



DOE Bioenergy Technologies Office: Project Peer Review

Syngas Mixed Alcohol Cost Validation

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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] <small>projected</small>
Years	10 (<i>FY04 to FY13</i>)
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)

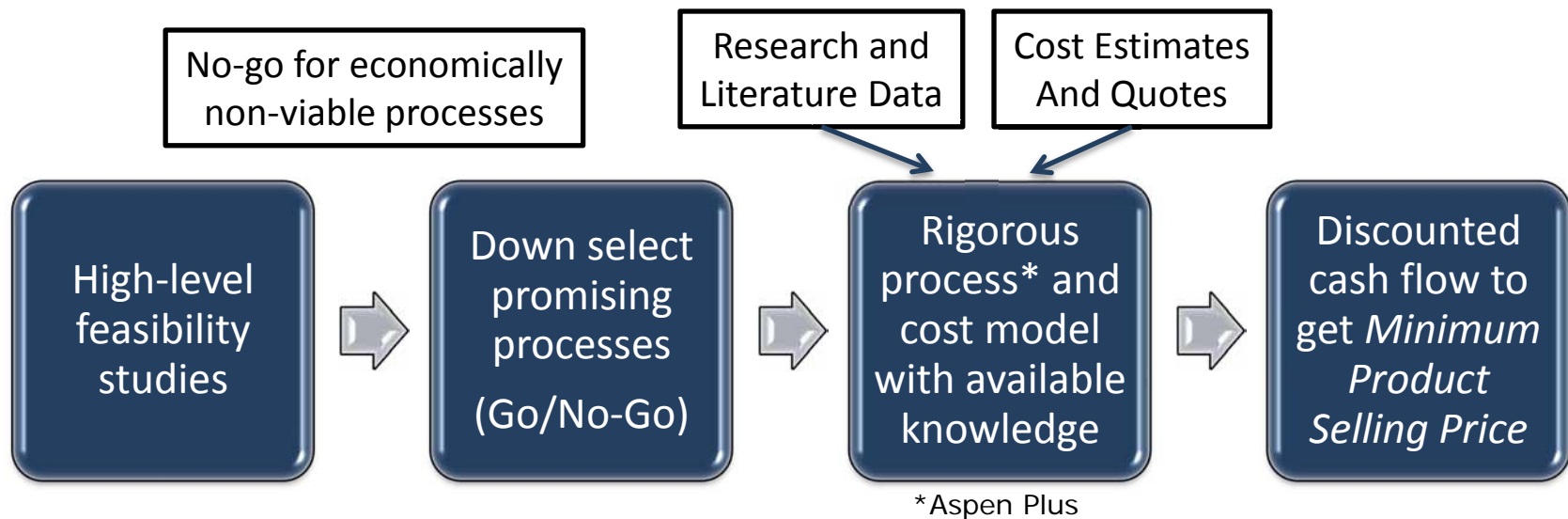
Managed by setting milestones in Annual Operating Plan prior to the start of each fiscal year. [PMP in Additional Slides.](#)

*MYPP: Multi-Year Program Plan, April 2012



- 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)

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 nth 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)



