Chemical Looping Technology – Reaction, Reactor and Solids Flow Issues

by

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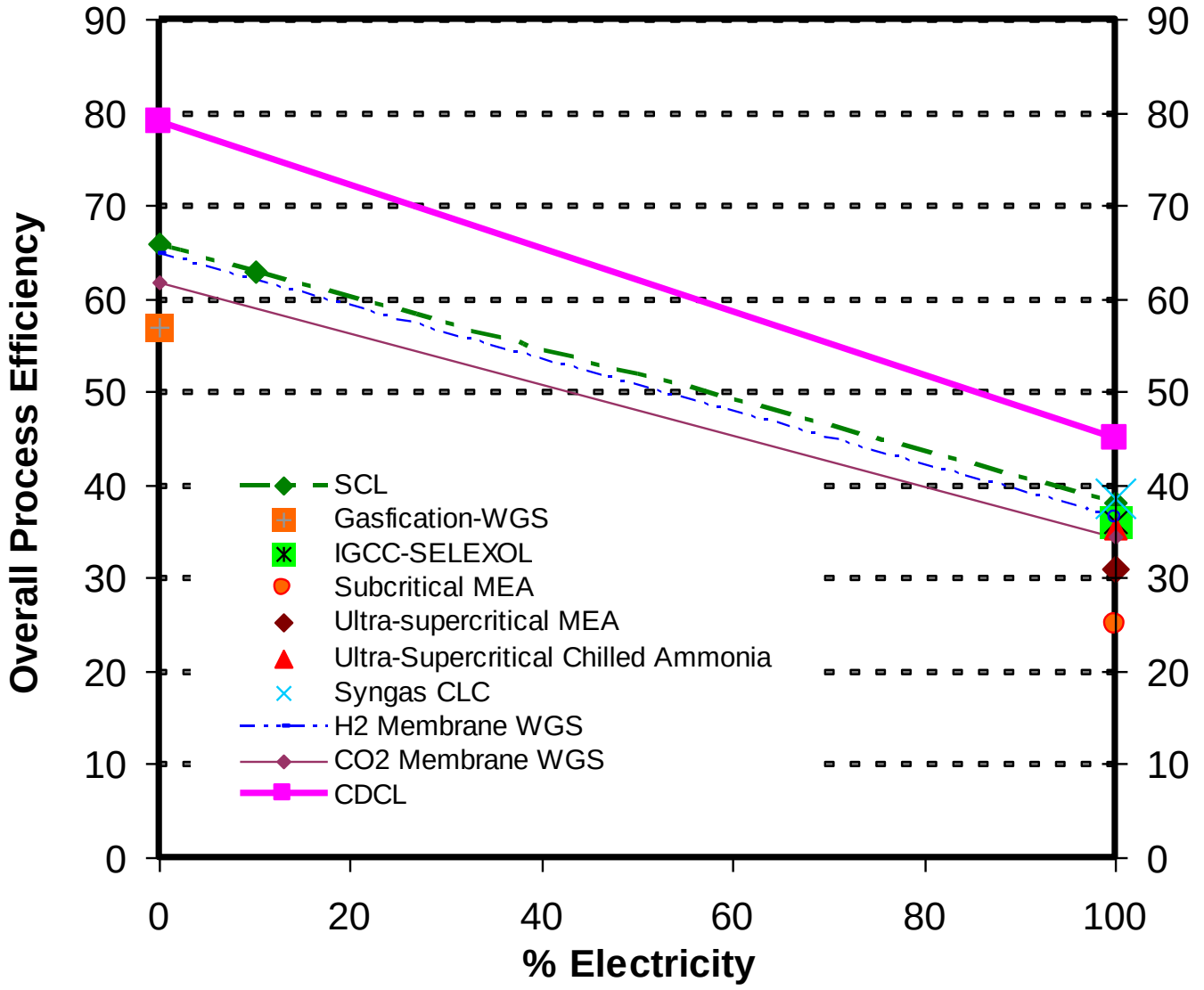
Comparison Among Gaseous Chemical Looping, Direct Coal Chemical Looping and Traditional Coal to Hydrogen/Electricity Processes



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

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.

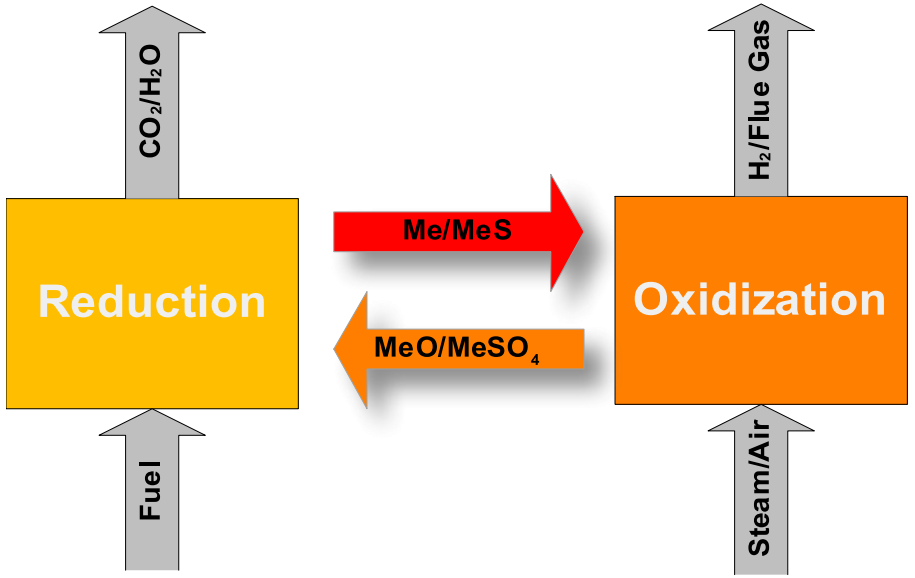
Topics

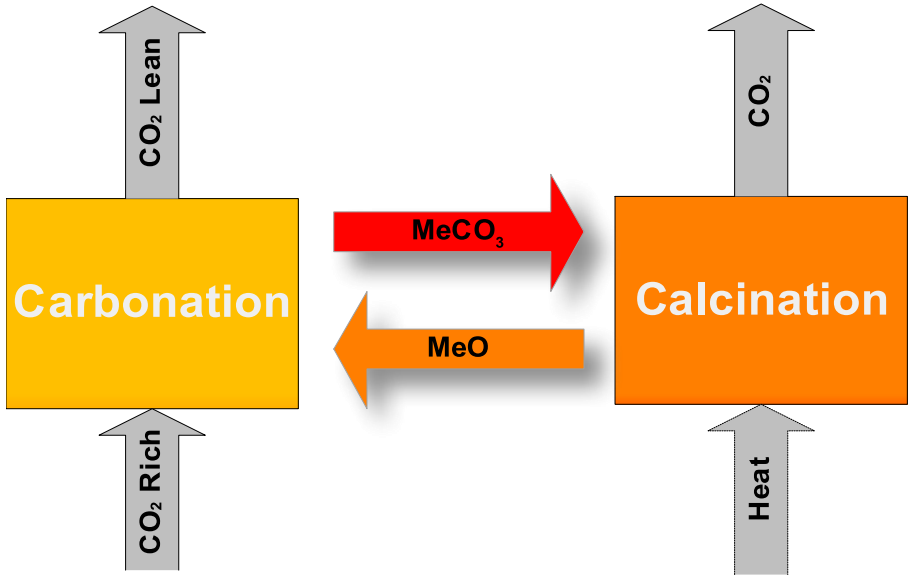
- Two Types of Chemical Looping Systems
- Particle Synthesis and Ionic Diffusion Mechanism
- Modes of Reactor Operation
- Stability of Solids Flow
- Chemical Looping System Efficiency
- Commercialization Potential

Chemical Looping 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/$MeCO_3$



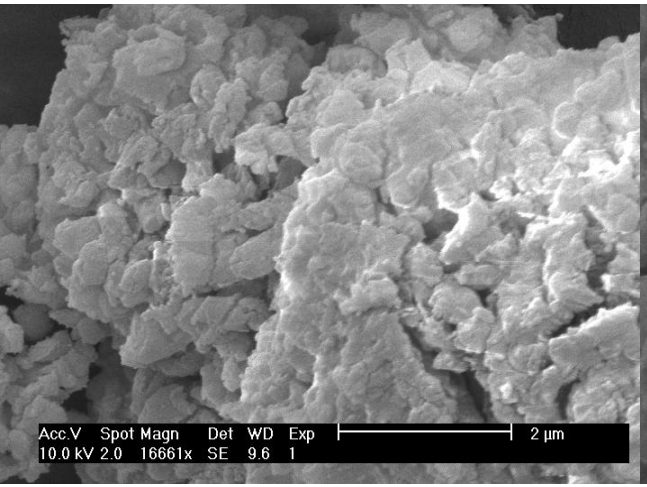


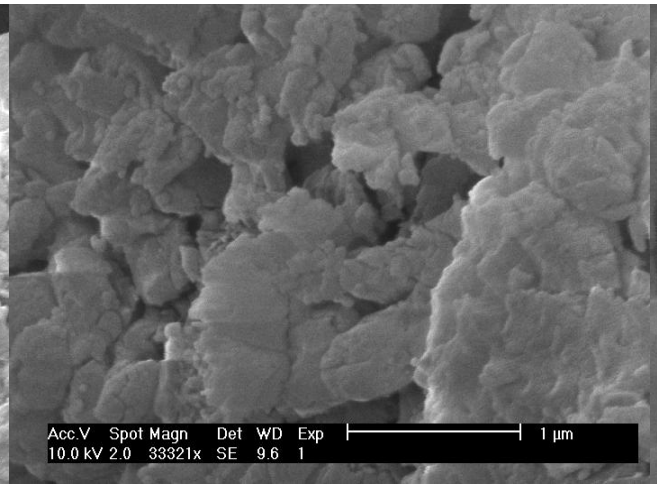
"1st International Conference on Chemical Looping", Lyon, France, March 17-19 (2010).

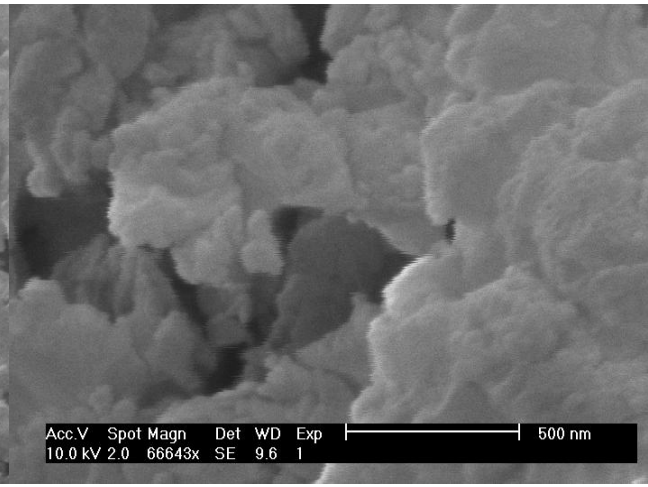
"1st Meeting of High Temperature Solids Looping Cycle Network", Oviedo, Spain, September 15-17 (2009).

