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Technoeconomic Analysis of a Solar Thermochemical Fuel Production Process using a Packed-Bed Redox Reactor

Alon Lidor, Zachary Hart, Janna Martinek
National Renewable Energy Laboratory

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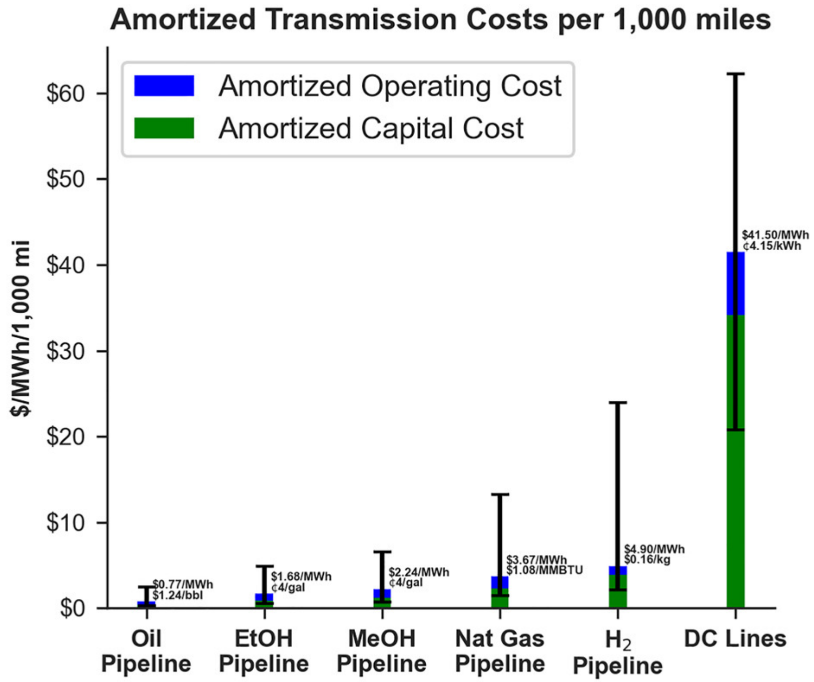
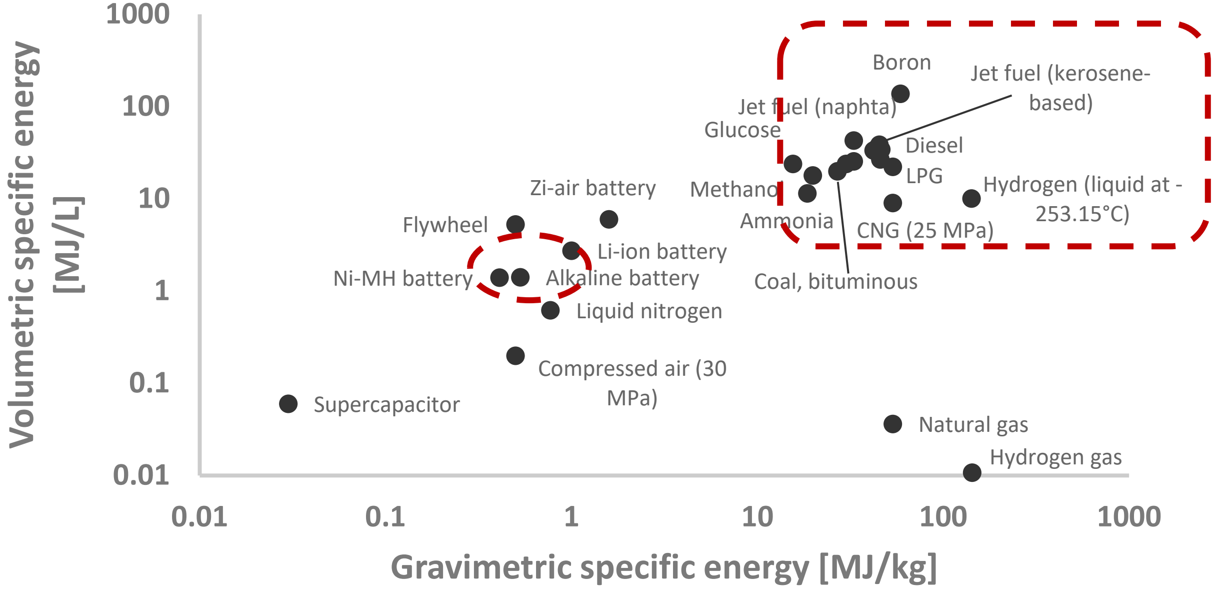
Background

- Liquid fuels are critical in many sectors due to high specific energy ($12 - 13\,\frac{\mathrm{kWh}}{\mathrm{kg}}$, $9 - 11\,\frac{\mathrm{kWh}}{\mathrm{L}}$), ease of storage/transport, wide infrastructure, and ability to produce high-temperature heat





D. DeSantis, B. D. James, C. Houchins, G. Saur, and M. Lyubovsky, “Cost of long-distance energy transmission by different carriers,” *iScience*, vol. 24, no. 12, p. 103495, Dec. 2021, doi: 10.1016/j.isci.2021.103495.

Background

- Liquid fuels are critical in many sectors due to high specific energy ($12-13\,\frac{\mathrm{kWh}}{\mathrm{kg}}$, $9-11\,\frac{\mathrm{kWh}}{\mathrm{L}}$), ease of storage/transport, wide infrastructure, and ability to produce high-temperature heat
- Thermochemical fuel production via the 2-step redox cycle using CO_2 and H_2O as the feedstock can produce sustainable syngas:

Reduction: $\frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{ox}}} \rightarrow \frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{O}_2$ $(T > 1500^{\circ}\mathrm{C}$, $\Delta_{\mathrm{r}}H_{\mathrm{red}} > \max(\Delta_{\mathrm{r}}H_{\mathrm{WT}}, \Delta_{\mathrm{r}}H_{\mathrm{CDT}})$, low $p_{\mathrm{O}_2})$

Oxidation: $\frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{CO}_2 \rightarrow \frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{ox}}} + \mathrm{CO}$ $(T < 1000^{\circ}\mathrm{C}$, $\Delta_{\mathrm{r}}H_{\mathrm{ox}} = \Delta_{\mathrm{r}}H_{\mathrm{red}} - \Delta_{\mathrm{r}}H_{\mathrm{CDT}} < 0)$

$\frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{H}_2\mathrm{O} \rightarrow \frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{ox}}} + \mathrm{H}_2$ $(T < 1000^{\circ}\mathrm{C}$, $\Delta_{\mathrm{r}}H_{\mathrm{ox}} = \Delta_{\mathrm{r}}H_{\mathrm{red}} - \Delta_{\mathrm{r}}H_{\mathrm{WT}} < 0)$

- Syngas can be converted into liquid fuels via Fischer-Tropsch or MeOH synthesis
- CST is proposed as the thermal driving force (high fluxes, high temperatures)

Definitions: δ – non-stoichiometry, $\Delta\delta = \delta_{\mathrm{red}} - \delta_{\mathrm{ox}}$ - non-stoichiometry extent

Motivation – Challenges in Solar Thermochemical Fuel Production

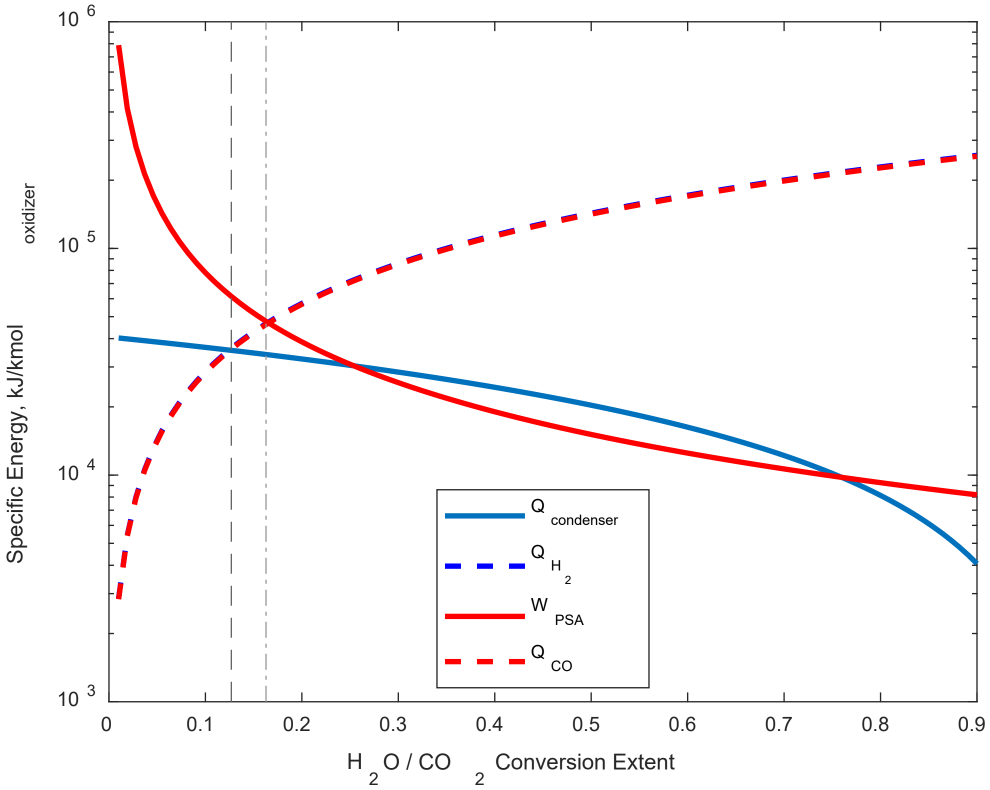
- State-of-art: $\eta_{\text{reactor}} = 4.1\%$ (co-splitting) or 5.6% (CO_2 splitting)

50 kW_{th} solar input reactor

Zoller, S., et al., "A solar tower fuel plant for the thermochemical production of kerosene from H_2O and CO_2", *Joule*, Vol. 6, pp. 1606-1616, 2022.

Motivation – Challenges in Solar Thermochemical Fuel Production

- State-of-art: $\eta_{\text{reactor}} = 4.1\%$ (co-splitting) or 5.6% (CO_2 splitting)
- Low conversion in the syngas production step – high energy penalty



Condensing at $T = 100°C, p = 1$ bar
PSA data from Capstick et al. (2023)

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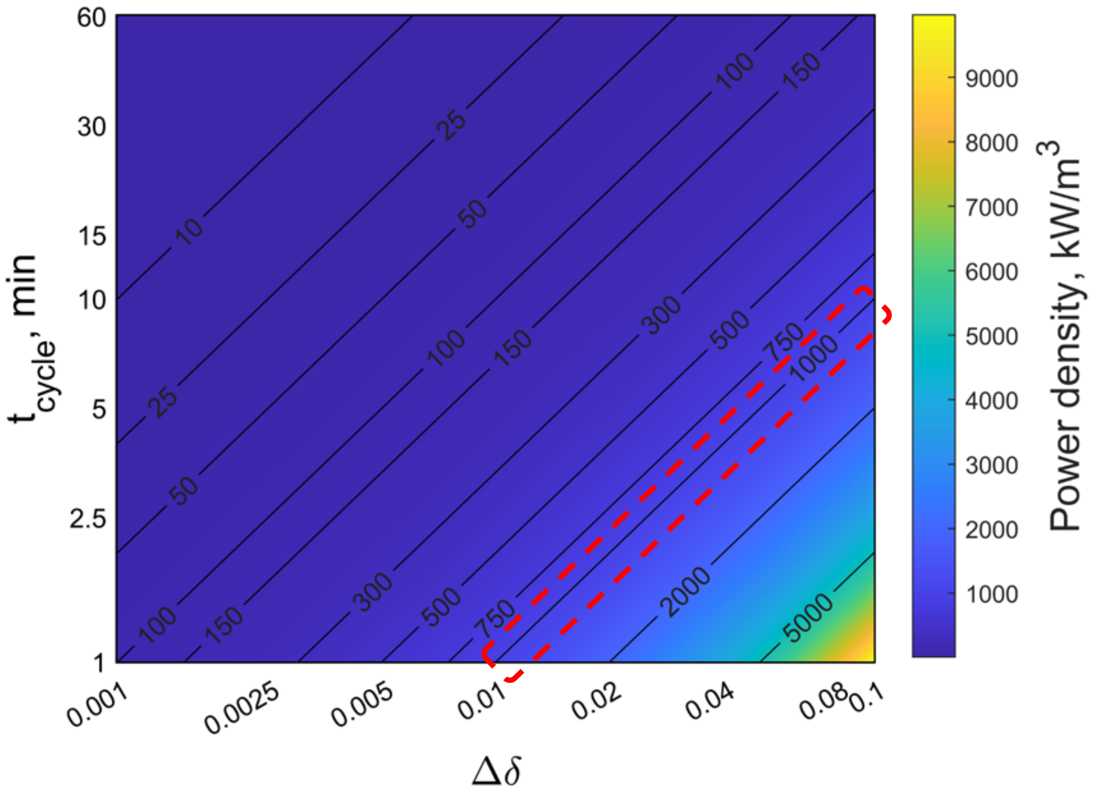

CeO$_2$, $\phi_{\mathrm{redox}} = 0.5$

From Lidor and Bulfin (2024)

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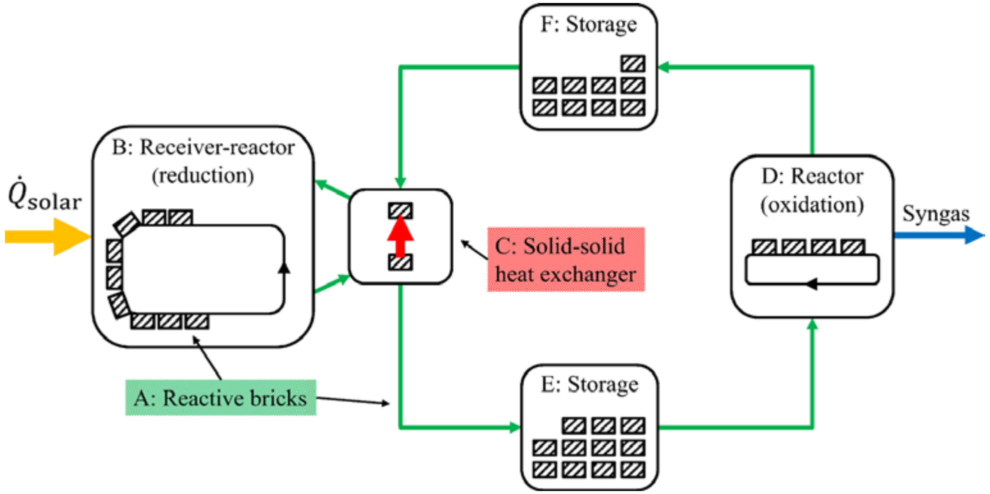
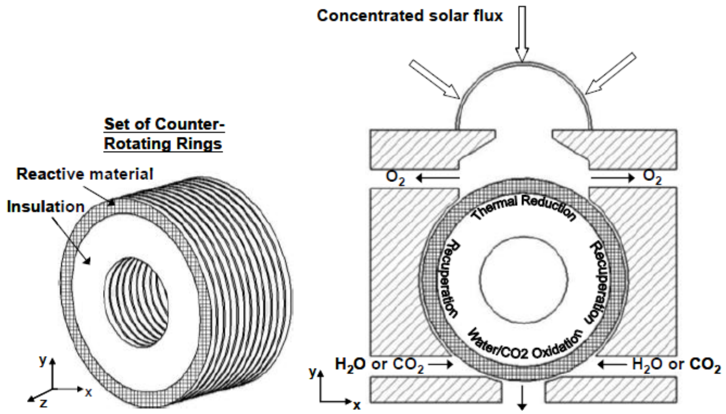


