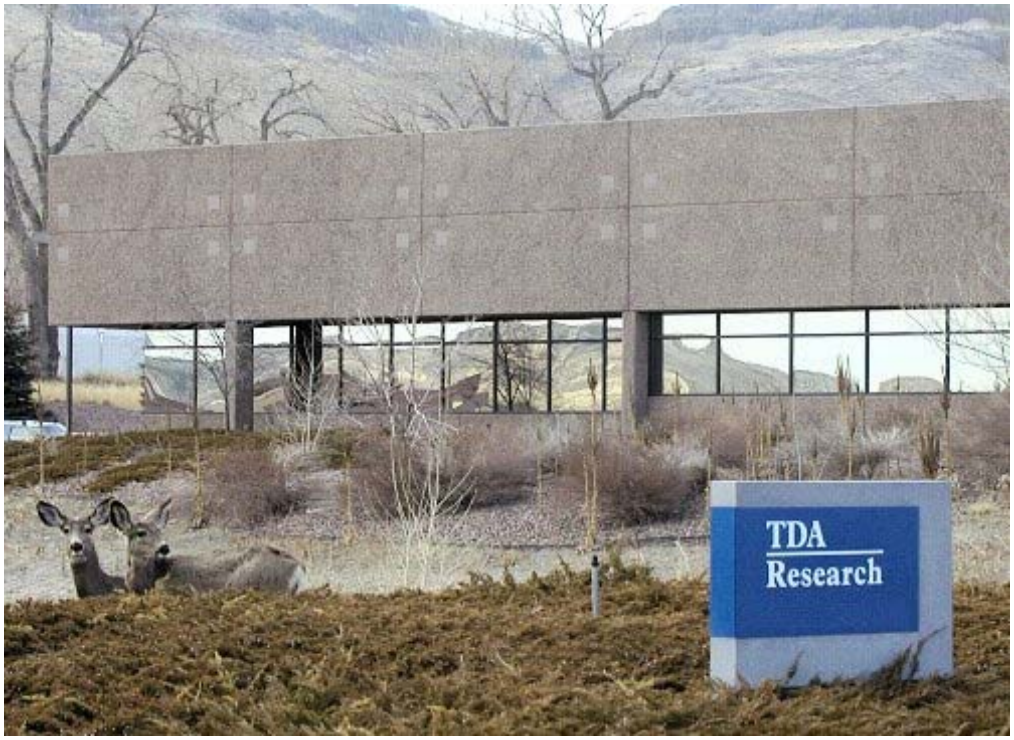
Advanced Reactor Design for Integrated WGS/ Pre-combustion CO_2 Capture (Contract No. DE-FE-0012048)



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DOE Gasification Systems and Coal & Coal-Biomass to Liquids Workshop

Morgantown, WV

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TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Project Objective

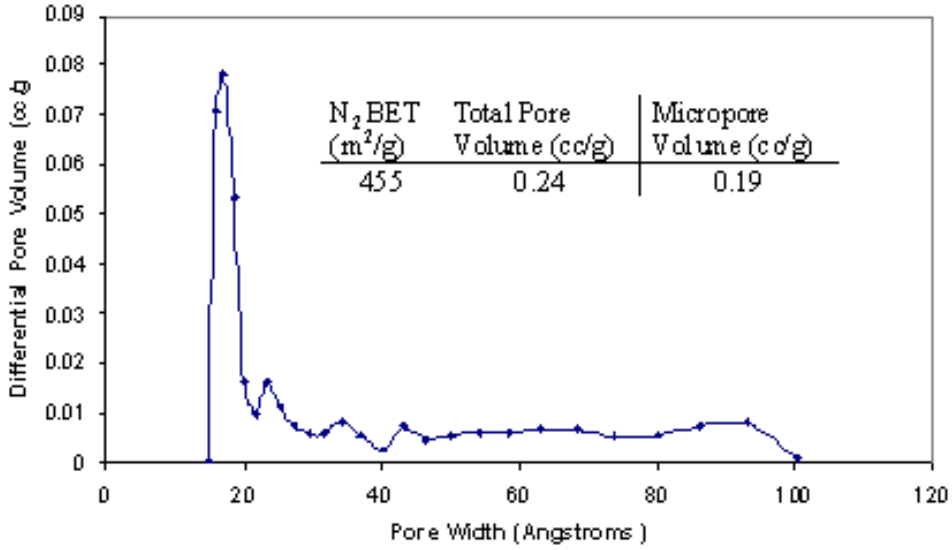
- **The project objective is to demonstrate techno-economic viability of an integrated WGS catalyst/CO_2 removal system for IGCC power plants and CTL plants**
  - A high temperature PSA adsorbent is used for CO_2 removal above the dew point of the synthesis gas
  - A commercial low temperature catalyst is used for water-gas-shift
- Critical Need
  - Develop an effective heat management system
- **Project Tasks**
  - Reactor design aided by CFD modeling to identify the best thermal management option in the integrated WGS/CO_2 removal bed
  - Evaluate the optimum reactor design at bench-scale
  - Demonstrate technical viability of the best design in slipstream tests at the NCCC using real-coal derived syngas
  - Engineering and cost analysis using Aspen Plus™

Project Partners

- **In the next phase of the project a larger slipstream evaluation will be carried out at 10 SCFM at Wabash River IGCC plant and NCCC (DE-FE-0023684)**

TDA's Approach

- **TDA's sorbent is mesoporous carbon modified with surface functional groups that remove CO_2 via strong physical adsorption**
  - CO_2-surface interaction is strong enough to allow operation at elevated temperatures
  - Because CO_2 is not bonded via a covalent bond, the energy input for regeneration is low
- **Heat of CO_2 adsorption is 4.9 kcal/mol for TDA sorbent**
  - Comparable to that of Selexol
- **Net energy loss in sorbent regeneration is similar to Selexol, but a much higher IGCC efficiency can be achieved due to high temperature CO_2 capture**



- **Pore size can be finely tuned in the 10 to 100 A range**
- **Mesopores eliminates diffusion limitations and rapid mass transfer, while enables high surface area**

US Pat. Appl. 61787761, Dietz, Alptekin, Jayaraman "High Capacity Carbon Dioxide Sorbent"

