Oxy-Combustion System Process Optimization
(Contract No. DE-FE-0029090)

Gökhan Alptekin, PhD
Ambal Jayaraman, PhD
Jerrod Hohman
TDA Research, Inc.

Dr. Ashok Rao
University of California Irvine

DOE-NETL's 2020 FE R&D Virtual Project Review Meeting – Transformative Power Generation

September 28, 2020

Project Summary

- **The objective is to optimize the Pressurized Oxy-Combustion (POxC) process to minimize the Cost of Electricity (COE)**
  - System analysis and design work to optimize POxC process, including thermal management, heat integration, power cycle optimization using process design and modeling supported with Aspen Plus® process simulations
  - Develop a new chemical absorbent-based CO_2 purification system to remove the residual oxygen that contaminates the recovered CO_2
- **Major Project Tasks**
  - Sorbent Optimization and Evaluation
    - Performance validation via long-term cycling tests
  - Process, System Design and Modeling
  - Techno-economic analysis
    - Various configurations with different ASU and O_2 removal options
    - High fidelity engineering analysis and process simulation

Project Partners

Project Duration

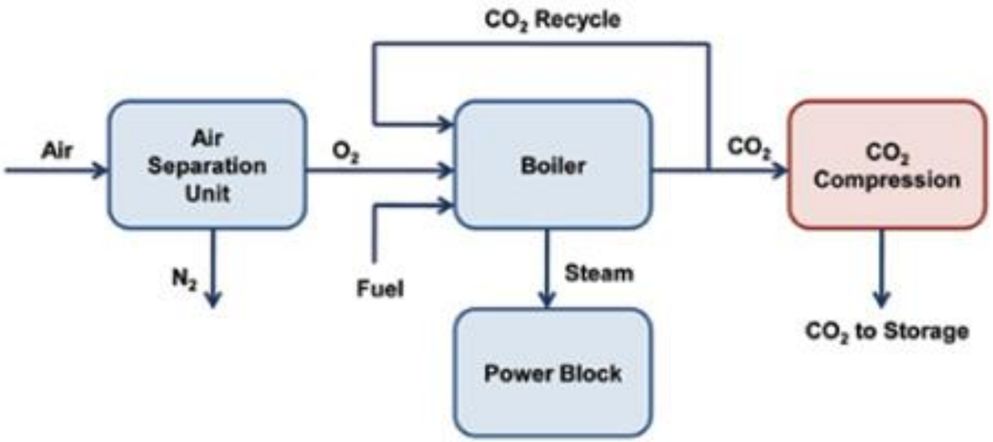
- **Start Date = October 1, 2016**
- **End Date = September 30, 2020**

Budget

- **Project Cost = $1,375,042**
- **DOE Share = $1,099,998**
- **TDA and UCI = $275,044**

Oxy-Combustion & Carbon Capture

- In oxy-combustion fuels is burned in O_2 instead of air, which results in a flue gas of primarily CO_2 with trace levels of impurities
- POxC reduces energy and capital costs of the equipment used to purify and compress the CO_2
- DOE/NETL objective is to optimize the POxC process to limit the COE increase to less than 20% over the no-capture case
- The main cost contributors to POxC process includes:
  - Air Separation Unit
  - CO_2 Purification system



	COE ($/MWh)	Increase in COE(%)*
NETL Non-Capture Ref., Air-fired SC w/o CCS	58.90	--
NETL Base Case Current Technology	91.07	54.6
NETL Cumulative Technology Case	78.15	32.7
Proposed Goal	70.68	20.0

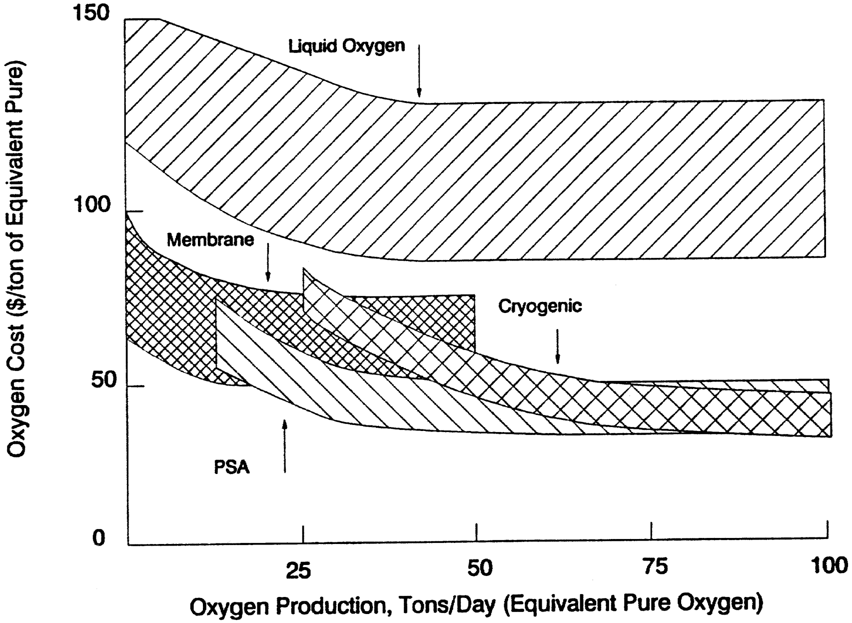
**Relative to the non-capture case*

Source: Cost of Electricity for Low Pressure Oxy-Combustion Technologies (NETL 2012)

Air Separation Options

- **ASU is one of the largest cost contributors to oxy-combustion (consumes over 5% of plant power and constitutes ~20% of plant cost)**
- **Cryogenic air separation is the choice of technology at large-scale**
  - 600 MW plant requires ~170 ton O_2/day
- **Cryo-separation is highly energy intensive due to the thermal inefficiencies inherent in the low operating temperatures**
- **Alternatives**
  - Ion Transport Membranes
    - High TRL
  - Sorbent-Based Air Separation System (TDA Technology developed under DE-FE0026142)
    - Low TRL

Source: Air Products and Chemicals, Inc.



