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Chemical Looping Technology Advancements for Natural Gas Utilization

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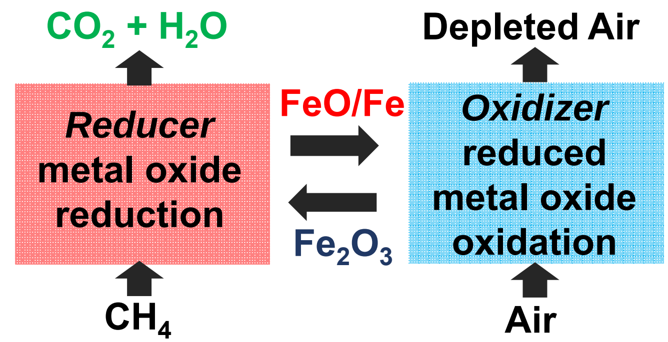
Chemical Looping Redox Applications

Combustion: Complete Fuel Oxidation

Reducer: Fe_2O_3 + CH_4 → **FeO/Fe** + **CO_2 + H_2O**
(oxidized) (reduced)

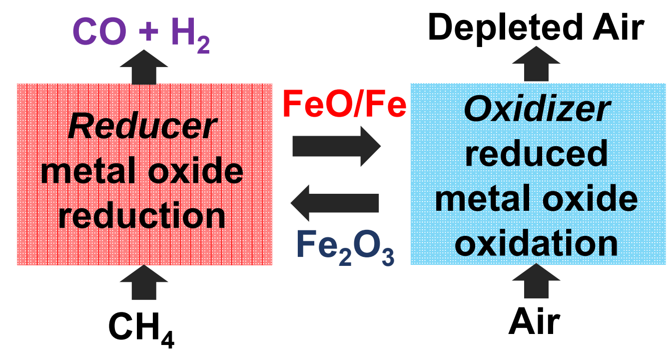
Oxidizer: **FeO/Fe** + Air (O_2) → **Fe_2O_3**

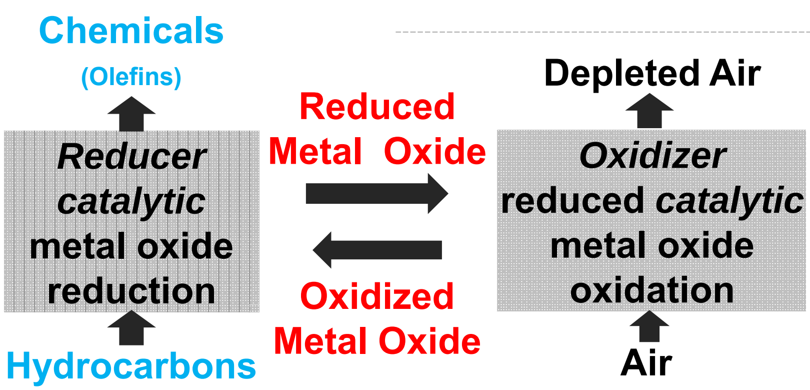


Gasification: Partial Fuel Oxidation

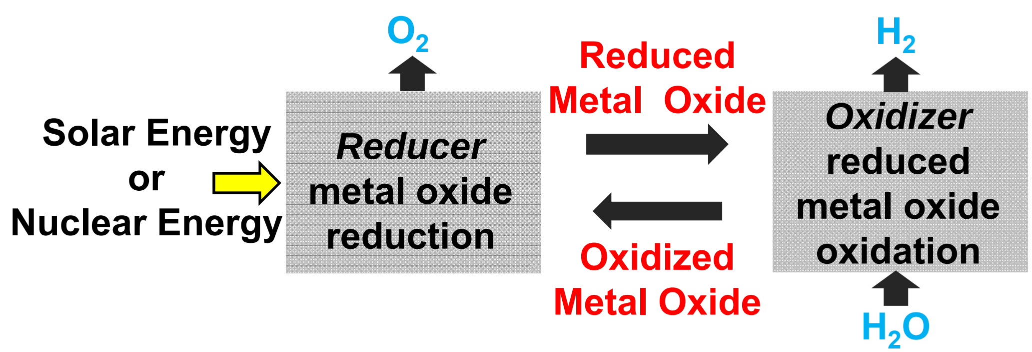
Reducer: Fe_2O_3 + CH_4 → **FeO/Fe** + **CO + H_2**
(oxidized) (reduced)

