

# Chemical Looping Processes

by



**L. S. Fan**  
Department of Chemical  
and Biomolecular  
Engineering  
The Ohio State University  
Columbus, Ohio 43210  
U.S.A.

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## *My Graduate Students and Research Associates*

Ted Thomas	Fanxing Li	Zhenchao Sun
Himanshu Gupta	Shwetha Ramkumar	S. Rao
Puneet Gupta	Liang Zeng	William Wang
Alissa Park	FuChen Yu	Songgeng Li
Mahesh Iyer	Deepak Sridhar	Andrew Tong
Luis Velazquez-Vargas	Ray Kim	Nihar Phalak
Bartev Boghos Sakadjian	Fei Wang	Siwei Luo
Danny Wong		Yao Wang
		Niranjani Deshpande

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## *Government Agencies and Industrial Corporations*

- Department of Energy
  - Clear Skies
  - Noblis/Metritek
- Ohio Coal Development Office
  - CONSOL Energy
  - PSRI
  - AEP
- Department of Defense
  - Duke Energy
  - Babcock & Wilcox
  - Air Products
  - Shell
  - CRI/Criterion
  - First Energy
  - Carmeuse Lime and Stone
  - LittleFord Day
  - Specialty Minerals Inc.

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## Scope

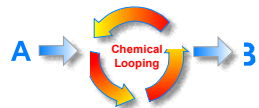
- Rationale for Chemical Looping
  - Non-Fossil Fuel Chemical Looping Processes
  - Fossil Fuel Chemical Looping Processes – Historical Development
- Modern Chemical Looping Combustion and Gasification Processes
  - Modern Chemical Looping Process Configurations
  - Ongoing Chemical Looping Testing
- Chemical Looping Particles and Their Reactivity
  - Chemical Looping Particle Selection, Properties, and Effects on Reactor Design
  - Oxygen Transfer Mechanisms
- Chemical Looping Process Simulation
- Novel Applications of Chemical Looping
  - Hydrogen Production and Liquid Fuel and Chemical Syntheses
  - High Efficiency Electricity Generation
- Chemical Looping – Challenges and the Path Forward

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## Rationale for Chemical Looping

- A given reaction step can be decomposed into multiple subreactions in a reaction scheme using **chemical intermediates** that are reacted and regenerated through the progress of the subreactions. A reaction scheme of this nature is referred to as **chemical looping**.
- An **ideal** chemical looping scheme is to design the subreactions in such a manner that the **exergy loss** of the process resulting from this reaction scheme can be **minimized** while allowing the **separation** of the desired or undesired products generated from the reactions to be accomplished with **ease**, thereby yielding an overall **efficient** and **economical** process system.



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## Non-Fossil Fuel Based Chemical Looping Systems

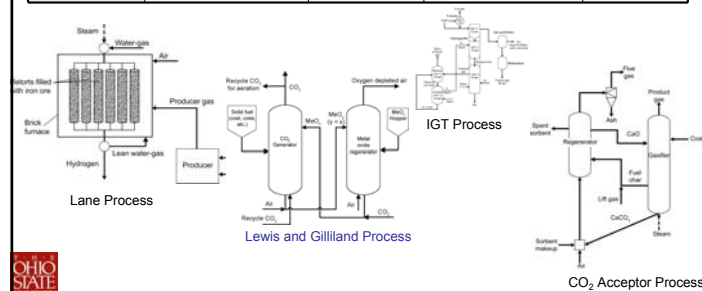
Application	Water Splitting	FMC's H <sub>2</sub> O <sub>2</sub> Process	DuPont's Maleic Anhydride Production
Reaction Scheme	$ZnO \rightarrow Zn + \frac{1}{2} O_2$ $Zn + H_2O \rightarrow ZnO + H_2$		Oxidized VPO + Butane → Maleic anhydride + Reduced VPO Reduced VPO + Air → Oxidized VPO + N <sub>2</sub> and remaining O <sub>2</sub>
Net Reaction	$H_2O \rightarrow H_2 + 0.5O_2$	$H_2 + O_2 \rightarrow H_2O_2$	Butane + Air → Maleic anhydride + N <sub>2</sub> and remaining O <sub>2</sub>
Looping Media	$ZnO \leftrightarrow Zn$		Oxidized VPO ↔ Reduced VPO