Source: Kobayashi, 2002

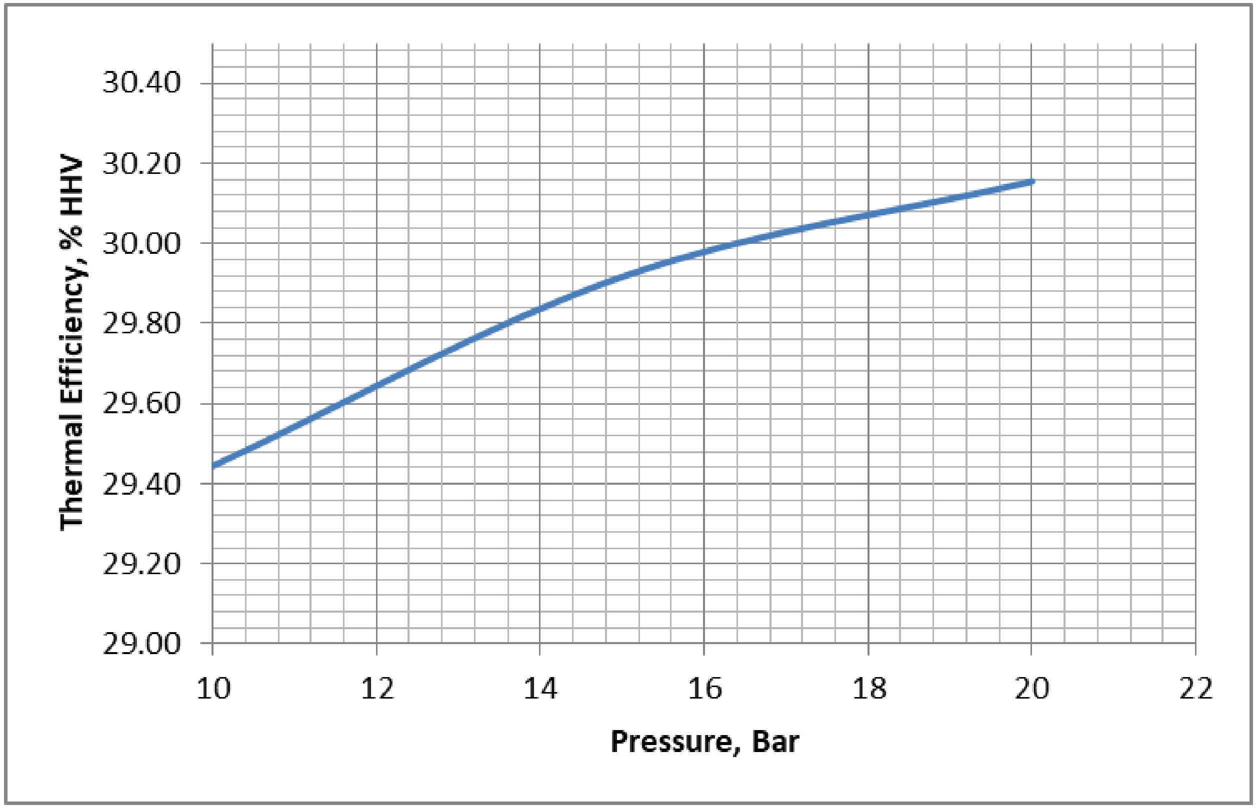
Process Optimization Case Matrix

Case	Power Cycle psig/°F/°F	Subsystem Concept Evaluated	Oxidant
1 (Base)	Supercritical Steam 3500/1100/1100	**Current ASU – Cryogenic ASU**	95% O_2, Cryogenic ASU
2	Supercritical Steam 3500/1100/1100	**Advanced O_2 Membrane with Preheat in Boiler**	~100% O_2, Advanced O_2 Membrane (Ion Transport)
3	Supercritical Steam 3500/1100/1100	**Advanced O_2 Membrane with Preheat by Natural Gas Combustion**	~100% O_2, Advanced O_2 Membrane (Ion Transport)
4	Supercritical Steam 3500/1100/1100	**Advanced O_2 Sorbent (TDA) with Boiler Heat**	95%+ O_2, Advanced O_2 Sorbent (TDA)
5	Supercritical Steam 3500/1100/1100	**Advanced O_2 Sorbent (TDA) with Natural Gas Combustion Heat**	95%+ O_2, Advanced O_2 Sorbent (TDA)
6A, 6B & 6C	Supercritical Steam 3500/1100/1100	**CO_2 Purification by Catalytic De-oxidation with Natural Gas**	Three cases chosen from Case 1 through Case 5 (Cryo, TDA & Ion Transport ASU)
7A, 7B & 7C	Supercritical Steam 3500/1100/1100	**CO_2 Purification by Chemical Looping Combustion or CLC (TDA) with Natural Gas**	Three cases chosen from Case 1 through Case 5 (Cryo, TDA & Ion Transport ASU)
8A, 8B & 8C	Supercritical Steam 3500/1100/1100	**Advanced CO_2 &/or ASU Compression**	Three cases chosen from above (cryo, TDA & Ion Transport ASU)
9A, 9B & 9C	Advanced-supercritical Steam 3500/1110/1150	**Advanced-supercritical Steam Cycle with Advanced Materials**	Same as Case 8 except steam cycle (Cryo, TDA & Ion Transport ASU)
10A, 10B & 10C	Ultra-supercritical Steam 4000/1350/1400	**Ultra-supercritical Steam Cycle with Advanced Materials**	Same as Case 8 except steam cycle (Cryo, TDA & Ion Transport ASU)
11A, 11B & 11C	Ultra-supercritical Steam 4000/1350/1400	**Ultra-supercritical Steam Cycle with Co-sequestration**	Same as Case 10 without CO_2 treating to remove SOx & NOx (Cryo, TDA & Ion Transport ASU)
12A, 12B & 12C	Supercritical CO_2 Conditions: 5030/1400	**Supercritical CO_2 Cycle with Advanced Materials**	Similar to Case 8 except working fluid (Cryo, TDA & Ion Transport ASU)

TDA RESEARCH

Pressurized Oxy-combustion

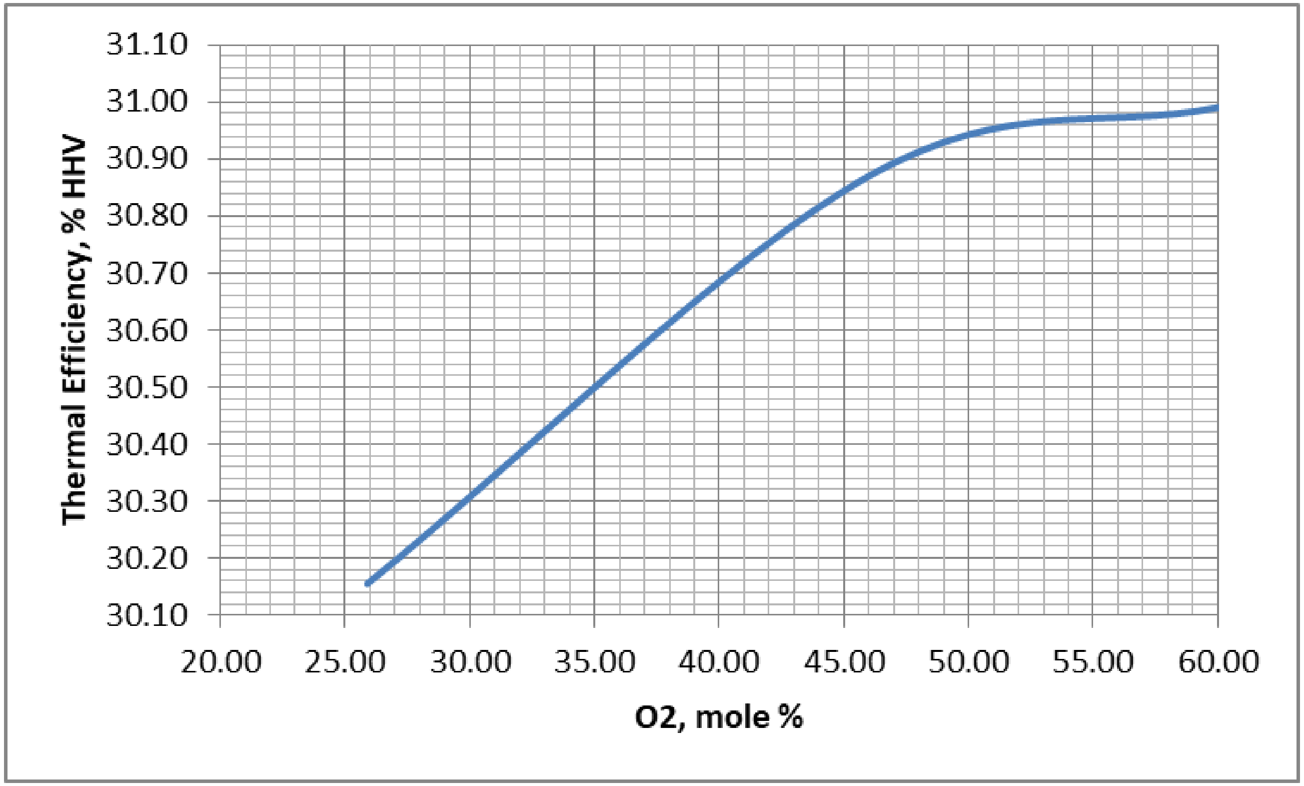
Operating Pressure of Circulating Fluidized Bed Combustion (CFBC) Boiler



- Higher operating pressures provided higher net thermal plant efficiency
  - Improving from 29.44% for 10 bar to 30.16% to 20 bar
  - We fixed our operating pressure at 20 bar in our Techno-economic Analysis

Flue Gas Recycle Ratio

Optimized O_2 Concentration in the Boiler Feed with Flue Gas Recycle



- Net thermal plant efficiency increases with increase in O_2 concentration and reaches a maximum around 60% O_2
- We fixed our flue gas recycle ratio such that O_2 concentration in the boiler is 60% for our Techno-economic Analysis

TDA RESEARCH

Plant Performance Summary: Cases 1-5

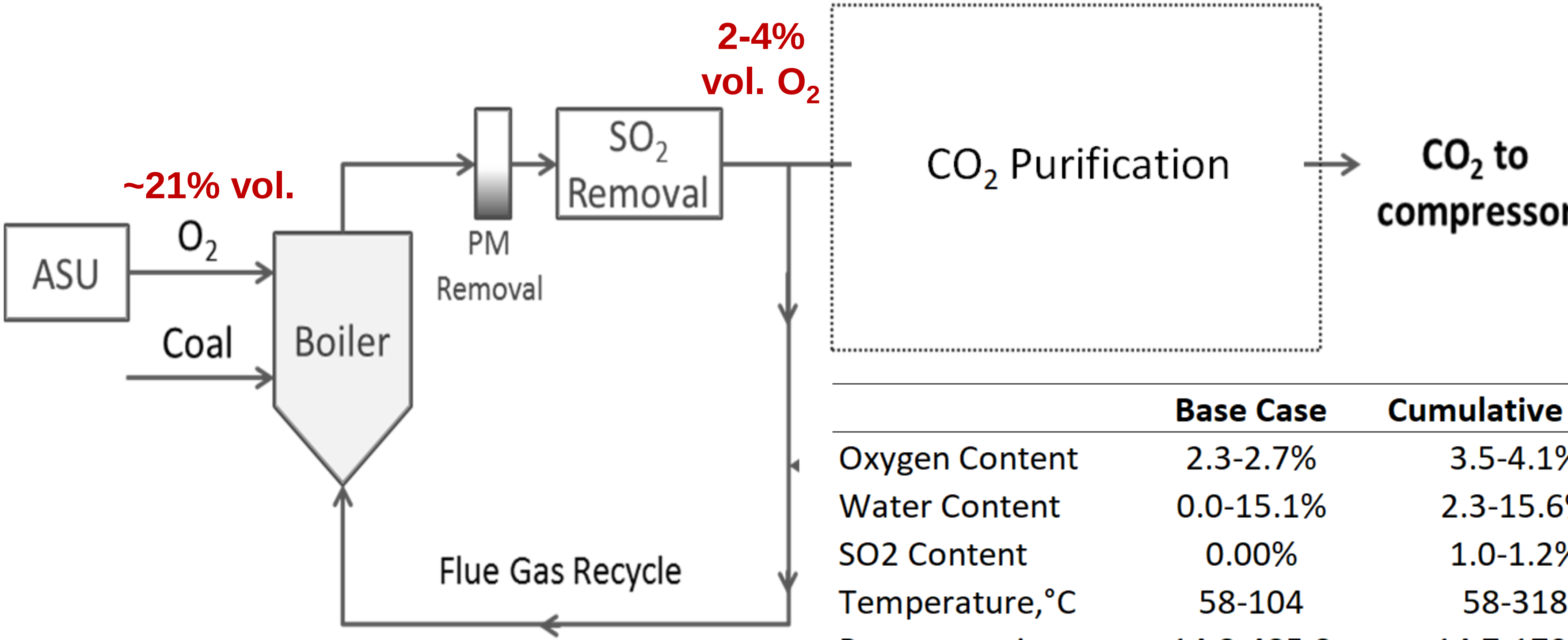
Case #	1	2	3	4	5
ASU Type	Cryo	ITM	ITM	TDA	TDA
CO_2 Purification	-	-	-	-	-
GROSS POWER GENERATED (AT GENERATOR TERMINALS) (KWE)					
STEAM TURBINE	785,587	794,691	785,071	723,700	715,557
DEPLETED AIR EXPANDER	-	217,964	215,454	80,118	80,714
TOTAL GENERATED (KWE)	785,587	1,012,655	1,000,524	803,818	796,271
TOTAL AUXILIARIES (KWE)	235,587	462,655	450,524	253,818	246,271
NET POWER (KWE)	550,000	550,000	550,000	550,000	550,000
NET PLANT EFFICIENCY (% HHV)	31.24	30.55	30.76	32.61	33.00
THERMAL INPUT					
COAL (KWT HHV)	1,760,447	1,800,104	1,705,240	1,686,511	1,569,989
NATURAL GAS (KWT HHV)	-	-	82,751	-	96,584
TOTAL (KWT HHV)	1,760,447	1,800,104	1,787,991	1,686,511	1,666,573
CARBON CAPTURED (%)	99.5	99.5	96.8	99.5	99.5

