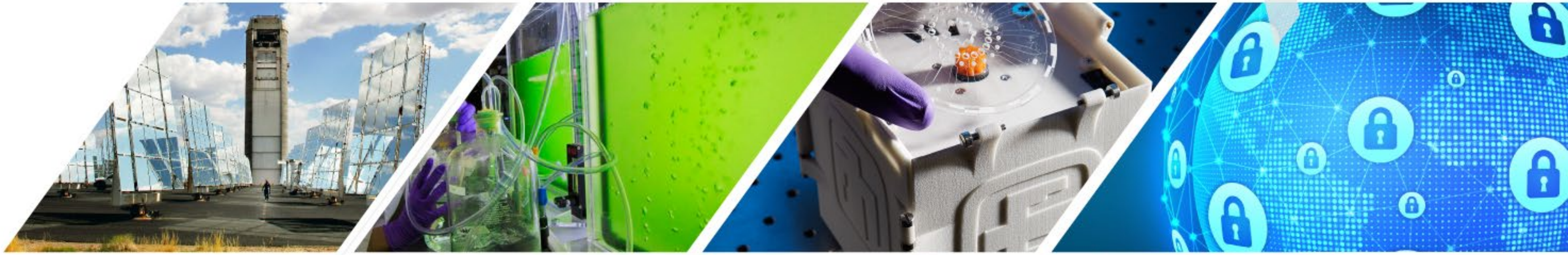

Energy & Homeland Security

Particle-Based Solar Thermochemical Applications for Decarbonization

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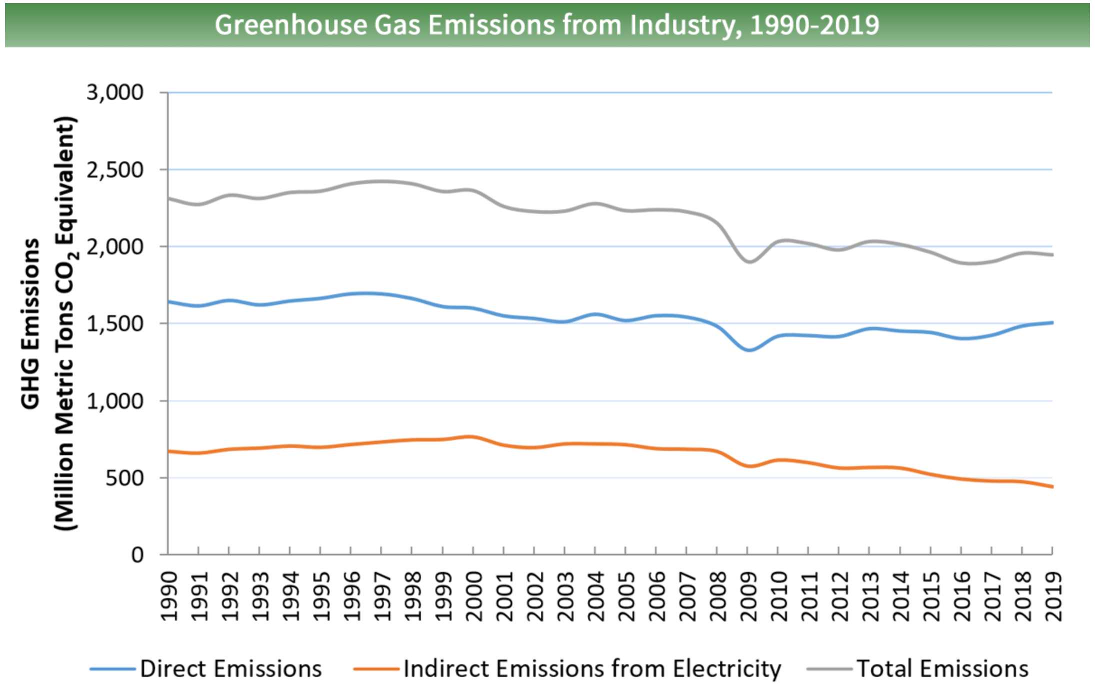
PROBLEM STATEMENT

Total US GHG Emissions in 2019 = 6,558 Million Metric Tons of CO_2 equivalent

- Greenhouse gas emissions from industry primarily come from burning fossil fuels for energy, as well as greenhouse gas emissions from certain chemical reactions necessary to produce goods from raw materials.
- Direct and Indirect Emissions
    - Direct emissions: produced on-site by burning fuel for power or heat, through chemical reactions, and from leaks from industrial processes or equipment
        - Largest source: Consumption of fossil fuels for energy
    - Indirect emissions: produced off-site by burning fossil fuel at a power plant to make electricity, which is then used by an industrial facility to power industrial buildings and machinery