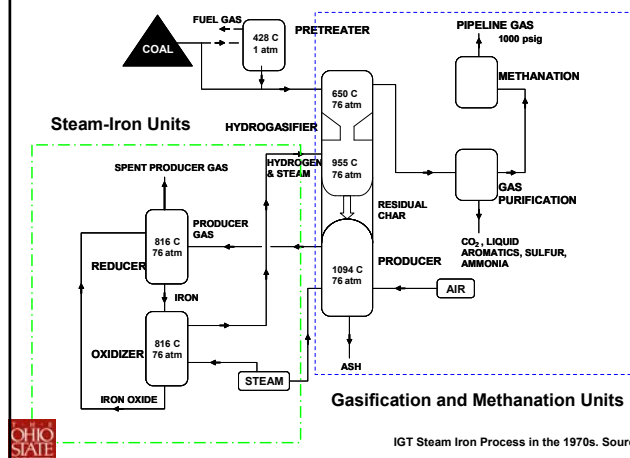
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## Historical Development of Chemical Looping Technologies for Fossil Energy Conversions

Technologies	Lane Process and Messerschmitt Process	Lewis and Gilliland Process	IGT HYGAS Process	CO <sub>2</sub> Acceptor Process
Time	Early Twentieth Century	1950s	1970s	1970s
Looping Media	Fe/FeO/Fe <sub>3</sub> O <sub>4</sub>	Cu <sub>2</sub> O/CuO	FeO/Fe <sub>3</sub> O <sub>4</sub>	CaO/CaCO <sub>3</sub>
Reactor Design	Fixed bed	Fluidized bed	Staged fluidized bed	Fluidized bed



## Case Study: IGT Steam-Iron HYGAS Process



IGT Steam Iron Process in the 1970s. Source: USDOE

## IGT Steam Iron HYGAS Process

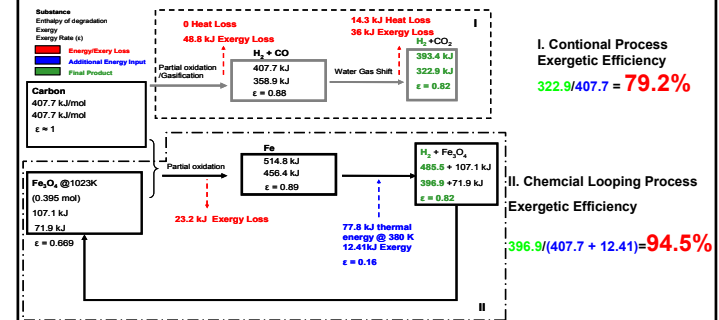
	MO=> M	M=> MO
Gas Conversion (%)	65	45
Solid inlet	80% Fe <sub>3</sub> O <sub>4</sub> - 20% FeO	95% FeO- 5% Fe
Temperature (°C)	900	900
Reactor	Fluid Bed	Fluid Bed

- 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<sub>2</sub>
- Poor Thermo



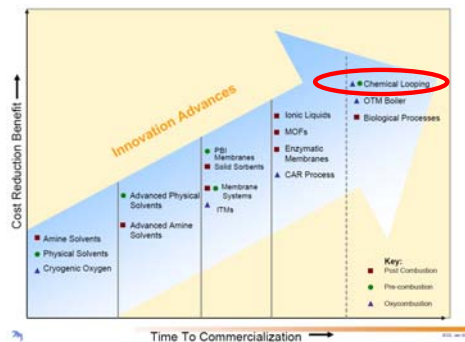
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## Exergy Analysis on Hydrogen Production



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## CO<sub>2</sub> Capture Technologies