Oxidizer: **FeO/Fe** + Air (O_2) → **Fe_2O_3**





Chemicals Production: Selective Oxidation

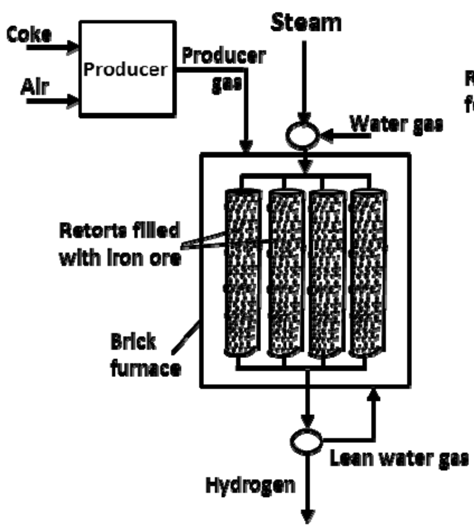


Solar/Nuclear Chemical Looping: Water Splitting

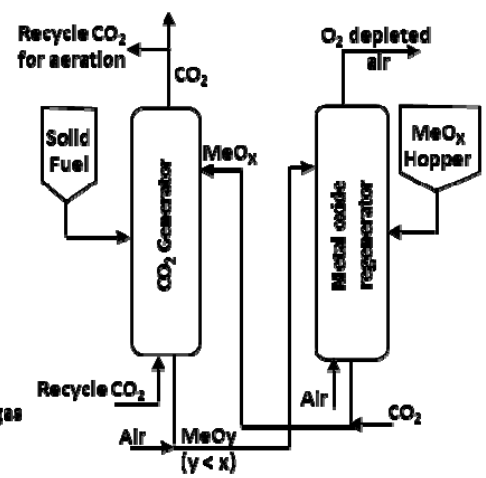
Luo, S., Zeng, L., Fan, L.-S., *Annual Review of Chemical and Biomolecular Engineering*. July 2015.
Chung, E.Y., Wang, W.K., Alkhatib, H., Nadgouda, S., Jindra, M.A., Sofranko, J.A., Fan, L.-S. 2015 AIChE Spring Meeting. April 2015.
Chueh, W. C., Falter, C., Abbott, M., Scipio, D., Furler, P., Haile,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

Historical Development of Chemical Looping Technology for Hydrogen Production and Combustion Applications

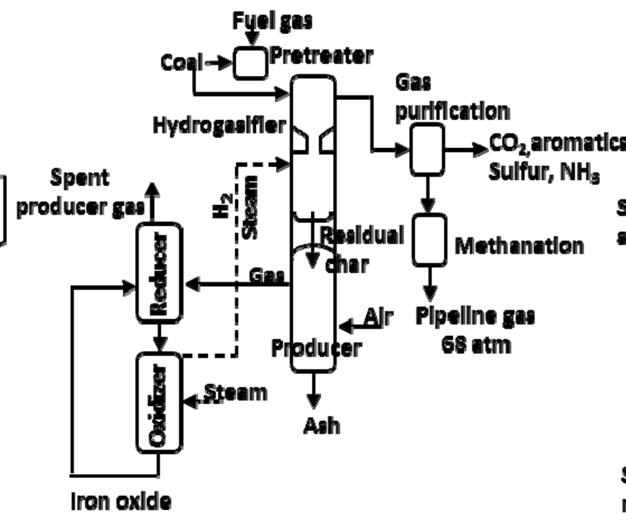
Technologies	Lane Process & Messerschmitt Process	Lewis and Gilliland Process	IGT HYGAS Process	CO_2 Acceptor Process
Time	Early Twentieth Century	1950s	1970s	1970s
Looping Media	$Fe/FeO/Fe_3O_4$	Cu_2O/CuO	FeO/Fe_3O_4	$CaO/CaCO_3$
Reactor Design	Fixed Bed	Fluidized Bed	Staged Fluidized Bed	Fluidized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