US Pat. Appl. 61790193, Alptekin, Jayaraman, Copeland "Pre-combustion Carbon Dioxide Capture System Using a Regenerable Sorbent"

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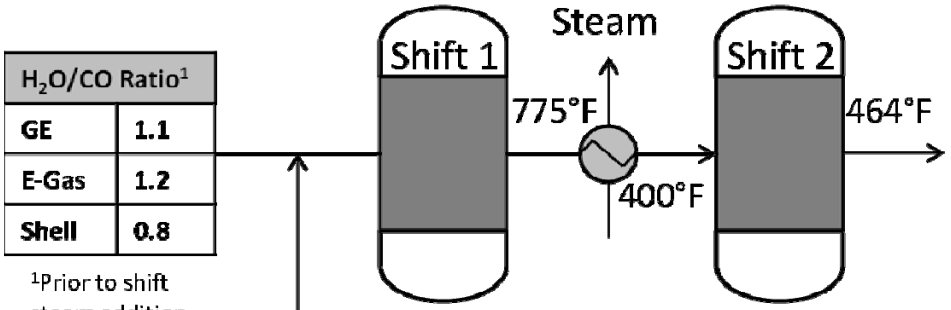
Further Energy Savings

- **Conventional IGCC plants use multi-stage WGS reactors with inter-stage cooling**
  - WGS is an equilibrium-limited exothermic reaction
- **Water is supplied at concentrations well above required by the reaction stoichiometry to completely shift the CO to CO_2**



H_2O/CO Ratio[1]	
GE	1.1
E-Gas	1.2
Shell	0.8

[1]Prior to shift steam addition

	H_2O/CO added	Energy Value (MW_{th})
GE	0.9	286
E-Gas	1.05	372
Shell	1.0	437

$$H_2O + CO \leftrightarrow CO_2 + H_2$$

3-stage WGS unit is described in the DOE/NETL-2007/1281

- **A high temperature CO_2 adsorbent combined with a LT shift catalyst enables high CO conversion *at low steam:carbon ratios***

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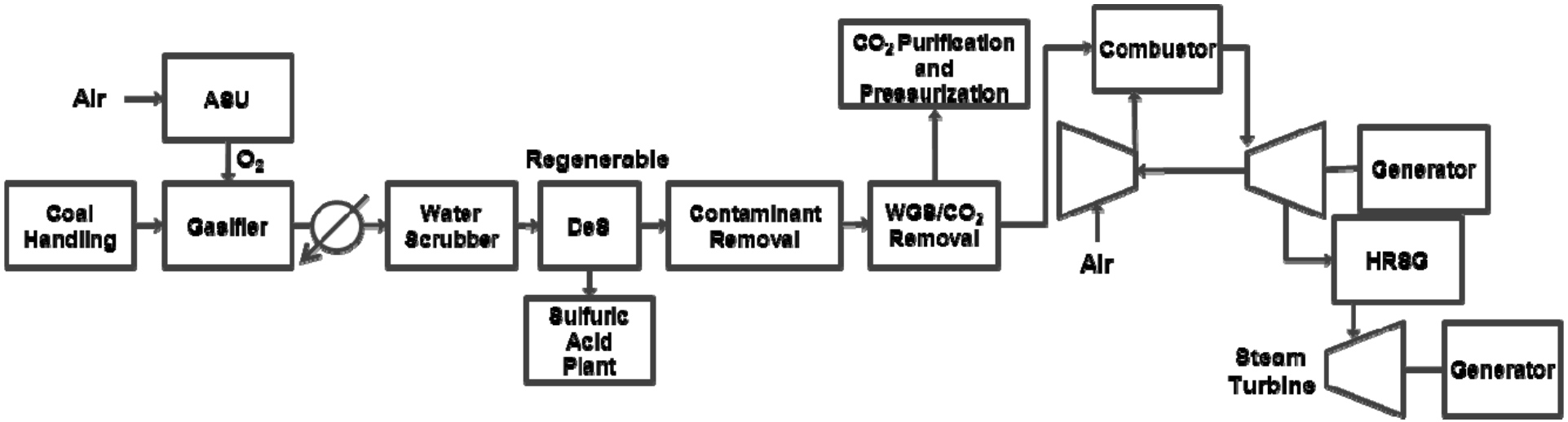
Integrated WGS/CO_2 Capture System



- **Reducing the use of excess steam improves power cycle efficiency**
  - Lower energy consumption to raise the steam
- **Process intensification reduces the number of hardware components and cost**

Sorbent's point of view:

- **Less dilution with water increases CO_2 partial pressure and in turn improves sorbent's working capacity**