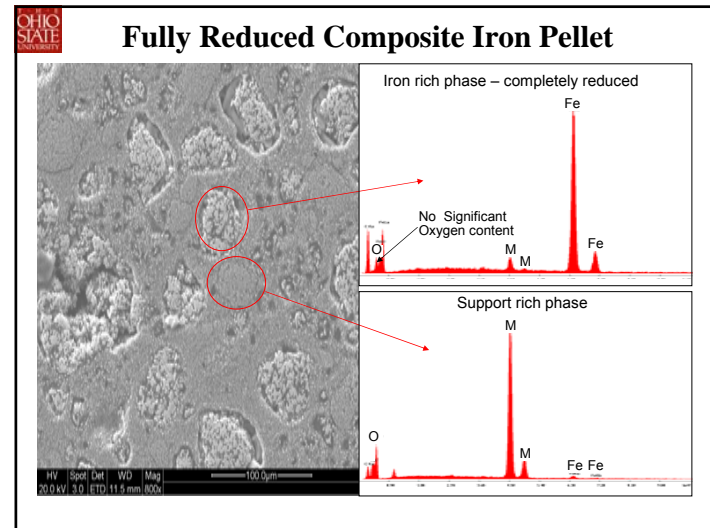
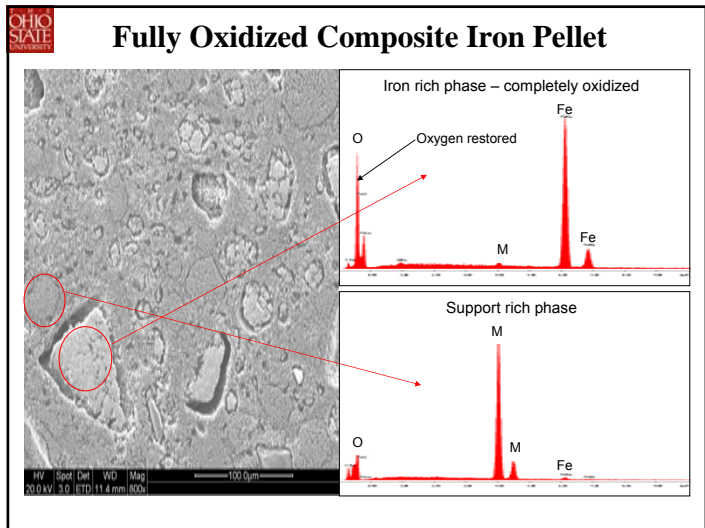
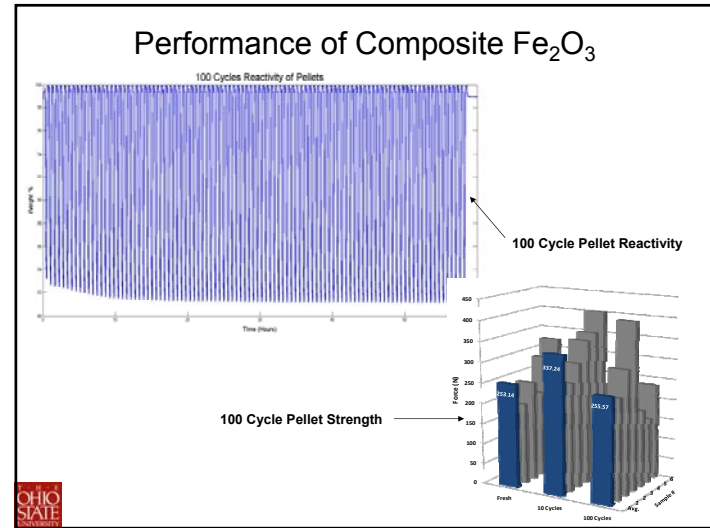
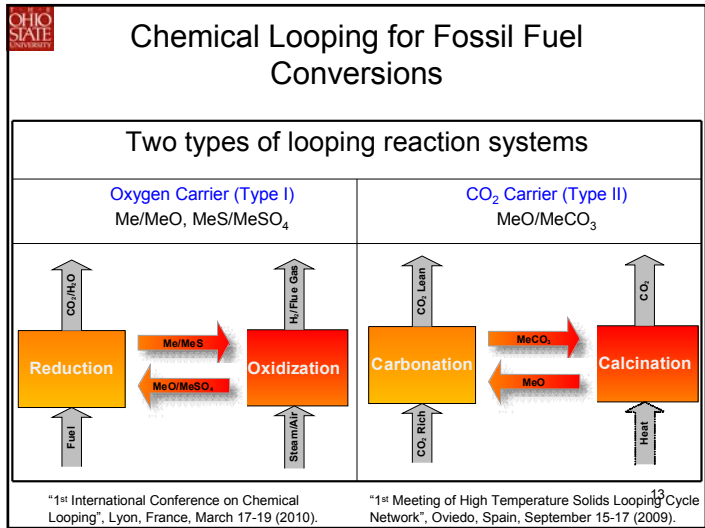
Figuerola, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D., Advances in CO<sub>2</sub> capture technology - The US Department of Energy's Carbon Sequestration Program. *International Journal of Greenhouse Gas Control* 2008, 2, (1) 1-9-20.

