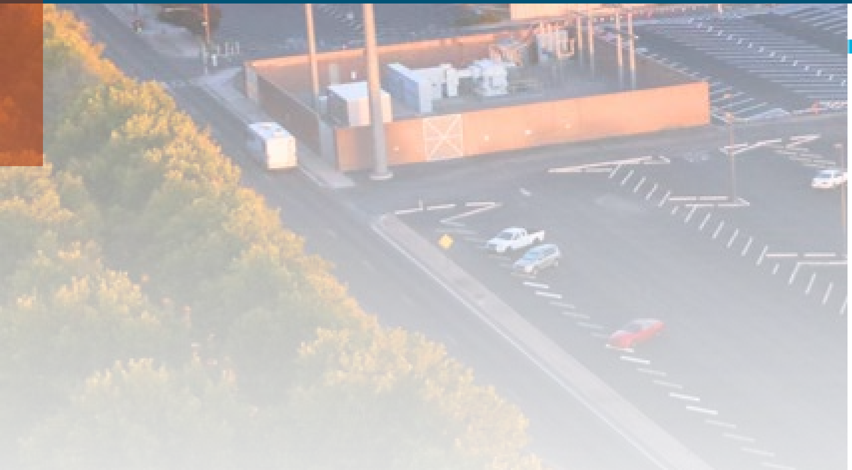
Unlocking Solar Thermochemical Potential: Leveraging CSP Experience for Solar Thermochemistry



Andrea Ambrosini

Sandia National Laboratories

SETO CSP Virtual Workshop

19 Nov 2020

Sandia National Laboratories

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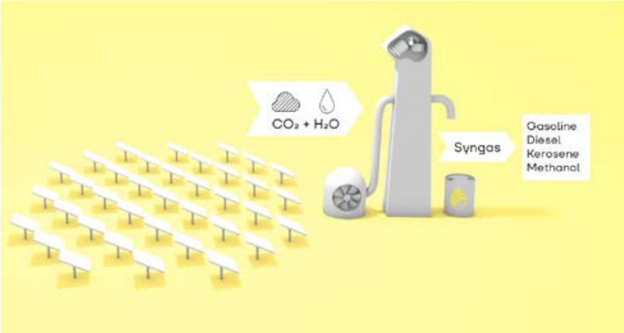
Solar Flux as a Thermal Energy Input

- **Motivation**
  - Decarbonizing industrial processes such as steel, ore refining, cement, fuel or chemical production, and food products
  - Can provide both heat and electricity for processing
  - Ability to achieve high temperatures
- **Key Considerations**
  - Intermittency
  - Integration into existing technology?
  - On-site production vs. transportation costs
    - Point of production does not always equal point of use
  - Location
  - Scale
  - Cost
- I will address some of these considerations in the context of solar thermal production of ammonia



Solar fuels (Synhelion.com)

