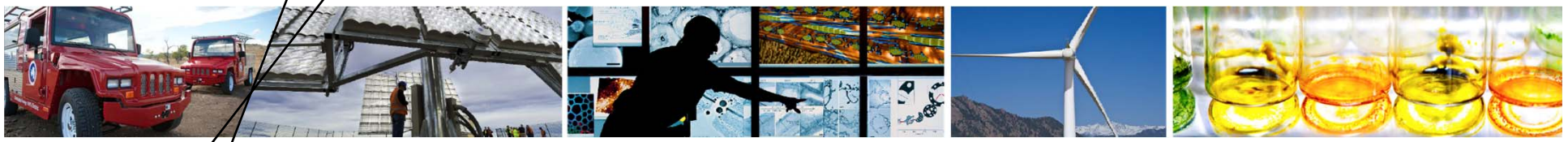
TCPDU Operations in Support of 2012 Thermochemical Joule Milestone



IEA Task 33 NREL Workshop

Richard Bain

9 May 2013

Presentation

- Objectives of Testing
- TCPDU Design
- Operating Parameters
- Unit Operations Characteristics
- Product Gas
- Conversions Achieved

Acknowledgements

The dedication and extra effort of the TCPDU staff instrumental in the successful completion of pilot operations supporting the 2012 DOE Thermochemical Joule Milestone is gratefully acknowledged.

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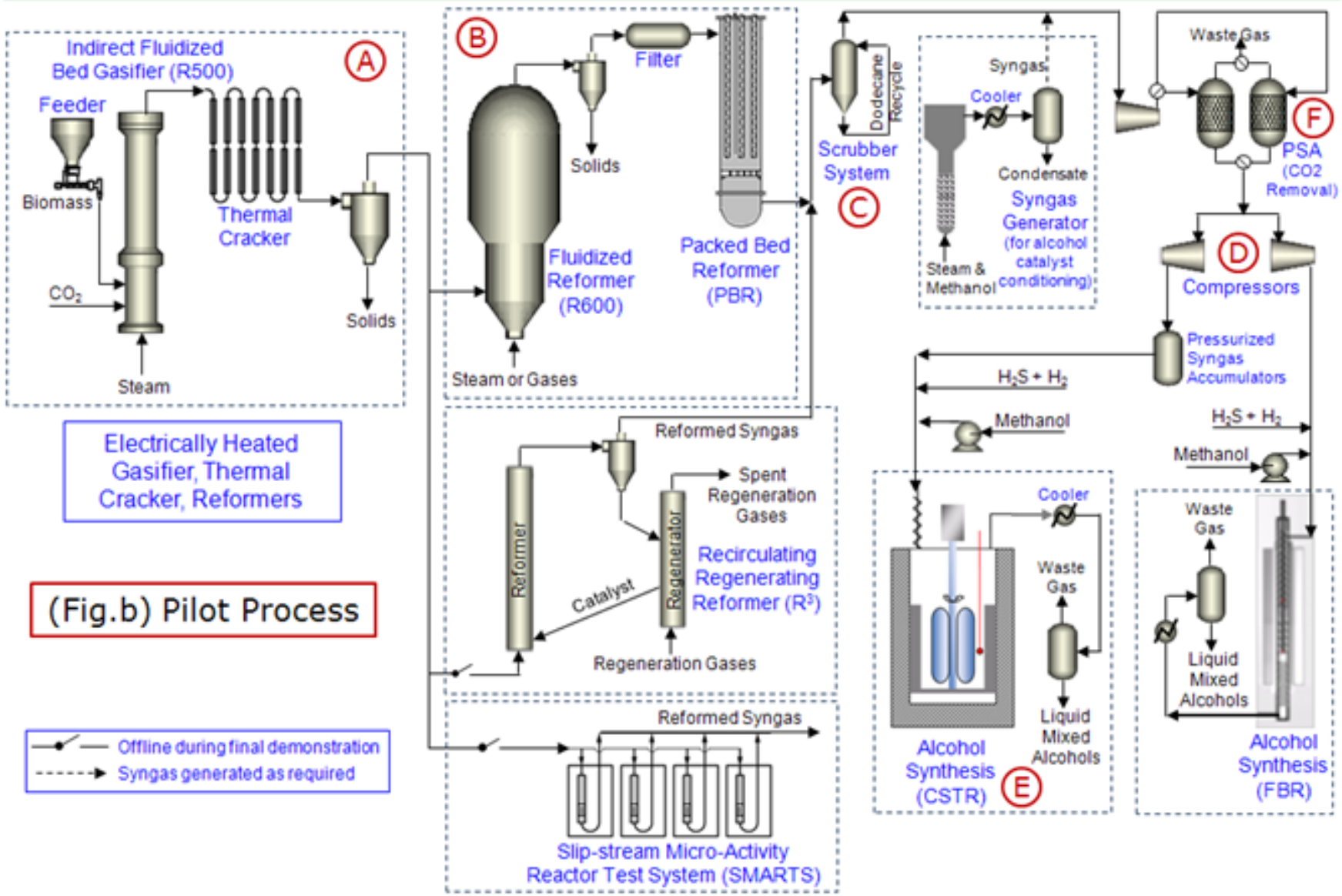
Objectives

- Demonstrate Long Term Operability of the Thermochemical PDU (TCPDU)
  - Gasifier (fluid bed reactor and thermal cracker)
  - Char cyclones
  - Fluid bed reformer (NREL Ni catalyst)
  - Packed bed filters
  - Packed bed catalytic reactor
  - Scrubber
  - Blower
- Generate a Conditioned Syngas Meeting the Biomass Program 2012 Purity Targets
- Provide Conditioned Syngas to the Mixed Alcohol Synthesis System as Part of an Integrated 200 hour Campaign to Produce Mixed Alcohols from a NREL Mixed Alcohol Catalyst

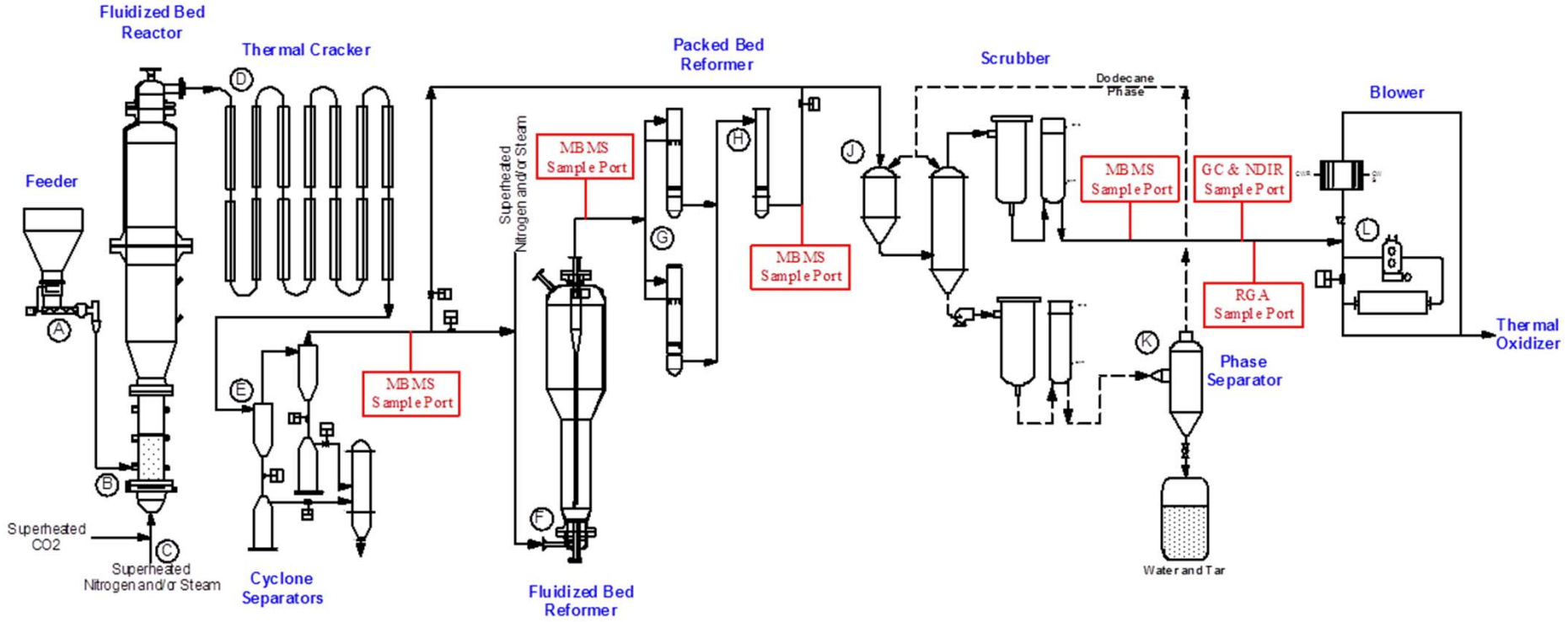
Steam reforming targets for the 2012 demonstration

