Poison-Resistant Water Gas Shift Catalyst for Biomass and Coal Gasification

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Research

2019 Crosscutting Research
Gasification Research

DE-SC0004378

About TDA

- **Founded in 1987**
  - Privately held
  - 80 employees, 27 Ph.D.'s -chemistry/engineering
  - Over $18 million in annual revenue
- **Facilities**
  - Combined 50,000 ft^2 laboratory and office space near Denver, Colorado
  - Catalyst development: Continuous PFR, CSTR, batch, large scale, high P&T systems
  - Sorbents for gas cleanup
  - Materials processing and testing
  - Process development (e.g. gas sweetening)
- **Business Model**
  - Identify opportunities with industry
  - Perform R&D
  - Secure intellectual property
  - Commercialize technology via spin-offs, licensing, joint ventures, internal business units


Wheat Ridge Facility


Golden Facility

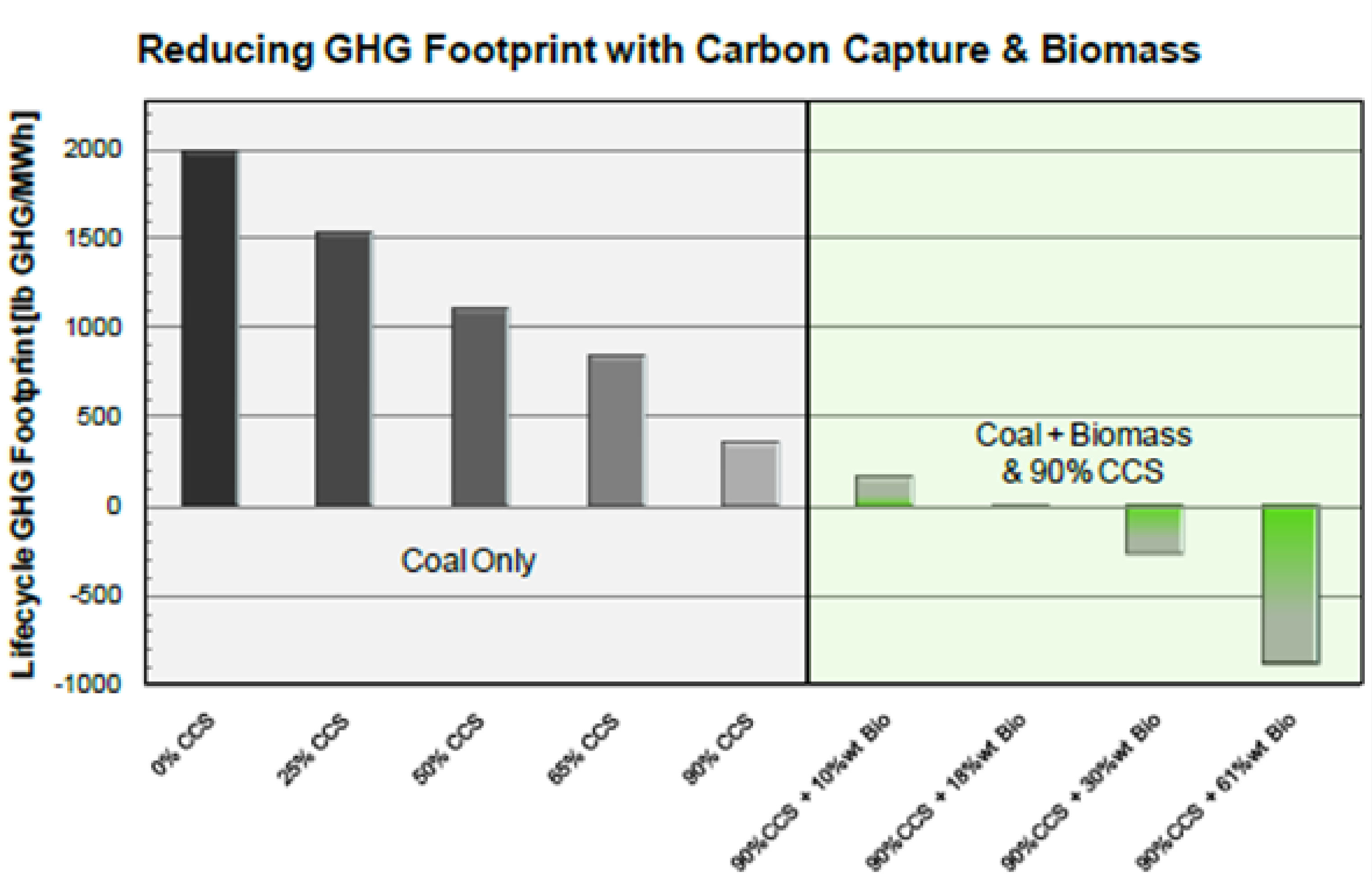
Sour Water Gas Shift
for
Co-Gasified Biomass & Coal

Background

Co-Gasification of Biomass & Coal

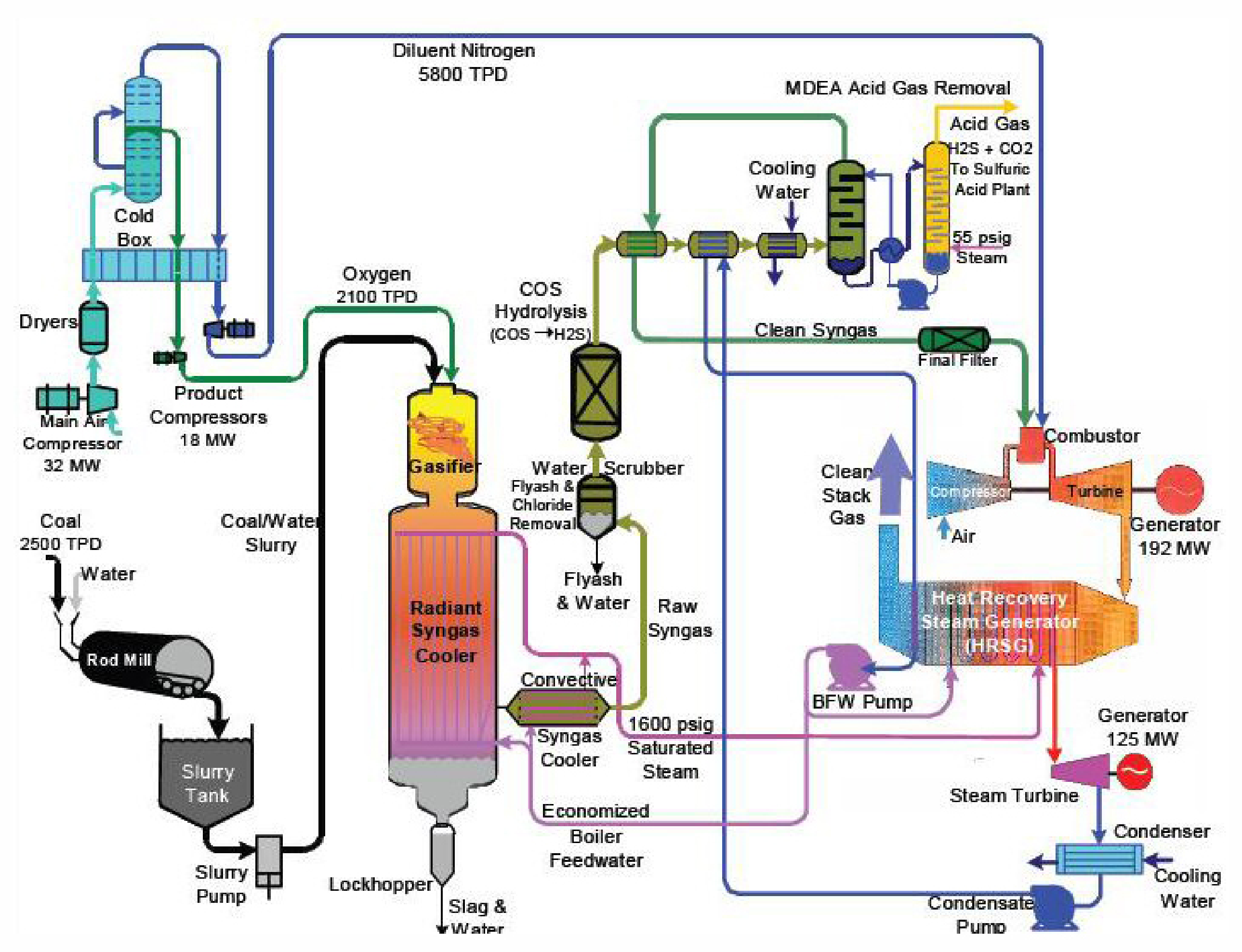
- **The U.S. has an estimated 250 billion tons of recoverable coal (EIA)**
  - 200+ years at current consumption rate of ~10^9 ton/y
- **Decrease CO_2 emissions**
  - More than 500 million tons/y of agricultural residue in the U.S.
  - Coal + biomass gasified to syngas
  - Gasifier produces a concentrated stream of CO_2 for sequestration
  - Syngas can then be shifted and converted to diesel fuel using Fischer Tropsch synthesis (e.g. wax and crack) or H_2 used for power and/or chemicals production

Gasification of Biomass/Coal Mixtures



- Greenhouse gas emissions can be dramatically reduced by gasifying biomass with coal and using carbon capture/sequestration