ASU Type

- TDA high temperature ASU provides highest net thermal plant efficiency
- ITM based ASU provides the lowest net thermal plant efficiency
- Using natural gas instead of boiler to preheat the air provides better net thermal plant efficiency for high temperature ASUs

Case	Power Cycle psig/°F/°F	Subsystem Concept Evaluated	Oxidant
1 (Base)	Supercritical Steam 3500/1100/1100	Current ASU	95% O_2, Cryogenic ASU
2	Supercritical Steam 3500/1100/1100	Advanced O_2 Membrane with Preheat in Boiler	~100% O_2, Advanced O_2 Membrane (Ion Transport)
3	Supercritical Steam 3500/1100/1100	Advanced O_2 Membrane with Preheat by Natural Gas Combustion	~100% O_2, Advanced O_2 Membrane (Ion Transport)
4	Supercritical Steam 3500/1100/1100	Advanced O_2 Sorbent (TDA) with Boiler Heat	95%+ O_2, Advanced O_2 Sorbent (TDA)
5	Supercritical Steam 3500/1100/1100	Advanced O_2 Sorbent (TDA) with Natural Gas Combustion Heat	95%+ O_2, Advanced O_2 Sorbent (TDA)

CO_2 Purification Need in POxC



	Base Case	Cumulative Case
Oxygen Content	2.3-2.7%	3.5-4.1%
Water Content	0.0-15.1%	2.3-15.6%
SO2 Content	0.00%	1.0-1.2%
Temperature,°C	58-104	58-318
Pressure, psia	14.8-485.8	14.7-179.9

Source: Cost of Electricity for Low Pressure Oxy-Combustion Technologies (NETL 2012)

- **The oxygen content in the CO_2 product has to be reduced to less than 1,000 ppmv prior to CO_2 compression**
- **Heat integration/optimization is critical**
    - **10-15% of plant's energy output**

CO_2 Purity Specifications

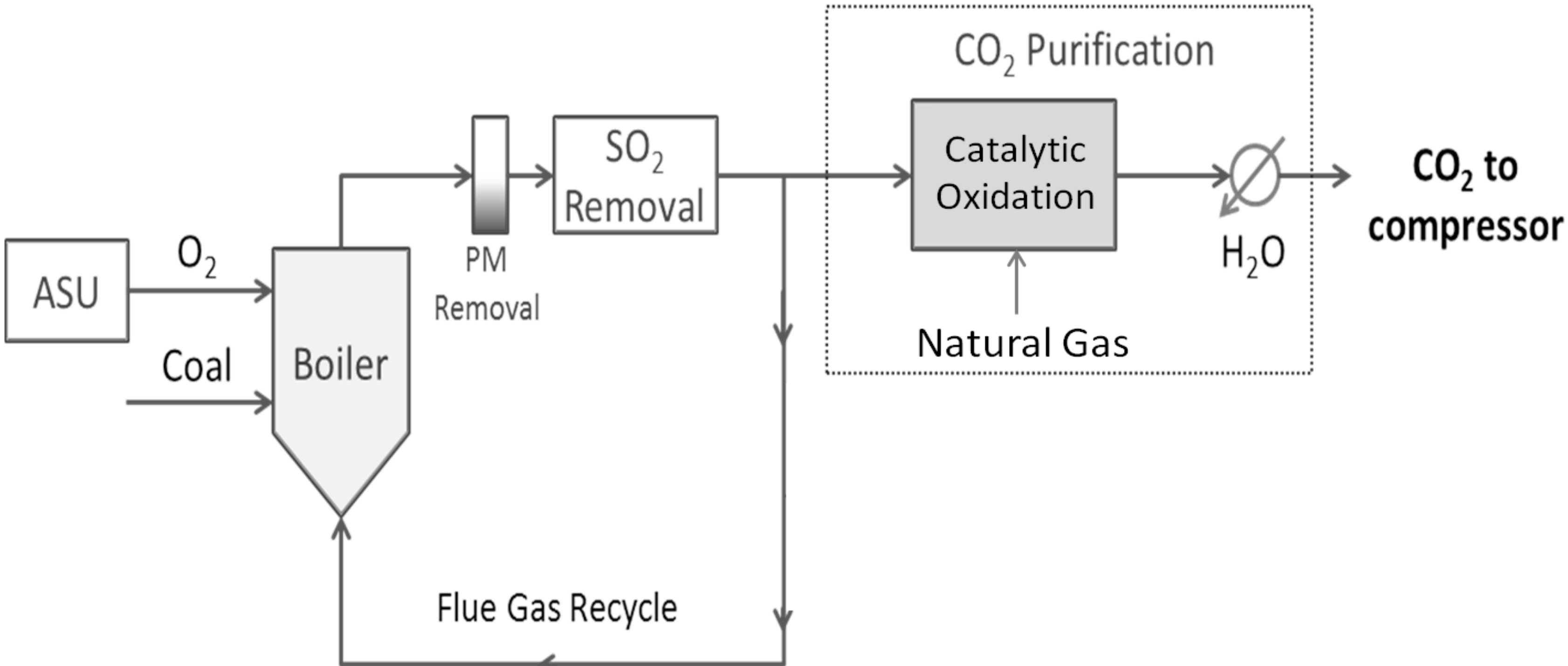
Component	Unit	Carbon Steel Pipeline		Enhanced Oil Recovery		Saline Reservoir Sequestration		Saline Reservoir CO_2 & H_2S Co-sequestration	
	(Max unless Otherwise noted)	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature
CO_2	vol% (Min)	95	90-99.8	95	90-99.8	95	90-99.8	95	20 – 99.8
H_2O	ppmv	500	20 - 650	500	20 - 650	500	20 - 650	500	20 - 650
N_2	vol%	4	0.01 - 7	1	0.01 - 2	4	0.01 - 7	4	0.01 – 7
O_2	vol%	0.001	0.001 – 4	0.001	0.001– 1.3	0.001	0.001– 4	0.001	0.001 – 4
Ar	vol%	4	0.01 – 4	1	0.01 – 1	4	0.01 – 4	4	0.01 – 4
CH_4	vol%	4	0.01 – 4	1	0.01 – 2	4	0.01 – 4	4	0.01 – 4
H_2	vol%	4	0.01 - 4	1	0.01 – 1	4	0.01 – 4	4	0.02 – 4
CO	ppmv	35	10 - 5000	35	10 - 5000	35	10 - 5000	35	10 - 5000
H_2S	vol%	0.01	0.002 – 1.3	0.01	0.002 – 1.3	0.01	0.002 – 1.3	75	10 - 77
SO_2	ppmv	100	10 - 50000	100	10 - 50000	100	10 - 50000	50	10 - 100
NO_x	ppmv	100	20 - 2500	100	20 - 2500	100	20 - 2500	100	20 - 2500
NH_3	ppmv	50	0 - 50	50	0 - 50	50	0 - 50	50	0 - 50
COS	ppmv	trace	trace	5	0 - 5	trace	trace	trace	trace
C_2H_6	vol%	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
C_3+	vol%	<1	0 - 1	<1	0 - 1	<1	0 - 1	<1	0 - 1
Particulates	ppmv	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
HCN	ppmv	trace	trace	trace	trace	trace	trace	trace	trace
Glycol	ppbv	46	0 - 174	46	0 - 174	46	0 - 174	46	0 - 174

* Not enough information is available to determine the maximum allowable amount for HCl, HF, Hg, MEA and Selexol solvent.

- **Stringent requirements for O_2 (and other contaminants) in compressed CO_2**
  - **<0.001% vol. O_2**

