2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

3.2.5.8 – Integrated Catalyst Fundamentals

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May 21, 2013

Thermochemical Conversion

Organizations: NREL, PNNL

Goal Statement

Project Goal – Develop and demonstrate warm and hot gas conditioning processes for biomass-derived syngas for ethanol synthesis so that DOE can meet or exceed ethanol cost targets

- **Down select and demonstrate the best syngas cleaning process** that achieve ethanol cost targets
- **Validate** the performance of the best catalyst and/or sorbent process that cleans biomass syngas for downstream ethanol synthesis
- **Collaborate with the Engineering tasks to demonstrate best syngas cleaning process** for 2012 pilot scale demonstration of cost competitive EtOH production

Quad Chart Overview

Timeline

Project start date: 2006
Project end date: 2012
Percent complete:100%

Barriers

Catalyst reforming activity

Catalyst tolerance to gas impurities

Budget

Funding for FY 2012:
$2M (NREL), $0.6M (PNNL)

Funding for FY 2013:
$2M (NREL), $0 (PNNL)

FY 2014 projected budget: $0

Years the project has been funded/average annual funding:
7y/$2.6M

Partners

Reforming catalyst development

- Johnson Matthey
- CoorsTek
- NexTech, GTI

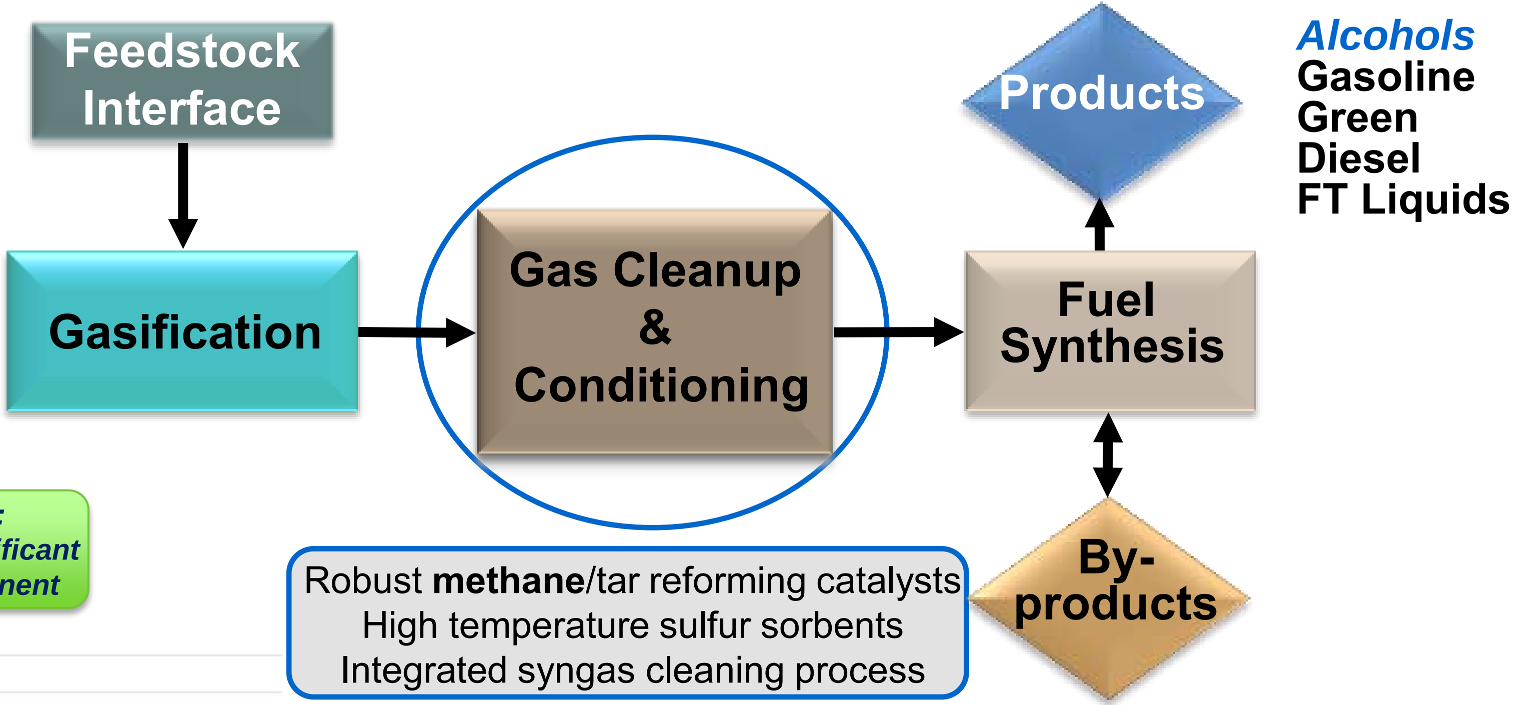
Catalyst evaluation

- Rentech

Catalyst characterization

- CU, CSM, USF

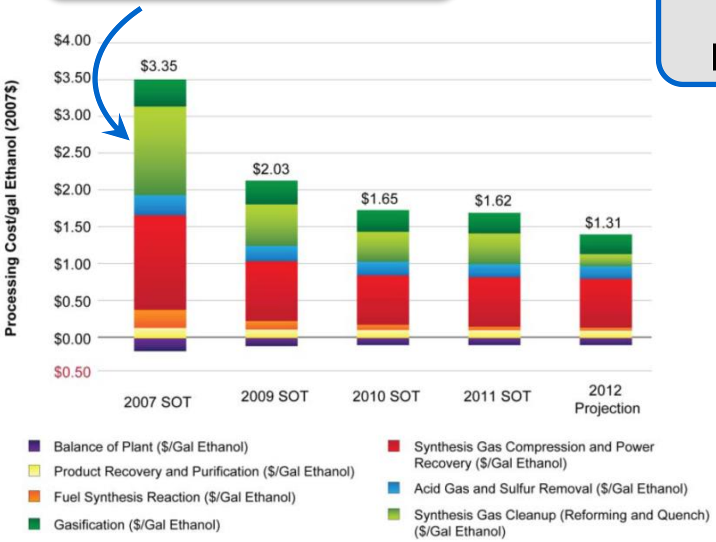
Project Overview



Alcohols
Gasoline
Green
Diesel
FT Liquids

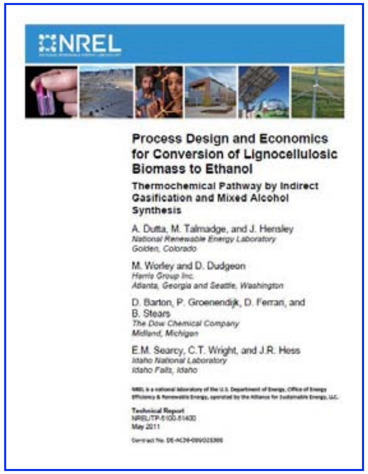
Robust **methane**/tar reforming catalysts
High temperature sulfur sorbents
Integrated syngas cleaning process

Project rationale:
Syngas cleaning significant process cost component



<u>Syngas Cleaning Targets</u>

Methane conversion: 80%
Benzene conversion: 99%
Tars/HC conversion: 99%
Meet $2.05/gal



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

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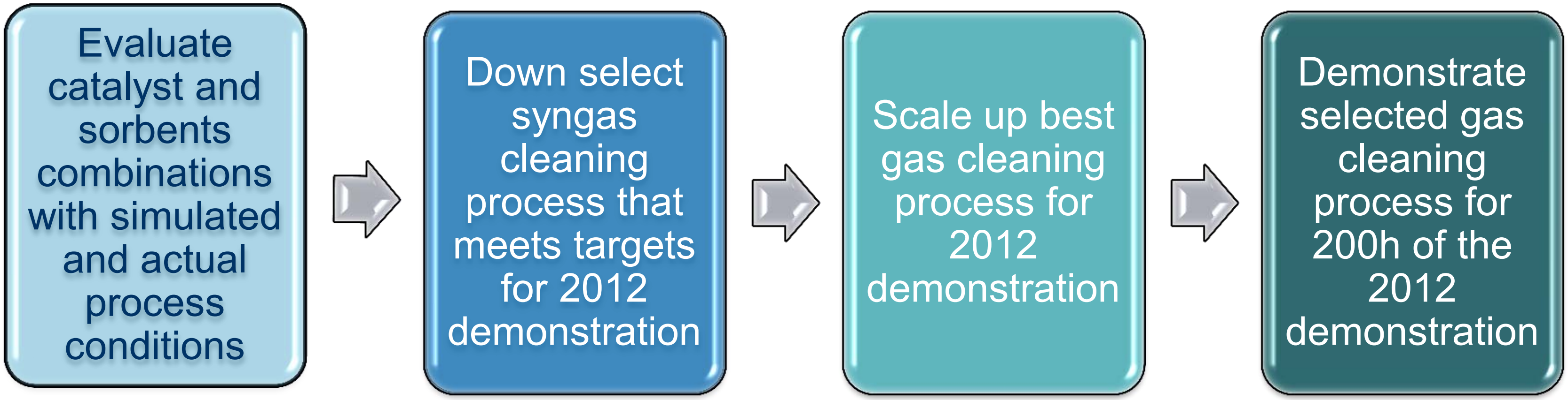
Idaho National Laboratory
Idaho Falls, Idaho

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

1 - Approach



Evaluate catalyst and sorbents combinations with simulated and actual process conditions

Down select syngas cleaning process that meets targets for 2012 demonstration

Scale up best gas cleaning process for 2012 demonstration

Demonstrate selected gas cleaning process for 200h of the 2012 demonstration

***2012 cost target: modeled MESP of $2.05/gal**

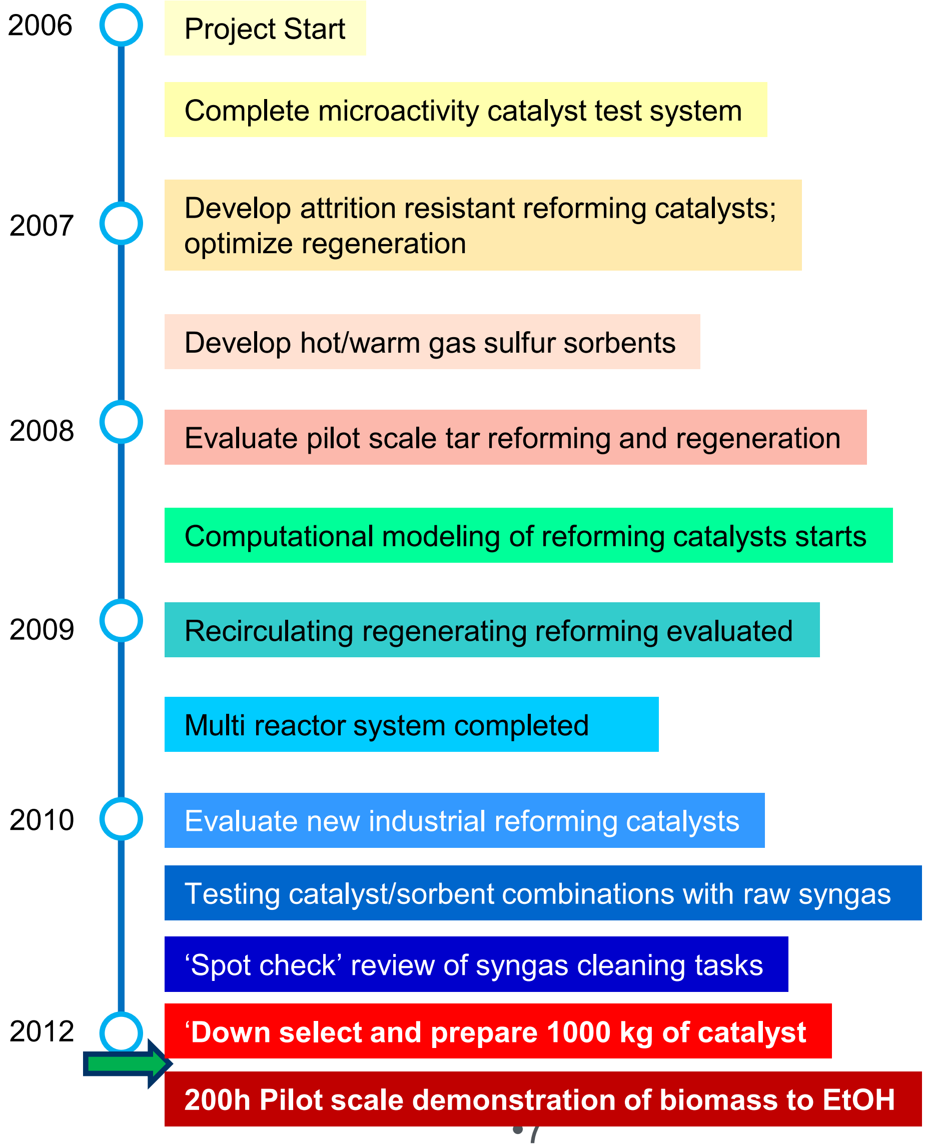
- Reduce syngas *inorganic contaminants* before tar cracking/methane reforming via *hot and warm gas sorbents, gasification catalysts*
- Catalytic reforming of *tars/methane* in biomass syngas with contaminants using optimized *nickel and Rh based reforming catalysts and contaminant resistant catalysts*
- Select optimized syngas cleaning process utilizing one/some combination of these approaches
- Validate process with biomass syngas at the pilot scale for 200h time on stream (TOS)
- ***Management Approach**: DOE approved management plans detail schedules, milestones, deliverables, and risk abatement*