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*

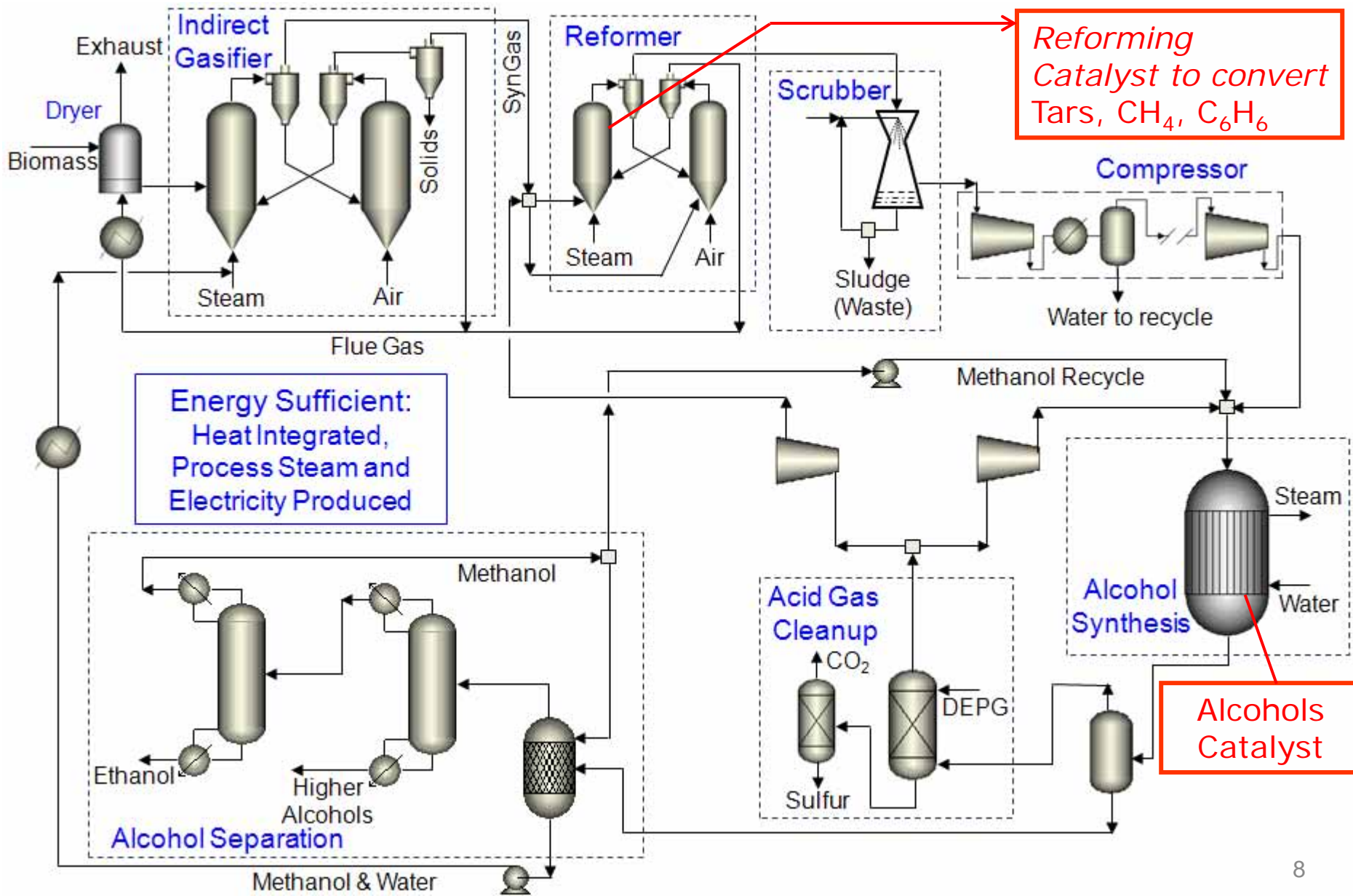
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy
Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5100-51400
May 2011

