Coal Direct Chemical Looping (CDCL) Retrofit to Pulverized Coal Power Plants for In-Situ CO_2 Capture

Award #: DE-NT0005289

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WILLIAM G. LOWRIE
DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING

Clean Coal Research Laboratory at The Ohio State University

Coal-Direct Chemical Looping

Cold Flow Model

Sub-Pilot Scale Unit

Syngas Chemical Looping

Sub-Pilot Scale Unit

250kW$_{th}$ Pilot Unit
(Wilsonville, Alabama)

Calcium Looping Process

Sub-Pilot Unit

CCR Process

120kW$_{th}$ Demonstration Unit

F-T Process

HPHT Slurry Bubble Column

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Coal Direct Chemical Looping Retrofit to Pulverized Coal Power Plants for In-Situ CO_2 Capture

Period of Performance: 2009-2013

Total Funding ($3.98 million):

- U.S. Department of Energy, National Energy Technology Laboratory ($2.86 million)
- Ohio Coal Development Office ($300,000)
- The Ohio State University ($487,000)
- Industrial Partners ($639,000)

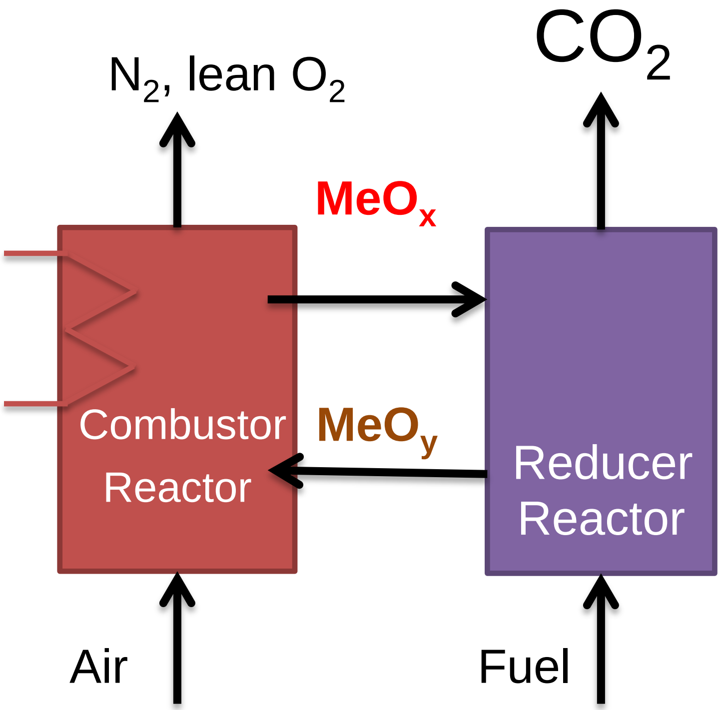
Major Tasks:

- Phase I: Selection of iron-based oxygen carrier particle - COMPLETE
- Phase II: Demonstration of fuel reactor (coal char and volatile conversion) at 2.5 kW_t scale and cold flow model study - COMPLETE
- Phase III: Demonstration of integrated CDCL system at 25 kW_t scale and techno-economic analysis of CDCL process – IN PROGRESS

This material is based upon work supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-NT0005289 and the Ohio Coal Development Office of the Ohio Air Quality Development Authority under Contract Number CDO-D-08-02.

Coal-Direct Chemical Looping Process Development

Chemical Looping Process Concept



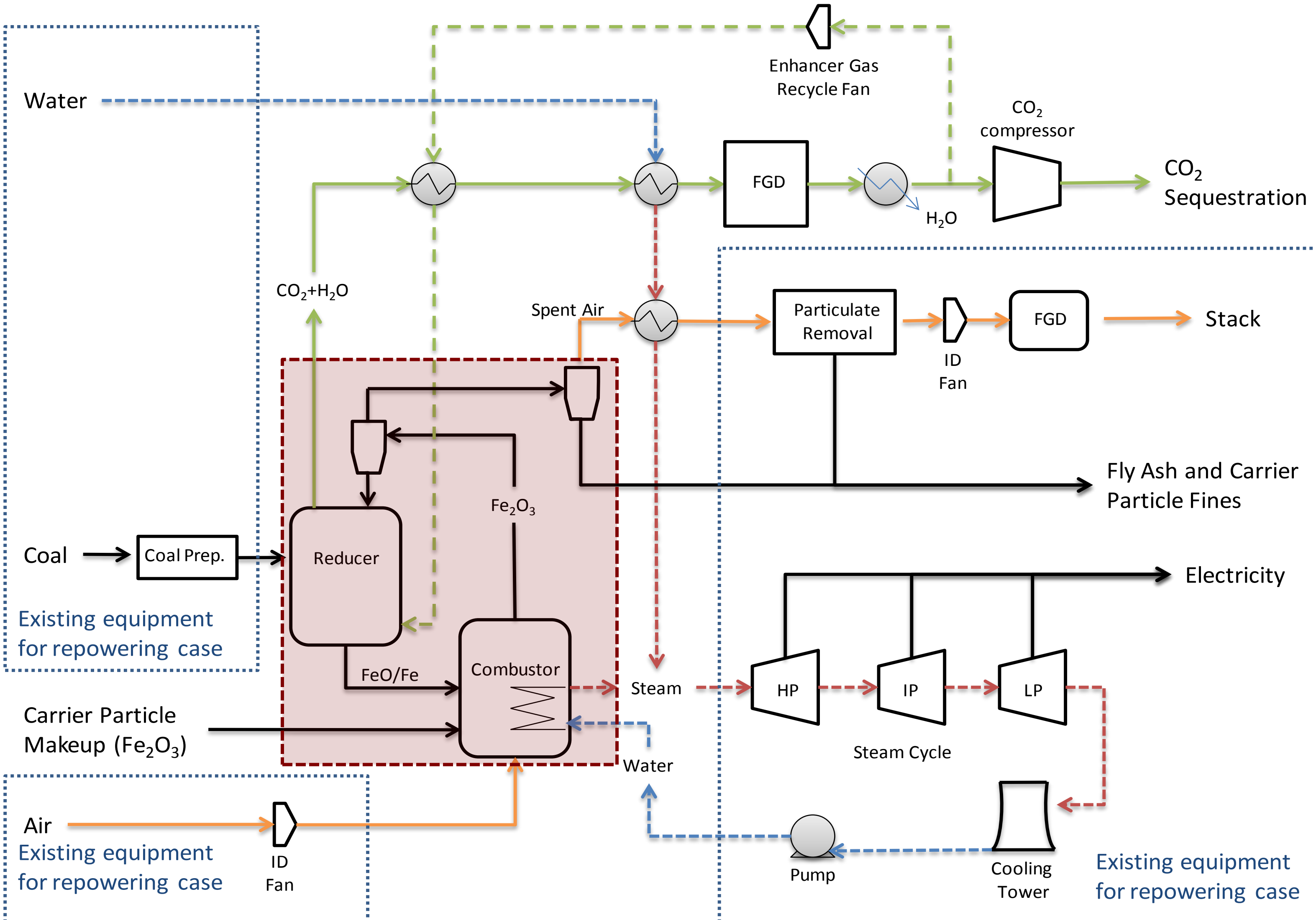
Reducer: MeO_x + Fuel → MeO_y + CO_2 + H_2O

Combustor: MeO_y + Air → MeO_x + **Heat**

Overall: Coal + Air → CO_2 + H_2O + **Heat**

$y < x$

Coal-Direct Chemical Looping Process for Retrofit/Repower



Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

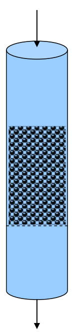
The CDCL process can be also used for high efficient hydrogen production

OSU CDCL Process Development

Phase I

More than **300** types of particle tested. A low cost, robust, highly reactive, and O^{2-} conductive composite particle is obtained.