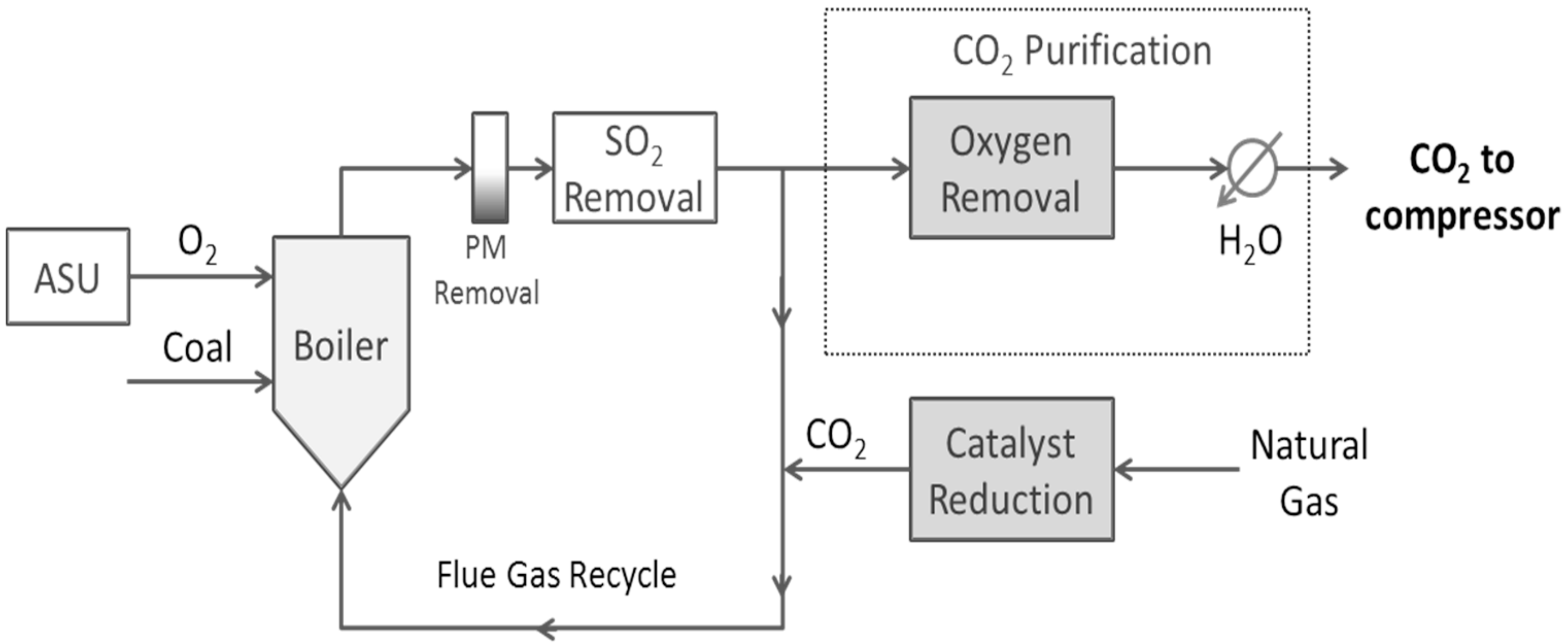
TDA RESEARCH

CO_2 Purification via Catalytic Oxidation



- **Catalytic oxidation is mature technology**
- **Challenges with catalytic oxidation**
  - **To meet the O_2 concentration requirements, natural gas has to be used in greater quantities than required by the reaction stoichiometry**
  - **Excess natural gas ending in the CO_2 will reduce system efficiency**
  - **Limit on CH_4 is high (1% vol.) but tighter on heavier HCs**

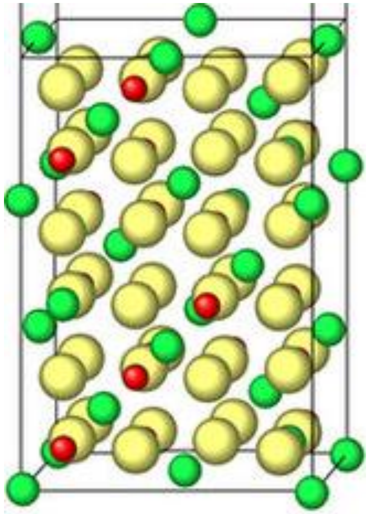
TDA's CO_2 Purification System



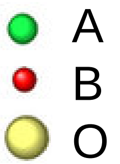
- **TDA proposes a chemical absorbent-based oxygen removal system**
  - **Low O_2 concentration in the treated CO_2 can be readily achieved**
  - **Excess natural gas can be recycled back to the boiler**
- **Does not use precious metal catalysts; low cost metal oxide catalyst could polish off impurities**

TDA’s Sorbent

- **TDA sorbent consists of a high surface area (>100 m²/g) mixed metal oxide $A_xB_yO_z$ phase that selectively reacts with the oxygen in the compressed CO_2 at moderate temperatures (<200 to 500°C)**



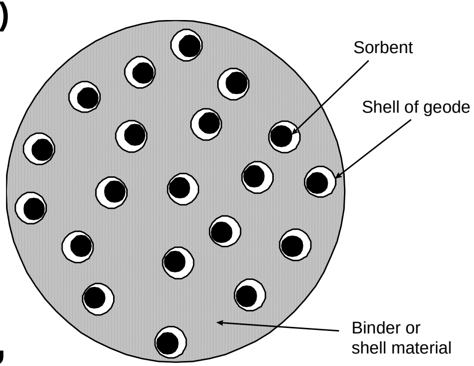
Crystal model for $A_xB_yO_z$

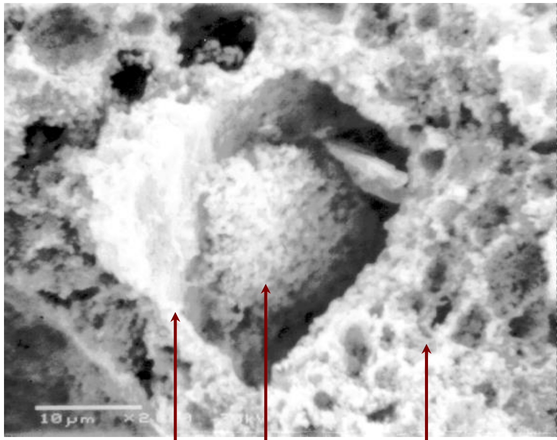


$$2M + O_{2(g)} = 2MO$$

$$4MO + CH_{4(g)} = 4M + CO_{2(g)} + 2H_2O_{(g)}$$

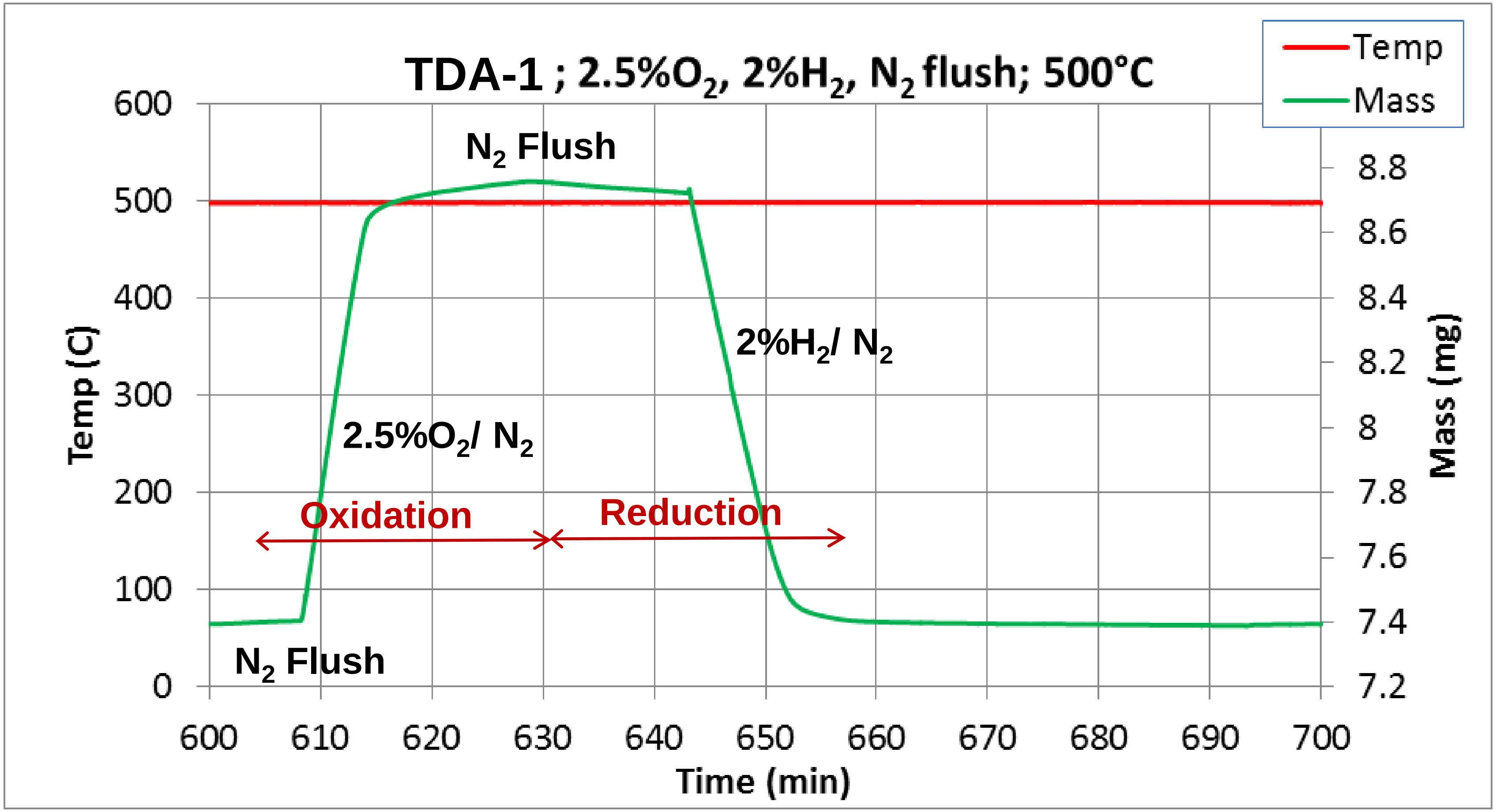
- **Sorbent can effectively reduce O_2 content to less than 100 ppmv**
  - **No equilibrium limitations**
- **TDA’s sorbent uses a unique structure referred to as a “geode”**
  - **High mechanical integrity**
  - **High chemical stability**
  - **High surface area**





