2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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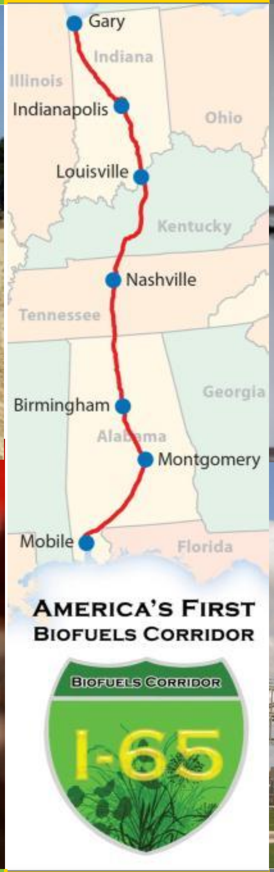

Integrated Gasification and Fuel Synthesis WBS# 3.2.5.7

Stephen Phillips and Mark Davis

May 22, 2013

Technology Area Review: Gasification

Organizations:
National Renewable Energy Laboratory

Goal Statement

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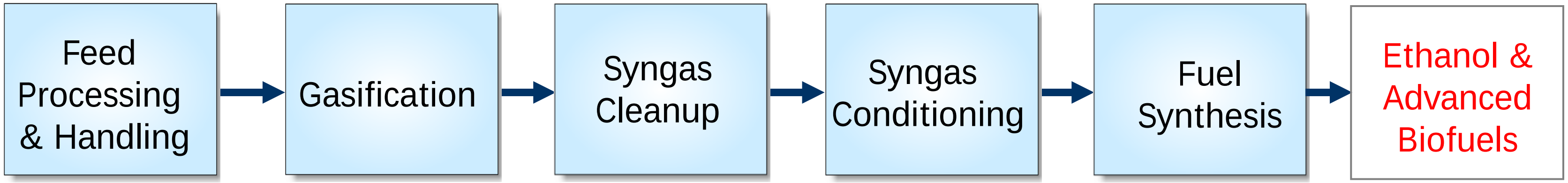
Project Goal:

Demonstrate integrated production of cost competitive ethanol from mixed alcohols produced from biomass-derived syngas at pilot scale

Objectives

- Integrate unit operations for gasification, reforming, conditioning and fuels synthesis to characterize and demonstrate performance
- Evaluate the performance of all unit operations using state-of-the-art analytical techniques to quantify key contaminants and gases
- Validate syngas quality by operating integrated gasification, cleanup and fuel synthesis process
- Provide performance input to Techno-economic Analysis (TEA) models



Quad Chart Overview

Timeline

- Project start: 2002
- Project end: 2012
- 100% complete

Budget

Funding for FY 2012 $2.1MM
Funding for FY 2013 $0.0 MM
FY 2014 projected budget $1.0MM
Average yearly funding $1.8MM (since 2007)

Barriers

- Tt-C: Gasification of Wood and Herbaceous Feedstocks
- Tt-F Gas Cleanup and Conditioning
- Tt-H Validation of Syngas Quality
- Tt-K Thermochemical Process Integration

Partners

- Wasson ECE Instrumentation
- TDA Research Inc.
- UOP LLC

Project Overview

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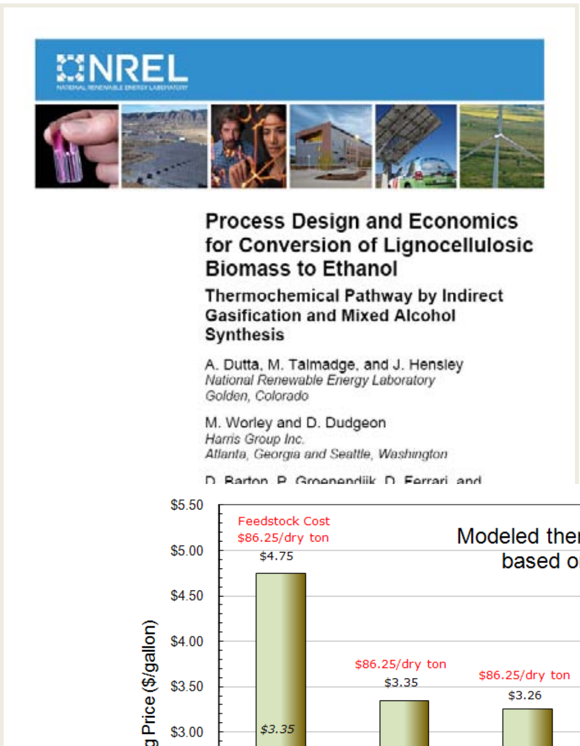
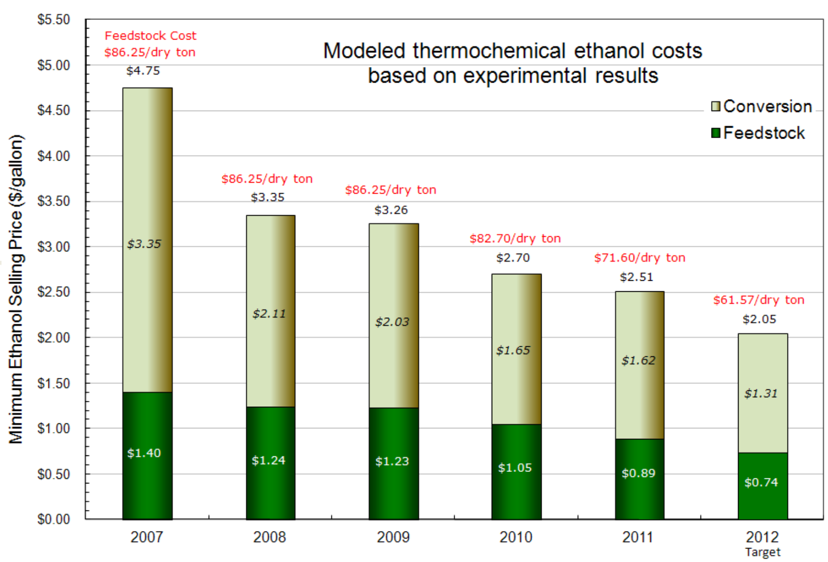
2002	**Project Start** — Project objective is to progress continually towards 2012 demonstration
	Developed tar sampling and analysis methods using Molecular Beam Mass Spec (MBMS)
2004	Installed Full Stream Reformer (catalytic fluidized bed reactor) for external partner and tested on biomass derived syngas. Reactor sent to partner's facility.
	Evaluated early NREL reforming catalyst in slipstream FBR reactor and TCPDU
	Installed new Full Stream Reformer (catalytic fluidized bed reactor) and continued reforming tests on biomass derived syngas.
2006	Evaluated impact of feedstock and operating conditions on gas composition and tar formation
2008	Achieved 15 hours of reforming with periodic batch regeneration on single batch of CAT 32b
	Achieved reforming conversion targets (56% methane conversion) with real syngas in Full Stream Reformer using single load of CAT 51 and batch-mode regeneration.
2010	Achieved 2012 continuous reforming conversion targets (80% methane conversion) slipstream reactor. Upgraded GC system and MS. Placed orders for balance of plant equipment.
	Evaluate new reforming catalysts from commercial companies. Pilot scale continuous reformer/regenerator, gas cleanup and synthesis equipment delivered and installed.
2012	**Demonstrate integrated biomass to fuels process at NREL TCPDU/TBPP**