Macroscopic Properties of Calcium Oxide

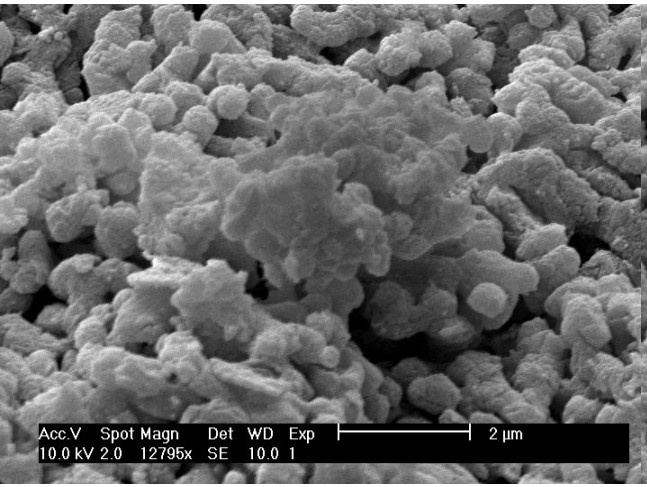
Sintered_CaO

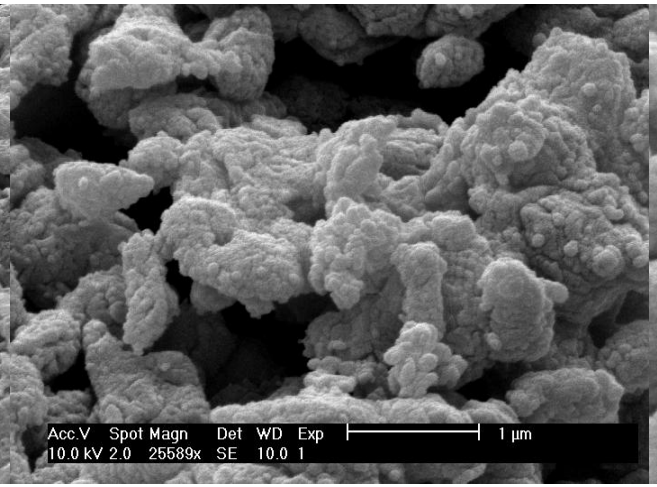


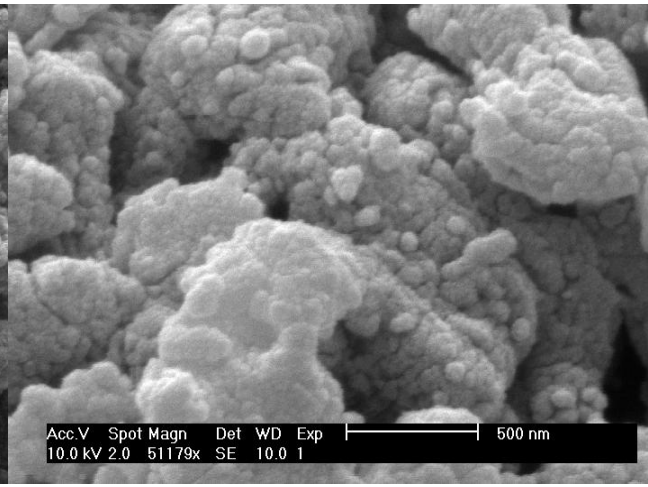




Hydrated_CaO

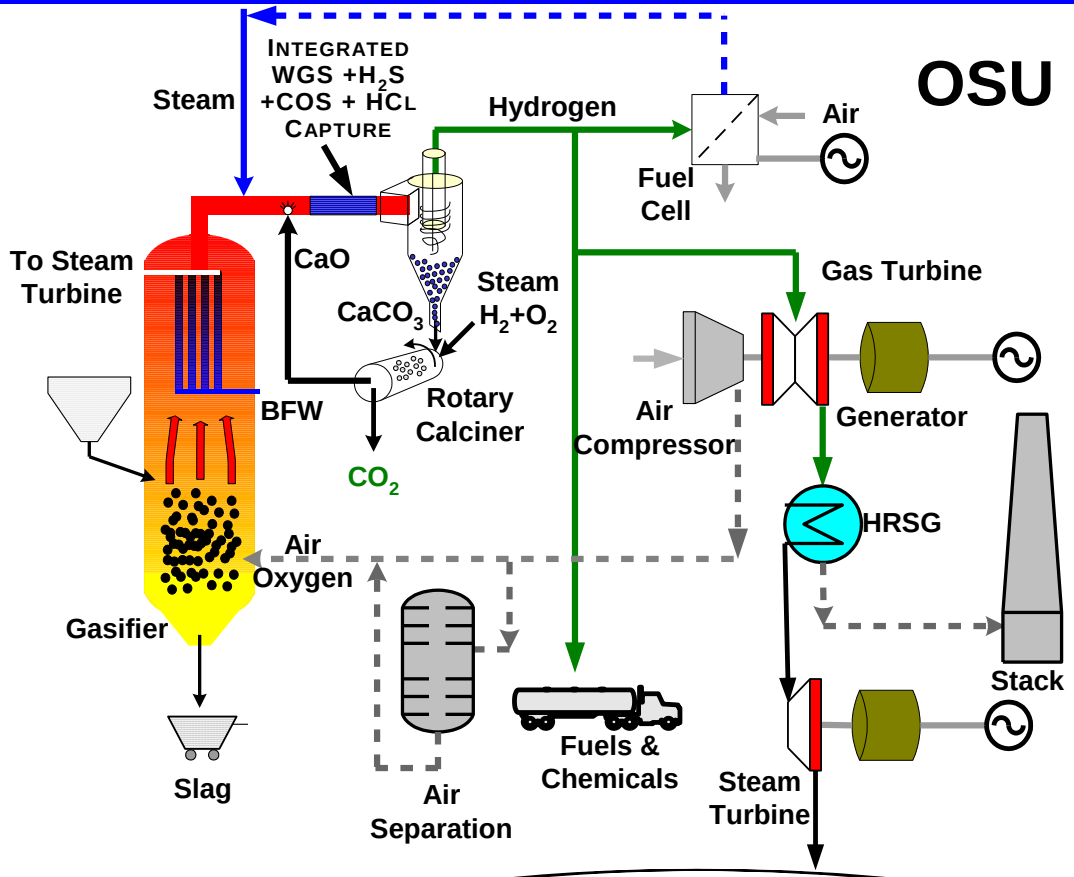


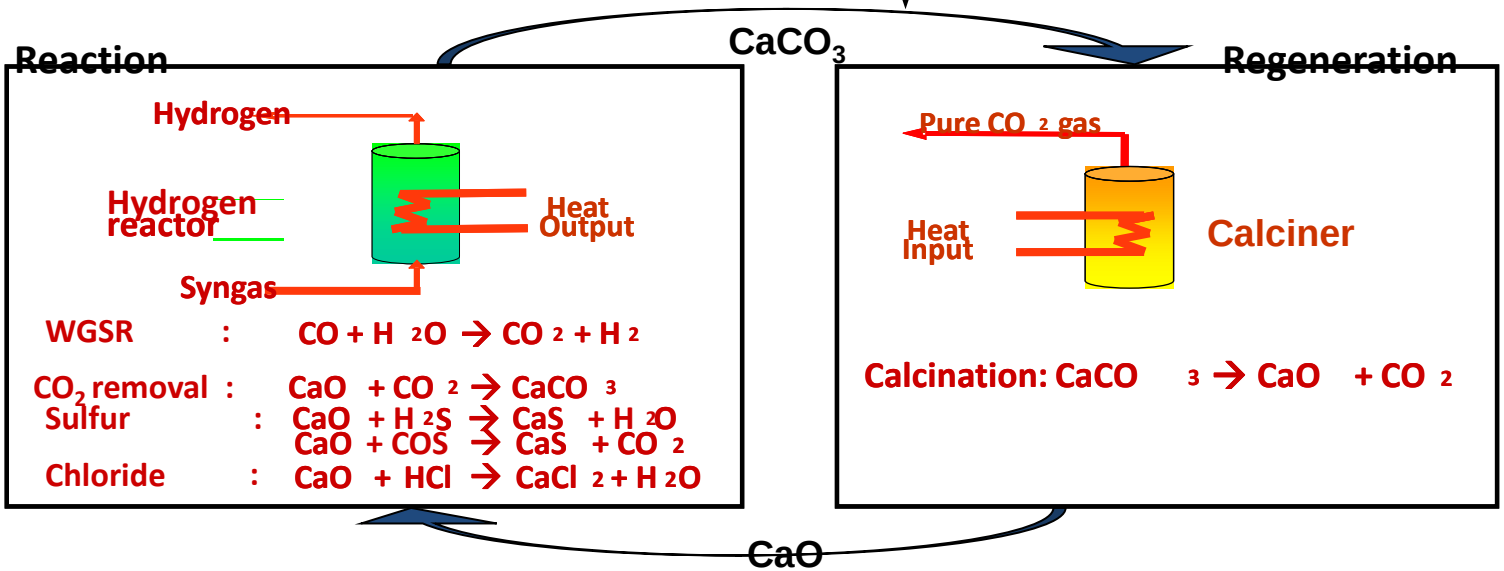




- Hydrated_CaO has smaller particles size
- Hydration caused cracks on the surface

OSU Calcium Looping Process





Calcium Looping Sub-pilot Unit for Hydrogen production

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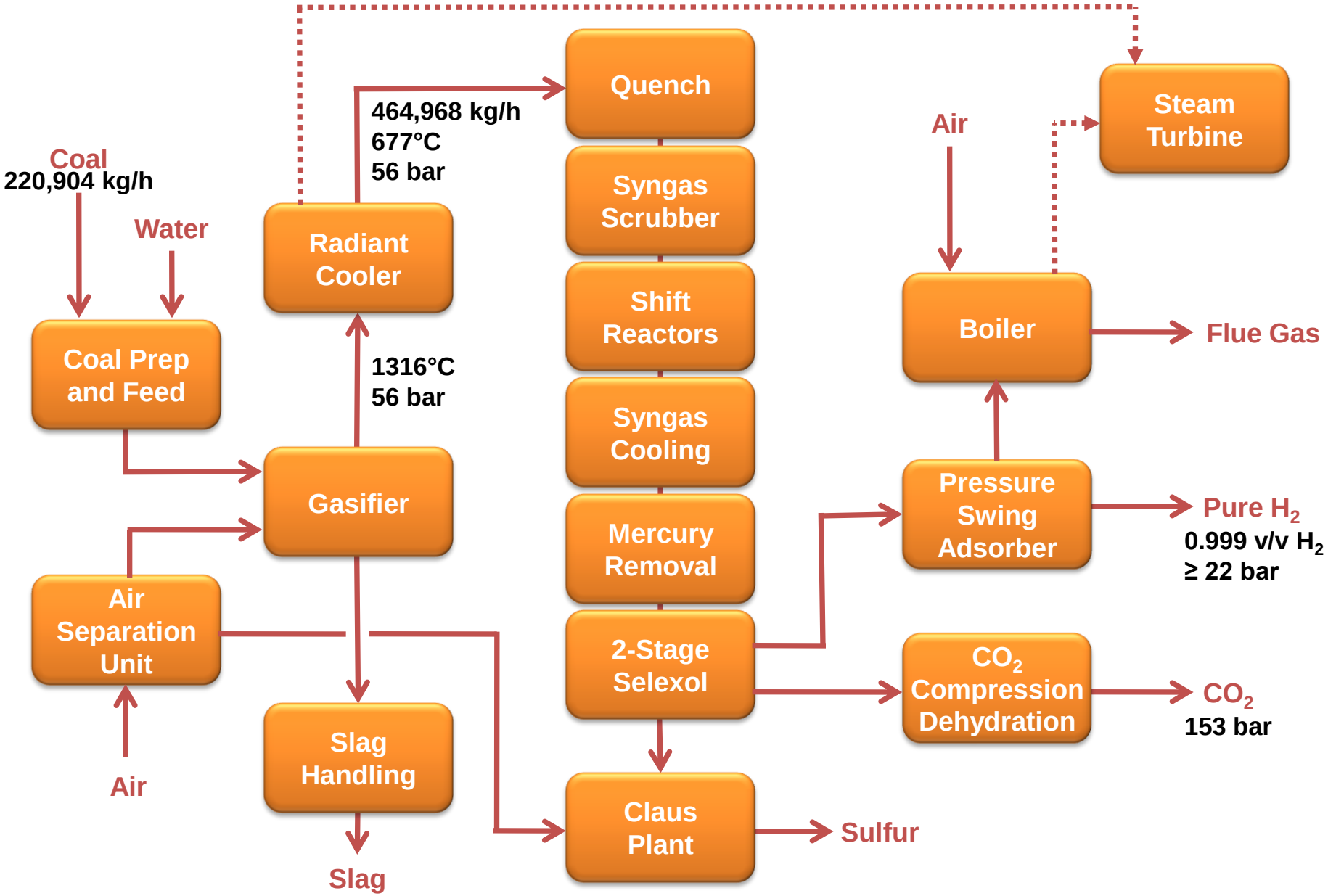
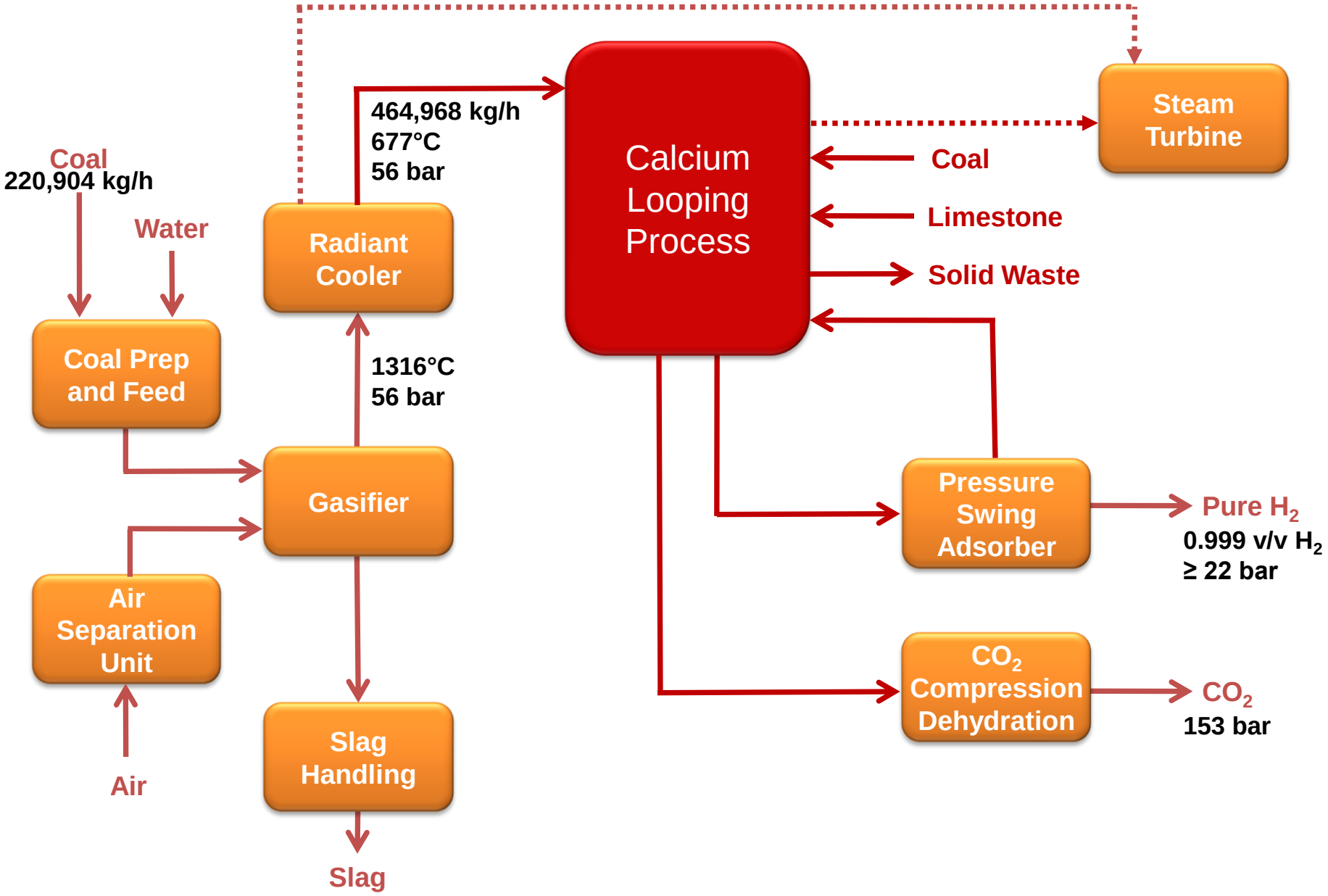
Base Coal-to-Hydrogen Process