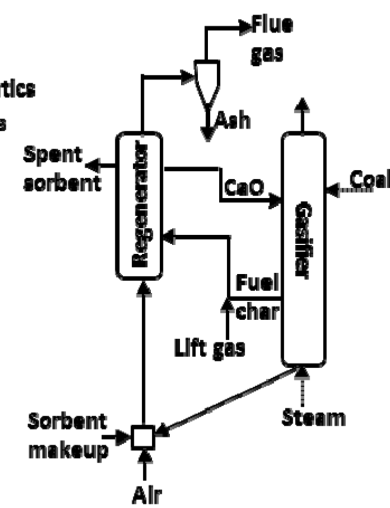
Lane Process



Lewis and Gilliland Process



IGT Process



CO_2 Acceptor Process

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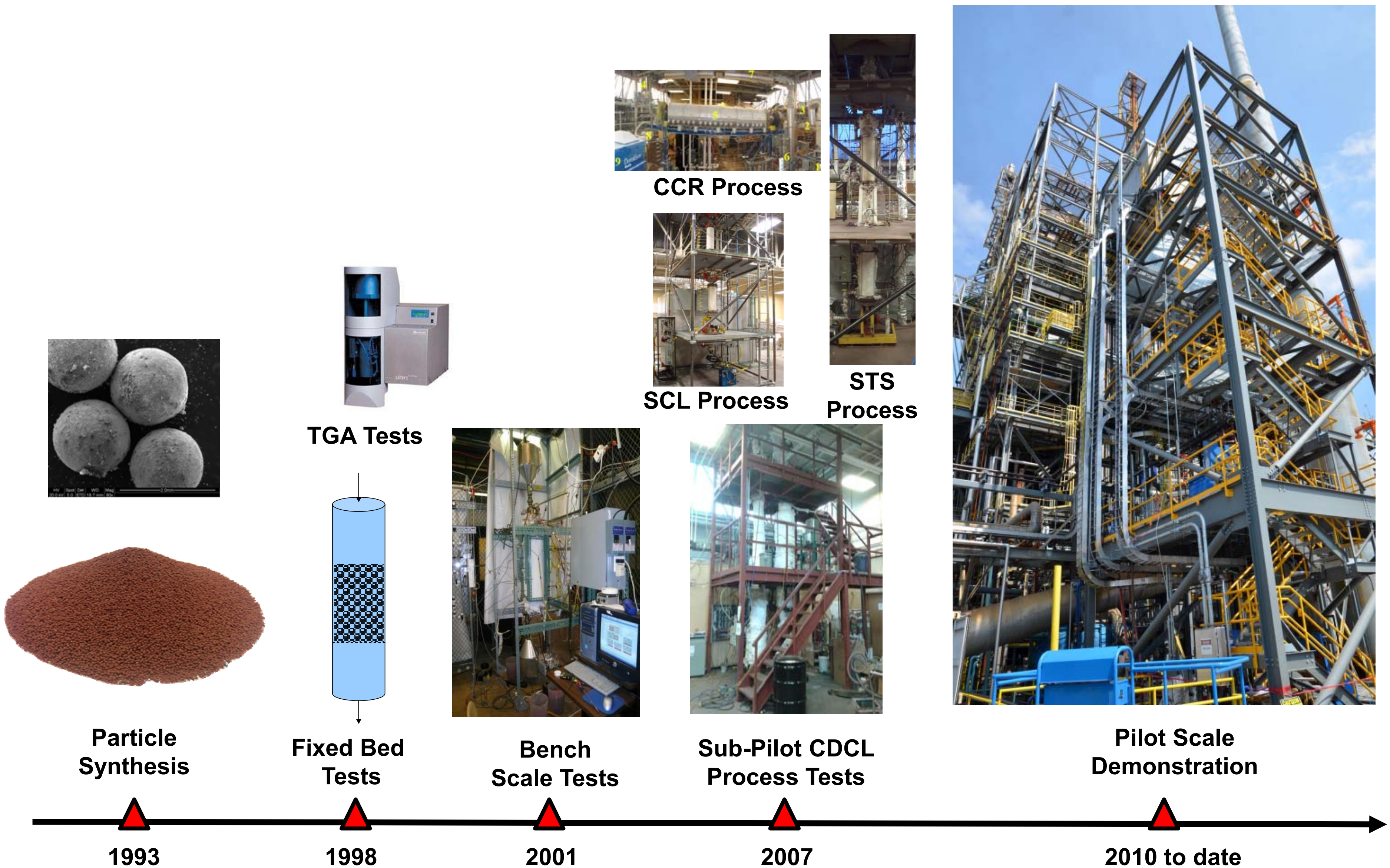
Messerschmitt, A. U.S. Patent 971,206, 1910.; Lane, H. U.S. Patent 1,078,686, 1913.
Dobbyn, R.C., Ondik, H.M., et al . U.S. DOE Report DOE-ET-10253-T1, 1978.
Lewis, W.K., Gilliland, E.R. U.S. Patent 2,655,972, 1954.
Institute of Gas Technology. U.S. DOE Report EF-77-C-01-2435, 1979.

