Chemical Looping Technology

by

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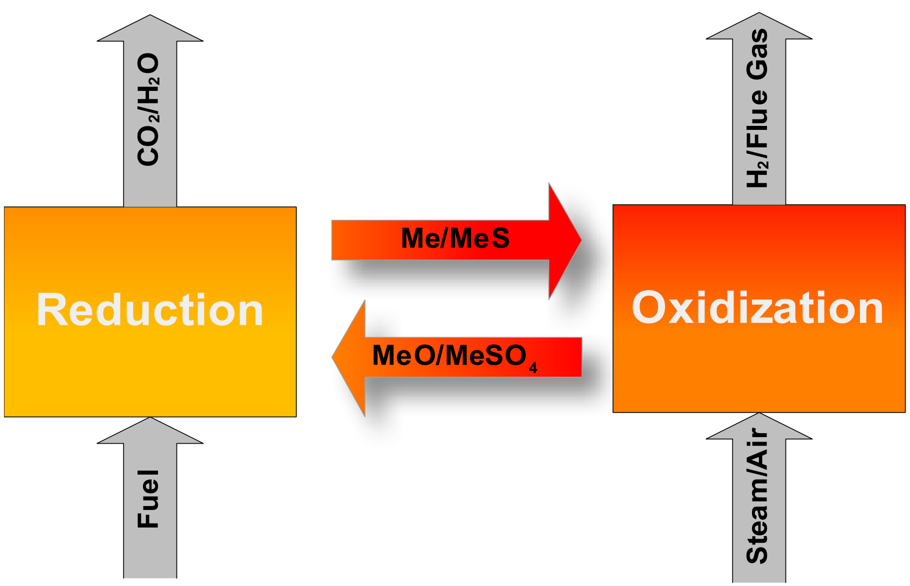
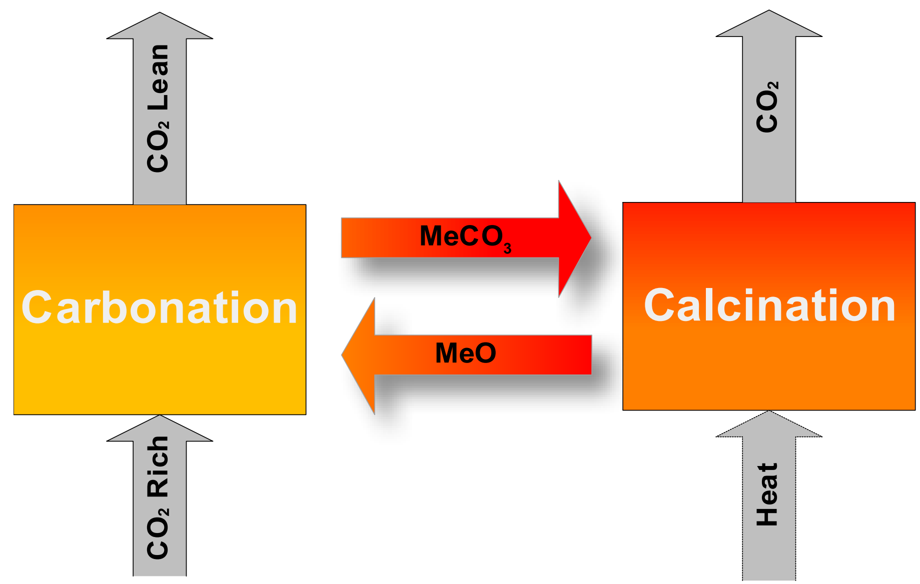
Full Oxidation in Chemical Looping Applications for Fossil Fuel Conversions

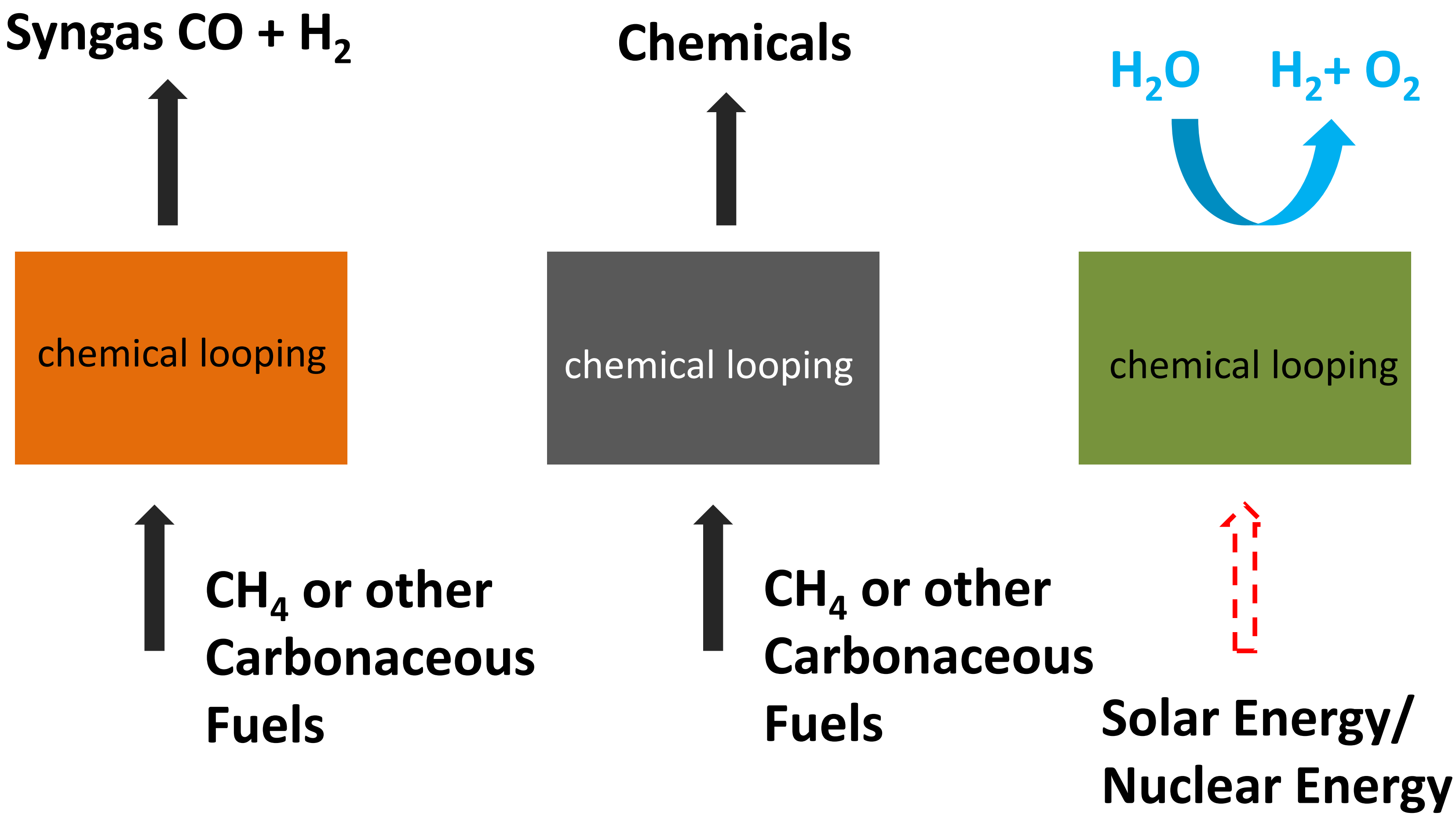
Two typical types of looping reaction systems