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

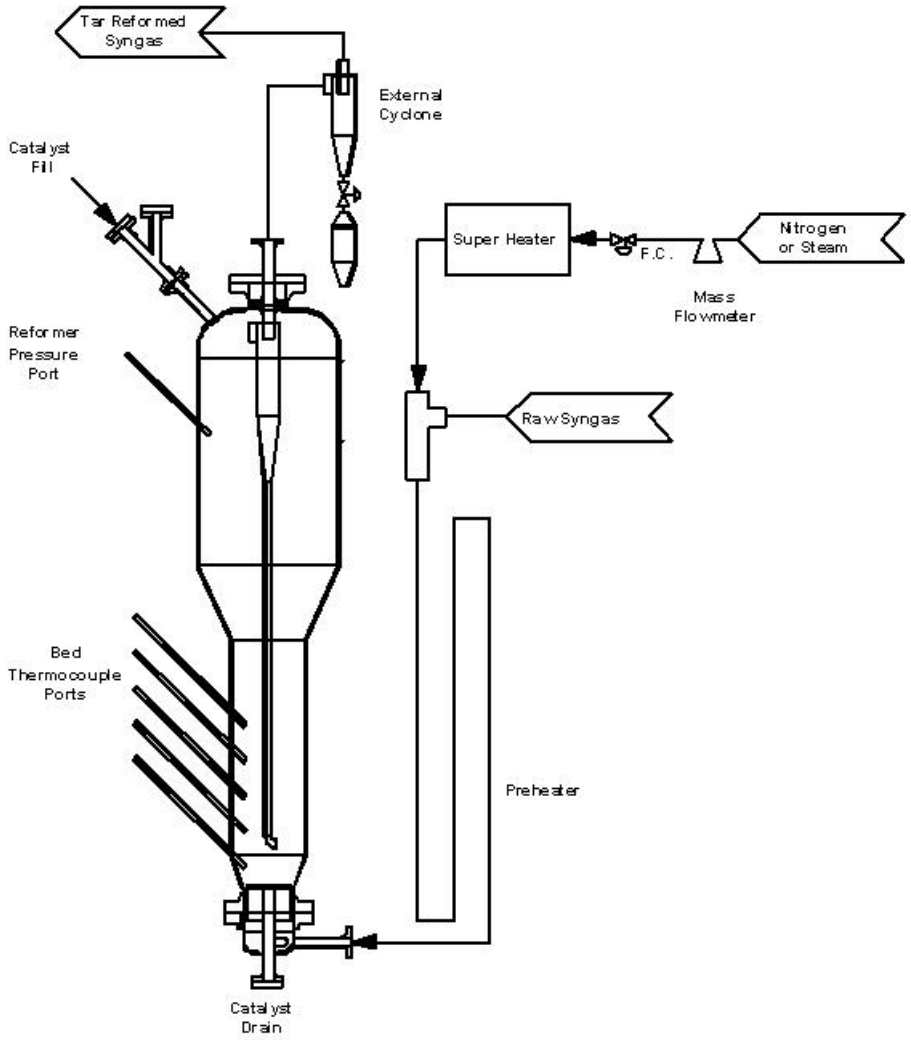
Integrated NREL Thermochemical Pilot Process



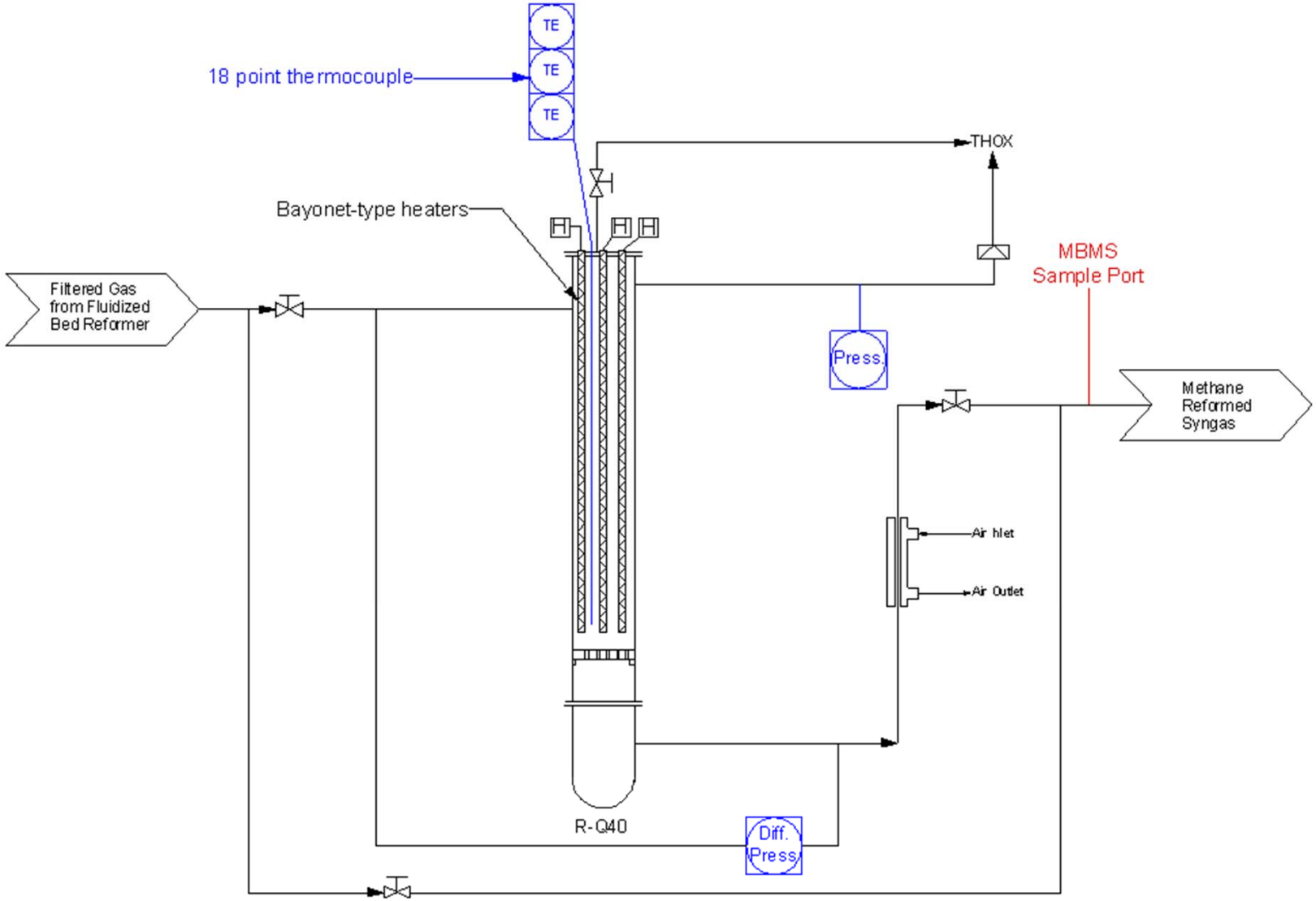
NREL Thermochemical Pilot Development Unit (TCPDU)



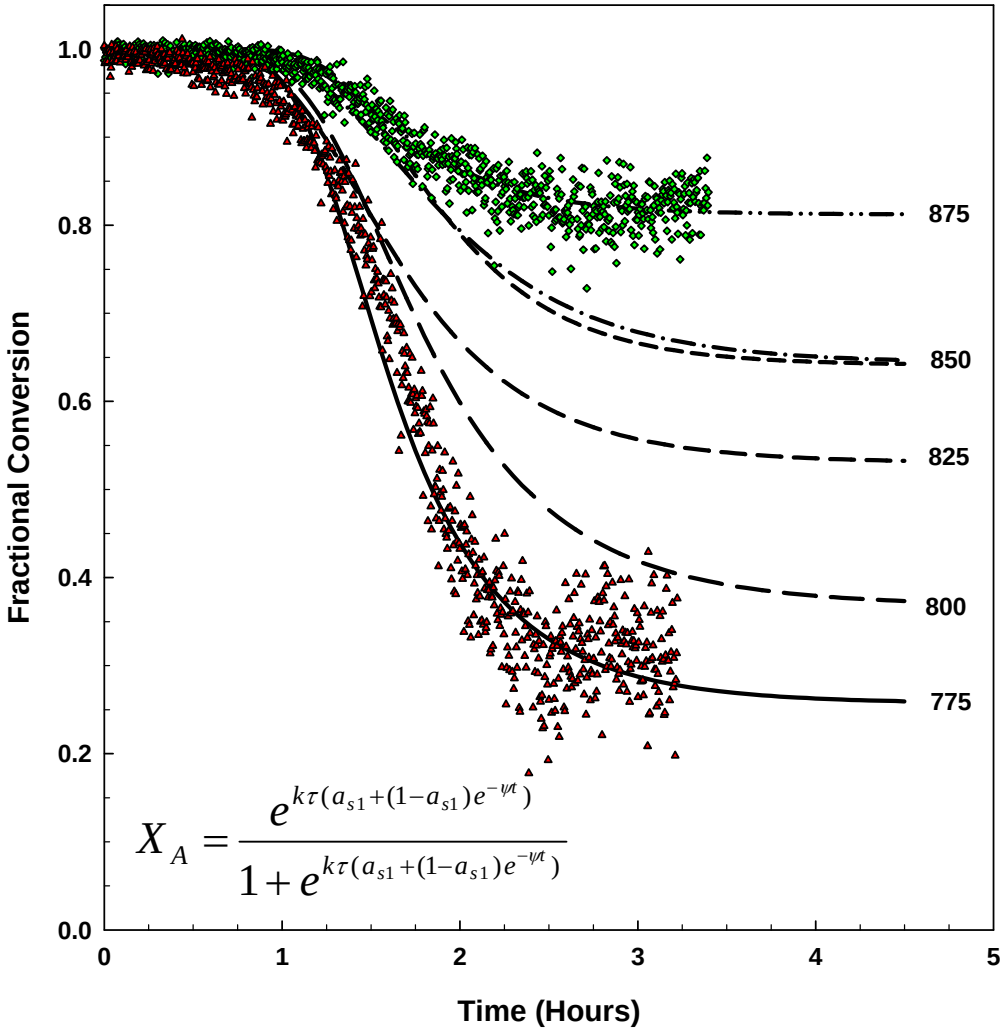
Schematic of the fluidized bed reformer (R600)