Evolution of OSU Chemical Looping Technology



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

Chemical Looping Advantages

Process Intensification: Eliminate Multiple Conventional Unit Operations

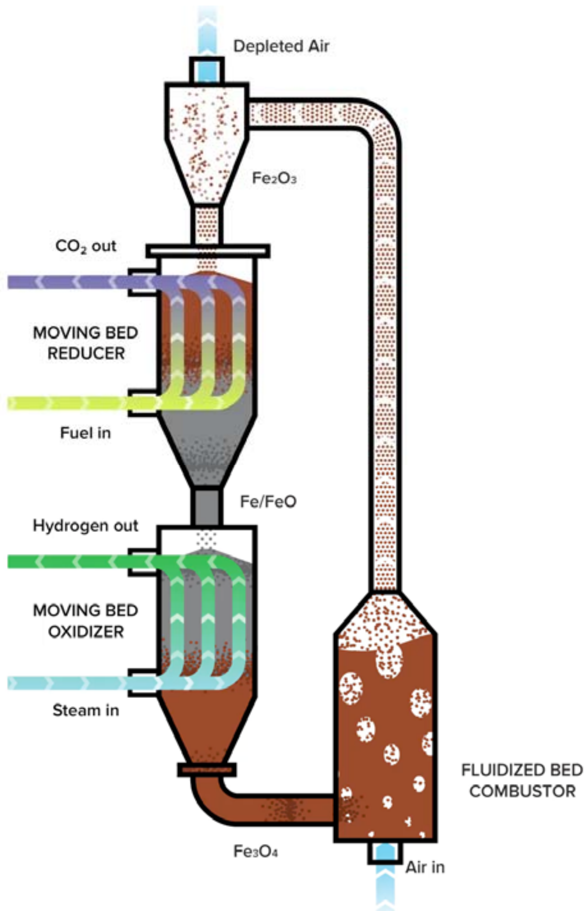
Hydrogen Production

Liquid Fuels and Chemicals

Chemical Looping Advantages

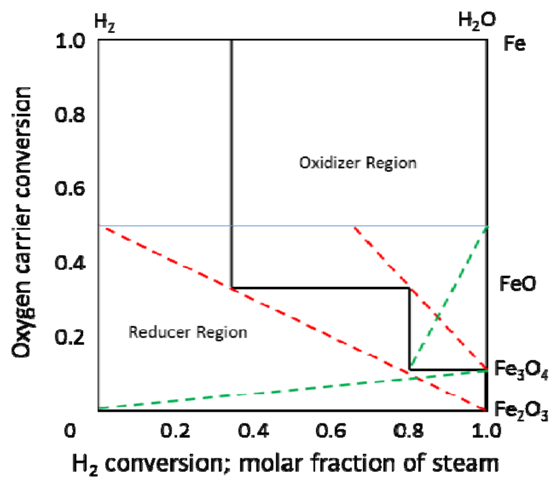
Process Intensification: Eliminate Multiple Conventional Unit Operations

Full Oxidation of NG: H_2 Production Application



Main Reactions

Reducer:	$C_xH_yO_z + Q + Fe_2O_3 \rightarrow CO_2 + H_2O + Fe$
Oxidizer:	$Fe + H_2O \rightarrow Fe_3O_4 + H_2 + Q$
Combustor:	$Fe_3O_4 + O_2 \rightarrow Fe_2O_3 + Q$
Total:	$C_xH_yO_z + H_2O + O_2 \rightarrow CO_2 + H_2$

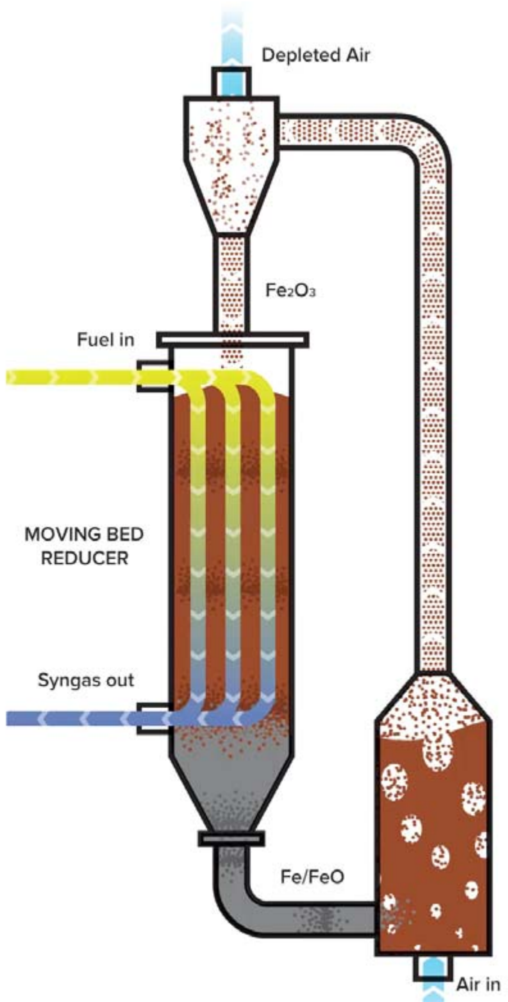


- Major Cost in Conventional SMR is H_2 Purification
- Nearly pure H_2 produced from oxidizer
- No downstream AGR required
- Versatile: Steam export

Chemical Looping Advantages

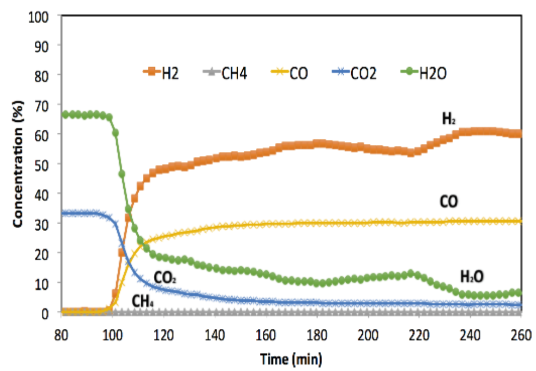
Process Intensification: Eliminate Multiple Conventional Unit Operations

