

A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO₂ Capture

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MEGA SYMPOSIUM

August 30, 2010

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

TDA Research, Inc.

- **Privately Owned / Began operations in 1987**
- **~13 million revenue in 2009**
- **84 full-time technical staff**
 - Primarily chemists and engineers, more than half with advanced degrees (26 PhDs)

Wheat Ridge Facility



12345-12355 W 52nd Avenue

22,000 ft² offices and labs

**Synthetic Chemistry, Catalyst/Sorbent
Synthesis and Testing, Machine and
Electronics Shops, SEM, TOF Mass Spec**

Golden Facility



4663 Table Mountain Drive

27,000 ft² offices and labs

**27 fume hoods, Synthetic Chemistry,
Catalytic Process Development**

Project Summary

- **The objective of this work is to develop a new pre-combustion CO₂ capture technology and demonstrate its technical and economic viability**
- **The novelty is a low cost, high capacity regenerable sorbent that can remove CO₂ above the dew point of the gas**
- **The sorbent is a mesoporous carbon that removes CO₂ by physical adsorption**

Year 1

- Scale-up sorbent production
- Extensive evaluations at the bench-scale
- Detailed process design

Year 2

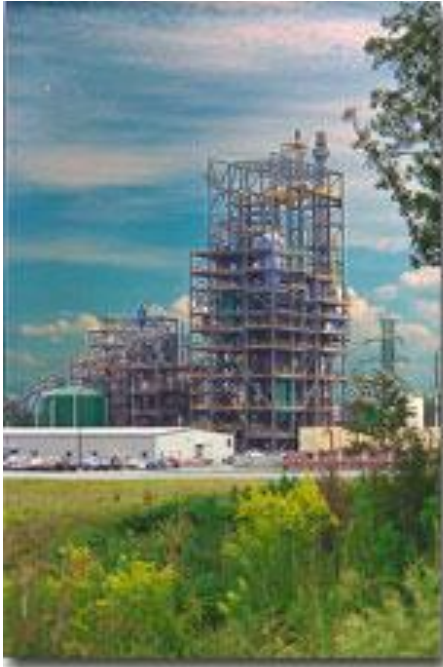
- Complete/demonstrate sorbent life for 10,000 cycles
- Slipstream demonstration using actual synthesis gas
- Based on performance data and optimum design, conduct an economic analysis to estimate the cost of CO₂ capture

Demonstration Sites

- Two 3-week test campaigns for proof-of-concept demonstrations

Wabash River IGCC Plant, Terre Haute, IN

- Largest single-train gasifier with 262 MW power output
- Oxy-blown E-Gas™ Gasifier
- Operates on petcoke or bituminous coal



National Carbon Capture Center, Wilsonville, AL

- Pilot-scale gasifier
- Air-blown transport gasifier (similar to KBR Halliburton's gasification technology)
- Operates on lignites (low quality, high sodium, high ash lignites)

Project Partners

TDA Research



KBR



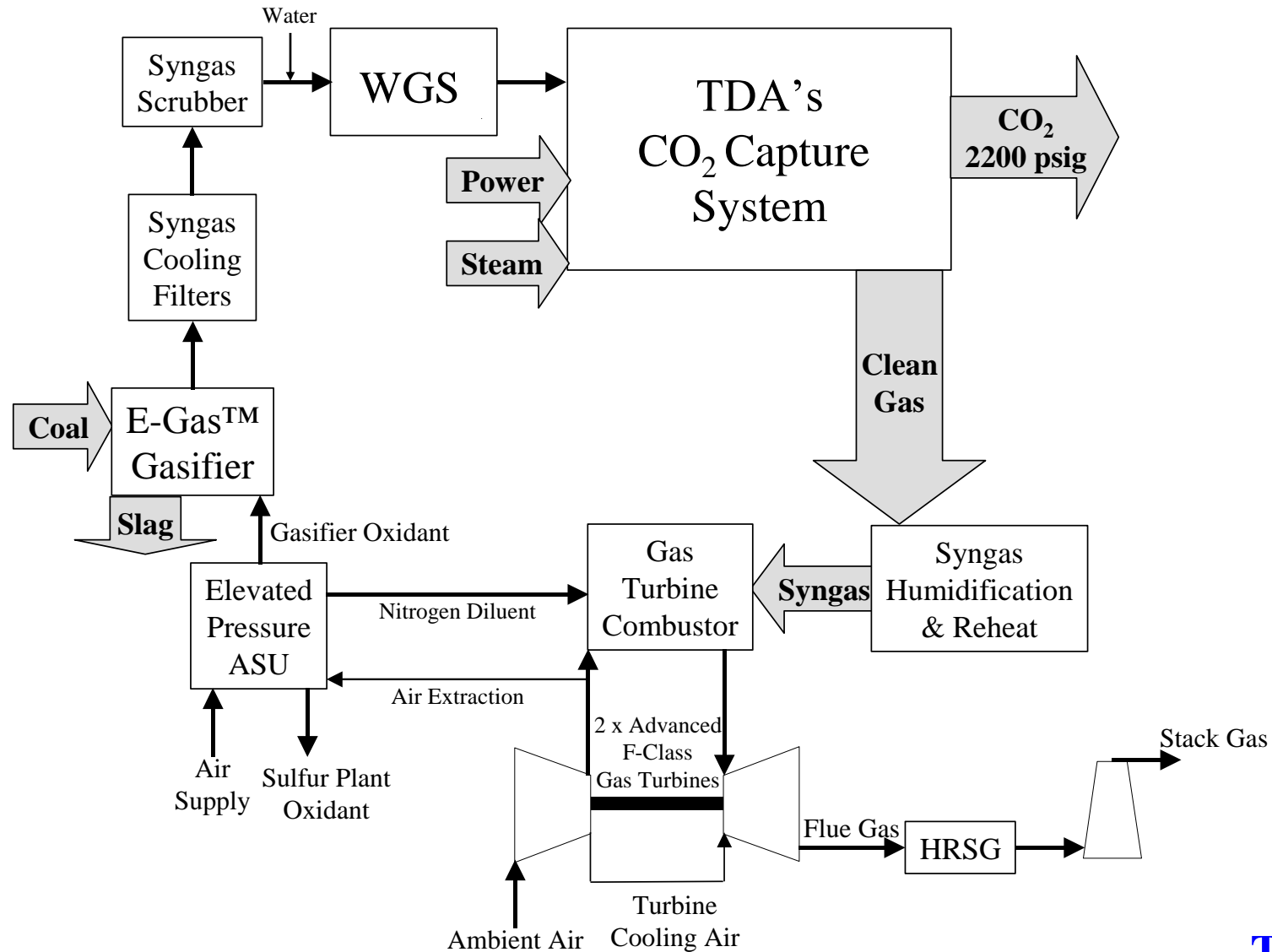
Carbon Capture Technologies

- **The baseline capture technologies uses low temperature solvents**
 - Physical solvents – Selexol, Rectisol
 - Chemical solvents – Amines
- **A major issue with these technologies is that they require to cool the gas below its dew point**
 - For a GE gasifier with water quench, the dew point is $\sim 245^{\circ}\text{C}$ (480°F)
- **Warm temperature gas cleaning has major benefits:**
 - Improves the efficiency of the power cycle
 - A previous Siemens analysis indicates $\sim 4\%$ efficiency decrease
 - Eliminate the need for any heat exchange equipment
 - Eliminate the difficulties processing the condensate
- **Warm gas CO_2 capture technologies are being developed**
 - H_2 membranes
 - High temperature chemical absorbents
 - Hydrotalcites

