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

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AND BIOMOLECULAR ENGINEERING

Clean Coal Research Laboratory at The Ohio State University

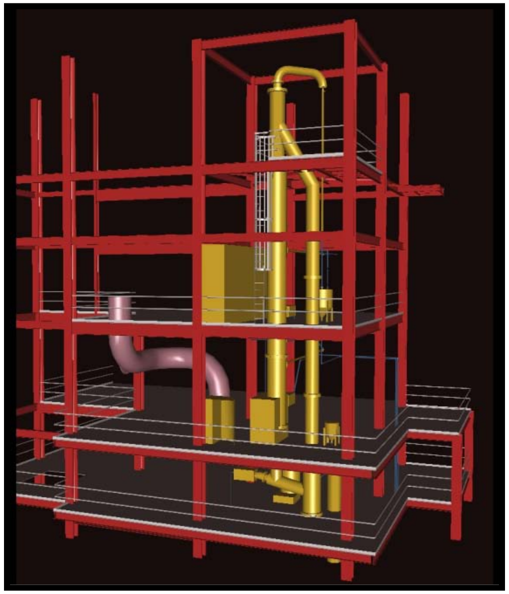
Coal-Direct Chemical Looping

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

HPHT Slurry Bubble Column

Partners

Government Agencies

- DOE/NETL: Bruce Lani, Timothy Fout, David Lang
- OCDO/ODOD: Chad Smith

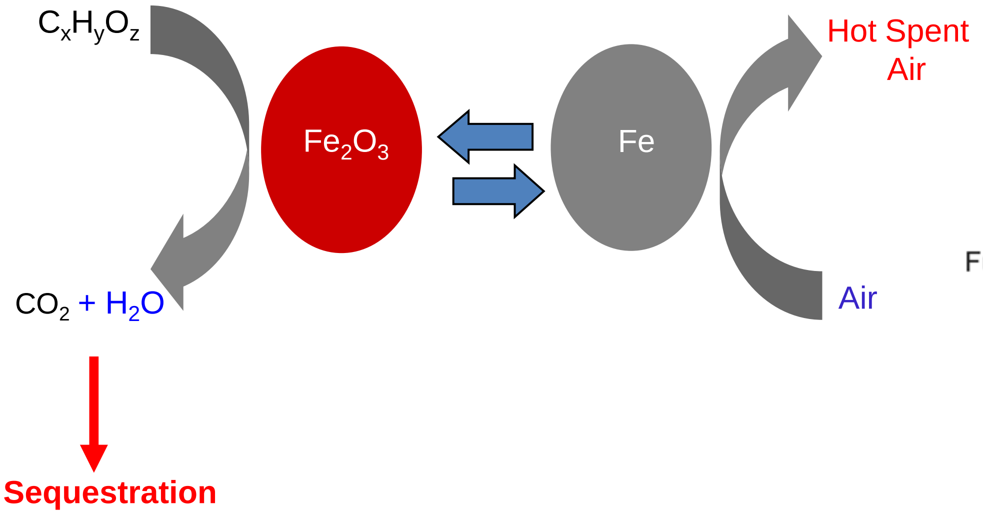
Industrial Collaborators

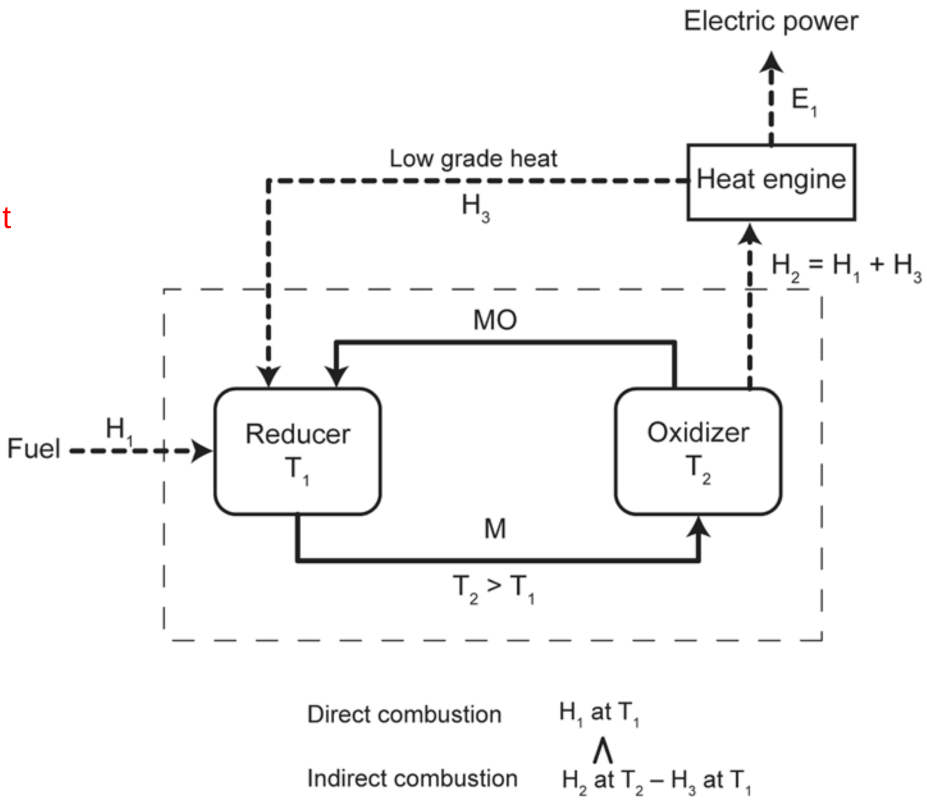
- Babcock & Wilcox (B&W): Tom Flynn, Luis Vargas, Doug Devault, Bartev Sakadjian and Hamid Sarv
- ClearSkies: Bob Statnick
- CONSOL Energy: Dan Connell, Richard Winschel, and Steve Winberg
- Air Products: Robert Broekhuis, Bernard Toseland
- Shell/CRI

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





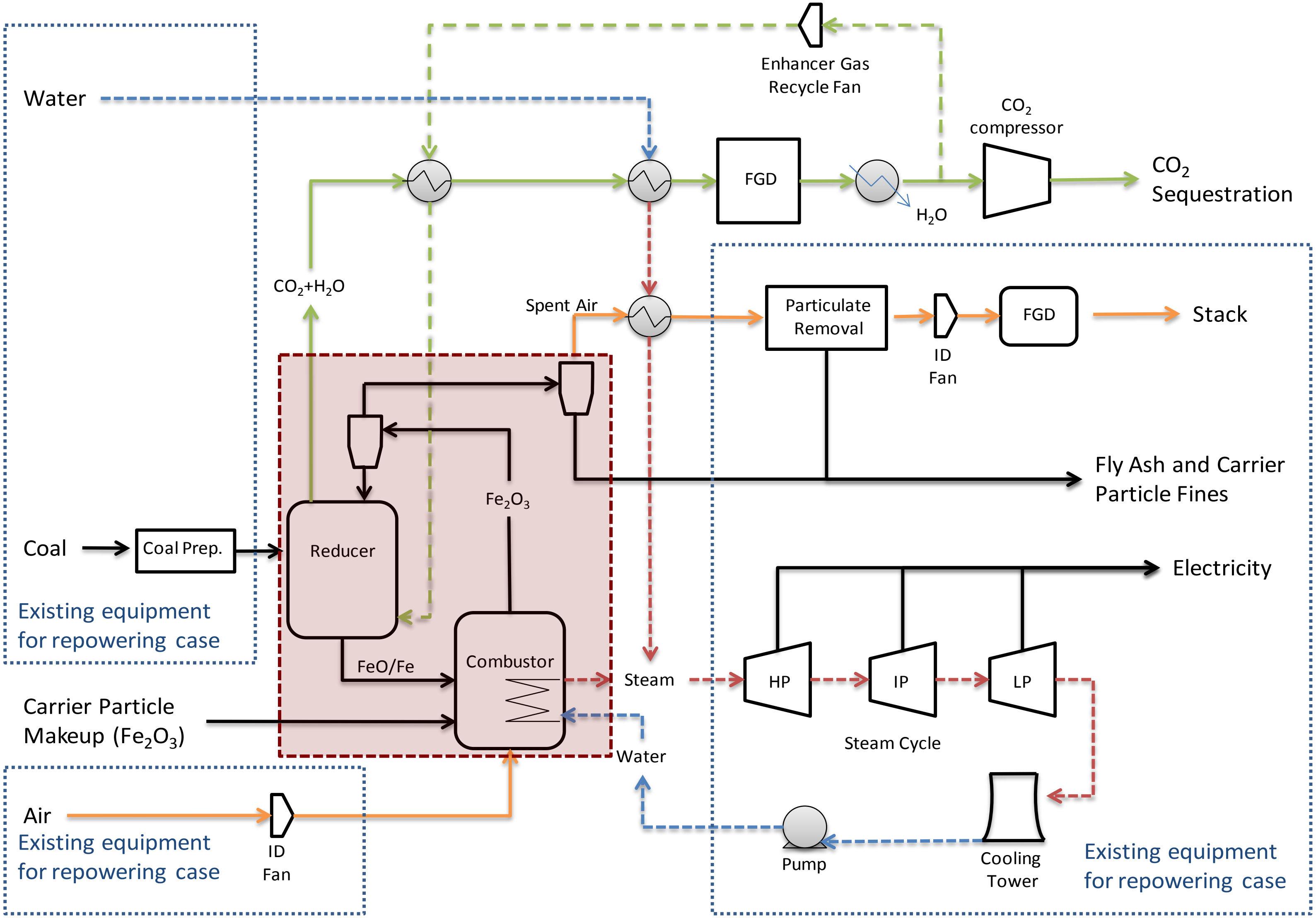
Reducer: Coal + Fe_2O_3 → Fe/FeO + CO_2 + H_2O (endothermic)