Siegrist et al., *Journal of Solar Energy Engineering*, 2019



Diver et al., *ASME 4th International Conference on Energy Sustainability,* 2010

Motivation – Challenges in Solar Thermochemical Fuel Production

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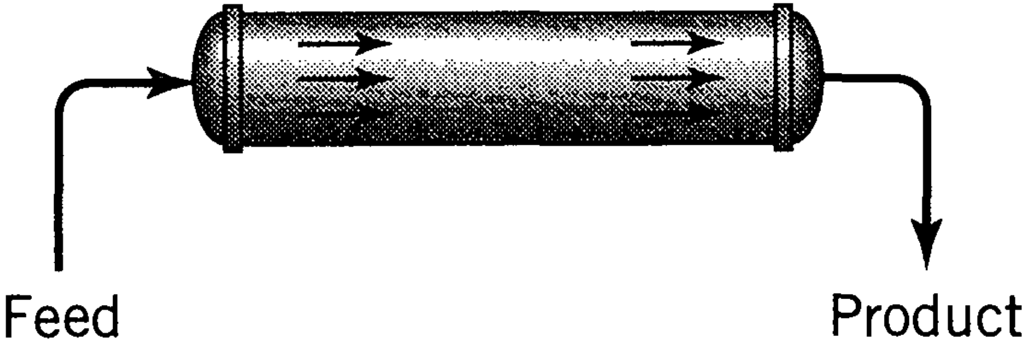
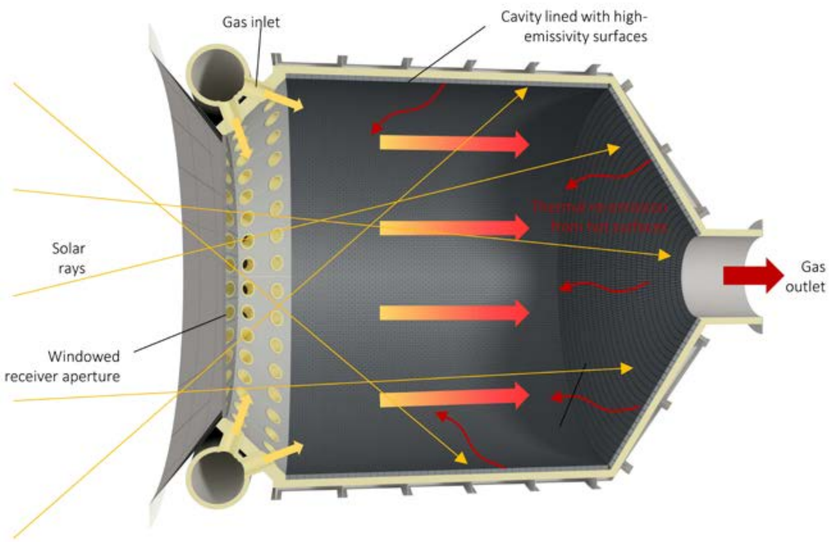
- Low conversion in the syngas production step – high energy penalty
- Low power output density → large oxide mass and reactor volume
- Challenges with moving oxide systems
- Conflicting requirements for high-T solar receivers and chemical reactors



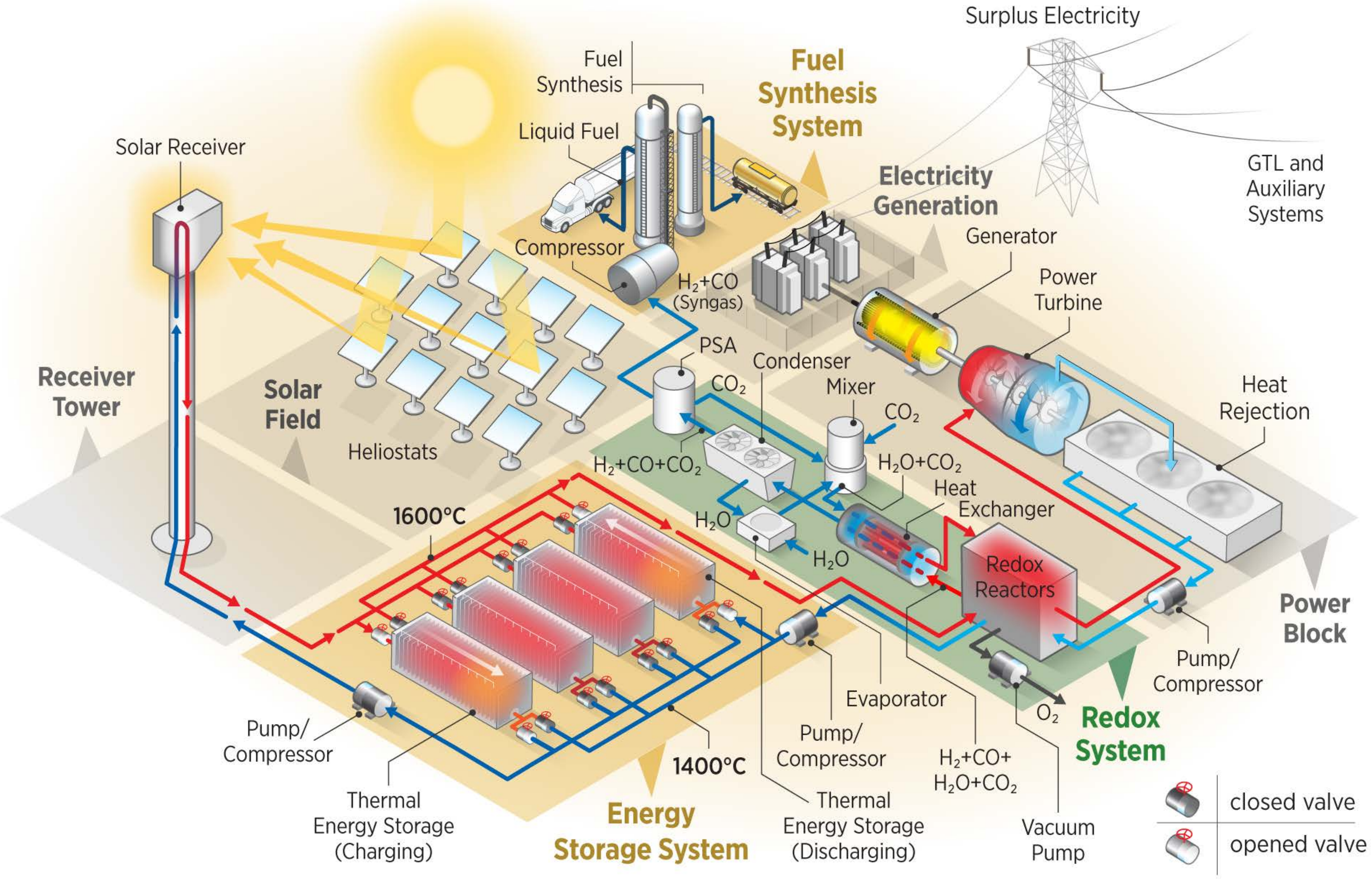
Levenspiel (1999)



Ackermann et al. (2020)

The Proposed Solar Fuel Plant Approach

- Decoupling the solar receiver and reactor
- Packed bed reactor design
- Combining CST+PV
- Adding thermal energy storage (TES)
- Separating the CO_2 and H_2O splitting reactors



Credit: NREL (Alfred Hicks)

Redox Subsystem – CO_2 splitting

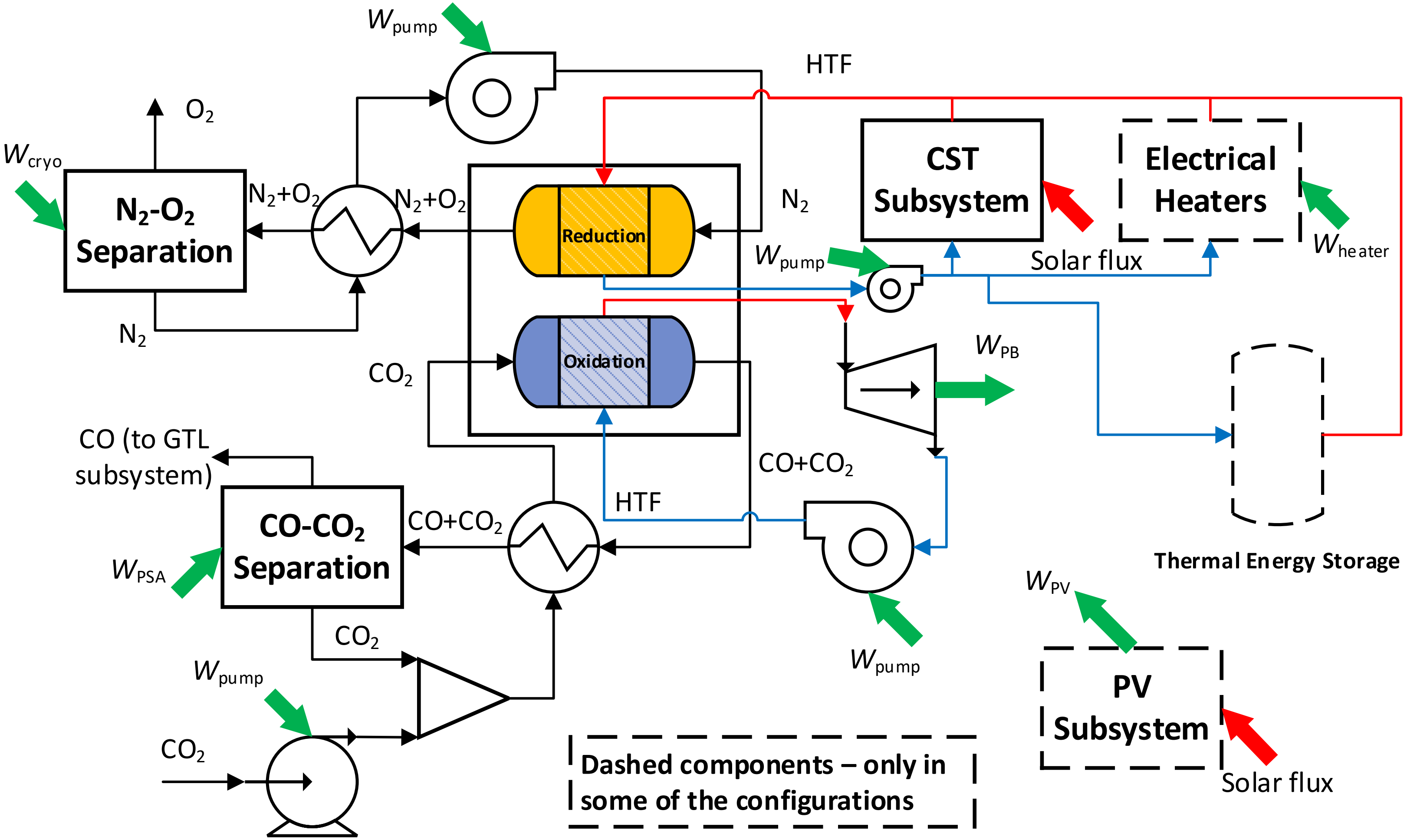
Four configurations:

1. CST
2. CST+PV
3. CST+PV+Electric Heaters
4. CST+TES

CO-CO_2 separation:

- Pressure swing adsorption (PSA)
- Membrane separation*
- Amine scrubbing*

* Not implemented yet



(for simplicity, TES charging mode not shown)

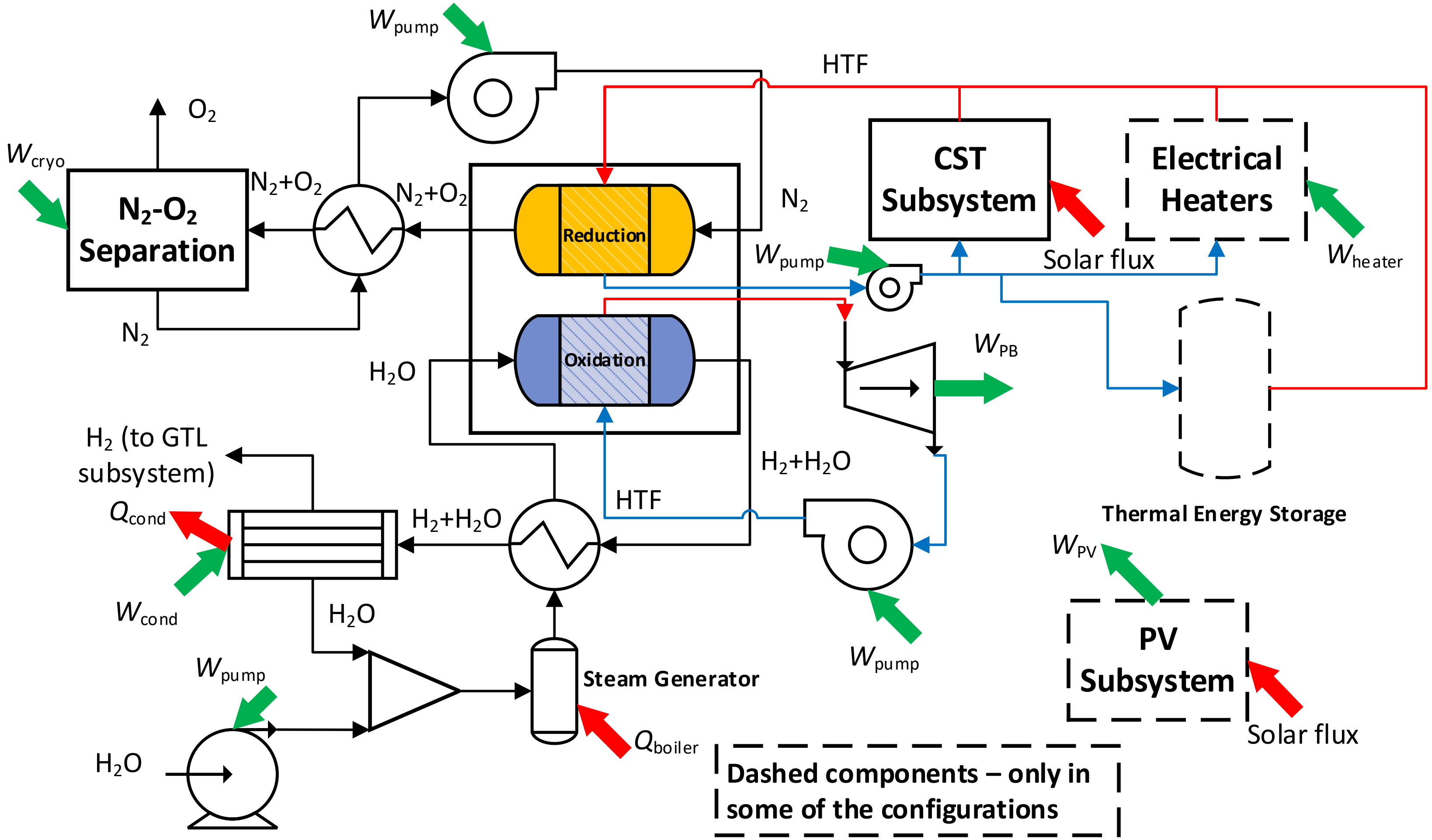
Redox Subsystem – H_2O splitting

Four configurations:

1. CST
2. CST+PV
3. CST+PV+Electric Heaters
4. CST+TES

H_2-H_2O separation:

- Condenser + boiler
- Mechanical vapor recompression*
- High-T membrane*



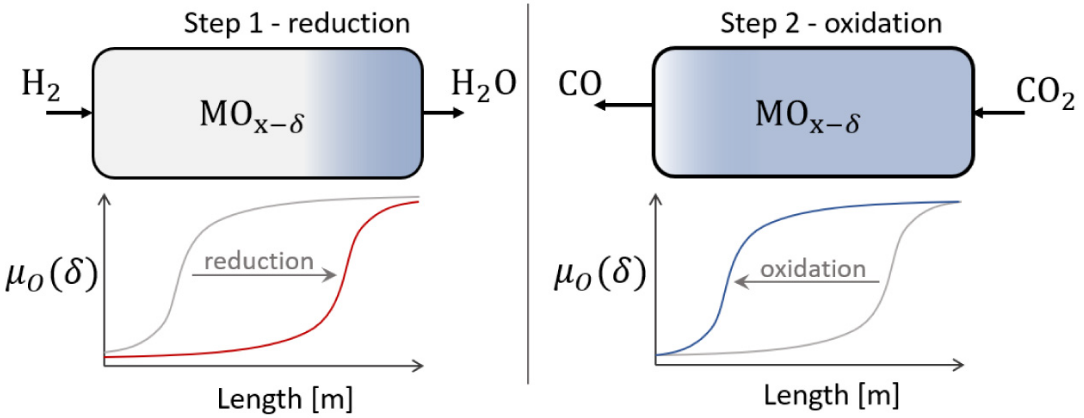
(for simplicity, TES charging mode not shown)