4 - Critical Success Factors

- Reforming Catalysts:
  - **Success:** Ability to reform methane, benzene, and total tars in biomass syngas to 80%, 99%, and 99% conversion, respectively while meeting $2.05/gal EtOH
  - **Challenge:** Maintaining the syngas cleaning targets for 200h in actual biomass syngas – successfully produced clean syngas in the 2012 demonstration – data open for industrial use
- Syngas cleaning and conditioning
  - **Success:** Demonstrated single or combined process to achieve methane, benzene and tar conversions in biomass derived syngas that meet the $2.05/gal cost target
  - **Challenge:** Achieving the cost targets with biomass syngas - successfully demonstrated a combined cleaning process at the pilot scale in 2012

1 - Approach

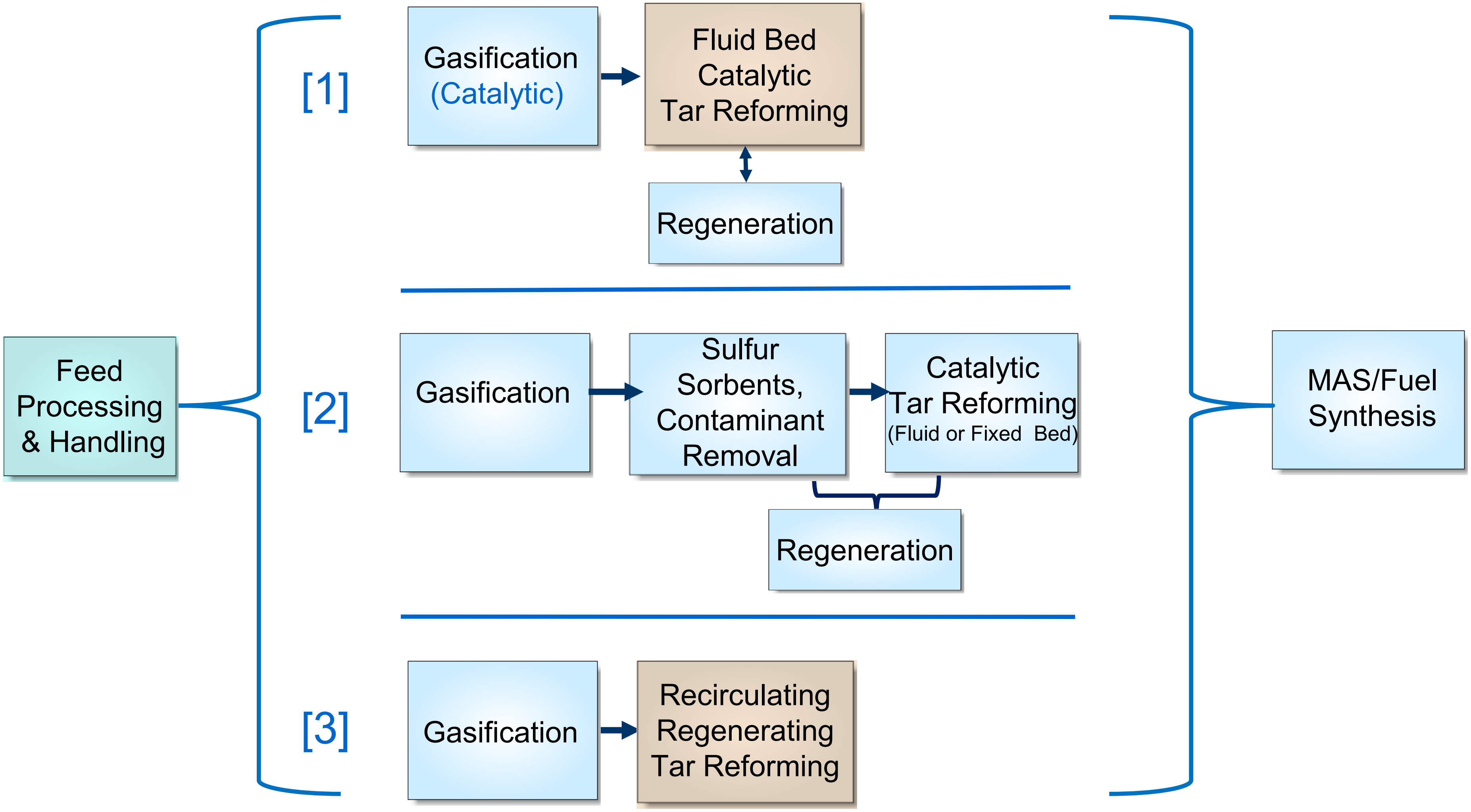
- **Identify and benchmark** the state of the art in tar reforming catalysts and sulfur sorbents
- **Identify and develop** candidate catalysts and sorbents with potential for improved performance
- **Provide performance information** for technoeconomic modeling of thermochemical biomass to ethanol processes
- **Validate** catalyst performance at the pilot scale
- **Down select/demonstrate optimized** syngas cleaning process for 2012 pilot scale EtOH production



2006
Project Start
Complete microactivity catalyst test system
2007
Develop attrition resistant reforming catalysts; optimize regeneration
Develop hot/warm gas sulfur sorbents
2008
Evaluate pilot scale tar reforming and regeneration
Computational modeling of reforming catalysts starts
2009
Recirculating regenerating reforming evaluated
Multi reactor system completed
2010
Evaluate new industrial reforming catalysts
Testing catalyst/sorbent combinations with raw syngas
'Spot check' review of syngas cleaning tasks
2012
'Down select and prepare 1000 kg of catalyst
200h Pilot scale demonstration of biomass to EtOH

2 –Progress

Biomass Syngas Cleaning Strategies



Process Intensification

2 –Progress

Catalyst Modeling

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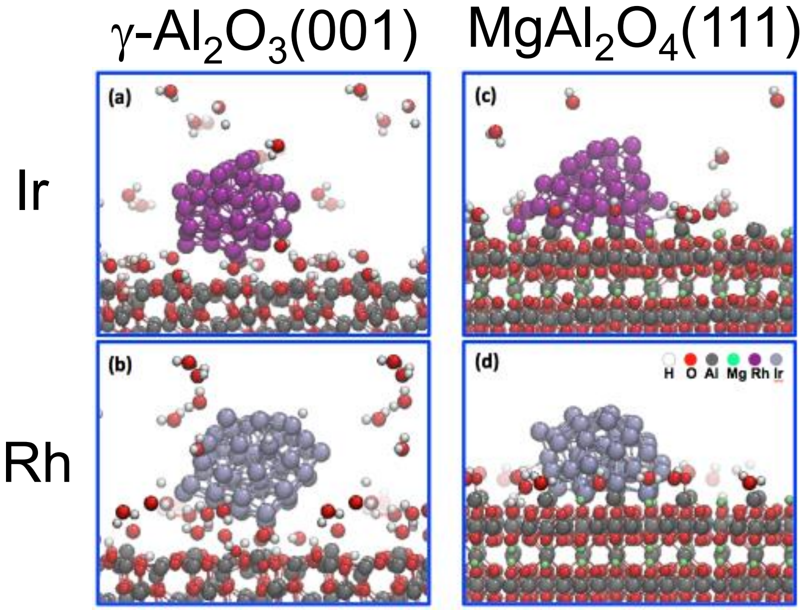


Cluster Binding Energy Per Metal Atom E_b

Surface	E_b(eV)
Ir/Al_2O_3	0.08
Ir/$MgAl_2O_4$	0.58
Rh/Al_2O_3	0.14
Rh/$MgAl_2O_4$	0.58

Rh and Ir clusters are weakly bound on γ-Al_2O_3, however strongly bound on $MgAl_2O_4$ spinel catalytic structure.

Accomplishment: *Ab-initio* work assisted in the development of new methane and tar reforming catalytic materials which offer excellent dispersion and resistance to high temperature sintering.

Catalyst formulations and tools for their development are being carried over into a new project (FY13) aimed at steam reforming the organics present in bio-oil aqueous phases