1 - Approach



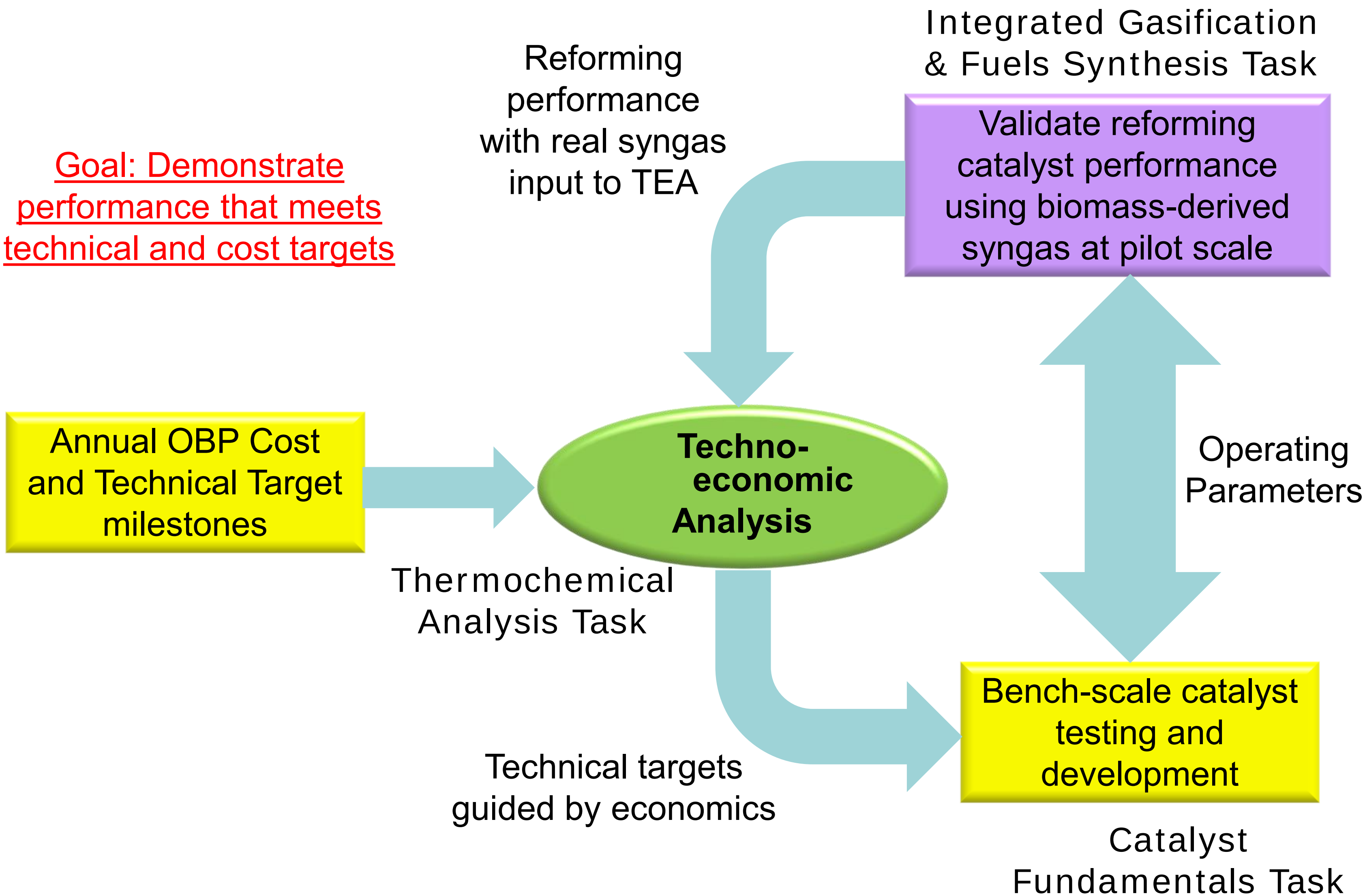


Technical Approach: Mimic commercial process model to demonstrate integrated process performance of key unit operations based on a conceptual design.

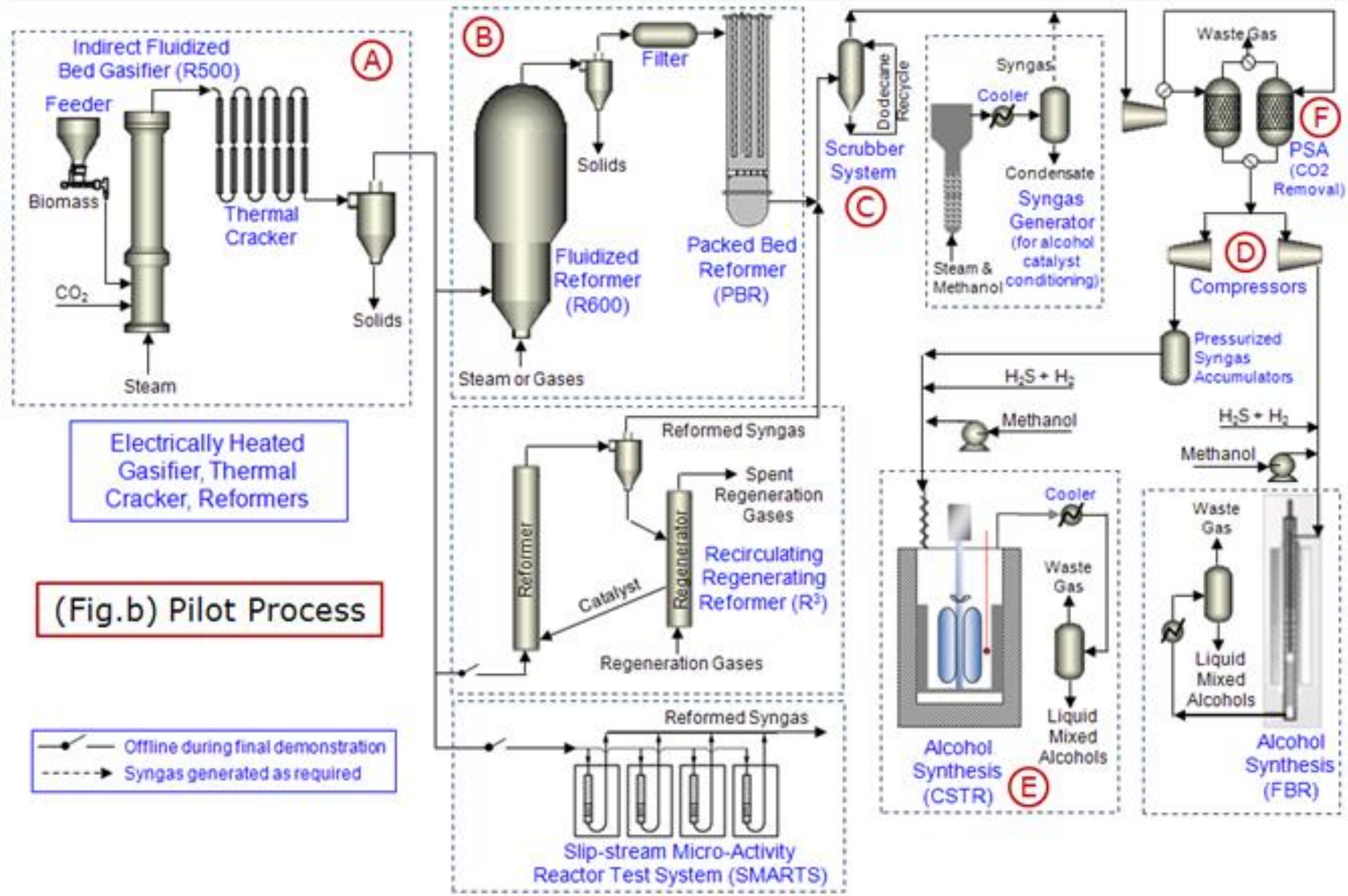
Management Approach: DOE-approved Project Management Plans detail schedules /milestones/risk abatement

1 - Approach

<u>Goal: Demonstrate performance that meets technical and cost targets</u>



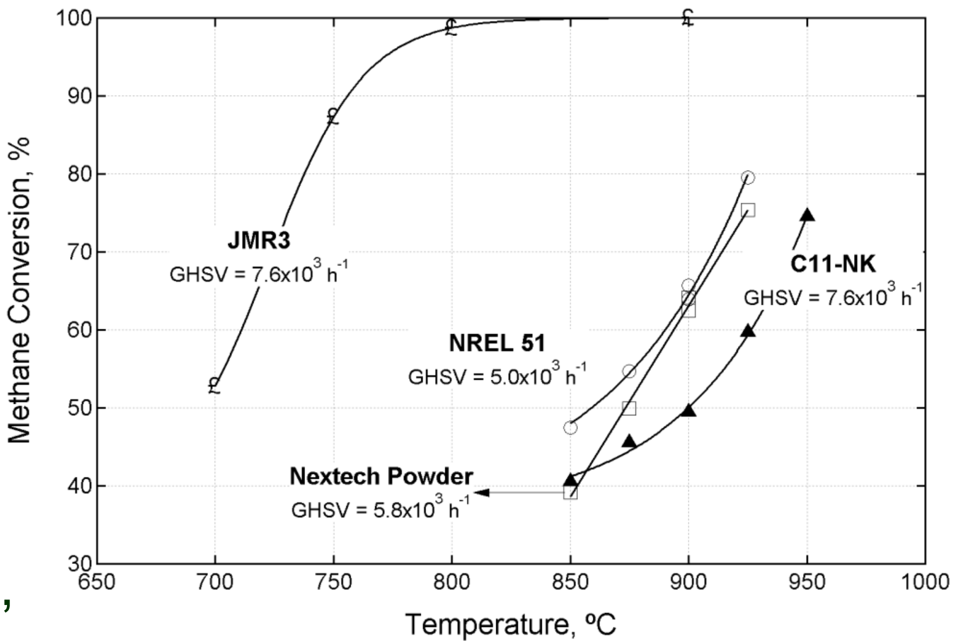
2 - Technical Accomplishments/ Progress/Results



