

Thermodynamic limits of redox-based thermochemical processes (REDOTHERM)

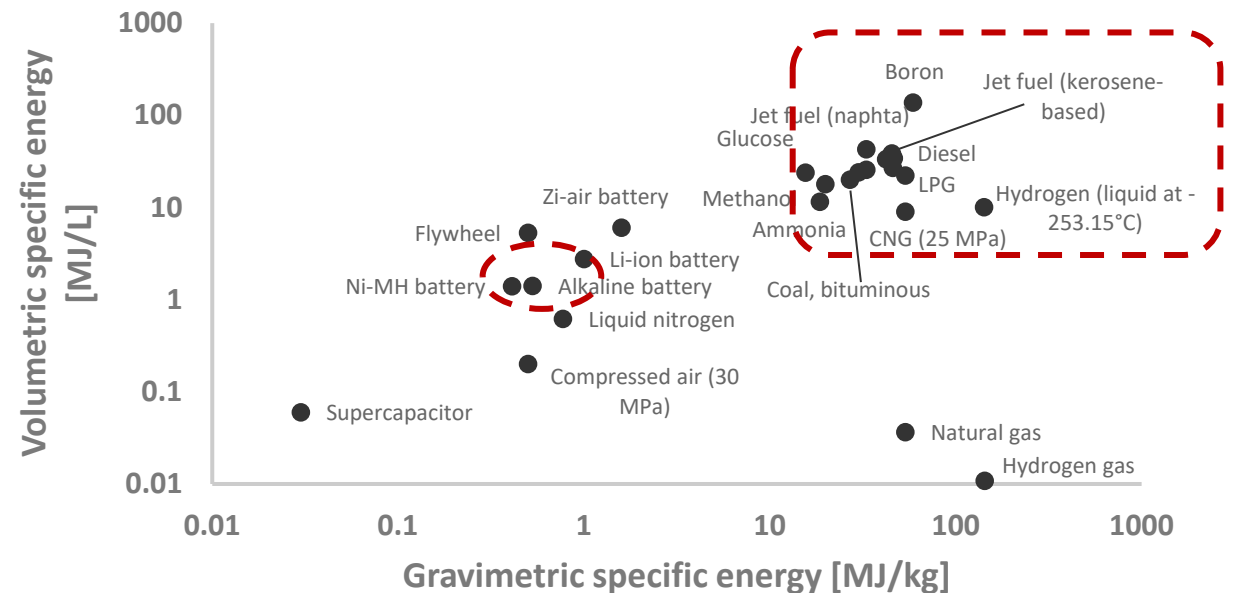
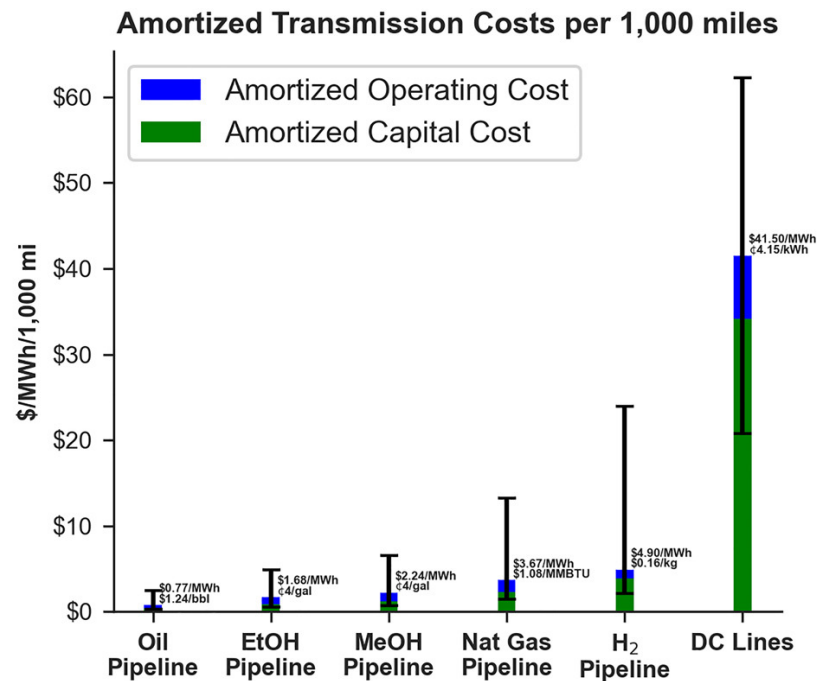
Alon Lidor

National Renewable Energy Laboratory

Oct 10, 2024

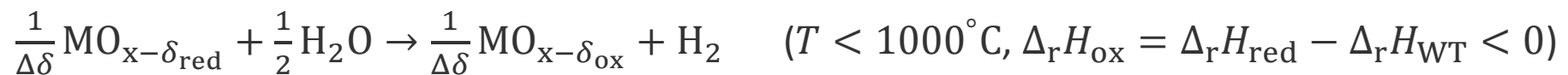
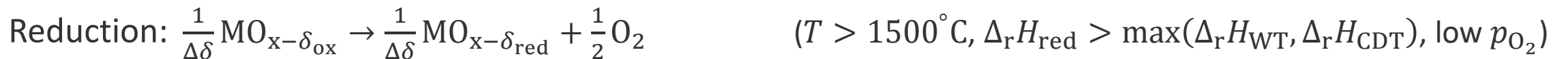
Background

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



Background

- Liquid fuels are critical in many sectors due to high specific energy ($12 - 13 \frac{\text{kWh}}{\text{kg}}$, $9 - 11 \frac{\text{kWh}}{\text{L}}$), 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:



- 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)

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)

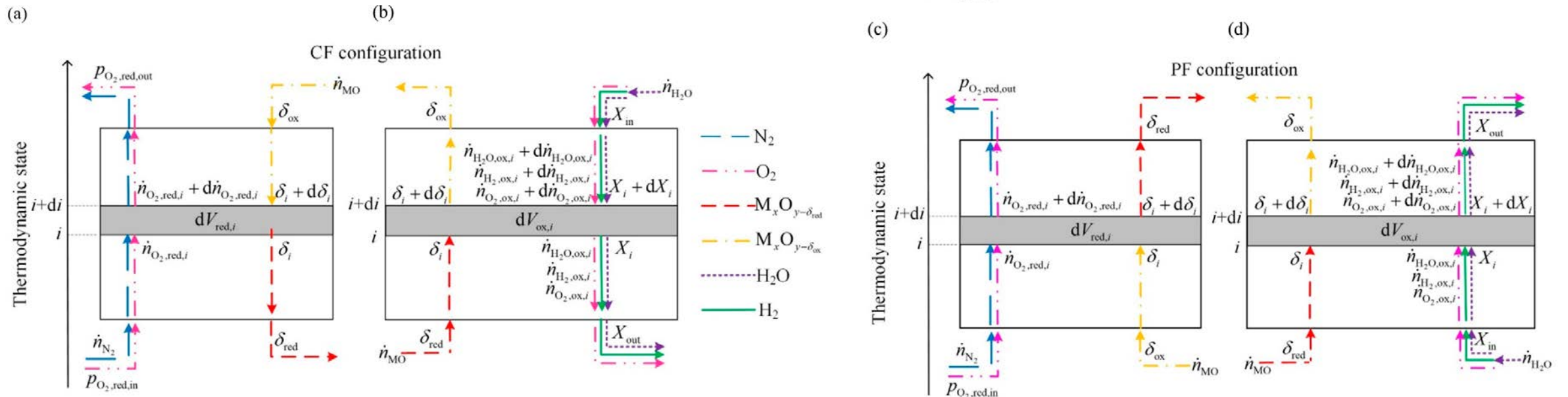
Objectives

- 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 ($dG \leq 0$) 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](https://doi.org/10.1021/acs.energyfuels.8b02081).

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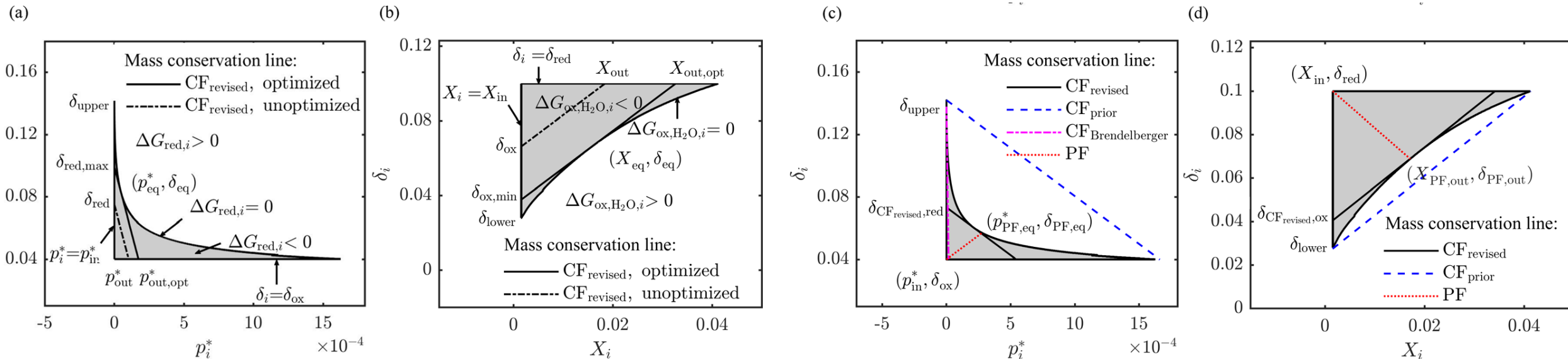
[3] A. de la Calle, I. Ermanoski, J. E. Miller, and E. B. Stechel, "Towards chemical equilibrium in thermochemical water splitting. Part 2: Re-oxidation," *International Journal of Hydrogen Energy*, vol. 72, pp. 1159–1168, Jun. 2024, doi: [10.1016/j.ijhydene.2024.05.298](https://doi.org/10.1016/j.ijhydene.2024.05.298).

[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](https://doi.org/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](https://doi.org/10.1039/C8CP07077F).