Schematic of the PBR

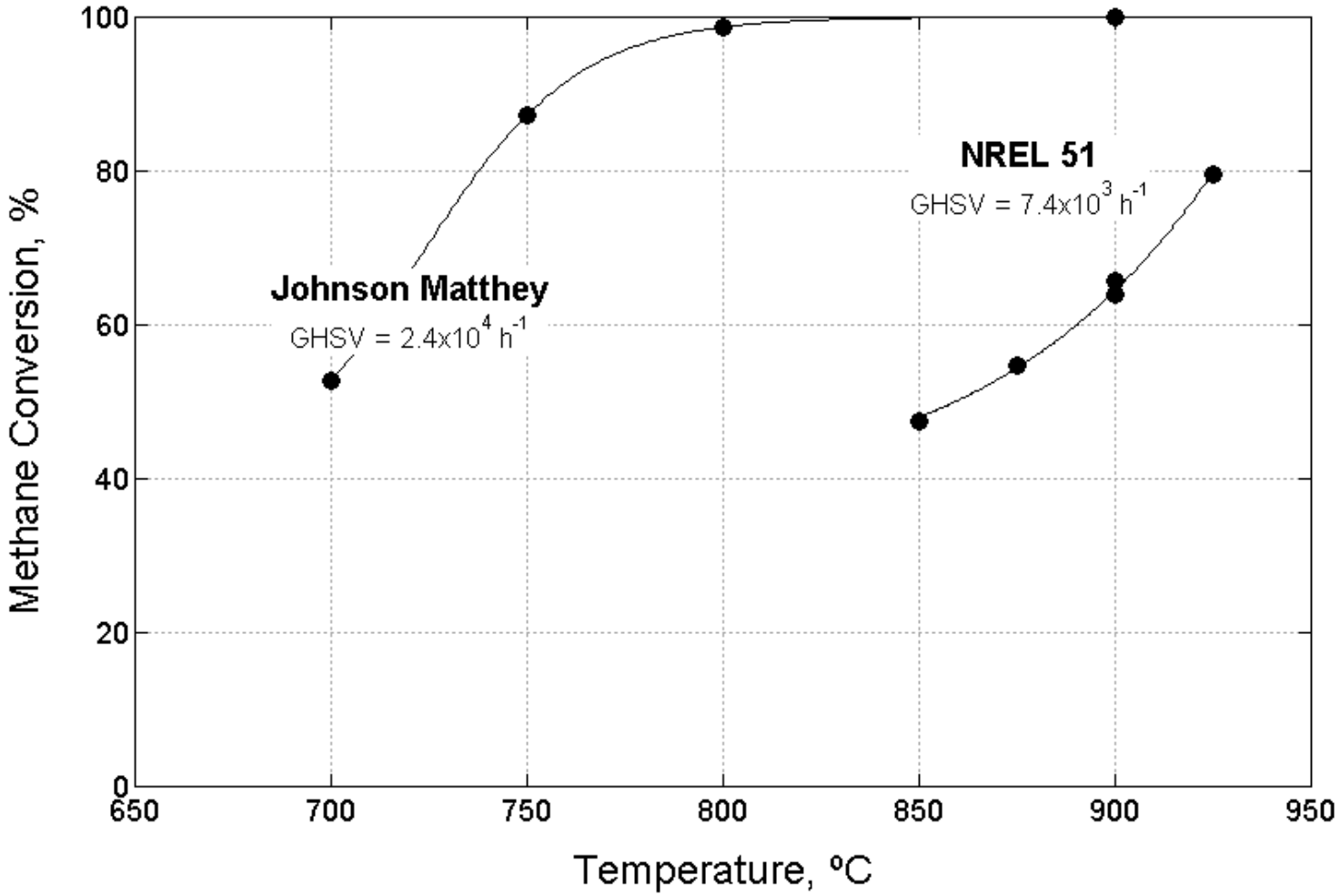


Benzene Fractional Conversion, N1D1 Model



Bain, R. L., D. C. Dayton, D. L. Carpenter, S. R. Czernik, C. J. Feik, R. J. French, K. A. Magrini-Bair and S. D. Phillips (2005). "An Evaluation of Catalyst Deactivation During Catalytic Steam Reforming of Biomass-Derived Syngas," *I&ECR*, 44, p 7945-7956

Catalyst Performance in SMARTS Reactor



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-h^{-1}
CO_2 flow to 8FBR Gasifier	4.0 kg-h^{-1}
Biomass (oak) feed rate	7.5 kg-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-h^{-1}

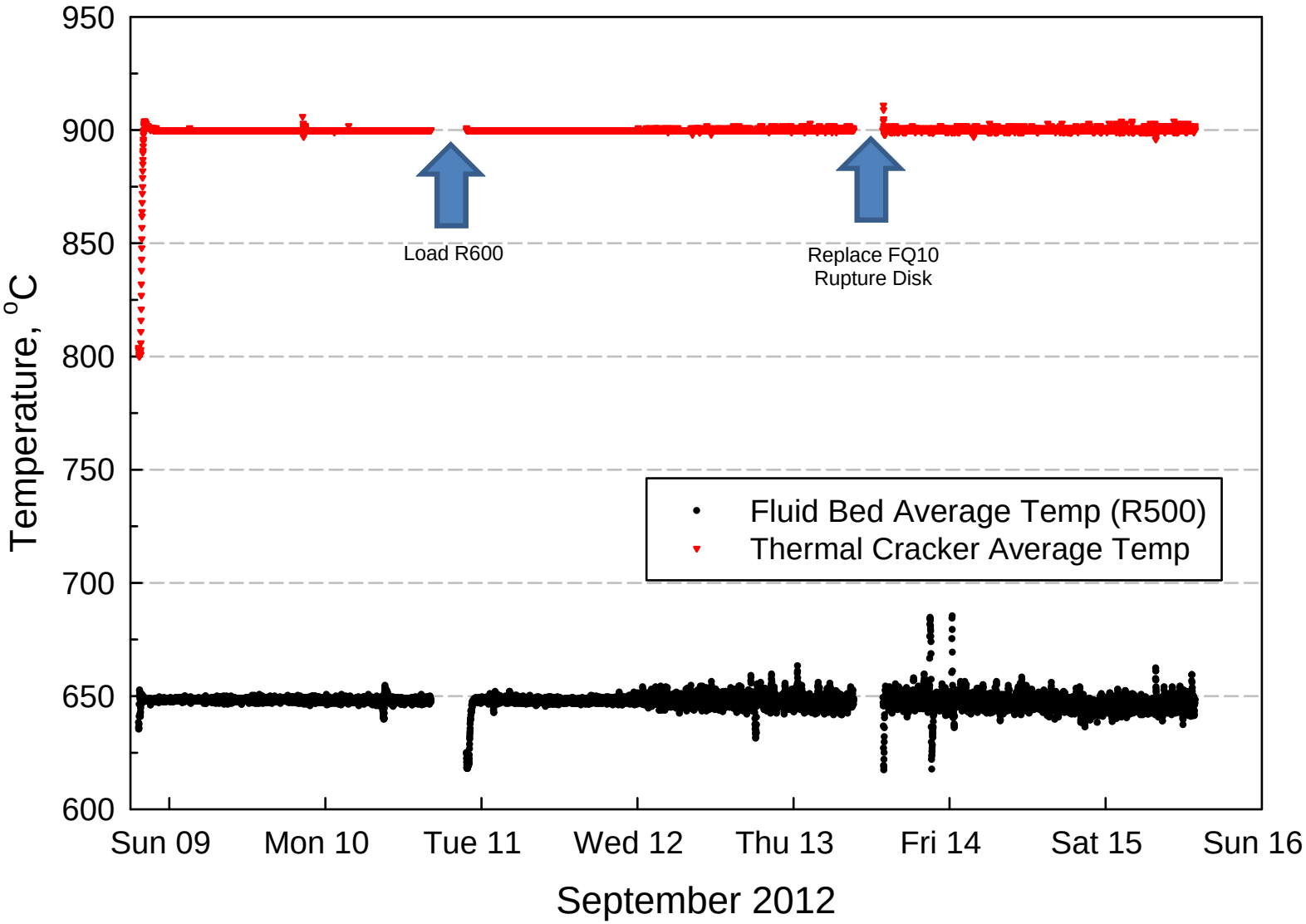
Overall nitrogen-free mass balance for 150 h of gasifier operation

