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SolarPACES
Concentrating Solar Power, Thermal, and Chemical Energy Systems

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Rome, Italy
30th SolarPACES Conference

Thermodynamic limits of redox-based thermochemical processes (REDOTHERM)

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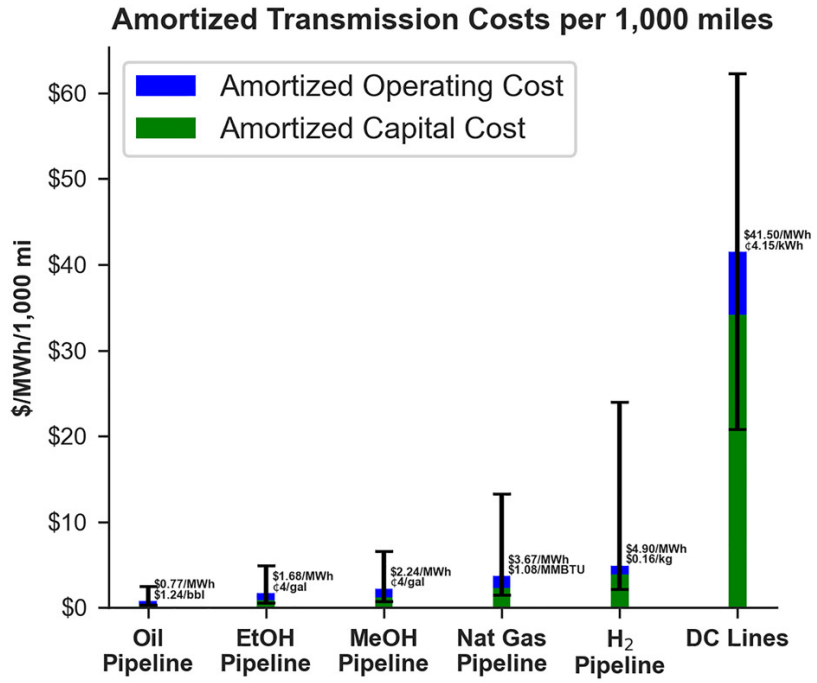
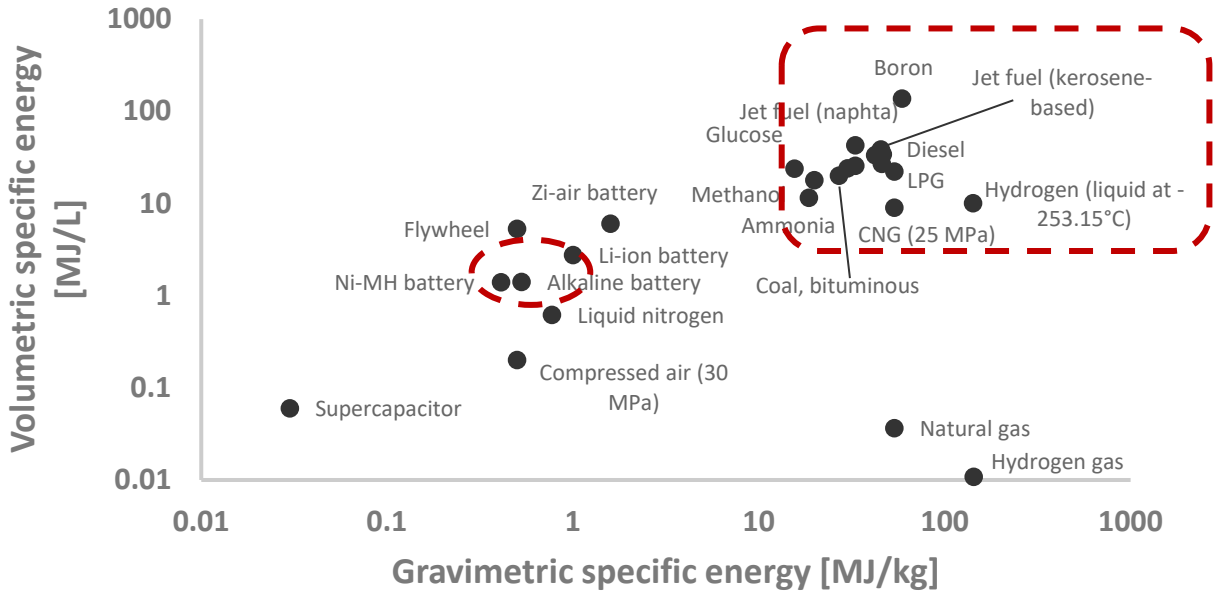
Background

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

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

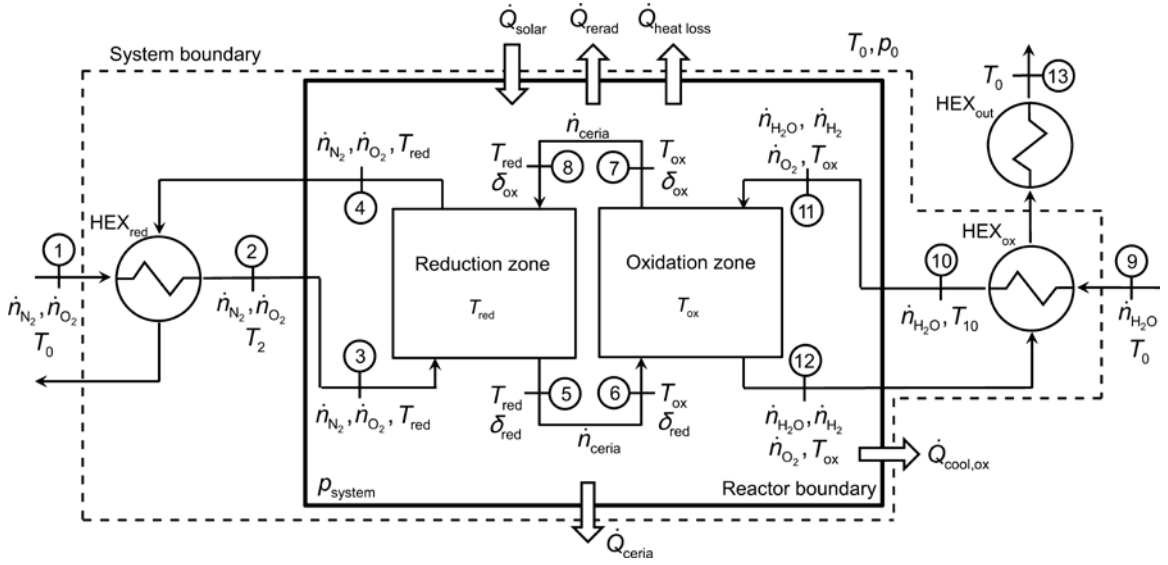
$\frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{H_2O} \rightarrow \frac{1}{\Delta\delta}\mathrm{MO}_{\mathrm{x}-\delta_{\mathrm{ox}}} + \mathrm{H}_2$ $\quad (T < 1000^{\circ}\mathrm{C}, \Delta_{\mathrm{r}}H_{\mathrm{ox}} = \Delta_{\mathrm{r}}H_{\mathrm{red}} - \Delta_{\mathrm{r}}H_{\mathrm{WT}} < 0)$

- 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 and Objective

- Moving oxide systems have high theoretical performance (countercurrent effect)
- Multiple models in the literature incorporate incorrect thermodynamics (enforcing equilibrium on both reactor inlet and outlet – causing $\Delta_r G > 0$ in the reactor)
- Incorrect thermodynamics impact system performance and TEA results (underestimation of sweep gas and oxidizer gas requirements)



R. Bader, L. J. Venstrom, J. H. Davidson, and W. Lipiński, "Thermodynamic Analysis of Isothermal Redox Cycling of Ceria for Solar Fuel Production," *Energy & Fuels*, vol. 27, no. 9, pp. 5533–5544, Sep. 2013, doi: 10.1021/ef400132d.

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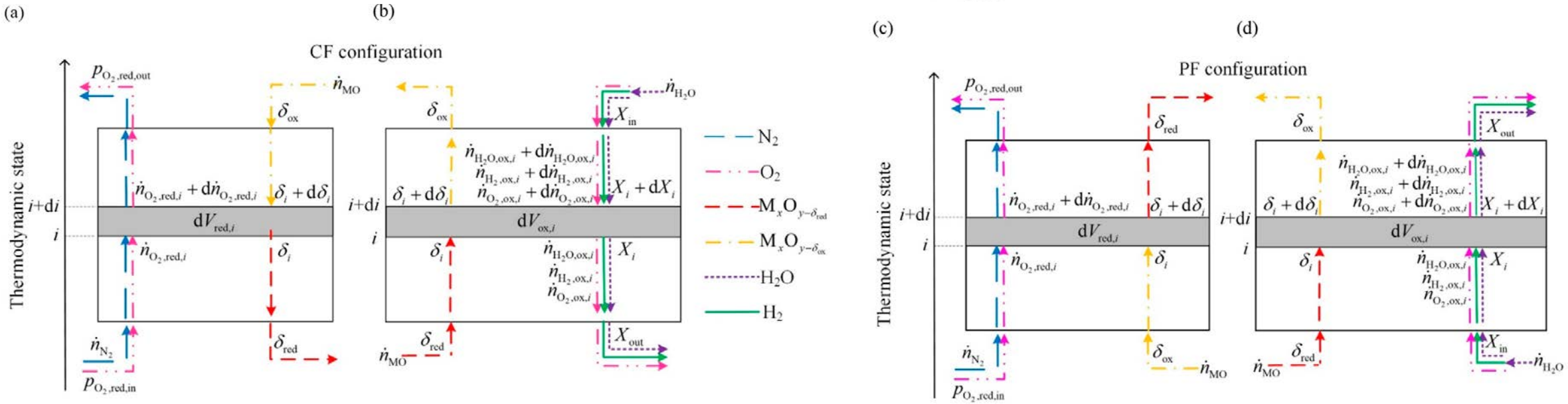
Objectives

- Developing a simple thermodynamics model incorporating thermodynamics limits
- Integrating energy/sizing correlations for the required auxiliaries
- Publishing an open-source code to be used by the community

Useful tool for redox material screening research, quick feasibility studies, promoting the field (like so many CST tools such as SAM, SolarPILOT, SolTrace, etc.)

Previous Work

- Adding Gibbs' criteria ($\mathrm{d}G \leq 0$) to a 1D countercurrent flow model (Li et al. [1-2])



[1] S. Li, V. M. Wheeler, P. B. Kreider, and W. Lipiński, "Thermodynamic Analyses of Fuel Production via Solar-Driven Non-stoichiometric Metal Oxide Redox Cycling. Part 1. Revisiting Flow and Equilibrium Assumptions," *Energy & Fuels*, vol. 32, no. 10, pp. 10838–10847, Oct. 2018, doi: 10.1021/acs.energyfuels.8b02081.

[2] S. Li, V. M. Wheeler, P. B. Kreider, R. Bader, and W. Lipiński, "Thermodynamic Analyses of Fuel Production via Solar-Driven Non-stoichiometric Metal Oxide Redox Cycling. Part 2. Impact of Solid–Gas Flow Configurations and Active Material Composition on System-Level Efficiency," *Energy & Fuels*, vol. 32, no. 10, pp. 10848–10863, Oct. 2018, doi: 10.1021/acs.energyfuels.8b02082.

[3] A. de la Calle, I. Ermanoski, J. E. Miller, and E. B. Stechel, "Towards chemical equilibrium in thermochemical water splitting. Part 2: Re-oxidation," *International Journal of Hydrogen Energy*, vol. 72, pp. 1159–1168, Jun. 2024, doi: 10.1016/j.ijhydene.2024.05.298.

[4] A. de la Calle, I. Ermanoski, and E. B. Stechel, "Towards chemical equilibrium in thermochemical water splitting. Part 1: Thermal reduction," *International Journal of Hydrogen Energy*, vol. 47, no. 19, pp. 10474–10482, Mar. 2022, doi: 10.1016/j.ijhydene.2021.07.167.

[5] B. Bulfin, "Thermodynamic limits of countercurrent reactor systems, with examples in membrane reactors and the ceria redox cycle," *Physical Chemistry Chemical Physics*, vol. 21, no. 4, pp. 2186–2195, 2019, doi: 10.1039/C8CP07077F.

