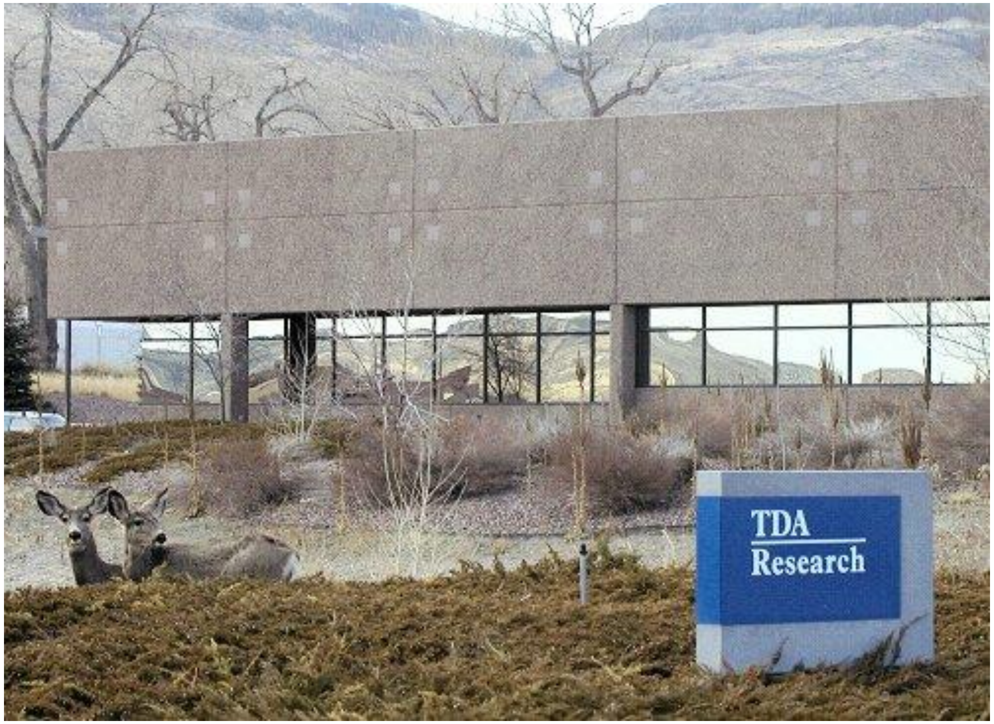
A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture

Contract No. DE-FE0000469
Project Review Meeting



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September 17, 2010

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

Project Summary

- **The objective of this work is to develop a new pre-combustion CO_2 capture technology and demonstrate its technical and economic viability**
- **A low cost, high capacity regenerable sorbent is developed to remove CO_2 above the dew point of the gas**
- **The sorbent is a mesoporous carbon grafted with surface functional groups to remove CO_2 via physical adsorption**
- **Year 1**
  - Sorbent optimization and scale-up sorbent production
  - Bench-scale evaluations
  - Process design and optimization
- **Year 2**
  - Complete/demonstrate sorbent life for 10,000 cycles
  - Slipstream demonstration using actual synthesis gas
  - Based on field performance data and optimum design, conduct an economic analysis to estimate the cost of CO_2 capture

Project Partners

TDA Research

Project Performance Dates

- **Project Start Date = November 15, 2009**
- **Project End Date = November 15, 2011**

Budget

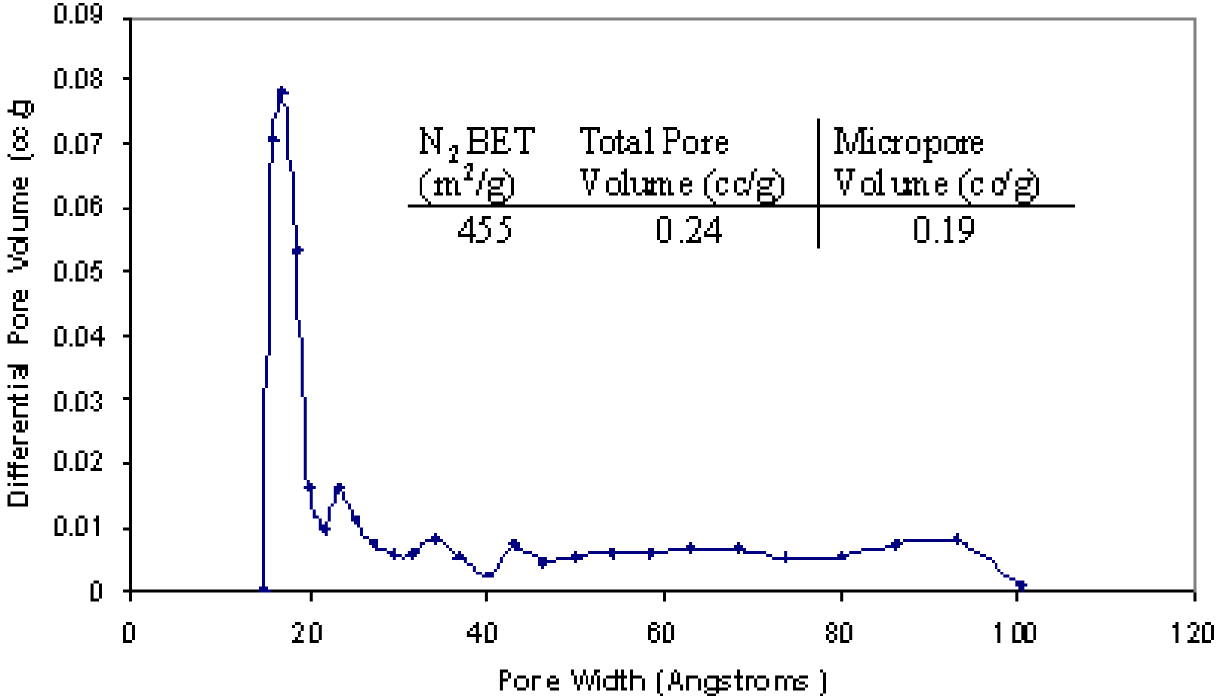
- **Project Cost = $2,500,000**
- **DOE Share = $2,000,000**
- **TDA and its partners = $500,000**

TDA's Approach

- TDA is developing a high temperature physical adsorbent to remove CO_2
- The sorbent consists of a carbon material 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
- Calorimetry measurements and isosteric calculations suggest that heat of adsorption on TDA sorbent is ~4.9 kcal mol per mole of CO_2
  - Selexol ~4 kcal/mol CO_2
  - Amine solvents ~14.4 kcal/mol
  - Chemical absorbents Na_2CO_3 29.9 kcal/mol
- Net energy loss in sorbent regeneration is similar to Selexol's
  - A much better IGCC efficiency due to higher temperature CO_2 capture
  - Warm gas clean-up improves cycle efficiency 2 to 4%