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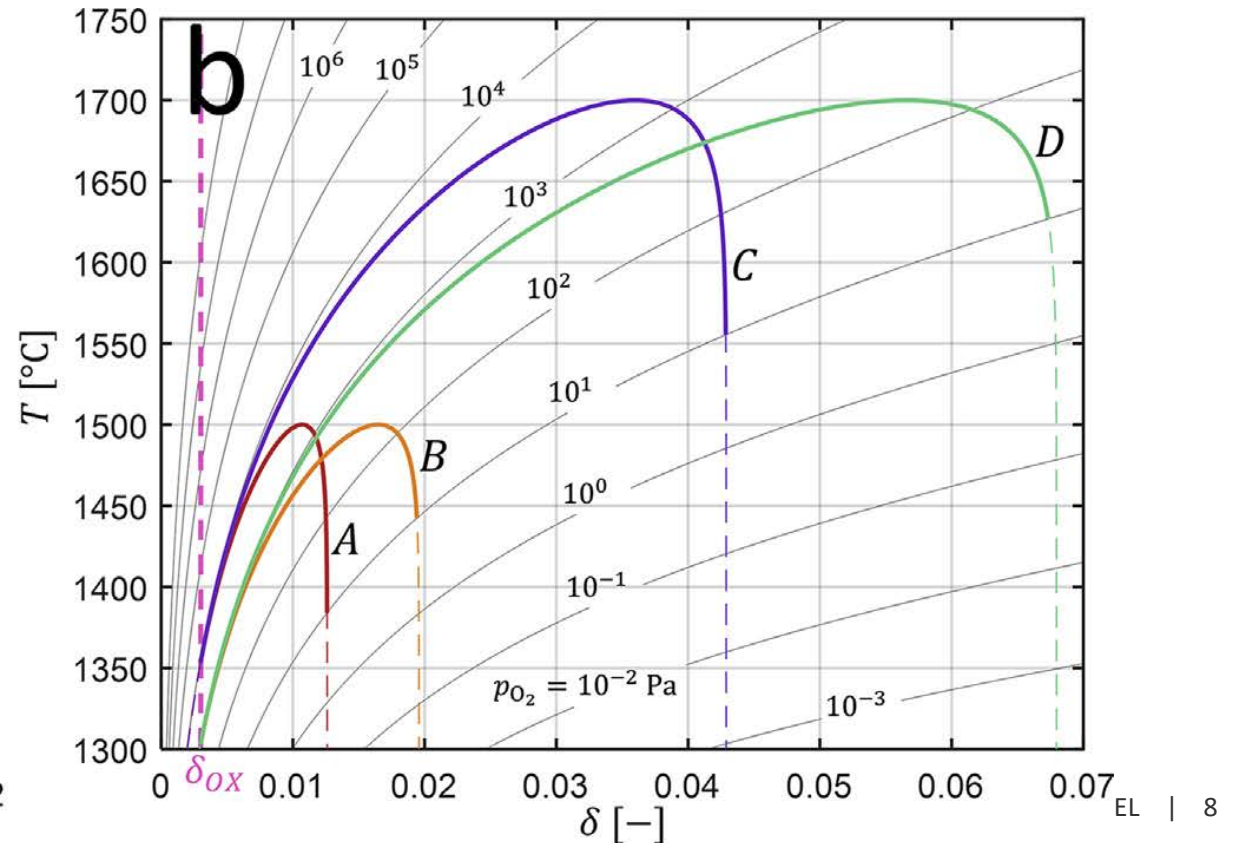
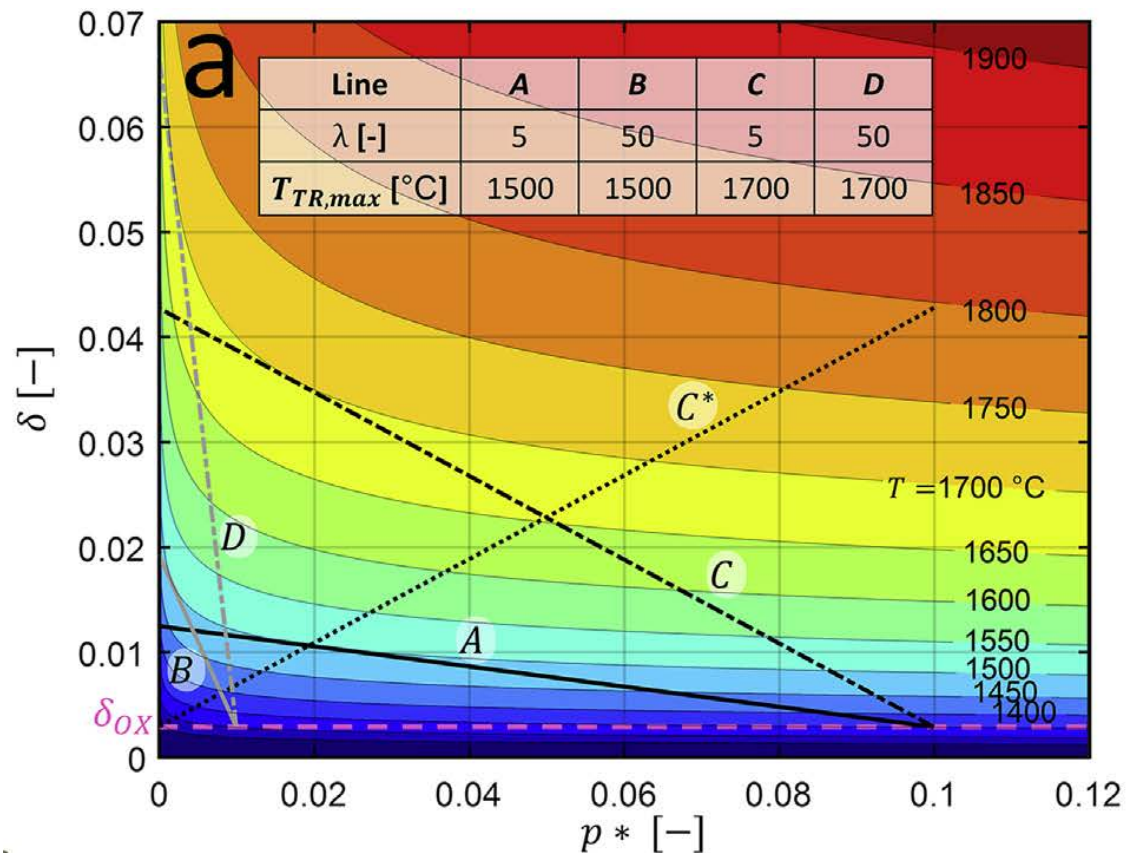
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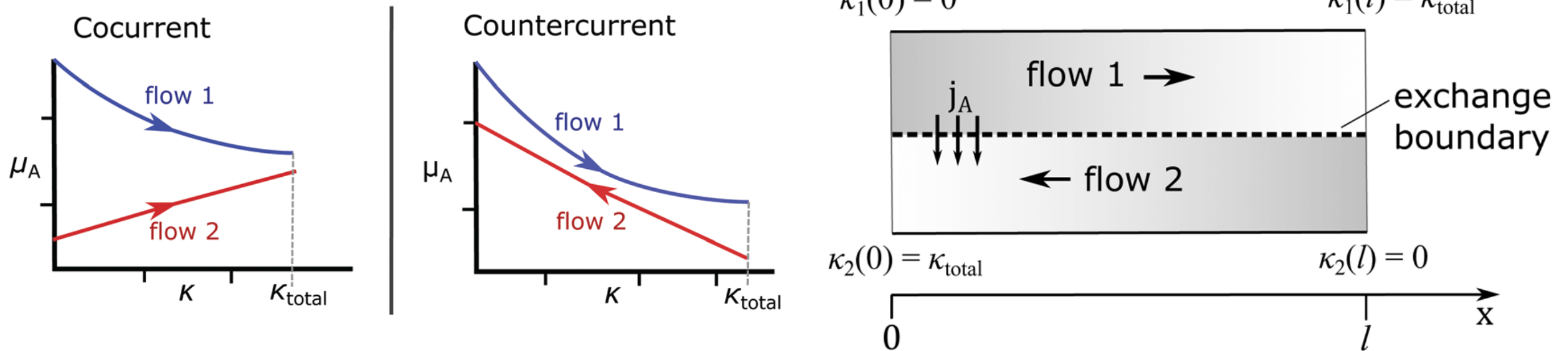
Previous Work

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- Extending the analysis to identify required temperature profile to obtain $\Delta_r G = 0$ all along the reactor (de la Calle et al. [3-4])



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- Alternative method (reduction only) – using non-dimensional exchange coordinate (Bulfin [5])



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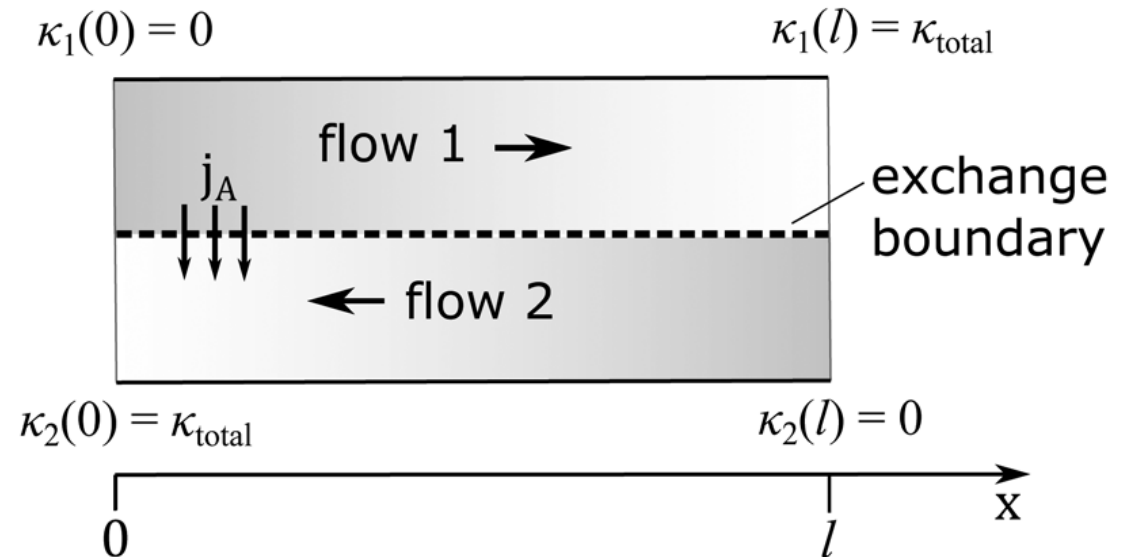
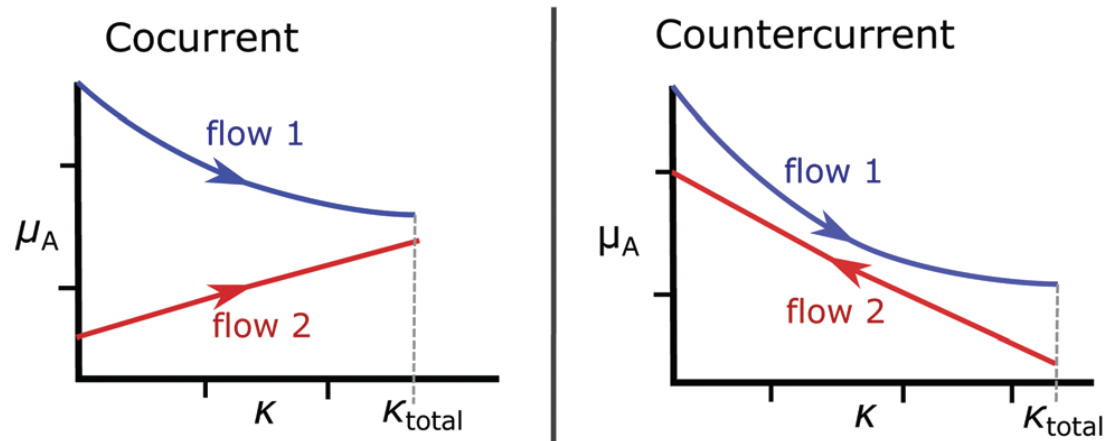
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Thermodynamic Model