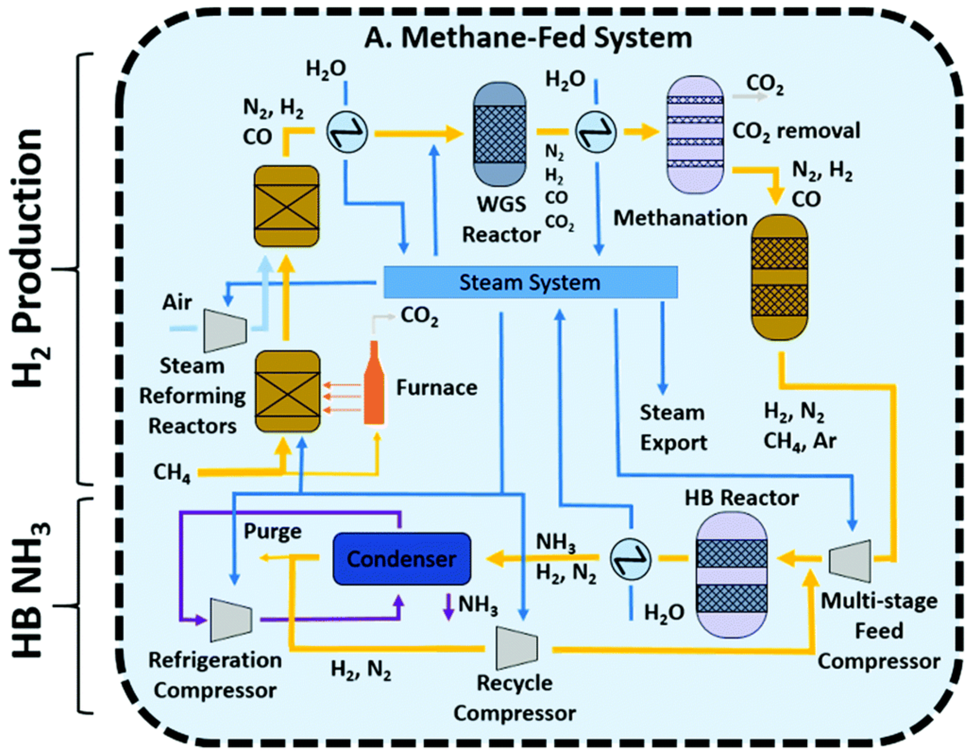
Steel production

Sustainable pasta production; Mmmm, pasta. (DLR/Barilla)

Deep decarbonization

Example: Ammonia Production

- Ammonia (NH_3) is an energy-dense chemical and a vital component of fertilizer, hydrogen carrier, and energy supplier
- NH_3 synthesized via the Haber-Bosch process
  - Requires high pressures (15-25 MPa) and temperatures (400-500 ^{o}C)
  - Consumes > 1% of global energy use
  - Heat, power, and hydrogen are all sourced from hydrocarbons
- Process including H_2 production generates about 2.3 t of fossil-derived CO_2 per t of NH_3, and is responsible for ~1.4% of global CO_2 emissions
- Steam reforming of natural gas for H_2 generation accounts for 84% of req'd energy