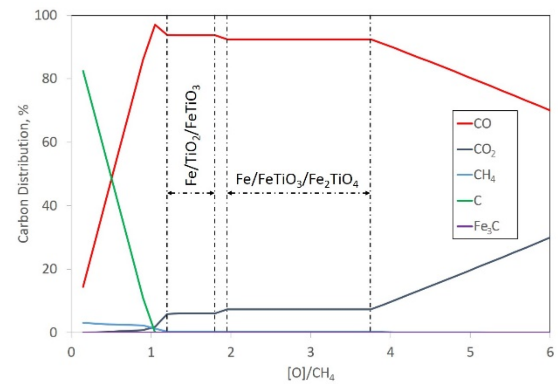
Partial Oxidation of NG: Gas to Liquids and Chemicals Application



Main reactions

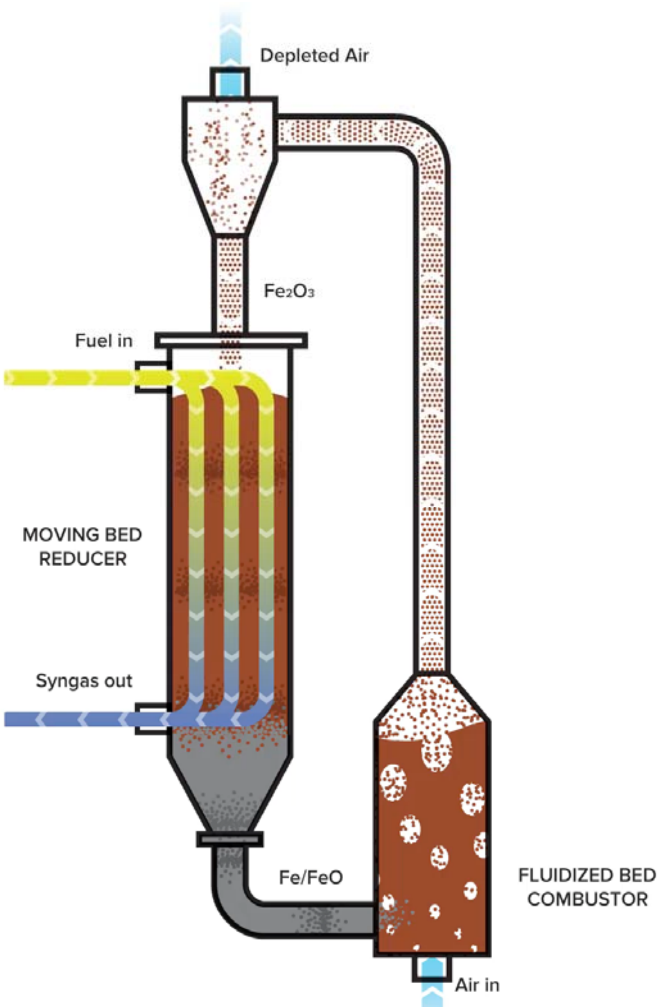
Reducer:	$C_xH_yO_z + CO_2 + H_2O + Fe_2O_3 + Q \rightarrow CO + H_2 + Fe/FeO$
Combustor:	$Fe/FeO + O_2\ (Air) \rightarrow Fe_2O_3 + Q$
Net:	$C_xH_yO_z + H_2O + CO_2 + O_2\ (Air) \rightarrow CO + H_2$





- ATR reactor accounts for nearly 50% GTL plant costs
- Removal of ATR, increased carbon conversion efficiency to syngas results in 60% reduction in capital cost for syngas production
- Capable of zero or negative CO_2 emissions from GTL plant

Chemical Looping Challenges



- High solid circulation rate
  - solid flow control
  - Pressure balance/gas seal
  - Possible max flux flow limitations
- Oxygen carrier performance
  - Attrition resistance – operating cost
  - Reaction kinetics – reactor volume/capital cost
  - Sustained reactivity – operating cost
- Process development
  - Heat integration
  - Transient operations
    - Ramp up/down

Chemical Looping Development Pathway

Proof of Concept:
- Oxygen Carrier Reactivity
- Reactor design verification
- Initiate TEA

Lab Testing

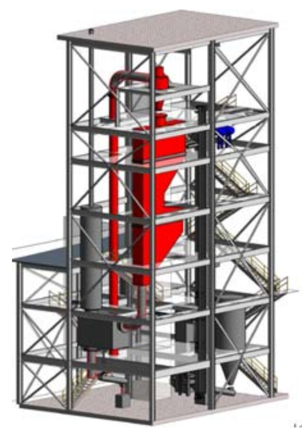
Integrated Operations:
- Scalable component design
- Sustained particle reactivity/strength
- Reactor operation procedure and controls development

Bench
($1kW_{th}$-$100\ kW_{th}$)

Pilot Operations
- Adiabatic reactor design and testing
- Feed point spacing
- HMB verification
- Process control development