TDA’s geode sorbent structure as seen in SEM

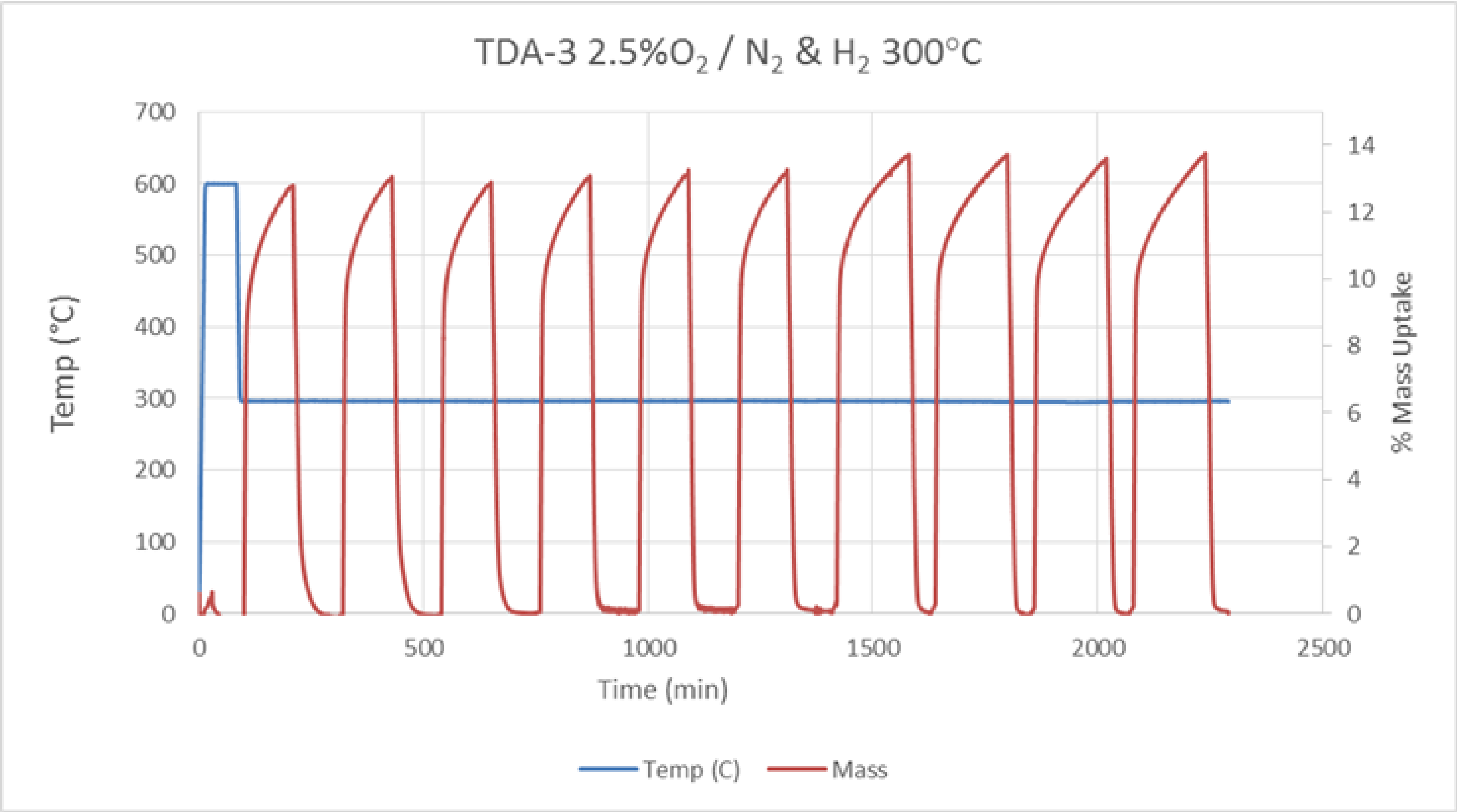
Typical RedOx Cycle - TGA Tests



- Fast oxidation/reduction kinetics at 500ºC
- 18-20% O_2 uptake capacity (kg O_2 removed per kg sorbent)

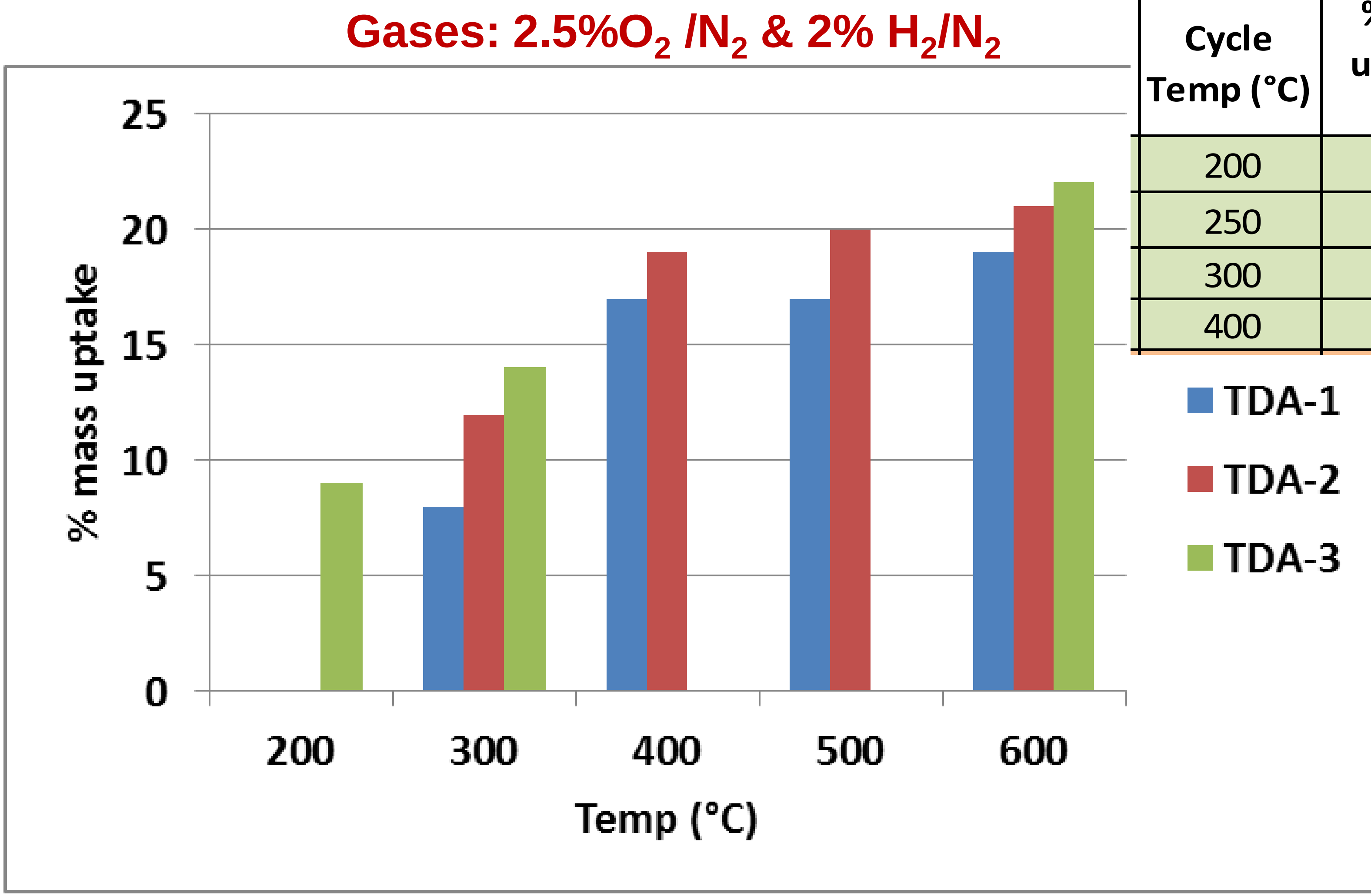
TDA RESEARCH

TGA Cycles at 300ºC



- **Formulations were modified using promoters to improve kinetics and oxygen uptake at lower temperatures**
- **Modified samples showed high capacity (12+% wt. O_2) at 300ºC**