2011 Joule Target

Title: Evaluate performance and regenerability of industrial reforming catalysts for syngas conditioning

Performance Measure: Industrial reforming catalyst evaluation with model and raw syngas towards meeting the 2011 syngas cleaning targets of > 80% methane conversion, > 99% benzene conversion, and > 99.9% total tar conversion with increased time between conversion.

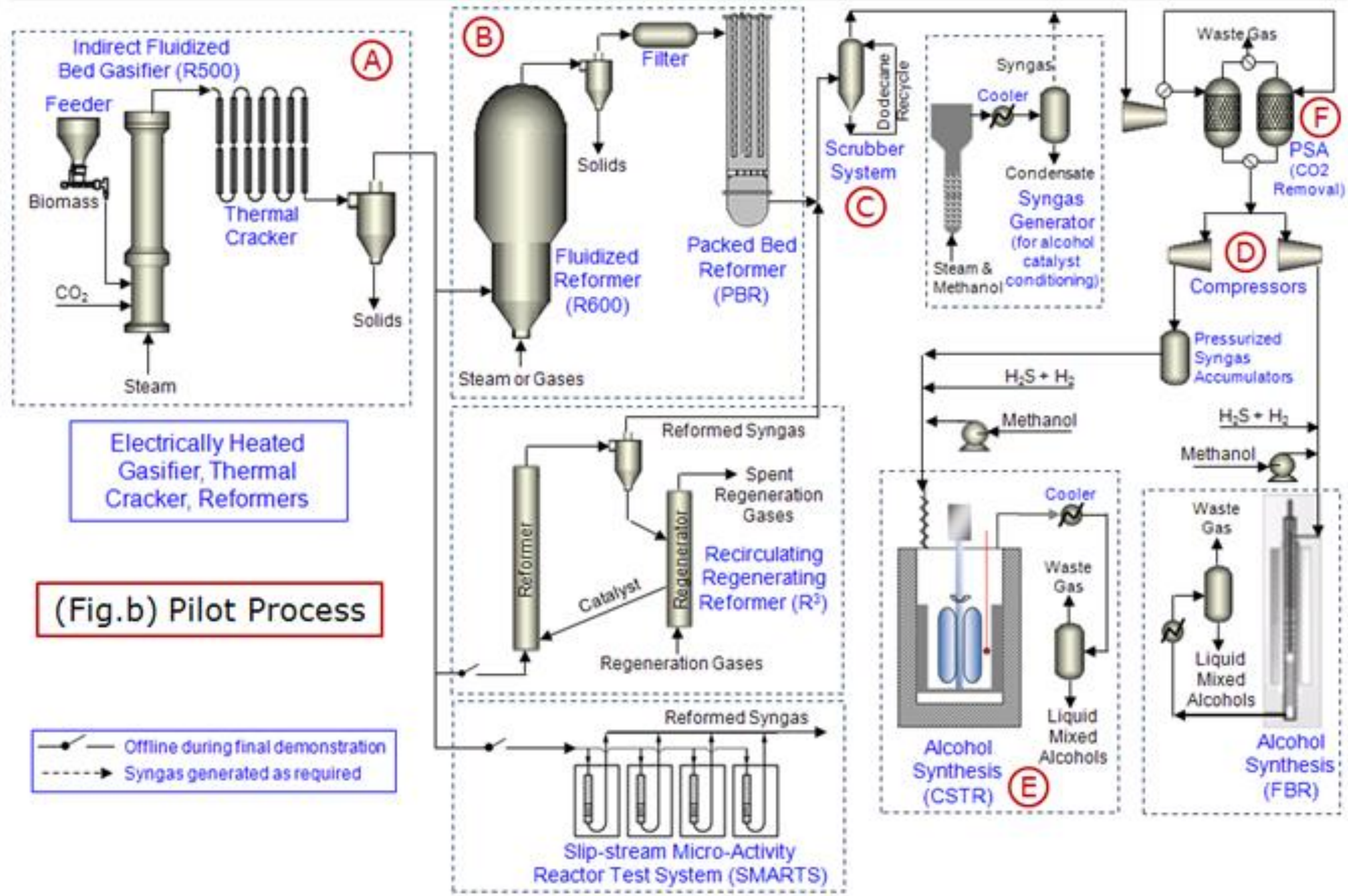


Single stage gasification mode where biomass and steam fed directly into the thermal cracker. This configuration lacks secondary tar cracking and produces more complex tars

Results

- ✓ JMR3 achieves 100% methane conversion at 830ºC
- ✓ JMR3 was evaluated for 200 hrs maintaining 95% methane conversion
- ✓ NREL 51 performed achieves 80% (target) methane conversion at 925ºC

2 - Technical Accomplishments/ Progress/Results



2 - Technical Accomplishments/ Progress/Results

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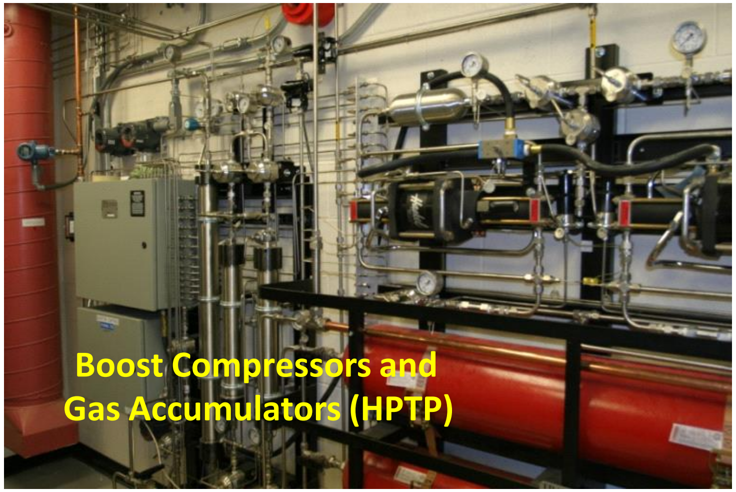
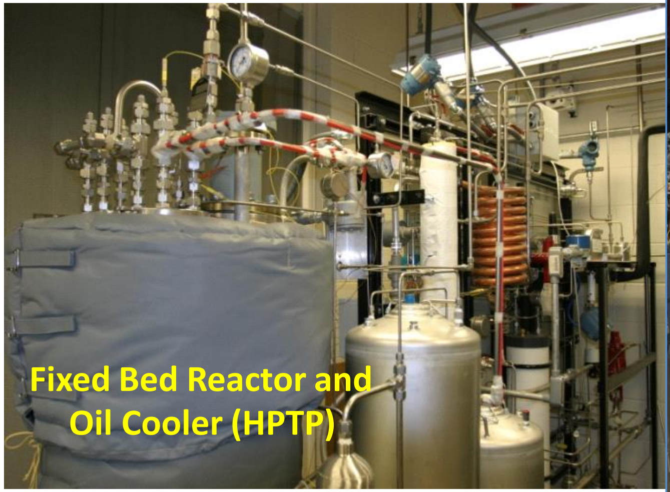
Completed fabrication/installation of an integrated system using the NREL thermochemical biorefinery facility (TCBR) for obtaining milestone data

- biomass gasification
- catalytic syngas reforming
- gas conditioning and compression
- mixed alcohol synthesis