- 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: $\omega_{\text{red}} = \frac{\dot{n}_{\text{sweep}}}{\dot{n}_{\text{MO}}}$
- O₂ impurity at inlet: ϕ_{red}
- O₂ chemical potential (MO):

$$p_{\text{O}_2} = f(\delta(\Delta h, \Delta s), T)$$

$$p_{\text{O}_2, \text{sg}}^{\text{red}}(\kappa) = \frac{\phi \omega_{\text{red}} + \kappa}{\omega_{\text{red}} + \kappa}$$

$$p_{\text{O}_2, \text{MO}}^{\text{red}}(\kappa) = f(T, 2\kappa)$$

- Reduction extent relation to exchange coordinate: $\delta = 2\kappa$
- Equilibrium thermodynamics: $\delta = f(T, p_{\text{O}_2})$

Oxidation (This work)

- Oxidizer gas-MO ratio: $\omega_{\text{ox}} = \frac{\dot{n}_{\text{oxidizer}}}{\dot{n}_{\text{MO}}}$
- Gas composition at inlet ($x_{\text{reac},0} / x_{\text{prod},0}$): from equilibrium of water/CO₂ thermolysis or specified
- O₂ chemical potential (MO):

$$p_{\text{O}_2} = f(\delta(\Delta h, \Delta s), T)$$

$$p_{\text{O}_2, \text{feed}}^{\text{ox}}(\kappa) = p^\circ \left(K \frac{\omega_{\text{ox}} x_{\text{reac},0} - 2\kappa}{\omega_{\text{ox}} x_{\text{prod},0} + 2\kappa} \right)^2$$

$$p_{\text{O}_2, \text{MO}}^{\text{ox}}(\kappa) = f(T, \delta_{\text{red}} - 2\kappa)$$

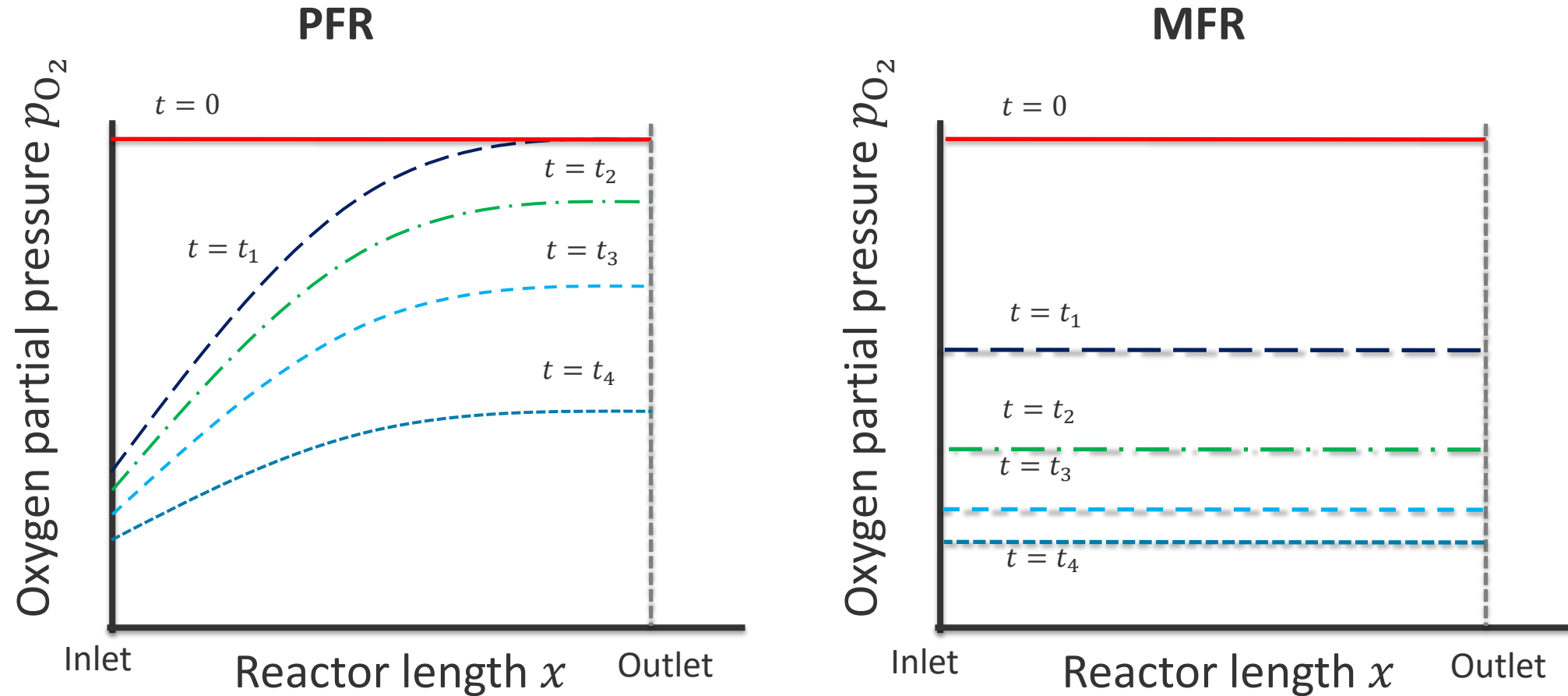
Methodology and Implementation

- Solving numerically from $\kappa = 0$ until κ_{total} (chemical potentials meet) or κ_{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 ($T_{\text{red}}, T_{\text{ox}}, \omega_{\text{red}}, \omega_{\text{ox}}$) 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](https://doi.org/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 CO₂ 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](https://doi.org/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: $T_{\text{red}}, \omega_{\text{red}} (p_{\text{red}}, \phi_{\text{red}})$
 - Oxidation: $T_{\text{ox}}, \omega_{\text{ox}} (p_{\text{ox}}, x_{\text{reac},0}, x_{\text{prod},0})$
- **Materials implemented:**
 - CeO₂
 - CeZr20 (Ce_{0.8}Ze_{0.2}O₂)
 - LCMA6464 (La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O₃)
 - LSM40 (La_{0.6}Sr_{0.4}MO₃)
 - Fe33Al67 (Fe_{0.33}Al_{0.67}O₄)
- **Oxidizers:**
 - H₂O or CO₂
- **Oxidizer feedstock composition:**
 - calculated equilibrium composition of H₂, H₂O, and O₂ (or CO, CO₂, and O₂)
 - specific value can be provided
- **Flow patterns:**
 - Parallel flow (PF)
 - Countercurrent flow (CF)

Performance Metrics

Nonstoichiometry extent

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

Conversion extent

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

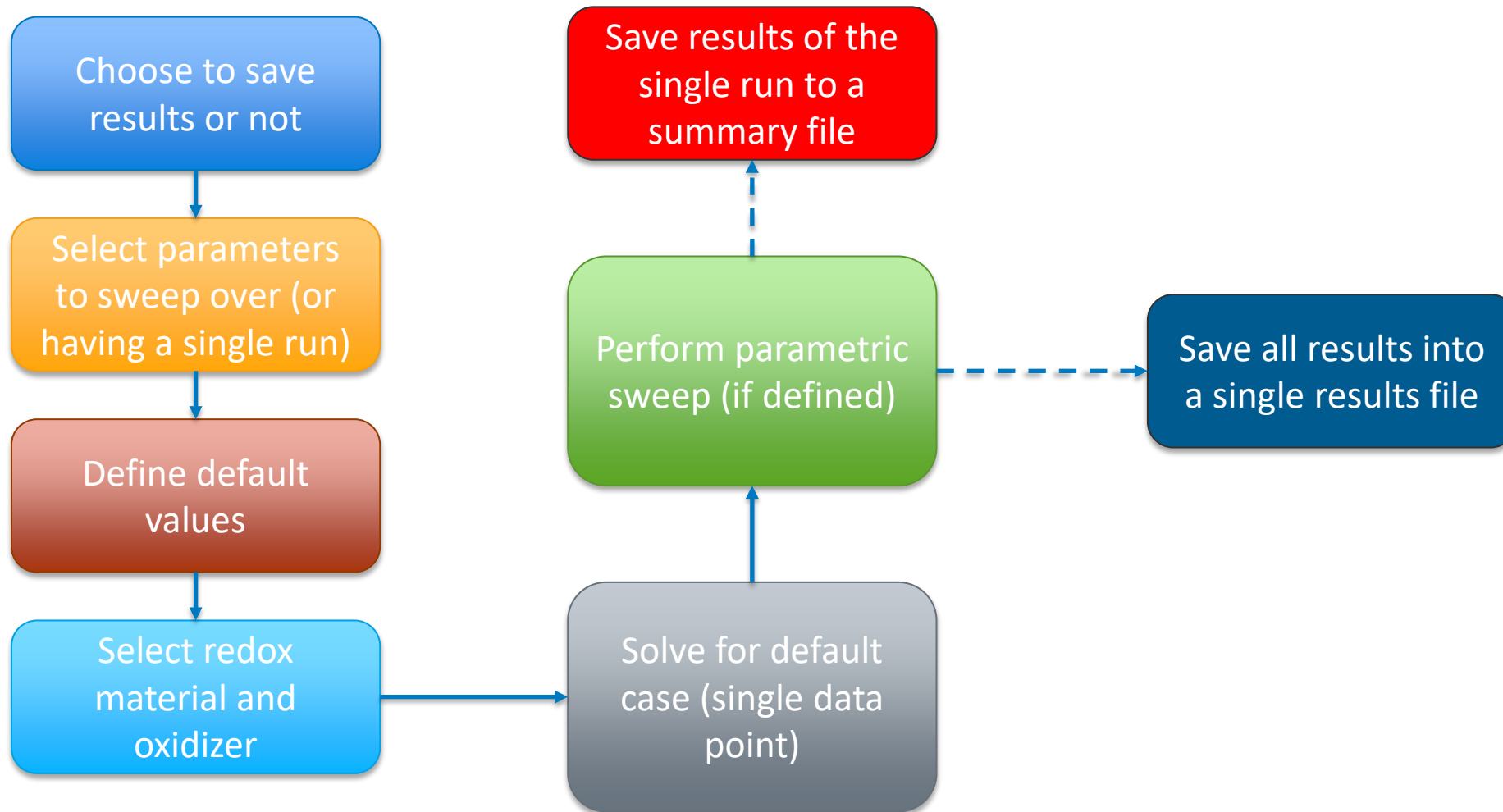
Specific energy terms:

$$F_i = \frac{Q_i}{Q_{\text{fuel}}}$$

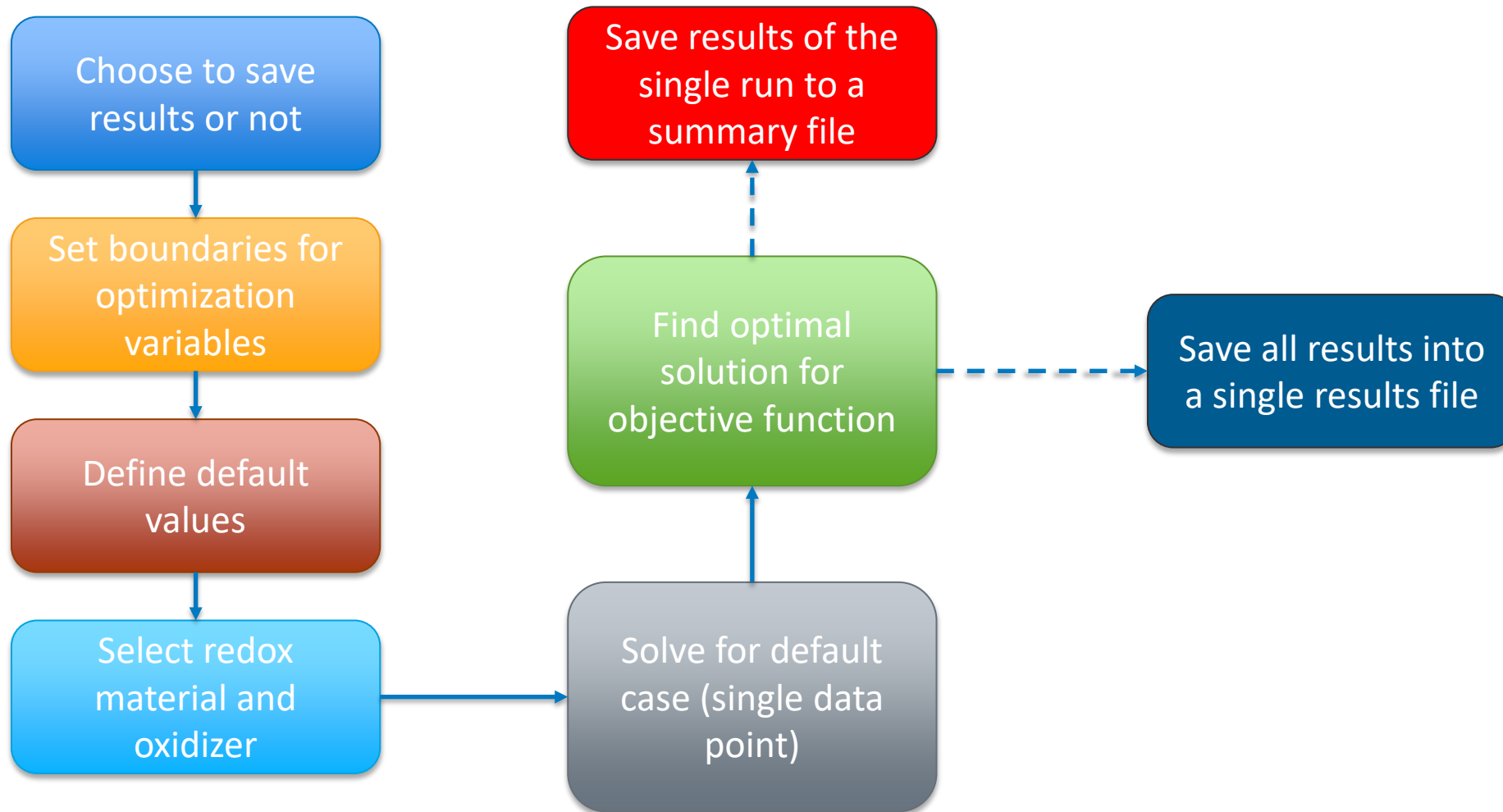
Process efficiency (excluding optical/receiver efficiency)

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

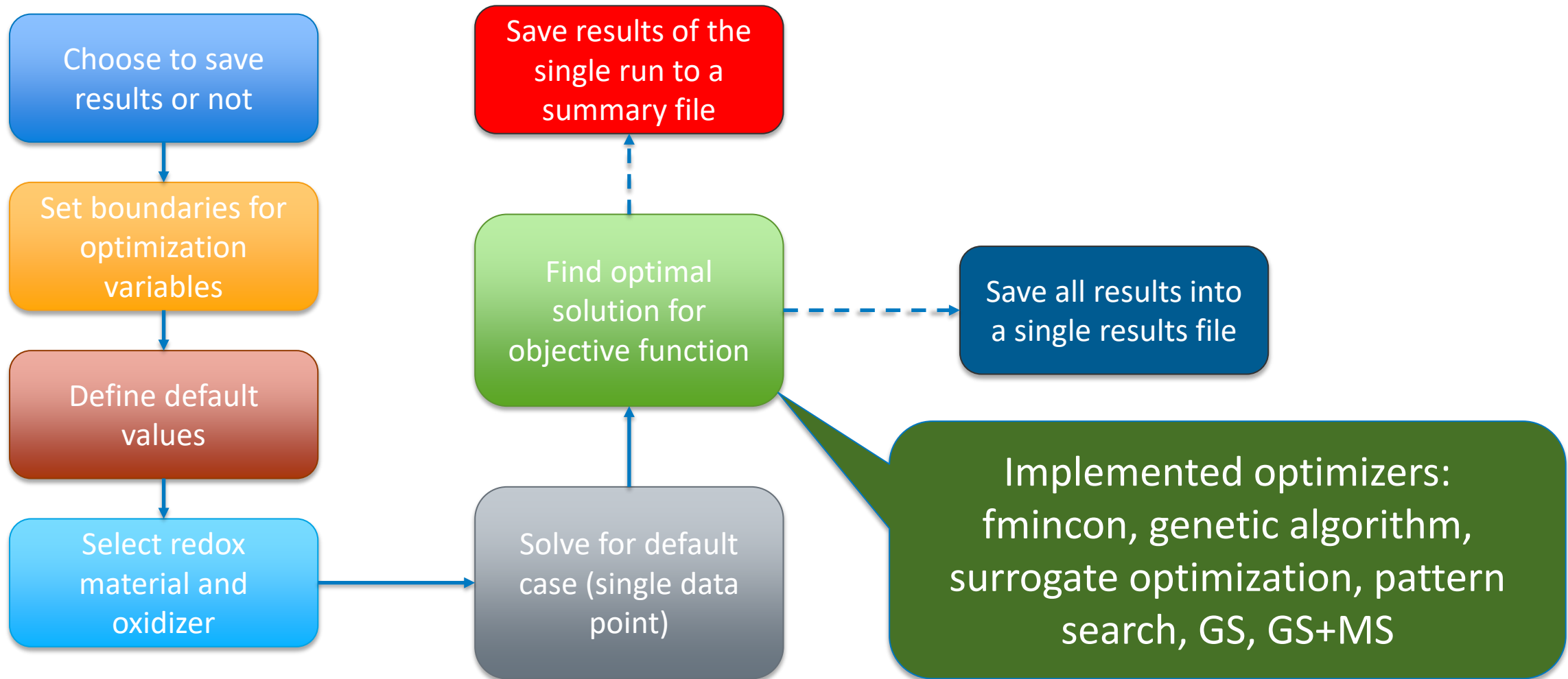
Code Logic Flow Chart – Parametric Sweep



Code Logic Flow Chart - Optimization



Code Logic Flow Chart - Optimization

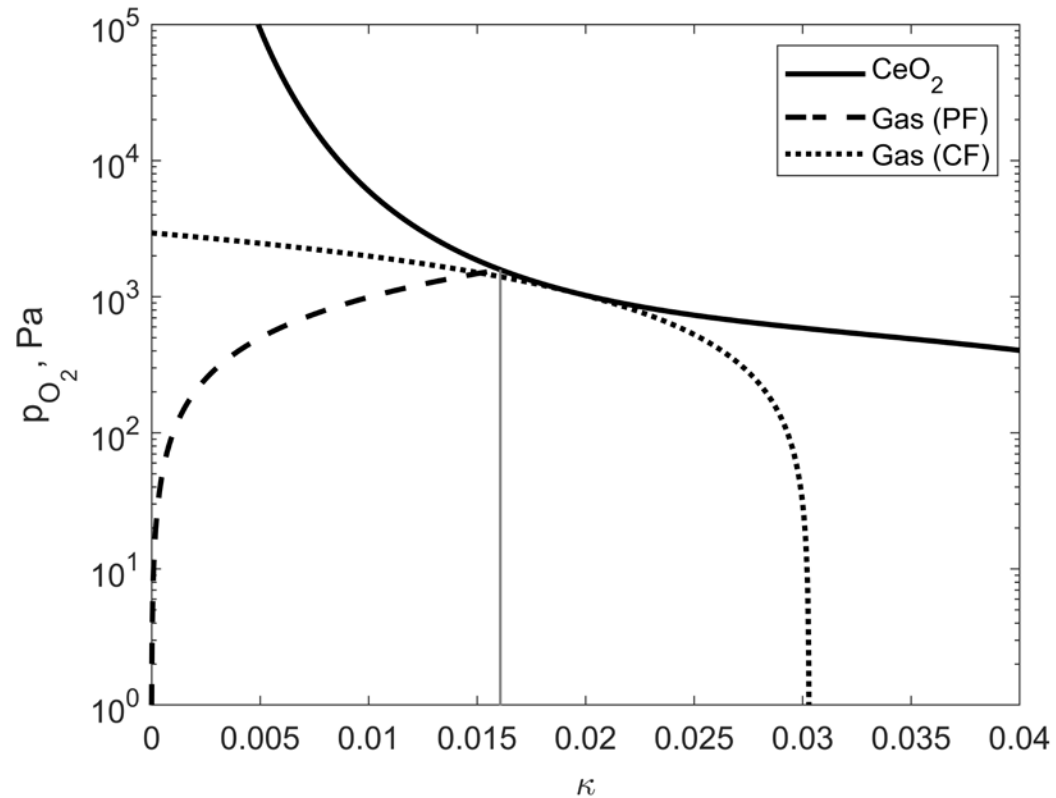


Results

Results (CeO₂)