Oxygen Carrier (Type I)	CO_2 Carrier (Type II)
Me/MeO, MeS/$MeSO_4$	MeO/$MeCO_3$
	

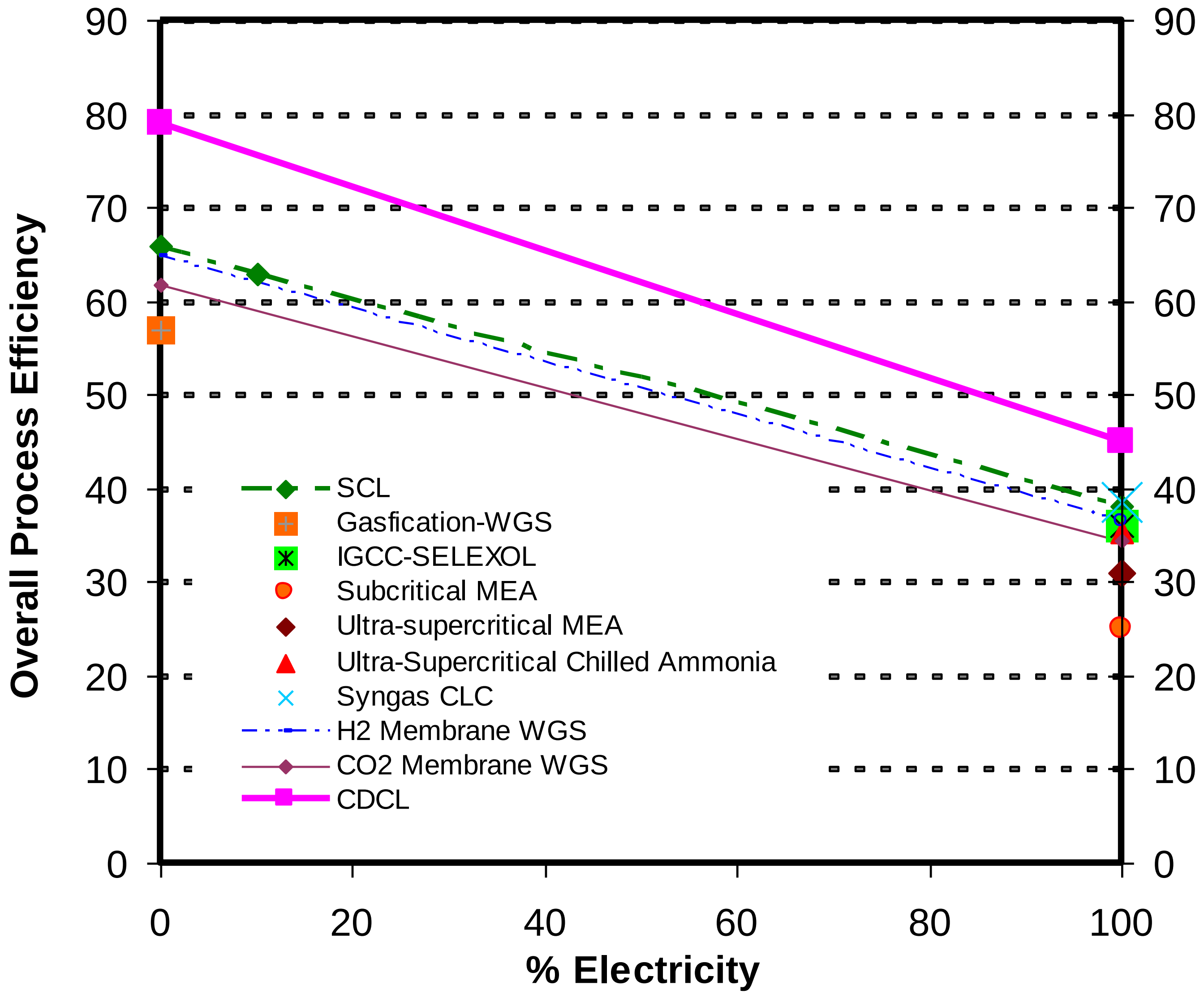
"1st International Conference on Chemical Looping", Lyon, France, March 17-19 (2010).

"1st Meeting of High Temperature Solids Looping Cycle Network", Oviedo, Spain, September 15-17 (2009).

Selective Oxidation in Chemical Looping Applications for Fossil Fuel Conversions and Solar Chemical Looping Systems

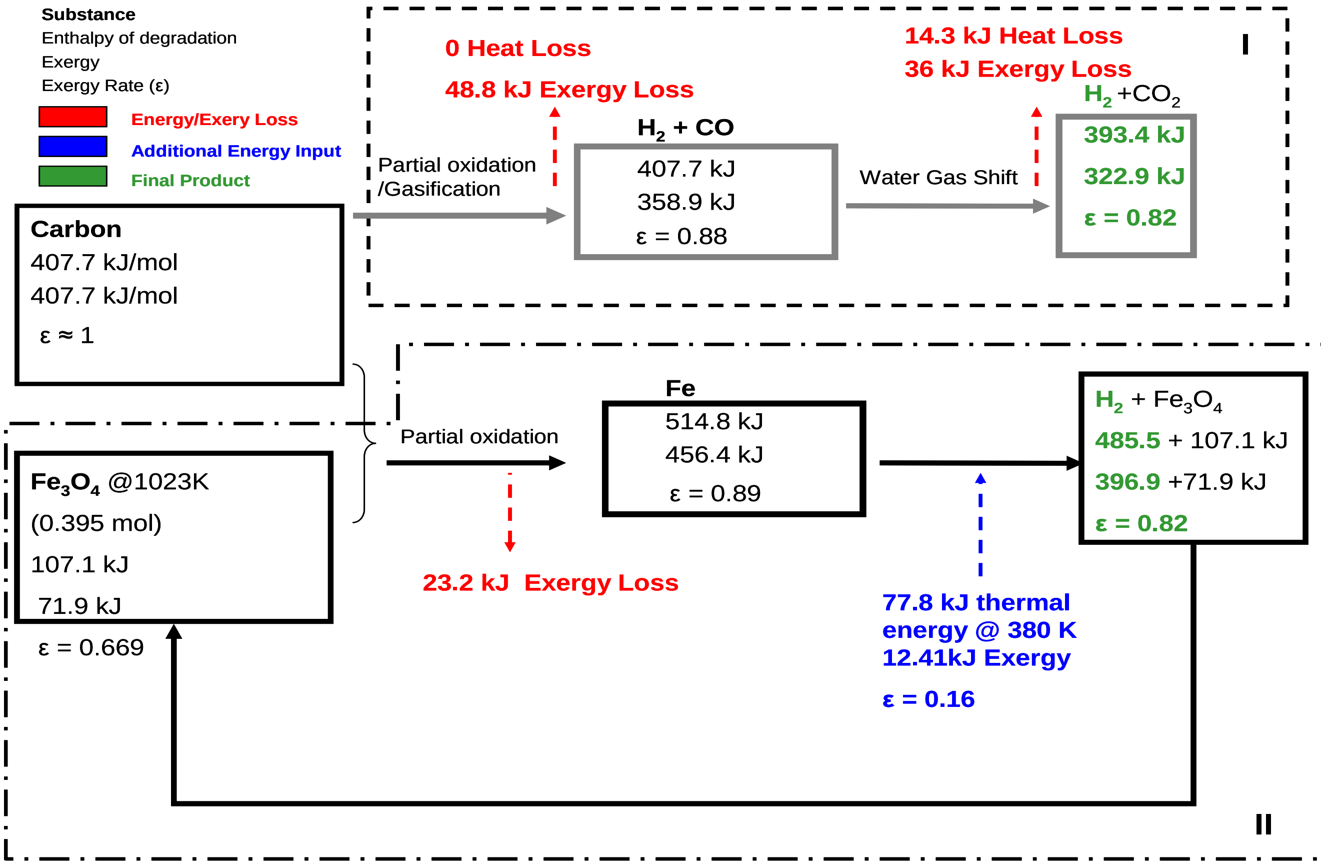


Comparison of OSU SYNGAS and Coal Direct Chemical Looping (CDCL) Processes with Traditional Coal to Hydrogen/Electricity Processes