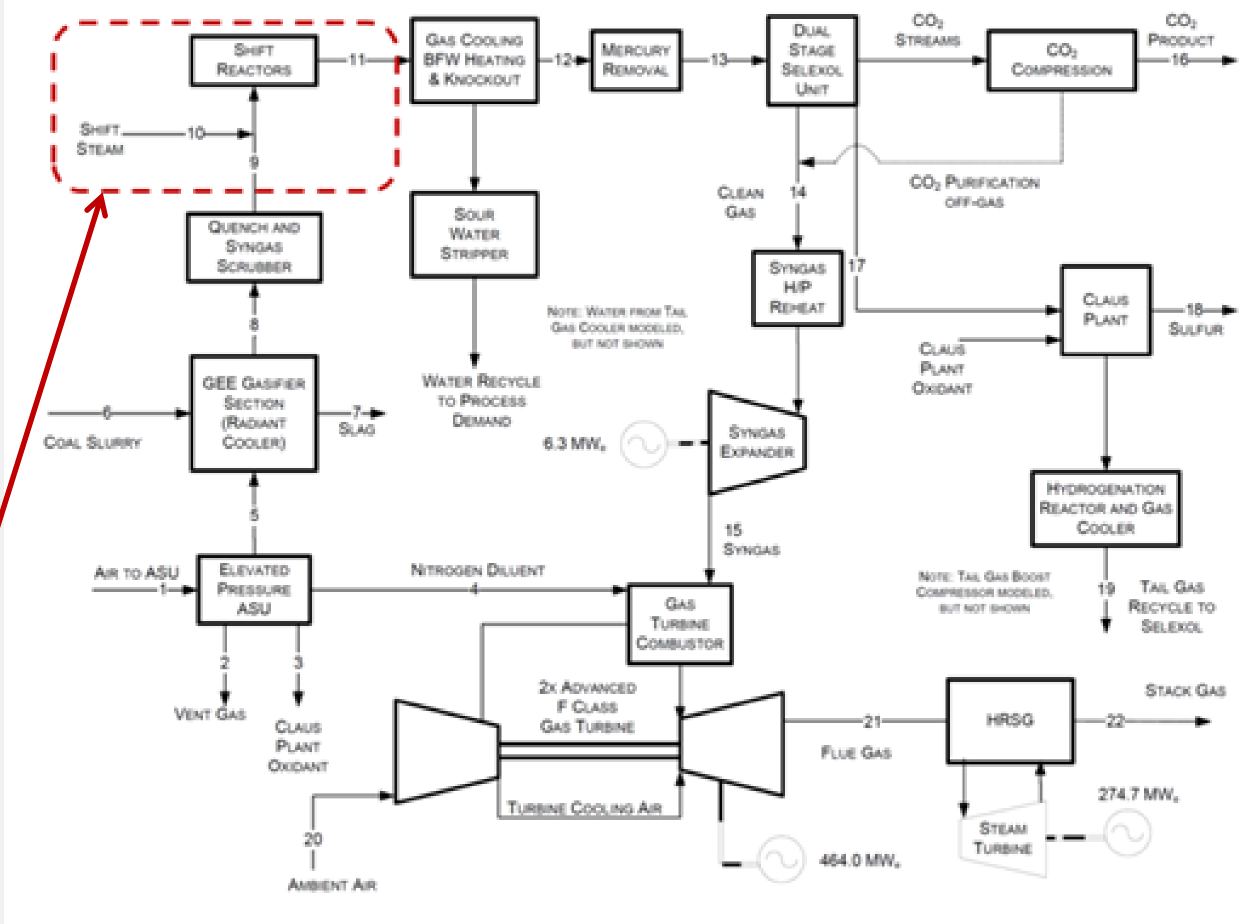
Scrubber Removes Particulates and Contaminants



(Tampa Electric) Entrained particulates, soluble contaminants such as ammonia and chlorides are removed by scrubbing

Texaco/GE 700 MW$_e$ IGCC

- While equilitrium is favored at lower temperatures, higher temperatures favor kinetics
- Ideal if we can find a catalyst with **high** kinetics at **low** temperatures
- TDA's catalyst lowers the shift temperature, which increases the concentration of H_2 in the syngas



Sour Water Gas Shift (SWGS)

- Goal is to develop a sour shift catalyst that has higher CO conversion than current commercial catalysts due to its ability to operate at lower temperatures where the WGS equilibrium is more favorable
- Catalyst also needs to be resistant to poisons in biomass/coal-derived syngas
  - Increased H_2 production
  - Useful for DOE’s coal/biomass gasification programs (poison resistant)
  - Would also benefit refiners that use POX to generate syngas

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

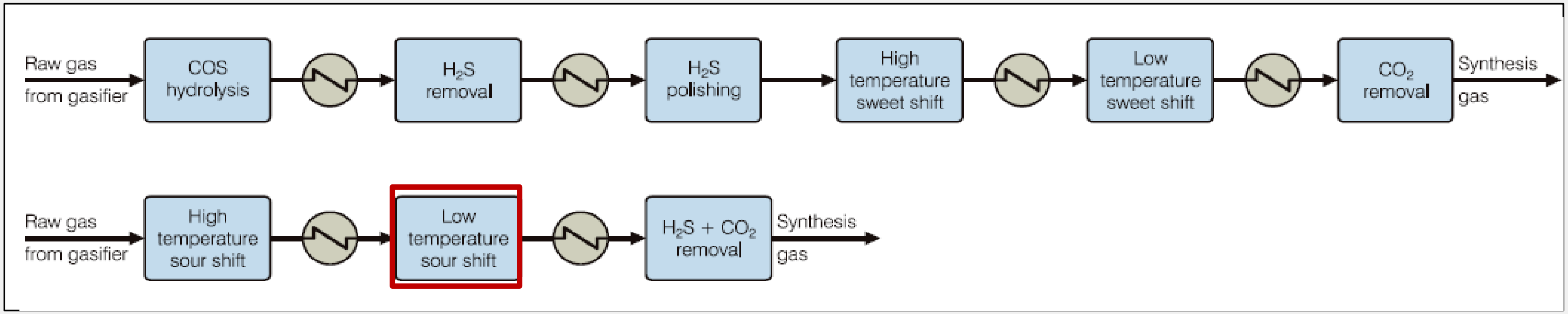
CO(g)+H2O(g)=CO2(g)+H2(g)					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
C	kcal	cal/K	kcal		
0	-9.848	-10.103	-7.088	4.696E+005	5.672
100	-9.747	-9.797	-6.091	3.698E+003	3.568
200	-9.580	-9.403	-5.131	2.346E+002	2.370
300	-9.374	-9.008	-4.211	4.034E+001	1.606
400	-9.142	-8.636	-3.329	1.205E+001	1.081
500	-8.896	-8.295	-2.483	5.033E+000	0.702
600	-8.646	-7.992	-1.668	2.616E+000	0.418

K increases as T decreases

$$K = \frac{P_{H_2} P_{CO_2}}{P_{H_2O} P_{CO}}$$

Advantages of Sour Shift

- **Sweet (no H_2S) shift (example 2 stages)**
  - Fe- based high temperature shift (HTS) catalysts have some sulfur resistance
  - Low temperature shift (LTS) Cu-ZnO catalysts are severely poisoned by sulfur
  - H_2S must be removed upstream of the shift

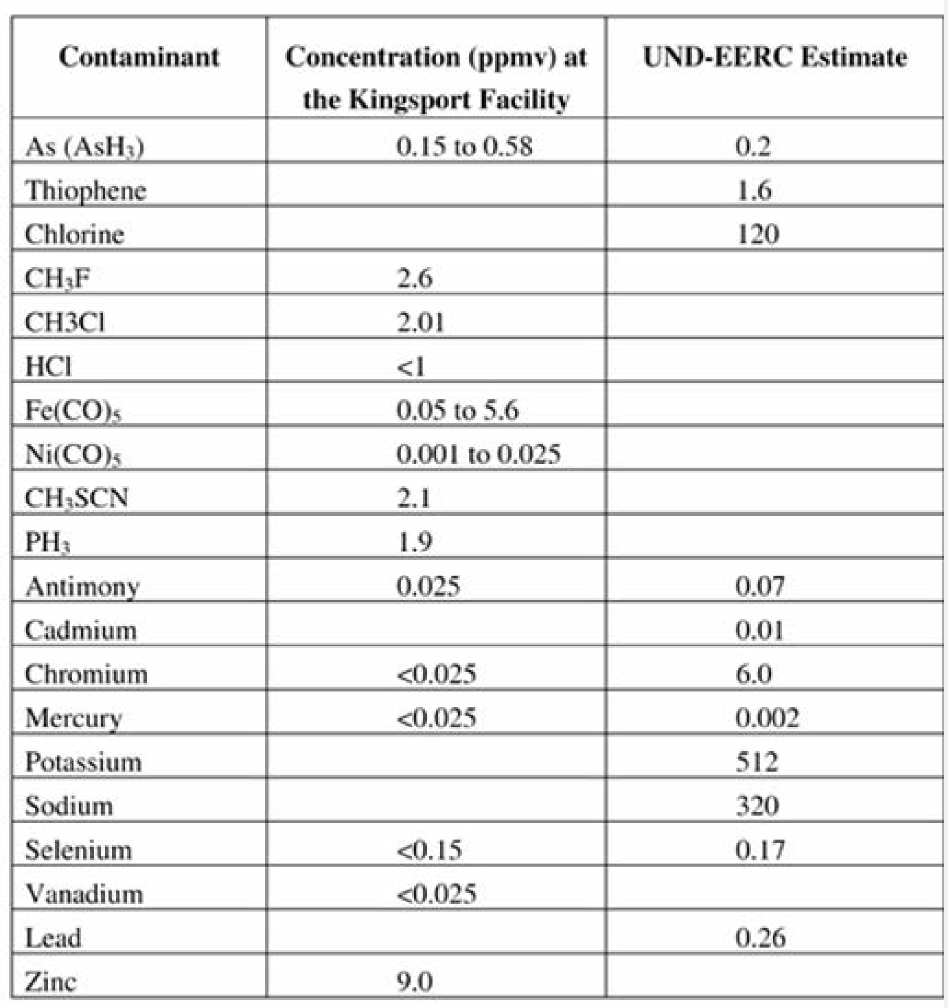


- **Sour shift (leave H_2S in the gas)**
  - Process is much simpler
  - Promoted Co-Mo/Al_2O_3 catalysts actually require H_2S to remain active
  - SWGS catalyst can be used for both HTS and LTS
  - WGS is equilibrium limited, lower temperatures give greater CO conversion
  - **TDA's catalyst further lowers the operating temperature for sour LTS**

Contaminants in Coal Derived Syngas

- Many of the volatile components are well known catalyst poisons
- Exactly how they affect SWGS catalysts when present in syngas derived from coal + biomass is part of this work

Krishnan, G.; Jayaweera, P.; Bao, J.; Perez, K.; Lau, H.; Hornbostel, M.; Sanjurgo, A.; Albritton, J.R. and Gupta, R.P. (2008) “Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life,” Final Technical Report, SRI Project No. P16935, Contract No.: DE FC26 05NT42627.

