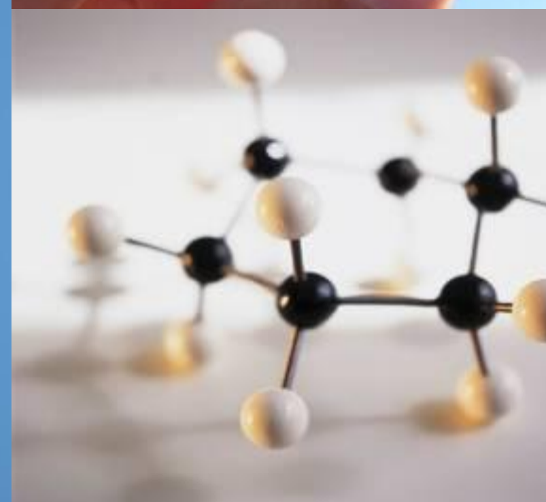





DOE Bioenergy Technologies Office: Project Peer Review

Syngas Mixed Alcohol Cost Validation

May 21, 2013

Abhijit Dutta, NREL

Goal Statement

Enable research and development of **cost-competitive biomass to liquid fuels** by providing:

- Techno-economic analysis (TEA)
- Feedback to the research efforts

Specific objective in 2012: Provide TEA and **validate** DOE BETO's goal to demonstrate technologies capable of producing **cost competitive ethanol** from biomass by the year 2012.

Quad Chart Overview

Timeline for Mixed Alcohols

Start Date	Oct 1, 2006
End Date	Sept 30, 2012
% Complete	100%

WBS 3.6.1.1 Budget (100% DOE)

Year	Total [Gasification/Pyrolysis]
FY12	$860k [$700k/$160k]
FY13	$1,000k [$250k/$750k]
FY14	$1,050k [$350k/$700k] projected
Years	10 (*FY04 to FY13*)
Avg./yr	$760k [$669k/$91k]

Changing with Research Needs

Before FY07	H_2 & syngas applications
FY07 to FY12	Mixed alcohols focus
After FY12	Hydrocarbon fuels focus

Barriers (from MYPP*)

- Tt.-F. Syngas Cleanup and Conditioning
- Tt-G. Fuel Synthesis
- Tt-H. Validation of Syngas Quality

Partners

- Harris Group (engineering firm, subcontract for capital costs)
- Rentech (tar reforming)
- The Dow Chemical Company (alcohol synthesis)
- Idaho National Lab (feedstock)
- PNNL (alcohol synthesis)

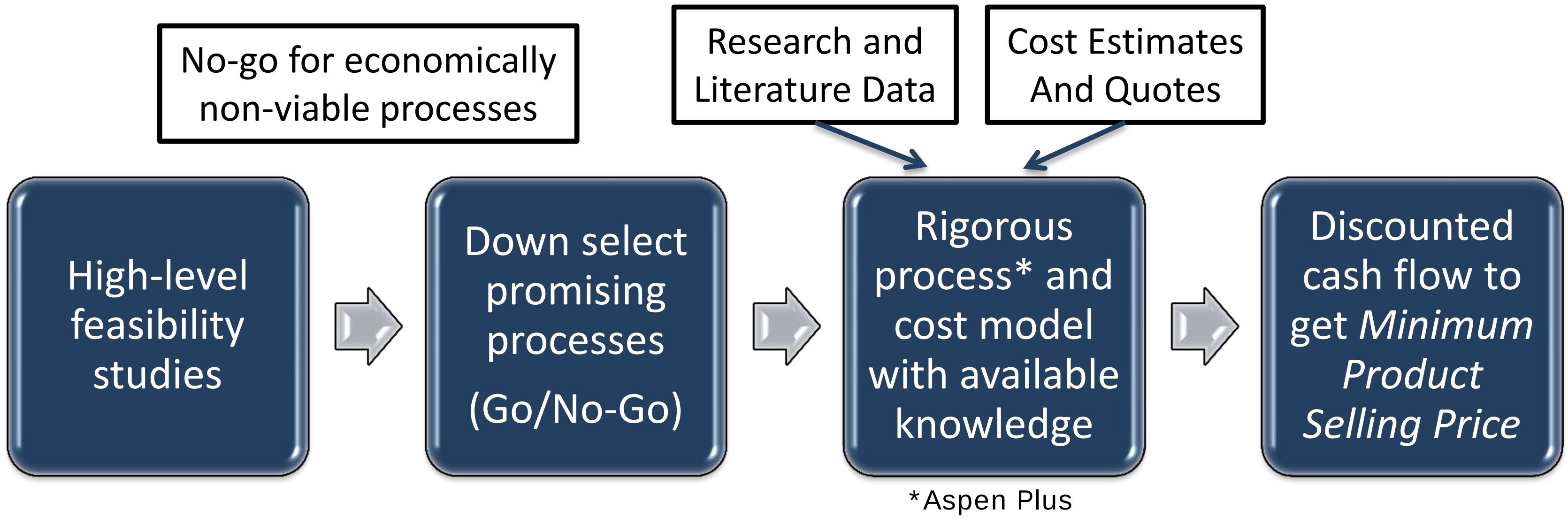
Managed by setting milestones in Annual Operating Plan prior to the start of each fiscal year. PMP in Additional Slides.

*MYPP: Multi-Year Program Plan, April 2012

Project Overview

- FY04 to FY06: Focus on hydrogen from biomass via gasification
- FY07 to FY12: Focus on cost-competitive ethanol
  - 2007: Established benchmark process, technical & cost targets for production of cost-competitive ethanol by 2012
  - Track research progress via annual State of Technology
  - FY10: Thorough reassessment of project after start of Dow Chemical CRADA
    - Updated TEA based on Dow Chemical kinetic model for alcohol synthesis
    - Published new benchmark design with updated targets in 2011
    - Platform objective: $2.05/gallon modeled ethanol cost by 2012
  - 2012 validation (*focus of this presentation*)
    - Used experimental results and projected commercial scale mature plant costs using assumptions consistent with benchmark model
- FY13 and beyond: Focus on liquid hydrocarbon fuels
  - Analyze alternate liquid fuels pathways & targets

Approach



- Sensitivity studies to cover uncertainties
- Determine areas where research will have biggest market impact and help set research goals
- Use a benchmark model to track the progress of research towards commercialization
- *Annual Operating Plan* prepared prior to each fiscal year, with milestones and deadlines to be met. (Details in additional slides)
- Risk management of uncertainties in analysis conclusions:
  - More peer review, interaction with industry, and collaborations
  - Use of engineering firms for better capital cost information

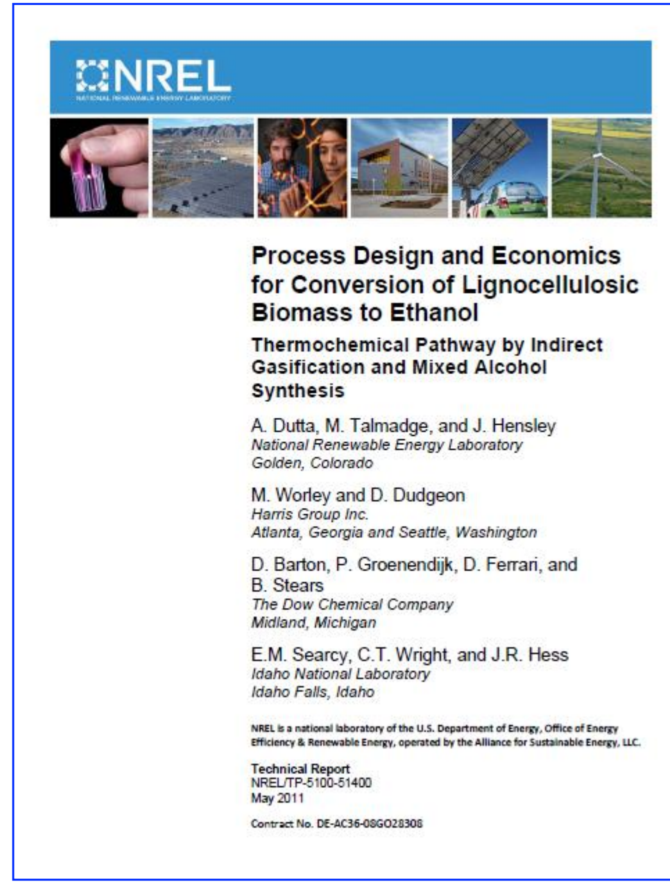
Accomplishments Since 2011 Review (Overview)

- Biomass to mixed alcohols:
  - Updated design report published – peer reviewed, co-authors from Dow Chemical (alcohol synthesis), INL (feedstock), Harris Group (engineering firm for cost validation)
  - Validation of technologies for cost-competitive ethanol (met modeled $2.05/gallon ethanol cost in a mature plant)
- Alternate syngas pathways milestone report (June 2012)
- Contributed to BETO's future conversion pathways work
- Constant interaction with research & experimental efforts
- Subcontract for update on gasifier & reformer costs and technology (NREL report published)
- Pyrolysis (separate presentations in bio-oil review)

