Chemical Looping Combustion, Gasification and Reforming

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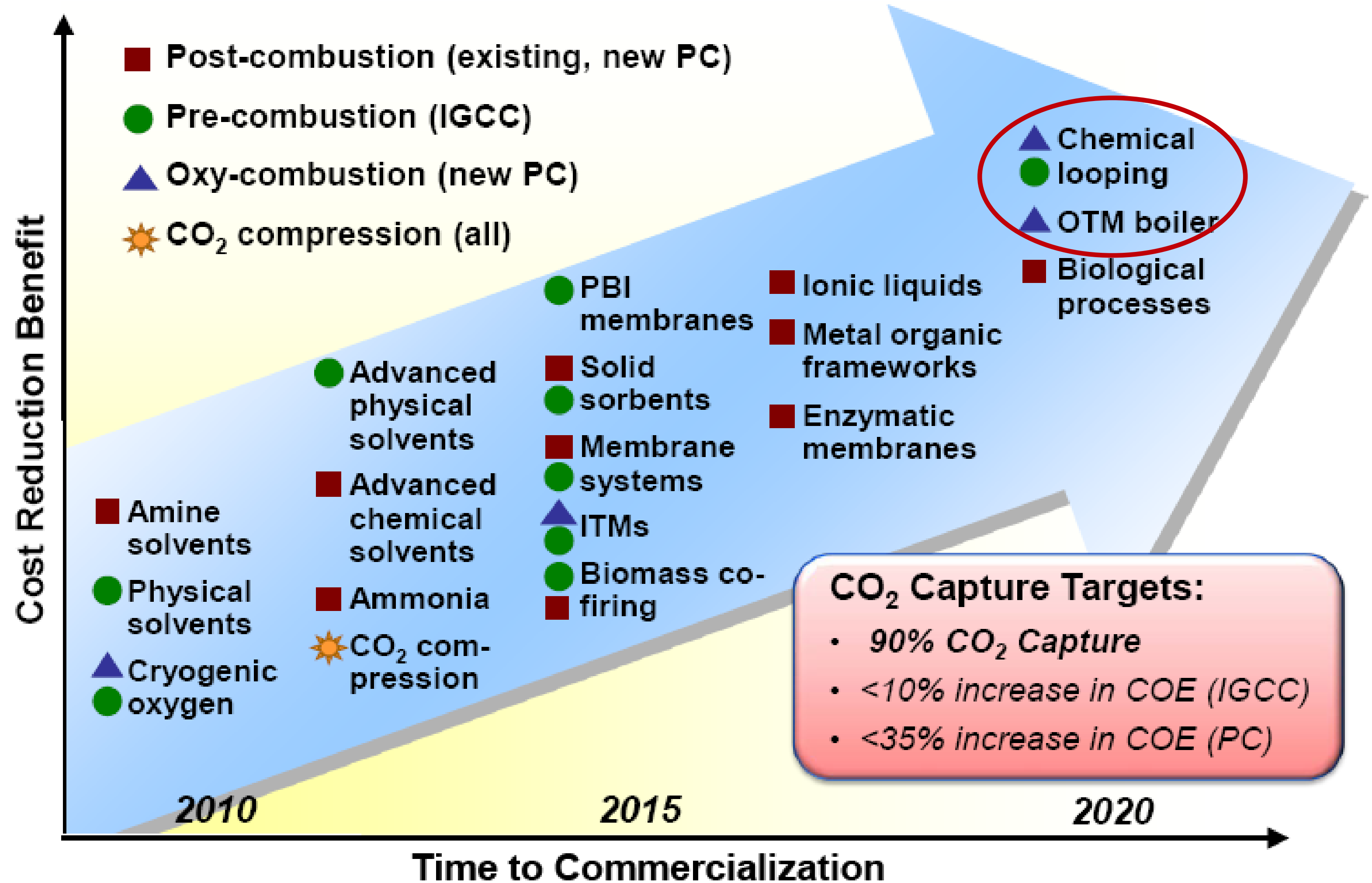
L.S. Fan "Chemical Looping Technology for Fossil Energy Conversions", Wiley/AIChE (2010).
L.S. Fan "Chemical Looping Partial Oxidation: Gasification, Reforming and Chemical Syntheses", Cambridge University Press (2017).

CO_2 Capture from Fossil Energy

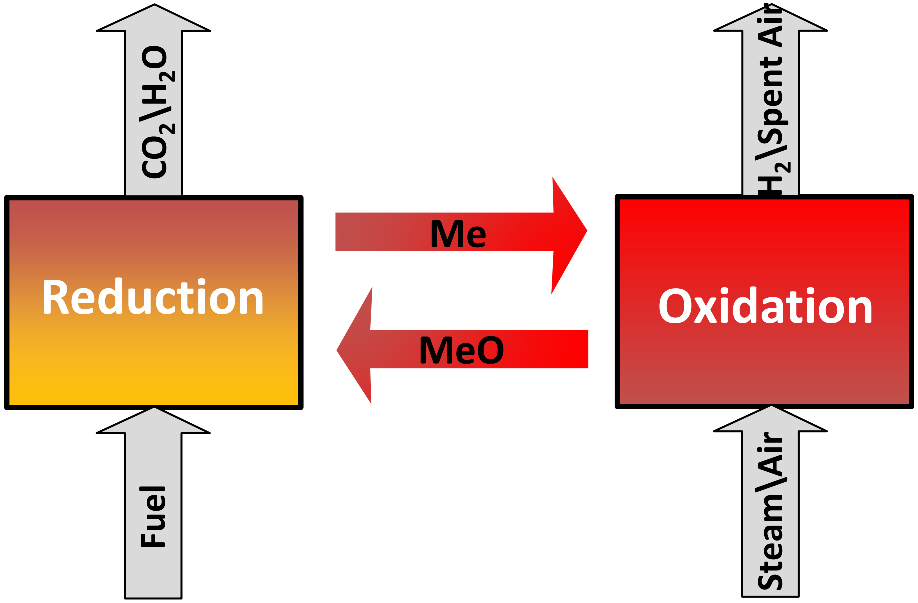
Technological Solutions

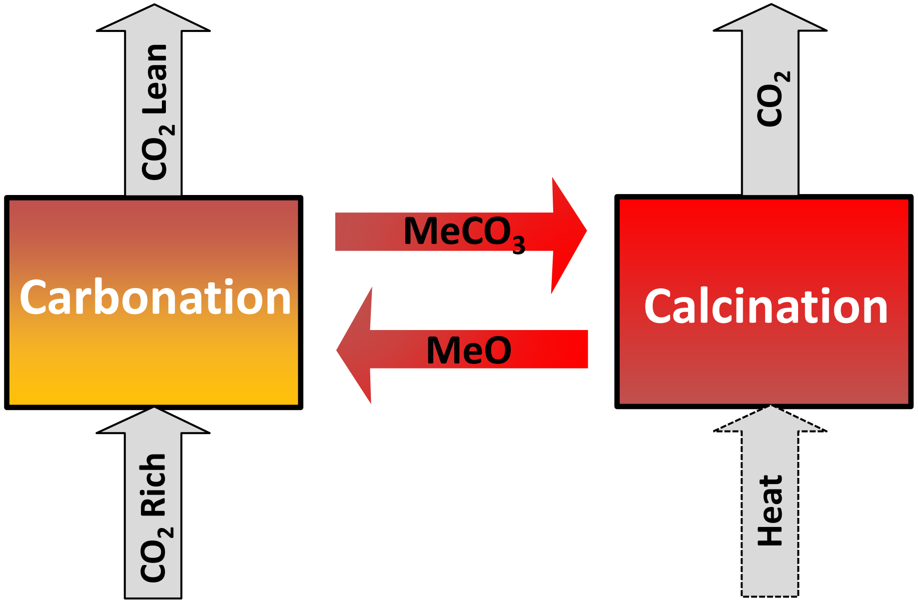


Figueroa, J.D., Fout, T., Plasynski, S., McIlvried, H., Srivastava, R.D., *International Journal of Greenhouse Gas Control.* 2008.

Chemical Looping Reaction Systems

Two Types	
Type 1 Oxygen Carrier Me/MeO	**Type 2** CO_2 Carrier $MeO/MeCO_3$



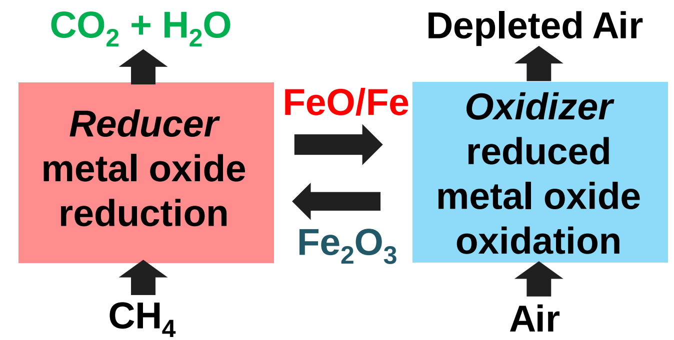


Metal Oxide as Oxygen Carrier:
Chemical Looping Redox Applications

Combustion: Complete Fuel Oxidation

Reducer: $Fe_2O_3 + CH_4 \rightarrow$ **FeO/Fe** + $CO_2 + H_2O$
(oxidized) (reduced)