	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**

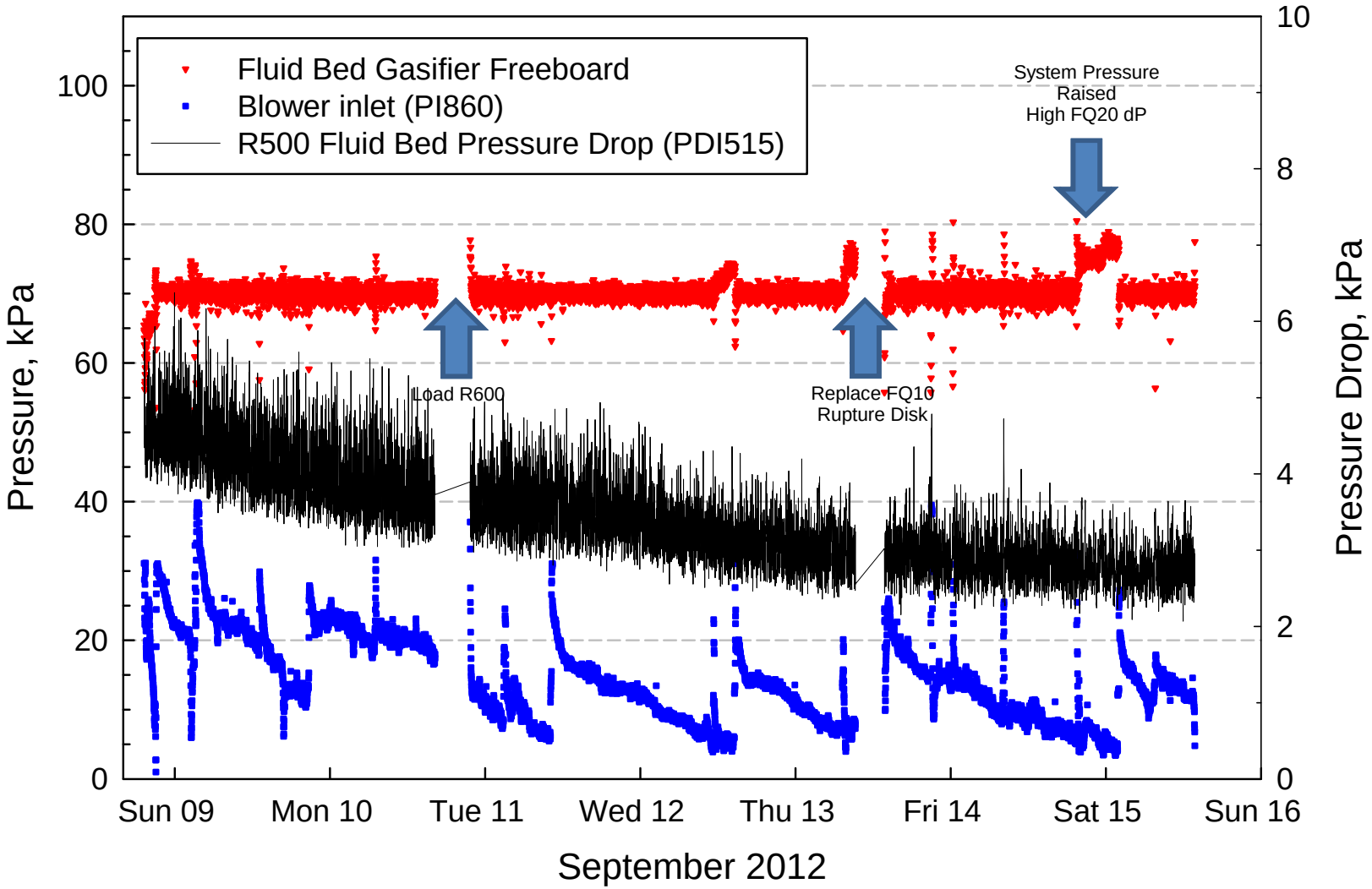
Gas Composition Through Gasifier/Reformer (N_2 Free)

Configuration	Gasifier Only	G + R600	G + R600 + PBR	Gasifier Only	G + R600+PBR
Carrier	Steam + CO2	Steam + CO2	Steam + CO2	Steam	Steam
S/B	1.79	1.79	1.79	2.0	2.0
CO2/B	0.53	0.53	0.53		
No. Samples	28	138	166	35	658
Gas Composition, Mole % Nitrogen Free					
H2	20.10 +/- 0.85	39.90 +/- 1.38	44.41 +/- 1.31	37.48 +/- 0.27	59.78 +/- 5.78
CO	16.27 +/- 0.45	17.47 +/- 1.21	15.22 +/- 0.45	17.09 +/- 0.33	11.52 +/- 2.87
CO2	50.91 +/- 0.52	38.96 +/- 0.94	38.60 +/- 1.21	25.94 +/- 0.26	26.73 +/- 3.23
CH4	8.90 +/- 0.25	2.84 +/- 0.86	0.77 +/- 0.17	13.08 +/- 0.20	0.88 +/- 1.10
C2H6	0.23 +/- 0.24	0.00 +/- 0.00	0.00 +/- 0.00	0.04 +/- 0.00	0.00 +/- 0.05
C2H4	1.89 +/- 0.04	0.00 +/- 0.00	0.00 +/- 0.00	2.58 +/- 0.07	0.05 +/- 0.30
C2H2	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.78 +/- 0.01	0.01 +/- 0.10
C3H8	0.02 +/- 0.02	0.03 +/- 0.07	0.01 +/- 0.01	0.79 +/- 0.01	0.00 +/- 0.06
C3H6	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.03
1-C4H8	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00
2-t C4H8	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00
2-c C4H8	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00
Ar/He	1.68 +/- 0.05	0.80 +/- 0.51	0.99 +/- 0.04	2.23 0.03	1.03 +/- 0.17
H2S (ppmv)	9.71 +/- 5.12	4.37 +/- 5.94	11.69 +/- 4.58	ND	ND
COS (ppmv)	0.00 +/- 0.00	0.00 +/- 0.00	0.00 +/- 0.00	ND	ND
H2/CO	1.24 +/- 0.05	2.30 +/- 0.24	2.92 +/- 0.07	2.19 +/- 0.04	5.36 +/- 1.17

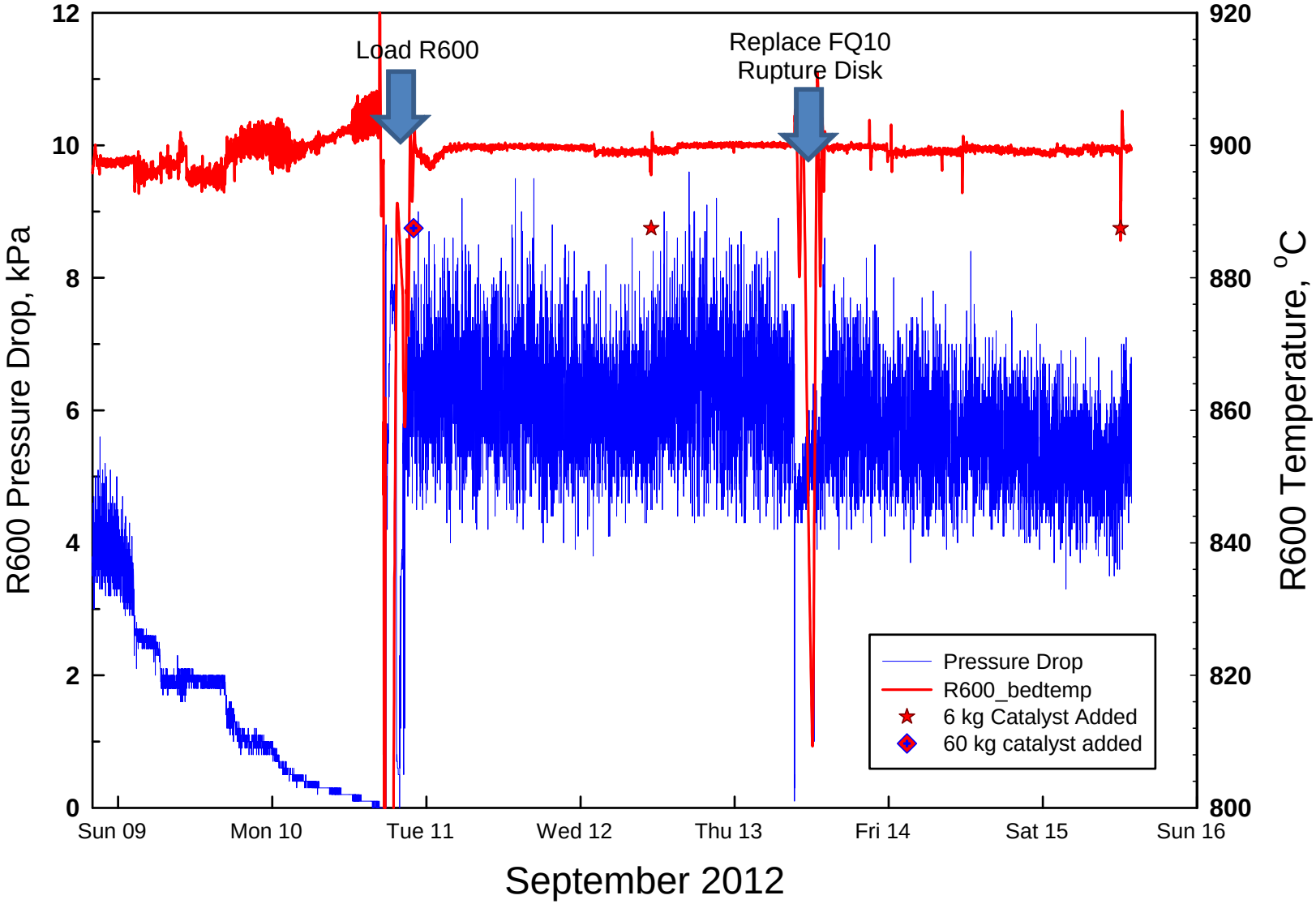
Fluid Bed Gasifier and Thermal Cracker Temperatures
NREL TCPDU