Mixed alcohols demonstration presented, rest shown in Additional Slides section

Updated Biomass to Mixed Alcohols Design Report

- Published 2011 (updates 2007 report)
- Recent vendor-based capital costs
- Key assumptions:
  - 2000 dry metric tonnes/day
  - \$61.57/dry ton (30% moisture)
  - 40% equity financing, 10% IRR
  - 60% debt financed at 8% for 10 years
  - Costs in 2007 dollars for a mature n^{th} plant
- State of technology & targets presented
- Peer reviewed by experts from 11 institutions. Transparent: All reviewer comments in Appendix O
- Represented initial Dow Chemical catalyst with a 20% activity improvement target (without loss in alcohols selectivity)


NREL

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

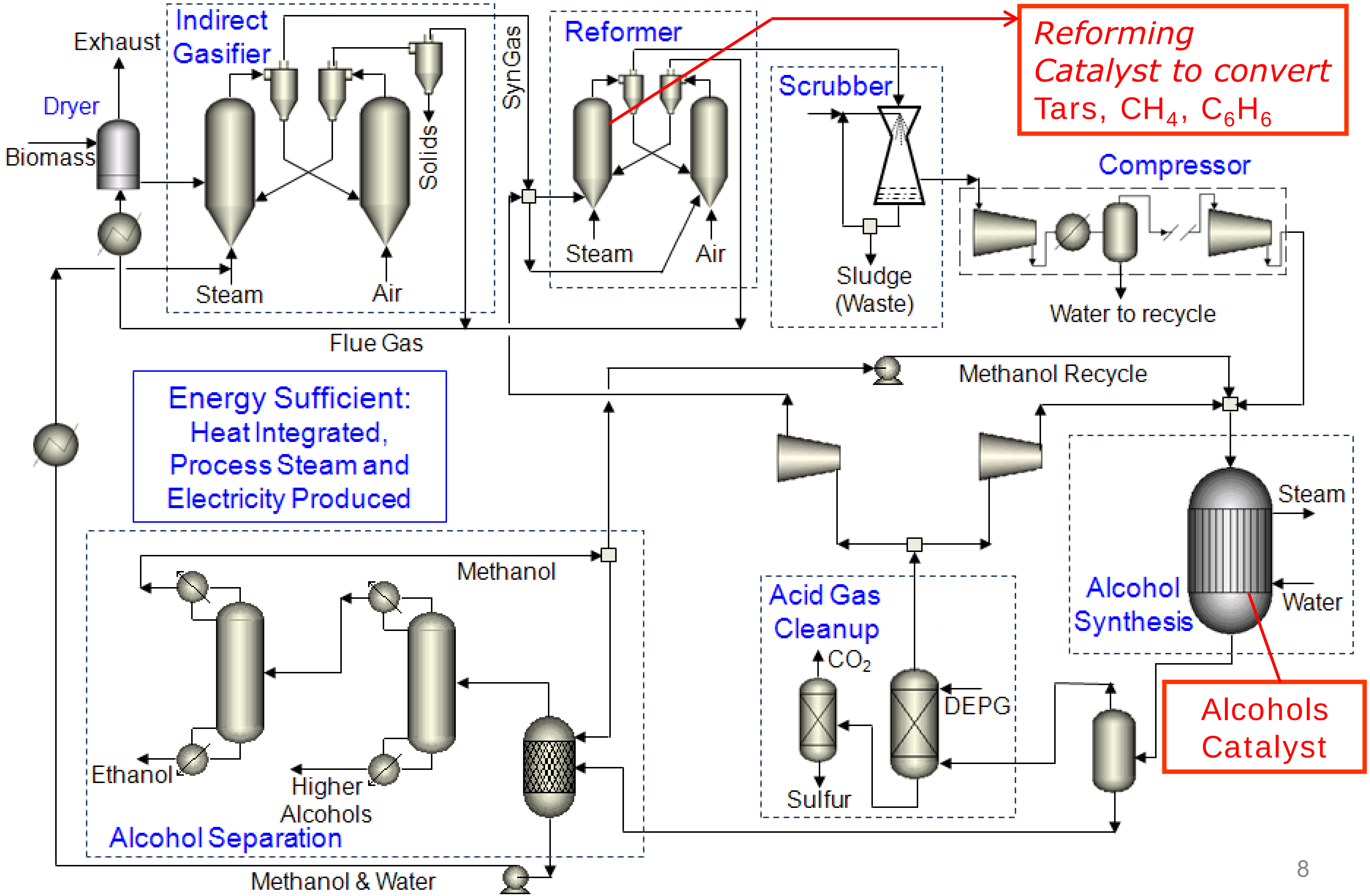
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5100-51400
May 2011