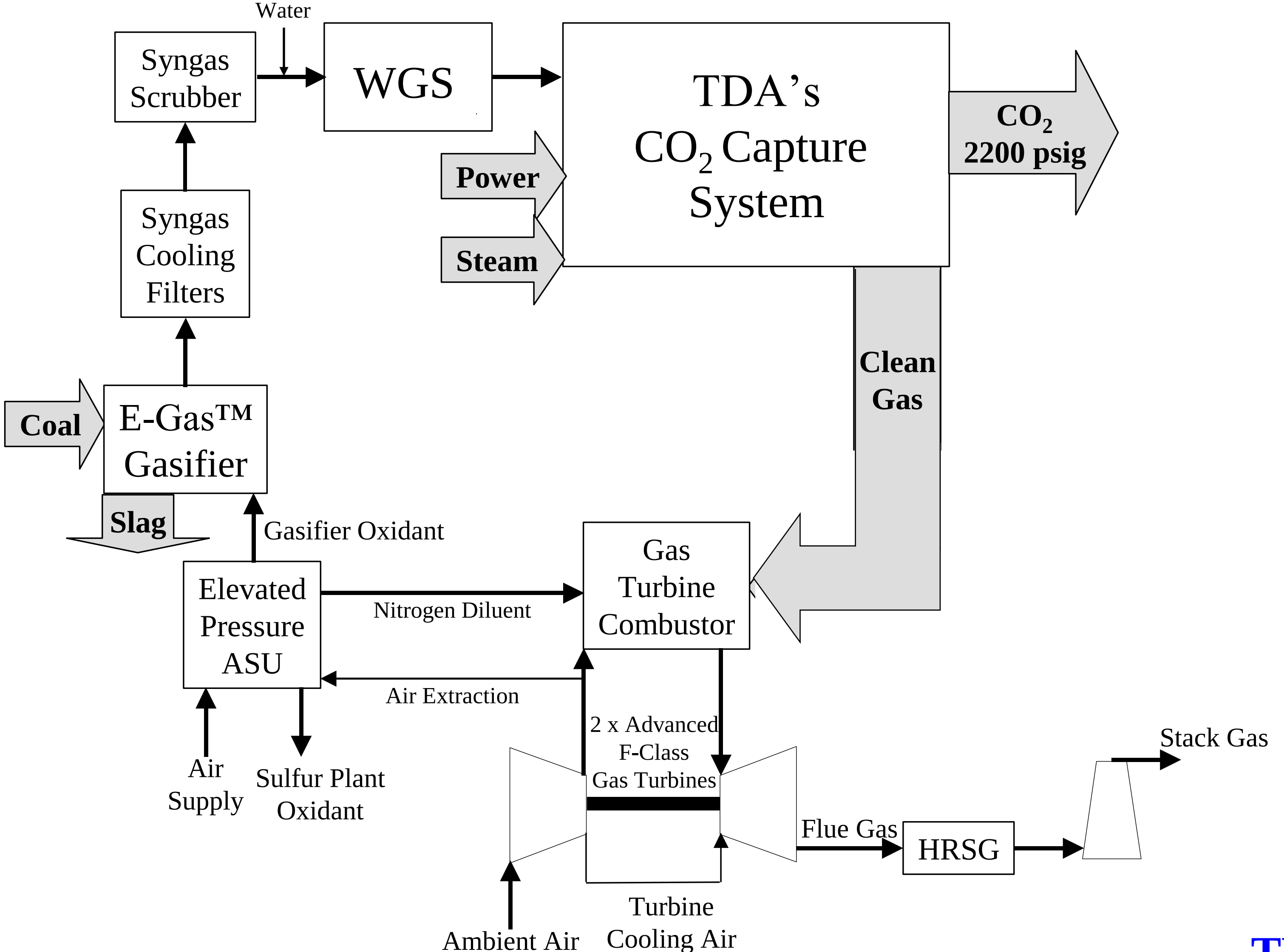
TDA's Sorbent

- The carbon is previously developed for ultracapacitors applications
  - Meso-range pores (20 to 100 Å) are large enough to allow transport of liquid electrolyte in and out of the pores
  - Macro-porosity is avoided to have a reasonably high surface area



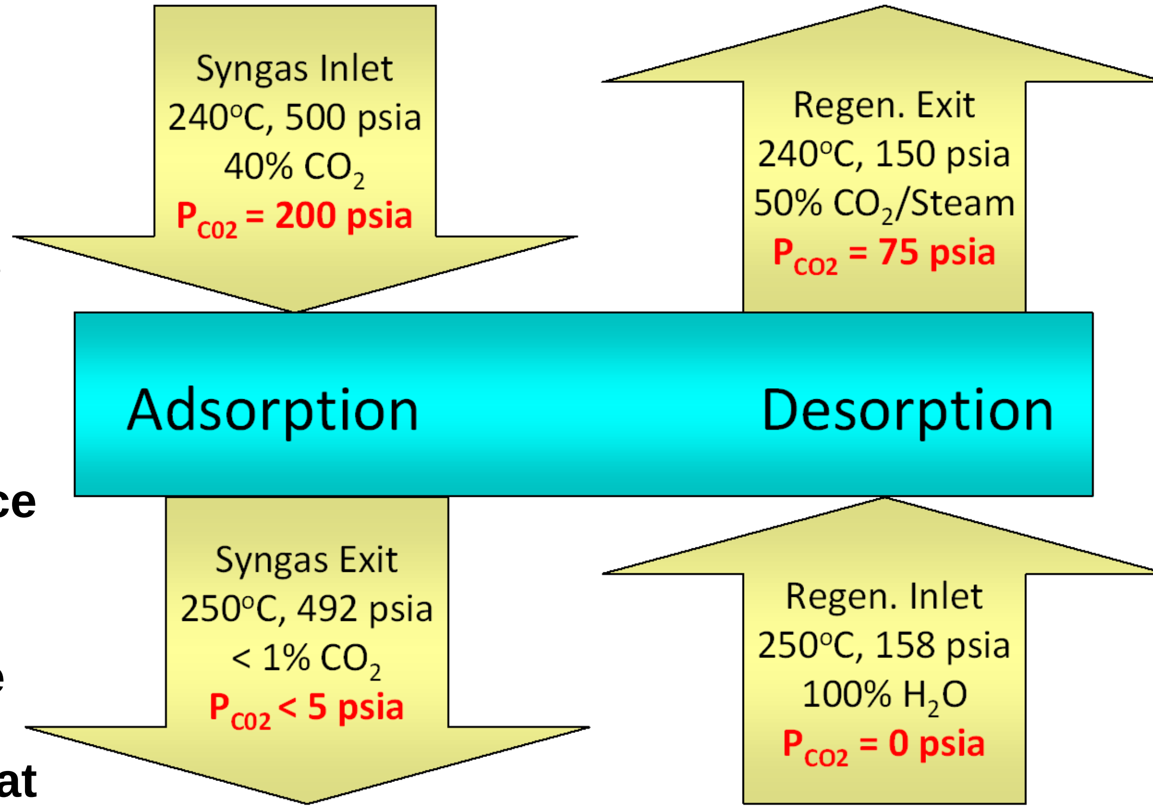
- The proprietary preparation method of the carbon also allows us to introduce functional groups

IGCC-Integrated CO_2 Capture System



Regeneration Options

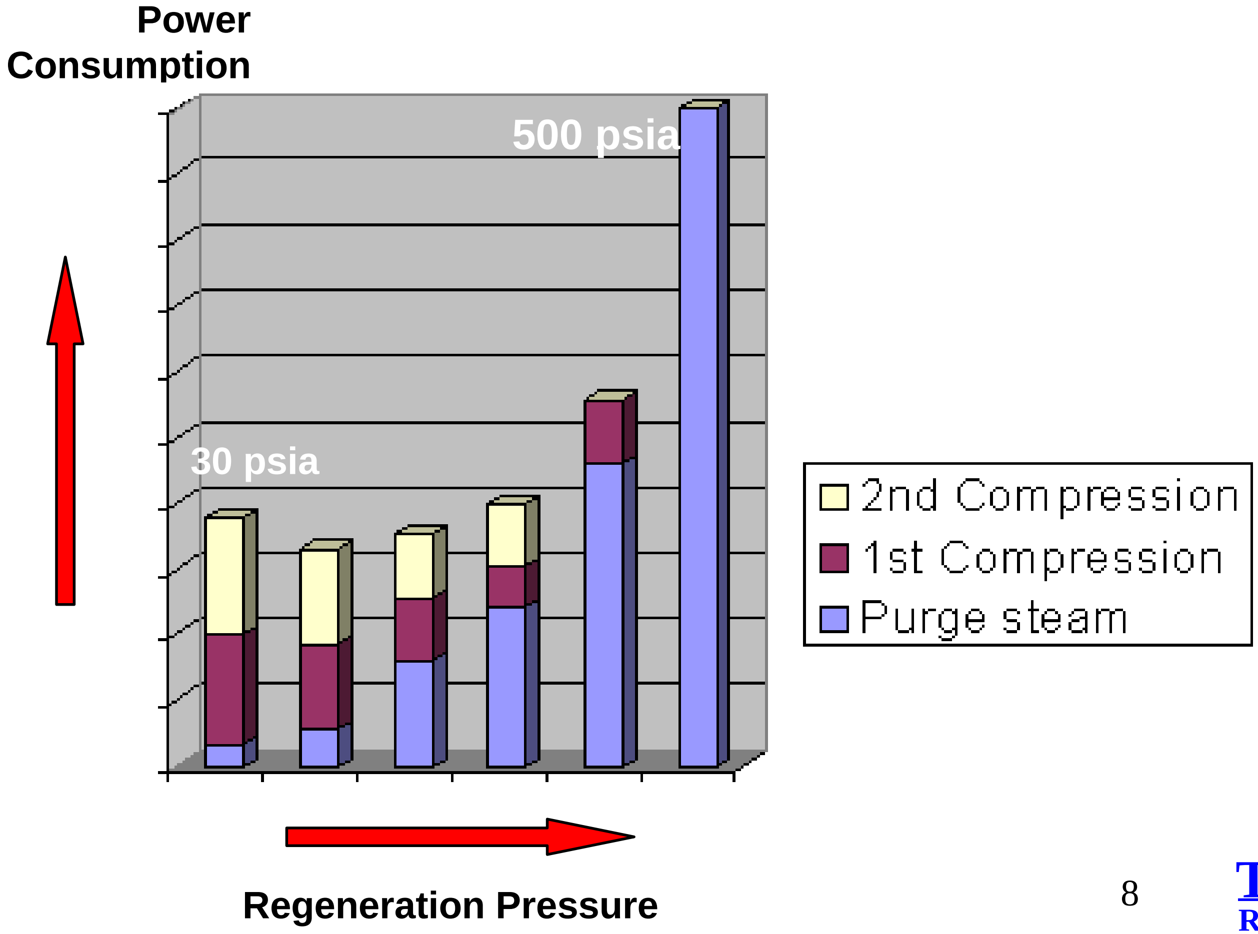
- **The physical adsorbent provides flexibility in the selection of regeneration options:**
  - **Temperature swing**
  - **Pressure swing**
  - **Concentration swing**
  - **Possible combinations**



- **Isothermal operating capability is critical to eliminate heat/cool transitions which will reduce cycle time and increase sorbent utilization**
- **Steam consumption can be reduced significantly if the steam purge is carried out at low pressure**
- **System operation is similar to that of the PSA (operating temperature will be high)**

Trade-off Analysis

- Regeneration pressure vs. steam consumption
- Higher regeneration pressure reduces power input for CO_2 compression, while pure concentration swing requires extracting large amounts of high pressure steam from steam cycle



