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

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Clean Coal Research Laboratory at The Ohio State University

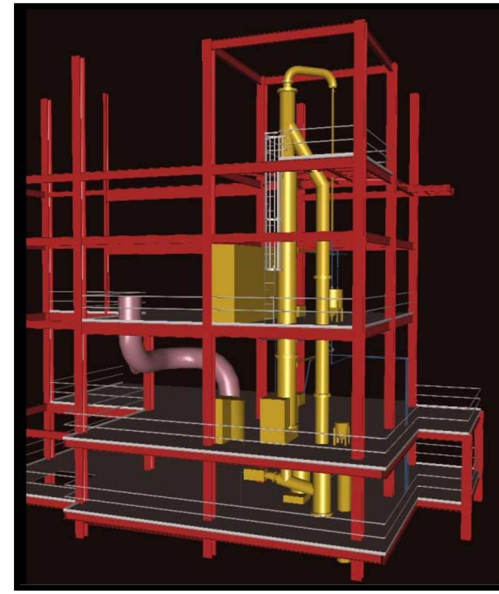
Coal-Direct Chemical Looping

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

HPHT Slurry Bubble Column

THE OHIO STATE UNIVERSITY

Partners

Government Agencies

- DOE/NETL: Bruce Lani, Timothy Fout, David Lang
- OCDO/ODOD: Bob Brown, Mario Marrocco

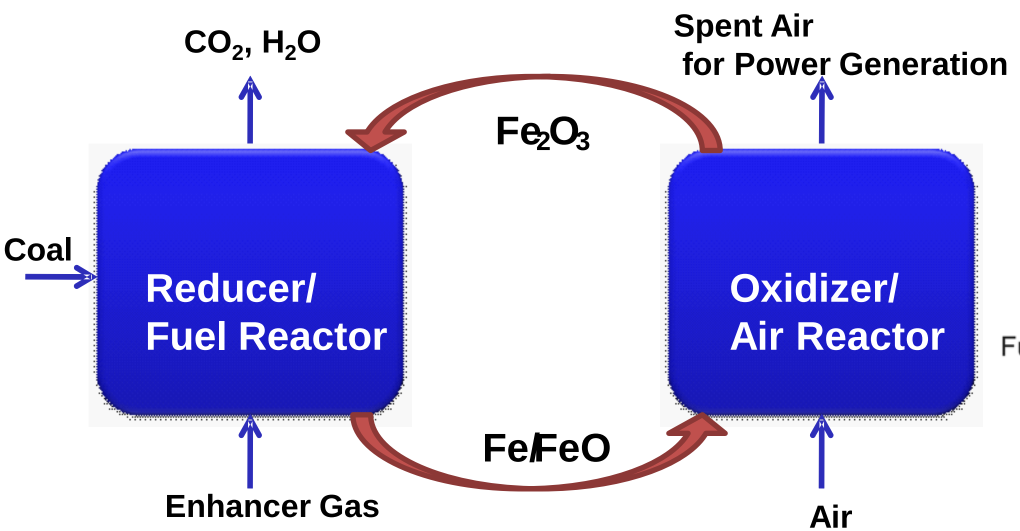
Industrial Collaborators

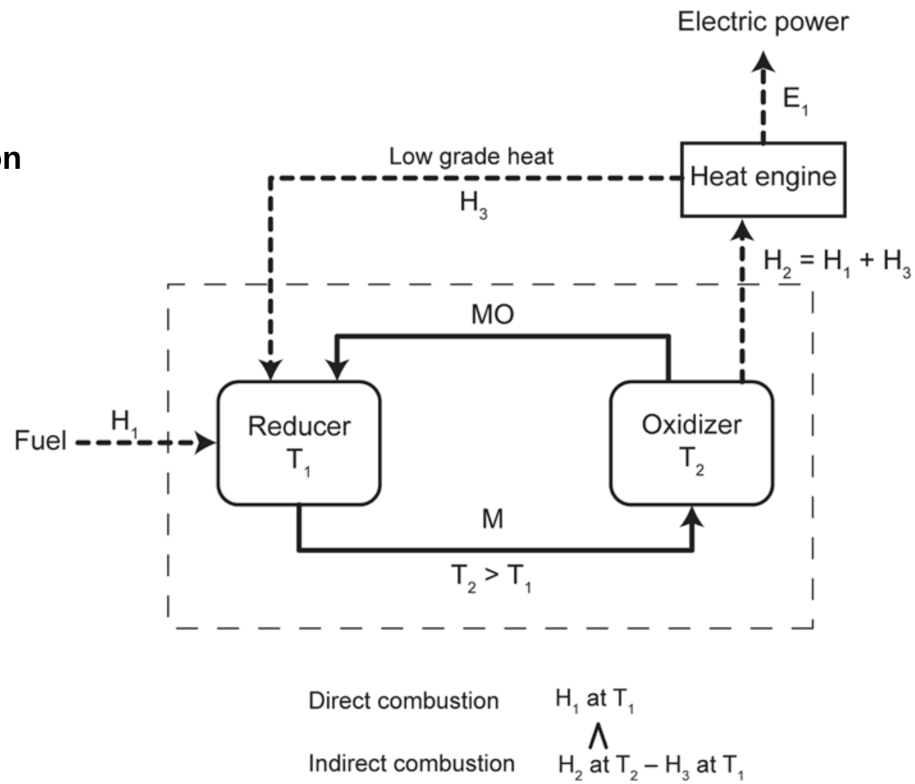
- Clear Skies: Bob Statnick
- B&W: Tom Flynn, Luis Vargas, Doug Devault, Bartev Sakadjian and Hamid Sarv
- CONSOL Energy: Dan Connell, Richard Winschel, and Steve Winberg
- Air Products: Robert Broekhuis, Bernard Toseland
- Shell/CRI: Tom Brownscombe

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

- Period of Performance: 2009-2012
- 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
  - Phase II: Demonstration of fuel reactor (coal char and volatile conversion) at 2.5 kW_t scale and cold flow model study
  - Phase III: Demonstration of integrated CDCL system at 25 kW_t scale and techno-economic analysis of CDCL process

CDCL Process Concept



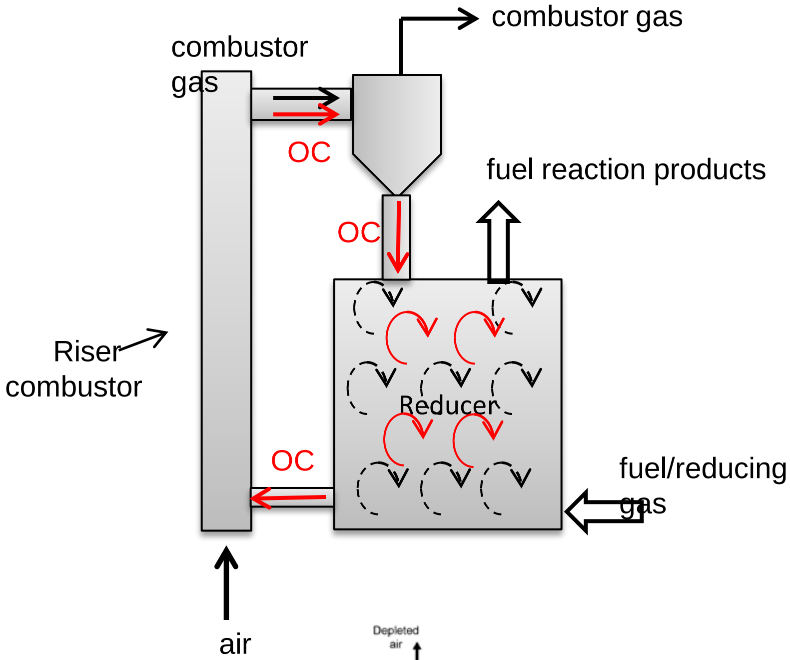


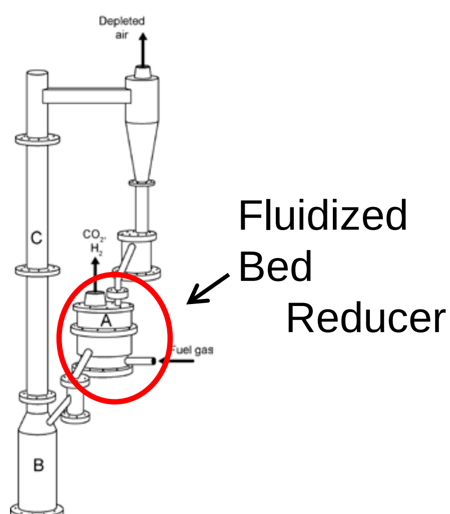
Reducer:	Coal + Fe_2O_3 → Fe/FeO + CO_2 + H_2O	(endothermic)
Oxidizer:	Air + Fe/FeO → Fe_2O_3 + Spent Air	(exothermic)
Overall:	Coal + Air → CO_2 + H_2O + Spent Air	(exothermic)

CDCL Process reduces exergy loss by recuperating the low grade heat while producing a larger amount of high grade heat

Modes of CFB Chemical Looping Reactor Systems

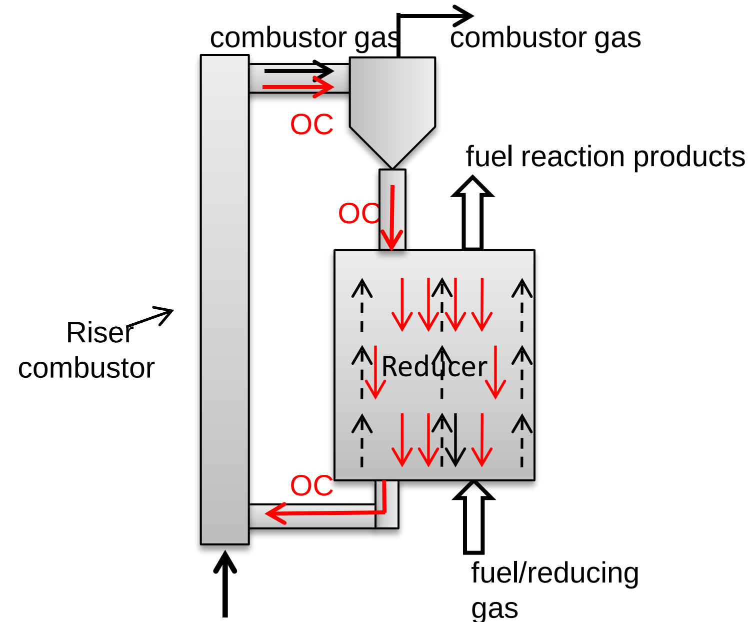
Mode 1- reducer: fluidized bed or co-current gas-solid (OC) flows