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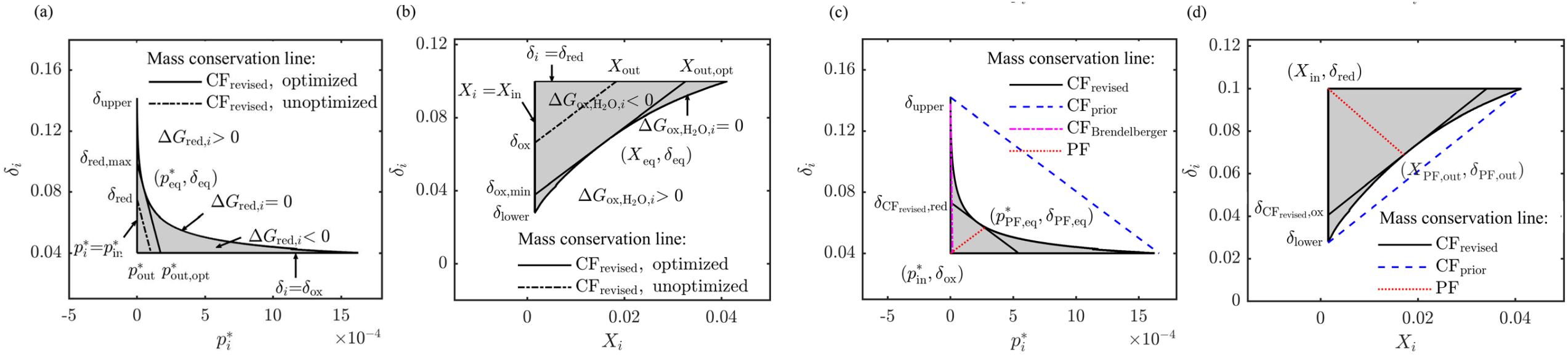

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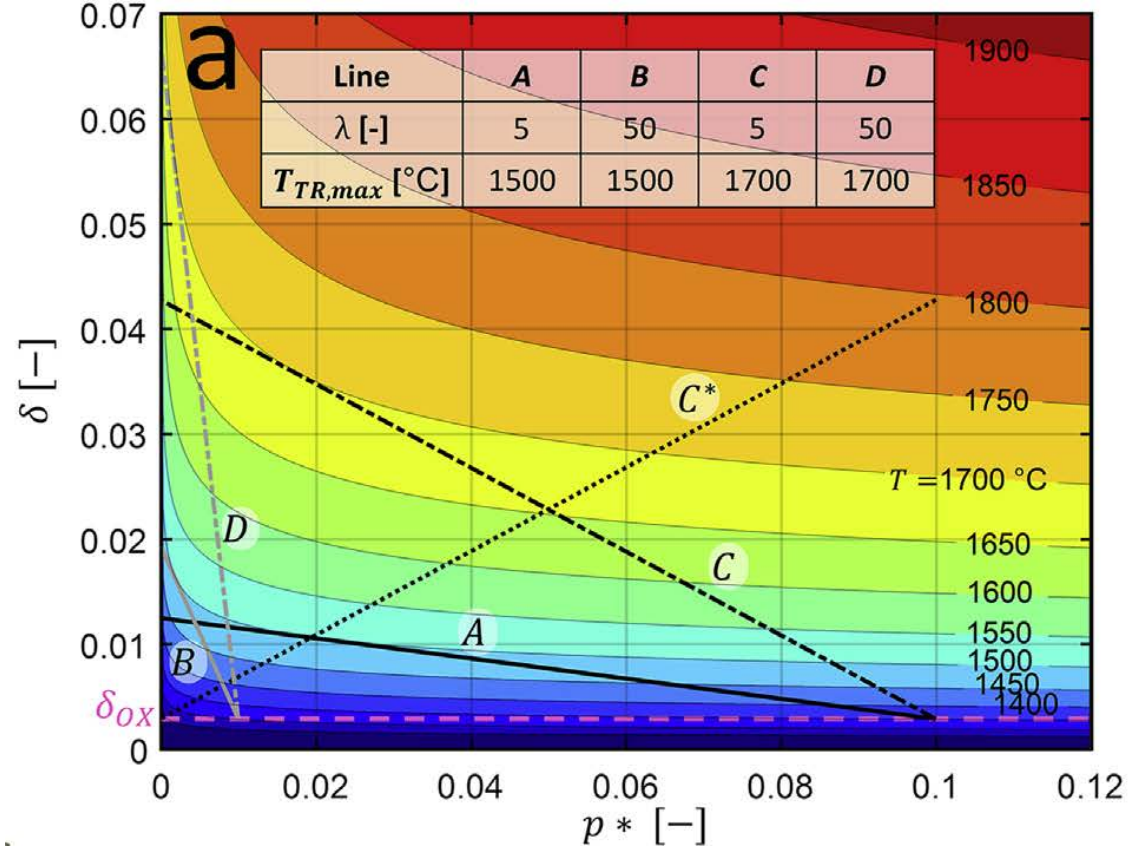

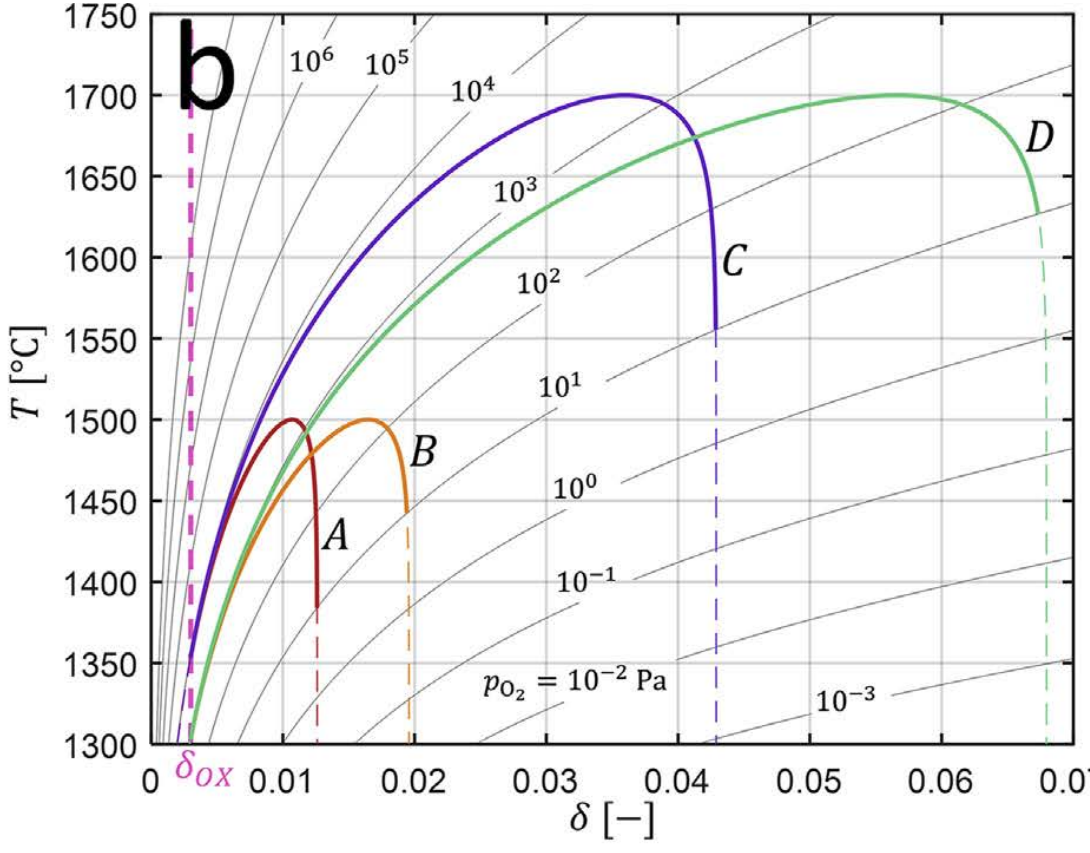

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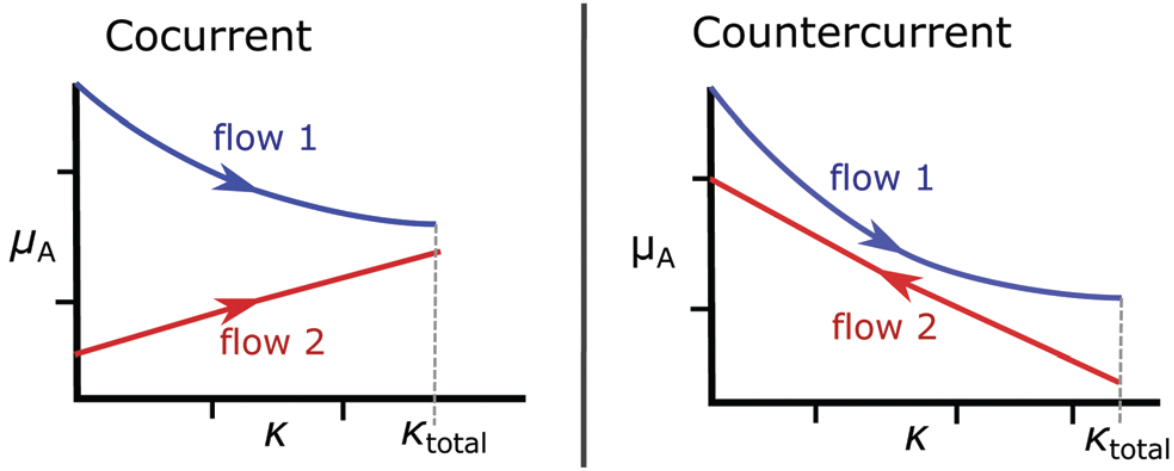

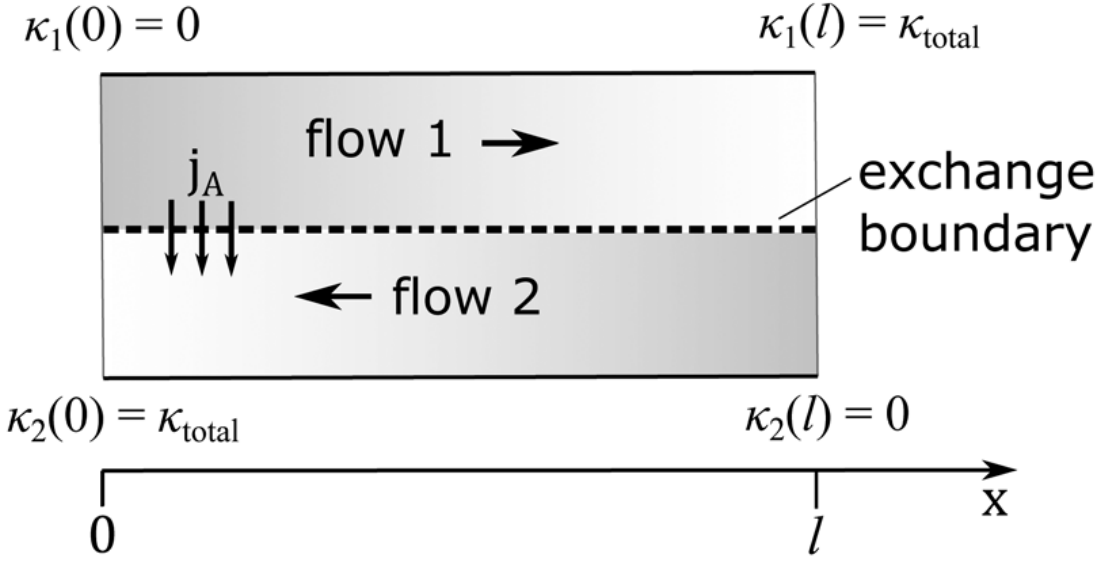

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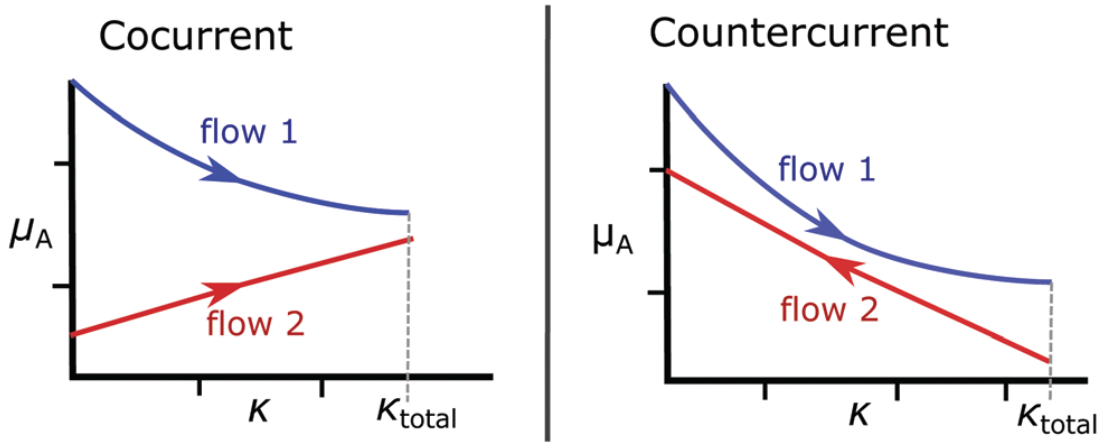
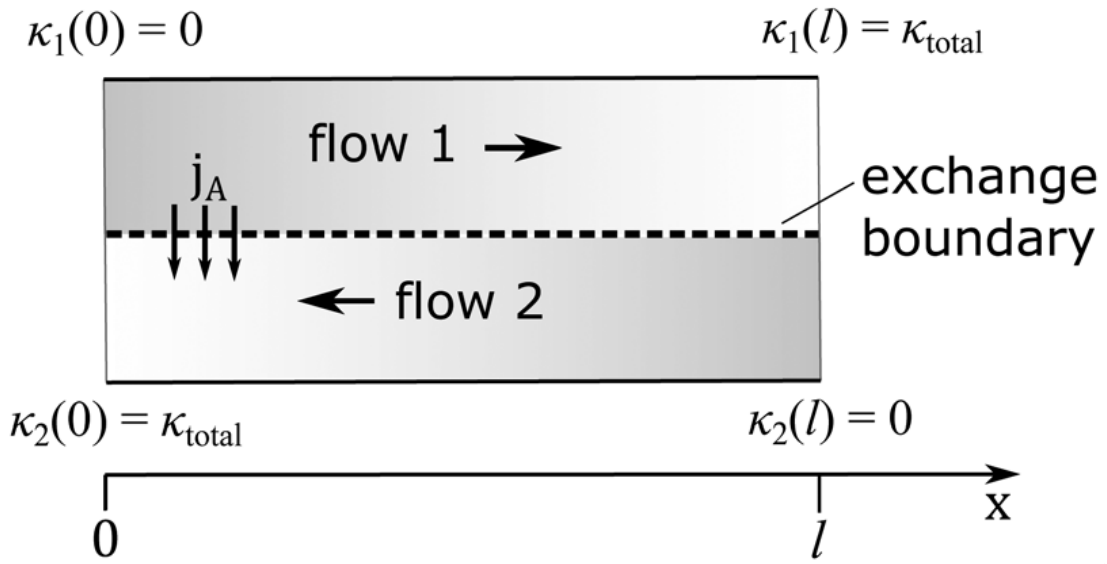
Thermodynamic Model