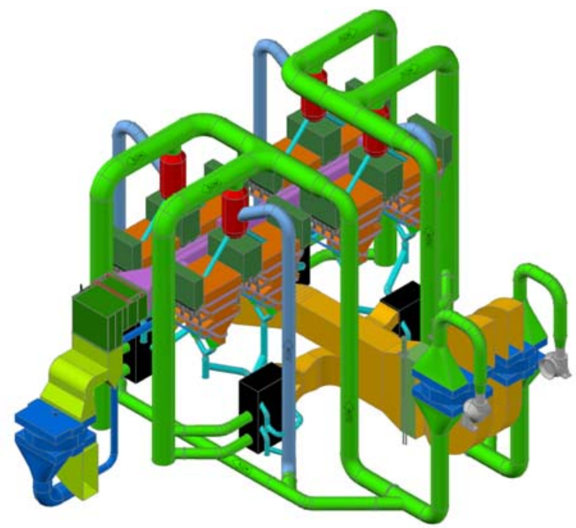
Small Pilot
($100kW_{th}$-$3\ MW_{th}$)

Product Production
- Heat integration
- Product quality assessment



Large Pilot
($10\ MW_{th}$ – $50\ MW_{th}$)

Verify costs and performance

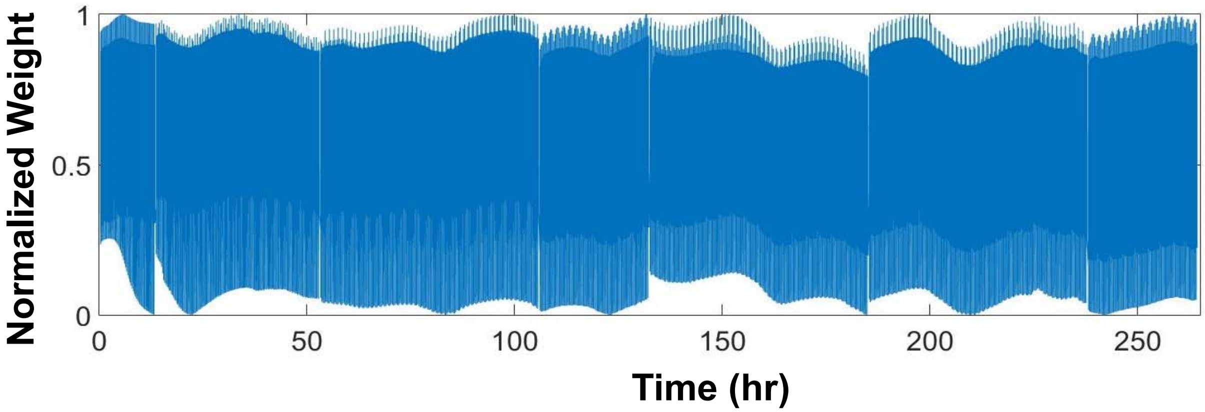


Commercial Offering

Time

Laboratory Studies

Oxygen Carrier Development

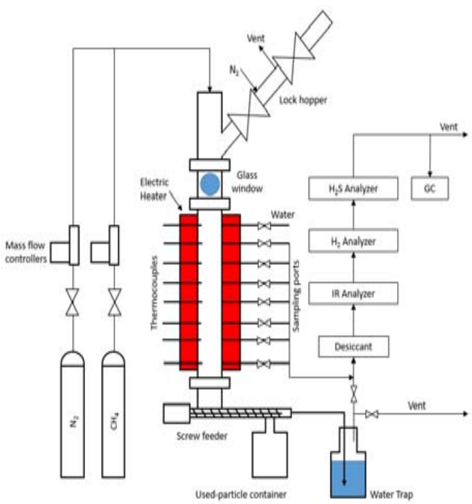