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

Exergy Analysis on Hydrogen Production



I. Contional Process Exergetic Efficiency

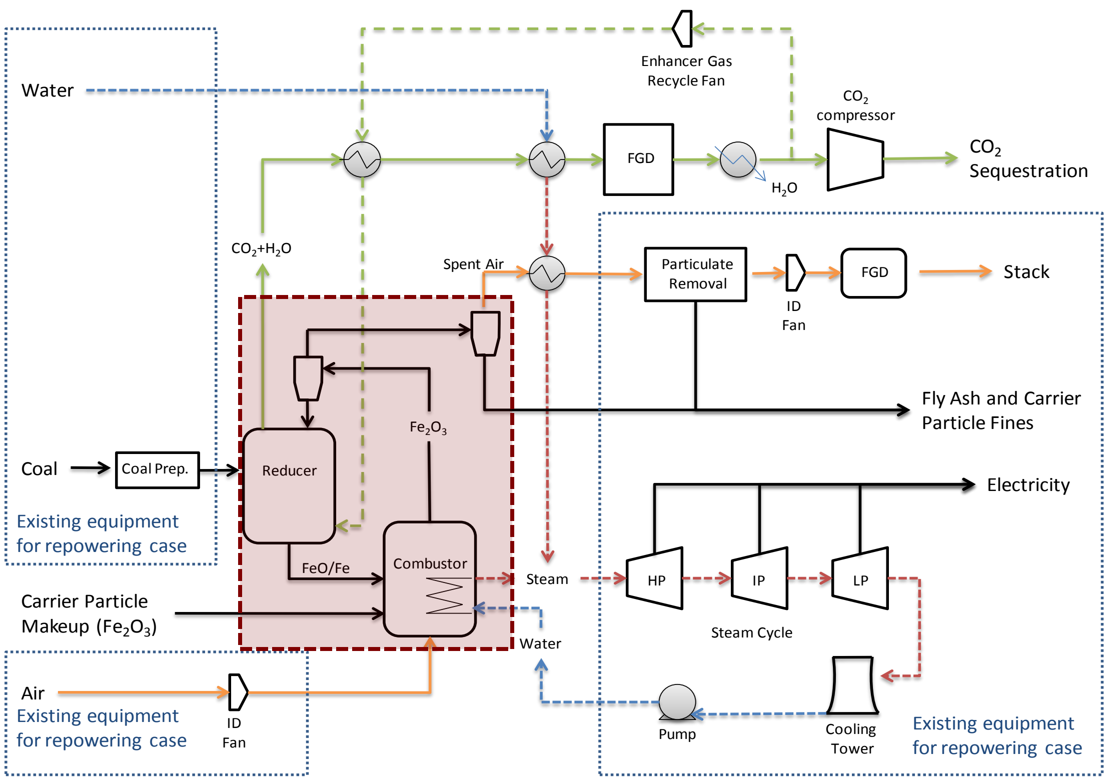
322.9/407.7 = 79.2%

II. Chemcial Looping Process

Exergetic Efficiency

396.9/(407.7 + 12.41)=94.5%

Economics on Chemical Looping Process



	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%

- Retrofit to conventional coal combustion process
- CDCL replaces existing PC boiler
  - Additional equipment for CO_2 compression and transportation required
- Techno-Economic analysis performed comparing CDCL to Base Plant with no CO_2 capture and 90% CO_2 capture via post-combustion MEA process

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

Large Scale Chemical Looping Process Demonstration

Organization	Process/Type	Capacity	Features
Hunosa, Spain	*CaOling* – CaO looping / Type II	2 MW_{th}	Pilot plant to capture CO_2 from the flue gas from 50 MWe coal power plant
Technical University of Darmstadt, Germany	LISA – limestone-based absorption of CO_2 / Type II	1 MW_{th}	Capture plant is an extension to a 1052 MWe hard coal-fired power plant
Industrial Technology Research Institute (ITRI), Taiwan	Carbonation-calcination and carbonation-calcination-hydration (Ohio State CCR process) looping reactions to capture CO_2 / Type II	2 MW_{th}	Limestone sorbents are used with spent CaO fed to cement industry
Technical University of Darmstadt, Germany	ECLAIR - emission free chemical looping coal combustion process using ilmenite / Type I	1 MW_{th}	The pilot unit is for solid fuel conversion and designed based on CFB concept
Alstom, U.S.	Calcium sulfate chemical looping combustion / Type I	3 MW_{th}	The oxygen carriers are $CaS/CaSO_4$
Ohio State University, U.S.	High pressure syngas chemical looping (SCL) gasification process using iron based oxygen carrier / Type I	250 kW_{th} - 3MW_{th}	SCL enables high purity hydrogen production with in-situ CO_2 capture via countercurrent moving bed reactor design; Syngas is from KBR gasifier

B&W and OSU Chemical Looping Combustion – 3 MW_{th} Pilot Demonstration (see B&W press release; work in progress)