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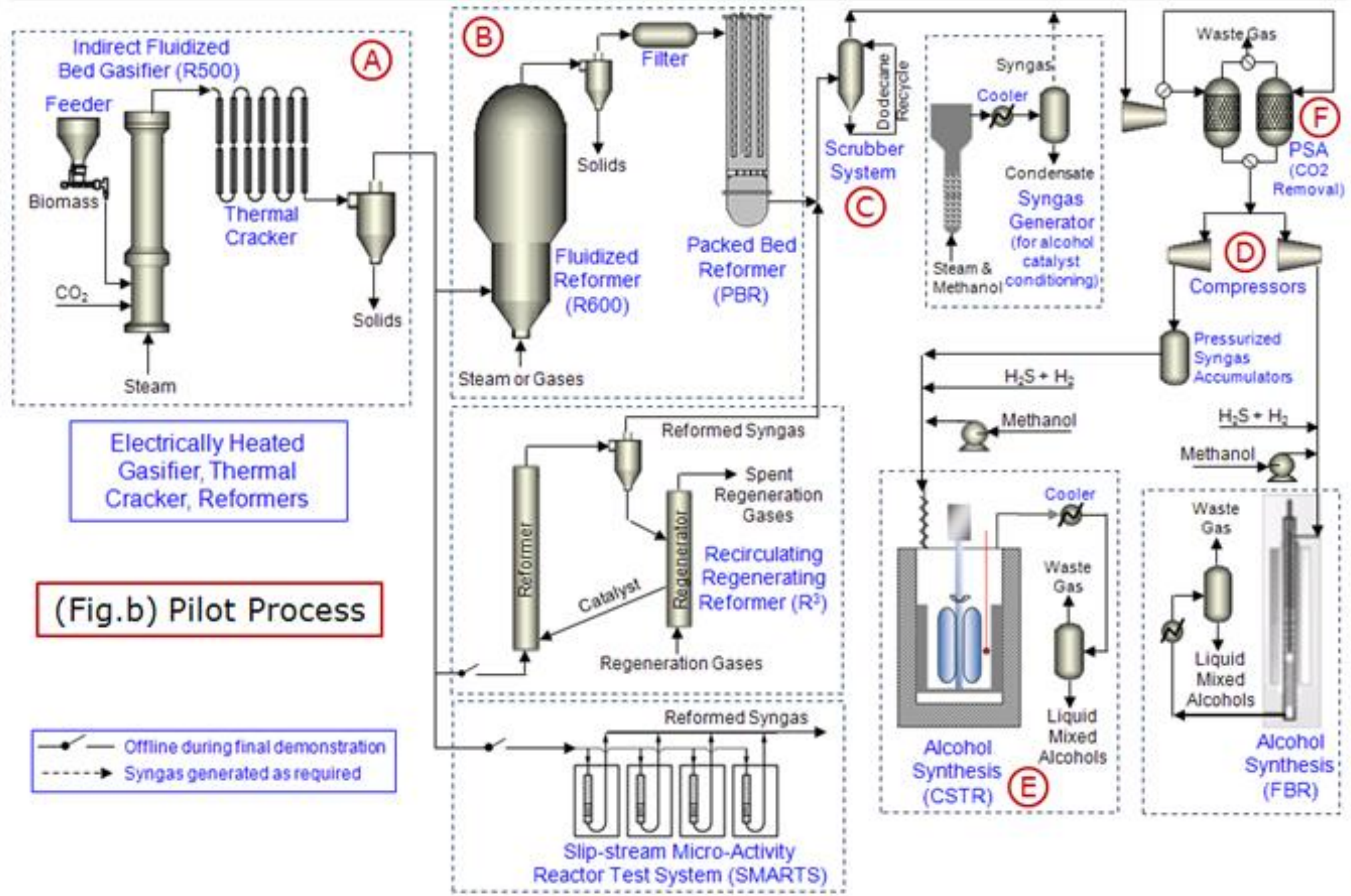

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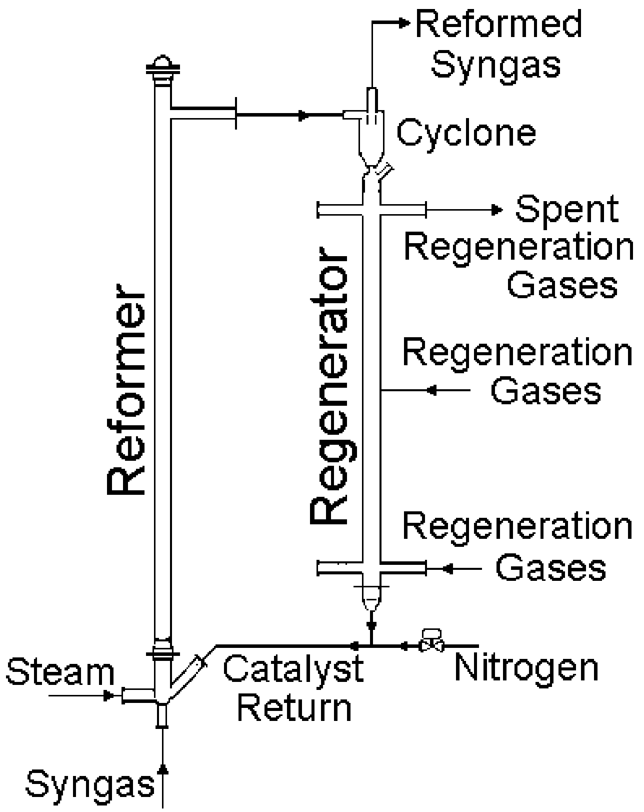
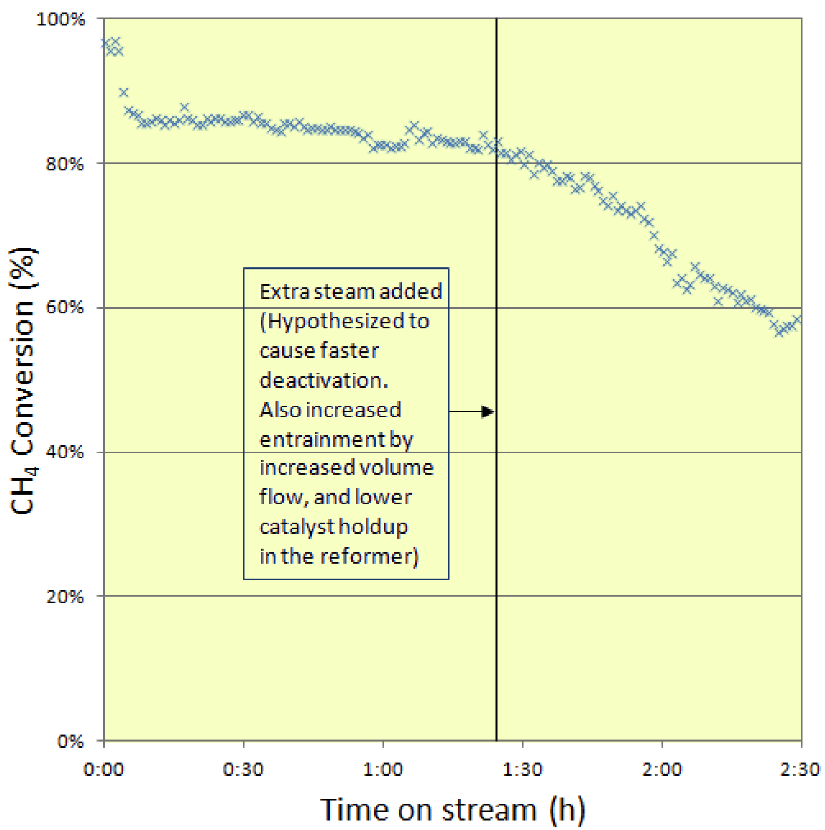