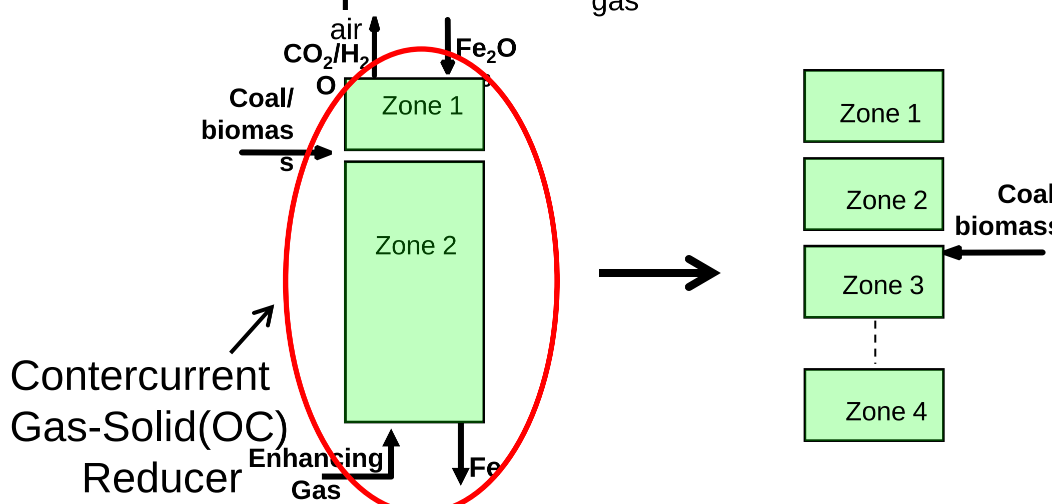




Chalmers University 10-kW$_{th}$ CLC System

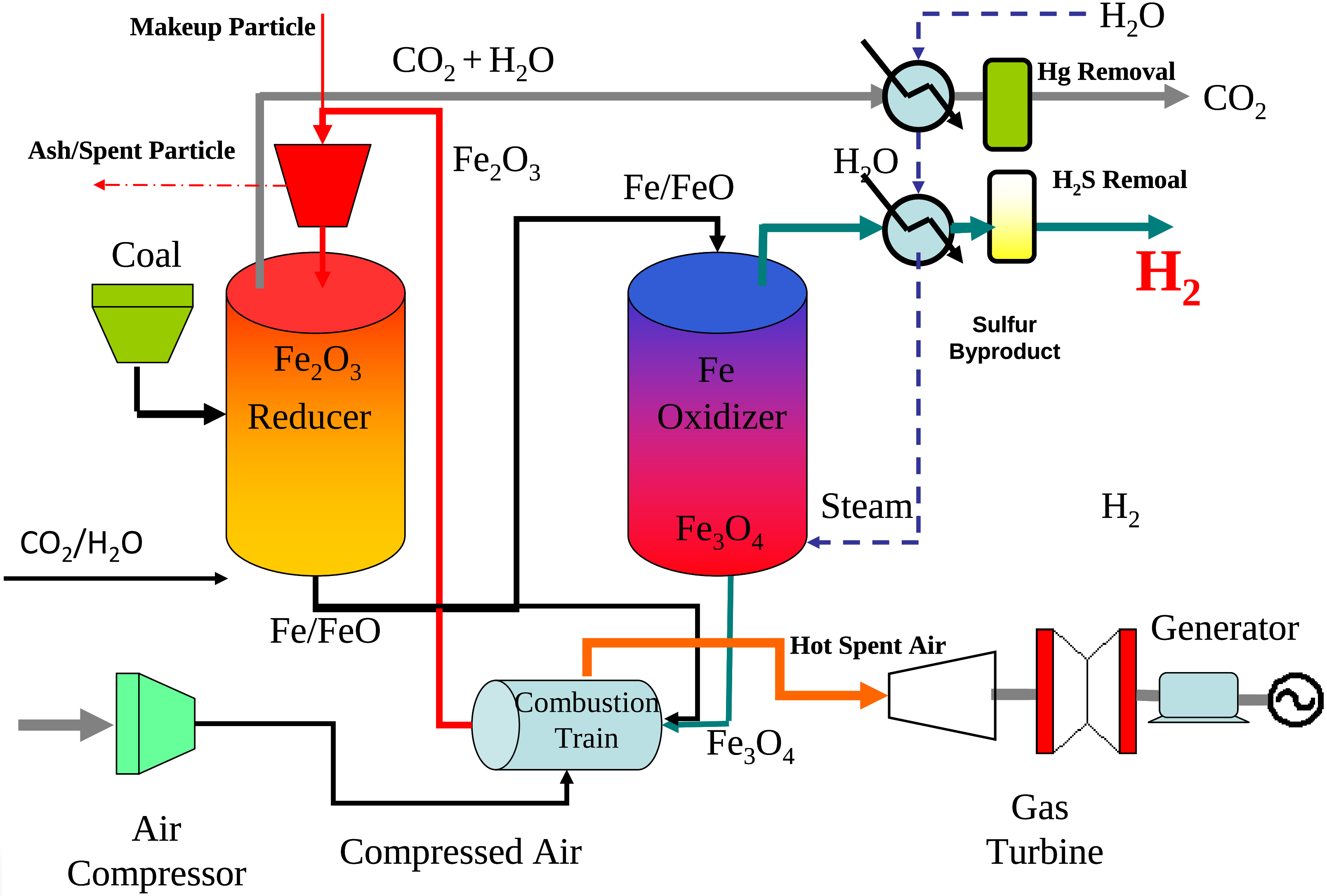
Mode 2 - reducer: gas-solid (OC) counter-current dense phase/moving bed flows





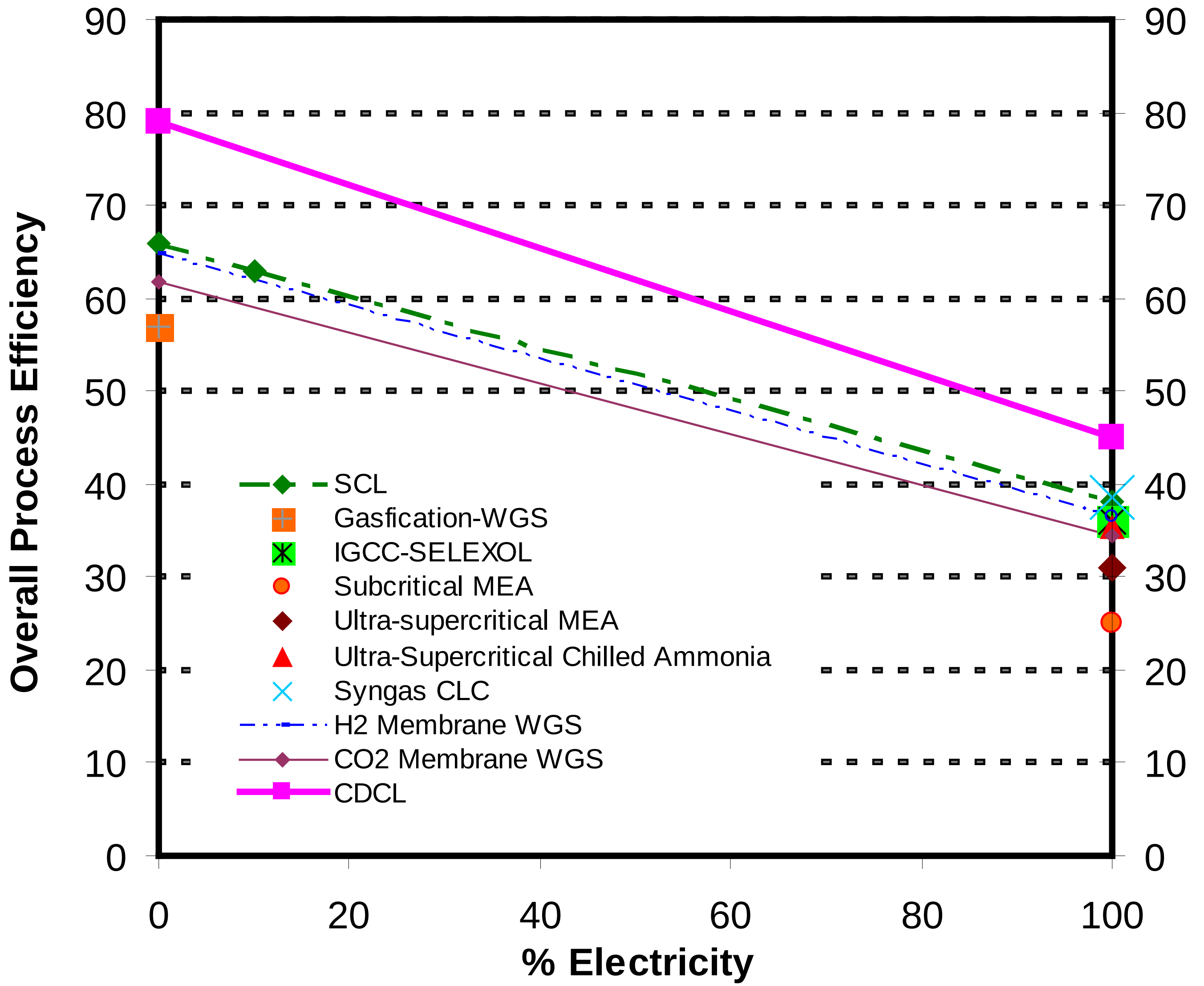
Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

Coal-Direct Chemical Looping Process for Electricity Generation or Electricity and Hydrogen Co-generation



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)

Comparison Among Gaseous Chemical Looping, Direct Coal Chemical Looping and Traditional Coal to Hydrogen/Electricity Processes



Assumptions used are similar to those adopted by the USDOE baseline studies.