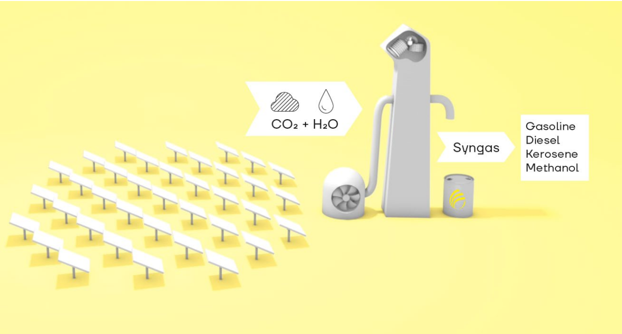
U.S. Environmental Protection Agency (2021). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2019

https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

Concentrating solar can address decarbonization from both direct and indirect sources

- Industrial processes such as steel or cement manufacture, ore refining, fuel or chemical production, and food products
- Can provide both heat and electricity for processing
- Ability to achieve high temperatures
- Potential for storage of both heat and energy over varying time scales


Steel production



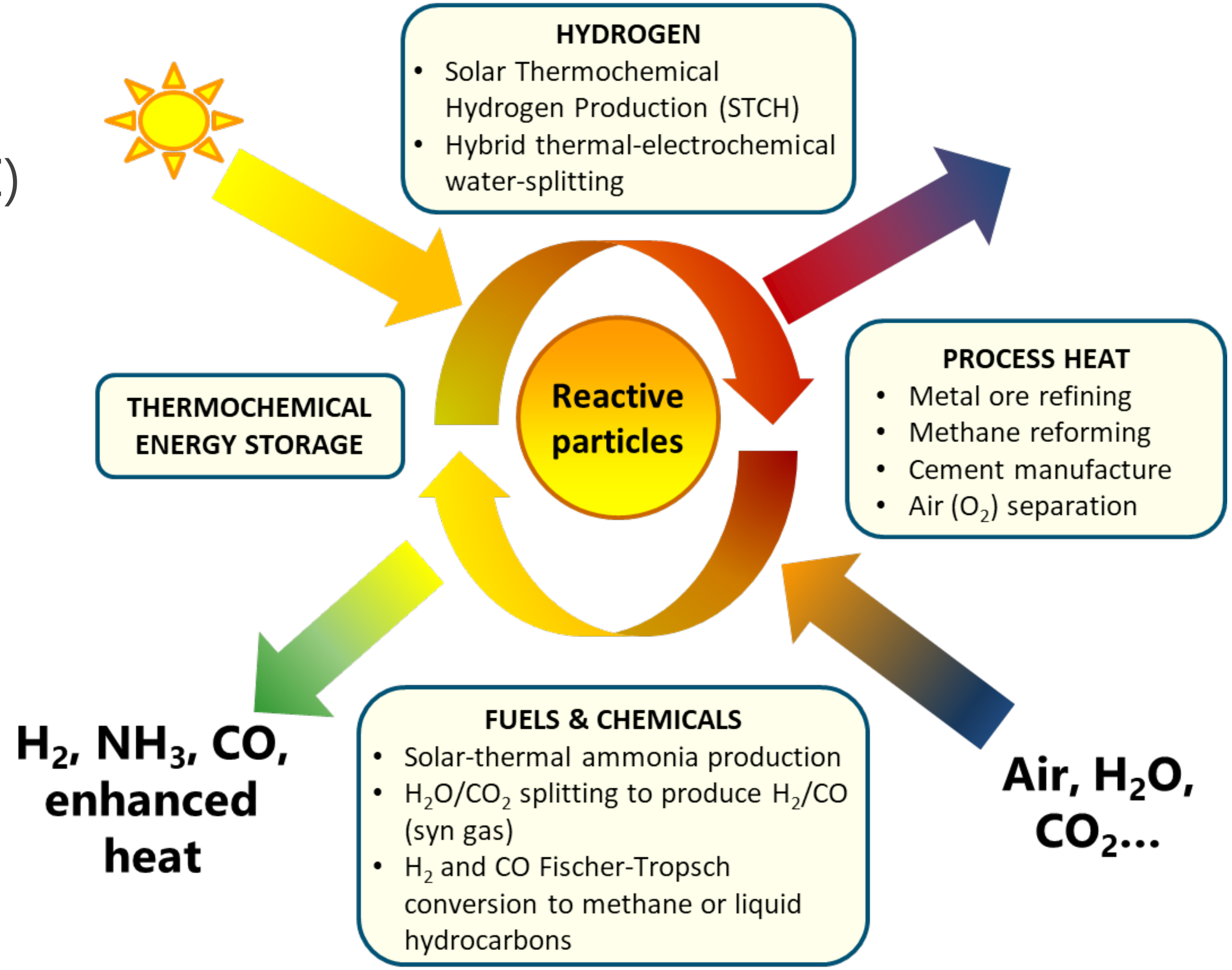
Solar fuels (Synhelion.com)

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

SOLAR THERMOCHEMISTRY (STC)