## Desired Properties for Modern Chemical Looping Processes

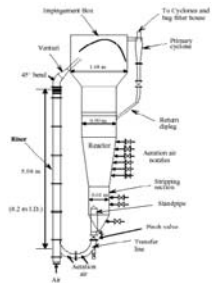
- Versatility
  - Fuel Flexibility: natural gas, syngas, liquid fuels, petrol coke, coal, biomass...
  - Product Variability: electricity (CLC), hydrogen (CLG), liquid fuels, chemicals...
  - Integration with Other Conventional and State-of-the-art Technologies
- In-situ Pollutant Control and CO<sub>2</sub> Separation
- High Efficiency
- Low Cost



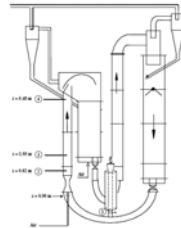
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## Circulating Fluidized Bed Systems



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



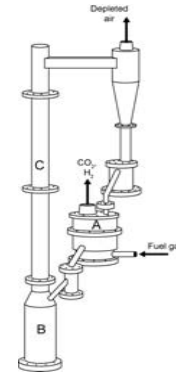
Two Loop High Density CFB System  
(Kulah et al., 2008)

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, 2006; Hamburg, Germany.

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## Chalmers University of Technology Gaseous Fuel CLC

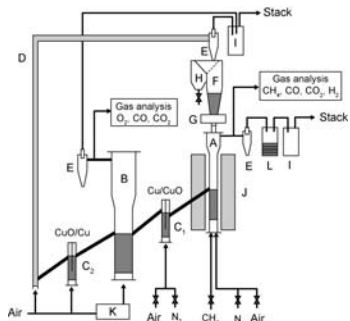


Up to 99% gaseous fuel conversion; Satisfactory (Ni) particle performance;  
Solids inventory: 100 - 200 kg/MW<sub>th</sub>; Solids circulation rate: 4 kg/s-MW<sub>th</sub>

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Photo Courtesy of Professor Anders Lyngfelt

## Instituto de Carboquimica (CSIC) 10 kW<sub>th</sub> Gaseous Fuel CLC



Nearly 100% gaseous fuel conversion; Satisfactory (Cu) particle performance;  
Solids inventory: ~2,100 kg/MW<sub>th</sub>; Solids circulation rate: 6 kg/s-MW<sub>th</sub>

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Photo Courtesy of Dr. Luis F. de Diego of CSIC

## Korea Institute of Energy (KIER) Research 50 kW<sub>th</sub> Gaseous Fuel CLC

1<sup>st</sup> Generation Unit



2<sup>nd</sup> Generation Unit



~99% gaseous fuel conversion achieved; Ni and Co particle tested;  
Solids inventory: ~600 kg/MW<sub>th</sub>;

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Photo courtesy of Dr. Ho-Jung Ryu of KIER

**OHIO STATE UNIVERSITY** **Vienna University of Technology 120 kW<sub>th</sub> Gaseous Fuel CLC**

**90 – 99% gaseous fuel conversion; satisfactory (Ni) particle performance; Fe ore not reactive enough; Solids inventory: ~240 kg/MW<sub>th</sub>; Solids circulation rate: ~11 kg/s-MW<sub>th</sub>**

Photo courtesy of Dr. Tobias Pröll of the Vienna University of Technology

**OHIO STATE UNIVERSITY** **Chalmers University of Technology Solid Fuel CLC**

**South African coal and pet coke tested; Iron based oxygen carrier used; 50 – 80% solid fuel conversion; 70 – 80% reducer outlet CO<sub>2</sub> concentration; Reducer solids inventory: 800 – 1500 kg/MW<sub>th</sub>**