Scope - Technical Status Report

1. Particles/TGA/Fixed Bed Reactivity Experiments
2. CDCL Moving Bed Reactor Configuration
3. Bench Moving Bed Studies of Stages I and II Reactions
4. Data Analysis
5. CDCL Scale-Up to 25KWth Unit
6. Net Power Calculation
7. Phase III Work

1. Oxygen Carrier Particle Development

Selection of Primary Metal

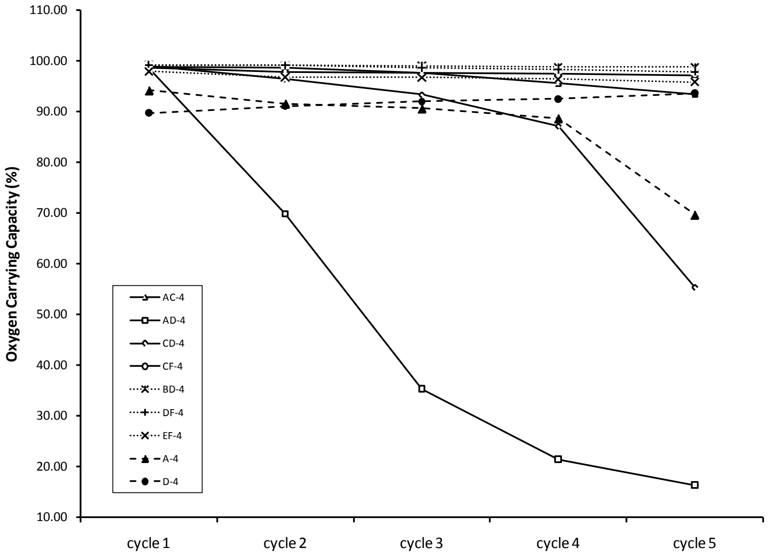
Primary Metal	Fe	Ni	Cu	Mn	Co
Support Materials	Al_2O_3, SiO_2, $MgAl_2O_4$, TiO_2, Bentonite, etc				
Cost	+	–	–	~	–
Oxygen Capacity[1](wt %)	**30**	**21**	**20**	**25[3]**	**21**
Thermodynamics for CLC	+	~	+	+	+
Kinetics/Reactivity[2]	–	+	+	+	–
Melting Points	+	~	–	+	+
Strength	+	–	~	~	~
Environmental& Health	~	–	–	~	–
Hydrogen Production	+	–	–	–	–

1. Maximum theoretical oxygen carrying capacity; 2. Reactivity with CH_4; 3. Mn_3O_4 is the highest oxidation state based on thermodynamics, although not thermodynamically favorable, Mn is assumed to be the lowest oxidation state

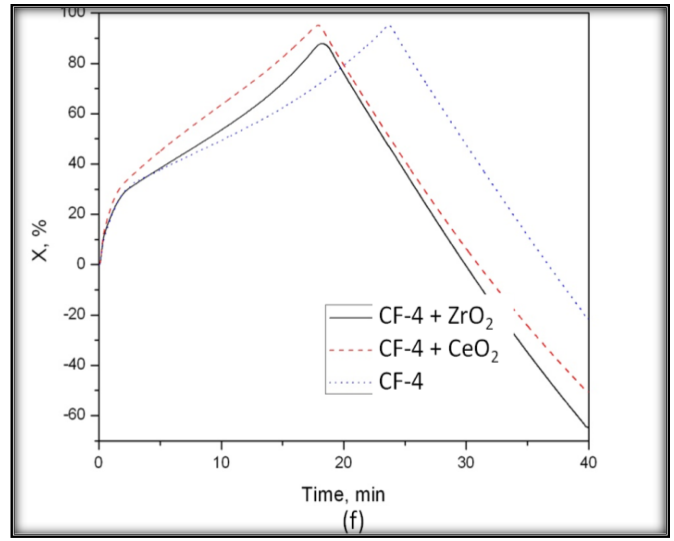
1. Oxygen Carrier (OC) Particle Development (cont.)

OC (over 150 particles) Performance with Volatile

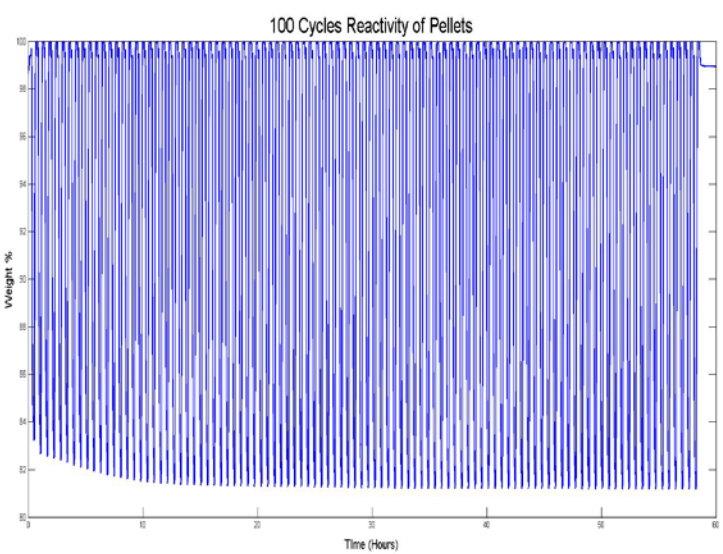
High Reactivity



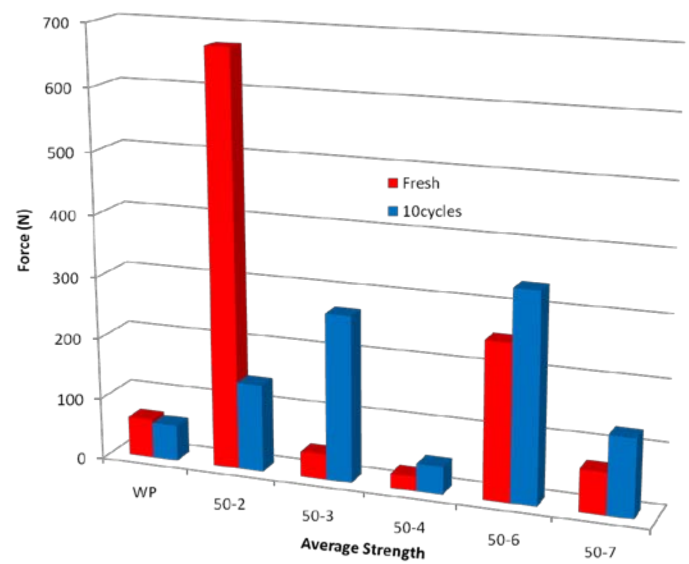
High Carbon Deposition Tolerance



High Recyclability



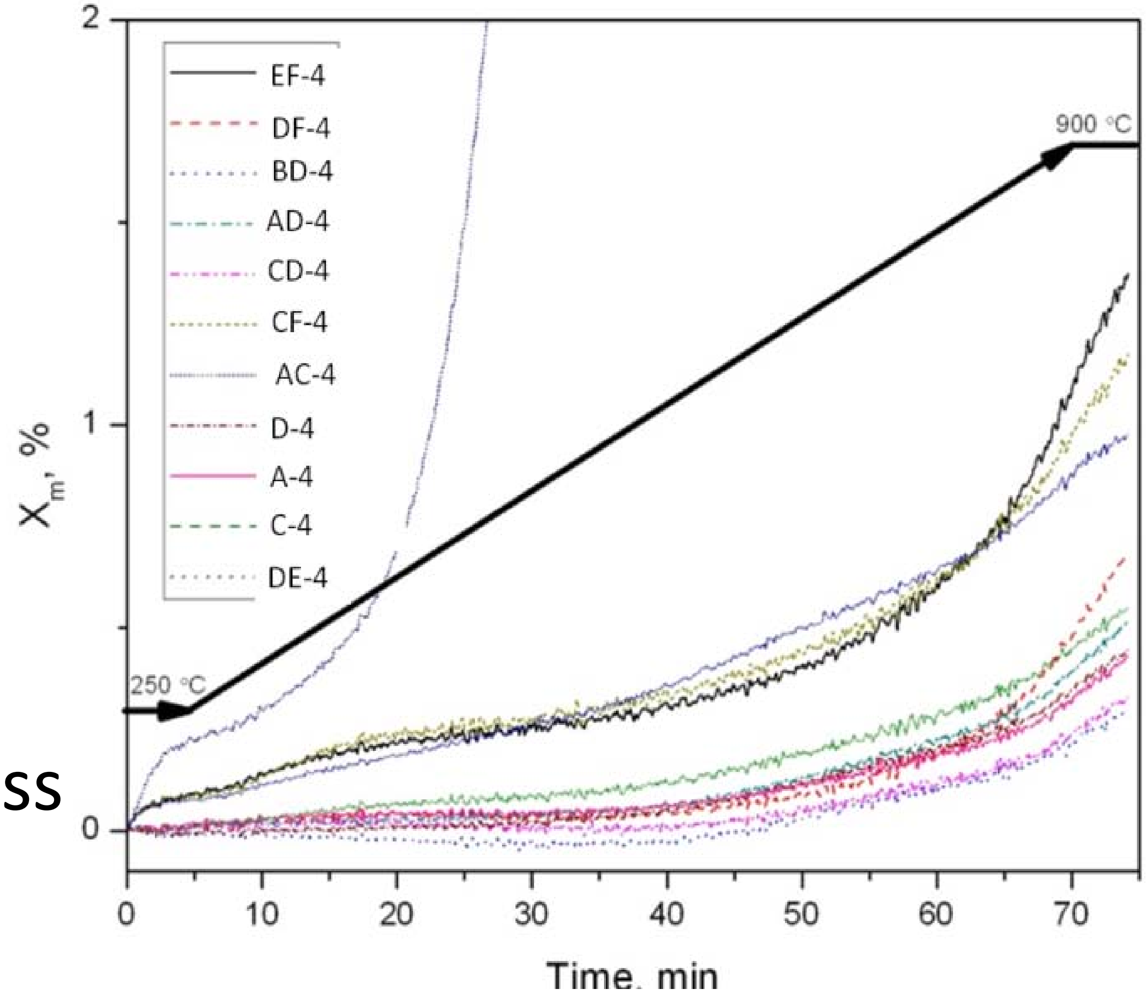
High Pellet Strength



1. Oxygen Carrier Particle Development (cont.)

Direct Reaction between OC and Char

- OC/Char = 5~10
- Temperature
  - 25°C to 250°C
  - 250°C for Drying
  - 250°C to 900°C
- Less than 2 wt.% Loss