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

Coal-Direct Chemical Looping Process for Retrofit/Repower

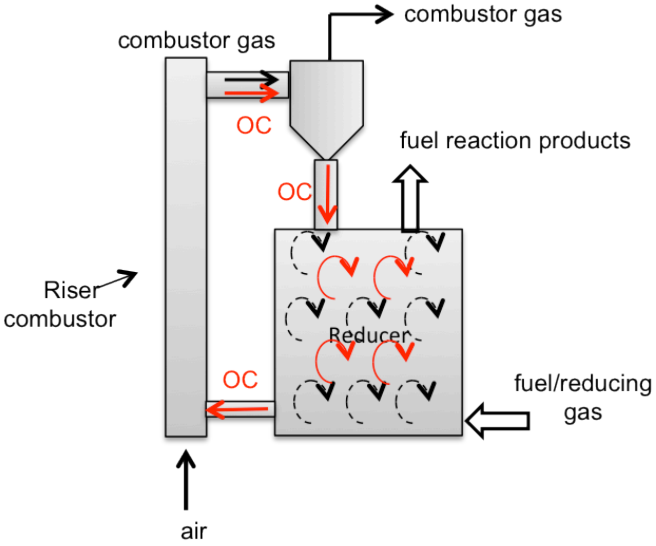


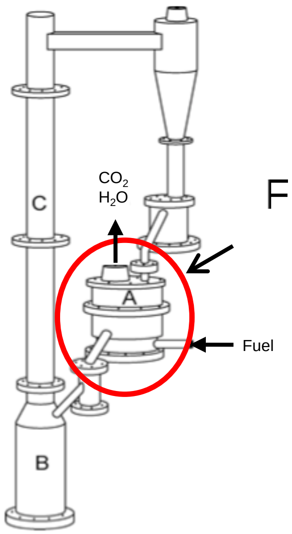
Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

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

Modes of CFB Chemical Looping Reactor Systems

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

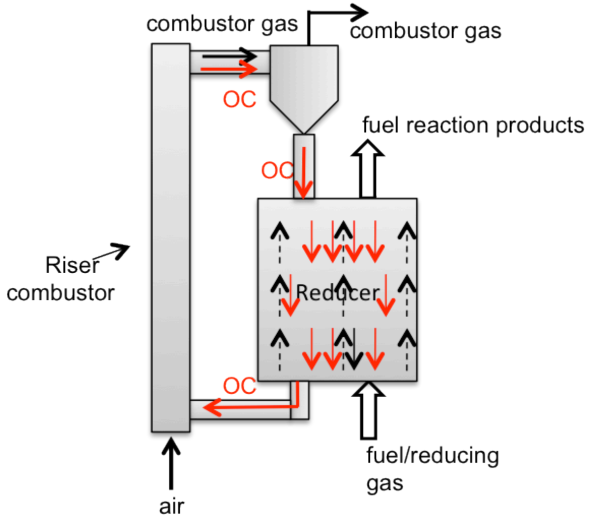


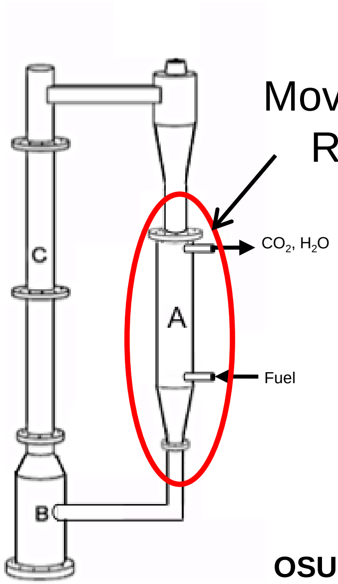


Fluidized Bed Reducer

Chalmers University CLC System

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





Moving Bed Reducer

OSU CLC System

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 Design Comparison Mode 1 versus Mode 2 Using Fe-Carrier

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

CDCL Fuel Feed Tests Studied

Fuel Feedstock	Type	Fuel Flow (lb/hr)	Enhancer	Fuel Conversion
Coal volatile	CH_4	0.1-0.4	H_2	99.80%
Coal char	Lignite	0.7-2.0	CO_2/H_2O	94.90%
	Metallurgical Coke	0.05-3	CO_2/H_2O	50-97.30%
Coal	Sub-Bituminous	0.05-7	CO_2/H_2O	60 – 99+%
	Bituminous	0.05-3	CO_2/H_2O	70 – 95%
	Anthracite	0.2-0.7	CO_2/H_2O	95.50%
Biomass	Wood pellets	0.1	CO_2	75 – 99%

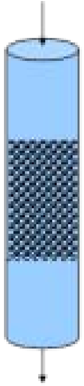
- Combined >530 hours of operational experience
- CO/H_2 Fuel feedstock tested in SCL sub-pilot process for over 300 hours of successful operation
- Successful results for all coal feedstock tested

OSU CDCL Chemical Looping Process Development

Scale

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

300+ hours operation with ***>99%*** volatile conversion in Stage I test, ***>95%*** char conversion in Stage II Test

Bench Scale Tests

Fuel Tested

- Syngas
- Natural gas
- Biomass
- Met coke
- Lignite char
- PRB
- Illinois 6
- Pittsburgh 8
- Anthracite

Sub-Pilot CDCL Integrated Tests

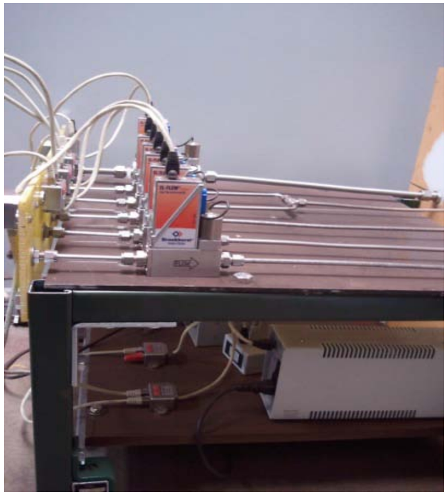
200+ hours operation with ***>80%*** solid fuel conversion, smooth solid circulation, gas sealing and in-situ ash removal

Time

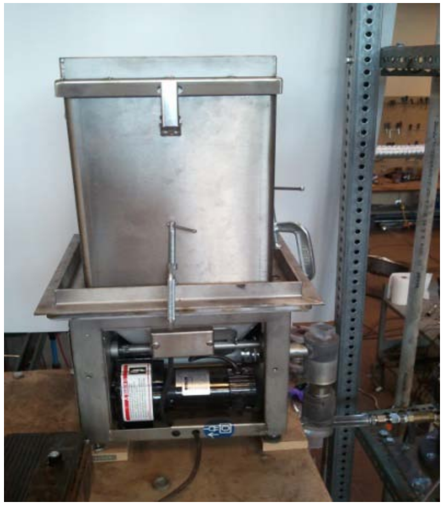
25 kW_{th} Sub-Pilot Demonstration

- Fully assembled and operational
- >200 hours of Operational experience
  - 3-day continuous operation
- Harmonious solid circulation
- Confirmed non-mechanical gas sealing under reactive conditions
- 12 test campaigns completed