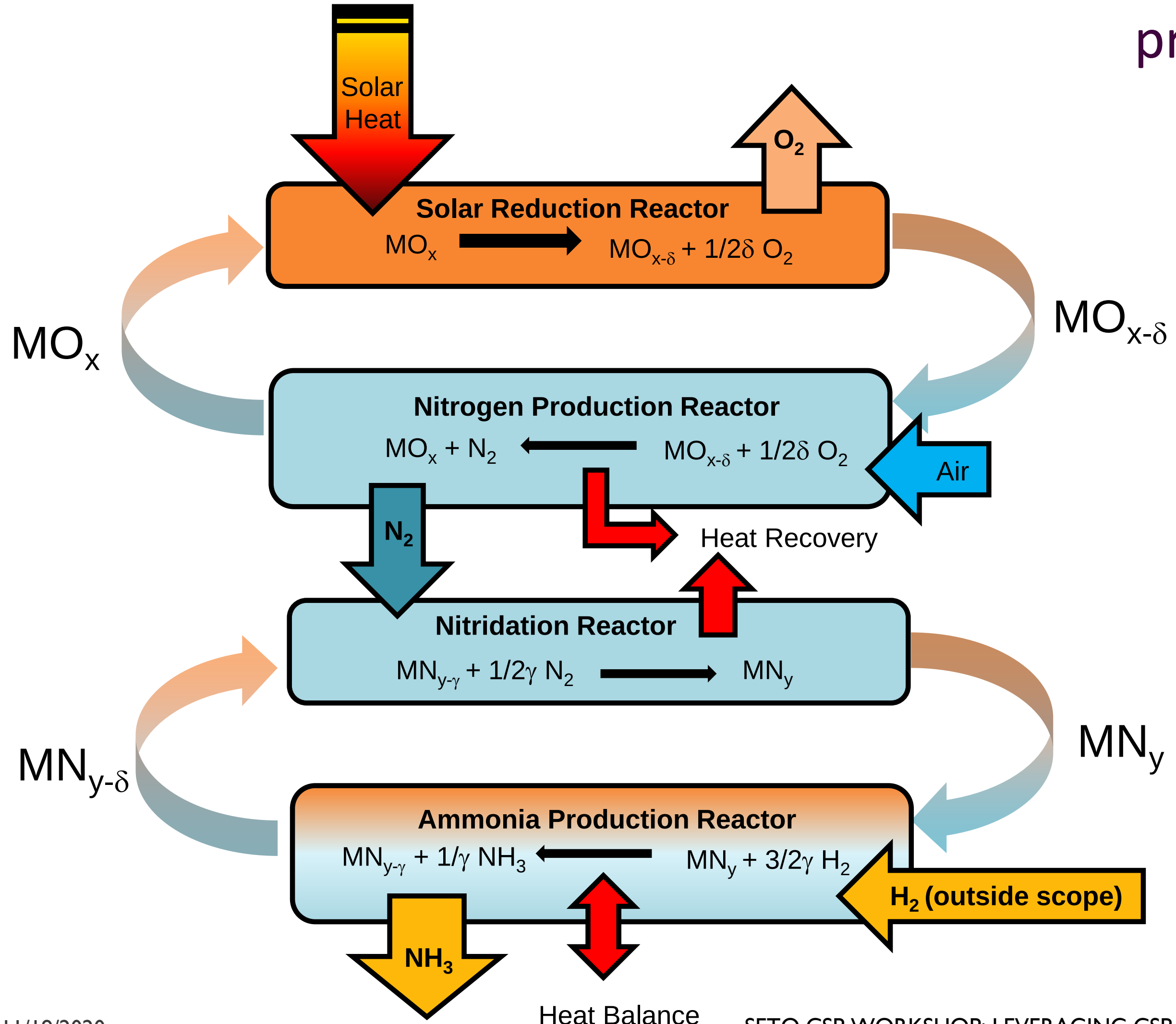


Schematic diagram of a typical conventional methane-fed Haber Bosch process (*Energy Environ. Sci.*, 2020,13, 331-344.)

Can NH_3 be synthesized via a renewable, carbon-neutral technology powered by concentrating solar ?

Solar Thermal Ammonia Production (STAP)

An advanced solar thermochemical looping technology to produce and store nitrogen (N_2) from air for the subsequent production of ammonia (NH_3) via an advanced two-stage process

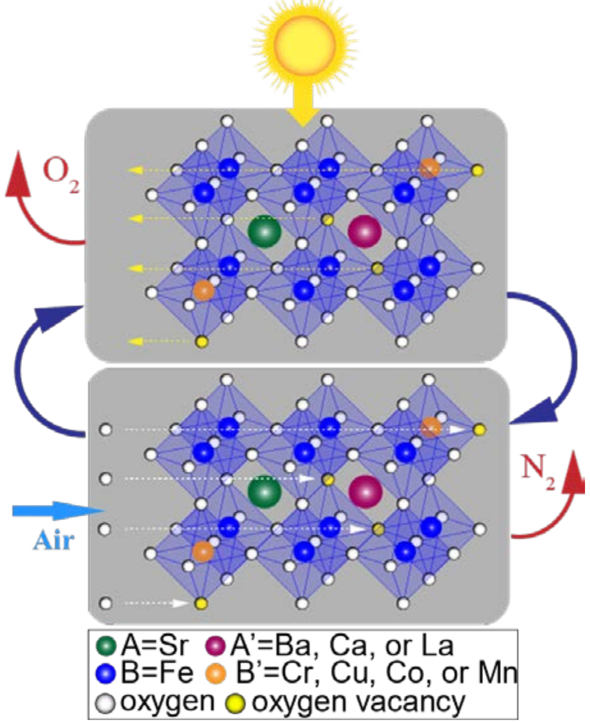


- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically
- The project consists of four thrusts:
  - N_2 production via air separation
  - NH_3 production via a cyclic nitride reaction
  - Reactor modeling and design
  - Systems analysis
- Low TRL