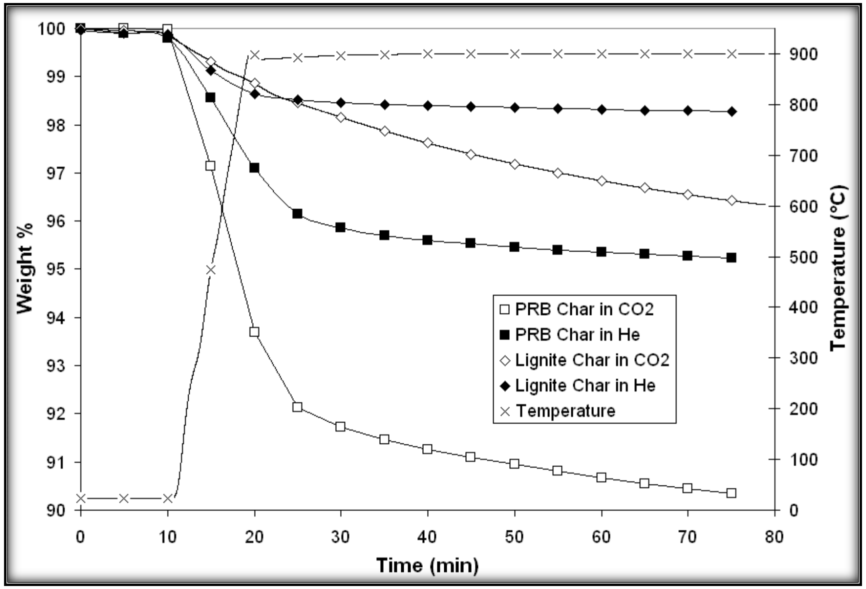


Slow solid-solid reaction between OC and char is slow. Enhancement is needed.

1. Oxygen Carrier Particle Development (cont.)

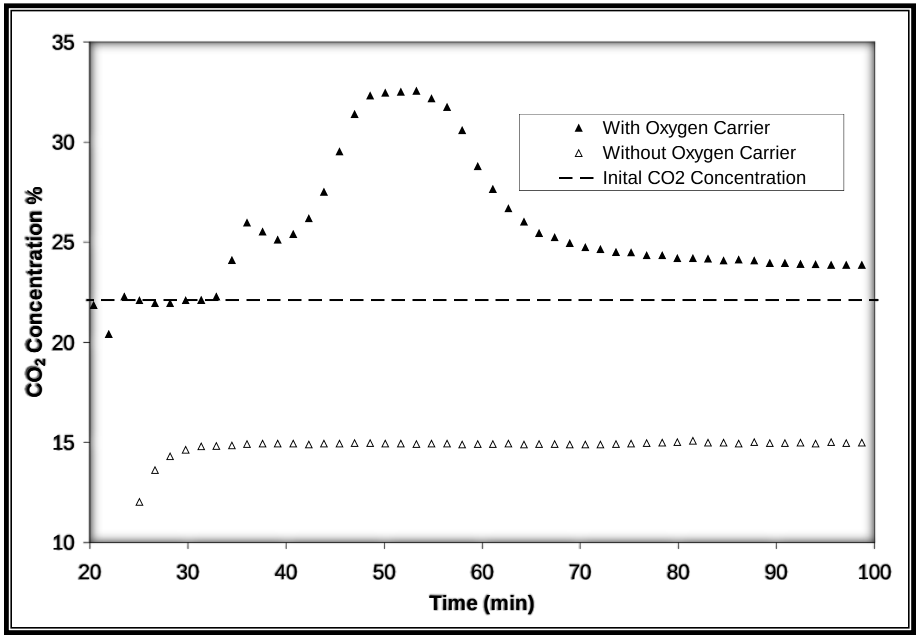
Enhancement of Char Conversion

TGA-FTIR Coupling



- Char and OC in He
- Reaction Initiated at 400-450°C
- Max. Intensity at 900°C
- CO_2 Formation Observation
- Enhanced Reaction at Higher T

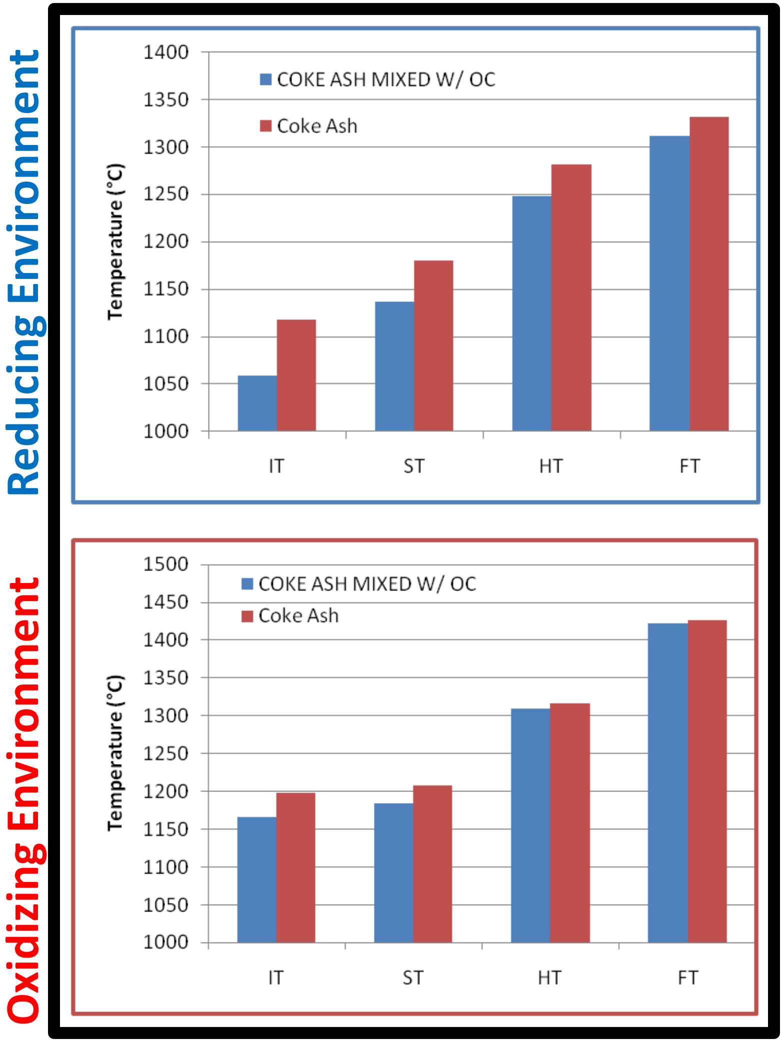
Fixed Bed Experiment

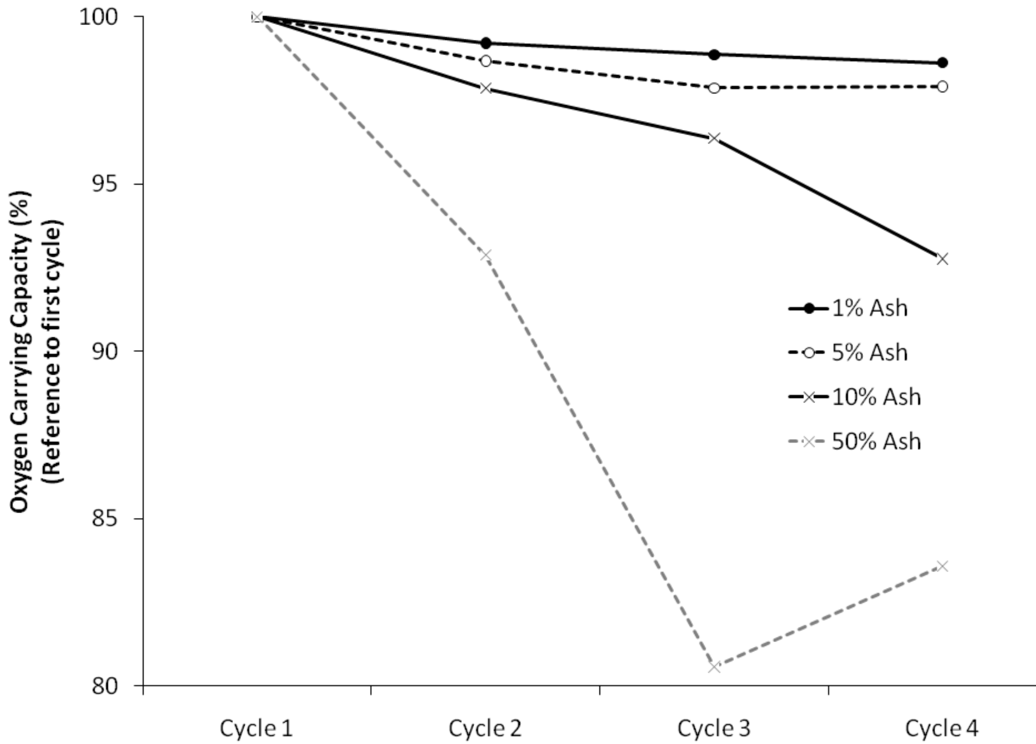


- Gas Analysis
- ~22 vol.% Initial CO_2
- Slow Char Conversion w/o OC
- ~70 min. for PRB Char Conversion