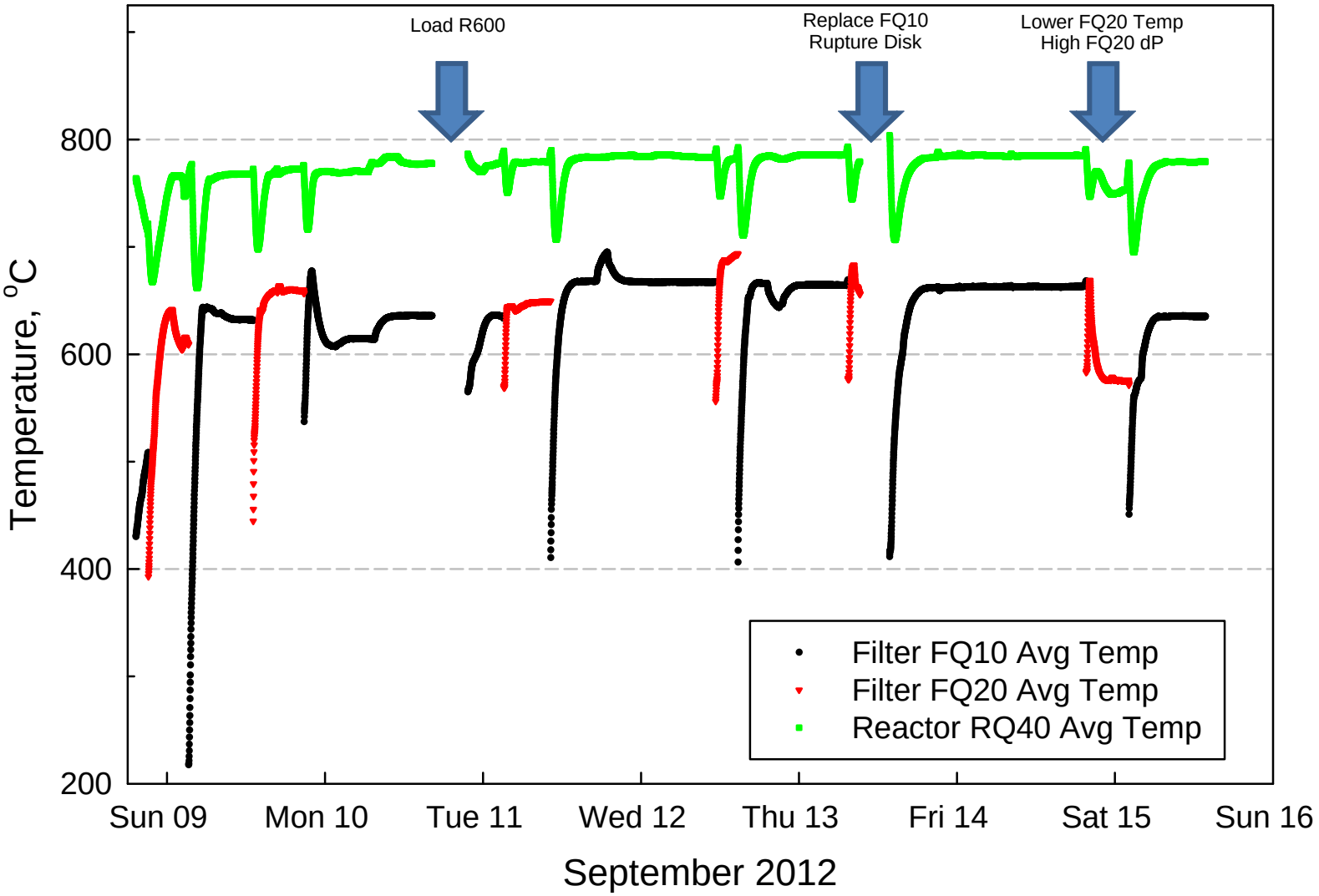
Fluid Bed Gasifier and Blower Inlet Pressures
NREL TCPDU