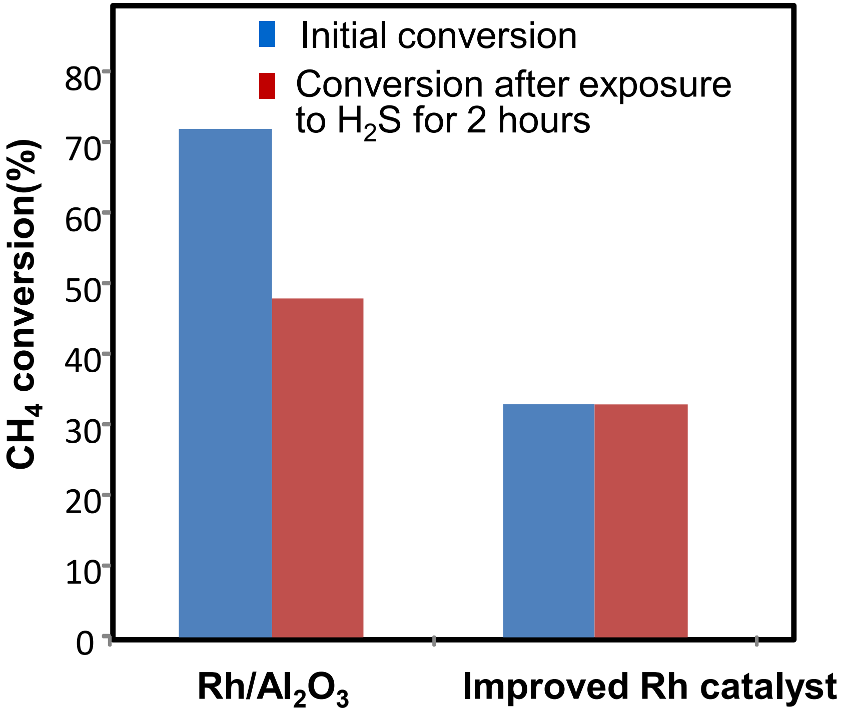
2 –Progress

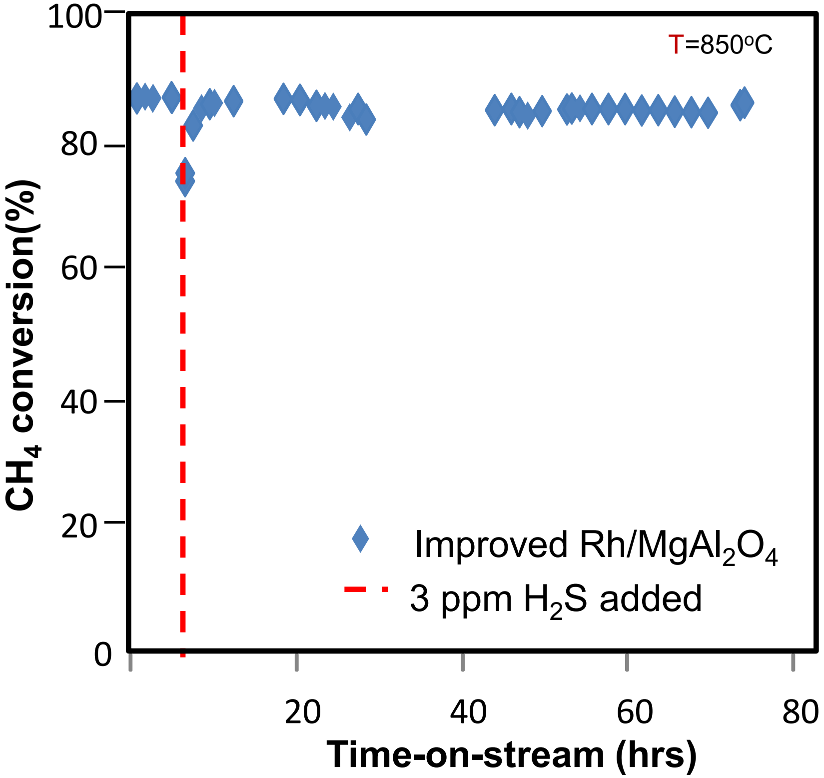
Reforming Catalyst Development

T=850^{o}C, GHSV= 110,000h^{-1}, simulant mix containing 5.7% CH_4

H_2S Tolerance: Pre and Post catalytic performance after reforming in 50 ppm H_2S for 2 hours shows activity recovery for the improved Rh-based catalyst

Catalyst Stability Evaluation: A further improved $Rh/MgAl_2O_4$ catalyst shows long term stability during H_2S exposure





Accomplishment: Improved H_2S tolerance and stability performance during H_2S exposure for improved $Rh/MgAl_2O_4$ catalyst

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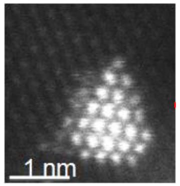
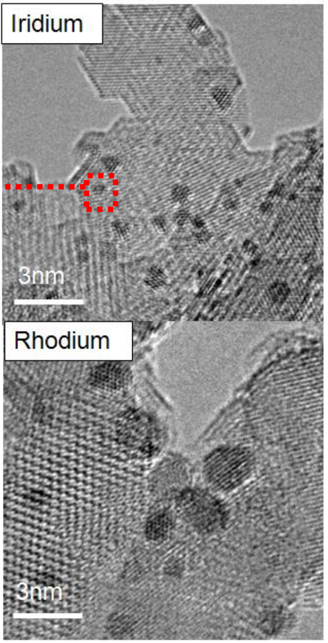
2 –Progress

Reforming Catalyst Development

- PGM-based catalysts developed as alternatives to conventional Ni-based
- Evaluated in the presence of tars, light hydrocarbons, and H_2S
- Rh and Ir-metals supported by a highly stable spinel structure exhibit:
  - **high dispersion** (1-3 nm metal cluster sizes)
  - **excellent activity** ➔ 13-17 X higher turnover (conversion/site/s) as compared to Ni
  - **resistance to thermal sintering and coking**
- HRTEM and XPS provided structural information related to size, shape, and the way the particles interact which supported *ab-initio* work that assisted in new methane and tar reforming catalytic materials





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2 –Progress

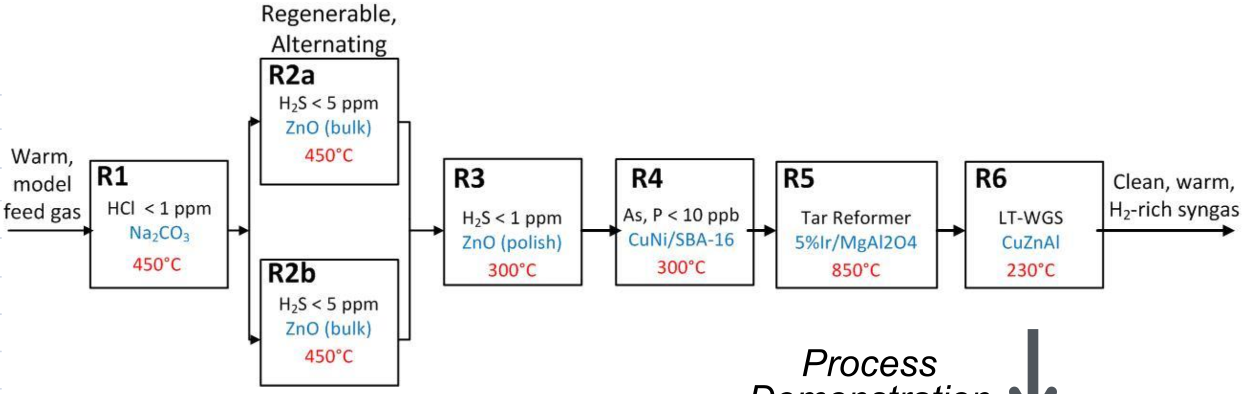
Warm gas cleanup

Thermally-efficient process developed for cleanup of tars and inorganics

Feed Composition:

Syngas and carriers		
H_2	16.5	%
CO	8.3	%
CO_2	8.3	%
CH_4	5.7	%
C_2H_4	0.8	%
H_2O	46.1	%
He	bal.	
N_2	0.8	%

Tar simulants		
Benzene	4,006	ppm
Naphthalene	492	ppm
Contaminants		
HCl	51	ppm
H_2S	1,065	ppm
AsH_3	6	ppm
NH_3	232	ppm



Process Demonstration

Accomplishments:

Reforming catalyst

- Complete conversion of tar & hydrocarbons
- Complete ammonia decomposition

High temperature sorbents

- S, Cl, As, P removal

Integrated process demonstration

- Stable operation for 175 hours

System currently being utilized for coal-gasification cleanup R&D (DOE-FE)

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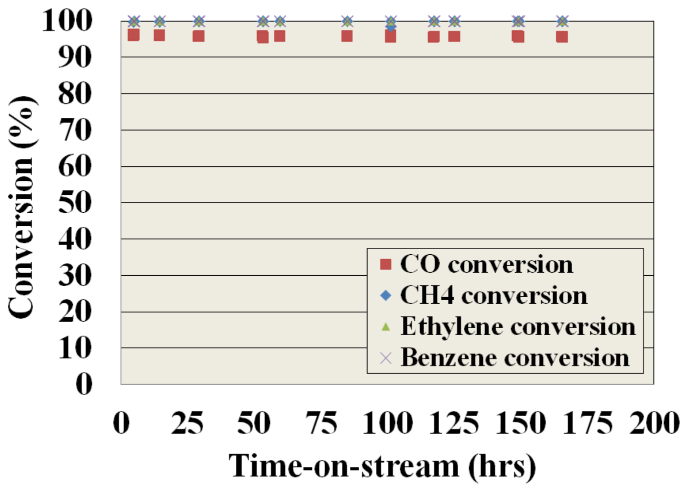
Water-gas-shift catalyst (R6)*

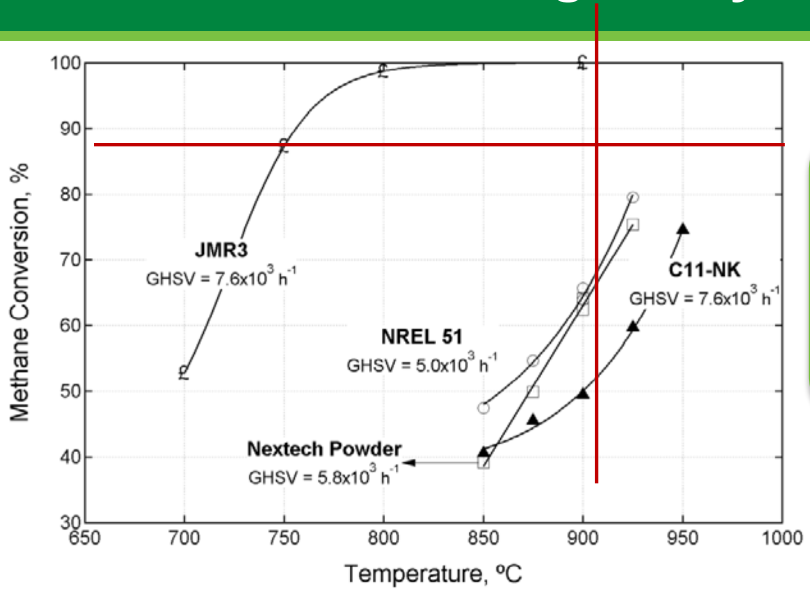
230°C, 1 atm, 8,000 hr^{-1}



*poison-sensitive catalyst

Progress

Down Select Reforming Catalyst



Commercial, emerging and NREL catalysts were evaluated for tar reforming performance:
- cost was a critical factor
- NREL 51 and JMR3 chosen for 1° and 2° polishing reforming

Oak Syngas

	Dual Stage Gasification Average mol-%
He	2.17
H_2	**35.64**
CH_4	12.52
CO	**19.17**
Propylene	0.15
Propane	0.02
CO_2	**26.13**
Acetylene	0.40
Ethane	0.36
Ethylene	3.43
H_2S	**39.00**

Tar concentrations (mg Nm^{-3}) measured via an on-line molecular beam mass spectrometer (MBMS).

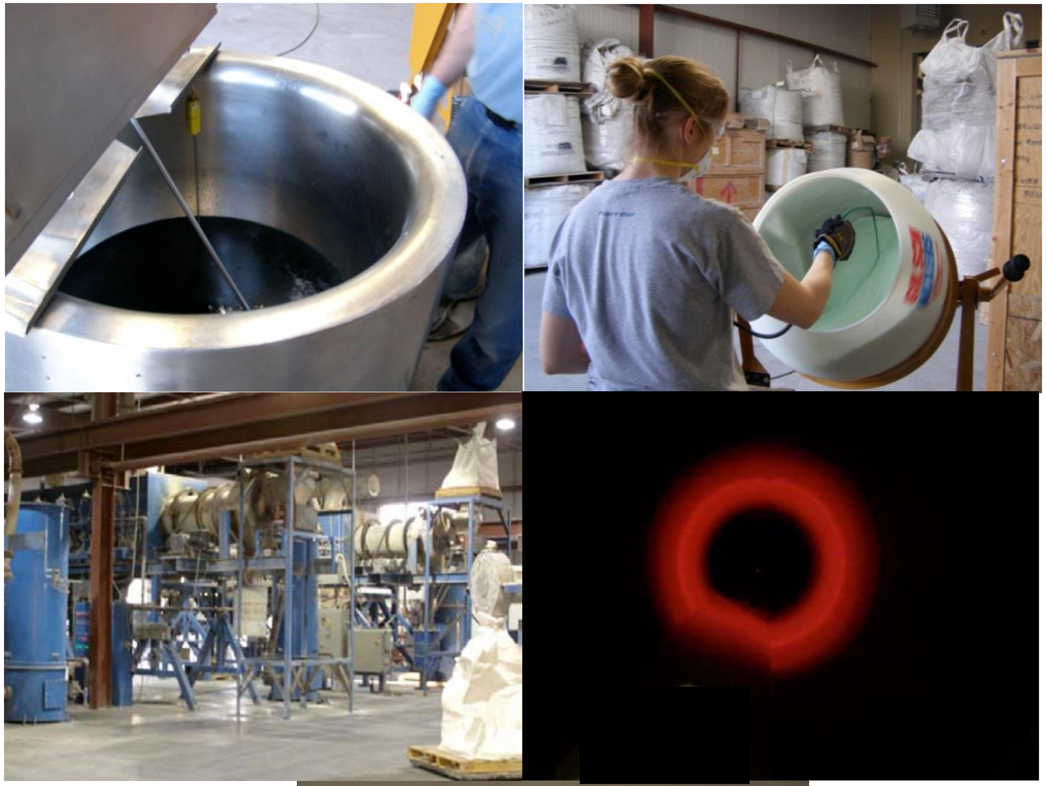
	Empty Reactor		NREL 51	Nextech	C11-NK	JMR3
Temperature, ° C	500	900	900	900	900	900
Benzene	1697	1747	0	2	18	0
Toluene	547	244	0	8	2	10
Phenol	79	7	6	1	1	10
Cresol	8	0	2	3	3	3
Naphthalene	581	488	1	0	3	4
Anthracene/Phenanthrene	89	89	26	11	42	7
Other Tar (m/z = 128)	825	305	22	1	45	70
Heavy Tar (m/z = 178)	101	76	62	1	101	91
Total Tar (m/z > 78)	2230	1209	119	26	196	195