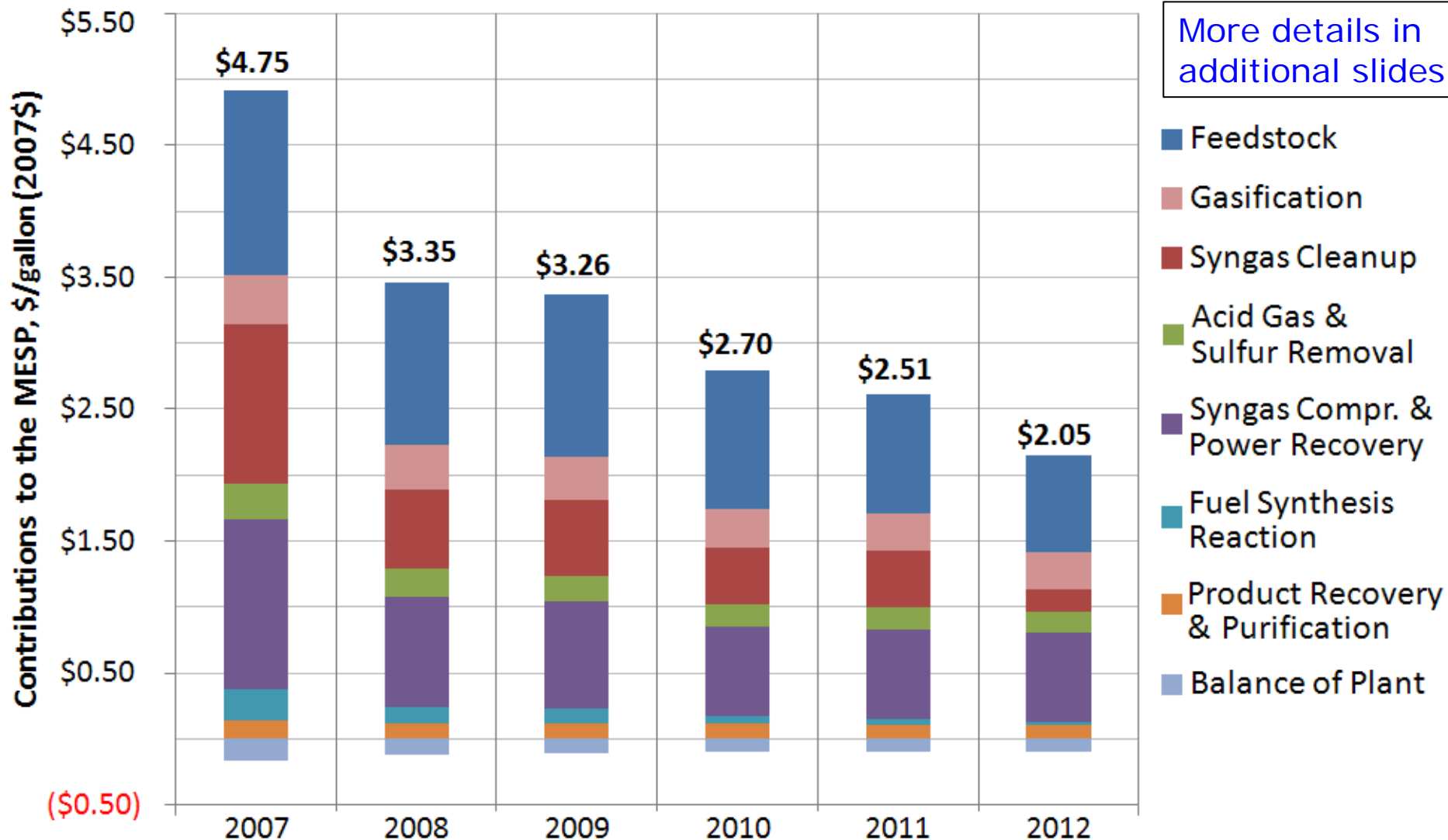
Contract No. DE-AC36-08GO28308

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

Benchmark Design

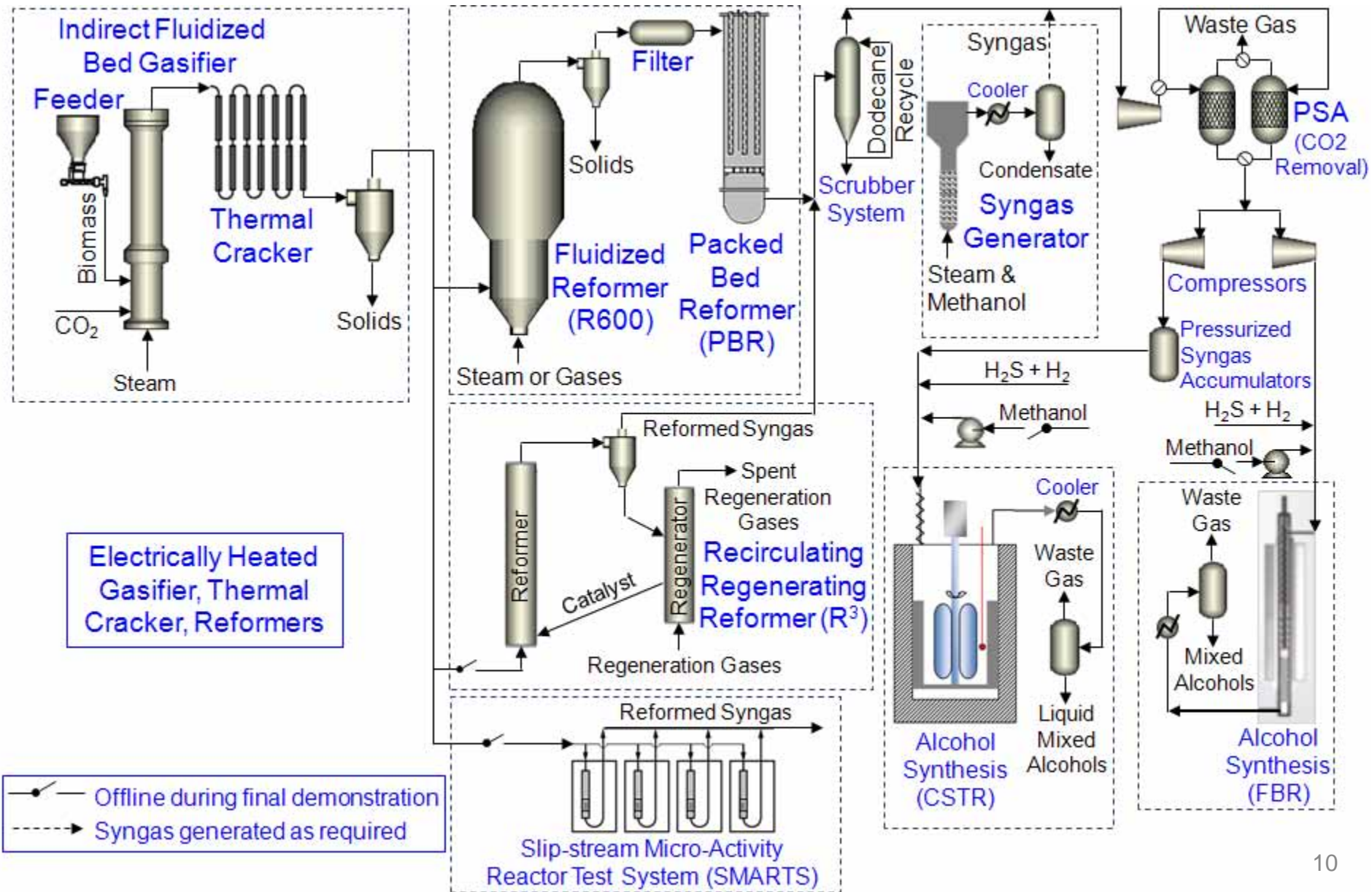


Design Cost by Area (2007 to 2012)



- 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 H₂:CO ratio
 - Partially offset by adding CO₂ 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 CO₂ removal was less than optimal, high CO₂ in syngas
- Alcohol synthesis:
 - Pilot-scale CSTR vs. modeled industrial scale fixed bed
 - Lower total pressure, lower CO partial pressure, higher H₂: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 ₂ S 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 ₆ H ₆)	99%	97% [§]	99.9%	-
Tars	99%	99.9%	99.9%	99.9%