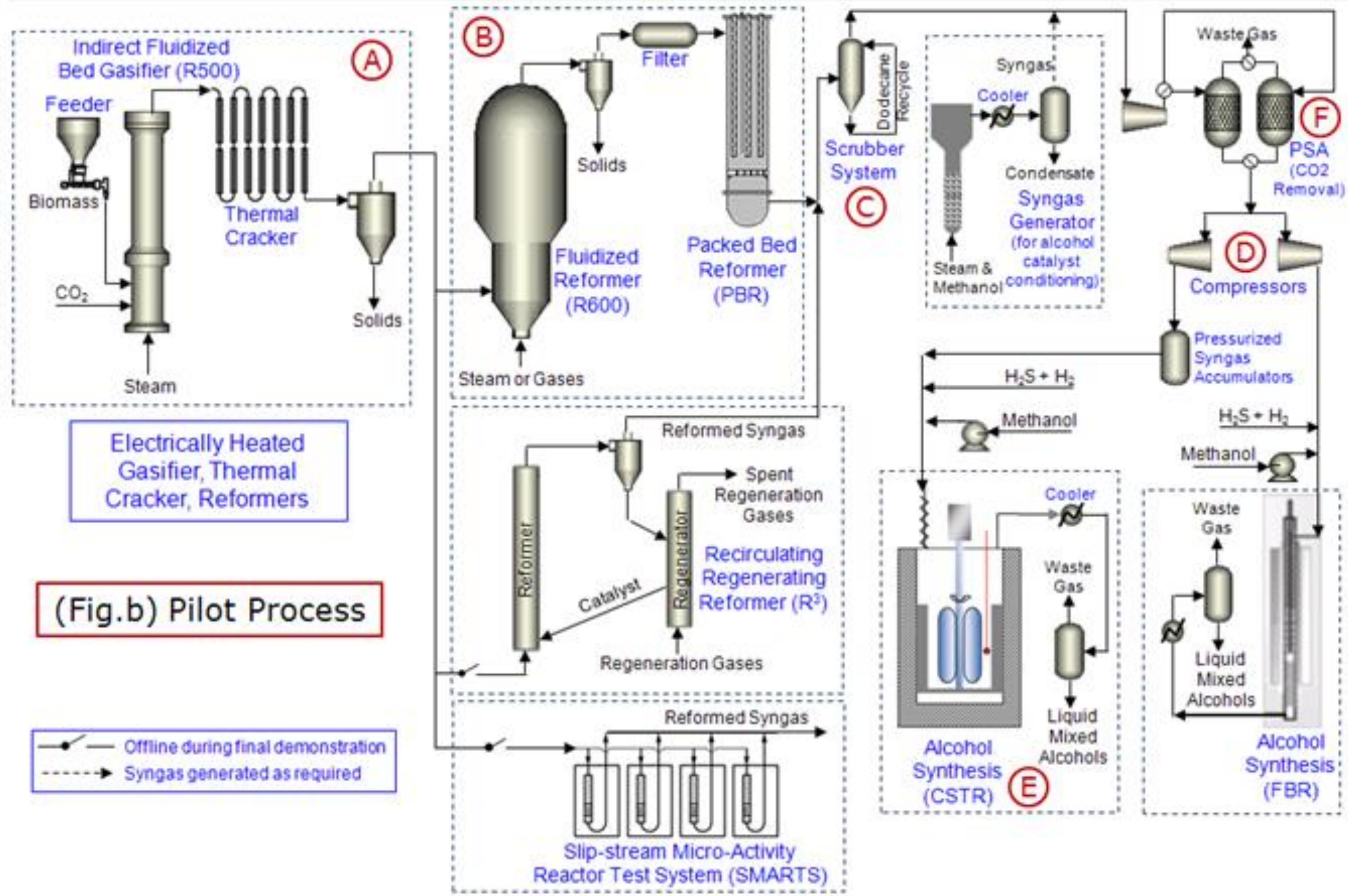
R[3] System



R[3] system run on 7/4/2012

Successful continuous reforming when no plugging during shakedown, with approximately 35 reforming-regeneration cycles/hour

2 - Technical Accomplishments/ Progress/Results



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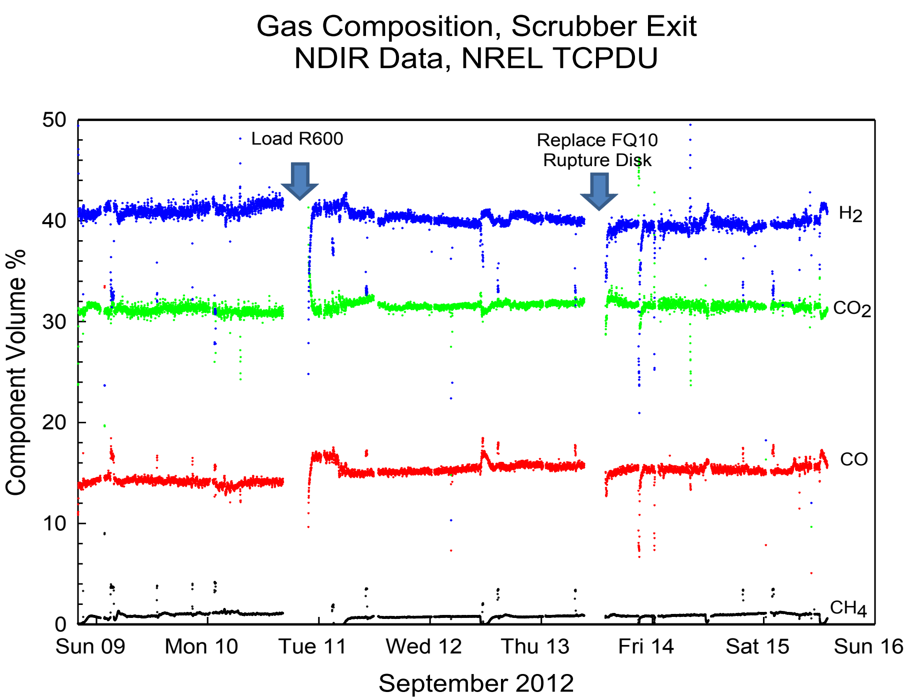
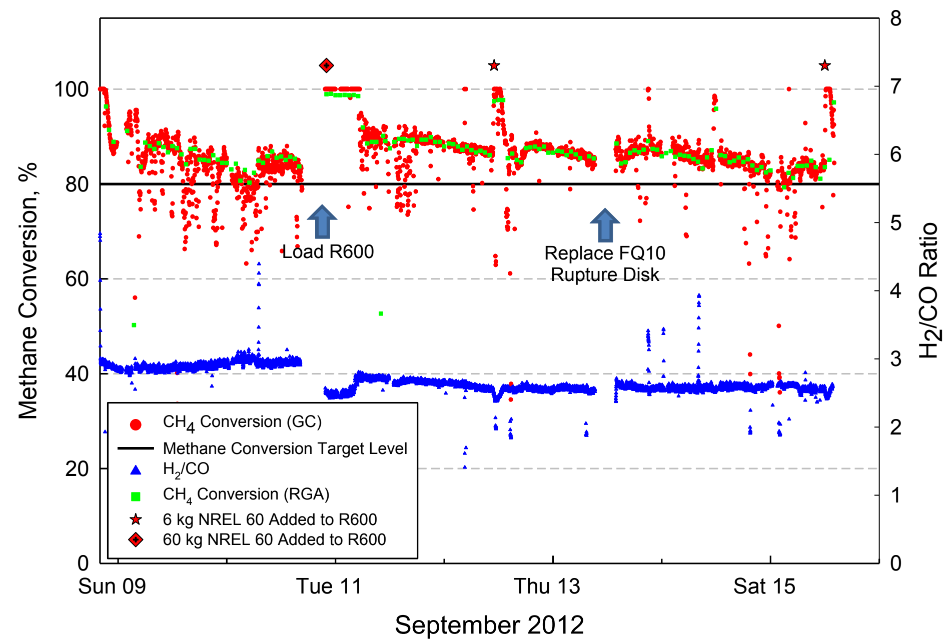




- Methane conversion was consistently above the target of 80%
- Tar conversion was 99% (technical target was 99%)
- Benzene conversion was 97% (technical target was 99%)

TCPDU 2012 syngas conditioning and fuel synthesis

Reformed syngas

Compress to 800 psi

Remove CO_2 with Pressure Swing Adsorber

Compress to 3000 psi and store

GTL in 10L CSTR

GC Analysis of ‘bag samples’