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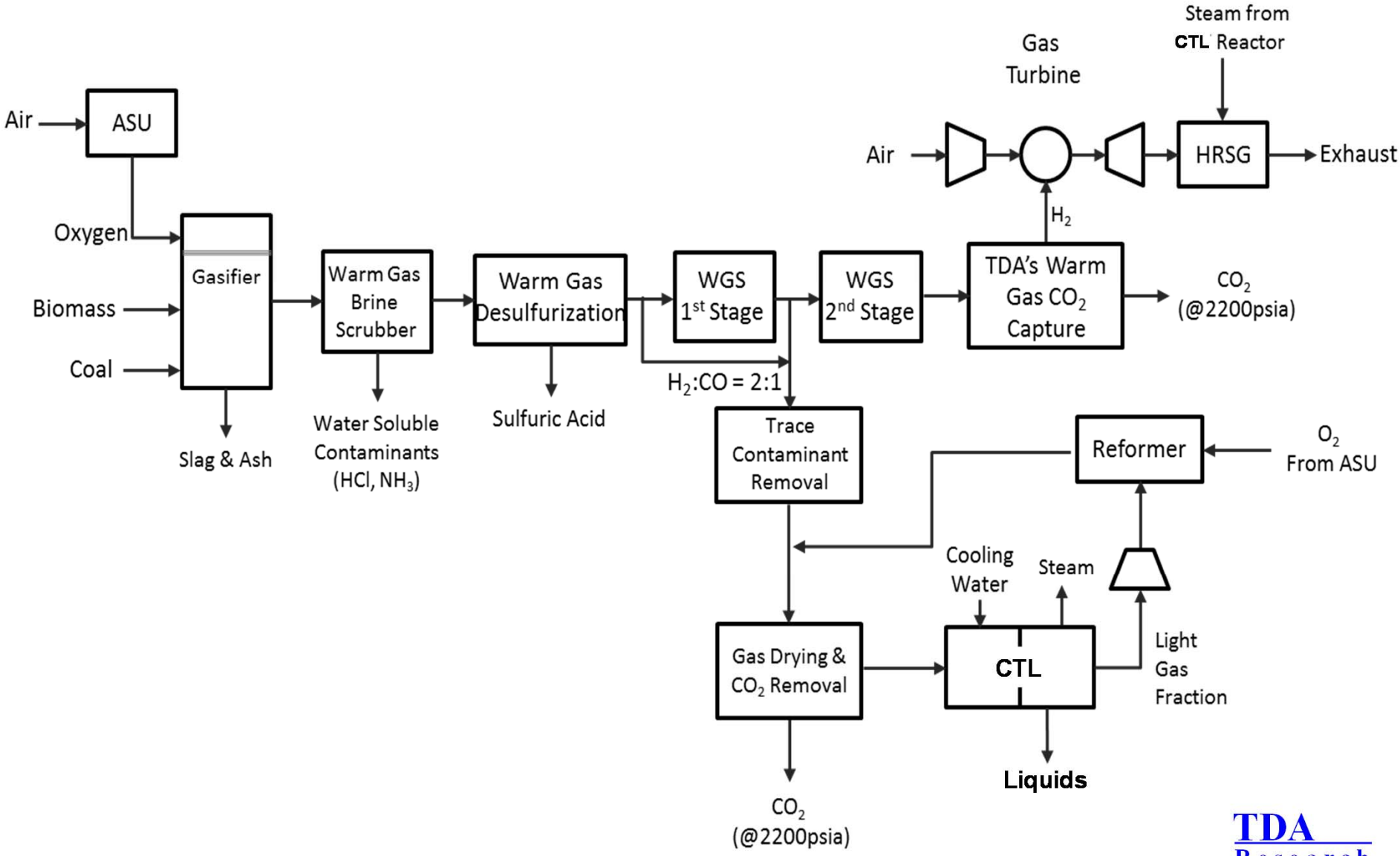
Application to CTL



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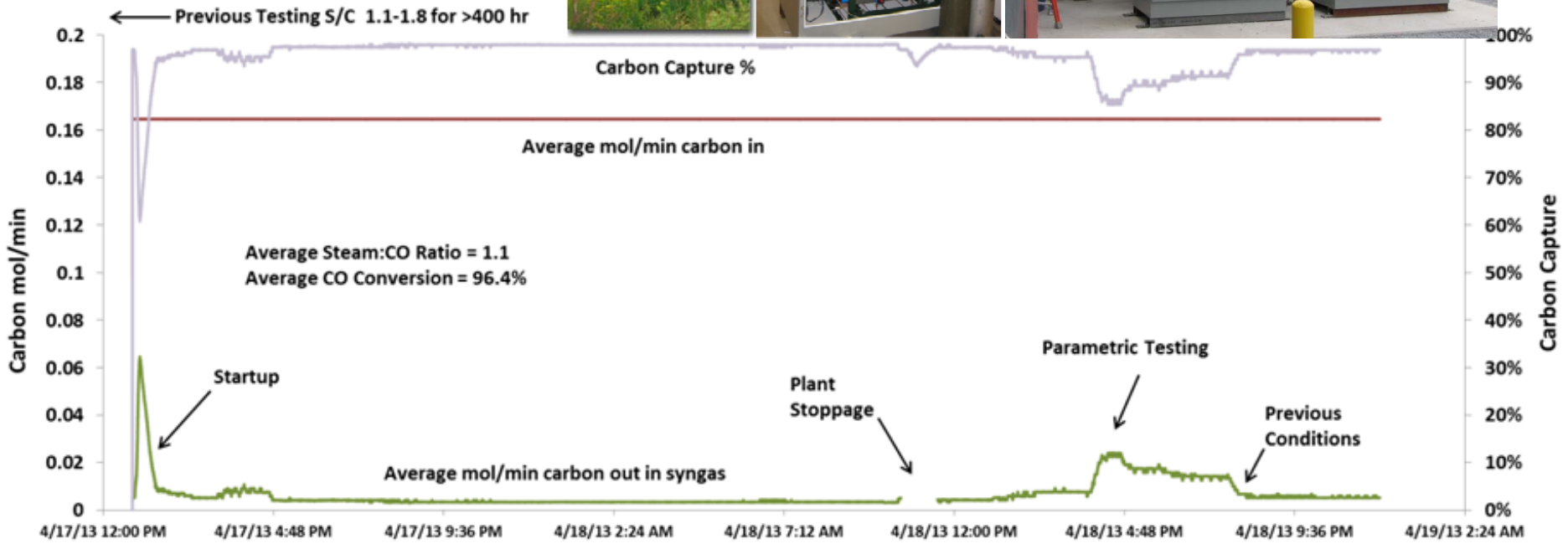
NCCC Field Test – Early Work



- **Prototype system achieved 90+% carbon capture under Steam:CO ratio of 1:1.1 with average CO conversion of 96.4%**
- **All objectives met (no coking etc.) but observed high reactor T**