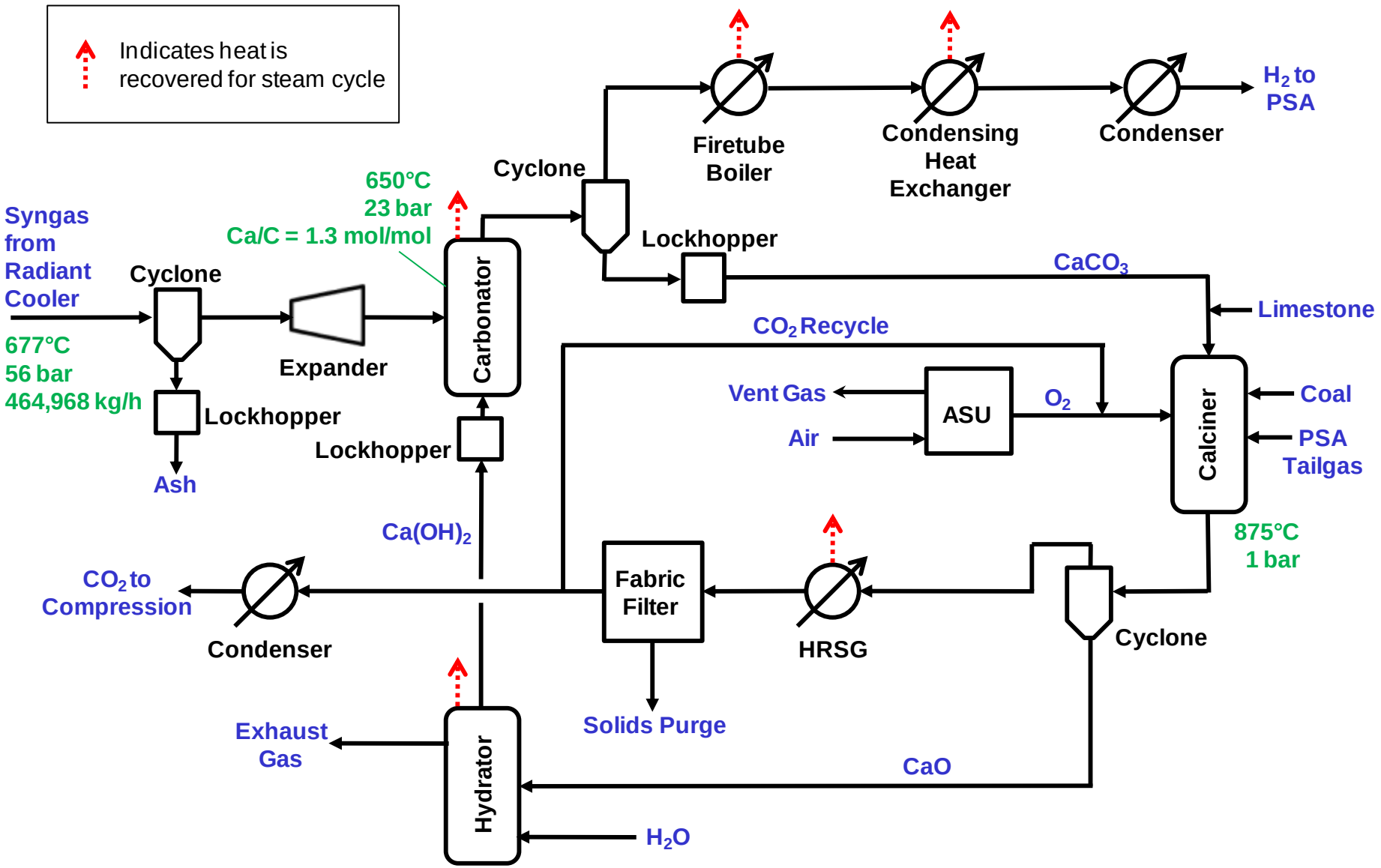


CLP Coal-to-Hydrogen Process



CLP Process Flow Diagram

Coal-to-Hydrogen Plant



Economic Analysis Results

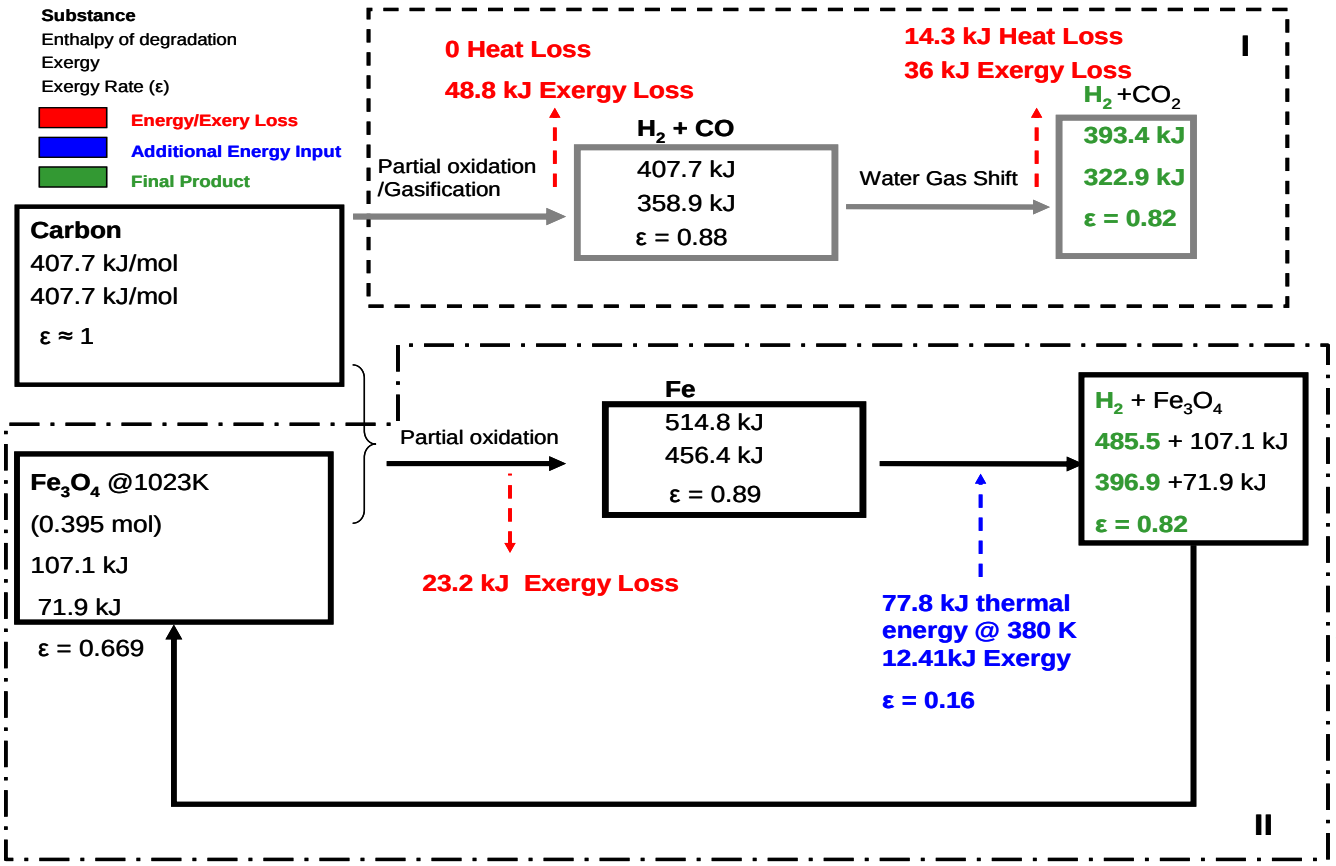
Coal-to-Hydrogen and SMR Cases

	Coal-to-Hydrogen Case		SMR Case	
	Base Plant	CLP Plant	Base Plant	CLP Plant
First-Year Capital ($/kg)	$2.26	$2.58	$0.62	$0.96
Fixed O&M ($/kg)	$0.43	$0.57	$0.16	$0.26
Fuel ($/kg)	$0.36	$0.55	$1.22	$1.40
Electric Power[a] ($/kg)	-$0.03	-$1.13	$0.14	-$0.70
CO_2 Emissions ($/kg)	$0.06	$0.00	$0.03	$0.00
Other Variable O&M ($/kg)	$0.04	$0.14	$0.02	$0.05
TOTAL FIRST-YEAR COH ($/kg)	**$3.12**	**$2.72**	**$2.19**	**$1.98**
TOTAL FIRST-YEAR COE ($/MWh)	**$105.00**	**$91.61**	**$105.00**	**$94.91**

[a]Computed using electricity price equal to the total COE value shown in the table.

Δ = -13% **Δ = -10%**

Exergy Analysis on Hydrogen Production



I. Contional Process

Exergetic Efficiency

322.9/407.7 = 79.2%

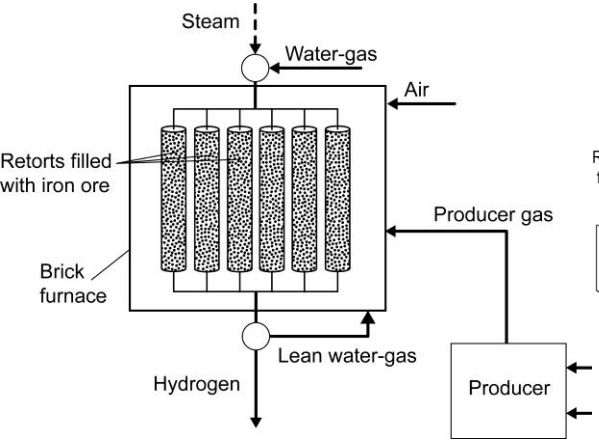
II. Chemcial Looping Process

Exergetic Efficiency

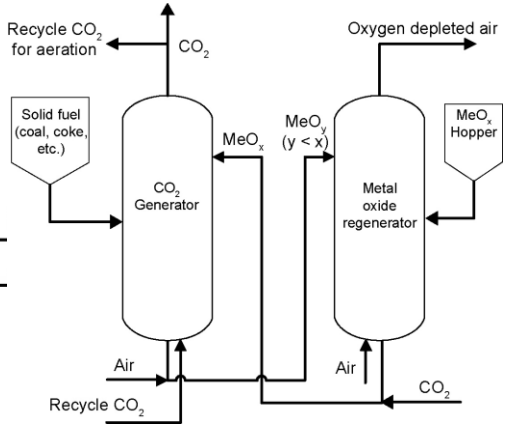
396.9/(407.7 + 12.41)=94.5%

Historical Development of Chemical Looping Technologies for Fossil Energy Conversions

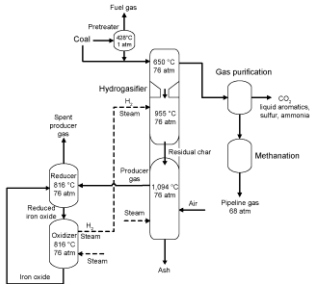
Technologies	Lane Process and Messerschmitt Process	Lewis and Gilliland Process	IGT HYGAS Process	CO_2 Acceptor Process
Time	Early Twentieth Century	1950s	1970s	1970s
Looping Media	$Fe/FeO/Fe_3O_4$	Cu_2O/CuO	FeO/Fe_3O_4	$CaO/CaCO_3$
Reactor Design	Fixed bed	Fluidized bed	Staged fluidized bed	Fluidized bed



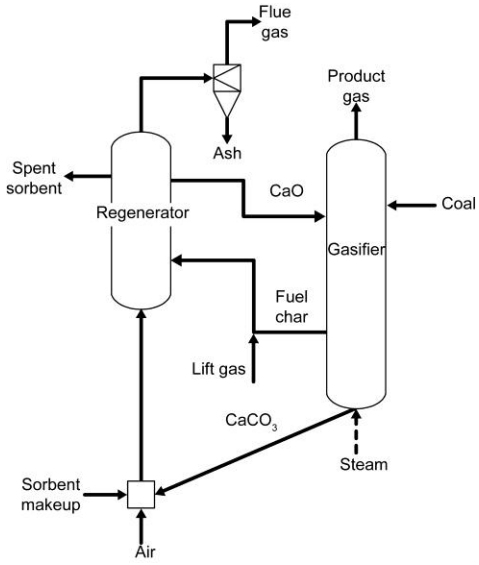
Lane Process



Lewis and Gilliland Process



IGT Process



CO_2 Acceptor Process

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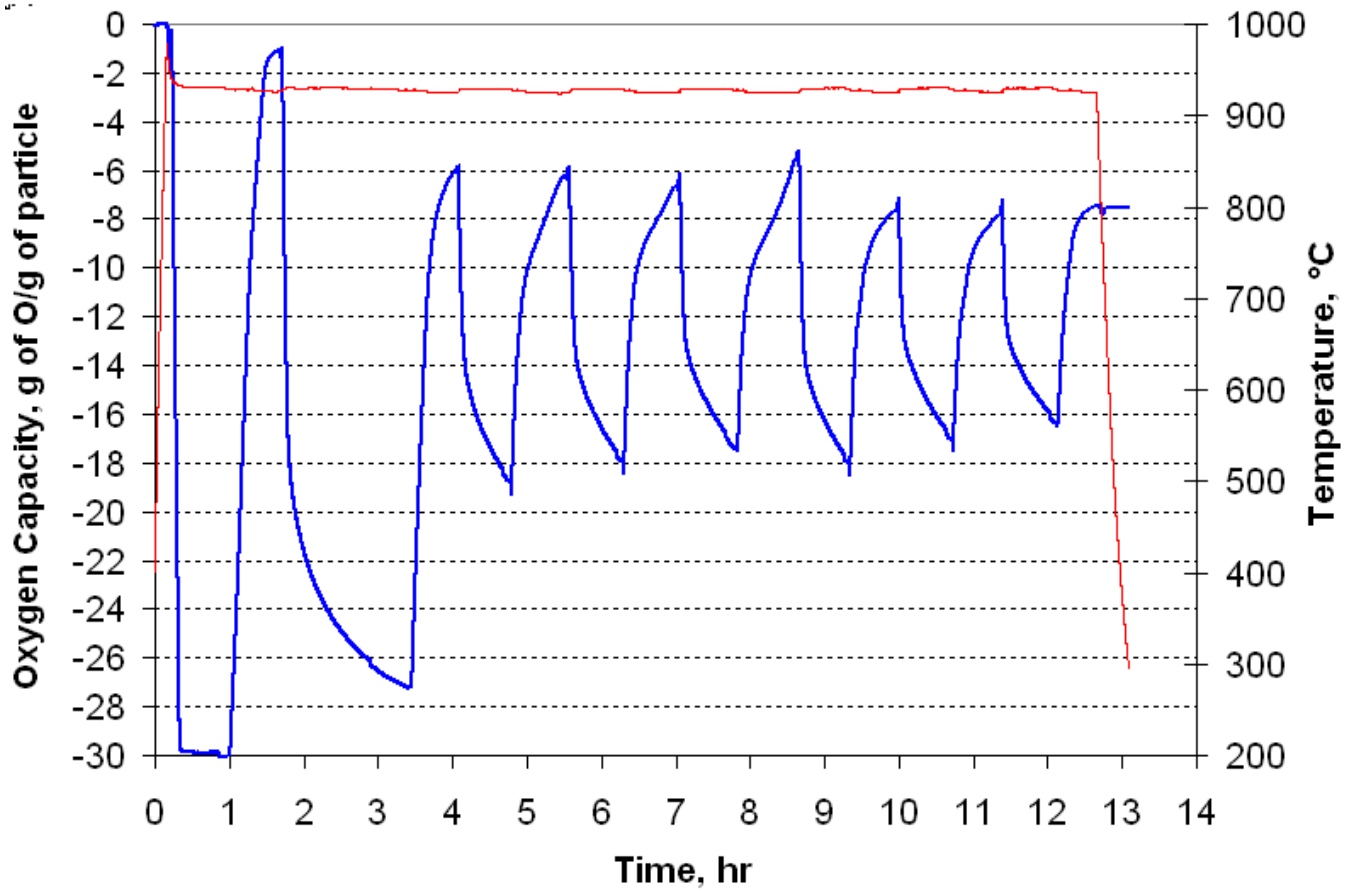
IGT Steam Iron HYGAS Process

	MO=> M	M=> MO
Gas Conversion (%)	65	45
Solid inlet	80% Fe3O4- 20% FeO	95% FeO- 5% Fe
Temperature (°C)	900	900
Reactor	Fluid Bed	Fluid Bed