1. Oxygen Carrier Particle Development (cont.)

Ash Study

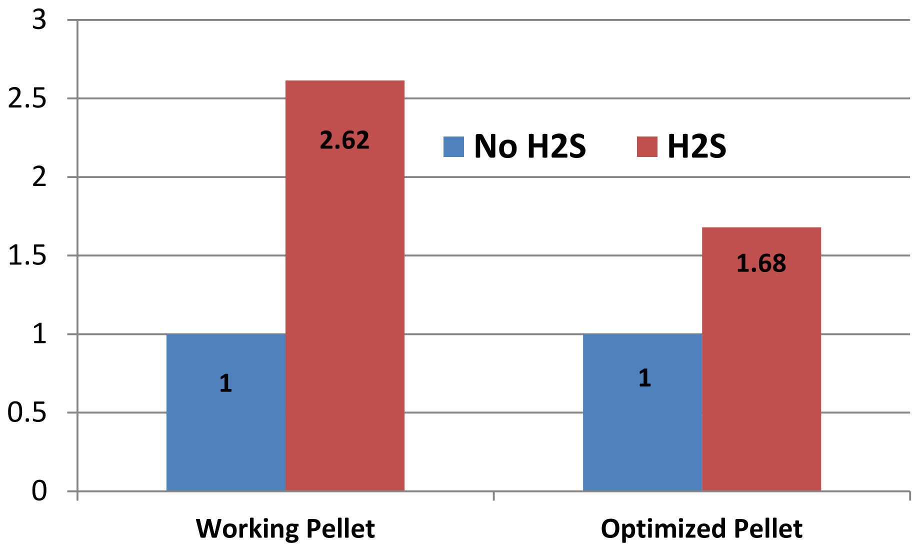


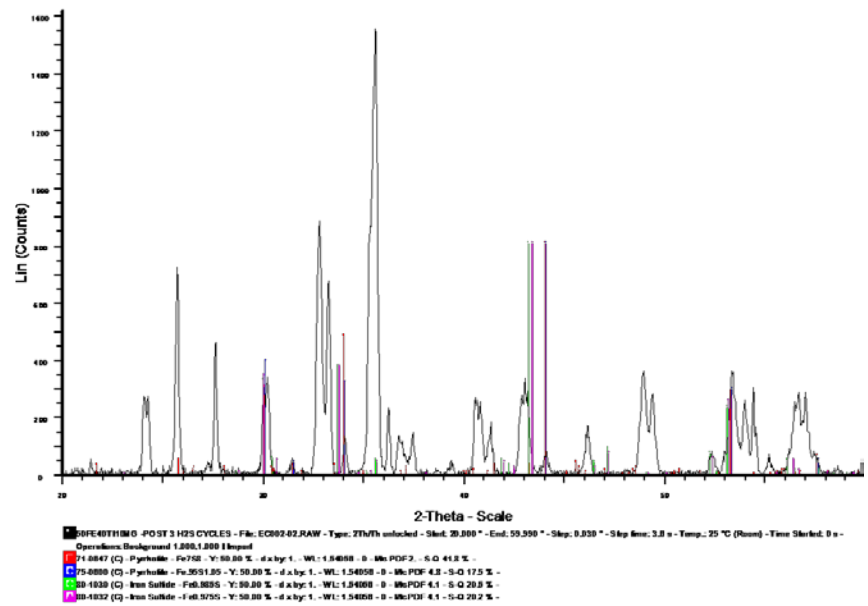


- •Effect of OC on bituminous coal ash deforming temp. is minimal.
- •Useful Data for combustor operation & Ash separation
- •Effect of ash on the reactivity and recyclability of oxygen carriers

1. Oxygen Carrier Particle Development (cont.)

Effect of Sulfur

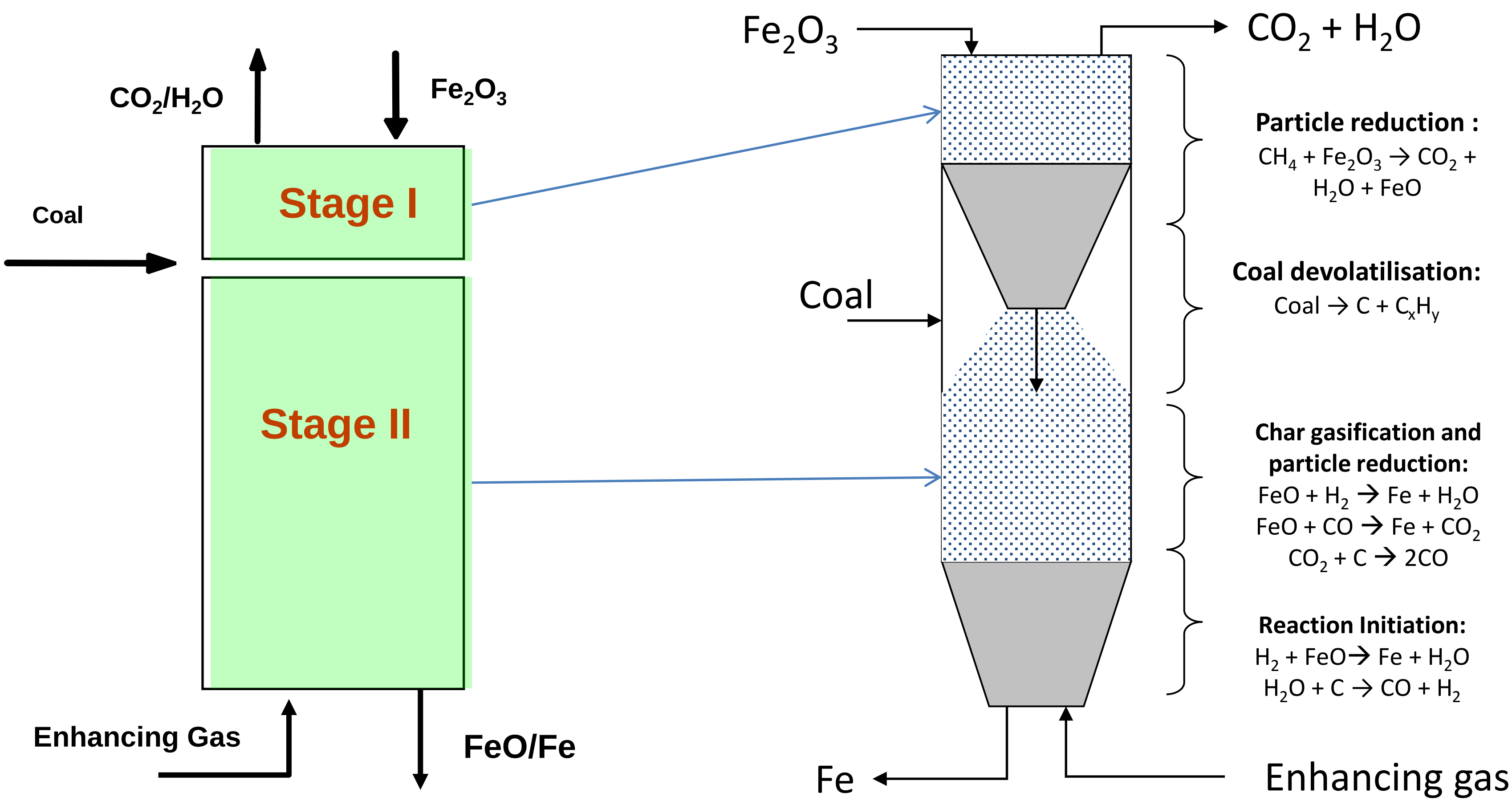




Effect of sulfur on the time of reduction for oxygen carrier particles

XRD results shows the formation of $Fe_{0.877}S$ after reduction

2. CDCL Moving Bed Reactor Configuration



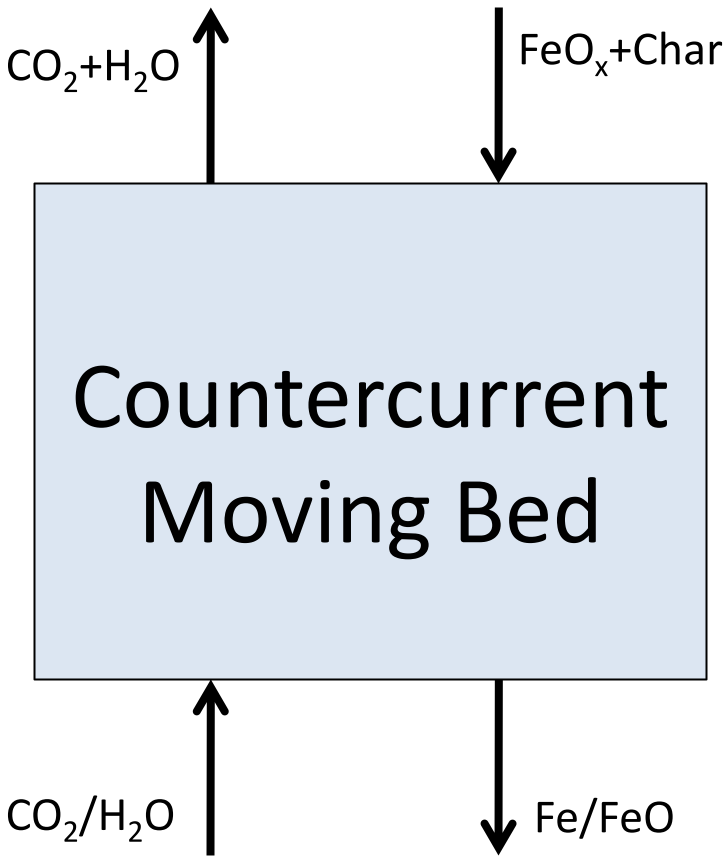
Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, “Combustion Looping Using Composite Oxygen Carriers” U.S. Patent No. 7,767,191 (2010, priority date 2003)