Solar thermochemistry harnesses concentrated solar heat to drive chemical reactions that would normally be energy- or resource-intensive

- High temperature applications (600-1500 °C)
- Synergistic with CSP particle technology
- Chemical and sensible heat storage
- Many technologies still low TRL
- Must increase efficiency and decrease costs to make technology more competitive



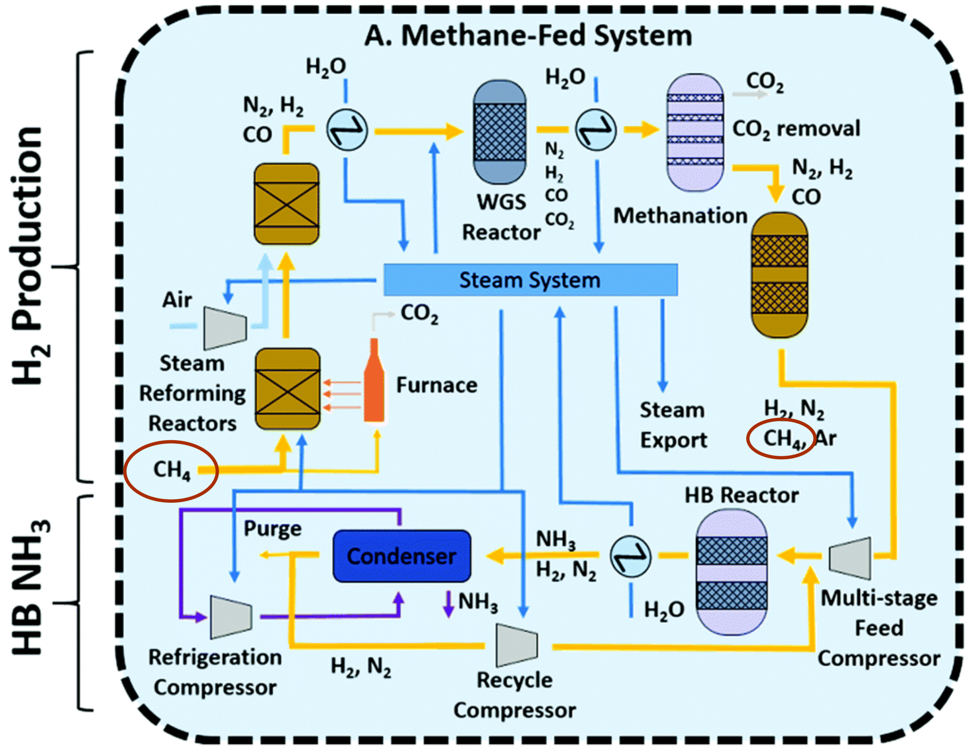
SYSTEM CHALLENGES AND CONSIDERATIONS

In order to de-risk and advance STC technology, one must consider many moving parts

- Materials: Identify, synthesize, characterize novel working materials for STC processes
- Reactor/Receivers: On-sun receiver/reactor designs for STC are more complex
  - High temperatures may necessitate exotic building materials
  - STC processes may require increased residence times on-sun to achieve desired temperature
  - Potential need for inert atmospheres or vacuum pumping
  - Gas separations
- Intermittency: How to enable 24/7 operation?
- Techno-economics: Provide a pathway to scale-up and integration

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 ^{0}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