All catalysts reformed all tars in dual stage syngas at 900ºC

Catalysis and Engineering Teams

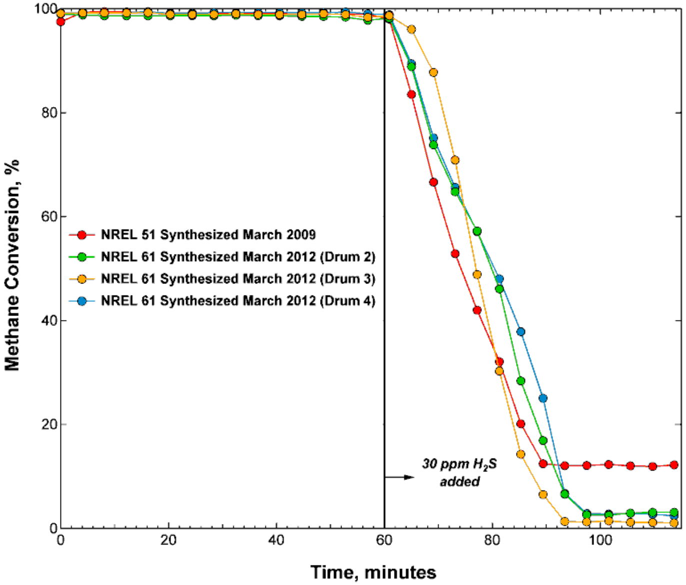
Progress

1000 kg Catalyst Preparation



	NiO Crystallite Size (nm)	H$_2$ Consumption (μmol/g)	
		TPR #1	TPR #2
Cat. 51	20	1158	957
Cat. 60 (average)	19	1240	1084
Cat. 60, Drum 1	21	1210	1099
Cat. 60, Drum 2	19	1241	992
Cat. 60, Drum 3	18	1241	1071
Cat. 60, Drum 4	18	1245	1203
Cat. 60, Drum 5	19	1264	1057

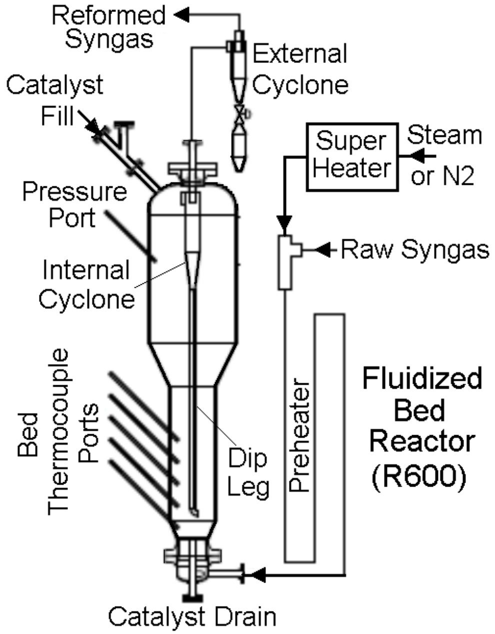
NiO crystal size determined by XRD and H$_2$ consumption from TPR.



Micro activity test (MATS) data for core samples 2-4 and catalyst 51. Methane conversion measured catalyst reforming activity at 850 °C with 30 ppmv of H$_2$S added after 60 minutes in oak simulated syngas.

Catalysis Team

Progress
Continuous Syngas Production

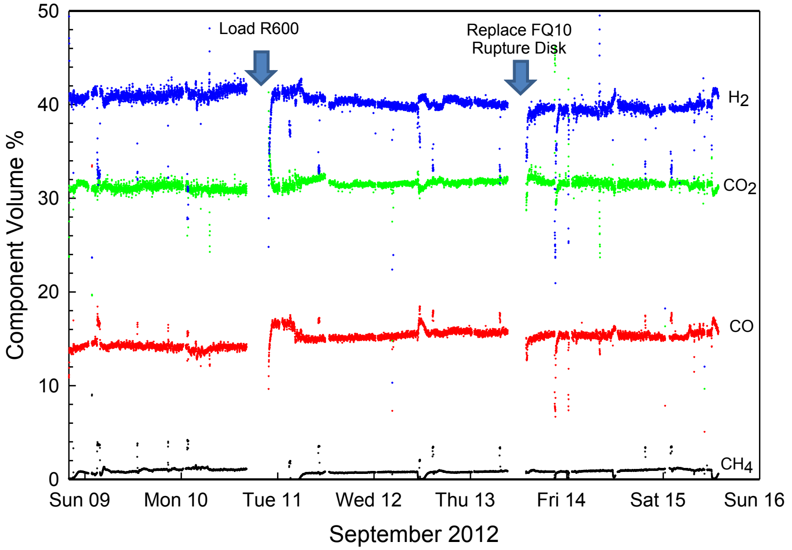


Clean syngas was produced for 200h TOS that met the technical conversion targets:

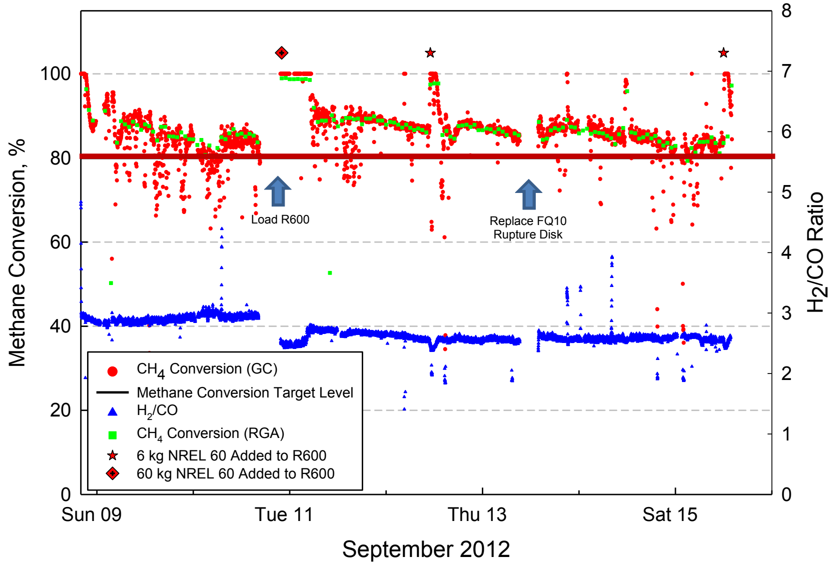
- 80% methane
- 99% benzene
- 99% total tars and HC

Representative tar species, concentration, and conversion

Concentrations (g-N^{-1}-m^3)	Post Gasifier	Post Reformer	Post Reformer Conversion (%).	Post PBR	Post PBR Conversion (%)
Argon (40)	6.37	3.57		3.57	
Benzene (78)	7.18	2.26	44	0.29	99
Toluene (92)	1.11	0.02	97	0.00	100
Phenol(94)	0.05	0.00	100	0.00	100
Naphthalene (128)	2.78	0.33	79	0.00	100
Anth, Phen (178)	0.92	0.04	92	0.00	100
"Other Tar" (as 128)	3.66	0.03	98	0.00	100
"Heavy Tar" (as 202)	4.70	0.01	100	0.00	100
"Total Tar (-78)"	13.21				

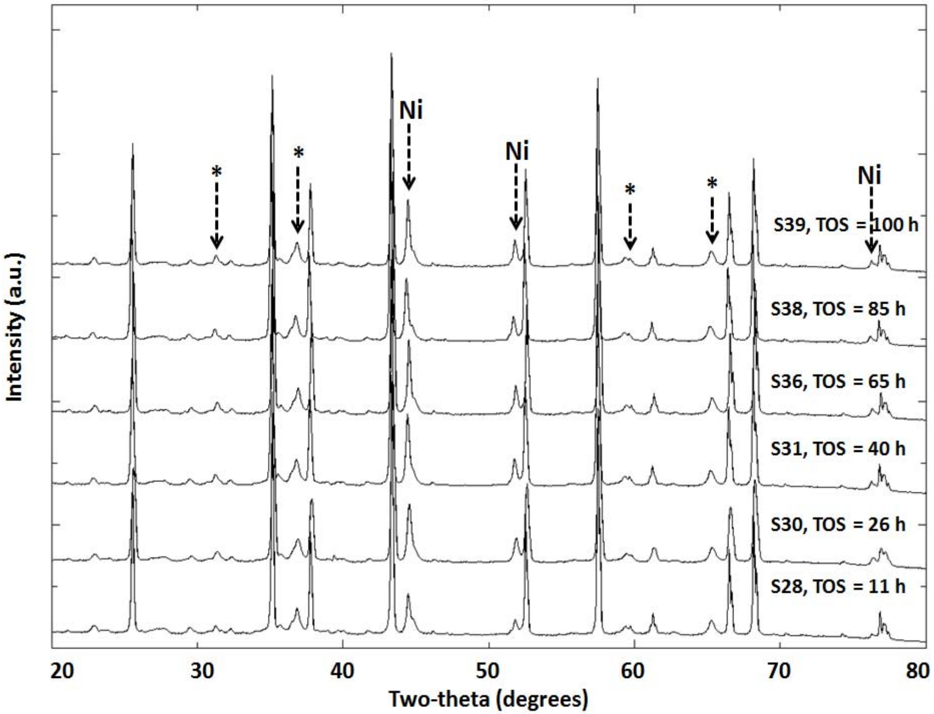


Average steady state conversions during integrated run



Progress

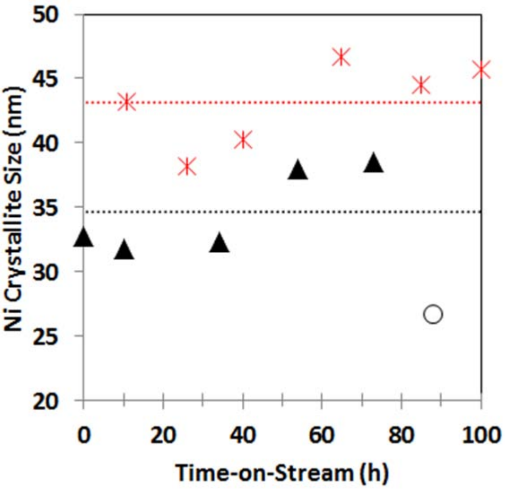
Post use characterization

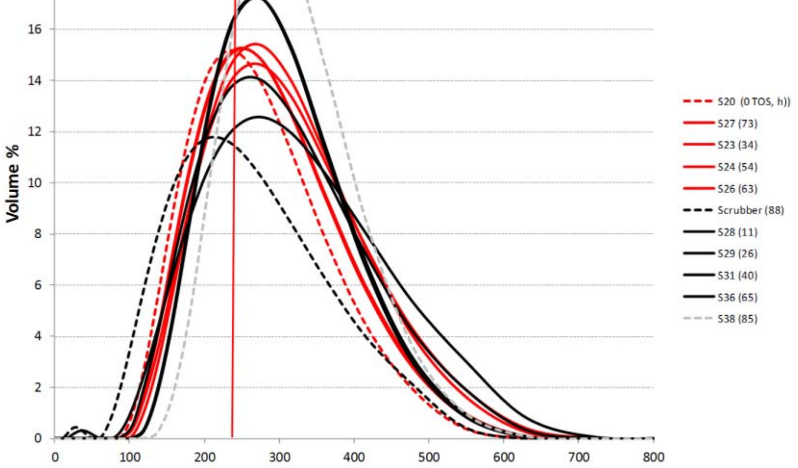


XRD patterns of NREL catalyst samples and scrubber contents collected during Run B (0-100h). Little change in Ni crystal structure.