25 kW$_{th}$ Sub-Pilot Demonstration

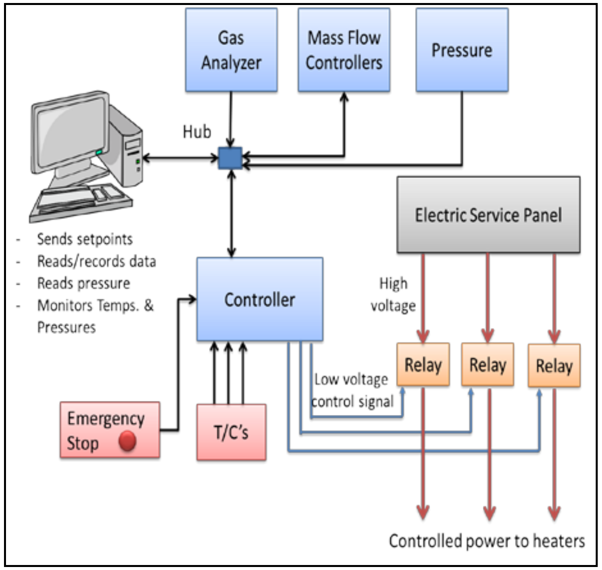


Gas Flow Control System



Coal Injection System

Gas Storage



Gas Analyzer

Mass Flow Controllers

Pressure

Hub

Electric Service Panel

- Sends setpoints
- Reads/records data
- Reads pressure
- Monitors Temps. & Pressures