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Sorbent Production Scale-up

- 11” diameter
- Computer controlled
- 1000 C temp. limit
- 12 kg capacity
- 2-4 kg carbon/run

- Trial runs at Hazen Research was carried out using a continuous rotary kiln
- TDA purchased a continuous rotary kiln that will be installed before the end of the year

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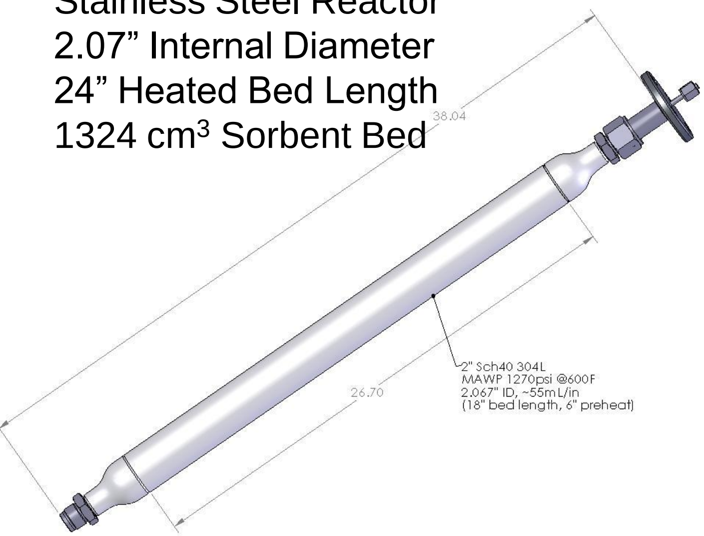
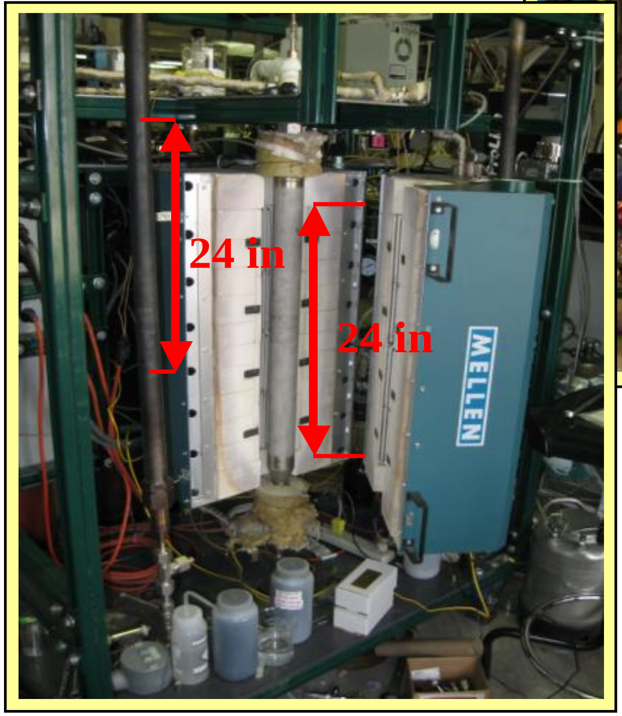
Experimental Apparatus

- **Three fixed-bed test apparatus are used for evaluations**
  - Adsorption Isotherms – 120 cc
  - Large Flow Reactor – 1,200 cc
  - Contaminant Reactor – 30-120 cc
  - All systems are capable of evaluating sorbent at 0.7 – 1.4 mm particle size

2" Schedule 40
Stainless Steel Reactor
2.07" Internal Diameter
24" Heated Bed Length
1324 cm^3 Sorbent Bed





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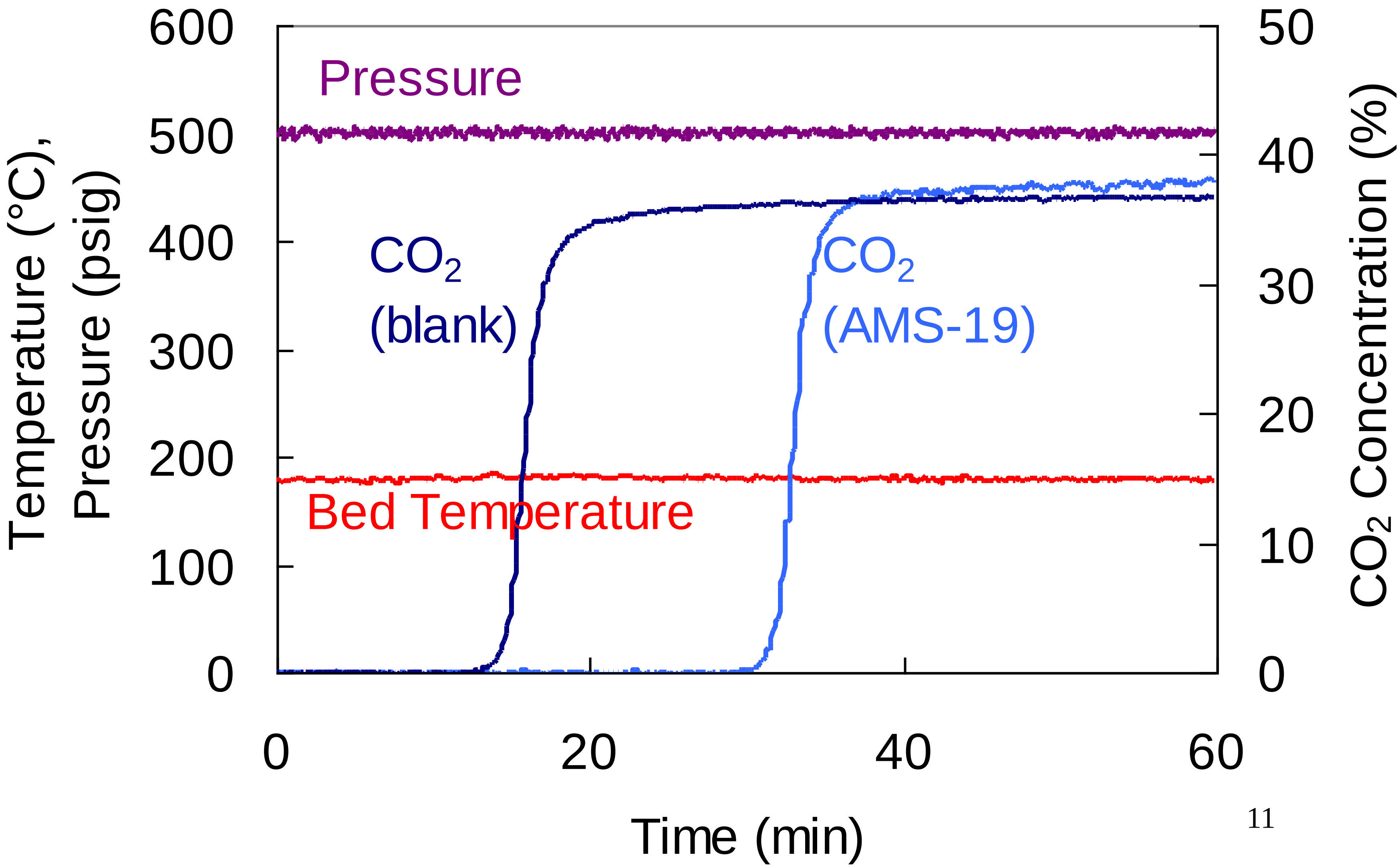
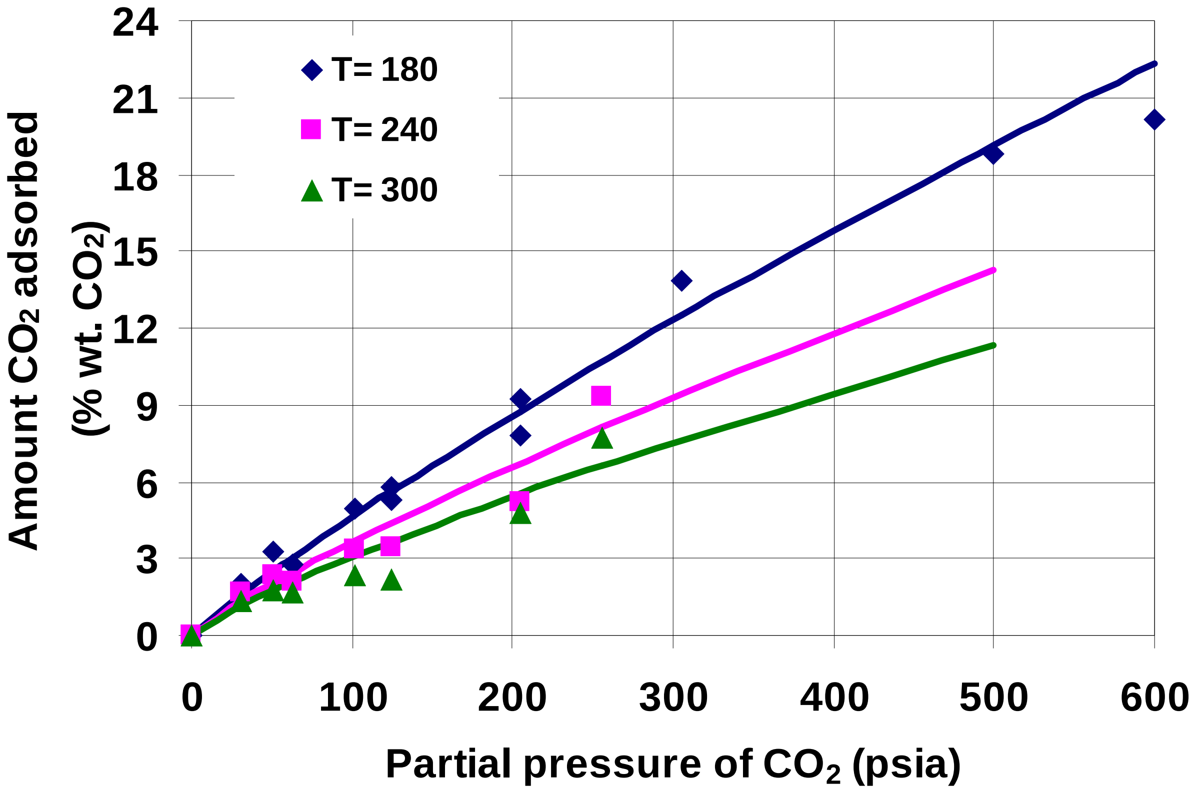
Typical CO_2 Adsorption Profile