TGA



Fixed Bed Tests

Phase II

300+ hours operation with ***>99%*** volatile conversion, ***>95%*** char conversion

Bench Scale Tests

100+ hours of operation and testing

Cold Model Tests

Phase III

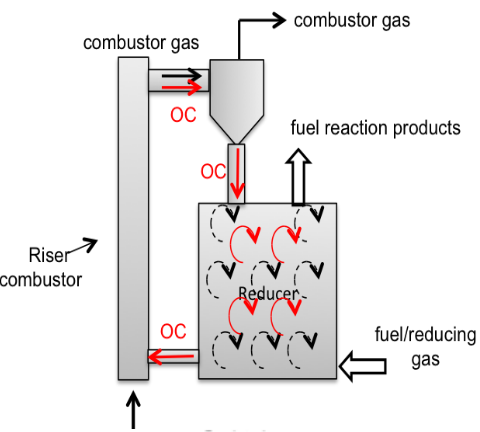
640+ hours operation with ***>99%*** solid fuel conversion, smooth solid circulation, gas sealing and in-situ ash removal

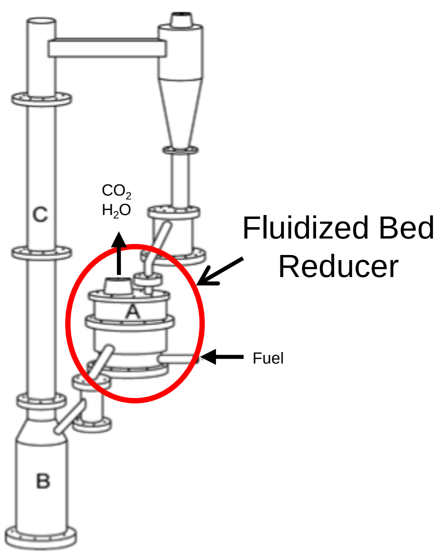
Sub-Pilot Integrated Tests

Phase III Results

Modes of CFB Chemical Looping Reactor Systems

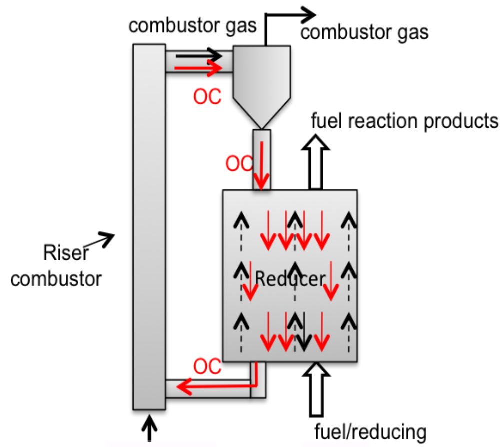
Mode 1- reducer: fluidized bed or co-current gas-solid (OC) flows

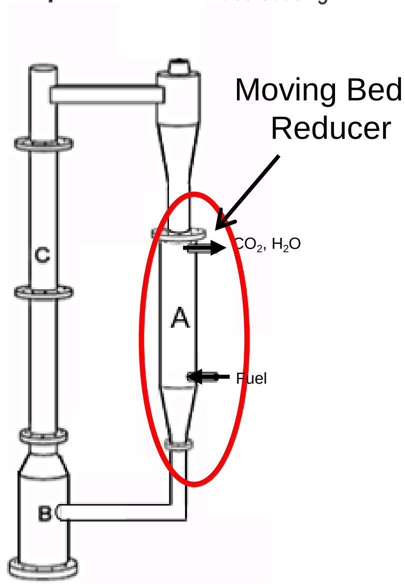




Chalmers University CLC System

Mode 2 - reducer: gas-solid (OC) counter-current dense phase/moving bed flows





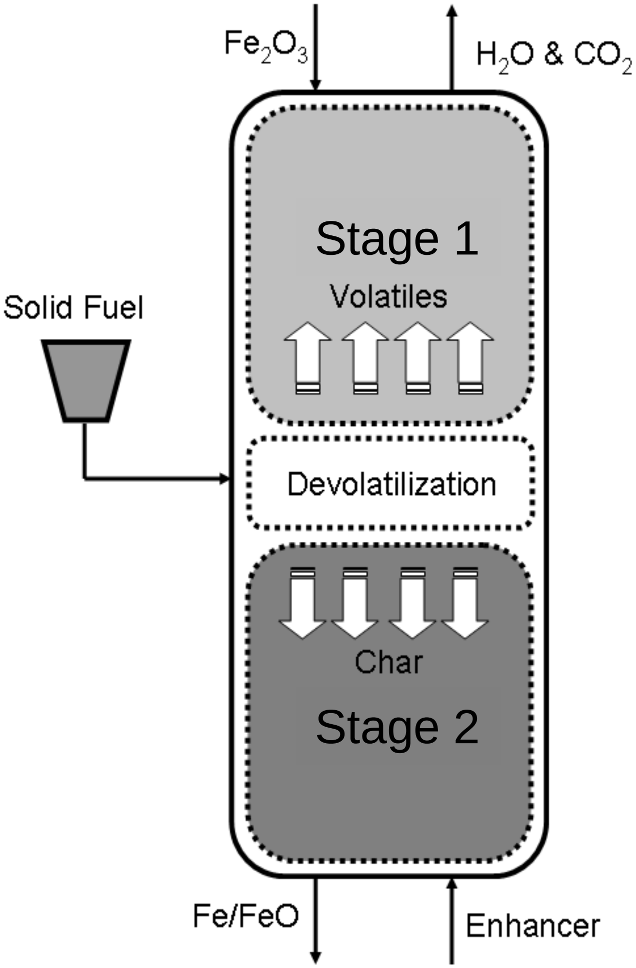
OSU CLC System

Reducer	Mode 1	Mode 2
Operation Regime	Bubbling, turbulent, fast fluidized, or spouted bed	Moving packed, or multistage fluidized bed
Gas Solid Contacting Pattern	Mixed/Cocurrent	Countercurrent
Controllability on Fuel and OC Conversions	Poor, due to back mixing and gas channeling	High
Maximum Iron oxide Conversion	11.1% (to Fe_3O_4)	>50% (to Fe & FeO)
Solids circulation rate	High	Low
Ash Separation Technique	Separate Step	In-Situ
Subsequent Hydrogen Production	No	Yes
Particle size, μm	100-600	1000-3000
Reducer gas velocity*, m/s	<0.4	>1.0
Reactor size for the same fuel processing capacity	Large	Small
Hydrodynamics effects on scaling up	Large	Small

*Reducer gas velocity calculated at 900 °C, 1 atm

Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010)

Reducer Reactor Design



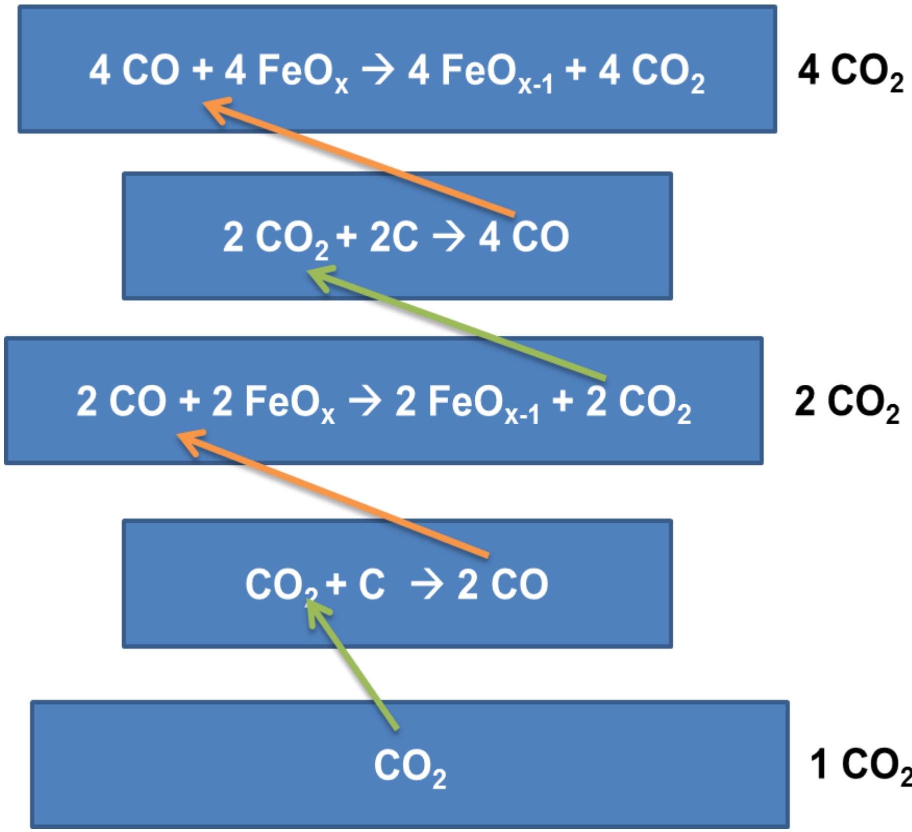
Particle reduction :
$CH_4 + Fe_2O_3 \rightarrow CO_2 + H_2O + FeO$