Catalysis Team

Ni crystallite size determined from XRD analysis.



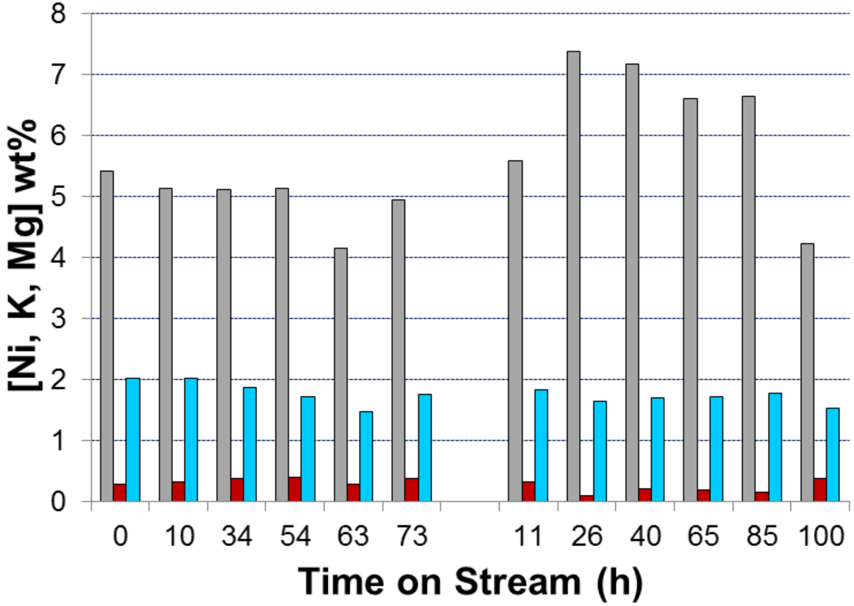


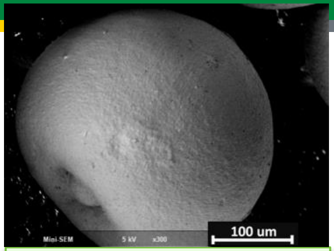
Particle size distribution of NREL catalyst samples and scrubber contents collected during Run B (0-100h). Little change in particle size with TOS.

Post use catalyst characterization indicates little change in catalyst morphology with TOS.
The reforming catalysts performed to meet the syngas quality targets

Progress

Post use characterization

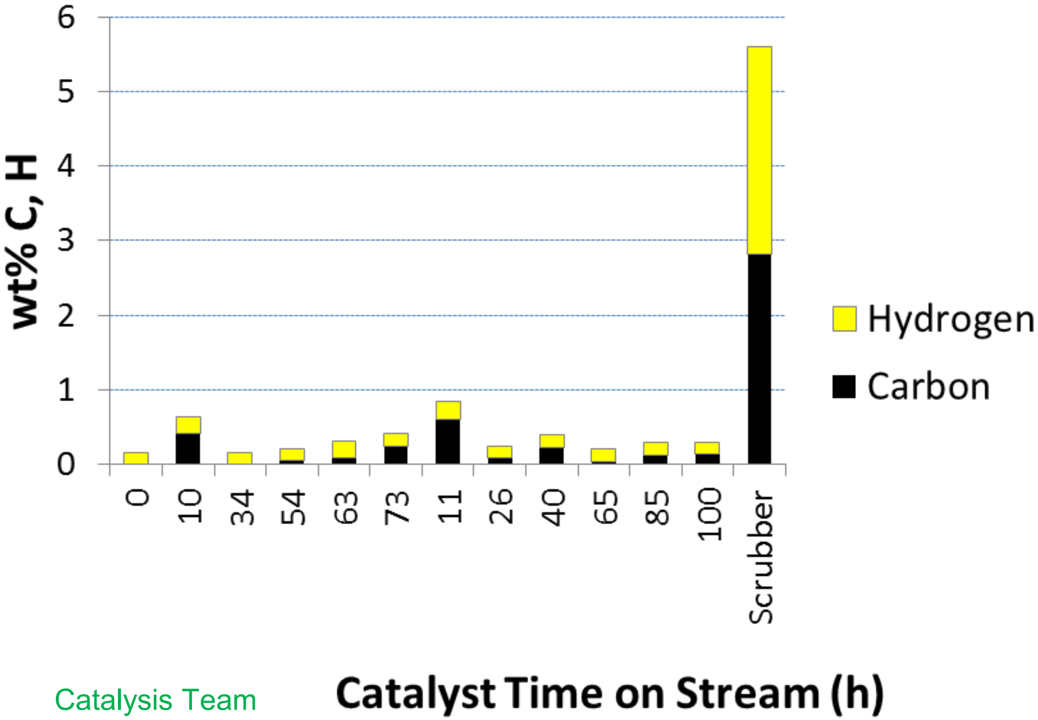




Tar reforming catalyst

Little change in morphology post reaction

CH analysis of catalyst and scrubber samples– distinguish between coke and char



The Ni-based reforming catalyst performed as expected with little change in morphology, composition or performance after > 200 TOS.

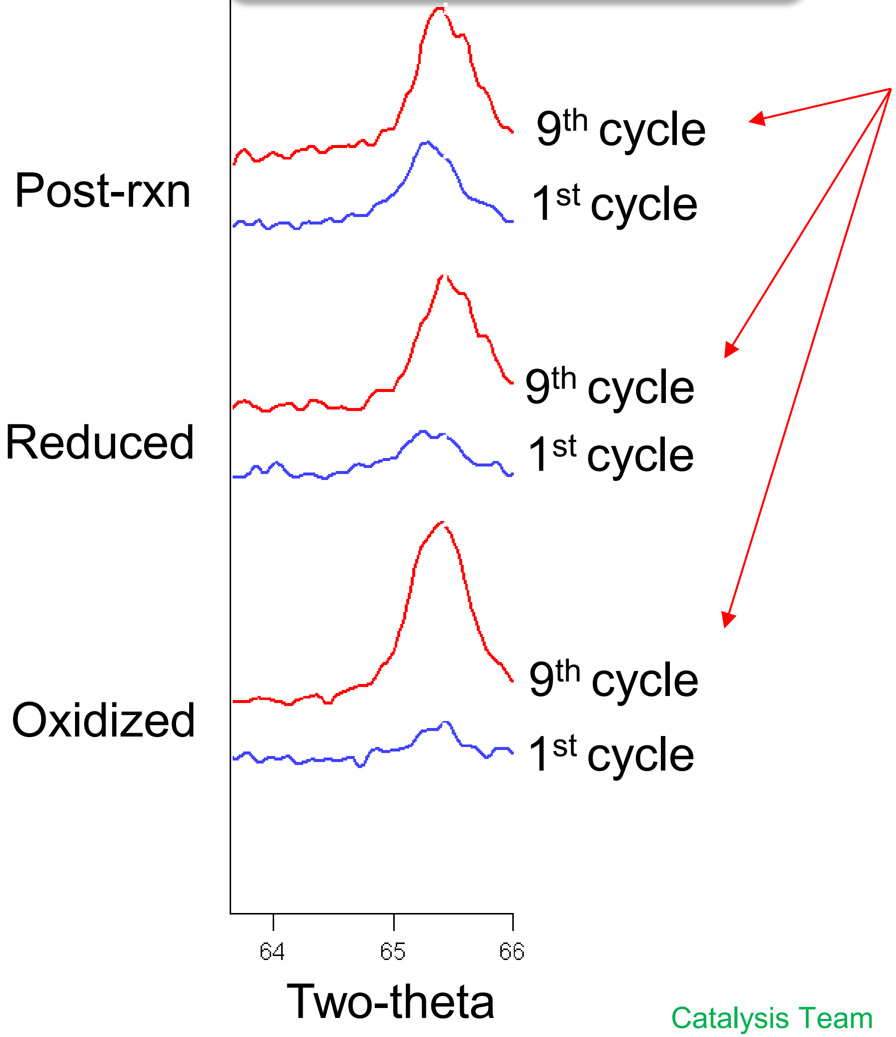
Catalyst formulations and tools for their development are being carried over into a new project (FY13) aimed at reforming the organics present in bio-oil aqueous phases to fuels/chemicals.

Catalysis Team

Progress

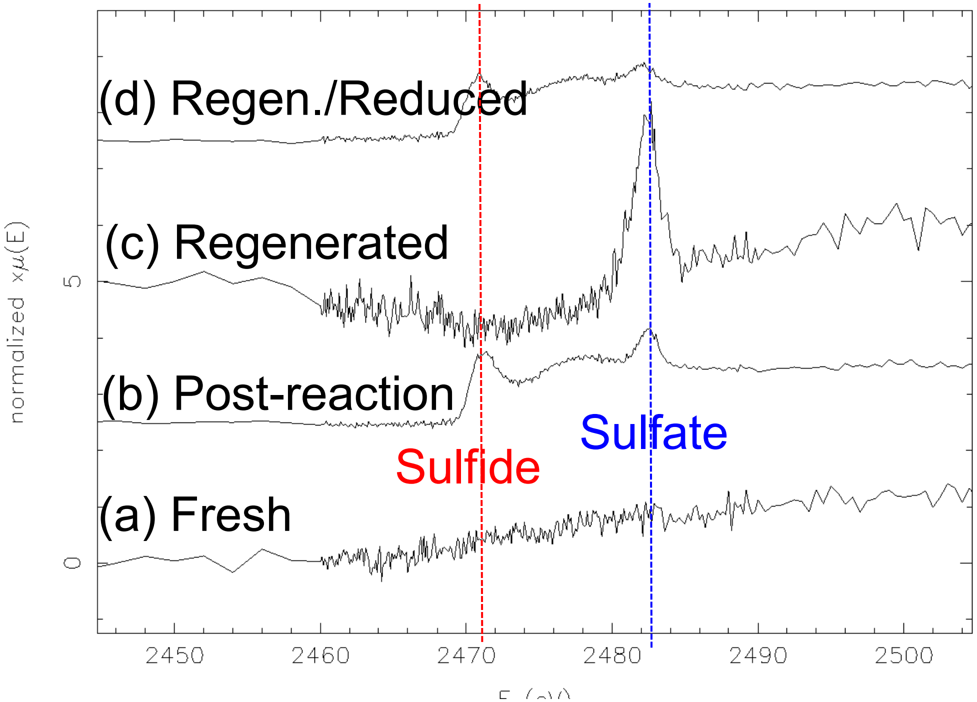
Post use characterization

XRD shows nickel oxidation to form $NiAl_2O_4$



$NiAl_2O_4$ content (intensity) increases with catalyst age

XANES shows sulfur retention and transformation from sulfides to sulfates during regeneration