TDA's Sorbent

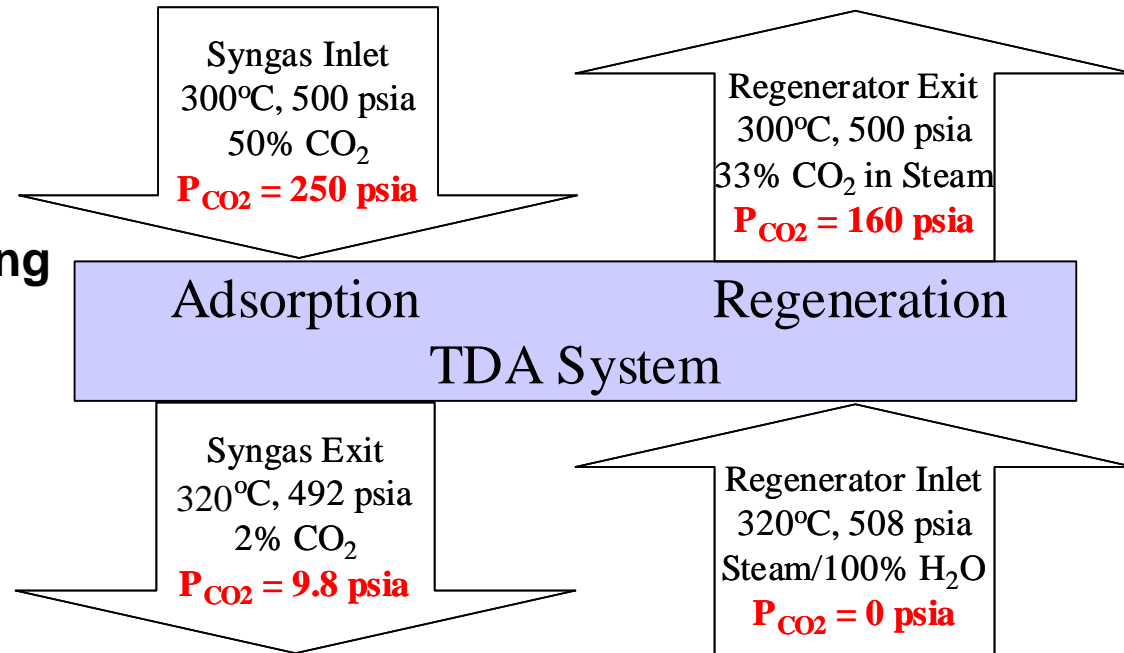
- **The sorbent consists of a carbon material modified with surface functional groups that remove CO₂ via strong physical adsorption**
 - The CO₂-surface interaction is strong enough to allow operation at elevated temperatures
 - Because CO₂ is not bonded via a covalent bond, the energy input for the regeneration process is low
- **Calorimetry results and isosteric estimations suggest that the heat of adsorption on TDA sorbent is ~4.9 kcal mol per mole of CO₂**
 - Selexol ~4 kcal/mol CO₂
 - Amine solvents ~14.4 kcal/mol
 - Chemical absorbents Na₂CO₃ 29.9 kcal/mol
- **The net energy loss due to sorbent regeneration is expected to be similar to Selexol's but;**
 - A much better IGCC efficiency due to higher temperature CO₂ capture
 - CO₂ recovery at pressure

IGCC-Integrated CO₂ Capture System



System Operation

- CO₂ system uses two (or more) beds that switches positions
- The physical adsorbent provides flexibility in selecting regeneration options:
 - Temperature swing
 - Pressure swing
 - Concentration swing
 - Possible combinations



- Isothermal operating capability will be critical to eliminate heat/cool transitions which will reduce cycle time and increase sorbent utilization
 - Operation of the system will be very similar to that of the PSA (but the operating temperature will be high)
- A trade-off analysis is carried out to optimize the CO₂ recovery pressure (that reduces compression costs for sequestration) and the steam consumption

Experimental Setup

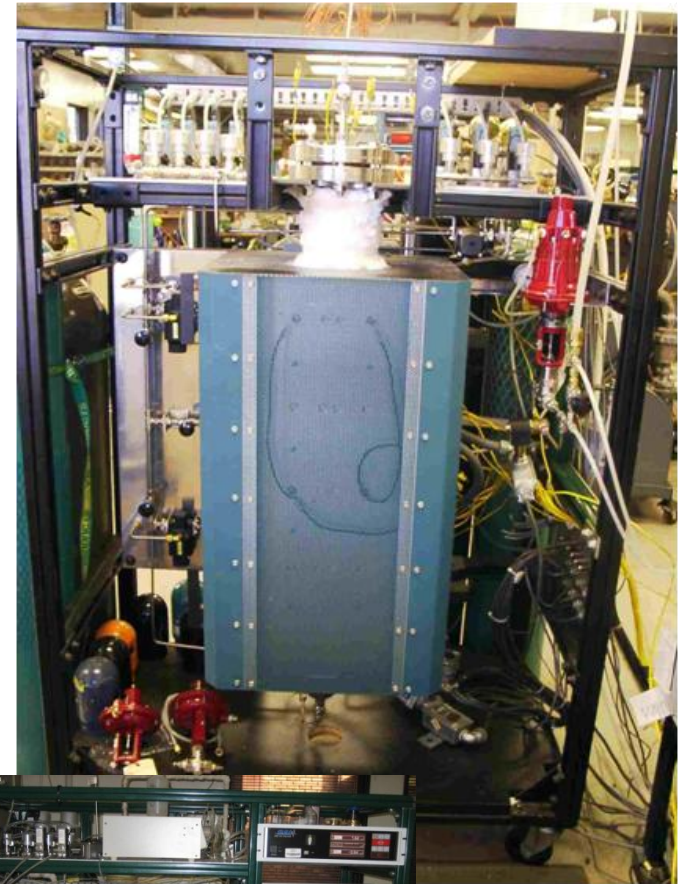
- **Three fixed-bed reactors are used for evaluations**
 - Adsorption Tests – 120 cc
 - Flow Reactor – 1,000 cc
 - Contaminant Reactor – 30-120 cc
 - All systems are capable of evaluating sorbent at 0.7 – 1.4 mm particle size

Adsorption Conditions

- 300 – 750 psig
- 180 – 300°C

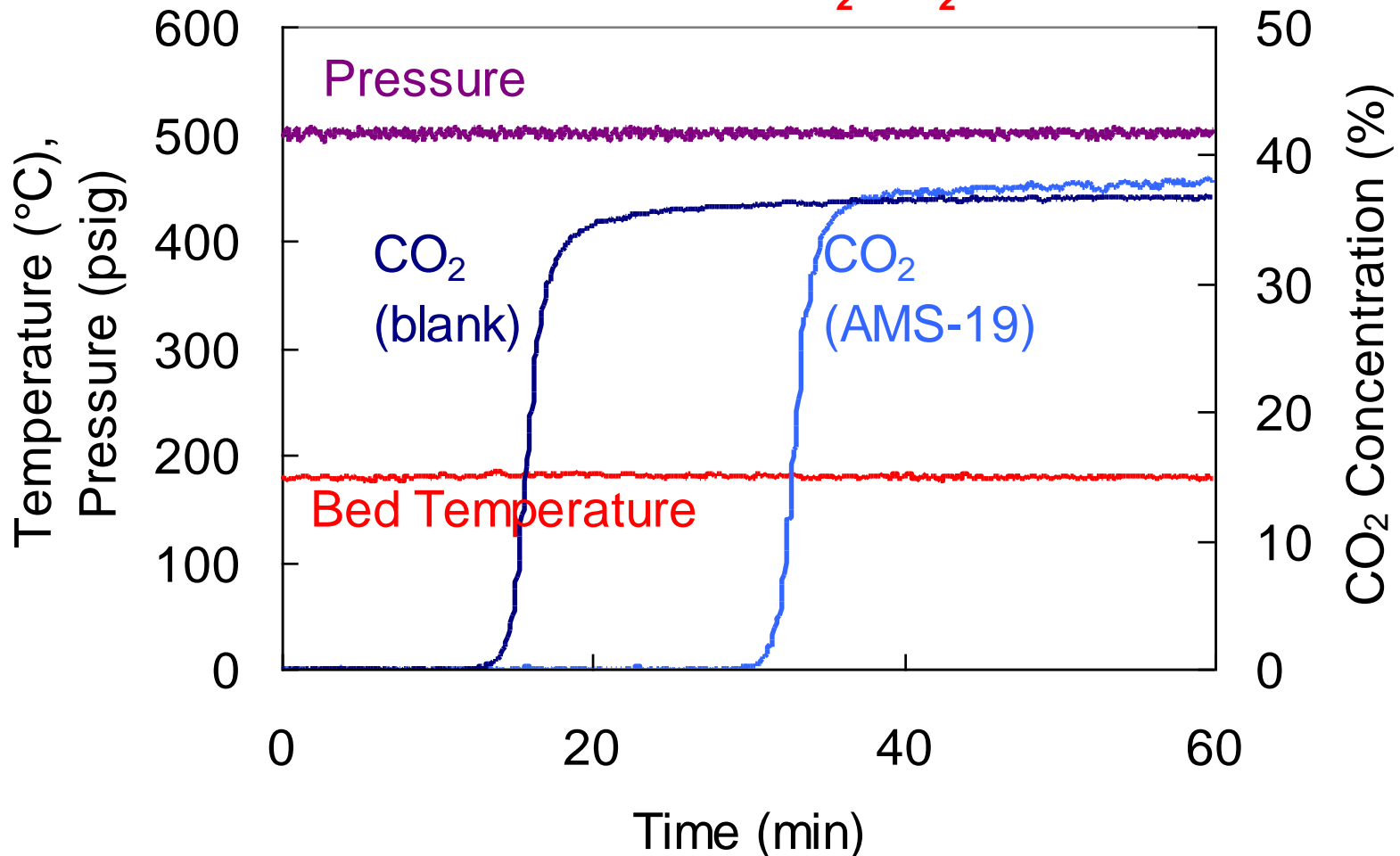
Desorption Conditions

- Concentration swing (0-30% $\text{H}_2\text{O}/\text{N}_2$)
- Pressure swing (0 – 750 psig)
- Temperature Swing ($\Delta T = 0 - 100^\circ\text{C}$)