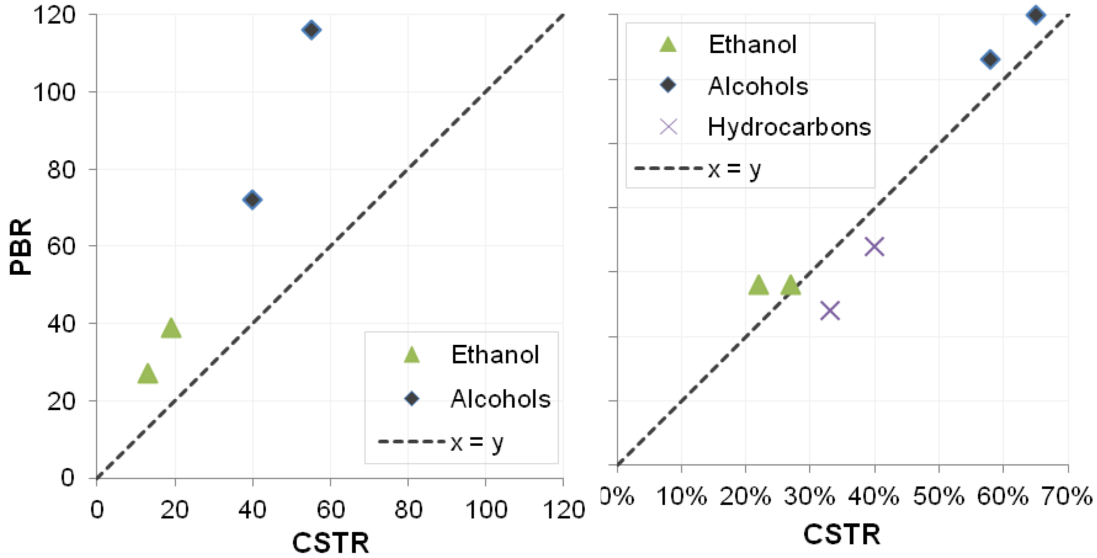
2 - Technical Accomplishments/ Progress/Results

Results

- Performance extrapolates to 2012 design (targets)
- Selectivity from CSTR same as from tubular reactor
- Productivity from CSTR less than from tubular reactor (expected for this type of reactor)

Productivity

Selectivity



Parity: bench scale tube reactor (PBR) and pilot scale CSTR

3 - Relevance

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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."

- ✓ Integrated processes and demonstrated all technologies required to convert biomass into mixed alcohols from which liquid fuel (ethanol) can be separated. Core topic areas included gasification, syngas cleanup and conditioning, and fuels synthesis
- ✓ Performance targets guided by techno-economic analysis of R&D results

Project accomplishments met the FY 2012 strategic and performance goals:

- ✓ Installed plant equipment required for 2012 demonstration.
- ✓ Demonstrated reforming and regeneration catalyst meets technical targets using real syngas.
- ✓ Integrated gasification, reforming, acid gas removal, and mixed alcohol synthesis was demonstrated at pilot scale for 330 h using both industrial and in-house catalysts.
- ✓ Demonstrated cost reductions that make cellulosic ethanol production cost competitive with gasoline production at ~$110/bbl crude oil

4 - Critical Success Factors

Success Factor	Outcome
Achieving steady state operation in integrated pilot plant that meets technical targets at each unit operation	Steady state operations were maintained hundreds of hours and two MoS fuel synthesis catalysts were evaluated. Syngas clean up metrics were achieved using biomass materials.
Ability to reliably measure gas composition and contaminants at process relevant levels	Online analytical measurements of tars (pre and post reforming), methane, CO, CO_2 and H_2 were used to evaluate process performance.
Data collected demonstrating TEA model assumptions and cost targets for achieving cost competitive ethanol production	The data collected from the experimental runs were integrated with the design case demonstrating a path forward for cost competitive fuels from biomass materials.

Lessons learned from the TC Demonstration

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- Opportunities to develop and evaluate conversion technology options before “locking in” performance measures and targets
- Evaluate individual unit operations targets at PDU scale
- Begin bench scale integration early – but it must be process-relevant.
- Maintain focus on a single (or very small number of) feedstock(s)
- Early availability of FULLY COMMISSIONED equipment for pilot-scale demonstrations
- Tracking of progress to TEA/LCA targets is critical

5. Future Work

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Leveragability to Hydrocarbons

- Syngas generation and clean-up directly applicable
  - Hybrid processes such as syngas fermentation.
- Modeling and analytical characterization techniques still important to understanding gasification processes
- Pilot/bench scale equipment can be leveraged fairly easily
- Would need a program to develop fuel synthesis strategies/catalysts that are compatible with the scale of biomass
- There is significant interest in catalytic conversion of mixed oxygenates to hydrocarbons

Summary

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- Integrated gasification, reforming, acid gas removal, and mixed alcohol synthesis was demonstrated at pilot scale for 330 h using both industrial and in-house catalysts.
- Analytical measurements of syngas composition, tars and methane were used to show that the technical targets could be achieved.
- The information collected was used in conjunction with a conceptual design case to show a route for the production of ethanol meeting the cost target of $2.05 per gallon.
- The equipment, analytical methodologies, and experienced can be leverage for the production of hydrocarbons.

Acknowledgements

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2012 Demonstration TCPDU Team

<u>Operations:</u>

Rich Bain

Danny Carpenter

Calvin Feik

Joseph Gardner

Katie Gaston

Ray Hansen

Dave Isham

Christa Loux

Bill Michener

Marc Oddo

Steve Phillips

Marc Pomeroy

Kristin Smith

Mike Sprague

Jim Stunkel

Adam Unruh

<u>Support:</u>

Helena Chum

Sheila Grady-McBride

Kim Magrini-Bair

Joany Tarud

Adam Bratis

Robert Baldwin

DOE Bioenergy Technologies Office (BETO)

Responses to Previous Reviewers' Comments

Reviewer Comment

This work is the integration of gasification and fuel syn work, actual testing of the system. This is important, but the Range Fuels project highlights the problem with changes after even 200 hrs. of testing. The key activity is to test the presence of 'known and unknown' compounds. They clearly understand the need to do 'real' testing, to inform performance and TEA, and the need to connect all the elements of the system.

Presenter Response

The MYPP 2012 target (pp. 1-22 of OBP MYPP, November 2010) being addressed by this task is: "By 2012, validate integrated conversion process to produce ethanol from mixed alcohols via gasification of woody feedstocks at scale sufficient to enable transfer to pilot scale operation." This project is not integrated demonstration at the pilot scale scheduled as a 2015 target in the MYPP; it is a technical demonstration of the integrated unit operations from gasification through fuel synthesis. The time-on-stream target of 200 hours represents our minimum operational goal to validate that the integrated unit operations work together while achieving the programmatic technical targets. The performance from the process will be fed into the TEA model to estimate the production cost for the desire ethanol product. A much longer testing period (>1000 hours minimum) needs to be demonstrated before this technology is considered "ready" for the Demo plant scale. The work completed for this project will provide the capability to do the extended testing, but this long-term testing is outside the project scope and resources.

Responses to Previous Reviewers' Comments

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Reviewer Comment

Economic challenges are not really addressed, however technical challenges are adequately addressed.

Presenter Response

Economic factors are addressed by a different project within the group of projects being done at NREL. We work closely with the TEA task to provide relevant data for their models and to implement feedback from TEA into the technical side of the project. Comprehensive chemical analyses of the gases and catalysts used in the process will be a critical part of the technical demonstration. Continued emphasis on state-of-the-art chemical analyses, especially for heteroatom measurements, will be important for providing maximum value to industrial users of the information gathered during the coming year of the project.

Responses to Previous Reviewers' Comments

Reviewer Comment

May want to include a team from Cat companies, who are the customer for the data, to make sure that the baseline data and the detection limits are useful.

The project has done a good of harvesting technology from the other projects in the Thermochem Platform. The project needs to consider how to transfer technology out of the project, i.e. commercialization partners, improvement needs, etc.

Presenter Response

The completion of the integrated process for biomass to liquid fuels via gasification and synthesis will provide a platform for industrial collaboration at all steps of the conversion process. The technical demonstration is not only a first look at the specific catalysts and integrated processes being tested, it is also a demonstration of the unit operations that will be available for testing new catalysts, cleanup systems, gasification processes, etc. with industrial partners and to support larger scale demonstrations by providing a highly instrumented facility and protocols to investigate problem areas that arise during scale up and commercialization.

Publications, Presentations, and Commercialization

1. 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.
2. 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.
3. 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
4. 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.