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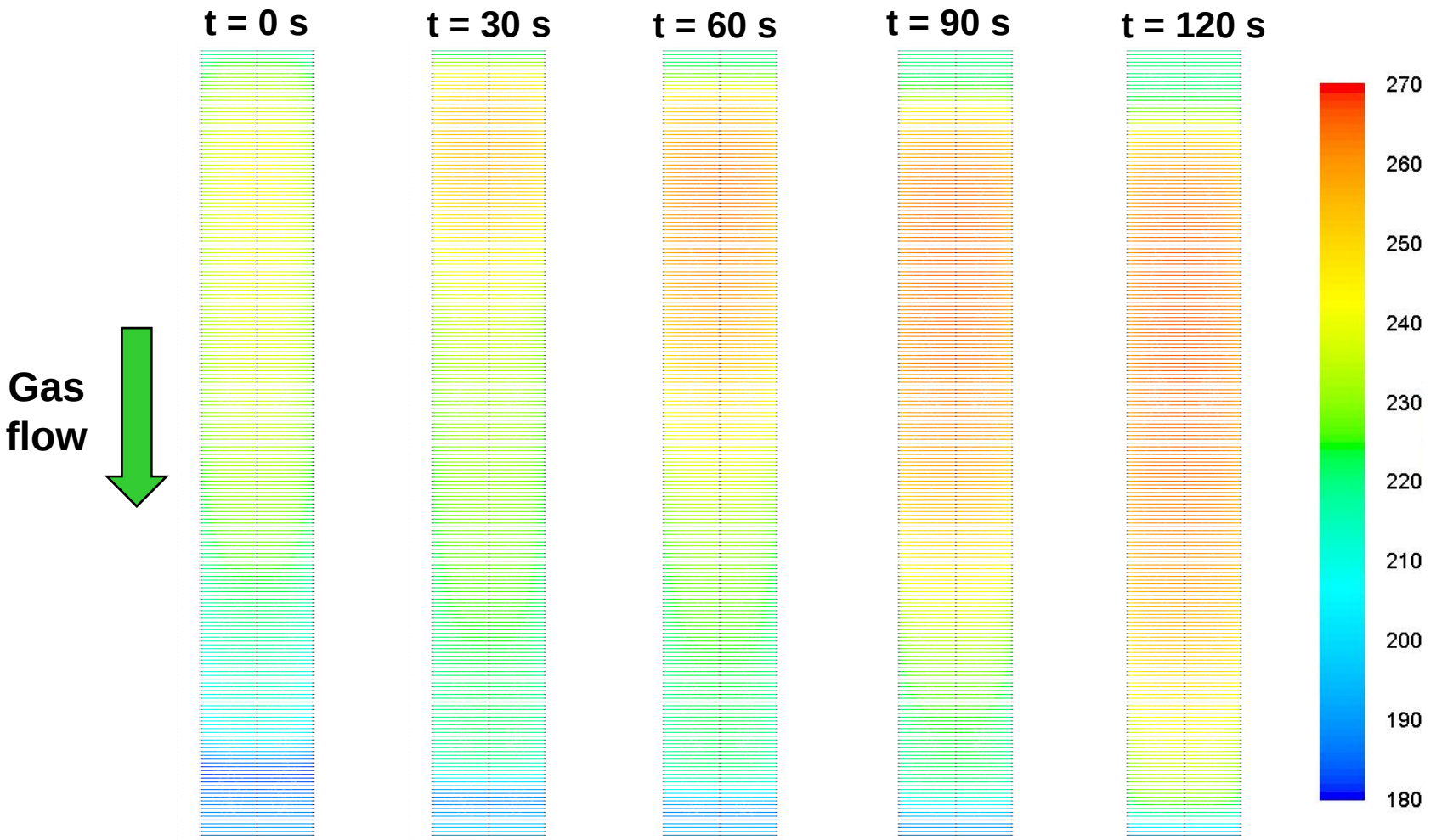
Technology Status/R&D Needs

- **Sorbent is developed under a separate DOE project (DE-FE0000469)**
- **WGS catalyst is commercially available mature technology**
- **Early-stage concept demonstration has already been completed (under DE-FE0007966)**
  - Integrated sorbent/catalyst operation
  - Pointed out the need to incorporate effective heat management
- **Key R&D need is the design/development of a high fidelity prototype to fully demonstrate the concept using actual coal-derived synthesis gas**
  - Early-stage prototype demonstration of an integrated system with heat management is also under progress (under DE-FE-00012048)
  - Slipstream test at the NCCC at ~0.2 kg/hr CO_2 removal
- **A larger-scale (10 kg/hr CO_2 removal) test will be carried out at the Wabash River IGCC plant (under DE-FE-00012048)**

T Profiles - During CO_2 Capture Only



- **Heat generated during adsorption is removed during regeneration**
  - Near isothermal operation

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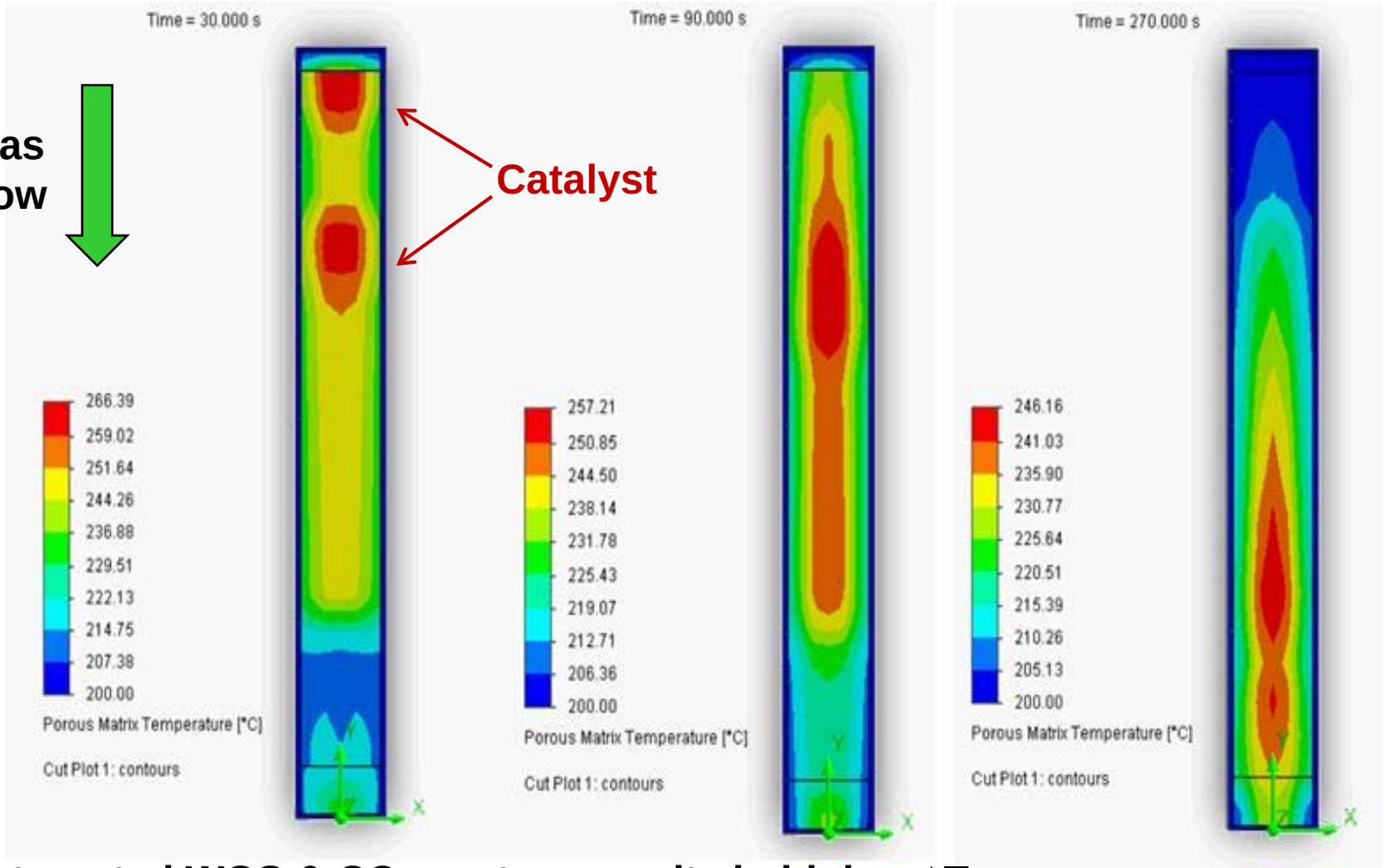
Heat Wave WGS & CO_2 Capture