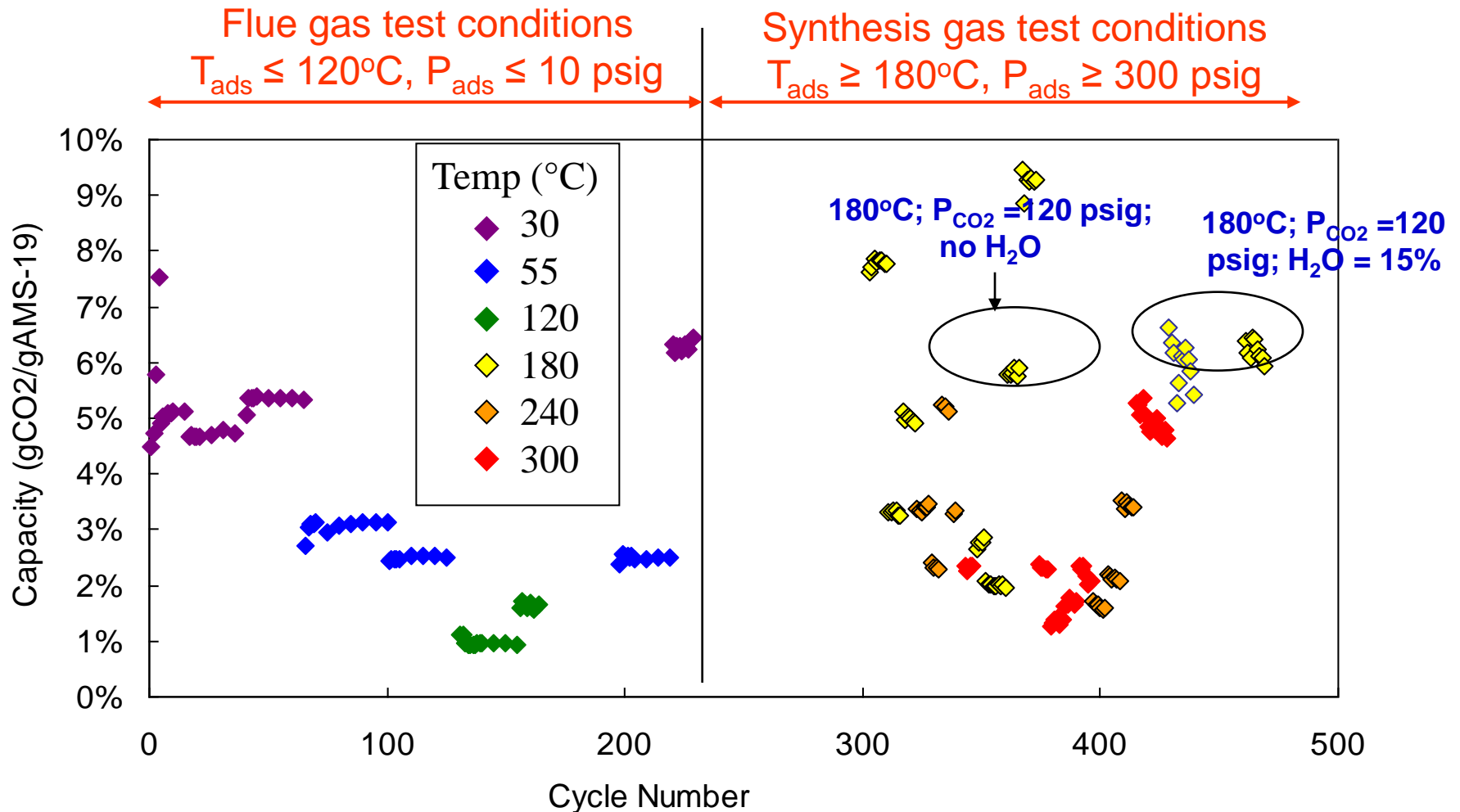


Typical Test Profile (Adsorption Tests)

$T=180^{\circ}\text{C}$, $P = 500$ psig, $P_{\text{CO}_2} = 200$ psig (Adsorption), Regeneration under 10% $\text{H}_2\text{O}/\text{N}_2$