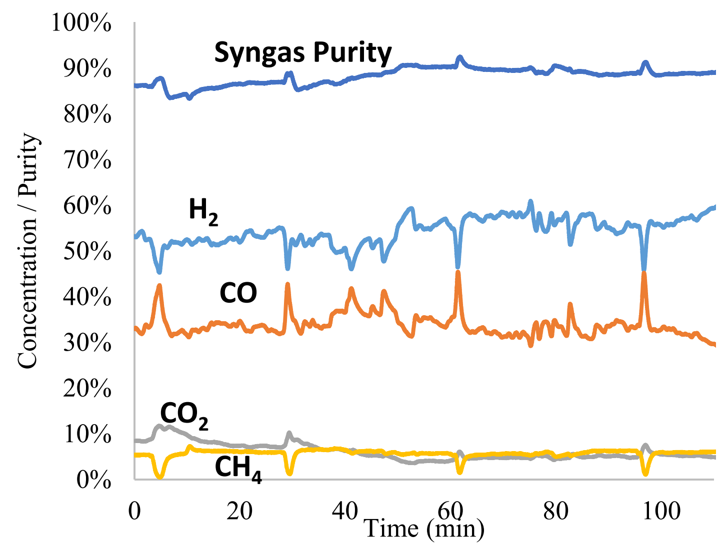
before

after

Co-Current Moving Reducer Testing

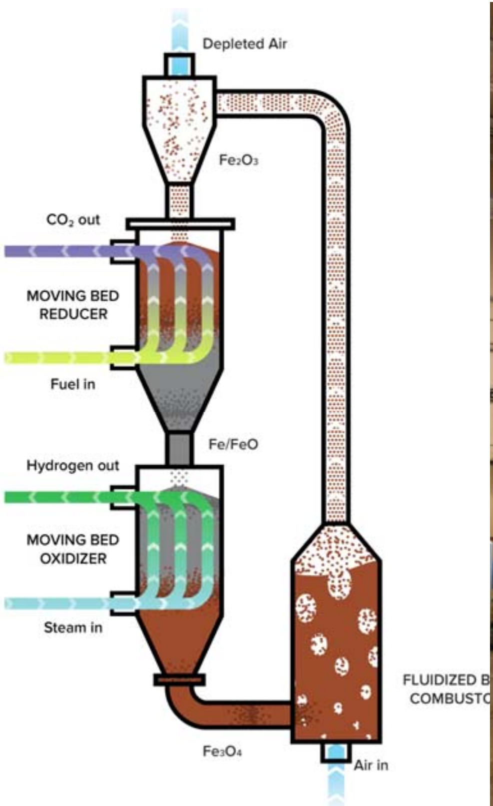
Test Apparatus

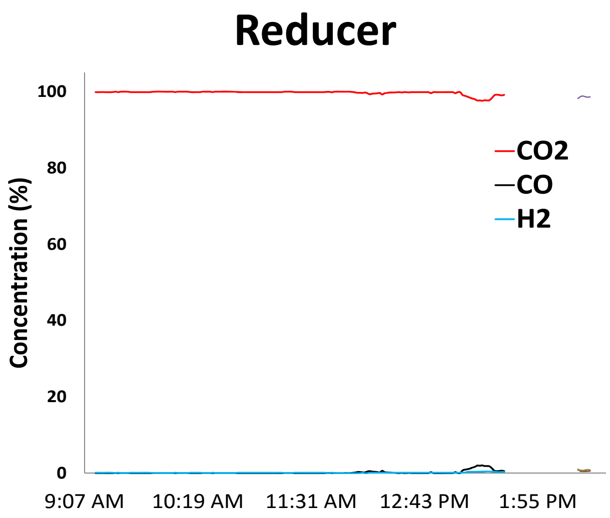


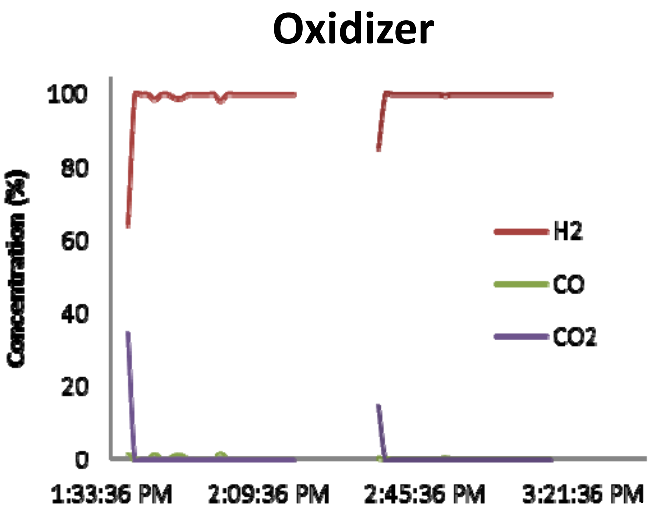


Fan, L.-S. Chemical Looping Systems for Fossil Energy Conversions. Wiley, 2010.
Li, F., Kim, H.R., Sridhar, D., Wang, F., Zeng, L., Fan, L.-S. *Energy & Fuels*. 2009.