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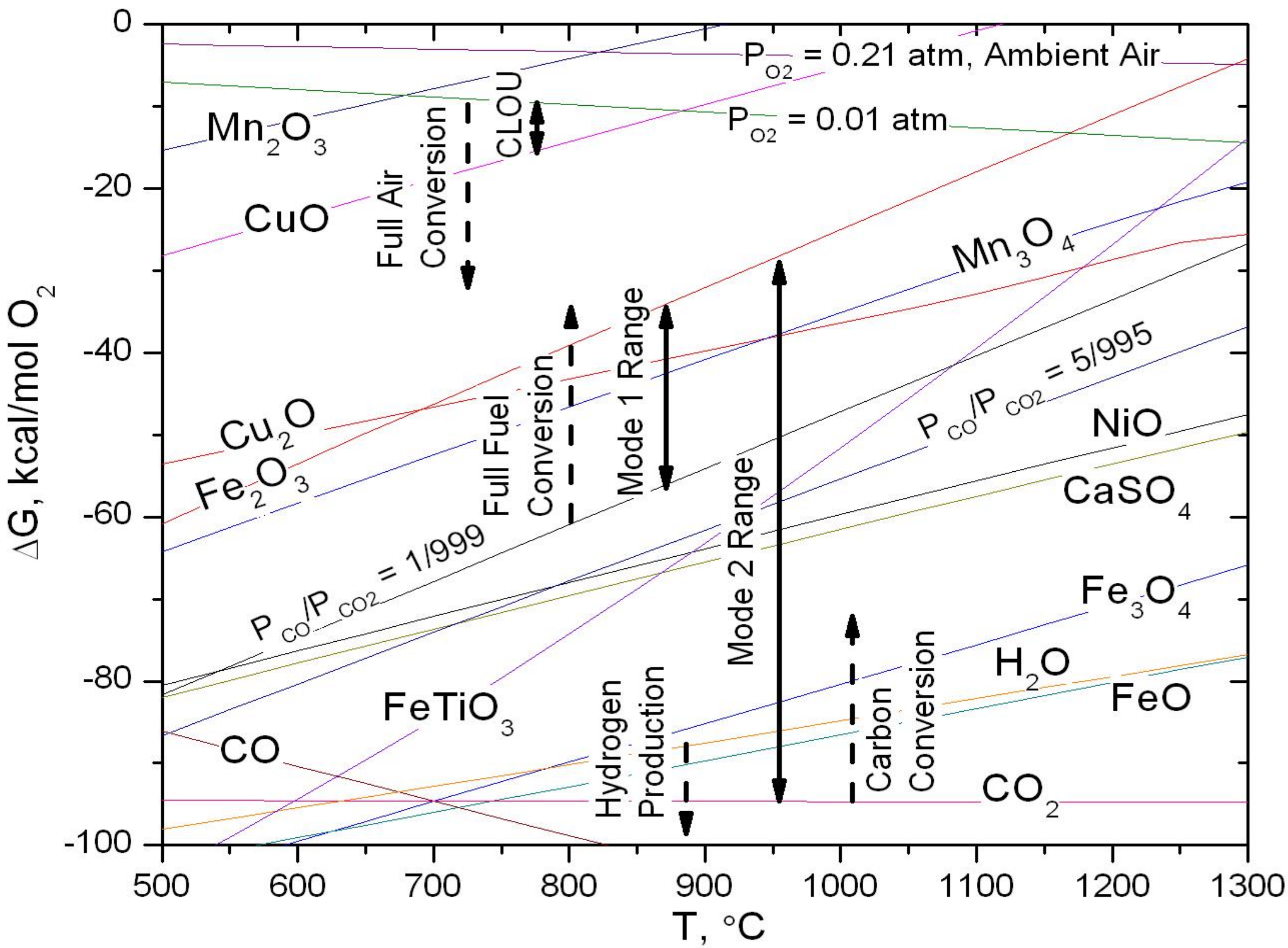
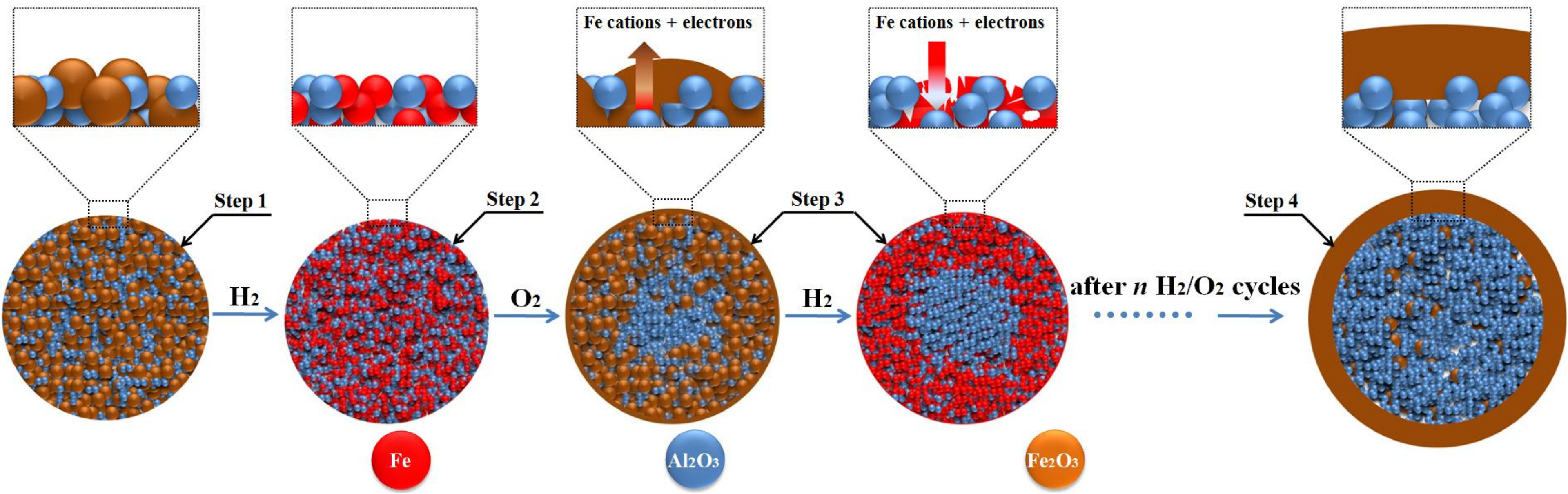
Oxygen Carrier Particle Development

Ellingham Diagram: Selection of Primary Metal



Core-Shell Particle Formation through Cyclic Gas-Solid Reactions



$$4Fe_{(s)} + 3O_{2\,(g)} \rightarrow 2Fe_2O_{3\,(s)} \qquad (1)$$

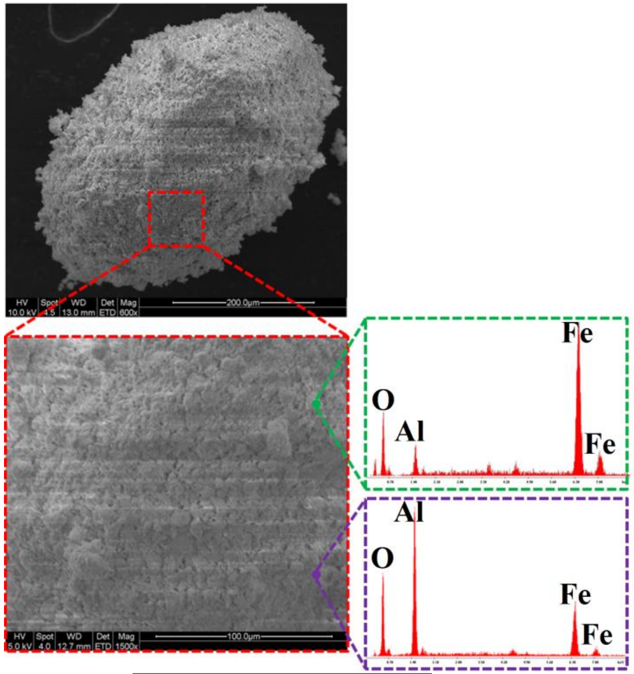
$$Fe_2O_{3\,(s)} + 3H_{2\,(g)} \rightarrow 2Fe_{(s)} + 3H_2O_{(g)} \qquad (2)$$

If the cyclic reactions proceed through Fe cation diffusion, core-shell structure forms, *e.g.* Fe_2O_3 + **Al_2O_3**.

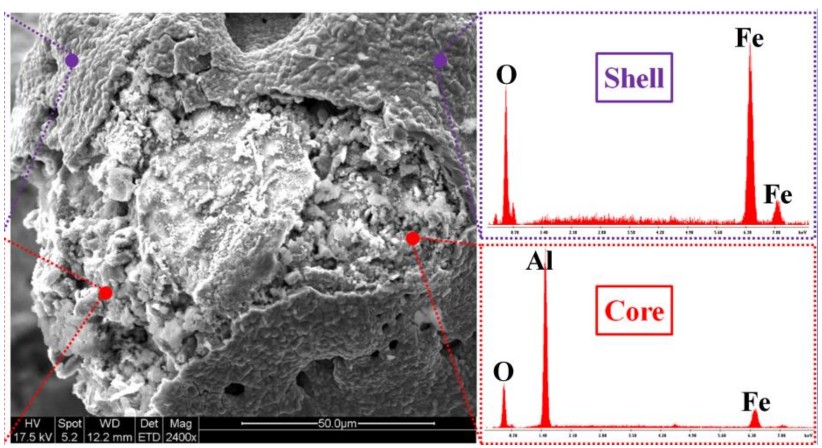
If the cyclic reactions proceed through O anion diffusion, core-shell structure does not forms, *e.g.* Fe_2O_3 + **TiO_2**.