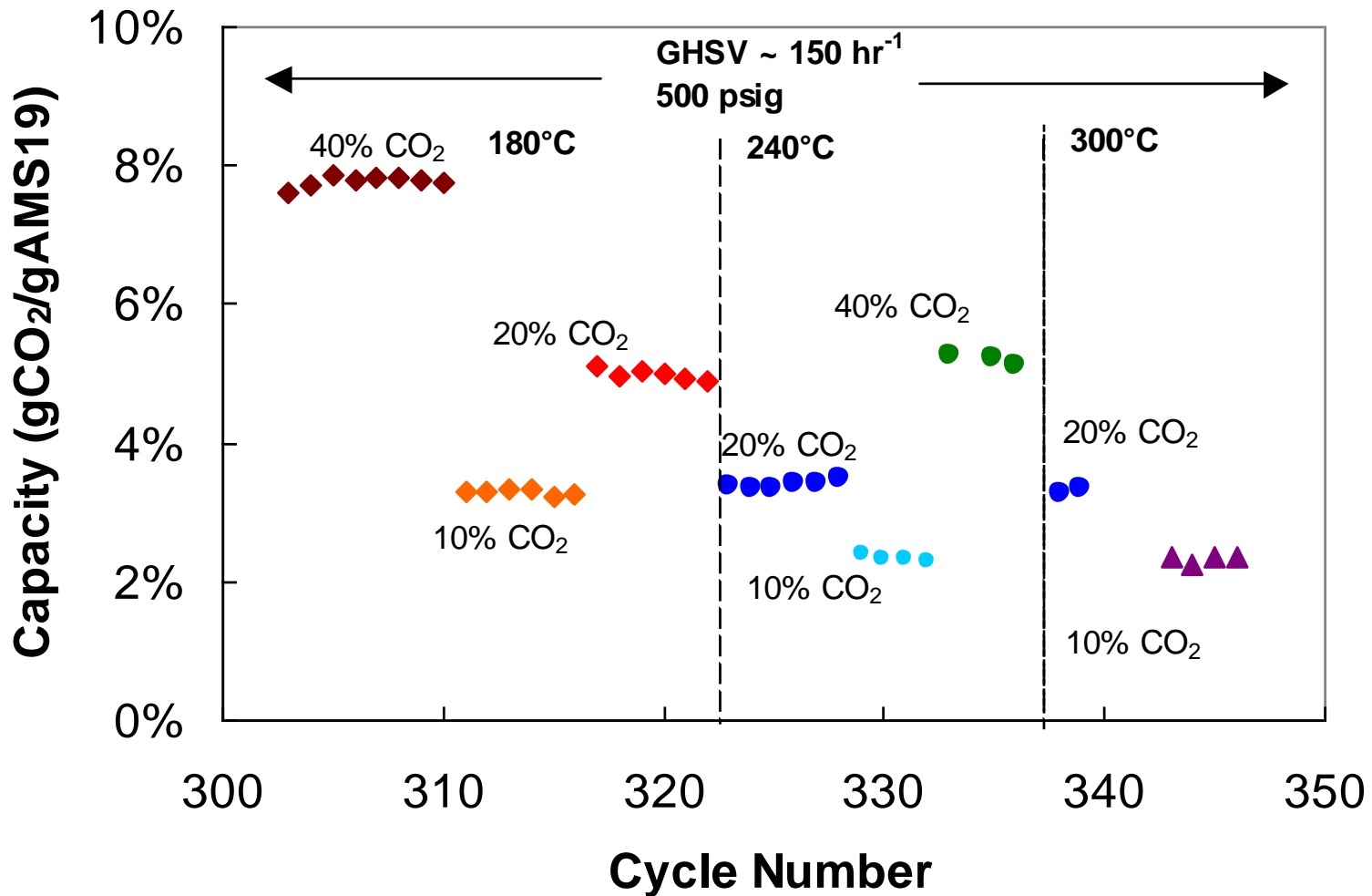


Multiple Cycle Data



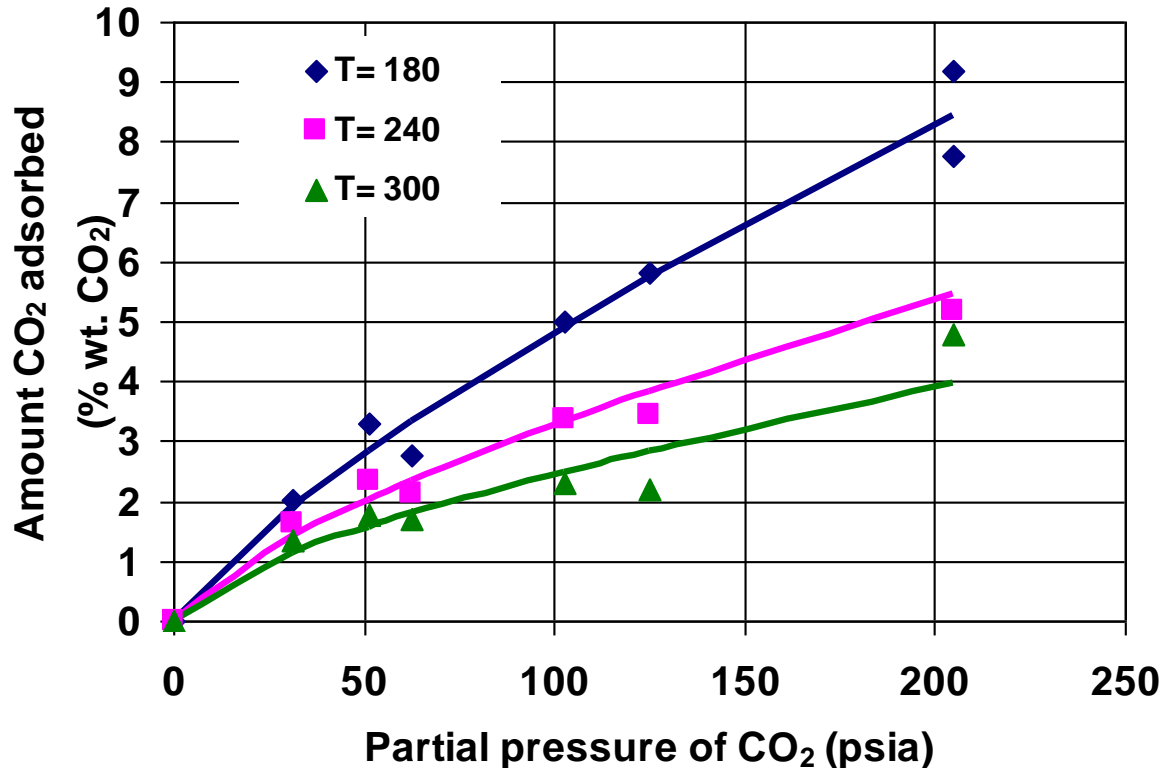
- Sorbent maintained a stable CO₂ capacity for more than 450 cycles
- Water does not affect the sorbent performance

Impact of T and P_{CO2}



- As expected sorbent capacity decreases with temperature and lower partial pressure of CO₂

Isotherm Data



Langmuir-Freundlich Isotherm

$$q = \frac{q_s B P^n}{1 + q_s B P^n}$$

$$q_s = k_1 e^{k_2/T}; B = k_3 e^{k_4/T}; n = k_5 e^{k_6/T}$$

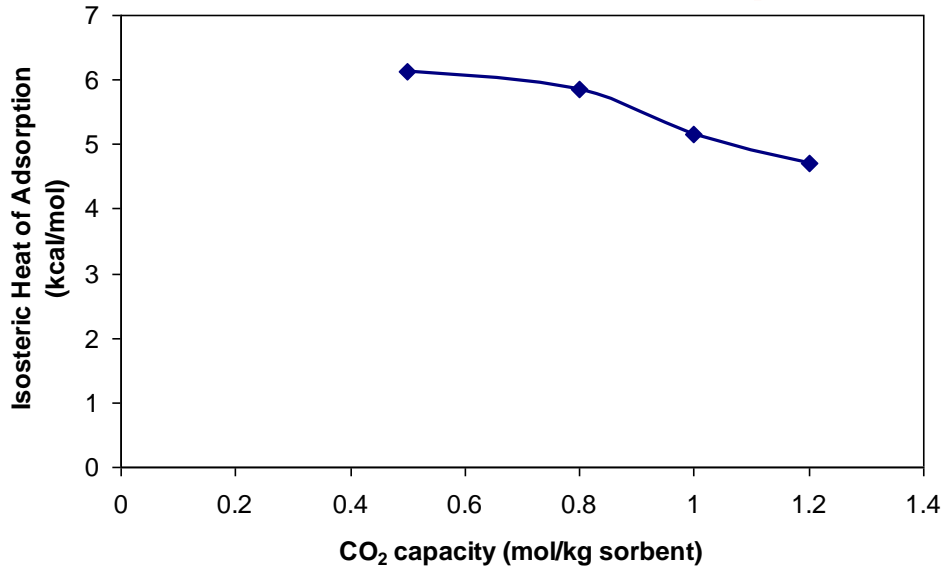
q (mol CO₂/kg); P (psia); T (K)

k1	54.30	k4	90.47
k2	92.48	k5	0.35
k3	3.42E-04	k6	381.77

- Data from bench-scale fixed-bed adsorption experiments were fitted with Langmuir-Freundlich Isotherm

Isosteric Heat of Adsorption

Isosteric Heat of Adsorption

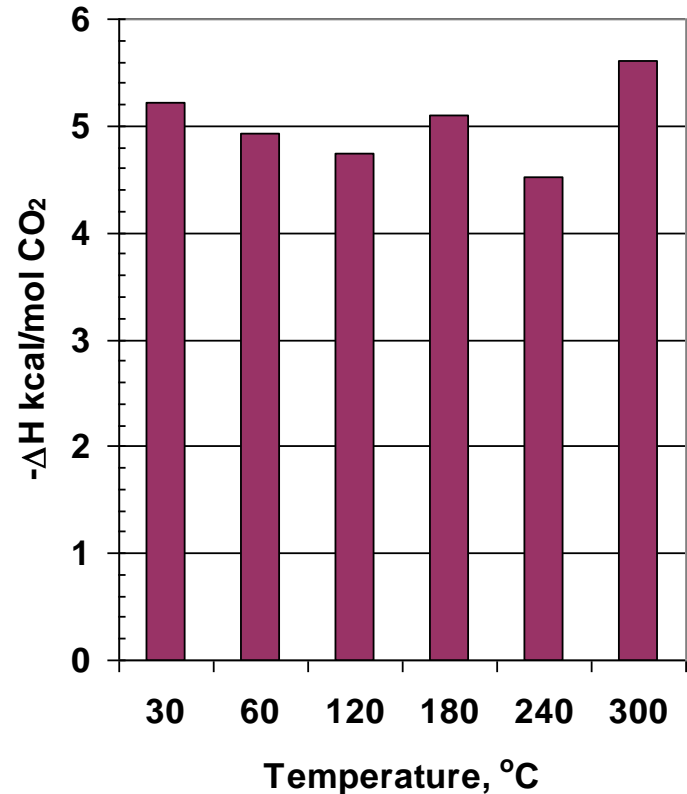


Clausius-Clapeyron Equation

$$\frac{\Delta H_{ads}}{R} = \frac{d \ln P}{d \left(\frac{1}{T} \right)} \ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H_{ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Isosteric heat of adsorption is estimated to be less than <6 kcal/mol