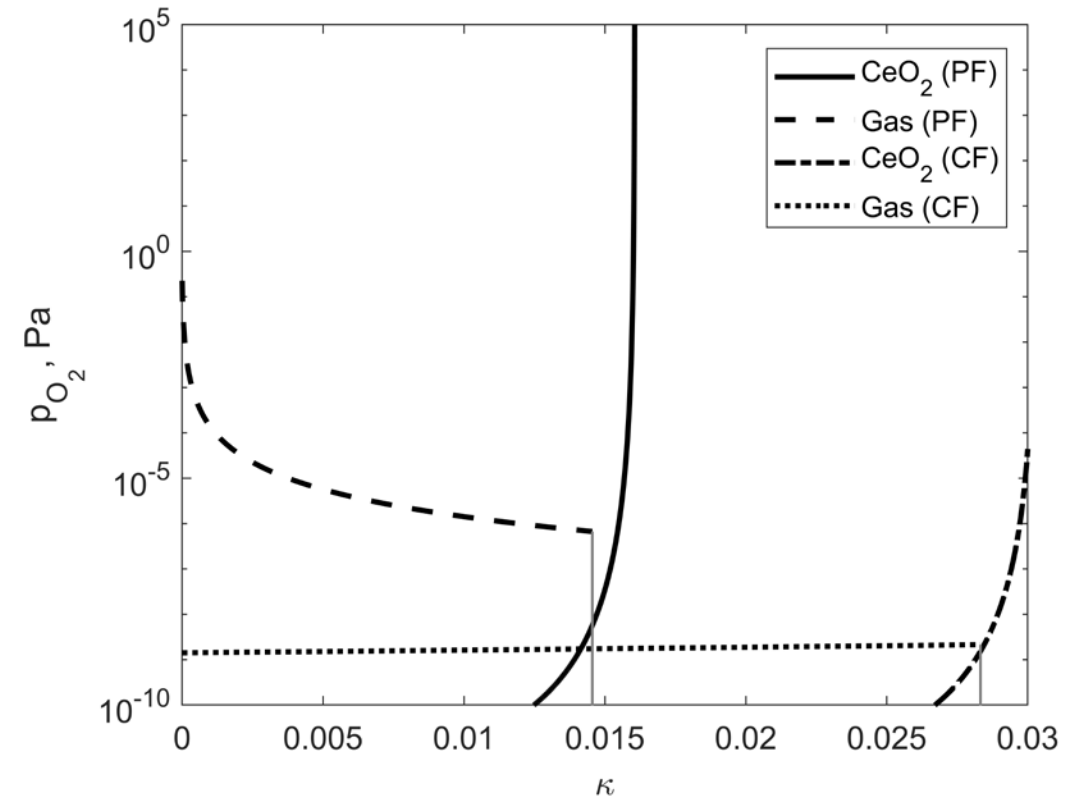
Reduction

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



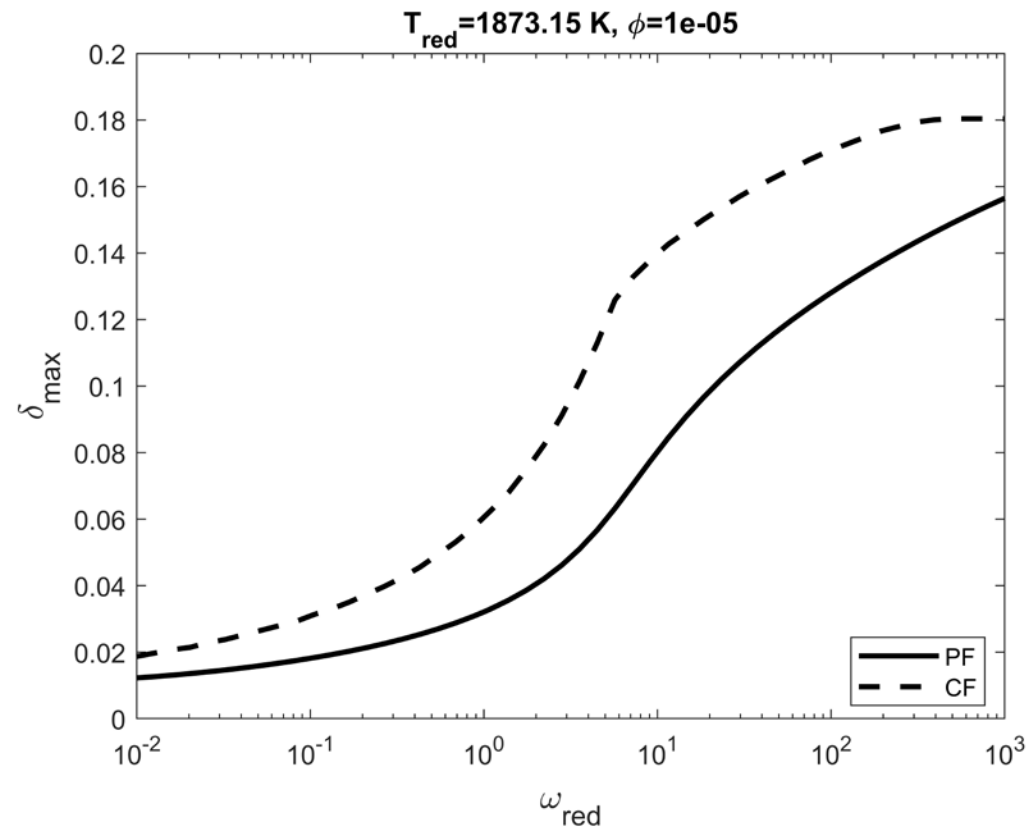
Oxidation

- $\omega_{\text{ox}} = 1, x_{\text{H}_2} = 4.8 \cdot 10^{-6}$
- $T_{\text{ox}} = 900^\circ\text{C}, p = 1 \text{ bar}$