*Al_2O_3 is only a physical support, while TiO_2 alters the solid-phase ionic diffusion mechanism

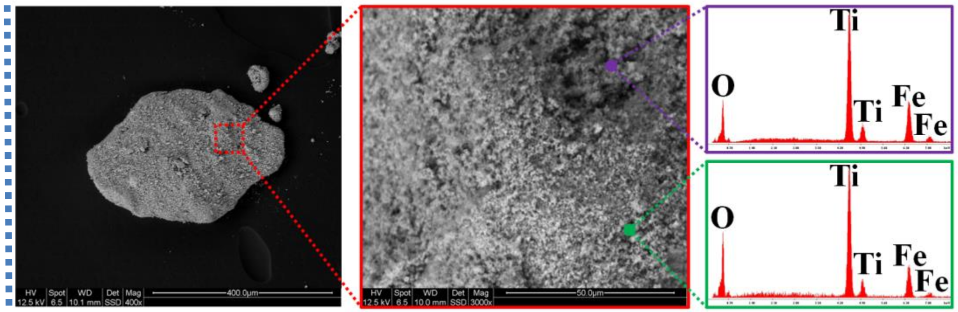
Fe_2O_3+Al_2O_3 VS Fe_2O_3+TiO_2



after 50 redox cycles

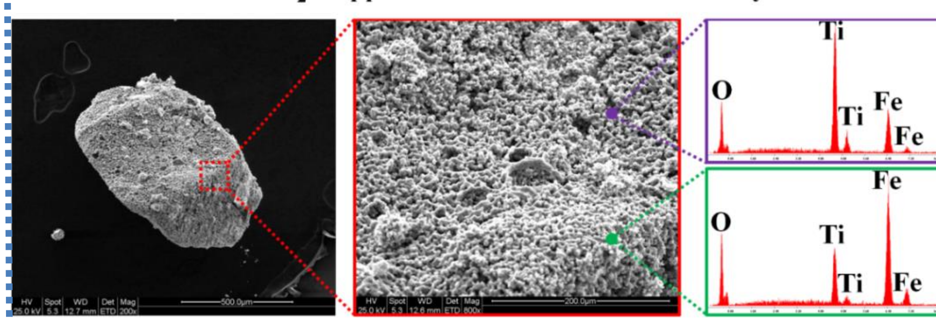


Raw TiO_2-Supported Particle



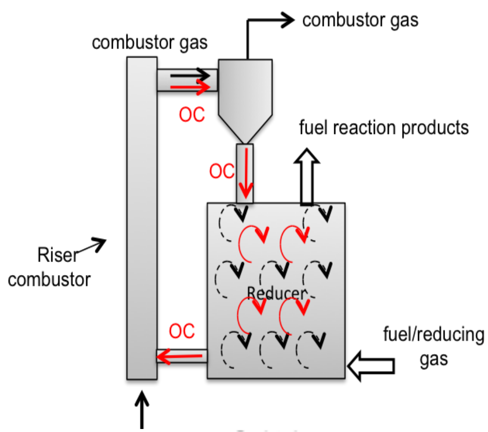
after 50 redox cycles

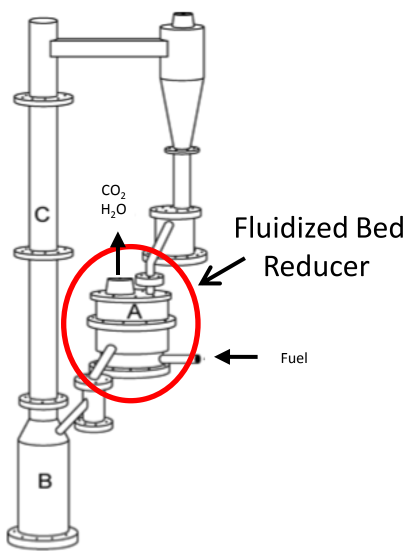
TiO_2-Supported Particle after 50 Redox Cycles



Modes of CFB Chemical Looping Reactor Systems

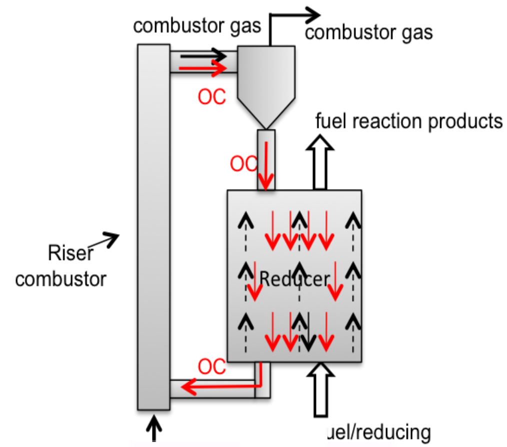
Mode 1- reducer: fluidized bed or co-current gas-solid (OC) flows

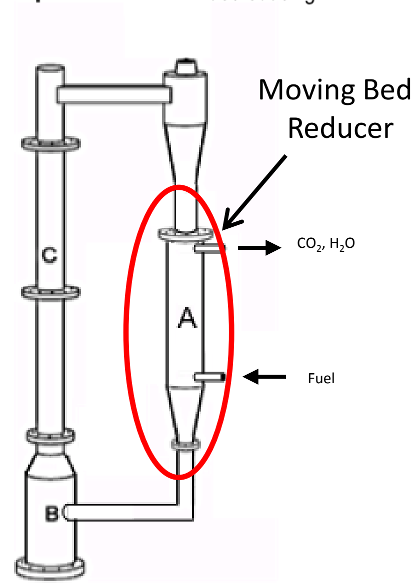




Chalmers University CLC System

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

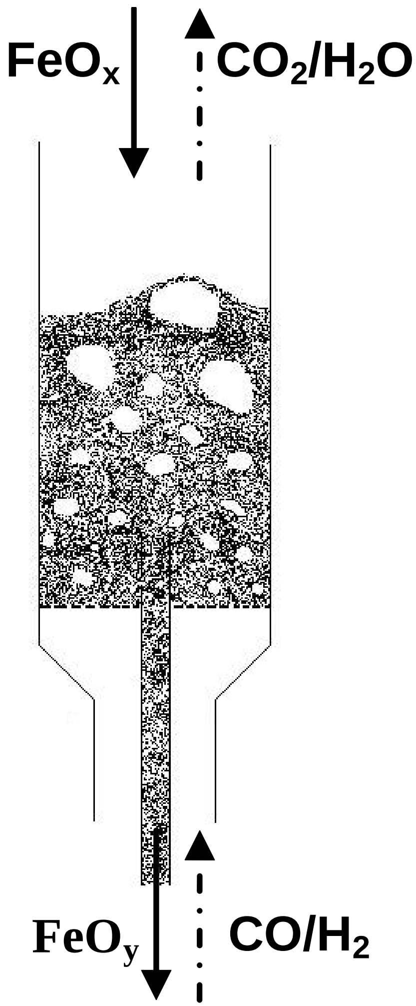




OSU CLC System

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).