Calorimetry Measurements



$$-\Delta H_{ads} = 4.9 \pm 0.4 \text{ kcal/mol}$$

- DSC experiments confirms the low heat of adsorption

Conditions for Synthesis Gas Tests

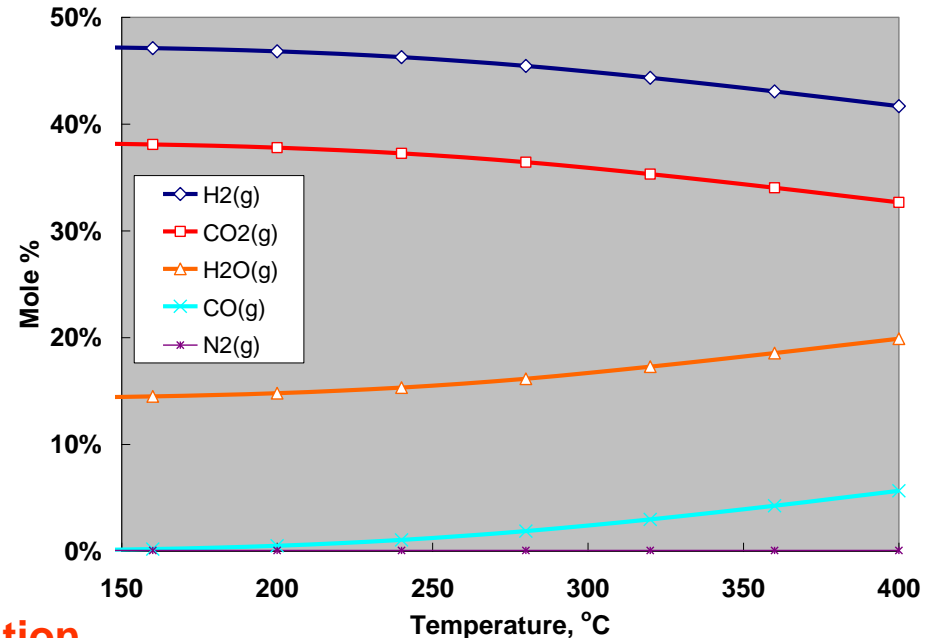
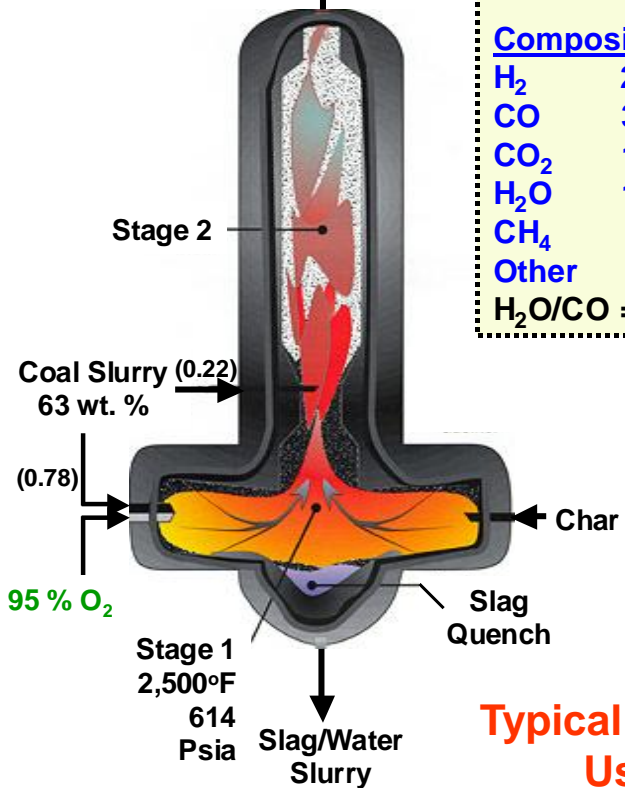
Synthesis gas

Synthesis Gas
1,700°F, 614 psia

Composition (Mole%):

H ₂	26%
CO	37%
CO ₂	14%
H ₂ O	15%
CH ₄	4%
Other	4%
H ₂ O/CO = 0.4	

To Cooler, Acid Gas
Removal and Shift



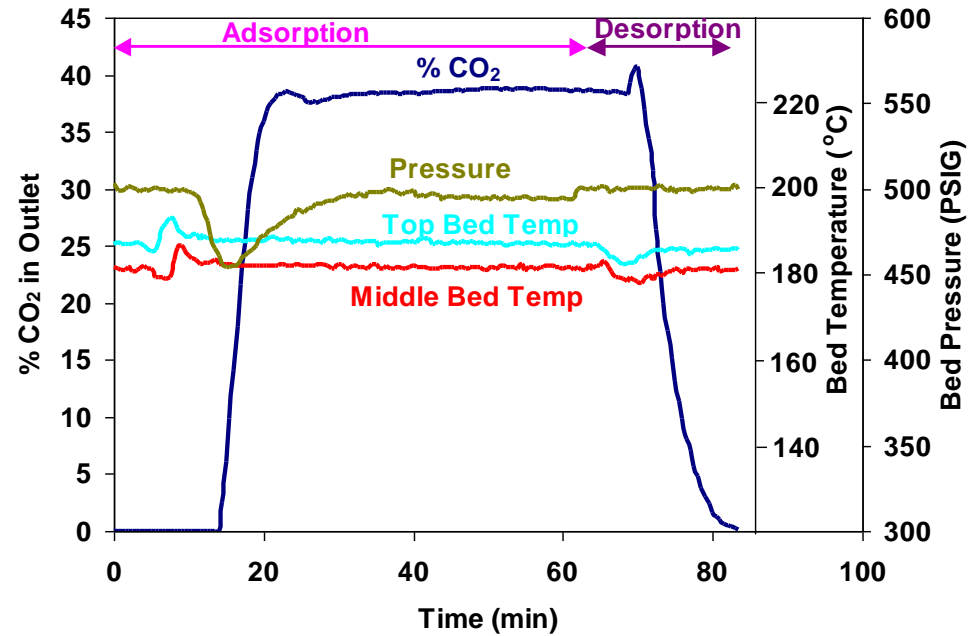
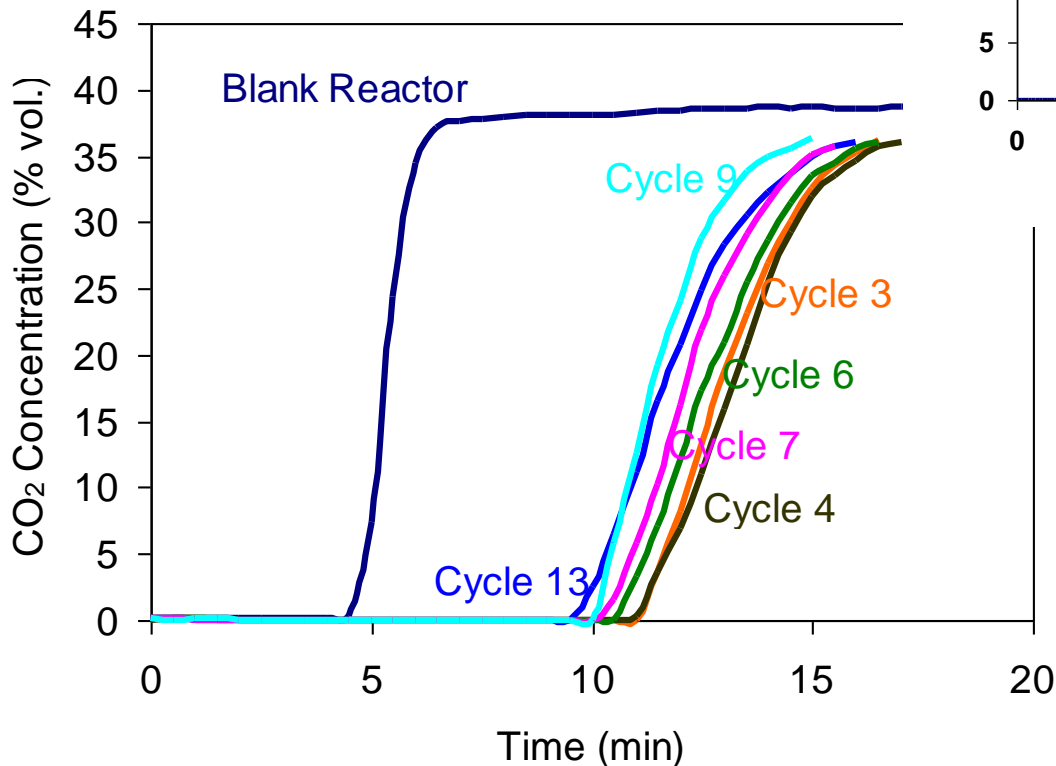
Typical Gas Composition
Used During Tests