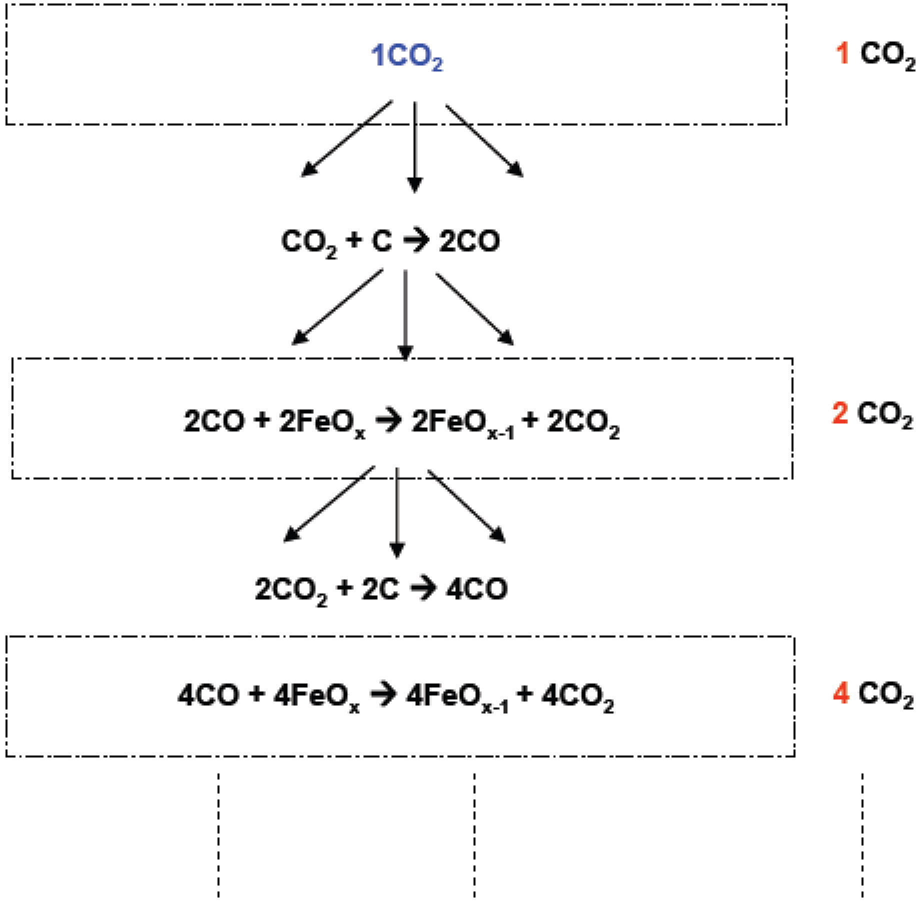
Two-stage moving bed

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

2. CDCL Moving Bed Reactor (cont.)

Stage II Configuration

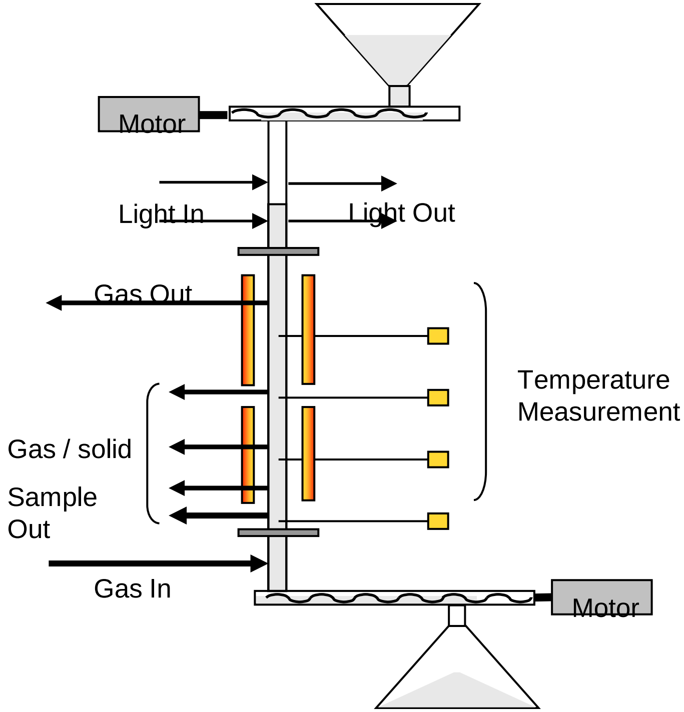


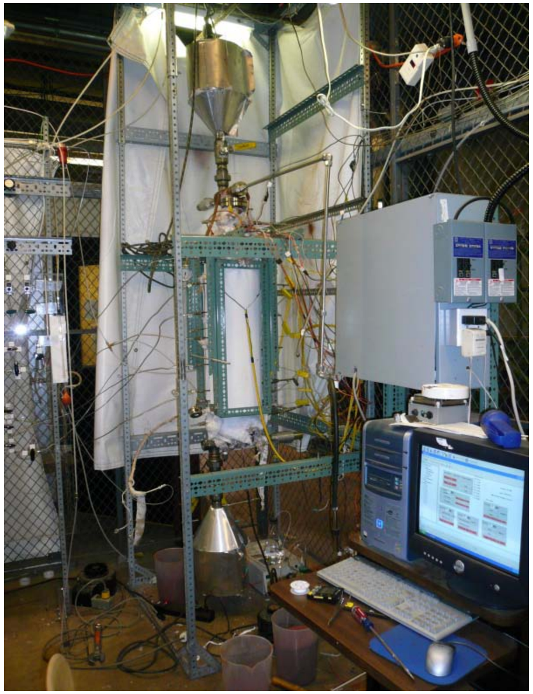


3. Bench Scale Testing

Stage I Test: Volatile Conversion

- Iron catalysts have the capability to crack volatiles to methane[1]
- Methane is the most stable volatile[2]
- Moving bed reactor for gas solid reaction study

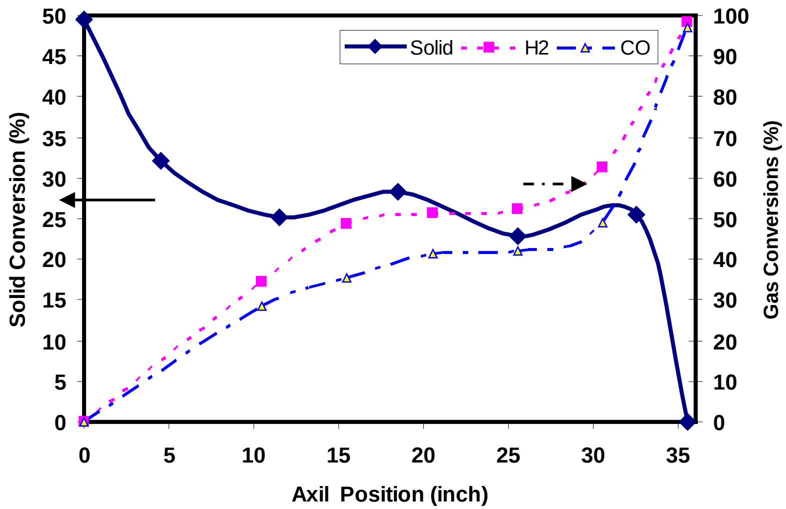




1. Simell, P. A., et al, "Catalytic Purification of Tarry Fuel Gas with Carbonate Rocks and Ferrous Materials," *Fuel*, 71(2), 211-218 (1992).
2. Gueret, C., M. Daroux, and F. Billaud, "Methane Pyrolysis: Thermodynamics," *Chemical Engineering Science*, 52(5), 815-827 (1997).

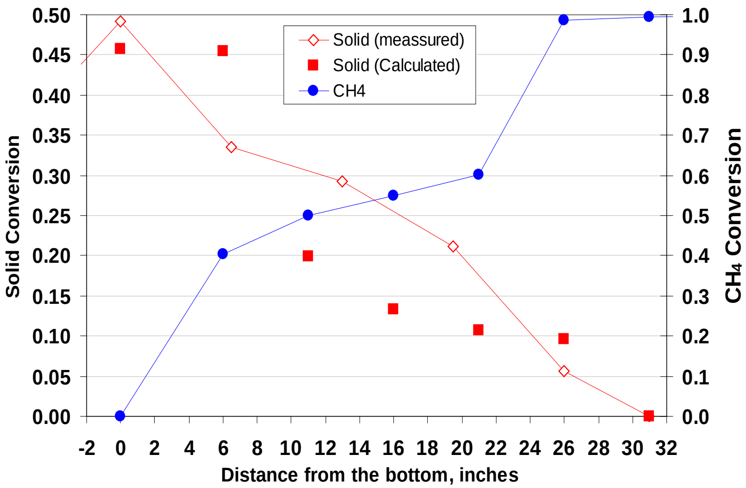
3. Bench Scale Testing (cont.)
Stage I Test: Volatile Conversion