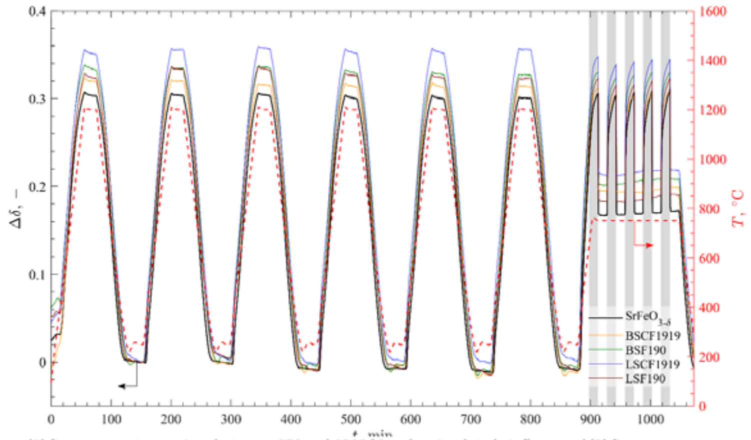
Materials

Materials choice influences every aspect of system design

- Materials must be carefully and comprehensively characterized
  - Reactivity
  - Durability: is structural integrity maintained
  - Thermodynamics: enthalpy, reactivity, reaction temperature
  - Kinetics: does the reaction proceed quickly (determines time on-sun)
  - Cyclability: can they be cycled repeatedly with no loss of performance
  - Particle size: affects kinetics, heat and mass transfer
  - Chemical stability: no undesired phase changes, deactivation
- Economic considerations
  - Synthesis: an they be easily synthesized and scaled up?
  - Cost/Availability: avoid critical elements



Metal oxide for air separation



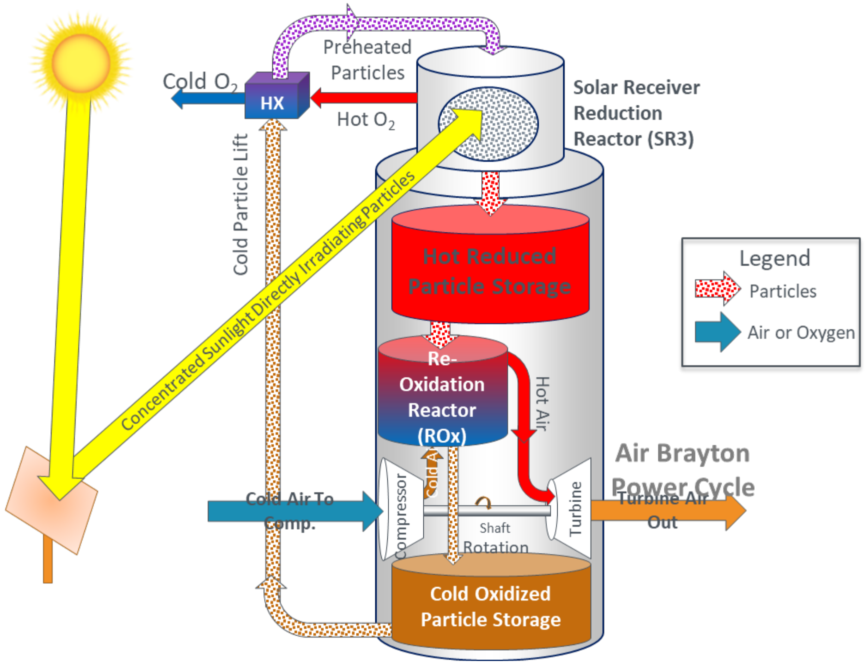
(1) five temperature swings between 250 and 1200 °C under simulated air flows and (2) five pressure swings between 0% and 20% O_2–Ar at 750 °C

TGA showing redox capacity and cyclability

Intermittency

To maximize productivity, a plant must be able to operate 24/7

- A feature of CSP is the ability to store heat for off-sun operation or electricity generation
  - Storage can be sensible (molten salt, particles), latent (phase change), or thermochemical (sensible + reaction enthalpy)
  - Solids are generally easier to store– they are dense, do not require compression, noncorrosive, stable at T > 1100 °C, and are amenable to multiple scales
    - Thermochemical materials have added benefit of storing energy in the form of chemical bonds, irrespective of storage temperature
- H_2 generated on-site via solar thermochemical water splitting can also act as a chemical storage material, in addition to as a feedstock for chemical processes, e.g., ammonia production