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Steam reforming targets for the 2012 demonstration

Species	Conversion
Methane	80%
Benzene	99%
Tars	99%
Catalyst replenishment rate (for fluidizable catalyst)	0.1% of inventory per day

Proximate and ultimate analysis of white oak pellets

Loss on drying (wt%)	6.12
Proximate Analysis (wt% dry)	
Volatile matter	79.74
Fixed carbon	13.75
Ash	0.39
Ultimate Analysis (wt% dry)	
Carbon	52.79
Hydrogen	6.42
Nitrogen	0.09
Oxygen	40.69
Sulfur	0.01
HHV (MJ/kg)	18.68

Operating parameters for the gasification system

Parameter	Value
Steam flow to 8FBR Gasifier	13.4 $kg\text{-}h^{-1}$
CO_2 flow to 8FBR Gasifier	4.0 $kg\text{-}h^{-1}$
Biomass (oak) feed rate	7.5 $kg\text{-}h^{-1}$
8FBR Gasifier Temperature	650 °C
8FBR Pressure	70 - 75 kPa
8FBR Initial Olivine	23.25 kg
Thermal Cracker Temperature	900 °C
Plant Heat Trace Temperatures	550 °C
Fluidized Bed Tar Reformer Temperature	900 °C
R600 Initial Catalyst	60 kg
PPBR Upstream Filters (FQ10 & FQ20) Heaters Temperature Set Point	700 - 850°C
PPBR (RQ40) Heaters Temperature Set Point	840 °C
Flow Set Point to Fuel Synthesis Room	6.5 $kg\text{-}h^{-1}$

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

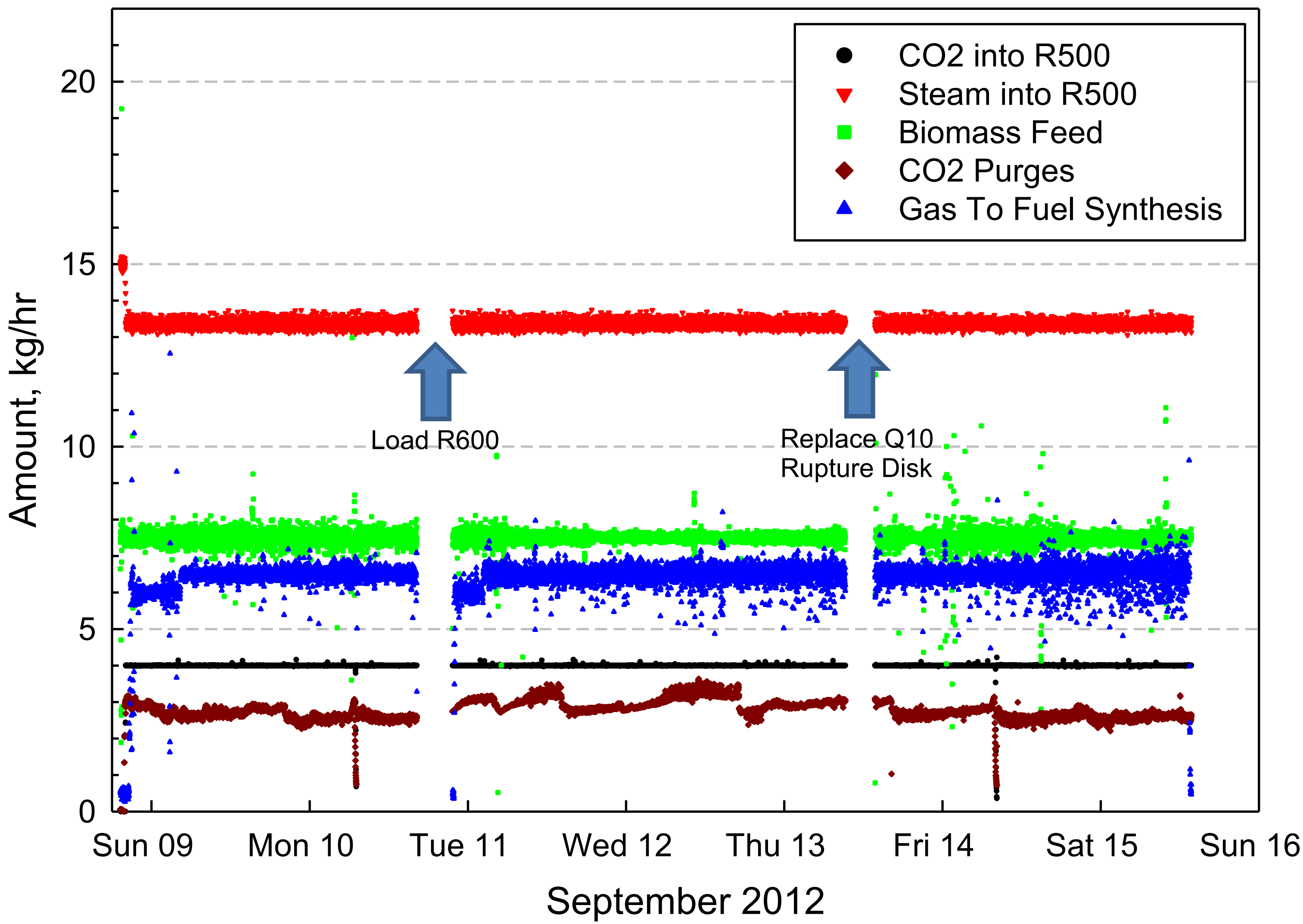
Overall nitrogen-free mass balance for 150 h of gasifier operation

	Flow, kg/h
Oak in	7.48
Steam in	13.36
CO_2 in	6.78
He & Ar Tracers in	0.35
N_2 in	(not measured)
SUM of INPUTS	**27.97**
Gas out of Scrubber	20.39
Char out	0.74
Water out	8.20
N_2 out	-2.48
SUM of OUTPUTS	**26.85**
Overall Closure	**96.00**

Gas composition through gasifier/reformers (nitrogen free)

Configuration	Gasifier Only	G + R600	G + R600 + PBR
Carrier	Steam + CO2	Steam + CO2	Steam + CO2
Feed	Oak	Oak	Oak
S/B	1.79	1.79	1.79
CO2/B	0.53	0.53	0.53
No. Samples	28	138	166
Gas Composition, Mole % Nitrogen Free			
H2	20.103 +/- 0.850	39.901 +/- 1.380	44.405 +/- 1.312
CO	16.268 +/- 0.452	17.469 +/- 1.213	15.225 +/- 0.454
CO2	50.909 +/- 0.524	38.958 +/- 0.939	38.605 +/- 1.212
CH4	8.898 +/- 0.251	2.837 +/- 0.861	0.769 +/- 0.166
C2H6	0.233 +/- 0.238	0.000 +/- 0.000	0.000 +/- 0.000
C2H4	1.888 +/- 0.038	0.000 +/- 0.000	0.000 +/- 0.000
C2H2	0.000 +/- 0.000	0.000 +/- 0.000	0.000 +/- 0.000
C3H8	0.017 +/- 0.023	0.031 +/- 0.073	0.011 +/- 0.014
C3H6	0.001 +/- 0.003	0.000 +/- 0.000	0.000 +/- 0.001
1-C4H8	0.000 +/- 0.000	0.000 +/- 0.000	0.000 +/- 0.000
2-t C4H8	0.000 +/- 0.000	0.000 +/- 0.000	0.000 +/- 0.000
2-c C4H8	0.000 +/- 0.000	0.000 +/- 0.000	0.000 +/- 0.000
Ar/He	1.682 +/- 0.049	0.803 +/- 0.505	0.985 +/- 0.041
H2S (ppmv)	9.71 +/- 5.12	4.37 +/- 5.94	11.69 +/- 4.58
COS (ppmv)	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00
H2/CO	1.24 +/- 0.05	2.30 +/- 0.24	2.92 +/- 0.07