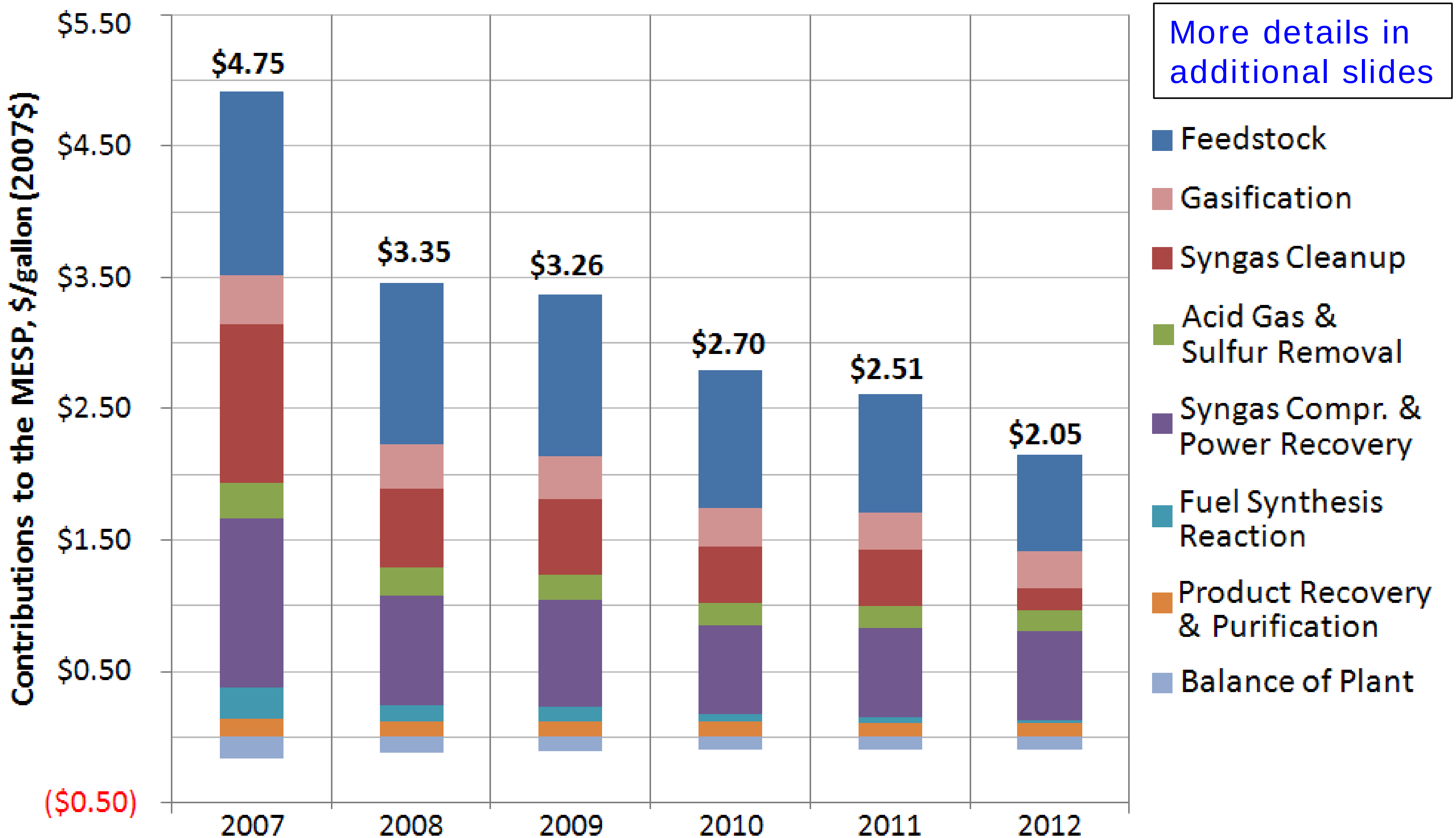
Contract No. DE-AC36-08GO28308

http://www.nrel.gov/docs/fy11osti/51400.pdf

Benchmark Design

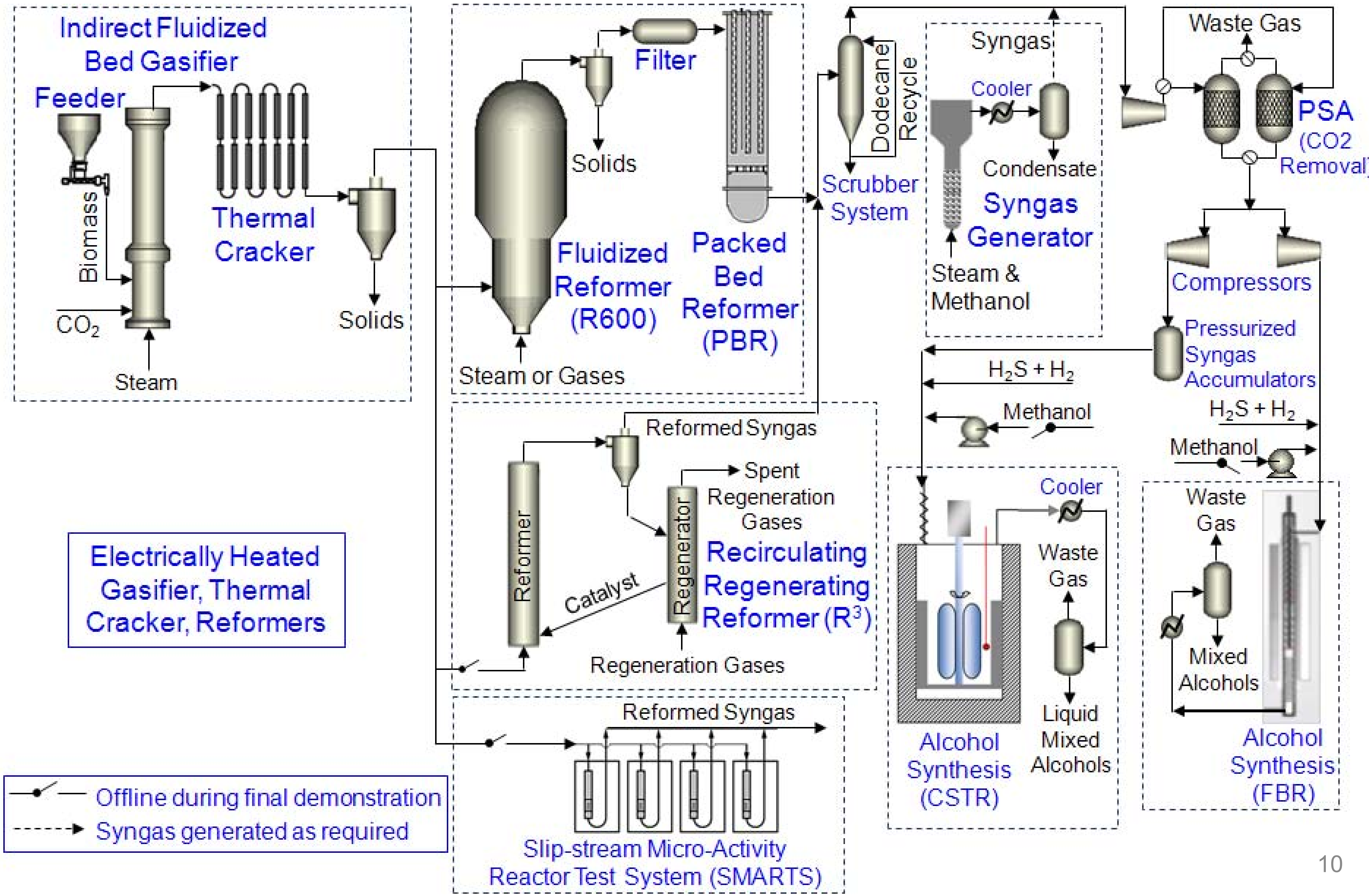


Design Cost by Area (2007 to 2012)



- MESP (Minimum Ethanol Selling Price), net value shown above each bar.
- Costs include electricity charge/credit by area, & higher alcohols credit in fuel synthesis

Experimental Setup



Model vs. NREL Demonstration Expt. (key differences)‡

- Higher steam in NREL gasifier to meet fluidization needs
  - Result: Higher than design H_2:CO ratio
  - Partially offset by adding CO_2 and water gas shift
- Reformer:
  - Recirculating-regenerating system, shakedown could not be completed for reliable operations during demo (see additional slide)
  - Used steady-state (no regeneration) fluidized bed with NREL catalyst, followed by packed bed with Johnson Matthey catalyst
- PSA-based CO_2 removal was less than optimal, high CO_2 in syngas
- Alcohol synthesis:
  - Pilot-scale CSTR vs. modeled industrial scale fixed bed
  - Lower total pressure, lower CO partial pressure, higher H_2:CO ratio, no methanol recycle

‡Discussed in detail in publication prepared for submission to journal (I&ECR). More information in additional slides.

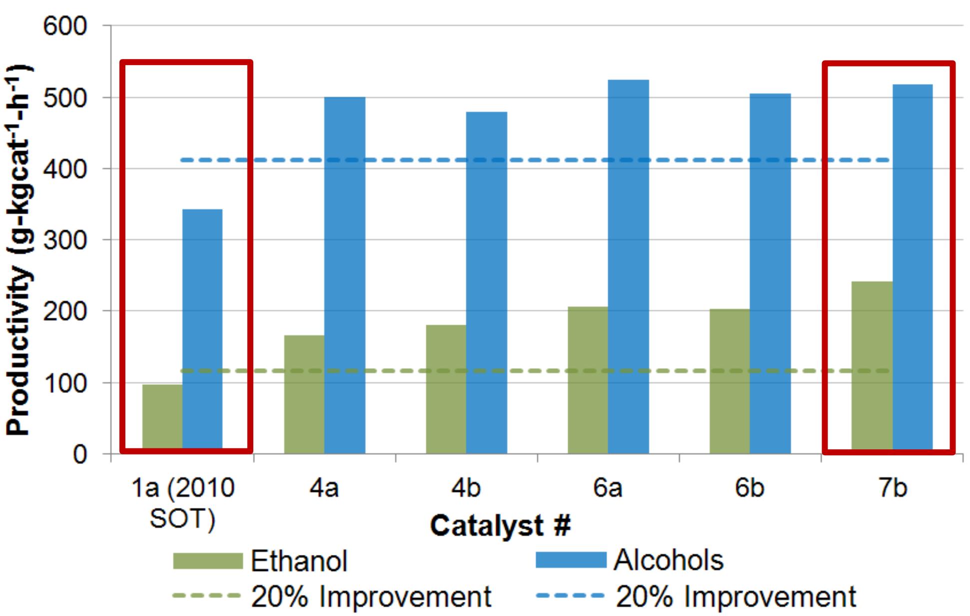
2012 Technical Targets & Performance (Reforming)

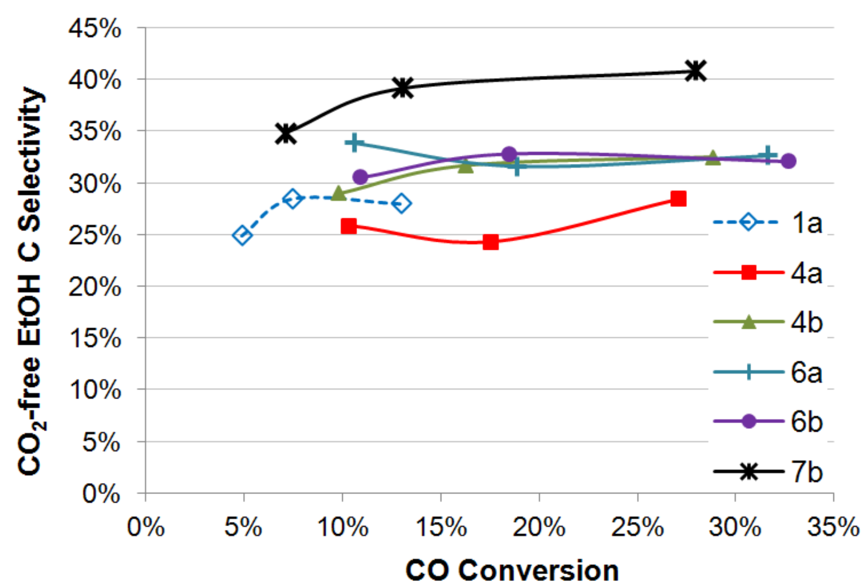
System	Design Target: Dual bed with regeneration	NREL Pilot: Steady fluidized bed (R600) followed by packed bed reformer (PBR)	Rentech directed pilot runs: Dual bed reformer-regenerator system (NREL catalyst was one of several considered for Rentech runs)	
Catalyst	R&D target	R600:NREL, PBR:JMR†	NREL	NREL
Cat. loss (%/day)	0.1	N/A	0.15‡	0.15‡
Inlet				
Feed	Gasifier products with recycled process gases	Gasifier products including steam required for gasifier fluidization and added CO_2	Biomass derived syngas from 1 ton/day pilot gasifier	Natural gas reformed with CO_2 only, spiked with elevated H_2S and tar species
Steam:Carbon#	2.0	6.2	1.8	0
CO_2:Carbon#	1.1	2.3	1.1	1
Conversions				
Methane (CH_4)	80%	86%	95%	>80%
Benzene (C_6H_6)	99%	97%§	99.9%	-
Tars	99%	99.9%	99.9%	99.9%

†JMR = Johnson Matthey reforming catalyst (noble metal). ‡ 0.15% (vs. 0.1% target) results in 1.4 cents increase in the MESP. This 1.4 cent increase can be offset by ≥ 84% CH_4 conversion. § 99% C_6H_6 conversion achieved with same catalyst at 800°C (vs. 780°C during pilot operations).
Carbon calculation excludes CO, CO_2, and subtracts oxygen already present in species to be reformed.