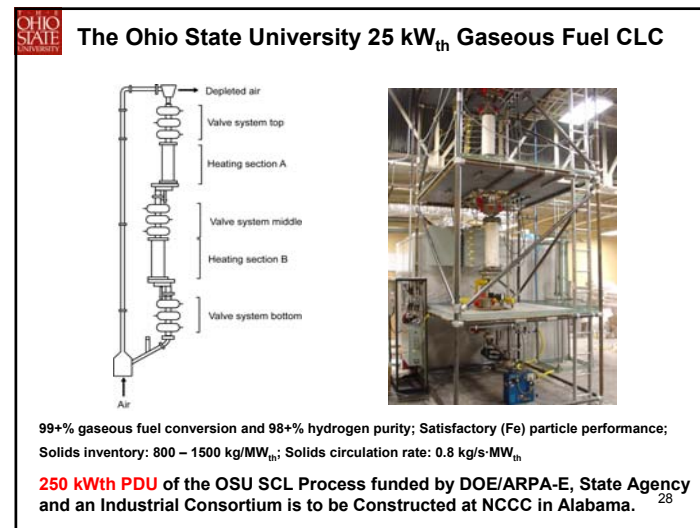
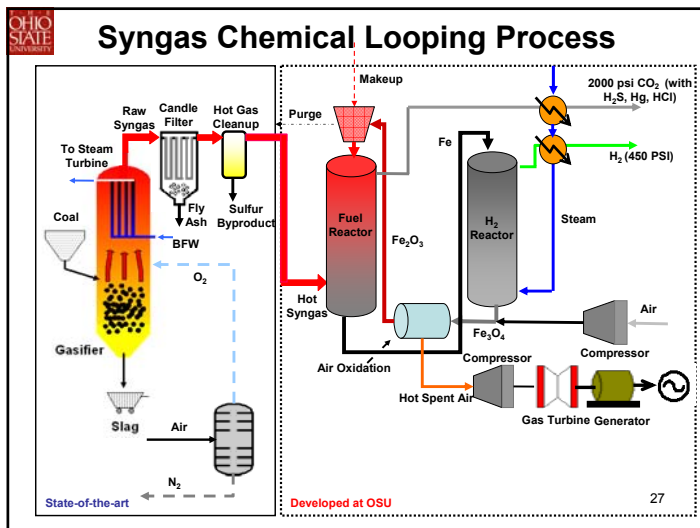
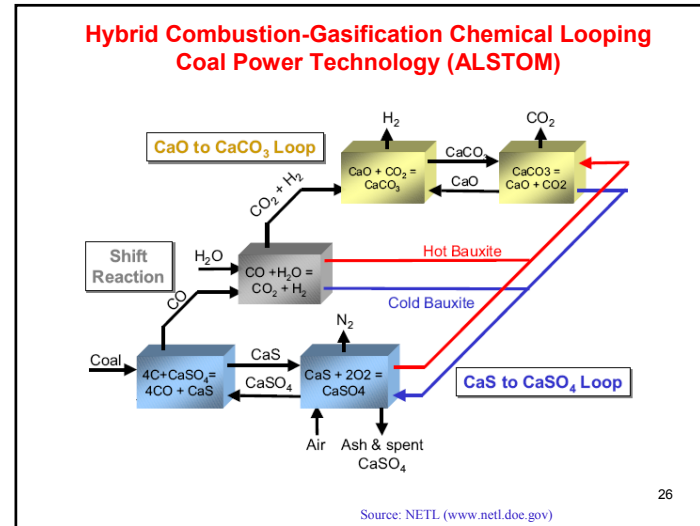
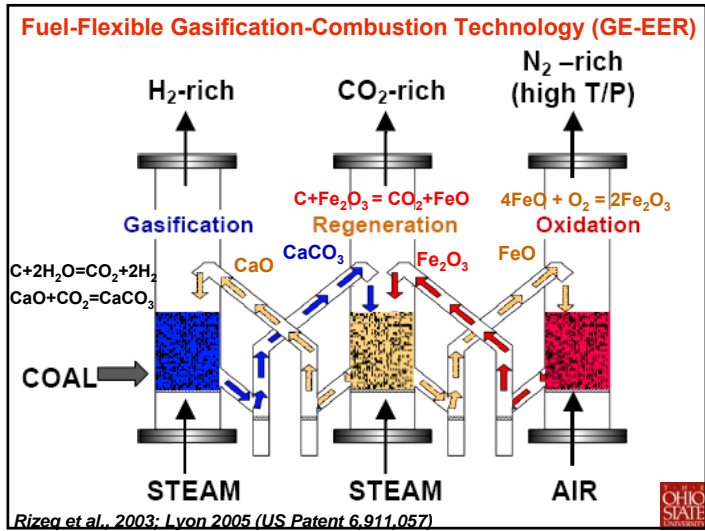
Photo Courtesy of Professor Anders Lyngfelt