* Not implemented yet

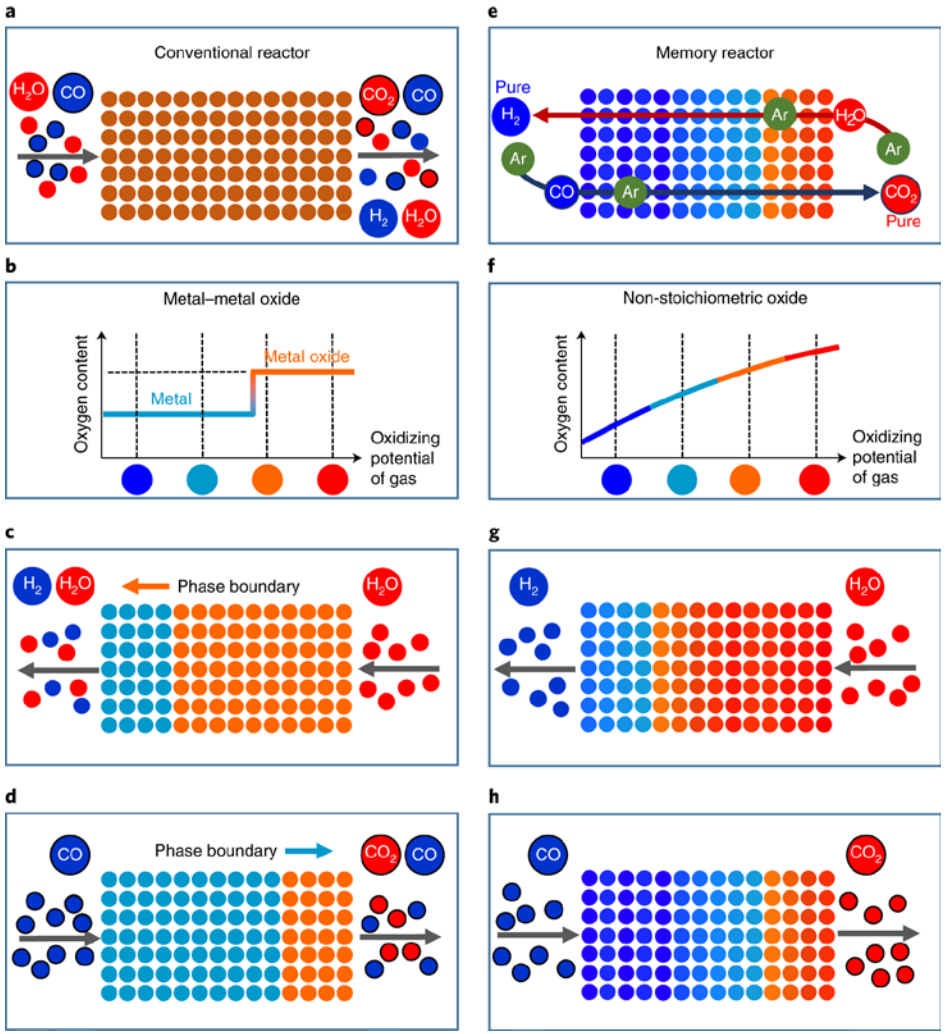
Our Approach – Countercurrent Stationary System

Indirectly-heated counter-current chemical regenerator:

- High conversion
- No moving parts (fixed bed design)
- Flexible heating method (CST, hybrid, etc.)
- Modular design



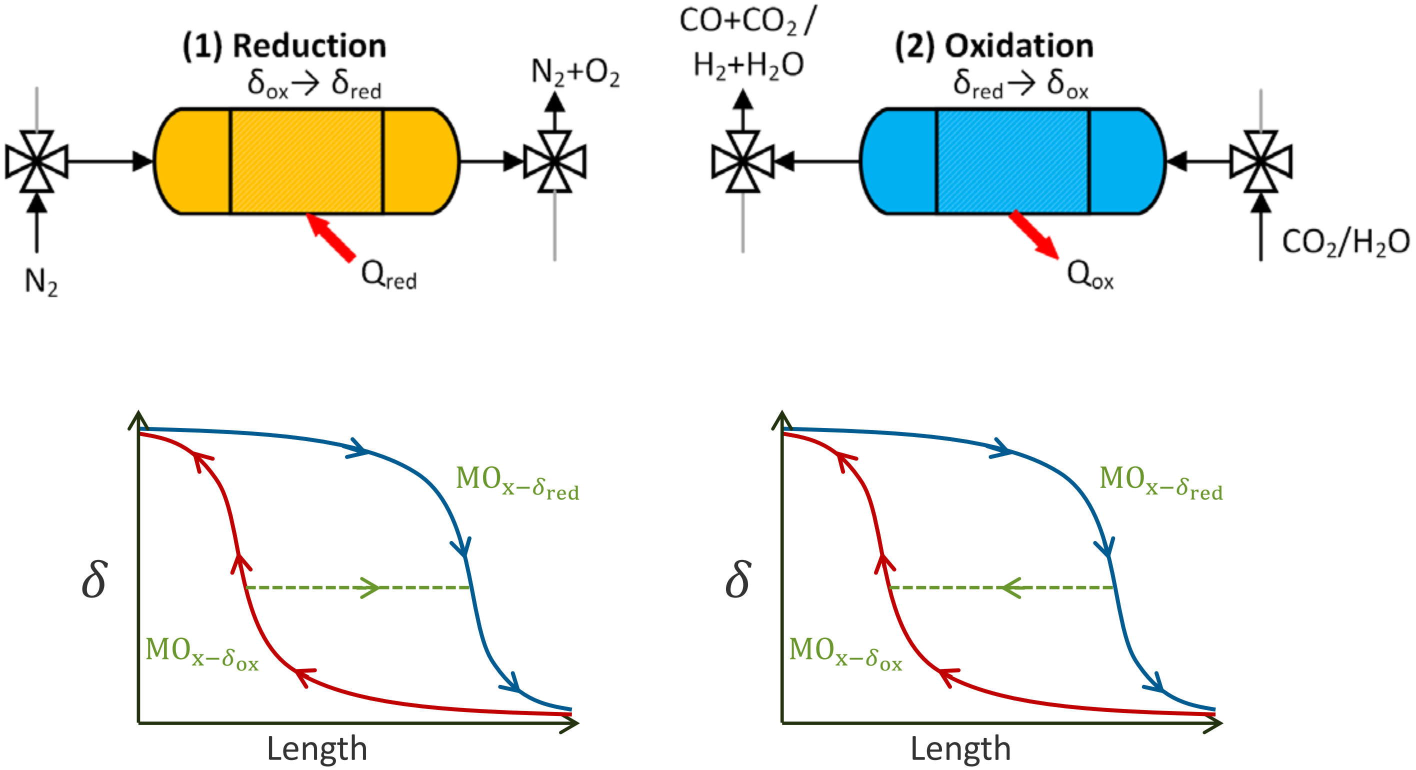
RWGS: Bulfin et al. (2023)



WGS: Metcalfe et al. (2019)

Our Approach – Countercurrent Stationary System

- Using the same countercurrent concept for thermal reduction
- Temperature-swing, sweep gas operated reactors
- Isothermal redox steps (T_{red} and T_{ox} held constant respectively)
- Splitting CO_2 and H_2O in separate reactors



Redox Reactors Model

Reactor:

- 1D convection-diffusion with multiple species (reactant, product, O_2)
- Pressure gradients calculated using the Ergun equation
- Providing the endothermic reduction heat, extracting exothermic oxidation heat
- Splitting CO_2 and H_2O in separate reactors
- Calculating number of reactors needed to obtain continuous syngas production

Auxiliary units:

- Sweep gas purification: **PSA, cryogenic separation**, thermochemical O_2 separation
- H_2-H_2O separation: **condensation**, **mechanical vapor recompression***, **electrochemical membrane separation***
- CO-CO_2 separation: membrane separation, **PSA**, scrubbing, syngas conditioning

System and TEA Model

- Four configurations: CST, CST+PV, CST+PV+Electric heaters, CST+TES
- System can operate at full or part load
- Fischer-Tropsch solved using model reaction assuming full conversion [1]
- Brayton power cycle utilizing oxidation heat for power generation
- TEA methodology based on “NETL Guidelines for Energy Systems” [2]
- CST subsystem designed with SolarPILOT [3] (assuming radiative, convective, and piping losses)
- Cost functions: solar components (CST, PV) from NREL ATB [4], chemical plant [5-7]

[1] A. de Klerk, *Fischer-Tropsch Refining*. Wiley, 2011. doi: 10.1002/9783527635603.
[2] J. Theis, “Quality Guidelines for Energy Systems Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance,” National Energy Technology Laboratory (NETL), Pittsburgh, PA, Morgantown, WV, and Albany, OR (United States), NETL-PUB-22580, Feb. 2021. doi: 10.2172/1567736.
[3] M. J. Wagner and T. Wendelin, “SolarPILOT: A power tower solar field layout and characterization tool,” *Solar Energy*, vol. 171, pp. 185–196, Sep. 2018, doi: 10.1016/j.solener.2018.06.063.
[4] B. Mirletz *et al.*, “Annual Technology Baseline: The 2024 Electricity Update,” National Renewable Energy Laboratory (NREL), Golden, CO (United States), NREL/PR-7A40-89960, Jul. 2024. Available: https://www.osti.gov/biblio/2425927
[5] B. T. Gorman, M. Lanzarini-Lopes, N. G. Johnson, J. E. Miller, and E. B. Stechel, “Techno-Economic Analysis of a Concentrating Solar Power Plant Using Redox-Active Metal Oxides as Heat Transfer Fluid and Storage Media,” *Front. Energy Res.*, vol. 9, Dec. 2021, doi: 10.3389/fenrg.2021.734288.
[6] E. Lewis *et al.*, “Comparison of Commercial, State-of-the-Art, Fossil-Based Hydrogen Production Technologies,” National Energy Technology Laboratory (NETL), Pittsburgh, PA, Morgantown, WV, and Albany, OR (United States), DOE/NETL-2022/3241, Apr. 2022. doi: 10.2172/1862910.
[7] G. Towler and R. Sinnott, *Chemical Engineering Design*, 3rd ed. Elsevier, 2022. doi: 10.1016/C2019-0-02025-0.

Results

Base Case Parameters (1)

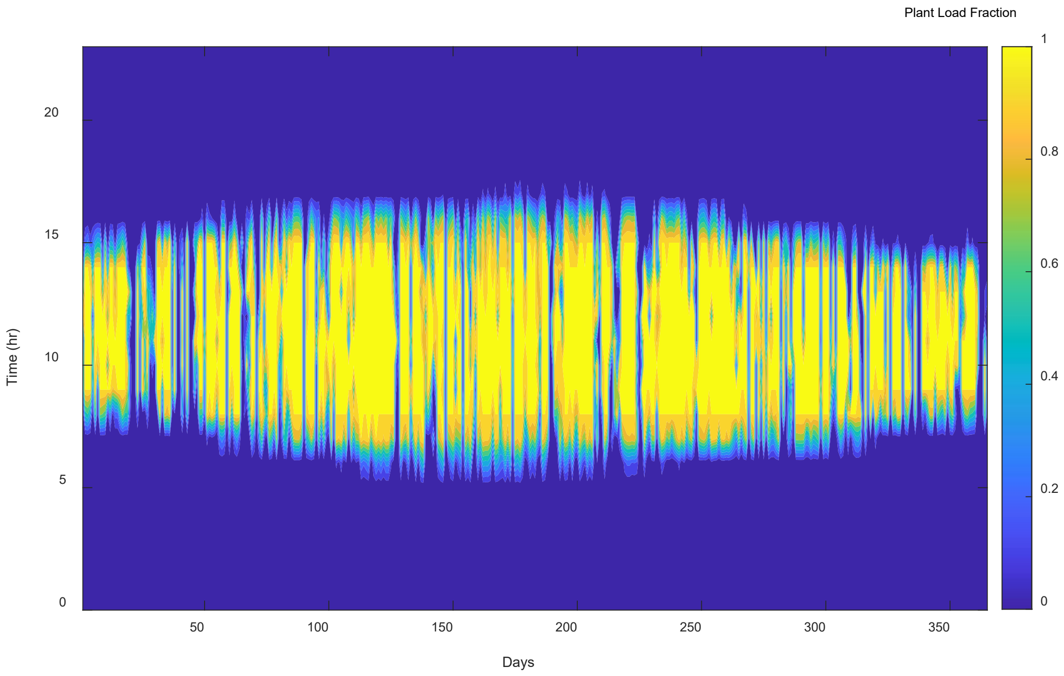
	Parameter	Value	Unit	Ref.
Redox reactors	Packed bed void fraction, ε	0.5		
	Redox material	CeO_2		
	Reduction temperature, T_{red}	1600	°C	
	Reduction pressure, p_{red}	1	bar	
	Oxidation temperature, T_{ox}	650	°C	
	Oxidation pressure, p_{ox}	1	bar	
	Sweep gas purity, $x_{\mathrm{O_2,in}}$	10^{-5}		
	Solid heat recovery effectiveness, $\varepsilon_{\mathrm{HR}}$	0.5		[8-9]
	Exothermic heat recovery effectiveness, $\varepsilon_{\mathrm{ex}}$	0.85		
	Gas-gas heat recovery effectiveness, $\varepsilon_{\mathrm{gg}}$	0.85		
	Reduction time, t_{red}	150	s	
	Oxidation time, t_{ox}	$t\left(X = 0.5X_{\mathrm{eq}}\right)$	s	
Gas-to-liquid	Fischer-Tropsch temperature, T_{FT}	200	°C	[1]
	Fischer-Tropsch pressure, p_{FT}	10	bar	[1]
	Fischer-Tropsch conversion, X_{FT}	1		
	Syngas composition H_2:CO	2: 1		[1]
CST	Plant thermal design point power, P_{DP}	300	$\mathrm{MW_{th}}$	[3]
	Design point field efficiency, η_{field}	0.451 / 0.652		[3]
	Receiver thermal efficiency, η_{rec}	0.613 / 0.9		[3]

Base Case Parameters (2)