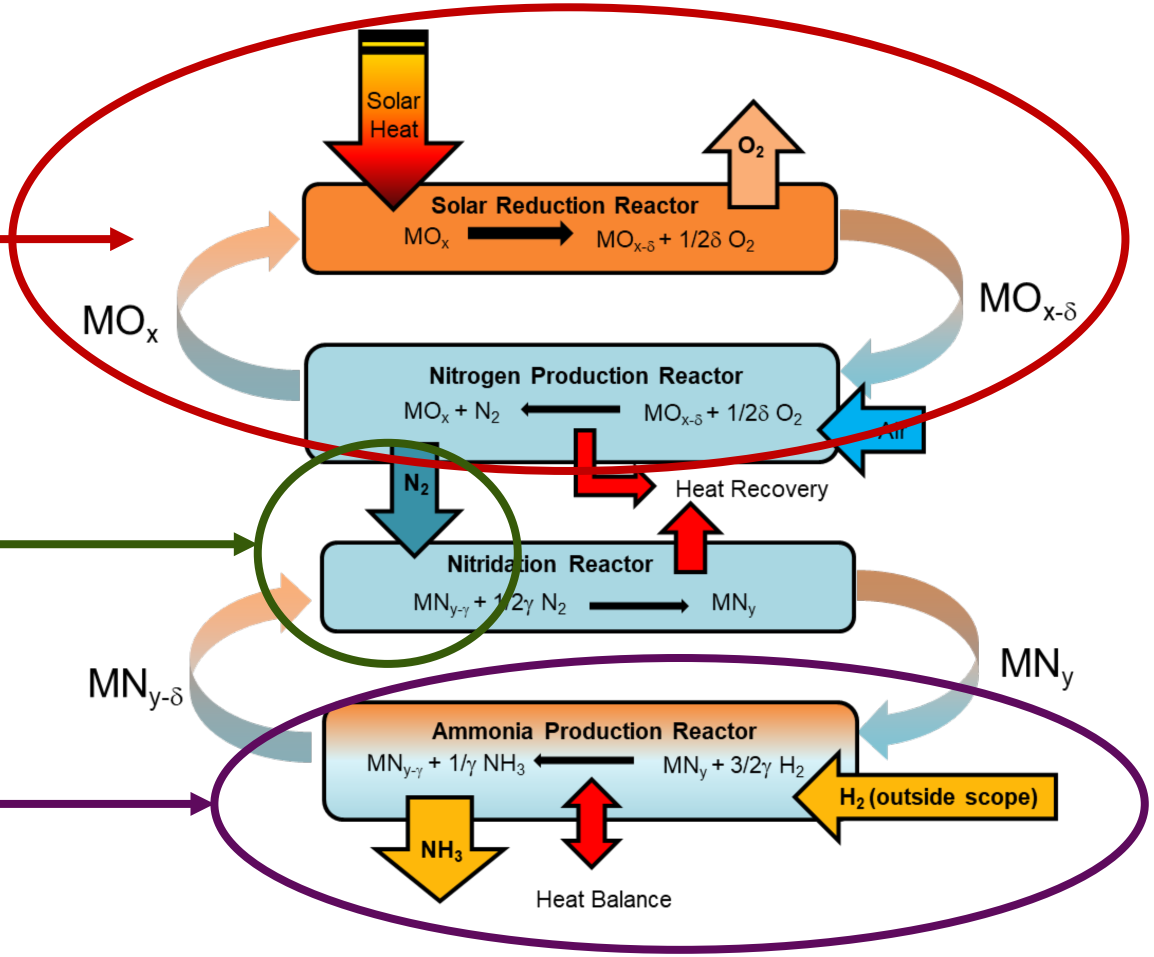


PROMOTES: High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage

Intermittency (cont'd)

To maximize productivity, a plant must be able to operate 24/7

- Process can be decoupled:
  - High temperature cycle, e.g., air separation, can be performed on-sun
  - Resulting N_2 can be stored as compressed gas or chemically, as the nitride (MN_y)
  - Ammonolysis can be run off-sun or evening utilizing recuperated or stored heat
- Similar decoupling can apply to other chemical processes