2012 Tech. Targets & Performance (Alcohol Synthesis)

2012 target: 20% activity (productivity) increase over catalyst "1a", while maintaining selectivity, for desired products (ethanol and other alcohols)





Comparative bench scale experiments at 325°C, CO & H_2 partial pressures 700 psi at space velocities (NTPL/kg-cat/h): 6k for productivity; 6k, 10k & 14k for selectivity

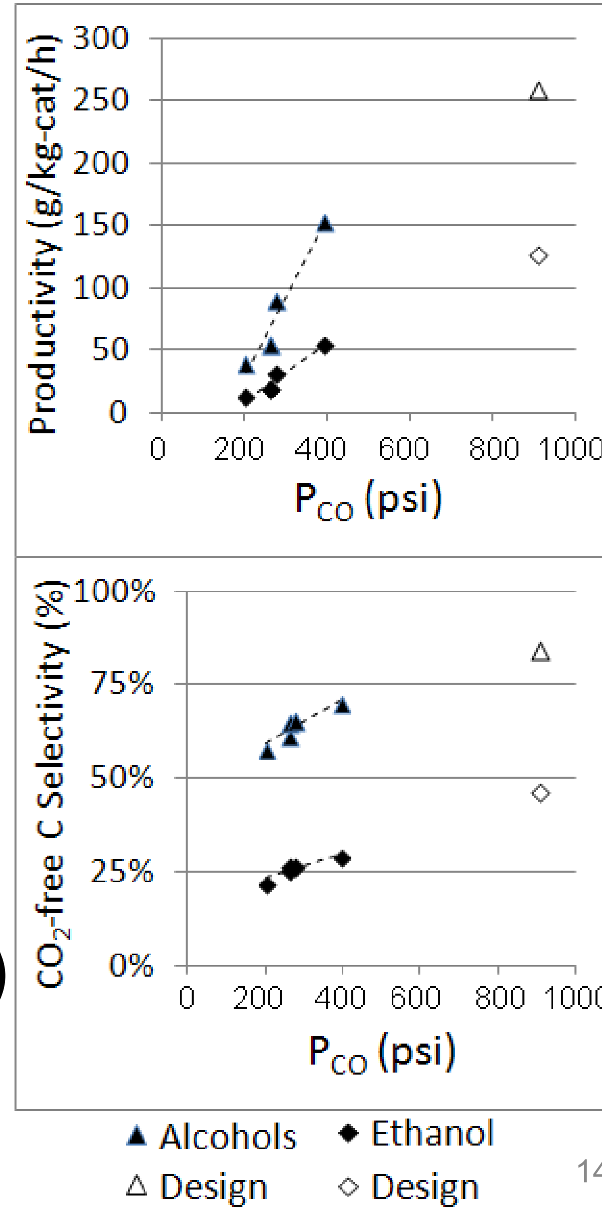
- Catalyst "7b" showed the best performance, chosen among multiple formulations
- Ethanol productivity was 51% over "1a" after binder addition and pelletization

Alcohol Synthesis: Pilot Experiments vs. Design Case

Condition	NREL Pilot Plant‡	Design Case
H_2:CO ratio	3.5	1.5
CO_2 (mole %)	28%	14%
N_2 (mole %)	8% (from purge)	-
Max. system pressure (psi)	2000	3000
CO partial pressure (psi)	400 (max achieved)	900
Synthesis reactor	CSTR	Fixed bed
Methanol recycle (mole %)	0%	2.6%

‡Representative approx. values. Conditions varied during pilot operations.

- Lower CO partial pressure in pilot
- CO partial pressure extrapolation suggests *single-pass* targets can be met at higher design pressure (figs. on right: 30% CO conv.)
- No noticeable negative impact of using biomass-derived syngas vs. simulated syngas

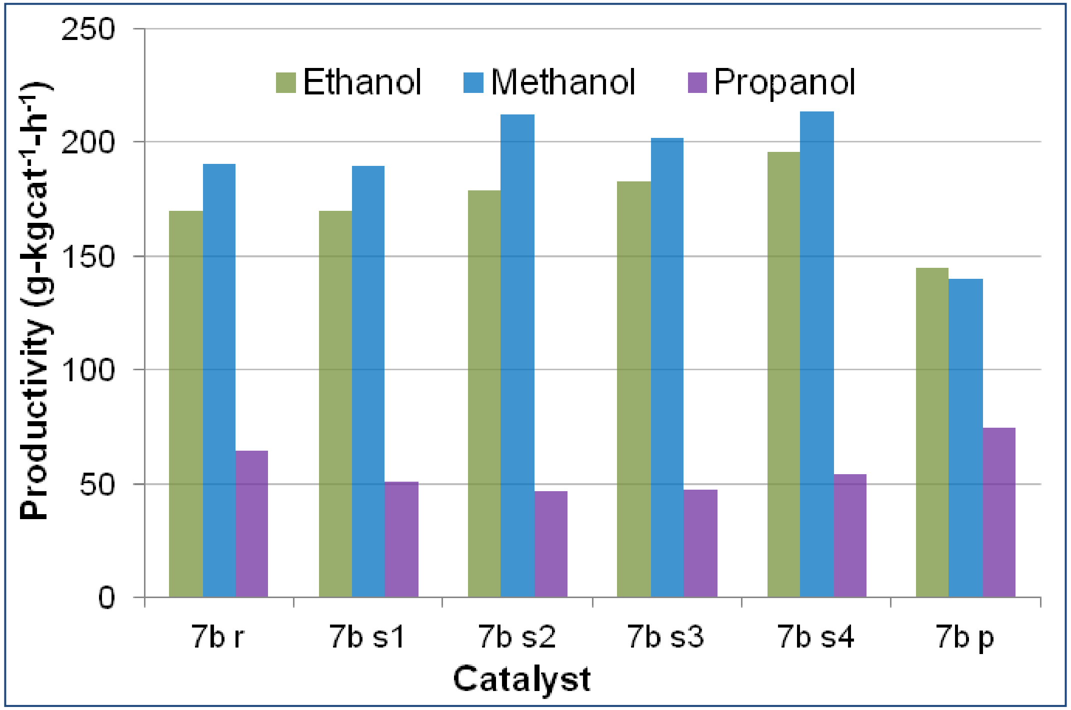


Alcohol Synthesis at a Lower Pressure‡

- Picked a bench-scale fixed bed reactor data point at industrially relevant condition (≈ 30% CO conversion)
- Used updated Dow Chemical kinetic model for improved catalyst
- Modified model scaling factors in kinetic model to mimic isothermal fixed bed *performance* in an industrial scale reactor (to the extent possible) with close parity achieved for key variables:
  - Methanol recycle at inlet ≈2.9 mole %, CO partial pressure ≈ 615 psi, H_2:CO ≈ 1.25
  - CO_2-free Selectivities : Ethanol ≈57%, Total Alcohols ≈ 70%. Model pressure = 1845 psi
- Lowered productivities in economic model to account for 24 wt% binder in pellets: total alcohols = 76% & consequent ethanol productivity ≈ 72% of experimental results
- This case met the \$2.05/gallon ethanol target (with 0.15% reformer catalyst loss & 86% CH_4 conversion in reformer)

‡More details in design report & publication prepared for submission to journal (I&ECR)