Fluid bed reformer temperature and pressure drop



Packed Bed Reactor Subsystem Temperatures
NREL TCPDU



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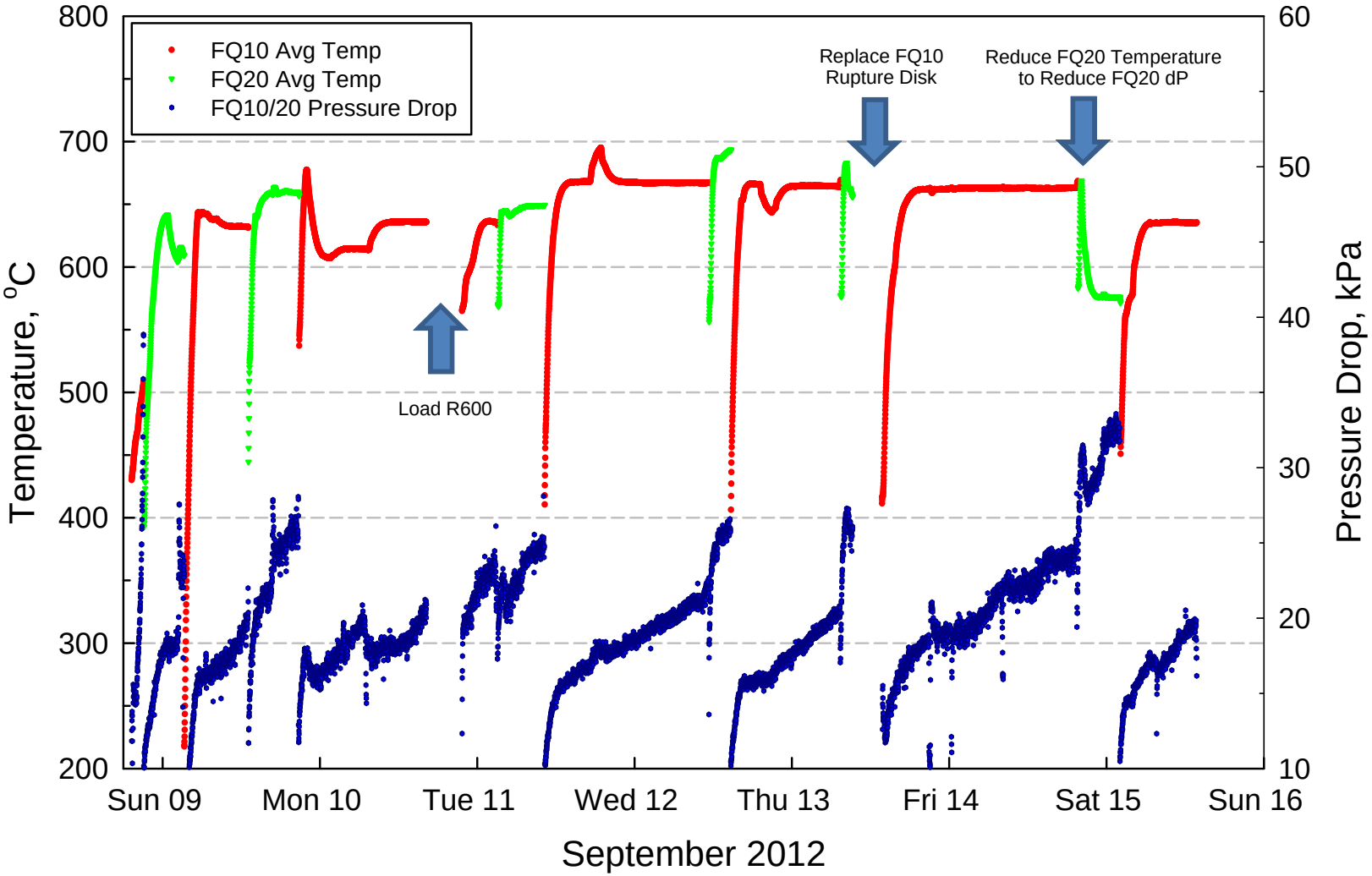
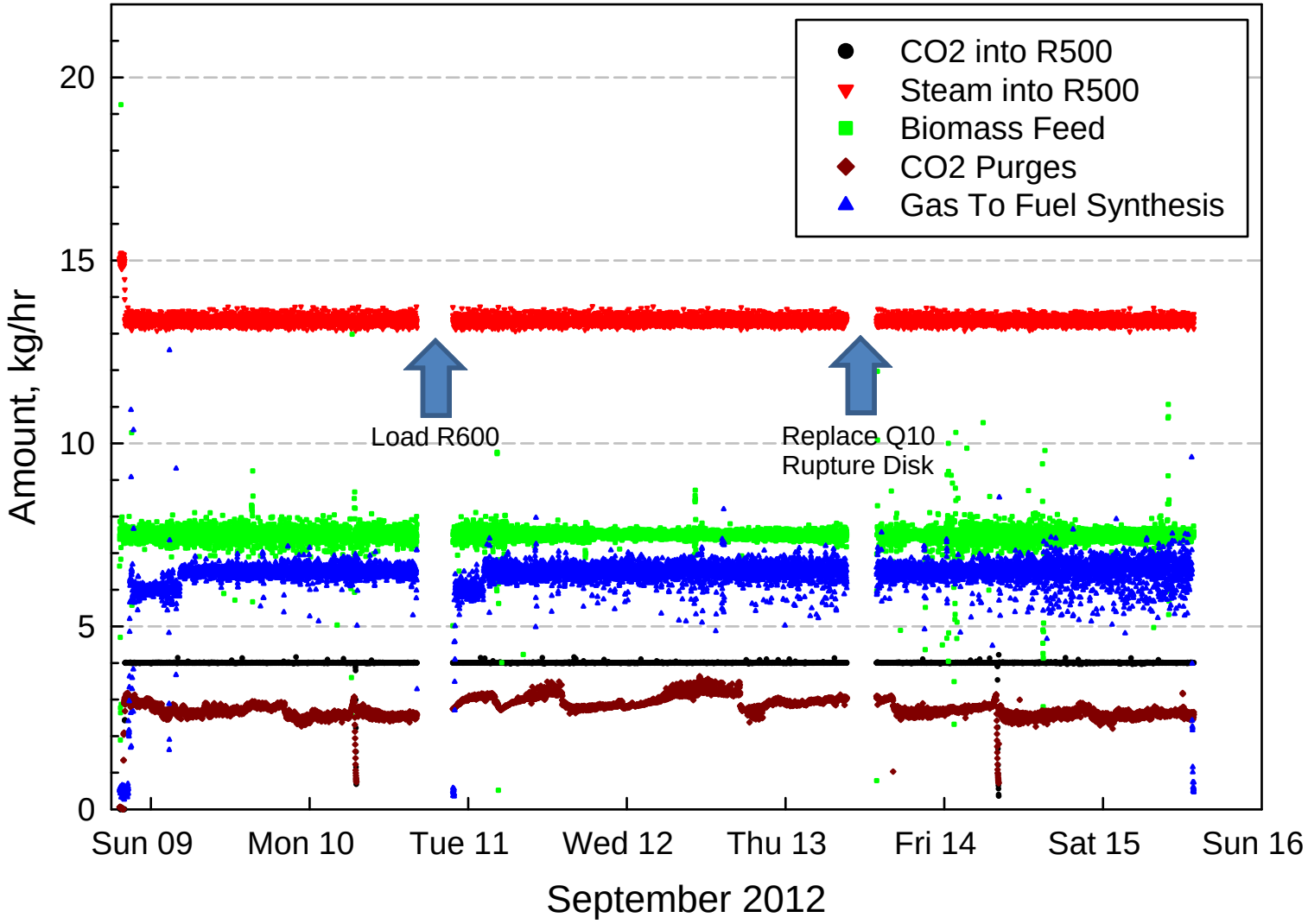
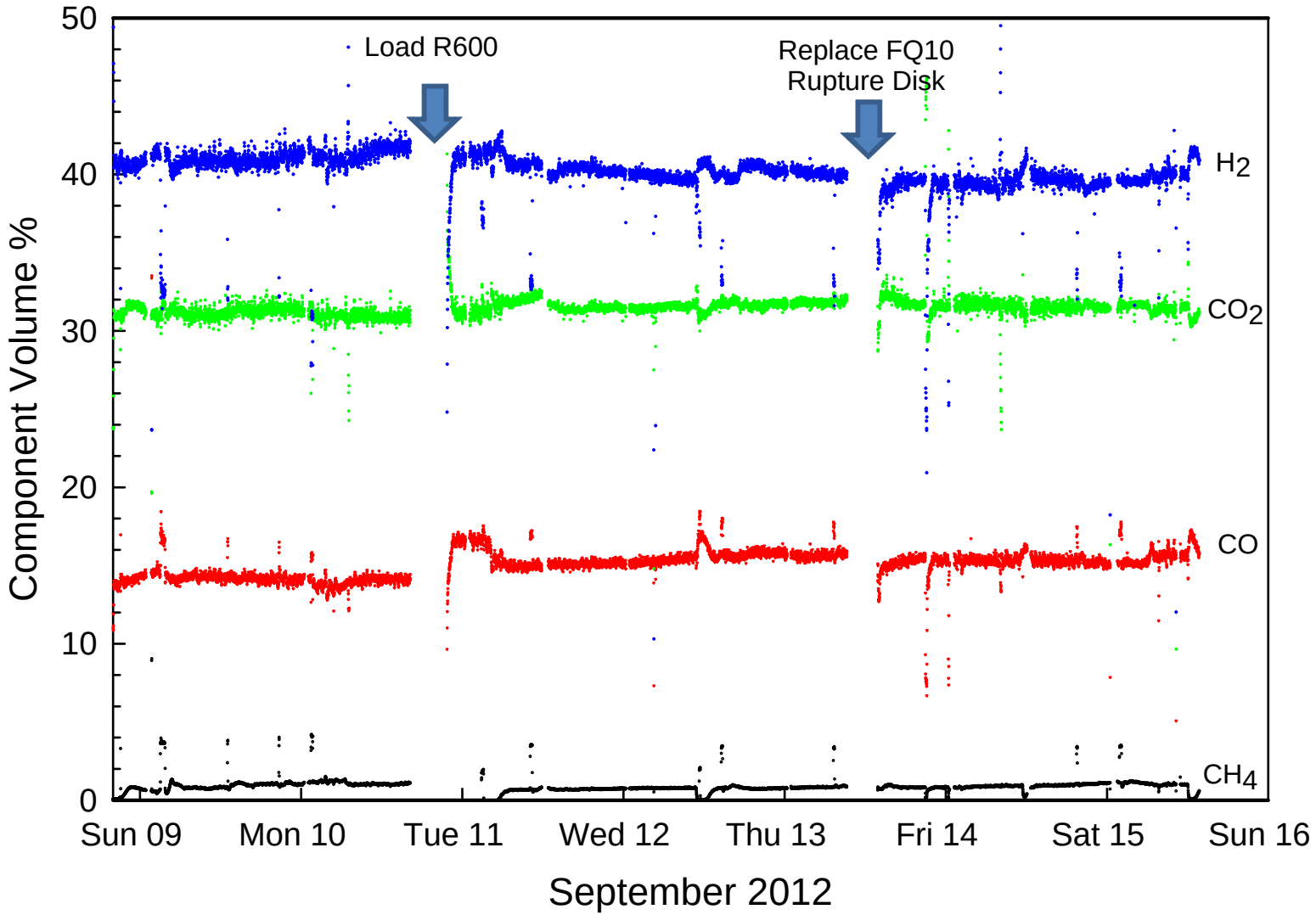
Packed Bed Filters Temperatures and Pressure Drop
NREL TCPDU