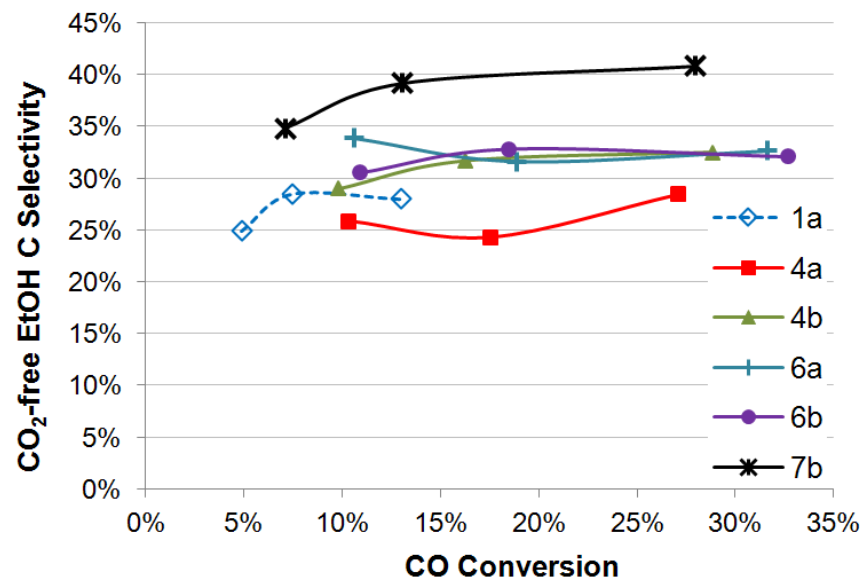
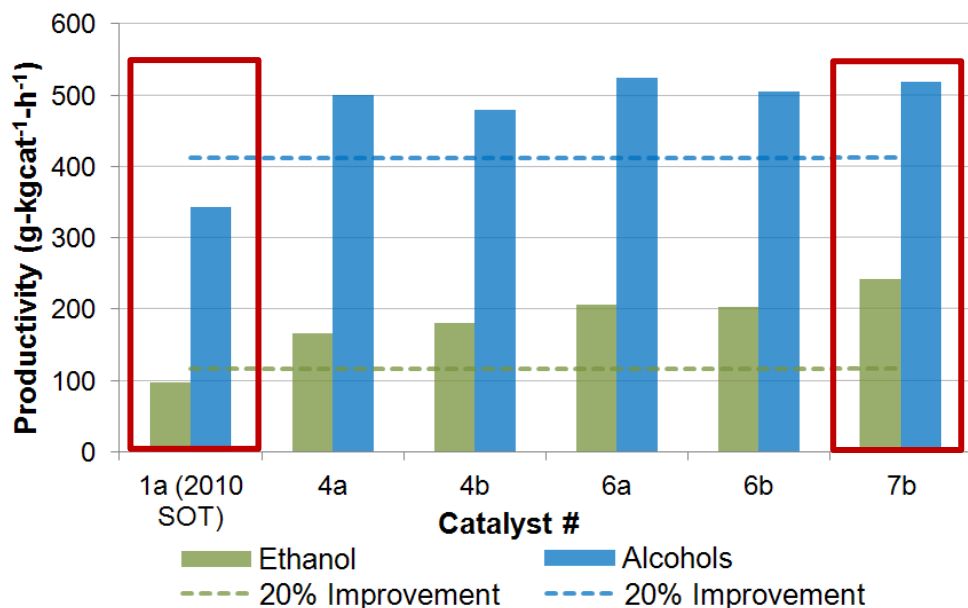
[†]JMR = Johnson Matthey reforming catalyst (noble metal). [‡] 0.15% (vs. 0.1% target) results in 1.4 cents increase in the MESP. This 1.4 cent increase can be offset by $\geq 84\%$ CH₄ conversion. [§] 99% C₆H₆ conversion achieved with same catalyst at 800°C (vs. 780°C during pilot operations).