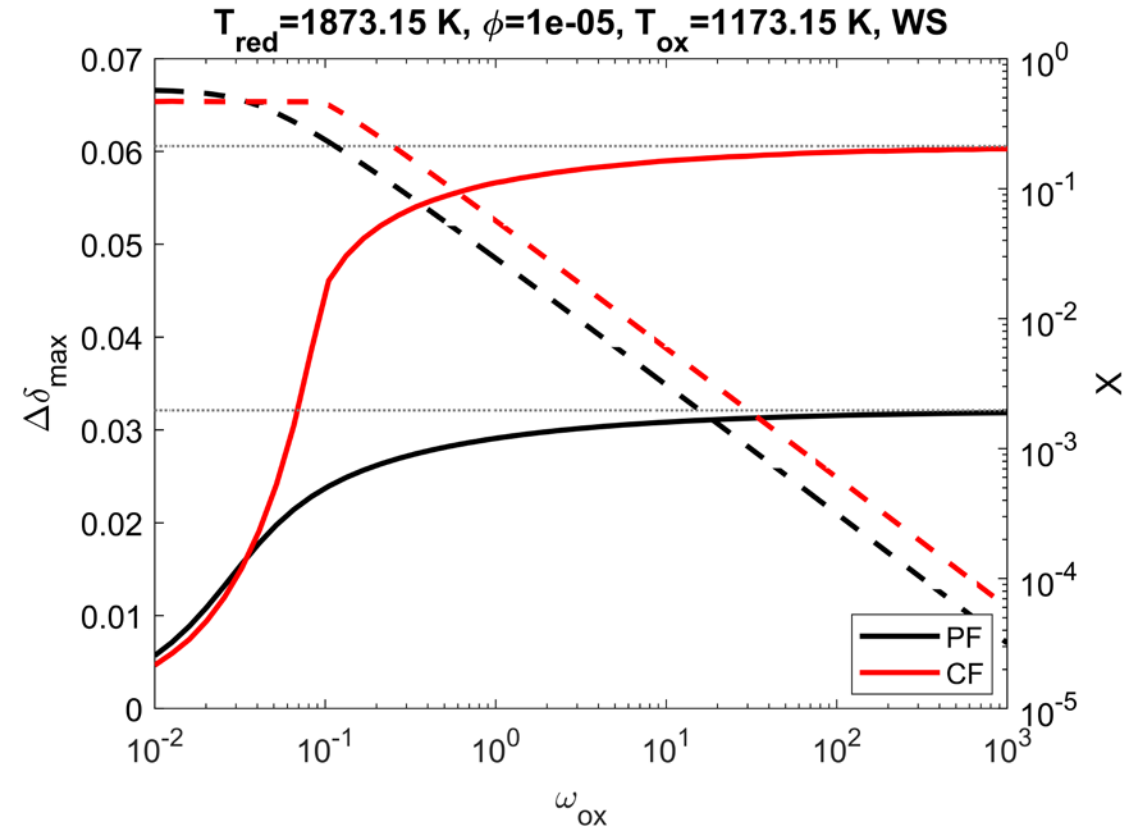


Results (CeO₂) – Single Para Sweep

Reduction

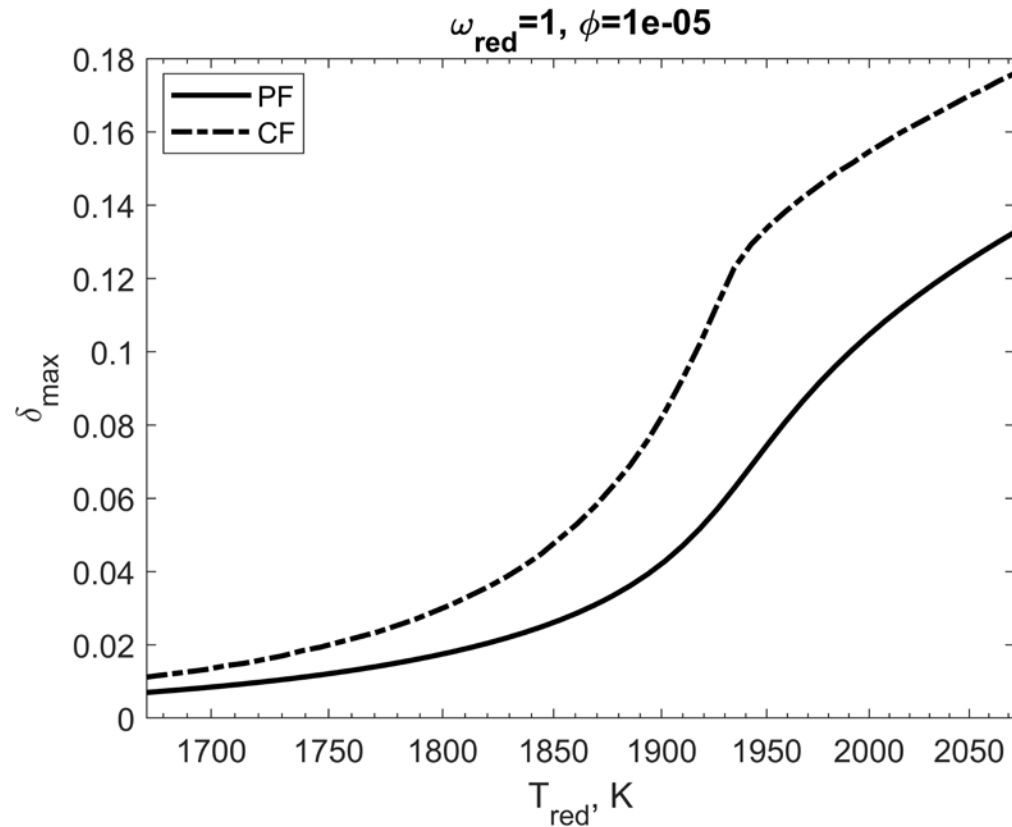


Oxidation

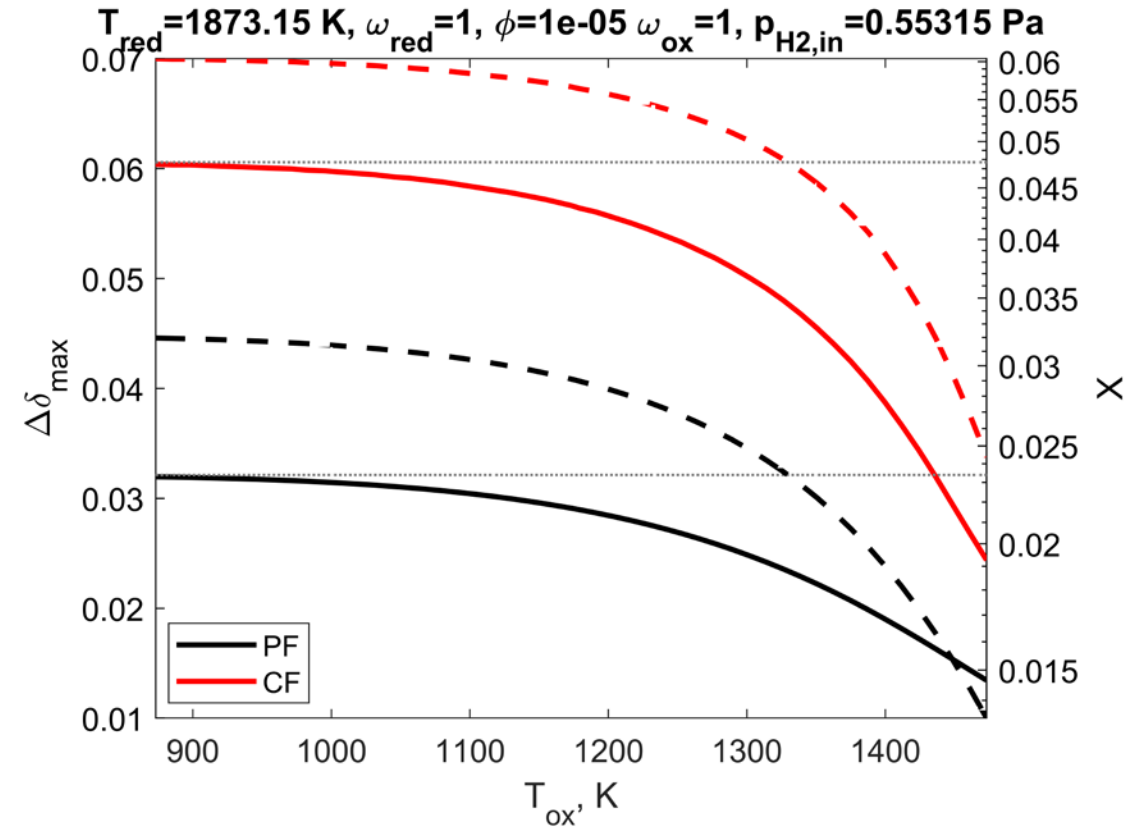


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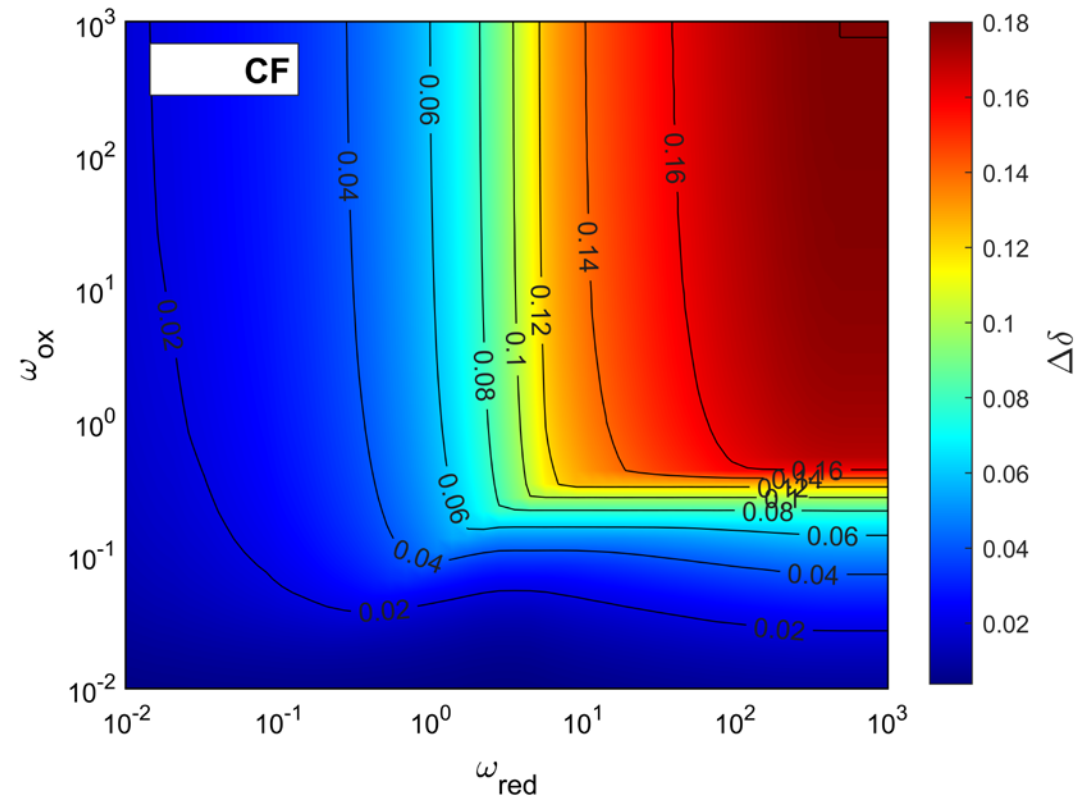
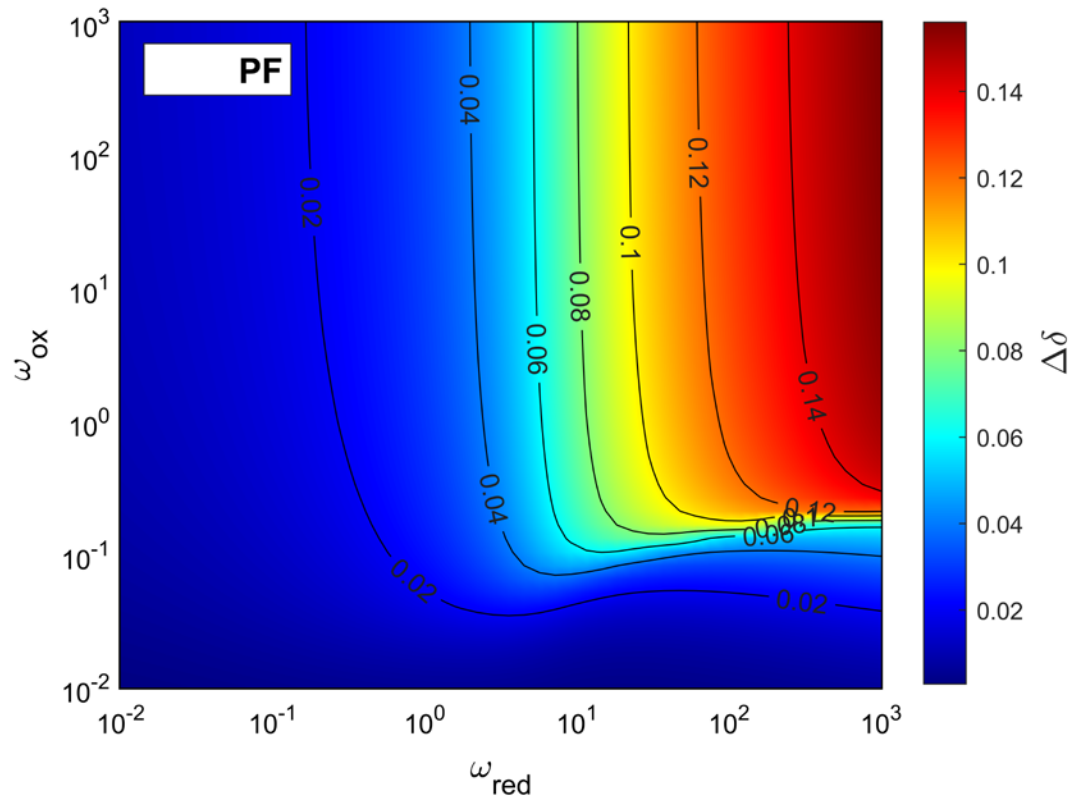