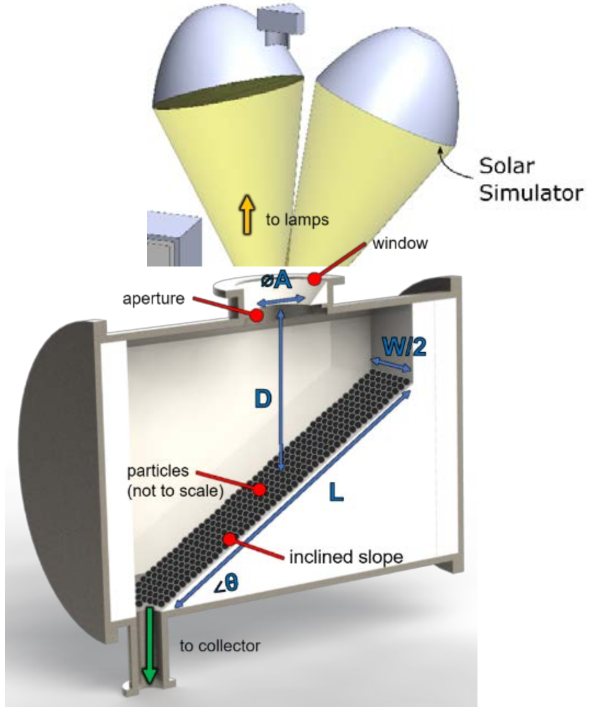
New vs. Existing Plants

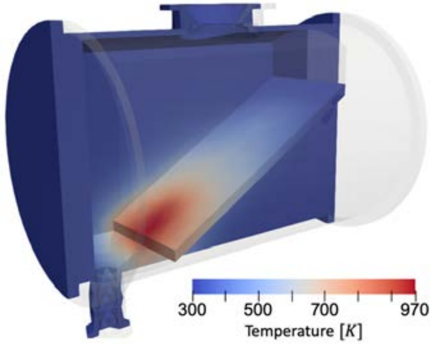
- Co-locate CSP plant with existing Haber-Bosch infrastructure
  - Hybrid model: CSP replaces methane reforming to synthesize H_2 for H-B process via thermochemical water splitting
  - Retains H-B infrastructure; no need to build new plant or transportation lines
  - Not completely green
  - Can be a bridge to fully green process
  - Also an option (or necessity) for processes such as steel production, ore refining, food processing
- Construct new plant for renewable NH_3 synthesis utilizing alternative process, e.g. STAP
  - Large up-front CapEx
  - Complete decarbonization of process – both environmentally sound and fiscally beneficial in case of carbon tax
  - Potential savings in long run due to less expensive, cyclable materials, lower temperatures and pressures
  - Consider smaller, distributed plants

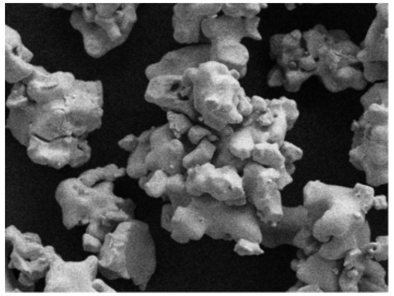
Receiver/Reactors

Design and scale of receiver/reactor must be assessed early in the process

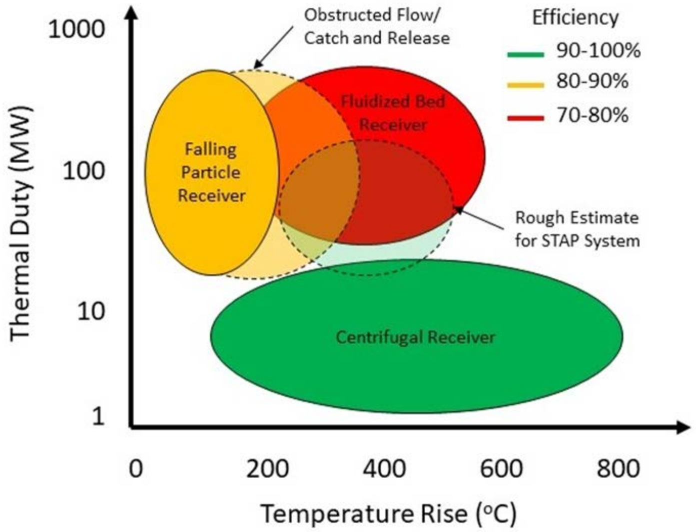
- Many considerations:
  - Direct or indirect irradiation?
  - Temperature requirements?
  - Size?
  - Window or windowless receiver?
  - Particle or monolith working material?
  - Batch or moving particle reactor?
  - Sweep gas or pumping?
- Requires combination of experiment and modeling
  - Decisions will be informed by properties of reactive material
    - In the case of STAP, oxide and nitride particles
  - Heat and mass transfer modeling, supported by experimental data, will inform scale and design