Coal devolatilisation:
$Coal \rightarrow C + C_xH_y$

Char gasification and particle reduction:
$FeO + H_2 \rightarrow Fe + H_2O$
$FeO + CO \rightarrow Fe + CO_2$
$CO_2 + C \rightarrow 2CO$

Reaction Initiation:
$H_2 + FeO \rightarrow Fe + H_2O$
$H_2O + C \rightarrow CO + H_2$

Enhancer Gas



Two-stage moving bed

- Stage I for gaseous volatiles
- Stage II for coal char

Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

<u>Phase III</u>: Integrated CDCL System Testing

- Fuel Design Input: 25 kW_{th}
- Fully assembled and operational
- **640+** hours of operational experience
- **200+** hours continuous successful operation
- Smooth solid circulation
- Confirmed non-mechanical gas sealing under reactive conditions

Phase III: Integrated CDCL System Testing

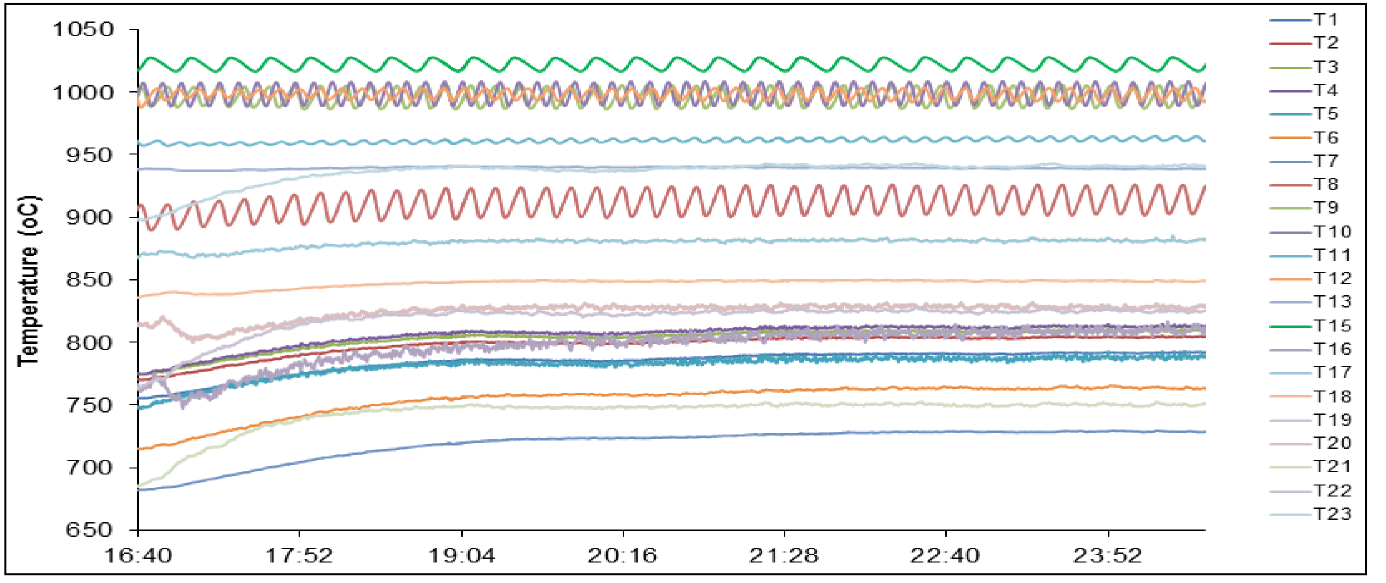
Fuel Feedstock Studied

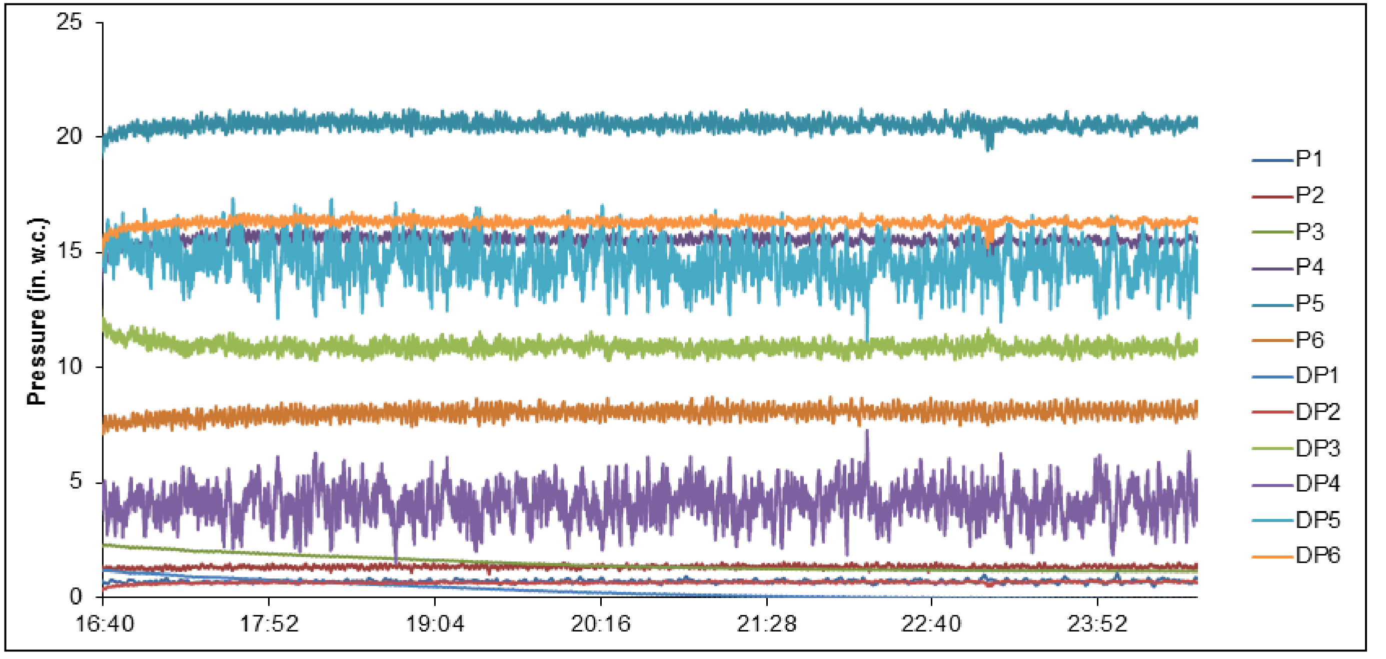
Fuel Feedstock	Type	Fuel Flow (lb/hr)	Enhancer
Syngas	CO/H_2	0.1-1.71	N/A
Coal volatile/ Natural Gas	CH_4	0.1-0.4	N/A
Coal char	Lignite	0.7-2.0	CO_2/H_2O
	Metallurgical Coke	0.05-3	CO_2/H_2O
Coal	Sub-Bituminous	0.05-7.38 **(25 kW_{th})**	CO_2/H_2O
	Bituminous	0.05-3	CO_2/H_2O
	Anthracite	0.2-0.7	CO_2/H_2O
	Lignite	2.84-6.15 (**20 kW_{th}**)	CO_2
Biomass	Wood pellets	0.1	CO_2
Coke	Petroleum Coke	1.98-5.95	CO_2/H_2O

- Combined >940 hours of sub-pilot operational experience
- Achieved high conversion on all fuel feedstock
- Successful results for all coal/coal derived feedstock tested