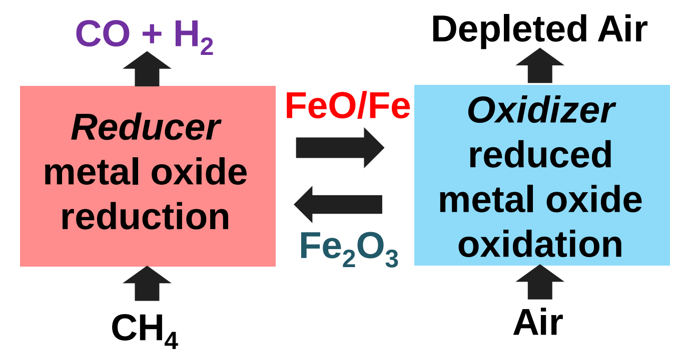
Oxidizer: **FeO/Fe** + Air (O_2) $\rightarrow$ Fe_2O_3

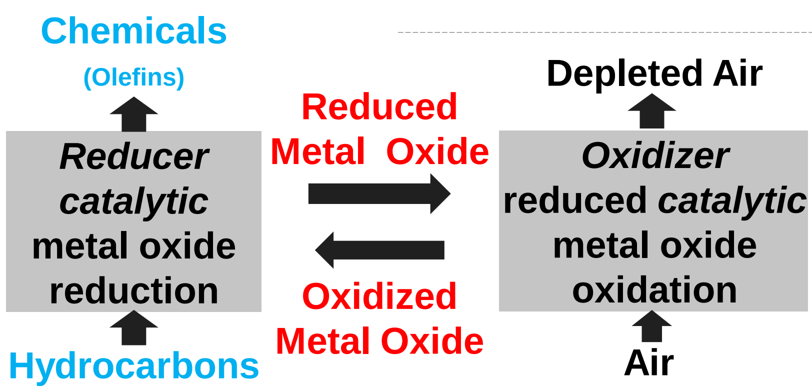


Gasification: Partial Fuel Oxidation

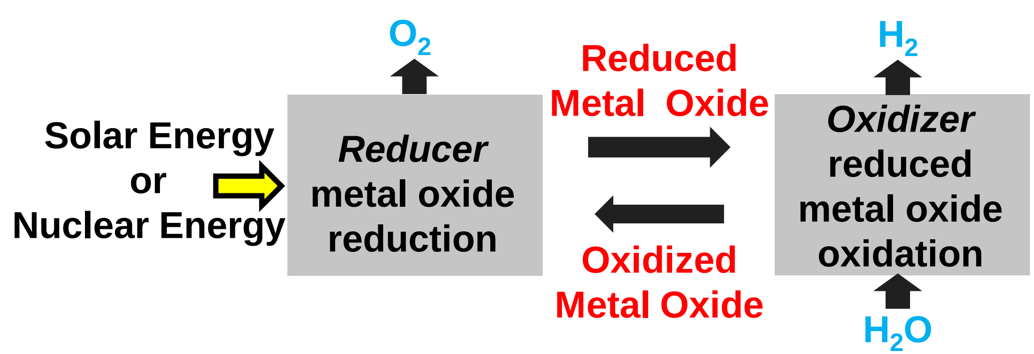
Reducer: $Fe_2O_3 + CH_4 \rightarrow$ **FeO/Fe** + $CO + H_2$
(oxidized) (reduced)

Oxidizer: **FeO/Fe** + Air (O_2) $\rightarrow$ Fe_2O_3





Chemicals Production: Selective Oxidation

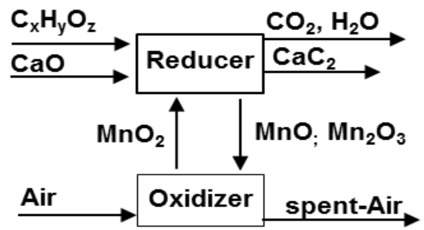


Solar/Nuclear Chemical Looping: Water Splitting

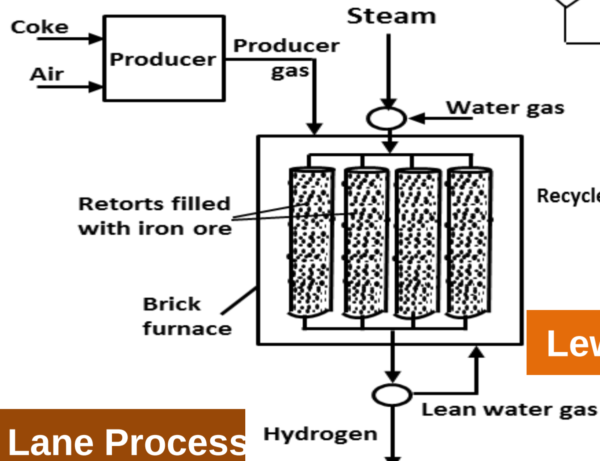
Luo, S., Zeng, L., Fan, L.-S., *Annual Review of Chemical and Biomolecular Engineering*. July 2015.
Chung, E.Y., Wang, W.K., Alkhatib, H., Nadgouda, S., Jindra, M.A., Sofranko, J.A., Fan, L.-S. 2015 AIChE Spring Meeting. April 2015.
Chueh, W. C., Falter, C., Abbott, M., Scipio, D., Furler, P., Haile, S.M., Steinfeld, A. *Science*. 2010.

Historical Development of Chemical Looping Technologies for Hydrogen Production and Combustion Application

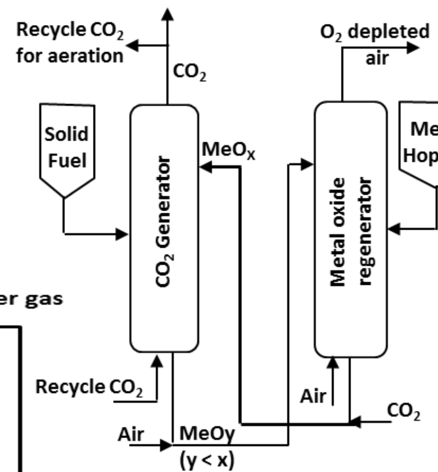
Technologies	Bergmann Process	Lane Process & Messerschmitt Process	Lewis and Gilliland Process	IGT HYGAS Process	CO_2 Acceptor Process
Time	1897	1910	1950s	1970s	1970s
Looping Media	$MnO_2/MnO/Mn_2O_3$	$Fe/FeO/Fe_3O_4$	Cu_2O/CuO	FeO/Fe_3O_4	$CaO/CaCO_3$
Reactor Design	Blast Furnace	Fixed Bed	Fluidized Bed	Staged Fluidized Bed	Fluidized Bed