[#] Carbon calculation excludes CO, CO₂, 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 & H₂ 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

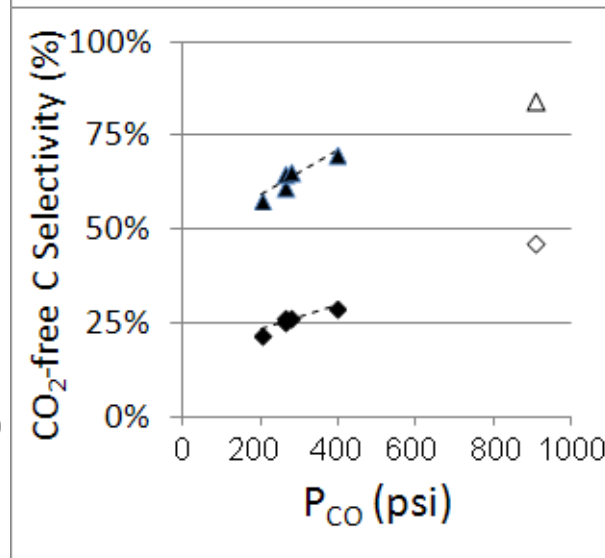
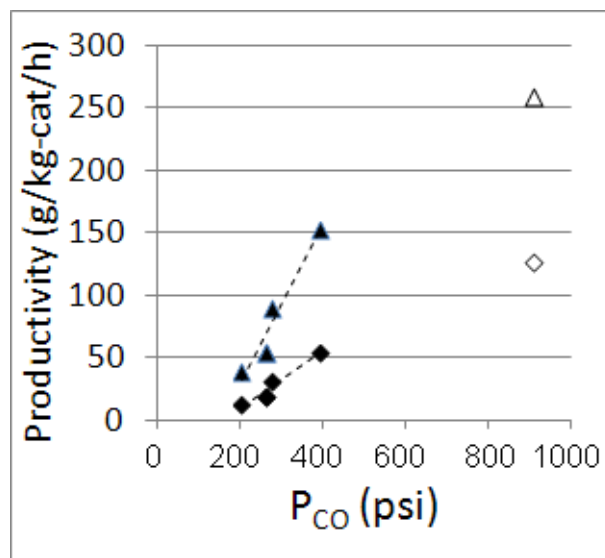
Alcohol Synthesis: Pilot Experiments vs. Design Case