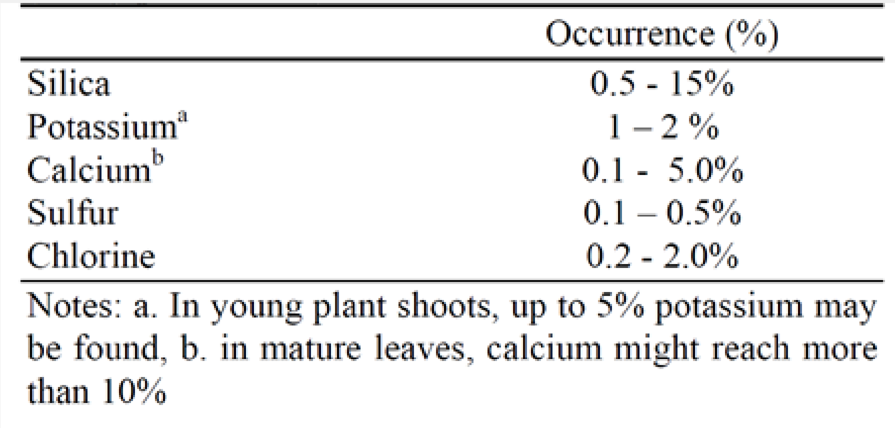


Contaminant	Concentration (ppmv) at the Kingsport Facility	UND-EERC Estimate
As (AsH$_3$)	0.15 to 0.58	0.2
Thiophene		1.6
Chlorine		120
CH$_3$F	2.6	
CH3Cl	2.01	
HCl	<1	
Fe(CO)$_5$	0.05 to 5.6	
Ni(CO)$_5$	0.001 to 0.025	
CH$_3$SCN	2.1	
PH$_3$	1.9	
Antimony	0.025	0.07
Cadmium		0.01
Chromium	<0.025	6.0
Mercury	<0.025	0.002
Potassium		512
Sodium		320
Selenium	<0.15	0.17
Vanadium	<0.025	
Lead		0.26
Zinc	9.0	

Contaminants in Biomass Derived Syngas

- Many of the elements found in biomass can be volatilized at high temperatures in the presence of steam during gasification

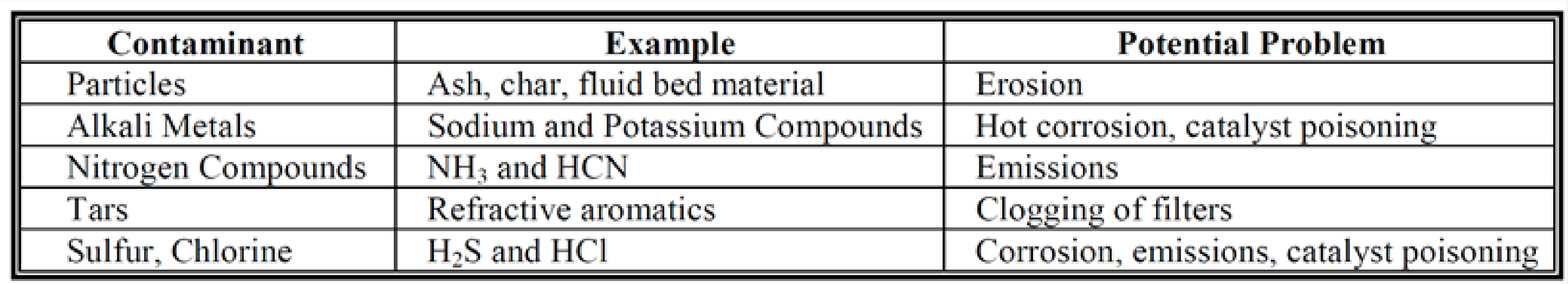
  - K as KOH and KCl
  - Si as $HSiO_4$
  - Cl as HCl (and alkali chlorides)
  - S as H_2S (needed by the SWGS catalyst)
  - N as HCN (trace) and NH_3



	Occurrence (%)
Silica	0.5 - 15%
Potassium[a]	1 – 2 %
Calcium[b]	0.1 - 5.0%
Sulfur	0.1 – 0.5%
Chlorine	0.2 - 2.0%

Notes: a. In young plant shoots, up to 5% potassium may be found, b. in mature leaves, calcium might reach more than 10%

Bakker, R.R. and Elbersen, H,W, (2005) "Managing Ash Content and -Quality in Herbaceous Biomass: An Analysis from Plant To Product," *14th European Biomass Conference*, 17-21 October 2005, Paris, France, p.p. 210-213



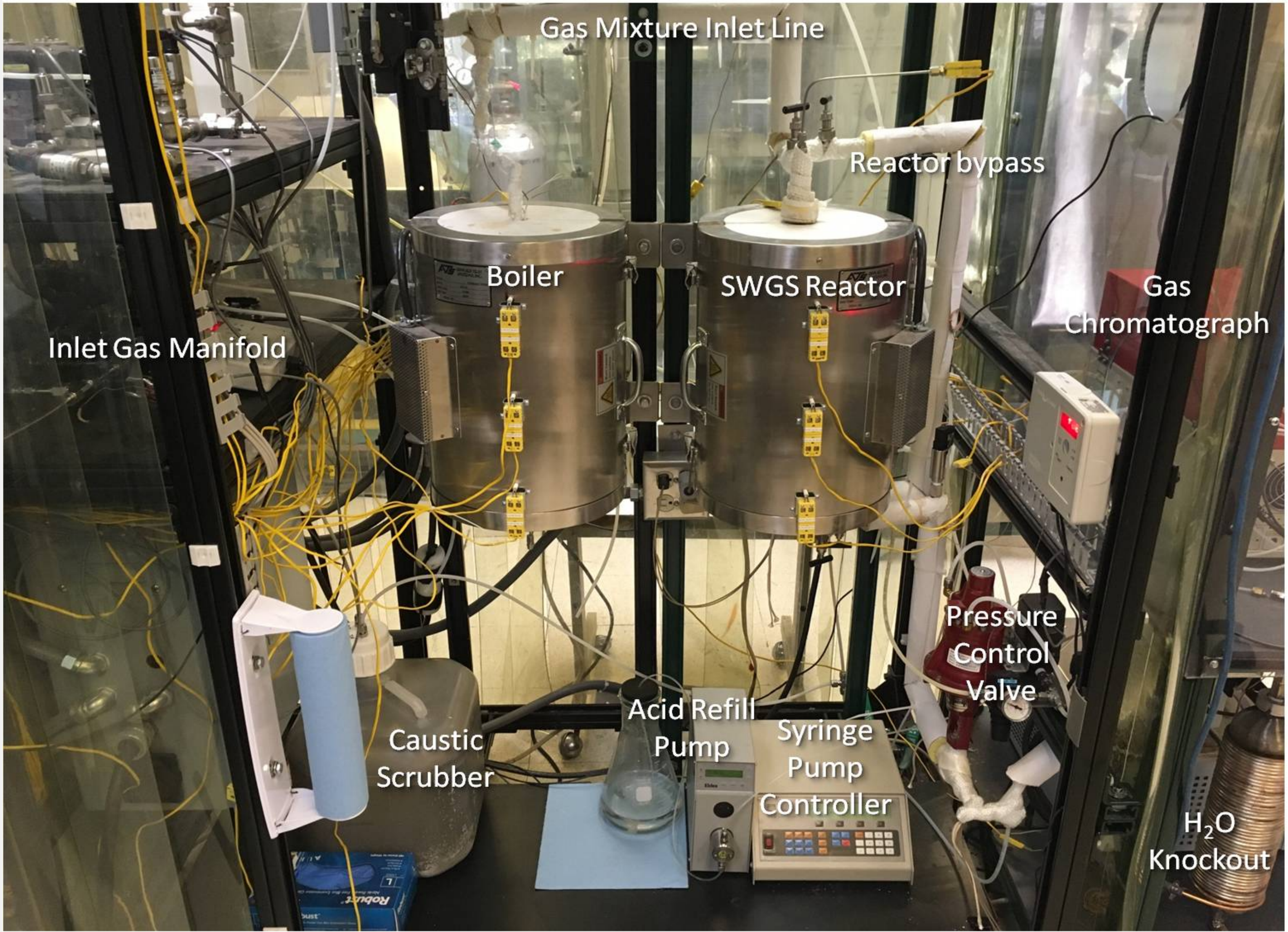
Contaminant	Example	Potential Problem
Particles	Ash, char, fluid bed material	Erosion
Alkali Metals	Sodium and Potassium Compounds	Hot corrosion, catalyst poisoning
Nitrogen Compounds	NH_3 and HCN	Emissions
Tars	Refractive aromatics	Clogging of filters
Sulfur, Chlorine	H_2S and HCl	Corrosion, emissions, catalyst poisoning

Ciferno, J.P. and Marano, J.J. (2002) Benchmarking Biomass Gasification Technologies for Fuels, Chemicals and Hydrogen Production," Prepared for, U.S. DOE/NETL, online at http://www.netl.doe.gov/technologies/coalpower/gasification/pubs/pdf/BMassGasFinal.pdf.