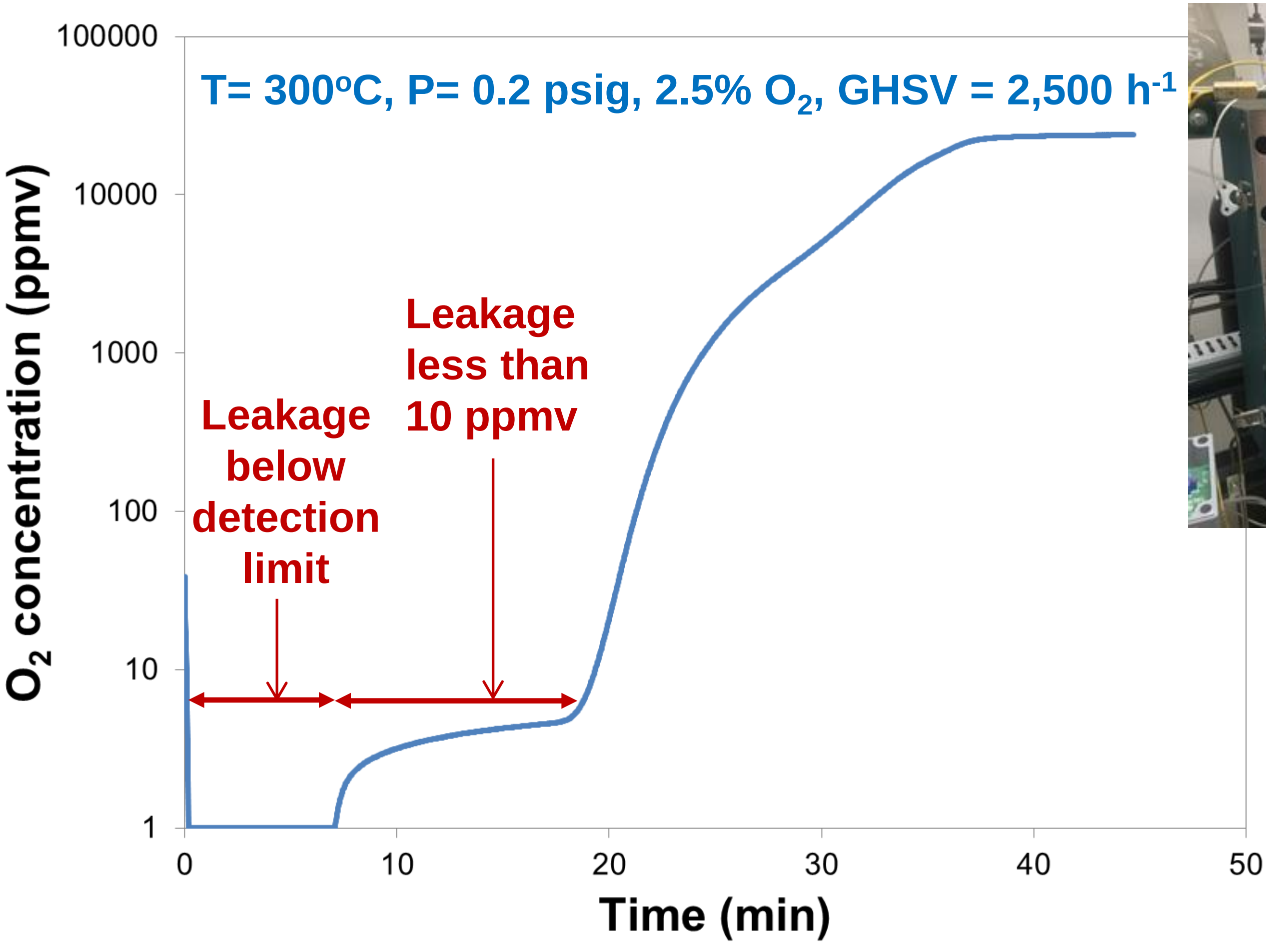
Impact of Temperature



Cycle Temp (°C)	% oxygen uptake (by mass)
200	6.0
250	12.5
300	17.3
400	20.5

- TDA-3 showed better oxygen uptakes at all temperatures

Breakthrough Tests

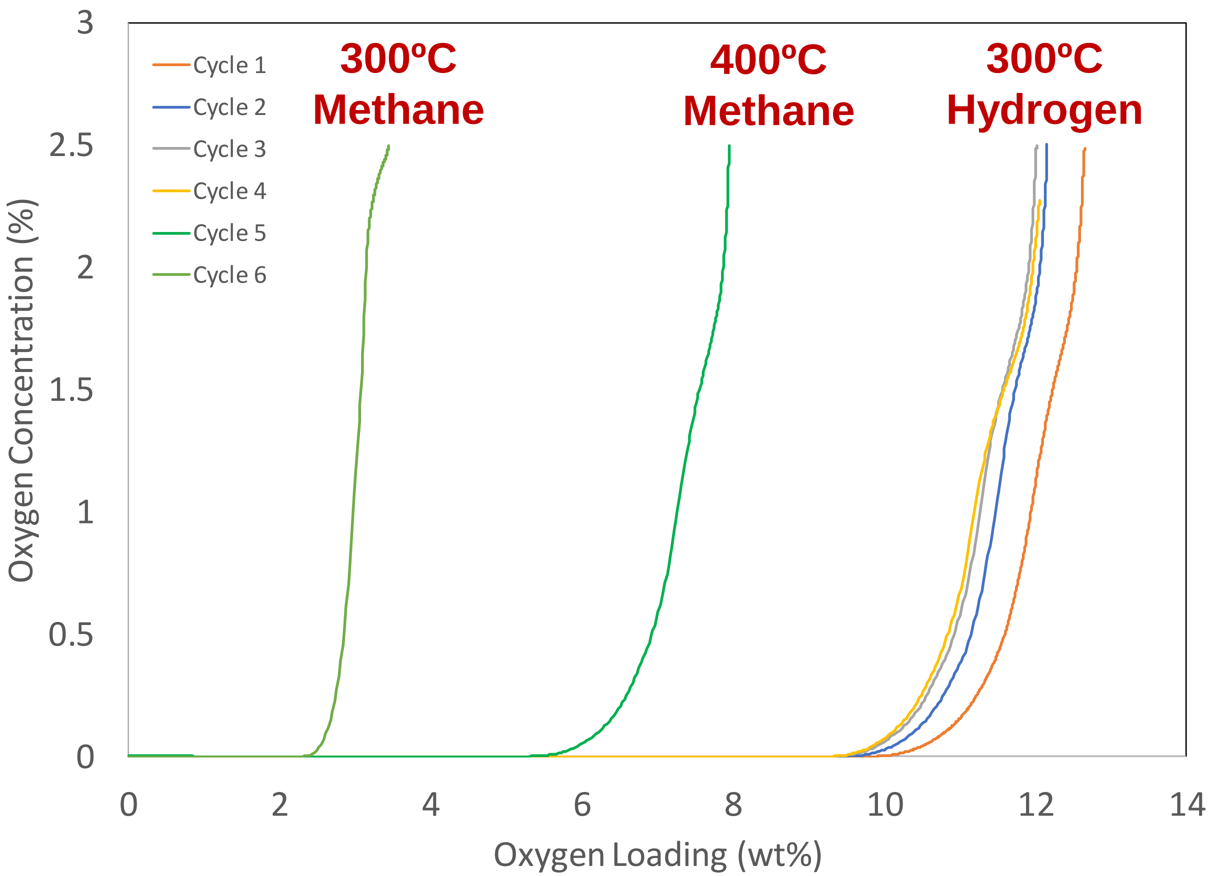


Bench-scale tests in a fixed bed reactor (25 cc sorbent)

An electro-chemical O_2 analyzer (ZR800 Zirconia Analyzer) with 1 ppmv O_2 detection capability

- **Breakthrough tests confirmed very high oxygen removal efficiency**
- **O_2 concentration in treated gas can be lowered to <10 ppmv**

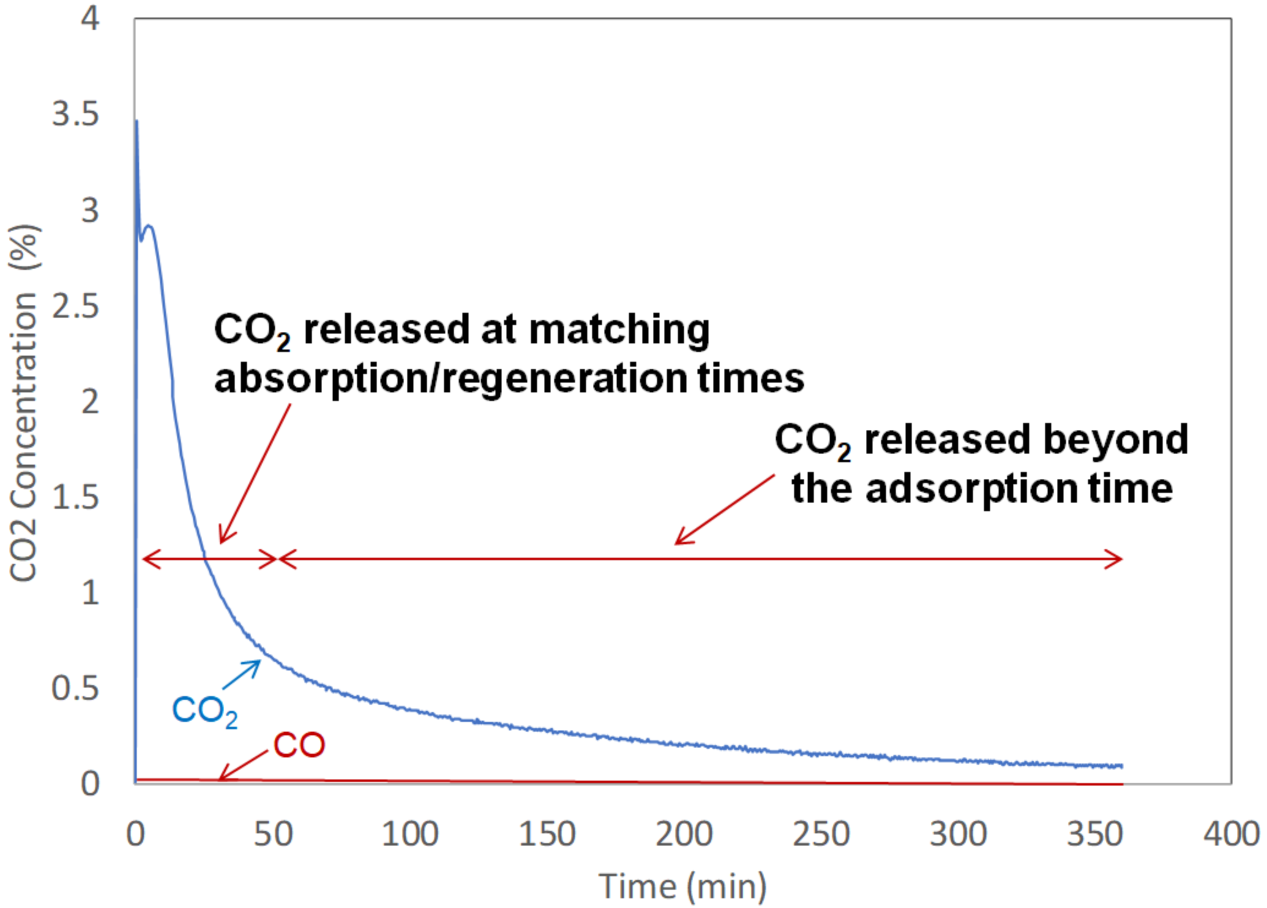
Using Methane as Reduction Gas



- When CH_4 is used instead of hydrogen the oxygen uptake decreased due to incomplete regenerations (lower reduction rates with CH_4)
- However, still had a good oxygen working capacity in excess of 5% wt.