CO₂ = 40%
H₂ = 45%
CO = 2%
& 13% H₂O

Equilibrium Gas Compositions
50% excess water

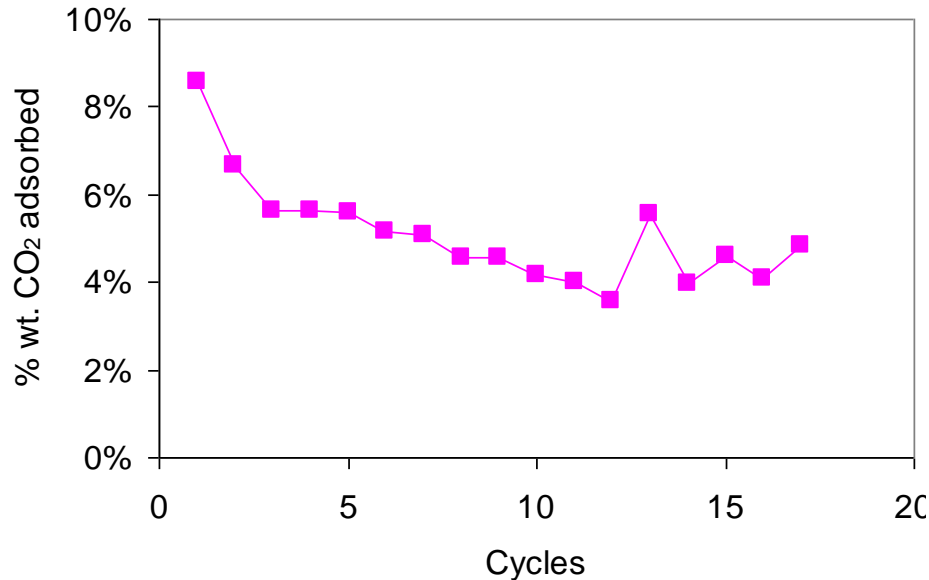
CO₂ Breakthrough Profile in Syngas

**T=180°C, P_{CO2} = 200 psig
(Adsorption) in simulated
syngas, Regeneration under
15% H₂O in N₂, P = 500 psig,
GHSV = 350 h⁻¹**



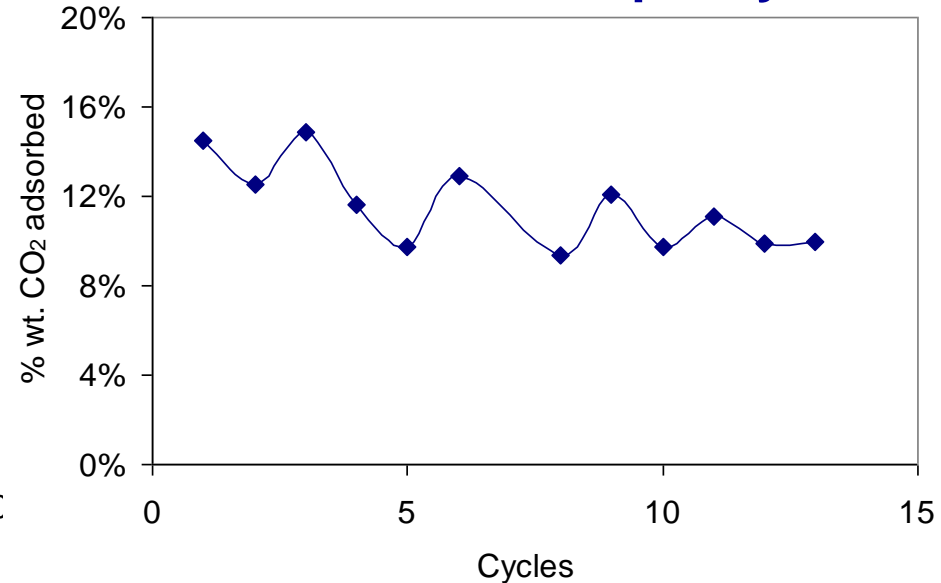
CO₂ Capacity in Flow Experiments

Breakthrough Capacity



- **Breakthrough capacity = ~5-6% wt. (lb CO₂ per lb of sorbent)**
- **CO₂ concentration at the exit is 10% of the inlet – aka 90% capture**

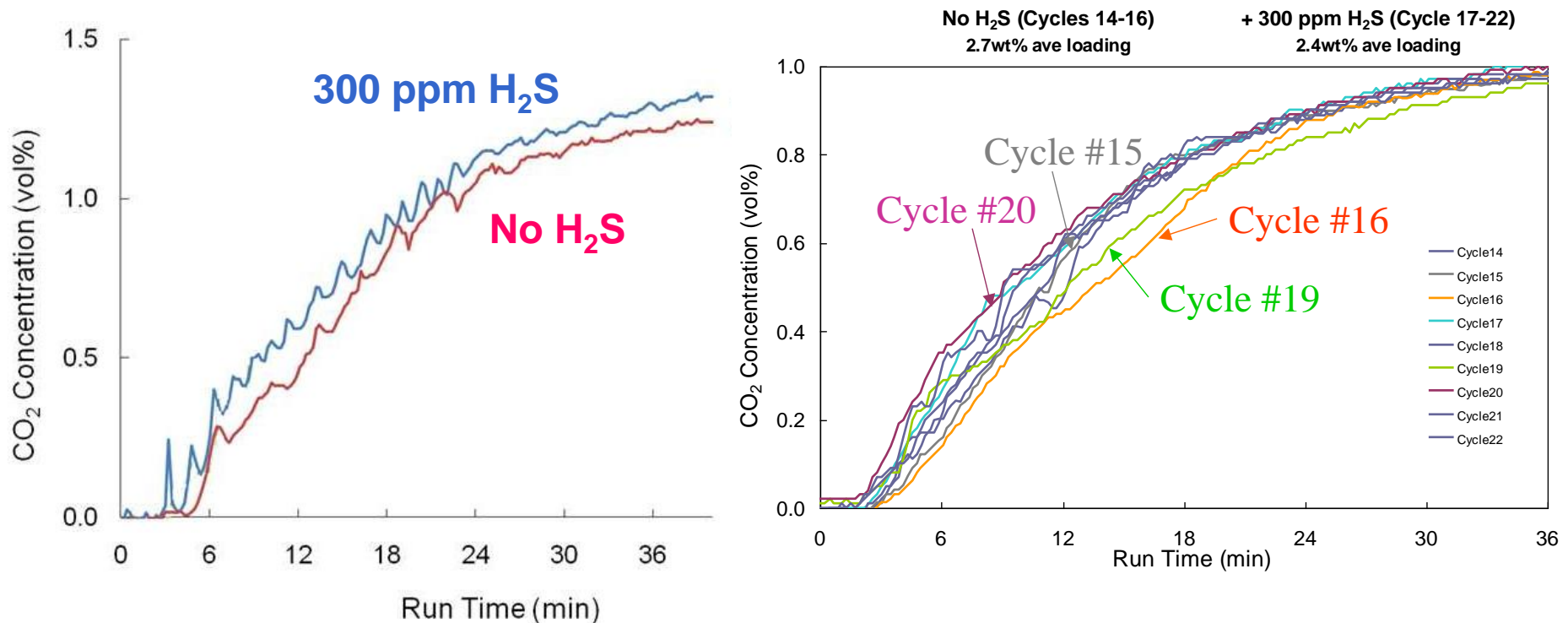
Saturation Capacity



- **Saturation capacity = 9-11% wt. (lb CO₂ per lb of sorbent)**
- **CO₂ concentration at the exit is 90% of the inlet**