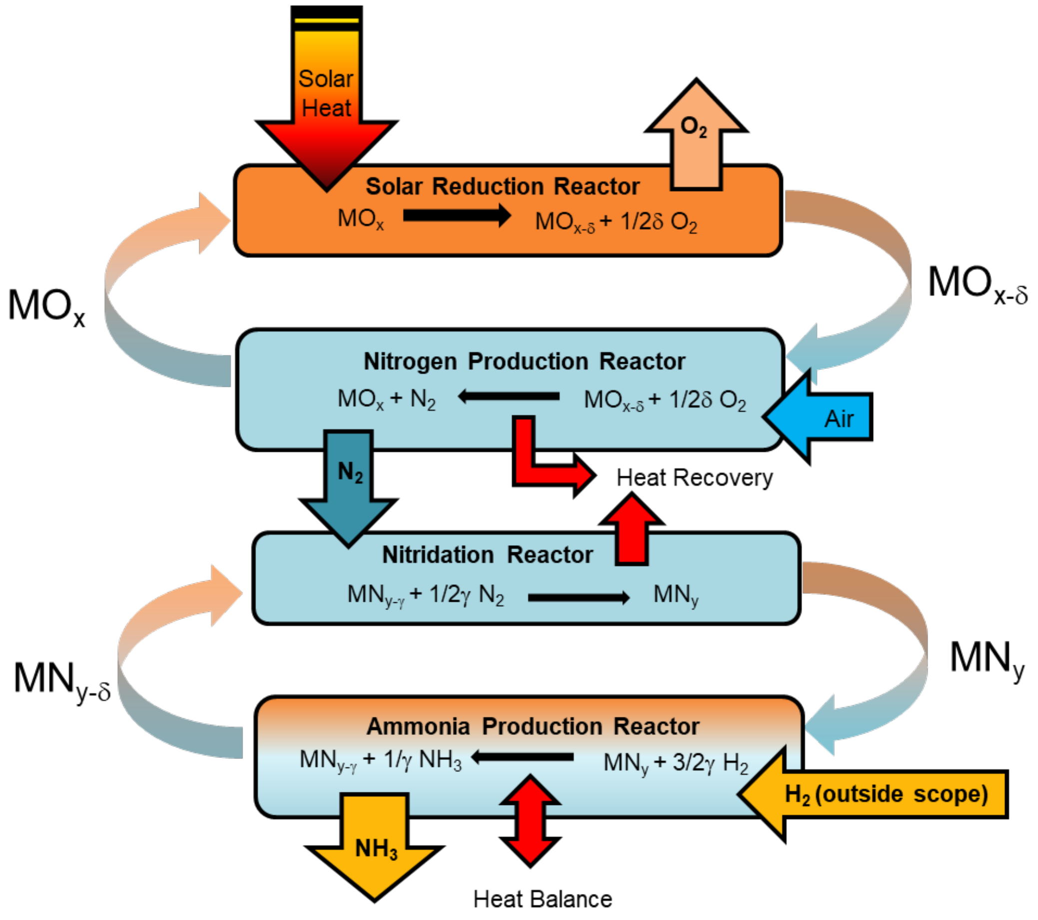


Schematic diagram of a typical conventional methane-fed Haber Bosch process (*Energy Environ. Sci.*, 2020,13, 331-344.)

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)

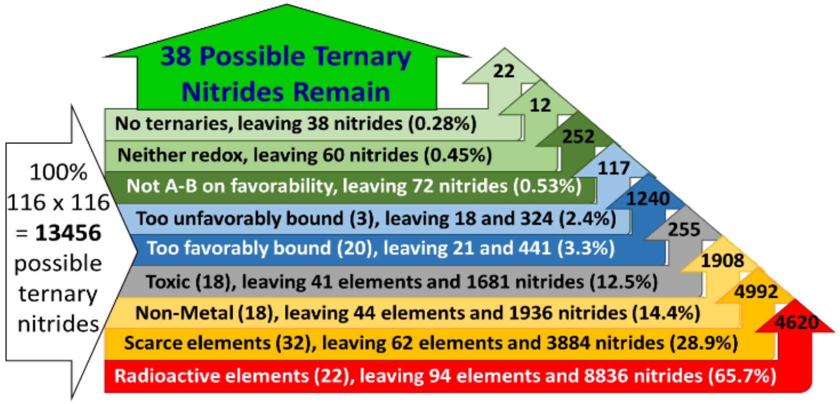


- Two cycles
  - N_2 separation from air using redox-active metal oxides (on-sun, moving particles)
  - Production of NH_3 from produced N_2 and green H_2 using metal nitrides (off-sun, batch)
- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- The process consumes neither the oxide nor the nitride particles, which are cyclable
- Low TRL: How do we develop and de-risk? What are key challenges?

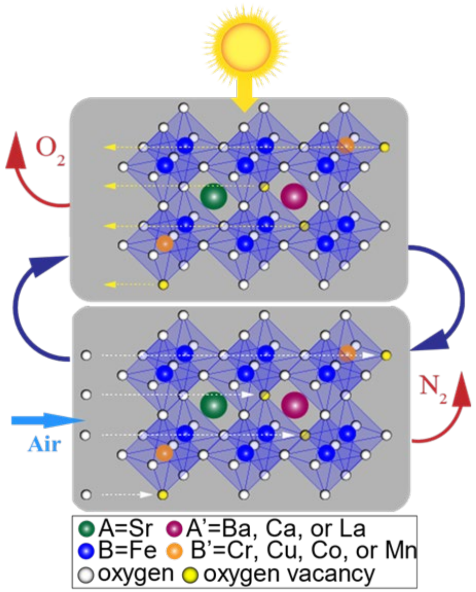
KEY CHALLENGES: MATERIALS

Materials choice influences every aspect of STAP system design

- Materials discovery and synthesis
  - Selection and synthesis of working materials
  - Nitride compounds less common than oxide materials
    - Smaller pool of reported materials
    - More difficult to synthesize
- Materials must be carefully and comprehensively characterized
  - 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
  - Cost/Availability: avoid critical elements
  - Ease of synthesis and scale-up