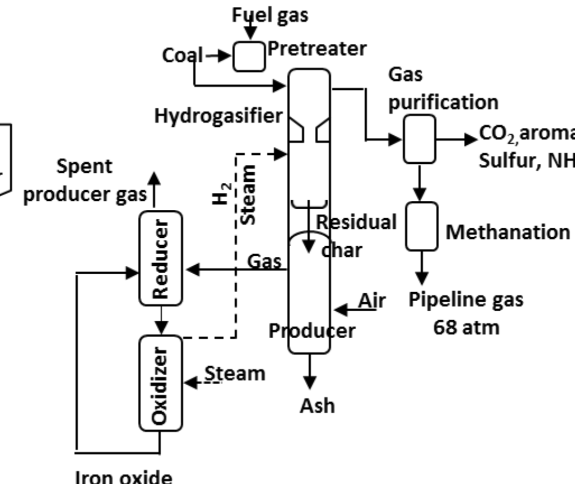
Bergmann Process



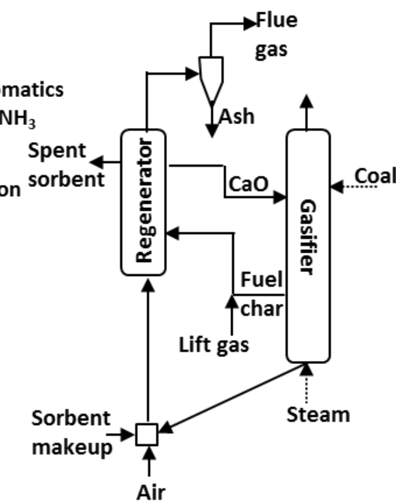
Lane Process



Lewis and Gilliland Process



IGT Process

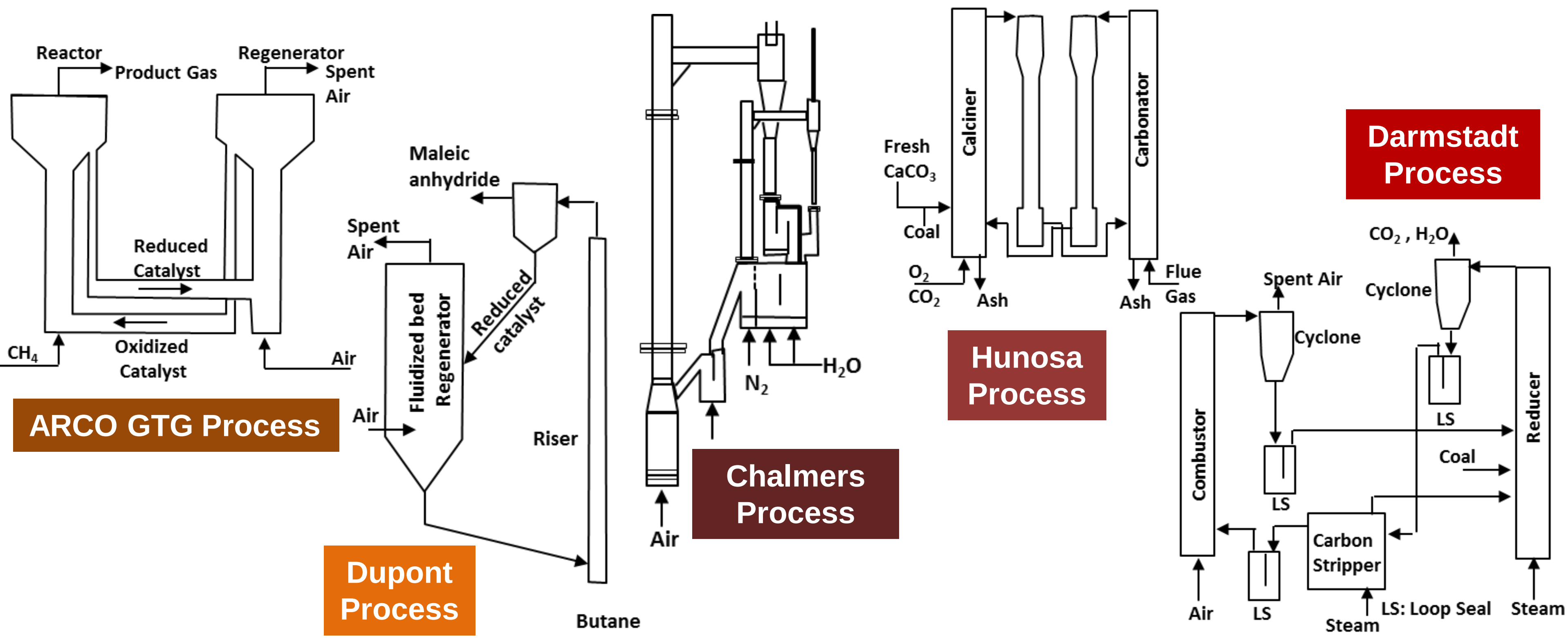


CO_2 Acceptor Process

Bergmann, F. German Patent 29,384, 1897;
Messerschmitt, A. U.S. Patent 971,206, 1910.; Lane, H. U.S. Patent 1,078,686, 1913.
Dobbyn, R.C., Ondik, H.M., et al . U.S. DOE Report DOE-ET-10253-T1, 1978.
Lewis, W.K., Gilliland, E.R. U.S. Patent 2,655,972, 1954.
Institute of Gas Technology. U.S. DOE Report EF-77-C-01-2435, 1979.

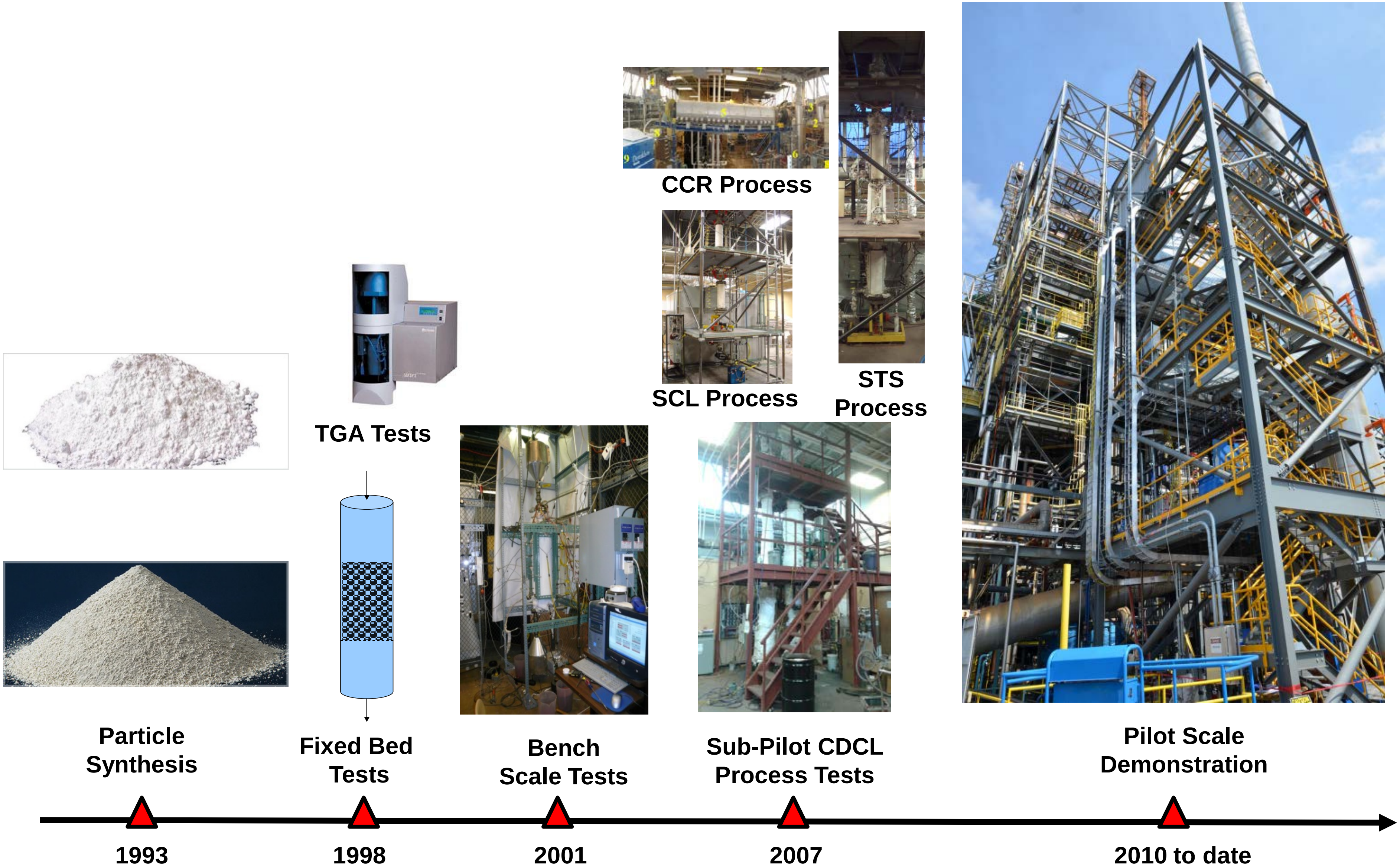
Recent Chemical Looping Technology Development

Technologies	ARCO GTG	Dupont	Chalmers	Hunosa	Darmstadt
Time	1980's	1990s	2000 onwards	2010 onwards	2010 onwards
Capacity		180M lb/yr	100 kW_{th}	2 MW_{th}	1 MW_{th}
Looping Media	Supported Mn	VPO	Ni; Fe; Mn; Cu	$CaO – CaCO_3$	$FeTiO_3$
Reducer Design	Fluidized Bed	Fluidized Bed	Fluidized Bed	Circulating Fluidized Bed	Fluidized Bed



Jones, C.A., Leonard, J.J., Sofranko, J.A. *Energy & Fuels*. 1987.
Contractor, R.M. *Chemical Engineering Science*. 1999.
Arias, B., Diego, M.E., Abanades, J.C., Lorenzo, M., Diaz, L., Martinez, D., Alvarez, J., Sanchez-Biezma, A. *International Journal Greenhouse Gas Control*. 2013.
Dudukovic, M.P. *Science*. 2009.
Ströhle, J., Orth, M., Epple, B. *Applied Energy*. 2014.

Evolution of OSU Chemical Looping Technology



Fan, L.-S., Zeng, L., Luo, S. *AIChE Journal*. 2015.

A Quick Look at the Periodic Table

Cost Range ($/kg)