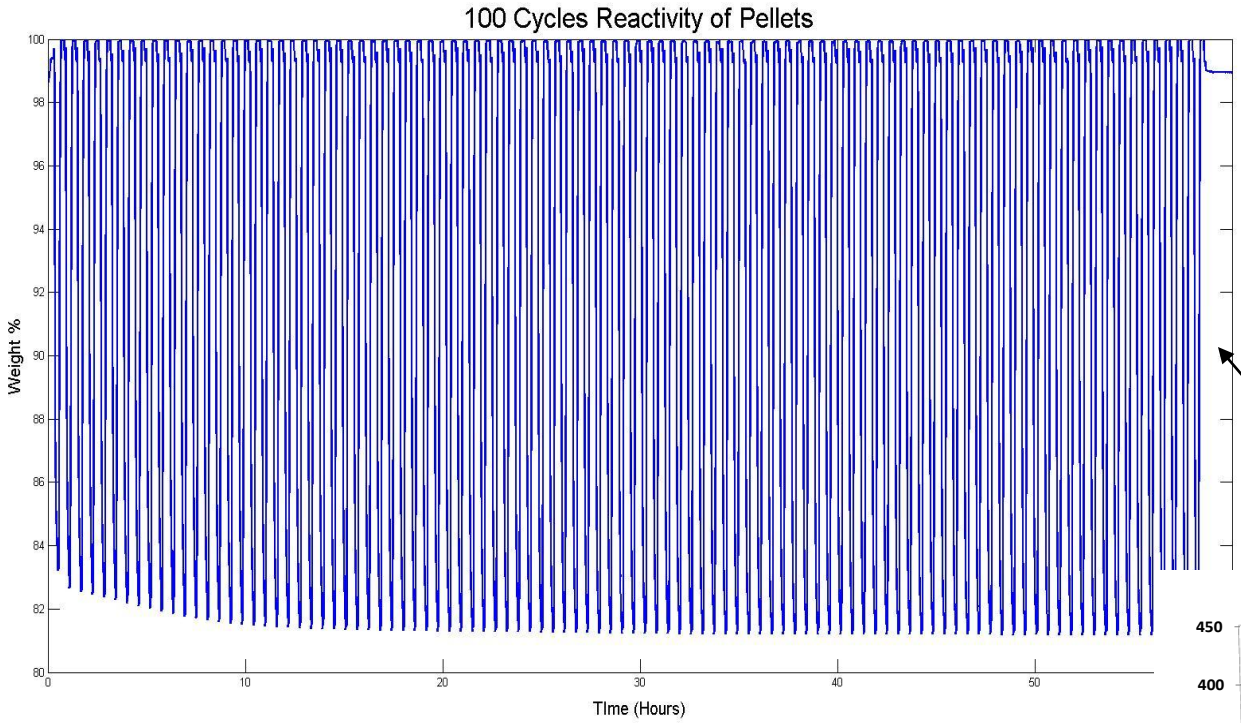
- Poor solid phase conversions: Used only about 25% oxygen capacity of the particles.
- Low gas phase conversions:
- Used iron ore: Low reaction rates
- Only about 40% efficient
- The process not geared towards making pure CO_2

Poor Thermo

Recyclability of Commercial Fe_2O_3

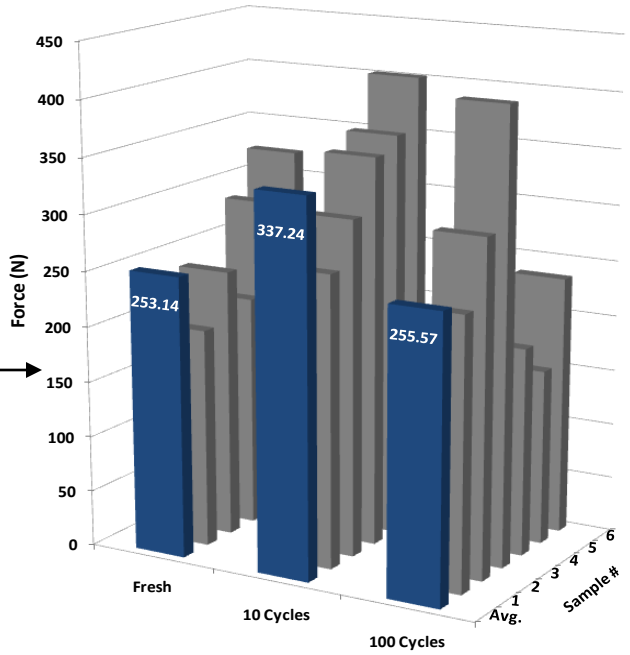


Performance of Composite Fe_2O_3



100 Cycle Pellet Reactivity

100 Cycle Pellet Strength



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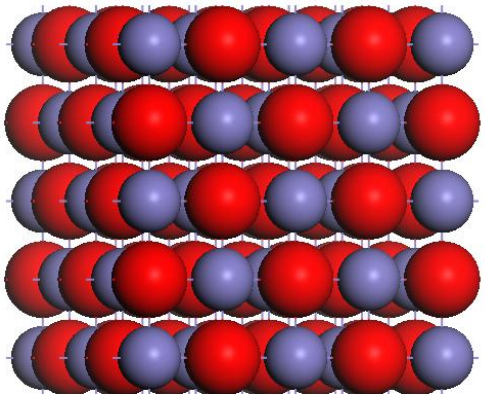
Oxygen Carrier Selection

Primary Metal	Fe	Ni	Cu	Mn	Co
Potential Supports	Al_2O_3, TiO_2, MgO, Bentonite, SiO_2, 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	+	–	–	–	–

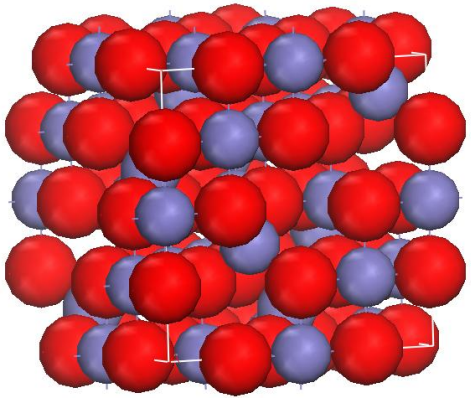
1. Maximum theoretical oxygen carrying capacity; 2. Reactivity with CH_4; 3. Mn_3O_4 is the highest oxidation state based on thermodynamics, although not thermodynamically favorable, Mn is assumed to be the lowest oxidation state