Reaction Products - 400ºC CH_4 Reduction

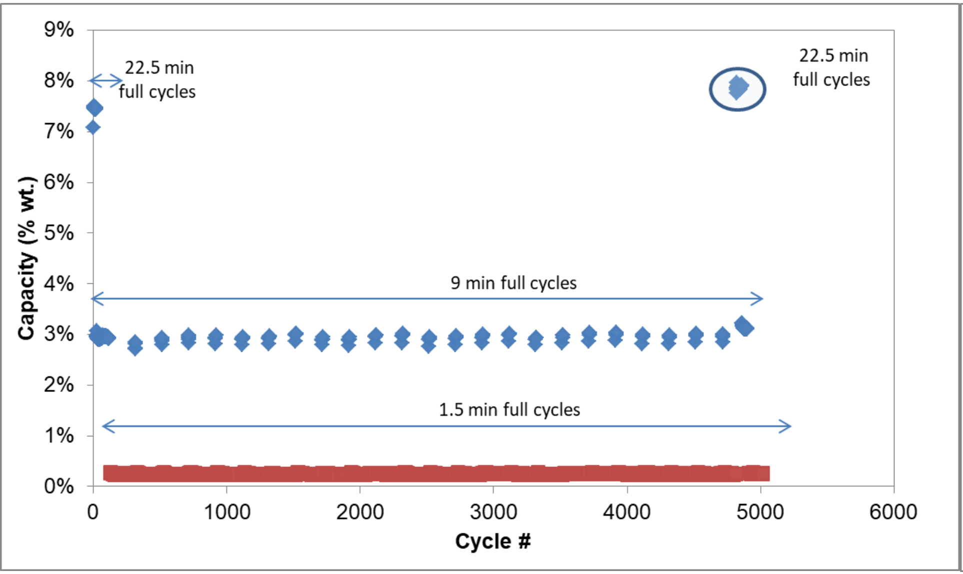
Absorption = 2.5% vol. O_2, GHSV= 2,500 h^{-1}

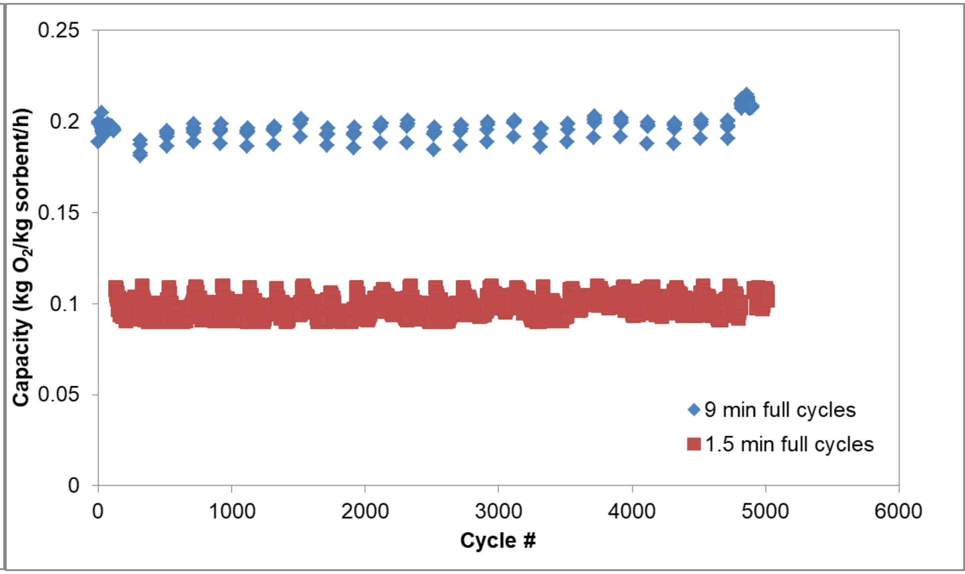


- **CH_4 reduction primarily generated CO_2 (<50 ppm CO observed)**
- **Longer regenerations are needed for full reduction, short regeneration still had working capacity**

Long-Term Stability Tests

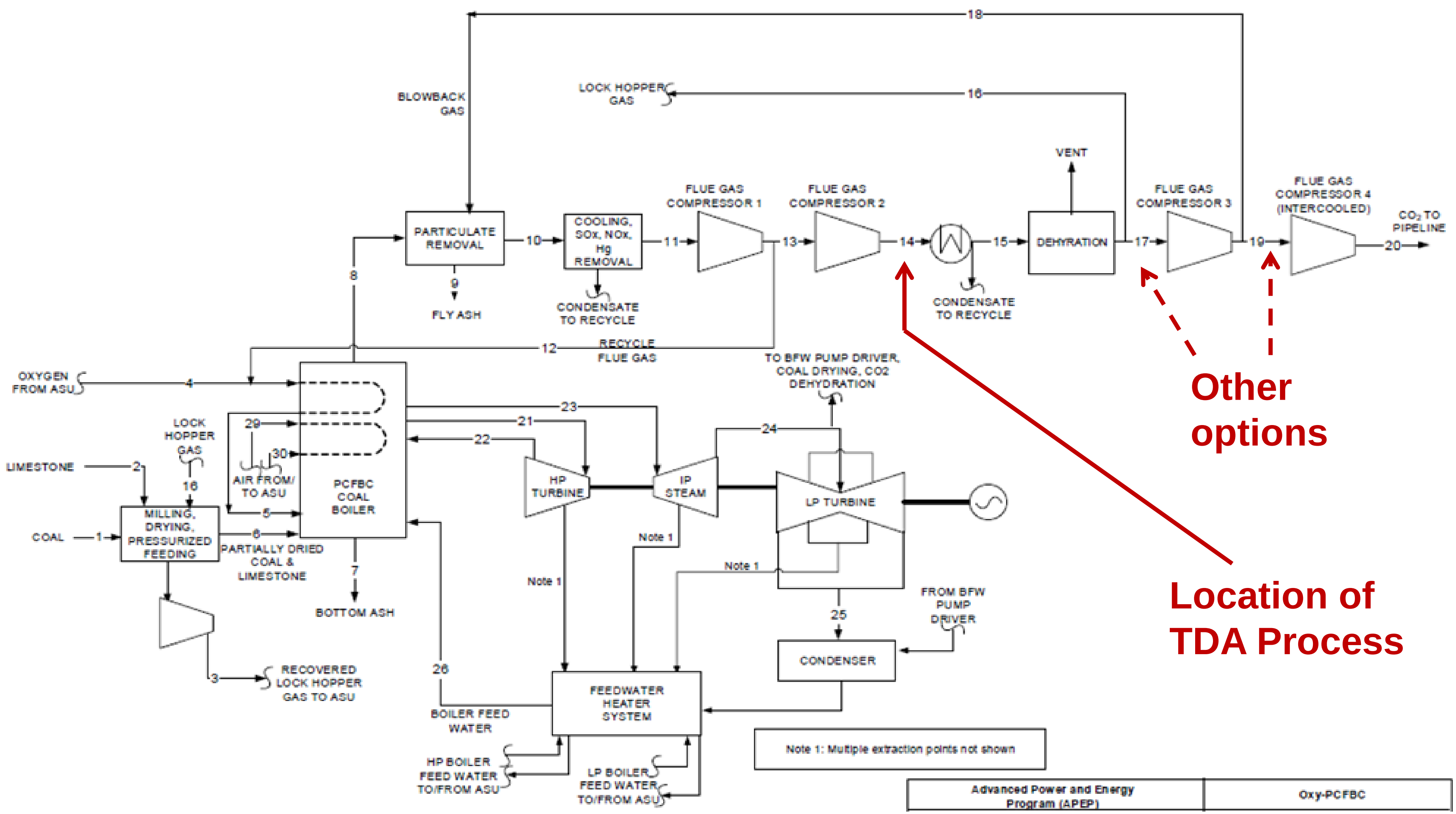
Absorption = 2.0% vol. O_2, Desorption = 1.6% H_2, GHSV= 68,500 h^{-1}





- **TDA's CO_2 purification sorbent maintains its capacity through 5,000+ absorption/ regeneration cycles**
- **Sorbent achieves a stable working capacity of 3% wt. O_2 (9 min cycle time) with extended cycle time of 22.5 min this increases to above 7.5% wt. O_2**

CO_2 Purification Process Design



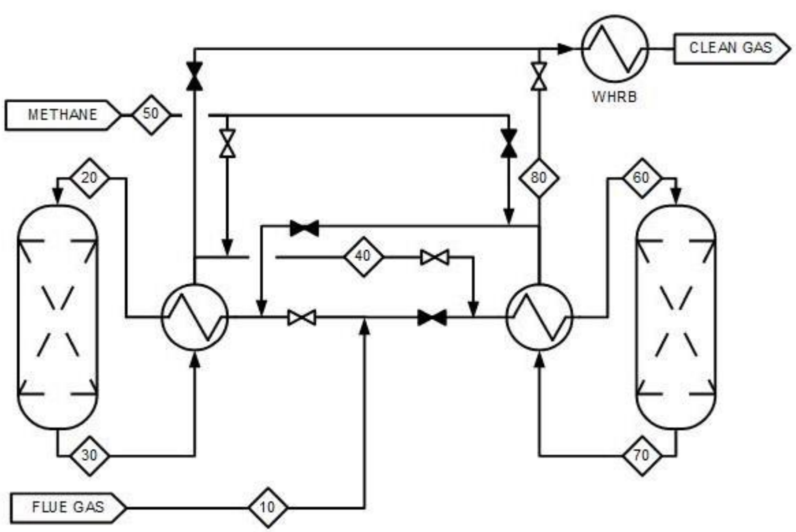
System Integration

- **Both absorption and regeneration processes are exothermic**
- **Absorption**

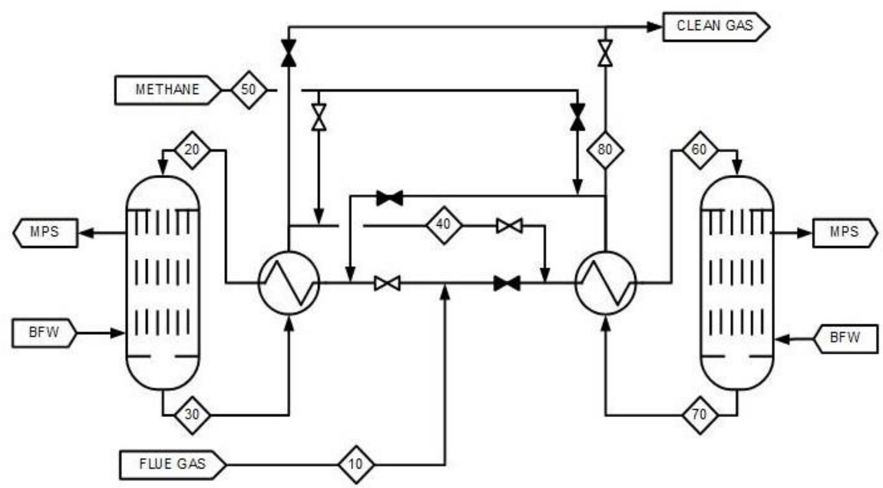
  $4M + 2O_2 \rightarrow 4MO$ **ΔH_{rxn} = -140-150 kcal/mole**
- **Regeneration**