Chemical Looping Reactor Design



Fluidized Bed

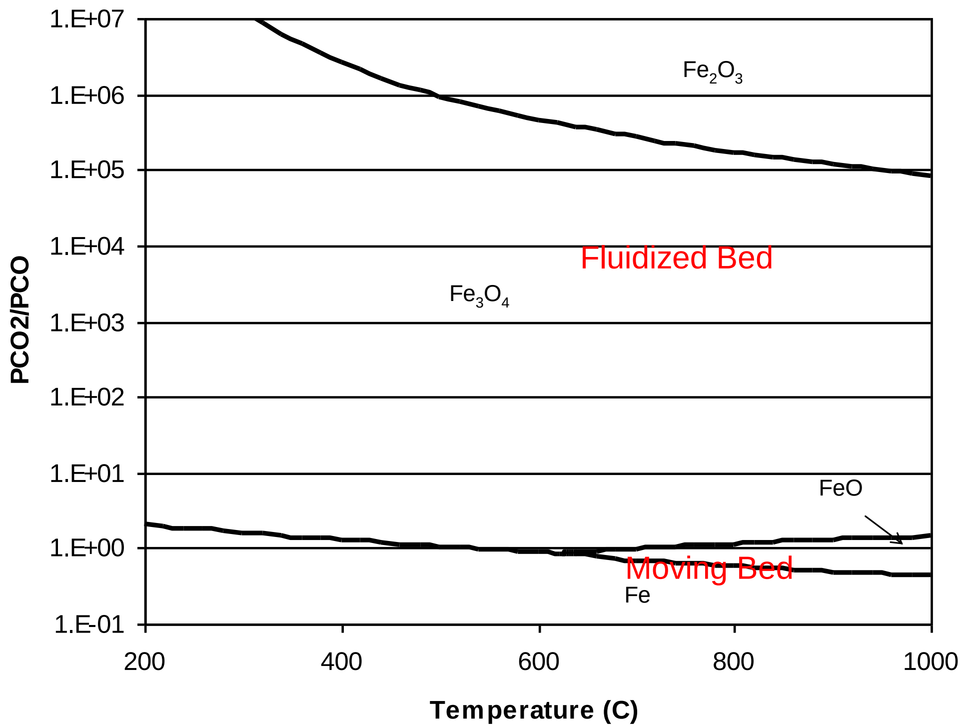
(x>y)

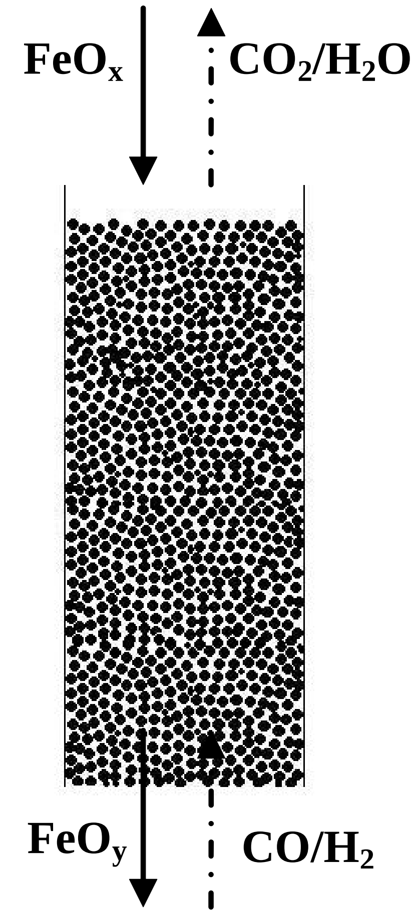
Fluidized Bed *v.s.* Moving Bed

11.11% ← Maximum Solid Conversion → **50.00%**

> U_{mfv} ← Gas Velocity → **< U_{mfv}**

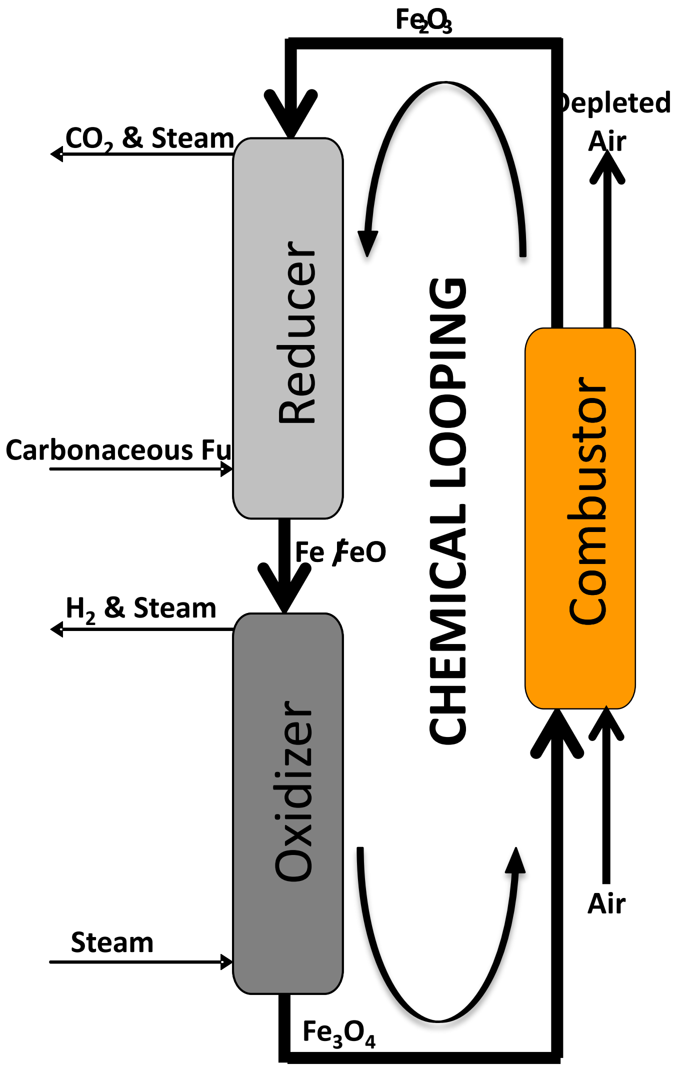
Small ← Particle Size → **Large**





Moving Bed

OSU SYNGAS Chemical Looping Process



Main reactions:

Reducer	$C_xH_yO_z + Fe_2O_3 \rightarrow CO_2 + H_2O + Fe$
Oxidizer	$Fe + H_2O \rightarrow Fe_3O_4 + H_2$
Combustion Train	$Fe_3O_4 + O_2 \rightarrow Fe_2O_3 + Heat$

Overall reaction

$$C_xH_yO_z + H_2O/O_2 \rightarrow CO_2 + H_2/Heat$$

Possible Oxygen Carriers:

Fe_2O_3 – Fe / FeO

General Observations:

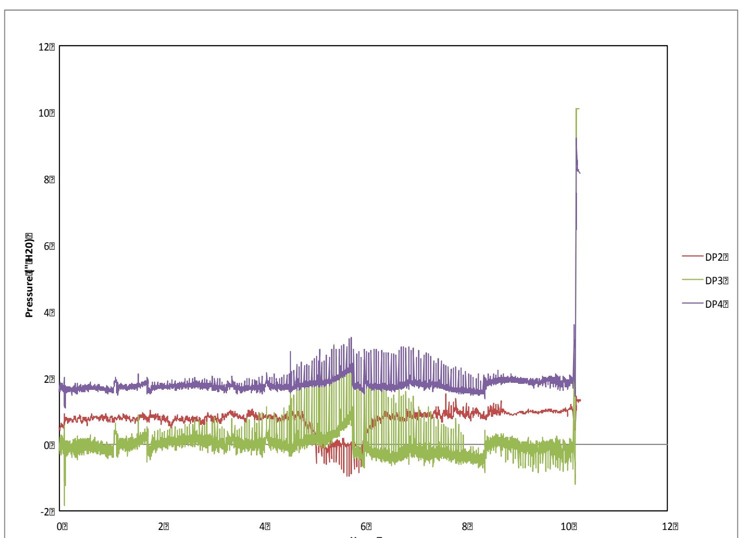
- 2 Moving Bed + 1 Entrained bed reactors
- Very High Fuel Conversion
- Near 100% in-situ CO_2 capture
- High Purity H_2 generation
- High Solid Conversion
- Low Solid Circulation Rate

25 kW$_{th}$ OSU Sub-Pilot SCL Unit

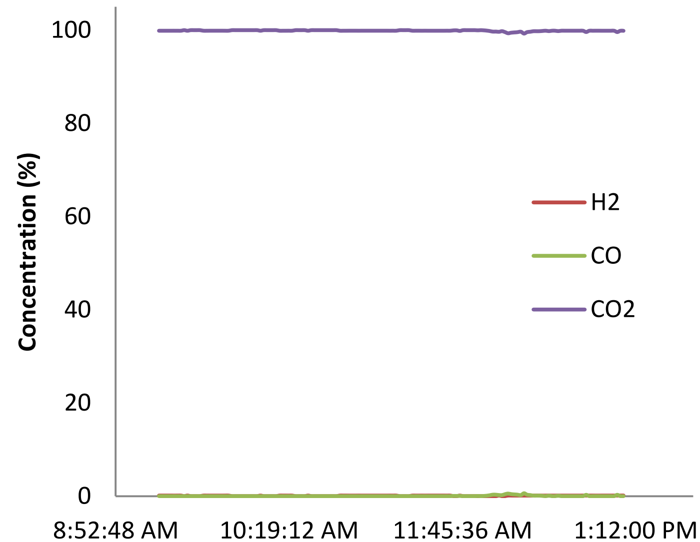
Recent Unit Demonstration

- Over 300+ hours operation
- Average CO_2 purity generated throughout run > 99%
- >99.99% hydrogen purity at steady state
- Steady Pressure Profile throughout Test run