Controller

High voltage

Relay

Relay

Relay

Low voltage control signal

Emergency Stop

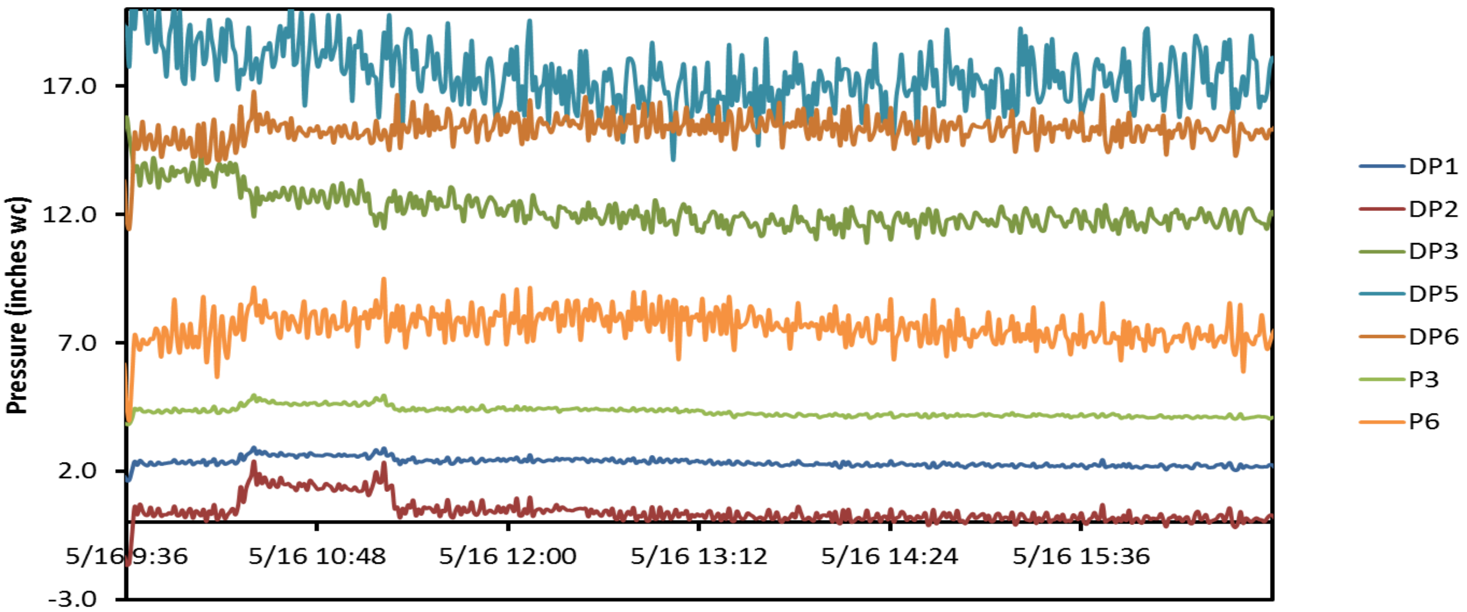
T/C's

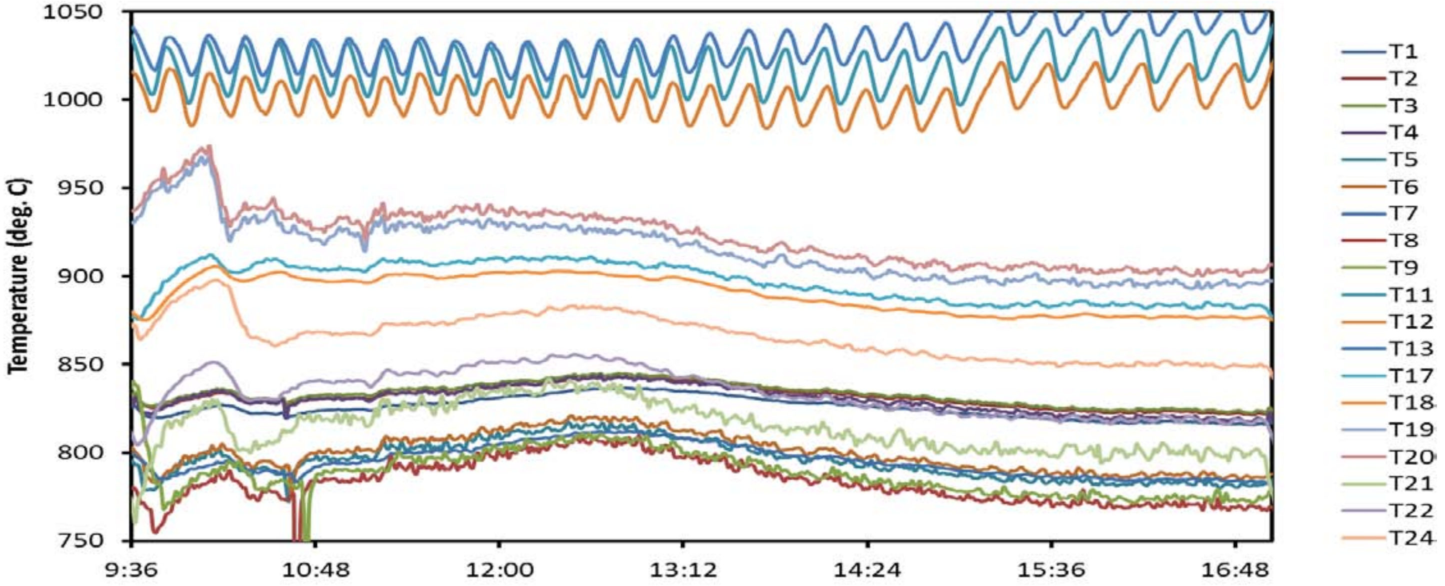
Controlled power to heaters

Process Control & Automation

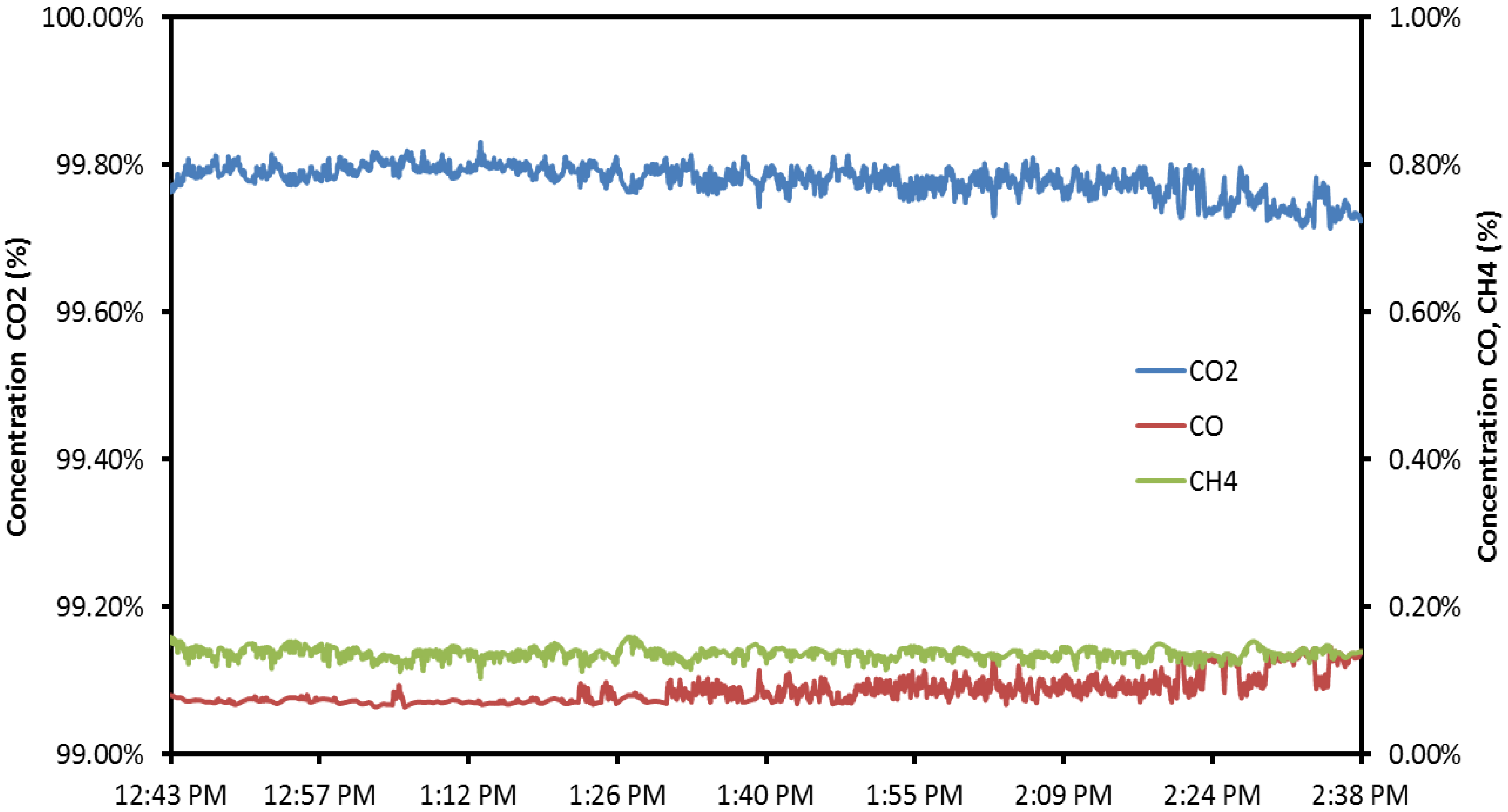
Gas Analyzer

3-day Sub-Pilot Continuous Run - *Sample Results*





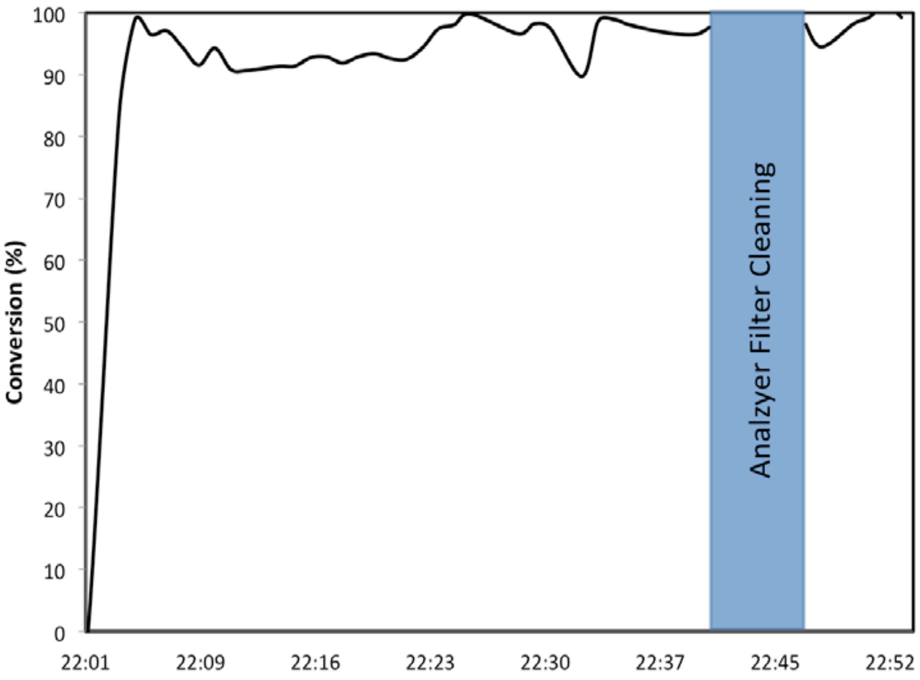
3-day Sub-Pilot Continuous Run - *Sample Results*



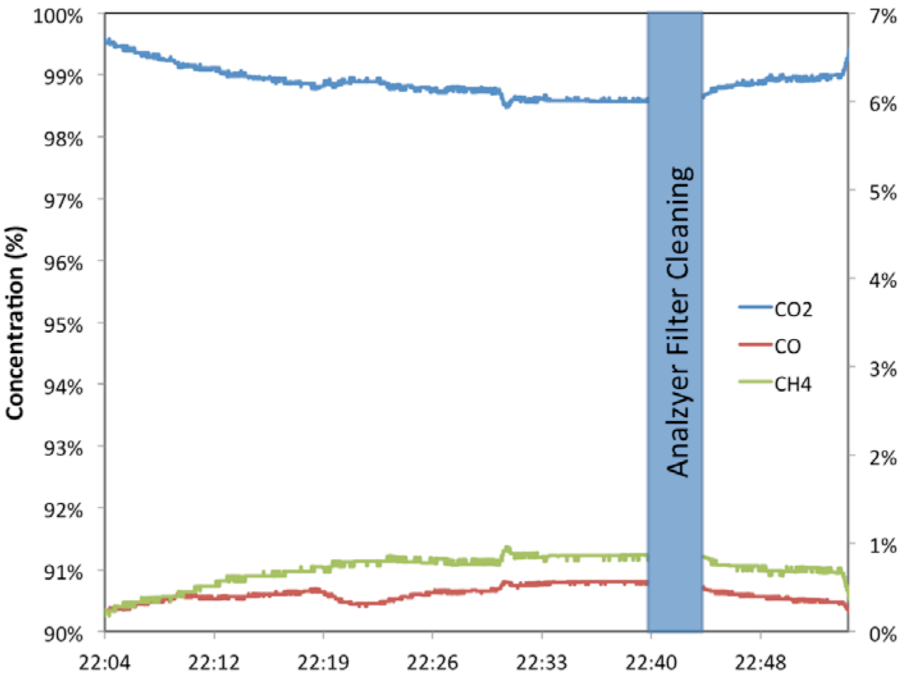
Reducer Gas Outlet Concentration Profile (Run 2A)

Sub-Pilot Continuous Run - *Sample Results*

Carbon Conversion Profile



Gas Concentration Profile

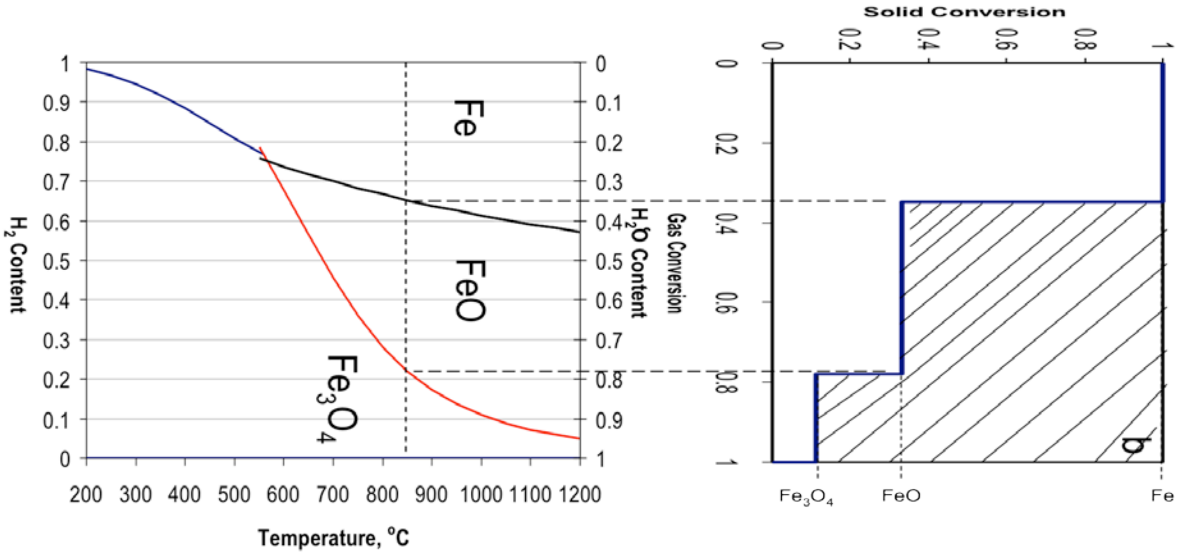


- ~24-hour Operation
- 90-99+% Carbon Utilization
- ~99 vol.% CO_2 Purity
- ~0.6 vol.% CO and ~0.2 vol.% CH_4
  - Higher than metallurgical coke due to higher volatile contents