Additional Slide: Impact of Pelletized Catalyst



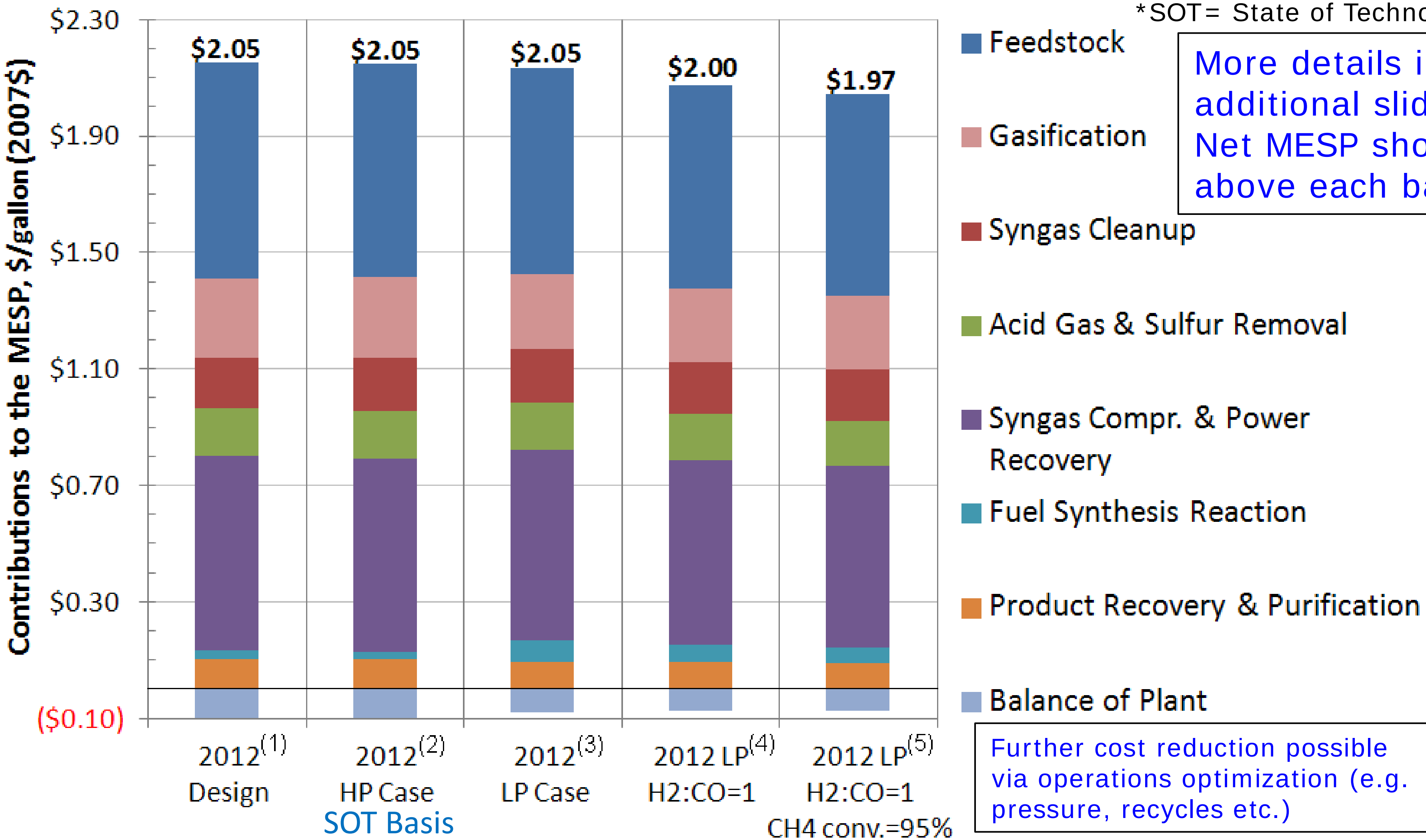
Comparative catalyst productivities for multiple catalyst batches

Formulation →	7b r	7b s1	7b s2	7b s3	7b s4	Avg. of samples	Binder Factor*	Avg Factored	Pelletized 7b p
Ethanol	170	170	179	183	196	179.6	0.72	**129.3**	**145**
Methanol	190	190	212	202	213	201.4	0.76	**153.1**	**140**
Propanol	65	51	47	47	55	53	0.76	**40.3**	**75**

*Binder factors based on factors used in the model to account for higher capital & catalyst costs

Cost Target Validation Cases (SOT* & Sensitivity Cases)

*SOT= State of Technology



More details in additional slides. Net MESP shown above each bar.

Further cost reduction possible via operations optimization (e.g. pressure, recycles etc.)

(1) 2012 design target, (2) Based on demonstration of technical targets. Reformer 0.15% catalyst loss/day, 84% CH_4 conversion. Extrapolation of alcohol synthesis to design case pressure. (3) Low pres. (LP) alcohol syn. based on expt. (details in previous slide). Reformer: 0.15% loss/day, 86% CH_4 conv. (4) Case 3, plus lower H_2:CO ratio of 1.0, based on Rentech demo of reforming with steam and/or CO_2. (5) Case 4, plus 95% CH_4 conv. demo by Rentech

Sustainability Metrics for the Conversion Process‡

Analysis done to support program goals towards sustainable process designs

GHG emissions ($gCO_{2\ equivalent}$/MJ LHV)	0.27†
Consumptive water use (gallons/gallon ethanol equivalent)	1.6
Ethanol yield (gallons/dry US ton)	84
Total alcohols (gallons/dry US ton)	94
Carbon efficiency	32%
LHV efficiency (fuel/dry wood)	45%
Net fossil fuel consumption LHV basis (Joules fossil fuel/1000 Joules in products)	5.5

- Includes indirect contributions from raw materials in conversion process (excluding feedstock production and logistics)
- Above data based on 2012 HP (high-pressure) case shown earlier

†Excludes biogenic CO_2

‡More details in design report & publication prepared for submission to journal (I&ECR)

Relevance

- Direct impact on achieving 2012 goals for cost-competitive thermochemical ethanol*
  - Provided cost reassessments for alternate scenarios based on available experimental information, indicating cost-competitive options
  - Feedback when research results deviated from expectations
  - Reach out to industrial partners to get relevant data for techno-economics
  - Results published (& will be) for use by interested industrial & other entities
- Work on future cost competitive liquid fuels (beyond ethanol) will impact future biomass derived fuels (pathways analysis in additional slides)
  - Future processes for non-ethanol products from biomass derived syngas
  - Study of pyrolysis-based processes
- Use of the work done (application of outputs)
  - Results made publicly available. Techno-economics of the researched (or potential) technology can (and has been) used by industry/academia for preliminary conclusions or starting point for their own evaluations.

*Table B-7 in Appendix B of the April 2012 MYPP. Mixed alcohols not shown in Nov 2012 version of MYPP because project was completed

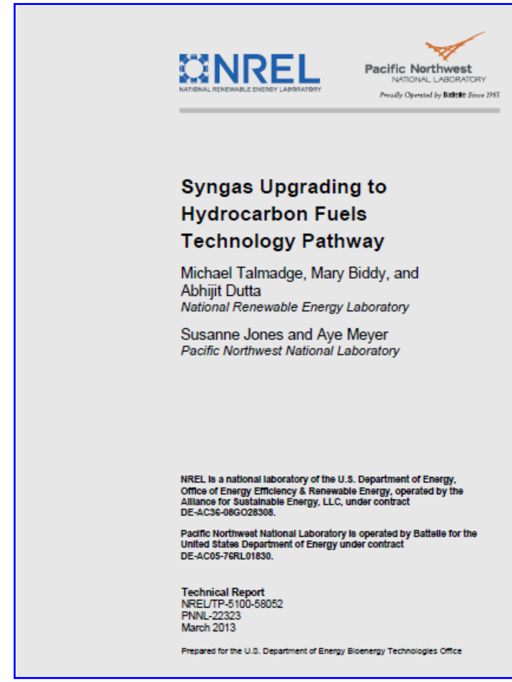
Success Factors and Challenges

- Incorporate continuous feedback to and from researchers:
  - Update models based on research findings
  - Advise on research direction based on feasibility
    - Alert the task leaders about potential problems and opportunities after analyzing research data or sensitivity studies
    - Set technical targets based on the intersection of economic viability & research feasibility
- Future pathways assessments‡ with realistic & objective inputs for:
  - (1) Feasible yields, (2) capital costs, (3) operating costs
  - Otherwise wrong processes will be down-selected, hurting actual viability
  - Overcome by: Periodic stakeholder buy-in, external peer reviews, actively seek collaborations. Make all assumptions transparent.
- Quantification of sustainability impacts & more sustainable designs
  - Assessments will be especially important when considering natural gas use
- Publications and public presentations of major analysis work

‡Assessments will potentially impact decision making for future biofuels research

Future Work

- Continue to support needs of the program*
  - Leverage clean syngas technology from this work for future pathways
  - Immediate work: Set benchmark targets for future hydrocarbon pathways*
  - State of Technology reassessments for the pathways to quantify progress
  - Help BETO with go/no-go decisions for pathways & provide input for MYPP


NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Pacific Northwest
NATIONAL LABORATORY

Syngas Upgrading to Hydrocarbon Fuels Technology Pathway

Michael Talmadge, Mary Biddy, and Abhijit Dutta
National Renewable Energy Laboratory

Susanne Jones and Aye Meyer
Pacific Northwest National Laboratory

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, under contract DE-AC36-08GO28308.

Pacific Northwest National Laboratory is operated by Battelle for the United States Department of Energy under contract DE-AC05-76RL01830.