Down-select of nitride candidates

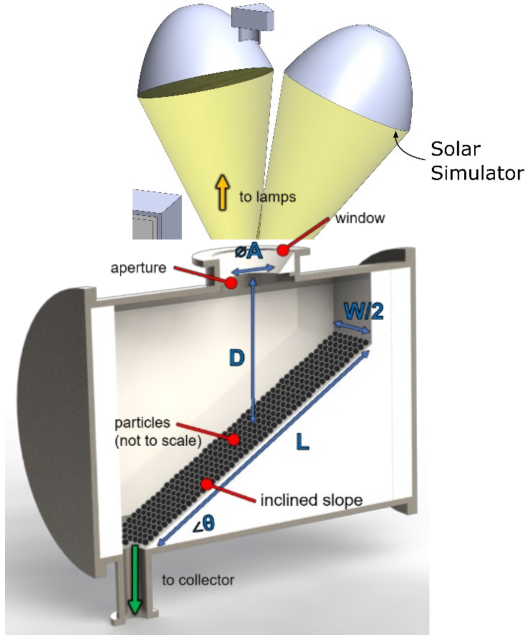


Metal oxide for air separation

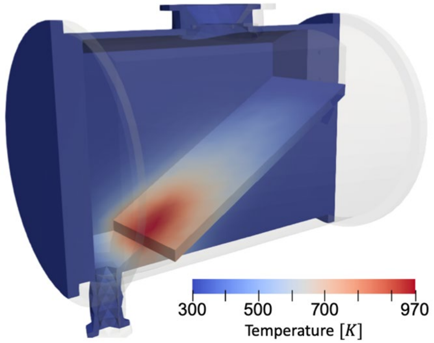
KEY CHALLENGES: RECEIVER/REACTORS

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

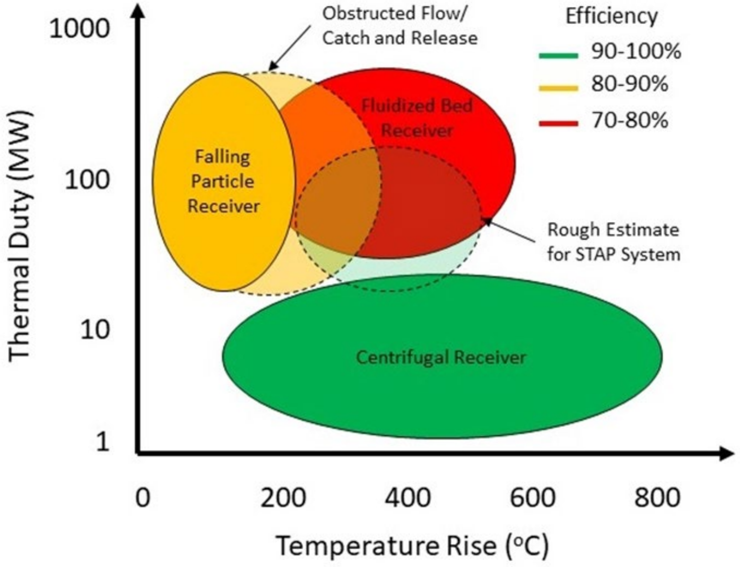
- Requires combination of experiment and modeling
  - Decisions informed by properties of reactive materials (oxide and nitride particles)
  - Heat and mass transfer modeling, supported by experimental data, inform scale and design
- Key considerations (for STAP metal oxide reduction step):
  - Direct or indirect irradiation? Direct
  - Temperature requirements? T_{red} ~ 800 °C
  - Window or windowless receiver? Windowless
  - Batch or moving particle reactor? Moving particle
  - Sweep gas or pumping? Neither



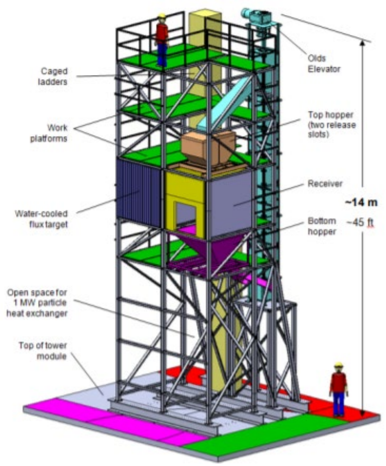
Benchtop reduction reactor design

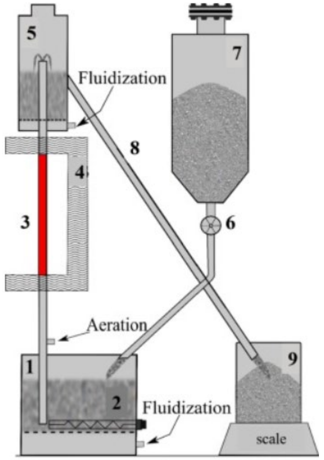


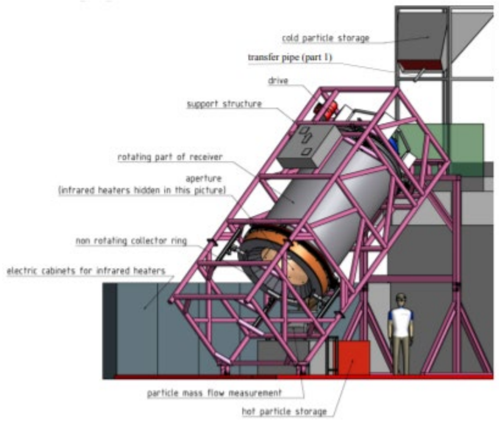
POTENTIAL MOVING PARTICLE RECEIVER DESIGNS