Structures of Iron Oxide

FeO

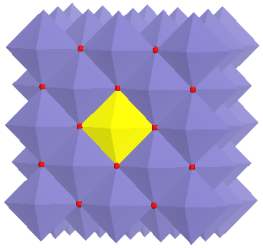


Fe_3O_4



NaCl Type

- oxygen close-packed cubic pattern
- iron occupy all **octahedral** interstices



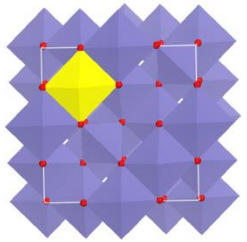
inverse Spinel Type

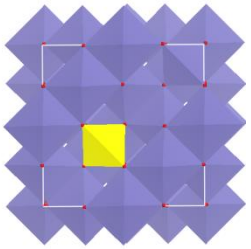
octahedral interstices

1/2 occupation rate

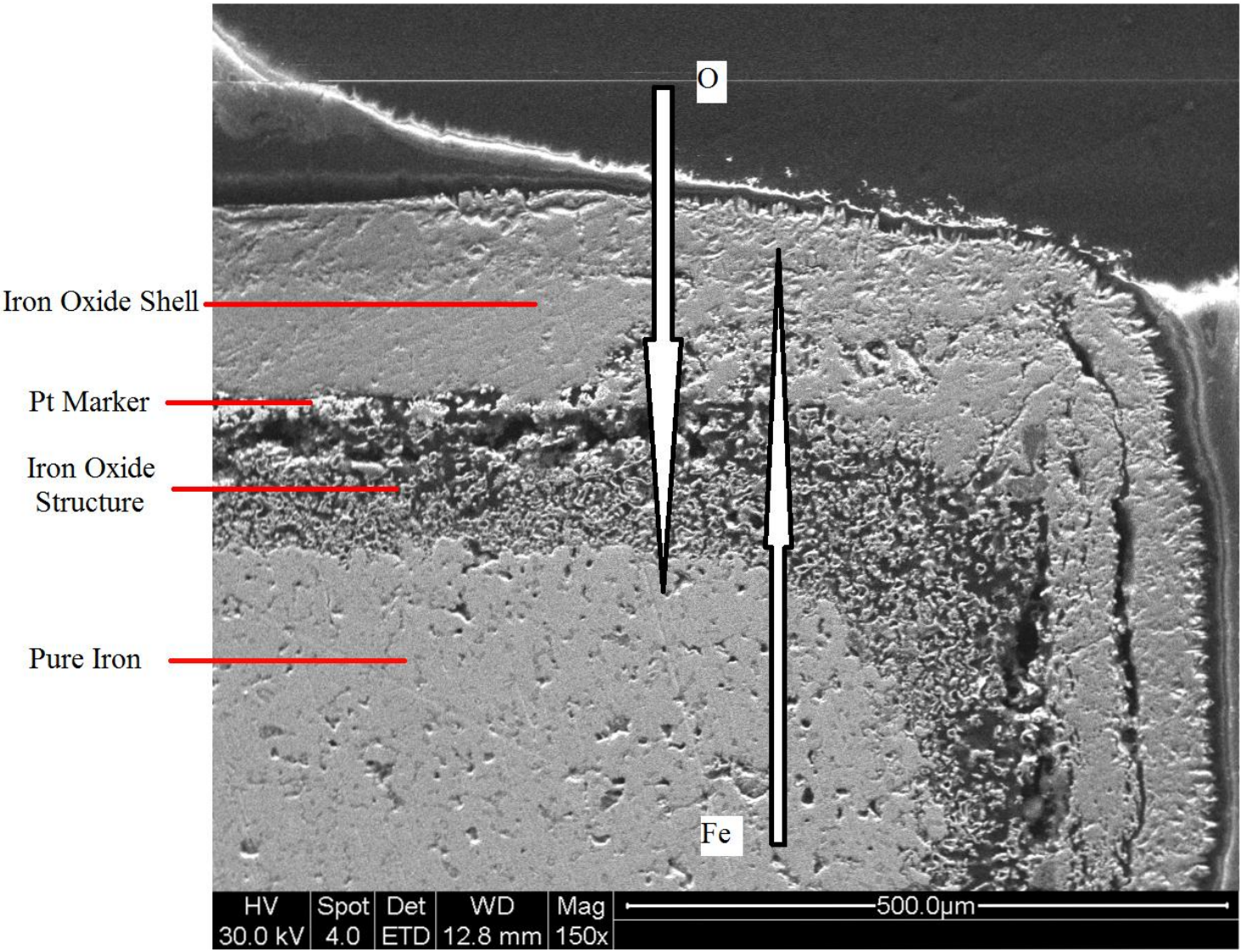
tetrahedral interstices

1/8 occupation rate



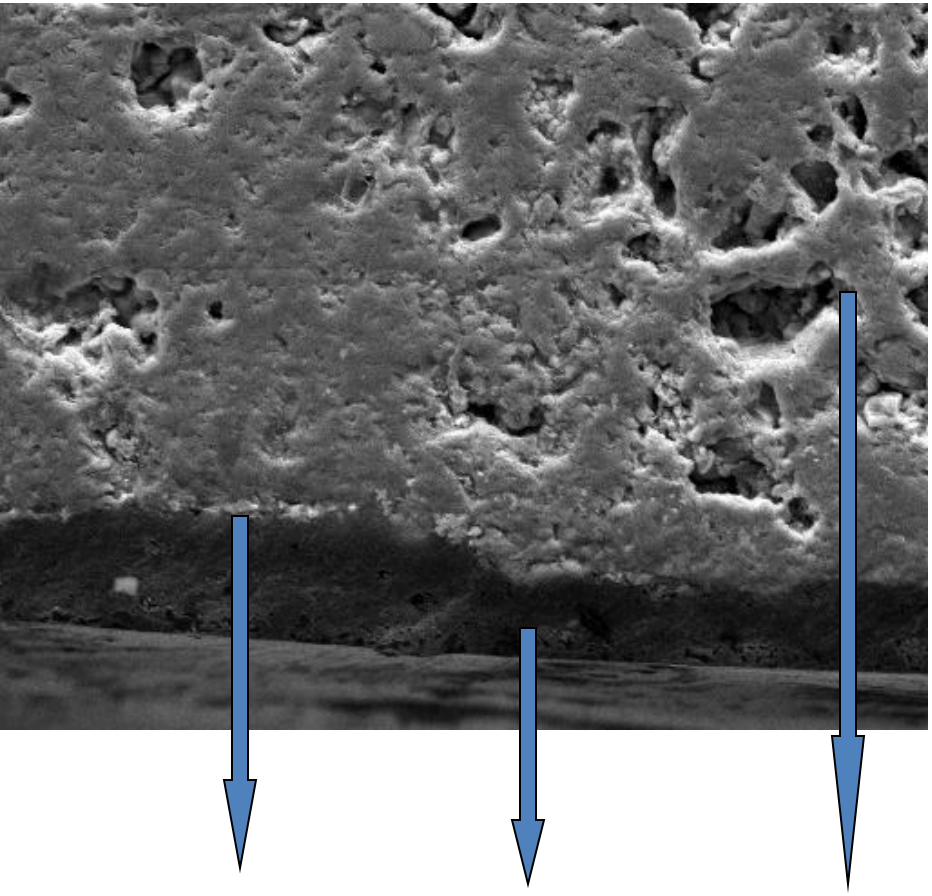


Pellet Reaction Mechanism – Ionic Diffusion for Unsupported Iron



Pellet Reaction Mechanism – Ionic Diffusion for Supported Iron

Partially oxidized Fe with support

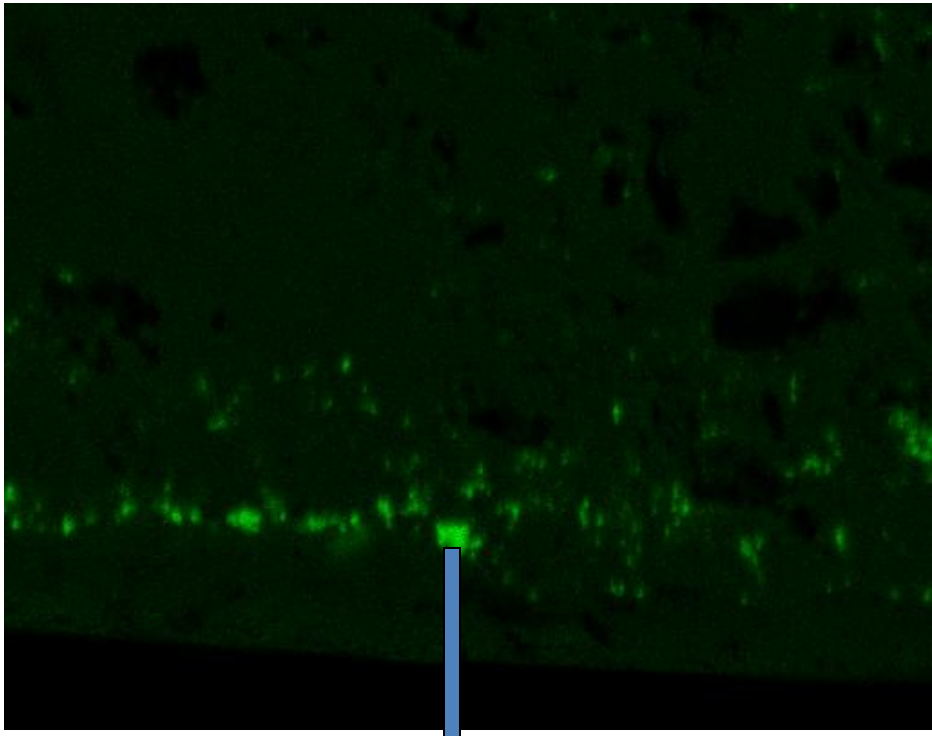


Pt

Epoxy Resin

Pellet bulk phase

Pt mapping

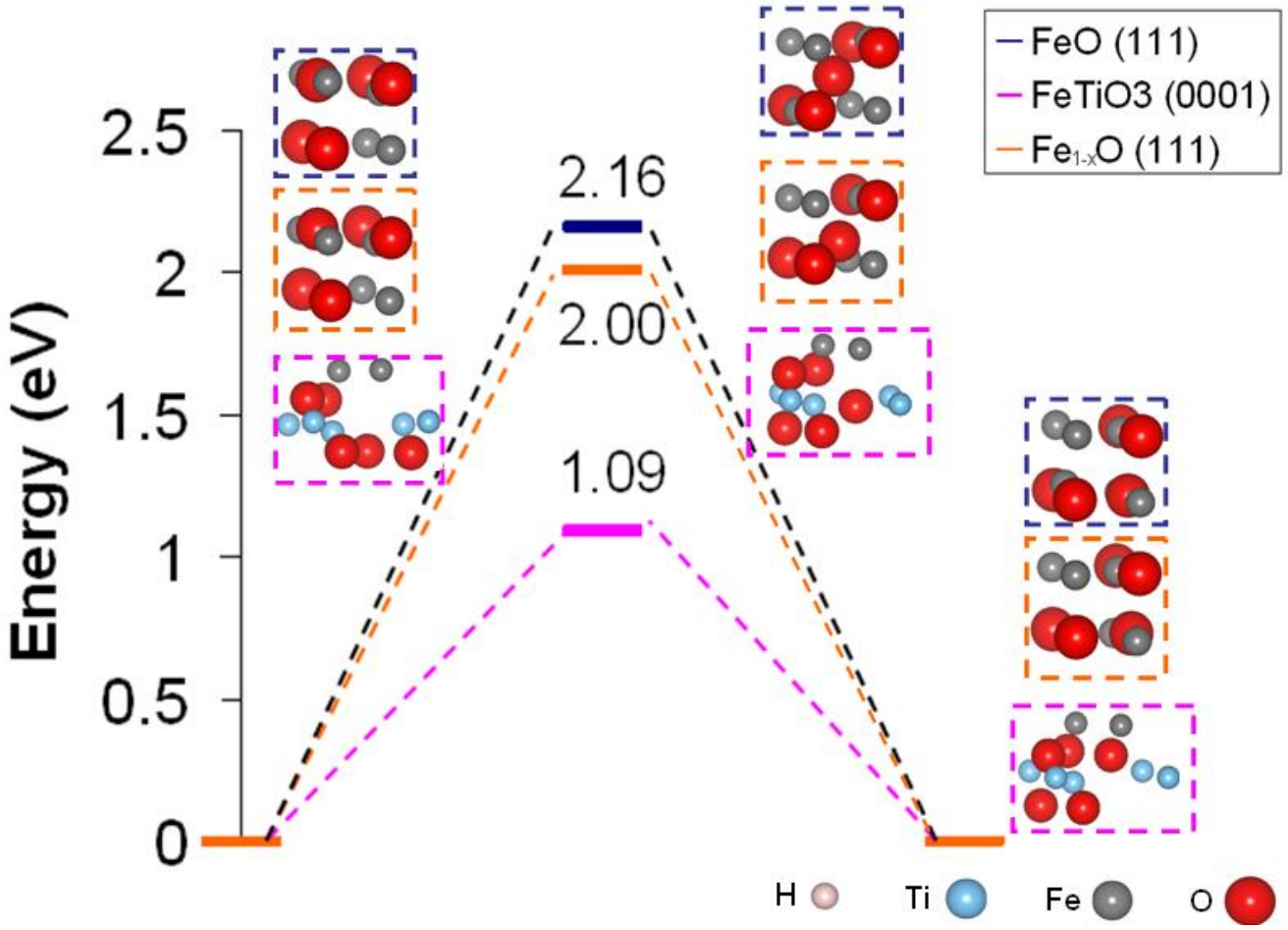


Pt

Role of Support – Oxidation of Fe and Fe/TiO_2

Simulation

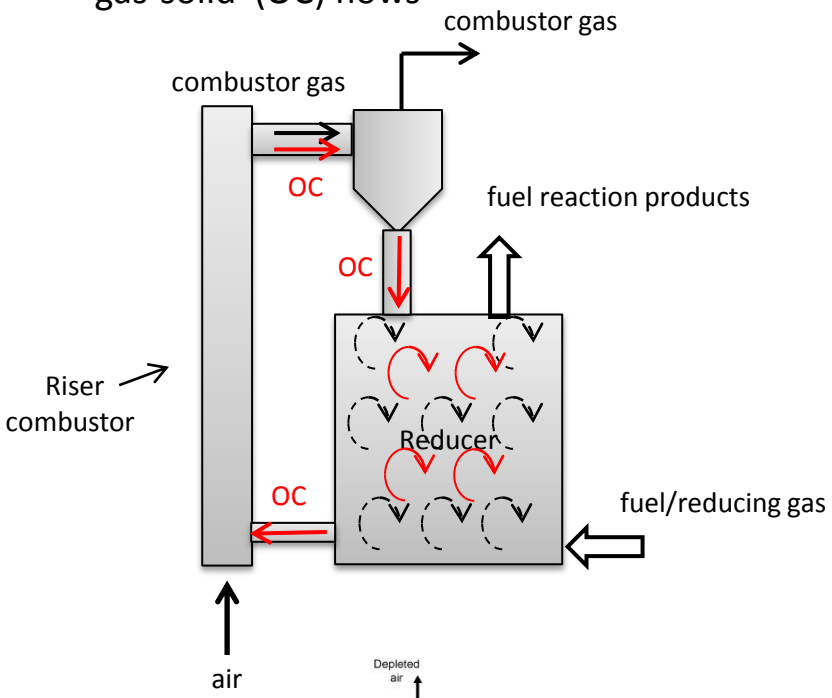
Oxygen anion transfer in Wüstite and Ilemnite

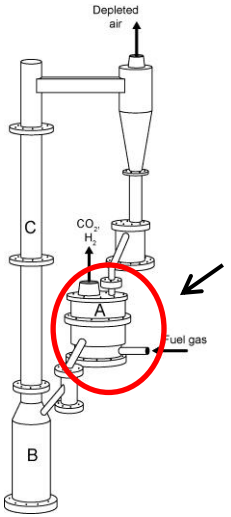


Energy barrier for O^{2-} can be reduced after support addition

Modes of CFB Chemical Looping Reactor Systems

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

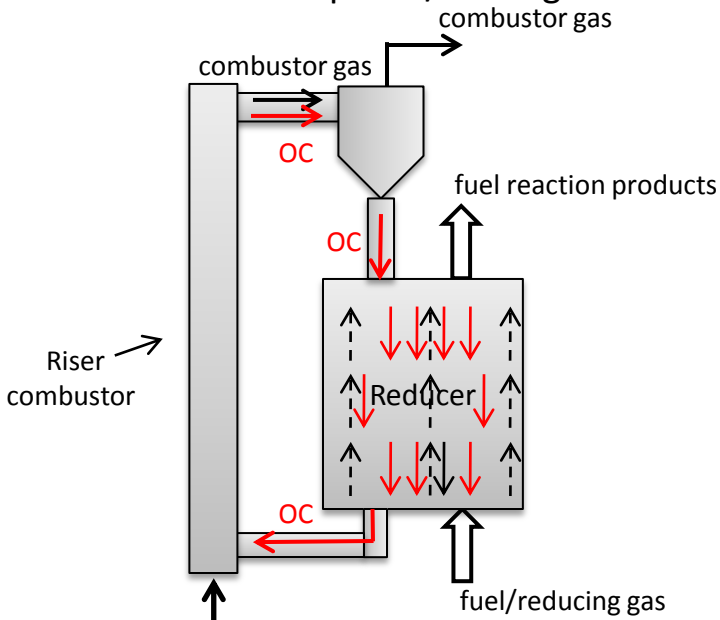


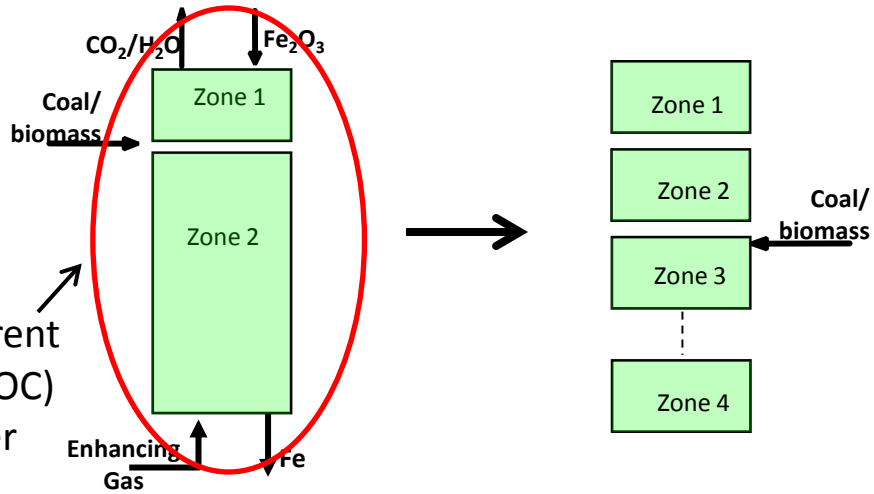


Fluidized Bed Reducer

Chalmers University 10-kW_{th} CLC System

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



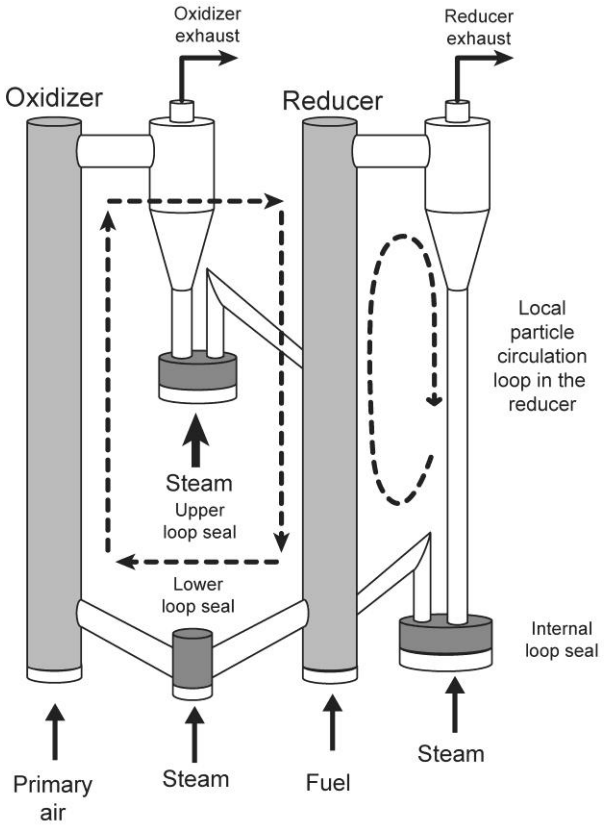


Contercurrent Gas-Solid(OC) Reducer

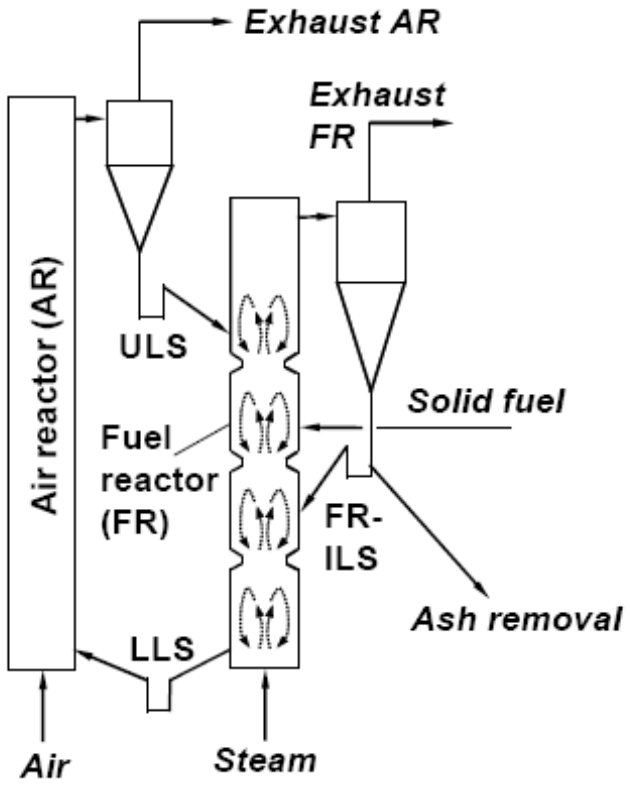
Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

Design Variation from Mode 1 to Mode 2

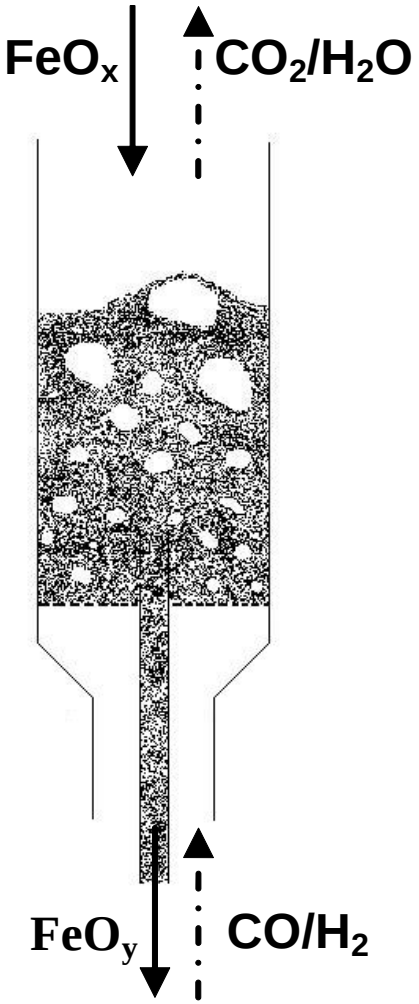
Original VUT 120-kW$_{th}$ CLC System (2007)



Modified VUT 120-kW$_{th}$ CLC System (2010)