Phase III: Integrated CDCL System Testing

200+ Sub-Pilot Continuous Run Results

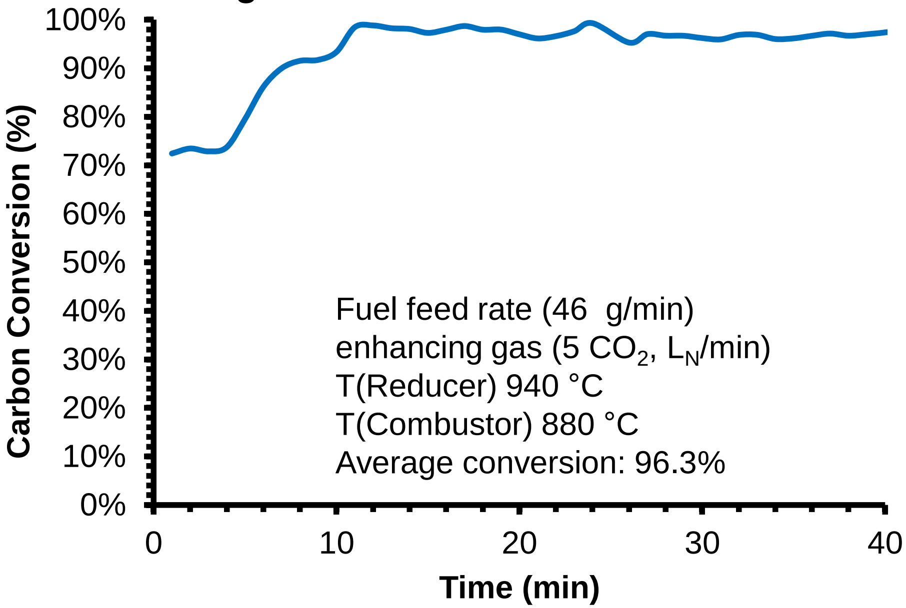




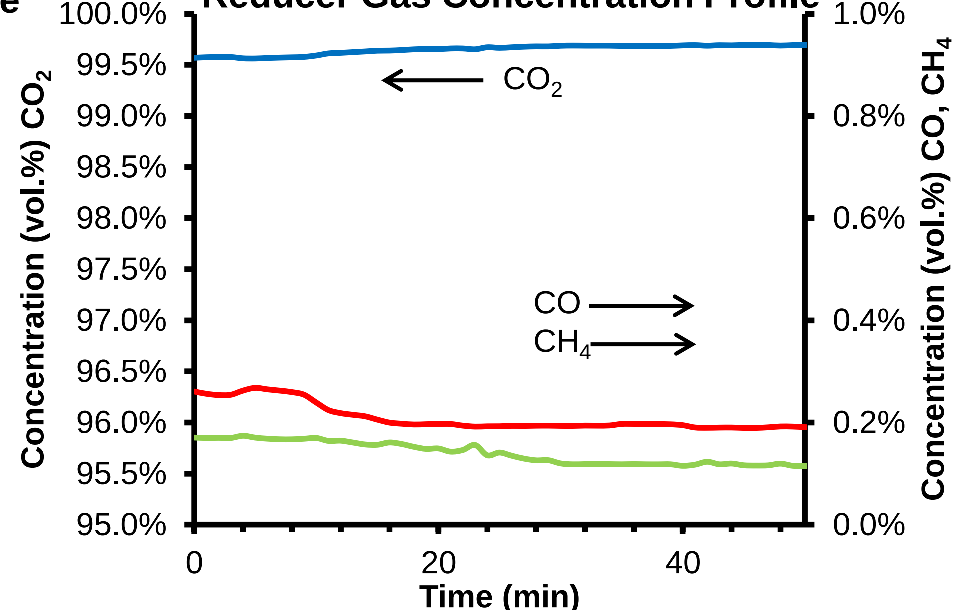
Phase III: Integrated CDCL System Testing

200+ Sub-Pilot Continuous Run Results

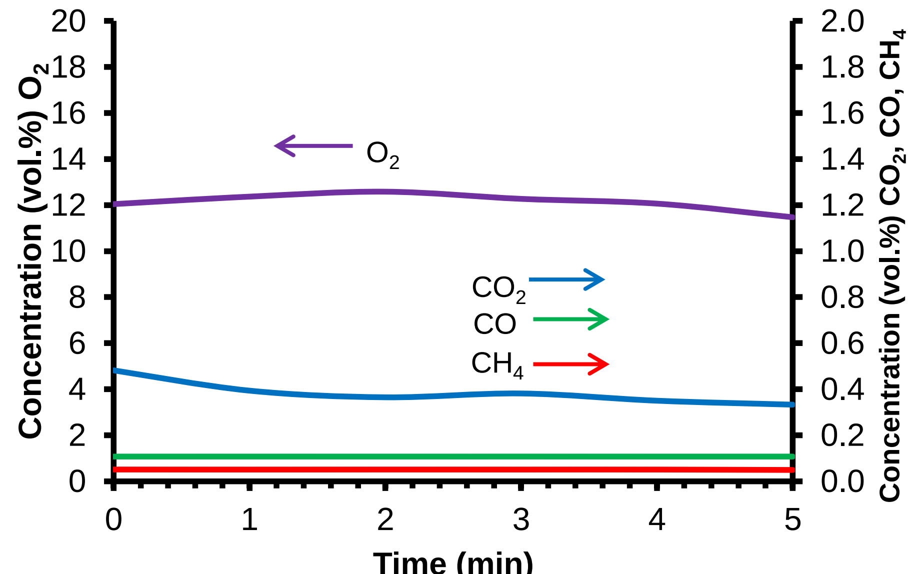
Once-Through Reducer Carbon Conversion Profile



Reducer Gas Concentration Profile



Combustor Gas Concentration Profile



- **Continuous steady carbon conversion from reducer throughout all solid fuel loading (5-25kW_{th})**
- **<0.25% CO and CH_4 in reducer outlet = full fuel conversion to CO_2/H_2O**
- **<0.1% CO, CO_2, and CH_4 in combustor = negligible carbon carry over, nearly 100% carbon capture**

Phase III: Integrated CDCL System Testing

Parametric Studies Performed

Fuel Type	Fuel Flow (g/min)	Enhancing Gas Flow (L_n/min)	CO_2 Purity (%)	Reducer Carbon Conv. (%)
Subbituminous	23	5.0, CO_2	99.7%	96.9%
Subbituminous	23	3.0, CO_2	99.6%	96.5%
Subbituminous	22	1.0, CO_2	99.0%	88.0%
Subbituminous, lower port	22	1.0, CO_2	98.0%	~100%
Subbituminous	32	5.0, CO_2	99.7%	96.9%
Subbituminous	46	5.0, CO_2	99.7%	96.9%
Subbituminous	56	5.0, CO_2	99.5%	96.9%
Subbituminous	68	5.0, CO_2	98.5%	99.9%
Subbituminous	15	5.0, H_2O	98.9%	97.8%
Subbituminous	22	5.0, H_2O	94.0%	99.8%
Subbituminous	38	5.0, H_2O	99.3%	96.3%
Lignite	22	5.0, CO_2	99.6%	97.7%
Lignite	46	5.0, CO_2	99.6%	96.3%

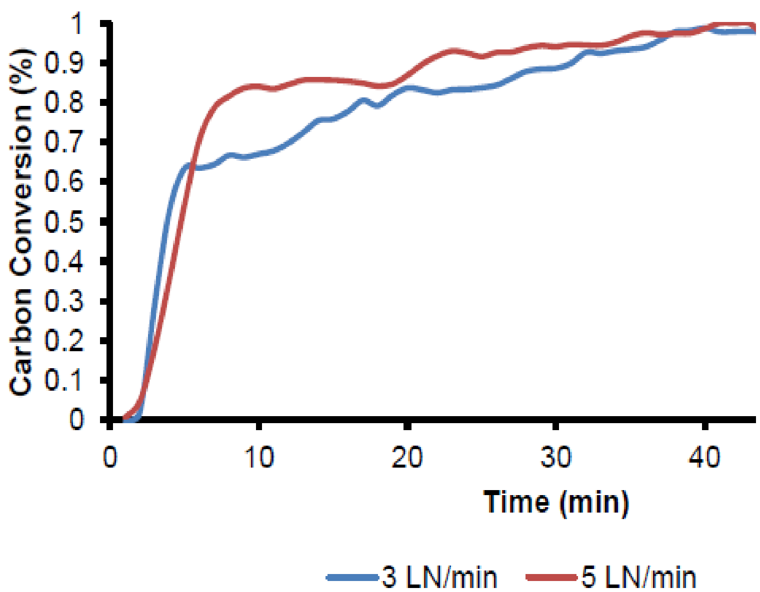
Parameters studied include

- Fuel flow rate
- Fuel type
- Enhancer gas type (CO_2, H_2O)
- Enhancer gas flow rate
- Injection location