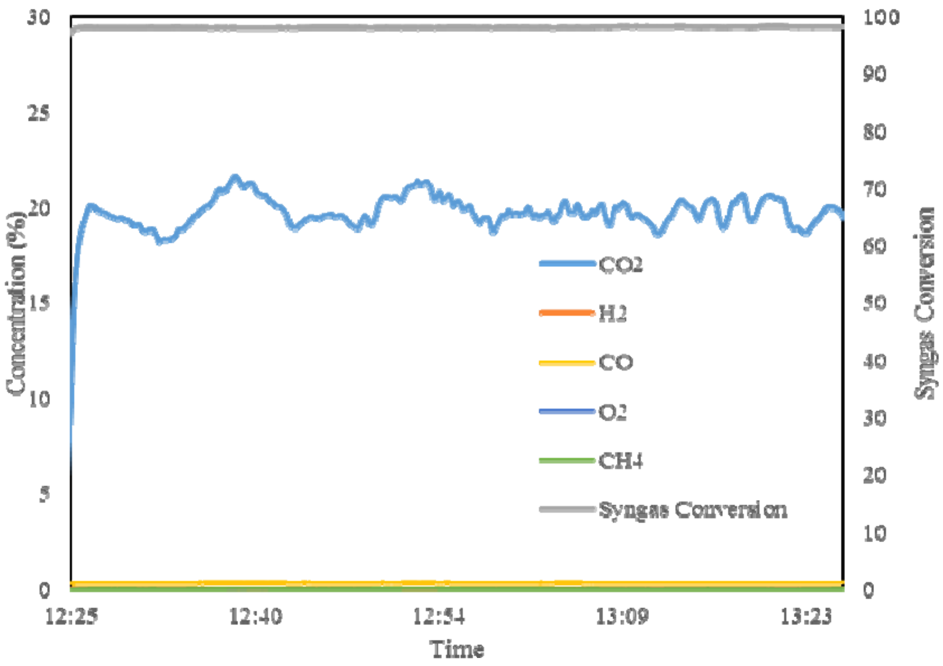
Bench-Scale Testing







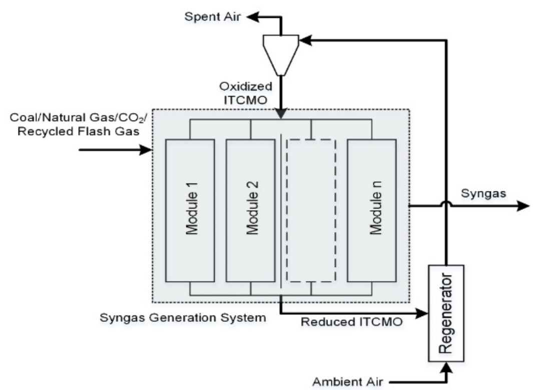
Pilot Plant Development



- Syngas operation initiated
  - 350 lb/hr syngas processed
- Achieved >98% syngas conversion
- Pressure balance and gas sealing maintained
- Elevated combustor temperatures confirm redox reactions

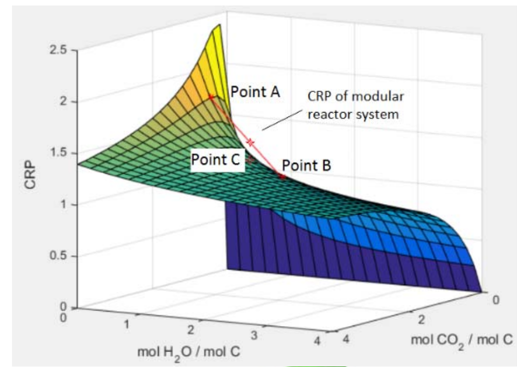
Chemical Looping Development Pathway

Modular Reactor Design



- Chemical looping inherent low capital cost technology
- Reduce risks for large scale-up

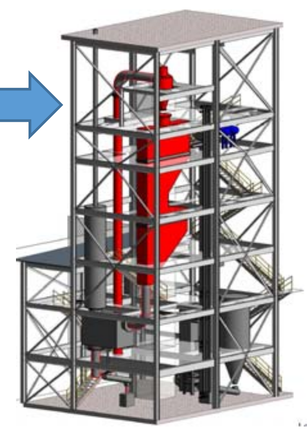
Modular Reactor Optimization



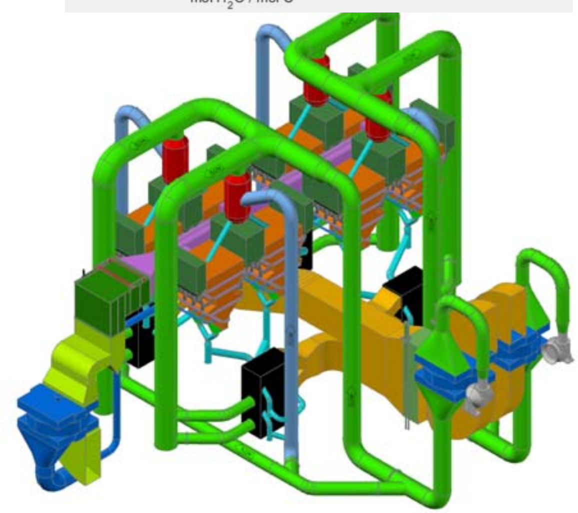
Lab Testing

Bench ($1kW_{th}$-$100\ kW_{th}$)

Small Pilot ($100kW_{th}$-$3MW_{th}$)



Large Pilot ($10\ MW_{th}$ – $50\ MW_{th}$)



Commercial Offering

Time

Summary

- Chemical Looping technologies represent promising means of utilizing natural gas for industrial gases and high value chemicals
  - Eliminate separation costs for high purity H_2 production
  - Eliminate air separation unit and carbon emissions for GTL plant
- Modular design and optimization work supports large scale-up
- Major economic opportunity for chemical looping process exists at intermediate natural gas processing capacities