Technical Report
NREL/TP-5100-58052
PNNL-22323
March 2013

Prepared for the U.S. Department of Energy Bioenergy Technologies Office

- Continue to improve modeling information and techniques
  - Interact with researchers to capture key information in simulations, including compounds, property methods, and reactions
  - Seek reliable yield information, capital and operating costs from industry & engineering firms
- Continue to integrate sustainability metrics into the analysis

*List of pathways, future milestones & Gantt Chart are in Additional Slides

Summary

- **Approach:** Techno-economic analysis with various levels of detail based on available information
- **Technical Accomplishments:** Cost validation of biomass derived syngas to mixed alcohols using experimental information. Other analysis include pathways to hydrocarbon fuels from biomass.
- **Relevance:** Work used for BETO decision making and MYPP input
- **Success Factors and Challenges:** Use of objective and realistic model inputs when data lacking. Use reliable information from: industry, national labs and academia to fill information gaps. Conduct peer reviews.
- **Future Work:** Analysis of hydrocarbon pathways for the future
- **Technology Transfer and Partnerships:** For the biomass to mixed alcohols research, key partnerships developed with Rentech and Dow Chemical, with active participation of this task in using Dow Chemical's fundamental kinetic model for the alcohol synthesis catalyst to better capture catalyst behavior in an industrial reactor

Thank you

DOE BETO for funding and support

- Paul Grabowski
- Kristen Johnson, Zia Haq, Alicia Lindauer (for Analysis & Sustainability)

NREL

- Jesse Hensley
- Michael Talmadge
- Eric Tan
- Richard Bain
- Kim Magrini
- Whitney Jablonski
- Daniel Carpenter
- Mark Davis
- Adam Bratis
- Entire thermochemical team for tireless efforts during the 2012 demonstration
- Biorefinery analysis team

Rentech

- George Apanel

The Dow Chemical Company

- David Barton
- Peter Groenendijk
- Daniela Ferrari

Harris Group

- Matt Worley
- Doug Dudgeon

Johnson Matthey

INL

- Erin M. Searcy
- Chris T. Wright
- J. Richard Hess
- Jake Jacobson
- David Muth

PNNL

- Susanne B. Jones
- Aye Meyer
- Corinne Valkenburg
- Jonathan Male

Additional Slides

- Mixed alcohols:
  - Industrial partners and commercialization
  - Technical and cost targets (2007 to 2012)
  - Details of design cost by area (2007 to 2012)
  - Details of cost target validation cases (SOT and sensitivity)
  - NREL recirculating regenerating reformer system
- Responses to comments from 2011 review
- Publications and presentations since 2011 review (3 slides)
- Project Management Plan for FY11 to FY14 (2 slides)
- Detailed list of accomplishments (3 slides)
- Future milestones
- Constant interaction with research (2 slides)
- Syngas to non-ethanol products
- Gasifier and reformer cost: Harris Group subcontract
- Biorefinery sizing
- List of acronyms

Industrial Partners and Commercialization

- Close collaboration with industrial partners and expected continued efforts by partners towards future commercialization:
  - Rentech: Successful pilot-scale tests using NREL fluidizable catalyst in reforming-regenerating dual bed system
  - Dow Chemical: Alcohol synthesis catalyst improvements
  - Johnson Matthey: NREL pilot runs showed their fixed-bed catalyst can meet technical targets for reforming biomass-syngas. (Catalyst & cost analysis not allowed per agreement)
- NREL fluidizable reforming catalyst licensed by industrial partners & DoD, with the aim of commercialization

Mixed Alcohols: Tech. & Cost Targets (2007 to 2012)

	2007	2008	2009	2010	2011	2012
Minimum Ethanol Selling Price ($/gal)	**$4.75**	**$3.35**	**$3.26**	**$2.70**	**$2.51**	**$2.05**
Feedstock Contribution ($/gal)	$1.40	$1.24	$1.22	$1.05	$0.90	$0.74
Conversion Contribution ($/gal)	$3.35	$2.11	$2.03	$1.65	$1.62	$1.31
Ethanol Yield (Gallon/dry ton)	62	70	70	79	80	84
Mixed Alcohol Yield (Gallon/dry ton)	67	77	78	88	89	94
Feedstock						
Feedstock Cost ($/dry ton)	$86.25	$86.25	$86.25	$82.70	$71.60	$61.57
Syngas Generation						
Syngas Yield (lb/lb dry feed)	0.78	0.78	0.78	0.78	0.78	0.78
CH_4 Concentration in raw syngas(mol %-dry basis)	15	15	15	15	15	15
Syngas Cleanup and Conditioning						
Tar Reformer – CH_4 conversion (%)	20	50	56	80	80	80
Tar Reformer – Benzene conversion (%)	80	98	98	99	99	99
Tar Reformer – Total Tar conversion (%)	97	97	97	99	99	99
Tar Reformer – Exit CH_4 concentration (mol %)	13	5	4	2	2	2
Catalyst Replacement (% inventory/day)	1.0	1.0	1.0	1.0	1.0	0.1
Catalytic Fuel Synthesis						
Compression for fuel synthesis (psia)	3,000	3,000	3,000	3,000	3,000	3,000
Single pass CO conversion (%)	25	24	25	26	29	29
Overall CO conversion (%)	55	68	70	80	79	79
CO Selectivity to alcohols - CO_2 free basis (%)	78	81	81	81	81	81
Total Alcohol Productivity (g/kg/hr)	282	330	337	360	358	368
CO Selectivity to ethanol - CO_2 free basis (%)	59	63	63	63	63	63
CO Selectivity to methanol - CO_2 free basis (%)	13.6	12.4	12.2	11.8	10.4	10.2
Ethanol Productivity (g/kg/hr)	101	128	132	143	153	160

Details of Design Cost by Area (2007 to 2012)*

Processing Area Contributions ($/gallon ethanol)	2007	2008	2009	2010	2011	2012
Feedstock	$ 1.40	$ 1.24	$ 1.22	$ 1.05	$ 0.90	$ 0.74
Gasification	$ 0.37	$ 0.33	$ 0.33	$ 0.29	$ 0.29	$ 0.28
Synthesis Gas Cleanup (Reforming and Quench)	$ 1.22	$ 0.61	$ 0.58	$ 0.42	$ 0.43	$ 0.17
Acid Gas and Sulfur Removal	$ 0.27	$ 0.21	$ 0.20	$ 0.17	$ 0.17	$ 0.17
Synthesis Gas Compression and Power Recovery	$ 1.28	$ 0.84	$ 0.81	$ 0.67	$ 0.67	$ 0.67
Fuel Synthesis Reaction	$ 0.24	$ 0.12	$ 0.11	$ 0.06	$ 0.04	$ 0.03
Product Recovery and Purification	$ 0.14	$ 0.12	$ 0.12	$ 0.11	$ 0.11	$ 0.10
Balance of Plant	$ (0.17)	$ (0.12)	$ (0.11)	$ (0.09)	$ (0.09)	$ (0.10)
Total Processing Cost (excl. feedstock)	**$ 3.35**	**$ 2.11**	**$ 2.03**	**$ 1.65**	**$ 1.62**	**$ 1.31**
Total MESP (Min. Ethanol Selling Price)	**$ 4.75**	**$ 3.35**	**$ 3.26**	**$ 2.70**	**$ 2.51**	**$ 2.05**

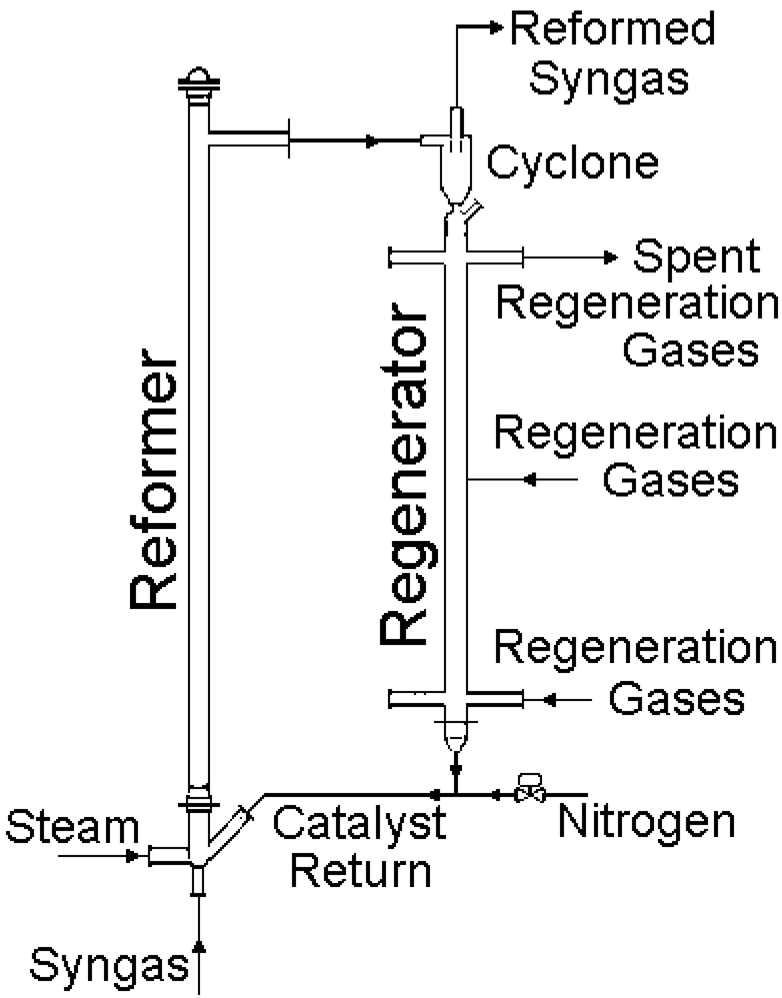
*Cost numbers rounded off (small differences may occur upon addition).
More details in Appendix I of the 2011 design report:
(http://www.nrel.gov/docs/fy11osti/51400.pdf)