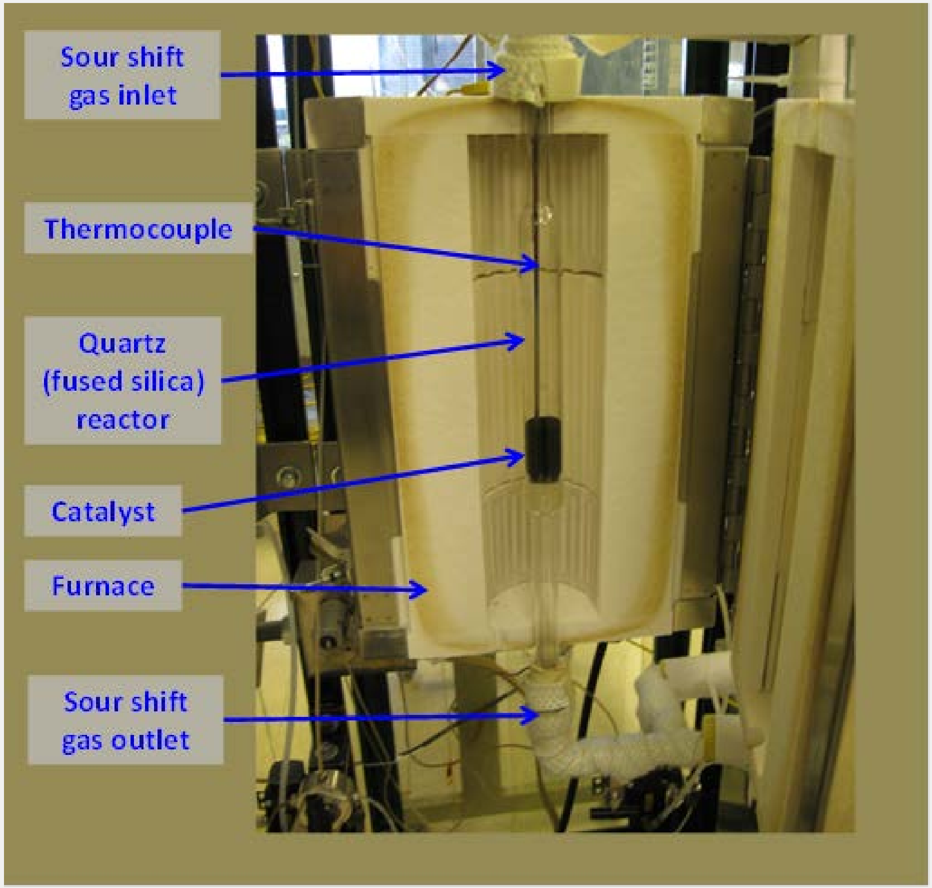
Sour Water Gas Shift
for
Co-Gasified Biomass & Coal

Experimental

Catalyst Test Apparatus



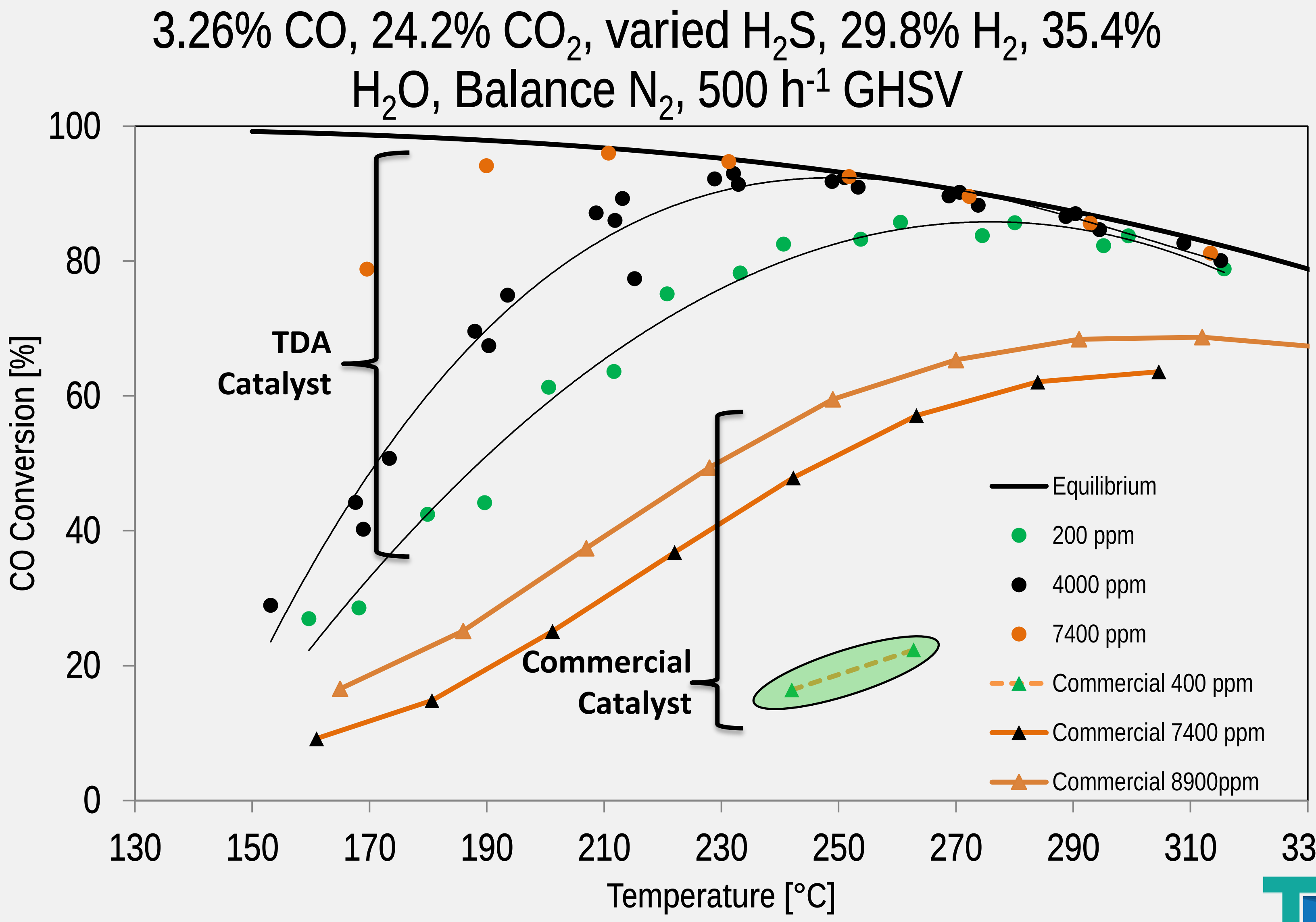
SWGS Catalytic Reactors



Low pressure screening

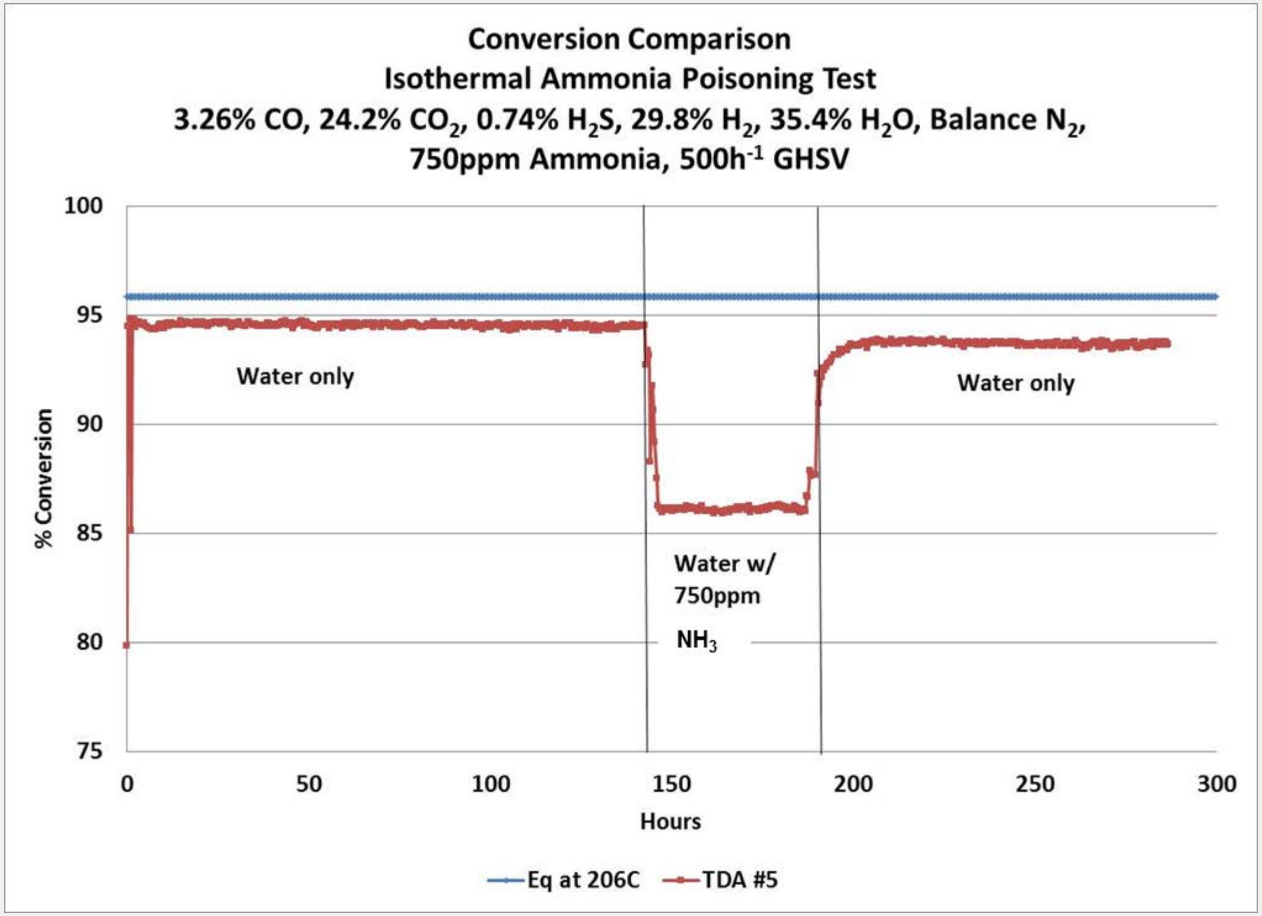
High pressure testing

TDA Catalyst is More Active – more H2S the Better



TDA Catalyst NH_3 Poisoning Test

(LTS, 2nd Bed)



