio and low productivity due to low partial pressures of H_2 and CO especially.
- Catalyst performance recovered when returned to bottled syngas (no evidence of rapid deactivation)

Performance Validation

Pilot Operation in Biomass-Derived Syngas

- Catalyst showed similar performance in activation gas and biomass-derived syngas
  - Higher H_2:CO in biomass syngas leading to increase in CH_4 selectivity
- Selectivity consistent over 1000 h in operation



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.”*
  - **Industry/government collaboration** to improve biomass to ethanol processes
  - Research and development **validated concurrently at partners’ facilities**
  - 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 **valuable information and insights for improved technoeconomic analysis** and benchmarking of today’s technology
  - Informed process models with industry know-how and experience
  - **Demonstrated catalyst operation integrated with a biomass gasification pilot plant**

Success Factors

- Technoeconomic Analysis:
  - **Improve predictive capabilities of process models** to obtain more robust TEA predictions *ACHIEVED*
  - Define a path to cost-competitive ethanol via mixed alcohol catalyst improvements *ACHIEVED*

- Performance Validation:
  - **Achieve reasonable parity** between kinetic models and laboratory data *GOOD AGREEMENT WITH SELECTIVITY, CONSERVATIVE IN ESTIMATES OF ALCOHOL PRODUCTION*
  - Demonstrate ability of mixed alcohol catalyst to operate in biomass-derived syngas *ACHIEVED*
  - Suggest practical limits to CH_4 and CO_2 in syngas *ACHIEVED*

Challenges

- Kinetics and Validation:
  - Incorporate formation of minor species (esters, aldehydes) into kinetic models
  - Model performance at **lower pressures** with **high recycle rates of methanol** (proved difficult in this work)
  - Model validation of pilot data (high H_2:CO feeds)
- Catalyst testing:
  - Long periods of operation in biomass syngas
  - **Pilot-scale** generation of large volumes of biomass syngas with **low H_2:CO**
  - Integrated high pressure acid gas removal at pilot scale
- Market and regulatory:
  - **Price of materials**: feedstock, steel, molybdenum, cobalt, gasoline, ethanol
  - Product purity requirements: fuel or chemical use?

Future Work

This CRADA was successfully executed

If additional CRADA funds become available the following research and development is warranted:

- **Greater depth of pilot scale testing**
  - Operation in a tubular packed bed reactor
  - Experiments with real, not simulated, product and reactant recycle
  - Evaluation of performance in biomass syngas with different compositions
  - Longer periods of pilot performance testing
- **Additional Model Validation**
  - Improved matching of NREL catalyst performance in Dow kinetic model
  - Better agreement with results of methanol recycle

Summary

- All line items in the CRADA statement of work were completed, resulting in a *successful project*
- The Dow/NREL collaboration **was a major contributing factor to achievement of FY12 MESP targets**
  - *Industrial insights* into process design, sensitivity analysis, and validation were invaluable to NREL
  - Access to advanced predictive tools (from Dow) was essential for generating robust and defendable MESP predictions
- Dow mixed alcohol catalysts were successfully operated in biomass-derived syngas and showed no signs of deactivation as a result
- Future research in this area should include:
  - Pilot studies with increasing scale and run time with lower H_2:CO syngas in packed bed reactors
  - Additional updates and improvements to predictive models, informed by bench- and pilot-scale data
  - Reactor operation with fully-integrated recycle

Acknowledgements

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Whitney Jablonski
Jessica Olstad
Steve Phillips
Mark Jarvis
Dave Barton (Dow)
Daniela Ferrari (Dow)
Brien Stears (Dow)
Peter Groenendijk (Dow)
Billy Bardin (Dow)