- Estimated $T_{receiver}$ ≤ 800 °C and $\Delta T_{receiver}$ = 200 – 500°C, based on:
  - Materials implications
  - System modeling
- Two possible options among existing technologies:
  - Expand falling particle receiver envelope
  - Target smaller systems with centrifugal receiver







	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

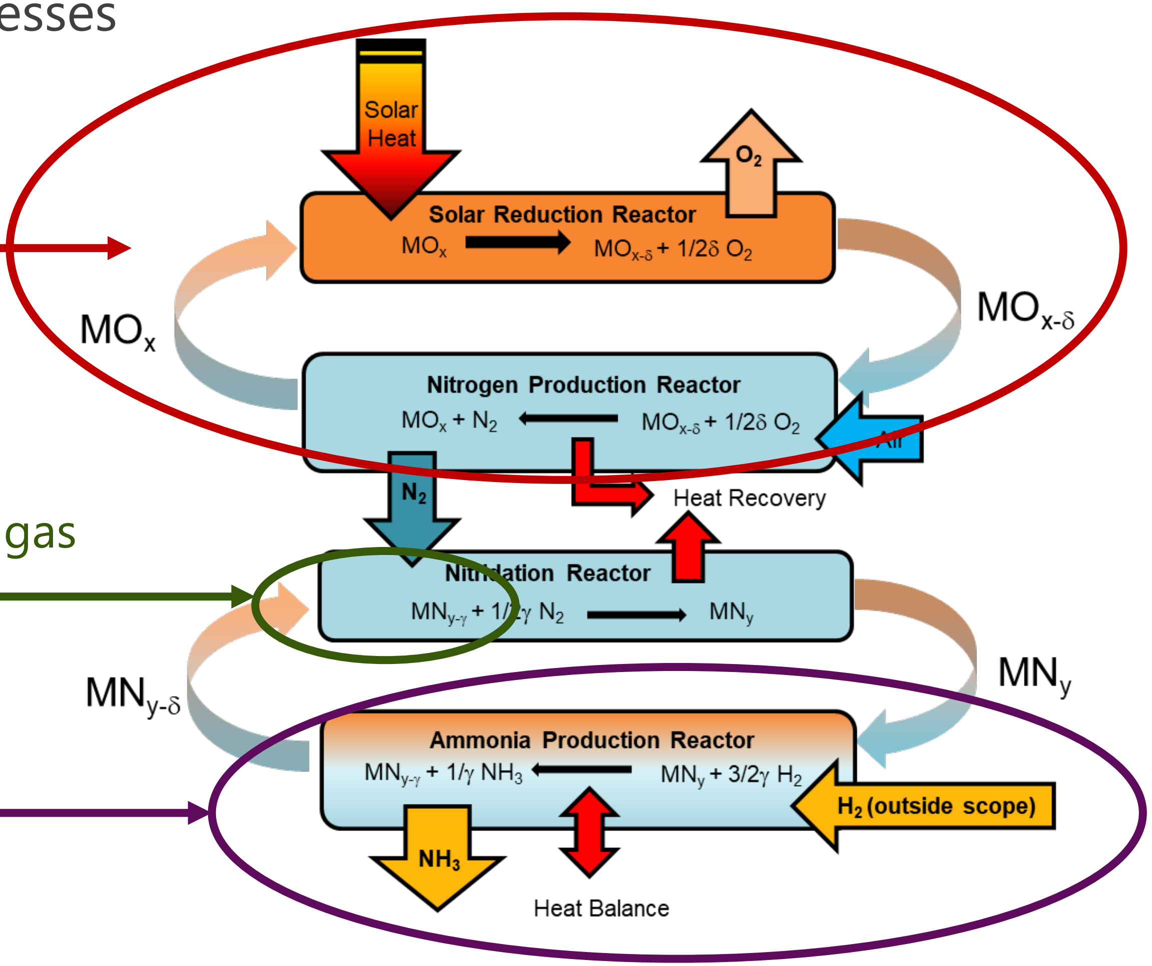
To maximize productivity, a plant must be able to operate 24/7

- STAP process can be decoupled
- Similar decoupling can apply to other chemical processes

High temperature air separation cycle can be performed on-sun

Resulting N_2 can be stored as compressed gas or chemically, as the nitride (MN_y)