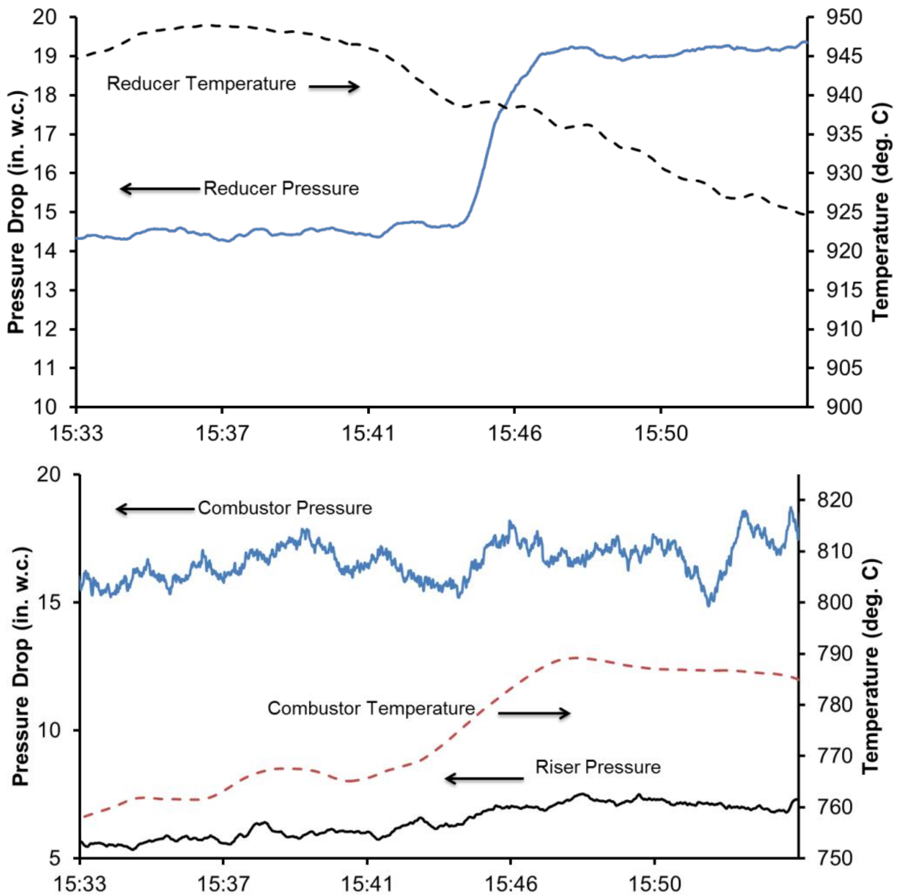
Data from Kim et al., *Fuel* (2013) **108** , 370–384
Bayham et al., *Energy Fuels* (2013) **27**, 1347−1356

Phase III: Integrated CDCL System Testing

Unsteady State Studies Performed



Effect of enhancing gas on approach to steady state



Effect of coal injection on system temperatures and pressures

Bayham et al., *Energy Fuels* (2013) **27**, 1347−1356

Supporting Work: Phases I, II

Phase I: Oxygen Carrier Particle Development

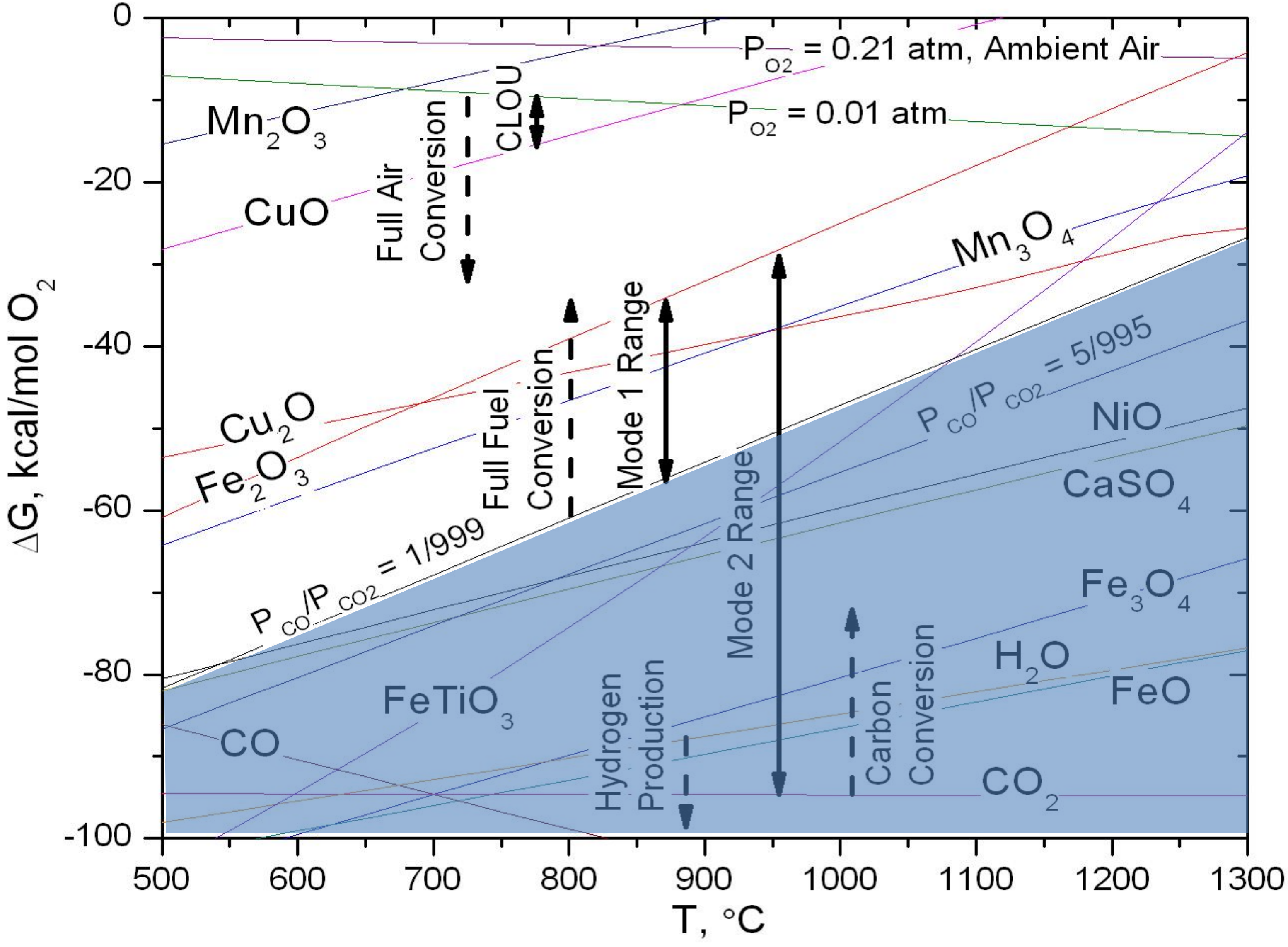
Primary Metal Properties

Redox Pair	Fe_2O_3-Fe_3O_4	Fe_2O_3-Fe	CuO-Cu_2O	CuO-Cu	$CaSO_4$-CaS	Mn_3O_4-MnO	NiO-Ni
Reducer Mode	1	2	1	1	1	1	1
Melting point, °C	1566-1538	1566-1535	1326-1235	1326-1085	1460-2525	1567-1650	1955-1455
Cost, $/ton[1]	319	319	7679		27	1000	21804
Recyclability Test, cycles	>100	>100[3]	>33[4]		<5	5[5]	5[5]
Theoretical OCC, kg O2/kg	0.033	0.3	0.1	X		0.07	
Conversions[2]		50-60%	60%		X		X
Support, %	X	40-60	60-80			X	
Actual OCC, kg O2/kg		0.06-0.11	0.012-0.024				
Crushing Strength, N		>60	<0.5				

1. Primary material cost, dollars in 2010 from US Geological Survey;
2. The actual conversion limited by both thermodynamics and kinetics;
3. Li, F. et al. *Energy Fuels* **2009**, *23*, 4182 – 4189.;
4. Eyring, EM. et al. *Oil Gas Sci. Technol.* **2011**, *66*, 209–221. ;
5. Lyngfelt, A. *Oil Gas Sci. Technol.* **2011**, *66*, 161-172.