- 750 ppmv NH_3
- Slightly higher loss of activity at higher NH_3 concentration
- Most of activity recovered when NH_3 is stopped

TDA Catalyst Scale-Up and Characterization

- In preparation for field testing at EERC, a total of 40 kg SWGS catalyst was shipped
- Combination of rotating coating pan and insipient wetness methods used
- Catalyst coated in two stages
- Dried after each stage
- Calcined overnight to produce final product
- Each batch of TDA catalyst and commercial catalyst were tested against predicted EERC conditions
- All five large batches were similar in appearance and performance

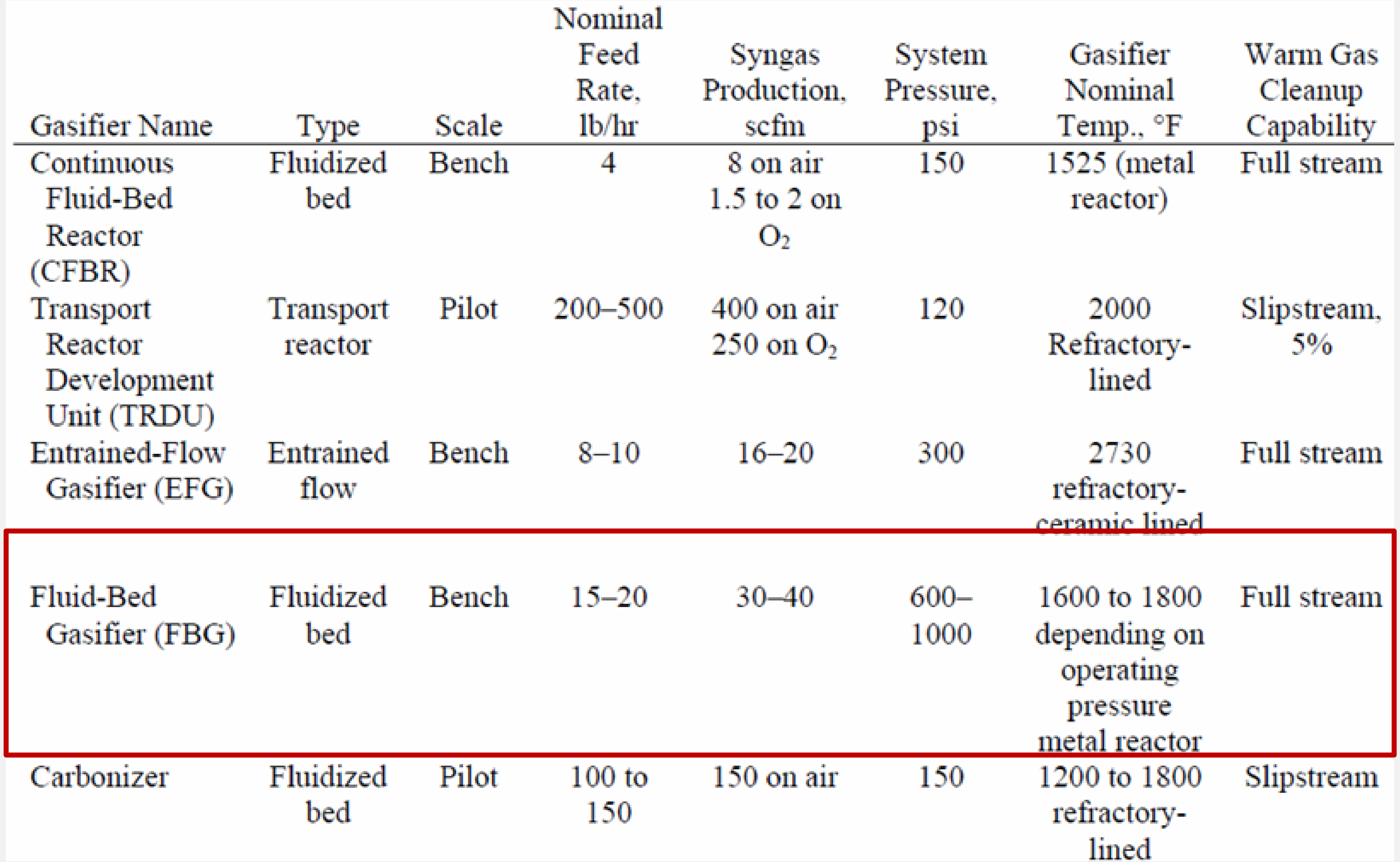
Sour Water Gas Shift for Co-Gasified Biomass & Coal

Field Test

Energy and Environmental Research Center (EERC)

- SWGS Reactors: 4.813 in. ID x 29 in. tall fixed beds
- Each reactor volume is 527 cubic inches (8.64 L)
- Maximum operating pressure is 1000 psig, at 1000°F (538°C)
- Four reactors in series that can be valved-off/around and bypassed as needed
- Three laser gas analyzers (LGA) using Raman spectroscopy
  - Capable of measuring up to eight gas species simultaneously
  - Can detect H_2, CO, CO_2, CH_4, N_2, O_2, H_2S, H_2O, and total hydrocarbons.
- Gas chromatographs as backup gas analysis
- Test campaigns using high pressure fluidized bed gasifier (HPFBG)
  - Operating pressure is about 700-720 psig

EERC High P Fluidized Bed Gasifier (HPFBG)



Gasifier Name	Type	Scale	Nominal Feed Rate, lb/hr	Syngas Production, scfm	System Pressure, psi	Gasifier Nominal Temp., °F	Warm Gas Cleanup Capability
Continuous Fluid-Bed Reactor (CFBR)	Fluidized bed	Bench	4	8 on air 1.5 to 2 on O_2	150	1525 (metal reactor)	Full stream
Transport Reactor Development Unit (TRDU)	Transport reactor	Pilot	200–500	400 on air 250 on O_2	120	2000 Refractory-lined	Slipstream, 5%
Entrained-Flow Gasifier (EFG)	Entrained flow	Bench	8–10	16–20	300	2730 refractory-ceramic lined	Full stream
Fluid-Bed Gasifier (FBG)	Fluidized bed	Bench	15–20	30–40	600–1000	1600 to 1800 depending on operating pressure metal reactor	Full stream
Carbonizer	Fluidized bed	Pilot	100 to 150	150 on air	150	1200 to 1800 refractory-lined	Slipstream

Energy and Environmental Research Center (EERC)