Chemical Looping Reactor Design

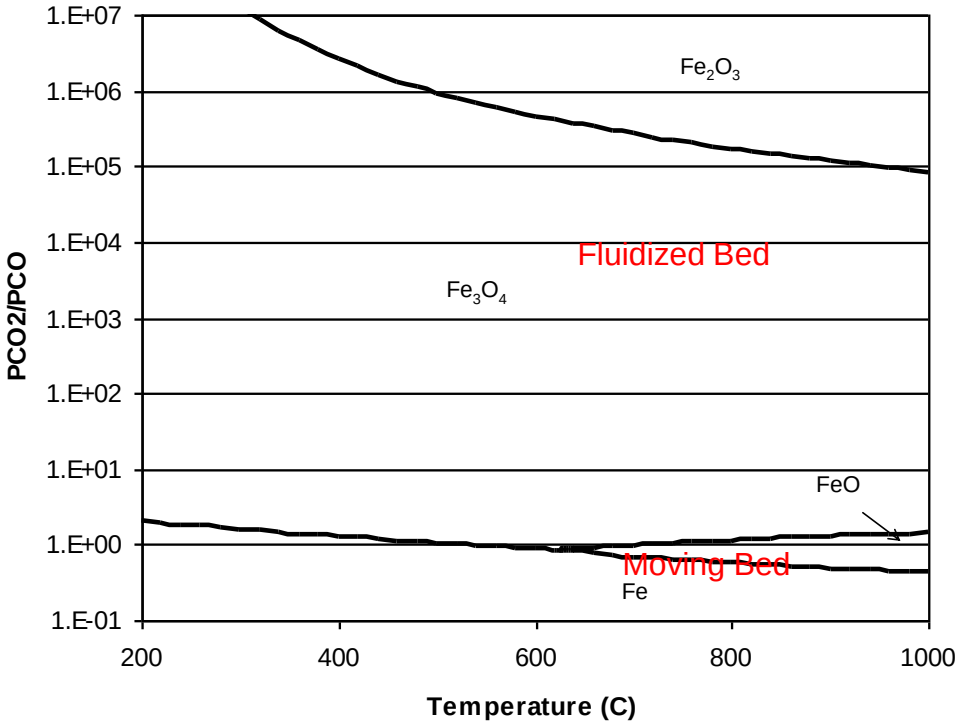


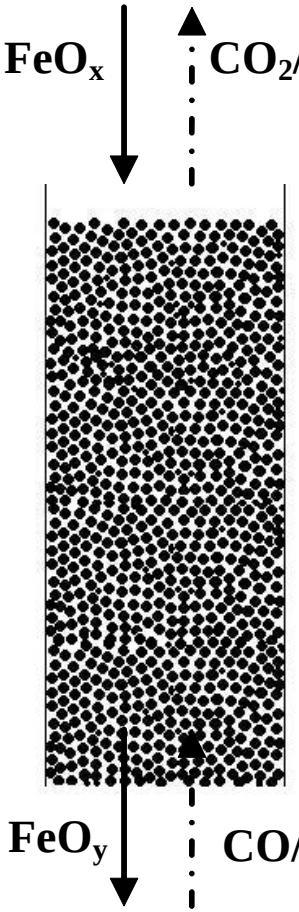
Fluidized Bed

(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**





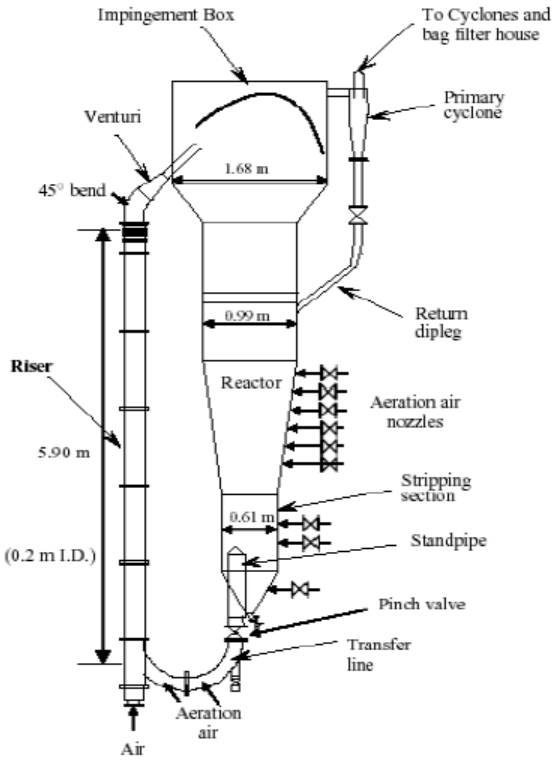
Moving Bed

4000 – 10000 kg/s or 14,000 – 36,000 ton/hour

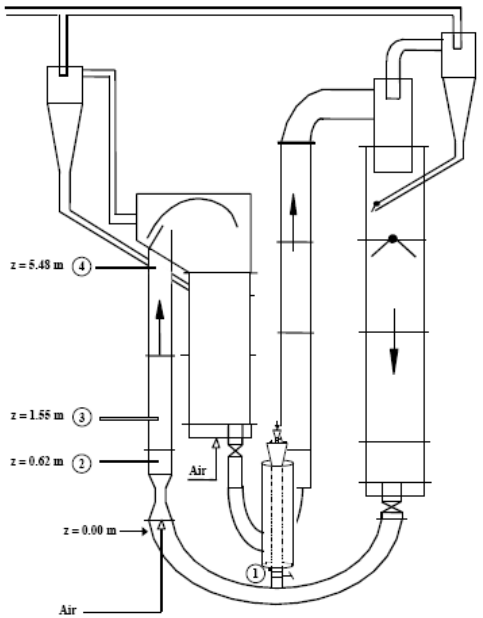
< 3,000 ton/hour

Particle Type	Ni		Cu				
Type of Data	Lab	CFB 120	Lab			CFB 300W	Moving Bed -H_2 25 kW
Particle Type	$NiO/MgAl_2O_4$	$NiO/MgAl_2O_4$	CuO/Al_2O_3	CuO/Al_2O_3	$Fe_2O_3/MgAl_2O_4$	Fe_2O_3/Al_2O_3	Composite Fe_2O_3
Air Flow Rate @1000 MWth and 10% Excess (mol/s)	11784						1309
Volumetric Air Flow Rate at 1 atm and 900 ºC (m^3/s)	1134						126
Particle Circulation Rate @ 1000 MWth (*kg/s*)	**4000**	**10000**	**3000**	**6000**	**8000**	**10000**	**800**
Reducer Solids Inventory (tonne)	230	160	70	total 2100	500	1200	1500 Total
Oxidizer Solids Inventory (tonne)	390	80	390		n/a	350	
Medium Particle Size (μm)	153	120	300	200	153	151	2000
Particle Density (g/cm^3)	1.9	5	2.5	2.5	4.1	2.15	2.5
Ut (m/s)	2	0.8	2	1.2	1.1	0.6	11
Uc (m/s)	4	4.8	4.9	4.2	4.8	3.6	4
Use (m/s)	6	6.7	7.5	6.1	6.9	4.9	9.7
Typical Riser Superficial Gas Velocity (m/s)	7.00						12
Bed Area Turbulent Section (if Required) at 1 atm (m^2)	231.47						25.18
Bed Area Required for Riser Section at 1 atm (m^2)	162.03						10.49
Corresponding **Riser Diameter (m)**	**14.37**						**3.66**
Solids Flux at 1 atm (kg/m^2s)	24.69	61.72	18.52	37.03	49.37	61.72	76.23
Number of Beds Needed given 8 m ID Riser	3.23						<1
Number of Beds Needed given 1.5 m ID Riser	91.73						5.94
Ug for a Single 1.5 m ID Riser at 1 atm (m/s)	642.14						71.29
Ug for a Single 8 m ID riser at 1 atm (m/s)	22.58						2.5 (Ug < Ut; N/A)
Required Pressure for a Single 1.5m ID Riser (atm)	91.73						10.00
Solids Flux for a Single 1.5 m ID Riser (kg/m^2s)	2264.69	5661.71	1699	3397.03	4529.37	5661.71	452.88
Required Pressure for a Single 8 m ID Riser (atm)	3.23						26 Ug < Ut; N/A
Solids Flux for a Single 8 m ID Riser (kg/m^2s)	79.62	199.04	59.71	119.43	159.24	199.04	

Circulating Fluidized Bed Systems



Single Loop High Density CFB System (Kirbas et al., 2007)



Two Loop High Density CFB System (Kulah et al., 2008)

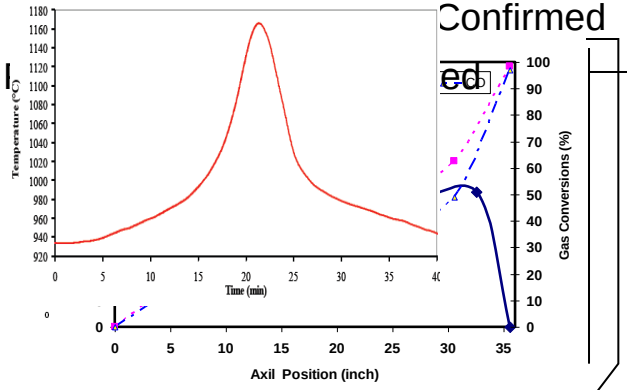
Kirbas G, Kim SW, Bi X, Lim J, Grace JR. Radial Distribution of Local Concentration Weighted Particle Velocities in High Density Circulating Fluidized Beds. Paper presented at: The 12th International Conference on Fluidization - New Horizons in Fluidization Engineering; May 13-17, 2007; Vancouver, Canada.

Kulah G, Song X, Bi HT, Lim CJ, Grace JR. A NOVEL SYSTEM FOR MEASURING SOLIDS DISPERSION IN CIRCULATING FLUIDIZED BEDS. Paper presented at: 9th International Conference on Circulating Fluidized Beds; May, 13 – 16, 2008; Hamburg, Germany.

OSU Syngas Chemical Looping Process Development

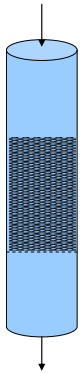
Maximum Operating Temperature Determined

Confirmed

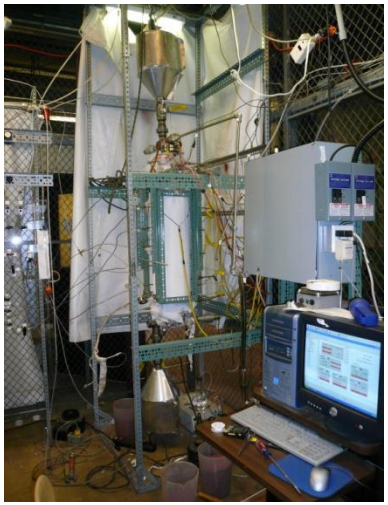


Scale

Particle



Fixed Bed Tests

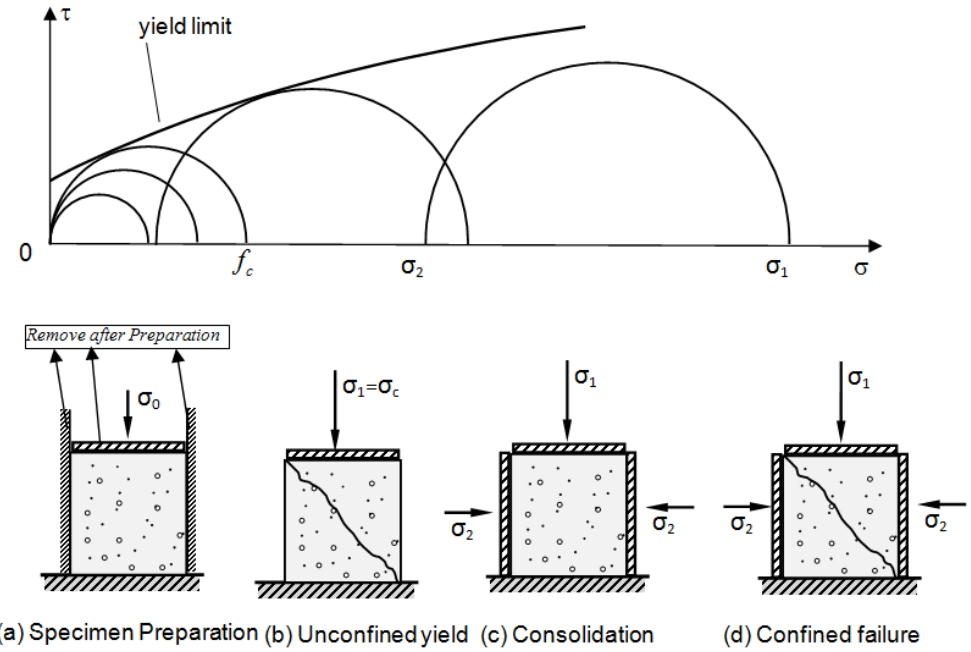


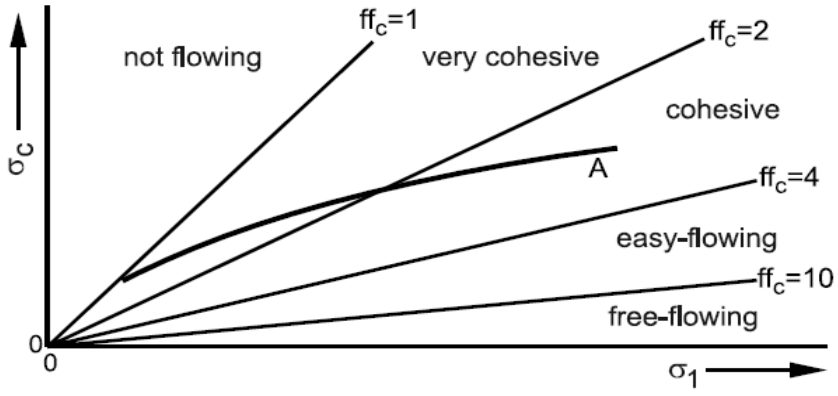
Bench Scale Tests

Sub-Pilot SCL
Integrated Tests

Time

Flow Properties of Bulk Solids

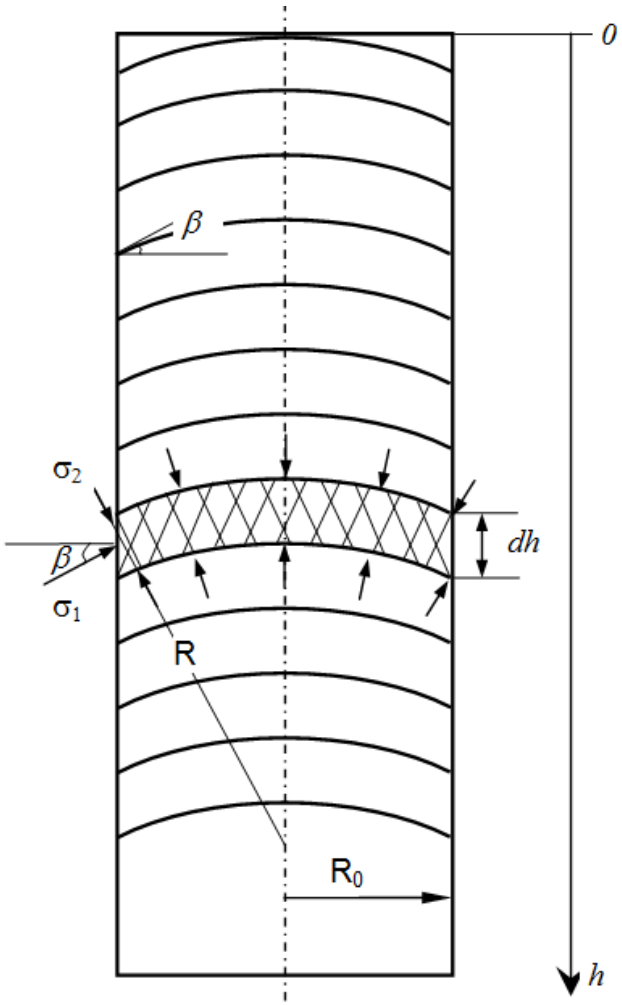




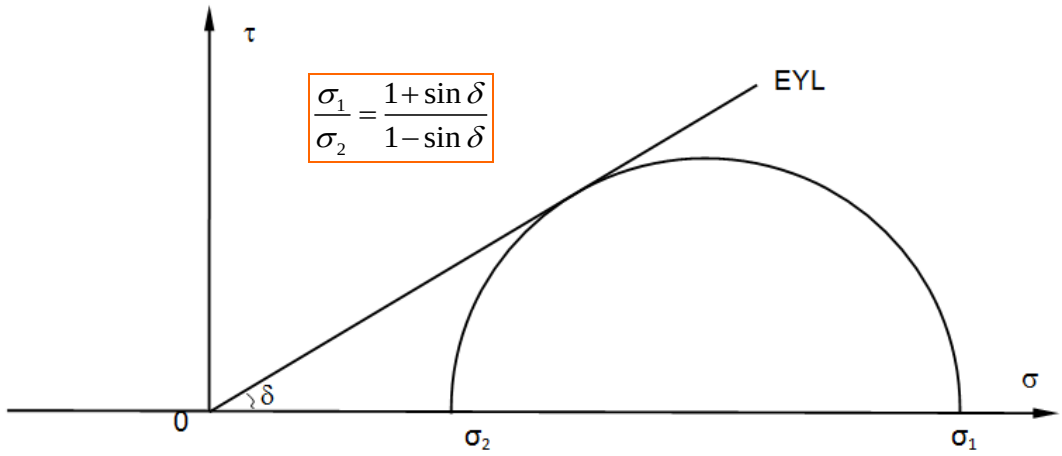
$ff_c = \frac{\sigma_0}{f_c}$: flowability of bulk solids