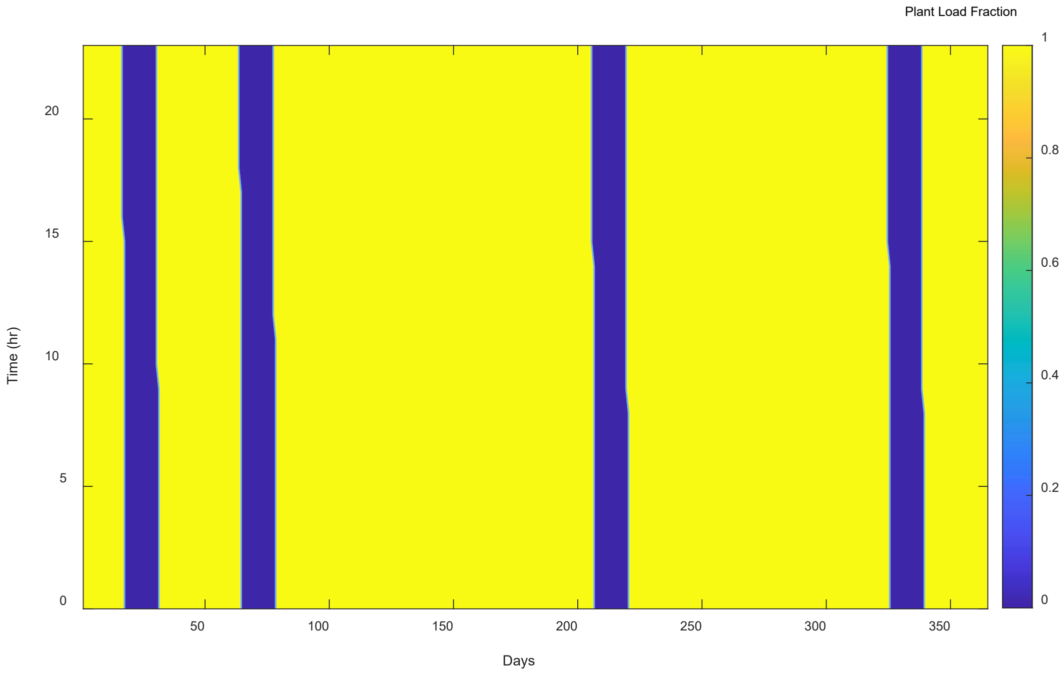
	Parameter	Value	Unit	Ref.
Thermal Energy Storage	Hourly losses fraction, $f_{\mathrm{th,loss}}$	0.01	$\mathrm{MW\ MWh^{-1}\ d^{-1}}$	[12]
	Charging efficiency, $\eta_{\mathrm{th,ch}}$	0.99		[12]
	Discharging efficiency, $\eta_{\mathrm{ch,dis}}$	0.9		[12]
	Max charging rate fraction, $f_{\mathrm{th,ch}}$	0.3	$\mathrm{MW\ MWh^{-1}}$	[12]
	Max discharging rate fraction, $f_{\mathrm{th,dis}}$	0.1	$\mathrm{MW\ MWh^{-1}}$	[12]
	Initial state of charge, $\mathrm{SOC_{init}}$	0.5		[12]
	Minimum state of charge, $\mathrm{SOC_{min}}$	0.05		[12]
Elec. Heat	Work-to-heat efficiency, η_{wth}	0.99		
Auxiliary	PSA efficiency (CO_2-CO), η_{PSA}	0.05		[11]
	PSA pressure, p_{PSA}	8	bar	[11]
	Power block cycle efficiency, η_{PB}	0.535		[5]
	Pump/compressor efficiency, η_{pump}	0.85		
	Cryogenic air separation energy, w_{sep}	15	$\mathrm{kJ\ mol_{N_2}^{-1}}$	[10]
Financial	O_2 selling price, C_{O_2}	150	$\$\ t^{-1}$	
	CST and PV costs	2035 ATB		[4]
	TES installed cost, $C_{\mathrm{e,TES}}$	10	$\$\ \mathrm{kWh^{-1}}$	[12]
	Redox reactor cost function	SMR reformer, higher f_{m}, redox cost		[6]
	Fixed charge rate, FCR	7.07	%	[2]
	Total as-spent cost to total overnight cost, TASC/TOC	1.093		[2]

Results – Annual Simulation

CST



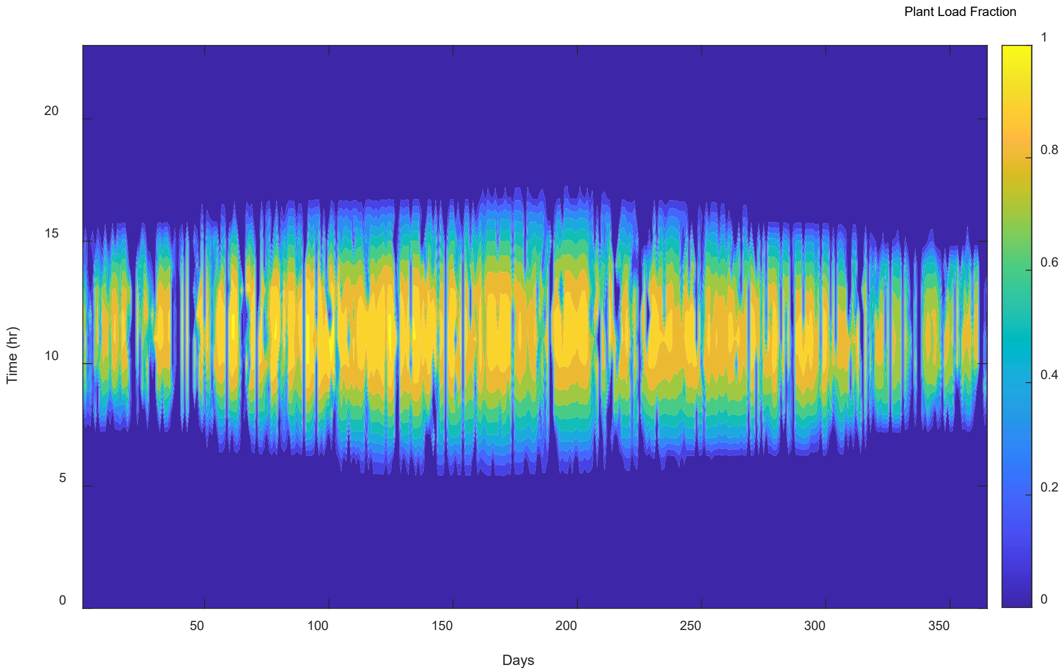
CST+TES



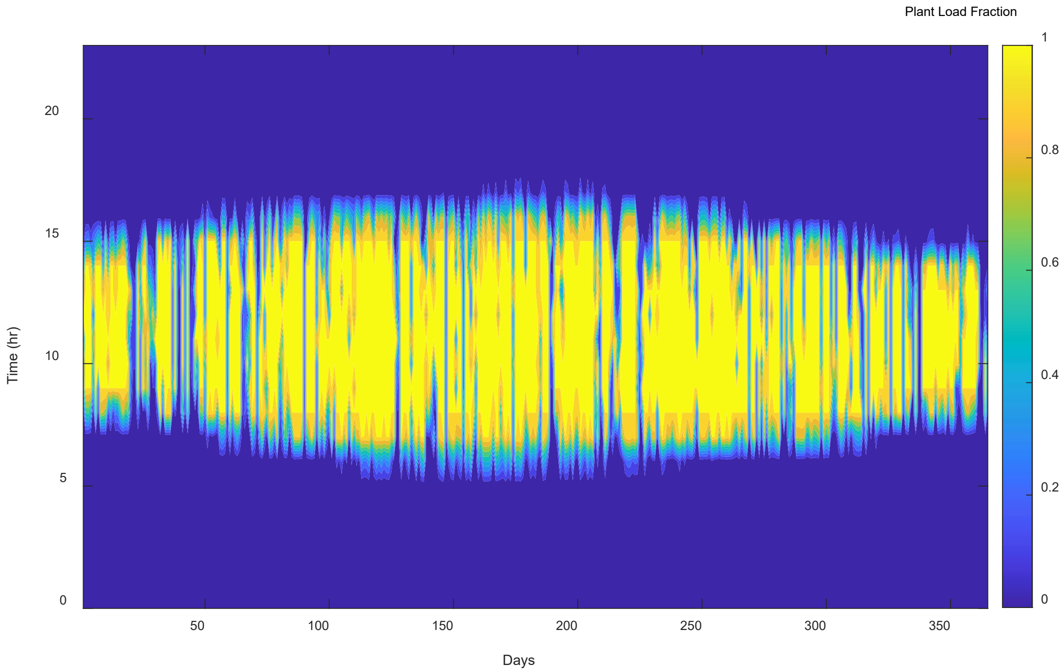
TES allows for high capacity factors

Results – Annual Simulation

CST+PV



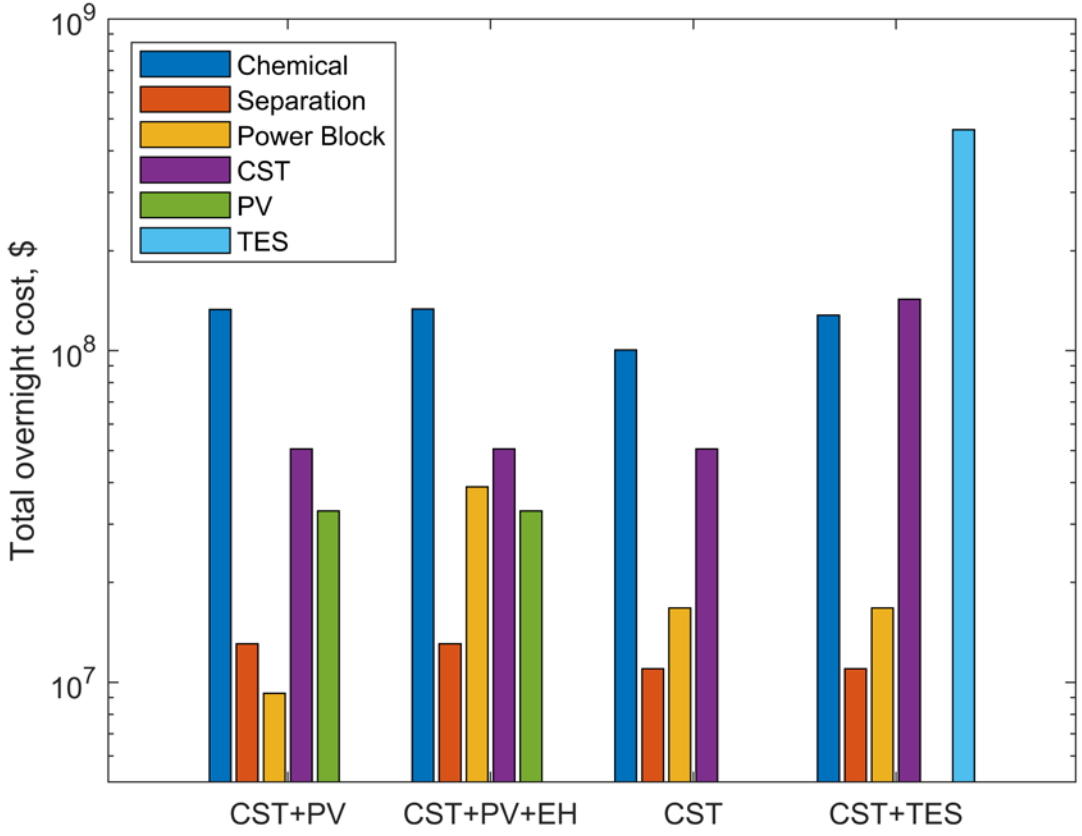
CST+PV+Electrical Heaters



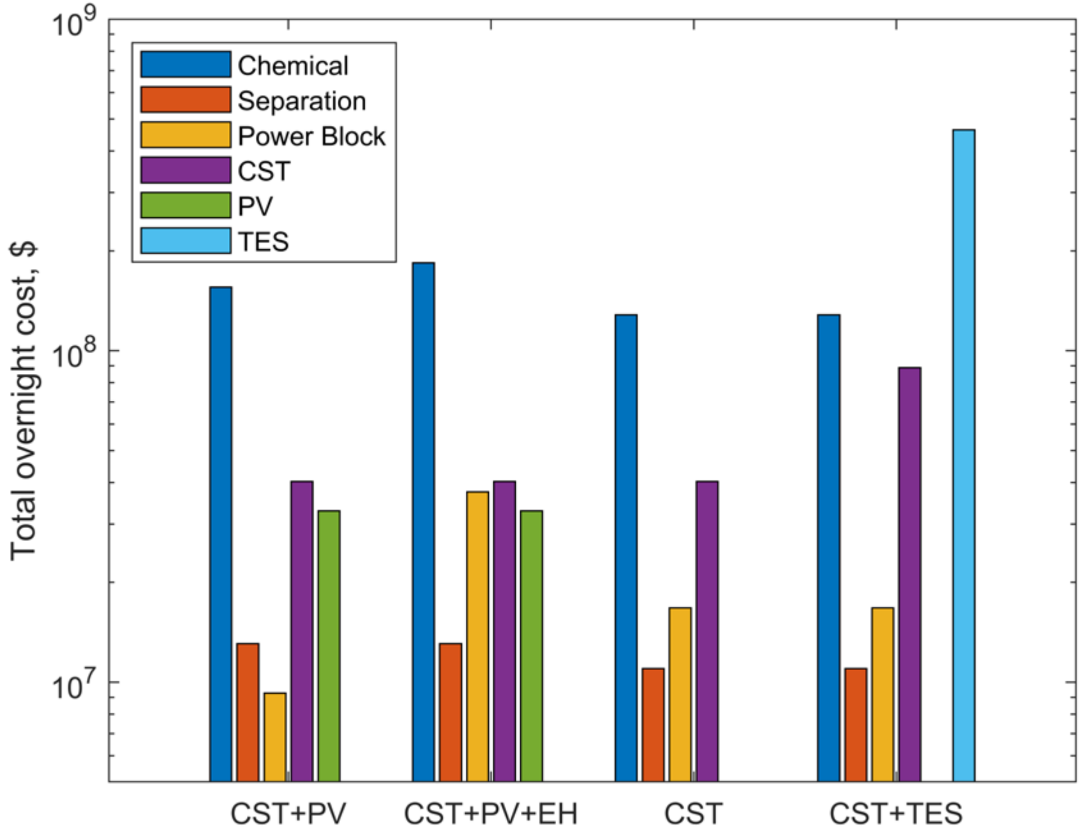
CST+PV without electrical heaters has the lowest capacity factor

Results – Total Costs

“SOA” Receiver



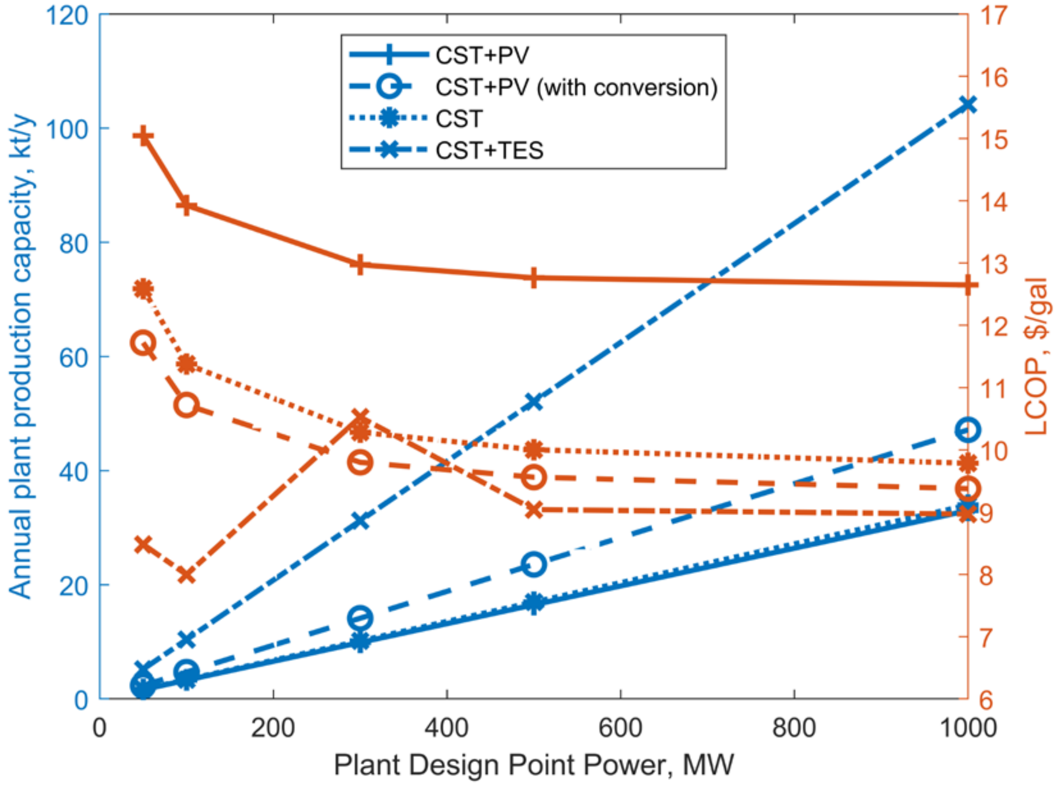
“Next-Gen” Receiver



Chemical plant cost doesn’t include separation and power block – when summed together, this is the largest CAPEX item (excluding TES)