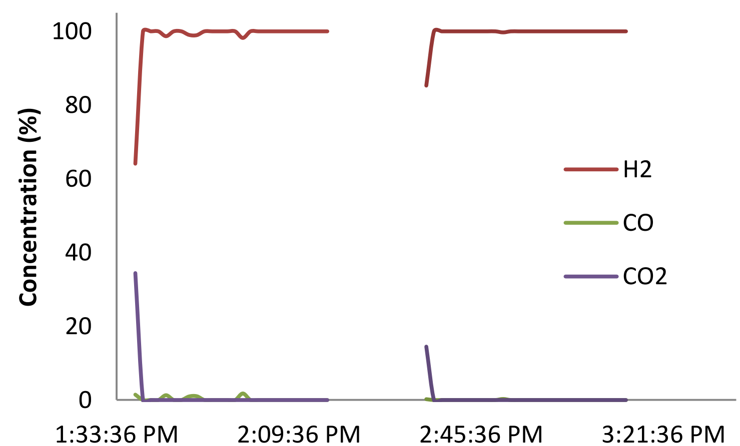
Differential Pressure Profile



Reducer Gas Composition

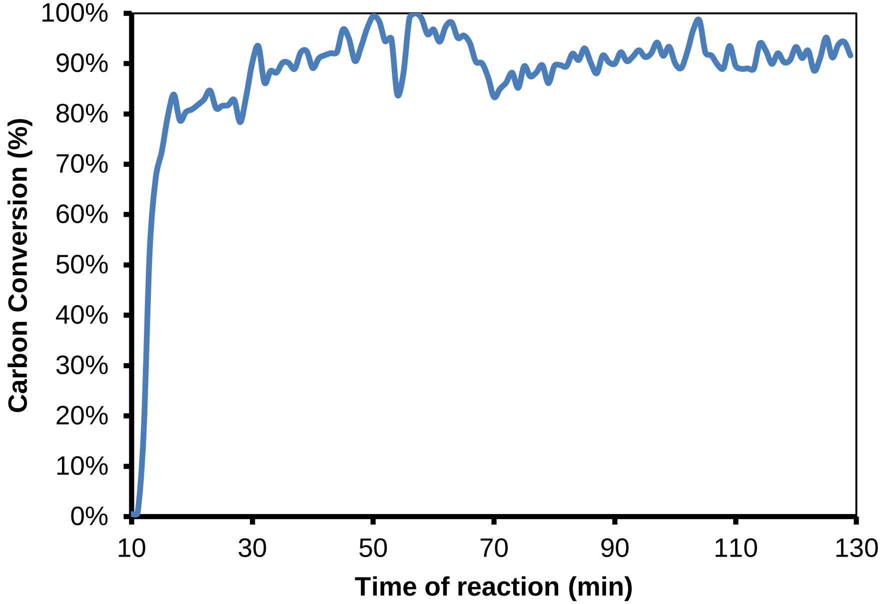


Oxidizer Gas Composition

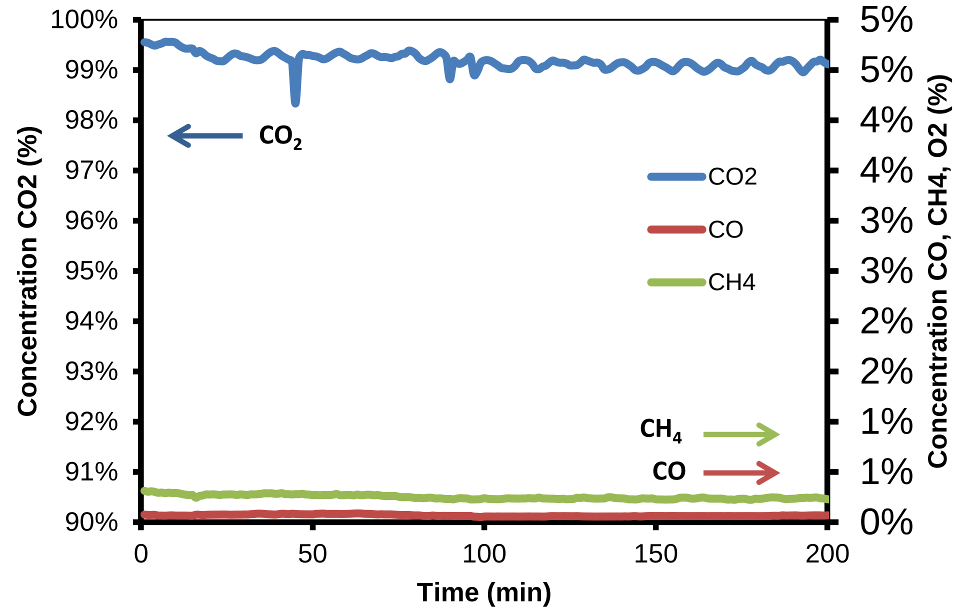


200+ Hour Sub-Pilot Continuous Run - *Sample Results*

Once-Through Reducer Carbon Conversion Profile

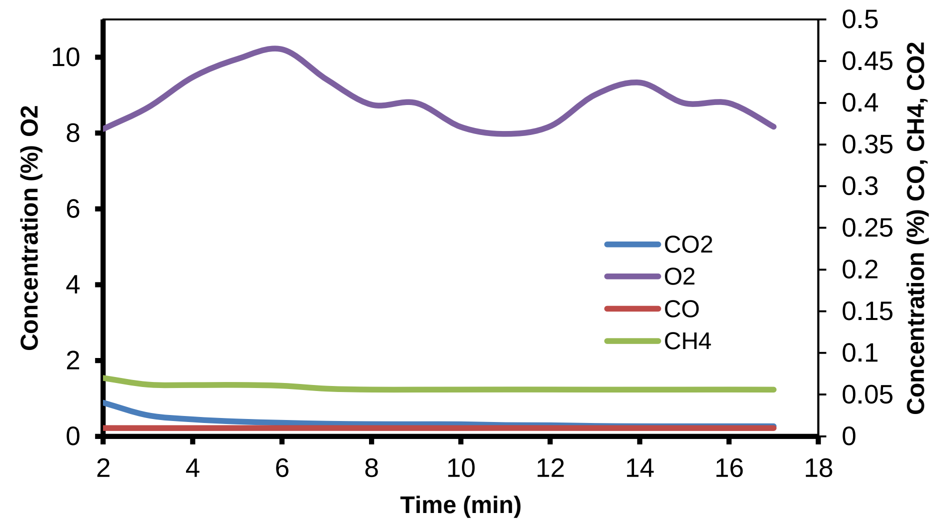


Reducer Gas Concentration Profile



- Continuous steady >90% 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

Combustor Gas Concentration Profile



CDCL NO_x/SO_x Analysis

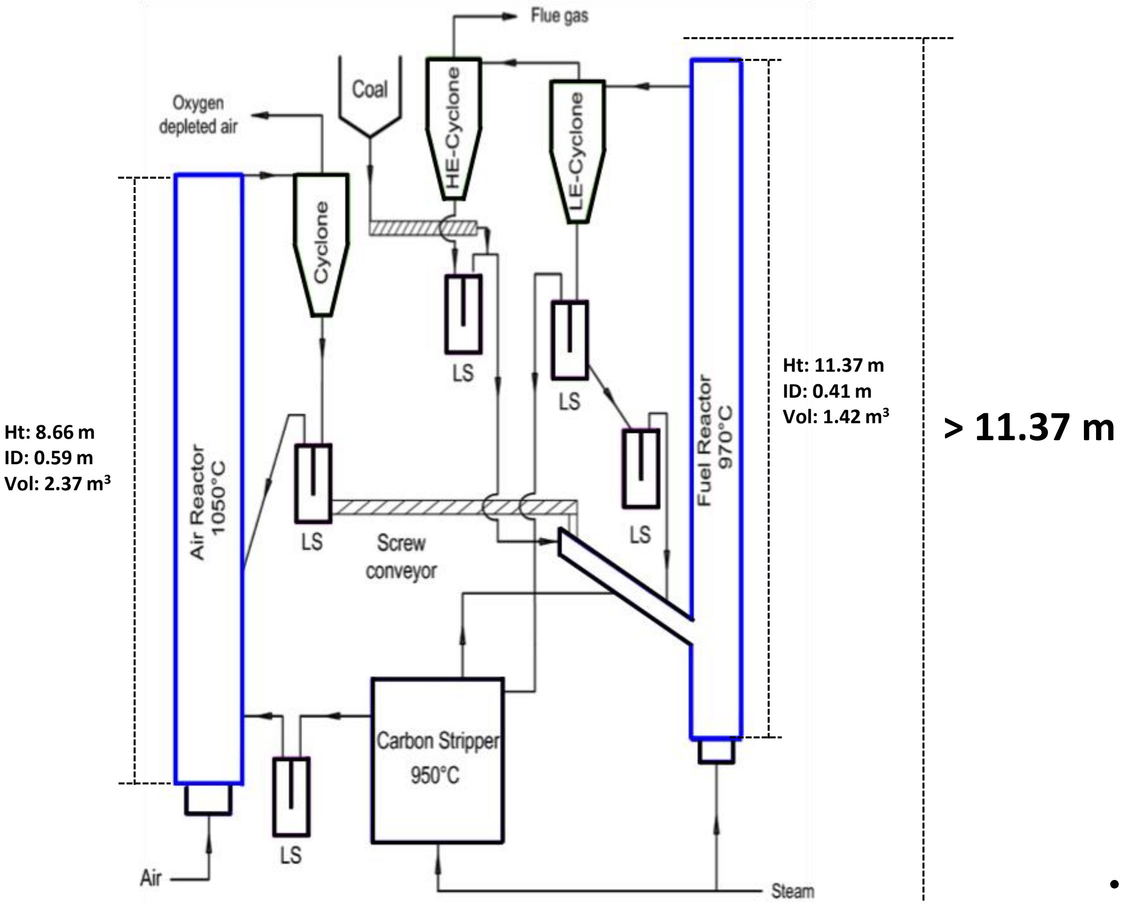
	Reducer	Combustor
SO_x (ppm)	190-1170	0 - 70
NO_x (lb/MMBTU)	0.100 – 0.200*	~ 0

*Conventional PC Boiler NO_x Generation = 0.2 – 0.5 lb/MMBTU[1]

1. NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 1 & 3b

1 MW$_{th}$ Chemical Looping Combustion System

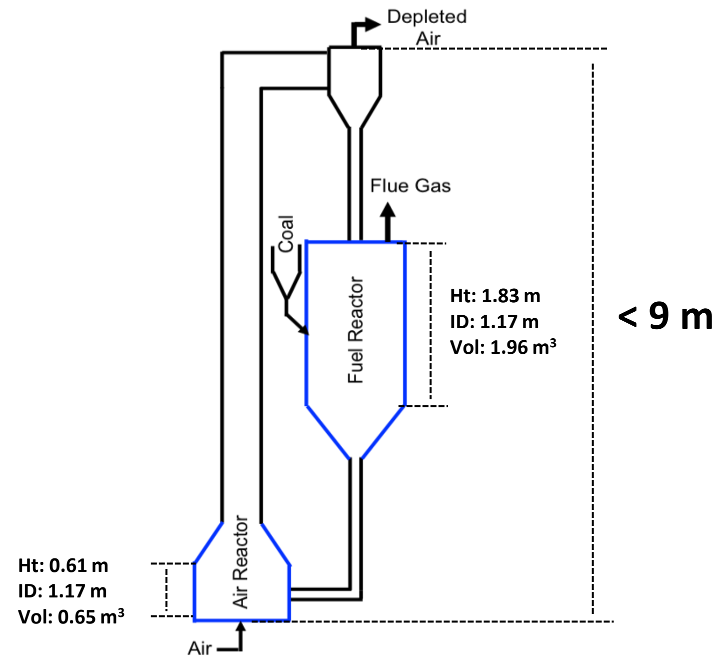
Alstom – Darmstadt MeO$_x$[1]



Total Reactor Volume: 3.80 m^3

- Mechanical solid conveying
- Carbon stripper required
- Multiple components – difficult to integrate

The Ohio State University - CDCL



Total Reactor Volume: 2.61 m^3

- No internal mechanical moving parts
- Packed moving bed design increases oxygen carrier conversion reducing solid flow rate
- In-situ ash separation
- Scalable reactor design
- Simple design – no loop seals/carbon strippers

1. Abdulally, I. et al. Clearwater Clean Coal & Fuel Conference 2012 43–54.