T=180°C, P = 500 psig, P_{CO2} = 200 psig



Isotherm Data



Langmuir-Freundlich Isotherm

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

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

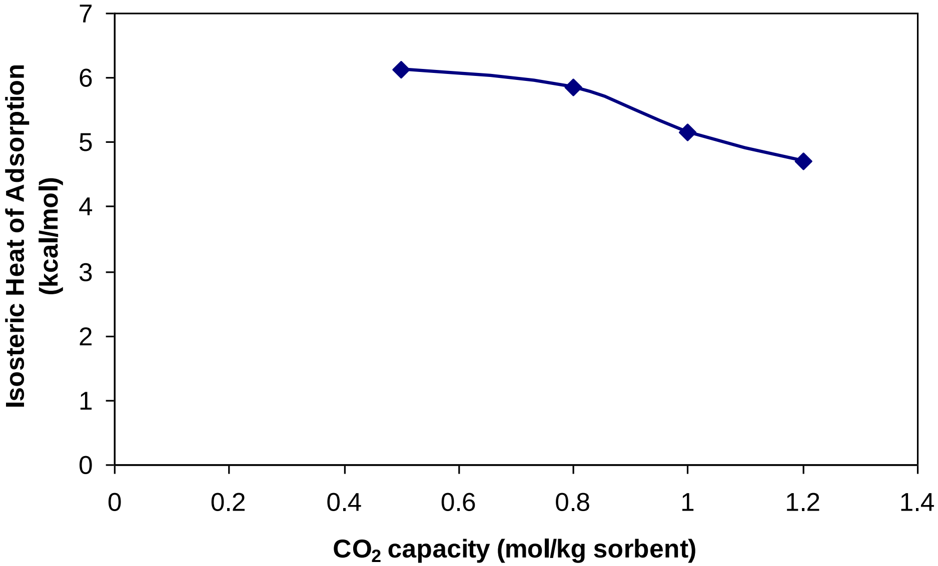
q (mol CO_2/kg); P (psia); T (K)

k1	58.05	k4	47.07
k2	46.55	k5	0.59
k3	2.2E-04	k6	201.46

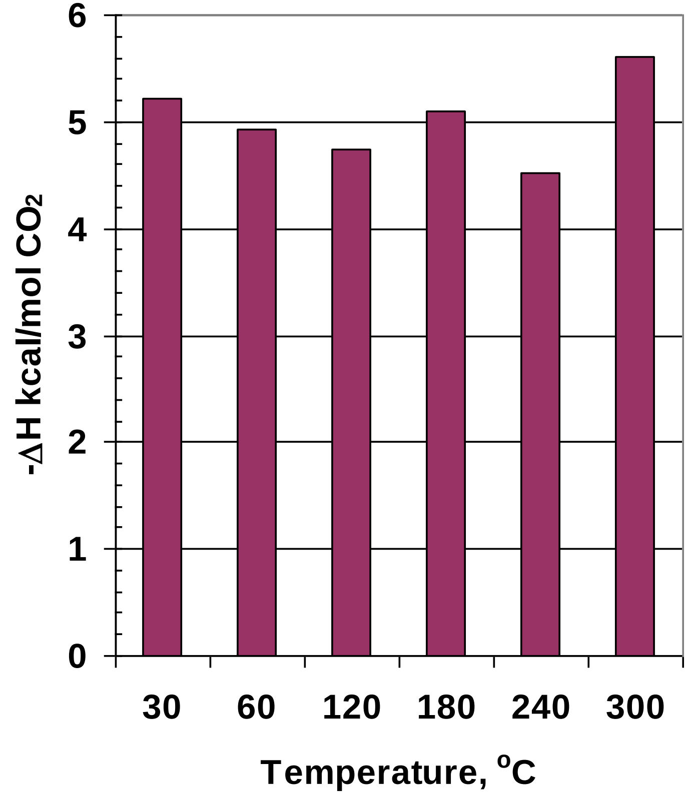
- **Data from bench-scale fixed-bed adsorption experiments were fitted with Langmuir-Freundlich Isotherm**

Heat of CO_2 Adsorption

Isosteric Heat of Adsorption



Calorimetry Measurements



Clausius-Clapeyron Equation

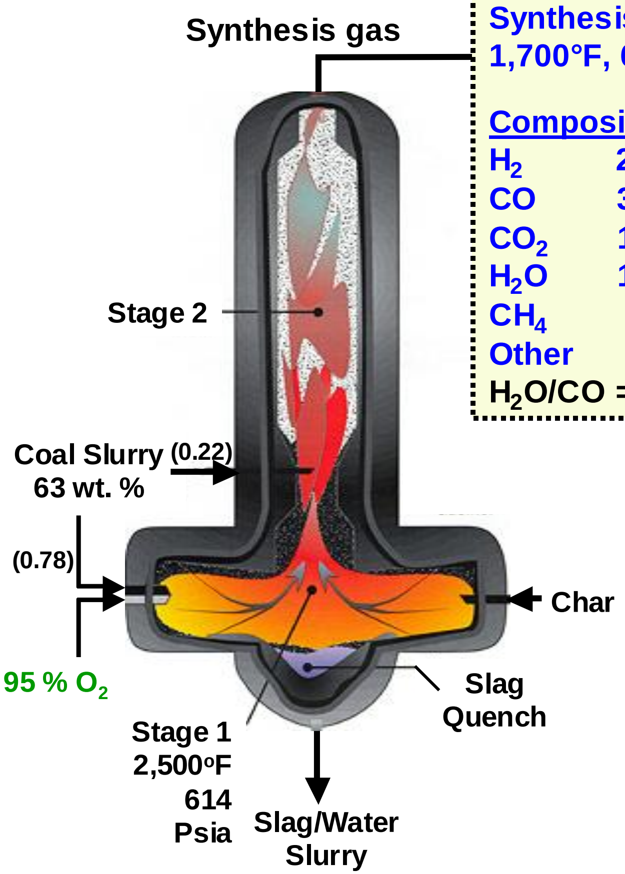
$$\frac{\Delta H_{ads}}{R} = \frac{d(\ln P)}{d\left(\frac{1}{T}\right)} \qquad ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{ads}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- **Isosteric heat of adsorption is estimated to be less than 4-6 kcal/mol**

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

- **DSC experiments confirms the low heat of adsorption**

Test Conditions for Sorbent Evaluation



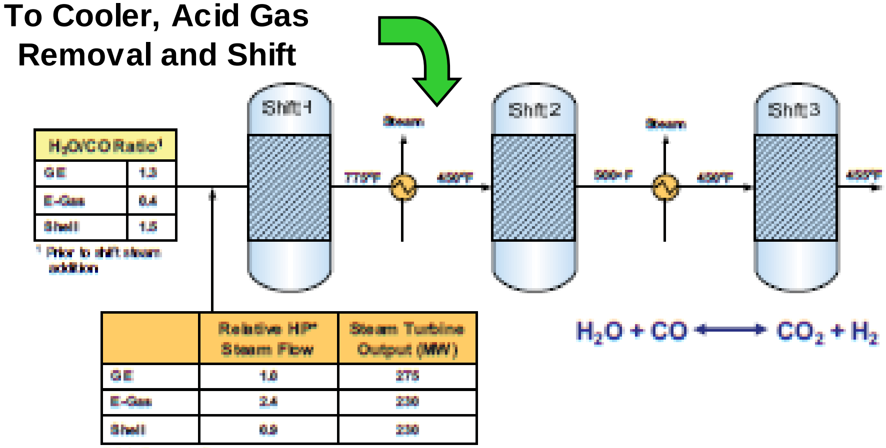
Synthesis Gas
1,700°F, 614 psia

Composition (Mole%):