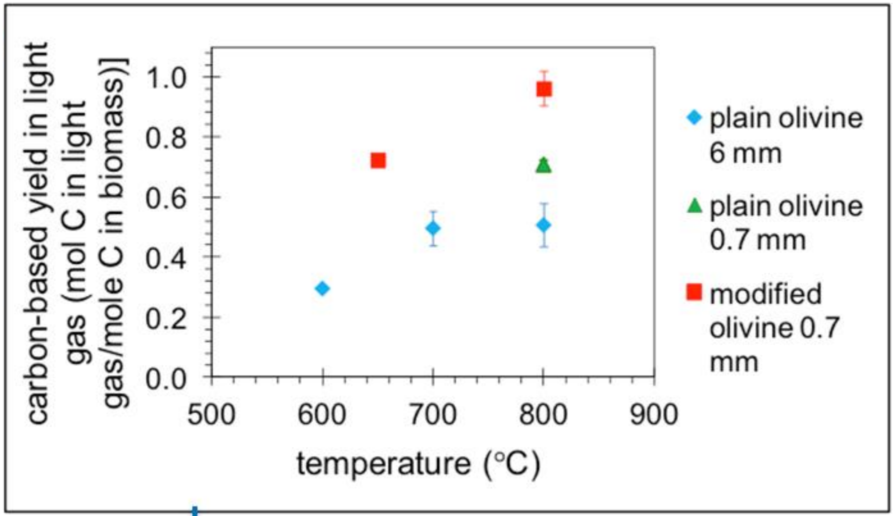


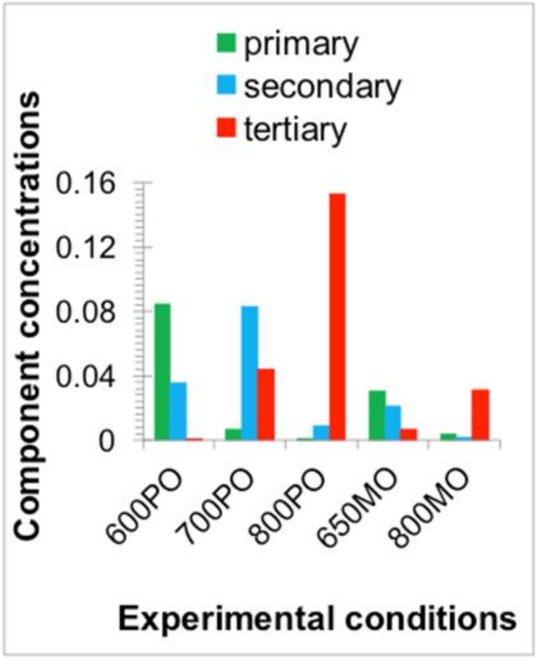
Catalysis Team

Progress

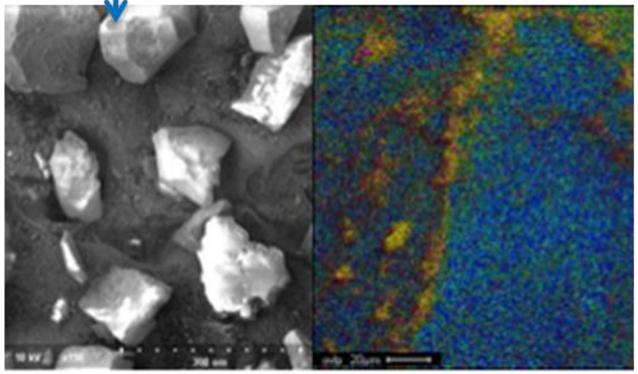
Catalytic Gasification

- Modified olivine with catalytic activities used in gasifier
- Directly produce clean syngas (process intensification).
- Improve carbon-based yield →
- Reduce tar by 70−80%





PO = plain olivine
MO = modified olivine
First 3 digits are experimental temperature



(a) Ni ceria olivine (b) EDS image of modified olivine surface: Ni (yellow), Ce (magenta), Mg (blue), Si (teal/green).

Catalysis Team

3 - 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."*
  - **Single and dual technology approaches** to cleaning biomass derived syngas for fuel synthesis demonstrated at the pilot scale for 200h TOS
  - Research and development **validated with the 2012 demonstration**
  - Research is **integrated with other core topic areas** including gasification and ethanol synthesis
- Project addresses three pathways:
  - M 4.12.3: Validate syngas cleanup performance
  - M 6.12.1: Produce mixed alcohols from syngas
  - M 6.12.3: Validate integrated process at pilot scale
- Project accomplishments in FY2011-13:
  - Provided **pilot scale information** for technoeconomic analysis and benchmarking of catalytic syngas cleaning
  - **Demonstrated improvements in catalyst and sorbent performance**
  - ***Demonstrated and validated a pilot scale integrated process to continuously produce biomass derived ethanol in 2012***

4 - Critical Success Factors

- Reforming Catalysts:
  - **Success:** Ability to reform methane, benzene, and total tars in biomass syngas to 80%, 99%, and 99% conversion, respectively while meeting $1.57/gal EtOH
  - **Challenge**: Maintaining the syngas cleaning targets for 200h in actual biomass syngas – successfully produced clean syngas in the 2012 demonstration – data open for industrial use

- Syngas cleaning and conditioning
  - **Success**: Demonstrated single or combined process to achieve methane, benzene and tar conversions in biomass derived syngas that meet the $1.57/gal cost target
  - **Challenge:** Achieving the cost targets with biomass syngas - successfully demonstrated a combined cleaning process at the pilot scale in 2012

Summary

- Hot syngas treatment to remove methane and tars is a key element in achieving DOE cost goals for mixed alcohols from biomass

- Alternative approaches comprised development and demonstration of 1) robust catalytic methane and tar reforming processes and 2) hot/warm gas adsorbent processes to reduce catalyst poisons

- Catalyst development (lab and industry-Johnson Matthey) has increased the tolerance and stability of reforming catalysts towards sulfur containing syngas with PGM metals

- A combination approach for syngas cleaning was selected and successfully demonstrated at the pilot scale for 200h TOS with oak derived syngas using a primary Ni based reforming catalyst followed by a PGM polishing catalyst

- On-going and future research is focused on continuing to improve catalyst performance and assessing other syngas cleaning requirements for DoD and industry applications

- NREL reforming catalyst licensed by 2 companies

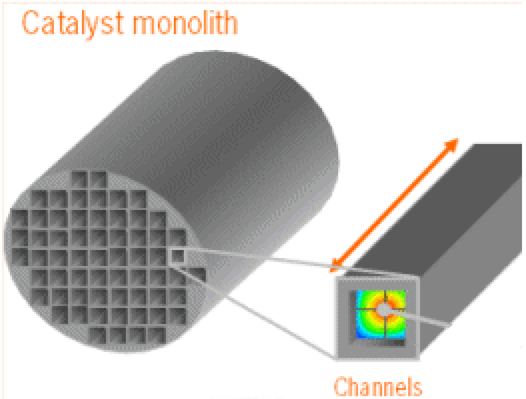
5. Future Work

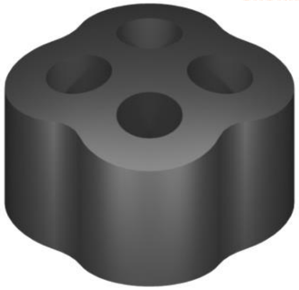
2 DOD waste to energy projects

- Lockheed Martin
- University of North Dakota

Use forward operating base (FOB) waste for feedstock

- Paper, plastics, packaging, food
- Gasify waste to syngas for genset operation
- NREL catalyst to be used for tar reforming (methane can be combusted)
  - Evaluating particulate and solid catalysts (monoliths)
  - Providing regeneration processes if needed
  - Providing post use catalyst characterization (identify and understand contaminant issues)





- Steam reforming aqueous bio-oil fractions
- Warm cleanup sorbent technology is being further developed for coal-gasification application (DOE-FE)
- Catalytic gasification to reduce tar formation at the source

Acknowledgements

NREL

Rich Bain
Whitney Jablonski
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Singfoong Cheah
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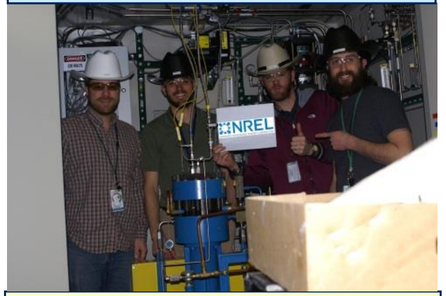
Luc Moens
Mark Davis
Marc Oddo
Joe Gardner
Mark Nimlos
Katherine Gaston
Steve Landin
Steve Deutch
Liz Rowsell
Andrew Steele
Rich Bolin
Danny Carpenter
Steve Phillips
Katie Gaston
Calvin Feik
Ray Hansen
Kristen Smith
Mike Sprague
David Isham
Adam Bratis

TCPDU Team

EtOH Team



Catalysis Team

PNNL

Robert Dagle
Mark Gerber
Karl Albrecht
Vanessa Lebarbier
Matthew Flake
Haiying Wan
Libor Kovarik
Roger Rousseau
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Liyu Li
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Jim Rainbolt
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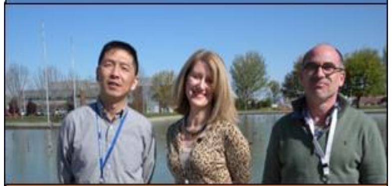
Computational Team



Experimental Team

Additional Slides

Responses to Previous Reviewers' Comments

- Comment (weakness) – It would be helpful to see more information on the project management plan
- Response – Project management plan in the milestone format will be included in the 2013 review

Project Management

Detailed Milestones for FY2011- FY2012

Due Date	Milestone Type	Milestone Title	Status
6/1/2011	D (NREL)	Conduct spectroscopic study of tar reforming catalysts used in H_2S-laden syngas	Complete
4/30/2011	D (NREL)	Development of catalyst modeling capabilities for prediction of emerging materials	Complete
6/30/2011	J (NREL)	Evaluate performance and regenerability of at least 3 reforming catalysts for biomass syngas conditioning	Complete
7/31/2011	E (	Optimize high capacity sulfur sorbents for H_2S removal from biomass derived syngas	Complete
8/31/2011	(NREL)	Optimize high capacity sulfur sorbents for H2S removal from biomass derives syngas	Complete
8/31/2011	D (NREL)	Kinetic/mechanistic study and rate law development of catalytic methane steam reforming	Complete
8/31/2011	D	Meet 2011 syngas cleaning technical targets via nickel based reforming catalyst development using model and actual (if available) syngas	Complete
9/15/2011	D	Determine the impact on syngas composition from catalytic gasification in a fluid bed research gasifier	Complete
9/30/2011	D (PNNL)	In the presence of benzene and naphthalene, maintain at least 70% methane conversion after 100 hrs time-on-stream with preferred catalyst	In progress
12/31/2011	D (NREL)	Assess factors controlling sulfur sequestration during pyrolysis and gasification	Complete
12/31/2011	D (NREL)	Characterize and evaluate Rentech reforming catalysts used in recirculating regenerating reforming tests	Complete
12/31/2011	D (NREL)	Select best syngas cleaning process and materials for 2012 pilot scale demonstration	Complete

Path to achieving thermochemical conversion strategic goals for biomass syngas cleaning through catalyst improvements and demonstration

Project Management

Detailed Milestones for FY2011- FY2012

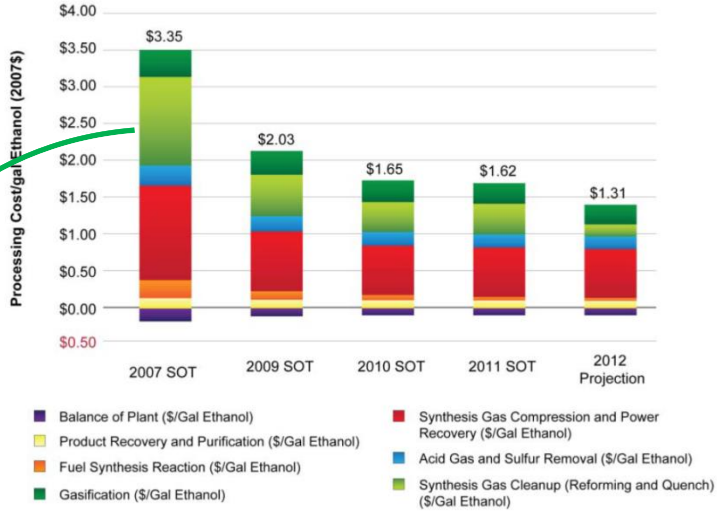
Due Date	Milestone Type	Milestone Title	Status
3/30/2012	D (NREL)	Prepare, characterize and evaluate 1000 kg of reforming catalyst for use in the 2012 demonstration	Complete
6/30/2012	E (PNNL)	Demonstrate 250 hour-long tests with both preferred and commercial Ni catalyst in the presence of benzene, naphthalene, and H_2S contaminant	In-progress
9/30/2012	D (PNNL)	Demonstrate 75% methane regeneration recovery of preferred catalyst after deactivation from tars and light hydrocarbons	In- progress
9/15/2012	D (NREL)	Characterize thermochemical biomass conversion catalysts pre-, post-reaction, and using in-situ techniques during regeneration	Complete
9/30/2012	D (NREL)	Demonstration of integrated process with pilot-scale fuel synthesis (Dow CRADA)	Complete
9/30/2012	J (NREL)	Demonstrate at pilot scale with IGFS task biomass syngas conditioning for cost competitive EtOH synthesis (200h)	Complete