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



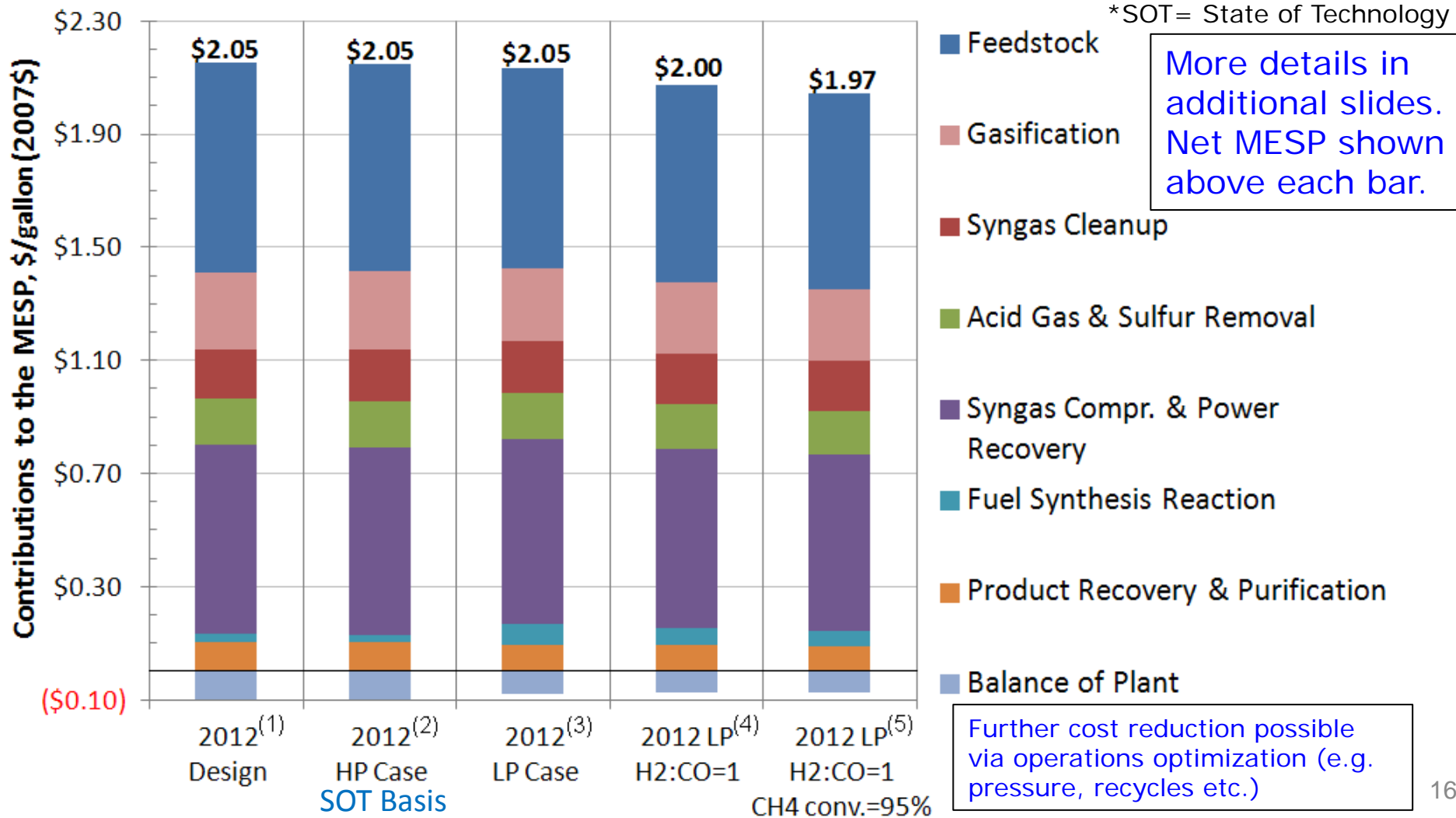
▲ Alcohols ◆ Ethanol
 △ Design ◇ Design

Alcohol Synthesis at a Lower Pressure[‡]



- Picked a bench-scale fixed bed reactor data point at industrially relevant condition ($\approx 30\%$ 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, $H_2:CO \approx 1.25$
 - CO_2 -free Selectivities : Ethanol $\approx 57\%$, Total Alcohols $\approx 70\%$, Model pressure = 1845 psi
- Lowered productivities in economic model to **account for 24 wt% binder in pellets**: total alcohols = **76%** & consequent ethanol productivity \approx **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)

Cost Target Validation Cases (SOT* & Sensitivity Cases)



(1) 2012 design target, (2) Based on demonstration of technical targets. Reformer 0.15% catalyst loss/day, 84% CH₄ 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% CH₄ conv. (4) Case 3, plus lower H₂:CO ratio of 1.0, based on Rentech demo of reforming with steam and/or CO₂. (5) Case 4, plus 95% CH₄ 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 CO₂

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



- 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

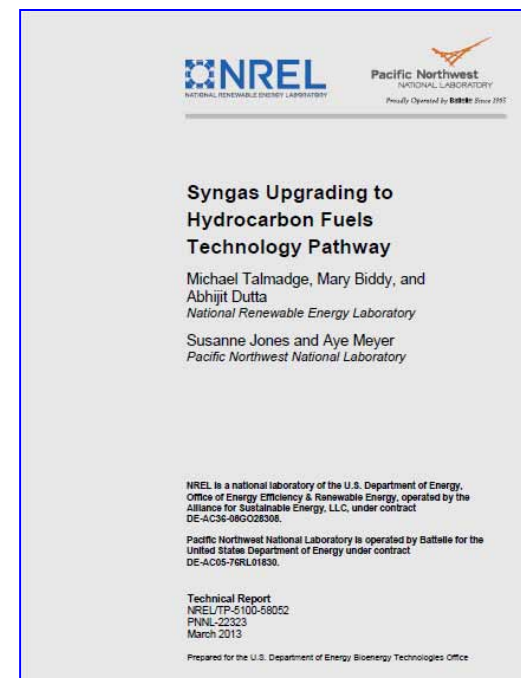


- Incorporate continuous **feedback to and from researchers**:
 - Update models based on research findings
 - Advise on research direction based on feasibility
 - Alert the task leaders about potential problems and opportunities after analyzing research data or sensitivity studies
 - Set technical targets 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