Mode II: Moving Bed (OSU) Reactor Development

CDCL Moving Bed Reactor – Stage I

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 $y = \dfrac{3n_{Fe_2O_3} + 4n_{Fe_3O_4} + n_{FeO}}{n_{Fe}}$

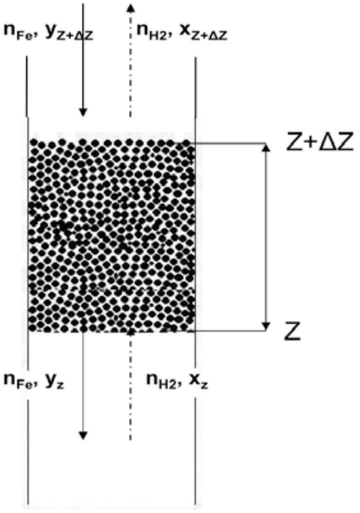
Fixed gas molar flowrate $n_{H2} + n_{H2O}$,

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

Oxygen Balance

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

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

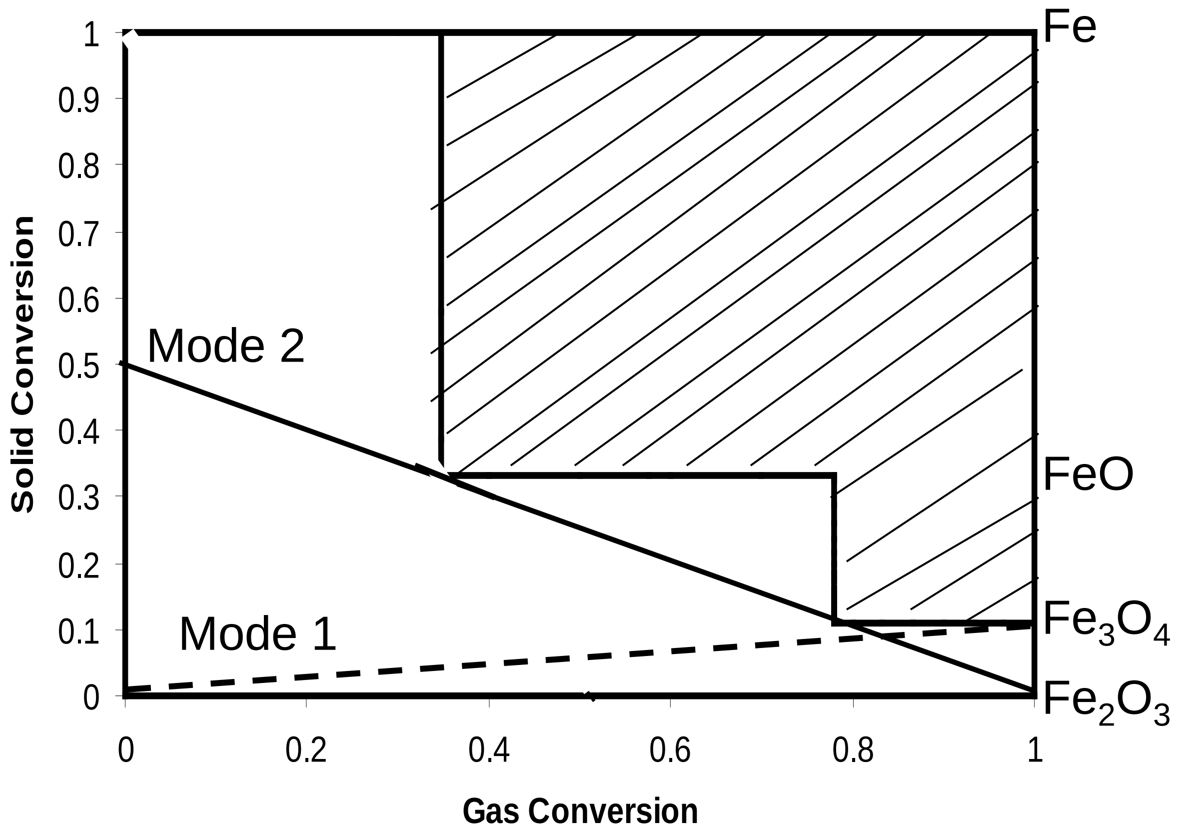


Countercurrent moving bed: straight operation line with negative slope

Similarly, Concurrent fluidized bed: straight operation with positive slope

CDCL Moving Bed Reactor – Stage I

Operation Diagram

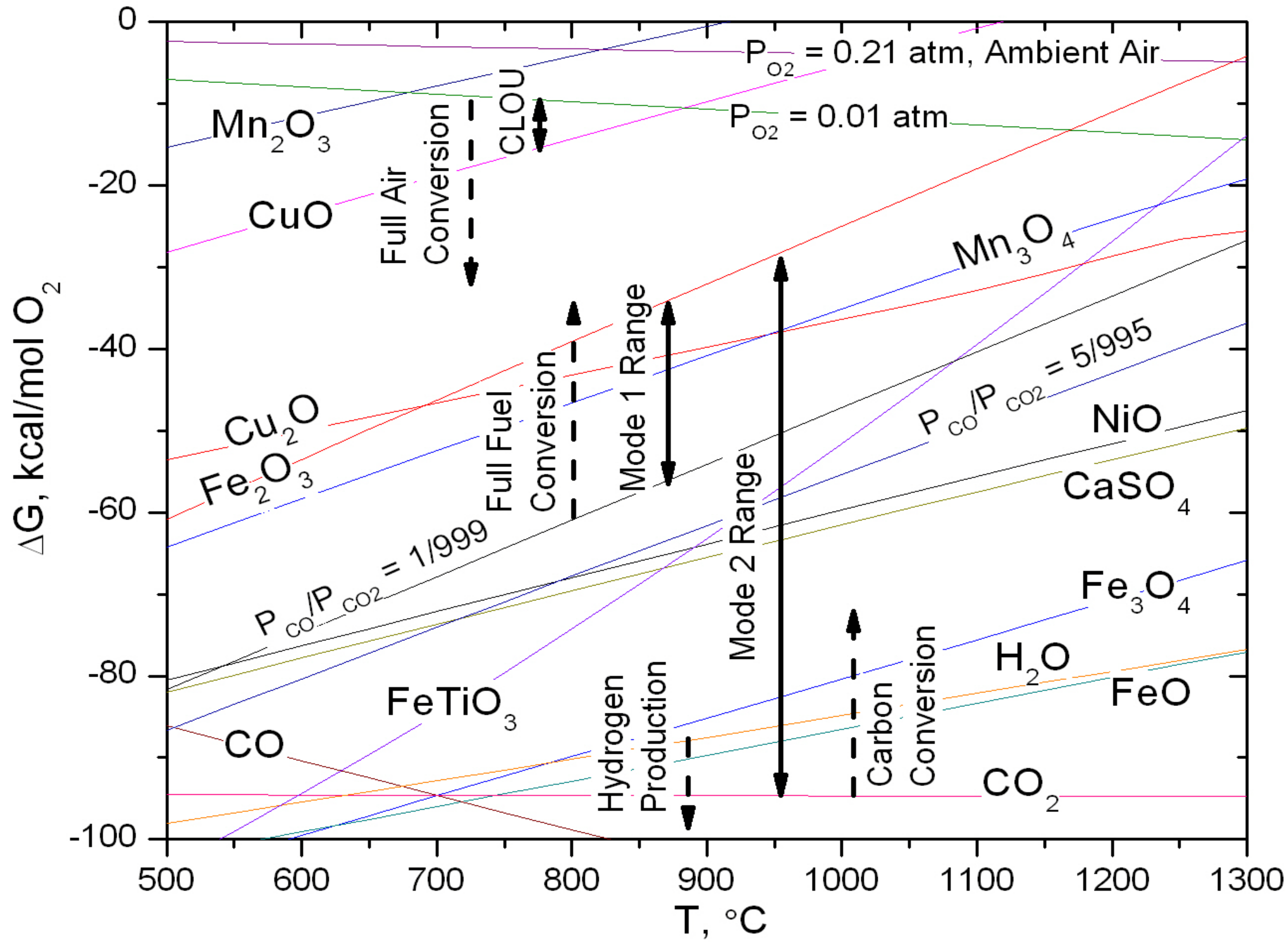


The operating line is straight when feeding ratio is fixed: solid line represents countercurrent moving bed operation, dash line represents co-current fluidized bed operation