Phase I: Oxygen Carrier Particle Development

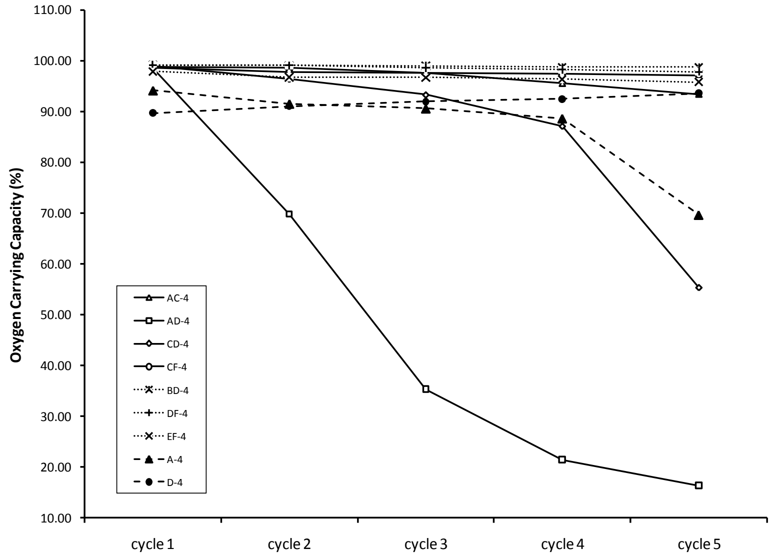
Ellingham Diagram: Selection of Primary Metal



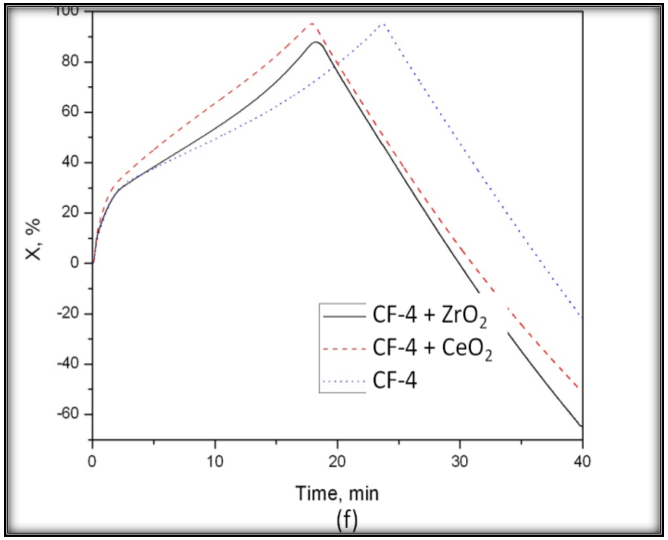
Phase I: Oxygen Carrier Particle Development

OSU Particle (over 300 particles) Performance

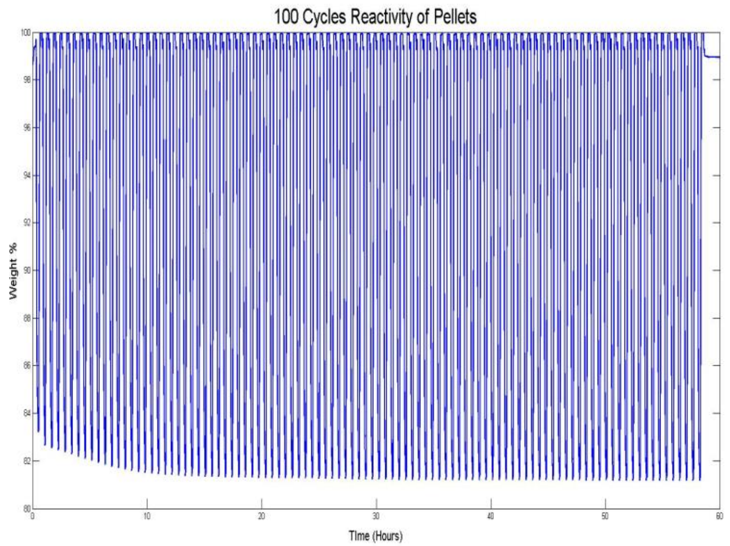
High Reactivity



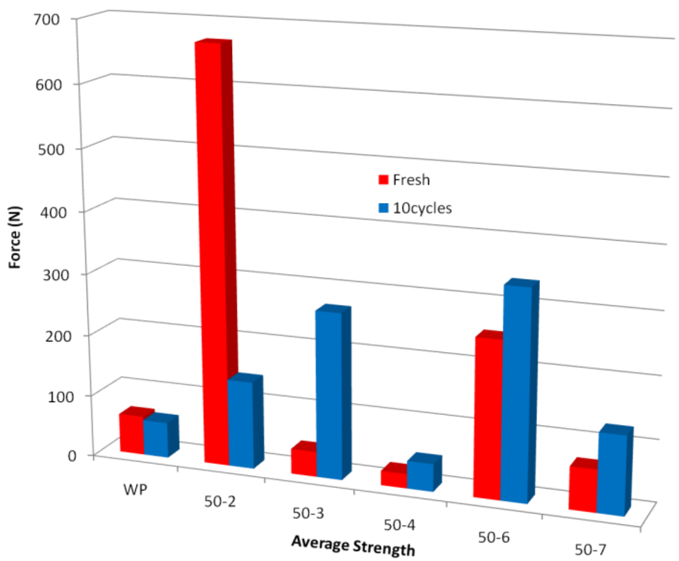
High Carbon Deposition Tolerance



High Recyclability

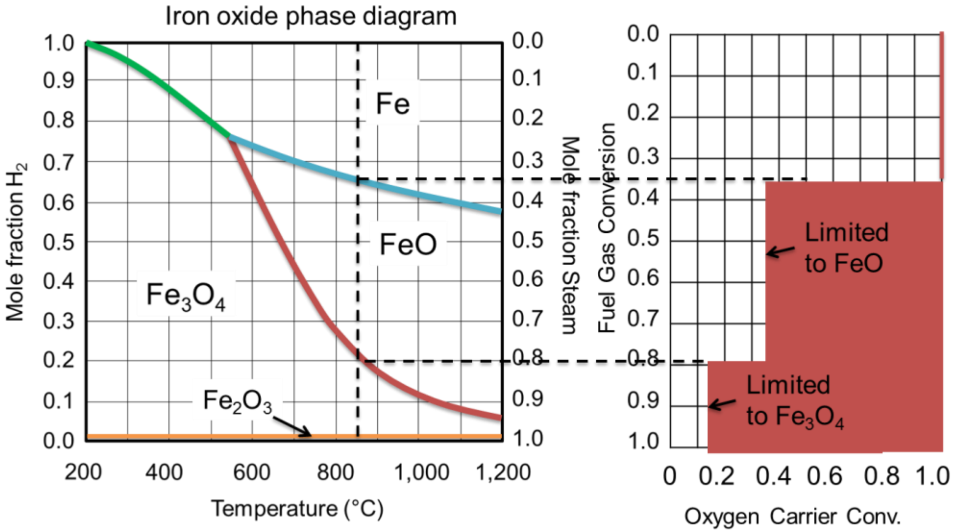


High Pellet Strength



Phase II: Reducer Reactor Design and Testing

Phase Diagram – Thermodynamic Restrictions



Shaded area is not reducer operation zone

Operating Equation for Moving Bed Reducer

Fixed solid molar flowrate n_{Fe},

Oxygen content for solid $y = \dfrac{3n_{Fe_2O_3} + 4n_{Fe_3O_4} + n_{FeO}}{n_{Fe}}$