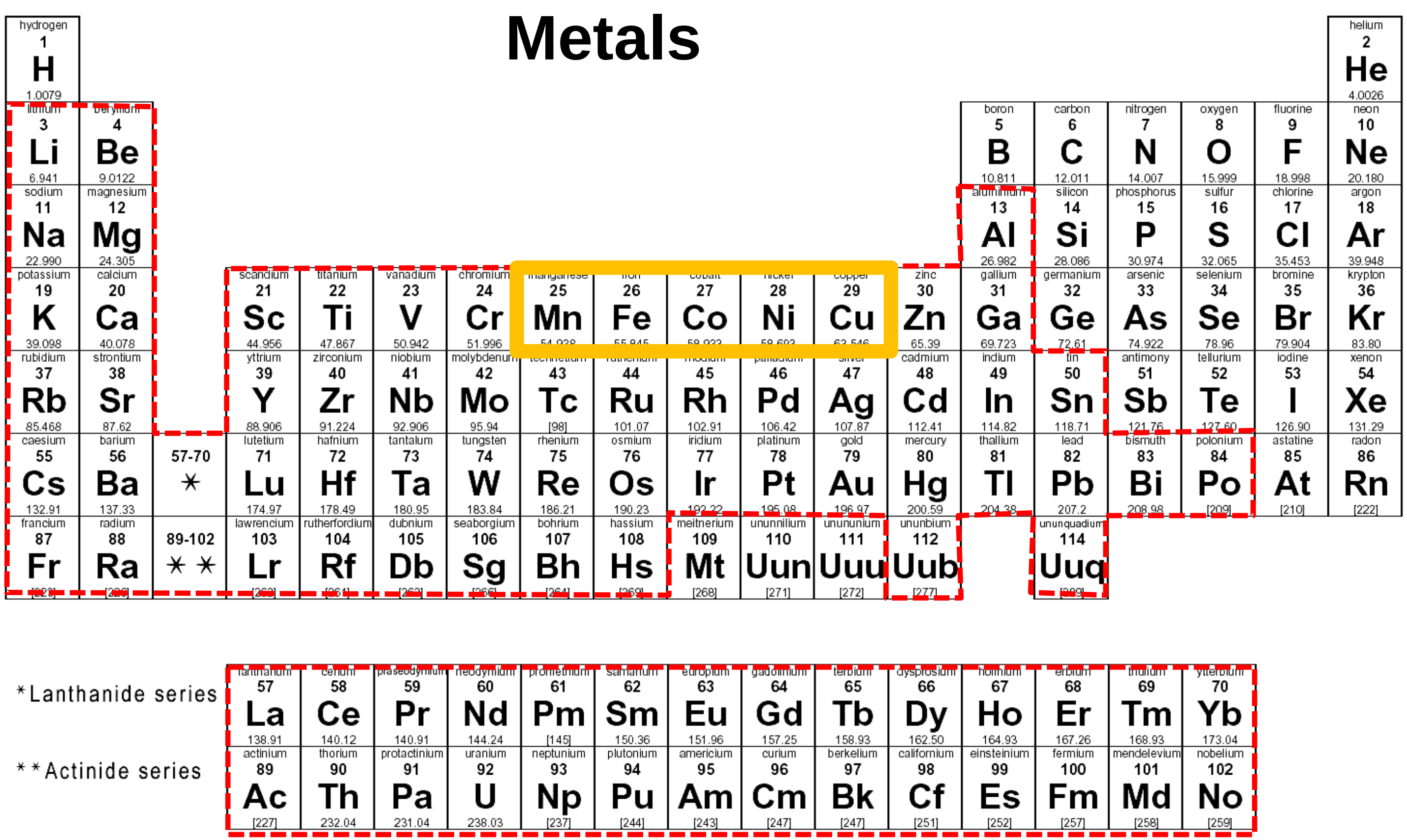
< $1/kg
Fe, K, Ca, Ti, Al, Ba, Na, Sr

$1/kg to $10/kg
Mn, Mg, Cu, Zn, Ce, Cd, Pb, Zr, Cr, La, Rb

$10/kg to $100/kg
Bi, Co, Hg, Sn, Ni, W, V, Li, Y, Nd, Gd

$100/kg to $1000/kg
Ga, In, Ag, Pr, Eu, Er

> $1000/kg
Tl, Dy, Ir, Lu, Ho, Tm, Yt, Ru, Au, Pt, Pd, Rh, Ra, Po, Cs, Sc



http://mineralprices.com/
http://www.infomine.com/investment/
http://minerals.usgs.gov/minerals/pubs/commodity/
Hammond, C.; The Elements, Handbook of Chemistry and Physics, 81st edition

Oxygen Carrier Selection

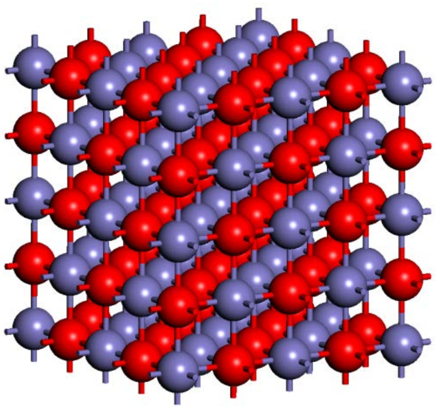
Primary Metal	Fe	Ni	Cu	Mn	Co
Potential Supports	Al_2O_3, TiO_2, MgO, Bentonite, SiO_2, etc				
Cost	+	–	–	~	–
Oxygen Capacity[1](wt %)	30	21	20	25[3]	21
Thermodynamics for CLC	+	~	+	+	+
Kinetics/Reactivity[2]	–	+	+	+	–
Melting Points	+	~	–	+	+
Strength	+	–	~	~	~
Environmental& Health	~	–	–	~	–
Hydrogen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

Structure Variations of Iron Oxide

Under Redox Reaction

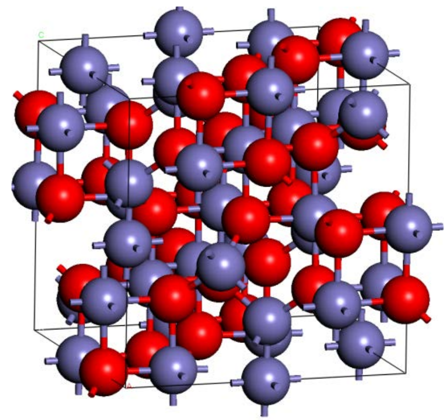
FeO
Wüstite



Ox

Re

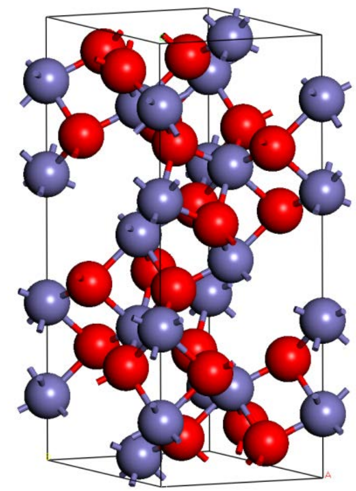
Fe_3O_4
Magnetite



Ox

Re

Fe_2O_3
Hematite



FCC - Rocksalt Type

oxygen close-packed cubic pattern

iron occupy all **octahedral** interstices

FCC - Inverse Spinel Type

octahedral interstices

1/2 occupation rate

tetrahedral interstices

1/8 occupation rate

HCP - Corundum Type

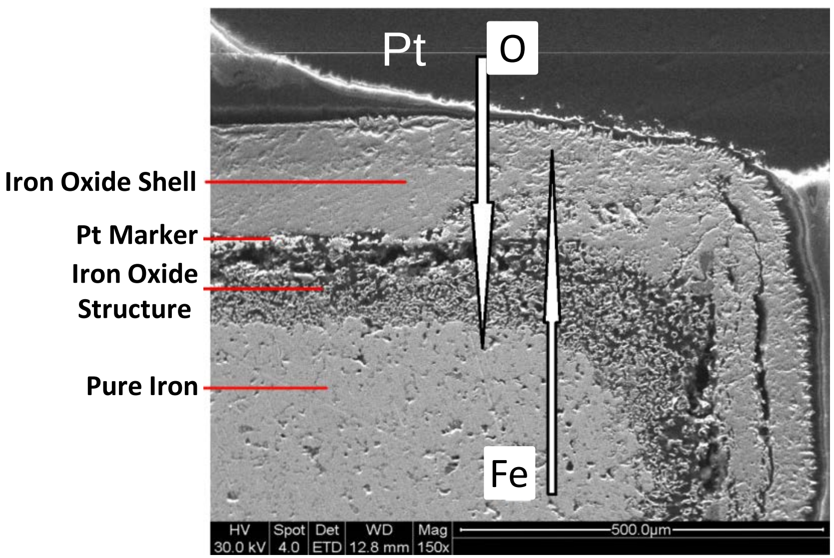
2/3 **octahedral** sites in the basal plane filled

Pellet Reaction Mechanism

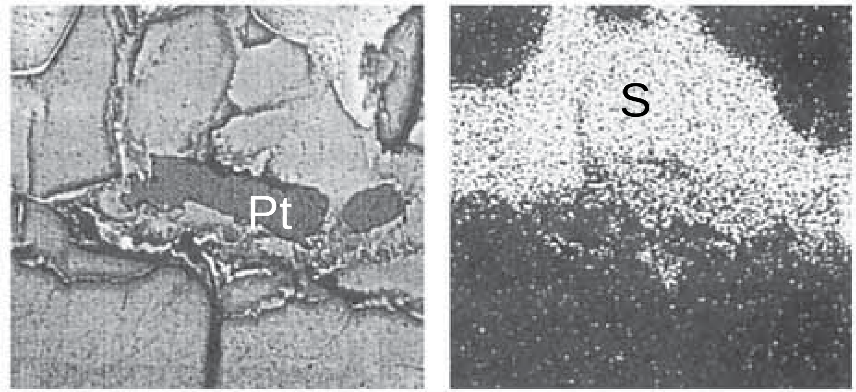
Ionic Diffusion for Unsupported Metal/Metal Oxides