Impact of Sulfur

300 ppmv H₂S, simulated synthesis gas, T= 300°C, P= 500 psig, GHSV of 1,500 h⁻¹



- Sorbent maintains its CO₂ capacity in presence of H₂S

Removal of Trace Contaminants

AsH₃ Removal

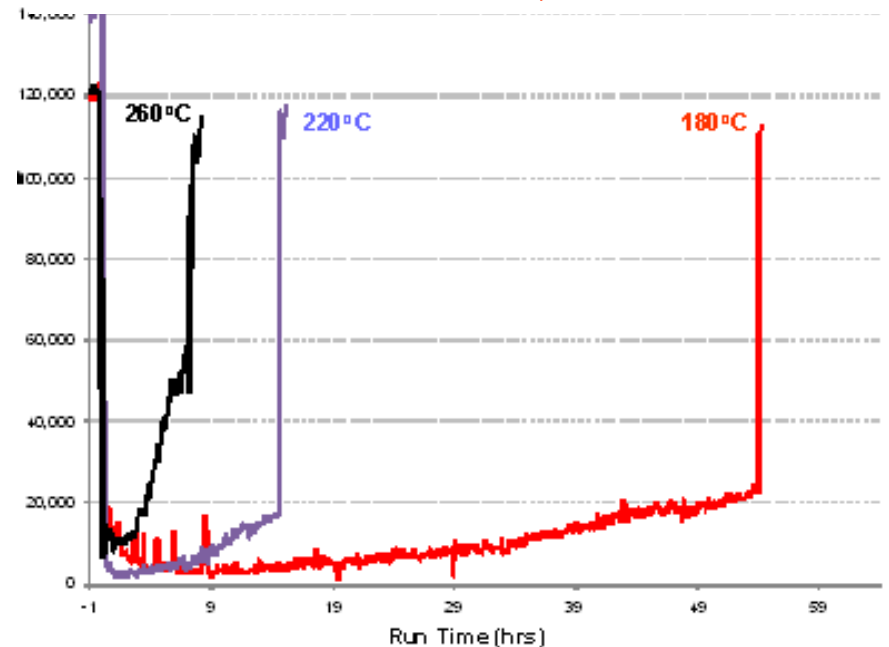
4.6 ppmv AsH₃, 50 ppmv H₂S, 41% CO, 10% CO₂, 29% H₂, 18% H₂O bal. N₂. T= 220°C, P= 500 psig, GHSV=60,000 h⁻¹



- **Modified sorbent achieved 2.79% wt. arsine capacity (lb of arsenic per lb of sorbent) at 10 ppbv breakthrough**

Hg Removal

Hg Conc.= 140,000 ng/m³, in simulated synthesis gas T= 180°C, P= 500 psig, GHSV of 75,000 h⁻¹



- **Baseline sorbent shows promising Hg capacity**

System Analysis

- **UCI will carry out the process simulation using AspenPlus™ and evaluate the cost analysis of the new CO₂ capture system integrated with CoP/E-Gas™ system**
- **The analysis will include three simulations:**
 - E-Gas™ based IGCC plant with no CO₂ capture
 - E-Gas™ based IGCC plant with Selexol-based CO₂ capture
 - E-Gas™ based IGCC plant with TDA's CO₂ capture system
- **This will be a comparative analysis using Selexol as the baseline CO₂ capture system**
- **First objective is to repeat the results of a previous DOE study to validate the model**
- **Same assumptions and cost guidelines will be adopted**
 - Consistent design requirements
 - Up-to-date performance and capital cost estimates
 - Technologies built now and deployed by 2012

Specifics of the Analysis

General Assumptions

Start-up	2012
Plant Life (years)	20
Capital Charge Factor (%)	
High Risk	17.5
Low Risk	16.4
Dollars (2007)	
Coal (\$/MM Btu)	
Capacity Factor (%)	80
CO ₂ Compression Pressure (psig)	2,200
Transport Distance (miles)	50

Coal Type

Illinois #6 Coal Ultimate Analysis (weight %)

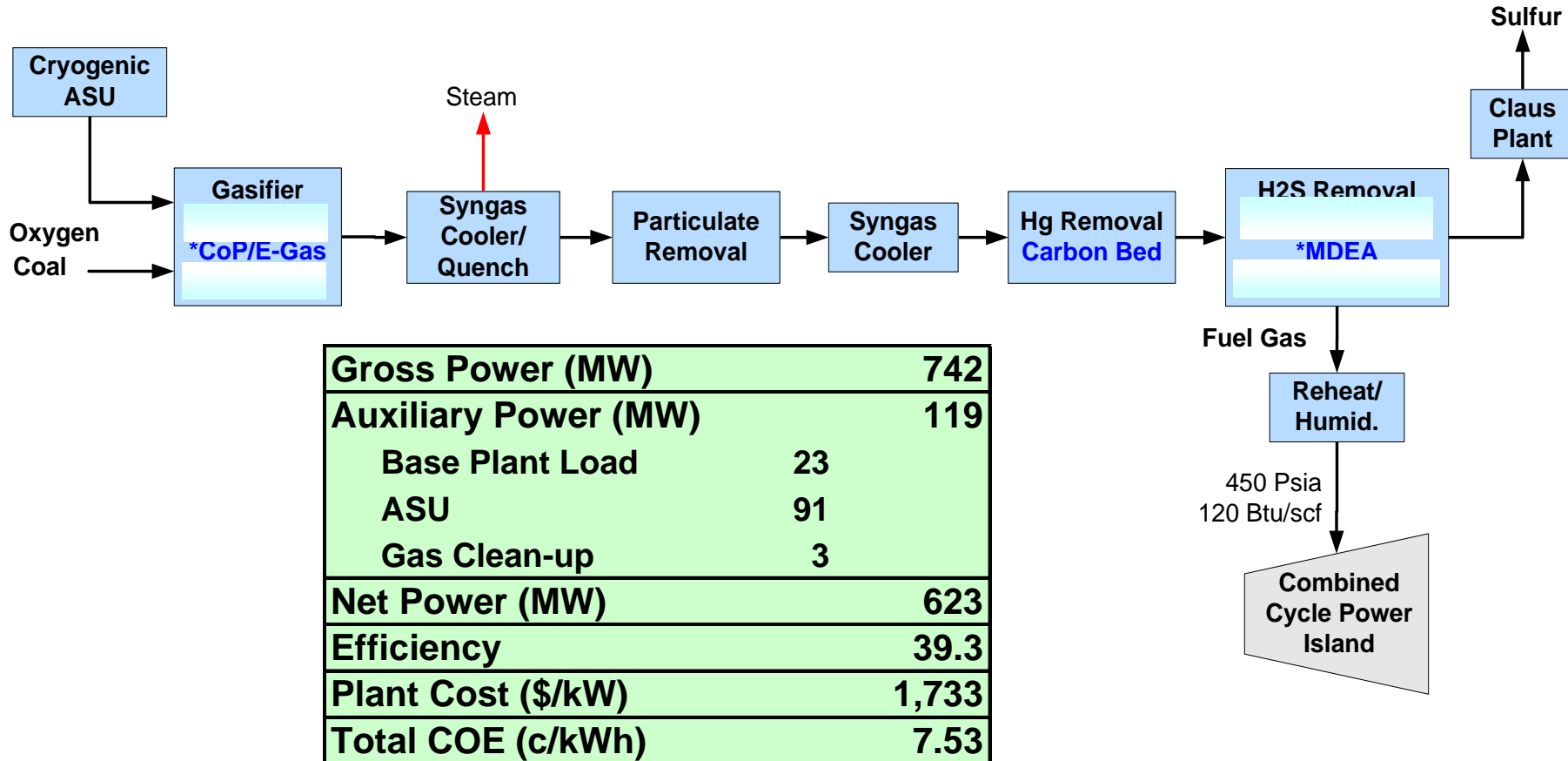
	As Rec'd	Dry
Moisture	11.12	0
Carbon	63.75	71.72
Hydrogen	4.50	5.06
Nitrogen	1.25	1.41
Chlorine	0.29	0.33
Sulfur	2.51	2.82
Ash	9.70	10.91
Oxygen (by difference)	6.88	7.75
	100.0	100.0
HHV (Btu/lb)	11,666	13,126

Emission Requirements

Pollutant	Emission Requirement
SO ₂	0.0128 lb/MMBtu
NO _x	15 ppmv (dry) @ 15% O ₂
PM	0.0071 lb/MMBtu
Hg	> 90% capture