Oxygen Carrier Development

Oxygen Carrier Particle Development

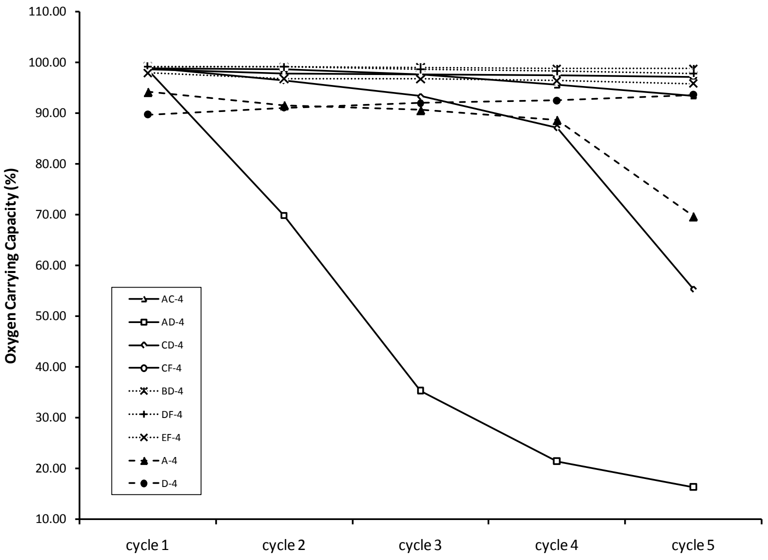
Ellingham Diagram: Selection of Primary Metal



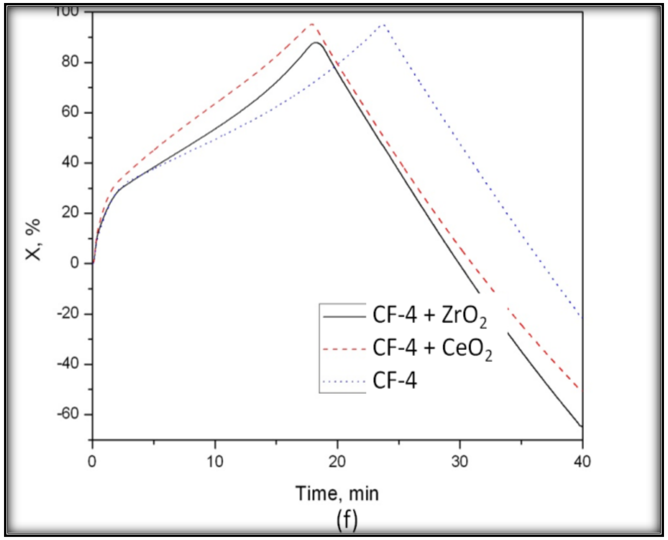
Oxygen Carrier Particle Development

OSU Particle (over 300 particles) Performance

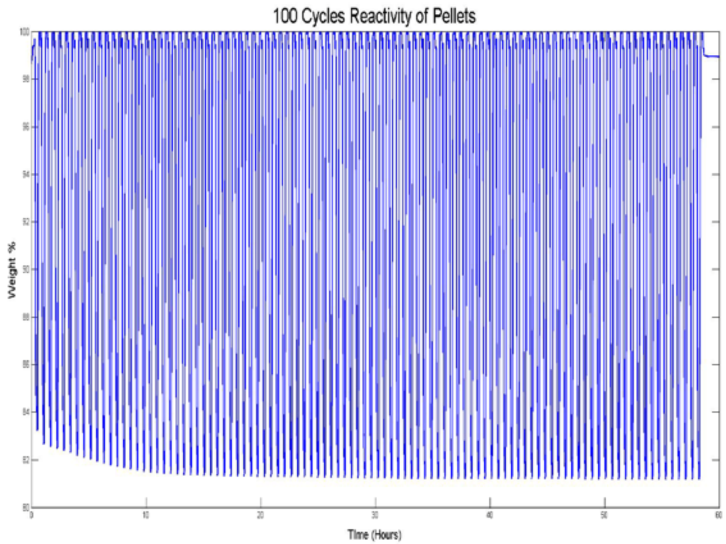
High Reactivity



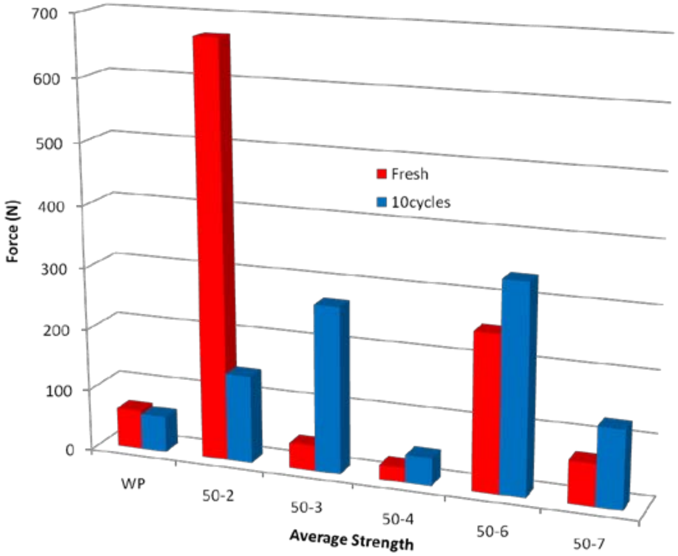
High Carbon Deposition Tolerance



High Recyclability



High Pellet Strength



Data Analysis and Modeling

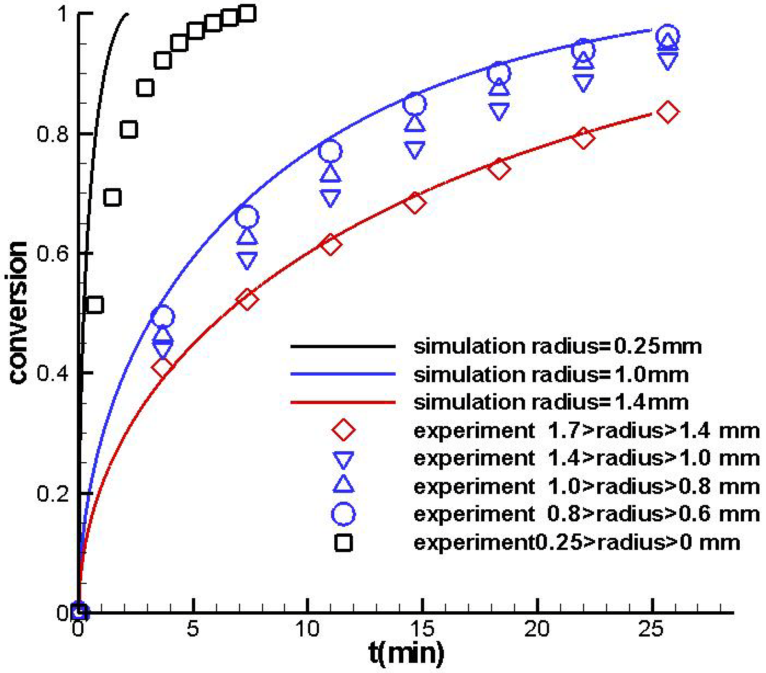
TGA - Oxygen Carrier Particle Reduction Kinetics

Three-interface unreacted shrinking core model (USCM) *

- Isothermal and isobaric conditions
- The pellet volume is unchanged
- First order reversible reaction

Three factors that affect the overall reaction rate

- **Diffusion through the gas film**
- **Intraparticle diffusion**
- **Chemical reaction at reaction interface**



Reaction rates at each reaction step:

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

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

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

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

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

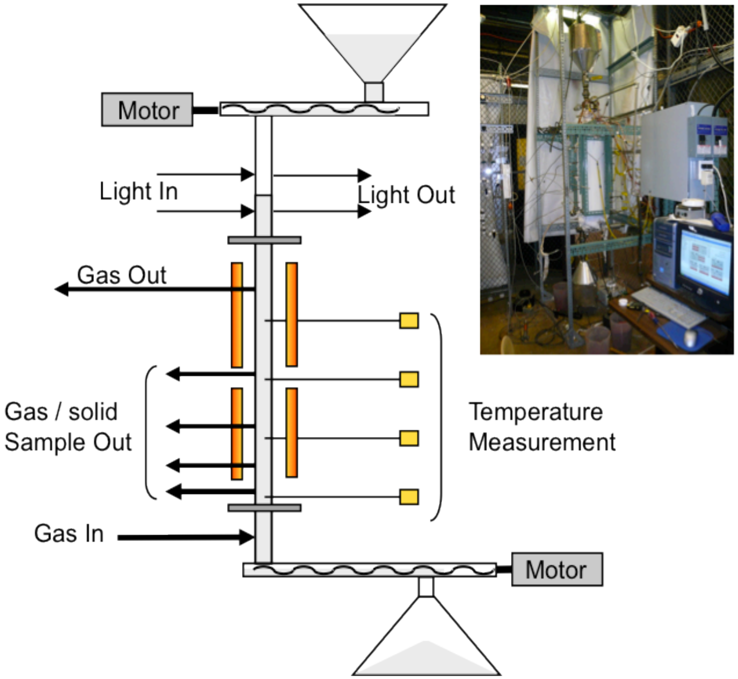
$$F = 1/k_f$$

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

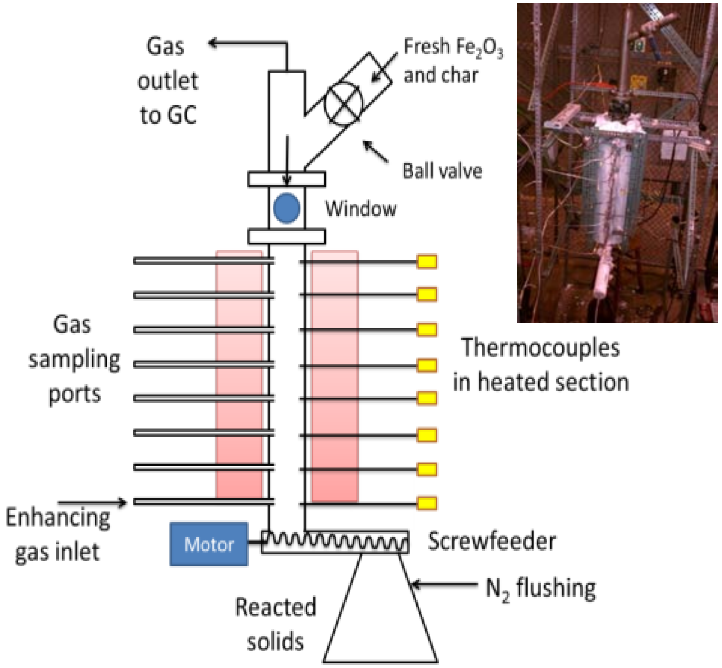
Yanagiya T., Yagi J., Omori Y. 1979 reduction of iron oxide pellets in moving bed. Ironmaking and steelmaking, No.3 93-100

Bench Scale 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

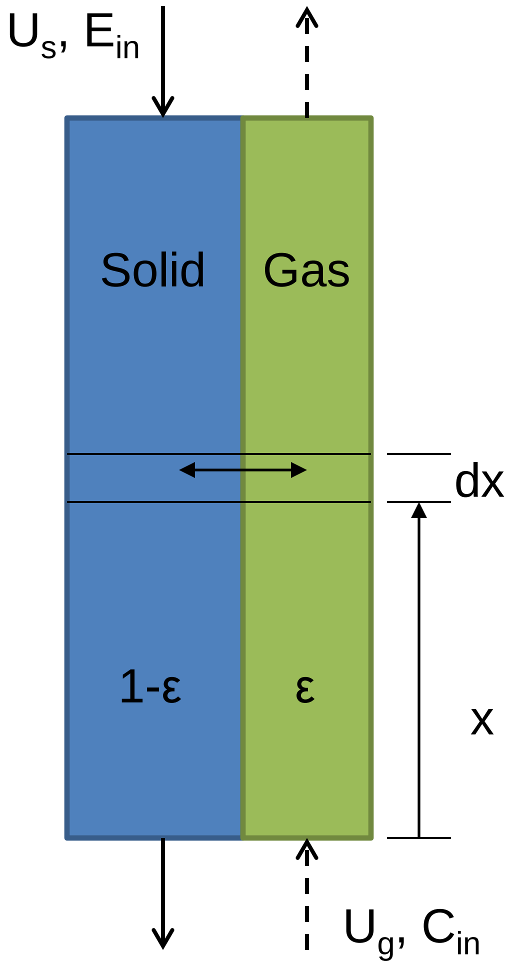
Bench Scale Testing - 1-D Reducer Modeling

- 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
  - Gas Phase
  - Solid Phase

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

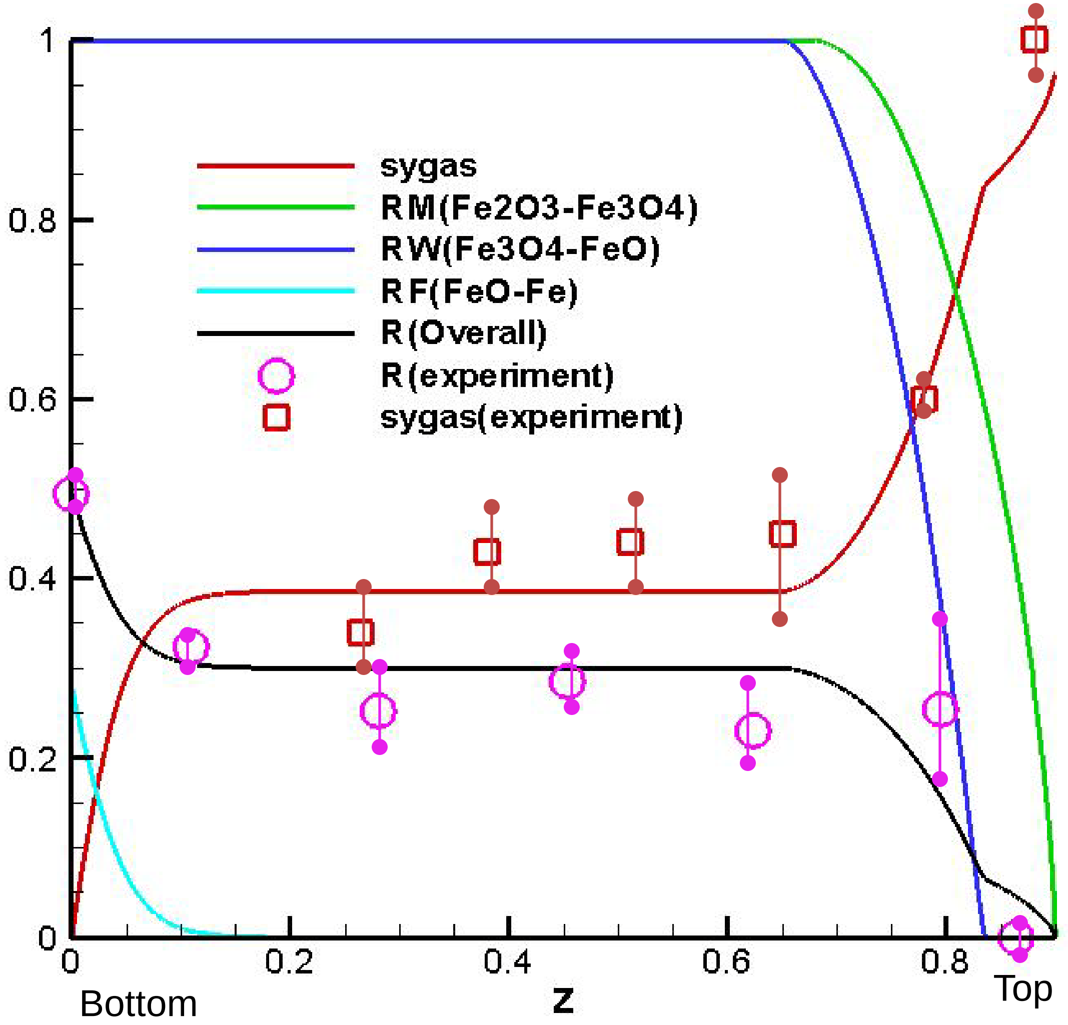
$$\frac{\partial E_i}{\partial t} = -Us_i \frac{\partial E_i}{\partial x_i} + \sum_l \upsilon_{li} \frac{6(1-\varepsilon) r_l}{d_p}$$

- Numerical Methods
  - Temporal terms are discretized by third order Runge-Kutta schemes
  - Spatial terms are discretized by fifth order schemes