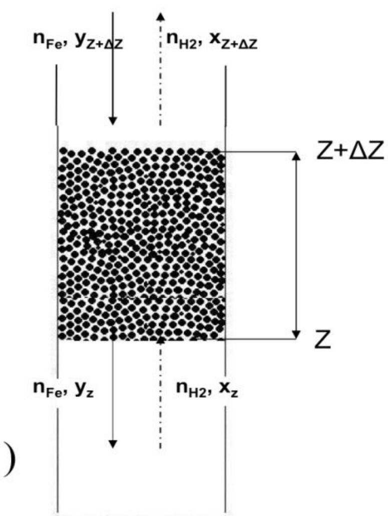
Fixed gas molar flowrate $n_{H2} + n_{H2O}$,

Oxygen content for gas $x = \dfrac{n_{H_2O}}{n_{H_2} + n_{H_2O}}$

Oxygen Balance

$$n_{Fe}(y_{z+\Delta z} - y_z) = (n_{H_2} + n_{H_2O})(x_{z+\Delta z} - x_z)$$

$$\Delta z \rightarrow 0 \Rightarrow dy/dx = (n_{H_2} + n_{H_2O})/n_{Fe}$$



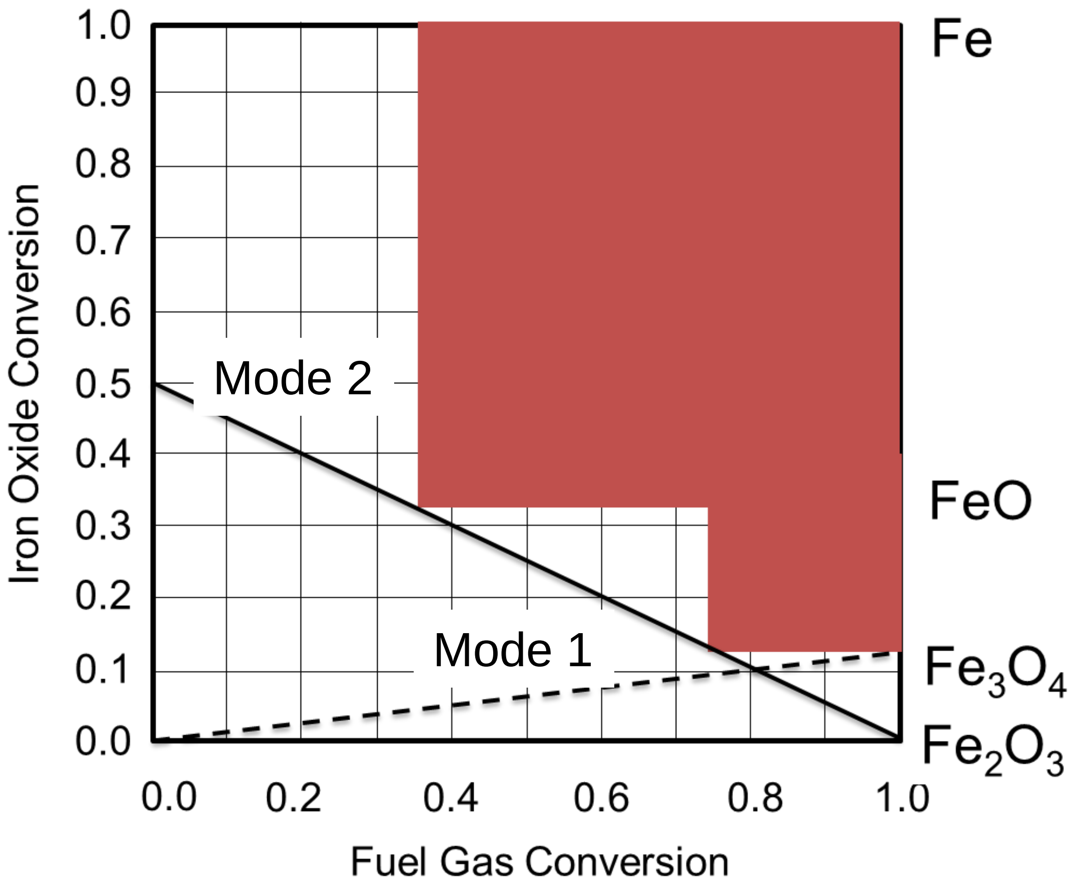
Countercurrent moving bed: straight operation line with negative slope

Similarly, Concurrent fluidized bed: straight operation with positive slope

Fan, L-S. "Chemical Looping Systems for Fossil Energy Conversion, Wiley AIChE, 2010.

Phase II: Reducer Reactor Design and Testing

Operation Diagram

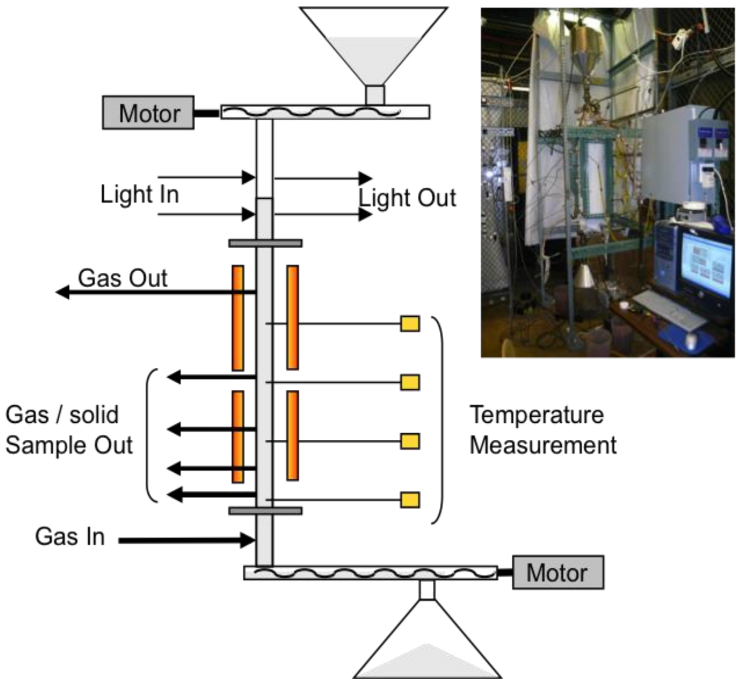


The operating line is straight when feeding ratio is fixed: solid line represents countercurrent moving bed operation, dash line represents co-current fluidized bed operation

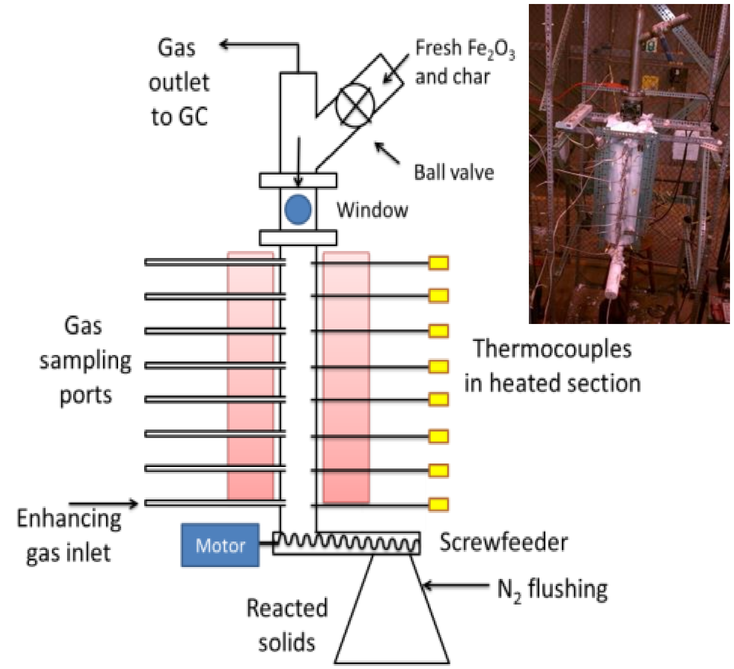
Fan, L-S. “Chemical Looping Systems for Fossil Energy Conversion, Wiley AIChE, 2010.

Phase II: Reducer Reactor Design and Testing

Stage I – Volatile Conversion



Stage II – Char Conversion



Summary of Bench Scale Unit Testing Results

Type of Fuel	Stage I - Coal Volatile		Stage II - Coal Char		Coal		
	CO, H_2	CH_4	Lignite char	Bituminous char	PRB	Bituminous	Anthracite
Fuel Conversion, %	99.9	99.8	94.9	95.2	>97	>95	95.5
CO_2 purity, %	99.9	98.8	99.23	99.1	-*	-	97.3

- Conducted in co-current mode, no gas analyzer was used to monitor the CO_2 purity.