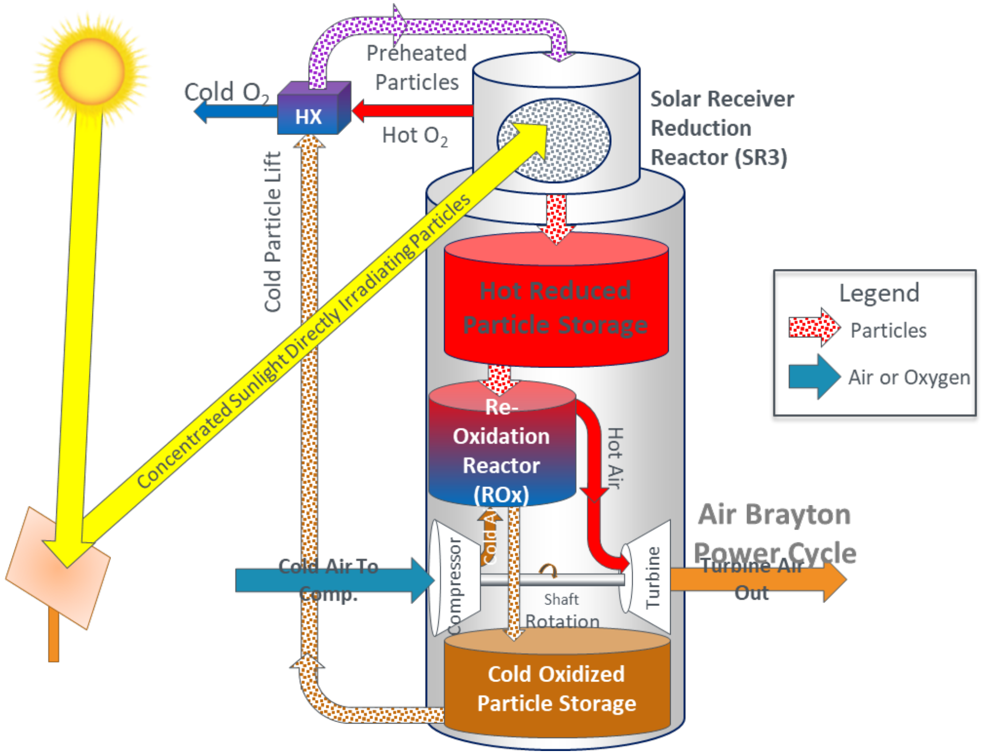
Ammonolysis can be run off-sun or evening utilizing recuperated or stored heat



KEY CHALLENGES: STORAGE

Thermochemical Energy Storage (TCES) can store high temperature, high quality heat

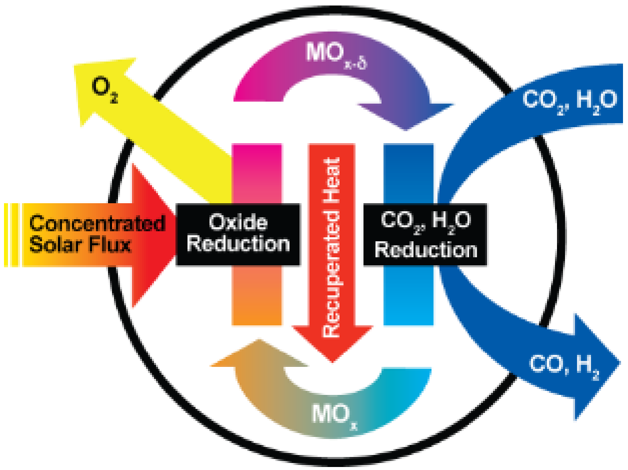
- A feature of CSP is the ability to store heat for off-sun operation or electricity generation
  - Particles are generally easier to store– they are dense, do not require compression, noncorrosive, stable at T > 1100 °C, and are amenable to multiple scales
  - Thermochemical materials have added benefit 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 long-term chemical storage material, as well as a feedstock for chemical processes, e.g., ammonia production



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

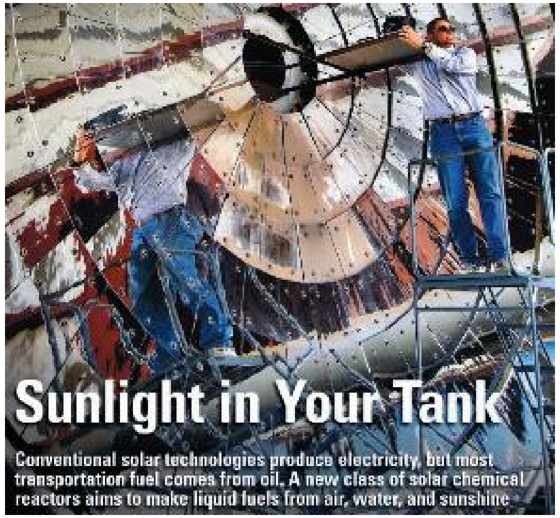
KEY CHALLENGES: STC PRODUCTION OF HYDROGEN

A green, renewable source of hydrogen is essential for decarbonizing ammonia production