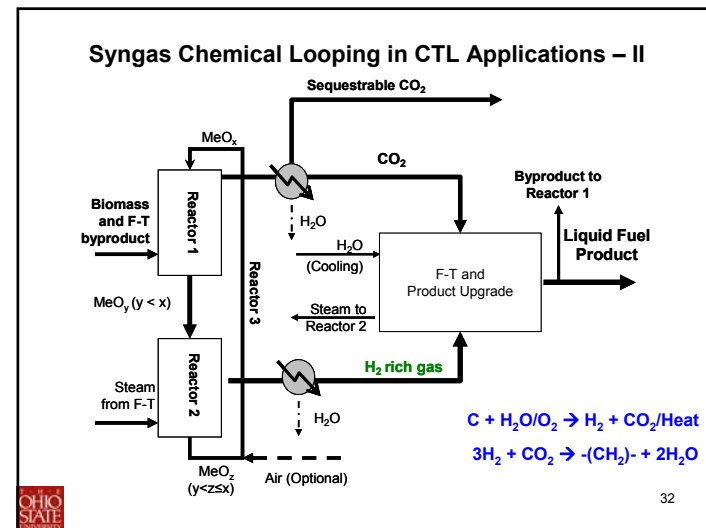
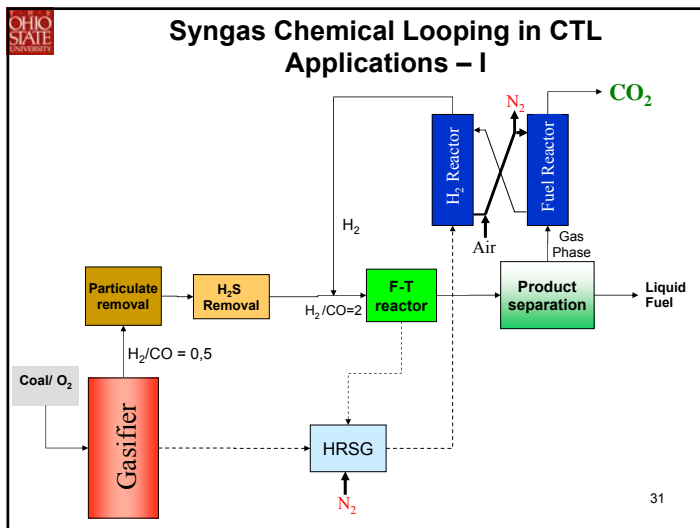
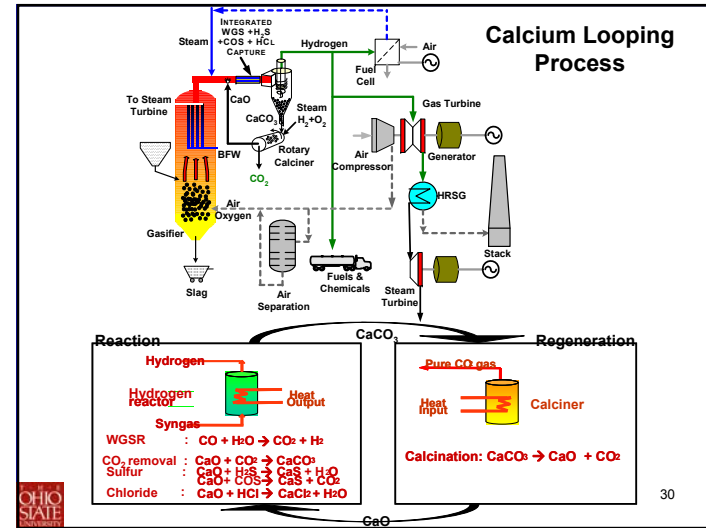
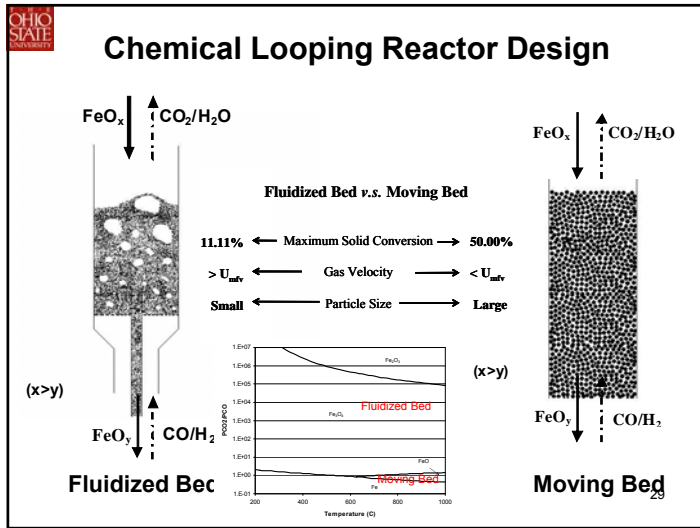
Particle Type	Ni		Cu		Fe		Moving Bed -H <sub>2</sub> 25 kW
	Lab Scale	CFB 120 kW	Lab Scale	CFB 10kW	Lab Scale	CFB 300W	
Particle Type	NiO/MgAl <sub>2</sub> O <sub>4</sub>	NiO/MgAl <sub>2</sub> O <sub>4</sub>	CuO/Al <sub>2</sub> O <sub>3</sub>	CuO/Al <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub> /MgAl <sub>2</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Composite Fe <sub>3</sub> O <sub>4</sub>
Air Flow Rate @1000 MWth and 10% Excess (mol/s)	11784						1309
Volumetric Air Flow Rate at 1 atm and 900 °C (m <sup>3</sup> /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 <sup>3</sup> )	1.9	5	2.5	2.5	4.1	2.15	2.5
U <sub>t</sub> (m/s)	2	0.8	2	1.2	1.1	0.6	11
U <sub>c</sub> (m/s)	4	4.8	4.9	4.2	4.8	3.6	4
U <sub>se</sub> (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 <sup>2</sup> )	231.47						25.18
Bed Area Required for Riser Section at 1 atm (m <sup>2</sup> )	162.03						10.49
Corresponding Riser Diameter (m)	14.37						3.66
Solids Flux at 1 atm (kg/m <sup>2</sup> s)	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
U <sub>g</sub> for a Single 1.5 m ID Riser at 1 atm (m/s)	642.14						71.29
U <sub>g</sub> for a Single 8 m ID riser at 1 atm (m/s)	22.58						2.5 (U <sub>g</sub> < U <sub>t</sub> ; 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 <sup>2</sup> s)	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						U <sub>g</sub> < U <sub>t</sub> ; N/A
Solids Flux for a Single 8 m ID Riser (kg/m <sup>2</sup> s)	79.62	199.04	59.71	119.43	159.24	199.04	U <sub>g</sub> < U <sub>t</sub> ; N/A