- Integrated WGS & CO_2 capture results in higher ΔT
- Not ideal for CO_2 capture (the WGS heat accumulates in the beds)

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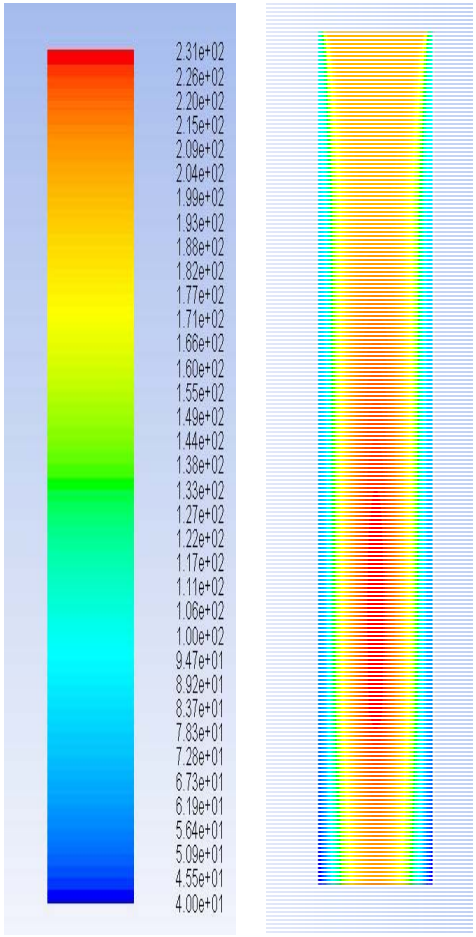
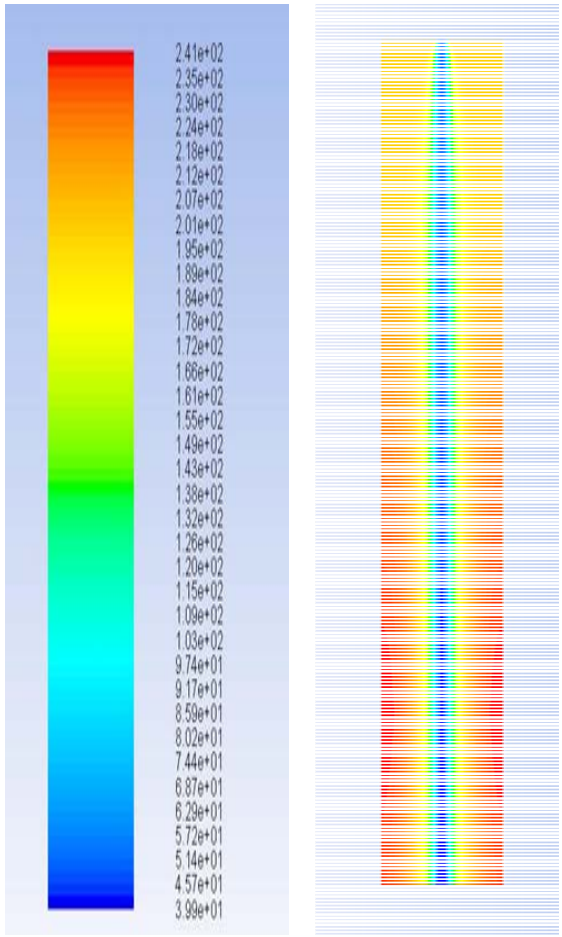
Conventional Heat Management Options

10 kg/hr CO_2 Removal Pilot Test System – 6" reactors

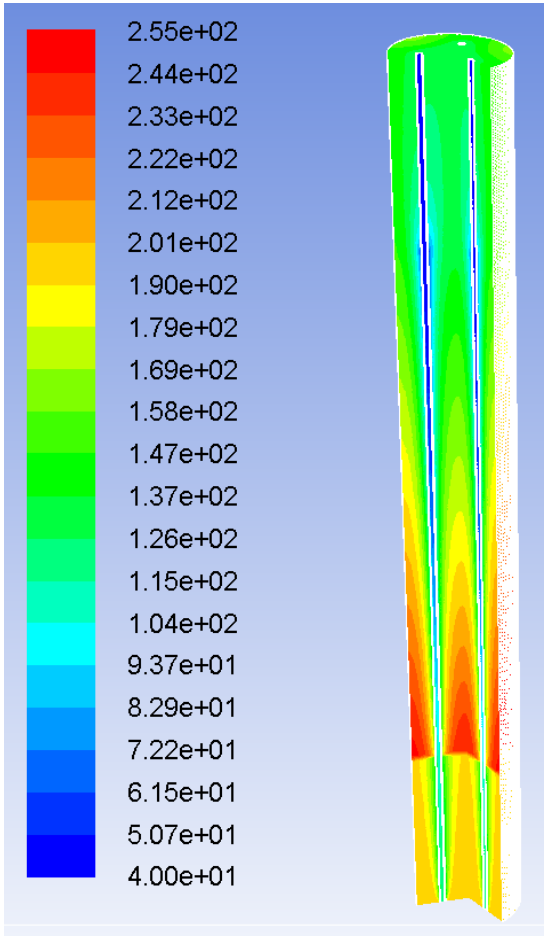
Cooling Jacket



Immersed Tube (1)