- Based on the methodology of Bulfin (2019) – extending to include oxidation
- Solved for a 0D isothermal isobaric reactor, used to calculate upper thermodynamic limit (no real process limitations such as heat/mass transfer are included)
- Defining an exchange coordinate: $\kappa(x) = \frac{\int_0^x |j_A(x)| dx}{\dot{n}_1}$ $(j_A = [\text{mol m}^{-1}\ \text{s}^{-1}])$
- Exchange species: O_2
- Parallel flow (cocurrent): $\kappa_1 = \kappa_2 \equiv \kappa$
- Countercurrent flow: $\kappa_1 = \kappa_2 - \kappa_{\text{total}} \equiv \kappa$





Thermodynamic Model

Reduction (Bulfin, 2019)

- Sweep gas-MO ratio: $\omega_{\mathrm{red}} = \frac{\dot{n}_{\mathrm{sweep}}}{\dot{n}_{\mathrm{MO}}}$
- O_2 impurity at inlet: ϕ_{red}
- O_2 chemical potential (MO):

$$p_{\mathrm{O_2}} = f(\delta(\Delta h, \Delta s), T)$$

$$p^{\mathrm{red}}_{\mathrm{O_2,sg}}(\kappa) = \frac{\phi\omega_{\mathrm{red}} + \kappa}{\omega_{\mathrm{red}} + \kappa}$$

$$p^{\mathrm{red}}_{\mathrm{O_2,MO}}(\kappa) = f(T, 2\kappa)$$

Oxidation (This work)

- Oxidizer gas-MO ratio: $\omega_{\mathrm{ox}} = \frac{\dot{n}_{\mathrm{oxidizer}}}{\dot{n}_{\mathrm{MO}}}$
- Gas composition at inlet ($x_{\mathrm{reac,0}}$ / $x_{\mathrm{prod,0}}$): from equilibrium of water/CO_2 thermolysis or specified
- O_2 chemical potential (MO):

$$p_{\mathrm{O_2}} = f(\delta(\Delta h, \Delta s), T)$$

$$p^{\mathrm{ox}}_{\mathrm{O_2,feed}}(\kappa) = p^{\circ}\left(K\frac{\omega_{\mathrm{ox}}x_{\mathrm{reac,0}} - 2\kappa}{\omega_{\mathrm{ox}}x_{\mathrm{prod,0}} + 2\kappa}\right)^2$$

$$p^{\mathrm{ox}}_{\mathrm{O_2,MO}}(\kappa) = f(T, \delta_{\mathrm{red}} - 2\kappa)$$

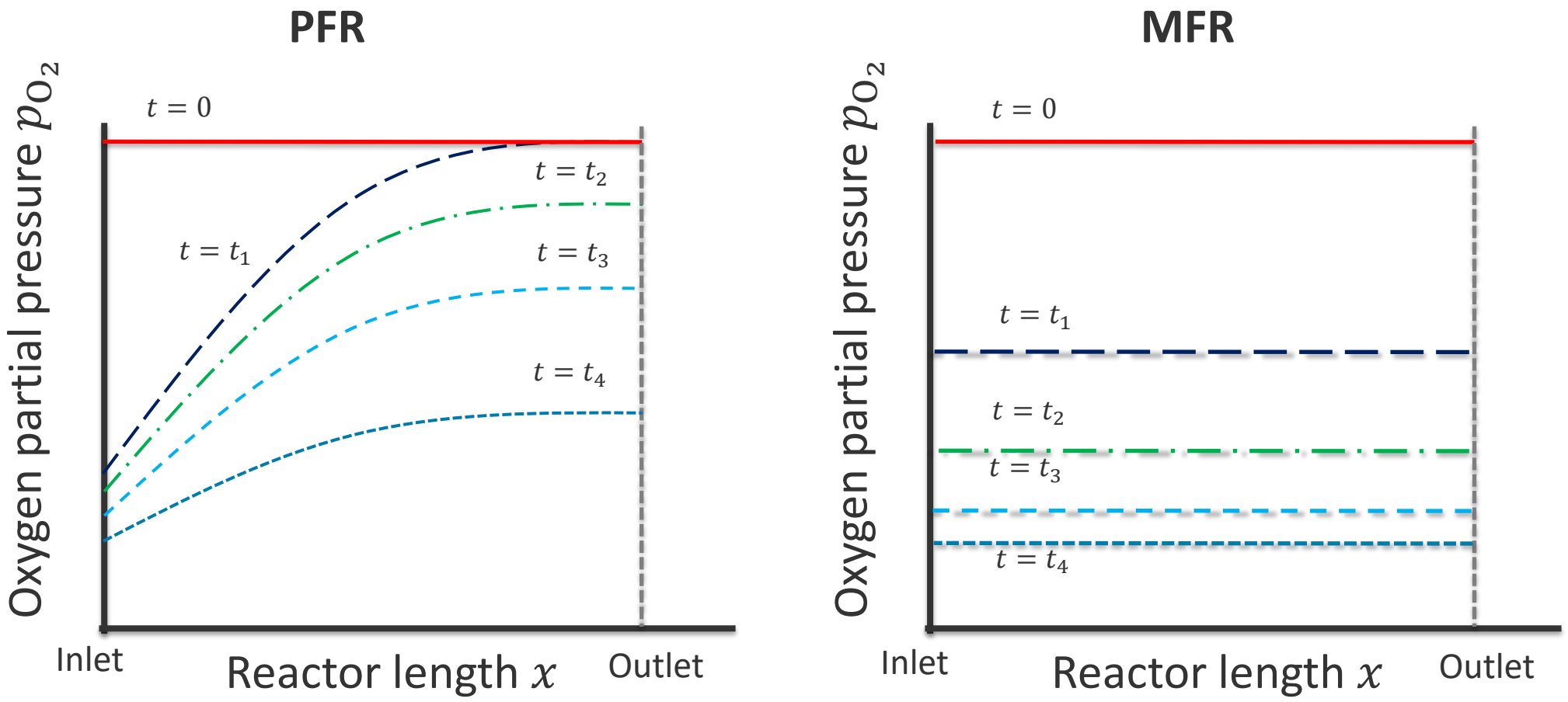
- Reduction extent relation to exchange coordinate: $\delta = 2\kappa$
- Equilibrium thermodynamics: $\delta = f\left(T, p_{\mathrm{O_2}}\right)$

Methodology and Implementation

- Solving numerically from $\kappa = 0$ until κ_{total} (chemical potentials meet) or $\kappa_{\max}$
- Implemented in MATLAB
- Developed as a tool (to be put as open source on GitHub)
- Multiple materials (needs functions of $\Delta H_{\text{red}}(\delta)$ and $\Delta S_{\text{red}}(\delta)$)
- Numerical solution, runtime 1-2 s (for a single set of parameters)
- Has parametric sweep options (T_{red}, T_{ox}, ω_{red}, ω_{ox}) and calculations of efficiency, conversion, and energy terms
- Has an optimization functionality for $\Delta\delta, X, \eta$ (4 optimization variables)
- Implemented comparison with 0D MFR approach [6-7] (**still finicky sometimes, very sensitive to IC and material**)

[6] T. C. Davenport, C.-K. Yang, C. J. Kucharczyk, M. J. Ignatowich, and S. M. Haile, "Maximizing fuel production rates in isothermal solar thermochemical fuel production," *Applied Energy*, vol. 183, pp. 1098–1111, Dec. 2016, doi: 10.1016/j.apenergy.2016.09.012.
[7] L. J. Venstrom, R. M. D. Smith, R. B. Chandran, D. B. Boman, P. T. Krenzke, and J. H. Davidson, "Applicability of an Equilibrium Model to Predict the Conversion of CO 2 to CO via the Reduction and Oxidation of a Fixed Bed of Cerium Dioxide," *Energy and Fuels*, vol. 29, no. 12, pp. 8168–8177, 2015, doi: 10.1021/acs.energyfuels.5b01865.

MFR Assumption – Validity in Large Packed Bed Reactor



Unlike the MFR assumption, packed bed reactor undergoing chemical looping will exhibit chemical potential gradient

Implementation

- **Parametric sweeps over:** Reduction: $T_{\mathrm{red}}, \omega_{\mathrm{red}}$ $(p_{\mathrm{red}}, \phi_{\mathrm{red}})$
  Oxidation: $T_{\mathrm{ox}}, \omega_{\mathrm{ox}}$ $(p_{\mathrm{ox}}, x_{\mathrm{reac},0}, x_{\mathrm{prod},0})$
- **Materials implemented:** CeO_2
  CeZr20 ($Ce_{0.8}Ze_{0.2}O_2$)
  LCMA6464 ($La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O_3$)
  LSM40 ($La_{0.6}Sr_{0.4}MO_3$)
  Fe33Al67 ($Fe_{0.33}Al_{0.67}O_4$)
- **Oxidizers:** H_2O or CO_2
- **Oxidizer feedstock composition:** calculated equilibrium composition of H_2, H_2O, and O_2 (or CO, CO_2, and O_2)
  specific value can be provided
- **Flow patterns**: Parallel flow (PF)
  Countercurrent flow (CF)

Performance Metrics

Nonstoichiometry extent

$$\Delta\delta = \delta_{\mathrm{red}} - \delta_{\mathrm{ox}}$$

Conversion extent

$$X = 1 - \frac{n_{\mathrm{ox}}}{n_{\mathrm{ox},0}}$$

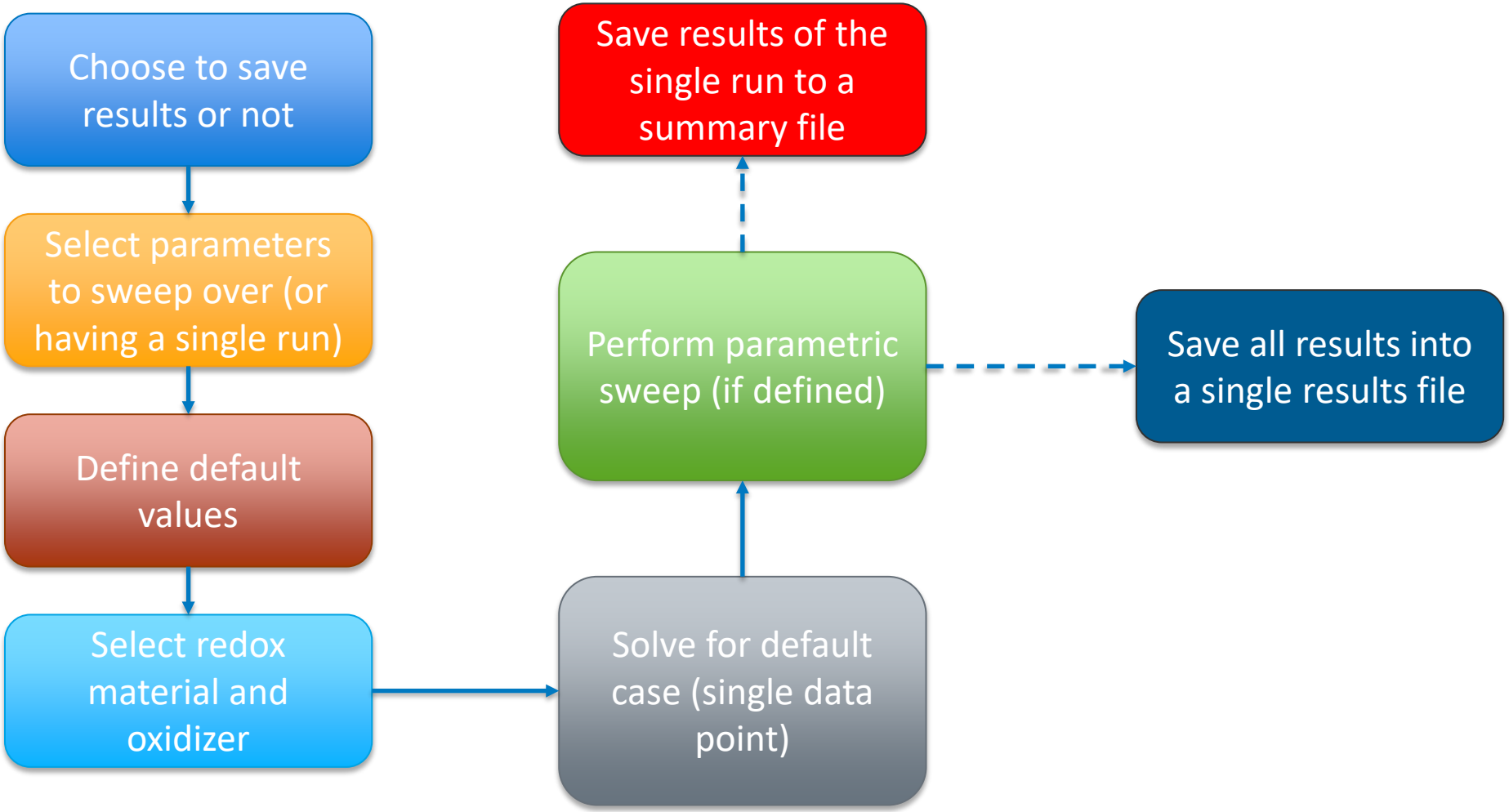
Specific energy terms:

$$F_{\mathrm{i}} = \frac{Q_{\mathrm{i}}}{Q_{\mathrm{fuel}}}$$

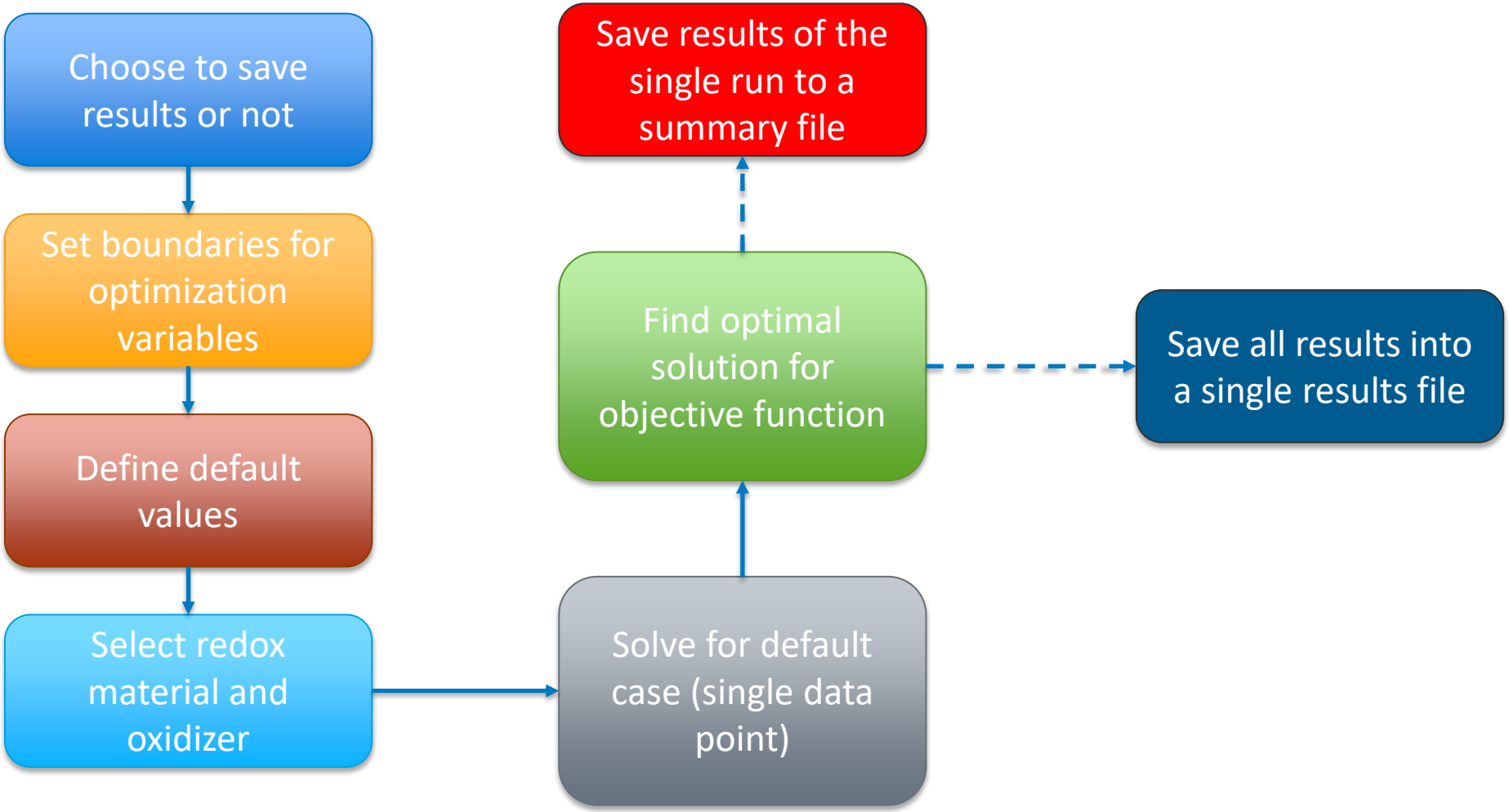
Process efficiency (excluding optical/receiver efficiency)

$$\eta = \frac{\dot{n}_{\mathrm{prod}}\mathrm{HHV}_{\mathrm{prod}}}{Q_{\mathrm{sens,MO}} + Q_{\mathrm{sens,gas}} + Q_{\mathrm{chem}} + W_{\mathrm{inert}} + W_{\mathrm{sep}} + W_{\mathrm{aux}}} = \frac{1}{\sum F_{\mathrm{i}}}$$

Code Logic Flow Chart – Parametric Sweep



Code Logic Flow Chart - Optimization



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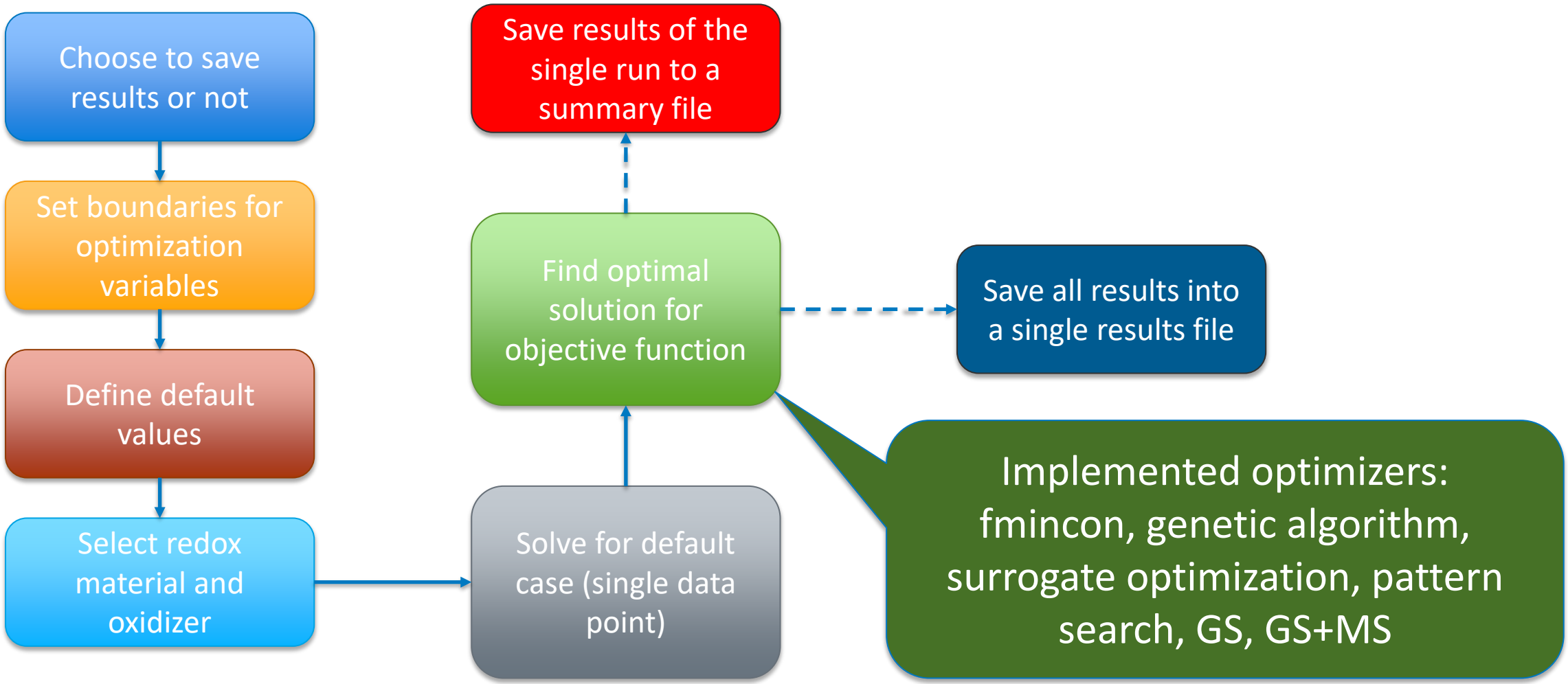
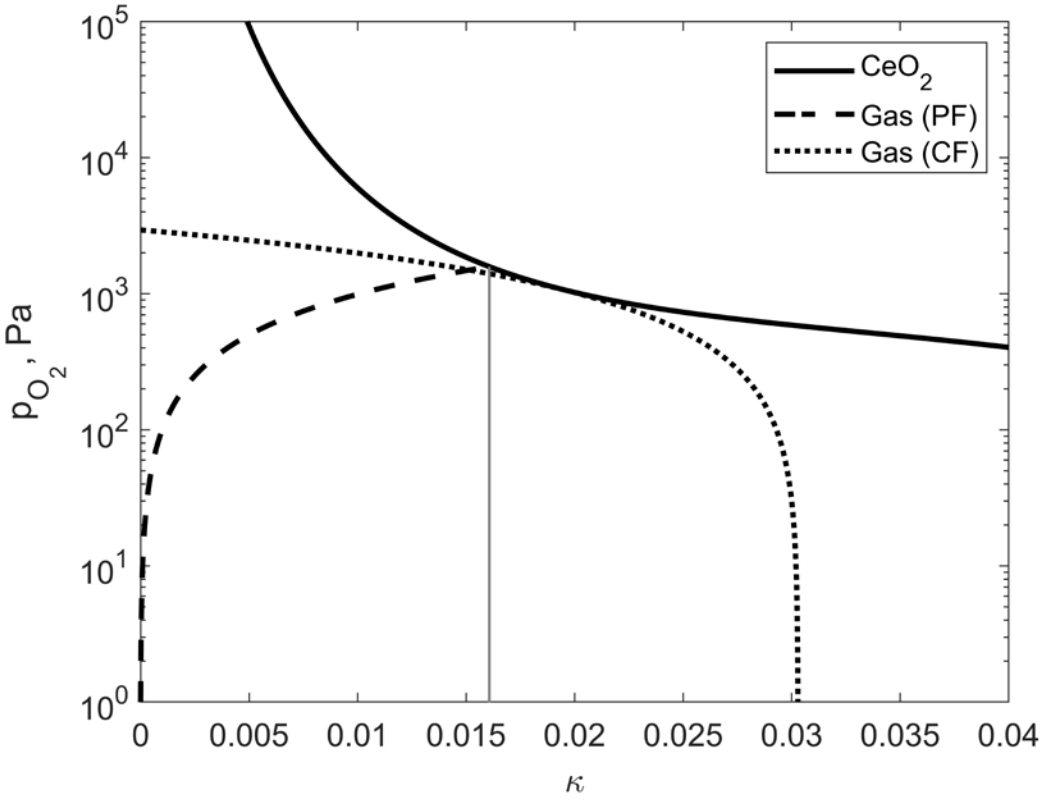


Results

Results (CeO_2)