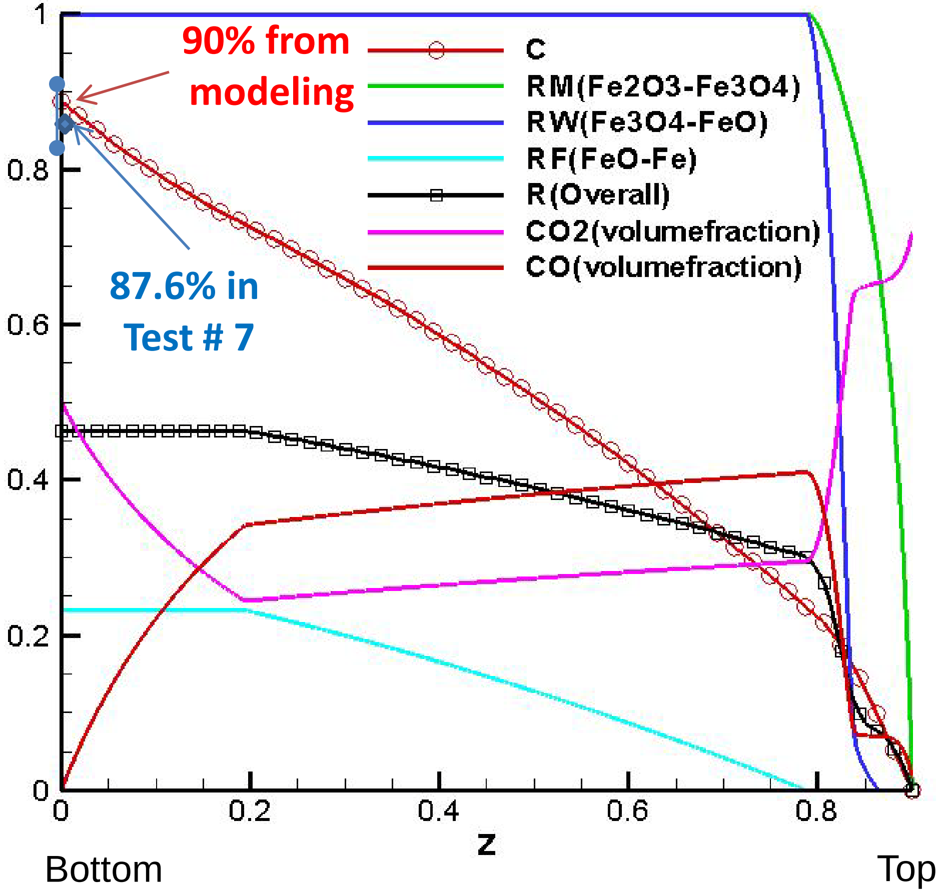
Bench Scale Testing - Stage I Modeling

- Reactor modeling validated by previous bench scale syngas test results
  - o Reaction ： Iron Oxide reduced by sygas:
  - o Initial mole fraction of sygas in gas: 72.9%
  - o Mass fraction of Iron Oxide in particle ： 60%
  - o Solid feedrate: 12.87g/min
  - o Diameter of the reducer: 4.06 cm
  - o Density of solids ： 2500 g/cm^3
  - o Voidage of reducer 0.40g
  - o Diameter of solid: 4mm
  - o Gas feedrate: 1.683 mol/s
  - o Temperature: T=1273K
  - o Pressure: P=1 atm



Bench Scale Testing - Stage II Modeling

Stage II Modeling Results



90% from modeling

87.6% in Test # 7

Stage II Bench Test Results

#	OC flowrate (g/min)	CO_2 flowrate (mL/min)	N_2, flowrate (mL/min)	T, (C)	X_C (%)
7	WP-5mm, 9.6	200	200	1000	87.6
17	OP-1.5mm, 10.9	200	200	1000	95.2

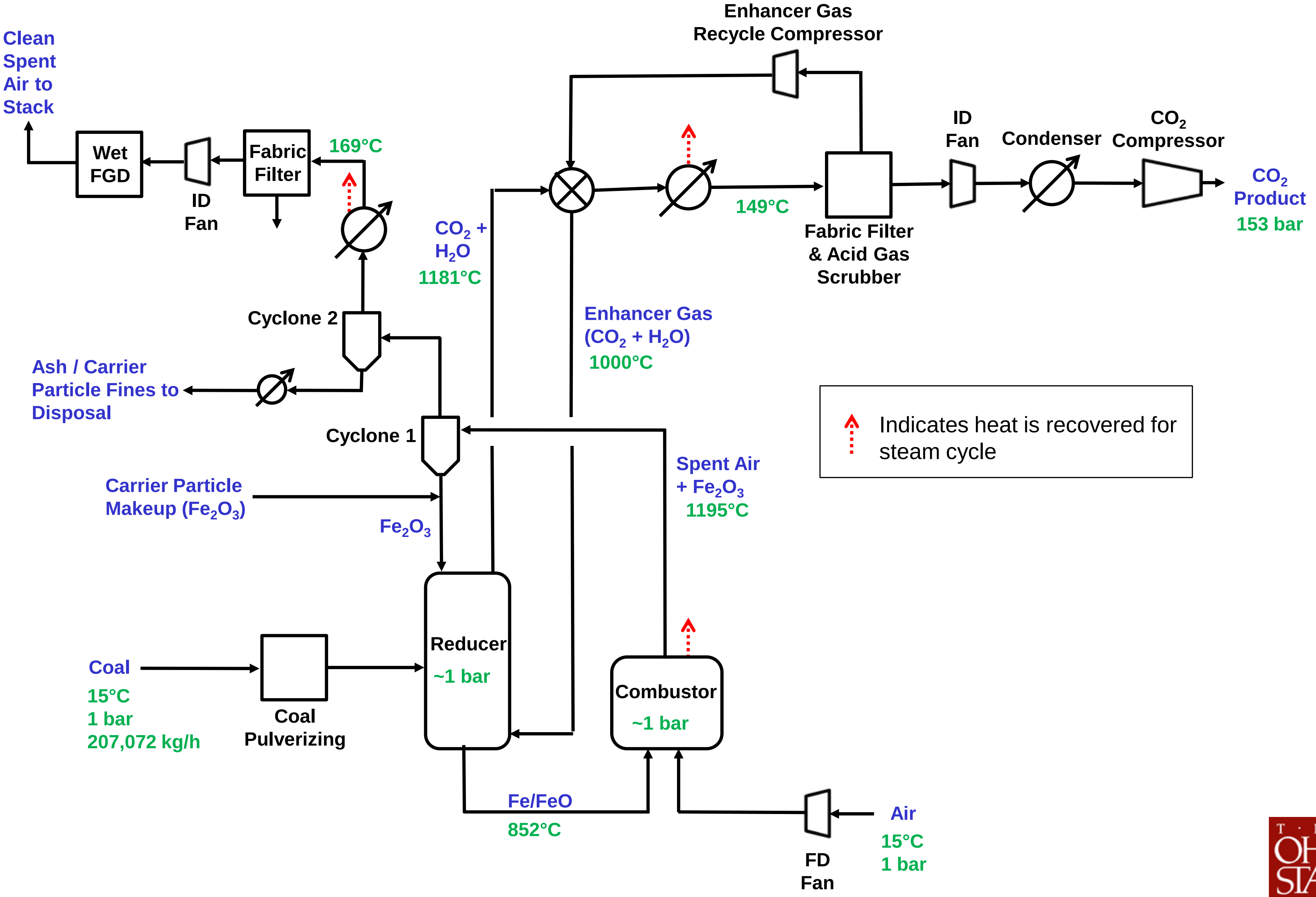
Both individual particle kinetics model and moving bed reactor model have been developed and validated by experimental results, and helped the reducer design and operation optimization.

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)
  - $\geq$ 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

Process Simulation and Analysis



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%

Accomplishments/Future Plans

Completed

- Synthesis/screening of >300 oxygen carrier particles and selected particles with optimal performance for further testing
- 300 hrs of 2.5 kW_t bench-scale operations achieving volatile and coal char conversions of >95%
- Cold flow model demonstrations evaluating solids/gas handling
- >230 hrs of integrated 25 kW_t sub-pilot scale operations achieving 90-99+% coal conversion
- CDCL process can achieve 97% CO_2 capture and compression with 10.6% energy penalty relative to a conventional, supercritical PC plant without CO_2 capture
- 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

- Continued integrated 25 kWth sub-pilot demonstration
  - Extended continuous demonstration
  - Varied operating parameters (e.g. coal type, enhancer gas, solid circulation)

Thanks