Immersed Tubes (3)



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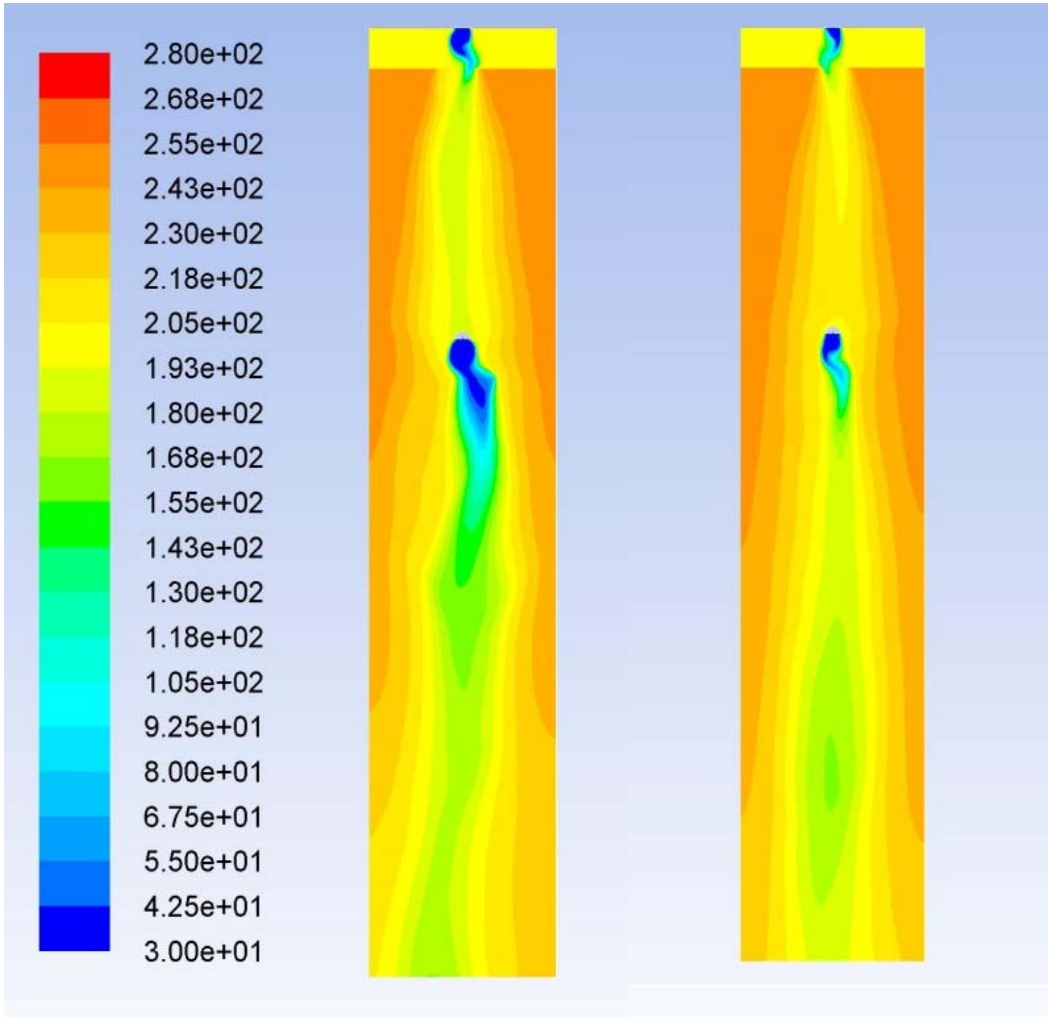
Heat Integrated WGS & CO_2 Capture

- **Advanced heat management concept based on direct water injection has proven to achieve much better temperature control**
  - Also much better heating efficiency (i.e., kJ heat removed per kg water)
- **Objective is more uniform cooling without having hot or cold spots**
- **We are also optimizing how the WGS catalyst and the sorbent to be distributed in the combined WGS catalyst /CO_2 capture sorbent beds**

Temperature Contours (°C)