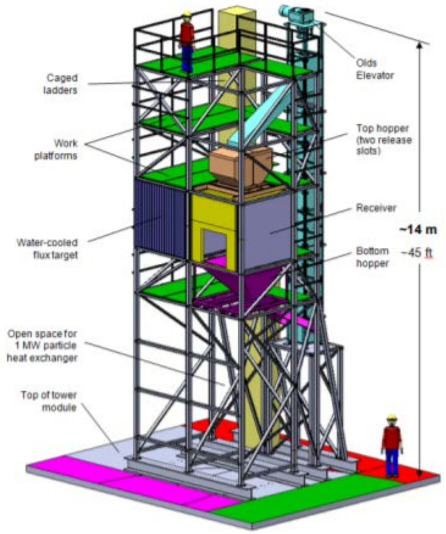


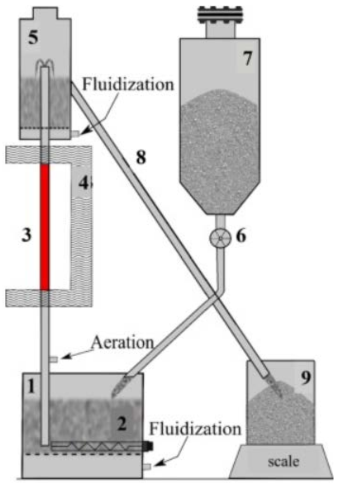


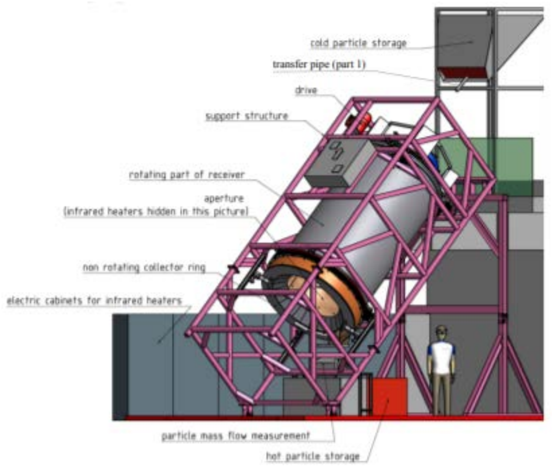
Receiver Designs



From material implications and system modeling, best estimate for receiver conditions is a temperature rise of 200-500 °C and scale <100 MW