H_2	26%
CO	37%
CO_2	14%
H_2O	15%
CH_4	4%
Other	4%

$H_2O/CO = 0.4$

To Cooler, Acid Gas Removal and Shift



Equilibrium Gas Compositions
2:1 H_2O:CO

Gas Composition	
Ar	0.49%
CH_4	1.52%
CO	0.59%
CO_2	32.26%
H_2	40.07%
H_2O	24.36%
N_2	0.71%

- **Dew point of before CO_2 capture – 190°C**
- **Dew point of after CO_2 capture – 207°C**
- **We selected 240°C as operating temperature**

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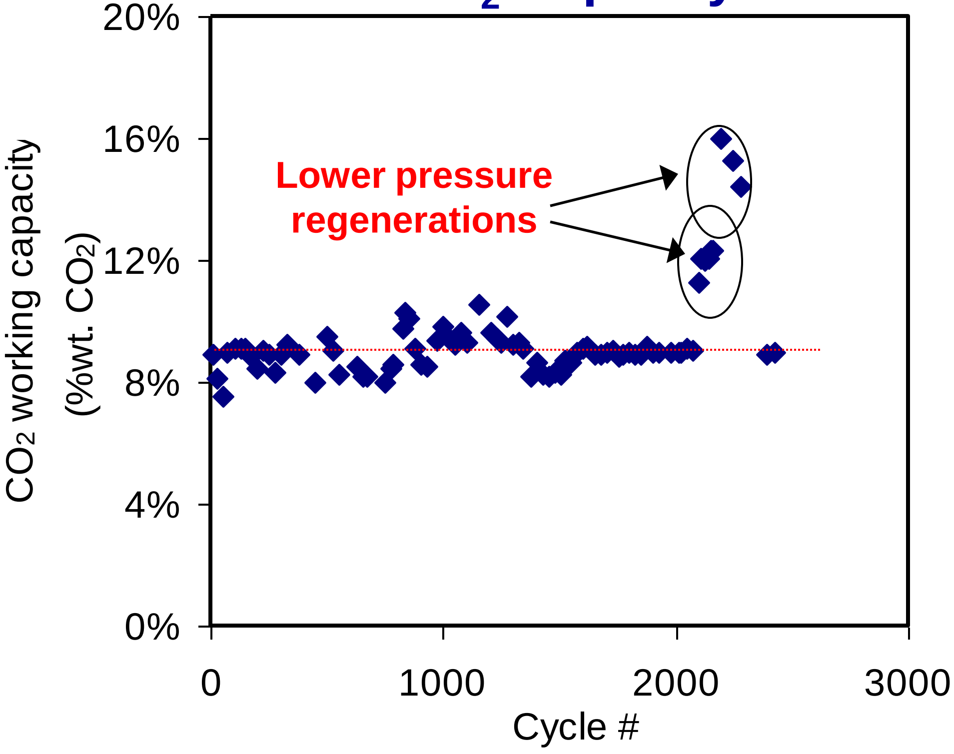
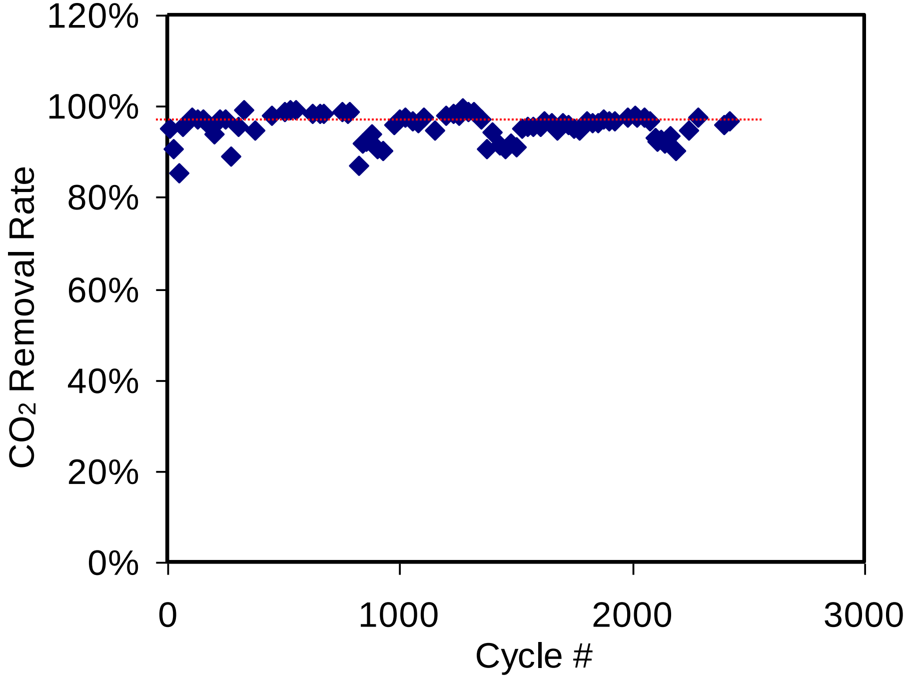
Multiple Cycle Tests

H_2=40%, CO_2=32%, N_2=3%, CO=1%, 24% H_2O;
T_{ads} = 240°C ; P_{ads} = 500 psig; T_{des} = 240°C ; P_{des} = 150 psig

CO_2 Capacity



CO_2 Removal Efficiency



- **Sorbent maintained its CO_2 capacity (8+%wt.) and removal efficiency (95+%) for 2,400 cycles**

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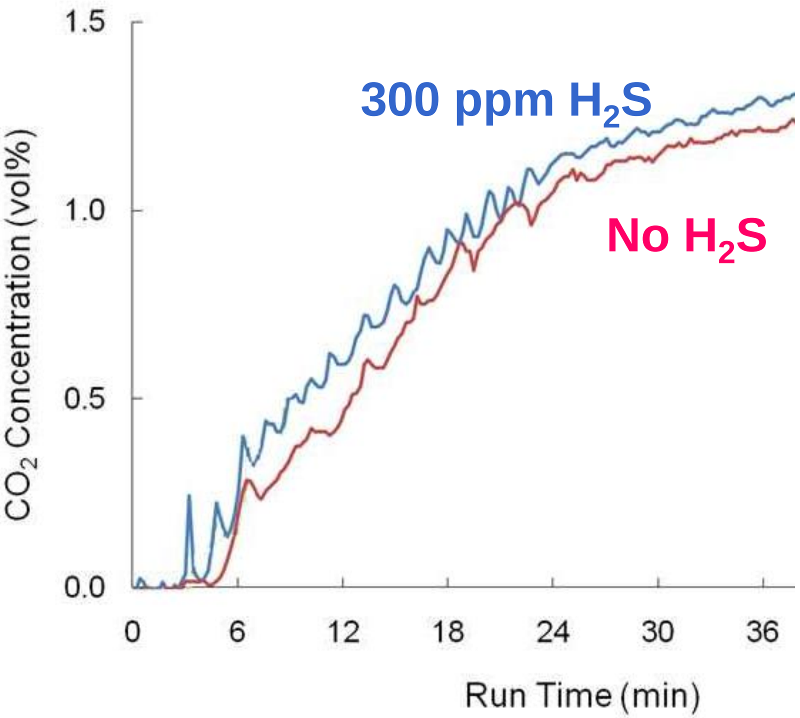
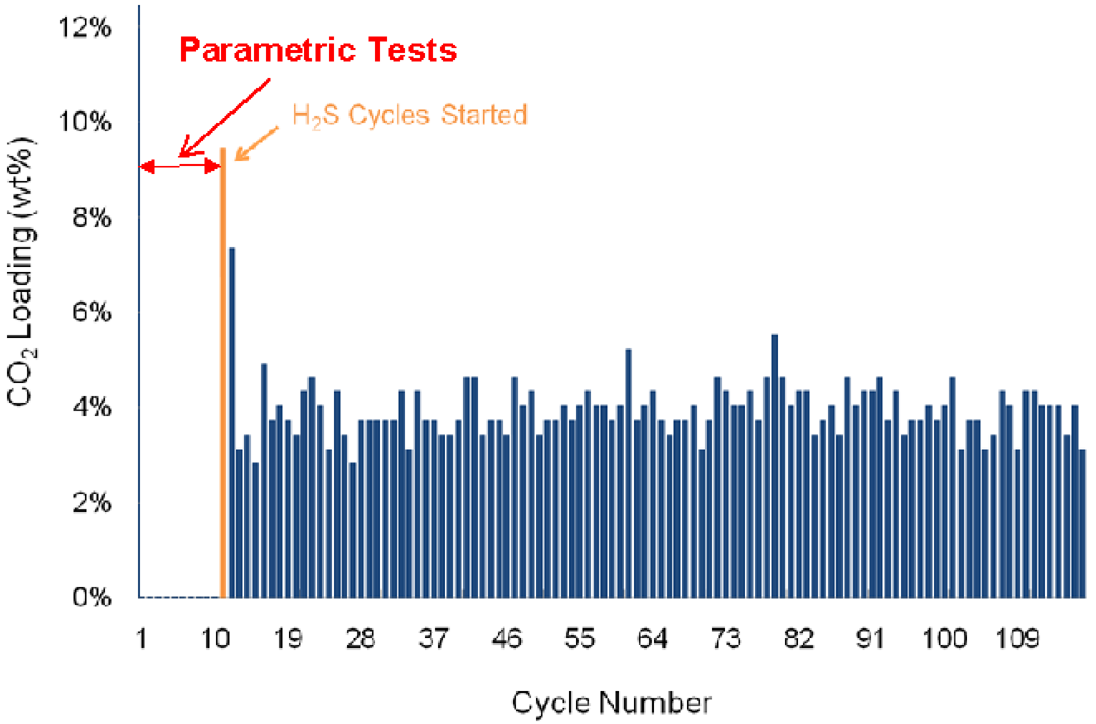
Impact of Sulfur