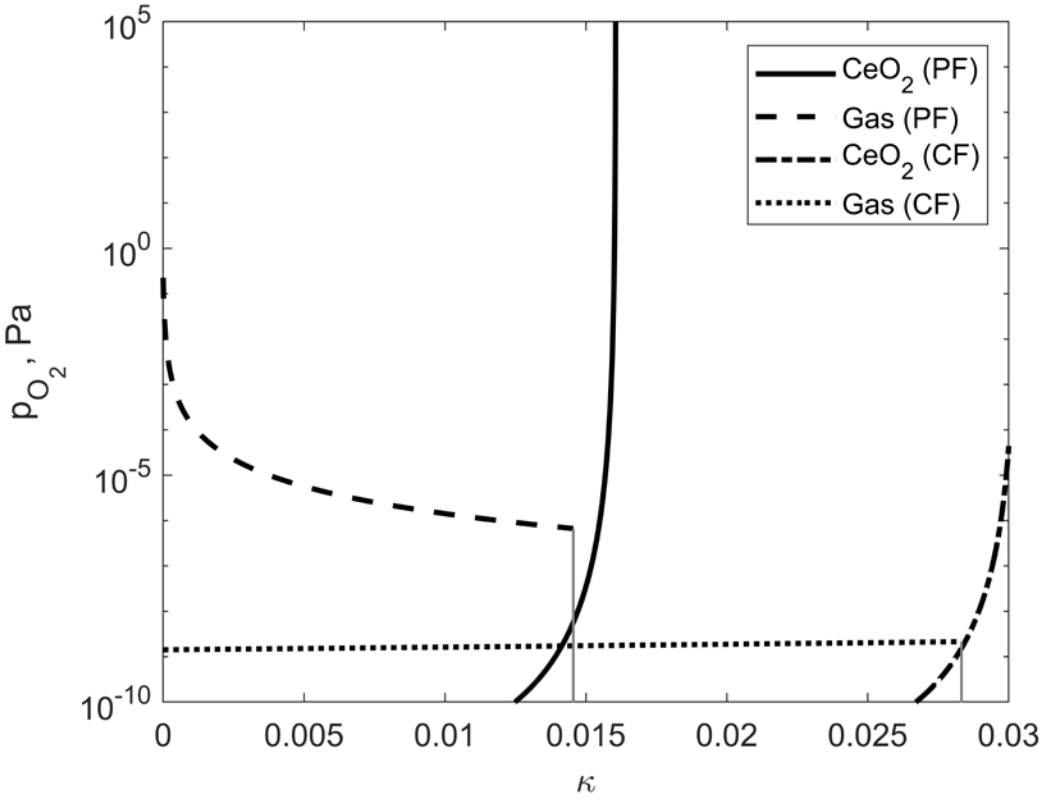
Reduction

- $\omega_{\mathrm{red}} = 1, \phi_{\mathrm{red}} = 10^{-5}$
- $T_{\mathrm{red}} = 1600°\mathrm{C}, p = 1\ \mathrm{bar}$



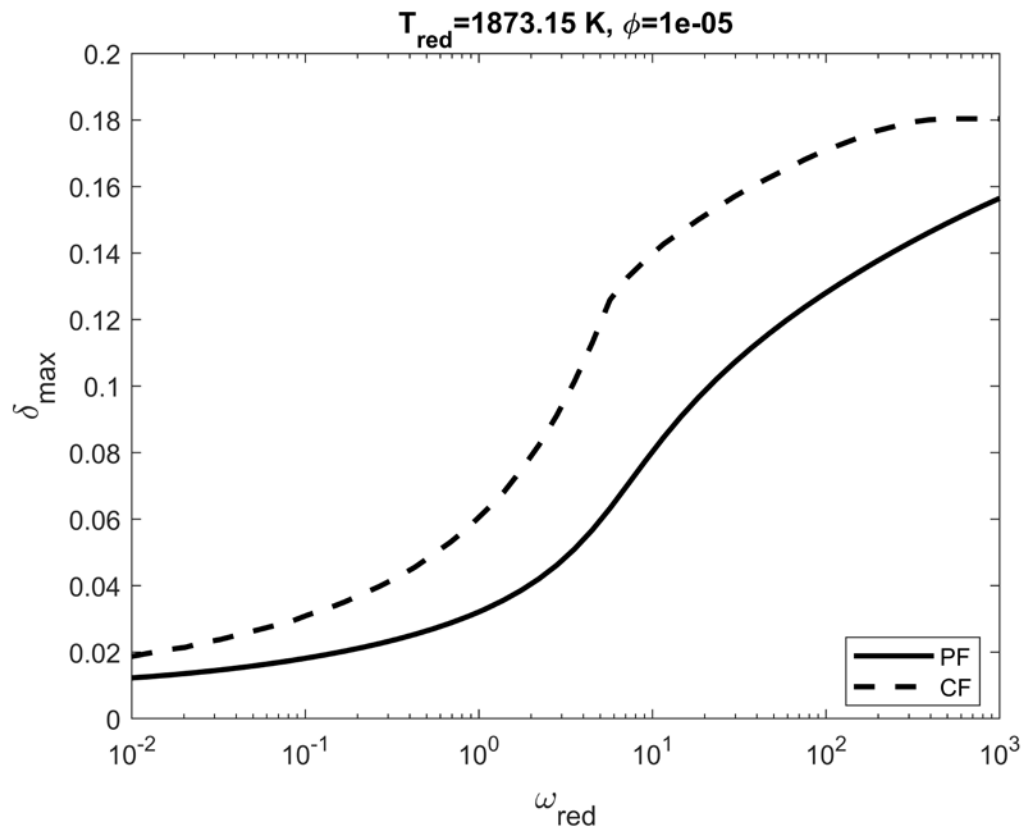
Oxidation

- $\omega_{\mathrm{ox}} = 1, x_{\mathrm{H_2}} = 4.8 \cdot 10^{-6}$
- $T_{\mathrm{ox}} = 900°\mathrm{C}, p = 1\ \mathrm{bar}$



Results (CeO_2) – Single Para Sweep

Reduction



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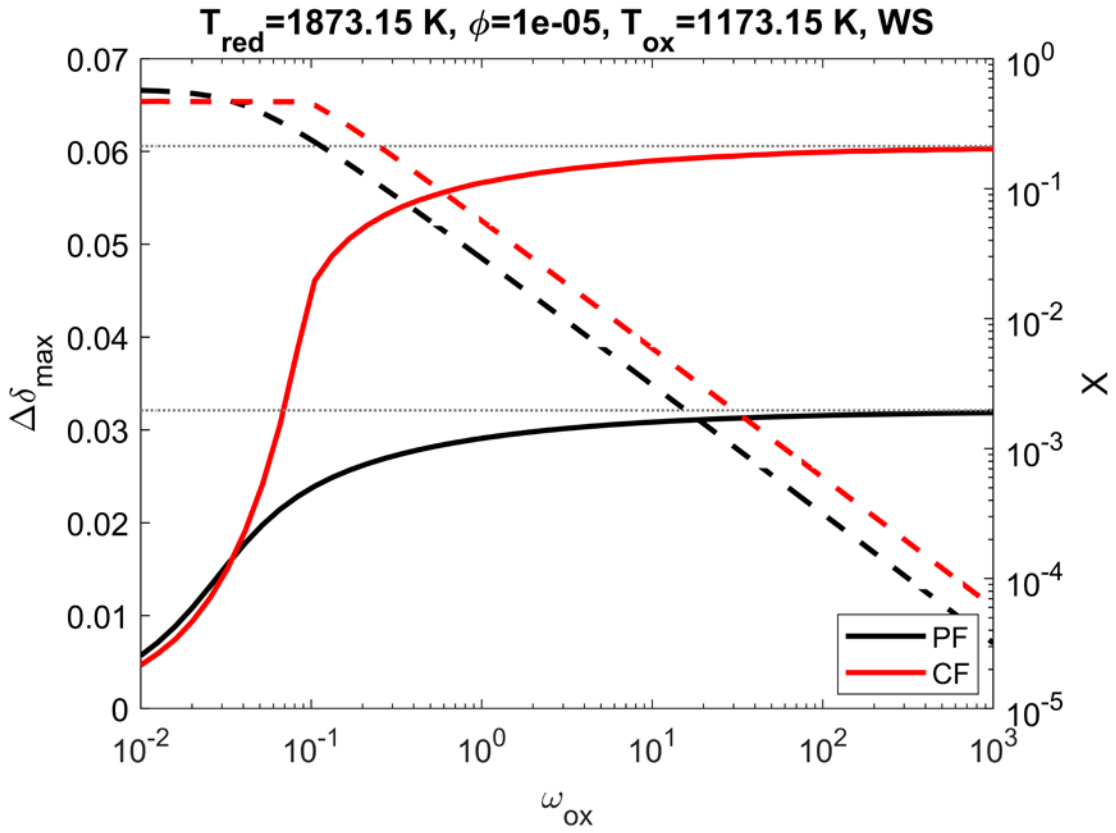

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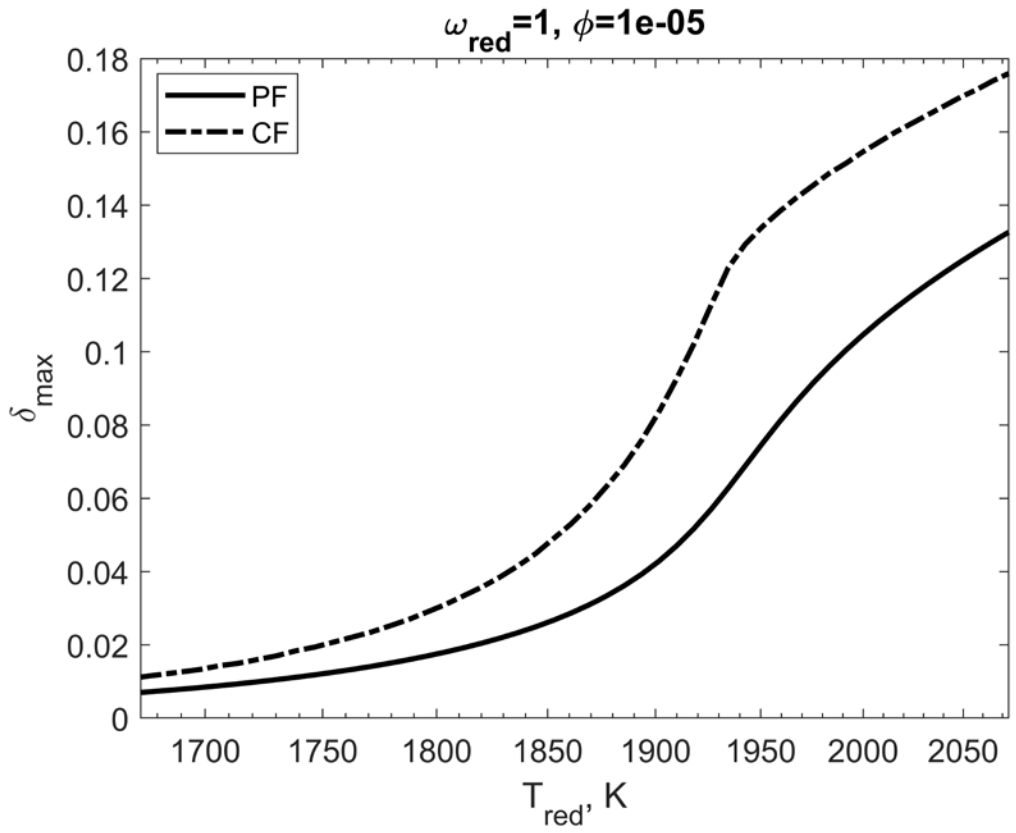