Consolidation and Yield of Bulk Solids

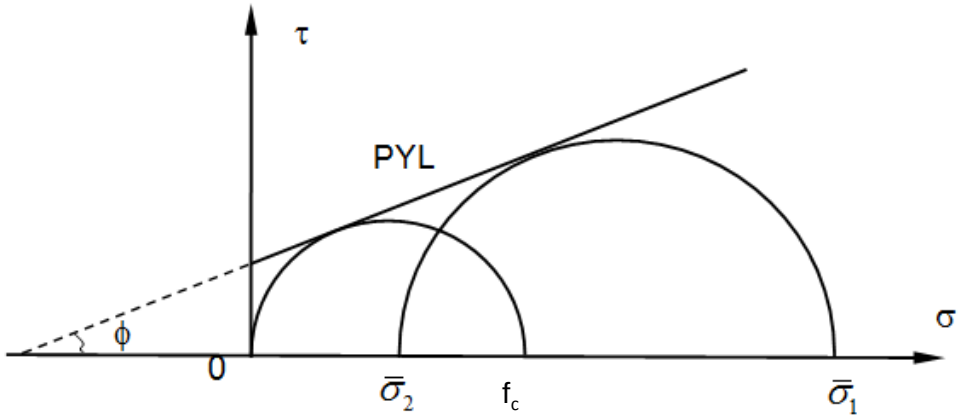
Stress of Bulk Solids in Vertical Reactor



Piling of Bulk Solids



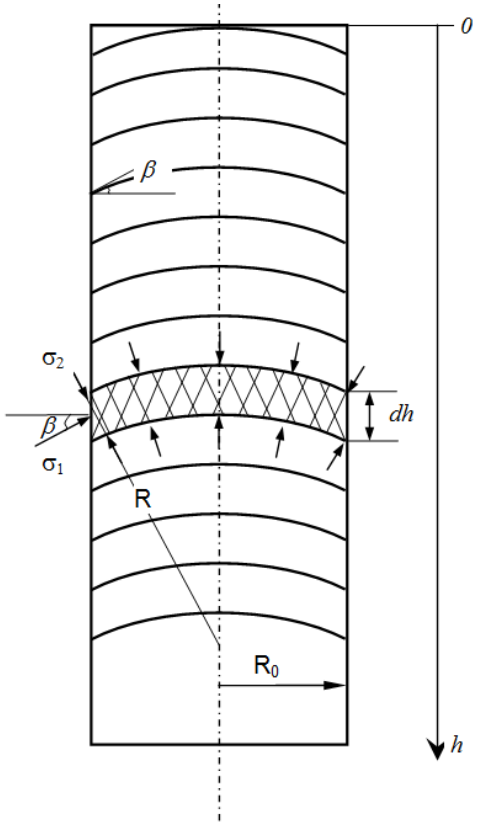
Flowing Condition



Arching Condition

Stress Condition of Bulk Solids

Stress Distribution in Flowing Solids



Limitation from wall: fully developed wall angle

$$\tau_{xy} = \frac{\sigma_1+\sigma_2}{2}\sin\delta\sin 2\beta = \frac{\sigma_1+\sigma_2}{2}(1+\sin\delta\cos 2\beta)\tan\varphi$$

$$\sin(2\beta-\varphi) = \frac{\sin\varphi}{\sin\delta} = \sin\nu$$

$$\Rightarrow \beta = \frac{\nu+\varphi}{2}$$

φ: angle of friction between the powder and the wall

$$\Delta W = \Delta F_{lift} + \Delta F_{upward}$$

$$\Delta W = \pi R_0^2 \Delta h \rho_s g \qquad \Delta F_{support} = \pi R_0^2 \Delta\sigma_2 \qquad \Delta F_{lift} = \pi R \Delta h(\sigma_1-\sigma_2)\sin 2\beta$$

$$\rho_s g = \frac{2\sin\delta\sin 2\beta}{R_0(1-\sin\delta)}\sigma_2 + \frac{d\sigma_2}{dh}$$

$$\begin{cases} a = \dfrac{2\sin\delta\sin 2\beta}{R_0(1-\sin\delta)} \\ b = \dfrac{R_0(1-\sin\delta)}{2\sin\delta\sin 2\beta}\rho_s g \end{cases}$$

$$\sigma_2 = b + (\sigma_0 - b)e^{-ah}$$

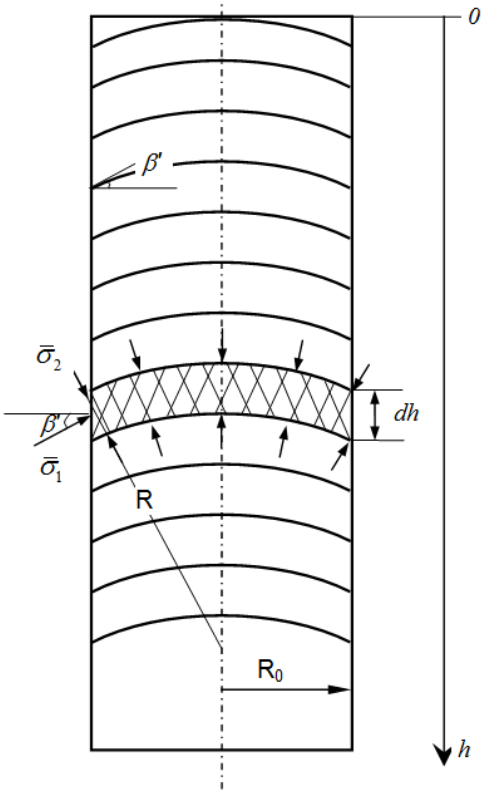
σ_0: external normal stress at the top of the solid surface

With counter-current interstitial gas flow

Drag force can be treated as a reduction of gravity

$$b = \frac{R_0(1-\sin\delta)}{2\sin\delta\sin 2\beta}(\rho_s g - F_D)$$

Stress Distribution in Arched Solids



Limiting Condition: Maximum lift force ⟹ $\beta' = \min(\phi, \pi/4)$

$$\rho_s g = (\bar{\sigma}_1 - \bar{\sigma}_2)\sin 2\beta' + \frac{d\bar{\sigma}_2}{dh}$$

$$\bar{\sigma}_2 = b + (\bar{\sigma}_0 - b)e^{-ah}$$

$$\begin{cases} a = \dfrac{2\sin\phi\sin 2\beta'}{R_0(1-\sin\phi)} \\ b = \dfrac{R_0(1-\sin\phi)}{2\sin\phi\sin 2\beta'}\rho_s g - \dfrac{f_c(1-\sin\phi)}{2\sin\phi} \end{cases}$$

With counter-current interstitial gas flow:

$$b = \frac{R_0(1-\sin\phi)}{2\sin\phi\sin 2\beta'}(\rho_s g - F_D) - \frac{f_c(1-\sin\phi)}{2\sin\phi}$$

Requirement for arching: $\bar{\sigma}_2 = 0$

Reactor Size Criteria for Arching

- No External Stress on Top

$$\bar{\sigma}_2 = b(1 - e^{-ah})$$

$$b = 0 \Rightarrow \frac{R_0(1-\sin\phi)}{2\sin\phi\sin 2\beta'}\rho_s g = \frac{f_c(1-\sin\phi)}{2\sin\phi}$$

$$\boxed{R_0 \geq \frac{f_c \sin 2\beta'}{\rho_s g}}$$

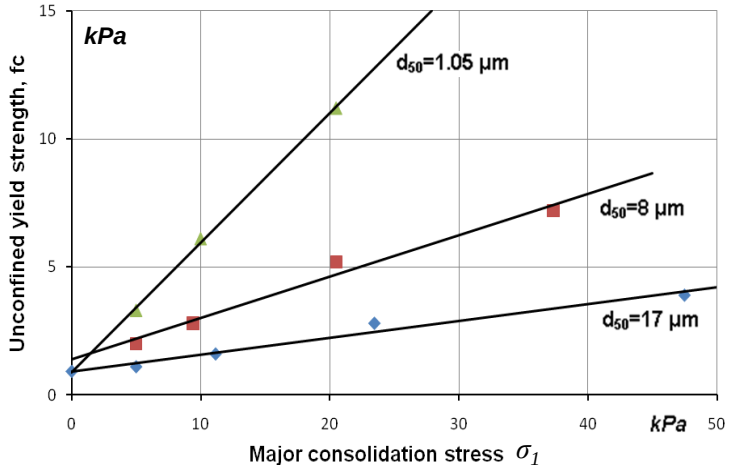
Influence of Some Critical Parameters

1. Gas Flow

$$R_0' \geq \frac{f_c \sin 2\beta'}{\rho_s g - F_D} > R_0$$

Counter-Current Interstitial gas flow causes reduction of gravity, and thus needs a larger reactor size

2. Particle Size



unconfined yield strength of some alumina-powders (*)

$$R_0 \geq \frac{f_c \sin 2\beta'}{\rho_s g}$$

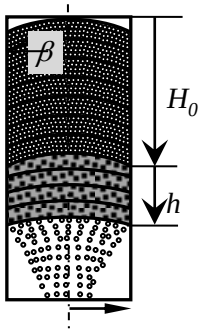
$$f_c \propto \frac{1}{d_p^n}$$

Smaller particles need larger reactor size

3. Mixing with Fine Powders

The flowability governed by flow properties of the fine powders as shearing takes place across the fines.

4. Layer of Fine Powders



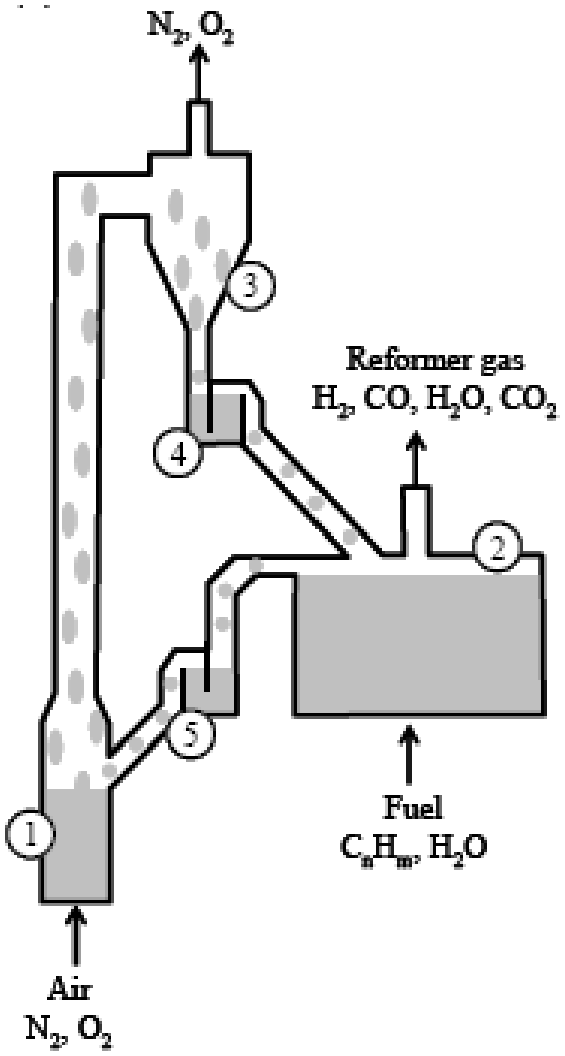
Arching Criteria:

depend on height of fine powder layer

$$h = -\frac{1}{a'} \ln \frac{b'}{b' - \bar{\sigma}_0'}$$

*: Kohler, T. and H. Schubert, *Influence of the Particle-Size Distribution on the Flow Behavior of Fine Powders.* Particle & Particle Systems Characterization, 1991. **8**(2): p. 101-104

European Chemical Looping Reforming/Gasification Application - I



Reducer:

$$MeO + CH_4 \rightarrow Me + CO + 2H_2$$

Oxidizer:

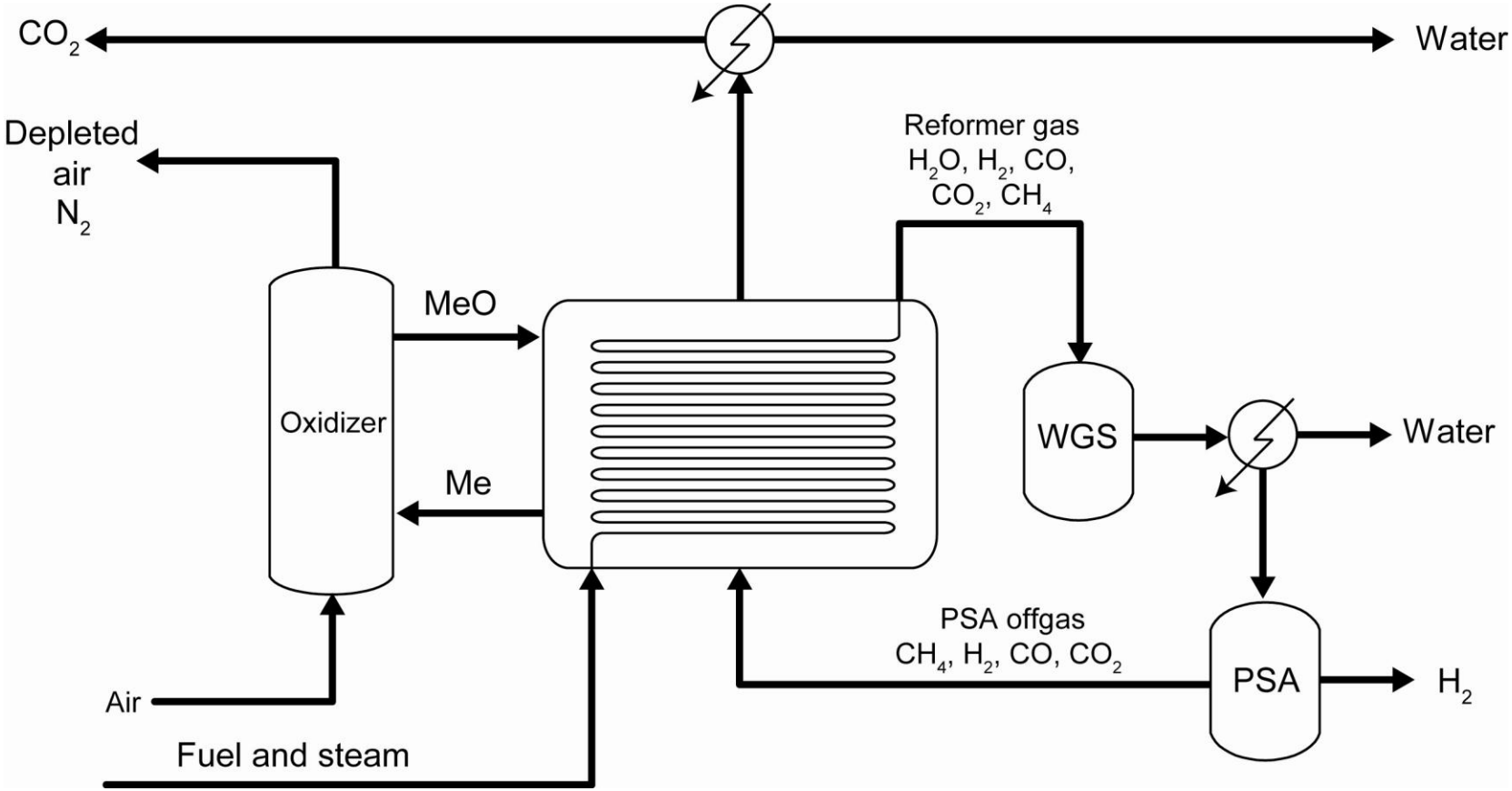
$$Me + O_2 \rightarrow MeO$$

Overall Reaction:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$$

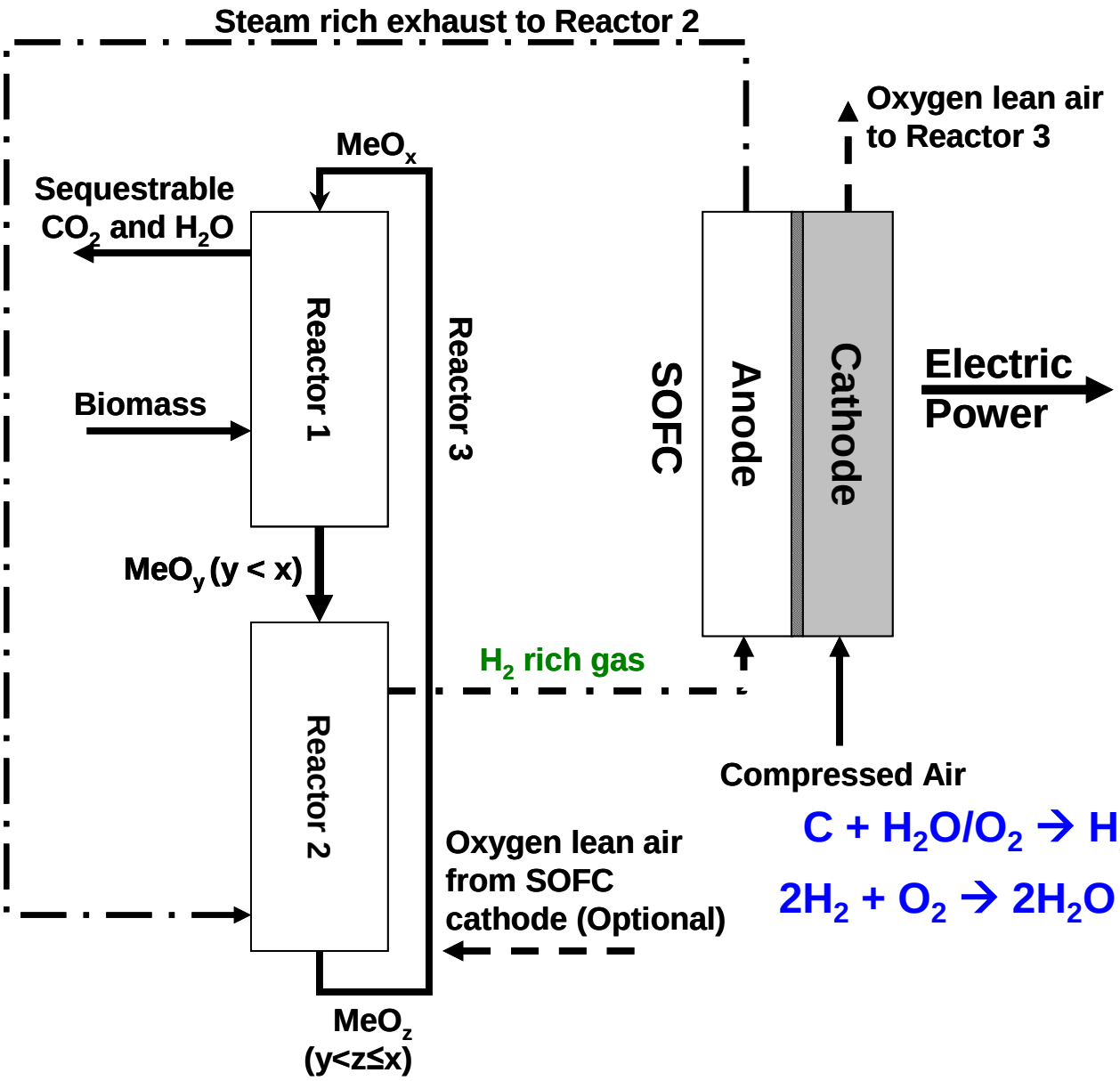
Juan adanez, *International Journal of Hydrogen energy, 2011*

European Chemical Reforming/Gasification Application - II

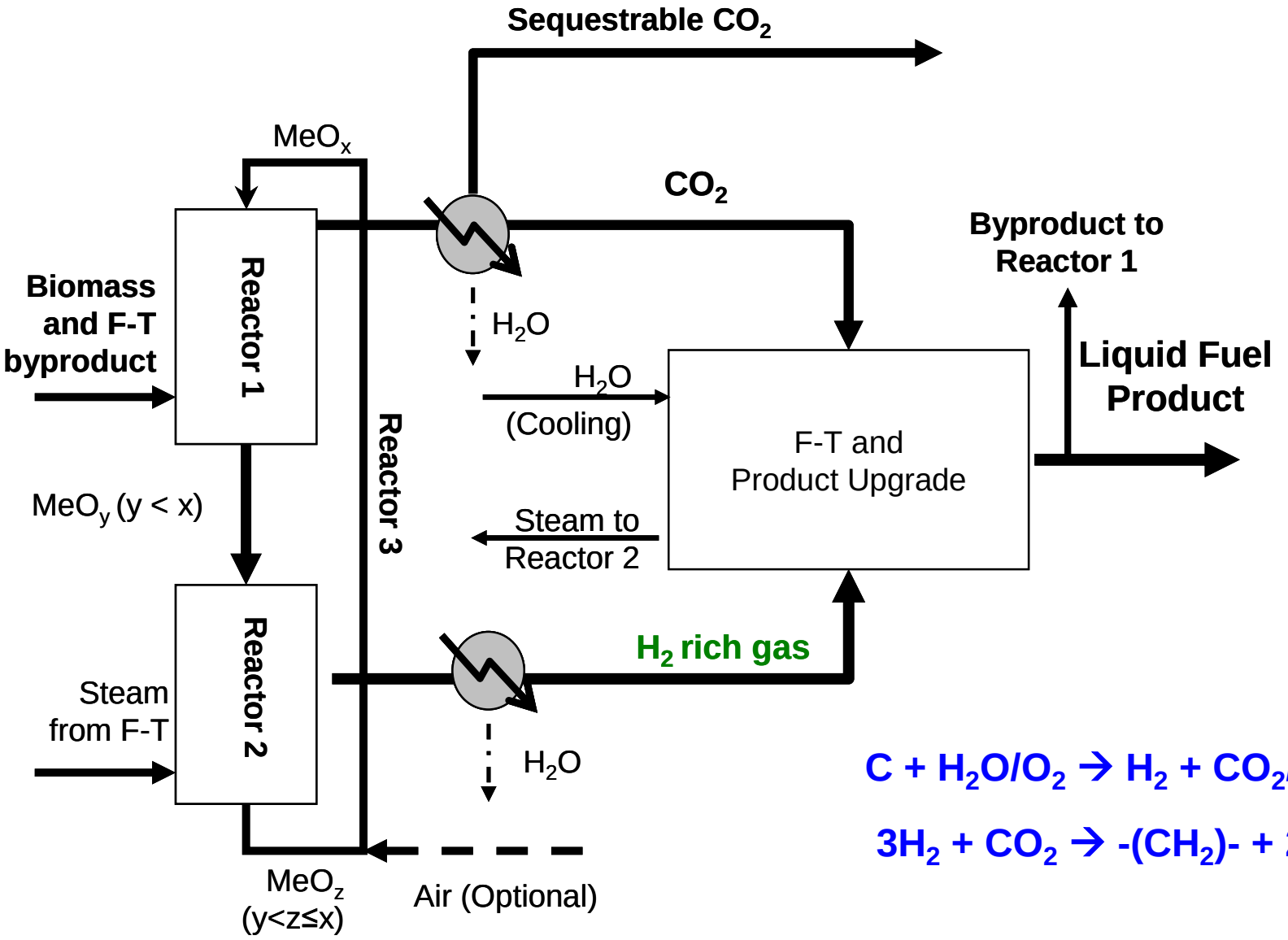


Ryden, M., and A. Lyngfelt, *International Journal of Hydrogen energy, 2006*

OSU Chemical Looping Integrated with Fuel Cell Application – 3



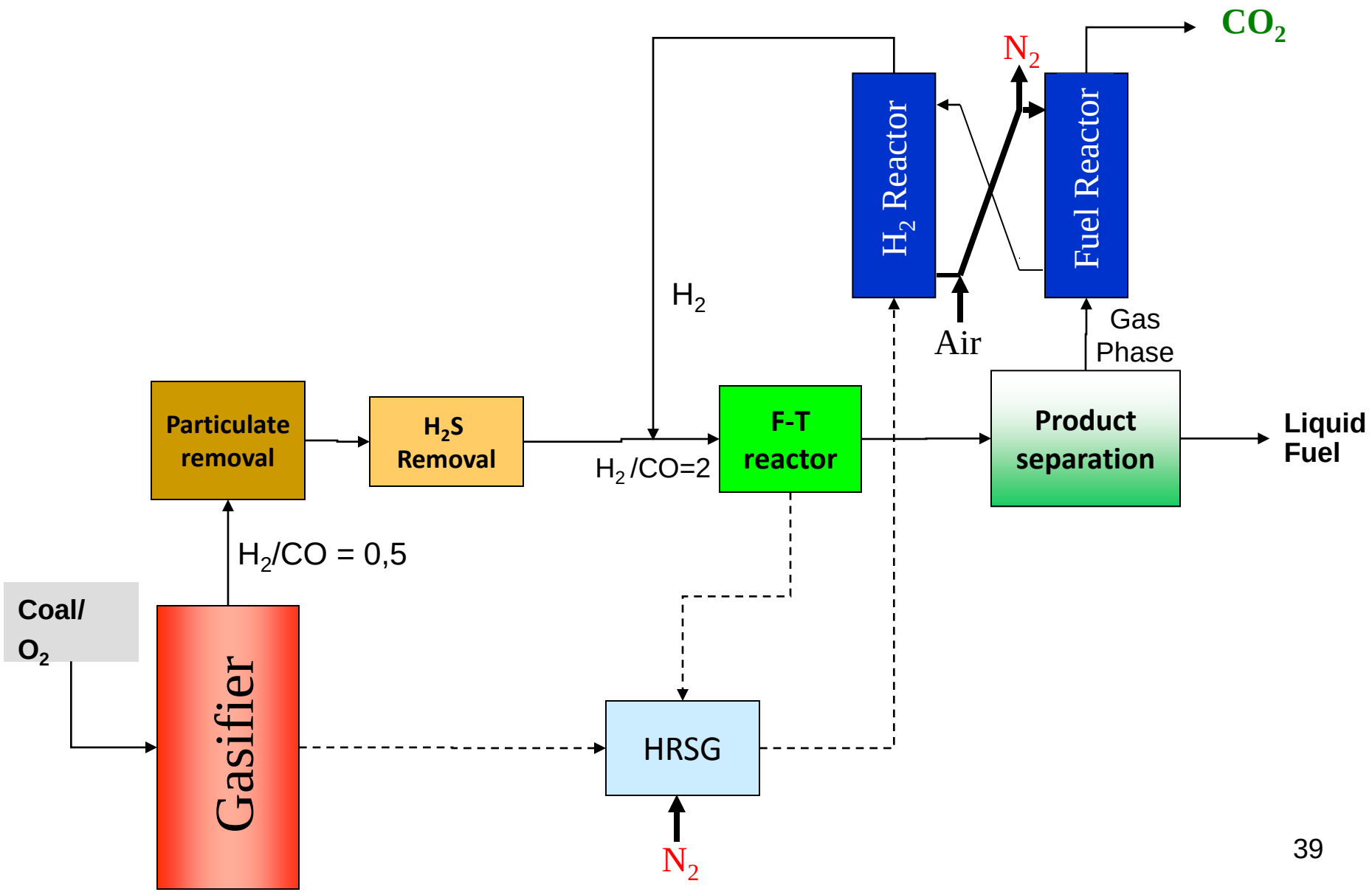
OSU Syngas Chemical Looping in CTL Applications – II



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

$3H_2 + CO_2 \rightarrow -(CH_2)- + 2H_2O$

OSU Syngas Chemical Looping in CTL Applications – I



Upcoming large-scale demonstrations of chemical looping technology

Organization/Location	Process	Size	Features
HUNOSA, Spain	$CaCO_3$ – CaO (CaOling) looping for post **combustion** CO_2 capture	2 MWth	CO_2 is from the flue gas generated from 50 MWe coal power plant .
Technical University of Darmstadt, Germany	$CaCO_3$ – CaO (LISA) looping for post **combustion** CO_2 capture	1 MWth	Capture plant is an extension to a 1052 MWe hard coal-fired power plant; carbonator and calciner both are CFBs.
Technical University of Darmstadt, Germany	ECLAIR – ilmenite Redox with coal for looping **combustion** application	1 MWth	Solid fuel conversion uses a fluidized bed reducer operated in a CFB looping system
Alstom, U.S.	$CaCO_3$ – CaO looping for CO_2 capture /$CaSO_4$ –CaS redox with coal for looping **combustion** application	3 MWth	Process uses two calcium – based loops in a chemical looping system
OSU, U.S.	Iron based oxygen carrier redox with gaseous fuels for H_2 production in a Syngas Chemical Looping (SCL) **gasification** process	250 kWth	High pressure SCL enables high purity H_2 generation and high purity CO_2 generation using a countercurrent moving bed reactor

Concluding Remarks

- Chemical Looping embodies all elements of particle science and technology - particle synthesis, flow and contact mechanics, gas-solid reaction engineering…
- Success achieved in the operation of sub-pilot units reflect the likelihood of commercialization of this technology in the near future