Outward growth mode

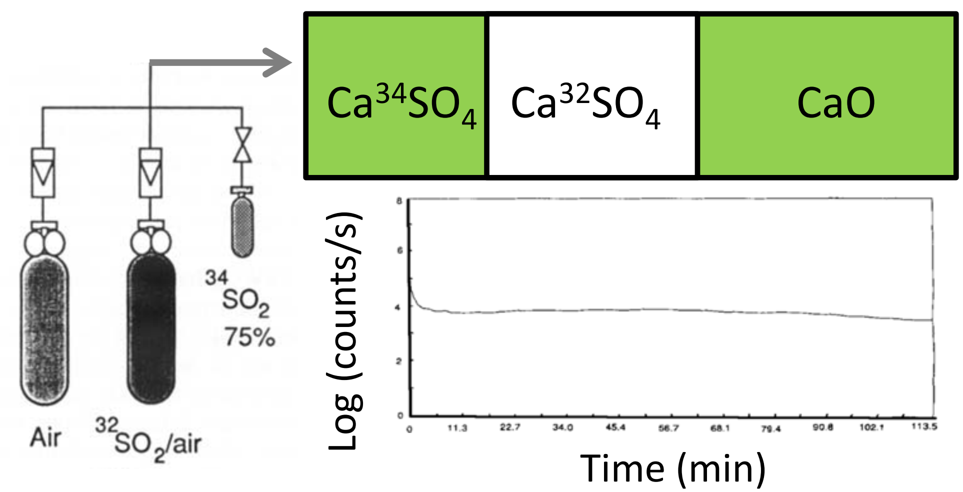
$$2Fe+3/2O_2 \rightarrow Fe_2O_3$$



$$CaO+SO_2+1/2O_2 \rightarrow CaSO_4$$



SIMS with $^{34}SO_2$

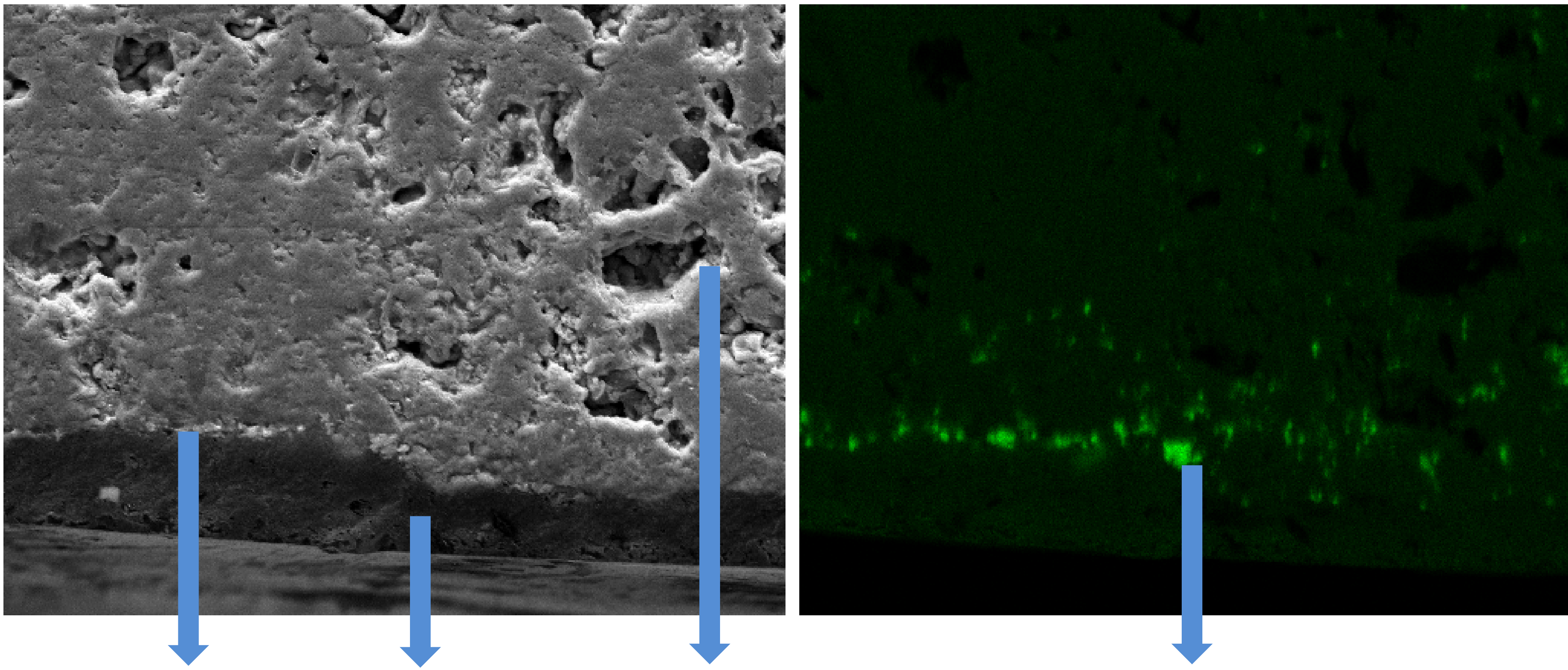


Li, F., Luo, S., Sun, Z., Bao, X., Fan, L.-S. *Energy & Environmental Science*, 2011.
Hsia, C., Raghunathan, K., St. Pierre, G.R., Fan, L.-S. *AIChE Journal,* 1993.
Hsia, C., St. Pierre, G.R., Fan, L.-S. *AIChE* Journal, 1995.