Path to achieving thermochemical conversion strategic goals for biomass syngas cleaning through catalyst improvements and demonstration

Responses to Previous Reviewers' Comments

- Comment (suggestion) – The project needs to project contribution to cost of the syngas cleanup and conditioning technologies

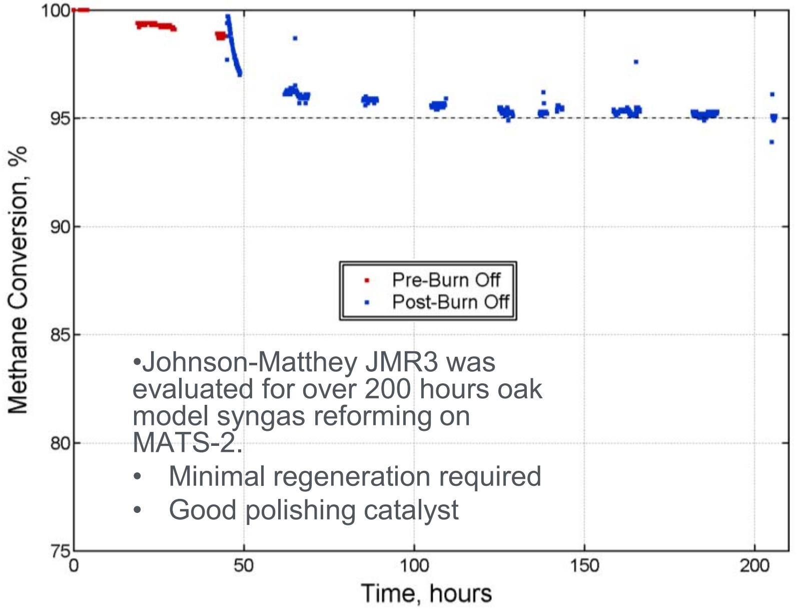
- Response – The SOT for thermochemical ethanol production from biomass derived syngas shows that syngas cleaning and conditioning comprises % of the overall process cost. The SOT report is available at: http://www.nrel.gov/biomass/pdfs/51400.pdf



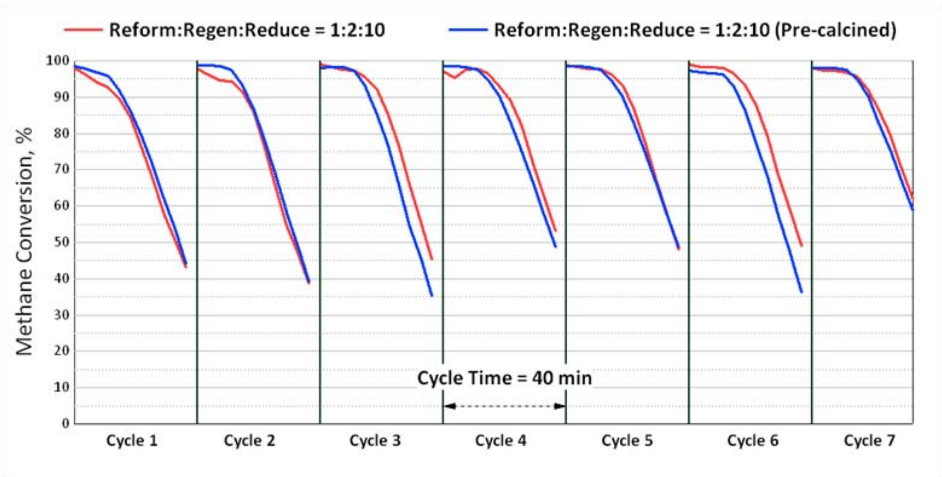
Project rationale:
Syngas cleaning significant process cost component

Responses to Previous Reviewers' Comments

- Comment (weakness) – Regarding catalyst life, when will hundreds to thousands of hours be demonstrated?
- Response – Increasing catalyst time on stream (life) work will be conducted in support of the 2012 demonstration at the labs scale and actually demonstrated at the pilot scale for hundreds of hours with the condition that NREL staff time is limited for conducting long term tests that span thousands of hours TOS. Lab scale tests comprise cycling the catalyst between reforming and regeneration cycles to assess both performance in closely modeled syngas and regeneration extent (milestone report available).



- Johnson-Matthey JMR3 was evaluated for over 200 hours oak model syngas reforming on MATS-2.
  - Minimal regeneration required
  - Good polishing catalyst



•: Consecutive model syngas reforming cycles in the MATS system at 900°C, at a GHSV of 119,000 h^{-1}, and S/C of 7.5 with catalyst 56. Reforming was conducted for 40 minutes with 53 ppmv of H_2S added ten minutes into the reforming cycle. Regeneration was conducted for 60 minutes at 850°C with the same steam content and a GHSV of 114,000 h^{-1}. Reduction conditions were 850° C for 300 minutes in 28% H_2 in inert.

Publications

1. Mei D, VMC Lebarbier, RJ Rousseau, VA Glezakou, KO Albrecht, L Kovarik, MD Flake, and RA Dagle "A Comparative Investigation of Benzene Steam Reforming over MgAl2O4 Spinel Supported Rh and Ir Catalysts." *ACS Catalysis* **(2013)** in press.

2. Howard CJ, RA Dagle, VMC Lebarbier, JE Rainbolt, L Li, and DL King. "Progress towards Biomass and Coal-Derived Syngas Warm Cleanup: Process Demonstration for Biomass Application." *Industrial and Engineering Chemistry Research* **(2013)** in revision.

3. Mei D, VA Glezakou, VMC Lebarbier, L Kovarik, H Wan, K Albrecht, RJ Rousseau, and RA Dagle. "Highly Active and Stable Ir/MgAl2O4 and Rh/MgAl2O4 Catalysts for Methane Steam Reforming: A Combined Theoretical and Experimental Study." In preparation for consideration in *Journal of Catalysis* **(2013)**.

4. Lebarbier VMC, K Albrecht, L Kovarik, H Wan, MD Flake, M Gerber, and RA Dagle. "Tar Reforming for Biomass-Derived Syngas Cleanup: Activity and Stability Comparisons among Noble Metals." In preparation for consideration in *Applied Catalysis A: General* **(2013)**.

5. Lebarbier VMC, Y Su, M Flake, MA Gerber, and RA Dagle. "Effect of the Rh particle size on the sulfur tolerance of Rh/Al2O3 catalysts for the steam reforming of biomass-derived methane." In preparation for consideration in *Catalysis Communications* **(2013)**.

6. Cheah, S., Olstad, J.L., Jablonski, W.S., and Magrini-Bair, K.A. Regenerable manganese-based sorbent for clean-up of simulated biomass-derived syngas. *Energy and Fuels*, 25: 379-387 **(2011)**.

7. Magrini-Bair, K. A., Jablonski, W. S., Parent, Y. O., Yung, M. M. **(2012).** Bench and Pilot Scale Studies of Reaction and Regeneration of Ni-Mg-K/Al2O3 for Catalytic Conditioning of Biomass Derived Syngas. Topic Catal. Vol. 55, pp. 209-217.

8. Parent, Y. O., Magrini-Bair, K. A., Landin, S. M., and Ritland, M. A**.(2011).** Attrition Resistant Fluidizable Reforming Catalyst. US Patent 7,915,196.

9. Robert M. Baldwin, Kimberly A. Magrini-Bair, Mark R. Nimlos, Perrine Pepiot, Bryon S. Donohoe, Steven D. Phillips. Current Research on Thermochemical Conversion of Biomass at the National Renewable Energy Laboratory. *Applied Catalysis B: Environmental* 115–116 **(2012)** 320–329.

10. M. M. Yung, S. Cheah, K. A. Magrini-Bair, J. N. Kuhn, "Transformation of sulfur species during steam/air regeneration on a Ni biomass conditioning catalyst," *ACS Catalysis* 2 **(2012)** 1363-1367.

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11. Dutta, A.; Cheah, S.; Bain, R.; Feik, C.; Magrini-Bair, K.; Phillips, S. Integrated Process Configuration for High-Temperature Sulfur Mitigation during Biomass Conversion via Indirect Gasification. *Industrial & Engineering Chemistry Research* 51(24):8326–33 (2012), DOI: 10.1021/ie202797s

12. A.M. Robinson, M.E. Gin, M.M. Yung, "Methane steam reforming kinetics on a Ni/Mg/K/Al2O3 catalyst," accepted in *Topics in Catalysis* (2013).

13. M. Rangan, M.M. Yung, J.W. Medlin, "NiW and NiRu bimetallic catalysts for ethylene steam reforming: Alternative mechanisms for sulfur resistance," *Catalysis Letters* 142 (2012) 718-727.

14. M. Rangan, M.M. Yung, J.W. Medlin, "Experimental and computational investigations of sulfur-resistant bimetallic catalysts for reforming of biomass gasification products," *Journal of Catalysis* 282 (2011) 249-257.

15. Singfoong Cheah, Yves Parent, Whitney S. Jablonski, Todd Vinzant, and Jessica L. Olstad. "Manganese and ceria sorbents for high temperature sulfur removal from biomass-derived syngas—the impact of steam on capacity and sorption mode," Fuel, 2012, 97, 612-620.

16. Q. Xu, S. Cheah, and Y. Zhao. (2013) Initial reduction of the NiO(100) surface in hydrogen. *The Journal of Chemical Physics* (submitted).

17. S. Cheah, S. Czernik, R.M. Baldwin, K. Magrini-Bair, J.E. Hensley. Catalysts and sorbents for thermochemical conversion of biomass to renewable biofuels--material development needs. In *Materials Challenges in Alternative and Renewable Energy;* Wicks, G., Simon, J., Zidan, R., Lara-Curzio, E., Adams, T., Zayas, J., Karkamkar, A., Sindelar R., and Garcia-Diaz, B., Eds.; *Ceramic Transactions*; Wiley, Vol. 224; pp 349–362 (2011), DOI: 10.1002/9781118019467.ch34.

18. S. Cheah, K.R. Gaston, Y. Parent, M.W. Jarvis, T.B. Vinzant, K.M. Smith, N. Thornburg, M.R. Nimlos, K.A. Magrini-Bair. Nickel cerium olivine catalyst for catalytic gasification of biomass. *Applied Catalysis B,* 134-135: 34-45 (2013) DOI:10.1016/j.apcatb.2012.12.022.

19. Singfoong Cheah, Jessica L. Olstad, Whitney S. Jablonski, and Kimberly A. Magrini-Bair. Regenerable Manganese-Based Sorbent for Cleanup of Simulated Biomass-Derived Syngas. Energy and Fuels, 2011, 25(1), 379-387.

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1.Kovarik L, RA Dagle, H Wan, JH Kwak, BC Kabius, CM Wang, S Thevuthasan, and CHF Peden. "Atomic Level Characterization of Transition-metal Catalytic Clusters and Nanoparticles on MgAl2O4 Substrate." SEDP Program, Richland, WA, May 2011.