Details of Cost Target Validation Cases (SOT & Sensitivity Cases)

Processing Area Contributions ($/gallon ethanol)	2012[1] Design	2012[2] HP Case	2012[3] LP Case	2012 LP[4] H_2:CO=1	2012 LP[5] H2:CO=1 CH4 conv.=95%
Feedstock	$ 0.74	$ 0.73	$ 0.70	$ 0.70	$ 0.69
Gasification	$ 0.28	$ 0.28	$ 0.26	$ 0.26	$ 0.25
Synthesis Gas Cleanup (Reforming and Quench)	$ 0.17	$ 0.18	$ 0.19	$ 0.18	$ 0.18
Acid Gas and Sulfur Removal	$ 0.17	$ 0.16	$ 0.16	$ 0.15	$ 0.15
Synthesis Gas Compression and Power Recovery	$ 0.67	$ 0.66	$ 0.66	$ 0.64	$ 0.63
Fuel Synthesis Reaction	$ 0.03	$ 0.03	$ 0.07	$ 0.06	$ 0.05
Product Recovery and Purification	$ 0.10	$ 0.10	$ 0.09	$ 0.09	$ 0.09
Balance of Plant	$ (0.10)	$ (0.10)	$ (0.08)	$ (0.07)	$ (0.07)
Total Processing Cost (excl. feedstock)	**$ 1.31**	**$ 1.31**	**$ 1.35**	**$ 1.31**	**$ 1.28**
Total MESP (Min. Ethanol Selling Price)	**$ 2.05**	**$ 2.05**	**$ 2.05**	**$ 2.00**	**$ 1.97**
Ethanol Yield (gallons/dry ton)	83.8	84.1	87.4	88.5	89.0

Note: Cost numbers rounded off (small differences may occur upon addition)
(1) 2012 design target, (2) Based on demonstration of technical targets. Reformer 0.15% catalyst loss/day, 84% CH_4 conversion. Extrapolation of alcohol synthesis to design case high pressure (HP). (3) Low pres. (LP) alcohol syn. based on expt. Reformer: 0.15% loss/day, 86% CH_4 conv. (4) Case 3 with lower H_2:CO ratio of 1.0, based on Rentech demo of reforming with steam and/or CO_2. (5) Case 4 with 95% CH_4 conv. based on demo by Rentech.

NREL Recirculating Regenerating Reformer System



- Allows continuous catalyst regeneration
- Reforming in entrained bed
- Fluidized bed regenerator
- Further shakedown necessary to resolve plugging problems
- Successful continuous reforming when no plugging during shakedown, with approximately 35 reforming-regeneration cycles/hour

Responses to Comments from 2011 Review

Following addresses the only weakness identified in the comments:

- The gasification block is still limited, and is not sensitive to changes in feedstock composition.
  - The correlations used were developed based on data from the BCL indirect gasifier (Appendix G of the 2011 design report http://www.nrel.gov/docs/fy11osti/51400.pdf). The correlations can predict yield variations based on temperature. Changes in yields are also predicted based on the elemental (ultimate) analysis of the feedstock. The model is thus sensitive to changes in feedstock elemental composition, but does not have the capability to capture variations in the proximate analysis. The correlations adequately represent syngas from woody biomass, which was the base case for the 2011 mixed alcohols process design. In addition, sensitivity studies were conducted for other feedstocks, and yield variations with ash and moisture were also shown. Although, gasifier output correlations were developed with many more input parameters using experimental data from the NREL pilot gasification system (NREL Report: http://www.nrel.gov/docs/fy09osti/44868.pdf), we did not use them for the mixed alcohols design because the BCL system is more representative of an industrial design.

Publications & Presentations (since 2011 review) – 1

Publications

Dutta, A.; Talmadge, M.; Hensley, J.; Worley, M.; Dudgeon, D.; Barton, D.; Groendijk, P.; Ferrari, D.; Stears, B.; Searcy, E. M.; Wright, C. T.; Hess, J. R. (2011). Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol: Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis. 187 pp.; NREL Report No. TP-5100-51400. http://www.nrel.gov/docs/fy11osti/51400.pdf

Dutta, A.; Talmadge, M.; Hensley, J.; Worley, M.; Dudgeon, D.; Barton, D.; Groenendijk, P.; Ferrari, D.; Stears, B.; Searcy, E.; Wright, C.; Hess, J. R. (2012). Techno-Economics for Conversion of Lignocellulosic Biomass to Ethanol by Indirect Gasification and Mixed Alcohol Synthesis. Environmental Progress and Sustainable Energy. Vol. 31(2), July 2012; pp. 182-190. http://dx.doi.org/10.1002/ep.10625

Talmadge, M.; Biddy, M.; Dutta, A.; Jones, S.; Meyer, A. (2013). Syngas Upgrading to Hydrocarbon Fuels Technology Pathway. 10 pp.; NREL Report No. TP-5100-58052; PNNL-22323. http://www.nrel.gov/docs/fy13osti/58052.pdf http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22323.pdf

Phillips, S. D.; Tarud, J. K.; Biddy, M. J.; Dutta, A. (2011). Gasoline from Woody Biomass via Thermochemical Gasification, Methanol Synthesis, and Methanol-to-Gasoline Technologies: A Technoeconomic Analysis. Industrial and Engineering Chemistry Research. Vol. 50(20), 19 October 2011; pp. 11734-11745. http://dx.doi.org/10.1021/ie2010675

Publications & Presentations (since 2011 review) – 2

Publications

Dutta. A.; Cheah, S.; Bain, R.; Feik, C.; Magrini-Bair, K.; Phillips, S. (2012). Integrated Process Configuration for High-Temperature Sulfur Mitigation during Biomass Conversion via Indirect Gasification. Industrial and Engineering Chemistry Research. Vol. 51(24), 20 June 2012; pp. 8326-8333. http://dx.doi.org/10.1021/ie202797s

Worley, M.; Yale, J. (2012). Biomass Gasification Technology Assessment: Consolidated Report. 358 pp.; NREL Report No. SR-5100-57085. http://www.nrel.gov/docs/fy13osti/57085.pdf

Survey and Down-Selection of Acid Gas Removal Systems for the Thermochemical Conversion of Biomass to Ethanol with a Detailed Analysis of an MDEA System. Task 1: Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis; Task 2: Detailed MDEA Process Analysis. (2011). 96 pp.; NREL Report No. SR-5100-50482. http://www.nrel.gov/docs/fy11osti/50482.pdf

Biddy, M.; Dutta, A.; Jones, S.; Meyer, A. (2013). Ex-Situ Catalytic Fast Pyrolysis Technology Pathway. 9 pp.; NREL Report No. TP-5100-58050; PNNL-22317. http://www.nrel.gov/docs/fy13osti/58050.pdf http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22317.pdf

Biddy, M.; Dutta, A.; Jones, S.; Meyer, A. (2013). In-Situ Catalytic Fast Pyrolysis Technology Pathway. 9 pp.; NREL Report No. TP-5100-58056; PNNL-22320. http://www.nrel.gov/docs/fy13osti/58056.pdf http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22320.pdf

Publications & Presentations (since 2011 review) – 3

Publications

Publication with supporting role for this task: Hensley, J. E.; Lovestead, T. M.; Christensen, E. D.; Dutta, A.; Bruno, T. J.; McCormick, R. L. Compositional Analysis and Advanced Distillation Curve for Mixed Alcohols Produced via Syngas on a K-CoMoSx Catalyst. Energy and Fuels, Just Accepted Publication Date (Web): April 19, 2013. DOI: 10.1021/ef400252x

In preparation (internal reviews ongoing before submission): Dutta, A.; Hensley, J.; Bain, R.; Magrini, K.; Tan E.; Apanel, G.; Barton, D.; Groenendijk, P.; Ferrari, D.; Jablonski, W.; Carpenter, D. Techno-economic analysis for the production of mixed alcohols via indirect gasification of biomass based on demonstration experiments. Expected submission May-June 2013.

In preparation (Multi-lab, contribution to conversion TEA & sustainability by NREL): Muth, D.J.; Langholtz M.H.; Argo, A.; Tan, E.C.D.; Dutta, A.; Eaton, L.M.; Brandt, C.C.; Jacobson, J.J.; Searcy, E.M.; Cafferty, K.G.; Wu, M.M.; Chiu, Y. Investigation of Thermochemical Biorefinery Sizing and Environmental Sustainability Impacts for Conventional Supply System and Distributed Preprocessing Supply System Designs. Expected submission in 2013.

Presentations (presenter’s name in bold)

Presentation at TC Biomass 2011: **Dutta, A.**; Talmadge, M.; Hensley, J. Techno-economic Assessment of the Production of Mixed Alcohols via Indirect Gasification of Lignocellulosic Biomass.

6 abstracts submitted to TC Biomass 2013, based on work under this task. Acceptance decisions pending.