Pellet Reaction Mechanism

Ionic Diffusion for Supported Iron

Partially oxidized Fe with support **Pt mapping**

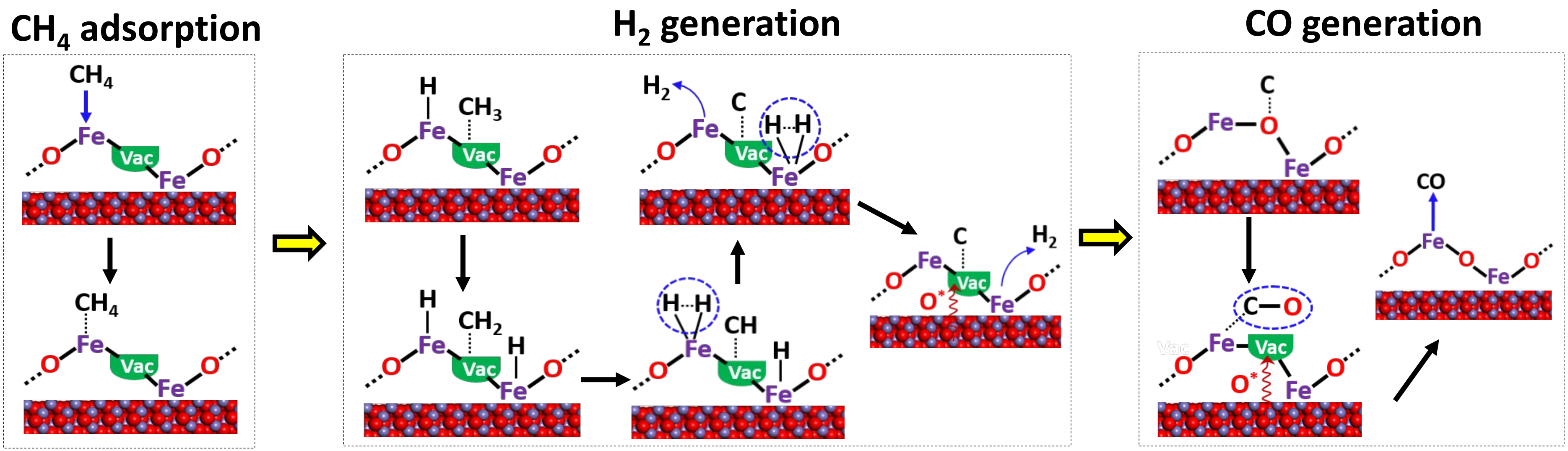


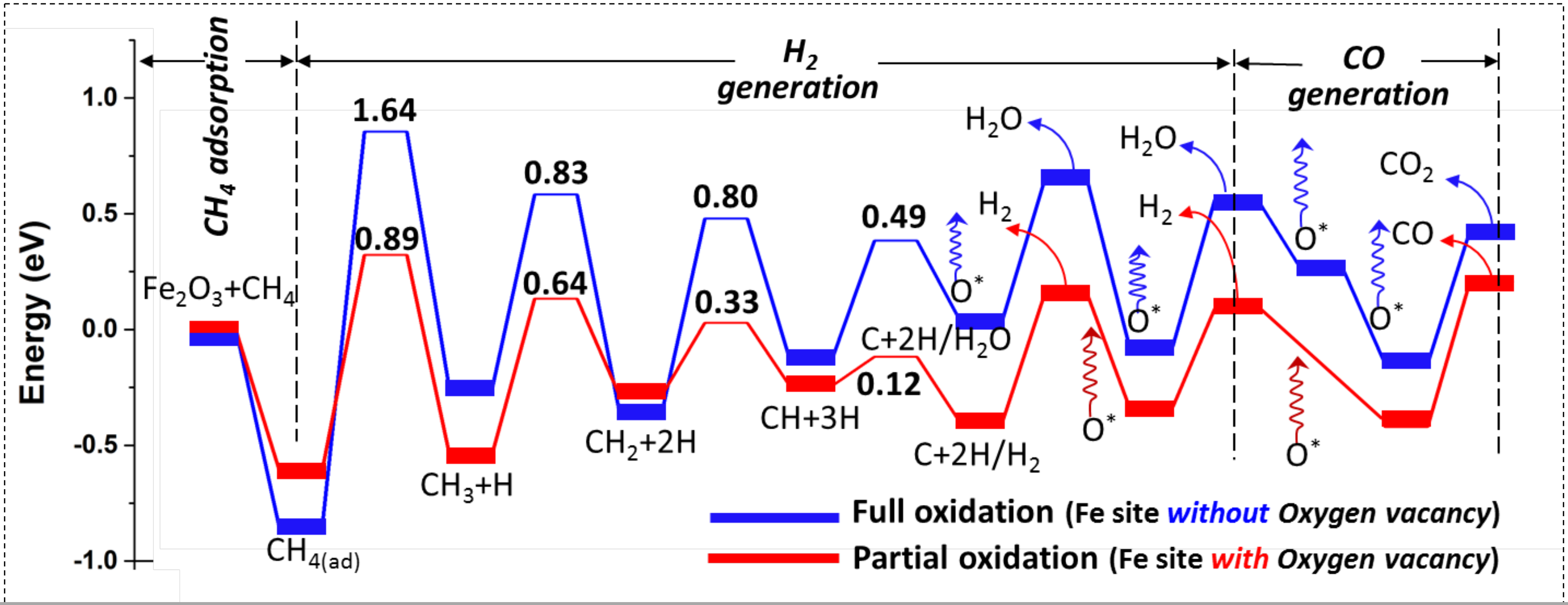
Pt Epoxy Resin Pellet Bulk Phase Pt

Sun, Z., Zhou, Q., Fan, L.-S. *Langmuir*, 2012

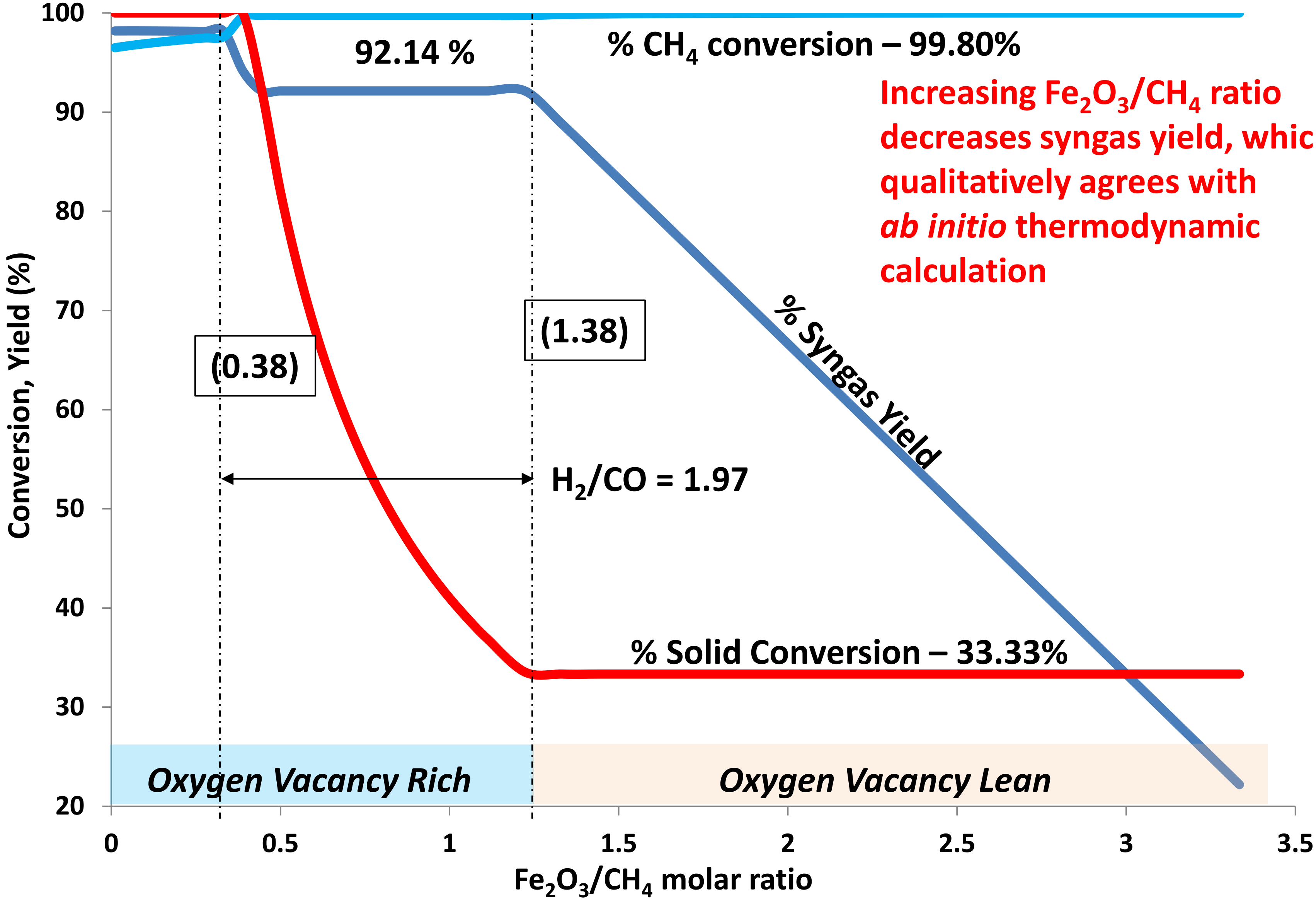
Methane Partial Oxidation Pathway

Fe Site with Oxygen Vacancy



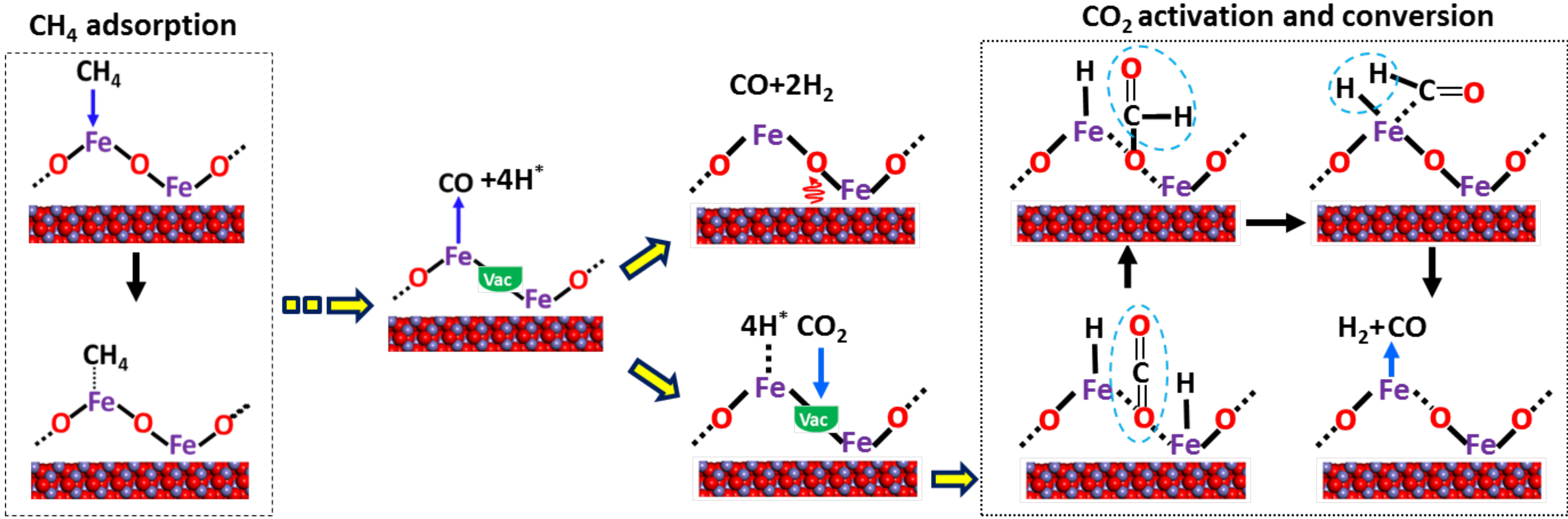


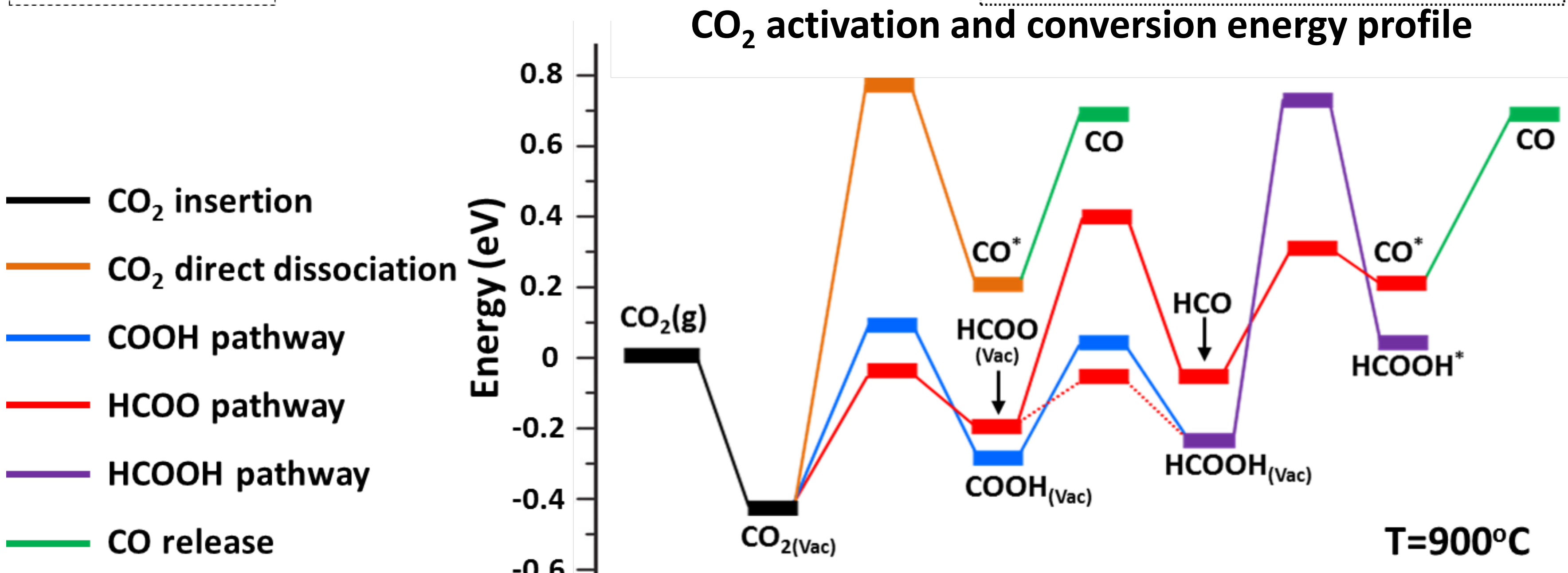
Classical Thermodynamics: CH_4 and Fe_2O_3



Increasing Fe_2O_3/CH_4 ratio decreases syngas yield, which qualitatively agrees with *ab initio* thermodynamic calculation

Methane Partial Oxidation Pathway with CO_2





OSU Chemical Looping Platform Processes

Two Basic Modes

Counter-current: Full Combustion

Co-current: Full Gasification

mplicity:
ne Loop
ue Reducer
figuration:
ving Bed
que Flow
ontroller:
echanical L-
Valve

M

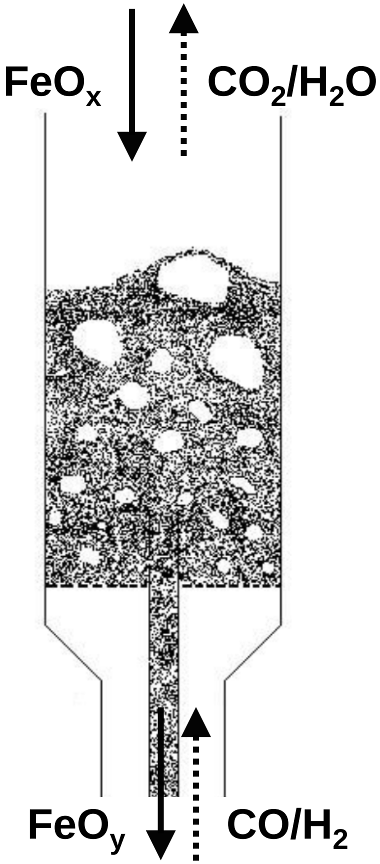
ED
R

M

ED
R

Fan, L.-S., Zeng, L., Luo, S. *AIChE Journal*. 2015.