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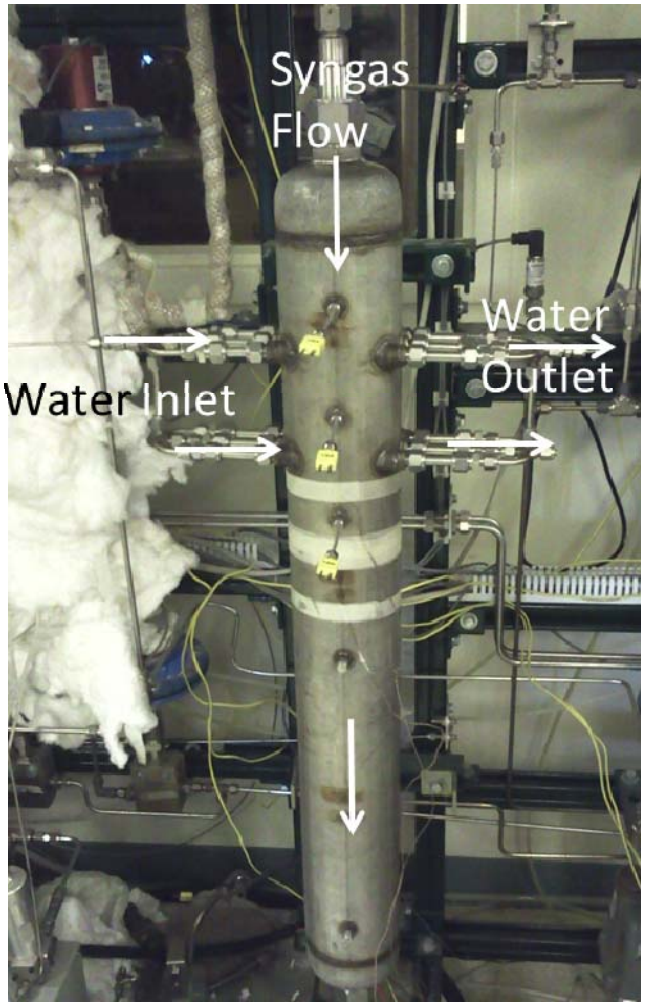
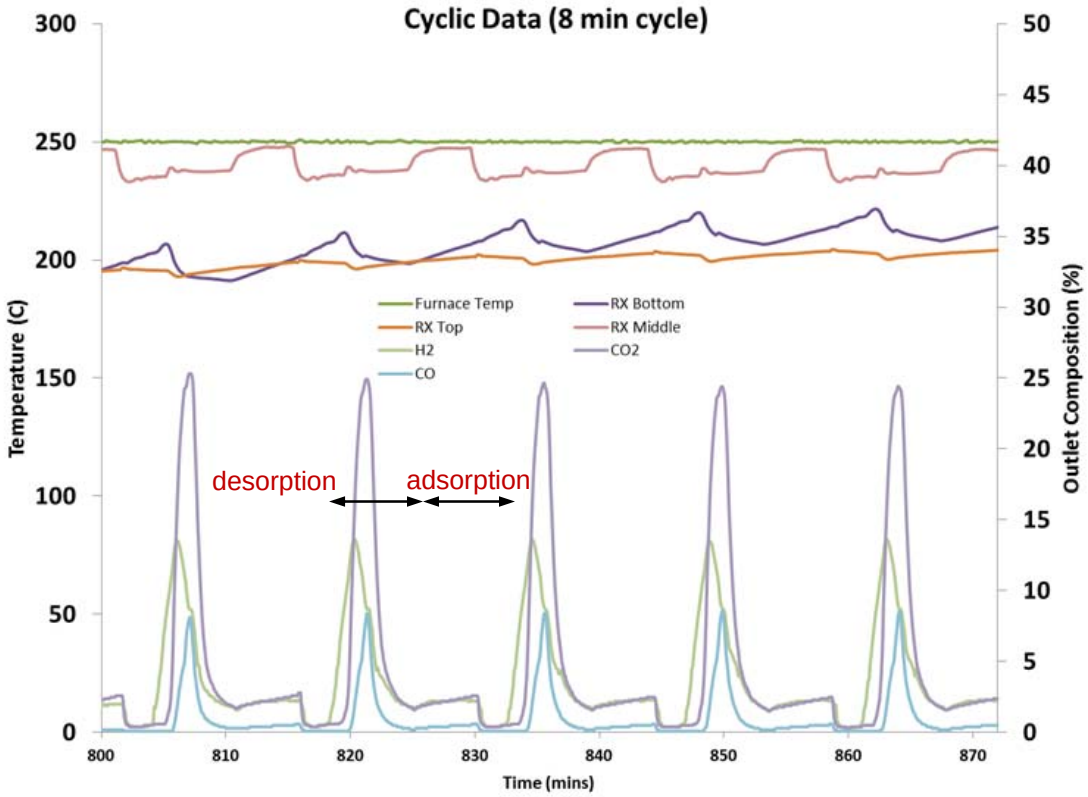
Bench-Scale Evaluations





- **8L reactors were modified with the heat management options**
- **Successful proof-of-concept demonstrations have been completed**

- **ΔT <10°C was maintained over extended cycling (much lower than those observed in early field tests)**

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Process Simulation and Analysis

IGCC plant with E-Gas™ Gasifier operating on Bituminous Coal

#	CO_2 Capture	Notes	Steam/ Water Addition	Overall Steam:CO Ratio	Net Efficiency % HHV
1	Conventional Technology	Reference IGCC Case with Steam addition to 1st WGS reactor feed	Steam	2.25	31.04
2	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed; water injection into combined WGS+PSA reactor	Water	1.50	34.30
2-1	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed; no water injection into combined WGS+PSA reactor	None	1.24	34.55 (87% carbon capture)
2-3	TDA/Advanced Technology	No 1st WGS reactor & water injection into combined WGS+PSA reactor	Water	2.21	33.73
2A	TDA/Previous Technology	Steam addition to 1st WGS reactor feed; no water injection into 2nd WGS reactor (not combined with PSA)	Steam	2.25	33.81

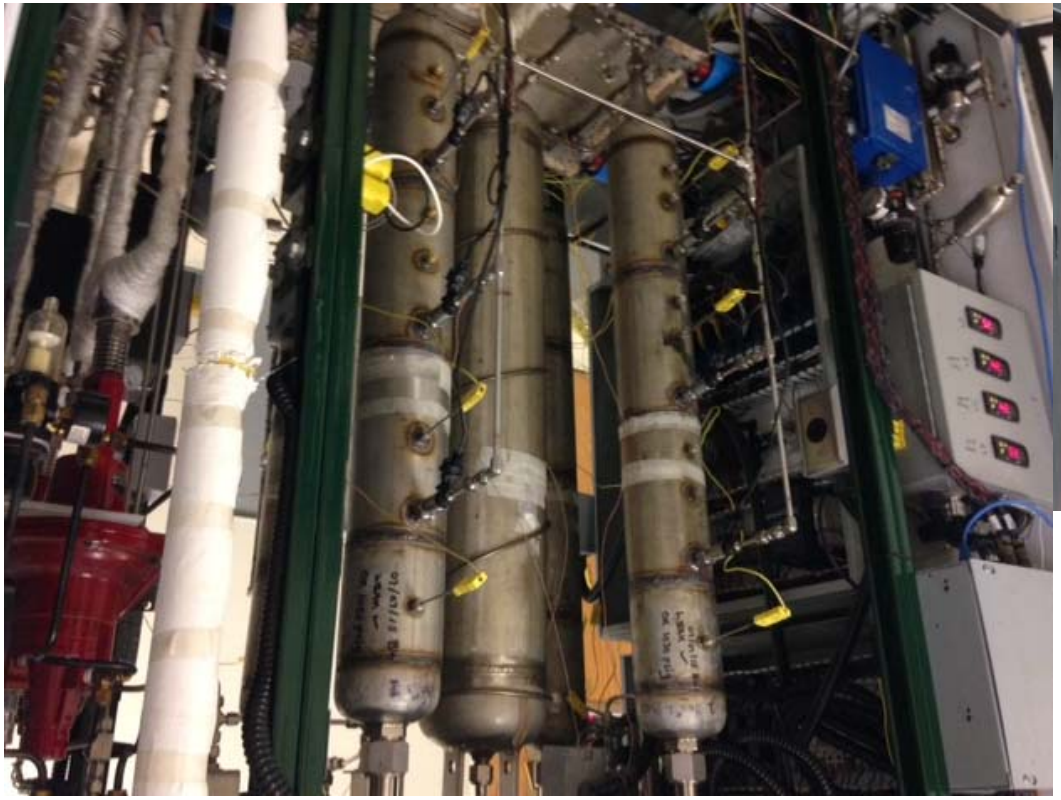
- **Reducing Steam:CO ratio to 1.50 w/ water addition to Integrated WGS/CO_2 Removal Reactor (2nd stage) provides a net plant efficiency of 34.30%**
  - **0.5% point improvement over TDA's previous technology**