1st Simulation

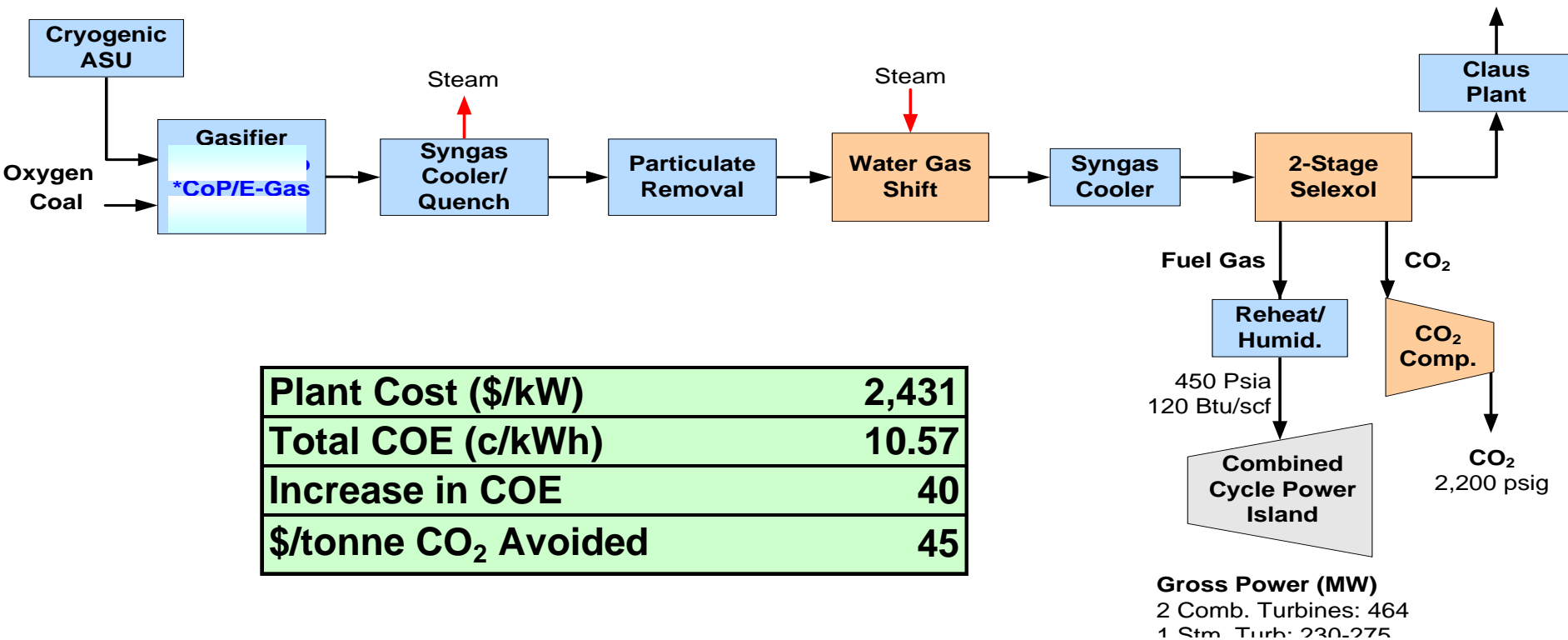
Current Technology- IGCC Power Plant (no CO₂ Capture)



Ref: Cost and Performance Baseline for Fossil Energy Plants, NETL, 2007

2nd Simulation

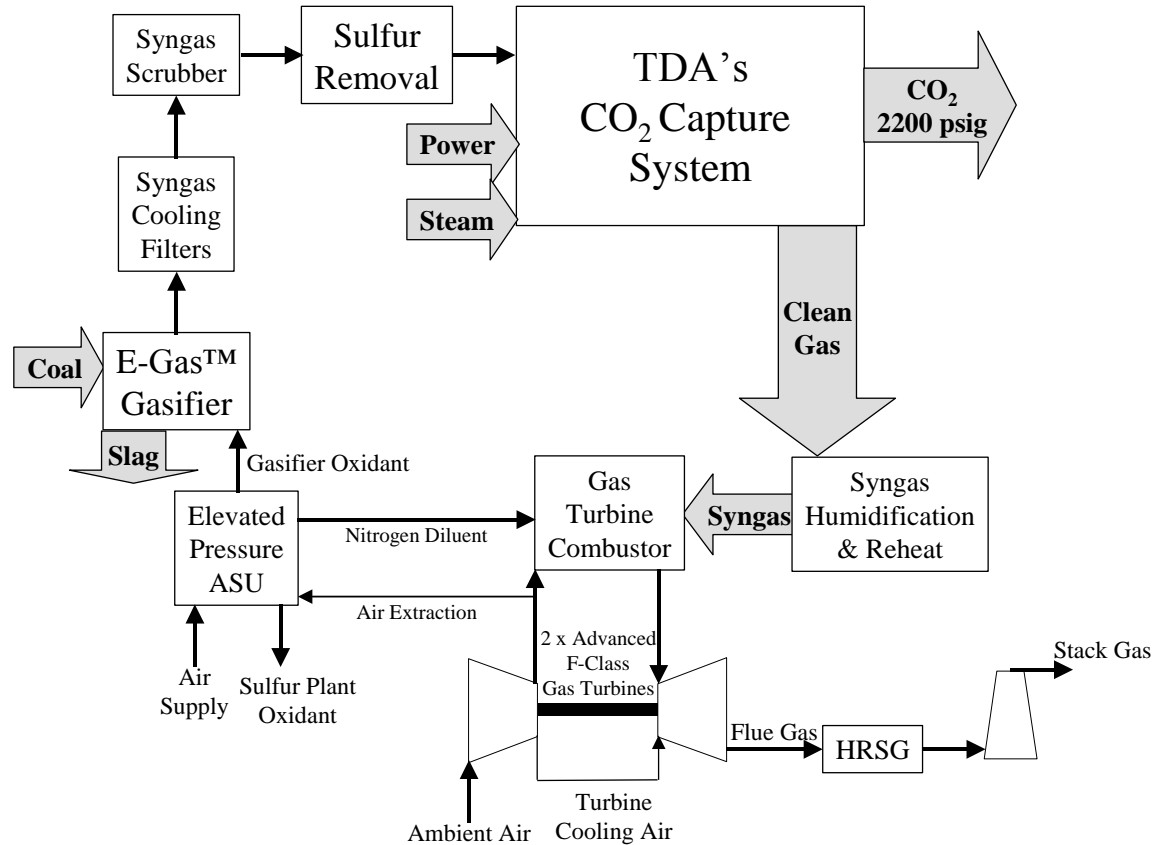
IGCC Power Plant with CO₂ Scrubbing



Ref: Cost and Performance Baseline for Fossil Energy Plants, NETL, 2007

3rd Simulation

IGCC with TDA's CO₂ Capture Technology



- Use project data for CO₂ system design and published data for sulfur removal
 - CoP's S-Sorb Technology
 - RTI's warm gas desulfurization

1st Order Cost Analysis

CO2 Removal (80% utilization)	319,703 ton/year 46.36 ton/hr
Sorbent Capacity	8% wt.
Sorbent Need	193.2 ton
Full-cycle Time	10 min
Cost of Sorbent	\$2.25 per lb
Sorbent Cost	\$956,188
Impact on \$/ton CO2	\$2.99 per ton
<hr/>	
Heat of Regeneration	5 kcal/mol 113,636 kcal/ton
Cost of Energy	\$1.75 MM Btu
Impact on \$/ton CO2	\$0.79 per ton

- **The contribution of the cost of the sorbent and the heat for regeneration (assuming no recovery) is less than 16% for the target \$23/ton CO₂**

Conclusions

- TDA is developing a new sorbent technology for pre-combustion CO₂ capture
- The sorbent can achieve a high CO₂ capacity
 - Up to 16% wt. with 5-6% wt. Working capacity
- The heat of CO₂ adsorption is very comparable to that of Selexol's
- The sorbent can be regenerated by pressure swing or concentration swing
- The sorbent may serve as a universal scrubber
- Preliminary cost analysis is promising

Acknowledgements

- **The authors acknowledges the funding from DOE (Contract No: DE-FE0000469)**
- **Contract Monitor: Sara Zenner**
- **Program Manager: Sean Pylanski**