Reducer Design Concept: Combustion



Fluidized Bed

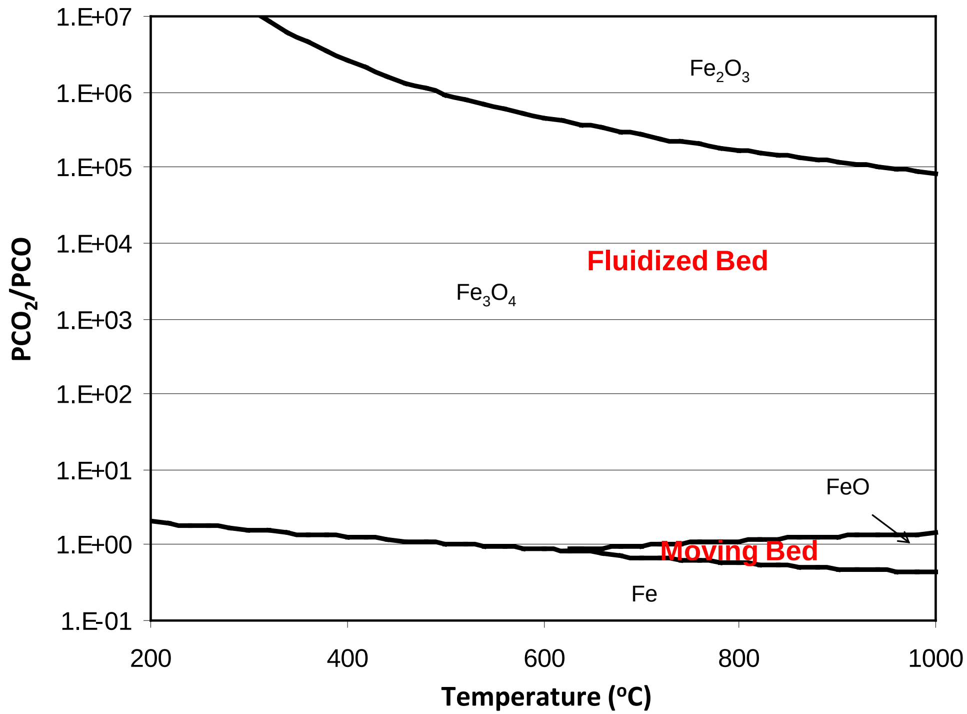
Fluidized Bed *v.s.* Moving Bed

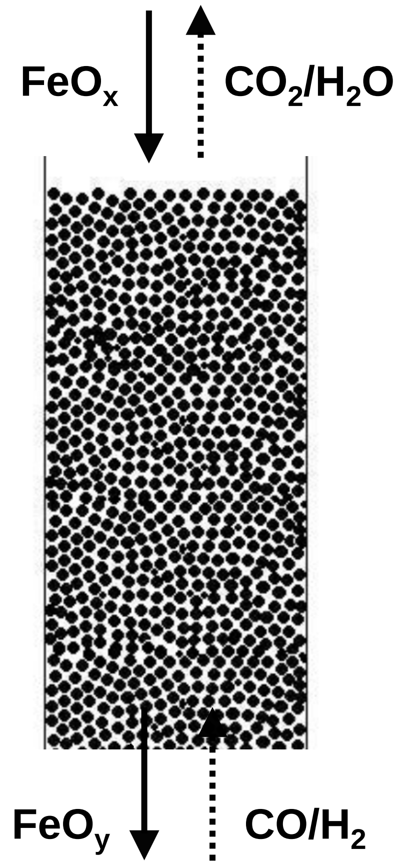
(x>y)

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

> U$_{mfv}$ ← Gas Velocity → **< U$_{mfv}$**

Small ← Particle Size → **Large**



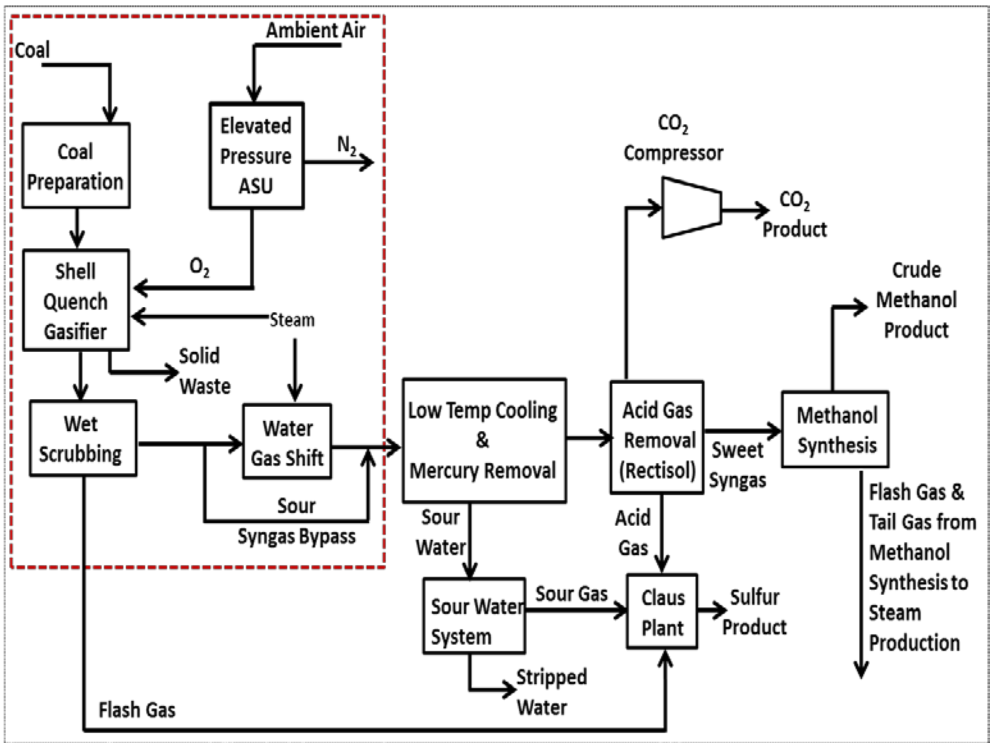


Moving Bed

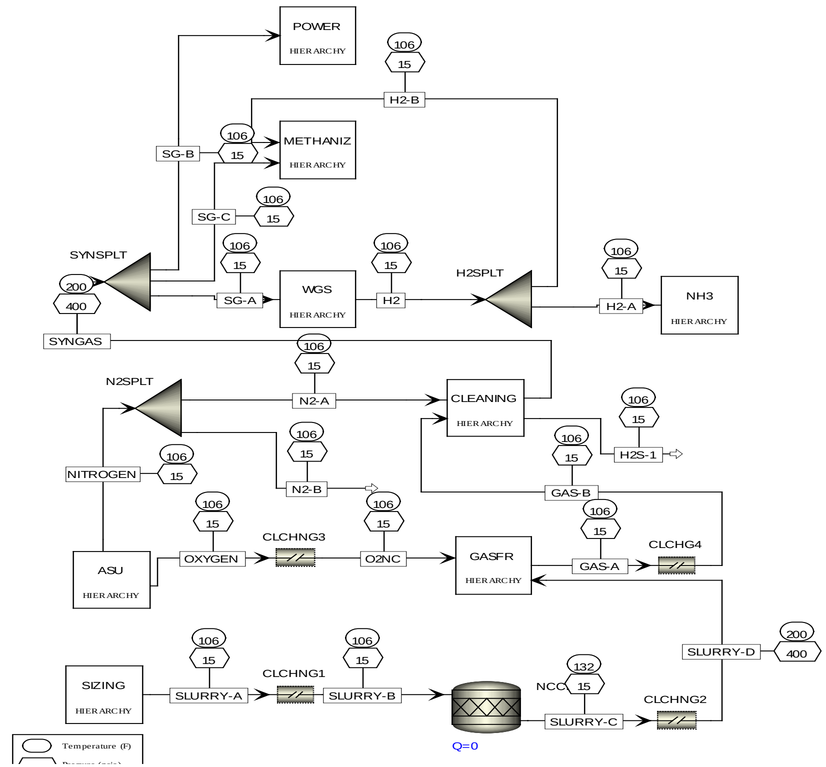
Fan, L.-S. Chemical Looping Systems for Fossil Energy Conversions. Wiley, 2010.