DOE BeTO agreement #10841

Questions

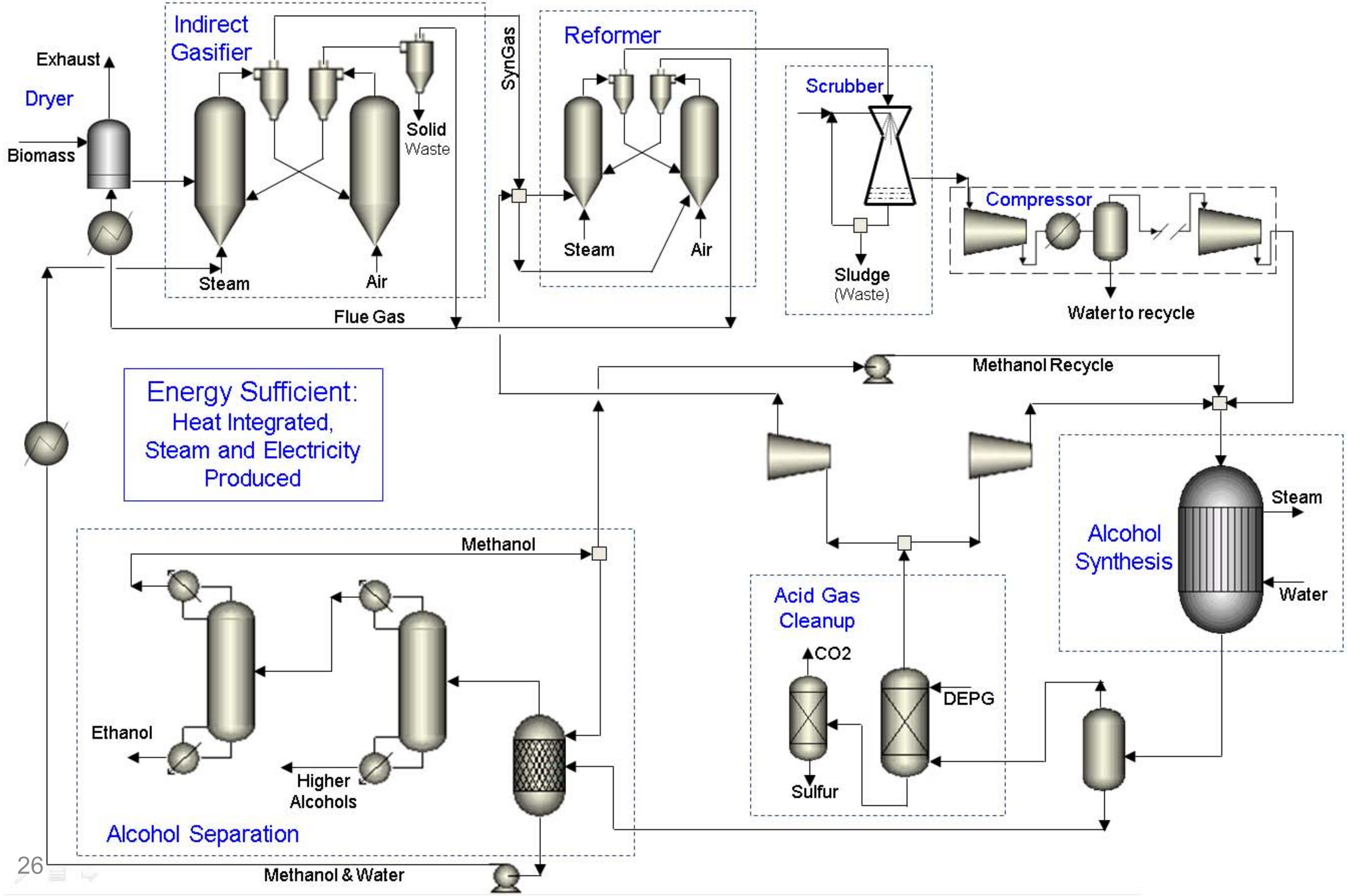
Additional Slides

Glossary of Terms

BeTO	Bioenergy Technology Office
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.
CRADA	Cooperative Research And Development Agreement
CSTR	Continuously-Stirred Tank Reactor
DOE	Department of Energy
INL	Idaho National Laboratory
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
NREL	National Renewable Energy Laboratory
P	Pressure
PMP	Project Management Plan
T	Temperature
TEA	Techno-Economic Analysis - includes mechanical process design, cost and revenue estimates, and sensitivity analysis

Process Development

Improved Process Design After Discussion with Dow Engineers



Energy Sufficient:
Heat Integrated,
Steam and Electricity
Produced

Additional Required Slides for Peer Evaluation

Responses to Previous Reviewers’ Comments

Not Applicable—this project was reviewed as a part of the Advanced Thermochemical Biofuels (W.B.S. 3.2.2.1) project in 2011. No questions or concerns were raised with respect to joint work with Dow.

Publications, Presentations, Reports
(FY11 to Present)

Publications

- 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.
- 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.

Presentations

- Hensley, JE; Thibodeaux J, “Effective Limits of CO_2 and CH_4 Recycle to Mixed Alcohol Reactors Operated with Metal Sulfide Catalysts.” Presented by JE Hensley at *American Institute of Chemical Engineers annual meeting*, **November 10, 2010**, Salt Lake City, UT.

Reports

- 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.
- Hensley, JE, **2010** “Mixed Alcohol Catalyst Evaluation of Upper Levels of Inert Species,” *NBC-10772*, National Renewable Energy Laboratory, Golden, CO.
- 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.