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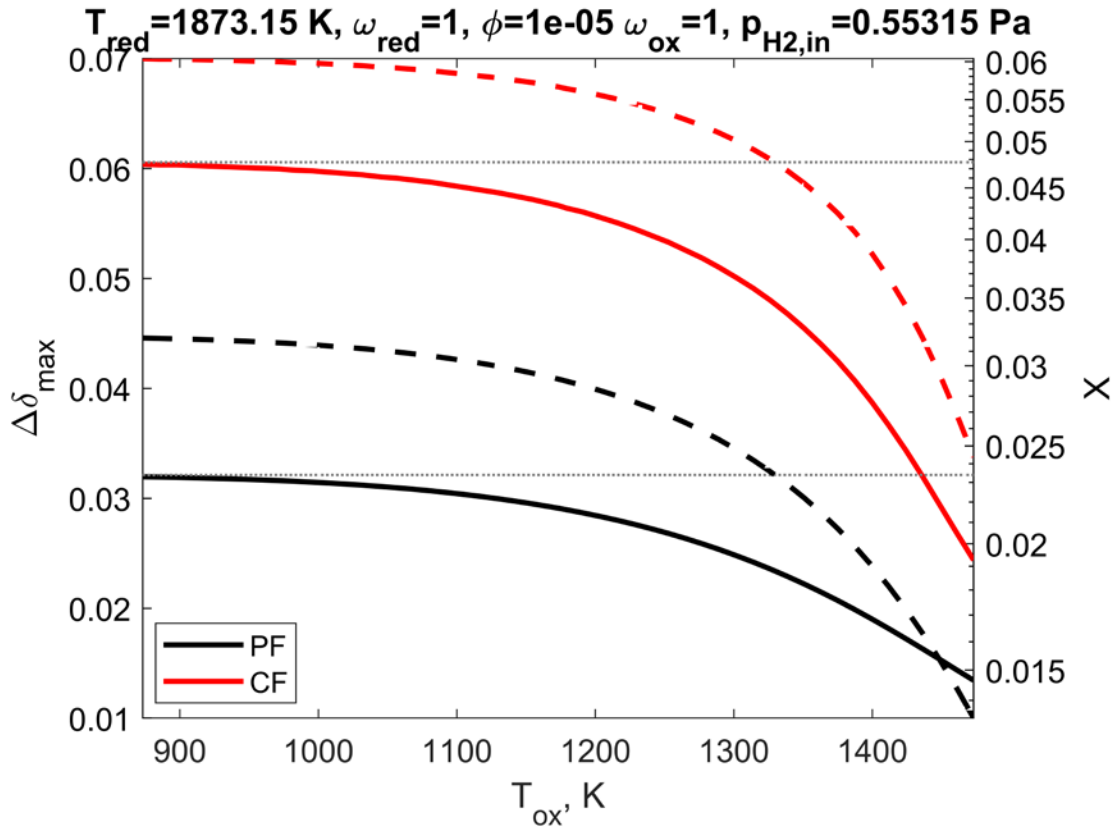
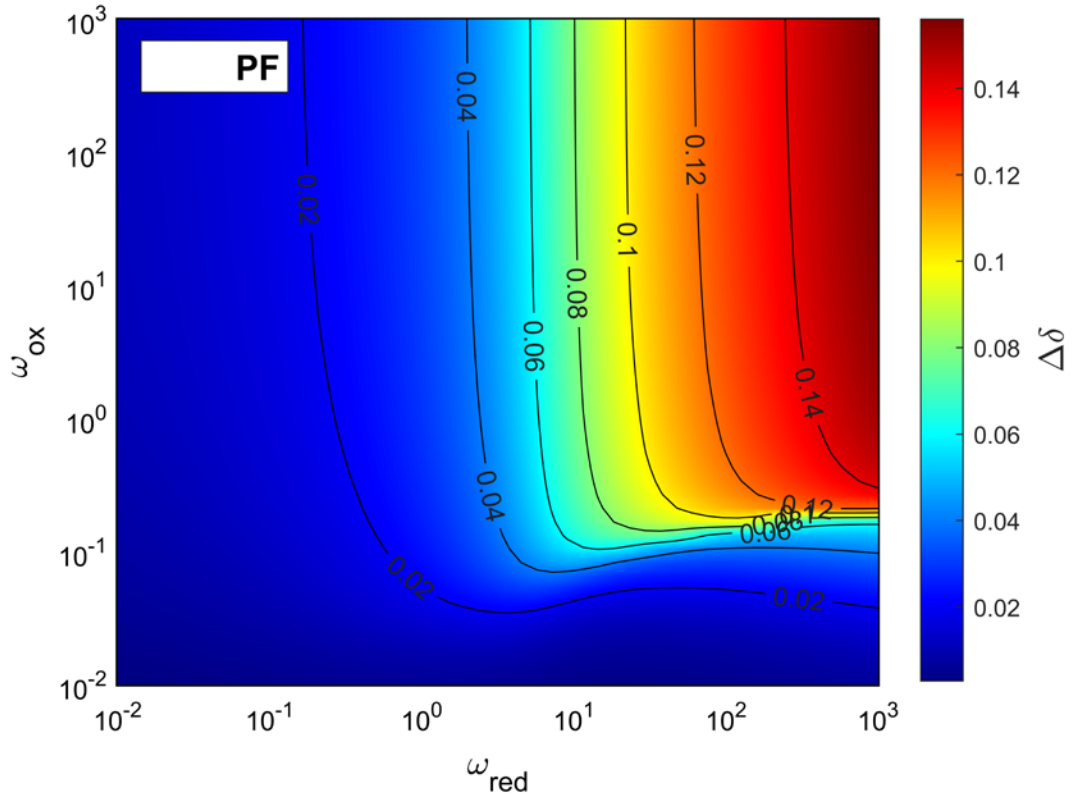
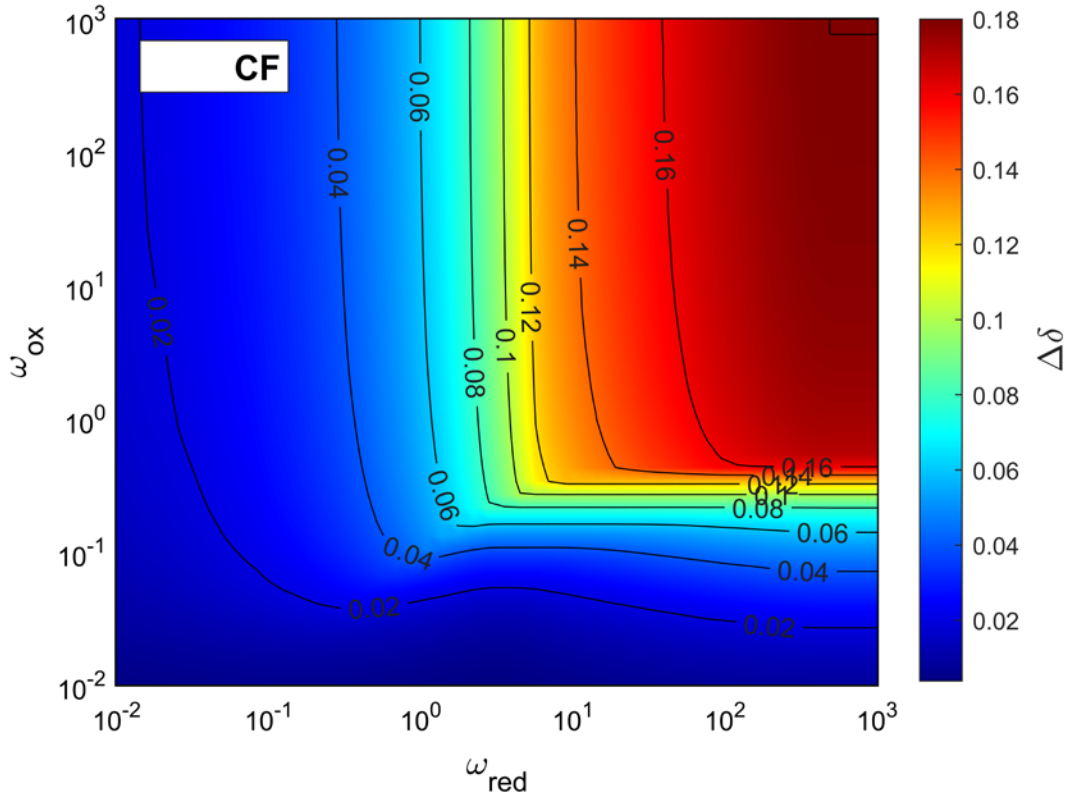


Results (CeO_2) – Two Parameters Sweep

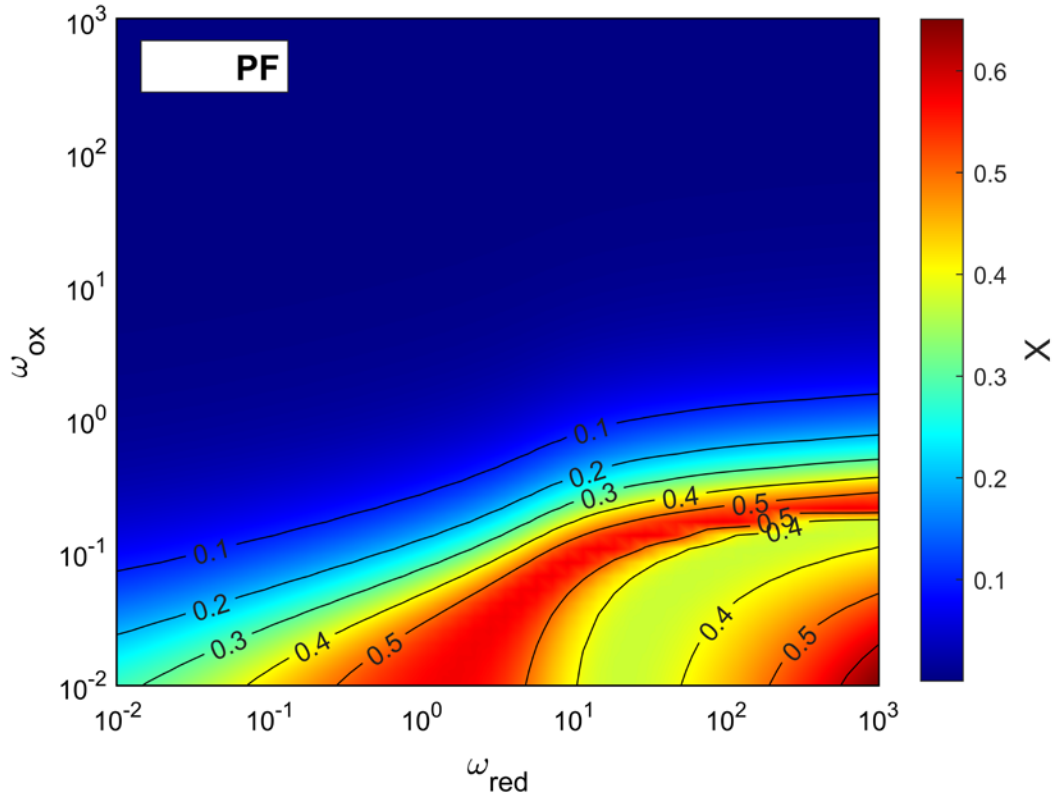
Molar flow rate ratios sweep – reduction extent

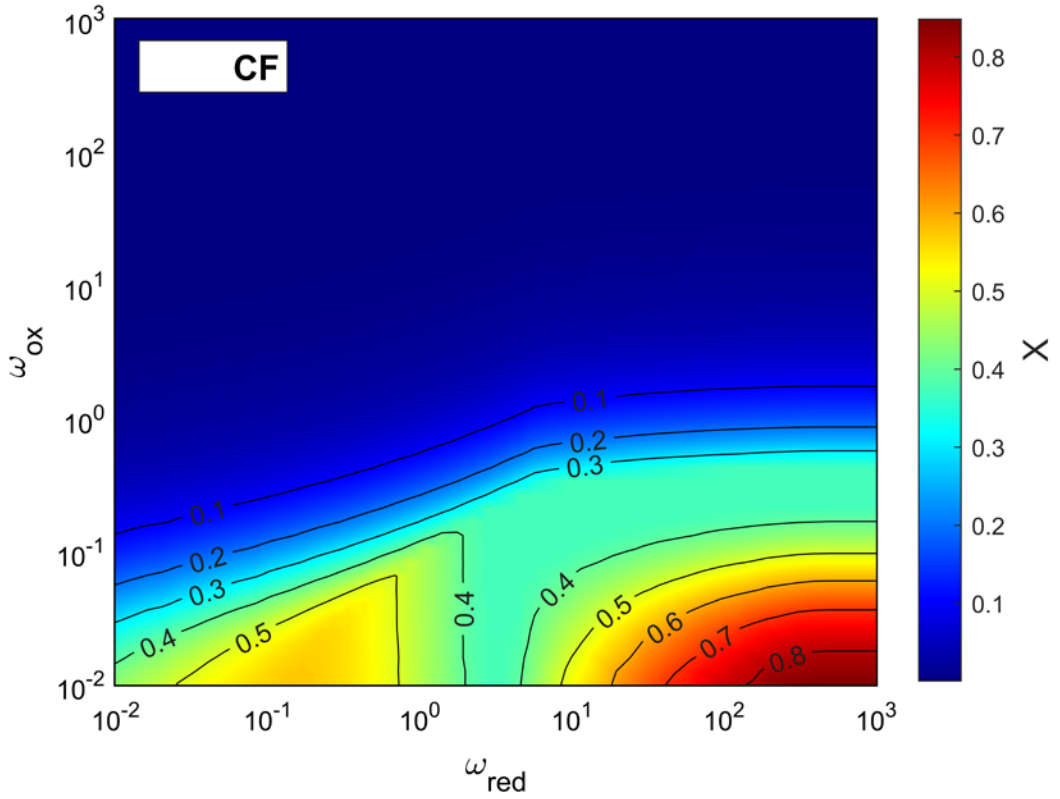




Results (CeO_2) – Two Parameters Sweep

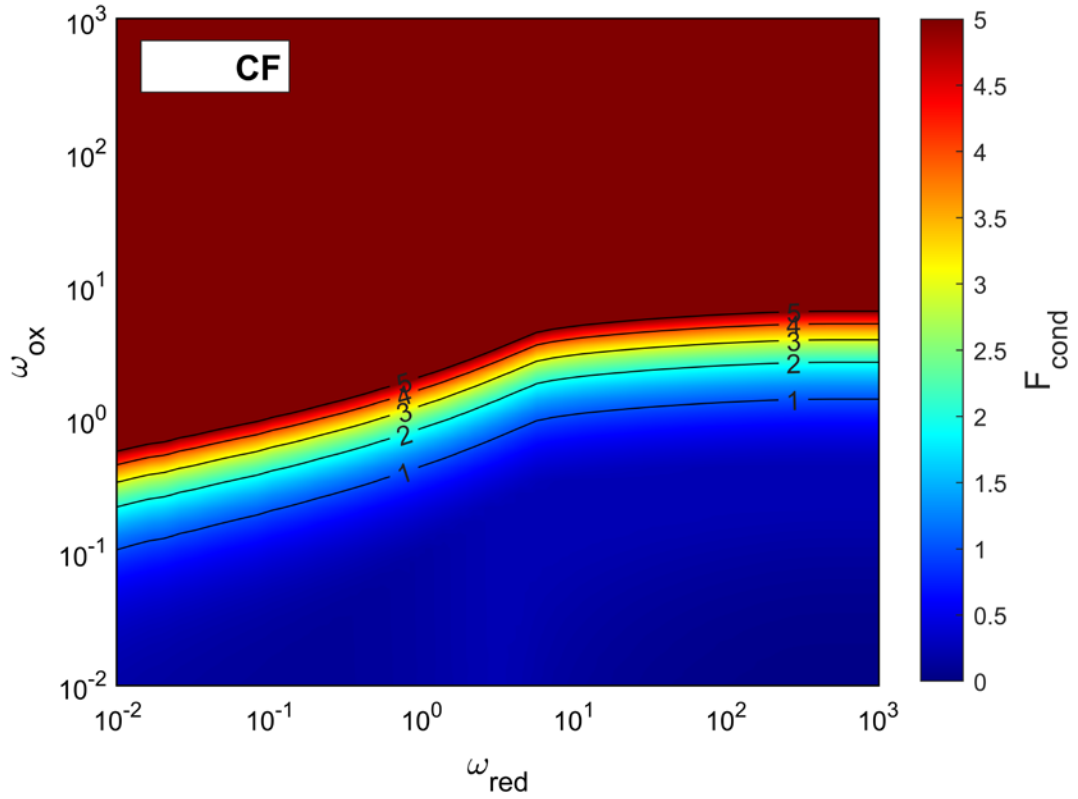
Molar flow rate ratios sweep - conversion