Oxidation



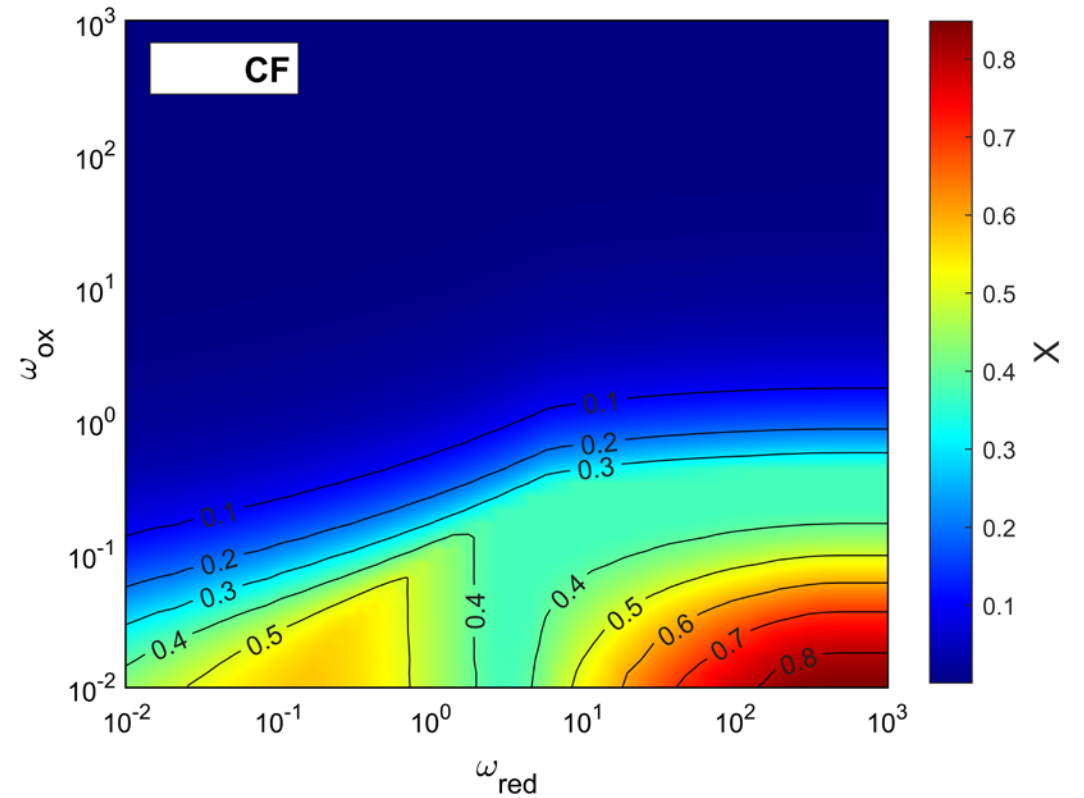
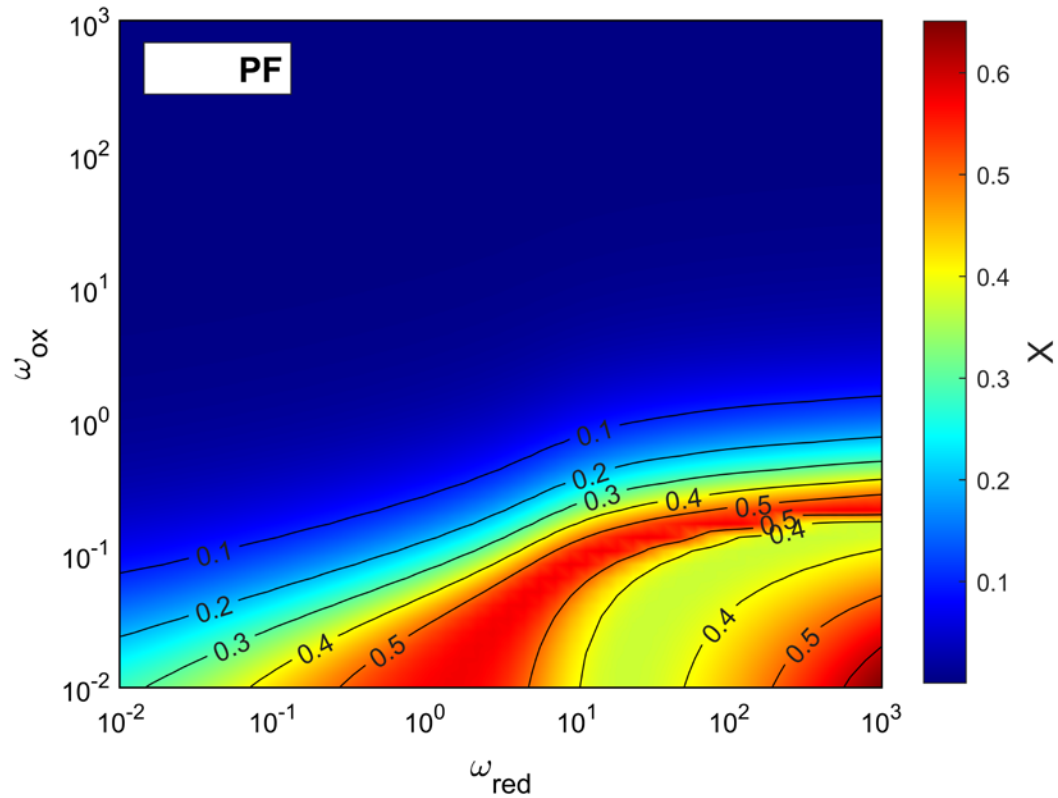
Results (CeO₂) – Two Parameters Sweep

Molar flow rate ratios sweep – reduction extent



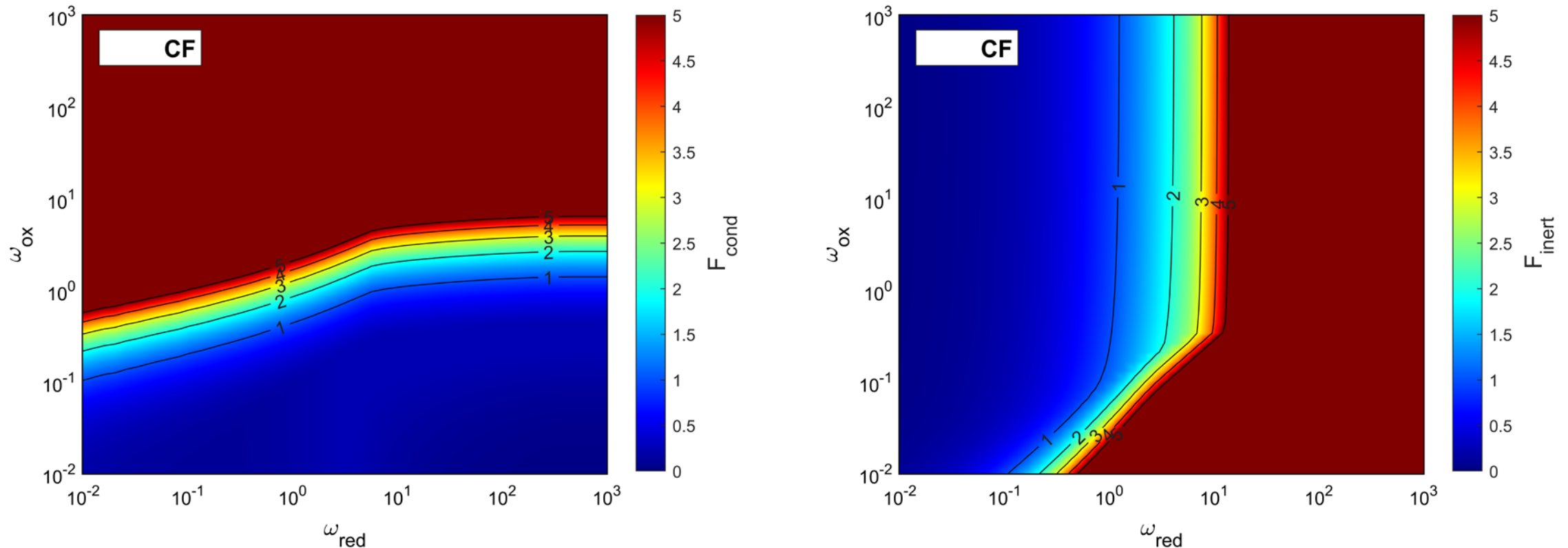
Results (CeO₂) – Two Parameters Sweep

Molar flow rate ratios sweep - conversion



Results (CeO₂) – Two Parameters Sweep

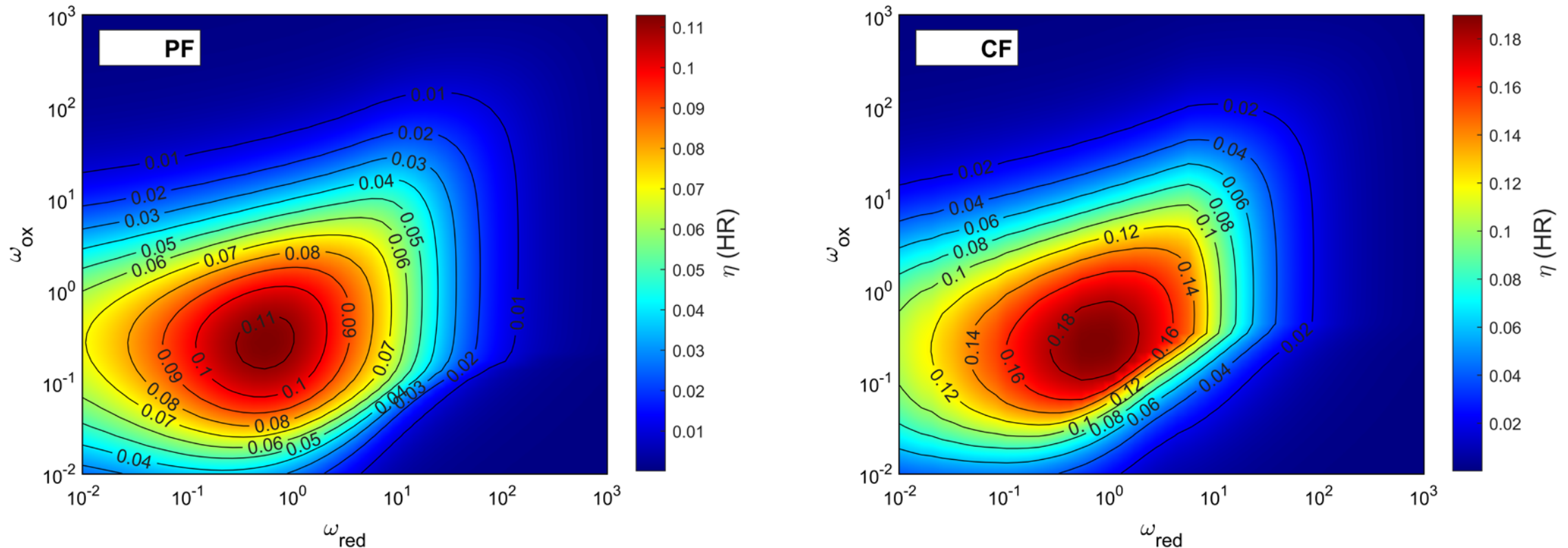
Condensation (boiling) and inert gas separation (via cryogenic separation) specific energy requirements