300 ppmv H_2S, simulated synthesis gas, T= 240°C, P= 500 psig



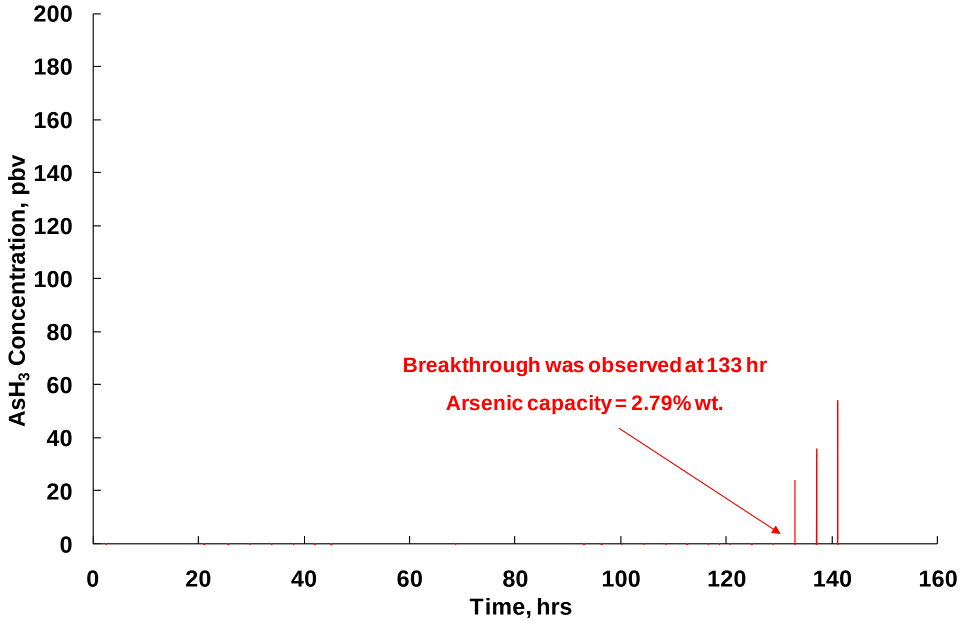


- **Presence of H_2S did not have a significant impact on sorbent performance**

Removal of Trace Contaminants

AsH_3 Removal

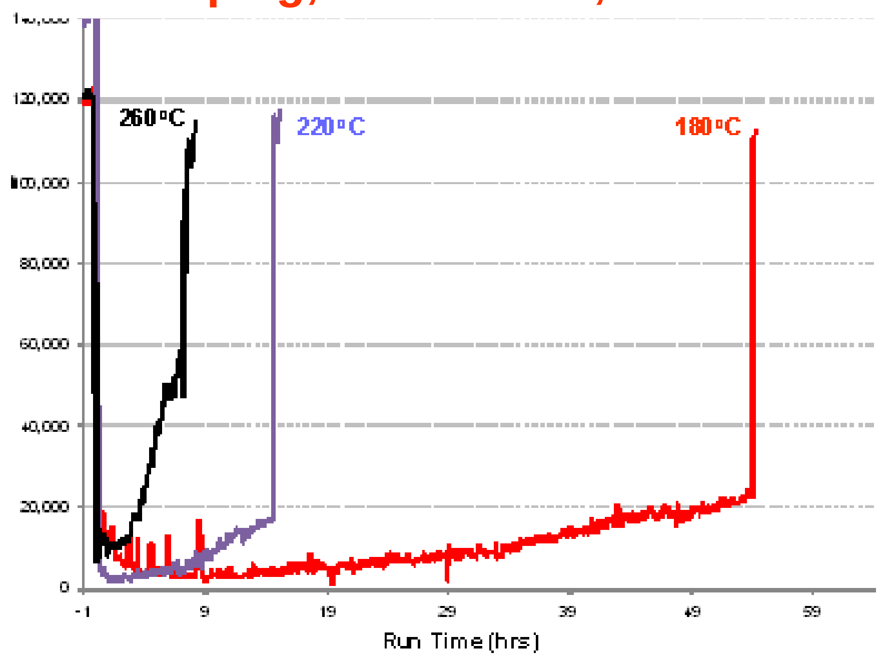
4.6 ppmv AsH_3, 50 ppmv H_2S, 41% CO, 10% CO_2, 29% H_2, 18% H_2O bal. N_2. T= 220ºC, P= 500 psig, GHSV=60,000 h^{-1}



- **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= 180-260ºC, P= 500 psig, GHSV of 75,000 h^{-1}



- **Baseline sorbent shows promising Hg capacity**

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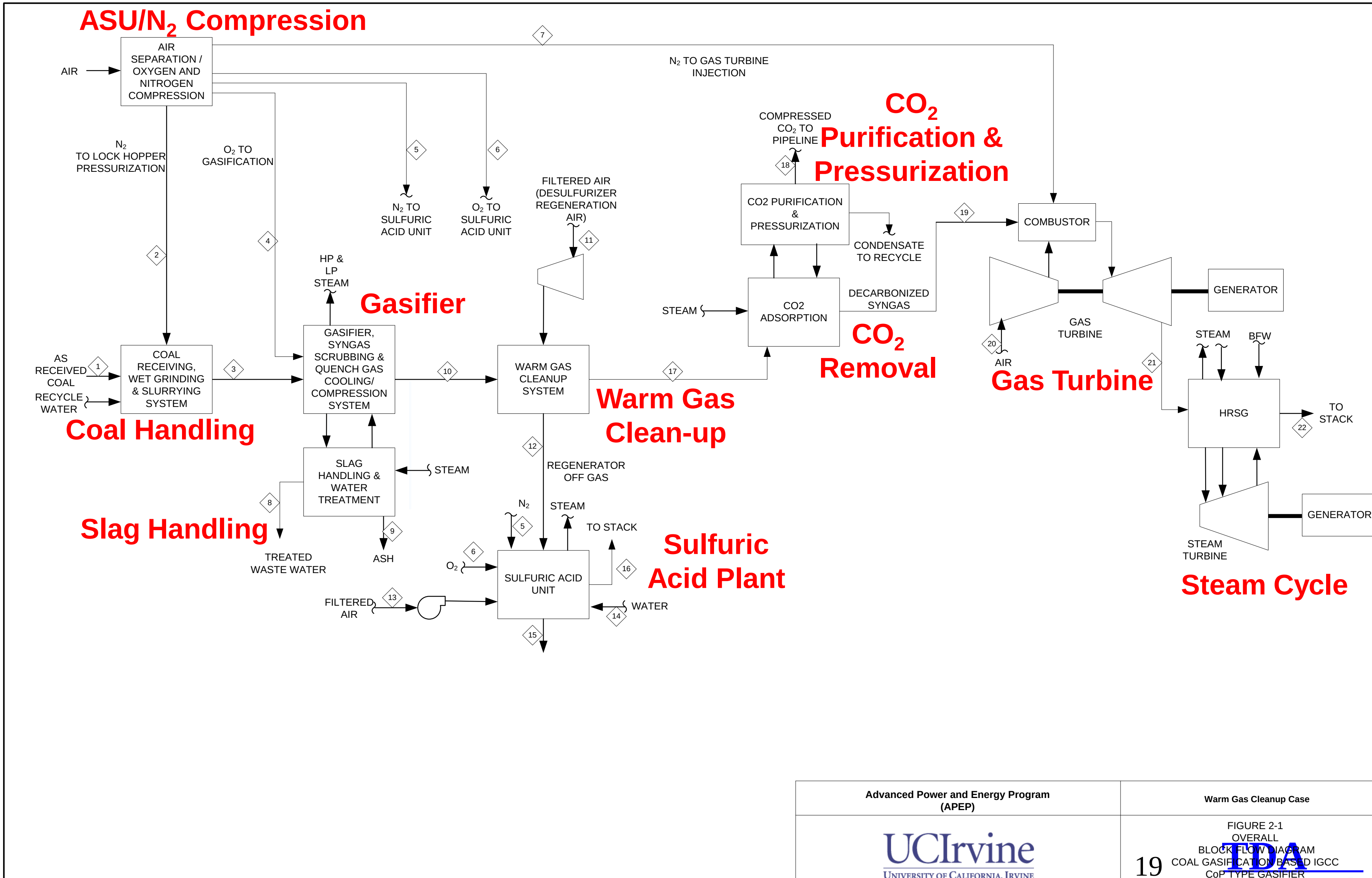
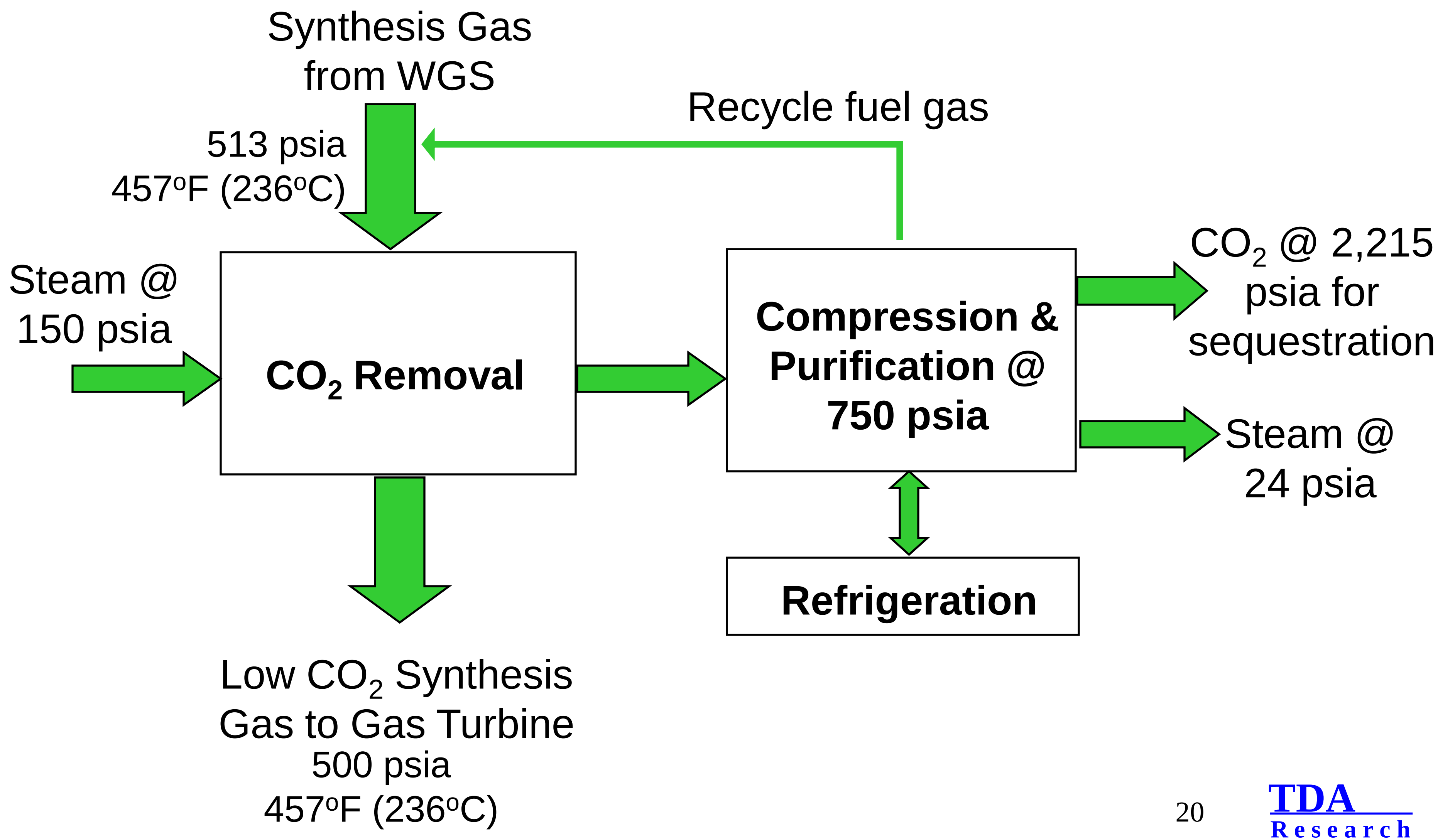
System Analysis