Biomass, steam, and gas flow rates



Average steady state tar conversions during integrated run

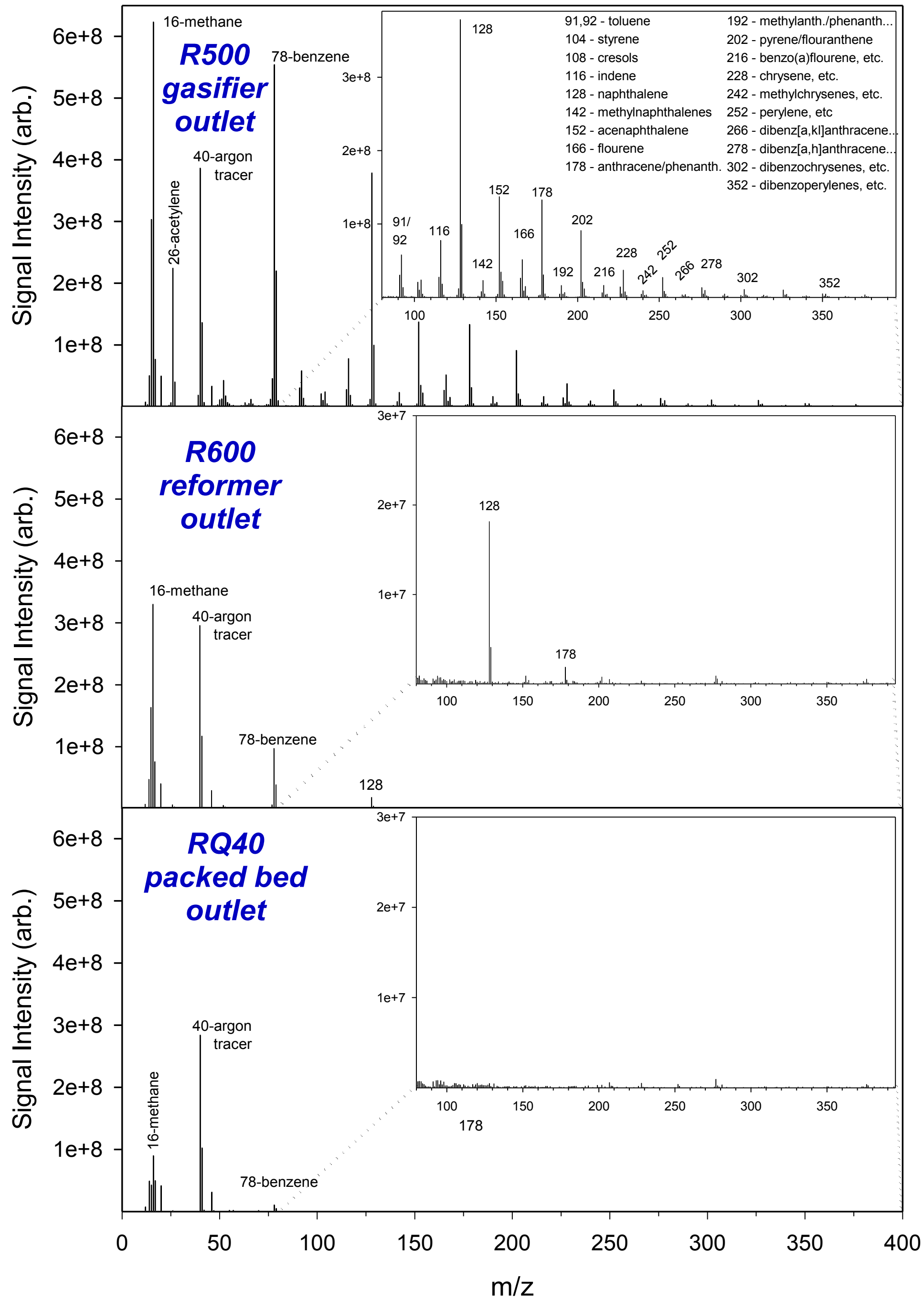
Compound	Conversion[†]
Benzene	97%
Naphthalene*	100%
Benzo(a)Pyrene*	100%

* Surrogates used to represent tars.

[†] 100% conversion indicates that effluent concentration is below detection limits

Mass spectral peak assignments of common hydrocarbons sampled with the TMBMS during steam gasification.

Molecular Weight	Formula	Chemical Name(s)
15,16	CH_4	methane
26	C_2H_2	acetylene
78	C_6H_6	benzene
91,92	C_7H_8	toluene
94	C_6H_6O	phenol
104	C_8H_8	styrene
106	C_8H_{10}	(m-, o-, p-) xylene
108	C_7H_8O	(m-, o-, p-) cresol
116	C_9H_8	indene
118	C_9H_{10}	indan
128	$C_{10}H_8$	naphthalene
142	$C_{11}H_{10}$	(1-, 2-) methylnaphthalene
152	$C_{12}H_8$	acenapthylene
154	$C_{12}H_{10}$	acenaphthene
166	$C_{13}H_{10}$	fluorene
178	$C_{14}H_{10}$	anthracene, phenanthrene
192	$C_{15}H_{12}$	(methyl-) anthracenes/phenanthrenes
202	$C_{16}H_{10}$	pyrene/fluoranthene
216	$C_{17}H_{12}$	methylpyrenes/benzofluorenes
228	$C_{18}H_{12}$	chrysene, benz[a]anthracene, …
242	$C_{19}H_{14}$	methylchrysenes, methylbenz[a]anthracenes
252	$C_{20}H_{12}$	perylene, benzo[a]pyrene,
266	$C_{21}H_{14}$	dibenz[a,kl]anthracene,
278	$C_{22}H_{14}$	dibenz[a,h]anthracene,



Mass spectra for gases at the outlet of the gasifier, fluid bed reformer, and PPBR

1 Reformers benzene and tar conversion

	Benzene			Naphthalene			Heavy Tar		
Inlet concentration, ppmv	1840	+/-	90	430	+/-	20	350	+/-	60
R600									
AVE Conversion, %	73.1	+/-	6.1	90.9	+/-	6.1	99.2	+/-	2.0
MAX conversion, %	78.2			95.0			100.0		
MIN conversion, %	56.5			72.6			93.2		
R600 + PBR									
AVE Conversion, %	97.0	+/-	1.8	99.9	+/-	0.1	100.0	+/-	0.1
MAX conversion, %	99.2			100.0			100.0		
MIN conversion, %	91.7			99.5			99.5		

2

Benzene, naphthalene, and heavy tar conversions

Date	Time	*% benzene conversion*		*% naphthalene conversion*		*% "heavy tar" conversion*	
		R600	**R600 +PBR**	**R600**	**R600 +PBR**	**R600**	**R600 +PBR**
9/10/12	11:00	n/a	93.5	n/a	99.8	n/a	100
9/10/12	12:30	60.9	92.6	81.1	99.9	100	100
9/10/12	15:30	56.5	91.7	72.6	99.5	93.2	100
9/11/12	11:30	n/a	97.5	n/a	99.8	n/a	99.5
9/11/12	12:30	76.7	97.1	93.4	100	100	100
9/11/12	13:30	74.3	97.2	92.6	100	98.9	100
9/11/12	14:15	n/a	98.3	n/a	100	n/a	100
9/11/12	15:45	75.1	98.1	91.0	100	100	100
9/11/12	16:30	n/a	98.2	n/a	99.9	n/a	100
9/11/12	18:45	n/a	98.0	n/a	99.9	n/a	100
9/12/12	10:30	69.2	96.6	91.9	100	100	100
9/12/12	11:30	n/a	99.1	n/a	100	n/a	100
9/12/12	13:30	75.7	98.1	94.3	100	100	100
9/12/12	15:00	75.6	97.6	93.8	100	100	100
9/12/12	16:00	77.4	96.8	95.0	100	100	100
9/12/12	17:00	77.3	97.2	93.9	100	100	100
9/13/13	15:00	78.2	97.1	93.1	100	100	100
9/13/12	16:45	n/a	97.5	n/a	99.7	n/a	100
9/14/12	10:45	n/a	97.3	n/a	99.9	n/a	100
9/14/12	11:45	n/a	99.2	n/a	99.9	n/a	100
9/14/12	13:45	78.0	97.4	94.6	100	99.1	100
9/14/12	14:45	75.9	97.9	93.8	100	n/a	n/a
9/14/12	17:00	n/a	96.9	n/a	99.8	n/a	n/a
9/15/12	10:00	n/a	96.8	n/a	99.9	n/a	100
9/15/12	11:00	n/a	97.0	n/a	99.9	n/a	100
9/15/12	12:05	98.7	n/a	99.5	n/a	100	n/a

•**Average R500 outlet concentrations (wet basis):**

•Benzene: 6.40±0.33 g/Nm^3 (1840±90 ppmv)
•Naphthalene: 2.44±0.10 g/Nm^3 (430±20 ppmv)
•"Heavy Tar": 3.95±0.79 g/Nm^3 (350±60 ppmv)