Project Management Plan (FY11 & FY12)

All milestones and target dates have been met *to date*

Fiscal Year 2011	Oct-10	Nov-10	Dec-10	Jan-11	Feb-11	Mar-11	Apr-11	May-11	Jun-11	Jul-11	Aug-11	Sep-11
State of Technology (SOT) Update for FY10	►											
Biomass to Gasoline NREL Design Report		■		●								
Gasifier/Reformer Equipment Cost (Harris Group)				■					■			
Final Results from Updated Ethanol Design Report to DOE				■		►						
Publication of Nexant Acid Gas Removal Report								●				
Publication - Mixed Alcohols (MA) NREL Design Report								●				
Presentation - MA process at TC Biomass 2011												■
Properties and Compounds for Pyrolysis Modeling									▼			
Status of Mixed Alcohol Catalysts (joint milestone)												►
Economic Impacts of FY11 MA Research & SOT												▲

Fiscal Year 2012	Oct-11	Nov-11	Dec-11	Jan-12	Feb-12	Mar-12	Apr-12	May-12	Jun-12	Jul-12	Aug-12	Sep-12
Journal Pub. - TEA of biomass to gasoline via methanol	●											
Pioneer plant cost estimates for mixed alcohols process												
Capitals costs of fluidized biomass conversion equipment			▼									
TEA of pyrolysis vapor phase upgrading (new model)						▼						
TEA of non-ethanol products from biomass-syngas									►			
Journal Pub. - Process configuration for sulfur removal									●			
Journal Pub. - TEA of biomass to Mixed Alcohols (MA)										●		
Future pathways tech memos (with Analysis task & PNNL)												■
Study of impact of MA biorefinery sizing. DOE multi-lab												■
Validation of 2012 Mixed Alcohols Targets												▲

▲=Joule Milestone, ►=D-Milestone, ▼=E-Milestone
■=Deliverable (e.g. presentation), ●=Event (e.g. publication)
Note: Events were added for past occurrences

Project Management Plan (FY13 & FY14)

All milestones and target dates have been met *to date*

Fiscal Year 2013	Oct-12	Nov-12	Dec-12	Jan-13	Feb-13	Mar-13	Apr-13	May-13	Jun-13	Jul-13	Aug-13	Sep-13
Gasifier technology assessment subcontract report		■										
Fluidized bed reactor design - initial report			▼									
Pyrolysis vapor phase upgrading (VPU) model for expt support						▼						
Presentation of Biorefinery Sizing for MA to DOE: Multi-lab							■					
Expected Journal Submission of MA Cost Validation								■				
Future pathways tech memos (with Analysis task & PNNL)				■		●						
Fast pyrolysis with upgrading design report (with PNNL)									■		■	▲
Expected presentations at TC Biomass 2013												■

Fiscal Year 2014 (Preliminary Plan)	Oct-13	Nov-13	Dec-13	Jan-14	Feb-14	Mar-14	Apr-14	May-14	Jun-14	Jul-14	Aug-14	Sep-14
Update on pyrolysis VPU model to support expt work			▼									
Fluidized bed reactor design - status update						▼		■				
Hydrocarbons from biomass derived syngas design report									■			▲
Pyrolysis in-situ and ex-situ upgrading design report									■			▲

▲=Joule Milestone, ►=D-Milestone, ▼=E-Milestone
■=Deliverable (e.g. presentation), ●=Event (e.g. publication)
Note: Events were added for past occurrences

Accomplishments (since 2011 review) – 1

Date*	Topic	Result
3/11	Draft version of mixed alcohols design report with final numbers for the MYPP	D-Milestone report to DOE for publication in MYPP
5/11	Publication of mixed alcohols design report	NREL external publication
5/11	Publication of Nexant subcontract report on acid-gas removal from biomass-derived syngas	NREL external publication
6/11	Properties and compounds for pyrolysis modeling	NREL E-Milestone report
9/11	Presentation of mixed alcohols design at the TC Biomass 2011 international conference	External presentation
9/11	Status of mixed alcohol catalysts (joint milestone with Advanced Fuel Synthesis)	D-Milestone
9/11	Mixed alcohols FY11 State of Technology	Joule Milestone report to DOE for MYPP input
10/11	Journal publication of the techno-economics of biomass to gasoline via methanol	Journal: Industrial and Engineering Chemistry Research

*Date of milestone report submission, publication or approx. completion of work

Accomplishments (since 2011 review) – 2

Date*	Topic	Result
10/11	Pioneer plant mixed alcohols cost estimates	Prepared for DOE management
12/11	Capital costs of fluidized biomass conversion equipment (Harris Group subcontract work)	NREL E-Milestone report
3/12	Develop new model for pyrolysis vapor phase upgrading	NREL E-Milestone report
6/12	Non-ethanol products from biomass syngas	NREL D-Milestone report, future presentation and publication
6/12	Journal publication: Process configuration for efficient sulfur removal	Journal: Industrial and Engineering Chemistry Research
7/12	Journal publication: TEA of mixed alcohols	Journal: Environmental Progress & Sustainable Energy
9/12	Initial Tech Memos for future conversion pathways (with Analysis task & PNNL)	Input to DOE for future planning
9/12	Validation of 2012 mixed alcohols targets based on demonstration experiments	NREL Joule Milestone report

*Date of milestone report submission, publication or approx. completion of work

Accomplishments (since 2011 review) – 3

Date*	Topic	Result
11/12	Gasifier technology assessment report (Harris subcontract)	NREL external publication
12/12	Fluidized bed reactor design – initial report	NREL E-Milestone report
3/13	Update of pyrolysis vapor phase upgrading model for experimental support	NREL E-Milestone report
3/13	Publication of Tech Memos for future conversion pathways (joint with Analysis task and PNNL)	NREL and PNNL external reports

*Date of milestone report submission, publication or approx. completion of work

Future Milestones (FY14 milestones may change)

Due Date	Milestone Type	Milestone Title
6/30/13	DL	Pyrolysis with upgrading updated design report peer review
9/30/13	Joule	Completed pyrolysis with upgrading design report
12/31/13	E	Update on pyrolysis vapor upgrading model to support expt.
3/31/14	E	Update on progress: Fluidized bed reactor design
6/30/14	DL	Hydrocarbons from syngas design report draft peer review
6/30/14	DL	In-situ/ex-situ pyrolysis vapor upgrading peer review
9/30/14	Joule	Completed hydrocarbons from syngas design report
9/30/14	Joule	Completed pyrolysis in-situ/ex-situ upgrading design report

Constant Interaction with Research – 1

- Examples
  - Analysis of data from Recirculating Regenerating Reformer, with recommendations for future operations. Analysis showed that reforming met the CH_4 conversion targets whenever space velocities were in the expected design range. Conversion drop correlated with significant increases in space velocity, mostly because of plugging
  - Biorefinery analysis personnel contributed to plant operations by providing simulated gas compositions for different operating scenarios during the 2012 demonstration

Constant Interaction with Research – 2

- Examples
  - Provided estimated flow rates for design of pyrolysis equipment
  - Provided simulated distillation results from Aspen Plus for an experiment-based journal article on mixed alcohol properties (Hensley et al., Energy and Fuels, web: April 2013)
  - Provided simulated scenarios during safety assessments for the pilot plant

Syngas to Non-Ethanol Products

- Milestone report submitted June 2012 (external publication and presentation in preparation)
- Phase I
  - Derive syngas cost from mixed alcohols design report model
  - Use literature techno-economic information and reduce to a common basis to derive cost ranges for many fuels and chemicals from syngas
- Phase II
  - Develop detailed models for some specific pathways: e.g. syngas fermentation, alcohols to hydrocarbons

Gasifier & Reformer Costs: Harris Group

Key Reasons for Subcontract to Engineering Firm:

- Front end of process (gasification and gas cleanup) is key for any fuel synthesis process and we need to reduce uncertainties in cost and technology

Phase I:

- Survey of gasifier (and reformer) technologies and vendor quotes (already included in updated 2011 mixed alcohols design report)

Phase II:

- Study cost impacts of various parameters, based on engineering design principles

Publication of detailed results in Nov 2012 report (http://www.nrel.gov/docs/fy13osti/57085.pdf)

Biorefinery Sizing

- Collaborative work involving INL, ORNL, NREL, ANL
- NREL contribution to conversion aspects of the mixed alcohols process
- Study shows the overall cost and sustainability impacts of using:
  - Conventional and advanced format feedstocks
  - Plant sizes
  - Feedstock processing to different ash and moisture levels
- Journal article in preparation

List of Acronyms

- BETO = Bioenergy Technologies Office
- DoD = Department of Defense
- DOE = US Department of Energy
- FY = Fiscal Year
- HP = High Pressure
- INL = Idaho National Laboratory
- IRR = Internal Rate of Return
- LHV = Lower Heating Value
- LP = Low Pressure
- MESP = Minimum Ethanol Selling Price
- MYPP = Multi-Year Program Plan
- NREL = National Renewable Energy Laboratory
- PMP = Project Management Plan
- PNNL= Pacific Northwest National Laboratory
- SOT = State of Technology