- **UCI carries out a process simulation using AspenPlus™ and evaluate the cost CO_2 capture**
- **The analysis includes three simulations:**
  - **E-Gas™ based IGCC plant with Selexol-based CO_2 capture**
    - Calibration Case
    - Compare/validate model results with prior DOE/NETL analysis
  - **E-Gas™ based IGCC plant with Selexol - 90% CO_2 capture**
  - **E-Gas™ based IGCC plant with TDA's CO_2 capture system**
- **Same assumptions and cost guidelines will be adopted**
  - **Consistent design requirements**
  - **Up-to-date performance and capital cost estimates**

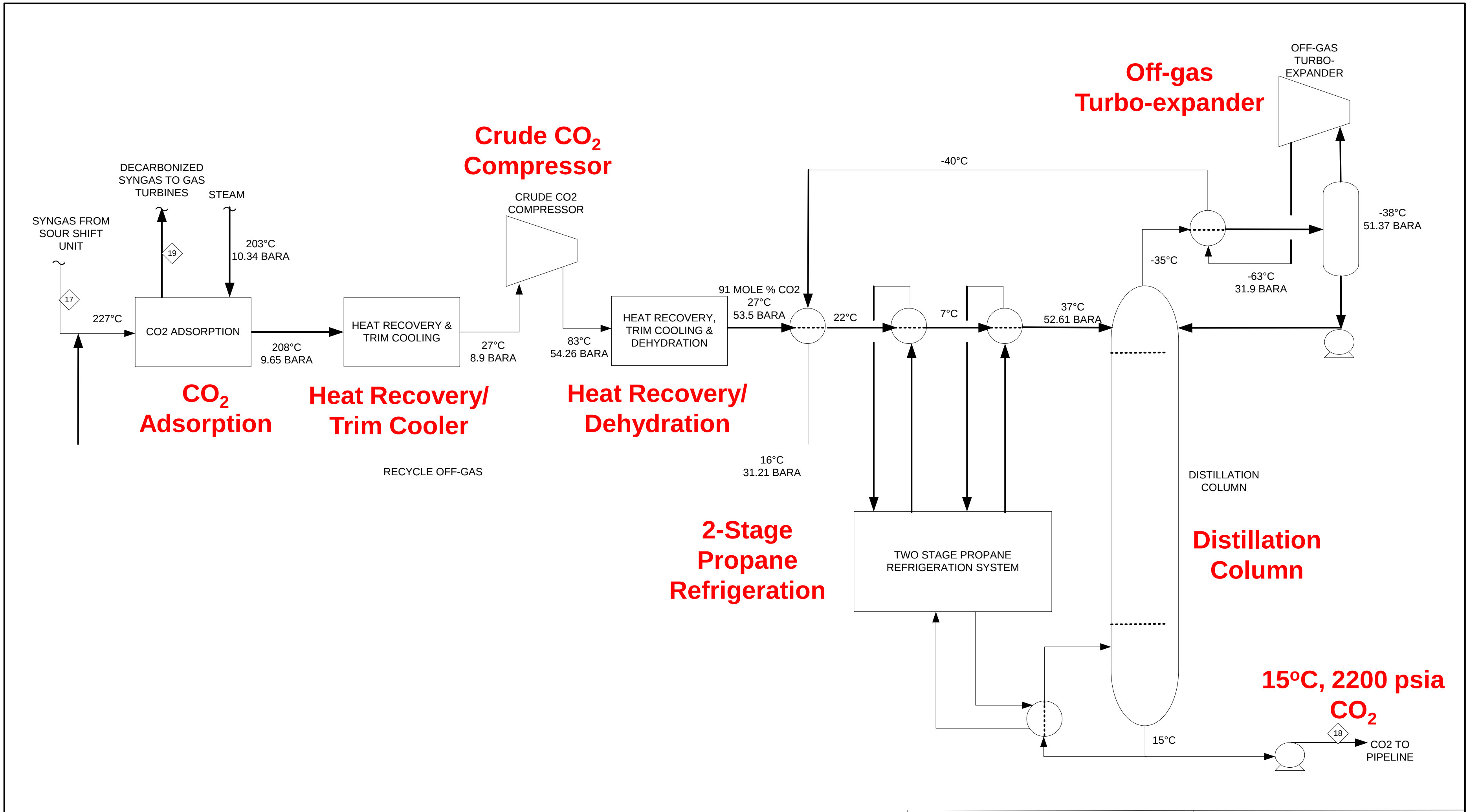
System Modeling



CO_2 Capture System Integrated with CO_2 Liquefaction



CO_2 Purification & Compression



Advanced Power and Energy Program (APEP)	Warm Gas Cleanup Case
UCIrvine University of California, Irvine	FIGURE 1-2 CO2 PURIFICATION SYSTEM COAL GASIFICATION BASED IGCC CoP TYPE GASIFIER