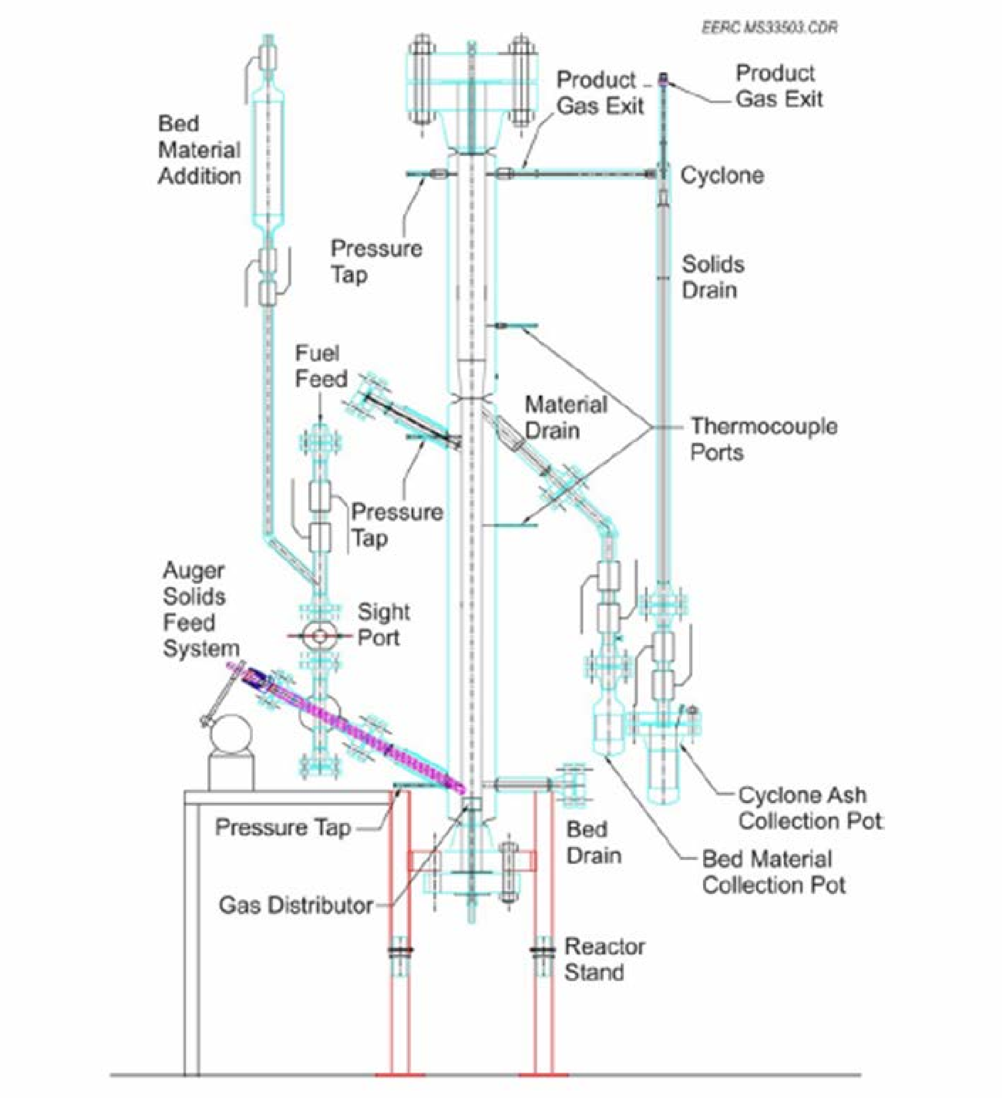
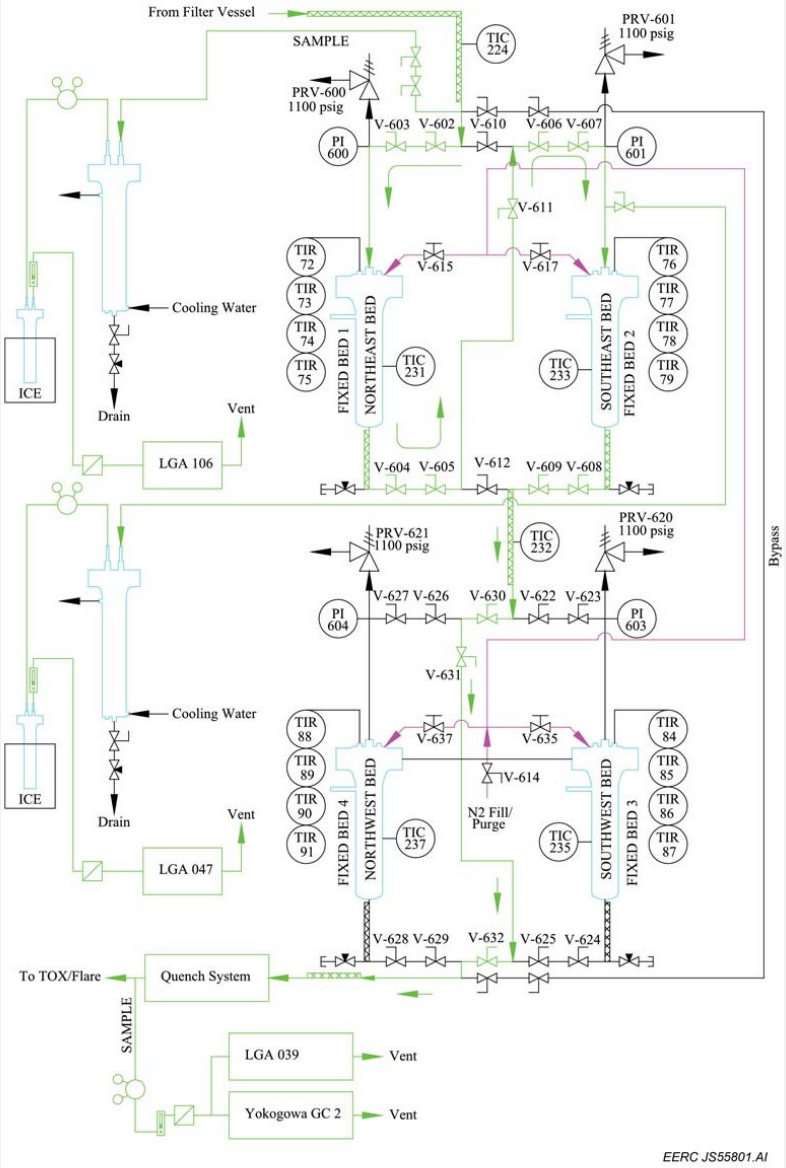


Figure B-4. Design drawing of the pressurized, fluidized-gasification reactor.

Energy & Environmental Research Center®
Putting Research into Practice

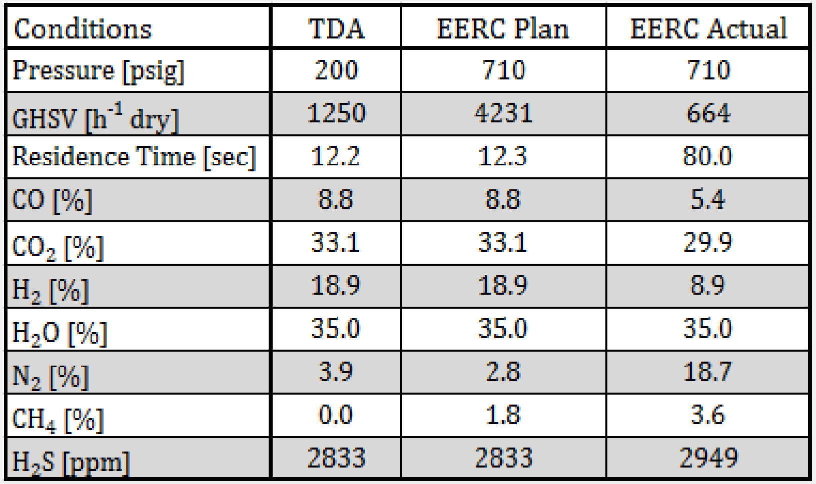
EERC Fixed Bed Reactors



EERC JS55801.AI

- 4 Fixed Bed Reactors
  - Flexible flow configurations
- 3 Laser Gas Analyzers
  - Measuring each stage of shift

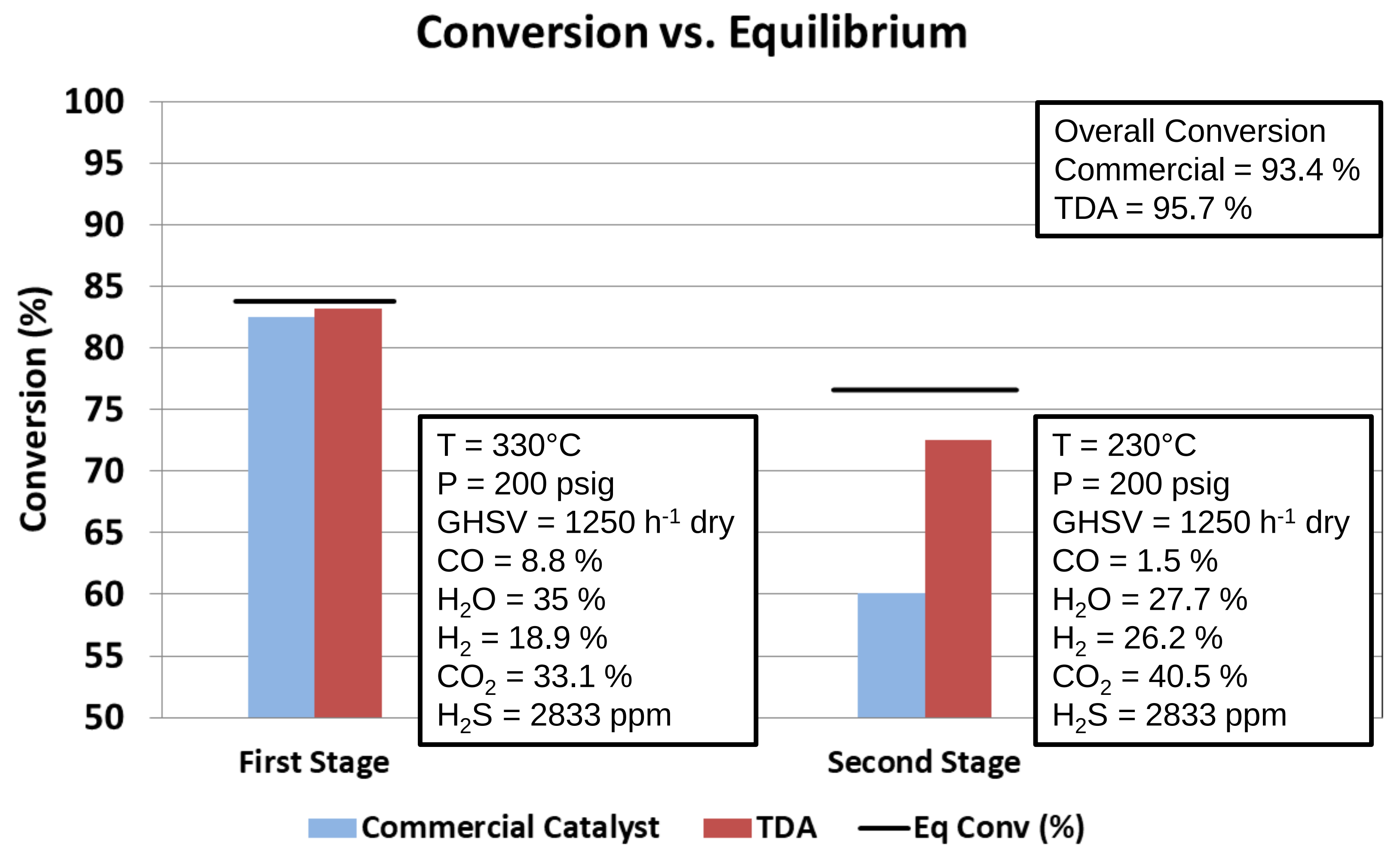
EERC Test Plan



Conditions	TDA	EERC Plan	EERC Actual
Pressure [psig]	200	710	710
GHSV [h^{-1} dry]	1250	4231	664
Residence Time [sec]	12.2	12.3	80.0
CO [%]	8.8	8.8	5.4
CO_2 [%]	33.1	33.1	29.9
H_2 [%]	18.9	18.9	8.9
H_2O [%]	35.0	35.0	35.0
N_2 [%]	3.9	2.8	18.7
CH_4 [%]	0.0	1.8	3.6
H_2S [ppm]	2833	2833	2949

- Parallel research effort with an existing test campaign for a precombustion CO_2 solvent developed by DOE’s NETL
- Solvent testing requires high pressure and the use of SWGS catalyst to increase CO_2 concentrations
- Full test campaign split into multiple runs
- Load TDA catalyst and existing commercial catalyst in parallel
  - Ability to switch catalyst on the fly
- Catalyst performance simulated under EERC conditions using TDA’s catalyst testing apparatus
  - TDA max reactor pressure is 200 psig
  - Reactor residence time simulated