Competing requirements – different areas are beneficial for different terms

Results (CeO₂) – Two Parameters Sweep

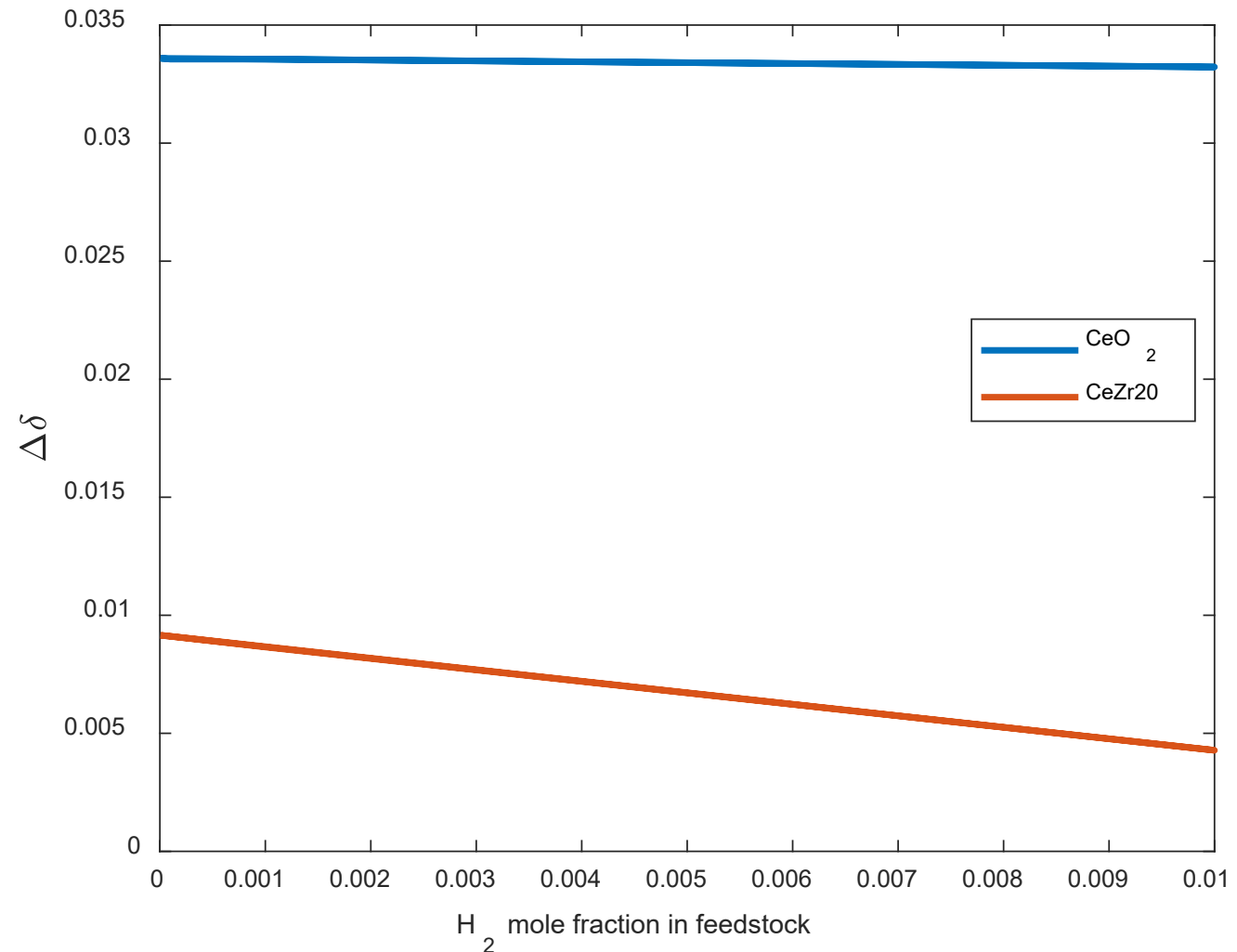
Molar flow rate ratios sweep – efficiency (with HR): $\varepsilon_s = 0.5$, $\varepsilon_g = 0.8$, $\varepsilon_{ox} = 0.8$



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

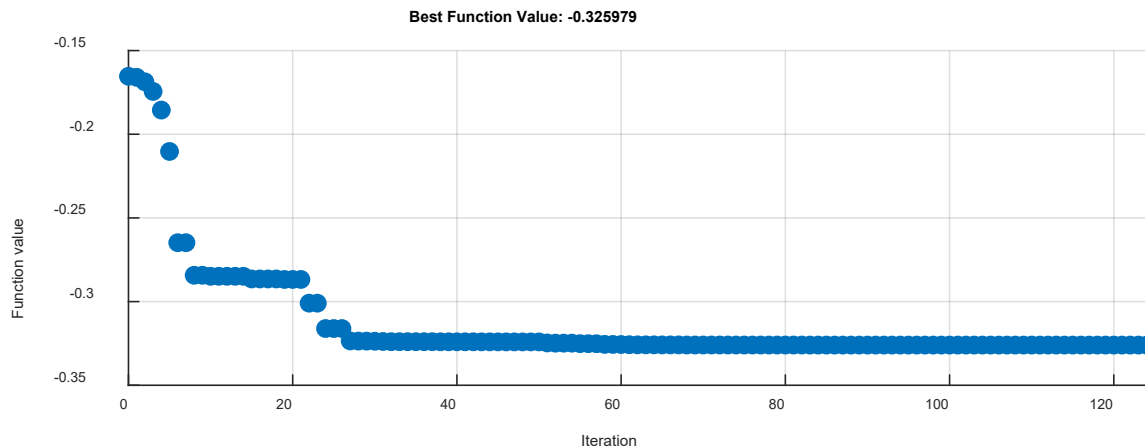
Results – Effect of Feedstock Composition

- 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 than CeO_2
- Relevant for “high-conversion” cycles (incomplete separation or multiple passes)

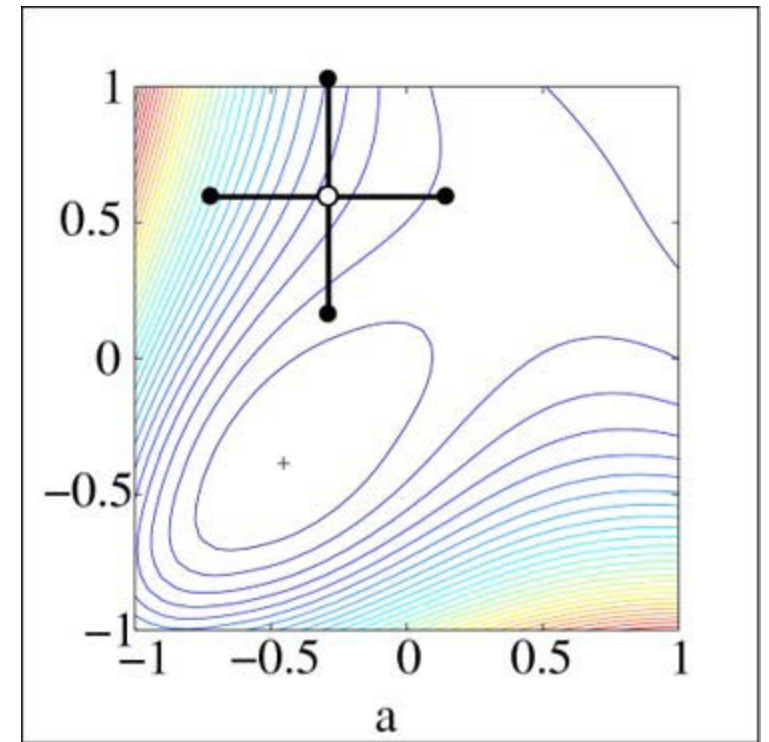


Results (CeO₂) – Optimization

- 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:
 $T_{\text{red}} = 1973 \text{ K}, T_{\text{ox}} = 1029 \text{ K},$
 $\omega_{\text{red}} = 0.4375, \omega_{\text{ox}} = 0.1836$
- Except T_{red} , no “instinct” on the effects of the other variables



Pattern Search Optimization



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

Code on GitHub (not public yet!)

Navigation bar: NREL / REDOTHERM, Search (Type / to search), +, Home, Pull requests, Issues, Code, Actions, Projects, Security, Insights, Settings.

Repository header: REDOTHERM (Private), Watch 2, Fork 0, Star 0.

Branches: main (1 Branch), 0 Tags. Search: Go to file. Actions: Add file, Code.

Commit history:

Author	Message	SHA	Time
alidor	Made the MFR results analysis optional (using a flag)	b0e63f5	last month
			2 Commits

File list:

File Name	Message	Time
functions	Made the MFR results analysis optional (using a flag)	last month
Redox_Countercurrent_Thermo_Main.m	Made the MFR results analysis optional (using a flag)	last month
Redox_Countercurrent_Thermo_Plot_Results.m	Made the MFR results analysis optional (using a flag)	last month

README section: Add a README. Help people interested in this repository understand your project by adding a README.

Right sidebar:

- About: No description, website, or topics provided.
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Code is Interactive and Well-Documented

The screenshot displays the MATLAB R2023b environment. The top menu bar includes HOME, PLOTS, APPS, EDITOR, PUBLISH, and VIEW. The ribbon contains various toolbars for file operations (New, Open, Save, Print), navigation (Go To, Find, Bookmark), code editing (Refactor, Analyze), and execution (Run, Step, Stop). The current folder is C:\Users\alidor\Documents\GitHub\REDOTHERM. The workspace shows variables like X_sol, xCO2_in, xCO_in, xH2_in, xH2O_in, xO2_CDS_in, xO2_ox_in, xO2_WS_in, Y, and Y0.

```
144 end
145 % MFR input data
146 n_MO = 1e4; % Amount of metal oxide (for MFR) [mol]
147 t_red = 600; % Reduction duration (for MFR) [s]
148 t_ox = 600; % Oxidation duration (for MFR) [s]
149 % Oxidizer composition selection
150 x_ox_in = input('Enter the oxidizer mole fraction in the oxidizer stream (leave empty to use equilibrium compo
151 if isempty(x_ox_in)
152     ox_comp_flag = 0;
153 else
154     ox_comp_flag = 1;
155 end
156 % Select redox material
157 redox_material = input("Select redox material: 1-CeO2,2-CeZr2O,3-LCMA,4-LSM40,5-Fe33A167 [1-CeO2]: ");
158 if isempty(redox_material)
159     redox_material = 1;
160 end
161 % NOTE: the initial delta for MFR can't be too low due to numerical
162 % stability issues (solution converges to zero), but it must not be too
```

The Command Window shows the following interactive prompts:

```
Save figures? Y/N [N]:
Enter minimum flow rate ratio of sweep gas to oxide [omega_red_min=0.1]: 0.01
Enter maximum flow rate ratio of sweep gas to oxide [omega_red_max=1000]:
Enter minimum flow rate ratio of oxidizer to oxide [omega_ox_min=0.1]: 0.01
Enter maximum flow rate ratio of oxidizer to oxide [omega_ox_max=100]:
Enter minimum reduction temperature in deg. C [Tred_min=1200]: 1400
Enter maximum reduction temperature in deg. C [Tred_max=1700]:
Enter minimum oxidation temperature in deg. C [Tox_min=600]:
```

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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Thank you for your attention!

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