2.Dagle RA, H Wan, L Kovarik, MD Flake, Y Su, KO Albrecht, DL King, JF White, and MA Gerber. "Noble-Metal Based Catalysts for Biomass-Derived Methane and Tar Reforming." North American Catalysis Society Meeting, Detroit, MI, June 2011.

3.Kovarik L, CM Wang, SVNT Kuchibhatla, RA Dagle, JH Kwak, BC Kabius, J Szanyi, and CHF Peden. "Probing Atomic and Electronic Structure of Catalysts by Combination of In-situ and Ex-situ Chemical Imaging ." Chemical Imaging Initiative Annual Review, Richland, WA , July 2011.

4.Kovarik L, BC Kabius, CM Wang, S Thevuthasan, H Wan, RA Dagle, JH Kwak, and CHF Peden. "Atomic Level Characterization of Transition-metal Catalytic Clusters and Nanoparticles on MgAl2O4 Substrates." Microscopy and Microanalysis 2011, Nashville, TN, August 2011.

5.Albrecht KO, RA Dagle, MA Gerber, MD Flake, DL King, and L Kovarik. "Noble-Metal Based Catalysts for Biomass-Derived Tar and Methane Reforming ." American Chemical Society Fall National Meeting, Denver, CO, August 2011.

6.Kovarik L, I Arslan, CM Wang, SVNT Kuchibhatla, JH Kwak, J Szanyi, RA Dagle, CHF Peden, and ND Browning.“ Probing Atomic And Electronic Structure Of Catalysts And Energy Storage Materials By Combination Of In-Situ And Ex-Situ Chemical Imaging ." Chemical Imaging Initiative Annual Review, Richland, WA, July 2012.

7.Lebarbier VMC, RA Dagle, D Mei, KO Albrecht, L Kovarik, VA Glezakou, and RJ Rousseau. “Highly active Ir/MgAl2O4 and Rh/$MgAl_2O_4$ catalysts for tar and methane steam reforming” American Chemical Society Spring National Meeting, New Orleans, LA, April 2013.

8.Mei D, VMC Lebarbier, RJ Rousseau, VA Glezakou, KO Albrecht, L Kovarik, MD Flake, and RA Dagle. "Benzene Steam Reforming over the MgAl2O4 Supported Rh and Ir Catalysts: A Combined Experimental and Theoretical Study ." To be orally presented at the North American Catalysis Society Meeting, Louisville, KY, June 2013.

9.Albrecht KO, RA Dagle, Lebarbier VMC, D Mei, VA Glezakou, L Kovarik, and RJ Rousseau. 2012. "Highly Active and Stable Ir/$MgAl_2O_4$ and Rh/MgAl2O4 Catalysts for the Steam Reforming of Tars and Methane: A Combined Theoretical and Experimental Study." To be orally presented at the North American Catalysis Society Meeting, Louisville, KY, June 2013.

10. J. Olstad, K. Magrini, R. Boardman, G. Gresham. “Determining and Addressing Feedstock Variability for Thermochemical Biomass Conversion”, presented in the session: Feedstock, Supply Chain, and Logistics of Forest Biorefineries, AIChE’s Annual Meeting, October 16-21, 2011, Minneapolis, MN.

Presentations

11. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, "Sulfur Species During Deactivation and Regeneration of Ni-Based Catalysts Used for Conditioning Biomass-Derived Syngas," American Institute of Chemical Engineers Annual Meeting, Minneapolis, MN, October 2011.
12. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, "Sulfur Removal, Retention, and Transformation During Steam Regeneration of Nickel Tar Reforming Catalysts," Western States Catalysis Club Annual Meeting, Boulder, CO, March 2012.
13. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, "Removal and transformation of sulfur species during regeneration of poisoned nickel biomass conditioning catalysts," 243rd American Chemical Society, San Diego, CA, March 2012.
14. W.S. Jablonski, S.D. Phillips, K.A. Magrini, M.M. Yung, K.R. Gaston, "Evaluation of Industrial Catalysts Performance on the Pilot-Plant Scale," American Institute of Chemical Engineers Annual Meeting, Minneapolis, MN, October 2011.
15. K. Magrini, M.M. Yung, J. Olstad, "Impact of Biomass Feedstock on Syngas Composition," International Biomass Conference & Expo, Denver, CO, April 2012.
16. K. Magrini, W. Jablonski, M. Yung, J. Olstad, Y. Parent, Producing Clean Biomass Syngas for Fuel Synthesis: Reforming Catalyst Development, World Renewable Energy Forum, May 12, 2012, Denver, CO.
17.. Kimberly Magrini-Bair and Singfoong Cheah. Attrition Resistant Fluidizable Reforming Catalyst. Oral presentation on behalf of Dr. Magrini at the Colorado Center for Biorefining and Biofuels (C2B2) Semi-Annual Meeting, March 20–21, 2012.
18. Singfoong Cheah, Katherine Gaston, Yufeng Zhao, Qiang Xu, Mark Nimlos, Kimberly Magrini-Bair. "Development of catalyst for catalytic gasification of biomass." Poster presentation at the Gordon Research Conference on Catalysis, New London, NH, June 24–29, 2012.
19. K. Magrini, M. Yung, W. Jablonski, J. Olstad, Y. Parent, Producing Clean Syngas via Catalytic Reforming for Fuels Production, ACS National Meeting, Catalysis for Renewable Energy Session, Philadelphia, PA, August 2012.

Presentations

20. K. Magrini, W. Jablonski, Y. Parent, M. Yung, J, Olstad. Developing sulfur tolerant reforming catalysts for biomass syngas cleaning. Tcbiomass 2011, the International Conference on Thermochemical Conversion Science, September 27-30, 2011, Chicago, IL.
21. K. Magrini-Bair. Process Engineering: Catalysis and Thermochemical Biomass Conversion. Colorado Center for Biofuels and Biorefining Short Course, March 9, 2011, Golden, CO.
22. K. Magrini, M. Gerber and R. Dagle. Catalyst Fundamentals, Thermochemical Conversion Platform Review, February 18, 2011, Denver, CO.
23. K. A. Magrini and Mark. R. Nimlos, Tar Cracking and Fuel Synthesis, Thermochemical Conversion of Biomass – 2012, October 24, 2012, Raleigh, NC.
24. K. A. Magrini, AAAS Series Cutting Edge: Biofuels, University of California Berkeley, October 24, 2012, Berkeley, CA.
25. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, "Understanding sulfur poisoning and regeneration of nickel biomass conditioning catalysts using X-ray absorption spectroscopy," ACS National Meeting, Catalysis Division, New Orleans, LA, April 2013.
26. M.M. Yung, "Thermochemical Biomass Catalytic Conversion R&D at NREL," Georgia Institute of Technology Chemical Engineering Department Seminar, Atlanta, GA, February 2013.
27. J.N. Kuhn, M.M. Yung, K.A. Magrini, S. Cheah, "Spectroscopic characterization of sulfur poisoning and regeneration for Ni-based biomass conditioning catalysts," American Institute of Chemical Engineers Annual Meeting, Pittsburgh, PA, October 2012.
28. M.M. Yung, K.A. Magrini, "Producing Clean Syngas via Catalytic Reforming for Fuels Production", ACS National Meeting, Catalysis for Renewable Energy Session, Philadelphia, PA, August 2012.
29. S. Cheah, M. Yung, K. Magrini, "Sulfur speciation in biochar and sulfur transformation in biomass conditioning catalysts," 2012 LCLS/SSRL Annual Users' Meeting & Workshops, SLAC National Accelerator Laboratory, Menlo Park, CA, October 2012

Presentations

30. M.M. Yung, K.A. Magrini, “Impact of Biomass Feedstock on Syngas Composition,” International Biomass Conference & Expo, Denver, CO, April 2012.
31. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, “Sulfur Removal, Retention, and Transformation During Steam Regeneration of Nickel Tar Reforming Catalysts,” Western States Catalysis Club Annual Meeting, Boulder, CO, March 2012.
32. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, “Removal and transformation of sulfur species during regeneration of poisoned nickel biomass conditioning catalysts,” 243rd American Chemical Society, San Diego, CA, March 2012.
33. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, “Sulfur Species During Deactivation and Regeneration of Ni-Based Catalysts Used for Conditioning Biomass-Derived Syngas,” American Institute of Chemical Engineers Annual Meeting, Minneapolis, MN, October 2011.
34. W.S. Jablonski, S.D. Phillips, K.A. Magrini, M.M. Yung, K.R. Gaston, “Evaluation of Industrial Catalysts Performance on the Pilot-Plant Scale,” American Institute of Chemical Engineers Annual Meeting, Minneapolis, MN, October 2011.
35. M.M. Yung, W.S. Jablonski, K.A. Magrini, “Characterization of promoted, Ni-based, tar reforming catalysts”, Colorado Center for Biorefining and Biofuels Annual Review Meeting, Golden, CO, March 2011.
36. Y. Zhao, Q. Xu, and S. Cheah. “Deoxygenation of lignin-derived monomeric compounds: computational and experimental results.” Abstract accepted for poster presentation at the 23rd North American Catalysis Society Meeting, Louisville, KY, June 2–7, 2013.
37. Y. Zhao, Q. Xu, and S. Cheah. “Modeling hydrogen reduction and hydrodeoxygenation of oxygenates.” Invited oral presentation at the Theory and Simulation in Energy and Fuel Production and Utilization special session, Division of Energy and Fuels, 245th ACS National Meeting, New Orleans, LA, April 7–11, 2013.
38. M. Rangan, M.M. Yung, J.W. Medlin, “Experimental and computational investigations of bimetallic catalysts for reforming of biomass tars,” North American Catalysis Society Meeting, Detroit, MI, June 2011.
39. M.M. Yung, “Biomass Conversion Research for Biofuels Production,” Colorado Center for Biorefining and Biofuels Seminar, Golden, CO, July 2011.

Presentations

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41. H.A. Fuster, M.E. Gin, M.M. Yung, “Characterization of a novel catalyst for methane-steam reforming,” Colorado Center for Biorefining and Biofuels Undergraduate Research Poster Session, Boulder, CO, August 2011.
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43. S. Cheah, D. Carpenter, S. Malone, C. Feik, M. Yung, and J. Olstad. “Sulfur speciation and partitioning during thermochemical conversion of cellulosic biomass to biofuel.” Oral presentation at the Biomass and Liquid Fuels, Advancement in RE Energy special technical session, World Renewable Energy Forum, Denver, CO, May 13–17, 2012.
44. K. Barthelemy, Y. Parent, and S. Cheah. “Effects of Synthesis Parameters on the Structure and Properties of a Modified Olivine Catalyst.” Oral presentation at the Western States Catalysis Club Annual Symposium, Boulder, CO, March 9, 2012.
45. S. Cheah, W. Jablonski, Y. Parent and K. Magrini-Bair. “Sulfur Removal from Biomass Syngas at High Temperatures: the Impact of Steam and Other Process Parameters.” Poster presentation at the TCBiomass Conference, Chicago, IL, September 27–30, 2011.
46. S. Cheah and K.R. Gaston. “Catalytic Gasification of Biomass for Syngas Generation.” Oral presentation at the Division of Fuel Chemistry special symposium on Green Chemistry for Sustainable Production of Fuels, Chemicals, and Energy, the 242nd American Chemical Society National Meeting, Denver, CO, August 28-September 1, 2011.
47. K. Barthelemy and S. Cheah. “Effects of Synthesis Parameters on Structure and Properties of a Modified Olivine Catalyst.” Summer intern poster presentation, NREL, August 18, 2011.
48. S. Cheah and K.R. Gaston. “Catalytic Gasification of Biomass for Syngas Generation.” Oral presentation at the 22nd North American Catalysis Society Conference, Detroit, MI, June 5-10, 2011.

Supplemental Information

Reformer Performance

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.

A. Dutta and G. Apanel