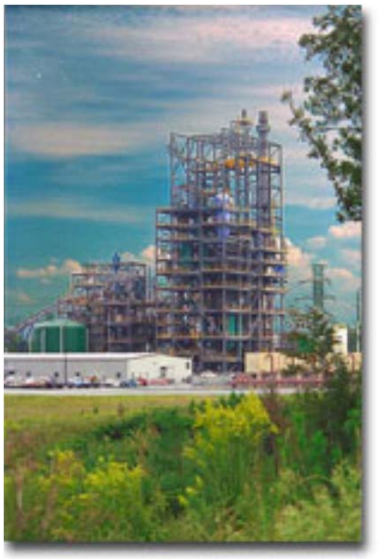
IGCC plants with Shell Gasifier

Case #	Coal Type	CO_2 Capture	Notes	Overall Steam: CO Ratio	Net Efficiency % HHV
3	Bituminous	Conventional Technology	Reference IGCC Case (H2O/CO in 1st WGS reactor feed = 1.8 mole/mole per corresponding DoE case)	1.8	31.08
4	Bituminous	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed (H2O/CO in 1st WGS reactor feed = 1.11 mole/mole); water injection into combined WGS+PSA reactor	1.38	33.71
5	Lignite	Conventional Technology	Reference IGCC Case (H2O/CO in 1st WGS reactor feed = 1.8 mole/mole)	1.8	30.89
6	Lignite	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed (H2O/CO in 1st WGS reactor feed = 1.60 mole/mole); water injection into combined WGS+PSA reactor	1.78	32.79

- **Different gasifiers and coal are being evaluated**
  - **Better plant efficiency for all coals and gasifiers**

Slipstream Evaluation at NCCC





- **Plan to participate two test campaigns at the NCCC**
  - **September – October 2015**
  - **April 2015**

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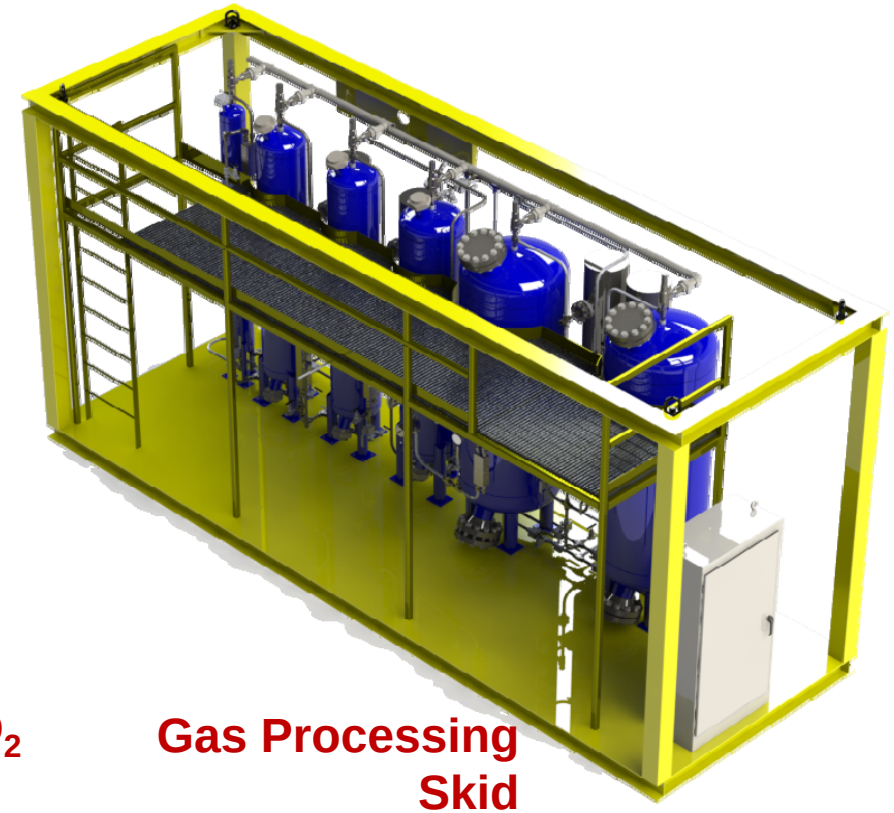
Larger Field Evaluation

Integrated WGS/CO_2 Capture Unit



Gas Processing Skid

- Process Design Package (PDP) is complete and being reviewed by the host sites Wabash River IGCC Plant and NCCC
- An additional test with Praxair is also planned
- With DOE's consent, these skids can be made available for other tests

Vision for Commercialization

- Slipstream to pilot-scale demonstrations to increase technical maturity from TRL = 4 to TRL = 6
- Develop a complete technology package for licensing
  - Intellectual Property
  - Process Design Package
  - Sorbent Manufacturing






- Privately Owned / Began operations in 1987
- Two facilities in Wheat Ridge and Golden, CO
  - 50,000 ft^2 of office and lab space
- 82 full-time technical staff
  - More than half with advanced degrees (28 PhDs)

TDA Research

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