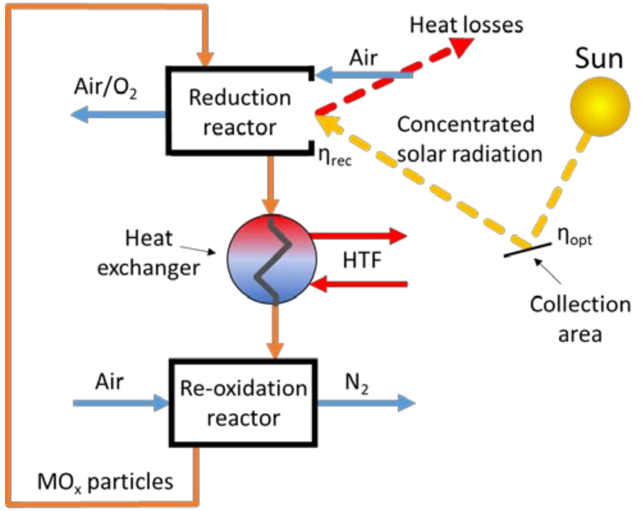




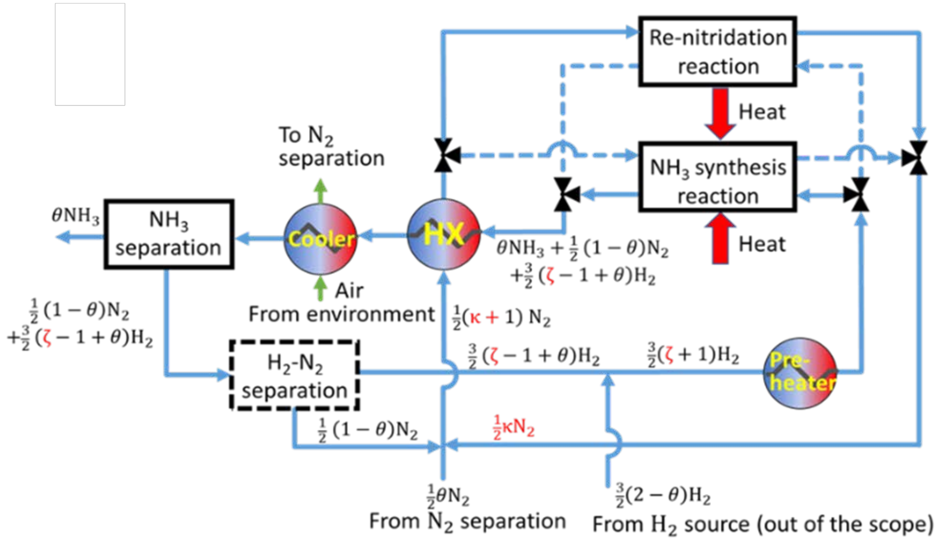
	Falling Particle Receiver (SNL)	Fluidized Bed Receiver (PROMES-CNRS)	Centrifugal Receiver (DLR)
Advantages	• Direct irradiance can lead to high efficiency • No high-cost nickel materials • Demonstrated at 1MW scale with significant operational experience	• Direct control over residence time and temperature rise • Possible to control oxygen partial pressure with enclosed tubed • Particle loss can be controlled	• Direct irradiance leads to high efficiency • Direct control over residence time and temperature rise • Particle loss can be controlled • Low particle velocity and nod angle minimizes advective loss
Disadvantages	• Advective loss is sensitivity to particle and wind velocity • Particle loss is an economic concern • Requires face-down configuration at 100 MW scale (taller tower) • Difficult to achieve curtain opacity with high temperature rise	• Tube bundles have flux limitations, which reduces efficiency • Fluidization gas is an energy parasitic • Limited experience with scaling or multi tube receivers	• Commercial scale size limits (~10 MW) • Requires multiple apertures for surround field

Techno-economics and Systems Analyses

- To attract industry and investment, it's essential to model systems and techno-economics from the beginning of a project
- Continuously refine model as data is collected
- Techno-economic considerations:
  - CAPEX (infrastructure, construction costs, raw materials, labor…)
  - Capacity
  - Energy inputs/outputs
  - O&M
  - Lifecycle
  - Return on investment
- Systems analysis:
  - Solar input
  - Balance of plant
  - Scale
  - Operating conditions
  - Efficiency
  - *Are there any show-stoppers?*



System description of air separation cycle



System description of ammonia synthesis cycle

Acknowledgements

Sandia National Laboratories — Kevin Albrecht, H. Evan Bush, Matthew W. Kury

ASU LightWorks, Arizona State University — Ellen B. Stechel, James E. Miller, Ivan Ermanoski, Xiang Michael Gao, Alberto de la Calle

Georgia Tech Solar Fuels and Technology Lab — Peter Loutzenhiser, Nhu “Ty” Nguyen, Tyler Farr

Solar Energy Technologies Office, U.S. Department Of Energy — Dr. Levi Irwin (DOE Project Manager)

U.S. Department of Energy — This work is supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office (SETO) Award Number DE-EE0034250.

THANK YOU FOR YOUR ATTENTION