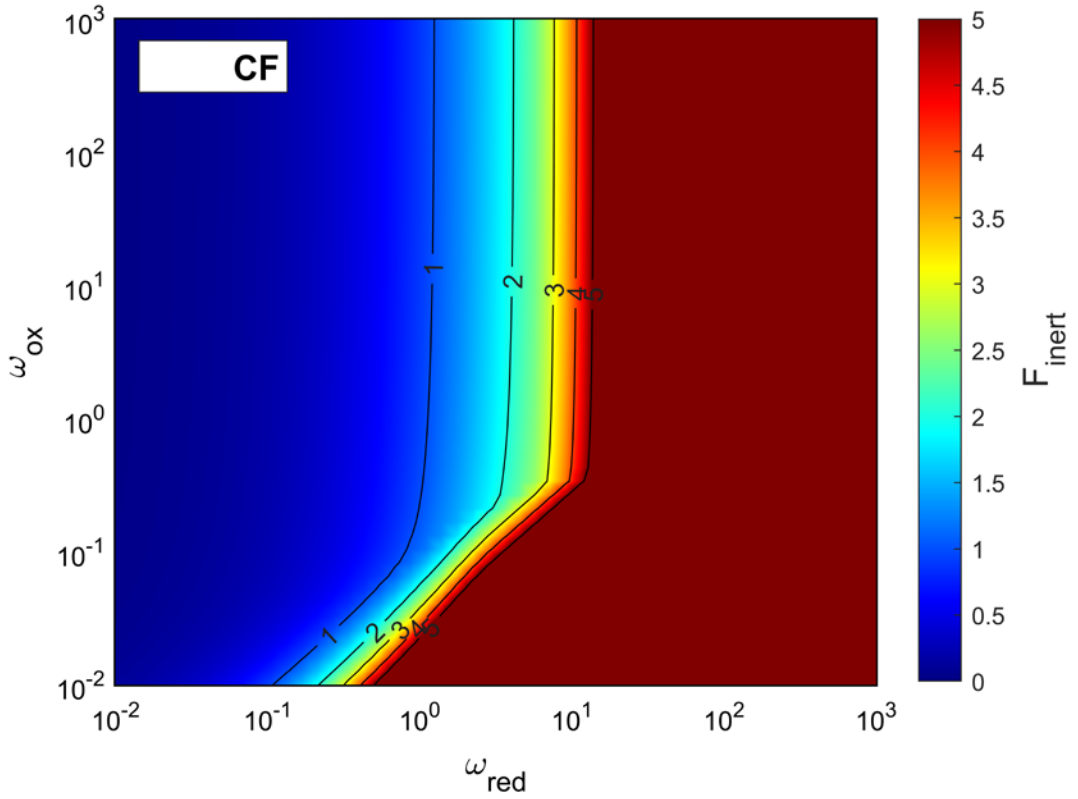




Results (CeO_2) – Two Parameters Sweep

Condensation (boiling) and inert gas separation (via cryogenic separation) specific energy requirements

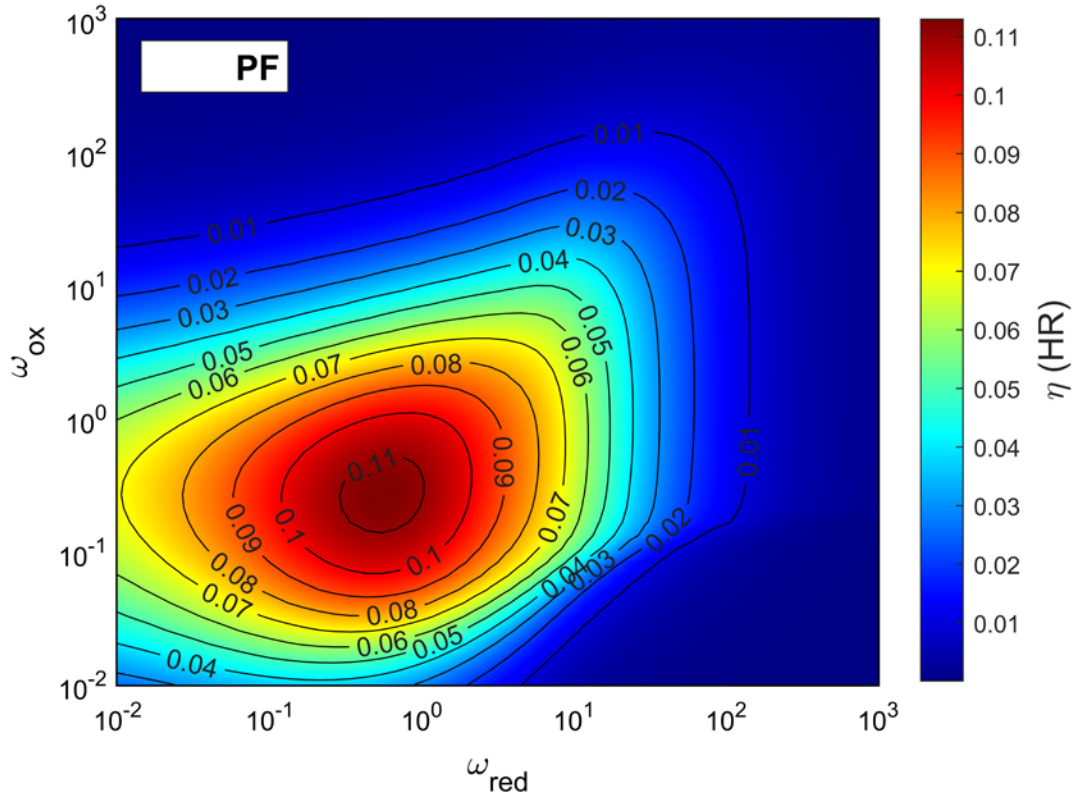


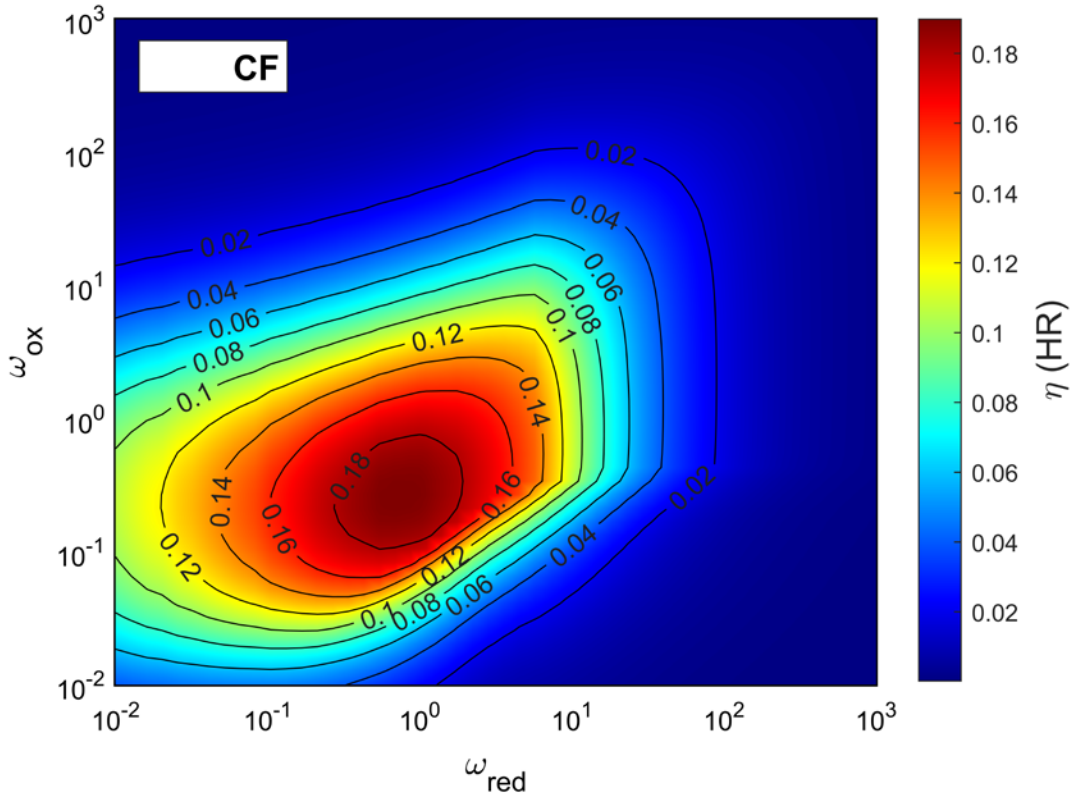


Competing requirements – different areas are beneficial for different terms

Results (CeO_2) – Two Parameters Sweep

Molar flow rate ratios sweep – efficiency (with HR): $\varepsilon_s = 0.5, \varepsilon_g = 0.8, \varepsilon_{ox} = 0.8$

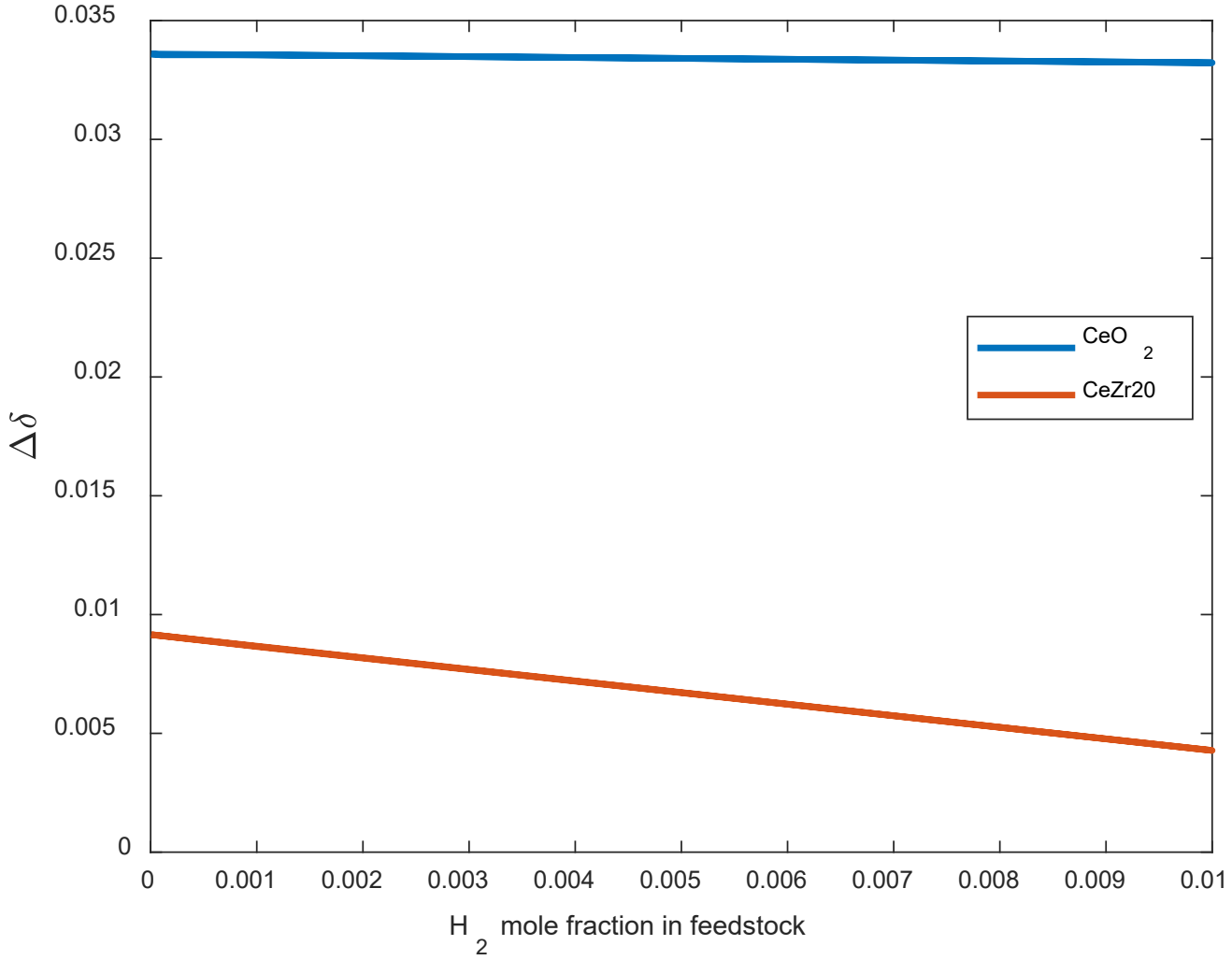




Highest efficiency is found in a "mean" performance area for the different terms

Results – Effect of Feedstock Composition

- Comparing the extent of nonstoichiometry for different materials under high H_2 mole fraction at the inlet during oxidation
- CeZr20 is more sensitive to H_2 mole fraction that CeO_2
- Relevant for “high-conversion” cycles (incomplete separation or multiple passes)