Results – Receiver Power

“SOA” Receiver



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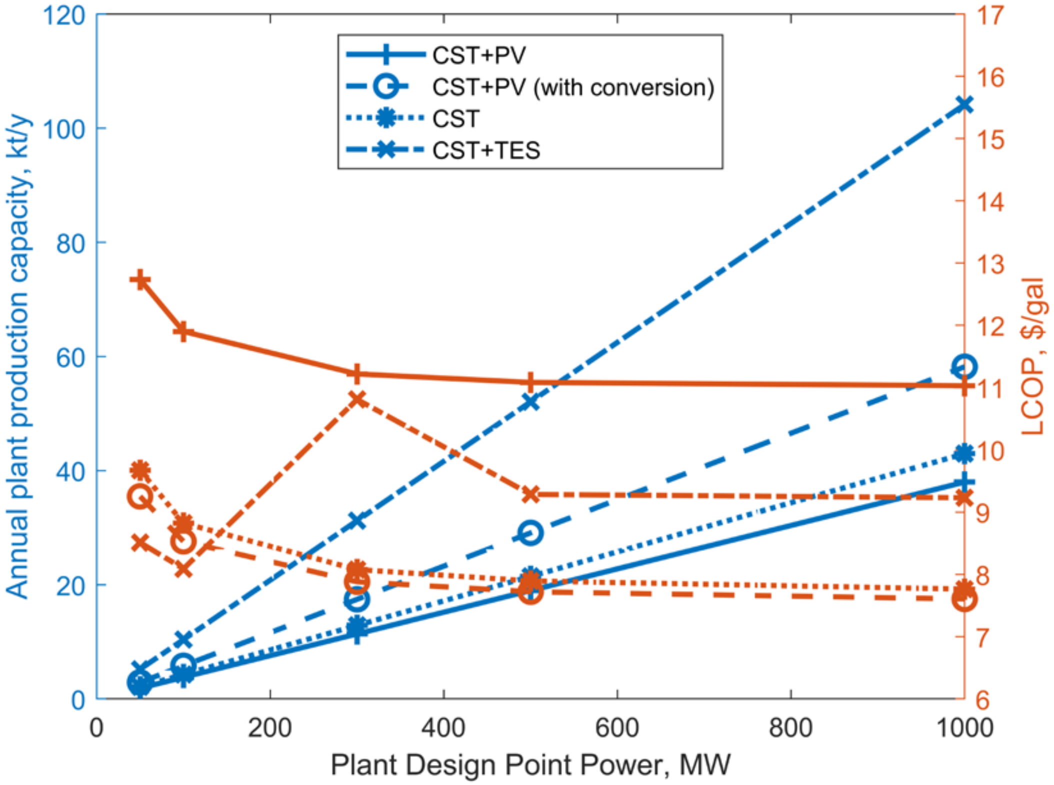
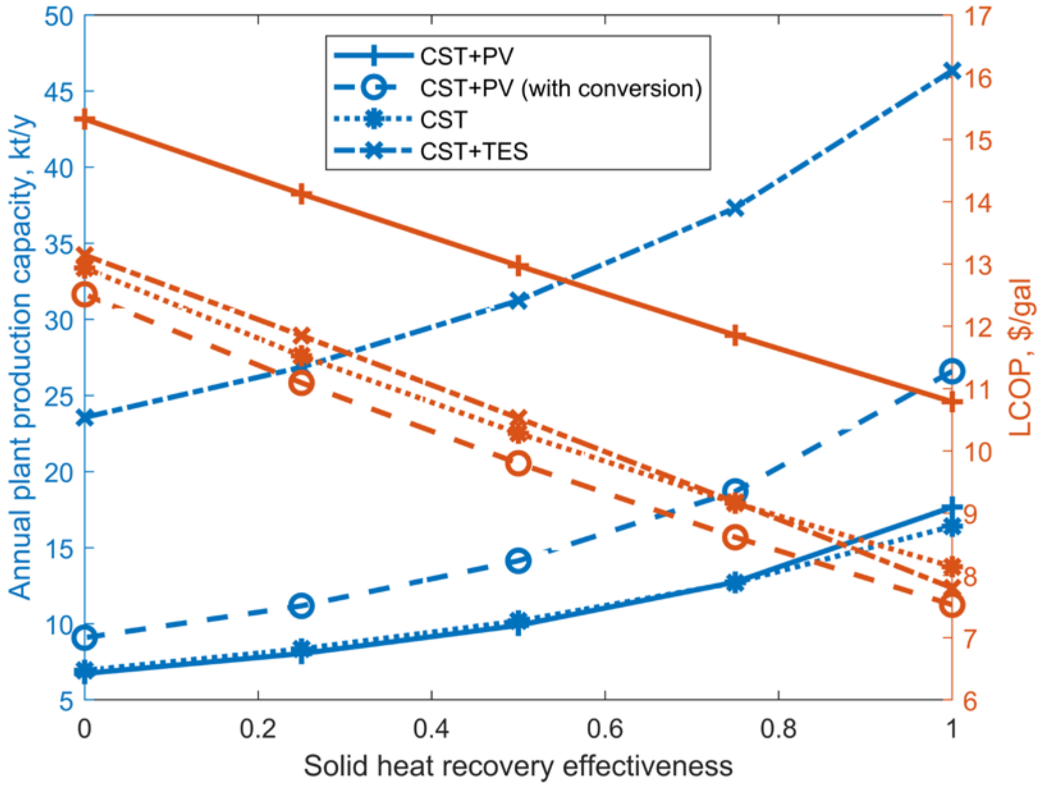


CST+TES affected by different scaling law for TES (optimal $\frac{C_{\mathrm{TES}}}{P_{\mathrm{receiver}}} = 8.5 - 19$)

Results – Solid Heat Recovery

“SOA” Receiver



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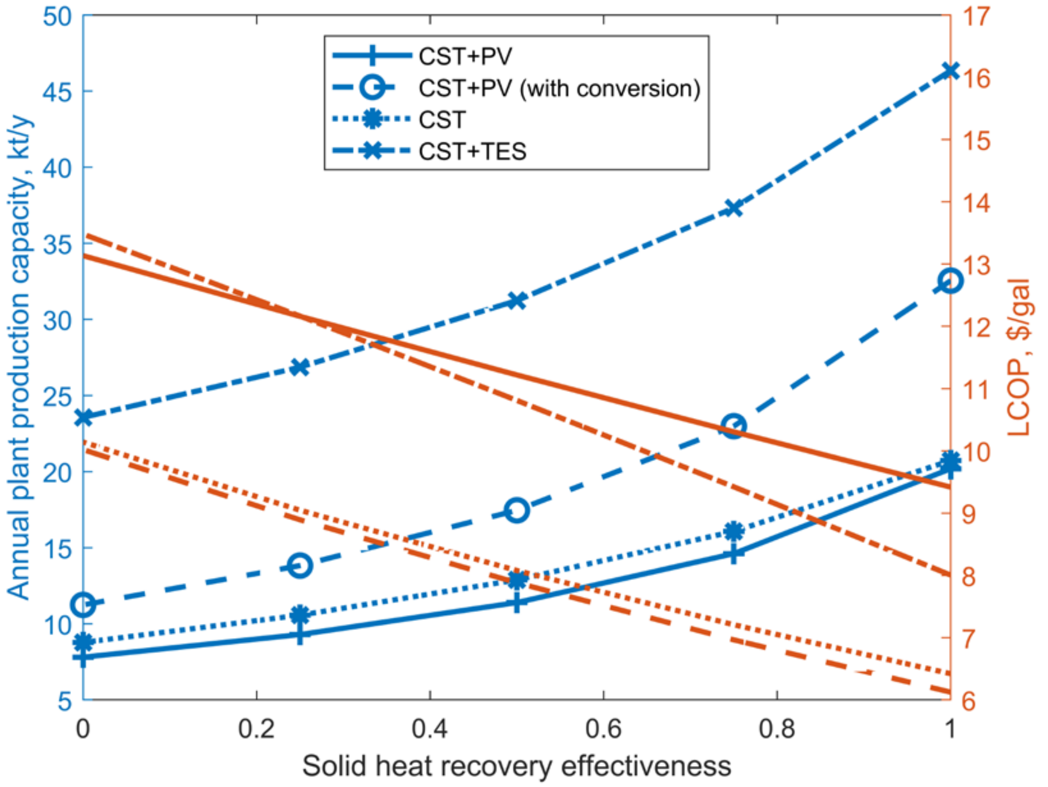
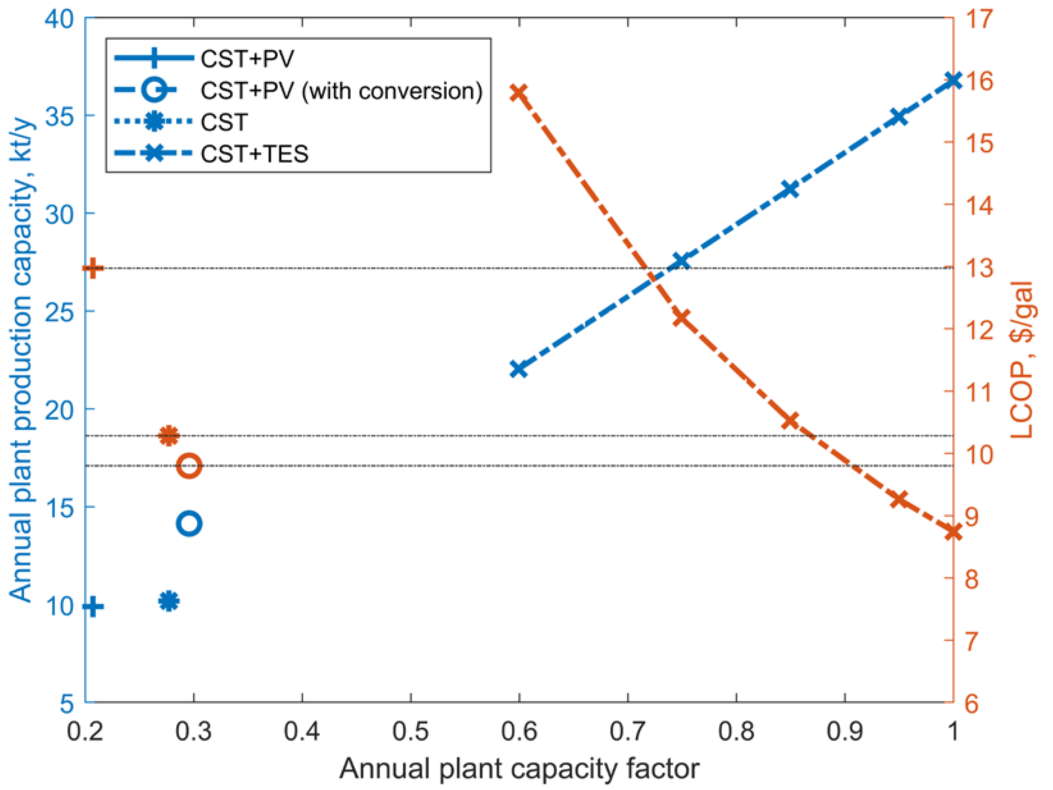
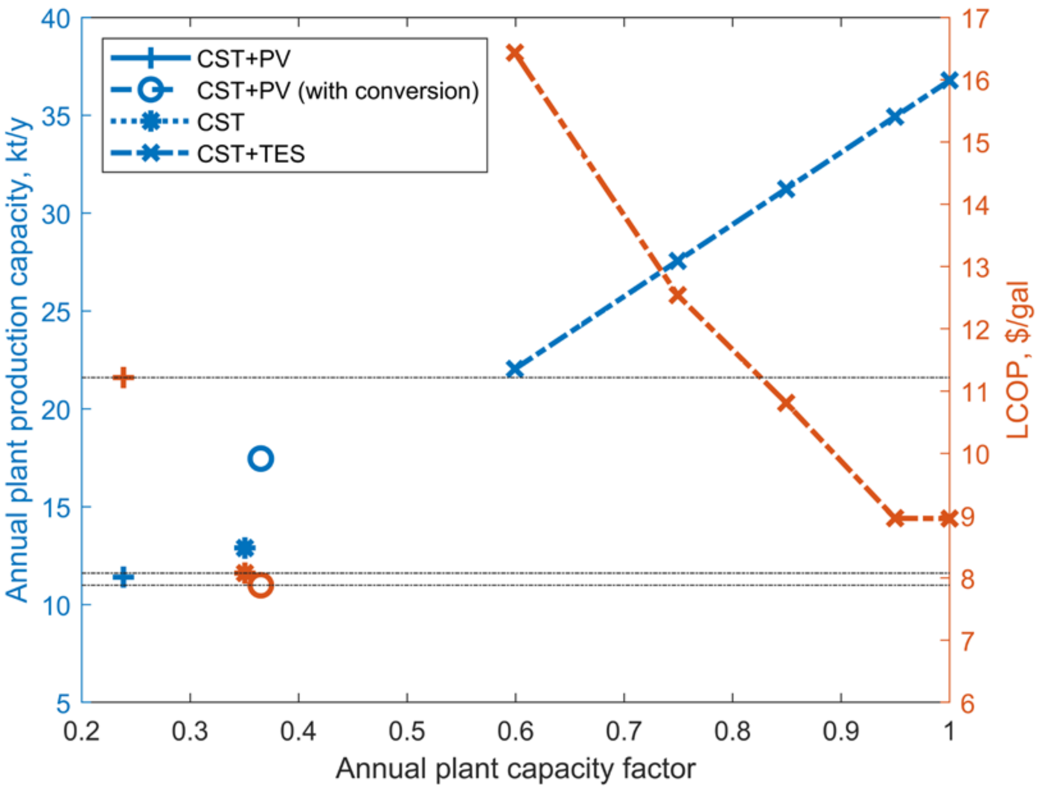


Results – Annual Capacity Factor (CST-TES)