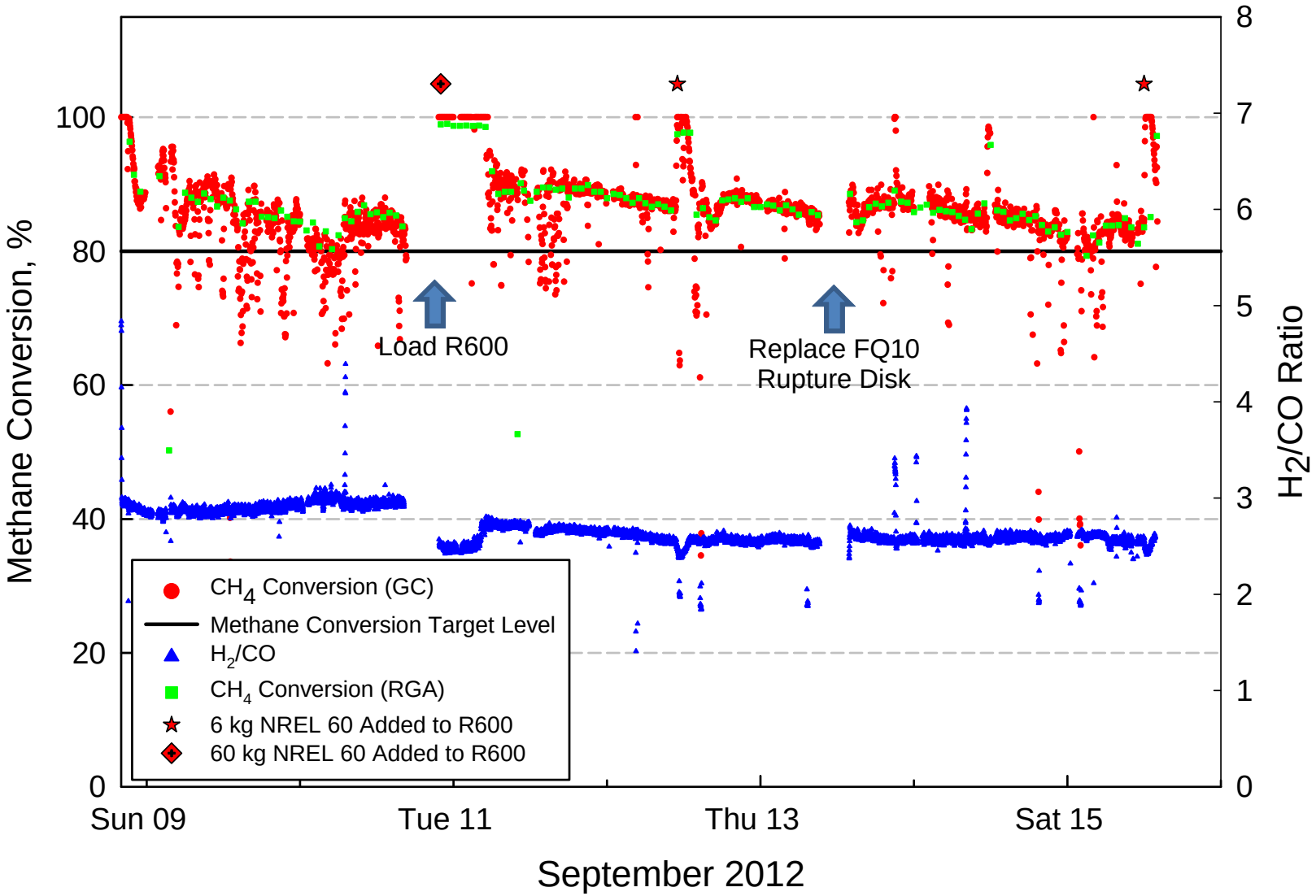
Biomass, steam, and gas flow rates



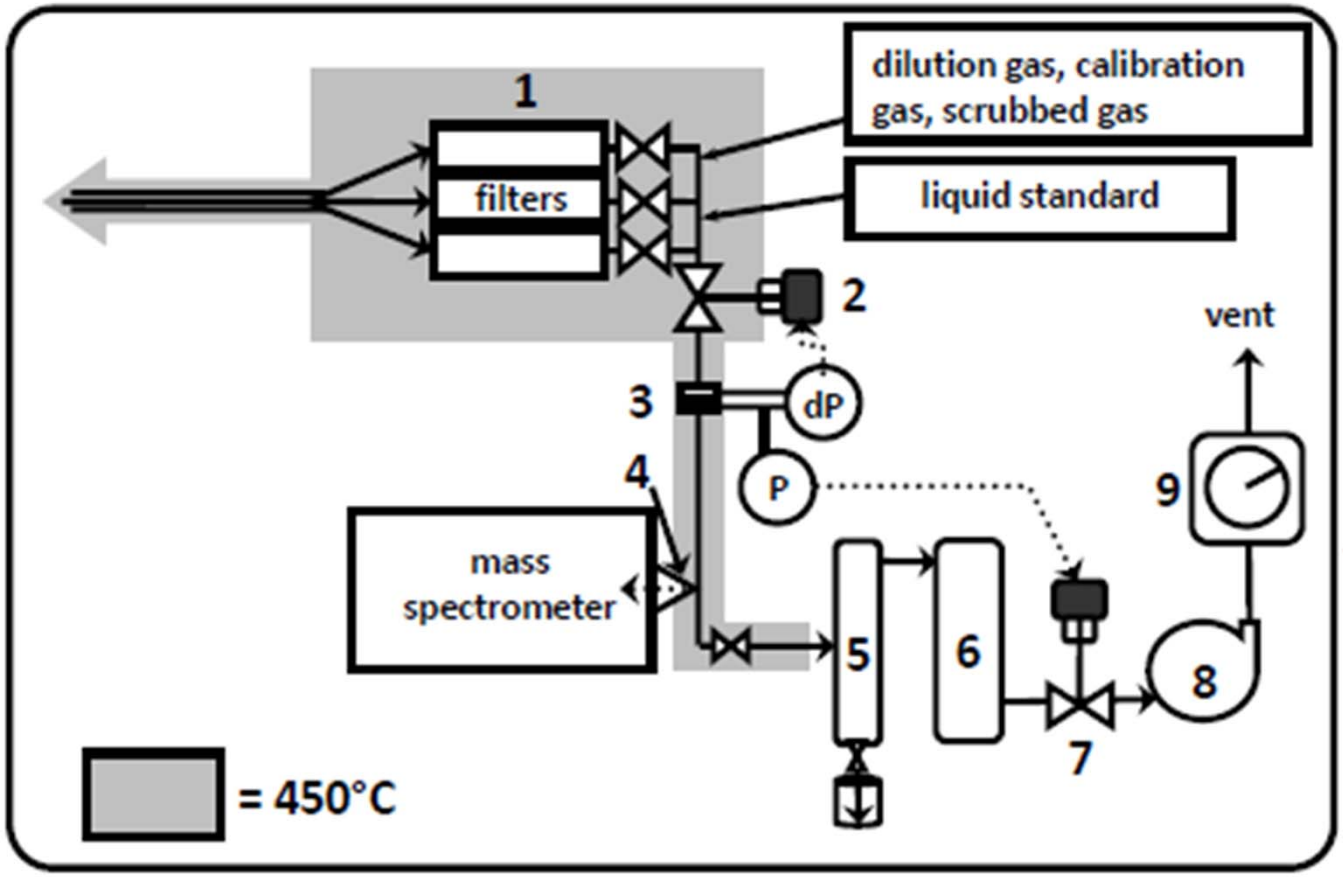
Gas Composition, Scrubber Exit
NDIR Data, NREL TCPDU



Methane conversion across sum of reformers and H_2:CO ratio at scrubber exit



Schematic of the Molecular Beam Mass Spectrometer



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,

Average steady state tar conversions during integrated run

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

* Surrogates used to represent tars.

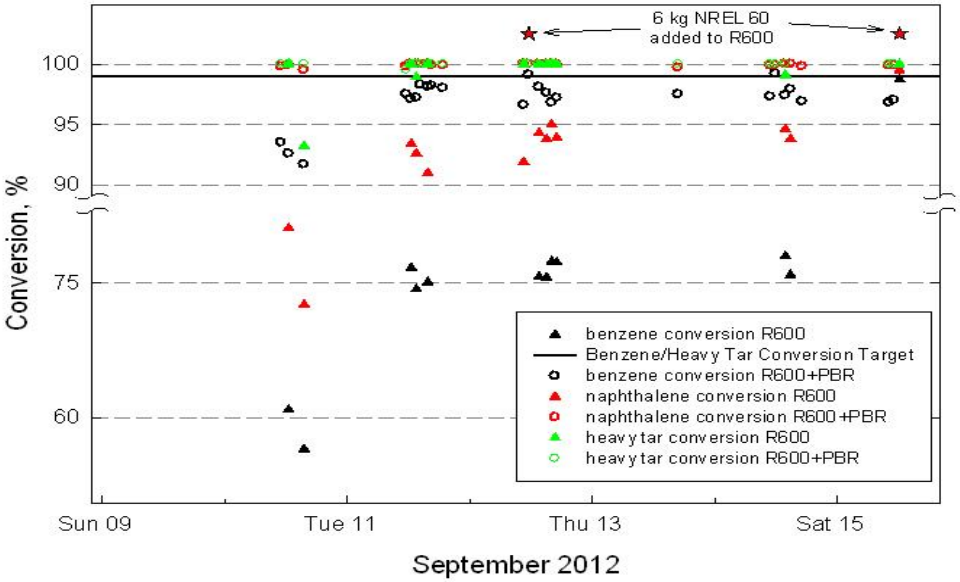
† 100% conversion indicates that effluent concentration is below detection limits