SWGS Lab Testing w/EERC Conditions



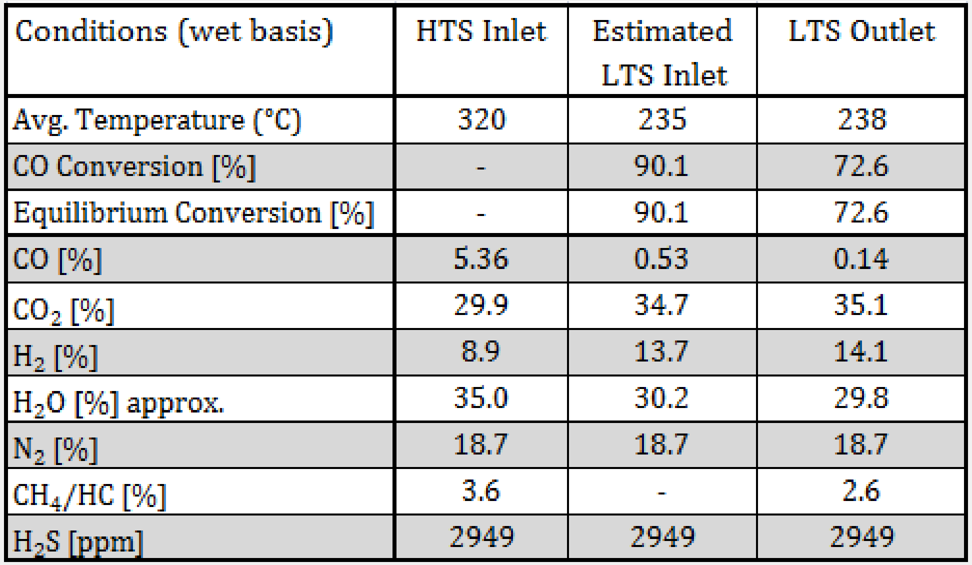
Overall Conversion
Commercial = 93.4 %
TDA = 95.7 %

T = 330°C
P = 200 psig
GHSV = 1250 h^{-1} dry
CO = 8.8 %
H_2O = 35 %
H_2 = 18.9 %
CO_2 = 33.1 %
H_2S = 2833 ppm

T = 230°C
P = 200 psig
GHSV = 1250 h^{-1} dry
CO = 1.5 %
H_2O = 27.7 %
H_2 = 26.2 %
CO_2 = 40.5 %
H_2S = 2833 ppm

- TDA Catalyst more active in both stages.
- Clearly outperforms in overall conversion.

EERC Results – Oct/Nov 2018



Conditions (wet basis)	HTS Inlet	Estimated LTS Inlet	LTS Outlet
Avg. Temperature (°C)	320	235	238
CO Conversion [%]	-	90.1	72.6
Equilibrium Conversion [%]	-	90.1	72.6
CO [%]	5.36	0.53	0.14
CO_2 [%]	29.9	34.7	35.1
H_2 [%]	8.9	13.7	14.1
H_2O [%] approx.	35.0	30.2	29.8
N_2 [%]	18.7	18.7	18.7
CH_4/HC [%]	3.6	-	2.6
H_2S [ppm]	2949	2949	2949

- Successfully completed two testing runs (Oct/Nov 2018)
- Total of 216 hr (9 days) on-stream
- Catalyst beds running at equilibrium maximum values of conversion
- No catalyst degradation over time

EERC Results – Oct/Nov 2018

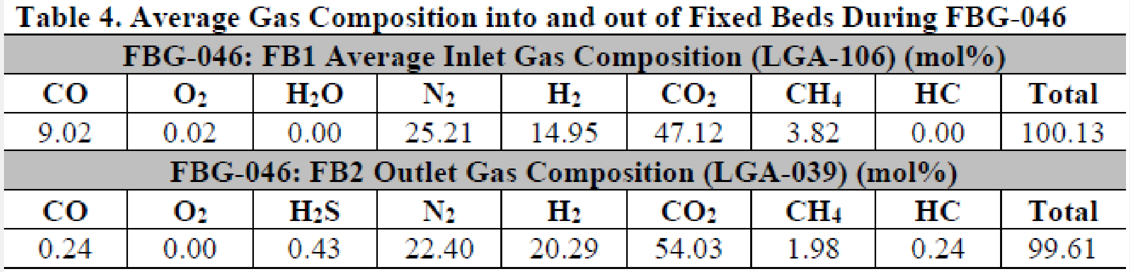


Table 4. Average Gas Composition into and out of Fixed Beds During FBG-046

FBG-046: FB1 Average Inlet Gas Composition (LGA-106) (mol%)

CO	O_2	H_2O	N_2	H_2	CO_2	CH_4	HC	Total
9.02	0.02	0.00	25.21	14.95	47.12	3.82	0.00	100.13

FBG-046: FB2 Outlet Gas Composition (LGA-039) (mol%)

CO	O_2	H_2S	N_2	H_2	CO_2	CH_4	HC	Total
0.24	0.00	0.43	22.40	20.29	54.03	1.98	0.24	99.61

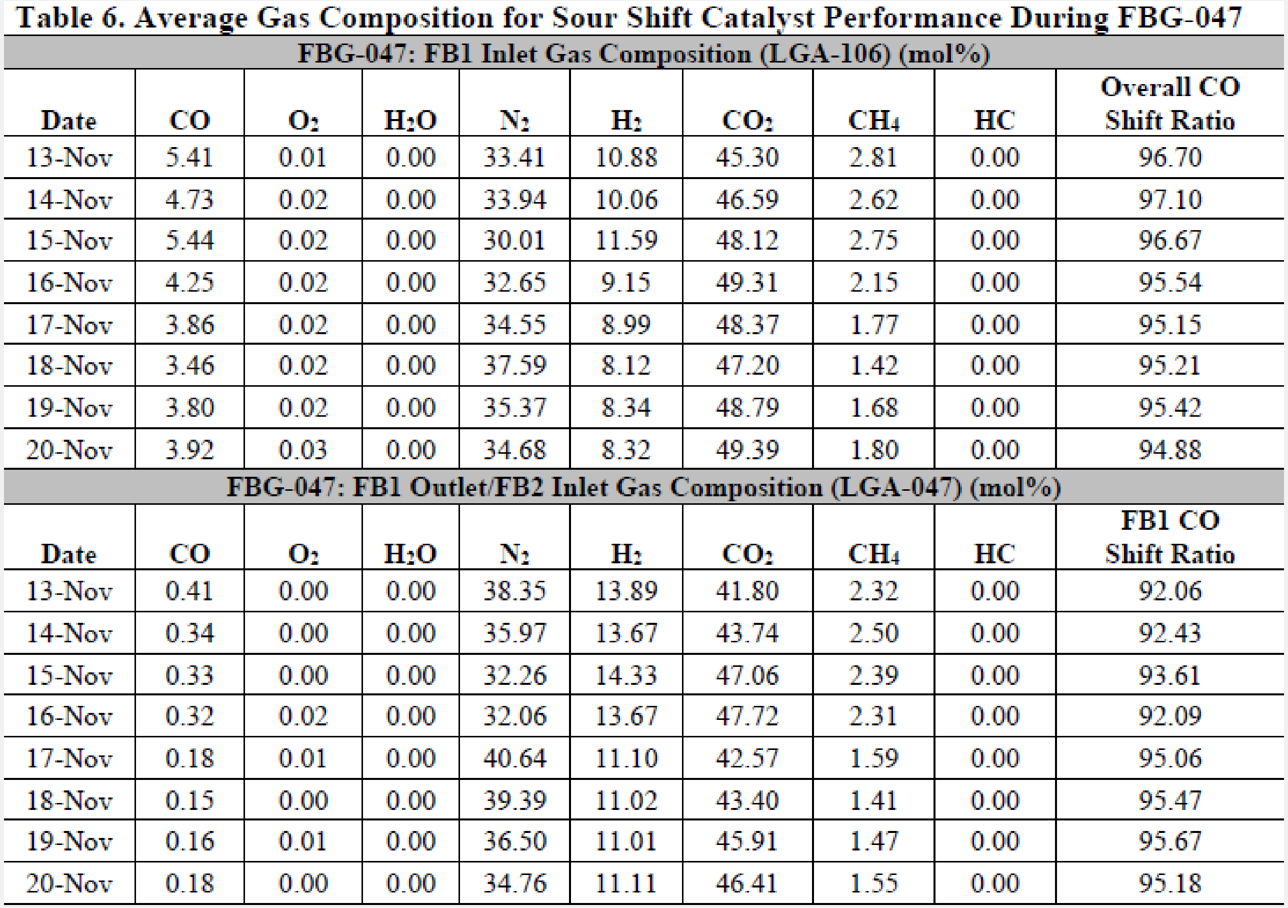


Table 6. Average Gas Composition for Sour Shift Catalyst Performance During FBG-047