“SOA” Receiver



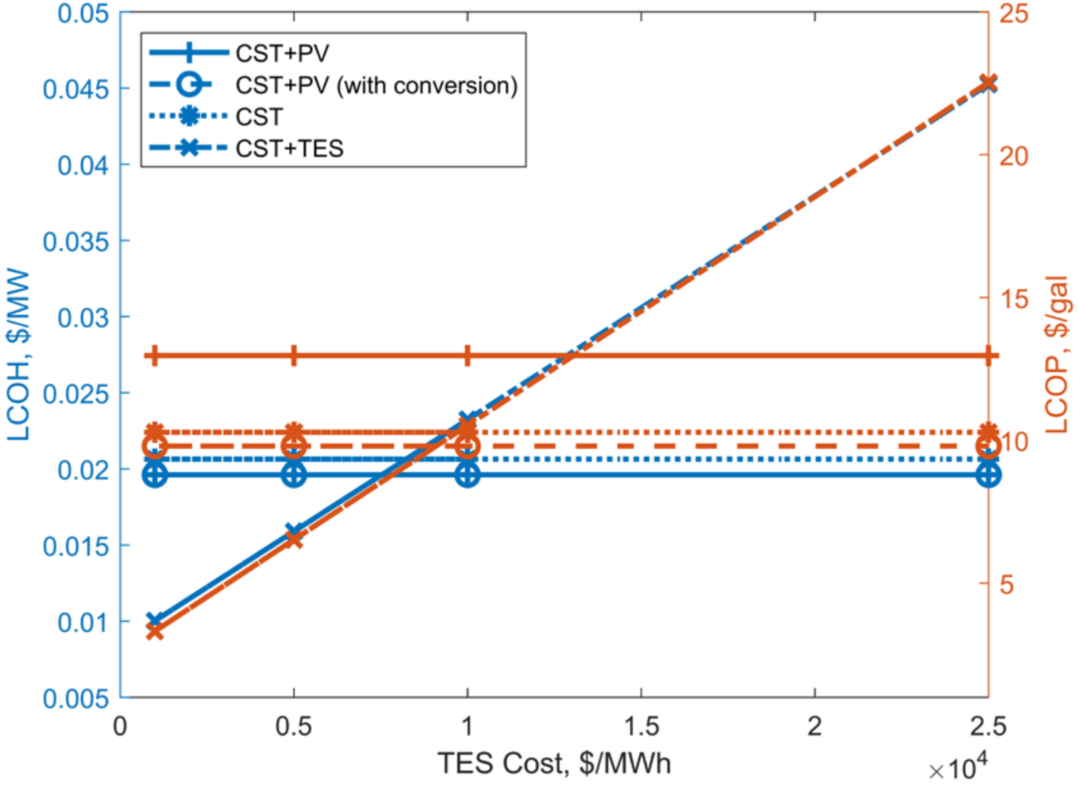
“Next-Gen” Receiver



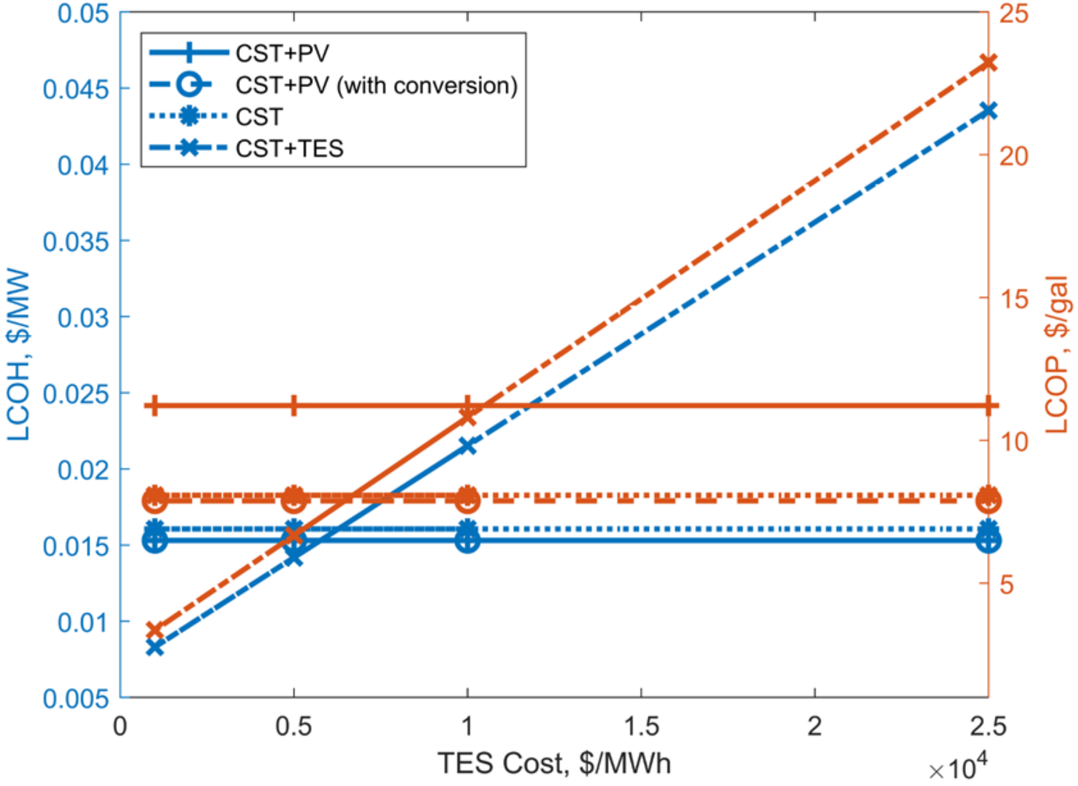
- High-performance receiver effect outweighs CST+TES benefits
- Sensitivity analysis of CST cost scaling power needed to better understand CST-TES cost relations

Results – TES Cost (CST-TES)

“SOA” Receiver



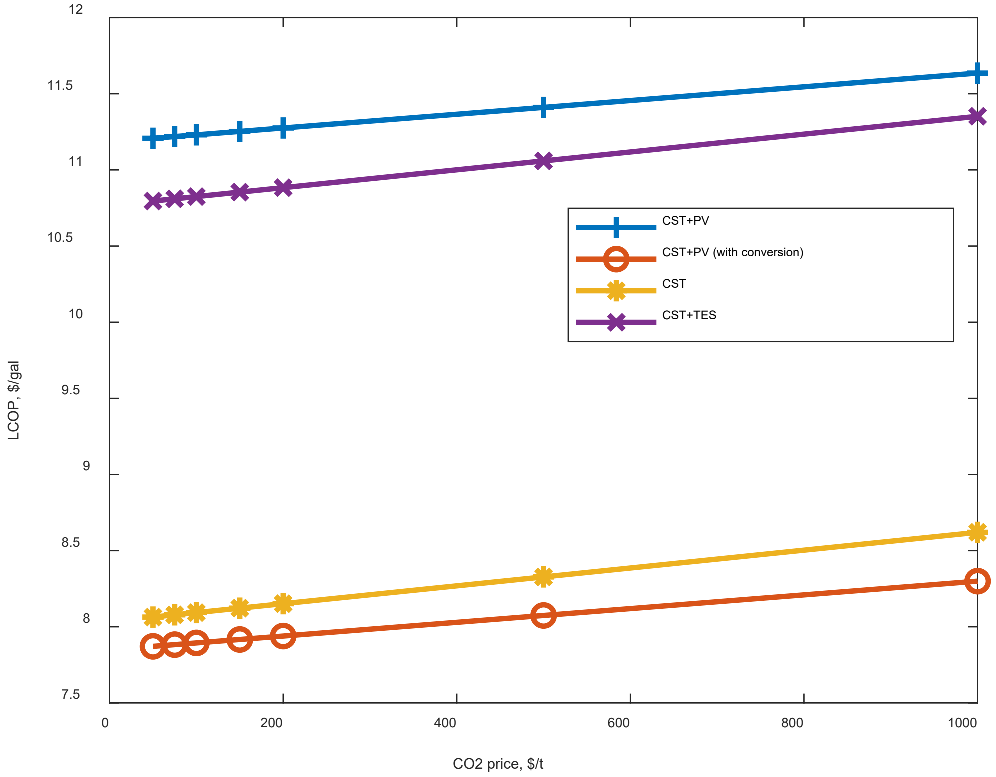
“Next-Gen” Receiver



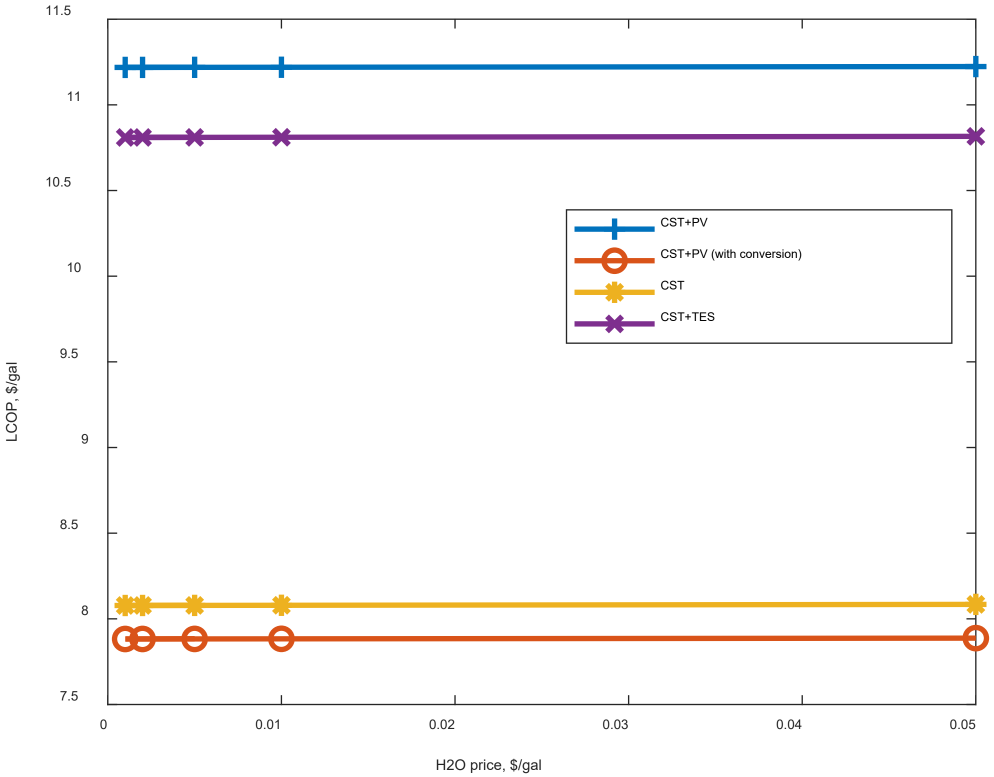
TES cost<$10/kWh needed to provide economical value

Results – Feedstock Price

“Next-Gen” Receiver – CO_2



“Next-Gen” Receiver – H_2O



CO_2 price affects production costs more than H_2O

Summary

- TEA modeling framework coupled with physics-based system performance
- Levelized cost of fuel <$9/gal (excluding incentives)
- TES improves fuel cost with “SOA” receiver
- High SM needed (~10) to utilize TES, annual CF>0.85 possible
- CST and PV results in the highest cost without energy conversion (generation mismatch)

Future work:

- Adding start-up/shutdown effects
- Including additional technology options for auxiliaries
- Sensitivity analysis for CST cost function
- Refining cost models
- More detailed TES performance modeling

References for Model Assumptions, Values, and Calculation Methods

[1] A. de Klerk, *Fischer-Tropsch Refining*. Wiley, 2011. doi: 10.1002/9783527635603.

[2] J. Theis, “Quality Guidelines for Energy Systems Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance,” National Energy Technology Laboratory (NETL), Pittsburgh, PA, Morgantown, WV, and Albany, OR (United States), NETL-PUB-22580, Feb. 2021. doi: 10.2172/1567736.

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[7] G. Towler and R. Sinnott, *Chemical Engineering Design*, 3rd ed. Elsevier, 2022. doi: 10.1016/C2019-0-02025-0.

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Solar-driven Chemical Looping RWGS Regenerative Reactor for Syngas Production (REGENLOOP)

New DOE SETO award

- RWGS system with high energy and CO_2 conversion efficiencies
- CST-compatible reactor for Gen3 CST temperature range
- Simple, scalable, and cost-effective design for indirect operation
- Evaluate commercial viability

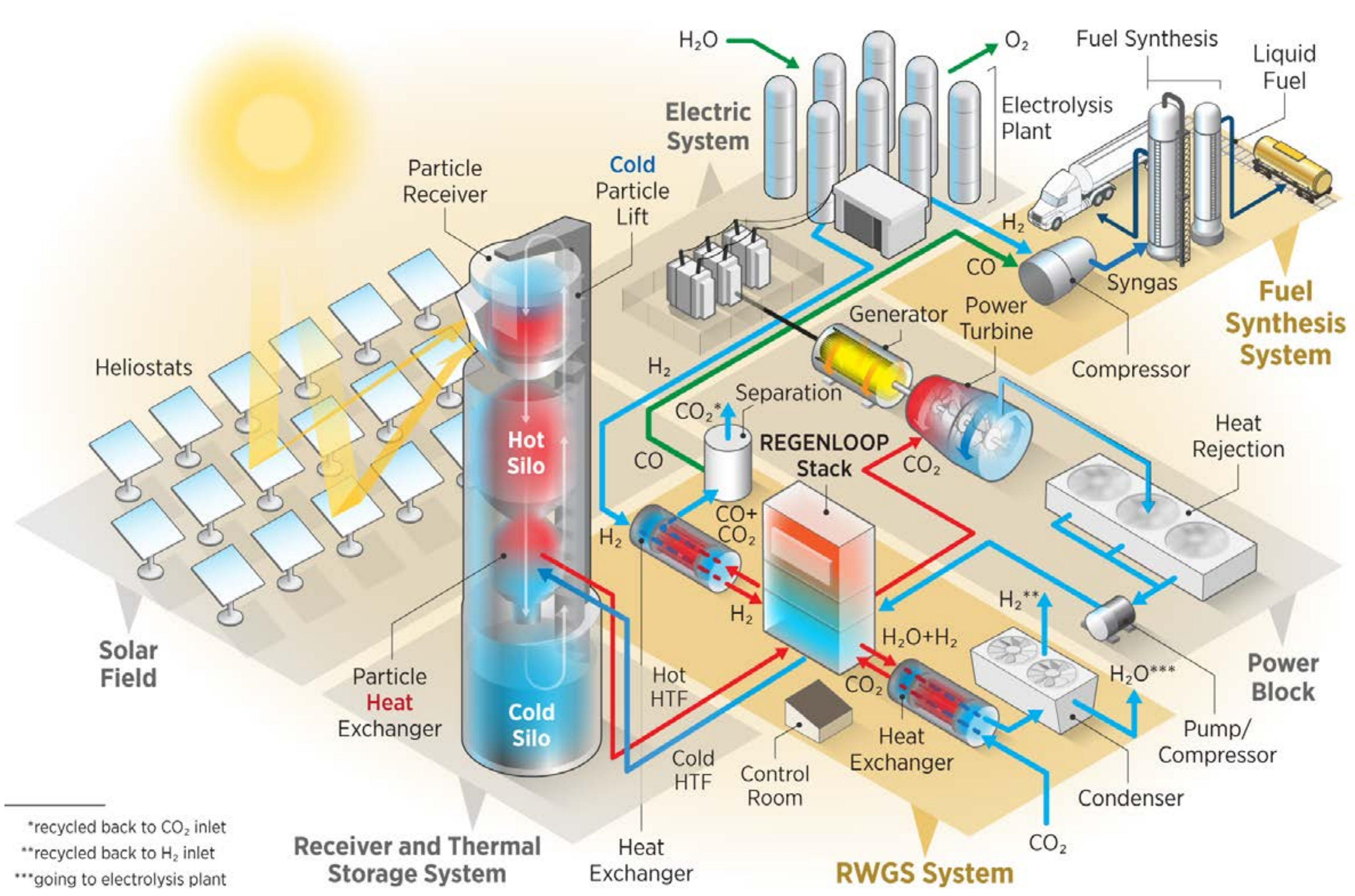
NREL Transforming ENERGY

Georgia Institute of Technology 1885 Progress and Service

LYDIAN

AMS CREATE NEW

UCC University College Cork, Ireland
Coláiste na hOllscoile Corcaigh



*recycled back to CO_2 inlet
**recycled back to H_2 inlet
***going to electrolysis plant

Credit: Alfred Hicks @ NREL

Acknowledgements:
Zachary Hart
Janna Martinek
Craig Turchi

Thank you for you attention!