**HyPr-RING Process (AIST, Japan)**

**Solid fuels used, one calcium sorbent, one chemical loop, one steam turbine, ~90% hydrogen purity**

Photo Courtesy of Dr. Shiyong Lin





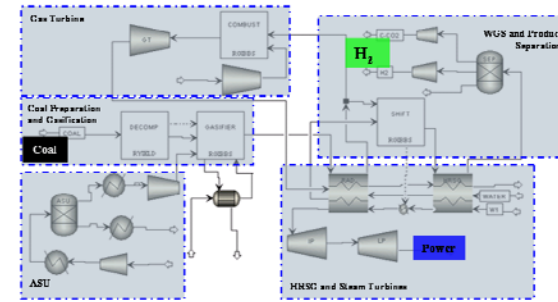
## ASPEN® Simulation Assumptions

- A Shell SCGP gasifier is considered
- A feeding rate of 132.9 t/hr of Illinois #6 coal is used (approximately 1,000 MW in HHV)
- Carbon regulation mandates > 90% carbon captured
- The H<sub>2</sub> coming out of the system is compressed to 6 MPa for transportation while the CO<sub>2</sub> is compressed to 15.3 MPa for geological sequestration
- 1% heat loss is assumed, heat can be integrated with a 100% efficiency
- The isentropic efficiencies is 0.8 for compressors, 0.85 for all turbines
- **Performance data obtained from bench scale unit is used for looping simulations**



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## Traditional Coal to Hydrogen Process



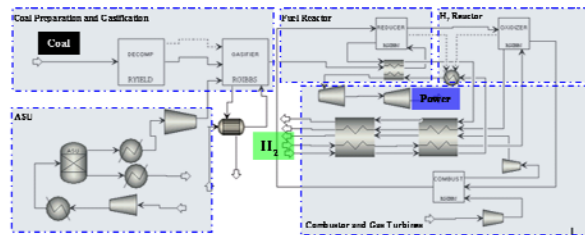
Assumption used is similar to those adopted by Mitretek Systems in their report to USDOE/NETL\*.

\* Gray D. and Tomlinson G. Hydrogen from Coal. Mitretek Technical Paper. DOE contract No:DE-AM26-99FT40465. (2002)



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## Syngas Chemical Looping Process



Practical factors that are taken into account in the simulation:

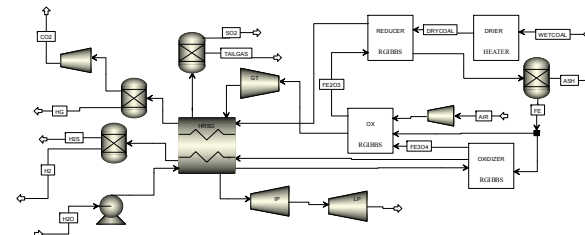
- Pressure drop of the major chemical looping units,
- Energy consumption for particle transportation
- Energy loss due to the purging of the particles

*The simulation results represent a conservative estimation of SCL performance based on current demonstration outcome*



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## Coal-Direct Chemical Looping Process



Practical factors that are taken into account in the simulation:

- No ASU and gasifier are required
- Pressure drop of the major chemical looping units
- Energy loss due to the purging of the particles

*The simulation results represent a very conservative estimation of CDCL performance based on thermodynamic equilibrium analysis*



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### ASPEN® Simulation Comparison of SCL, CDCL, and Traditional Coal to Hydrogen/Electricity Processes

	IGCC Process	SCL Process Electricity	CDCL Process Electricity	Conventional to Hydrogen Process	SCL Process Hydrogen	CDCL Process Hydrogen
Coal Feed (ton/hr)	132.9	132.9	132.9	132.9	132.9	132.9
Carbon Capture (%)	90	100	100	90	100	100
Hydrogen (ton/hr)	0	0	0	14.4	15.6	20.0
Net Power (MW)	321	365	435	2.1	26	3
Efficiency (%HHV)	32.1	36.5	43.5	57.8	64.1	79.0

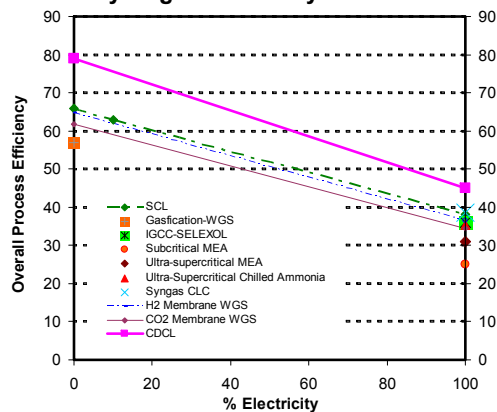
Process unit performance conditions correspond to those given in "Cost and Performance Baseline for Fossil Energy Plants", DOE/NETL-2007/1281.



## Concluding Remarks

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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.



## Thank You

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