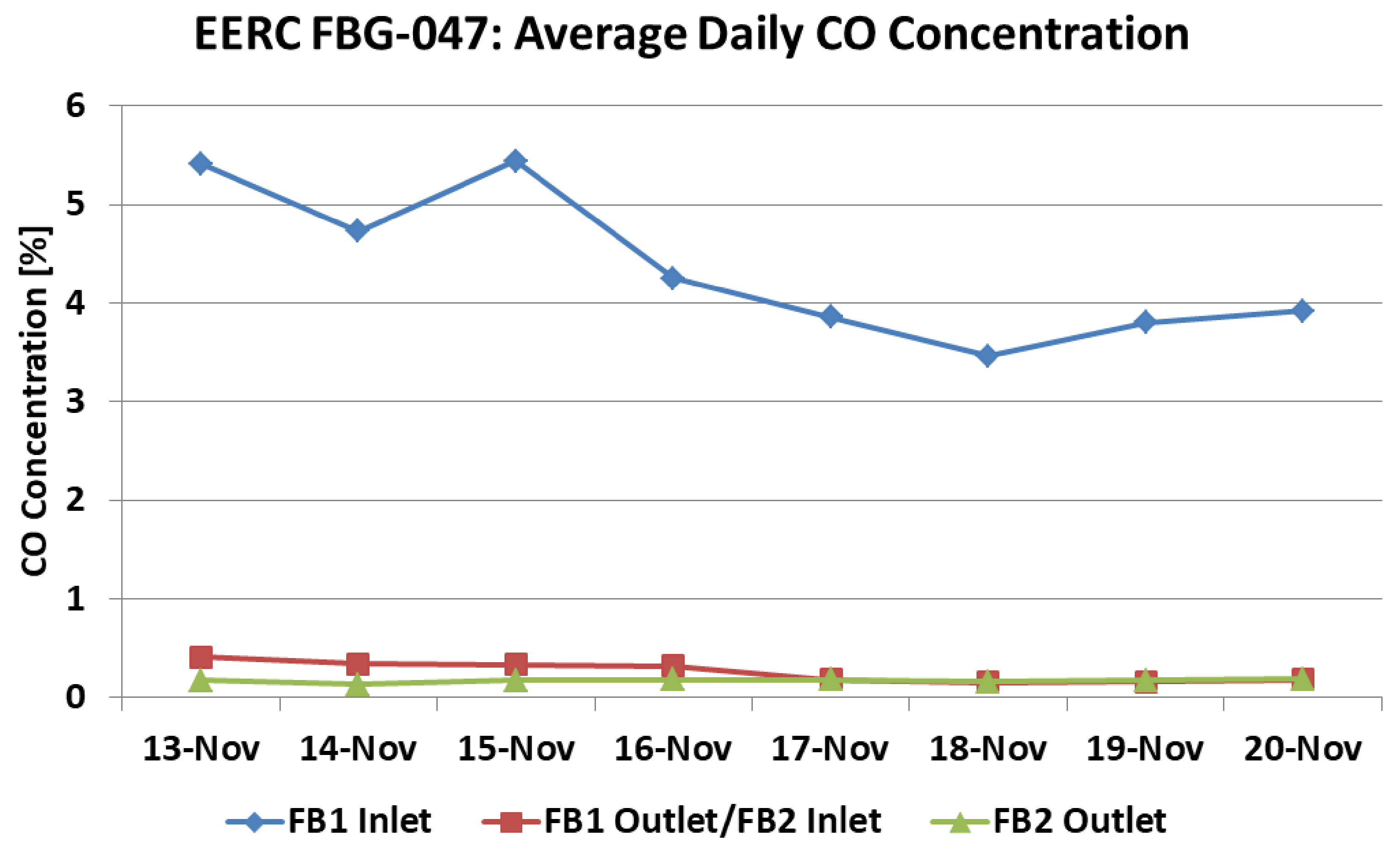
FBG-047: FB1 Inlet Gas Composition (LGA-106) (mol%)

Date	CO	O_2	H_2O	N_2	H_2	CO_2	CH_4	HC	Overall CO Shift Ratio
13-Nov	5.41	0.01	0.00	33.41	10.88	45.30	2.81	0.00	96.70
14-Nov	4.73	0.02	0.00	33.94	10.06	46.59	2.62	0.00	97.10
15-Nov	5.44	0.02	0.00	30.01	11.59	48.12	2.75	0.00	96.67
16-Nov	4.25	0.02	0.00	32.65	9.15	49.31	2.15	0.00	95.54
17-Nov	3.86	0.02	0.00	34.55	8.99	48.37	1.77	0.00	95.15
18-Nov	3.46	0.02	0.00	37.59	8.12	47.20	1.42	0.00	95.21
19-Nov	3.80	0.02	0.00	35.37	8.34	48.79	1.68	0.00	95.42
20-Nov	3.92	0.03	0.00	34.68	8.32	49.39	1.80	0.00	94.88

FBG-047: FB1 Outlet/FB2 Inlet Gas Composition (LGA-047) (mol%)

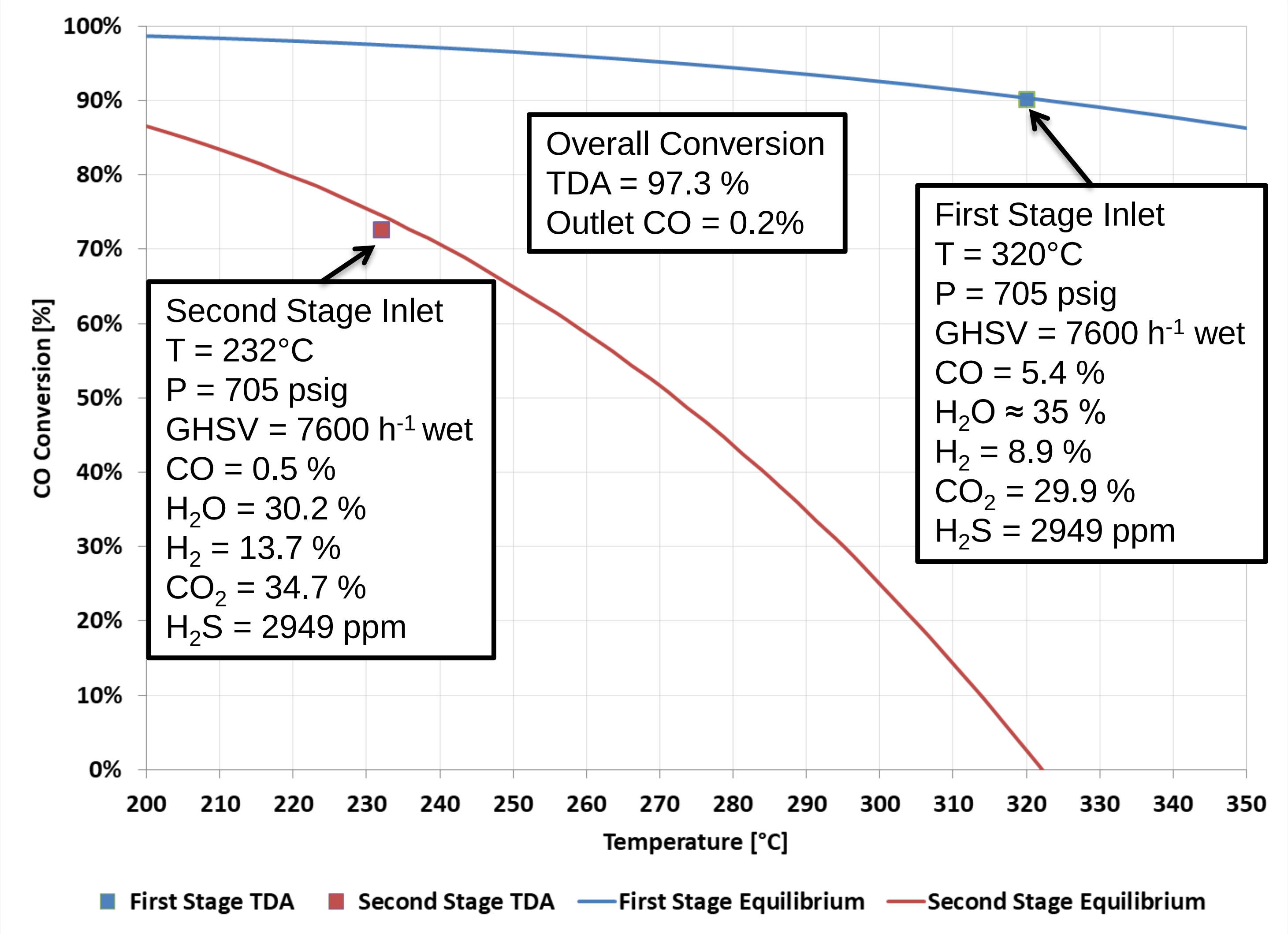
Date	CO	O_2	H_2O	N_2	H_2	CO_2	CH_4	HC	FB1 CO Shift Ratio
13-Nov	0.41	0.00	0.00	38.35	13.89	41.80	2.32	0.00	92.06
14-Nov	0.34	0.00	0.00	35.97	13.67	43.74	2.50	0.00	92.43
15-Nov	0.33	0.00	0.00	32.26	14.33	47.06	2.39	0.00	93.61
16-Nov	0.32	0.02	0.00	32.06	13.67	47.72	2.31	0.00	92.09
17-Nov	0.18	0.01	0.00	40.64	11.10	42.57	1.59	0.00	95.06
18-Nov	0.15	0.00	0.00	39.39	11.02	43.40	1.41	0.00	95.47
19-Nov	0.16	0.01	0.00	36.50	11.01	45.91	1.47	0.00	95.67
20-Nov	0.18	0.00	0.00	34.76	11.11	46.41	1.55	0.00	95.18

EERC Results – Oct/Nov 2018



- Total of 216 hr (9 days) on-stream
- No catalyst degradation over time

TDA SWGS Catalyst Performance at EERC



Overall Conversion
TDA = 97.3 %
Outlet CO = 0.2%

First Stage Inlet
T = 320°C
P = 705 psig
GHSV = 7600 h^{-1} wet
CO = 5.4 %
H_2O ≈ 35 %
H_2 = 8.9 %
CO_2 = 29.9 %
H_2S = 2949 ppm

Second Stage Inlet
T = 232°C
P = 705 psig
GHSV = 7600 h^{-1} wet
CO = 0.5 %
H_2O = 30.2 %
H_2 = 13.7 %
CO_2 = 34.7 %
H_2S = 2949 ppm

Tested on coal-derived syngas, TDA operating on equilibrium curve.

Ongoing Work with EERC

- EERC to keep TDA's catalyst in their shift reactors
- Under contract through end of July 2019
- May 2019 test scheduled with EERC
- EERC Modifications to more effectively test low temperature shift catalytic activity
  - Adjust conditions to increase CO concentration in coal-derived syngas
  - Build a heat exchanger to better control the second bed inlet temperature
  - Inject CO prior to second stage bed to increase the CO concentration by 1 mol %

Acknowledgements

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- Josh Stanislowski, EERC