Syngas Experiment



Nearly 100% conversion of syngas achieved

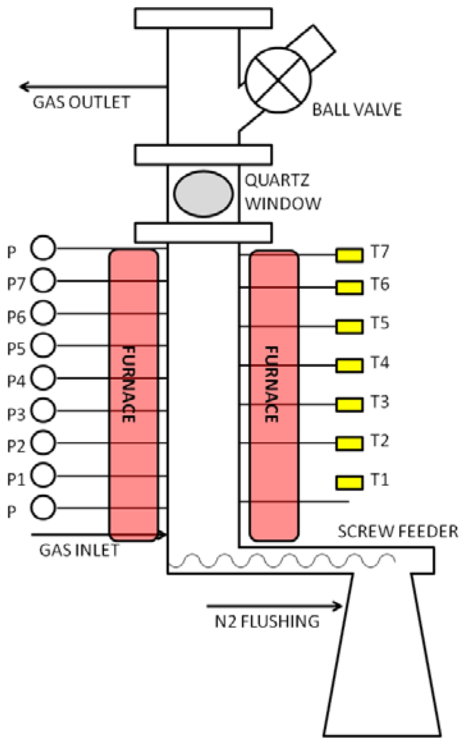
CH_4 Experiment

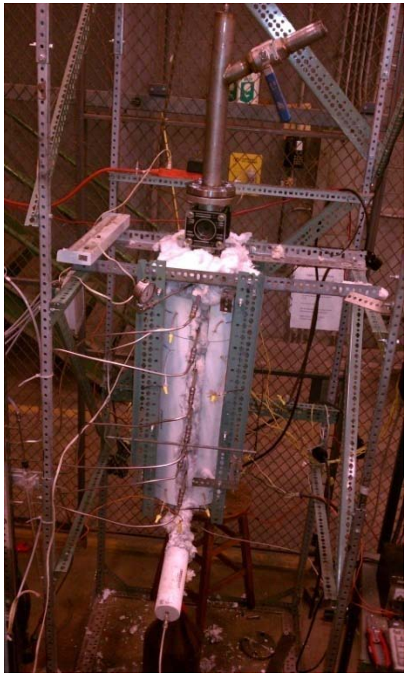


Nearly 100% conversion of CH_4 achieved

Syngas, Methane, and Other Hydrocarbons can be Fully Converted to CO_2 and H_2O in Stage I

3. Bench Scale Testing (cont.)
Stage II Test: Char Conversion

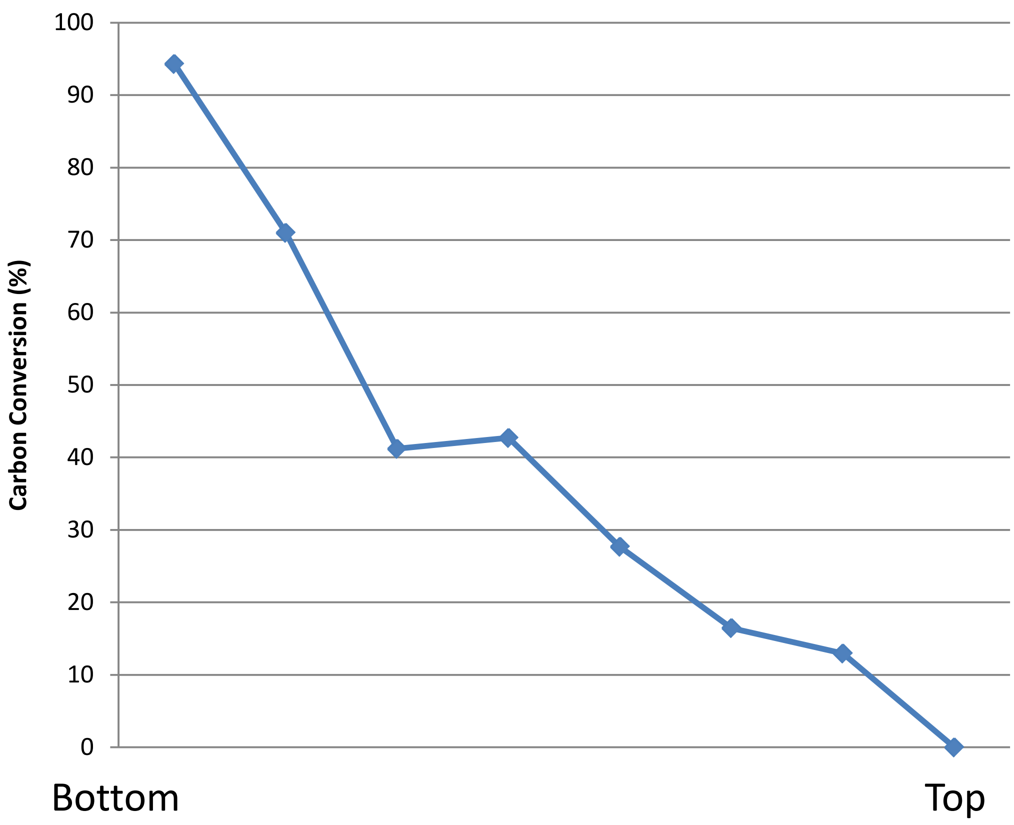


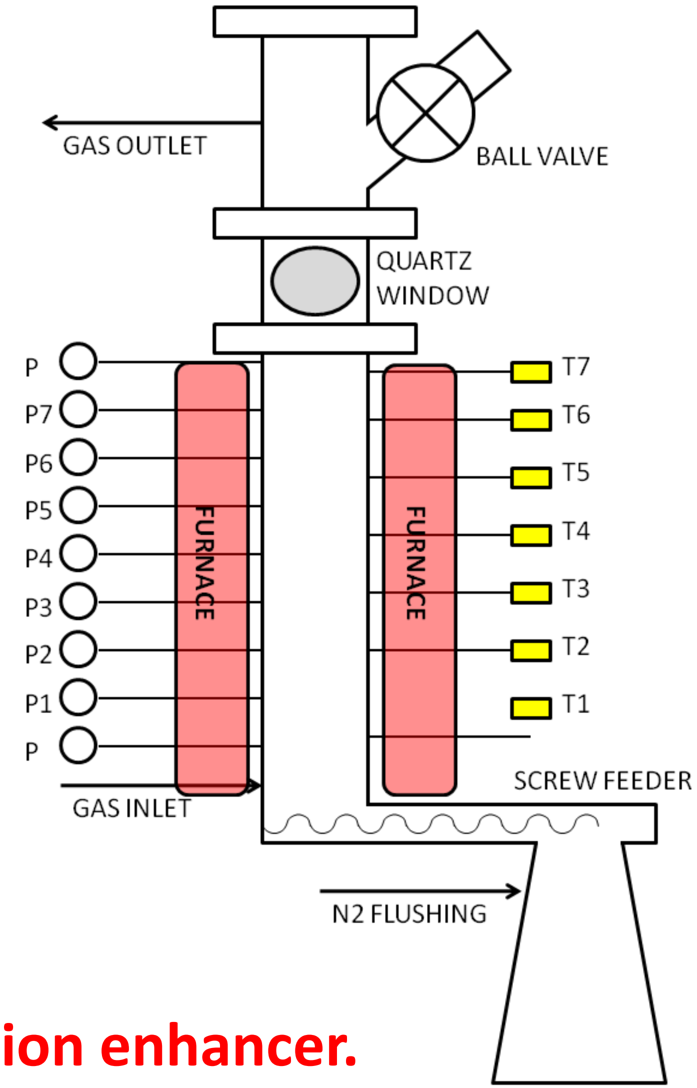


- 2.5kW$_{th}$ Capacity
- Bituminous Char Used
  - Low volatiles (2.89%)
  - High Carbon (84.4%)
- Gasification Enhancer
  - CO_2
  - H_2O
- Reaction Temperature Range: 950-1050°C
- Analysis Methods
  - Outlet Flowrate
    - C (Solid) → CO_2 + CO + CH_4(Gas)
    - Inlet Flow < Outlet Flow
  - Gas Chromatogram (GC)
    - Gas Sampling at Ports

3. Bench Scale Testing (cont.)

Stage II Test: Char Conversion



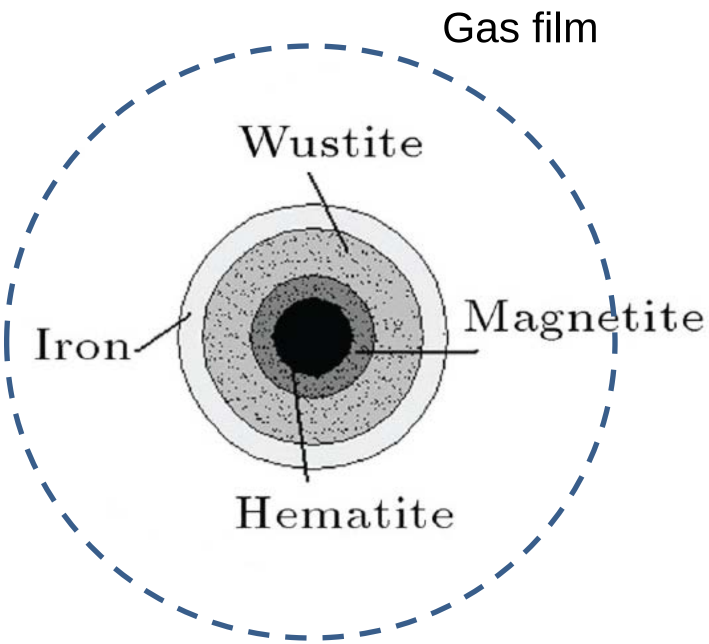


97% Char conversion with H_2O as gasification enhancer.