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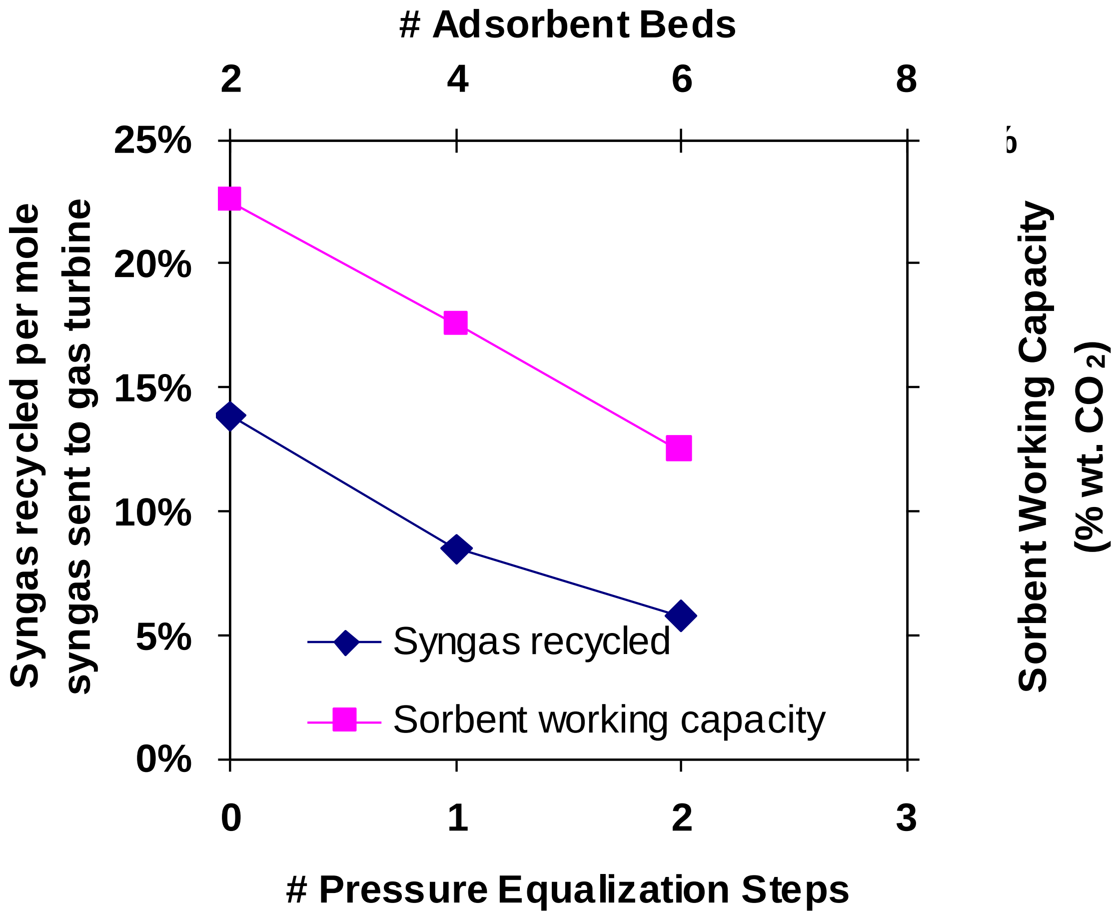
Trade-off Analysis

- **Synthesis gas recycle versus # of beds**
- **Contamination of CO_2 by the process gas left in the reactor ullage can be minimized by increasing # of pressure equalization steps**



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UCI System Analysis Results

	Calibration Case	IGCC-Selexol 90% Capture	IGCC - TDA WGC 90% Capture
CO2 Capture, %	88.2	90	90
Gross Power Generated, kWe	696,770	691,624	691,460
Gas Turbine Power	464,336	461,986	459,990
Steam Turbine Power	232,434	229,638	231,470
Auxiliary Load Summary	171,998	175,498	151,082
Coal Handling	3,252	3,252	3,252
Slag Handling	1,107	1,107	1,107
Air Separation	108,714	111,464	86,584
Selexol Unit	14,827	15,153	-
CO2 Compressor	19,464	19,888	35,003
Sulfur Removal	199	199	4,889
Other Losses	24,435	24,435	20,245
Net Power, kWe	524,772	516,126	540,378
Net Plant Efficiency, % HHV	**32.1**	**31.6**	**33.1**

- **The IGCC plant with TDA's CO_2 capture technology system achieves higher efficiency (33.1%) than IGCC with Selexol (31.6%)**
  - **At 90% CO_2 capture**

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Summary of Results (Year 1)

- **Completed sorbent optimization**
  - Identified an optimum chemical composition
  - Production scale-up
- **Demonstrated high CO_2 capacity in bench-scale experiments**
  - Saturation capacity approaching 20% wt. CO_2
  - 6 to 8% wt.working capacity
- **Long-term durability was demonstrated through 2,400 cycles**
- **System simulation indicates that TDA's CO_2 technology will provide higher net plant efficiency than that of IGCC-Selexol**

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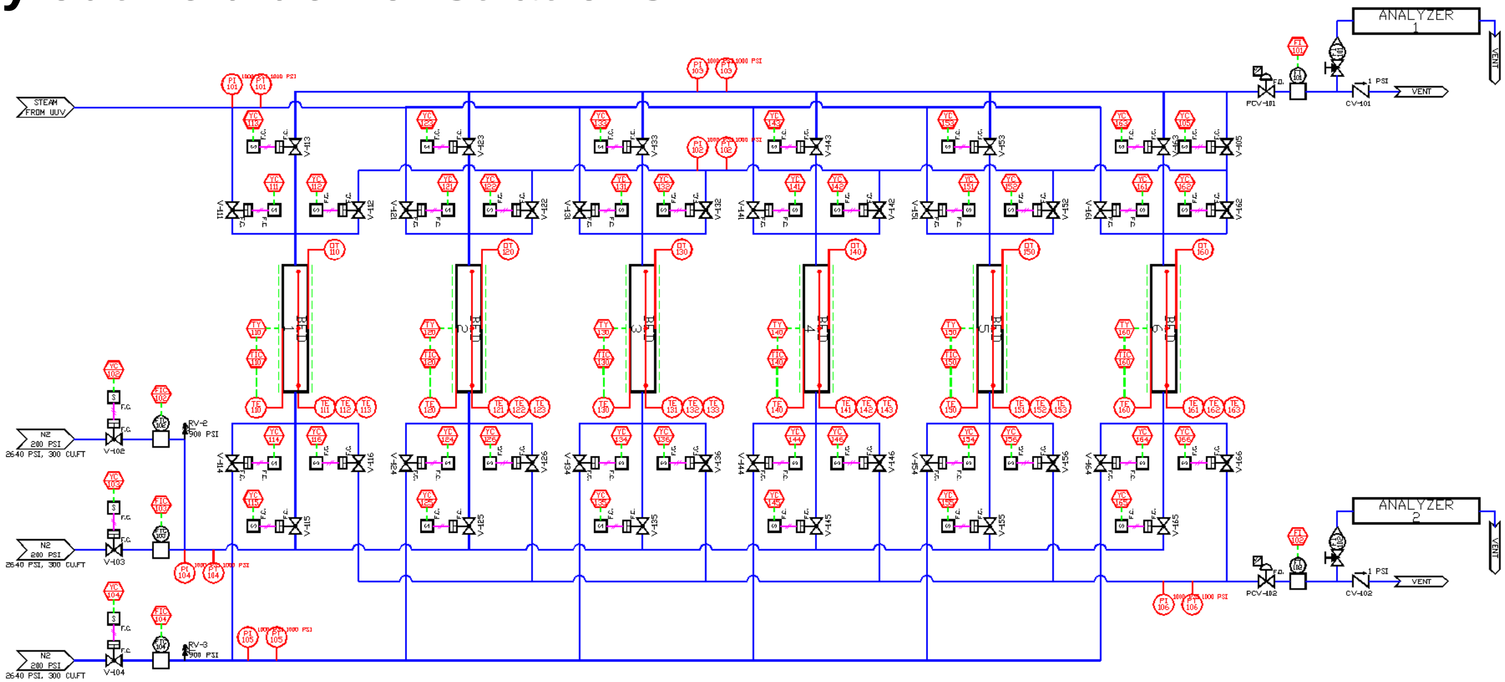
Year 2 Tasks

- **Complete 10,000 cycles to demonstrate sorbent life**
- **Complete the process design and optimization**
  - **Estimate the cost of capital equipment**
  - **Economic analysis**
- **Complete the fabrication of a skid-mounted unit for field evaluations**
- **Carry out field demonstrations**

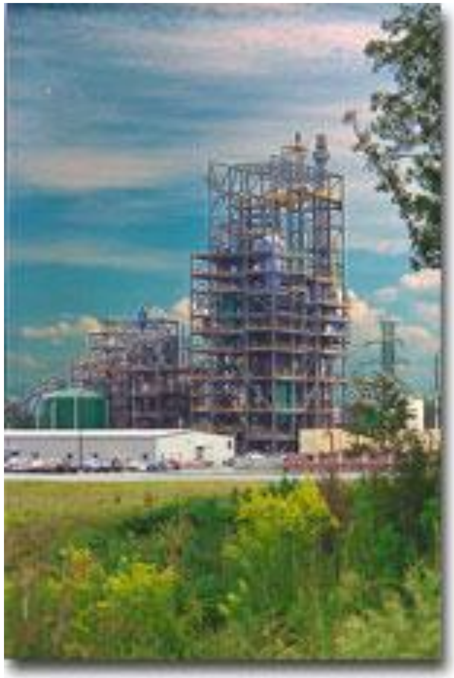


Demonstration Sites

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

<u>Wabash River IGCC Plant, Terre Haute, IN</u>

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



<u>National Carbon Capture Center, Wilsonville, AL</u>

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

Acknowledgments

- **DOE Monitor**
  - Dr. Arun Bose
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  - Dr. Ashok Rao
- **CoP**
  - Dr. Albert Tsang
- **MWV**
  - Paula Walmett