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)



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		

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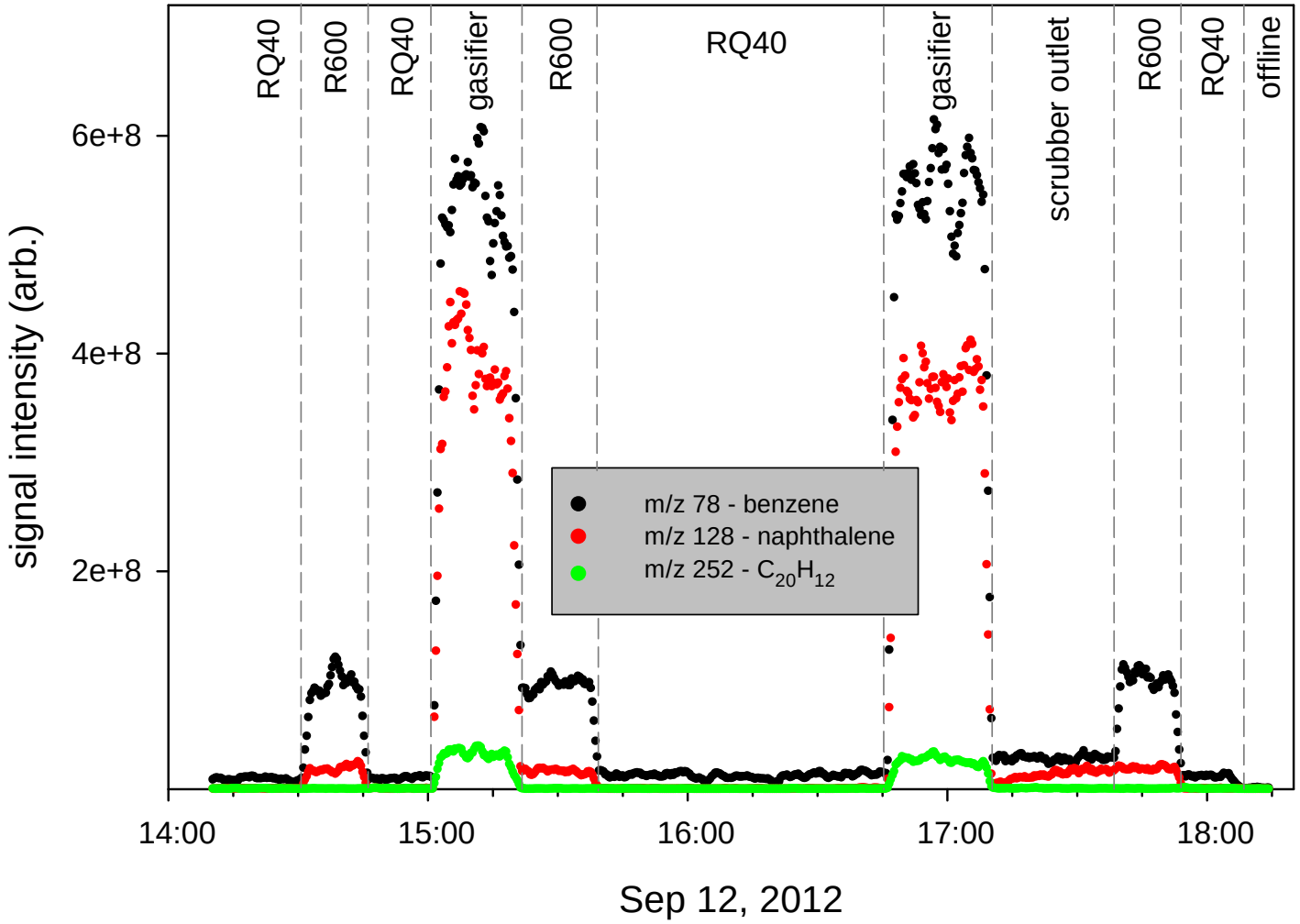
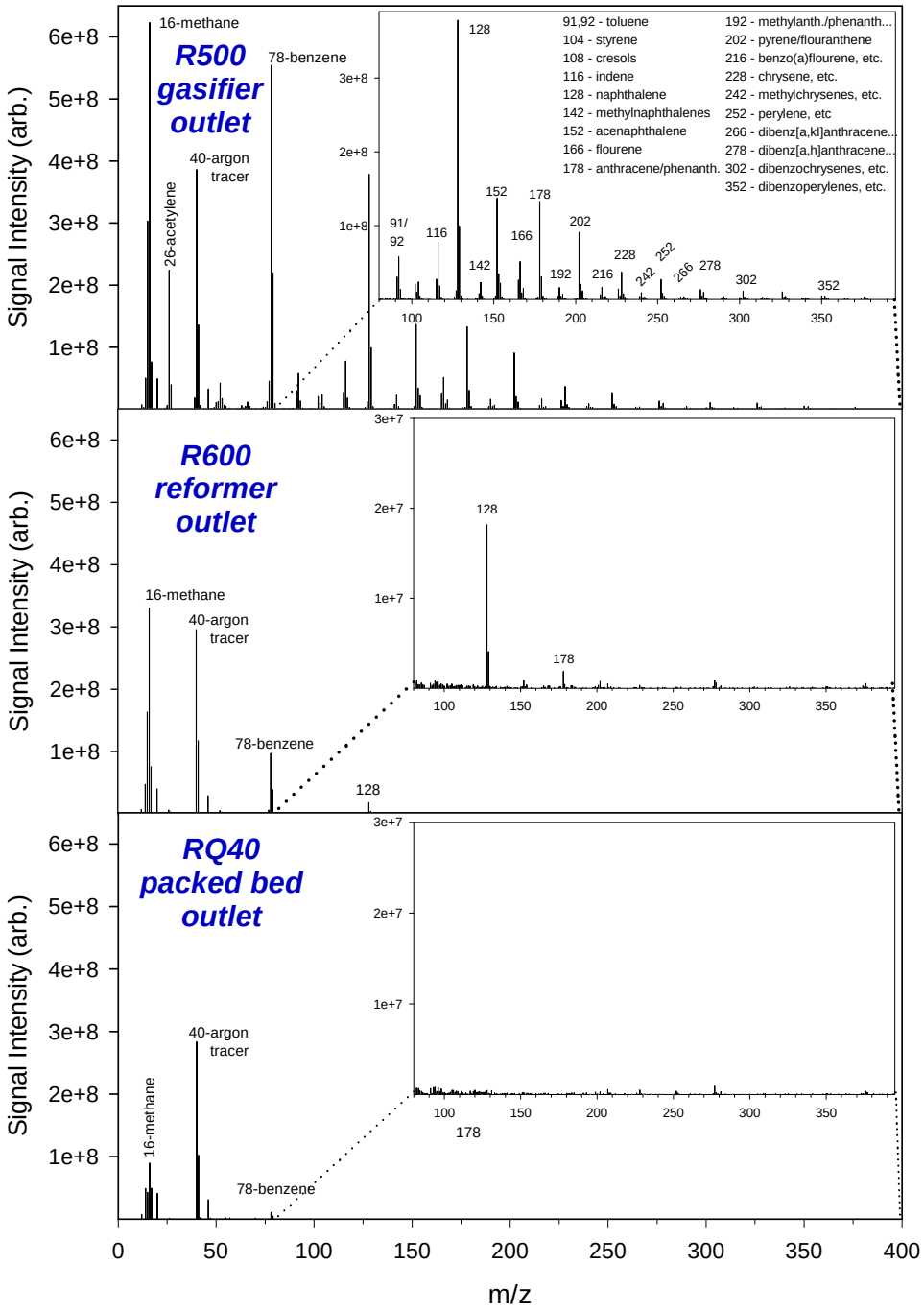
MBMS Ion traces - gasifier/reformer/PBR/scrubber
NREL TCPDU





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

Summary Results

Key technical targets for tar reforming and mixed alcohol synthesis consistent with those outlined for 2012 in the Office of Biomass Programs' Multi-Year Program Plan were met or exceeded. Successful production of mixed alcohols from biomass was demonstrated in an integrated pilot plant process, with additional bench-scale experiments conducted to further validate performance measures beyond the constraints of the integrated runs.

When the technological improvements are translated into an estimated n^{th} plant commercial cost of production (MESP) using NREL's techno-economic models (described in report NREL/TP-5100-51400 available at http://www.nrel.gov/docs/fy11osti/51400.pdf), the resulting MESP is $2.05/gallon and the conversion cost is $1.31/gallon, as shown below in Table ES-1. Furthermore, the $61.57/dry ton feedstock cost was demonstrated by the Idaho National Laboratory.

The catalysts developed to meet technical targets are robust and can be produced at scale.

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.