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**
- 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



- **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



- 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



- 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)



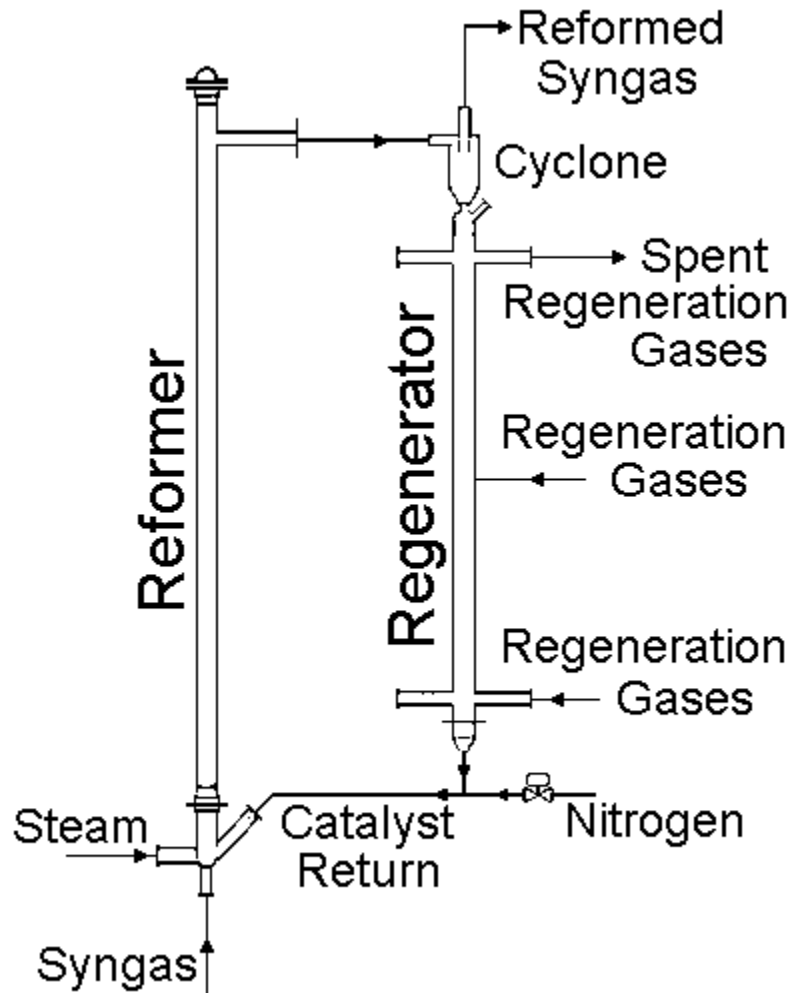
Processing Area Contributions (\$/gallon ethanol)	2012 ⁽¹⁾ Design	2012 ⁽²⁾ HP Case	2012 ⁽³⁾ LP Case	2012 LP ⁽⁴⁾ H ₂ :CO=1	2012 LP ⁽⁵⁾ H ₂ :CO=1 CH ₄ conv.=95%
Feedstock	\$ 0.74	\$ 0.73	\$ 0.70	\$ 0.70	\$ 0.69
Gasification	\$ 0.28	\$ 0.28	\$ 0.26	\$ 0.26	\$ 0.25
Synthesis Gas Cleanup (Reforming and Quench)	\$ 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% CH₄ 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% CH₄ conv. (4) Case 3 with lower H₂:CO ratio of 1.0, based on Rentech demo of reforming with steam and/or CO₂. (5) Case 4 with 95% CH₄ 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



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

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.; Bidy, 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.

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- 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>
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- 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>
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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



- 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



- 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



- 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



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>)



- 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