300+ hours operation with >95% conversions of various types of fuel

Techno-Economic Analysis

Process Simulation and Analysis

Systems Analysis Methodology

- Performance of CDCL plant modeled using Aspen Plus® software
- Results compared with performance of conventional pulverized coal (PC) power plants with and without CO_2 capture
  - U.S. Department of Energy, National Energy Technology Laboratory; *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity* (November 2010)
    - Case 11 – Supercritical PC plant without CO_2 capture ("Base Plant")
    - Case 12 – Supercritical PC plant with MEA scrubbing system for post-combustion CO_2 capture ("MEA Plant")
- All plants evaluated using a common design basis
  - 550 MW_e net electric output
  - Illinois No. 6 coal: 27,113 kJ/kg (11,666 Btu/lb) HHV, 2.5% sulfur, 11.1% moisture as received
  - Supercritical steam cycle: 242 bar/593°C/593°C (3,500 psig/1,100°F/1,100°F)
  - ≥ 90% CO_2 capture efficiency (MEA and CDCL Plants)
  - CO_2 compressed to 153 bar (2,215 psia)
- Results are preliminary, will be used to guide further design improvements

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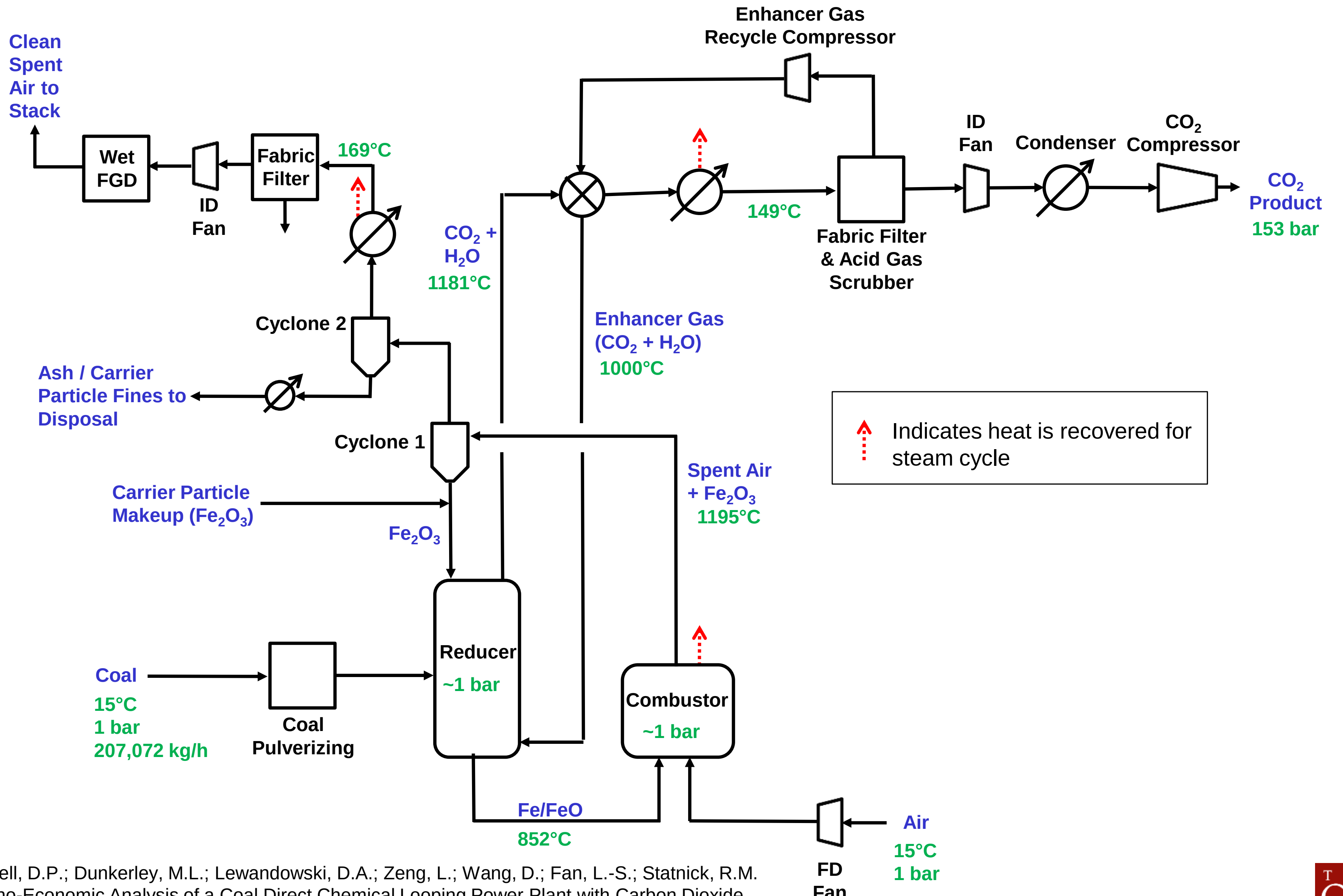
Process Simulation and Analysis



Connell, D.P.; Dunkerley, M.L.; Lewandowski, D.A.; Zeng, L.; Wang, D.; Fan, L.-S.; Statnick, R.M. Techno-Economic Analysis of a Coal Direct Chemical Looping Power Plant with Carbon Dioxide Capture. In Proceedings of the 37th International Technical Conference on Clean Coal and Fuel Systems, Clearwater, FL, June 3-7, 2012.

Aspen Plus® Modeling Results

	Base Plant	MEA Plant	CDCL Plant
Coal Feed, kg/h	185,759	256,652	207,072
CO_2 Emissions, kg/MWh_{net}	802	111	28
CO_2 Capture Efficiency, %	0	90.2	97.0
Solid Waste,[a] kg/MWh_{net}	33	45	43
Net Power Output, MW_e	550	550	548
Net Plant HHV Heat Rate, kJ/kWh (Btu/kWh)	9,165 (8,687)	12,663 (12,002)	10,248 (9,713)
Net Plant HHV Efficiency, %	39.3	28.5	35.2
Energy Penalty,[b] %	-	27.6	10.6

[a]Excludes gypsum from wet FGD. [b]Relative to Base Plant; includes energy for CO_2 compression.

First-Year Cost of Electricity

	Base Plant	MEA Plant	CDCL Plant
First-Year Capital ($/MWh)	31.7	59.6	44.2
Fixed O&M ($/MWh)	8.0	13.0	9.6
Coal ($/MWh)	14.2	19.6	15.9
Variable O&M ($/MWh)	5.0	8.7	8.7
TOTAL FIRST-YEAR COE ($/MWh)	**58.9**	**100.9**	**78.4**

Δ = +71%

Δ = +33%

Connell, D.P.; Dunkerley, M.L.; Lewandowski, D.A.; Zeng, L.; Wang, D.; Fan, L.-S.; Statnick, R.M. Techno-Economic Analysis of a Coal Direct Chemical Looping Power Plant with Carbon Dioxide Capture. In Proceedings of the 37th International Technical Conference on Clean Coal and Fuel Systems, Clearwater, FL, June 3-7, 2012.

Accomplishments

Completed

- >640 hrs of integrated 25 kW_t sub-pilot scale operations achieving 90-99+% coal conversion
- The longest demonstration to date is >200 hours continuous with smooth operations and high fuel conversions.
- The CDCL process has the potential to meet DOE's goal of ≥90% CO_2 capture at no more than a 35% increase in cost of electricity

Future work

- Test other fuels such as woody biomass and corn stover
- Work closely with B&W to scale-up to pilot plant (3 MW_{th})

Partners

Government Agencies

- DOE/NETL: Bruce Lani, Timothy Fout, David Lang
- OCDO/ODSA: Chad Smith, Greg Payne

Industrial Collaborators

- Babcock & Wilcox (B&W): Tom Flynn, Luis Vargas, Doug Devault, Bartev Sakadjian and Hamid Sarv
- Clear Skies Consulting LLC: Bob Statnick
- CONSOL Energy: Dan Connell, Richard Winschel, and Steve Winberg
- Air Products: Robert Broekhuis, Bernard Toseland
- Shell/CRI

Thanks