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The Model

- 1D convection-diffusion with multiple species (reactant, product, O$_2$)

$$\varepsilon \frac{\partial C_{\mathrm{i}}}{\partial t} = D_{\mathrm{eff}} \frac{\partial^2 C_{\mathrm{i}}}{\partial x^2} - u \frac{\partial C_{\mathrm{i}}}{\partial x} + C_{\mathrm{oxide}} \frac{d\delta}{dt}$$

Reduction:

$$\frac{d\delta}{dt} = k_0\left(\delta_{\mathrm{eq}}\left(T_{\mathrm{red}}, c_{\mathrm{o}_2}, \delta\right) - \ \delta\right) H\left(\delta_{\mathrm{eq}}\left(T_{\mathrm{red}}, c_{\mathrm{o}_2}, \delta\right) - \ \delta\right)$$

Oxidation:

$$\frac{d\delta}{dt} = -k_0\left(\delta_{\mathrm{eq}}\left(T_{\mathrm{red}}, c_{\mathrm{o}_2}, \delta\right) - \ \delta\right) H\left(\ \delta - \delta_{\mathrm{eq}}\left(T_{\mathrm{red}}, c_{\mathrm{o}_2}, \delta\right)\right)$$

The TEA Model

- Levelized cost of fuel:

$$\mathrm{LCOP} = \frac{\mathrm{FCR} \cdot \mathrm{TCC} + \mathrm{FOC} - \mathrm{REV}}{m_{\mathrm{fuel}}} + \mathrm{VOC} + \mathrm{LCOE}_{\mathrm{PV}} \frac{P_{\mathrm{PV}}}{m_{\mathrm{fuel}}} + \mathrm{LCOH}_{\mathrm{CST}} \frac{P_{\mathrm{CST}}}{m_{\mathrm{fuel}}}$$

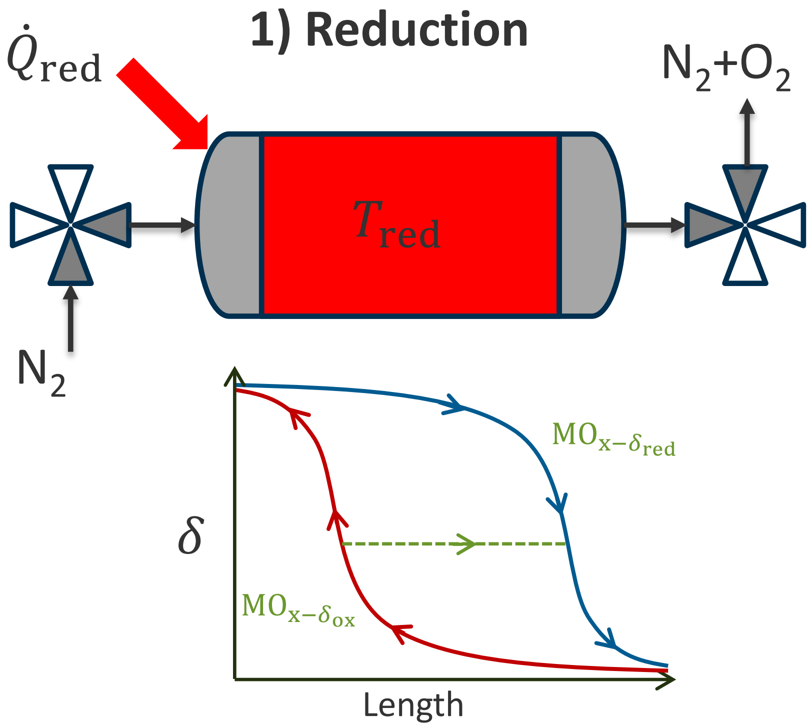
- TCC – total capital cost of chemical plant (equal to TASC – total as-spent cost) – accounting for financing over a period (as opposed to overnight cost):

$$\mathrm{TCC} = \frac{\mathrm{TASC}}{\mathrm{TOC}} \mathrm{TOC}$$

- REV – revenues (from selling O_2); FOC – fixed operating costs; VOC – variable operating costs
- TOC - total overnight cost (includes capital costs of all components and extras)

$$\mathrm{TOC} = \sum_{j=1}^{M} C_{\mathrm{e},j}\left[\left(1 + f_{\mathrm{p}}\right) f_{\mathrm{m}} + \left(f_{\mathrm{er}} + f_{\mathrm{el}} + f_{\mathrm{i}} + f_{\mathrm{c}} + f_{\mathrm{s}} + f_{\mathrm{l}}\right)\right]$$

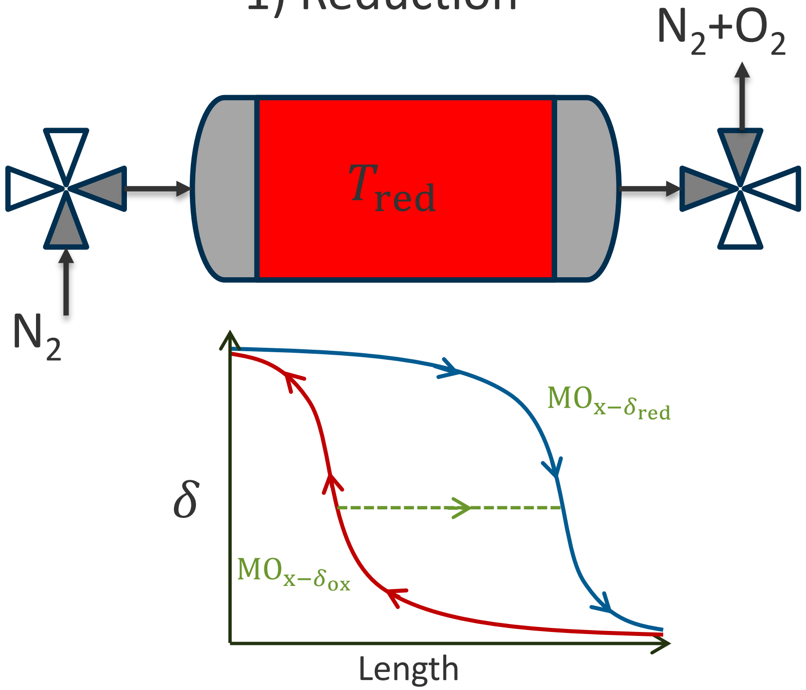
Cycle Process - Reduction



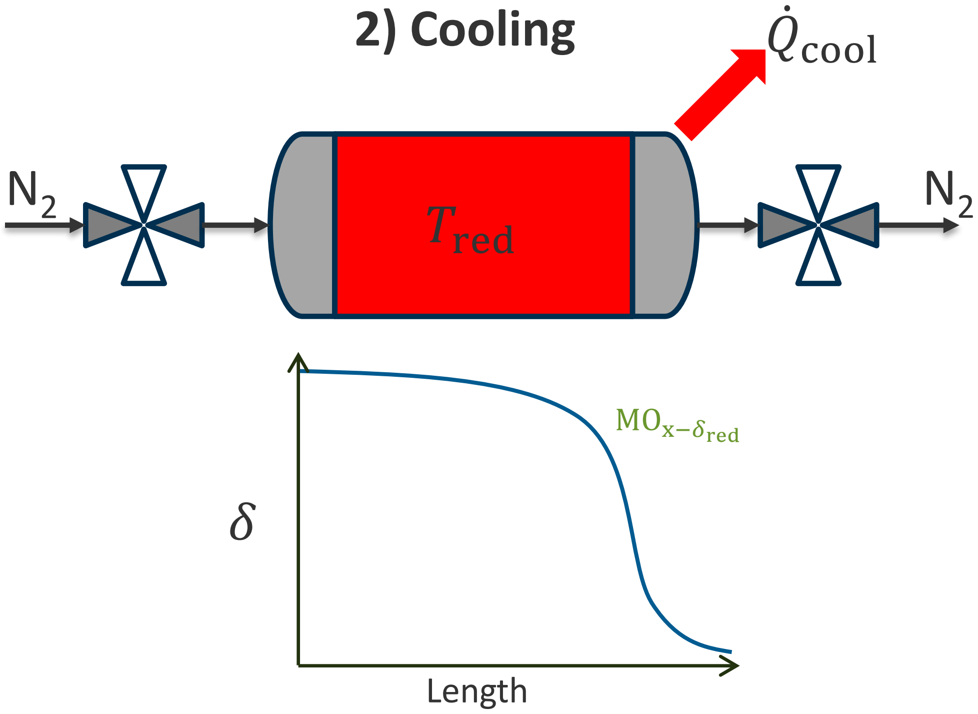
Reduction enthalpy provided indirectly using HTF and/or excess sweep gas heating (high h)

Cycle Process - Cooling

1) Reduction



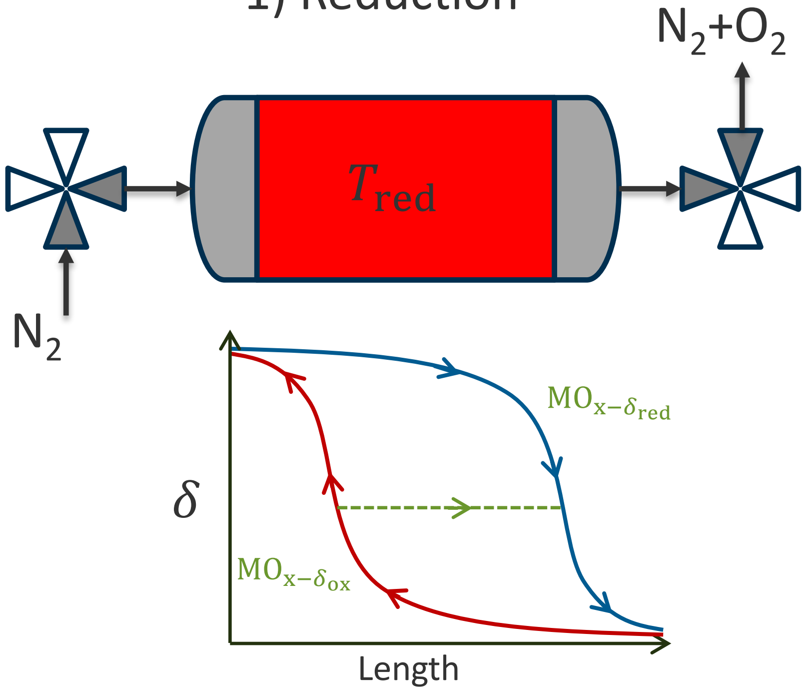
2) Cooling



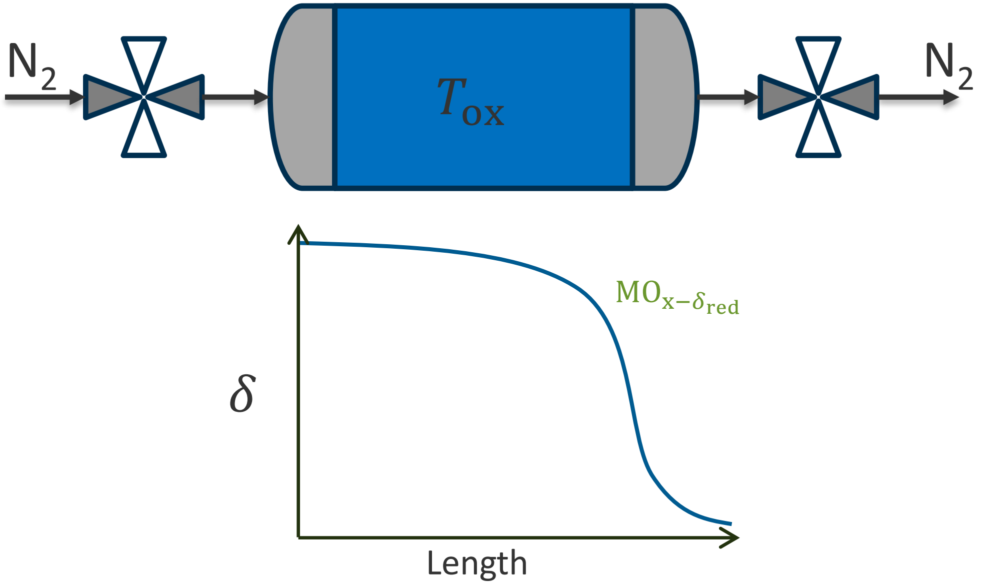
Cooling is performed via the HTF tubes, directly through the reactor (inert HTF), or a combination
Heat could be stored or used for power/heat

Cycle Process - Cooling

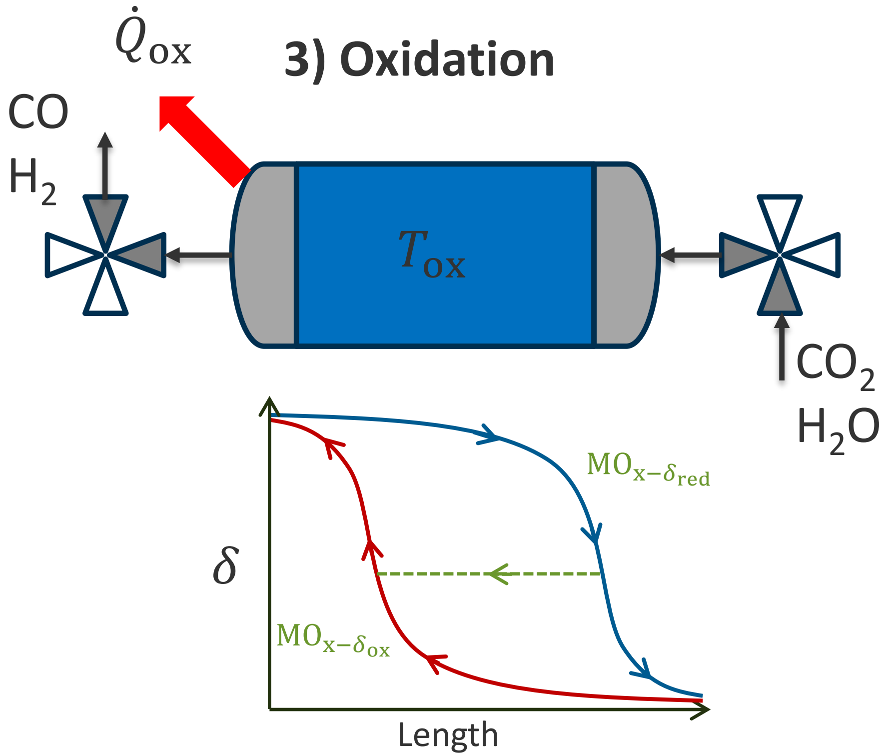
1) Reduction



2) Cooling

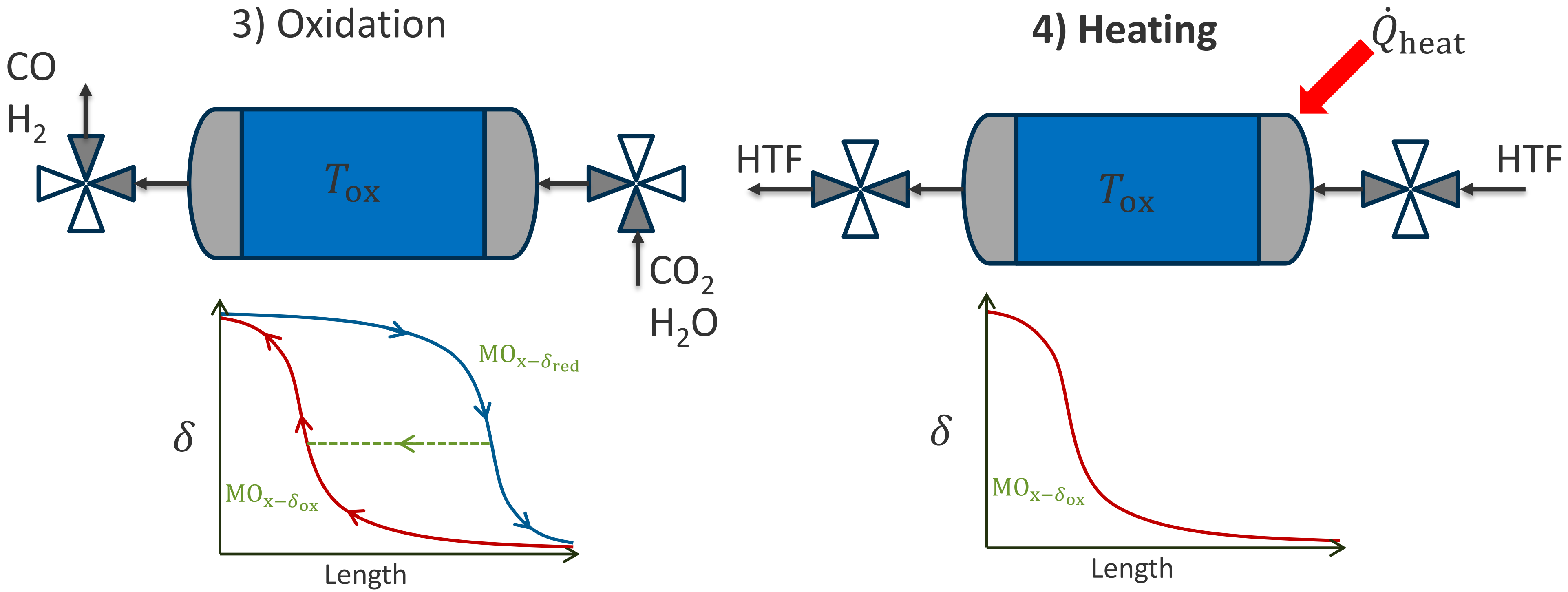


Cycle Process - Oxidation



Extracting the exothermic heat is performed via the HTF tubes, by flowing reactant at $T < T_{\mathrm{ox}}$, or a combination