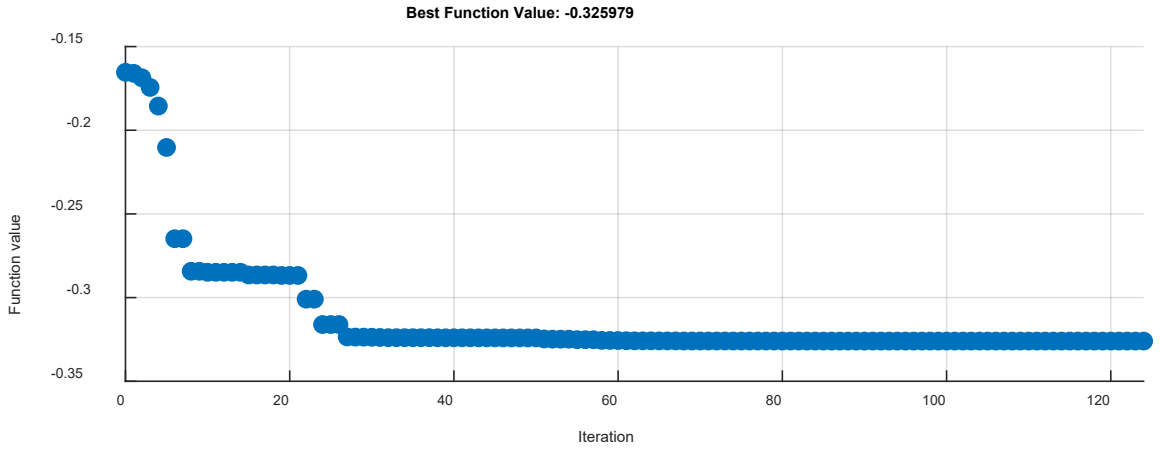


Results (CeO_2) – Optimization

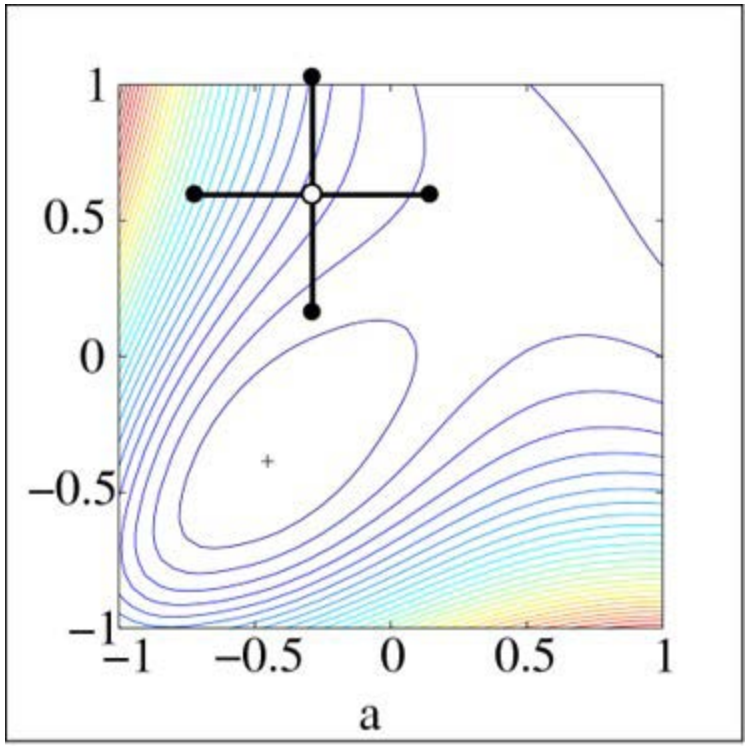
- Much faster than 2-parameter sweeps (~30-60 min compared to 4-8 hours for 50x50 points)
- Increased η from 18% to 32.6% at:

$$T_{\mathrm{red}} = 1973\ \mathrm{K}, T_{\mathrm{ox}} = 1029\ \mathrm{K},$$
$$\omega_{\mathrm{red}} = 0.4375, \omega_{\mathrm{ox}} = 0.1836$$

- Except T_{red}, no "instinct" on the effects of the other variables

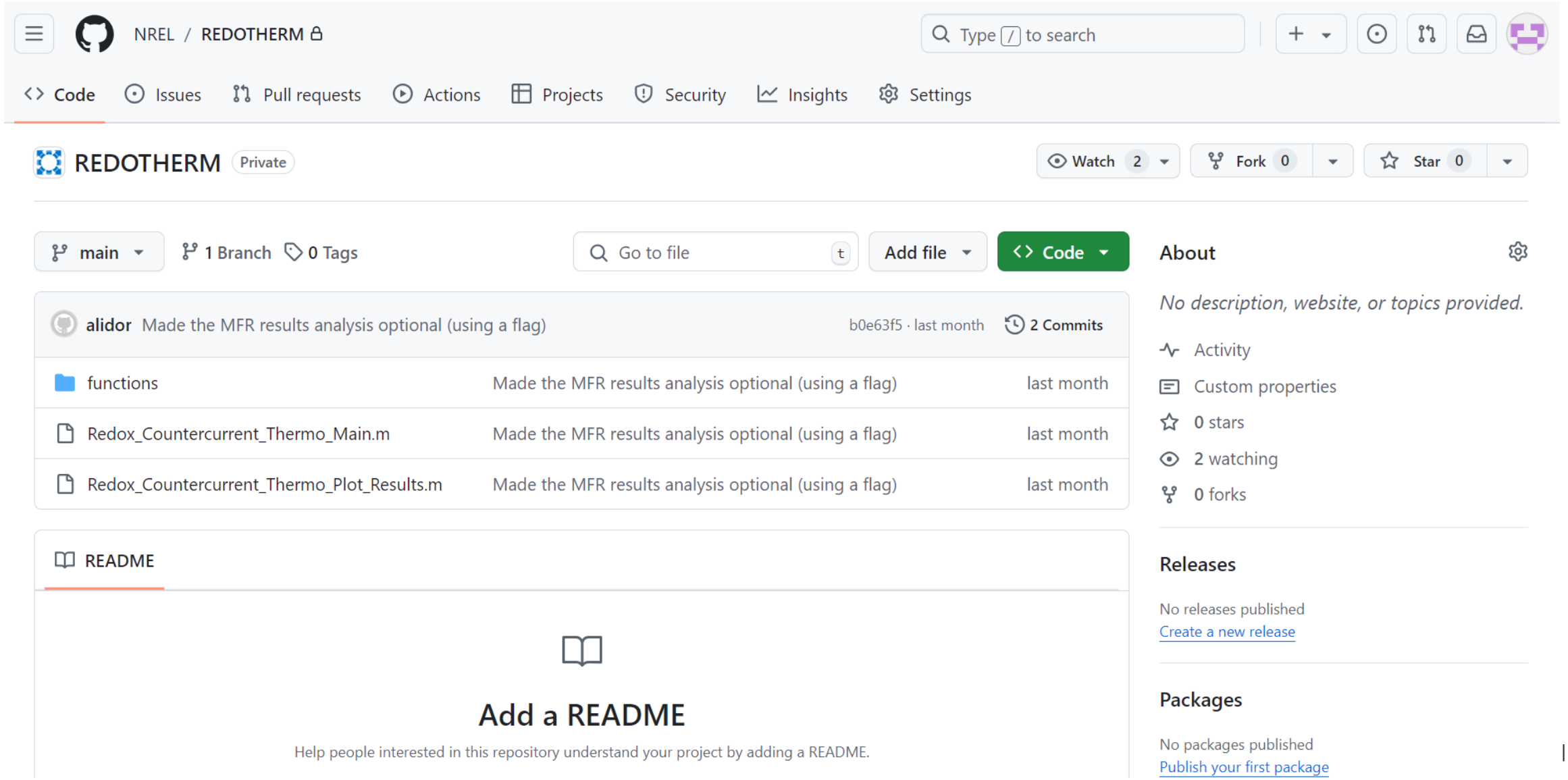


Pattern Search Optimization

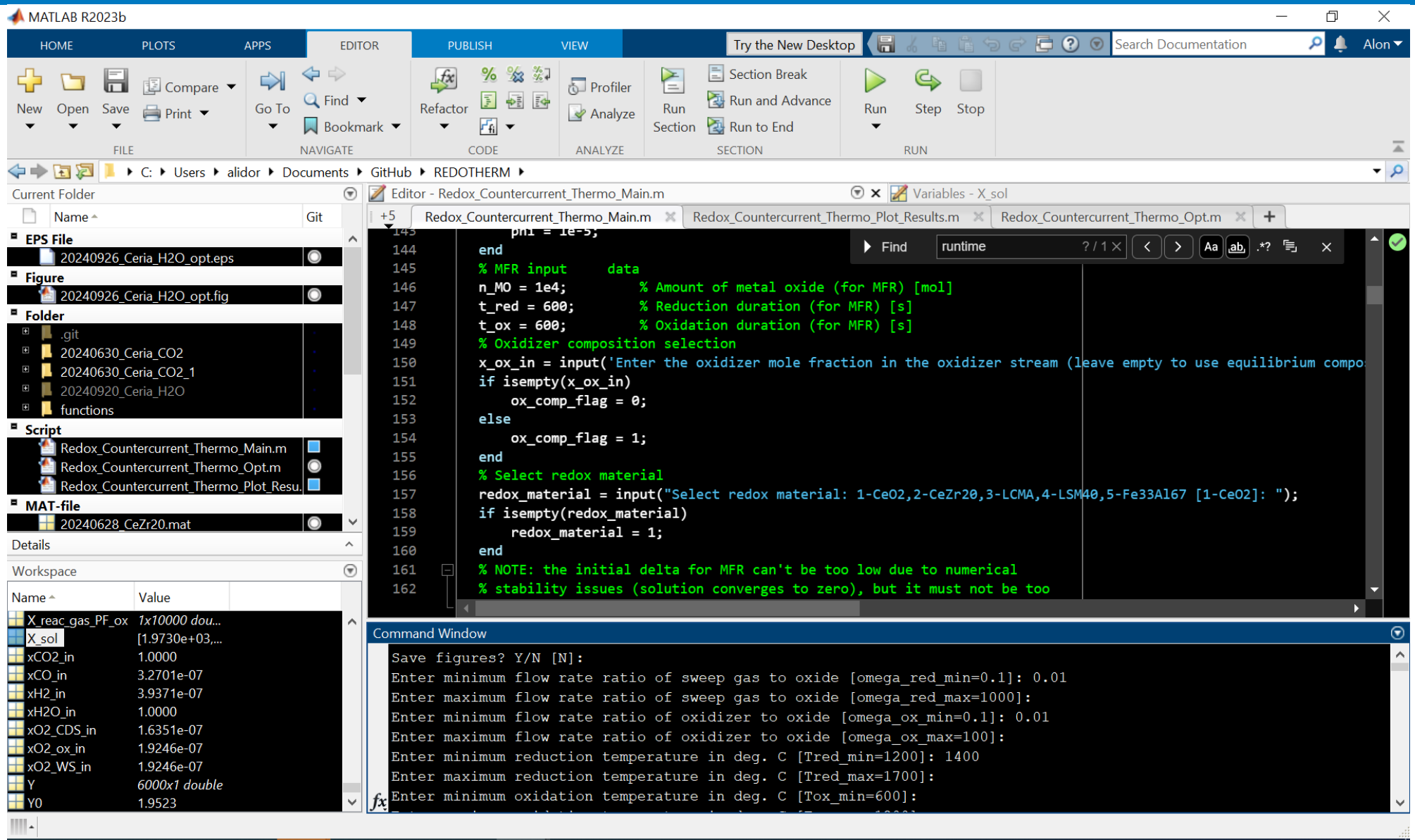


https://en.wikipedia.org/wiki/Pattern_search_(optimization)

Code on GitHub (not public yet!)



Code is Interactive and Well-Documented



Summary

- Thermodynamic model with "correct" $\Delta_r G$ limits implemented in MATLAB
- Both parametric sweeps and optimization solutions are implemented
- Publication will be submitted to *Frontiers in Energy Research* special issue *"Advanced Water Splitting Technologies Development: Best Practices and Protocols Volume II"*
- Code on GitHub will be made public together with the journal publication https://github.com/NREL/REDOTHERM

Future work:

- Adding multiple options for the auxiliary units (product separation, etc.)
- Including vacuum pumping
- Adding options for variable temperature $T(\kappa)$

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Brendan Bulfin

Thank you for you attention!

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