Thermochemical metal oxide cycle

Ceria falling particle reactor



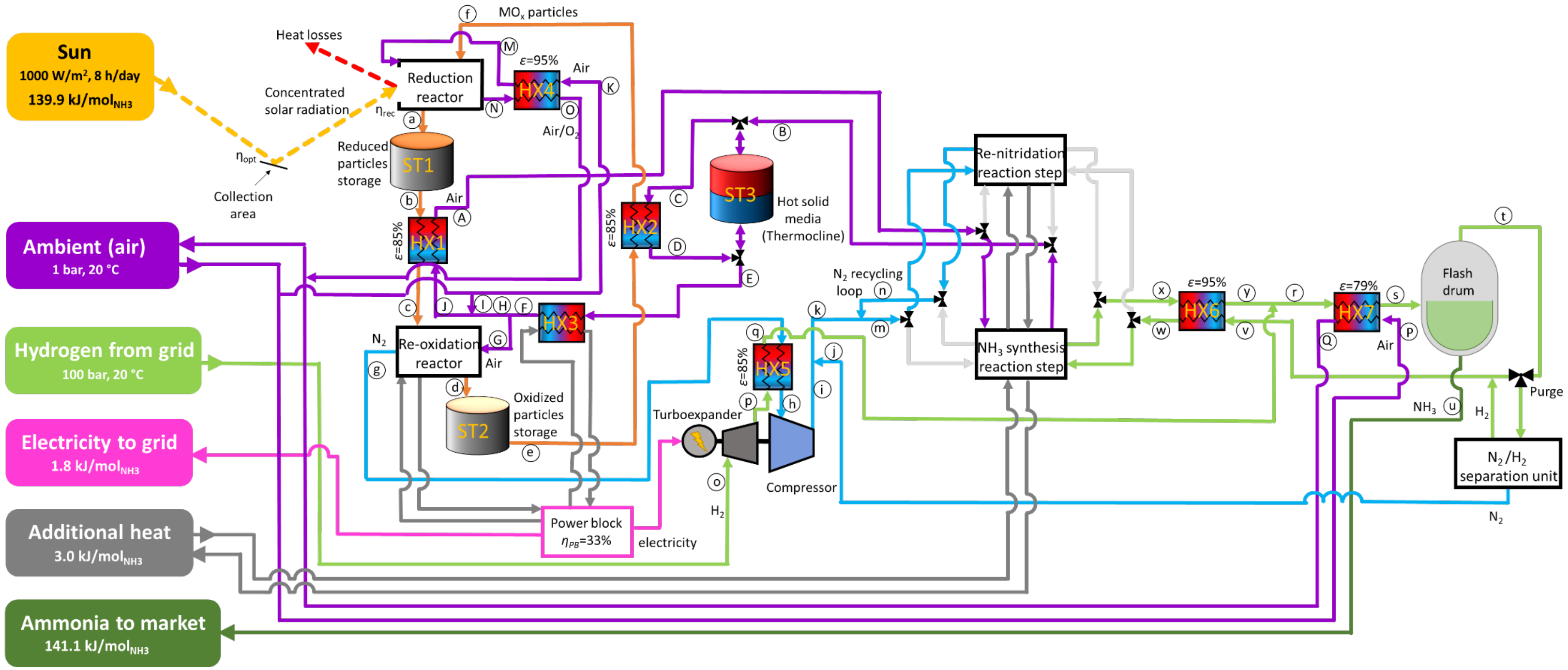
"Sunshine to Petrol"

- Solar thermochemical water splitting via utilization of metal oxide particles to produce H_2
  - One of several paths to water splitting (electrolysis, hybrid technologies)
- H_2 can also be used as a medium for long-term energy storage, fuel, and reducing agent for other chemical processes, e.g., in steel production
- Many similar challenges as other STC processes

TECHNO-ECONOMICS AND SYSTEMS ANALYSES

Materials, reactors, systems performance, and techno-economics must all balance. The best element in isolation not necessarily the best for the system.

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



CONCLUSIONS AND CHALLENGES

- Concentrating solar has the potential to decarbonize industry by addressing both direct and indirect GHG emissions
- Solar-thermal chemistry (STC) can utilize high temperatures from concentrating solar resources and leverage particle technology to effect chemical reactions that would normally be carbon-intensive
- The example of solar thermal ammonia production illustrates the considerations and challenges facing commercialization, including:
  - Materials
  - Reactors
  - Receivers
  - Storage Intermittency
  - Scale-up
  - Cost/efficiencies
  - Technoeconomic and systems analysis
- Other STC processes face similar challenges

Overcoming these challenges will help meet the goal to "deliver an equitable, clean energy future, and put the United States on a path to achieve net-zero emissions, economy-wide, by no later than 2050."

(Executive Order 14008, "Tackling the Climate Crisis at Home and Abroad," January 27, 2021.)

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