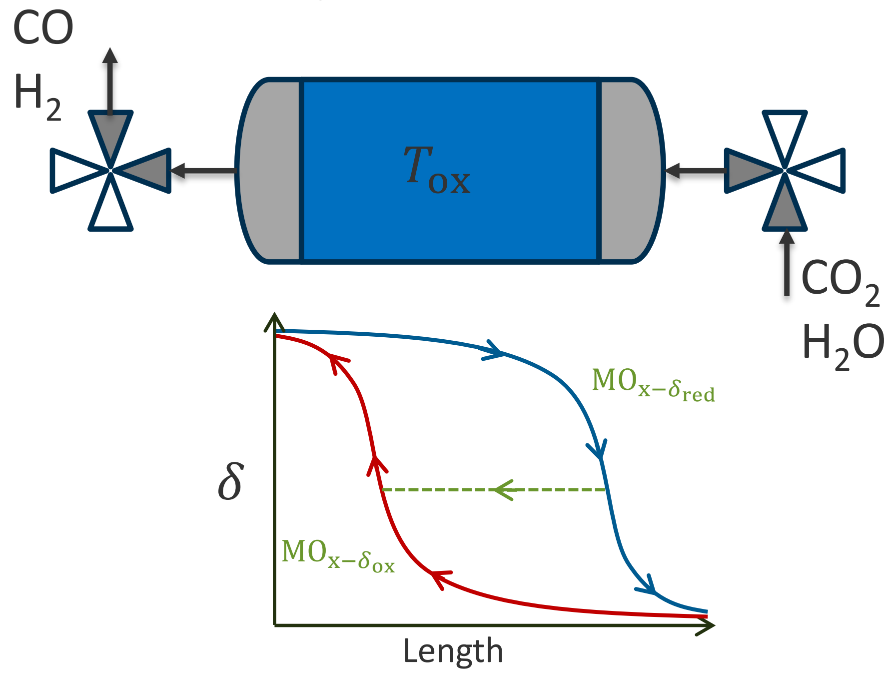
Cycle Process - Heating



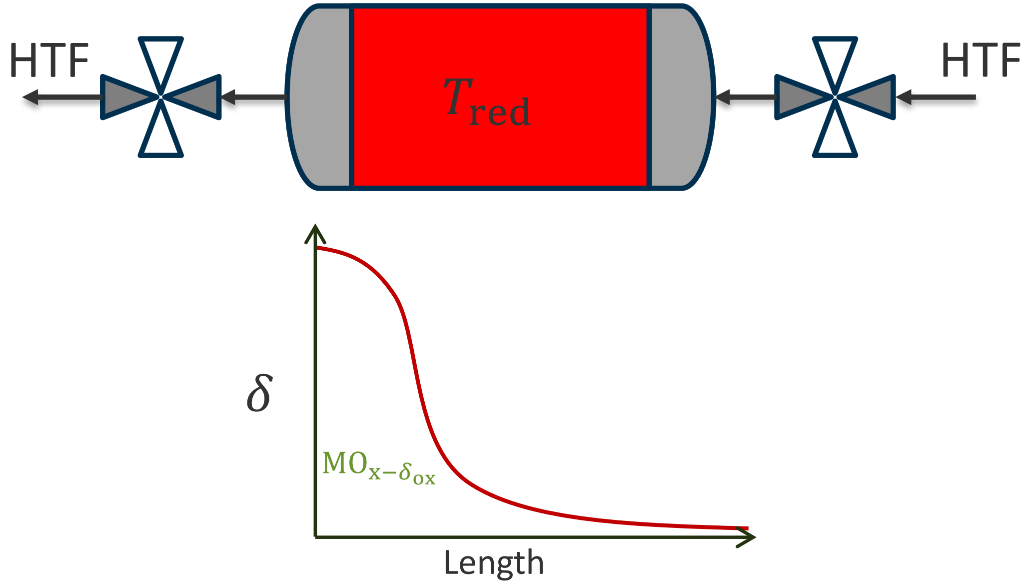
Heating is performed via the HTF tubes, directly through the reactor (using HTF), or a combination
Depending on heating rates, reduction could be started during heating

Cycle Process - Heating

3) Oxidation



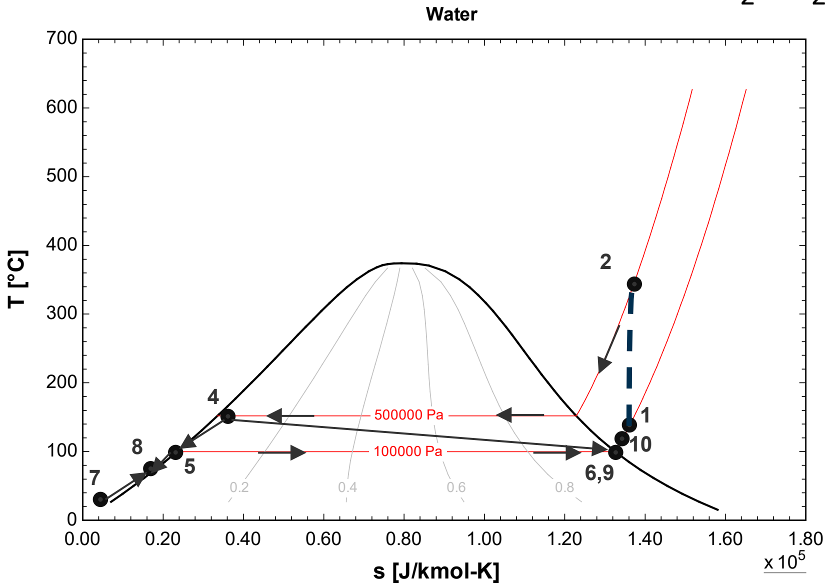
4) Heating

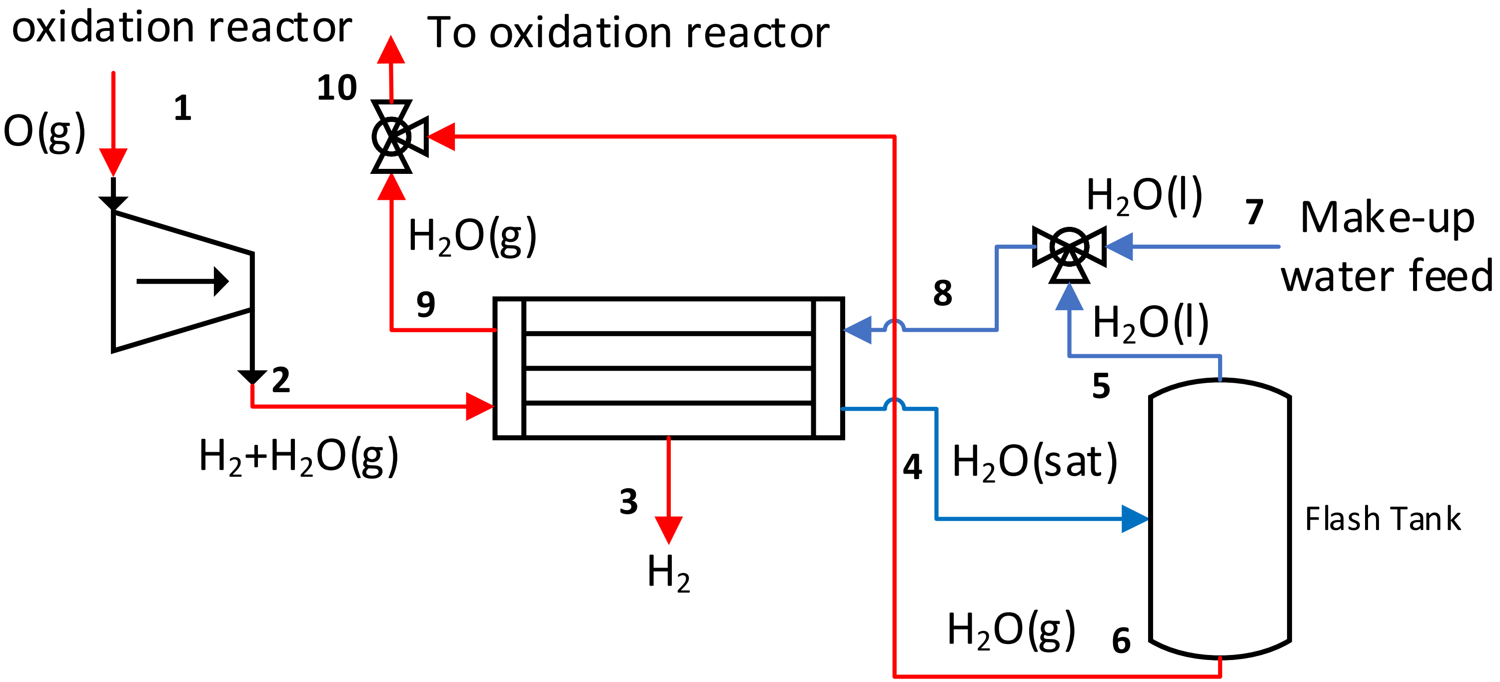


Alternative H_2-H_2O Separation

Mechanical Vapor Recompression (MVR)

- Method used to recover low-grade waste steam in plants
- Compressing the vapor -> creating ΔT between streams -> simultaneous evaporation and condensing





The Model

Reactor:

- 1D convection-diffusion with multiple species (reactant, product, O_2)
- Temperature-swing, sweep gas operated reactors
- Isothermal redox steps (T_{red} and T_{ox} held constant respectively)
- Splitting CO_2 and H_2O in separate reactors
- Calculating number of reactors needed to obtain continuous syngas production

Auxiliary units:

- Sweep gas purification: **PSA, cryogenic separation**, thermochemical O_2 separation
- H_2-H_2O separation: **condensation**, **mechanical vapor recompression**, **electrochemical membrane separation**
- CO-CO_2 separation: membrane separation, **PSA**, scrubbing, syngas conditioning

Software: MATLAB, Cantera, CoolProp, COMSOL

Performance Indicators

- Reactor efficiency

$$\eta = \frac{\sum_{\mathrm{i=product}} n_{\mathrm{i}} \mathrm{HHV_i}}{Q_{\mathrm{sens}} + Q_{\mathrm{red}} + W_{\mathrm{pump}} + W_{\mathrm{inert}}}$$

- Conversion extent

$$X = 1 - \frac{n_{\mathrm{ox,out}}}{n_{\mathrm{ox,in}}}$$

- Power output

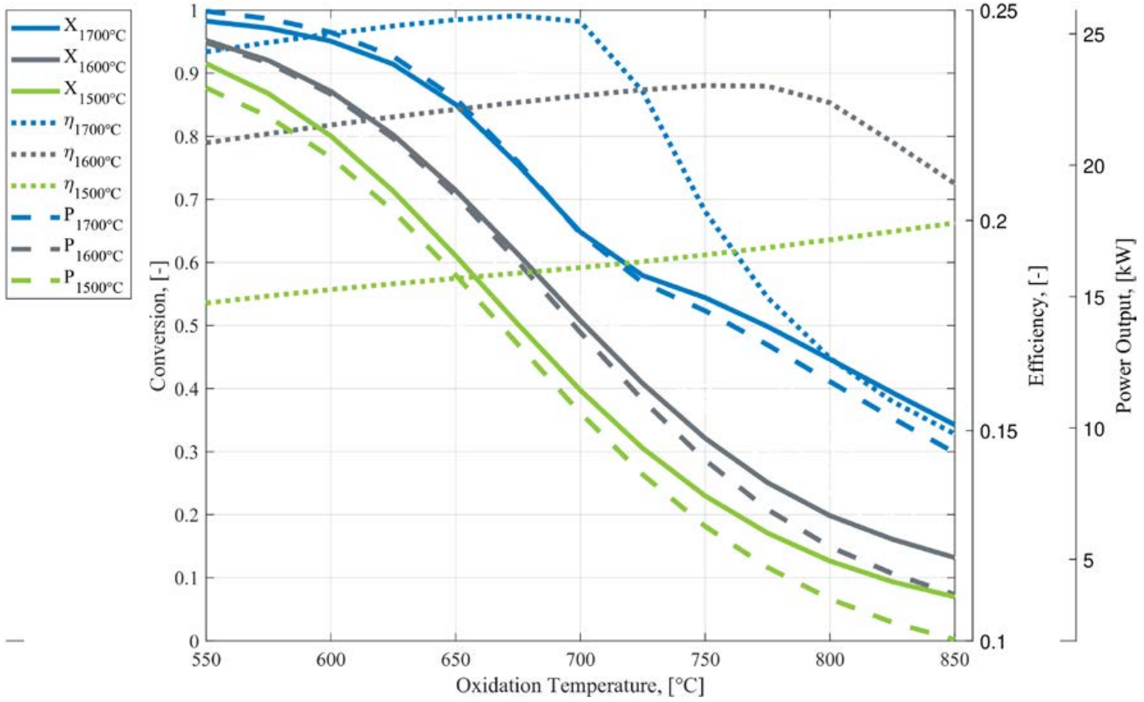
$$P = \frac{\sum_{\mathrm{i=product}} n_{\mathrm{i}} \mathrm{HHV_i}}{t_{\mathrm{cycle}}}$$

- Power density / specific power

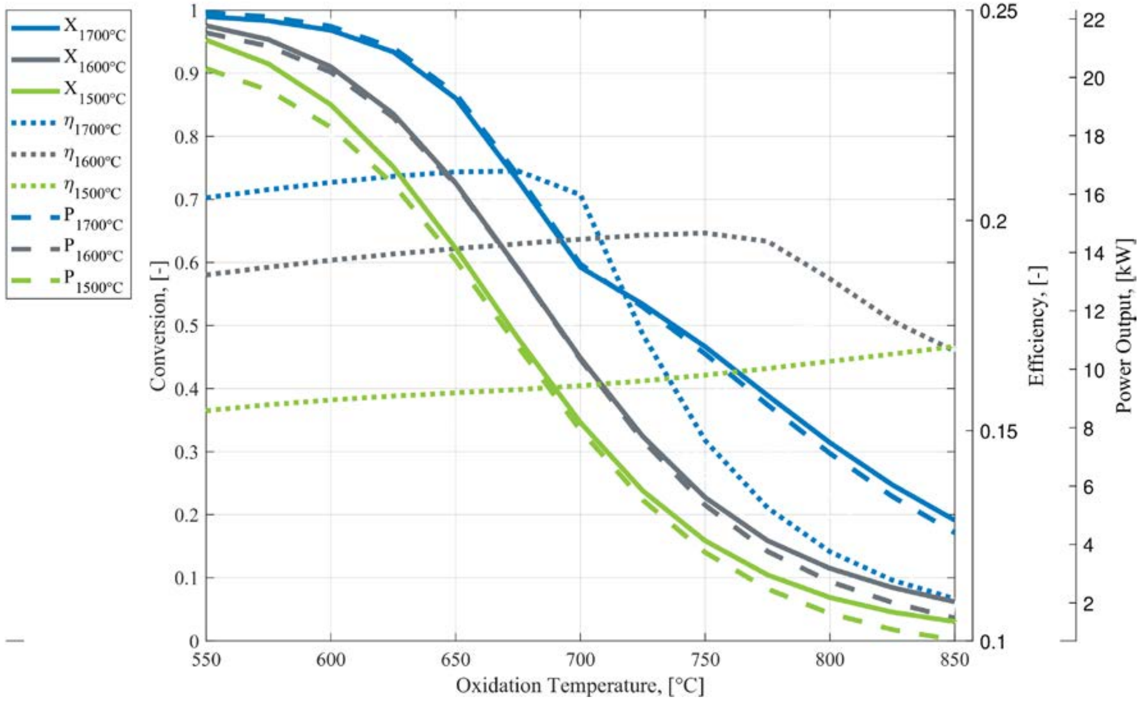
$$\frac{P}{V_{\mathrm{PB}}} \text{ or } \frac{P}{m_{\mathrm{oxide}}}$$

Results – Temperature Effects

H_2O splitting



CO_2 splitting



- Clear trade-offs between efficiency and conversion/power output
- Optimal T_{ox} for different T_{red}
- $\eta > 0.2$ with $X > 0.2$ at $T_{\text{red}} = 1600^{\circ}\text{C}$ (without any solid sensible heat recovery)