  $4MO + CH_4 \rightarrow CO_2 + 2H_2O + 4M$ **ΔH_{rxn} = -40-50 kcal/mole**

- **Various heat removal options were investigated**

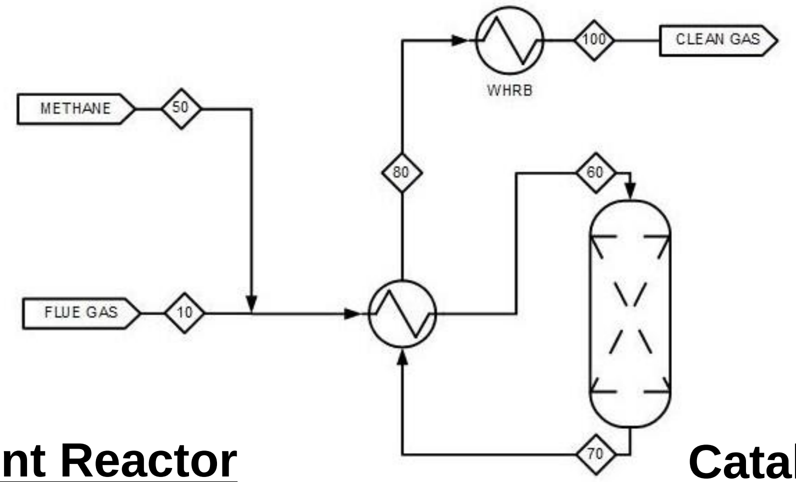


Adiabatic Design



Isothermal Design

CatOx vs. Sorbent-Based O_2 Removal



Isothermal Sorbent Reactor

Reactor Type – 2 x Packed Tube Feed-Product Exchangers

- Adsorber – 63 MW_{th} /Regen – 61 MW_{th}

Operating Temperatures

- Absorber Bed – 425°C
- Regeneration Bed – 425°C
- Outlet Flue Gas – 126°C

Heat Recovery – 39 MW_{th} from the shell side of the reactors

- Steam Generated – 59,640 kg/hr @ 45 bar (medium pressure)

Catalytic Reactor

Reactor Type – Single Fixed Bed Feed-Product Exchangers

- Reactor– 44 MW_{th}

Operating Temperatures

- Catalyst Bed – 520°C
- Outlet Flue Gas – 165°C

Heat Recovery – 31 MW_{th} from waste heat recovery boiler

- Steam Generated – 48,400 kg/hr @ 45 bar (medium pressure)

Plant Performance : Cases 6-7

Case #	1	6A	6B	6C	7A	7B	7C
ASU Type	Cryo	Cryo	ITM	TDA ASU	Cryo	ITM	TDA ASU
CO_2 Purification	-	Catalytic	Catalytic	Catalytic	TDA Sorbent	TDA Sorbent	TDA Sorbent
GROSS POWER GENERATED (AT GENERATOR TERMINALS) (KWE)							
sCO_2 EXPANDER							
STEAM TURBINE	785,587	784,107	779,662	713,618	783,135	780,538	713,955
DEPLETED AIR EXPANDER	-	-	209,582	79,305	-	209,932	79,213
TOTAL GENERATED (KWE)	785,587	784,107	989,244	792,923	783,135	990,470	793,168
TOTAL AUXILIARIES (KWE)	235,587	234,107	439,244	242,923	233,135	440,470	243,168
NET POWER (KWE)	550,000	550,000	550,000	550,000	550,000	550,000	550,000
NET PLANT EFFICIENCY (% HHV)	31.24	30.80	30.75	32.74	30.91	30.70	32.77
THERMAL INPUT							
COAL (KWT HHV)	1,760,447	1,733,581	1,660,466	1,537,853	1,727,623	1,663,167	1,536,058
NATURAL GAS (KWT HHV)	-	52,114	127,956	142,244	51,896	128,232	142,077
TOTAL (KWT HHV)	1,760,447	1,785,695	1,788,422	1,680,097	1,779,520	1,791,400	1,678,135
CARBON CAPTURED (%)	99.5	99.5	96.8	99.5	99.5	96.8	99.5

CO_2 Purification Module

- TDA's sorbent based CO_2 purification process provides slightly better net thermal plant efficiency than regular catalytic oxidizers

Case	Power Cycle psig/°F/°F	Subsystem Concept Evaluated	Oxidant
1 (Base)	Supercritical Steam 3500/1100/1100	**Current ASU – Cryogenic ASU**	95% O_2, Cryogenic ASU
6A, 6B & 6C	Supercritical Steam 3500/1100/1100	**CO_2 Purification by Catalytic De-oxidation with Natural Gas**	Three cases chosen from Case 1 through Case 5 (Cryo, TDA & Ion Transport ASU)
7A, 7B & 7C	Supercritical Steam 3500/1100/1100	**CO_2 Purification by Chemical Looping Combustion or CLC (TDA) with Natural Gas**	Three cases chosen from Case 1 through Case 5 (Cryo, TDA & Ion Transport ASU)

Plant Performance : Cases 7-8

Case #	7A	7B	7C	8A	8B	8C
ASU Type	Cryo	ITM	TDA	Cryo	ITM	TDA
CO_2 Purification	Sorbent	Sorbent	Sorbent	Sorbent	Sorbent	Sorbent
Compression scheme	Regular	Regular	Regular	Advanced	Advanced	Advanced
GROSS POWER GENERATED (AT GENERATOR TERMINALS) (KWE)						
STEAM TURBINE	783,135	780,538	713,955	782,862	782,910	712,582
DEPLETED AIR EXPANDER	-	209,932	79,213	-	210,048	78,984
TOTAL GENERATED (KWE)	783,135	990,470	793,168	782,862	992,958	791,566
TOTAL AUXILIARIES (KWE)	233,135	440,470	243,168	232,862	442,959	241,566
NET POWER (KWE)	550,000	550,000	550,000	550,000	550,000	550,000
NET PLANT EFFICIENCY (% HHV)	30.91	30.70	32.77	30.95	30.69	32.87
THERMAL INPUT						
COAL (KWT HHV)	1,727,623	1,663,167	1,536,058	1,725,373	1,664,097	1,531,745
NATURAL GAS (KWT HHV)	51,896	128,232	142,077	51,865	128,295	141,663
TOTAL (KWT HHV)	1,779,520	1,791,400	1,678,135	1,777,237	1,792,392	1,673,409
CARBON CAPTURED (%)	99.5	96.8	99.5	99.5	96.8	99.5

Compression scheme

- TDA's sorbent based CO_2 purification process provides slightly better net thermal plant efficiency than regular catalytic oxidizers

Case	Power Cycle psig/°F/°F	Subsystem Concept Evauated	Oxidant
7A, 7B & 7C	Supercritical Steam 3500/1100/1100	**CO_2 Purification by Chemical Looping Combustion or CLC (TDA) with Natural Gas**	Three cases chosen from Case 1 through Case 5 (Cryo, TDA & Ion Transport ASU)
8A, 8B & 8C	Supercritical Steam 3500/1100/1100	**Advanced CO_2 &/or ASU Compression**	Three cases chosen from above (cryo, TDA & Ion Transport ASU)

Plant Performance : Power Cycles

Case #	8C	9C	10C	11C*	12C
Power Cycle	Supercritical Steam	Adv. Supercritical Steam	Ultra Supercritical Steam		Supercritical CO_2
ASU Type	TDA ASU	TDA ASU	TDA ASU	TDA ASU	TDA ASU
CO_2 Purification	TDA Sorbent	TDA Sorbent	TDA Sorbent	TDA Sorbent	TDA Sorbent
GROSS POWER GENERATED (AT GENERATOR TERMINALS) (KWE)					
sCO_2 EXPANDER					692,220
STEAM TURBINE	712,582	713,792	697,408	693,710	8,292
DEPLETED AIR EXPANDER	78,984	78,594	72,247	70,877	71,217
TOTAL GENERATED (KWE)	791,566	792,385	769,655	764,587	771,728
TOTAL AUXILIARIES (KWE)	241,566	242,385	219,655	214,587	221,728
NET POWER (KWE)	550,000	550,000	550,000	550,000	550,000
NET PLANT EFFICIENCY (% HHV)	32.87	33.03	36.55	36.99	38.65
THERMAL INPUT					
COAL (KWT HHV)	1,531,745	1,524,175	1,399,025	1,383,354	1,380,651
NATURAL GAS (KWT HHV)	141,663	140,965	105,743	103,524	42,553
TOTAL (KWT HHV)	1,673,409	1,665,140	1,504,768	1,486,878	1,423,204
CARBON CAPTURED (%)	99.5	99.5	99.5	99.5	99.5

* Same as Case 10 without CO_2 treating to remove SOx & NOx (Cryo, TDA & Ion Transport ASU)

- Ultra supercritical steam cycle provides a significant improvement in net thermal plant efficiency of about 3% point over other supercritical steam cycles
- Supercritical CO_2 power cycle provides about 2% point over ultra supercritical steam cycle

Acknowledgements

- DOE/NETL funding under the DE-FE-0029090 project is greatly appreciated
- DOE Project Manager, Diane R. Madden
- Dr. Ashok Rao, UCI