4. Data Analysis

Oxygen Carrier Particle Reduction Kinetics

- Three-interface Unreacted shrinking core model (USCM) *
  - Diffusion through the gas film
  - Intraparticle diffusion
  - Chemical reaction at reaction interface, first order reversible reaction
  - Isothermal and isobaric conditions
  - The pellet volume is unchanged



$$r_1 = \frac{P}{\tilde{R}T\omega}\left\{\begin{array}{l} A_3(A_2+B_2+B_3+F)+(A_2+B_2)(B_3+F)(y-y_1^*) \\ -[A_3(B_2+B_3+F)+B_2(B_3+F)](y-y_2^*)-A_2(B_3+F)(y-y_3^*) \end{array}\right\}$$

$$r_2 = \frac{P}{\tilde{R}T\omega}\left\{\begin{array}{l} [(A_1+B_1+B_2)(A_3+B_3+F)+A_3(B_3+F)](y-y_2^*) \\ -[B_2(A_3+B_3+F)+A_3(B_3+F)](y-y_1^*)-(A_1+B_1)(B_3+F)(y-y_3^*) \end{array}\right\}$$

$$r_3 = \frac{P}{\tilde{R}T\omega}\left\{\begin{array}{l} [(A_1+B_1)(A_2+B_2+B_3+F)+A_2(B_2+B_3+F)](y-y_3^*) \\ -A_2(B_3+F)](y-y_1^*)-(A_1+B_1)(B_3+F)(y-y_2^*) \end{array}\right\}$$

$$A_i = \frac{1}{(1-R_i)^{2/3}}\frac{1}{k_i(1+1/K_i)} \qquad B_1 = \frac{(1-R_2)^{1/3}-(1-R_1)^{1/3}}{(1-R_1)^{1/3}(1-R_2)^{1/3}}\frac{d_p}{2D_1}$$

$$B_2 = \frac{(1-R_3)^{1/3}-(1-R_2)^{1/3}}{(1-R_2)^{1/3}(1-R_3)^{1/3}}\frac{d_p}{2D_2} \qquad B_3 = \frac{1-(1-R_3)^{1/3}}{(1-R_3)^{1/3}}\frac{d_p}{2D_3}$$

$$F = 1/k_f$$

$$\omega = (A_1+B_1)[A_3(A_2+B_2+B_3+F)+(A_2+B_2)(B_3+F)]+A_2[A_3(B_2+B_3+F)+B_2(B_3+F)]$$

Yanagiya T., Yagi J., Omori Y. 1979 reduction of iron oxide pellets in moving bed. Ironmaking and steelmaking, No.3 93-100

4. Data Analysis (cont.)
Stage I Modeling: Volatile Conversion

- Assumptions:
  - Both gas and solid streams are in plug flow.
  - Three-interface USCM for representing the overall reaction rate of the pellet
  - Negligible temperature difference between gas and solid.
- Governing Equations
  - C_i: CO, CO_2, H_2, H_2O
  - E_i: Fe_2O_3,Fe_3O_4,FeO,Fe

$$\frac{\partial \varepsilon C_i}{\partial t} = -Ug_i \frac{\partial \varepsilon C_i}{\partial x_i} + \sum_l \upsilon_{li} \frac{6(1-\varepsilon) r_l}{d_p}$$

$$\frac{\partial E_i}{\partial t} = -Us_i \frac{\partial E_i}{\partial x_i} + \sum_l \upsilon_{li} \frac{6(1-\varepsilon) r_l}{d_p}$$

- Numerical Methods
  - Both temporal and spatial terms are discretized by fifth order schemes
  - Executed in Fortran
- The overall fraction reduction could be expressed as follows

$$R = 0.1111 R_M + 0.1889 R_W + 0.7 R_F$$

- R_M conversion of reaction from Fe_2O_3 to Fe_3O_4
- R_W conversion of reaction from Fe_3O_4 to $Fe_{0.952}O$
- R_F conversion of reaction from $Fe_{0.952}O$ to Fe

5. CDCL Scale-Up to 25KWth Unit

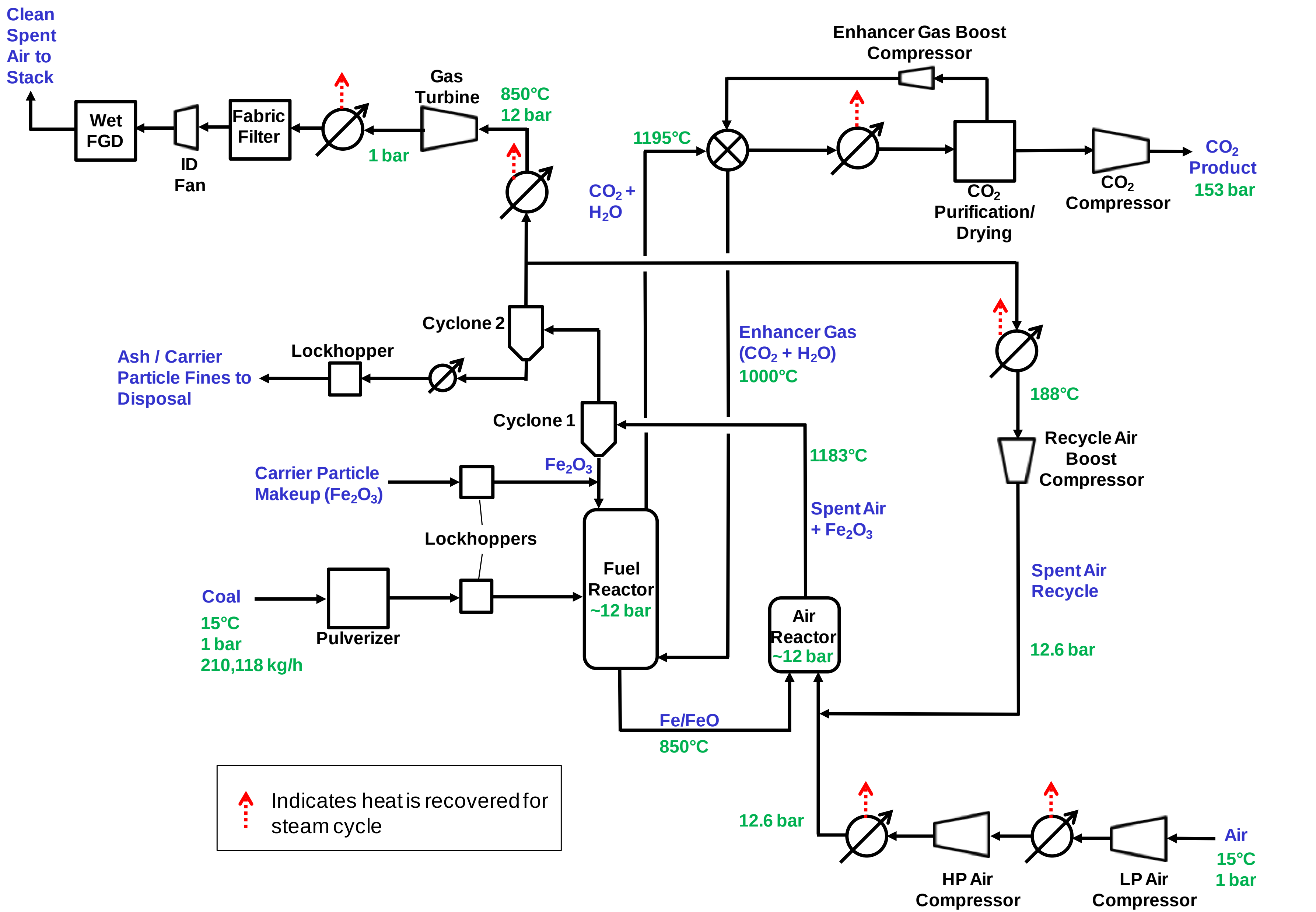
- Cold Flow Model Study
  - Feasibility of Reactor Design
  - Hydrodynamic Study of OC, Coal and Ash
  - OC/Coal Residence Time
  - Coal Injection Study
  - Fine Removal Device

6. 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 9 – Subcritical PC plant without CO_2 capture ("Base Case")
    - Case 10 – Subcritical PC plant with MEA scrubbing system for post-combustion CO_2 capture ("MEA Case")
- All plants evaluated using a common design basis
  - 550 MW_e net electric output
  - Illinois No. 6 coal (11,666 Btu/lb HHV, 2.5% sulfur, 11.1% moisture as received)
  - Subcritical steam cycle: 2,400 psig/1,050°F/1,050°F (166 bar/566°C/566°C)
  - ≥ 90% CO_2 capture efficiency (MEA and CDCL Cases)
  - CO_2 compressed to 2,215 psia (153 bar)
- Results are preliminary, will be used to guide further design improvements

6. Process Simulation and Analysis (cont.)



Aspen Plus® Modeling Results

	Base Plant	MEA Plant	CDCL Plant
Coal Feed, kg/h (lb/h)	198,391 (437,378)	278,956 (614,994)	210,118 (463,231)
CO_2 Emissions, kg/MWh_{net} (lb/MWh_{net})	856 (1,888)	121 (266)	~0 (~0)
CO_2 Capture Efficiency, %	0	90	~100
Solid Waste,[a] kg/MWh_{net} (lb/MWh_{net})	35 (77)	49 (108)	39 (87)
Net Power Output, MW_e	550	550	550
Net Plant HHV Heat Rate, kJ/kWh (Btu/kWh)	9,788 (9,277)	13,764 (13,046)	10,357 (9,817)
Net Plant HHV Efficiency, %	36.8	26.2	34.8
Energy Penalty,[b] %	-	29	5

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

7. Accomplishments / Phase III Plans

- Completed synthesis / screening of >150 oxygen carrier particles and selected particles with optimal performance for further testing
- Demonstrated >99% conversion of CH_4 (volatiles) at 2.5 kW_t scale
- Demonstrated 90-95% conversion of coal char at 2.5 kW_t scale using enhancer gas (CO_2 & H_20)
- Performed cold flow modeling to demonstrate and evaluate solids handling
- Plans for Phase III (2011.8 -2012.8)

Phase III												
Task	1	2	3	4	5	6	7	8	9	10	11	12
Subtask 8.2: Sub-pilot Scale CDCL System Construction and Shakedown												
Milestone - Proof-of-concept Scale Reactor												
Task 9.0: Integrated System Performance												
Subtask 9.1: Continuous in-situ CO_2 Capture												
Milestone - continuous operation of Unit												
Task 10.0: Techno-Economic Analysis performed by CONSOL												
Milestone - Techno -economic Analysis Report												

Thanks