Coal Gasification for Methanol Production: DOE Baseline (Traditional) Process

Simplified Block Flow diagram



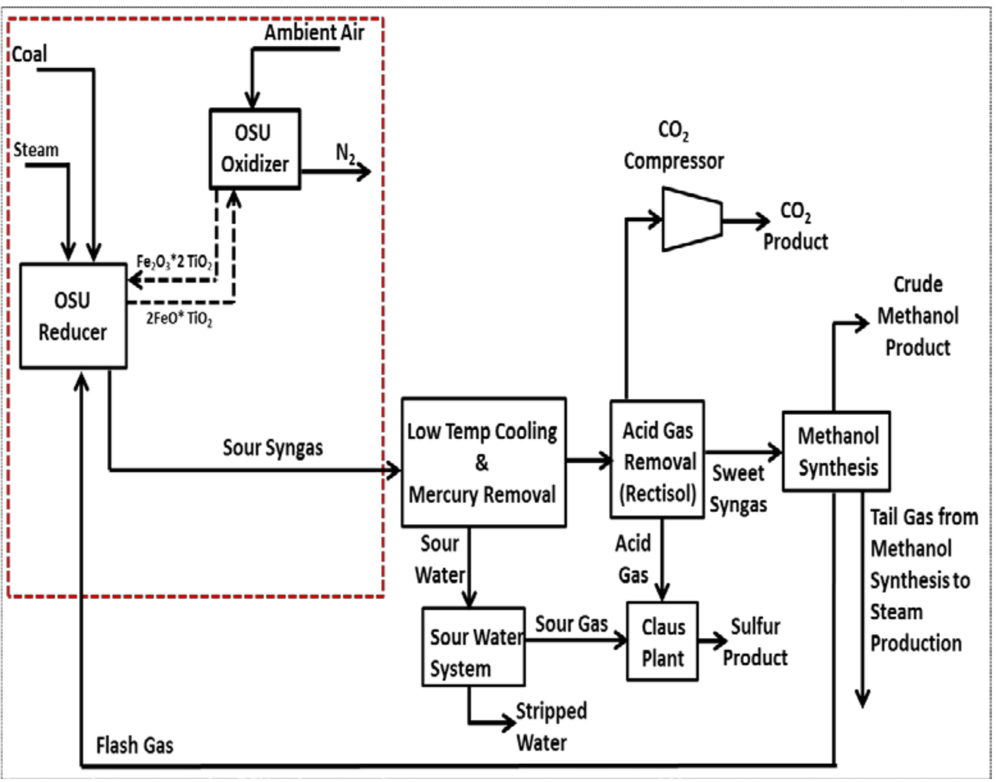
ASPEN PLUS v8.4 Condensed Flow Diagram with hierarchy blocks



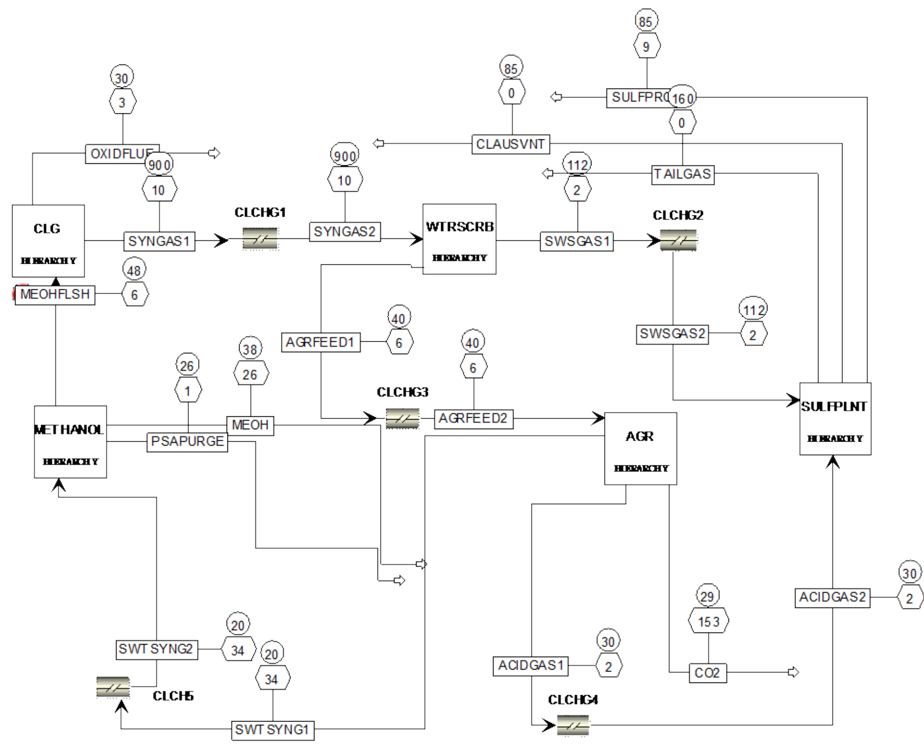
Kathe, M., Xu, D., Hsieh, T. L., Simpson, J., Statnick, R., Tong, A., Fan, L.-S. 2014. OSTI: 1185194.

Coal Gasification for Methanol Production: OSU Process

Simplified Block Flow diagram

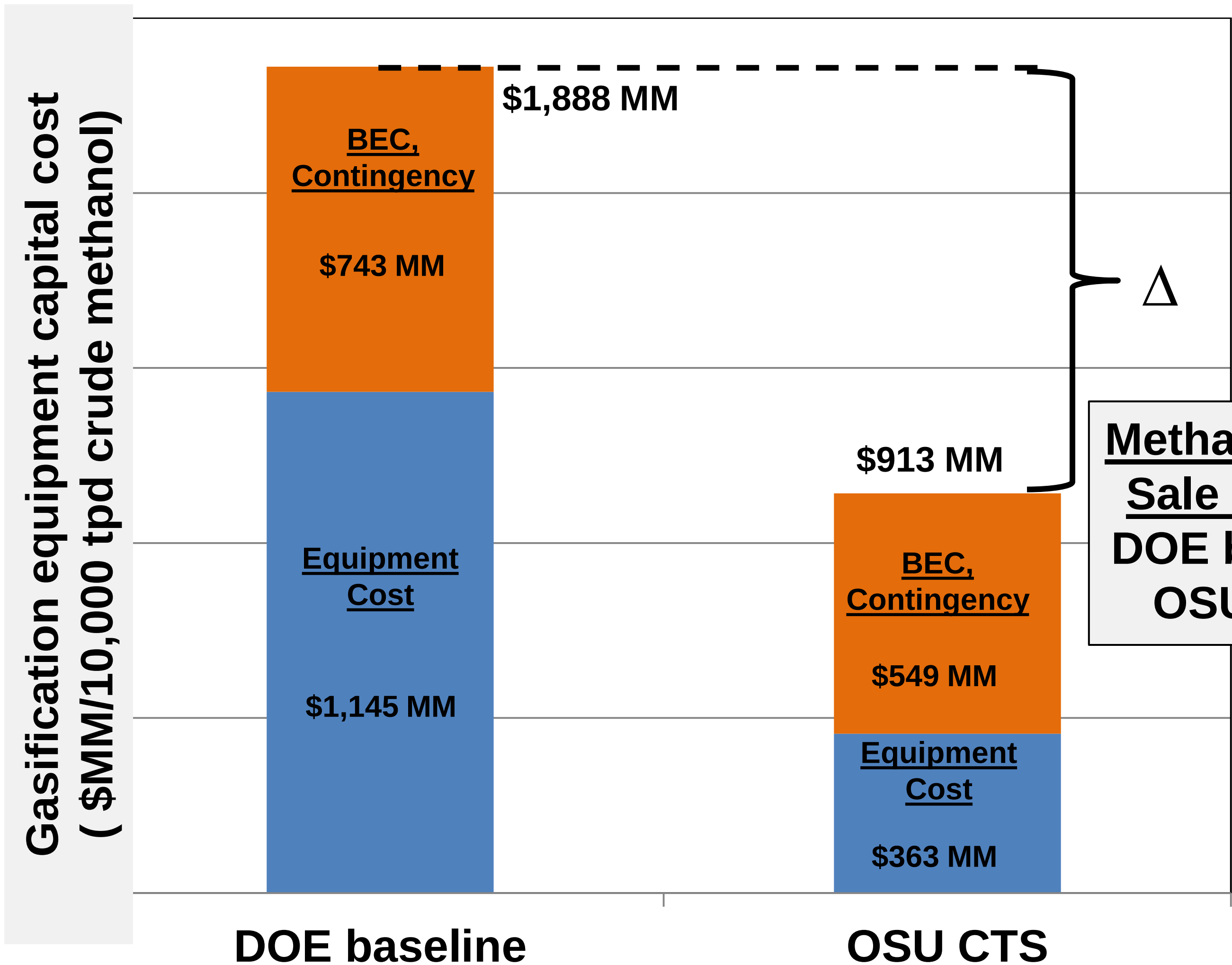


ASPEN PLUS v8.4 Condensed Flow Diagram with hierarchy blocks



Kathe, M., Xu, D., Hsieh, T. L., Simpson, J., Statnick, R., Tong, A., Fan, L.-S. 2014. OSTI: 1185194.

Cost Analysis: Total Plant Capital Cost for 10,000 ton/day Methanol Production from Coal



Methanol Required Sale Price ($/gal):
DOE baseline: 1.78
OSU CTM: 1.41

Kathe, M., Xu, D., Hsieh, T. L., Simpson, J., Statnick, R., Tong, A., Fan, L.-S. 2014. OSTI: 1185194.

Concluding Remarks

- **With major advances recently in oxygen carrier development and good results obtained in pilot plant demonstration, commercialization of chemical looping technology for combustion, gasification and reforming applications will be expected in the near future**
- **Metal Oxide Reaction Engineering and Particle Science and Technology are two underpinning science and engineering fields of close relevance to successful chemical looping technology development**

Sponsors

U.S. Department of Energy

National Science Foundation

Ohio Development Services Agency

THE OHIO STATE UNIVERSITY

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Test Site Host

National Carbon Capture Center